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The Role of Sediments in the Chemistry of Aquatic Systems—Proceedings of the Sediment Chemistry Workshop, February 8–12, 1982

Edited by Wesley L. Bradford *and* Arthur J. Horowitz

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The Role of Sediments in the Chemistry of Aquatic Systems— Proceedings of the Sediment Chemistry Workshop, February 8-12, 1982

Edited by Wesley L. Bradford *and* Arthur J. Horowitz

ABSTRACT

A workshop on sediment chemistry was held at the U.S. Geological Survey National Headquarters in Reston, Virginia, February 8-12, 1982, to discuss the state of the science and possible future directions for research and operational programs in the Water Resources Division of the U.S. Geological Survey. Technical papers presented broad overviews of current conceptual models for and research on the interactions between sediments, water, and biota with respect to the occurrence, distribution, movement, and fate of metals and organic substances in aquatic systems. Five separate disciplines within the overall theme were discussed: physical and chemical partitioning of inorganic constituents; analysis association, and effects of organic constituents; bioavailability of sediment-bound metals; concepts and methods regarding physical properties of sediments; and simulation of transport-related properties. The discussions of the participants regarding needs and possible future directions are summarized. The papers and discussions should help guide individual investigators and policy/program managers alike for the next several years.

WORKSHOP SUMMARY

INTRODUCTION

"Sediment" is defined in the "National Handbook of Recommended Methods for Water Data Acquisition" (1977), chapter 3, as "(1) particles derived from rocks or biological materials that have been transported by a fluid, and (2) solid material (sludges) suspended in or settled from water." Sediment includes, for purposes of this discussion, "suspended sediment", material that is being actively transported by the fluid, and "bed material", material that is temporarily stationary in the bottom of the water course. The term "sediment" when used alone implies both suspended and bed material.

It is widely recognized that, in most aquatic systems, the suspended sediment and the top few centimeters of bed material contain many times the amounts of certain trace metals and organic compounds than are dissolved in the overlying water column. The strong association of numerous toxic chemicals—both organic (such as PCB's, DDT, Mirex, and Kepone) and inorganic (such as arsenic, mercury, cadmium, and lead)—with sediment means that much of the downstream transport of these materials cannot be detected or evaluated solely through the sampling and analysis of water. Moreover, bed materials are a reservoir of these chemicals, which could, under certain physicochemical conditions, dissolve into the water column or otherwise enter the food web. Finally, both organic and inorganic compounds can degrade or react with other constituents to form soluble, and possibly even more toxic, forms (for example, the conversion of elemental mercury to methylmercury). Thus, to develop a comprehensive picture of water quality that accurately depicts the distribution, transport, and availability of organic and inorganic constituents, data on sediments, as well as on water, must be used.

Through the use of data on the physical and chemical characteristics of sediment, it may be possible to identify sources and sinks as well as the fate and possible effects of potentially toxic or environmentally necessary elements and compounds. Similarly, such information is a requisite for transport modeling, for attempts to estimate cycling rates (development of global geochemical cycles), and for determination of the availability of these constituents to an ecosystem. Also, historical information on the distribution and concentration of various chemical compounds is lacking. Because bed materials act as reservoirs for these materials, a detailed investigation based on core samples can provide a much-needed historical record as well as perspective with which present-day levels can be compared and contrasted. This is especially true where chemical analyses are used in conjunction with radiometric age dating techniques (such as ^{210}Pb and ^{14}C).

One of the major shortcomings of the present technology used by the U.S. Geological Survey, Water Resources Division (WRD), to assess water quality is a lack of adequate methodology for collecting and analyzing sediments for trace metals and organic compounds. The methodology required should permit the design of adequate sampling schemes, should address collection and preservation techniques, should permit determination of how these compounds are both physically (such as association with particular size fractions) and chemically (such as adsorbed, bound in Fe–Mn hydrous oxides) entrained or partitioned in sediments, and should provide some measure of bioavailability.

Many of the guidelines and techniques currently used by WRD, such as the analytical procedure for determining total recoverable metals in sediments, resulted from a series of meetings held in 1971–72 in response to the problem of mercury in the environment (B.F. Jones, oral commun., 1982). However, many of these are not adequate to meet present and future needs. Additionally, since that time, many advances have been made in the field of sediment chemistry that should be evaluated and, if suitable, be made available to operational arms of WRD. Finally, new areas of research should be identified so that the WRD can meet future needs for water-quality information.

STRUCTURE AND GOALS OF THE WORKSHOP

To provide a mechanism for guiding and evaluating a program in sediment chemistry, the Quality of Water Branch, WRD, established a Sediment Chemistry Task Group. The group's efforts were initiated during the week of February 8, 1982, with a workshop. Participants were invited on the basis of expertise and interest in the field of sediment chemistry and transport, and represented all segments of the WRD (District, Central Laboratory System, National Research Program, and Regional and Branch staff). Speakers presented papers on five separate topics within the general theme. These papers, which form the body of this circular, are detailed overviews intended to provide a "feel" for the state of the science, to outline directions for future research and field investigations, and to serve as a point of reference for future investigators in these areas.

Workshop speakers and topics were as follows:

A.J. Horowitz, Doraville, Ga., Cochairman—Inorganic partitioning
S.N. Luoma, Menlo Park, Calif.,—Sediment-biota interactions
T.M. Lai, Lakewood, Colo.,—Physical properties
J.A. Leenheer, Lakewood, Colo—Organic partitioning
J.P. Bennett, Reston, Va.,—Sediment transport modeling

Workshop participants were:

G.L. Pederson, Atlanta, Ga.
S.W. McKenzie, Portland, Oreg.
J.R. Elder, Tallahassee, Fla.
V.C. Kennedy, Menlo Park, Calif.
D.K. Nordstrom, Menlo Park, Calif.
J.T. Turk, Lakewood, Colo.
D.K. Helsel, Columbus, Ohio
H.R. Feltz, Reston, Va.
E. Callender, Reston, Va.
W.L. Bradford, Reston, Va., Co-chairman
B.A. Malo, Reston, Va.
R.L. Wershaw, Lakewood, Colo.
R.H. Meade, Jr., Lakewood, Colo.

The workshop had several clearly defined goals. First was to identify operational needs regarding methods and procedures (e.g., the procedures for sediment chemical analysis that will yield data most useful for assessment of aquatic impacts from sediment-borne trace metals). Second was to provide the participants with up-to-date overviews of current research in the field of sediment chemistry and transport. This was accomplished through half-day presentations and discussions on the broadly selected topics listed above. Third was to identify various procedures for immediate implementation and subject areas for additional research or methods development.

Regarding the first and third goals, during the workshop four broad subject areas were identified and discussed: (1) sources, sinks, transport, and storage; (2) analytical methods; (3) sampling methods; and (4) technology transfer. The group reached consensus in all four areas as to directions WRD's program should be headed. A synopsis of these discussions is presented in the next section. It represents the culmination of several days of indepth review, debate, and compromise among the participants, in an effort to distill into a few words the major themes and messages of the workshop.

The overview papers and discussions of the workshop participants presented herein formed the technical basis for a new program of research and field investigations begun in Fiscal Year 1984 by the Geological Survey, the Hazardous Substances-Surface Water and Sediment Program.

SYNOPSIS OF DISCUSSIONS

SOURCES, SINKS, TRANSPORT, AND STORAGE

The ultimate goal of an integrated sediment chemistry program is to identify and quantify the sources, sinks, transport mechanisms, and potential environmental effects of organic and inorganic constituents residing on or interacting with sediments. Although this goal is not achievable without many years of dedicated investigation, some along avenues that cannot be foreseen, there have been many technological advances during the last 10 years that can be employed immediately or after a short-term investment in research that will foster an advance toward this goal. The implementation of these advances and consideration of future directions for research in this area are the subjects of this discussion.

The pursuit of the ultimate goal is stimulated by the realization that chemical compounds associated with sediments affect, or may affect, the fitness of aquatic systems to support aquatic life. Additional stimulus comes from other considerations:

1. Storage and transport of chemical constituents on sediments are significant parts of global geochemical cycles. Computed global material budgets are becoming increasingly useful tools in estimating fluxes of important mineral resources and for indicating the relative importance of pollutant sources and sinks, and may provide insight into the fates and effects of chemical constituents.
2. The concentrations of chemical constituents on sediments are often good indicators of chemical anomalies, including anthropogenic inputs. For this reason, monitoring the chemical composition of sediments may be the most cost-effective method of assessing the impact of man's activities on aquatic environments.
3. Knowledge of chemical composition of sediments may be useful in investigating historic changes in inputs (both natural and man-induced) of trace metals and organic compounds to aquatic systems. Conversely, the chemical composition can, on occasion, be used in studies of historic sediment transport.
4. Because of the time scales involved in sediment transport and storage, and because of the persistence of many chemical constituents, problems can arise in aquatic systems from constituents that have their origins in events decades or more earlier. Many examples can be seen today of effects on aquatic systems from pollutants disposed of 40 years ago, and more, by methods appropriate at that time.

A full identification and quantitative understanding of sources, sinks, and transport mechanisms must involve development of detailed structure- and process-imitating models. It is recognized that such models will be enormously complex, and that the conceptual models needed to guide their development are not yet available. The development of structure- and process-imitating models should proceed in tandem with investigations that build a conceptual framework. Multidisciplinary research should be encouraged to synthesize current techniques and demonstrate linkages among contaminants associated with water, sediments, and biota.

In the discussions that follow, an attempt has been made to identify technologies that are available now and may be readily implemented to provide badly needed upgrading of current WRD programs, technologies that show promise of benefiting the program but need additional development before being implemented, and technologies that, it is anticipated, will be needed to achieve the ultimate goal and to which research should be directed.

ANALYTICAL METHODS

CHEMICAL ANALYSES

Readily implemented:

- Analyses for total trace metal concentrations should be performed on samples totally digested by an appropriate technique. Data would permit comparisons between samples and between areas, comparisons with data collected outside WRD, and comparisons of element ratios with natural abundances to determine anomalies. The primary uses would be to determine changes in space and time and to detect anomalous concentrations.
- Analyses for trace metals should also be performed on an extract obtained with cold 0.5 *M* HCl digestion for 2 hours with agitation. This method is simpler and more cost effective than the current procedure, and concentrations of some trace metals, particularly iron, correlate more closely with concentrations found in biological tissue.
- The detection limit, accuracy, and precision of trace metal analyses required should be judged from the average composition of shale or granite, whichever proves more restrictive (see Krauskopf, 1967).

Development needed:

- Organic extraction methods should be updated to improve the recoveries of organic constituents, to recover volatile constituents, and to evaluate and apply recent developments in analytical methodology.
- Methods of determining the partition coefficients of both organic and inorganic materials should be developed. The partition coefficients are needed for modeling of storage and transport processes and for describing movement and ultimate fates of chemical constituents in the aquatic environment.
- Biological tissue analysis should be provided as a standard service at the Central Laboratory. Tissue analysis will be necessary to gather data on bioavailability, and the service would provide Districts the capability of conducting studies with indicator species. A procedure that should be examined, among others, is HNO_3 refluxing.
- Evaluation and implementation of methods for routine direct analysis of suspended sediments for trace metals and organic compounds is extremely important. Current methods of estimating concentrations in suspended sediments (total minus dissolved) are subject to large errors because the estimate is the difference between two large numbers; also, there are problems with subsampling the whole water sample and with providing a total sample digestion or an efficient extraction of organic materials.

Research needs:

- New methods of data analysis should be developed including methods of identifying contamination over native concentrations.
- Guidelines are needed regarding concentrations of chemical constituents in sediments that affect biota in aquatic systems.
- The inorganic solubility controls on organic solutes, and vice versa, should be studied. Knowledge of these controls is essential in determining and modeling the fate of organic compounds in aquatic environments.
- Methods of comparing the concentrations of chemical constituents in biota and sediments should be developed. Such comparisons are needed to establish a consistent methodology and to build a data base that will permit more rational studies of bioavailability.

MINERALOGICAL ANALYSES

Readily implemented:

- None can be identified.

Development needed:

- The Central Laboratory should have the capability to perform mineralogical analyses of sediment samples. This would aid in characterizing a system, in providing a means of distinguishing natural from anthropogenic inputs, and in identifying anomalies. It would also aid in identifying phases having high and low sorptive capacities to complement cation-exchange capacity and other measurements.

Research needs:

- Sediments should be examined for surface phenomena by scanning electron microscopy (SEM) or other means. SEM would provide a better characterization of fine-grained material than does x-ray diffraction and could be used to examine surficial coatings and their chemistry.

PHYSICAL PROPERTIES

Readily implemented:

- None can be identified.

Development needed:

- Methods should be evaluated for separation of various size fractions down to <2 μm, and one or more methods should be implemented that do not alter the sample chemical composition significantly and can be used in laboratories or field service units. Knowledge of the chemical composition of various size fractions is needed to gain insight into the potential for physical dispersion and transport of chemical constituents on sediments.
- Determinations of surface area by dye tests should be provided. These are needed to normalize partition coefficients to surface areas (giving distribution coefficients) and will be needed for modeling of constituent movement.
- The need for surface-area determinations by monolayer gas adsorption (BET) should be evaluated and, if appropriate, the capability established within WRD. This is the accepted method for determining surface areas on a wide range of materials, and it should be compared with the dye method to increase understanding of its utility and applicability.
- Methods of determining exchange characteristics should be evaluated and implemented. These are needed for chemical modeling and for estimating absorption capacity. Methods would include determining surface charge, cation exchange capacity, buffering capacity of water, and others.

SAMPLING METHODOLOGY

It is often necessary to compare the concentrations of chemical constituents on bed materials between and within regions and streams, and with time. There are many situations in which concentrations of constituents in various size fractions are needed to help address questions that cannot be adequately addressed by analyzing a single size fraction. Finally, it is unclear how to determine a constituent load on suspended sediments with minimal effort.

It is not advisable to have a single procedure for all sediment investigations. To do so would constrain programs in an undesirable way. The emphasis of the following discussion is on procedures for monitoring programs that are designed to compare sediment chemical composition among rivers and to evaluate changes in sediment chemical composition in a single river over a period of years.

Readily implemented:

- When only one sample is to be collected annually at a site, it should be collected after an extended period of low flow typical of the stream. It is generally believed that random variations affecting chemical composition are minimal during this period.
- At the first visit, and periodically thereafter, three to five bed-material samples (more in large rivers) should be collected in the cross section and a standard total size fraction analysis performed. Chemical analyses should be performed on the <16-μm fraction of each sample at a minimum, but preferably on all fractions from <2 mm to <2 μm to indicate variation across the channel and to provide a basis for determining the fraction or fractions to be analyzed and the numbers of samples in the cross section needed in the future.
- Bed-material samples should be taken with a BM-54, BM-60, or BM-80 from the surface to the depth of penetration.
- Bed-material samples should be wet-sieved using native water in the field to separate the <62-μm fraction using a stainless steel sieve (organic analysis) or a plastic sieve (inorganic analysis). Sieved material should be dewatered in the field, if possible, by filtration through 0.45-μm membrane filter (inorganic analysis) or an organic-free glass-fiber or silver membrane filter (organic analysis). This method represents current preference; other methods are possible and may prove preferable upon further evaluation.

Development needed:

- Tests for contamination of a sample intended for inorganic analysis by crimped (not soldered) stainless steel sieves should be performed. If contamination is insignificant, the plastic sieve may be eliminated.
- The glass-fiber filter, 0.3-μm nominal pore size, should be tested for loss of the <16-μm fraction. If losses are insignificant, an

organic-free glass-fiber filter may be used for dewatering all samples.

- Better methods are needed for the collection of suspended-sediment samples at the leading edge (rising limb) of the storm-runoff hydrograph. Accurate data in this region of a hydrograph are needed to compute storm loads and to gain a better understanding of transport processes during storms.

Research needed:

- Differences between oxic and anoxic bed materials that are significant to monitoring programs with respect to sampling procedures should be determined, as should constituents that require different sampling procedures.

TECHNOLOGY TRANSFER

TRAINING

Readily implemented:

- A training course should be established and coordinated by the Quality of Water Branch to begin developing the expertise for using sediment-chemistry information in field investigations.

ADVISORY GROUPS AND WORKSHOPS

Readily implemented:

- Workshops on sediment-constituent relations should be held biennially at the National Training Center. Non-WRD investigators should be included as guest speakers. These workshops should be oriented toward the objective of periodic review of the field of sediment chemistry for guidance on new operational techniques and research directions.
- Regional workshops for District water-quality specialists should be convened periodically to address problems and methods in sediment studies. A group of speakers from USGS's Quality of Water Branch, National Research Program, and Regional offices and from outside WRD could present workshops in all regions.
- A Sediment Chemistry Task Group composed of two representatives each from the Operational Program, the National Research Program, and the Central Laboratory and coordinated by the Quality of Water Branch should be maintained to advise the WRD on operational, development, and research needs and on the suitability of new methodology for transfer to the operational programs.
- A team of advisers from the National Research Program should be selected. Their availability should be made known to Regional and District Water Quality Specialists, who would advise project leaders in making contacts.

CONCLUDING REMARKS

As the WRD moves into this new and enormously complex area of inquiry, the state of the science will change rapidly and the remarks of the participants recorded here in summary and in individual contributions following may be superseded many times over. Nevertheless, it is the hope of the editors of and contributors to this circular and the participants in this workshop that a good beginning has been made, that these efforts will stimulate further investigations by all groups within the WRD, and that new programs will be developed thereby.

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A REVIEW OF PHYSICAL AND CHEMICAL PARTITIONING OF INORGANIC CONSTITUENTS IN SEDIMENTS

By Arthur J. Horowitz

INTRODUCTION

Historically, investigators in the Water Resources Division (WRD) have attempted to measure inorganic constituent concentrations in aquatic systems by analyzing water samples. This entails the determination of concentrations of total and dissolved constituents, respectively, in unfiltered and filtered water. Concentrations associated with suspended sediment are not determined directly but by the difference between total and dissolved concentrations. It is well recognized that this approach casts doubt on the accuracy and precision of the sediment-borne concentrations because the concentration of the suspended sediment is often a small difference between two larger concentration values. As a result, water quality tends to be evaluated on the kinds and concentrations of various constituents found in solution (Feltz, 1980). However, in most aquatic systems, the suspended sediment plus the top few centimeters of bed sediment (which are usually involved actively in downstream transport) contain many times the concentration of certain inorganic constituents than are dissolved in the water column. The strong association of numerous inorganic elements and compounds (e.g., As, Hg, Cd, Pb, Zn) with suspended and bed sediments means that the distribution, transport, and availability of these constituents cannot be evaluated accurately solely through the sampling and analysis of the dissolved phase. Moreover, bed sediments are a reservoir of these constituents, which could, under certain physicochemical conditions, dissolve into the water column or otherwise enter the food chain. Finally, several inorganic constituents can degrade or react with other constituents to form soluble and possibly even more toxic forms (e.g., the conversion of elemental mercury to methyl mercury). Thus, to develop a comprehensive understanding of inorganic water quality, one that incorporates the distribution, transport, and availability of constituents, data on suspended and bed sediments as well as on the dissolved phase must be used.

Currently, the WRD lacks the capability to accurately determine either the total concentration of inorganic constituents or their partitioning in suspended and bed sediments. The term "total" refers to the concentration of inorganic constituents after complete dissolution or decomposition of the sample and should not be confused with the term "total recoverable," which refers to a variable fraction of the total that may be obtained by a defined chemical attack or extraction. The term "partitioning" implies both a physical and a chemical separation. "Physical partitioning" refers to the separation of a sediment sample into various physical categories such as by grain size, specific gravity, magnetic properties, and mineralogy. "Chemical partitioning" refers to the separation of various inorganic constituents with respect to their association with other materials in the sample (e.g., humic acids, carbonates, manganese oxides, sulfides, silicates) as well as to the type of association that exists (e.g., adsorption, complexation, substitution within mineral phases). For convenience, the two types of partitioning are discussed separately; in fact, the two types are closely related, and the dividing line between them is far from clear.

Data on both total concentration and concentrations present in the "partitions" mentioned above are necessary to begin to identify sources and sinks and the fate and potential effects of toxic or environmentally necessary inorganic constituents. Similarly, such information is a requisite for transport modeling, for estimating cycling rates, and for inferring the availability of inorganic constituents to an ecological system.

