Metal Associations in Suspended Sediments and Bed Sediments from the Mississippi River

by

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ABSTRACT

The role of silt-size (1-63μm) and colloidal-size (0.005-1μm) suspended sediment and bed sediment in the fate and transport of metals (Cr, Cu, Pb, Fe, and Mn) in the Mississippi River was investigated. To examine metal-sediment interactions, a sequential extraction method was developed to operationally differentiate among inorganic, organic, and refractory mineral metal associations in the sediment. Inorganically bound metals, those loosely-held to the sediment surface and associated with carbonates, manganese oxides, and amorphous oxides, were released using the reducing agent hydroxylamine hydrochloride. To solubilize organically bound metals, an oxidizing solution of potassium persulfate was employed. The remaining refractory mineral fraction was completely digested using a mixture of aqua regia and HF. Concentrations of Cr, Cu, Pb, Fe, and Mn in each extract were determined using inductively-coupled plasma atomic emission spectroscopy and inductively-coupled plasma mass spectroscopy. A significant fraction of sediment bound Cu (30-40%), Pb (10-30%), Fe (15-25%), and Mn (85-90%) was extracted by the hydroxylamine reagent. The fraction of total sediment bound metals in the persulfate extract was insignificant for all metals except Cr (10-20%) and Fe (15-25%). Refractory mineral associations represented a significant fraction of Cr (70-90%), Cu (50-60%) and Fe (10-20%) and a negligible fraction of Pb and Mn. Suspended sediment from the free-flowing lower Mississippi River exhibited lower and less variable non-residual metal concentrations than sediment from the impounded upper river. Occasional increases in the non-residual metal concentrations in the colloids with no corresponding increase in the silts suggested that the colloids and silts may not be at equilibrium which may have important implications in modeling metal transport. Colloids contributed only slightly to the sediment bound non-residual metal load in the lower river, but carried a significant fraction of the load in the upper river. The significance of metal transport by colloids relative to dissolved metal transport could not determined since concentrations of both dissolved metals and colloid associated metals expressed in micrograms per liter of river water were typically below or near analytical detection limits. Bed sediments from pools in the upper Mississippi River clearly indicated anthropogenic metal inputs from metropolitan and mining sources. Investigation of the role of inorganic and organic components in metal sorption onto sediments was inconclusive due to the inability of the sequential extraction method to effectively distinguish between adsorption on hydrous iron oxides and interaction with organic matter.

TABLE OF CONTENTS

Page

APPENDIX

DATA SUPPLEMENT: Excel spreadsheet files on 3.5" 1.44 Mb DS,HD computer diskette[1]

FILES: SSMC.XLS (Suspended Sediment Metal Concentrations)
BSMC.XLS (Bed Sediment Metal Concentrations)
HSD.XLS (Hydrologic and Sedimentologic Data)

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[1] If the accompanying data supplement diskette is missing, data can be obtained by writing either of the following addresses:

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Boulder, CO 80301

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LIST OF FIGURES

LIST OF TABLES

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INTRODUCTION

The Mississippi River and its tributaries drain approximately 40 percent of the conterminous United States with a discharge of suspended sediment to the Gulf of Mexico averaging 210 million tons per year (Meade, 1988). Suspended sediments are an important determinant of river quality because the major fraction of dissolved metals (and organic contaminants) transported by alkaline waters such as the Mississippi River become associated with sediments (Forstner and Wittmann, 1979). Although sediments sorb dissolved metals, these sediment-bound metals may be released back into the aquatic environment due to changes in chemical conditions of the system. Determination of the sediment components controlling metal ion sorption is important since the potential mobility of sediment-bound metals is largely determined by the specific association of the metal ions in sediment.

While many investigators have attempted to determine metal associations in sediments primarily using sequential extraction techniques, elucidation of the role sediment components play in controlling metal transport has proved inconclusive. Several researchers have shown that metal ion partitioning between inorganic and organic sediment components is a competitive process determined by the concentrations of the individual substrates, while others have concluded that one component of the sediment, either iron and manganese oxides or organic material, dominates the scavenging of dissolved metals in the aquatic environment. Luoma and Bryan (1981) used a statistical approach to support a concentration-dependent competition between inorganic and organic substrates for various trace metals. The work of Lion and others (1982) also supported particulate component competition, but the study was limited to surface adsorption characteristics of each of the components. According to a study of the partitioning of copper, zinc, and lead onto stream sediments by Filipek and others (1981), organic-metal associations were dominant even in the presence of large concentrations of iron and manganese oxides. Wilhelm and others (1979) suggested that iron and manganese coatings control the metal distribution when the organic carbon content in sediments and soils is below 5%. In contrast, Hoffman and Fletcher (1981) found that in some cases, the organic matter in soils and sediments played only a minor role relative to hydrous oxides in trace metal scavenging despite being a major component of the sample. Similar results were reported by Smith (1992) for the sorption of trace metals onto streambed sediment in acid-mine drainage. Clearly, a greater understanding of the nature of trace metal transport on sediment is needed.

This research attempts to quantify inorganic, organic, and refractory mineral associations of chromium, copper, lead, iron, and manganese in the silt-size (1-63μm) and colloidal-size (0.005-1 μm) suspended sediments as well as bed sediments from the Mississippi River in order to determine the distribution, fate, and transport of sediment bound metals in the river and to examine the relative importance of the inorganic and organic sediment components in controlling trace metal transport. Inorganically bound metals are defined here to include those metals loosely-held to the sediment surface and associated with carbonate minerals, manganese oxides, and amorphous iron oxides. Included in the organically bound definition are those metals associated with oxidizable components, largely organic matter as well as some sulfides. The refractory mineral metal associations encompass those metals incorporated into the mineral crystal lattice. To determine these metal-sediment associations, a sequential extraction scheme is developed to operationally differentiate among the geochemical components.

The chapters in this thesis are organized in the following sequence. Chapter 1 provides background information on important trace metal sinks associated with sediments and outlines the usefulness and limitations of sequential extraction methods in determining these metal-sediment associations. Development and evaluation of a sequential extraction method to identify inorganic, organic, and residual metal associations in sediments is presented in Chapter 2. Results of the sequential extractions of Mississippi River suspended sediments and bed sediments are reported in Chapter 3. Chromium, copper, lead, iron, and manganese distributions in the sediments are discussed, focusing on downriver trends, seasonal variations, and differences between silt and colloidal transport of metals. In Chapter 4 the nature of inorganic and organic components in the Mississippi River sediment and their role in trace metal transport are discussed. The geochemical implications of the sequential extraction results for chromium, copper, and lead are also examined. Conclusions and suggestions for future work are presented in Chapter 5.

CHAPTER 1

BACKGROUND

Sediment particles can be considered to be clay minerals acting as a substrate for the transport of iron and manganese oxides coatings, organic material, carbonates, and sulfides (Jenne, 1977). Each of the components associated with the clay-matrix vehicle may scavenge trace elements from the aqueous phase. Metals can be sequestered through numerous mechanisms including adsorption, precipitation, or incorporation into the mineral crystal lattice. The relative importance of each individual sink is dependent on the reduction and oxidation potentials and the pH of the system, as well as the abundance of the component and its affinity for a particular trace element. Whether or not a bound metal is remobilized due to chemical changes in the aquatic milieu is largely determined by the specific association of the metal in the sediment.

Iron and Manganese Oxides

The iron and manganese oxide components of the sediment are considered by some to be a primary control on metal ion sorption in the aquatic environment (Singh and Subramanian, 1984; Jenne, 1968). The amorphous forms of iron and manganese oxides which exist in surficial waters promote both surface sorption and diffusion into the oxide lattice of metal ions. Dissolution of these oxides may occur primarily by a decrease in the redox potential and/or pH of the system, thereby releasing the associated metals back into the aqueous environment.

Forms

Iron and manganese hydroxides and oxides in surficial waters commonly exist as coatings on minerals and as discrete particles. These oxides are generally amorphous in character. The important forms of iron oxides in surficial waters are $Fe(OH)_3$, Fe_3O_4 (magnetite), amorphous FeOOH, and α-FeOOH (geothite) (Forstner and Wittmann, 1979). In the case of manganese oxides, important forms in surficial waters include $Mn(IV)_{1-x}Mn(II)_xO_{2-2x}(OH)_{2x}$ (nsutite) and $(Na,Ca)Mn_7O_{14}\cdot 2.3H_2O$ (birnessite) (Potter and Rossman, 1979).

The iron and manganese oxides coatings on the Mississippi River sediments have not been characterized in this study. Although X-ray diffraction (XRD) analyses of several silt samples indicated the presence of iron hydroxides (Dunn, 1992), information concerning the form of the oxides using XRD was not obtainable because of the amorphous nature of the iron and manganese oxides coatings.

Both iron and manganese oxides maintain a low degree of crystallinity in the aquatic environment for several reasons. In the case of iron oxides, the extreme insolubility of Fe(III) oxides coupled with a high rate of oxidation and precipitation results in formation of amorphous iron oxides as a thermodynamically metastable phase (Jenne, 1977). Manganese oxides are usually more amorphous than iron oxides due to their formation of nonstoichiometric oxides with variable oxidation states (+2, +3, or +4). Isomorphic substitution is also greater in manganese oxides as a consequence of a slower precipitation rate (Jenne, 1977). Further crystallization of both oxides is inhibited by foreign ions adsorbed to the surface and incorporated into the lattice.

The amorphous character of the oxides is largely responsible for the scavenging of trace metals (Kuhnel and others, 1975). By providing many accessible surface sites, the extensive surface area of the oxides facilitates both adsorption and lattice substitution of metal ions (Wadsley and Walkley, 1951). The surface area of manganese oxides may be as high as a few hundred square meters per gram (Anderson and others, 1973; Loganathan and Burau, 1973), while that of iron oxides may range from about 200 to over 300 square meters per gram (Bigham and others, 1990; Eggleton and Fitzpatrick, 1988).

Scavenging Mechanisms

Both specific and non-specific adsorption of metal ions may occur at the oxide surface. Specific adsorption, also referred to as chemical adsorption, results in the formation of inner-sphere complexes of the sorbate with surface functional groups. The commonly accepted mechanism for specific adsorption of metal cations onto the oxide surface is the displacement of H^+ ions bound to the surface oxygen by the metal cation (Stumm and Morgan, 1981; Loganathan and Burau, 1973). The surface coordination reactions can be viewed as following:

$$=\text{MeOH} \quad + \quad M^{z+} \quad <\!\!\text{----}\!\!> \quad =\text{MeOM}^{z-1} \quad + \quad H^{+} \text{ and}$$

$$\begin{array}{c} =\text{MeOH} \\ | \\ =\text{MeOH} \end{array} \quad + \quad M^{z+} \quad <\!\!\text{----}\!\!> \quad (=\text{MeO})_2M^{(z-2)+} \quad 2\,H^{+}$$

in which =MeOH and =MeO are oxide surfaces and M^{z+} is the metal cation to be adsorbed. If the metal occurs in an oxyanion form, the anion can be viewed as exchanging with the bound OH^- ion as shown by the following scheme (Stumm and Morgan, 1981) :

$$=\text{MeOH} \quad + \quad MO_x^{z-} <\!\!\text{----}\!\!> \quad =\text{Me}(MO_x)^{z-1} + \quad OH^{-}$$

in which MO_x^{z-} is the oxyanion adsorbed.

Adsorption can also occur due to electrostatic attraction between a charged oxide surface and an oppositely charged ion; this is referred to as non-specific or physical adsorption. The charge of the oxide surface is determined by H^+ or OH^- ions adsorbed to the surface as well as the other specifically adsorbed ions and isomorphic substitution within the crystal lattice (Stumm and Morgan, 1981). In non-specific adsorption, the sorbed ion retains its solvation shell and forms outer-sphere complexes with the oxide surface.

Although both specific and non-specific adsorption are possible mechanisms for the sequestering of metal ions, Murray and others (1968) and Gadde and Laitinen (1974) found that sorption of multivalent metal ions by hydrous iron and manganese oxide surfaces is dominated by specific adsorption. Rudin and Motschi (1983) also found many of the metal ions to form inner-sphere complexes with the oxide surface.

Since the pH of the system largely determines the nature of the oxide surface sites, both specific adsorption and electrostatic attraction of ions are extremely pH-dependent. In acidic conditions the protonated oxide surface sites, $=MeOH_2^+$ or $=MeOH$, are dominant while an increase in pH results in a corresponding increase in the activity of $=MeO^-$. The anionic oxide surface sites formed at higher pH conditions generally favor specific and non-specific adsorption of metal cations while inhibiting the sorption of oxyanions (Stumm and Morgan, 1981).

In addition to sorption processes, incorporation of metal ions into the oxide lattice may occur either through diffusion processes or coprecipitation. Following the fast initial uptake of metal ions by the hydrous iron and manganese oxides, a period of slow uptake attributed to the incorporation of the ions into the crystal lattice has been observed (Anderson and others, 1973; McKenzie, 1970). Loganathan and Burau (1973) studied the sorption of Zn^{2+} and Co^{2+} on hydrous manganese oxide and found that the metal ions not only displaced surficially bound H^+, but manganese ions in the crystal structure as well. In addition, metal ions may be physically trapped in the lattice during the precipitation of the oxides. This generally occurs when dissolved iron and manganese enter an oxidizing environment with other metal ions.

Dissolution of iron and manganese hydrous oxides and the subsequent release of associated metal ions may occur in response to a decrease in oxidation potential or pH or to an increased concentration of complexing agents in the system (Gadde and Laitinen, 1974; Suter and others, 1991). Reducing conditions result in the conversion of iron and manganese hydrous oxides to the reduced Fe^{2+} and Mn^{2+} aqueous ions, respectively. Solubilization due to reduction of the oxides may occur when iron and manganese oxides are buried beneath the oxidized/reduced boundary in the bottom sediments (Duchart and others, 1973). In addition, the decomposition of organic matter mediated by microorganisms often results in a reducing environment. During anaerobic respiration organic matter may reduce iron and manganese oxides by providing electrons and hydrogen ions (Jenne, 1968).

The effect of hydrogen ions on the dissolution of iron and manganese oxides is twofold. A decrease in pH promotes the reduction and subsequent dissolution of both iron and manganese oxides as shown by their respective reduction half-reactions:

$$Fe(OH)_{3(s)} + 3\,H^+ + e^- \text{ <----> } Fe^{2+} + 3\,H_2O,$$

$$MnO_{2(s)} + 4\,H^+ + 2e^- \text{ <----> } Mn^{2+} + 2\,H_2O.$$

Protons can also bond to the oxygen on the oxide surface enhancing the nonreductive release of Fe^{3+} or Mn^{4+} from the lattice by weakening the critical iron- or manganese-oxygen bond (Furrer and Stumm, 1986; Zinder and others, 1986). Additionally, complexing agents in the system can facilitate the nonreductive dissolution of oxides by a similar mechanism in which ligands complex iron on the oxide surface and form soluble iron ligand complexes (Zinder and others, 1986). Dissolved organics can promote the dissolution of metal oxides through this complexing mechanism (Jenne, 1977).

Organic Matter

In addition to affecting the stability of iron and manganese oxides, organic matter itself may scavenge trace metals from the aqueous environment. Organic matter, along with iron and manganese oxides, is considered to play a major role in the sequestering of trace metals (Filipek and others, 1981). Unlike iron and manganese oxides, relatively little is known about the structure of organic material in the sediment or the mechanisms by which organic matter scavenges metal ions.

Forms

Organic matter in the aquatic environment is a complex mixture of components of biological as well as of anthropogenic origin. Included in this mixture may be viable organics such as bacteria and phytoplankton and nonviable organics such as proteins, lipids and carbohydrates, as well as the broad category of humic substances (Leenheer, 1991). Reuter and Perdue (1977) estimate that 60 - 80% of the dissolved and particulate organic carbon in natural waters exists as humic substances. Humic substances can be divided into three main classes:

1) Humin: high molecular weight compounds, insoluble in aqueous solutions.
2) Humic acids: intermediate molecular size, insoluble at low pH.
3) Fulvic acids: low molecular weight, soluble over the entire pH range.

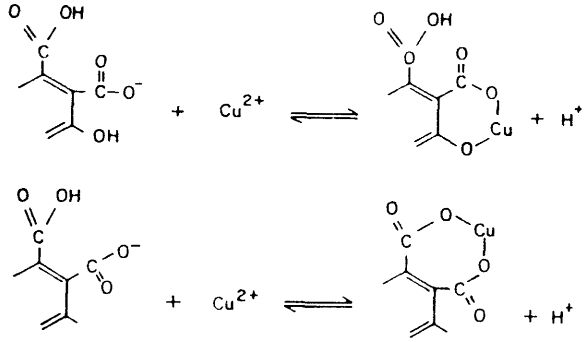
Humic substances are polyprotic acids, and their properties are largely determined by carboxylic and phenolic functional groups. In most surficial waters with a pH between 5 and 8, humic and fulvic acids exist as polyanions due to ionization of the acidic groups (Malcolm, 1985) Although humic and fulvic acids can form both soluble and insoluble complexes with multivalent cations, because of the greater proportion of acidic functional groups in fulvic acids, as well as its lower molecular weight, fulvic acid complexes are usually more soluble than humic acid complexes (Stevenson, 1985).

The nature of organic compounds in surficial waters is affected by numerous variables. Salinity, dissolved oxygen, hydrological conditions, anthropogenic inputs, and seasonal changes including temperature variations and changes in allochthonous inputs may all influence the character of organic compounds in the aquatic environment (Leenheer, 1991). According to Stevenson (1982), the inorganic substrate to which the organic coatings are bound also partly determines the nature of coatings on aquatic sediments. Humic and fulvic acids, as well as other organic matter with similar functional groups, can bind to clays weakly through van der Waal's forces, hydrogen-bonding and electrostatic attraction and strongly through coordination reactions. The latter mechanism occurs by bridging the negatively charged clay surface and the anionic organic molecule with multivalent cations. Although bridging by divalent cations such as Ca^{2+} results in weakly bound humic material, Fe^{3+} and Al^{3+} bind humic substances very strongly to the clay surface. When clay minerals are coated with hydrous oxides, humic substances can bind strongly to the oxide surfaces by coordination with iron or aluminum.

Organic matter on the Mississippi River silts and colloids has been characterized by Leenheer and others (1991). Infrared spectral data revealed that organic matter associated with the colloids is largely composed of glycolipoproteins. Scanning electron microscopy showed the presence of bacteria which are essentially glycolipoproteins. The organic material on the silt fraction is lower in lipids and higher in proteins and sugars relative to the organic matter on the colloidal fraction. Humic substances also comprise a portion of the organic matter.

Scavenging Mechanisms

The mechanisms by which organic matter in aquatic sediments scavenges trace metals are not well understood due to the physical and chemical complexity of the organic matter (Leenheer, 1991). Metal ions are most likely sorbed to the surface of the organic material. As with iron and manganese oxides, the functional groups in particulate organics can form either inner- or outer-sphere complexes with trace metals. Stevenson (1982) and Schnitzer (1969) attribute trace metal binding in humic substances to carboxylic and phenolic functional groups, especially those similar to salicylate and phthalate groups. The proposed metal-humic interaction can be viewed as follows:



Because of the large amount of proteinaceous material in the organic matter of the Mississippi River sediments, nitrogen functional groups and sulfur groups may also play a role in scavenging metal ions and binding to mineral surfaces.

As with iron and manganese oxides, the pH of the system affects the extent of trace metal ion sorption to the organic matter. Because an increase in the pH results in increased ionization of the acidic functional groups on the organic matter, the sorption of metal cations is favored at higher pH conditions.

Degradation of the organic matter and the subsequent release of bound trace metals occurs primarily through oxidation processes. Oxidizing conditions can be generated by biological activity or aeration. Organic matter can also be decomposed in anoxic conditions through biological processes.

Carbonates and Sulfides

The role of carbonates in sequestering metals has often been given little or no attention (Forstner and Patchineelam, 1980). However, in systems in which carbonates are major components of the sediments or when trace metal concentrations are high enough to saturate the other trace metal sinks, carbonates may be important in trace metal transport (Jenne, 1977). Sediments in the Mississippi River have a carbonate component due to the geology of the basin (Boyer, 1980), and the presence of calcite, dolomite, and siderite is indicated in the mineralogical analyses of several Mississippi River silts (Dunn, 1992).

Mechanisms of removing metal ions from solution include coprecipitation with carbonate minerals or exchange with calcium or magnesium ions at the carbonate surface. Additionally, as carbonate crystals grow, sorbed metals can be incorporated into the carbonate mineral. Heavy metals often form relative insoluble carbonates and may themselves precipitate as carbonates (Fergusson, 1990). Forstner and Patchineelam (1980) attributed enrichment of copper and zinc in the carbonate fraction of Rhine River sediments to their formation of discrete metal carbonate precipitates. Conditions of carbonate precipitation include the following: 1) CO_2 loss due to plant assimilation, 2) evaporation concentration, or 3) mixing of different waters (Forstner and Wittmann, 1979). Under acidic conditions carbonate minerals are generally soluble, and coprecipitated trace metals are released.

Sulfides may also play a minor role as trace metal scavengers through the precipitation of trace metal ions as sulfides. This mechanism is largely limited to reducing environments. Several trace-metal-bearing sulfide minerals of notable occurrence are galena (PbS), sphalerite (ZnS), and chalcopyrite (CuS). These metal sulfides may be an important source of trace metals in the Mississippi River system due to several adjacent mining districts, the lead-zinc mining district near Galena, Illinois and the New Lead Belt in southeastern Missouri. Galena, sphalerite, and chalcopyrite are all mined in both areas. In addition, pyrite (FeS_2) which may contain coprecipitated trace metals was identified in all three of the Mississippi River silt samples for which mineralogy was determined (Dunn, 1992). Under oxidative conditions sulfide minerals dissolve releasing associated metals.

Clays and Refractory Minerals

Although clays and refractory minerals in the sediment may contain trace metals in their structures, these components do not actively participate in the scavenging of trace metal ions from the aquatic environment (Jenne, 1977). The primary importance in metal transport is their role as a substrate onto which the other trace metal sinks, iron and manganese oxides, organic matter, carbonates, and sulfides, can attach. Clay minerals typical of the Mississippi River include smectite, kaolinite, chlorite, and mixed-layer varieties (Dunn, 1992). The XRD data on several representative mainstem silts indicated that quartz and feldspar are major sediment components as well (Dunn, 1992).

Sequential Extractions

Using total metal concentrations in sediments to assess the associated level of metal pollution assumes that all metals in the sediment are equally accessible to the environment. However, total concentrations may not be meaningful since metals incorporated into the mineral crystal lattices are usually not available for short-term chemical and physical processes. Investigators have often relied on sequential extraction techniques to evaluate the fraction of metals in a sediment sample that potentially may be remobilized into the environment due to various chemical changes occurring in the system. These extraction procedures involve applying a sequence of reagents to the sediment sample, each reagent aimed at selectively dissolving a specific component, or phase, of the sediment. Numerous schemes have been developed utilizing a wide array of extractants and conditions. Most sequential extractions involve five or six fractions in which each reagent in the sequence becomes more chemically vigorous. Fractions commonly targeted are identified as the exchangeable, carbonate, manganese and iron oxides, organic, and refractory mineral phases. In this study, a more simplistic extraction scheme is developed for determining trace metal associations on sediments in order to achieve fast and simple analysis of large numbers of samples, a realistic comparison of a wide compositional range of samples, and minimal trace metal contamination.

Although sequential extractions are widely used to identify different metal associations, considerable criticism of sequential extraction techniques is found in the literature stressing both the conceptual and operational problems associated with the procedures. Martin and others (1987) and Nirel and Morel (1990) point out that simulating conditions found in nature, weak reagents and slow reactions, with laboratory conditions, strong reagents and fast reactions, is a tenuous exercise. Operational problems include nonselectivity of extractants and redistribution of the extracted metal among the phases during the extraction. The conceptual model of sediment composed of discrete phases which may be selectively dissolved fails to consider the heterogeneity of the real sample. For example, interactions between the iron oxides and organic matter may be significant (Karlsson and others, 1987; Maher, 1984).

Various researchers have attempted to ascertain the specificity of sequential extraction schemes by studying artificially prepared and spiked soils (Kim and Fergusson, 1991; Kheboian and Bauer, 1987; Martin and others, 1987) and by tracing major cations extracted with each phase (Tessier and others, 1979; Maher, 1984). Incomplete and nonselective attack of various extractants as well as the possible formation of insoluble residues during the procedures were observed to varying degrees in all tested cases.

Redistribution of the extracted metal onto the remaining phases has also been reported to varying extents by numerous investigators. While Kheboian and Bauer (1987), Rendell and others (1980), Tipping and others (1985), and Gruebel and others (1988) found readsorption to be significant, Belzile and others (1989) argued that the reported redistribution has been overestimated because the conditions used were considerably different than those of normal extractions of natural sediment. Minimal readsorption was further supported by the results of Kim and Fergusson (1991). Although investigators disagree on the extent of the operational problems associated with sequential extractions, the general conclusion that can be drawn is that mineralogical designations to the sediment components dissolved in the individual extraction steps are largely operational in nature.

Another operational complication involves sample preparation. Concern over the effect of sample preservation, usually freeze-drying or oven-drying, on the crystallinity of the mineral phases has been voiced by Rapin and others (1986). However, phases stored in suspension may be more doubtful due to continuous aging (Kheboian and Bauer, 1987). According to Rapin and others (1986), no preservation technique tested, freeze-drying, oven-drying, freezing, or wet storage, maintains the initial partitioning of the metal.

Despite their considerable limitations, sequential extractions are still the best technology available to give insight into metal speciation on sediment particulates and to identify metal ions susceptible to short-term chemical and physical processes. The merits and usefulness of the procedure have been pointed out by various investigators (Chao, 1984; Martin and others, 1987). However, application of sequential extractions requires awareness of existing limitations, and indiscriminate use of resulting data may lead to erroneous interpretations. Consequently, the operational problems of the developed extraction procedure are investigated and evaluated in this study.

CHAPTER 2

METHOD DEVELOPMENT

The sequential extraction scheme developed for the Mississippi River sediments was designed with the following objectives. The procedure must be relatively simple and fast in order to process large numbers of samples, yet must yield useful information regarding trace metal associations in the sediments. Conventional published procedures are either single-leaching extractions which permit only limited data interpretation (Martin and others, 1987) or elaborate schemes with as many as eight steps (Miller and others, 1986) which are both time- and labor-intensive. The most widely applied extraction method is that developed by Tessier and others (1979) involving five steps and requiring approximately 24 hours to complete (Mahan and others, 1987). These complex methods can also lead to artifacts in the determination of trace metal loads since each reagent used in the extraction method can be a source of trace metal contamination. Another disadvantage of elaborate sequential extraction procedures is the difficulty of realistically comparing the detailed results for a wide compositional range of samples. Finally, the developed scheme must attempt to minimize operational problems, in particular, redistribution and reagent nonselectivity.

To meet these goals a three-step extraction was developed, fashioned after the proposed scheme of Salomons and Forstner (1980), involving both a reduction step and an oxidation step followed by a total digestion of the residual material. The procedure was designed to distinguish among the primarily inorganic, primarily organic, and refractory mineral metal associations. The inorganically bound metals as defined here include those that are loosely-held to the sediment surface (exchangeables) as well as those associated with carbonate minerals, manganese oxides, and amorphous iron oxides. Included in the definition of organically bound metals are those associated with oxidizable sediment components, largely organic matter as well as some sulfides. The residual phase associated metals are those incorporated in refractory minerals such as silicates. However, as previously noted, distinctions among individual components of real sediments are not clear, making mineralogical assignments to the extraction steps largely operational.

Extractants

Inorganic Fraction: After a review of the literature, 0.25 M hydroxylamine·HCl in 0.25 M hydrochloric acid was chosen to dissolve the inorganic components. The hydroxylamine reagent releases exchangeable metal ions due to its high ionic strength and dissolves carbonates as a result of acidification. The solubility of manganese oxides in hydroxylamine·HCl is well known (Canney and Nowlan, 1964; White, 1969). Manganese oxides are more soluble than amorphous iron oxides and are often selectively extracted using 0.1 M hydroxylamine·HCl in 0.01 M HNO_3 (Chao, 1972; Chao and Theobald, 1976). Consequently, the more vigorous conditions used in this procedure result in effective dissolution of manganese oxides by reducing MnO_2 to Mn^{2+} by the following reaction:

$$MnO_{2(s)} + 4\,H^+ + 2e^- \longleftrightarrow Mn^{2+} + 2\,H_2O, \quad E^o = 1.22\ V,$$

$$2NH_3OH^+ \longleftrightarrow N_2 + 2e^- + 4H^+ + 2H_2O, \quad E^o = 1.87\ V,$$

i.e.,

$$MnO_{2(s)} + 2NH_3OH^+ \longrightarrow Mn^{2+} + N_2 + 4\,H_2O, \quad E^o = 3.09\ V.$$

In the case of amorphous iron oxides, 0.25 M hydroxlamine·HCl in 0.25 M HCl at 50^oC has been reported by Chao and Zhou (1983) to be the preferred reagent for dissolution of amorphous iron oxides due its efficiency and selectivity. Only minor dissolution of the crystalline iron oxide was observed (<1% of total iron) thereby isolating the scavenging impact of the more active amorphous forms. The general reduction reaction of iron oxides may be expressed as follows:

$$2Fe(OH)_{3(s)} + 2e^- + 6H^+ \longleftrightarrow 2Fe^{2+} + 6H_2O, \qquad E^o=1.06\ V,$$

$$2NH_3OH^+ \longleftrightarrow N_2 + 2e^- + 4H^+ + 2H_2O, \qquad E^o=1.87\ V,$$

i.e.,

$$2Fe(OH)_{3(s)} + 2NH_3OH^+ + 2H^+ \longleftrightarrow 2Fe^{2+} + N_2 + 8H_2O, E^o=2.93\ V.$$

Organic Fraction: An oxidizing agent is commonly used to decompose organic material associated with the sediment thereby releasing associated trace elements. The oxidizing reagent chosen was 0.17 M potassium persulfate in 0.2% (v/v) sulfuric acid. While persulfate has not commonly been employed in extraction schemes, it has been used in standard wet-ashing methods for the determination of organic carbon (U.S. Geological Survey Techniques of Water-Resources Investigation, 1983). The disadvantages of the more widely used acidified hydrogen peroxide are the incomplete oxidation of organic materials (Farmer and Mitchell, 1963) and the rather lengthy reaction time of 5 hours required. Other oxidizing reagents employed, mainly hypochlorite (Hoffmann and Fletcher, 1981) or pyrophosphate (Learned and others, 1981; Eisenreich and others, 1980), not only suffer from lengthy extraction times but involve high pH conditions as well, resulting in possible precipitation of released metal ions (Miller and others, 1986).

