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A PRIMER ON TRACE METAL-SEDIMENT CHEMISTRY

UNITED STATES GEOLOGICAL SURVEY

Open-File Report 84-709

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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by Arthur J. Horowitz

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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 which control, and which 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 is organized in the same way as the instructional session. It contains all the diagrams and tables used for the course, along with a descriptive text. Additionally, a large list of selected references on the subject of trace metal-sediment chemistry is provided. 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.

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply SI units	By	To obtain inch-pound units
centimeter (cm)	0.3937	inch (in)
millimeter (mm)	0.03937	inch (in)
micrometer (µm)	0.00003937	inch (in)
square micrometers (μm^2)	0.00154997	square inches (in^2)
metric ton	1.102	ton, short (t)
kilogram (kg)	2.2046226	pounds, avdp (lb)
gram (g)	0.035273962	ounces, avdp (oz)
milligram (mg)	0.000035273962	ounces, avdp (oz)
microgram (µg)	3.5273962×10^{-8}	ounces, avdp (oz)
square meters per gram (m^2/g)	305.186	square feet per ounce (ft^2/oz)
square centimeters per gram (cm^2/g)	3.05186	square inches per ounce (in^2/oz)
liter (L)	33.81497	ounce, fluid (oz)
cubic meters per second (m^3/s)	35.31	cubic feet per second (ft^3/s)
microgram per kilogram (µg/kg)	1.000	part per billion (ppb)
microgram per liter (µg/L)	1.000	part per billion (ppb)
microgram per gram (µg/g)	1.000	part per million (ppm)
milligram per kilogram (mg/kg)	1.000	part per million (ppm)
concentration of 1%	10,000	part per million (ppm)

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ABSTRACT

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

The sampling and analysis of suspended and bottom sediments is 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 for several other reasons. Riverine transport of trace metals is dominated by sediment. In addition, bottom sediments serve as a source for suspended sediment, and can provide an historical record of chemical conditions through time. This will help establish area baseline metal levels against which exisiting 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 in terms of 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, organic matter) and how the metals are entrained by the sediments (such as adsorption, complexation, 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. Under this heading, such subjects as bioavailability, amount of constituent transport, location of chemical sinks, ultimate fate, and potential toxic effects, could be placed.

Historically, the U.S. Geological Survey has attempted to assess trace metals in aquatic systems by analyzing water samples. This has entailed the determination of 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 not determined directly, but 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 suspended sediment, and the top few centimeters of bottom sediment, contain many times the concentration of metals than are dissolved in the water column. The strong association of numerous trace metals (for example, arsenic, cadmium, mercury, lead, zinc) 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, bottom sediments can act as a reservoir for many trace metals. As a result, they must be given serious consideration in the planning and design of any water quality study. There are several reasons for this. Firstly, an undisturbed sediment sink contains an historical record of chemical conditions through time. 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. Secondly, under changing environmental or physicochemical conditions (such as pH, Eh, dissolved oxygen, bacterial action), sediment-bound trace metals can dissolve into the water column, possibly enter the food chain, and have significant environmental impacts. Thirdly, 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 one of the major, if not the major, source of suspended sediment. As such, they must be investigated in order to determine transport potential. Under changing hydrologic conditions (such as a major storm, or spring runoff), a localized pollution problem can suddenly become widespread, and have significant environmental impact.

The above 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 this 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 is a requisite for transport modeling, for estimating geochemical cycles, and for inferring the availability of various trace metals to an ecological system. For purposes of this 'Primer', and for convenience, the following glossary and concepts should be kept in mind.

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 which is actively transported by a fluid.

Bottom Sediment, Bed Material - material which 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 micrometer filter.

Suspended Load, Suspended Constituent - operationally defined as that material that is retained by a 0.45 micrometer filter during the filtration of a whole water sample.

Trace Metal, Heavy Metal, Metal - these terms are used interchangeably throughout this 'Primer'.

Total Concentration - refers to the true concentration of metal in a sediment sample which has been determined by the complete dissolution of the sample. Unless otherwise stated, concentrations in this 'Primer' are totals.

Totally Recoverable Concentration - refers to the concentration of metal in a sediment sample which has been extracted with a solution which 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 has been extracted from an article by Chapman and others (1982) which deals with the design of monitoring studies for priority pollutants. They point out that an investigator must decide two basic questions in order to design an effective monitoring program--what samples should be collected, and for what should they be analyzed? This requires an understanding of the relative importance of each constituent based on chemical behavior and biological significance. These, in turn, determine what type of sample(s) that should be collected (water, sediment, biota). All the inorganic priority pollutants, with the exception of antimony (Sb), are persistant and can bioaccumulate, and all tend to be found in either sediment (bottom and suspended) or biota (table 1.1)

Table 1.1--Recommendations for types of environmental sampling for monitoring purposes (from Chapman and others, 1982)

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

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

1.0 Importance of sediments to aquatic trace metal chemistry.

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. As such, riverine transport of these constituents can be dominated by suspended sediment. Figure 1.2, from Gibbs (1977), graphically displays this phenomenon, and is based upon the analysis of dissolved and suspended loads for selected trace metals in the Amazon and Yukon Rivers.

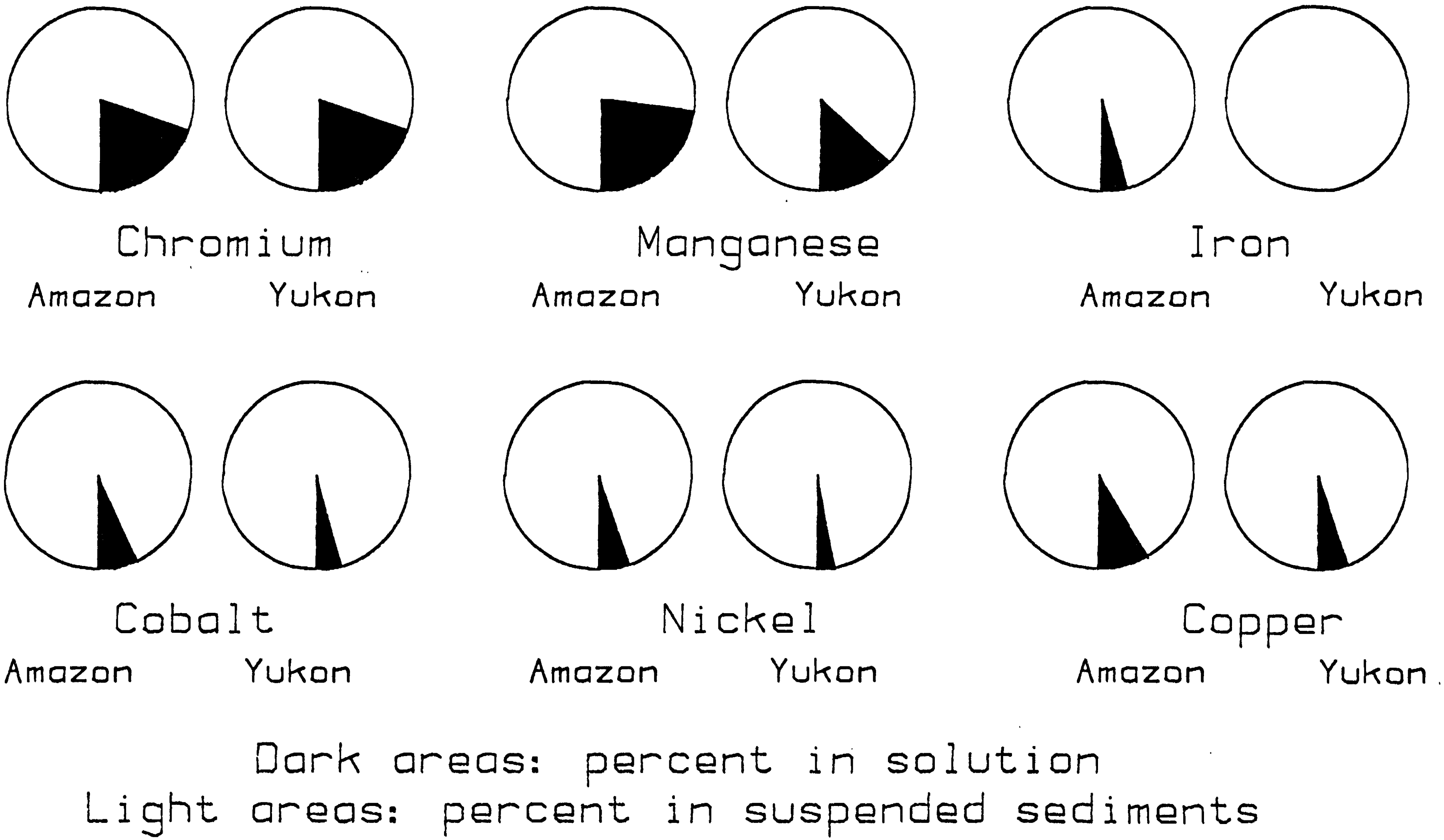

Figure 1.2-Transport phases of selected trace metals in rivers

(Reprinted from Gibbs, 1977 and published with permission)

1.0 Importance of sediments to aquatic trace metal chemistry.

1.3 Riverine transport of trace metals by suspended sediment.

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. 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. Please note that even relatively low suspended sediment associated-trace metal concentrations can involve significant weights of constituent transport. For example, the arsenic (As) concentration in Willamette River suspended sediment is only 0.002 milligrams per kilogram (2 ppb) and yet, this means that 0.9 metric tons of As were transported by the river each day (metric t/d). At the other end of the spectrum, examine the iron (Fe) data for the Mississippi River. Suspended sediment Fe concentrations are 46,000 micrograms per kilogram (46 ppm), and this led to the transport of some 75,000 metric t/d of Fe.

