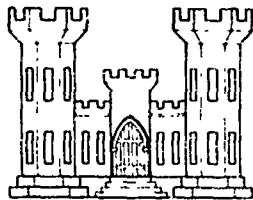
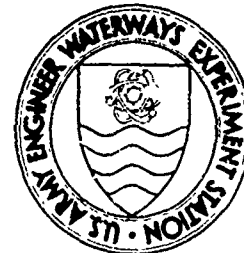


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DREDGED MATERIAL RESEARCH PROGRAM



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TRANSFORMATIONS OF HEAVY METALS AND PLANT NUTRIENTS IN DREDGED SEDIMENTS AS AFFECTED BY OXIDATION REDUCTION POTENTIAL AND pH VOLUME II: MATERIALS AND METHODS/RESULTS AND DISCUSSION

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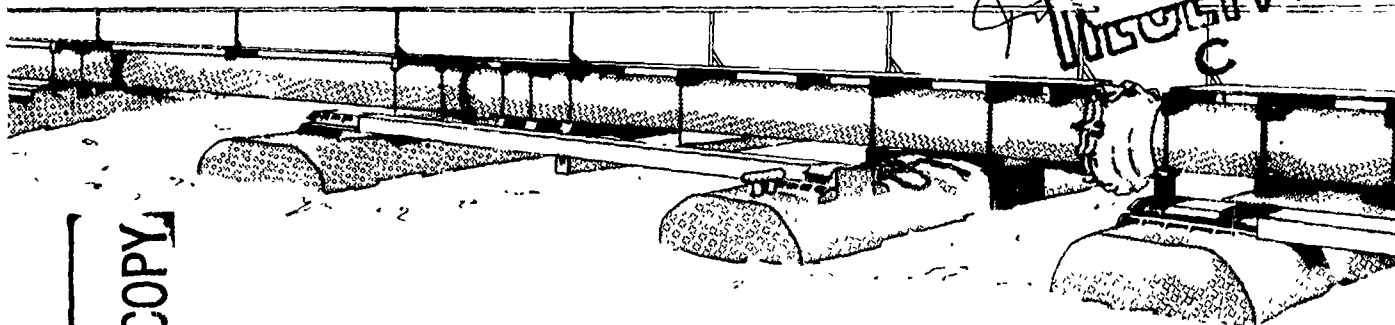
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May 1977
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reduction potential on the capacity of the sediment materials to retain high levels of added toxic metals. The effects of pH and oxidation conditions on the formation, stability, and molecular weight distribution of soluble metal complexes with selected trace metals were also studied.

These studies indicated that pH and redox potential do influence the chemical form and distribution of the metals studied, although the response to changes in the physicochemical environment were frequently not the same for the different metals.

Soluble and exchangeable levels of mercury were not greatly influenced by changes in pH and oxidation intensity. However, small increases in these forms were noted under strongly reduced, acid conditions and oxidized, mildly alkaline conditions. Soluble and especially insoluble large molecular weight humic materials apparently are principal regulatory factors controlling the retention and availability of mercury.

Levels of soluble and exchangeable lead were less affected by oxidation intensity than pH and increased considerably when pH was lowered to 5.0. Lead was strongly associated with the reducible phase (hydrrous oxides), and lead recovered in this chemical form increased with increasing oxidation intensity. Much of the remaining potentially available lead was associated with large molecular weight humic materials recovered from oxidized systems with a mild extraction using a synthetic organic chelate.

Unlike mercury and lead, cadmium release to soluble and exchangeable forms was favored by oxidized conditions, particularly at pH 5.0 and 6.5. As oxidation intensity increased, this cadmium was apparently released from large molecular weight organics.

The report also discusses the effects of pH and redox potential on the chemical transformations of iron, manganese, zinc, copper, phosphorus, and ammonium-nitrogen in the sediment materials studied.

The results of this study suggest that pH and redox potential are important in regulating the chemical availability of a number of nutrients and potentially toxic trace metals. The metal regulatory processes involved included precipitation with sulfide, adsorption or coprecipitation with colloidal hydrrous oxides, and complex formation with soluble and insoluble organics. In many cases, changes in acidity or oxidation-reduction conditions resulted in considerable transformations among potentially available forms, but little conversion to the soluble and exchangeable chemical forms thought to be most readily available. Cadmium was a notable exception, as considerable proportions of the total cadmium content could be transformed to soluble and exchangeable forms as a result of comparatively mild changes in physicochemical parameters.

Where dredged material disposal is accomplished by open water dumping, it is probable that little change in oxidation-reduction conditions occurs to the typically reduced bulk solid phase before these solids settle to the bottom of the water column at the disposal site and again become a reduced sediment material. Toxic substance release by open water disposal methods can better be approximated by short-term studies such as the elutriate test. The availability response described in this report is thought to be applicable in open water disposal where little change in physicochemical parameters of bulk solids is expected to occur as well as to upland application of dredged material for disposal or resources utilization purposes. Where upland methods are used, gradual drainage and subsequent oxidation may occur over extended time intervals concurrently with probable redox potential mediated changes in pH which may affect metal availability.

The results of this study and its applicability to upland disposal methods suggest that plants should be included in research of this type to determine if conditions enhancing chemical availability do indeed increase bioavailability of these metals to flora and fauna populations when dredged materials are introduced into wetland ecosystems.

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EXECUTIVE SUMMARY

The volume of sediments dredged annually from navigable waters in the United States exceeds 200 million cu m. Currently, most dredged material disposal is accomplished either by discharge into open water at sites removed from shipping channels or by land disposal where solids settle from suspension and are confined, usually within a dike structure. Disposal of dredged material may, under some conditions, adversely affect environmental quality. This concern is compounded by the large quantities of dredged material involved. Waterways are the recipients of much of the toxic metals, pesticides, biostimulants, and other organic and inorganic wastes released into the environment. In waterways, sediments and suspended solids exhibit a strong affinity for most chemical contaminants. As a consequence, considerable quantities of undesirable materials may accumulate in the sediment solid phase.

Some sediment-bound materials, such as nitrogen, phosphorus, and certain metals, are known to diffuse from interstitial water into overlying surface water. Thus an equilibrium may exist which results in the maintenance of low levels of certain materials in the water column as a consequence of their release from undisturbed sediments. However, there may be a much greater exchange of potential pollutants between sediments and surface waters when sediments are disturbed during dredging and dredged material disposal.

In recent years, much concern has been focused on the possible deleterious effects on water quality resulting from the release of toxic metals from dredged sediments. Even more recently, attention has been drawn to the possible uptake and concentration of toxic metals by plants grown on dredged sediments transported to land.

Sediment-bound pollutants range widely in availability to aquatic and benthic organisms and to plants grown on dredged sediments. Some chemical combinations are readily available to the biological community, and other chemical forms are essentially unavailable. Soluble and exchangeable metallic cations are examples of readily available materials. Metals bound within the crystal lattice of primary minerals are essentially unavailable. Between these extremes may be a considerable quantity of toxic or biostimulatory substances which are potentially available to terrestrial plants and aquatic and benthic populations as a result of chemical transformations in the sediment-water system. When sediments are disturbed during dredging and dredged material disposal, physical and chemical changes may occur, possibly influencing the bioavailability of sediment-bound toxins and biostimulants.

Several factors have been found to influence the exchange of materials between disturbed sediments and surface waters. These factors include the solid-to-liquid ratio, the degree of agitation, sediment particle size, time of contact, and chemical characteristics of the water and sediments. The pH and oxidation-reduction (redox) potential of

sediment-water systems are chemical characteristics known to have both direct and indirect effects on chemical transformations, possibly affecting the bioavailability of toxic metals and nutrients. The soluble concentration of a metal in an aqueous environment is regulated to a considerable extent by elemental speciation, or the ions and covalent compounds formed in a given chemical environment. Redox potential and pH are important parameters influencing elemental speciation in aqueous systems.

The pH and redox potential of sediment-water systems also affect the bioavailability of potentially toxic metals by influencing the chemistry of numerous other substances which regulate the availability of metals. Some of these processes include metal-sulfide precipitation; adsorption to colloidal hydrous oxides, such as those of iron and manganese; and metal complexation with soluble and insoluble organics.

Currently, little is known about the chemical transformations of sediment-bound toxic metals and biostimulants resulting from their being disturbed, transported, and disposed of in an environment which may differ considerably from that of an undisturbed sediment at the bottom of a waterway. Even less is known about the influence of pH and redox potential, and particularly changes in these parameters, on the chemical transformations affecting the bioavailability of metals and nutrients during dredging and dredged material disposal. A striking change in the chemical environment of dredged material may occur as typically reduced bottom sediments are dispersed in an oxygenated water column or deposited

on land for disposal. Transformations in the chemical forms of environmental contaminants which affect their bioavailability may occur due to changes in pH or redox potential of the dredged material.

The influence of pH and redox potential on the chemistry of many elements can be derived from thermodynamic considerations for simple inorganic systems such as a metal in water. For aqueous systems consisting of a limited number of elemental components, the regulation of chemical form characterized by distinct redox potential-pH boundary conditions between the various possible chemical forms. In recent years, such thermodynamic calculations have been expanded to describe metal chemistry in more complex aqueous systems which include both organic and inorganic chemical constituents. Such studies are useful in identifying regulatory mechanisms affecting metal solubility and availability. However, these models of simple aqueous systems cannot approach the complexity of natural sediment-water systems due to the qualitative diversity and quantitative variability of the chemically reactive constituents present in natural systems. This suggests a somewhat empirical approach is necessary to study the influence of pH and redox potential on metal and nutrient chemistry in sediment-water systems.

The objective of this study was to determine the influence of pH and redox potential in regulating chemical transformations affecting the bioavailability of toxic metals and nutrients in sediment-water systems. In particular, this research was planned to answer how changes

in pH and redox potential encountered by a sediment material during dredging and dredged material disposal might affect the release of toxic metals and plant nutrients. It is believed that an increased understanding of the regulatory influence of pH and redox potential on toxic metal and plant nutrient chemistry in sediment-water systems may contribute in developing effective dredged material disposal criteria.

Sediment materials from four locations were selected to include a range of physical and chemical sediment properties in the research materials studied. The sediments were incubated at controlled pH and redox potential levels as a suspension of approximately the same solids-to-water ratio encountered in a dredged slurry. Four redox potential treatments were selected to represent oxidation levels ranging from strongly reduced to well oxidized. The pH levels studied ranged from moderately acid to weakly alkaline (pH 5.0, 6.5, and 8.0).

The nature of oxidation-reduction reactions is such that the pH of reduced sediments generally falls within a fairly narrow range around neutrality (represented by the pH 6.5 and 8.0 treatments). However, moderately acid environments may be encountered by dredged materials. The pH 5.0 treatment may be particularly applicable to some dredged materials transported to land for disposal. Drainage and subsequent oxidation of the surface layer of reduced sediments containing considerable sulfide may result in the formation of a weak sulfuric acid solution. This may contribute to the formation of an acid environment, not only

in the surface oxidized layers, but in underlying reduced layers as a consequence of leaching.

Dredging and dredged material disposal may also affect redox potential. Though it is likely the redox potential of sediments from most navigable waterways ranges from moderately reduced to strongly reduced, well-oxidized environments may be encountered by initially reduced sediments as a consequence of dredging and/or dredged material disposal. Some chemical changes affecting aqueous metal chemistry as a consequence of an altered redox potential may be almost immediate. An example is the oxidation of soluble ferrous iron as reduced interstitial water is mixed with oxygenated surface waters. The colloidal hydrous ferric oxides and hydroxides thus formed may be effective scavengers for soluble heavy metals. In contrast to the rapid oxidation of soluble ferrous iron, quantitative and qualitative changes in organic matter may occur gradually if the oxidation-reduction environment of a sediment is altered for extended periods.

Changes in redox potential of dredged sediments may depend on the methods of dredging and dredged material disposal. It is likely that there will be little change in redox potential in the bulk of the dredged solids which are transported relatively short distances, dumped in open waters for disposal, and settle rapidly to the bottom. However, there is some opportunity for oxidation to occur where: (1) hydraulically dredged sediments are transported for extended distances, (2) interstitial

water and its soluble components are mixed with surface water, and
(3) finely divided solids remain in suspension for considerable length
of time following open-water disposal. Also, it is likely that the
surface horizons of reduced dredged material transported to land for
disposal will eventually become oxidized as excess water drains and
is replaced by air.

A laboratory study was conducted in which sediment suspensions were
incubated under conditions of controlled pH and redox potential. All
incubation flasks were equipped with glass (pH) and platinum electrodes
connected to potentiometers to measure pH and redox potential, respectively.
The pH was controlled by manual additions of acid or base. In the ab-
sence of oxygen, sediments tend to become more reduced with time. Thus
redox potential was adjusted and then maintained at the selected levels
by slowly bubbling air containing the normal contents of oxygen through
the sediment suspensions whenever the redox potential decreased below
the specified level. Air was automatically added as required by an air
pump activated by a meter relay which was, in turn, connected to the
recorder output of the potentiometer monitoring redox potential. When-
ever the redox potential dropped below a preset level, the meter relay
started the air pump, which resulted in a slow, gradual increase in sus-
pension redox potential. Using this system, suspension redox potential
could be maintained within a relatively narrow range.

After equilibration for several days under a controlled environment,

a sequential chemical fractionation procedure was used to determine the influence of pH and redox potential on the chemical forms of iron, manganese, zinc, copper, mercury, cadmium, lead, ammonium-nitrogen, and phosphorus in the sediment materials. The chemical fractionation procedure was designed to determine the quantity and/or proportion of elements in readily bioavailable forms (soluble and exchangeable) as well as in chemical forms which are thought to be less available, but potentially capable of being chemically transformed to the more bioavailable forms. Chemical fractionation was conducted under an oxygen-free atmosphere to prevent changes in redox potential during extraction and filtration procedures.

Following the initial chemical fractionation in which the influence of pH and redox potential on the geochemical distribution of indigenous metals and nutrients was determined, incremental additions of selected heavy metals were added to the sediment suspensions. This study was conducted to determine the capacity of the various processes regulating metal availability to transform added soluble toxic metals to relatively unavailable chemical forms under conditions of controlled pH and redox potential.

Another study was conducted to determine the influence of various levels of dissolved oxygen on the redox potential and pH of a sediment material and the subsequent effect on the readily bioavailable chemical forms of selected trace metals and nutrients.

Metal complex formation with soluble organics has been reported to enhance the solubility of metal ions in surface waters and sediments. A series of experiments were conducted to determine the ionic nature and particle-size distribution of soluble metal-organic complexes, and the effects of pH and redox potential on these properties.

The formation of metal sulfides is reported to be an important factor limiting the solubility of toxic heavy metals. Several hundred μg sulfide/g oven dry solids generally were found in strongly reduced sediment materials from three of the four sites studied. Most of the sulfide was likely precipitated with the excess ferrous iron present in these materials. In all strongly reduced (-150 mv) materials containing sulfide, an increase in redox potential to moderately reducing (50 mv) levels resulted in no measurable sulfide after a 2- to 3-week period. However, there was no great increase in soluble levels of any metal as the redox potential increased above the stability field for sulfide. A small increase in readily available zinc and cadmium was noted, possibly as a consequence of sulfide oxidation, but the increases were modest relative to levels found in potentially available forms. There was some evidence that processes affected by redox potential other than sulfide precipitation were equally as important, or perhaps more important, in complexing with metals under strongly reduced conditions. For example, metal complex formation with insoluble organics was thought to be an effective scavenger for most metals, particularly at low redox potentials.

In simulated highly contaminated sediments, insoluble sulfide complex formation was thought to significantly reduce the bioavailability of zinc, lead, and possibly cadmium. However, sulfide apparently had only a moderate influence in reducing the solubility of indigenous zinc and cadmium and little effect on the availability of most other metals in the sediment materials studied.

Comparatively large quantities of reduced soluble and easily exchangeable iron and manganese were found relative to levels of toxic metals. Oxidation of the readily available iron and manganese occurred as sediment redox potential and pH increased. This oxidation is thought to occur rapidly. During dredging and dredged material disposal as typically reduced sediments are dispersed in an oxygenated environment, considerable quantities of freshly formed hydrous ferric and manganic oxides and hydroxides are formed which may effectively adsorb soluble heavy metals. Though the scavenging effect of hydrous oxides is thought to be enhanced by increasing pH and redox potential, considerable quantities were found at all pH-redox potential combinations studied. Most of the total zinc, copper, and lead were found associated with the hydrous oxide (reducible) phase. The reductant extractable levels of copper and lead increased markedly with increasing redox potential.

The presence of sulfide apparently affected the solubility of indigenous zinc more than any other metal studied. Although zinc solubility was apparently reduced in the presence of sulfide, there was

some indication that more zinc was soluble than would be expected based on the dissociation constant of zinc sulfide. Similar conclusions were made for most potentially toxic metals studied. Zinc complex formation with soluble organics was not thought to account for the enhanced zinc solubility at certain pH-redox potential combinations, but inactivation of most of the sulfide by the excess ferrous iron present in strongly reduced sediments may have been a contributing factor. Most of the potentially reactive zinc was associated with the hydrous oxide phase, and lesser amounts were found with insoluble organics. There was not a great release from the potentially available forms to the more available soluble and exchangeable forms at any pH-redox potential combination studied.

Some zinc may be released from sulfide-bearing sediments during dredging and dredged material disposal, which results in an increase in redox potential above the sulfide stability boundary for sufficiently long periods for sulfide oxidation to occur. However, little release would be expected from increasing the oxidation status of reduced sediments which contained no sulfide.

This study indicated that changes in the pH or redox potential environment of sediments, possibly induced by dredging, will result in little increase in readily bioavailable copper. Precipitation or adsorption to colloidal hydrous oxides in oxidized environments and formation of insoluble complexes with organics and perhaps sulfide in

reduced sediment materials contributed to the strong affinity of sediment solids for copper over the range of pH and redox potential studied.

The predominant factors regulating the bioavailability of mercury were found to depend on the mercury levels present. In simulated highly contaminated sediments, a large release of mercury to soluble and exchangeable forms was favored by decreasing pH and increasing redox potential. The solubility of indigenous mercury in the four sediment materials studied did not show such clear, progressive increases with incremental changes in pH and redox potential. However, apparent solubilization of indigenous mercury did occur at certain pH-redox potential combinations in some of the sediment materials under strongly reduced conditions, in moderately and weakly acid environments, and under oxidized conditions at pH 8.0. The greater solubility of mercury in some suspensions containing sulfide relative to better oxidized treatments suggested that the mercury sulfide complex was not the predominant factor regulating mercury solubility in the strongly reduced sediment material. The increased solubility of mercury was apparently due to the formation of soluble, uncharged mercury complexes, possibly with soluble organics. Sediment organics were indicated to be the predominant factor regulating mercury availability in reduced as well as oxidized environments, although there was considerable evidence that the stability of the insoluble organo-mercury complex decreased with increasing oxidation levels. Dredging and dredged material disposal could possibly affect

the bioavailability of mercury by altering the oxidation status and/or pH of sediments. .. change in the sediment chemical environment resulting in a lower redox potential in moderately and weakly acid sediments, and an increase in redox potential under mildly alkaline conditions may result in a small increase in soluble mercury in some sediment materials. In highly contaminated sediments, a reduction in pH or an increase in sediment oxidation may result in large increases of readily available mercury.

Though a slight increase in soluble lead may have occurred with decreasing pH and redox potential, it was generally concluded that these parameters had no important effects on soluble lead. Considerably more lead was found in an exchangeable form, and this lead was affected by both pH and redox potential. Exchangeable lead levels were generally greatest under a moderately reducing environment at low pH. At lower redox potentials, lead sulfide formation was thought to limit exchangeable lead, while an increase in reducible lead likely decreased the exchangeable pool as the materials became better oxidized. Most potentially available lead was associated with the hydrous oxide (reducible) and insoluble organic-bound phases. In simulated highly contaminated sediments, lead was more strongly bound to sediment solids than equivalent levels of zinc, mercury, and cadmium.

This study indicated that changes in the sediment chemical environment resulting from dredging and dredged material disposal will have

little effect on soluble lead. Exchangeable lead levels may increase somewhat if a sediment pH is reduced to moderately acid levels.

A much greater proportion of potentially available indigenous cadmium was found in the soluble and exchangeable forms than for other toxic metals studied. Redox potential and pH were found to greatly influence the readily available cadmium levels. Though the presence of sulfide may reduce cadmium solubility to some extent in highly contaminated sediments, cadmium retention by insoluble organics was indicated to be important in regulating cadmium solubility. A reduction in the stability of the cadmium-insoluble organic complex with increasing redox potential was thought to contribute to increased cadmium solubility as a sediment material became oxidized.

This study indicated that a dredged sediment encountering a more acid environment may release cadmium to the soluble and easily exchangeable forms, as was noted for other metals such as iron, manganese, and zinc. However, unlike other metals studied, there was a comparatively large increase in soluble and exchangeable indigenous cadmium with increasing redox potential over the entire redox potential range studied in both moderately acid (pH 5.0) and near-neutral (pH 6.5) sediment materials. Thus a typically reduced dredged sediment material subjected to an oxidizing environment for a sufficiently long time could be expected to release much of its potentially bioavailable cadmium to the readily available forms.

Dredging and dredged material disposal of reduced sediments may increase both the ammonium-nitrogen and phosphorus content of surface waters. This increase is a consequence of mixing surface waters with reduced sediments and interstitial water containing relatively large quantities of readily available forms of these nutrients. Both redox potential and pH were found to influence their bioavailability. An increase in the oxidation status of interstitial water during dredging would tend to reduce soluble phosphorus and ammonium-nitrogen levels, thus countering the expected increase resulting from mixing. However, nitrogen cycling in sediment-water systems is complex. Processes other than a reduction in ammonium levels with increasing redox potential should be considered before evaluating the effects of dredging on nitrogen availability.

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TRANSFORMATIONS OF HEAVY METALS AND PLANT NUTRIENTS IN DREDGED
SEDIMENTS AS AFFECTED BY OXIDATION REDUCTION POTENTIAL AND pH

VOLUME II: MATERIALS AND METHODS/RESULTS AND DISCUSSION

INTRODUCTION

The volume of sediments dredged from navigable waters in the United States exceeds 250 million cu m annually.¹ Disposal of dredged material may adversely affect environmental quality, and this concern is compounded by the large quantities of material involved. Currently, most dredged material disposal is accomplished either by discharge into open water at sites removed from shipping channels or by land disposal in which the solid material settles from suspension and is confined, usually within a dike structure on land.

In recent years, much concern has been focused on the possible deleterious effects on water quality resulting from dredging and dredged material disposal, especially regarding possible release of toxic metals from dredged sediments. Sediment-water systems are the final recipients of much of the toxic metals, pesticides, biostimulants, and other organic and inorganic wastes released into the environment from both point and nonpoint pollution sources. In addition, many atmospheric pollutants eventually migrate to waterways as a result of precipitation and land drainage. In waterways, sediments and suspended solids exhibit a pronounced affinity for most chemical contaminants. As a consequence, considerable quantities of these materials may accumulate in the sediment phase.

Sediment-bound pollutants range in availability to aquatic and benthic organisms from chemical combinations which are readily available to the biological community to forms which are essentially

unavailable. Soluble and exchangeable metallic cations are examples of readily available materials. Metals bound within the crystal structure of primary minerals are essentially unavailable. Between these extremes may be a considerable quantity of toxic or biostimulatory substances which are potentially available to aquatic and benthic populations as a result of chemical transformations within the sediment-water system. When sediments are disturbed, as during dredging and dredged material disposal, physical and chemical changes may occur, possibly influencing the bioavailability of sediment-bound toxins and biostimulants. These changes may be harmful or possibly beneficial.

Currently, little is known about the transformations of sediment-bound toxic metals and biostimulants resulting from their being disturbed, transported, and disposed of in an environment that may differ from that of the undisturbed sediment at the bottom of a waterway. A striking change in the chemical environment of dredged material may occur as reduced bottom sediments are dispersed in an oxygenated water column or deposited on land for disposal. Transformations in the chemical forms of environmental contaminants which affect their bioavailability may occur due to changes in pH or in the oxidation-reduction status (as indicated by redox potential) of the dredged material.

The influence of pH and redox potential on the chemistry of many elements can be derived from thermodynamic considerations for simple systems such as a metal in water. For such simple aqueous systems, pH-redox potential diagrams and associated calculations can be utilized to predict the chemical form and concentration of an element under a

specified pH and redox potential environment. In recent years, such thermodynamic calculations have been expanded to describe metal chemistry in more complex aqueous systems which include specified levels of a few additional organic and inorganic chemical constituents.^{2,3} Such studies are useful in identifying regulatory mechanisms affecting metal concentrations. However, these models of simple aqueous systems cannot approach the complexity of natural sediment-water systems due to the qualitative diversity and quantitative variability of chemically reactive constituents present in natural systems. This suggests a somewhat empirical approach to the study of the influence of pH and redox potential on metal chemistry in sediment-water systems.

The objective of this study is to determine the influence of sediment pH and redox potential on chemical transformations of selected toxic metals and plant nutrients in sediments. The chemical forms of these materials and transformations among chemical forms influenced by changes in pH and oxidation intensity were determined by various chemical extractions. Hence availability in this report refers to chemical availability, as biological incorporation was not determined. However, the generally assumed biological availability of soluble and easily exchangeable toxic metals and nutrients should approximate or at least reflect qualitatively how changes in the study parameters affect biological availability. Additional chemical extractants used in this study indicate the role of various regulatory processes in limiting the availability of metals and nutrients. Although no distinction was made between chemical and biological transformations, it should be kept in mind that either

or both processes are involved in regulating the chemical and biological availability of these materials. The research methods in this study utilize some of the expertise developed over the years in the Laboratory of Flooded Soils and Sediments, Louisiana State University, in determining the effects of pH and redox potential in the regulation of certain chemical transformations in natural systems. A better understanding of the role of these environmental parameters in regulating the chemistry and thus bioavailability of chemical pollutants in waterways should contribute to establishing sediment disposal criteria for developing effective disposal guidelines.

MATERIALS AND METHODS

Site Selection

The influence of pH and redox potential on the chemistry of selected metals and plant nutrients in sediment-water systems was studied on sediment samples from four sites. The sites were selected with the objective of including sediments which varied considerably in their physical, chemical, and biological properties, as well as in the expected degree of pollution from cultural activities affecting the waterways. The selected sampling sites included (1) Bay Ronfleur, a coastal bay near Grand Isle, Louisiana, and part of the greater Barataria Bay area; (2) Mobile Bay, Mobile, Alabama; (3) the Mississippi River, near New Orleans, Louisiana; and (4) Calcasieu River at Lake Charles, Louisiana (Figure 1).

The Barataria Bay sampling site (Bay Ronfleur) was a small, partially enclosed bay of approximately 1.5 sq km located 3 km west of the southern tip of Grand Isle, Louisiana. This bay is little influenced by man's activities and should be representative of natural, unpolluted estuaries of the Louisiana Gulf Coast. The water depth at the sampling site near the south end of the bay was approximately 1 m.

The sampling site in Mobile Bay was 800 m east of the Mobile Bay ship channel near buoy #38. This is approximately 8 to 9 km south of Pinto Island and the main harbor area of Mobile Bay. The water depth at the time of sampling on an outgoing tide was 2.5 to 3 m.

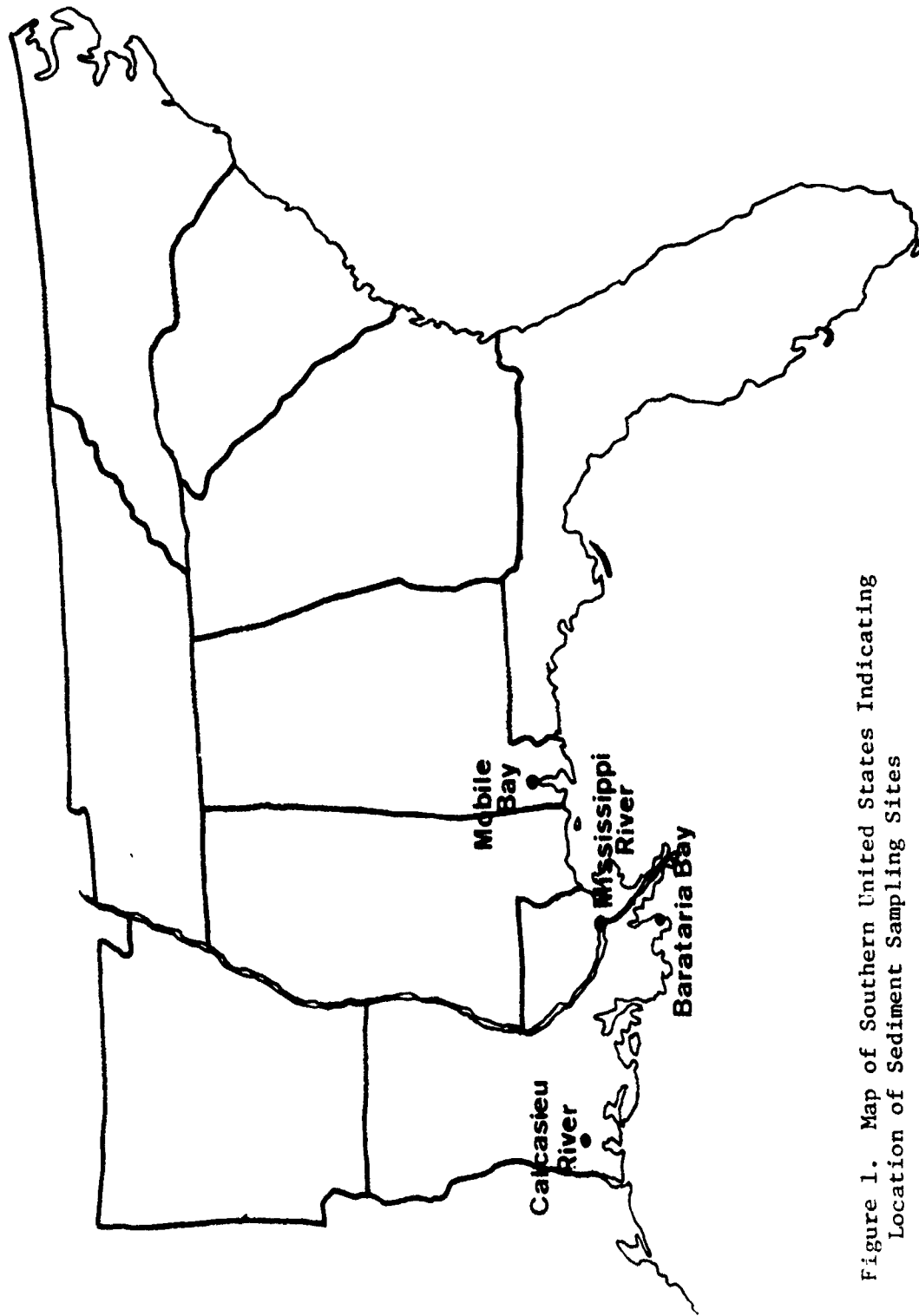


Figure 1. Map of Southern United States Indicating Location of Sediment Sampling Sites

A sediment sample was obtained from the Mississippi River just out of the main channel at the entrance to the Algiers Lock. This site is at mile #88 and is just a few km downstream from the main harbor area of New Orleans.

A sediment sample from Lake Charles, Louisiana, was obtained from a site about 200 m east of the Calcasieu River ship channel near the I-210 bridge. This site is approximately 1 km south of Coon Island and is downstream from the main industrial and harbor complex of Lake Charles. The water was 3 to 4 m deep at the sampling site. A more detailed map of each sampling site is presented in Appendix A.

Sediment Sampling and Storage

Sediment samples were taken with a Peterson dredge lowered by rope over the side of a boat. At each sampling site, the boat was maneuvered or allowed to drift so that the total sediment taken during a 15- to 30-minute sampling time was a composite of the bottom sediment over a traverse of 50 to 100 m. The sediment material collected was sealed in 20-ℓ metal tubs lined with two large-capacity polyethylene bags for transport to the laboratory. Approximately 100 to 150 ℓ of sediment was taken at each site. Surface water samples were taken at the same time in acid-rinsed polyethylene carboys.

In the laboratory, sediment material from each container was composited in a 120-ℓ polyethylene tub. After thorough mixing, 3-ℓ aliquots of the composite sediment material were placed in 4-ℓ glass storage containers and sealed with a gas-tight cap. The atmospheric oxygen overlying

the sediment in each storage container was then displaced by purging with nitrogen gas injected through a rubber septum fitted into each container cap. The sediment material was then stored at 4°C until needed, as were surface water samples.

Sediment Characterization

pH and Redox Potential of Bulk Sediment Samples

The pH and redox potential of the bulk sediment material were measured upon returning to the laboratory. A standardized pH electrode was inserted into a bulk sediment aliquot and allowed to stand undisturbed for a few minutes before a reading was made.

Several bright platinum electrodes were inserted into aliquots of bulk sediment material to measure redox potential. Readings were taken occasionally over the course of 1 to 2 days until the measured potentials had stabilized, then an average of the readings from the electrodes was recorded.

Mineralogy

The preparatory steps for mineralogical analysis of the silt, coarse clay, and fine clay fractions of the sediment samples from the four study sites were as follows: (1) destruction of carbonates; (2) decomposition of organic matter and manganese oxides; (3) removal of free iron oxides; (4) dispersion in sodium carbonate; (5) separation of sand, silt, and clay; and (6) separation of coarse clay (2.0-0.2 μ) from fine clay (<0.2 μ). These procedures are described in detail by

Jackson.⁴ The procedures for magnesium and potassium exchange saturation, glycerol solvation, and mounting of mineral specimens for X-ray diffraction analysis are described by Whittig.⁵ Crystalline minerals in the sediment materials were identified by interpretation of X-ray diffraction patterns.^{5*}

Organic Carbon and Carbonate Content

Total carbon in the sediment materials was determined by dry combustion and expressed as percent carbon (dry weight basis).⁶ Carbonate carbon was measured by the pressure-calculator method.⁷ Organic carbon was calculated by subtracting the carbonate carbon from the total carbon content.

Oxygen-Consumption Rates

The reduced sediment samples were transferred to bottles fitted with serum caps. The bottles were then purged with air (21 percent oxygen) and incubated with continuous shaking at 30°C. At the end of 1, 2, 4, 6, 8, 12, and 24 hours, small gas samples were withdrawn from the bottles into a cell provided with an oxygen electrode. The decrease in oxygen content of the gas samples with incubation time was determined.

Particle-Size Distribution

The particle-size distribution of the whole sediment materials

*Personal Communication, Dr. A. G. Caldwell, Department of Agronomy, Louisiana State University, Baton Rouge, Louisiana, June 16, 1975.

was measured by the hydrometer method of particle-size analysis.⁸

Cation Exchange Capacity

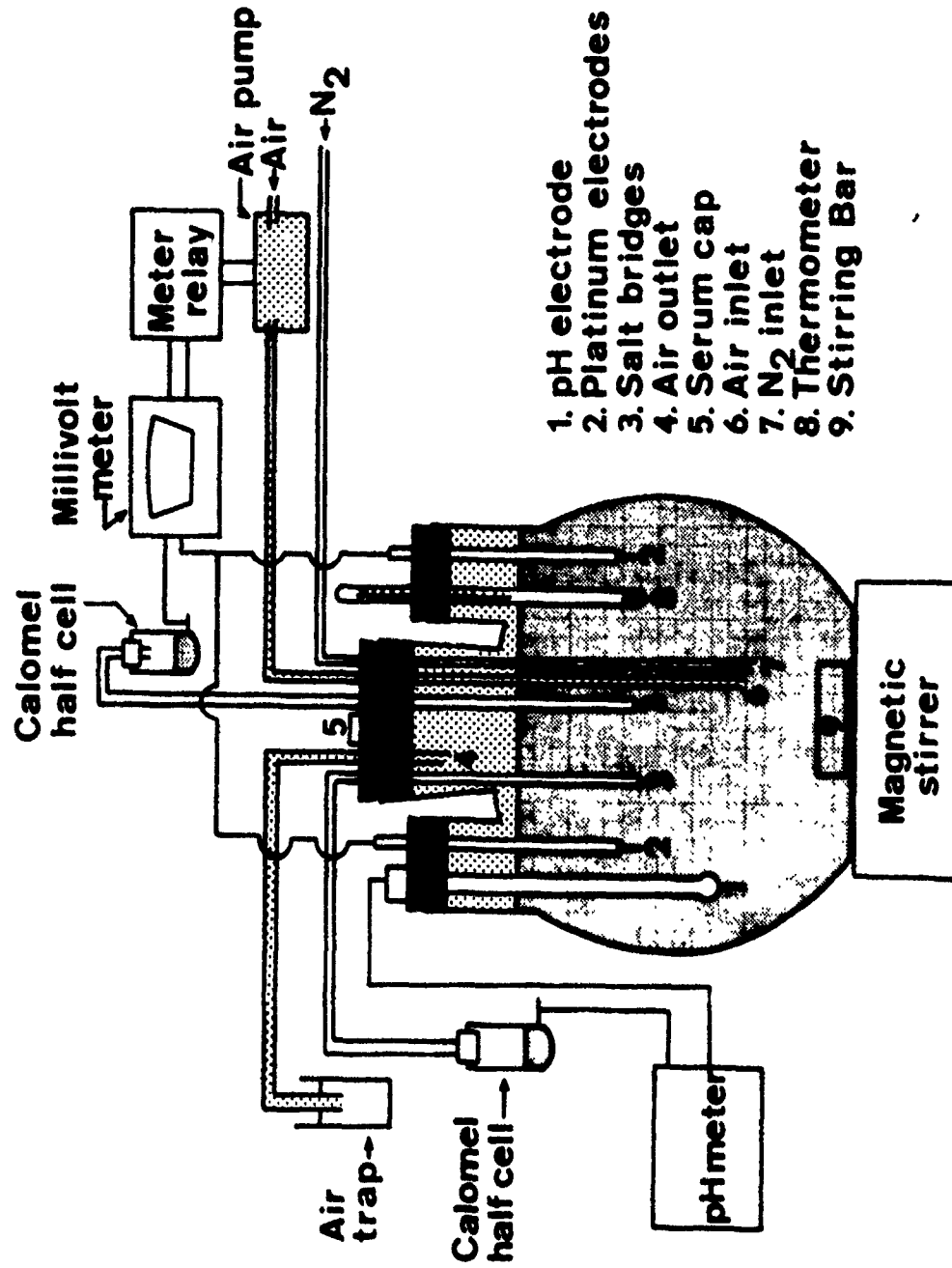
Cation exchange capacity was determined by the ammonium saturation procedure described by Chapman.⁹

pH and Redox Potential Control

A 2-l, 3-necked, flat-bottomed flask was used to contain sediment suspensions incubated under conditions of controlled pH and redox potential (Figure 2). A suspension was maintained by continuous stirring of the sediment-surface water mixture using a motor-driven magnetic stirrer. Two-inch (5.08-cm) teflon-coated magnetic stirring bars were inserted into an equal length of flexible polyvinyl chloride (Tygon) tubing to prevent excessive wear to the bar due to abrasion. As indicated in Figure 2, each flask was fitted with two platinum electrodes, a glass electrode for measuring pH, a thermometer, one large serum cap, separate inlet tubes for air and nitrogen, and an outlet tube, the end of which was submerged to prevent gaseous oxygen diffusion into the flask.

The suspensions were maintained at $30^{\circ}\text{C} \pm 1^{\circ}$. Temperature was regulated by inserting thin asbestos sheets as required between the flask and the underlying magnetic stirrer to control the heat transfer from the stirrer motor.

Suspension pH was adjusted to the proper level and then maintained using a syringe to add 1 N hydrochloric acid or 1 N sodium hydroxide through the serum cap located in the center rubber stopper. The suspension pH was measured continuously using a glass electrode and a saturated



1. pH electrode
2. Platinum electrodes
3. Salt bridges
4. Air outlet
5. Serum cap
6. Air inlet
7. N₂ inlet
8. Thermometer
9. Stirring Bar

Figure 2. pH and Redox Potential Control Apparatus for Incubating Sediment Suspensions

calomel reference electrode connected to the suspension with a saturated potassium chloride-agar salt bridge. This reference electrode assembly, coupled with the glass electrode, was more satisfactory in long-term sediment suspension studies than commercial combination pH electrodes. The commercial combination pH electrodes used initially required more frequent restandardization, particularly in reduced sediment suspensions. This was attributed to possible metal sulfide precipitation in the fritted ceramic junction of the silver-silver chloride reference electrode, which contributed a junction potential to the electrode system which was not constant with time.

Bright platinum electrodes immersed in the sediment suspension were connected to a potentiometer (Beckman Zeromatic, SS-3) for redox potential measurements. A separate saturated calomel reference electrode, as described for pH measurements, was used to complete the cell. A meter relay (General Electric, Type 196) was connected to the recorder output of the potentiometer and activated an aquarium pump when the redox potential of the suspension dropped below the desired level. The airflow from the aquarium pump was regulated by a valve from 0.5 to 2.0 ml/minute to allow slow oxidation of the suspension during the aeration cycle. When the suspension was again oxidized to the proper level, the meter relay automatically switched off the aerator.

In the absence of oxygen, sediments exhibit a natural tendency to become more reduced. Thus, the redox potential of a sediment suspension can be maintained over a considerable range of oxidation-reduction levels by regulating the addition of air. An additional gas inlet to the flask

supplied oxygen-free nitrogen gas. Nitrogen gas was effective in purging excess oxygen from the system at the end of the aeration cycle, removing possible oxygen contamination from small leaks, and preventing a buildup of gaseous decomposition products such as carbon dioxide. Continuous purging with nitrogen may artificially reduce the sediment carbonate content, possibly an important regulatory mechanism for some trace metals in sediment-water systems. On the other hand, it is possible that little or no gaseous purging may result in an excessive buildup of carbon dioxide, as considerable microbial activity is expected in the incubated sediments. Thus, the experimental procedure used could possibly affect the regulatory role of metal carbonate chemistry in an undetermined manner. Passing a slow, continuous stream of nitrogen gas through the suspension allowed the redox potential to be controlled within 5 to 10 mv of the desired potential. In studies in which a continuous nitrogen flow was not used, redox potential was somewhat more difficult to control, but ranged from 10 to 35 mv of desired level.

A zinc acetate trap at the end of the outlet tube prevented atmospheric oxygen diffusion into the suspension and served as a trap for determining possible hydrogen sulfide evolution from reduced suspensions.

Chemical Extraction of Sediments under an Oxygen-Free Atmosphere

During studies of sediment-water systems in which redox potential may affect chemical transformations of environmental contaminants, it is important that the oxidation-reduction status of the sediment material

not be altered during the chemical fractionation procedure. Such transformations may occur rapidly. When a typically dark, reduced sediment is exposed to the atmosphere, oxidation may begin immediately as evidenced by the formation of a lighter colored, thin surface horizon within a few minutes. Continued exposure to air results in an increase in the depth of the partially oxidized layer and a greater degree of oxidation. The thin oxidized layer formed at the surface of a sediment sample after exposure to the atmosphere may represent only a small proportion of the total sediment material volume. However, this oxidation process could result in unwanted chemical transformations during extraction procedures. This would especially be true if the sediment material were mixed while exposed to air or shaken in the presence of air with an oxygen-saturated chemical extractant for extended periods. For example, soluble trace metals in a reduced sediment-water system may be subject to rapid adsorption on freshly formed colloidal hydrous oxides of iron and manganese. It has been suggested that the oxidation of soluble ferrous iron (Fe^{2+}) to insoluble ferric iron (Fe^{3+}) during dredging is almost immediate.¹⁰ Several literature reports suggest that such freshly formed oxides of iron and manganese may be more effective scavengers for soluble trace metals than aged hydrous oxides.^{10,11,12} Thus, ordinary air is a potentially serious contaminant during chemical extractions, and considerable care must be exercised to minimize oxidation of sediment material during laboratory extractions.

In this study, centrifugation and chemical extractions were conducted under an oxygen-free nitrogen atmosphere in 500-ml polycarbonate

centrifuge bottles. Many of these bottles were found to have air leaks around the screw cap. Sealing gaskets cut from thin polyvinyl chloride sheeting were placed in the caps to prevent air leaks. A silicon rubber serum cap was sealed into a hole drilled into each bottle cap to permit sample and extractant transfer to and from the bottle without oxygen contamination. The sealed centrifuge bottles were purged with oxygen-free nitrogen prior to adding a sediment suspension aliquot.

A plastic syringe fitted with a glass pipette was purged with nitrogen and then used to transfer suspension from the 2- ℓ incubation flasks to the centrifuge bottles. The transfer was made by inserting the glass pipette through the serum caps in the top of the incubation flask and centrifuge bottle. After centrifugation, the supernatant solution was transferred under a nitrogen atmosphere through a filter and collected in a receiving flask (Figure 3). For this transfer, a syringe needle connected to a low-pressure nitrogen source was inserted through the serum cap in the centrifuge bottle. A glass pipette connected by polyvinyl chloride plastic tubing to a gas-tight, 300-ml-capacity filtering funnel was also inserted into the atmosphere above the supernatant solution within the centrifuge bottle. A vacuum applied to the filtering flask displaced the atmospheric oxygen in the filtering apparatus by pulling nitrogen through the system. After purging for several minutes, the glass sampling tube was pushed down into the supernatant solution, which was then drawn into the filter reservoir. The supernatant solution was thus filtered into a receiving flask containing a sample preservative under an oxygen-free atmosphere.

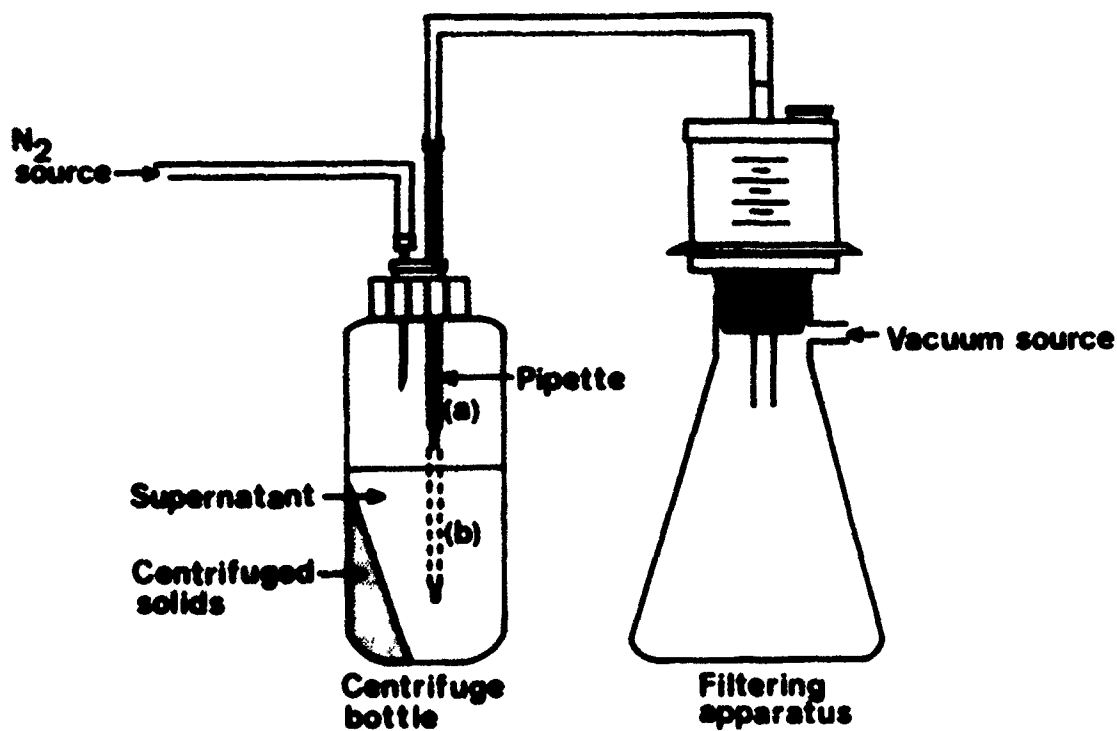


Figure 3. Apparatus for Filtering Supernatant Solutions Under a Nitrogen Atmosphere: (a) pipette in N_2 purge position, and (b) pipette in filtering position

A sample preservative is necessary to prevent the precipitation of some soluble metallic ions as the solution becomes oxidized upon exposure to air and storage. Prior to analysis, metallic ions can be maintained in solution either by acidification to pH 1 or 2,^{13,14} or by complexing with a soluble chelating agent.^{15,*} In this study, both techniques were

*Personal Communication, Dr. M. G. Verloo, Department of Agricultural Sciences, State University, Ghent, Belgium, October 9, 1974.

employed. In sample solutions containing considerable soluble organic matter, some humic acid material which is soluble at the pH of extraction may precipitate upon acidification to pH 1 or 2 and become an effective scavenger in removing certain trace metals from solution.¹⁶ Humic acids are not precipitated when a chelating compound such as EDTA (ethylenediaminetetraacetic acid) is used to maintain metal ions in solution. However, caution must be exercised in determining the milliequivalents of EDTA required, as an excess may precipitate in solutions of relatively low ionic strength which are stored at low temperatures for extended periods.

After filtration of the initial water-soluble fraction, additional extractions in the sequential fractionation procedure were also conducted under an inert atmosphere. A measured quantity of extracting solution was injected through the serum cap in the centrifuge bottle before dispersing the centrifuge solids. The bottle was immediately connected to a vacuum and an oxygen-free nitrogen source. Sufficient vacuum was applied until the extracting solution approached a boil, as indicated by the formation of gas bubbles within the solution. Then the atmosphere was replaced to just greater than 1-atmosphere pressure with oxygen-free nitrogen gas. This sequence was repeated 4 or 5 times prior to dispersing and shaking the sediment material with a chemical extractant. The purpose of this procedure was to remove dissolved oxygen from the extracting solution and any traces of gaseous oxygen in the centrifuge bottle.

Incubation of Sediment Material Prior to Chemical Fractionation

A container of stored sediment material to be incubated under conditions of controlled pH and redox potential was turned on a roller-mixer overnight prior to being weighed into the incubating flasks to ensure a homogeneous sample. A predetermined amount of reduced, wet sediment material, equivalent to 200 g of oven dry solids, was placed in each of four incubation flasks. Sufficient stored surface water from the sampling site was added to each flask to produce a sediment-water mixture with a solids:water ratio of 1:8. Two platinum electrodes, a standardized pH electrode, and associated reference electrodes were positioned in the flask and connections made with nitrogen and air inlet tubes and a gas outlet tube as previously described.

Stirring of the sediment-water mixture was begun, and the redox potential of the suspension was adjusted to near the desired level. Four to five days were usually required to approximate the most oxidizing redox potential levels. The suspension pH was adjusted to the proper level at this time, and further refinement of the pH and redox potential continued for 2 to 5 additional days. Each experimental run included four redox potentials ranging from strongly reduced to well-oxidized at one specified pH.

After incubation of the sediment suspensions for 4 to 5 days at controlled pH and redox potential levels, radioisotopes of mercury and cadmium or lead were added. The sediment suspensions were incubated

an additional 4 to 7 days at the specified pH and redox potential levels to permit equilibration of the added isotopes with the various chemical forms of these trace metals in the suspension prior to chemical fractionation.

Chemical Fractionation

The order in which the four sediment materials were studied during the course of this research was as follows: (1) Barataria Bay, (2) Mobile Bay, (3) Mississippi River, and (4) Calcasieu River. As early data were evaluated, it was thought that some modifications in the originally planned chemical fractionation procedure might provide additional information. Also, as additional experience in methodologies was gained, some changes in laboratory extraction techniques were found to be beneficial and were thus employed in subsequent work. Thus, the materials and methods used for each sediment material, though basically the same, will be presented separately to fully explain the procedural modifications used on each.

Barataria Bay

After the desired levels of redox potential and pH were reached and maintained in the sediment suspensions for several days, 0.25 μCi of carrier-free ^{203}Hg and 0.20 μCi of carrier-free ^{109}Cd per g oven dry solids were added to each treatment. Duplicate 25- to 30-ml suspension aliquots for each treatment were withdrawn and dried at 105°C for 24

hours to determine the solids:water ratio. After one week of equilibration, sediment suspensions were withdrawn and fractionated according to the following scheme: (1) total water-soluble, (2) soluble organic bound, (3) exchangeable, (4) reducible, (5) sodium citrate-sodium dithionite extractable (hereafter called the dithionite extractable), and (6) total elements. Total water-soluble, soluble organic bound, and total elements were determined on separate sample aliquots. Fractions 3, 4, and 5 were sequentially carried out on duplicate aliquots in the order mentioned. The fractionation procedure is described below.

Total Water-Soluble. About 150 ml of sediment suspension was pipetted out through the rubber septum in each incubation flask with a glass pipette fitted to a plastic syringe. These suspensions were transferred to preweighed, airtight centrifuge bottles. Just before sampling, the centrifuge bottles and the pipette-syringe assembly were purged with nitrogen to remove any atmospheric oxygen. The centrifuge bottles were reweighed to determine the weight of suspensions withdrawn and the amount of solids present. The suspensions were centrifuged for 20 minutes at 6000 rpm, and the supernatant was transferred to polyethylene bottles containing sufficient 6 N hydrochloric acid to lower the pH to ≈ 2 . This transfer was carried out in a glove bag under a nitrogen atmosphere. The acidified samples were then stored at 4°C until analyzed for their metal and nutrient content.

Soluble Organic Bound. About 150 ml of sediment suspension was withdrawn from each incubation flask and centrifuged as outlined for the total water-soluble fraction. The supernatant was then transferred to an airtight centrifuge bottle containing 18 g cation exchange resin (Chelex-100, sodium form, 100-200 mesh). This transfer was carried out in a glove bag under a nitrogen atmosphere. The centrifuge bottles containing the resin were purged with nitrogen prior to transferring the supernatant. The solution-exchange resin mixture was shaken for 2 hours on a mechanical shaker and centrifuged for 20 minutes at 6000 rpm. The supernatant was poured into polyethylene bottles containing sufficient 6 N hydrochloric acid to lower the pH to ≈ 2 . This transfer was carried out in a glove bag under a nitrogen atmosphere. The extracts were stored at 4°C.

Exchangeable. Fifty ml of sediment suspension was pipetted into each of two centrifuge bottles containing 10 ml of a 5 N sodium acetate solution adjusted to the pH of the suspension. The centrifuge bottles containing sodium acetate were weighed and purged with nitrogen before transferring the suspension. The centrifuge bottles were reweighed to record the amount of suspension taken and then purged again with nitrogen. The suspensions were shaken for 2 hours using a mechanical shaker and centrifuged. The supernatant was transferred to polyethylene bottles containing sufficient 6 N hydrochloric acid to lower the pH to ≈ 2 to prevent precipitation of metal ions. The supernatant from both

centrifuge bottles was composited and stored at 4°C. The quantity of elements in the exchangeable fraction was calculated as follows:

Exchangeable element = mass of element in the sodium acetate extract minus mass of element in the total water-soluble fraction.

Reducible. Two-hundred and fifty ml of oxalate reagent (0.1 M oxalic acid plus 0.175 M ammonium oxalate, pH 3.25) was added to the residual sediment material from the exchangeable fraction and the centrifuge bottle purged with nitrogen. The mixture was shaken for 2 hours on a mechanical shaker and centrifuged for 20 minutes at 6000 rpm. The supernatant was transferred to polyethylene bottles containing sufficient 6 N hydrochloric acid to lower the pH to ≈ 2 and stored at 4°C. The two extracts were not composited.

Dithionite Extractable. A freshly prepared 20-percent sodium dithionite solution was shaken with equal weight of cation exchange resin (Chelex-100, sodium form, 100-200 mesh) for 5 hours, centrifuged, and the supernatant collected. The purpose of treating sodium dithionite with a cation exchange resin was to remove zinc contamination present in this reagent. Fresh dithionite reagent was prepared just prior to each extraction as sodium dithionite loses reducing power with time. To the residual material in the centrifuge bottles from the reducible fraction, 10 ml of freshly cleaned 20-percent sodium dithionite solution, 20 g of sodium citrate, and 240 ml of distilled deionized water were

added and the contents shaken for 18 hours on a mechanical shaker.¹⁸ The mixture was centrifuged for 20 minutes at 6000 rpm and the unacidified supernatant was stored in polyethylene bottles at 4°C.

Total Elements. Nine ml of sediment suspension from each treatment was transferred to Teflon beakers. Thirty ml of concentrated hydrofluoric acid and 20 ml of concentrated nitric acid were added to the beakers. The beakers were loosely covered with Teflon caps and allowed to stand for 2 hours under a fume hood. Four ml of 6 N perchloric acid was then added and the mixture heated at a low temperature on a hot plate until the dense fumes of perchloric acid subsided. The mixture was cooled and the sides of beakers washed with a minimum of distilled, deionized water, and the material was then evaporated to dryness. The residue was dissolved in hot concentrated hydrochloric acid and diluted to 50 ml. The digest was stored in polyethylene bottles for total iron, manganese, zinc, copper, cadmium, lead, and phosphorus analyses.

Total Mercury. Nine ml of sediment suspension was transferred to 125-ml Pyrex Erlenmeyer flasks, and 25 ml of 2:1 mixture of concentrated sulfuric acid and redistilled concentrated nitric acid was added. The contents were mixed well and the flasks placed in an ice bath to prevent possible mercury volatilization. After cooling, the flasks were transferred to a water bath maintained at 50 to 60°C and digested for about 5 hours, after which the supernatant was clear. The samples were

removed from the water bath and allowed to cool in an ice bath. Five ml of 5-percent potassium permanganate solution (w/v) was added and the mixture allowed to stand for 15 minutes. Additional potassium permanganate solution was added as necessary to maintain an excess, as indicated by a purple color. Two ml of 5-percent potassium persulfate (w/v) was added and the samples left overnight to ensure complete oxidation of organo-mercury. The digest was stored for total mercury analysis. A reagent blank was carried through the procedure with the samples.

Mobile Bay

Five to six days prior to chemical fractionation, this sediment suspension received 0.3 μCi of carrier-free ^{203}Hg and ^{210}Pb per g solids (dry weight basis). A 25-ml suspension aliquot from each incubation flask was placed in 50-ml beakers and dried 24 hours at 105°C to determine the precise solids:water ratio at the time of chemical fractionation. The Mobile Bay sediment suspensions were sequentially fractionated according to the following scheme: (1) total water-soluble, (2) soluble organic bound, (3) exchangeable, (4) reducible, (5) DTPA (diethylenetriaminepentaacetic acid) extractable, and (6) total elements. The following paragraphs describe the details of the fractionation procedure.

Total Water-Soluble. Suspension samples were obtained through a rubber septum located in the top of each incubation flask with a 1-ml glass pipette which was connected to a large-capacity plastic syringe.

The pipette and syringe were purged with nitrogen to remove atmospheric oxygen contamination immediately prior to sample removal. A 125-ml aliquot was withdrawn from each treatment flask and injected through a septum in the top of a tared, sealed, 500-ml polycarbonate centrifuge bottle in which the atmosphere had been replaced with nitrogen. The centrifuge bottles were then reweighed so that the exact amount of solid material present could be calculated from the solids:water ratio and the suspension weight. The suspensions were centrifuged at 6000 rpm for 20 minutes, and the supernatant solution was filtered under an oxygen-free atmosphere through a 0.45- μ pore size membrane filter into a receiving flask containing 4 ml of 0.5 N EDTA. A measured aliquot of EDTA solution was used as a sample preservative at a rate of approximately 1 ml per 25 ml of sample solution for all extractions unless otherwise stated. After the contents of the receiving flasks were swirled to mix the sample and preservative thoroughly, the receiving flasks were opened to the atmosphere and poured into an acid-rinsed polyethylene bottle for storage. All samples were stored at 4°C until analyzed for their trace metal and nutrient content.

Soluble Organic Bound. A 125-ml suspension aliquot was removed from the incubation flask, centrifuged, and filtered as described for the total water-soluble fraction. However, the supernatant solution was passed through a cation exchange resin bed (Chelex-100, sodium form, 100-200 mesh) connected in series with the filtering funnel to remove

soluble free cations.^{16,*} A flow rate of < 4 ml/minute/cm² of resin bed surface was used.¹⁹ Solution containing cations bound to soluble organic matter was collected in the receiving flask and stored for subsequent analysis as described for the total water-soluble fraction.

Exchangeable. A 2-N sodium acetate solution was prepared and passed through a sodium-saturated cation exchange resin bed (Chelex-100, sodium form, 100-200 mesh) to remove possible trace metal contamination in this reagent.¹⁹ This extractant was diluted with distilled, deionized water to 1 N and the pH adjusted to the pH of the suspension by addition of 8 N distilled hydrochloric acid. To determine the easily exchangeable metals, sufficient extractant to give a 10:1 extractant:solids ratio (w/w) was injected through the septum in the top of the centrifuge bottles containing the residual solid material from the total water-soluble fraction. The centrifuge bottles were then connected to a high vacuum source and a compressed nitrogen source. Sufficient vacuum was applied to the bottle such that gas bubbles evolved from the solution; then the atmosphere within the bottles was replaced with nitrogen. This cycle was repeated several times to ensure removal of both dissolved and gaseous oxygen from the centrifuge bottle. The sediment-extractant mixture was then shaken for 2 hours, centrifuged, and the supernatant filtered through a 0.45- μ pore size membrane filter into a receiving flask containing a

*Personal communication, Dr. John Sims, Department of Agronomy, University of Kentucky, April 11, 1974.

premeasured aliquot of EDTA as a preservative. The sediments were washed with 50 ml of deionized water using the same procedure described for the sodium acetate extraction except that a 15-minute shaking time was used. The filtered supernatant was combined with the sodium acetate extract.

Reducible. A solution of 0.15 M oxalic acid and 0.25 M ammonium oxalate was prepared and passed through an ammonium-saturated cation exchange resin bed (Chelex-100, sodium form, 100-200 mesh) to remove possible trace metal contamination in this reagent. A 300-ml aliquot of this extractant (approximately a 20:1 extractant:solids ratio) was added to the residual solid material previously extracted for exchangeable metals. The procedure for this extraction and the subsequent water wash was the same as described previously for the exchangeable fraction.

DTPA Extractable. An extracting solution of 0.05 M DTPA and 0.2 M sodium acetate was prepared and the pH adjusted to 7.0. An amount of 150 ml of this extractant, equivalent to a 10:1 extractant:solids ratio (w/w), was added to the residual material from the previous extraction. The extraction procedure was the same as described previously for the exchangeable fraction; however, no EDTA was required as a sample preservative. Strong synthetic complexing agents such as EDTA or DTPA have been used to measure naturally complexed, chelated, and adsorbed micro-nutrients in soils.²⁰

Total Elements. Aliquots were taken for total elemental analysis and digested as described for the Barataria Bay sediment material.

This fractionation sequence was repeated the following day such that data of two extractions from each treatment were available. An aliquot was also taken at the conclusion of the chemical fractionation procedure for a total sulfide analysis. The zinc acetate solution connected to the gas outlet tube of the flask was also analyzed for sulfide to detect possible gaseous hydrogen sulfide loss from the stirred suspensions.

Mississippi River

After the sediment suspensions were equilibrated for several days at the controlled redox potential levels at each pH, 2.4 µg mercury/g solids (oven dry basis) tagged with 0.4 µCi ^{203}Hg /g solids was added to each treatment. The suspensions also received 0.2 µCi of carrier-free ^{109}Cd per g solids. Four days after these additions, sediment suspensions were sampled in duplicate for chemical fractionation according to the procedures described for the Mobile Bay study. However, the extraction with DTPA was not followed by a water wash. The residual material from the DTPA extraction was further treated to determine the quantity of metals bound to insoluble organic matter as follows.

Insoluble Organic Bound Elements (Mercury Excluded). The residue from the DTPA extraction was digested at 95°C with 30-percent hydrogen

peroxide for several hours to a pale bleached color, indicating the organic matter was destroyed.²¹ The residual material was then extracted with 1 N sodium acetate adjusted to pH 2.5, similar to the procedure described for extracting exchangeable metals. The extraction was followed by a water wash, which was composited with the initial extraction, and the samples were stored at 4°C.

Insoluble Organic-Bound Mercury. The DTPA residue from one replication of different redox potential treatments maintained at pH 5 was digested at 50 to 60°C with 30-percent hydrogen peroxide to reduce possible mercury volatilization during digestion. The remaining extraction procedure was the same as described in the previous paragraph.

Calcasieu River

The chemical fractionation of the Calcasieu River sediment material and the laboratory procedure used were basically the same as described for the Mobile Bay suspensions and included the modifications described for the study of the Mississippi River materials. The radioisotopes added to the Calcasieu River suspensions were ²⁰³Hg and ²¹⁰Pb. A study of this material at pH 5 was not attempted due to time limitations.

Table 1 lists the experimental variables included in the study of the four sediment materials.

Table 1
List of Experimental Variables Included in the Study of the Four Sediment Materials

Variable	Site			
	Barataria Bay	Mobile Bay	Mississippi River	Calcasieu River
pH	5.0, 6.5, 8.0	5.0, 6.5, 8.0	5.0, 6.5, 8.0	6.5, 8.0
Redox potential, mv	-150, 0 200, 450	-150, 50 250, 500	-150, 50 250, 500	-150, 50 250, 500
Radioisotopes	203Hg, 109Cd	203Hg, 210pb	203Hg, 109Cd	203Hg, 210Pb
Chemical Fractions	Total water soluble Soluble or-ganic bound Exchangeable Oxalate reducible Dithionite reducible Residual	Total water soluble Soluble or-ganic bound Exchangeable Oxalate reducible DTPA extractable Total	Total water soluble Soluble or-ganic bound Exchangeable Oxalate reducible DTPA extractable Insoluble organic	Total water soluble Soluble or-ganic bound Exchangeable Oxalate reducible DTPA extractable Insoluble organic
	Total	Total	Total	Total

Adsorption-Desorption Study for Zinc, Mercury,
Cadmium, and Lead

Following the initial fractionation procedure, a study was conducted on the remaining suspension in which increasingly larger increments of three trace metals were added at 24-hour intervals to three of the sediment materials. Twenty-four hours after each addition, suspension aliquots were taken to determine the influence of pH and redox potential on the distribution of these metals in the total water-soluble and exchangeable fractions. The extraction procedures were similar to those previously described. Each metal was added as a soluble salt.