Considerably faster reaction times for the complete oxidation of organic material in fresh water by persulfate have been reported by Goulden and Anthony (1978) when reaction conditions are optimized. These optimal conditions include an acidic pH range and an excess of persulfate. The concentration of 0.17 M represents the maximum $K_2S_2O_{8(s)}$ that easily dissolves in water. Under acidic conditions, the persulfate oxidation reaction for an organic compound represented by the simple CH_2O molecule may be expressed as follows:

$$2S_2O_8^{2-} + 4e^- + 4H^+ \longleftrightarrow 4HSO_4^- \qquad E^o=2.123V$$

$$CH_2O + H_2O \longleftrightarrow CO_2 + 4e^- + 4H^+ \qquad E^o=0.083V$$

i.e.,

$$CH_2O + 2S_2O_8^{2-} + H_2O \longrightarrow CO_2 + 4HSO_4^- \qquad E^o=2.206V.$$

Residual Fraction: Dissolution of the remaining silicates and other refractory minerals usually involves either decomposition by thermal fusion with alkali fluxes or dissolution by a combination of strong mineral acids. Although fusion is effective, large excesses of alkali salts must be added to the sample introducing the possibility of matrix effects and contamination when analyzing the resultant solutions for trace metals (Tessier and others, 1979). Digestions by acids typically employ hydrofluoric acid along with a combination of hydrochloric, nitric, sulfuric, or perchloric acid to dissolve silicates. The specific reagents chosen for the digestion were hydrofluoric, nitric, and hydrochloric acids (Nadkarni, 1986).

Acid digestions on a conventional hot plate require constant operator attention to prevent evaporation to dryness or boiling-over losses and require considerable time. Mahan and others (1987) estimate dissolution time for 200 mg sediment samples to be about 4 hours. Microwave digestion techniques, on the other hand, have been shown to be fast, efficient decomposition procedures for most geological samples (Lamothe and others, 1986; Revesz and Hasty, 1987; Matthes and others, 1983; Nadkarni, 1986). In addition to the rapid rate of microwave heating, use of sealed microwave digestion vessels results in considerably higher temperatures than the atmospheric boiling point of the mineral acid mixture, retention of volatile elements such as mercury and cadmium, and decreased potential for air-borne contamination of the sample (Neas and Collins, 1988). These advantages make the microwave oven approach ideal for use in the residual digestion step of the sequential extraction scheme.

After the digestion, excess HF must be removed from the sample digest before analysis of the trace metals since HF attacks the sample introduction components of the inductively coupled plasma instruments. This HF removal may be carried out by evaporation in the presence of either sulfuric or perchloric acid or by the addition of boric acid to convert HF to inactive fluoroboric acid. The latter technique was used since it requires less time and attention.

Extraction Conditions

The outcome of an extraction scheme is affected by specific operating conditions: the temperature, solid-solvent concentration ratio, and duration of the extraction. Consequently, each parameter chosen operationally defines the sequential extraction scheme and has been optimized in arriving at the final procedure. Since practical considerations prohibit method optimization for every sediment sample collected for analysis, the extraction procedure has been developed and assessed using a few representative sample types and reference standards composed of similar material.

The temperatures for the hydroxylamine and persulfate extractions were based on those recommended in the literature. Chao and Zhou (1983) studied the hydroxylamine dissolution at $50^{o}C$ and $70^{o}C$ and concluded that $50^{o}C$ provides more selectivity in dissolving amorphous iron oxides than 70°C. In the case of the persulfate extraction, 95°C was chosen to optimize the rate of oxidation. Above 100°C the thermal decomposition of persulfate slows the oxidation reaction (Goulden and Anthony, 1978).

The volume of reagent used to extract the sediment sample must be large enough to insure that during the course of the extraction, the concentration of the extractant does not significantly change and the pH remains relatively constant (Beckett, 1989). For the inorganic extraction, the ratio recommended by Chao and Zhou (1983) is 25 mL of 0.25 M hydroxylamine hydrochloride/0.25 M HCl for a 100 mg sediment sample. Preliminary calculations considered sediment containing the highest concentrations of carbonates and manganese and iron oxides expected in our study using existing data on Mississippi River sediments as a compositional guideline. Using the maximum values of approximately 9% total iron and 0.3% total manganese (Young, 1991) and assuming a worst case scenario in which all of the iron and manganese exist as amorphous oxides, the number of moles of hydroxylamine used for the extraction exceeded the maximum moles consumed by at least a factor of 30. A maximum value of 2.5% carbonate carbon in the Mississippi River sediments (J.A. Leenheer, unpub. data, 1993) results in at least a fifteen fold excess of acid. The pH of the extractant was monitored during the course of the sample digestion and remained below pH 1 for the duration of the extraction.

In the case of the organic fraction, the volume chosen was based on the maximum percent organic carbon value of approximately 10% reported for the Mississippi River silts and bed sediments (Leenheer, 1993). A volume of 12.5 mL 0.17 M $K_2S_2O_8$ yields a stoichiometric ratio of 2.6 mole $K_2S_2O_8$/ mole organic carbon which should result in a complete reaction according to Goulden and Anthony (1978). In addition, this volume gives adequate head space in the 30 mL digestion tubes to allow for the evolution of gases. The pH of the persulfate solution never exceeded 3 throughout the duration of the sample extraction. In the case of Mississippi River colloidal material, the percent organic carbon is considerably higher than that of the silts or bed sediments, occasionally as high as 30% in the upper reaches of the river (Leenheer and others, 1993). To completely oxidize organic material in these sediments multiple persulfate extractions were necessary.

Optimal times of the hydroxylamine and persulfate extractions were determined by measuring the concentrations of major, minor, and trace elements of interest in the supernatant of a representative mainstem Mississippi River sediment at successive extraction time intervals. When the rate curve reached a plateau, the extraction was considered to be complete. The rate curves for calcium, magnesium, manganese, iron (Fig. 1a and 2a) and the trace metals, cobalt, copper, lead, and zinc (Fig. 1b and 2b), leveled by 40 minutes for the hydroxylamine extraction at 50°C and by 60 minutes for the persulfate extraction at 95°C. However, the iron and magnesium curves for the persulfate extractions had slight positive slopes throughout the time interval, meaning that iron and magnesium were still being removed from the sediment. Mahan and others (1987) observed similar rate curves suggesting that while efficient separation of minor and trace elements are obtained, major components, iron and magnesium in this case, may continue to be leached because of possible attack on the remaining phases. Although the other trace elements extracted leveled during the time interval studied, copper appeared to exhibit a slightly positive slope during the entire course of the persulfate extraction indicating that copper was still being solubilized. Without the corresponding organic carbon data for successive time intervals, it is difficult to ascertain whether or not oxidation of all organic material during the persulfate extraction was complete. A possible explanation is that copper may be associated with organic material or sulfides which are

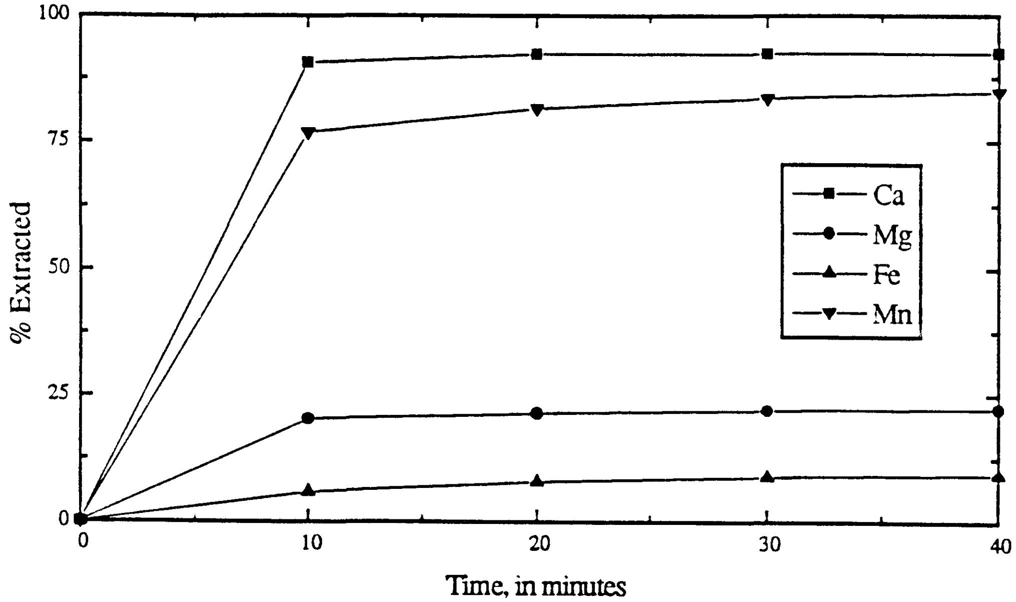


Figure 1a. Hydroxylamine extraction rate curves for calcium, magnesium, iron, and manganese.

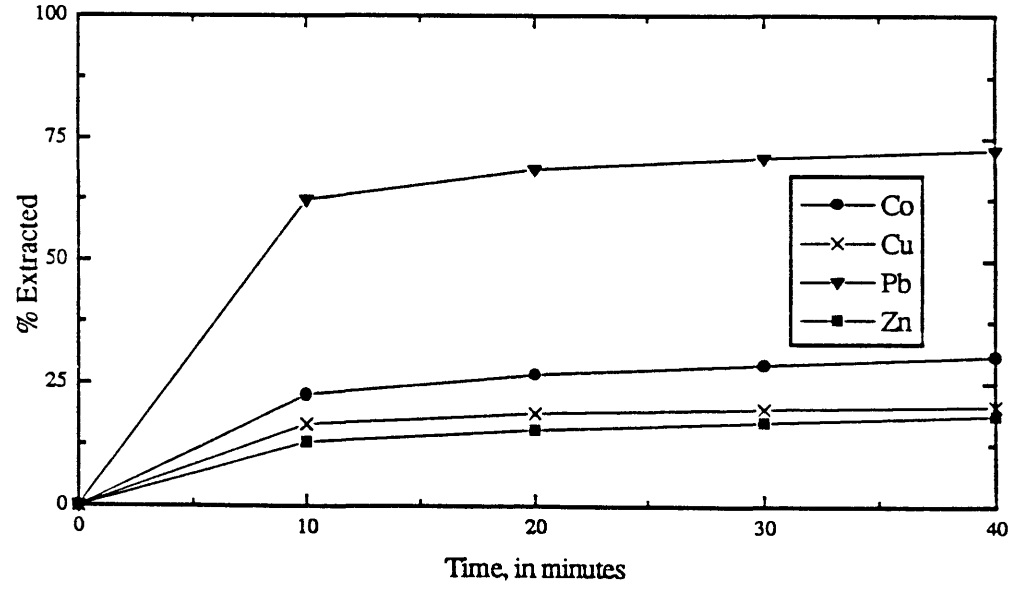


Figure 1b. Hydroxylamine extraction rate curves for cobalt, copper, lead, and zinc.

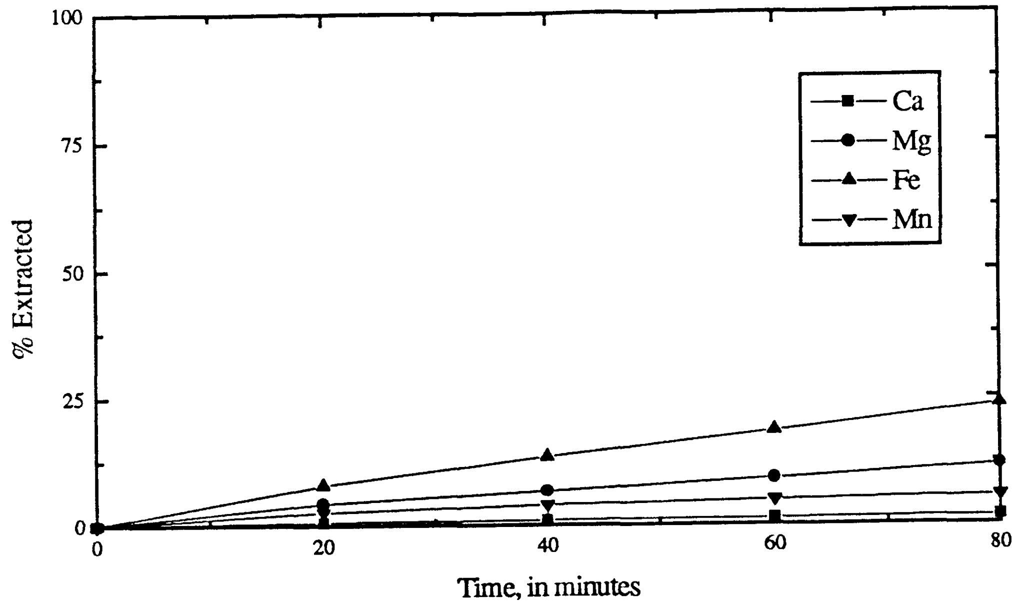


Figure 2a. Persulfate extraction rate curves for calcium, magnesium, iron, and manganese.

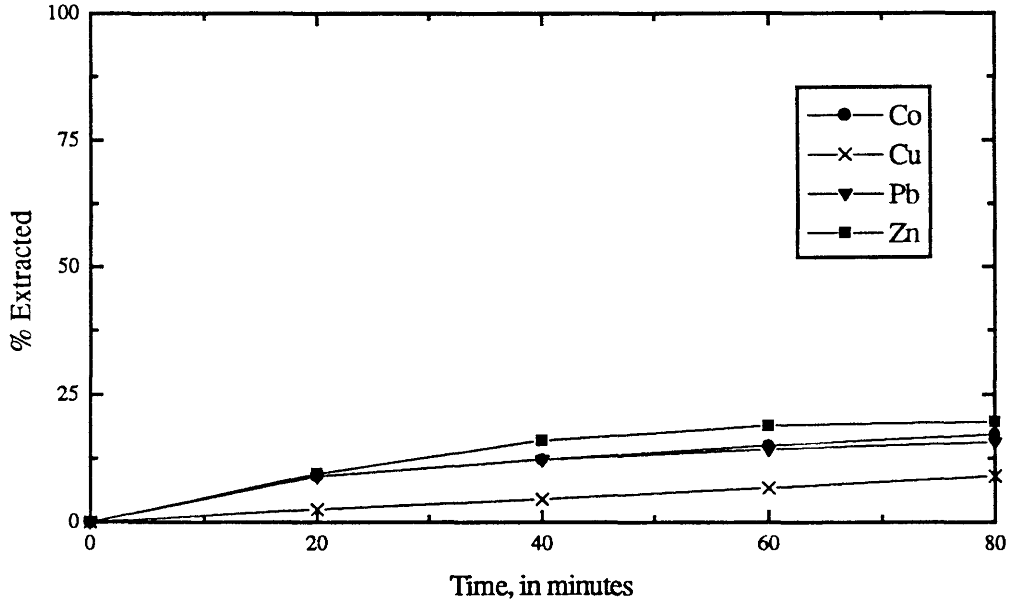


Figure 2b. Persulfate extraction rate curves for cobalt, copper, lead, and zinc.

more resistant to oxidation or with other resistant minerals, while the other trace metals are associated with the easily and moderately oxidizable organics.

The initial time chosen for the microwave digestion was 3 minutes at 630 W (Nadkarni, 1984). However, the presence of solids after 3 minutes prompted an additional 3 minute digestion. Although the second digestion dissolved more of the residual phase, black particulates formed a ring on the wall of the Teflon centrifuge tubes. This substance was slightly soluble in sulfuric acid and analysis by inductively coupled plasma-mass spectroscopy (ICP-MS) confirmed it to be a titanium-containing phase. Nadkarni (1984) also reported the existence of a titanium mineral in sediments not attacked by the acid mixture. To examine the assumption that no appreciable trace elements were associated with these black particles, the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2704 Buffalo River sediment, was digested under the specified conditions. Despite undissolved black particulates in the sample, recoveries for all elements analyzed were within reported uncertainty limits with the exception of titanium and silicon which were low (see Table 1). Cobalt was greater than the certified value, possibly due to a mass spectral interference from the borate molecular ion (58 amu) in the digestion matrix.

A schematic of the final sequential extraction procedure is shown in Figure 3, and the detailed extraction scheme is outlined in the following section.

Table 1. Comparison of certified values, total digest concentrations, and the sum of the extract concentrations for NIST SRM 2704 Buffalo River sediment.

[The uncertainty represents 1 standard deviation of the analysis of 4 samples for the total digest values and 19 samples for the sum;---- indicates concentrations below detection limits in the individual extracts.]

	Concentration (microgram per gram)		
Element	Certified	Total digest	Sum
Aluminum	61100 ± 1600	60300 ± 200	50600 ± 3200
Barium	414 ± 12	424 ± 29	388 ± 14
Cadmium	3.45 ± 0.22	3.56 ± 0.08	---- ± ----
Calcium	26000 ± 300	26600 ± 2000	26000 ± 2000
Chromium	135 ± 5	138 ± 10	120 ± 8
Cobalt	14.0 ± 0.6	21.9 ± 4.0	13.5 ± 0.8
Copper	98.6 ± 5.0	92.0 ± 4.2	113.5 ± 6.8
Iron	41100 ± 1000	42200 ± 4600	40200 ± 2600
Lead	161 ± 17	130 ± 17	141 ± 8
Magnesium	12000 ± 200	11800 ± 200	11700 ± 480
Manganese	555 ± 19	561 ± 33	554 ± 31
Silicon	290800 ± 1300	161000 ± 14000	144200 ± 11000
Titanium	4570 ± 180	2600 ± 600	1980 ± 350
Vanadium	95 ± 4	90 ± 5	82 ± 4
Zinc	438 ± 12	446 ± 36	447 ± 27

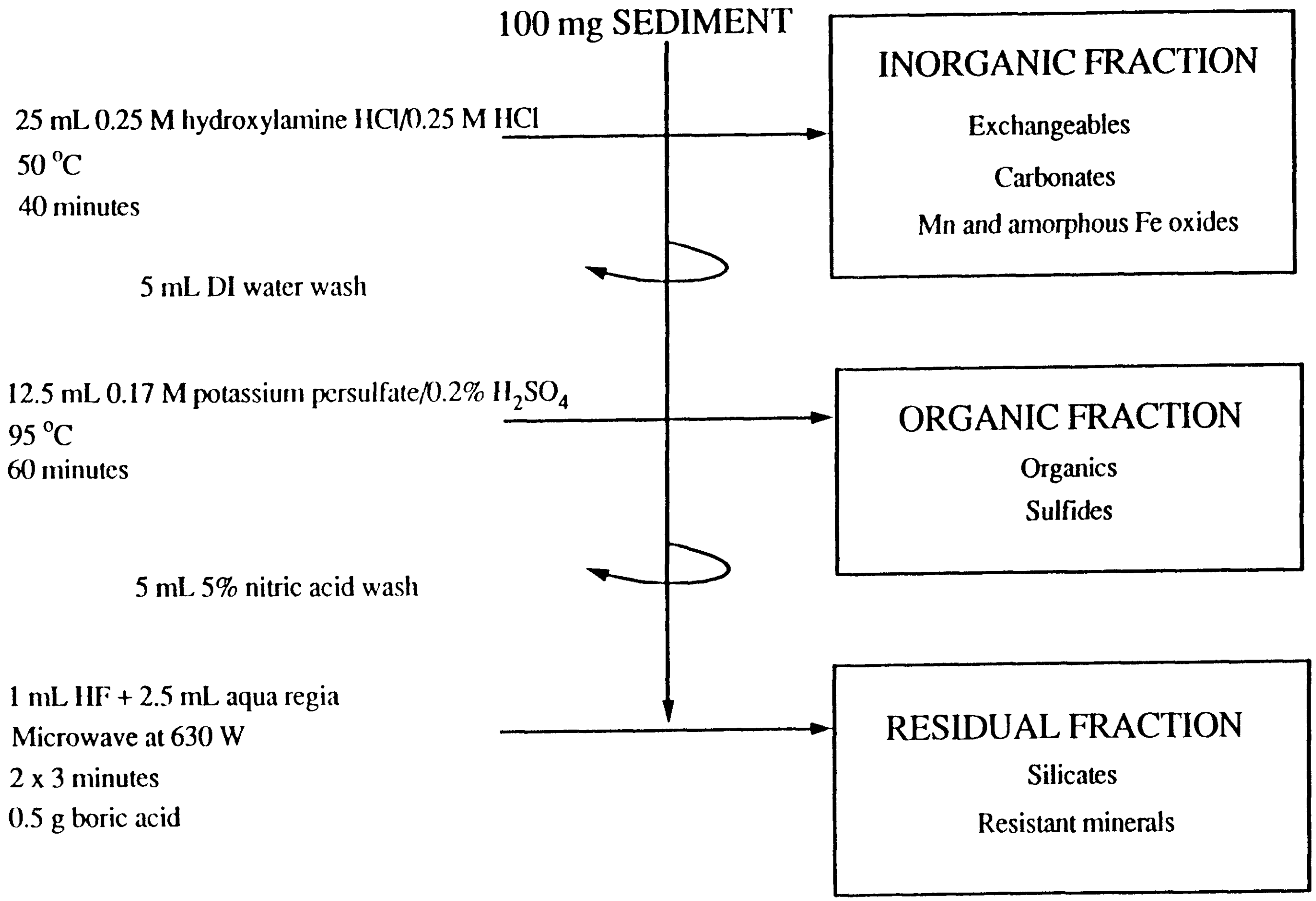


Figure 3. Sequential extraction schematic diagram.

Extraction Procedure

Sample Collection and Preparation: Silt-size (1 - 63 μm) and colloidal-size (0.005-1 μm) suspended sediment from the mainstem Mississippi River and its principal tributaries, the Minnesota, Illinois, Missouri, and Ohio Rivers, were collected using depth-integrated sampling techniques as described by Meade and Stevens (1990). Approximately 100 L of raw river water was collected and processed to separate the suspended sediment into two size fractions using continuous-flow centrifugation to isolate the silt-size material, followed by tangential flow ultrafiltration to isolate the colloidal-size fraction. Processing details can be found in Leenheer and others (1989). Suspended sediment from the smaller tributaries was collected by grabbing 40 L from the surface. The silt and colloid fractions were not separated. The collected sediment was concentrated into approximately 1 L of processed water and frozen for shipping and storage. Prior to extraction, the samples were thawed, centrifuged to remove the excess water, and freeze-dried (Brinton and others, 1993). The dried sample was then gently ground with an agate mortar and pestle to insure homogeneity. To obtain a representative subsample, the sediment was "coned and quartered" on a Teflon sheet (Reeves and Brooks, 1978). Precisely weighed samples of approximately 100 mg were placed into 30 mL Teflon centrifuge tubes.

Bed sediment cores from the Mississippi River above St. Louis were collected along transects in the shallow pools formed behind each dam. Details concerning the collection of the bed sediments is outlined in Moody and Anderson (1993). The top 2 centimeters of each core in a given pool were combined, sieved through a 2 millimeter nylon mesh screen, dewatered through centrifugation, coned and subsampled. More complete processing details are found in Brinton and others (1993). Bed sediment samples were not freeze-dried and sample dry weights were determined on separate samples. Because no attempt was made to separate particle sizes, the bed sediment samples contained a mixture of sand, silt, and colloidal size particles.

Procedure: To each of the samples, 25 mL 0.25 M $NH_2OH{\cdot}HCl$/0.25 M HCl was added. Sample centrifuge tubes were capped and placed in a 48-50°C water bath with an ultrasonic probe immersed in the bath for agitation. After 40 minutes the samples were removed from the bath and centrifuged at 17,000 x g and 0-5°C for 30 minutes. Following centrifugation, the supernatant was transferred with a pipette to a class A 50 mL glass volumetric flask. (All glassware used in the extraction procedure was leached in 10% HCl / 10% HNO_3 for 24 hours and rinsed with deionized (DI) water prior to use.) To wash the remaining solid, 5 mL DI water was added to the sample. After another 30 minutes of centrifugation, the DI wash was combined with the hydroxylamine extract in the volumetric flask and diluted to the 50 mL mark with DI water.

Next, 12.5 mL 0.17 M $K_2S_2O_8$ / 0.2% H_2SO_4 was added to the sample residue, the centrifuge tube capped and placed in a 90-95°C water bath while using ultrasonification for 1 hour. The sample was then centrifuged at the previously specified conditions. After 30 minutes in the centrifuge, the persulfate supernatant was transferred to a 50 mL volumetric flask. To minimize subsequent adsorption of released metals back onto the oxidized sediment surface, the sample residue was then washed with 5 mL of 5% HNO_3 (Wilbur and Hunter, 1979) and centrifuged. The nitric acid wash was added to the persulfate extract, and the solution was diluted to the 50 mL mark with 5% HNO_3 to prevent any precipitation of metal ions.

Finally, 1 mL HF and 2.5 mL aqua regia were added to the remaining sample residue. The centrifuge tube with a vented cap was placed inside a Teflon microwave digestion vessel. The sample was heated in a CEM MDS-81D microwave for 3 minutes at 630 W. To prevent the digestion vessel from venting acid fumes and losing volatile metals, the sample was allowed to cool in the microwave before heating a second time for another 3 minutes. After the sample had cooled from the second heating and was no longer under pressure, the centrifuge tube was removed from the digestion vessel and 0.5 g boric acid was added to the digest. To dissolve the boric acid, the sample was warmed in a water bath (~50°C) for about 30 minutes. Finally, the digest was filtered through a 0.4 μm acid rinsed Nuclepore filter and brought to volume in a 50 mL volumetric flask with DI water.

The sample extracts were transferred from the glass volumetric flasks to pre-cleaned 60 mL polyethylene bottles to await analysis using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-MS. Concentrations of major and minor metals (>500 μg/L) were determined on each of the extracts using a Jarrell-Ash AtomComp Model 975 ICP-AES, while trace metal concentrations less than 500 μg/L were typically determined using a Sciex Elan Model 250 ICP-MS. All standards were matrix-matched to the sample extracts to correct for spectral interferences. (Detection limits for trace metal determinations are tabulated in the Appendix in Table A-1.) System operating conditions used are outlined in Garbarino and Taylor (1979; 1993) with several modifications. To maximize the signal to background intensity ratios for the extracts on the ICP-AES, incident RF power was decreased from 1.25 to 0.9 kW. The ICP-MS operating conditions were modified by increasing the rinse time between samples from 100 to 150 seconds and the read delay time from 50 to 55 seconds to minimize any contamination from previously analyzed extracts.

The chemicals employed in the extractions were of 99.9% purity or better, and the nitric acid was prepared using an isopiestic distillation method (Kuehner and others, 1972). To remove trace amounts of lead in the potassium persulfate reagent solution, the solution was eluted through a Chelex 100 column before acidification with sulfuric acid. Analyses of reagent and process blanks by ICP-AES and ICP-MS revealed no significant metal contamination. Trace metal concentrations for process blanks are tabulated in the Appendix in Table A-2. To insure consistency, fresh reagents were prepared prior to each set of extractions.

Evaluation

An important aspect in the development of an extraction scheme is to evaluate its accuracy and precision. Unfortunately, no sediment reference material exists in which the mineralogical phases and their associated metals are known. Despite this limitation, the accuracy of the extraction technique may be evaluated to some degree by examining the extent of redistribution of metals during the extraction steps, the selectivity of the reagents, and the mass balance of extracted metals.

Redistribution

To evaluate the degree of redistribution of extracted metal ions to the remaining sediment, a spike of 10 μg/L cadmium, chromium, cobalt, copper, lead, and zinc was added to the hydroxylamine and persulfate reagents during the extraction of a representative Mississippi River sediment. A spike concentration of 10 μg/L (5 μg/g) represents a realistic concentration of trace metals solubilized during the course of the extraction of the river sediments. The results of the redistribution experiment are shown in Figures 4a and 4b. The average recovery of spiked metal ions was essentially 100%

within the analytical precision obtainable, indicating that redistribution was not apparent for either extraction step. The high chromium spike recoveries in the persulfate extraction may be partly a result of mass spectral interferences by persulfate-derived $^{34}S^{18}O$ and $^{36}S^{16}O$ ions. Since both analytical methods rely on matrix matching to correct for spectral interferences, the degree of success depends on how well the blank and calibration standard matrices match the samples.

