Metal Biogeochemistry in Surface-Water Systems—

A Review of Principles and Concepts

Cover.—Symbols of the elements discussed in this report are shown. The triangular background represents three-phase partitioning of the elements in aquatic systems—the soluble phase, the suspended sediment phase, and the bottom sediment phase.

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METRIC CONVERSION FACTORS

For readers who wish to convert from the metric system of units to the inch-pound system of units, the conversion factors are listed below:

Multiply	By	To obtain
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
millimeter (mm)	0.03937	inch (in.)
micrometer (μm)	3.937×10^{-5}	inch (in.)
gram (g)	0.03527	ounce (oz)
kilogram (kg)	2.205	pound (lb)
megagram (Mg)	1.102	ton, short (t)
milligram (mg)	0.00003527	ounce (oz)
microgram (μg)	3.527×10^{-8}	ounce (oz)
square centimeter (cm^2)	0.1550	square inch (in^2)
square meter per gram (m^2/g)	305.0	square foot per ounce (ft^2/oz)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
gram per cubic centimeter (g/cm^3)	6.243×10^{-5}	pound per cubic foot (lb/ft^3)
milligram per liter (mg/L)	1.0	parts per million (ppm)
microgram per liter (μg/L)	1.0	parts per billion (ppb)
microgram per gram (μg/g)	1.0	parts per million (ppm)
milligram per kilogram (mg/kg)	1.0	parts per million (ppm)
microgram per kilogram (μg/kg)	1.0	parts per billion (ppb)
degree Celsius (° C)	$1.8 \times$ (° C + 32)	degree Fahrenheit (° F)

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Abstract

Metals are ubiquitous in natural surface-water systems, both as dissolved constituents and as particulate constituents. Although concentrations of many metals are generally very low (hence the common term "trace metals"), their effects on the water quality and the biota of surface-water systems are likely to be substantial. Biogeochemical partitioning of metals results in a diversity of forms, including hydrated or "free" ions, colloids, precipitates, adsorbed phases, and various coordination complexes with dissolved organic and inorganic ligands.

Much research has been dedicated to answering questions about the complexities of metal behavior and effects in aquatic systems. Voluminous literature on the subject has been produced. This paper synthesizes the findings of aquatic metal studies and describes some general concepts that emerge from such a synthesis. Emphasis is on sources, occurrence, partitioning, transport, and biological interactions of metals in freshwater systems of North America. Biological interactions, in this case, refer to bioavailability, effects of metals on ecological characteristics and functions of aquatic systems, and roles of biota in controlling metal partitioning.

This discussion is devoted primarily to the elements aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, and zinc and secondarily to cobalt, molybdenum, selenium, silver, and vanadium. Sources of these elements are both natural and anthropogenic. Significant anthropogenic sources are atmospheric deposition, discharges of municipal and industrial wastes, mine drainage, and urban and agricultural runoff.

Biogeochemical partitioning of metals is controlled by various characteristics of the water and sediments in which the metals are found. Among the most important controlling factors are pH, oxidation-reduction potential, hydrologic features, sediment grain size, and the existence and nature of clay minerals, organic matter, and hydrous oxides of manganese and iron. Partitioning is also controlled by biological processes that provide mechanisms for detoxification of metals and for enhanced uptake of nutritive metals. Partitioning is important largely because availability to biota is highly variable among different phases. Hence,

accumulation in biological tissues and toxicity of an element are dependent not only on total concentration of the element but also on the factors that control partitioning.

INTRODUCTION

During the past several decades, there has been a growing awareness of widespread and often serious environmental problems that have resulted from pollution by metals. Problems posed by elevated concentrations of toxic metals in the aquatic environment include hazards to human health and varying degrees of toxicity to most plant and animal species. Some species may be so severely affected that they are eliminated from contaminated ecosystems. Food web structures of entire communities thus may be significantly altered. There also is the possibility of accumulation of metals in biological tissues (bioaccumulation) through various levels of the food chain and of latent effects resulting from gradual bioaccumulations.

Stimulated by this awareness of the metal contamination problem, a great deal of research in the water resources area has been directed at investigations of metals in aquatic systems. Most of the research has dealt with metals of known or suspected toxicity, although there has also been a considerable amount of interest in the nutritive value of metals. Some elements that are toxic at high concentrations may have nutritive value for aquatic biota in unpolluted systems containing very low concentrations of those elements.

Aquatic metal investigations are numerous and diverse. The diversity of research sites, objectives, and study designs that have been applied in these investigations has produced an almost equal variety in results. Therefore, it is difficult to review aquatic trace metal literature and to extract general rules that meaningfully apply to a variety of aquatic systems. Perhaps the most unquestionable generality is that the biogeochemistry of metals in natural water systems is extremely complex. A knowledge of trace metal chemistry is, in fact, only a beginning to acquiring some understanding

of the complexity of trace metals in natural waters. Biological and physical processes exert an important influence over the forms in which the elements occur and the pathways that lead to those forms. It has become apparent that biota not only are affected by the presence of toxic metals but also have a great deal of control over the concentrations and toxicities of those same metals in the aquatic environment.

Considerably more research is needed to improve our understanding of the complexities of aquatic metal biogeochemistry. As in any scientific pursuit, however, the investigators undertaking such studies need to be familiar with what has already been done. The primary purpose of this report is to help fill that need.

Purpose and Scope

This report provides a synthesis of the current (1986) state of our understanding of metals in surface-water systems. It is intended to aid the reader in identifying important concepts and principles that have emerged from the diverse collection of published research in this area. It also identifies and discusses some findings that are controversial—those where the results or conclusions of some studies differ from others—and offers possible explanations for the apparent inconsistencies.

Recent publications have already provided many syntheses of aquatic metal biogeochemistry research. Notable among these are books by Jarvis (1983), Forstner and Wittmann (1981), and Salomons and Forstner (1984). These monographs provide a comprehensive coverage of examples that document principles developed over the past quarter century of research. Shorter papers, such as that of Komarovskiy and Polishchuk (1981), provide information on more specific topics. Thorough discussions of general water chemistry concepts, including principles of trace metal behavior in natural waters, were written by Stumm and Morgan (1981) and Hem (1985). Kuwabara and Helliker (1988) discussed various concepts of trace contaminant transport in streams and provided extensive reference citations. Leland and Kuwabara (1986) produced a recent summary of current knowledge of toxicology of trace metals. Review papers published annually in the *Journal of Water Pollution Control Federation* are good sources of bibliographic information. Three papers in the 1985 review issue (Lathrop and Davis, 1985; Pritchard, 1985; Roush and others, 1985) contained numerous citations of literature dealing with metals in surface waters.

This paper is not intended to provide a complete bibliography of trace metal research, which would only duplicate other readily available reviews. Instead, I hope that this discussion will complement other publications that provide thorough annotated bibliographies. The focus is on concepts rather than specific studies. Of course, the concepts have evolved through analysis and reanalysis of diverse study results, and pertinent references are cited in the subsequent discussion of these concepts.

Nearly all the publications referenced in this paper appeared in readily available technical journals, most of them within two decades prior to this writing. Recent studies, although not necessarily more significant than earlier studies, are more likely to characterize the current status of knowledge. Reports having limited distribution were generally avoided unless judged especially significant.

Emphasis in this paper is on freshwater systems, both lotic and lentic. Considerably more work has been done on marine and estuarine systems than on freshwater environments. While studies of marine and estuarine systems are by no means ignored in this review, reference to them is limited to cases whose results contribute substantially to our understanding of metals in freshwater, as well as in marine systems.

Terminology and Elements Included

The terms "trace metals," "toxic metals," "trace elements," "heavy metals," and simply "metals" are often used interchangeably. I acknowledge that such usage is rather unfortunate because it leads us to ignore the slight distinctions among all of the sets of elements that these terms represent. However, maintaining total accuracy in terminology becomes cumbersome, especially because some of the elements under study, such as arsenic and selenium, are nonmetals. For simplicity, the term "metals" will be used in this review to include a group of elements that are of greatest interest and concern in aquatic systems. A list of these elements and their abundances in the Earth's upper crust is given in table 1. Some other elements not on the list are considered occasionally in this report, primarily for comparison with elements of primary or secondary focus.

Table 1. Principal elements discussed in this report and their abundances in the Earth's crust

Element	Abundance in Earth's upper crust (micrograms per gram)
Aluminum	[1]84,700
Arsenic	[2]2.5
Cadmium	[2].14
Chromium	[1]35
Cobalt	[1]10
Copper	[1]25
Iron	[1]35,000
Lead	[1]15
Manganese	[1]600
Mercury	[2].11
Molybdenum	[2]3.8
Nickel	[1]20
Selenium	[2].12
Silver	[2].07
Vanadium	[1]60
Zinc	[1]52

[1]Taylor and McLennan, 1981.
[2]Turekian and Wedepohl, 1961.

Acknowledgments

SOURCES OF METALS IN THE AQUATIC ENVIRONMENT

Metals are common in the Earth's crust, as well as in products and wastes of human activity. Hence, the sources of metals in the aquatic environment are both natural and anthropogenic.

Aluminum and iron are among the most common elements in the Earth's crust (table 1). Erosion of materials from the watershed substrate supplies large quantities of these elements as background levels in natural waters. In the case of aluminum, anthropogenic sources are generally assumed to supply insignificant quantities of the metal, relative to amounts that are already in the system due to natural processes. This characteristic makes aluminum a useful reference metal in assessing the degree of pollution of other elements whose sources are primarily anthropogenic (Bruland and others, 1974; Forstner and Wittmann, 1981; Thomas and others, 1984). Concentrations of elements having anthropogenic sources may be normalized to concentrations of aluminum to identify changes over time due to new sources. Considerable care must be used in applying this procedure, however, especially when there are pH changes that may mobilize significant amounts of aluminum. Titanium, which also may be used as a reference metal (Forstner and Wittmann, 1981), has the advantage of being less subject to mobilization under low pH conditions.

This discussion is devoted primarily to the elements aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, and zinc and secondarily to cobalt, molybdenum, selenium, silver, and vanadium. Sources of these elements are both natural and anthropogenic.

Metals of anthropogenic origin may be transmitted to surface waters through various pathways, including atmospheric deposition, localized industrial and municipal discharges (point sources) of wastewaters or byproducts, drainage from mining areas (which may be either point or nonpoint sources), and urban and agricultural surface-water runoff (nonpoint sources). Documentation of some of these types of input is limited, but for other types, it is quite abundant.

Long-term records of contaminant inputs to lakes are commonly contained in sediment cores (Feltz, 1980). A number of investigators have taken advantage of this occurrence to describe trends of metal inputs to lakes (Nriagu and others, 1979; Dillon and Evans, 1982; Davis and others, 1983; Evans and others, 1983; Mudroch, 1983; Ochsenbien and others, 1983; Ouellet and Jones, 1983; Thomas, 1983; Thomas and others, 1984). Typically, the cores contain concentration peaks at or near the surface in recent sediments. This condition is nearly always interpreted as a reflection of increasing anthropogenic inputs in recent decades.

Atmospheric Deposition

Numerous investigations have shown that atmospheric deposition is an important source of metals to lakes. Most notable of the airborne contaminants is lead, due to its widespread discharge into the atmosphere from exhausts of gasoline engines. The atmospheric pathway is most likely to be significant for large, shallow lakes and for reservoirs near urban areas. Three factors contribute to the importance of atmospheric input in such systems: (1) proximity to sources of atmospheric pollutants, (2) relatively high ratios of lake-surface area to lake volume, and (3) relatively low ratios of watershed area to lake-surface area.

Sedimentary records from lakes in southern Ontario, Canada, were used by Dillon and Evans (1982) to examine the importance of various sources of lead in the lakes. The elevated lead levels in the upper layers of the sediments of all of the lakes indicated the effects of anthropogenic lead inputs in recent years. However, little variation among lakes was found, regardless of factors such as size of watershed, ratio of watershed to lake-surface area, or lake residence time. It was concluded that the uniform input rate could be explained only if the primary entry pathway was atmospheric. Where spatial differences did occur, they were attributed to redistribution of sediments. Later work by the same group (Evans and others, 1983) gave similar results for zinc and cadmium.

The importance of atmospheric deposition as an input pathway for lead, zinc, and cadmium was corroborated in a similar study by Thomas and others (1984). Enrichment factors for metals were calculated by dividing surface sediment concentrations by background and normalizing to aluminum concentrations. Very little enrichment of copper was found. Arsenic enrichment was attributed to agricultural use in the basin. However, substantial enrichments of lead,

zinc, and cadmium were observed, and these enrichments approximately corresponded to atmospheric fluxes previously determined for the area. Atmospheric flux of mercury has been shown to be significant in coastal waters (Windom and others, 1975), and atmospheric transport may also play an important role in redistribution of mercury to inland waters.

Lakes that are in geologically similar watersheds and in the same general vicinity are not necessarily similar in atmospheric metal inputs. The differences may be due to local anthropogenic activities. These effects may be sorted out by correcting for bedrock (background) contributions to the metal loading (Davis and Galloway, 1981).

The Great Lakes are subject to considerable influence from atmospheric deposition. Because of their size, their watershed area to lake-surface area ratios are relatively low,

Figure 1. Chromium concentrations in river bed sediments of the Schuylkill River, Pa. A, Location of the main stem of the Schuylkill River. B, Relation of bed-sediment chromium concentrations to river mile (from Stamer and others, 1985, p. A20).

and approximately 50 percent of the water entering the lakes falls as precipitation directly on their surfaces. Schmidt and Andren (1984) examined the results of numerous studies that produced atmospheric loading estimates for metals in the Great Lakes and found that there was a great deal of discrepancy. Such discrepancy may have been partially attributable to real spatial and temporal differences, but whatever the cause, it precluded the possibility of precise determinations of atmospheric deposition of the metals. However, rough estimates did allow the authors to conclude that more than half of the zinc and 90 percent of the lead entered the lakes through atmospheric pathways.

One of the studies on the Great Lakes (Sievering and others, 1981) indicated the importance of dry deposition as a source of metals to the lakes. At least 40 percent of the total lead input, 20 percent of the total zinc input, and 15 percent of the total iron input were attributed to dry deposition alone. These results suggest some urgency for further examination of dry deposition and wet deposition separately. Studies of dry deposition have been hampered by difficulties in analyzing and interpreting dry deposition data (Schmidt and Andren, 1984).

Atmospheric deposition may cause enrichment at the surface microlayer of natural waters (Elzerman, 1981; Barnes and others, 1982). Dissolved and particulate matter may accumulate in the surface microlayer [0.01- to 1.0-mm (millimeter) thickness] at higher concentrations than in the adjacent bulk water. All material directly deposited on water bodies from the atmosphere must obviously contact this layer. In doing so, the material may be retained there, at least temporarily causing surface microlayer enrichment. Surface enrichment of metals, often retained by surface tension or organic slicks, has been documented in seawater (Piotrowicz and others, 1972; Hunter, 1980; Hardy and others, 1985), but little is known about surface enrichment in freshwater systems. Metal enrichment in this unique environment (Hardy, 1982) may induce effects that are distinct from those in the bulk solution.

Other investigations in various parts of the country have shown quite consistently the importance of atmospheric deposition as a source of metals in lakes, especially as a source of lead. Rainwater in Florida contained elevated concentrations of lead near the urban areas of the southern part of the State (Irwin and Kirkland, 1980). An oligotrophic lake in northern Wisconsin had appreciable lead accumulation in its sediments, mostly attributable to atmospheric inputs (Talbot and Andren, 1984). In a subalpine catchment in the northern Cascade Range in Washington, more than 50 percent of lead, copper, arsenic, and other trace metals could be accounted for by atmospheric deposition (Dethier, 1979).

The widespread occurrence of lead emissions in the atmosphere near aquatic systems is an important consideration in selecting sampling sites for monitoring studies. Care should be taken to avoid locating sampling sites near highway bridges or sites of airborne emissions from industry. Unlike
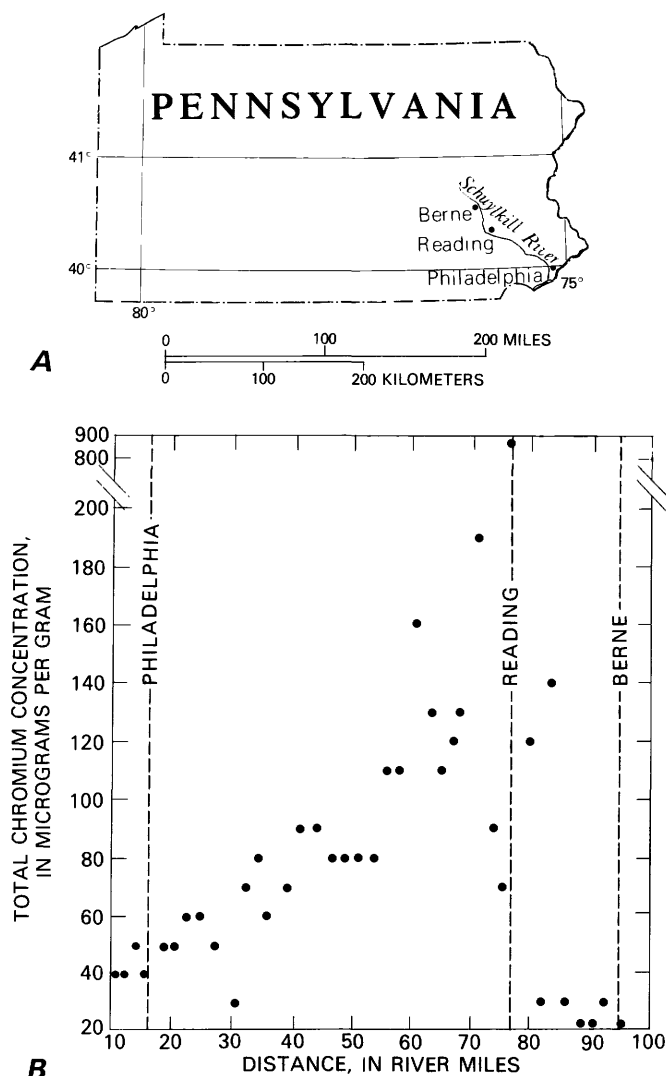
discharges directly into the streamflow, atmospheric transport may affect metal concentrations both upstream and downstream of the source.

Industrial and Municipal Point Sources

Because anthropogenic sources account for many occurrences of elevated metal concentrations in natural waters, investigations of the biogeochemistry of metals are often carried out in systems where such sources are common. However, very few of these studies have actually identified the sources of the metals. The studies tend to be oriented toward descriptions of behavior of the elements once they are in the system, rather than toward identification of their sources. In the few cases where source monitoring has been conducted, results show quite consistently that, for both water and sediments, concentrations are appreciably higher near the point source and they diminish rapidly as distance from the source increases.

The most extensive documentation of industrial and municipal point-source contamination has been from studies of the Rhine River in Europe (Salomons and Forstner, 1984). Metal "mapping" in the sediments showed marked increases in cadmium, lead, zinc, mercury, copper, and chromium in a downstream direction. Cadmium exhibited the most dramatic increases, reaching concentrations more than 100 times natural background values. Virtually all of these increases were associated with industrial activity along the river.

Stamer and others (1985) found elevated concentrations of chromium and other metals in the sediments of the Schuylkill River, Pa., just downstream of effluent discharges. Figure 1 shows the relation of chromium concentrations to river mile.[1] Reading, at river mile 76, is an industrial area that seems to be the major site of chromium input to the river. Metal concentrations gradually decreased with distance farther downstream. Profiles for other metals, particularly copper and nickel, were similar, although their concentrations upstream of Reading were higher than those of chromium. Both natural and anthropogenic sources of copper and nickel appeared to be significant.