Barataria Bay

After the initial chemical fractionation, incremental additions of 1, 6, 12, 20, 45, 100, and 215 μg each of mercury, cadmium, and zinc/g solids were made to the remaining suspensions at 24-hour intervals. Twenty-four hours after each addition, sediment suspensions were extracted for the total water-soluble fraction as outlined for the Barataria Bay fractionation scheme. To the residual sediment material from the total water-soluble fraction, 1 N sodium acetate adjusted to the pH of suspensions was added to obtain a 10:1 sodium acetate:solids ratio (w/w). The extraction for the exchangeable fraction was then carried out as outlined earlier for the initial fractionation study.

Mobile Bay

Increments of 1, 5, 20, 80, 150, and 250 μg each of mercury, lead, and

zinc/g solids were added at 24-hour intervals to the Mobile Bay sediment material. Total water-soluble and exchangeable metals were determined for each incremental addition as described for Barataria Bay.

Mississippi River

In the Mississippi River sediment suspensions, increments of 1, 5, 25, 75, 150, and 250 μg each of mercury, cadmium, and zinc/g solids were added at 24-hour intervals. Twenty-four hours after each addition, concentrations of these elements were measured in the water-soluble and exchangeable fraction. After the equilibration of the 150- $\mu\text{g/g}$ addition (accumulative addition of 256 $\mu\text{g/g}$), the sediment suspensions were extracted for total water-soluble, soluble organic bound, exchangeable, reducible, DTPA extractable, and insoluble organic bound fractions according to the scheme outlined for the initial chemical fractionation of Mississippi River sediment suspensions.

Effect of Dissolved Oxygen on the Transformation of Metal Ions and Nutrient Elements in Barataria Bay Sediment Suspensions

An experiment was set up in the laboratory to investigate the influence of various levels of dissolved oxygen on the transformation of metal ions and nutrient elements in Barataria Bay sediments. The objective was to simulate dredging and dredged material disposal where reduced bottom sediments were dispersed in oxygenated surface water or were transported to a landfill area where gaseous atmospheric oxygen

may diffuse into the dredged material. Changes in the oxidation-reduction conditions of dredged material influence the availability of toxic metals and biostimulants and hence their uptake by organisms. This study investigated some of these chemical transformations as a function of oxygen concentration and time.

A predetermined amount of reduced, wet sediment material equivalent to 300 g oven dry solids was placed in each of three 3-l, 3-necked, flat-bottomed flasks. Sufficient stored overlying water was added to attain a solids:water ratio of 1:8. After 10 days of preincubation at 30°C under an argon atmosphere, sediment suspensions were continuously stirred with oxygen-free argon to create a highly reduced system. Suspension pH and redox potential were recorded according to the system outlined earlier in this section (see Figure 2 for details). After the suspensions reached a minimum redox potential (7 days), pretreatment sediment suspension aliquots were pipetted out and extracted according to the fractionation scheme summarized below:

1. Water-soluble
2. Soluble organic bound
3. Exchangeable (0.5 N sodium acetate, pH 6.5)
4. Easily reducible (0.1 M hydroxylamine hydrochloride in 0.01 N nitric acid, pH 2.0, solids:extractant ratio of 1:50, shaking time of 30 minutes, centrifuge)²²

5. Reducible (0.1 M oxalic acid plus 0.175 M ammonium oxalate, pH 3.25, solids:extractant ratio of 1:50)

Water-soluble and soluble organic bound fractions were determined on separate samples. Fractions 3, 4, and 5 were sequentially extracted in the indicated order on duplicate samples.

Detailed methods of extraction have been described earlier under the heading "Chemical Fractionation, Barataria Bay."

After the zero-time sampling (pretreatment), sediment suspensions were constantly purged with 0.11 percent, 2.11 percent, and 21 percent oxygen at a flow rate of 20 ml/minute. Changes in pH and redox potential were recorded with time. Suspension samples were taken for fractionation as a function of redox potential and time, as indicated in Table 2.

The sampled sediment suspensions were extracted for different chemical fractions outlined earlier and the extracts analyzed for iron, manganese, zinc, copper, ammonium-nitrogen, and phosphorus.

Studies of Metal Complexation with Soluble Organics

Efficiency of Chelex-100 Resin for Separating Water-Soluble Free and Complexed Ions

According to data given by the manufacturers, Chelex-100 cation exchange resin has an exchange capacity of about 2.9 meq/g dry material. The reported moisture content of this resin is 71 to 75 percent. Ten g of Chelex-100 resin (2.6 g dry resin) have an exchange capacity of 7.5

Table 2

Sampling Parameters of the Dissolved Oxygen Experiment

Sample Number	% Oxygen		
	0.11	2.11	21.00
	Redox Potential		
	mv		
1	-200 (0)	-200 (0)	-260 (0)
2	-210 (8)	-160 (8)	-160 (0.5)
3	-170 (120)	-50 (48)	-40 (3.5)
4	----	+100 (168)	+150 (7)
5	----	+640 (288)	+610 (132)

Note: Zero in parentheses indicates zero-time (pretreatment) sampling. Number in parentheses indicates hours after initiating oxygen treatments.

meq. Small columns 16 mm in diameter and 10 mm long were filled with 10 g of Chelex-100 resin and placed in a vacuum flask as shown in Figure 4. Based on the stoichiometry of the reaction between copper and the disodium salt of EDTA, cupric sulfate and EDTA were mixed to give five solutions containing 0, 25, 50, 75, and 100 percent, respectively, of complexed copper. Each solution contained 100 ppm of total copper. These solutions had an average specific conductivity of 2.040 mmhos/cm,

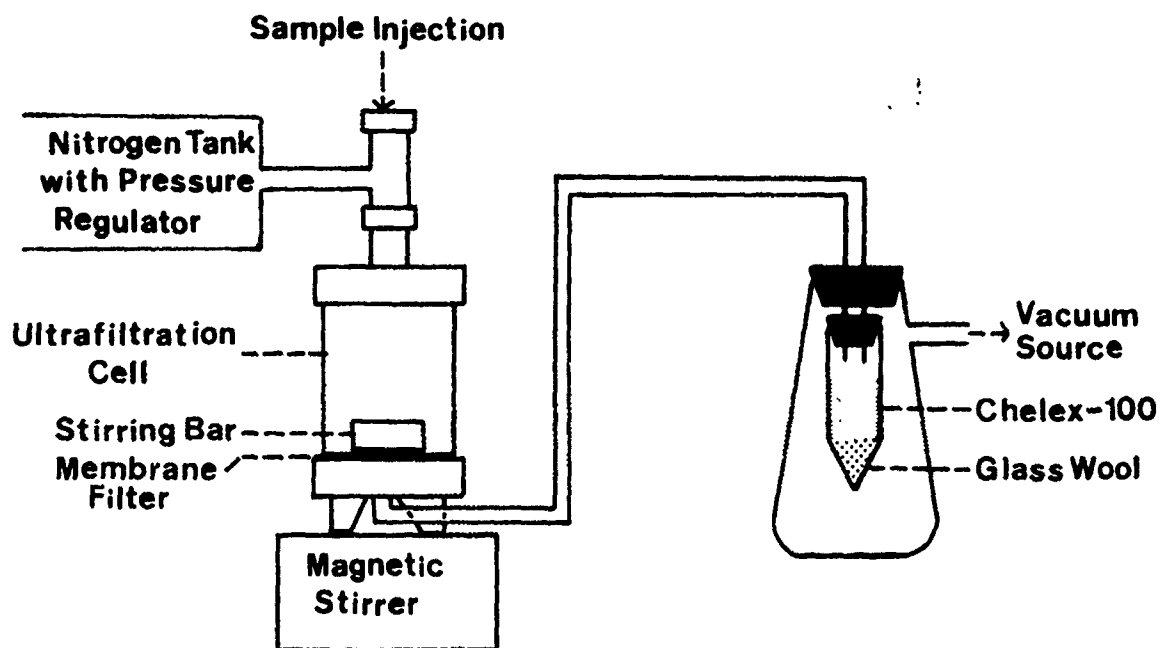


Figure 4. Pressure Filtration Apparatus for Separating Free Cations and Selected Size Fractions of Cation-Soluble Organic Complexes.

which corresponds to a salt concentration of 0.014 N based on a 0.01 N potassium chloride solution having a specific conductance of 1.413 mmhos/cm at 25°C. One-hundred-ml portions of this sample solution thus contained an average of 1.4 meq soluble salts, and 50-ml portions contained 0.7 meq.

Fifty-ml portions of these solutions were passed through the resin bed at a rate of 5 ml/min.

Influence of Zinc, Lead, and Copper Additions on the Free and Chelated Forms of Soluble Iron and Manganese

A 241.5-g portion of anaerobic Barataria Bay sediment material containing 100 g oven dry solids and 141.5 g water was weighed into a 2-l Erlenmeyer flask. To this, 658.5 g water was added to obtain a mixture with a solids:water ratio of 1:8. One-half g of ground grass was added as a carbon source for micro-organisms. Four replicate flasks were set up. The containers were purged with oxygen-free nitrogen once a day and shaken manually twice a day to achieve anoxic conditions. Redox measurements were made to confirm anaerobic conditions existed.

After 5 days of anaerobic incubation, 100 µg/g of zinc, lead, and copper were added to three different containers.

After another 10 days, pH and redox potential were measured and a 150-ml aliquot from each flask was withdrawn and transferred anaerobically to polycarbonate centrifuge bottles which had previously been purged with nitrogen. The sediment material was centrifuged for 20

minutes at 6000 rpm. The supernatant was filtered through a 0.45- μ membrane filter under an oxygen-free atmosphere as described previously.

The separation of free and chelated ions was accomplished by passing a portion of the sample solution through a membrane filter connected in series to a Chelex-100 cation exchange resin column.

To all filtered solutions, 100 mg of EDTA was added to prevent precipitation of insoluble metal compounds upon oxidation prior to analysis.

Influence of pH and Redox Potential on the Particle-Size Distribution of Water-Soluble Iron, Manganese, Mercury, and Lead in Barataria Bay Sediments

For this experiment, a 1:8 solids:water mixture of reduced Barataria Bay sediment material was incubated anaerobically for 15 days. Ground grass (0.5 percent) was added as a carbon source for micro-organisms. The sediment mixture was filtered through a Whatman No. 42 filter and transferred to a 2-l, 3-necked flask. The flask was provided with a combination pH electrode, inlet, and outlet tubing for passing air or N₂ through the solution, a serum cap and a magnetic stirrer as shown in Figure 5. Each of six flasks was filled with 1500 ml of the filtered solution. The solutions in three flasks were purged with oxygen-free nitrogen, keeping the solution under reducing conditions. The remaining three solutions were aerated with compressed air to create oxidizing conditions.

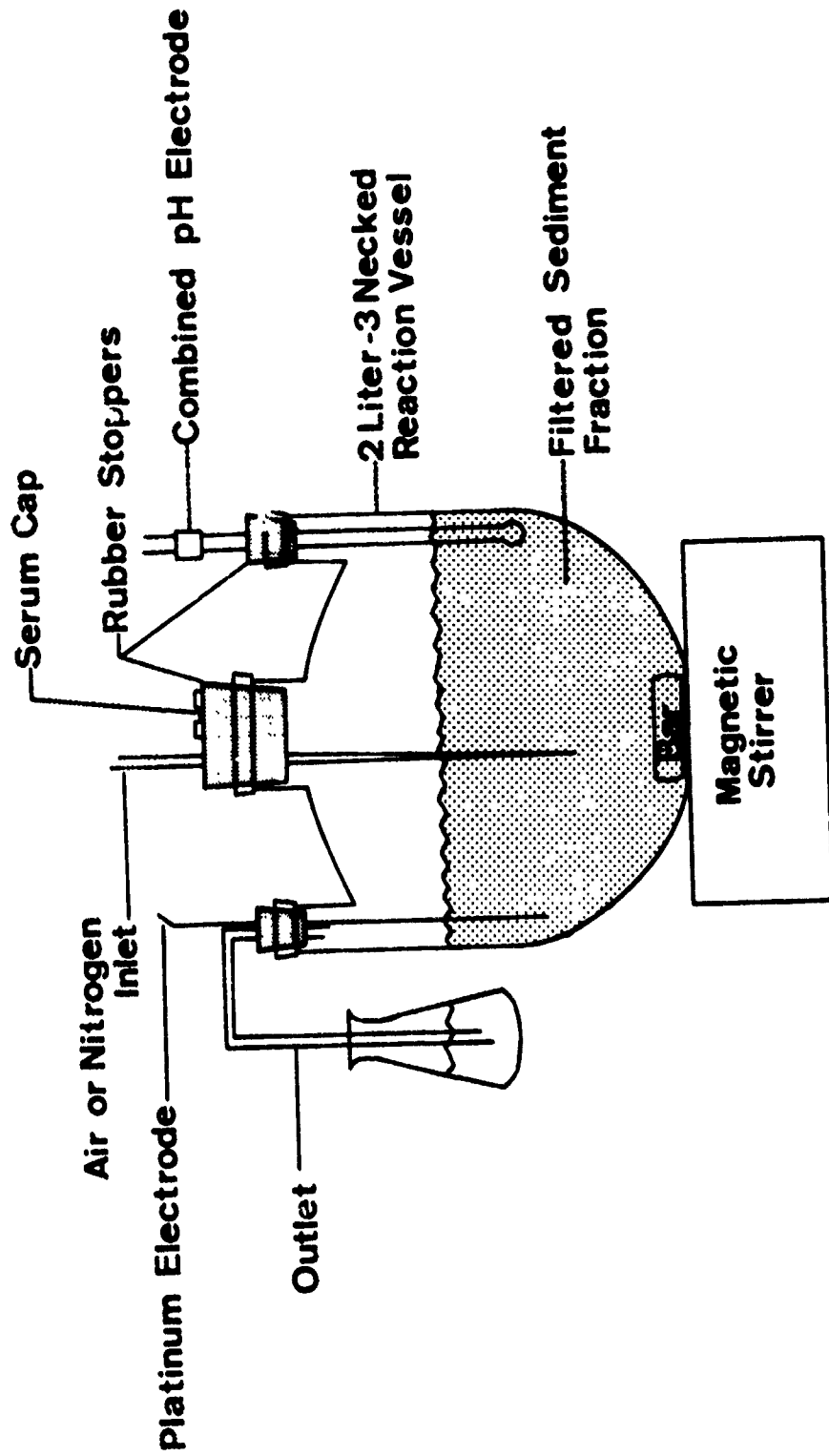


Figure 5. Incubation Flask for Barataria Bay Sediment Solutions Maintained at Controlled pH and Oxidation-Reduction Levels

After the redox potential of the solutions was stabilized (some 4 days), 20 μCi each of ^{203}Hg and ^{210}Pb were added to separate oxidized and reduced solutions, and the pH was adjusted to 8.0 by adding sodium hydroxide.

After another 2 days of equilibration, solution samples (pH 8.0) were taken, and the pH was lowered to 7.0 by adding dilute hydrochloric acid. When pH and redox potential were again stabilized (2-3 days), additional solution samples were taken, and the pH was adjusted to 6.0. This procedure was repeated until pH 4.0 was obtained, at which the last sample was taken.

The samples were filtered through different Millipore filter types using a modified "Millipore stirred molecular filtration cell" permitting filtration under completely anaerobic conditions. The filter types used were HA (0.45- μ pore size), pellicon PSAC (1000 nominal molecular weight limit), PSED (25,000 nominal molecular weight limit), and PSJM (100,000 nominal molecular weight limit). Some solutions were also run through a VC type filter (0.10- μ pore size), which was not available during the first portion of this experiment.

The water-soluble fraction (<0.45 μ) was also run through a Chelex-100 cation exchange resin column to determine the amount of free cations in these solutions.

Analytical Procedures

Atomic Absorption

Flame atomic absorption (Perkin-Elmer Model 107 Atomic Absorption

Spectrophotometer) was used for metal analyses in samples containing sufficient concentrations to be measured by this procedure. Total water-soluble and exchangeable cadmium and lead were measured by flameless atomic absorption (Perkin-Elmer Model 360 Atomic Absorption Spectrophotometer, Perkin-Elmer Model 2100 HGA graphite furnace). Indigenous components of the sample matrix as well as added chemical extractants contributed to considerable broad-band, nonatomic absorption in the graphite furnace. Deuterium arc (D_2) background correction alone was not sufficient to reduce broad-band absorption to acceptable levels. This type of interference was minimized by optimizing the sample and instrument operating parameters for each element as well as for the type of sample. Among the variables controlled to reduce interference were sample size, sample dilution, furnace charring and atomization temperatures, enhancement of interfering components' volatilization during charring cycle by chemical modification of the sample, and D_2 background correction.

A brief description of the procedures used with the graphite furnace are presented in Table 3.

Generally, a 1:2 dilution of the total water-soluble samples with deionized, distilled water was helpful in reducing background absorption without reducing metal concentration to low levels approaching the detection capabilities of the procedure. Where chemical extractants were used, a somewhat greater dilution was necessary.

The validity of D_2 background correction is open to serious question

Table 3

Instrument and Sample Parameters Used with Graphite
Furnace Atomic Absorption Technique

Parameter	Element	
	Cadmium	Lead
Sample size	20 μ l	50 μ l
Sample treatment	dilution, 20 μ l 5% NH_4NO_3	dilution, 20 μ l 5% NH_4NO_3
Drying time	30 sec	40 sec
Drying temperature	125°C	125°C
Charring time	25 sec	25 sec
Charring temperature	400°C	500°C
Atomization time	7 sec	10 sec
Atomization temperature	2400°C	2600°C
D ₂ background correction	yes	yes

whenever broad-band, nonatomic absorption approaches 1% absorption.²³

Treatment of samples with 20 μ l of a 5-percent ammonium nitrate solution directly within the graphite furnace was effective in reducing the sample matrix interference for most samples to levels which could be handled by D₂ background correction.

The previously discussed procedures were used to optimize sample and instrument parameters, and the method of standard additions was used for all determinations made by graphite furnace atomic absorption. An

example of this technique for cadmium is presented in Figure 6.

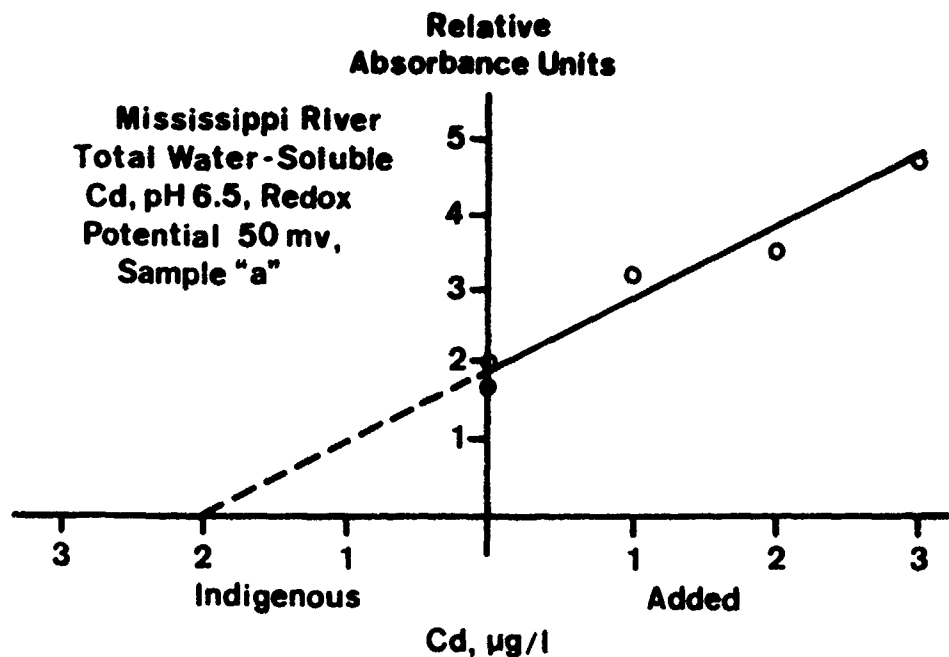


Figure 6. Soluble Cadmium Determination by Method of Standard Additions

Mercury was measured by flameless atomic absorption using a Coleman MAS-50 Mercury Analyzer System. Using this procedure, the minimum detectable mercury concentration was $0.01 \mu\text{g}/100 \text{ ml}$ sample volume.

Gamma Radiation Counting

The radioisotopes used in this study were gamma emitters. Gamma radiation counts were measured with an ORTEC solid scintillation gamma counting system.

Phosphorus

Phosphorus in the water-soluble and sodium acetate extracts was determined colorimetrically by the ascorbic acid method.²⁴ This method is based on reduction of the ammonium molybdiphosphate complex by ascorbic acid in the presence of antimony.

Ammonium-Nitrogen

Ammonia in the water-soluble and sodium acetate extracts was determined by the steam distillation method.²⁵ Distilled ammonia was collected in 0.1 N sulfuric acid. The samples were then nesslerized and ammonia was determined colorimetrically.²¹

Total and Volatile Sulfide

Sulfide was determined by the iodimetric procedure recommended for sewage by the American Public Health Association.²⁶ Total sulfide includes hydrogen sulfide as well as metallic sulfides present in the sediment material. Volatile sulfide evolved during sediment incubation was trapped in a zinc acetate solution attached to the incubation vessel's gas outlet. The zinc sulfide formed reacted with iodine solution, and the excess iodine was titrated with sodium thiosulfate using starch as an indicator. Total (metallic) sediment sulfide was transformed to hydrogen sulfide by treating the suspensions with sulfuric acid and collecting the gaseous hydrogen sulfide evolved in zinc acetate. The sulfide in the precipitate formed was determined as described above.

RESULTS AND DISCUSSION

Characterization of Sediment Material

pH and Redox Potential

The pH and redox potential of the bulk sediment material upon returning to the laboratory are given in Table 4. The pH ranged from 7.30 to 6.95 for the Barataria Bay and Mississippi River material, respectively.

Table 4
pH and Redox Potential of Bulk Sediment Samples

Sediment Material	pH	Redox Potential, mv
Barataria Bay	7.30	-60
Mobile Bay	7.25	-160
Mississippi River	6.95	+70
Calcasieu River	7.00	-100

Mineralogy

The predominant minerals identified by X-ray diffraction in the silt, coarse clay, and fine clay fractions of the sediment materials studied are presented in Table 5. The minerals within each size fraction are listed in decreasing order of abundance based on the relative peak areas of the X-ray diffractograms. The number in parentheses after

Table 5
 Predominant Minerals in Decreasing Order of Abundance in the Silt, Coarse
 Clay, and Fine Clay Fractions of the Research Sediment Materials Studied

Site	Particle-Size Fraction		
	Silt (50 → 2 μ)	Coarse Clay (2 → 0.2 μ)	Fine Clay (<0.2 μ)
Barataria Bay	Illite (20)* Quartz (10) Potassium Feldspars (10) Kaolinite (5)	Montmorillonite (15) Illite (15) Kaolinite (10)	Montmorillonite (40) Illite (5) Kaolinite (5)
Mobile Bay	Illite (10) Potassium Feldspars (10) Quartz (10) Kaolinite (5)	Kaolinite (25) Montmorillonite (20) Illite (15) Vermiculite (10)	Montmorillonite (25) Kaolinite (25) Chlorite-Vermiculite (5)
Mississippi River	Illite (10) Plagioclase Feldspars (10) Potassium Feldspars (10) Quartz (5) Kaolinite (5)	Montmorillonite (15) Vermiculite (15) Kaolinite (10) Illite (5) Potassium Feldspars (5)	Montmorillonite (40) Chlorite-Vermiculite (15) Kaolinite (10)
Calcasieu River	Quartz (10) Potassium Feldspars (10) Plagioclase Feldspars (5) Illite (5) Kaolinite (5)	Kaolinite (15) Montmorillonite (10) Vermiculite (10) Quartz (10) Illite (5)	Montmorillonite (25) Kaolinite (20) Vermiculite (5)

*Numbers in parentheses indicate an estimate of percent of total crystalline minerals within designated size fraction and site based on determining peak area percentages of X-ray diffractograms. 27, **

**Personal Communication, Dr. A. G. Caldwell, Department of Agronomy, Louisiana State University, June 16, 1975.

each mineral refers to the percent of the indicated mineral of the total crystalline minerals present within the designated sediment material and size fraction. Though X-ray diffraction is an excellent qualitative tool, quantitative mineralogical evaluations by this technique are subject to considerable error. Thus the percentages given in Table 5 should be interpreted as approximations of the relative proportions of minerals present for comparisons between sites and particle-size fractions for these sediment materials.

Organic and Carbonate Carbon Content

The total carbon content of the sediment materials studied is presented in Table 6.

Table 6

Organic and Carbonate Carbon Content of Sediment Materials

Sediment Material	Organic Carbon --- % ---	Carbonate Carbon --- % ---
Barataria Bay	2.99	0.07
Mobile Bay	1.82	0.08
Mississippi River	1.16	0.19
Calcasieu River	2.37	0.07

The carbonate carbon contents of the Barataria Bay, Mobile Bay, and Calcasieu River sediment materials were similar (0.07 to 0.08 percent).

The carbonate carbon content of the Mississippi River sediment material was over twice as great (0.19 percent) as found for the other materials studied.

The Barataria Bay material contained the highest level of organic carbon and the Mississippi River, the least. The low level of organic carbon in the Mississippi River sediment material may limit microbial activity in this material relative to the other sites studied. This likely contributed to the greater degree of oxidation and the lighter color of the Mississippi River sediment samples.

Oxygen-Consumption Rates

Oxygen-consumption rates of the four sediment materials should reflect the availability of an organic energy source to micro-organisms as well as the demand for oxygen for the chemical oxidation of inorganic materials such as ferrous iron and sulfide. Figure 7 shows oxygen-consumption rates for the four sediment materials. In general, it is seen that oxygen consumption increases with the total carbon content (Table 6). However, the relative oxygen-consumption rates for the Barataria Bay and Calcasieu River sediment material are an exception to this generalization. The differences in the soluble and exchangeable iron (Tables B1 and B4) and the sulfide content of these sediments do not seem adequate to explain the greater oxygen-consumption rate of the Calcasieu River sediment material. Some sediment characteristics may

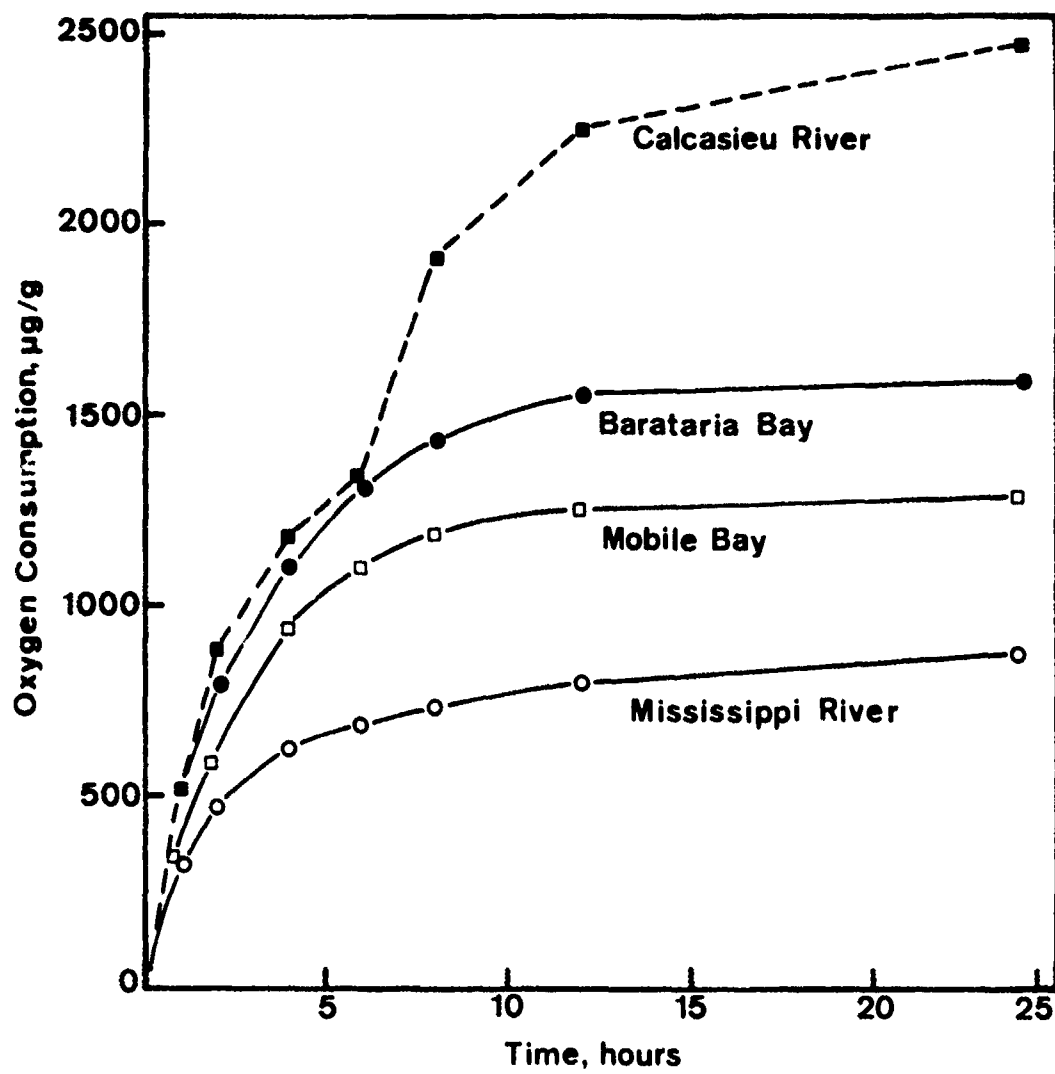


Figure 7. Oxygen-Consumption Rates for Sediment Materials Studied

be limiting microbial activity, or the microbial availability of the organic carbon from the two sources may differ.

Particle-Size Distribution

The particle-size distribution of the sediment materials is indicated in Figure 8. The clay fraction is known to be the most important size fraction for sorption-desorption reactions of metals and nutrients with mineral soil and sediment materials. The sediment materials from Mobile Bay and Calcasieu River were found to have a clay content of around 45 percent. The Mississippi River sediment material had 36 percent clay and the Barataria Bay material contained 28 percent clay.

Cation Exchange Capacity

The cation exchange capacity of all the sediment materials group around two levels (Table 7). The Barataria Bay and Mississippi River sediment materials were found to have a cation exchange capacity of around 19 meq/100 g of oven dry solids, while the measured cation exchange capacity of the Mobile Bay and Calcasieu River sediment materials was around 35 meq/100 g.

The greater cation exchange capacity of the Mobile Bay and Calcasieu River sediment materials corresponds well with their greater

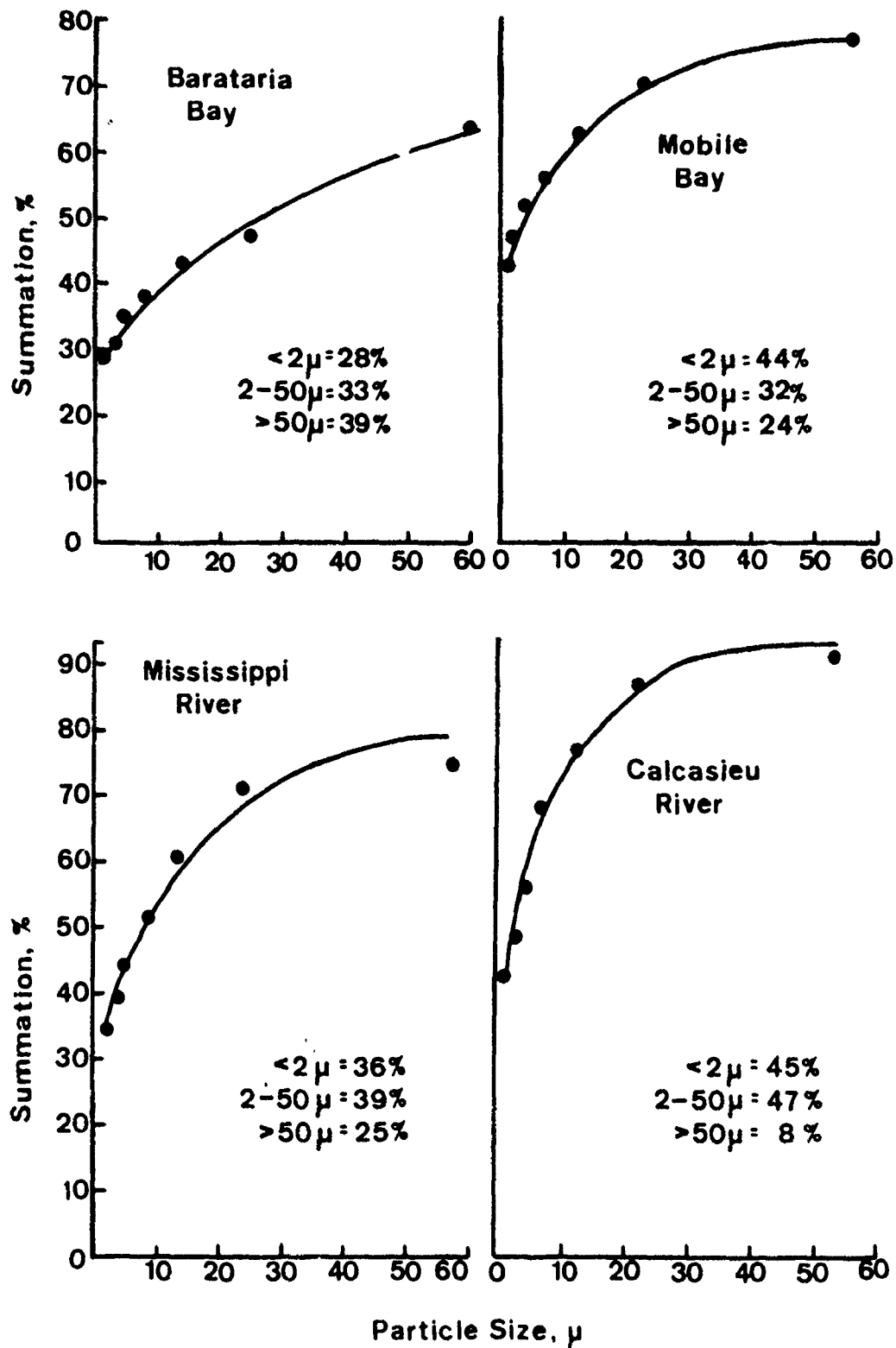


Figure 8. Particle-Size Distribution of Sediment Materials Studied

Table 7

Cation Exchange Capacity of Sediment Materials

Sediment Material	Cation Exchange Capacity
	--milliequivalents per 100 grams--
Barataria Bay	19.2
Mobile Bay	32.6
Calcasieu River	34.9
Mississippi River	19.2

proportion of clay-size particles. With the exception of the Barataria Bay material, there is also a trend for cation exchange capacity to increase with the organic carbon content. Soil and sediment organic material contributes a greater cation exchange capacity per unit weight than do clay minerals, especially at neutral and alkaline pH levels. The proportional contribution of organic matter to total cation exchange capacity is generally greater for sediments than for soils, as most sediments contain higher levels of organic material than cultivated soils.

There seems to be little and perhaps even a negative correlation between the measured cation exchange capacity and the expected contribution to exchange capacity due to the type and relative proportions of specific clay minerals identified in the sediment materials (Table 5).

In the sediment materials studied, it is believed that the contribution to cation exchange capacity from organic matter and the relative total clay content generally overrides the significance of the sediment material mineralogy in influencing cation exchange capacity.

Trace Metal and Nutrient Chemistry of Sediment Materials
as Influenced by pH and Redox Potential

Quantitative data for the water-soluble metals discussed in this report are expressed as $\mu\text{g metal/g}$ oven dry solids rather than $\mu\text{g/l}$, as commonly done for dissolved metals. This is to facilitate comparisons between metal levels in this fraction with levels determined in other chemical forms which are traditionally expressed on a weight-metal/weight-solids basis. Though the actual solution:solids ratio in each incubation flask may have varied slightly around the planned 8:1 ratio, dividing the reported levels by eight (8) will closely approximate the concentration of metals in the total water-soluble fraction on a solution basis.

However, one should keep in mind that the water-soluble phase in this study is not representative of surface water, nor does it accurately represent interstitial water, as the surface water:sediment ratio used in this study is typical of a dredged material slurry. Additionally, maintaining this sediment-water mixture in suspension by continuous stirring may enhance the release of metals from the solid to the solution phase.

For these reasons, concentration of water-soluble metals given in this report cannot be compared with the reported quantity of dissolved metals in surface and interstitial waters found in the published literature. However, the data given in this report should indicate qualitatively, if not quantitatively, the influence of pH and redox potential on the distribution of metals among various chemical forms and the chemical transformations expected as the pH and redox potential environment of a sediment-water system is altered.

Sulfide-Sulfur

In reduced soils and sediments containing sulfide, the precipitation of trace and toxic metals such as iron, zinc, copper, lead, cadmium, and mercury as a sulfide is thought to be an important regulatory mechanism limiting the soluble levels of these metals.^{28,29,30,31,32} In this report, the sulfide data are presented prior to the discussion of the effect of pH and redox potential on metal chemistry in order to consider the role of sulfide regulation of metal solubility as the data for each element are discussed (Table 8).

No sulfide was detected in any sediment suspension incubated at 50, 250, or 500 mv. This corresponds to literature reports that a redox potential of -150 mv is approaching the upper limit for sulfide stability.^{33,34,35} No sulfide was detected in the strongly reduced Barataria Bay sediment material incubated at pH 8.0, and none was measured in the

Table 8
 Total Sulfide Content of Sediment Materials Incubated at a
 Redox Potential of -150 mv

Sediment Material	Total Sulfide		
	pH 5.0	pH 6.5	pH 8.0
	µg S/g solids		
Barataria Bay	510	631	n.d.*
Mobile Bay	1,230	607	434
Mississippi River	n.d.	n.d.	n.d.
Calcasieu River	----**	675	195

*Not detectable. **Data not available.

Mississippi River sediment material at any pH level studied. Where sulfide was measured, a decrease in pH was generally found to increase the total sulfide content.

No volatile sulfide (H_2S) was detected in the outlet gas stream of the incubated sediment materials at any pH-redox potential combination. Presumably, all of the sulfide was complexed in a solid phase as a metal sulfide. Due to the high levels of soluble ferrous iron measured in the strongly reduced sediment suspensions, it is likely that most of the sulfide was present as sparingly soluble ferrous sulfide.

In contrast to the known low solubility of many metal sulfides, there are numerous reports in the literature where the soluble levels of

metals in reduced sulfide-bearing waters and sediments has been found to exceed the levels predicted from the solubility of their sulfides. Several mechanisms have been summarized from the available literature, reported, and proposed to account for these observations. These mechanisms include the formation of soluble metal sulfide complexes,^{36,37} metal solubility regulation by equilibrium with unknown metastable solids,³⁸ and metal complexing with organic ligands. In addition, it has been proposed that some trace metal ions may be kept from precipitation with sulfide where a sufficiently large concentration of soluble iron is present to complex with and precipitate the sulfide.²

Iron

Iron in surface waters and sediments is not considered to have deleterious effects on aquatic and benthic organisms. Although the U.S. Public Health Service³⁹ and U. S. Environmental Protection Agency⁴⁰ consider 0.3 mg/l as the maximum permissible level of iron in drinking water, these levels were selected primarily for esthetic rather than health reasons. However, iron is known to be an important factor in regulating the concentration of trace and toxic metals. In sediment-water systems, a considerable quantity of iron may be subject to transformations between the reduced ferrous (Fe^{2+}) and the oxidized ferric (Fe^{3+}) form. These transformations of iron depend on changes in pH and redox potential. Such changes could occur during dredging and dredged material disposal when typically reduced sediments are mixed with an oxygenated

water column or transported to land for disposal.

Table 9 indicates the total iron content of the sediment materials studied and the proportion of iron recovered by the sequential chemical fractionation procedure applied to each.

Table 9
Total Sediment Iron Content and the Proportion Recovered
in Potentially Active Chemical Forms by the
Fractionation Procedure Applied to Each Sediment Material

Sediment Material	Total Iron	Potentially Reactive Iron*
	-- $\mu\text{g Fe/g solids}$ --	-- % of total --
Barataria Bay	23,800	27
Mobile Bay	37,400	51
Mississippi River	29,400	46
Calcasieu River	26,000	16

*Sum of iron extracted by the sequential chemical fractionation procedure from the pH-redox potential treatment yielding largest iron recovery.

The total iron content ranged from 23,800 $\mu\text{g/g}$ for the Barataria Bay sediment material to 37,400 $\mu\text{g/g}$ for the Mobile Bay material. The potentially reactive iron given in Table 9 is the sum of iron recovered by the sequential fractionation procedure in the pH-redox potential treatment yielding the greatest iron recovery. These levels are not intended to represent the absolute amount of iron potentially capable

of chemical transformations in these sediment materials since elemental recovery depends on the severity of the extractions included in a chemical fractionation procedure. Nor should these levels be used for strict comparisons between the sediment materials studied as the chemical fractionation procedures varied somewhat. However, these data are useful in approximating the potentially reactive iron in the different sediment materials over the range of pH and redox potentials studied. About half of the iron in the Mobile Bay and Mississippi River sediment materials was recovered in the chemical forms studied, primarily in the reducible fraction. A much smaller proportion of the total iron was recovered by chemical extractions of Barataria Bay and Calcasieu River materials, suggesting either less weathering of the clay minerals in these sediments, or solubilization and subsequent mobilization of iron released by mineral weathering under long-term exposure to reducing environments.

The influence of pH and redox potential on the quantity of total water-soluble and exchangeable iron was similar for the four sediment materials studied. As the results from all sampling sites were somewhat similar, and because iron is not considered a potentially toxic or nuisance element, the data from representative sediment materials will be presented to illustrate the chemistry of iron in sediment samples from all four sites. Data for the remaining materials studied are available in Appendix B.

Figures 9 and 10 indicate the influence of pH and redox potential on the total water-soluble iron in the Mississippi River and Mobile Bay sediment suspensions, respectively. Relatively large quantities of iron were maintained in solution under a low pH-redox potential environment. The soluble iron in the Mississippi River sediment material was over 2,700 $\mu\text{g/g}$ solids at -150 mv, pH 5.0. As the redox potential increased from -150 mv, at pH 5.0, there was a marked decline in the soluble iron to around 1,900 $\mu\text{g/g}$ at 50 mv and to about 400 $\mu\text{g/g}$ at 250 mv. Little to no soluble iron was detected by flame atomic absorption at the two higher redox potential levels studied in any of the other sediment materials. At pH 6.5, soluble iron decreased from 142 $\mu\text{g/g}$ solids at -150 mv to 30 $\mu\text{g/g}$ at 50 mv and was not detected at higher oxidation levels. No soluble iron was detected at pH 8.0. Iron in the Mobile Bay sediment suspensions responded to pH and redox potential in a similar manner (Figure 10). Though there were some quantitative differences, exchangeable iron extracted from these suspensions followed the same trends with changes in pH and redox potential as were found for total water-soluble iron (Figures 11 and 12).

Gotoh and Patrick⁴¹ reported similar results for soluble and exchangeable iron in rice soils. In both of these chemical fractions, the oxidation of soluble ferrous (Fe^{2+}) iron to the sparingly soluble ferric (Fe^{3+}) form is responsible for the reduced availability of iron as pH and redox potential are increased.

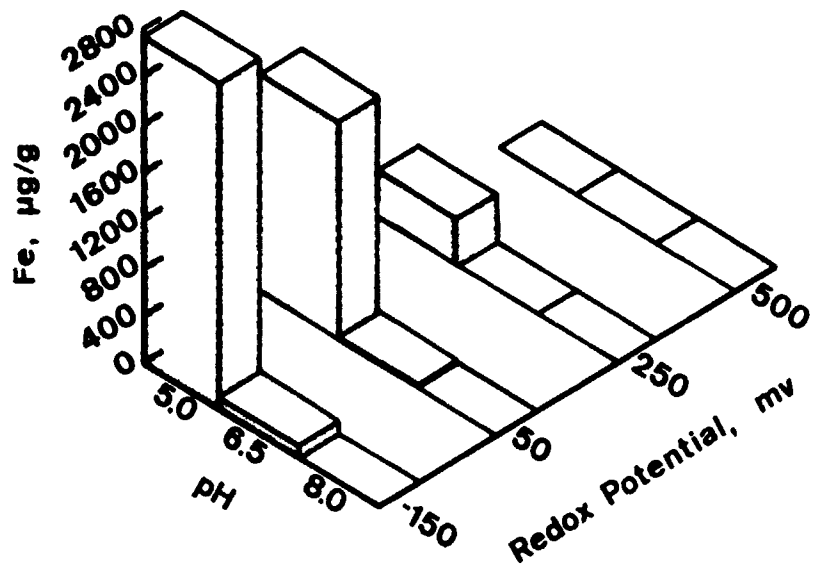


Figure 9. The Effects of pH and Redox Potential on Total Water-Soluble Iron in Mississippi River Sediment Suspensions

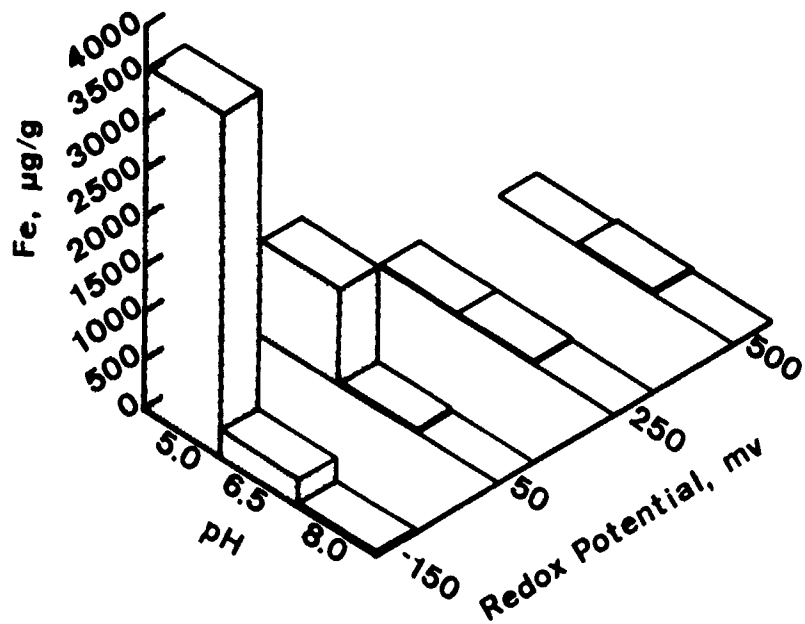


Figure 10. The Effects of pH and Redox Potential on Total Water Soluble Iron in Mobile Bay Sediment Suspensions

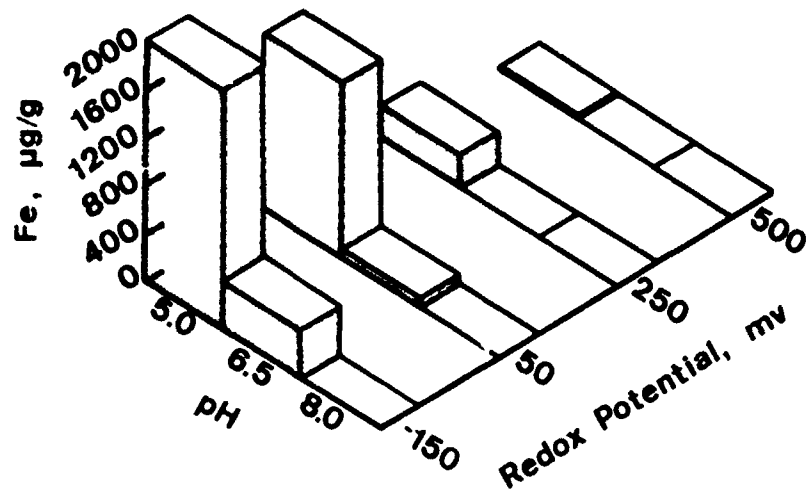


Figure 11. The Effects of pH and Redox Potential on Exchangeable Iron in Mississippi River Sediment Suspensions

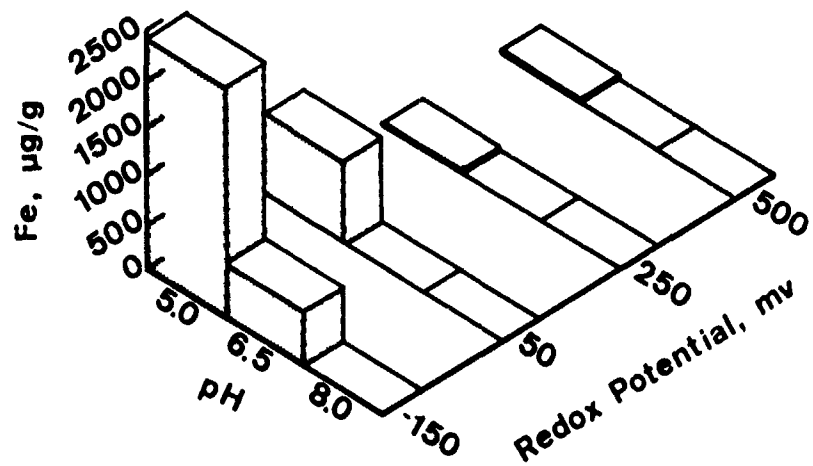


Figure 12. The Effects of pH and Redox Potential on Exchangeable Iron in Mobile Bay Sediment Suspensions

The rapid oxidation of ferrous iron as pH and redox potential are increased is possible only if the soluble ferrous iron is not complexed with some ligand that prevents or retards its oxidation. Theis and Singer⁴² have shown that considerable quantities of ferrous iron may be maintained in solution in aqueous aerobic environments for periods up to several days due to the complexation of ferrous iron with naturally occurring soluble organic material. In the sediment materials included in this study, data indicate that while some soluble ferrous iron is complexed in reduced sediment environments, most of the soluble ferrous iron is either present as free ions or only weakly bound and thus readily released from naturally occurring organic chelates (see Soluble Organic Bound Fraction, Appendix B). The small proportion of iron present in a complexed form should not significantly affect the rapid oxidation of ferrous iron and the potential trace metal adsorption activity of freshly formed ferric oxides and hydroxides as the ferrous iron is transported into an oxidized environment.

No sulfide was detected at any pH-redox potential combination in the Mississippi River sediment suspension and in the Barataria Bay sediment material incubated at pH 8.0; however, several hundred μg sulfide-sulfur/g solids were detected at all pH levels under the most reducing (-150 mv) conditions for the remaining sediment materials (Table 8). Considerable dissolved iron was measured at -150 mv in all sediment materials at pH 5.0 and 6.5. Due to the low solubility of ferrous sulfide,

it is reasonable to assume that essentially all of the sulfide was precipitated as ferrous sulfide at pH 5.0 and 6.5 and that the soluble iron measured under these conditions is that quantity of iron which exceeded the capacity of sulfide precipitation. At pH 8.0, -150 mv, it is likely that the total sulfide content of the sulfide-containing sediments exceeded the available ferrous iron as no soluble iron was detected. However, it is also possible that the formation of less soluble iron compounds, such as carbonates and phosphates, may also limit soluble ferrous iron.

In this report, reducible iron refers to that iron extracted with an ammonium oxalate-oxalic acid extractant. A number of reducing reagents and procedures are discussed in the literature, some of which are reported to be more selective for one chemical form of a particular element than another. It is doubtful that any chemical extractant is highly selective for a particular elemental form, as it is unlikely that sharp boundaries exist between metal and nutrient bonding strengths to different adsorbents and their susceptibility to different chemical extractants. However, the reducing reagent used in this study is reported to preferentially attack poorly crystallized oxides and hydroxides of iron and manganese while having little effect on crystalline materials.^{43,44} Thus it is thought that reducible iron may correlate with that iron effective in trace metal adsorption.

Figures 13 and 14 indicate the influence of pH and redox potential

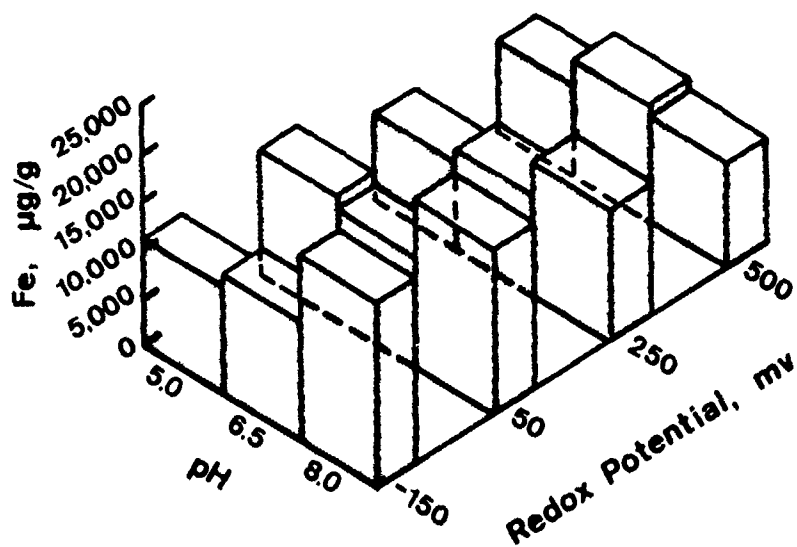


Figure 13. The Effects of pH and Redox Potential on Reducible Iron in Mobile Bay Sediment Suspensions

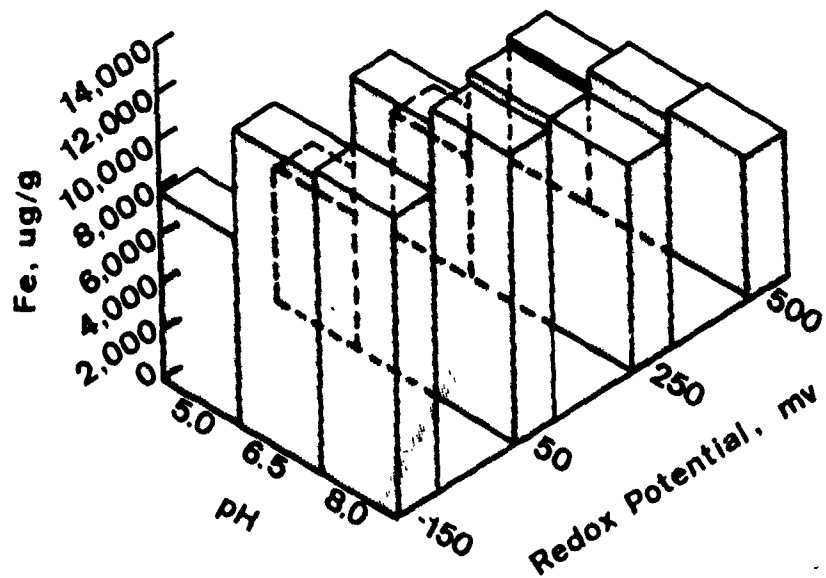


Figure 14. The Effects of pH and Redox Potential on Reducible Iron in Mississippi River Sediment Suspensions

on the reducible iron in the Mobile Bay and Mississippi River sediment material, respectively. Oxalate extractable iron was found to be greatest under reducing conditions and decreased somewhat as redox potential increased. This was also the general trend for the Calcasieu River sediment material but not for the Barataria Bay material. The Mobile Bay, Mississippi River, and Calcasieu River sediment materials possibly contained more poorly crystalline iron compounds under reducing conditions. Though a quantitative comparison between the extracted iron from these sediment materials cannot be made with the Barataria Bay material due to a different oxalate reagent concentration used, it was noted that reducible iron recovery in this material increased with increasing redox potential.

Unlike the readily transformed water-soluble and exchangeable iron, which decreased from a few thousand $\mu\text{g/g}$ solids under reduced, acid conditions to undetectable levels at higher pH-redox potential combinations, the relatively large quantities of reducible iron are not influenced to as great a degree. Reducible iron is not simply that quantity of ferrous iron that was lost from the soluble and exchangeable fractions as the suspension redox potential increased. Instead, reducible iron is thought to include considerable levels of oxidized iron compounds which persist even under moderate and strongly reducing conditions. Gotoh and Patrick,⁴¹ using citrate-dithionite-bicarbonate solution, extracted 6,000 to 11,000 $\mu\text{g/g}$ of reducible iron under strongly reduced conditions. The iron compounds dissolved consisted of iron oxides and hydroxides, which strongly suggests the presence of ferric iron under reduced conditions. Thus, iron

extracted with reducing agents includes a relatively large proportion of the total iron present in sediment materials under both oxidizing and reducing conditions. Apparently, much of this iron is only slowly capable of chemical transformations, either to more crystalline forms or to the more mobile water-soluble and exchangeable forms.

Discrete particles of hydrated ferric oxides as well as coatings of this amorphous material on crystalline minerals in sediments are thought to be effective scavengers for soluble trace metals. Literature reports and data from this study presented above indicate that considerable amounts of colloidal ferric oxides and hydroxides may be present in both oxidized and reduced sediments. It is also known that both ferrous and ferric iron are present in soils and sediments as a large number of compounds with considerable structural and crystalline variability. Thus the chemistry of iron in sediments and its capacity for trace metal adsorption is dependent on the composite contributions from the many iron compounds present. In general, poorly crystalline iron and manganese compounds are thought to be more effective metal scavengers. Thus sediment environmental conditions conducive to formation and/or maintenance of poorly crystalline hydrous oxides should enhance the role of hydrous oxides as regulators of trace metal solubility.

Freshly oxidized and precipitated ferric compounds, which are formed from the considerable quantities of soluble and exchangeable iron when reduced sediments are transported to an oxidized environment, are thought to be much more effective in adsorbing trace metals from solution than aged ferric oxides.^{10,11,12} There is evidence that the aging effect is

due to a decrease in surface area or perhaps improved crystallinity under oxidized conditions with time.^{11,45}

Data shown in Figures 9, 10, 11, and 12 indicate that in reduced acid and near-neutral sediment materials, the level of ferrous iron potentially capable of transforming to an effective trace metal scavenger exceeds the expected levels of trace metals by several orders of magnitude. In slightly alkaline to alkaline sediment materials, there is far less soluble ferrous iron available for oxidation. Though little or no iron was detected in some of the sediment suspensions by flame atomic absorption at pH 8.0, it is likely that more soluble iron was present under reducing conditions than under oxidizing conditions, but that the levels involved were below the sensitivity of the analytical procedures used (1 μg iron/g). Trace levels (≈ 0.5 to 5.0 mg/l) of soluble iron have been found in reduced interstitial waters of Lake Ontario where the pH ranged between 7 and 8.⁴⁶

In contrast to the rapid formation of poorly crystalline hydrous oxides, which may act as effective metal adsorbents in recently oxidized sediments, the maintenance of hydrous oxides in poorly crystalline forms may be favored by prolonged reduced environments. As previously discussed, the quantity of poorly crystalline (oxalate-extractable) iron compounds was greater in the strongly reduced Mobile Bay, Mississippi River, and Calcasieu River sediment suspensions than in the better oxidized treatments. Patrick and Khalid⁴⁷ reported more oxalate-reducible iron was extracted from rice soils when incubated under anaerobic conditions than when incubated under aerobic conditions. Thus the presence of poorly crystalline hydrous oxides may be favored by two contrasting environments:

one being a recently oxidized environment and the other, a long-term reduced environment.

Trace metal adsorption to oxides and hydroxides of iron is generally thought to be favored in oxidized environments, but more reducible and presumably poorly crystalline iron was generally extracted from the -150 mv treatment. Data to be presented later will show several trace metals recovered in the reducible fraction do tend to increase with redox potential. However, there was some indication that other metals and nutrients may be more strongly associated with iron in a strongly reducing environment. This suggested that the oxalate-extractable iron includes much iron in a form or forms which are not well correlated with the form of iron effective in adsorbing trace metals. The iron in an active adsorbing form may be a proportionally small part of the total and is thus masked by the total iron extracted.

Figure 15 summarizes the influence of redox potential on the distribution of iron in the various chemical forms studied in the Mississippi River sediment material incubated at pH 6.5. The results were similar for the other sediment materials studied. Trends with redox potential and quantities extracted were generally comparable to the other pH levels studied with the notable exception that total water-soluble and exchangeable iron levels were much greater under reduced conditions at pH 5.0 and were less at pH 8.0. An increase in redox potential resulted in a reduction of both soluble and exchangeable iron. The reducible fraction contained by far more iron than the other fractions studied, and the level of this iron generally decreased with increasing redox

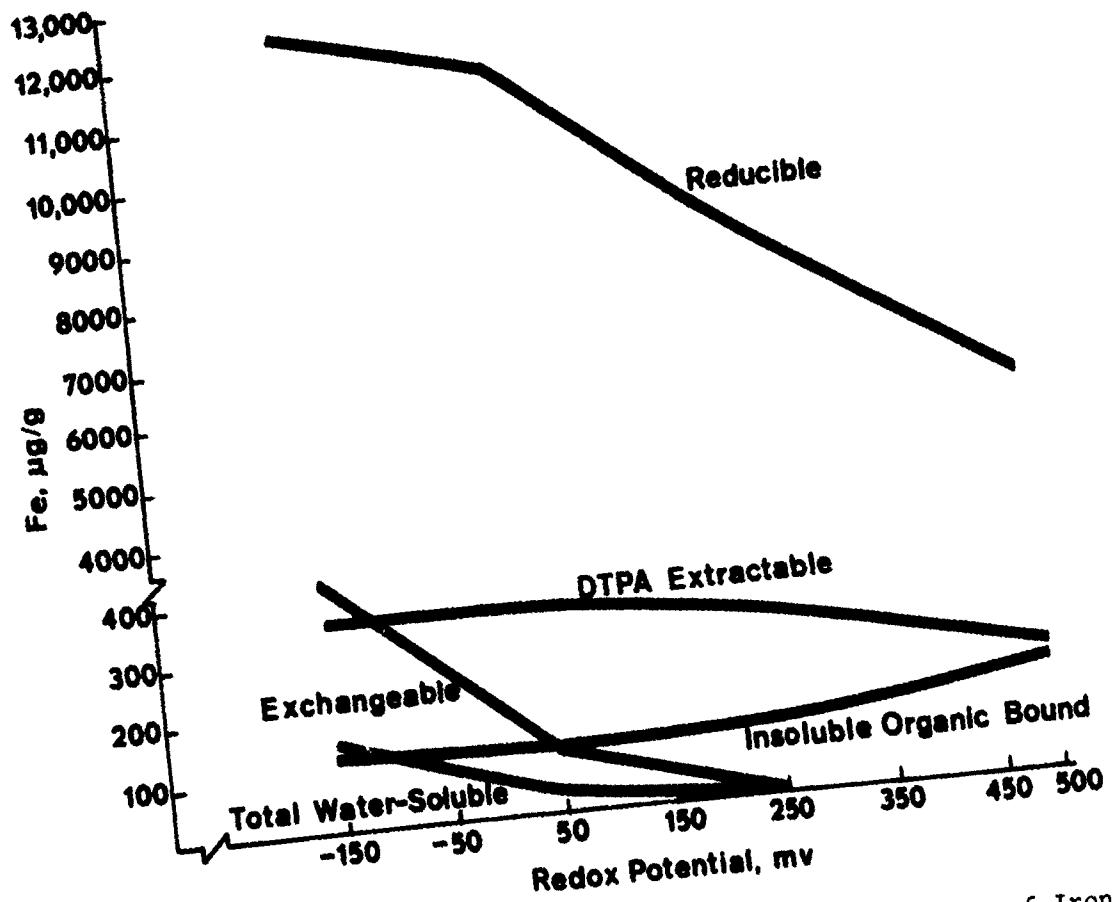


Figure 15. The Effects of Redox Potential on the Distribution of Iron Among Selected Chemical Forms in Mississippi River Sediment Suspensions Incubated at pH 6.5 (total iron, 29,400 µg/g)

potential. It is apparent from Figure 15 that if the iron removed from the total water-soluble and exchangeable fractions became oxidized as the redox potential increased, either (1) the oxalate extractant failed to recover this iron or (2) the transformation of soluble and exchangeable iron to the reducible form was small relative to the loss of total poorly crystalline iron as the redox potential increased. It is also possible that under reduced conditions, the oxalate-extractant is more effective in dissolving oxides and hydroxides of iron.

Comparatively little iron was recovered in the DTPA-extractable and insoluble organic bound fractions relative to that recovered in the reducible form. Also apparent is that over half of the iron in this material was not accounted for with the fractionation procedure used. Much of this iron is likely an essential component of crystalline minerals. However, residual iron probably includes much iron that is still subject to chemical transformations or to more severe extractions. For example, the large quantity ($>6000 \mu\text{g/g}$) of iron removed from the reducible fraction as redox potential increased was not detected in other more easily available fractions measured in this study. This iron was likely transformed to what was termed the residual iron fraction. Other sediment materials studied showed comparable results.

Manganese

Manganese, like iron, is an essential element to flora and fauna. Also, similar to iron, it is usually not detrimental to water quality as a consequence of its nutritional or toxicological properties. Like

iron, manganese is of interest because of its reported scavenging effect for soluble trace and toxic metals in surface waters, soils, and sediments. 11,12,48

Table 10 indicates the total quantity of manganese present in the research materials studied. Also included in this table is the sum of

Table 10

Total Manganese and Proportion Recovered in Potentially Active
Chemical Forms by Fractionation Procedure
Applied to Each Sediment Material

Sediment Material	Total Manganese	Potentially Reactive Manganese*
	-- µg Mn/g O. D. solids --	-- % of total --
Barataria Bay	300	84
Mobile Bay	590	82
Mississippi River	950	97
Calcasieu River	320	86

*Sum of manganese extracted by sequential chemical fractionation procedure from the pH-redox potential treatment yielding largest manganese recovery.

the manganese extracted by the sequential fractionation procedure used at the pH-redox potential combination yielding the greatest manganese recovery. Though most was recovered in the less mobile chemical forms, the proportionally large recovery indicates that almost all of the total manganese in these sediment materials is potentially capable of transformations affecting the levels of chemically reactive manganese.

Due to the similarity of the manganese data for the different sediment materials, selected data will be used to discuss the manganese chemistry of the four sediment materials studied. Additional data is given in Appendix C.

Figures 16 and 17 indicate the total water-soluble manganese present in the Mobile Bay and Mississippi River sediment materials, respectively. There is a marked tendency for the total water-soluble manganese to decrease with increasing redox potential in the Mississippi River sediment material. At pH 5.0, under strongly reducing to moderately oxidizing conditions, over half of the total manganese was present in solution. A smaller decrease in manganese levels with increasing redox potential was noted at pH 5.0 and 8.0 in the Mobile Bay sediment material, and no response to redox potential was apparent at pH 6.5. For reasons not apparent, manganese in the various chemical fractions studied from the Mobile Bay sediment material did not respond to changes in redox potential as distinctly as did manganese in the other sediment materials studied. For all of the sediment materials, there was a sharp decrease in the water-soluble manganese as pH increased.