PHYSICAL PARTITIONING OF SEDIMENTS

SURFACE AREA AND GRAIN SIZE

One of the most significant factors controlling the capacity of sediment (both suspended and bed) to retain inorganic constituents is grain size (Goldberg, 1954; Krauskopf, 1956; Goldberg and Arrhenius, 1958; Hirst, 1962; Jenne, 1968; Kharkar and others, 1968; Gibbs, 1973; Horowitz, 1974; Gibbs, 1977; Stoffers and others, 1977; Jones and Bowser, 1978; Filipek and Owen, 1979; Jenne and others, 1980; Thorne and Nickless, 1981). This control is expressed primarily by the finer size fractions and results from both physical and mineralogical factors. Clay-sized sediments (<2 μm) have surface areas measured in square meters per gram, for example, whereas sand-sized particles have surface areas usually measured in tens of square centimeters per gram (Grim, 1968; Jackson, 1975; Jones and Bowser, 1978). As a result of the importance of surface reactions to inorganic-sediment interactions, fine-grained sediments are the main site for the transport and collection of these materials (Krauskopf, 1956; Jenne, 1968; Gibbs, 1973; Jones and Bowser, 1978; Jenne and others, 1980). Additionally, Jenne (1976) indicates that clay-sized particles can also be viewed as mechanical substrates upon which inorganic constituents can concentrate; as such, surface area is extremely significant and increases with decreasing grain size. It should be borne in mind that inorganic substances can concentrate on larger substrata, including sand, pebbles, cobbles, and boulders (Filipek and others, 1981; Robinson, 1982); however, higher concentrations are more commonly associated with fine-grained material.

MINERALOGY AND COMPOSITION

Compositional control entails a number of considerations. However, it generally appears that the most significant sedimentary "collectors" of inorganic constituents are thermodynamically unstable, amorphous or cryptocrystalline mineral phases capable of extensive substitution, and tend to be concentrated in the finer size ranges (<62 μm) (Jones and Bowser, 1978). The most common materials meeting these criteria are clay minerals, organic matter, and manganese and hydrous iron oxides. Forstner (1982) has listed these materials according to their ability to collect inorganic constituents as follows: manganese oxides>humic substances>hydrous iron oxides>clay minerals. This sequence is based on chemical extraction studies. Within each category there is substantial variability, depending on the geochemical character of the environment (e.g., pH, Eh), the available substrates (e.g., type of clay minerals, presence of organic matter), and the metals involved.

Hydrous iron (Fe) and manganese (Mn) oxides have long been known to be excellent scavengers of metals in solution (Goldberg, 1954; Krauskopf, 1956). The most spectacular demonstration of this effect are the Mn nodules located at the sediment–water interface on deep ocean floors or lake beds (Mero, 1962; Moore and others, 1973). Manganese micronodules are found in grab and core samples, indicating that they are ubiquitous and play a significant role throughout the sediment column as inorganic collectors in aquatic environments (Goldberg and Arrhenius, 1958; Jenne, 1968; Chester and Hughes, 1969; Moore and others, 1973; Dymond and others, 1973; Duchart and others, 1973; Cronan and Garrett, 1973; Horowitz, 1974; Lee, 1975; Horowitz and Cronan, 1976; Jones and Bowser, 1978; Forstner, 1982). Micronodules have been found in a variety of sizes, but, as their name implies, they tend to occur in the smaller (<20 μm) size ranges (Goldberg and Arrhenius, 1958; Chester and Hughes, 1969; Dymond and others, 1973; Horowitz, 1974). In soils and suspended sediment, as well as in many bed sediments, hydrous Fe and Mn oxides commonly occur as coatings on various minerals and finely dispersed particles (Forstner and Wittmann, 1979). Forms most capable of concentrating inorganic constituents range from amorphous to microcrystalline to crystalline and have 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 act as significant concentrators of inorganic substances in aquatic systems.

The ability of organic matter (humic substances, primarily) to concentrate inorganic constituents in and on soils and suspended and bed sediments is well recognized (Goldberg, 1954; Krauskopf, 1956; Kononova, 1966; Swanson and others, 1966; Saxby, 1969; Schnitzer and Kahn, 1972; Gibbs, 1973; Bunzl and others, 1976; Jenne, 1976; Stoffers and others, 1977; Nriagu and Coker, 1980; Ghosh and Schnitzer, 1981; Forstner, 1982). Gibbs (1973), among others, has indicated the importance of organic molecules in controlling metal concentrations on and in suspended and bed sediments, and in sediment–water interactions. Saxby (1969) has shown that the relative attraction between metals and organic matter associated with colloidal, suspended, and bed sediment can range from weak and readily replaceable (adsorption) to strong (chemically bonded). The ability of organic matter to concentrate inorganic constituents varies with the constituent and the type of organic matter (Swanson and others, 1966; Saxby, 1969; Rashid, 1974; Bunzl and others, 1976; Jonasson, 1977). Organic matter can concentrate between 1 percent and 10 percent dry weight of Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, V, and Zn (Swanson and others, 1966). The ability to concentrate various inorganic constituents appears to be related to the stability of the organic-inorganic constituent complex. In soils, the sequence is Pb>Cu>Ni> Co>Zn>Cd>Fe>Mn >Mg, the Irving-Williams Series (Irving and Williams, 1948). Similar results have been found for aquatic organic matter (Swanson and others, 1966; Saxby, 1969; Rashid, 1974; Bunzl and others, 1976; Jonasson, 1977). The concentration of aquatic organic matter, as indicated by such parameters as total organic carbon and total organic nitrogen, tends to show a strong positive correlation with decreasing grain size and increasing surface area (Kuenen, 1965; Forstner and Wittmann, 1979). For further discussion of the role of organic matter in aquatic systems, see the paper by Leenheer in this circular.

Clay minerals can act as significant concentrators of inorganic constituents 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, 1982). Clay mineral capacity, especially for cations, is governed by broken chemical bonds around the edges of mineral grains, the substitution of Al for 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 bed sediments and has evaluated the capacity of various types of clays as regards their ability as inorganic concentrators as follows: montmorillonite>vermiculite>illite= chlorite> kaolinite.

The process by which clay minerals concentrate inorganic constituents is not well understood. Studies indicate that reaction rates can be quite fast (tens of minutes), depending on a number of physicochemical factors such as valence, ionic radii, concentration of the constituent, type of clay, pH of the solution, and nature and concentration of competing substrates (Forstner and Wittmann, 1979). An empirical affinity sequence for heavy metals and clay minerals indicates Pb>Ni>Cu>Zn (Mitchell, 1964). More recent studies in European rivers indicate that clay minerals may not play a significant role in the direct concentration of inorganic constituents by, for example, adsorption (Forstner and Wittman, 1979). This would support the view of Jenne (1976) that the major role of clay minerals as inorganic concentrators is as mechanical substrates for the precipitation and flocculation of organic matter and secondary minerals (e.g., hydrous Fe and Mn oxides).

SIZE FRACTIONATION TECHNIQUES FOR CHEMICAL ANALYSIS

The separation of bulk bed-sediment samples into various size fractions has been going on for many years, and the techniques are well documented. More recently, the same types of procedures have been applied to suspended sediments. The separation of sediments for chemical analysis poses several special problems and limitations. The two most serious involve contact with metal sieves (brass, stainless steel) and the use of liquid media. The former involves separations of material larger than 63 μm (silt-sand size break), and the latter involves separations smaller than 63 μm.

Metal sieves cause difficulties for two reasons. The abrasion caused by sediment grains during the sizing process may contaminate the sediment with finely divided bits of metal. This is particularly true for brass sieves. Stainless steel meshes are less subject to abrasion. However, the meshes of all metal sieves are held in their frames by solder or weld, which are quite soft and more subject to abrasion than the meshes. Polyester meshes held in plexiglass or acrylic frames are preferable to metal sieves but still tend to abrade easily. Accurately made meshes are available down to 30 μm.

Particle size separations below 63 μm generally employ a liquid medium and are based upon Stokes Law. The most common procedures employed in the WRD are pipet and bottom tube withdrawal using distilled or native water as the settling medium. To improve dispersion and to facilitate settling, a dispersant such as sodium hexametaphosphate is added; if significant amounts of organic matter are present, hydrogen peroxide is also added and the sample heated to decompose organic material binding the mineral grains (Guy, 1969). Dispersants can alter sediment chemistry by adding major cations such as sodium (Na) and calcium (Ca), and may cause the release of inorganic constituents held in ion exchange or on adsorption sites. Hydrogen peroxide, in conjunction with heating, can solubilize organic matter and organic coatings and may attack clay minerals. These effects make results of subsequent chemical analysis of the separated size fractions dubious, because they might not reflect natural chemical content and, further, would make it extremely difficult to relate the size fraction chemistry back to the chemistry of the unsized initial sample.

If neither dispersants nor hydrogen peroxide are used, settling could be an acceptable procedure depending on the settling medium. Settling in native water collected at the same time as the sediment sample is preferable to settling in distilled water because of differences in ionic strength. Distilled water has a significantly lower ionic strength than most natural waters, and its use could lead to the changes in inorganic constituents held as adsorbates or in ion exchange sites. Despite this, Jenne and others (1980) recommend the use of distilled water, and appear to have carried out successful sizing procedures for subsequent chemical analysis. Pilkington and Warren (1979) have had success using acetone as a settling medium. If little or no inorganic constituents are held as adsorbates or in ion exchange sites (Forstner and Wittmann, 1979), the ionic strength of the settling medium could be insignificant. However, other workers (Nissenbaum, 1972; Dymond and others, 1973) have reported that even distilled water is capable of leaching significant amounts of inorganic constituents from sediments. Therefore, the use of any medium but native water must be approached with caution.

Sizing by settling in liquid media has one additional problem. The procedures require removal of fixed-volume aliquots over time. Unlike sieve analyses, each aliquot contains the entire range of particles smaller than a certain size. For example, the <32-μm fraction also contains 16 μm, 8 μm, 4 μm, 2 μm, and smaller particles (Guy, 1969). Therefore, any attempt to determine the chemical concentration of a specific size fraction (e.g., 16–32 μm, 8–16 μm) must be done indirectly by the subtraction of the analytical results from two withdrawal aliquots. This type of procedure has the same drawbacks as the current method of determining chemical concentrations in suspended sediments.

The problems associated with liquid-medium sizing procedures, for the range <2 μm to 62 μm, could be avoided by using dry separation methods. Several procedures are currently available. One problem associated with dry procedures is obtaining a disaggregated sample. Air or oven drying produces a hard cake or sediment clumps, which are not amenable to sizing procedures. However, freeze-drying (lyophilization) leaves a friable, reasonably dissaggregated sediment sample (Charm, 1967; Horowitz, 1974). If this procedure is preceded by ultrasonic shaking, disaggregation is nearly complete. Very fine sieves (as small as 5 μm) are available and, if used with ultrasonic shakers, could be employed for sizing sediment. Unfortunately, these sieves are metallic and very fragile, and the possibility of metal contamination remains. An alternative is air elutriation which uses air spirals of varying magnitudes to accomplish size separations (Ashley, 1979). These size separations are reproducible, and experimental evidence indicates that chemical analyses of the various size fractions separated in this manner can also be related back to bulk chemical analyses (Horowitz, 1974).

Many investigators have indicated that the <2-μm fraction may be most important as regards the retention of various inorganic constituents (Armstrong, 1958; Durum and Haffty, 1963; Hem and Robertson, 1967; Hem and others, 1973; Kennedy and others, 1974; Jenne and others, 1980). Sediment size separations below 2 μm have been attempted only in liquid media, by settling, centrifugation, or filtration (Jackson, 1958; Kennedy and others, 1974). Problems with liquid-medium size separations have already been discussed. Dry techniques have not been attempted. A procedure that might be applicable for dry separations of <2 μm size material is that used for the sampling and sizing of airborne particulates. The equipment comes under the general heading of air-impact samplers or cyclone samplers (Liu and others, 1980). Experiments with sediment would have to be carried out in order to evaluate the utility of this equipment for sediment size separations for subsequent chemical analysis.

UTILITY OF SIZE FRACTIONATION FOR CHEMICAL ANALYSIS

The chemical analysis of sedimentary material, both bulk and separated size fractions, can offer a powerful interpretive or predictive tool to differentiate hydrologic settings or systems. Horowitz (1974), Summerhayes and others (1976), and Jenne and others (1980) have indicated that chemical analysis of specific size fractions can facilitate intra- and interareal comparisons because it can eliminate differences imposed by size variations. For example, if a constituent is known to be associated with a particular size fraction and comes from a point source, other size particles from other sources could act as diluents for the constituent-bearing fraction. Thus, tracing the extent or areal distribution of the constituent from a particular source could become impossible using the bulk sample alone. For example, Horowitz (1974) was able to determine the presence and chemical contribution of Icelandic volcanic ash and glass in an apparently biogenic-rich sediment several hundred kilometers from the Icelandic coast by analyzing individual size fractions. By combining grain size chemistry with such factors as streamflow velocities, current speeds, or tidal bore rates, it may be possible to develop predictive models for inorganic constituent transport rates. Transport rates are also needed for the development of models of geochemical cycles.

Although the <2-μm fraction of a sediment sample may represent a small percentage of the bulk sedimentary composition, its effect on sediment chemistry can be dramatic. The data in table 1 show trends that are typical for sediments from the Atlantic and Pacific Oceans for Cu.

The sample displays a bimodel grain size distribution with peak concentrations at <2 μm and at 10-20 μm. Typically, the <2-μm material is either waterborne or due to in-place chemical weathering or precipitation. The 10-20-μm fraction comes from aeolian contributions and authigenic mineral formation (Rex and Goldberg, 1958). Although the <2-μm fraction represents only about 20 percent of the bulk sample, its Cu contribution amounts to 75 percent of the total Cu in the sample. On the other hand, the 10-20-μm fraction Cu contribution amounts to only 9 percent of the total Cu, even though it is the largest single size fraction in the sample.

TABLE 1.—*Distribution of Cu in a marine sediment sample, by size fraction*

[Previously unpublished data from Horowitz, University of Miami, 1970]

Size fraction (μm)	Percent of fraction in sample	Cu concentration (mg/kg)	Contribution to sample (mg/kg)[1]
<2	20	750	150.0
2-6	15	60	9.0
6-10	18	110	19.8
10-20	30	60	18.0
20-32	10	25	2.5
32-64	7	20	1.4
Total	100%		200.7

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[1] Contribution to the sample was calculated by multiplying the chemical concentration in each size fraction by the percentage that size fraction represented in the bulk sample.

The data presented in table 2 provide a second illustration of the utility of chemically analyzing separate sedimentary size fractions. Both samples are marine sediment. One sample (AD 600) was collected from a seismically active area, the other (AD 500) from a seismically quiet area. The samples have similar total Mn concentrations (~3,550 mg/kg) and similar grain size distributions, but there are significant differences in the content between size fractions. Sample AD 600 has two significant Mn peaks, one in the <2-μ m fraction and the other in the 10-20-μ m fraction. Sample AD has a similar Mn concentration for all size fractions from <2 to 32 μm. Subsequent mineralogical analysis and chemical partitioning studies indicated that the Mn peaks in AD 600 were due to Mn oxide coatings and Mn micronodules and the Mn in AD 500 were due to volcanic ash and glass. Differentiation of the two samples cannot be made on the basis of either grain size distribution or bulk chemical data. Mineralogical examination might have revealed the different source materials, but such examinations are very difficult, particularly when dealing with clays and cryptocrystalline material (volcanic ash and glass versus Mn oxides). The chemical analyses of the various size fractions provided a means for clearly differentiating the two samples.

CHEMICAL PARTITIONING OF SEDIMENTS

To better understand the distribution of inorganic constituents in sediments, and to be able to

TABLE 2.—*Distribution of Mn in two marine sediment samples, by size fraction*

[Previously unpublished data from Horowitz, Imperial College, London, 1973]

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

[1] Contribution to the sample was calculated by multiplying the chemical concentration in each size fraction by the percentage that size fraction represented in the bulk sample.

predict how these constituents will behave under changing physicochemical conditions, it is important to understand how and where they are held. Conceptually, particles could be separated according to size and mineralogy either instrumentally (e.g., by magnetic separators, heavy mineral flotations) or manually (picking out mineral grains with the aid of a microscope) prior to chemical analysis (Francis and Brinkley, 1976; Pilkington and Warren, 1979). A physical separation alone, however, would not enable identification of phases attached to the particles such as hydrous Fe and Mn oxides and organic coatings. (Instrumentation for examination of coatings is developing rapidly; this approach may be practical in the future.) By current practice, some physical separation techniques may alter the sample chemistry, and some are very time consuming. In addition, it is virtually impossible to physically separate the individual mineral grains in the finer size ranges, such as the clay minerals (Pilkington and Warren, 1979).

Chemical partitioning of sediments involves the use of various sequential chemical extractions to dissolve individual phases (Chester and Hughes, 1967; Brannon and others, 1976; Nriagu and Coker, 1980). These methods have the advantage of being relatively simple to carry out compared with actual mineral separations but the disadvantage of being more difficult to interpret than the direct chemical analysis of individual mineral grains or phases. This difficulty results, in part, from the lack of specificity of some of the chemical extractants.

Other, indirect approaches to partitioning involve the statistical treatment of bulk sediment chemical data or the construction of mathematical models that attempt to predict phase associations. Factor analysis has been applied to bulk sediment chemical data to identify the various phases present in complex marine sediments (Leinen and others, 1980; Pisias and Leinen, 1980). Mathematical models, based on thermodynamic or experimentally derived data, that attempt to predict phase associations on the basis of pH, Eh, substrates, and concentrations in solution have been developed (Oakley and others, 1980; Swallow and Morel, 1980; Benjamin and Leckie, 1981). Both types of methods are probably the easiest to apply since only bulk sediment chemical data and supporting physical and chemical measurements in the water phase are required. However, as the authors of the papers cited above have noted, statistical analysis is rarely unambiguous and the models, at the present stage of development, are oversimplifications of complex environmental systems.

Approaches to chemical partitioning are of two types: attempts to determine how inorganic constituents are retained on or by sediments (mechanistic) and attempts to determine where inorganic constituents are retained (phases or sites).

According to Gibbs (1973), there are five major mechanisms for inorganic accumulation in or on sediments: (1) adsorption on fine-grained material, (2) precipitation of metal compounds, (3) coprecipitation with hydrous Fe and Mn oxides and carbonates, (4) association either by adsorption or by organometallic bonding with organic matter, and (5) incorporation in crystalline minerals. Individual constituents may be associated with several phases (interstitial water, clays, sulfides, carbonates, humic acids, pyroclastics, and others). Partitioning by phases or sites has been attempted by Jones and Bowser (1978) and by Pilkington and Warren (1979).

In terms of such factors as bioavailability and residence times, and for the investigation of geochemical cycles, the mechanistic approach may be more relevant. For the determination of transport rates and the identification and location of sources and sinks, the phase approach may be more useful. Regardless, very few attempts to chemically partition complex sediment samples entail a purely mechanistic or phase approach, but combine aspects of both.

PARTIAL CHEMICAL EXTRACTIONS

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, with some emphasis on Mn nodules and oxides (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 Messiha-Hanna, 1970; Cronan and Garrett, 1973; Horowitz, 1974; Horowitz and Cronan, 1976). These early procedures usually involved two-step or three-step separations, used in a sequence of increasing strength, which attempted to partition trace metals. For example, Chester and Hughes (1966, 1967, 1969) employed two reagents, 25-percent volume/volume acetic acid and a combined acid-reducing agent made from hydroxylamine hydrochloric acid in 25-percent volume/volume acetic acid. Metals extracted by the former were said to be associated with carbonates or held as adsorbates. The additional metals extracted by the latter were thought to be associated with ferromanganese oxides. The constituents extracted by both reagents were said to be authigenic and to have a hydrogenous character. Metals associated with the residue after both extractions were termed detrital or were said to have a lithogenous character. Chester and Hughes found that such metals as Mn, Ni, Pb, and Co were hydrogenous and that others, such as Cr, V, Fe, and Ba were lithogenous. It should be pointed out that the terms "hydrogenous" and "lithogenous" have operational definitions in that they refer to the constituents removed by the extraction reagents; they do not refer to a phase in the thermodynamic sense (Jones and Bowser, 1978).