Wiener and others (1984) reported that Upper Mississippi River concentrations of several metals, particularly cadmium, lead, and mercury, tended to be highest at or near the Twin Cities metropolitan area. However, various other inputs in the system were indicated by scattered concentration peaks both upstream and downstream of the Twin Cities.

A number of investigations in the Great Lakes indicated that industrial and municipal effluents are important sources of metal inflow to the lakes. Examination of mercury concentrations in Lake Ontario sediments by Thomas (1972) showed increased accumulation relating to industrial pollution that dated back to the turn of the century. Although

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[1]River mile = distance of 1 mile, measured upstream from the river mouth, along a line located in the established course of the stream.

there was a tendency for greater concentrations to occur in fine-grained sediments near the center of the lake, high concentrations [up to 2,000 μg/kg (micrograms per kilogram)] were found in nearshore areas. These nearshore concentrations indicate that the principal inflow was from the Niagara River. A more generalized study (Fitchko and Hutchinson, 1975) provided data for 10 metals from the mouths of 116 tributaries to the Great Lakes system. Most of the tributaries that drained urban-industrial areas had elevated metal concentrations, while most of the relatively undisturbed tributaries did not. Also, concentrations tended to be higher in tributaries of the lower Great Lakes (Erie, Ontario, and Michigan) than in the upper Great Lakes (Superior and Huron), correlating to proximity of urban industrial activity. Nriagu and others (1979) calculated annual inputs and sediment retention of cadmium, copper, lead, and zinc in Lake Erie. The sedimentary records showed evidence of high anthropogenic inputs. The authors pointed out that sewage discharges, in particular, were an important source of metals to the lake.

In a study of Chesapeake Bay, Helz (1976) found that the relative importance of natural and anthropogenic sources varied among different metals and among different parts of the bay. Wastewater was the primary source of cadmium, and atmospheric deposition was the primary source of lead, regardless of location in the bay. However, for many other metals, including manganese, iron, cobalt, nickel, and zinc, industrial discharges were the primary contributors in nearshore areas, and natural sources were more important for the bay as a whole. Because only part of the input was removed by sedimentation, anthropogenic inputs were judged to have significant input on water quality.

In a large city, one might expect to find substantial impact of anthropogenic inputs. Evaluating the sources of metals in New York City wastewaters, which ultimately reach New York Harbor, Klein and others (1974) reported that nonindustrial inputs, especially wastewater from residential areas, are more important than industrial discharges for metals such as copper, zinc, and cadmium. For nickel and chromium, the electroplating industry was the major contributor, but residential wastewater was still very significant. These findings complicate the problem of how to regulate sources of contamination. Obviously, regulation of one perceived point-source (in this case, the electroplating industry) might reduce total pollution but would not eliminate the problem.

Drainage from Mining Areas

Acid mine drainage is a source of extremely high concentrations of metals at some sites around the country. Not only do the mines constitute a rich source of metals, but also the oxidation of sulfides in pyrite and in other ores releases sulfate, producing low pH in drainage waters (Wentz, 1974). The acidity tends to solubilize the metals and to greatly increase their mobility (Moran and Wentz, 1974).

The Coeur d'Alene River in Idaho, the south fork of which receives drainage from a mining district, is an example of a river that is severely impacted by mine drainage (Funk and others, 1975). Dissolved metal concentrations range as high as 23 mg/L (milligrams per liter) zinc, 0.35 mg/L cadmium, and 2.8 mg/L lead. Complete inhibition of growth of the green alga *Selenastrum capricornutum* occurs at 0.12 mg/L zinc and 0.080 mg/L cadmium (Bartlett and others, 1974). As expected, no populations of *S. capricornutum* were found in the waters of the Coeur d'Alene River.

Another North American system that has been severely affected by mining is the Belle Fourche River and its tributary Whitewood Creek near Lead, S. Dak. Between 1880 and 1977, about 100 million Mg (megagrams) of mine tailings containing arsenopyrite and other metallic sulfides were discharged into the creek (Marron, 1987). Arsenic concentrations in stream sediments are as high as 5,400 ppm (parts per million) 25 km (kilometers) downstream of the town of Lead. The contaminated flood-plain sediments will remain for centuries as a source of metals to adjacent streams. A study of this system is being conducted by the U.S. Geological Survey.

A lead-zinc-copper mine that discharges tailings into a British Columbia lake has caused substantial increases in metal concentrations in the lake during the mine's 18 years of operation (Austin and others, 1985). Changes in water chemistry have affected community structure of periphyton and phytoplankton. Metal-sensitive species have dramatically decreased in abundance and have been replaced by more tolerant species. Species diversity also has decreased.

Mining activity may alter speciation and transport of metals in drainage streams, not only by releasing metals directly into the drainage waters, but also by causing other perturbations that affect the metals. Modification of pH is one important example of such perturbations. Others are increased sedimentation due to construction and land disturbance and increased input of organic material (Smith and others, 1983). Cabrera and others (1984) observed that simultaneous release of organics and metals from old mine spoil heaps resulted in high metal concentrations downstream.

The effects of coal mining on water quality were examined by Wirries and McDonnell (1983). Data from inactive coal mine drainages in eight States showed that concentrations of aluminum, manganese, nickel, and zinc were found to exceed Federal effluent quality guidelines in 40 to 60 percent of the samples collected. High concentrations of a number of metals in streams that drain coal mining areas tend to be associated with sulfate concentrations greater than 2,000 mg/L (Toler, 1982).

Drainage waters from areas where specific precious metals are mined are likely to contain high concentrations of various other metals. Tin and tungsten mines in Tasmania produced severe pollution of two drainage streams (Tyler and Buckney, 1973). Contaminants, including sulfuric acid, cadmium, copper, iron, lead, and manganese, were at such high levels that the waters were unusable for domestic or agricultural use. In South Africa, gold and uranium mining activity produced enrichment of lead, cadmium, mercury, arsenic, and selenium (Wittman and Forstner, 1977). Mining of barium can release several toxic metals, principally lead and zinc (Smith and others, 1983).

Nonpoint Sources

In areas remote from urban-industrial development, nonpoint sources are usually the predominant contributors of metals in aquatic systems (McElroy and others, 1975). Surface-water runoff represents a major component of the water budget of many surface-water systems, especially those without channelized tributaries (Winter, 1981). It is thus a major potential contributor to contaminant loading, especially in agricultural or silvicultural areas. Nutrient loading from point sources has been demonstrated and quite well documented, but similar studies of metal loading from non-atmospheric, nonpoint sources have been very limited.

One of the major nonpoint sources for water bodies near urban development is storm water runoff from man-made impervious surfaces. Studies that show elevated contaminant concentrations near densely populated areas lead to the conclusion that urban storm water runoff is an important source of the contaminant (Ellaway and others, 1982; Renwick and Edenborn, 1983). Runoff from basins in south Florida that included a highway and commercial development was compared to atmospheric deposition by Miller and Mattraw (1982). Runoff loads of zinc were more than half of the atmospheric loads. Runoff loads of lead equaled or even exceeded those from atmospheric deposition.

Erosion has been a major contributor of nutrients and metals to Lake Erie (Kemp and others, 1976). Large quantities of fine-grained sediments were released by erosion and could have been transported long distances in the lake (up to 150 km). Surface enrichment factors of cadmium, copper, mercury, lead, and zinc in the lake sediments were significant and reflect the importance of anthropogenic inputs that reached the lake largely by way of erosion.

Another area where erosion is the primary contributor of nutrients and metals is the Lake Tahoe basin (Leonard and others, 1979). The biological impact of such inflow in this system is eutrophication rather than accumulation of toxic levels of contaminants. Earlier work had shown that primary productivity in the lake was limited not only by macronutrients but also by some metals, including iron and zinc, that may be transported in large quantities to the lake during snowmelt runoff (Goldman, 1964).

The Mississippi River drains more than 40 percent of the land area of the contiguous United States. Analyses of its sediments thus provide indicators of broad regional contamination. Trefry and others (1985) used sediment analyses from the Mississippi River Delta to determine trends in lead contamination and effects of regulations limiting lead additives in gasoline. Some sediment core data, taken from near

the river mouth, showed peak lead concentrations in sediments deposited in approximately 1970, corresponding quite closely with the maximum annual consumption of lead in gasoline. The results implied that lead in gasoline had been an important source of lead pollution on a nationwide scale and that reduction of this source was quite effective in reducing lead inputs to the environment.

Other Sources

Ground-water flow is likely to be an important hydrologic control on contiguous surface-water systems (Winter, 1983). However, its role in supplying metals to those same systems is sharply limited because most metals are readily sorbed to soils and aquifer materials. Even relatively mobile metallic elements, such as sodium, potassium, and lithium, are sorbed to sedimentary materials (Bencala and others, 1983, 1984). However, there are appreciable differences in distribution coefficients, depending on the metal and substrate. Removal of the metals during ground-water transport generally results in negligible metal input by this pathway.

Some work has been done to investigate the importance of volcanoes as a source of metals in aquatic systems. Kitano and others (1983) described metal input and speciation in rivers near Mount Ontake, Japan, following its 1979 eruption. Volcanic material contained various metals incorporated in sulfides and silicates. Within the river sediments, diagenesis yielded transformation to various other forms. The 1980 eruption of Mount St. Helens did not produce appreciable increases in dissolved concentrations of most metals in the Columbia River estuary (Riedel and others, 1984). Of seven metals measured, only manganese and copper showed slightly elevated concentrations due to leaching from the volcanic material.

OCCURRENCE AND DISTRIBUTION OF METALS IN AQUATIC SYSTEMS
In Water

Reconnaissance studies that describe occurrence of trace metals over regions are generally limited to areas no larger than States or small groups of States. On a national scale, the most complete work of this nature was done by Durum and associates (Durum and Haffty, 1963; Durum and others, 1971). The 1971 report gives data for 720 samples collected in 1970 from sites throughout all 50 States and Puerto Rico. All samples were filtered, acidified, and analyzed for arsenic, cadmium, hexavalent chromium, cobalt, lead, mercury, and zinc. The filtration, through a 0.45-μm (micrometer) membrane filter, creates a commonly used operational definition of the dissolved fraction.

Data on the occurrence of metals in surface and ground waters are available for each State and territory of the United States in annual reports published by the U.S. Geological Survey. Each of these reports is available as a

U.S. Geological Survey Water-Data Report XX–nn (where "XX" is the State abbreviation and "nn" is the year). Water-quality and physical data from more than 14,000 sites around the country are included in these reports. Most of the trace metals are reported as their concentrations, in micrograms per liter, in the dissolved form. In some cases, results of analyses of "total recoverable" and "total in bottom material" are also included.

In Sediments

No complete nationwide reconnaissance of metals in sediments of freshwater systems has been reported. Local studies that give results of monitoring in North America are available, but comparisons among them are not practical because of the differences in sampling and analytical techniques. One of the most significant problems in interstudy comparisons is the effect of grain size. In some studies, only selected size fractions are collected, whereas most studies do not include any size separation at all, and results are given as total concentrations.

Table 2 lists studies that included determinations of metal concentrations in sediments. Analytical procedures varied; hence, some data represent total metal concentrations, whereas other data represent certain extractable fractions. The studies listed are limited to those that were conducted in freshwater systems or estuaries in the United States and Canada. The information in the table indicates the locality of each study, the metals monitored, and whether or not grain-size fractions were separated.

Although nationwide monitoring information on stream sediments is not available, such information is available for soils and other surficial material in a report by Shacklette and Boerngen (1984). Analytical data were presented for 47 elements analyzed in substrate samples from more than 1,300 sites uniformly distributed throughout the conterminous United States. For most elements, analyses were performed by emission spectrography and yielded total concentration data. A separate map for each element was produced and was accompanied by frequency distribution data.

The soil data showed some patterns of geographical distribution of elements on a nationwide scale. Aluminum and the alkali-alkaline earth metals are considerably more abundant in the western part of the country than in the eastern areas. Soils of the Pacific Northwest have relatively high concentrations of aluminum, cobalt, iron, scandium, and vanadium, whereas in the Rocky Mountain region, copper, lead, and zinc are relatively abundant. Mercury concentrations tend to be high in soils of the Gulf Coast and the upper Atlantic Coast. Among individual States, Florida had the most striking geochemical pattern, showing low concentrations of most of the elements included in the study.

Additional soils survey work by the U.S. Geological Survey included an extensive nationwide reconnaissance entitled National Uranium Resources Evaluation (NURE). Ap-

Table 2. Published reports of metal concentrations in sediments in surface waters of North America
[If any attempt was made to separate grain-size fractions, it is so indicated. Studies whose primary focus was on processes governing metal concentrations, rather than on the concentrations themselves, are not included]

Location	State or Country	Elements monitored (Al As Cd Co Cr Cu Fe Pb Mn Hg Ni Zn)	Others	Grain-size separations	Reference	Date
Lakes	Wis.	`------X----X-X----X------X-X-`			Iskandar and Keeney	1974
Lake George	N.Y.	`-----------X-X-X----X-------X-`			Schoettle and Friedman	1974
Great Lakes tributaries		`------X-X-X-X----X-X-X-X-X-`	Ag		Fitchko and Hutchinson	1975
Reservoirs	Okla.	`------X-------------X---------X-`			Pita and Hyne	1975
Lake Erie		`X --- X ------ X X X X X --- X`	Si, K, Na, Mg		Kemp and others	1976
Streams	Maine	`--------- X --- X X X X ------ X`			Chork	1977
Narragansett Bay	R.I.	`X --- X X X X X X X --- X X`	V		Goldberg and others	1977
Willamette River	Oreg.	`--- X X --- X X --- X --------- X`		X	Rickert and others	1977
Chesapeake Bay	Md.	`X --- X X X X X X X --- X X`	Ag, V		Goldberg and others	1978
Bayou Chico estuary	Fla.	`------------ X X X X X --- X ---`	Rb, Ti, Zr		Pilotte and others	1978
Iowa River	Iowa	`------------------ X --- X ---------`	Ba, Rb, Sr, Zr	X	Tsai and others	1978
Hudson River	N.Y.	`------------- X X X X ------ X`		X	Williams and others	1978
Lake Michigan	Mich.	`------------ X X X --- X ------ X`		X	Filipek and Owen	1979
Lakes	Canada	`------ X ------ X X ------ X --- X`			Jackson	1979
Lake Erie		`------ X ------ X --- X --------- X`			Nriagu and others	1979
Potomac River	Va.	`--- X X --- X X X X X X X X`			Feltz	1980
Great Bear Lake	Canada	`--- X --- X --- X --- X X X X ---`	Ra, Th		Moore and Sutherland	1981
Ontario lakes	Canada	`----------------- X`			Dillon and Evans	1982
Ontario lakes	Canada	`------ X ----------------- X`			Evans and others	1983
Rivers	Del.	`------ X --- X X X X X ------ X`			Hoffman and Biggs	1983
Eastern North America lakes		`X ----------------- X --- X --- X`			Ouellet and Jones	1983
Saw Mill River	N.Y.	`--- X X X X X X X X X X X X`		X	Rogers	1983
Lake Ontario		`--- X X --- X X --- X --- X X`			Thomas	1983
Indian River	Fla.	`--------------- X`			Trefry and others	1983
Fontana Lake	N.C.	`X ------------ X X --- X X --- X`	Mg		Abernathy and others	1984
Apalachicola River	Fla.	`X X X X X X X X X X X X X`	Ag, Mo, Sn, Si	X	Elder and Mattmraw	1984
Chesapeake Bay		`------ X ------ X --- X --------- X`			Di Giulio and Scanlon	1985
Schuylkill River	Pa.	`--- X ------ X X --- X --- X X X`	Be	X	Stamer and others	1985
Waterways	La.	`X --- X --- X --- X X ------ X X`			White and Tittlebaum	1985

proximately one million samples (at least one from every 2-degree quadrangle) were analyzed. Uranium was the primary target element in the study, but information on a number of other elements was also produced. NURE reports are available at the U.S. Geological Survey library in Reston, Va.

PARTITIONING OF METALS AMONG DIFFERENT PHASES
General Characteristics of Partitioning

Partitioning is defined as the process by which any solute, including contaminants, may transfer among the different phases and biological components of a surface-water system. Transfer pathways are nearly always bidirectional; hence, a substance that resides in any particular phase rarely stays permanently in that phase and may move to a different phase as conditions change.

Figure 2 illustrates diagrammatically the general nature of partitioning of trace metals among different phases in aquatic systems. Three broad abiotic phase categories are depicted at the apexes of the "triangle." Biological com-

ponents (plankton, nekton, and benthos) are also involved in metal partitioning and are shown as components in the phase diagram.

Some of the conditions that influence the directions and magnitudes of metal transfers among phases are shown on the perimeter of the partitioning triangle (fig. 2). The soluble phase is favored under conditions of low pH, low Eh (reducing environment), low particulate loads (both organic and inorganic), and high concentrations of dissolved organic matter. If pH and particulate loads increase, while hydraulic energy of the system is high enough to sustain suspension of the particles, partitioning is likely to shift toward the suspended phase. Finally, high pH and Eh, combined with elevated concentrations of organic matter in the bottom sediments, are conditions that favor partitioning in the bottom sediment phase.

In most surface-water systems, biota are abundant and diverse and constitute important partitioning components themselves. High productivity among planktonic (free-floating) and nektonic (swimming) organisms usually implies uptake of contaminants by these organisms from both sol-

uble and suspended phases. An abundant benthic community is likely to incorporate and accumulate contaminants from water or ingestion of sediments or planktonic organisms.

Metals in the soluble phase tend to approach an equilibrium condition where all dissolved forms coexist in accordance with the dissociation constant of each metal-ligand association. Such a steady state is rarely reached in natural waters, however, due to the continually fluctuating nature of controlling factors such as pH, redox potential, and temperature.

One form of the metal within the dissolved phase is the "free ion," so named because it is not associated with dissolved ligands. However, it should not be considered a "bare metal ion" (for example, Cu^{2+}), because such an ion cannot exist as a separate entity in water (Manahan, 1972, p. 19). Instead, the free ion is a hydrated form having the general formula $M(H_2O)_x{}^{n+}$, where $M =$ metal and $n =$ its ionic charge. Other dissolved species of the metal are those involving association with one or more ligands, either inorganic or organic, which form soluble complexes with the metal.

Within the suspended particulate phase, metals may be associated with inorganic particles, organic particles, or biota. The dominant mechanism of such association is adsorption, or linkage to the surfaces of solid particles due to charge attractions between the surfaces and the dissolved ions. Adsorption reactions are readily reversible, and the system thus approaches, but rarely reaches, an equilibrium state involving adsorbed and desorbed forms. For biota, another dominant mechanism of incorporation of metals is

absorption, or assimilation into cells. For many metals, biological uptake by algae involves initial adsorption followed by actual cellular uptake or absorption (Crist and others, 1982). Absorption is accompanied by discharge of the metals in waste products of the same organisms, again resulting in continual input and output.

Metals within the bottom-material particulate phase are also associated with inorganic particles, organic particles, and biota. The benthic fauna and aquatic vegetation that are involved are different species than those which are in overlying waters, but the mechanisms of incorporation are virtually the same, involving both adsorption and absorption. The inorganic and organic particles include many of those that may be in the suspended phase, but, because of their density, the particles settle into the bottom material.

Analysis of Metal Species

Most research having to do with metals in aquatic systems addresses one or more facets of the partitioning "triangle" (fig. 2). A considerable amount of attention has been centered directly on rates and significance of various pathways of interaction among different metal species. Any aquatic trace metal study, even if not process oriented, must involve examination of the results, if not the mechanisms, of partitioning. At the very least, separate analyses are done for water and bottom material, although the "water" phase usually contains some fraction of the suspended material. In addition, many studies require focus on one or more species. This places special demands on methodology for sample treatment and analyses.