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

[1] Discharge, in cubic feet per second
[2] Sediment concentration, in milligrams per liter
[3] Concentration, totally recoverable, in milligrams per liter
[4] 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])

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[3]	Transport[4]	Concentration[3]	Transport[4]	Concentration[3]	Transport[4]
Sediment[2]	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

1.0 Importance of sediments to aquatic trace metal chemistry.

1.4 Comparison of trace metal concentrations in suspended and bottom sediments versus dissolved levels.

Bottom and suspended sediment contain significantly higher concentrations of trace metals than are found in solution. What is meant by significantly more? An examination of the data presented in table 1.4 will provide an approximate answer to this question. Table 1.4.1 contains data from the Elbe River, Federal Republic of Germany and compares and contrasts dissolved metal concentrations with those found associated with bottom sediments. The bottom sediment concentrations can be more than 100,000 times higher than the dissolved levels (see lead levels for water and sediment for Hamburg). Similar results were obtained during the Schuylkill River Basin assessment study for dissolved and totally recoverable analyses (Feltz, 1980, table 1.4.2). Table 1.4.3 contains data from the Amazon and Yukon Rivers and compares and contrasts dissolved metal concentrations with those found for suspended sediment. The suspended sediment concentrations for the Amazon and the Yukon are approximately 10,000 times 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, Federal Republic of Germany (from Forstner and Wittmann, 1979)

[1] (W) - concentration in water
[2] (S) - concentration in sediment
[3] All concentrations in milligrams per kilogram

Location		Cadmium[3]	Chromium[3]	Copper[3]	Lead[3]	Zinc[3]
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	1600
Hitzacker	(W)	0.0008	0.020	0.020	0.008	0.140
	(S)	23	250	200	200	750

Table 1.4.2. -- Comparison of metal concentration in river water and bottom sediment from the Schuylkill Basin (from Feltz, 1980)

[1] (W) - concentration in water
[2] (S) - concentration in sediment, totally recoverable
[3] All concentrations in milligrams per kilogram

Location		Cadmium[3]	Chromium[3]	Copper[3]	Lead[3]	Zinc[3]
Phoenixville	(W)[1]	0.013	0.001	0.005	0.190	0.080
	(S)[2]	30	130	190	250	1000
Norristown	(W)[1]	0.010	<0.001	0.007	0.110	0.120
	(S)[2]	10	30	70	400	1000
Philadelphia	(W)[1]	0.002	<0.001	0.004	0.001	<0.001
	(S)[2]	10	50	80	180	170

Table 1.4.3 -- Comparison of metal concentration in river water and suspended sediment from the Amazon and Yukon Rivers (from Gibbs, 1977)

[1] (W) - concentration in water
[2] (S) - concentration in suspended sediment
[3] All concentrations in milligrams per kilogram

Location		Chromium[3]	Manganese[3]	Iron[3]	Cobalt[3]	Nickel[3]	Copper[3]
Amazon	(W)[1]	0.019	0.110	5.1	0.004	0.010	0.026
	(S)[2]	195	1100	56,000	41.4	105	265
Yukon	(W)	0.019	0.200	8.9	0.006	0.020	0.060
	(S)	115	1300	63,000	40.6	135	415

1.0 Importance of sediments to aquatic trace metal chemistry.

1.5 Historical records

An undisturbed sediment sink can contain an historical record of chemical conditions through time. If a sufficiently large and stable (neither physical nor chemical alteration has occurred) sink can be found, and studied, it will allow the investigator to establish chemical changes over time, and will also help establish area baseline levels against which existing conditions can be compared and contrasted. When chemical analyses are used in conjunction with radiometric dating techniques (Pb^{210}, C^{14}), historical changes in water quality can be elucidated. Figure 1.5 provides two examples of historical records detailing changes in mercury (Hg) concentration through time. The data from Lake Ontario indicates that high concentrations of Hg occur in the top 6 centimeters, below 8 centimeters, the concentration decreases significantly. At about 25 centimeters depth, concentrations reach a low of 140 milligrams per kilogram (140 ppb), which corresponds to a period of active deforestation by settlers around 1800 to 1820. This activity, in fact, diluted the Hg levels below normal background for the area through increased erosion, and deposition of non-Hg bearing material. The levels found below 30 centimeters are believed to reflect natural background levels of between 0.3 and 0.4 milligrams per kilogram (300 to 400 ppb). Industrial input is believed to have begun around 1900 (∼9cm) and there has been a steady rise until around 1940 (∼ 5 cm) when concentrations leveled off at about 4 times natural levels. A similar pattern can be seen in sediments from Lake Windermere in England. Since 1400, Hg levels rose steadily as a result of such activities as 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 approximately 4 to 5 times higher than natural background concentrations.

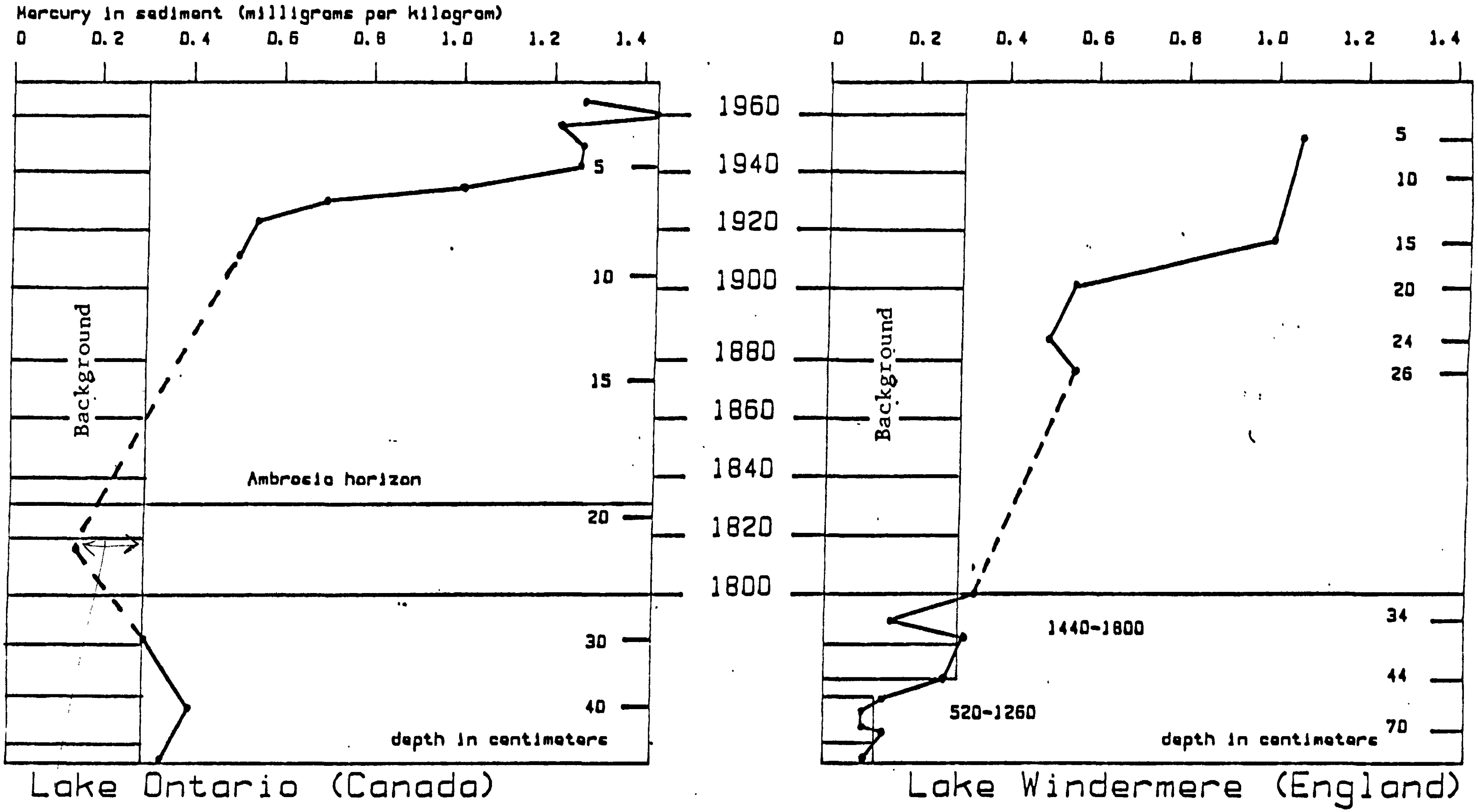

Figure 1.5 - Examples of mercury concentration changes through time

(Reprinted from Thomas, 1972, and Forstner and Wittmann, 1979, with permission)

2.0 Physical factors affecting sediment-trace metal concentrations.

2.1 Introduction.

The previous material was based upon 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, in order to understand the factors affecting sediment chemistry, as well as to enable an investigator to intelligently address such topics as trace metal transport, potential environmental impact, and to permit the comparison of sample data from the same or different areas, a number of physical and chemical factors need to be examined. These factors fall under the general heading of the various components or properties of a sediment. Physical partitioning refers to the separation of a sediment sample (bottom or suspended) into various physical categories such as by grain size, surface area, specific gravity, magnetic properties, mineralogy, and so forth. Chemical partitioning refers to the separation of various trace metals with respect to their association with other materials within the sediment (such as organic matter, carbonates, manganese oxides, sulfides, or silicates) as well as to the type of association that exists (such as adsorption, complexation, and substitution within mineral lattices). 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 as will be seen, both are interrelated. The factors involved in partitioning are listed in table 2.1.

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

Physical
Grain Size
Surface Area
Composition
Cation Exchange Capacity
Specific Gravity
Magnetic Properties
Surface Charge

Chemical - Mechanistic
Adsorption
Precipitation
Co-Precipitation
Organometallic Bonding
Incorporation in Crystalline Minerals

Chemical - Phase
Interstitial Water
Carbonates
Clay Minerals
Organic Matter
Hydrous Iron and Manganese Oxides
Sulfides
Silicates

2.0 Physical affecting sediment trace metal concentations.

2.2 Grain size ranges and affect 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 contains a listing of size classes (names) and the size range the names represent. For lakes, rivers, estuaries, and oceans, and for sediment chemistry in general, most sediments tend to be composed of materials smaller than 2000 micrometers (very coarse sand).

There is a very strong positive correlation between decreasing grain size and increasing trace metal concentrations. This correlation is the result of numerous factors which are both physical and mineralogical (compositional) in nature. Clay-sized sediments (less than 2 to 4 micrometers, see Table 5) have surface areas measured in square meters per gram as opposed, for example, to sand-sized particles whose surface areas tend to be measured in tens of square centimeters per gram (Grim, 1968; Jones and Bowser, 1978). Because surface chemical reactions are extremely important to aquatic trace metal-sediment interactions, fine-grained sediments, because of their large surface areas, are the main site 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). It should be borne in mind that metal concentrations can and do accumulate on many substrates, including sand, pebbles, cobbles, and boulders (Filipek and others, 1981; Robinson, 1982); however, high concentrations are more commonly associated with fine-grained material.