Cronan and Garrett (1973), Horowitz (1974), and Horowitz and Cronan (1976) used similar procedures, with the addition of a stronger extraction (hot 50-percent volume/volume hydrochloric acid), to investigate metalliferous surface and basal marine sediments. In these sediments, much of the Mn was hydrogenous while most of the Fe was soluble in the hydrochloric acid. Other metals, such as Ni, Cu, and Co, were removed in varying concentrations, by all extractions. The extraction data indicated that metal partitioning in basal and surface metalliferous sediments was similar, suggesting that the mode of formation of the two was the same. This could not have been inferred on the basis of bulk sediment chemical data alone because the data were insufficient to differentiate between metals that were authigenic or detrital in origin.

Further advances in chemical partitioning using sequential partial extractions have been made by workers in such divergent fields as soil science, biology, freshwater geochemistry, and airborne particulate chemistry (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). Many of these studies employed partial chemical extractions in an attempt to differentiate between anthropogenic and natural metal sources and to predict or estimate bioavailability.

As attempts to more clearly determine inorganic-sediment chemical partitioning proceeded, the sequential extraction schemes became more complex. For example, Summerhayes and others (1976) and Stoffers and others (1977) carried out a six-step sequential extraction procedure on sediments from Buzzards Bay, Mass., which included (1) 1:1 methanol:benzene (bitumen fraction extraction, (2) cation exchange extraction, (3) humic acid extraction, (4) fulvic acid extraction, (5) authigenic mineral extraction, and (6) resistant mineral extraction. Forstner (1982) recommends a seven-step sequence including (1) exchangeable cations, (2) carbonate fraction, (3) easily reducible phases, (4) moderately reducible phases, (5) nonsilicate Fe phases, (6) organic fractions, and (7) detrital silicates. Working with riverine and estuarine sediments, Brannon and others (1976) used an equally complex series of extractions to investigate partitioning; Schmidt and others (1975) used a nine-step sequence to study Cu partitioning in Sequim Bay, Oreg., sediments.

The foregoing review is not intended to be exhaustive but simply to highlight the extent to which chemical extractions have been used to determine partitioning in sediments. As a summary, most of the various extractants are listed in table 3; more than 30 different reagents have been tried.

Although sequential chemical extractions have been used widely, as an interpretative and pre-

TABLE 3.—*Reagents employed in sequential partial chemical extractions*

Phase/Mechanism	Extractant	Reference
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* HN_2OH•HCl w/25% v/v HOAc	Chester and Hughes, 1967
Moderately reducible	Oxalate buffer	Schwartmann, 1964
(hydrous Fe oxides).	Dithionate/citrate buffer	Holmgren, 1967
Easily reducible (Mn and amorph. oxides).	0.1 *M* NH_2OH•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 2.5	Engler and others, 1976
	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 *M* 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
	0.1 *N* NaOH w/H_2O_2 w/HNO_3, pH 2	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	$HF/HClO_4/HNO_3$	Forstner and Wittmann, 1979
	Borate fusion w/HNO_3	Forstner and Wittmann, 1979

dictive tool, on a variety of soils and sedimentary material from differing environments, they should not be viewed as a panacea; there are serious problems with a number of the procedures currently in use. In some cases, the extraction steps are not as "selective" as may be indicated (Malo, 1977; Pilkington and Warren, 1979). Reducible fractions, upon retreatment, often release additional constituents (Heath and Dymond, 1977). Under basic conditions, which occur during humate extractions with sodium hydroxide (Schnitzer and Kahn, 1972, 1978) or sodium pyrophosphate (Kononova, 1966), soluble basic metal oxides may form (Patchineelam and Forstner, 1977; Burton, 1978). Also, as Forstner (1982) points out, readsorption of metals can occur after dilute acid or hydrogen peroxide extractions, and extraction efficiencies are affected by the length of treatment and the ratio of extractant volume to sediment.

Despite these drawbacks, there are several advantages to sequential partial chemical extractions. Compared with picking out individual components and chemically analyzing them, the extractions are simpler and less labor intensive. They permit differentiation between samples that have similar bulk chemistries. They represent one of the few practical methods currently available for determining concentration mechanisms and, as such, provide a possible means of estimating bioavailability. Finally, they also can provide a means of predicting how various inorganic constituents associated with sediments might behave under changing physicochemical conditions.

CHEMICAL ANALYSIS OF SEPARATED PHASES

Studies involving physical mineralogical separations followed by chemical analysis to determine inorganic partitioning are not as common as partial chemical extractions. The approach has been used on nearshore sediments (Pilkington and Warren, 1979) in industrial mineral processing (Muller and Burton, 1965), and soil mineralogy (Francis and others, 1972). The approach involves three stages: size fractionation, followed by a mineralogical separation of each size fraction, followed by the chemical analysis of each mineral or organic phase.

An example is the procedure used by Pilkington and Warren (1979). Size fractionation was accomplished by suspending the sediment in acetone, ultrasonically shaking to provide disaggregation, and separation into three size ranges by settling. Mineralogical separations were achieved on the basis of specific gravity differences using heavy mineral flotation with tetrabromoethane: acetone to produce density ranges from 2.75 to 2.20. The liquids were layered in centrifuge tubes, the sediment placed on top, and the tube spun in a centrifuge. Mineralogical identifications were made on each density fraction, many of which were found to be mixtures. Where sufficient material was available, mineralogy was partially quantified using x-ray diffraction or differential thermal analysis. Each density fraction was then subjected to chemical analysis. Because of the initial size and density separations, the uncertainty in assigning chemical partitioning was reduced. Pilkington and Warren (1979) indicated that the use of neither acetone nor tetrabromoethane affected the chemistry of the various size and density fractions. However, they do add the caveat that this type of procedure is of limited value when there is a significant proportion of $< 2\text{-}\mu m$ particles. A similar procedure was used by Francis and Brinkley (1976) to partition ^{137}Cs in micaceous minerals in a contaminated sediment; a mechanical rotor system was used for density separations.

Jones and Bowser (1978) used chemical treatments (analagous to partial chemical extractions) to determine mineralogy of lacustrine sediments; then, using bulk chemical data along with the x-ray-determined mineralogy, attempted to assign concentrations to various phases. Connection between phase and chemical composition was inferred from the amounts of constituents released by each chemical extraction.

Besides the problems associated with significant quantities of fine-grained material, there are other potential drawbacks to separating phases prior to chemical analysis. Although the reagents involved seemed to have little or no effect on sediment chemistry (Pilkington and Warren, 1979), the method has received limited testing (only two nearshore sediments were partitioned). Based upon the work of Nissenbaum (1972), which showed significant loss of inorganic adsorbates in distilled water, it is questionable whether acetone and tetrabromoethane will leave all sediment types unaffected. Nevertheless, if the reagents can be shown not to alter the chemistry, the technique might have considerable practical application.

Relatively new chemical analytical techniques can also be used to directly determine chemical partitioning in sediments. These methods permit quantitative analysis of various minerals or mineral assemblages, in place and sometimes nondestructively, from areas as small as 1 μm (Johnson and Maxwell, 1981). Such techniques as x-ray photoelectron spectroscopy have been used on many types of geological materials, including sediments, with mixed success (Jones and Bowser, 1978; Johnson and Maxwell, 1981). Many of these procedures permit the user to select the site for analysis, thus making phase associations possible for the derived chemical data. The electron microprobe uses a narrowly focused electron beam to cause x-ray emissions which are detected and analyzed with a wavelength or energy dispersive spectrometer (Skoog and West, 1980). X-ray photoelectron spectroscopy (ESCA), ultraviolet photoelectron spectroscopy, electron impact spectroscopy, and Auger spectroscopy all use a beam of photons to produce an excited ion and an electron. All are coupled with electron spectrometers as detectors which sort electrons according to energy, permitting detection and quantitation (Skoog and West, 1980).

Although these techniques are promising, several problems limit their utility, the foremost being 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 mg/kg and can be significantly higher (Johnson and Maxwell, 1981). This tends to limit the usefulness of these procedures to major elements such as Fe, Mn, and Na, and would exclude such environmentally important trace elements as Pb, Cd, Ag, and Cu. Another problem is surface roughness. These techniques require a smooth surface for maximum efficiency; even fine-grained sediments may lack sufficient smoothness.

STATISTICAL TREATMENT OF DATA AND MATHEMATICAL MODELING

Statistical manipulation of chemical and mineralogical data can be used to clarify the processes by which various inorganic constituents are partitioned on or in suspended and bed sediments, especially when dealing with large data sets (Jones and Bowser, 1978). Statistical treatments range from calculation of correlation coefficients through highly complex cluster and multivariate techniques. For example, Rossman and others (1972) used correlation coefficients to partition bulk chemical data for Fe and Mn nodules from Green Bay, Wis. Because the Fe and 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 partitioning with either the Fe or Mn phases. The Fe phase appears to concentrate Si and PO_4^{3-}, while the Mn phase appears to concentrate Ba, Ni, Co, Mo, Mg, and Sr.

Leinen and others (1980) and Pisias and Leinen (1980) used an extended version of Q-mode factor analysis (a 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 separated five geochemically and mineralogically separate end members (phases): (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 inorganic constituents associated with suspended sediment in the Amazon River. The major transport phases and their relative importance for carrying transition metals are as follows: crystalline particles=hydrous oxide coatings > solid organic material > absorbates.

Luoma and Bryan (1981) applied 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 bed sediments from a number of estuaries. The analyses 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 partitioning of Ag, Cd, Cu, Pb, and Zn, while humic material is also important for the partitioning of Ag and Cu. The results of this study support the view that partitioning is a dynamic process in which various substrates compete for different inorganic constituents and that the relative concentrations of differing substrates strongly influence partitioning (see also Oakley and others, 1980, 1981; Benjamin and Leckie, 1981). Although not specifically stated, it is implied that partitioning can and will change with varying physicochemical conditions (changes in Eh, pH, solute concentrations, solute form, etc.) and with transport and mixing processes owing 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) and Pisias and Leinen (1980) on the Nazca Plate sediments were also applied to relatively homogeneous sediments from other Pacific areas and produced much more ambiguous results (Pisias and Leinen, 1980). Another problem associated with this type of technique is also associated with partial chemical extractions: a lack of sufficient specificity to truly identify phases (identification is by inference). However, the greatest difficulty arising from the interpretation of the statistical treatments 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 that cannot be ascribed to a rational environmental setting or process. 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; Oakley and others, 1980; Pisias and Leinen, 1980; Swallow and Morel, 1980; Benjamin and Leckie, 1981; Oakley and others, 1981). The development of mathematical models and their application to natural environments for determining or predicting sediment-chemical partitioning depend 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 that describe the strength and stability range of inorganic-substrate binding, quantification of inorganic speciation in various strength solutes, Eh, and pH.

Swallow and Morel (1980) studied the behavior of Cu and Pb in the presence of hydrous Fe oxides in artificial 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 hydrous Fe oxide substrate, as well as the precipitation of the hydrous oxides in the presence or absence of the metals in question, had no significant effect. Although the concentration of Cu and Pb in the presence of hydrous Fe oxides in seawater is somewhat analogous to surface complexation, the oxides are better viewed as a three-dimensional metal absorbing sponge that accommodates metal ions into the solid as they hydrolize. These conclusions were based on laboratory experiments. The process was subsequently modeled successfully.

Davis and Leckie (1978) also studied the uptake of Cu and Ag by hydrous Fe oxides and found, as did Swallow and Morel (1980), that uptake varied with pH. However, it was also determined that organic ligands strongly affect trace metal absorption and may enhance or depress the concentration capabilities of the Fe oxides. Some ligands bind to the surface of the hydrous oxides and increase surface collection efficiency, while other ligands remain in solution and compete with hydrous 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 on sediments coated with Fe oxides. This result has been confirmed using mathematical models for several metals, including Cu, Pb, Cd, Co, Ni, and Zn (Vuceta and Morgan, 1978; Benjamin and Leckie, 1981). This is also in agreement with partial extraction studies (Forstner, 1982). Additionally, Benjamin and Leckie (1981) indicate that metal adsorption from aqueous solutions depends on adsorbent and adsorbate concentration and on 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 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. On the basis of these studies, an attempt was made to predict bioavailability through the construction of a mathematical model which was tested in the laboratory using a deposit-feeding polychaete worm. Although the results were ambiguous, the authors concluded that the bioavailability of Cu and Cd from geochemical phases (clay, humic acid, hydrous oxides) to the polychaete could be more significant than the bioavailability of Cu and Cd dissolved in the seawater at natural concentrations.

Mathematical modeling shows some promise for understanding the processes involved and for predicting inorganic partitioning in aqueous-sedimentary systems. However, there are a number of problems associated with modeling 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. Moreover, even in multiphase systems (Oakley and others, 1980, 1981), substrates have been relatively simple compared with 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). Finally, some of the results reported from modeling studies appear to contradict direct observations. For example, Swallow and Morel (1980) claim that adsorption of metals by hydrous Fe oxides is independent of the presence of the metals when hydrous oxide precipitation occurs. The proposed mechanism for metal concentration by hydrous Fe oxides, when studied in the natural environment, has almost invariably been coprecipitation (Cronan, 1974); this conclusion is supported by partial extraction studies (Chester and Hughes, 1966, 1976; Forstner, 1982).

SUMMARY

1. To develop a comprehensive understanding of inorganic water quality, one that incorporates the distribution, transport, and availability of inorganic constituents, data on suspended and bed sediments as well as on the dissolved phase must be employed.

2. Adequate assessment of the role of sediments in water quality requires the capability to determine both total inorganic constituent concentrations and inorganic-sediment partitioning. The term "partitioning" includes a physical and a chemical aspect.

3. The most important aspects of physical partitioning of inorganic-sediment systems are grain size and composition. Compositional control is dominated by hydrous Fe and Mn oxides, organic matter, and clay minerals. Both increasing surface area and increasing concentration of compositional controls show a strong positive correlation with decreasing grain size.

4. To better understand the distribution of inorganic constituents in or on sediments, and to be able to predict how these constituents will behave under differing physicochemical conditions, it is important to know how they are chemically partitioned—that is, how and where they are held (chemically partitioned).

5. Inorganic constituents may be bound on or in sediments by such means as adsorption, complexation, precipitation, and incorporation within lattices (mechanistic) and may be held in such locations as interstitial waters, clays, sulfides, carbonates, organic matter, and hydrous oxides of Fe and Mn (phase).

6. Although there are problems associated with each type of procedure currently used to chemically partition sediments, the most likely means of determining chemical partitioning are partial chemical extractions, the physical separation of various phases followed by chemical analysis, and the statistical treatment of sediment chemical data. Mathematical models, while providing useful information on partitioning processes, are not yet capable of predicting behavior in complex environmental systems.

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ANALYSIS, ASSOCIATION, AND EFFECTS OF ORGANIC CONSTITUENTS OF AQUATIC SEDIMENT

By Jerry A. Leenheer

INTRODUCTION

Organic constituents have long been recognized as one of the most important factors affecting the chemical, physical, and biological properties of aquatic sediments in diverse environments, but definition of the nature and aquatic effects of these constituents has been limited by the complexity of natural organic constituents in sediment, by the difficulty of isolating both natural and contaminant organic substances from sediment for study, and by the lack of interdisciplinary investigations needed to characterize sediment organic constituents.

Aquatic sediment also serves as the primary substrate for various organisms, and this further complicates chemical and physical studies because of biodegradation and biosynthesis of sediment organic constituents. However, given today's state-of-the-sciences, these investigative difficulties are not insurmountable, and a good opportunity exists for major advances in the chemistry of organic substances in sediments by applying recent findings in the diverse fields of aquatic biology, hydrology, physics, and soil science, as well as the various disciplines of chemistry.

The objective of this paper is to identify data and procedural needs for studies of sediment organic chemistry conducted by the U.S. Geological Survey Water Resources Division's operational and research programs. To put these needs in perspective, an overview of current knowledge and research in sediment organic chemistry is presented first.

ASSOCIATION OF ORGANIC CONSTITUENTS WITH SEDIMENTS

NATURAL ORGANIC CONSTITUENTS

The association of natural organic substances can be approximately described by the representation in figure 1. A more structurally precise representation of the association of organic substances with sediment colloids is given by Stevenson (1976), but organic substances are a useful conceptual simplification of natural organic constituents of sediments and will be used throughout this paper. The molecular weight of organic substances in natural surface waters ranges from 500 to 2,000 g/mole (Daltons) (Thurman and others, 1982), but organic substances associated with a suspended lake sediment were found to range between 1,000 to 3,000 Daltons (Davis and Gloor, 1981), and with an aquatic bed sediment, 5,000 to 200,000 Daltons (Kemp and Wong, 1974). Most organic substances associated with sediment can also be described as humic acids having negative charge characteristics which dominate the surface charge properties of many soils and sediments (van Raij and Peech, 1972).

The diverse functional groups possessed by organic substances impart polar amphoteric properties which bind them to inorganic sediments by multiple bonding mechanisms. The high nitrogen content of organic matter associated with aquatic sediments (C:N=7-9:1) versus the low nitrogen content of dissolved organic matter (C:N=20-50:1) (Malcolm and Durum, 1976) indicates the importance of nitrogen-

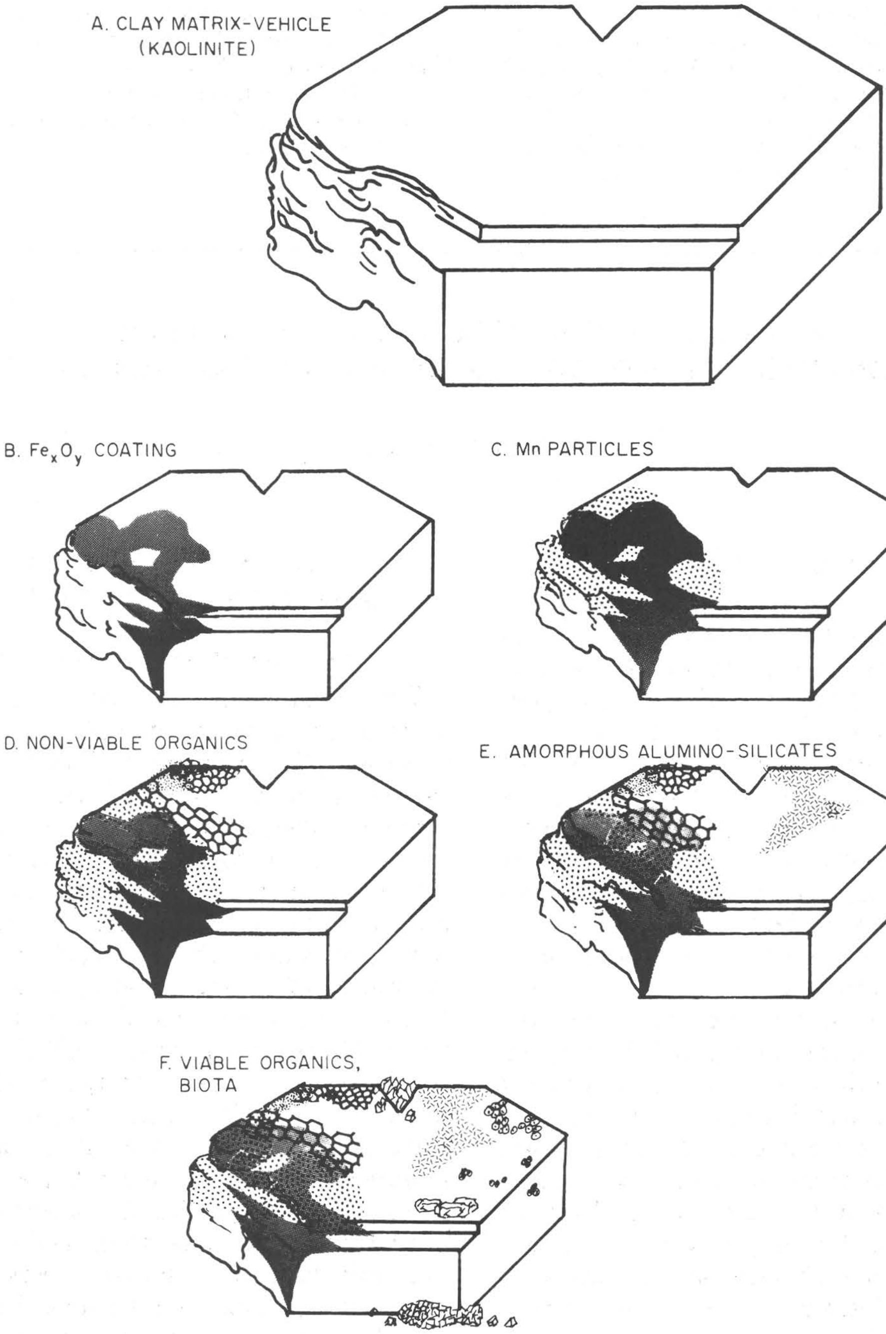
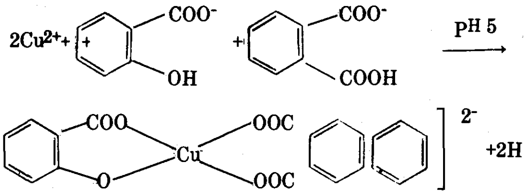


FIGURE 1.—Diagrammatic representation of the important inorganic and organic sinks on the surface of a clay mineral particle (from Jenne, 1977).

containing functional groups in organic substance-sediment interactions. Polysilicic acid surfaces such as clay mineral surfaces are known to form reversible hydrogen bonds with amide and amino functional groups of proteins in the pH range 3 to 9 (Holt and Went, 1959). Wershaw and Pinckney (1980) found strong chemical bonding between clays and amino functionalities of humic acid; this bond was disrupted by destruction of the amino group with nitrous acid.