High pH
High particulate organic matter concentration
High suspended sediment load
High hydraulic energy

SUSPENDED SEDIMENT PHASE

Plankton, nekton

SOLUBLE PHASE

Low pH
Low Eh
Low particulate organic matter concentration
Low suspended sediment load
High dissolved organic matter concentration

BOTTOM SEDIMENT PHASE

Benthos

High pH
High Eh
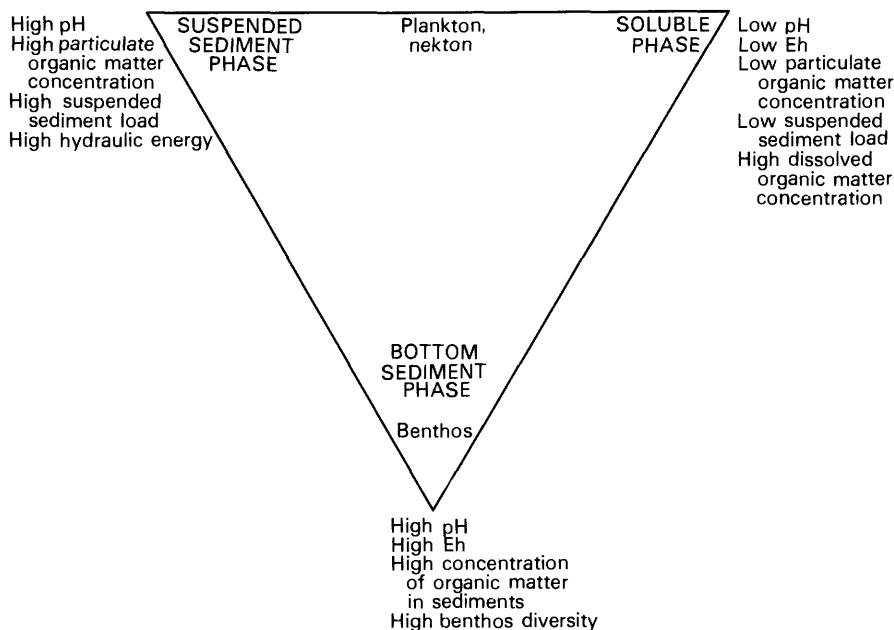High concentration of organic matter in sediments
High benthos diversity

Figure 2. Metal partitioning in aquatic systems among three major phases (inside the triangle) and some environmental conditions that favor each phase (outside the triangle). Biological components (plankton, nekton, and benthos) are positioned according to the phases with which they are most closely associated.

There has been a considerable amount of work done during the past three decades to develop sequential partial extraction procedures that allow reliable measurement of speciation (or fraction analysis) of a metal. Each step of a sequential partial extraction scheme produces an extract that theoretically contains only one metal fraction from the original sample, and analyses may then be performed on each fraction separately. A thorough history of the development of this methodology was provided in discussions by Chao (1984), Horowitz (1985), and Horowitz (in press).

Although most sequential partial extraction procedures that have been described in the recent literature are similar, there is no standardized procedure. In general, most procedures are constructed on the premise that the metal fractions of primary importance in natural water systems are as follows:

1. the dissolved fraction,
2. the exchangeable fraction, only loosely bound to colloidal or particulate material,
3. the carbonate fraction, associated with sediment carbonates,
4. the iron and manganese oxide fraction, adsorbed to surfaces of iron-manganese hydrous oxide particles or coatings,
5. the organic fraction, bound to various forms of organic matter, and

6. the crystalline fraction, held within the crystal structure of minerals, not readily removed and not available to biota.

Table 3 summarizes three partial extraction procedures for separating metal fractions in sediments. The approaches of Tessier and others (1979) and Popp and Laquer (1980) are similar, the principal difference being that the latter does not include steps that separate out the carbonate and organic fractions. The alkaline acetate treatment is used in both procedures to extract the exchangeable fraction, and the citrate-dithionite combination is used in both to extract the metals bound to hydrous iron-manganese oxides. The use of hydrogen peroxide and dilute nitric acid to extract the organically bound fraction was omitted by Popp and Laquer (1980) because the river (the Rio Grande) where their investigation was carried out carries a very small organic fraction in the sediment phase. However, the hydrogen-peroxide extraction step has been used quite commonly in other studies (Gupta and Chen, 1975; Kitano and others, 1980).

The approach of Kitano and others (1980) reflects a somewhat different fractionation scheme (table 3). Dilute hydrochloric acid, rather than acetate, is used in the first step, giving a slightly more vigorous attack that extracts ion-exchangeable metals, some sulfides, and most carbonates. Hence, there is no true separation of exchangeable and carbonate-bound fractions. The remaining sulfides are ex-

Table 3. Summary of three sequential partial extraction procedures for separating metal fractions in particulate material

[Extraction steps proceed from top to bottom, the residue from each step being used for the subsequent treatment. For each method, table shows reagents used, concentrations of those reagents, temperature (in ° C), and pH at which extraction is conducted. For more details, consult source material. RT=room temperature; heat=direct heat application; M=molar; N=normal; conc.=concentrated]

Fraction removed in extract	References									
	Tessier and others, 1979				Popp and Laquer, 1980			Kitano and others, 1980		
	Reagents	Concentration	Temperature	pH	Reagents	Concentration	Temperature	Reagents	Concentration	Temperature
Exchangeable	$MgCl_2$ or $NaOAc$	1 M 1 M	RT RT	7 8.2	NH_4OAc	1 M				
Bound to carbonates.	$NaOAc$ + $HOAc$	1 M conc.	RT	5				HCl	0.1 N	RT
Bound to Fe/Mn oxides.	$Na_2S_2O_4$ + Na citrate + H citrate– or $NH_2OH.HCl$ + $HOAc$	.3 M .175 M .025 M .04 M –25%	96 96		$Na_2S_2O_4$ + Na citrate	.115 M .094 M				
Bound to organic matter.	HNO_3 + H_2O_2 + NH_4OAc + HNO_3	.02 M –30% 3.2 M 20%	85	2				H_2O_2 + HCl –	30% –0.05 N	heat
Crystalline	HF + $HClO_4$	conc. conc.	heat		HF + HNO_3	conc. conc.	heat	HF + HNO_3 – + $CHlO_4$	conc. conc.	heat

tracted with the organics by the hydrogen-peroxide step. Finally, the silicates are released by vigorous attack with three strong acids (hydrofluoric, perchloric, and nitric).

In addition to these partial extraction schemes for fractionation of particulate material, there has been some success with procedures for separating different forms of dissolved metals. Voltammetric procedures, particularly anodic stripping voltammetry (Batley and Florence, 1976; Figura and McDuffie, 1979), are commonly used for this type of separation. Ion exchange (Figura and McDuffie, 1979) and dialysis (Hart and Davies, 1977) are alternative procedures that may be used independently or in combination with each other to separate labile metal fractions.

Rapin and others (1986) discussed some of the pitfalls in sample treatment that may lead to erroneous results in partial extraction procedures to determine metal partitioning. Freezing or short-term wet storage at 1 to 2° C was recommended to minimize deterioration of sediments during storage. Drying of sediments should be avoided.

Factors That Control Metal Partitioning

Hydrogen-Ion Activity (pH)

The overwhelming importance of hydrogen ion activity is one of the most recurring themes in literature on aquatic trace metals. Innumerable studies have demonstrated dramatic changes in speciation that may be expected with relatively small changes in pH. Furthermore, the pH ranges within which such changes occur are usually near neutrality and are common to natural waters. Major pathways of trace metal partitioning, including complexation, sorption, precipitation, biological uptake, and their respective reverse pathways, are all highly pH dependent. The importance of accurate pH measurements in any assessment of metal behavior in aquatic systems cannot be overemphasized.

The critical role of pH in metal speciation is manifested in the frequency with which pH is shown as the primary independent variable in speciation diagrams and models. One leading example is shown in figure 3 (Stumm and Morgan, 1970, p. 270). It illustrates how Cu(II) species predominance is controlled by pH. The abundance of a species is measured as its activity relative to the activity of Cu^{+2}. At the given total copper concentration, the copper species are dominated by two solids: tenorite (CuO) above pH 7 and malachite $[Cu_2(OH)_2(CO_3)]$ below pH 7. Among the aqueous species, the free metal ion is expected to dominate below pH 6, but various carbonate and hydroxide complexes become important at higher pH levels.

The diagram in figure 3 is based on chemical-equilibrium calculations and given concentrations of dominant inorganic ligands such as carbonate and sulfate. Other similar models, derived from similar types of computations, have been published by various authors (for example, Zirino and Yamamoto, 1972; Morel and others, 1973; Elder and Horne, 1978; Vuceta and Morgan, 1978; McKnight and

Morel, 1979; Davis, 1984). The models all show similar overall patterns of pH dependence. The pH effect varies as ligand concentrations vary, and the precise positions of boundaries among different species depend on the particular conditions, including the total metal concentration. Nevertheless, the consistently important role of pH in controlling speciation is obvious from all models. The sensitivity to small pH changes in common natural water pH ranges is usually very high.

Effect of pH on Solubility

The hydroxide precipitates of most metals are quite insoluble under natural water pH conditions. Because the hydroxide ion activity has a direct relation to pH, however, the solubility of hydroxide precipitates increases sharply as pH decreases. Complexations with other ligands may tend to keep the metal in solution, but these complexations are also pH dependent. For example, the carboxyl functional group $(-COO^-)$ is rendered nonfunctional as a metal binding site by coordination with a hydrogen-ion (COOH). The probability of this occurrence is clearly dependent on hydrogen ion activity.

The variation of copper solubility as a function of pH, illustrated in figure 3, is one example of the role of pH in influencing solubility of metals. Similar sensitivity to pH in near-neutral ranges has been determined for cadmium (Morel and others, 1973) and iron (Hem, 1985). A detailed discussion of solubility variations of metals as a function of pH was provided by Garrels and Christ (1965, chaps. 7 and 11).
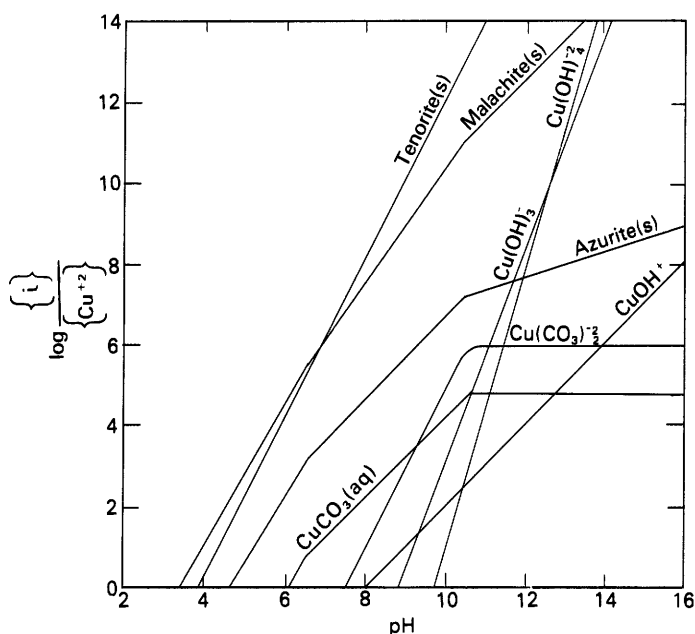
Figure 3. Activity ratio diagram showing speciation of Cu(II) as a function of pH (from Stumm and Morgan, 1970, p. 270). Total Cu concentration is 0.01 M. Vertical axis is logarithmic and is based on ratio of activity of any Cu species to activity of the free cupric ion. s, solid; aq, aqueous.

The effect of pH on adsorption of metals to surfaces of iron and aluminum oxides has been studied in considerable detail by Leckie and coworkers (Benjamin and Leckie, 1981; Davis and Leckie, 1978a, b). Sorption capacity of oxide surfaces generally ranges from near 0 percent to near 100 percent over a pH range of approximately 2 units.

The term "adsorption edge" implies a rapid change of adsorption capacity as a function of pH and concentrations of adsorbent and adsorbate. Plots of adsorption edges for cadmium, copper, lead, and zinc on oxide substrates (Benjamin and Leckie, 1981) illustrate this pH effect. An example, shown in figure 4, illustrates the sensitivity of cadmium adsorption on amorphous iron hydroxide. The pH range of 5 to 9 brackets neutral conditions and common natural water situations. Within this range, there is a span of approximately 2 pH units through which small changes in pH have a large effect on adsorption of the metal to the hydroxide surface. The positions of the curves along the pH axis are variable, depending on concentrations of adsorbing substance, metal ions, and competing ligands. However, the similarity of the shapes of the curves indicates that the intensity of pH effect is nearly independent of adsorbent concentration.

Similar effects of pH on adsorption of copper on iron oxyhydroxides were reported in earlier papers by Davis and Leckie (1978a, b). Nearly identical results were achieved by Davies-Colley and others (1984). The strong influence of pH can be expected to apply generally to all metal adsorption on solid surfaces, as shown by the investigations of sorption to various clays and soil minerals by Huang and others (1977) and Reid and McDuffie (1981).

Mixing of waters of widely different pH may have significant chemical and biological consequences. Examples of pH-mixing effects were observed by Theobald and others (1963) and McKnight and Feder (1984) at the confluence of a high-pH stream with a low-pH stream. The acidic waters carry relatively high concentrations of aluminum, iron, zinc, and other metals, and the precipitation of these metals as hydrous oxides below the confluence limits the abundance of periphyton and benthic invertebrates.

Effect of pH on Organometallic Interactions

The affinities of metals for organic molecules are the result of linkages between the charged metal ion and oppositely charged coordination sites, such as the carboxyl and sulfhydryl groups, on the organic molecule. The positively charged hydrogen ion is a competitor with the metals for such coordination sites. Thus, hydrogen-ion activity is as important in determining the degree of organometallic interaction as are the concentrations of the organic and metallic reactants themselves.

Sorption of metals on humic acids is an example of an organometallic interaction for which there is some documentation of dependence on pH. Kerndorff and Schnitzer (1980) showed sharp increases in sorption efficiencies with a pH rise from 2 to 6 (fig. 5). However, the maximum slopes for chromium, lead, copper, and aluminum occur at much lower pH levels than those of cadmium, zinc, nickel, cobalt, and manganese. Iron and mercury show very
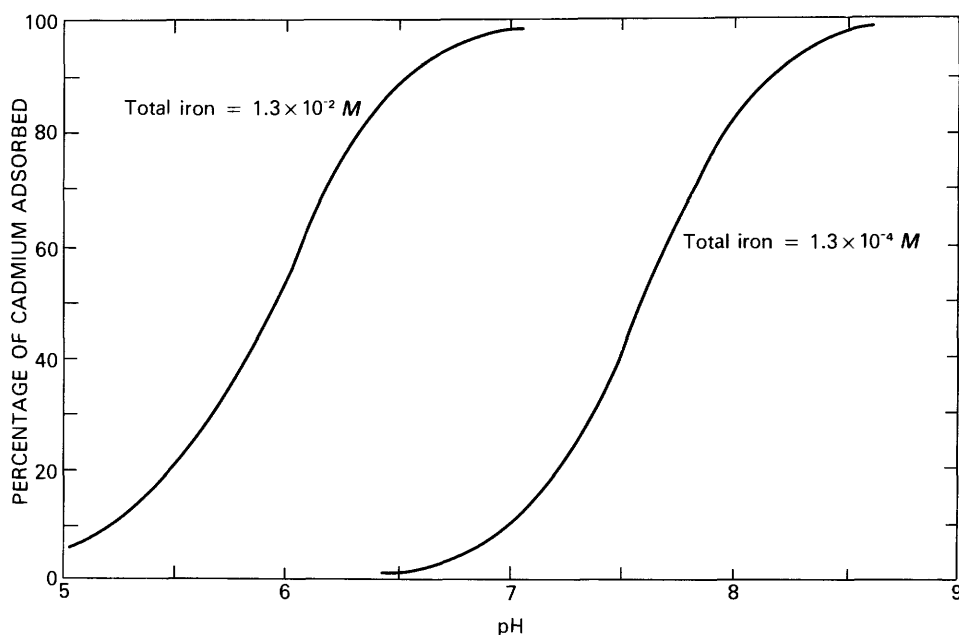
Figure 4. Adsorption of cadmium on amorphous ferric hydroxide, as a function of pH and concentration of total iron (from Benjamin and Leckie, 1981). Total cadmium concentration is 5×10^{-7} molar (M), temperature is 20° C, and sodium nitrate concentration is 0.1 M.

strong humic-acid affinities at any pH greater than 2. Because of these differences in responses among different metals, pH changes produce changes in the order of sorption. For example, as seen in figure 5, the sorption order at pH 2.4 is Hg > Fe > Pb > Cu > Al > Ni > Cr = Zn = Cd = Co = Mn, whereas at pH 5.8, the order is Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn.

This comparison of sorption capacities is similar but not equivalent to the frequently cited "Irving-Williams series" (Irving and Williams, 1948). Comparing the stabilities of metal-ligand complexes of six metals, the Irving-Williams series reflects an increase in stability as an inverse function of ionic radius. According to the series $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, copper forms the most stable complexes of the six metals. Like the sorption capacity order, this series is also pH dependent.

Effect of pH on Biological Uptake

Given the general concepts that (1) metal speciation is highly pH dependent and (2) bioavailability is highly dependent on speciation, it follows that hydrogen-ion activity is very important in affecting uptake of metals by biota. This importance has been documented in various studies. Schecher and Driscoll (1985) observed that removal of copper and lead by the blue-green alga Nostoc muscorum was highly pH dependent (fig. 6). Within acid-pH range, the sorption edges
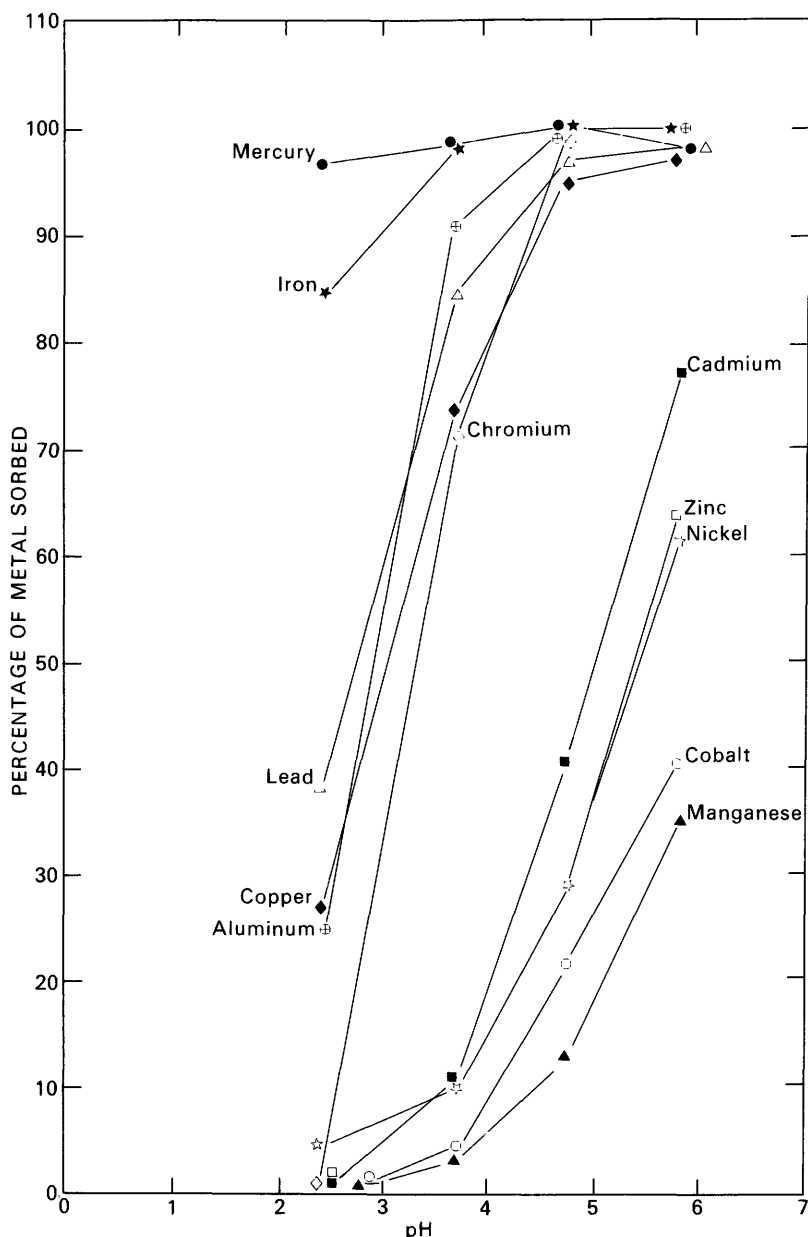
Figure 5. Adsorption of various metals on humic acids, as a function of pH (from Kerndorff and Schnitzer, 1980, p. 1704). Each initial metal concentration = 0.0005 molar.

shown were similar to the pattern of adsorption on inorganic oxide surfaces. The percentage of metal removed increased sharply with increasing pH. Above pH 7, however, the effect was reversed, and removal decreased with increasing pH. The departure from the adsorption curve in the alkaline range was attributed to release of organic materials capable of complexing metals. Precipitation of the metal hydroxides was considered in calculating the percent removal by biological uptake. Les and Walker (1984) also observed increased binding of copper, zinc, and cadmium by the blue-green alga *Chroococcus paris* with pH increases from 4 to 7. No data were given for the pH effect above pH 7.