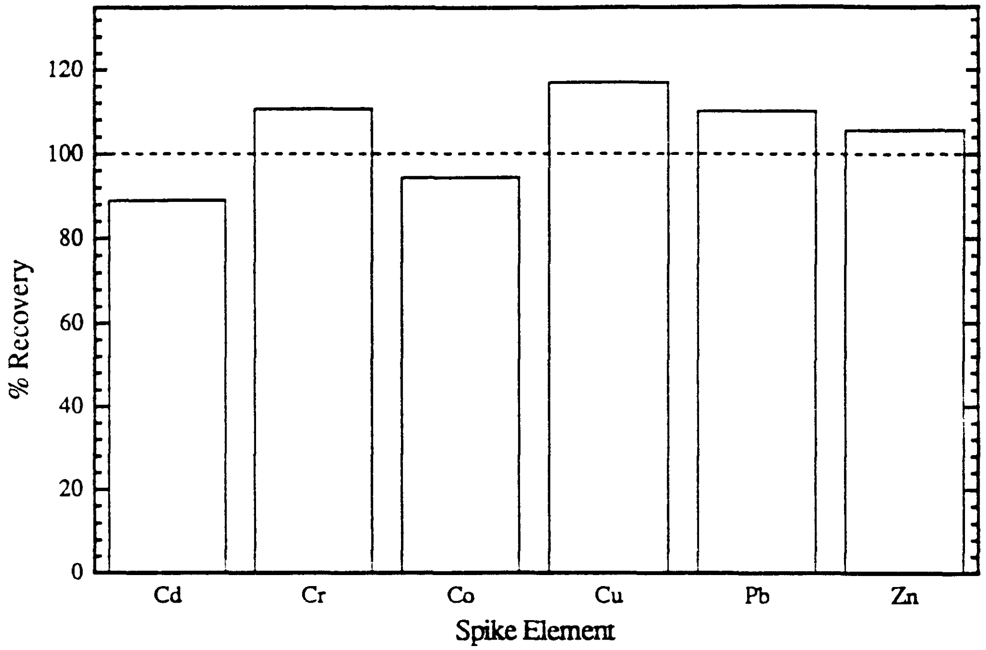


Figure 4a. Recovery of 10 μg/L trace metal spike for hydroxylamine extraction.

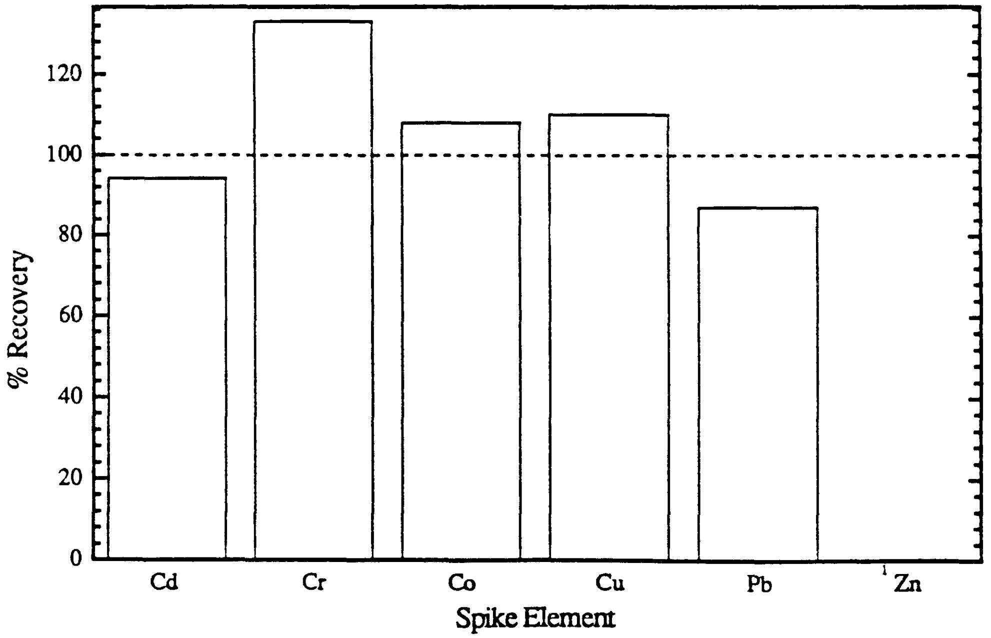


Figure 4b. Recovery of 10 μg/L trace metal spike for persulfate extraction.
[1] Zinc is near its detection limit of 8 μg/L in the persulfate matrix.

Specificity

In order to be a useful tool in examining metal associations, the extraction scheme must attempt to target the phase of interest without significant dissolution of the remaining sediment components. A reagent's selectivity may be assessed by monitoring the solubilization of elements which are a major phase component. For example, the dissolution of a silicate crystal lattice by the reagent may be estimated by the concentrations of silica and aluminum in the leachates since these elements reside predominantly in the residual fraction as refractory minerals. Silica and aluminum data obtained from the proposed extraction scheme show that dissolution of the crystal structure by the hydroxylamine and persulfate reagents is minimal. In the case of the hydroxylamine extraction, an average of less than 3% of the total measured silica and less than 5% of the total aluminum were leached from the Mississippi River silts and colloids. The more aggressive conditions of the persulfate extraction resulted in a slightly higher average percentage of approximately 7% of the total aluminum and 5% of the total measured silica extracted.

Approximately 92% of the total calcium was released in the hydroxylamine extraction compared to 3.5% released in the persulfate extraction, indicating that the hydroxylamine reagent effectively attacks carbonate minerals since calcium most likely exists primarily as carbonates in these samples. In addition, 92% of the total manganese was extracted by the hydroxylamine reagent with 2% solubilized by the persulfate extraction. This suggests that manganese oxides are efficiently dissolved under the reducing conditions of the hydroxylamine extraction. In contrast, iron does not exhibit a clear association with the hydroxylamine phase with an average of approximately 24% of the total iron in the hydroxylamine extractant and 16% in the persulfate extractant. At first glance, this may appear to be a problem since the hydroxylamine reagent should efficiently dissolve the amorphous iron oxides. The occurrence of pyrite in the Mississippi sediment (Dunn, 1992) may account for a portion of the iron released since pyrite is oxidized by the persulfate. In addition, the iron distribution possibly reflects the fact that the iron and manganese oxide fraction and the organic fraction may not be clearly differentiated, especially in the case of organic rich sediments. Organic coatings on iron and manganese oxides and complexation of iron with organics could explain the release of iron in the persulfate oxidation (Maher, 1984). This complication serves to emphasize the operationally-defined nature of sequential extractions.

Unfortunately no data on the effect each reagent has on sediment bound organic matter were obtained. Measurement of organic carbon on the residual material after the hydroxylamine and persulfate extraction is necessary to fully determine the specificity of the extractions.

Mass Balance

To insure that a mass balance of the extracted metals was obtained during the sequential extraction procedure, concentrations of the metals in the total digest were compared to the sum of the concentrations in the hydroxylamine extraction, the persulfate extraction and the residual digestion. The results of 15 Mississippi River sediment samples are shown in Table 2. The sum divided by the total yields a value of between about 95 and 120 percent for all the elements analyzed with the exception of silicon. In addition, the NIST SRM 2704 Buffalo River sediment sum of extracted element concentrations was compared to the total digest concentrations as well as to the certified values. The results, tabulated in Table 1, show that with the exception of aluminum, silicon, and titanium, there is close agreement between values with the total digest and sum of the three extract concentrations, generally within reported uncertainty limits of the certified value.

Precision

To evaluate the precision of the sequential extraction, a NIST SRM 2704 Buffalo River sediment sample was extracted along with each set of sample extractions. These samples were extracted and analyzed over the course of four consecutive months. The resulting precision of each of the extraction steps represents the variability associated with the entire process, from subsampling and extracting the sediment to the analysis of the sample extracts. The precision obtainable in the hydroxylamine extraction is generally less than 15% relative standard deviation (see Table 3), although considerable variations in silicon and vanadium are apparent. The concentration of vanadium in the hydroxylamine extract is very near its detection limit by ICP-AES, explaining its large relative standard

Table 2. Mass balance results of sequential extractions.

[Sum is the summation of the concentrations in the hydroxylamine, persulfate, and residual extracts; total is the concentration in the total digest of the sample; the uncertainty represents 1 standard deviation of 15 Mississippi River samples.]

Element	Sum/Total (%)
Aluminum	98 ± 2
Barium	96 ± 2
Calcium	103 ± 5
Chromium	107 ± 6
Copper	120 ± 11
Iron	104 ± 1
Lead	112 ± 3
Magnesium	99 ± 1
Manganese	98 ± 2
Silicon	135 ± 4
Vanadium	99 ± 2
Zinc	115 ± 10

Table 3. Precision of sequential extractions of NIST SRM 2704 Buffalo River sediment.

[Statistics are based on 19 samples; RSD is the relative standard deviation.]

	HYDROXYLAMINE			PERSULFATE			RESIDUAL		
Element	Average (µg/g)		RSD (%)	Average (µg/g)		RSD (%)	Average (µg/g)		RSD (%)
Aluminum	1310	±	12	4300	±	30	45000	±	6
Barium	57	±	10	7	±	26	324	±	4
Calcium	23800	±	8	375	±	80	2100	±	3
Chromium	27.3	±	11	39.6	±	17	52.9	±	4
Cobalt	2.8	±	8	4.4	±	16	6.3	±	6
Copper	55.7	±	13	22.7	±	14	35.1	±	12
Iron	6200	±	7	11000	±	22	23000	±	4
Lead	122	±	7	8.7	±	10	10.1	±	10
Magnesium	4670	±	8	1650	±	14	5400	±	4
Manganese	300	±	8	54	±	20	200	±	7
Silicon	950	±	32	4200	±	23	139000	±	8
Vanadium	4	±	25	6	±	33	72	±	8
Zinc	270	±	8	69	±	13	108	±	12

deviation. The precision obtainable in the persulfate extraction is generally lower than that of the hydroxylamine extraction with the relative standard deviation typically between 10 and 20%. The large variabilities of barium, calcium, and vanadium are most likely due to their low levels in the persulfate extract, near their detection limits by ICP-AES. In the case of the residual fraction, the relative standard deviation is 12% or less for all the elements analyzed.

Although the scheme does not overcome the operationally defined nature of sequential extractions, evaluation of the procedure indicates no apparent redistribution of metal ions during the extraction and minimal attack of the refractory minerals by the hydroxylamine and persulfate reagents. The mass balance evaluation shows that the procedure results in neither significant loss nor gain of extracted metals. In addition, precision data show that the relative standard deviation obtainable for each extraction step is relatively low considering the many sources of variability in the entire procedure.

CHAPTER 3

RESULTS AND DISCUSSION

Silts and Colloids

The developed sequential extraction method was applied to silts and colloids collected at sites on the Mississippi River and selected tributaries shown in Figure 5 on three sampling trips over the course of two years. Flow profiles for the Mississippi River and major tributaries for each sampling trip are shown in Figure 6 (Moody and Meade, 1993). The summer cruise, July-August 1991, took place during high flow conditions in the upper section of the Mississippi River due to local precipitation events and low flow conditions in the lower stretch of the Mississippi River. The late fall cruise, October-November 1991, was during low flow conditions for the entire Mississippi River. For the final cruise in April-May 1992, the upper stretch of the Mississippi River had flows similar to those of the October-November 1991 trip, but the Mississippi River below the Iowa River confluence had high flow conditions due to several run-off events.

Silt and colloid concentrations at each sampling site for the three cruises are shown in Figure 7. Both the silt and colloid concentrations increase downriver with the silt fraction composing approximately 80-95% of the total suspended sediment concentration. The increase of suspended sediment concentrations from the upper to the lower segment of the Mississippi River is largely due to hydrological differences between the two river sections. While the Mississippi River above St. Louis, MO is a series of shallow pools

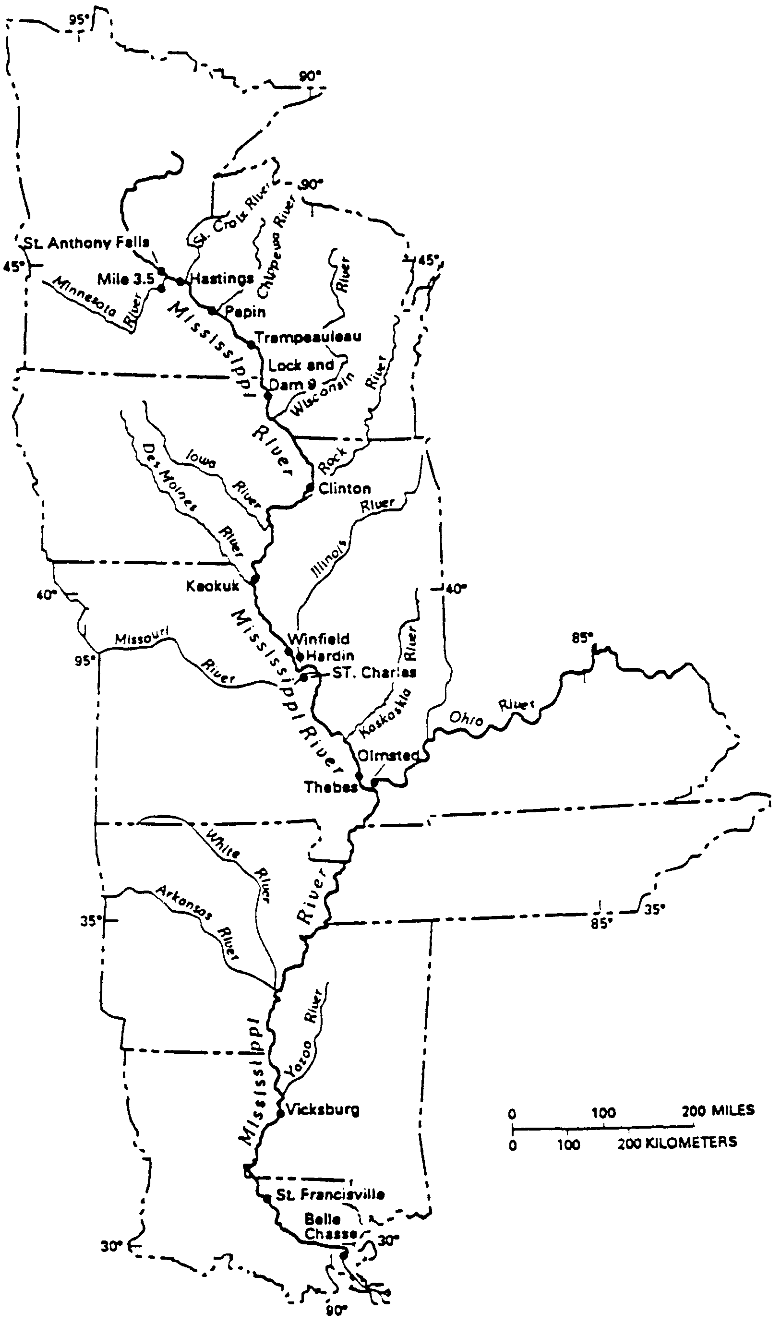


Figure 5. Sampling sites on the Mississippi River and tributaries.

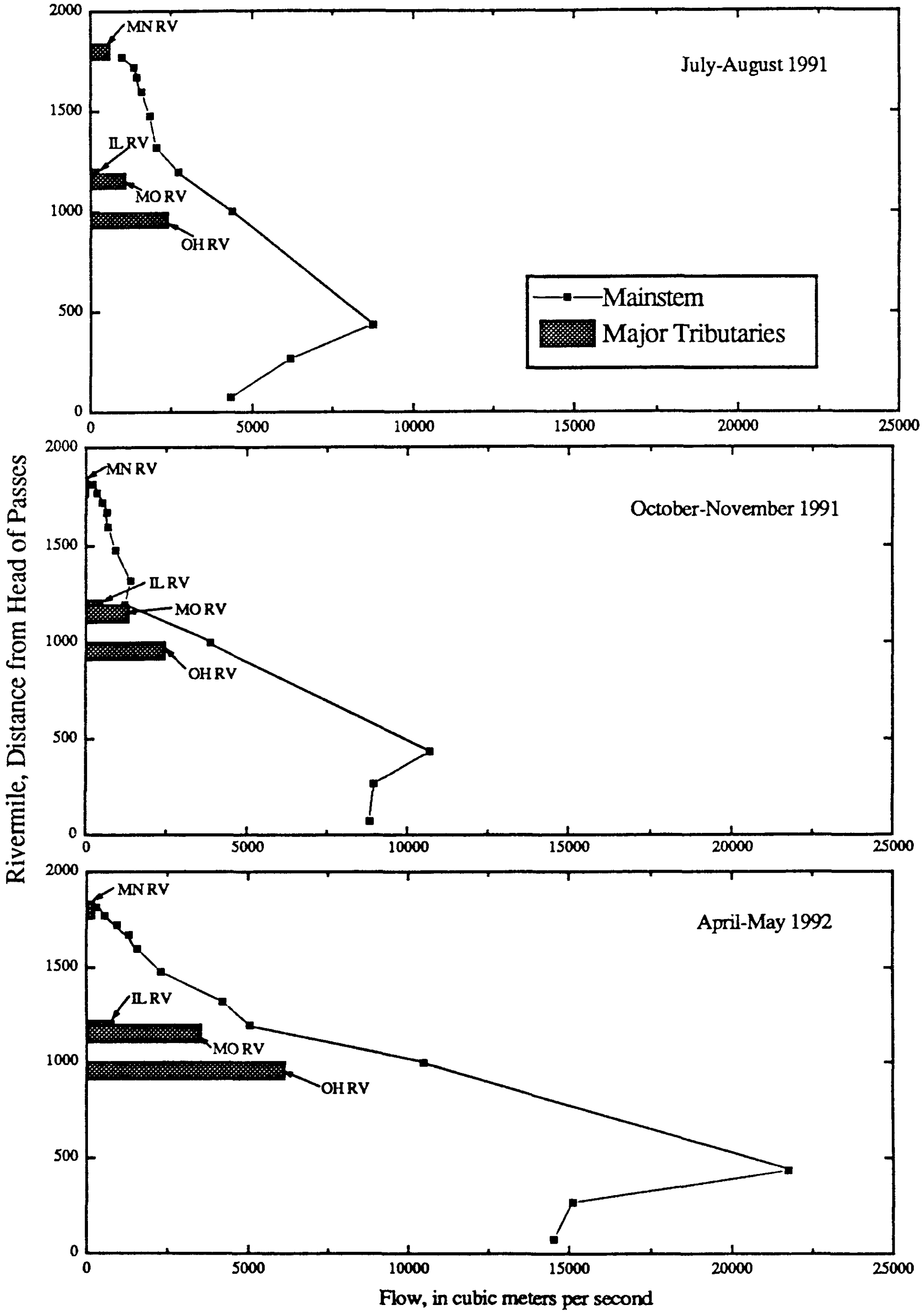


Figure 6. Flow profiles for Mississippi River and major tributaries for July-August 1991, October-November 1991, and April-May 1992 sampling cruises.

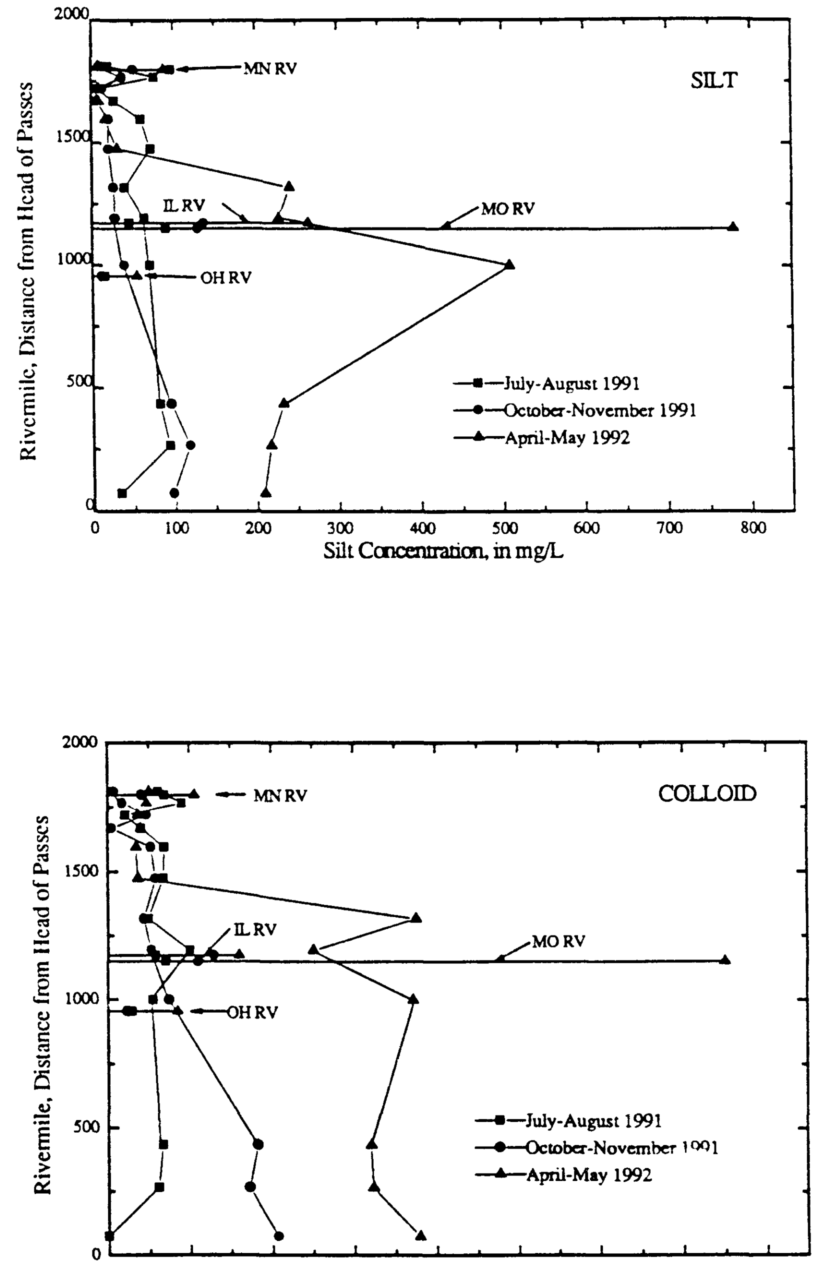


Figure 7. Silt and colloid concentrations in the Mississippi River and major tributaries for July-August 1991, October-November 1991, and April-May 1992 sampling cruises.

created by an extensive system of locks and dams, the Mississippi River below St. Louis, MO is a free-flowing river. Because locks and dams hinder the normal flow of the river much of the suspended sediment is deposited in the pools that form behind the dams resulting in lower suspended sediment concentrations (Nielsen and others, 1984). In contrast, the Mississippi River below St. Louis, MO flows unimpeded and is fed by several major tributaries which increase the sediment load in the lower river considerably, the most significant of which is the Missouri River.

Suspended sediment loads expressed in kilograms of sediment transported per day have been calculated from silt and colloid concentrations and discharge data (Moody and Meade, 1993) for all sites sampled on the three cruises with the results shown in Figure 8. Data for suspended sediment load calculations can be found in the Excel file HSD.XLS (hydrologic and sedimentologic data) on the accompanying 3.5" computer diskette. While sampling sites on the upper reach of the river have a relatively low suspended sediment load due to a combination of low sediment concentration and low discharge, the load increases substantially below the confluence of the Missouri River due to its large sediment input. The impact of the Missouri River on the suspended sediment load is most dramatic for the April-May 1992 trip with a sediment load more than twice that of the Mississippi River at Winfield, MO.

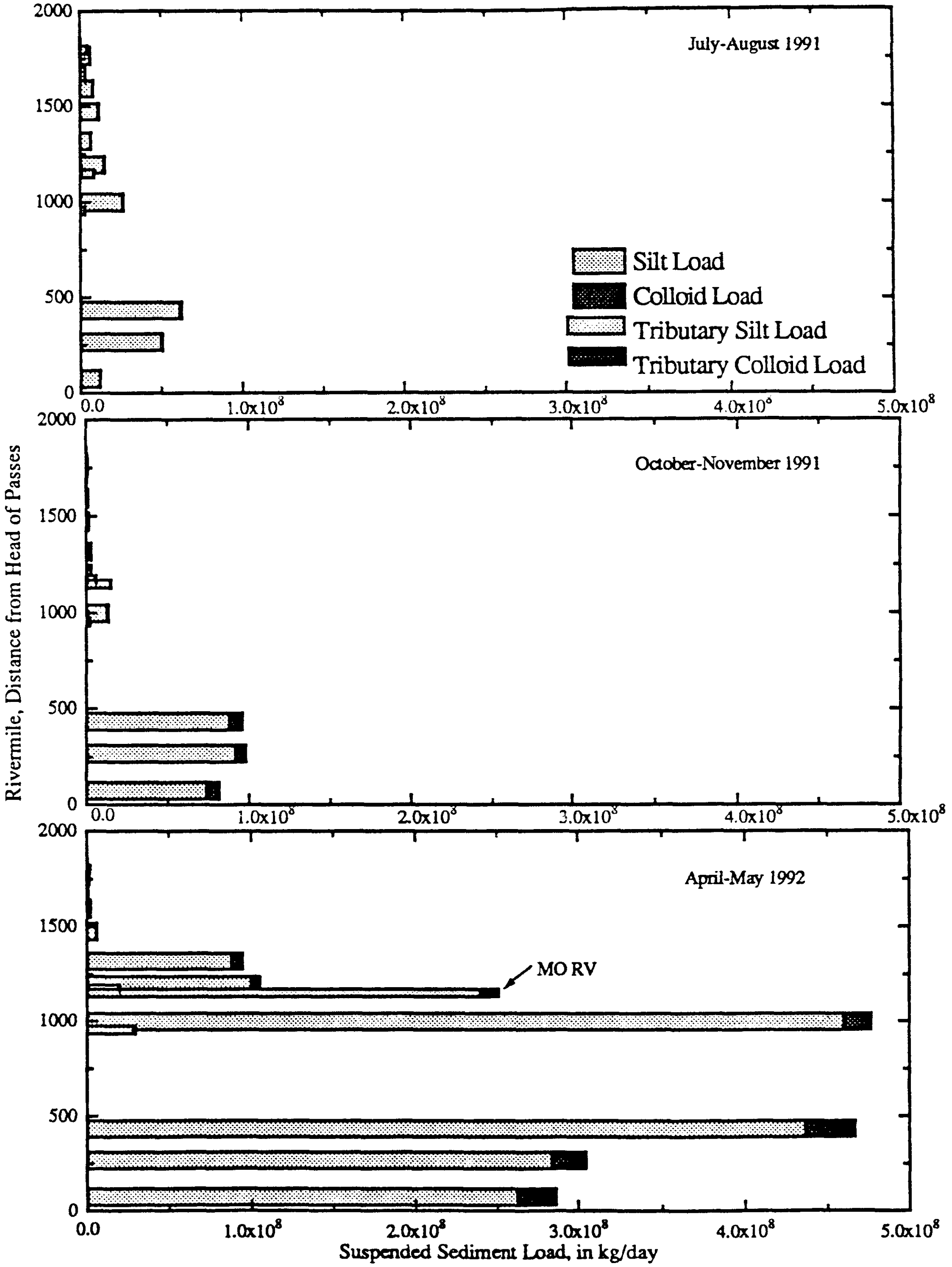


Figure 8. Suspended sediment load in the Mississippi River and major tributaries for July-August 1991, October-November 1991, and April-May 1992 sampling cruises.

Suspended sediment samples from all sites and tributaries (see Fig. 5) were extracted for the July-August 1991 cruise while samples from selected sites were extracted for the fall and spring cruises. In cases for which the sample collected was under 200 mg, only a total digestion on the sample was performed. Concentrations of metals in the hydroxylamine, persulfate, and residual extracts are reported as micrograms of extracted metal per gram of silt or colloid. Concentrations of chromium, copper, lead, iron, and manganese in each extract and total organic carbon concentrations (Leenheer and others, 1993) are tabulated in Tables 4a-f (July-August 1991), Tables 5a-f (October-November 1991), and Tables 6a-f (April-May 1992). Complete tables of concentrations of all metals determined in each extract are found in the Excel file SSMC.XLS (suspended sediment metal concentrations) on the accompanying 3.5" computer diskette.