Negatively charged clays and negative carboxyl groups on organic substances can associate through "bridge bonds" formed by polyvalent cations such as calcium or magnesium; these bridge bonds balance the ionic charge between the clay and organic substances. Polyvalent cations also form mixed clay-organic substance complexes, as summarized by Schnitzer (1978). Phthalic and salicylic complexing sites found in organic substances are thought to be the most important, and iron, lead, copper, nickel, cobalt, and zinc form the strongest metal complexes (Schnitzer, 1978), as shown below:



Alumninum and iron sesquioxide coatings on clay minerals have weakly basic surfaces which can interact with organic substance acid functional groups through hydrogen bonding or ligand exchange, in which organic acid functional groups bond directly with the metal atoms of the oxide lattice (Davis, 1980). These sesquioxide-organic substance interactions may be quantitatively significant because of the ubiquitous nature of sesquioxide coatings on sediments.

Lastly, sediment-bound organic substances may interact with dissolved organic substances to form loosely bound aggregates. DeHaan and DeBoer (1978) found that fulvic acids, proteins, and carbohydrates in lake water form loosely bound complexes in the pH range 3-9, and it is probable that such loosely bound aggregates also occur between organic coatings on sediment and dissolved organic matter.

An important conclusion currently being arrived at by investigators of organic substance-sediment associations is that the surfaces of most aquatic sediments are partially to completely covered by organic substance coatings. These coatings can modify the chemical and physical properties of the surface such that the underlying mineral surface exerts only a minor influence on the surface properties of the sediment particle.

ORGANIC CONTAMINANTS

Organic contaminants (largely manmade) introduced into aquatic systems usually differ greatly from natural organic substances. Their molecular weights are generally below 500, they have few organic functional groups and, as a consequence, are more nonpolar and less soluble in water, and their concentrations are usually a small percentage of natural organic constituents.

Organic contaminants associate with sediment mineral surfaces through the same binding mechanisms discussed in the previous section, but the mineral surfaces of most aquatic sediments are partially to completely covered with organic substance coatings at the time organic contaminants are introduced to water; therefore, binding of organic contaminants is controlled by organic substance surface chemistry.

Probably the most important mechanism of organic contaminant association with sediment is hydrophobic bonding or partitioning of nonpolar hydrocarbon moieties of organic contaminants with hydrocarbon portions of the organic substance structure ("like dissolves like"). The hydrophobic effect, as described by Tanford (1973), is more a thermodynamic phase-partitioning effect driven by the increase in entropy associated with hydrogen-bond formation in the water structure than a weak bonding mechanism sometimes described as van der Waals bonding. Nonpolar hydrocarbon moieties reside in the voids of the molecular structure of liquid water. Solubilities of hydrocarbon moieties are inversely proportional to their size. Increasing size requires larger voids in the water structure which disrupts hydrogen bonds. Because the effect is not favored energetically, water has a tendency to "squeeze out" hydrophobic constituents onto any interface less polar than water. The phenomenon is called the hydrophobic effect. Organic contaminants of low water solubility, such as chlorinated hydrocarbon insecticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons, adsorb on sediment primarily through the hydrophobic effect. Hydrophobic sorption of organic contaminants on sediments was successfully modeled by the linear relationship found to exist between the organic carbon content of sediment and partition coefficients in two-phase water-organic solvent systems (Lambert, 1968). Most of the chemical models correlate the water-octanol distribution coefficient of an organic contaminant with the organic carbon content of natural sediment (Brown and Flagg, 1981). However, as the polar character of the organic contaminant increases, the water-octanol partition coefficient model becomes less applicable (Brown and Flagg, 1981).

Weak-base organic contaminants, such as the triazine- and aniline-based herbicides, interact with organic substances on sediment through hydrogen bonding to weakly acidic carboxyl, enolic, and phenolic hydroxyl functional groups (Bartha and Hsu, 1976). Strongly basic organic contaminants, such as the bipyridylium herbicides, form protonated cations in water and bind to strong-acid groups of organic substances by cation exchange and to electron-donating groups by formation of charge-transfer complexes (Kahn, 1973).

Aromatic amine and phenol contaminants associate with organic substance structures through sorption interactions, but a more important associative mechanism is oxidative coupling of these compounds with phenolic constituents of the organic substance structure (Sjoblad and Bollag, 1981), which converts these compounds to an integral structural component of organic substances. This type of association, called molecular conjugation, is frequently accomplished by enzymatic and microbiological degradation processes. Other types of organic contaminant conjugates include glycoside, glucuronide, amino acid, sulfate ester, glutathione, acyl, and alkyl conjugates (Kaufman and others, 1976).

Organic acid contaminants that exist as negatively charged anions at environmental pH levels (pH 5-9), the phenoxyacid herbicides, for example, are repelled by negatively charged sediment surfaces and remain in aqueous solution. organic substance coatings may increase the degree of repulsion due to enhancement of the negative charge of the sediment surface and deactivation of basic sesquioxide sites where acid sorption might occur.

ANALYSIS OF ORGANIC CONSTITUENTS IN SEDIMENTS

NATURAL ORGANIC CONSTITUENTS

Analysis of organic substance constituents of aquatic sediments is usually performed at three levels of specificity: (1) determination of organic elemental composition (Whitby and Schnitzer, 1978; Wetzel, 1983), (2) determination of compound groups, such as amino acids, amino sugars, carbohydrates, humic compounds, and lipids, released from organic substances by extraction and hydrolysis (Kemp and Johnson, 1979), and (3) structural characterization of extracted organic substance constituents (Kemp and Mudrochova, 1973; Whitby and Schnitzer, 1978). Organic matter in the modern sediments of Lakes Ontario, Erie, and Huron consists of humic compounds (68–83 percent), amino acids (19–20 percent), lipids (2–8 percent), carbohydrates (2–6 percent), and amino sugars (0.5–4 percent) (Kemp and Johnson, 1979). Humic acid is precipitated upon acidification to pH 1, and fulvic acid remains in solution. Structural characterization studies of humic compounds are carried out by alkaline permanganate oxidation, methylation of oxidation products, and gas chromatographic–mass spectrometric determination of the oxidation products (Whitby and Schnitzer, 1978). Pyrolysis-gas chromatography and catalytic hydrogenation have been used to a lesser extent (Schnitzer, 1978), and, recently, proton and C–13 nuclear magnetic resonance spectroscopy have greatly advanced structural studies of humic substances (Hatcher and others, 1981).

The conventional soil organic matter extraction procedure, using sodium hydroxide (NaOH), when applied to aquatic sediments give humic preparations of higher ash contents than those derived from soil (Whitby and Schnitzer, 1978). Povoledo and Pitze (1979) found that low-ash humic acids could be prepared from aquatic sediments by extraction with neutral sodium pyrophosphate ($Na_4P_2O_7$) instead of sodium hydroxide followed by treatment of the crude humic acid with dilute hydrofluoric acid, dialyses, and subfractionation with ultrafiltration membranes. Sodium pyrophosphate extraction may be preferable to sodium hydroxide extraction to prevent oxidation of humic constituents in aquatic sediments, which often are found under more reducing conditions than surface soils. An alternative to organic matter extraction is hydrofluoric acid dissolution of the sediment mineral matrix which leaves organic substance constituents isolated as an acid-insoluble residue (Leenheer and Moe, 1969).

Aquatic organic substance–sediment constituents have generally received less study than soil organic substance constituents, and most analytical procedures are adaptations from soil organic matter studies. It should be recognized that compared with surface soils, aquatic sediments exist under more reducing conditions, have inputs of organic matter produced in the aquatic environment, and are saturated with water. The analyst should take these differences into account in the application of soil procedures to chemical characterization of organic substance structures in aquatic sediments.

ORGANIC CONTAMINANTS

Organic contaminants must usually be isolated from the sediment and water matrix before analysis. These extraction and isolation procedures are combinations of water and soil extraction procedures and include batch solvent extraction (Goerlitz and Law, 1974), Soxhlet solvent extraction (Bellar and others, 1980), steam distillation (Veith and Kiwus, 1977), dynamic headspace extraction (May and others, 1975), and sweep codistillation (Shaw and others, 1976). Batch solvent extraction is the most commonly used procedure: moist sediment is extracted with polar-nonpolar solvent pair combinations such as acetone-methylene chloride, acetone-hexane, and methanol-benzene. The polar solvent removes the water from the sediment surface, allowing extraction of the organic contaminant into the organic phase. The crude extract is then back-extracted with water to remove water and the polar solvent, the elemental sulfur produced as a byproduct of oxidation of sulfide by the solvent is removed from the extract by reaction with copper or mercury, and the extract is freed of extracted polar constituents by direct phase column chromatography on Florisil, alumina, or silica. The solvent is evaporated using Kuderna-Danish concentrators, and the contaminants are determined with gas and liquid chromatographic procedures which use mass spectrometric, ultraviolet, or infrared detectors. This extraction, concentration, and detection scheme has been used with great success for nonpolar organic contaminants but will not work with polar contaminants which are not efficiently solvent-extracted. Techniques such as steam distillation, acid or base extraction combined with ion exchange fractionation, and freeze-drying followed by derivative formation are better matrix-isolation procedures for polar organic contaminants.

Bound contaminant residues in soil are defined as "that unextractable and chemically unidentifiable pesticide residue remaining in fulvic acid, humic acid, and humic fractions after exhaustive sequential extraction with nonpolar organic and polar solvents" (Kaufman, 1976). This definition is also applicable to aquatic sediments. There is considerable discussion on the question of how bound contaminant residues can best be released from soils and sediments (Kearney, 1976). A commonly used procedure is the classical base-extraction and acid-precipitation method for humic and fulvic acids from soils, but pyrophosphate extraction and dimethyl formamide/oxalate extraction are also advocated by certain groups of investigators. Even stronger degradative methods such as acid hydrolysis, base saponification, alkaline permanganate oxidation, and reductive degradation methods are used by many workers to identify bound and conjugated residues in soil and sediment organic matter. Methods for extracting and identifying a number of pesticide conjugates in plants and soil are summarized well in Kaufman and others (1976).

AQUATIC EFFECTS OF ORGANIC CONSTITUENTS IN SEDIMENTS

NATURAL ORGANIC CONSTITUENTS

The organic substance structure contains many negatively charged functional groups and metal complexation sites; therefore, aquatic sediments coated with organic substance structures can retain metals by cation exchange and complexation. Rashid (1969) found that organic matter contributed 80 to 95 percent to the total cation-exchange capacities of a number of marine sediments. Aquatic effects of the metal-binding capacities are important from the following standpoints: (1) contributions of exchangeable metal cation plant nutrients (e.g., K, Ca, Mg), (2) buffering of water chemistry by exchange of cations, and (3) toxic effects of bound trace metals.

Toxic effects of sediment-bound trace metals have long been the focus of many research studies. Mathematical models have been developed and tested for trace-metal partitioning on sediment (Oakley and others, 1981). Oxidation of organic matter in sediment frequently causes reducing conditions in sediment, which releases bound trace metals into the water as their more soluble reduced species (Lu and Chen, 1977). Certain bound trace metals, especially mercury, can be methylated or converted to other organometallic forms by microorganisms (Fujita and Iwashima, 1981) which can bioaccumulate in fish.

The buffering capacity of weak-acid exchange sites of sediment organic matter effectively neutralizes acid inputs (such as acid rain) when these exchange sites contain cations other than hydrogen and aluminum. Affinities of hydrogen ion and acidic hydroxy oxides of aluminum for weak-acid exchange sites are much greater than those of most other metal cations and, consequently, sediment organic matter may serve as a sink for acidity.

Organic matter associated with sediment usually contains phosphorus, nitrogen, and sulfur. Mineralization or direct utilization of organic forms of these elements can increase the primary productivity of water to the point where eutrophic conditions occur (Lee and others, 1978). The role of organic matter in sediment in nutrient cycling, in oxygen depletion, as a substrate for micro- and macro-organisms, as a source of and a sink for carbon in maintaining the global carbon-dioxide balance, and in the diagenesis of fossil fuel deposits encompasses the sciences of limnology and oceanography, which can be treated adequately only in a detailed text (Wetzel, 1983).

Lastly, a largely unrecognized but important aquatic effect of natural organic matter in sediment is its flocculating and aggregating action on sediment. The multiple binding sites and associative mechanisms previously discussed with the organic substance model (fig. 1) can aggregate sediment particles through various organic linkages. This aggregation phenomenon was thought to be the cause of the formation of a series of uniquely shaped river islands in the "black water" of the Rio Negro in Brazil (Leenheer and Menezes-Santos, 1980). Inorganic sediments in glacier-melt rivers do not have organic coatings. This sediment may not flocculate at the same rate as sediment having organic coatings, and this may cause the milky appearance characteristic of such waters.

ORGANIC CONTAMINANTS

Organic contaminants in aquatic sediments have been the focus of intense studies after discoveries of organic contaminant concentration and transport in sediment, uptake of contaminants from sediment by benthic organisms, and bioconcentration of contaminants in the food chain. Halogenated contaminants, such as chlorinated hydrocarbon insecticides, polychlorinated biphenyls, and polybrominated biphenyls, have the undesirable properties of low water solubility, toxicity, a high tendency to bioaccumulate, and long half-lives in the environment. They are lipophilic and, therefore, concentrate in fatty tissues of aquatic and terrestrial organisms. A good correlation, covering more than eight orders of magnitude in solubility, has been observed between the reciprocal of aqueous solubility for stable organic compounds and bioconcentration factors in trout (Chiou and others, 1977). Sorption of organic contaminants on sediment decreases their toxicity (Steen and others, 1980), and eventual burial by sedimentary processes and microbial degradation slowly removes them from the aquatic ecosystem. Although half-lives of tens to hundreds of years have been postulated for persistent organic contaminants, they may reenter the aquatic ecosystem when contaminated sediments are remobilized through floods or dredging operations.

The second major aquatic effect of organic contaminants on sediment are their general deleterious effects on water quality. Untreated or partially treated domestic sewage, paper-mill wastes, tannery wastes, brewery wastes, and other industrial-plant wastes containing natural products frequently contain biodegradable organic detritus which is incorporated into suspended and bed sediment after waste discharge into water. If the organic loading of these wastes exceeds the capacity of the aquatic ecosystem to completely degrade them, the receiving waters may become depleted of oxygen and the resulting reducing conditions may release toxic trace metals from sediment, cause fish mortality, produce sulfide precipitates and gases, and cause taste and odor problems from reduced organic compounds.

Lastly, certain organic contaminants can modify the physical properties of sediment. Adsorbed oils, greases, and detergents can alter the density and surface area of sediment such that sedimen-tation rates are changed. The surface charge of sediment can be altered by adsorption of anionic or cationic surfactants such that sediment is either flocculated or dispersed.

PROPOSED OPERATIONAL PROGRAMS IN SEDIMENT ORGANIC CHEMISTRY

Following are four proposed studies that the Water Resources Division operational programs in district offices can perform with existing technology and resources to obtain data for new and expanded knowledge of the nature and aquatic effects of organic constituents in sediment.

FIELD SEPARATION OF DISSOLVED AND SEDIMENT PHASES OF SAMPLES FOR ORGANIC CONTAMINANT ANALYSIS

Most organic contaminant analyses in water and sediment currently performed by the Water Resources Division are "total recoverable" analyses with no prior separation of suspended sediment from the water samples. It is difficult to use data from these analyses for studies of organic contaminant partitioning into dissolved and sediment phases. Turk and Troutman (1981) used field filtration of water through a 0.45-μm-porosity silver membrane filter to define polychlorinated biphenyl transport in the Hudson River in both dissolved and sediment phases to illustrate differences in the mechanism of transport with change in flow.

Two important considerations in sediment separation from water for organic contaminant analysis are (1) field rather than laboratory separation of dissolved and sediment phases to avoid changes in organic contaminant distribution with sample transport, preservation, and storage, and (2) judicious selection of water–sediment separation equipment to avoid organic contaminant loss through volatilization, degradation, or adsorption. Such equipment exists and can be evaluated through studies of organic contaminant recovery.

When water–sediment separation techniques are tested and adopted for sediment organic-contaminant studies, a valuable ancillary study would be to perform multiple successive equilibrations of contaminated sediment with contaminant-free water to obtain data on the desorption potential of a specific contaminant on a sediment.

TAILORING SEDIMENT SAMPLING AND SUBSAMPLING TECHNIQUES FOR ORGANIC CONTAMINANT ANALYSIS

Organic contaminant concentrations are usually highest on fine-grained sediments because they possess a relatively large surface area and high organic matter content. Because the cost of analysis for a specific organic contaminant of a sediment sample is relatively high, it might be more cost-effective to analyze the sediment size fraction that has the highest concentration of the analyte, particularly during reconnaissance. Sufficient historical data are available in the sediment literature for most organic contaminants to permit selection of the correct size fraction for analysis. A reasonable prediction of contaminant concentrations of other size fractions, and, ultimately, the whole unfractionated sediment sample, could be based on correlatable parameters such as surface area and organic carbon content. Quantitative determination of contaminant concentrations in a fractioned sediment using specific size-fraction analysis would likely be more accurate because analytical methodology would be more sensitive and accurate.

LONG-TERM SITE-SPECIFIC STUDIES

Most site-specific studies in the Water Resources Division are from 2 to 5 years in duration. This time period is too short in many cases to get long-term data needed for accurate determination of contaminant transport rates and half-lives. A national operational program could be implemented whereby specific sites where aquatic sediments are contaminated, such as the Hudson River sediments by PCB, are analyzed at infrequent intervals to obtain long-term data. A small program using existing methodology could obtain long-term data on 10 to 20 sites scattered over the United States. This program should be national in scope to minimize differences in data gathering and interpretation. Existing data should be used as the beginning data base.

CORRELATION OF SEDIMENT ORGANIC CONTAMINANT ANALYSES WITH BIOASSAY ANALYSES

Aquatic effects of organic contaminants in sediments are best measured in the laboratory by various bioassay techniques. The Water Resources Division operational program is strong in chemical analytical capability but weak in bioanalytical capability. There are currently available some fairly simple and inexpensive bioassay tests of sediment toxicity, such as in vitro enzyme (Buikema and others, 1980) which could be performed by district personnel, and the results correlated with organic contaminant analyses on a split of the same sediment sample. This correlation would extend the interpretive value of organic contaminant analysis of sediments.

PROPOSED RESEARCH PROGRAMS IN SEDIMENT ORGANIC CHEMISTRY

The Water Resources Division research program has, in the past, concentrated on dissolved and total organic constituents in water. A greater emphasis on sediment organic constituents is warranted, owing to the fundamental lack of knowledge in this field and the importance of aquatic effects from these constituents. Following are five areas of research in sediment organic chemistry which the Water Resources Division might consider undertaking.