Essentially none of the total water-soluble manganese was found associated with soluble organic matter (Appendix C). This agrees with published data for soils where manganese has been reported to be not complexed or only weakly complexed with organics in soil solution.⁴⁸

The response of exchangeable manganese to pH and redox potential was similar to that found for the water-soluble fractions (Figures 18

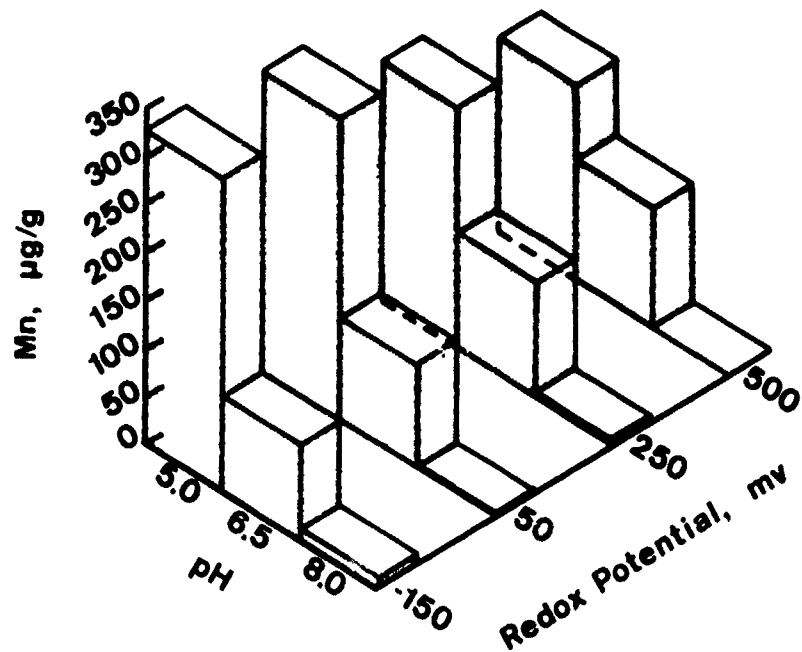


Figure 16. The Effects of pH and Redox Potential on Total Water-Soluble Manganese in Mobile Bay Sediment Suspensions

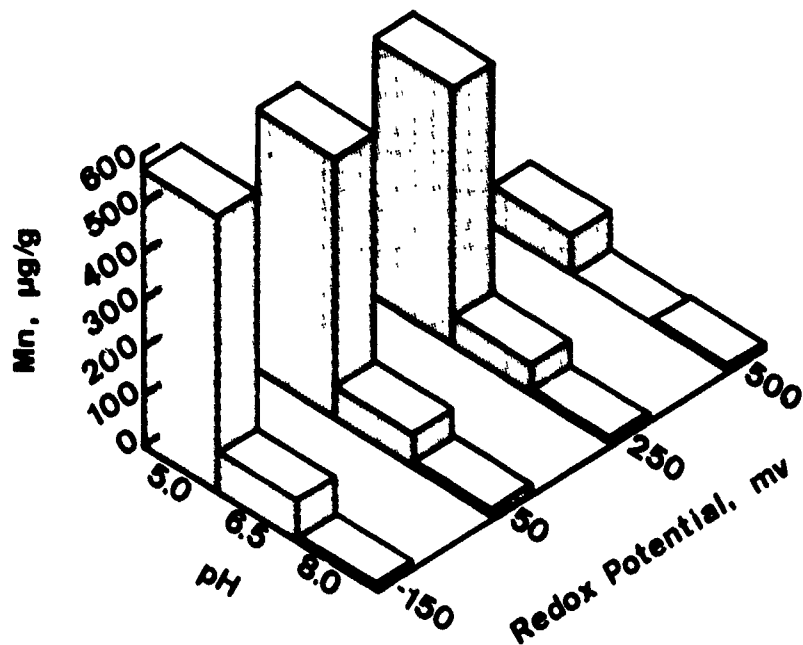


Figure 17. The Effects of pH and Redox Potential on Total Water-Soluble Manganese in Mississippi River Sediment Suspensions

and 19). Exchangeable manganese decreased as pH and redox potential increased. Generally, there was less exchangeable manganese than water-soluble manganese at pH 5.0, but the opposite was found at pH 8.0.

As indicated in Figures 16 through 19, considerable quantities of manganese are present in readily available forms under acid reducing conditions. This manganese is thought to be in the divalent cationic form (Mn^{2+}). Most of this manganese is transformed by oxidation to less mobile manganese oxides as the pH or oxidation levels of a sediment-water system is increased.⁴⁹ Over 150 oxides of manganese ranging from $MnO_{1.2}$ to MnO_2 have been identified.⁵⁰ As with iron, manganese oxides and hydroxides are known to be important adsorbents for trace metals. Morgan and Stumm⁵¹ found that freshly precipitated manganese dioxide has a significant sorption capacity for heavy metals, and it was suggested that aging of these oxides could likely reduce sorption capacity. During dredging and dredged material disposal, the formation of hydrous oxides of manganese, as reduced sediment material containing dissolved divalent manganese is dispersed in an oxygenated water column, may result in adsorption of metals by these freshly formed hydrous oxides. This could be a significant factor in regulating the bioavailability of toxic metals, especially where dredged material is disposed by land application methods where gradual drainage and subsequent oxidation may occur. Water-soluble and exchangeable manganese levels were more dependent on pH than redox potential. However, decreases in these readily mobile manganese forms were frequently noted as redox potential increased above the 200 or 250 mv levels. Similar redox potentials

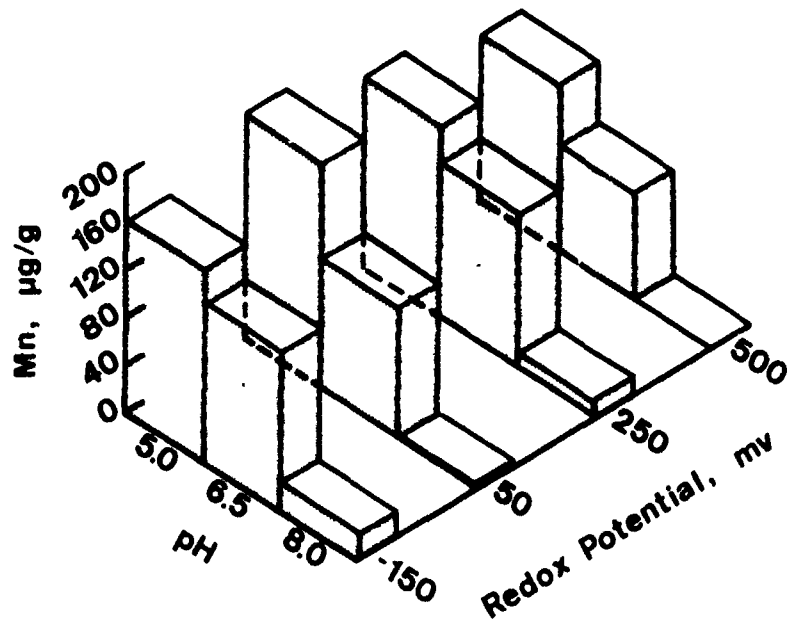


Figure 18. The Effects of pH and Redox Potential on Exchangeable Manganese in Mobile Bay Sediment Suspensions

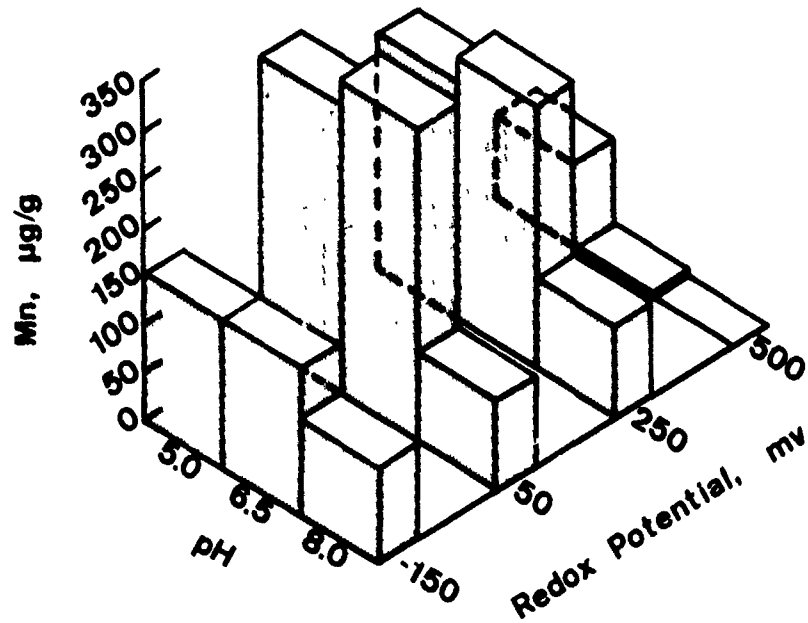


Figure 19. The Effects of pH and Redox Potential on Exchangeable Manganese in Mississippi River Sediment Suspensions

for manganese conversion from the water-soluble and exchangeable forms to less available forms have been reported for flooded rice soils.⁵² Surface waters which are mixed with dredged sediments generally contain some dissolved oxygen. Where dissolved oxygen is present, the minimum redox potential expected at pH 7 is 300 to 400 mv.⁵³ Thus for dredged sediments mixed with large volumes of aerobic surface waters, it is likely that the redox potential environment of interstitial waters and sediments containing manganese will be increased beyond the critical redox potential for manganese oxidation, at least during mixing. However, the kinetic stability of reduced manganese may limit the quantity oxidized unless disposal conditions result in extended exposure of the manganese to an oxidized environment.

Unlike iron, the manganese that was removed from the water-soluble and exchangeable forms as redox potential and pH were increased was generally recovered in the reducible fraction (Figures 20 and 21). A sharp increase in reducible manganese as the redox potential increased from mildly oxidizing (200 to 250 mv) to strongly oxidizing (450 to 500 mv) was well correlated with the drop in water-soluble and exchangeable manganese that occurred between these oxidation levels. A comparatively small proportion of the manganese was recovered by the DTPA extraction and the hydrogen peroxide digestion-sodium acetate extraction procedure. This indicated the organic manganese pool was not as large as the pool associated with poorly crystalline oxides.

Figure 22 summarizes the distribution of manganese among the various

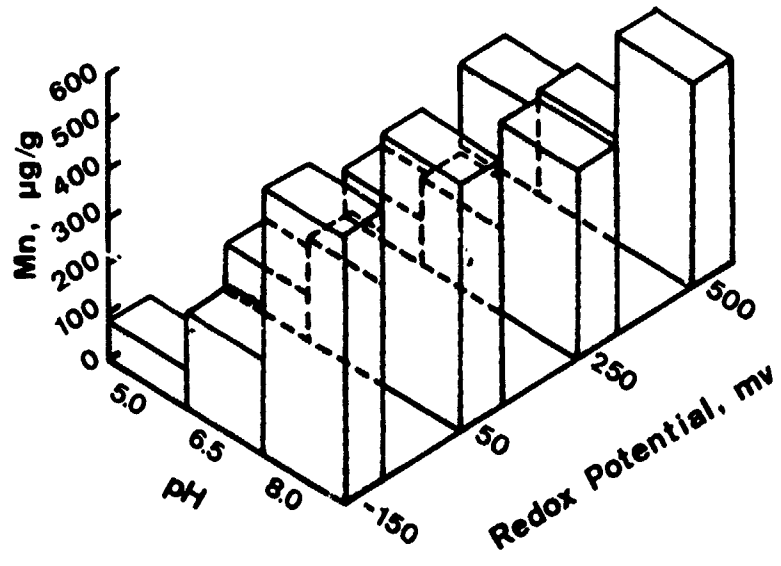


Figure 20. The Effects of pH and Redox Potential on Reducible Manganese in Mobile Bay Sediment Suspensions

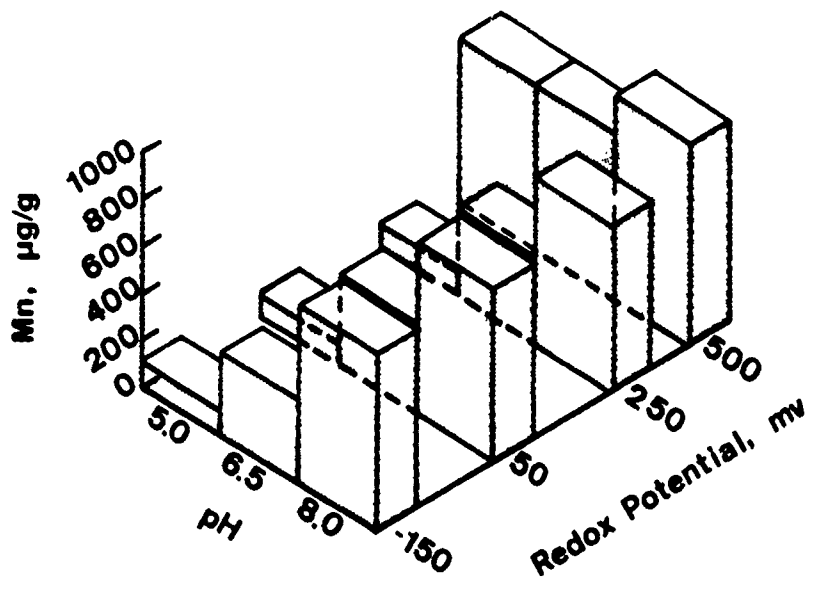


Figure 21. The Effects of pH and Redox Potential on Reducible Manganese in Mississippi River Sediment Suspensions

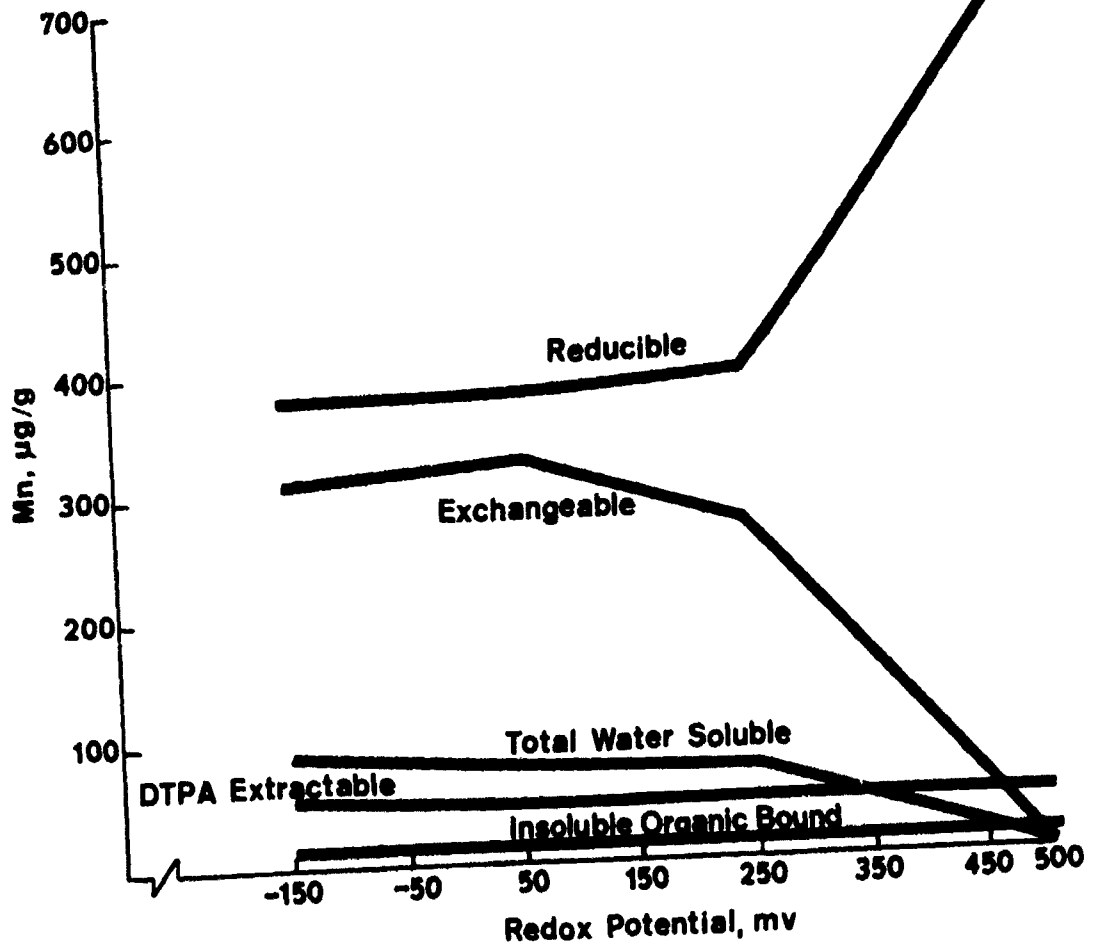


Figure 22. The Effects of Redox Potential on the Distribution of Manganese Among Selected Chemical Forms in Mississippi River Sediment Suspensions Incubated at pH 6.5 (total manganese, 950 µg/g)

chemical forms studied in the Mississippi River sediment material incubated at pH 6.5. Much of the manganese was found in the water-soluble and exchangeable forms under reducing and moderately oxidizing conditions. However, as the redox potential increased from 250 to 500 mv, there was a sharp decline in these manganese forms accompanied by an increase in reducible manganese. Upon oxidation, much of the easily mobilized manganese in the reduced Mississippi River sediment material appeared to transform to oxidized manganese compounds. These oxides of manganese may be important in regulating the release of trace and toxic metals from disturbed sediments. The reduction in the readily bioavailable forms as pH increased was also accompanied by an increase in reducible manganese. At pH 8.0, considerably less reduced manganese was available in the water-soluble and exchangeable forms for oxidation as the redox potential increased above 250 mv. Though quantitative differences in manganese recovery were apparent between the sediments studied, the nature of the response of manganese to changes in pH and redox potential were similar for all of the materials.

Zinc

The total zinc in the four sediment materials studied is indicated in Table 11. Also presented in this table is the sum of the zinc extracted by the chemical fractionation procedure applied to each sediment material at the pH-redox potential combination giving the highest zinc recovery (Appendix D). The total sediment zinc content ranged from around 200 $\mu\text{g/g}$ solids for the Mobile Bay material to around 100 $\mu\text{g/g}$ solids for the

Table 11

Total Zinc and Proportion Recovered in Potentially
Active Chemical Forms by the Fractionation Procedure
Applied to Each Sediment Material

Sediment Material	Total Zinc	Potentially Reactive Zinc*
	-- $\mu\text{g Zn/g O. D. solids}$ --	-- % of total --
Barataria Bay	78	85
Mobile Bay	205	64
Mississippi River	113	41
Calcasieu River	93	39

*Sum of zinc extracted by the sequential chemical fractionation procedure from the pH-redox potential treatment yielding largest zinc recovery.

remaining three sediments. The proportion of the total zinc recovered by the sequential chemical fractionation procedure was also variable, ranging from around 40 to 85 percent. This wide recovery range indicates a measure of total zinc may not correlate well with the chemically active zinc in these sediment materials. Presumably, much of the remaining zinc is in other chemical combinations which are relatively unavailable or associated with minerals as a primary constituent. There appeared to be no simple relationship between total zinc or potentially reactive zinc and sediment physical and chemical characteristics.

The influence of pH and redox potential on total water-soluble zinc

is indicated in Figures 23 and 24 for the Mobile Bay and Mississippi River sediment materials, respectively. The soluble zinc in the Barataria Bay and Calcasieu River sediment suspensions responded similarly to changes in pH and oxidation-reduction intensities. It is apparent from these figures that pH has a large influence on soluble zinc. The highest levels were recovered at pH 5.0 with water-soluble zinc decreasing as pH increased. At pH 8.0, traces of water-soluble zinc ($<5.0 \mu\text{g/g}$) were detected by flame atomic absorption only in the Calcasieu River sediment material (Appendix D). No soluble zinc was detected at pH 8.0 in any other sediment material.

The reduction in soluble zinc to undetectable levels at pH 8.0 is likely a result of zinc carbonate formation. Where dissolved carbon dioxide is present, zinc is reported to precipitate as the sparingly soluble carbonate as pH is increased between 7 and 8.⁵⁴

Water-soluble zinc in the sediment materials studied was present in a free cationic state rather than complexed with soluble organic material (Appendix D). In three sediment materials, no zinc complexed with soluble organic material was detected by flame atomic absorption at any pH-redox potential combination studied. In the Calcasieu River material incubated at pH 6.5, a small proportion (≈ 10 percent) of the total water-soluble zinc was present in a complexed form.

Exchangeable zinc levels exhibited the same response to controlled pH and redox potential as did soluble zinc. In general, the levels

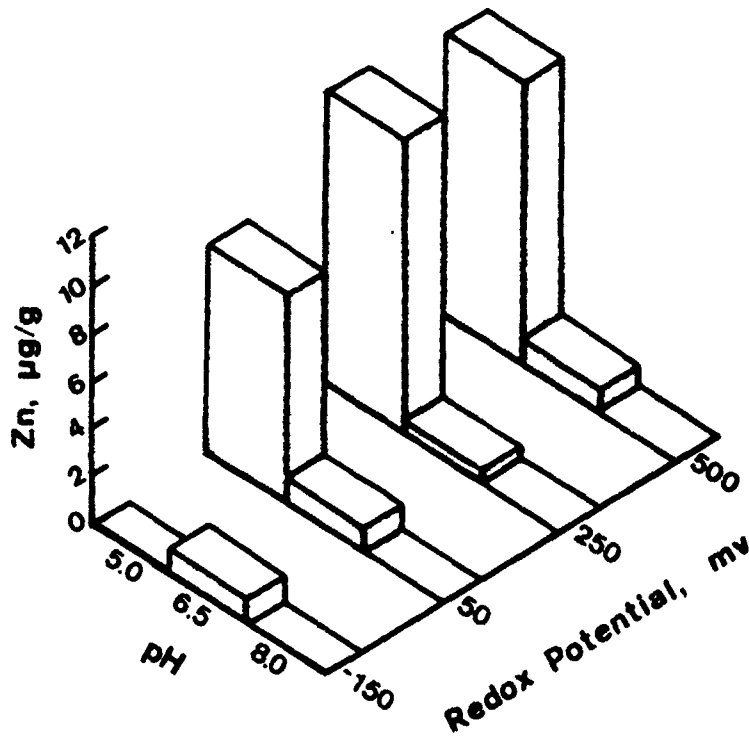


Figure 23. The Effects of pH and Redox Potential on Total Water-Soluble Zinc in Mobile Bay Sediment Suspensions

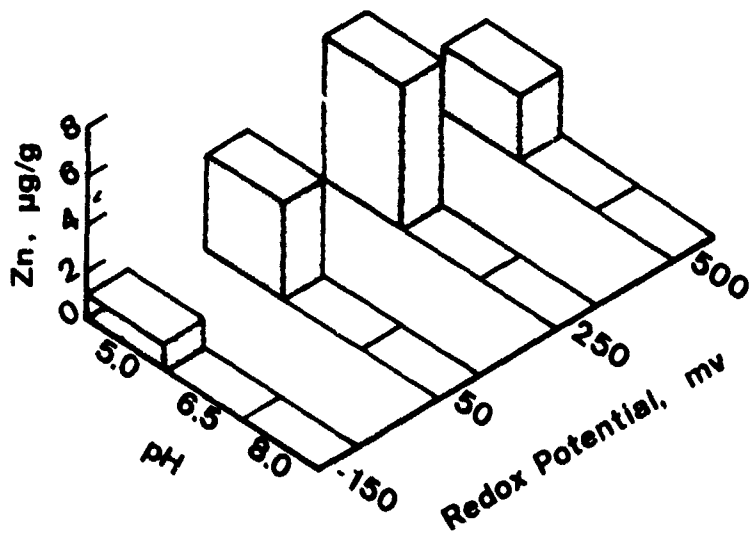


Figure 24. The Effects of pH and Redox Potential on Total Water-Soluble Zinc in Mississippi River Sediment Suspensions

recovered ranged from about the same to about twice that of the soluble fraction (Figures 25 and 26).

In reduced sediment-water systems containing sulfide, the formation of zinc sulfide is expected to limit the concentration of soluble zinc. In the absence of sulfide, a low pH-redox potential environment is known to favor increased zinc solubility. The results obtained with the incubated suspensions are somewhat inconclusive regarding the sulfide regulation of soluble zinc in these sediment materials.

In the Mobile Bay sediment suspension, considerable sulfide was measured at -150 mv at all pH levels, and no sulfide was detected at higher redox potentials. Except for the pH-6.5, -150-mv treatment where zinc contamination in one subsample was thought to elevate soluble zinc levels, very little zinc was extracted in the soluble and exchangeable fractions at -150 mv redox potential relative to the more oxidized treatments. The formation of zinc sulfide in this strongly reducing environment was thought to be contributing to low levels of zinc in readily bioavailable forms in this sediment material. Though the soluble zinc at pH 5.0, -150 mv is relatively low compared to more oxidized treatments, the fact that any soluble zinc was measured in sulfide-containing sediments by flame atomic absorption suggests that the formation of zinc sulfide may not be the limiting factor for zinc solubility.

The levels of soluble and exchangeable zinc in the Mississippi River sediment material at the -150-mv redox potential treatment were low relative to the more oxidized treatments; however, no sulfide was found in

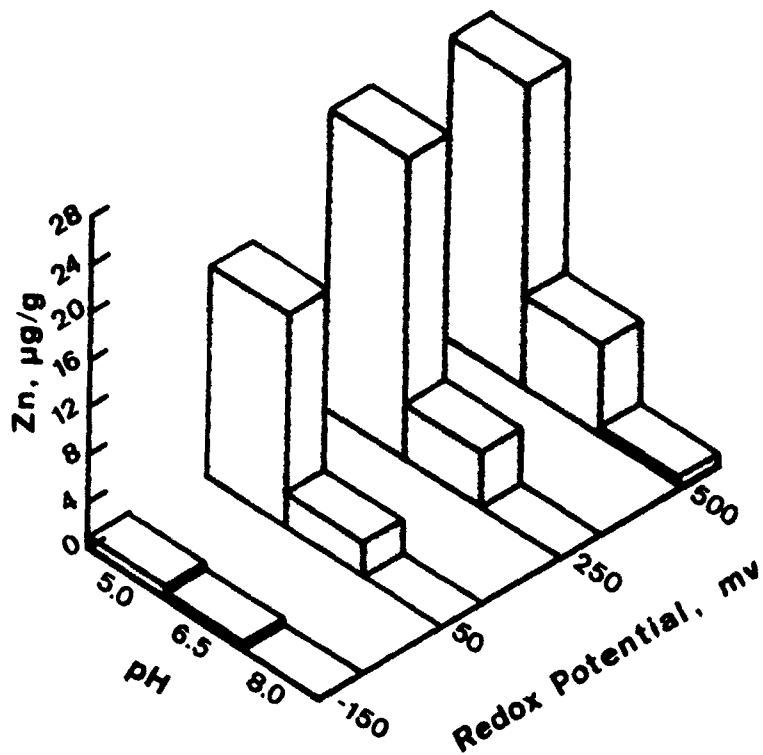


Figure 25. The Effects of pH and Redox Potential on Exchangeable Zinc in Mobile Bay Sediment Suspensions

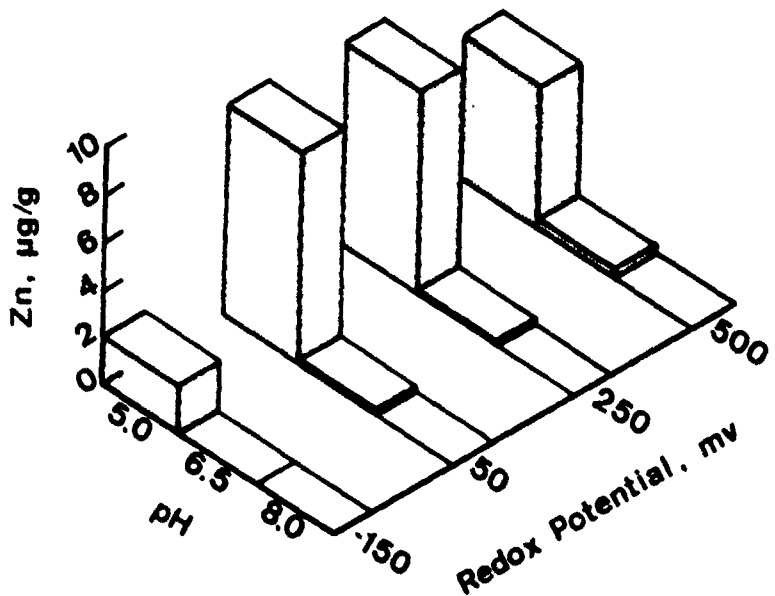


Figure 26. The Effects of pH and Redox Potential on Exchangeable Zinc in Mississippi River Sediment Suspensions

these reduced suspensions. This suggests two possibilities. First, a low sulfide concentration of a few $\mu\text{g/g}$, which is beneath the sensitivity of the total sulfide analysis technique used, may have gone undetected in this sediment material and could have contributed to reduced soluble zinc levels. Or, some other regulatory factor directly or indirectly dependent on oxidation-reduction intensity could have reduced soluble zinc levels. An explanation for the reduction in soluble zinc under a reduced environment in the absence of sulfide is not apparent from redox potential-pH diagrams of zinc in simple aqueous systems.⁵⁴

Another possible mechanism of a decrease in soluble zinc under strongly reduced conditions in the absence of sulfide would be chelation of zinc by naturally occurring insoluble organics. It has been reported that organic matter degradation under anaerobic conditions differs both qualitatively and quantitatively from aerobic decomposition.^{53,55} More large molecular weight material of possible greater metal chelating capacity may be present in a reduced soil or sediment. Where DTPA and hydrogen peroxide-sodium acetate extractions were used, there was little or no difference in zinc recovery at -150 mv relative to the better oxidized treatments.

Zinc recovered in the Mobile Bay and Mississippi River reducible fraction (oxalate extractable) was greatest at -150 mv, particularly at pH 5.0 (Figures 27 and 28). This was also the case for the other sediment materials incubated at pH 5.0. Considerable quantities of iron and manganese oxides have been found in reduced soil materials.^{41,52} Reducible zinc may be associated with these hydrous oxides. Patrick and Khalid⁴⁷

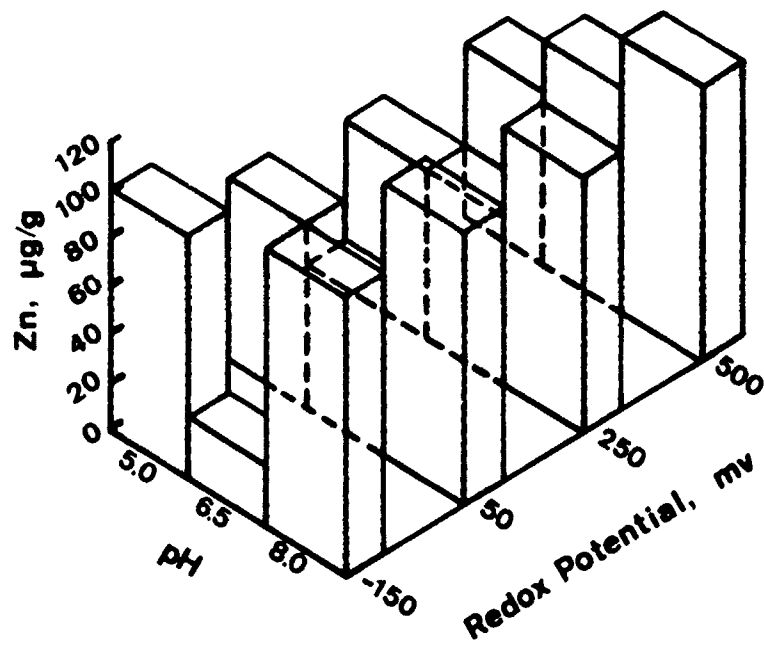


Figure 27. The Effects of pH and Redox Potential on Reducible Zinc in Mobile Bay Sediment Suspensions

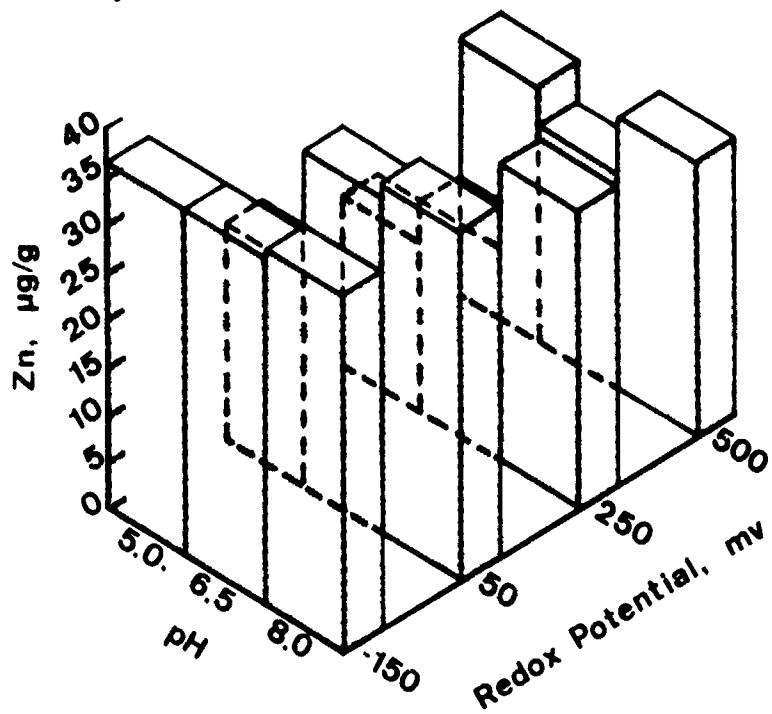


Figure 28. The Effects of pH and Redox Potential on Reducible Zinc in Mississippi River Sediment Suspensions

have demonstrated that greater quantities of poorly crystalline hydrous oxides of iron affecting phosphorus availability in flooded soils may exist under reduced rather than oxidized conditions. As previously discussed, oxalate-extractable (poorly crystalline) iron from all but the Barataria Bay material was also greatest under strongly reducing conditions. Thus the adsorption of zinc to poorly crystalline hydrous iron oxides, which may be particularly surface-active in these sediments at pH 5.0, may be contributing to the low recovery of zinc at -150 mv in the soluble and exchangeable fractions where sulfide is present, as well as in the absence of sulfide.

The soluble and exchangeable zinc in the Barataria Bay sediment suspension, which did contain considerable sulfide at -150 mv, showed somewhat similar trends to the Mississippi River material (Appendix D). However, zinc contamination may be responsible for some of the measured soluble and exchangeable zinc from the Barataria Bay sediment material. The high soluble and exchangeable zinc levels at -150 mv relative to the other sediment materials containing sulfide may have resulted from zinc adsorbed to suspended particulate matter in the supernatants of the centrifuged suspensions being decanted into storage bottles. These extractions were not filtered through a 0.45- μ membrane filter as were the supernatants from the other sediment materials studied.

The response of reducible zinc to redox potential was variable, depending on pH. At pH 5.0, the reducible zinc in all sediment materials decreased as redox potential increased above -150 mv. The association of

zinc with poorly crystalline oxides of iron under anaerobic conditions has been suggested previously as a possible contributing factor to the higher levels of zinc found in the reducible fraction and the relatively low soluble zinc in the absence of sulfide in the pH-5.0, -150-mv treatment. At pH 6.5, the pattern of reducible zinc distribution as a function of redox potential varied with sediment material. An increase in reducible zinc with oxidation was noted in the Mobile Bay material, and the opposite was found in the Mississippi River sediment material. No trends with redox potential were apparent in the other materials studied.

Figures 29 and 30 summarize the influence of redox potential on the distribution of zinc among the chemical fractions studied in the Mobile Bay and Mississippi River sediment materials incubated at pH 5.0 and 6.5, respectively. These data are representative of these pH levels in all the materials studied. Most of the zinc recovered in the chemical extraction procedure used was associated with the reducible fraction, presumably adsorbed with hydrous oxides of iron and perhaps manganese. A relatively small proportion of the recovered zinc was associated with organic materials as evidenced by the low recovery in the DTPA extractable and insoluble organic-bound fractions.

These results are similar to published work indicating that zinc correlates less well with mineralogy and organic matter than numerous other trace metals,⁵⁶ and that relative to iron, manganese, and copper in near-surface, reducing sediments, a greater proportion of zinc was recovered in the reducible phase rather than from a hydrogen peroxide-treated (oxidizable) fraction.³⁸

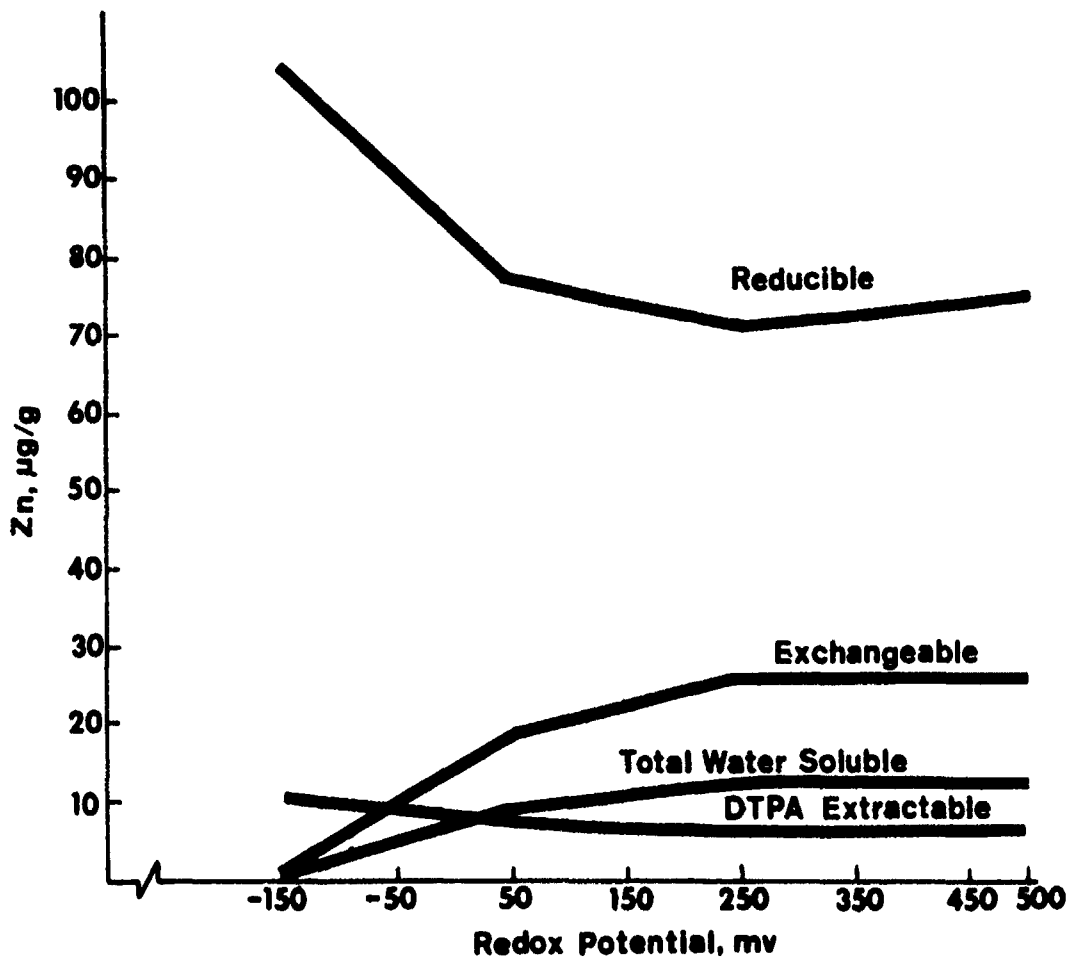


Figure 29. The Effects of Redox Potential on the Distribution of Zinc Among Selected Chemical Forms in Mobile Bay Sediment Suspensions Incubated at pH 5.0 (total zinc, 205 µg/g)

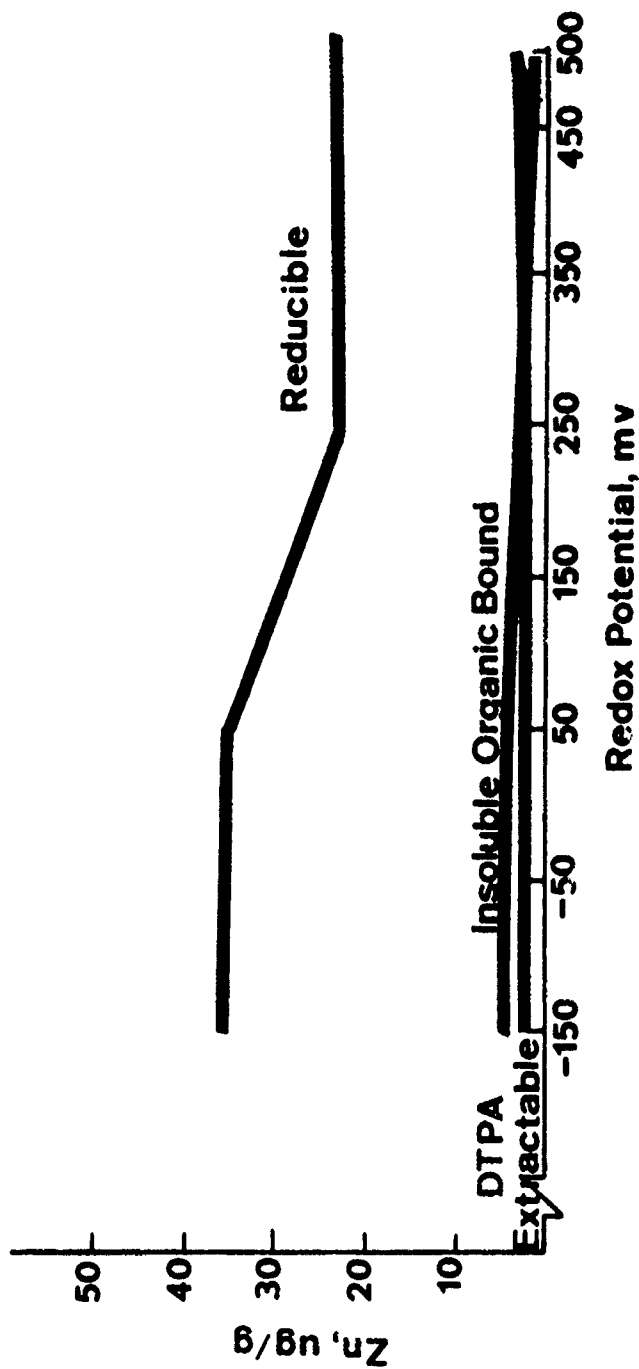


Figure 30. The Effects of Redox Potential on the Distribution of Zinc Among Selected Chemical Forms in Mississippi River Sediment Suspensions Incubated at pH 6.5 (total zinc, 113 $\mu\text{g/g}$)

Copper

The total copper content in the sediment materials studied ranged from about 14 to 21 $\mu\text{g/g}$ (Table 12). Also indicated in this table is the proportion of the total copper which was recovered in the chemical fractions studied in each sediment material (Appendix E).

Table 12

Total Copper and the Proportion Recovered in Potentially Active Chemical Forms by the Fractionation Procedure Applied to Each Sediment Material

<u>Sediment Material</u>	<u>Total Copper</u> $\mu\text{g/g}$	<u>Potentially Reactive Copper*</u> %
Barataria Bay	14.6	60
Mobile Bay	14.7	64
Mississippi River	18.2	90
Calcasieu River	21.4	64

*Sum of copper extracted by the sequential chemical fractionation procedure from the pH-redox potential treatment yielding the largest copper recovery.

The percentage recovery of copper by the fractionation procedures used indicates that more than half of the sediment-bound copper is potentially capable of transformations affecting its bioavailability.

Soluble copper was detected by flame atomic absorption only in the Mobile Bay and Mississippi River sediment materials. Figure 31 indicates the influence of pH and redox potential on soluble copper in the

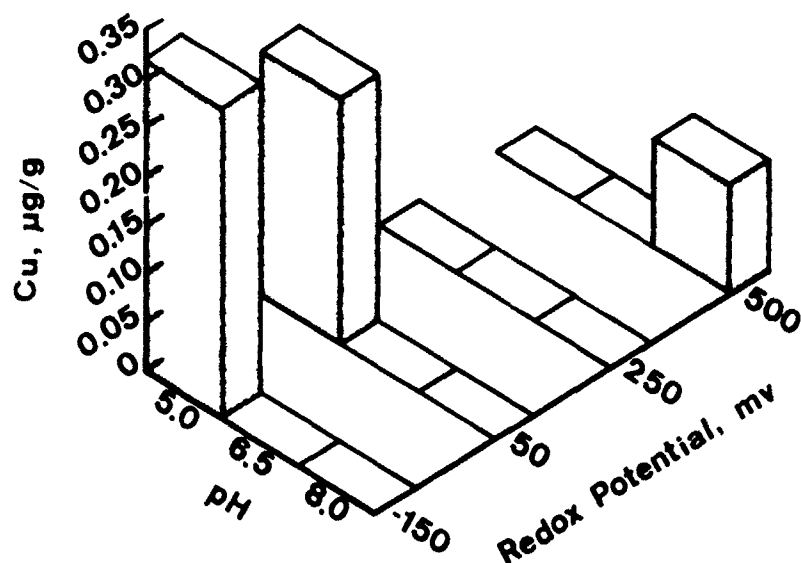


Figure 31. The Effects of pH and Redox Potential on Total Water-Soluble Cooper in Mobile Bay Sediment Suspensions

Mobile Bay sediment material. Low levels of soluble copper were detected at pH 5.0 in strongly and moderately reducing sediment suspensions. Some copper was measured at -150 mv in the presence of considerable sulfide. Copper sulfide is reported to form one of the least soluble sulfides of trace and toxic metals.³⁶ The data suggest that even in the presence of sulfide, some copper may remain uncomplexed with sulfide. At pH 5.0 there was no evidence that the measured water-soluble copper was complexed with soluble organics and thus possibly less susceptible to sulfide precipitation. At pH 8.0, under oxidizing conditions for Mobile Bay and at all levels of oxidation for the Mississippi River sediment material, a low level of soluble copper was again detected by flame atomic absorption. There was some indication that at this pH, soluble organic complexes may have contributed to the total soluble copper levels. However, at pH

8.0, the experimental error was relatively large on these measurements and the quantitative relationship between the total soluble copper and that which was not retained within a cation exchange resin column was poor.

No exchangeable copper was detected at any pH-redox potential combination in any of the sediment materials studied.

Reducible copper was little affected by sediment pH, but was much influenced by redox potential (Figures 32 and 33). Most of the copper extracted by the total sequential fractionation procedure was recovered in the reducible fraction. Unlike reducible zinc, which was greatest at -150 mv, pH 5.0 and responded little to redox potential at higher pH

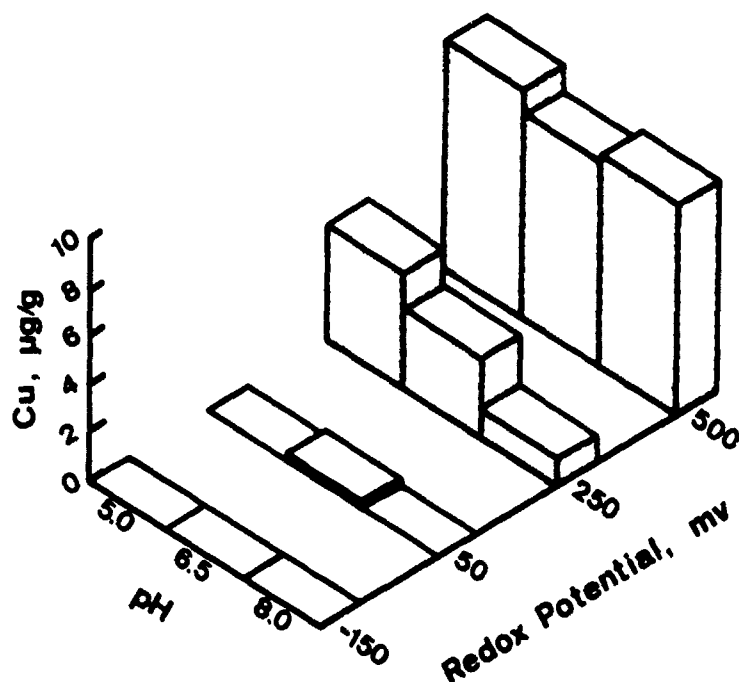


Figure 32. The Effects of pH and Redox Potential on Reducible Copper in Mobile Bay Sediment Suspensions

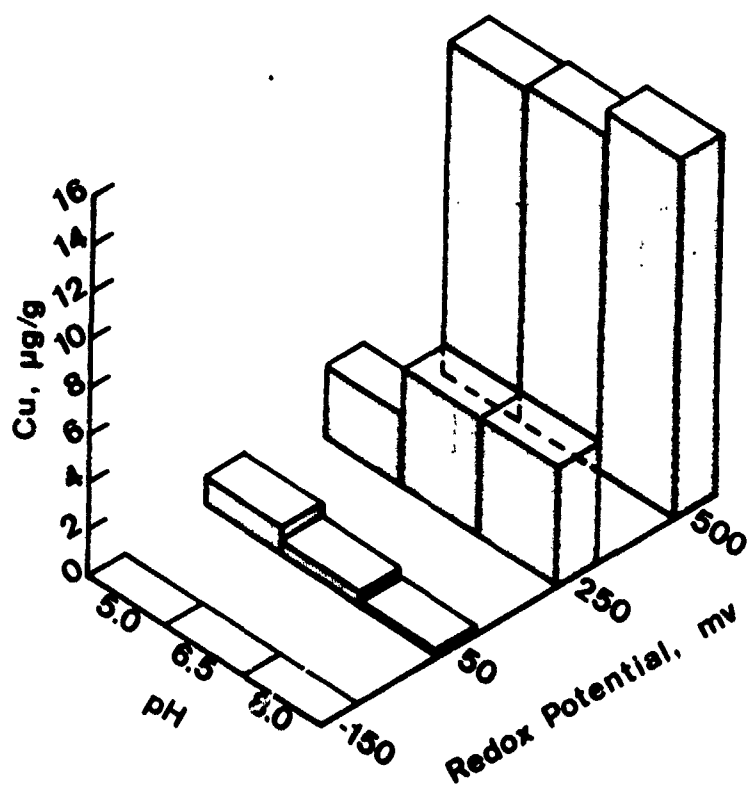


Figure 33. the Effects of pH and Redox Potential on Reducible Copper in Mississippi River Sediment Suspensions

levels, reducible copper increased with increasing redox potential at all pH levels studied. This suggested that copper may be associated

with the poorly crystalline hydrous oxides of iron and manganese under oxidizing conditions. If the copper and zinc extracted by the oxalate reagent are indeed desorbed from colloidal hydrous oxides of iron and manganese, these two elements may be associated with different forms of the hydrous oxides, which vary depending on pH and redox potential.

As previously discussed, the relative levels of reducible zinc extracted responded to changes in pH and redox potential similar to reducible iron, especially at pH 5.0. In these sediment materials, reducible copper may be more closely associated with manganese than iron. A better correlation of copper with manganese than iron has been reported for other soils and sediments.^{56,57,58} Though the response of oxalate-extractable manganese to increasing redox potential up to 250 mv was not as apparent as for copper, reducible manganese did generally increase with redox potential, especially as redox potential was increased from 250 to 500 mv.

Figure 34 summarizes the distribution of copper in the chemical forms studied in the Calcasieu River sediment material incubated at pH 8.0. The marked increase in reducible copper and the smaller increase in DTPA-extractable copper as redox potential increased was accompanied by a decrease in the insoluble organic-bound copper. These results suggest that under strongly and moderately reduced conditions, copper may be predominately associated with sediment organics. However, in an oxidized environment, the stability of the copper-organic complex may be

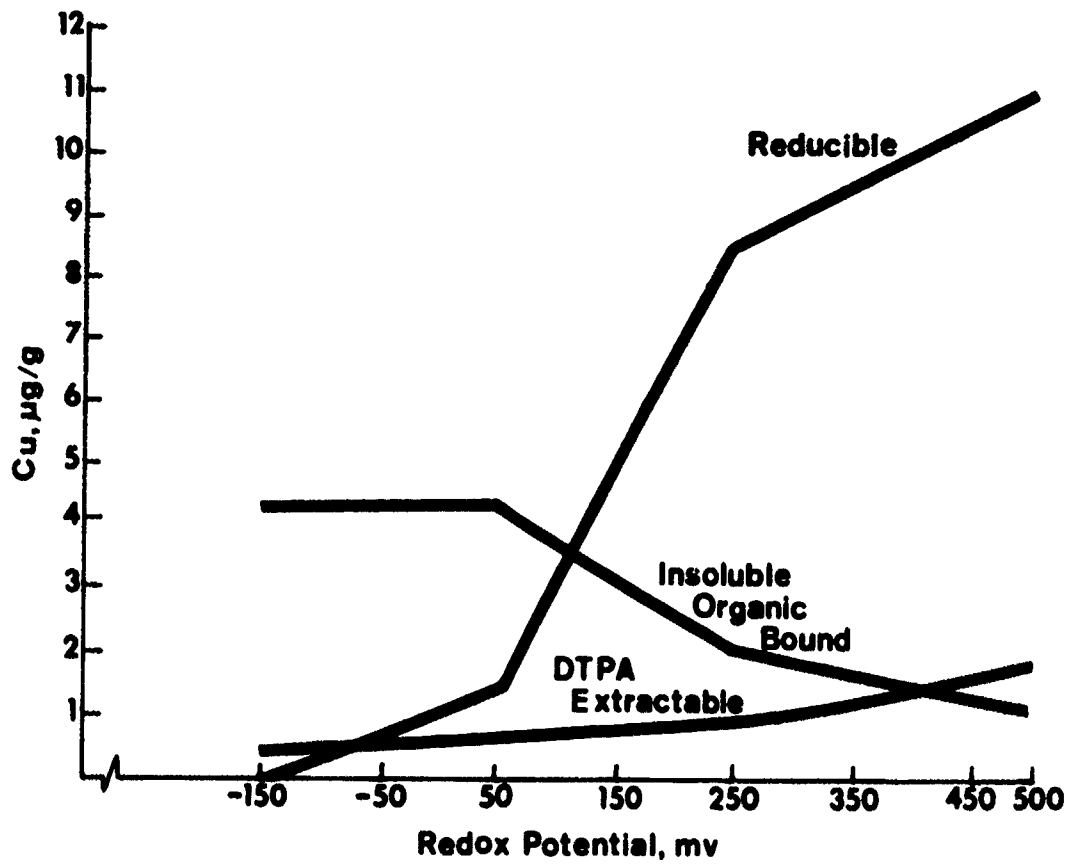


Figure 34. The Effects of Redox Potential on the Distribution of Copper Among Selected Chemical Forms in Calcasieu River Sediment Suspensions Incubated at pH 8.0 (total copper, 21.4 µg/g)

reduced, and adsorption to colloidal hydrous oxides of iron and manganese may be the primary regulatory factor for copper. Total copper recovery was not equal at all redox potentials; this suggests that either some copper was present in forms not susceptible to the fractionation procedures used or that during the course of a sequential fractionation, some copper mobilized by one extractant was immobilized again, perhaps in a form previously extracted. It is likely that some of the insoluble organic-bound copper mobilized during digestion with hydrogen peroxide may have been reabsorbed by colloidal hydrous oxides of iron and manganese likely formed during this intense oxidation procedure.

Mercury

The total mercury content of the sediment materials studied is indicated in Table 13.

Table 13
Total Sediment Mercury Content

Sediment Material	Total Mercury
	--µg Hg/kg solids--
Barataria Bay	18
Mobile Bay	95
Mississippi River	2
Calcasieu River	285

The comparatively low mercury level of the Barataria Bay sediment material likely reflects a small input of mercury into this waterway from cultural activities. The other three waterways are thought to have received considerably more mercury input from industrial and municipal waste discharges. The greater mercury levels of the Mobile Bay and Calcasieu River sediment material relative to the Mississippi River sediment sample may be attributed to a greater mercury retention capacity for these sediments. Both the Mobile Bay and Calcasieu River sediments exhibited a greater cation exchange capacity and clay and organic carbon content than did the Mississippi River sediment. A higher organic content could contribute to increased retention of mercury entering these waterways. Also, the strongly reduced Mobile Bay and Calcasieu River sediments contained considerable sulfide whereas sulfide was not detected in the Mississippi River sediment material. As a consequence of the extremely low solubility of mercuric sulfide, it is likely that the sulfide-bearing sediments served as a much more effective sink for mercury discharged into surface waters than the Mississippi River sediment sampled.

The influence of pH and redox potential on the chemical form and distribution of mercury in all sediment materials was studied using radio-tracer techniques (Appendix F). In addition, measurements of indigenous mercury levels were attempted (Appendix G). However, in spite of the sensitivity of the cold vapor atomic absorption procedure for mercury analysis,

the quantities of mercury in the approximately 50 ml of solution available for analysis were generally too low for satisfactory analysis in the chemical extracts studied.

No mercury analysis was attempted on the Barataria Bay sediment suspension extracts due to the low mercury content of this sediment. Because of the very low total mercury content of the Mississippi River sediment, an addition of 2.4 μg Hg/g solids was made, hopefully to increase the mercury content of the various chemical extractions to measurable levels.

Most of the mercury added to the Mississippi River sediment material, as well as the indigenous mercury in the Mobile Bay and Calcasieu River materials, was partitioned in forms not susceptible to the chemical extractants used. Where low mercury levels approaching the minimum detectable limits were recovered by the chemical fractionation procedure, there was generally a poor correlation between the effect of pH and redox potential on the distribution of the added mercury radioisotope and mercury levels determined by atomic absorption.

More mercury was generally extracted in the DTPA fraction than was found in the other chemical forms, and the distribution of mercury in this form was very similar to the distribution of the mercury isotope. The improved similarity in distribution of the two forms of mercury where greater quantities were extracted is likely due to less experimental error associated with analysis of the higher mercury levels.

Due to the inability of the atomic absorption technique to accurately measure the low levels extracted, the following discussion on the influence of pH and redox potential on the chemical distribution of mercury in these sediment materials will be based primarily on the radiotracer techniques used.

Chemical and microbial transformations of mercury in the range of pH-redox potential levels typically encountered in sediment-water systems may result in the formation of some elemental mercury (Hg^0). Elemental mercury is relatively volatile. However, significant quantities of mercury were not volatilized during incubation of these sediment suspensions. Quantitative recovery of the mercury initially added to the Mississippi River sediment suspensions at the time of chemical fractionation indicated little volatile losses of mercury. In addition, no significant ^{203}Hg activity was found in potassium permanganate-sulfuric acid mercury traps connected to the incubation vessel's gas outlet tube.

Figures 35 and 36 indicate the influence of pH and redox potential on the recovery of added ^{203}Hg in the total water-soluble and the soluble organic-bound fractions, respectively, from the Mobile Bay sediment suspension. Figures 37 and 38 represent these same fractions from the Mississippi River suspension, and Figures 39 and 40 indicate these results for the Calcasieu River sediment material. There is evidence that the enhanced activity of mercury in the total water-soluble fraction

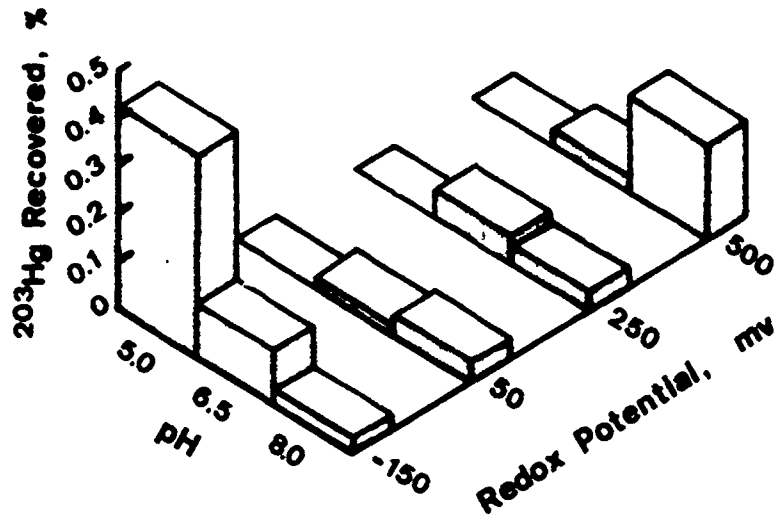


Figure 35. The Effects of pH and Redox Potential on Total Water-Soluble ^{203}Hg in Mobile Bay Sediment Suspensions

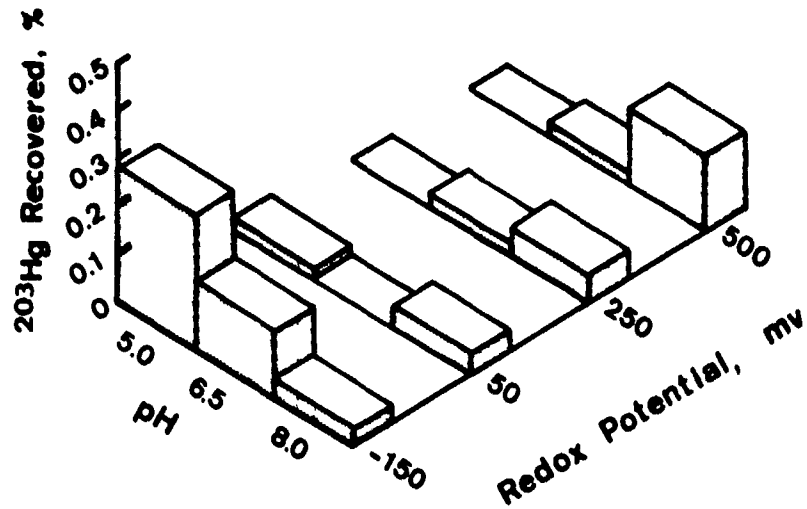


Figure 36. The Effects of pH and Redox Potential on Soluble Organic-Bound ^{203}Hg in Mobile Bay Sediment Suspensions

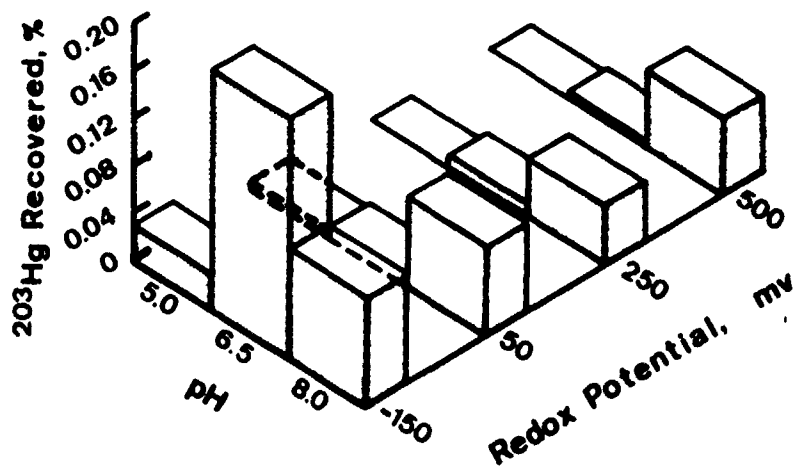


Figure 37. The Effects of pH and Redox Potential on Total Water-Soluble ^{203}Hg in Mississippi River Sediment

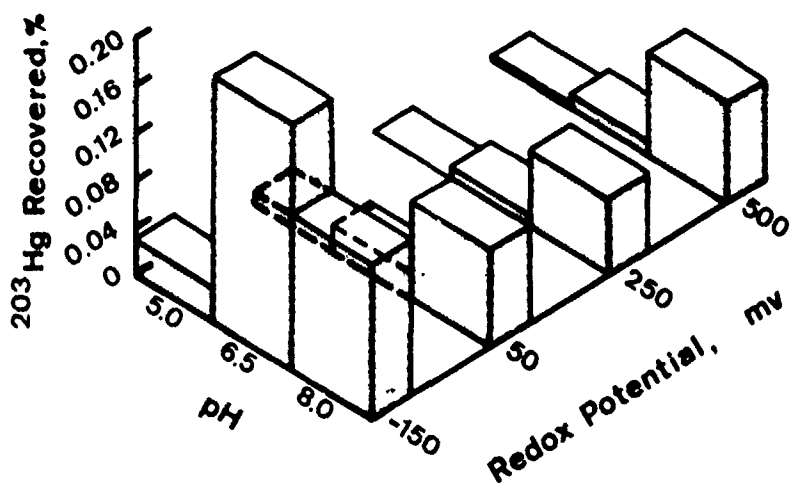


Figure 38. The Effects of pH and Redox Potential on Soluble Organic-Bound ^{203}Hg in Mississippi River Sediment Suspensions

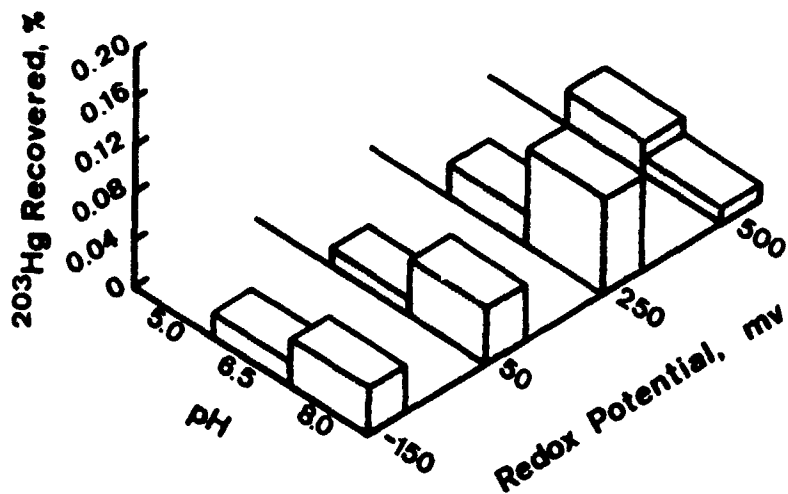


Figure 39. The Effects of pH and Redox Potential on Total Water-Soluble ^{203}Hg in Calcasieu River Sediment Suspensions

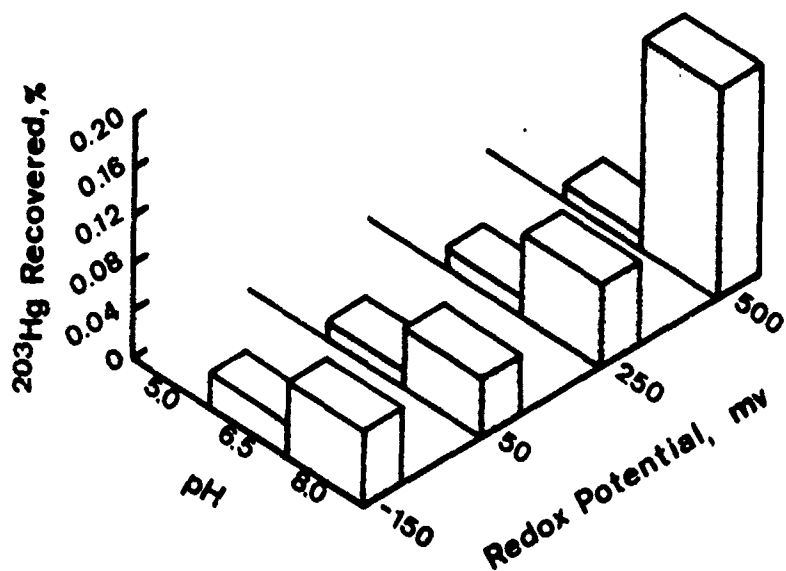


Figure 40. The Effects of pH and Redox Potential on Soluble Organic-Bound ^{203}Hg in Calcasieu River Sediment Suspensions

under reduced acid and oxidized alkaline environments was due to the formation of inorganic nonionic or negatively charged mercury complexes, as indicated by Hem,⁵⁹ or by complexation with soluble organic materials as suggested by Lindberg and Harriss.³⁷

In no case for any of the sediment materials was ²⁰³Hg recovery in the total water-soluble fraction greater than 0.5 percent. Under most pH-redox potential combinations, recovery was less than 0.1 percent. There was little evidence for a general pH effect in any sediment material except that slightly more mercury may have been solubilized at pH 8.0 than at other pH levels studied in the Mississippi River and Calcasieu River materials. However, at certain pH-redox potential combinations, there was an apparent enhancement of ²⁰³Hg activity in the total water-soluble fractions relative to levels in adjacent pH-redox potential treatments in all but the Barataria Bay material. Generally, this occurred under strongly reducing conditions (-150 mv) at pH 5.0 and 6.5 and in the well-oxidized treatment at pH 8.0 (as indicated for Mobile Bay in Figure 35).

