# A Primer on Trace Metal-Sediment Chemistry

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# PREFACE

This Primer was originally developed as a companion volume to a short course on trace metal-sediment chemistry. The purpose of the course was to expose the participants to the basic principles and techniques that control and are used to elucidate trace metal sediment interactions. Participants were not expected to walk away from the course as experts in sediment chemistry; however, they were expected to have a good knowledge of the basic principles governing this complex subject.

This Primer, organized in the same way as the instructional session, contains all the diagrams and tables used for the course, along with a descriptive text. It also includes a large list of selected references on the subject of trace metal-sediment chemistry. This list is by no means exhaustive. Many of the references were used in developing the material in the course and in the Primer. The other references are provided for information on techniques and methods, and as examples of how sediment chemistry can be used to deal with various types of environmental studies.

# CONTENTS

# A PRIMER ON TRACE METAL-SEDIMENT CHEMISTRY

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## Abstract

In most aquatic systems, concentrations of trace metals in suspended sediment and the top few centimeters of bottom sediment are far greater than concentrations of trace metals dissolved in the water column. Consequently, the distribution, transport, and availability of these constituents can not be intelligently evaluated, nor can their environmental impact be determined or predicted solely through the sampling and analysis of dissolved phases. This Primer is designed to acquaint the reader with the basic principles that govern the concentration and distribution of trace metals associated with bottom and suspended sediments.

The sampling and analysis of suspended and bottom sediments are very important for monitoring studies, not only because trace metal concentrations associated with them are orders of magnitude higher than in the dissolved phase, but also because of several other factors. Riverine transport of trace metals is dominated by sediment. In addition, bottom sediments serve as a source for suspended sediment and can provide a historical record of chemical conditions. This record will help establish area baseline metal levels against which existing conditions can be compared.

Many physical and chemical factors affect a sediment's capacity to collect and concentrate trace metals. The physical factors include grain size, surface area, surface charge, cation exchange capacity, composition, and so forth. Increases in metal concentrations are strongly correlated with decreasing grain size and increasing surface area, surface charge, cation exchange capacity, and increasing concentrations of iron and manganese oxides, organic matter, and clay minerals. Chemical factors are equally important, especially for differentiating between samples having similar bulk chemistries and for inferring or predicting environmental availability. Chemical factors entail phase associations (with such sedimentary components as interstitial water, sulfides, carbonates, and organic matter) and ways in which the metals are entrained by the sediments (such as adsorption, complexation, and within mineral lattices).

## INTRODUCTION

The basic goal of most chemically oriented water-quality studies is to describe or evaluate existing environmental conditions and to attempt to identify the source or sources of the constituents under investigation. An equally important goal is to attempt to predict or determine potential impacts. This heading could accommodate such subjects as bioavailability, amount of constituent transport, location of chemical sinks, ultimate fate, and potential toxic effects.

Historically, the U.S. Geological Survey has attempted to assess trace metals in aquatic systems by analyzing water samples. This assessment has entailed determining concentrations of total and dissolved elements and compounds through the collection and analysis, respectively, of unfiltered and filtered water. Concentrations associated with suspended sediment (particulates, seston) are determined indirectly by the difference between total and dissolved concentrations. It is recognized that this approach casts doubt on the reliability of reported suspended-sediment chemical analyses. As a result, water quality tends to be evaluated on the kinds and concentration of various constituents found in solution (Feltz, 1980). However, in most aquatic systems, the concentration of trace metals in suspended sediment and the top few centimeters of bottom sediment is far greater than the concentration of trace metals dissolved in the water column. The strong association of numerous trace metals (for example, As, Cd, Hg, Pb, Zn) with seston and bottom sediments means that the distribution, transport, and availability of these constituents can not be intelligently evaluated solely through the sampling and analysis of the dissolved phase.

Additionally, because bottom sediments can act as a reservoir for many trace metals, they must, for several reasons, be given serious consideration in the

1

planning and design of any water-quality study. First, an undisturbed sediment sink contains a historical record of chemical conditions. If a sufficiently large and stable sink can be found and studied, it will allow the investigator to study changes over time and, possibly, to establish area baseline levels against which existing conditions can be compared and contrasted. Second, under changing environmental or physico-chemical conditions (like pH, Eh, dissolved oxygen, bacterial action), sediment-bound trace metals can dissolve into the water column, possibly enter the food chain, and have a significant environmental impact. Third, several relatively inert or otherwise environmentally harmless inorganic constituents can degrade, or react with others, to form soluble and potentially toxic forms (for example, the conversion of elemental mercury to methyl-mercury). Finally, bottom sediments should be regarded as a major, if not the major, source of suspended sediment. Therefore, they must be investigated to determine transport potential. Under changing hydrologic conditions (such as a heavy storm or spring runoff), a localized pollution problem can suddenly become widespread and result in significant environmental impact.

The foregoing discussion indicates that data on suspended and bottom sediments, as well as on the dissolved phase, are a requisite for the development of a comprehensive understanding of the impact of trace metals on water quality. Through the use of such additional data, it may be possible to begin to identify sources and sinks and the fate and potential effects of toxic or environmentally necessary metals. Similarly, sediment-chemical data are a requisite for transport modeling, for estimating geochemical cycles, and for inferring the availability of various trace metals in an ecological system.

## GLOSSARY

**Sediment**—Particles derived from rocks or biological materials that have been transported by a fluid, or solid material suspended in or settled from water.

**Suspended sediment, seston, particulates**—Material actively transported by a fluid.

**Bottom sediment, bed material**—Material that is temporarily stationary in the bottom of a water course.

**Dissolved load, dissolved constituent**—Operationally defined as that material that passes through a 0.45-$\mu$m (micrometer) filter.

**Suspended load, suspended constituent**—Operationally defined as that material that is retained by a 0.45-$\mu$m (micrometer) filter during the filtration of a whole water sample.

**Trace metal, heavy metal, metal**—Terms used interchangeably throughout this Primer.

**Total concentration**—Refers to the true concentration of metal in a sediment sample as determined by the complete dissolution of the sample. Unless otherwise stated, concentrations in this Primer are totals.

**Total recoverable concentration**—Refers to the concentration of metal in a sediment sample that has been extracted with a solution that does not completely dissolve the sediment. In other words, this is an *operationally* defined concentration, the definition being dependent upon the extraction solution.

# 1.0 IMPORTANCE OF SEDIMENTS TO AQUATIC TRACE METAL CHEMISTRY

## 1.1 Monitoring Studies

Table 1.1-1 has been extracted from an article by Chapman and others (1982) dealing with the design of monitoring studies for priority pollutants. The authors point out that, to design an effective monitoring program, an investigator must decide two basic questions: what samples should be collected, and for what should they be analyzed? This decision requires an understanding of the relative importance of each constituent on the basis of its chemical behavior and biological significance. These factors, in turn, determine what type of sample(s) should be collected (water, sediment, biota). All the inorganic priority pollutants, with the exception of antimony, are persistent and can bioaccumulate, and all tend to be found in either sediment (bottom and suspended) or biota (table 1.1-1).

**Table 1.1-1.** Recommendations for types of environmental sampling for monitoring purposes
[Data from Chapman and others, 1982]

| Metal | Category rank* | Water | Sediment | Biota |
|---|---|---|---|---|
| Antimony | 3 | X | | |
| Arsenic | 1 | | X | X |
| Beryllium | 1 | | X | X |
| Cadmium | 1 | | X | X |
| Chromium | 1 | | X | X |
| Copper | 1 | | X | X |
| Lead | 1 | | X | X |
| Mercury | 1 | | X | X |
| Selenium | 1 | | X | X |
| Silver | 1 | | X | X |
| Thallium | 1 | | X | X |
| Zinc | 1 | | X | X |

*Category rank: 1 and 2 - persistent and may bioaccumulate
3 and 4 - persistent and nonaccumulative
5 - nonpersistent

## 1.2 Comparison of Dissolved and Suspended Trace Metal Concentrations

As stated previously, both bottom and suspended sediments contain significantly more trace metals than are found in the dissolved phase. Hence, riverine transport of these constituents can be dominated by suspended sediment. Figure 1.2-1 is based upon the analysis of dissolved and suspended loads for selected trace metals in the Amazon and Yukon Rivers and graphically displays this phenomenon (adapted from Gibbs, 1977).
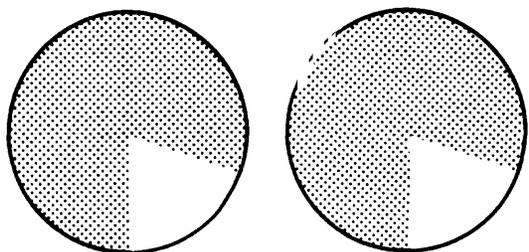
Chromium
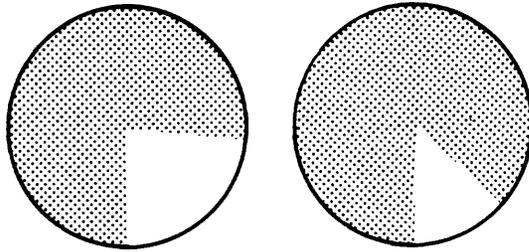
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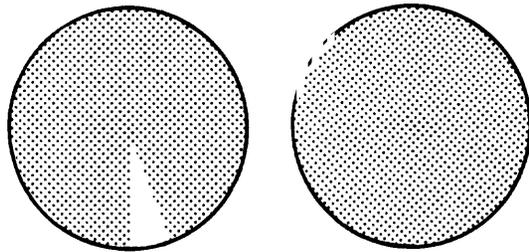
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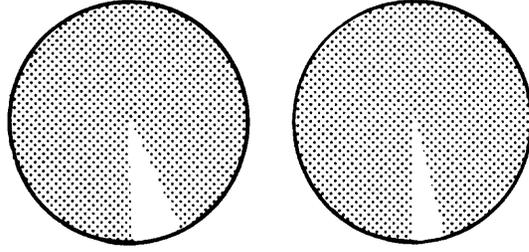
Cobalt
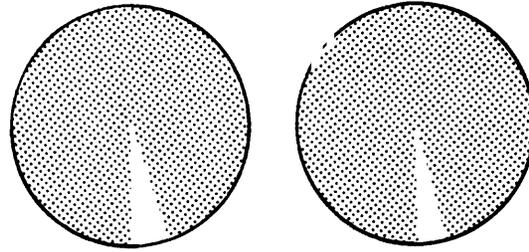
Nickel
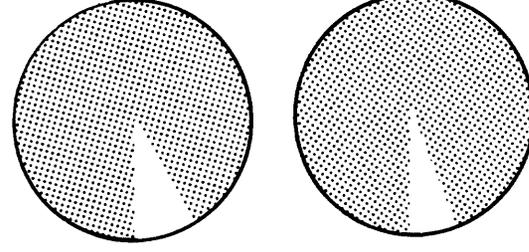
Copper

**AMAZON RIVER   YUKON RIVER**

**AMAZON RIVER   YUKON RIVER**

EXPLANATION

Dark areas:   percentage in suspended sediments
Light areas:   percentage in solution

Figure 1.2-1.—Transport phases of selected trace metals in rivers. (Data from Gibbs, 1977)

## 1.3 Riverine Transport of Trace Metals by Suspended Sediments

As a further indication that riverine transport of metals may be dominated by the suspended-sediment load, it is worthwhile to determine, in relatively simple terms, what order of magnitude of material is being transported. Examine the data in table 1.3-1. The discharge equation used to generate the data comes from Porterfield (1972), and the basic data for the actual calculations come from the annual reports of Pennsylvania, Oregon, and Louisiana. Note that even relatively low concentrations of trace metals in suspended sediment can involve significant weights of constituent transport. For example, the arsenic concentration in Willamette River suspended sediment is only 0.002 mg/kg (2 ppb), and yet this means that 0.9 t/d of As is transported by the river. At the other end of the spectrum, examine the iron data for the Mississippi River. Suspended-sediment iron concentrations are 46 mg/kg (46 ppm); thus some 75,000 t/d of Fe is transported.

**Table 1.3-1.** Transport of metals associated with suspended sediment in selected rivers

| Element | Susquehanna River 03/08/79 | | Willamette River 01/16/80 | | Mississippi River 01/18/81 | |
|---|---|---|---|---|---|---|
| Discharge[1] | 346,000 | | 189,000 | | 671,000 | |
| | Concentration[2] | Transport[3] | Concentration[2] | Transport[3] | Concentration[2] | Transport[3] |
| Sediment[4] | 406 | 344,200 | 106 | 49,000 | 641 | 1,050,000 |
| Iron | 12 | 10,200 | 4.4 | 2,040 | 46 | 75,600 |
| Manganese | 0.590 | 430 | 0.100 | 46 | 1.3 | 2,150 |
| Zinc | 0.070 | 59 | 0.030 | 14 | 0.090 | 148 |
| Lead | 0.018 | 15 | 0.005 | 2.3 | 0.030 | 49 |
| Copper | 0.015 | 13 | 0.006 | 2.8 | 0.018 | 30 |
| Cobalt | 0.010 | 8.5 | – | – | 0.005 | 8.2 |
| Chromium | 0.003 | 6.8 | 0.010 | 4.6 | 0.028 | 46 |
| Nickel | – | – | 0.004 | 1.9 | 0.035 | 58 |
| Arsenic | – | – | 0.002 | 0.9 | 0.012 | 20 |

[1]Discharge, in cubic feet per second
[2]Concentration, total recoverable, in milligrams per liter
[3]Sediment and chemical transport in metric tons per day, calculated from Porterfield, 1972: (concentration, in milligrams per liter) (discharge, in cubic feet per second) 0.00245
[4]Sediment concentration, in milligrams per liter

## 1.4 Comparison of Trace Metal Concentrations in Suspended and Bottom Sediments Versus Dissolved Levels

Bottom sediment and suspended sediment contain significantly higher concentrations of trace metals than are found in solution. What is meant by significantly higher? Examination of the data presented in the accompanying tables provides an approximate answer to this question. Table 1.4-1 contains data from the Elbe River, FRG (Federal Republic of Germany), and compares and contrasts dissolved metal concentrations with those associated with bottom sediments. The bottom-sediment concentrations can be more than 100,000 times higher than the dissolved levels (see,

for example, lead levels for water and sediment for Hamburg). During the Schuylkill River Basin assessment study, similar results were obtained for dissolved and total recoverable levels (Table 1.4-2, from Feltz, 1980). Table 1.4-3 shows data from the Amazon and Yukon Rivers and compares and contrasts dissolved metal concentrations with those in suspended sediment. The suspended-sediment concentrations for the Amazon and the Yukon are approximately 10,000 and 7,000 times higher, respectively, than the dissolved load.

**Table 1.4-1.** Comparison of metal concentration in river water and bottom sediment from the Elbe River, FRG. (All concentrations in milligrams per kilogram)
[Data from Forstner and Wittmann, 1979]

| Location | | Cadmium | Chromium | Copper | Lead | Zinc |
|---|---|---|---|---|---|---|
| Stade | (W)[1] | 0.0005 | 0.003 | 0.005 | 0.005 | 0.025 |
| | (S)[2] | 5 | 100 | 100 | 200 | 600 |
| Hamburg | (W) | 0.0007 | 0.010 | 0.012 | 0.005 | 0.120 |
| | (S) | 32 | 500 | 450 | 500 | 1,600 |
| Hitzacker | (W) | 0.0008 | 0.020 | 0.020 | 0.008 | 0.140 |
| | (S) | 23 | 250 | 200 | 200 | 750 |

[1](W)–concentration in water
[2](S)–concentration in sediment


**Table 1.4-2.** Comparison of metal content in river water and bottom sediment from the Schuylkill Basin. (All concentrations in milligrams per kilogram)
[Data from Feltz, 1980]

| Location | | Cadmium | Chromium | Copper | Lead | Zinc |
|---|---|---|---|---|---|---|
| Phoenixville | (W)[1] | 0.013 | 0.001 | 0.005 | 0.190 | 0.080 |
| | (S)[2] | 30 | 130 | 190 | 250 | 1,000 |
| Norristown | (W) | 0.010 | <0.001 | 0.007 | 0.110 | 0.120 |
| | (S) | 10 | 30 | 70 | 400 | 1,000 |
| Philadelphia | (W) | 0.002 | <0.001 | 0.004 | 0.001 | <0.001 |
| | (S) | 10 | 50 | 80 | 180 | 170 |

[1](W)–concentration in water
[2](S)–concentration in sediment, totally recoverable


**Table 1.4-3.** Comparison of metal content in river water and suspended sediment from the Amazon and Yukon Rivers. (All concentrations in milligrams per kilogram)
[Data from Gibbs, 1977]

| Location | | Chromium | Manganese | Iron | Cobalt | Nickel | Copper |
|---|---|---|---|---|---|---|---|
| Amazon | (W)[1] | 0.019 | 0.110 | 5.1 | 0.004 | 0.010 | 0.026 |
| | (S)[2] | 195 | 1,100 | 56,000 | 41.4 | 105 | 265 |
| Yukon | (W) | 0.019 | 0.200 | 8.9 | 0.006 | 0.020 | 0.060 |
| | (S) | 115 | 1,300 | 63,000 | 40.6 | 135 | 415 |

[1](W)–concentration in water
[2](S)–concentration in suspended sediment

## 1.5 Historical Records

An undisturbed sediment sink can contain a historical record of chemical conditions. If a sufficiently large and stable sink (one in which neither physical nor chemical alteration has occurred) can be found and studied, the investigator can establish the occurrence of chemical changes over time and may establish area baseline levels with which existing conditions can be compared. When chemical analyses are used together with radiometric dating techniques ($Pb^{210}$, $C^{14}$), historical changes in water quality can be elucidated. Figure 1.5-1 gives two examples of historical records detailing changes in mercury concentration through time. The data from Lake Ontario indicate that high concentrations of mercury occur in the top 6 cm; below 8 cm, the concentration decreases significantly. At about 25-cm depth, the concentration reaches a low of 0.140 mg/kg (140 ppb), which corresponds to a period of active deforestation by settlers around 1800 to 1820. That activity, in fact, diluted the mercury levels below normal background for the area through increased erosion and deposition of non-mercury-bearing material. The levels found below 30 cm are believed to reflect natural background levels of 0.3 to 0.4 mg/kg (300 to 400 ppb). Industrial input is believed to have begun around 1900 (~9 cm); there ensued a steady rise until around 1940 (~5 cm), when concentrations leveled off at about four times natural levels. A similar pattern can be seen in sediments from Lake Windermere in England. Since 1400, mercury levels have risen steadily as a result of erosion, industrialization, mining, quarrying, use of fossil fuels, and sewage disposal. The onset of industrial input occurred around 1880 (~24 cm), and today's levels are about four to five times higher than natural background concentrations.
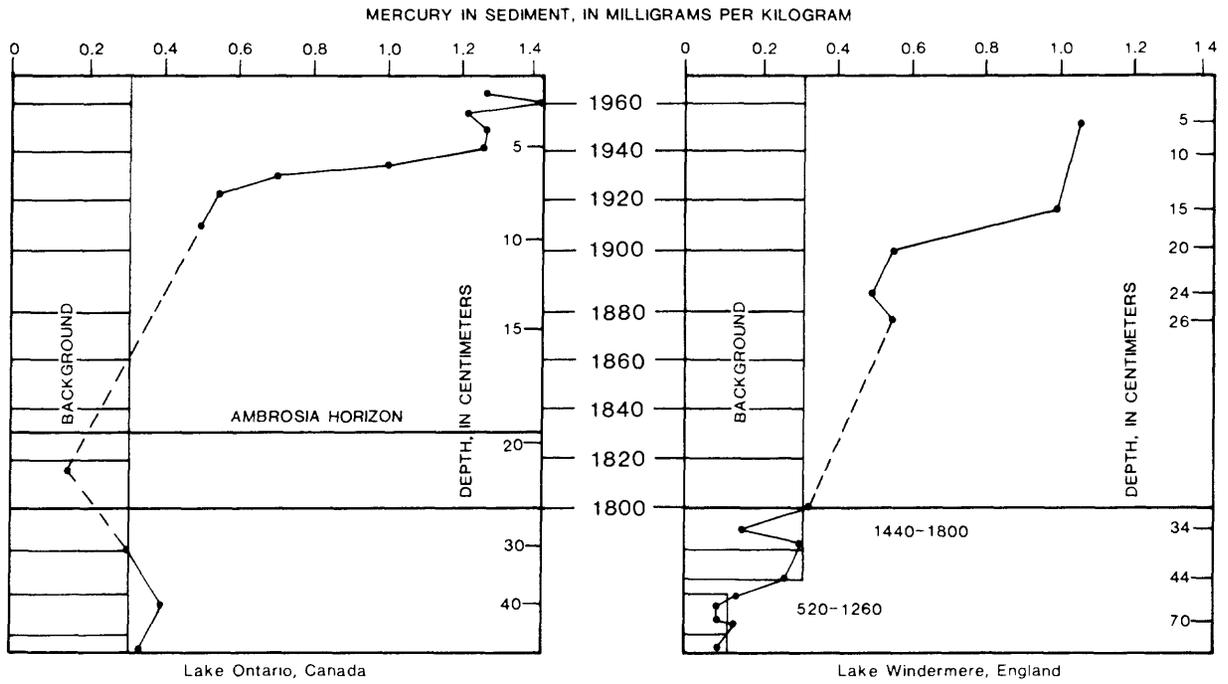
MERCURY IN SEDIMENT, IN MILLIGRAMS PER KILOGRAM