DEVELOPMENT OF A COMPREHENSIVE TESTING REGIME AND CHEMICAL MODEL FOR ORGANIC CONTAMINANT ASSOCIATION WITH SEDIMENT

Most current models of organic contaminant association with sediment use water-octanol partition coefficient data combined with organic carbon content of sediment. Contaminated sediments often contain a mixture of polar and nonpolar organic contaminants which associate with sediments through multiple mechanisms, as discussed previously in this report, and the water-octanol partition coefficient model quantifies only the hydrophobic effect. A regime of n_1 tests performed on x contaminant correlated with a regime of n_2 tests performed on y sediment could lead to a comprehensive chemical model of the association between x contaminant and y sediment.

High-performance liquid chromatography of x contaminant on reverse-phase packings, ion-exchange packings, ligand-exchange packings, and direct-phase packings should provide quantitative data on x contaminant interactions through the hydrophobic effect, ion-exchange, metal complexation, and hydrogen bonding. Measurement of y sediment surface area, carbon content, and model solute interactions which quantify the hydrophobic effect, ion exchange, ligand exchange, and hydrogen bonding should provide necessary data on the sediment phase. Correlation of the two data sets should provide a comprehensive chemical model for organic contaminant association with sediment. This comprehensive model should be very useful in predicting the potential for sediment contamination with discharge of a certain waste and showing the associative mechanisms and strength of association in already contaminated sediments.

IMPROVED METHODOLOGY FOR ISOLATION AND ANALYSIS OF ORGANIC CONTAMINANTS FROM SEDIMENT

Isolation of organic contaminants from moist aquatic sediments is especially difficult because both water and sediment phases must be considered. Organic solvent extraction techniques generally work well for loosely bound, semivolatile, nonpolar organic contaminants; more strongly bound contaminants, both volatile or nonvolatile, are difficult to solvent-extract and analytically determine after extraction. Recently, there have been many promising developments in extractive methodology such as supercritical fluid Soxhlet extraction, thermal desorption of volatiles and semivolatiles followed by analyte concentrator traps, and matrix dissolution prior to analyte extraction. A research project should evaluate the applicability of these advances in extractive methodology to organic contaminant analysis of aquatic sediments.

Also needed is a hierarchy of extractive methods and analyses that can be applied to determine an unknown set of organic contaminants on sediment. A possible analytical scheme is shown in figure 2. The approach uses successively stronger extraction techniques, which permits interpretation of the nature and strength of association between the organic contaminant and sediment.

INORGANIC SOLUBILITY CONTROLS ON NATURAL AND MANMADE ORGANIC SOLUTES IN WATER

Very little research has been performed on this subject as applied to aquatic sediments. Most

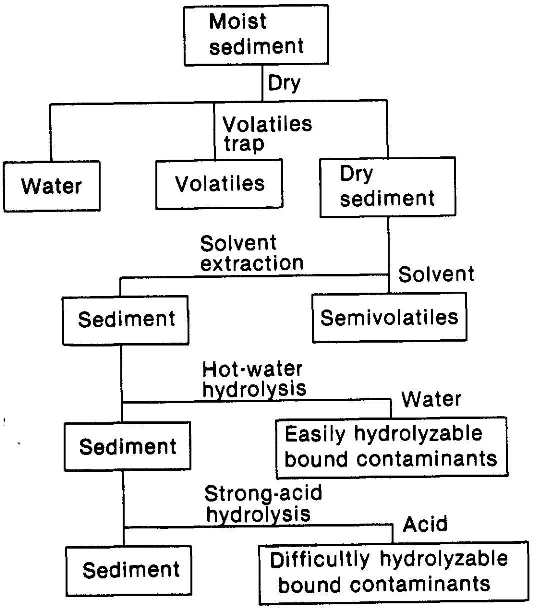


FIGURE 2.—Proposed analytical scheme for organic contaminant analysis of sediment.

research in this area consists of fundamental physical chemistry studies of solubility phenomena. When organic solutes precipitate owing to an inorganic solubility control, they become part of the sediment system. Inorganic solubility controls likely to be involved in aquatic systems are silicic acid hydrogen-bonded complexes with organic bases, mutidentate inorganic cation complexes with organic ligands, and alkali-metal ion-pair complexes with organic acids. Studies of these inorganic solubility controls may explain why soluble organic base contaminants partition into sediment, why soluble fulvic acids precipitate in brackish esturaries, and why trace metal-organic solute complexation frequently results in precipitation.

ORGANIC CHEMISTRY CHANGES ASSOCIATED WITH THE AEROBIC/ANAEROBIC BOUNDARY IN BED SEDIMENT

The aerobic/anaerobic boundary in bed sediment, or the change of entire aquatic systems from aerobic to anaerobic conditions, has been associated with the release of both inorganic and organic contaminants from sediment. Organic contaminants also usually decompose at slower rates and less completely under anaerobic conditions, and this adds to their hazard. The mechanisms of release and of alteration in chemical structure associated with anaerobic sediments are poorly understood. The Water Resources Division research program is especially strong in studies of humic substances in water. Broadening of certain humic substance studies to include anaerobic sediments should give a much better fundamental understanding of processes responsible for release of contaminants.

EARLY DIAGENESIS OF ORGANIC MATTER IN AQUATIC SEDIMENTS

Many geochemical studies have been performed in this area with regard to the formation of fossil fuel resources, but few studies have approached the subject from a water-quality perspective. The objectives of studies in this area would be to define both the nature of and the decay and synthetic processes that form organic matter in aquatic sediments in diverse environments with respect to the properties (such as organic contaminant conjugation) that affect water quality. Studies would have to be broadly based and interdisciplinary, coupling field and laboratory studies in the sciences of aquatic biology, chemistry, geology, hydrology, and others. These studies would focus on how plant and animal matter, which releases natural products of defined composition (sugars, proteins, lipids, etc.), is transformed into organic matter in aquatic sediments.

CONCLUSIONS

There are many needs in the field of organic chemistry of aquatic sediments for both the operational and research programs of the Water Resources Division. These needs have arisen because of the important role that sediments play in the aquatic ecosystem. They have persisted because of the complex nature of sediment organic constituents and because of the general lack of interdisciplinary scientific investigations in sediment chemistry. The Water Resources Division has a unique opportunity to make a substantial contribution to the field of organic chemistry of aquatic sediments because of its broad mission objectives in water-quality investigations, its technical expertise and research facilities, and its nationwide operational program and broad data base.

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BIOAVAILABILITY OF SEDIMENT-BOUND METALS

By Samuel N. Luoma

INTRODUCTION

Trace metals are natural components of the biosphere. Although some metals are essential for life, all metals are toxic at sufficiently high concentrations. For a number of metals, the difference between the required concentration and the toxic concentration is very small. Recent research (e.g., Sunda and Guillard, 1976; Engel and Sunda, 1979) has verified earlier speculation that many aquatic organisms live perilously close to the threshold of trace metal toxicity, even in environments unperturbed by man. The development of mechanisms that facilitate survival at the threshold of trace metal toxicity may have been an essential component in the evolution of aquatic species. The most obvious of such mechanisms would involve detoxification of metals after their transport from the environment into biological tissues (at some metabolic expense). More subtly, organisms also appear to generally avoid the geochemical forms of trace metals that are most abundant, employing the geochemical complexity of metal reactions in aquatic environments as a buffer to avoid the potential toxic effects of those metals.

Because many biological systems exist at the margin of metal toxicity, the physical and geochemical redistribution of metals in aquatic environments by human activities has a strong potential to disrupt aquatic ecosystems. Predicting the effects of metals on aquatic ecosystems, or demonstrating that an effect has occurred, is difficult because current understanding of the geochemical processes affecting the availability of metals to the organisms involved is poor.

Metals concentrate in suspended and bed sedimentary particles in aquatic environments. The transport of metals from those particles to biological food webs is strongly influenced by the geochemical selectivity of the organisms that contact the particles. This review considers how biological and geochemical processes affect the bioavailability of particle-bound metals. This requires assessing the state of knowledge concerning the biological characteristics of metal uptake, in general, since those characteristics determine the selectivity of the organism. It is also necessary to consider what is known about the availability of metals from food, in general, since ingestion is the route of direct metal transfer from particles to organisms. Finally, particle–organism interactions themselves are discussed. Particles may also transfer metals indirectly by desorption into water. This process is not discussed because chemical reactions within the water itself ultimately influence the availability of such metals, and uptake of metals from solution is a broad subject beyond the scope of this paper. One final goal is to assess how consideration of processes affecting metal bioavailability can be incorporated into operational programs that assess metal concentrations in sediments.

CHARACTERISTICS OF THE BIOLOGICAL UPTAKE OF METALS

Studying the availability of trace metals requires employing some measure of metal transport into biological tissues. Both bioaccumulation and biological response (either a nutritional or a toxic response) have been employed in such a context. A biological response cannot occur without bioaccumulation; however, bioaccumulation need not elicit a response, since the ultimate response also depends on the biochemical transport and fate of the metal (e.g., both detoxification and luxury uptake have been documented). Thus, bioaccumulation is the most direct measure of bioavailability, although measurement of a response is sometimes more practical. The processes that could uncouple response from uptake will not be discussed; however, some discussion of the characteristics of uptake itself is a necessary prelude to discussions of environmental influences on metal availability.

The net accumulation of most substances into biological tissues nearly always reflects some equilibration between influx and efflux of the substance. Since an efflux has been demonstrated (although it is often slow) for nearly all metals in a variety of organisms (Cutshall, 1974; Bryan, 1979; Coombs, 1980), it is likely that equilibration theory applies to trace metal kinetics in aquatic organisms. Support for an underlying control of uptake by equilibration kinetics is also found in the net uptake differences observed among metals. Metals that exchange rapidly (e.g., Co) are accumulated less efficiently than metals that exchange slowly (e.g., Hg).

Although body burdens of metals may reflect a balance between fluxes, equilibrium (or, more properly, steady state) is seldom, if ever, attained. Positive correlations between size or age and concentrations of some metals have been observed in fish (Cutshall and others, 1977) and invertebrates (Boyden, 1977; Bryan and Uysal, 1978). Such correlations are most common in metal-enriched environments (Boyden, 1977; Bryan and Uysal, 1978; Strong and Luoma, 1981) and appear to reflect lifelong, net metal accumulation (Cross and others, 1973). Recent studies point to mechanisms that might explain how lifelong metal accumulation could occur in enriched environments coincident with metal fluxes that should eventually lead to a steady-state concentration. One mechanism is the occurrence of slowly exchanging (or perhaps conservative) pools of metals stored for detoxification; the other involves the synthesis of metal-specific binding proteins.

Some metals may be assimilated after uptake into physiological pools that exchange very slowly or not at all. Pentreath (1973a) and Renfro and others (1975) first demonstrated in fish and shrimp that pools of Zn did not exchange readily with ^{65}Zn in solution or in food. More recently, studies involving invertebrates and fish have shown that metals (e.g., Zn, Cu, Pb) may be sequestered in membrane-bound vesicles, presumably for detoxification (Walker and others, 1975; Brown, 1977; Walker, 1977; George and others, 1978a; Janssen and Scholz, 1979). These vesicle-bound metals are especially prevalent in metal-enriched environments. Although the metal-rich vesicles may be excreted (George and others, 1978a; Coombs, 1980), their turnover is likely to be slow, and direct exchange with incoming metal minimal. The storage of metals in vesicles could lead to lifelong metal uptake if the rate of vesicle synthesis necessary for detoxification exceeds the rate of metal excretion from the organism.

Metal-specific binding proteins (metallothionein-like proteins) have also been observed in aquatic organisms (Brown and Parsons, 1978; Engel and Fowler, 1979). Synthesis of such proteins is induced by metal exposure. Paradoxically, in mammals, metal uptake also may be stimulated by metallothionein synthesis (Cousins, 1979), resulting in a positive feedback which could enhance metal accumulation in tissues. A similar process, in which the onset of synthesis of metallothionein-like proteins accelerates metal uptake, has been postulated in aquatic organisms

(Noel-Lambot and others, 1980). An ongoing synthesis of binding protein violates one of the requirements for equilibration of metal levels in a tissue, that of a constant size of the pool of binding sites. Again, the result may be long-term net metal accumulation in metal-enriched environments, even where environmental concentrations of metals are constant.

The processes that control metal uptake by biological tissues will influence the interpretation of bioavailability studies. Positive feedbacks which enhance metal accumulation may cause overestimation of availability under some circumstances. In contrast, unpublished work (F. L. Harrison, Lawrence Livermore Laboratory, oral commun., 1982) suggests that high metal exposures may poison the synthesis of binding proteins and cause an underestimate of availability. Short-term experiments may end before induction of binding proteins becomes significant, or exchange with conservative metal pools is possible, leading to an underestimate of important components of uptake. In long-term experiments, the important influences of growth (Strong and Luoma, 1981) on uptake must be considered. Laboratory manipulations may also affect the kinetics of metal accumulation. For example, efflux rates of metals in some animals held in a natural setting exceed efflux rates measured in the laboratory (Benayoun and others, 1974; Fowler and Benayoun, 1976; Fowler and Unlu, 1978), perhaps reflecting differences in growth rates of animals in different circumstances (Fowler and Benayoun, 1976; Farmer and others, 1979), but certainly affecting conclusions concerning metal availability. Similarly, starved animals may accumulate metals more rapidly than feeding animals (Cross and others, 1969; Luoma and Jenne, 1976a; Klump, 1980), affecting comparisons where starvation is necessary. Thus, consideration of the kinetic characteristics of metal uptake is essential in interpreting bioavailability studies and in extrapolating between the laboratory and nature.

Some discussions in the literature have suggested that some organisms may regulate concentrations of some metals, uncoupling uptake from any dependence on the concentrations of available metal (Bryan, 1979). Zinc concentrations in the polychaete *Nereis diversicolor* show little variation over wide variations in environmental levels of Zn (Bryan and Hummerstone, 1973), suggesting efficient regulation. However, at least 40 percent of the total Zn in *N. diversicolor* occurs in the jaws of the animal (Bryan and Gibbs, 1979). Some concentration dependence of Zn uptake in other tissues might be more obvious if the conservative component of Zn in the jaws could be excluded from tissue analyses. Similarly, fish may regulate concentrations of essential metals (such as Zn and Cu) in some tissues but not in others. Some regulation of Cu in some molluskan bivalves might also occur (Bryan, 1979), but Cu uptake is not totally uncoupled from Cu exposure. The uptakes of nonessential metals such as Pb, Cd, Ag, and Hg most certainly are determined by exposure concentrations (for a comprehensive review see Bryan, 1979). In general, then, regulatory uncoupling of uptake from concentration dependence is the exception rather than the rule, and the exposure level of available metal is the most important control on bioaccumulation.

MECHANISMS OF UPTAKE

The biological mechanisms of metal accumulation determine the geochemical form of metal available for uptake. The biological interface between the environment and eukaryotic (all organisms except bacteria and blue-green algae) biological tissues is a nonpolar lipid membrane impregnated with more polar molecules which sequester and help transport essential polar substances across the membrane (these are called carrier molecules; fig. 3). Most metals are highly polar and not soluble in the lipid membrane. Nevertheless, kinetic characteristics suggest that most trace metals traverse the environmental interface of organisms via diffusion, rather than an energy-dependent, active transport process (Coombs, 1980). Facilitated diffusion is a common mode of membrane transport (Neame and Richards, 1972). The substance to be transported first complexes with a carrier molecule on the external surface of the membrane and then is transported into the cell by the carrier if an external-to-internal diffusion gradient exists. Several authors have reviewed the possible importance of such carriers in the biological uptake of trace metals (Lunde, 1974; Coombs, 1980).

Metals occur as strongly bound complexes within tissues (Chou and others, 1978). Rapid

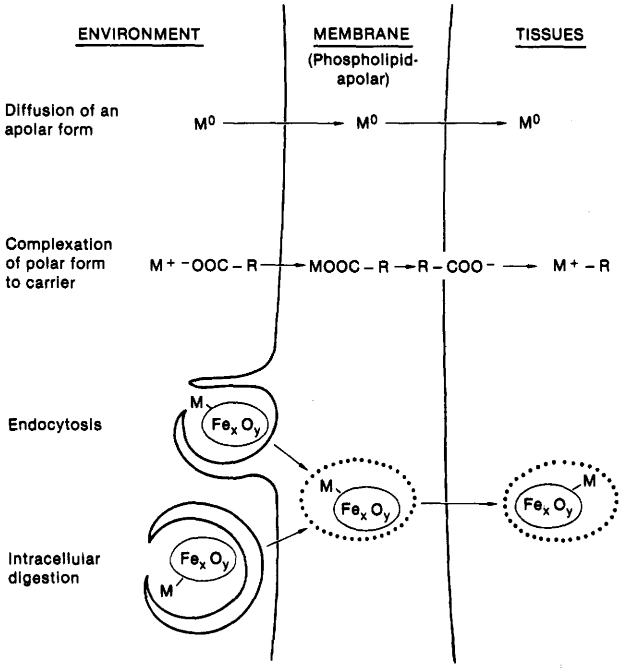


FIGURE 3.—Simplified schematic characterization of the environmental interface of an organism, illustrating mechanisms of transport of metals (M) into biological tissues. (From Luoma, 1983.)

complexation to strong, slowly exchanging ligands could maintain a sufficient diffusion gradient to allow the degree of bioconcentration characteristic of most metals (Luoma, 1974, 1977a). This process is well established for bioconcentration of major cations (Fletcher, 1970).

The characteristics of biological membranes suggest that metal forms that are lipid-soluble or of reduced polarity will be accumulated readily, crossing the membrane via diffusion. Reduced polarity, together with high solubility in biological membranes, is the most likely explanation for the exceptionally high bioavailability of methylmercury (Phillips and Buhler, 1978). In a similar context, a likely reason that octanol-water partitioning coefficients are such useful indicators (Neely and others, 1974) of the bioavailability of synthetic and petroleum-based trace organic substances is their relationship to membrane solubility (Riley and others, 1981). However, low-polarity forms of many metals are rare; thus, mechanisms other than diffusion through the lipid membrane probably are involved in most metal uptake.

If facilitated diffusion is important in uptake, then metal transport will be linked to complexation with carrier molecules. The carrier may be viewed simply as a competing ligand in metal speciation. Free metal ions would be available for complexation, as would complexes compatible with the binding capabilities of the carrier or metals bound to ligands of weaker stability than the carrier. Kinetics may limit the process of complexation to the membrane. For example, the reaction of Cr (III) with organic ligands is 3 to 12 orders of magnitude slower than the reactions of other metals (Sutin, 1966), perhaps explaining the low availability of this form of the metal (Jenne and Luoma, 1977).

A second important characteristic of carrier-mediated transport is that the number of carrier sites is limited. Therefore, gross influx (measured in the early phases of uptake, before significant efflux occurs) should be a *saturable* function of exposure concentration. Luoma (1977a) observed such kinetics in Hg uptake by a polychaete (*Nereis succinea*) and a small shrimp (*Palaemon debilis*). Coombs and George (1978) found that Cd uptake by oyster gills (in place) was similarly characterized by saturable kinetics during influx. Antagonism of uptake also could occur between metals transported by the same carrier at metal concentrations sufficient to saturate carrier sites.

Carrier molecules may be quite selective in the molecules or elements they transport (Neame and Richards, 1972). Specific carriers appear to occur for some specific metal complexes. For example, assimilation of cobalt into the tissues of crustaceans occurs more efficiently when the metal is administered as cobalamine than as $CoCl_2$, presumably in equilibrium with free Co^{+2} (Lowman and Ting, 1973). Since cobalamine is an essential vitamin, specific carrier-mediated mechanisms for its uptake are likely. Similarly, Fe uptake by blue-green algae is preceded by complexation with specifically exuded Fe-binding molecules called siderochromes or siderophores (Murphy and others, 1976; McKnight and Morel, 1980). Because of their unique capability for transporting siderochrome-bound Fe (presumably via carriers specific for the molecule), blue-green algae may dominate other types of phytoplankton in Fe-limited environments (Murphy and others, 1976). Carrier systems for cobalamine and siderochrome-Fe have developed in response to specific nutritional needs; however, these are probably exceptional among metals.