The Mississippi River results indicated slightly increased soluble mercury concentrations at pH 5.0, -150 mv and considerable enhancement of ²⁰³Hg recovery at pH 6.5, -150 mv. The activity of ²⁰³Hg was notably greater in the pH 8.0, 500 mv water-soluble Calcasieu River material. The greater mercury solubility under strongly reducing conditions for the Mobile Bay material, which contains considerable total sulfide, indicates

sulfide precipitation of mercury is not regulating mercury solubility as would be predicted from the very low solubility of mercury sulfide. Where dissolved mercury has been reported to exceed the solubility of its sulfide in interstitial waters of reduced sediments, the presence of mercury as a relatively soluble polysulfide or as a soluble mercury-organic complex has been suggested.³⁷ Hem⁵⁹ suggested that under mildly reducing conditions, mercury solubility can be reduced to extremely low levels due to the precipitation of mercury as a sulfide. However, it was suggested that further reduction may increase the solubility of mercury somewhat by reducing the precipitated mercury to the free metal.

A noticeable increase in ^{203}Hg recovery under well-oxidizing conditions at pH 8.0 occurred in both the Mobile Bay and Calcasieu River sediment materials. Hem presented a pH-redox potential diagram indicating the stability of aqueous mercury species in a simple inorganic system containing chloride and sulfur. A redox potential of 500 mv at pH 8.0 is shown to be more within the indicated stability field for the uncharged mercuric hydroxide $[\text{Hg}(\text{OH})_2^0]$ species than any other pH-redox potential included in this study. This compound was reported to be a relatively soluble form of mercury.

However, Hem acknowledges the limitations of theoretical evaluations for describing the important factors regulating mercury solubility in natural systems, especially regarding the exclusion of organic complexes in such models. Thus the apparent increased solubility of mercury in a

strongly reduced environment and in a well-oxidized sediment suspension at pH 8.0 is poorly understood, but may be due to the formation of relatively soluble complexes with sulfur or organics or as a hydroxide under alkaline conditions.

The influence of pH and redox potential on exchangeable mercury was very similar to that found for the total water-soluble fraction (Figures 41, 42, and 43). There was an apparent pH-related increase in exchangeable mercury only in the Mississippi River sediment material at pH 8.0.

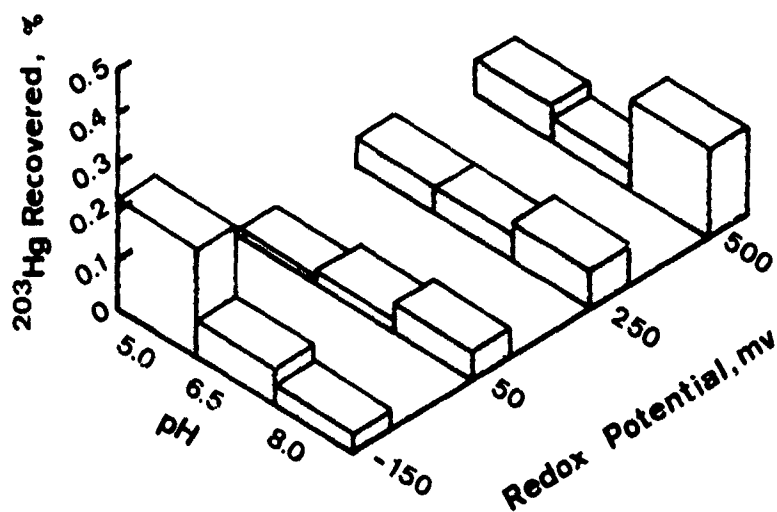


Figure 41. The Effects of pH and Redox Potential on Exchangeable ^{203}Hg in Mobile Bay Sediment Suspensions

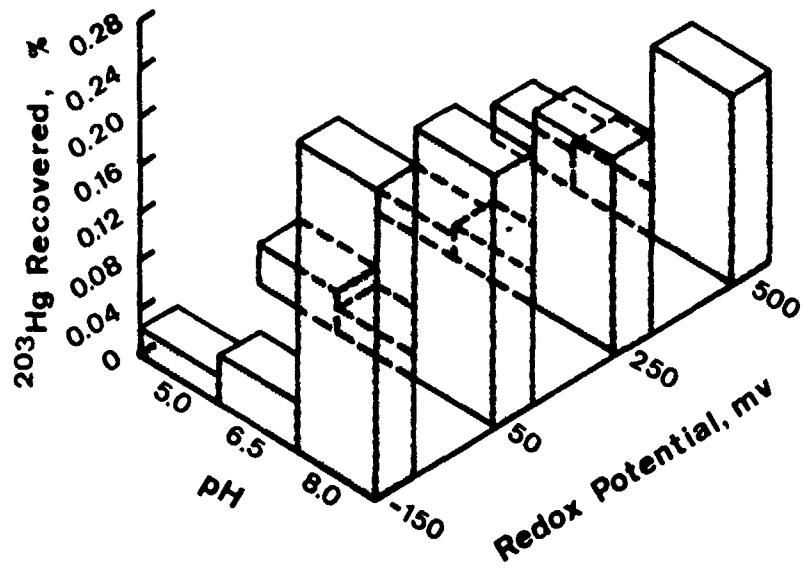


Figure 42. The Effects of pH and Redox Potential on Exchangeable ^{203}Hg in Mississippi River Sediment Suspensions

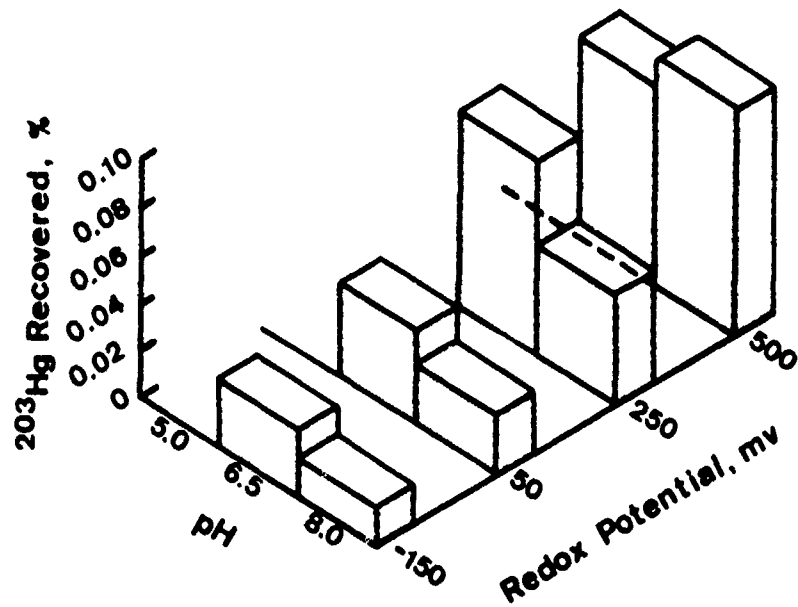


Figure 43. The Effects of pH and Redox Potential on Exchangeable ^{203}Hg in Calcasieu River Sediment Suspensions

which may be due to an interaction between certain sediment chemical properties regulating mercury availability. An increase in pH tends to increase the pH-dependent cation exchange capacity of organic matter and clay minerals, particularly the 2:1 type clay minerals, which predominated in this sediment material. Also, the smaller quantity of organic matter in the Mississippi River sediment material may have complexed less mercury in a chelated form, resulting in more mercury being found in this more mobile form. The increased level of mercury in the exchangeable form at the same pH-redox potential combinations found to enhance soluble mercury results in approximately twice as much mercury being present in readily bioavailable forms as would be found from a measure of soluble mercury alone.

Oxalate-extractable (reducible) mercury recovered from these sediment materials is indicated in Figures 44, 45, and 46. There were no important influences of pH noted in this reaction. At pH 5.0 and 6.5, recovery of mercury in this fraction at -150 mv was greater than at 50 mv in all sediment materials studied. Though the magnitude of this difference was small, this greater recovery at -150 mv than at 50 mv may be related to the generally larger recovery of poorly crystalline (oxalate-extractable) iron under strongly reduced conditions.

At each pH level, reducible mercury recovered was usually greatest at the highest redox potential. This suggests a relationship between mercury and the hydrous manganese oxides extracted in this fraction.

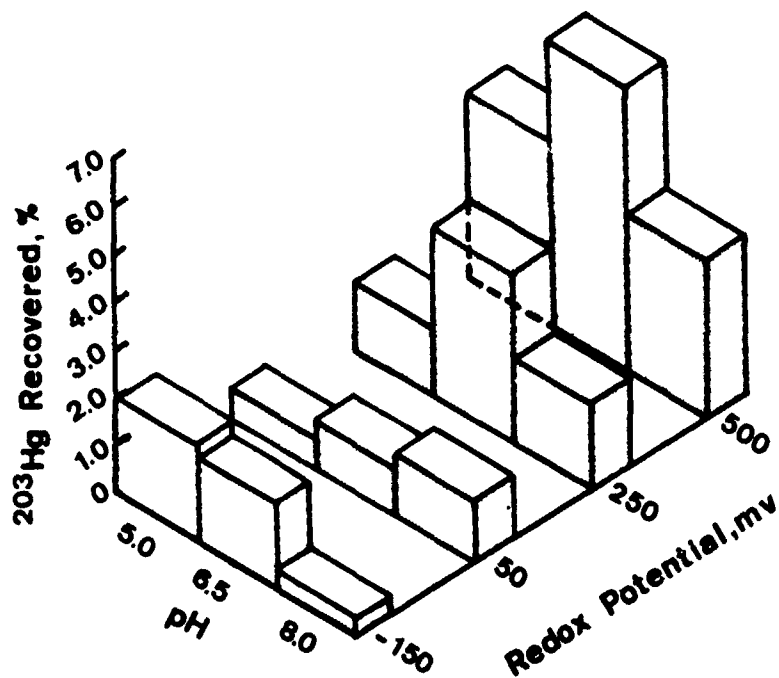


Figure 44. The Effects of pH and Redox Potential on Reducible ^{203}Hg in Mobile Bay Sediment Suspensions

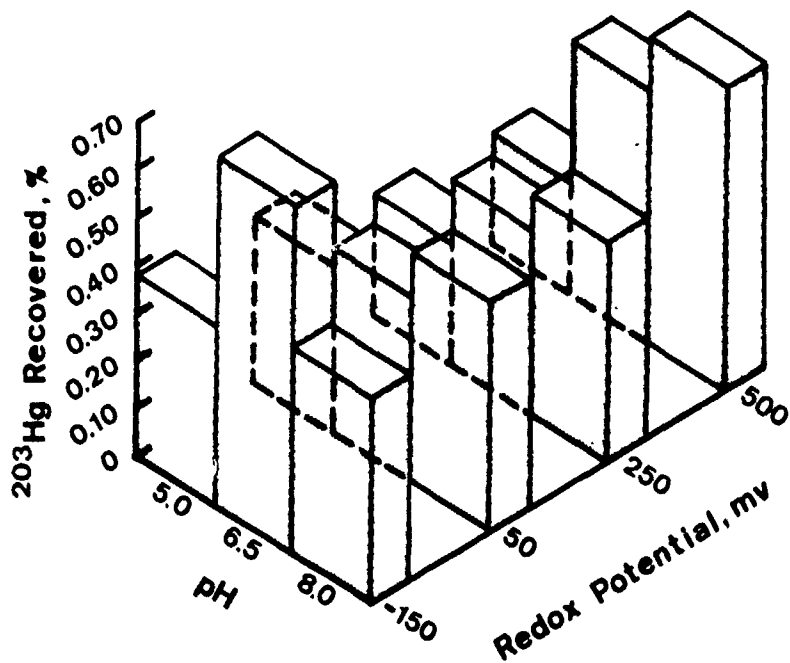


Figure 45. The Effects of pH and Redox Potential on Reducible ^{203}Hg in Mississippi River Sediment Suspensions

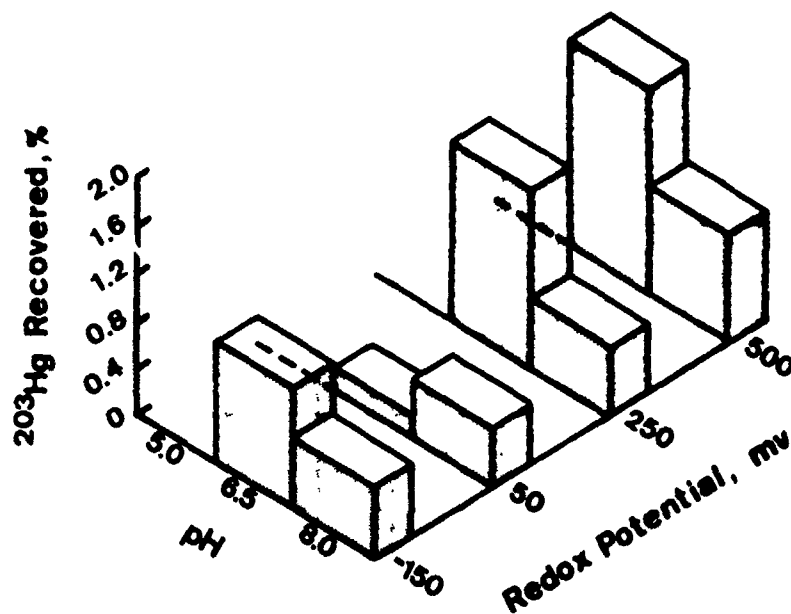


Figure 46. The Effects of pH and Redox Potential on Reducible ^{203}Hg in Calcasieu River Sediment Suspensions

A sodium dithionite-sodium citrate extraction of the Barataria Bay sediment material resulted in approximately a 10-fold increase (1 to 5 percent recovery of added ^{203}Hg) in mercury extracted over the oxalate extraction. This reagent is believed to solubilize elements associated with better crystalline hydrous oxides. As found with the oxalate extraction in the Barataria Bay sediment suspension, there was little influence of pH and redox potential on this form of mercury.

Figures 47, 48, and 49 indicate the influence of pH and redox potential on the recovery of added ^{203}Hg by a DTPA extraction of the Mobile Bay, Mississippi River, and Calcasieu River sediment suspensions respectively. The mercury recovery by this reagent was generally greater

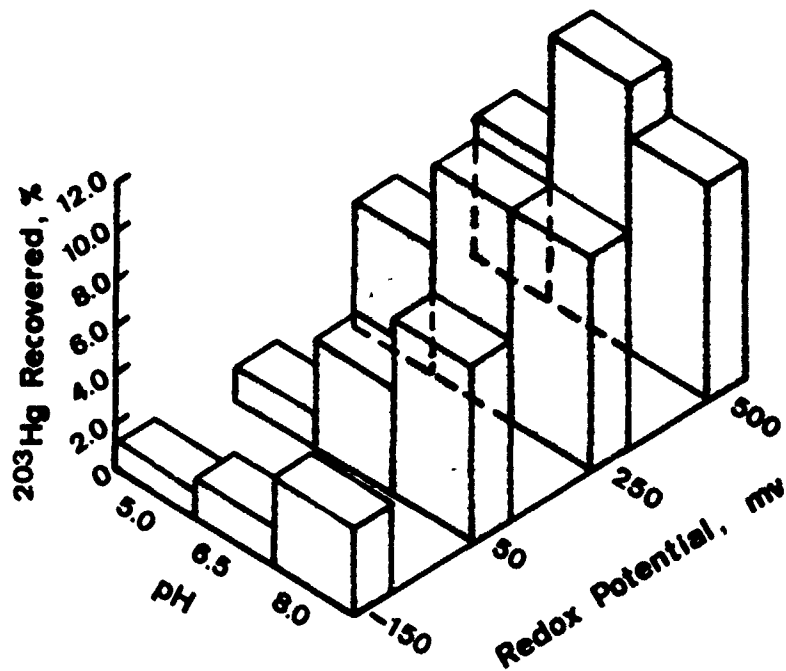


Figure 47. The Effects of pH and Redox Potential on DTPA-Extractable ^{203}Hg in Mobile Bay Sediment Suspensions

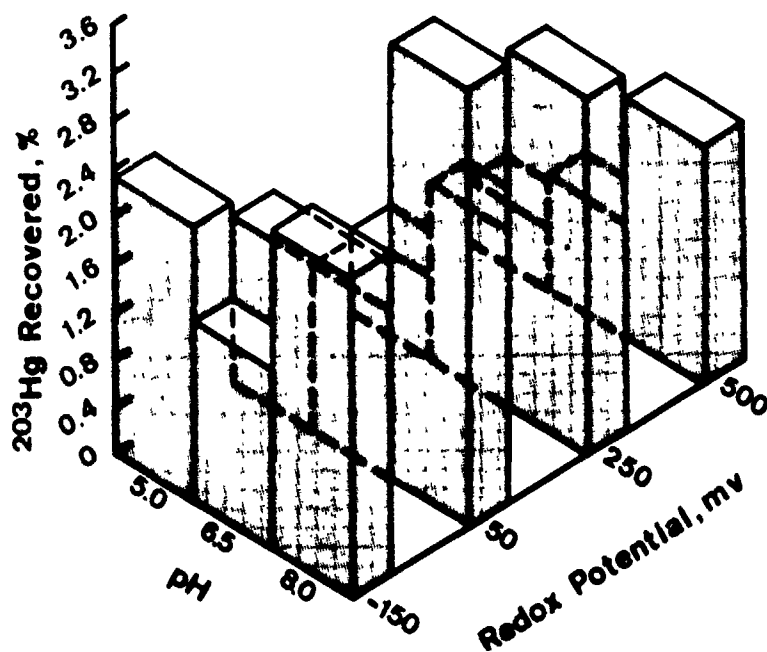


Figure 48. The Effects of pH and Redox Potential on DTPA-Extractable ^{203}Hg in Mississippi River Sediment Suspensions

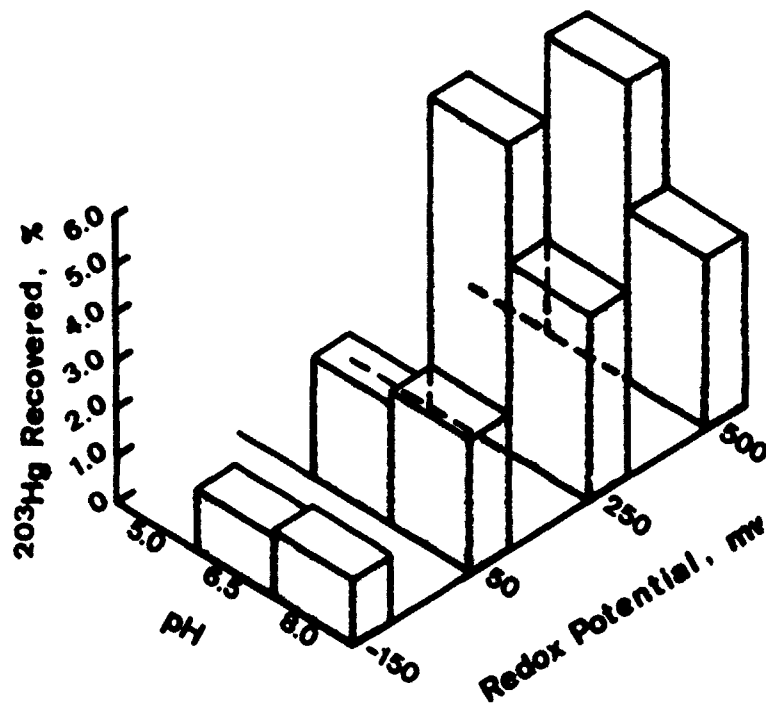


Figure 49. The Effects of pH and Redox Potential on DTPA-Extractable ^{203}Hg in Calcasieu River Sediment Suspensions

than for all other chemical forms studied and was within the range of accurate determination by the cold vapor atomic absorption technique. As a consequence, there was generally good agreement between the influence of pH and redox potential on the distribution of DTPA-extractable mercury using atomic absorption and radiotracer methods.

The greater recovery of mercury in this fraction indicates that complexation of mercury with organics is an important regulatory factor for mercury in sediments.

There was no apparent effect of pH on DTPA-extractable mercury, and no consistent influence of redox potential found on this form of mercury in the Mississippi River sediment material. However, in the Mobile Bay and Calcasieu River sediment suspensions, which contained considerably

more organic matter, DTPA-extractable mercury increased with an increase in redox potential. This may reflect a weakening of the bond between naturally occurring organics and mercury as the organic material is subjected to an oxidizing environment. A decrease in mercury-organic complex stability as a reduced sediment is oxidized has been suggested elsewhere.⁶⁰

Figures 50 and 51 indicate the influence of redox potential on the distribution of ^{203}Hg within the chemical forms studied for the Mississippi River and Mobile Bay sediment suspensions incubated at pH 6.5 and 8.0, respectively. The influence of pH and redox potential on mercury in these fractions has been discussed above; however, this figure indicates the relative quantities of ^{203}Hg associated with each fraction and the proportion unrecovered by the sequential chemical fractionation procedure employed. Unlike iron and manganese, of which a considerable proportion of the total levels were recovered in the readily bioavailable forms (soluble and exchangeable) under acid reduced conditions, less than 0.5 to 1 percent of the added ^{203}Hg was retained in readily bioavailable forms. Under aerobic conditions, reducible ^{203}Hg generally accounted for less than 5 percent of the total recovery, whereas well over half of the iron, manganese, copper, and zinc was associated with the reducible fraction at a high redox potential. The greatest recovery of added ^{203}Hg occurred in the DTPA-extractable fraction, which indicates the strong association of mercury with organics. The total ^{203}Hg

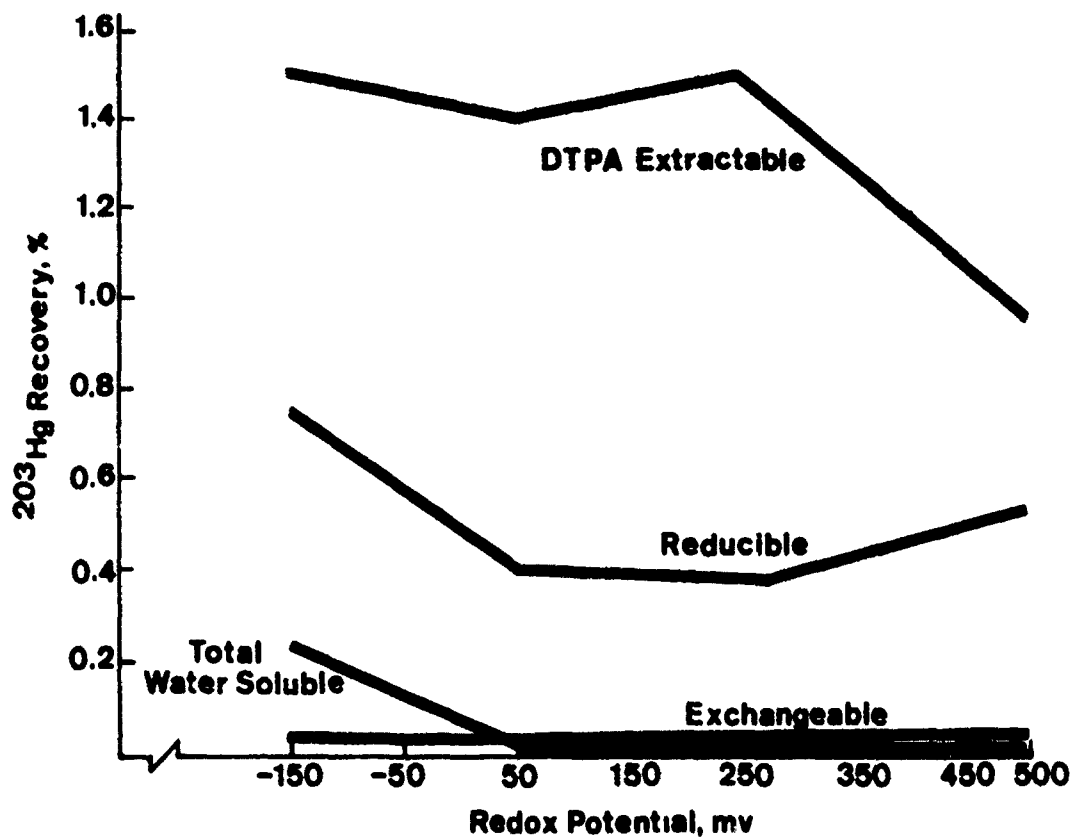


Figure 50. The Effects of Redox Potential on the Distribution of ^{203}Hg Among Selected Chemical Forms in Mississippi River Sediment Suspensions Incubated at pH 6.5

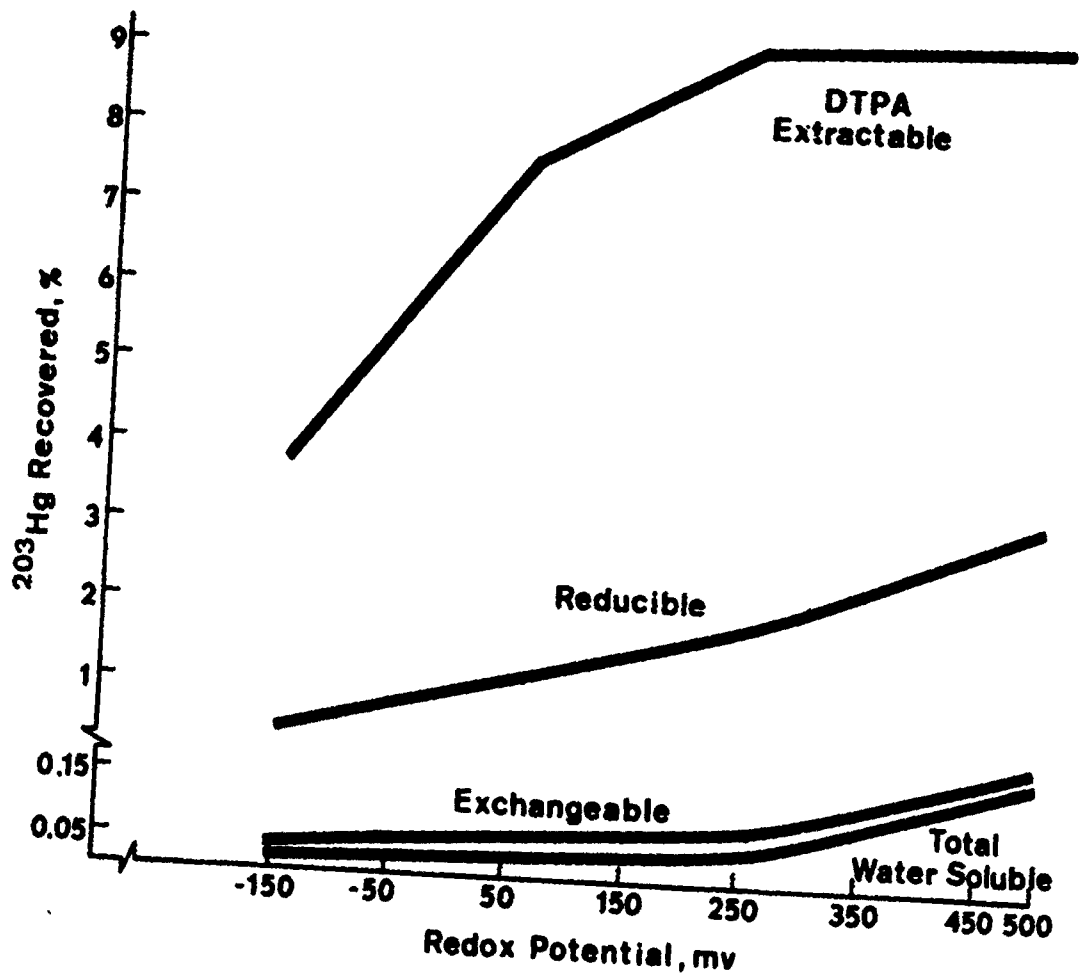


Figure 51. The Effects of Redox Potential on the Distribution of ^{203}Hg Among Selected Chemical Forms in Mobile Bay Sediment Suspensions Incubated at pH 8.0

recovered by the sequential chemical fractionation procedure accounts for only 10 to 20 percent of the ^{203}Hg added. The data indicate that most of the mercury associated with reduced as well as oxidized sediments is associated in forms which are relatively immune to moderate chemical attack.

Though slight increases of soluble and exchangeable mercury may occur in strongly reduced, acid, and well-oxidized alkaline environments, the proportion of the total mercury transformed to these readily bioavailable forms by pH-redox potential changes is a very small part of the total mercury pool.

Lead

The total lead content of the sediment materials studied ranged from 36 to 53 $\mu\text{g/g}$ (Table 14).

Table 14
Total Sediment Lead Content

Sediment Material	Total Lead
	$\mu\text{g Pb/g solids}$
Barataria Bay	37
Mobile Bay	36
Mississippi River	44
Calcasieu River	53

In this study, the influence of pH and redox potential on the levels of lead in selected chemical forms was studied using radiotracer and atomic absorption techniques. The Mobile Bay and Calcasieu River sediment suspensions were incubated with ^{210}Pb . Indigenous levels of soluble and exchangeable lead were measured in all sediment materials using the heated graphite atomic absorption technique. Sufficient lead was generally found in the remaining chemical forms studied to measure by conventional flame atomic absorption.

The added isotope of ^{210}Pb was so strongly complexed with the solid phase that it was difficult to assess the influence of pH and redox potential on soluble lead in these sediment materials. No clear trends with either parameter were apparent from the radiotracer or atomic absorption data. In strongly reduced sediments containing sulfide, the activity of ^{210}Pb and the analytically determined soluble lead levels were usually, but not always, lower than at the next higher oxidation level. Lead sulfide complex formation may be contributing to the depressed solubility of lead in strongly reduced sediments. However, the soluble lead measured from the strongly reduced suspensions was greater than expected, based on the low solubility of lead sulfide.

That lead solubility is enhanced by the formation of soluble lead-organic complexes has been reported by a number of investigators.^{16,61,62}

In this study there was some indication that the soluble ^{210}Pb was in a noncationic form in the Mobile Bay material incubated at pH 8.0

and in the Calcasieu River material incubated at pH 6.5. However, soluble ^{210}Pb recovery in all samples was too low to make definitive conclusions regarding the ionic nature of this lead.

Considerably more ^{210}Pb was found in the exchangeable form than in the soluble form, and both pH and redox potential influenced exchangeable ^{210}Pb activity (Figures 52 and 53). The activity of ^{210}Pb decreased with increasing pH, ranging from a few percent of that added in the Mobile Bay suspension incubated at pH 5.0 to essentially no ^{210}Pb recovery at pH 8.0. The Calcasieu River material, though similar in cation exchange capacity, released two or more times the ^{210}Pb activity in the exchangeable form as did the Mobile Bay material at similar pH levels. Though several factors could contribute to reduced levels of exchangeable lead as pH is increased above 5.0, thermodynamic equilibrium data of simple aqueous systems suggest that the formation of the sparingly soluble lead carbonate may occur as pH is increased. At all pH levels studied, where appreciable ^{210}Pb was recovered, maximum recovery generally occurred in the moderately reduced treatment (50 mv) with less activity found in the more reduced and more oxidizing treatments. This was generally the case with lead measured by flameless atomic absorption. The often low levels determined at -150 mv may be associated with the formation of insoluble lead sulfide. The decrease in lead usually found in the two oxidized treatments may be attributed to the well-known scavenging effect of colloidal ferromanganese oxides for lead in an oxidized environment.

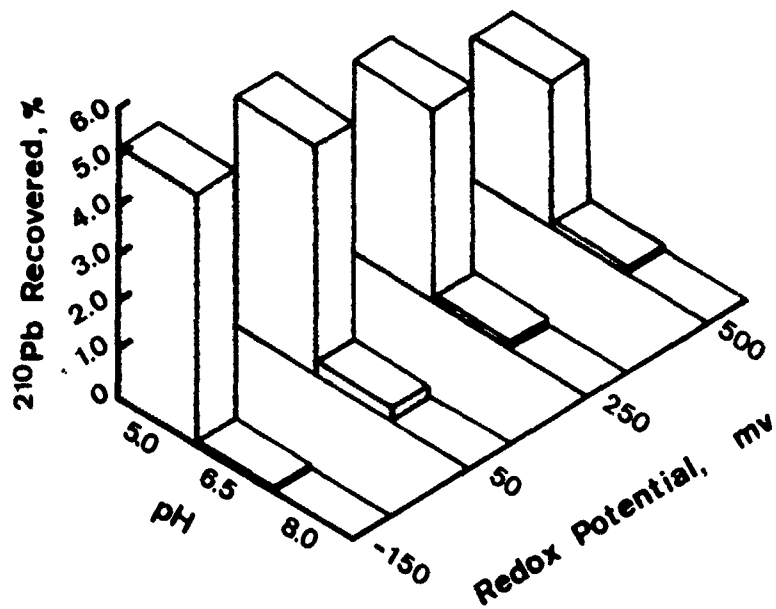


Figure 52. The Effects of pH and Redox Potential on Exchangeable ²¹⁰Pb in Mobile Bay Sediment Suspensions

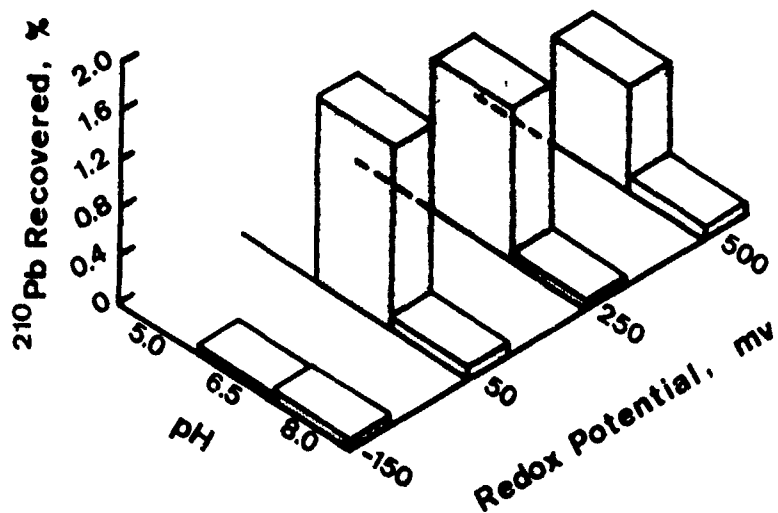


Figure 53. The Effects of pH and Redox Potential on Exchangeable ²¹⁰Pb in Calcasieu River Sediment Suspensions

A large proportion of the added ^{210}Pb was recovered in the reducible fraction, indicating that much of the chemically active lead in sediment-water systems is associated with hydrous oxides (Figures 54 and 55). There was little effect of pH on reducible lead, but the quantity of lead in this form was strongly influenced by redox potential as indicated by isotope activity and flame atomic absorption data (Appendix I). The recovery of ^{210}Pb at all pH levels in the Mobile Bay material ranged from around 25 to 30 percent under a strongly reducing environment to around 50 percent from the well-oxidized suspensions. Indigenous lead in this chemical form ranged from levels undetectable by flame atomic absorption ($2 \mu\text{g/g}$) in strongly reduced suspensions to just over $10 \mu\text{g Pb/g}$ solids at 500 mv (Appendix I). Where reducible lead was detected, redox potential was found to exert a similar influence in the remaining sediment suspensions studied.

Several reports indicate that lead may associate with the hydrous oxide phase.^{10,63} A reduction in soluble lead in dredged suspensions in Mobile Bay has also been attributed to the scavenging property of freshly precipitated ferric compounds as a reduced sediment was dispersed in oxygenated water.⁶⁴ A slight reduction in soluble lead in a dredge discharge supernatant in the Calcasieu River, Louisiana, relative to nearby surface waters may also be due to the adsorption of lead by freshly formed colloidal hydrous oxides.

Lead is reported to form very stable complexes with both synthetic

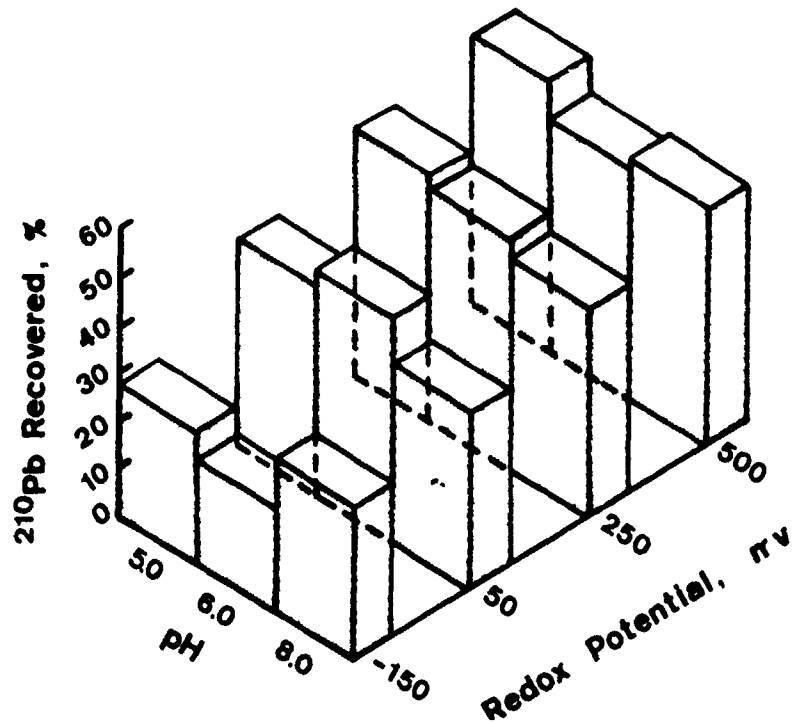


Figure 54. The Effects of pH and Redox Potential on Reducible ^{210}Pb in Mobile Bay Sediment Suspensions

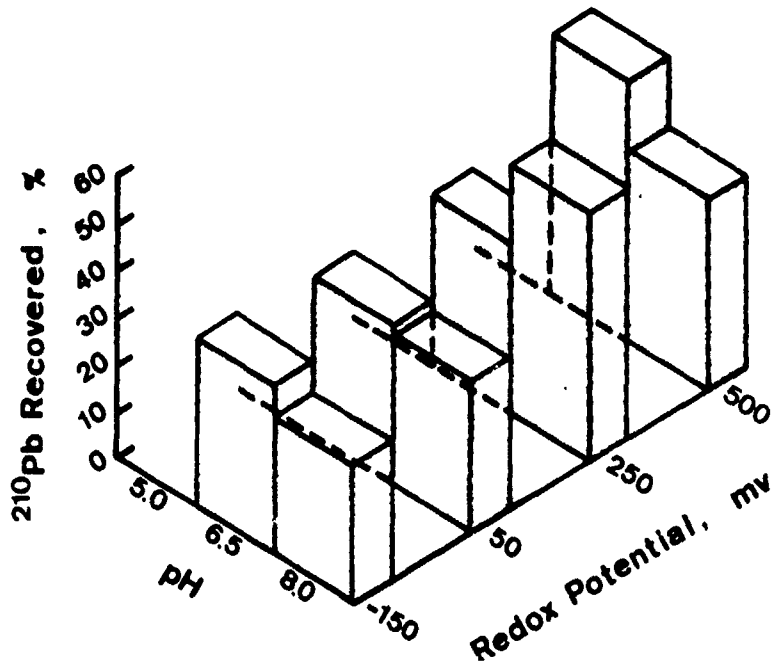


Figure 55. The Effects of pH and Redox Potential on Reducible ^{210}Pb in Calcasieu River Sediment Suspensions

organic chelates and with natural soil-derived organics,^{29,65} and the stability of the lead-soil-organic complex is pH dependent.⁶⁶ This study also indicated that complex formation with organics is an important mechanism regulating the availability of lead. The influence of pH and redox potential on the ²¹⁰Pb activity recovered in the DTPA-extractable fraction of the Mobile Bay and Calcasieu River sediment suspensions is indicated in Figures 56 and 57, respectively. Indigenous lead measured by flame atomic absorption followed very similar patterns (Appendix I). Little influence of pH was apparent on this form of lead. Strongly reduced (-150 mv) sediment suspensions released less ²¹⁰Pb and indigenous lead to the DTPA extractant than better oxidized suspensions. This indicates that the lead-organic complex may be more stable under a strongly reduced environment. This was supported by the finding that where a hydrogen peroxide digestion was included (insoluble organic bound), the quantity of indigenous lead released was always greatest from the strongly reduced treatments and decreased with increasing redox potential (Appendix I).

Figure 58 indicates the effect of redox potential on the distribution of ²¹⁰Pb in the Mobile Bay sediment material incubated at pH 6.5. Essentially none was recovered in the total water-soluble fraction. The exchangeable ²¹⁰Pb activity accounted for only a few tenths of one percent of that added at pH 6.5 (recall that at pH 5.0, the recovery of ²¹⁰Pb in the exchangeable form was 3 to 5 percent). More lead was associated with the reducible phase than with any other fraction in this sediment

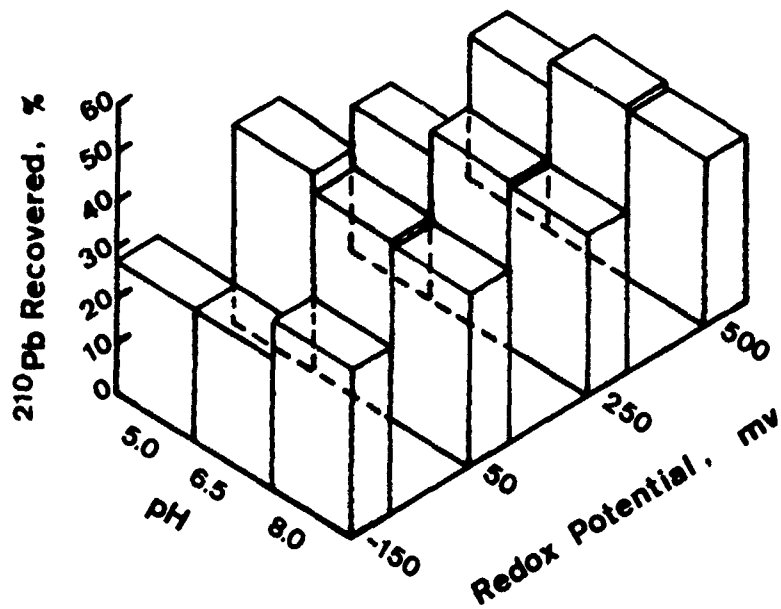


Figure 56. The Effects of pH and Redox Potential on DTPA-Extractable ^{210}Pb in Mobile Bay Sediment Suspensions

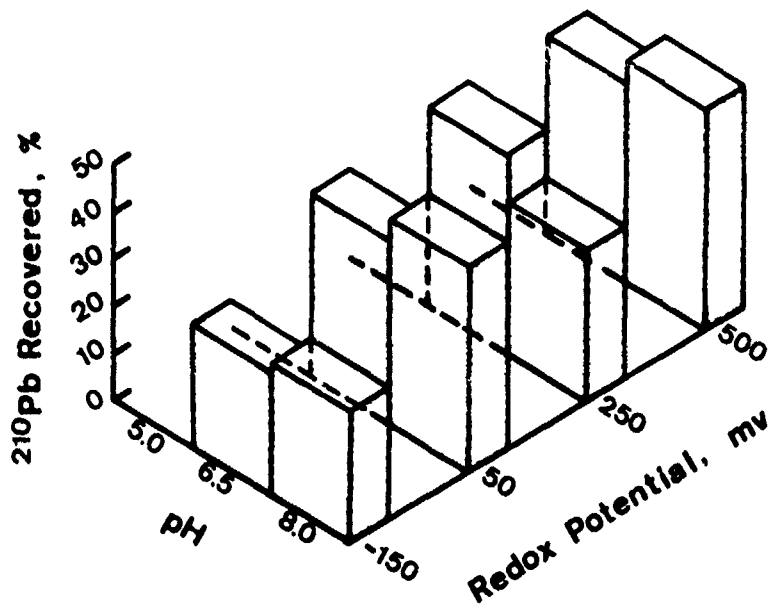


Figure 57. The Effects of pH and Redox Potential on DTPA-Extractable ^{210}Pb in Calcasieu River Sediment Suspensions

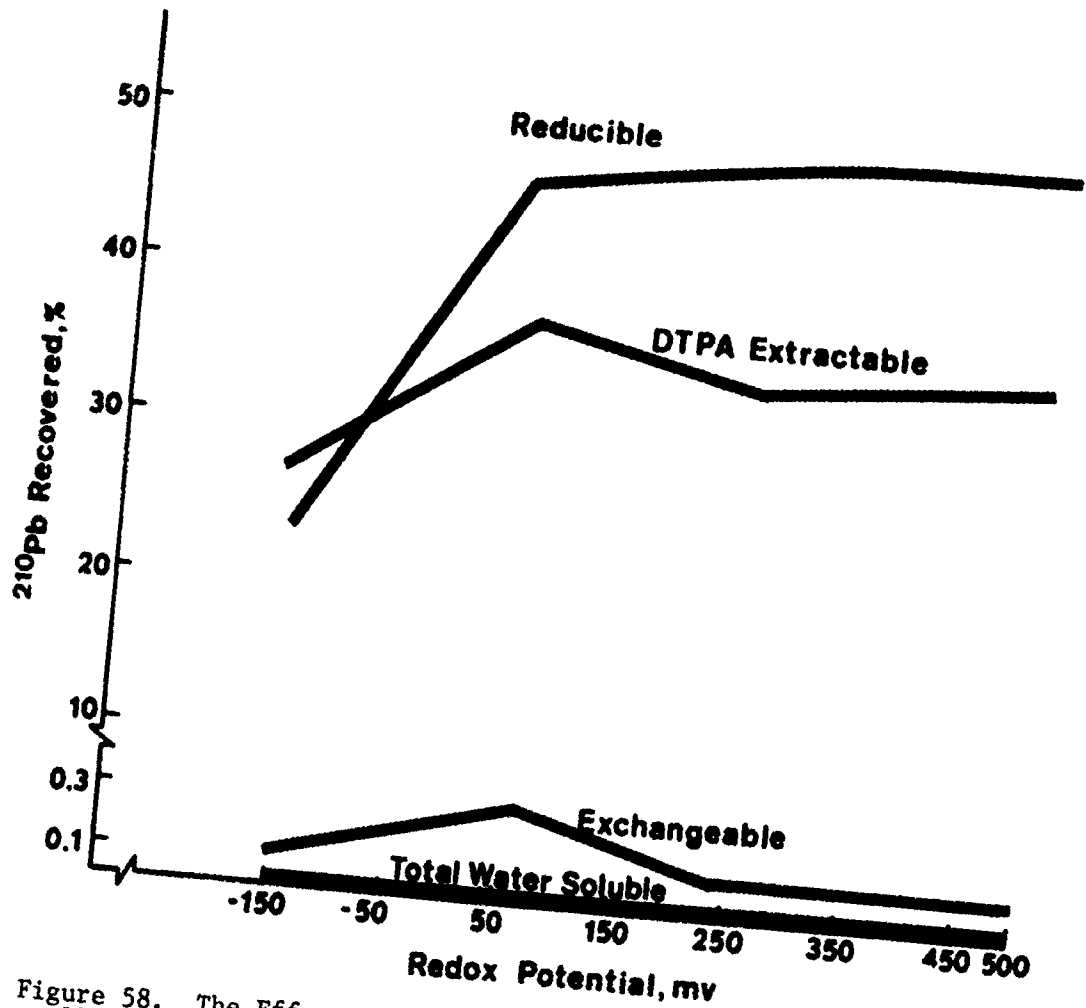


Figure 58. The Effects of Redox Potential on the Distribution of ²¹⁰Pb Among Selected Chemical Forms in Mobile Bay Sediment Suspensions Incubated at pH 6.5

material. The increase in reducible lead with redox potential was found in the Mobile Bay and Calcasieu River sediment suspensions at all pH levels.

As previously suggested, an increase in redox potential may reduce the stability of lead-organic complexes. The increase in DTPA-extractable lead as redox potential is increased from -150 to 50 mv may result from a reduced lead-natural chelate stability as redox potential increases. Further increases in DTPA-extractable ^{210}Pb with stepwise increases in redox potential were not apparent and likely reflect both a weakening of the lead-organic bonds and the competition of hydrous oxides for lead in an oxidized environment.

Figure 59 shows the effect of redox potential on the distribution of indigenous lead among the chemical fractions containing substantial portions of the total lead in the Calcasieu River sediment material incubated at pH 6.5. As indicated from ^{210}Pb data, reducible lead was found to increase with each stepwise increase in redox potential. There was an apparent inverse relationship between DTPA extractable and hydrogen peroxide-digestible (insoluble organic bound curve) lead. This suggested that digestion with hydrogen peroxide dissolved the fraction of lead more strongly incorporated into insoluble organic material which the DTPA extractant was unable to extract.

Though some of the lead released from one form by a chemical extractant may be retained by another regulatory process prior to extraction,

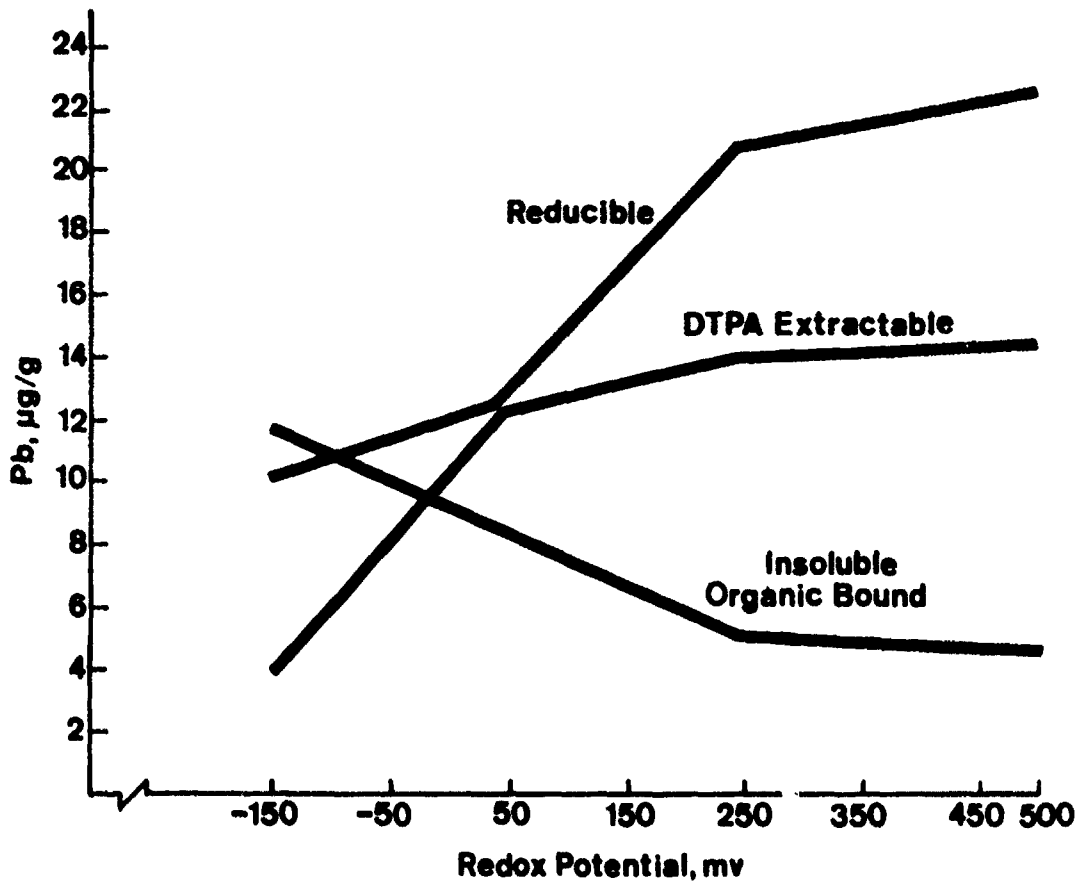


Figure 59. The Effects of Redox Potential on the Distribution of Lead Among Selected Chemical Forms in Calcasieu River Sediment Suspensions Incubated at pH 6.5 (total lead, 53 µg/g)

it is apparent from the sum of the lead found associated with hydrous oxides and insoluble organics under oxidizing conditions that up to 75 percent of the total lead in this sediment may be subject to chemical transformations affecting its availability.

Cadmium

The total cadmium content of the sediment materials studied is indicated in Table 15. The sediment materials studied contained approximately the same total cadmium content.

Table 15

Total Sediment Cadmium Content	
Sediment Material	Total Cadmium
	µg Cd/g solids
Barataria Bay	4.1
Mobile Bay	3.4
Mississippi River	4.7
Calcasieu River	3.2

The influence of pH and redox potential on the distribution of cadmium among selected chemical forms was studied by determining the gamma activity of added ^{109}Cd in the various chemical extracts as well as by quantitative measurements of indigenous cadmium by flame and flameless atomic absorption. The Barataria Bay and Mississippi River

sediment suspensions were incubated with ¹⁰⁹Cd. Soluble and exchangeable cadmium were determined for all four sediment materials by flameless atomic absorption using the heated graphite furnace technique. Conventional flame atomic absorption, which is a relatively sensitive analytical tool for cadmium, was used for the remaining chemical fractions since more cadmium was removed by the harsher chemical extractants used to determine cadmium in the less readily bioavailable forms.

The chemistry of pH and redox potential regulation of soluble cadmium levels in natural surface waters and sediments is not found in the literature. This is due to the variability in types and quantities of components comprising natural systems and the unknown interactions of these components in complexing with trace metals. However, pH-redox potential diagrams from thermodynamic calculations have been developed for cadmium in simple aqueous systems. Such models include typical levels of a few predominant inorganic ligands known to complex with metals and are useful in understanding the nature of control of metal solubility. In many cases these stability diagrams may be applicable to natural systems. Hem⁵⁴ has constructed a pH-redox potential diagram for predominant solid and dissolved cadmium species for an inorganic aqueous system containing sulfur and carbon dioxide. Cadmium carbonate formation is thought to be important in regulating cadmium solubility. Stability fields for cadmium species in pH-redox potential diagrams indicate that cadmium carbonate precipitation may be limiting cadmium solubility

as pH increases from near-neutral levels to around pH 8.0.^{54,67} Where considerable chloride is present, a soluble chloride or chloride-hydroxide complex may form, which competes with the formation of an insoluble cadmium-ligand complex. These soluble compounds may, in some cases, enhance cadmium solubility in the presence of carbon dioxide.

With the exception of sulfide precipitation, little is known about the possible mechanisms regulating cadmium solubility as the oxidation status of a sediment-water system is changed. Where a change in redox potential crosses the stability boundary for sulfide, cadmium solubility may be associated with the resultant formation or destruction of the cadmium sulfide complex. However, there is little information available on the solid phases influencing cadmium solubility as redox potential is increased outside the stability field for cadmium sulfide.

Figures 60 and 61 indicate the influence of pH and redox potential on the ¹⁰⁹Cd recovered in the water-soluble fraction for the Barataria Bay and Mississippi River sediment suspensions, respectively. Figures 62 and 63 indicate the cadmium measured by flameless atomic absorption in these suspension extracts. There was generally less experimental error associated with the radiotracer technique as indicated by a smaller standard deviation about the mean of duplicate determinations (Appendixes J and K). However, the responses of both forms of cadmium to changes in pH and redox potential were found to be similar. There is a general pH effect on water-soluble cadmium resulting in less dissolved

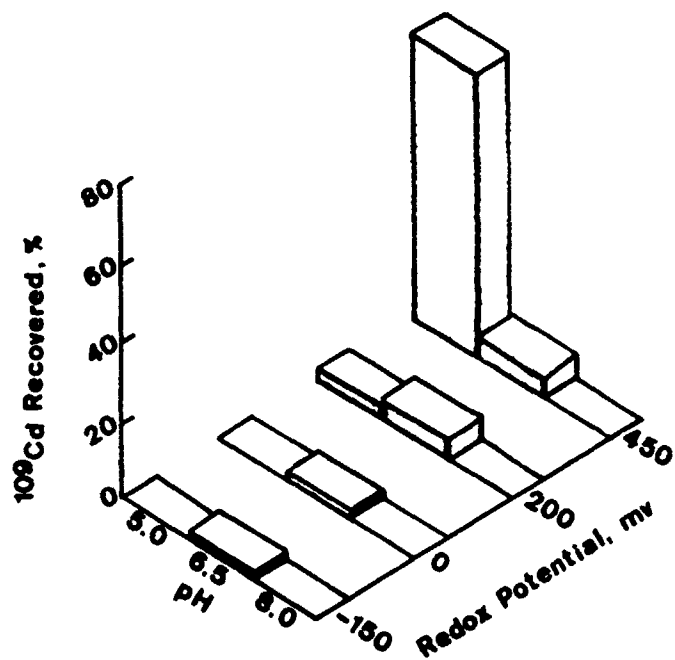


Figure 60. The Effects of pH and Redox Potential on Total Water-Soluble ^{109}Cd in Barataria Bay Sediment Suspensions.

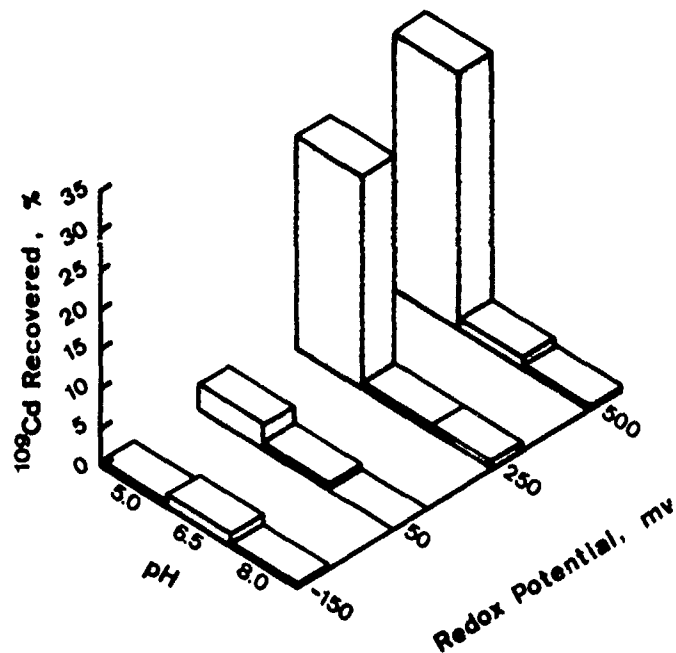


Figure 61. The Effects of pH and Redox Potential on Total Water-Soluble ^{109}Cd in Mississippi River Sediment Suspensions.

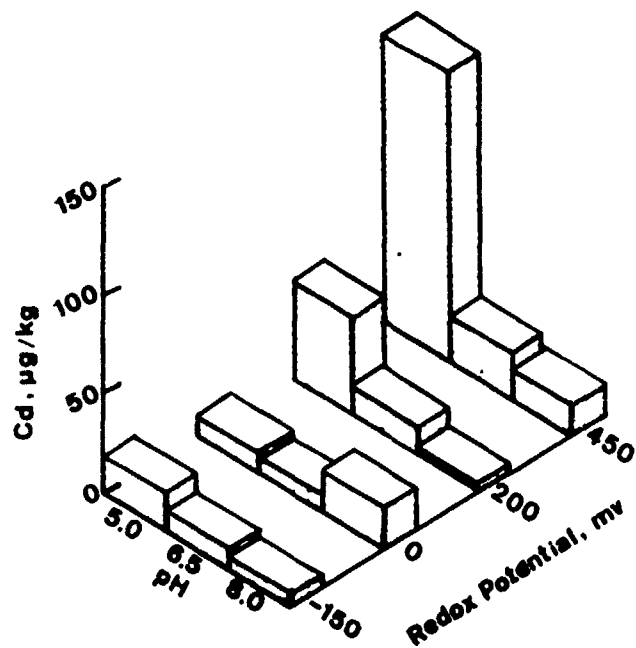


Figure 62. The Effects of pH and Redox Potential on Total Water-Soluble Cadmium in Barataria Bay Sediment Suspensions Measured by Flameless Atomic Absorption

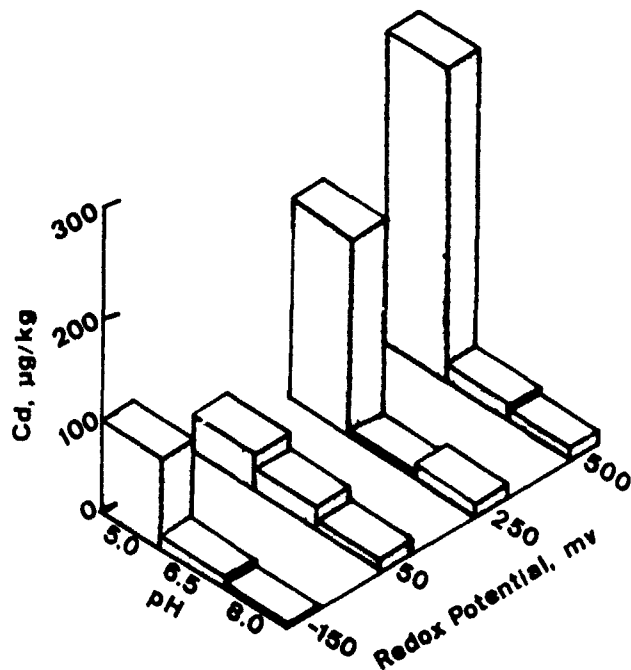


Figure 63. The Effects of pH and Redox Potential on Total Water-Soluble Cadmium in Mississippi River Sediment Suspensions Measured by Flameless Atomic Absorption

cadmium as pH is increased from 5.0 to 8.0. This pH effect is especially apparent in the oxidized treatment and is likely due to cadmium carbonate formation. The formation of uncharged soluble organic or inorganic cadmium complexes apparently had little influence on cadmium solubility. Essentially all of the total water-soluble ^{109}Cd was retained by a cation exchange resin in these two sediment materials. There was a marked increase in soluble cadmium concentrations from reduced to oxidized treatments over the entire redox potential range studied at pH 5.0 for both of these sediments. There was no apparent influence of redox potential on the low cadmium levels found at pH 8.0 in either sediment material.

The low recovery of soluble ^{109}Cd from the -150-mv treatment fits the expected pattern of sulfide precipitation in reduced sediments. This may be the case for the Barataria Bay suspensions incubated at pH 5.0 and 6.5. However, no total sulfide was detected in the reduced Mississippi River suspension at any pH level. Either undetectable levels of sulfide were present in this system, or another mechanism limiting cadmium solubility was active under strongly reduced conditions. The data seem to suggest that cadmium adsorption to a solid phase other than sulfide is involved. While there was generally a reduction in water-soluble ^{109}Cd and indigenous cadmium associated with a decrease in redox potential, the levels began to decrease before the redox potential stability boundary for sulfide was encountered. Also, where sulfide

was detected, soluble cadmium levels measured by atomic absorption did not decrease appreciably as the redox potential was lowered across the sulfide stability boundary. Considerably more water-soluble cadmium was found in the Mobile Bay and Calcasieu River suspensions incubated at pH 6.5 and 8.0 (Figures 64 and 65). Though no influence of redox potential was found for soluble cadmium in the Calcasieu River suspension, possibly due to the large experimental variation between duplicate samples, a general increase in soluble cadmium was associated with an increase in the degree of oxidation in the Mobile Bay suspensions at all pH levels.

The greater quantity of soluble cadmium from the Mobile Bay and Calcasieu River sediment materials may be due, in part, to an equilibrium with a larger exchangeable cadmium pool. These two sediment materials were found to have both a greater cation exchange capacity and a greater quantity of exchangeable cadmium at pH 6.5 and 8.0 than the Barataria Bay and Mississippi River sediment materials. There are numerous studies indicating that cation exchange in soils and sediments is an important factor in retaining cadmium and possibly regulating its solubility.^{62,67,68} Price⁶⁷ has shown a definite correlation between the soluble and exchangeable forms of cadmium.