Table 4a. Chromium concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on July-August 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of chromium per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

JULY-AUGUST 1991		**CHROMIUM (µg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	16.6	15.8	59.2	---	---	---
Minnesota River at mile 3.5	1798	3.4	7.5	60.1	6.7	39.9	231.7
MS RV at Hastings, MN	1766	6.7	16.7	66.8	---	---	---
MS RV near Pepin, WI	1719	9.9	28.9	78.5	29.3	138.7	251.3
MS RV at Trempealeau,WI	1668	6.4	16.7	63.9	53.2	163.9	167.2
MS RV below L & D 9	1594	5.0	13.3	58.0	15.7	33.6	68.8
MS RV at Clinton, IA	1474	7.1	15.5	61.1	15.1	44.6	63.9
MS RV at Keokuk, IA	1317	1.8	8.6	49.5	12.2	40.3	58.2
MS RV near Winfield, MO	1193	4.2	6.7	56.8	10.5	23.7	71.2
Illinois River at Hardin, IL	1172	5.6	13.5	60.9	13.3	36.5	81.0
MO RV at St. Charles, MO	1149	3.5	9.5	62.9	2.2	14.9	89.5
MS RV at Thebes, IL	998	4.2	9.7	54.3	11.0	31.2	82.6
Ohio River at Olmsted, IL	954	5.7	12.4	75.4	13.4	27.3	74.6
MS RV below Vicksburg, MS	433	3.7	10.4	62.4	1.8	9.7	75.2
MS RV near St. Francisville, LA	266	4.3	8.4	63.1	---	---	---
MS RV below Belle Chasse, LA	73	5.2	12.4	67.4	---	---	---

Table 4b. Copper concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on July-August 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of copper per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

JULY-AUGUST 1991		**COPPER (µg/g)**					
		SILT			COLLOID		
Sites on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	17.8	5.8	28.6	---	---	---
Minnesota River at mile 3.5	1798	17.5	4.9	31.8	147.0	48.3	67.7
MS RV at Hastings, MN	1766	22.9	6.8	23.3	---	---	---
MS RV near Pepin, WI	1719	31.1	8.4	25.9	68.8	31.1	17.5
MS RV at Trempealeau,WI	1668	17.9	6.0	24.4	97.1	29.8	38.4
MS RV below L & D 9	1594	15.4	4.5	23.0	30.4	12.5	30.4
MS RV at Clinton, IA	1474	19.9	5.4	25.0	32.6	24.5	21.4
MS RV at Keokuk, IA	1317	17.8	5.2	26.2	31.8	23.3	19.8
MS RV near Winfield, MO	1193	14.0	3.3	36.5	27.2	15.6	32.5
Illinois River at Hardin, IL	1172	20.2	5.1	27.6	36.2	17.9	27.7
MO RV at St. Charles, MO	1149	17.6	3.2	32.4	25.0	7.5	30.5
MS RV at Thebes, IL	998	17.7	3.6	28.1	69.2	19.3	32.4
Ohio River at Olmsted, IL	954	24.8	4.9	35.4	22.9	13.9	23.0
MS RV below Vicksburg, MS	433	15.7	3.9	27.2	19.2	5.2	24.8
MS RV near St. Francisville, LA	266	16.6	2.6	30.3	---	---	---
MS RV below Belle Chasse, LA	73	21.8	4.3	27.2	---	---	---

Table 4c. Lead concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on July-August 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of lead per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

JULY-AUGUST 1991		**LEAD (µg/g)**					
		SILT			COLLOID		
Sites on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	26.8	2.2	4.8	---	---	---
Minnesota River at mile 3.5	1798	15.6	2.0	4.9	58.3	4.6	4.6
MS RV at Hastings, MN	1766	26.5	2.5	5.2	---	---	---
MS RV near Pepin, WI	1719	53.8	4.6	5.4	73.6	6.9	1.8
MS RV at Trempealeau,WI	1668	26.5	1.4	5.0	85.4	11.2	4.0
MS RV below L & D 9	1594	18.9	2.0	5.5	48.3	5.2	4.9
MS RV at Clinton, IA	1474	30.3	2.3	5.1	47.5	5.5	3.0
MS RV at Keokuk, IA	1317	26.5	1.5	4.7	43.9	4.1	2.6
MS RV near Winfield, MO	1193	21.9	2.0	6.3	34.3	4.5	4.7
Illinois River at Hardin, IL	1172	27.5	2.0	6.4	51.4	4.8	3.8
MO RV at St. Charles, MO	1149	18.0	2.0	6.6	30.9	3.2	5.8
MS RV at Thebes, IL	998	20.4	2.0	6.0	36.3	7.0	4.9
Ohio River at Olmsted, IL	954	24.2	2.3	9.9	38.6	5.4	6.7
MS RV below Vicksburg, MS	433	19.2	2.3	7.5	29.7	4.2	8.3
MS RV near St. Francisville, LA	266	18.8	2.5	7.5	---	---	---
MS RV below Belle Chasse, LA	73	20.8	2.4	7.4	---	---	---

Table 4d. Iron concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on July-August 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in milligrams of iron per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

JULY-AUGUST 1991		**IRON (mg/g)**					
		SILT			COLLOID		
Sites on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	13.9	7.31	20.0	---	---	---
Minnesota River at mile 3.5	1798	5.07	7.26	26.7	8.54	4.84	41.5
MS RV at Hastings, MN	1766	6.30	7.01	26.8	---	---	---
MS RV near Pepin, WI	1719	10.7	9.09	24.9	12.4	6.69	10.8
MS RV at Trempealeau,WI	1668	12.2	5.62	22.6	32.5	13.2	23.3
MS RV below L & D 9	1594	6.64	7.54	23.9	10.5	9.37	25.5
MS RV at Clinton, IA	1474	7.11	6.78	25.5	8.15	14.2	13.4
MS RV at Keokuk, IA	1317	7.95	3.69	21.0	5.11	11.4	15.7
MS RV near Winfield, MO	1193	6.19	6.91	24.7	5.17	10.7	21.8
Illinois River at Hardin, IL	1172	6.15	7.26	29.3	4.32	9.24	23.6
MO RV at St. Charles, MO	1149	4.38	6.76	29.2	4.87	4.69	38.9
MS RV at Thebes, IL	998	4.82	6.60	27.4	4.36	9.60	28.2
Ohio River at Olmsted, IL	954	7.33	7.70	24.7	6.01	11.0	20.4
MS RV below Vicksburg, MS	433	6.82	7.75	28.3	12.2	8.47	36.0
MS RV near St. Francisville, LA	266	6.71	7.61	28.1	---	---	---
MS RV below Belle Chasse, LA	73	6.40	7.53	30.5	---	---	---

Table 4e. Manganese concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on July-August 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of manganese per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

JULY-AUGUST 1991		**MANGANESE (µg/g)**					
		SILT			COLLOID		
Sites on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	5900	70	150	---	---	---
Minnesota River at mile 3.5	1798	2010	30	140	5480	50	140
MS RV at Hastings, MN	1766	2290	30	170	---	---	---
MS RV near Pepin, WI	1719	4340	90	170	12900	70	40
MS RV at Trempealeau,WI	1668	3700	30	190	4280	110	180
MS RV below L & D 9	1594	2780	40	180	3700	120	90
MS RV at Clinton, IA	1474	2300	30	180	4670	90	80
MS RV at Keokuk, IA	1317	2470	30	140	3300	80	60
MS RV near Winfield, MO	1193	2850	40	140	4690	70	80
Illinois River at Hardin, IL	1172	2250	40	150	2810	60	70
MO RV at St. Charles, MO	1149	1270	20	160	3360	30	140
MS RV at Thebes, IL	998	1450	40	140	2540	60	110
Ohio River at Olmsted, IL	954	1530	40	220	2540	90	120
MS RV below Vicksburg, MS	433	2250	30	180	3010	40	170
MS RV near St. Francisville, LA	266	1910	20	170	---	---	---
MS RV below Belle Chasse, LA	73	1170	20	160	---	---	---

Table 4f. Organic carbon concentrations for silts and colloids collected on July-August 1991 cruise (From Leenheer and others, 1993).

[Rivermile is the distance upriver from Head of Passes; concentrations are percent organic carbon in sediment.]

JULY-AUGUST 1991 SITES on Mainstem and Major Tributaries	River mile	**Organic Carbon (%)** SILTS	COLLOIDS
MS RV above St. Anthony Falls, MN	1812	7.45	26.23
Minnesota River at mile 3.5	1798	2.92	10.31
MS RV at Hastings, MN	1766	3.65	15.59
MS RV near Pepin, WI	1719	8.69	21.41
MS RV at Trempealeau, WI	1668	5.62	24.75
MS RV below Lock and Dam 9	1594	4.30	18.51
MS RV at Clinton, IA	1474	4.51	22.80
MS RV at Keokuk, IA	1317	5.46	24.70
MS RV near Winfield, MO	1193	3.38	17.21
Illinois River at Hardin, IL	1172	3.13	16.50
Missouri River at St. Charles, MO	1149	2.15	6.90
MS RV at Thebes, IL	998	2.92	13.01
Ohio River at Olmsted, IL	954	4.24	21.96
MS RV below Vicksburg, MS	433	2.10	8.32
MS RV near St. Francisville, LA	266	1.94	8.13
MS RV below Belle Chasse, LA	73	2.43	7.06

Table 5a. Chromium concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on October-November 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of chromium per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

OCTOBER-NOVEMBER 1991		**CHROMIUM (μg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	11.1	17.1	38.3	---	---	---
Minnesota River at mile 3.5	1798	<1.0	6.1	42.4	12.5	21.5	42.6
MS RV near Pepin, WI	1719	5.8	13.6	50.5	---	---	---
MS RV at Clinton, IA	1474	2.8	15.4	50.5	---	---	---
MS RV near Winfield, MO	1193	3.4	6.3	49.1	---	---	---
Illinois River at Hardin, IL	1172	3.1	13.1	55.2	6.6	17.7	91.2
MO RV at St. Charles, MO	1149	1.3	11.7	51.9	2.1	9.8	68.2
MS RV at Thebes, IL	998	3.1	10.4	51.5	2.8	5.5	56.6
Ohio River at Olmsted, IL	954	3.8	10.2	60.3	---	---	---
MS RV below Vicksburg, MS	433	1.5	10.0	63.9	2.3	10.2	111.0
MS RV near St. Francisville, LA	266	2.3	15.2	62.4	3.2	14.9	101.0
MS RV below Belle Chasse, LA	73	1.5	12.6	68.3	<1.0	14.4	98.9

Table 5b. Copper concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on October-November 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of copper per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

OCTOBER-NOVEMBER 1991		**COPPER (µg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	7.8	7.8	19.6	---	---	---
Minnesota River at mile 3.5	1798	13.2	3.3	29.5	12.0	12.0	14.8
MS RV near Pepin, WI	1719	18.2	5.0	30.7	---	---	---
MS RV at Clinton, IA	1474	13.9	3.7	29.4	---	---	---
MS RV near Winfield, MO	1193	13.0	2.9	31.7	---	---	---
Illinois River at Hardin, IL	1172	17.3	5.6	34.9	34.9	4.8	37.3
MO RV at St. Charles, MO	1149	15.8	3.3	35.4	22.8	3.0	32.2
MS RV at Thebes, IL	998	15.1	3.5	34.3	18.2	5.2	24.5
Ohio River at Olmsted, IL	954	27.3	12.3	39.5	---	---	---
MS RV below Vicksburg, MS	433	15.5	3.1	36.1	22.2	4.2	31.7
MS RV near St. Francisville, LA	266	12.9	2.7	24.9	22.4	2.9	32.8
MS RV below Belle Chasse, LA	73	15.4	2.9	25.6	23.2	5.1	33.5

Table 5c. Lead concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on October-November 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of lead per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

OCTOBER-NOVEMBER 1991		**LEAD (μg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	2.5	2.5	3.3	---	---	---
Minnesota River at mile 3.5	1798	13.0	<0.3	4.2	2.4	2.4	3.9
MS RV near Pepin, WI	1719	44.1	2.0	4.0	---	---	---
MS RV at Clinton, IA	1474	30.4	1.5	5.0	---	---	---
MS RV near Winfield, MO	1193	24.7	1.1	5.6	---	---	---
Illinois River at Hardin, IL	1172	27.6	1.1	7.5	48.1	2.8	7.0
MO RV at St. Charles, MO	1149	18.8	0.9	6.5	29.4	1.7	6.7
MS RV at Thebes, IL	998	28.6	2.1	9.2	36.2	2.5	3.5
Ohio River at Olmsted, IL	954	24.9	0.9	10.3	---	---	---
MS RV below Vicksburg, MS	433	21.3	1.5	8.9	29.5	3.6	8.4
MS RV near St. Francisville, LA	266	18.5	1.3	8.1	31.1	2.3	9.0
MS RV below Belle Chasse, LA	73	17.3	1.2	8.4	25.3	3.3	9.0

Table 5d. Iron concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on October-November 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in milligrams of iron per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

OCTOBER-NOVEMBER 1991		**IRON (mg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	9.75	8.87	13.7	---	---	---
Minnesota River at mile 3.5	1798	5.86	3.27	17.2	4.24	6.51	15.6
MS RV near Pepin, WI	1719	10.0	5.22	20.3	---	---	---
MS RV at Clinton, IA	1474	11.0	5.08	24.9	---	---	---
MS RV near Winfield, MO	1193	7.40	4.89	23.8	---	---	---
Illinois River at Hardin, IL	1172	5.54	6.86	28.9	7.55	4.76	41.4
MO RV at St. Charles, MO	1149	5.48	5.00	28.5	7.02	4.44	38.6
MS RV at Thebes, IL	998	5.91	4.32	27.3	4.42	3.66	27.1
Ohio River at Olmsted, IL	954	8.99	6.47	26.2	---	---	---
MS RV below Vicksburg, MS	433	7.58	5.93	33.1	7.30	6.08	40.3
MS RV near St. Francisville, LA	266	6.65	3.74	26.9	7.67	5.80	37.5
MS RV below Belle Chasse, LA	73	6.79	4.05	24.5	7.09	8.79	40.6

Table 5e. Manganese concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on October-November 1991 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of manganese per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

OCTOBER-NOVEMBER 1991		**MANGANESE (μg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	2860	50	140	---	---	---
Minnesota River at mile 3.5	1798	2020	30	110	1780	50	60
MS RV near Pepin, WI	1719	5950	70	180	---	---	---
MS RV at Clinton, IA	1474	3250	50	140	---	---	---
MS RV near Winfield, MO	1193	2480	40	150	---	---	---
Illinois River at Hardin, IL	1172	972	20	160	1340	40	130
MO RV at St. Charles, MO	1149	1890	20	160	1060	30	140
MS RV at Thebes, IL	998	2120	20	160	1260	30	90
Ohio River at Olmsted, IL	954	4080	40	240	---	---	---
MS RV below Vicksburg, MS	433	1920	30	180	630	30	160
MS RV near St. Francisville, LA	266	1580	10	160	630	20	150
MS RV below Belle Chasse, LA	73	1110	10	140	300	20	150

Table 5f. Organic carbon concentrations for silts and colloids collected on October-November 1991 cruise (From Leenheer and others, 1993).

[Rivermile is the distance upriver from Head of Passes; concentrations are in percent organic carbon in sediment.]

OCTOBER-NOVEMBER 1991 SITES on Mainstem and Major Tributaries	River mile	**Organic Carbon (%)** SILTS	 COLLOIDS
MS RV above St. Anthony Falls, MN	1812	13.73	30.85
Minnesota River at mile 3.5	1798	5.83	15.34
MS RV near Pepin, WI	1719	9.70	30.54
MS RV at Clinton, IA	1474	6.23	18.83
MS RV near Winfield, MO	1193	5.71	16.39
Illinois River at Hardin, IL	1172	2.19	10.45
MO RV at St. Charles, MO	1149	2.05	6.25
MS RV at Thebes, IL	998	2.89	10.29
Ohio River at Olmsted, IL	954	3.45	13.63
MS RV below Vicksburg, MS	433	1.53	5.91
MS RV near St. Francisville, LA	266	2.23	5.86
MS RV below Belle Chasse, LA	73	1.52	5.02

Table 6a. Chromium concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on April-May 1992 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of chromium per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

APRIL-MAY 1992		**CHROMIUM (µg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	<1.0	21.6	56.0	7.6	23.5	91.0
Minnesota River at mile 3.5	1798	<1.0	10.5	50.6	1.1	21.6	63.1
MS RV near Pepin, WI	1719	3.4	27.9	81.5	6.1	33.6	39.5
MS RV at Clinton, IA	1474	5.7	8.1	46.7	---	---	---
MS RV near Winfield, MO	1193	4.6	8.4	63.0	<1.0	9.8	89.6
Illinois River at Hardin, IL	1172	8.3	12.7	59.3	4.2	14.6	88.9
MO RV at St. Charles, MO	1149	<1.0	6.8	61.0	<1.0	6.5	96.5
MS RV at Thebes, IL	998	<1.0	9.5	74.8	<1.0	7.7	90.3
Ohio River at Olmsted, IL	954	4.9	16.6	72.1	2.8	13.0	84.8
MS RV below Vicksburg, MS	433	<1.0	8.9	67.3	2.0	9.1	93.3
MS RV near St. Francisville, LA	266	6.2	10.7	69.2	2.0	8.9	91.3
MS RV below Belle Chasse, LA	73	<1.0	8.8	84.4	2.7	10.4	103.0

Table 6b. Copper concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on April-May 1992 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of copper per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

APRIL-MAY 1992		**COPPER (µg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	30.2	18.6	18.1	30.7	10.3	12.8
Minnesota River at mile 3.5	1798	11.3	3.4	21.4	21.3	8.1	16.7
MS RV near Pepin, WI	1719	20.6	8.1	21.4	41.7	15.4	7.4
MS RV at Clinton, IA	1474	11.4	3.6	27.0	---	---	---
MS RV near Winfield, MO	1193	11.2	4.1	29.2	18.8	3.9	56.9
Illinois River at Hardin, IL	1172	15.7	5.0	37.2	34.1	6.0	36.2
MO RV at St. Charles, MO	1149	12.4	3.0	32.5	18.3	3.0	38.1
MS RV at Thebes, IL	998	12.7	5.0	35.5	24.4	3.0	34.4
Ohio River at Olmsted, IL	954	20.6	9.0	28.9	26.2	7.1	34.2
MS RV below Vicksburg, MS	433	15.2	4.0	34.0	25.1	4.1	41.2
MS RV near St. Francisville, LA	266	14.7	4.6	30.7	22.4	3.1	35.3
MS RV below Belle Chasse, LA	73	14.7	3.9	36.6	31.6	3.1	37.3

Table 6c. Lead concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on April-May 1992 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of lead per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

APRIL-MAY 1992		**LEAD (µg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	18.3	2.6	18.1	39.4	4.8	3.2
Minnesota River at mile 3.5	1798	11.5	0.5	4.2	35.5	3.0	2.1
MS RV near Pepin, WI	1719	26.2	3.1	3.5	51.6	5.5	1.0
MS RV at Clinton, IA	1474	21.8	1.8	4.2	---	---	---
MS RV near Winfield, MO	1193	18.4	2.8	5.5	28.3	4.8	7.7
Illinois River at Hardin, IL	1172	25.8	2.4	7.5	49.7	4.4	6.5
MO RV at St. Charles, MO	1149	14.7	3.0	7.5	22.9	4.8	8.2
MS RV at Thebes, IL	998	18.2	2.5	6.9	26.4	4.3	7.6
Ohio River at Olmsted, IL	954	30.7	4.2	8.6	44.0	7.6	9.6
MS RV below Vicksburg, MS	433	20.6	2.9	7.8	32.1	4.1	9.2
MS RV near St. Francisville, LA	266	19.8	2.9	7.9	25.4	3.9	8.2
MS RV below Belle Chasse, LA	73	21.2	4.0	8.2	35.8	4.1	8.7

Table 6d. Iron concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on April-May 1992 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in milligrams of iron per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

APRIL-MAY 1992		IRON (mg/g)					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	16.2	7.57	12.7	49.8	9.37	5.26
Minnesota River at mile 3.5	1798	4.59	4.00	18.6	3.65	6.15	14.9
MS RV near Pepin, WI	1719	9.84	7.66	19.2	26.0	8.69	9.49
MS RV at Clinton, IA	1474	9.55	5.90	21.8	---	---	---
MS RV near Winfield, MO	1193	6.60	5.17	28.6	7.25	6.84	41.8
Illinois River at Hardin, IL	1172	5.81	5.93	25.5	9.03	6.71	36.1
MO RV at St. Charles, MO	1149	4.03	4.89	30.8	4.25	6.05	51.1
MS RV at Thebes, IL	998	4.61	8.55	29.8	6.44	5.88	48.7
Ohio River at Olmsted, IL	954	6.47	13.2	26.7	6.86	9.18	36.7
MS RV below Vicksburg, MS	433	5.14	8.10	28.5	7.70	6.39	41.9
MS RV near St. Francisville, LA	266	6.04	11.2	35.0	7.60	7.37	42.3
MS RV below Belle Chasse, LA	73	5.81	6.47	36.3	7.61	7.30	46.7

Table 6e. Manganese concentrations in hydroxylamine (HA), persulfate (PS), and residual (RES) extracts for silts and colloids collected on April-May 1992 cruise.

[Rivermile is the distance upriver from Head of Passes; concentrations are in micrograms of manganese per gram of sediment; ---indicates inadequate sample amounts collected for extraction.]

APRIL-MAY 1992		**MANGANESE (µg/g)**					
		SILT			COLLOID		
SITES on Mainstem and Major Tributaries	River mile	HA	PS	RES	HA	PS	RES
MS RV above St. Anthony Falls, MN	1812	3390	50	130	1650	90	20
Minnesota River at mile 3.5	1798	1740	10	140	950	30	50
MS RV near Pepin, WI	1719	3480	50	110	1120	60	30
MS RV at Clinton, IA	1474	2610	30	150	---	---	---
MS RV near Winfield, MO	1193	1490	20	150	3570	30	150
Illinois River at Hardin, IL	1172	1030	20	160	5260	40	110
MO RV at St. Charles, MO	1149	1000	20	150	3420	30	160
MS RV at Thebes, IL	998	920	20	150	3650	20	150
Ohio River at Olmsted, IL	954	1810	40	200	2480	50	160
MS RV below Vicksburg, MS	433	1160	20	160	3830	20	140
MS RV near St. Francisville, LA	266	1300	30	170	3570	20	140
MS RV below Belle Chasse, LA	73	1500	30	180	3170	20	160

Table 6f. Organic carbon concentrations for silts and colloids collected on April-May 1992 cruise (From Leenheer and others, 1993).

[Rivermile is the distance upriver from Head of Passes; concentrations are in percent organic carbon in sediment.]

APRIL-MAY 1992 SITES on Mainstem and Major Tributaries	River mile	**Organic Carbon (%)** SILTS	COLLOIDS
MS RV above St. Anthony Falls, MN	1812	16.83	14.18
Minnesota River at mile 3.5	1798	2.82	14.39
MS RV near Pepin, WI	1719	11.45	27.06
MS RV at Clinton, IA	1474	6.12	23.22
MS RV near Winfield, MO	1193	2.40	8.06
Illinois River at Hardin, IL	1172	2.01	8.99
MO RV at St. Charles, MO	1149	1.23	4.11
MS RV at Thebes, IL	998	1.42	5.25
Ohio River at Olmsted, IL	954	2.31	9.91
MS RV below Vicksburg, MS	433	1.77	4.77
MS RV near St. Francisville, LA	266	1.79	4.68
MS RV below Belle Chasse, LA	73	1.76	4.59

Metal Partitioning

The distribution of chromium among the hydroxylamine, persulfate and residual extracts is shown in Figures 9a (silts) and 9b (colloids). The results indicate that 70-90% of the total chromium in the Mississippi River suspended sediments is associated with refractory minerals, and consequently largely unavailable to the environment. The high amount of chromium in the residual digestion, generally 60-80 µg/g, is consistent with rock minerals composing the river basin. Containing an average chromium concentration of 75 µg/g, Pierre shale and similar rocks such as sandstone, siltstone, and claystone, are common in the Mississippi River basin (Boyer, 1984). Chromium extracted by the persulfate reagent represents the next largest association in the silt and colloid, generally 10-20% of the total sediment bound chromium. Concentrations of chromium in the hydroxylamine extract are typically a factor of 2 to 10 less than the persulfate-extractable chromium concentrations. Nearly 15% of the 70 analyzed suspended sediments are below the hydroxylamine chromium detection limit of 1 µg/g.

As shown in Figures 10a (silts) and 10b (colloids), copper is predominantly in the refractory mineral phase with concentrations again consistent with the mineralogy of the river basin. Representing about 50-60% of the total copper, the copper concentrations determined in the residual digestions, typically 25-35 µg/g, are comparable to an average copper concentration of 34 µg/g found in the rock types of the Mississippi River basin (Boyer, 1984). The hydroxylamine-extractable copper also represents a significant and occasionally the dominant association of the sediment bound copper. In general, 30-40% of the total copper is extracted by the hydroxylamine reagent. Of considerably lesser significance is the persulfate-extractable association of copper. Copper concentrations in the persulfate extract typically represent only one-fourth of copper concentrations in the hydroxylamine extract.

The partitioning of lead is shown in Figures 11a (silts) and 11b (colloids). Unlike chromium and copper, only a minor fraction of the lead in the sediment (~10-30%) is associated with the refractory mineral phase. Average lead concentration reported for the shales, sandstones, siltstones, and claystones characteristic of the river basin is approximately 20 μg/g (Boyer, 1984), a level at least twice as high as the concentrations of 5-10 μg/g determined in this study. This suggests that lead associated with native minerals may not be completely refractory in nature. A significant fraction of the total lead, 65-80%, is liberated by the hydroxylamine extraction, while the lead concentration in the persulfate extract represents only about one-tenth of the hydroxylamine lead and is generally less than the lead concentration in the residual digest.

Figures 12a and 12b show the distribution of iron in the silts and colloids, respectively. Iron occurs predominantly in the residual extract for all silts and most of the colloids analyzed. Residual iron concentrations are generally between 20 and 30 mg/g for the silts, which translate to approximately 55-70% of the total iron in the sediment. In the case of the colloids, iron in the residual extract is quite variable, ranging from 5 to 49 mg/g. On the average, residual iron in the colloids represents about 60% of the total iron. Depending on the specific sampling cruise and the location on the river, the next largest association of iron may either be with the hydroxylamine- or the persulfate- extractable fraction. Nearly equal concentrations of iron are extracted by the hydroxylamine and persulfate reagents, both liberating about 20% of the total iron. In the case of the mainstem silts, hydroxylamine iron concentrations are slightly higher than persulfate iron concentrations for the upper reaches of the river in July-August 1991 and April-May 1992 and for the entire river in October-November 1991. For mainstem colloids from the upper river in July-August 1991 and from the entire river in April-May 1992, hydroxylamine iron concentrations are generally higher than iron concentrations in the persulfate extract. The limited data for October-November 1991 colloids suggest that concentrations of hydroxylamine-extractable iron are also slightly higher than persulfate iron concentrations.

Sequential extraction results for sediment bound manganese are shown in Figures 13a (silts) and 13b (colloids). Approximately 90% of the total manganese in the Mississippi River suspended sediments is liberated by the hydroxylamine extraction with concentrations of manganese in the persulfate extract typically representing only 1-5% of the total manganese. For most sediment samples, the residual manganese comprises less than 10% of the total sediment bound manganese. Residual concentrations of manganese are approximately 150 μg/g with the exception of several colloids which have lower residual concentrations of 20 to 100 μg/g.

To aid in the discussion that follows, organic carbon concentrations on the silts and colloids are shown in Figure 14.

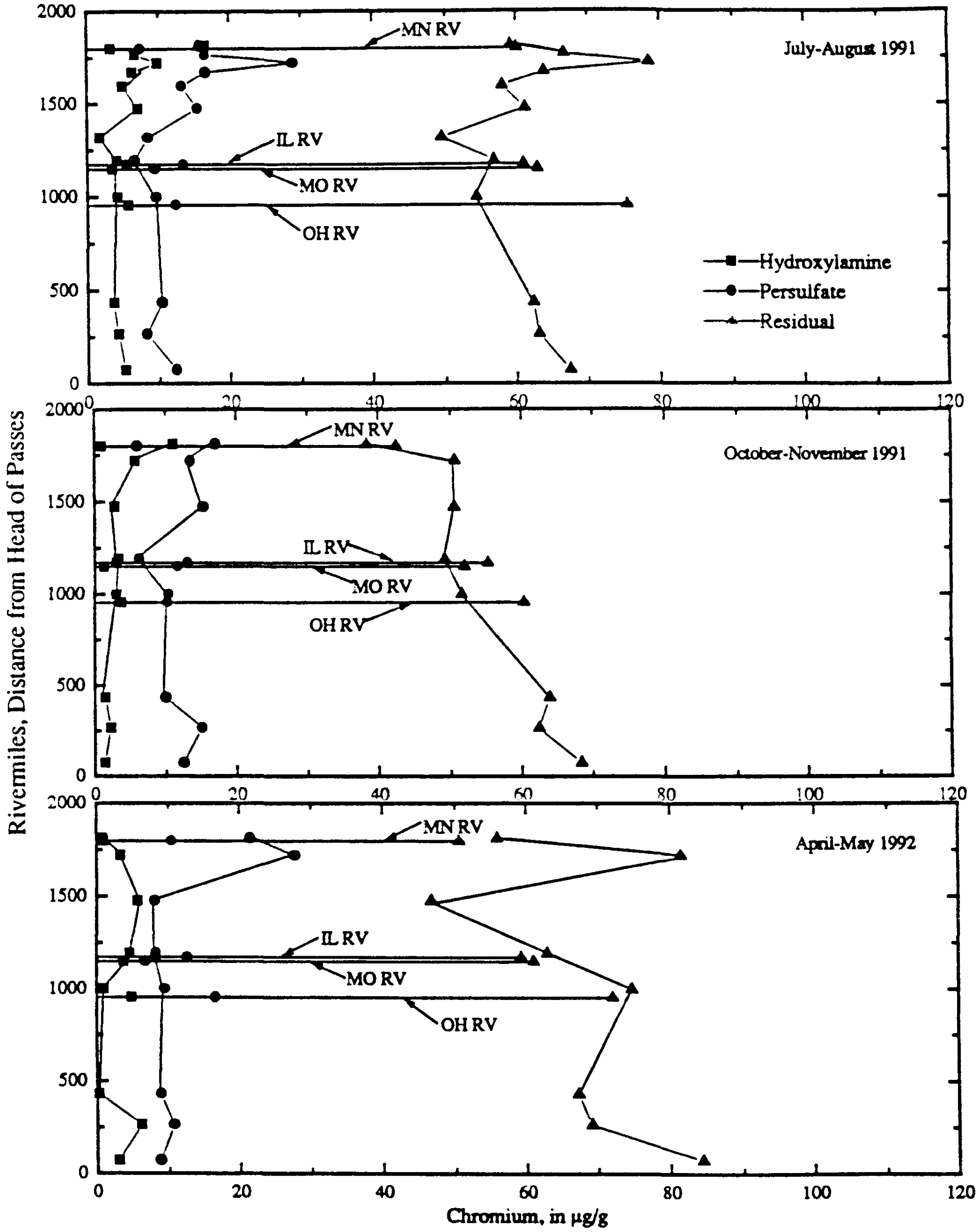


Figure 9a. Chromium concentrations in hydroxylamine, persulfate, and residual extracts of silts from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported chromium concentrations are approximately 11%, 17%, and 4% in the hydroxylamine, persulfate, and residual digests, respectively.)