Other mechanisms of carrier-facilitated metal uptake which are possible include (1) transport via carriers specific for nutritionally essential cations, (2) nonspecific complexation of metal forms with carrier molecules, which could result in either "accidental" transport across the interface or immobilization at the external interface if the carrier-metal complex cannot move through the membrane,(3) transport of metals complexed with essential nutrients (e.g., amino acids or proteins) on carriers specific for the nutrient, and (4) transport of nutritionally inessential metal complexes. The lack of uptake of metals complexed with synthetic organic compounds such as EDTA or NTA (Sunda and Guillard, 1976; Anderson and Morel, 1978; Jackson and Morgan, 1978) and inorganic species such as $CuCO_3$ (Magnusson and others, 1979) suggests that little uptake occurs via mechanism 4. However, little is known about the relative importance of the first three modes of uptake in aquatic organisms.

Uptake by passive diffusion of polar metals through nonpolar membranes could occur via pores that have been observed in the membranes. However, the exclusion of most metal complexes, which is consistently observed in aquatic studies, seems inconsistent with such a nonspecific uptake mechanism.

Metal uptake by endocytosis also has been documented, at least in mollusks, and may be important in many aquatic invertebrates. Endocytosis (or pinocytosis) is the engulfment of particulate metal by the epithelial cell membrane, which then pinches off to form membrane-limited vesicles within the cell (fig. 3; Coombs, 1980). Alternatively, specific amoebocytes or digestive vesicles may engulf metals outside the cell membrane (as in the lumen of the digestive tract) and then move back into the tissues carrying their particulate burden. Digestion by engulfment within vesicles is common in many invertebrates, accounting for a major fraction of the digestion accomplished by mulluskan species such as *Macoma balthica* (Owen, 1966). Direct microscopic observation of the transport of iron hydroxide particles, iron-ferritin complexes, and iron-transferin complexes by endocytosis in mussels was reported by George and others (1977). Vesicles rich in Cu, Zn, and Pb, similar to those observed by George and others (1977) during endocytosis have been reported in scallops (George and others, 1978b), barnacles (Walker, 1977), and crustacean isopods (Brown, 1977). Thus, some uptake of particulate and complexed metals by endocytosis in invertebrates seems likely, especially during digestion. It is unlikely such uptake would be confined to a single metal species (George and others, 1977). However, the contribution of endocytosis to metal uptake has not been quantified.

Digestive processes also play a role in determining metal uptake from food and ingested water. Enzymatic cleavage of proteins could facilitate metal assimilation if metals are transported with amino acids. The most important factor in the digestive tract probably is pH; however, pH of less than 5 is uncommon in the digestive tract of lower trophic level invertebrates. Little is known about conditions inside digestive vesicles or amoebocytes in the many species of invertebrates that employ intracellular digestion. Lower pH, longer digestive times, and great digestive efficiency might be expected in upper trophic level and air-breathing organisms (since the latter must rely on food for calcium). High concentrations of some metals (e.g., Hg) occur in large predatory fish and in air-breathing animals linked to aquatic food chains. However, biomagnification through several trophic levels, which could result from rigorous extraction of metals during digestion, has not been observed for most metals (Bryan, 1979).

The poor correlation between low digestive pH and greater metal uptake may reflect a balancing influence of pH on carrier molecules. At low pH, the strength of metal binding to organic ligands, such as those on carrier molecules, is greatly reduced (Davis and Leckie, 1978). Thus, although low pH may strip more available metal from food, the carriers in such an environment are less efficient in complexing that metal for transport. In support of this hypothesis, Miller and MacKay (1980) showed that below pH 4.7, pH affected Cu availability to trout in an antagonistic manner, while at pH 5.4 and above the interaction was synergistic.

In summary, physiological characteristics suggest that metal forms of reduced polarity should be highly available for uptake by diffusion through membranes. Forms that readily complex with carrier molecules or nutritionally essential complexes should be available for carrier-facilitated uptake. Kinetics or conditions at the membrane (e.g., pH in the digestive tract) might affect the efficiency of carrier complexation.

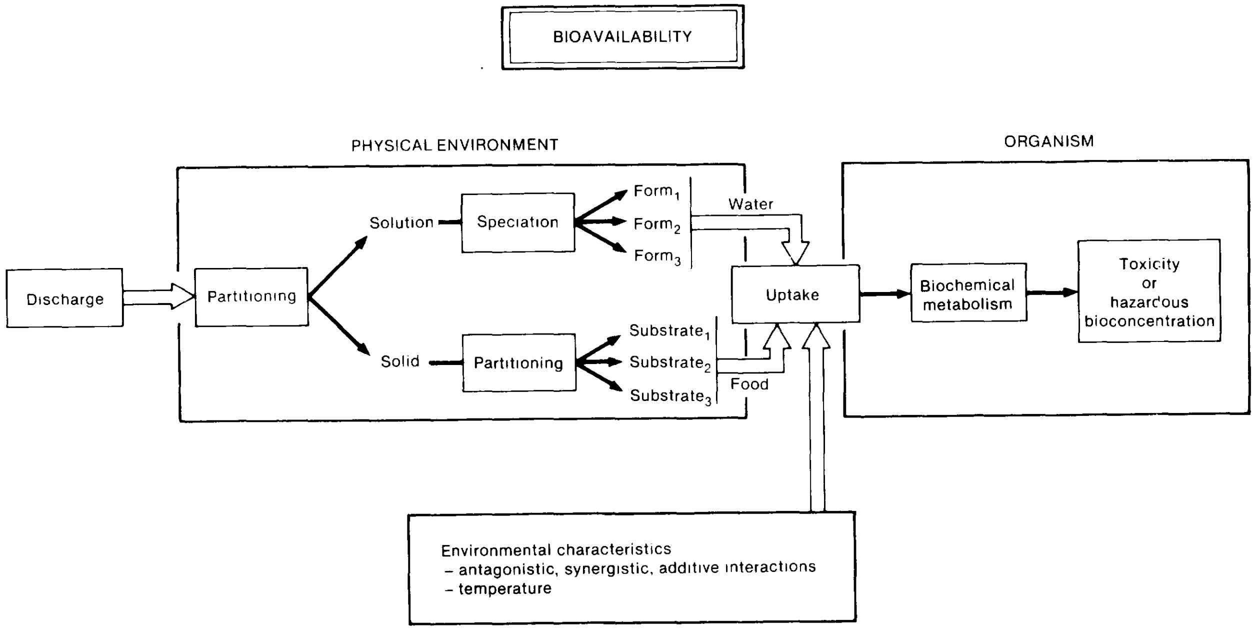


FIGURE 4.—Simplified schematic illustration of the various processes that affect the availability of trace contaminants to organisms.

Metals associated with the types of particles that are engulfed by amoebocytes or during endocytosis might also be accumulated, as might metals strongly complexed with nutritionally important molecules. Little is known about the importance of the latter two possibilities, however.

TRANSPORT FROM FOOD

The vectors of metal transport to organisms are food and water (fig. 4). The quantity of metal taken up by an organism is the sum of the quantities obtained from each vector. Uptake from a vector is determined by (1) the metal concentration in the medium of exposure, (2) the rate of exposure (e.g., feeding rate), and (3) specific geochemical and physiological reactions which determine the proportion of the total metal that is available for transport by the organism.

Early studies of metal uptake (e.g., Townsley, 1967) showed that the bioavailability of metals from solution is considerably greater than is the availability of metals bound to solids (in food). However, metal concentrations in solid form are orders of magnitude higher than concentrations in solution. Because availability balances concentration, the relative importance of food and water as vectors of uptake is highly variable, and study of each vector individually is important. Only the food vector is considered in this review.

The high concentrations of metals in the food of most organisms, relative to water, suggest that food should be a dominant vector of metal uptake. Establishing the importance of metal uptake from food has proved to be a difficult problem, however. Three general approaches have been employed: (1) experimental separation of the food and water vectors and comparison of their importance, (2) use of mass-balance models in combination with experimental studies of uptake, and (3) comparisons of tissue distributions observed in laboratory studies with observations of animals in nature.

Direct comparisons of metal uptake from food and solution at distribution ratios characteristic of nature seem the most obvious method of comparing vectors of uptake. In all such experiments, uptake from food must be determined by the difference between uptake from food plus water and uptake from water alone. The results of such experiments have not yielded consistent conclusions for a given metal. For example, rainbow trout showed no uptake of Pb from food; uptake from spiked food and freshwater did not exceed uptake from solution alone (Hodson and others, 1978). Similar results were observed with freshwater isopods (Brown, 1977), although some uptake from food was observed in Pb-tolerant isopods. In contrast, in long-term studies, abalone fed (ad libitum) Pb-contaminated brown algae accumulated substantial concentrations of Pb (Stewart and Schulz-Baldes, 1976). Jennings and Rainbow (1979) observed no difference between crabs (*Carcinus maenus*) fed a small ration of Cd-spiked *Artemia* (brine shrimp) in Cd-contaminated water and crabs held in the water alone. Janssen and Scholz (1979) observed similar results with mussels (*Mytilus edulis*) exposed to Cd, as did Sick and Baptist (1979) with marine zooplankton (*Pseudodiaptomus coronatus*). Renfro and others (1975) showed no detectable uptake of Zn from food by shrimp or crab, but some uptake by fish. However, in a similar experimental design, Young (1975) observed that food was a very important source of Zn uptake by snails (*Littorina obtusata*). More uptake from food and water than from water alone was also observed for Fe by mussels and shrimp (Fowler and Benayoun, 1976), Ag by estuarine clams (Amiard, 1978), Co by freshwater fish and crayfish (Amiard-Triquet, 1979), and Hg in salmon and trout (Spinelli and Mahnken, 1976; Hartman, 1978; Phillips and Buhler, 1978). Singh and Ferns (1978) observed uptake of Mn, Co, Cu, Cr, Pb, Zn, Ni, and Cd in trout fed metal-contaminated activated sludge or commercial pellets.

All such experiments may underestimate the contribution of food to metal uptake by overestimating uptake from solution or by failing to employ realistic feeding rates. First, organisms held in labeled water alone are held without food. Starved animals accumulate at least some metals (Hg, Zn, Cd, Pu) more rapidly from solution than do feeding animals (Cross and others, 1969; Luoma and Jenne, 1976a). One reason for this may be that food in the digestive tract enhances metal efflux by inhibiting reabsorption of excreted metals (Luoma, 1974). Second, metal uptake from food depends on weight-specific feeding rates (Luoma, 1976; Sick and Baptist, 1979). Controlled experiments seldom provide the quantity or quality of food characteristic of natural conditions. Finally, the presence and abundance of food may affect feeding rates, and thus rates of water transport across the gills of organisms, thereby affecting the uptake of metals from both food and water (Janssen and Scholz, 1979).

Experiments that have incorporated mass-balance models have considered the importance of feeding rate. Concentration factors determined from uptake experiments with solute metals alone have been used in some such models. Solute metal concentrations observed in nature have then been employed to predict the solute component of the metal burden in the organism. Pentreath (1973a, b) concluded from such experiments that the Zn, Mn, Co, and Fe in demersal fish (plaice) could not be explained by radionuclide uptake from solutions and must be obtained primarily from food. Similar conclusions were drawn about As uptake by shrimp (Fowler and Unlu, 1978). However, Renfro and others (1975) showed that biological pools of Zn that do not exchange with ^{65}Zn in either food or solution may occur, negating the basis of Pentreath's conclusions. In other approaches, the efficiency of assimilation of metals from food was determined in short-term experiments and then metal uptake from food was calculated from estimates of feeding rate and concentrations in natural foods. Uptake efficiencies for most metals (except methylmercury; Phillips and Buhler, 1978) are generally low, less than 20 percent (Pentreath, 1973a; Kerfoot and Jacobs, 1976; Jennings and Rainbow, 1979; Sick and Baptist, 1979). The bulk of the ingested metal passes through the organism unassimilated and is excreted in feces (Boothe and Knauer, 1972; Small and others, 1972; Benayoun and others, 1974). Despite the inefficiencies of uptake, calculations have suggested that food could be the dominant source of Zn to macrozooplankton (euphausiids; Small and others, 1972), Cs to both plaice (the demersal marine fish *P. platessa*) and trout (*Salmo-trutta;* Hewitt and Jeffries, 1978), Se to marine zooplankton (Fowler and Benayoun, 1976), Pu to crabs (Fowler and Guary, 1977), Cd to euphasiid zooplankton (Benayoun and others, 1974), Cr to oysters (Preston, 1971), Hg to mussels (Fowler and others, 1978), and As to both snails (*Littorina littoralis;* Klumpp, 1980) and lobster (Cooney and Benson, 1980). In contrast, calculations by Sick and Baptist (1979) suggested that food was not an important source of Cd to zooplankton at food levels available in nature, and Kerfoot and Jacobs (1976) drew similar conclusions about Cd uptake by oysters and clams in the enriched environment of a biological sewage treatment facility.

All the model estimates rely on poorly known values for uptake from solution alone, possibly unreliable estimates of assimilation efficiencies (Amiard and Amiard-Triquet, 1977), and limited knowledge of feeding rates and sources of food. Thus, such calculations are indirect estimates, at best.

Tissue distributions of metals also differ with the source of uptake, as do physiological kinetics. Differences in tissue distribution between animals exposed to metals in food and those exposed to metal-enriched solutions have been observed for Hg in oysters (Cunningham and Tripp, 1975), Zn in euphausiid crustaceans (Fowler and others, 1970), and Zn, Mn, Co, Hg, and Fe in mussels (Pentreath, 1978) and fish (Pentreath, 1976a, b, c). Surface adsorption is especially important in crustaceans exposed to solute metals (VanWeers and Petten, 1975), and in contamination of "external organs" (e.g., mantle, gills) in mollusks (Amiard, 1978). In contrast, exposure to metals in food appears to result in greater metal accumulation in digestive organs and muscle in most species (Tenore and others, 1968). Surface adsorption may accentuate the apparent efficiency of whole-body metal uptake from solution often observed in studies with species such as zooplankton (VanWeers and Petten, 1975; Sick and Baptist, 1979) and may lead to underestimates of the significant transport of metals from food to internal tissues.

Pentreath (1976a, b, c) compared tissue distributions of Hg in fish (the plaice, *P. platessa*) exposed to organic and inorganic Hg in food and in solution. Only animals exposed to methylmercury in food showed distributions similar to those observed in fish from nature, leading to the conclusion that food was the source of the metal. Bryan and Uysal (1978) concluded from tissue distributions that Cd, Co, Pb, and Zn, but possibly not Ag and Cu, in the burrowing clam *Scrobicularia plana* originated largely from food.

The source of metal uptake may also affect distributions of metals at the biochemical level. Proportionately less Cd is bound to low molecular weight protein and more to a medium molecular weight (12,000 g/mole) protein in the mid-gut gland of crabs (*C. maenus*) exposed to Cd in food than in those exposed to solute Cd (Jennings and Rainbow, 1979). These biochemical differences may be the cause of kinetic differences among animals exposed to different sources of metals. Efflux of Ag, Cs, Mn, and Zn in both fish and invertebrates appears to be slower when food is the source of the metals than when uptake is from solution (Amiard, 1978; Suzuki and others, 1979). Different tissue distributions and biochemical distributions could suggest differences in the predominant form of metal transported via food and solution, since it seems likely that a single form of a metal would be metabolized similarly whatever its site of uptake.

The characteristics of metal uptake may also differ when metals are introduced via different vectors. If efflux rates are slower when uptake is from food than when uptake is from solution, then equilibration should occur more slowly when food is the source of metal. Where studies have been conducted over sufficient time periods, continuing long-term uptake from food has been evident (Stewart and Schulz-Baldes, 1976). If long-term exposure to metal enrichment is necessary to simulate the kinetics of metal uptake from food, then uptake from food, which is insignificant in short-term exposures characteristic of laboratory situations, may not replicate events occurring over the lifetime of an organism in nature.

Differences in metal availability among food types and the variety of foods ingested by many organisms also make it difficult to draw broad conclusions about the contribution of food to uptake. Metals in synthetic foods are consistently more available than are metals in natural foods labeled "in vivo." Higher Zn uptake from synthetic food than from labeled prey organisms was observed in freshwater fish (Merlini and others, 1976). Demersal marine fish (*P. platessa*) accumulated twofold more ^{65}Zn from synthetic foods (gelatin or starch) than when fed ^{65}Zn-labeled polychaetes (*Nereis diversicolor*) (Pentreath, 1973a). Similar results were observed with ^{60}Co and ^{59}Fe (Pentreath, 1973b). Efficiencies of Hg assimilation by northern pike (*Esox lucius*) ranged from 38 to 89 percent when the animals were fed synthetic food or tissue homogenates, but were only 20 percent in animals fed live carp labeled "in vivo."

Metal availability may also differ among prey species. For example, plaice feed on a variety of benthic organisms, including amphipods, sessile polychaetes such as *Arenicola marina*, and errant polychaetes such as *Nephthys sp.* and *Nereis diversicolor* (Pentreath and Jeffries, 1971). The errant polychaetes are digested most efficiently. When plaice were fed a mixture of food types labeled with fluctuating concentrations of ^{137}Cs, fluctuations of ^{137}Cs in the predator followed those in only one species of errant polychaete (*Nephthys* sp.), suggesting that this species alone was the primary source of available ^{137}Cs.

Similar studies showed that retention by plaice of methylmercury (MeHg) from the polychaetes *N. diversicolor* and *A. marina* exceeded retention observed when the fish were fed MeHg-enriched shrimp or mussels (Pentreath, 1976b). Sick and Baptist (1979) observed up to 550-percent greater uptake of Cd by copepods (*P. coronatus*) fed the algae *Dunaliella viridis* than when *Skeletonema costatum* was the food source. The difference in availability between species increased at higher concentrations of Cd. Higher concentrations of Hg in piscivorous sharks compared with sharks that are benthic predators (Walker, 1976) may reflect a greater availability of Hg from fish tissues than from benthic organisms. Higher concentrations of methylmercury in fish tissues may also influence such differences, however. Finally, in general, it has been observed in the mammalian literature that Zn in plant tissue is less available to feeding organisms than Zn in animal tissues (Evans and others, 1974).

Some of the differences in metal availability from different foods may relate to differences in the strength of metal binding to different ligands in prey tissues. The importance of binding differences among ligands is indicated in two studies of metal transfer to predators from prey that are in kinetically different phases of uptake. Phillips and Gregory (1979) observed that methylmercury uptake was more efficient in pike fed prey exposed to high concentrations of Hg for short periods than in pike fed prey equilibrated for long periods in vivo. Longer equilibration of an organism results in proportionately greater quantities of Hg occurring in slowly exchanging and (presumably) more strongly bound pools of Hg (Luoma, 1977a). Similarly, Merlini and others (1976) first fed snails freshly labeled with ^{65}Zn to fish, and then fed the fish snails that had been labeled and then allowed to lose Zn for a period of time. Rapidly exchanging (loosely bound) pools of Zn in the snails would be depleted during the period of efflux, resulting in proportionately more slowly exchanging Zn in the second group of snails than in the first. The fish exhibited more efficient Zn uptake from the first group of snails than from the second group.

In summary, trace metals in food are less available to aquatic organisms than trace metals in solution. However, because of high concentrations, food appears to be an important source of at least some metals to some organisms. There is probably no simple answer to the question of whether food or water is the most important source of metals. The availability of metals differs among different types of food and may even differ within a food type over time. Concentrations also fluctuate with time and space. Metals in solution are subject to the same temporal and spatial variations in availability and concentration. Models that incorporate knowledge of the controls on metal availability from both vectors will be essential to predicting metal burdens in organisms from environmental exposures. Unfortunately, studies of differences in metal availability from different foods are sufficiently rare that few generalizations are possible. Studies that link the biochemical partitioning of metals to different ligands in foods with the trophic transfer of those metals are subject to major difficulties. However, such work is essential to understanding the transfer of metals to organisms from their environment.

THE ROLE OF SEDIMENTS

The most concentrated environmental pool of trace metals in aquatic ecosystems occurs in suspended and bed sediments. Organisms are directly exposed to sediment-bound metals through surface contact and accidental or intentional ingestion during feeding. Sediments also may control solute metal concentrations in interstitial water or in waters overlying the sediment bed, thus affecting biological exposure to the solute vector of uptake.

