DREDGED MATERIAL RESEARCH PROGRAM

CONTRACT REPORT D-77-4

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

VOLUME I: LITERATURE REVIEW

by

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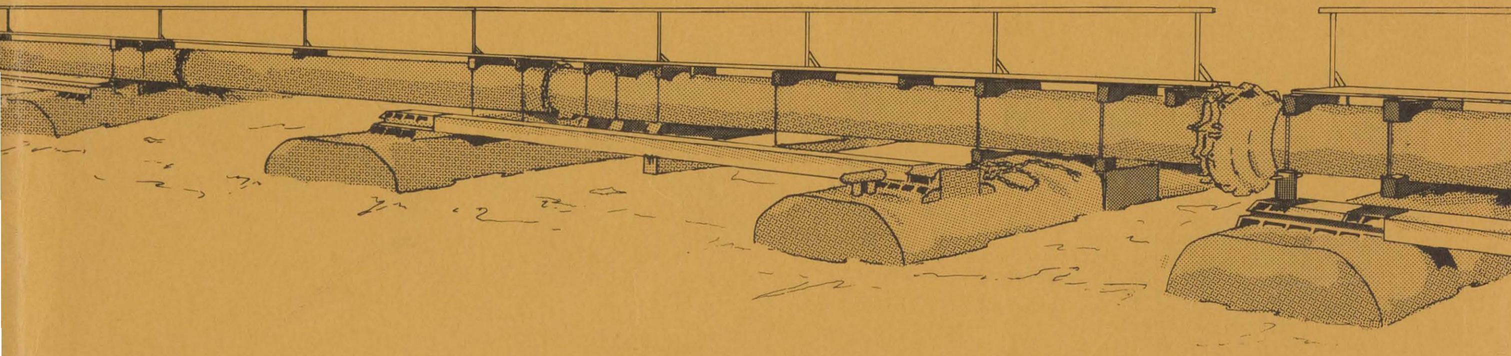

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TO: All Report Recipients

1. The Dredged Material Research Program (DMRP) is a broad, multifaceted investigation of the environmental impacts of dredged material disposal and includes consideration of the development of new or improved disposal alternatives. In the early stages of the DMRP's problem definition and assessment and research program development phases, it became apparent that an understanding of the actual pollution potential of dredging and discharging of sediments required substantial state-of-the-art improvement in a number of fundamental aspects. Particularly critical were basic matters of sediment chemistry relating to physicochemical parameters such as pH, redox potential, and dissolved oxygen. These are dominant factors regulating the mobilization of chemical constituents or pollutants from dredged material discharged into aquatic or terrestrial environments. Contaminated sediments are often involved in dredging projects and during the discharge activity changes in the physicochemistry of the system can significantly enhance or retard release of contaminants from the sediment.

2. The contract report transmitted herewith represents the results of one of several research efforts completed as part of Task 1C (Effects of Dredging and Disposal on Water Quality) of the DMRP. Task 1C is part of the Environmental Impact and Criteria Development Project of the DMRP. Among other considerations this project includes determining on a regional basis the short- and long-term effects on water quality due to dredging and discharging bottom sediment containing contaminants.

3. This research was conducted (as Work Unit 1C05) to study the transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Specific objectives were to review thoroughly the scientific literature concerning cause-and-effect relationships and to conduct specific laboratory investigations where data and evaluations were not available.

4. The first volume of this two-volume report includes an extensive bibliography and thorough discussion on the occurrence and chemistry of selected heavy metals and plant nutrients in relation to expected physicochemical changes during discharge of dredged material into various environments. The second volume contains reports on laboratory investigations of the effects of pH and oxidation-reduction conditions on the

distribution of toxic heavy metals and plant nutrients among selected chemical forms in sediment-water systems from four geographical locations. Particular emphasis was placed on how these physicochemical parameters might affect the chemical availability of these nutrients and toxic substances and thus reflect changes in their bioavailability.

5. From the literature review, it was concluded that changes in the physicochemical nature of sediments could enhance release of toxins or biostimulants; however, too few investigations have been conducted to draw broadly applicable conclusions regarding the effects on water quality. The laboratory investigations demonstrated that physicochemical changes during aquatic disposal resulted in little change and subsequent release of chemical constituents; however, when upland discharge methods were used, long-term and gradual changes in the physicochemical parameters occurred that could significantly affect toxic metal availability. It was further concluded that a thorough evaluation of the physicochemical nature of a dredging and discharge activity should be conducted prior to selection of a discharge alternative.

6. The information and data published in this report are contributions to the further understanding of the complex nature of sediment, water, and chemical/biological interactions and establish a baseline from which to develop meaningful evaluations for the selection of an environmentally compatible disposal alternative. It is expected that the methodology employed in this study and the resultant interpretation of the chemical interactions will be of significant value to those persons concerned with CE dredged material permit programs.

JOHN L. CANNON
Colonel, Corps of Engineers
Commander and Director

[illegible]

SUBJECT: [illegible]

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report, which includes a bibliography of 414 references, discusses literature on the occurrence and chemistry of selected trace metals and plant nutrients in sediment-water systems. The effects of pH and oxidation-reduction conditions on metal and nutrient chemistry were stressed where this information was available. The toxic and nutrient elements included are lead, cadmium, mercury, arsenic, selenium, copper, zinc, manganese, iron, nitrogen, phosphorus, and sulfur. The report also reviews the scope and limitations (Continued)

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20. ABSTRACT (Continued)

of various selective chemical fractionation procedures developed to determine the chemical forms of trace metals and nutrients in soil and sediment-water systems.

This review determined that many laboratory studies simulating the transport of reduced sediments to an oxygenated environment have reported some release of toxic metals and biostimulants and others have shown no release of many elements. However, too few studies of actual dredging and dredged material disposal operations have been completed to draw broadly applicable conclusions regarding the effects of dredging on water quality. Where dredging activities have resulted in minimal change in metal ion concentration, it may be that some regulating processes influenced by oxidation-reduction reactions tend to be activated as others are inactivated. Because of the numerous potential interactions of dredging and dredged material disposal with surrounding ecosystems, it is suggested that some site-specific evaluation of possible adverse environmental impact should be conducted for each proposed dredging project.

Though adsorption and release reactions in disturbed sediment-water systems are frequently not of the magnitude predicted from metal-ligand solubilities and thermodynamic considerations of simple aqueous systems, it is apparent from the literature that pH and redox potential do influence the availability of metals and plant nutrients by affecting regulatory processes. Studies of the effects of redox potential and pH in sediment-water systems should therefore be useful in determining the nature of the regulatory process involved and the sediment-water characteristics which may contribute to significant release of metals and nutrients to benthic and aquatic organisms.

EXECUTIVE SUMMARY

Trace metals and plant nutrients in sediment-water systems are present in a number of forms. These forms vary widely in bioavailability. Some forms are readily available to aquatic and benthic organisms while others are essentially unavailable, regardless of the environmental stress applied to the system. Thus the total elemental composition of a particular sediment, as determined by a bulk chemical analysis, is not indicative of the pollution potential of a given sediment.

In general, undisturbed sediments and the natural sedimentation process have a net scavenging effect on most chemical pollutants added to waterways such that the content of metals and other pollutants in sediments is greater than their levels in the overlying water column. This pollutant accumulating capacity of sediments has been used to identify sources of some pollutants after the natural or background levels of a particular pollutant in an area have been determined. Some sediment-bound materials, such as nitrogen, phosphorus, and some metals, have been shown to diffuse from the interstitial waters of sediments into the overlying water column, particularly when the chemical environment of the water column is favorable for the presence of the metals or nutrients in a soluble form. Thus a dynamic equilibrium is established which may result in the maintenance of low levels of certain materials in the water column as a result of their release from undisturbed sediments. However, there may be a much greater exchange of potential pollutants between sediments and the water column when sediments are disturbed as during dredging and dredged material disposal.

Several factors have been shown to influence the exchange of materials between sediments and the overlying water column. These factors include the solid-liquid ratio, the degree of agitation, particle size, time of contact, chemical characteristics of the water and sediments, pH, and the degree of oxidation or reduction (redox potential) of the sediment-water system. It is the purpose of this report to review some of the literature available on the chemistry of selected trace metals and plant nutrients in sediment-water systems with particular attention given to the effects of redox potential and pH on the exchange of these materials between sediment and water. The toxic and nutrient elements included are lead, cadmium, mercury, arsenic, selenium, copper, zinc, manganese, iron, nitrogen, phosphorus, and sulfur.

Though both dissolved oxygen and redox potential have utility in describing the oxidation or reduction status of an aqueous system, the concept of redox potential is in many ways more applicable to sediment systems in quantifying the degree of oxidation. In the presence of measurable dissolved oxygen, most chemical species subject to oxidation-reduction type reactions are found in the oxidized state and a redox potential measurement would indicate oxidizing conditions.

In the absence of measurable dissolved oxygen, an aqueous system may be only moderately reduced or very reduced. The degree or intensity of reduction is indicated by the redox potential. Over the range of potentials found in nature, redox potential has been found to play an important regulatory role in the chemical forms and oxidation states of many metals and plant nutrients in soils and sediment-water systems. In nature, both sediments and surface waters are found to range from well oxidized to very reduced. Some aqueous systems are subject to seasonal changes from one extreme to the other. In general, the sediments of large waterways, such as used for navigation, tend to be depleted of dissolved oxygen and thus reduced while the overlying water is oxidized as dissolved oxygen is usually present. During dredging and dredged material disposal, reduced sediments containing metals, nutrients, and other potential toxicants become well mixed with oxidized surface waters at the site of dredging and dredged material disposal. The transfer of sediment material from a reduced sediment environment to an oxidized water column could strongly influence chemical transformations of toxicants and nutrients affecting their bioavailability. In the literature, models based on both thermodynamic calculations and experimental data from soil, sediment, and water systems have demonstrated the importance of redox potential in regulating the solubility and speciation of metals and nutrients such as lead, mercury, iron, phosphorus, manganese, and nitrogen. In sediments exhibiting a wide range of oxidation-reduction levels with depth, many other metals have shown a tendency to accumulate in various horizons representing different oxidation-reduction intensities. From the literature available, it is apparent that a reducing environment, as indicated by a low redox potential, tends to favor the reduced, ionic form of many metals. In the reduced ionic state, some metals are considerably more soluble and thus more mobile than in their oxidized states.

The pH of sediment-water systems also plays an important regulatory role in the forms and chemical transformations of trace metals and plant nutrients. In general, the solubility and mobility of metals are enhanced as a system becomes more acid. As either acid or alkaline eroded soil material becomes incorporated into sediments and is reduced, there is a tendency for its pH to approach neutrality. The tendency for sediment material to become buffered around neutrality is due to substances produced as a result of the reduction process. Iron and manganese compounds are thought to be involved in the pH buffering of submerged soils and sediments. Upon reoxidation of sediments as a result of their resuspension in an oxygenated water column or perhaps other methods of disposal, a temporary or permanent pH change may occur which could influence the mobility and bioavailability of some sediment-bound pollutants.

The literature described how pH and redox potential are not entirely independent properties of aqueous systems. All important reduction reactions that occur in natural systems involve the consumption of hydrogen ions. Thus a change in either of these properties induces a change in the other. The interdependence of pH and redox potential is complex and the redox potential-pH slope of a given aqueous system is determined by the chemical components of that system. Consequently, a detailed study of the effects of redox potential and pH on the chemical transformations of metals and plant nutrients must describe or consider both of these parameters.

As previously mentioned, low pH and redox potential in sediment-water systems tend to favor the formation of soluble species of many metals, whereas in oxidized, non-acid systems, slightly soluble or insoluble forms tend to predominate. However, pH, and particularly redox potential, may regulate other processes which counter these generalities. There is considerable evidence in the literature that sulfide is important in this respect. In a reduced environment, slow mineralization of the ample organic material usually present in sediments results in the formation and accumulation of sulfide.

The extremely low solubility of divalent metal sulfides in aqueous systems is well documented in the literature. Where considerable sulfide is present, sulfide precipitation is thought to be a very effective process for immobilizing trace metals in reduced sediments. Thus, a reducing environment which causes a metal to be present in a soluble, ionic form may also contribute to its being effectively immobilized by sulfide precipitation. However, in the case of mercury, there is some evidence that sulfide may polymerize and form a soluble compound which maintains a somewhat greater level of mercury in solution in the interstitial waters than would be predicted from solubility product calculations.

Sparingly soluble metal sulfides which are stable in reduced environments may oxidize to relatively soluble metal sulfates in aerobic environments. The resuspension of reduced sediments in an aerobic water column as a result of dredging and open water disposal probably results in minimal release of sulfide-bound metals. The released sediment material will rapidly settle out and again become part of the anaerobic sediment phase at the disposal site before significant oxidation of the bulk solids occurs. However, upland application of dredged material for either disposal or resource utilization purposes may offer considerably greater opportunity for metals release by sulfide oxidation since the dredged material may be subject to long-term oxidized soil environments.

Conversely, another redox potential-pH regulated process occurs in sediment-water systems which is thought to be effective in removing soluble metals from an oxidized water column. The resuspension of reduced sediments in the overlying water results in the release of soluble iron and manganese in quantities considerably greater than that of trace metals. The reduced forms of iron and manganese oxidize quickly in aerated water columns to form solid hydrous oxides of large surface area and sorptive capacity for trace metals. These hydrous oxides are known to be effective scavengers of many trace metals. The resulting particulate material settles out of suspension to become reincorporated with the sediment. The literature suggests that the scavenging effect of hydrous oxides may be particularly effective in dredging situations due to the considerable quantities of manganese and iron released, and the relatively rapid oxidation of these elements. It has also been suggested in some reports that freshly formed hydrous oxides of iron and manganese, such as would be found during dredging and dredged material disposal, may be more effective scavengers than aged oxides.

There are several reports available indicating quantitatively or qualitatively the effects of redox potential and/or pH on the forms and transformations of metals in simple aqueous systems and the calculations for developing redox potential-pH diagrams. Also, there are laboratory data available indicating the importance of these parameters on the chemistry of some metals. In simple aqueous systems consisting of a limited number of elemental components, the regulation of chemical form by pH and redox potential is characterized by distinct redox potential-pH boundary conditions between the various forms. However, in natural sediment-water systems typically consisting of a heterogeneous mixture of both inorganic and organic compounds, the factors influencing the immobilization or release of potential pollutants is much more complex. Thermodynamic calculations based on simple systems cannot yet be extrapolated to natural systems. Additional factors which complicate the understanding of metal chemistry include cation exchange and other surface adsorption reactions as well as complexation with organic matter.

The reactions of metals with organics is particularly important in sediment chemistry as indicated by studies in which selected organics are used to simulate the complexation effects of certain naturally occurring organic components. Such studies cannot accurately simulate a natural system, but are useful in demonstrating the importance of organics in trace metal regulation in sediment-water systems. Recent work has shown that soluble natural organics may form a sufficiently stable complex with the reduced soluble form of some metals such that the metal is maintained in a water-soluble form for several hours or days in an oxidizing environment.

Due to the diversity of organic materials capable of binding metals in sediment-water systems, the fixation or release of metals in natural sediments does not exhibit the rather precise, predictable redox potential-pH boundary conditions shown by simple aqueous systems. However, redox potential and pH have been shown to influence metal-organic complex formation and stability. The effects of redox potential and pH on trace metal transformations in natural systems must therefore be studied empirically.

Plant nutrient transformations are also affected by redox potential and pH. The mineralization of organic nitrogen and the biological oxidation and reduction of its inorganic nutrient forms affecting nitrogen availability are particularly responsive to the oxidation-reduction status of sediment-water systems. Recent work has shown that the presence of an oxidized water column or thin oxidized surface horizon over a reduced sediment is conducive to the removal of potentially bioavailable nitrogen from sediment-water systems. Organic nitrogen within a sediment is slowly mineralized to the reduced ammonium form. Ammonium nitrogen thus formed may move due to a concentration gradient to the oxidized environment at the sediment surface where it may be oxidized to nitrate. The nitrate thus formed is quite mobile. Some may move into the reduced portion of the sediment by diffusion in response to a concentration gradient where it is subject to denitrification and removal from the sediment-water system as nitrogen gas. During dredging, a considerable amount of ammonium nitrogen which accumulates in the interstitial waters of reduced sediments may be dispersed into the water column.

The sorption and release of phosphorus from sediments is also affected by redox potential-pH influences. There is a considerable amount of information in the literature on the chemistry of phosphorus in soils and sediments and some information on the effects of pH and the oxidation-reduction environment on phosphorus. In general, reducing conditions have been found to favor the desorption of phosphorus from soil and sediment materials, while an oxidizing environment favors phosphorus immobilization or fixation. However, under some conditions, the oxidation of reduced material has been found to contribute to some release of adsorbed phosphorus. The chemistry of phosphorus is as complex as the sediment chemistry of trace metals, if not more so, and many interacting factors appear to regulate phosphorus availability in sediment-water systems.

A number of selective fractionation procedures have been developed to determine the chemical forms of trace metals and nutrients in soil and sediment-water systems. The purpose of selective chemical extraction of sediments has been to determine either the origins of sediment-bound material or its bioavailability. Only a portion of the total toxicants or biostimulatory materials in sediments are potentially available to aquatic and benthic organisms, and the chemical forms actually available are subject to regulation by several factors including redox potential and pH.

Though certain limitations exist in the use of selective extraction procedures, these methods have been found useful in characterizing chemical forms which are either readily available or potentially available to organisms after some transformations. However, the utility of chemical fractionation procedures may be impaired by some of the techniques used to characterize sediments. For example, drying and grinding some soil and sediment samples prior to chemical fractionation has been shown to influence the quantity of elements measured in some chemical forms. When studying reduced sediment-water systems, sample contact with air or oxygenated extractants may also induce transformations of metals and nutrients affecting their release by chemical fractionation procedures is presented in order to identify an appropriate procedure for the sequential chemical extraction of sediments. Attention is focused on the potentially bioavailable forms of sediment-bound materials and on the influence of sample preparation and chemical extraction techniques which may affect the interpretation of data.

In conclusion, many laboratory studies simulating the transport of reduced sediments to an oxygenated environment have reported some release of toxic metals and biostimulants. Other studies have shown this release to be minimal. At the present time, too few studies have been completed of actual dredging and dredged material disposal operations to make final conclusions concerning water quality degradation as a result of dredging which are broadly applicable to most waterways. In the few good studies which have been conducted in recent years, a large release of toxic metals from dredging activities has not been found. However, a relatively small but temporary increase in some toxic metal levels in surrounding surface waters has sometimes been noted. In certain cases, dredging activities have apparently reduced the toxic metal content of surface waters which contact the disturbed sediments.

Where dredging activities have resulted in a minimal change in metal concentration upon dispersion of reduced sediments in surface waters, a possible explanation may be that certain regulating processes likely influenced by oxidation-reduction reactions tend to be activated as others are inactivated. A suggested explanation in the literature is the release of metals by sulfide oxidation in an oxygenated water system being compensated for by metal precipitation with freshly formed hydrous oxides of iron and manganese. More research should be done using a three-dimensional sampling network around the dredging and dredged material disposal sites at many locations covering a wide range of sediment-water characteristics to determine possible nutrient or toxic metal release during dredging.

Though adsorption and release reactions in disturbed sediment-water systems are frequently not of the magnitude predicted from metal-ligand solubilities and thermodynamic considerations of simple aqueous systems, it is apparent from the literature that pH and redox potential do influence the availability of metals and plant nutrients by affecting regulatory processes. Studies of the effects of redox potential and pH in sediment-water systems should be useful in determining the nature of the regulatory process involved and sediment-water characteristics which may contribute to significant release of metals and nutrients to benthic and aquatic organisms.

PREFACE

Volume I of this report presents a literature review of transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH. Volume II describes a laboratory study designed to determine how changes in pH and oxygen-reduction conditions, such as may occur during dredging and dredged material disposal, might affect the chemical availability of certain nutrients and toxic substances and thus reflect possible changes in their bioavailability. The report was prepared by personnel of the Laboratory of Flooded Soils and Sediments, Agronomy Department, Louisiana Agricultural Experiment Station, Louisiana State University (LSU), Baton Rouge, Louisiana. This investigation was conducted under Contract No. DACW39-74-C-0076, entitled "Research Study of Eh, pH, and DO Effects on Chemical Constituent Migration During Open-Water Disposal," dated 6 March 1974, between the U. S. Army Engineer Waterways Experiment Station (WES) and the Agronomy Department, LSU. The project was sponsored by the Office, Chief of Engineers, and was monitored by the Environmental Effects Laboratory (EEL), WES, as part of the Dredged Material Research Program (DMRP) study on effects of dredging and disposal on water quality under Work Unit 1C05, "Study of Eh, pH, and DO Effects on Chemical Constituent Migration During Open-Water Disposal of Dredged Material."

The principal investigator was Dr. W. H. Patrick, Jr., LSU. Drs. R. A. Khalid, R. P. Gambrell, and M. G. Verloo, LSU, also participated in the study. This report was written by Drs. Patrick, Khalid, Gambrell, and Verloo.

The authors wish to express their appreciation to Dr. K. R. Reddy for determining organic carbon content and relative oxygen consumption rates on the sediment samples and to Mr. C. N. Reddy for measuring the particle size distribution and cation exchange capacity of the sediment materials, as well as assisting in ammonium nitrogen and orthophosphate analyses on sediment extracts. The authors wish to thank Mr. R. D. DeLaune for helpful suggestions contributed during the study and for review comments during manuscript preparation. The authors are

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The Contract Manager was Mr. Ronald E. Hoeppel, Environmental Impact and Criteria Development Project, DMRP. The Project Manager was Dr. Robert M. Engler, Chief, Environmental Impact and Criteria Development Project, DMRP. The study was conducted under the general supervision of Dr. John Harrison, Chief, EEL.

Contracting Officer was COL G. H. Hilt, CE, Director of WES. Technical Director was Mr. F. R. Brown.

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CONVERSION FACTORS,
U. S. CUSTOMARY TO METRIC (SI) UNITS OF MEASUREMENT

U. S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

Multiply	by	to Obtain:
cubic yards	0.7645549	cubic meters
pounds (mass)	0.4535924	kilograms
tons	907.1847	kilograms

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

VOLUME I: LITERATURE REVIEW

INTRODUCTION

Approximately 380 million cubic yards* of sediment are dredged each year in the United States.[1] Maintenance dredging accounts for about 80 percent of this total while new projects account for the remainder. Disposal of such large volumes of dredged sediment is generally accomplished by one of two methods. The dredged sediment is either transported to and disposed of in selected open-water sites away from the shipping channel, or it is transported onto land. Either method of disposal may present a threat to the surrounding environment.

Mining activities, municipal and industrial waste discharges, as well as agricultural drainage, may result in undesirable levels of biostimulants, toxic metals, pesticides, and organic waste entering waterways, either in solution, or associated with suspended solids. In a waterway, these chemical contaminants, particularly toxic metals and biostimulants, are partitioned between the overlying water column and the accumulated sediments beneath the water column. Many of these contaminants can enter into various combinations with the sediment such that most of added pollutants are associated with the sediment phase.

Sediment-bound pollutants range in availability from chemical combinations that are unavailable to the aquatic and benthic populations of the waterway to forms that are readily available. For example, toxic metals bound within the crystal lattice of a mineral particle are considered unavailable, while materials dissolved in interstitial water, or surface-adsorbed ions which may be easily displaced into solution by ion exchange reactions,

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*A table of factors for converting U. S. customary units of measurement to metric (SI) units is found on page xvii.

are considered available. Between these two extremes, a considerable amount of toxins or biostimulants may be present in chemical combinations potentially available to organisms. This sediment-associated reservoir of potentially contaminating substances is in dynamic equilibrium with material in the overlying water column. Sediment-bound toxic or biostimulatory substances may be effectively removed from the water column such that there is no deleterious effect on the water quality. Or, reactions in the sediment phase may maintain levels in the water column that will have a beneficial or harmful influence on the biological population. When sediments are disturbed, such as during dredging, transformations possibly affecting the bioavailability of the toxic substances and biostimulants may result from both physical and chemical changes in the sediment which occur during transport and disposal.

Currently, relatively 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 the 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 of the dredged material.

It is the objective of this study to determine the influence of sediment pH and oxidation-reduction conditions on the chemical and biological transformations of selected toxic metals and plant nutrients in sediments. From this study, it is hoped that a better understanding will be gained of the effects of dredging and dredged material disposal on the chemistry of these substances affecting their bioavailability. The results should give some insight into the importance of considering the influence of pH and redox potential on sediment chemistry when developing sediment disposal criteria.

CHARACTERISTICS OF SEDIMENTS

Sediments are primarily detached soil particles transported by water, ice, wind, or gravity, and deposited at a new location.[2] The overall process of detachment, transportation, and consolidation is called sedimentation.[3] Suspended solids also result from the detachment and transportation of mineral and organic particles by water and constitute a part of sediments.

Dredged material is basically composed of solids and liquids which consist of a wide range of constituents, many of which may be classified as pollutants. Dredged material solids consist of soil particles, rock, wood, pieces of metal, broken glass, and other debris. The main constituents of the dredged material are soil particles, organic matter, and water.

The sediment in water may be a major pollutant as it interferes with the beneficial use of water.[4] Water characteristics such as turbidity, taste and odor, temperature, and abrasiveness may be influenced by the physical presence of sediments.

Turbidity is the optical property of water causing light to be scattered and absorbed rather than transmitted. It is caused by silt and clay particles, organic matter, bacteria, plankton, and other finely divided material. Turbidity results in reduction of light penetration, which may restrict or eliminate photosynthesis, causing a reduction of primary productivity at various levels in the aquatic food chain.[2,5] Turbidity also directly affects fish production, spawning, and gill functioning.[6]

Temperature fluctuations due to suspended sediments are of little significance to aquatic organisms.[7] Substantial seasonal variations in temperature in estuarine and coastal areas in the temperate regions, however, may influence the distribution of aquatic life.[8]

Mineralogy

Particle size distribution of sediments is important because of surface area exposed for chemical reactions. One of the dominant features of the sediments in reservoirs, lakes, and the sea is the presence of fine-size particles. Clay- and silt-size fractions dominate, and there is an almost complete absence of sand-size particles.[4] A physical analysis of 303 sediment samples, representing 32 lakes, conducted by the Illinois Experiment Station, showed that 90 percent of the samples had a sand content of less than 10 percent. In 65 percent of the samples, the sand content was less than 2 percent.[4] Particle size analysis of sediments collected from various locations in San Francisco Bay[9] gives a range of various fractions as follows:

Sand	5.6 - 27.5%
Silt	30.1 - 45.8%
Clay	42.0 - 55.8%

The variation in the distribution of various size fractions in lakes and estuaries is mainly due to the mode of sediment transport in the streams and the textural composition of the soils eroded. However, the proportion of coarse particles in sediments generally decreases as the sediments are transported. Frequent large variations of the textures in the Lower Nile sediments are considered typical of delta sedimentation where meandering rivers continually sort and redeposit the sediments.[10]

The clay fraction has a profound effect on the hydrological performance and the erodability of soils.[11] Clay is an active mineral ingredient of soil, and the various clay minerals differ in their capacity to hold nutrients and other chemicals which may be carried into the lake with the sediments. Clays differ in their dispersion properties and thereby in their transportability by water.

Lund et al.[11] compared the mineralogical composition of soils to sediments within a watershed and found that only small differences exist between the soil clay of the watershed and that of the resulting sediment clays. The common clay minerals observed were montmorillonite, vermiculite, mica, kaolinite, and amorphous alumina. Montmorillonite occurred in larger proportions in the sediment clay whereas quartz was found in abundance in the soils. Montmorillonite, chlorite, and hydrous micas were reported in the San Francisco Bay sediments with montmorillonite being the largest contributor to ion exchange capacity of the bulk sediment.[9] However, studies conducted on sediments of Lake Superior showed that the bottom sediments were composed largely of chemically inert quartz (SiO_2) grains with small (10 percent) amounts of black magnetic ilmenite.[12] The clay fraction of Nile sediments was dominated by expanding clay minerals - smectite and smectite-illite with minor amounts of kaolinite.[10] The clay minerals in the Nile delta show strong similarities with soil clays and do not appear to have been altered following burial or deposition in saline water.

Clay minerals play an important role in the sorption reactions controlling the exchange of nutrients, heavy metals, pesticides, and other materials between sediment and water. Sorbed substances may be held or fixed in forms that reduce their availability to plants and water and thus may be transported with mobile sediments to a new location.[2] Some clay minerals, such as montmorillonite and vermiculite, have a cation exchange capacity (CEC) on the order of 100 meq / 100 g and adsorb more nutrients than do clay minerals like kaolinite with a low CEC. Kennedy,[13] in a study of the clay minerals present in rivers of the United States, found that typical CEC values of the particulate matter present in most rivers ranged from 10 to 75 meq/100 g. By comparing the concentration of various alkali and alkaline earth metals in the river water with those present on the surface of clays, Kennedy[13] concluded that significant cation transport in rivers occurs via sorption of these species on the surface of particulate matter.

Toth and Ott[14] determined that the CEC values of the bottom sediments from rivers and bays were considerably higher than those of soils which ranged from 1-15 meq/100 g. The CEC values of the sediments, which included rivers, bays, and freshwater impoundments, ranged from 7 to 100 meq/100 g, with more variation occurring in the freshwater impoundments. These investigators also observed that the organic matter content of the sediments accounted for about 80 percent of the CEC, which signifies the importance of sediment organic matter in sorption reactions. Barnegat Bay, New Jersey sediment samples had the highest CEC values (85 to 100 meq/100 g) and also had the highest organic matter content, 13 to 24 percent. Toth and Ott[14] suggested that sediment exchange properties could be utilized in determining saltwater intrusions and pollution effects.

The sorption of organics by clay minerals has also been reported in the literature. Bader[15] found that various kinds of clay minerals could sorb large amounts of organics and that this sorption correlated with the CEC of the clay. The amount of specific organic compounds that was removed during a 20-minute contact period with each mineral decreased in the order montmorillonite > illite > kaolinite > quartz. This sequence was identical with the CEC of the minerals tested (montmorillonite, 80-150 meq/100 g;

illite, 10-40 meq/100 g; kaolinite, 3-15 meq 100 g; and quartz, negligible). Bader[15] also found that a significant part of this adsorption (about 80 percent) was irreversible, that is, the material could not be leached from the clay minerals. The proposed mechanisms to account for the observed retention were the formation of a clay-organic complex, entrapment of organic molecules or the alteration of organic molecules.

An important aspect of the Bader[15] investigation is that the formation of an organic-mineral complex would increase the rate of influx of dissolved organic matter into the sediments. Since the association reaction is not reversible, the sediments would tend to be a sink for organic matter rather than a source. This clay-organic complex may serve as a sink for nutrient elements, toxic metals, and organic contaminants and thereby remove them from solution.

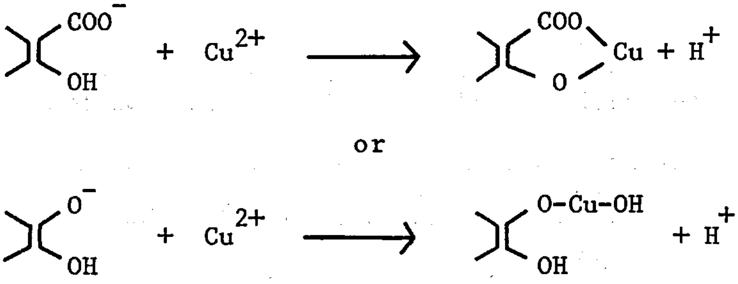
The deposition of sediments and the nutrient sorption and release by sediments are important to lake eutrophication. Their physical presence in the waterways necessitates dredging of the deposited material, which increases tremendously the cost of maintaining these waterways for navigation. The chemical composition of sediments, which includes chemical toxicants as well as growth stimulants, may cause water-quality problems, especially when sediments are disturbed as during dredging and dredged material disposal. The chemical reactions taking place in the sediments and the exchange of various ions between sediments and overlying water will be discussed in other sections of this report.

Organic Matter

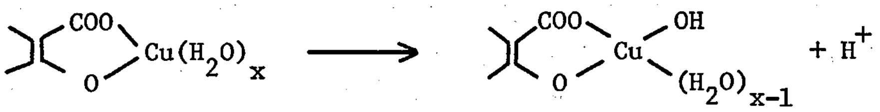
More and more scientific disciplines are becoming interested in the study of naturally occurring organics in the environment. Though the original interest came from soil chemists, oceanographers, geochemists, biologists, and on vironmental specialists are now convinced of the important influences humic materials have on inorganic substances occurring in water-sediment systems.

An important property of the naturally occurring organics is their ability to form stable combinations with metal ions. In addition to affecting soil genesis processes, soil or sediment structure, and the availability of plant nutrients, organo-metallic complexes may also influence the transport and fixation of toxic elements, which are important phenomena in sediments and dredged materials. Many chemical compounds are able to interact with metal ions. However, the most abundant class of compounds in soils and sediments are the humic substances known as humic and fulvic acids. Proteins, amino acids, and other biochemically synthesized compounds are examples of naturally occurring nonhumic substances that might be found in natural systems and are also capable of complexing metals in soluble forms. More complex insoluble forms of organic matter are also capable of interacting with metal ions.

The most probable reaction mechanism between humic compounds and metal ions is the formation of complex bonds with carboxyl and phenolic groups. According to Van Dijk,[16] the following mechanisms may be involved in the binding of copper by humic acids:

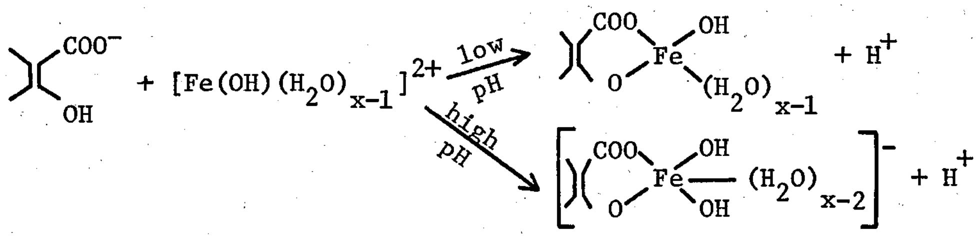


These reactions are favored by low pH levels. At higher pH levels, hydroxyl complexes may be formed according to the reaction:



It is assumed that other metals behave in the same way.

For ferric ions, the following hypothetical structure is given:



The equilibrium reaction between b molecules of a cation M^{x+} and c molecules of a ligand, L^{y-}, can be given as: $bM^{x+} + cL^{y-} \rightleftharpoons (M_bL_c)^{bx-cy}$ and the stability constant of the complex is:

$$K = \frac{(M_bL_c)^{bx-cy}}{(M^{x+})^b (L^{y-})^c}$$

The values of these stability constants depend on the pH and the ionic strength. In general, the stability of humic complexes increases with pH due to the ionization of more functional groups of the humic-polyelectrolyte molecule. Increasing ionic strength results in a decrease in the measured stability.

According to Schnitzer and Hansen,[17] the value of log K for fulvic acid complexes with different divalent cations varies between 2.9 for divalent manganese and 4.7 for divalent copper at pH 3 and zero ionic strength. For comparison, the log K value for copper-ethylenediaminetetraacetate(EDTA) at pH 3 is 8.3, which means that metal-fulvic acid complexes are some 10^5 times less stable than the copper EDTA complex.[18] Ong and Bisque[19] have shown that the humic acids in a solution behave as negatively charged hydrophilic colloids that are coagulated by cations, thus forming insoluble heavy metal-organic compounds. For optimum extraction of these insoluble complexes, polar solvents with high dielectric constants at a high pH have to be used.[20] These solvents favor the dispersion and solubilization of the humic compounds by disrupting the hydrogen bonds between the humic molecules. Accordingly, solutions of alkali in water seem to be the most useful extractants.

The concentration of organic materials in sediments is highly variable. A concentration range between 0.09 and 3.22 percent (organic matter = organic carbon X 1.8) with a median of 2.5 percent has been reported for San Francisco Bay sediments.[9] In Mobile Bay, Lindberg and Harriss[21] found concentrations between 10.2 and 19.3 percent in the 0- to 10-cm sediment layer, while in Everglades sediments, values up to 68.8 percent have been determined.

Even though only a small percentage of this organic matter may be dispersed in the overlying water column during dredging operations, it may affect the heavy metal chemistry in natural systems.

The levels of dissolved organic carbon in natural waters range from several parts per billion to several hundred parts per million.[22] Most of the soluble humic substances occurring naturally in water will be fulvic acids because of their higher solubility. Fulvic acids also contribute to the yellow color of interstitial water, as well as some lake waters. Fulvic acids are generally considered to be degradation products of the more insoluble humic acids.

More information on the nature of humic materials and their effects on the environment may be found in Schnitzer and Khan.[23]

Sediment pH

Krauskopf[24] defined the pH of a solution as the negative logarithm of the hydrogen-ion concentration, $[H^+]$, where concentration is given in moles/liter. This relationship may be expressed as:

$$pH = -\log [H^+]$$

Stumm and Morgan[25] discussed the concept of pH in terms of hydrogen-ion activity, $\{H^+\}$, and showed how this is approximated by the hydrogen-ion concentration:

$$p^aH = -\log \{H^+\} = -\log [H^+] - \log f H^+$$

where p^aH is the negative log of the hydrogen ion activity and the activity coefficient, $f = \{H^+\}/[H^+]$.