Figures 66 and 67 indicate the influence of pH and redox potential on the ¹⁰⁹Cd activity in the exchangeable form in the Barataria Bay and Mississippi River sediment suspensions. Comparison of these figures with the exchangeable cadmium determined by atomic absorption (Appendix K)

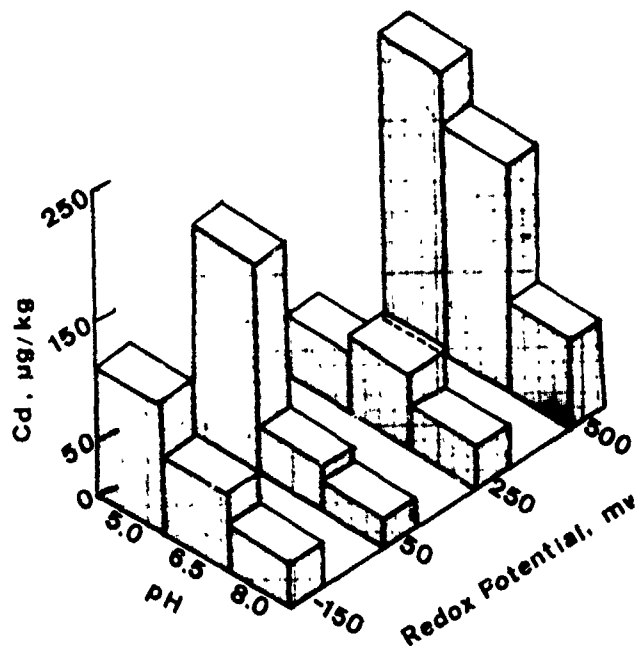


Figure 64. The Effects of pH and Redox Potential on Total Water-Soluble Cadmium in Mobile Bay Sediment Suspensions

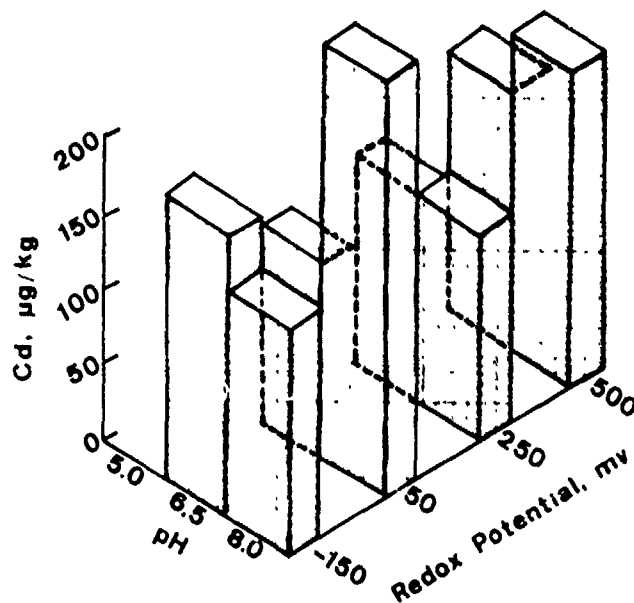


Figure 65. The Effects of pH and Redox Potential on Total Water-Soluble Cadmium in Calcasieu River Sediment Suspensions

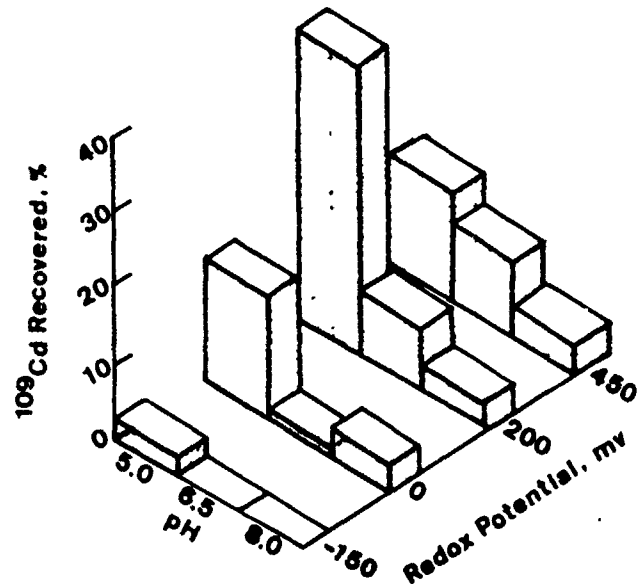


Figure 66. The Effects of pH and Redox Potential on Exchangeable ¹⁰⁹Cd in Barataria Bay Sediment Suspensions

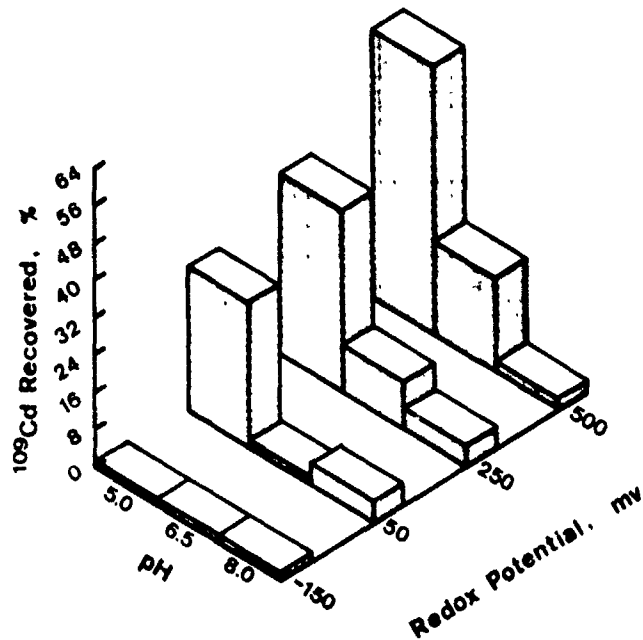


Figure 67. The Effects of pH and Redox Potential on Exchangeable ¹⁰⁹Cd in Mississippi River Sediment Suspensions

indicates that the response trends obtained by both techniques are somewhat similar. The relatively low recovery of ^{109}Cd (≈ 14 percent) from the Barataria Bay suspension incubated at pH 5.0, 450 mv, was due to the large proportion of added ^{109}Cd (≈ 73 percent) recovered in the preceding water-soluble extraction. The reason for the large discrepancy between soluble and exchangeable ^{109}Cd activity and measured indigenous cadmium as the redox potential increased from 200 to 450 mv in this pH treatment was not apparent.

The greatest recovery of exchangeable ^{109}Cd from the Barataria Bay and Mississippi River suspensions was 39 and 57 percent, respectively, at pH 5.0 and about 10 and 20 percent, respectively, at pH 6.5. When this is included with that cadmium recovered in the soluble fraction, it is apparent that, relative to other trace metals such as mercury, a considerable portion of the total sediment cadmium may be present in the most readily bioavailable forms, depending on pH and the degree of oxidation. This rather striking effect of both pH and redox potential suggests considerable cadmium release to relatively mobile forms may occur as a cadmium-contaminated sediment is transported from a near-neutral pH, reducing environment to a moderately acid, oxidizing environment. Most open-water disposal methods probably result in minimal oxidation of the bulk dredged solids during the relatively short transit times in an oxidized water column. However, substantial reductions in the pH of noncalcareous materials and increases in oxidation intensity may occur in some cases where upland disposal results in gradual drainage and subsequent oxidation of dredged materials. Under these conditions,

cadmium levels of subsurface drainage water may be increased, and cadmium availability to plants growing on the material may be enhanced.

The adsorption of trace metals such as cadmium by hydrous oxides of iron and manganese is reported to be an important factor in regulating the dissolved levels of metals in sediment-water systems. However, in the sediment materials studied, relatively large quantities of relatively mobile soluble and exchangeable cadmium were often found at pH-redox potential combinations which favored the formation of hydrous oxides. Reducible ^{109}Cd showed little response to pH or redox potential in the Barataria Bay and Mississippi River sediment suspensions. Cadmium measured by flame atomic absorption was somewhat erratic, but also showed no response to pH and redox potential. There was also little relation between the indigenous cadmium and the iron and manganese extracted with the oxalate reagent. Indeed, the isotope data indicated a negative correlation between oxalate-extractable cadmium and the poorly crystalline hydrous oxides reported to be solubilized by this chemical reducing agent. Thus, in this study, there was little evidence indicating cadmium adsorption to hydrous oxides as an important factor in limiting its chemical availability.

The influence of pH and redox potential on the DTPA- and hydrogen peroxide-extractable ^{109}Cd from the Mississippi River sediment suspension is shown in Figures 68 and 69. Where DTPA extractions were made in the remaining sediment materials and cadmium was determined by atomic absorption, the response to changes in redox potential was generally similar.

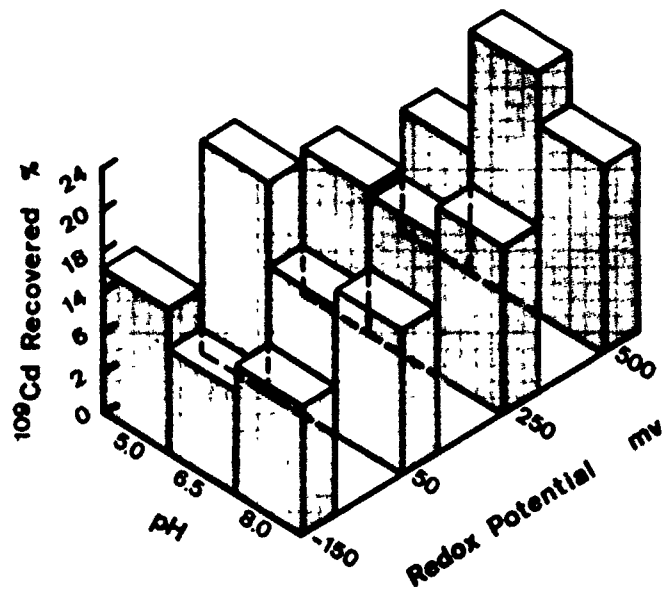


Figure 68. The Effects of pH and Redox Potential on DTPA-Extractable ¹⁰⁹Cd in Mississippi River Sediment Suspensions

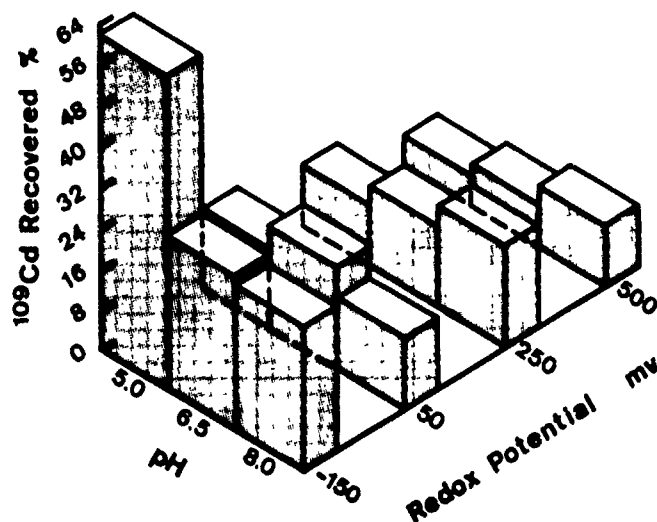


Figure 69. The Effects of pH and Redox Potential on Insoluble Organic-Bound ¹⁰⁹Cd in Mississippi River Sediment Suspensions

Assuming the DTPA-extractable cadmium represents a portion of that cadmium complexed with organics in the solid phase, the increase in extractable ^{109}Cd with increasing redox potential indicates a weakening of the cadmium-organic complex as a sediment-water system becomes better oxidized. This may contribute to the increased levels of readily bioavailable cadmium found as redox potential increased, which was discussed above. Also apparent is that the cadmium present in the residual solid organic phase decreases with an increase in redox potential, again suggesting that the cadmium-organic complex is more stable in reducing environments (Figure 69). This process may be responsible for the low solubility of cadmium in a strongly reduced environment, particularly where no sulfide was detected. The slower and less complete degradation of organic matter under reducing conditions may be contributing to these observations.

Figure 70 indicates the influence of redox potential on the distribution of ^{109}Cd in the Mississippi River sediment suspension incubated at pH 6.5. Relative to other metals discussed, a large proportion of the potentially chemically active cadmium may be recovered in the readily bioavailable water-soluble and exchangeable forms, particularly as pH is lowered (recall previous discussion). The comparatively easy release of sediment-bound cadmium may be due, in part, to a weaker bonding of this element with the solid phase than for other metals studied. There was little relationship between redox potential and that cadmium supposedly extracted from hydrous oxides. Also, it has been reported that cadmium

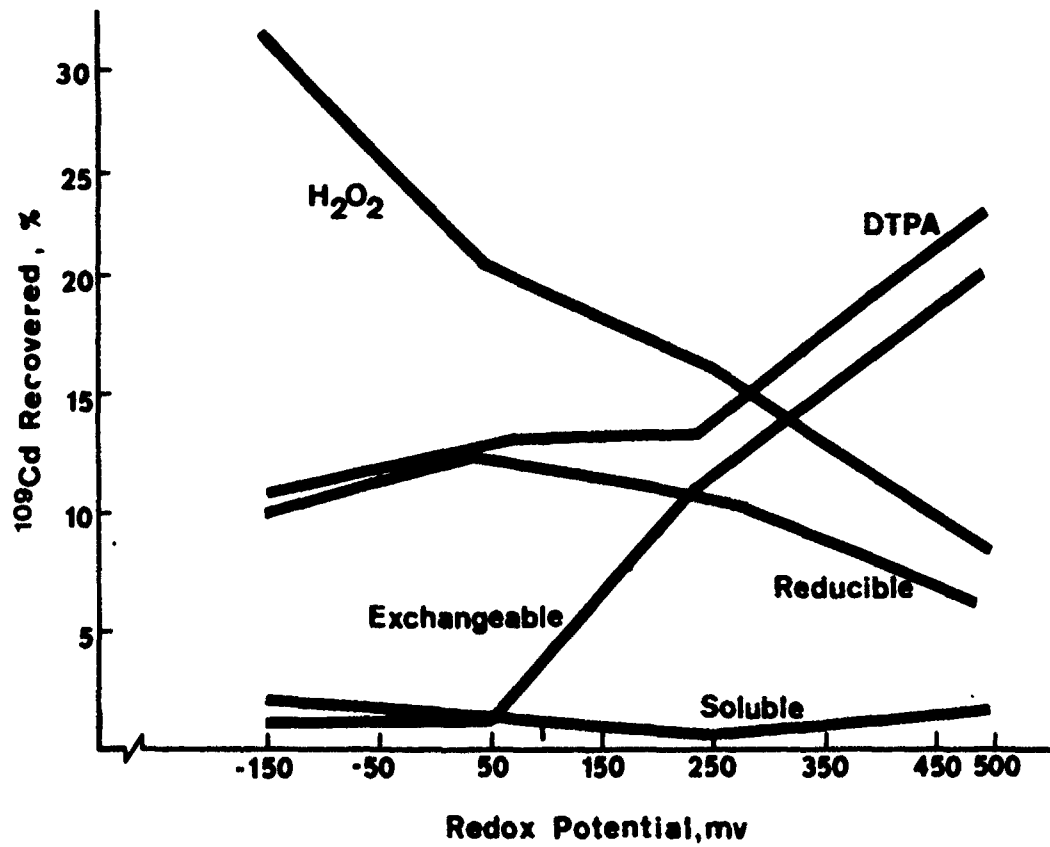


Figure 70. The Effects of Redox Potential on the Distribution of ^{109}Cd Among Selected Chemical Forms in Mississippi River Sediment Suspensions Incubated at pH 6.5

forms less stable complexes with organics than many other metals.⁵⁴

Nitrogen

Both pH and redox potential were found to influence the levels of soluble and exchangeable ammonium-nitrogen in all sediment materials studied. However, the means of duplicate samples and the general response trends of ammonium-nitrogen levels to incremental changes in pH and redox potential were considerably more variable than for other metals and nutrients studied. Possible contributing factors to the variable response to pH and redox potential include the continuous production of ammonium during incubation by mineralization of organic nitrogen, and the possible irreversible loss of ammonium from reduced sediments by nitrification during the air pumping cycle used to control suspension redox potential.

The results for the incubated Barataria Bay and Calcasieu River materials best summarized the overall influence of pH and redox potential on ammonium-nitrogen for these incubated suspensions. Ammonium data for the remaining sediment materials is given in Appendix L. Total water-soluble ammonium generally decreased with an increase in pH, especially as the pH increased from 6.5 to 8.0 (Figures 71 and 72). Volatilization of ammonia from the suspensions incubated at pH 8.0 and 30°C may have contributed to the observed pH effects.

There was also a general reduction in soluble and exchangeable ammonium-nitrogen as redox potential increased. Oxidation of the ammonium to nitrite and subsequently to nitrate by aerobic chemoautotrophic bacteria was thought to be the primary process accounting for the redox potential effect.

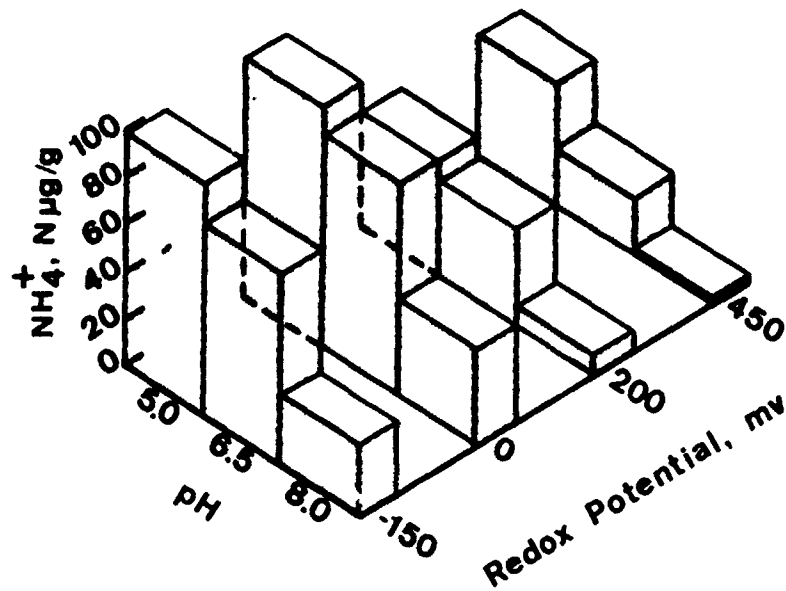


Figure 71. The Effects of pH and Redox Potential on Total Water-Soluble Ammonium-Nitrogen in Barataria Bay Sediment Suspensions

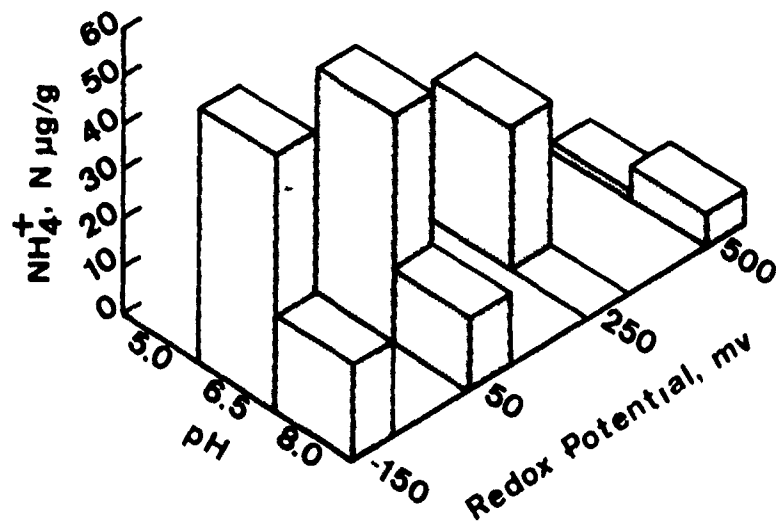


Figure 72. The Effects of pH and Redox Potential on Total Water-Soluble Ammonium-Nitrogen in Calcasieu River Sediment Suspensions

The exchangeable ammonium content of these sediment suspensions responded similarly to changes in pH and redox potential (Figures 73 and 74). Approximately the same quantities of ammonium-nitrogen were recovered in this form.

From these figures, it is apparent that a substantial decrease in readily bioavailable ammonium-nitrogen may occur as a strongly reduced sediment becomes well oxidized. However, it is likely that much of the ammonium-nitrogen lost as a result of oxidation was transformed to the equally bioavailable nitrate form. The ultimate fate of the sediment-derived inorganic nitrogen is complicated. Some ammonium-nitrogen associated with a reduced sediment may be released to surface waters as a sediment is disturbed. This released ammonium-nitrogen may be utilized by aquatic organisms, reabsorbed by cation exchange mechanisms, or transformed to nitrate. Nitrate may also enhance the trophic status of receiving surface waters or may, under certain conditions, move into reduced sediments and be removed from the sediment-water system by denitrification.

Phosphorus

The data for water-soluble and exchangeable phosphorus is given in Appendix M for the four sediment materials studied. The following general observations may be made from these data:

a. An increase in redox potential from -150 mv to +50 mv significantly reduced the concentration of phosphorus in both the water-soluble and exchangeable fractions at pH 6.5 and 8.0. Further increases in redox potential from 50 to 500 mv had no noticeable effect on water-soluble or exchangeable phosphorus in these two pH treatments. At pH 5.0, a

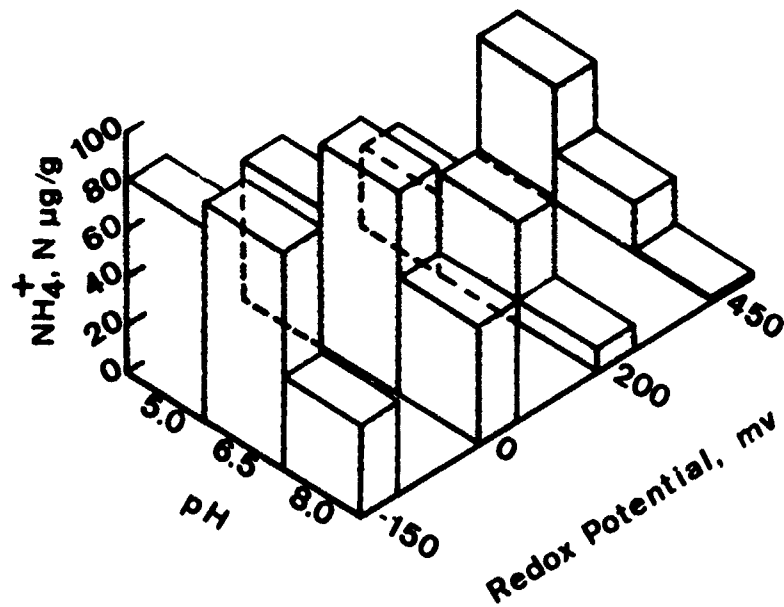


Figure 73. The Effects of pH and Redox Potential on Exchangeable Ammonium-Nitrogen in Barataria Bay Sediment Suspensions

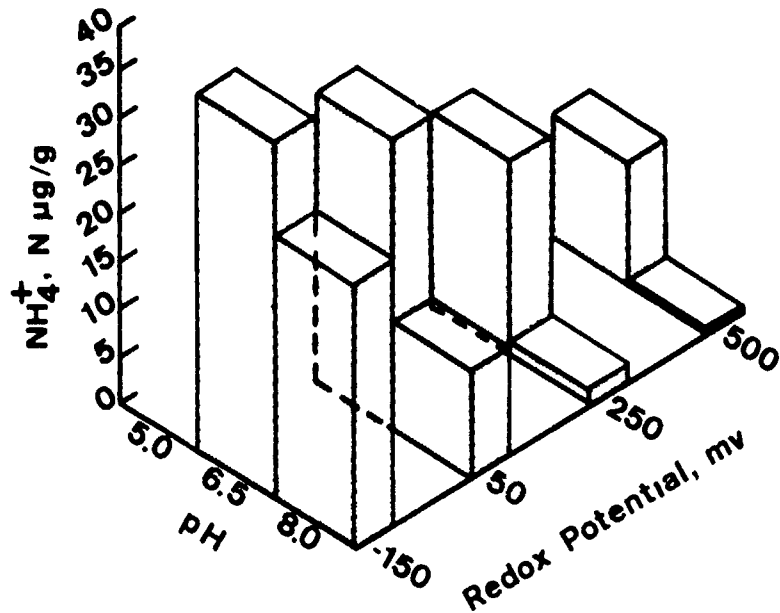


Figure 74. The Effects of pH and Redox Potential on Exchangeable Ammonium-Nitrogen in Calcasieu River Sediment Suspensions

reduction in soluble and exchangeable phosphorus was not apparent until the redox potential increased beyond the 50-mv level.

b. The effect of pH on the solubility of phosphorus was variable depending on the oxidation-reduction conditions. For example, under very reduced conditions (-150 mv), the concentration of water-soluble phosphorus increased greatly as pH increased from 5.0 to 6.5. An increase in pH from 6.5 to 8.0 did not change phosphorus concentrations to any significant level except in the Mississippi River sediment suspensions, where an increase in suspension pH from 6.5 to 8.0 resulted in a 40-percent increase in phosphorus levels. The effect of pH at 50-mv redox potential was very small or nonexistent. In the more oxidized suspensions (250 mv and 500 mv), an increase in pH from 5.0 to 8.0 was accompanied by a substantial increase in water-soluble phosphorus.

c. The effect of pH on the exchangeable phosphorus was very similar to that of the water-soluble fraction discussed above.

d. Generally more phosphorus was present in the exchangeable fraction than in the water-soluble fraction, especially under low pH and more reduced conditions.

The influence of pH and redox potential was similar for the different sediment materials; thus the results from the Mobile Bay sediment suspension will be used to represent the response of water-soluble and exchangeable phosphorus to pH and redox potential (Table 16).

The solubility of phosphorus in acid sediments is known to be influenced largely by the reduction of ferric iron to ferrous iron, which combines with phosphate to form ferrous phosphate. This results in more

Table 16

Water-Soluble Plus Exchangeable Phosphorus ($\mu\text{g/g}$)
in Mobile Bay Sediment Suspensions

Redox Potential mv	pH		
	5.0	6.5	8.0
-150	27.1	95.5	91.1
+50	28.2	15.9	35.4
+250	18.1	17.0	29.8
+500	7.1	16.5	32.2

phosphorus on the exchange complex and in solution. Oxidation of ferrous iron to ferric iron will reduce soluble phosphorus concentrations. In this study, the water-soluble and exchangeable phosphorus levels are strongly influenced by iron concentrations in these fractions (See Appendix B for iron data). A decrease in water-soluble and exchangeable iron is accompanied by a reduction in phosphorus levels as the redox potential is increased from -150 mv to 500 mv.

Higher concentrations of water-soluble plus exchangeable phosphorus were measured in suspensions incubated at 50-, 250-, and 500-mv redox potentials at pH 8.0, compared to pH 5.0 and 6.5 (Table 16). At pH 8.0, the solubility of phosphorus is governed by the solubility of calcium phosphate compounds. It is very likely that under moderately reduced and oxidized conditions, calcium phosphate is more available than iron phosphates. This may explain greater phosphorus concentrations at pH

8.0 than at pH 5.0 under these conditions. However, this study was not designed to compare relative solubility of various phosphorus compounds, and the discussion will be limited to simple comparisons.

To summarize, more phosphorus was present in solution and in the exchangeable form under reduced conditions than under oxidized conditions. This effect was observed at pH 5.0, 6.5, and 8.0. A strong positive relationship between iron and phosphorus was observed in the present study, confirming the literature reports that phosphorus solubility is strongly influenced by iron compounds. The concentration of phosphorus in the easily available water-soluble and exchangeable fractions was strongly influenced by suspension pH. In moderately reduced and oxidized environments at pH 8.0, the phosphorus levels in the various sediment materials seemed to be controlled by calcium phosphate solubility.

Influence of pH and Redox Potential on the
Adsorption/Desorption Behavior of Zinc, Mercury,
Cadmium, and Lead in Sediment Suspensions

After the initial fractionation, incremental additions of soluble mercury, zinc, cadmium, and lead were made to the remaining suspensions incubated at different pH and redox potential levels. Twenty-four hours after each addition, the amount of these metals remaining in the equilibrium solution (water-soluble) was determined. The residual solid material remaining from the water-soluble extraction was extracted with 1 N sodium acetate adjusted to the pH of the incubated suspensions to determine exchangeable levels of the added metals. Zinc and mercury sorption studies

were carried out on Barataria Bay, Mississippi River, and Mobile Bay sediment suspensions. Sorption behavior of cadmium was investigated in the Barataria Bay and Mississippi River sediment suspensions. Adsorption behavior of incremental additions of lead was investigated in Mobile Bay sediment suspensions incubated at different pH and redox potential levels. The results of this study are discussed in the order of zinc, mercury, cadmium, and lead.

Zinc

In the Barataria Bay sediment suspensions, the amount of zinc remaining in the equilibrium solution was strongly affected by both redox potential and pH (Table N1). In the most reduced treatment (-150 mv), a negligible amount of zinc was recovered in the water-soluble fraction. This means that essentially all of zinc added at pH 5.0, 6.5, and 8.0 was retained by the solid material when the suspensions were strongly reduced. At pH 5.0 and 6.5, the recovery of soluble zinc increased with an increase in the intensity of oxidation. Generally, more zinc was recovered at pH 5.0 compared to pH 6.5. Although detectable levels of zinc were recovered only at the highest levels of zinc added at pH 8.0, the effect of redox potential on the concentration of zinc in solution was different than found at pH 5.0 and 6.5. More zinc was present in solution at -150- and 0-mv redox potentials than at -200- and +450-mv redox potentials. The absence of sulfide in the strongly reduced sediment at pH 8.0 may have contributed to the increased soluble zinc at -150 mv in this pH treatment.

These results indicate that the maximum adsorption or precipitation of added zinc occurred at pH 8.0 at all levels of redox potentials studied. The amount of zinc retained by the sediments decreased with decreasing pH. At lower pH values, strongly reduced treatments (-150 mv) retained more zinc than weakly reduced and well-oxidized treatments, possibly due to zinc sulfide precipitation.

Exchangeable zinc increased with larger incremental additions at pH 5.0 and 6.5. Recovery of exchangeable zinc increased with increased redox potential, which means that a greater proportion of the adsorbed zinc was more loosely bound under oxidized conditions at pH 5.0 and 6.5. No detectable zinc was recovered at pH 8.0 under reduced or oxidized conditions, except at the highest incremental addition (400 μg zinc/g) where a maximum of 1.75 percent of the adsorbed zinc was recovered at -150 mv. Although a decrease in exchangeable zinc with increasing redox potential was noticed at pH 8.0, lower pH values combined with oxidized conditions generally favored greater recovery of the freshly adsorbed zinc.

In Mobile Bay sediment suspensions, zinc retention was favored by increasing pH and decreasing redox potential (Figure 75), as was found for Barataria Bay sediment suspensions. However, differences in the amount of zinc adsorbed at +50, +250, and +500 mv incubated at pH 5.0 and 6.5 were not as apparent for the Mobile Bay suspensions, especially at high levels of zinc added. Recovery of the zinc initially retained by sediment solids in the exchangeable form decreased significantly with an increase in sediment pH (Table N2). This effect was noticed at all redox potential levels studied. Considerably less exchangeable zinc was

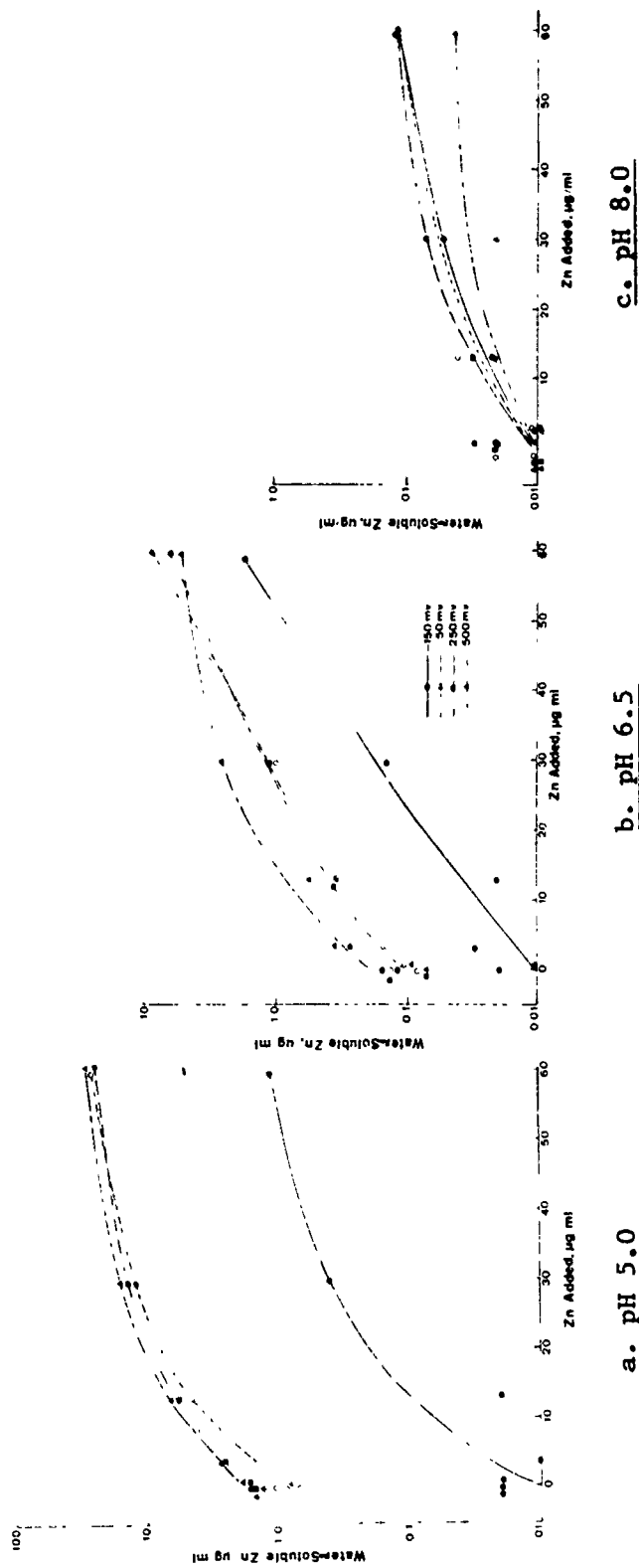


Figure 75. The Effect of Redox Potential on Water-Soluble Zinc 24 Hours After Incremental Zinc Additions to Mobile Bay Sediment Suspensions Incubated at pH 5.0, 6.5, and 8.0

found at -150 mv, as compared to +50, +250, and +500 mv in suspensions incubated at pH 5.0 and 6.5. The differences between the +50-, +250-, and +500-mv treatments were more pronounced at lower levels of zinc added at pH 5.0 and 6.5. At levels greater than 105 $\mu\text{g/g}$ zinc added, comparative amounts of exchangeable zinc were recovered in these treatments. At pH 8.0 exchangeable zinc levels were negligible.

The effect of pH on the amount of zinc remaining in solution in the Mississippi River sediment suspensions follows the same general trend of pH 5.0 > pH 6.5 > pH 8.0 (Figure 76). At the highest level of zinc added (500 μg zinc/g), about 45 percent of the total zinc was recovered in the equilibrium solution at pH 5.0 at all oxidation levels. At pH 6.5, recovery of the added zinc ranged from 2.36 to 11.27 percent. The concentration of zinc in solution at pH 8.0 was around 0.1 percent. Generally, a strongly reduced suspension did not decrease soluble zinc as much as found in the other sediment materials. The lack of measurable sulfide in these strongly reduced suspensions may account for increased zinc solubility.

Recovery of the freshly adsorbed zinc in the exchangeable form increased greatly as pH dropped from 8.0 to 6.5 and 5.0 (Figure 76). The effect of various redox potential treatments on exchangeable zinc was not similar at different pH levels maintained. For example, at higher levels of zinc added at pH 8.0, more zinc was recovered under reduced conditions than under oxidized conditions. At lower concentrations, essentially no exchangeable zinc was found. In contrast, at pH 5.0 and

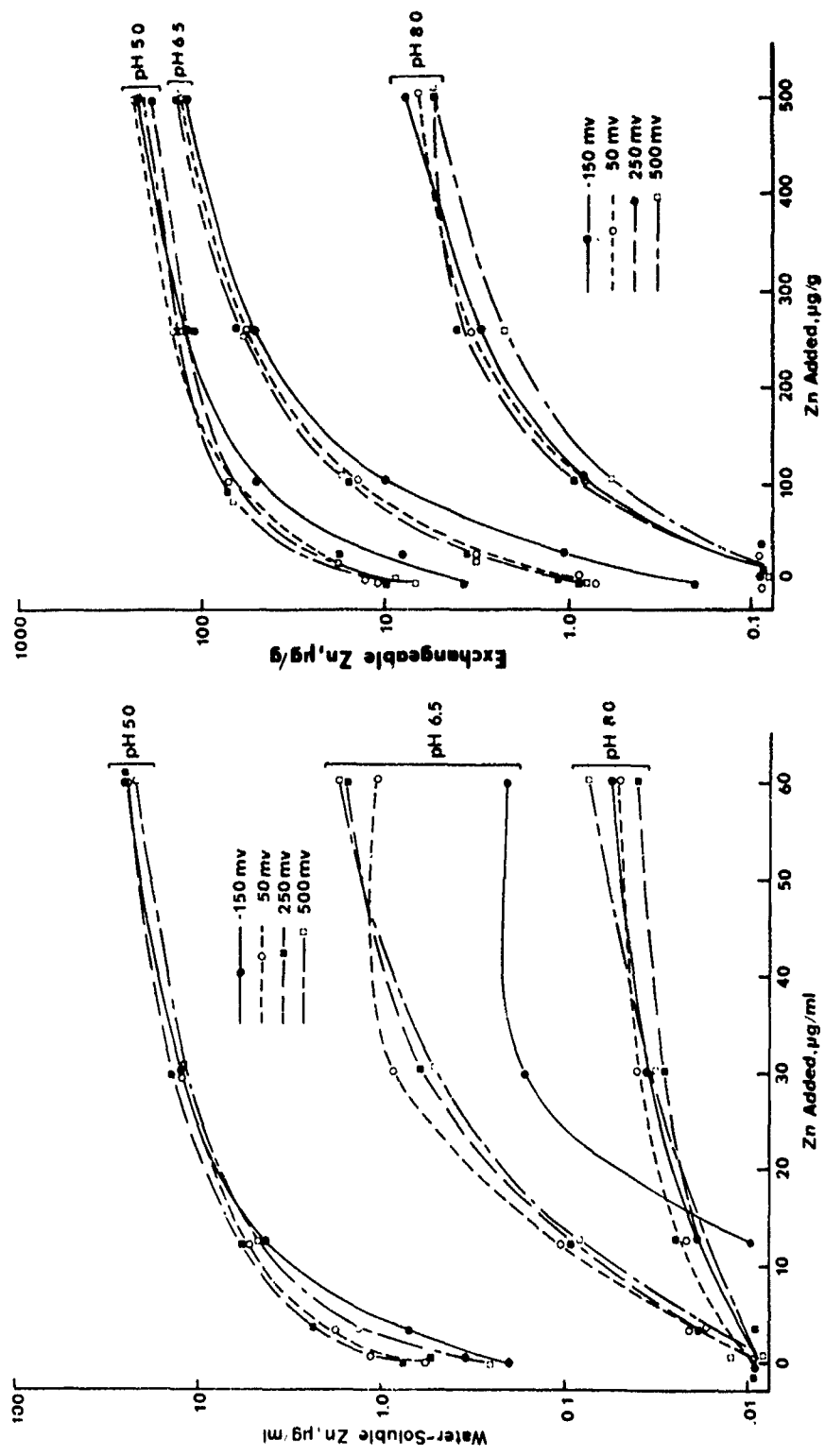


Figure 76. The Effect of pH and Redox Potential on Zinc 24 Hours After Incremental Zinc Additions to Mississippi River Sediment Suspensions

6.5, the effect of a strongly reduced environment (-150 mv) in decreasing exchangeable zinc levels was noticeable up to 260 µg/g zinc added. Again, it should be recalled that no sulfide was detected in the strongly reduced Mississippi River sediment suspensions.

Some of the important results presented above may be summarized as follows:

a. The adsorption-precipitation pattern of increasingly larger additions of zinc to Barataria Bay, Mobile Bay, and Mississippi River sediment suspensions followed a general trend of $\text{pH } 5.0 < \text{pH } 6.5 \ll \text{pH } 8.0$. Essentially all of the zinc added at pH 8.0 was adsorbed by sediment solids as little to no water-soluble zinc was detected.

b. The effect of redox potential on zinc adsorption by Barataria Bay and Mobile Bay sediment suspensions incubated at pH 5.0 and 6.5 was generally in the order of $-150 \text{ mv} \gg +50 \text{ mv} > +250 \text{ mv} \geq +500 \text{ mv}$. There was little difference in the magnitude of zinc adsorbed between various redox potential treatments by Mississippi River sediment suspensions, although slightly more zinc was retained under strongly reduced conditions.

c. The sediment materials used in this study differ in their capacity to retain added zinc.

d. The freshly adsorbed zinc recovered in the exchangeable form increased with decreasing sediment pH, indicating that under acid conditions, zinc was less tightly bound to sediment solids than under alkaline conditions. Exchangeable zinc at pH 8.0 was negligible.

e. The effect of redox potential treatments on exchangeable zinc levels was more pronounced in Barataria Bay and Mobile Bay sediment suspensions, and this effect was more noticeable at lower levels of zinc added.

Several factors affecting the adsorption behavior of zinc may be influenced by pH. Literature reports indicate that cation exchange capacity of soils and sediments decreases as pH decreases,⁶⁹ and this may influence zinc adsorption capacity. Shuman⁷⁰ reported that low pH reduced zinc adsorption more for sandy soils than for those high in colloidal-size materials. Sediment pH also influences the solubility of various zinc compounds present in sediments. For example, acid conditions favor the soluble divalent, cationic form of zinc. As pH increases from 5.0 to 8.0, zinc carbonate formation is reported to reduce zinc solubility. Zinc hydroxide may also form around pH 8.0. Carbonates and hydroxides form precipitates of zinc which are characterized by low solubility and greater stability. These effects of pH on zinc speciation are discussed in detail by Hem.⁵⁴ Reduced cation exchange capacity of the organic component of sediments at lower pH may partially explain lower zinc adsorption at pH 5.0 compared to that at pH 6.5 and 8.0.

It is well known that in reduced sediments rich in sulfides, the precipitation of heavy metals as insoluble sulfides is important in controlling the solubility of trace metals.^{29,31,32,54} In this study, Barataria Bay and Mobile Bay sediments contained several hundred ppm of

total sulfide under strongly reduced conditions (Table 8), and the removal from solution of the high zinc levels added at -150 mv is believed to be due to the precipitation of zinc sulfide. In the Mississippi River sediments where no sulfide was detected under strongly reduced conditions, the concentration of zinc remaining in solution increased with increasing levels of zinc added at pH 5.0 and 6.5. In the Mobile Bay sediment suspension, the precipitation of zinc sulfide at pH 8.0, in addition to carbonate or hydroxide formation, may be contributing to the reduced solubility of zinc.

The results indicate that under oxidized conditions at low pH, most of the zinc added was present in the readily bioavailable form (water-soluble + exchangeable). However, under reduced conditions, at pH 5.0 and at all redox potential treatments at pH 6.5 and 8.0, most of the zinc adsorbed was not recovered in the sodium acetate fraction. This indicates the chemically precipitated or strongly adsorbed zinc under these conditions is not in a readily available form.

A sequential chemical fractionation of the Mississippi River sediment suspension after the addition of 260 μg zinc/g solids indicated that the zinc not recovered in the readily bioavailable water-soluble and exchangeable forms was present in the reducible fraction (Table N4). This fraction is thought to consist of heavy metals strongly adsorbed to, or coprecipitated with oxides and hydroxides of iron and manganese and is considered potentially bioavailable. A change in pH or dissolved oxygen concentration, as may occur during dredging and dredged material disposal,

may transform metals in the reducible form to more bioavailable forms.

Mercury

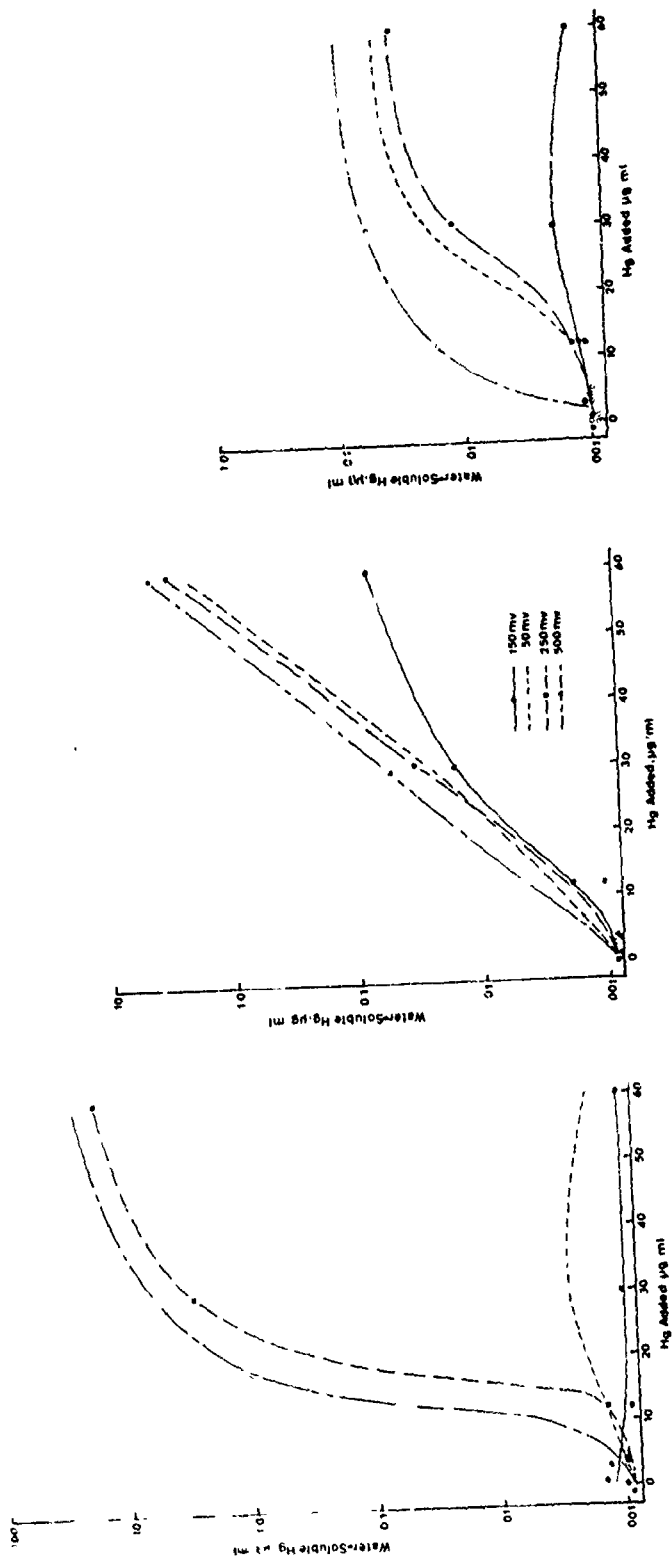
Soluble and Exchangeable Levels Following Incremental Mercury Additions.

It is well established that most of the mercury discharged into sediment-water systems is associated with the solid phase and is not readily bioavailable.^{37,71,72} Mercury forms strong stable bonds with carbonate, hydroxide, sulfide, and organic matter present in the natural water systems.²⁹ However, some of this mercury may be converted to more readily available forms if the physical and chemical environment is changed.

The effects of pH and redox potential on the capacity of Barataria Bay, Mobile Bay, and Mississippi River sediment material to retain increasing amounts of mercury added as mercuric chloride dissolved in hydrochloric acid was investigated. Subsequent removal of the freshly adsorbed or precipitated mercury by 1 N sodium acetate was also studied. The sediment materials selected for study differ in their physical, mineralogical, and chemical characteristics (Tables 4 and 8). One of the regulatory processes that controls soluble mercury concentrations under reduced conditions is the formation of insoluble mercuric sulfide. Mobile Bay sediment suspensions contained several hundred ppm of total sulfide under reduced conditions (-150 mv) incubated at pH 5.0, 6.5, and 8.0. In the Barataria Bay sediment material, sulfide was present at pH 5.0 and 6.5. No sulfide was detected at any pH in the Mississippi River

sediment material. An attempt was made in this study to relate the sorption of mercury to various sediment parameters which are known to affect mercury transformations in sediment-water systems.

The influence of redox potential on the amount of mercury remaining in the equilibrium solution (water-soluble) in the Mobile Bay sediment suspensions 24 hours after each addition is plotted against the accumulative mercury additions in Figures 77a,b, and c for pH 5.0, 6.5, and 8.0, respectively. The data indicate that pH and redox potential greatly influence the recovery of soluble mercury in the equilibrium solution. The concentration of mercury in the water-soluble fraction increased with increasing redox potential, and this trend was observed at all pH values studied. However, it is very important to note that under very reduced conditions at low levels of mercury added ($\approx 25 \mu\text{g/g}$), the mercury concentration in the equilibrium solution was greater than or equal to that in the more oxidized treatments. At higher levels of mercury added, the recovery of soluble mercury under more oxidized conditions increased sharply. This effect was more pronounced at pH 5.0 and 6.5, compared to pH 8.0. Although the effect of increasing oxidation levels on the relative amounts of soluble mercury present at pH 8.0 was evident, the quantities of mercury in the equilibrium solution were very small relative to that added. The concentration of mercury in the water-soluble fraction in the -150-mv redox potential treatment did not show any significant increase with incremental mercury additions, and this trend was observed at all pH levels studied.



a. pH 5.0

b. pH 6.5

c. pH 8.0

Figure 77. The Effect of Redox Potential on Water-Soluble Mercury 24 Hours After Incremental Mercury Additions to Mobile Bay Sediment Suspensions Incubated at pH 5.0, 6.5, and 8.0

It is evident from these results that under strongly reduced conditions (-150 mv), essentially all of the soluble mercury added was retained by the sediment material in an insoluble form at all pH levels studied. Appreciable amounts of sulfide were detected in the -150-mv redox potential treatment incubated at pH 5.0, 6.5, and 8.0. Precipitation of mercury as a sulfide under the above conditions may very likely be a principal mechanism in retaining mercury in an insoluble form under reduced conditions. Several research reports indicated that sulfide has a very strong mercury-binding capacity and thus may be important in keeping mercury in an insoluble form.^{29,32,36,72} Other important factors which may be responsible for the adsorption of freshly added mercury to sediment material include organic matter, the amount and type of clay minerals, oxides and hydroxides of iron and manganese, and carbonate and phosphate compounds. However, it is difficult at this point to differentiate between various mechanisms involved in complexing added mercury.

The results also show that the adsorption of added mercury by the more oxidized suspensions (250 mv and 500 mv) tremendously decreased with a decrease in suspension pH from 8.0 to 5.0. There are two important observations that need to be pointed out here: (1) mercury adsorption decreased with an increase in oxidation levels and (2) the magnitude of adsorption decreased sharply with a decrease in pH. It is likely that under more oxidized conditions where no sulfide was detected, the decrease in mercury-binding capacity of the sediments was due to greater decomposition of organic material under oxidized conditions. The effect

oxidized treatments (250 mv and 500 mv) at pH 5.0, 14 to 21 percent of the freshly adsorbed mercury was recovered at the highest level added.

The adsorption study of mercury in the Mobile Bay sediment suspensions indicated that changes in oxidation-reduction status or pH of sediments may strongly influence the easily bioavailable water-soluble and exchangeable mercury levels. Also, alkaline pH and anaerobic environments were found to increase the mercury-binding capacity of sediments. Acid pH and oxidized conditions favor the transformation of mercury to more easily extractable forms, especially at higher concentrations of added mercury.

In Barataria Bay sediment suspensions, the adsorption behavior of increasing concentrations of added soluble mercury was investigated at pH 6.5 and 8.0 only. The data presented in Table O1 show that a very small fraction of the total mercury was recovered in the equilibrium solution, which means that essentially all of the mercury added was adsorbed by the sediment material. A slightly higher concentration of mercury was found in the oxidized treatments (200 mv and 450 mv) as compared to reduced treatments (0 mv and -150 mv). No significant effect of pH on the concentrations of mercury measured in the water-soluble fraction was observed. Exchangeable mercury levels were negligible, indicating that the freshly adsorbed mercury was strongly bound. Redox potential and pH did not influence recovery of freshly adsorbed mercury in the exchangeable form to any appreciable degree. These results indicate that greater than 99 percent of the added mercury was not present in the easily bioavailable water-soluble and exchangeable fraction at the pH levels studied.

In the very reduced treatment (-150 mv) at pH 6.5, the presence of considerable sulfide may explain in part the removal of soluble mercury as a mercuric sulfide precipitate. Some of the mechanisms that may be responsible for mercury adsorption in the Barataria Bay sediments have been discussed above.

Mississippi River sediment suspensions are characterized by the absence of sulfide. Sulfide precipitation has been considered one of the main regulatory processes complexing mercury under reduced conditions. Comparison of mercury adsorption data obtained from Mobile Bay sediment suspensions with that from Mississippi River sediment suspensions will enable comparison of the effects of sulfide with other adsorbents responsible for mercury retention in sediments.

The influence of redox potential on the amount of mercury remaining in the equilibrium solution in the Mississippi River sediment suspensions 24 hours after each addition is plotted against the cumulative mercury additions in Figures 78a, b, and c for pH 5.0, 6.5, and 8.0, respectively. An examination of these figures indicates that both redox potential and pH had tremendous effects on the levels of soluble mercury. The recovery of soluble mercury generally increased with increasing redox potential. However, under strongly reducing conditions at low levels of mercury added (up to $\approx 15 \mu\text{g/g}$), the recovery of soluble mercury was found to equal or exceed that for all but the most oxidized treatment. This trend did not continue at greater levels of mercury additions. At low mercury levels, it is likely that some mercury-complexing ligand whose

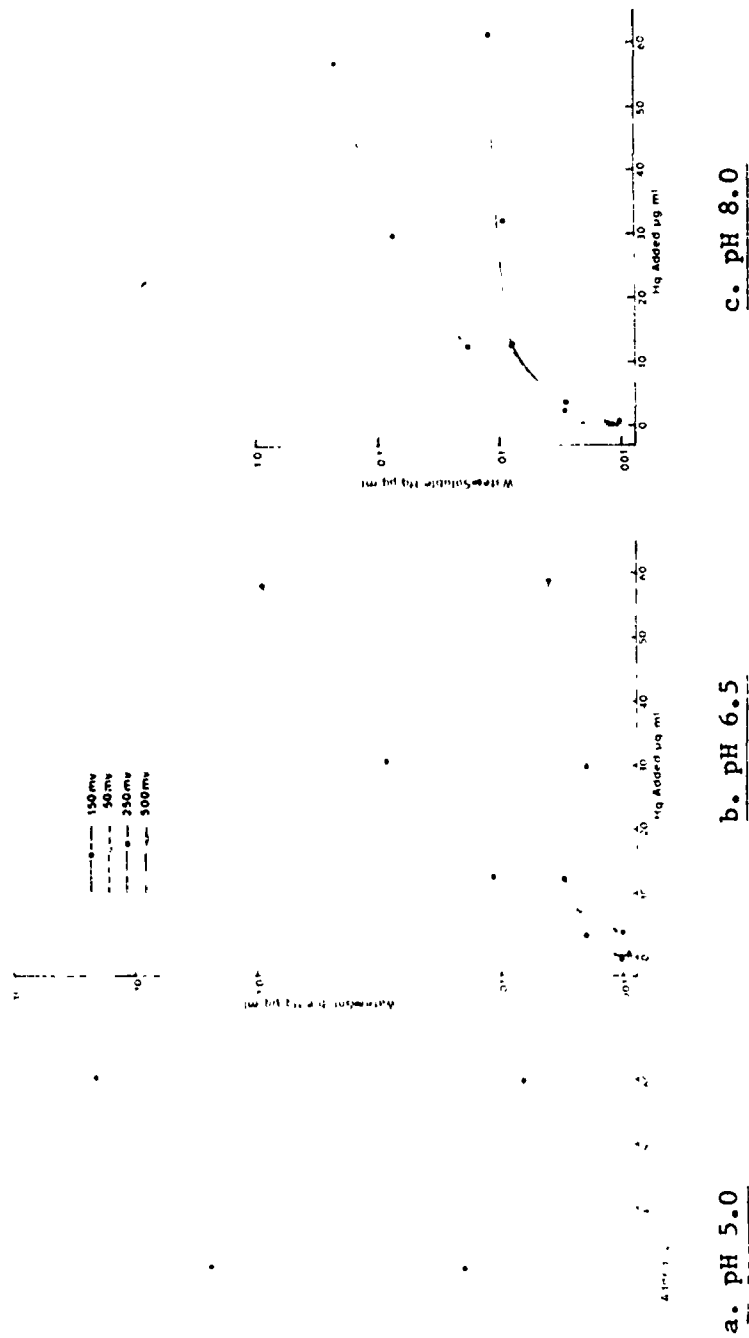


Figure 78. The Effect of Redox Potential on Water-Soluble Mercury 24 Hours After Incremental Mercury Additions to Mississippi River Sediment Suspensions Incubated at pH 5.0, 6.5, and 8.0

solubility is favored by reducing conditions is contributing to the initial upward slope of the -150-mv curve. Soluble organics in a reducing environment may be involved. As additional mercury is added, the regulatory factors increasing mercury solubility under reducing conditions may be overwhelmed and other regulatory factors become dominant. At the higher levels of mercury added, the concentration of mercury recovered in the equilibrium solution generally increased with the intensity of oxidation, and this effect was more pronounced at the lower pH values studied. For example, at 500 mv, 50 to 75 percent of the added mercury was recovered in the equilibrium solution at pH 5.0. At pH 6.5, the recovery was in the range of 1 to 13 percent. Less than 0.5 percent of the total mercury added was present in solution at pH 8.0.

Under very reduced and moderately reduced conditions, essentially all of the mercury added was adsorbed by the sediment material. Greater decomposition of organic matter under oxidized conditions may partially explain a reduction in the capacity of oxidized sediments to sorb mercury. Under oxidized conditions, a decrease in pH from 8 to 5 tremendously decreased the capacity of sediments to retain added mercury at concentrations greater than 6 $\mu\text{g/g}$ sediment. The chloride content of the sediment suspensions increased with decreasing pH because hydrochloric acid was used to maintain pH at 6.5 and 5.0. Sodium hydroxide was used to maintain pH 8. Significant reductions in the capacity of illite, montmorillonite, kaolinite, and hydrous manganese oxides to adsorb mercury due to high chloride contents have been reported in the literature.^{73,74}

Thus the chloride added as a result of pH control may be contributing to the pH response under the conditions of this experiment.

Recovery of the freshly adsorbed mercury in the exchangeable form was determined by extracting the residual solid material remaining from the water-soluble extraction with 1 N sodium acetate adjusted to the pH of the incubated suspensions. The amount of exchangeable mercury is presented in Figures 79a, b, and c for pH 5.0, 6.5, and 8.0, respectively. Recovery of the adsorbed mercury in the exchangeable form was also greatly influenced by both pH and redox potential. Exchangeable mercury increased with an increase in the intensity of oxidation, especially at pH 5.0 and 6.5. The recovery of exchangeable mercury in the strongly reduced and moderately reduced treatments was negligible at all pH levels studied. Maximum recovery occurred at 500 mv at pH 5.0 where more than 75 percent of the freshly adsorbed mercury was recovered in the exchangeable fraction. Mercury was more strongly retained in a reduced, alkaline environment.

The results of this study suggest that reduced sediments have a large capacity for removing mercury from solution in relatively immobile forms. However, oxidized sediment-water systems support considerably higher concentrations of mercury in the relatively mobile soluble and exchangeable forms. Also, a decrease in sediment pH may reduce sediment sorption capacity, adding mercury to the overlying surface water.

It is evident from these studies that under very reduced conditions (-150 mv), essentially all of the mercury added to Mobile Bay, Barataria

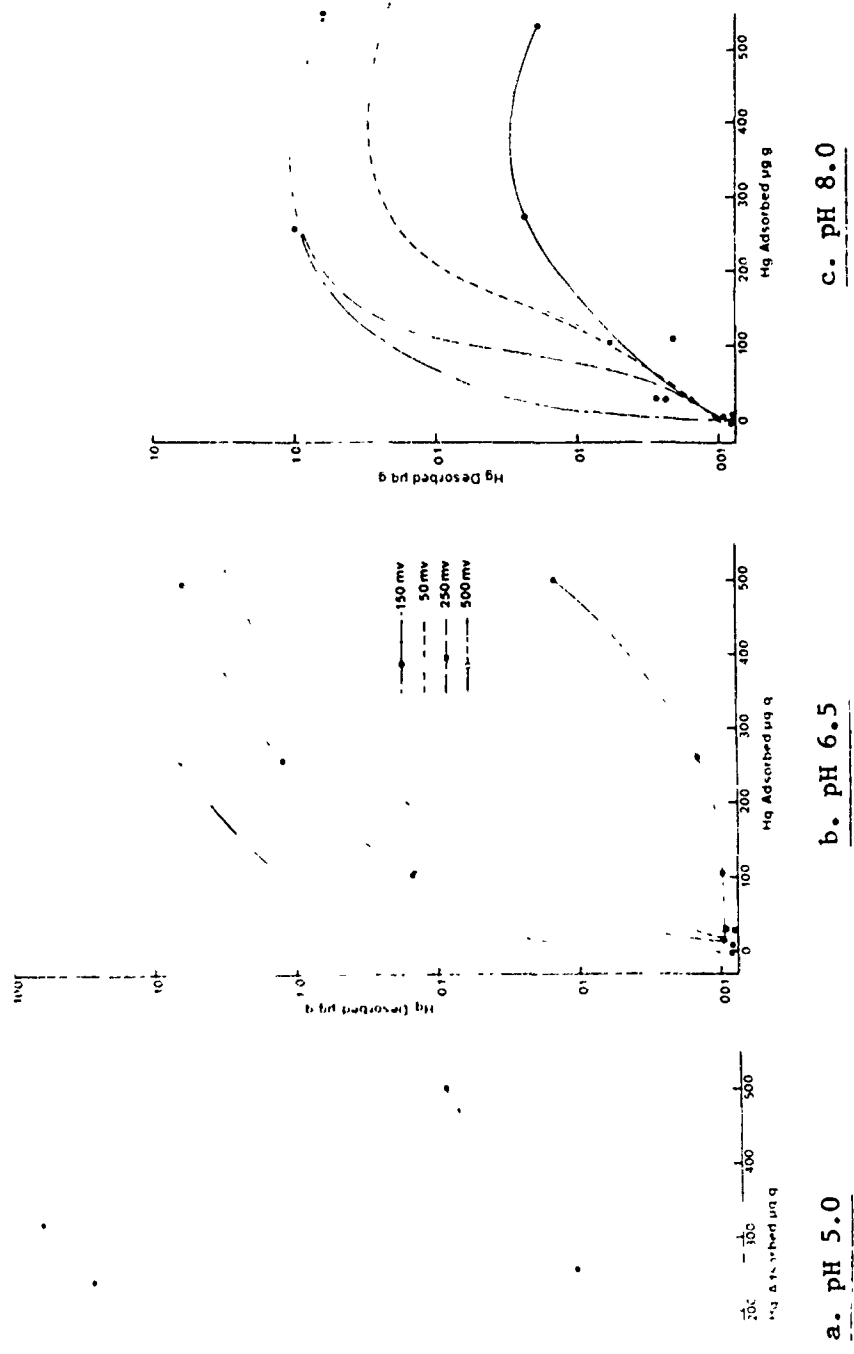


Figure 79. The Effect of Redox Potential on the Desorption of Freshly Adsorbed Mercury in Mississippi River Sediment Suspensions Incubated at pH 5.0, 6.5, and 8.0

Bay, and Mississippi River sediments was adsorbed by the sediment material. Also, that a negligible amount of this adsorbed mercury was removed by a weak exchanger indicates that mercury was very tightly held in some form in the sediments.

Precipitation of mercury as a sulfide in the Mobile Bay material at pH 5.0, 6.5, and 8.0 and at pH 6.5 in the Barataria Bay material may be responsible for this mercury retention. Absence of measurable sulfide in the Mississippi River sediment suspensions incubated at pH 5.0, 6.5, and 8.0 and in Barataria Bay suspensions incubated at pH 8.0 strongly suggests that mercury adsorption in reduced sediments may not be explained fully by sulfide precipitation. Other regulatory factors such as organic matter complexation, adsorption by oxides and hydroxides of iron and manganese, and fixation by clay may play an important role in scavenging mercury from solution. Results discussed elsewhere in this report suggest that most of the mercury adsorbed under reduced conditions was strongly complexed to the insoluble organic material. A significant fraction of adsorbed mercury was also recovered in the reducible fraction which includes metals bound by oxides and hydroxides of iron and manganese.

Influence of pH and Redox Potential on the Distribution of a High-Level Mercury Addition among Selected Chemical Forms in Mississippi River Sediment Material. The distribution of added soluble mercury (260 $\mu\text{g/g}$) in selected chemical fractions of the Mississippi River sediment material was strongly influenced by changes in pH and redox potential (Table 04). In the well-oxidized treatment at pH 5.0, about 90 percent of the added

mercury was recovered in the readily bioavailable water-soluble and exchangeable forms. Recovery in water-soluble and exchangeable forms was reduced to 6 percent at pH 6.5 and to less than 1 percent at pH 8.0. Very little readily bioavailable mercury was recovered in the strongly reduced and moderately reduced treatments at all pH levels studied. Reducible mercury increased with increasing redox potential, indicating some mercury adsorption to poorly crystalline hydrous oxides of iron and manganese. The greatest recovery of mercury at pH 6.5 and 8.0 was in the strongly chelated or complexed form (DTPA extractable).

At low-level mercury additions to the Mississippi River sediment material, recovery in the readily bioavailable soluble and exchangeable forms was favored by a strongly reducing and alkaline (pH 8.0) sediment environment (Table F3). However, at high concentrations of added mercury, an oxidized, acid environment enhanced the readily available forms (Table 04). These contrasting results clearly demonstrate that the availability of mercury will depend on the level of mercury present in sediments and the mercury-binding capacity of the various regulatory mechanisms and factors.