**Figure 1.5-1.**—Examples of mercury concentration changes through time. (Data from Thomas, 1972; Aston and others, 1973)

# 2.0 PHYSICAL FACTORS AFFECTING SEDIMENT-TRACE METAL CONCENTRATIONS

## 2.1 Introduction

The preceding material is based on the determination of total bottom or suspended sediment chemical concentrations. This type of chemical information is a typical and standard starting point for most water-quality studies. However, to understand the factors affecting sediment trace metal chemistry, to enable an investigator to address such topics as trace metal transport and potential environmental impact intelligently, and to permit the comparison of sample data from the same or different areas, a number of physical and chemical factors must be examined. They fall under the general heading of the various components or properties of a sediment. *Physical partitioning* is the separation of a sediment sample (bottom or suspended) into various physical categories (by grain size, surface area, specific gravity, magnetic properties, mineralogy, and so forth). *Chemical partitioning* is the separation of various trace metals with respect to their association with other materials within the sediment (organic matter, carbonates, manganese oxides, sulfides, or silicates) and to the type of association that exists (adsorption, complexation, substitution within mineral lattices, and so forth). The separation into physical and chemical categories is somewhat arbitrary; for example, composition could just as easily be placed under chemical partitioning. For convenience, the two types of partitioning are discussed separately, but they are interrelated. The factors involved in partitioning are listed in table 2.1-1.

## 2.2 Grain-Size Ranges and Effect of Grain Size

One of the most significant factors controlling both suspended- and bottom-sediment capacity for retaining trace metals is grain size (Goldberg, 1954; Krauskopf, 1956; Goldberg and Arrhenius, 1958; Hirst, 1962; Jenne, 1968; Kharkar and others, 1968; Gibbs, 1973; Horowitz, 1974; Stoffers and others, 1977; Gibbs, 1977; Jones and Bowser, 1978; Filipek and Owen, 1979; Jenne and others, 1980; Thorne and Nickless, 1981). Table 2.2-1 lists the sediment particle-size classes (names) and the size ranges the names represent. In lakes, rivers, estuaries, and oceans—and in sediment chemistry in general—most sediments tend to be composed of materials smaller than 2,000 μm (very coarse sand).

There is a very strong positive correlation between decreasing grain size and increasing trace metal concentrations. This correlation results from numerous factors that are both physical and mineralogical (compositional). Clay-sized sediments (less than 2 to 4 μm, table 2.2-1) have surface areas measured in square meters per gram as opposed, for example, to sand-sized particles with surface areas commonly measured in tens of square centimeters per gram (Grim, 1968; Jones and Bowser, 1978). Surface chemical reactions are extremely important to aquatic trace metal sediment interactions; thus, fine-grained sediments, because of their large surface areas, are the main sites for the collection and transport of inorganic constituents (Krauskopf, 1956; Jenne, 1968; Gibbs, 1973; Jones and Bowser, 1978; Jenne and others, 1980). However, Jenne (1976) indicates that clay-sized particles may be viewed simply as mechanical substrates upon which trace metals can concentrate (without chemical interaction). Bear in mind that metal concentrations can and do accumulate on many substrates, including sand, pebbles, cobbles, and boulders (Filipek and others, 1981; Robinson, 1982); nevertheless, high concentrations are more commonly associated with fine-grained material.

**Table 2.1-1.** Examples of types of physical and chemical partitioning

| Physical | Chemical Mechanistic | Chemical Phase |
|---|---|---|
| Grain size | Adsorption | Interstitial water |
| Surface area | Precipitation | Carbonates |
| Composition | Co-precipitation | Clay minerals |
| Cation exchange capacity | Organometallic bonding | Organic matter |
| Specific gravity | Incorporation in crystalline minerals | Hydrous iron and manganese oxides |
| Magnetic properties | | Sulfides |
| Surface charge | | Silicates |

**Table 2.2-1.** Sediment particle size and classes
[Data from Guy, 1969]

| Class Name | Millimeters | Micrometers |
|---|---|---|
| Boulders | >256 | |
| Large cobbles | 256 – 128 | |
| Small cobbles | 128 – 64 | |
| Very coarse gravel | 64 – 32 | |
| Coarse gravel | 32 – 16 | |
| Medium gravel | 16 – 8 | |
| Fine gravel | 8 – 4 | |
| Very fine gravel | 4 – 2 | |
| Very coarse sand | | 2,000 – 1,000 |
| Coarse sand | | 1,000 – 500 |
| Medium sand | | 500 – 250 |
| Fine sand | | 250 – 125 |
| Very fine sand | | 125 – 62 |
| Coarse silt | | 62 – 31 |
| Medium silt | | 31 – 16 |
| Fine silt | | 16 – 8 |
| Very fine silt | | 8 – 4[1] |
| Coarse clay[1] | | 4 – 2 |
| Medium clay | | 2 – 1 |
| Fine clay | | 1 – 0.5 |
| Very fine clay | | 0.5 – 0.25 |

[1]Many sedimentologists consider that the clay/silt break occurs at 2 $\mu$m rather than at 4 $\mu$m.

15

## 2.3 Chemical Analysis of Various Grain Sizes in Bottom Sediments

How significant is the effect of grain size on chemical composition in bottom sediments? Table 2.3-1 contains data for a marine sample that was broken down into various size fractions; each fraction was then subjected to chemical analysis. The sediment displays bimodal grain-size distribution with peaks in the ranges of less than 2 μm and 10 to 20 μm; this is typical for marine material (Rex and Goldberg, 1958).

The less than 2-μm fraction has, by far, the highest copper concentration of all the fractions. Al-though the less than 2-μm fraction represents only some 20 percent of the bulk sediment, its copper contribution amounts to 75 percent of the total copper in the sample. The 10 to 20-μm fraction copper contribution amounts to only 9 percent of the total copper, although it is the largest single size fraction in the sample. This type of pattern is similar to ones for other metals such as Cd, Ni, Co, Zn, and Pb.

**Table 2.3-1.** Distribution of copper by size fraction in a bottom sediment sample

| Size Fraction (μm) | Percent of Sample | Chemical Concentration (mg/kg) | Contribution to Sample[1] (mg/kg) |
|---|---|---|---|
| <2 | 20 | 750 | 150 |
| 2 - 6 | 15 | 60 | 9 |
| 6 - 10 | 18 | 110 | 19.8 |
| 10 - 20 | 30 | 60 | 18 |
| 20 - 32 | 10 | 25 | 2.5 |
| 32 - 64 | 7 | 20 | 1.4 |
| | 100 | | 200.7 |

[1]Calculated by multiplying chemical concentration by percent of sample.

*2.4 Chemical Analysis of Various Grain Sizes in Suspended Sediments*

Are the patterns just described for bottom sediments also typical of suspended matter? Data presented in figure 2.4-1 should clarify this point. All the inorganic constituents investigated—Mn, Fe, Cr, Ni, Cu, and Co—have their highest concentrations in the less than 2-micrometer fraction (fig. 2.4-1). Further, this illustration also shows that the majority of the metal transport can be attributed to the less than 2-$\mu$m fraction. These data also imply that most *chemical* transport may occur under relatively low discharge because high metal concentrations are associated with the fine-grained material, which requires relatively low discharge conditions for suspension and transport.

Figure 2.4-1.—Distribution of metals by particle size, and relative mass transport by suspended sediment. (Data from Gibbs, 1977)

## 2.5 Effect of Grain Size on Trace Metal Concentrations in Samples Collected From the Same Basin

The effect of grain size on sediment-trace metal concentrations should be fairly evident now, in light of the preceding discussions. Further, it should be apparent that the finer grain sizes contain the majority of the metals associated with sediments. However, it is important to understand the significant implications such relations have for such common practices as trying to trace the extent of pollutant discharge from a point source, and for comparing sediment-chemical concentrations within and between depositional basins.

The data in figure 2.5-1 come from bottom sediments collected from the River Ems in Europe (de Groot and others, 1982). The manganese concentrations vary over a wide range, from some 7,000 to about 25,000 mg/kg; cobalt, iron, and mercury also show wide concentration ranges. Solely on the basis of bulk chemical analysis, there appears to be no interrelation between the various samples, and all that an investigator could report would be the wide range of concentrations. However, if the chemical data are plotted against grain-size information, very distinct patterns emerge. There is a strong positive correlation between increasing chemical concentration and the increasing percentage of fine-grained material. This relation, which is common in sediments, can provide a means for tracing the extent of pollutant transport or dispersion from a point source because, as material moves away from the source, it is usually diluted by other constituents and other grain sizes. As a result, the use of bulk chemical data would make it difficult to trace the extent of dispersion because of the effects of dilution. However, these effects could be reduced, and the extent of transport determined, either by separating out the constituent-bearing size fraction or by determining the percentage of the constituent-bearing size fraction in a bulk sediment sample and recalculating the bulk data accordingly. Recalculation methods are discussed in section 4.0 of this Primer.
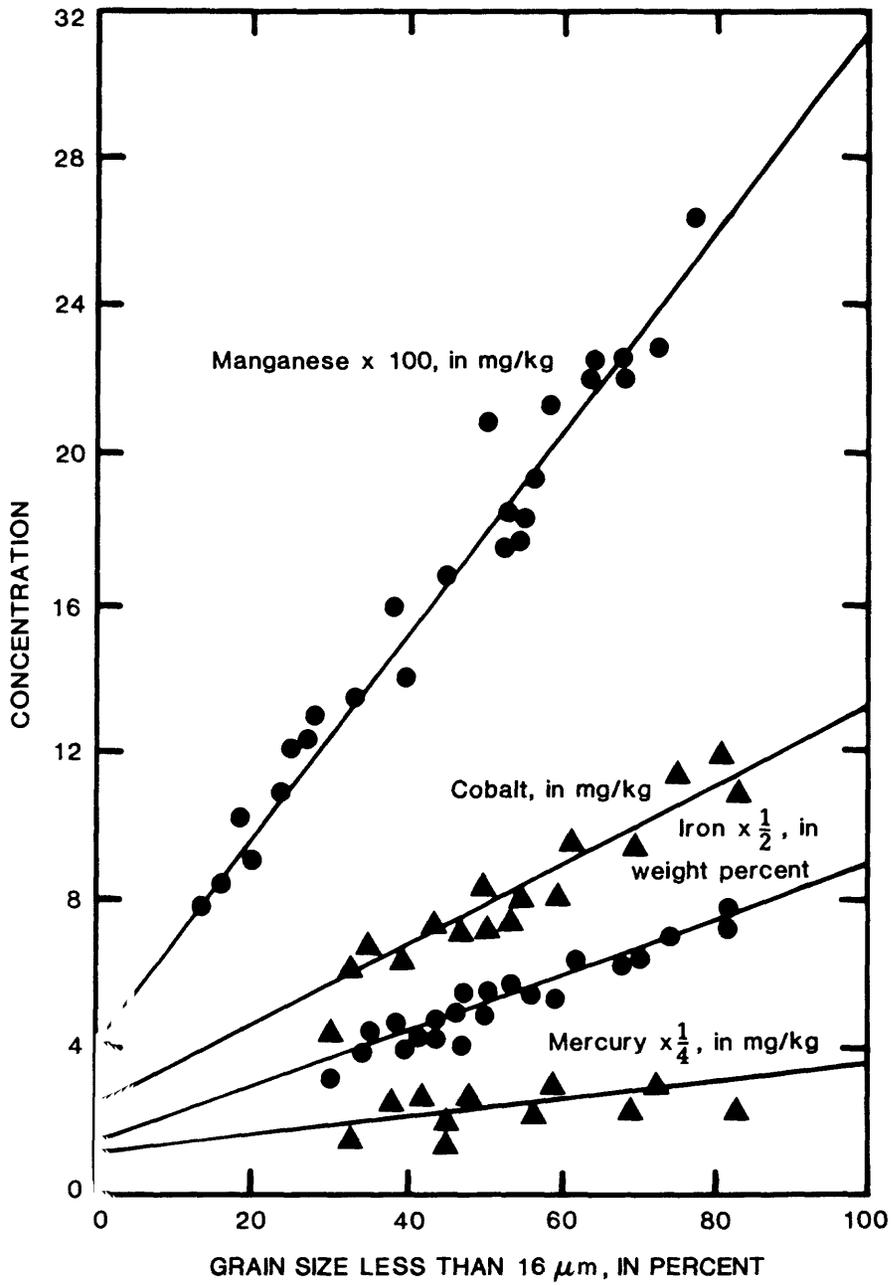
**Figure 2.5-1.**—Relation between metal concentration and grain size for the River Ems, FRG. (Data from deGroot and others, 1982)

## 2.6 Comparison of Samples Having Similar Bulk Chemistries But Differing Grain-Size Distributions

Keep in mind that two sediments with the same bulk chemical concentrations are not necessarily the same. The sources for the constituents in question may be different, the constituents may be held in different chemical forms, they may be associated with different size fractions, and so forth. As an example, examine the data in table 2.6-1. Both samples are marine in origin. Sample AD 600 comes from a hydrothermally active area, while sample AD 500 comes from a nonhydrothermal area. Both samples in this table have similar manganese concentrations (~3500 mg/kg) and similar grain-size distributions. However, the chemical data for each grain-size range indicate significant differences between the two sam-

ples in the distribution of Mn. Sample AD 600 has two major Mn peaks, one in the less than 2 $\mu$m fraction, and the other in the 10-to-20 $\mu$m fraction. Sample AD 500 has similar Mn concentrations for all size fractions ranging from 2 $\mu$m to 32 $\mu$m. Subsequent mineralogical and chemical analyses have indicated that manganese oxide coatings and micronodules caused the Mn peaks in AD 600, while the Mn in AD 500 came from volcanic ash and glass. Differentiation of the two samples could not have been made solely on the basis of either grain-size distribution or bulk chemical data, but can be made on the basis of size-fraction chemical analysis.

**Table 2.6-1.** Comparison of manganese distributions in two samples having similar grain-size distributions and bulk concentrations

| Size Fraction (μm) | Percent of Sample | Sample AD 600 | | Percent of Sample | Sample AD 500 | |
|---|---|---|---|---|---|---|
| | | Concentration (mg/kg) | Contribution[1] (mg/kg) | | Concentration (mg/kg) | Contribution[1] (mg/kg) |
| <2 | 20 | 5,000 | 1,000 | 18 | 4,000 | 720 |
| 2 - 6 | 12 | 1,000 | 120 | 13 | 3,800 | 494 |
| 6 - 10 | 14 | 1,000 | 140 | 15 | 3,800 | 570 |
| 10 - 20 | 30 | 7,100 | 2,130 | 25 | 4,000 | 1,000 |
| 20 - 32 | 10 | 1,000 | 100 | 15 | 4,000 | 600 |
| 32 - 64 | 7 | 500 | 35 | 5 | 2,000 | 100 |
| 64 - 125 | 4 | 300 | 12 | 5 | 1,000 | 50 |
| 125 - 250 | 3 | 300 | 9 | 4 | 500 | 20 |
| | 100 | | 3,550 | 100 | | 3,550 |

[1]Contribution calculated by multiplying chemical concentration by percent of sample.