A wide variety of characteristics affect the way metals bind to sediments, and thus the potential biological availability of sediment-bound metals (see Luoma and Davis, 1983, for a comprehensive review). First, concentrations of sediment-bound metals are strongly dependent on the surface area of the sedimentary particles. Thus, fine-grained sediments bind metals more efficiently than do coarse-grained, sandy sediments.

Second, several sedimentary components (substrates) are involved in metal binding. The most important of these include iron and manganese hydrous oxides (known also as sesquioxides), organic materials (viable and nonviable) and, to a lesser extent, clays and carbonates (Jenne, 1977; Luoma and Davis, 1983). Each of these components may occur in a number of forms, each of which binds metals differently. Deposit- and suspension-feeding organisms are exposed to all of these substrates in their quest for nutrients. Nearly all silt-clay particles in surficial estuarine sediments occur as organic-mineral aggregates (Johnson, 1974), making chemical separation of particle types difficult for feeding organisms. Furthermore, most deposit feeders choose their food only on the basis of particle size, or particle density (Newell, 1965; Bubnova, 1974; Whitlatch, 1974; Self and Jumars, 1978), although particle-size selectivity may differ among species. For example, the clam, *Macoma balthica*, digests various types of particles > 80 μm in size (Yonge, 1949). The average particle size in the digestive gland of *Macoma inquinata* is 10 μm, while particles in the gut of *Macoma secta* average 300 μm (Reid and Reid, 1969). The more selective feeder, *Pectinaria gouldii* (a polychaete worm), ingests particles <75 μm and >25 μm, but employs no detectable chemical selection (Whitlatch, 1974). "Selective" suspension-feeding organisms also may inadvertently ingest a variety of metal-binding substrates when heavy concentrations of resuspended materials are mixed with phytoplankton in the water column, or may employ some suspended sediment as an essential source of nutrients.

Redox also affects the form of sediment-bound metals. Under reducing conditions, oxides of Fe and Mn are solubilized, iron sulfide is precipitated in abundance (and may bind trace metals; Jenne, 1977), and metal sulfides may be formed. In oxygenated waters, however, reducing conditions occur only in sediments below the sediment–water interface. Most benthic organisms are exposed primarily to metals associated with oxidized particles (Luoma and Davis, 1983). Many infaunal organisms feed at the oxidized sediment–water interface or irrigate burrows with water from the oxidized surface. Meiofauna live exclusively above the redox interface (Coull, 1979), and epibenthic organisms are in contact, almost exclusively, with the oxidized environment at the surface of the sediment. Where reducing conditions occur, they undoubtedly affect the availability of sediment-bound metals; in general, however, benthic animals are exposed only to oxidized sediments.

The distribution of metals among the various substrates in oxidized sediments is complex. Hydrous oxides of iron, manganese, and aluminum, aluminosilicate minerals, organic matter, and carbonates all may be present. All are capable of sequestering metals from the overlying water by coprecipitation, adsorption, or ion exchange. At equilibrium, the partitioning of metals among the substrates is controlled by:

1. mass action, as determined by substrate abundance and the binding site density of each substrate;
2. the binding intensity of the metal ion to each substrate (intensities differ among metals);
3. solution parameters such as pH and dissolved ligand concentrations which may influence the speciation of dissolved metal ions; and
4. the concentrations of other metal ions that may compete with trace metals for available binding sites (e.g., Ca^{2+}, Mg^{2+}).

Because substrate concentrations may vary dramatically with space and time in some environments (Luoma and Bryan, 1981), the kinetics of metal redistribution among substrates may also play a role in determining metal partitioning, because systems are rarely at equilibrium.

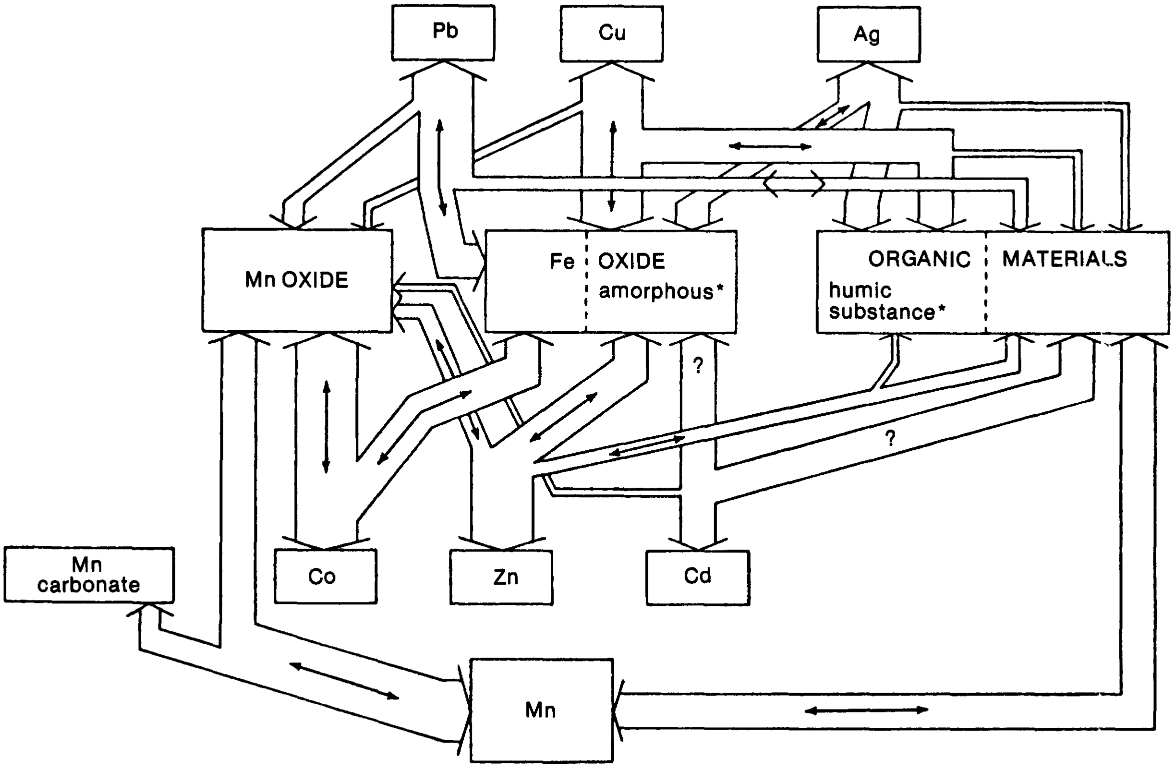
The total binding sites of pure substrates do not necessarily equal the binding sites available when metals partition in oxidized sediments because of the complex nature of the particles involved. Concentrations of iron and organic materials correlate with the abundance of fine particles, suggesting that these types of ligands occur as surface coatings (Jenne, 1977). Relatively rapid (several days) coating of particles by bacteria and their exudates has been observed in the laboratory (Corpe, 1975). Simultaneous flocculation of colloidal iron oxides and colloidal organic material at the freshwater/seawater interface, generating complex, aggregated particles in which these two substrates are intermixed, also has been observed (Sholkovitz, 1976). Although manganese concentrations do not correlate well with the abundance of fine particles in sediments, manganese hydrous oxides may also occur in aggregate particles. Sundby and Silverbert (1981) demonstrated that 80 percent of the manganese in near-bottom suspended sediments occurred as "weak enrichments (>1 percent) on a background of otherwise undistinguished particles." Manganese was also observed as a stronger enrichment (1-20 percent) in 10–20-μm-sized particles which were more obviously aggregates. These results are all consistent with suggestions (Jenne, 1977) that many natural particles are a complex, interlayered, intermeshed mixture of iron hydrous oxide coatings, organic coatings, and minute but discrete manganese hydrous oxide particles, often adsorbed on the surfaces of clay particles. Microscopic observations show that nearly all clay-silt-sized particles in estuarine surface sediments resemble such complex aggregates (Johnson, 1974).

Layering and aggregation may strongly influence the partitioning of metals among binding sites on the substrates involved. The total site density available for metal binding may not change, but the types of sites available and the intensity of binding could certainly be affected (Davis and Leckie, 1978; Hunter, 1980). For example, different types of model particles rapidly take on a common surface charge, different from their surface charges in artificial freshwater or artificial seawater, when immersed in natural seawater (Neihof and Loeb, 1972). Adsorption coating of particles by both microorganisms (Corpe, 1975) and humic materials (Davis and Gloor, 1981; Tipping, 1981) has been observed. Balistrieri and others (1981) presented evidence that the scavenging of trace metals by suspended marine particulate matter is better correlated with the complexation properties of organic ligands than with the properties of oxide surfaces. Coating of suspended particles with adsorbed organic particulates derived from biological processes, for example, packaging in fecal pellets, could explain such results.

Although adsorption of organics may cover binding sites on suspended inorganic particles, this effect may be balanced in some environments (e.g., the sediment-water surface) by the regeneration of sites on fresh amorphous oxides. For example, when iron and manganese are buried, they are solubilized in the reducing environment of the anoxic subsurface sediments. Diffusion to the sediment surface may then occur, followed by reprecipitation as highly reactive amorphous oxides containing high densities of uncoated sites available for reaction with trace metals (Luoma and Davis, 1983). For another view of sediment-organic interactions, see the paper by Leenheer in this circular.

In general, differences in binding intensities among metals suggest that partitioning among substrates will be metal-specific (fig. 5). The immense variability of substrate concentrations among some sediments (Luoma and Bryan, 1981) suggests that partitioning of a specific metal also will be dynamic in both time and space. No one substrate is likely to dominate partitioning of all metals in all sediments (Luoma and Davis, 1983). The myriad forms of substrates available to bind metals, the differences in binding to these different substrates which characterize different metals, and the complex, aggregated nature of the component mixtures in sediments cause difficulties in precisely defining partitioning of metals among components in natural sediments. Direct means of determining how a metal is partitioned in a sediment are not available. Operational methods of extracting specific forms of metals from sediments have proved, in fact, to be highly nonspecific (Luoma and Jenne, 1976b; Guy and others, 1978). Methods for mathematically modeling metal partitioning in sediments, anologous to speciation models of metals in solution, may offer some hope for estimating partitioning but are not fully developed (Luoma and Davis, 1983). Qualitative, indirect methods such as statistical correlations (Luoma and Bryan, 1981) or studies with well-defined model sediments (Oakley and others, 1980, 1981) can be used to estimate partitioning. However, determining the effects of partitioning on the biological availability of sediment-bound metals from such methods is difficult.

Aside from the problems of determining how metals are bound in particulates and the general difficulties of studying metal uptake from ingestion, several unique problems may confound the interpretation of laboratory studies of metal transfer from sedimentary particles to organisms (Luoma and Jenne, 1976a). First, the distribution of metals between solid and solution differs among sediments. In closed experiments, desorption of metals from sediments to "clean" water or adsorption of metals from labeled water to "clean" sediments may be quantified in a distribution coefficient, but the sediment-water distribution observed in a closed laboratory exper-



*Operationally defined

FIGURE 5.—Partitioning of Ag, Cd, Co, Cu, Pb, and Zn among binding components important in oxidized sediments, as indicated by statistical associations (from Luoma and Bryan, 1983).

iment may not be the same as the distribution in open systems in nature. Furthermore, the form of the solute metal in the laboratory solution will most certainly not be the same as would occur in many natural systems, thus affecting the bioavailability from the solute vector. Thus, metal availability from a sediment cannot be determined for any environment beyond that precise laboratory aquarium unless the vectors of uptake are separated. Second, because metal concentrations in sediments are high, undigested sediment in the digestive tract may bias the results of whole-body metal analyses—especially in small animals (Elwood and others, 1976; Flegal and Martin, 1977). Third, redistribution of metals among different binding components may occur if changes in sediment chemistry occur (Oakley and others, 1980). If one type of labeled particle is introduced to an experiment (or an environment) containing several types of unlabeled particles, there is no assurance that the exclusive binding of the metal to the original particle type is maintained.

Few laboratory experiments have considered these limitations. Several studies that demonstrated that fish accumulate Hg (Jernelov, 1970; Gillispie, 1972) and other metals (DeLisle, 1975) in a closed sediment-water system did not differentiate the vector of uptake. Similarly, experiments that showed that metal uptake differed among different types of sediments (Chipman and others, 1968; Beasley and Fowler, 1976; Pesch, 1979; Phelps, 1979) may have reflected differences in distribution coefficients rather than actual differences in availability from different ingested sediments. Renfro and Benayoun (1976) compared uptake from organic materials and Fe oxides labeled with ^{65}Zn when each was mixed with sediments from the Mediterranean Sea and fed to a polychaete (*N. diversicolor*). Only small differences between treatments were observed. However, no controls on metal redistribution among particle types, or between particle and solution, were established. Substantial uptake of ^{115m}Cd from sediments by the polychaete *Neries japonica* (Ueda and others, 1976) was demonstrated, but the kinetics of uptake (Luoma and Jenne, 1976a) suggested that undigested sediments were an important component of the ^{115m}Cd content of the organism.

To separate the vectors of uptake, Dean (1974) exposed tubificid worms to sediments labeled with ^{65}Zn and ^{59}Fe in a rapidly exchanging flow-through system. After depuration of digestive tracts for 4 hours, no uptake from ingestion of either nuclide by the worms was evident. Harrison and others (1976) compared oysters (*Crassostrea gigas*) exposed to water and particles with oysters exposed to particle-free water (particles were removed by filtration) in the discharge canal of a nuclear power plant. The former group of oysters contained more ^{60}Co, ^{65}Zn, and ^{54}Mn than the latter. Little uptake of ^{60}Co from solution was evident. Kudo and Mortimer (1979) also showed much higher concentrations of Hg in fish ("guppies") held in contact with labeled sediments than in fish physically separated from sediment by nylon mesh. No control of undigested stomach or intestinal content was established in the whole-body analyses employed in either of the latter two studies, however.

In studies with deposit-feeding clams, Luoma and Jenne (1976a, 1977) separated the vectors of ^{110m}Ag (the superscript "m" implies a metastable form of the isotope), ^{109}Cd, ^{60}Co, and ^{65}Zn uptake by enclosing some of the experimental animals in dialysis bags. Nuclide concentrations in enclosed animals were subtracted from those in feeding animals to obtain an estimate of uptake from ingestion alone. The contribution of undigested sediment was estimated from uptake kinetics, and the animals were fed individual, well-defined components of sediment for 13 days. Metals bound to iron hydrous oxides, manganese hydrous oxides, organic materials, and carbonates were considered in different experiments. Although uptake from solution occurred more rapidly than uptake from sediments, significant bioaccumulation from ingestion alone was observed. Furthermore, uptake from ingestion alone differed among sediment types by as much as a thousandfold (fig. 6). Differences in availability among sediment types differed among metals. Since experiments with all metals were conducted simultaneously, a common biological control (feeding rate) could not explain the differences. The biological availability of the metals was obviously influenced by binding to different substrates. The differences among sediments in uptake from ingestion correlated significantly with equilibrium sediment–water distribution coefficients for Ag, Co, and Zn. This suggested that the strength of metal binding to different substrates controlled the availability of metals to organisms ingesting those sedimentary components.

Laboratory experiments show that some direct transfer of metals from sedimentary particles to organisms is possible, and that factors other than concentration (e.g., the distribution of metals among substrates) may affect metal uptake from particles. Field studies are necessary to determine the relative importance of particles as a direct vector of metal uptake, however.

If exposures to sediments control metal bioaccumulation by benthos, then metal concentrations in organisms in nature might correlate with concentrations in sediments. Strong correlations are most commonly not observed, however. Poor correlations between marine or estuarine benthic organisms and their sedimentary habitat have been reported by Cross and others (1970), Halcrow and others (1973), Valiela and others (1974), Huggett and others (1975), Luoma (1977b), and Schell and Nevissi (1977). The poor correlations between metal concentrations in benthic organisms and sediments could mean that metals in benthos are not derived from sediments or from sources coupled to sediments. However, the poor correlations could also result from statistical problems in the comparison, or from an influence of variables other than metal concentrations in sediment on metal bioavailability.

Two especially important problems have characterized statistical comparisons of metal concentrations in benthos and their food: (1) the actual food of the organisms has not always been used in the comparison, and (2) an adequate data range has not always been employed.

Obviously, metal concentrations in filter-feeding organisms that depend primarily on phytoplankton for food (e.g., oysters, mussels, and some species of clams) or in herbivorous grazing animals would not necessarily correlate with metal concentrations in sediments, even if food

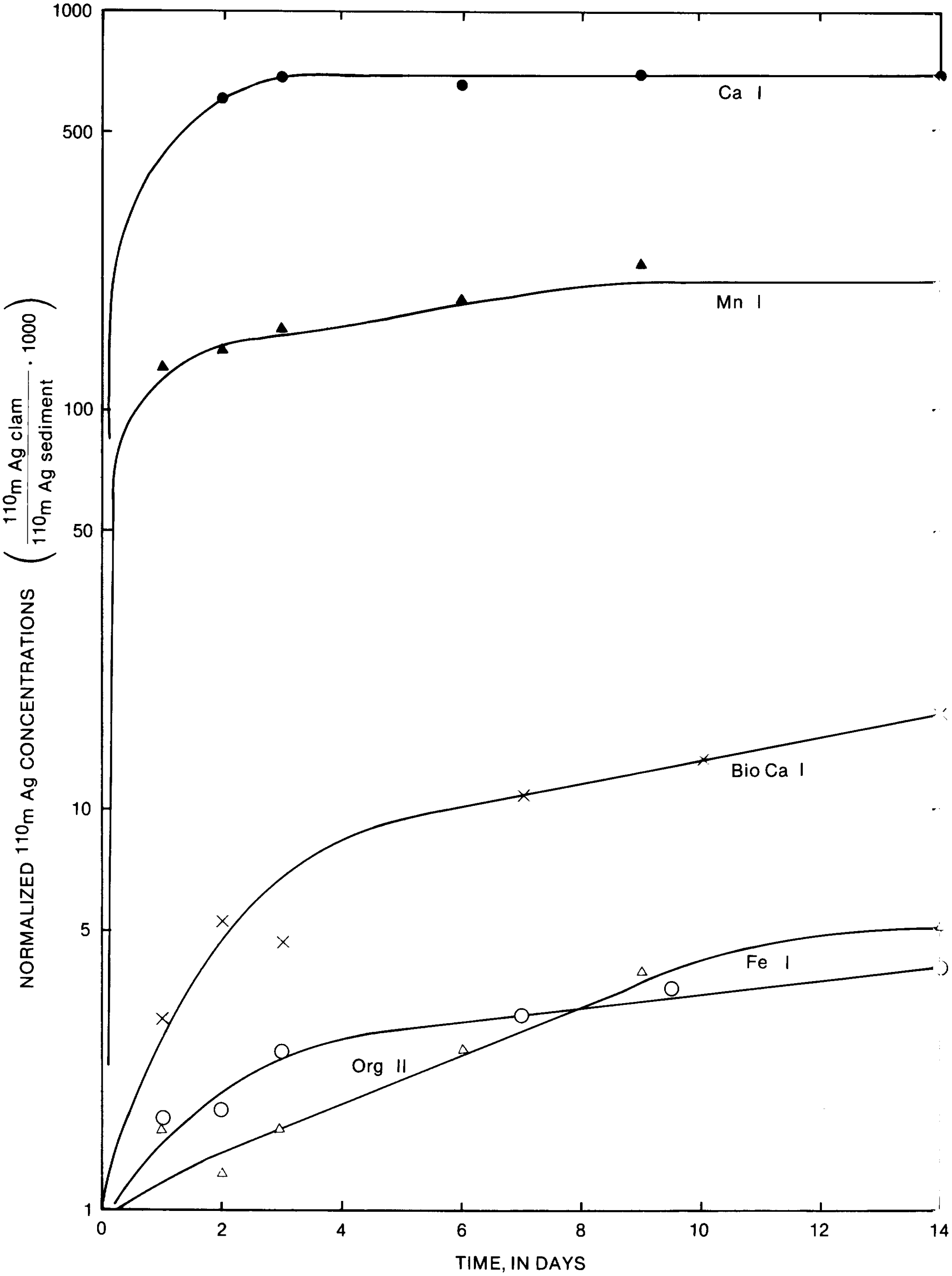


FIGURE 6.—Differences in uptake of $^{110\mathrm{m}}$Ag when different types of well-defined sediments were ingested by the deposit-feeding clam *Macoma balthica*. Sediment types are amorphorus iron oxides (Fe), decaying marsh grass fragments (org), manganese oxides (Mn), crushed bivalve shells (BioCa), and calcium carbonate (Ca) (from Luoma and Jenne, 1977).