In summary, it was found that redox potential and pH influence the chemical forms and distribution of mercury in Mississippi River sediment material over a large range of mercury content and that mercury mobilization or retention in a specified sediment environment may depend on the amount of mercury present relative to the capacity of the mercury-binding capacity. Where large levels of mercury were added, pH and

redox potential were shown to greatly affect the quantity of water-soluble and easily exchangeable mercury. Among the regulatory factors influenced by pH and redox potential are the rate and intermediate products of organic matter decomposition, the cation exchange properties of organics and clay, the nature and quantity of potential adsorbents, such as colloidal hydrous oxides of iron and manganese, and the speciation of mercury in sediment-water systems. These regulatory factors in turn influence the exchange of mercury between sediments and dredged material and the overlying water. Thus pH and the degree of oxidation or reduction are important considerations in determining the chemistry and bioavailability of mercury in sediment-water systems.

Cadmium

Soluble and Exchangeable Levels Following Incremental Cadmium Additions.

Adsorption/desorption behavior of incremental additions of soluble cadmium was studied in Barataria Bay and Mississippi River sediments incubated at various pH-redox potential combinations. Earlier data on the distribution of ^{109}Cd in various chemical fractions in these sediment materials indicated that most of the ^{109}Cd added to low-pH, oxidized treatments was recovered in the easily bioavailable water-soluble and exchangeable fractions (see Tables J1 and J2 for Barataria Bay and Mississippi River sediments, respectively). Under reduced conditions, a greater proportion of ^{109}Cd added to Barataria Bay suspensions was present in the reducible fraction, presumably adsorbed by oxides and hydroxides of iron and manganese. In reduced Mississippi River

sediments, however, a small proportion of the ^{109}Cd was found in the reducible fraction. More ^{109}Cd was recovered in the DTPA-extractable (strongly chelated or adsorbed to organic matter) and hydrogen peroxide digested-sodium acetate extractable fractions. As the levels of ^{109}Cd in the water-soluble and exchangeable form decreased with changes in pH and redox potential, this bioavailable cadmium was transformed to the more strongly adsorbed reducible and organic fractions. These data and the available literature indicate that the speciation of cadmium and its distribution in sediment-water systems is strongly affected by sediment properties such as cation exchange capacity, mineral colloids, organic matter, carbonates, sulfides, and chlorides present. The purpose of this study was to investigate the influence of pH and redox potential on the adsorption of increasing concentrations of added cadmium and relate this to sediment parameters. Recovery of the freshly adsorbed cadmium in the exchangeable form was also determined under these conditions.

The concentration of cadmium determined in the equilibrium solution 24 hours after each addition to Barataria Bay sediment suspensions is given in Table P1. These data show that in reduced sediment suspensions (-150-mv, 0-mv redox potential) incubated at pH 5.0 and 6.5, at all but the highest level of cadmium added, no appreciable increases in soluble cadmium with increasing concentrations added were observed. However, in the 0-mv treatment at the highest cadmium level studied, 6

and 15 percent of the 400 μg cadmium/g added was recovered in the equilibrium solution at pH 5.0 and 6.5, respectively. In the more oxidized treatments (200 and 450 mv) at pH 5.0 and 6.5, a substantial amount of cadmium was present in the water-soluble fraction, and the proportion of cadmium remaining in the equilibrium solution increased with increasing concentration of cadmium added. At pH 8.0, the recovery of cadmium in the water-soluble fraction in the more reduced treatments was greater than that at pH 5.0 and 6.5, and the concentrations in the equilibrium solution increased with incremental additions. This may be related to the absence of sulfide at pH 8.0. In more oxidized suspensions, the concentration of soluble cadmium followed a general pattern of pH 5.0 > pH 6.5 > pH 8.0. No significant effect of redox potential on cadmium levels in the water-soluble fraction was observed at pH 8.0.

Recovery of the freshly adsorbed cadmium in the exchangeable form was negligible in the -150-mv redox potential treatment incubated at pH 5.0 and 6.5 (Table P1). In the moderately reduced treatment (0 mv), the pattern was similar to that at -150 mv, except at the highest cadmium level added where 6 and 10 percent of the freshly adsorbed cadmium was recovered in the exchangeable fraction at pH 5.0 and 6.5, respectively. Levels of exchangeable cadmium were much greater at 200 mv and 450 mv, particularly at higher incremental additions at pH 5.0 and 6.5. At pH 8.0, the amount of exchangeable cadmium increased with increasing redox potential up to 40 μg cadmium/g added. Beyond that point, no

effect was noticed. The effect of pH on recovery of freshly adsorbed cadmium in the exchangeable form was variable depending on the oxidation-reduction condition of the sediment suspensions. For example, in the very reduced and moderately reduced treatments, the cadmium recovered increased from undetectable levels at pH 5.0 and 6.5 to appreciable concentrations at pH 8.0. On the other hand, in the moderately oxidized and well-oxidized treatments, exchangeable cadmium decreased with increasing pH.

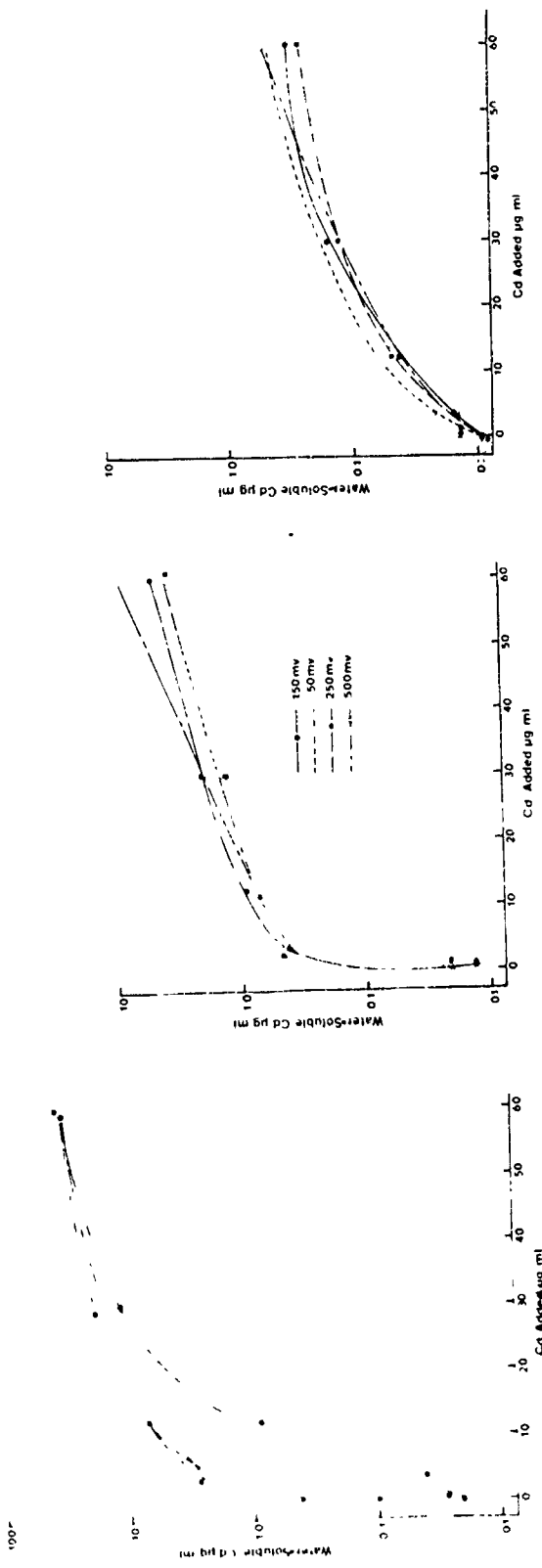
In reduced sediments containing sulfide, the formation of insoluble metal sulfides is thought to limit the concentration of heavy metals in solution. Several hundred μg total sulfide/g solids was detected in the very reduced treatments (-150 mv) incubated at pH 5.0 and 6.5 (Table 8). No sulfide was present in any other pH-redox potential combination in this sediment material. Very low cadmium concentrations were found in the equilibrium solution in the -150-mv, pH 5.0- and 6.5-treatments after incremental additions. The low soluble cadmium levels and the subsequent low recovery of adsorbed cadmium in the exchangeable fraction may be explained by cadmium sulfide precipitation. However, essentially complete adsorption of 185 μg cadmium/g in the moderately reduced treatment (0 mv) at pH 5.0 and 6.5 and subsequent negligible recovery of adsorbed cadmium in the exchangeable form suggest that sulfide precipitation alone cannot explain cadmium adsorption under reduced conditions. Adsorption of soluble cadmium by oxides and hydroxides of iron and manganese, complexation with organic material, and adsorption by crystalline minerals may, in

part, account for the cadmium not recovered in the easily bioavailable water-soluble and exchangeable fractions.

In the more oxidized treatments (200 and 450 mv), an increase in sediment pH resulted in reduced levels of dissolved cadmium and may be related to the formation of comparatively less soluble compounds. At pH 5.0, higher concentrations of cadmium present in the equilibrium solution may be due to the formation of relatively soluble cadmium chloride complexes, due to excess chloride present at pH 5.0 since hydrochloric acid was used to lower suspension pH. The precipitation of cadmium as a hydroxide and carbonate with an increase in pH may, in part, explain lower levels of water-soluble cadmium at pH 6.5 and 8.0.⁵⁴

In Mississippi River sediment suspensions, the amount of cadmium remaining in equilibrium solution after incremental cadmium additions decreased with increasing suspension pH (Figures 80a, b, and c). This effect was noticed at all levels of redox potential studied. The effect of redox potential on water-soluble cadmium was evident only at pH 5.0. Except at the highest levels added, the soluble cadmium concentration in the -150-mv treatment was considerably lower than in the 50-, 250-, and 500-mv treatments. No significant effect of redox potential was observed at pH 6.5 and 8.0.

Exchangeable cadmium generally decreased with an increase in suspension pH at levels of cadmium additions greater than 31 $\mu\text{g/g}$ (Figures 81a, b, and c). Like water-soluble cadmium the effect of redox potential

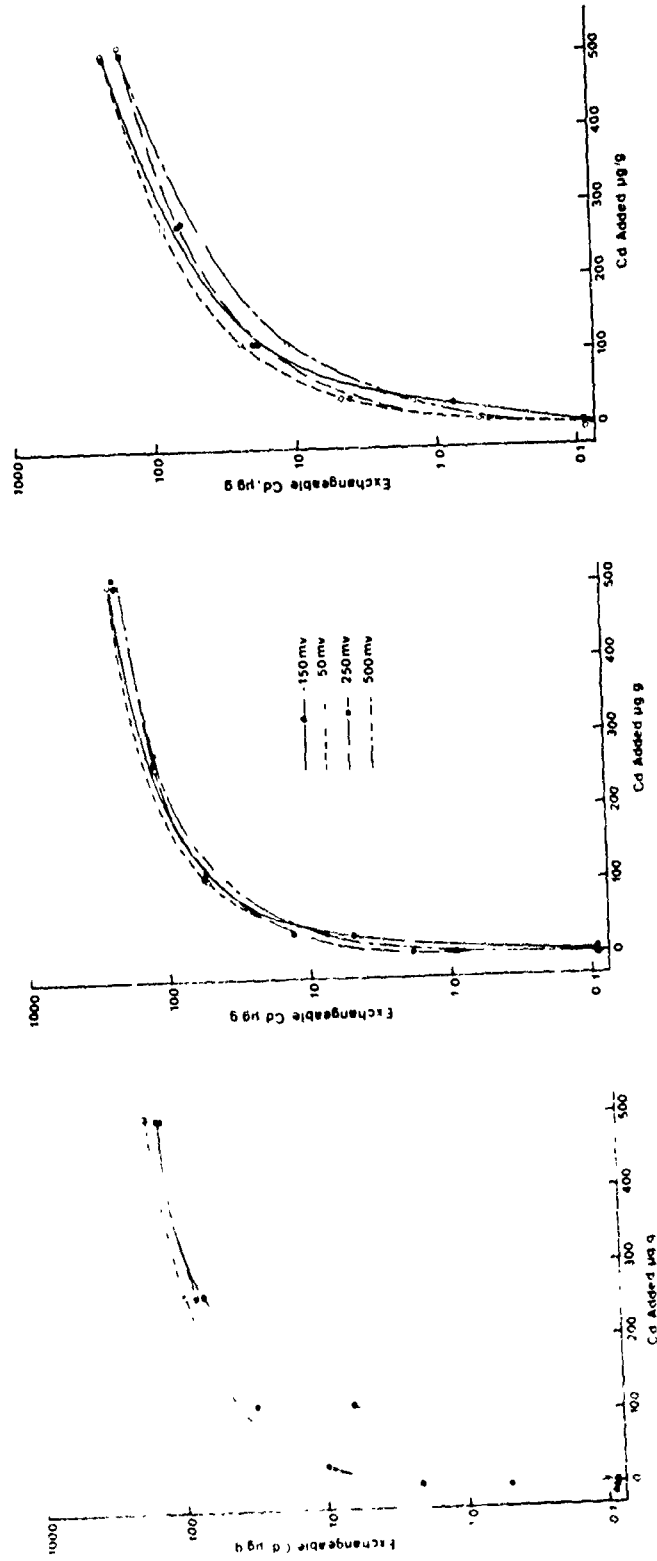


c. pH 8.0

b. pH 6.5

a. pH 5.0

Figure 80. The Effect of Redox Potential on Water-Soluble Cadmium 24 Hours After Incremental Cadmium Additions to Mississippi River Sediment Suspensions Incubated at pH 5.0, 6.5, and 8.0



c. pH 8.0

b. pH 6.5

a. pH 5.0

Figure 81. The Effect of Redox Potential on Exchangeable Cadmium 24 Hours After Incremental Cadmium Additions to Mississippi River Sediment Suspensions Incubated at pH 5.0, 6.5, and 8.0

on exchangeable cadmium was apparent only at pH 5.0 where less cadmium was desorbed in the -150-mv treatment.

When the results obtained from Barataria Bay and Mississippi River sediment suspensions were compared, it was apparent that these two sediment materials differ markedly in their behavior to adsorb soluble cadmium. The following paragraphs are a discussion of some of these differences.

a. Comparatively more cadmium was present in the equilibrium solution in the most reduced treatment (-150 mv) at pH 5.0 and 6.5 in the Mississippi River suspensions than in the Barataria Bay suspensions. It should be recalled from earlier discussions that appreciable amounts of sulfide were measured at pH 5.0 and 6.5 in the Barataria Bay suspensions, whereas no sulfide was detected in the Mississippi River material at any pH level. Precipitation of cadmium as cadmium sulfide in the Barataria Bay suspensions may contribute to lower cadmium concentrations in the equilibrium solution. A similar trend was observed in levels of exchangeable cadmium. Another possible mechanism responsible for greater cadmium adsorption in the more reduced treatments in Barataria Bay sediments may be the higher content of organic material capable of strongly chelating cadmium in an insoluble form. An absence of sulfide and a lower organic matter content may, in part, explain the comparatively greater water-soluble cadmium recovered in Mississippi River suspensions in this treatment.

b. In the Barataria Bay sediment suspensions incubated at pH 8.0, more cadmium was determined in the equilibrium solution as compared to Mississippi River sediment suspensions. This difference was noted at all redox potential levels.

It should be pointed out that the redox potential levels maintained and the incremental levels of cadmium added varied slightly between these sediment materials. As discussed in earlier paragraphs, cadmium solubility at higher pH values is strongly influenced by the formation of sparingly soluble hydroxide and carbonate compounds. In addition to the greater initial carbonate content of the Mississippi River sediment, certain experimental conditions may have enhanced carbonate activity in the Mississippi River suspension relative to the Barataria Bay suspensions. During the suspension incubation period prior to chemical fractionation, a constant stream of nitrogen or nitrogen plus air was passed through Barataria Bay suspensions. This may have purged most of the carbon dioxide, resulting in lower concentration of carbonate. In Mississippi River suspensions, nitrogen or air only was used when necessary to regulate redox potential. The possible difference in carbon dioxide and thus carbonate content of the two suspensions may partially explain the greater cadmium concentration in the Barataria Bay equilibrium solution.

The effect of pH was similar in both sediment materials incubated at the two highest oxidation levels. The water-soluble cadmium levels

decreased with increasing pH. Some of the factors influencing this change were discussed earlier in this section.

In conclusion, the levels of mobile water-soluble and exchangeable cadmium are thought to be strongly influenced by precipitation with sulfide, complexation with organic matter, and by cadmium carbonate formation in natural sediments. Although cadmium availability is generally reduced by an increase in sediment pH, the effect of pH is greatly modified by the presence or absence of sulfide and the organic matter content. In general, a decrease in pH and an increase in redox potential will transform more strongly adsorbed cadmium to an easily exchangeable and/or water-soluble form.

Influence of pH and Redox Potential on the Distribution of a High-Level Cadmium Addition among Selected Chemical Forms in Mississippi River Sediment Material. The data presented in Table P3 show that cadmium concentration in the water-soluble fraction decreased sharply with an increase in suspension pH. This influence of pH was observed at all levels of redox potential maintained. The effect of redox potential on water-soluble cadmium was noticeable only at pH 5.0 where the concentration of cadmium at -150 mv was lower than at higher redox potential treatments. The exchangeable cadmium was also low in this treatment, suggesting that under reduced conditions at pH 5.0, cadmium was more strongly adsorbed than under oxidized conditions. Most of the adsorbed cadmium was recovered in the insoluble organic-bound fraction. Oxidation of organic matter may

reduce the chelating capacity of organic complexes, resulting in additional cadmium present in the easily available water-soluble and exchangeable fractions.

The relative distribution of added cadmium in the various chemical fractions was dependent on pH. The quantity of cadmium in the fractions studied followed the general order of:

pH 5.0 = Water-soluble > Exchangeable >> DTPA Extractable

≈ Reducible ≈ Insoluble Organic Bound

pH 6.5 = Exchangeable > DTPA Extractable > Insoluble Organic Bound

> Water-soluble ≥ Reducible

pH 8.0 = Exchangeable > DTPA Extractable > Insoluble Organic Bound

> Reducible > Water-soluble

These trends strongly indicate that at high concentrations of soluble cadmium added in near-neutral or slightly alkaline sediments, a substantial part will be present either in the exchangeable form or strongly chelated and complexed with insoluble organic matter. A decrease in sediment pH from 8.0 to 6.5 resulted in an increase in the exchangeable fraction at the expense of organic-bound fractions (DTPA extractable and insoluble organic bound). Apparently, the cadmium-binding capacity of organic material is reduced at lower sediment pH. Also at pH 6.5, the reduction in cadmium carbonate stability may result in more cadmium on the exchange complex. A decrease in suspension pH to 6.5 also resulted in an 8- to 20-fold increase in water-soluble cadmium as compared to pH 8.0. A further decrease in sediment pH to 5.0 was accompanied by a large

increase in water-soluble cadmium, accounting for 40 to 58 percent of the total cadmium added. Exchangeable cadmium accounted for 30 to 40 percent of the total cadmium added. Other fractions accounted for only a small proportion of cadmium adsorbed. The water-soluble cadmium was present in a free ionic form, as essentially all of the total water-soluble cadmium was retained when passed through a cation exchange resin column.

The fraction of cadmium adsorbed by or coprecipitated with amorphous and poorly crystalline oxides and hydroxides of iron and manganese as indicated by oxalate extraction (reducible fraction) ranged from 1.6 to 9 percent of total cadmium added. Levels of reducible cadmium were slightly higher at pH 8.0 compared to pH 5.0 and 6.5. These low levels of cadmium associated with iron and manganese oxides and hydroxides at various pH-redox potential combinations suggest that adsorption by colloidal hydrous oxides is not a major control mechanism influencing cadmium availability. Under the conditions of this experiment, adsorption of cadmium on the exchange complex and complexation with insoluble organic matter constitute the major pools of reactive cadmium, influencing its availability in sediment-water systems in the absence of sulfide.

Lead

Adsorption of increasing concentrations of soluble lead added to Mobile Bay sediment suspensions was studied under controlled conditions of pH and redox potential. Subsequent recovery of the freshly adsorbed lead in the exchangeable form was also investigated by extracting the

residual solid material remaining from the water-soluble fraction with 1 N sodium acetate adjusted to the pH of the suspensions.

The data presented in Appendix Q show that essentially all of the soluble lead added was adsorbed by the solid complex at all pH levels studied. The concentration of lead remaining in the equilibrium solution after the addition of 500 μg lead/g ranged from levels undetectable by flame atomic absorption ($\approx 2 \mu\text{g/g}$ solids or $0.25 \mu\text{g/ml}$) to less than 2.4 percent of total added. In the very reduced treatment (-150 mv) incubated at pH 5.0, the level of lead in the water-soluble fraction was below the detection limits even at the highest incremental addition. Measurable amounts of lead were found in the more oxidized treatments. A similar trend was observed at pH 6.5 where water-soluble lead in the -150-mv treatment was lower than found in the higher redox potential treatments. Mobile Bay sediment suspensions are characterized by the presence of appreciable amounts of sulfide under strongly reduced conditions. The undetectable or low levels of soluble lead measured at -150 mv in samples incubated at pH 5.0 and 6.5 may be explained in part by the formation of insoluble lead sulfide. No soluble lead was detected at pH 8.0 in any redox potential treatment.

The results discussed above indicate that 98 to 100 percent of lead added was retained by the solid material at all pH-redox potential combinations. Several mechanisms are known to complex lead in an insoluble form. These include adsorption on the exchange complex, adsorption to

colloidal hydrous oxides, formation of lead carbonate and lead oxide, and complexation with insoluble organic matter. Under reduced conditions, the presence of sulfide may exert a considerable influence on lead solubility. Data on the distribution of ^{210}Pb (see Appendix H) show that 25 to 50 percent of the added ^{210}Pb in the initial fractionation was recovered in the reducible fraction, indicating that much of the active lead was associated with hydrous oxides such as those of iron and manganese.

Recovery of the freshly adsorbed lead in the exchangeable form was strongly influenced by redox potential and pH (Appendix Q). In the very reduced treatment (-150 mv) at pH 5.0 and 6.5, only 1 to 2 percent of the freshly adsorbed lead was recovered. Exchangeable lead was found only at the highest lead increment. The formation of lead sulfide likely contributed to the unavailability of lead in the strongly reduced suspensions. At higher redox potential levels incubated at pH 5.0, exchangeable lead increased with incremental additions. A maximum of 39 to 52 percent of the freshly adsorbed lead was extracted by sodium acetate at 500 μg lead/g added. Exchangeable lead ranged from 6 to 10 percent at pH 6.5 and decreased below detection limits at pH 8.0.

These results indicate that the presence of lead in readily bioavailable forms is strongly pH dependent. At pH 5.0 in the absence of sulfide, 50 to 80 percent of the added lead was not released in soluble or exchangeable forms. Ninety to 100 percent of that added was not recovered

in readily available forms at higher pH levels. Essentially complete adsorption of soluble lead and negligible levels of exchangeable lead under strongly reduced conditions may be largely due to sulfide precipitation. Under more oxidized conditions, a decrease in exchangeable lead with increasing suspension pH may be due to greater adsorption by colloidal hydrous oxides, complexation with insoluble organic matter, and formation of insoluble compounds of lead oxide and lead carbonate. The relative contribution of these control mechanisms in regulating lead solubility is discussed in an earlier section under lead chemistry.

Effect of Dissolved Oxygen on the Chemical Form

and Distribution of Metal Ions and

Nutrient Elements in Barataria Bay Sediment Suspensions

This experiment was planned to study the effect of various concentrations of oxygen on chemical transformations of selected elements as a function of redox potential and pH changes with time in Barataria Bay sediment suspensions. The results are discussed in the order of redox potential, pH, iron, manganese, zinc, copper, nitrogen, and phosphorus.

Redox Potential

The data plotted in Figure 82 indicate that aeration of a sediment-water system, in an otherwise closed system with a nitrogen-oxygen gas mixture containing 21 percent oxygen and 2.11 percent oxygen completely oxidized reduced sediment suspensions in 2.5 and 9 days, respectively.

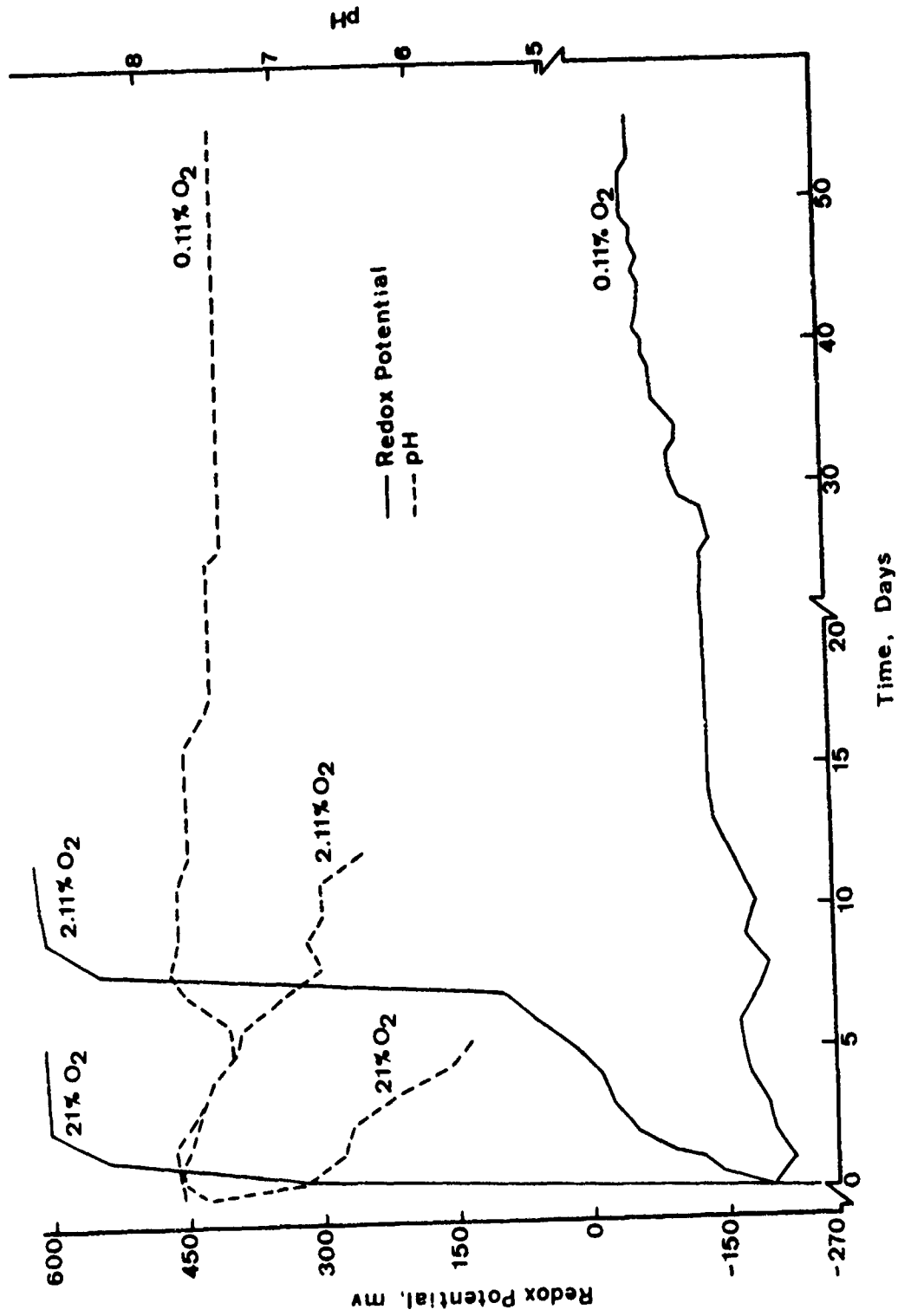


Figure 82. The Effect of Dissolved Oxygen and Incubation Time on the Redox Potential and pH of Barataria Bay Sediment Suspensions

In these suspensions, the redox potential increased to around 600 mv. No further increase in redox potential was observed upon subsequent purging at these oxygen levels. The redox potential of the suspension treated with 0.11 percent oxygen increased slowly with time. After 5 days, the redox potential of this suspension increased by only 30 mv. After 56 days, the redox potential increased to -65 mv, a moderately reduced condition.

These data demonstrate that both concentration of oxygen and time of exposure have a strong effect on the oxidation-reduction status of sediment suspensions which may influence the bioavailability of toxic metals and nutrients.⁷⁵

pH

The influence of varying oxygen levels on suspension pH is also indicated in Figure 82. In the 21-percent oxygen treatment, the pH of the sediment suspension decreased from an initial value of 7.7 to 5.7 after 5.5 days of constant purging. Where sediment suspensions were purged with 2.11 percent oxygen, the pH dropped from 7.7 to 6.5 after 12 days. The 0.11-percent oxygen treatment reduced suspension pH from an initial pH of 7.8 to 7.5 after 56 days of constant purging. This small change in suspension pH corresponded to the relatively small change in redox potential found at the 0.11-percent oxygen level. This suggests that changes in pH and redox potential are interrelated. However, data show that the two higher oxygen levels induced a greater

differential in pH than in redox potential.

Iron

The concentration of dissolved oxygen may influence several sediment parameters. Some of the sediment properties affected include pH, redox potential, organic matter decomposition, and cation exchange properties. The time of equilibration with different oxygen levels may strongly modify equilibrium conditions, making it difficult to single out specific effects of certain sediment components. For example, purging with 21 percent oxygen for extended periods of time will not only oxidize ferrous iron to ferric iron, a form active in adsorbing trace metals, but will also oxidize sulfide to sulfate, possibly releasing metals in a soluble form. Also, reducing sediment pH as a result of oxidation may favor solubilization of certain metals. Each affected process may increase or decrease elemental mobility, and only net effects can be observed in terms of concentrations of the various elements involved.

The concentration of water-soluble iron in various oxygen treatments was below the detectable limit of flame atomic absorption analysis ($\approx 0.4 \mu\text{g}$ iron/ml in solution, Table R1). Purging with 0.11 percent oxygen did not appreciably reduce exchangeable iron concentration with time. When sediment suspensions were purged with 2.1 percent oxygen for 288 hours, exchangeable iron decreased to nondetectable levels (Table R1). This decrease may be due to oxidation during this period, resulting in ferric

compounds not extracted with 0.5 N sodium acetate. In the 21-percent oxygen treatment, however, the exchangeable iron at the end of 132 hours purging was greater than initial levels. Apparently a decrease in pH from the initial value of 7.7 to 5.7 at the end of the incubation period may have resulted in the transformation of potentially reactive ferric hydroxides to a more available exchangeable fraction due to acidic pH.

The residual solid material from the sodium acetate extraction was shaken with 0.1 M hydroxylamine hydrochloride solution prepared in 0.01 M nitric acid.²² This extraction procedure is reported to selectively dissolve manganese oxides from soils and sediments while having little effect on iron oxides. Elements recovered by this procedure are termed easily reducible. Iron in this fraction ranged from 780 to 1600 $\mu\text{g/g}$, which comprised 15 to 67 percent of the total reducible fraction (easily reducible + reducible). The implications of the greater proportion of iron extracted by this reagent than reported elsewhere²² will be discussed in the manganese section following iron. The effect of the 0.11-percent oxygen treatment during 120 hours of constant purging on easily reducible iron was negligible. In the 2.11-percent and 21-percent oxygen treatments, easily reducible iron decreased with increasing redox potential. Purging with 21 percent oxygen was more effective in reducing extractable iron levels than the 2.11-percent oxygen treatment.

The oxalate-extractable iron (reducible) increased with incubation time at all levels of dissolved oxygen. At the end of the experiment,

the quantity of reducible iron extracted decreased with a decrease in oxygen levels in the order of 21 percent > 2.11 percent > 0.11 percent. The increased oxalate-extractable (reducible) iron with time may be due to lower sediment pH values at the end of the incubation. The measured pH at the final sampling times was 5.7, 6.5, and 7.5 for the 21-, 2.11-, and 0.11-percent oxygen treatments, respectively. Also, intense oxidation conditions due to greater dissolved oxygen levels may affect the oxidation of organic matter and release more iron from insoluble organics to be transformed to the reducible fraction.

This study indicates that dissolved oxygen levels strongly influenced the quantity of reducible iron, a form which may act as a scavenger for heavy metals. In this study, pH was not controlled, and there was relatively little change in soluble and exchangeable iron.

Manganese

The effect of dissolved oxygen concentration on water-soluble manganese as a function of time was variable (Table R2). In the 0.11-percent oxygen treatment, little trend in soluble manganese with time was observed. Since there was only a slight increase in redox potential after 5 days, the system was still very reduced. Purging with 2.11-percent and 21-percent oxygen levels resulted in a gradual decrease in the water-soluble manganese with increasing redox potential. Ten to 63 percent of the water-soluble manganese was associated with the soluble organic complex. The high proportion of uncharged soluble manganese

under oxidized conditions resulted from relatively little changes in this fraction with time, while a substantial decrease in total water-soluble manganese occurred in some treatments.

Sodium acetate-extractable manganese (exchangeable) generally increased only slightly with increasing redox potential in the 2.11-percent and 21-percent oxygen treatments. No change in manganese concentrations was noticed with the 0.11-percent oxygen treatment.

There was little trend in easily reducible manganese with time. This extraction is reported to selectively extract oxides and hydroxides of manganese, and these data show that 55 to 77 percent of total reducible manganese was present in the easily reducible form. The purpose of this selective extraction was to differentiate metal ions associated with manganese oxides from those associated with iron oxides. Though this fraction dissolved a greater proportion of the reactive manganese, the dissolution of iron from iron oxides was eight to ten orders of magnitude greater. This substantial proportion of reactive iron extracted with manganese makes it difficult to relate associated metals to hydrous oxides of manganese only.

The oxalate-extractable manganese (reducible) increased with incubation time in the 0.11-percent and 21-percent oxygen treatments. The effect of incubation time (or increasing redox potential) was not consistent in the 2.11-percent oxygen treatment. Total reducible manganese (easily reducible + reducible) may act as an absorbent for heavy metals and regulate their exchange between sediments and overlying water

as discussed earlier in this report.

Zinc

Water-soluble zinc ranged from nondetectable levels to over 4 $\mu\text{g/g}$, depending on oxygen treatments and time of incubation (Table R3). The highest concentrations were observed at redox potential levels of 150 and 610 mv in the 21-percent oxygen treatment. This may be due to a decrease in suspension pH, which solubilized more zinc. At higher pH values, most of the zinc will be in the sparingly soluble zinc carbonate form.

Exchangeable zinc exceeded 1 $\mu\text{g/g}$ only in the 21- and 2.11-percent oxygen treatments which became well oxidized. Again, the corresponding decrease in pH may have contributed to this observation. Zinc associated with the easily reducible fraction decreased with incubation time in the 0.11-percent treatment. In the 2.11-percent oxygen treatment, easily reducible zinc decreased initially up to -160 mv, but a further increase in redox potential to -50, +100, and +640 mv was accompanied by an increase in easily reducible zinc. In the 21-percent oxygen treatment, easily reducible zinc increased consistently with an increase in redox potential. No consistent relationship was found between easily reducible manganese and zinc or between easily reducible iron and zinc.

Reducible zinc decreased with increasing redox potential in the 2.11-percent oxygen treatment. In the 0.11-percent oxygen treatment,

reducible zinc increased slightly with incubation time. Little trend was noted in the 21-percent oxygen treatment.

Soluble and adsorbed zinc in the sediment-water system is strongly influenced by several factors including sulfide precipitation, adsorption by oxides and hydroxides of iron and manganese, formation of zinc carbonate and hydroxides, and decomposition of organics bonded to zinc. The extraction of zinc from sediment material will be simultaneously influenced by these and other processes which may result in variable mobilization trends as the oxidation status of a sediment changes.

Copper

Water-soluble, exchangeable, and easily reducible copper could not be detected by flame atomic absorption. Reducible copper was detected only at redox potentials of 100 mv and higher. Reducible copper in the 2.11-percent oxygen treatment increased from 1.98 to 5.26 $\mu\text{g/g}$ with an increase in redox potential from 100 mv to 640 mv. A similar trend was observed in the 21-percent oxygen treatment where an increase in redox potential from 150 mv to 610 mv was accompanied by an increase in reducible copper from 1.76 to 10.46 $\mu\text{g/g}$. These trends in reducible copper were strongly related with reducible iron, indicating that copper was adsorbed by oxides and hydroxides of iron under the conditions of this experiment.

Ammonium-Nitrogen

The levels of sodium acetate-extractable ammonium-nitrogen were

found to be influenced by the concentration of oxygen and the equilibration time (Table R4). This effect was largely a function of redox potential. In both the 21-percent and 2.11-percent oxygen treatments, the concentration of ammonium-nitrogen decreased as redox potential increased. In the 2.11-percent oxygen treatment, nitrification of ammonium-nitrogen commenced sometime between 48 and 168 hours after the treatments began. It is possible that where the purging gas contained only 2.11 percent oxygen, most of the initially added oxygen was consumed in the oxidation of iron and manganese, and little oxygen was available for nitrification. In the 21-percent oxygen treatment, sufficient oxygen was available for several oxidation processes to proceed simultaneously. No change in the level of ammonium-nitrogen was observed in the 0.11-percent oxygen treatment. In this treatment the sediment suspensions remained very reduced during the 56-day incubation.

Phosphorus

Water-soluble phosphorus decreased with increasing redox potential in the 21-percent and 2.11-percent oxygen treatments (Table R4). Oxidation of ferrous iron to ferric oxyhydroxides to which phosphate can absorb is important in regulating the concentration of soluble phosphorus. The comparison of iron (Table R1) and phosphorus data (Table R4) show that water-soluble phosphorus was strongly related with easily reducible and water-soluble iron. The concentration of soluble phosphorus in the 0.11-percent oxygen treatment increased slightly with time, which means that

under reduced conditions more phosphorus was solubilized with time. Some of the effects of redox potential on phosphorus transformations have been discussed earlier in this report.

Metal Complexation with Soluble Organics

in Barataria Bay Sediment Material

Efficiency of Chelex-100 Resin for Separating Water-Soluble Free and Complexed Ions

In this study, five solutions containing varying proportions of free copper and an EDTA-copper complex were prepared to determine the efficiency of Chelex-100 cation exchange resin for separating free and complexed ions. A comparison of the theoretical and experimentally measured amounts of complexed ions in the five prepared solutions are presented in Table 17.

This ion exchange technique was effective for the separation of EDTA-complexed and free copper ions. The stoichiometry of trace metal complexation with naturally occurring ligands in sediment-water systems is unknown due to the diverse nature of the natural organic ligands present. However, it is reasonable to assume that this type of complexation is an important regulatory mechanism for soluble trace metals in surface waters and sediments.

Table 17

Efficiency of Chelex-100 Resin for Separating Soluble Free
Cationic and Complexed Copper

Total Copper Concentration	Complexed, Theoretical	Complexed, Experimental	Deviation
-- $\mu\text{g Cu/ml}$ --	-- % --	-- % --	-- % --
100	100	99.70	-0.10
100	75	76.32	+1.32
100	50	47.28	-2.72
100	25	25.56	+0.56
100	0	0.03	+0.03

The Effect of Zinc, Lead, and Copper Additions on the Chelation of Soluble
Iron and Manganese

Total soluble and soluble-complexed iron, manganese, and zinc were determined in a reduced Barataria Bay sediment-water mixture. Additions of 100 μg zinc, copper, and lead/g solids were then made to determine the influence of these added cations on the distribution of iron, manganese, and zinc between the free cationic and soluble-complexed state.

Table 18 gives the concentrations of total water-soluble iron, manganese, and zinc in the filtered solutions before and after passing through the Chelex-100 resin column.

Table 18

Water-Soluble Iron, Manganese, and Zinc before and
after Passing Through a Chelex-100 Resin Column

Sample	Iron		Manganese		Zinc	
	Total	After Resin Treatment	Total	After Resin Treatment	Total	After Resin Treatment
	----- mg/l -----					
Sediment Solution	1.08	0.68	0.80	0.00	0.11	0.10
Solution + 100 $\mu\text{g/g Zn}^{++}$	0.93	0.53	0.70	0.00	0.10	0.10
Solution + 100 $\mu\text{g/g Cu}^{++}$	0.73	0.33	0.75	0.00	0.11	0.10
Solution + 100 $\mu\text{g/g Pb}^{++}$	1.10	0.30	0.88	0.00	0.10	0.10

At the time of sampling, the average redox potential and pH of the incubated sediments were -259 mv and 7.55, respectively.

The addition of zinc, copper, and lead to the sediment had an effect on the soluble levels of iron and manganese. Differences in the zinc concentration seem too low to be significant. The addition of zinc and copper lowered the concentration of water-soluble iron and manganese in the sediment, while a lead addition increased their soluble concentrations.

Different proportions of iron, manganese, and zinc were found to be in a free cationic state as determined by passing the solution phase through the cation exchange resin. Soluble iron was partially retained by the resin, manganese was completely bound, and no zinc was retained by the exchange resin.

Assuming that the quantity of these elements not retained by the resin was chelated, a distribution of the total water-soluble elements between the chelated and free cationic fractions may be calculated (Table 19).

Table 19

The Distribution of Soluble Iron, Manganese, and Zinc Between Free and Chelated Forms and the Effect of Added Zinc, Copper, and Lead on this Distribution

Sample	Iron		Manganese		Zinc	
	Free	Chelated	Free	Chelated	Free	Chelated
	-----		%		-----	
Sediment Solution	37.2	62.8	100	0.0	9.0	91.0
Solution + 100 µg/g Zn ⁺⁺	43.2	56.8	100	0.0	0.0	100.0
Solution + 100 µg/g Cu ⁺⁺	55.2	44.8	100	0.0	4.7	95.3
Solution + 100 µg/g Pb ⁺⁺	72.7	27.3	100	0.0	0.0	100.0

In the original sediment, 62.8 percent of the water-soluble iron was chelated, and the addition of zinc, copper, or lead to the sediment resulted in a decrease in chelated iron. These data indicate that the stability of iron chelated under reduced conditions is rather low and that other heavy metals may displace iron from these complexes. Given the same concentrations of added ions, lead was more effective in displacing iron from chelates than copper and zinc.

Soluble manganese was not chelated and appeared to be completely cationic in nature. This manganese was probably present in the divalent cationic form (Mn^{2+}).

Zinc was found to be completely complexed and was not affected by the addition of other heavy metals to the system. It should be noted that although 100 μg zinc/g was added to the sediment suspension, no increase in soluble zinc was noted (Table 18). An identical observation was made for copper and lead. The total water-soluble copper was less than 10 $\mu g/l$ while lead was less than 100 $\mu g/l$.

Possible explanations for this behavior include the formation of insoluble sulfides in the reduced sediment and the binding of metals by insoluble organic compounds.

Additional information on the behavior of these elements was obtained by filtering the water-soluble fraction ($<0.45 \mu$) through a "pellicon membrane Millipore filter" with a nominal molecular weight limit of 25,000. Only particles having molecular weights less than 25,000 can pass this membrane filter.

Table 20 indicates that all soluble iron and zinc was associated with particles of an apparent molecular weight greater than 25,000. All soluble manganese was apparently associated with particles of molecular weight less than 25,000.

Table 20
Percentage of Water-Soluble Iron, Manganese, and Zinc
Having a Molecular Weight Greater than 25,000

Sample	Percentage of Elements Having a Molecular Weight of > 25,000		
	Iron	Manganese	Zinc
Sediment Solution	100	0	100
Solution + 100 µg/g Zn ⁺⁺	100	0	100
Solution + 100 µg/g Cu ⁺⁺	100	0	100
Solution + 100 µg/g Pb ⁺⁺	100	0	100

These results for manganese and zinc confirm what was obtained by passing the water-soluble fraction through a Chelex-100 resin column (Tables 18 and 19). All water-soluble manganese was bound by the resin and had a molecular weight smaller than 25,000. As stated earlier, the most probable form of manganese under these conditions is Mn²⁺.

Zinc was not bound by the resin, and these data indicate that all water-soluble zinc was bound to particles having a molecular weight

greater than 25,000. These soluble "particles" (operationally defined as $<0.45 \mu$) may be colloidal organic matter, although 25,000 is a relatively high average molecular weight for soluble organic compounds.

All zinc and iron were associated with particles with an apparent molecular weight greater than 25,000. These data only partially confirm the conclusions drawn from Table 19, which showed that some free cationic iron was in solution, the proportion of which increased by adding other metal ions to the sediment. On the other hand, these results may suggest that a considerable amount of the iron is very loosely bound and can be easily released.

Additional information is given by noting the color of the water-soluble fraction. After passing through the 0.45μ -filter, the solution had a yellow color. Color was not altered by passing this solution through a Chelex-100 resin column. However, the solution passing the pellicon membrane filter lost all color and was completely clear. This indicated that all colored material, presumably organic material with fulvic acid properties, had a molecular weight greater than 25,000, and that all iron was bound to this material. A portion of this iron seems to be very loosely bound and can be released either by the competitive action of other metal ions or by a weak acid ion exchange resin such as Chelex-100.

In the water-soluble fraction of a reduced Barataria Bay sediment, zinc was firmly bound by soluble organic material in a molecular weight

fraction greater than 25,000. The water-soluble manganese was present in a free cationic form, probably as Mn^{2+} .

Iron was completely bound in a fraction with a molecular weight greater than 25,000, but may be easily displaced by other materials, indicating that under these experimental conditions, the stability of iron chelates is rather weak.

Influence of pH and Redox Potential on the Particle-Size Distribution of Water-Soluble Iron, Manganese, Mercury, and Lead

In this study, a series of filters of varying pore size and nominal molecular weight limits were used to determine the influence of pH and redox potential on the particle-size distribution of soluble iron, manganese, mercury, and lead in solution extracted from Barataria Bay sediment.

The pH and redox potential at sampling time in the oxidizing and reducing solutions are given in Figure 83. The average slope of the curves was found to be -59 mv/pH in both cases.

Iron. The concentration of iron in the different fractions under reducing conditions is given in Table 21.

Total iron refers to the iron measured prior to filtration through membrane filters. All other values refer to the iron concentration in the solution passed through a filter with a designated pore size or molecular weight limit.

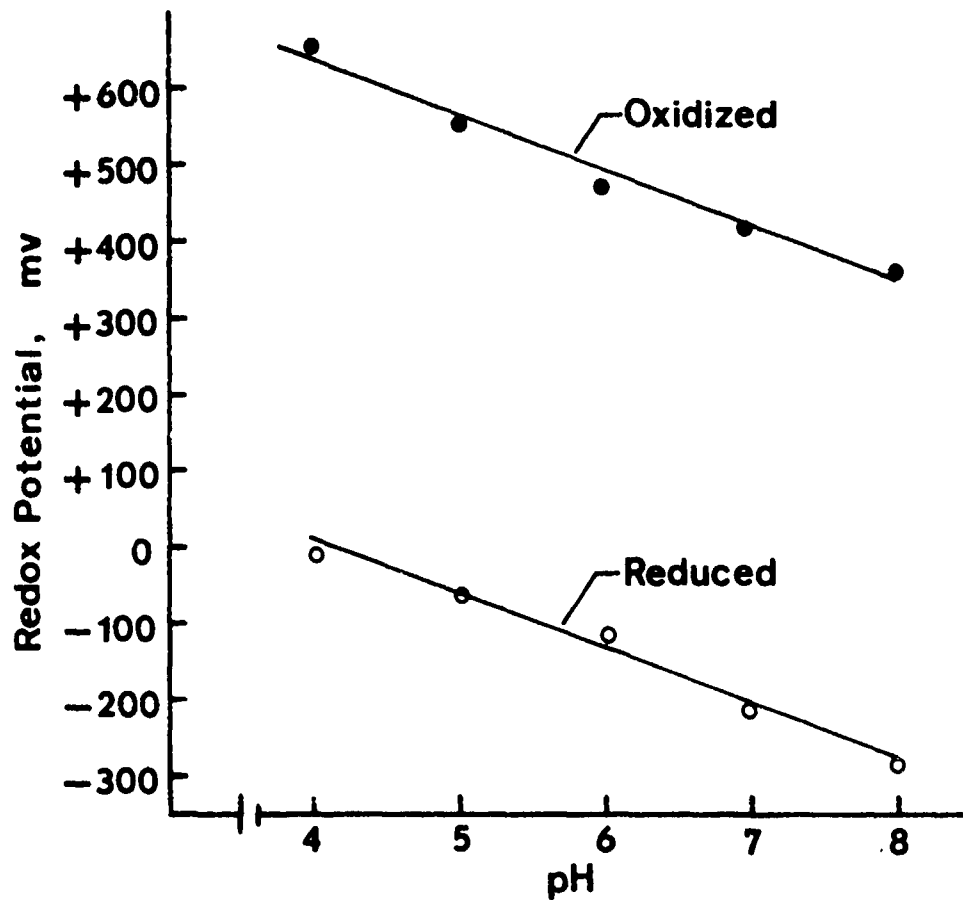


Figure 83. The pH and Redox Potential of Oxidized and Reduced Barataria Bay Sediment Suspensions at Time of Sampling

Table 21
Concentration of Iron in Different Size Fractions
Under Reducing Conditions

Fraction	pH 4	pH 5	pH 6	pH 7	pH 8
	----- mg Fe/l -----				
Total	1.74	1.75	1.74	1.71	1.71
0.45 μ	1.57	1.50	1.45	1.25	1.30
100,000 MW*	1.52	1.38	1.23	0.32	0.05
25,000 MW*	1.52	1.38	1.20	0.09	0.05
1,000 MW*	1.46	1.38	1.20	0.00	0.00
Not Exch.**	0.11	0.00	0.00	0.09	0.37

*Molecular Weight.

**Not Exchangeable by Chelex-100 resin.

Although the color of the freshly filtered sediment solution was yellow, the color changed from a dark brownish-green to blue at pH 8 after 2 days. At lower pH levels, the color after 2 days was greenish-yellow to yellow. Once filtered through the 0.45- μ filter, all solutions were yellow. However, this color was completely lost after filtering through a 100,000 molecular weight pellicon filter. Table 22 shows the change in optical density of the different solutions with pH. Measurements were made at 425 nm.

It was apparent that the intensity of color in the water-soluble (<0.45 μ) fraction decreased with decreasing pH and that no colored

Table 22

Optical Density of Sample Solution vs. pH at 425 nm

Fraction	pH 4	pH 5	pH 6	pH 7	pH 8
	----- Optical Density -----				
Total	0.125	0.125	0.125	0.110	0.115
0.45 μ	0.046	0.058	0.059	0.062	0.099
100,000 MW	0.010	0.010	0.010	0.010	0.010
25,000 MW	0.010	0.010	0.010	0.010	0.010
1,000 MW	0.010	0.010	0.010	0.010	0.010
Not exch.	0.046	0.058	0.059	0.062	0.099

material was adsorbed by the resin. The nature of this colored material with an apparent molecular weight greater than 100,000 will be discussed after considering additional data. From the data in Table 21, the quantity of iron in the different size fractions was calculated, and the results are shown in Figure 84. The fraction greater than 100,000 molecular weight contains in fact particles smaller than 0.45 μ , but having a molecular weight greater than 100,000. It was found that under reducing conditions, the predominant fraction at lower pH values (4 to 6) was in the low molecular weight range. The ion exchange data (Figure 85) showed that under these conditions, almost 100 percent of the water-soluble

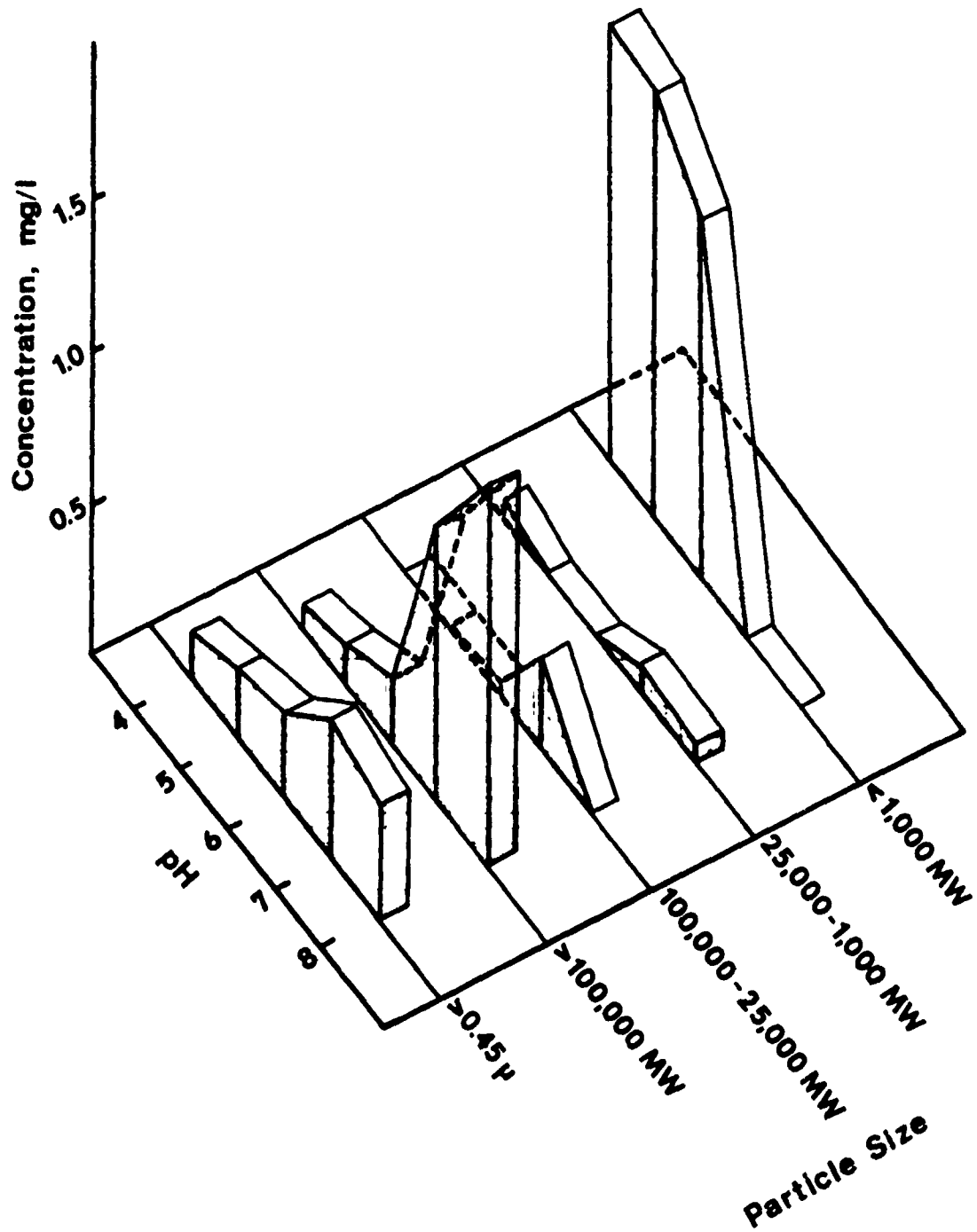


Figure 84. The Effect of pH on the Particle Size Distribution of Soluble Iron in Reduced Barataria Bay Interstitial Water

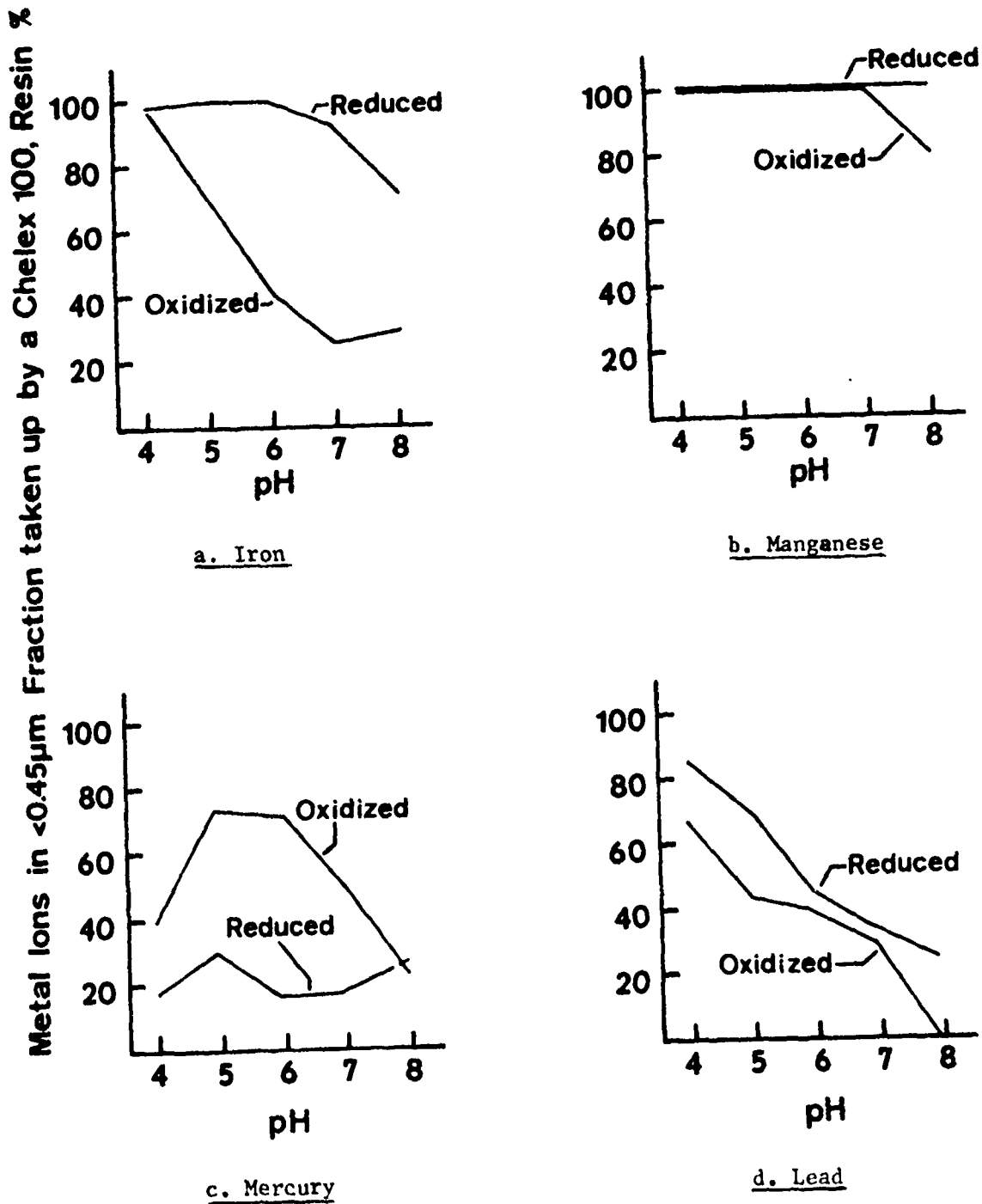


Figure 85. The Effects of pH and Redox Potential on the Cationic Nature of Soluble Iron, Manganese, Mercury, and Lead in Baratataria Bay Sediment Suspensions

(<0.45 μ) iron was taken up by the Chelex resin, indicating that this iron was cationic and probably Fe^{2+} . At pH 7 and 8, no iron remained in the low molecular weight fraction, and most was shifted to the greater than 100,000 molecular weight fraction. However, the ion exchange data showed that more than 70 percent (pH 8.0) can be taken up by the resin, which indicated that the stability of iron compounds in these larger molecular weight fractions is relatively low.

The concentration of iron in the different size fractions under oxidizing conditions is given in Table 23.

Table 23
Concentration of Iron in Different Size Fractions
Under Oxidizing Conditions

Fraction	pH 4	pH 5	pH 6	pH 7	pH 8
	----- mg Fe/l -----				
Total	1.78	1.60	1.67	1.64	1.66
<0.45 μ	1.18	0.86	0.87	0.93	1.05
<0.10 μ	1.11	0.51	0.31	0.36	0.43
<100,000 MW	0.93	0.18	0.00	0.00	0.00
<25,000 MW	0.93	0.17	0.00	0.00	0.00
<1,000 MW	0.93	0.16	0.00	0.00	0.00
Not Exch.	0.00	0.26	0.52	0.68	0.77

Oxidizing the previously reduced solution resulted in a color change from yellow to a red-yellow, but, as for the reduced solution, all colored material was retained by the 100,000 molecular weight filter.

Figure 86 shows that under oxidizing conditions, most iron was associated with larger particle sizes ($>0.45 \mu$ and $>100,000$ MW). Only at pH 4 and 5 did some of the water-soluble iron appear in the lowest molecular weight fraction. The $>0.45\text{-}\mu$ fraction retained the red-yellow hematite-like material, while the yellow soluble compounds together with the soluble iron were retained by the 100,000 molecular weight filter.

The ion exchange data in Figure 85 indicated that under oxidizing conditions at all pH values above pH 4, less iron was retained by the resin than under reducing conditions. This suggested the iron-yellow material complex was more stable at higher redox potentials. The total soluble iron at pH 4 was found to be completely cationic. However, thermodynamic data given in the literature indicate that free ferric ions cannot exist at pH 4; thus these ions must consist of Fe^{2+} stabilized at lower pH or perhaps stable oxides such as FeOH^{++} .

Considering the nature of the yellow-colored soluble material referred to previously, it is obvious that it is organic and is not caused by colloidal iron or manganese oxides. Manganese cannot be involved in the color formation as the color still exists when all manganese from the solution has been removed by the exchange resin. A similar reasoning is valid for iron. In the reduced solution at lower pH, all soluble

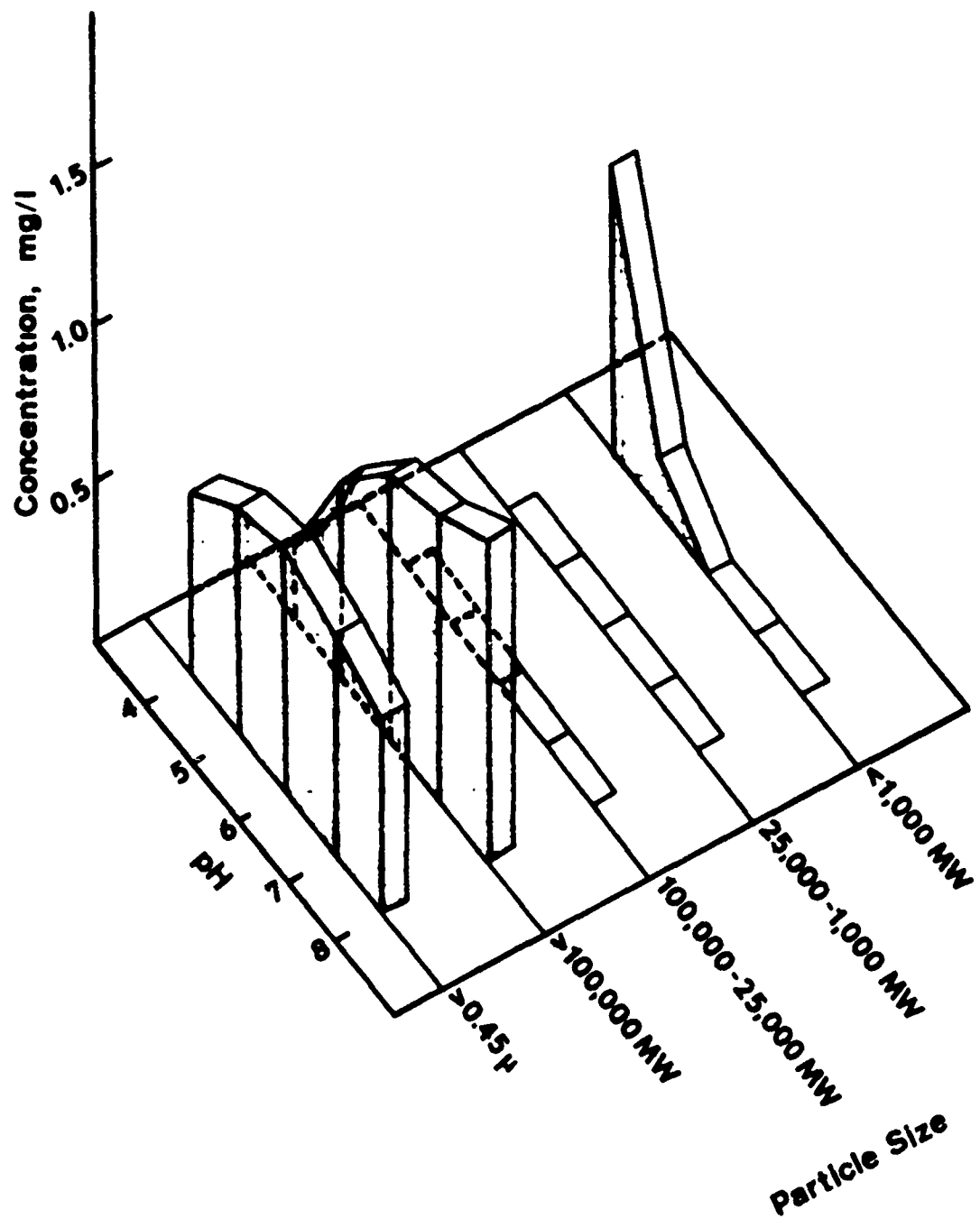


Figure 86. The Effect of pH on the particle Size Distribution of Soluble Iron in Oxidized Barataria Bay Interstitial Water

iron was taken up by the resin but the color persisted. It may be concluded that the yellow-colored soluble material is organic, with an apparent molecular weight greater than 100,000. It is obvious that the intensity of the yellow color may be affected by iron and manganese in solution, and it is generally known that the optical density of a soluble chelate increases with increasing stability of the complex. Table 22 shows an increase in optical density in the soluble fraction (<0.45 μ) with increasing pH, indicating that more stable complexes were formed at higher pH. This is also suggested by the ion exchange data in Figure 85.

Manganese. The concentration of manganese in the different fractions under reducing and oxidizing conditions are given in Tables 24 and 25, respectively.