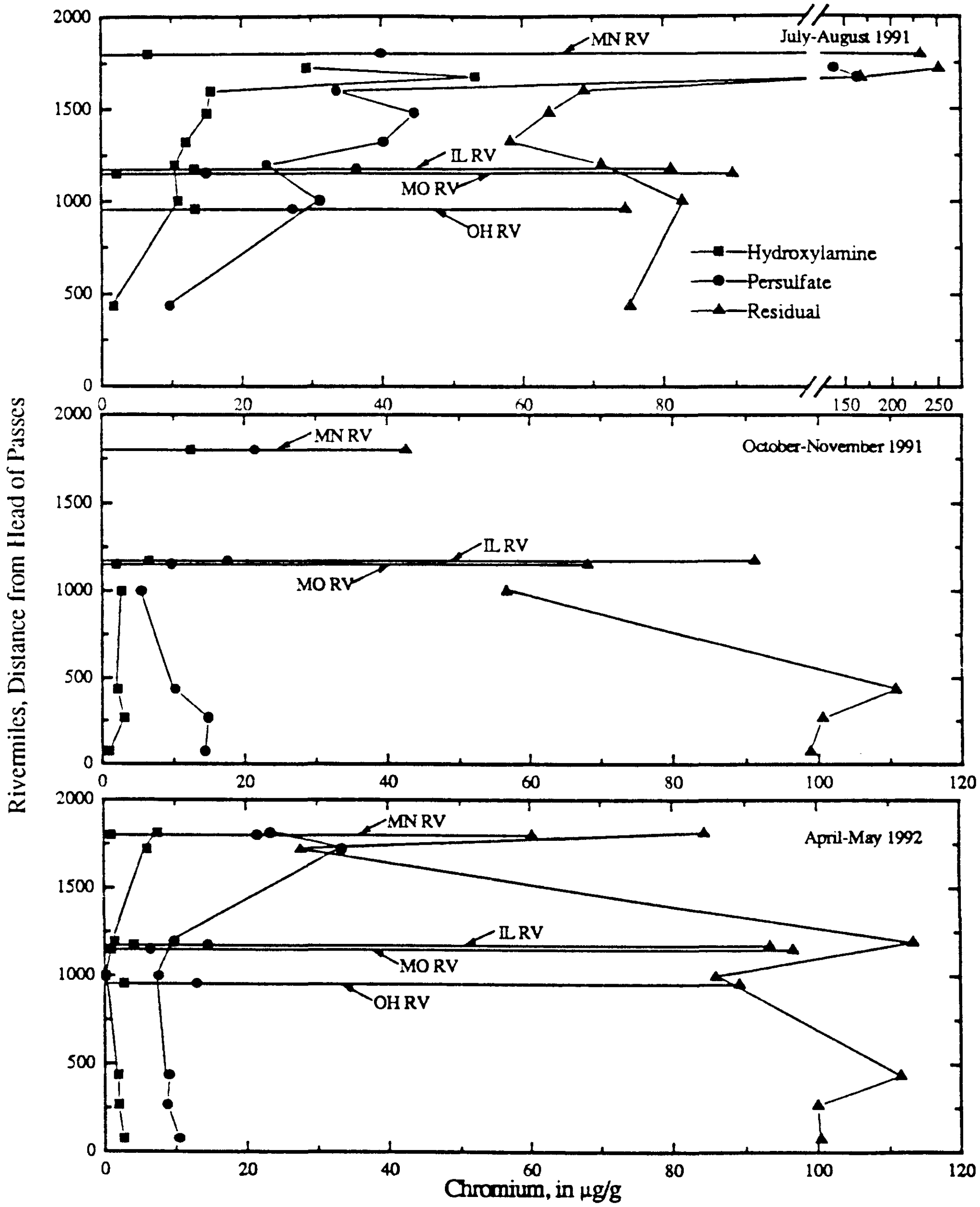


Figure 9b. Chromium concentrations in hydroxylamine, persulfate, and residual extracts of colloids from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported chromium concentrations are approximately 11%, 17%, and 4% in the hydroxylamine, persulfate, and residual digests, respectively.)

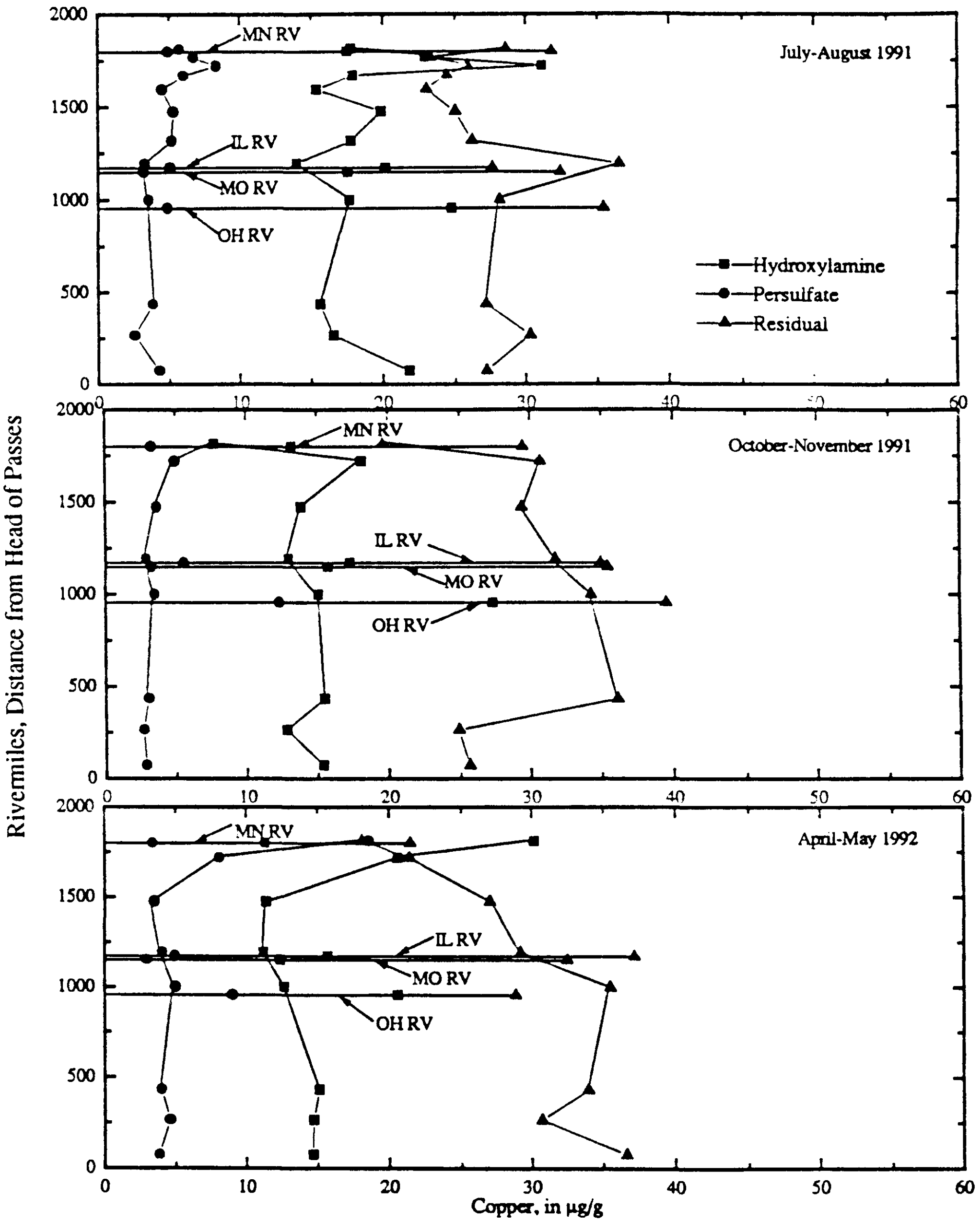


Figure 10a. Copper concentrations in hydroxylamine, persulfate, and residual extracts of silts from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported copper concentrations are approximately 13%, 14%, and 12% in the hydroxylamine, persulfate, and residual digests, respectively.)

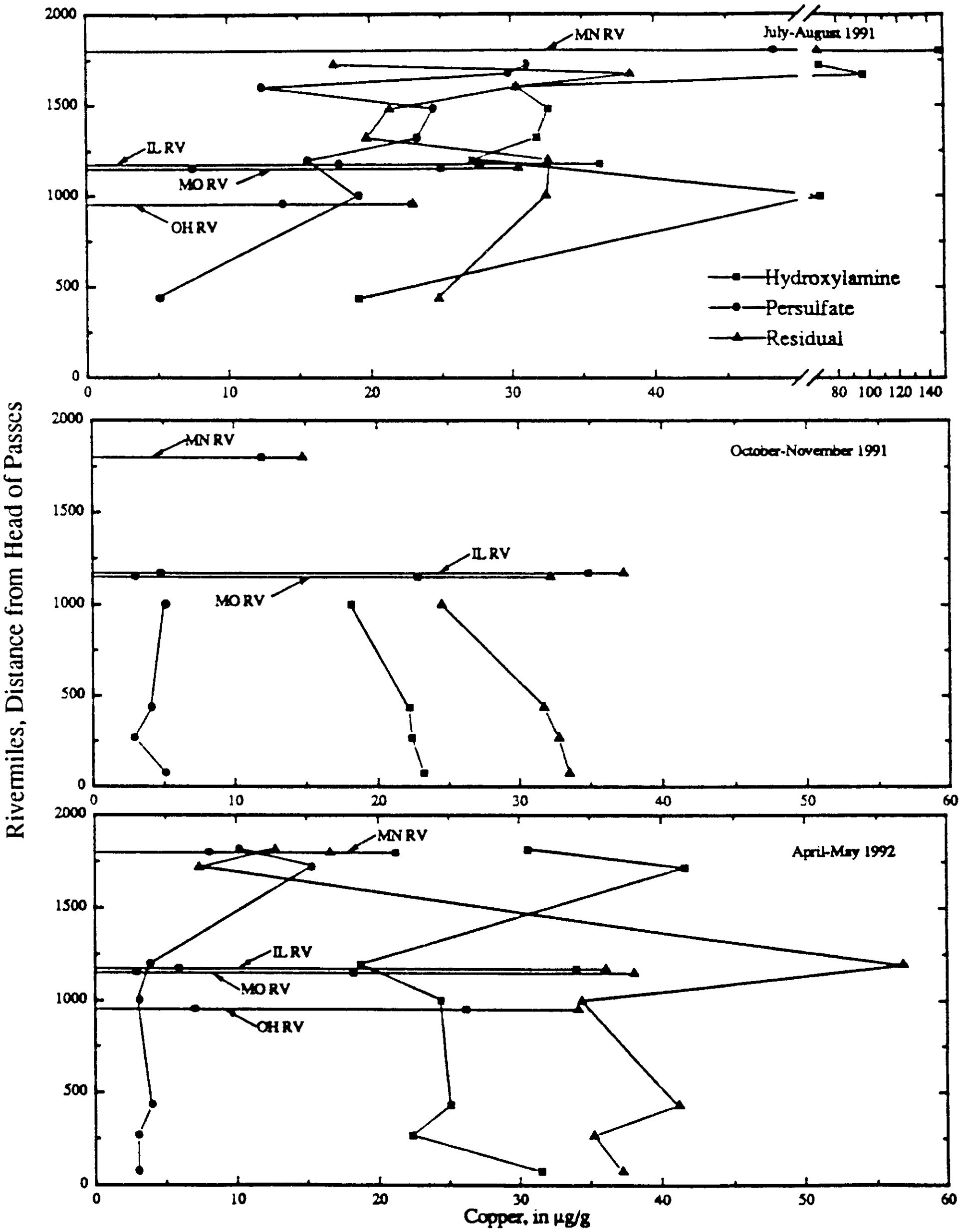


Figure 10b. Copper concentrations in hydroxylamine, persulfate, and residual extracts of colloids from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported copper concentrations are approximately 13%, 14%, and 12% in the hydroxylamine, persulfate, and residual digests, respectively.)

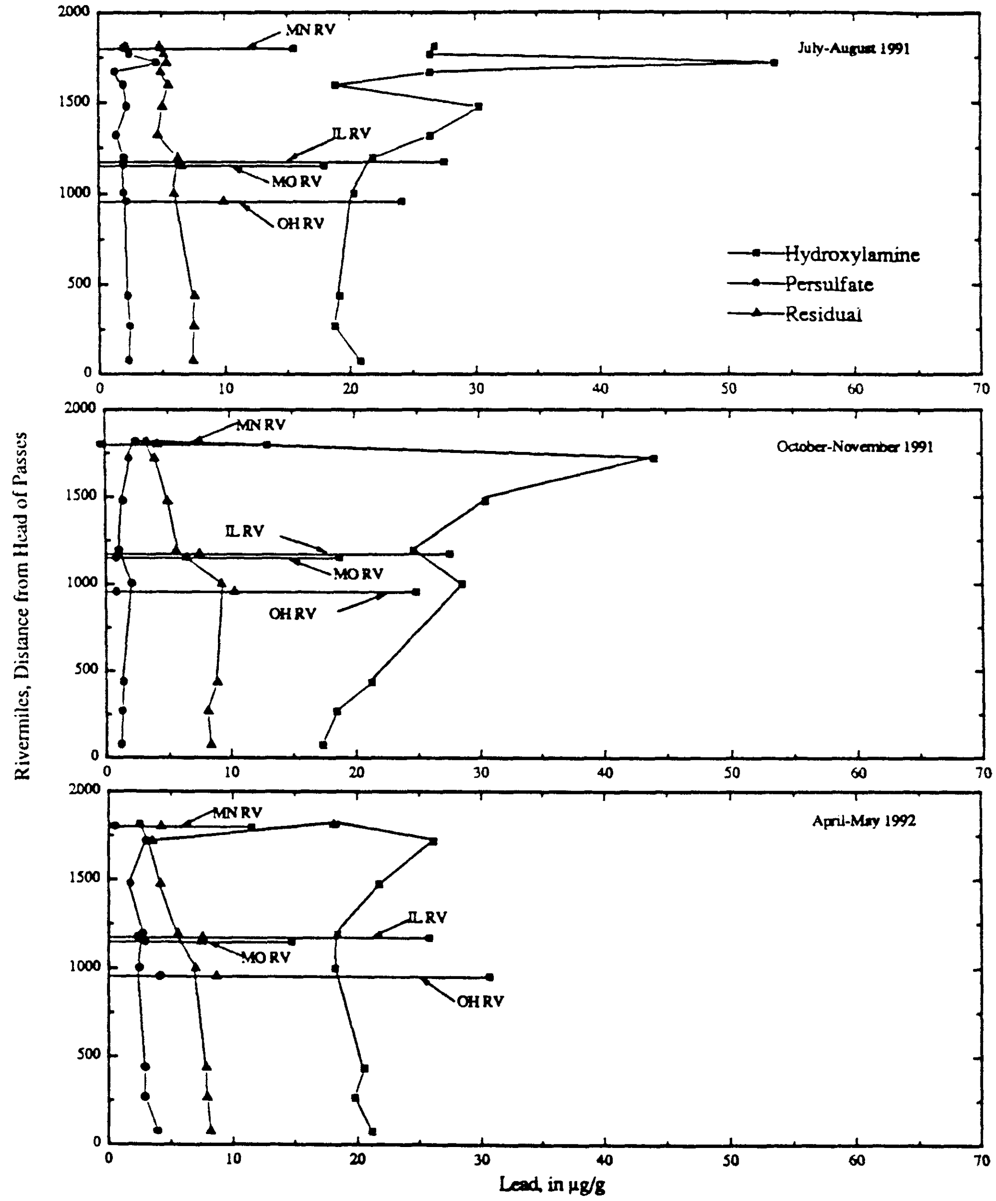


Figure 11a. Lead concentrations in hydroxylamine, persulfate, and residual extracts of silts from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported lead concentrations are approximately 7%, 10%, and 10% in the hydroxylamine, persulfate, and residual digests, respectively.)

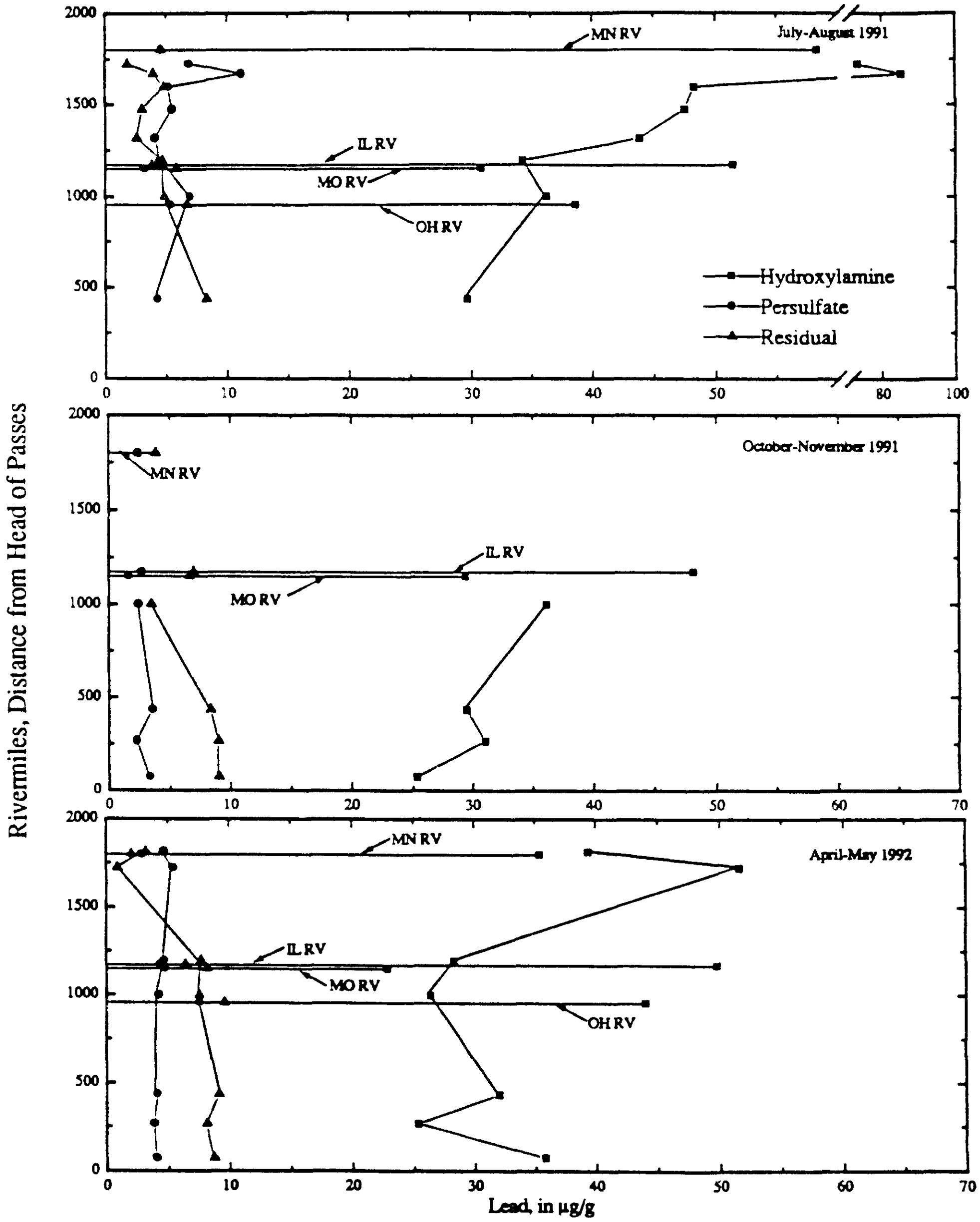


Figure 11b. Lead concentrations in hydroxylamine, persulfate, and residual extracts of colloids from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported lead concentrations are approximately 7%, 10%, and 10% in the hydroxylamine, persulfate, and residual digests, respectively.)

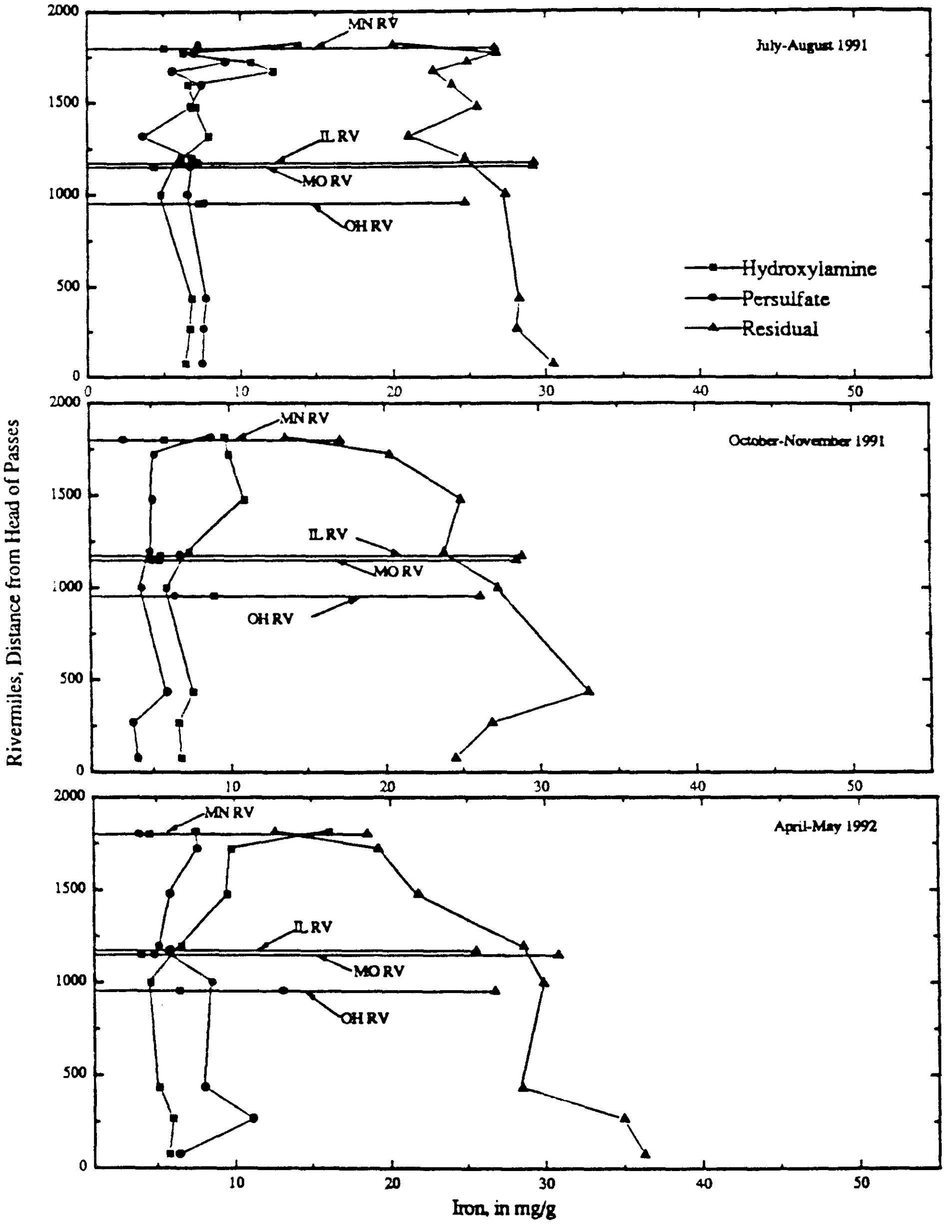


Figure 12a. Iron concentrations in hydroxylamine, persulfate, and residual extracts of silts from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported iron concentrations are approximately 7%, 22%, and 4% in the hydroxylamine, persulfate, and residual digests, respectively.)

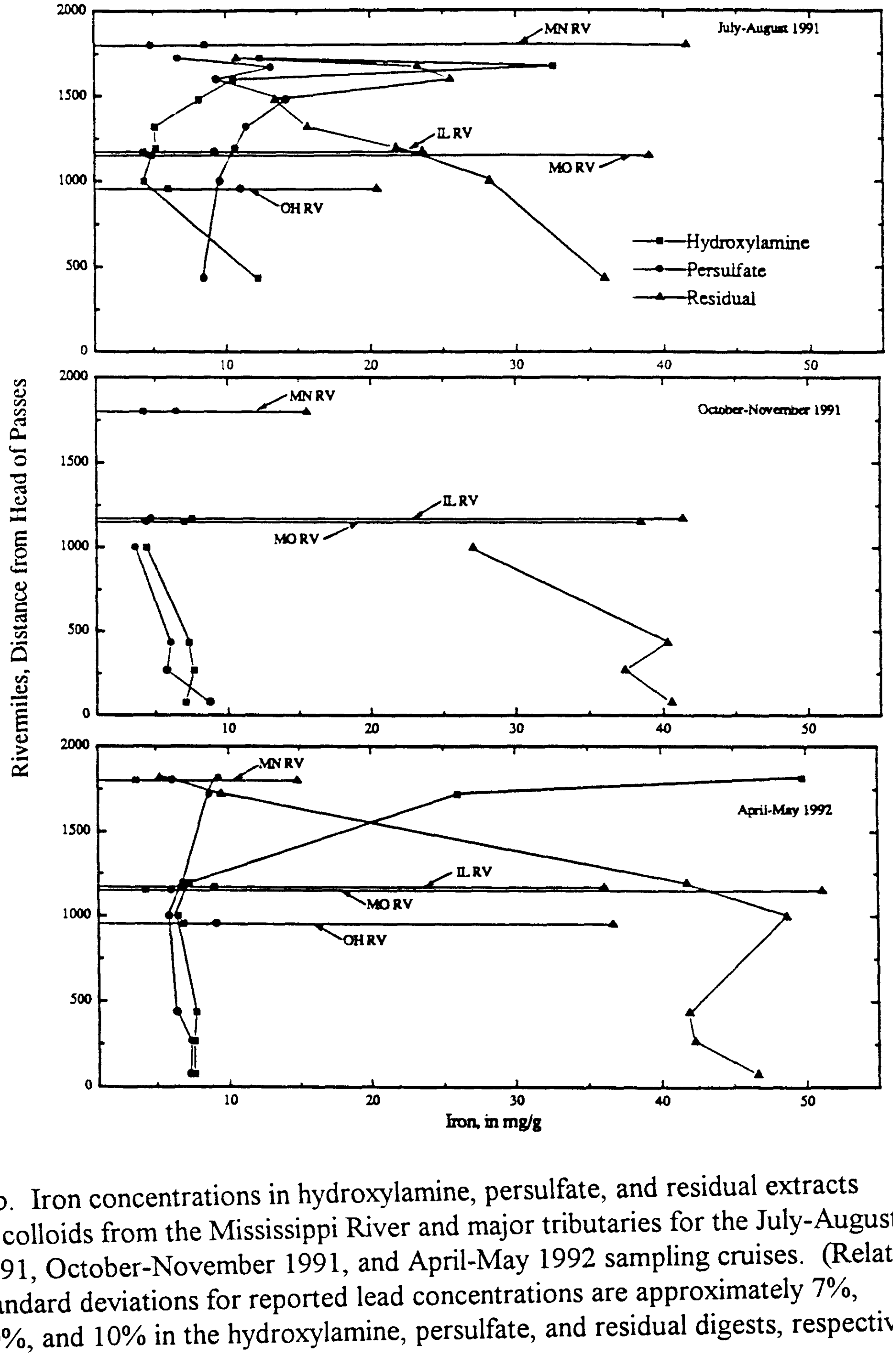


Figure 12b. Iron concentrations in hydroxylamine, persulfate, and residual extracts of colloids from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported lead concentrations are approximately 7%, 10%, and 10% in the hydroxylamine, persulfate, and residual digests, respectively.)

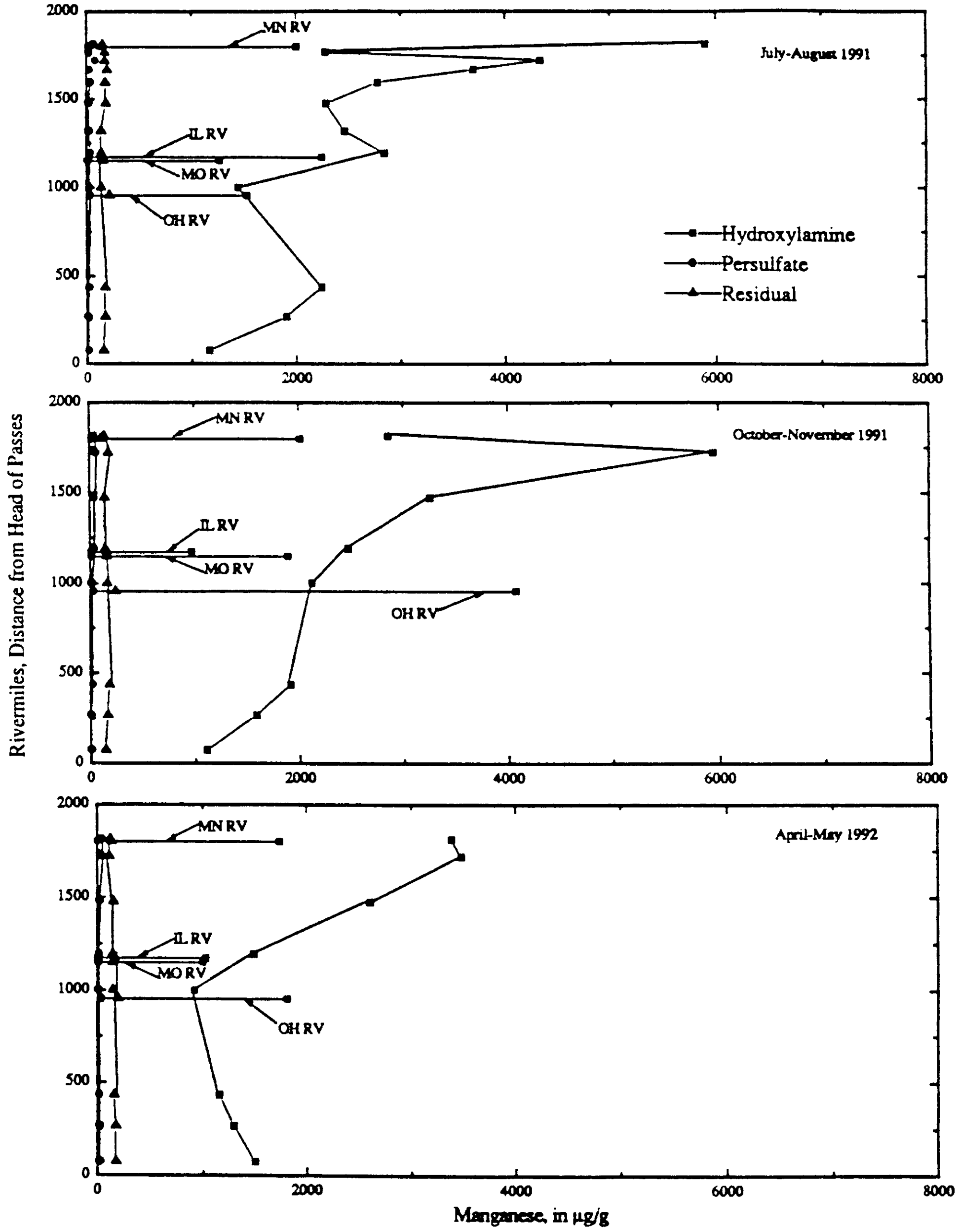


Figure 13a. Manganese concentrations in hydroxylamine, persulfate, and residual extracts of silts from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported manganese concentrations are approximately 8%, 20%, and 7% in the hydroxylamine, persulfate, and residual digests, respectively.)