Table 2.2. -- Sediment particle size and classes (from Guy, 1969)

Class Name	Millimeters (mm)	Micrometers (μm)
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		2000 - 1000
Coarse sand		1000 - 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 μm rather than at 4μm

2.0 Physical factors affecting sediment-trace metal concentrations.

2.3 Chemical analysis of various grain sizes in bottom sediment.

How significant is the effect of grain size on chemical composition for bottom sediments? Table 2.3 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 less than 2 micrometer and the 10 to 20 micrometer ranges; this is typical for marine material (Rex and Goldberg, 1958)

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

MARINE

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

Size Fraction (micrometers)	Percent of Sample	Chemical Concentration (milligrams per kilogram)	Contribution to Sample[1] (milligrams per kilogram)
<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

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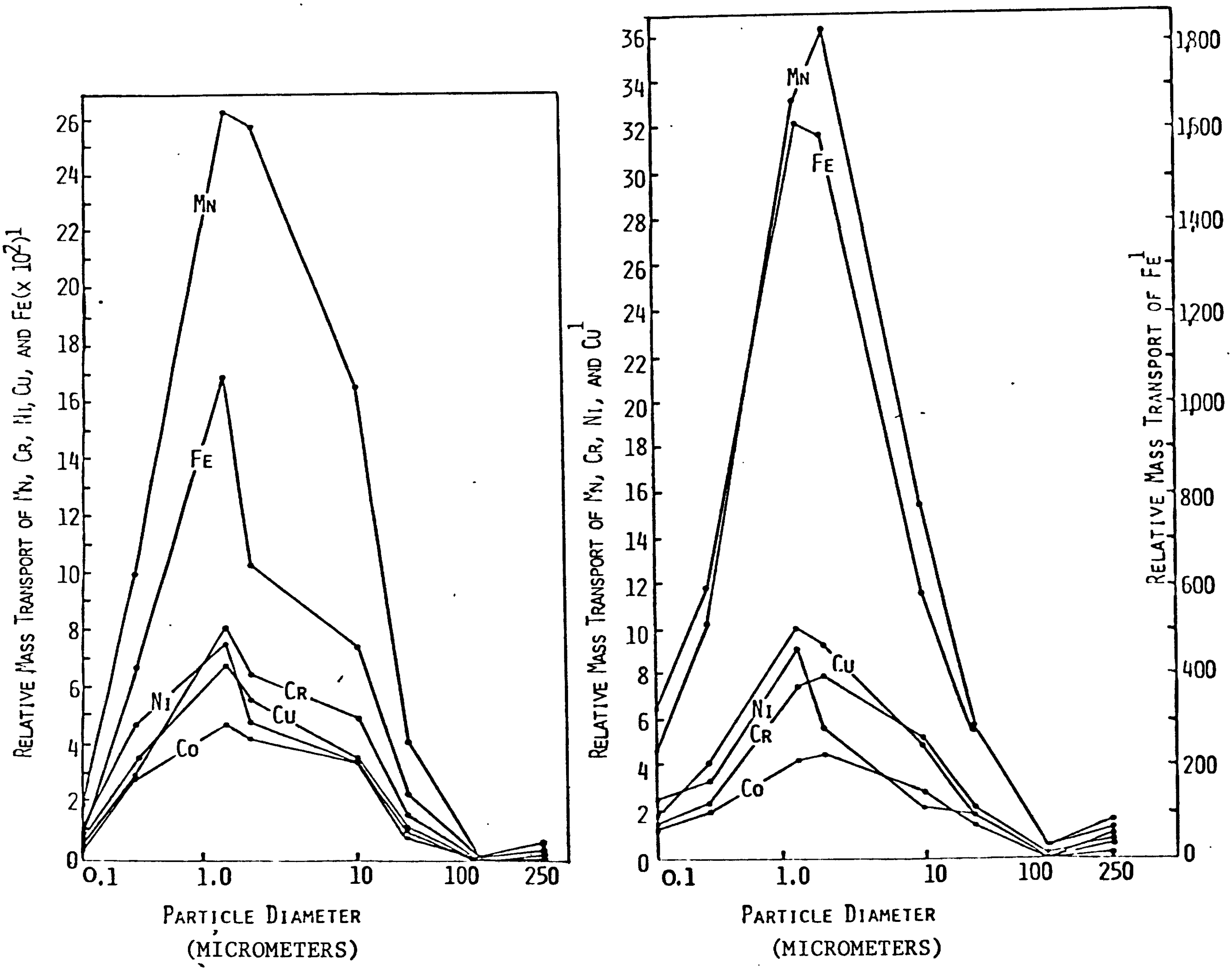
[1] Calculated by multiplying chemical concentration by percent of sample

2.0 Physical factors affecting sediment-trace metal concentrations.

2.4 Chemical analysis of various grain sizes in suspended sediment.

Are the patterns just described for bottom sediments also typical for suspended matter? Examination of the data presented in figure 2.4 should clarify this point. All the inorganic constituents investigated: manganese (Mn), iron (Fe), chromium (Cr), nickel (Ni), copper (Cu), and cobalt (Co), have their highest concentrations in the less than 2 micrometer fraction (figure 2.4). Further, this illustration also shows that the majority of the metal transport can be attributed to the less than 2 micrometer fraction. These data also imply that the majority of chemical transport may occur under relatively low discharge, because high metal concentrations are associated with the finer-grained material which requires relatively low discharge conditions for suspension and transport.



[1] Mn - manganese
Fe - iron
Cr - chromium
Ni - nickel
Cu - copper
Co - cobalt
Relative Mass Transport - calculated from size distribution data of material transported by each river and the metal concentrations for each size fraction , as a relative term, it has no units

Figure 2.4 - Distribution of metals by particle size, and relative mass transport by suspended sediment
(Reprinted from Gibbs, 1977, and published with permission)

2.0 Physical factors affecting sediment-trace metal concentrations.

2.5 Effect of grain size on trace metal concentrations for samples from the same basin.

The effect of grain size, on sediment-trace metal concentrations should be fairly evident now, based upon the previous discussions. Further, it should also be apparent that the finer grain sizes contain the majority of the metals associated with sediments. However, it is also important to understand the significant implications such relationships 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 comes from bottom sediments collected from the River Ems in Europe (de Groot and others, 1982). The manganese (Mn) concentrations vary over a wide range, from some 7000 to about 25,000 milligrams per kilogram; cobalt (Co), iron (Fe), and mercury (Hg), also display wide concentration ranges. Based solely upon bulk chemical analysis, there would appear to be no interrelationship between the various samples, and all an investigator could report would be the wide range of concentrations. However, if the chemical data is 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, by either separating out the constituent-bearing size fraction, or determining the percentage of the constituent-bearing size fraction in a bulk sediment sample and recalculating the bulk data accordingly (recalculation methods will be discussed later in the Primer).

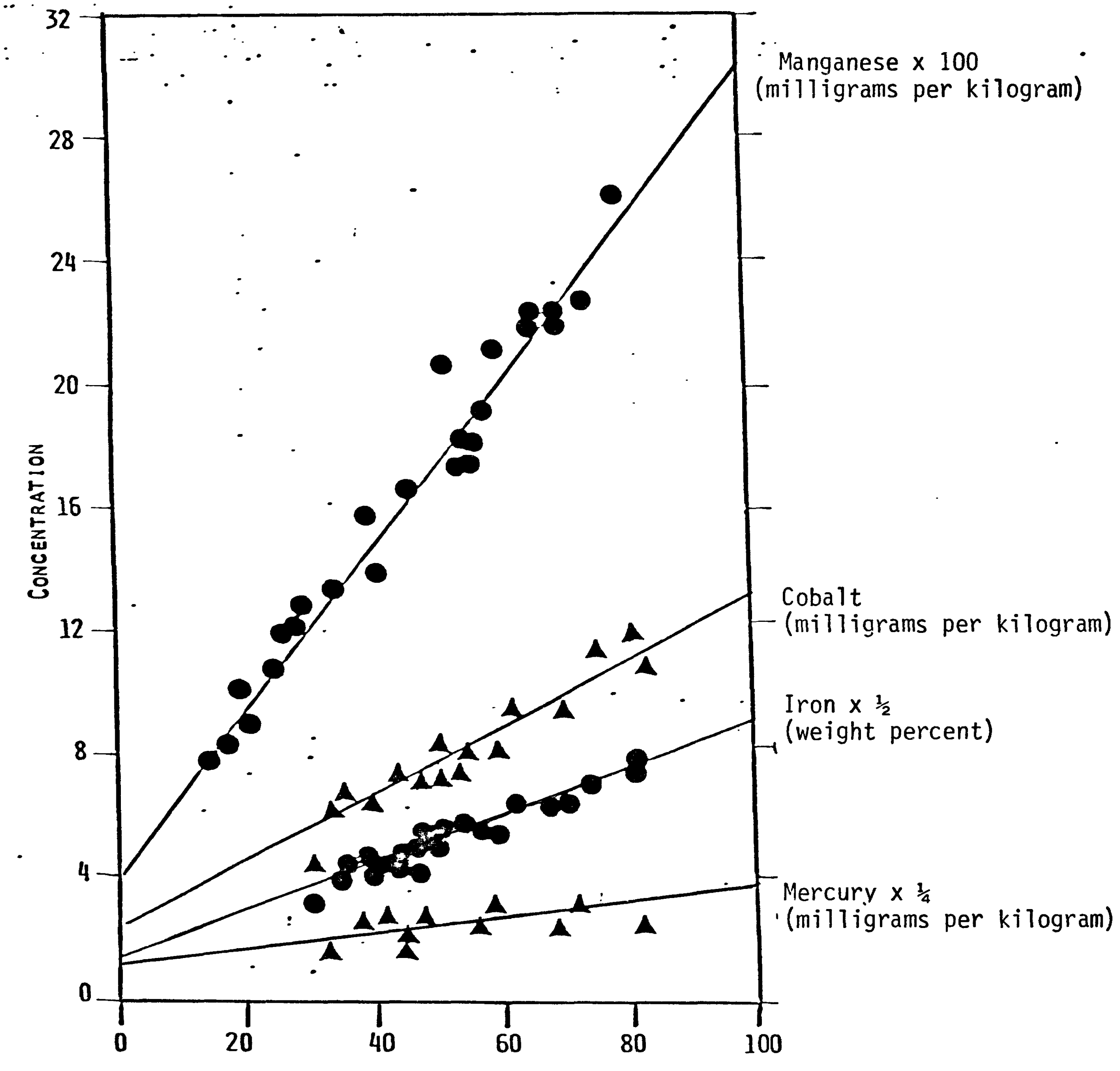


Figure 2.5 - Relation between metal concentration and grain size for the River Ems, Federal Republic of Germany
(Reprinted from deGroot and others, 1982 and published with permission)

2.0 Physical factors affecting sediment-trace metal concentrations.

2.6 Comparison of samples having similar bulk chemistries but differing grain size distributions.

It should be borne in mind that just because two sediments have the same bulk chemical concentrations, does not mean they are 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 of this, examine the data in table 2.6. Both samples are marine in origin. Sample AD 600 comes from a hydrothermally active area while sample AD 500 comes from a non-hydrothermal area. Both samples have similar manganese (Mn) concentrations (3,500 milligrams per kilogram), and as shown by the data in table 2.6, similar grain size distributions. However, the chemical data for each grain size range indicates significant differences between the two samples in the distribution of Mn. Sample AD 600 has two major Mn peaks, one in the less than 2 micrometer fraction, and the other in the 10 to 20 micrometer fraction. Sample AD 500 has similar Mn concentrations for all size fractions ranging from 2 to 32 micrometers. Subsequent mineralogical and chemical analyses indicated that the Mn peaks in AD 600 were due to manganese oxide coatings and micronodules while the Mn in AD 500 was due to volcanic ash and glass. Differentiation of the two samples could not have been made solely on the basis of either grain size distribution, nor on bulk chemical data, but could be made on the basis of size fraction chemical analysis.