Table 24
Concentration of Manganese in Different Size
Fractions Under Reducing Conditions

Fraction	pH 4	pH 5	pH 6	pH 7	pH 8
	mg Mn/l				
Total	1.17	1.15	1.19	1.16	1.16
<0.45 μ	1.17	1.15	1.16	1.16	1.13
<100,000 MW	1.17	1.15	1.15	1.16	1.05
<25,000 MW	1.17	1.15	1.15	1.16	1.05
<1,000 MW	1.16	1.13	1.15	1.16	1.05
Not Exch.	0.00	0.00	0.00	0.00	0.00

Table 25
 Concentration of Manganese in Different Size
 Fractions Under Oxidizing Conditions

Fraction	pH 4	pH 5	pH 6	pH 7	pH 8
	----- mg Mn/l -----				
Total	1.30	1.23	1.23	1.26	1.27
<0.45 μ	1.17	1.16	1.20	1.18	1.00
<0.10 μ	1.17	1.16	1.20	1.06	0.84
<100,000 MW	1.17	1.16	1.10	1.06	0.63
<25,000 MW	1.17	1.16	1.10	1.02	0.63
<1,000 MW	1.17	1.16	1.10	1.02	0.63
Not Exch.	0.00	0.00	0.00	0.00	0.20

From Figures 87 and 88 it is seen that in both reducing and oxidizing conditions, all soluble manganese was in the lowest molecular weight fraction. Ion exchange data (Figure 85) show that manganese was completely removed from solution by the cation exchange resin. It was concluded that the primary soluble form of manganese was Mn^{2+} and that only a minor fraction became colloidal upon oxidation. It is obvious that there is a great difference between the behavior of iron and manganese in these systems and that the often assumed similarity between

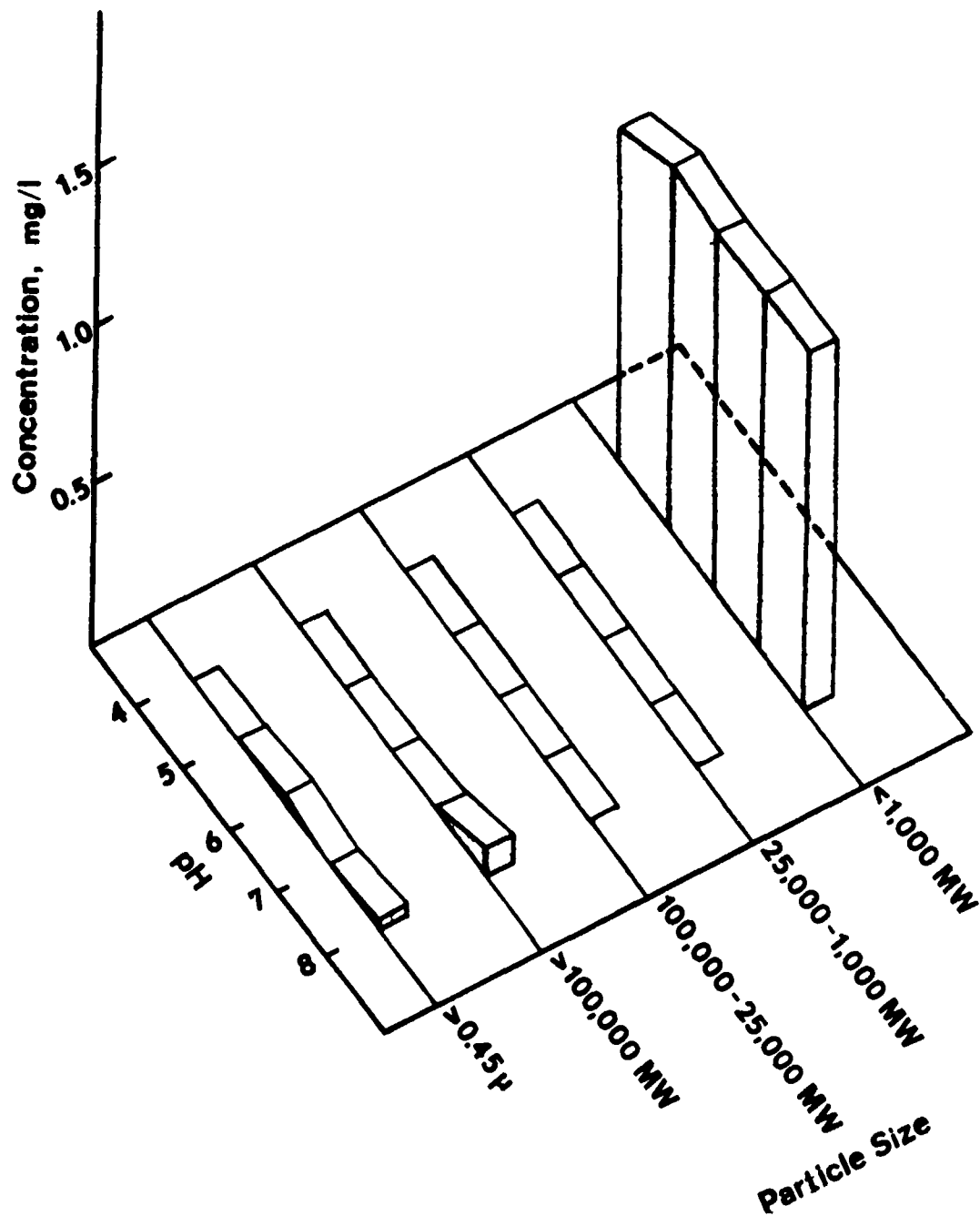


Figure 87. The Effect of pH on the Particle Size Distribution of Soluble Manganese in Reduced Barataria Bay Interstitial Water

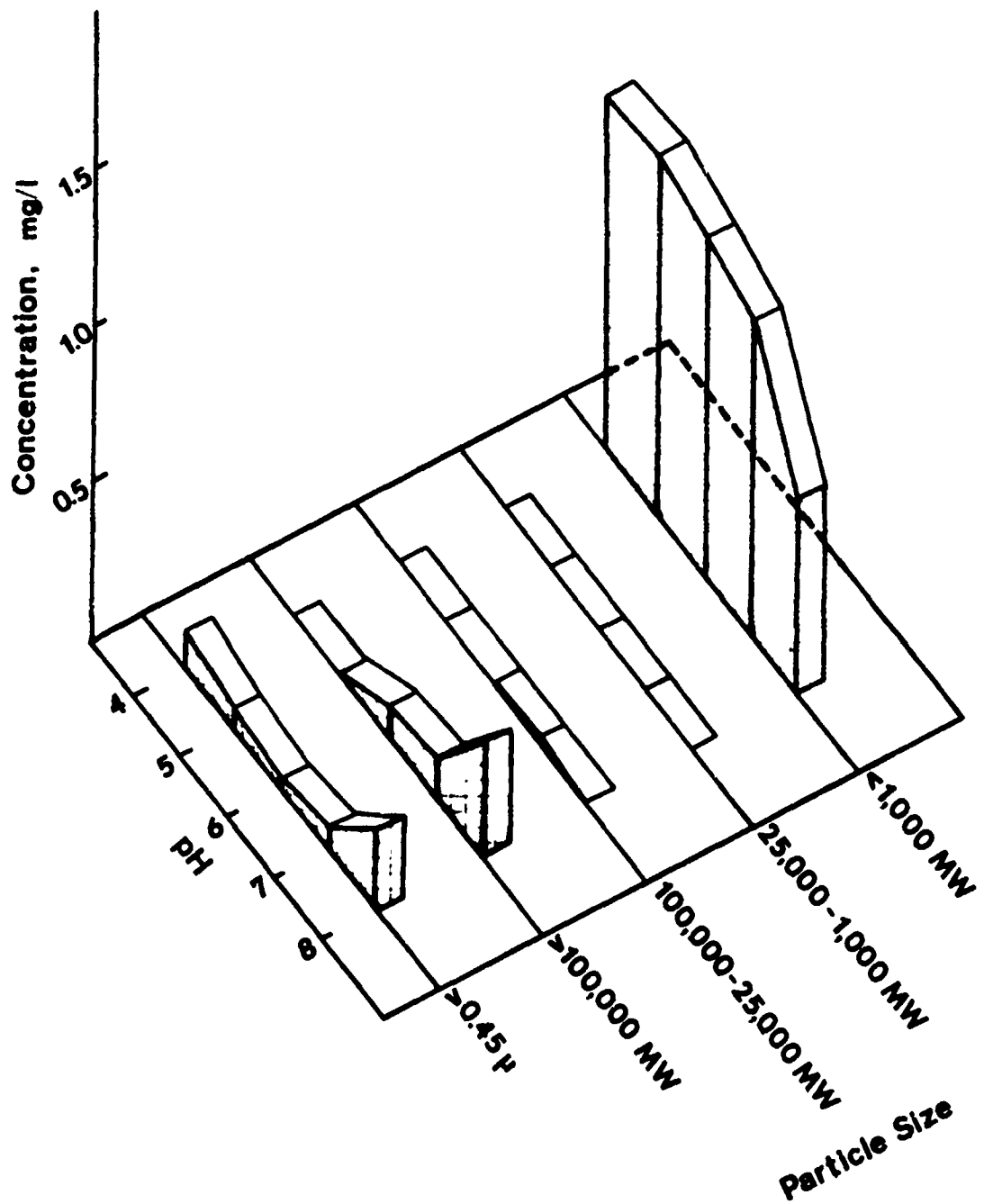


Figure 88. The Effect of pH on the Particle Size Distribution of Soluble Manganese in Oxidized Barataria Bay Interstitial Water

their chemistry may be invalid.

Mercury. Mercury was added as the ^{203}Hg isotope. The quantities of ^{203}Hg referred to in Tables 26 and 27 are relative to the total quantity added (assumed to be 100 units).

Table 26
Relative Activity of ^{203}Hg in Different Size
Fractions Under Reducing Conditions

Fraction	Relative Activity				
	pH 4	pH 5	pH 6	pH 7	pH 8
	----- % -----				
Total	100	100	100	100	100
<0.45 μ	6.0	7.2	12.3	14.9	22.3
<0.10 μ	2.2	2.0	2.5	---	---
<100,000 MW	0.1	0.1	0.2	0.1	0.1
<25,000 MW	0.1	0.1	0.1	0.1	0.1
<1,000 MW	0.0	0.1	0.0	0.1	0.1
Not Exch.	5.0	5.1	10.3	12.2	16.6

From Figures 89 and 90, it is apparent that mercury was associated with the larger particle-size fractions. Under oxidized conditions, more mercury was shifted to the soluble 100,000 and lower molecular

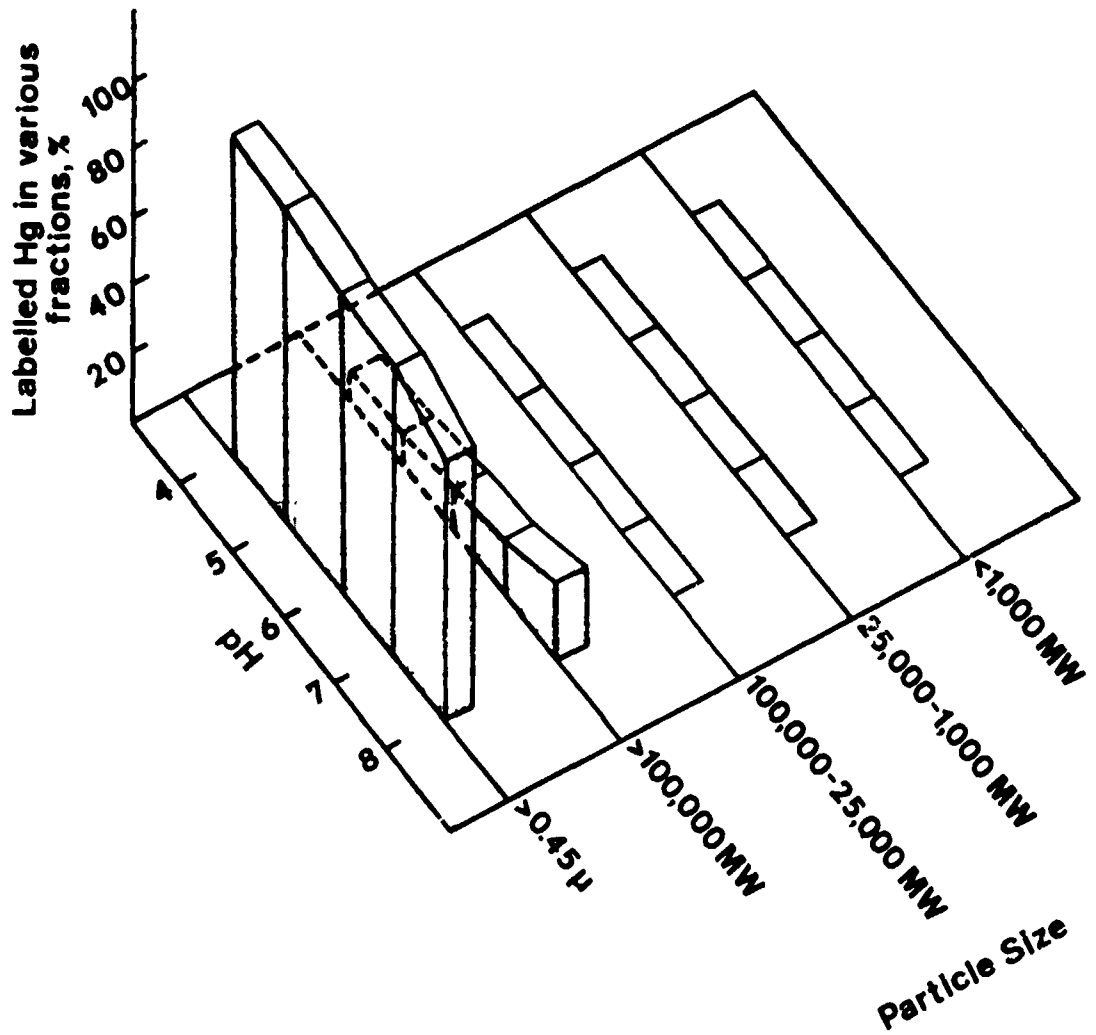


Figure 89. The Effect of pH on the Particle Size Distribution of Soluble Mercury in Reduced Barataria Bay Interstitial Water

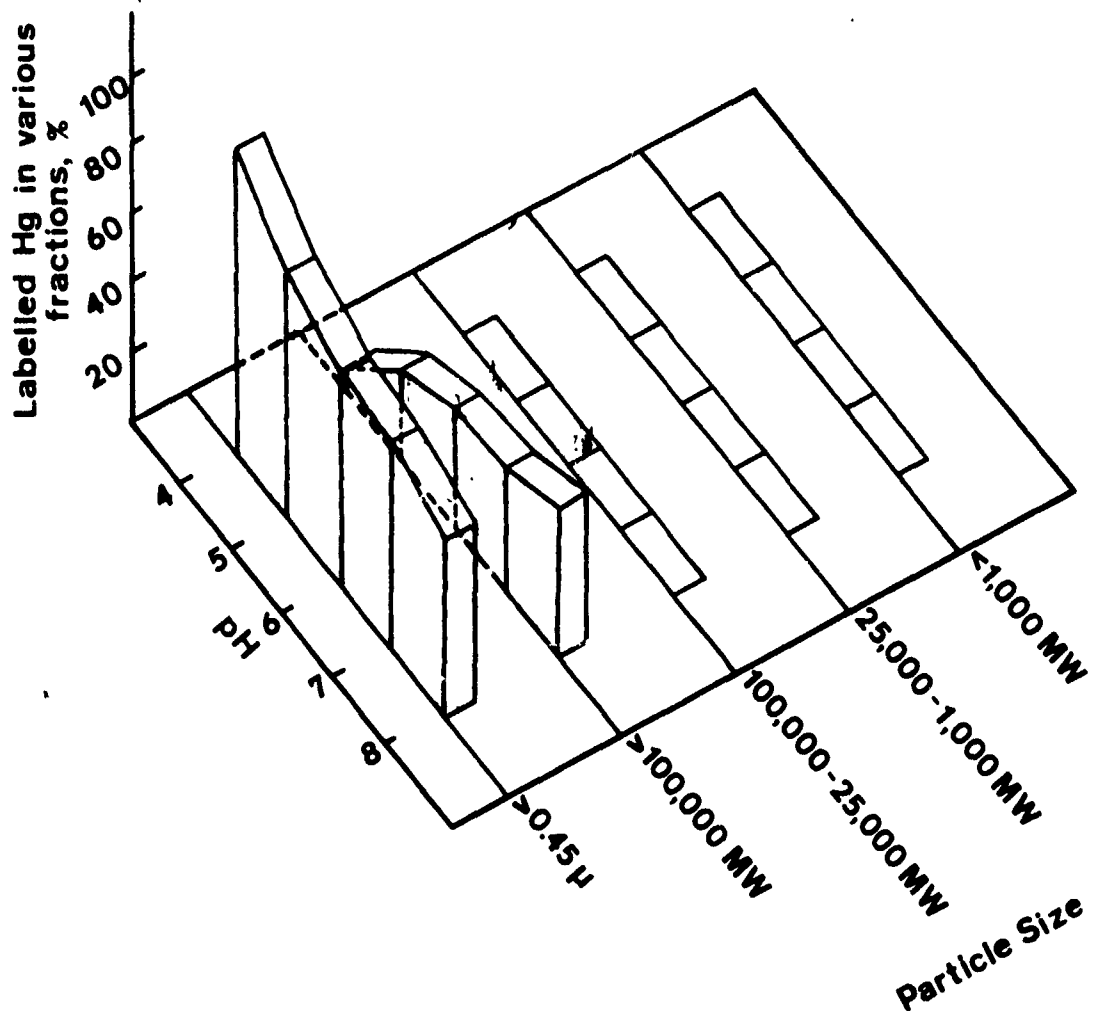


Figure 90. The Effect of pH on the Particle Size Distribution of Soluble Mercury in Oxidized Barataria Bay Interstitial Water

Table 27
 Relative Activity of ^{203}Hg in Different Size
 Fractions Under Oxidizing Conditions

Fraction	Relative Activity				
	pH 4	pH 5	pH 6	pH 7	pH 8
	----- % -----				
Total	100	100	100	100	100
<0.45 μ	7.8	26.1	35.5	36.7	45.3
<0.10 μ	4.2	4.0	5.4	6.8	11.9
<100,000 MW	0.2	0.5	0.8	0.6	0.7
<25,000 MW	0.2	0.3	0.4	0.3	0.1
<1,000 MW	0.2	0.2	0.3	0.2	0.0
Not Exch.	4.9	6.8	10.2	18.3	35.1

weight fractions, but the amounts were too small to be presented in the figure.

Ion exchange data (Figure 85) show that a relatively small percentage of the water-soluble mercury was removed from solution by the Chelex-100 resin under reducing conditions, indicating that these fractions form a stable compound with the yellow-colored material. It was also found that under oxidizing conditions, more mercury was taken up by the resin as mercury was shifted to a soluble form.

The larger particle-size fraction (>0.45 μ m) associated with mercury was thought to be the very insoluble mercuric sulfide in the reduced solution, while oxidation resulted in a partial release of mercury, which may then be coprecipitated with iron oxides (exchangeable by the resin) or form stable compounds with soluble organics.

Lead. Lead was added as the ^{210}Pb isotope. The relative amounts of ^{210}Pb refer to a total added quantity of 100 in the different filtrates of reduced and oxidized solutions indicated in Tables 28 and 29, respectively.

Table 28
Relative Activity of ^{210}Pb in Different Size Fractions Under Reducing Conditions

Fraction	Relative Activity				
	pH 4	pH 5	pH 6	pH 7	pH 8
	----- % -----				
Total	100	100	100	100	100
<0.45 μ	22.6	1.3	1.5	1.7	2.1
<0.10 μ	19.2	1.0	0.2	0.1	0.3
<100,000 MW	13.6	0.1	0.1	0.1	0.0
<25,000 MW	11.1	0.1	0.1	0.1	0.0
<1,000 MW	9.5	0.1	0.1	0.1	0.0
Not Exch.	3.3	0.4	0.8	1.1	1.6

Table 29
Relative Activity of ^{210}Pb in Different Size
Fractions Under Oxidizing Conditions

Fraction	Relative Activity				
	pH 4	pH 5	pH 6	pH 7	pH 8
	----- % -----				
Total	100	100	100	100	100
<0.45 μ	13.1	1.3	1.6	1.3	1.6
<0.10 μ	12.9	0.3	0.1	0.5	0.3
<100,000 MW	11.0	0.1	0.1	0.1	0.0
<25,000 MW	10.5	0.1	0.1	0.1	0.0
<1,000 MW	9.3	0.1	0.1	0.1	0.0
Not Exch.	1.5	1.2	1.0	0.9	1.6

As for mercury, it is seen from Figures 91 and 92 that almost all lead was immobilized in the >0.45- μ fraction under reducing and oxidizing conditions. Only at pH 4 was an appreciable portion of the total lead added recovered in the lowest molecular weight fraction (\approx 9 percent).

Ion exchange data (Figure 85) indicated that lead in the soluble fractions (less than 2 percent of the total) is in a stable complex form at higher pH levels and shows a decrease in stability with decreasing pH.

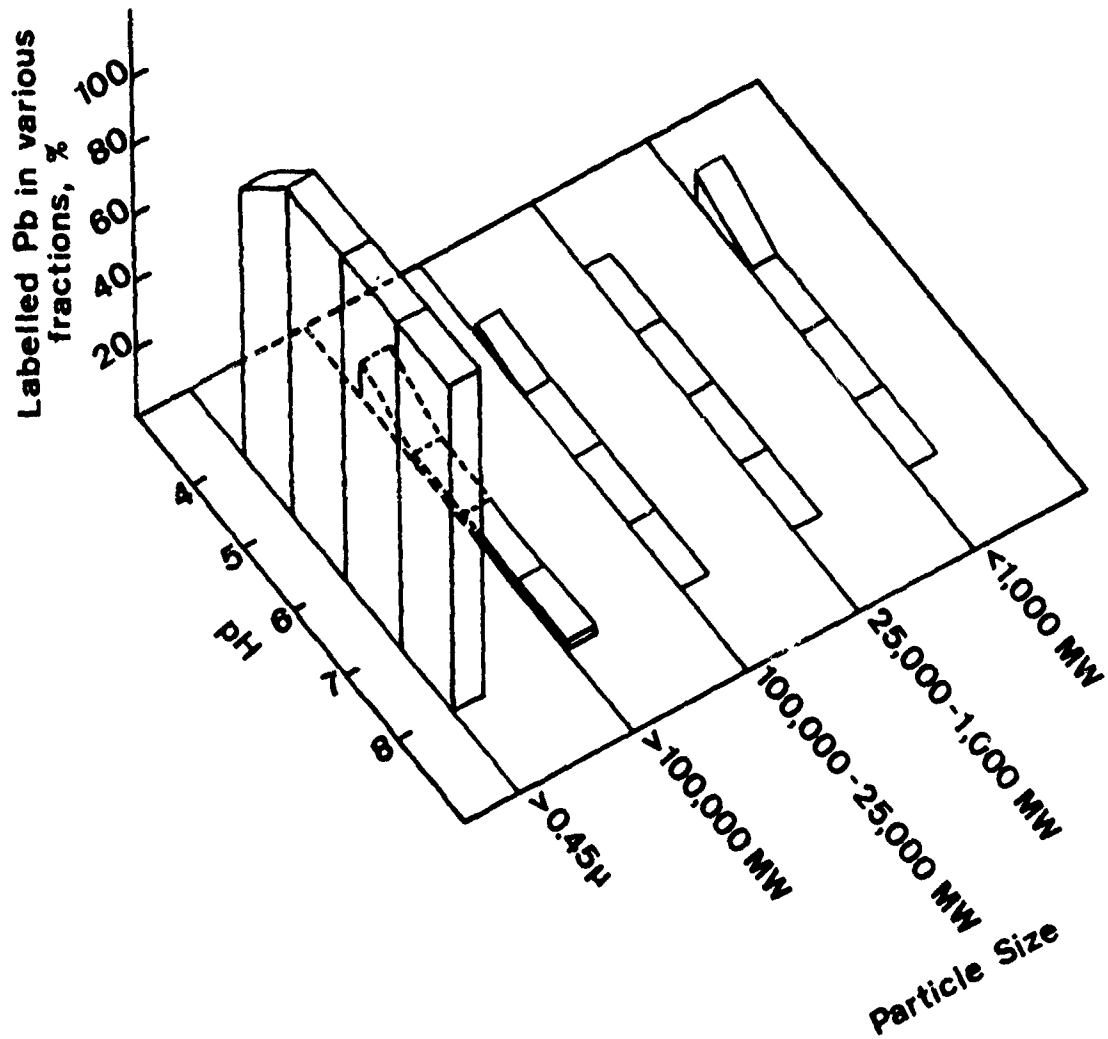


Figure 91. The Effect of pH on the Particle Size Distribution of Soluble Lead in Reduced Barataria Bay Interstitial Water

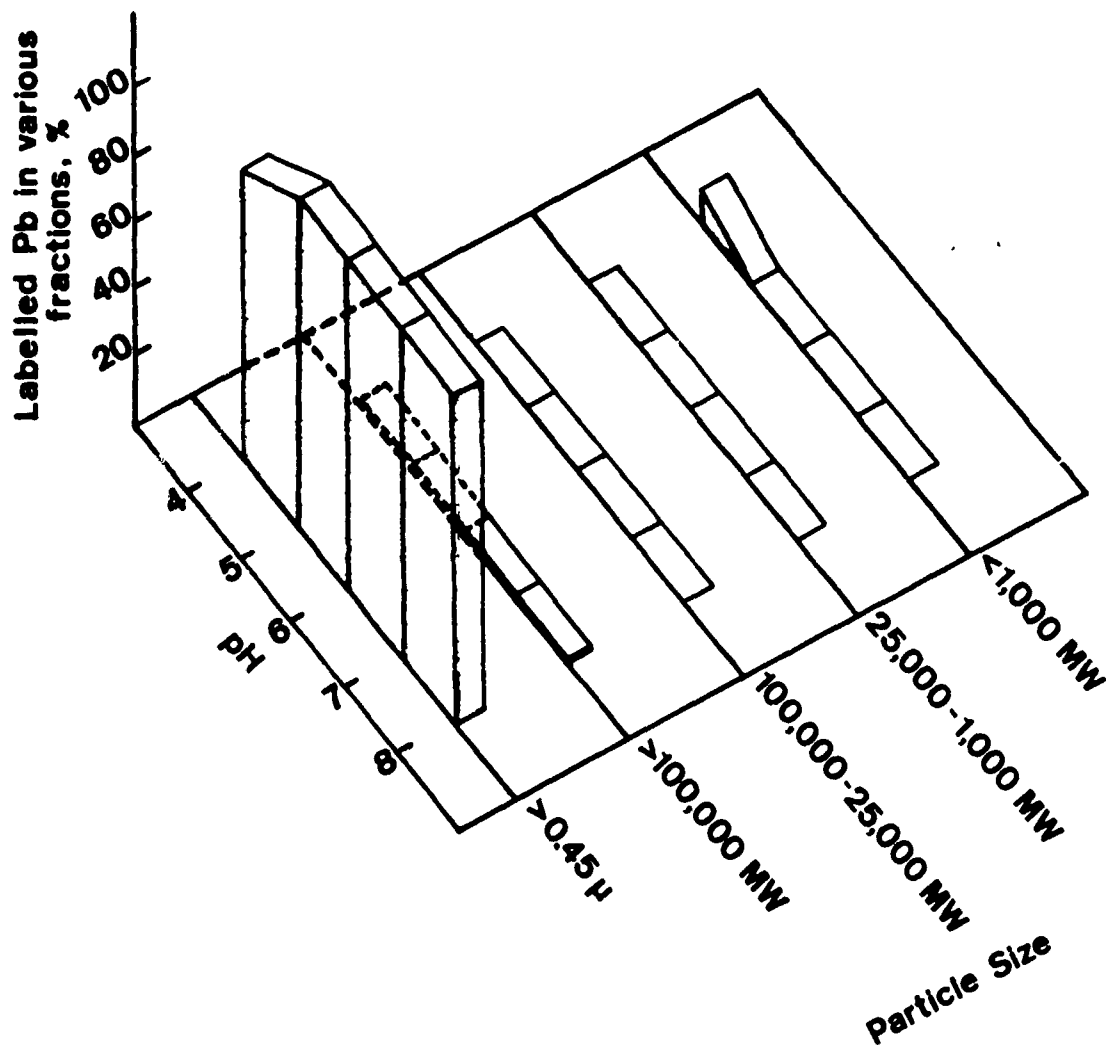


Figure 92. The Effect of pH on the Particle Size Distribution of Soluble Lead in Oxidized Barataria Bay Interstitial Water

CONCLUSIONS

Sulfide-Sulfur

Several hundred μg sulfide-sulfur/g solids were generally found under strongly reduced (-150 mv) environments at all pH levels studied in the Barataria Bay, Mobile Bay, and Calcasieu River sediment suspensions. Barataria Bay material incubated at pH 8.0 was an exception. No sulfide was detected in the strongly reduced Mississippi River material at any pH. This observation corresponded with the comparatively small organic carbon content and greater natural redox potential of this material. No sulfide was detected at 50, 250, or 500 mv in any sediment suspension. No volatile sulfide (H_2S) was detected in any treatment, presumably due to the moderate pH levels and the excess ferrous iron in these sediments, which forms a stable complex with sulfide.

Where sediments are dredged, transported, then redeposited in open water for disposal, it is likely that most metal-sulfide complexes will remain stable during a brief exposure to an oxygenated aqueous environment before again becoming part of the reduced sediments at the disposal site. However, release of sulfide-bound metals may be important in surface layers of land-applied dredged material where gradual drainage and subsequent oxidation may occur over extended periods of time.

Though metal sulfide formation is reported to be an important regulatory factor limiting the soluble levels of toxic and trace metals in strongly reduced sediment-water systems containing sulfide, there was

generally no great release of any metal when the redox potential was raised beyond the stability boundary for sulfide. If considerable quantities of metals were precipitated as sulfide, it was apparent that other processes regulating the solubility of metals became active as a sediment-water environment changed to favor the oxidation of sulfide and the subsequent release of sulfide-bound metals. There was a moderate increase in the soluble and exchangeable forms of some metals such as zinc and cadmium as the redox potential increased from strongly reducing levels favoring sulfide stability to redox potentials just above the sulfide stability boundary. However, the quantities of these metals released, possibly by sulfide oxidation, were modest compared to the quantities of potentially reactive metals present in the sediments. There was some evidence that processes affected by redox potential other than sulfide precipitation were equally as important as, or perhaps more important than, sulfide in complexing with metals under strongly reduced conditions. Metal complex formation with insoluble organics was thought to be an effective scavenger for metals, especially at low redox potentials.

Iron

Relatively large quantities of iron subject to chemical transformations induced by changes in pH and redox potential were found in all sediment materials studied. Both pH and redox potential strongly affected the readily available soluble and exchangeable iron. In strongly reduced sediments incubated at pH 5.0 and 6.5, soluble and exchangeable iron

levels of several hundred to a few thousand $\mu\text{g/g}$ oven dry solids were generally found. As the suspensions were oxidized to 250 and 500 mv and/or increased in pH to mildly alkaline levels, these readily available forms of iron decreased to very low levels. The soluble ferrous iron was likely oxidized to ferric iron that precipitated as insoluble ferric oxides and hydroxides included in the reducible form. The greatest quantity of iron was recovered in the reducible form in all sediment materials studied. Though levels of reducible iron were not influenced by changes in pH and redox potential to as great a degree as were levels of soluble and exchangeable iron, these data indicate that several thousand μg iron/g solids in a form potentially effective as a trace metal adsorbent was present over the entire range of pH and redox potential studied. In addition to the poorly crystalline ferric oxides likely formed from soluble and exchangeable iron as the pH and redox potential were increased, large levels of reductant extractable iron were also recovered from strongly reduced sediment materials.

Studies conducted to determine the ionic nature of soluble iron indicate that much of this iron may be present as soluble organic complexes. However, the stability of the iron-organic complex was shown to be very low such that most iron was released in a cationic form by brief contact with a weak cation exchange resin, particularly at concentrations greater than a few μg iron/ml. Due to the low stability of the iron-soluble organic complex, essentially all soluble iron was believed to behave essentially as free cationic iron. Thus during dredging

and dredged material disposal, the initial presence of iron as a soluble organic complex is not believed to significantly affect the chemical transformation of soluble ferrous iron to ferric compounds potentially active as trace metal adsorbents.

The quantity of soluble and exchangeable ferrous iron potentially available for oxidation to surface-active forms exceeded the quantities of soluble toxic metals by several orders of magnitude. Thus the quantities of freshly formed hydrous ferric oxides produced as a reduced sediment is oxidized as well as the levels of colloidal iron oxides and hydroxides extracted from strongly reduced sediments suggested the presence of a relatively large amount of iron potentially active as a metal adsorbent. As indicated in subsequent paragraphs, some of the potentially toxic metals studied were strongly associated with the reducible phase thought to consist of colloidal hydrous oxides such as those of iron and manganese.

Manganese

As with iron, the levels of potentially reactive manganese capable of forming compounds active in the adsorption of other metals was far greater than the quantities of toxic metals found. Both pH and redox potential were found to regulate levels of soluble and exchangeable manganese. Generally, these forms of manganese decreased with an increase in both pH and redox potential, particularly as the redox potential increased above 250 mv. The decrease in soluble and exchangeable

manganese as pH and redox potential increased was accompanied by an increase in reducible manganese. As recently formed hydrous oxides of manganese are thought to be effective adsorbents for trace and toxic metals, the transformation of soluble and exchangeable manganese to an oxidized form as reduced sediments are mixed with oxygenated surface waters may be an important regulatory mechanism reducing soluble levels of toxic metal during dredging and dredged material disposal.

Experiments designed to study the nature of soluble manganese indicate that essentially all soluble manganese was present as a free divalent cation.

Zinc

Total zinc in the sediment materials studied ranged from around 100 to 200 $\mu\text{g/g}$. From 40 to 85 percent of this was recovered in potentially reactive forms by the chemical fractionation procedure applied.

Both pH and redox potential strongly influenced soluble and exchangeable zinc. Exchangeable zinc levels were generally greater than soluble levels. The levels of both forms decreased with an increase in pH. Zinc hydroxide and carbonate formation likely contributed to the reduced solubility of zinc with increasing pH.

Studies conducted at pH 7.5 suggested that low levels of soluble zinc at this pH are rather strongly complexed with soluble ligands. However, at lower pH levels, which favor increased soluble zinc levels, zinc was either not complexed or only weakly complexed, as most was

retained by brief contact with a cation exchange resin.

This study indicated that zinc sulfide formation is an important regulatory process affecting soluble and exchangeable zinc. In strongly reduced sediments containing sulfide, soluble zinc increased as the redox potential increased above the stability field for sulfide. In strongly reduced sediments in which no sulfide was detected, there was considerably less influence of increasing redox potential above the strongly reduced levels. The importance of sulfide regulation of soluble zinc was most apparent in the zinc addition study where the presence of measurable sulfide generally reduced soluble zinc at the highest levels added by a factor of 5 to 100, compared to strongly reduced sediments containing no sulfide. The presence of any measurable indigenous soluble zinc by flame atomic absorption in strongly reduced sediments containing sulfide suggested that some zinc may be solubilized by complex formation with soluble organics or perhaps because of the unavailability of the sulfide ligand, which may be tied up predominantly as ferrous sulfide.

Most of the indigenous zinc recovered in potentially chemically reactive forms by the fractionation procedure used was recovered in the reducible form. Reducible zinc was consistently higher in the pH-5.0, -150-mv treatment, which corresponded with the greatest reducible iron levels. This suggested an association between zinc and colloidal hydrous iron oxides in reduced, moderately acid environments. There was a slight trend for levels of DTPA-extractable and hydrogen

peroxide-digestible zinc to decrease with increasing redox potential.

Based on the results of this study, it is anticipated that most of the total sediment-bound zinc would not be affected by changes in either pH or redox potential encountered during dredging and dredged material disposal. However, some changes in the readily bioavailable soluble and exchangeable forms could be expected by a change in the pH or oxidation environment of a sediment. In strongly reduced sediments containing sulfide, an increase in readily available zinc may be expected if the redox potential increases beyond the sulfide stability boundary for sufficiently long periods for sulfide oxidation to occur. This might occur in finely divided dredged material which remains in suspension for considerable periods and particularly in the surface horizon of dredged material deposited on land where slow drainage and subsequent oxidation of the surface horizon may occur. Only a small release by insoluble organics would be expected as a result of a change in the pH or oxidation environment of a dredged material, and, as for sulfide release, this would be expected only if the more oxidized environment persisted for sufficient time for quantitative and qualitative changes in the sediment organic matter to occur.

Copper

Total copper in the sediment materials studied ranged from around 15 to 21 $\mu\text{g/g}$ solids. Maximum recovery by the chemical fractionation procedure used ranged from 60 to 90 percent. This indicated much of

the total copper was in chemical combinations potentially capable of being transformed to readily available forms. However, measurable soluble copper was found by flame atomic absorption only under strongly and moderately reduced conditions at pH 5.0 in Mobile Bay sediment material and at pH 8.0 in Mobile Bay and Mississippi River material. At pH 8.0, there was a slight trend for soluble copper to increase with redox potential.

In the Mobile Bay sediment suspension incubated at pH 5.0, -150 mv, the small amounts of soluble copper detected were present in a sediment material containing around 1000 μg sulfide/g solids. As copper sulfide is reported to form one of the least soluble sulfides of trace and toxic metals, these data again suggested that there may be some competition for the available sulfide such that all of the copper does not form a stable sulfide complex. There was no evidence that a soluble copper-organic complex contributed significantly to the soluble copper found in the acid, sulfide-bearing sediment material, as all soluble copper was retained by brief contact with a cation exchange resin.

In all sediment materials studied, reducible copper levels were strongly correlated with redox potential. Reducible copper was generally undetectable in strongly reduced suspensions by flame atomic absorption. However, recovery in this fraction increased with increasing redox potential to approximately 50 percent of the total sediment copper content under well-oxidized conditions. These data and the literature

available suggest that reducible copper may be predominately associated with hydrous oxides of manganese.

Copper levels associated with insoluble organics decreased with increasing redox available, suggesting that the copper-organic complex is more stable under reducing conditions and decreases in stability as a sediment becomes better oxidized. Also to be considered is the possible increased competition for available copper by adsorption to hydrous oxides as a reduced sediment-water system becomes oxidized.

This study indicated that changes in the pH or redox potential environment of sediments induced by dredging and dredged material disposal will result in little or no increase in readily bioavailable copper. Precipitation or adsorption to colloidal hydrous oxides in oxidized environments and copper complex formation with insoluble organics and perhaps sulfide in reduced sediment materials contributed to the strong affinity of sediment solids for copper over the range of pH and redox potential studied.

Mercury

In the sites studied, there seemed to be some relation between the expected influence of cultural activities and the total sediment mercury content. Also, there was some tendency for the total sediment mercury content to correlate with reduced conditions favoring sulfide stability and particularly with the total organic carbon content.

Indigenous soluble mercury levels were generally too low for accurate analysis. Thus the influence of pH and redox potential on the

distribution of a radioisotope of mercury equilibrated with the sediment suspensions was studied. The recovery of the added radioisotope in the soluble form did not exceed 0.5 percent at any pH-redox potential combination, and in most cases the recovery in this form was less than 0.1 percent. These data indicate that the proportion of potentially available mercury in the soluble phase is very small over the entire pH-redox potential range studied.

There was no general trend in mercury solubility with changing pH or redox potential. However, certain pH-redox potential combinations did enhance mercury solubility relative to adjacent pH-redox potential treatments. In two of the materials studied, strongly reducing environments at pH 5.0 and 6.5 resulted in considerably greater recovery of the labelled mercury in a soluble form. Also in two materials, a well-oxidized environment at pH 8.0 enhanced mercury solubility.

Again, greater dissolved mercury in some reduced suspensions containing sulfide relative to more oxidized treatments suggested that the mercury sulfide complex is not the predominant factor regulating dissolved levels of mercury. The increased solubility of mercury was apparently due to the formation of soluble, uncharged mercury complexes, as most of the soluble mercury was not retained by a cation exchange resin. These soluble complexes may be either organic or inorganic. Oxidation of reduced sediment solution extracts resulted in more of the soluble mercury becoming associated with a smaller molecular weight material. These oxidized complexes were less stable as measured by

comparative mercury release to a cation exchange resin.

In suspensions treated to represent highly contaminated sediments, mercury solubility was strongly influenced by both pH and redox potential. For example, in Mississippi River sediment suspensions to which several hundred μg mercury/g solids had been added, recoveries in soluble and easily exchangeable forms in well-oxidized treatments were about 90, 6, and less than 1 percent at pH 5.0, 6.5, and 8.0, respectively. Other sediment materials gave comparable results. The influence of redox potential on readily bioavailable mercury was also accentuated in highly contaminated sediments. In strongly reduced Mobile Bay sediments receiving 500 μg mercury/g solids, soluble mercury did not exceed 0.6 $\mu\text{g}/\text{g}$ at any pH level. In contrast, soluble mercury levels recovered from well-oxidized treatments were 217, 31, and 0.8 $\mu\text{g}/\text{g}$ at pH 5.0, 6.5, and 8.0, respectively. It was found that in highly contaminated sediments, changes in either pH or redox potential over the range studied may change levels of soluble mercury by a factor of 100 to 1000 and more.

There was evidence that colloidal hydrous oxides may play a role in regulating the availability of mercury. Reducible mercury was associated with reducible iron under strongly reduced, moderately acid environments, and with reducible manganese in oxidized, nonacid sediments. However, sediment organics were indicated to be the predominant factor regulating mercury availability in the overall study in reduced as well as oxidized environments. Where up to 500 $\mu\text{g}/\text{g}$ of mercury was

added, only trace recoveries ($<0.6 \mu\text{g/g}$) of soluble and exchangeable mercury in reduced sediments were measured from any sediment material. As no sulfide was detected in the strongly reduced Mississippi River material, another important and effective regulatory mechanism for mercury in strongly reduced sediments was suggested. With each incremental increase in redox potential, there was a corresponding increase in the bioavailable forms of mercury, possibly resulting from a reduced stability of the mercury-organic complex with increasing oxidation levels. In the well-oxidized treatments receiving high-level mercury additions, the release of mercury to readily bioavailable forms was strongly associated with organic carbon levels. The recovery of soluble plus exchangeable mercury in the well-oxidized suspensions receiving the highest mercury addition from three sediment materials incubated at pH 6.5 and the corresponding organic carbon contents were: Barataria Bay (400 $\mu\text{g/g}$ added) 3 μg , 3.0 percent organic carbon; Mobile Bay (500 $\mu\text{g/g}$ added) 34.6 μg , 1.8 percent organic carbon, and Mississippi River (500 $\mu\text{g/g}$ added) 83.1 μg , 1.2 percent organic carbon. Comparable recovery relationships were found at other pH levels in moderately oxidized and well-oxidized sediment suspensions.

In studies of indigenous mercury levels as well as where increasingly larger increments of mercury were added, it was apparent that mercury solubility under strongly reduced conditions may be enhanced over mercury solubility in better oxidized treatments at relatively low sediment mercury contents. However, as additional mercury was added

over approximately the 25- $\mu\text{g/g}$ level, soluble mercury in strongly reduced treatments did not increase appreciably, whereas soluble mercury in the better oxidized treatments increased sharply, particularly at the higher levels added. Thus the predominant factors controlling the solubility of mercury apparently depend on the mercury levels present. As the mercury content exceeds the capacity of one regulatory process, the influence of pH and redox potential on the distribution of potentially bioavailable mercury may change depending on the interaction of controlling factors at the greater mercury levels.

Data indicate that a change in the sediment chemical environment resulting in a lower redox potential in moderately and weakly acid sediments and an increase in redox potential under mildly alkaline conditions may result in a small increase in soluble mercury in some sediment materials. In highly contaminated sediments, a reduction in pH or an increase in sediment oxidation may result in large releases of mercury.

Lead

Very little radiotracer lead was recovered in a soluble form at any pH-redox potential combination studied, and consequently there were no clear trends of the influence of these parameters on lead solubility. In a separate study where 500 $\mu\text{g/g}$ solids of lead, zinc, and mercury had been added to Mobile Bay sediment suspensions, the lowest release occurred with lead. However, flameless atomic absorption data generally indicated a small increase in soluble lead with decreasing pH and with decreasing

redox potential at pH 5.0 and 6.5.

There was some indication that soluble organic complexes contributed to total soluble lead in Mobile Bay suspensions incubated at pH 8.0 and Calcasieu River suspensions incubated at pH 6.5. Studies done on solution extracts of Barataria Bay sediment samples indicated that the proportion of lead complexed with organics increased with increasing pH.

Considerably more lead was found in the exchangeable form, and this lead was affected by both pH and redox potential. In the oxidized treatments, the recovery of the added lead isotope in the exchangeable form decreased from several percent of that added at pH 5.0 to almost undetectable levels at pH 8.0. Lead sulfide formation apparently had an important influence on exchangeable lead. In moderately and weakly acid Mobile Bay sediment suspensions receiving up to 500 μg lead/g solids, there was a sharp increase in soluble and exchangeable lead as the redox potential was increased from -150 to 50 mv where sulfide disappeared. Subsequent increases in redox potential did not result in further increases in these two forms of lead. This indicated that lead sulfide formation may play an important role in regulating exchangeable lead in strongly reduced sediments.

Where a carrier-free isotope was added, the maximum recovery of exchangeable lead generally occurred at 50 mv. Smaller recoveries at the lower redox potential may have been due to lead sulfide formation. Smaller recoveries in better oxidized treatments may have resulted from the scavenging effect of hydrous oxides. Recovery of the added lead

isotope as well as indigenous lead in the reducible form increased with increasing redox potential. Approximately half of the lead isotope was recovered in this form in well-oxidized treatments at all pH levels.

Much of the remaining added lead isotope was recovered in an organic chelate-extractable form. The recovery of this form of lead and of hydrogen peroxide-digestible lead indicated that the stability of lead-inorganic complexes may be reduced by an increase in redox potential, though this did not appear to be the case for sediments receiving high level lead additions.

Unlike mercury, for which most of the added radioisotope was not recovered by the sequential chemical fractionation procedure used, most of the added lead isotope was recovered in the reducible and DTPA-extractable forms. Thus there was some indication that more lead may, in chemical combinations, be potentially capable of being transformed to readily bioavailable forms than mercury in all but highly contaminated sediments.

In highly contaminated sediments (represented by materials receiving 500 μg metal/g solids), more mercury was released under acid, oxidizing conditions than lead. In these sediments, there was little lead release in the readily bioavailable soluble and exchangeable forms and relatively little effect of redox potential on these forms up to lead contents of several hundred $\mu\text{g}/\text{g}$ solids.

The data indicate that changes in sediment pH and redox potential, possibly induced by dredging and dredged material disposal, will result

in relatively small changes in soluble lead unless the sediments contain high levels of lead. An increase in acidity may increase soluble lead somewhat. A change in redox potential will likely have minimal effects on soluble lead. However, exchangeable lead may be increased considerably by an increase in sediment acidity.

Cadmium

There was generally good agreement between flameless atomic absorption and radiotracer techniques in determining the influence of pH and redox potential on soluble and exchangeable cadmium in the sediment materials studied. A much greater proportion of potentially available indigenous cadmium was found in the soluble and exchangeable chemical forms than was the case for mercury and lead. Most of the soluble cadmium was apparently present in a free cationic state. The relative levels of exchangeable cadmium corresponded to the cation exchange capacity of the sediments studied.

Both pH and redox potential were shown to strongly influence the readily bioavailable cadmium. As pH was increased from 5.0 to 8.0, cadmium availability decreased. Soluble and exchangeable cadmium generally increased with increasing redox potential at pH 5.0 and 6.5 such that much of the equilibrated isotope was recovered in these forms in moderately and weakly acid suspensions. Only the Mobile Bay soluble cadmium responded to increasing redox potential at pH 8.0.

Recovery of the added cadmium radioisotope in a soluble form from the Mississippi River material under well-oxidized conditions was around

34 and 2 percent at pH 5.0 and 6.5, respectively. Corresponding recovery in the exchangeable fraction was 57 and 21 percent. Labelled cadmium recovery in the Barataria Bay material studied showed similar trends.

Where high levels of cadmium were added to Mississippi River sediment suspensions, there was comparatively little effect of redox potential on soluble and exchangeable cadmium. Where high levels of cadmium were added to Barataria Bay sediment material, there was a marked increase in levels of soluble and exchangeable cadmium with an increase in redox potential, especially as redox potential increased above the stability field for sulfide. Since the Mississippi River material did not contain measurable sulfide, there was some indication that cadmium sulfide formation may have resulted in much reduced levels of soluble and exchangeable cadmium relative to better oxidized treatments.

However, the role of sulfide in regulating cadmium availability was not as apparent at low cadmium levels based on tracer and flameless atomic absorption data. The somewhat progressive increases in soluble cadmium levels with increasing redox potential in sulfide and nonsulfide-bearing sediments suggested that some other process was limiting cadmium availability in strongly and moderately reduced sediments, possibly cadmium retention by insoluble organics.

There was little effect of pH and redox potential on reducible cadmium. However, organic chelate-extractable cadmium generally increased with increasing redox potential while total insoluble organic-bound

(hydrogen peroxide-digestible) cadmium decreased. This suggested that cadmium-organic complex stability decreases with increasing redox potential. This would support the finding where high levels of cadmium were added that redox potential had a greater influence on cadmium availability in the sediment material containing the greatest quantity of organic matter.

This study indicates that a dredged sediment encountering a more acid environment may release cadmium to the soluble and easily exchangeable forms as was noted for other elements such as iron, manganese, and zinc. However, radiotracer and atomic absorption data indicate that, unlike other metals studied, there was a comparatively large increase in soluble and exchangeable indigenous cadmium with increasing redox potential over the entire redox potential range studied in both moderately acid (pH 5.0) and near-neutral (pH 6.5) sediment materials. Thus, a typically reduced dredged sediment material subjected to an oxidizing environment for a sufficiently long time could be expected to release much of its potential bioavailable cadmium in readily available forms.

Relative Bioavailability of Mercury, Lead, and Cadmium

There is little research data to substantiate exactly which chemical pools of metals and nutrients are readily available to benthic organisms and plants grown on dredged materials. It is generally accepted that elements in the soluble form are most readily incorporated into living tissue and that the easily exchangeable pool also represents readily available sources as this pool may be in equilibrium with and

replenish the soluble pool. However, other chemical pools also contribute to the uptake of metals and nutrients. It is also likely that the relative contribution of the various chemical combinations to total elemental uptake varies with biological species and that uptake by an organism is influenced by the chemical and physical environment. Nevertheless, it is useful to determine the influence of the chemical and physical environment on the response of nutrients and potentially toxic metals to selected chemical extracts in sediment-water systems. In this study, soluble and 1 N sodium acetate-extractable (easily exchangeable) were termed readily available. Reducible, DTPA-extractable, and hydrogen peroxide-digestible elements were considered potentially available, either directly, or as a result of chemical transformations mobilizing these forms.

The recovery of added isotopes indicated that of the potentially reactive indigenous quantities of mercury, lead, and cadmium in the sediment-water systems studied, mercury was least associated with the readily bioavailable forms. Lead ranked next, depending on pH and redox potential. A relatively large proportion of the added cadmium isotope was recovered in soluble and exchangeable forms. The remaining cadmium was recovered in potentially available forms. Though little of the added lead isotope was recovered in readily available forms, most was recovered in the reducible and DTPA-extractable forms (potentially available). Mercury was tightly bound to sediment solids, and most of the mercury was not recovered by the fractionation procedure applied (mercury

was quantitatively recovered in the extraction for total elemental content).

The heavy metal addition study indicated the relative bioavailability of these metals may be altered in highly contaminated sediments where pH and redox potential strongly influence the quantities recovered in soluble and easily exchangeable forms.

Ammonium-Nitrogen

Soluble and exchangeable ammonium-nitrogen decreased as pH increased, especially as the pH increased from 6.5 to 8.0. Volatilization may have contributed to this nitrogen loss in sediment suspensions maintained at pH 8.0 and 30°C. An increase in redox potential also resulted in a reduction of soluble and exchangeable ammonium. It is likely that much of the readily available ammonium-nitrogen was transformed to the equally bioavailable and somewhat more mobile nitrate form as a consequence of increasing the oxidation levels of sediments. Dredging and dredged material disposal will likely cause a temporary increase in the ammonium-nitrogen content of surface waters contacting dredged material due to mixing of interstitial water containing high levels of ammonium. A number of biological, chemical, and possibly physical processes will influence the ultimate fate of released inorganic nitrogen. Thus, an evaluation of possible changes in the trophic status of receiving waters must consider the complex cycling of nitrogen in sediment-water systems.

Phosphorus

Soluble and exchangeable phosphorus decreased with increasing redox potential and increased somewhat with increasing pH. Both effects were thought to be due to phosphorus interactions with sediment iron. Changes in readily available phosphorus were associated with levels of soluble and exchangeable iron as redox potential was altered, especially in moderately and weakly acidic sediment suspensions. Neutral and mildly alkaline pH levels favor the formation of calcium phosphates over iron phosphate, which may have contributed to the increase in phosphorus availability at pH 8.0 relative to the lower pH levels studied.

Soluble phosphorus levels in surface waters may be enhanced when mixed with reduced sediments and interstitial waters. However, increases in the redox potential of interstitial water containing elevated phosphorus levels would tend to counter the possible release of phosphorus caused by dredging and dredged material disposal.

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APPENDIX A: SAMPLING SITE LOCATION MAPS

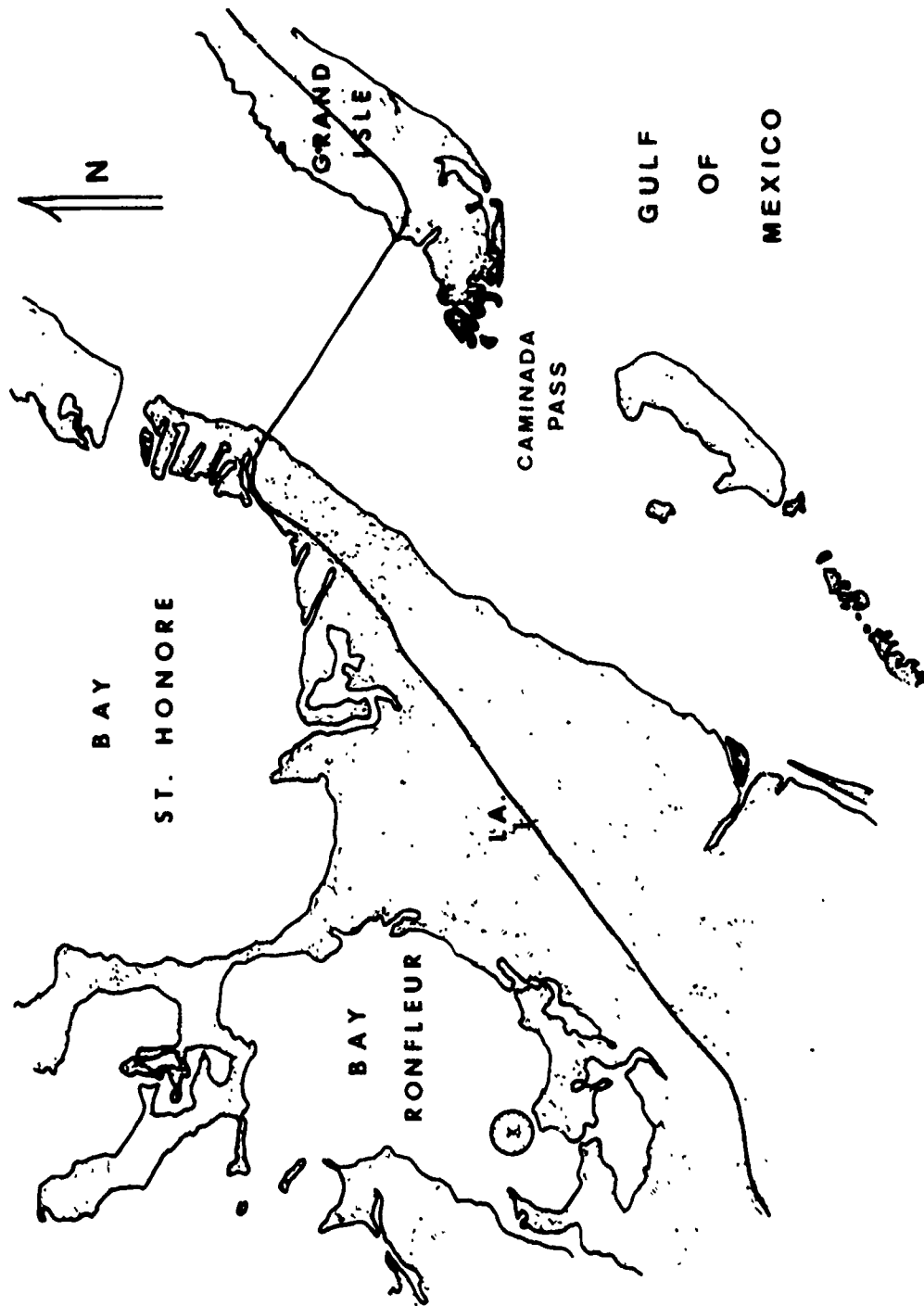


Figure 1. Sampling Site in Barataria Bay (Bay Ronfleur) near Grand Isle Louisiana

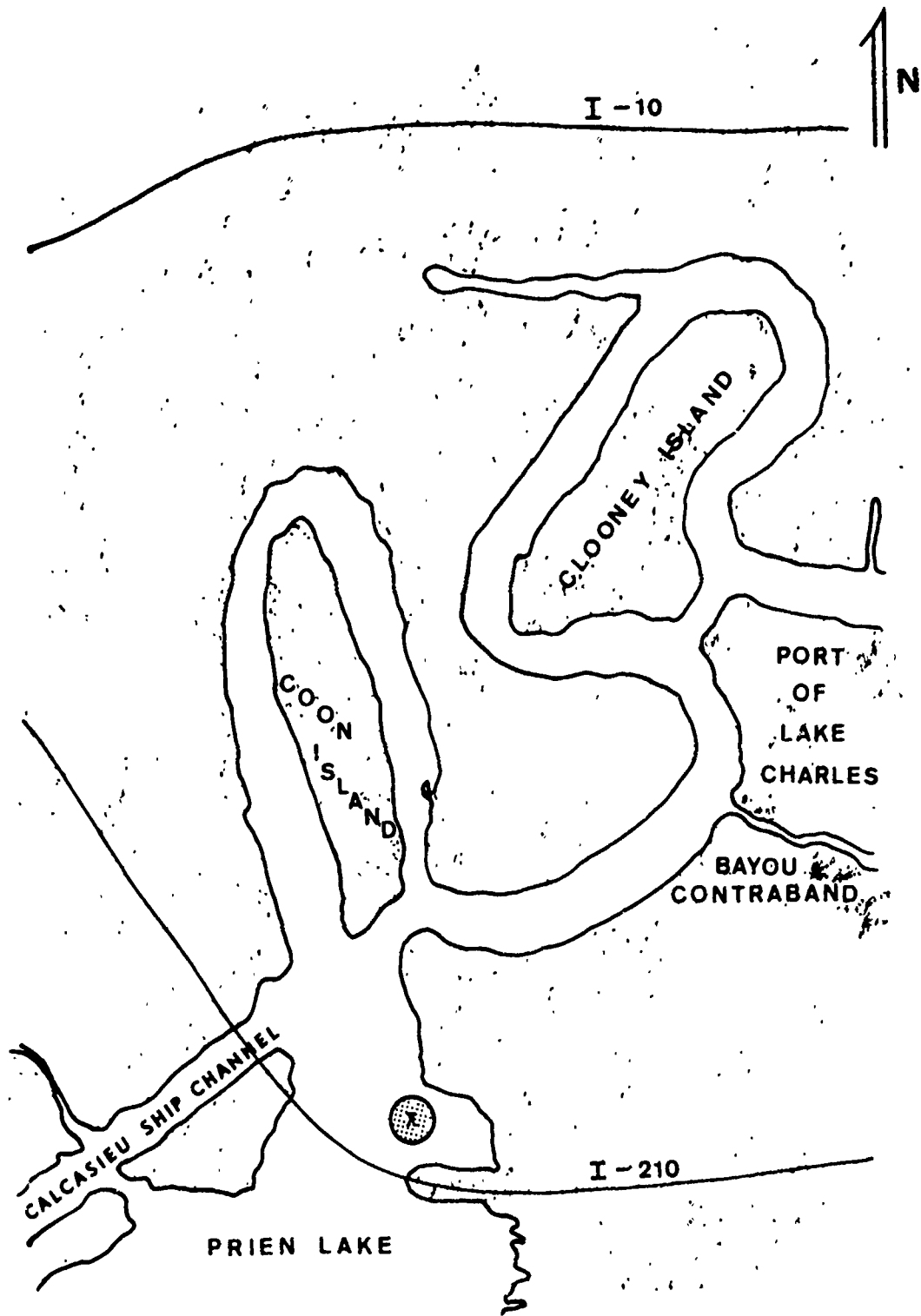


Figure A4. Sampling Site in Calcasieu River, Lake Charles, Louisiana

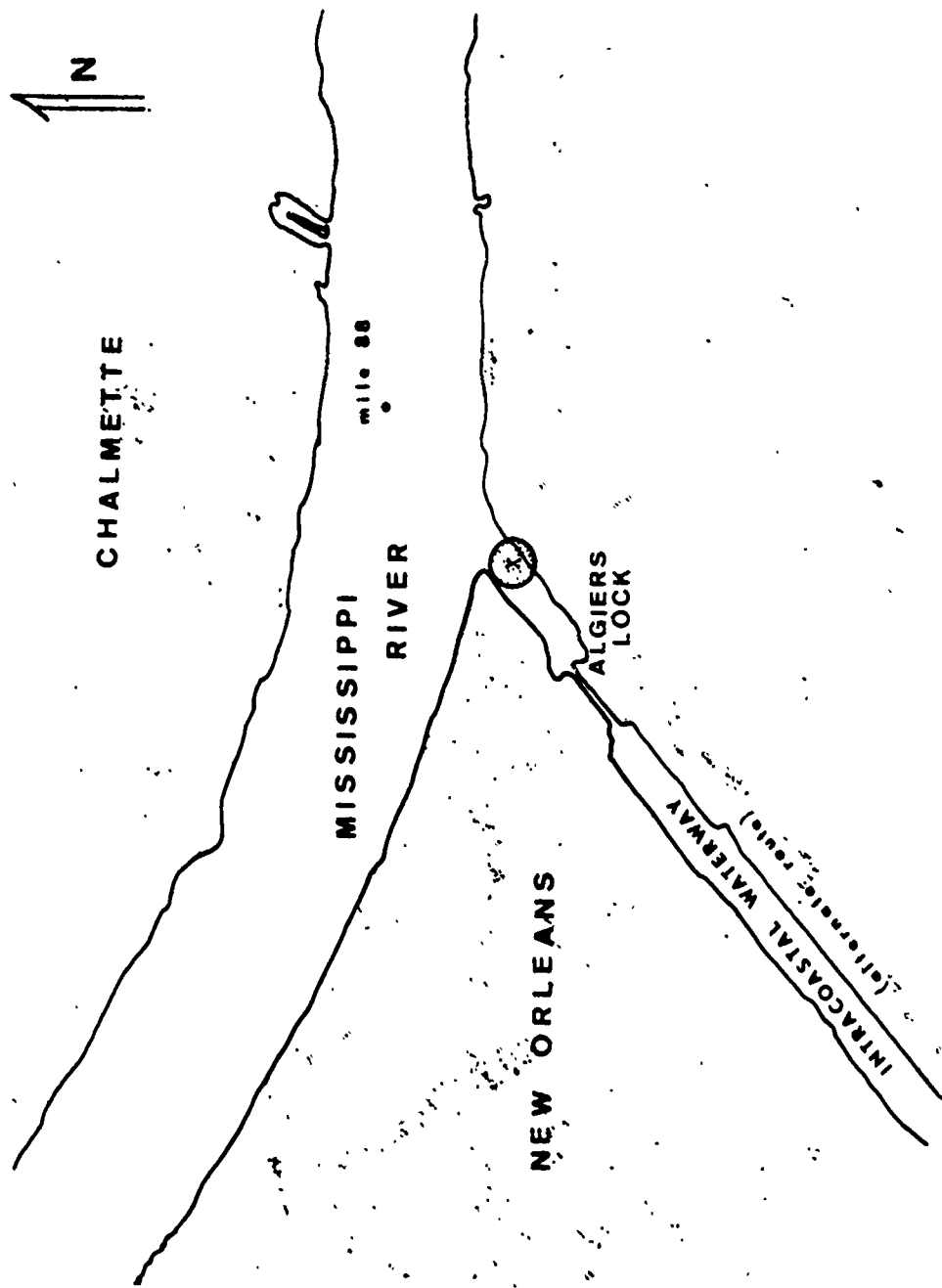


Figure A3. Sampling Site in Mississippi River, New Orleans, Louisiana

- APPENDIX B: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF IRON
- APPENDIX C: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF MANGANESE
- APPENDIX D: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF ZINC
- APPENDIX E: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF COPPER
- APPENDIX F: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF ^{203}Hg
- APPENDIX G: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF MERCURY
- APPENDIX H: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF ^{210}Pb
- APPENDIX I: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF LEAD
- APPENDIX J: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF ^{109}Cd
- APPENDIX K: EFFECT OF pH AND REDOX POTENTIAL ON CHEMICAL FORM AND DISTRIBUTION OF CADMIUM
- APPENDIX L: EFFECT OF pH AND REDOX POTENTIAL ON WATER-SOLUBLE AND EXCHANGEABLE NH_4^+-N
- APPENDIX M: EFFECT OF pH AND REDOX POTENTIAL ON WATER-SOLUBLE AND EXCHANGEABLE PHOSPHORUS
- APPENDIX N: EFFECT OF pH AND REDOX POTENTIAL ON WATER-SOLUBLE AND EXCHANGEABLE ZINC 24 HR AFTER ACCUMULATIVE ADDITIONS OF ZINC
- APPENDIX O: EFFECT OF pH AND REDOX POTENTIAL ON WATER-SOLUBLE AND EXCHANGEABLE MERCURY 24 HR AFTER ACCUMULATIVE ADDITIONS OF MERCURY
- APPENDIX P: EFFECT OF pH AND REDOX POTENTIAL ON WATER-SOLUBLE AND EXCHANGEABLE CADMIUM 24 HR AFTER ACCUMULATIVE ADDITIONS OF CADMIUM
- APPENDIX Q: EFFECT OF pH AND REDOX POTENTIAL ON WATER-SOLUBLE AND EXCHANGEABLE LEAD 24 HR AFTER ACCUMULATIVE ADDITIONS OF LEAD
- APPENDIX R: EFFECT OF DISSOLVED OXYGEN ON CHEMICAL FORM AND DISTRIBUTION OF IRON

Table B1. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Iron in Barataria Bay Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	0	200	450	200	450	-150	0	200	450		
Water Soluble	1890	860	8	12	171.0	181.0	6.0	5.9	3.5	1.2	2.1	1.8
soluble Organic Round	16.0	18.6	1.4	1.6	9.9	9.6	1.7	1.6	2.3	1.2	2.1	1.8
Exchangeable	421	451	48	31	243.0	38.0	5.0	2.9	8.4	4.2	3.7	3.8
Reducible ⁺	1760	1400	3330	4670	3570	3640	4710	5100	4820	4060	4070	5720
Dithionite ⁺ Extractable ⁺	298	276	780	433	354	454	419	498	443	807	822	803

*Determined by flame atomic absorption. ⁺ Mean of duplicate samples.