## 2.7 Effect of Grain Size on Sediment-Associated Chemical Transport at Differing Discharge Rates

It has now been reasonably well established that trace metals tend to be concentrated in the finer grain sizes of both suspended and bottom sediments. It has also been shown that larger sized material can act as a diluent for the constituent-rich finer grain sizes. What, then, is the implication for suspended-sediment constituent concentrations under differing discharge conditions? The immediate assumption might be that as both discharge and the suspended-sediment load increase, associated constituent concentrations also increase. However, a little thought and an examination of the data presented in figure 2.7-1 should dispel this assumption. As discharge increases, the size of sediment grains being suspended and transported will also increase. When fine-grained material, rich in trace metals, is diluted with metal-poor, larger sized material, suspended-sediment concentration decreases, as it does for chromium (fig. 2.7-1). Remember that the weight of chromium or other metals transported will not decrease and may, in fact, increase (see table 1.3-1 for calculations concerning transport); only the concentration in the suspended load will decrease. (This relation is applicable to large rivers; caution should be exercised in applying it to small rivers.) The data presented in figure 2.7-1, and as also shown by figure 2.4-1, reemphasize the point that most chemical transport may occur under relatively low flow conditions, because of the high concentrations of metals associated with small-size fractions that do not require high velocities to move them.
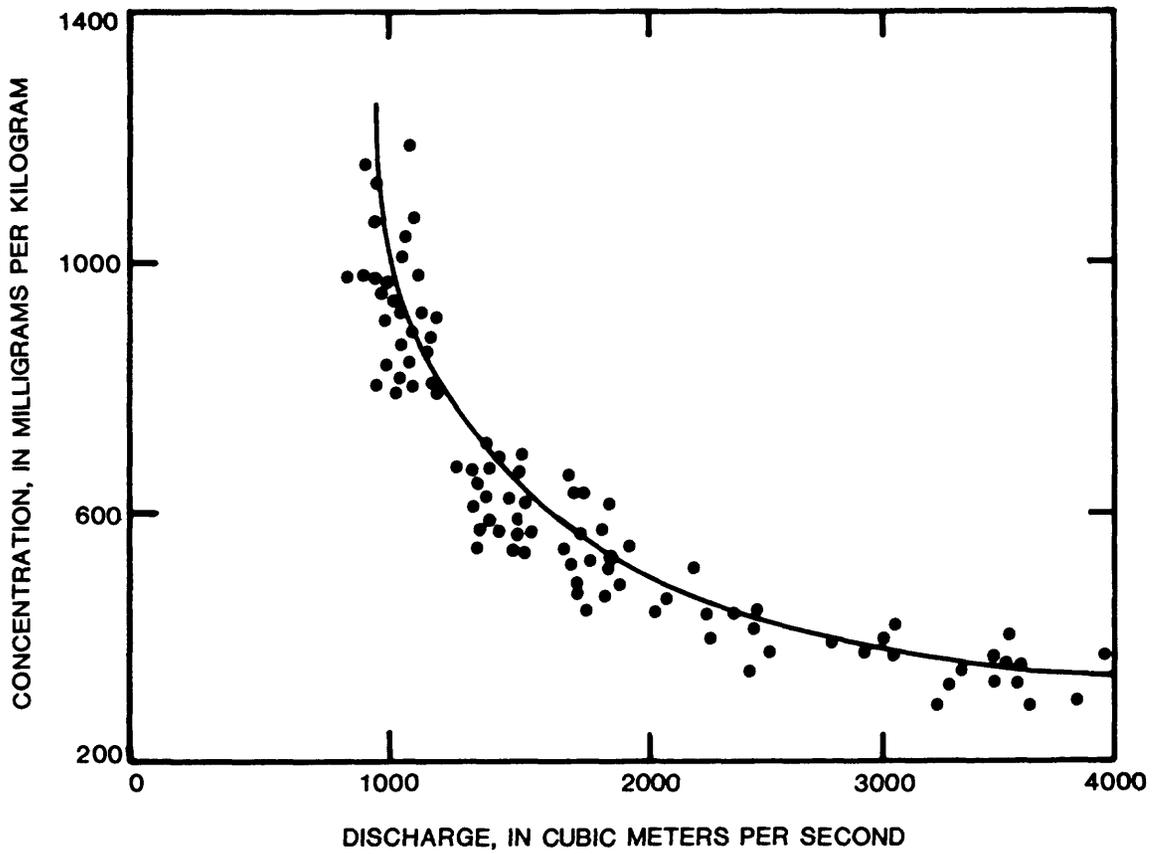
**Figure 2.7-1.**—Metal transport versus water discharge for chromium in suspended sediments for the Rhine River, FRG. (Data Forstner and Wittmann, 1979)

## 2.8 Effect of Surface Area

The preceding discussions have demonstrated the importance of grain size to sediment-trace metal concentrations. A number of other factors also have significant effects on metal concentrations (see table 2.1-1); there is a "common thread" for all these factors: *grain size*. As grain size decreases, these additional factors become more important, and a positive correlation usually exists between them and increasing metal concentration. In some instances, it is impossible to differentiate between effects caused by factors like surface area, cation exchange capacity, and surface charge, and effects due to grain size. Hence, if only one physical parameter of a sediment sample is to be determined, in order to aid in interpreting chemical data, grain size is by far the parameter of choice, because it integrates all the others.

Surface area is almost indistinguishable from grain size; as grain size decreases, surface area increases sharply. As an example, examine the data in table 2.8-1. The surface area for simple spheres of differing diameters (grain size) has been calculated (Jackson, 1979). Sand-sized particles have surface areas on the order of tens to hundreds of square centimeters per gram, silt-sized particles have surface areas on the order of hundreds to thousands of square centimeters per gram, and clay-sized particles have surface areas on the order of tens of square meters per gram. Bear in mind that these numbers are for *spheres*. Obviously, real sediments are composed not of spheres, but of irregular grains. Jackson (1979) has calculated that the surface area of montmorillonite (a platey clay mineral) can theoretically be more than 800 square meters per gram (if it were a sphere of 2 $\mu$m in diameter, its surface area would only be 1.13 square meters per gram). Actual measurements of real materials, including montmorillonite, indicate that surface area can be and usually is less than the theoretical value but is still much larger than that of a sphere of equivalent diameter (Forstner and Wittmann, 1979). These surface areas were measured for selected materials with less than 2-$\mu$m diameter:

| Material | Surface area |
|---|---|
| Calcite | 12.5 m²/g |
| Clay minerals | |
| Kaolinite | 10 to 50 m²/g |
| Illite | 30 to 80 m²/g |
| Montmorillonite | 50 to 150 m²/g |
| Iron hydroxide | 300 m²/g |
| Organic matter (humic acids) | 1,900 m²/g |

**Table 2.8-1.** Calculated surface areas assuming sphericity
[Data from Jackson, 1979]

| Size Class | Diameter ($\mu$m) | Surface Area ($m^2$/g) | Surface Area ($cm^2$/g) |
|---|---|---|---|
| Very coarse sand | 2,000 | 0.00113 | 11.3 |
| Very fine sand/coarse silt | 62 | 0.036 | 360 |
| Very fine silt/coarse clay | 4 | 0.57 | 5,700 |
| Medium clay | 2 | 1.13 | 11,300 |
| Fine clay | 1 | 2.26 | 22,640 |
| Very fine clay | 0.5 | 4.52 | 45,280 |
| Colloids | 0.1 | 22.6 | 226,400 |

## 2.9 Importance of Surface Area to Sediment-Trace Metal Concentrations

Why is surface area so important in controlling sediment-trace metal concentrations? It is because all the various means by which sediment tends to collect metals fall into the general category of so-called surface reactions or surface chemistry. It follows that materials with large surface areas (small grain size) are the main sites for the transport and collection of these constituents (Krauskopf, 1956; Jenne, 1968; Gibbs, 1973; Jenne, 1976; Jones and Bowser, 1978; Jenne and others, 1980). The major mechanism for the collection of trace metals on surfaces is adsorption. This process entails the condensation of atoms, ions, or molecules on the *surface* of another substance. Materials having large surface areas are good adsorbers. Adsorption can occur with or without cation exchange (see section 2.10), and should not be confused with absorption, which involves penetration of a substance into the body, or inner structure, of another material. Additionally, Jenne (1976) indicates that materials with large surface areas can be viewed simply as mechanical substrates upon which inorganic constituents can concentrate without any chemical interaction between the material and the constituent. Thus, deposited materials like organic matter and hydrous iron and manganese oxides, rather than the original surface, may act as metal collectors. Obviously, as surface area increases, so does the amount of these collectors, thus increasing the metal-concentrating capacity of the surface.

An example of how surface area affects inorganic concentrations is shown in figure 2.9-1. The data come from the Ottawa and Rideau Rivers and clearly show that as surface area increases, the concentrations of both nickel and copper increase. This pattern is also typical of many other metals like Fe, Mn, Zn, Pb, and Cd. Bear in mind that the surface areas plotted on these graphs (fig. 2.9-1) are actual measurements—they were not calculated. Do not assume, for example, that a surface area of 22.6 $m^2/g$ implies a sediment particle size of some 0.1 $\mu m$, which would be the case if the particle were a sphere (see section 2.8).
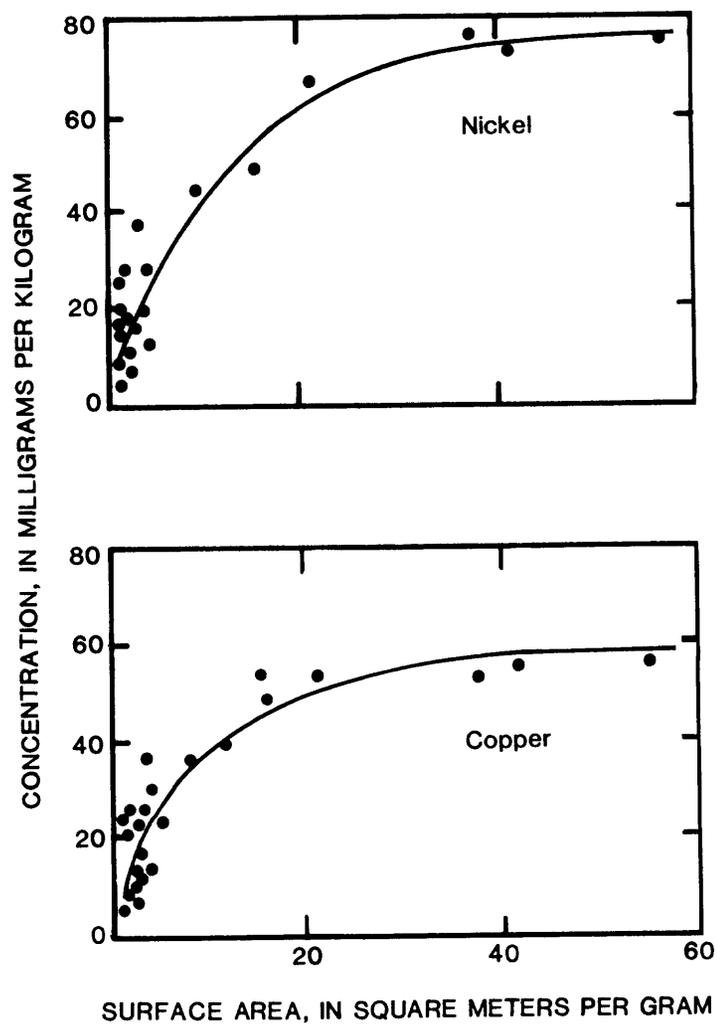
**Figure 2.9-1.**—Effect of surface area on metal concentration from the Ottawa and Rideau Rivers, Canada. (Data from Oliver, 1973)

*2.10 Cation Exchange Capacity*

Many different materials that are common components of sediment and that have large surface areas, such as clay minerals, iron hydroxides, manganese oxides, and organic matter, are capable of sorbing cations from solution and releasing equivalent amounts of other cations back into solution. This process is called ion exchange. Since most trace metals are cations (have a positive ionic charge), and the surfaces of most materials with a capacity for this process have a net negative charge, the process is termed cation exchange. The ability of a particular material to sorb cations can be measured and is called CEC (cation exchange capacity). The actual mechanism by which cation exchange occurs is a matter of some debate, but appears to be due to the sorptive properties of negatively charged anionic sites such as SiOH, $Al(OH)_2$, and AlOH (clay minerals); FeOH (iron hydroxides); and COOH and OH (organic matter) (Forstner and Wittmann, 1979). CEC may also occur between the layers of certain silicates, like expandable clays (montmorillonite, smectites), which, depending on how one chooses to define the layers, might not be viewed as "surfaces" (Grim, 1968).

The data in table 2.10-1 include measured cation exchange capacities for selected materials commonly associated with this phenomenon. The data also show that as grain size decreases and surface area increases, CEC increases significantly (tables 2.10-2 and 2.10-3). Note that CEC results from the availability of "unbalanced" negatively charged sites; thus, it could readily be stated that it is a result of a net negative surface charge (another important physical factor—see table 2.1-1).

**Table 2.10-1.** Cation exchange capacity of selected materials

| Material | Exchange Capacity (mEq/100 g) | Reference |
|---|---|---|
| Kaolinite | 3 - 15 | 1 |
| Illite | 10 - 40 | 1, 2 |
| Chlorite | 20 - 50 | 1 |
| Montmorillonite | 80 - 120 | 1, 2 |
| Smectites | 80 - 150 | 2 |
| Vermiculite | 120 - 200 | 2 |
| Iron hydroxide | 10 - 25 | 1 |
| Soil humic acids | 170 - 590 | 1 |
| Manganese oxides | 200 - 300 | 1 |

1 - From Forstner and Wittmann (1979)
2 - From Drever (1982)

**Table 2.10-2.** Variation of cation exchange capacity with particle size for kaolinite
[Data from Grim, 1968]

| Particle size (μm) | 10-20 | 5-10 | 2-4 | 1-0.5 | 0.5-0.25 | 0.25-0.1 | 0.1-0.05 |
|---|---|---|---|---|---|---|---|
| Cation exchange capacity (mEq/100 g) | 2.4 | 2.6 | 3.6 | 3.8 | 3.9 | 5.4 | 9.5 |

**Table 2.10-3.** Variation in cation exchange capacity with particle size for illite
[Data from Grim, 1968]

| Particle size (μm) | | 1-0.1 | 0.1-0.06 | <0.06 |
|---|---|---|---|---|
| Cation exchange capacity (mEq/100 g) | Sample A | 18.5 | 21.6 | 33 |
| | Sample B | 13.0 | 20.0 | 27.5 |
| | Sample C | 20.0 | 30.0 | 41.7 |

## 2.11 Significant Sedimentary Trace Metal Collectors

As has been shown, a number of physical factors affect the ability of a sediment to collect and concentrate trace metals. With these factors as a basis, plus additional chemical work, it is possible to identify the compounds and substances that are most significant in providing a sediment with the capacity to concentrate metals. These compounds and substances have large surface areas, cation exchange capacities, and high surface charges, and they tend to be found in the finer size fractions. Further, sedimentary metal collectors tend to be thermodynamically unstable and are amorphous or cryptocrystalline (Jones and Bowser, 1978). The most common materials meeting these criteria are clay minerals, organic matter, hydrous manganese oxides, and hydrous iron oxides.

Table 2.11-1 lists the various important features of metal sedimentary collectors. Forstner (1982a) has listed these materials in descending order according to their ability to collect and concentrate trace metals: manganese oxides, humic substances (organic matter), hydrous iron oxides, and clay minerals. These results are based upon sequential extraction studies (see section 3.5). Within each category there is substantial variability depending upon the geochemical character of the environment (type of clay minerals present, concentration of organic matter, pH, Eh) and the various metals involved.

## 2.12 Iron and Manganese Oxides

The characteristics of iron and manganese oxides are outlined in table 2.12-1. These substances have long been known as excellent scavengers of trace metals from solution (Goldberg, 1954; Krauskopf, 1956). Although the most spectacular demonstration of this effect is the manganese nodules located at the sediment-water interface on deep ocean floors or on lake beds (Mero, 1962; Moore and others, 1973), the separation and identification of manganese micronodules in core and grab samples indicate that they are ubiquitous and play a significant role throughout the sediment column as metal collectors in aquatic environments (Goldberg and Arrhenius, 1958; Chester and Hughes, 1967; Jenne, 1968; Cronan and Garrett, 1973; Duchart and others, 1973; Dymond and others, 1973; Moore and others, 1973; Horowitz, 1974; Lee, 1975; Horowitz and Cronan, 1976; Jones and Bowser,

1978; Forstner, 1982a,b;). Micronodules have been found in a variety of size ranges but, as their name implies, tend to be found in the smaller (less than 20 $\mu$m) size ranges (Goldberg and Arrenius, 1958; Chester and Hughes, 1969; Dymond and others, 1973; Horowitz, 1974). In soils, suspended sediment, and in bottom sediment, iron and manganese oxides also commonly occur as coatings on various minerals and finely dispersed particles (Forstner and Wittmann, 1979). Those forms most capable of concentrating metals range from amorphous to microcrystalline to crystalline and have large surface areas—on the order of 200 to 300 m$^2$/g (Fripiat and Gastuche, 1952; Buser and Graf, 1955). Regardless of form, whether micronodules or coatings, hydrous iron and manganese oxides are significant concentrators for trace metals in aquatic systems.

**Table 2.11-1.** Compositional controls on metal concentration

| Important Features |
| --- |
| 1. Thermodynamically unstable |
| 2. Amorphous or cryptocrystalline |
| 3. Capable of extensive substitution |
| 4. High cation exchange capacity |
| 5. Large surface area |
| 6. High surface charge |
| 7. Small particle size |

| Most Significant Collectors |
| --- |
| 1. Hydrous iron oxides |
| 2. Hydrous manganese oxides |
| 3. Organic matter |
| 4. Clay minerals |

| Relative Capacity of Collectors[1] |
| --- |
| Manganese oxides > organic matter > iron oxides > clay minerals |

[1]From Forstner (1982a)

**Table 2.12-1.** Iron and manganese oxides

| Characteristics |
| --- |
| 1. Fine grained |
| 2. Amorphous or poorly crystallized |
| 3. Large surface area |
| 4. High cation exchange capacity |
| 5. High negative surface charge |

## 2.13 Organic Matter

The characteristics of aquatic and soil organic matter are outlined in table 2.13-1. The ability of organic matter to concentrate trace metals in and on soils as well as suspended and bottom sediments is well recognized (Goldberg, 1954; Krauskopf, 1956; Kononova, 1966; Swanson and others, 1966; Saxby, 1969; Schnitzer and Kahn, 1972; Gibbs, 1973; Bunzl and others, 1976; Jenne, 1976; Singer, 1977; Stoffers and others, 1977; Nriagu and Coker, 1980; Ghosh and Schnitzer, 1981; Forstner, 1982a,b). Aquatic organic matter, generally termed humic substances, has been subdivided by Jonasson (1977) into four categories: humins, humic acids, fulvic acids, and yellow organic acids (see table 2.13-1). Gibbs (1973), among others, has indicated the importance of organic molecules in controlling trace metal concentrations on and in suspended and bottom sediments, and in sediment-water interactions. Saxby (1969) has shown that the relative attraction between metals with colloidal, suspended, and bottom sediment-associated organic matter can range from weak and readily replaceable (adsorption) to strong (chemically bonded). The ability of organic matter to concentrate metals varies with the constituent and the type of organic matter (Swanson and others, 1966; Saxby, 1969; Rashid, 1974; Bunzl and others, 1976; Jonasson, 1977). Organic matter can concentrate between 1 percent and 10 percent dry weight of Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, V, and Zn (Swanson and others, 1966). The ability to concentrate various trace metals appears to be related to a number of factors, including large surface area, high cation exchange capacity, high negative surface charge, and physical trapping (table 2.13-1). It is also related to the stability of the organic-metal constituent complex. In soils, the sequence in descending order is Pb, Cu, Ni, Co, Zn, Cd, Fe, Mn, Mg—the so-called Irving-Williams Series (Irving and Williams, 1948) (table 2.13-1). Similar results have also been found for aquatic organic matter (Swanson and others, 1966; Saxby, 1969; Rashid, 1974; Bunzl and others, 1976; Jonasson, 1977). The concentration of aquatic organic matter, as indicated by such constituents as total organic carbon and total organic nitrogen, tends to show a strong positive correlation with decreasing grain size and increasing surface area (Kuenen, 1965; Forstner and Wittmann, 1979).

## 2.14 Clay Minerals

The characteristics of clay minerals are outlined in table 2.14-1. These materials can act as significant collectors and concentrators of trace metals in aquatic systems (Goldberg, 1954; Krauskopf, 1956; Goldberg and Arrhenius, 1958; Hirst, 1962; Grim, 1968; Kharkar and others, 1968; Gibbs, 1973; Jenne, 1976; Jones and Bowser, 1978; Forstner and Wittmann, 1979; Forstner, 1982a,b). Clay mineral capacity for cation exchange is governed by broken chemical bonds around the edges of mineral grains, the substitution of $Al^{+3}$ (aluminum) for $Si^{+4}$ (silicon) with the associated charge imbalance, and the presence of expandable lattices (Grim, 1968). Hirst (1962) has pointed out the importance of different clay minerals in controlling the background levels of metals in bottom sediments and has evaluated the capacity of various types of clays with respect to their ability as trace metal concentrators in descending order, as follows: montmorillonite, vermiculite, illite equal to chlorite, kaolinite. The actual process by which clay minerals concentrate constituents is not well understood; however, laboratory studies indicate that it can be rapid (in tens of minutes) and depends upon a number of physicochemical factors like the valence, ionic radii, and concentration of the constituent, the type of clay, the pH of the solution, and the nature and concentration of competing substrates (Forstner and Wittmann, 1979). An empirical affinity sequence for some heavy metals and clay minerals gives, in descending order, lead, nickel, copper, and zinc (Mitchell, 1964). Recent studies in some European rivers appear to indicate that clay minerals may not play a significant role in the direct chemical concentration of inorganic constituents by, for example, adsorption (Forstner and Wittmann, 1979). That would support the view of Jenne (1976) that the major role of clay minerals as metal concentrators is to act as mechanical substrates for the precipitation and flocculation of organic matter and secondary minerals (for example, hydrous iron and manganese oxides). In other words, the clays are coated with material that, rather than the clays themselves, actually carries out the concentration of trace metals.