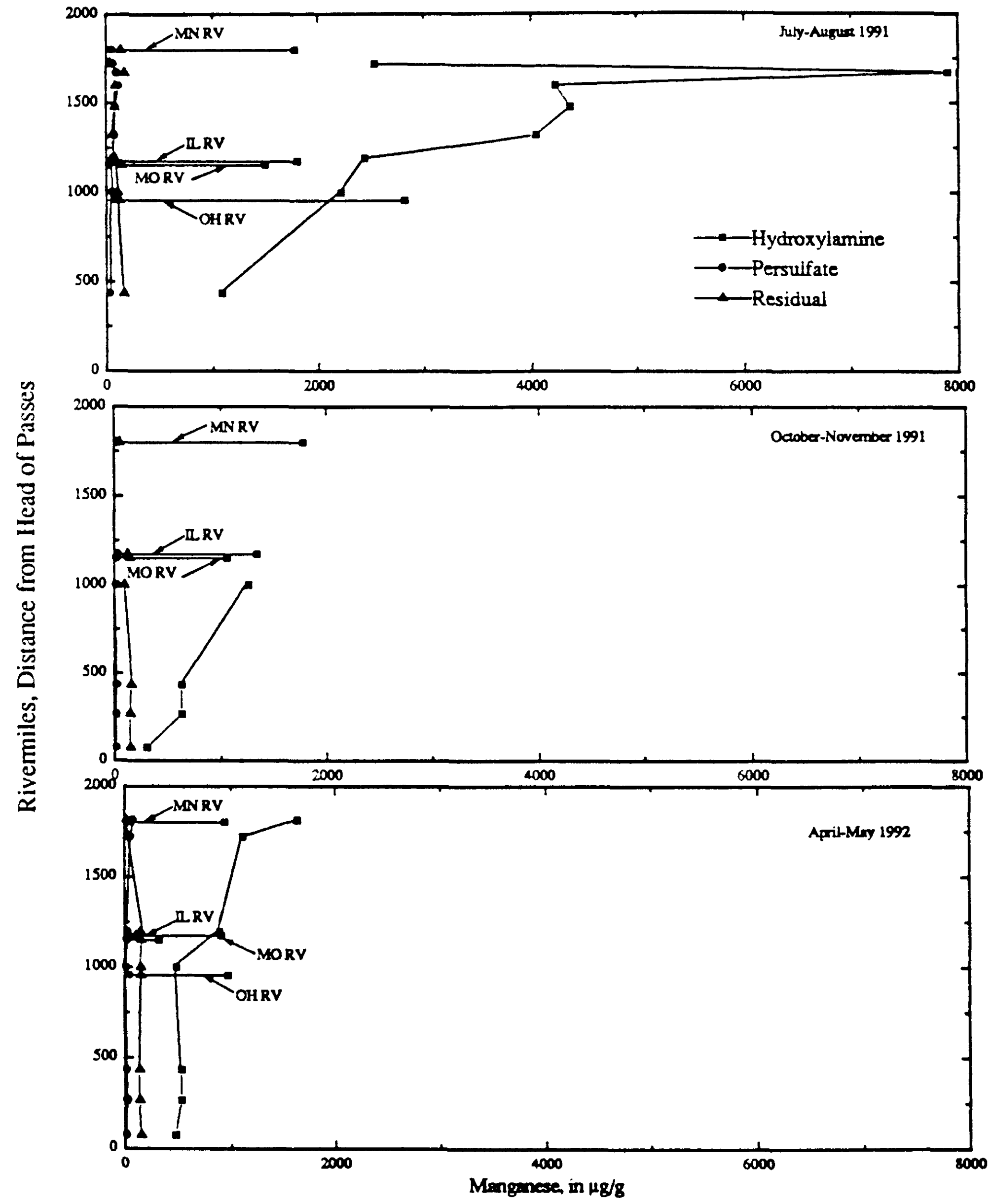


Figure 13b. Manganese concentrations in hydroxylamine, persulfate, and residual extracts of colloids from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises. (Relative standard deviations for reported manganese concentrations are approximately 8%, 20%, and 7% in the hydroxylamine, persulfate, and residual digests, respectively.)

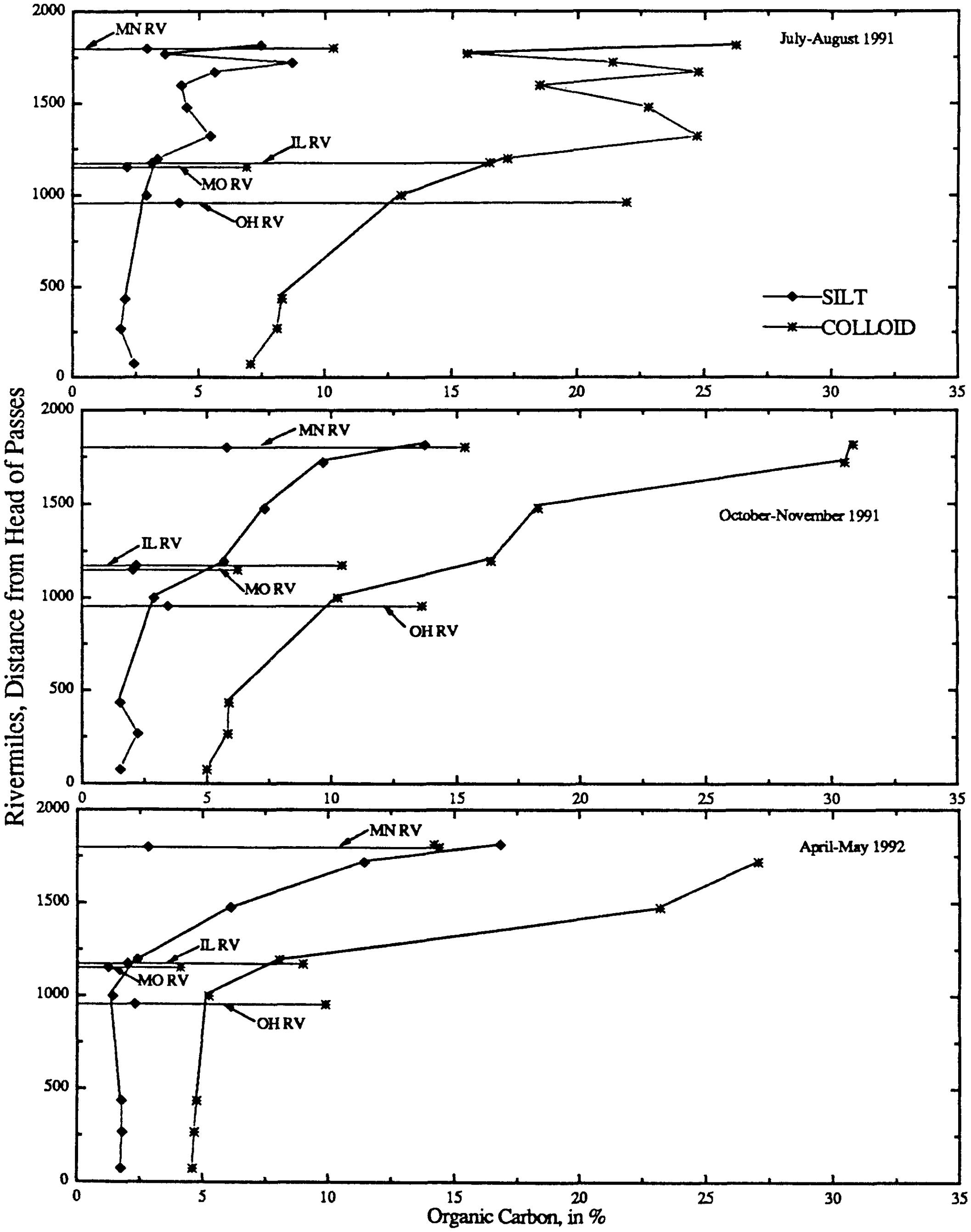


Figure 14. Organic carbon concentrations for silts and colloids from the Mississippi River and major tributaries for the July-August 1991, October-November 1991, and April-May 1992 sampling cruises (From Leenheer and others, 1993).

Downriver Trends and Seasonal Variations

Concentrations of hydroxylamine- and persulfate-extractable (referred to hereafter as non-residual) chromium, copper, lead, iron, and manganese associated with the suspended sediments are generally higher and more variable in the Mississippi River above the confluence of the Missouri River than below the Missouri River confluence. Silts sampled from the Mississippi River at Pepin, WI usually have the highest concentrations of the metals in the hydroxylamine and persulfate extracts while silts with the lowest metal concentrations in the non-residual extracts are from the Mississippi River at Thebes, IL, Vicksburg, MS, St. Francisville, LA, and Belle Chasse, LA. In the case of the major tributaries, silts from the Illinois River and Ohio River are generally higher and those from the Missouri River are lower in non-residual metal concentrations than the mainstem silts. Although the data set for the colloids is incomplete, the colloids also appear to exhibit a general decrease downriver in chromium, copper, lead, iron, and manganese concentrations in the non-residual fraction with the highest concentrations for colloids from the Mississippi River at Pepin, WI and Trempealeau, WI. Similar to the case for silts, the lowest concentrations of the metals in the non-residual fraction of the colloids are below the Missouri River confluence with the Illinois and Ohio Rivers colloids higher and the Missouri River colloids lower in non-residual metal concentrations relative to the mainstem Mississippi River colloids.

The downriver decrease in non-residual metal concentrations associated with the suspended sediment may be a result of an increase in suspended sediment concentrations in the free-flowing lower river and dilution by relatively non-polluted Missouri River suspended sediments. Hydrous oxide coatings and organic matter concentrate on the lower concentrations of suspended sediment in the upper river. Consequently, metals introduced into this reach of river have less particulate matter of higher scavenging capacity with which to bind than in the free-flowing lower river, resulting in higher non-residual metal concentrations per gram of suspended sediment in the upper Mississippi River. The high non-residual metal concentrations for suspended sediments at Pepin, WI, located immediately below Lake Pepin on the Mississippi River, may be due to the sharp decrease in suspended sediment concentration as a result of Lake Pepin's efficiency as a sediment trap. In addition, the high non-residual metal concentrations on the silts at Pepin, WI may be a function of the particle size distribution in the silts with a larger percentage of particles in the smaller end of the silt size range following sedimentation of larger sediment particles in Lake Pepin. The increase in surface area associated with the decrease in particle size may account for the apparent non-residual metal enrichment.

Both the silts and colloids exhibit greater variability in the non-residual metals concentrations in the upper section of the Mississippi River than in the river below the Missouri River confluence. This trend is most evident for the July-August 1991 trip for which the complete set of Upper Mississippi River silts were extracted and analyzed. The range of non-residual metal concentrations on the silts in the Mississippi River above the Missouri River for all sampling trips is approximately 1.5 to 17.5 times the non-residual metal concentration range below the confluence of the Missouri River. The same trend is apparent but more difficult to distinguish for the colloids because of missing data for the lower river on the July-August 1991 trip and the upper river on the October-November 1991 trip. The lack of variability of non-residual metal concentrations in the lower river suspended sediment is probably a result of the well-mixed, highly integrated nature of the free-flowing lower river as opposed to the impounded segment above St. Louis. Because of the smaller scale of the upper reach of the Mississippi River, this section of the river is also more sensitive to changes in the system such as variations in tributary and anthropogenic inputs.

Non-residual metal concentrations on suspended sediment in the upper reaches of the river also seem to be influenced most strongly by seasonal variations, while concentrations of hydroxylamine- and persulfate-extractable metals on the silt fraction are relatively constant in the lower river from season to season. Although seasonal differences in non-residual metal concentrations for the silts are observed in the upper river, no systematic seasonal trend is apparent for the metals as a group. The limited colloid data suggest larger seasonal variations in non-residual metal concentrations in the upper river as well. One particular seasonal trend evident for the colloids is the increased non-residual metal concentrations in the upper river for the July-August 1991 sampling trip compared to the April-May 1992 trip. For example, non-residual metal concentrations for July-August 1991 colloids at Pepin, WI are generally 2-5 times greater than for April-May 1992.

Silts vs. Colloids

Colloids in the Mississippi River are generally enriched relative to silts in non-residual chromium, copper, and lead. Higher non-residual metal concentrations in the Mississippi River colloids are likely due to the larger surface area of the smaller colloid particles available for metal-surface interactions as well as increased organic carbon content on the colloids, generally 3-5 times that of the silts. In general, non-residual chromium, copper, and lead concentrations associated with the colloids are a factor of 1.5 to 2 times higher than in the silts with the exception of the July-August 1991 upper river colloids which are enriched relative to the silts by a factor of 2 to 10. This enrichment is a result of the higher non-residual metal concentrations associated with the colloids noted previously for the July-August 1991 trip.

Several possibilities exist to explain this enrichment in the upper river July-August 1991 colloids. Although the concentration of organic carbon on the colloids is relatively invariant for all trips, the nature of organic matter may be considerably different in July-August due to the high biological activity during the late summer. It is possible that colloidal organic material in July-August is more active in scavenging metals. Unfortunately, existing data on the character of the colloidal organic matter is limited mainly to its nitrogen content which is of little use in characterization due to the large agricultural nitrogen inputs (Leenheer and others, 1993).

Another possibility for the high non-residual metals for colloids in July-August 1991 is the difference between silt and colloid transport in the river. Since colloids essentially travel with the flow of the river while silt particles are continually being deposited and resuspended, the non-residual metals associated with the colloids in a given sample may reflect transient changes in the water quality of the river, whereas non-residual metals on silts in a given sample may represent a more time-averaged picture of suspended sediments in the river. On the July-August 1991 trip higher levels of metals may have been introduced into the upper river resulting in higher non-residual metal concentrations on the colloids, while changes in non-residual metals on the silt particles may have been masked due to deposition and resuspension dynamics in the river.

This possibility suggests that silts and colloids in the river may not be in equilibrium with respect to their associated non-residual metals. At several sites on the river, a spike is indicated for the colloidal non-residual metal concentrations but not for the corresponding silt. For example, a significant increase in non-residual metal concentrations is indicated for the colloids at Trempealeau, WI, while a significant decrease is indicated for the silts for the July-August 1991 trip. A similar discrepancy is noted at Thebes, IL in July-August 1991 for non-residual copper and at St. Francisville, LA and Belle Chasse, LA in April-May 1992 for hydroxylamine copper and lead.

Transport

To evaluate the amount of sediment bound metal transported by the Mississippi River at a given location, non-residual metal loads have been calculated corresponding to the hydroxylamine and persulfate extraction steps. This provides an estimate for the metal load most available for short term chemical processes. Metal loads, expressed in kilograms of metal per day, were determined by multiplying the concentration of the metal on the sediment by the water discharge (Moody and Meade, 1993) and the sediment concentration in the river. A correction factor was applied to the metals transported by the silt fraction to account for the estimated loss of silt in the processing procedure (Brinton and others, 1993). Data used to calculate loads can be found in the Excel files, SSMC.XLS (suspended sediment metal concentrations) and HSD.XLS (hydrologic and sedimentologic data) files on the accompanying 3.5" computer diskette.

The hydroxylamine- and persulfate-extractable chromium, copper, and lead loads in the suspended sediment of the Mississippi River and major tributaries for the three sampling cruises are shown in Figures 15a-c. Results are shown as stacked bar graphs such that the entire bar represents the sum of hydroxylamine and persulfate metal load on the silt and the colloid fraction. The major mode of sediment transport for chromium is the persulfate-extractable silt fraction. In contrast, copper and lead are transported primarily by the hydroxylamine-extractable silt-sized material. Although metal concentrations are generally higher for the colloid fraction than for the silt fraction, actual non-residual metal loads for the colloid fraction represent only about 10% of the total non-residual metal load in the lower river, but as high as 40% in the upper river. The significance of non-residual metal loads transported by colloids relative to dissolved metal loads (Antweiler and others, 1993) can not be determined since both the dissolved metal concentrations and colloid associated metal concentrations in terms of micrograms of metal per liter of river water were below or near analytical detection limits.

Whereas the highest metal concentrations are typically found on the silts and colloids in the Upper Mississippi River and decrease downriver, metal loads exhibit the reverse trend with the highest load in the lower river due to its substantially higher sediment loads (see Fig. 8). The decrease in the metal load from Vicksburg, MS to St. Francisville, LA is the result of the diversion of up to 30% of the Mississippi River's flow into the Acthafalaya River at the Old River Outflow. Between St. Francisville, LA and Belle Chasse, LA a decrease in the metal load is generally observed and is most pronounced in July-August 1991. The decrease in load in this reach of the river is most likely due to deposition of suspended sediment at low water discharge (Meade and others, 1990).

Unlike the metal concentrations, metal loads show clear seasonal variations primarily due to seasonal variations in discharge and suspended sediment concentrations. The upper section of the Mississippi River transports a significant metal load during the high-flow conditions of July-August 1991, while during low flow conditions of October-November 1991 and April-May 1992, the non-residual metal load is negligible relative to that in the lower Mississippi River. High flow conditions in the lower river in April-May 1992 result in non-residual metal loads 2-32 times greater than loads in the lower river in either October-November 1991 or July-August 1991.

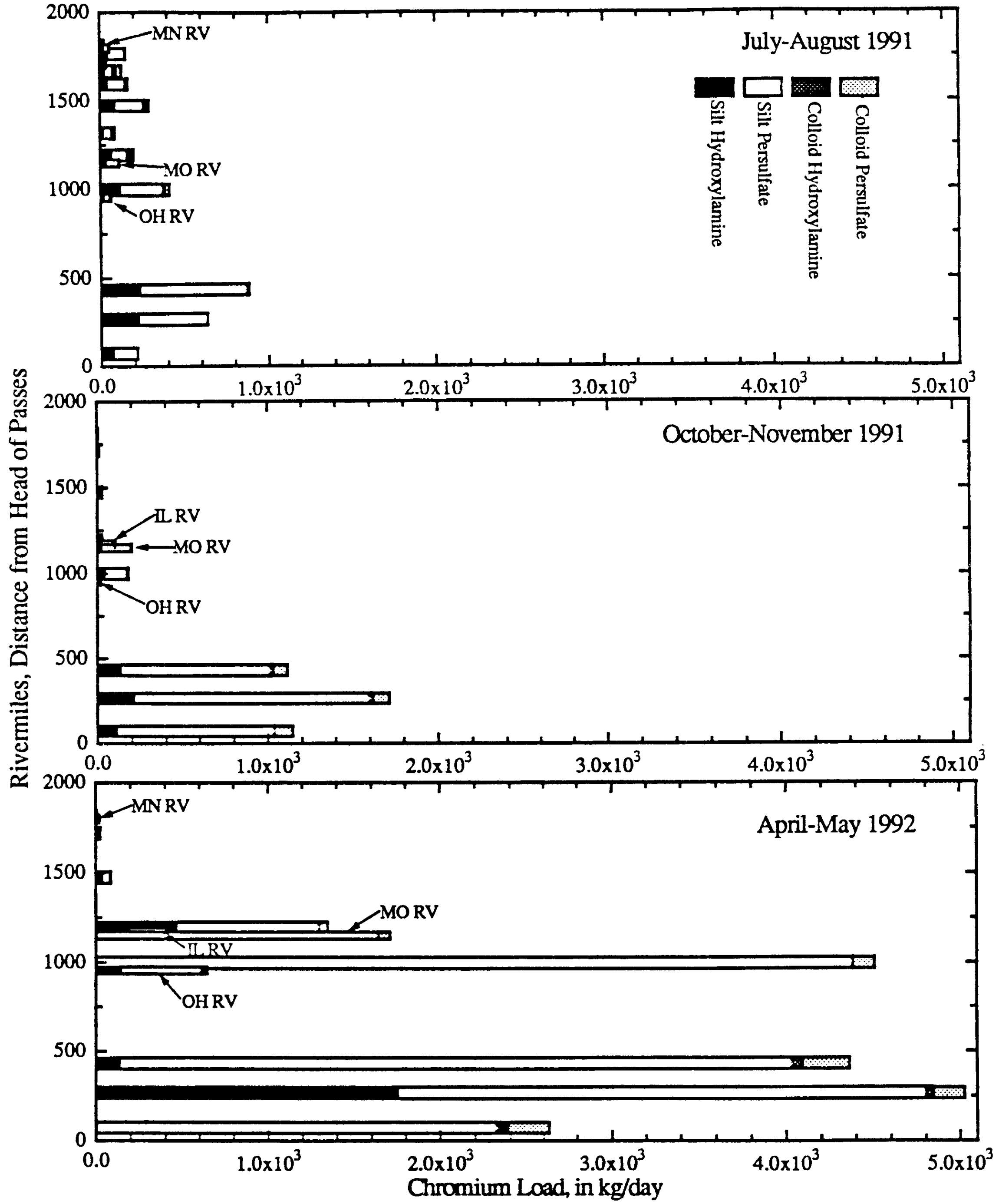


Figure 15a. Non-residual chromium loads in the Mississippi River and major tributaries for July-August 1991, October-November 1991, and April-May 1992 sampling cruises.

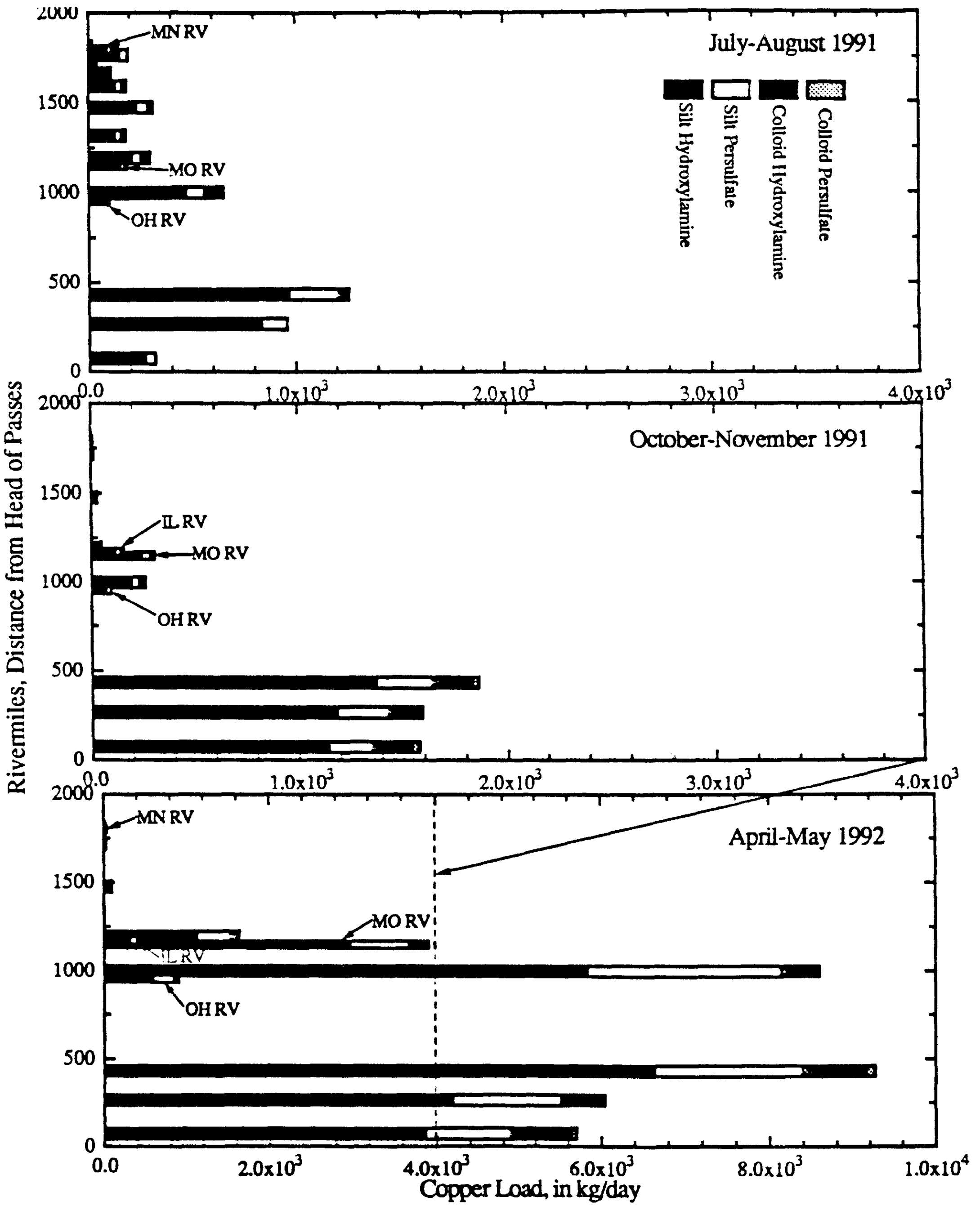


Figure 15b. Non-residual copper loads in the Mississippi River and major tributaries for July-August 1991, October-November 1991, and April-May 1992 sampling cruises.

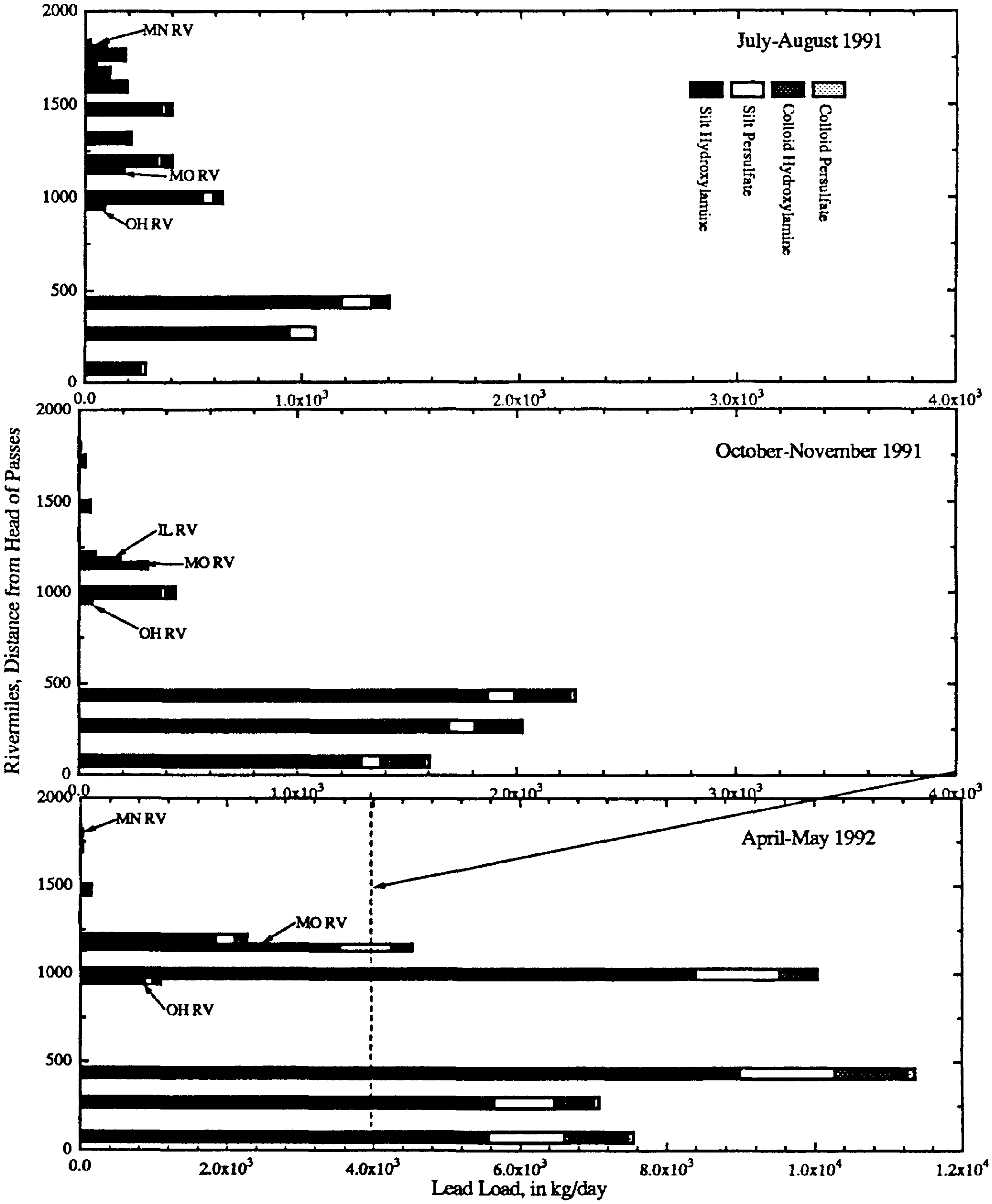


Figure 15c. Non-residual lead loads in the Mississippi River and major tributaries for July-August 1991, October-November 1991, and April-May 1992 sampling cruises.