It was suggested that since the activity coefficient in a constant ionic medium remains very close to one, hydrogen-ion concentration ($-\log [H^+]$) may be used as an estimation of hydrogen-ion activity ($-\log \{H^+\}$). Solution pH is normally determined in relation to a standard buffer whose pH has been estimated in terms of p^aH. Some of the problems related to activity-concentration relationships, pH measurements, and operational scale are discussed by Krauskopf,[24] Stumm and Morgan,[25] Bates,[26] and Sillen.[27]

The pH of an environment is also a measure of the availability of protons for reaction with a base and is thus analogous to redox potential, which is a measure of the availability of electrons for oxidation-reduction type reactions. The relationship between pH and redox potential will be discussed in another section of this report.

The pH levels of sediments and submerged soils are normally buffered around neutrality (pH 7). Aerobic, acid soils tend to increase in pH upon flooding and subsequent reduction, while aerobic soils with a pH greater than seven tend to decrease in pH as they become reduced. Upon reaeration, the pH of reduced soils and sediment materials will tend to return to levels exhibited prior to flooding. This buffering action of flooded soils and sediments is due to substances produced as a result of reducing conditions. Hydroxides and carbonates of iron and manganese and carbonic acid may be involved in buffering the pH of waterlogged soils.[28] Ponnamperuma[29] related the increase in pH of acid soils to the reduction of iron in the system where ferric oxide hydrate ($Fe_3(OH)_8$) was a dominant solid phase and ferrous iron and carbonic acid were dominant dissolved species. Yamane[30] proposed that ferric carbonate ($FeCO_3$) instead of ferric oxide hydrate was a dominant solid species. Yamane[30] also suggested that ferrous iron, calcium ions, and carbonic acid were important components of the system influencing pH after submergence.

The pH of sediments and overlying waters is also affected by deposition of ions of the various buffer systems, gaseous exchange with the atmosphere, temperature and salinity changes, and photosynthesis and respiration. The pH of the sediments may vary considerably from point to point in one area and from area to area. In general, for freshwater bodies, the pH of the overlying water is more uniform and is lower than that of the surface layer of sediment, especially during the day when photosynthetic activity is high.[31]

The pH in sediments of lakes and estuaries normally decreases with increasing depth, especially in the presence of sulfides.[31,32,33] The pH values generally recorded for surface sediments range from 7.9 to 9.2, and from 6.1 to 9.0 at some depth within the sediment.[8,31] The pH of seawater normally lies between 7.8 and 8.3 in the surface waters, the range being confined to these limits by the natural buffer systems present.[34]

Vanderpost[33] found an average pH of 7.6 in the top 3 cm of sediments in Lake Ontario. The pH decreased with depth to 7.1 at 15 cm. Kemp and Mudrochova,[35] working with Lake Ontario sediments, found a similar decrease in pH with sediment depth. This decrease of pH with depth is thought to be the result of the bacterial production of CO_2 during decomposition of organic matter.[36]

Input of waste materials from surrounding industrial areas and the loading of nutrients, chemical fertilizers, and suspended soil particles from cultivated lands can be a significant source of pollutants entering streams and lakes which eventually alter sediment chemistry. Such changes have been observed in the Great Lakes in the last few years.[37] Schelske and Roth[38] conducted a survey of pollution problems of the Great Lakes and reported that higher pH values in Lake Erie were due to an outflow of pollutants from Lake Huron. The sequence of flow in these lakes is: Lake Superior to Lake Huron and to Lake Erie, and the pH values observed were 8.03, 8.50, and 8.77, respectively. The pH of sediment samples from three different locations in San Francisco Bay were reported to vary between 6.6 and 7.4. The differences were attributed to industrial effluents entering the bay.[9]

The pH of sediments is an important factor in exchange reactions between sediments and water as it influences the solubilities of various compounds. In general, the solubility of metals tends to increase with decreasing pH.[39] The pH of sediment and overlying water modify oxidation-reduction reactions, and thus the transformations of various nutrient elements and trace metals.[40,41,42,43] Sediment pH can also influence the sorption and desorption of organic molecules.[44,45] Lee[46] indicated that minor changes in the pH, in the neutral pH range, could have a pronounced effect on the contaminants released from dredged material. Lee and Plumb[39] recommended that the pH of all elutriate test solutions should be measured and recorded, and that the tests be conducted at essentially the same pH that prevails in the environments under consideration.

Redox Potential

The redox potential of soil, water, and marine systems is a measure of electrochemical potential or electron availability within these systems. Electrons are essential to all inorganic and organic chemical reactions. A chemical species which loses electrons is said to become oxidized. Alternately, reduction is described as the gain of electrons. Thus a measure of the redox potential (electron availability) of a system reflects the degree of oxidation or reduction of the various chemical species in the system.

In an aqueous system, the degree of oxidation is limited by the electrochemical potential at which water becomes unstable and is oxidized to molecular oxygen. Similarly, the limit of reducing conditions in an aqueous system is the potential at which the hydrogen in water is reduced to molecular hydrogen.[47] Within these limits imposed by the stability of water, the oxidation states of hydrogen, carbon, nitrogen, oxygen, sulfur, and many metals may be affected by redox potential, though the measured redox potential is largely determined by a few of the more abundant of these elements in the system.[48]

In theory, redox potential measurements are to be made with electrodes inert to the chemical species in the sample. In practice, no electrode material is completely inert. However, gold or platinum electrodes have been used successfully in making redox potential measurements. Redox potential measurements can quantitatively describe the ionic distribution only between chemical species which may interact with the transfer of electrons, such as ferrous and ferric iron in an aqueous system or nitrite and nitrate nitrogen. In a natural system, there are usually many redox couples present, and not all redox couples are chemically interactive with others. Unless the concentration of a given redox couple is relatively high, inert electrodes (generally platinum) used for redox measurements are not specific for a single redox couple. Thus the electrode responds to the electrochemical potentials of all redox couples present.

If an equilibrium were assumed in a system containing many redox couples, the tendency for some chemical species to donate electrons is balanced by the tendency for others to accept electrons. The measured redox potential would be a mixed potential which reflects a weighted average of the potentials contributed by each of the redox couples present in the system.[49] Due to the almost continuous addition of organic matter, which may be oxidized and thus serve as an electron donor, a redox equilibrium is almost never attained in a natural system.[48] Laitinen[50] has described how several redox couples, each having greatly different potentials as separate redox systems, may be added together to produce a mixed potential which differs several hundred millivolts (mv) from the potential of the individual couples.

The previous discussion briefly described some of the problems associated with redox potential measurements. However, the problems should not mask the utility of these measurements. In spite of the theoretical limitations involved in the use of redox potentials to quantitatively describe a specific ionic distribution in a mixed system, these measurements have been successfully applied in soil and sediment chemistry to characterize the oxidation-reduction transformations of many metals and plant nutrients.[51,52,53,54,55]

Sediments generally contain a considerable amount of residual organic material. This organic matter is derived primarily from the death and decay of plant and animal tissue from the aquatic and benthic organisms in the sediment-water system. Additional organic carbon is added from soluble and particulate organic material associated with surface and subsurface soil drainage and waste discharges into receiving waters. As a result, there is usually an ample supply of substrate for the large population of anaerobic and facultative anaerobic bacteria within the sediments, and biological activity is high.

As this predominately heterotrophic bacterial population utilizes the available oxidizable organic matter as an energy source, some reducible substance in the sediment environment must be available to accept the electrons resulting from oxidation of the organic food source. This process is respiration. Where oxygen is available, bacterial populations adapt to use it as a terminal electron acceptor. When the demand for oxygen exceeds the supply, anaerobic and facultative anaerobic organisms become active. Under these conditions, reducible compounds such as nitrate, the oxidized forms of iron and manganese, and other inorganic or organic species are reduced by microbial respiration to the extent that these reducible substances are available. In such a sediment where the demand for oxygen exceeds the supply, oxygen is rapidly depleted as are the oxidized forms of many of the redox couples within the sediment. The degree of sediment reduction is then indicated by a low redox potential.

The dissolved oxygen content throughout the water column in most shallow bodies of water remains high due to: (1) the exchange of oxygen at the air-water interface and subsequent downward diffusion of oxygen or mixing of the water by currents resulting from temperature gradients or wind, (2) oxygen production by photosynthetic algae, and (3) the relatively low demand for oxygen within the water column. At the sediment-water interface of a sediment supporting considerable biological activity, an oxygen concentration gradient will exist between the interstitial water and the overlying water. This results in oxygen diffusing from the water column into the surface layer of sediments and the maintenance of an oxidized layer at the top of the sediment.[56] The rate of oxygen diffusion through the interstitial water in the sediment pores is about one-tenthousandth of the rate of gaseous oxygen diffusion.[57] Due to this slow diffusion of oxygen into the sediment, the oxidized layer at the surface is usually very thin. Beneath this thin oxidized layer, the sediment may be highly reduced.

Redox Potential in Soils and Sediments

In order to have some concept of the degree of oxidation or reduction indicated by redox potential measurements, one must be able to associate numerical redox values with the chemical transformations occurring. Patrick and Mahapatra[58] suggested four general ranges of redox conditions in soils and indicated the approximate critical reducing potential for several chemical species. At pH 7, oxidized soils are characterized by a redox potential of > +400 mv; moderately reduced soils, from +400 to +100 mv; reduced soils, from +100 to -100 mv; and highly reduced soils are characterized by a redox potential between -100 and -300 mv. At pH 7, as the redox potential decreases below about +225 mv, nitrate-nitrogen is reduced. Manganic manganese is reduced at about +200 mv, ferric iron at about +120 mv, and sulfate is reduced to sulfide at about -150 mv.

In some early studies of the redox potential of marine sediments, ZoBell[59] reported data on over 1,000 sediment samples. Redox potential values ranging from +350 to -500 mv were measured. He found that well oxidized sediments generally had a coarse texture and contained little organic carbon. Reduced sediments were characterized by the presence of considerable organic carbon in fine-textured sediments.

Hallberg[60] reported the metal distribution, redox potential, and other characteristics in a sediment profile of an intertidal area of an island off the coast of Holland. The redox potential at 0.5 cm was about +300 mv but decreased to about -220 mv at the 10 to 15 cm depth.

Berryhill, Swanson, and Love[61] reported that the sediment redox potential of five selected sites in the Pamlico Sound, North Carolina, range from about -100 to -300 mv while the water just above the sediment at these sites ranged from < -100 to > +100 mv.

Weiler[62] reported the sediment redox potential and interstitial water composition of several sites in western Lake Ontario. At all sites, the overlying water was well oxidized (> +400 mv). Beneath 10 cm, the redox potential of three sites was found to be strongly reducing (< -100 mv). However, the subsurface redox potential at one site containing almost no organic carbon was only moderately reduced (> +200 mv at 30 cm).

Ho and Lane[63] reported that the redox potential of Barataria Bay, Louisiana, sediments averaged -220 mv.

Mortimer[64] reported the redox potential profile across a sediment-water interface for sites in Lake Windermere, England. In the overlying water column, the measured potentials were about +200 to +300 mv. Four to 5 cm below the sediment-water interface, the redox potential had decreased to strongly reducing levels of about -200 mv. In the 0- to 4-cm increment beneath the interface, the redox potential decreased abruptly from +300 to -200 mv with most of the potential drop in the upper 2 cm.

Windom[32] reported redox potential profile measurements of an estuarine waterway channel along the southeastern Atlantic coast and an adjoining marsh area after dredged material deposition. The redox potential of two channel sites ranged from about -50 to -150 mv from the surface to a depth of 80 cm. One study area in a nearby marsh prior to dredged material disposal was generally more reduced than the channel sediments beneath the 20 cm depth (-200 to -300 mv), but was less reduced at the surface (approximately +100 to 0 mv). Another nearby marsh study area showed a similar redox profile. Measurements taken a few months after dredged material deposition on these marshes showed that the upper part of the marsh, which was composed of the added dredged material, had a redox profile very similar to the channel sediments. Beneath the added material, a redox potential profile characteristic of the marsh prior to disposal was noted (with the exception that the better oxidized horizon representing the former surface of the marsh became more reduced).

Vanderpost[33] reported the redox profile of overlying water and sediments from a site in western Lake Ontario. During a summer measurement, the redox potential decreased from greater than about +300 mv, 1 meter above the sediment-water interface, to +200 mv in the water at the interface. Within the sediment, the redox potential showed a gradual decline from about +50 mv at the 0- to 3-cm depth to -250 mv at the 9- to 12-cm depth. During the winter months, the redox profile shifted to levels approximately 100 mv higher than measured in July. Seasonal fluctuations in redox potential profiles have also been reported by Mortimer[64] and are likely a reflection of the temperature influence on biological activity. In climates where the temperature of water and sediment layers changes considerably during the year, it is likely that temperature-induced changes in biological activity may contribute to redox changes within the sediment which seasonally affect the exchange of trace metals and plant nutrients with the overlying water column. This temperature effect could possibly be of importance in influencing transformations resulting from dredged material disposal such that some dredging operations should be planned for specific seasons.

From the redox potential profiles presented, it is seen that the redox potential of sediments generally ranges from oxidized to somewhat poorly reduced at the sediment-water interface to very reduced well beneath the surface. Thus the chemical environment affecting transformations may vary considerably within a sediment profile or between the sediment and the overlying water column. When these two environments are mixed, as during dredging and disposal, it is possible that transformations affecting the bioavailability of sediment-bound toxins and biostimulants will occur.

Relationship between Redox Potential and pH

As previously discussed, the redox potential of soil or sediment is often the determining factor in regulating the chemical form a nutrient or toxic metal may take. In a similar manner, pH has an influence on the stability of these forms. Thus, to predict a chemical environment in which a particular chemical species may be found, one would have to describe the range of both the redox potential and the pH at which that species is stable.[24] There is an interaction between pH and redox potential of many chemical species such that a change in one of these parameters will result in a shift in the other. Thus the redox potential describing the stability boundary between an oxidized and reduced species at one pH level may differ if the pH of the system is altered. The relationship between redox potential and pH is usually (but not necessarily) linear.[65] Thus the slope of the change in redox potential per unit change in pH may be used in defining the stability boundaries of a chemical species over a range of redox potentials and pH levels.

Baas Becking et al.[47] pointed out that there are four general types of chemical reactions in natural systems. The type reactions and examples presented were:

- a. reactions involving neither electrons or protons, i.e., $Fe_2O_3 + H_2O \rightleftarrows 2FeOOH$
- b. reactions involving protons, i.e., $H_2CO_3 \rightleftarrows H^+ + HCO_3^-$
- c. reactions involving electrons, i.e., $Fe^{++} \rightleftarrows Fe^{+++} + e^-$
- d. reactions requiring both electron and proton transfer, i.e., $FeSO_4 + 2H_2O \rightleftarrows SO_4^= + FeOOH + 3H^+ + e^-$

Reactions of the first type are not influenced by, nor do they have an effect on, the redox potential and pH of natural systems. Reactions of the second type were said to be associated primarily with the dissociation of acids, while reactions of the third type are related to the oxidation or reduction of metal ions resulting in a change in their valence state. Reactions of the fourth type, involving both electrons and protons, were said to be typical of most reactions in the natural environment. Therefore, most reactions depend upon both the redox potential and the pH of their environment.

As a consequence of involving both electrons and protons, there is a definite relationship between the influence of redox potential and pH on most reactions.

Baas Becking et al.[47] expressed the relationship between redox potential and pH with the following equation:

$$Eh = E_o - 59(a/n)pH$$

where Eh is redox potential, E_o is the standard potential at equal activities of the oxidized and reduced species, a is the number of protons involved in the reaction, and n is the number of electrons. This equation described the slope or gradient of the equilibrium line between the stable forms of a chemical species involved in a redox type reaction. These authors pointed out that many researchers have assumed that a=n, which always results in a redox potential slope of -59 mv per pH unit. However, they state that the ratio of a to n may vary from 0 to ∞, and present a table involving four common reactions of iron in which the a/n ratio is 1, 2, 3, and 4. The resulting redox potential-pH slopes for these four reactions varied from -59 mv per pH unit to -237 mv per pH unit.

Ponnamperuma[29] also discussed the relationship between redox potential and pH. A table of important reduction reactions in nature was presented which indicated that all involved protons as well as electrons. An equation was developed describing the relationship between redox potential and pH for the equilibrium of a typical oxidation-reduction reaction:

$$Ox + ne^- + mH^+ \rightleftarrows Red$$

Where protons are not involved in a redox reaction, the redox potential (Eh) is given by:

$$Eh = E_o + \frac{RT}{nF} \ln \frac{(Ox)}{(Red)}$$

where E_o is the standard potential, n is the number of electrons, and O_x and Red are the activities of the oxidized and reduced species, respectively. In a reaction involving protons, H^+, an additional term is included which indicates the relationship between redox potential and pH in oxidation-reduction reactions involving protons:

$$Eh = E_o + \frac{RT}{nF} \ln \frac{(Ox)}{(Red)} + \frac{mRT}{nF} \ln H^+$$

where H^+ is the hydrogen ion activity and m is the number of hydrogen ions.

Expressing redox potential as the negative log of electron activity, pE, and the activity of the oxidized and reduced species as their negative logs, p(Ox) and p(Red), the above equation may be expressed as:

$$pE = pE_o - \frac{1}{n} p(Ox) + \frac{1}{n} p(Red) - \frac{m}{n} pH$$

Thus, as a reduction reaction progresses, the change in pH is not regulated solely by the number of hydrogen ions consumed or hydroxyl ions produced. Instead, the change in pH is determined by the ratio of hydrogen ions consumed to electrons consumed.

As discussed above, it is possible to determine the redox potential/pH slope of simple systems theoretically. Krauskopf[24] has illustrated this with the ferrous-ferric iron equilibrium in an aqueous medium (Figure 1). The redox potential/pH slopes of both the $O_2 - H_2O$ and $H_2O - H_2$ stability boundaries is -59 mv/pH unit. The slope between ferrous and ferric iron is -177 mv/pH unit. In simple chemical systems such as just described, the experimentally derived redox potential/pH slope may coincide closely with values predicted theoretically.[66] However, in soil and sediment systems containing many redox couples in widely varying concentrations, there is little, if any, basis for expecting the redox potential/pH slopes to coincide

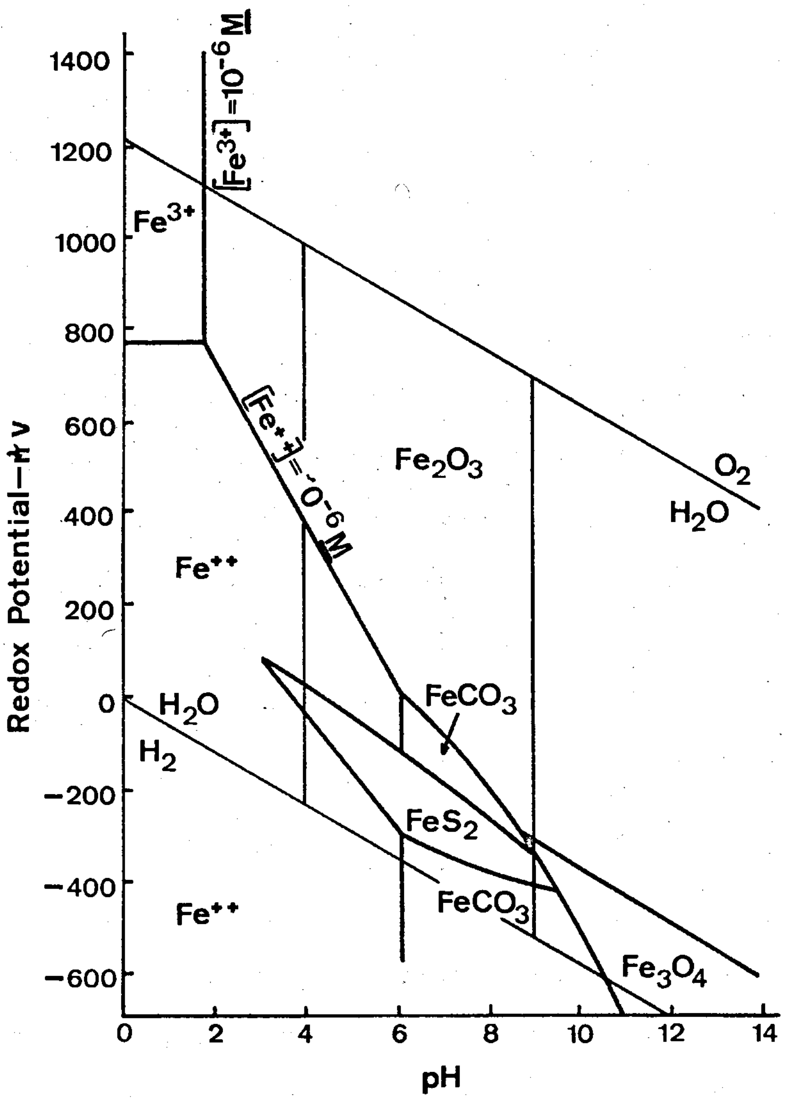


Figure 1. Redox Potential-pH Diagram for Simple Ions and Hydroxides of Iron at 25°C.[24] "From Introduction to Geochemistry by K. B. Krauskopf. Copyright 1967, McGraw-Hill Book Company. Used with permission of McGraw-Hill Book Company.

with the slopes found in the more simple, mono-elemental systems. Bohn[65] explained that the expected dissimilarity in redox potential/pH slopes in different systems is due to the fact that both redox potential and pH in natural systems are controlled by many complex reactions and that these reactions are not necessarily the same. For example, many carbonates, insoluble hydroxides, and silicates are important to pH buffering but are not sensitive to changes in redox potential.[65]

As a result of the interacting effects of pH and redox potential on chemical transformations, it is apparent that: (1) both pH and redox potential should be considered in any experimental study in determining the influence of redox potential and pH on sediment chemical transformations and (2) it is necessary to experimentally cover the expected range of redox potential and pH encountered in sediments and dredged material. Predicting the effect of pH and redox potential on chemical forms of metals found in sediments and water by extrapolating beyond the experimental range may result in invalid conclusions.

Biological Activity

Concern over environmental pollution of waterways has historically focused on aquatic organisms living within the water column. However, another important community of organisms, both plant and animal, is the benthos which live within, on the surface of, or closely associated with the sediment and other material at the base of the water column. Benthic organisms may be categorized by a number of systems. Perkins,[8] in an extensive discussion of benthos, conveniently groups these organisms by size. Other classification considerations, such as tolerance to salinity, depth range in which the organism is found, mobility, surface or subsurface habitat, feeding habits, nature of substratum, and others are also discussed.

Bella[67] advocated a classification of benthal systems based on the amount of iron available to react with free sulfide, and the hydrogen acceptors in the sediments available for decomposition of deposited organic material. Since the amount of free sulfide and hydrogen acceptors is closely related to redox potential, it is apparent that sediment redox conditions are important to the kind and distribution of benthic organisms present. Any changes in the redox characteristics of a sediment occurring at a dredging or disposal site may affect the benthic community. Thus, dredging and disposal may affect bottom-living organisms physically by destroying or smothering their substratum habitat or chemically by changing the redox environment of the sediment, which can alter benthic respiratory activity as well as affect the chemistry and availability of biostimulants and toxins.

Although dredging and dredged material disposal may have short- and long-term influences on both aquatic and benthic life, the benthic organisms require special consideration due to their generally much slower mobility and potentially slower repopulation rate after their habitat has been destroyed or altered.

The biology of benthal communities involves complicated interactions of chemical, physical, and biological factors, and it is beyond the scope and intent of this discussion to present a detailed picture of this system. However, an overall perspective of the diversity of roles of these bottom-living organisms is sufficient to indicate their importance and the reason concern is given them with regard to detrimental changes in their environment resulting from waste disposal.

Bottom-rooted plants and algae (benthic organisms) attached to the substratum contribute to varying degrees to the overall primary productivity of a waterbody. These photosynthetic plants serve as a food source for heterotrophic benthic and aquatic organisms. Green[68] discussed the importance of benthos in the food web. Although some plant material is directly consumed by estuarine animals, most of the vegetation is converted to detritus before it is utilized as a food source. This detritus, much of which becomes intimately associated with the sediment, forms the substratum for benthic bacteria which provide an important source of food for many benthic and aquatic fauna in an estuary. It was suggested that the total organic nitrogen available to the estuarine community may be increased by these bacteria since many are capable of nitrogen fixation. Thus benthic bacteria are an important food source to many species of benthic fauna, which are, in turn, the food source for predators higher up the food chain. Darnell[69] presented a tropic spectrum of the most important fish in Lake Pontchartrain, an estuary in Louisiana. Of 30 or so consumer species studied, over half were found to depend substantially on benthos as a food source. Man is also a direct consumer of several benthic species such as oyster and crab.

In addition to their participation in the food web, benthos contribute to important chemical changes in their sediment environment which may regulate the bioavailability of toxic metals and biostimulants. The relatively abundant organic energy source in sediments results in a high level of biological activity, especially in benthic microbial populations.[56] Their respiratory requirements for a hydrogen acceptor result in the rapid utilization of dissolved oxygen in the interstitial water. Thus oxygen and oxidized forms of other ionic species, such as nitrate nitrogen, ferric iron, and manganic manganese, may be depleted in all but a thin layer of sediment material just beneath the sediment-water interface.[56,70] The resulting reduced environment of the sediment, as indicated by a low redox potential, can contribute to chemical changes within the sediment and interstitial water which affects the water solubility and mobility of certain toxins and/or biological stimulants.

Complex organic decomposition products resulting from the biological decay of plant and animal tissue are formed in sediments. These organic compounds can form a variety of organo-mineral complexes with trace metals and plant nutrients. The chemistry of these chelated metals is complex and poorly understood. These organo-mineral complexes may have a significant influence on the bioavailability of toxic metals and plant nutrients in sediment-water systems by serving as sources or sinks for these materials, or by affecting their mobility. The nature of these complexes is discussed more fully elsewhere in this report.

CHEMISTRY OF TOXIC METALS AND PLANT NUTRIENTS IN SEDIMENTS AND DREDGED MATERIAL

The following section is a review primarily of the chemistry of selected trace metals and plant nutrients in soil and sediment-water systems. A brief discussion of their effects on environmental quality is also included. Though sediments and soils are quite different in many respects, the reported chemistry of these elements in soils, especially flooded soils, may be similar in many respects to their chemistry in sediment-water systems. Thus literature concerning trace metals and plant nutrients from both of these systems has been used in the following discussion.

Lead

The average concentration of lead in the earth's crust is about 15 ppm by weight. Lead is the most abundant of the heavy elements having atomic numbers greater than 60. The relative abundance of lead is due to its three predominant isotopes being end products of naturally occurring neutron capture processes which result in the formation of lead from the radioactive decay of other elements.[71] The slow radioactive decay of uranium and thorium is reported to account for about a third of the lead currently found in the earth's crust.

Though about 20 lead-containing minerals are known, galena (PbS) is the most economically significant mineral, as it accounts for about 80 to 90 percent of the lead mined.[71,72]

Lead in the Environment

Lead was one of the earliest used metals because of its resistance to corrosion and the relative ease with which it could be smelted, worked, and incorporated into alloys. Man was first exposed to potentially harmful levels of lead over 4,000 years ago as a result of smelting metal ores.[73] Lead continues to be one of man's most important metals and has been used extensively since the Industrial Revolution.

Goyer and Chisolm,[74] reporting the data of Lutz, stated that lead production in the United States was around 500,000 tons in 1969, but that the total used amounted to about 1,500,000 tons. Secondary recovery and imports accounted for the difference in production and consumption. Lead is used in a diversity of manufacturing processes and products. About 20 percent of the lead was reported to be used in the production of storage batteries, and 40 percent was used as an additive to gasoline.[74]

The combustion of lead-containing fuel is reported to be the primary source of lead in the atmosphere, resulting in a release of approximately 180,000 tons into the environment each year. This source is thought to account for about 98 percent of all known atmospheric lead emissions.[75]

Much of the lead emitted by automotive exhaust falls on or near the roadway. Singer and Hanson[76] reported that about half of the automobile lead emission is deposited within 30 meters of the highway. Cannon and Bowles[77] found up to 3000 ppm lead in plants growing beside a highway.

Much of the lead is in a fine particulate form and is dispersed as an aerosol over a wide area by wind. This lead is eventually removed from the atmosphere by precipitation or aggregation and falls to the earth's surface. Thus soils serve as an intermediate recipient of airborne lead deposits. Soil lead may cycle through plants and enter food webs, or it may enter waterways through surface and subsurface drainage. This is in addition to lead entering waterways via industrial and municipal waste discharges and direct fallout into water from lead-containing aerosols. As for many other potentially toxic materials, the sediment-water system is the final recipient of much of the lead discharged into the environment.

Due to the diversity of uses for lead, the quantities utilized, and the considerable period of history that lead has been a part of man's technology, it is somewhat difficult to determine what background or natural levels of this element should be in many soils, organisms, or sediments. Lead in arctic snow deposits has shown a steady increase since about 1750 and a sharp increase in the last 20 years as a result of airborne lead contamination.[78] Thus current reported levels tend to include lead that has accumulated in the environment for decades and perhaps a century or more.

Concentrations of lead in a typical urban atmosphere are reported to range from 1 to 3 $\mu g/m^3$ and up to 40 $\mu g/m^3$ in air near heavily travelled roadways.[79] An average of 1.2 μg of lead is estimated to fall per square centimeter of earth annually.[75]

Unless there is a nearby source of contamination, surface waters generally contain little lead. In areas near limestone deposits and galena ores, natural waters have been found to contain up to 0.8 mg of soluble lead per liter. A survey of 876 surface water samples tested between 1962 and 1964, reported by Kopp and Kroner,[80] showed that only five water samples contained more than 50 μg lead/l. They reported the lead content of U. S. waters ranged from 2 to 140 μg/l with a mean concentration of 23 μg/l. Of representative drinking water samples collected from 1963 to 1965, about 14 percent contained more than 10 μg lead/l, but fewer than 1 percent contained more than 30 μg lead/l. The U. S. Public Health Service has set 0.05 mg lead/l (50 μg/l) as the safe limit of lead in drinking water.[81]

Due to the large quantities of particulate lead emitted into the atmosphere annually, it is likely that the soil levels of lead could be increasing. Snyder et al.[82] reported that the lead content of agricultural soil in Illinois has increased from about 12 μg/g to 25 μg/g in the last 40 years. Typical soils contain about 10 μg lead/g, but the range commonly found in soils is 2 to 200 μg/g.[83]

The average American ingests approximately 300 μg lead/day in his diet.[75] About 10 percent of this amount is absorbed and the remainder is excreted. The quantity of lead inhaled by a person working and living in a large city may be an additional 50 to 60 μg lead/day and 30 to 40 percent of this amount may be retained.

A daily body absorption of about 100 μg lead/day is required before the blood lead concentration exceeds 40 μg lead/100g. This level of lead is associated with measurable and possibly adverse metabolic effects,[75] and has been suggested as a maximum safe threshold level of lead in blood. Goyer and Chisolm[74] reported that the blood level of lead in a healthy population ranges from 15 to 40 μg/100g with the mean level around 20 μg lead/100 g. They presented survey data showing a correlation between environmental lead exposure and blood levels and concluded that the lead content of blood in the general population falls below that known to affect the body. However, a National Academy of Science report[84] indicated that the suggested maximum safe level in blood is only about 2.5 times that found in the blood of a typical suburban male working in a city.

In man, organs and systems most affected by lead are the nervous system, red blood cells, and the kidneys. Goyer and Chisolm[74] presented a review of the pathology of lead on the human body and the clinical effects associated with the lead toxicity. This aspect of lead intoxication is well known and need not be discussed in this report. They concluded that with the exception of urban children in deteriorated housing (lead-based paint threat), drinkers of lead-contaminated illegal whisky, and those occupationally exposed industrial workers, most people are not absorbing sufficient lead to adversely affect their health.

There is no evidence that lead concentrations in livestock and aquatic animals currently used for human consumption pose any threat to human health.[84] The concentration of lead in surface waters which has been shown to adversely affect aquatic organisms appears large relative to the concentrations normally found in surface waters.

From literature reports, it seems that most studies on the effects of lead on aquatic organisms have been short-term studies using relatively high concentrations of lead. By comparison, few studies have looked for chronic effects due to long-term exposure to low lead concentrations. Both types of studies are useful and may be applicable to specific environmental lead pollution problems. The following discussion will consider results and interpretations from a few short- and long-term studies.

Dorfman and Whitworth[85] reported that a lead dosage of 25 mg/l reduced growth of brook trout, but no effect could be detected on growth at lower lead levels. Malacea and Gruia[86,87] concluded that a maximum permissible level of 0.1 mg lead/l was adequate for the protection of aquatic organisms.

Lloyd[88] reported that the toxicity of lead, zinc, and copper salts to rainbow trout increased as the dissolved oxygen content of the water decreased.

Rather than a change in the nature of the toxic material due to a redox potential type transformation of the toxicant, an increase in exposure due to increased respiratory flow was suggested as the cause.

Pickering and Henderson[89] studied the acute toxicity of some heavy metals to several species of fish. The 96-hour median tolerance limit for the most sensitive of the species was 7.33 mg lead/1.

Teulon and Simeon[90] reported that two species of carp tolerated lead in water up to 9.6 g/1.

Ayling[91] studied the uptake of several metals including lead in the Pacific oyster, taken from the Tamar River in Australia. Of the five metals studied, lead uptake mechanisms appeared to differ from the other metals studied. Zinc and cadmium accumulation depended primarily on their levels in the sediment while copper and chromium uptake was related to the size of the oyster. However, lead seemed to be "randomly incorporated" or independent of the two correlations noted for the other metals.

Buhler[92] summarized the data of several investigators pertaining to the relative toxicity of metallic ions to fish. The experimental lead concentrations reported to produce toxicity in fish ranged from 0.2 to 7.3 mg/1. Different experimental conditions such as species of fish and length of exposure likely contributed to the wide range reported to be toxic. Buhler[92] also discussed a report prepared by the American Fisheries Society in 1970 which indicates that as little as 10 ppb of lead in water may be toxic under some conditions.

Davies and Everhart[93] reported the toxicity of lead to rainbow trout in short- and long-term studies. The occurrence of abnormal black tails in trout due to chronic lead exposure was used as an indicator to determine the maximum acceptable toxicant concentration ("MATC") in both hard and soft waters in long-term studies. Also determined was the median tolerance limit (TL_{50}), the level at which half of the organisms show acute toxicity symptoms during a specified time interval. In hard water, the 96-hour TL_{50} and "MATC" levels of total lead were reported to be 471 mg lead/l and 0.12 to 0.36 mg lead/l respectively. The corresponding values for free or soluble lead in the same water was 1.38 mg/l and 0.018 to 0.032 mg/l. In the soft water experiments, all lead was considered to be free lead, and the 18-day TL_{50} and "MATC" levels were 140 μg lead/l and 6.0 to 11.9 μg lead/l, respectively.

Unlike many short-term studies in which concentrations must reach relatively high levels to show an effect of lead on fish, this study indicated that a long-term lead exposure of around 10 μg lead/l in some waters may produce chronic physiological symptoms.

Lead Levels in Surface Waters and Sediments

In order to get an idea of the quantities of lead potentially involved in transformations affecting its bioavailability, it is necessary to know the levels typically found in water and sediments in unpolluted systems as well as in those that have received considerable lead from waste discharges.

Sediment samples collected from several sites in the San Francisco Bay were analyzed for selected heavy metals and showed lead levels ranging from just over 100 ppm from the Oakland Inner Harbor to levels considerably less than 50 ppm in sediment samples taken away from the shoreline.[9]

Bischoff and Sayles[94] reported the lead content of deep (∿4000 meters) sediment samples in the eastern Pacific Ocean. On a calcium carbonate-free basis, the levels reported were 0.05 and 0.07 percent for samples 751 and 585 cm beneath the sediment-water interface. These sediments were only moderately reducing as the redox potential was just over 100 mv.

Preston et al.[95] conducted a survey of selected heavy metals in seawater and biological indicators in coastal waters around the British Isles. The mean lead content of filtered water from several sites ranged from <0.05 to 0.21 μg/1. The mean lead content from filtered water from two sites near the shoreline in the Irish Sea was over 1 μg/1. Comparison of their 1970 data with similar 1961 data indicated that there was no increase in the metal content in these waters during the intervening time, even in contaminated areas.

Iskandar and Keeney[96] reported the heavy metal content of sediment cores from selected Wisconsin lakes. Of all the metals studied in these sediments, the concentration of lead showed the most marked decrease with sediment depth in all lakes. This was thought to be the result of lead fallout resulting from the combustion of lead-containing fuels in internal combustion engines. The lead levels below the 50-cm depth were believed to indicate precultural concentrations and showed a considerable range from <0.1 to 20 μg/g sediment. The top 5 cm of four lakes in forested watershed basins contained 3, 10, 33, and 20 μg lead/g sediment. In contrast, the surface 5 cm of sediments from four lakes influenced considerably by man's activities contained 51, 124, 44, and 32 μg lead/g sediment.

The soluble and particulate levels of heavy metals in streams and lakes of the Cayuga Lake Basin of upstate New York were determined.[97] Although the average lead content of soil samples from that region was 7.9 ppm, the lead content of suspended particulate matter in the streams was around

480 ppm. Thus the lead content of the suspended particulates was around 60 times the level in soils of that area.

Berryhill et al.[61] reported the elemental lead content of sediment and organic extracts from sediments for two small estuaries of the Pamlico Sound area of North Carolina. The lead content of the whole sediment sample from several sites in both estuaries ranged from 0.0015 to 0.007 percent (15 to 70 ppm).

Oliver[98] found the mean background level of lead in sediments from the Ottawa and Rideau Rivers near Ottawa, Canada, to be 26 and 42 ppm, respectively. Lead levels of 390 ppm were found in sediments near a sewage plant. Where snow had been dumped in the Rideau River, sediment lead levels up to 1344 ppm were reported. The source of this lead was thought to be automobile exhausts which contaminated the snow.