**Table 2.13-1.** Organic matter

| Characteristics |
| --- |
| 1. Concentration increases with decreasing grain size |
| 2. Large surface area |
| 3. High cation exchange capacity |
| 4. High negative surface charge |
| 5. Capable of physical trapping |

| Types[1] |
| --- |
| 1. Humins |
| 2. Humic acids |
| 3. Fulvic acids |
| 4. Yellow organic acids |

| Metal Affinities[2] |
| --- |
| Lead > copper > nickel > cobalt > zinc > cadmium > iron > manganese > magnesium |

[1]From Jonasson (1977)
[2]From Irving and Williams (1948)

**Table 2.14-1.** Clay minerals

| Characteristics |
| --- |
| 1. Fine grained |
| 2. Large surface area |
| 3. Moderate to high cation exchange capacity |
| 4. High negative surface charge |
|    a. Broken bonds on mineral edges |
|    b. Substitution of aluminum(III) for silicon(IV) |

| Capacity for Metal Concentration[1] |
| --- |
| Montmorillonite > vermiculite > illite=chlorite > kaolinite |

[1]From Hirst (1962)

# 3.0 CHEMICAL FACTORS AFFECTING SEDIMENT-TRACE METAL CONCENTRATIONS

*3.1 Introduction to Chemical Partitioning*

Now that we have discussed physical partitioning and elucidated the major physical factors affecting interactions between trace metals and sediments, it is time to examine chemical partitioning. Just as aquatic systems are physically dynamic (water moving in a streambed, wind-created waves in a lake) they are also chemically dynamic. The key to understanding and predicting metal transport and environmental availability, as well as to identifying sources and sinks for aquatic metal constituents, is the identification and quantification of the metal associations in sediments (suspended and bottom) and the reactions among sediment, water, and biota (see table 3.1-1).

A search of the literature on sedimentary chemical partitioning shows that two approaches have been used. The first approach aims at determining how trace metals are retained on or by sediments—the so-called mechanistic approach. According to Gibbs (1977), there are five major mechanisms for inorganic accumulation in or on sediments (suspended and bottom):

1. Adsorption on fine-grained material
2. Precipitation of metal compounds
3. Co-precipitation with hydrous iron and manganese oxides and carbonates
4. Association either by adsorption or organometallic bonding with organic matter
5. Incorporation in crystalline minerals (table 3.1-2)

Adsorption was discussed in section 2.9. Precipitation and coprecipitation are readily understandable terms. Organometallic bonding is the attachment of a metal directly to carbon; such bonds can be formed by almost any metal and by several nonmetals (silicon, phosphorus). Examples are diethylzinc, methyl- and dimethyl mercury, and tetraethyl lead. Incorporation in crystal minerals is also called substitution. This entails the substitution of one element for another within a fixed crystal structure; substitution is governed by ionic radius and charge. In general—and there are exceptions—substitution may take place when ionic radii are within ±15 percent and when the charge is the same, or differs by no more than ±1.

The second approach seeks to determine where inorganic constituents are retained on or by sediments (phase or site)—the so-called phase approach (see table 3.1-2). This has been attempted because individual constituents (like Fe, Mn, Cd, Pb, Zn, Ni, Co, and Cu) may be, and usually are, associated with several phases. The term *phase* is used in the thermodynamic sense and incorporates categories like interstitial water, clay minerals, sulfides, carbonates, humic acid, manganese oxides, and so forth (table 3.1-3). Despite this relatively simple division into two approaches, very few attempts to chemically partition complex sediment samples entail a purely mechanistic or phase approach; rather, they combine aspects of both.

**Table 3.1-1.** Chemical partitioning

Aquatic systems are chemically dynamic. The key to understanding and predicting metal transport and environmental availability, as well as to identifying sources and sinks, lies in identifying and quantifying the metal associations in sediments and the reactions that occur between sediment, water, and biota.

**Table 3.1-2.** Mechanisms for metal accumulation in sediments
[Data from Gibbs, 1977]

1. Adsorption on fine-grained material
2. Precipitation of metal compounds
3. Co-precipitation with hydrous iron and manganese oxides and carbonates
4. Association either by adsorption or organometallic bonding with organic matter
5. Incorporation in crystalline minerals

**Table 3.1-3.** Examples of phases where metal accumulates in sediments

1. Interstitial water
2. Carbonates
3. Clay minerals
4. Organic matter
5. Hydrous iron and manganese oxides
6. Sulfides
7. Silicates

*3.2 Utility of Chemical Partitioning Data*

The preceding discussion outlined the concept of chemical partitioning. It is important, at the same time, to understand the practical implications of the concept and to grasp its importance to the environment and to water-quality studies. Because aquatic systems are chemically dynamic, the goal of water-quality projects should be not only to describe existing conditions at some point in time and infer their effect on the environment, but also to attempt to predict likely occurrences later, or when physicochemical conditions change.

Table 3.2-1 points out some of the potential uses of chemical partitioning and indicates some of the potential changes that can result from altered physicochemical conditions. The table is divided into three major categories: bioavailability, transport modeling, and remobilization. Bioavailability is a common term encompassing a concept that most individuals can grasp. However, determining actual bioavailability is another matter entirely. Bioavailability is always operationally defined, usually as the result of some chemical test or toxicity experiment. Unfortunately, no one has yet come up with a universally accepted method of determining

bioavailability, and thus the concept remains subject to much interpretation and argument.

Because aquatic systems are both physically and chemically dynamic, both aspects must be considered when discussing sediment-associated chemical transport. Physical transport of sediment is relatively straightforward and involves hydrodynamics. A number of existing physical-transport models have already been tested and used. However, in order to predict chemical transport adequately, an effective model must be able to take into account chemical changes that result from altered environmental conditions. The first step toward creating such a model is an understanding of the chemical reactions that can take place in a system and requires input regarding the existing chemical phases and the way in which trace metals are held. This type of data can only be obtained by chemical partitioning.

Under the heading, "Remobilization," table 3.2-1 gives practical examples of how changing physicochemical conditions affect sediment-trace metal concentrations. The types of changes are typical of many common environments and should be familiar occurrences to most water-quality investigators.

*3.3 Chemical Partitioning Methods*

Table 3.3-1 outlines the most common methods by which chemical partitioning is ascertained. The

methods and their practical uses and limitations are discussed in the following pages.

**Table 3.2-1.** Rationale for the determination of chemical partitioning

I. Bioavailability
II. Transport modeling
III. Remobilization
    A. Elevated salt levels–alkali and alkaline earth displacement
        1. Deicing salts
        2. Saline effluents
        3. Saltwater intrusion
        4. Estuarine, fresh, and saltwater mixing
    B. Redox changes–dissolution of iron and manganese oxides and hydroxides with subsequent metal release
        1. Eutrophication
        2. Organic inputs
    C. pH reduction–dissolution of carbonates and hydroxides, desorption by $H^+$
        1. Acid mine drainage
        2. Acid rain
        3. Acidic industrial effluents
    D. Increases in complexing agents–form stable soluble metal complexes
        1. Tannic acid
        2. Peat and lignite
        3. Nitriloacetic acid–detergent additive in place of phosphate
    E. Microbial activity–solubilization of metals by direct and indirect action
        1. Alkylation of metals (mercury, arsenic, lead, selenium, and so forth)—for example, methyl mercury
        2. Destruction of organic matter
        3. Metabolic activity decreasing pH or oxygen

**Table 3.3-1.** Methods for determining chemical partitioning

1. Manual selection of phases and analysis
2. Instrumental selection of phases and analysis
3. Partial chemical extractions
4. Density gradients and analysis
5. Statistical manipulations of bulk chemical data
6. Mathematical modeling

## 3.4 Chemical Partitioning—Instrumental Methods

Ideally, chemical partitioning can be accomplished by separating out specific mineral or organic sediment phases, whether instrumentally (for example, magnetic separators, heavy mineral flotation) or manually (picking out mineral grains with the aid of a microscope), and subjecting them to chemical analysis. In actual practice, some separation techniques may change the sediment chemistry, and most are extremely time consuming. Moreover, it is virtually impossible to separate the individual constituents in the finer size range (e.g., clay minerals) although that is likely to be the size range of maximum interest.

Relatively new chemical analytical techniques may be used to determine chemical partitioning in sediments directly (table 3.4-1). These methods permit the quantitative analysis of various minerals or mineral assemblages in natural mixtures, without separation and sometimes nondestructively, from areas as small as 1 square micrometer (Johnson and Maxwell,

1981). Such techniques as x-ray photoelectron spectroscopy have been used on many types of geological materials, including sediments, with mixed success (Jones and Bowser, 1978; Johnson and Maxwell, 1981). Many of these procedures permit the user to select the analytical site visually, thus making possible the determination of phase association for the derived chemical data. Although these techniques are promising, several problems limit their use. Foremost is the problem of determining correction factors for the various counting systems used and for background interference. Because of the complexity of these correction factors, detection limits are usually higher than 100 mg/kg (100 ppm) and can be significantly higher (Johnson and Maxwell, 1981). This problem tends to limit the usefulness of these procedures to major elements such as Fe, Mn, and Na, and could exclude such environmentally important trace metals as Pb, Cd, Ag, and Cu.

**Table 3.4-1.** Instrumental techniques for determining chemical partitioning

1. Electron microprobe–Electron beam producing x-ray emissions
2. X-ray photoelectron spectroscopy (ESCA, XPS)–Photon producing electrons
3. U.V. photoelectron spectroscopy–Photon beam producing ionization and electrons
4. Auger electron spectroscopy (AES)–Electron beam producing ionization and secondary electrons
5. Secondary ion mass spectroscopy (SIMS)–Positive ion beam producing chemical fragments
6. Ion scattering spectroscopy (ISS)–Ion beam producing primary ions

*3.5 Chemical Partitioning—Partial Extraction*
*Methods*

One of the oldest and most commonly used methods of chemically partitioning sediments involves the use of partial chemical extractions. Much of the original work in this area was carried out on marine material (Goldberg and Arrhenius, 1958; Hirst and Nicholls, 1958; Arrhenius and Korkish, 1959; Chester, 1965; Lynn and Bonatti, 1965; Chester and Hughes, 1966; 1967; 1969; Chester and Messiah-Hanna, 1970; Cronan and Garrett, 1973; Horowitz, 1974; Horowitz and Cronan, 1976). These early procedures usually involved two- or, at most, three-step sequential extractions plus a total analysis, used in increasing strength, which attempted to partition trace metals. The concept of sequential extractions is based on the idea that a particular reagent is either phase-specific or mechanistic-specific (for example, acetic acid *will only* attack and dissolve carbonates; ammonium acetate at pH 7 *will only* remove adsorbates). Table 3.5-1 lists most of the extractants that have been used over the years to partition sediments and soil chemically.

After the initial work on marine sediments, further advances in chemical partitioning using sequential partial extractions have been made by workers in many diverse fields (Bruland and others, 1974; Gupta and Chen, 1975; Brannon and others, 1976; Chen and others, 1976; Gambrell and others, 1977; Luoma and Jenne, 1977; Malo, 1977; Stoffers and others, 1977;

Forstner and Wittmann, 1979; Tessier and others, 1979; Nriagu and Coker, 1980; Diks and Allen, 1983). These studies used sequential chemical extractions in an attempt to differentiate between anthropogenic and natural inorganic pollutants and to try to predict or estimate bioavailability. The sequences became more and more complex as attempts to clarify chemical partitioning increased. Some procedures involved six, seven, and even nine steps (Schmidt and others, 1975; Brannon and others, 1976; Summerhayes and others, 1976; Stoffers and others, 1977; Forstner, 1982a,b).

Sequential extractions have been used widely and on many types of material, but they are not a panacea. The major problem is that the extraction reagents are not as "selective" as many users assert (Malo, 1977; Pilkington and Warren, 1979). Also, as Forstner (1982a) points out, extraction efficiencies vary according to length of treatment and sediment-to-extractant ratio. However, sequential procedures also have advantages. They permit differentiation between samples having similar bulk chemistries. Also, they represent one of the few practical methods for the determination of concentration mechanisms and thus provide a possible means for estimating bioavailability (see Diks and Allen, 1983). Finally, they offer a potential means of providing the requisite chemical partitioning data needed for transport modeling.

**Table 3.5-1.** Reagents employed in sequential partial chemical extractions

| Classification | Reagent | Reference |
|---|---|---|
| Adsorbates and Exchangeables | 0.2 BaCl$_2$-triethanolamine, pH 8.1 | Jackson, 1958 |
| | 1 M NH$_4$OAc, pH 7 | Jackson, 1958 |
| | Distilled deionized water | Nissenbaum, 1972 |
| | 1 M NH$_4$OAc | Gupta and Chen, 1975 |
| | 1 M MgCl$_2$, pH 7 | Tessier and others, 1979 |
| | 1 M NaOAc, pH 8.2 | Tessier and others, 1979 |
| Carbonates | 1 M HOAc (25% v/v HOAc) | Chester and Hughes, 1967 |
| | 1 M NaOAc, pH 5 w/ HOAc | Tessier and others, 1979 |
| | CO$_2$ treatment | Pachineelam, 1975 |
| | Exchange columns | Deurer and others, 1978 |
| Detrital/Authigenic | EDTA treatment | Goldberg and Arrhenius, 1958 |
| Hydrogenous/Lithogenous | 0.1 M HCl | Piper, 1971 |
| | 0.3 M HCl | Piper, 1971 |
| Reducible | 1 M NH$_2$OH·HCl w/ 25% v/v HOAc | Chester and Hughes, 1967 |
| Moderately Reducible | Oxalate buffer | Schwertmann, 1964 |
| (hydrous iron oxides) | Dithionate/citrate buffer | Holmgren, 1967 |
| Easily Reducible | | |
| (Mn and amorphous oxides) | 0.1 M NH$_2$OH·HCl w/ 0.01 M HNO$_3$ | Chao, 1972 |
| Organics | Na hypochlorite w/ dithionate-citrate | Gibbs, 1973 |
| | 30% H$_2$O$_2$ at 95°C, pH 2 | Engler and others, 1974 |
| | 30% H$_2$O$_2$ w/ 0.02 N HNO$_3$, pH 2 extracted w/ 1 M NH$_4$OAc in 6% HNO$_3$ | Gupta and Chen, 1975 |
| | 30% H$_2$O$_2$ w/ 0.02 N HNO$_3$, pH 2 extracted w/ 0.01 M HNO$_3$ | Gupta and Chen, 1975 |
| | 1:1 methanol-benzene (bitumen) | Summerhayes and others, 1976 |
| | 0.1 N NaOH (humic acids) | Schnitzer and Kahn, 1978 |
| | 0.02 M HNO$_3$ w/ H$_2$O$_2$, pH 2 w/ HNO$_3$ at 85°C, w/ 3.2 M NH$_4$OAc in 20% HNO$_3$ | Tessier and others, 1979 |
| | 30% H$_2$O$_2$ in 0.5 N HCl, heat | Kitano and others, 1980 |
| Sulfides | 30% H$_2$O$_2$ at 95°C, extracted w/ 1 N NH$_4$OAc | Gupta and Chen, 1975 |
| | 0.1 N HCl w/ air | Kitano and others, 1980 |
| Detrital Silicates | HF/HClO$_4$/HNO$_3$ | Johnson and Maxwell, 1981 |
| | Borate fusions w/ HNO$_3$ | Johnson and Maxwell, 1981 |

## 3.6 Chemical Partitioning of Suspended Sediments by Partial Extraction

For an example of the type of information that can be obtained using partial chemical extractions, examine the data in figure 3.6-1. The information was generated by a four-step chemical extraction sequence performed on suspended sediment from the Amazon and Yukon Rivers (Gibbs, 1977). Most of the chromium, cobalt, and copper is concentrated in mineral lattices; most of the manganese and nickel is associated with ferromanganese coatings. The iron was evenly divided between mineral lattices and ferromanganese coatings. Adsorption was not a significant contributor to the concentration of any of the metals studied, and organic matter was a significant collector only in the case of cobalt and nickel.

With these results as a basis, it is possible to discuss potential environmental availability. Metals associated with crystal lattices are essentially unavailable. Metals associated with ferromanganese coatings probably will be stable or environmentally unavailable unless there is a significant decrease in dissolved oxygen or a significant increase in biological activity. Ferromanganese-associated metals may be released in the digestive systems of certain organisms (Diks and Allen, 1983). Organics-associated metals could be available, particularly if ingested by an organism. Adsorbed metals are readily available but, as can be seen, represent a relatively small percentage of the metals present in the suspended matter.