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

	Sample AD 600			Sample AD 500		
Size Fraction (micrometers)	Percent of Sample	Concentration (milligrams per kilogram)	Contribution[1] (milligrams per kilogram)	Percent of Sample	Concentration (milligrams per kilogram)	Contribution[1] (milligrams per kilogram)
<2	20	5000	1000	18	4000	720
2 - 6	12	1000	120	13	3800	494
6 - 10	14	1000	140	15	3800	570
10 - 20	30	7100	2130	25	4000	1000
20 - 32	10	1000	100	15	4000	600
32 - 64	7	500	35	5	2000	100
64 - 125	4	300	12	5	1000	50
125 - 250	3	300	9	4	500	20
	100		3550	100		3550

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

2.0 Physical factors affecting sediment-trace metal concentrations.

2.7 The effect of grain size on sediment associated chemical transport under differing discharge rates.

It has now been reasonably 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 discharge increases, and the suspended sediment load increases, associated constituent concentrations will also increase. However, a little thought, and examination of the data presented in figure 2.7, 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 concentrations will decrease, as it does for chromium (Cr) as shown in figure 2.7. It should be borne in mind that the weight of Cr, or other metals, transported will not decrease, and may, in fact, increase (see table 1.3 for calculations concerning transport), only the concentration in the suspended load will decrease (this relation is applicable to large rivers, and caution should be exercised in applying it to small rivers). The data presented in this figure, as also shown by figure 2.4, reemphasizes the point that a majority of 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.

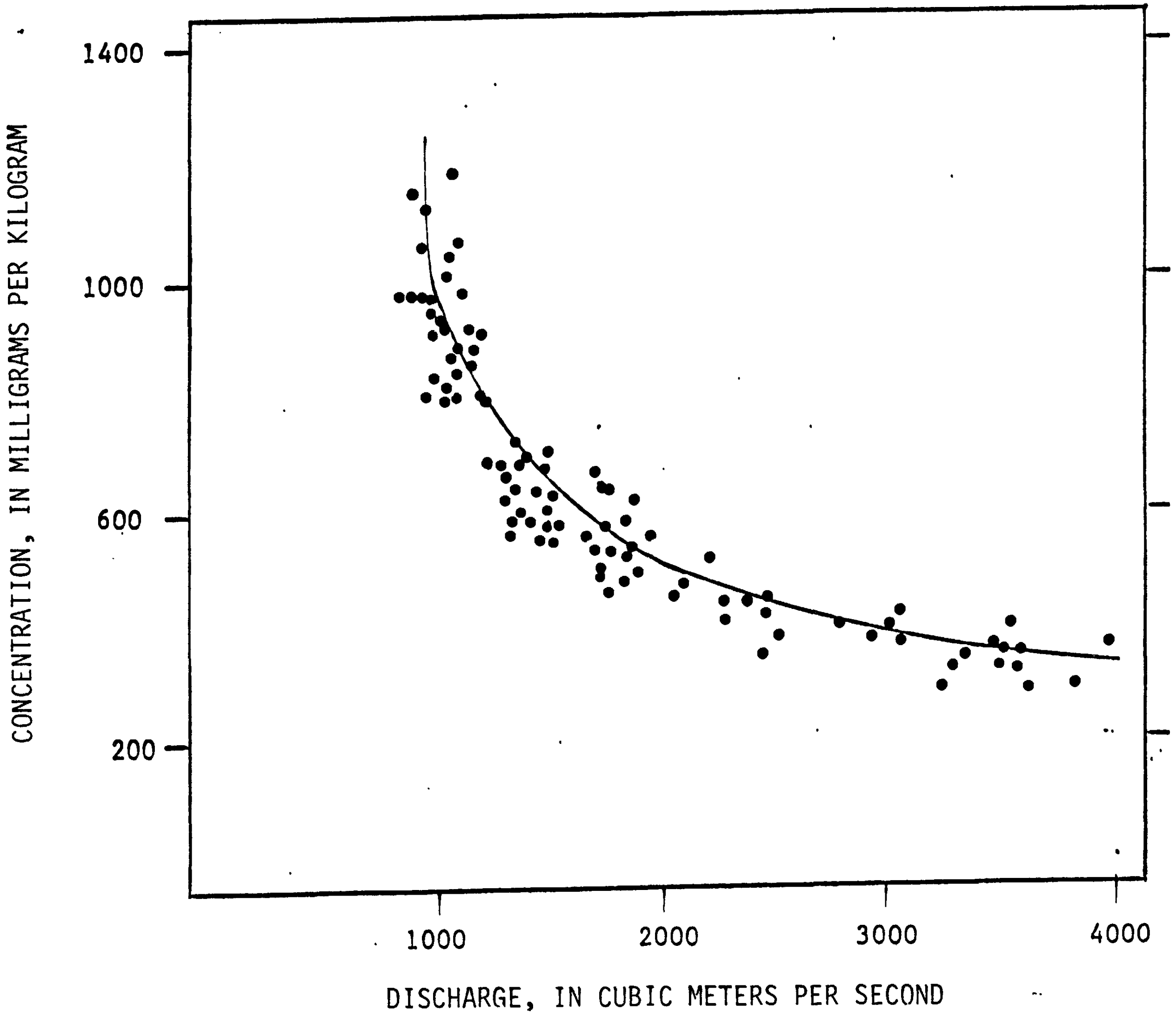


Figure 2.7 - Metal transport versus water discharge for chromium in suspended sediments for the River Rhine, Federal Republic of Germany
(Reprinted from Forstner and Wittmann, 1979, and published with permission)

2.0 Physical factors affecting sediment-trace metal concentrations.

2.8 The effect of surface area.

From the previous discussions, the importance of grain size to sediment-trace metal concentrations should be apparent. There are a number of other factors which also have significant effects on metal concentrations (see table 2.1). As shall be shown, there is a 'common thread' for all of these factors; it is grain size. As grain size decreases, these additional factors become more important, and there is usually a positive correlation between them, and increasing metal concentration. In some instances, it is impossible to differentiate between the effects due to such factors as surface area, cation exchange capacity, and surface charge, and those due to grain size. As a result, if it is possible to determine only one physical parameter on a sediment 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 presented in table 2.8. The surface area for simple spheres of differing diameters (grain size) has been calculated. 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, while clay-sized particles have surface areas on the order of tens of square meters per gram. Bear in mind that these values are for spheres. Obviously, real sediments are not composed of spheres, but 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 was a sphere of 2 micrometers 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 and usually is less than the theoretical value, but is still much larger than that of a sphere of equivalent diameter (Forstner and Wittman, 1979). For selected materials of less than 2 micrometers:

Calcite	12.5 square meters per gram
Clay Minerals	
Kaolinite	10 to 50 square meters per gram
Illite	30 to 80 square meters per gram
Montmorillonite	50 to 150 square meters per gram
Iron Hydroxide	300 square meters per gram
Organic Matter (humic acids)	1900 square meters per gram

Table 2.8. -- Calculated surface areas assuming sphericity (from Jackson, 1979)

Size Class	Diameter (micrometers)	Surface Area (square meters per gram)	(square centimeters per gram)
very coarse sand	2000	0.00113	11.3
fine sand/coarse silt	62	0.036	360
fine silt/coarse clay	4	0.57	5700
medium clay	2	1.13	11,300
fine clay	1	2.26	22,640
ery fine clay	0.5	4.52	45,280
colloids	0.1	22.6	226,400

2.0 Physical factors affecting sediment-trace metal concentrations.

2.9 Importance of surface area to sediment metal concentrations.

Why is surface area so important in controlling trace metal-sediment 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. As such, material with a large surface area (small grain size) is the main site 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 is a process which entails the condensation of atoms, ions, or molecules to 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 material 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. This means that such materials as organic matter, and hydrous iron (Fe) and manganese (Mn) oxides, can deposit on a surface and then these materials, rather than the surface itself, can act as metal collectors. Obviously, as surface area increases, the amount of these collectors can increase, thus increasing the metal-concentrating capacity of the surface.

An example of how surface area affects inorganic concentrations is presented in figure 2.9. The data come from the Ottawa and Rideau Rivers and it clearly shows that as surface area increases, the concentrations of both nickel (Ni) and copper (Cu) increase. This pattern is typical for many other inorganic constituents as well, such as iron (Fe), manganese (Mn), zinc (Zn), lead (Pb), and cadmium (Cd). Bear in mind that the surface areas plotted on these graphs (figure 2.9) are actual measurements, and have not been calculated. Do not assume that, for example, a surface area of 22.6 square meters per gram implies a sediment particle size of some 0.1 micrometers, which would be the case if the particle was a sphere (see section 2.8).

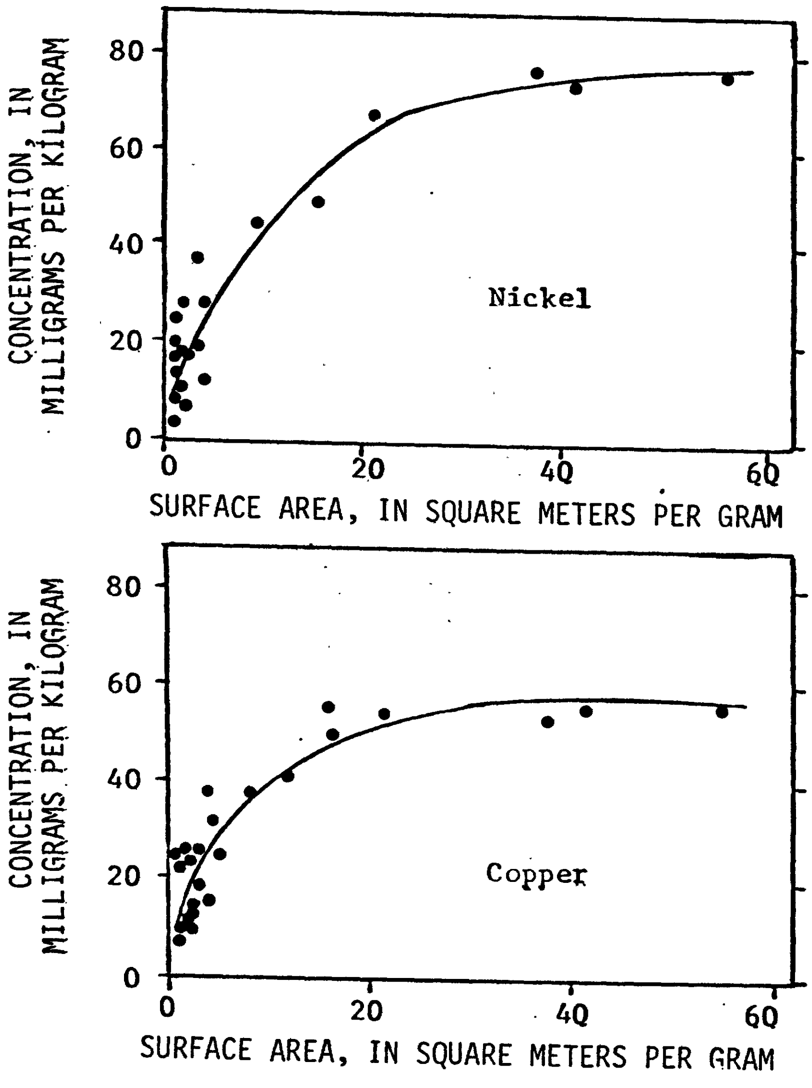


Figure 2.9 - Effect of surface area on metal concentration from the Ottawa and Rideau Rivers, Canada (Reprinted from Oliver, 1973, and published with permission)

2.0 Physical factors affecting sediment-trace metal concentrations.

2.10 Cation exchange capacity.

Many different materials, which are common components of sediment, and which 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 cation exchange capacity (CEC). 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 Wittman, 1979), CEC may also occur between the layers of certain silicates, such as expandable clays (montmorillonite, smectites), which, depending on how one chooses to define the layers, might not be viewed as 'surfaces' (Grim, 1968).