Chester and Hughes[99] reported the trace metal distribution from a 5220-m-deep sediment core sample in the North Pacific. In this sample, the measured lead content of the sediment to the 860-cm depth ranged from 12 ppm to 36 ppm with little or no trend with depth. The concentration of lead in seawater is 0.004 mg/l.[100]

Windom[101] determined the content of trace metals in water and sediment samples in relation to a dredged shipping channel in Mobile Bay, Alabama. The lead content of the sediments ranged up to 40 ppm with most samples containing between 20 and 35 ppm. The lead content of the overlying water ranged to 12 μg/l with most reported values considerably less than 10 μg/l.

Lead Chemistry in Surface Waters and Sediments

Lead Inorganic Chemistry. The chemistry of trace metals in natural systems is immensely complex. For most metals, it is not possible to predict quantitatively the concentrations of the numerous possible forms of a particular metal in a typically heterogeneous natural system based on the behavior of the metal in pure systems. Lisk[102] presents a literature summary of selected chemical data for several trace elements. The solubility product constant (K_{sp}) of lead carbonate, hydroxide, phosphate, sulfide, and sulfate were listed as 10^{-14}, 10^{-15}, 10^{-42}, 10^{-28}, and 10^{-8} respectively. Thus in the presence of these ligands, lead is only sparingly soluble. However, in natural systems, it is usually not possible to explain trace metal levels by a straightforward application of solubility data. To project or speculate on the predominant regulatory mechanisms affecting trace metal chemistry and its concentration in natural systems, one must first consider what is known about metal chemistry in pure or simple chemical systems. Then one must try to explain how other complex factors, such as trace metal-sediment organic matter associations, interact with the known chemistry of the metal. Understanding trace metal chemistry in a static natural system is difficult, to say the least, but inadequate since sediment-water systems are dynamic, especially when disturbed as during dredging. The chemical environment affecting the complex trace metal regulatory mechanisms is subject to considerable variability when a sediment is disturbed.

Krauskopf[103] presented a discussion of the factors regulating the concentration of several trace metals in seawater and results of precipitation and adsorption studies. The current seawater concentrations of the metals are generally several orders of magnitude less than the calculated levels based on their estimated supply to the sea during geologic time. It was concluded that precipitation reactions with other common constituents of seawater such as carbonate, chloride, hydroxide, sulfate, and even the less common ions such as flouride, bromide, iodide, phosphate, etc., are not the factors limiting the concentration of these elements in normal, aerated seawater. Due to the low solubility of the metal sulfides, it was suggested that precipitation with sulfide may control metal solubility under some local reducing environments, but that sulfide was not thought to be the chief control mechanism in most of the oceans. However, sulfide precipitation reactions could be an important mechanism for immobilizing lead within a reduced sediment. Due to the extreme insolubility of lead sulfide as indicated by its solubility product of 10^{-28}, lead should be effectively removed from the interstitial water and unavailable to organisms in reduced sediments containing sulfide.[102]

It should be kept in mind that only a portion of the total amount of any metal in natural water is present in true solution. Metals bound in living organisms, present as suspended colloidal particles, or adsorbed on suspended colloidal particles likely account for much of the total metal available; and these forms may be in equilibrium with metal in solution.

In seawater the principal ionic form of lead is lead chloride ($PbCl^+$), and divalent lead is the next most abundant ionic species.[103] Lead carbonate is thought to be the compound in aerated seawater limiting the concentration of lead in solution.

Krauskopf[103] also conducted studies on trace metal interactions with selected adsorbents in seawater to get some information on the importance of various adsorption reactions in immobilizing trace metals. It was acknowledged that the reactions with adsorbents used under laboratory conditions may not correspond closely with reactions in nature, but his data certainly indicate which type of adsorption reactions are likely significant concentration controlling factors. The absorbents and amounts of absorbents used were ferric oxide (0.03 g/l), apatite (0.1 g/l), montmorillonite clay (20 g/l), and peat moss (20 g/l). In three days or less, the ferric oxide and apatite adsorbed 86 and 90 percent of the initial 0.5 mg lead/l added, respectively. Clay and peat moss each adsorbed more than 96 percent of the lead added. In this paper, the possibility of organic processes being active in regulating the concentration of trace metals is acknowledged, but not discussed in detail since it was thought to be impossible to even qualitatively evaluate the role of organic processes in trace metal regulation. Literature data were presented which showed that trace metals may be enriched by a factor of several hundred to many thousands in living organisms. Upon the death and settling of the organisms, it was suggested that a portion of the metal may remain with the organic fraction during decay. Eventually, the organic-bound metal would be buried where it may form relatively stable complexes in a reduced sediment environment, thus enriching the trace metal levels of sediments at the expense of levels in solution in the overlying water column.

Hallberg[60] investigated the horizontal and vertical distribution of acid soluble metals in an intertidal area. In addition, data were obtained on particle size, organic matter content, carbonate level, and redox potential. Among the metals examined, lead was significantly correlated with cobalt, zinc, iron, magnesium, and potassium. Lead was also significantly correlated with the <60-μ size fraction and the organic matter content. No correlation existed between redox potential and lead levels. Redox potential was strongly dependent on depth, as expected, while it was suggested that differing geologic factors over geologic time may have contributed to the metal content of the four horizons studied.

A weak but significant correlation has been found between surface area and lead in sediments from two Canadian rivers.[98]

Netzer et al.[104] studied the removal of heavy metals from simulated wastewater by using lime to increase pH and thus induce precipitation of metal hydroxides. Before addition of lime, a solution of 102-ppm lead as lead nitrate in distilled water had a pH of 5.2. Increasing the pH to 7.05 by the addition of calcium oxide removed 63.7 percent of the initial lead. Subsequent pH levels attained and the percent of lead removed by precipitation and flocculation were: pH 7.95 (88.3 percent), pH 9.2 (89.5 percent), pH 10.55 (97.2 percent), and pH 10.8 (98.6 percent). Additional increases in pH resulted in a slight decline in the amount of lead removed, but pH ranges above this would have little applicability to natural sediment-water systems.

Hahne and Kroontje,[105] using a mathematical approach, assessed the significance of lead and other metal complexes with hydroxide and chloride ions on the mobilization of soluble inorganic forms of these trace metals in the environment. The effects of pH and chloride ions were first considered separately since both of these ions exhibit considerable range in nature. In chloride-free water, as pH was increased, divalent lead (Pb^{+2}) predominated up to pH 5, at which point a charged hydroxide of lead ($PbOH^{+}$) increased as divalent lead decreased. These two forms accounted for equal proportions of the total lead at pH 6. Between pH 6 and 10, the positively charged hydroxide of lead ($PbOH^{+}$) was the dominant form in this simple water system. Where the fraction of total lead was plotted against chloride concentration, divalent lead (Pb^{+2}) predominated up to about 3500 mg chloride/l.

At greater chloride levels, up to that of seawater (19,000 mg/1), positively charged lead chloride ($PbCl^+$) was the chief ionic form. Their calculations indicated that uncharged lead chloride ($PbCl_2$) accounted for most of the total lead only at chloride concentrations approached in seawater.

When the influence of both anions was considered together at pH 8.5, the positively charged hydroxide of lead ($PbOH^+$) was the dominant form at all chloride levels commonly found in natural fresh waters.

Though this system is certainly simplified in comparison to natural waters, as only hydroxide and chloride were available to react with lead, these mathematical calculations would suggest that in natural systems, inorganic lead tends to form cationic monovalent and divalent species which are subject to surface adsorption reactions and electrostatic bonding to functional groups. At the low chloride levels encountered in most fresh waters, divalent lead would appear to be the predominant ionic species up to pH 6, above which most of the lead is found as the positively charged hydroxide ($PbOH^+$).

If this mechanism for determining the form of inorganic lead is active in nature, it may have important implications on the fate of lead in sediment-water systems. For instance, below pH 6, soluble divalent lead may be much more subject to removal by organic chelating reactions than the monovalent form of lead found above pH 6 due to the formation of much stronger complexes between organic matter and divalent metals.[106]

The previous two literature reports dealt with lead chemistry in simple systems. Though numerous and complex factors regulate lead in a natural system, evaluating the effects of selected factors individually, where data are available, may add to our knowledge about the chemistry of lead in sediment-water systems.

Bloomfield, Kelso, and Piotrowska,[107] in a simulated soil system, have shown that metal oxides, including lead, are released in a soluble form when incubated with anaerobically decomposing plant material. Previous work indicated that much of the mobilized lead was complexed with soluble organic material produced by the decomposition of the added plant material.[108]

A similar experiment under aerobic conditions indicated that approximately one-third as much lead is mobilized per gram of plant material by decomposition in oxygenated systems.[109] When reduced soil systems were reoxidized, soluble lead tended to be immobilized.[110]

Studies by Bloomfield and others[107,108,109,110] seem to suggest that the soluble metal organic complexes formed under anaerobic conditions are more stable than complexes formed under aerobic conditions. Under anaerobic conditions, the stability of the metal complexes and thus their mobility may be enhanced by the absence of ferromanganese oxides, which compete for trace metals and tend to immobilize them.

Redox potential gradient is one of the most important factors influencing the exchange of substance between sediment and water.[111,112] Gorham and Swaine[113] studied the distribution of metals in oxidate crusts (enriched in iron and manganese oxides), oxidized surface sediment, reduced subsurface sediment, and glacial clays from lakes in the English Lake District of Canada. The redox potential in these four horizons would be expected to generally decrease with depth. Lead appeared correlated with sediment organic matter. Sediments containing considerable organic deposits contained more lead than did white glacial clays which contained little organic carbon.

Several distinct patterns were noted when the proportional concentrations of the 27 elements in each sediment horizon were plotted. Lead, zinc, and cobalt exhibited similar patterns. Their concentrations were lowest in the white clay (the deepest sediment) and generally increased with decreasing depth up to the surface oxidized layer. The greatest levels of lead were found in the oxidized crust and were thought to be due to the scavenging effect of ferromanganese minerals, though lead showed less correlation with iron and manganese than did several of the other metals.

Stumm and Morgan[25] presented redox potential-pH diagrams for simple lead systems. The following two diagrams for lead-water and lead-water-carbonate systems were derived from their figures (Figures 2 and 3). In the lead-water system, lead was shown to exist in the divalent soluble state (presumably, this includes the charged hydroxide of lead, $PbOH^+$, discussed by Hahne and Kroontje[105]) up to a pH of about 8. Above pH 8, the insoluble lead oxide (PbO) would form in this system. When the simple lead-water system was expanded to include a specified concentration of carbon dioxide, there was a pronounced reduction in the stability field for divalent lead. At a total carbon concentration of 10^{-2} M lead precipitated to form lead carbonate ($PbCO_3$) above a pH of about 5.0. In addition to indicating the importance of carbonate to the aquatic chemistry of lead, this example illustrates the complexity of trace metal chemistry as more and more regulatory factors are considered.

Redox potential-pH diagrams can be expanded to cover more complex systems when the concentrations of all components are known. For instance, chloride, sulfate, phosphate, and other ions may complex with lead under specified redox potential-pH conditions. Thus the forms of lead in complex

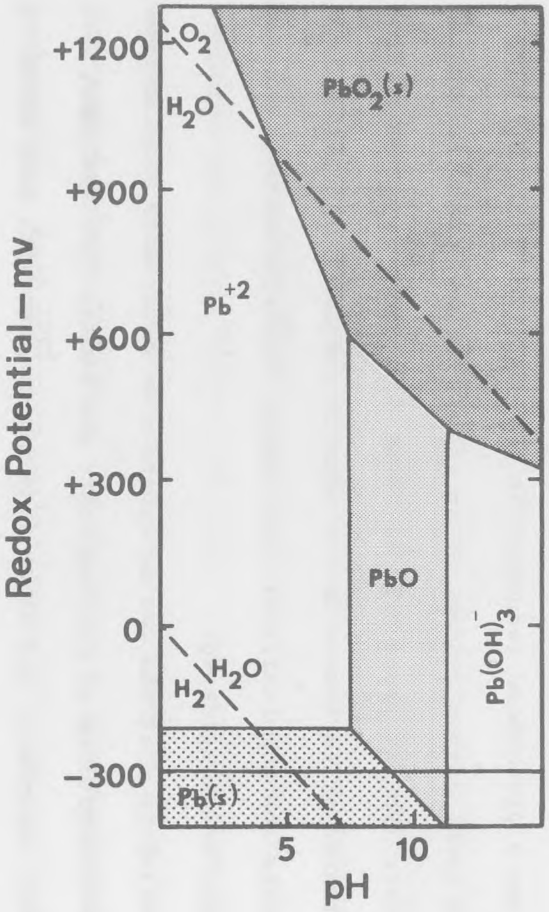


Figure 2. Redox Potential-pH Diagram for the Lead-Water System: Lead (Total) = 10^{-4}*M*.[25] "From *Aquatic Chemistry*, Werner Stumm and James J. Morgan, copyright 1970, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc."

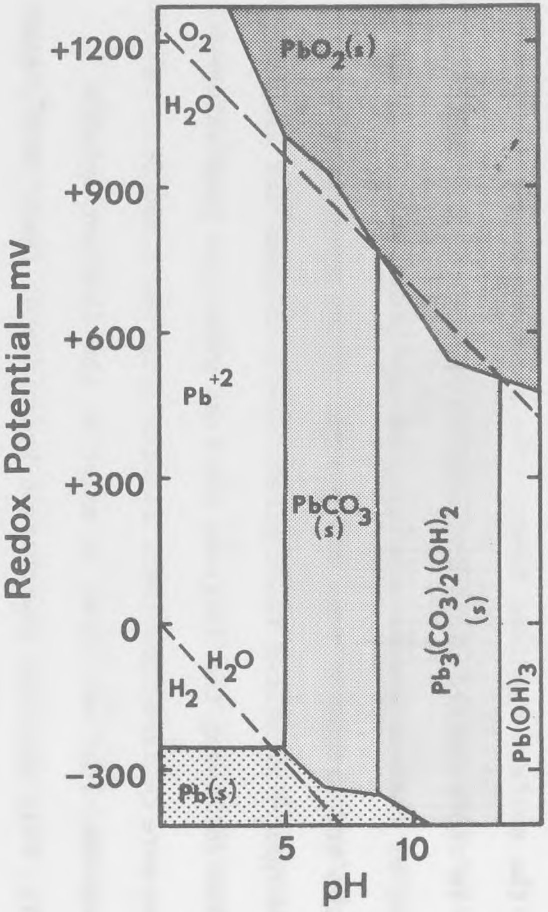


Figure 3. Redox Potential-pH Diagram for the Lead-Water-Carbonate System: Lead (Total) = 10^{-4}*M*.[25] "From *Aquatic Chemistry*, Werner Stumm and James J. Morgan, copyright 1970, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

water systems can be determined where the concentrations and chemistry of all the components are known. However, in natural sediment-water systems, the factors affecting lead chemistry may be in a dynamic state and the chemistry of all the components is not known. Such is the case with interactions between organic matter and metals.

In a study of San Francisco Bay sediments incubated under oxidizing and reducing conditions, it was concluded that the redox potential was the most important of several environmental parameters tested in controlling the solubility of lead as well as several other metals.[9] Significantly higher lead levels were generally found under oxidized conditions. It was thought that this was due to the release of lead from sulfides in aerated sediments and the inability of components in oxidized sediments to complex with lead as effectively as sulfide.

Lead Reactions with Organic Materials. The chemistry of the organic component of sediment-water systems is poorly understood, and little quantitative information is available about its complexing properties except that stable organo-metallic combinations do form. As an indication of the strength of these complexes, Lisk[102] presents information from Sillen and Martell on the stability constants of metals with EDTA, an organic chelating agent which is known to form very stable complexes with divalent metals. The magnitude of the stability constant indicates the strength or stability of the complex. Several metals and their accompanying stability constants were listed as follows: barium (7.8), cadmium (16.6), lead (18.3), lithium (2.8), mercury (21.8), nickel (18.6), and silver (7.3). Thus lead is shown to form quite strong complexes with synthetic chelating agents.

Stevenson and Ardakani[114] summarized the studies of Schnitzer and Skinner in which the stability constants for nine divalent metal ion-fulvic acid preparations were determined. Though the organic matter was derived from a soil, the data from sediment-derived organic material would likely show similar results. The values presented by Stevenson and Ardakani are shown below:

log K, pH 3.5

Cu >	Fe >	Ni >	Pb >	Co >	Ca >	Zn >	Mn >	Mg
5.8	5.1	3.5	3.1	2.2	2.0	1.7	1.5	1.2

log K, pH 5.0

Cu >	Pb >	Fe >	Ni >	Mn >	Co >	Ca >	Zn >	Mg
8.7	6.1	5.8	4.1	3.8	3.7	2.9	2.3	2.1

From these data, two general conclusions can be made. First of all, it is apparent that lead forms relatively stable complexes in comparison to most other divalent metals under the conditions specified. Secondly, it is apparent that the stability constants increased as pH increased from 3.5 to 5.0. This was attributed to the greater number of functional groups, such as carboxylic acid groups (-COOH) which ionize as pH increases. In reducing sediments where the pH tends to approach 7, it follows that even more stable organo-metallic complexes may be present as a result of greater ionization of the organic material.

On the other hand, calculations by Hahne and Kroontje,[105] discussed previously, indicate that at a greater pH, especially above pH 6.0, inorganic lead available for complexing with organic matter may be in a monovalent form. This may reduce the complexation of inorganic lead at higher pH levels, as Rashid[106] has shown that marine humic acid complexes are more stable with divalent metals.

Verloo[115] reported the influence of pH on the stability of lead with extracts of soil organic matter over a wide pH range. Below pH 4, free cationic lead was the predominant form. At pH 4.0, 63 percent of the lead was in cationic form and 26 percent was precipitated as an insoluble organic complex. At pH 5.0, lead was divided almost equally between the free cationic, soluble organic, and insoluble organic fractions. The insoluble organic lead fraction reached a maxima at pH 6 (35 percent of the total), while the soluble organic fraction accounted for 50 percent of the total at this pH. From pH 7 to 10, the soluble organic fraction contained most of the lead. Thus over a wide pH range, two stability maxima were noted for lead-organo complexes. The first was in an acid environment where mostly insoluble complexes formed and the second was in an alkaline range where soluble lead-humates predominated.

Bloomfield and Pruden[116] studied the availability of indigenous levels of trace metals in sewage sludge incubated anaerobically for three months followed by aerobic incubation for three months. As with other published reports, it was apparent that different trace metals frequently show widely different trends. With lead, there was a marked increase in the water-soluble and acetic acid-extractable fraction after anaerobic incubation for one month. Subsequent changes in lead levels were relatively small during the remaining two months of anaerobic incubation and three months of aerobic incubation. There may have been a slight trend for these fractions to continue a slow increase under aerobic incubation. The EDTA extractable lead increased continuously during anaerobic incubation, but showed an even greater rate of release during the three-month aerobic incubation period. This may suggest that there is some loss of stability of the organometallic complexes upon oxidation, or that the organic material itself is less stable and subject to more rapid decomposition under aerobic conditions, resulting in a decrease of the naturally occurring chelating agents. In general, liming sludge soil mixtures was shown to increase acetic acid and EDTA-extractable lead.

Effects of Dredging on Lead Transformations

Some studies have been done in recent years on the effect of dredging on trace metal levels in waterways. Windom[32] reported the effect of dredging on water quality for two sites adjacent to the Intercoastal Waterway in Georgia. The lead content of filtered river water upstream from the dredge was essentially the same as the lead content of effluent from a weir outlet where the sediment had been disposed of by confinement behind a dike. The lead content of the filtered water collected from the dredge discharge pipe was considerably lower (<2 μg/l) than measured in the upstream water. From subsequent laboratory experiments, it was concluded that some of the reduced iron within the sediment may have oxidized rapidly to ferric hydroxide which has a well known scavenging effect on trace metals in solution.[117]

Windom[101] noted that the north-south distribution of sediment iron and lead levels in Mobile Bay were similar, increasing toward the southern end of the bay where contact is made with seawater. It was suggested that the chemistry of these metals could be similar or that lead tended to accumulate with iron because of the scavenging activity of precipitated ferric hydroxide. The decreasing level of lead in the overlying water also corresponded to patterns of soluble iron in the water going down the bay. Samples obtained from around an operating dredge showed that the water content of lead and other metals downstream from the dredge was about the same or possibly lower than levels upstream from the dredge. It was suggested again that this may have been due to iron scavenging. Where dredged material was disposed of in open water, only in very localized areas downstream from the dredge was any increase in metals noted.

In a study of the effects of dredging on several water quality factors in the Calcasieu River, Louisiana, the dissolved lead concentration of the dredge discharge supernatant was slightly less than the lead content of the nearby surface water.[118] Though lead release during dredging at this site did not apparently occur, the river is somewhat atypical since the reported soluble lead content of the surface water (230 μg/l) is much greater than normally found in surface waters. Supernatant from an on-land dredged material disposal site also contained slightly less soluble lead than found in nearby surface waters.

Cadmium

Cadmium is a relatively rare metal and its abundance in the earth's crust is estimated at only 0.5 gram per ton.[119] Cadmium is closely related to zinc in its chemical properties and in nature is always found associated with zinc. It is a divalent metal, readily forming halides of which the chloride is most reactive. It is soluble in most inorganic and some organic acids, but insoluble in alkalies. Cadmium is soluble in ammonium nitrate, forming a cadmium-ammonium complex. In the presence of sulfide, cadmium precipitates out of solution as cadmium sulfide (CdS). The sulfide can be redissolved in sulfuric or hydrochloric acid for quantitative determinations.

Cadmium metal is primarily used as a protective coating for iron and steel, and to a smaller extent, for copper. It is also employed in small amounts in bearing metals used for high-speed automotive, aircraft, and marine engines that operate at high temperatures. Cadmium is also a constituent of solders, alloys, and storage batteries.[119]

Cadmium is toxic to man and to other living organisms in virtually all of its chemical forms. Chronic exposures to small dosages of cadmium have been related to kidney disorder, lung damage, bone and cardiovascular diseases, reduced longevity, and a host of other human maladies.[73,120,121,122] The most severe and classical clinical symptom of chronic exposure to small quantities of cadmium is exemplified by itai-itai disease in people living in the Jinto River Valley of Japan.[123,124] This unusual renal disease may lead to secondary softening of bones and eventual multiple spontaneous fractures. This disease occurred as a result of ingestion of rice irrigated with cadmium-contaminated water from the Jinto River. The cadmium source was waste discharges from zinc and lead mines and smelting plants.[123]

In the United States, the primary environmental concern over cadmium has been its possible relation to the development of cardiovascular diseases, particularly hypertension. Cadmium levels in the air of 28 American cities have been closely correlated with the incidence of death from hypertension and arteriosclerotic heart diseases.[122] The subject of cadmium toxicology has been extensively reviewed by Friberg et al.,[125] Schroeder,[73] and Sandstead et al.[84]

Cadmium in the Environment

The environmental presence of cadmium is normally linked to that of zinc because of their geochemical kinship and incomplete technical separation.

The recovery of cadmium from sphlerite (ZnS) ranges from 1 to 50 kg per ton, averaging 5 kg per ton. The cadmium content of the resulting technical zinc may still be as high as 0.5 kg per ton.[126] Cadmium also enters the environment from smelting of metals other than zinc; attrition of automobile tires; and the combustion of petroleum products, coal, wood, paper, and urban organic trash. The cadmium concentration of four brands of tires ranged from 20 to 90 ppm. The cadmium concentration in diesel and heating oil samples has been found to range from 0.07 to 1.0 ppm and from 0.42 to 0.54 ppm, respectively.[127] The cadmium concentrations of five samples of motor oil were found to average 0.48 ppm, and the total U. S. aerial discharge of cadmium from motor oil in 1968 was estimated at 850 kg.[128] Since cadmium is primarily released into the atmosphere as airborne particulates, cadmium will eventually be deposited on the surface of soils, plants, and water by rain, snow, or dust fallout. Lagerwerff and Specht[127] found that the concentration of cadmium in soil and vegetation along a highway decreased with distance from traffic. The cadmium concentration was related to the concentration of motor oil and automobile tires and their residues deposited along the roadside.

In Japan, levels of 1 to 50 ppm have been found in rice fields in areas under observation for suspected cadmium contamination causing itai-itai.[123] Cadmium is also added to the soil as an impurity with superphosphate fertilizers, as a constituent of fungicides, and in sewage sludge applied to land.[120,129] The metal is easily absorbed through the roots of important food crops, especially grain crops such as wheat, corn, rice, oats, and millet.[130]

Cadmium Levels in Surface Waters and Sediments

The cadmium concentration of seawater is reported to vary from 0.075 to 0.32 μg/l.[131] Goldberg et al.[132] found an average of 0.1 μg/l of cadmium in seawater. The principal species reported were divalent cadmium (Cd^{2+}) and cadmium sulfate ($CdSO_4$).

The average cadmium concentration in the main streams and lakes draining 16 major U. S. watersheds, measured between 1962 and 1967, was 9.5 μg/l, and ranged from 0 (Tennessee, Missouri, and lower Mississippi Rivers) to 50 μg/l in Lake Erie.[80] Drinking water from New England municipal systems analyzed in 1962 and 1963 had the lowest concentration, and water from 21 south-central systems, the highest concentrations of cadmium, averaging 0.12 and 11.2 μg/l, respectively.[133] Where ground water is the source of municipal water, the cadmium content is normally high. Older piping in private dwellings may cause the cadmium content of drinking water to be even higher.[120] The U. S. Geological Survey[134] recently found that 4 percent of the surface waters measured in the United States contained levels of cadmium that exceed the 10 μg/l drinking water standard of the U. S. Public Health Service.[81] Forty-two percent of the samples measured contained between 1 and 10 μg/l, and 54 percent were found to contain less than 1 μg/l.

Kubota et al.[97] analyzed trace elements in the water and suspended particulates in the water of the Cayuga Lake Basin, New York. These samples were thought to be indicative of the natural levels due to soil weathering and geochemical processes. The mean concentration of cadmium in Cayuga Lake water was higher (0.54 μg/l) than in waters of the tributary streams (0.17 μg/l) feeding the lake. Also, the mean concentration of cadmium in the stream particulate matter was appreciably greater than that in soils of the area surrounding the streams (15.6 vs. 0.2 mg/1, respectively). They suggested that the cadmium content of particulates in the streams may represent inputs from industrial, automotive, and household waste. The levels of cadmium found in the Cayuga Lake Basin were low in comparison with the levels in major rivers of this country,[80] and well below maximum permissible levels safe for municipal drinking waters.[81]

Windom[32] found soluble cadmium to range from 0.05 to 0.49 μg/l in the Savannah River. These levels were thought to be relatively low considering the water is heavily polluted with industrial and municipal waste.

The average concentration of cadmium, expressed in μg/l, in the northern half of the Southeastern United States continental shelf waters was 0.11, compared to 0.06 in the southern half.[135] This slightly higher concentration of cadmium in the north was probably caused by the continental runoff, the effects of which were evident across the entire shelf. The concentration of cadmium in the Northwest Atlantic Ocean appears to be relatively uniformly distributed with a mean value of 0.11 μg/l.[136] Similar values have been reported between the English Channel and the Irish Sea.[137]

Taylor[138] conducted a study to provide information on the distribution of trace metals in the sediments of relatively unpolluted coastal area of Tor Bay, England; to establish a baseline for any future investigation related to the discharge of polluted effluents. The cadmium concentration ranged from 0.2 to 0.7 μg/g with an average value of 0.37 μg/g, a value much lower than found in the estuarine sediments.

Iskandar and Keeney[96] compared the heavy metal concentrations of precultural sediment deposits (140 to 400 years old) with that of recent sediment deposits (0-10-cm depth) in 10 Wisconsin lakes to evaluate the rate and extent of accumulation of heavy metals due to man's activities. The results showed that the cadmium concentration decreased with depth, especially when the surficial sediment levels were compared with those below the 50-cm depth. Surficial sediments of all lakes contained cadmium ranging from 2.1 to 4.6 μg/g sediment, whereas levels in sediments below 50 cm ranged from 0.7 to 2.7 μg/g. The study indicated that the lakes are receiving significant quantities of cadmium, the sources of those additions, however, were not discussed. Pacific Northwest Laboratories[9] conducted a similar study in the San Francisco Bay area and reported the cadmium concentration in the 0- to 30-cm deposits ranged from 0.81 to 1.56 μg/g sediment. The concentrations of cadmium in the 30- to 60-cm depth were slightly lower.

Bloom et al.[22] have reported comparable concentrations ranging from 2.5 to 9.2 μg/1 of cadmium in the interstitial waters of Great Lakes and New York Harbor sediments. However, the total cadmium concentrations in the sediments collected from New York area were appreciably higher than those collected from the Great Lakes (mean levels of 22.5 and 10.1 μg/g sediment, respectively). The high concentrations of total cadmium in the New York dredging area reflect the influence of industrial effluent discharges into the bay, and also the capacity of sediments to incorporate heavy metals into the solid phase.

Surveys of cadmium concentrations in surface waters and sediments of the United States and elsewhere reveal that the effect of cadmium contamination from industrial and other sources is reflected by greater cadmium levels in the solid components of sediment-water systems. Thus sediments act as a sink for cadmium; and the magnitude of this scavenging action of sediments depends not only on the concentration of the element in the effluent, but also on the physical, chemical and biological properties of the sediments. To appreciate the complexity of heavy metals transformations in sediment-water systems, one must understand the various kinds of exchange reactions taking place between water and sediments and the factors affecting these reactions.

Cadmium Chemistry of Surface Waters and Sediments

Solubility calculations made by Krauskopf[103] indicate that seawater is greatly undersaturated with respect to cadmium. The estimated amount of cadmium added to seawater over geologic time from the weathering of terrestrial materials far exceeds the quantity presently found in solution, the latter amount being 0.04 to 0.08 percent of the former.[139,140] The literature cited in the preceding section also indicates that the interstitial and overlying waters represent a very small fraction of the total cadmium present in the sediments. As the technological use of cadmium increases, an increase in the amount introduced into the environment is assured.[141] Thus there is a need for a thorough understanding of the mechanisms responsible for the net removal of this element from solution.

Cadmium generally exists in the aquatic environment in four different forms: (1) as a part of living organisms, (2) as colloidal particles, (3) adsorbed on the mineral and organic complexes, and (4) in true solution.[103] Based on the mathematical models and experimental data, Krauskopf[103] advocated that the low cadmium concentration in seawater could possibly be the result of: (1) local precipitation of sulfides, (2) adsorption by various adsorbents present in the sediments, and/or (3) organic concentration by living organisms. Presley et al.[142] attributed the various degrees of metal enrichment in the interstitial waters of a reducing fjord to organic complexing and equilibration with unidentified solid mineral phases. Price[143] reviewed the existing literature on the distribution of cadmium in the various sediment components and established five tentative sites for controlling the equilibrium concentration of cadmium in the marine environment:

a. In solution
b. On exchange sites of clays and organic debris
c. As a carbonate
d. As a sulfide
e. As organically fixed by the micro-organisms

Some of these phases will be discussed in more detail in the following sections.

Solution. The principal species of cadmium present in seawater are divalent cadmium ions (Cd^{2+}) and cadmium sulfate ($CdSO_4$).[34] Gardiner[144] presented experimental evidence that a substantial proportion of the total cadmium in river and lake water is usually present as the free cadmium ion and that this portion will be larger the lower the pH value and the lower the sewage effluent present in the water.

In addition to the free ions, cadmium is also present in solution complexed with a variety of inorganic and organic ligands.[144,145] Hem[145] suggested that the concentrations of cadmium in fresh water were lower than the maximum permitted by the solubility products of carbonates and hydroxides. Complexation of cadmium with carbonate in river and lake water has also been reported by Gardiner.[144]

Although both inorganic and organic ligands can chelate cadmium, the organic complex has several times the metal binding capacity of the inorganic constituents. The soluble organic fraction is composed of various types of chemical compounds such as humic acids, fulvic acids, carbohydrates, proteins, hydrocarbons, etc., some of which can complex metallic ions.[146] Studies conducted by Gardiner[144] showed that humic substances account for most of the complexation, followed in importance by carbonates. The author reported that complexing abilities of extracted humic acid and natural humic material in sewage effluent were comparable. This study also suggested that the ratio of complexed to uncomplexed cadmium depends only on the stability constant and the concentration of the ligand and not on the total cadmium concentration, provided the ligand remains in excess.

Rashid and Leonard[147] have shown that metal ions remain in solution in the chemical environment in the presence of humic substances which should otherwise precipitate if not complexed. No information is available at present on the role of complexation in cadmium toxicity to aquatic life. Although humic materials found in soils and sediments are recognized as chelating agents, the nature and chemical composition of these materials is not well understood. For a detailed account of the nature and chemistry of humic materials, the reader is referred to Schnitzer and Khan[23] and Jellinek.[146]

Sorption on the Solid Phase. Since concentrations of cadmium in the overlying waters are usually far lower than the maximum permitted by the solubility product of the carbonate, the least soluble salt in most natural waters, sorption on the solid phase of sediment is a major factor in influencing the net removal of this element from solution.[145] The rate of adsorption and desorption depends mainly on the type of solid, its state of subdivision, the concentration of the metal ion present, the time of contact, and the concentration of ligands present. Humic materials appear to be the most important component of marine sediments responsible for adsorption.[148]

Price[143] studied the effects of adsorption, precipitation as a sulfide or carbonate, and organic fixation by micro-organisms on the relative mobility of cadmium in a salt marsh. The results show that cation exchange processes adsorb cadmium from interstitial water in increasingly significant amounts as the solution concentration of cadmium approaches those found in nature (less than 20 μg/1).

Hydrous manganese and iron oxides in soils and sediments are strong scavenging agents for heavy metal ions. Geochemists have utilized the heavy metal scavenging properties of these hydrous oxides in mineral exploration studies.[117,149] Krauskopf[103] proposed that hydrated manganese dioxide and hydrated ferric oxides were the most efficient adsorbents for removing trace metals from the seawater. Kopp and Kroner[80] suggested that cadmium, like zinc, was largely adsorbed from solution on hydrolyzate sediments or precipitated as a carbonate in the rivers and lakes in the United States. However, no experimental evidence was provided to substantiate this mechanism for cadmium.

Jenne[117] suggested that adsorption on clays, concentration by organic matter, and precipitation as carbonates or discrete oxides and hydroxides as mechanisms governing the concentration of heavy metals in soils and fresh water are inadequate to explain the fixation of cobalt, nickel, copper, and zinc (no direct reference to cadmium). Surface and nonsurface sorption of these metals by ubiquitous hydrous manganese and iron oxides better explains the reported data in literature. Morgan and Stumm[150] found that freshly precipitated manganese dioxide has a very significant sorption capacity for heavy metals. They reported that the distribution coefficient for heavy metals on freshly precipitated manganese dioxide was greater than the distribution coefficient for alkaline or alkaline earth metals, suggesting a preferential sorption of heavy metals on hydrous metal oxides even in the presence of large amounts of other cations. Lee[151] reviewed earlier work on the role of hydrous metal oxides in the transport of heavy metals in the environment and strongly supported Jenne's proposal[117] that these oxides act as sink for heavy metals.

Hydrous metal oxide coatings on the surface of mineral particles also play a dominant role in the chemistry of heavy metals. Plumb and Lee[152] have reported that taconite tailings derived from iron ore mining in the Mesabi Range in northern Minnesota show significant sorption capacity for various metal ions such as copper, zinc, and cadmium and also for phosphate. This capacity was manifested even though the tailings, which were composed primarily of quartz and of an iron-magnesium silicate (cummingtonite), were a fraction of 1 percent of the total sediment under Lake Superior conditions. The iron released from the taconite particles would precipitate on the surface as a ferric hydroxide and would tend to remove phosphate and heavy metals. A significant part of this removal was associated with surface coatings of the mineral fragments. Unfortunately, most of the work reported in this paper had only an indirect reference to cadmium, and the literature on the cadmium adsorption phenomenon is meager and inconclusive.

Adsorption of cadmium on clay also plays an important role in cadmium fixation. Using samples of 30 surface soils equilibrated with three cadmium concentrations (5, 10, and 50 μg/g), John[153] reported 98.7, 98.0, and 88.2 percent of added cadmium adsorbed, respectively. Haghiri[154] found that soil organic matter plays an important role in retaining soil cadmium. However, it was suggested that the effect of organic matter in adsorbing large quantities of cadmium was predominantly through its CEC rather than chelating ability. Lagerwerff and Brower[126] likewise found significant amounts of cadmium adsorbed by soils, and noted that the adsorption of cadmium increased as the proportion of exchange sites initially holding sodium ions increased. Since the divalent cadmium ion was thought to be preferentially adsorbed, they concluded that the effect of different sodium levels on cadmium sorption indicated an exchange mechanism was active in cadmium retention.

Bittell and Miller[155] investigated the adsorption of cadmium and lead on various clay minerals and found that in the presence of calcium ions, lead was preferentially adsorbed as compared to cadmium. They concluded that more cadmium will be in soil solution and thus available to plants. Since cadmium uptake is related at least partially to solution concentration,[156] this may imply that clay may not tie up as much cadmium in the presence of lead.

Hahne and Kroontje[105] developed mathematical models based on metal solubility products to study the complexation of several heavy metals with hydroxyl and chloride ions at concentrations found in the environment. They reported that cadmium will be present in the divalent ionic form at pH 6 to 7; and, assuming that no other precipitation reactions occur, cadmium will be available for adsorption on suspended mineral colloids and complexation with organic matter. The formation of $Cd(OH)_2$ was reported to begin at pH 9.0 and peak at pH 11.0, though, as the authors stated, such high pH values are not normally encountered in the environment. Based on the distribution of chloride and hydroxyl species in seawater of about pH 8.5, they predicted that chloride complexes will predominate over hydroxy complexes such that the main inorganic cadmium species in seawater are $CdCl_2$ and $CdCl_3$. However, no experimental data were presented to substantiate the theoretical formations.