Table B4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Iron in Calcasieu River Sediment Suspensions*

FRACTION	pH 6.5			pH 8.0				
	Redox Potential, mv			Redox Potential, mv				
	-150	50	250	500	-150	50	250	500
	----- $\mu\text{g Fe/g oven dry solids}$ -----							
Water Soluble	58 [†] ±3 [‡]	53 ±4	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.
Soluble Organic Bound	5 ±3	n.d.	n.d.	n.d. [¶]	n.d.	n.d.	n.d.	n.d.
Exchangeable	230 ±3	195 ±16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Reducible	2961 ±33	2867 ±3	2693 ±0	3097 ±177	3153 ±246	2575 ±245	2624 ±110	2532 ±92
DTPA Extractable	436 ±79	327 ±94	284 ±±6	261 ±78	443 ±80	346 ±46	261 ±12	359 ±16
Insoluble Organic Bound	596 ±42	564 ±14	710 ±26	674 ±32	594 ±84	750 ±175	664 ±47	673 ±120

*Determined by flame atomic absorption. [†]Mean of duplicate samples. [§]Not detectable. [‡]Standard deviation. [¶]Lost one sample.

Table C1. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Manganese in Barataria Bay Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv					
	-150	0	200	-150	0	200	-150	0	200			
	----- $\mu\text{g Mn/g oven dry solids}$ -----											
Water Soluble	108	87	114	110	69.0	93.0	63.0	5.9	12.8	0.2	n.d. [§]	n.d.
Soluble Organic Bound	2.1	1.9	1.8	1.7	1.4	2.0	2.0	0.4	n.d.	n.d.	n.d.	n.d.
Exchangeable	31	54	47	33	47.0	36.0	13.0	1.4	11.8	1.7	1.5	3.2
Reducible [†]	31	20	40	49	36	47	71	118	148	155	170	218
Dithionite Extractable [†]	6.0	5.2	7.5	6.1	6.5	5.1	3.4	2.0	22.0	30.0	21.0	30.0

*Determined by flame atomic absorption. [§]Not detectable. [†]Mean of duplicate samples.

Table C2. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Manganese in Mobile Bay Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0						
	-150	50	250	500	-150	50	250	500	-150	50	250	500	
	Redox Potential, mv												
Water Soluble	330 [†]	317	252	204	106	116	122	122	122	8.1	3.0	5.0	0.4
	±9 [‡]	±5	±2	±5	±1	±2	±1	±2	±2	±0.4	±2.2	±0.8	±0.6
Soluble Organic Bound	3.3	4.8	1.8	1.6	n.d. ^{§¶}	n.d. [¶]	n.d. [¶]	n.d. [¶]	0.4 [¶]	0.6	0.4	n.d.	n.d.
	±0.7	±2.2	±0.3	±0.1						±0.8	±0.6		
Exchangeable	164	186	162	135	126	113	131	89	89	21.2	3.4	5.7	n.d.
	±9	±2	±1	±3	±48	±26	±6	±39	±39	±2.4	±4.8	±4.3	
Reducible	96	96	98	188	202	210	184	234	234	558	522	400	436
	±3	±1	±2	±1	±32	±14	±1	±50	±50	±5	±26	±4	±3
DTPA Extractable	14.5	10.8	12.3	15.1	105.5	42.4	25.2	27.6	27.6	58.7	47.7	66.4	47.2
	±3.4	±1.6	±1.5	±0.2	±63.9	±29.8	±10.3	±2.4	±2.4	±11.8	±2.7	±24.4	±18.0

*Determined by flame atomic absorption. [†]Mean of duplicate samples. [‡]Standard deviation. [§]Not detectable. [¶]Lost one sample.

Table C3. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Manganese in Mississippi River Sediment Suspensions*

FRACTION	pH 5.0						pH 6.5						pH 8.0										
	-150		50		500		-150		50		250		500		-150		50		250		500		
	Redox Potential, mv																						
Water Soluble	µg Mn/g oven dry solids																						
	569 [†]	544	±15	±3	537	92	±5	90	75	69	n.d. [‡]	8.1	7.5	9.0	1.3	±6 [‡]	±0	±6	±5	±0.3	±0.1	±0.4	±0.1
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.8	0.5	0.7	n.d.	n.d.	n.d.	n.d.	n.d.	±0.1	±0.4	±0.0
	307	303	±1	±9	254	85	±5	310	325	274	3.2	109	96	99	n.d.	±30	±35	±68	±17	±3.5	±5.5	±5.9	n.d.
Exchangeable	108	100	±17	±4	97	687	±1	380	379	387	712	731	743	710	856	±0	±13	±14	±18	±88	±21	±19	±7
	12.5	12.6	±2.9	±0.9	12.4	31.9	±0.7	51.3	44.1	45.9	40.2	58.7	57.1	54.8	48.5	±2.2	±2.6	±4.3	±5.1	±1.8	±1.5	±1.2	±1.0
DTPA Extractable	2.0	2.3	±0.0	±0.2	2.4	5.5	±1.4	11.7	11.1	13.5	10.4	33.5	33.4	34.8	19.8	±0.8	±1.0	±1.4	±0.5	±1.5	±1.0	±5.9	±2.5
	±0.8	±0.0	±0.2	±1.4	±0.2	±1.4	±1.7	±1.0	±1.4	±0.5	±1.7	±1.5	±1.0	±5.9	±2.5	±0.8	±1.0	±1.4	±0.5	±1.5	±1.0	±5.9	±2.5

*Determined by flame atomic absorption. [†]Mean of duplicate samples. [‡]Not detectable. [§]Standard deviation.

Table C4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Manganese in Calcasieu River Sediment Suspensions*

FRACTION	pH 6.5				pH 8.0			
	-150		500		-150		500	
	50	250	500	500	50	250	500	500
Water Soluble	17.6 [†]	22.7	22.4	n.d. [‡]	4.8	4.8	4.8	n.d.
	±0.3 [‡]	±0.4	±0.3		±0.0	±0.2		n.d.
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d. [‡]	n.d.	n.d.	n.d.	n.d.
Exchangeable	68.2	73.3	64.4	1.1	16.4	13.3	n.d.	n.d.
	±2.6	±0.4	±5.9	±1.6	±3.0	±1.7		
Reducible	181	194	156	244	230	176	240	221
	±7	±46	±2	±23	±16	±32	±11	±12
DTPA Extractable	22.6	18.2	25.2	25.4	32.0	25.4	18.6	34.8
	±3.5	±2.9	±4.2	±12.5	±8.7	±4.1	±1.9	±3.3
Insoluble Organic Bound	12.0	12.1	15.8	18.0	14.5	22.4	11.0	20.8
	±2.3	±1.8	±1.6	±8.0	±6.4	±9.7	±4.4	±2.0

*Determined by flame atomic absorption. [†]Mean of duplicate samples. [‡]Not detectable. [§]Standard deviation. [¶]Lost one sample.

Table D2. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Zinc in Mobile Bay Sediment Suspensions*

FRACTION	pH 5.0						pH 6.5						pH 8.0												
	-150		50		250		500		-150		50		250		500		-150		50		250		500		
	Redox Potential, mv																								
Water Soluble	µg Zn/g oven dry solids																								
	0.13 [†]	8.81	12.33	11.72	1.26 [Ⓞ]	1.01	0.57	0.98	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d.	
Soluble Organic Bound	±0.18 [‡]	±0.88	±0.96	±0.18	±1.41	±0.64	±0.11	±0.12	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d.	
	n.d.	0.13	n.d.	n.d.	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d.	
Exchangeable	1.2	18.4	25.2	24.8	0.7	3.0	4.6	7.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2 [Ⓞ]
	±0.7	±0.2	±0.7	±0.2	±0.1	±0.3	±0.2	±1.8	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d. [‡]	n.d.	±1.6
Reducible	104.8	76.6	70.8	74.4	25.7	62.2	71.0	95.3	118.8	114.0	107.1	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5
	±9.3	±1.7	±3.3	±5.2	±8.6	±12.0	±7.1	±0.8	±2.5	±1.9	±5.1	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3	±4.3
DTPA Extractable	10.3	7.7	5.9	6.0	20.1	11.5	8.8	11.1	11.8	9.6	14.4	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1	12.1
	±2.5	±2.2	±1.0	±0.1	±6.1	±5.9	±4.5	±2.5	±2.0	±2.0	±6.8	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1	±1.1

*Determined by flame atomic absorption. †Mean of duplicate samples. ‡Possible contamination. §Not detectable. ¶Standard deviation. ††Lost one sample.

Table D3. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Zinc in Mississippi River Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	Redox Potential, mv											
Water Soluble	1.02 [†]	4.16	6.20	2.56	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	±0.40 [‡]	±0.20	±0.08	±0.15	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Exchangeable	2.30	8.78	8.49	6.04	n.d.	0.36	0.30	0.51	n.d.	n.d.	n.d.	n.d.
	±0.00	±0.80	±0.35	±0.09	n.d.	±0.16	±0.05	±0.21	n.d.	n.d.	n.d.	n.d.
Reducible	36.04	22.57	16.72	25.80	35.74	34.58	22.57	23.09	36.96	35.72	31.90	29.46
	±0.10	±2.70	±1.40	±4.50	±0.71	±3.10	±0.65	±0.42	±0.43	±2.37	±0.71	±1.90
DTPA Extractable	2.86	2.69	2.30	2.57	2.54	2.35	1.99	2.42	2.72	2.95	2.34	2.55
	±0.33	±0.35	±0.23	±0.18	±0.07	±0.23	±0.19	±0.22	±0.02	±0.31	±0.04	±0.16
Insoluble Organic Bound	4.45	3.37	2.53	1.27	3.78	4.08	2.49	1.85	6.89	7.86	7.01	5.08
	±0.54	±0.07	±0.40	±0.22	±1.20	±0.64	±0.73	±0.43	±0.52	±0.40	±1.10	±0.02

*Determined by flame atomic absorption. [†]Mean of duplicate samples. [‡]Not detectable. [§]Standard deviation.

Table D4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Zinc in Calcasieu River Sediment Suspensions*

FRACTION	pH 6.5			pH 8.0			
	Redox Potential, mv			Redox Potential, mv			
	-150	50	250	-150	50	250	
	----- $\mu\text{g Zn/g oven dry solids}$ -----						
Water Soluble	2.27 [†] ±2.19 [‡]	1.67 ±0.43	1.33 ±0.13	1.19 ±0.09	n.d. [§] 0.30 ±0.07	0.33 ±0.19	0.10 ±0.14
Soluble Organic Bound	0.23 ±0.04	0.26 ±0.14	0.20 ±0.07	0.05 [¶]	0.34 ^{¶¶} n.d.	n.d.	n.d.
Exchangeable	0.59 ±0.10	1.72 ±0.00	1.96 ±0.16	2.39 ±0.63	n.d.	n.d.	n.d.
Reducible	27.0 ±4.0	23.0 ±1.5	27.8 ±0.3	27.6 ±0.9	23.8 ±6.1	20.4 ±3.5	25.8 ±0.7
DTPA Extractable	4.65 ±2.08	3.98 ±0.88	4.10 ±0.65	4.20 ±1.04	3.34 ±1.02	3.16 ±0.62	2.81 ±0.12
Insoluble Organic Bound	1.93 ±0.64	2.05 ±0.28	0.82 ±0.19	0.45 ±0.29	1.10 ±0.08	3.12 ±0.57	0.18 ±0.25

*Determined by flame atomic absorption. †Mean of duplicate samples. ‡Possible contamination.

§Not detectable. ¶Standard deviation. ¶¶Lost one sample.

Table E1. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Copper in Barataria Bay Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	0	200	450	-150	0	200	450	-150	0	200	450
	Redox Potential, mv											
Water Soluble	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Reducible	n.d.	0.59 [†]	3.92	8.20	n.d.	n.d.	3.90	5.80	n.d.	5.72	7.76	8.73
Dithionite Extractable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	µg Cu/g oven dry solids											

*Determined by flame atomic absorption. [§]Not detectable. [†]Mean of duplicate samples.

Table E2. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Copper in Mobile Bay Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0							
	-150	50	250	Redox Potential, mv			-150	50	250	-150	50	250	500	
				-150	50	250								
	----- µg Cu/g oven dry solids -----													
Water Soluble	0.32 [†] ±0.03 [‡]	0.26	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12 ±0.17
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12 ±0.17
Exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Redecible	n.d.	n.d.	4.84 ±0.23	9.38 ±1.14	0.28 ±0.40	3.34 ±0.04	8.45 ±0.04	1.44 ±0.49	8.70 ±0.44	n.d.	n.d.	n.d.	n.d.	n.d.
DTPA Extractable	0.09 ±0.13	0.21 ±0.08	0.66 ±0.02	0.64 ±0.06	0.28 ±0.06	0.55 ±0.25	0.72 ±0.25	0.35 ±0.10	0.66 ±0.30	n.d.	n.d.	n.d.	n.d.	0.12 ±0.12

*Determined by flame atomic absorption. [†]Mean of duplicate samples. [‡]Standard deviation. [§]Not detectable. [¶]Lost one sample.

Table E3. The effect of pH and Redox Potential on the Chemical Form and Distribution of Copper in Mississippi River Sediment Suspensions*

FRACTION	pH 5.0			pH 6.5			pH 8.0			
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv			
	-150	50	250	-150	50	250	-150	50	250	
Water Soluble	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	0.10 [†]	0.07	0.07	0.14
							±0.00 [‡]	±0.04	±0.04	±0.00
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.21	0.16	0.14
							±0.04	±0.03	±0.03	±0.00
Exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Reducible	n.d.	1.30	2.92	n.d.	0.82	5.03	n.d.	0.21	4.91	14.98
		±1.80	±0.01		±0.06	±0.23		±0.28	±0.47	±1.21
DTPA Extractable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.45	0.95	0.49	0.60
							±0.04	±0.23	±0.09	±0.04
Insoluble Organic Bound	4.60	3.86	3.17	4.01	3.88	2.40	11.16	12.71	6.90	0.61
	±1.42	±0.33	±0.77	±0.13	±0.32	±0.74	±0.16	±0.11	±0.18	±0.23

*Determined by flame atomic absorption. [§]Not detectable. [†]Mean of duplicate samples. [‡]Standard deviation.

Table E4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Copper in Calcasieu River Sediment Suspensions*

FRACTION	pH 6.5			pH 8.0		
	Redox Potential, mv			Redox Potential, mv		
	-150	50	250	-150	50	250
	----- $\mu\text{g Cu/g oven dry solids}$ -----					
Water Soluble	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d. [¶]	n.d.	n.d.
Exchangeable	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Reducible	n.d.	n.d.	10.22 [†]	12.42	1.30	8.49
			$\pm 0.08^{\ddagger}$	± 1.47	± 0.24	± 0.02
DTPA Extractable	n.d.	n.d.	1.58	1.26	0.52	0.77
			± 0.64	± 0.72	± 0.50	± 0.12
Insoluble Organic Bound	3.01	2.85	0.59	n.d.	4.28	2.01
	± 0.59	± 0.70	± 0.11		± 0.17	± 0.22

† determined by flame atomic absorption. ‡ Not detectable. § Lost one sample. ¶ Mean of duplicate samples. †† Standard deviation.

Table F1. The Effect of pH and Redox Potential on the Chemical Form and Distribution of ²⁰³Hg Added to Barataria Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv					
	-150	0	200	450	-150	0	200	450	-150	0	200	450
	----- % ²⁰³ Hg Recovered -----											
Water Soluble	0.02	0.12	0.02	0.08	0.08	0.10	0.05	0.05	0.05	0.09	0.15	0.10
Soluble Organic Bound	0.04	0.05	0.01	0.19	0.04	0.03	0.02	0.01	0.02	0.04	0.05	0.04
Exchangeable	0.46	n.d. [§]	0.01	0.01	0.07	0.13	0.09	0.08	0.07	0.08	0.07	0.08
Reducible [†]	0.46	0.23	0.47	0.46	0.10	0.08	0.13	0.17	0.41	0.48	0.38	0.48
Dithionite Extractable [†]	3.46	3.69	5.46	4.05	1.83	1.39	1.89	1.51	6.29	4.74	4.46	4.83

[§]Not detectable. [†]Mean of duplicate samples.

Table F2. The Effect of pH and Redox Potential on the Chemical Form and Distribution of ²⁰³Hg Added to Mobile Bay Sediment Suspension.

FRACTION	pH 5.0			pH 6.5			pH 8.0						
	-150	50	250	Redox Potential, mv			-150	50	250	-150	50	250	500
				50	250	500							
	----- % of ²⁰³ Hg recovered -----												
Water Soluble	0.43 [†]	n.d. [‡]	n.d.	0.01	0.12	0.02	0.07	0.03	0.03	0.03	0.04	0.05	0.19
	0.12 [‡]			±0.00	±0.01	±0.01	±0.04	±0.02	±0.02	±0.00	±0.02	±0.01	±0.01
Soluble Organic Bound	0.29	0.01	0.01	0.01	0.15 [‡]	0.01 [¶]	0.02 [¶]	0.03 [¶]	0.04	0.04	0.03	0.06	0.17
	±0.16	±0.00	±0.00	±0.00					±0.00	±0.00	±0.00	±0.01	±0.02
Exchangeable	0.22	0.03	0.05	0.08	0.09	0.02	0.05	0.07	0.04	0.04	0.07	0.08	0.19
	±0.05	±0.00	±0.01	±0.01	±0.02	±0.01	±0.02	±0.03	±0.03	±0.03	±0.00	±0.02	±0.04
Reducible	2.02	0.62	2.36	3.90	1.84	1.12	3.52	6.14	0.42	1.28	1.82	1.82	3.28
	±0.21	±0.24	±0.24	±0.38	±0.46	±0.22	±0.16	±0.58	±0.14	±0.14	±0.62	±0.62	±0.01
DTPA Extractable	1.44	1.74	5.87	6.38	1.89	4.84	9.39	11.42	3.75	7.68	9.14	9.14	9.31
	±0.21	±0.08	±0.62	±0.59	±0.87	±2.18	±3.22	±1.85	±0.11	±0.46	±0.46	±0.46	±0.77

[†]Mean of duplicate samples. [‡]Not detectable. [¶]Standard deviation. [§]Lost one sample.

Table F3. The Effect of pH and Redox Potential and the Chemical Form and Distribution of ²⁰³Hg Added to Mississippi River Sediment Suspensions (2.4 µg Hg/g oven dry solids added)

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	Redox Potential, mv											
Water Soluble	0.03 [†]	n.d. [‡]	n.d.	n.d.	0.23	0.01	0.01	0.01	0.09	0.08	0.05	0.07
	±0.00 [‡]				±0.04	±0.01	±0.00	±0.00	±0.02	±0.02	±0.00	±0.01
Soluble Organic Bound	0.03	0.01	n.d.	0.01	0.25	0.02	0.01	0.01	0.13	0.08	0.07	0.09
	±0.00	±0.00		±0.00	±0.06	±0.01	±0.01	±0.00	±0.01	±0.00	±0.01	±0.01
Exchangeable	0.02	0.04	0.02	0.03	0.04	0.02	0.03	0.04	0.26	0.21	0.17	0.16
	±0.01	±0.02	±0.00	±0.00	±0.00	±0.00	±0.01	±0.01	±0.01	±0.09	±0.00	±0.02
Reducible	0.37	0.35	0.23	0.23	0.74	0.40	0.38	0.53	0.43	0.48	0.45	0.62
	±0.15	±0.35	±0.00	±0.03	±0.31	±0.15	±0.25	±0.30	±0.02	±0.09	±0.06	±0.12
DTPA Extractable	2.26	1.44	0.72	0.51	1.50	1.40	1.49	0.95	2.71	3.68	3.01	2.00
	±0.63	±0.12	±0.04	±0.01	±0.05	±0.03	±0.05	±0.11	±0.14	±0.15	±0.14	±0.29
Insoluble Organic Bound	5.17 [‡]	5.91 [‡]	6.62 [‡]	17.86 [‡]	----- [‡]	----- [‡]	----- [‡]	----- [‡]	----- [‡]	----- [‡]	----- [‡]	----- [‡]

[†]Mean of duplicate samples. [‡]Not detectable. [§]Standard deviation. [¶]Only one sample processed for Hg analysis. ^ϕSample not processed for Hg analysis.

Table F4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of ^{203}Hg Added to Calcasieu River Sediment Suspensions

FRACTION	pH 6.5						pH 8.0					
	Redox Potential, mv			% ^{203}Hg recovered			Redox Potential, mv			% ^{203}Hg recovered		
	-150	50	250	500	-150	50	250	500	-150	50	250	500
Water Soluble	0.02 [†]	0.02	0.02	0.03	0.04	0.04	0.08	0.17	±0.01	±0.00	±0.01	±0.02
	±0.00 [‡]	±0.00	±0.00	±0.01	±0.01	±0.01	±0.01	±0.02	±0.01	±0.00	±0.01	±0.02
Soluble Organic Bound	0.03	0.02	0.02	0.02 [¶]	0.07	0.05	0.07	0.18	±0.00	±0.00	±0.03	±0.01
	±0.00	±0.00	±0.00	±0.00	±0.02	±0.00	±0.02	±0.01	±0.02	±0.00	±0.03	±0.01
Exchangeable	0.03	0.04	0.08	0.08	0.02	0.03	0.05	0.10	±0.00	±0.00	±0.02	±0.01
	±0.00	±0.00	±0.00	±0.01	±0.00	±0.01	±0.01	±0.01	±0.00	±0.01	±0.02	±0.01
Reducible	1.18	0.25	1.53	1.70	0.60	0.53	0.56	0.92	±0.24	±0.04	±0.14	±0.09
	±0.24	±0.04	±0.08	±0.12	±0.00	±0.14	±0.23	±0.09	±0.00	±0.14	±0.23	±0.09
DTPA Extractable	1.27	2.47	6.51	6.17	1.31	2.81	3.93	3.63	±0.25	±0.15	±0.68	±0.11
	±0.25	±0.15	±0.63	±0.19	±0.08	±0.68	±0.99	±0.11	±0.08	±0.68	±0.99	±0.11

[†]Mean of duplicate samples. [‡]Standard deviation. [¶]Lost one sample.

Table G1. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Mercury in Mobile Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	Redox Potential, mv											
Water Soluble	9.42 [†]	2.54	4.93	0.21 [‡]	4.58	7.38	2.94	4.68	6.78	9.20	4.02	5.10
	±2.31 [‡]	±0.00	±2.32		±0.59	±1.65	±0.28	±2.21	±1.83	±3.32	±2.10	±2.41
Exchangeable	1.78	1.80	1.20	0.66	0.54	0.60	0.40	0.82 [‡]	1.42	0.14	0.43	n.d. [§]
	±0.16	±1.38	±0.95	±0.57	±0.15	±0.01	±0.29		±0.37	±0.19	±0.21	
Reducible	8.18	2.20	5.83	4.40	2.32	1.65	2.04	0.90	7.80	3.84	5.51	3.44
	±0.12	±0.78	±0.77	±0.53	±2.13	±0.54	±0.02	±0.53	±0.78	±1.14	±1.47	±0.23
DTPA Extractable	1.08	1.12	13.14	16.86	2.32	3.34	5.84	5.54	12.68	7.51	9.82	10.72
	±0.83	±0.15	±1.75	±9.75	±2.39	±1.11	±2.45	±1.46	±6.33	±1.03	±3.53	±4.67

[†] Mean of duplicate samples. [‡] Lost one sample. [‡] Standard deviation. [§] Not detectable.

Table 62. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Mercury in Mississippi River Sediment Suspensions (2.4 µg Hg/g oven dry solids added)

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	µg Hg/kg oven dry solids											
Water Soluble	7.75 [†] ±0.00 [‡]	7.22 ±0.92	8.38 ±6.51	7.72 ±3.03	4.46 ±0.52	2.37 ±0.49	2.07 [‡] ±0.49	3.15 [‡] ±0.49	14.74 ±8.42	2.13 ±2.01	1.05 ±0.49	1.08 ±2
Soluble Organic Bound	4.15 ±1.69	2.42 ±0.27	1.89 ±0.87	1.10 ±0.01	4.97 ±2.29	2.36 ±0.01	2.42 ±2.20	0.78 ±0.14	4.21 ±0.28	3.87 ±2.52	5.24 ±1.69	4.50 ±0.01
Exchangeable	5.68 ±0.93	4.82 ±0.02	3.73 ±0.16	3.53 ±0.93	1.24 ±0.64	0.50 ±0.16	1.06 ±0.93	0.63 ±0.63	6.56 ±0.61	2.98 ±0.01	0.73 ±0.76	3.01 ±0.01
Reducible	40.26 ^ε	17.46 ^ε	5.56 ^ε	14.24 ^ε	26.28	21.45	20.79	20.13	9.18	24.33	20.61	9.45
DTPA Extractable	62.62 ^ε	39.43 ^ε	24.89 ^ε	11.15 ^ε	±3.78	±0.08	±3.27	±5.45	±7.23	±2.86	±4.60	±4.97
Insoluble Organic Bound	93.57 [‡]	100.67 [‡]	118.97 [‡]	235.35 [‡]	29.35 ±6.33	25.74 ±0.61	25.60 ±1.38	14.45 ±2.52	31.96 ±1.57	48.24 ±5.31	45.94 ±2.81	19.37 ±0.10

[†]Mean of duplicate samples. [‡]Lost one sample. [‡]Standard deviation. ^εComposite for two samples. [‡]Only one sample processed for Hg analysis. [‡]Sample not processed for Hg analysis.

Table G3. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Mercury in Calcasieu River Sediment Suspensions

FRACTION	pH 6.5				pH 8.0			
	Redox Potential, mv				Redox Potential, mv			
	-150	50	250	500	-150	50	250	500
	----- µg Hg/g oven dry solids -----							
Water Soluble	10.76 [†]	5.04	1.52	1.22	2.74	2.62	1.07	0.98
	±6.60 [‡]	±1.87	±0.01	±0.16	±0.00	±1.56	±0.00	±1.10
Exchangeable	3.00	4.92	4.69	n.d. [§]	1.41	0.15	0.14	0.62
	±1.91	±4.69	±0.51		±0.17	±0.21	±0.20	±0.01
Reducible	6.43	4.28	5.61	11.40	10.08	13.31	5.76	5.11
	±0.04	±0.18	±0.25	±7.13	±0.53	±4.38	±0.02	±0.54
DTPA Extractable	2.06	2.46	4.11	4.86	1.94	2.50	2.90	3.46
	±0.91	±0.00	±0.49	±0.20	±0.23	±0.34	±0.69	±0.05

[†]Mean of duplicate samples. [‡]Standard deviation. [§]Not detectable.

Table III. The Effect of pH and Redox Potential on the Chemical Form and Distribution of ²¹⁰Pb Added to Mobile Bay Sediment Suspensions

FRACTION	pH 5.0						pH 6.5						pH 8.0														
	-150		50		250		-150		50		250		-150		50		250		-150		50		250		500		
	Redox Potential, mv																										
Water Soluble	% of ²¹⁰ Pb recovered																										
	n.d. [§]	0.02 [†]	0.01	0.02	0.02	0.02	0.02	n.d.	0.02	0.02	0.02	0.02	n.d.	0.01	0.14	0.04	0.06	0.01	0.01	0.01	0.01	0.04	0.04	0.06	0.06	0.06	0.06
Soluble Organic Bound	±0.00 [‡]	±0.00 [‡]	±0.00	±0.01	±0.01	±0.01	±0.02	±0.02	±0.02	±0.02	±0.02	±0.02	±0.02	±0.02	±0.04	±0.05	±0.03	±0.01	±0.01	±0.01	±0.01	±0.04	±0.05	±0.05	±0.03	±0.03	±0.03
	0.01	n.d.	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.06	0.05	n.d.	n.d.	n.d.	n.d.	0.07	0.06	0.06	0.05	0.05	0.05
Exchangeable	±0.00	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01
	5.33	4.81	4.01	3.14	3.14	3.14	0.11	0.28	0.12	0.12	0.12	0.11	0.11	0.04	0.04	0.01	0.02	0.04	0.04	0.04	0.04	0.04	0.01	0.01	0.02	0.02	0.02
Reducible	27.64	44.62	51.86	57.19	57.19	57.19	23.18	46.75	49.21	49.86	49.86	49.86	49.86	32.13	37.41	44.60	50.90	32.13	32.13	32.13	32.13	37.41	44.60	50.90	50.90	50.90	50.90
	±1.63	±0.20	±0.24	±1.54	±1.54	±1.54	±7.16	±14.50	±2.20	±2.06	±2.06	±2.06	±2.06	±1.39	±0.81	±0.07	±1.77	±1.39	±1.39	±1.39	±1.39	±0.81	±0.07	±1.77	±1.77	±1.77	±1.77
DTPA Extractable	27.17	41.68	32.20	30.60	30.60	30.60	27.53	37.37	34.26	35.28	35.28	35.28	35.28	34.78	36.95	39.38	34.96	34.78	34.78	34.78	34.78	36.95	39.38	34.96	34.96	34.96	34.96
	±3.17	±2.43	±0.60	±0.48	±0.48	±0.48	±10.97	±10.66	±3.52	±2.26	±2.26	±2.26	±2.26	±0.27	±2.41	±6.21	±1.26	±0.27	±0.27	±0.27	±0.27	±2.41	±6.21	±1.26	±1.26	±1.26	±1.26

§Not detectable. †Mean of duplicate samples. ‡Standard deviation. ¶Lost one sample.

Table 11. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Lead in Barataria Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv					
	-150	0	450	-150	0	200	450	-150	0	200	450	
Water Soluble ^o	870	580	140	250	740	470	110	140	180	190	300	340
Exchangeable ^o	6250	4750	1210	2700	2450	3300	2050	3100	2400	1400	2200	2970
Reducible*	8.7	n.d. [§]	n.d.	n.d.	n.d.	11.5	13.2	9.4	n.d.	n.d.	n.d.	n.d.
	±0.0					±2.3	±0.0	±0.0				

^oDetermined by flameless atomic absorption, µg/kg.

*Determined by flame atomic absorption, µg/g.

§Not Detectable.

Table 12. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Lead in Mobile Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
Water Soluble ^O	530	390	400	190	170	100	130	170	130	170	270	160
	±90	±60	±310	±70	±140	±70	±10	±50	±80	±100	±120	±80
Exchangeable ^O	n.d. [§]	290	140	250	420	220	110	100	70	230	50	580
	---	±100	±70	±50	±190	±30	±30	±90	±40	±150	±70	±40
Reducible*	n.d.	6.0	9.9	11.6	n.d.	3.2	4.7	10.3	5.5	6.4	5.6	10.2
		±1.2	±2.4	±0.1		±4.5	±6.7	±1.2	±0.1	±1.1	±0.0	±1.2
DTPA Extractable*	4.1	6.0	4.8	4.0	3.9	5.3	4.6	5.9	6.4	6.8	6.2	6.1
	±0.3	±0.0	±0.0	±0.4	±1.5	±0.9	±1.0	±0.9	±1.0	±1.5	±1.5	±0.5

^ODetermined by flameless atomic absorption, µg/kg.

[§]Not detectable.

*Determined by flame atomic absorption, µg/g.

Table 13. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Lead in Mississippi River Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
Water Soluble ^o	690	620	1030	1460	120	130	540	1020	140	60	50	40
	±150	±160	±440	±370	±20	±0	±230	±240	±100	±40	±20	±20
Exchangeable ^o	2810	1650	1390	2760	5450	5670	4130	5730	2590	1670	3390	1780
	±1180	±370	±90	±450	±840	±160	±1800	±590	±150	±870	±1110	±160
DTPA Extractable*	5.0	9.1	9.1	9.6	5.5	7.4	7.6	8.4	4.7	5.8	5.4	4.8
	±0.0	±0.6	±0.0	±0.5	±0.2	±0.3	±0.3	±0.2	±0.5	±0.0	±0.5	±0.5
Insoluble Organic Bound [§]	4.3	n.d. [§]	n.d.	n.d.	5.3	4.2	4.4	3.4	7.1	6.2	4.7	3.9
	±0.7				±1.3	±0.2	±1.2	±1.1	±0.1	±0.1	±0.8	±0.1

^oDetermined by flameless atomic absorption, µg/kg.

*Determined by flame atomic absorption, µg/g.

[§]Not detectable.

Table 14. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Lead in Calcasieu River Sediment Suspensions

FRACTION	pH 6.5				pH 8.0			
	Redox Potential, mv				Redox Potential, mv			
	-150	50	250	500	-150	50	250	500
Water Soluble [⊙]	330	140	90	60	70	100	120	180
	±250	±70	±30	±10	±10	±10	±10	±90
Exchangeable [⊙]	n.d. [§]	310	340	330	640	1580	370	190
	---	±30	±60	±224	±10	±140	±70	±10
Reducible*	10.1	12.5	20.8	22.3	n.d.	9.1	16.5	18.4
	±1.4	±0.0	±1.6	±0.6		±1.0	±2.3	±0.3
DTPA Extractable*	3.9	12.4	13.9	14.3	6.6	13.4	12.0	15.5
	±1.5	±1.0	±0.8	±1.4	±0.1	±0.2	±0.9	±0.7
Insoluble Organic Bound*	11.6	8.3	5.0	4.5	9.0	5.6	3.4	2.2
	±0.9	±0.5	±0.4	±0.6	±1.7	±1.0	±0.4	±0.5

[⊙]Determined by flameless atomic absorption, µg/kg.

[§]Not detectable.

*Determined by flame atomic absorption, µg/g.

Table J2. The Effect of pH and Redox Potential on the Chemical Form and Distribution of ^{109}Cd Added to Mississippi River Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0		
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv		
	-150	50	250	-150	50	250	-150	50	250
Water Soluble	1.11 [†]	3.40	27.29	33.69	0.58	0.31	1.89	1.06	0.19
	± 0.14 [‡]	± 2.85	± 0.96	± 0.44	± 0.81	± 0.21	± 0.27	± 1.51	± 0.27
Soluble Organic Bound	0.11	0.77	0.28	0.58	0.31	0.31	1.89	n.d. [§]	0.19
	± 0.16	± 0.55	± 0.40	± 0.81	± 0.84	± 0.55	± 0.21	± 0.03	± 1.51
Exchangeable	1.98	31.17	39.12	57.47	1.31	1.21	11.35	4.99	3.32
	± 0.73	± 14.76	± 0.69	± 2.51	± 0.31	± 0.47	± 1.48	± 3.25	± 0.02
Reducible	11.60	21.61	11.19	14.01	9.77	12.26	10.95	7.37	13.56
	± 2.23	± 7.79	± 2.81	± 1.92	± 3.27	± 2.70	± 2.29	± 1.29	± 7.31
DTPA Extractable	14.13	20.62	14.05	11.60	10.85	12.67	13.64	16.34	18.21
	± 2.58	± 0.93	± 0.71	± 2.39	± 2.11	± 0.37	± 3.93	± 0.29	± 0.98
Insoluble Organic Bound	62.16	16.24	12.48	6.09	31.38	20.21	16.22	20.25	12.11
	± 1.14	± 4.81	± 2.23	± 0.23	± 0.37	± 0.58	± 4.42	± 0.92	± 1.75

[†]Mean of duplicate samples. [‡]Not detectable. [§]Standard deviation.

Table K1. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Cadmium in Barataria Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv	µg Cd/kg oven dry solids	Flame atomic absorption	Redox Potential, mv	µg Cd/kg oven dry solids	Flame atomic absorption	Redox Potential, mv	µg Cd/kg oven dry solids	Flame atomic absorption			
Water Soluble ⁰	20	11	49	142	10	10	17	19	7	21	5	16
Exchangeable ⁰	18	32	86	104	25	98	99	69	15	47	125	92
Reducible*	n.d. ⁵	n.d.	300 ⁴	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
			420 ⁴									

⁰Determined by flameless atomic absorption. ⁴Determined by flame atomic absorption. ⁵Not detectable. [†]Mean of duplicate samples. ^{*}Standard deviation.

Table K2. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Cadmium in Mobile Bay Sediment Suspensions

FRACTION	pH 5.0						pH 6.5						pH 8.0							
	-150		50		250		-150		50		250		-150		50		250		500	
	Redox Potential, mv						µg Cd/kg oven dry solids													
Water Soluble ^o	113 [†]	175	51	235	66	40	65	188	39	29	35	76								
	±26*	±39	±5	±92	±18	±1	±12	±74	±14	±4	±2	±5								
Exch. geable ^o	102	108	102	97	206	149	115	253	238	340	237	262								
	±26	±51	±7	±8	±26	±17	±22	±254	±106	±38	±57	±109								
Reducible*	590	680	160	500	260	320	400	n.d. [§]	460	370	180	n.d.								
	±110	±0	±230	±0	±360	±0	±120		±140	±10	±260									
DTPA Extractable*	110	170	160	160	330	270	240	240	n.d.	n.d.	n.d.	60								
	±0	±0	±0	±0	±150	±0	±50	±40				±80								

^oDetermined by flameless atomic absorption. [†]Mean of duplicate samples. [‡]Standard deviation. [§]Determined by flame atomic absorption. [¶]Not detectable.

Table K3. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Cadmium in Mississippi River Sediment Suspensions

FRACTION	pH 5.0						pH 6.5						pH 8.0												
	-150		50		250		500		-150		50		250		500		-150		50		250		500		
	µg Cd/kg oven dry solids																								
Water Soluble ⁰	95 [†]	37	196	310	16	23	9	14	14	14	14	14	14	4	14	14	13								
	±4 [‡]	±7	±10	±114	±2	±20	±2	±0	±0	±0	±0	±0	±0	±2	±2	±2	±5								
Exchangeable ⁰	169	278	120	375	99	67	152	197	197	197	197	197	197	76	62	87	89								
	±58	±80	±59	±83	±25	±38	±68	±34	±34	±34	±34	±34	±34	±47	±26	±41	±31								
Reducible*	480	n.d. [§]	190	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	570	490	190	n.d.								
	±140		±260											±260	±140	±270									
DTPA Extractable*	220	230	220	260	330	390	400	560	560	560	560	560	560	190	230	300	380								
	±0	±0	±0	±60	±10	±120	±20	±10	±10	±10	±10	±10	±10	±50	±0	±0	±0								
Insoluble Organic Bound*	240	120	n.d.	n.d.	480	470	470	290	290	290	290	290	290	510	520	390	310								
	±0	±170			±50	±60	±120	±50	±50	±50	±50	±50	±50	±190	±170	±0	±80								

⁰Determined by flameless atomic absorption. [†]Mean of duplicate samples. [‡]Standard deviation. [§]Determined by flame atomic absorption. [¶]Not detectable.

Table K4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Cadmium in Calcasieu River Sediment Suspensions

FRACTION	pH 6.5			pH 8.0				
	Redox Potential, mv							
	-150	50	250	500	-150	50	250	500
	----- $\mu\text{g Cd/kg oven dry solids}$ -----							
Water Soluble [⊖]	184 [†]	126	133	167	148	270	134	204
	$\pm 47^{\ddagger}$	± 22	± 64	± 10	± 35	± 67	± 34	± 44
Exchangeable [⊖]	473	1030	303	388	68	17	17	24
	± 252	± 1230	± 165	± 121	± 87	± 10	± 7	± 1
Reducible [*]	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	160
								± 230
DTPA Extractable [*]	n.d.	70	70	n.d.	n.d.	170	200	200
		± 100	± 100			± 40	± 0	± 0
Insoluble Organic Bound [*]	600	420	420	430	320	120	150	190
	± 120	± 120	± 120	± 110	± 0	± 160	± 0	± 50

[⊖]Determined by flameless atomic absorption. [†]Mean of duplicate samples. [‡]Standard deviation.

^{*}Determined by flame atomic absorption. [§]Not detectable.

Table L1. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable $\text{NH}_4^+\text{-N}$ in Barataria Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	0	200	450	-150	0	200	450	-150	0	200	450
	Redox Potential, mv											
Water Soluble	97.4	98.2	46.2	50.6	79.9	87.2	41.6	22.3	33.2	40.5	6.8	3.3
Exchangeable	81.1	58.0	33.6	50.7	90.5	84.5	42.5	21.0	40.0	48.5	10.7	1.0
	----- $\mu\text{g N/g oven dry solids}$ -----											

Table L2. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable $\text{NH}_4^+\text{-N}$ in Mobile Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	Redox Potential, mv											
Water Soluble	148.5 [†]	36.0	45.8	22.1	71.6	17.0	24.0	25.5	6.4	17.1	37.7	4.2
Exchangeable	99.5	10.0	0.2	0.6	16.6	3.3	3.8	1.4	12.5	14.9	15.0	0.6
	±57.7 [‡]	±18.6	±25.7	±2.8	±6.6	±19.3	±20.3	±14.8	±4.0	±0.0	±2.4	±0.6
	±124.3	±12.6	±0.4	±0.8	±8.2	±2.4	±3.6	±0.3	±0.6	±14.6	±3.7	±0.8
	----- $\mu\text{g N/g oven dry solids}$ -----											

[†]Mean of duplicate samples. [‡]Standard deviation.

Table 13. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable $\text{NH}_4^+\text{-N}$ in Mississippi River Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	Redox Potential, mv											
Water Soluble	57.6 [†]	159.9	97.5	2.7	38.1	15.3	10.6	1.8	9.6	5.5	3.2	0.9
	±1.8 [‡]	±4.1	±46.2	±0.0	±25.0	±1.0	±6.6	±0.0	±0.7	±0.0	±2.0	±1.3
Exchangeable	39.2	104.7	27.5	19.0	29.4	92.4	11.0	0.0	53.2	17.7	6.8	0.7
	±11.6	±64.4	±31.1	±7.9	±6.3	±67.9	±10.1	±0.0	±23.8	±3.4	±4.3	±1.0

Table 14. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable $\text{NH}_4^+\text{-N}$ in Calcasieu River Sediment Suspensions

FRACTION	pH 6.5			pH 8.0				
	-150	50	250	500	-150	50	250	500
	Redox Potential, mv							
Water Soluble	54.4 [†]	47.2	30.8	2.3	21.8	15.6	n.d. [‡]	7.8
	±6.1 [‡]	±11.8	±0.5	±0.6	±5.9	±4.4	---	±11.0
Exchangeable	37.2	30.0	21.4	13.9	28.2	11.6	1.2	0.6
	±11.5	±6.4	±3.6	±13.7	±0.8	±0.1	±0.0	±0.0

[†] Mean of duplicate samples. [‡] Not detectable. [§] Standard deviation.

Table M1. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Phosphorus in Barataria Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	0	200	450	-150	0	200	450	-150	0	200	450
	Redox Potential, mv											
----- µg P/g oven dry solids												
Water Soluble	79.5	45.1	1.4	6.5	31.4	5.9	4.5	4.9	12.7	12.5	15.4	14.9
Exchangeable**	63.3	44.9	13.0	14.0	21.6	15.4	11.5	12.8	6.4	12.2	14.9	14.3

**Sodium acetate-extractable P includes water-soluble phase.

Table M2. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Phosphorus in Mobile Bay Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	Redox Potential, mv											
----- µg P/g oven dry solids												
Water Soluble	79.3 [±]	8.5	5.0	3.9	42.5	5.5	6.7	6.3	43.3	16.7	12.2	14.0
	+1.5 [±]	+0.6	+0.6	+5.6	+2.9	+0.5	+1.1	+1.6	+2.9	+1.8	+1.2	+3.7
Exchangeable	191.7	19.7	13.1	13.2	53.0	10.4	10.3	10.2	47.8	18.7	17.6	18.2
	+28.5	+2.3	+1.4	+1.6	+3.3	+0.0	+0.1	+0.1	+2.7	+0.6	+0.0	+0.9

-Mean of duplicate samples.

*Standard deviation.

Table M3. The Effect of pH and Redox Potential on Water Soluble and Exchangeable Phosphorus in Mississippi River Sediment Suspensions

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	Redox Potential, mv			-150	50	250	500	
	µg P/g oven dry solids									-150	50	250
Water Soluble	146.9 [†]	59.3	7.7 [¶]	4.6 [¶]	37.6	13.0	5.9 [¶]	7.1 [¶]	52.8	26.2	16.5	16.4
	±13.4 [‡]	±28.7			±8.7	±4.0			±6.6	±0.7	±1.3	±3.2
Exchangeable	450.8	144.3	32.5 [¶]	36.6 [¶]	66.4	26.7	16.9	21.9	117.2	85.7	66.4	76.9
	±22.3	±3.7			±16.5	±6.7	±1.7	±1.3	±2.3	±6.8	±2.6	±2.6

[†]Mean of duplicate samples.

[¶]Lost one sample.

[‡]Standard deviation.

Table M4. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Phosphorus in Calcasieu River Sediment Suspensions

FRACTION	pH 6.5						pH 8.0		
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv		
	-150	50	250	-150	50	250	50	250	500
	----- µg P/g oven dry solids -----								
Water Soluble	89.3 [†]	31.8	29.1	24.6	42.6	13.4	8.4	16.6	
	±2.7 [#]	±2.0	±1.3	±9.3	±9.2	±0.6	±2.8	±5.9	
Exchangeable	84.8	39.9	34.5	38.4	18.5	8.4	16.1	20.1	
	±15.8	±2.1	±0.5	±1.1	±1.1	±0.9	±5.3	±0.3	

[†]Mean of duplicate samples.

[#]Standard deviation.

Table N3. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Zinc 24 Hours After Accumulative Additions of Zinc to Mississippi River Sediment Suspensions*

Accumulative Zn Added $\mu\text{g/g}$	pH 5.0						pH 6.5						pH 8.0											
	-150		50		250		500		-150		50		250		500		-150		50		250		500	
	Redox Potential, mv						Water-Soluble Zn, $\mu\text{g/g}$ oven dry solids						Exchangeable Zn, $\mu\text{g/g}$ oven dry solids											
0	1.02	4.16	6.20	2.56	2.56	2.56	n.d. ⁵	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
1	1.74	4.97	6.59	2.19	2.19	2.19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
6	6.22	10.19	4.69	4.60	4.60	4.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
31	3.07	14.72	20.31	11.10	11.10	11.10	n.d.	0.17	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
106	37.79	45.62	49.79	41.98	41.98	41.98	n.d.	0.86	0.82	0.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
260	109	111	120	106	106	106	0.87	7.49	5.40	4.71	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
500	232	226	228	212	212	212	1.77	9.21	14.26	15.28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
0	2.30	8.29	8.49	6.05	6.05	6.05	n.d.	0.36	0.37	0.51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
1	3.86	11.90	10.40	7.91	7.91	7.91	0.21	0.77	0.91	0.86	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
6	4.24	12.99	10.74	9.47	9.47	9.47	0.21	0.94	1.21	0.97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
31	8.47	22.35	18.46	18.00	18.00	18.00	1.06	3.34	3.74	3.32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
106	50.02	72.62	71.08	72.72	72.72	72.72	10.46	14.81	16.90	17.31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
260	120	144	114	126	126	126	53	61	65	66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
500	209	234	192	212	212	212	128	131	138	139	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	

*Determined by flame atomic absorption. ⁵Not detectable.

Table N4. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Zinc in Mississippi River Sediment Suspensions (260 µg Zn/g oven dry solids added)*

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	500	-150	50	250	500	-150	50	250	500
	µg Zn/g oven dry solids											
Water Soluble	109.30	110.96	119.57	106.25	0.88	7.49	5.40	4.77	0.31	0.53	0.26	0.32
Soluble Organic Bound	1.45	1.77	0.67	0.76	0.87	7.49	5.40	4.71	Ω	Ω	Ω	Ω
Exchangeable	120.35	143.95	113.88	126.24	52.60	61.03	65.08	66.02	3.09	9.93	4.15	2.32
Reducible	72.16	73.54	60.36	84.58	247.10	256.50	212.80	234.75	289.30	264.50	269.99	310.89
DIPA Extractable	2.31	1.93	2.10	2.79	6.93	6.23	6.35	7.37	8.64	8.47	7.51	9.68
Insoluble Organic Bound	15.92	4.39	4.17	2.02	15.47	9.04	13.14	6.70	7.24	6.50	6.79	3.86

*Determined by flame atomic absorption. Ω Not sampled.

Table G1. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Mercury 24 Hours After Accumulative Additions of Hg to Barataria Bay Sediment Suspensions

Accumulative Hg Added µg/g	pH 6.5				pH 8.0			
	Redox Potential, mv		Water-Soluble Hg, µg/g oven dry solids		Redox Potential, mv		Water-Soluble Hg, µg/g oven dry solids	
	-150	0	200	450	-150	0	200	450
0	n.d. ⁵	n.d.	n.d.	n.d.	0.006	0.003	0.004	0.002
1	0.009	0.010	0.008	0.006	0.004	0.005	0.004	0.005
7	0.026	0.036	0.014	0.025	0.018	0.024	0.022	0.026
19	0.050	0.029	0.023	0.066	0.034	0.025	0.018	0.022
40	0.066	0.062	0.046	0.042	0.027	0.032	0.036	0.035
85	0.029	0.048	0.066	0.048	0.042	0.052	0.085	0.054
185	0.186	0.184	0.167	1.276	0.058	0.120	0.299	0.251
400	0.220	0.239	0.418	0.611	0.484	0.791	1.066	1.149
	Exchangeable Hg, µg/g oven dry solids							
0	0.015	0.015	0.011	0.011	n.d.	n.d.	n.d.	n.d.
1	0.017	0.015	0.013	0.011	0.012	0.003	0.009	0.005
7	0.011	0.020	0.028	0.022	0.008	0.003	0.010	0.002
19	0.041	0.050	0.046	0.015	0.009	0.008	0.011	0.005
40	0.051	0.046	0.045	0.039	0.017	0.018	0.021	0.010
85	0.072	0.089	0.096	0.081	0.016	0.025	0.018	0.029
185	0.270	0.250	0.200	0.425	0.014	0.014	0.078	0.078
400	0.149	0.197	0.222	2.443	0.171	0.158	0.313	0.276

⁵Not detectable.

Table O2. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Mercury 24 Hours After Accumulative Additions of Mercury to Mobile Bay Sediment Suspensions

Accumulative Hg Added μg/g	pH 5.0			pH 6.5			pH 8.0									
	-150	50	250	500	Redox Potential, mv		Water-Soluble Hg, μg/g oven dry solids		-150	50	250	500				
					-150	250	500	0.005	0.007	0.003	0.005					
0	0.009	0.002	0.005	n.d. ⁵	0.007	0.006	0.005	0.005	0.007	0.003	0.005	0.007	0.009	0.004	0.005	
1	0.007	0.002	0.003	0.001	0.007	0.006	0.005	0.005	0.007	0.006	0.005	0.008	0.006	0.006	n.d.	
6	0.012	0.001	0.003	0.001	0.005	0.005	0.003	0.003	0.005	0.005	0.003	0.008	0.004	0.005	0.003	
26	0.012	0.005	0.008	0.008	0.006	0.007	0.004	0.004	0.006	0.007	0.004	0.010	0.006	0.007	0.006	
106	0.002	0.012	0.035	0.226	0.014	0.035	0.071	0.071	0.014	0.035	0.008	0.010	0.019	0.029	0.157	
260	0.004	0.024	25.000	53.800	0.120	0.182	4.050	4.050	0.120	0.182	0.275	0.075	0.204	0.115	0.515	
500	0.007	0.015	148.800	217.320	0.569	19.980	31.010	31.010	0.569	19.980	25.580	0.024	0.403	0.296	0.827	
					Exchangeable Hg, μg/g oven dry solids											
0	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	n.d.	n.d.	n.d.	n.d.	
1	0.005	0.001	0.001	0.001	0.007	0.003	0.001	0.001	0.007	0.003	0.003	n.d.	n.d.	n.d.	n.d.	
6	0.004	0.001	0.001	0.004	0.008	0.002	0.002	0.002	0.008	0.002	0.003	0.011	0.010	0.006	0.003	
26	0.003	0.002	0.003	0.002	0.012	0.008	0.005	0.005	0.012	0.008	0.005	0.001	0.002	0.002	0.007	
106	0.004	0.003	0.272	1.380	0.016	0.016	0.048	0.048	0.016	0.016	0.016	0.002	0.004	0.008	0.072	
260	0.004	0.006	10.780	15.050	0.014	0.073	0.140	0.140	0.014	0.073	0.095	0.001	0.045	0.041	0.219	
500	0.019	1.710	48.130	58.710	0.395	2.070	2.890	3.570	0.395	2.070	2.890	0.003	0.149	0.180	0.284	

⁵Not detectable.

Table O3. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Mercury 24 Hours After Accumulative Additions of Mercury to Mississippi River Sediment Suspensions

Accumulative Hg Added $\mu\text{g/g}$	pH 5.0				pH 6.5				pH 8.0			
					Redox Potential, mv							
	-150	50	250	500	-150	50	250	500	-150	50	250	500
0	0.008	0.007	0.008	0.008	0.004	0.002	0.002	0.003	0.015	0.002	0.001	0.001
1	0.002	0.003	0.002	0.005	0.006	0.005	0.004	0.002	0.011	0.008	0.008	0.008
6	0.004	0.003	0.002	0.011	0.005	0.007	0.010	0.003	0.008	0.011	0.011	0.017
31	0.005	0.004	0.002	3.930	0.018	0.008	0.005	0.091	0.022	0.022	0.024	0.109
106	0.025	0.011	0.016	55.650	0.028	0.024	0.099	0.951	0.068	0.083	0.158	0.350
260	0.099	0.053	21.120	158.300	0.017	0.214	0.780	8.730	0.077	0.146	0.669	0.938
500	0.061	0.052	187.500	374.000	0.038	1.760	8.160	62.780	0.109	0.567	2.026	2.167
0	0.006	0.005	0.004	0.003	Exchangeable Hg, $\mu\text{g/g}$ oven dry solids				0.006	0.003	0.001	0.003
1	0.001	0.001	0.002	0.001	0.001	n.d. ⁵	0.001	0.001	n.d.	n.d.	n.d.	n.d.
6	0.001	0.001	0.001	0.005	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001
31	0.002	0.001	0.001	0.037	n.d.	n.d.	n.d.	0.085	0.003	0.002	0.003	0.039
106	0.005	0.013	3.280	19.850	0.001	0.019	0.155	1.223	0.002	0.005	0.064	0.104
260	0.012	0.070	32.400	67.860	0.005	0.453	1.280	6.550	0.025	0.289	1.082	0.910
500	0.097	0.068	72.800	96.360	0.015	3.300	7.010	20.270	0.021	0.222	0.672	0.675

⁵Not detectable.

Table 04. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Mercury in Mississippi River Sediment Suspensions
(260 µg Hg/g oven dry solids added)

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	-150	Redox Potential, mv		-150	50	250	500		
					50	250						
Water Soluble	0.03	0.05	21.12	158.30	0.17	0.21	0.78	8.73	0.08	0.15	0.67	0.94
Soluble Organic Bound	0.01	0.01	0.06	0.24	0.02	0.13	0.33	0.76	Ω	-----	-----	-----
Exchangeable	0.01	0.07	32.40	67.84	0.01	0.45	1.28	6.55	0.02	0.29	1.08	0.91
Reducible	0.31	0.88	3.34	3.28	1.23	2.36	7.07	13.17	1.10	1.18	2.11	4.93
DTPA Extractable	2.37	3.78	7.27	10.94	1.63	12.81	49.68	85.00	8.90	11.60	30.22	69.52
Insoluble Organic Bound	28.73	29.28	30.98	9.35	-----	-----	-----	-----	-----	-----	-----	-----

Not sampled.

Table P1. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Cadmium 24 Hours After Accumulative Additions of Cadmium to Barataria Bay Sediment Suspensions*

Accumulative Cd Added	pH 5.0			pH 6.5			pH 8.0					
	Redox Potential, mv			Redox Potential, mv			Redox Potential, mv					
	-150	0	200	450	-150	0	200	450	-150	0	200	450
0	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	0.36	0.40	0.83	1.26	0.33	0.46	0.57	0.54	0.32	0.32	0.36	0.33
7	0.36	0.35	5.12	4.95	0.39	0.40	2.13	1.91	0.27	0.37	0.41	0.44
19	0.31	0.31	13.34	13.46	0.33	0.35	7.35	5.77	0.27	0.64	0.83	1.05
40	0.37	0.36	32.96	25.43	0.33	0.41	20.02	19.5 [§]	1.15	1.77	1.88	2.42
85	0.48	0.48	78.00	58.46	0.39	0.41	36.57	37.46	4.65	4.44	5.38	5.46
185	0.60	0.51	169.10	159.40	0.69	0.59	125.30	133.37	14.97	13.40	12.66	12.05
400	0.34	26.24	293.00	337.70	0.65	58.55	279.10	297.40	64.82	60.15	52.96	34.43
					Exchangeable Cd, µg/g oven dry solids							
0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	n.d.	n.d.	0.92	0.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7	n.d.	n.d.	2.92	1.83	n.d.	n.d.	1.32	1.24	n.d.	n.d.	0.26	0.27
19	n.d.	n.d.	6.59	4.96	n.d.	n.d.	3.55	4.47	0.26	0.62	1.12	1.08
40	n.d.	0.48	12.78	7.63	n.d.	n.d.	4.41	10.84	1.35	2.39	3.02	3.21
85	n.d.	0.40	23.06	14.33	n.d.	n.d.	21.16	24.36	7.54	7.06	8.76	7.97
185	n.d.	1.13	41.31	40.96	n.d.	n.d.	51.53	51.74	19.57	19.46	20.75	21.32
400	0.16	22.31	55.97	66.80	n.d.	34.83	98.78	106.11	74.85	58.02	58.12	53.32

*Determined by flame atomic absorption. [§]Not detectable.

Table P2. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Cadmium 24 Hours After Accumulative Additions of Cadmium to Mississippi River Sediment Suspensions

Accumulative Cd Added $\mu\text{g/g}$	pH 5.0						pH 6.5						pH 8.0													
	-150		50		250		-150		50		250		-150		50		250		-150		50		250		500	
	Redox Potential, mv						Water-Soluble Cd, $\mu\text{g/g}$ oven dry solids						Exchangeable Cd, $\mu\text{g/g}$ oven dry solids													
0	n.d. ⁵	.12	.22	.56	n.d.	n.d.	.12	.18	.18	.18	.18	.18	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12
1	.18	.42	.81	1.01	1.01	1.01	.12	.18	.18	.18	.18	.18	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12
6	.24	2.07	3.49	3.07	3.07	3.07	.12	.18	.18	.18	.18	.18	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12	.12
31	.36	17.85	23.37	19.21	19.21	19.21	3.71	3.91	4.00	4.00	4.00	3.85	3.71	3.91	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
106	7.58	53.18	56.52	50.69	50.69	50.69	8.10	6.38	6.37	6.37	6.24	6.24	8.10	6.38	6.37	6.37	6.24	6.24	6.24	6.24	6.24	6.24	6.24	6.24	6.24	6.24
260	104	103	148	137	137	137	17.21	11.74	11.14	11.14	16.32	16.32	17.21	11.74	11.14	11.14	16.32	16.32	16.32	16.32	16.32	16.32	16.32	16.32	16.32	16.32
500	281	301	301	287	287	287	42.87	33.08	34.29	34.29	84.74	84.74	42.87	33.08	34.29	34.29	84.74	84.74	84.74	84.74	84.74	84.74	84.74	84.74	84.74	84.74
0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	n.d.	.35	.51	.87	.87	.87	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	n.d.	2.56	2.11	2.65	2.65	2.65	n.d.	.86	1.84	1.84	0.89	0.89	n.d.	.86	1.84	1.84	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89
31	n.d.	12.62	10.19	13.12	13.12	13.12	5.16	12.14	13.57	13.57	7.79	7.79	5.16	12.14	13.57	13.57	7.79	7.79	7.79	7.79	7.79	7.79	7.79	7.79	7.79	7.79
106	6.47	41.61	32.36	39.51	39.51	39.51	53.64	54.64	55.67	55.67	39.97	39.97	53.64	54.64	55.67	55.67	39.97	39.97	39.97	39.97	39.97	39.97	39.97	39.97	39.97	39.97
260	75	101	81	101	101	101	122	119	118	118	107	107	122	119	118	118	107	107	107	107	107	107	107	107	107	107
500	147	180	142	171	171	171	235	246	238	238	209	209	235	246	238	238	209	209	209	209	209	209	209	209	209	209

⁵Not detectable.

Table P3. The Effect of pH and Redox Potential on the Chemical Form and Distribution of Cadmium in Mississippi River Sediment Suspensions
(260 µg Cd/g oven dry solids added)*

FRACTION	pH 5.0			pH 6.5			pH 8.0					
	-150	50	250	Redox Potential, mv			-150	50	250	500		
				50	250	500						
Water Soluble	103.75	139.84	147.75	136.81	17.22	11.74	11.17	16.34	1.42	1.56	1.12	0.70
Soluble Organic Bound	0.44	0.29	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	-----Ω	-----	-----	-----
Exchangeable	78.00	101.35	81.53	101.17	122.02	119.26	118.26	107.09	62.20	81.01	60.32	43.51
Reducible	13.40	4.19	6.11	7.13	9.55	9.93	9.57	22.52	16.73	14.75	15.48	22.94
DTPA Extractable	11.58	8.41	7.06	9.74	30.80	28.82	31.24	47.66	46.58	42.71	50.37	65.01
Insoluble Organic Bound	40.10	2.61	1.18	0.95	19.73	17.55	12.61	9.27	45.63	29.19	31.93	36.65

*Determined by flame atomic absorption. [§]Not detectable. ^ΩNot sampled.

Table Q. The Effect of pH and Redox Potential on Water-Soluble and Exchangeable Lead 24 Hours After Accumulative Additions of Lead to Mobile Bay Sediment Suspensions*

Accumulative Pb Added µg/g	pH 5.0			pH 6.5			pH 8.0				
	-150	50	250	Redox Potential, mv			-150	50	250	500	
				-150	50	250					
0	n.d. [‡]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
106	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
260	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
500	n.d.	7.38	7.17	7.27	7.32	11.98	6.68	3.93	7.32	11.98	6.68
					Water-Soluble Pb, µg/g oven dry solids						
0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
106	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
260	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
					Exchangeable Pb, µg/g oven dry solids						
0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	n.d.	7.73	5.92	6.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
106	n.d.	3.75	26.74	27.74	n.d.	3.03	n.d.	n.d.	n.d.	n.d.	n.d.
260	n.d.	85.09	72.63	78.17	n.d.	14.51	11.48	n.d.	n.d.	n.d.	n.d.
500	4.31	255.64	190.87	218.04	5.54	48.36	31.43	n.d.	n.d.	n.d.	n.d.

*Determined by flame atomic absorption. ‡Not detectable (minimum detection limit ~ 2 µg/g in water-soluble and exchangeable fraction).

Table R1. The Effect of Dissolved Oxygen on the Chemical Form and Distribution of Iron in Barataria Bay Sediment Suspensions

Fraction	0.11% Oxygen			2.11% Oxygen			21% Oxygen					
	Redox Potential, mv	µg Fe/g oven dry solids		Redox Potential, mv	µg Fe/g oven dry solids		Redox Potential, mv	µg Fe/g oven dry solids				
Water Soluble	-200 (0) †	-170 (120)	-200 (0)	-160 (8)	-50 (48)	100 (168)	640 (288)	-260 (0)	-160 (0.5)	-40 (3.5)	150 (7)	610 (132)
Soluble Organic Bound	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Exchangeable	9.18	3.05	5.39	5.86	10.19	6.91	n.d.	6.17	10.00	3.78	5.06	15.57
Easily Reducible [‡]	1603	1491	1573	1406	1396	1024	944	1419	1530	1440	1045	781
Reducible [†]	1459	1729	2320	2187	2188	2330	3376	2101	2350	2224	2459	4420

‡ Zero-time (pretreatment) sampling.

† Sampling time in hours after zero-time.

‡ Not detectable.

† Mean of duplicate samples.

Table R3. The Effect of Dissolved Oxygen on the Chemical Form and Distribution of Zinc in Barataria Bay Sediment Suspensions

Fraction	0.11% Oxygen			2.11% Oxygen			21% Oxygen						
	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv				
	-200 (0) †	-210 (8) ‡	-170 (120)	-200 (0)	-160 (8)	-50 (48)	100 (168)	640 (288)	-260 (0)	-160 (0.5)	-40 (3.5)	150 (7)	610 (132)
	µg Zn/g oven dry solids												
Water Soluble	n.d. §	0.30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.30	n.d.	2.92	4.38
Soluble Organic Bound	n.d.	n.d.	0.24	0.19	n.d.	0.23	0.23	0.62	n.d.	n.d.	0.20	0.80	0.45
Exchangeable	n.d.	n.d.	0.28	n.d.	n.d.	n.d.	n.d.	1.61	n.d.	n.d.	0.47	0.50	1.96
Easily Reducible ⁺	13.87	4.28	5.46	10.92	2.67	3.14	9.60	16.17	4.51	5.51	5.16	4.54	15.71
Reducible [†]	16.29	20.24	22.56	17.50	16.71	15.48	8.46	5.84	13.92	15.22	13.37	13.83	10.66

‡ Zero-time (pretreatment) sampling.

† Sampling time in hours after zero-time.

§ Not detectable.

+ Mean of duplicate samples.

Table R4. The Effect of Dissolved Oxygen on the Distribution of Ammonium-Nitrogen, Phosphorus, and Copper in the Water-Soluble and Exchangeable Fractions in Barataria Bay Sediment Suspensions

Fraction	0.11% Oxygen		2.11% Oxygen				21% Oxygen						
	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv	Redox Potential, mv						
Exchangeable	-200 (0) ^ψ	-210 (8) ^φ	-170 (120)	-200 (0)	-160 (8)	-50 (48)	100 (168)	640 (288)	-260 (0)	-160 (0.5)	-40 (3.5)	150 (7)	610 (132)
Water Soluble	27.94	33.90	36.93	28.21	29.66	13.41	5.59	3.87	37.23	35.69	13.34	6.15	4.07
Reducible [†]	n.d. [§]	n.d.	n.d.	n.d.	n.d.	n.d.	1.98	5.26	n.d.	n.d.	n.d.	1.76	10.46
Ammonium-Nitrogen, µg N/g oven dry solids													
Phosphorus, µg P/g oven dry solids													
Copper, µg Cu/g oven dry solids													

^ψ Zero-time (pretreatment) sampling

^φ Sampling time in hours after zero time.

[§] Not detectable.

[†] Mean of duplicate samples.