Chromium

Manganese

Iron

Cobalt
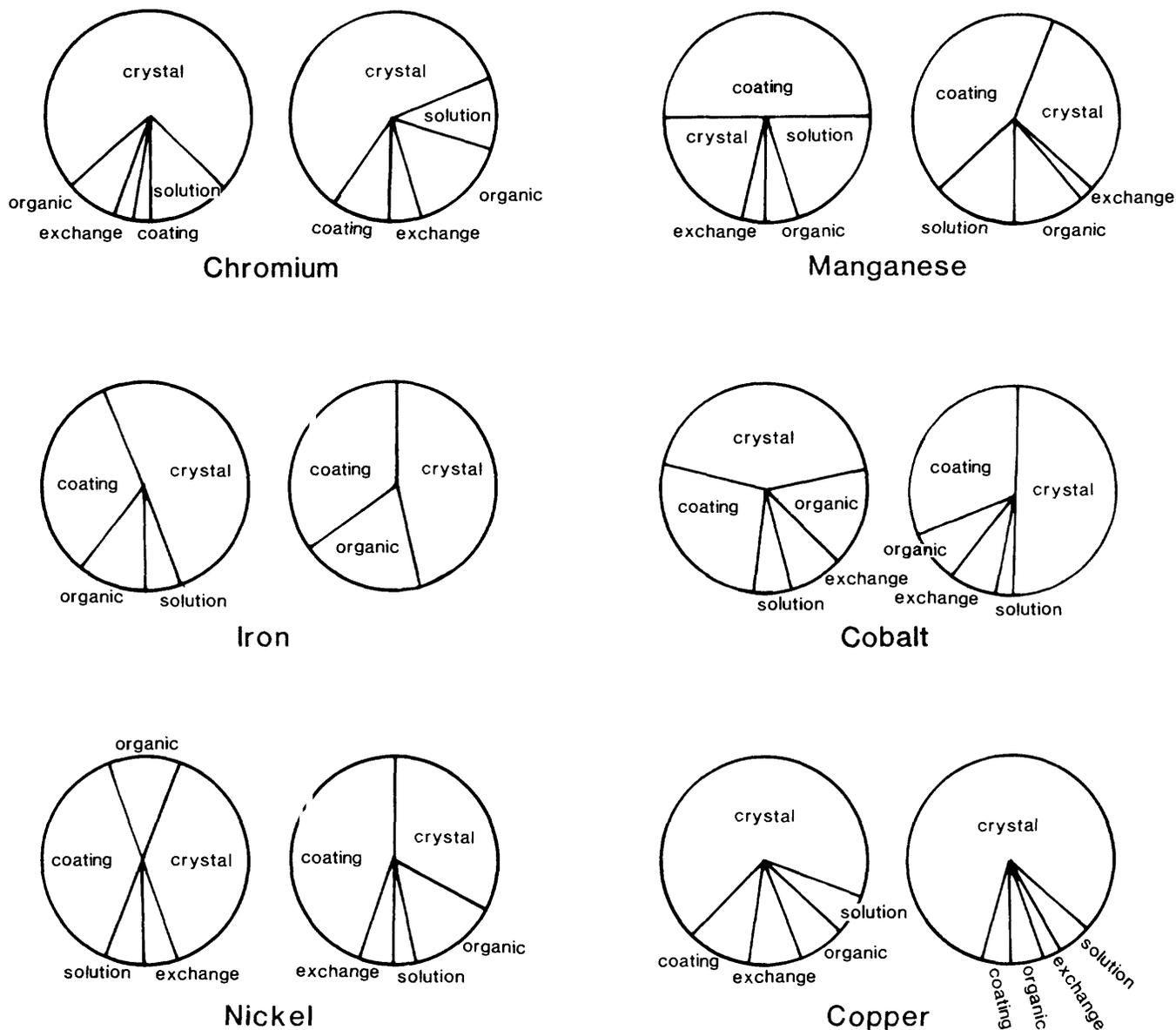
Nickel

Copper

AMAZON RIVER    YUKON RIVER        AMAZON RIVER    YUKON RIVER

Solid phases, in percent

| Phase | Chromium | Manganese | Iron | Cobalt | Nickel | Copper |
|---|---|---|---|---|---|---|
| Absorbed | 3.5 | 0.8 | 0.007 | 6.5 | 3.2 | 3.5 |
| Coatings | 5.2 | 54.8 | 43.6 | 28.8 | 47.2 | 5.7 |
| Organics | 11.0 | 6.7 | 9.0 | 16.4 | 15.0 | 4.5 |
| Crystalline | 80.3 | 37.8 | 47.4 | 48.3 | 34.6 | 86.2 |

Figure 3.6-1.—Chemical partitioning of selected metals in the Amazon and Yukon Rivers. (Data from Gibbs, 1977)

## 3.7 Chemical Partitioning of Bottom Sediments by Partial Extraction

The data in table 3.7-1 provide another example of the utility of partial chemical extractions. This information was generated by carrying out a four-step sequential extraction on two marine bottom sediment samples, both having similar Mn concentrations. Sample 1 comes from a hydrothermally active region, and sample 2 comes from a hydrothermally inactive region. Ordinarily, hydrothermally active areas display high Mn concentrations. Two questions about these samples need to be addressed: Are the samples geochemically similar, as implied by the bulk chemical results? If they are dissimilar, why?

The acetic acid extraction is designed to remove adsorbates and metals associated with carbonate minerals. For this extraction, the two sediments are similar. The hydroxylamine extraction is designed to break down manganese oxides. For this extraction, it is obvious that the samples are dissimilar. The sample from the hydrothermally active area has three times as much Mn associated with oxides as has the sample from the inactive area. The hot HCl (hydrochloric acid) attack is designed to break down all but the most resistant silicates and aluminosilicates. Here, too, the samples are dissimilar; much more manganese is held in this fraction in the hydrothermally inactive sample than in the active one. These results show that the sequential partial extractions provided a means of determining how manganese was held in the samples; they also permitted the differentiation of the two samples. This differentiation would have been impossible solely on the basis of bulk chemical data.

**Table 3.7-1.** An example of manganese partitioning in bottom sediment samples using partial chemical extractions

| Extraction | Active Hydrothermal Area | | Inactive Hydrothermal Area | |
|---|---|---|---|---|
| | Concentration Remaining (mg/kg) | Percentage of Total Removed | Concentration Remaining (mg/kg) | Percentage of Total Removed |
| Bulk | 1,400 | | 1,200 | |
| Acetic acid | 1,300 | 7 | 1,100 | 8 |
| Hydroxylamine | 600 | 50 | 900 | 17 |
| Hot HCl | 200 | 29 | 200 | 58 |

*3.8 Chemical Partitioning by Density Gradient and Mineralogy*

Another method employed to determine chemical partitioning uses physical separations, determination of mineralogy, and subsequent chemical analysis (Muller and Burton, 1965; Francis and others, 1972; Pilkington and Warren, 1979; Dossis and Warren, 1980). Table 3.8-1 shows an example of the results of this type of procedure. Each sample was broken down into four size fractions by settling in acetone (Pilkington and Warren, 1979). Each size fraction was further subdivided into density subfractions by heavy liquid flotations using tetrabromoethane (bromoform). Each density subfraction was subjected to mineralogical analysis by x-ray diffraction or differential thermal analysis. Finally, each size or density subfraction was chemically analyzed. The data in table 3.8-1 are the chemical results from two samples, A and D, and represent the six density subfractions of the 1,000-to-10-$\mu$m size separation of each. It is apparent that the lighter (least dense) fraction of sample A contains the

highest concentrations of the metals investigated, while the heaviest (most dense) fraction of sample D contains the highest concentrations. This is true despite the fact that in both cases, these density subfractions constitute only minor components of each sample (8.5 percent for A, and 1.3 percent for D). Because the mineralogy of each density subfraction is known, establishing chemical partitioning is much more direct and certain than with partial chemical extractions.

This type of procedure also has drawbacks. It is not very useful when there is a large percentage of fine particles, because of difficulties involved in carrying out density separations on material finer than 10 $\mu$m (Pilkington and Warren, 1979). There is no assurance, without individual testing, that the acetone or bromoform will not alter the chemistry. Finally, the method is extremely labor-intensive and consequently expensive to carry out.

**Table 3.8-1.** Density gradients and chemical analysis

[Data from Dossis and Warren, 1980]

[Procedure: 1. Sizing in acetone (>1,000, 1,000 to 10, 10 to 1, and <1 μm)
2. Density separations using bromoform (<2.20, 2.20 to 2.55, 2.55 to 2.66, 2.66 to 2.75, 2.75 to 2.95, and >2.95 g/cc)  3. Phase identification by x-ray diffraction or differential thermal analysis  4. Chemical analysis of each density subfraction]

| | | Concentration of Metals by Density Subfraction | | | | | | |
| Sample | Density Subfraction | Weight Distribution (percent) | Zinc (μg/g) | Lead (μg/g) | Cadmium (μg/g) | Zinc in Fraction (percent)[1] | Lead in Fraction (percent)[1] | Cadmium in Fraction (percent)[1] |
|---|---|---|---|---|---|---|---|---|
| AS2 | D1 | 8.5 | 486 | 436 | 22 | 37 | 43 | 38 |
| | D2 | 6.5 | 204 | 166 | 9.4 | 12 | 13 | 13 |
| | D3 | 45.7 | 74 | 45 | 1.9 | 30 | 24 | 18 |
| | D4 | 20.3 | 85 | 61 | 5.4 | 15 | 15 | 23 |
| | D5 | 19.0 | 35 | 23 | 1.9 | 6 | 5 | 8 |
| | D6 | 0.1 | | | | | | |
| DS2 | D1 | 2.3 | 1,580 | 1,370 | 25.3 | 3 | 4 | 4 |
| | D2 | 27.5 | 1,170 | 1,140 | 22.7 | 13 | 43 | 38 |
| | D3 | 61.6 | 183 | 168 | 1.7 | 5 | 14 | 7 |
| | D4 | 3.6 | 648 | 992 | 4.1 | 1 | 5 | 1 |
| | D5 | 3.6 | 740 | 1,100 | 7.3 | 1 | 6 | 2 |
| | D6 | 1.3 | 148,000 | 15,000 | 607 | 79 | 28 | 49 |

[1]Percent in fraction calculated by multiplying the concentration by the weight distribution for each subfraction, summing, and then dividing each fractional contribution by the total.

### 3.9 Chemical Partitioning by Mathematical Manipulation or Modeling

Thus far, the discussion of chemical partitioning has concentrated on direct determination by either chemical or instrumental means. Attempts also have been made to determine chemical partitioning indirectly, using various statistical manipulations and by constructing mathematical models.

The statistical manipulation of chemical data can be used to clarify the processes by which various trace metals are partitioned on or in seston and bottom sediments, especially when dealing with large data sets (Jones and Bowser, 1978). Statistical treatment of chemical data, or chemical and mineralogical data, ranges from the calculation of relatively simple correlation coefficients through highly complex cluster and multivariate techniques. For example, Rossman and others (1972) used correlation coefficients to partition bulk chemical data for ferromanganese nodules from Green Bay. Because iron and manganese are the major elements in the samples and appear to form two distinct phases, they show strong negative correlations. Additional calculations, using chemical data on other elements, indicate that they partition with either the iron or manganese phases. The Fe phase appears to concentrate Si and $PO_4$ while the Mn phase appears to concentrate Ba, Ni, Co, Mo, Mg, and Sr.

Leinen and others (1980), Pisias and Leinen (1980), and Leinen and Pisias (1984) used an extended version of Q-mode factor analysis (a method for determining associations among samples) and linear programming to partition (identify phases of) chemical data from sediments collected on the Nazca Plate in the Pacific Ocean. The procedure identified five geochemically and mineralogically separate end members (groups), which were termed (1) detrital, (2) hydrothermal, (3) biogenic, (4) authigenic hydrogenous, and (5) biogenic residual. Gibbs (1967; 1977) used multiple regression analysis to evaluate the major transporting mechanisms for metal constituents associated with seston in the Amazon River. The major transport phases and their relative importance for carrying transition metals are, in decreasing order, metals held in crystal lattices equal to metals associated with hydroxide coatings; metals associated with organic matter; and metals held as adsorbates on minerals.

Luoma and Bryan (1981) applied statistical techniques (linear regressions on log-transformed data) to assess the "competition" between various substrates for different metals using data obtained from various partial chemical extractions on bottom sedi-

ments from a number of estuaries. Their statistical work assessed the utility of the various extractions in determining phase associations and bioavailability. Substrate (phase) characterization seems best accomplished by iron and manganese, and humic acid extractions. Extractable Fe phases seem more important than total Fe for the concentration of Ag, Cd, Cu, Pb, and Zn, while humic material is also important for the concentration of Ag and Cu. The results of this study support the view that the concentration of metals is a dynamic process in which various substrates "compete" for different constituents, and that the relative concentrations of differing substrates strongly influence partitioning (Oakley and others, 1980; 1981; Benjamin and Leckie, 1981). Although not specifically stated, partitioning can change with varying physicochemical conditions (changes in Eh, pH, solute concentrations, solute form, and so forth) and with transport and mixing processes, because of the addition, dilution, or removal of available substrates.

Statistical manipulations of sediment-chemical data pose some problems. For example, when the procedures used successfully by Leinen and others (1980), Pisias and Leinen (1980), and Leinen and Pisias (1984) on the Nazca Plate sediments were applied to relatively homogeneous sediments from other Pacific areas, they produced much more ambiguous results. Another problem associated with this type of technique is also associated with partial chemical extractions: a lack of sufficient specificity to identify phases positively (accomplish partitioning); identification is by inference. However, the greatest difficulty arising from the interpretation of the statistical treatment of sediment-chemical data is that it must be made with a view to real processes and relations (Jones and Bowser, 1978). This becomes increasingly important as the statistical manipulations become more complex. The manipulations may produce statistically significant results, but they can not be ascribed to a rational environmental setting or process; in such cases they serve no useful purpose. Remember, applied statistics are an empirical tool used to clarify and evaluate processes and do not represent an end in themselves (Jones and Bowser, 1978).

According to Luoma and Bryan (1981), mathematical models designed to predict sediment chemical partitioning may represent the most viable approach to the problem. Others share this view (Leinen and others, 1980; Swallow and Morel, 1980; Oakley and others, 1980; Pisias and Leinen, 1980; Benjamin and Leckie, 1981; Oakley and others, 1981). The development of mathematical models and their application to natural environments for determining and predicting

sediment-trace metal partitioning depend on a number of factors like thermodynamic data, results of partial extraction studies, ability to identify and quantify substrates, development of constants that describe the strength and stability range of metal-substrate binding, quantification of metal speciation in various strength solutions, Eh, pH, and so forth.

Swallow and Morel (1980) studied the behavior of copper and lead in the presence of hydrous iron oxides in artificial seawater and under varying pH conditions. It was found that adsorption of both metals increased with increasing pH. Further, it seemed that other factors such as the ionic strength and background electrolyte levels of the solution, the aging of the iron oxide substrate, and the precipitation of the oxides in the presence or absence of the metals in question, had no significant effect. Although the behavior of copper and lead with oxides in seawater is somewhat analogous to surface complexation, the oxides are better viewed as a three-dimensional, metal-absorbing "sponge" that accommodates metal ions into the solid as they hydrolize. These conclusions were based on experiments carried out in the laboratory; a mathematical model (expression) was developed to predict copper and lead behavior experimentally determined in the presence of iron oxides.

Davis and Leckie (1978) also studied the uptake of copper and silver by iron oxides. As did Swallow and Morel (1980), they found that uptake varied with pH. They also determined that complexing ligands strongly affect trace metal adsorption and may enhance or depress the concentration capabilities of the iron oxides. Some ligands, which bind to the surface of the oxides, increase their collection efficiency, while other ligands remain in solution and compete with oxide surfaces for metals, thus decreasing collection efficiency. These results suggest that the distribution of metals in aquatic systems may be controlled more by surface binding on sediments coated with organic matter than by those coated with iron oxides. Using purely mathematical models, this result has been confirmed for several metals including Cu, Pb, Cd, Co, Ni, and Zn (Vuceta and Morgan, 1978; Benjamin and Leckie, 1981). This is also in agreement with partial extraction studies (Forstner, 1982a,b). Further, Benjamin and Leckie (1981) indicate that metal adsorption from aqueous solutions also depends on adsorbent and adsorbate concentration and on the speciation of metals in solution.

Using copper and cadmium, Oakley and others (1980; 1981) attempted to develop a mathematical model capable of predicting partitioning and, ultimately, bioavailability. The study employed a ternary substrate system composed of clay (bentonite), humic

substances, and hydrous iron and manganese oxides, in seawater. Laboratory experiments showed that clay was the dominant sink for copper except where humic substances constituted more than 90 percent of the substrate; clay was also the dominant sink for cadmium, except where hydrous iron and manganese oxides constituted more than 90 percent of the substrate. Also, clay was the dominant sink for both copper and cadmium when it constituted more than 60 percent of the substrate. On the basis of these laboratory studies, an attempt was made to predict bioavailability through the construction of a mathematical model; it was tested in the laboratory using a polychaete worm that fed on the substrate. The results were somewhat ambiguous; nevertheless, the authors stated that they were sufficiently satisfied to conclude that the bioavailability of copper and cadmium from geochemical phases (clay, humic acid, hydrated oxide) could be more significant than the bioavailability of copper and cadmium dissolved in the seawater, at natural concentrations.

Mathematical modeling shows some promise for determining the processes involved and for predicting metal partitioning in aqueous-sedimentary systems. However, a number of problems are associated with the models. The experiments and calculations on which the models were based were carried out using laboratory-generated or purified substrates to eliminate interpretational ambiguities; even in multiphase systems (Oakley and others, 1980; 1981), the substrates were relatively simple compared to the natural environment. Also, we lack adequate data on the identity and structure of organic constituents and on the stability constants for many metal-ligand, ligand-substrate, and metal-substrate interactions in aquatic systems (Vuceta and Morgan, 1978). The results of some modeling studies appear to contradict each other: for example, the results from Swallow and Morel (1980) compared with those of Vuceta and Morgan (1978) and Benjamin and Leckie (1981). Finally, some of the reported results from modeling appear to contradict direct observations. For example, Swallow and Morel (1980) assert that adsorption of metals by hydrous iron oxides is independent of the presence or absence of the metals when oxide precipitation occurs. The suggested mechanism for metal concentration by hydrous iron oxides, when studied in the natural environment (manganese nodules), has almost invariably been coprecipitation (Cronan, 1974). This conclusion is supported by partial extraction studies (Chester and Hughes, 1966; 1967; Forstner, 1982a) and by direct examination of nodule layers (Cronan, 1974).

# 4.0 SEDIMENT-TRACE METAL DATA MANIPULATIONS

*4.1 Corrections for Grain-Size Differences*

The discussion of physical and chemical partitioning showed that many factors affect the distribution and concentration of trace metals associated with both suspended and bottom sediments. Hence it can be very difficult to determine the presence or absence of significant distribution patterns from a point source, for example. However, certain mathematical or graphic manipulations of chemical data may help the investigator determine if significant patterns do exist.

Figure 4.1-1 shows the relation between grain size and chemistry. As pointed out earlier, metals tend to concentrate in the finer size ranges (less than 16 or 20 μm in diameter), and the addition of larger grained material can be viewed as a diluent. Such diluents can readily hide a significant pattern (de Groot and others, 1982). One way to deal with the dilution problem is to separate out the less than 20-μm (16-μm) fraction and chemically analyze it. However, a reasonably good result may be obtained by determining the less than 20-μm (16-μm) percentage in the bulk sample of each sediment and normalizing the chemical data to it. The mathematics are very simple and straightforward.

The dilution factor is calculated thus:

$$\frac{100}{100\text{-percent of size fraction greater than 20 }\mu\text{m}}$$

Then this product gives the normalized chemical data (in mg/kg):

(dilution factor)×(chemical concentration in mg/kg)

As an example, assume a sediment has 20 percent less than 20-μm grain size and a zinc concentration of 100 mg/kg.