Environmental acidification effects on toxicity of 10 metals to aquatic biota were considered by Campbell and Stokes (1985). They pointed out that pH decreases in the range of 7 to 4 may affect metal uptake, not only by altering metal speciation in solution, but also by altering the organisms' sensitivity to the metal at the cell surface. Metals may be grouped into two categories according to how their toxicity is affected by pH. Type I metals, including cadmium, copper, and zinc, produce less biological effect at lower pH. Type II metals, of which lead is an example, become more bioavailable as pH decreases.

Bioassays of nutrient uptake by the green alga *Scenedesmus quadricauda* in the presence of cadmium and copper (Peterson and others, 1984; Peterson and Healey,

1985) demonstrated that toxicity of the metals is highly pH dependent. The concentration of cadmium needed to cause a 50-percent reduction in phosphorus uptake, for example, decreased two hundredfold with a change in pH from 5.5 to 8.5. This result is consistent with Campbell and Stokes' (1985) description of type I metals and appears contradictory to the principle that metal complexation increases with pH to cause a decrease in bioavailability and toxicity. The explanation suggested by the authors was that the free ionic species (Cd^{+2}) is the dominant cadmium species over the entire pH range tested. Hence, there was no direct appreciable change in cadmium bioavailability. At the same time, the one-thousandfold decrease in hydrogen ion activity resulted in diminished competition from hydrogen ions for cellular binding sites, indirectly causing greater bioavailability of the cadmium. This explanation was supported by the experiments with copper, which showed similar increases in copper toxicity from pH 5 to pH 6.5 but little effect above pH 6.5. Unlike cadmium and zinc, copper speciation is dominated by inorganic complexation in alkaline conditions (fig. 3), and the bioavailability is diminished significantly. The drop in competitive complexation by hydrogen ions is apparently balanced by the corresponding reduction in copper bioavailability.

Implications of Acidic Atmospheric Deposition

Because of the likelihood of rapid desorption of metals as pH drops below neutrality, one of the most dramatic effects of acid deposition and lake acidification tends to be metal mobilization. One notable example is aluminum. Although it is the third most common element in the Earth's crust (table 1), aluminum was hardly noticed as a potential problem in natural water systems until acid deposition began to receive national attention. Recent studies have shown that, below pH 5, significant amounts of aluminum may be leached from soils (Cronan and Schofield, 1979) and solubilized through association with organic matter (Campbell and others, 1983) or inorganic ligands (Hayden and Rubin, 1974; Driscoll and others, 1980). Nordstrom and Ball (1986) pointed out the importance of the pH range 4.6 to 4.9 in aluminum behavior. Below this range, aluminum behaves conservatively, and its activity is controlled by the solubilities of sulfate minerals. Above this pH range, aluminum becomes nonconservative.

Studies of fish responses to acidification (Driscoll and others, 1980; Gunn and Keller, 1984; Robinson and Deano, 1985) have shown that aluminum is more toxic to fish than previously believed. Other biotic responses, such as increased drift of benthic invertebrates (Hall and others, 1985), have been reported. Therefore, increased mobilization of this metal may pose a significant environmental threat.

Oxidizing or Reducing Conditions

Aquatic systems are commonly characterized by a rather sharp demarcation between oxidizing and reducing en-
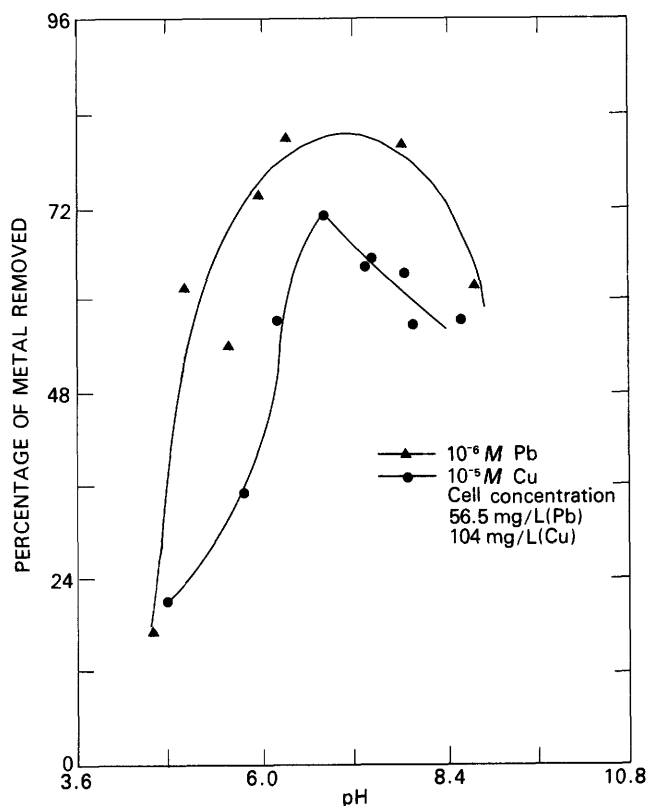

Figure 6. Removal of dissolved copper and lead by *Nostoc muscorum* as a function of pH (from Schecher and Driscoll, 1985, p. 90). *M*, molar.

vironments. In stratified lakes, this boundary is likely to be at the thermocline because of the isolation of the hypolimnetic waters from surface oxygenation. In more actively mixed waters, the boundary is likely to be in the interstitial water of the sediment-water interface. The boundary is characterized by a sharp change in reduction-oxidation potential (redox potential or Eh).

The order of metal solubility and the relative stabilities of different metal-containing minerals are controlled to a large extent by pH and reduction-oxidation potential (Krumbein and Garrels, 1952). Concentrations of dissolved oxygen and dissolved sulfide, influenced by the redox potential but more easily measurable than Eh, are important controls on precipitate formation (Berner, 1981). The oxides are one of the predominant precipitates in oxic waters, whereas the sulfides are predominant under anoxic conditions. The increasing order of solubility (based on data from Ringbom, 1963, p. 341–347) is as follows:

Oxides: $Fe(III) < Hg << Cu < Pb = Zn < Ni < Cd < Mn(II)$;
Sulfides: $Hg << Cu << Pb = Cd = Ni < Zn < Fe(II)$ $< Mn(II)$.

The position of iron in the sequence changes dramatically with the change in redox potential. Under oxidizing conditions, the ferric hydroxide precipitate is highly insoluble. Under anoxic conditions, the iron is reduced to ferrous iron, and its tendency to precipitate as the sulfide is lower than that of many other elements. However, concentrations of ferrous iron may far exceed those of other elements because of solubilization from the sediments under reducing conditions. The iron may be so abundant that it consumes most of the sulfide, leaving very little to precipitate other elements (Morel and others, 1973).

Combined Eh-pH Effect

The sensitivity of iron speciation to both Eh and pH is illustrated by the stability-field diagram of Hem (1985, fig. 14, p. 80) (fig. 7). Shaded areas indicate conditions in which iron exists as a solid; unshaded areas represent dissolved species. There are two general regions, representing Eh-pH combinations, where iron solubility is very low. One is a condition of strong reduction in the presence of sulfur, resulting in precipitation of the sulfide. This condition covers a broad pH range; given sufficient reducing potential, it may occur at any natural water pH. The second condition is one of moderate oxidation, above pH 4, where the ferric hydroxide may precipitate. Outside of these regions, especially at low pH, iron is relatively soluble, either as ferric complexes when Eh is high or as free ferrous ion under more reducing conditions.

The stability field diagram (fig. 7) is somewhat variable depending on temperature, pressure, and activities of iron and anions. Unless there are drastic changes in conditions, however, the changes are manifested only as slight shifts in the region boundaries. The general stability-field pattern remains. The diagram represents inorganic inter-

actions only; under conditions of high organic carbon concentrations, where organic complexation prevails, the field compartmentalization would be quite different.

The redox and pH control of iron speciation is especially significant because of its indirect effect on speciation of other metals. Formation of hydroxides and oxides of iron, as well as manganese, provides ideal surfaces for sorption of dissolved metal ions. Conversely, changes in Eh-pH conditions that redissolve the iron-manganese oxyhydroxides may release various dissolved metals into the water column.

Other Effects of Redox Changes

Because of the solubilization of iron and manganese in reduced form, a change from oxidizing to reducing environment is generally believed to favor release of metals
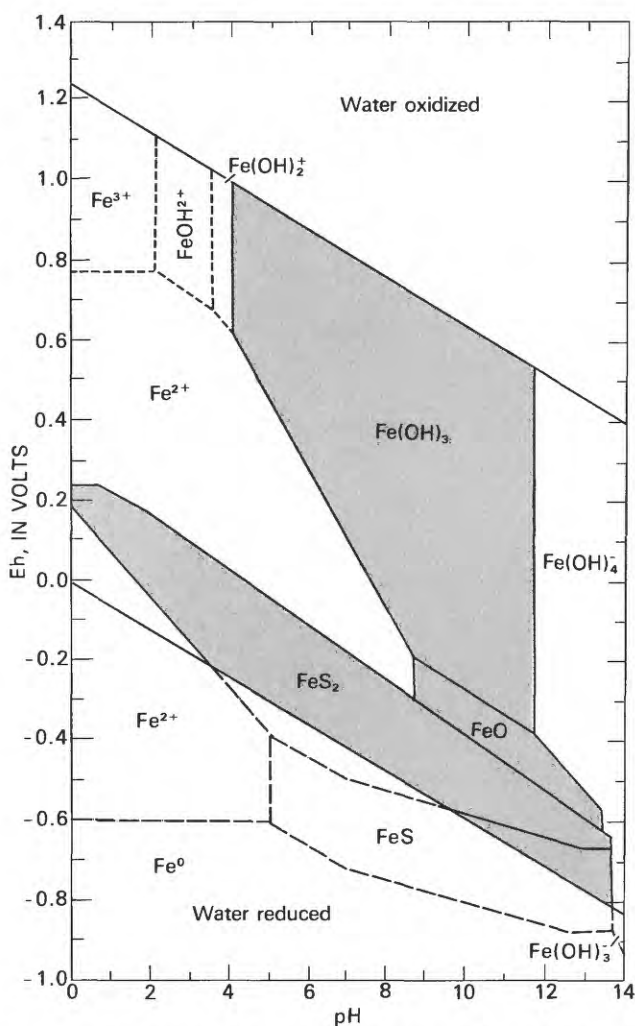
Figure 7. Stability field diagram for solid and dissolved forms of iron, as a function of Eh and pH at 25° C and 1 atmosphere pressure (from Hem, 1985, p. 80). Activity of sulfur species = 96 milligrams per liter as sulfate; carbon dioxide species = 61 milligrams per liter as bicarbonate; and dissolved iron = 0.0056 milligrams per liter.

from the sediments. There is some evidence, however, that metal release may actually be diminished under anoxic conditions, because of effects of the anoxia on other constituents of the medium. One of the most important is the reduction of sulfate to sulfide. Metals that may be released by solubilization of iron and manganese oxides may rapidly reprecipitate as sulfides. Nondetectable concentrations of cadmium, copper, and nickel in Narragensett Bay pore water (Elderfield and others, 1981) were attributed to sulfide precipitation.

The reducing environment may cause changes in pH that have marked impact on metal speciation. DeLaune and Smith (1985) observed that oxygenation of anoxic Mississippi River Delta sediments was followed by pH decreases because of oxidation of amorphous metal sulfide and pyrite. The pH change was greatest in saline environments, but even freshwater sediments exhibited a pH drop of approximately 2 units. The resulting acidity caused solubilization of various metals in saline environments. In no case did the authors observe decreased solubility in the more oxidizing conditions. Apparently, the solubilization due to acidification predominated over desolubilization due to higher oxidation potential.

Adsorption to Hydrous Oxides of Iron and Manganese

Among the various aquatic constituents whose solubility and speciation are largely controlled by pH and redox potential, hydrous oxides of iron and manganese may be the most important. These iron-manganese oxide particles are very important substrates for sorption of dissolved trace metals, and as such, they have major effects on the speciation of trace metals in aquatic systems. The role of iron and manganese precipitates in metal speciation merits further attention.

Early discussions of the importance of sorption of metals on iron and manganese hydrous oxides were focused on geochemistry in marine systems (Goldberg, 1954; Krauskopf, 1956). The sorption process involving iron and manganese oxides in freshwater systems was discussed by Jenne (1968). Emphasizing the strong sorptive capacity of the hydrous oxide surfaces, Jenne pointed out that the effects of these surfaces on trace metal speciation can be far greater than their concentrations would suggest. The reason is that amorphous iron and manganese oxides tend to exist as coatings (usually on clay particles) rather than as discrete particles; thus, they have a high surface to volume ratio.

Since the publication of Jenne's paper, the roles of iron and manganese oxides have been tested and discussed frequently. One of the important considerations is the effects of redox potential and pH on adsorption rates. Reducing conditions and low pH are likely to prevent oxide formation, even with much iron and manganese available. Consequently, oxide adsorption of metals depends not only on the total concentrations of iron and manganese but also on the conditions that allow the oxides to exist in appreciable quantities.

Because of the Eh and pH control, the hydrous oxides can be either sources or sinks of trace metals in most systems. As conditions change, the direction of metal speciation can rapidly change from sorption of dissolved metals on particulate matter to mobilization of particulate metals back into the dissolved phase (Jenne, 1976).

The effect of pH on surface charge of inorganic particles (fig. 8) (Stumm and Morgan, 1981, p. 613) shows that manganese oxides are almost always negatively charged under natural water conditions, whereas amorphous iron oxyhydroxides may be either positively or negatively charged. This difference may explain why positively charged metal ions such as copper and zinc are commonly sorbed to both iron and manganese oxides, but anions such as silica, phosphate, and arsenate are sorbed only to the iron oxide surfaces (Jones and Bowser, 1978).

Oxidation of iron and manganese to form the hydrous oxides is commonly catalyzed by the same elements that are subsequently sorbed to them. Copper, for example, has been shown to catalyze oxidation of both iron and manganese (Jenne, 1968).

Various studies have confirmed active metal sorption by iron-manganese hydrous oxides. Rogers and others (1984) found that mercury has a strong affinity for both $Fe(OH)_3$ and MnO_2, and it tends to desorb very slowly. Mercury affinity for oxides of nontransition elements such as aluminum and silicon is weaker. Amirhaeri and others (1984) used a chemiluminescence technique to show the rate of Cr(III) adsorption by iron oxide. Approximately 80 percent of dissolved Cr(III), at an initial concentration of 1 $\mu g/L$, was removed within 3 minutes. Pierce and Moore (1982) measured adsorption isotherms and found up to 90 percent removal of arsenate on amorphous iron oxides. Arsenate was more rapidly adsorbed than arsenite.

A significant fraction of the metals transported by rivers is sorbed to iron and manganese hydrous oxide coatings. Gibbs (1973) compared the quantities of riverine metal transport in two large rivers in very different environments. In the Amazon and Yukon Rivers, he found that copper, chromium, cobalt, and nickel were present in the form of hydrous iron-manganese oxide coatings in amounts up to 50 percent of total metal transport.

In short, there is no apparent disagreement to the general statement that iron and manganese hydrous oxides play significant roles in trace metal speciation. From a physicochemical standpoint, the interaction is a virtual certainty. The hydrous oxide coatings are highly charged (Stumm and Morgan, 1981), and they have a surface area of some 200 to 300 m^2/g (square meters per gram) (Horowitz, 1985). Quantification of the actual metal fractions involved is more difficult. The wide discrepancies observed in different studies probably reflect real variability attributable to different environmental conditions, especially reducing potential and pH. Furthermore, competing ligands may interfere considerably with sorption of

metals to hydrous iron and manganese oxides (Vuceta and Morgan, 1978). More study of this type of interaction is needed.

Concentration of Organic Matter

Metal affinity for dissolved and particulate organic matter is very high relative to other possible binding sites. Productivity and decomposition in terrestrial biotic communities ensure a substantial and continuous supply of organic matter in most watersheds. Anthropogenic inputs have added considerably to the magnitude and complexity of organic loads in surface waters. The combination of strong metal binding or sorbing capacities and abundance in surface waters renders the organics an extremely important influence on trace metal chemistry.

Effect of Organic Complexation on Solubility of Metals

In the absence of competing dissolved ligands, the solubility of metals is controlled by the solubility product, which represents the equilibrium reaction:

$$MA_n(s) = M^{2+} + nA^{(-2/n)} \qquad K_{sp} = [M^{2+}][A]^n \qquad (1)$$

where

M = a divalent metal;

A = an anion (usually hydroxide or carbonate in oxic waters or sulfide in anoxic waters), which forms a precipitate with the metal;

n = 2 if anionic charge = 1; n = 1 if anionic charge = 2;

K_{sp} = solubility product; and

(s) = solid (precipitate).

If a competing ligand is added to this system, it adds a branch, or side reaction, as follows:

$$MA_n(s) = M^{2+} + nA^{(-2/n)} \qquad (2)$$
$$+$$
$$L = ML_{(aq)} \quad K_s = \frac{[ML_{(aq)}]}{[M^{2+}][L]}$$
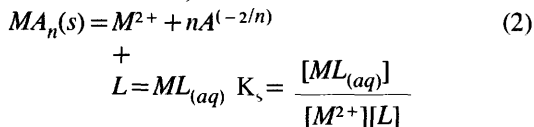
where

L = a dissolved ligand (usually charged, but the charge is omitted here for simplicity) and

K_s = stability constant of the M-L complexation.

As free metal ions are formed by dissolution of the solid phase, they are incorporated in the complexation side reaction. This removes free metal ions from solution and forces still more dissolution. In theory, an equilibrium would eventually be reached that conforms to both the solubility product, K_{sp}, and the stability constant, K_s.

Sholkovitz and Copland (1981) cautioned that solubilities of metals in natural freshwaters may be very different from those observed in artificial solutions or chemical models. The primary reason is interaction with organic substances. For example, a number of metals may be held in dissolved state by complexation with humic acids, even in alkaline conditions (pH as high as 9). At very low pH levels (less than 3), humics may be precipitated, taking the metals with them. Iron is one of the elements most affected by this association with humic acids. More than 70 percent of iron is removed by humics at pH 2. This removal rate is very different than inorganic solubility considerations would predict. On the other hand, manganese and cobalt association with humic acid precipitation is negligible.