The data presented in table 2.10.1 include measured cation exchange capacities for selected materials commonly associated with this phenomena. The data also indicate that as grain size decreases, and surface area increases, CEC increases significantly (tables 2.10.2 and 2.10.3). It should be pointed out that CEC results from the availability of 'unbalanced' negatively charged sites and as such, it could readily be stated that it is a result of a net negative surface charge (another important physical factor, see table 2.1).

Table 2.10.1. -- Cation exchange capacity of selected materials

Material	Exchange Capacity (milliequivalents per 100 grams)	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 - Forstner and Wittmann (1979)
2 - Drever (1982)

Table 2.10.2. -- Variation of cation exchange capacity with particle size for kaolinite (from Grim, 1968)

Particle Size (micrometers)	10-20	5-10	2-4	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05
Cation Exchange Capacity milliequivalents per 100grams)	2.4	2.6	3.6	3.8	3.9	5.4	9.5

Table 2.10.3. -- Variation of cation exchange capacity with particle size for illite (from Grim, 1968)

Particle Size (micrometers)		1-0.1	0.1-0.06	< 0.06
Cation Exchange Capacity (milliequivalents per 100grams)	Sample A	18.5	21.6	33
	Sample B	13.0	20.0	27.5
	Sample C	20.0	30.0	41.7

2.0 Physical factors affecting sediment-trace metal concentrations.

2.11 Significant sedimentary trace metal collectors.

As has been demonstrated previously, there are a number of physical factors which affect the ability of a sediment to collect and concentrate trace metals. Based on these factors, plus additional chemical work, it is possible to identify those compounds and substances which are most significant in providing a sediment with the capacity to concentrate inorganic substances. Besides having large surface areas, cation exchange capacities, and high surface charges, they tend to be found in the finer size-fractions. Additionally, sedimentary metal collectors tend to be thermodynamically unstable and are amorphous or cryptocrystalline (Jones and Bowser, 1978). The various important features of metal-sedimentary collectors are listed in table 2.11.

The most common materials meeting these criteria are clay minerals, organic matter, hydrous manganese oxides, and hydrous iron oxides (table 2.11). Forstner (1982a) has listed these materials, in descending order, as regards 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. 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.

Table 2.11. -- 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)

2.0 Physical factors affecting sediment-trace metal concentrations

2.12 Iron and manganese oxides.

The characteristics of iron (Fe) and manganese (Mn) oxides are outlined in table 2.12. These substances have long been known as excellent scavengers of trace metals in solution (Goldberg, 1954, Krauskopf, 1956). Although the most spectacular demonstration of this effect is the Mn 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 Mn micronodules in core and grab samples indicates 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 micrometers) size ranges (Goldberg and Arrenius, 1958; Chester and Hughes, 1969; Dymond and others, 1973; Horowitz, 1974). In soils and suspended sediment, as well as in bottom sediment, Fe and Mn oxides also commonly occur as coatings on various minerals and finely dispersed particles (Forstner and Wittman, 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 square meters per gram (Fripiat and Gastuche, 1952; Buser and Graf, 1955). Regardless of form, whether micronodules or coatings, hydrous Fe and Mn oxides constitute significant concentrators for trace metals in aquatic systems.

Table 2.12. -- 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

2.0 Physical factors affecting sediment-trace metal concentrations.

2.13 Organic matter.

The characteristics of aquatic and soil organic matter are outlined in table 2.13. The ability of organic matter to concentrate trace metals in and on soils, suspended, and bottom sediments is well recognized (Goldberg, 1954; Krauskopf, 1956; Konanova, 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 is generally termed humic substances and has been subdivided into four categories: humins, humic acids, fulvic acids, and yellow organic acids by Jonasson (1977) (table 2.13). 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 cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), silver (Ag), vanadium (V), and zinc (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). 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). Similar results have also been found for aquatic organic matter (Swanson and others, 1966; Saxby, 1969; Rashid, 1974; Bunzl and others, 1976; Janasson, 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 (Kuenan, 1965; Forstner and Wittman, 1979).

Table 2.13. -- 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

[1] From Jonasson (1977)

Metal Affinities[2]

lead > copper > nickel > cobalt > zinc > cadmium > iron > manganese > magnesium

[2] From Irving and Williams (1948)

2.0 Physical factors affecting sediment-trace metal concentrations.

2.14 Clay minerals.

The characteristics of clay minerals are outlined in table 2.14. 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 aluminum (Al) for silicon (Si) 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 as regards 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 such as 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 Wittman, 1979). An empirical affinity sequence for some heavy metals and clay minerals indicates in descending order, lead, nickel, copper, 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). This 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 which actually carries out the concentration of trace metals rather than the clays themselves.

Table 2.14. -- 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 the subject of physical partitioning has been discussed, and the major physical factors affecting trace metal-sediment interactions have been elucidated, it is time to examine chemical partitioning. Just as aquatic systems are physically dynamic (such as 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 identifying sources and sinks for aquatic metal constituents, lies in identifying and quantifying the metal associations in sediments (suspended and bottom), and the reactions which occur between sediment, water, and biota (see table 3.1.1).

A search of the literature on sedimentary chemical partitioning indicates that two approaches have been used. The first attempts to determine how trace metals are retained on or by sediments - the so-called mechanistic approach. According to Gibbs (1973), there are five major mechanisms for inorganic accumulation in or on sediments (suspended and bottom): 1) adsorption on fine-grained material, 2) precipitation of inorganic compounds, 3) co-precipitation with hydrous iron (Fe) and manganese (Mn) oxides and carbonates, 4) association either by adsorption or organo-metallic bonding with organic matter, and 5) incorporation in crystalline minerals (table 3.1.2).

Adsorption is discussed in section 2.9. Precipitation and co-precipitation are readily understandable terms. Organometallic bonding refers to the attachment of a metal directly to carbon; such bonds can be formed by almost any metal, and several non-metals (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; such substitution is governed by ionic radius and change. In general, and there are exceptions, substitution takes place when ionic radii are within ±15 percent and when charge is the same, or differs by no more than ± 1.

The second approach attempts to determine where inorganic constituents are retained on or by sediments (phase or site) - the so-called phase approach. This has been attempted because individual constituents (such as iron, manganese, cadmium, lead, zinc, nickel, cobalt, and copper) may, and usually are, associated with several phases. The term phase is used in the thermodynamic sense and incorporates such categories as: 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, but 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 identifying sources and sinks, lies in identifying and quantifying the metal associations in sediments, and the reactions which occur between sediment, water, and biota.

Table 3.1.2. -- Mechanisms for metal accumulation in sediments (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 by adsorption or chemical 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

3.0 Chemical factors affecting sediment-trace metal concentrations.

3.2 Utility of chemical partitioning data.

The previous 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, it should be the goal of water quality projects to not only describe existing conditions at some point in time, and how they will affect the environment, but to also attempt to predict what is likely to occur later in time, or when physicochemical conditions change.

Table 3.2 attempts to point out some of the potential uses of chemical partitioning, and indicates some of the potential changes which can result from altered physicochemical conditions. The table is divided into three major categories: bioavailability, transport modeling, and remobilization. Bioavailability is an oft-used term which encompasses 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 type of chemical test or toxicity experiment. Unfortunately, no-one has yet come up with a universally accepted method of determining bioavailability and thus, the concept still remains subject to a tremendous amount of interpretation and argument.

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

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

Table 3.2. -- 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 (NTA) - 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

3.0 Chemical factors affecting sediment-trace metal concentrations.

3.3 Chemical partitioning methods.

Table 3.3 outlines the most common methods by which chemical partitioning is ascertained. Each method, and its practical uses and limitations, will be discussed in the following pages.

Table 3.3. -- 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

3.0 Chemical factors affecting sediment-trace metal concentrations.

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 floatations) 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 alter the sediment chemistry, and most are extremely time-consuming. In addition, it is virtually impossible to separate the individual constituents in the finer size ranges, such as clay minerals, and this is likely to be the size range of maximum interest.

Relatively new chemical analytical techniques may be utilized to directly determine chemical partitioning in sediments (table 3.4). These methods permit the quantitative analysis of various minerals, or mineral assemblages, in natural mixtures, without separation and sometimes non-destructively, 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 visually select the analytical site, thus making the determination of phase association possible for the derived chemical data. Although these techniques are promising, several problems limit their utility. The foremost is the determination of 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 milligrams per kilogram (100 ppm) and can be significantly higher (Johnson and Maxwell, 1981). This tends to limit the usefulness of these procedures to major elements such as iron (Fe), manganese (Mn), and sodium (Na), and could exclude such environmentally important trace metals as lead (Pb), cadmium (Cd), silver (Ag), and copper (Cu).

Table 3.4. -- 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

3.0 Chemical factors affecting sediment-trace metal concentrations.

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-Hannah, 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 lists most of the extractants which have been used over the years, to chemically partition sediments and soil.