Dilution factor:

$$\frac{100}{100-80}=\frac{100}{20}=5$$

Then the normalized chemical data are

$$(5)\times(100)=500 \text{ mg/kg Zn}$$

Remember that the underlying assumption for this type of correction is that all of the constituent of interest is found in the less than 20-μm (16-μm) fraction. This is almost certainly not true, but it does help to clarify a distribution pattern that has been obscured because of the presence of varying amounts of diluent.
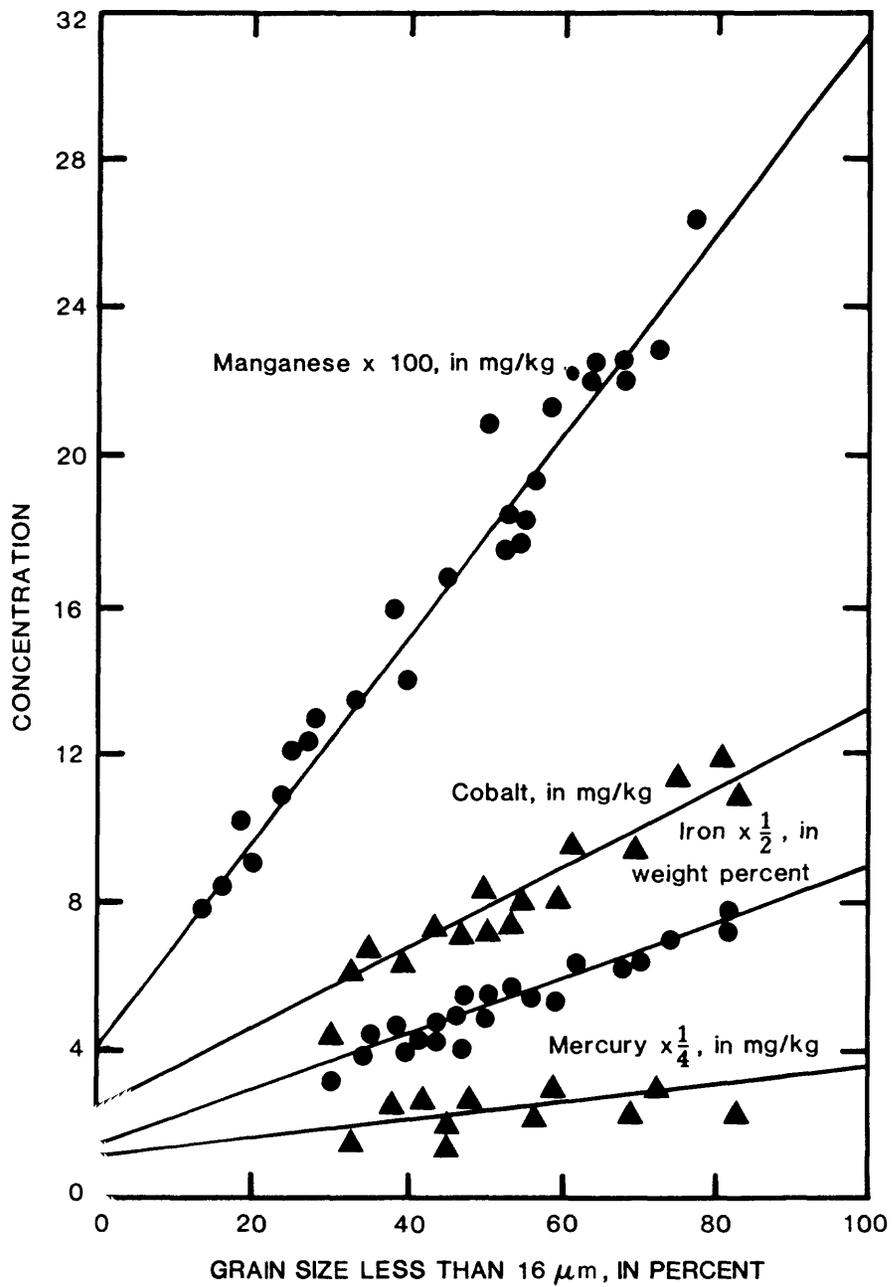
**Figure 4.1-1.**—Relation between metal concentration and grain size for the River Ems, FRG. (Data from deGroot and others, 1982)

# 4.0 SEDIMENT-TRACE METAL DATA MANIPULATIONS—Continued

## 4.2 Carbonate Corrections

Another commonly used correction factor is the normalization of data to a carbonate-free basis. As with the grain-size correction, the assumption is made that the carbonate fraction does not contain any of the inorganic constituents of interest. Data in figure 4.2-1, for a marine bottom-sediment sample, certainly support this view, with the possible exception of lead and cadmium. As with the grain-size example, the carbonate fraction could be physically separated and chemically analyzed, but with extreme difficulty. The usual procedure is to determine the carbonate content and then normalize the data accordingly. The mathematics for normalizing chemical data are simple and straightforward.

The dilution factor is given by:

$$\frac{100}{100 - \text{percent carbonate}}$$

Then the normalized chemical data are the product (in mg/kg):

(dilution factor)×(chemical concentration in mg/kg)

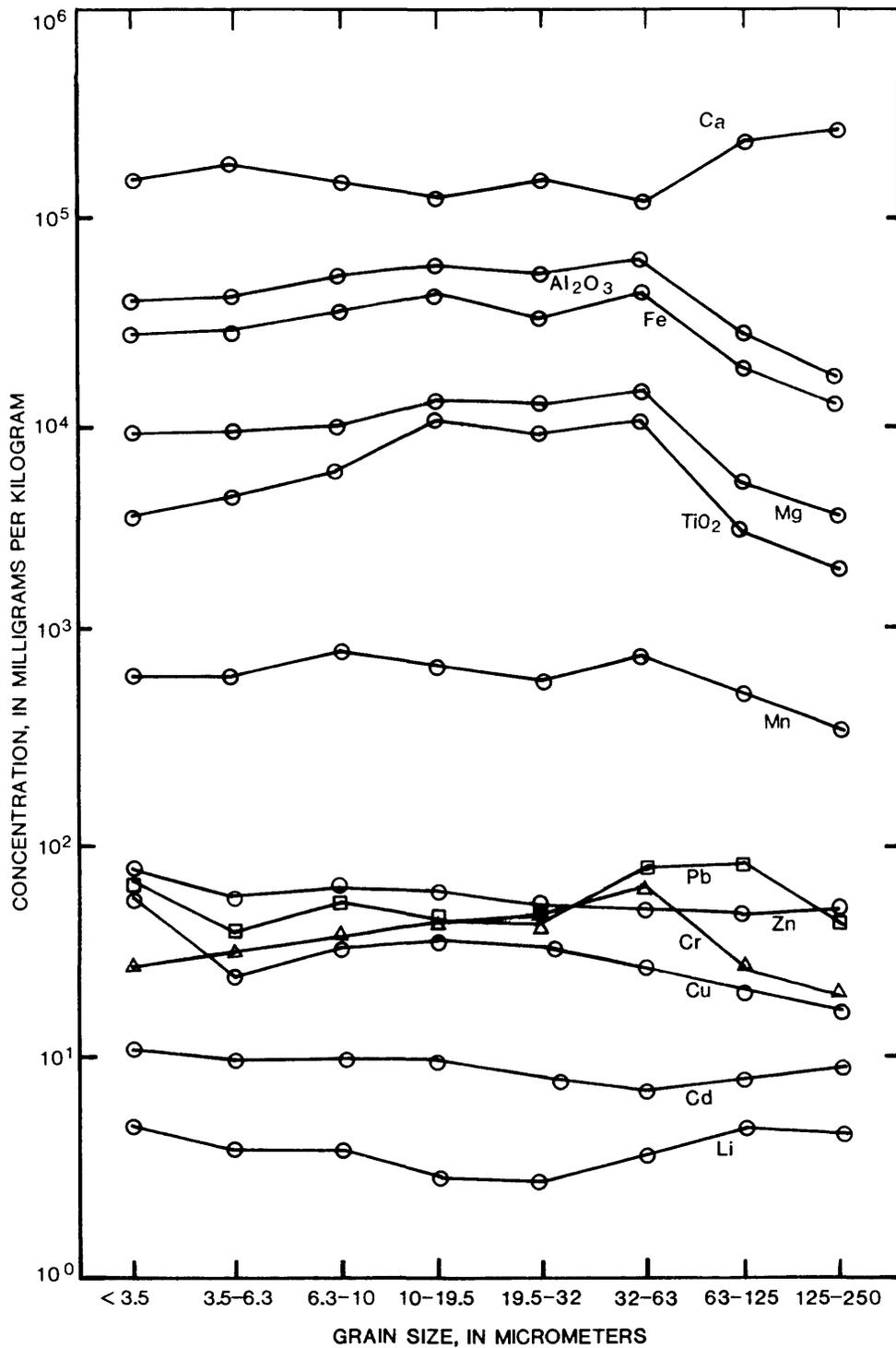As an example, assume a sediment has 25 percent carbonate, and a zinc concentration of 50 mg/kg.

The dilution factor is then

$$\frac{100}{100-25} = \frac{100}{75} = 1.33$$

The normalized chemical data are thus:

$$(1.33) \times (50) = 66.7 \text{ mg/kg Zn}$$

As an example of how a carbonate correction can clarify a pattern, examine the data in figure 4.2-2. The dashed line represents uncorrected data and the solid line the corrected data. The difference between the two patterns is striking. However, bear in mind that this type of correction assumes that all of the constituents of interest are concentrated in the noncarbonate fraction. This is almost certainly not true for every situation or trace metal, as the data in figure 4.2-3 show. The pattern for calcium which represents the dominant form of carbonate ($CaCO_3$), is the same as those for other constituents. Thus, before applying any correction to chemical data, an investigator must be certain that the underlying assumption upon which the correction is based is valid or, at least, fairly reasonable.

Figure 4.2-1.—Variation in metal content with grain size from the same bottom-sediment sample.
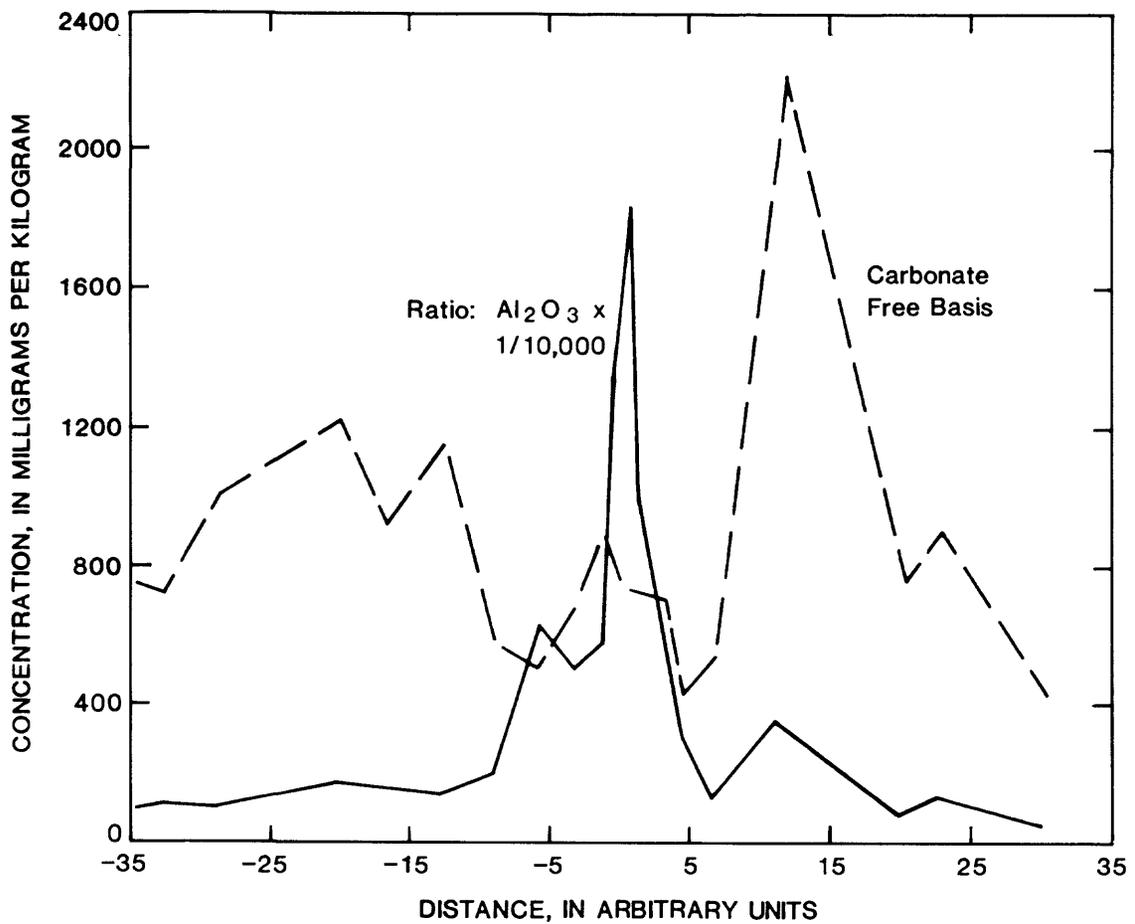
**Figure 4.2-2.**—Distribution of zinc from a point source.

# * WSP 2277—A primer on trace metal-sediment chemistry *

ERRATUM: The graphs above the captions of figures
4.2–2 (page 56) and 4.3–1 (page 59) are
erroneously transposed.

**Figure 4.2-3.**—Variation in metal content with grain size from the same bottom-sediment sample.
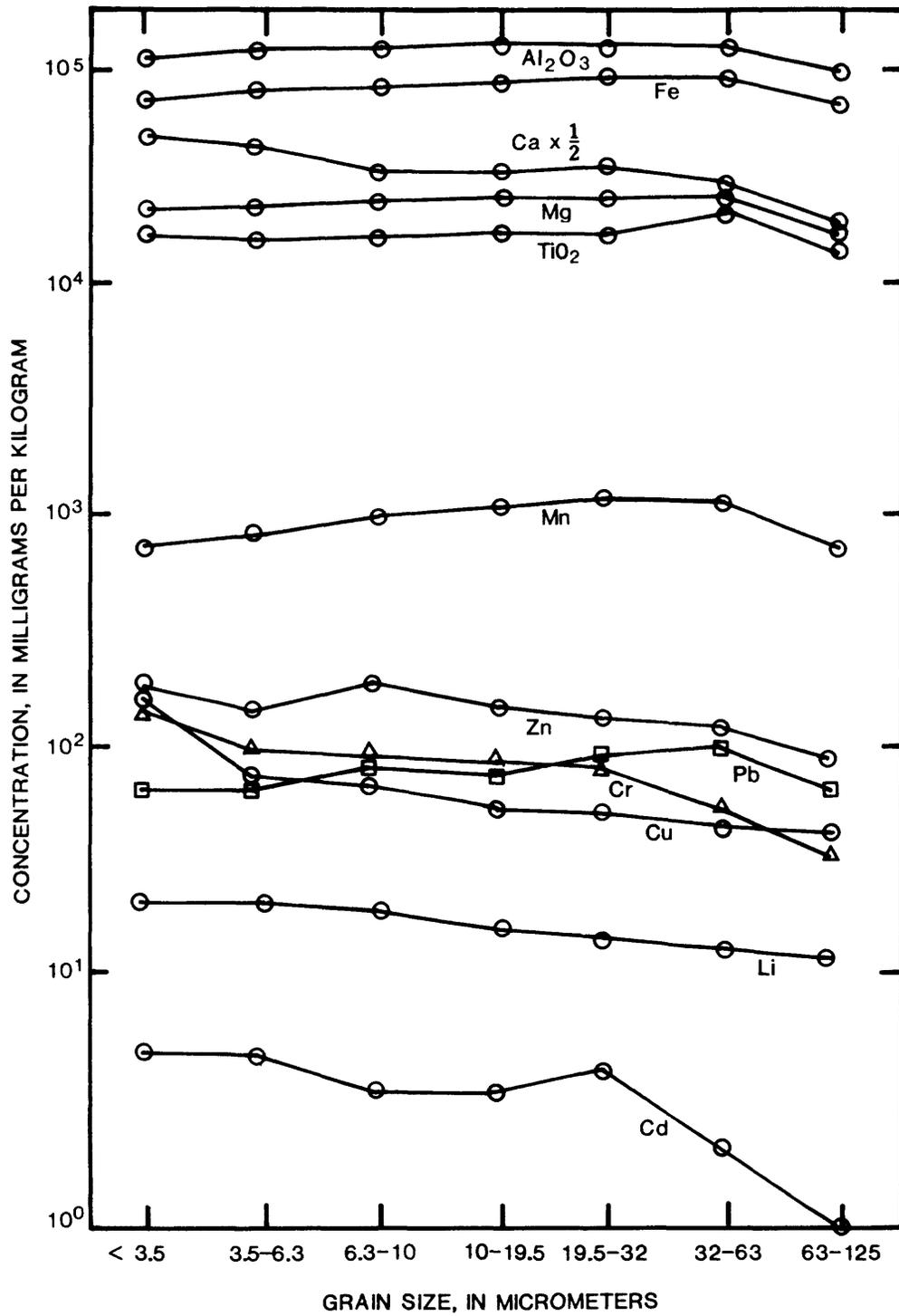
**EXPLANATION**

Al$_2$O$_3$ --aluminum     TiO$_2$ —titanium     Cr—chromium

Fe--iron                  Mn--manganese         Cu--copper

Ca x $\frac{1}{2}$—calcium   Zn—zinc              Li--lithium

Mg—magnesium              Pb—lead               Cd--cadmium

## 4.3 Normalization to "Conservative" Elements

One final commonly employed method of normalizing bulk sediment data entails a comparison with so-called conservative elements. These elements are assumed to have had a uniform flux from crustal-rock sources to the sediments over a long period of time; consequently, compensation for changes in levels of various diluents can be made (Forstner and Wittmann, 1979). The most commonly used conservative elements are aluminum (Piper, 1973; Bruland and others, 1974), and titanium (Forstner and Wittmann, 1979). The mathematics of this type of correction is a simple ratio:

$$\frac{\text{Concentration of inorganic constituent}}{\text{Concentration of conservative element}}$$

However, unlike the grain-size and carbonate corrections, the resulting values are simply ratios rather than chemical concentrations. This makes comparison with data from other areas difficult, unless the data are similarly recalculated; also, a ratio rather than a concentration is conceptually more difficult to grasp. Nevertheless, normalizing to a conservative element can significantly clarify distribution patterns, as shown in figure 4.3-1. The data in that figure are from a series of marine sediment samples. The dashed line represents bulk copper data corrected to a carbonate-free basis, while the solid line depicts the same bulk copper data normalized to aluminum (as $Al_2O_3$).
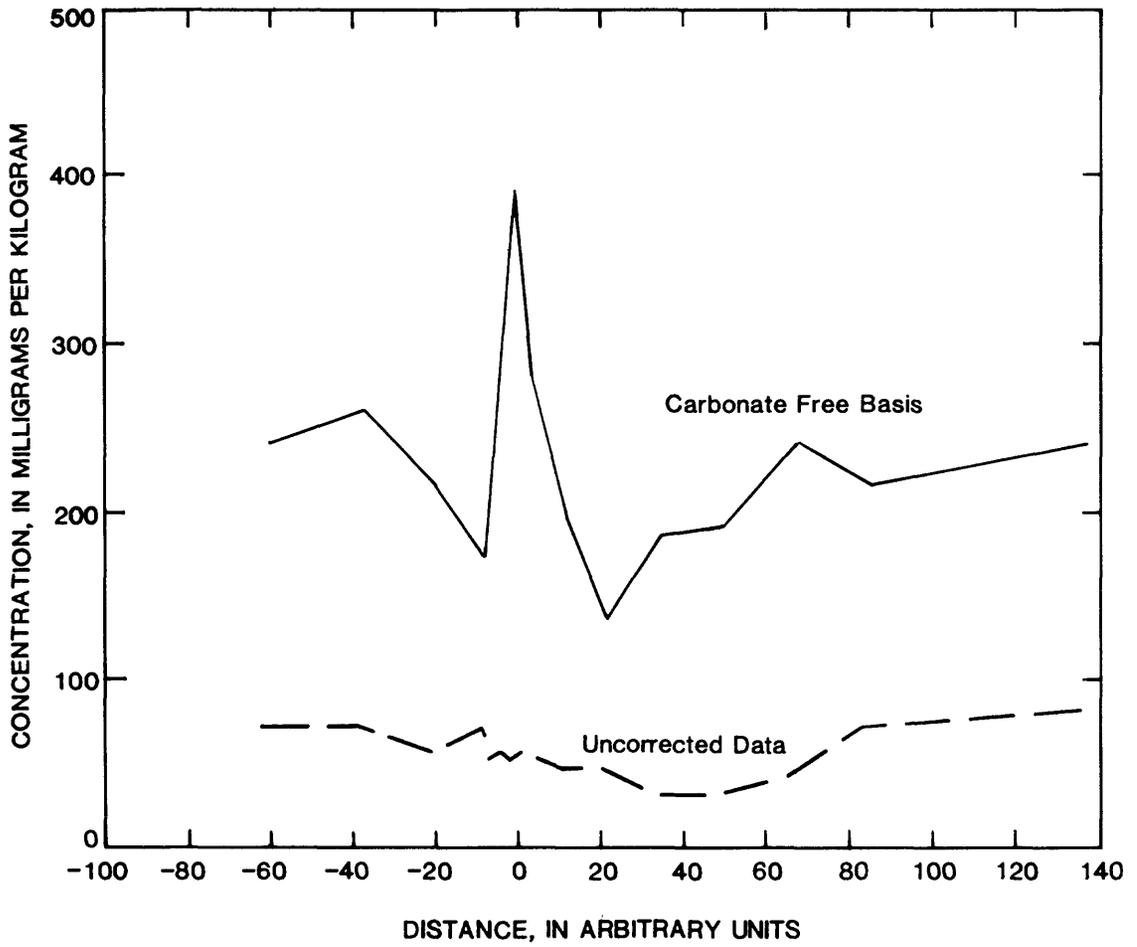
**Figure 4.3-1.**—Distribution of copper from a point source. (Data from Piper, 1973)

Several final points need to be discussed. Some are not solely related to sediment chemistry but apply to the subject, and they should be considered when planning, carrying out, and interpreting the results of water-quality investigations.