The studies discussed above indicate that the presence of mineral colloids, organic matter, carbonates, and sulfides may have a tremendous effect on modifying the exact distribution and speciation of cadmium in natural aquatic systems.

Reaction with Sulfide. Sulfate reduction is known to take place in the presence of sulfate-reducing micro-organisms (Desulfovibrio desulfuricans), in submerged soils, lake and river sediments, and marine deposits depleted of dissolved oxygen, but containing an ample organic energy source.[157,158,159,160] Harter and McLean[161] determined that sulfate-reducing microorganisms function best at redox potential of -75 mv or less and that at redox potential levels below -75 mv, sulfate reducers were extremely active. Connell and Patrick[159,160] demonstrated that the critical redox potential for the inception of sulfate reduction was about -150 mv.

Heavy metals are reported to form sulfide complexes in a reduced environment which regulate their concentration in solution.[103,162] Krauskopf[103] speculated that the concentration of cadmium in seawater could be controlled at least in part by the precipitation of sulfides in locally reduced environments, provided that circulation of ocean water was sufficiently rapid. Holmes et al.[163] suggested that the cadmium introduced into Corpus Christi Bay Harbor from industrial effluent in the summer when the harbor was stagnant, reacted with the sulfide ions present below the surface water and precipitated according to the following reaction:

$$CdCl^{+}_{(aq)} + HS^{-} \longrightarrow CdS_{(s)} + Cl^{-}_{(aq)}$$

This precipitation process is accelerated as the low redox potential boundary rises and more metal diffuses into the reducing layer, resulting in a cadmium sulfide-rich sediment. In the winter months, however, the increased flow of oxygen-rich water into the bay results in the desorption of some of the precipitated metal. During mixing, cadmium is adsorbed on suspended sediment and transported through the bay. They warned that this transport of metals previously deposited on the floor may be detrimental to the aquatic environment long after the effluent from industrial process is stopped and that this should be taken into account in coastal management.

Gardiner[148] suggested that when sediments carrying adsorbed cadmium are buried under succeeding layers and become anaerobic, cadmium sulfide will probably be produced and the metal become fixed. About 92 percent of the total cadmium was found in the organic and sulfide phases in the San Francisco Bay dredged sediments.[9] This study concluded that the most important geological phases for all metals in terms of total metal content appeared to be the organic, sulfide, and mineral lattice phases.

Studies also indicate that solution concentrations of cadmium may be reduced by incorporation into plant and micro-organism tissues. Certain plants are capable of accumulating large amounts of cadmium when grown in a medium containing a few tenths of a ppm of cadmium.[156] Ferrell et al.[164] reported that the concentration of cadmium in the shell material of modern oysters (Crassostrea virginica) was considerably higher than the concentration in ambient seawater. Similar findings were reported for the soft tissue of this species by Kofler and Mayer.[165] An investigation of the heavy metal uptake by Pacific oyster (Crassostrea gigas) from the contaminated sediment of Tasmar River, Tasmania, revealed that the concentration of cadmium, zinc, and copper found in the oysters were 10 to 40 times the concentrations in inhabited mud.[91] Ayling[91] reported that cadmium was accumulated in the oysters by a process that depends primarily on the concentration in the mud. The mean concentrations of cadmium in oysters and mud samples ranged from 4.2 to 134 μg/g and 0.4 to 5.7 μg/g, respectively.

Price[143] indicated that ingestion and fixation of cadmium by micro- and macrofauna represent a significant immobilization of this metal, particularly under anaerobic conditions. Fixation of cadmium by organic materials in the sediments has also been reported by Krauskopf[103] and Gardiner.[144,148]

Price[143] studied the influence of redox potential and pH on the transformations of cadmium in Barataria Bay marsh sediments and reported that cadmium in solution decreased with increasing pH and redox potential due to cadmium carbonate ($CdCO_3$) formation. Likewise, cadmium in solution decreased with decreasing redox potential due to sulfide formation. However, the experimental data indicated that the solution phase was supersaturated with respect to both salts such that the lowest measured cadmium level in solution was over 200 μg/l. Thus these discrete cadmium solid species could hardly exert control at cadmium levels found in nature (20 μg/l).

Although the literature reported here is indicative of the different forms of cadmium existing in the sediment-water systems, it does not offer much information on the behavior of this element under conditions where redox potential or sediment pH is altered during dredging and disposal operations in navigable waterways. Chemical equilibrium models discussing the influences of oxidation-reduction potentials and pH on the theoretical speciation of cadmium have been extensively discussed,[25,105,162] but the experimental evidence of these reactions in the aquatic environment is lacking.

Mercury

Geochemistry and Cycling in the Environment

Mercury is a naturally occurring metallic element and is one of the least abundant elements found in the earth's crust. One estimate ranks mercury 74th in abundance in a list of 90 elements.[166] It is found in the atmosphere, water, soil, rocks, and biological ecosystems of the earth in a number of chemical forms. In the elemental state, it exists as a liquid at the surface of the earth and as such will vaporize into the atmosphere and condense as determined by its vapor pressure and the barometric pressure and temperature of its environment.[167] It may also exist in a cationic form which results in its electrostatic adsorption to minerals and humic substances such as found in soils, rocks, and water. In addition, mercury is found in several organic combinations. Some organo-mercurial substances are manufactured because of their commercial importance, and some are known to be produced in natural ecosystems. Organo-mercurial compounds are environmentally important because of their mobility and well-known toxicological properties.

The U. S. Geological Survey[167] reported that the range of mercury in a broad category of rocks was from 10 to 20,000 µg/kg. Although greater than background levels are found in many ores, only cinnabar ores contain sufficient mercury to serve as a commercial source for this metal. Rocks near ore deposits or organic-rich shales contained the most mercury. In soils, the U. S. Geological Survey[167] found an average concentration of 71 μg/kg mercury. Mercury is found in the atmosphere because of its tendency to vaporize. In most areas surveyed, the concentration of mercury in air ranged from 0.003 $\mu g/m^3$ to 0.009 $\mu g/m^3$. Concentrations ranging up to 20 $\mu g/m^3$ were found in the air over mercury, copper, and other precious metal mines.[167] Precipitation washes mercury out of the atmosphere into soil and surface waters. Mercury washed into soil from the atmosphere may be bound tightly to the mineral and humic material in the upper few centimeters of soil. Mercury is naturally distributed in ground and surface waters as a result of contact with water in the atmosphere, soil, and rock during surface and subsurface drainage. The natural levels of mercury in surface waters, except where influenced by special geologic conditions, is generally less than 0.1 μg/l. Higher concentrations of mercury are likely to occur in underground water because of groundwater's longer contact time with mercury-containing mineral and organic material and certain environmental factors.

Because of its tendency to be sorbed readily by a variety of earth materials, bottom sediments and suspended particulate matter in water are more likely to contain higher concentrations of mercury than the associated overlying water, regardless of the source of the mercury.

Suspended material in surface waters may contain from 5 to 25 times the mercury found dissolved in the surrounding water in areas of industrial pollution. Although normal stream water with a pH of 5 to 9 can contain up to about 25 μg/l of mercury when saturated, the concentration downstream from a mercury source is generally much lower because of dilution, vaporization, precipitation, sorption, and chemical reactions.[167]

Mercury occurs in the environment as a result of natural processes, but man-made sources of this element have added substantially to the total load of mercury in the ecosystem.

The principal forms of mercury pollutants commercially discharged into the environment and the primary sources of these compounds are the following: (1) metallic mercury, Hg° (chloralkali and instrument plants); (2) inorganic divalent mercury, Hg^{2+} (chloralkali plants); (3) phenylmercury, $C_6H_5Hg^+$ (paints, pulp, and paper plants); (4) methylmercury, CH_3Hg^+ (agriculture); and (5) methyoxyethyl-mercury, $CH_3OHgC_2H_5$ (agriculture).[168] Losses to the environment of mercury and mercury compounds from industrial processes in this country are estimated at 600 tons per year and superimpose a significant amount of man-made pollution upon the pattern established by nature.[167] Recent studies by an Interior Department task force revealed mercury contents of many industrial outfalls and sludge banks to range from a trace to 100,000 μg/kg.[167]

The single largest source of mercury pollution during 1968 was derived from inventory losses suffered by the chloralkali plants.[169] Mercury catalysts employed for acetaldehyde and vinyl chloride manufacture and mercury formulations used as seed dressings have also promoted serious consequences, even though such usage represents a small percent of the total mercury consumption.[170] The dissipative uses of mercury include paints, agriculture, dental fillings, catalysts, paper and pulp manufacture, and pharmaceuticals, a total of 26 percent of the mercury demand of 1968.[167] Other man-made sources include unsalable outputs as mine tailings and vapor released by the mining and smelting of mercury. Although these sources are difficult to quantify, nevertheless, high stream and lake water levels of mercury have been attributed to dump material and tailings. Also during the refining process, ore is heated to liberate mercury as a vapor, which is then collected in condensers. Stack losses during the process should not exceed 2 to 3 percent, although much higher losses have occurred. A stack loss of 3 percent would mean that about 31 tons were emitted into the atmosphere from smelting during 1968.[171]

Klein and Goldberg[172] estimate that the annual worldwide production of mercury is over 7,000 metric tons and that from 25 to 50 percent of this may be discharged into the environment. This quantity of mercury from man's activities compares with 230 tons estimated to reach the world's oceans from natural weathering of mercury-containing rocks and minerals and 36,000 tons emitted into the atmosphere by natural evaporation.[173] Thus mercury pollution from technology should probably be considered a problem, not so much from total quantities discharged, but from the standpoint that man-made inputs of mercury into the environment tend to be concentrated in relatively localized areas, particularly in water courses near large industrial or metropolitan areas.

From results of various tests throughout this country, some believe that mercury is present in excessive amounts in all segments of the environment.[169]

Mercury is subject to many complex transitions and pathways between its source (mined cinnabar ores) and the surface waters and underlying sediments which generally serve as sinks for this metal. Waterways have historically been the recipient of industrial, municipal, and agricultural waste discharges containing mercury as well as other metals. This is the basis for concern over trace metal transformations induced by dredging and dredged material disposal which may affect the bioavailability of these metals.

Mercury and Environmental Quality

Mercury has been known to be detrimental to human health for a long time. But only in this century, or perhaps more accurately since the midpoint of this century, has the mercury threat to man and his environment become understood sufficiently well for mercury pollution to receive the attention it deserves. In the early 1950's a mysterious disease appeared in Japan, which seriously affected scores of people, many of them fatally.[174] The disease occurred most frequently in fishermen and their families and was linked at first to fish in their diet and ultimately to industrial mercury-containing waste discharges into Minamata Bay. Since then, the occurrence of a few similar episodes in various parts of the world and the discovery of significant levels of mercury in some fish in many countries have resulted in much research into the effects of mercury on environmental quality.

Goldwater and Clarkson[175] have compiled data from several sources available on mercury levels in food from the mid-1930's to the mid-1960's. While acknowledging the possibility of variation due to differing analytical procedures, they concluded that mercury levels in food probably did not change significantly during this period, but that the mercury concentrations in certain foods may have increased some in the last few years. However, it was suggested that inorganic mercury in food and water currently poses little threat to human health.

Though mercury is not known to be an essential element in the biosphere, it is assimilated by all organisms in environments which contain it. Fruit, vegetables, and grain have been shown to contain mercury up to a few hundredths of a ppm.[176,177,178]

The mercury content of marine algae ranges from 0.023 to 0.037 μg/g, which is several hundred times the accepted concentrations for seawater.[179]

The degree of toxicity of environmental mercury is very much dependent upon its form and how it enters an organism. Metallic mercury can be swallowed without adverse effects, while inhalation of metallic mercury vapors, usually as a result of occupational exposure, has long been known to have an adverse effect on human health.[175] Inorganic mercury salts as well as certain organic mercury compounds are known to be only moderately toxic. The greatest danger to human health is from certain alkylmercury compounds.[174] Though several are known to be extremely toxic, methylmercury has received the most attention as it was apparently the form responsible for the Minamata Bay incident. Methylmercury has been found to be the predominant form of mercury in the biological cycle.[179] Since most of the mercury released into waterways is in the inorganic form and most mercury in fish is present as methylmercury, there is much interest in the mechanisms and location of mercury transformations in sediment, water, and biological systems resulting in its accumulation in the food chain.

Inorganic mercury has been shown to be methylated biologically from micro-organisms isolated from sediments.[168,180] Once formed, methylmercury may complex with anions and diffuse to surface sediments or the overlying water column and be assimilated by organisms.

Harriss et al.[181] have reported the effects of several organo-mercury compounds on phytoplankton. The degree of toxicity was indicated by the compounds' effect on photosynthesis as measured by fixation of carbon-14-labelled sodium bicarbonate ($NaHCO_3$). The four compounds tested gave significant reductions in photosynthetic ability and cell growth in concentrations as low as 1 µg/kg. A concentration of 50 µg/kg completely inhibited carbon-14 fixation and cell growth. The authors concluded that the maximum permissible concentrations for mercury in drinking water (5 μg/l in the U. S.) are well above the levels which would have adverse effects on phytoplankton.

Lagerwerff[182] reported that the average daily intake of mercury in the United States is 40 to 100 μg per person, depending on the amount and kind of meats (particularly fish) in the diet; and that the work in Sweden suggests that a daily intake of 300 μg mercury per day is associated with minimum blood levels at which toxic symptoms have been found.

The previous discussion of the effect of mercury in the environment, though brief and incomplete, indicates that mercury is a potentially serious environmental contaminant, and that the sediment-water system and associated organisms are important to the chemical and biochemical transformations affecting its availability and toxicity. Wallace et al.[179] and Lagerwerff[182] present a more complete review of mercury in the environment, and the clinical aspects of mercury in man thatbeen reviewed by Goldwater and Clarkson.[175]

Mercury Levels in Sediment-Water Systems

Since water and sediments are recipients of much of the waste mercury in the environment, it is important to know something of the levels of mercury found in the sediment-water system. Goldwater and Clarkson[175] stated that little attention was given to mercury in water in the United States prior to 1970. Therefore, it is difficult to determine what background or natural levels were prior to the widespread use of mercury for industrial and agricultural purposes during the last 20 years.

In 1970, the U. S. Geological Survey[167] reported the results of a survey of the mercury content of selected streams in the U. S. and found a range of values from <0.1 to 6.0 μg/l. Most streams contained less than 1 μg/l and many less than 0.1 μg/l. Walters et al.[183] reported the mercury content with depth in water samples from the western basin of Lake Erie and found the sample means ranged from about 0.10 to 0.15 μg/l.

The mercury content of seawater is 0.03 μg/l.[100] Chau and Saitoh[184] reported that the mercury levels of all of the Great Lakes are similar and range from 0.13 μg/l to 0.18 μg/l. Most of these reported mercury levels in surface water are for total mercury and do not distinguish between mercury in solution and that adsorbed on finely divided, suspended particulate matter.

Though it appears that only low levels are found in most waters, much higher concentrations are found near the sources of mercury-contaminated discharges into waterways.[167]

Several recent reports are available on the mercury content of sediments. Syers, Iskandar, and Keeney[185] determined the vertical distribution of sediment mercury in several hard- and soft-water lakes in Wisconsin and found that background levels in sediment deposited prior to the time of cultural uses of mercury ranged from 0.01 to 0.24 μg/g. In lakes contaminated by cultural uses of mercury, the measured concentration was higher in surface horizons and decreased with increasing depth. This indicates that mercury is relatively immobile in undisturbed sediments. Thomas[186] reported background levels of mercury in Lake Ontario sediments to be 0.03 to 0.06 μg/g. Andren and Harriss[187] reported data for total mercury and methylmercury in Mobile Bay, Mississippi River Delta, and Florida Everglades sediments. Of the samples collected, the total mercury in each of the sediments ranged from 0.21 to 0.60 μg/g, 0.08 to 0.57 μg/g, and 0.12 to 0.49 μg/g, respectively. Oliver[98] reported the background levels of selected trace metals in Ottawa and Rideau River sediments near Ottawa, Canada, and found 0.28 and 0.20 μg/g mercury, respectively. However, sediment samples collected near three known discharges of mercury-contaminated wastes were around 2 μg/g, and this level dropped to about 0.75 μg/g approximately one mile downstream from each discharge site. In contrast, a sediment sample obtained near a sewage treatment plant contained over 200-μg/g mercury.

From seven sediment sampling sites in the Florida Everglades, Lindberg and Harriss[21] found that mercury ranged from 0.28 to 1.50 μg/g in the surface 10 cm. They found 0.50 and 0.22 μg/g total mercury in the surface 10 cm from two sites in Mobile Bay. This was of interest since Mobile Bay was thought to receive considerably more mercury in effluents from anthropogenic sources. The mercury content of the interstitial water ranged from 0.26 to 3.60 μg/l in the top 10 cm of the Everglades sediment samples and was around 1 μg/l for the same depth interval in the Mobile Bay samples. This was reported to be 2.6 to 36 times the concentration of dissolved mercury in the overlying surface waters at these sites.

Skoch and Turk[188] reported the sediment mercury content at sites in Lake Erie as a function of different sampling techniques and time during the 1964 to 1968 period. Sediment levels of mercury generally ranged from 0.5 to 1.0 μg/g and varied considerably with time. Fluctuations in the mercury content generally followed changes in other sediment components such as iron and organic carbon.

From the previous references, it is apparent that the total mercury content of sediments is three orders of magnitude or greater than the concentrations reported in natural waters.

This reservoir of mercury in sediments and the greater soluble mercury in the interstitial water fraction make it important to understand the chemical and physical factors which are involved in the exchange of mercury between sediments and the overlying water. It is also important to understand the effects of altering the physical and chemical environment of sediments, as occurs during dredging and disposal, on the levels of mercury in water.

Chemistry of Mercury in Sediments and Overlying Water

From the previous discussion it is apparent that most of the mercury associated with undisturbed sediments is not in a soluble form. Since the physical and chemical behavior of mercury in the environment is dependent upon the species with which mercury complexes, the forms of mercury in sediment-water systems must be characterized.

Lisk[102] summarized several literature reports on the physicochemical data for selected metals. The solubility product constant (Ksp) for mercury with carbonate, hydroxide, and sulfide reported were 10^{-16}, 10^{-25}, and 10^{-53}, respectively. The reported stability constant (log K) with EDTA, an organic chelate, was 21.8, indicating a strong bonding with organic matter. These values indicate that mercury forms strong, stable bonds with many of the components found in natural water systems. For comparison, the solubility product constant and stability constant for mercury with every species mentioned above was greater than for lead, cadmium, nickel, and silver.

Hahne and Kroontje[105] calculated the effects of chloride and pH on the forms of mercury in aqueous systems from formation and solubility product constants. In a pure water system, the mercuric hydroxide ($Hg(OH)_2$)

precipitate complex predominated at pH levels common to sediments and soils. Unlike zinc, cadmium, and lead, mercury was shown to form several chloride complexes at low chloride concentrations. For a mercury-chloride system, the predominant species reported as chloride concentration increased were $HgCl^+$, $HgCl^2$, and $HgCl_3^-$. The chloride concentrations at which each of these compounds predominated were reported to be 0.0035 mg/l, 3.5 mg/l, and 3,550 mg/l, respectively. Above 3,550-mg/l chloride, the $HgCl_4{}^{2-}$ form predominated. When chloride and pH were considered in a mixed system at pH 8.5, mercuric hydroxide ($Hg(OH)_2$) was the dominant form expected at chloride concentrations normally found in freshwater systems. It should be kept in mind that in a natural system, there are many other species with which mercury can complex.

Morel, McDuff, and Morgan[43] also used models to predict the forms of various metals found in mixed inorganic systems in the pH range from 5 to 9.5. They listed mercuric chloride ($HgCl_2$) and mercuric hydroxide ($Hg(OH)_2$) as the predominant mercury species expected in an aerobic system. Mercuric chloride ($HgCl_2$) was more important at the lower pH levels computed, and mercuric hydroxide ($Hg(OH)_2$) predominated at a higher pH. In a reduced environment, the predominant species expected as pH increased over the range of 5 to 9.5 were HgS, Hg^0, $HgS_2{}^{-2}$, and $Hg(SH)_2$.

Mercury may interact with organic matter to form combinations which are soluble or insoluble. These reactions are important in influencing the bioavailability of mercury. The formation of soluble mercury compounds is generally expected to increase its bioavailability whereas mercury complexation with insoluble organic material decreases its bioavailability. Mercury is generally found to be positively related to the organic carbon content of the sediments.[186,188] However, a good correlation is not always found. Syers, Iskandar, and Keeney[185] have shown that the mercury and organic carbon profiles of selected Wisconsin lake sediments can bear a close resemblance or almost no similarity.

In a study of mercury-organic matter associations in sediments, Lindberg and Harriss[21] reported that interstitial dissolved mercury is much greater than is dissolved mercury in the overlying surface water. They presented evidence that this may be due in part to formation of soluble mercury-organo complexes. For samples from both the Everglades and Mobile Bay, total mercury was significantly related to the total organic matter content (r=0.80). In addition, they found a good correlation between dissolved mercury and dissolved organic carbon in the surface interstitial waters (r=0.81), but a poor correlation in subsurface layers in the Everglades sediment.

The total mercury content was greater in the relatively unpolluted Everglades sediment, most likely because of the much greater total organic matter at these sites. However, the ratio of total and dissolved mercury to total and dissolved organic carbon respectively, was greater for the more polluted Mobile Bay sediments, indicating the importance of organic matter complex formation with mercury added from waste discharges.

The strong correlation between mercury and dissolved organic carbon suggests that soluble organo-metallic complexes are involved in the mercury and other trace metal enrichments in the interstitial water. These researchers[21] fractionated the dissolved organic carbon into four molecular weight fractions (>100,000; 100,000-50,000; 50,000-500; and <500) and found a good correlation (r=0.94) between dissolved mercury and dissolved organic carbon in all four molecular weight fractions for both sites studied.

For the Everglades samples, most of the soluble mercury (and thus dissolved organic carbon) was found in the <500 molecular weight fraction while the >100,000 molecular weight fraction contained most of both interstitial water components from Mobile Bay.

From this report, it appears that much of the interstitial soluble mercury may be present as organo-metallic complexes rather than as free ions. It is likely that this would be true of the low soluble mercury levels found in surface waters. Also, based on the general relationships reported for total mercury and total organic carbon, a large proportion of the total sediment mercury load may be present as an insoluble organo-mercuric complex in some sediments. However, other sediment constituents, such as sulfide precipitates, which may or may not be correlated with total organic matter, may be important complexing agents for mercury and should also be considered. The availability of mercury complexed with insoluble organic matter would depend greatly upon the stability of the complex and little information is available on the topic. Lindberg and Harriss[21] reported that increasing salinity tends to have a negative effect on mercury-organic matter complexation, which suggests that some mercury may be released from organic complexes if a sediment is transported to a more saline environment for disposal. Also, they found a decreasing correlation between dissolved mercury and dissolved organic carbon with increasing depth, which may suggest a lack of organo-metallic complex stability with time.

There are numerous chemical and biological transformations of mercury which affect its oxidation state and availability. Baughman et al.[189] recommended that research should be done to determine the influence of the redox properties of sediments on the oxidation-reduction reactions of mercury.

In a strongly reducing environment, mercury may be present in the elemental form as (Hg^0) or as the sulfide (HgS). Under oxidizing conditions, the sulfide complex may be slowly transformed into mercuric sulfate ($HgSO_4$), which dissociates rapidly, releasing inorganic mercury into the web of geochemical and biological interactions. An oxidizing environment will also promote the conversion of metallic mercury to ionic mercury, particularly if there is soil material present with which the resulting inorganic mercury can firmly bind. Mercuric compounds which are transported to the earth's surface will generally degrade to metallic mercury and may volatilize under the action of sunlight.[171] However, mercury compounds which are washed into anaerobic river and lake bottoms may be converted to the insoluble and unavailable sulfide form (if hydrogen sulfide is present) or to metallic mercury, depending somewhat on the pH.[43]

Alberts, Schindler, and Miller[190] report the reduction of the mercuric ion to elemental mercury in the presence of humic acid. In the study described, about 33 percent of the initial mercuric ion was reduced to metallic mercury in 290 hours. The process was thought to occur chemically rather than biologically.

According to Hem (Jonasson[171]), under the usual conditions of temperature and pressure that occur in river, lake water, and water-saturated sediment, mercury can be present in one or more of three different oxidation states. The most reduced of these forms is the metal which is a liquid at ordinary temperatures. The metal has a high vapor pressure and is therefore very easily volatilized. The other two forms are ionic. The more reduced of the two ionic forms is the mercurous ion (Hg_2^{2+}), where the valence of mercury is +1. Under oxidizing conditions, especially at low pH, the stable form is the mercuric ion (Hg^{2+}). At the conditions of pH and redox potential likely to occur in aerobic or anaerobic sediments (pH 5 to 9 and redox potential less than 500 mv), metallic mercury (Hg^0) and mercuric sulfide (HgS) are the principal species likely to enter into an equilibrium affecting the solubility of mercury. Mildly reducing conditions, as are likely to occur in many lake and streambed sediments, can cause mercury to be precipitated as the sulfide. Very strongly reducing conditions, however, may increase the solubility by converting the mercuric ion to free metal. In solutions that are high in chloride, the solubility of mercury in oxygenated water may be greatly increased by the formation of the uncharged $HgCl_2$ complex, or anionic complexes such as $HgCl_4^{2-}$.

Even though it has been shown that the greatest amount of pollutant mercury is in the inorganic form, the predominate form found in the biological cycle is methylmercury.[179] As previously discussed, organo-mercury compounds, especially methylated forms, are by far the more toxic forms of mercury.[51] Inorganic mercury can apparently be easily converted to methylmercury. The mercuric (Hg^{2+}) ion is converted to methylmercury in rotting fish and by micro-organisms.[168] Where mercury is present in anaerobic sediments, as the insoluble sulfide, methylation does not occur. However, if the sulfide is incubated in an aerobic sediment, methylation may occur as mercuric sulfide (HgS) is oxidized to mercuric sulfate ($HgSO_4$).[191]

Andren and Harriss[187] studied levels of methylmercury in estuarine sediments from Mobile Bay, the Mississippi River, and the Everglades. They found that methylmercury accounted for an average of only 0.03 percent of the total sediment mercury and never more than 0.07 percent in the sediments studied. They concluded that methylation of mercury plays only a small role in influencing levels of dissolved mercury in interstitial water and suggested that the future studies of the toxicological nature of methylmercury should emphasize the biological production of this form of mercury from inorganic mercury. Presumably, they mean methylmercury production within the consuming organisms or perhaps in the organisms used as food by other species.

Sorption-Desorption Reactions of Mercury. There is relatively little quantitative data on the sorption and desorption reactions of ionic mercury by soils and sediment material in the literature. Possible binding mechanisms are: (1) sorption by hydrated metal oxides, (2) surface sorption or ion exchange on soil minerals, and (3) sorption or chemical bonding with organic matter.[192] Sorption-desorption reactions of mercury with sediment minerals may result in mercury removal from water or a net release into water.

Bothner and Carpenter[193] reported sorption-desorption laboratory studies of mercury with suspended matter in the Columbia River. From 60 to 75 percent of the total naturally occurring mercury in unfiltered water was associated with the particulate materials.

In sorption studies using inorganic radiotracers, they found about 50 percent of the added mercury was taken up by the suspended matter in 10 hours with a small additional uptake between 10 to 60 hours. Methylmercury was sorbed at similar rates and concentrations. They also reported that about half of the inorganic mercury was loosely held as it could be removed or desorbed by filtered river water containing low levels of mercury. Following a series of freshwater rinses, a seawater rinse resulted in small additional amounts of inorganic mercury being removed. More (60 to 75 percent) of the methylmercury could be removed by filtered river water, but again, subsequent washes with filtered seawater removed only a small additional amount.

Though this work suggests that the transition of suspended matter from fresh to salt water results in little increase in desorption of mercury, it should be kept in mind that the study was conducted in a continuously aerobic environment. In a dredging situation, the dispersal of anaerobic freshwater sediments into an oxygenated water column with subsequent reduction upon settling may result in greater release due to an interaction between the increased ionic strength or salinity and a change in the oxidation state of the sediment material. These authors mention the work of DeGroot using suspended matter from river and offshore sediments in Europe in which salt water did significantly increase desorption. Unlike the Columbia River study,[193] DeGroot's material was likely reduced before it was placed in suspension. Feick et al.[192] showed that calcium chloride ($CaCl_2$) and sodium chloride (NaCl) used for deicing roads can greatly increase the release of mercury from highly contaminated sediments.

Reimers and Krenkel[194] reported an extensive study on the kinetics of mercury adsorption and desorption on selected sediment mineral components and simulated organic components in well-oxidized environments. They used montmorillonite, illite, kaolinite, three sand fraction sizes, and three organic functional groups (carboxyl, amine, and mercaptan attached to long aliphatic chains) to represent sediment components. Using the sediment components described, they studied the effects of three pH levels (5, 7, and 9) and three chloride levels (≃0, ≃100, and ≃10,000 μg/g) on mercury adsorption. Both inorganic and methylmercury were studied. The capacity of the clay minerals to adsorb inorganic mercury was reduced by an increase in the chloride concentration. Kaolinite exhibited the greatest reduction in mercury adsorption as chloride concentration was increased. Clay mineral type could therefore play an important role in determining trace metal release from freshwater dredged material disposed of in salt water. Since little pH effect was noted and because a mercury chloride complex does not exist at high pH, the authors suggested the reduction in mercury sorption with increasing chloride concentration might be due to a competitive ion effect between mercury and sodium. This suggests that ion exchange with clay minerals may be an important regulatory mechanism for mercury. The carboxyl functional group (stearic acid) showed a similar response to chloride levels while the other functional groups showed no chloride effect. Although there was no pH effect with kaolinite, sand, and stearic acid, illite and montmorillonite did show a pH effect with highest sorption capacity occurring at pH 5 at the lower chloride levels. They concluded that desorption of inorganic mercury was slight for all components investigated except for illite at high chloride concentrations and pH levels greater than 7, and in sands when the chloride concentration was high.

Lockwood and Chen[195] examined the adsorption of the mercuric ion (Hg^{2+}) by hydrous manganese oxides. Considering the influence of pH, ionic strength, and sodium chloride levels on this process, they concluded that hydrous oxides of manganese may be important in scavenging mercury in fresh or brackish natural water systems. It was pointed out that mercury differs from many other divalent metals used in adsorption studies since the dominant species above pH 3 is the uncharged metal oxide hydrate ($Hg(OH)_2$). When the chloride in solution is considerably less than that in seawater, mercuric chloride ($HgCl_2$) may also adsorb to a considerable degree. The presence of chloride at concentrations approaching that of seawater retards mercury adsorption up to pH 10. They noted a pH effect on adsorption rates. Where the pH was lower than 7, the rate of adsorption up to apparent equilibrium values was much faster than when the pH was above 7. In addition to the rate of adsorption decreasing as pH increases, they presented data indicating that the total mercury adsorbed decreases as pH increases above 4.

Mercury Precipitation with Sulfide. Mercuric sulfide (HgS) is an extremely insoluble compound. Dissolved sulfide typically found in reduced soils and sediments should effectively remove mercury from solution by precipitation.[103,179] Engler and Patrick's work[196] with several metal sulfides indicated that mercuric sulfide was more stable in reducing soils than sulfides of manganese, iron, zinc, and copper, as measured by labelled sulfur-35 uptake by rice plants (Oryza sativa L.). However, they pointed out that mercury toxicity may have been a factor in this particular experiment.

Lindberg and Harriss[21] found that the measured mercury content of interstitial water from Mobile Bay and Everglades sediments was 10^{13} to 10^{31} times greater than the concentration calculated from the solubility of mercuric sulfide. It was suggested that mercuric sulfide may be present in a relatively soluble polysulfide complex which might account for much of the dissolved mercury observed in these samples. They refer to previous calculations by Lindberg supporting the contention that polysulfide complexes may be involved in producing mercury enrichment of interstitial water.

Effects of Dredging on Mercury Transformations

Windom[32] conducted a study to evaluate how a Georgia salt marsh sediment responded chemically to dredged material disposal. Sediment samples were analyzed before and after deposition for sulfide and selected metal concentrations, redox potential, and pH. Samples collected from the dredge discharge pipe and allowed to settle after collection showed that dissolved mercury, unlike the other metals studied, did not show an initial lowering followed by an increase to near normal upstream river levels. Instead, the dissolved mercury content in this simulated settling experiment showed little change from upstream levels during the six-day settling study. The dissolved concentration in effluent water from a diked disposal area showed no increase over the mercury content of the river water upstream from the dredge.

In a later report, Windom[101] investigated changes in heavy metal concentrations as a result of dredging in the Mobile Bay ship channel. Dissolved mercury showed no clear increase in samples collected from around an operating dredge. A subsequent sampling network was set up around the discharge end of a disposal pipeline. Although the discharge may have had some influence on the concentration of other metals studied, there was little indication of any influence on the dissolved mercury level. In a simulated dispersion study in which the dissolved metal content of a water-sediment system was determined periodically after an initial dispersion, there was little change in the level of mercury relative to its initial concentration in the water.

In another study of mercury chemistry as influenced by dredging in Mobile Bay, Lindberg, Andren, and Harriss[197] concluded that mercury deposited into Mobile Bay is effectively removed by sediments. They reported the results of a study in which pH, redox potential, dissolved mercury, salinity, and dissolved organic carbon were measured in well-mixed sediment-surface water systems of marsh sediments near Mobile Bay as well as dredged material from the bay. Upon resuspension and continuous mixing, they observed an initial increase in dissolved mercury in both systems which corresponded to a drop in redox potential and a change in pH. However, a subsequent decline in mercury levels and the appearance of a second mercury concentration peak did not seem related to redox potential in either system. In the marsh sediment, dissolved mercury corresponded fairly well with fluctuations in dissolved organic carbon, but this was not the case for the dredged material suspensions. After the initial increase in mercury concentration upon suspension of the sediment, it was suggested that the subsequent decline in dissolved mercury levels might be attributed to the scavenging effect of iron and manganese oxides likely formed upon suspension of the sediments in an oxygenated water column. However, Windom[101] has presented evidence suggesting that hydrous ferric oxide may have little influence on the dissolved mercury concentration in Mobile Bay. Mercury levels did not follow the changes in iron concentration in Mobile Bay as did some other metals such as lead and cadmium.

Arsenic

Arsenic is a toxic metal in all of its chemical forms, and, in sufficient concentration, it will cause death or injury to humans, animals, and plants. The chronic clinical symptoms due to ingestion and inhalation have been described by Dinman,[198] and, unlike symptoms of acute arsenic intoxication, early manifestations include subjective complaints and such nonspecific symptoms as weakness, malaise, abdominal complaints, and pains involving the extremities. The most common ailments of those occupationally exposed to arsenic are dermatitis, perforation of the nasal septum, and even ulceration of the skin. Penrose and Woolson[199] reported that chronic arsenic poisoning from high levels in drinking water has been observed in Taiwan, Ontario, Minnesota, Chile, and elsewhere. However, in their review of the occurrence of arsenic in the environment, no instances of poisoning by arsenic accumulated naturally by food organisms were discovered.

Arsenic and cancer, especially skin cancer, have been associated for over 100 years, but the objective validity of the association has not been established.[199,200] The belief that arsenic can cause human cancers is supported by epidemiological data showing correlations between incidences of cancer and high levels of arsenic in water supplies and by industrial studies of occupational exposure to arsenic.[201,202] Tseng et al.[203] established a strong geographical correlation between arsenic levels in water in the "black-foot disease" area of Taiwan and the skin cancer rate. They also established a statistically indisputable association between skin cancer and hyperpigmentation, hyperkeratosis, and the black-foot syndrome. However, attempts to induce cancer in animals under controlled conditions have been unsuccessful.[204,205] Although the relationship between arsenic and cancer remains unclear,[199,200,206] the potential carcinogenicity of arsenic is perhaps the single most important aspect of concern with arsenic in the environment.

Occurrence and Sources of Arsenic in the Environment

Though present in small quantities, arsenic is considered to be ubiquitous in the upper lithosphere. Concentration in rocks ranges from 1.5 to 10 μg/kg.[200] It is frequently found in combination with sulfur, selenium, telurium, and as sulfosalts and arsenides of various heavy metals such as copper, iron, nickel, and cobalt. Arsenopyrite (FeAsS) is the most abundant and widespread mineral of arsenic found in nature.

Arsenic for commercial use is recovered as a by-product from the treatment of sulfidic lead and copper ores. It is mainly used in herbicides and insecticides. Other uses of arsenic include the manufacture of alloys, semiconductors, pigments, medicine, and chemical warfare agents, such as the nerve gas lewisite.

The natural weathering of arsenic-containing rocks is the main source of the trace amounts of arsenic commonly found in unpolluted waters. The major sources of arsenic pollution related to civilization include industrial wastes, increased land erosion, mining processes, burning of coal, and the use of arsenic-based insecticides and herbicides.

Concentrations of arsenic in seawater range from 2.0 to 6.0 μg/l.[34] Arsenite is the main inorganic form of the arsenic present in seawater.[199] Arsenic levels in freshwater vary depending on the source of contamination and geological processes. Levels ranging from 1 to 10 μg/l are generally found in the uncontaminated waters. However, levels of 0.4 to 10,000 μg/l arsenic have been reported in the literature.[199] The U.S. Public Health Service recommends a maximum of 10 μg arsenic/l in the drinking water and states that values exceeding 50 μg/l would indicate water unfit to drink.