Other Factors Affecting Attainment of Equilibrium

One important factor that is ignored in this simplified view of metal-ligand-precipitate interaction is the effect of kinetics. Reaction rates in natural water systems may vary from nanoseconds to decades (Morgan and Stone, 1985), and the rates are subject to considerable variation with temperature. In the double equilibrium represented by equation 2, one reaction may be several orders of magnitude faster than the other. Hence, the theoretical equilibrium may never be reached in natural water environments because a rate-limiting step prevents attainment of a steady-state condition
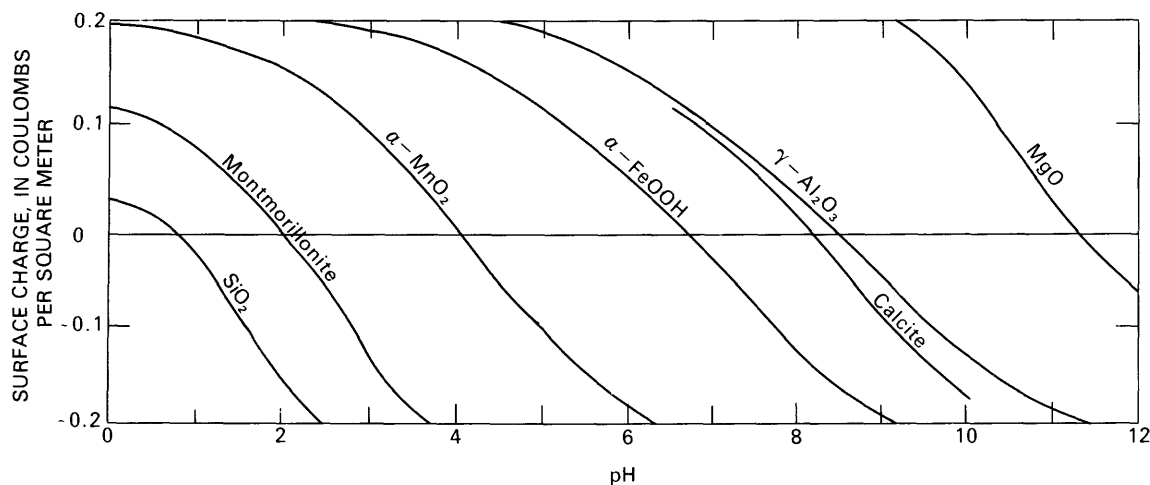
Figure 8. Charge variation on surfaces of some common suspended solids, as a function of pH (adapted from Stumm and Morgan, 1981, p. 613). The curves are meant to exemplify trends and are not necessarily quantitative.

(Hem, 1985, p. 25). Types of reactions that are typically slow include certain metal-ion oxidations and polymerizations, aging of oxide and hydroxide precipitates, dissociation of metal-organic chelates, and precipitation of metal-ion silicates and carbonates (Stumm and Morgan, 1970, p. 66).

A second factor that complicates the interaction is that each of the reactants may enter into additional side reactions (Elder, 1975). The charge on the organic ligand, for example, depends on the ligand's degree of association with hydrogen ions (protonation), which, in turn, depends on pH. If conditions that control such side reactions change, there is a domino effect on the association reactions and an appreciable shift in speciation.

Effect of Organic Complexation on Adsorption of Metals

The effect of organometallic complexation on metal adsorption is similar to the effect on solubility; it creates a multicomponent interaction among the adsorbing surface, the organic ligand, the metal, and the other constituents of the system. At least three simultaneous types of association compete with each other: sorbing surface-to-metal, sorbing surface-to-ligand, and metal-to-ligand. The "winner" of this interaction depends on the relative concentrations of the three reactants and on the relative association constants of the three complexes.

The variability of effects of complexing ligands on adsorption was directly addressed by Davis and Leckie (1978b). By using model experimental systems to determine uptake of Cu(II) and Ag(I) on amorphous iron oxide, the authors observed that some ligands enhance uptake, whereas others retard it. The mechanism of enhancement, as described by the authors, is adsorption of the ligand in a configuration that leaves a strongly complexing functional group directed outward toward solution. This functional group is then available for binding the metal. Examples are thiosulfate, glutamic acid, and ethylenediamine. Retardation occurs in two ways: (1) when the ligand is not adsorbed but instead competes with the adsorbing surface for coodination of the metal ion or (2) when the ligand is adsorbed with its functional group involved in the surface bonding, leaving no binding sites available for metal ions. The first type of retardation is caused primarily by inorganic ions such as chloride or cyanide; the second type may be caused by organic ligands such as picolinic acid or salicylic acid.

Later work by Davis (1984) further confirmed the importance of adsorbed organic matter in determining trace metal partitioning and demonstrated how different metals are affected in different ways. An alumina surface covered with adsorbed organic matter (extracted from lake sediments) had greater adsorptive capacity for Cu(II) than did uncovered alumina. The enhancement could again be explained by affinity to exposed functional groups. However, Cd(II) adsorption to alumina was not significantly affected by the organic

coating because cadmium affinity for the organic functional groups is weak.

Other investigations of complexation effects on adsorption provide additional documentation of both enhancement and retardation. Elliott and Huang (1979) reported that Cu(II) adsorption to alumina was greater in the presence of organic chelating agents than in their absence. They also pointed out that maximum adsorption should occur at a ligand to metal ratio of 1:1. At higher ratios, the excess ligand would compete for the surface-binding sites, and, at lower ratios, a smaller proportion of the metal would be in the form of preferentially sorbed organometallic chelate. Baccini and others (1982) obtained nearly opposite results with the same reactants—Cu(II) and alumina. Natural organic matter from lake water was found to retard adsorption because the organic matter tended to saturate the binding sites of the mineral surface. The explanation for the different results of these two studies may be parallel to the interpretation offered by Davis and Leckie (1978b). The organic chelators in the experiments of Elliott and Huang (1979) may adsorb with functional groups available for binding metal ions, whereas the natural organic matter used by Baccini and others (1982) may adsorb without leaving this kind of functional group exposure.

A study of the influence of surfactants on metal-ion adsorption by clays (Beveridge and Pickering, 1983) illustrated some of the complexities of the interaction between organic binding and surface adsorption of metals. The effect of the surfactants was found to be dependent on the charge of the surfactant, as well as on the type of clay. Cationic surfactants reduced metal sorption on montmorillonite by competing for surface sites, but the surfactants had little or no effect on sorption on two other clays (kaolinite and illite). Nonionic surfactant effects were variable with both the clay type and the metal involved. Anionic surfactants did not interfere directly with adsorption but reduced the concentrations of dissolved metals by precipitating them.

Laxen (1985) demonstrated again the variability of complexation effects on adsorption. Adsorption of cadmium, nickel, and lead to iron hydrous oxides was enhanced by humic acids. The effect on copper adsorption was more uncertain. Laxen recognized that humic acids could work both ways—to facilitate adsorption of the metal or to keep the metal in solution by forming stable soluble complexes. He suggested that complexation with the sorbed humic acid is generally stronger than complexation with the dissolved humic fraction.

Fulvic acids typically constitute about 50 percent of the total dissolved organic carbon in surface waters (McKnight and others, 1983). Complexation by fulvic acids may also be important in affecting adsorption (Saar and Weber, 1982). Again, adsorption may be either favored or retarded, depending on whether the fulvic acids themselves tend to be dissolved or adsorbed to sediments. Because fulvic acids are more hydrophilic than humic acids, the effect of

fulvic acids on metals may be more likely to favor dissolution and mobility.

Effect of Organics on Other Reactions Incorporating Metals

Just as organic complexation may have either a positive or a negative effect on adsorption and solubility, it may also either increase or decrease biological uptake of metals. Vymazal (1984) observed that increases of humic substance concentration from 1.6 to 2.7 mg/L significantly decreased uptake of metals by periphytic algae. Baccini and Suter (1979) reported similar results. Uptake of copper by phytoplankton was positively correlated to the concentration of Cu^{2+} in solution, hence negatively correlated to the proportion of complexed copper. On the other hand, complexing agents may increase retention of metals in phytoplankton cells by increasing the solubility of the metals and facilitating their translocation across the cell wall and plasma membrane (Schulz-Baldes and Lewin, 1976). The translocation mechanism is important for blue-green algae that produce siderophores to improve the organism's capacity to incorporate iron (Murphy and others, 1976; McKnight and Morel, 1980).

Important oxidation-reduction reactions also are controlled to some extent by organics. The oxidation of ferrous iron may be inhibited by organic matter, even in highly oxidizing environments (Theis and Singer, 1973). Two explanations for this interaction were given by the authors: (1) iron(II)-organic complexes that are resistant to oxidation may be formed and (2) the ferric iron that is produced is promptly reduced again by the organics.

Overall Effect on Metal Speciation

In view of the variable effects of organics on metal behavior in aquatic systems, it is not surprising that studies of metal-organic interactions have produced notably inconsistent results. The presence of organic ligands in natural waters causes metal speciation to deviate considerably from predictions based solely on equilibrium constants of inorganic association and precipitation reactions. Each of the different types of association reactions tends to pull the system in a different direction. Various physical, chemical, and biological controls determine what type of association predominates at any given moment. The end result is that the presence of organic ligands is likely to have some effect on metal speciation, but the magnitude, and even the direction, of that effect is variable.

Biological Activity

Recent studies indicate that aquatic biota are not only affected by changes in bioavailability of metals due to partitioning but also play important roles in controlling partitioning mechanisms and pathways. Transformations of metals from one species to another are commonly mediated directly

by microbiota. Extracellular sequestering agents may be secreted by organisms in response to environmental stimuli and may act as important chelators of metal ions. Metals that are ingested or otherwise assimilated by organisms may undergo species transformations internally before reentering the aquatic system.

Methylation and Other Bacterially Mediated Transformations

Bacteria play very active roles in species transformations of metals. One of the most important microbially mediated transformations from a human health standpoint is methylation (Summers and Silver, 1978; Thayer and Brinckman, 1982). Transfer of a methyl group from methyl B12 (methylcobalamin) to the metal ion may proceed either aerobically or anaerobically and gives the organism a means of detoxification in metal-contaminated systems (Wood and Wang, 1985). Methyl mercury is an especially hazardous product of this process; it is responsible for the catastropic cases of "Minamata disease" in Japan. Microbial methylation of mercury, which is most active at the surface of bottom sediments, is favored by high temperatures and organic enrichment. It is inhibited by oxygenation of sediments (Callister and Winfrey, 1986). Other elements that are known to undergo biomethylation are chromium, arsenic, selenium, and tin (Ridley and others, 1977). Methyl forms of other toxic elements, including cadmium and lead, have been observed but their formation is less clearly understood.

Numerous other types of microbial transformations of metals are important controls on metal cycles and biological availability in aquatic systems. Oxidation-reduction reactions at the sediment-water interface or the anoxic-oxic boundary in stratified lakes are largely mediated by bacteria, which gain energy from the conversions (Goldman and Horne, 1983, p. 105). Sulfate reduction by bacteria (Lovley and Klug, 1983) produces the sulfide ion, which binds and precipitates many metals. Thus, the process has major significance in controlling metal partitioning in anoxic waters.

Algal Activity—Extracellular Sequestering Agents

Another type of biological activity that has recently been shown to have important effects on speciation and bioavailability of metals is extracellular production of sequestering agents capable of significantly altering the metal complexing capacity of the medium. Most commonly observed as a function of blue-green algae, this extracellular chelator release provides the organism with selective advantages over other species. As nitrogen fixers, some blue-green algae are able to capitalize on limitation of other species in nitrogen-poor waters and undergo dramatic population blooms (Horne and Goldman, 1972). However, their nitrogen-fixing capability is dependent on an adequate supply of iron (Murphy and others, 1976; Wurtsbaugh and Horne, 1983). To contend with the likely shortage of available iron in surface waters of lakes, the algae are capable of producing

siderophores (trihydroxamates) that selectively chelate ferric iron (Murphy and others, 1976). The siderophores serve as carrier molecules, specifically for blue-green algae, transporting iron across the cell membranes. At the same time, they render the iron less available to other algal species and thus suppress competitive growth.

The work of McKnight and Morel (1980) provided evidence that the hydroxamate siderophores released by blue-green algae are not as selective to iron as previously believed. Copper is also complexed by the siderophores. The resulting removal of free cupric ions from solution probably diminishes toxicity of copper by making it less available. Unlike the iron-siderophore complex, the copper-siderophore counterpart is apparently not assimilated by blue-green algal cells. This may be attributable to known differences in coordination numbers and molecular geometries of the two complexes. The blue-green algae thus derive secondary benefit from siderophore production. Other metals also may be complexed in similar fashion.

Figure 9 (from McKnight and Morel, 1980) illustrates siderphore complexation of copper. The graph represents titration of copper solutions with media from two separate cultures of the blue-green alga *Anabaena cylindrica*. One
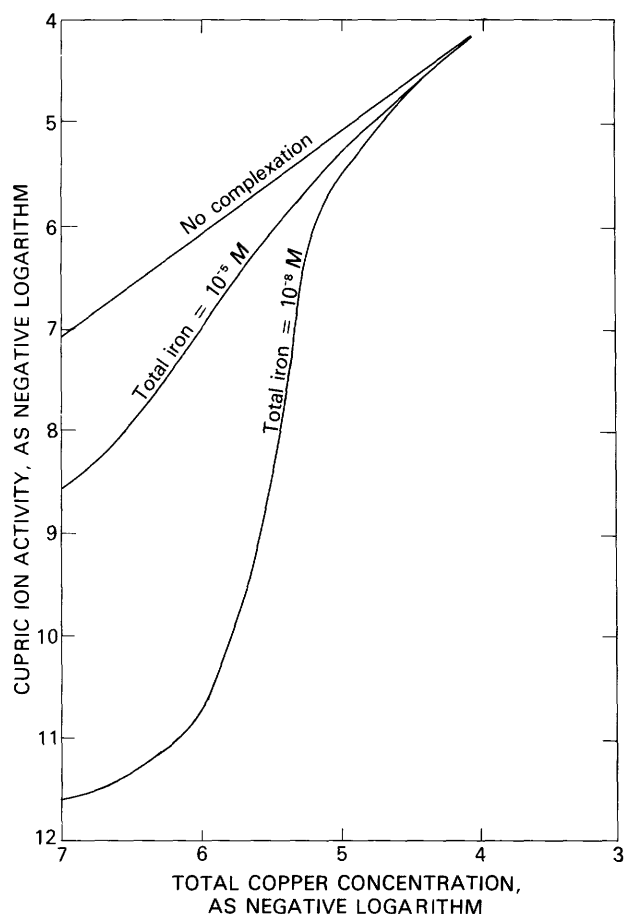
Figure 9. Free cupric-ion activity as a function of total copper concentrations and concentration of total iron, in cultures of *Anabaena cylindrica* (from McKnight and Morel, 1980, p. 64). *M*, molar.

culture was incubated at an iron concentration of 10^{-8} *M* (molar) and the other at an iron concentration of 10^{-5} *M*. Free cupric-ion activity is plotted as a function of total copper; both variables are represented as negative logarithms. The solid line represents no complexation; hence, cupric-ion activity equals total copper concentration.

Extensive complexation of copper occurred in media from the iron-limited *Anabaena* cultures, as shown by the curves (fig. 9) which drop well below the no-complexation line. Furthermore, more severe iron limitation produced the greatest copper complexation and left cupric-ion activity several orders of magnitude lower than total copper concentration. The lower iron concentrations stimulated production of siderophores, including some that were strong copper-binding agents (stability constant $> 10^8$).

Earlier studies by McKnight and Morel (1979) indicated that copper complexation by extracellular algal products is common to many algal species. Green algae and other eucaryotic species produced copper-complexing agents, although of lower complexing strength than those produced by blue-green algae. For all species, the benefit was the same—detoxification of copper. This study was an extension of work by Swallow and others (1978), who had found that very few algal species produced exudates that could alter cupric-ion concentrations. The later study extended the analyses to lower exudate concentrations, at which considerably more copper complexation was found to occur. However, green algal adaptation to copper (Kuwabara and Leland, 1986) could not be explained by media conditioning by algal exudates.

Further evidence of detoxification of copper by algal extracellular products was provided by Van den Berg and others (1979). A diatom, a blue-green alga, and a green alga were all shown to produce an exudate that diminished the toxicity of copper to photosynthetic activity of *Chlorella vulgaris*.

Enhancement of Iron-Manganese Oxide Formation

Iron and manganese oxidation in natural water systems may be catalyzed by microbial activity (Emerson and others, 1982; Nordstrom, 1985). The tendency for metals to be associated with hydrous oxides or concretions of iron and manganese is, therefore, partially dependent on biological characteristics of the system. This relation was demonstrated experimentally in the field by Kepkay (1985), by using azide-poisoned and nonpoisoned dialysis enclosures. Formation of manganese concretions, as well as uptake of dissolved copper, iron, manganese, and nickel, proceeded at a higher rate in nonpoisoned cells. Nordstrom (1985) demonstrated similar effects on iron oxidation by *Thiobacillus ferrooxidans* in a stream degraded by acid-mine drainage in California.

Other Biological Effects on Partitioning

Assimilation in biological tissue, resulting in bioaccumulation, is an important process affecting speciation

and transport of metals. The biota constitute a major reservoir for both toxic and nontoxic metals. Uptake by biota of a metal creates a multitude of transport possibilities, either by transfer through various trophic levels (Mathis and Kevern, 1975) or by transformation in the organism and subsequent release into the abiotic environment (Starkel, 1985). Further discussion of bioaccumulation and effects on biota follows in the Bioavailability and Bioaccumulation section of this paper.

Bioturbation of bottom sediments by benthic organisms may cause resuspension of previously deposited metals and result in increases in the metal concentrations in overlying water (Krantzberg and Stokes, 1985). Some benthic organisms may also alter sediment redox potential, which, in turn, affects metal cycling.

Hydraulic Energy—Flow and Turbulence

Water movement plays an important role in partitioning of metals in both riverine and lacustrine systems. In rivers and streams, the capacity for transporting suspended sediments depends on hydraulic flow, turbulence, and morphological characteristics (Guy, 1970). Therefore, the proportion of metals in the suspended phase increases with fluid energy. In lakes and reservoirs, the mixing characteristics of the system greatly influence the relation between metal partitioning and hydrologic factors.

Riverine Hydrologic Effects

In contrast to the correlation between riverine discharge and suspended sediment loads, dissolved metal concentrations are not necessarily an increasing function of discharge (Yeats and Bewers, 1982). If the major inflows to a river carry metal concentrations that are relatively constant, and if there are no major seasonal shifts in predominance between high-concentration and low-concentration sources, then increasing discharge is unlikely to produce either a dilution effect or a flushing effect. This is commonly the case in large rivers (Yeats and Bewers, 1982; Elder and Mattraw, 1984). Highly concentrated point-source inputs, which might cause discharge-related variability of metal loads in small rivers, are likely to be masked beyond detection in the volume of a large river.

Other studies have provided examples of both positive and negative effects of discharge on dissolved-metal concentrations in rivers. Positive effects may occur where new sources are activated by high discharges, resulting in maximum metal concentrations on the falling limb of the flood peak (Bradley, 1984). Negative effects are likely when heavy pollution produces high inputs of dissolved, labile forms of metals. The dissolved concentrations may decrease during high flow because of removal by sedimentation as the ions are adsorbed by suspended-sediment particles (Benes and others, 1985).