Sampling and program design are extremely important to the ultimate success of a study. More time, effort, and money have been wasted in environmental studies because of poor program design than for any other reason (Keith and others, 1983; Hakanson, 1984). The decision on how, where, and when to sample must be predicated on what an investigator is trying to discover and how the data are to be used. For example, if a large areal study is needed, a type of random sampling should be used to characterize distributions. If random sites are not carefully selected but just picked, it is possible that only interpretations based on that specific set of sites can be made, and generalizations about the entire area will be difficult or impossible. It is a good idea to obtain statistical help in developing a program plan if an investigator lacks expertise in this area. It is fairly safe to say, although statistical proof is lacking, that more errors are introduced into a study by improper sampling design and handling than could ever be attributed to analytical errors in the laboratory.

Of the many types of sampling programs, four generally used procedures are discussed here.

1. Simple random sampling—the selection of sites such that every possible sample has an equal opportunity of being chosen. This method is very efficient in homogeneous study areas. However, it may be ineffective in heterogeneous areas and could lead to overlooking important sites or data.
2. Stratified random sampling—dividing a heterogeneous area into homogeneous subareas within which sampling locations are randomly selected. This often permits the elucidation of subtle but real differences.
3. Systematic sampling—establishing a constant interval of distance between sampling sites determined by the number of samples to be collected. The initial sampling site is randomly determined. The advantage of such a scheme is its ease of application; the disadvantage is that it can produce very biased results.

4. Fixed transect—sampling at fixed and predetermined sites that need not be at constant intervals. This method of sample design, while extremely simple, has this drawback: Because not all possible sampling sites have an equal chance of being selected, any statistical inferences or conclusions are associated only with the selected sites, and areal conclusions may not be valid.

The computer has been a boon to scientific investigators because it permits the handling of large data sets and the application of many complex statistical manipulations. This can also be viewed as a curse, because many investigators use statistical manipulations as a replacement for thinking about what their data are telling them. Remember that statistically significant results must be matched by realistic environmental interpretations; otherwise, all the work that has gone into a study can be wasted. Before embarking on a major statistical program, understand what the implications of each manipulation are. In fact, it is more advisable to develop a theory or hypothesis and test its statistical validity than to manipulate data statistically and then try to fashion a theory to fit the statistics. Statistics is a tool, not an answer.

Understand and appreciate the limits of laboratory analytical data. Try to develop a feeling for analytical precision and accuracy. Precision means reproducibility; accuracy means how close the number is to the true value. Do not overinterpret analytical results. For example, if analytical accuracy is $\pm 10$ percent and all the results differ by $\pm 5$ percent, then to all intents and purposes, the results are the same.

Use and build upon the work of others. Although no one receives credit for re-inventing the wheel, there is nothing wrong with using a successful investigator's sampling and interpretation program that has been applied elsewhere. You might save time, initially, by ignoring previous work, during the planning of a study or during data analysis and report preparation. However, most studies do not produce new advances. Good science tends to be built upon much retesting and repetition; occasionally, advances are made, and, rarest of all, a giant step occurs. Remember, the purposes of good science and of most studies are to answer specific questions as capably as possible within time and financial constraints—not to find the ultimate solution.

# SELECTED REFERENCES

Ackermann, F., Bergmann, H., and Schleichert, U., 1983, Monitoring of heavy metals in coastal and estuarine sediments—a question of grain size: <20 μm versus <60 μm: Environmental Technology Letters, v. 4, p. 317-328.

Armstrong, F., 1958, Inorganic suspended matter in seawater: Journal of Marine Research, v. 17, p. 23-25.

*Arrhenius, G., and Korkish, J., 1959, Uranium and thorium in marine minerals: First International Oceanographic Congress, American Association for the Advancement of Science, preprints, 497 p.

Ashley, H., 1979, Particle size analysis by elutriation and centrifugation as exemplified by the Bahco Microparticle Classifier, in Stockham, J., and Fachtman, E., eds., Particle size analysis: Ann Arbor, Mich., Ann Arbor Press, p. 101-110.

*Aston, S., Bruty, D., Chester, R., and Padgham, R., 1973, Mercury in lake sediments. A possible indicator of technological growth: Nature (London), v. 241, p. 450-451.

Aulio, K., 1980, Accumulation of copper in fluvial sediments and yellow water lilies (Nuphar lutea) at varying distances from a metal processing plant: Bulletin of Environmental Contamination and Toxicology, v. 25, p. 713-717.

Benjamin, M., Hayes, K., and Leckie, J., 1982, Removal of toxic metals from power-generation waste streams by adsorption and coprecipitation: Journal of the Water Pollution Control Federation, v. 54, p. 1472-1481.

*Benjamin, M., and Leckie, J., 1981, Conceptual model for metal-ligand-surface interactions during adsorption: Environmental Science and Technology, v. 15, p. 1050-1057.

————1982, Effects of complexation by Cl, $SO_4$, and $S_2O_3$ on adsorption behavior of Cd on oxide surfaces: Environmental Science and Technology, v. 16, p. 162-170.

Berner, R., 1981, A new geochemical classification of sedimentary environments: Journal of Sedimentary Petrology, v. 51, p. 359-365.

Bostrom, K., Burman, J., Ponter, C., and Ingri, J., 1981, Selective removal of trace elements from the Baltic by suspended matter: Marine Chemistry, v. 10, p. 335-354.

*Brannon, J., Engerl, R., Rose, J., Hunt, P., and Smith, I., 1976, Distribution of Mn, Ni, Zn, Cd, and As in sediments and the standard elutriate: U.S. Army Engineers Waterways Experimental Station, Environmental Effects Laboratory, Miscellaneous Papers, D 76-18, 38 p.

Breward, N., and Peachey, D., 1983, The development of a rapid scheme for the elucidation of the chemical speciation of elements in sediments: The Science of the Total Environment, v. 29, p. 155-162.

*Bruland, K., Bertine, K., Koide, M., and Goldberg, E.,

1974, History of metal pollution in the southern California coastal zone: Environmental Science and Technology, v. 8, p. 425-432.

*Bunzl, K., Schmidt, W., and Sanson, B., 1976, Kinetics of ion exchange in soil organic matter, IV, adsorption and desorption of $Pb^{+2}$, $Cu^{+2}$, $Cd^{+2}$, $Zn^{+2}$, and $Ca^{+2}$, by peat: Journal of Soil Science, v. 27, p. 32-41.

Burton, J., 1978, The modes of association of trace metals with certain compounds in the sedimentary cycle, in Goldberg, E., ed., Biogeochemistry of estuarine sediments, Paris, UNESCO Press, p. 33-41.

*Buser, W., and Graf, F., 1955, Differenzierung von mangan (II)-manganit and δ-$MnO_2$ durch oberflächenmessung nach brunauer-emmet-teller: Helvetica Chimica Acta, v. 38, p. 830-842.

Calmano, W., and Forstner, U., 1983, Chemical extraction of heavy metals in polluted river sediments in central Europe: The Science of the Total Environment, v. 28, p. 77-90.

Calmano, W., Wellershaus, S., and Forstner, U., 1982, Dredging of contaminated sediments in the Weser estuary: chemical forms of some heavy metals: Environmental Technology Letters, v. 3, p. 199-208.

*Chao, T., 1972, Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride: Soil Science Society of America Proceedings, v. 36, p. 764-768.

————1984, Use of partial dissolution techniques in geochemical exploration: Journal of Geochemical Exploration, v. 20, 101-136.

Chao, T., and Zhou, L., 1983, Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments: Soil Science Society of America Journal, v. 47, p. 225-232.

Chapman, P., Romberg, G., and Vigers, G., 1982, Design of monitoring studies for priority pollutants: Journal of the Water Pollution Control Federation, v. 54, p. 292-297.

Charm, W., 1967, Freeze drying as a rapid method of disaggregating silts and clays for particle size analysis: Journal of Sedimentary Petrology, v. 37, p. 970-971.

*Chen, K., Gupta, S., Sycip, A., Lu, J., Knezevic, M., and Choi, W., 1976, The effect of dispersion and resedimentation on migration of chemical constituents during open water disposal of dredged material: Contract Report, U.S. Army Engineers Waterways Experimental Station, Vicksburg, Miss. 221 p.

*Chester, R., 1965, Geochemical criteria for differentiating reef from non-reef facies in carbonate rocks: American Association of Petroleum Geologists Bulletin, v. 49, p. 253-276.

*Chester, R., and Hughes, M., 1966, The distribution of manganese, iron, and nickel in a North Pacific deep sea clay core: Deep Sea Research, v. 13, p. 627-634.

*————1967, A chemical technique for the separation of ferromanganese minerals, carbonate minerals, and adsorbed trace elements from pelagic sediments: Chemical Geology, v. 2, p. 249-262.

---

*References cited in the text or diagrams are marked with an asterisk(*).

*————1969, The trace element geochemistry of a north Pacific pelagic clay core: Deep Sea Research, v. 16, p. 639-654.

*Chester, R., and Messiah-Hanna, R., 1970, Trace element partition patterns in North Atlantic deep sea sediments: Geochimica et Cosmochimica Acta, v. 34, p. 2212-1128.

*Cronan, D., 1974, Authigenic minerals in deep sea sediments, in Goldberg, E., ed., The Sea, v. 5, New York, John Wiley, p. 491-525.

*Cronan, D., and Garrett, D., 1973, The distribution of elements in metalliferous Pacific sediments collected by the DSDP: Nature Physical Science, v. 242, p. 88-89.

*Davis, J., and Leckie, J., 1978, Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides: Environmental Science and Technology, v. 12, p. 1309-1315.

*de Groot, A., Zshuppe, K., and Salomons, W., 1982, Standardization of methods of analysis for heavy metals in sediments: Hydrobiologia, v. 92, p. 689-695.

*Deurer, R., Forstner, U., and Schmoll, G., 1978, Selective chemical extraction of carbonate-associated metals from recent lacustrine sediments: Geochimica et Cosmochimica Acta, v. 42, p. 415-427.

*Diks, D., and Allen, H., 1983, Correlation of copper distribution in a freshwater-sediment system to bioavailability: Bulletin of Environmental Contamination and Toxicology, v. 30, p. 37-43.

*Dossis, P., and Warren, L., 1980, Distribution of heavy metals between the minerals and organic debris in a contaminated marine sediment, in Baker, R., ed., Contaminants and sediments, v. 1, Ann Arbor, Mich., Ann Arbor Science Publishers, Inc., p. 119-142.

*Drever, J., 1982, The geochemistry of natural waters: Englewood Cliffs, N.J., Prentice-Hall, Inc., 388 p.

*Duchart, P., Calvert, S., and Price, N., 1973, Distribution of trace metals in the pore waters of shallow water marine sediments: Limnology and Oceanography, v. 18, p. 605-610.

Durum, W., and Haffty, J., 1963, Implications of minor element content of some major streams of the world: Geochimica et Cosmochimica Acta, v. 27, p. 1-11.

*Dymond, J., Corliss, J., Heath, G., Field, C., Dasch, J., and Veeh, H., 1973, Origin of metalliferous sediments from the Pacific ocean: Geological Society of America Bulletin, v. 84, p. 3355-3372.

*Engler, R., Brannon, J., and Rose, J., 1974, A practical selective extraction procedure for sediment characterization: American Chemical Society, v. 168, Atlantic City, N.J., 17 p.

Etchebar, H., and Jouanneau, J., 1980, Comparison of different methods for the recovery of suspended matter from estuarine waters: deposition, filtration, and centrifugation; consequences for the determination of some heavy metals: Estuarine and Coastal Marine Science, v. 11, p. 701-707.

*Feltz, H., 1980, Significance of bottom material data in evaluating water quality, in Baker, R., ed., Contaminants and sediments, v. 1, Ann Arbor, Mich., Ann Arbor Science Publishers, Inc., p. 271-287.

*Filipek, L., Chao, T., and Carpenter, J., 1981, Factors affecting the partitioning of Cu, Zn, and Pb in boulder coatings and stream sediments in the vicinity of a polymetallic sulfide deposit: Chemical Geology, v. 33, p. 45-64.

*Filipek, L., and Owen, R., 1979, Geochemical associations and grain size partitioning of heavy metals in lacustrine sediments: Chemical Geology, v. 26, p. 105-117.

*Forstner, U., 1982a, Chemical forms of metal enrichment in recent sediments, in Amstutz, G., and others, eds., Ore genesis, New York, Springer-Verlag, p. 191-199.

*————1982b, Accumulative phases for heavy metals in limnic sediments: Hydrobiologia, v. 91, p. 269-284.

Forstner, U., and Patchineelam, S., 1980, Chemical associations of heavy metals in polluted sediments from the Lower Rhine River, in Kavanaugh, M., and Leckie, J., eds., Particulates in water, Advances in chemistry series, v. 189, American Chemical Society, Washington, D.C., p. 177-193.

Forstner, U., and Stoffers, P., 1981, Chemical fractionation of transition elements in Pacific pelagic sediments: Geochimica et Cosmochimica Acta, v. 45, p. 1141-1146.

*Forstner, U., and Wittmann, G., 1979, Metal pollution in the aquatic environment: New York, Springer-Verlag, 486 p.

*Francis, C., Bonner, W., and Tamura, T., 1972, An evaluation of zonal centrifugation as a research tool in soil science, I, methodology: Soil Science Society of America Proceedings, v. 36, p. 366-376.

Francis, C., and Brinkley, F., 1976, Preferential adsorption of $Cs^{137}$ to micaceous minerals in contaminated freshwater sediment: Nature (London), v. 260, p. 511-513.

*Fripiat, J., and Gastuche, M., 1952, Etude physiochimique des surfaces des argiles—Les combinaisons de la kaolinite avec des oxides de fer trivalent: Publications de L'Institute National Pour L'Etude Agronomique du Congo Belge, v. 54, p. 7-35.

*Gambrell, R., Khalid, R., Verloo, M., and Patrick, W., 1977, Transformations of heavy metals and plant nutrients in dredged sediments as affected by oxidation-reduction potential and pH: U.S. Army Corps of Engineers, Vicksburg, Miss., Report D 77-4, 309 p.

*Ghosh, K., and Schnitzer, M., 1981, Fluorescence excitation spectra and viscosity behavior of a fulvic acid and its copper and iron complexes: Soil Science Society of America Journal, v. 45, p. 25-29.

*Gibbs, R., 1967, Amazon River: environmental factors that control its dissolved and suspended load: Science, v. 156, p. 1734-1737.

---

*References cited in the text or diagrams are marked with an asterisk (*).

*————1973, Mechanisms of trace metal transport in rivers: Science, v. 180, p. 71-73.

*————1977, Transport phases of transition metals in the Amazon and Yukon Rivers: Geological Society of America Bulletin, v. 88, p. 829-843.

*Goldberg, E., 1954, Marine geochemistry I-chemical scavengers of the sea: Journal of Geology, v. 62, p. 249-265.

*Goldberg, E., and Arrhenius, G., 1958, Chemistry of Pacific pelagic sediments: Geochimica et Cosmochimica Acta, v. 13, p. 153-212.

*Grim, R., 1968, Clay mineralogy, 2nd edition, New York, McGraw-Hill, 596 p.

*Gupta, S., and Chen, K., 1975, Partitioning of trace metals in selective chemical fractions of near-shore sediments: Environmental Letters, v. 10, p. 129-158.

*Guy, H., 1969, Laboratory theory and methods for sediment analysis; U.S. Geological Survey Techniques of Water Resources Investigations, book 5, chapter C1, 58 p.

*Hakanson, L., 1984, Sediment sampling in different aquatic environments—statistical aspects: Water Resources Research, v. 20, p. 41-46.

Hart, B., 1982, Uptake of trace metals by sediments and suspended particulates: a review: Hydrobiologia, v. 91, p. 299-313.

Heath, G., and Dymond, J., 1977, Genesis and transformation of metalliferous sediments from the East Pacific Rise, Bauer Deep, and Central Basin, northwest Nazca Plate: Geological Society of America Bulletin, v. 88, p. 723-733.

Hem, J., and Robertson, C., 1967, Form and stability of aluminum hydroxide complexes in dilute solution: U.S. Geological Survey Water Supply Paper, 1827-A, p. A24.

Hem, J., Robertson, C., Lind, D., and Polzer, W., 1973, Chemical interactions of aluminum with aqueous silica at 25°C: U.S. Geological Survey Water Supply Paper, 1827-E.

*Hirst, D., 1962, The geochemistry of modern sediments from the Gulf of Paria: Geochimica et Cosmochimica Acta, v. 26, p. 1147-1187.

*Hirst, D., and Nicholls, G., 1958, Techniques in sedimentary geochemistry, I, separation of the detrital and nondetrital fractions of limestones: Journal of Sedimentary Petrology, v. 28, p. 468-481.

*Holmgren, G., 1967, A rapid citrate-dithionate extractable iron procedure: Soil Science Society of America Proceedings, v. 31, p. 210-211.

*Horowitz, A., 1974, The geochemistry of sediments from the northern Reykjanes Ridge and the Iceland-Faeroes Ridge: Marine Geology, v. 17, p. 103-122.

*Horowitz, A., and Cronan, D., 1976, The geochemistry of basal sediments from the North Atlantic Ocean: Marine Geology, v. 20, p. 205-228.

*Irving, H., and Williams, R., 1948, Order of stability of metal complexes: Nature (London), v. 162, p. 746-747.

*Jackson, M., 1958, Soil chemical analysis: Englewood Cliffs, N.J. Prentice-Hall, 498 p.

*————1979, Soil chemical analysis—advanced course, 2nd edition, Madison, Wis., published by the author, 898 p.