After the initial work on marine sediments, further advances in chemical partitioning using sequential partial extractions have been make 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 and predict or estimate bioavailability. The sequences became more and more complex, as attempts to more clearly determine 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, 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 claim (Malo, 1977; Pilkington and Warren, 1979). Also, as Forstner (1982a) points out, extraction efficiencies vary due to length of treatment and sediment to extractant ratio. However, sequential procedures also have advantages. They permit differentiation between samples which have similar bulk chemistries. Also, they represent one of the few practical methods for the determination of concentration mechanisms and as such, 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. -- Reagents employed in sequential partial chemical extractions

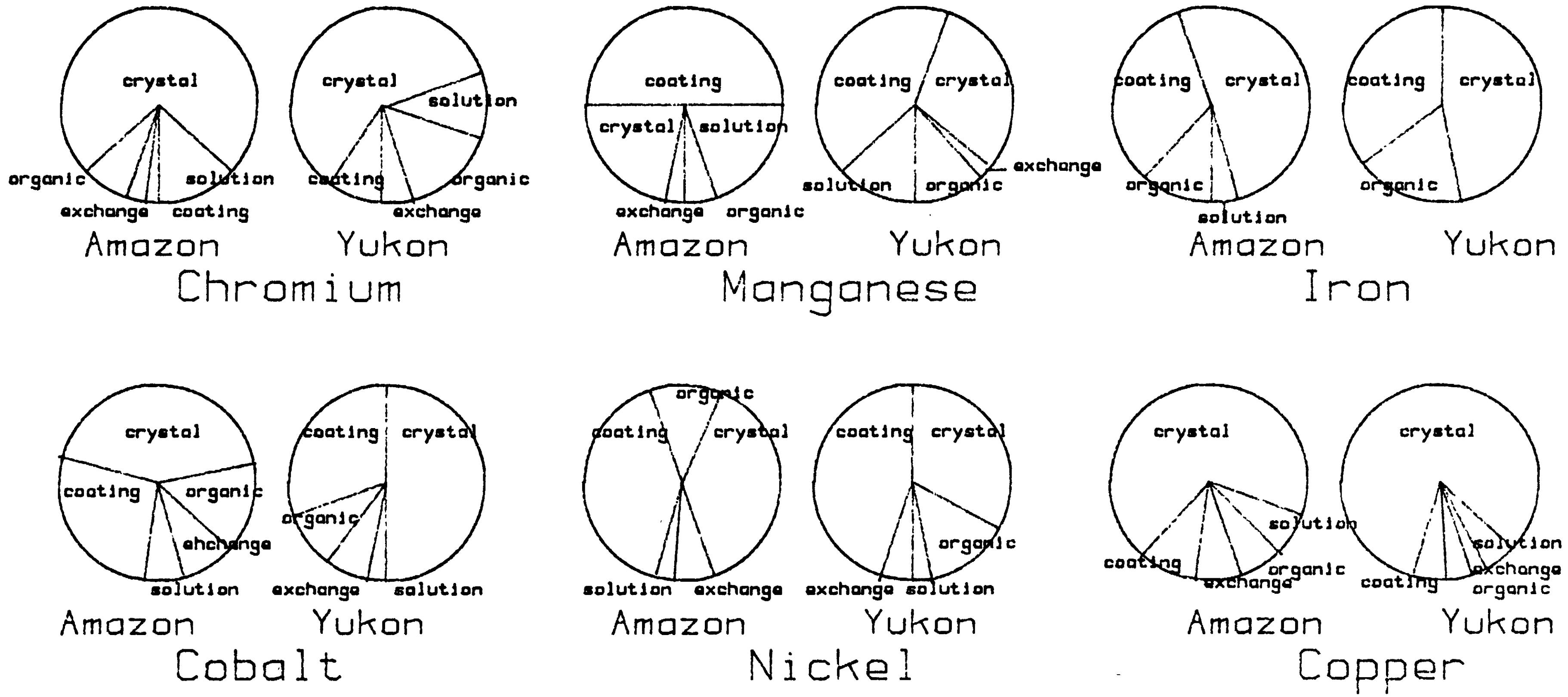
Adsorbates and Exchangeables	0.2 $BaCl_2$-triethanolamine, pH 8.1	Jackson, 1958
	1 M NH_4OAc, pH 7	Jackson, 1958
	Distilled deionized water	Nissenbaum, 1972
	1 M NH_4OAc	Gupta and Chen, 1975
	1 M $MgCl_2$, pH 7	Tessier and others, 1979
	1 M NaOAc, pH 8.2	Tessier and others, 1979
Carbonates	1 M HOAc (25% 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 $NH_2OH \cdot HCl$ 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 $NH_2OH \cdot HCl$ w/ 0.01 M HNO_3	Chao, 1972
Organics	Na hypochlorite w/ dithionate-citrate	Gibbs, 1973
	30% H_2O_2 at 95°C, pH 2	Engler and others, 1974
	30% H_2O_2 w/ 0.02 N HNO_3, pH 2 extracted w/ 1 M NH_4OAc in 6% HNO_3	Gupta and Chen, 1975
	30% H_2O_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_2O_2, pH 2 w/ HNO_3 at 85°C, w/ 3.2 M NH_4OAc in 20% HNO_3	Tessier and others, 1979
	30% H_2O_2 in 0.5 N HCl, heat	Kitano and others, 1980
Sulfides	30% H_2O_2 at 95°C, extracted w/ 1 N NH_4OAc	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

3.0 Chemical factors affecting sediment-trace metal concentrations.

3.6 Chemical partitioning of suspended sediment by partial extraction.

As an example of the type of information that can be obtained using partial chemical extractions, examine the data presented in figure 3.6. It was generated by carrying out a four-step chemical extraction sequence on suspended sediment from the Amazon and Yukon Rivers (Gibbs, 1977). The majority of the chromium (Cr), cobalt (Co) and copper (Cu) is concentrated in mineral lattices, the majority of the manganese (Mn) and nickel (Ni) is associated with ferromanganese coatings. The iron (Fe) was evenly divided between mineral lattices and ferromanganese coatings. Adsorption was not a significant contributor to the concentration of any of the metals studied while organic matter was a significant collector only in the cases of Co, and Ni.

Based upon these results, it is possible to discuss potential environmental availability. Those metals associated with crystal lattices are essentially unavailable. Those metals associated with ferromanganese coatings will probably be stable or environmentally unavailable unless there is a significant decrease in dissolved oxygen or a significant increase in biological activity. 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.



Solid phases, in percent

Phase	Chromium	Manganese	Iron	Cobalt	Nickel	Copper
Adsorbed	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-Chemical partitioning of selected metals in the Amazon and Yukon Rivers

(Reprinted from Gibbs, 1977 and published with permission)

3.0 Chemical factors affecting sediment-trace metal concentrations.

3.7 Chemical partitioning of bottom sediments by partial extraction.

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

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

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

Extraction	Active Hydrothermal Area		Inactive Hydrothermal Area	
	Concentration Remaining (milligrams/kilogram)	Percentage of Total Removed	Concentration Remaining (milligrams/kilogram)	Percentage of Total Removed
Bulk	1400		1200	
Acetic Acid	1300	7	1100	8
Hydroxylamine	600	50	900	17
Hot HCl	200	29	200	58

3.0 Chemical factors affecting sediment-trace metal concentrations.

3.8 Chemical partitioning by density gradient and mineralogy.

Another method that has been employed to determine chemical partitioning entails the use of physical separations, determination of mineralogy, and then subsequent chemical analysis (Muller and Burton, 1965; Francis and others, 1972; Pilkington and Warren, 1979; Dossis and Warren, 1980). An example of the results of this type of procedure is provided in table 3.8. 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 floatations 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 presented in table 3.8 are the chemical results from two samples, A and D, and are for the six density subfractions of the 1000 to 10 micrometer size separation of each. It is apparent that the lighter (least dense) fraction of sample A contains the highest concentrations of the inorganics investigated while the heaviest (most dense) fraction of sample D contains the highest concentrations. This is true although 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 miocrometers (Pilkington and Warren, 1979). There is no surety, without individual testing, that the acetone or bromoform will not alter the chemistry. Finally, it is extremely labor intensive and as such, expensive to carry out.

Table 3.8. -- Density gradients and chemical analysis
(from Dossis and Warren, 1980)

Procedure

1. Sizing in acetone
   (>1000, 1000 to 10, 10 to 1, and <1 micrometers)
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

ple	Density Subfraction	Weight Distribution (percent)	Zinc (micrograms per gram)	Lead (micrograms per gram)	Cadmium (micrograms per gram)	Zinc in Fraction (percent)[1]	Lead in Fraction (percent)[1]	Cadmium in Fraction (percent)[1]
2	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						
2	D1	2.3	1580	1370	25.3	3	4	4
	D2	27.5	1170	1140	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	1100	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 modelling.

Thus far, the discussion of chemical partitioning has concentrated on direct determination either by chemical or instrumental means. Attempts have also been made to determine chemical partitioning indirectly, through the use of various statistical manipulations and through the construction of 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, or chemical and mineralogical data, range 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. As the iron (Fe) and manganese (Mn) 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 Fe or Mn phases. The Fe phase appears to concentrate silicon (Si) and phosphate (PO_4), while the Mn phase appears to concentrate barium (Ba), nickel (Ni), cobalt (Co), molybdenum (Mo), magnesium (Mg), and strontium (Sr).

Leinen and others (1980), Pisias and Leinen (1980), and Leinen and Pisias (1984) used an extended version of Q-mode factor analysis (method for determining associations among samples) and linear programming, to partition (identify phases) 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, in decreasing order are: metals held in crystal lattices equal to metals associated with hydroxide coatings, metals associated with organic matter, 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 sediments from a number of estuaries. The statistical work assessed the utility of the various extractions in determining phase associations and bioavailability. Substrate (phase) characterization seems best accomplished by Fe and Mn, and humic acid extractions. Extractable Fe phases seem more important than total Fe for the concentration of silver

(Ag), cadmium (Cd), copper (Cu), lead (Pb), and zinc (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 influences partitioning (Oakley and others, 1980; 1981; Benjamin and Leckie, 1981). Although not specifically stated, partitioning can and will change with varying physicochemical conditions (changes in Eh, pH, solute concentrations, solute form, and so forth) and with transport and mixing processes, due to the addition, dilution, or removal of available substrates.

Statistical manipulations of sediment chemical data are not without problems. For example, the procedures used successfully by Leinen and others (1980), Pisias and Leinen (1980), and Leinean and Pisias (1984) on the Nazca Plate sediments were also applied to relatively homogeneous sediments from other Pacific areas and produced much more ambiguous results. Another problem associated with this type of technique is that which is also associated with partial chemical extractions; a lack of sufficient specificity to truly identify phases (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 relationships (Jones and Bowser 1978). This becomes increasingly important as the statistical manipulations become more complex. The manipulations may produce statistically significant results, but these can not be ascribed to a rational environmental setting or process; in such cases they serve no useful purpose. It should be remembered that 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. This view is shared by others (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 are dependent on a number of factors, such as thermodynamic data, results of partial extraction studies, the ability to identify and quantify substrates, the development of constants which describe the strength and stability range of metal-substrate binding, quantification of inorganic speciation in various strength solutes, Eh, pH, and so forth.

Swallow and Morel (1980) studied the behavior of Cu and Pb in the presence of hydrous Fe oxides in artifical seawater, 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, and the aging of the Fe oxide substrate, as well as the precipitation of the oxides in the presence or absence of the metals in question, had no significant effect. Although the behavior of copper (Cu) and lead (Pb) with oxides in seawater is somewhat analogous to surface complexation, the oxides are better viewed as a three-dimensional metal absorbing 'sponge' that accomodates metal ions into the solid as they hydrolize. These conclusions were based upon actual experiments carried out in the laboratory, and a mathematical model (expression) was developed to predict (describe) the experimentally determined Cu and Pb behavior, in the presence of iron (Fe) oxides.