The relation, if any, between metal concentration and discharge in riverine systems is a function of several factors, including dilution, desorption of metals from sediments, and resuspension of sediments. The relative importance of these processes changes as discharge changes, as illustrated in figure 10 (from Turk and Troutman, 1981). These curves were derived from a study of polychlorinated biphenyls in the Hudson River, but the trends also apply to other solutes, including some metals, that adsorb to sediments. The authors observed that, as river discharge increased from minimum levels to about 500 m^3/s (cubic meters per second), the contaminant concentration (dissolved plus particulate) decreased, but, as discharge rose further, contaminant concentration (dissolved plus particulate) increased again, reaching maximum levels at maximum discharge.

The explanation of the contaminant-discharge relation illustrated in figure 10 is that different processes predominate in different flow conditions. At low flows, desorption is the primary mechanism of contaminant movement from sediments to water. As discharge decreases, the dilution factor decreases, while desorption remains nearly constant, resulting in an inverse discharge-concentration relation. During high-flow periods, resuspension becomes the predominant mechanism of contaminant movement from sediments to water. As discharge increases, the transport of greater sediment loads more than compensates for the dilution effect, and contaminant concentrations increase.

An important result of the overall pattern illustrated in figure 10 is that the species composition of the contaminant load is highly dependent on discharge. Dissolved forms predominate in low-flow conditions, and particulate forms predominate in high-flow conditions. In view of the general rule that the soluble, labile species are more bioavailable than particulate species, the contaminants transported during low flows may be of disproportionately high biological importance.

The expectation that the dissolved to particulate species ratio should be relatively high at low flow is consistent with the observation by Jackson and others (1982) that dissolved mercury in the Wabigoon River, Canada, increased in summer, while particulate mercury declined. The same pattern was observed by Benes and others (1985) for lead in a smelter-polluted river. In the Fraser River system in British Columbia, Geesey and others (1984) found that the bulk of total copper, nickel, and zinc in the bottom sediments consisted of reactive species (extractable with dilute hydrochloric acid and peroxide). During periods of low flow, there was more rapid deposition of particulate metals, causing an increase in the concentrations of reactive metals in surface sediments.

Lacustrine Hydrologic Effects

In stratified lakes, the iron cycle sets up in a characteristic pattern, illustrated in figure 11 (from Davison and others, 1980, fig. 14). Sometimes described as the "iron wheel," this cycle exists because of the marked differences in solubility and mobility of the two oxidation states. Below

the oxic-anoxic boundary (near the top of the hypolimnion in a stratified lake), ferrous iron predominates. Although the ferrous sulfide is insoluble and represents a pathway for removal of iron from the hypolimnion, additional iron moves in the opposite direction because of dissolution of sedimentary oxides and hydroxides. Eddy diffusion in the upper layers of the hypolimnion, and turbulence in the epilimnion, mixes dissolved iron vertically through the water column. Therefore, the entire process is largely driven by wind mixing and the hydrodynamics of the system.

Similar effects characterize manganese cycles (Verdouw and Dekkers, 1980; Davison and Woof, 1984). The principal difference is that manganese sulfides and oxides are somewhat more soluble than their very insoluble iron counterparts, and the metal therefore tends to be more mobile.

The iron and manganese cycles are highly significant in the partitioning and transport of other metals in lakes because of the common association between the metals and the iron-manganese hydrous oxides. The cycling of iron and manganese provides the other metals with a mechanism for movement from the sediments upward through the water column to the photic and oxygenated zones of the lake.

As illustrated in the diagram (fig. 11), vertical eddy diffusion and turbulent mixing are important processes in the iron-manganese cycle. Evidence of vertical eddy diffusion in the upper hypolimnion was provided by Hesslein and Quay (1973). Turbulent mixing within the epilimnion and diel vertical shifts of the thermocline (Elder and others, 1979) make

further metal transport possible in the water column. Biological uptake of the elements in the epilimnion may be active and rapid, as this type of cycle is most likely to occur during summer months when biological productivity is at maximum levels.

In unstratified systems that are wind mixed from top to bottom, the hydrologic effect is similar to that in rivers. Higher mixing energy produces greater capacity for movement of bottom sediments and all materials associated with them, but calm conditions may favor high dissolved to particulate ratios.

Nature of Substrate Material

Metal partitioning depends largely on the types of suspended matter and dissolved ligands that are available for binding. In systems that contain elevated concentrations of organic matter (for example, those that receive large inputs from heavily forested watersheds), metals are predominantly chelated and adsorbed to organic matter. It is important in such systems to examine the ratio of particulate to dissolved organic matter (POM:DOM) and to identify, if possible, the major organic species present. Much of the organic speciation will depend on the degradation processes that may break down POM before its transport into the aquatic system. It will also depend on the timing and severity of hydrologic activity that may initiate transport before degradation has progressed appreciably. In watersheds that produce runoff containing predominantly inorganic loads, the clay to silt ratio
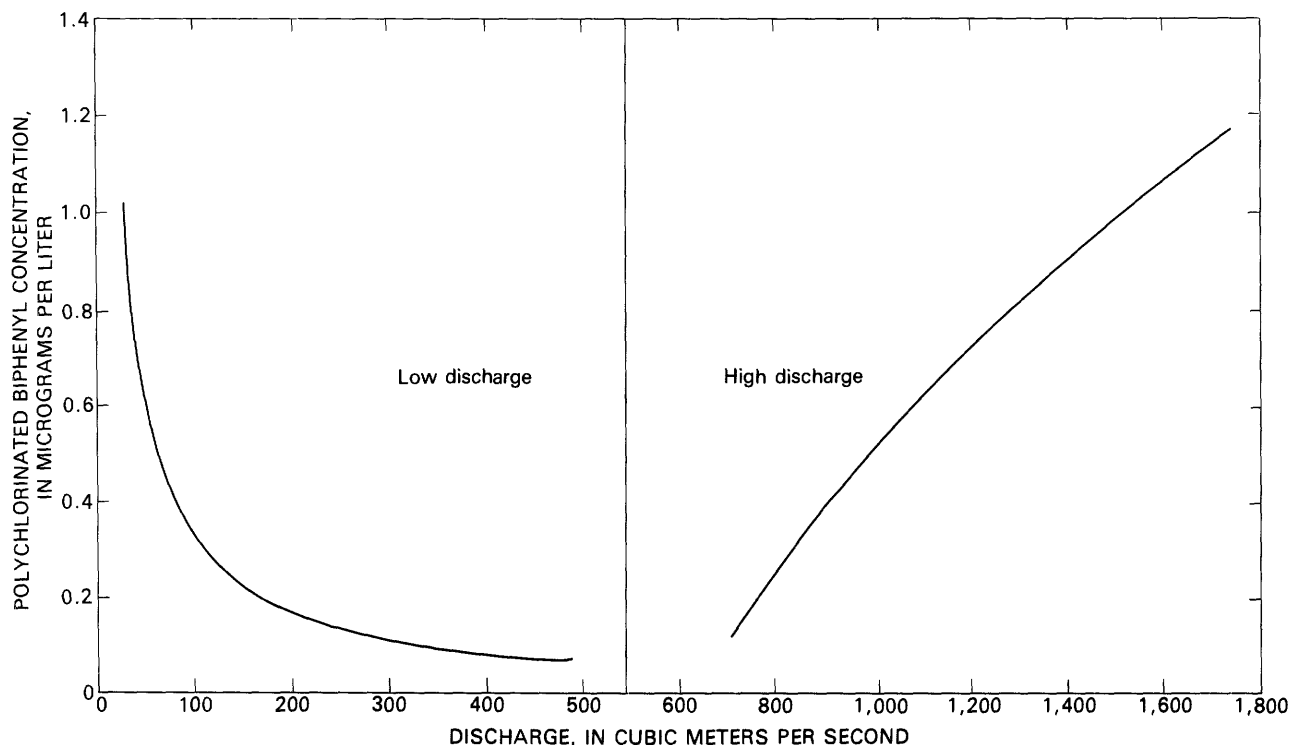

Figure 10. Polychlorinated biphenyl concentration in water (either dissolved or particulate), as a function of discharge in the Hudson River, N.Y. (from Turk and Troutman, 1981, p. 4).

and the composition of the clay load (fractions of different types of clays) will be important in affecting the adsorption-desorption processes associated with those particles.

Specific surface areas and exchange capacities of several sorption active surfaces were tabulated by Forstner and Wittman (1981, p. 209). This tabulation revealed substantial differences among clays, ferric hydroxide, and humic acids. Significant differences in exchange capacities existed for different types of clay minerals and for other important sorptive surfaces. Especially noteworthy was the very high exchange capacity of humic acids—170 to 590 milliequivalents per 100 grams. This was an order of magnitude greater than exchange capacities of most other surfaces listed. Similar data for fulvic acids, measured as the conditional formation constants for complexation of copper, were reported by McKnight and others (1983).

Sediment Grain Size

General Effects of Grain Size

Because the primary mechanisms of association between metals and sediments are complexation and adsorption processes at the particle surfaces, it follows that the extent of such association will be directly related to the total particle surface area.

For a perfectly spherical particle, the surface to volume ratio ($S:V$) may be expressed as a function of radius (R) as follows:

$$\frac{S}{V} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{R} \tag{3}$$

Hence, the $S:V$ ratio is inversely proportional to R. The result is that, for a constant mass, the surface area increases as particle size decreases. This is illustrated in figure 12, which shows the change in surface area as a hypothetical mass of uniform density is subdivided into smaller but equally sized spheroidal particles. The total surface area approximately doubles for every tenfold increase in number of particles. If these particles act as sorption surfaces, there should theoretically be a corresponding increase in adsorption sites. This relation is an oversimplification of natural phenomena, because natural particles are not perfect spheres and always have a certain degree of porosity, which adds considerably to their surface area. Nevertheless, the spherical-particle concept shows that, from a purely physical standpoint, smaller particle size correlates with greater surface area.

Grain-Size Effects in Natural Waters

The influence of surface area on metal adsorption was demonstrated by Oliver (1973), who determined metal concentrations on various sediment samples from the Ottawa and Rideau Rivers in Canada. True surface area of the sediments, determined by measuring nitrogen adsorption by a sorptometer, was an important factor in controlling sediment-metal concentrations. Concentrations increased with surface area,
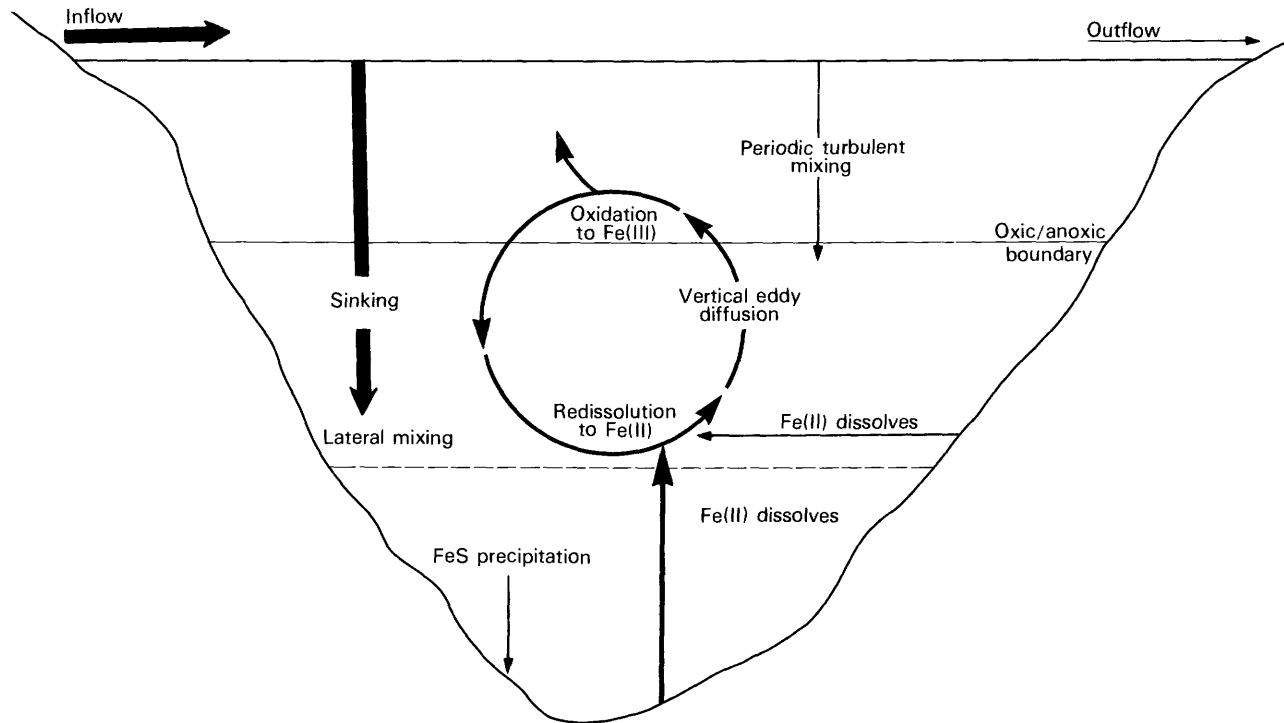

Figure 11. Iron cycle in a lake having an anoxic hypolimnion, showing various transport processes (from Davison and others, 1980, fig. 14). Relative importance of processes indicated by arrow thickness.

as shown in figure 13. The shape of the curve was found to be roughly the same for many other metals, including lead, zinc, copper, cobalt, iron, manganese, and chromium. The curve is also notably similar to the surface-particle relation shown in figure 12.

Other factors, however, usually cause the relation between particle size and metal concentration to deviate appreciably from the simple correspondence to physical changes in surface area. Gosz and others (1980) found that the origin of the sediments was an important factor. Sediments from limestone and sandstone generally showed the characteristic inverse relation between metal concentration and grain size, but this was not the case for sediments originating in basalt or granite. Some of the differences may be attributed to differences in the type of vegetation and organic-matter content. Rickert and others (1977) found that some metals are more likely than others to concentrate in the fine fractions. The observed concentrations of most metals were much higher in the <20-μm fraction than in the larger fraction, but chromium and mercury were notable exceptions. Association with relatively coarse organic particles of anthropogenic origin may account for the departure of chromium and mercury from the expected concentration-grain size relation.

As pointed out by Rickert and others (1977), the grain-size effect has major implications for analysis of data on total metal concentrations in sediments. Concentration differences among samples may reflect differences in proportion of fine material rather than reflecting variable metal loading.

In the Mattole River, Calif., a relatively pristine system, Jenne and others (1980) found concentration trends as a function of grain size for a large number of trace elements. Most metals conformed to the normal pattern of inverse relation between concentration and grain size. However, other elements, such as barium, sodium, and strontium, showed an opposite trend—their concentrations were higher in larger grain-size fractions. These differences were attributed to differences among metals in their tendency to sorb to clays, hydrous oxides, and organic matter, all of which are concentrated in fine fractions. The discussion included considerable description of methodology for sampling and processing both suspended and bed sediment to achieve grain-size fraction separation.

Bimodal Distribution

A common deviation from the inverse relation between metal concentration and grain size is bimodal distribution. This phenomenon is characterized by concentration peaks in the smallest grain-size fraction and in another fraction of larger particles. Concentrations in intermediate fractions are much lower.

In the Saddle River, N.J. (fig. 14), Wilber and Hunter (1979) found that zinc distribution in sediments was a decreasing function of grain size at an upstream site but was bimodal near the mouth of the river. In both cases, the highest concentrations were clearly in the smallest grain-size fraction ($<1\mu m$), but at the river mouth site, another concentration peak occurred in the largest size fraction (1,000–2,000 μm). The probable reason was that the downstream site was affected by municipal effluents. These effluents contained relatively high concentrations of coarse organic materials, which, because of their high metal sorptive capacity, carried disproportionately large amounts of zinc.
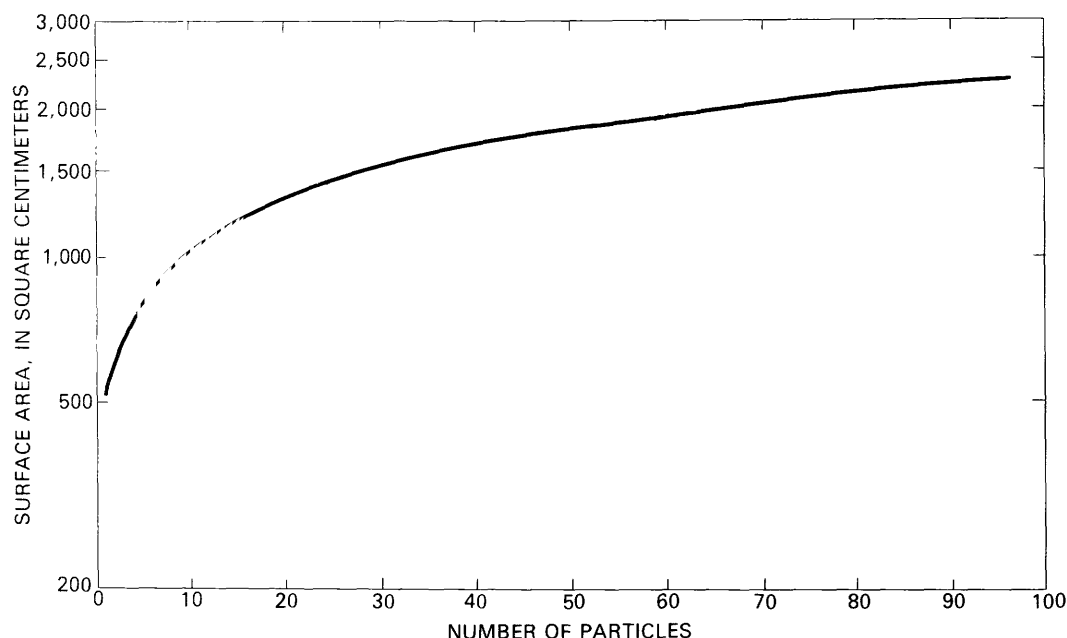

Figure 12. Total surface area of spherical particles whose total mass equals 1,000 grams and density equals 1 gram per cubic centimeter, as a function of the number of particles.

Bimodal metal distribution on different grain-size fractions has been observed in diverse environments, ranging from marine sediments (Horowitz, 1985) to small streams (Kennedy and others, 1985) and rivers (Rogers, 1983). In marine sediments, the secondary concentration peak in the larger grain-size fractions can be attributed to coatings and atmospherically deposited particles. Also, ferromanganese micronodules, rich in associated metals, generally fall in the size range of 10 to 20 μm (Horowitz, 1985). In the stream situation, described by Kennedy and others (1985), the bimodal distribution was attributable to variability of cation exchange capacity (CEC) in going from small to large particle sizes. In the midsize ranges, the grains tended to be composed of a higher proportion of minerals of low CEC, whereas both the smaller and the larger grains contained higher proportions of highly reactive clay-silt aggregates.

Effects of Grain Size on Metal Transport

Although metal concentrations and grain sizes are usually inversely correlated, it does not follow that metal transport in rivers is also inversely correlated to grain size. Larger grain size generally signifies higher discharge, although various other factors, such as particle shape, turbulence, and flow depth, are also important (Guy, 1970). Hence, greater total sediment loads and greater total metal loads may be expected if grain size increases. However, because of the effects of grain size on concentration, this increase in metal transport is not proportional to the increase in sediment load.

Although the dependence of metal concentrations on sediment grain size is well documented, the assessment of metal loading in sediments by examining only the small grain-

size fractions may be misleading (Forstner, 1982; Salomons and Forstner, 1984). The larger grain sizes are less subject to scour; hence, they are less mobile and more likely to provide an accurate long-term record at a given site. The midrange size fraction (20–200 μm) is the most common in most bulk sediments. The largest proportion of the total metal load may reside in this fraction because of its abundance, even if the concentrations are lower than in the smaller fractions. Therefore, particle-size distribution and chemical analysis of different size fractions are both necessary to fully describe particulate metal loading under different flow regimes.