Sediments from Lake Michigan analyzed for arsenic contained levels from 2 to 43 μg/g, with most containing between 4 and 9 μg/g.[207] Portmann and Riley[208] found 6.6 μg/g in a red clay sediment from a sampling site in the western Atlantic. Levels as high as 290 to 980 μg/g have also been reported in the sea bottom near a smelter.[199] Although significant amounts of arsenic have been found in sediments, very little is known of the significance of sediment-bound arsenic to the arsenic cycling in the environmental cycling of this element.

Arsenic Chemistry of Soils and Sediments

Arsenic exists in three oxidation states: metallic (As^0); trivalent (As^{3+}); and pentavalent (As^{5+}). The reduced state of arsenic (As^{3+}) is considerably more soluble than the oxidized state (As^{5+}).[209] Reed and Sturgis,[210] working with rice soils, provided conclusive evidence that reduced arsenic compounds were specially toxic to plants. They were unable to account for all of the arsenic lost in their field experiments and suggested that some may have been reduced to As^{3-} and lost as arsine (AsH_3).

Keaton and Kardos[211] demonstrated that the arsenate ($AsO_3{}^{3-}$) form of arsenic was fixed to a much greater extent than the arsenite (AsO_2^-) form and proposed that the "arsenic fixing power" of the soil was influenced by its state of oxidation. They found that additions of iron oxides to soils with high arsenic concentrations increased the redox potential of the soil. This resulted in a greater arsenate/arsenite ratio and subsequently an increase in the fixation of arsenic by the soil.

The studies cited above indicate that arsenic solubility in the soil solution is increased under reduced conditions, which implies that arsenic will be more available for micro-organisms and higher plants in a reduced aquatic environment. The effects of redox potential on the solubility of native and added arsenic in soils has been recently investigated by Deuel and Swoboda.[209] They showed that a reduced environment resulted in a greater water-soluble arsenic content. They also found that under reduced conditions, water-soluble arsenic was highly correlated to the total aluminum content in the soil. This study indicated that more arsenic was converted to soluble form when the samples were equilibrated at 38°C as compared to those equilibrated at 25°C, and this difference was attributed to the more reduced condition at 38°C. These researchers proposed that the increase in the soluble arsenic at lower redox potentials was due to the reduction of iron and not the reduction of arsenic itself. This conclusion was based on the observation that the amount of water-soluble arsenic became constant at about 3 percent of total arsenic in the equilibrated soil samples when all the ferric iron that was reacting with arsenate was reduced to the ferrous form and the arsenic was solubilized in the equilibrium with the reduced system. Had the arsenic been reduced, the total arsenic/soluble arsenic ratio would have decreased much more rapidly as the redox potential decreased, since arsenite is very soluble in comparison to arsenate. However, it should be pointed out that the lowest reduction potential obtained under the condition of the experiment was +25 mv, which represents only moderately reduced soil.

In addition to the redox potential, clay fraction and sesquioxides play a governing role in the sorption and desorption of arsenic in soils. Arsenic toxicity to plants decreases as the clay and iron oxide contents of soils increase,[212] presumably due to the lower levels of arsenic maintained in the soil solution. Several investigators have shown that soils high in reactive iron components, either native or added, sorb larger amounts of arsenic than soils of a similar texture low in iron.[211,213]

Jacobs et al.[214] conducted a series of laboratory experiments to study the possible mechanisms of arsenic sorption in soils. They reported that the amount of arsenic sorbed from solution increased as the free ferric oxide content of the soils increased. The preferential sorption of added arsenic by amorphous iron and aluminum components was evidenced by the quantitative removal of added arsenic from equilibrated soils by a single oxalate extraction, and the essentially complete recovery of added arsenic by ammonium fluoride (NH_4F) and sodium hydroxide (NaOH) reagents during chemical fractionation. Removal of amorphous iron and aluminum components by treatment with oxalate[215] eliminated or appreciably reduced the arsenic sorption capacity of the soil, which indicated that these components provide the sites for arsenic sorption, and thus should control the amount of arsenic that is readily soluble and available to plants.

The role of clay fraction in arsenic sorption has been investigated by several workers. For example, Johnson and Hiltbold[216] analyzed the arsenic content of the sand, silt, and clay fractions in soils and found that about 90 percent of the total arsenic content of the soil occurred in the clay fraction. They concluded from this that the clay fraction is the reservoir for arsenic accumulation and release. Similar results have been reported by Deuel and Swoboda[209] who recovered only 5 to 10 percent of the added arsenic in the water solution fraction in the Houston black clay. Inactivation of arsenic in soil as a function of clay content has also been shown by Crafts and Rosenfels.[217]

Because the size and molecular configuration of arsenate parallels closely that of phosphate, it has usually been assumed that the same mechanisms are involved in the sorption of arsenic and phosphorus by soils.[218] Rubins and Dean[219] showed that arsenate and phosphate could be alternately adsorbed and mutually replaced on soil colloids. Hingston et al.[218] obtained similar adsorption maxima for the sorption of arsenic and phosphorus on goethite. Other studies, however, have shown that phosphorus will displace arsenic much more readily than arsenic will displace phosphorus.[220,221]

Johnson and Hiltbold[216] extracted soil samples containing disodium methanearsonate (DSMA) with nine successive extracting solutions to determine the possible similarity of arsenic to soil phosphorus with regard to its distribution among various forms. The results indicate a considerable difference between arsenic and its distribution among chemical and mineralogical forms in the soil. Arsenic was much more extractable by mild salt solutions, suggesting a greater water solubility and a lower extent of adsorption, precipitation, or occlusion. While most of the soil phosphorus was associated with iron, either as precipitated iron phosphate or occluded with iron oxides, much of the arsenic not readily removed was associated with aluminum. These studies also showed that little, if any, of soil arsenic was in an organic form, while approximately 68 percent of the phosphorus in the surface soil appeared in organic combinations.

Although organic arsenic may constitute a small portion of total arsenic present in the soil, the amount of organic arsenic in sediments could be of significant proportions. Ruch et al.[207] observed a positive correlation between arsenic and organic carbon in the Lake Michigan sediments. Penrose and Woolson[199] suggested that arsenic present in sediments may have been derived from dead organic matter that had accumulated arsenic during life, or the complexing properties of the decomposing organic matter may have simply resulted in the nonbiological accumulation of arsenic from the water. No data were presented to support these hypotheses. Penrose and Woolson[199] reviewed the existing literature on the significance of arsenic in the aquatic environment and concluded that whereas high levels of arsenic in commercial marine species are a widespread phenomenon, very little is known about the arsenic cycle in the marine environment.

Based on the literature available, it may be summarized that the transformation of arsenic in the sediment-water system may be a function of redox potential and the composition of the sediments, which include mineral colloids, compounds of iron and aluminum, and the organic matter contents of the sediments. More work is needed to ascertain these assumptions.

Selenium

Selenium (Se) has been historically recognized as a toxicant associated with "alkali disease" and "blind staggers" in animals.[222] In both of these diseases, selenium toxicity results in myocardial necrosis, cerebral edema, and liver and kidney damage. Langer and Mackler[223] related selenium dust to severe irritation of nose and eyes, gastrointestinal disorders, and dental caries in men working in ore processing plants. The investigations have also been conducted on the carcinogenic and teratogenic effects of dietary selenium levels in animals, but the results are controversial. The incidence of these diseases and their possible relationship with selenium have been recently reviewed by Oldfield et al.[222]

In addition to being a toxicant, selenium has also been identified as an essential trace metal in animals. The critical level for dietary selenium below which deficiency symptoms are observed is reported to be 0.02 μg/g for ruminants and from 0.03 to 0.05 μg/g for poultry.[224] Minimum levels of 0.01 and 0.05 mg/l selenium in drinking water have been recommended by the U.S. Public Health Service and World Health Organization, respectively, to abate deficiency problems in human beings.[225] The subject of selenium deficiency in animals and human beings has been extensively reviewed by several workers.[83,222,224]

Sources and Occurrence of Selenium in the Environment

Selenium is most frequently found as an accessory metal in base metal ores of lead, copper, and nickel, and it occurs with native sulfur. Its abundance in the earth's crust is estimated to be 0.05 μg/g, and the selenium content in igneous rocks ranges from 0.004 to 1.5 μg/g.[226] The concentration of selenium in seawater is reported to be 3.0 μg/l.[34] The commercial source of selenium originates in the anodic slime from electrolytic copper refining.

Environmental pollution by selenium comes from burning of fossil fuel and trash, mining, and also as a contaminant in the air with sulfur dioxide (SO_2). However, Oldfield et al.[222] have indicated that airborne selenium may not be a major factor in environmental contamination by this element.

Selenium concentration in the river water in the United States is normally less than 0.5 μg/l.[222] Certain alkaline streams draining seleniferous lands in the western United States may, however, contain as much as 0.5 mg/l selenium.[227] Selenium content of sediments from 11 Wisconsin lakes and one South Dakota reservoir are reported to range from 1.3 to 3.5 μg selenium/g dry weight.[228] Wiersma and Lee[228] compared the selenium contents of lake sediments with the content reported in soils from different areas of the United States[229] and indicated that sediments contained considerably higher concentrations of selenium. This may imply that sediments serve as reservoirs for selenium. However, these workers found that most of the sediments from lakes in northern Wisconsin, a sparingly populated area with little industrial activity, contained high levels of selenium as did the sediments from the three Dane County lakes, an area of much higher population density and industrial activity. Based on their results, these investigators concluded that there were no signs of selenium buildup in sediments of these lakes as a result of environmental contamination. No attempt was made in this study to ascertain the mechanism whereby selenium cycles through the aquatic ecosystem.

Selenium Chemistry of Soils and Sediments

Most of the selenium added to soils is generally unavailable to plants.[83] Allaway[83] indicated that in some low-selenium soils, over 90 percent of the added selenium remained in the soil after three years of continuous cropping and plant removal. The low solubility of selenium in soils has been attributed to its presence as selenite in combination with ferric iron.[229,230]

The studies of Cary et al.[229] indicated that selenite is a major form of residual selenium in selenium-treated acid and neutral soils. Some form of hydrous iron oxide was suggested as the adsorbing solid phase. The other immobilization products of added selenium consisted of elemental selenium or selenide. They suggested that organic selenium compounds could also account for some residual selenium.

Geering et al.[230] constructed solubility diagrams to study the nature of iron complexes involved in the retention of soil selenium. Based on the plots of calculated ion activity values, these workers indicated that the selenium concentration in the soil solution was governed primarily by a ferric-oxide-selenite-adsorption complex (selenium oxidation state +4). They ruled out the possibility that crystalline ferric selenites were involved in governing the observed selenium solubility in the soils under study. They also reported that selenium may exist in the oxidation states of +6, 0, and -2, under certain conditions.

The effect of pH on the availability of selenium to plants was also investigated by Geering et al.[230] They reported that in acid soils (pH 4.5 to 6.5), selenium is usually bound as a basic ferric selenite of extremely low solubility and is essentially unavailable to plants. In alkaline soils (pH 7.5 to 8.5), however, selenium may be oxidized to selenate ions and become water soluble.

Hingston et al.[231] studied the adsorption of selenite on goethite and found that the specific adsorption of selenium increased the pH of the suspension and the negative charge of the oxide surface. They proposed that the mechanism of adsorption involved the release of water molecules from the surface when the selenite ion is adsorbed.

These findings may suggest that the forms and concentration of selenium in the soil solution are governed by various physical-chemical factors expressed in terms of chemical ligands, pH, dissociation constants, solubility products, and oxidation-reduction states. However, the current knowledge of the transformations of selenium in the sediments is very obscure. Wiersma and Lee[228] conducted a preliminary survey of the selenium concentrations in various lake sediments and discussed the adsorption of selenium by lake sediments in the light of the results reported by Cary et al.[229] and Delfino et al.[232] They interpreted the high correlation of selenium with iron, manganese, and phosphorus in the lake sediments to be due to sorption characteristics of sediments rather than to interrelated chemical reactions such as the precipitation of selenium with ferric hydroxide. Further studies are required to determine the mobility of the chemical forms of selenium in the sediments and the quantity of sediment-bound selenium directly available to the aquatic and benthic organisms.

Copper

Copper in the Environment

Copper is an essential element, being active in many enzymes and hemocyanin.[92] The average concentration of copper in the earth's crust is about 70 µg/g.[234] Soils contain about 20 µg/g, and 16 to 71 µg/g have been reported in some lake sediments.[96] The normal concentration in plants is between 5 and 20 µg/g.[235] The copper concentration in plants associated with good growth falls within narrow limits as <4 µg/g may be a deficient level while >20 µg/g may be toxic. Wilber[236] gives a copper concentration of 2.3 mg/l in seawater as the tolerance limit for several species of marine fishes.

Chemistry of Copper

The chemistry of zinc and copper seems closely related, although in general, copper compounds are less soluble. The stable form in natural conditions is the cupric ion (Cu^{++}). The cuprous ion (Cu^{+}) is unstable at ordinary temperatures. The adsorbed form in soils is the cupric ion (Cu^{++}), and this ion and various complexes are found in soil solutions.

Copper sulfide is a relatively stable compound in reducing environments, but yields cupric ions and sulfate (SO_4^{2-}) when oxidized.[24]

The copper solubility in soils, as given by Lindsay,[233] can be expressed by the equation:

$$[Cu^{2+}] = 10^{3.2}(H^+)^2$$

or

$$pCu = 2pH - 3.2$$

This indicates that at pH 5, the concentration of Cu in a soil solution is approximately $10^{-6.8}$ $\underline{M}$ or 0.01 mg/l. This level is far below that maintained by the solubility of $Cu(OH)_2$, $CuCO_3$, and $Cu_3(PO_4)_2$.

The chemistry of copper is more complex than zinc chemistry because it is found in two valence states in nature. The cuprous ion (Cu^+) is generally more common in minerals formed at a considerable depth, while the cupric ion (Cu^{2+}) is more abundant in compounds formed near the surface; however, many exceptions exist.[24]

Cupric ions can persist in acid to slightly alkaline oxidizing conditions, thus making copper one of the more mobile elements in the environment, though adsorption on both organic and mineral colloidal material may reduce its mobility.

In systems that are not acid and oxidizing, copper is much less mobile. Copper sulfide (CuS) is known to be insoluble, and the concentration of cupric ions in equilibrium with solid copper sulfide at a neutral sediment pH is too small to be of any significance in the transport of copper.

The solubility of copper is increased by complex formations. Although mineral complexes such as $CuCl^+$, $CuCl_2^-$, or $Cu(CO_3)_2^{2-}$ may be formed, these contribute relatively little to soluble copper levels.

Organic complexes may play a more important role in the solubility of copper, and copper has been shown to form more stable complexes with fulvic acids than other metals.[17] The importance of organic material in controlling the solubility of copper in natural water systems is not really clear. Although copper has been shown to form stable complexes with organic matter, in a recent study Sanchez and Lee[237] found that in Lake Monona, Wisconsin, the soluble organic complexes play a very minor role in the chemistry of copper in the lake water. The concentrations found could be readily explained by either the basic carbonates in an aerated system or the sulfides in an anoxic system. This lake had received 1.5 million pounds of copper sulfate ($CuSO_4$) for algae control during the past 50 years.

Jenne[117] has proposed that the hydrous metal oxides of manganese and iron are the principle control mechanisms for copper in soils and freshwater sediments. The regulatory properties of these hydrous oxides have been discussed in other sections of this report.

Zinc

Zinc in the Environment

Zinc is an essential element to life and is required for the activity of many enzymes.[92] The average amount in the earth's crust is about 132 μg/g[234] and it averages 50 μg/g in soils. In sediments, the reported concentrations are variable and have been found to range from 12 to 195 μg/g.[96] Man's activity seems to be an important factor in the increase of zinc in the environment. Plants generally contain between 25 and 150 μg/g zinc.[235] Concentrations >400 μg/g are toxic. Toxicological effects of zinc to man are relatively unimportant because there is a wide range between the usual environmental levels of zinc and levels known to be toxic. However, high concentrations of zinc may be detrimental to fish and other aquatic life.[238]

Chemistry of Zinc

Zinc is known to be the most mobile of the heavy metals. The zinc compounds formed with the common anions of surface waters are soluble in neutral and acid solutions. In reducing environments, zinc sulfide (ZnS) is a relatively insoluble and stable compound which may oxidize in the presence of dissolved oxygen as shown below:

$$ZnS + 2O_2 + 2HCO_3^- \rightarrow ZnCO_3 + H_2CO_3 + SO_4^= \quad \text{(Reference 24).}$$

Zinc carbonate ($ZnCO_3$) is thought to be less stable than zinc sulfide, though still relatively insoluble.

The zinc solubility in soils, as given by Lindsay,[233] can be expressed by the equation:

$$[Zn^{++}] = 10^6 [H^+]^2$$

or

$$pZn = 2pH - 6$$

which indicates that at pH 5, the concentration of zinc in solution is approximately 10^{-4} M or 6.5 mg/l.

Zinc ions are dominant up to pH values of about 9 in simple aqueous systems. In basic solutions, zinc hydroxide ($Zn(OH)_2$) precipitates if the concentration of zinc is 10^{-4} M. Zinc hydroxide shows minimal solubility at pH 9.5 and dissolves at higher pH values as the zincate anion,[24] $Zn(OH)_4^{2-}$. The redox potential-pH stability diagram given by Hem[145] indicates that between pH 7 and 8, zinc carbonate ($ZnCO_3$) will be formed when the concentration of dissolved carbon dioxide (CO_2) is 10^{-3} moles/l. At low redox values, zinc sulfide is the most stable combination. Jenne[117] has proposed that precipitation by the hydrous metal oxides of manganese and iron is the principal control mechanism for zinc in soils and freshwater sediments. The occurrence of these oxides as coatings on clay and silt enhances their chemical activity in excess of their total concentration. The uptake and release of the metals is governed by local conditions, including the concentration of other heavy metals, pH, and the amount and type of organic and inorganic compounds formed in the system. According to Jenne,[117] the aqueous environmental chemistry of zinc, copper, nickel, and cobalt cannot be explained without taking into account the hydrous oxides of iron and manganese as dominant regulating factors, although organic matter, clays, carbonates, and precipitation as discrete hydroxides are also involved.

Manganese

Manganese in the Environment

Manganese is an essential element and activates a number of enzymes nonspecifically. Two manganese-specific enzymes are arginase and pyruvate carboxylase.[92] It is also thought to be essential in photosynthesis.[240]

The total manganese concentration in soils has been found to range from 20 to 6000 μg/g. In sediments, levels between 11 and 1260 μg/g have been reported.[241,242] Plants can take up considerable amounts of manganese, and concentrations between 20 and 500 μg/g in dry matter are typical.[235] Levels in excess of 500 μg/g are probably toxic to many plants.

Manganese toxicity to man has been well documented in the scientific literature.[243] Almost all cases of manganese-caused diseases may be related to airborne manganese from industrial sources, by iron and steel industries in particular. It was stated that as much as 4 percent of the fumes produced by an electric arc furnace consisted of manganese oxides.[244]

Chemistry of Manganese

Manganese is one of the transition elements and may exist in a number of oxidation states (1+, 2+, 3+, 4+, 5+, 6+, and 7+). In nature, only the 2+, 3+, and 4+ oxidation states are found. In aqueous systems, the 2+ and 4+ states are of greatest importance since trivalent manganese is subject to autooxidation-reduction as shown by the following equilibrium reaction:[25]

$$2Mn^{3+} + 2H_2O \rightleftarrows MnO_{2(s)} + Mn^{2+} + 4H^{+} \ (\log K = 9 \text{ at } 25°C)$$

The general chemistry and geochemistry of manganese are complex due to the fact that nonstoichiometric oxides with mixed valences may be found. More than 150 oxides ranging from $MnO_{1.2}$ to MnO_2 have been described.[239] Also, the marked tendency to form coprecipitates, particularly with iron, contributes to the complexities of manganese chemistry. One of the most stable forms of manganese is manganese dioxide (MnO_2), which is solubilized according to the following equation:

$$MnO_{2(s)} + 2H^+ \rightarrow Mn^{2+} + 1/2\ O_2 + H_2O$$

In soil solutions, divalent manganese (Mn^{2+}) is the predominant species and its theoretical concentration increases 100-fold for each unit decrease in pH.[233]

The soluble form of manganese is the divalent cation (Mn^{2+}). It is the predominant form in aqueous environments depleted of dissolved oxygen. It has been reported that most of the soluble manganese in soil solution may be present as an organic complex.[245] However, Olomu et al.[246] recently reported that manganese either not complexed or weakly complexed with organic material in reduced extracts from six Manitoba soils. Most of the divalent manganese compounds present in natural water systems are very soluble, even at pH values greater than 7.

Under oxidizing conditions, manganese cannot exist as simple ions and theoretical predictions of solubility based on thermodynamic data become extremely difficult, especially if other cations are present in the solution.

Lindsay[233] reported that the soluble manganese in soils exceeds the solubility of manganese dioxide (MnO_2) but is considerably less than the solubility of other manganese compounds such as $Mn(OH)_3$, $Mn(OH)_2$, $MnCO_3$, and $MnSiO_3$.

The complexation of manganese by soil fulvic acids is rather weak. According to Schnitzer and Hansen,[17] the stability constant (log K) of these complexes varies between 2.2 at pH 3 to 3.7 at pH 5 at a constant ionic strength of $\mu = 0.1$. Although there may be some similarity between soils and sediments, it is risky to assume the behavior of one particular element is the same in both systems. The low complex stability of manganese may be the reason for the lack of information in literature on the specific behavior of manganese in sediments.

The plant response to soil-applied manganese-EDTA seems to be poor. It has been shown that while manganese sulfate ($MnSO_4$) is effective in correcting manganese deficiency in plants, manganese-EDTA applications may reduce plant yields.[247] A reason for this may be due to the substitution of iron for manganese in the weakly stable chelate molecule and a subsequent increase in iron uptake.

Gotoh and Patrick[40] showed that exchangeable manganese in waterlogged soil increased with decreasing pH and redox potential. Organic complexes of manganese are less stable than for many other metals, and it has been demonstrated that divalent manganese is less strongly adsorbed on soil particles and fine-grained sediments than most other heavy metal ions.[248]

More important seems to be the role of manganese oxides on the adsorption of other elements. Morgan and Stumm[249] found that freshly precipitated manganese dioxide has a very significant sorption capacity for heavy metals. This sorption had a marked pH dependence in the neutral to slightly alkaline pH range with sorption increasing as pH increases. Aging of the precipitates likely reduces sorption capacity.

Murray et al.[250] reported that sorption of cations on manganese dioxide is pH-dependent only at low concentration of the cations. They proposed that in dilute solutions, the adsorption occurs as counter ions in the diffuse double layer while at higher concentrations, the sorption occurred within the mineral lattice. The sorption of cations is due to the presence of a pH, dependent change[251] above the zero point of charge. The manganese hydroxides are negatively charged and sorb cations. The zero point of charge is between pH 2 and 7 for manganese dioxide, depending on its structure and age. Below this point, the oxide acts as an anion exchanger. In neutral solutions, the surface charge is mixed with both positive and negative charges such that there is a limited capacity for adsorption of cations and anions.

Iron

Iron Geochemistry

Iron is the most abundant element in the earth. It is the fourth most abundant element in the earth's mineral crust and is a constituent of all mineral classes.[248] The iron content in rocks generally ranges from several tenths of 1 percent in sedimentary rocks to several percent in igneous rocks, averaging 5 percent in the earth's crust.[252]

Because of the numerous stable compounds formed with sulfur, oxygen, and silicon, it is a chemically active metal in most geochemical environments. It is an essential element in the biochemistry of both plant and animals. Due to its widespread distribution and its two common valence states, elemental and combined iron are useful indicators of the degree of oxidation of natural environments.[248]

In mineral soil and sediment material, iron is found in several forms ranging from relatively inert to chemically active. Iron may be associated with clay minerals as: (1) an essential constituent, (2) a minor constituent within a mineral crystal as a result of isomorphous substitution, or (3) as an oxide coating on the surface of a mineral particle.[253] Changes in redox potential and/or pH may affect the association of iron with clay minerals by dissolution of surface iron oxide coatings, by influencing ion exchange reactions, or perhaps by decomposition of the crystal lattice under extreme conditions.

Iron and Environmental Quality

Iron is not generally considered to have deleterious effects on environmental quality. The U. S. Public Health Service and Environmental Protection Agency consider 0.3 mg/l the maximum permissible level of iron in drinking water.[81,254] This standard was selected primarily for esthetic rather than health reasons. Other than in waters affected by the mining and processing of ore, iron has been implicated in only a few instances as having an adverse effect on water quality. Morton and Lee[255] found that the concentration of iron under some conditions may regulate the predominate type of algae growth if not the total algae biomass. In the laboratory study reported, total iron levels between 0.1 and 1.0 mg/l were thought to contribute to the preponderance of scum-forming, blue-green algae over a less objectionable algae type. In concentrations normally found in unpolluted as well as polluted waters, iron is not known to be toxic.

Although some waste discharges into waterways may contain considerable amounts of total iron, high levels of iron in wastewater do not generally present environmental problems. This is because of natural processes which keep the inorganic, soluble, biochemically active iron content of most surface waters low as well as the large levels of total iron already present in the environment from natural sources.

Iron in the Sediment-Water System

The iron content of seawater is around 10 μg/l.[100] In fresh oxygenated waters, the soluble iron content is somewhat greater. The soluble iron content of surface water in upper Mobile Bay ranges from around ten to a few hundred μg/l.[101,256] In a reducing environment, much more iron may be soluble as a result of the formation of ferrous iron. While oxygenated interstitial water of Lake Ontario sediments contained less than 100 μg dissolved iron/l, the iron levels increased to about 2000 μg/l in interstitial water of underlying reduced sediments.[62]

The total iron content of sediments is high as indicated by a few examples. The iron content of sediment samples from two Wisconsin lakes were determined to be 1.9 and 6.6 percent.[257] The total iron content of numerous sediment samples collected over a wide area of Mobile Bay generally ranged from about 1.5 to 4 percent.[101]

Surface soils typically contain about 2.5 percent iron and commonly range from 0.5 to 5.0 percent. Hallberg[60] reported relatively low levels ranging from 0.09 to 0.36 percent in sediment layers of a tidal marsh in Holland while levels from 2 to more than 10 percent were reported for sediments from the Pamlico Sound, an estuary in North Carolina.[61]

Though iron is not considered to be a toxicant in sediment-water systems, its chemistry is important because of its interaction with metals which are considered toxic. The following discussion will first consider some aspects of the chemistry of iron; then iron chemistry will be related to the regulatory role of iron in the sediment-water chemistry of heavy metals.

Iron Chemistry in the Sediment-Water System

Though the levels of total iron in soils and sediments just discussed include iron which is an essential constituent of clay minerals and is thus unreactive in sediment-water chemistry, there is generally much potentially reactive iron present in sediments.

In nature, reactive iron commonly exists in two oxidation states: ferrous (Fe^{2+}) and ferric (Fe^{3+}). Low pH and redox potential levels favor the ferrous (reduced) form of iron, while high pH and/or redox levels result in a stable chemical environment for ferric (oxidized) iron.[41,104] Ferric iron reacts to form highly insoluble oxides or hydroxides which precipitate from solution forming discrete colloidal particles or coatings on clay minerals. In a reducing environment, oxidized chemical combinations of ferric iron are unstable and may reduce to ferrous iron, which is the soluble form of this metal. This soluble ferrous iron may be mobilized in response to a concentration gradient in a reduced environment.

Gorham and Swaine[113] determined the distribution of several metals in an oxidate crust, oxidized surface sediment, reduced subsurface sediment, and glacial clay in two Canadian lakes. The four horizons listed are in order from top to bottom, and the redox potential of these horizons would generally be expected to decrease with depth. The oxidate crust contained the greatest concentration of total iron. The surface oxidized sediment layer contained only 40 percent as much iron as the oxidate crust, and the reducing subsurface layer only 30 percent as much. This distribution suggests that soluble, ferrous iron may diffuse upwards toward the surface due to a concentration gradient. The oxidate crust and surface oxidized layer likely act as a sink for the ferrous iron where it becomes oxidized, precipitates, and is effectively removed from solution. This corresponds with the data of Weiler,[62] who found that the soluble iron in interstitial waters of Lake Ontario increased with depth.

Working with a swamp soil in developing models of oxygen consumption, Howeler and Bouldin[258] found that ferric iron was present only near the sediment surface where the total iron content was also greatest. Ferrous iron, on the other hand, was found to increase with depth.

Lindström[259] discussed iron cycling in sediment-water systems and described how iron can accumulate at the sediment-water interface by diffusion and oxidation-reduction processes.

A simplified redox potential-pH diagram for iron in water (Figure 1, p. 25) shows the influence of pH and redox potential on the stability of ferrous and ferric iron.[24] The figure shows that the stability boundary between ferrous and ferric iron is generally in the middle of the redox potential-pH conditions found in nature. Also apparent from the figure is the interaction of redox potential and pH on the stability boundary between oxidized and reduced iron.

This illustrative figure for a relatively simple aqueous iron system indicates the solubility of ferrous iron is controlled primarily by carbonate and sulfide formation. For example, in the presence of considerable carbonate, as in an alkaline environment, soluble iron can increase only to a certain level before precipitating as ferrous carbonate ($FeCO_3$). In the presence of sulfide, ferrous carbonate formation is limited by the much lower solubility of ferrous sulfide (FeS). Berner[260] concluded from theoretical considerations as well as sulfide and redox potential measurements that the chemical environment of interstitial waters generally falls outside the stability field for ferrous carbonate. Thus, in flooded soil and sediment systems containing considerable organic material, it is likely that ferrous sulfide will be the predominant inorganic form of iron. This form of iron contributes to the black color of reduced sediments.[248] Sulfide is reported to form from sulfate (SO_4^{2-}) when the redox potential drops below -150 mv at pH 7.[159]

The sulfides of most divalent metals are very insoluble. In the presence of excess sulfide, most metallic toxins may be effectively immobilized and unavailable to aquatic organisms. However, the formation of ferrous sulfide may, in some instances, reduce the effectiveness of sulfide immobilization of toxic metals. If the ferrous iron concentration is sufficiently large to precipitate most of the sulfide, then other metal ions may be kept from forming sulfide precipitates.[43]

Gotoh and Patrick[41] studied the effects of redox potential and pH on the transformations of iron in a waterlogged soil. The effects of redox potential levels from -250 to +300 mv and pH levels from 5 to 8 on the distribution between the water-soluble, exchangeable, and reducible forms of iron were determined. These fractions represent chemically reactive or potentially reactive forms of iron.

Water-soluble and exchangeable iron levels increased as both redox potential and pH decreased. The concentration of water-soluble iron ranged from undetectable at the higher pH and redox potential values to over 3,600 μg/g at pH 5, and a redox potential of -250 mv. At a given pH, a decrease in redox potential was accompanied by an increase in soluble iron. Where iron was measurable, there was an increase in soluble iron at each stepwise decrease in redox potential at a given pH. This was also true where pH was lowered and a constant redox potential was maintained. Thus, it was demonstrated that changes in the soluble iron concentration occurred sequentially over most of the pH-redox potential range studied. Similar results were found for iron exchangeable with 1 N ammonium acetate. The iron levels ranged from undetectable at high redox potential and pH levels to over 1,000 μg/g at low redox and pH levels. Reducible iron was thought to consist of ferric hydroxides and oxides and was also influenced by redox potential and pH. In a well oxidized suspension, reducible iron was around 11,000 μg/g at all pH levels. As the redox potential was decreased, less iron was found in this fraction at pH 5 and 6, indicating that this form of iron became reduced and solubilized at low redox potential levels. At -250 mv, the reducible iron decreased from around 11,000 μg/g to 6,800 and 8,200 μg/g at pH 5 and 6, respectively.

These data indicate that as insoluble oxides and hydroxides of iron become reduced, they are transformed into the chemically reactive water-soluble and exchangeable fractions. Likewise, as a soil or sediment system becomes oxygenated, as during dredged material disposal in open water, the water-soluble and exchangeable fractions are precipitated as iron oxides and hydroxides. In this particular soil, almost one-fourth (≃4,000 μg/g) of the total iron was subject to transformations with the reducible fraction under the range of pH and redox potentials studied. This sizable fraction is important to the well-known scavenging effect of iron for trace metals in sediment-water systems.

Iron Organic Matter Interactions

Iron and organic carbon have been found to be correlated in sediment-water systems.[60,242] Both oxidized and reduced forms of iron may complex with organic matter. Krauskopf[248] suggested that iron-organic matter complexes may be responsible for the enhanced solubility of ferric iron in some oxygenated natural waters where the measured soluble iron concentration has been found to be several orders of magnitude greater than that predicted from solubility product calculations.

Theis and Singer[261] have demonstrated that considerable quantities of ferrous iron can be maintained in solution in aerobic aquatic systems due to the complexation of reduced iron by naturally occurring organic matter. The complex is sufficiently strong to completely prevent the oxidation of ferrous iron for several days under normal atmospheric oxygen levels. In addition, this metal-organo complex reduced the rate of oxidation of the complexed organic compounds. The stability constant for a ferrous iron-tannic acid complex was reported to be about $10,^4$ indicating the relative strength of these metal-organo complexes. The stability of reduced metal-organo complexes such as discussed in this report could be important to transformations affecting trace metal bioavailability during dredging and dredged material disposal.

Stevenson and Ardakani[114] presented some data of Schnitzer and Skinner showing that the stability constant for a ferrous iron and fulvic acid preparation was about 5.8, which is just under that of lead, but greater than that for nickel, manganese, cobalt, calcium, zinc, and magnesium at pH 5.0.

Iron as a Scavenging Agent for Trace Metals

It has long been established in sediment chemistry studies that there is a relationship between trace metals and oxides of iron and manganese.[103, 262,263] Sorption of heavy metals by these compounds is thought to be an important mechanism in regulating heavy metal concentration. It has been suggested that manganese crusts and subsequent nodules in marine sediments, which are known to accumulate trace metals, may start their development on primary iron accumulations.[264] Some laboratory data support this contention.[66] The literature on the scavenging effect of hydrous oxides frequently includes both iron and manganese since it is the oxidized form of each involved in trace metal adsorption and since the reduction chemistry of these active forms is somewhat similar in response to redox potential changes. The role of hydrous iron and manganese oxides in the transport and regulation of trace metal concentrations in the environment has been reviewed by Jenne[117] and Lee.[151]

In reduced flooded soils and sediments, iron and manganese subject to pH and redox potential transformations exist as soluble ions or compounds.[70] As such, they are not effective trace metal scavengers. However, as a reduced soil, sediment, or water becomes aerated, the reduced forms of both of these ions will oxidize within the range of redox potential normally encountered in going from a reduced to an oxidized environment. Ferric hydroxide ($Fe(OH)_3$) is considered to be a common form of oxidized iron, but ferric iron may also exist in several other structural forms such as ferric oxide hydroxide ($FeOOH$) or ferric oxide (Fe_2O_3).[259]

Ferric oxide may form colloids of its own which polymerize and may precipitate as discrete particles. It may also form a coating on other colloidal-sized or larger particles such as clay minerals.[248] As precipitated colloidal particles or surface coatings, these materials are characterized by high surface area and are effective in adsorbing ions such as heavy metals from solution.[25]

There seems to be relatively little detailed information in the literature on the mechanism by which ferric oxides adsorb ions. Surface adsorption processes have been proposed and discussed based on the general chemical nature of ferric oxides. Surface charge of the coatings is likely important in adsorption reactions. In an acid environment, positive charges would tend to predominate on ferric oxides and would favor the adsorption of anions. As pH is increased above 4.8 to 6, colloidal ferric oxide particles tend to be negatively charged, favoring the adsorption of cations,[248] though both cations and anions show a strong tendency to interact with hydrous oxides over a considerable pH range.

Stumm and Morgan[25] describe the sorption of metal ions to iron and manganese oxides as ion exchange or surface complex formation reactions since hydrogen ions (H^+) or other cations are released during heavy metal adsorption. Heavy metals are thought to attach to specific sites at the surface while other cations such as sodium or potassium (Group I and II cations) are thought to adsorb in the diffuse region of the electric double layer near the surface.[250] An example of complex formation with zinc using -Me-OH to represent the surface active group of a hydrous metal oxide was given as follows:

$$\text{-Me-OH} + Zn^{2+} \rightarrow \text{-Me-O-}Zn^{1+} + H^+$$

A more detailed discussion of these sorption mechanisms can be found in Stumm and Morgan.[25]

Although there are data on the stability constants for the complexes formed by some metals with organic matter fractions and certain specific organic compounds, there are no such stability constant data for metals bound to hydrous oxides.[117]

In considering the relative importance of heavy metal complexation by hydrous oxides of iron and manganese vs. organic matter, Jenne[117] concluded from a survey of the literature that hydrous oxides may be the dominant control mechanism for heavy metals in environments where these oxides are found. It was suggested that complexation with organic matter may be the primary control mechanism only in environments where hydrous oxides of iron and manganese are not stable, such as in reduced sediments. Organic matter was thought to contribute indirectly to heavy metal scavenging by hydrous oxides. Periodic reducing conditions which would develop in soils of high organic matter content upon intermittent flooding would result in the dissolution of the hydrous oxides. Subsequent oxidation of the soil would result in the reformation of the hydrous oxides. It was suggested that this cycle favors the maintenance of the iron and manganese oxides in a state of high surface area, which is critical to maximizing its adsorption properties.

Lee[151] summarized several reports regarding the effect of hydrous metal oxides age on their heavy metal scavenging properties. It was concluded that the sorption capacity was dependent on age of the hydrous oxides in many instances and that the greatest interaction with heavy metals might occur if heavy metals were present at the time the hydrous metal oxide was formed. Structural changes that occur with time which improve the crystallinity of the hydrous oxide precipitates were thought to be responsible for the aging effect. Mackenzie and Meldau[265] have shown that aging of iron oxide gels results in the clumping together of primary particles into larger particles, which, in effect, results in a decrease in surface area with time.