Davis and Leckie (1978) also studied the uptake of Cu and silver (Ag) by Fe oxides. Like Swallow and Morel (1980), it was found that uptake varied with pH. However, it was also determined that complexing ligands strongly affect trace metal adsorption as well, and may enhance or depress the concentration capabilities of the Fe 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 those coated with Fe oxides. This result has been confirmed, using purely mathematical models, for several metals including Cu, Pb, cadmium (Cd), cobalt (Co), nickel (Ni), and zinc (Zn) (Vuceta and Morgan, 1978; Benjamin and Leckie, 1981). This is also in agreement with partial extraction studies (Forstner, 1982a,b). Additionally, Benjamin and Leckie (1981) indicate that metal adsorption from aqueous solutions also depends on adsorbent and adsorbate concentration, and the speciation of metals in solution.

Oakley and others (1980; 1981), using Cu and Cd, 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 Fe and manganese (Mn) oxides, in seawater. Laboratory experiments indicated that clay was the dominant sink for Cu except where humic substances constituted more than 90 percent of the substrate; clay was also the dominant sink for Cd, except where hydrous Fe and Mn oxides constituted more than 90 percent of the substrate. Additionally, clay was the dominant sink for both Cu and Cd when it constituted more than 60 percent of the substrate. Based upon these laboratory studies, an attempt was made to try and predict bioavailability through the construction of a mathematical model which was tested in the laboratory using a polychaete worm that fed on the substrate. Although the results were somewhat ambiguous, the authors stated that they were sufficient to conclude that the bioavailability of Cu and Cd from geochemical phases (clay, humic acid, hydrated oxide), to the polychaete worm, could be more significant than the bioavailability of Cu and Cd dissolved in the seawater, at natural concentrations.

Mathematical modeling shows some promise for determining the processes involved, and predicting metal partitioning in aqueous-sedimentary systems. However, there are a number of problems associated with them at the present time. The experiments and calculations on which the models have been based, were carried out using laboratory generated or purified substrates to eliminate interpretational ambiguities and even in multi-phase systems (such as, Oakley and others, 1980; 1981), have been relatively simple, compared to the natural environment. Also, there is a lack of 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) when compared with those of Vuceta and Morgan (1978) and Benjamin and Leckie (1981). Finally, some of the reported results from modeling studies appear to contradict direct observations. For example, Swallow and Morel (1980) claim that adsorption of metals by hydrous iron (Fe) oxides is independent of the presence, or absence of the metals, when oxide precipitation occurs. The proposed mechanism for metal concentration by hydrous Fe oxides, when studied in the natural environment (manganese nodules), has almost invariably been one of 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 discussions of physical and chemical partitioning has indicated that many factors affect the distribution and concentration of trace metals associated with both suspended and bottom sediments. As a result, it can be very difficult to determine if there are significant distribution patterns from, for example, a point source. However, there are certain mathematical or graphical manipulations which can be performed on chemical data, which will permit the investigator to determine if significant patterns do exist. Figure 4.1 shows the relationship between grain size and chemistry. As pointed out earlier, metals tend to concentrate in the finer size ranges (either less than 16 or 20 micrometers) and the addition of larger grain-sized 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 this dilution problem is to separate out the less than 20 micrometer (16 micrometer) fraction, and chemically analyze it. However, a reasonably good result may be obtained by determining the less than 20 micrometer (16 micrometer) percentage in the bulk sample of each sediment and normalizing the chemical data to it. The mathematics are very simple and straightforward.

dilution factor:

$$\frac{100}{100 - \text{percent size fraction less than 20 micrometers}}$$

then normalized chemical data (in milligrams per kilogram):

$$(\text{dilution factor})\ \begin{array}{l}\text{chemical concentration}\\ \text{in milligrams per kilogram}\end{array}$$

As an example, assume a sediment has a concentration of 20 percent less than 20 micrometers, and a zinc (Zn) concentration of 100 milligrams per kilogram.

dilution factor:

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

then normalized chemical data:

$$(5)\ (100) = 500 \text{ milligrams per kilogram Zn}$$

Remember, the underlying assumption for this type of correction assumes that all of the constituent of interest is found in the less than 20 micrometer (16 micrometer) fraction. This is almost certainly not true, but it does help to clarify a distribution pattern which has been obscured due to the presence of varying amounts of diluent.

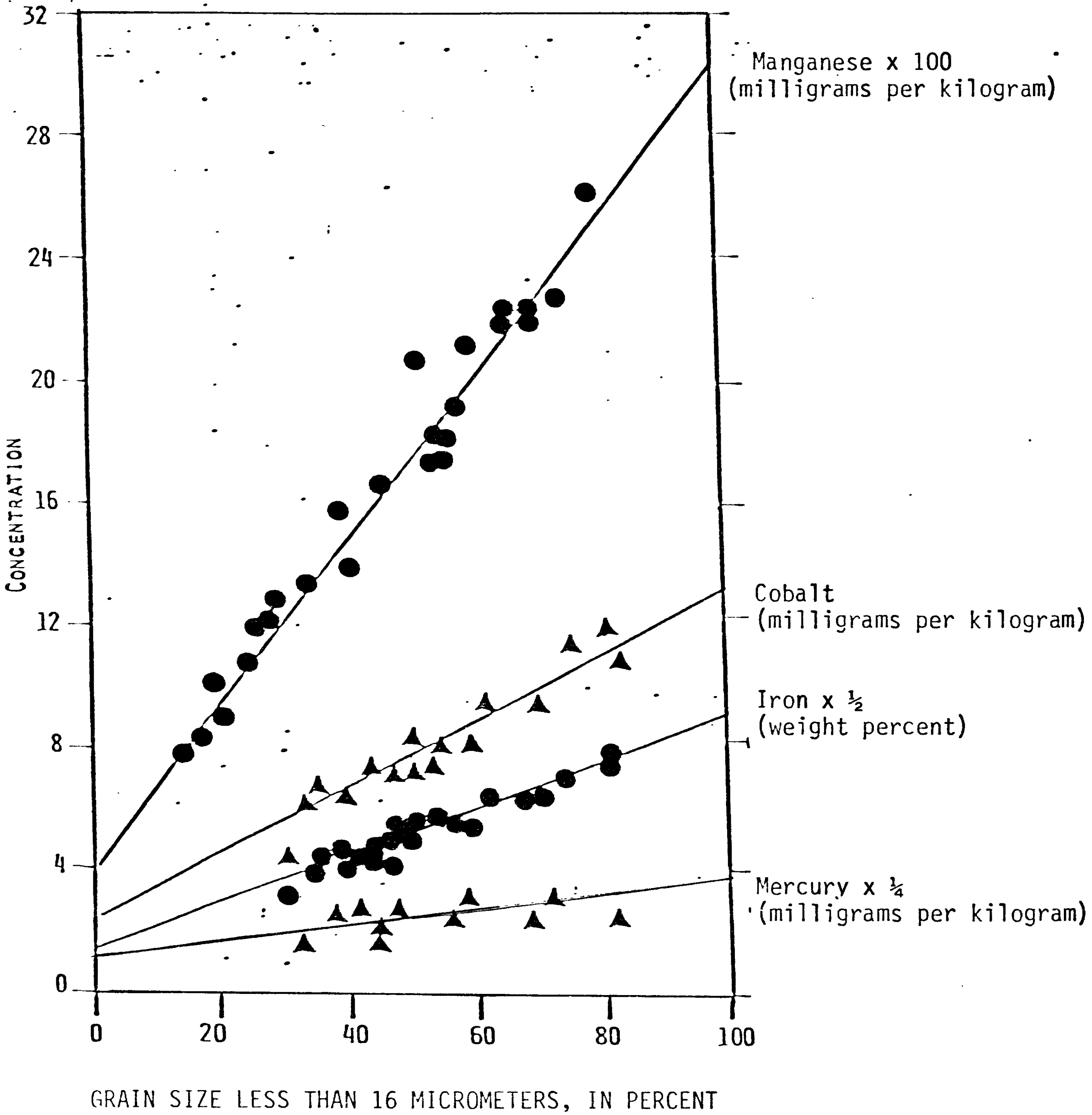


Figure 4.1 - Relation between metal concentration and grain size for the River Ems, Federal Republic of Germany
(Reprinted from deGroot and others, 1982, and published with permission)

4.0 Sediment-trace metal data manipulations.

4.2 Carbonate corrections.

Another commonly used correction factor involves normalizing 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. Examination of the data presented in figure 4.2.1, which is for a marine bottom sediment sample, would certainly support this view, with the possible exception of lead (Pb) and cadmium (Cd). As with the grain size example, the carbonate fraction could be physically separated and chemically analyzed, but this is extremely difficult. 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:

dilution factor:

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

then normalized chemical data (in milligrams per kilogram):

(dilution factor) chemical concentration
in milligrams per kilograms

As an example, assume a sediment has 25 percent carbonate, and a zinc (Zn) concentration of 50 milligrams per kilogram.

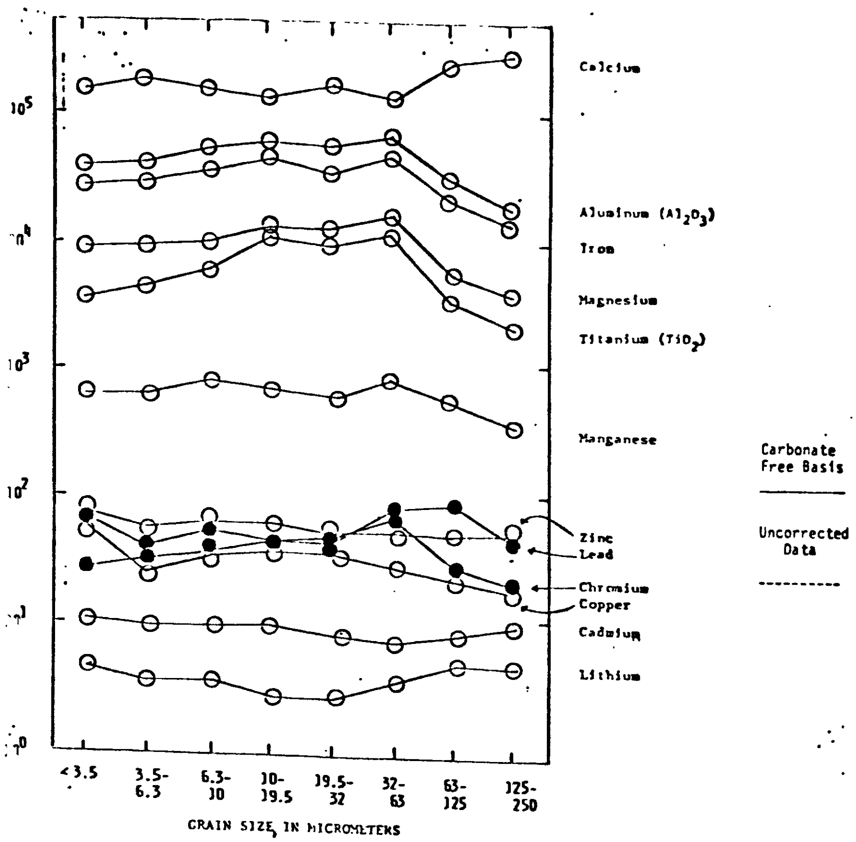
dilution factor:

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

then normalized chemical data:

(1.33) (50) = 66.7 milligrams per kilogram Zn

As an example of how a carbonate correction can clarify a pattern, examine the data presented in figure 4.2.2. The dashed line represents uncorrected data while the solid line represents the corrected data. The difference between the two patterns is striking. However, it should be borne in mind that this type of correction assumes that <u>all</u> of the constituents of interest are concentrated in the non-carbonate fraction. This is almost certainly not true for every situation or trace metal, as examination of the data in figure 4.2.3 shows. The pattern for calcium (Ca) 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.



re 4.2.1. - Variation in metal content with grain size from the same bottom sediment sample

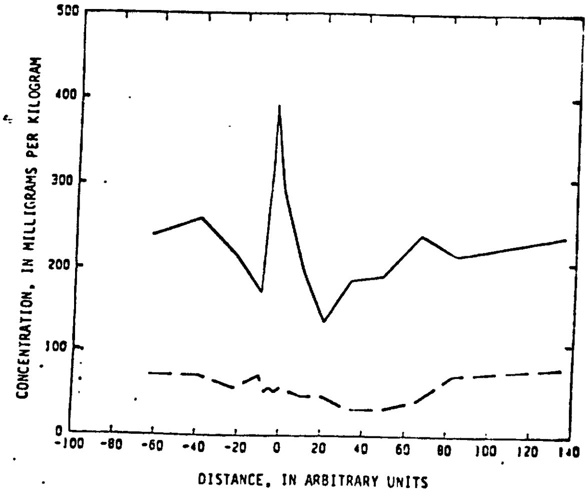


Figure 4.2.2 - Distribution of zinc from a point source

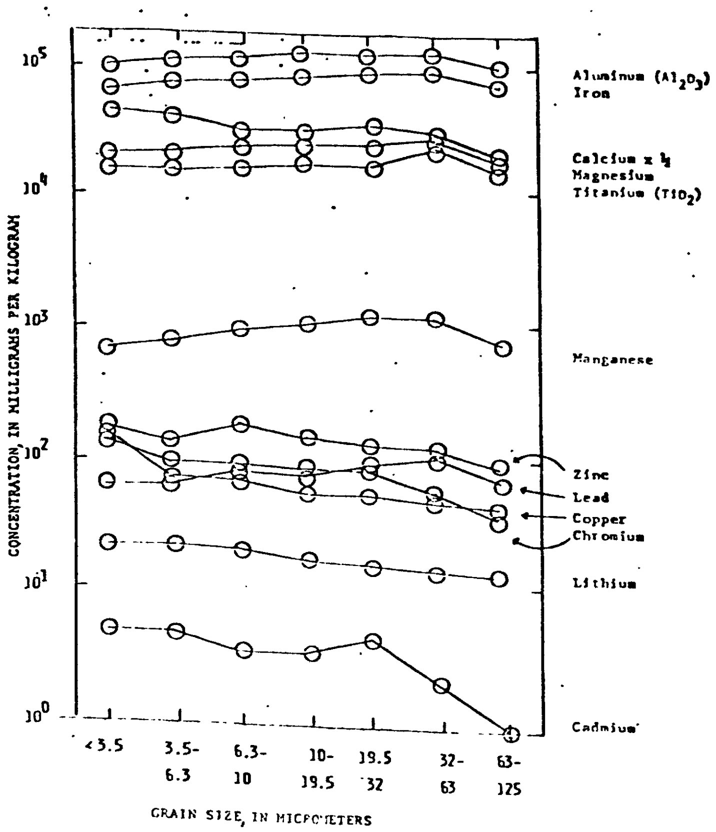


Figure 4.2.3. - Variation in metal content with grain size from the same bottom sediment sample

4.0 Sediment-trace metal data manipulations.

4.3 Normalization to 'conservative' elements.

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

$$\frac{\text{Concentration of Inorganic Constituent}}{\text{Concentration of Conservative Element}}$$

However, unlike the grain size and carbonate corrections, the resultant values are simply ratios, rather than some chemical concentration. As such, comparison with data from other areas is difficult unless similarly recalculated, and, a ratio, rather than a concentration, is conceptually more difficult to grasp. Despite this, normalizing to a conservative element can significantly clarify distribution patterns as shown in figure 4.3. The data comes from a series of marine sediment samples. The dashed line represents bulk copper (Cu) data corrected to a carbonate free basis, while the solid line depicts the same bulk Cu data normalized to Al (as Al_2O_3).

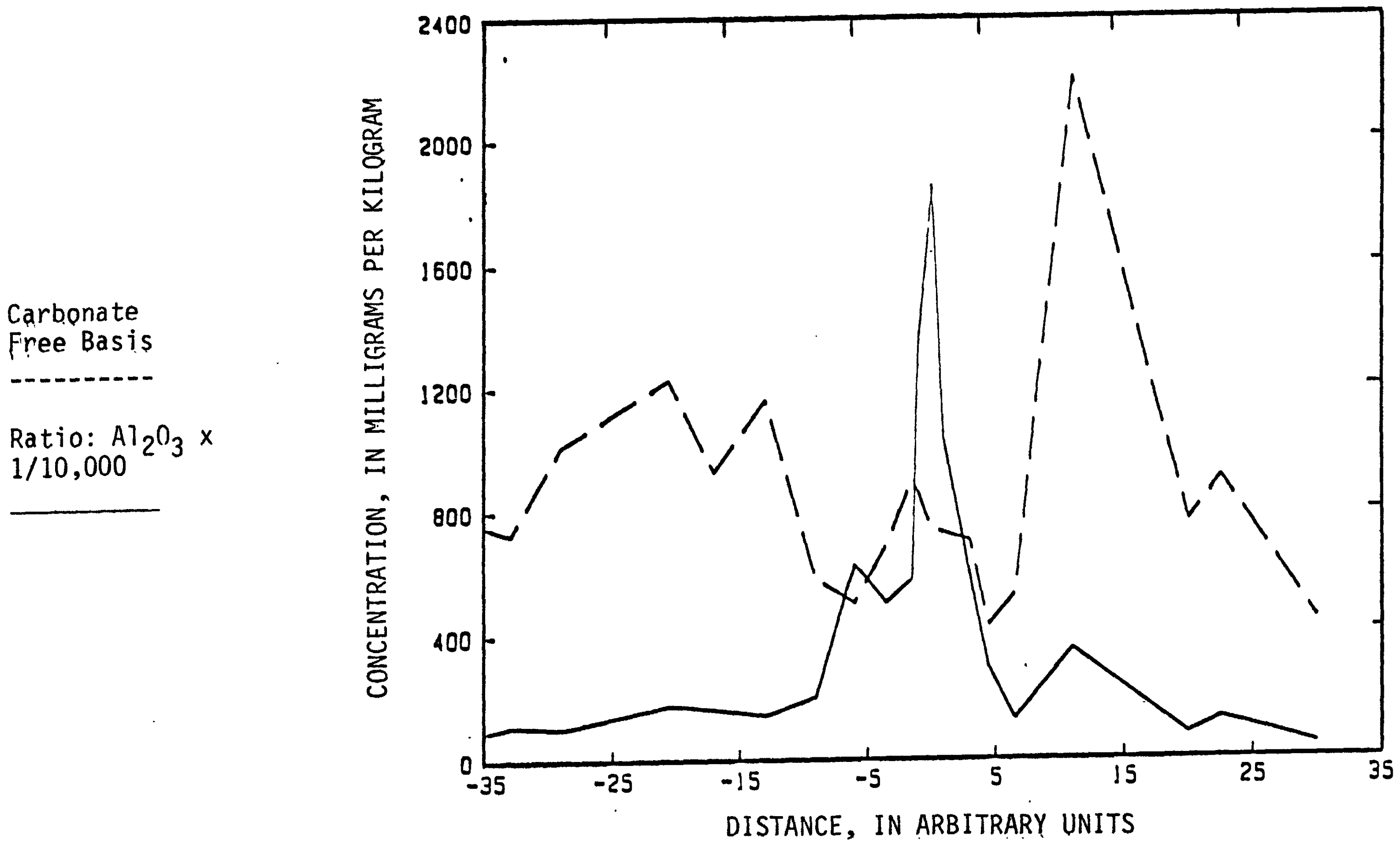


Figure 4.3 - Distribution of copper from a point source (data from Piper, 1973)

5.0 Sampling and data handling - general comments

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

Sampling and program design is extremely important to the ultimate success of a study. More time, effort, and money have been wasted in environmental studies as a result of poor program design, than any other cause (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 is to be used. For example, if a large areal study is needed, then a type of random sampling should be used to characterize distributions. If random sites are not selected, but just picked, it is possible then, 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 assistance in developing a program plan if an investigator is lacking in this area. There are many types of sampling programs, four generally used procedures are discussed below:

1) Simple Random Sampling - this entails the selection of sites such that every posssible sample has an equal opportunity of being chosen. It is very efficient if the study area is homogeneous; however, it may be ineffective in heterogeneous areas and could lead to missing important sites or data.

2) Stratified Random Sampling - this entails dividing a heterogeneous area into homogeneous sub-areas within which sampling locations are randomly selected. This often permits the elucidation of subtle, but real differences.

3) Systematic Sampling - this entails a constant distance interval between sampling sites and is 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, but the disadvantage is that it can produce very biased results.

4) Fixed Transect - this entails sampling at fixed and predetermined sites which need not be at constant intervals. This is an extremely simple method of sample design. However, since all possible sampling sites do not have an equal chance of being selected, any statistical inferences, or conclusions, are appropriately associated only with the selected sites, and areal conclusions may not be valid.

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 laboratory analytical errors.

The advent of the computer has been a boon to scientific investigators in that it has permitted the handling of large data sets as well as 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 is telling them. Remember, statistically significant results must be matched by realistic environmental interpretations, or all the work that has gone into a study can be wasted. Before embarking on a major statistical program, understand what the implications are for each manipulation. In fact, it is more advisable to develop a theory or hypothesis and test its statistical validity, than to statistically manipulate data and to then try and fashion a theory to fit the statistics. Statistics are a tool, not an answer!

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

Use and build upon the work of others. Time may be saved, initially, if previous work is ignored during the planning of a study, or during data analysis and report preparation. Bear in mind that no one receives credit for 're-inventing the wheel'. However, there is nothing wrong with using a successful investigator's sampling and interpretation program which has been applied elsewhere. 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, good science, and the purposes of most studies, are to answer specific questions as capably as possible, within time and financial constraints, not to find the ultimate solution.

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