Bed Sediments

In order to assess the degree of storage and the fate of trace metals in the upper Mississippi River, bed sediments from the broad shallow pools created by locks and dams were extracted and analyzed for associated metals. Bottom sediments were collected and analyzed from 25 of the 29 pools over the course of the three sampling cruises. In addition, a bed sediment sample from the Illinois River was collected and analyzed. The locations of the pool sites are shown in Figure 16. Concentrations of chromium, copper, lead, iron, and manganese in the hydroxylamine, persulfate, and residual extracts for the bed sediments are tabulated in Tables 7a-e with organic carbon concentrations tabulated in Table 7f (Leenheer and others, 1993). Concentrations of all metals determined in the extracts are compiled in the Excel file BSMC.XLS (bed sediment metal concentrations) on the accompanying 3.5" computer diskette.

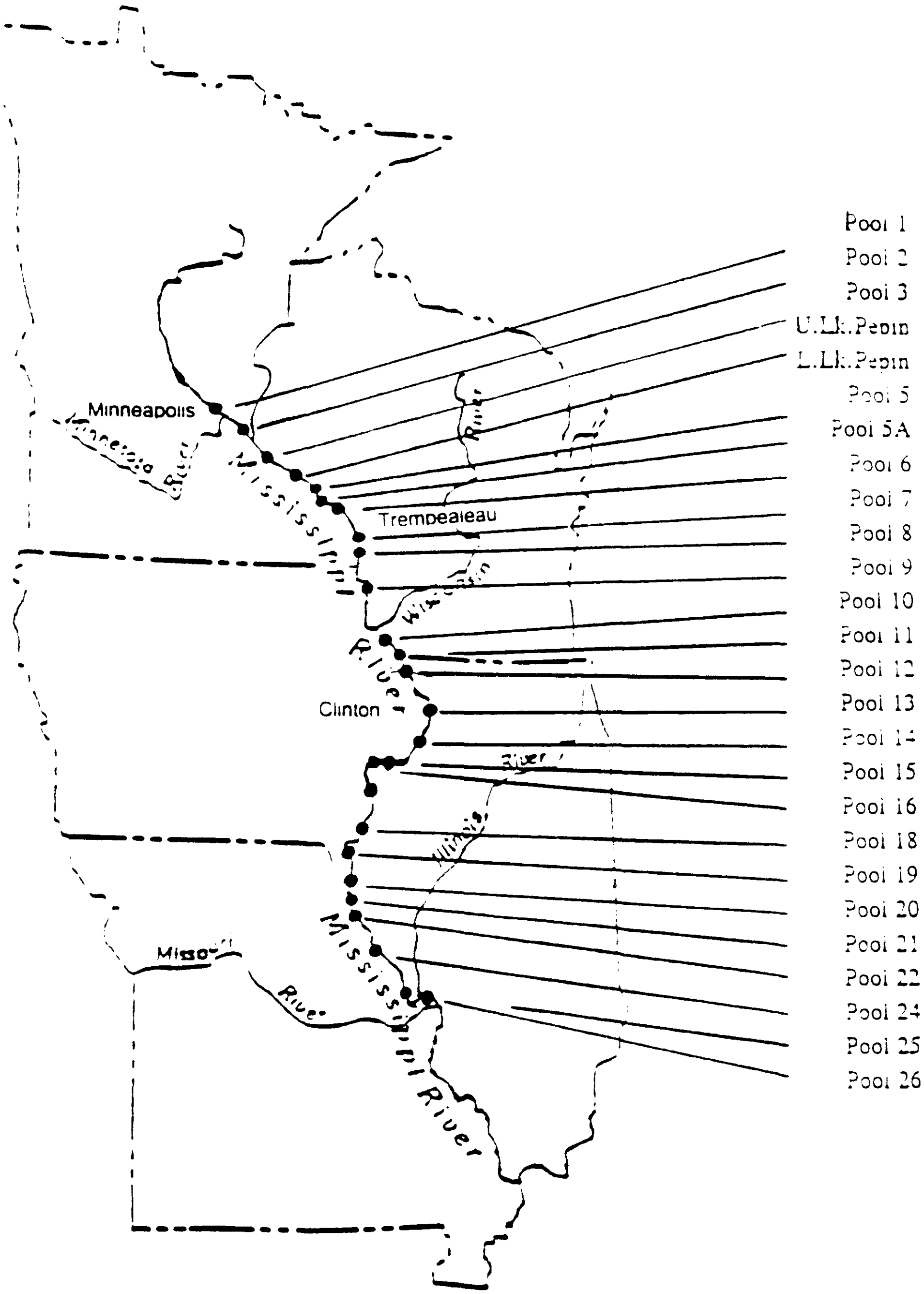


Figure 16. Location of pool sites for bed sediments in the Upper Mississippi River.

Table 7a. Chromium concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments in the Upper Mississippi River.

[Concentrations are in micrograms of chromium per gram of sediment.]

BED SEDIMENTS SITE	**CHROMIUM (µg/g)** Hydroxylamine	Persulfate	Residual
Pool 1	<1.0	1.6	15.0
Pool 2	1.7	4.8	30.8
Pool 3	<1.0	8.9	38.6
Upper Lake Pepin	3.1	14.9	50.1
Lower Lake Pepin	12.4	20.9	58.7
Pool 5	<1.0	2.9	14.2
Pool 5A	2.3	3.9	27.4
Pool 6	<1.0	2.0	12.1
Pool 7	<1.0	4.5	27.9
Pool 8	<1.0	3.8	19.8
Pool 9	<1.0	4.3	43.5
Pool 10	1.4	4.8	28.3
Pool 11	<1.0	4.2	21.9
Pool 12	<1.0	6.0	36.2
Pool 13	<1.0	3.5	21.9
Pool 14	1.2	2.2	15.6
Pool 15	<1.0	1.3	13.4
Pool 16	<1.0	3.3	17.1
Pool 18	<1.0	3.4	20.7
Pool 19	<1.0	6.3	49.8
Pool 20	<1.0	2.5	20.4
Pool 21	<1.0	1.8	11.5
Pool 22	<1.0	2.7	17.3
Pool 24	<1.0	3.6	29.2
Pool 25	1.9	3.0	25.8
IL RV	<1.0	5.8	52.7
Pool 26	<1.0	4.8	42.5

Table 7b. Copper concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments in the Upper Mississippi River.

[Concentrations are in micrograms of copper per gram of sediment.]

BED SEDIMENTS	**COPPER (µg/g)**		
SITE	Hydroxylamine	Persulfate	Residual
Pool 1	1.6	0.7	9.7
Pool 2	5.3	4.1	21.1
Pool 3	9.1	5.1	29.5
Upper Lake Pepin	19.5	4.6	32.5
Lower Lake Pepin	18.7	7.3	32.6
Pool 5	2.8	1.6	12.2
Pool 5A	3.8	1.9	20.0
Pool 6	1.2	0.6	14.6
Pool 7	4.9	1.6	26.2
Pool 8	2.9	1.2	20.6
Pool 9	5.5	1.6	25.2
Pool 10	4.8	2.5	21.8
Pool 11	3.3	1.5	17.1
Pool 12	6.9	2.2	34.8
Pool 13	3.5	1.1	23.4
Pool 14	2.4	1.2	14.3
Pool 15	1.6	0.8	9.1
Pool 16	2.9	1.1	22.1
Pool 18	3.5	1.2	20.7
Pool 19	7.2	2.5	38.9
Pool 20	2.6	1.0	21.5
Pool 21	1.7	0.8	4.9
Pool 22	2.8	0.9	17.2
Pool 24	3.8	1.7	14.3
Pool 25	3.5	1.7	20.3
IL RV	9.0	3.4	38.1
Pool 26	7.1	2.6	32.4

Table 7c. Lead concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments in the Upper Mississippi River.

[Concentrations are in micrograms of lead per gram of sediment.]

BED SEDIMENTS SITE	**LEAD (μg/g)** Hydroxylamine	Persulfate	Residual
Pool 1	6.9	1.2	6.6
Pool 2	10.0	1.7	6.5
Pool 3	13.3	2.0	7.3
Upper Lake Pepin	28.7	2.8	6.8
Lower Lake Pepin	36.2	2.2	6.2
Pool 5	4.6	0.4	4.1
Pool 5A	5.7	0.7	6.0
Pool 6	2.0	0.5	4.9
Pool 7	6.5	1.2	6.2
Pool 8	4.5	0.8	6.1
Pool 9	7.2	1.5	6.9
Pool 10	8.1	0.7	6.2
Pool 11	6.0	0.9	7.2
Pool 12	28.0	2.4	7.4
Pool 13	6.9	0.8	7.4
Pool 14	5.0	0.6	5.2
Pool 15	5.0	1.2	4.0
Pool 16	6.5	1.1	6.0
Pool 18	6.8	1.0	6.7
Pool 19	15.2	2.2	6.3
Pool 20	4.5	0.9	5.1
Pool 21	5.4	1.0	5.0
Pool 22	4.8	0.7	5.7
Pool 24	6.4	1.1	5.3
Pool 25	6.3	0.9	5.7
IL RV	13.3	2.7	6.1
Pool 26	11.9	2.7	5.3

Table 7d. Iron concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments in the Upper Mississippi River.

[Concentrations are in milligrams of iron per gram of sediment.]

BED SEDIMENTS	**IRON (mg/g)**		
SITE	Hydroxylamine	Persulfate	Residual
Pool 1	1.31	1.08	9.25
Pool 2	3.13	3.53	12.7
Pool 3	4.84	4.14	15.5
Upper Lake Pepin	9.36	6.12	20.8
Lower Lake Pepin	9.51	8.09	25.2
Pool 5	2.15	1.87	11.0
Pool 5A	3.79	3.76	11.5
Pool 6	1.83	1.75	8.95
Pool 7	3.70	2.43	13.8
Pool 8	3.44	2.40	10.3
Pool 9	3.99	3.51	17.2
Pool 10	4.64	4.22	10.7
Pool 11	3.53	2.99	10.5
Pool 12	5.46	4.29	12.9
Pool 13	3.00	1.81	9.39
Pool 14	2.22	2.47	5.76
Pool 15	1.34	1.58	7.66
Pool 16	2.96	2.62	8.48
Pool 18	2.87	2.24	6.82
Pool 19	5.92	3.89	16.6
Pool 20	2.05	2.19	7.32
Pool 21	1.13	1.49	7.84
Pool 22	2.38	1.84	7.27
Pool 24	2.51	2.97	13.0
Pool 25	2.61	3.47	9.79
IL RV	4.15	7.61	21.8
Pool 26	4.75	6.04	18.8

Table 7e. Manganese concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments in the Upper Mississippi River.

[Concentrations are in micrograms of manganese per gram of sediment.]

BED SEDIMENTS	**MANGANESE (µg/g)**		
SITE	Hydroxylamine	Persulfate	Residual
Pool 1	170	<10	110
Pool 2	710	10	120
Pool 3	1240	10	140
Upper Lake Pepin	1470	20	150
Lower Lake Pepin	1660	30	190
Pool 5	330	10	100
Pool 5A	570	10	130
Pool 6	350	10	130
Pool 7	430	10	130
Pool 8	520	10	130
Pool 9	600	10	150
Pool 10	620	10	110
Pool 11	640	10	120
Pool 12	840	10	140
Pool 13	550	<10	120
Pool 14	300	<10	60
Pool 15	220	<10	90
Pool 16	430	10	100
Pool 18	430	10	80
Pool 19	1270	10	140
Pool 20	320	<10	90
Pool 21	180	<10	80
Pool 22	340	<10	90
Pool 24	420	<10	100
Pool 25	510	10	90
IL RV	720	10	150
Pool 26	770	10	140

Table 7f. Organic carbon concentrations for bed sediments collected from navigation pools in the Upper Mississippi River (From Leenheer and others, 1993).

[Concentrations are percent organic carbon based on dry weight of the sediment.]

BED SEDIMENTS SITE	**ORGANIC CARBON (%)**
Pool 1	<0.1
Pool 2	1.4
Pool 3	1.9
Upper Lake Pepin	3.0
Lower Lake Pepin	3.5
Pool 5	1.0
Pool 5A	1.7
Pool 6	0.4
Pool 7	0.7
Pool 8	0.8
Pool 9	1.0
Pool 10	1.7
Pool 11	0.9
Pool 12	2.0
Pool 13	1.0
Pool 14	0.7
Pool 15	0.7
Pool 16	0.9
Pool 18	1.6
Pool 19	1.3
Pool 20	0.6
Pool 21	0.5
Pool 22	0.4
Pool 24	0.5
Pool 25	1.5
IL RV	1.6
Pool 26	1.5

Metal Partitioning

The distributions of chromium, copper, lead, iron, and manganese in the bed sediments determined by sequential extractions are shown in Figures 17 a-e. (Organic carbon concentrations are shown in Figure 17f.) Hydroxylamine, persulfate and residual distributions for chromium, copper, lead, manganese and iron associated with the bed sediments are comparable to those determined for the suspended sediment, suggesting similar metal-sediment associations.

One clear difference between bed and suspended sediments is the significantly lower concentrations of all metals in each extract of the bed sediments despite the fact that bed sediments originate from deposited suspended sediments. Concentrations are generally 2-10 times less than those determined for the suspended sediments. The reason for the lowered metal concentrations in bed sediments may be a function of their particle size distribution. Since processing of bed sediments removed only particles greater than 2 mm, a significant percentage of the sediment may be comprised of sand-size particulates. These large heavy particles add to the weight of the sample but add little to the metal content due to their low surface area and poor adsorptive properties. This results in a dilution of metal concentrations in all extracts.

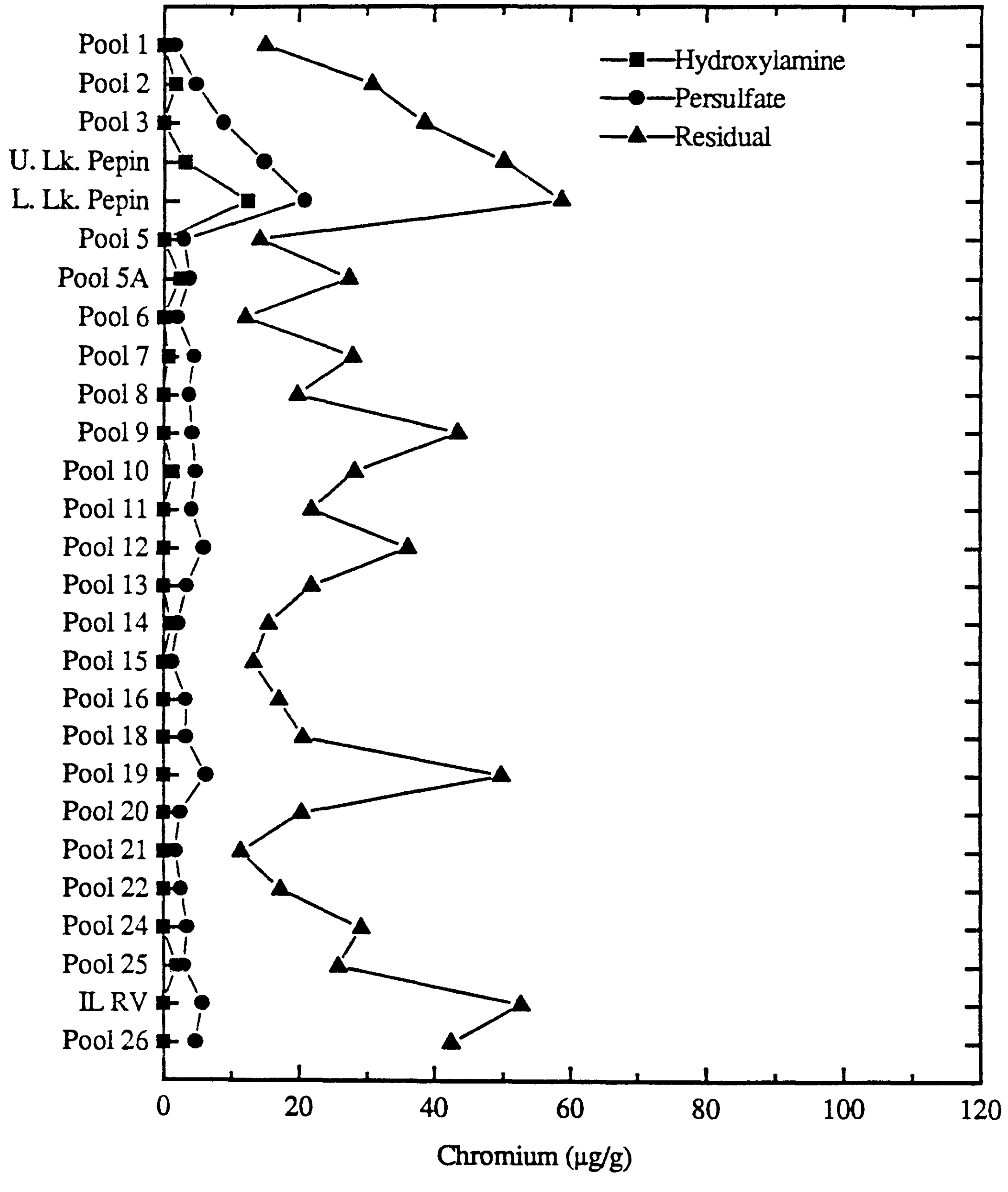


Figure 17a. Chromium concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments from the Upper Mississippi River. (Relative standard deviations for reported chromium concentrations are approximately 11%, 17%, and 4% in the hydroxylamine, persulfate, and residual digests, respectively.)

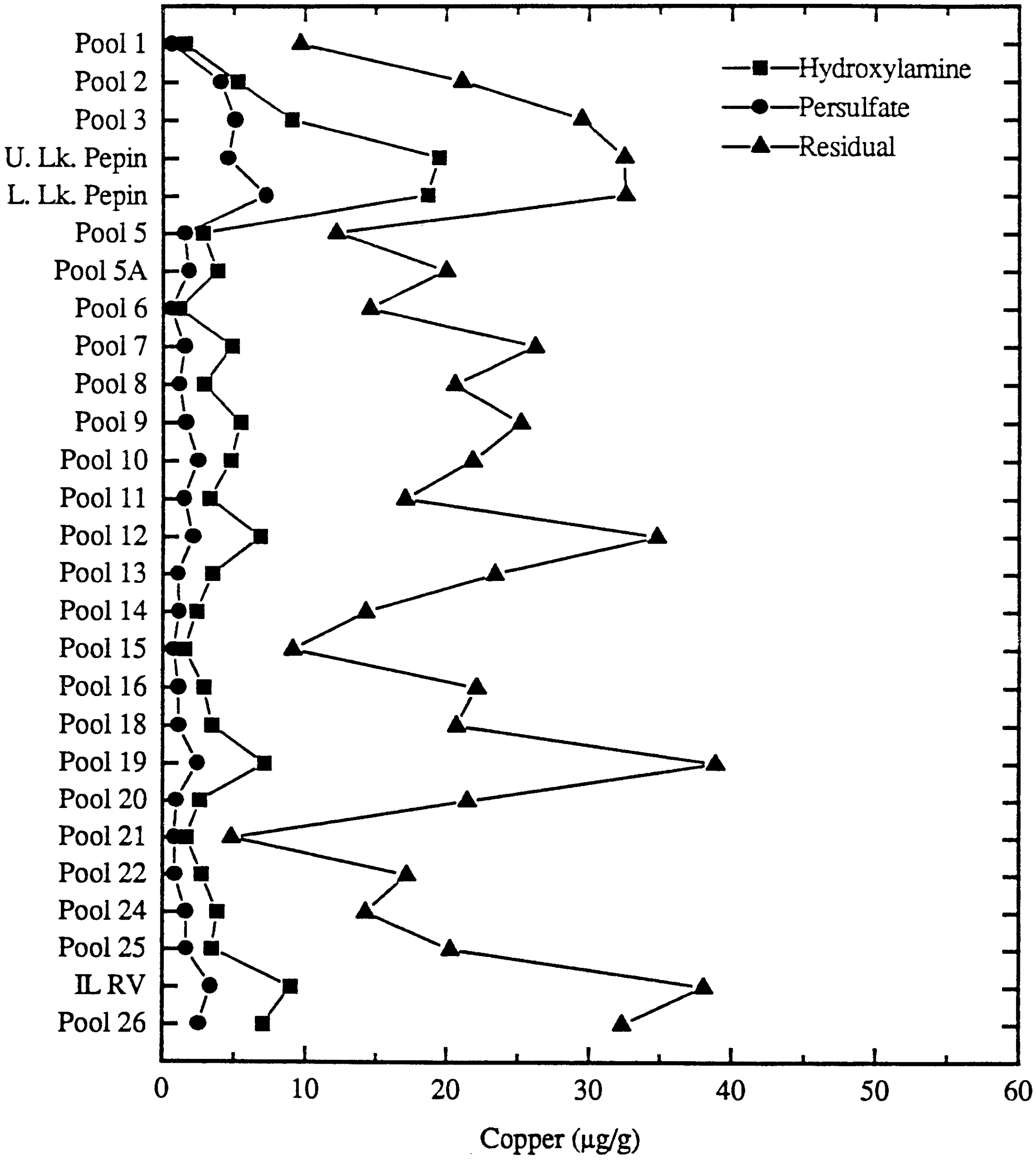


Figure 17b. Copper concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments from the Upper Mississippi River. (Relative standard deviations for reported copper concentrations are approximately 13%, 14% and 12% in the hydroxylamine, persulfate, and residual digests, respectively.)

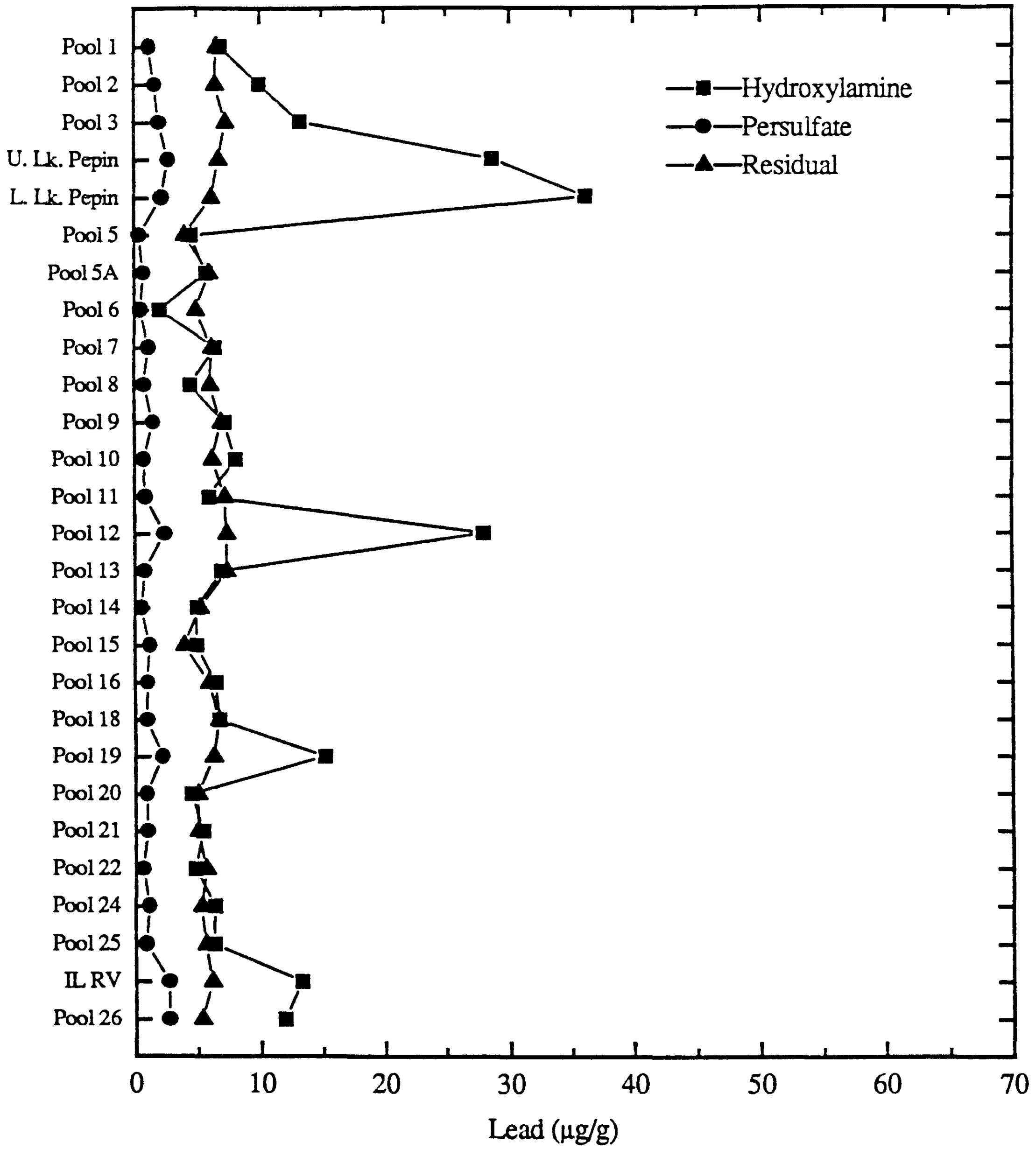


Figure 17c. Lead concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments from the Upper Mississippi River. (Relative standard deviations for reported lead concentrations are approximately 7%, 10%, and 10% in the hydroxylamine, persulfate, and residual digests, respectively.)

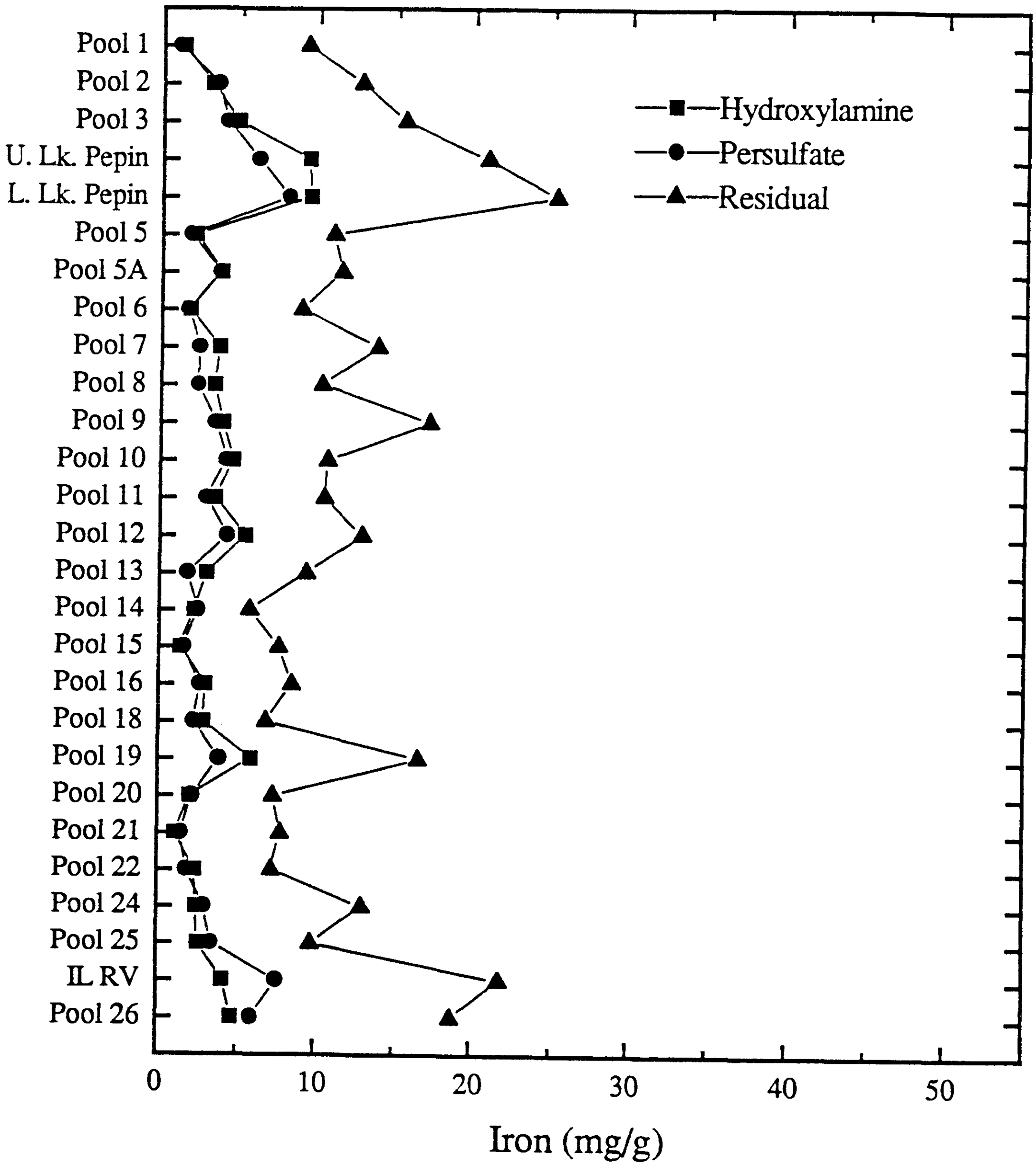


Figure 17d. Iron concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments from the Upper Mississippi River. (Relative standard deviations for reported iron concentrations are approximately 7%, 22%, and 4% in the hydroxylamine, persulfate, and residual digests, respectively.)