Several examples were given by Lee[151] in which the higher sorption of freshly precipitated hydrous metal oxides could be significant in natural water systems. If this effect is real, then it could also be of considerable importance in a dredging situation during which there is mixing of reduced sediments with an oxygenated water column. Hydrous metal oxides formed at this time could be important in regulating the concentration of trace metals mobilized during dredging and disposal. In most sediments, iron and manganese subject to redox potential-and pH-induced transformations would be present in a reduced state. Upon dredging and dredged material disposal, these ions would rapidly oxidize as they were mixed with and dispersed in oxygenated water. Windom[32] suggested that oxidation of ferrous iron during dredging is almost immediate. Thus, it would be expected that the freshly formed hydrous oxides of iron and manganese produced during dredging and disposal would be most effective in complexing with heavy metals and removing these ions from solution. The solid complexes formed with potentially toxic metals will tend to settle out of suspension. Once the metals are returned to the sediment, they may be held tightly by the hydrous oxides as long as they are stable. In an aerobic sediment or water system, the metal bonding may be considered almost irreversible. However, if the hydrous metal oxide becomes buried by other sediment material, it will dissolve as the buried horizon becomes reduced. Thus, the adsorbed metals will be released and may become mobile unless subjected to some other regulatory mechanism, such as complexation with insoluble organic matter or sulfide precipitation.

Sanchez and Lee,[237] working with copper in Lake Monona, Wisconsin, found that as hydrous metal oxides became reduced, sulfide precipitation immobilized the copper. This process might occur in most sediment material subject to cycles of oxidation and reduction.

There is some danger in making generalizations about sulfide precipitation of heavy metals becoming an effective sink as hydrous oxides are reduced. Patrick and DeLaune[70] have shown that oxidized forms of iron and manganese become unstable at considerably greater redox potentials than is required for sulfide formation. Thus in some sediments in which only mildly reducing environments are attained, or in oxidized sediment material that becomes reduced very slowly, redox potential levels could be intermediate between the critical potentials for hydrous oxide reduction and sulfide formation. In such an environment, organic matter complexation would likely be the primary mechanism regulating heavy metal concentration.

In a study of the effects of dredging and disposal on the solubility of trace metals in an estuarine area, Windom[32] reported sorption on ferric hydroxide was an important scavenging mechanism for several trace metals. The water-soluble levels of metals at the outlet of a dredge discharge pipe were less than the concentration upstream in the river or at a weir outlet from a diked disposal area. It was postulated that reduced iron within the sediments oxidized immediately to iron hydroxide when the sediment was suspended. This freshly formed material then removed the metals from solution such that the trace metals accumulated with the precipitated iron in the impounded sediments. In a subsequent lab study, it was shown that the iron hydroxide decomposed as the sediments again became reduced, releasing some metals to the overlying water column. It was believed that the iron precipitated with sulfide during reduction. This cycle of an initial lowering of water-soluble metals followed by an increase in concentration to levels normally found in the river occurred within a one-week period. Since most heavy metals form sulfides of lower solubility than ferrous sulfide, the release of some metals upon sediment reduction suggests that a time lag occurs between the reduction of hydrated ferric oxides and the production of sulfides by sulfate reduction. Such a time lag may have been involved in the release of metals from the sediment.

Another possibility previously mentioned is that where ferrous iron is present in large quantities, it may tend to tie up the sulfide to an extent that insufficient sulfide is available for precipitating with heavy metals.[43]

In a later study of the effects of dredging on the heavy metal content of water in Mobile Bay, Windom[101] suggested that iron precipitation played a role in decreasing the concentration of cadmium, copper, lead, and zinc, though levels of mercury did not seem to respond to the changes in iron concentration.

In a laboratory dredging study of Mobile Bay sediment samples, Lindberg et al.[197] reported that mercury levels in water initially increased. However, in this study, it was suggested that freshly formed colloidal hydrous oxides of iron may have played a role in the observed reduction of soluble mercury levels that occurred within a few hours of its release.

Nitrogen

Nitrogen in the Environment

Nitrogen is a common element in the earth's lithosphere, atmosphere, hydrosphere, and biosphere. Nitrogen-containing organic compounds are involved with the biochemistry of all living organisms. Of the earth's total nitrogen, 98 percent is in the lithosphere, and nitrogen in the atmosphere accounts for most of the remainder.[266] Thus, most of the earth's nitrogen is tied up as stable compounds in the lithosphere and is not readily available for interaction with the biosphere. The most significant biological exchange between these spheres is the cycling of nitrogen between the atmosphere and biosphere. Both inorganic and organic nitrogen are important to living organisms. Atmospheric nitrogen gas (N_2) is not biologically active, but does serve as a reservoir and a source for certain organisms which may fix or transform atmospheric nitrogen into mineral forms that can be assimilated by other living organisms. This process is termed nitrogen fixation. Hutchinson[267] states that few, if any, eucaryotic organisms are capable of biological nitrogen fixation. However, a large number of procaryotic organisms may reduce atmospheric nitrogen, either symbiotically (as with legumes) or independently. Hutchinson[267] also points out that chemical fixation by man is now approaching the rate of natural fixation.

Biologically active forms of nitrogen can be catagorized as: (1) organically combined nitrogen in living organisms and in organic detritus and (2) inorganic nitrogen compounds which are derived primarily from the biological degradation of organic matter. This mineralized inorganic nitrogen may again be assimilated by organisms either directly, or after some readily occurring biological transformations. The amount of inorganic nitrogen in this last category and the rate of transformation between the inorganic and organic bound fractions is significant in terms of water quality.

There are two primary causes for concern over excess nitrogen in the environment. Nitrogen in the nitrate form in food and drinking water may, under certain conditions, cause health problems for animals[268] and humans, particularly for infants.[269,270] The U. S. Public Health Service has established a somewhat arbitrary level of 10 mg/1 of nitrate-nitrogen in water as the maximum concentration safe for human consumption.[81] In addition to possible health problems, inorganic nitrogen may contribute to eutrophication as many interacting nutrient and environmental factors are involved in determining both the total biomass production and the predominate algae species present in the water.[267,271] Much of the available evidence indicates that phosphorus is frequently the single most limiting element for algae growth in surface waters, especially for freshwater lakes. Hutchinson[267] concluded this in a general review of eutrophication, and many experiments have shown phosphorus to apparently be the most limiting nutrient in freshwater lakes.[272,273] However, nitrogen has been shown to be the controlling factor for algae growth in some freshwater lakes,[274,275] and recent evidence indicates that nitrogen may be the limiting growth factor in many coastal waters.[276,277,278]

Although natural processes result in nitrogen as well as other nutrients entering surface waters, man is implicated when the trophic status of surface waters begins to change rapidly. Cultural activities may influence the amount of bioavailable nitrogen in lakes in two ways. Available nitrogen levels may be increased because of increased nitrogen entering a water body or as a result of changes in the sediment-water system which increase the availability of nitrogen to aquatic organisms. Examples of increasing nitrogen levels include industrial, municipal, and agricultural discharges of nitrogen-containing waste into waterways as well as increased nutrient load in surface runoff from agricultural and nonagricultural land. Nitrogen availability may be increased either by transport processes which move the nutrient to the habitat of the consuming organism or by chemical transformations which increase its bioavailability. Resuspension of sediments containing inorganic and organic nitrogen compounds from a reducing environment to an oxygenated water column, as would occur during dredging and dredged material disposal, may be important to the overall nitrogen budget of some surface waters.

Nitrogen Chemistry of Flooded Soils and Sediments

Most sediment nitrogen is in the organic form. Thus, total nitrogen tends to correlate with the total organic carbon content of sediments. However, the carbon : nitrogen ratio in sediments depends somewhat on the sources of the organic material incorporated into sediments. Decayed plant material generally has a carbon : nitrogen ratio of about 10.1, and a ratio near this may generally be expected when plant residues constitute much of the organic material entering the sediment. Finger and Wastler[279] studied the use of the organic nitrogen content and the carbon : nitrogen ratio to characterize the source of sediment organic material with regard to industrial and domestic waste discharges in the Charleston Harbor estuary. The organic nitrogen content from unpolluted sites above the waste discharge points and in the outer harbor were 0.0027 and 0.050 percent, respectively. The organic nitrogen in benthic deposits near points of industrial and domestic waste discharges ranged from 0.124 to 0.237 percent. Thus, the non-uniformity of organic nitrogen levels within one estuary indicates that sampling site selection is important in evaluating the consequence of altering the nitrogen cycle within a waterway. Lake sediment nitrogen contents ranging from a small fraction of a percent to several percent have been reported in the literature,[257,280,281] and these levels may decrease with sediment depth.[282,283] That the total sediment nitrogen content is far greater than the aquatic nitrogen levels in even the most eutrophic waters indicates the significance of sediment nitrogen as a potential source and/or sink for nitrogen in the overlying water column.

A considerable amount of information has accumulated over the years on the forms and cycles of nitrogen in soils.[284,285] In many respects, this information is applicable to sediments. There have been several recent reviews of the sequence of nitrogen chemical transformations in sediments and flooded soils.[28,29,286]

Most of the nitrogen in sediments is present in organic combination, which is only slowly made available to the biotic community.[280] Though the process is slow, it may be important to water quality because of the large reservoir of nitrogen in the sediment. Biochemical processes can transform organic-bound nitrogen to inorganic nitrogen compounds which are readily available for plant or algae growth. Thus the nitrogen in sediments may be an important source of this nutrient for the biotic community in the overlying water column.

Mineralization is the term that refers to the transformation of organic nitrogen to an inorganic form. Ammonium-nitrogen (NH_4^+-N) is the first inorganic product of mineralization. The ammonium ion may be assimilated by organisms directly or may be further transformed to other bioavailable nitrogen forms. Although mineralization will occur in anaerobic as well as aerobic soils and sediments, the oxidation status of the sediment has an influence on the rate of mineralization. Several reports have been published indicating that alternate aerobic and anaerobic conditions tend to maximize nitrogen loss from soils.[287,288] Mineralization of nitrogen is the first step in this process.

In a 128-day soil incubation study in which the number of complete aerobic and anaerobic cycles was varied, Reddy and Patrick[289] found that nitrogen loss was greater as the cycling frequency between aerobic and anaerobic incubation periods increased. Even a single cycle of 64 days each of aerobic and anaerobic incubations resulted in a greater total nitrogen loss than did either continuous aerobic or anaerobic incubations. Continuous anaerobic treatments resulted in the smallest total nitrogen loss. Although dredging may subject a sediment to only one cycle of aerobic and anaerobic conditions, and the duration of the cycle would be on the order of hours or days instead of months, the results of Reddy and Patrick's study[289] suggest that a change in the sediment redox environment during dredging and dredged material disposal may induce more rapid nitrogen transformations.

Austin and Lee[257] measured the influence of aerobic and anaerobic conditions on nitrogen release in sediment suspensions from two Wisconsin lakes. In deep-water sediments from Lake Mendota, a 200-day aerobic incubation resulted in 44 percent of the total hydrolyzable nitrogen[290] being released as dissolved inorganic nitrogen. In contrast, the anaerobically incubated sediment from the same site released only about 6 percent of its initial hydrolyzable nitrogen. The aerobic nitrogen release from this sediment was shown to continue for the duration of the 200-day experiment, but anaerobic release after 20 days was negligible. While it was acknowledged that continuous sediment mixing in the laboratory may enhance nitrogen release over that occurring in a natural environment, this study does indicate the influence of the oxidation-reduction environment on sediment nitrogen mineralization. The results of this and other studies suggest that resuspension of anaerobic sediment in an oxygenated water column, as would occur during open-water dredged material disposal, could increase the inorganic nitrogen content of the overlying water column. This would especially be true if some sediment material remained in suspension for a considerable period of time or if upon resettling of a suspended sediment which became oxidized during disposal, a relatively thick oxidized sediment layer formed which persisted for some time before again becoming anaerobic.

Ammonium-nitrogen produced in sediment-water systems is subject to one of several possible fates. Due to its cationic nature, it may be adsorbed by ion exchange mechanisms to mineral or organic material in the sediment where it may be retained or subsequently released. Ammonium-nitrogen is also available as a nutrient for microbes and plants where it is again organically combined. In an anaerobic flooded soil or sediment, ammonium-nitrogen may accumulate in the interstitial waters to concentrations that exceed the capacity for retention by cation exchange mechanisms due to the low assimilatory demand. Thus, the soluble ammonium ion in the interstitial water may diffuse across the sediment-water interface into the overlying water.[291] If the soil or sediment environment becomes oxidized or if ammonium-nitrogen diffuses from a reduced sediment into the overlying oxygenated water column, ammonium-nitrogen will be readily oxidized by chemoautotrophic bacteria, first to nitrite and then to nitrate.[292]

The nitrate anion (NO_3^-) is not subject to retention by ion exchange processes and is relatively mobile. Nitrate will move readily with the mass flow of water, or it may be mobilized by diffusion in response to a concentration gradient. Nitrate-nitrogen is an available nutrient for most plants and algae and can therefore be removed from water by incorporation into plant or algae tissue. Should an oxidized soil or sediment containing nitrate become reducing or should nitrate diffuse into an anaerobic sediment environment, it may be utilized as the terminal electron acceptor in microbial respiration resulting in its reduction to nitrous oxide (N_2O) or nitrogen gas. This process is known as denitrification. The gaseous products of denitrification can escape a flooded soil or sediment-water system and move into the atmosphere.[285]

This brief description of the general transformations of nitrogen, though simplified and somewhat incomplete, gives an introduction to the possible fate of sediment-derived nitrogen and the processes affecting its availability to the biotic community. From the previous discussion, it is apparent that the bioavailability of nitrogen in a sediment-water system may be influenced by an interaction of transport processes and factors affecting chemical transformations. When considering one of these influences, one must keep in mind the contributing role of the others in determining the overall fate of nitrogen. Certain aspects of the nitrogen cycle in sediments are covered more fully in the following discussion.

The ammonium-nitrogen content of interstitial water within a reduced sediment may accumulate to high concentrations relative to that of the overlying, aerobic water.[293,294,295] Nissenbaum, Presley, and Kaplan[293] reported that ammonium-nitrogen reached concentrations of 250 mg/l in interstitial water in a reduced fjord in British Columbia, but could not be detected in the overlying water column. In one unusually well-oxidized core sample in which the redox potential ranged from +340 to +380 mv (an oxidizing environment for nitrogen), no ammonium could be found. These researchers suggested that sulfide controls the redox potential of interstitial water since they always found negative redox potential values in the presence of sulfide and positive values where sulfide was not present. Though sulfide may indeed have a strong influence on the redox potential where it is present in considerable quantities, it is probably inaccurate to suggest that sulfide controls the redox potential. It is more likely that each influences the other and that several factors which contribute to a strongly reducing environment, as indicated by a low redox potential, also contribute to an environment which favors the formation and stability of sulfides.

Graetz, Keeney, and Aspiras[294] also found that the ammonium content of interstitial water was greater than found in an oxygenated overlying water column in simulated sediment-water systems. They noted that ammonium-nitrogen which did accumulate in anoxic overlying water during periods of density stratification was almost completely nitrified upon aeration of the water column. The loss of ammonium-nitrogen and subsequent appearance of nitrate-nitrogen in the water column upon aeration corresponded to changes in redox potential.

The probable increase in mineralization rates and thus bioavailable nitrogen when reduced sediments are dispersed in an oxygenated water column has been previously discussed. However, the greater dissolved ammonium-nitrogen content of interstitial water when mixed with overlying water during dredging and disposal may represent a significant source of nutrient nitrogen which is rapidly released in the water column.

Dredging and disposal of dredged material are certainly not the only mechanisms by which ammonium-nitrogen formed within sediments may be mobilized and move into the overlying water column to subsequently become oxidized to nitrate. Diffusion of interstitial dissolved ammonium-nitrogen into the thin oxygenated surface sediment horizon or across the sediment-water interface is also an important source of ammonium- and nitrate-nitrogen in the water column.[56,282,294] Kemp and Mudrochova[282] found that the upward diffusion of ammonium due to a concentration gradient in the interstitial water was active to a depth of approximately 150 cm. They also reported that the ammonification and nitrification of organic nitrogen in the top 6 cm of the sediment resulted in about 20 percent of the nitrogen loading into Lake Ontario sediments being lost to the overlying water, either in a nutrient form or as molecular nitrogen (N_2) or nitrous oxide (N_2O) gas, which would escape into the atmosphere. Chen et al.[296] showed that ammonium exchange with the overlying water column was considerable in the top 4 cm of the sediment studied, but was negligible beneath the 8-cm depth. Graetz, Keeney, and Aspiras[294] extrapolated laboratory data to determine the relative significance of nitrogen mineralization and upward diffusion on the total nitrogen input into Lake Mendota. They estimated that this process contributed approximately 30 percent of the nitrogen entering the lake from external sources. From these literature reports, it would appear that a considerable amount of sediment-bound nitrogen is released into the overlying water column from undisturbed sediments. This contrasts with the relatively permanent retention of heavy metals in undisturbed sediments. Though dredging and dredged material disposal may increase nitrogen release from sediments, the additional mineral nitrogen release may be relatively small compared to the quantities released by natural processes in many sediment-water systems.

Although mineralization, ammonium diffusion to the sediment-water interface, and nitrification contribute considerable amounts of nitrogen in a nutrient form to the overlying water, the role of sediments as a nitrogen sink may be more significant in the overall sediment-water nitrogen balance. Nitrate, which diffuses beneath the sediment-water interface and the thin oxidized sediment layer into a reduced sediment horizon, is subject to denitrification. Denitrification refers to the biological reduction of nitrate- and nitrite-nitrogen to volatile gases which may escape into the atmosphere.[285] Nitrous oxide and molecular nitrogen are the usual products of denitrification. Patrick[51] and Bailey and Beauchamp[53] have shown that nitrate is reduced by denitrification when the redox potential drops below about 340 mv at pH 5 or below about 225 mv at a pH of around 7. Many soil or sediment factors influence denitrification. However, this process will generally occur in a sediment or flooded soil where an ample energy supply (available organic matter) is supporting a high level of microbial activity such that the rate of oxygen replenishment is inadequate to meet the oxygen demand for microbial respiration.

There are many literature reports indicating that nitrate is readily reduced within sediments.[296,297] Engler and Patrick[56] have shown that the active site of nitrate reduction is at the sediment-water interface or just beneath this interface in the underlying reduced sediment. They concluded that nitrate in the overlying water moved into the sediment as a result of a concentration gradient. Extrapolated laboratory data indicated that denitrification in the saltwater marsh from which the sample was derived could remove about 7.4 kg nitrate-nitrogen/ha per day from the overlying water. A freshwater swamp removed about half this amount by the downward diffusion and subsequent reduction of nitrate.

From the previous discussion of the transport mechanisms and chemistry of nitrogen in sediment-water systems, it is apparent that the levels of inorganic nitrogen in water are determined by many complex processes which are occurring simultaneously. Dredging and dredged material disposal do not necessarily change the processes naturally occurring in the nitrogen cycle of sediment-water systems. However, they may significantly affect the rate of some of these processes and the resulting balance between processes that act as sources and sinks for inorganic nitrogen, particularly in a localized area. The influence of locally altering the natural nitrogen cycle in a water body on the overall nitrogen balance of that water would be difficult to evaluate, and the conclusions drawn from one area may or may not apply to a different water course. However, due to the large amounts of sediment material moved during dredging and the greater nitrogen content of sediment material relative to the amounts implicated in health and eutrophication problems, it is apparent that changes in nitrogen availability induced by dredging and dredged material disposal could possibly have an adverse effect on water quality.

Ritchie and Speakman[298] determined the influence of settling time on the quality of dredged material supernatant in simulated upland dredged material disposal facilities. The concentration of nitrate was less than 1 mg/l in all samples. The large amount of Kjeldahl nitrogen in the supernatant was reduced to about 8 percent of its initial level after one hour of settling and to about 3 percent after 18 hours. Three percent of the initial Kjeldahl nitrogen represented about 14 mg nitrogen/l in the sample reported. From a figure presented in this paper, it appears that the additional decrease in total Kjeldahl nitrogen after 40 hours of settling was not substantial.

Total dissolved Kjeldahl nitrogen of dredged discharge supernatant was increased by a factor of about 9 relative to that of nearby surface water in a study in the Calcasieu River, Louisiana.[299] The total Kjeldahl nitrogen of the supernatant from an enclosed disposal area was about twice that of the surface water in that area. In these two studies, dredged material disposal apparently did increase the total nitrogen potentially available for transformation into a nutrient form.

Due to the many interacting factors influencing eutrophication, it is not possible to set a threshold value of inorganic nitrogen applicable to most surface waters above which water quality will significantly deteriorate. However, based on the literature available, the suspension of several mg/l of Kjeldahl nitrogen removed from a reducing environment to an oxygenated water column could potentially increase the rate of ammonium and subsequent nitrate formation to levels well above those found to contribute to excessive algae growth.

Phosphorus

Phosphorus is present in the earth's crust in concentrations ranging from 0.23 to 0.26 percent, expressed as P_2O_5, and is found in the biosphere almost exclusively in a fully oxidized state.[300] Phosphorus is most concentrated in igneous rocks. Mining is the primary source of increasing phosphorus quantities in soils and sediments. The concentration of phosphorus in seawater is very small, averaging 0.07 mg/l, and it mainly occurs as an inorganic orthophosphate ion, PO_4^{3-}.[301] The most abundant species in seawater listed in order of increasing magnitude are H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-}. Traces of polyphosphates have also been reported,[302] which are considered possible indicators of pollution.

Phosphorus plays a governing role in the life cycles of the inhabitants of the earth. It is present mainly as a structural component of the nucleic acids, DNA and RNA, and plays a fundamental role in the very large number of enzymatic reactions that depend on phosphorylation. Phosphorus is a constituent of the cell nucleus and is essential for cell division and the development of meristematic tissue. It is also critically involved in all energy transfer steps in the cell since phosphorus is a component of compounds such as ATP which control energy transformation.

Although phosphorus is essential for food production, the presence of excess levels of this element in surface water may contribute to the deterioration of water quality. Because the rate of mining exceeds the rate of transport to the sea, an ecological imbalance may result causing pronounced pollution of inland and coastal waters.[303]

Phosphorus in the elemental form is toxic and subject to bioaccumulation in much the same way as is mercury.[37] Colloidal elemental phosphorus will poison marine fish, causing skin tissue breakdown and discoloration. Also, phosphorus is capable of being concentrated and will accumulate in organs and tissues.[304] Concentration of phosphorus by marine fish from water containing as little as 1 μg/l has been reported.[37]

Role of Phosphorus in Eutrophication

Eutrophication is a natural process of lake aging that progresses regardless of man's activities. It may be defined simply as the process of nutrient enrichment. However, the problem of eutrophication has become one of the major concerns of water-quality management of our day. The rate of eutrophication of streams and lakes in the United States is often enhanced by nutrient discharges from urban, industrial, and agricultural activities. One of the most important results of excessive nutrient input into the nation's waters is the development of an undesirable biological population which is a nuisance to man and also serves as a physical impediment to the use of water resources.

The normal nitrogen concentrations of most lakes are generally sufficient to support the vigorous biological growth observed in eutrophic lakes, while small quantities of naturally available phosphorus are not.[305] Although the relative importance of nutrients required for phytoplankton growth is a subject of recent controversy,[277,306,307] the supply of phosphorus to streams and lakes and its availability to the biota may be a prime factor controlling the rate and extent of eutrophication.[46,308,272]

Lee[46] studied the role of phosphorus in lake eutrophication and concluded that phosphorus was a key element in causing the excessive fertilization of natural waters. This conclusion was justified from several points of view. First, phosphorus is one of the elements present in natural waters at concentrations which limit algae growth in many lakes. Secondly, phosphorus is one element that is often derived from sources related to man's activities and is thus amenable to control. The third reason for the importance of phosphorus control as a means of reducing excessive fertilization is that a significant input reduction may be achieved by removing phosphorus from domestic wastewaters. Schindler[272] suggested that in most lakes, reducing the phosphorus input could cause a proportional abatement in phytoplankton bloom. Syers et al.[309] also suggested that since phosphorus is often the limiting nutrient in lake waters, measures implemented to retard or reverse eutrophication through nutrient control are most likely to succeed with phosphorus than with other nutrients.

Phosphorus Levels in Surface Waters

The total phosphorus content in surface water may be divided into soluble phosphorus and suspended insoluble phosphorus. The soluble phosphorus is composed of soluble inorganic orthophosphate, hydrolyzable polyphosphates, and organic phosphorus. The suspended insoluble phosphorus includes insoluble inorganic phosphorus compounds, sorbed or fixed phosphorus, and phosphorus in micro-organisms. Phosphorus levels reported in the literature for surface waters generally are soluble inorganic orthophosphate, unless otherwise specified.

As mentioned in the previous section, the phosphorus content of surface waters is frequently the limiting factor for the growth of algae and aquatic plants. Hutchinson[300] states that most relatively uncontaminated lake districts have surface waters containing 0.01 to 0.03 mg/l phosphorus. Holt et al.[310] have collected data on phosphorus levels of several lakes and streams as reported by several investigators. The concentration of dissolved inorganic phosphorus ranges from 0.018 to 0.18 mg/l and that of total dissolved phosphorus from 0.02 to 1.4 mg/l. They suggested that if the figure of 0.01 mg/l soluble inorganic phosphorus is taken as the point above which algae can flourish, most of the surface waters surveyed had the potential for supporting undesirable growth.

Schelske and Roth[38] conducted a limnological survey of Lakes Michigan, Superior, Huron, and Erie and reported a range of 2.7 to 22 μg/l phosphate-phosphorus in these lakes. They found higher phosphorus concentrations in Lake Erie than in Lake Huron, indicating an output of pollutants downstream from Lake Huron.

Sources of Environmental Phosphorus Pollution

The quantity of phosphorus present in the surface waters and sediments of streams and lakes is dependent on the human and livestock population density, the methods and intensity of fertilization, the land management practice (e.g. forests, grassland, cropland), the pedological characteristics of the soil, and on the type of sewage and waste treatment involved. The sources of phosphorus which enter streams and lakes may be described as either point sources or diffuse sources. Point sources of phosphorus include effluent from municipal sewage treatment plants, combined sewer overflows, storm sewers, and industrial effluent outfalls. In general, point sources consist of relatively small volumes of flow containing relatively high concentrations of phosphorus.

Diffuse sources of phosphorus consist of numerous low-intensity, widely distributed sources. A major source of phosphorus of diffuse origin is a consequence of erosion, since the soil particles that become part of the sediment load of streams retain much of the phosphorus that was originally bound to them. Selective erosion of finer soil particles can even result in higher phosphorus contents within the sediment than in the parent soil.[308]

Thus, all land areas susceptible to erosion, such as cultivated fields, stream banks, and construction sites, represent potential diffuse sources of phosphorus. In addition to sediment-bound phosphorus, surface runoff water will also contain dissolved phosphorus. Drainage tile effluents, rural septic tanks, feed lots, and ground water are also considered diffuse sources of phosphorus. In contrast to point sources, diffuse sources of phosphorus generally yield large volumes of flow containing relatively low concentrations of phosphorus.

The sources of phosphorus in surface waters may also be divided into those coming from industrial, municipal, and agricultural endeavors. Pollution from industrial sources mainly depends on the type of output and the chemicals involved in the production. Municipal sources are mainly related to sewage and the phosphate loading from detergents. Agricultural sources include precipitation, animal waste, discharges, and land runoff of native soil and fertilizer phosphorus.

The control of phosphorus loading from various sources needs separate planning; some of the problems in decreasing the phosphorus load from these sources are discussed by Lee,[46] Baker and Kramer,[308] and Klausner et al.[311]

Phosphorus Chemistry of Sediments and Submerged Soils

The forms and amounts of phosphorus in lake and estuarine systems are a function of the phosphorus input from rural and urban sources, the phosphorus output from the lake through surface streams and ground water seepage, and the interchange of phosphorus among the various sediment and water phosphorus components. Interchange between the dissolved and solid phase (particulate) phosphorus components occurs both through chemical and biochemical reactions. The biological incorporation of dissolved inorganic phosphorus into insoluble organic phosphorus, and the subsequent settling of insoluble inorganic and organic phosphorus gradually remove phosphorus from the surface water.[309] The direction of net transport of phosphorus is thus from the overlying water to the sediments. Although sediments act as a sink for phosphorus, release to the overlying water of dissolved inorganic phosphorus can occur if the concentration of interstitial phosphorus exceeds that of the overlying water,[312] and/or if anaerobic conditions exist in the sediments.[313]

Stumm[303] contended that phosphorus is deposited mainly through: (1) adsorption of phosphorus on clays, (2) chemical precipitation of phosphorus compounds like apatite, (3) incorporation of dissolved inorganic phosphorus into the detrital phosphorus, and (4) diagenetic replacement of calcite by substitution of carbonate by phosphate. The dynamics of availability of sediment phosphorus to the overlying water depends on the phosphorus concentration of interstitial water, which in turn, depends on the redox intensity and the affinity of the solid sediment phases of phosphorus.[303] Phosphorus behavior may be conveniently subdivided into the following components to better understand phosphate chemistry of sediments and submerged soils:

- _a_. Distribution of phosphorus in sediments and submerged soils as determined by chemical fractionation.
- _b_. Sorption and desorption of inorganic phosphorus by sediments.
- _c_. Role of redox potential and pH in the exchange of phosphorus between water and sediments.
- _d_. Chemical precipitation of phosphate compounds in the sediments.
- _e_. Status of organic phosphorus in sediments.

Forms of Phosphorus in Sediments and Submerged Soils as Determined by Chemical Fractionation. The phosphorus content of most mineral soils is low, ranging between 0.2 and 0.4 percent phosphorus pentoxide.[58] As an important soil constituent, phosphorus is present in organic and inorganic forms of which the inorganic forms are more mobile under waterlogged conditions. According to Chang and Jackson,[314] inorganic phosphate in the soil can be divided into four main groups: calcium phosphate, aluminum phosphate, iron phosphate, and reductant-soluble phosphate extracted after the removal of the first three forms. Calcium phosphate exists mainly as apatite; but dicalcium, monocalcium, and octacalcium phosphate exist in small amounts as transitional forms. The reductant-soluble phosphate plus the insoluble phosphorus fraction, which includes occluded iron and aluminum phosphate fractions[315] described by Bauwin and Tyner[316] as nonextractable phosphorus, are not important in the fertility of well-drained soils, but are believed to be of economic importance in waterlogged soils.

The reducing conditions caused by waterlogging activate forms of phosphate that are normally insoluble in well-drained soils.[55] For example, ferric phosphate is reduced to more soluble ferrous forms. Using multiple regression analysis, Mahapatra and Patrick[317] showed that iron phosphate, calcium phosphate, and aluminum phosphate accounted for most of the phosphate extracted under waterlogged conditions, while water-soluble and loosely bound phosphate, aluminum phosphate, and calcium phosphate were the important factors in determining extractable phosphate in previously air-dried samples.

Several forms of phosphate which are coprecipitated with ferric oxide are also released as a result of reduction of ferric oxides in the soil. Using labelled $AlPO_4 \cdot 2H_2O$, $FePO_4 \cdot 2H_2O$, and NaH_2PO_4, Patrick et al.[318] have observed that most of the added phosphorus was present in the aluminum and iron phosphate fractions with little phosphate finding its way into the calcium phosphate or reductant-soluble iron phosphate fractions. Flooding the soil increased the movement of all three phosphorus sources to the iron phosphate fraction at the expense of aluminum phosphate fraction. The chemical transformation of aluminum phosphate to iron phosphate may be due to the lower solubility product of iron phosphate.[319]

In acid sediments, phosphorus is combined largely with iron and aluminum; and in neutral and alkaline sediments, calcium phosphate predominates.[319] Frink,[320] investigating the forms and amounts of phosphorus in the sediments of a eutrophic lake, found that phosphorus combined with aluminum and iron increased in amount with depth of overlying water, whereas calcium phosphate decreased with water depth. Aluminum and iron were associated with the finer soil particles and were thus transported as suspensions to the deeper parts of the lakes before settling. Calcium phosphate was associated with the coarse particles and was therefore deposited in the shallow water. Frink also found that there was an overall shift from aluminum phosphate to iron phosphate in the acid, waterlogged soils, but that in the neutral lake deposits, aluminum phosphate tended to convert to calcium phosphate. Frink thus concluded that not all the calcium phosphate found in the mud had been transported in as a part of the sand fraction, but that some of it was formed by chemical transformations within the mud.

Association of phosphorus with iron compounds in the sediments has been suggested by several workers.[309,313,321,322,323,324] This relationship will be further discussed later in the section.

The fractionation scheme of Chang and Jackson,[314,315] which was designed for soils, has been widely used to study the forms of inorganic phosphorus in sediments and submerged soils.[317,320,325,326,327] This scheme was based on the ability of certain reagents to solubilize inorganic phosphorus contained in synthetic phosphates and phosphate minerals such as variscite, strengite; and apatite. According to this scheme, the ammonium chloride (NH_4Cl) extraction, the first step in the procedure, removed dissolved inorganic phosphorus in the interstitial water and the phosphate ions weakly sorbed by soil components. The sequential extraction with ammonium fluoride (NH_4F) and sodium hydroxide (NaOH) reagents selectively removed aluminum phosphate (variscite) and iron phosphate (strengite), respectively. Calcium phosphate, reductant-soluble phosphate, and occluded aluminum phosphate were then sequentially extracted as outlined in the scheme.[314,315]

Recent researchers have indicated that problems can arise when the Chang and Jackson[314,315] scheme is used to characterize lake sediment. For example, Fife[328] and Williams et al.[322] have shown that ammonium fluoride is not selective for aluminum-bound phosphorus in a variety of materials. Bromfield[329] reported that 50 to 75 percent of the inorganic phosphorus of "phosphated iron oxides" was removed by extraction with 0.5 M ammonium fluoride. Because of the lack of a relationship between inorganic phosphorus and aluminum in ammonium fluoride extracts of a wide range of surficial, non-calcareous sediments taken from Wisconsin lakes, Williams et al.[322] concluded that ammonium fluoride-extractable inorganic phosphorus was largely iron-bound. The problem of resorption of inorganic phosphorus released from both the calcareous and non-calcareous sediments during the same extraction further complicated the interpretation of the data.[321,322]

Williams et al.[322] proposed a fractionation scheme for calcareous materials, excluding an ammonium fluoride extraction and employing single extractions with sodium hydroxide (NaOH), citrate-dithionite-bicarbonate (CDB), and hydrochloric acid reagents. They reported that the proportion of iron plus aluminum-bound inorganic phosphorus in calcareous sediments ranged from 54 to 75 percent of total inorganic phosphorus. This indicated that, contrary to the results obtained with a scheme using ammonium fluoride, calcareous sediments may contain appreciable amounts of inorganic phosphorus in noncalcium-bound forms.

The acid oxalate solution has also been widely used to characterize the phosphorus retention capacity of soils and sediments. Saunders[330] obtained a very close relationship between oxalate-extractable iron plus aluminum and phosphorus retention in a variety of New Zealand soils. He suggested that this reagent extracts only amorphous compounds of iron and aluminum and the attack on the crystalline oxides and the crystalline clay minerals is very small. According to Saunders,[330] the aluminum and iron extracted by oxalate solution were derived from a complex gel, a phospho-silico-hydroxy humate of iron and aluminum, the type envisaged by Mattson et al.[331] The gel complex is considered to be an isoelectric amorphous precipitate formed by the precipitation of ionic forms of aluminum and iron after they have been released by weathering from primary and secondary minerals.

Shulka et al.[324] reported a close relationship between the ability of surficial Wisconsin lake sediments to sorb added inorganic phosphorus and the amount of iron removed by oxalate extraction. This finding, in conjunction with the elimination of inorganic phosphorus sorption capacity when the sediments were treated with oxalate, indicates that the sediment components which are responsible for the sorption of added inorganic phosphorus are oxalate-extractable. McKeague and Day[215] have shown that the oxalate reagent extracts short-range-order oxides and hydroxides, whereas crystalline iron oxides and hydrous oxides and iron-containing primary silicates are little attacked.

Williams et al.[323] reported that the levels of inorganic phosphorus in 16 non-calcareous and 9 calcareous surficial sediments from 14 Wisconsin lakes were closely related to the amounts of short-range-order hydrated iron oxides extracted by acid ammonium oxalate or neutral CDB. They indicated that CDB iron was directly proportional to oxalate iron and suggested that both reagents attacked the same form or forms of iron in the sediment. Research conducted elsewhere (McKeague and Day[215]), however, has shown that CDB extraction dissolved a large proportion of the crystalline iron oxides in addition to the amorphous materials. Bascomb[332] compared the extractability of various solutions and reported that CDB extraction also dissolves crystalline oxides in addition to the amorphous hydrous oxides.

Wentz and Lee[333] developed a dilute hydrochloric-sulfuric acid (pH 1.1) extraction procedure for the removal of available phosphorus from lake sediments. According to the authors, this procedure allows the extraction of relatively loosely bound forms of phosphorus, which include sorbed phosphorus, apatite (and presumably calcium phosphate also), and certain organic forms. In a later study, Wentz and Lee[334] found that available phosphorus, which comprised one-half of the total phosphorus, was most likely associated with the carbonate portion of the sediment.