Temperature, Light, Salinity, and Water Hardness

Numerous other characteristics of the aquatic environment exert various degrees of influence over metal partitioning. Among these are temperature, light, salinity, and water hardness.

The importance of temperature derives largely from high sensitivity of most chemical reaction rates to temperature changes (Morgan and Stone, 1985). An increase of 10° C can double the reaction rate (Hem, 1985). Because reaction rates determine the tendency of a system to attain equilibrium, temperature is a controlling factor on the chemical speciation of the system. Various chemical reactions also are sensitive to light. Among the important effects of light is photo-reduction of iron, releasing soluble Fe(II) from ferric hydroxides (McMahon, 1969; Miles and Brezonik, 1981; Collienne, 1983). Photo-oxidation of organic compounds may simultaneously release metals bound in organic complexes (Collienne, 1983). Temperature and light are also important controls on biological activity (Goldman and Horne, 1983),
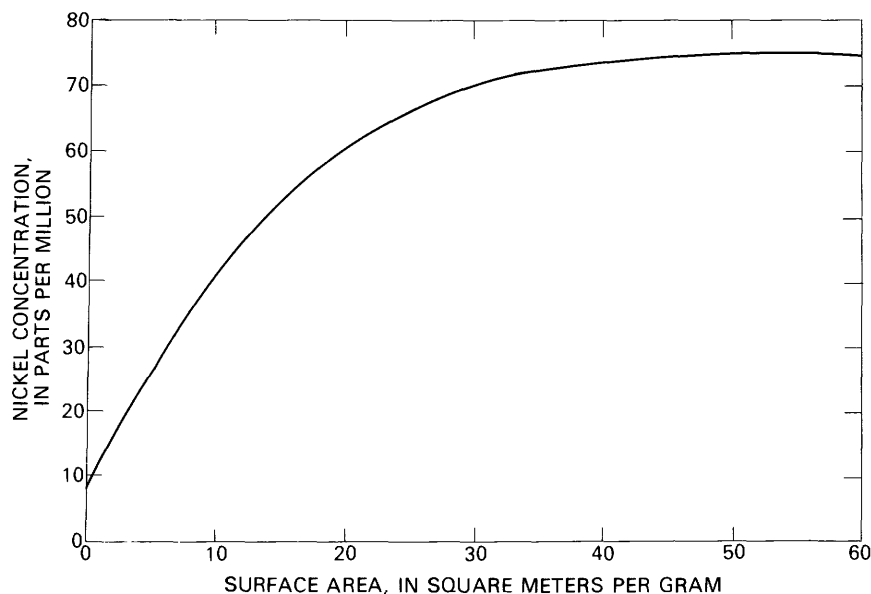

Figure 13. Nickel concentrations as a function of surface area in bottom sediments of the Ottawa and Rideau Rivers near Ottawa, Canada (from Oliver, 1973, p. 136).

which may affect speciation of metals associated with biological products.

High salinity or water hardness exerts important control on metal speciation. Major ions, particularly magnesium and calcium, interfere with complexation and adsorption, presumably by competing with trace metals for surface-binding sites (O'Connor and Kester, 1975; Gupta and Harrison, 1981; Millward and Moore, 1982). In addition, alkaline-earth ions, especially calcium, seem to control permeability of cell membranes to solutes (Oduleye, 1976). Reductions in metal toxicity attributable to increases in water hardness have been documented repeatedly (Howarth and Sprague, 1978; Chakoumakos and others, 1979; Chapman and Dunlop, 1981; Rai and others, 1981; Stendahl and Sprague, 1982).

EFFECTS OF METALS ON AQUATIC BIOTA
Bioavailability and Bioaccumulation

Bioaccumulation of metals in tissues of aquatic biota and the physiological and ecological effects of metal uptake are important results of metal contamination. Measurement of these factors is essential to complete understanding of the environmental effects of metals.

There is a tendency to assume that metal uptake rates of organisms are directly related to metal concentrations in their habitat medium, either sediments or water. In fact, this relation has often been documented. Dixit and Witcomb (1983) found high levels of copper, lead, and zinc in in-

vertebrate fauna of the River Irwell, England, and a linear relation between concentrations in the animals and those in the substrate. In a much less polluted system (Kootenay Lake, British Columbia), Evans and Lasenby (1983) found a correlation between concentrations of lead in crustaceans (*Mysis relicta*) and in sediments, even though *M. relicta* is a benthic detritivore only during daylight hours (it migrates upward to feed on plankton at night).

It is equally common, however, to find cases where there is no apparent relation between bioaccumulation and concentrations in the habitat medium. Heit and Klusek (1985) found no relation between trace element concentrations in fish dorsal muscle and those in surficial sediments, despite the bottom-feeding habits of the fish species studied. Elder and Mattraw (1984) found little evidence of correlation between metal bioaccumulation in *Corbicula manilensis* and concentrations of the same metals in the riverine sediments where the animals were found.

In view of the wide range of bioavailability of different forms of metals, it is indeed apparent that substrate concentration alone cannot be the sole factor that determines uptake by organisms. Marquenie (1985) discussed this phenomenon, with description of some case studies. For example, a contaminant contained in a fine sediment might be less toxic than the same contaminant at equal concentrations in coarse sediment, because the tendency to adsorb to fine particles diminishes the bioavailability of the metal.

Multielement Effects

During the past decade, a number of investigations have focused on bioaccumulation as influenced by effects of multiple elements. In particular, the investigations have shown that the concentrations of iron and manganese, in addition to those of the metal in question, influence the ultimate effect of the subject metal on the organism. While examining the inhibitory effects of cadmium on green algae (*Chlorella pyrenoidosa*), Hart and Scaife (1977) found that cadmium accumulation was effectively blocked by moderate concentrations of manganese or iron.

The effect of iron or manganese concentrations on metal bioavailability complicates the relation between concentration of a metal and its uptake by biota. Rather than a direct relation, bioaccumulation of a metal probably is related to an extractable metal to iron ratio or to an extractable metal to manganese ratio. More specifically, the ratio of the extractable metal concentration in the sediments to the concentration of amorphous oxides of iron and manganese might be the important control. As this ratio increases, the number of oxide-binding sites that are occupied by the adsorbate metal also increases, resulting in a progression toward saturation of the binding sites. Increased occupancy of the binding sites diminishes the likelihood that additional metal will be sorbed, leaving higher concentrations available for biological uptake.
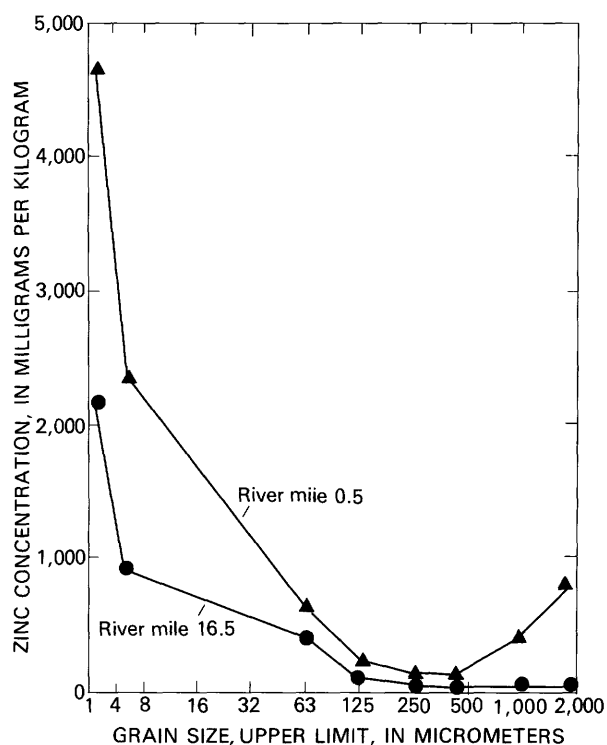

Figure 14. Concentration of zinc in sediments of the Saddle River, N.J., as a function of grain size (from Wilber and Hunter, 1979, p. 798).

The importance of element ratios in determining bioaccumulation was confirmed in a study by Luoma and Bryan (1978). They found that the lead to iron ratio in 1 N HCl extract of sediment could explain nearly all variability of lead concentrations in the bivalve *Scrobicularia plana* from English estuaries. There was no doubt that this ratio was a better factor than total sediment lead concentrations to use as a predictor of lead concentrations in *S. plana*. The model was consistent enough to be a quite reliable predictor of concentrations of metals in bivalves in all estuaries where it was tested. Its accuracy was corroborated by Langston (1980) in studies of arsenic availability to *S. plana* in English estuaries.

Similar study of another pelecypod mollusk (*Elliptio complanata*) by Tessier and others (1984) confirmed the findings of the *Scrobicularia plana* studies. Copper, zinc, and lead concentrations in *E. complanata* were found to be much more closely related to sediment extracts (using magnesium chloride, acetate, acetic acid, and hydroxylamine as extracting agents) than to total sediment metal concentrations. The authors suggested that the protective or competitive role of iron was the primary reason for the close relation between metal concentration in the organism and the total metal extract to iron extract ratio in the sediments.

All of these studies illustrated the importance of the association of metals with the amorphous iron oxides, as had been proposed by Jenne (1968) and documented by various authors since then. Amorphous iron oxide is likely to be a relatively small fraction of the total iron in the system, but it exerts a disproportionate control over speciation of metals. The selective extraction methods used in the studies by Luoma and Bryan (1978) and Tessier and others (1984) attack the amorphous iron oxide but not the more crystalline iron oxide phases. When more vigorous extraction procedures are used, the crystalline iron is removed, and the correlation with bioaccumulated metal becomes much weaker.

Mechanisms by which iron might exert such control over bioaccumulation of other metals were suggested by both Luoma and Bryan (1978) and Tessier and others (1984). Three scenarios were envisioned, all of which probably occur, depending on the species. The first is that iron and metal are ingested together and iron is solubilized by the acidic, reducing conditions in the digestive tract of the organism. Iron then competes with the other metal for uptake sites in the digestive system. The second is that both iron and metal are ingested together, but iron remains in particulate form. The iron oxide continues to compete with other binding sites for metals, just as it does outside the organism. Thus, availability of the ingested metal is reduced. The third scenario is that uptake of the metals is not through ingestion but through the gills and mantle and the association of iron oxide and metal in the external medium reduces the availability of the metal.

A study of bioaccumulation of lead in freshwater snails (Newman and McIntosh, 1983b) indicated that the pro-

tective role of iron and manganese is not universal. Although lead was slowly accumulated by the snails from aufwuchs (attached seston and biota) and sediments, bioaccumulation was not affected by iron or manganese concentrations in aufwuchs. The authors acknowledged that one reason for this may have been insufficient concentration differences to induce different responses. The lead to iron ratio ranged from 0.007 to 0.016. The other possible explanation offered was that the original hypothesis that iron or manganese oxides may interfere with lead accumulation may have been incorrect. The need for more research on this topic was emphasized.

Multielement effects involving other metals were described by Popham and D'Auria (1982) and by Calabrese and others (1984). Uptake of copper by the mussel *Mytilus edulis* was enhanced by high concentrations of lead, zinc, or silver. Copper was apparently accumulated preferentially to the other elements. The presence of the other metals may, in some way, facilitate transport of copper across the cell membrane, but specific explanations for this were not given.

Kuwabara (1985) found that interaction between zinc and phosphorus can increase the growth-limiting effect of phosphorus for algae (*Selanastrum capricornutum*). Elevated zinc concentrations may interfere with phosphorus metabolism. Other metals that are involved in nutrient assimilation and metabolism include manganese, iron, copper, molybdenum, and cobalt (Goldman and Horne, 1983).

Nonuniform Bioaccumulation Among and Within Individuals

Bioaccumulation and toxic effects of metals correlate in some cases with size and age of the organisms (Bryan and Hummerstone, 1978; Bryan and Uysal, 1978; Tsai and Chang, 1984). However, in other cases, there is no apparent relation between bioaccumulation and animal size (Harvey and Knight, 1978). Of the two gastropod species studied by Newman and McIntosh (1983a), one showed no relation between lead concentration and size, whereas the other showed a curvilinear relation. An explanation for the inconsistent importance of size in controlling bioaccumulation was given by Smock (1983), with reference to concentrations in aquatic insects. Two general patterns of relation to size were proposed, as illustrated in figure 15. The mode of uptake is shown to be a factor that affects bioaccumulation and the effects on the organism. Where adsorption on the exterior surfaces of the organism is the primary mechanism of uptake, the effect of size is precisely the same as it is in sediments—larger size means smaller surface-to-volume ratio and decreased uptake. This relation is illustrated by curve A in figure 15. If absorption is the primary mechanism of uptake—that is, if the metal is ingested with food and absorbed through the gut, size of the organism has little effect. If anything, there is a slight increase of metal concentration with increasing size, as illustrated in curve B in figure 15.

The results of Zaroogian and Johnson (1984) show that uptake of nickel by the bivalves *Crassostrea virginica* and *Mytilus edulis* is indeed dependent on size and follows the general pattern of curve A (fig. 15). These animals are filter feeders and might be expected to assimilate the metal internally, as had been demonstrated for another bivalve mollusk by Bryan and Uysal (1978). According to the model of Smock (1983), curve B should apply, and there should be no effect of size on metal concentration. The apparent contradiction indicates that the processes involved are not fully understood and that the effect of size may be more complicated than is indicated by Smock's model.

Bioaccumulation rates may vary considerably among different organs of the same individual. The freshwater mussel *Anodonta cygnea* was exposed to 10 μg/L mercury and 16 μg/L cadmium, and separate analysis of bioaccumulation in different organs were performed by Balogh and Salanki (1984). Both metals in nearly all organs accumulated linearly during the 840-hour experiment, but at different rates. A ten- to twentyfold difference was observed between kidney and adductor muscle accumulation.

Effects of Speciation on Bioaccumulation

Different metal species in sediments and water have different degrees of bioavailability. Aquatic biota respond quickly to changes in concentrations of free metal ions, but the availability of metals bound to organic and inorganic

Figure 15. Metal bioaccumulation by an organism, as a function of weight of the organism (from Smock, 1983, p. 319). Curve A, bioaccumulation primarily by adsorption; curve B, bioaccumulation primarily by absorption.

ligands, or adsorbed to suspended matter, is generally less than that of the free ions (Marquenie, 1985). Although studies of both speciation and biological effects of metals are common, there are relatively few studies that link measured concentrations of specific metal forms with bioaccumulation or biological responses.

Studies such as those by Diks and Allen (1983) and Kuwabara and others (1986) do provide some insight into the nature of speciation effects on bioaccumulation. Diks and Allen (1983) analyzed concentrations of copper in various sediment and water fractions from Illinois and Indiana rivers. These data were compared to metal concentrations in tissues of tubified worms that were exposed for up to 12 days to the same sediments and water. A high correlation ($R>0.97$) was found between the copper extracted from the amorphous manganese oxide fraction and the concentration of copper in the worms. Other copper fractions were less correlated to bioaccumulation. Kuwabara and others (1986) tested growth response of the green alga *Selenastrum capricornutum* to dissolved and particle-bound orthophosphate and zinc. The particle-bound fractions of both elements (adsorped to particles of titanium oxide) were less available to the algae than zinc and phosphorus in solution.

Toxicity
Use of Biota as Pollution Indicators

Increasing concern over hazardous waste contamination of natural water systems in recent years has led to increasing development of methodology for assessing contaminant effects. One area of development has been in the use of aquatic biota as indicators of contamination. This use generally entails one of two approaches: (1) examination of occurrence and distribution of natural populations in the affected habitat or (2) examination of response of nonnative organisms when placed in the affected habitat or a simulation of the habitat. The principal advantage of using bioindicators is that they integrate effects of whatever contaminants may be in the system. Conversely, one disadvantage is that observed effects are difficult to attribute to a particular contaminant in any system having multiple contaminants and sources.

Use of bioindicators to assess trace metal contamination has had some success in recent years. Examples are studies by Sheppard and Funk, 1975; Winner and others, 1980; Whitton and others, 1981; Bryan, 1983; Leland and Carter, 1985; and Swift, 1985. The results of all of these studies indicated that the existence of water-quality problems was signaled by changes in the biotic community—either in the community structure or community metabolic processes, or both.

In rivers, the distribution of different types of organisms can be a useful bioindicator. The characteristic continuum is that shredders and collectors dominate in headwaters, grazers and collectors in midwaters, and gatherers in large rivers (Vannote and others, 1980). Responses of ben-
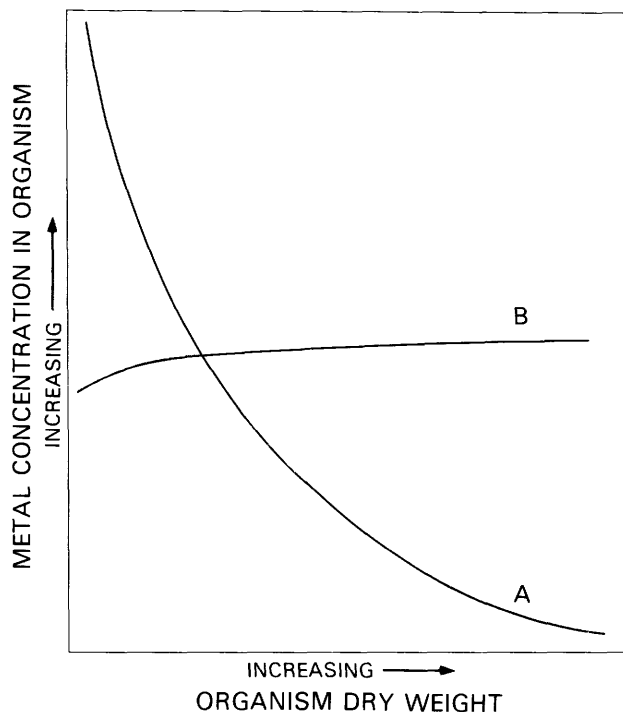
thic invertebrates to pollution abatement in the Penobscot River, Maine, were interpreted by Rabeni and others (1985) as illustrating a shifting of the riverine community continuum because of changes in contaminant levels. Pollution tended to shift this continuum in a downstream direction.

Whitton and others (1981) listed several advantages to using bioindicator species, particularly plants, to monitor heavy metals in rivers. The advantages are significant but should be interpreted with caution. For example, the metal composition of a particular plant species is likely to be less heterogeneous than that of the sediments. The restriction to "a particular species" is critical here, because differences among species in their resistance and adaptation to contaminants yield a great deal of cross-species heterogeneity (Luoma, 1977; Norris and Lake, 1984). Comparisons of bioaccumulation in different species should not be attempted as a means of comparing pollution effects in different systems. Even within one species, individual variations and factors that may not be taken into account, such as differences in size, age, or reproductive state, may produce heterogeneous results (Luoma, 1977; Ney and Van Hassel, 1983). If these variables are adequately taken into account, bioindicator organisms can be valuable tools for assessing problems of contamination, especially when used in combination with chemical analyses.

Norris and Lake (1984) noted that the reliability of using bioindicators depends on the metal being tested. Copper and zinc bioaccumulation by fish correlated quite well with water concentrations of the same elements, but the same degree of correlation could not be shown for cadmium. This difference probably is caused by distinct speciation patterns of the different elements and distinct pathways for their incorporation into biological tissues. Compartmentalized bioaccumulation among different tissues of rooted plants was demonstrated by Buhl and McConville (1984).

Among the advantages of using plants as bioindicators, Whitton and others (1981) included the integrated record that is produced. Knowing what facet of the system is being integrated, however, is also important. Some species of aquatic macrophytes extract metals primarily from the sediments, while others extract from the water (Heisey and Damman, 1982). Even an individual species may extract different metals from different phases. Campbell and others (1985) observed that most of the copper accumulated by the water lily *Nuphar variegatum* was derived from the sediments, whereas most of the zinc in the plant came from the water.