*Jenne, E., 1968, Controls of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significance of hydrous Mn and Fe oxides: Advances in Chemistry Series, v. 73, p. 337-387.

*————1976, Trace element sorption by sediments and soils—sites and processes, in Chappell, W., and Peterson, K., eds., Symposium on molybdenum, v. 2, New York, Marcel-Dekker, p. 425-553.

————1981, Speciation of aqueous contaminants—role of the geochemical model, in Proceedings of the NBS Workshop on Aqueous Speciation of Dissolved Contaminants, Gaithersburg, Md., CONF 810588-4, NTIS, 14 p.

*Jenne, E., Kennedy, V., Burchard, J., and Ball, J., 1980, Sediment collection and processing for selective extraction and for total metal analysis, in Baker, R., ed., Contaminants and sediments, v. 2, Ann Arbor, Mich., Ann Arbor Science Publishers, Inc., p. 169-189.

Jenne, E., and Luoma, S., 1977, Forms of trace elements in soils, sediments, and associated waters: an overview of their determination and biological availability, in Wildung, R., and Drucker, H., eds., Biological implications of metals in the environment, CONF-750929, NTIS, Springfield, Va., p. 110-143.

*Johnson, W., and Maxwell, J., 1981, Rock and mineral analysis, 2nd edition, New York, John Wiley, 489 p.

*Jonasson, I., 1977, Geochemistry of sediment/water interactions of metals, including observations on availability, in Shear, H., and Watson, A., eds., The fluvial transport of sediment-associated nutrients and contaminents, IJC/PLUARG, Windsor, Ontario, p. 255-271.

*Jones, B., and Bowser, C., 1978, The mineralogy and related chemistry of lake sediments, in Lerman, A., ed., Lakes: chemistry, geology, physics, New York, Springer-Verlag, p. 179-235.

*Keith, L., Crummett, W., Deegan, J., Libby, R., Taylor, J., and Wentler, G., 1983, Principles of environmental analysis: Analytical Chemistry, v. 55, p. 2210-2218.

Kennedy, V., Zellwager, G., and Jones, B., 1974, Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water: Water Resources Research, v. 10, p. 785-790.

Keulder, P., 1982, Particle size distribution and chemical parameters of the sediments of a shallow turbid impoundment: Hydrobiologia, v. 91, p. 341-353.

*Kharkar, D., Turekian, K., and Bertine, K., 1968, Stream supply of dissolved Ag, Mo, Sb, Se, Cr, Ca, Rb, and Cs to the oceans: Geochimica et Cosmochimica Acta, v. 33, p. 285-298.

---

*References cited in the text or diagrams are marked with an asterisk (*).

*Kitano, Y., Sakata, M., and Matsumoto, E., 1980, Partitioning of heavy metals into mineral and organic fractions in a sediment core from Tokyo Bay: Geochimica et Cosmochimica Acta, v. 44, p. 1279-1285.

*Kononova, M., 1966, Soil organic matter, 2nd ed., Nowakowski, T., and Newman, A., translators, New York, Pergamon Press, p. 377-419.

*Krauskopf, K., 1956, Factors controlling the concentration of thirteen rare metals in sea water: Geochimica et Cosmochimica Acta, v. 9, p. 1-32.

*Kuenen, Ph., 1965, Geological conditions of sedimentation, in Riley, J., and Skirrow, G., eds., Chemical oceanography, v. 2, New York, Academic Press, p. 1-22.

Laxen, D., and Chandler, I., 1983, Size distribution of iron and mangenese species in freshwaters: Geochimica et Cosmochimica Acta, v. 47, p. 731-741.

*Lee, G., 1975, Role of hydrous metal oxides in the transport of heavy metals in the environment, in Krenkel, P., ed., Heavy metals in the aquatic environment, New York, Pergamon Press, p. 137-147.

*Leinen, M., and Pisias, N., 1984, An objective technique for determining end member compositions and for partitioning sediments according to their sources: Geochimica et Cosmochimica Acta, v. 48, p. 47-62.

*Leinen, M., Pisias, N., Dymond, J., and Heath, G., 1980, Geochemical partitioning: application of an objective technique for end-member characterization: Geological Society of America Abstracts with Programs, v. 93, p. 470 (abstract).

Lion, L., Altmann, R., and Leckie, J., 1982, Trace metal adsorption characteristics of estuarine particulate matter: evaluation of contributions of Fe/Mn oxide and organic surface coatings: Environmental Science and Technology, v. 16, p. 660-666.

Liu, B., Raabe, O., Smith, W., Spencer, H., III, and Kuykendal, W., 1980, Advances in particle sampling and measurement: Environmental Science and Technology, v. 14, p. 392-397.

Loring, D., 1981, Potential bioavailability of metals in eastern Canadian estuarine and coastal sediments: Rapports et Procès-Verbaux des Réunions Conseil International Pour l'Exploration de la Mer, v. 181, p. 93-101.

Luoma, S., 1983, Bioavailability of trace metals to aquatic organisms—a review: The Science of the Total Environment, v. 28, p. 1-22.

Luoma, S., and Bryan, G., 1978, Factors controlling the availability of sediment-bound lead to the estuarine bivalve Scrobicularia plana: Journal of the Marine Biological Association of the United Kingdom, v. 58, p. 793-802.

————1979, Trace metal bioavailability: modeling chemical and biological interactions of sediment-bound zinc, in Jenne, E., ed., Chemical modeling in aqueous systems, ACS Symposium Series 93, American Chemical Society, Washington, D.C., p. 577-609.

————1979, Trace metal bioavailability: modeling chemical and biological interactions of sediment-bound lead to the estuarine bivalve Scrobicularia plana: Journal of the Marine Biological Association of the United Kingdom, v. 58, p. 793-802.

*————1981, A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants: The Science of the Total Environment, v. 17, p. 165-196.

Luoma, S. and Davis, J., 1983, Requirements for modeling trace metal partitioning in oxidized estuarine sediments: Marine Chemistry, v. 12, p. 159-181.

Luoma, S., and Jenne, E., 1976, Factors affecting the availability of sediment-bound cadmium to the estuarine deposit-feeding clam, Macoma balthica, in Radiological problems associated with the development of energy sources, Proceedings of the Fourth National Symposium on Radioecology, Corvallis, Oreg., ERDA Report CONF-759503, Stroudsburg, Pa., Dowden, Hutchinson, and Russ Publishers, 16 p.

*————1977, Estimating bioavailability of sediment-bound metals with chemical extractants, in Hemphill, D., ed., Trace substances in environmental health, v. 10, Columbia, Mo., University of Missouri Press, p. 343-351.

————1977, The availability of sediment-bound cobalt, silver and zinc to a deposit-feeding clam, in Wilding, R., and Drucker, H., eds., Biological implications of metals in the environment, CONF-750929, NTIS, Springfield, Va., p. 213-230.

*Lynn, D., and Bonatti, E., 1965, Mobility of manganese in diagenesis of deep sea sediments: Marine Geology, v. 3, p. 457-474.

*Malo, B., 1977, Partial extraction of metals from aquatic environments: Environmental Science and Technology, v. 11, p. 277-282.

Martin, H., Wilhelm, E., Laville-Timsit, L., and Lecomte, P., 1984, Enhancement of stream-sediment geochemical anomalies in Belgium and France by selective extractions and mineral separations: Journal of Geochemical Exploration, v. 20, p. 179-205.

*Mero, J., 1962, Occurrence of Mn nodules: Economic Geology, v. 57, p. 747-767.

*Mitchell, R., 1964, Trace elements in soil, in Bear, F., ed., Chemistry of the soil, New York, Reinhold Publishing Corp., p. 320-368.

*Moore, R., Meyer, R., and Morgan, C., 1973, Investigation of the sediments and potential manganese nodule resources of Green Bay, Wisconsin: University of Wisconsin Technical Report WIS-SG-73-213, Madison, Wis., 144 p.

Mora, S., and Harrison, R., 1983, The use of physical separation techniques in trace metal speciation studies: Water Research, v. 17, p. 723-733.

Mouvet, C., and Bourg, A., 1983, Speciation (including

---

*References cited in the text or diagrams are marked with an asterisk (*).

adsorbed species) of copper, lead, nickel, and zinc in the Meuse River: Water Research, v. 17, p. 641-649.

*Muller, L., and Burton, C., 1965, The heavy liquid density gradient and its application in ore dressing mineralogy: Proceedings of the eighth commonwealth mining and metallurgical congress, v. 6, Melbourne, Australia, p. 1151-1163.

Musani, Lj., Valenta, P., Nurnberg, H., Konrad, Z., and Branica, M., 1980, On the chelation of toxic trace metals by humic acid of marine origin: Estuarine and Coastal Marine Science, v. 11, p. 639-649.

Nembrini, G., Rapin, F., Garcia, J., and Forstner, U., 1982, Speciation of Fe and Mn in a sediment core of the Baie de Villefrance: Environmental Technology Letters, v. 3, p. 545-552.

Nishida, H., Miyai, M., Tada, F., and Suzuki, S., 1982, Computation of the index of pollution caused by heavy metals in river sediment: Environmental Pollution (Series B), v. 4, p. 241-248.

*Nissenbaum, A., 1972, Distribution of several metals in chemical fractions of a sediment core from the Sea of Okhotsk: Israeli Journal of Earth Science, v. 21, p. 143-154.

*Nriagu, J., and Coker, R., 1980, Trace metals in humic and fulvic acids from Lake Ontario sediments: Environmental Science and Technology, v. 14, p. 443-446.

*Oakley, S., Nelson, P., and Williamson, K., 1981, Model of trace-metal partitioning in marine sediments: Environmental Science and Technology, v. 15, p. 474-480.

*Oakley, S., Williamson, K., and Nelson, P., 1980, The geochemical partitioning and bioavailability of trace metals in marine sediments: Project completion report, OWRR Project No. A-044-ORE-WF3, October 1, 1977-September 31, 1979, Oregon State University, Corvallis, Oreg., 84 p.

*Oliver, B., 1973, Heavy metal levels of Ottawa and Rideau River sediment: Environmental Science and Technology, v. 7, p. 135-137.

Olsen, C., Cutshall, N., and Larsen, I., 1982, Pollutant-particle associations and dynamics in coastal marine environments: a review: Marine Chemistry, v. 11, p. 501-533.

*Patchineelam, S., 1975, Untersuchungen uber die hauptbindungsarten und die mobilisierburkeit von schwermetallen in fluviatilen sedimenten: unpublished Ph.D. dissertation, University of Heidelberg, 136 p.

Patchineelam, S., and Forstner, U., 1977, Bildungsformen von schwermetallen in marinene sedimenten: Senckenbergiana Maritima, v. 9, p. 75-104.

Pickering, W., 1981, Selective chemical extraction of soil components and bound metal species: Critical Reviews in Analytical Chemistry, v. 12, p. 233-266.

*Pilkington, E., and Warren, L., 1979, Determination of heavy metal distribution in marine sediments: Environmental Science and Technology, v. 13, p. 295-299.

*Piper, D., 1971, The distribution of Co, Cr, Cu, Fe, Mn, Ni, and Zn in Framvaren, a Norwegian anoxic fjord: Geochimica et Cosmochimica Acta, v. 35, p. 531-550.

*———1973, Origin of metalliferous sediments from the East Pacific Rise: Earth and Planetary Science Letters, v. 19, p. 75-82.

*Pisias, N., and Leinen, M., 1980, Geochemical partitioning of deep-sea sediments using an extended version of Q-mode factor analysis and linear programming: Geological Society of America Abstracts with Programs, v. 93, p. 500 (abstract).

*Porterfield, G., 1972, Computation of fluvial sediment discharge: U.S. Geological Survey Techniques of Water Resources Investigations, book 3, chapter C-3, p. 43-47.

*Rashid, M., 1974, Adsorption of metals on sedimentary and peat humic acids: Chemical Geology, v. 13, p. 115-123.

*Rex, R., and Goldberg, E., 1958, Quartz contents of pelagic sediments of the Pacific Ocean: Tellus, v. 10, p. 153-159.

Robinson, G., 1981, Adsorption of Cu, Zn, and Pb near sulfide deposits by hydrous manganese-iron oxide coatings on stream alluvium: Chemical Geology, v. 12, p. 233-266.

*———1982, Trace metal adsorption potential of phases comprising black coatings on stream pebbles: Journal of Geochemical Exploration, v. 17, p. 205-219.

———1983, Heavy-metal adsorption by ferromanganese coatings on stream alluvium: natural controls and implications for exploration: Chemical Geology, v. 38, p. 157-174.

*Rossman, R., Callender, E., and Bowser, C., 1972, Interelement geochemistry of Lake Michigan ferromanganese nodules: Proceedings of the 24th international geological congress, Montreal, Section 10, p. 336-341.

Saar, R., and Weber, J., 1981, Lead (II) complexation by fulvic acid: how it differs from fulvic acid complexation of copper (II) and cadmium (II): Geochimica et Cosmochimica Acta, v. 44, p. 1381-1384.

*Saxby, J., 1969, Metal-organic chemistry of the geochemical cycle: Reviews of Pure and Applied Chemistry, v. 19, p. 131-150.

Schalscha, E., Morales, M., Vergara, I., and Chang, A., 1982, Chemical fractionation of heavy metals in wastewater affected soils: Journal of the Water Pollution Control Federation, v. 54, p. 175-180.

*Schmidt, R., Garland, T., and Wildung, R., 1975, Copper in Sequim Bay sediments: Batelle Pacific Northwest Laboratory Annual Report, part 2, p. 136.

Schnitzer, M., and Kerndorff, H., 1981, Reactions of fulvic acid with metal ions: Water, Air, and Soil Pollution, v. 15, p. 97-108.

*Schnitzer, M., and Kahn, S., 1972, Humic substances in the environment, New York, Marcel-Dekker, 327 p.

*———1978, Soil organic matter, New York, Elsevier, p. 1-64.

*References cited in the text or diagrams are marked with an asterisk (*).

Schultz, L., 1964, Quantitative interpretation of mineralogical composition from x-ray and chemical data for the Pierre Shale: U.S. Geological Survey Professional Paper 391-C, 31 p.

*Schwertmann, U., 1964, Differenzierung der eisenoxide des bodens durch photochemische extraktion mit sauer ammonium-oxalat-losung: Zeitschrift fur Pflanzenerahrung, Dungung mit Bodenkunde, v. 105, p. 194-202.

*Singer, P., 1977, Influence of dissolved organics on the distribution, transport, and fate of heavy metals in aquatic systems, in Suffet, I., ed., Fate of pollutants in the air and water environment, part I, New York, John Wiley, p. 155-182.

Skei, J., and Paus, P., 1979, Surface metal enrichment and partitioning of metals in a dated sediment core from a Norwegian fjord: Geochimica et Cosmochimica Acta, v. 43, p. 239-246.

Skoog, D., and West, D., 1981, Principles of instrumental analysis, 2nd edition, Philadelphia, Pa., Saunders College Press, p. 452-457.

Slavek, J., and Pickering, W., 1981, The effect of pH on the retention of Cu, Pb, Cd, and Zn by clay-fulvic acid mixtures: Water, Air, and Soil Pollution, v. 16, p. 209-221.

Sposito, G., Lund, L., and Chang, A., 1982, Trace metal chemistry in arid-zone field soils phases: Soil Science Society of America Journal, v. 46, p. 260-264.

*Stoffers, P., Summerhayes, C., Forstner, U., and Patchineelam, S., 1977, Copper and other heavy metal contamination in sediments from New Bedford Harbor, Massachusetts: a preliminary note: Environmental Science and Technology, v. 11, p. 819-821.

Stover, R., Sommers, L., and Silviera, D., 1976, Evaluation of metals in wastewater sludge: Journal of the Water Pollution Control Federation, v. 48, p. 2165-2175.

*Summerhayes, C., Ellis, J., Stoffers, P., Briggs, S., and Fitzgerald, M., 1976, Fine-grained sediment and industrial waste distribution in New Bedford Harbor and western Buzzards Bay, Mass.: Woods Hole Oceanographic Institution Technical Report WHOI-76-115, 110 p.

*Swallow, K., and Morel, F., 1980, Adsorption of trace metals by hydrous ferric oxides in seawater: Environmental Protection Agency Report No. EPA 600/3-80-011, Environmental Research Laboratory, Narragansett, R.I., 52 p.

*Swanson, V., Frist, L., Rader, R., Jr., and Huffman, C., Jr., 1966, Metal sorption by northwest Florida humate: U.S. Geological Survey Professional Paper 550-C, p. 174-177

*Tessier, A., Campbell, P., and Bisson, M., 1979, Sequential extraction procedure for the speciation of particulate trace metals: Analytical Chemistry, v. 51, p. 844-851.

———1982, Particulate trace metal speciation in stream sediments and relationships with grain size: implications for geochemical exploration: Journal of Geochemical Exploration, v. 16, p. 77-104.

*Thomas, R., 1972, The distribution of mercury in the sediment of Lake Ontario: Canadian Journal of Earth Science, v. 9, p. 636-651.

*Thorne, L., and Nickless, G., 1981, The relation between heavy metals and particle size fractions within the Severn estuary (U.K.) inter-tidal sediments: The Science of the Total Environment, v. 19, p. 207-213.

van Valin, R., and Morse, J., 1982, An investigation of methods commonly used for the selective removal and characterization of trace metals in sediments: Marine Chemistry, v. 11, p. 535-564.

*Vuceta, J., and Morgan, J., 1978, Chemical modeling of trace metals in fresh waters: role of complexation and adsorption: Environmental Science and Technology, v. 12, p. 1302-1309.

Young, T., Depinto, J., and Seger, E., 1982, Transport and fate of heavy metals in Onondaga Lake, N.Y.: Bulletin of Environmental Contamination and Toxicology, v. 29, p. 554-561.

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*References cited in the text or diagrams are marked with an asterisk (*).

# CONVERSION FACTORS

| Multiply SI unit | By | To obtain inch-pound units |
| --- | --- | --- |
| cm (centimeter) | 0.3937 | inch (in) |
| mm (millimeter) | 0.03937 | inch (in) |
| $\mu$m (micrometer) | 0.00003937 | inch (in) |
| $\mu$m$^2$ (square micrometer) | 0.00154997 | in$^2$ (square inch) |
| t (metric ton) | 1.102 | ton, short (t) |
| kg (kilogram) | 2.2046226 | pound, avdp (lb) |
| g (gram) | 0.035273962 | ounce, avdp (oz) |
| mg (milligram) | 0.000035273962 | ounce, avdp (oz) |
| $\mu$g (microgram) | $3.5273962 + 10^{-8}$ | ounce, avdp (oz) |
| m$^2$/g (meter squared per gram) | 305.186 | ft$^2$/oz (foot squared per ounce) |
| cm$^2$/g (centimeter squared per gram) | 3.05186 | in$^2$/oz (inch squared per ounce) |
| L (liter) | 33.81497 | ounce, fluid (oz) |
| m$^3$/s (cubic meter per second) | 35.31 | ft$^3$/s (foot cubed per second) |
| $\mu$g/kg (microgram per kilogram) | 1.000 | part per billion (ppb) |
| $\mu$g/L (microgram per liter) | 1.000 | part per billion (ppb) |
| $\mu$g/g (microgram per gram) | 1.000 | part per million (ppm) |
| mg/kg (milligram per kilogram) | 1.000 | part per million (ppm) |
| concentration of 1 percent | 10,000 | part per million (ppm) |