Upchurch et al.[335] studied the distribution of available phosphorus, using the procedure developed by Wentz and Lee,[333] in sediments from the Pamlico Estuary. They reported that a high correlation (r=0.99) existed between available phosphorus and oxalate-extractable iron in the Pamlico Estuary. The amounts of iron extracted by dilute hydrochloric-sulfuric acid solution and the oxalate procedure were similar, with the oxalate values generally 15 to 20 percent higher than the acid values. Based on these relationships, they suggested that phosphorus is held to suspended sediments by some type of iron-inorganic phosphorus complex of limited solubility.

Sorption and Desorption of Phosphorus in Sediments. The ability of sediments to sorb added inorganic phosphorus has been studied in recent years with the objective of understanding the role of sediments in the removal of dissolved phosphorus from, or the release of dissolved phosphorus to, interstitial waters. The term sorption used in this section includes both adsorption (retention at the surface of the retaining component) and absorption (penetration into the retaining component). It has been shown that inorganic phosphorus, added at concentrations considerably greater than those present in the interstitial waters of sediments, is retained by oxides and hydrous oxides of iron and aluminum and calcium carbonate by a sorption rather than a precipitation mechanism.[218,336,337] The sorption is influenced by pH, redox potential, and the concentration of ions such as HPO_4^{2-} and HCO_3^- in the system.[338] Another system for adsorption and desorption of phosphorus involves the clay minerals such as kaolinite and montmorillonite,[320,327,338,339,340,341] and this system is pH-dependent, as discussed by Golterman.[339]

The role of aluminum-containing components in the sorption of inorganic phosphorus by lake sediments has been little studied in inorganic phosphorus fractionation studies. Harter[326] concluded that aluminum components were involved in the sorption of inorganic phosphorus by sediments from Bentam Lake, Connecticut. However, Frink[320] reported that the removal of aluminum interlayers from expandable layer silicates in the lake environments may have resulted in the formation of short-range-order alumino-silicates capable of sorbing inorganic phosphorus. Shulka et al.[324] reported evidence which suggests that aluminum-containing components, other than the small amount of aluminum in an iron-rich gel complex, are of little significance in the sorption of inorganic phosphorus by surficial Wisconsin sediments.

The role of iron components, such as ferric hydroxide, ferric oxyhydroxide, ferrous compounds, and amorphous oxides and hydroxides of iron, in controlling the levels of dissolved inorganic phosphorus in soils and sediments has been studied by several workers.[309,313,321,322,323,324,342] Shulka et al.[324] and Williams et al.[323] postulated that a gel complex of the type proposed by Mattson et al.,[331] largely consisting of hydrated iron oxide along with smaller amounts of organic matter, aluminum, and associated $Si(OH)_4$ and inorganic phosphorus, was the major contributor to the sorption of inorganic phosphorus by non-calcareous and calcareous sediments from Wisconsin lakes under laboratory and field conditions. Patrick and Khalid[313] suggested that the conversion of ferric oxyhydroxide to the more soluble and highly dispersed ferrous forms, under reduced conditions, increases the activity and the surface area of the iron compounds reactive with phosphorus. Singer[342] concluded that stoichiometric additions of ferrous iron can achieve efficient removal of orthophosphate from wastewater as ferrous phosphate. Singer[342] also suggested that ferrous phosphate may be of significance in influencing phosphorus transport during seasonal transformations in limnological systems.

The concept of a sediment functioning as a phosphate buffer in regulating dissolved inorganic phosphorus has been recognized by many workers,[313,326,343,344,345,346,347] with the ratio of relative phosphorus sorbed onto the solid phase vs. that in solution determining whether inorganic phosphorus is sorbed or desorbed.

Carritt and Goodgal[343] reported that the sorption (adsorption) of inorganic phosphorus is initially rapid, but that additional inorganic phosphorus is sorbed by a much slower, diffusion-controlled reaction (absorption). The model proposed to explain these two processes predicts that during desorption, both the amount and the rate of inorganic phosphorus removal from the complex would be dependent on the length of time the complex had to form. They supported this hypothesis with experimental evidence.

Pomeroy et al.[344] investigated the exchange of phosphate from estuarine sediments and found that the transfer was a two-step ion exchange process between clay minerals and water with half times of 15 seconds and approximately 30 minutes. The addition of formalin decreased the amount of exchanged phosphate by 50 to 100 percent, and this was thought to indicate the magnitude of biological fixation. They estimated the amount of phosphate transferred through the surface of submerged, undisturbed sediment to be on the order of 1 μ mole phosphate/m^2/day. Biological exchange in undisturbed sediment was minimal; but in suspended sediments, almost as much phosphate was biologically exchanged as was chemically exchanged with clay minerals.[344]

Li et al.[348] suggested that exchange rates were the combined effects of three separate first-order reactions. Reaction one, however, was much faster and accounted for 45 to 87 percent of the total exchangeable sediment phosphorus. Although the inorganic phosphorus was released into solution in anaerobic systems due to reduction of iron from the ferric to the ferrous state, the total pool of exchangeable phosphorus (sediment phase plus phosphorus in solution) was not greatly altered.[348] They also showed that sorbed added inorganic phosphorus showed approximately the same degree of exchangeability as native inorganic phosphorus in non-calcareous sediments, but was more exchangeable in calcareous sediments. These findings indicate that a large pool of sediment inorganic phosphorus has a high potential for interaction with the overlying water and for biological assimilation.

Adsorption isotherms have been widely used to study the rate and extent of phosphate sorption and desorption in soils and sediments. Equations such as the Freundlich and Langmuir adsorption isotherms describe the relationship between the amount of inorganic phosphorus adsorbed by the sediment and the equilibrium concentration in solution. The Freundlich equation predicts that sorption will continue indefinitely, with no saturation point, whereas the Langmuir equation is based on the assumption that a sorption maximum should be approached as concentration increases. The derivations of these equations will not be discussed, but some of the applications of these equations as an aid in nterpreting the phosphorus sorption behavior of sediments will be given.

Olsen[349] determined simultaneously the two opposite processes of sorption and desorption between water and sediments in well-defined oxidation and reduction states using phosphorus-32. For the oxidized sediments investigated, the phosphorus equilibrium was described as the difference between a gross adsorption and a liberation. Mathematical descriptions were given of the liberated amount (B) of phosphorus from the mud to water:

$$B = K^b \cdot C^w$$

and of the gross adsorbed amount (A) of phosphorus:

$$A = K \cdot C^v$$

The latter expression follows the Freundlich adsorption isotherm. They calculated the net amount of phosphorus adsorbed as a difference between A and B. When experimenting with muds in the reduced state, the reduction of ferric iron to the ferrous form complicated the process, and a direct mathematical description was thought impossible to derive.

In another study, Olsen and Watanabe[350] found that although the phosphorus sorption data followed the Freundlich equation, the Langmuir equation gave a better fit over a limited concentration range. Despite the concentration limitation, Olsen and Watanabe[350] considered the Langmuir equation preferable because (1) the Langmuir equation predicts a sorption maximum and (2) the Langmuir equation permits calculation of a constant which is related to the bonding energy between soil and phosphate.

Bache and Williams[351] determined phosphorus sorption isotherms covering a wide range of solution phosphorus concentrations (10^{-6} to 5×10^{-3} M phosphate) for 42 soils by a standardized technique modified from the Langmuir equation. The slope of a plot of the sorption (X) against the logarithm of the equilibrium solution phosphorus concentration (log c measured at $c = 10^{-4}M$) proved a suitable reference index to characterize phosphorus-sorbing properties of the soils. The quotient, x/log c, as the authors suggested, was a simple, yet adequate way of indicating a fundamental soil property, its phosphate sorption isotherm.

Kuo and Lotse[347] reported that the rate of phosphorus adsorption by sediments could be described by the equation:

$$X = KC_o t^{1/m}$$

where X = amount adsorbed in mg/g, C_o = initial phosphorus concentrate ion in ppm, t is reaction time, and K and 1/m are constants.

The calculated activation energy of adsorption was 2.7 kcal/mole. The rate of phosphorus adsorption was rapid initially, and decreased with prolonged reaction time. The initial rapid adsorption was probably a high energy adsorption associated with low surface saturation. The slow reaction was assumed to be a result of increased negative surface change, increased interaction energy and decreased adsorption energy. The authors[347] maintained that the relatively low activation energy was indicative of phosphorus adsorption being a diffusion-controlled process. This equation was developed from the Freundlich equation taking into account the fact that the slope of the plot is independent of reaction time.

The authors[347] also reported that while phosphorus adsorption by lake sediments could be described by the Freundlich equation over a large phosphorus concentration range, the Langmuir equation provided a good fit to the experimental data only at low phosphorus concentrations. The deviation from the Langmuir isotherms at high phosphorus concentrations was explained by an increase in total negative potential of the surface due to phosphorus adsorption and increased interaction between adsorbate molecules.

Kuo and Lotse[347] also reported that freshly adsorbed phosphorus was much more exchangeable than native phosphorus. This large difference in phosphorus release between untreated and phosphated sediments was attributed to an aging effect making adsorbed phosphorus more strongly bound by rearrangement of phosphate ions on the surface particles. This desorption study showed that $EDTA^{2-}$ was more effective in extracting adsorbed phosphorus than fluoride (F^-), bioxalate ($HC_2O_4^-$), and hydroxyl (OH^-) ions. The phosphate-replacing power of these anions was probably related to their ionic potential and complexing ability. It was suggested that phosphate released by $EDTA^{2-}$ and fluoride solutions most likely included phosphate held to the surface by electrostatic attraction ("specifically adsorbed" phosphate) and that held to the surface with coordinate covalent bonds (colloid-bound phosphate). These authors also concluded that desorption was diffusion-controlled and thus could be described by the proposed kinetic equation.

<u>Role of Redox Potential and pH in the Exchange of Phosphorus between Water and Sediments.</u> The cycling of phosphorus between the overlying water and sediments is a dynamic, steady-state system in which changes in the levels of phosphorus in the various components are rather small and slow under constant environmental conditions. The interchange of phosphorus between various components, however, can be extremely rapid[343,344,347,348] even though the phosphorus levels in the respective components remain unchanged.

The direction of phosphorus transfer is generally from the water to the sediment, presumably due to particle settling and sorption processes. However, the direction of transport of dissolved inorganic phosphorus will often be from the sediment to the overlying water due to direct biological uptake, the higher levels of inorganic phosphorus in the sediment interstitial water than in the overlying water, and the oxidation-reduction status of the sediments.[309]

Lee[352] conducted an extensive review of the factors involved in the various kinds of exchange reactions between water and sediments. According to Lee,[352] the direction of phosphate transport is a complex function of physical, chemical, and biological interactions in the environment.

It is well established that the oxidation-reduction potential controls the oxidation state of iron and thus affects the ability of sediments to retain or release inorganic phosphorus. Mortimer[111,112] showed that the disappearance of dissolved oxygen and the subsequent reduction of a sediment resulted in a severalfold increase of dissolved phosphorus and ferrous iron. Oxygenation of the sediment reversed the process and decreased the phosphorus concentration in solution.

Mortimer[64] conducted a quantitative study of the effect of dissolved oxygen in surface sediments on the chemistry of overlying water. The results show that a progressive decline in oxygen concentration from 2 mg/l to analytical zero at the interface was accompanied by a fall in electrode potential and this correlated with mobilization and transfer into the water of first manganese and then iron. There was a concurrent release of substantial quantities of phosphorus previously held in a complex form.

The high level of ferrous iron and dissolved inorganic phosphorus characteristic of deoxygenated lake bottom waters may be attributed in part to release of dissolved inorganic phosphorus from the sediments and suggest that ferric iron is involved in the immobilization of inorganic phosphorus in sediments. Other processes also occur in anaerobic environments which can release phosphate to the water column. Sulfate reducing bacteria reduce sulfate to sulfide, which can react with ferrous iron and form ferrous sulfide.[353] This reaction promotes the release of phosphorus.

Patrick[354] studied the state of extractable iron and phosphorus at controlled redox potentials in a submerged soil. The data indicated that extractable phosphorus increased over threefold between redox potentials +200 and -200 mv. Ferric iron predominated at potentials greater than +200 mv whereas extractable iron was present largely in the ferrous form below +200 mv. The sharp break in the phosphate release curve at +200 mv, the same potential at which ferric iron began to be reduced, indicates that the conversion of phosphate to an extractable form was dependent on the reduction of ferric compounds in the soil.

In a recent study, Patrick and Khalid[313] observed that anaerobic soils released more phosphate to soil solutions low in soluble phosphate and sorbed more phosphate from solutions high in soluble phosphate than did aerobic soils. The difference in behavior of phosphate under aerobic and anaerobic conditions was attributed to the change brought about in ferric oxyhydroxide by soil reduction. They suggested that a probably greater surface area of the gel-like reduced ferrous compounds in an anaerobic soil results in more soil phosphate being solubilized where solution phosphate is low, and more solution phosphate is being sorbed where solution phosphate is high.

Contrary to the popular belief discussed above, appreciable release of orthophosphate may also occur under aerobic conditions. Working with Lake Mandota sediments, Spear[355] reported that approximately 1 to 2 mg/l of orthophosphate was released when nitrogen gas was passed through the mud-water system. When oxygen or air was used in place of nitrogen in the same experiment, about 1 mg/l of orthophosphate was released. Similar results were obtained by Sridharan[356] and Bortleson.[357] They found that the amount of aerobic release was highly dependent on sediment type, which may vary considerably depending on the location sampled. These studies, however, indicate that phosphorus release under aerobic conditions was very slow as compared to the rate of release under anaerobic conditions.

In discussing these studies, Lee[352] has pointed out that these experiments were conducted in a well-mixed sediment-water system, and that the rate of release was controlled by the exchange reactions rather than the hydrodynamics of the system. An understanding of these exchange reactions is important in the dredging process, which consists of moving accumulated sediment from navigation channels and harbors and disposing of the sedimentary material at designated open-water sites or selected on-land disposal sites. The mixing of the sediments and sediment interstitial water with the overlying water at the dredging site may result in the release of potentially significant amounts of nutrients to aquatic ecosystems. Also, problems may arise primarily from the contamination of surface or ground waters from water that has contacted the dredged material at the on-land disposal sites.

The changes in pH of sediments may also effect the exchange of phosphorus between sediments and overlying waters. MacPherson et al.[358] found that the release of phosphorus from lake muds was minimum between pH 5.5 to 6.5. Four types of lake sediments -acid bog, productive, moderately productive, and unproductive - yielded similar release patterns. Acid bog and highly productive sediment released the most phosphate with lesser amounts leached from moderately productive and unproductive sediments. However, it is not possible to tell from their figures whether they measured changes in the sorption reaction caused by a pH effect or an effect caused by changing the ionic strength.[338] Hayes[359] obtained a maximum adsorption of phosphorus by mud at pH values between 5 and 7 when $H_2PO_4^-$ ions were dominant. Lee and Plumb[39] have reported that adsorption phenomenon is highly pH-dependent with maximum sorption occurring at pH values of 4 to 7. As the pH is increased or decreased, there is a rapid loss in sediment sorption capacity.

Burns and Ross[360] studied the effects of oxygenation on phosphorus release in Lake Erie sediments and stressed the importance of regeneration of phosphorus in the anoxic sediments. They suggested that in the case of overturn of anoxic water to the surface, the pH of the mixture containing both iron and phosphorus will rise and that iron will precipitate out as the hydroxide and not as the phosphate. The ferric hydroxide could then react with some (but not all) of the phosphate molecules, resulting in a decrease of soluble phosphorus. These theoretical assumptions were verified experimentally as soluble reactive phosphorus decreased by only 10 percent during an overturn, whereas the decrease would have been 55 percent if all the anoxic soluble reactive phosphorus in the hypolimnion had converted to the particulate form. The proportion of soluble reactive phosphorus to particulate phosphorus within the water column thus increased rather than decreased with the overturn. These results demonstrate that the phosphorus regenerated under anoxic conditions may become bioavailable, possibly contributing to the development of eutrophic conditions within the lake.

For a detailed account of the factors influencing the transfer of toxic metals and nutrient elements of ecological importance between sediment and overlying water, the reader is referred to Mortimer,[111,112] Lee,[352] Lee and Plumb,[39] and Stumm.[303]

Precipitation of Phosphorus Compounds in Sediments. The precipitation and dissolution of aluminum, iron, and calcium phosphates in sediments are considered an important buffer mechanism which regulates both the levels of phosphorus in the interstitial waters and the release of phosphorus to the overlying waters. An understanding of the geochemical processes involved in the formation of these compounds in freshwater environments is of considerable interest in eutrophication abatement programs.

The phosphate minerals known to exist in soils and sediments are variscite ($AlPO_4$), strengite ($FePO_4$), vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), anapaite ($Ca_2Fe(PO_4)_2 \cdot 4H_2O$), and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$).[42,309,361,362] However, the evidence for the existence of most of these minerals in the sediments has been based primarily on the solubility product criteria.

According to Stumm and Morgan,[25] the minimum solubility of variscite is at pH 6. At this pH, the precipitation of aluminum phosphate is theoretically possible if the level of dissolved inorganic phosphorus exceeds $3 \times 10^{-6}M$ (approximately 1 μg/ml). At pH 6, strengite, which has a minimum solubility at pH 5.5, sustains a level of phosphorus of approximately 1 μg/ml. Stumm[363] reported that the dissolved inorganic phosphorus concentration in lake waters rarely exceeds 0.3 μg/ml. Because sediment components can apparently regulate dissolved inorganic phosphorus levels to considerably less than 1 μg/ml (except under anoxic conditions where strengite instability is expected), it is unlikely that strengite would persist even if it existed initially in sediment.[309] Strengite and variscite are unstable at pH values > 1.4 and 3.1, respectively, based on ion product measurements.[364]

Patrick et al.[54] studied the dissolution of strengite in flooded soil under controlled redox potentials and pH. The results showed that strengite undergoes partial dissolution under the reducing conditions found in a flooded soil. The greatest release of phosphorus and iron occurred at a redox potential of -250 mv at pH 5.0. At pH 6.0, a more realistic value for a flooded soil, 21.5 percent of the total ^{59}Fe was extracted at a redox potential of -250 mv. Nriagu[361] suggested that the requirements for strengite formation include a high redox potential, large phosphorus concentrations, and low pH.

The occurrence of vivianite has been reported in the postglacial sediments from Lakes Superior, Erie, and Ontario.[362,365] Dell[362] reported that vivianite was formed authigenically within sediments and is thus a component of the phosphorus cycle in these lakes.

Nriagu[361] constructed solubility isotherms for synthetic vivianite in the three-component system, $Fe_3(PO_4)_2 - H_3PO_4 - H_2O$, and defined boundary conditions depicting the stability fields of vivianite. According to the diagrams constructed, vivianite is stable only at very high phosphorus concentrations, and the vivianite field would disappear if activity of $HS \geq 10^{-1.5}$ and activity of $HPO_4^{2-} < 1.0$. This indicates that iron phosphate minerals are unlikely to be formed in sulfide-generating anoxic environments unless abnormally high concentrations of phosphorus are present.

In a recent study, Nriagu and Dell[42] combined thermodynamic data with measurements on the interstitial waters of Lake Erie to define the chemical requirements for the formation of vivianite and other iron phosphates in Great Lakes sediments. They reported that for a range in pH values of 6.5 to 9, where redox potential $\leq$ 0 mv, vivianite is the most stable mineral in the natural geochemical environment. They suggested that ferrosoferric hydroxyphosphates were most stable at the redox potential and pH likely to be encountered at the mud-water interface. However, below the mud-water interface, the lower redox potential environment may cause these complexes to dissolve incongruently to form vivianite or a mixture of vivianite with reddingite or anapaite.

Contrary to the mechanism of phosphorus regeneration in limnetic environments discussed by Mortimer,[64,111,112] Nriagu and Dell suggested that the solubility of ferrous phosphate rather than the reduction of ferric oxyhydroxides controls the phosphorus concentration in the interstitial water, and indirectly regulates the release of phosphorus to the overlying water. Most of these findings are still based on the solubility product considerations, and the experimental data to substantiate these hypotheses are lacking.

The formation of hydroxyapatite in sediments has been suggested by Stumm and Leckie[312] and Williams et al.[321] Stumm and his coworkers[25,312] have indicated that hydroxyapatite precipitates in sediments by the interaction of dissolved inorganic phosphorus with calcium or calcite. Calculations based on the equilibrium constants and the free energy relationship for the conversion of calcite into apatite[25] indicate that at pH 8, $[HCO_3^-] = 10^{-3}\underline{M}$, a solution containing $10^{-4}\underline{M}\ HPO_4^{2-}$ should theoretically convert calcite into apatite.

Sutherland et al.[366] concluded that the dissolved inorganic phosphorus concentration in the Great Lakes could be explained by a simple equilibrium model involving hydroxyapatite. Although the concentration of dissolved inorganic phosphorus in lake and interstitial waters is often considerably higher than the equilibrium constants sustained by hydroxyapatite (0.03 μg/ml at pH 7.0),[363] this does not mean that this mineral will precipitate. For example, the Wisconsin lakes are supersaturated with hydroxyapatite, and yet small amounts of apatite are present in the surficial sediments of these lakes.[352]

Nriagu and Dell[42] report that for the pH and calcium and phosphorus concentrations likely to be encountered in many freshwater sediments, anapaite ($Ca_2Fe(PO_4)_2 \cdot 4H_2O$) rather than hydroxyapatite would be the stable calcium-bearing mineral. This observation conflicts with the suggestion of Sutherland et al.[366] that hydroxyapatite is the most stable diagenetic calcium phosphate. According to Lee,[352] there is little or no evidence that hydroxyapatite plays a major role in the chemistry of phosphorus in the sediments.

Organic Phosphorus in Sediments. Organic phosphorus constitutes 10 to 70 percent of the total phosphorus in lake sediments,[320,367] and thus constitutes a major reservoir of phosphorus. Organic compounds of phosphorus originate in the sediments, partly from plant and animal remains and partly from microbial synthesis from inorganic phosphorus compounds. Organic matter that enters the lake also deposits phosphorus largely as organic compounds that mineralize very slowly. Also, the biological incorporation of dissolved inorganic phosphorus into particulate organic phosphorus which subsequently settles removes phosphorus from the surface water and deposits it at the sediment surface.

Reported literature data show that organic phosphorus is correlated with organic matter in certain sediments.[320,323,368] In addition to organic matter, oxalate-extractable aluminum has been found to correlate significantly with total organic phosphorus.[323,368] Jackman[369] also reported a similar organic phosphorus-aluminum relationship for some soils which may indicate that aluminum stabilized organic phosphorus against decomposition in soils.

Specific organic phosphorus compounds found in sediments include adenosine triphosphate (ATP), and inositol penta- and hexa-phosphates.[368] The presence of nucleic acids, phospholipids, and phytin in waterlogged soils has also been indicated.[319] An extraction-fractionation procedure employed by Sommers et al.[368] to characterize lake sediments indicated that, although some differences exist, sediments in general contain similar forms and amounts of organic matter. The observed positive correlations between the organic matter and major organic phosphorus fractions of sediments suggest that differences in the organic phosphorus status were more a function of general organic matter transformation dynamics than of differences in the nature of the specific organic compounds and complexes constituting the sediment organic phosphorus fractions.

Sommers et al.[368] reported that much of the organic phosphorus (48 to 60 percent) was composed of high molecular weight humic-fulvic complex. Wildung and Schmidt,[305] working with sediments from the Upper Klamath Lake, Oregon, also found that approximately 50 percent of the total organic phosphorus was recovered in the fulvate and humate fractions with the remaining phosphorus present in the silicon fraction, as nonextractable sediment residual.

Selective extraction procedures for the identification and fractionation of organic phosphorus in soils and sediments has been proposed by several workers.[305,367,370,371] The details of these procedures will not be considered in this report. However, it should be pointed out that the rationale in the study of organic phosphorus compounds in sediments is such that the mineralization-immobilization balance is related to the types of organic phosphorus compounds present, and to the nature of the association between the organic phosphorus and other sediment parameters. The solubility and release of organic phosphorus increases with reduction and chelation and is directly proportional to the amount of utilizable organic matter.[372] Therefore, the study of the organic fraction of total sediment phosphorus is important to understanding the mechanism of phosphorus release to the overlying water and the aquatic organisms.

Sulfur

In most of the earth's crust, sulfur is a minor constituent and its concentration rarely exceeds 0.03 percent in common rock types.[24] Although not abundant, sulfur is widely distributed as a principal constituent of minerals that have formed throughout a broad spectrum of geologic environments which are representative of diverse physicochemical conditions. This chemical versatility of sulfur may be attributed to its activity in oxidized as well as reduced environments and its ability to combine with both metals and nonmetals by either covalent or ionic bonds.[373] The common sulfur-bearing minerals include sulfides, sulfosalts, and sulfates. A detailed account of these minerals is given by Staples[374] and Field.[373] The sulfide minerals are found in reducing environments, whereas the sulfates are representative of oxidizing conditions. The minerals pyrite (FeS_2) and gypsum ($CaSO_4 \cdot 2H_2O$) are the most abundant of these two forms.

The principal geologic sources of sulfur include native sulfur deposits associated with salt domes, sedimentary rocks, and volcanic exhalations. Though some sulfur is obtained as by-product recovery from the roasting or smelting of sulfide ores or from "sour" natural and refinery gases, deposits of native sulfur in salt domes and in sedimentary rock are quantitatively more important in domestic sulfur production.[373] According to Ambrose,[375] approximately 85 percent of the domestic sulfur production is converted to sulfuric acid for use in agricultural, chemical, and related industries.

Sulfur in the Environment

The potential pollutants of sulfur in the environment include sulfur oxides and hydrogen sulfide. Sulfur oxides (SO_2, SO_3, H_2SO_3, H_2SO_4) and sulfide and sulfate salts in the atmosphere are derived principally from the combustion of fossil fuels used to generate electricity, to heat buildings, and to power machines.[200] A survey conducted in 1966 indicated that the burning of coal, oil, and gasoline for power and heat accounted for 80 percent of the atmospheric sulfur dioxide emitted in the United States.[200] The remaining 20 percent of the total is generated by industrial processes--smelting, petroleum refining, and sulfuric acid manufacture. According to this study, the automobile and natural gas do not contribute significantly to sulfur oxide emissions. The background concentration of sulfur dioxide in the air is about 0.5 $\mu g/m^3$, but the average annual concentration in cities has been found to range from 27 $\mu g/m^3$ (Denver, 1966) to about 470 $\mu g/m^3$ (Chicago, 1964).[200] The U. S. Environmental Protection Agency[376] has set 80 $\mu g/m^3$ as the maximum permissible concentration of sulfur oxides for health reasons, and many cities in the United States exceed this limit. High concentrations of sulfur oxides are toxic and may cause injury to both plants and man. Some of the injurious effects of atmospheric sulfur oxides have been discussed elsewhere.[200,377,378]

Hydrogen sulfide can be toxic to soil micro-organisms and plants in flooded soils and to fish and other aquatic animals in marine environments. The production of hydrogen sulfide results from the reduction of sulfate by sulfate-reducing bacteria under oxygen-deficient conditions. The inhibition of enzymatic activity in soil and the reduced uptake of several plant nutrients have been attributed to the influence of hydrogen sulfide.[379,380,381,382] Fish and other aquatic animals have been killed in the deep water of the Caspian Sea; the Sea of Azov; Walvis Bay, South Africa; and Nörwegian fjords as a result of high levels of hydrogen sulfide produced in sediments.[8]

The concentration of sulfur is estimated to be about 885 mg/1 in seawater whereas freshwater contains only 5.5 mg/1 sulfur.[24] Deep-sea sediments contain about 1300 μg/g sulfur, and pyrite (FeS_2) is the most important species found in marine sediments. The high enrichment of sulfur in the oceans results from volcanic activity and leaching of surface igneous and metamorphic rocks. The sulfur is transferred into the ocean either by streams or rain where it may be reduced in sediments and anoxic waters by bacteria and converted to pyrite. The other sources of sulfur in water include industrial, agricultural, and sewage discharges into waterways.[383]

Sulfur Chemistry of Sediments

The geochemistry of sulfur, like iron and manganese, involves oxidation-reduction reactions. Its most common valences in sedimentary environments are -2 (sulfides), 0 (elemental sulfur), and +6 (sulfate). Sulfate is readily reduced to sulfide in sediments and submerged soils containing decomposable organic matter. Under conditions of oxygen deficiency, the sulfate-reducing bacteria, e.g. Desulfovibrio, use sulfate as a hydrogen acceptor to produce hydrogen sulfide.[284,379] The bacteria are widely and abundantly distributed in the sediments. They are obligate anaerobes which, though not rapidly killed by oxygen, cannot reproduce in the presence of oxygen.[8] In reduced sediments, hydrogen sulfide combines with certain metal ions to form metal sulfide precipitates. The precipitation of metal ions such as iron, manganese, zinc, copper, mercury, and other trace metals as sulfides in sediments and submerged soils is an important mechanism regulating the solution concentration of both sulfide and the metal ion, either of which could be toxic. However, an increase in dissolved oxygen concentration by currents or through dredging activities may result in the oxidation of sulfide to sulfate or to elemental sulfur, possibly mobilizing the toxic metals. It is evident that the nature of sulfide transformations and the chemical and biological conditions affecting these transformations must be characterized in order to appreciate the metal-sulfide association in sediments.

Effect of Redox Potential and pH on Sulfur Transformation. The major controlling factors related to reduction process in the sediments and submerged soils are the microbial population, organic matter content, redox potential and pH. Although *Desulfovibrio desulfuricans* is the most widely distributed sulfate reducer in nature,[384] *Desulfotomaculum*, *Clostridium nitrificans*, and *Bacillus megaterium* are also reported to reduce sulfate under certain conditions.[385,386,387] Organic matter acts as a substrate for the sulfate-reducing organisms, and a positive relationship between the accumulation of sulfide and the soil organic matter has been reported in the literature.[157,388]

Redox potential and pH are known to control the activity of sulfate-reducing organisms and thus limit the production of sulfides in the environment.[47, 159,160,161,284,389] The boundary conditions for sulfide stability in terms of redox potential-pH limits have been described by Baas Becking and associates,[47,390] Garrels and Christ,[162] and Krauskopf.[24]

Baas Becking and his associates[47,390] studied the chemical and physical conditions controlling the activity of Desulfovibrio in the natural environment and found that it cannot occur at a pH under 4.2, but can be found at greater pH values to well over pH 10. The highest redox potential at which sulfide may be produced is +110 mv, and it may be generated at potentials as low as -500 mv. They also reported that the intensity of sulfate reduction depends upon the sulfate content of the water and on the available hydrogen, both organic and inorganic. The iron concentration is also important as iron sulfide is the principal sulfide species formed.

Harter and McLean[161] determined that sulfate-reducing micro-organisms functioned best at Eh potentials of -75 mv or less. Their work was based on the relatively rapid rate of sulfide accumulation in soil at redox potentials of less than -75 mv. Connell and Patrick[159,160] demonstrated that the critical oxidation-reduction potential in an incubated soil for the reduction of sulfate was about -150 mv. They also reported that in aerobic soil, the oxidation of sulfide was rapid, with one-half of the sulfide being oxidized after 8 hours.

Alexander[284] found that the lower pH limit for the microbial evolution of hydrogen sulfide was 5.5. Connell and Patrick[159] showed that under controlled conditions, little or no sulfide accumulated with a pH outside the range 6.5 to 8.5. The maximum sulfide accumulation was found to be at pH 6.8 to 7.0. Bloomfield[391] reported that more free hydrogen sulfide was generated under alkaline conditions, but he added that iron was less mobile under alkaline conditions and that iron chemistry governed the distribution of sulfide in a reduced soil.

Chemical Forms of Sulfur in Sediments. The biological reduction of sulfates results in the production of hydrogen sulfide, which combines with any of the available metallic ions capable of forming stable sulfides under the prevailing conditions. Kaplan et al.[392] presented experimental evidence that the product of sulfate reduction is free sulfide, which is transformed in sediments to elemental sulfur, organic sulfur, and iron sulfide, the latter being the dominant form of sulfur and comprising mainly pyrite (FeS_2). They studied the distribution of various sulfur compounds in recent marine sediments off southern California and showed that the quantities of different compounds varied with environment and depth in the sediments. They also found that pyrite occurs in oxidizing as well as reducing sediments and constitutes up to 90 percent of the total sulfur. Using isotopic sulfur, they demonstrated that the sulfide released by biological reduction is first converted to hydrotroilite and then to pyrite. A similar pathway of pyrite formation was suggested earlier by Harmsen et al.[393] who stated that pyrite forms by the direct reaction of hydrotroilite and elemental sulfur:

$$FeS + S \rightarrow FeS_2$$

Stanton[394] has discussed in some detail the occurrence of sulfides in sediments. He stated that the iron sulfide and pyrite (cubic FeS_2) is by far the most common, and that pyrrhotite ($Fe_{1-x}S$), sphalerite (ZnS), chalcopyrite ($Cu_2Fe_2S_4$), and galena (PbS) are not so abundant or widespread, but are sometimes locally prominant and may attain quite high concentrations over restricted areas.

Research by Harter and McLean[161] demonstrated that in a soil producing considerable quantities of sulfide, almost all of the sulfide was precipitated as ferrous sulfide. The soil under study was high in extractable ferrous iron when flooded, and the extracted ferrous iron decreased with an increase in sulfide. The production of free hydrogen sulfide under flooded conditions has also been reported by several workers.[160,389]

The amount of sulfides present in the sediment may vary with the type of sediment and the physical, chemical, and biological conditions prevailing in the environment. Kaplan et al.[392] reported a value of about 1 percent total sulfide in Santa Barbara Basin sediments and 0.5 to 0.7 percent in the Santa Catalina Basin sediments. A study of the seasonal variations in the total sulfide content of marsh sediments at two sites in Barataria Bay gave a range of values for the two locations from 40 to 310 μg/g and from 16 to 240 μg/g during a 12-month period.[395] A sharp rise of total sulfides observed during the spring was attributed to the increased reduction associated with the heavier flooding of the marsh. The analysis of Los Angeles Harbor sediments showed that sulfide contents varied from 163 to 1673 mg/kg dry weight.[396] Chen et al.[396] indicated that silty clay sediments, rich in both organics and sulfide, exhibited a higher level of release during the quiescent settling tests. The presence of oxygen, however, was shown to oxidize the sulfides quickly. The sulfide content of San Francisco Bay dredged sediments has been found to range from 1000 to 3000 μg/g with the sulfide content increasing significantly with depth.[9] No free sulfides were detected in the overlying water.

May[256] has determined the presence of hydrogen sulfide in the Mobile Bay sediments and in the effluent during the dredging operations. No hydrogen sulfide was detected in water leaving a diked disposal area, indicating that oxidation of sulfide to sulfate or to elemental sulfur occurred in the supernatant water.

Effect of Sulfides on Heavy Metals in Sediments. The high concentration of sulfides in sediments plays an important role in limiting the release of toxic metal ions to the overlying water. The metal ions - iron, manganese, zinc, copper, lead, mercury, and cadmium - readily form insoluble and relatively stable sulfide compounds in soils and sediments where reducing conditions are intense and sulfide is present.[21,24,102,159,162,163,196] Some of these metallic sulfide precipitation mechanisms have been discussed earlier in the report in the discussions of the indivdual metals.

Lisk[102] described a relationship between metal toxicity and properties such as their electronegativities, the insolubility of their sulfides, and the stability of their chelates. For example, metals like mercury and copper, which are more electronegative, form sulfides of very low solubility, and have greater chelate stability, will be more toxic. The insolubility of various metallic sulfides was reported in the order of:

$$Hg > Cu > Pb > Cd > Co > Ni > Zn > Fe > Mn > Sn > Mg > Ca$$

Engler and Patrick[196] evaluated the effects of aerobic and anaerobic moisture conditions on the reactions of manganese, iron, zinc, copper, and mercury sulfides using ^{35}S. The results indicate that under anaerobic conditions, the metallic sulfides were very stable with little or no dissolution of the ^{35}S from the metal. Where there was release of ^{35}S under anaerobic conditions; the release was only slightly correlated with the calculated solubilities of the metal sulfides. The metal sulfides were relatively unstable under aerobic soil conditions and the degree of sulfide oxidation was related to some extent to the solubility product constant. The authors[196] also reported that the degree of oxidation of the metal sulfides and the uptake of ^{35}S by rice plants (Oryza sativa L.) were directly related to the solubility of the sulfides. The uptake of added ^{35}S was in the order of:

$$MnS > FeS > ZnS > CuS > HgS$$

For the metal ions involved, the toxicity to plants appeared to be inversely related to the solubility of their sulfide salts with divalent mercury being the most toxic and manganous manganese and ferrous iron being the least toxic.

Krauskopf[103] suggested that local precipitation of sulfides in a reducing environment was a possible control mechanism for copper, zinc, mercury, silver, cadmium, bismuth, and lead concentrations in seawater. The concentration of these metals, however, had no discernible relation to the calculated solubilities of their sulfides, indicating that this mechanism is not a major controlling factor. The sulfides of nickel, cobalt, tungsten, molybdenum, and vanadium, on the other hand, were far too soluble to explain the concentration of these metals. Piper[242] showed that the concentration of zinc in the suspended matter in the sulfide-bearing water of a Norwegian anoxic fjord was controlled by sulfide precipitation. A sevenfold increase in the concentration of zinc in the suspended matter below 40 m indicated that zinc was precipitating as a sulfide. This observation was confirmed by the fact that the activity product for zinc sulfide exceeded its solubility product ($10^{-20.6}$ vs. $10^{-22.9}$, respectively). The distribution of iron, manganese, cobalt, nickel, and copper in the sediments, on the other hand, was dominated by the mineralogy of the lithogeneous material and the abundance of organic matter.