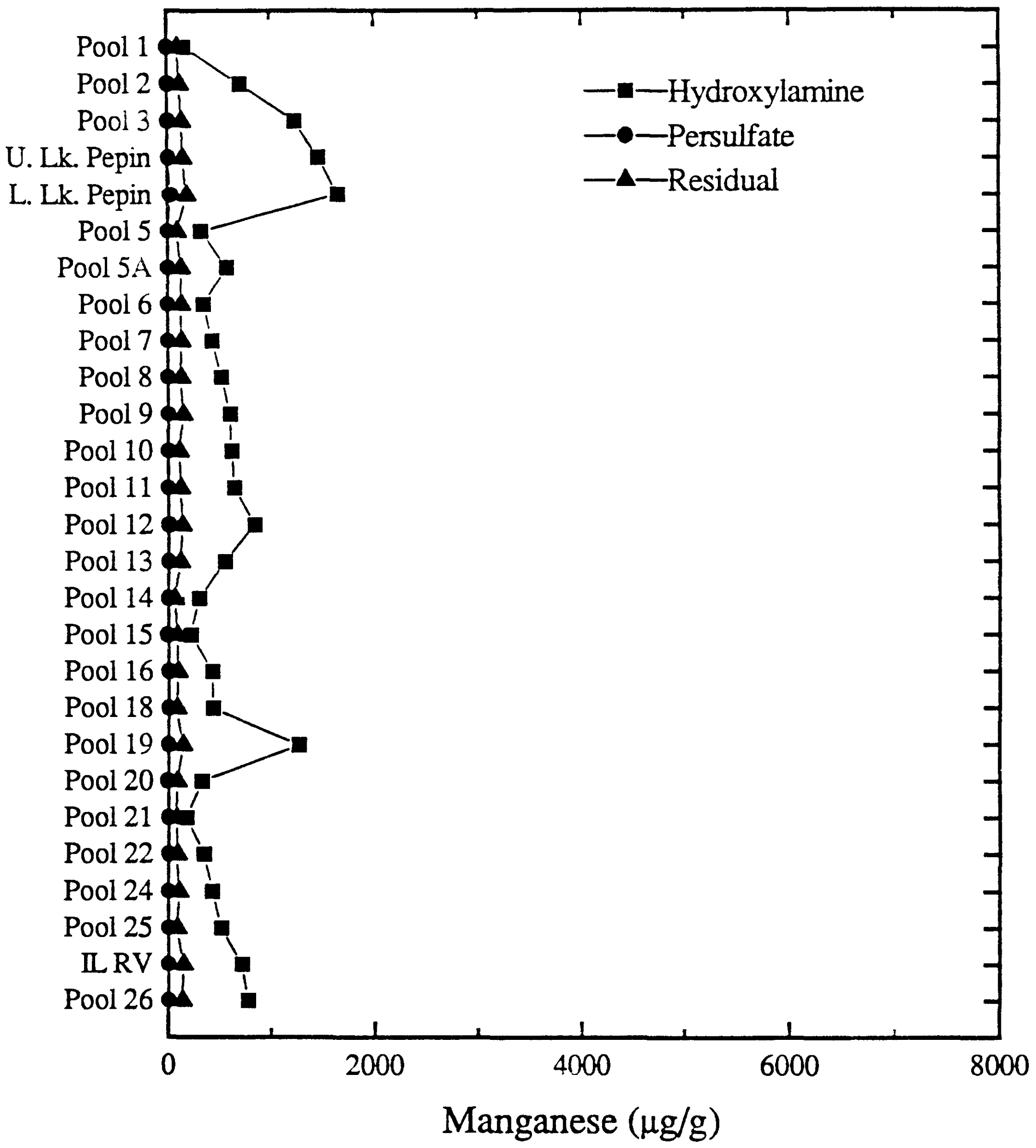


Figure 17e. Manganese concentrations in hydroxylamine, persulfate, and residual extracts for bed sediments from the Upper Mississippi River. (Relative standard deviations for reported manganese concentrations are approximately 8%, 20%, and 7% in the hydroxylamine, persulfate, and residual digests, respectively.)

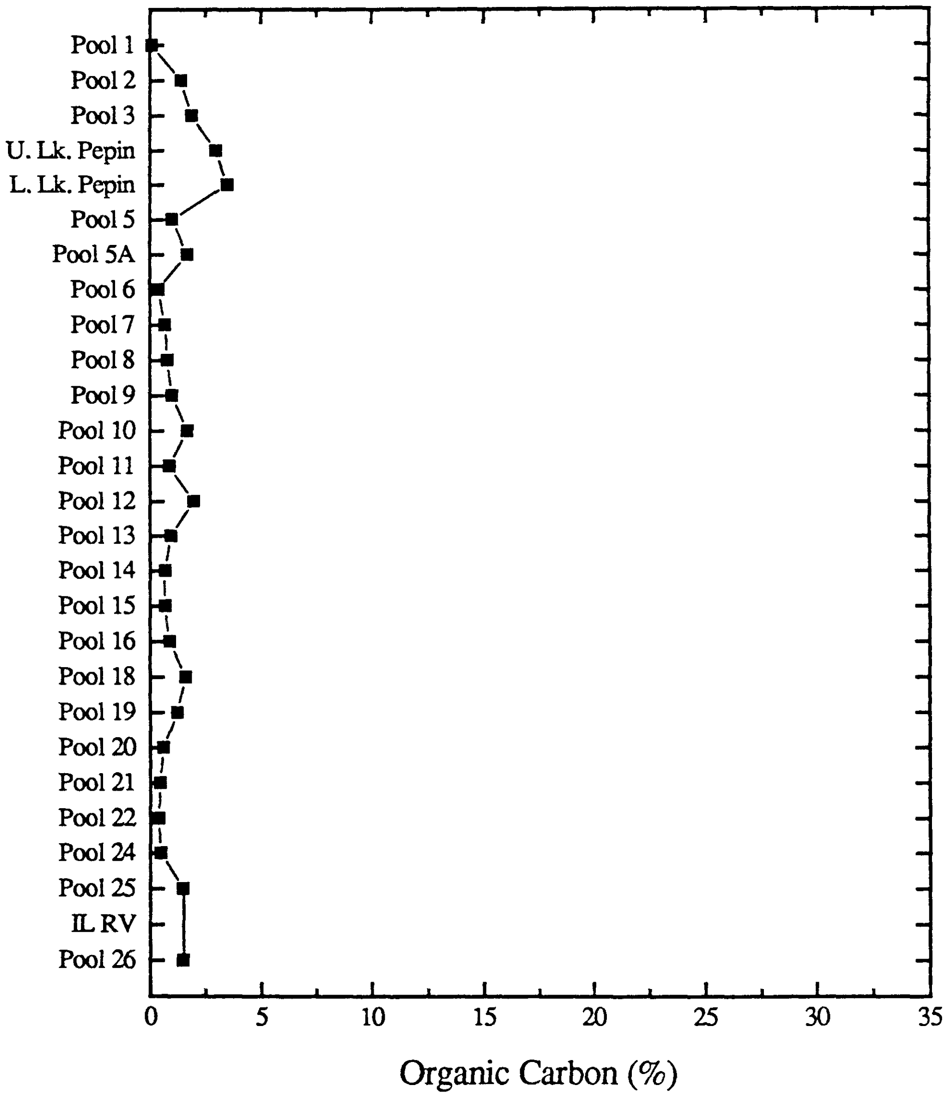


Figure 17f. Organic carbon concentrations for bed sediments from the Upper Mississippi River.

In the specific cases of copper, lead, and manganese, a larger decrease in metal concentrations is indicated in the hydroxylamine extract relative to the concentration decrease in either the persulfate or residual extract. The percentages of sediment-bound copper, lead, and manganese in the hydroxylamine extract are lower for bed sediments than for suspended sediments by about 15%, 20%, and 10%, respectively. The corresponding percent increase for each of these metals occurs in the percentage associated with the residual fraction, while the relative metal concentrations in the persulfate extract remain virtually unchanged from the suspended sediments. The difference between the redox potential in the river and in the bottom sediments may account for the decrease in the hydroxylamine-extractable copper, lead, and manganese the bed sediments. The bottom sediments may be sufficiently reducing to liberate a portion of the bound hydrous manganese oxides while leaving the more resistant amorphous iron oxides intact. The corresponding decrease in hydroxylamine-extractable copper and lead may be a direct result of the dissolution of hydrous manganese oxides which may be a sink for these two metals.

Downriver Trends

Non-residual metal concentrations exhibit definite trends in selected pools. The non-residual concentrations for all the metals steadily increase from Pool 1 at Minneapolis/St. Paul, MN to a maximum at lower Lake Pepin, presumably due to continual inputs from the Twin Cities area. A long and narrow lake, Lake Pepin functions as an efficient trap for Mississippi River suspended sediments. Consequently, bottom sediments in the lake have a large percentage of finer particles (McHenry and others, 1984) which results in higher associated metal content. Metal concentrations drop sharply in Pool 5 immediately after Lake Pepin. Non-residual metal concentrations are relatively constant in the remaining pools with a few notable exceptions. At Pool 12, a large increase in hydroxylamine lead can be attributed to mining activities in the Lead-Zinc District immediately upstream from Pool 12. A moderate increase in non-residual metal concentrations occurs at Pool 19, a deep navigation pool that acts as an important sediment trap (Leenheer and others, 1993). The next increase occurs in the Illinois River bed sediment and Pool 26 immediately downstream from the Illinois River confluence. This suggests that the Illinois River is the source of the high non-residual metal concentrations in Pool 26.

CHAPTER 4

GEOCHEMICAL IMPLICATIONS

In addition to the assessment of suspended sediment in the Mississippi River with regard to trace metal associations and transport, the other objective of this research is to examine the geochemical implications of the sequential extraction results. In particular, the sequential extraction scheme was developed to examine the role of hydrous iron and manganese oxides and organic matter in the transport of trace metals in the aquatic environment by attempting to separate and quantify metals associated with the inorganic and organic components. The purpose of this section is to critically evaluate the results and discuss possible interpretations.

Iron and Manganese Oxides and Organic Matter

In order to investigate the relative importance of iron and manganese oxides and organic matter on sediment in scavenging metals using sequential extraction data, the extractants must effectively differentiate metals associated with each component. Regression analyses of the mainstem silts sequential extraction data suggest that hydroxylamine-extractable iron, hydroxylamine-extractable manganese, and organic carbon concentrations are strongly and significantly related. (A relationship is considered to be highly significant with a probability, or confidence level, less than 0.05). Results from the regression analyses for hydroxylamine iron, hydroxylamine manganese and organic carbon are given in Table 8.

Table 8. Results for regression analyses between hydroxylamine iron, Fe(H) and hydroxylamine manganese, Mn(H) and between hydroxylamine iron and organic carbon on mainstem Mississippi River sediments.

[R is the regression coefficient; P is the probability; N is the number of values regressed;--- indicates inadequate number of values for a meaningful regression.]

		Fe(H)-Mn(H)			Fe(H)-Organic C		
TYPE	TRIP	R	P	N	R	P	N
Silt	July-August 1991	0.904	6E-5	12	0.800	2E-3	12
	Oct.-Nov. 1991	0.699	5E-2	8	0.771	2E-2	8
	April-May 1992	0.881	4E-3	8	0.963	1E-4	8
Colloid	July-August 1991	0.740	4E-2	8	0.322	4E-1	8
	Oct.-Nov. 1991	---	---	4	---	---	4
	April-May 1992	0.945	1E-3	7	0.617	1E-1	7
Beds	July 1991-May 1992	0.935	1E-14	31	0.855	9E-10	31

Although iron and manganese oxides are commonly related in the aquatic environment, the results for the silts and bed sediments suggest that hydrous iron oxides and organic matter may also interact significantly. The observed relation between hydroxylamine iron and organic carbon is most likely due to sorption of organic matter especially humic substances onto the amorphous iron coatings on the sediment (Greenland, 1971; Tipping, 1981). The implication of this relationship is that the hydroxylamine extraction may have liberated organics which were either sorbed to the surface of the oxide or incorporated within the amorphous iron oxide lattice. The results of Karlsson and others (1987) support this implication, reporting that a sequential extraction of mine drainage stream sediments using 0.043 M hydroxylamine hydrochloride in 25% acetic acid released up to 28% of the total humic and fulvic acids before the oxidation step. With regard to interpretation of the trace metal sequential extraction data, the strong relation between the amorphous iron oxide content and organic matter concentration implies that the hydroxylamine extraction does not disrupt purely inorganic metal associations.

In contrast to the silts and bed sediments, regression analyses of hydroxylamine iron, hydroxylamine manganese, and organic carbon on the colloids show that while a significant relationship exists between iron and manganese for July-August 1991 and April-May 1992, no significant relationship exists between the hydroxylamine iron and organic carbon. (An insufficient number of data points for the October-November 1991 colloids precluded a meaningful regression analysis). A possible explanation for the difference between the silts and bed sediments and the colloids may be that the colloids have considerably larger concentrations of organic carbon, generally 3 to 5 times the concentrations on the silts and over 10 times the concentrations on bed sediments, while the hydroxylamine iron concentrations are similar to those of the silts. This suggests that the relatively small amounts of amorphous iron oxides on the colloids no longer significantly influence sorption of relatively extensive organic coatings. Additionally, some of the colloidal particles are probably purely organic material contributing to the lack of relationship between organic carbon and hydroxylamine iron.

The sequential extraction data also indicate that a significant amount of iron is extracted for the silts, colloids, and bed sediments by the persulfate reagent. Several interpretations are possible for this result which were also mentioned in the method development chapter. Although it is unlikely that the hydroxylamine extraction was inefficient in its dissolution of amorphous oxides, organic matter may have an armoring effect on part of the iron coatings making them inaccessible to the reducing agent (Karlsson and others, 1987; Maher, 1984). This explanation seems most plausible for colloid samples for which organic matter is a relatively major component. However, since persulfate-extractable iron is generally not significantly higher for sediments with high organic carbon, this explanation does not appear to be fully adequate.

Another possibility is that the iron released by the persulfate extraction is due to the oxidation of pyrite. A typical persulfate iron concentration of 7000 μg/g translates to about 1.5% pyrite in the sample. This concentration of pyrite seems reasonable since pyrite was present in detectable amounts by X-ray diffraction in the Mississippi River sediments for which mineralogical analyses were done (Dunn, 1992). Several important pyrite deposits related to the mining of lead, zinc, and copper as well as pyrite-containing coal deposits are located adjacent to the Mississippi River such as in the Lead-Zinc District near Galena, IL and the New Lead Belt in southeastern Missouri. This interpretation would explain the higher persulfate iron below the confluence of the Missouri River particularly for the April-May 1992 trip. The increase in persulfate iron may be the result of an increase in pyrite in the suspended sediment due to the high flow conditions in the Mississippi River which may resuspend the heavier pyrite particles once deposited on the bottom sediment. Surface run-off may increase the pyrite concentrations in the river as well. The increase in persulfate iron in this reach of the river is primarily observed in the silt fraction because the dense pyrite particles are most likely fractionated in the silt size during centrifugation. The Ohio River which flows through a sulfide deposit (Lovering, 1972) also has substantial persulfate iron in both the silt and colloid under conditions of high flow in April-May 1992. Unfortunately, the implication of either the armoring effect of organics or the presence of pyrite as an explanation of the high persulfate iron is that metals released by the persulfate are not entirely associated with organic matter.

Because of the inability of the sequential extraction to differentiate between the hydrous oxides and organic matter, as suggested by the sequential extraction data, discerning the role of these components in the transport and scavenging of trace metals is complicated considerably. As a consequence, results of the sequential extraction may not necessarily reflect the actual trace metal association on the sediment, and these complications must be considered in the following discussion of the geochemical significance of the trace metal extraction results.

Chromium

Because chromium can exist as a cation, mainly $Cr(OH)_2^+$, in the +3 oxidation state or as an oxyanion, largely CrO_4^-, in the +6 oxidation state in the redox and pH conditions in the Mississippi River (Hem, 1977), its sorption behavior onto sediment is expected to be a function of its oxidation state. While the +6 oxidation state is thermodynamically stable in alkaline and mildly oxidizing waters, the +3 state is kinetically stable, and interconversions between the two states can occur under conditions present in natural waters (Moore and Ramamoorthy, 1984). Assuming chromium interacts with the sediment as the anion CrO_4^-, similar sediment-metal interactions may be expected for vanadium which also exists as an oxyanion ($H_2VO_4^-$) at pH 7-9 (Hem, 1977). However, the sequential extraction data for vanadium (see SSMC.XLS and BSMC.XLS) present an apparent and unexpected contradiction. Unlike chromium, the concentrations of the supposedly anionic vanadium (Hem, 1977) in the hydroxylamine extract are dominant over concentrations in the persulfate extract, a distribution similar to other metal cations.

Complicating the oxidation issue further, the significant amount of chromium extracted under the oxidizing conditions of the persulfate extraction suggests that chromium is most likely in the cationic +3 oxidation state, which forms stable complexes with organic compounds, in particular nitrogen-containing compounds (Cotton and Wilkinson, 1988). This interpretation seems reasonable given that the organic matter on the sediments in the Mississippi River is largely proteinaceous in nature (Leenheer and others, 1991). Apparently other factors in addition to the charge of the metal ion may be influencing sorption behavior onto the sediment.

Several researchers have found similar chromium associations in sediments. Rosental and others (1986) reported chromium in the sediments of False Bay, South Africa present dominantly in the residual and organic matter while only about 10% of the chromium was associated with the oxide coatings. Dudka and Chlopecka (1990) found chromium-organic associations to be more significant than chromium bound to oxide coatings for sludge and soil samples. By comparison, Gupta and Chen (1975) reported 75-88% of the non-residual chromium incorporated in oxide coatings for Los Angeles sediments. Extraction results of sediments from the Rhine River also indicated the dominant association of chromium with oxide coatings over organic matter (Forstner and Patchineelam, 1980).

Copper

In contrast to chromium, the concentration of copper extracted by hydroxylamine is considerably more significant than that found in the persulfate extract. This suggests that copper has a greater association with iron and manganese oxides and carbonates than with organic matter. Cupric cations may interact with oxide coatings and/or carbonate minerals through surface sorption, coprecipitation, or precipitation mechanisms detailed in Chapter 1. Extraction results for bed sediments seem to support the association of copper and manganese given the concurrent decrease in the fraction of both manganese and copper in the hydroxylamine extract discussed in Chapter 3. However, given the significant presence of organic material on the Mississippi River sediments and the strong affinity of organic matter for Cu^{2+} (Stumm and Morgan, 1981), the relatively small amounts of copper extracted by the persulfate oxidation reaction appears inconsistent. Although surface complex formation constants for metals and organic surfaces are difficult to quantify due the to structural complexity of organic material, mean pK values for copper binding at proton sites on fulvic-type materials have been reported to be 0.8 for carboxylic sites and 3.7 for phenolic sites (Tipping, 1993). Given these large equilibrium constants, a significant fraction of the copper would seem likely to be organically bound.

This apparent discrepancies may actually be due to an artifact of the extraction scheme. Several equilibria during the hydroxylamine extraction may affect organically bound copper. Excess hydrochloric acid used in the hydroxylamine extraction may disrupt humate-copper complexes as shown in the following reaction:

$$\text{R--COO-Cu}^{+} + \text{HCl} \longleftrightarrow \text{R--COOH} + \text{CuCl}^{+}.$$

This equilibrium is essentially the reverse of the organic surface-metal complex formation reaction which means the equilibrium constant for the protonation reaction is approximately $10^{0.8}$. With HCl concentrations of 0.25 M, this reaction is undoubtedly of significance. Because other metals that bind less strongly to humic substances than does copper are most likely affected similarly, the fraction of metals extracted by the hydroxylamine should probably be redefined to include not only inorganic metal associations, but metals bound surficially to humic substances as well.

Another reaction which may affect the results of copper in particular is the reduction of organically bound Cu(II) by hydroxylamine in the presence of excess chloride ion. Assuming the standard potential of 0.538 V for the reduction of aqueous Cu^{2+} in excess Cl^- (Huheey, 1983) as a rough estimate for the corresponding reduction of organically bound Cu(II), a standard potential of 1.87 V for the oxidation of hydroxylamine is sufficiently high for this reaction to occur.

The copper extracted by the persulfate oxidation reaction may be either due to association with the significant protein component of the Mississippi River organic material or to copper sulfide minerals. Proteins are strongly adsorbed to the sediment (J.A. Leenheer, oral commun., 1993) and are most likely not significantly affected by the hydroxylamine hydrochloride / hydrochloric acid reagent.

The existing literature on copper speciation on sediments sheds little light on the interpretation of the copper data. According to the published studies, the association of copper is quite variable depending on the specific river system or estuary. Copper on sediments from Baie de Nice (Rapin, 1984), Los Angeles Harbor (Gupta and Chen, 1975), Weser Estuary, Rotterdam Harbor, Neckar River, Meuse River, and Somme River (Calmano and Forstner, 1983) are reported to have greater inorganic than organic associations, while sediments from Yellow River, Yanaska River, St. Francis River, (Hong and Forstner, 1984), Garonne River, Gironde River, Rhine River, and Elbe River

(Calmano and Forstner, 1983) are reported to exhibit the reverse trend. Of particular relevance to this Mississippi River study are the investigations of copper transport by Presley and others (1980) on Lower Mississippi River sediments and by Eisenreich and others (1980) on Upper Mississippi River sediments. While Presley and others (1980) reported concentrations of copper associated with the hydrous oxides comparable to those determined in this study, they also reported slightly higher copper concentrations associated with the organic matter and lower concentration in the refractory minerals. In contrast, Eisenreich and others (1980) reported a greater proportion of copper associated with the organic fraction for Upper Mississippi River sediments.

Lead

In the case of lead, the results presented in Chapter 3 suggest inorganic associations to be dominant. Since lead exists in the aquatic environment as the cationic species, Pb^{2+} or $Pb(OH)^{+}$, at a pH of between 7 and 9 (Moore and Ramamoorthy, 1984), the most probable interaction is sorption of the lead cation to the negatively charged hydrous oxide surface. The decrease in hydroxylamine lead concomitant with a decrease in hydroxylamine manganese observed in the bed sediments implies that manganese oxides may indeed play a role in scavenging lead. Another source of lead in the inorganic fraction is most likely particulate lead. Particulate lead is largely mixed lead oxides originating from the breakdown of lead additives in gasoline during combustion (Pierrard, 1969). Since particulate lead is a distinct oxide particle not associated with the sediment, lead in the hydroxylamine fraction can not be considered to be entirely sediment bound. The relatively constant and low concentrations of lead in the persulfate extracts may be due to lead sulfide minerals common in the Mississippi River basin.

The importance of hydrous oxides relative to organic matter in scavenging lead is supported by numerous investigators. Lead distributions for sediment from rivers and estuaries from various geographical locations, tabulated by Nair and others (1991), indicate lead is predominately associated with the inorganic sediment component in all cases. Similar concentrations of inorganic lead, approximately 20 μg/g, were reported by Presley and others (1980) in the Lower Mississippi River sediments with slightly higher values reported for organic and residual associated lead.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

Concentrations of chromium, copper, lead, iron, and manganese associated with sediment from the Mississippi River determined by the developed sequential extraction method provide an estimate of non-residual and residual metal associations, and therefore, a measure of the bound metals most likely to be remobilized as a result of changes in the aquatic environment. While a major fraction of sediment bound chromium, iron, and to a lesser degree, copper, is associated with refractory minerals, the significant fraction of copper, lead, and manganese in the sediments is non-residual. The significantly higher and more variable non-residual metal concentrations of suspended sediment in the upper Mississippi River relative to the lower river are largely due to hydrological differences between the impounded upper river and the free-flowing lower river.

Occasional increases in non-residual metal concentrations for colloids with no corresponding increase in non-residual metal concentrations for silts may suggest that colloids and silts are not in equilibrium with respect to sorbed metal ions in the river. If colloids and silts in the river are not at equilibrium, then metal ions may be transported downriver by the colloids without significantly partitioning onto the silt fraction. This result may have important implications in modeling metal transport in river systems.

Colloids, although generally enriched in non-residual metal concentrations relative the silts, contribute a minor fraction of non-residual metal suspended sediment load in the lower river, but carry a significant fraction of sediment bound non-residual metals in the upper river. The contribution of colloid associated metals, typically analyzed by most workers with the "dissolved" phase (<0.4 µm), to "dissolved" metal results is difficult to determine since both colloid associated metal concentrations and dissolved metal concentrations in the Mississippi River were near or below analytical detection limits when expressed in micrograms per liter of river water.

Although extractions of Mississippi River sediment provide useful non-residual and residual metal data, elucidation of the specific inorganic and organic metal associations proves inconclusive. The indistinguishablility of the inorganic and organic components by the sequential extraction method greatly limits attempts to examine the role of either component in trace metal transport. To gain a better understanding of the complicated metal-sediment interactions, batch sorption reactions using pure hydrous oxide substrate and pure humic substrate are proposed. Sorption of metal cations can be studied on each phase separately as well as on hydrous oxide and organic mixtures to study competition effects. By varying the ratio of oxide and organic components as well as the order of deposition, the extent of additive or competitive sorption can be examined by determining the loss of metal ions in solution as well as determining metal associations on the solid through direct techniques such as electron microprobe. In addition, effects of metal competition and differences between the behavior of anions such as CrO_4^- and cations such as $Cr(OH)_2^+$ on sorption can be investigated. By controlling the heterogeneity of the sample and by eliminating the uncertainty of sequential extractions in characterizing metal-solid associations, more definitive results may possibly be obtained.

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APPENDIX

Table A-1: Detection limits and quantitation limits determined for trace metal analysis on the ICP-MS, in µg of metal per gram of sediment, for hydroxylamine, persulfate, and total digest matrices.

	Hydroxylamine		Persulfate		Total digest	
	DL[a]	QL[b]	DL[a]	QL[b]	DL[a]	QL[b]
^{52}Cr	0.3	1	0.4	0.5	2	1
^{59}Co	0.1	0.1	0.1	0.3	0.4	
^{60}Ni	0.2	0.3	0.3	1	1	2
^{63}Cu	0.1	0.2	0.2	0.4	0.8	1
^{66}Zn	0.1	0.5	4	10	5	20
^{111}Cd	0.1	0.3	0.5	1.5	0.7	3
^{208}Pb	0.1	0.3	1	1.5	0.6	2

[a] Detection limit in µg/g of sediment at the 99% confidence level calculated following the method of Skogerboe and Grant (1970).

[b] Quantitation limit in µg/g of sediment, the experimentally determined analyte concentration that can be reported with 99% confidence. Calculated as QL = t X s, where t = student t statistic at 99% confidence level and s = the standard deviation of the analyses of a synthetic standard at a concentration of 5 times the detection limit for the respective analyte.

Table A-2. Blank determinations for trace metals analyzed on the ICP-MS for the hydroxylamine, persulfate, and residual extracts.

[Concentrations are in micrograms per liter; - indicates less than; and * indicates analysis on ICP-AES.]

	HYDROXYLAMINE EXTRACT				
Date of extraction	Cr	Cu	Zn	Cd	Pb
9/7/92	-2	-0.3	-1	-0.5	-0.5
9/10/92	-2	-0.3	-1	-0.5	-0.5
9/24/92	-2	-0.3	-1	-0.5	-0.5
10/7/92	-2	-0.3	1	-0.5	-0.5
10/18/92	-2	-0.3	-1	-0.5	-0.5
10/26/92	-2	-0.3	-1	-0.5	-0.5
11/5/92	-2	-0.3	-1	-0.5	-0.5
11/17/92	-2	-0.3	-1	-0.5	-0.5
11/23/92	-2	-0.3	-1	-0.5	-0.5
12/1/92	-2	-0.3	-1	-0.5	-0.5
12/7/92	-2	-0.3	-1	-0.5	-0.5
2/10/93	-2	-0.3	-1	-0.5	-0.5
	PERSULFATE EXTRACT				
	Cr	Cu	Zn*	Cd	Pb
9/7/92	10	-0.3		-0.5	-0.5
9/10/92	-2	-0.3		-0.5	-0.5
9/24/92	-2	-0.3		-0.5	-0.5
10/7/92	-2	-0.3		-0.5	-0.5
10/18/92	-2	-0.3		-0.5	-0.5
10/26/92	10	-0.3		-0.5	-0.5
11/5/92	-2	-0.3		-0.5	-0.5
11/17/92	-2	-0.3		-0.5	-0.5
11/23/92	-2	-0.3		-0.5	-0.5
12/1/92	-2	-0.3		-0.5	-0.5
12/7/92	-2	-0.3		-0.5	-0.5
2/10/93	-2	-0.3		-0.5	-0.5
	RESIDUAL				
	Cr	Cu	Zn	Cd	Pb
9/7/92	-2	-0.3	-1	-0.5	-0.5
10/7/92	3	6	-1	-0.5	-0.5
10/18/92	-2	5	-1	-0.5	-0.5
10/26/92	-2	3	-1	-0.5	-0.5
11/5/92	2	13	7	0.9	1.598
11/17/92	-2	11	2	0.7	-0.5
11/23/92	2	16	6	1	-0.5
12/1/92	2	5	6	0.8	-0.5
12/7/92	-2	3	-1	-0.5	-0.5
12/27/92	-2	1	-1	-0.5	-0.5
2/10/93	-2	1	-1	-0.5	-0.5