Effects of Metals on Phytoplankton

A considerable amount of work has been done over the past several decades that demonstrates impacts of trace metals on phytoplankton activity in aquatic systems. Phytoplankton are quite sensitive to most metals, and most studies that examine algal response to changes in metal con-

centrations, whether in the laboratory or in the field, show positive results.

The effects of metals are not limited to toxicity; metals may also stimulate activity in some situations. The most common metal to show stimulatory effects is iron, but similar effects have also been observed for other metals, including manganese, cobalt, vanadium, and molybdenum (Wiessner, 1962; Goldman, 1972). Copper and zinc, which are frequently toxic to algae and other biota at relatively high concentrations, are essential micronutrients. Deficiency symptoms may develop in algae when copper or zinc concentrations fall below 10^{-7} or 10^{-6} M (Wiessner, 1962).

Copper and zinc are good examples of elements that have ambivalent biological impacts, especially with respect to phytoplankton. They may either be nutrients or toxicants at natural water total concentrations. This is explained by limited bioavailability of bound and precipitated species. If natural water ligands are present in concentrations that exceed that of the metal, complexation may leave a bioavailable metal fraction that is several orders of magnitude less than the total concentration and less than the micronutrient requirements for the metal (Manahan and Smith, 1973). Relatively small changes in the total ligand to metal ratio, or changes in ambient conditions, particularly pH, may shift the equilibrium such that the concentrations of the bioavailable metal become high enough to be toxic.

The stimulatory capacity of copper has some implications for possible "backfiring" when using this element as an algicide (Telitchenko and others, 1972). The amount of the copper addition is critical. Although too much may be costly and dangerous to other organisms, too little may serve only to raise the Cu^{2+} concentration slightly toward an optimal level and actually encourage algal growth (Elder and Horne, 1978).

Toxicity as a Function of Bioaccumulation

Results of studies show that the question of whether or not toxicity is related to the concentrations of metal accumulated by the organism does not have a simple answer. Cadmium and copper toxicity to daphnids was affected by humic-acid concentrations, but bioaccumulation was not affected (Winner, 1984). *Chlorella pyrenoidosa* growth was sensitive to cadmium in experiments performed by Hart and Scaife (1977), but a great deal of cadmium could be accumulated in the organism without shutting off its productivity, possibly because of production of protective cadmium sequestering agents. The relation between toxicity and bioaccumulation is clearly variable among different species and is probably dependent on the mechanism of uptake and metabolism (Leland and Kuwabara, 1985).

Baccini (1985) noted that, when a phytoplankton community is exposed to a trace metal stress, the community structure tends to shift toward those species that accumulate the lowest concentrations of the metal in their

tissues. Species that accumulate high concentrations suffer the greatest effects on metabolic rates and may eventually disappear from the community.

Effects of Metal Interactions

The biological effect of one metal may be influenced by the presence of others. In some cases, this effect may be to reduce toxicity (antagonism), and in other cases, the effect may be to increase it (synergism). Tolerance of white suckers to cadmium increased when they had been previously exposed to cadmium or mercury (Duncan and Klaverkamp, 1983). Several mechanisms for this enhanced tolerance were suggested, including decreased uptake, increased excretion, redistribution of metals to less sensitive biochemical storage sites, and induced synthesis of metallothionein (a protein that facilitates metal storage and detoxification). A similar conditioning effect of prior metal contamination was observed by Titus and Pfister (1984). Bacteria in sediments of the Ottawa River showed higher tolerance to cadmium when concentrations of various other metals were high.

Growth of copepods that were exposed to various pair combinations of arsenic, cadmium, copper, lead, mercury, and zinc was inhibited in all cases more than when exposed to single metals (Borgmann, 1980). However, very little synergism and no antagonism were observed; the toxicities of the metal pairs could be accounted for by summation of the individual toxicities. Hart and Scaife (1977) could not find any evidence of effects of metal interactions with most combinations of metals in their experiments with *Chlorella pyrenoidosa*. Cadmium accumulation, although unaffected by extracellular presence of cobalt, copper, molybdenum, or zinc, was almost totally blocked by manganese.

The capacity of an organism to develop tolerance to metals also was demonstrated by Seim and others (1984). Steelhead trout that were continuously exposed to copper were better able to grow and survive than if the exposure was intermittent (4.5 hours per day). Continuous exposure may allow the organism's defense mechanisms to develop more effectively than would be allowed by temporal variation in exposure levels. Unfortunately, the intermittent exposure situation is more common in natural waters.

TRANSPORT OF TRACE METALS IN RIVERS AND LAKES
Forms of Transport in Rivers

Riverine transport of trace metals is generally characterized by high proportions of particulate species, especially during high flows (Jackson and others, 1982; Yeats and Bewers, 1982; Benes and others, 1985). Even when soluble species dominate the composition of inflowing water, they have strong affinity to three types of suspended materials—organic detritus, clay mineral particles, and iron-manganese oxide coatings—all of which are abundant in most river waters. Many studies of metals in rivers indicate the relative amounts of metals in dissolved and particulate phases, but few go beyond that. However, some information is available to describe partitioning of metals transported in large rivers.

Some of the most detailed work on forms of metal transport in rivers has been done by Gibbs (1972, 1973, 1977). Five phase categories were recognized: (1) dissolved, (2) adsorbed on solids, (3) associated with particulate organic material, (4) as metallic coatings (adsorbed to hydrous oxides of iron and manganese coated on suspended particles), and (5) in crystalline material structures where the metals are almost totally unavailable for further cycling. Most work was done on two very large rivers—the Amazon and the Yukon. Striking similarities were found between the two rivers with respect to the relative proportions of different metals transported in the respective phases. The proportions varied among different metals, however. Manganese speciation was dominated by coatings, as might be expected, but relatively high proportions were also found in crystalline and dissolved forms. Chromium was distributed primarily between dissolved and crystalline species, with very little of the element associated with coatings. More than three-quarters of the copper was in crystalline form, with the remainder almost evenly distributed among the more available forms.

Rivers that carry heavy loads of suspended sediments are naturally those that exhibit the highest fractions of particulate metal transport. This may explain the similarity between the Amazon and the Yukon Rivers, both of which are characterized by heavy sediment loads (Gibbs, 1977). In contrast, the St. Lawrence River, which carries a relatively lighter suspended sediment load, displays lower particulate to dissolved metal ratios (Yeats and Bewers, 1982). Even then, the ratios are still much greater than unity.

A study of 20 of the world's major rivers by Martin and Meybeck (1979) also demonstrated how different metals vary considerably in form of transport. This variation was attributed primarily to differences in weathering rates and coordination chemistry. Dissolved fractions constitute a substantial fraction of the total transport of arsenic, copper, molybdenum, and zinc, whereas 90 percent of the elements chromium, cobalt, lead, manganese, and nickel are carried in particulate form. Some elements, such as zinc, may occur in higher concentrations in river water than can be accounted for by composition of watershed substrate materials. These high concentrations indicate remobilization of such elements from the bottom sediments, which provide an autochthonous source that adds to constituents in inflow from watershed drainage.

Differences in speciation behavior of cadmium, copper, lead, iron, and zinc in the Yarra River, Australia, were observed by Hart and Davies (1981). The analytical approach permitted separation of particulate, filterable, ion-exchangeable, dialysable, and bound-metal fractions. The dominant forms of the metals in the river were, respectively:

Cadmium:	free Cd^{2+}
Copper:	ion exchangeable
Iron:	bound (nonion exchangeable) and particulate
Lead:	$PbCO_3^0$
Zinc:	free Zn^{2+}

Of the ion-exchangeable fraction, organic complexes were important for copper but not so important for lead and zinc. Increases in concentrations of iron, lead, or zinc were manifested primarily as increases in bound and particulate, not ion-exchangeable, species. This trend presumably reflects equilibrium shifts toward adsorption when metals are introduced as the free ion or other labile forms.

Particulate transport is favored in relatively unpolluted systems, where metal inputs are principally from erosion of watershed substrates. In polluted systems, where sources are likely to deliver metals in a soluble phase or loosely associated with organic material, the proportion of dissolved metals tends to be higher (Salomons and Forstner, 1984, p. 162).

Studies in a variety of localities have demonstrated that the species of metals transported in rivers are transformed when the metals enter coastal estuaries (Kharkar and others, 1968; Hart and Davies, 1981; Ellaway and others, 1982; Danielsson and others, 1983). In most cases, these transformations were observed to proceed toward greater particulate fractions, as flocculation or coagulation was triggered by increased dissolved solids in the estuarine water. However, Kharkar and others (1968) reported that significant amounts of some metals are released from particles into dissolved forms when reaching the oceans. This release was calculated to contribute most of the dissolved cobalt supplied to the oceans from rivers. In their study of the Amazon plume, Boyle and others (1982) found that copper and nickel were relatively unreactive upon discharge to the ocean, but there was some indication of desorption of cadmium.

Transport in Lakes

Most investigations of metal transport and cycles in lakes and estuaries have focused on iron and manganese (Evans and others, 1977; Jones and Bowser, 1978; Davison, 1982; Morris and others, 1982; Davison and Seed, 1983; Sundby and Silverberg, 1985). The cycles of these two elements have significant influence over the cycles of other elements because of sorption and desorption from iron and manganese hydrous oxides.

Particle flux, or movement of suspended particles through the system and into the bottom sediments, is another important control on metal cycles in lakes (Baccini, 1985; Joshi, 1985; Sigg, 1985). Data from various lakes of different morphological features were used by Santschi (1984) to compare mean residence time of zinc with particle flux to the bottom, in grams per centimeter per day. A close inverse correlation was found. Elements that have the greatest

affinity for particles, such as iron and cobalt, are most likely to conform to this type of correlation with particle flux (Hesslein and others, 1980). Characteristics of the particles, especially ionic radius, electronegativity, mineralogy, and porosity, are also important in determining their capacity for transporting dissolved metals (Jackson and others, 1980).

OVERVIEW

The metals that have been discussed in this review are extremely important constituents of natural water systems. They are ubiquitous, and they are readily associated with other constituents—both abiotic and biotic. Characterized by a small ionic radius and high surface charge, their biogeochemical interactions are diverse and complex. Metals may accumulate in particulate matter and biota. In water, they commonly occur at concentrations of less than 1 μg/L, but even at such concentrations, they are likely to have important biological effects. Their effects on sensitive populations can substantially affect the structure and function of the aquatic community. Effects on human populations also are important. Transferred through food chains, or transported to potable water sources, metals can create special problems for human health and aquatic-resource management.

Research on occurrence, transport, biogeochemical cycles, and biological effects of metals in aquatic systems has been active, especially in the past two decades. In view of the complexity of metal behavior and extremely low levels of effective concentrations, researchers are faced with some formidable problems. With the aid of improved partial extraction techniques and analytical methodology, many studies have provided detailed insight into specific situations having well-defined conditions. When biota are involved, the success of the investigation usually depends on limitation of the study to one species or to a few very similar species. Generalizations of results from one situation to another are extremely difficult and usually unsuccessful. Models are useful to facilitate understanding of fundamental chemistry of the metals, but applied to natural systems, they are prone to inaccuracy because of the complexity and natural variability of environmental factors.

In spite of such difficulties, considerable progress has been made in understanding trace metal biogeochemistry. Although research results commonly conflict as a result of natural variability, a number of common themes emerge from the vast body of literature on the subject. Specific studies explore various facets of these basic themes and serve to provide additional documentation and detail to them. The following itemized statements synthesize important themes and represent the current state of our understanding of metals in surface waters, derived from results of research to date.

- Anthropogenic and natural processes are important as sources of trace constituents. Some metals, such as aluminum and iron, are very common in the Earth's

crust and are present in natural waters at substantial concentrations. These concentrations vary geographically (being controlled by the geologic characteristics of the watershed) but are likely to be quite stable over time. Other elements (for example, cadmium, mercury, selenium, and silver) are rare in the Earth's crust. Background concentrations of such elements are low but usually detectable by state-of-the-art analytical tools. The presence of any of the metals in natural waters at concentrations higher than background is usually attributable to one of three common anthropogenic sources: (a) deposition of atmospheric pollutants, (b) point-source discharges of municipal or industrial waste products, and (c) nonpoint-source runoff from agricultural or silvicultural areas or urban impervious surfaces.

- In areas of mining activity, mine drainage can significantly increase concentrations of various metals, such that the contaminated waters may be uninhabitable by most aquatic biota and the water may be unusable for agricultural or domestic purposes. The metal contaminants are by no means limited to those that are mined. Contaminants are released in the processing of mineral ores, and their transport is facilitated by the high acidity usually characteristic of mine drainage.

- Metals accumulate in sediments and biota at much higher concentrations than those that remain in the water. However, the dissolved fractions can be very important biologically because they represent a principal source of bioavailable metals.

- Anthropogenic input of metals is likely to increase the proportion of dissolved metals in the system, at least near the input source, because metal pollution is usually accompanied by other types of pollution, such as acidification or elevated concentrations of dissolved organic matter, which favor solubilization of the metals.

- Because of their charge and small ionic radius, free-metal ions in solution have a very strong tendency to become associated with various other constituents of the aquatic medium. Some of these associations cause precipitation, some lead to incorporation in colloidal or suspended particles, and some leave the metal in a dissolved state but bound with dissolved ligands as complexes or chelates (complexes with multiple binding sites). Nearly all of the association reactions that result in the formation of different forms, or species, of metal are reversible. Slight changes in environmental factors, such as temperature or pH, can produce appreciable shifts in species composition. The result is that, at any point in time, the metal exists as numerous species and the proportions of these species are highly subject to change. Activities of the dissolved free-ion species are generally several orders of magnitude lower than those of the total metal concentration.

- Two important partitioning processes—precipitation and adsorption—cause the predominance of particulate metal fractions over dissolved fractions. Metals are only slightly soluble in water (solubility products of hydroxides, carbonates, and sulfides are low), assuring low concentrations of the dissolved forms under common natural water conditions. If charged surfaces are present, which is virtually always the case in natural waters, adsorption is a predominant process, sometimes accounting for nearly 100 percent of the metal partitioning. Both precipitation and adsorption are reversible—a fact that is critical in trace metal cycling.

- Three types of particulate substances, abundant in natural waters, provide surfaces for metal adsorption. All have very strong affinities for metal ions. They are (a) clay-mineral particles, (b) particulate organic matter, and (c) hydrous oxides of iron and manganese.

- The most important single variable that controls metal partitioning is pH. Because the equivalence points of many metal-ligand associations fall within the pH range of 5 to 9, major shifts in proportions of different metal fractions can occur with relatively mild changes in pH, as are common in the natural environment. Studies of aquatic metal biogeochemistry must include reliable pH measurements.

- Complexation by dissolved organic ligands is almost certain to affect adsorption and bioavailability of the metal, but the direction of the effect may be either positive or negative, depending on the conditions and the metals and ligands involved. This effect can be predicted if association constants are known for the metal-to-ligand, metal-to-surface, and ligand-to-surface combinations.

- Amorphous hydrous oxides of iron and manganese are among the most important types of adsorption surfaces for trace metals. Because of their surface charge, these oxides have a strong affinity for other metals, and they are usually abundant in natural waters. Because they commonly occur as coatings on other particles, they tend to have high surface exposure relative to their mass, and their effect on metal adsorption may be disproportionately high.

- Changes in the redox potential between oxidizing and reducing conditions profoundly affect metal partitioning. Because of the solubilization of iron and manganese oxides, reducing conditions are generally expected to favor release of metals from sediments to water. However, this is not always the case, because other factors that accompany a redox drop may counteract the release from iron-manganese binding. Most important among such accompanying factors are increases in pH and reduction of sulfate to sulfide, both of which favor reprecipitation of released metals.

- Trace metal concentration in sediments generally increases with decrease in grain size, primarily because of the higher surface to volume ratio of finer particles. But this general rule may be altered by the nature of the particles. The existence of metal-rich nodules raises con-

centrations in large-size particles. This commonly results in a bimodal distribution, whereby elevated concentrations are observed in both very fine and coarse fractions, with smaller concentrations in intermediate-size fractions. The same type of distribution may occur in systems subject to large inputs of coarse organic particles, such as from a municipal-waste discharge because of strong affinity between metals and organic surfaces.

- In rivers and streams, hydrologic changes are important to both transport and speciation of metals. In medium- to high-discharge conditions, an increase in flow promotes higher metal concentrations because of the greater sediment load. The effect of this change is an even greater relative increase in metal transport (concentration × flow). In low-discharge conditions, concentrations tend to decrease as flow increases, because of dilution of metals desorbed from bottom sediments. During high flows, particulate to soluble fraction ratios are likely to be much higher than during low flows.

- In lakes and reservoirs, the hydrologic action is also critical to metal transport. In stratified systems, the highest concentrations of dissolved metals are in the hypolimnion, whereas the primary producing populations are in the epilimnion. The thermocline barrier to upward transport of nutrients and metals from hypolimnion to epilimnion may be partially overcome by current and eddy effects caused by wind action. Wind action can provide mobility of the elements from their sources to where their biological effects may be most evident.

- Metals tend to accumulate in bottom materials and biota. As a result, metal "sinks" exist in the bottom materials and biota. However, such accumulation is not necessarily equivalent to permanent removal from circulation through deposition in an immobile reservoir or to complete export from the system. Instead, the immobilization is often only a temporary stop in a continuous cycle through the system. The accumulated metals may be returned to general circulation upon suitable changes in environmental conditions.

- Bioaccumulation of a metal in native organisms may or may not correlate to concentrations of the same metal in the habitat medium—either water or sediments. If bioaccumulation does not correlate, the concentrations in the medium probably do not correspond to bioavailability. The latter situation is very common because of the abundance of iron and manganese oxides, particulate organic matter, and fine clay-mineral sediments in water systems. All of these substances strongly adsorb metals, diminishing their bioavailability, and thus "protect" the organisms from the contaminants.

- Toxicity of a metal to aquatic populations is manifested as impairment of metabolic functions or limitation of distribution or abundance of the populations. For any given population, toxicity may or may not be correlated to bioaccumulation of the metal by organisms in the population. Bioaccumulation occurs nonuniformly among different tissues and organs, and the distribution factors vary greatly among different species. Thus, some species may accumulate considerable toxic metal loads without suffering significant impairment, whereas others are much more sensitive. The duration and continuity of exposure also influence an organism's capacity to resist toxic effects.

- Bioaccumulation and toxicity can be affected by various characteristics of the organism, such as size, age, reproductive state, and feeding habits. However, there is no general pattern of such relation, and in many cases, the variables may be independent of each other. The magnitudes and directions of the relation, if any, depend to a large extent on the mechanism of uptake of metals by the organism.

- Biological effects of metals are not limited to toxicity. At concentrations higher than background, but within common natural water ranges, many metals may be nutritive, toxic, or variable between the two, depending on the biota present and the environmental conditions.

- The biological effect of one metal may be modified by the presence of others. If various metals are present at contaminant levels and a new contaminant is introduced, its effect may be greater or less than it would be in an uncontaminated situation. Its effect would depend on which of the following interactions predominates: (1) improved effectiveness of the organism's toxicity defense mechanisms, such as synthesis of metallothioneins, due to its prior exposure to toxic elements, (2) weakening of the organism's defense mechanisms caused by the stresses imposed by the existing contamination, and (3) cation exchange with the introduced metal that releases previously sorbed metals into a bioavailable pool. The amelioration of metal bioavailability by adsorption to hydrous oxides of iron and manganese is another example of effects of element interactions.

- Various forms of aquatic biota, particularly blue-green algae, can partially control bioavailability by production of extracellular sequestering agents. These substances are advantageous to the organism in at least three ways: (1) they facilitate uptake of limited quantities of nutritive elements such as iron; (2) they complex toxic elements, thereby diminishing their bioavailability; and (3) they reduce the availability of nutritive elements to competing species.

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