A selective extraction of San Francisco Bay dredged sediments determined that 92 percent of the cadmium, 45 percent of the lead, 43 percent of the copper, 39 percent of the zinc, 23 percent of the mercury, 19 percent of the manganese, and 6 percent of the iron was associated with organic and sulfide-like phases.[9] Significant correlations were also observed between the total heavy metal contents and the total sulfur. Based on these results, the study concludes that sulfides play an important role in the movement of trace metals within San Francisco Bay.

Hallberg[60] measured the vertical distribution of several metal ions (acid soluble) in sediments collected from an intertidal area on the island of Ameland, off the coast of Holland and studied interrelationships between different sediment parameters. The data indicate that the heavy metals in the reduced hydrogen sulfide-rich layers of the sediment may not necessarily be present only as sulfides. The adsorption and absorption by clay minerals and organic matter may account for some of the metal concentrations, as was evidenced by a high correlation between the metals, the organic matter, and the finest sediment fraction. The results of the study also suggest that there may be a competition for the heavy metals between the naturally occurring chelating agents and hydrogen sulfide. For example, if a metal-chelating compound has an upward diffusion rate in the sediment which is greater than that of hydrogen sulfide, the chelated metal will be withdrawn from the hydrogen sulfide zone. The chelating and complexing effect of decomposed organic matter was very striking in the case of copper, which was twice as concentrated in the oxidized layer as in the reduced layer. Iron, zinc, lead, and nickel were slightly more abundant in the reduced zone than in the oxidized zone, which suggested a greater influence of sulfide precipitation.

It is evident from these studies that the stability of metal-sulfide complexes in sediments is greatly modified by several sediment parameters and especially by the organic matter. The chelating and complexing properties of the organic ligands may keep the trace metals in solution which would be precipitated otherwise. The presence of organic material influences the transformations of heavy metals in sediment-water systems such that the metal-organic interaction is often greater than the interaction between metals and inorganic ligands.[43] This means that metal solubility predictions based on thermodynamic calculations must consider metal interactions with organic as well as inorganic substances for a meaningful interpretation.

The complexity of thermodynamic equilibrium in sediment systems is shown by Lindberg and Harriss,[21] who found mercury concentrations in the Everglades interstitial water to be 2.6 to 36 times higher than the average levels in the overlying waters. They reported that the calculated solubility of mercuric sulfide under pH and sulfide concentration levels measured in these cores was 10^{13} to 10^{31} times too small to account for the dissolved mercury concentrations. This high enrichment of mercury was thought to be due to the formation of soluble organo-metallic complexes and/or polysulfide complexes of relatively high solubility such as HgS_2H^- and $HgS(HS)^{2-}$.

Chen et al.[396] investigated the transport of heavy metals under oxidized and reduced conditions in Los Angeles Harbor sediments. The experiments were conducted in plexiglass columns set up in a dark, controlled temperature chamber (10 ± 2° C). The sediment-seawater columns were maintained at oxidized and reduced conditions for two months and samples analyzed at appropriate intervals. The results show that all metals except silver, chromium, and mercury were released under oxidized conditions. Cadmium, manganese, nickel, and zinc were released in high concentrations, with copper, iron, manganese, and lead released to a lesser extent. The authors[396] have speculated that this release was mainly due to carbonate, chloride, and organic complex formation.

Chen et al.[396] reported that iron and manganese were released to very high levels under reduced conditions and that sulfides of iron and manganese were not the controlling factors under reduced conditions. The concentrations of other trace metals were decreased to extremely low values during the initial contact period. As time passed, the concentrations of cadmium, copper, mercury, nickel, lead, and zinc were again increased. Under these experimental conditions, the increased cadmium concentration was close to the solubility of cadmium predicted from pH and the solubility of cadmium sulfide. The concentrations of copper, mercury, nickel, lead, and zinc in the interstitial water after 60 days of contact were higher than those predicted from the formation of sulfide complexes. The decrease in the soluble metal content for several metals during the initial contact period was explained by metallic sulfide formation. The metallic sulfide species are more stable compared to most of the chloride, carbonate, or organo species. The subsequent increase in trace metal levels under reducing conditions was attributed to desorption from iron and manganese or clay minerals, formation of more soluble sulfide complexes, formation of organo-metallic complexes, or slow kinetics of metal sulfide precipitation, which, as explained by the authors, is not clearly understood.

FORMS OF TRACE METALS IN SEDIMENTS AS DETERMINED BY CHEMICAL FRACTIONATION

It is necessary to know the chemistry of trace metals in sediments in order to understand the cycling of metals in both undisturbed and disturbed sediments. This knowledge is indispensable in evaluating the fate of these metals that are introduced as pollutants into the aquatic system as a by-product of modern civilization. With regard to water quality, it is important to determine whether the trace metals are (1) in solution or loosely adsorbed on solids, where they are readily available, (2) complexed with insoluble organic or inorganic substances where chemical or biological changes are required before they are released so that they are less available, or (3) in the crystal structure of deposited or suspended mineral particles where they are essentially unavailable. In recent years, there has been much interest in establishing the distribution of trace elements among the various components of the sediment-water system. The geochemistry and occurrence of these metals have been discussed in previous sections. In this section, the existing literature on the selective extraction of heavy metals will be reviewed in order to identify an appropriate procedure for the sequential chemical extraction of sediments. Such a procedure should help explain the transformations these metals undergo when sediments are subjected to different environmental conditions, especially during dredging and disposal operations.

Goldberg and Arrhenius[264] used a technique involving the chelation action of ethylenediaminetetraacetic acid (EDTA) to examine the distribution of trace metals between the components of marine sediments. According to the authors, this treatment completely dissolves manganese nodules, leaving the minerals as intact as possible. The use of EDTA was criticized on the grounds that the adsorption process was slow and that EDTA interferred with the elemental analysis of some trace metals in the solution.[397]

Arrhenius and Korkisch[398] used 1 M hydrochloric acid to separate the iron oxide fraction of the ferromanganese nodules. The results show that the ferromanganese nodules contain a reducible fraction, consisting of oxides of manganese, which can be separated using a reducing solution, hydroxylamine hydrochloride. Later studies, however, showed that the reagent will not only dissolve manganese oxide phases of ferromanganese nodules, but will also dissolve up to 50 percent of iron oxide present.[397]

Chester and Hughes[399] studied the distribution of nickel, manganese, and iron in North Pacific pelagic clay using dilute hydrochloric acid and EDTA. Fifty-six percent of the total nickel was bound in the manganese nodules, and 44 percent was in the clay lattices. There was no nickel present on the exchange sites. The distribution of manganese was such that 88 percent was recovered in the marine-derived nodules and 12 percent was bound to clay lattices. Ninety-five percent of iron was determined to be in the clay lattices; and only 5 percent was associated with iron oxides and manganese nodules. The investigators indicated that unless the various sediment fractions were considered separately, the relationship between trace metals and major elements could be masked in pelagic sediments.

In later studies, Chester and Hughes[99,397] advocated the use of a mixture of 1 M hydroxyalamine hydrochloride and 25 percent acetic acid in determining trace elements in marine sedimentary environments. Iron, manganese, copper, lead, cobalt, nickel, chromium, and vanadium in the North Pacific pelagic clay were chemically separated into three types: land derived (lithogeneous), nodular marine derived (hydrogeneous), and non-nodular marine derived. The lithogeneous contributions represented materials weathered from the continental areas, and, in most cases, atoms bound in the clay lattices. The hydrogeneous nodular fractions were comprised of manganese-rich nodules whereas the non-nodular material represented metals bound in hydrous iron-rich oxides. However, these workers cautioned that selective chemical attack does not permit a distinction to be made between trace metals removed from the seawater and those incorporated in preexisting mineral phases. The conclusions were based on the fact that the quantitatively important hydrogeneous phases, opal and authigenic clay minerals, could not be separated from minerals of the lithogenic origin.

Presley et al.[142] studied the distribution of iron, manganese, nickel, cobalt, copper, molybdenum, zinc, lithium, and strontium in a reducing fjord of British Columbia. The sequential extraction procedure employed was as follows:

a. Leaching with acetic acid in hydroxylamine hydrochloride.
b. Leaching with hydrogen peroxide.
c. Dissolution in hydrofluoric-nitric-perchloric acid mixture.

They stated that the first extraction removed metals bound to carbonates, hydrous oxides, and some sulfides. The second extraction removed metals bound to the sulfides and organic matter, and the third, residual dissolution, removed the lithogeneous mineral-bound metals. They also suggested that the trace metals that were chemically leachable were bound with amorphous oxides of iron and manganese and as sulfides with a minor contribution from exchangeable ions.

Nissenbaum[400] reports on the chemical fractionation of iron, manganese, strontium, copper, nickel, and zinc in a sediment core from the sea of Okhotsk in the North Pacific off the coast of Siberia. The sediment was leached successively with water, hydrogen peroxide, acetic acid, and hydrochloric acid and finally fused with sodium carbonate. The metals removed by these extractants were respectively designated as (1) water soluble; (2) organic- and sulfide-bound ions; (3) carbonate-bound, exchangeable, and some hydrous oxide-bound ions; (4) the remainder of the hydrous oxide-bound ions plus some metals in the clay lattice sites and silicate minerals; and (5) the remaining fraction of the silicate materials, which included resistant clays and detrital silicate minerals transported from the neighboring land area.

Although there is a considerable overlapping in the chemical and mineralogical makeup of the different extractants used by Nissenbaum,[400] these data do indicate the diagenetic transformations occurring in the sediments. For example, a gradual decrease in the acetic acid fraction combined with an increase in the hydrochloric and residual fractions along the entire length of the sediment core may occur by the recrystallization of the poorly crystalline ferromanganese oxides into more stable forms, or by diagenetic transformations of clay minerals in the silicone-rich environment. The appearance of iron in the hydrogen peroxide fraction was attributed to the probable lower redox potential values facilitating the formation of iron sulfide.

The studies cited above have been mainly concerned with the sedimentary geochemistry of pelagic sediments. The classification of various sediment components was related primarily to their origin into lithogeneous, hydrogeneous, biogeneous, and related categories. Studies of this kind are important in determining the origin of deposited sediment and the processes by which different chemical elements have been incorporated into the sediments with time. The purpose of this investigation, however, is to use an extraction procedure which should indicate those phases which participate in chemical and biological transformation in oxidized and reduced sediments. The selective extraction studies discussed earlier do not account for oxidation-reduction reactions which may cause phase differentiation of elements within the sediment. Most of the partitioning of elements in these studies has been done on dried and ground samples, which obviously changes the nature of amorphous materials, organic matter, and certain clays, resulting in a modification of exchange properties and other surface characteristics of the sediment.

The effect of drying on the cation exchange capacity (CEC) and exchangeable iron and manganese of sediments is demonstrated by Toth and Ott.[14] Air drying of the bottom sediments resulted in a 21-percent decrease in the CEC whereas ovendrying resulted in a net loss of 35 percent in the CEC values. During ammonium acetate extraction of dried sediment sample, organic matter exhibits a hysteresis effect and some sites become unavailable for ion retention. Another factor responsible for reduction in CEC values during the drying process is the oxidation of ferrous and manganese ions to ferric and manganic ions which tend to precipitate as insoluble oxides, thereby blocking exchange sites. The data indicate that drying bottom sediments reduces the exchangeable iron and manganese contents from very high to almost trace levels. Since heavy metals are related to iron and manganese compounds, phase differentiation of these compounds will alter the distribution of heavy metals in the sediments.[117,149]

The effects of atmospheric oxidation on chemical transformations in the interstitial water and sediments are well known.[40,41,55,64,160,313] Thus, the selection of an extraction procedure aimed to study the chemical and biological transformations in the sediments should preclude any atmospheric oxidation at certain operational steps. One of the main goals of this investigation is to predict the effects of dredging and disposal operations on the possible migration of toxic metal ions and plant nutrients from insoluble forms to soluble and exchangeable forms in dredged material sediments. Dredging usually results in the transport of bottom sediments from an oxygen-deficient, anaerobic environment to an environment in which oxygen is at least temporarily available. Some aerobic sediments are also mixed with anaerobic sediments by dredging. The changes in the physicochemical properties induced by dredging affect the activity of toxic metal ions and plant nutrients in lake and river sediments. The chemical fractionation procedure should be sensitive enough to register such changes, which are easily masked by oxygen contamination during extraction.

This laboratory has developed a selective extraction procedure applicable to many sediments and which takes into account the functional properties of various sediment components, rather than the traditional sedimentary geochemistry. This extraction procedure is based on the work of Patrick and Turner,[55] Patrick et al.,[54] Gotoh and Patrick,[40,41] and Engler et al.[401] with modifications incorporated as deemed necessary to make the procedure more reproducible as well as practical.

Patrick and Turner[55] studied the distribution of various forms of manganese in waterlogged soils and the influence of redox potential on these forms. The fractionation scheme involved sequentially extracted (1) water-soluble fraction, (2) exchangeable fraction, (3) easily reducible fraction, and (4) residual forms of manganese. Water-soluble manganese was rapidly filtered through a 0.45-μm membrane filter under argon, and exchangeable manganese was then extracted with 1 N ammonium acetate under argon. Easily reducible manganese was then removed by five successive extractions with 1 N ammonium acetate containing 0.2 percent hydroquinone. A mixture of nitric and perchloric acids was used for digestion of the residual fraction. A significant finding of this study was the conversion of easily reducible manganic compounds to the exchangeable manganous form upon reduction. Residual manganese was not affected by flooding the soil.

In later studies related to manganese and iron transformations in a waterlogged soil, Gotoh and Patrick[40,41] extracted the water-soluble plus exchangeable fraction by three successive extractions with 1 N ammonium acetate adjusted to the pH of the soil suspension. The water-soluble fraction was determined on a separate sample by filtration through a 0.45-μm membrane filter. These two extractions were made under a nitrogen atmosphere to protect iron and manganese from atmospheric oxidation. The reducible fraction was extracted with a sodium dithionite-sodium citrate solution buffered with sodium bicarbonate according to the procedure proposed by Mehra and Jackson.[402] This procedure has been shown to be effective in removing free iron oxides from soils without appreciable dissolution of iron silicate clays. Kilmer[403] also employed a sodium dithionite solution to remove free iron oxides from soils. A modification of Mehra and Jackson's method and Kilmer's procedure was suggested by Holmgren,[404] which eliminated the use of the sodium bicarbonate buffer. This modification was found to improve the effectiveness of the extractant as well as reproducibility for Oxisols and Ultisols containing much iron.

McKeague and Day[215] have demonstrated that dithionite-citrate-bicarbonate extraction dissolved a large proportion of the crystalline iron oxides in addition to amorphous materials. They presented experimental data indicating that oxalic acid and ammonium oxalate was a better extractant for amorphous iron and aluminum as very little was removed from crystalline materials.

Gibbs[405] evaluated the transport of iron, nickel, copper, chromium, cobalt, and manganese in the Amazon (Brazil) and Yukon (Alaska) Rivers: (1) in solution, (2) by adsorption, (3) as metallic coatings, (4) in solid organic material, and (5) in detrital crystalline material. The fraction of these elements present in a solution form was determined in filtered water samples acidified with distilled hydrochloric acid to pH 1.5. The adsorbed cations on the suspended material were extracted with a 1 N magnesium chloride solution adjusted to pH 7. The metallic coatings on the suspended material were removed with a sodium dithionite-citrate solution, and the solid organic material was oxidized by sodium hypochlorite, pH 8.5. The residual suspension was then fused with lithium metaborate and dissolved in nitric acid for metal analysis.

Gibbs[405] showed that ammonium acetate, a widely used extractant for adsorbed ions, also dissolved or complexed the metallic coatings of the sediment particles and was thus not a good measure of adsorbed cations. Magnesium chloride, on the other hand, did not dissolve the metallic coatings. Results of this study indicate that the transport mechanism for various metal ions was similar in samples collected from the Amazon and Yukon Rivers. Copper and chromium were transported mainly in the crystalline solids; manganese, coatings; and iron, nickel, and cobalt were distributed equally between precipitated metallic coatings and crystalline solids. The amounts of metal ions related to the soluble and adsorbed phases were generally very small, except for chromium and manganese where more than 10 percent of the total was present in solution. Gibbs concluded from his data that the chemistry of metallic ions under study varied such that no sweeping generalizations can be made regarding the incorporation of these metals into various sediment fractions.

Engler et al.[401] recently have developed a selective extraction scheme to separate metals bound in various sediment phases based on their chemical and biological transformations in aerobic and anaerobic sediments. The sequential extraction procedure proposed includes separation of various metal ions into:

a. Interstitial water phase (centrifugation followed by vacuum filtration under a nitrogen atmosphere).

b. Exchangeable phase (extraction with 1 N ammonium acetate buffered to the sediment pH).

c. Easily reducible phase (extraction with acidified hydroxylamine hydrochloride according to the method of Chao[149]).

d. Organic phase (digestion at 95°C with 30 percent hydrogen peroxide acidified to pH 2.5 followed by extraction with 1 N ammonium acetate buffered to pH 2.5).

e. Moderately reducible phase (extraction with sodium citrate-dithionite according to the procedure developed by Holmgren[404]).

f. Residual phase (the dissolution of residues from previous extraction with hydrofluoric, perchloric, nitric, and hydrochloric acids as suggested by Smith and Windom[406]).

Engler et al.[401] suggested that the proposed extraction should be done on relatively undisturbed sediments avoiding drying or atmospheric oxidation.

FIXATION AND RELEASE OF TRACE METALS AND PLANT NUTRIENTS DURING DREDGING AND DISPOSAL OPERATIONS

The exchange of potentially toxic metals and plant nutrients between the solid and the liquid phases during dredging and disposal operations is a function of several processes such as complexation, ion exchange, adsorption and desorption reactions, mineralization and immobilization, precipitation, and other reactions which may occur simultaneously in the same system. Redox potential of the sediment-water system is a major factor known to influence these processes, and a discussion on the relationship of fixation and release to redox potential has been presented in earlier sections. The purpose here is to point out that the lack of understanding of the interacting effects of certain of these processes stems from two opposite views of the effect of oxidation-reduction potentials. One view is that the presence of sulfide under reduced conditions will precipitate toxic metals, resulting in a very low solubility, and that the conversion of sulfide to sulfate will release these metals under oxidizing conditions. The opposite thought is that toxic metals will be more soluble under reduced conditions due to the reduction of iron and manganese hydrous oxides which tend to sorb or coprecipitate toxic metals under oxidized conditions.[117]

Evidence supporting the fixation of trace metals under reduced conditions is presented by Holmes et al.[163] who found the oxygenated water of Corpus Christi Bay, Texas, to be more enriched in zinc and cadmium than the reduced bottom waters. In summer, when the harbor was stagnant, cadmium and zinc precipitated in the anoxic sulfide-bearing waters. However, in winter, the presence of dissolved oxygen resulted in the desorption of sulfide-bound metals. Similar results were reported by Lu and Chen[407] under laboratory conditions. Sediment samples from the Los Angeles Harbor were mixed with seawater and equilibrated in columns under a range of conditions from oxidized to very reduced. The trace metals cadmium, copper, nickel, lead, zinc, iron, and manganese were found to be released under oxidized conditions compared to the concentrations in the original seawater. Under reducing conditions, large amounts of iron and manganese were released into the water column. The authors concluded that metal release under oxidizing conditions was the result of soluble complex formation, most likely of metal carbonates, chlorides, and organic compounds. Under reducing conditions, iron and manganese were released as a result of dissolution of previously insoluble hydrous oxides, but other trace metals were immobilized by the formation of sparingly soluble sulfides. The desorption of trace metals associated with sewage effluents upon mixing and dilution with the seawater under aerobic conditions was shown by Hendricks and Young.[408] They attributed these releases to the oxidation of organic particulates containing the metals, the oxidation of metal sulfides, surface desorption of the metals upon dilution, and soluble complex formation of both inorganic and organic compounds.

Evidence indicating that trace metals are more soluble under reducing conditions has been shown by several workers. Brooks et al.[409] found iron and nickel to be enriched in interstitial waters taken from reduced sediments in comparison to oxidized interstitial waters at the sediment surface. Windom[101] interpreted the observed decrease of iron, copper, and zinc at a dredge discharge pipe to be the effects of immediate oxidation and precipitation of iron and the scavenging effects of iron on trace metals resulting in their precipitation along with the freshly precipitated iron. The subsequent increase in trace metal concentrations in the water with time was explained by the reduction of ferric hydroxide precipitates and the production of ferrous sulfide thus releasing trapped metals to the water.

Dredging of waterways (rivers, bay areas, and lakes) normally results in the transport of bottom sediments from an oxygen-deficient, reduced environment to an environment in which oxygen is at least temporarily available. The changes in physicochemical and biological conditions of the sediments induced by dredging may influence the activity of toxic metal ions and plant nutrients. Since the behavior of various ions in the sediments is simultaneously affected by a variety of processes, the direction of change will largely depend on the dominating processes.

The distribution of various metal ion species in natural fresh waters is generally governed by oxidation-reduction reactions, pH, and the solubility of their carbonates, oxides, hydroxides, and sulfides.[43] Silicates may also exert some influence on the concentration of metal ions at high pH. The effects of these systems on the equilibrium speciation of various trace elements are summarized in Table 1. The computations indicate that under oxidizing conditions, free ions tend to dominate at low pH, and carbonate, oxide, hydroxide, and silicate solids precipitate at higher pH values. In reducing environments, insoluble sulfide species dominate. From Table 1, it is apparent that trace metals are either present as free ions or precipitated with superabundant ligands where the solubility of the precipitates regulates the concentration of free ions. The exception to this general rule under the conditions of the computations is the presence of soluble complexes of copper carbonate, mercuric chloride, and mercuric sulfide, which may exist in natural waters.

Table 1

Predominant Trace Metal Species under All Conditions of Computation in the Models (Morel et al.[43])

Metal	Species Accounting for more than 90%	Species Accounting for a few percent
Fe	$Fe(OH)_2^+$, $FePO_4(s)$, $Fe(OH)_3(s)$ $FeCO_3(s)$, $FeS(s)$, $FeSiO_3(s)$	
Mn	Mn^{++}, $MnCO_3(s)$, $MnO_2(s)$ $MnS(s)$	$MnHCO_3^+$, $MnSO_4$, $MnCl^+$
Cu	Cu^{++}, $Cu_2CO_3(OH)_2(s)$ $CuCO_3$, $Cu(OH)_2(s)$ $CuS(s)$	$CuSO_4$
Cd	Cd^{++}, $CdCO_3(s)$, $Cd(OH)_2(s)$ $CdS(s)$	$CdSO_4$, $CdCl^+$
Zn	Zn^{++}, $ZnCO_3(s)$, $ZnSiO_3(s)$ $ZnS(s)$	$ZnSO_4$, $ZnCl^+$
Hg	$HgCl_2$, $Hg(OH)_2(s)$ $HgS(s)$, $Hg(liq)$, HgS_2^{2-}, $Hg(SH)_2$	
Pb	Pb^{++}, $PbCO_3(s)$, $PbO_2(s)$ $PbS(s)$	$PbSO_4$, $PbCl^+$

Notes:

The species of each metal are listed in the order they are found with increasing pH. The species listed in the top line for each metal are for oxidizing conditions and the bottom line refers to a reducing environment.

Morel et al.[43] computed the equilibrium concentration of various trace metals for a well-oxygenated model and a reducing model for average concentrations of ligands found in natural waters (See Tables 2 and 3, respectively). It should be pointed out that the calculations were based on a pure inorganic system where organic complexation of metal ions was not considered. They studied the interactions between various metal ions and concluded that the inorganic constituents of fresh natural waters were relatively independent of each other.

Morel et al.[43] also investigated the effects of selected organic ligands introduced into a pure inorganic system on the solubility of various metal ions. Table 4 illustrates the addition of four organic ligands - citrate, glycine, nitrilotriacetate (NTA), and cysteine - to an inorganic system where computations were made under oxidizing conditions (See Table 2). A comparison between Table 2 and Table 4 emphasizes the importance of organic ligands in keeping metals in solution. Carbonates of cadmium and copper which precipitated in the pure inorganic system were not present as solid species after the introduction of organic ligands in the system. Also, the addition of organics partitioned the total metals into a larger number of relatively important complexes. The total concentration of various metal ions used in computations was the same for both inorganic system (Table 2) and for the system containing organic ligands (Table 4), the concentration of free ions in solution for certain metals decreased as a result of adding organics to the system. This phenomenon of decreasing concentration was more pronounced in the case of mercury, lead, and copper. The concentration of free zinc and cadmium in solution was only slightly affected by organics, and no effect was observed in manganese, iron, calcium, magnesium, and sodium. A decreased concentration of

Table 2

Results of an Equilibrium Computation for
Oxidizing Conditions: pε = 12, pH = 7
(Morel et al.[43])

Metal			Ligand				
			Carbonate CO_3	Sulfur S	Chlorine Cl	Phosphate PO_4	Hydroxide OH
	Total→ Conc. ↓		3.00	4.50	3.50	5.00	--
		Free Conc.→ ↓	6.41	4.60	3.50	11.84	7.00
Calcium, Ca	3.00	$\underline{3.02}$	$\underline{4.81}$	5.32	--	7.56_s	8.52
Magnesium, Mg	3.50	$\underline{3.51}$	$\underline{5.40}$	5.71	--	7.55	7.81
Sodium, Na	3.50	$\underline{3.50}$	8.61	7.30	--	--	--
Iron, Fe	5.00	15.40	--	17.20	17.90	15.44	7.40_s
Manganese, Mn	5.50	10.00	11.41	12.30	12.30	12.94	13.20_s
Copper, Cu	6.00	$\underline{6.70}$	$\underline{6.40}_s$	9.00	9.50	9.24	7.69
Cadmium, Cd	6.00	$\underline{7.19}$	10.50_s	9.50	8.09	15.63	9.29
Zinc, Zn	7.00	$\underline{7.01}$	--	9.31	9.21	10.45	9.61
Mercury, Hg	9.00	16.20	--	18.41	9.00	--	25.70
Lead, Pb	7.00	$\underline{7.69}$	--$_s$	9.70	9.39	--	$\underline{7.89}$

Notes: Numbers are negative logarithms of molar concentrations in solution. The presence of a solid is indicated by s. A blank signifies the absence of a computable species. Numbers underlined indicate species or solids that amount to more than 1% of the total metal.

Table 3

Results of an Equilibrium Computation
for Reducing Conditions:
$p\varepsilon = -4$, pH = 7 (Morel, et al.[43])

Metal	Total Conc. ↓	Free Conc. ↓	CO_3	S	Cl	PO_4	OH
	Total→		*3.00	4.50	3.50	5.00	--
		Free Conc.→	6.41	7.23	3.50	11.84	7.00
Ca	3.00	$\underline{3.01}$	$\underline{4.81}$	7.95	--	7.56_s	8.51
Mg	3.50	$\underline{3.51}$	$\underline{5.40}$	8.34	--	7.55	7.81
Na	3.50	$\underline{3.50}$	8.61	9.93	--	--	--
Fe	5.00	8.17	--	13.10_s	10.67	24.21	9.77
Mn	5.50	5.52	$\underline{6.93}$	10.45	7.82	8.46	8.72
Cu	6.00	$\underline{27.07}$	26.77	32.00_s	29.87	29.61	28.07
Cd	6.00	14.87	18.17	19.80_s	15.76	23.31	16.97
Zn	7.00	15.07	--	20.00_s	17.27	18.51	17.67
Hg	9.00	42.47	--	$\underline{10.62}_s$	35.27	--	--
Pb	7.00	19.47	--	24.10_s	21.17	--	19.67

Notes:

Numbers are negative logarithms of molar concentrations in solution. The presence of a solid is indicated by s. A blank signifies the absence of a computable species. Numbers underlined indicate species or solids that amount to more than 1% of the total metal.

Table 4

Results of an Equilibrium Computation for Oxidizing Conditions (pε = 12, pH = 7) for a System Containing Four Organic Ligands (Morel et al.[43])

Metal	Total Conc. ↓	Free Conc. ↓	CO_3	S	Cl	PO_4	*CIT	*GLY	*NTA	*CYST	OH
	Total→		†3.00	4.50	3.50	5.00	5.00	5.00	5.00	5.00	--
		Free Conc. →	6.41	4.60	3.50	11.84	17.68	8.10	10.06	11.07	7.00
Ca	3.00	$\underline{3.02}$	$\underline{4.81}$	5.32	--	7.55_s	5.90	9.92	5.28	--	8.52
Mg	3.50	$\underline{3.51}$	$\underline{5.40}$	5.71	--	7.54	7.09	10.01	$\underline{6.77}$	--	7.81
Na	3.50	$\underline{3.50}$	8.61	7.30	--	--	--	--	11.26	--	--
Fe	5.00	25.40	--	16.90	17.80	15.44	$\underline{6.68}$	14.00	$\underline{5.73}$	$\underline{5.55}$	7.40_s
Mn	5.50	10.00	11.41	12.30	12.30	12.94	12.38	15.50	11.26	16.37	13.20_s
Cu	6.00	10.05	9.75	12.35	12.85	12.58	$\underline{7.93}$	9.27	$\underline{6.01}$	--	11.05
Cd	6.00	$\underline{7.46}$	10.76	9.76	8.36	15.89	9.34	10.56	$\underline{6.02}$	--	9.56
Zn	7.00	$\underline{8.85}$	--	11.16	11.05	12.29	13.34	11.01	$\underline{7.01}$	$\underline{8.92}$	11.45
Hg	9.00	31.95	--	34.16	24.75	--	--	27.63	26.50	$\underline{9.00}$	57.21
Pb	7.00	10.20	--	12.21	11.90	--	11.31	12.60	$\underline{7.06}$	$\underline{7.88}$	10.40

*CIT = citrate, GLY = glycine, NTA = nitrilotriacetate, CYST = cysteine. †Numbers are negative logarithms of molar concentrations in solution. The presence of a solid is indicated by s. A blank signifies the absence of a computable species. Numbers underlined indicate species or solids that amount to more than 1% of the total metal.

soluble sulfide and chloride complexes of some metals were also observed after the addition of organics to the system. These authors suggested that under reduced conditions, a large concentration of ferrous iron may precipitate most of the sulfide and keep other trace metals from precipitating. Several other researchers[21,25,60,144,148,396] have also discussed the important role that organics play in complexing trace metal ions and keeping them in solution in natural waters. These reports have been discussed earlier under appropriate metals.

It is possible that the interaction of various ionic species present in a sediment-water system disturbed by dredging may result in minimum changes in the concentration of trace metals. Numerous studies reported in the literature on the effects of dredging on trace metal availability indicate that the damage to water quality or biological life is minimal or nonexistent in most of the cases.

May[256,410] has studied the effects of dredging operations on water quality in Alabama estuaries. In the study reported in 1973,[410] hydraulic and shell dredging and open-water dredged material disposal had little significant immediate effect on Mobile Bay water quality. About 96 percent of the sediment discharged by dredges settled very rapidly and was transported by gravity along the bottom as a separate flocculated density layer. Potentially harmful components of the mud such as heavy metals and pesticides were not released to the water column. May suggested that under such conditions, biological uptake of potentially deleterious components of the mud would not be expected.

In a second study, May[256] found that dredging, by confined dredged material disposal, did not degrade water quality in Chickasaw Creek, Alabama. The quality of water returned to the waterway was better than that in the stream before or during dredging due to an increase in dissolved oxygen and removal of solids and hydrogen sulfide. There was no significant increase in trace metals in the return waters from the confined dikes. Before and during dredging, bottom waters in the area had zero dissolved oxygen and surface waters ranged from 0 to 2.6 mg/l. At the dredged material area overflow where the supernatant water was returned to the creek, dissolved oxygen ranged from 4.2 to 5.2 mg/l. Trace metals present in the dredged sediment included lead concentrations up to 180 µg/g, zinc up to 1900 µg/g, cadmium up to 6 µg/g, copper up to 293 µg/g, and mercury up to 2 µg/g. However, these metals were not released into the water in a soluble form as levels in the return water were not significantly different from levels in the stream. Values reported for the concentration of trace metals in the stream were: lead, 20 to 200 µg/l; zinc, 20 to 40 µg/l; cadmium, <10 to 20 µg/l; copper, 10 to 50 µg/l; and mercury, <1.0 to 1.6 µg/l. May[256] proposed that the lack of significant changes in water quality following dredging and dredged material disposal may be due to the following possibilities: (1) although chemicals in the mud are influenced by redox conditions, the processes are either too slow or too quickly reversible to allow sediment constituents to become dissolved where dredged material is deposited in confined areas or in open water; (2) the materials (trace metals and other ions) are so strongly adsorbed to inorganic or organic matter that reducing conditions have little effect on their release; and (3) the materials are largely in refractory forms such as lignins, sulfide compounds, organic complexes, hydroxides, or in the elemental state, which are not readily soluble under conditions created by dredging. May suggested that these possibilities should be examined under rigidly controlled laboratory conditions.

Ritchie and Speakman[298] studied the effects of settling time of dredged sediments on the quality of water in Ashtabula and Fairport Harbors in Ohio and in confined disposal facilities. A settling time of 1 to 40 hours produced 95- to 99-percent reductions in the concentrations of most pollutants tested. Total phosphorus and Kjeldahl nitrogen were reduced from 10 and 700 mg/l, respectively, to less than 1 and 75 mg/l after 1 hour. Heavy metals present in potential toxic levels of up to 260 mg/l were reduced to below 0.3 mg/l after 1 hour and to 0.01 mg/l after 40 hours. Heavy metals studied were cadmium, chromium, zinc, mercury, lead, arsenic, copper, and nickel. The levels of zinc, cadmium, and chromium in the initial dredging sample were potentially toxic to aquatic organisms.

Windom[101] reported that the concentrations of heavy metals (iron, cadmium, copper, lead, mercury, and zinc) in upper Mobile Bay sediments appeared to be primarily a function of natural processes such as runoff which may result in the greater concentrations of metals southward. Dredging activities tended to accelerate this process to a small degree. Dispersion of dredged sediments from the Mobile Bay ship channel was not followed by metal release of any significant quantity except possibly a slight release of zinc and iron. Of the six metal levels studied, cadmium, mercury, and zinc were reported to be above EPA criteria in bay sediments, reflecting possible input from industries in the area.

Windom[411] found in his work on the environmental effects of dredging, that the only place where water quality problems are likely to occur during pipeline dredging was at the point of discharge from the dredged material area. He reported that the slurry taken from the pipeline initially showed lower soluble heavy metals than did preceding conditions at the dredging site.

The soluble lead, copper, and iron levels, however increased to levels above predredging values after 15 days of storage in large polypropylene containers. Windom attributed the initial decrease in heavy metal concentrations to the scavenging effects of ferric hydroxide organic complexes. Upon reduction, these stable organic complexes diffused back into the water column, resulting in the release of trapped metals. Zinc and mercury decreased in concentration with time of storage and may reflect uptake by micro-organisms. Free copper, Cu^{2+}, showed no change during or after dredging.

Westley et al.[412] revealed that neither clamshell nor pipeline dredging in the Southern Puget Sound Harbor had any measurable effect on water quality. However, the disposal of dredged material increased suspended solids and turbidity. Barge dumping caused very localized and short-term increases in ammonia, biological oxygen demand (BOD), and organic phosphate. No major changes occurred in the benthic community at the disposal site in the case of pipeline dredging, while in the barge disposal sites, a decrease in abundance and diversity of macroscopic benthic organisms was observed.

Slotta et al.[413] reported the effects of hopper dredging and in-channel disposal in Coos Bay, Oregon. The volatile solids of the dredged material decreased from 10 percent before dredging to 8 percent after disposal, indicating that organics were being dispersed during suspension. Total sulfides in the sediments ranged between 0 and 600 µg/g, but no measurable free sulfides were found at any sites either before or after dredging. The absence of free sulfides was attributed to the insoluble iron sulfide formation in the presence of sufficient ferrous iron at the sediment-water interface. Heavy metals were not investigated in this work.

Mudroch and Cheam[414] monitored changes in the pore water chemistry at the site of a trial dredged material disposal area in Lake St. Clair, Mitchell Bay, Ontario, for a period of 8 months after disposal in the test bay had ceased. The data collected during this period showed slight changes in the chemical composition of the pore water. The concentrations of aluminum, zinc, cadmium, lead, and copper in the pore water and the Mitchell Bay lake water were almost identical. The sampled pore water had a higher content of phosphorus, nitrogen, iron, organic carbon, mercury, and manganese relative to the surrounding Mitchell Bay lake water. The iron and phosphorus contents appeared to depend on the pH of the pore water, and the values increased markedly as pH values dropped. The authors concluded that the high phosphorus content found in the water column after dredging activities was related to the higher manganese and iron content in the water column. It was suggested that oxides and hydroxides of iron and manganese play an important part in controlling phosphorus concentrations in the sediment pore water. The quantities of nutrients released were negligible and had no adverse effects on water quality.

In a recent study of the San Francisco Bay dredged sediments,[9] it was found that in simulated dredging studies, larger concentrations of cadmium, copper, lead, and zinc were released to the water column under oxygen-rich conditions than under oxygen-deficient conditions. Iron acted in the opposite manner with more iron found in solution under reduced conditions. The greater concentrations under oxidized conditions were attributed to the release of trace metals bound to the sulfide phases upon oxidation. It was noted that the bay sediments contained 1000 to 3000 μg/g sulfide and thus represented a reduced environment. Under oxidized conditions, larger releases of cadmium and zinc were measured as salinity increased. A similar effect was observed in the case of iron under reduced conditions. Two possible mechanisms proposed which may explain this observation were the formation of soluble inorganic complexes with the increased level of chlorides, carbonates, and sulfates, or the release of trace metals bound to ion exchange sites with the greater cation competition of more saline waters. It was recommended that more study is needed to determine the amount of oxidation that actually takes place during dredging and disposal to fully evaluate the environmental effects.

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