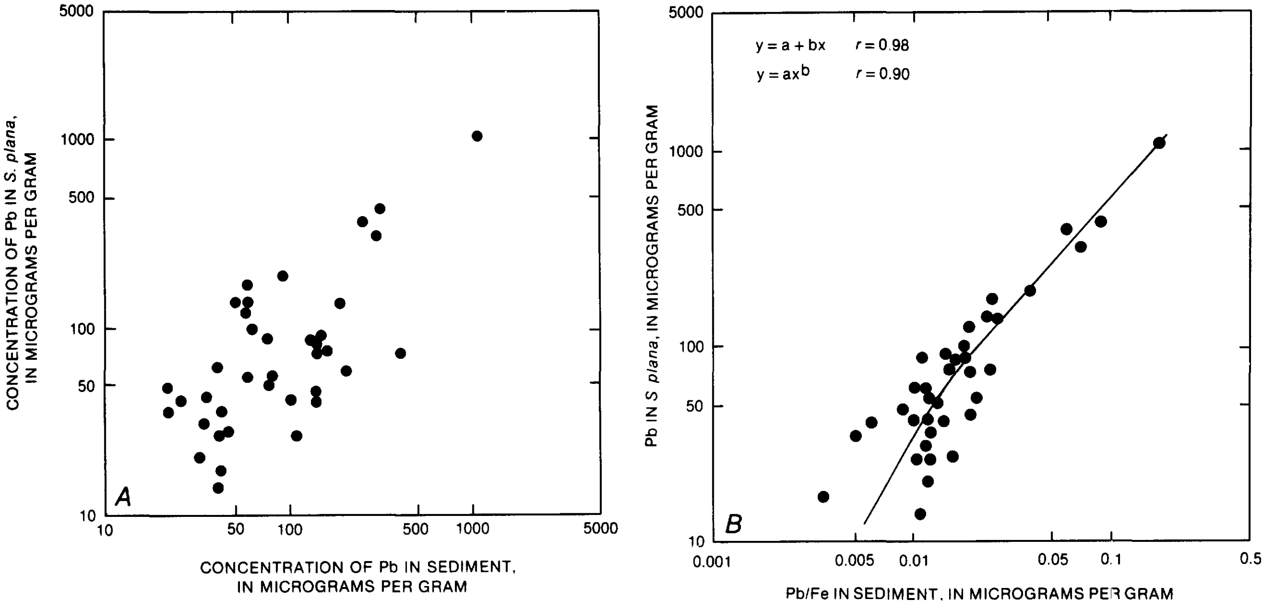


FIGURE 7.—Correlation of Pb in deposit-feeding bivalve *Scrobicularia plana* with Pb or Pb/Fe ratio in surficial estuarine sediments. *A*, Correlation with Pb; r=0.69 for power function fit. *B*, Correlation with Pb/Fe ratio (both extracted by 1 *N* HCl; r=0.95). (Data from 17 estuaries: from Luoma and Bryan, 1978.)

were the primary vector of metal uptake. For example, concentrations of most metals in grazing snails follow concentrations in algae, but not sediments, where sediments and algae are not correlated (Young, 1975; Bryan and Hummerstone, 1977). Even among deposit-feeding organisms, differences in food sources may affect metal exposure. For example, Phelps (1967) and Phelps and others (1969) reported consistent differences in Zn concentrations among benthic polychaetes from different feeding guilds (surface feeders versus subsurface feeders; selective versus nonselective feeders).

Most correlation studies also have been conducted within a single body of water, including only narrow concentration gradients in the comparison. Comparisons that have considered wider data ranges have shown some significant correlations between metal concentrations in deposit feeders and concentrations in sediments. Bryan (1974) found that concentrations of Cu, Pb, and Cd in the polychaete *N. diversicolor* correlated strongly with concentrations in sediments from the sediment-water interface when data were collected from several estuaries. Packer and others (1980) found that Cd and Zn concentrations in the polychaete *Arenicola marina* followed Cd and Zn in sediments from 24 stations on the coast of Wales. Significant correlations were not observed for Pb, Cu, and Mn, however. In an extensive survey, Luoma and Bryan (1978, 1979, 1981) compared concentrations of Ag, Cd, Co, Cu, Pb, and Zn in two deposit feeders, the burrowing clam *Scrobicularia plana* and the polychaete *N. diversicolor*, with concentrations in sediments over a wide range of conditions among 50 stations in 17 estuaries. The data range for all metals was two to three orders of magnitude. Statistically significant (but weak) correlations between total metals in sediments and the tissues of *S. plana* were observed for Pb (fig. 7*A*) and for all other metals except Cu. Stronger correlations were observed between sediments and *N. diversicolor* for Cu and Pb; however, over the broader data set, these correlations were not as strong as those observed by Bryan (1974). In general, the data suggested that total concentrations contributed to metal concentrations in the deposit feeders, but that an understanding of other contributing variables would be necessary to predict metal concentrations in organisms from concentrations in the environment.

Deviations in correlations between organisms and sediments could result from uptake from solution. However, even where the source of exposure that controls both the food and solute vectors is well defined, deviations of bioaccumulation from dependence on exposure alone are evident. For example, Bryan and Hummerstone (1977) observed differences in Ag and Cu concentrations in *S. plana* from two estuaries which could not be explained by Ag and Cu either in water or in sediment. In San Francisco Bay, spatial variations in Cu concentration indicated that a sewage outfall was the primary source of the metal for the burrowing clam *Macoma balthica.* Cu concentrations in the clams were consistently highest near the outfall and declined in both directions away from the outfall (Thomson and others, 1984). Sediment analyses also showed Cu enrichment of particles, per unit surface area, near the outfall. Temporal trends in Cu concentrations in surface sediments near the plant outfall followed temporal trends in Cu discharge determined from analyses of plant effluent. This indicated that Cu concentrations in surface sediments were an accurate indicator of Cu discharge from the plant. Comparisons of 5 years of near-monthly analyses of sediments and clams from this site showed that, although Cu levels in *M. balthica* were occasionally coupled to exposure, large fluctuations in Cu concentrations occurred in the clam which could not be explained by changes in exposure. Again, a general dependence on exposure was evident, but other variables also were obviously important in controlling bioaccumulation.

Employing the broad data set described earlier, Luoma and Bryan (1978, 1979, 1981) used multiple regression to identify the relative importance of several possible causes of spatial variation in concentrations of Ag, Cd, Co, Cu, Pb, and Zn in two deposit feeders, *S. plana* and *N. diversicolor*. Variables tested included (1) total metal concentrations in surface sediments, (2) the influence of physicochemical form on metal availability, (3) uptake from the solute vector, and (4) the effect of intermetal competitive inhibition or enhancement.

The influence of physicochemical form was tested in two ways. First, sediments were extracted with six different extractants. Previous laboratory work with model sediments and deposit-feeding clams (Luoma and Jenne, 1976b) had indicated that extractable fractions of some trace metals might correlate with the availability of those metals. Soil scientists also have employed extractants to test the bioavailability of soil-bound metals to crop plants (reviewed by Stearitt and Lester, 1980). Various extractable fractions of metals in aquatic sediments have been described as biologically available (Loring, 1978), although without empirical information.

Second, concentrations of substrates (Fe, Mn, total organic carbon, carbonates, humic substances) in sediments were included as independent variables in the regression calculations. Statistical studies of sediments alone indicated that metal partitioning shifted among such substrates as substrate concentrations changed (Luoma and Bryan, 1981). It was assumed that if changes in partitioning affected metal bioavailability (as suggested by Luoma and Jenne, 1977), then metal concentrations in organisms might show some correlation with the substrate concentrations which controlled partitioning. Uptake from the solute vector was assessed using metal concentrations in the seaweed *Fucus vesiculosus* as an indicator of biologically available metal in solution. Concentrations of Cu in *F. vesiculosus* correlated strongly with Cu in sediments; thus this technique could not be used to test uptake of biologically available Cu from solution. Because the data range for all variables was broad, few autocorrelations occurred among independent variables.

The multiple regression calculations showed that 70–80 percent of the variation in all metals in the organisms (except Cu in *S. plana*) could be explained by 2–5 of the independent variables (table 4). The solute vector was quite important in Cd uptake by both species and also affected Co and Zn uptake. No effect of uptake from solution was evident for Ag or Pb. Extraction of sediments improved prediction of metal availability from sediment (compared with predictions from total metal concentrations) for Ag, Cd, Co, and Zn. The best correlations were obtained with 1 *N* ammonium acetate for Zn (as reported in many soil studies, e.g., Stearitt and Lester, 1980) and with 1 *N* HCl for the other metals. The availability of Pb followed total concentrations in sediment as closely as extractable concentrations.

The same was true of Cu in correlations with *N. diversicolor*. With the exception of Cd, metal concentrations in sediment (extractable or total) explained 37-72 percent of the variation in concentrations in the deposit feeders.

Concentrations of binding substrates in sediments explained 8–49 percent of the variation in metal concentrations in *S. plana* and *N. diversicolor*. Concentrations of Pb in *S. plana* were very closely correlated (R^2=0.89) with Pb/Fe in sediments (where Fe was measured by HCl extraction; fig. 7*B*).

Luoma and Bryan (1978) suggested that the availability of Pb was enhanced at low concentrations of Fe in sediment because less Pb was strongly bound to iron hydrous oxides as the Pb/Fe ratio in sediments increased. Whatever the cause, the ratio Pb/Fe in sediments was an accurate predictor of Pb in *S. plana* in estuaries not included in the original regression calculations.

The substrates that correlated with concentrations of Ag, Cd, Co, and Zn in *S. plana* and *N. diversicolor* differed among metals but were usually similar for the two deposit feeders. In all cases, more than one substrate correlated significantly, and the predictive capabilities of the regressions were not as strong as observed with Pb. Nevertheless, the statistical importance of partial extractions and correlation with substrate concentrations in sediments suggested that the physicochemical partitioning of metals in sediments provided an important control on metal availability to deposit feeders.

Physicochemical conditions other than those statistically tested by Luoma and Bryan (1978, 1979, 1981) also appear to influence metal bioavailability from sediment. Increased pH appears to increase the availability of Hg (perhaps by stimulating conversion of Hg^{+2} to Hg^0), but not of Cu and Pb, to marsh plants (Gambrell and others, 1977). Strong reducing conditions cause a substantial decline in the availability of Cd to marsh plants (Gambrell and others, 1977). Unpublished data from the study of Luoma and Bryan also suggested that Cd was of lower availability in highly anoxic mudflats. The availability of Cu to the polychaete *Neanthes arenaceodentata* also is less from subsurface than from surface sediments (Pesch, 1979), presumably owing to differences in redox potential. In contrast, certain

TABLE 4—*Percentage of the total variation in concentration of Ag, Cd, Co, Cu, Pb, and Zn in two deposit feeders from 17 estuaries explained by statistical correlation (multiple regression) with metal in various locations*

[From Bryan, 1982]

Species	Metal	Metal in sediment extract[1]	Metal-binding substrate concentrations[2]	Metal in seaweed (fucus)[3]	Other metals in sediment[4]
Scrobicularia plana (a bivalve).	Pb[5]	50 ($\overset{+}{\text{HCl}}$)	28–49 ($\overset{-}{\text{Fe}}$)	?	0
	Ag	49 ($\overset{+}{\text{HCl}}$)	8 ($\overset{-}{\text{Mn}}$, $\overset{-}{\text{humics}}$, $\overset{+}{\text{TOC}}$)	0	28 ($\overset{-}{\text{Cu}}$)
	Co	47 ($\overset{+}{\text{HCl}}$)	18–21 ($\overset{+}{\text{humics}}$, $\overset{-}{\text{TOC}}$)	8	0
	Zn[6]	37 ($\overset{+}{\text{Am. acetate}}$)	23 ($\overset{+}{\text{humics}}$ $\overset{-}{\text{TOC}}$, $\overset{+}{\text{Mn}}$)	7	0
	Cd	29–31 ($\overset{+}{\text{HCl}}$)	20–23 ($\overset{+}{\text{Mn}}$, $\overset{-}{\text{TOC}}$, $\overset{+}{CO_3}$)	16	0
	Cu	No relation	10 ($\overset{-}{\text{TOC}}$ or $\overset{-}{\text{Fe}}$)	?	16 ($\overset{+}{\text{Ag}}$)
Nereis diversicolor (a polychaete).	Cu	72 ($\overset{+}{HNO_3}$)	7 ($\overset{+}{\text{Mn}}$)	?	8 ($\overset{-}{\text{Pb}}$)
	Co	66 ($\overset{+}{\text{HCl}}$)	0	4	5 ($\overset{-}{\text{Ag}}$)
	Pb	54 ($\overset{+}{HNO_3}$)	21 ($\overset{-}{\text{Fe}}$)	?	0
	Ag	41 ($\overset{+}{\text{HCl}}$)	34 ($\overset{+}{\text{Mn}}$, $\overset{+}{\text{Fe}}$, $\overset{-}{\text{humics}}$)	0	0
	Cd	16 ($\overset{+}{\text{HCl}}$)	23 ($\overset{-}{CO_3}$, $\overset{+}{\text{Mn}}$, $\overset{-}{\text{TOC}}$)	15	0
	Zn[7]	weak relation—regulation by organism			

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[1] Extractant giving the best correlation and sign of the slope of the relationship are in parentheses.

[2] Metal-binding substrates are indicative of metal partitioning. Substrates that correlate significantly and sign of the slope of the relationship are in parentheses.

[3] Metal in seaweed is indicative of biologically available metal in solution.

[4] Metal and sign of the slope of the relationship are in parentheses.

[5] Luoma and Bryan, 1978.

[6] Luoma and Bryan, 1979.

[7] Bryan and Hummerstone, 1973.

types of reducing conditions enhanced the bioavailability of Cu to the clams *S. plana* and *M. balthica* (Luoma and Bryan, 1982). Exceptionally high concentrations of Cu were observed in these animals in seven anoxic mudflats, and during an unusual period of anoxia in one mudflat. Greater enhancements of Cu availability generally accompanied lower concentrations of Fe in sediments, but the precise cause of the enhancement was not identified.

In a recent review, Bryan (1985) summarized, for a number of trace metals, the results of his extensive experience, and that of others, with processes controlling metal availability from sediments to aquatic organisms. He emphasized that the results were speculative; they sometimes differed among species, and definitive studies have been conducted with only a few species, and mostly in estuarine environments. His conclusions were as follows: (1) high concentrations of organic matter and Fe (probably as amorphous iron hydrous oxide) inhibit the availability of Hg, Pb, As, Zn, and possibly Ag and Cu. Sediments high in total organic carbon or extractable Fe may contain high concentrations of trace metals, but the metals do not appear to pass on to most biota; (2) under some circumstances or for some species, the solute vector of uptake is an especially important source of Cd, Zn, and possibly As and Ag; (3) total concentrations in sediments control Cu availability to polychaetes, but the controls on Cu availability to mollusks are not clear; anoxia may enhance Cu availability to mollusks, under some circumstances; (4) Zn availability is controlled by readily exchangeable Zn in sediment, uptake from the solute vector, and a negative influence of organic carbon; and (5) most metals (especially Hg, Pb, Zn, As, Cu, and Ag) would be expected to be of high bioavailability in coarser grained sediments enriched by anthropogenic metal input and in wastes (such as smelter wastes or mine wastes) low in organic material or Fe (this is consistent with the hypothesis of Luoma and Davis (1983) that the availability of some metals may be inversely related to total metal-binding-capacity in sediments). Some unknown attribute of sewage sludge enhances the availability of Ag and possibly Cd. Anoxic conditions reduce the availability of most metals (especially Cd) but may enhance the availability of Cu.

Table 5 summarizes the speculative conclusions presented to date on factors controlling metal availability from sediments to benthos.

TABLE 5.—*Summary of various factors that appear to inhibit or enhance the availability of sediment-bound trace metals to benthic organisms*

	Best extraction method	Vector	Inhibits availability	Enhances availability
Ag	HCl	Sediment (interstitial water)	Cu Extractable Fe?	Sewage factor
As	Total	Sediment Solute (polychaetes)	Extractable Fe	
Cd	HCl	Solute Sediment	Anoxia (S=)	Sewage factor?
Co	HCl	Sediment (Solute?)	Organic carbon	
Cu	Total HCl	Sediment (polychaetes)	Extractable Fe Organic carbon?	 Anoxia (mollusks)
Hg		Sediment	Organic carbon Extractable Fe	Moderate Eh Low organic carbor
Pb	Total HCl	Sediment	Extractable Fe Organic carbon	
Zn	1 *N* ammonium acetate	Sediment	Organic carbon	
	HCl	Solute		

RECOMMENDATIONS

It must be reemphasized that our knowledge of metal bioavailability from sediments is fragmentary at best. Definitive studies are less than 5 years old, have been conducted by only a few research groups, and consider only a few species, and nearly all have been conducted in estuaries. Most conclusions rest on statistical evidence that has not yet been mechanistically clarified by definitive laboratory studies. Additional comparative studies among estuaries, rivers, or coastal environments are needed, as are controlled studies testing some of the hypotheses generated by the statistical work.

Within the limitations of current knowledge, it is possible to recommend a few practical procedures that could enhance the biological relevance of sediment treatment by USGS operational programs. It must be recognized that these recommendations are preliminary and could change as knowledge increases. Furthermore, the objective here is to recommend the simplest possible procedures, so as to maximize their utility in an operational program.

The simplest, biologically relevant measurements of sediments could include

1. Measurement of total concentrations (or near-total concentrations using an HNO_3-reflux) of trace metals.
2. A simple extraction of sediments with 0.5 *N* HCl and analysis of trace metals in the extract.
3. Measurement of major sediment components that affect bioavailability, including
   - Total organic carbon.
   - Concentrations of Fe extracted by HCl. (Acid ammonium oxalate is a more widely accepted alternative for estimating amorphous Fe oxide. However, HCl and oxalate extractions of estuarine sediments usually yield similar results. For the sake of simplicity, measurement of Fe in the same HCl extract used for metals would not result in much loss of information.)
   - Total Mn.

Collection of such samples should be from microenvironments most relevant to organisms of interest in the systems involved. In estuaries, this means sediments should be collected from the thin oxidized layer at the sediment-water interface. In streams, reservoirs, or lakes, a similar procedure might be desirable. Sediments should be sieved prior to storage. Some investigators employ a 100-μm sieve; others suggest 60 μm. Sediments also should be frozen as soon as possible if they are to be stored prior to extraction so as to prevent redox changes that could affect extraction results.

A slightly more extensive program might include

1. Analysis of sediments for more specific forms of components important in metal binding, such as humic substances, or extractions of Mn that exclude one or more of the major forms. Although these procedures have not proved statistically useful in bioavailability studies in estuaries, they could provide valuable information in other systems.
2. Measurement of metal concentrations in a cosmopolitan species of algae, as an indicator of metal availability from the solute vector.
3. Some measure of redox state of the sediments.

This simple program would provide information about the major constituents that appear to affect metal bioavailability and the concentrations of metals that may competitively inhibit availability. Although no simple extraction scheme is likely to define the biologically available fraction of metals in sediment, HCl extractions appear to add biologically useful information. From such a program, general assessments of the vulnerability of different sedimentary environments to accumulation of biologically significant concentrations of trace metals may be possible.

CONCLUSIONS

The impacts of trace contaminants in aquatic environments cannot be assessed realistically without a greater understanding of the factors controlling biological availability. It has been established that direct uptake of (at least some) trace metals from particulates contributes to metal concentrations in benthic organisms. Important controls on metal uptake from sediment are the concentration of the exposure, the partitioning of the metals among substrates in the sediment, and the redox potential of the sediment. Important problems in physiology, geochemistry, and biogeochemistry remain unsolved. However, knowledge of certain processes is essential in determining the physicochemical forms of metals that are available for transport into biological tissues. These processes include (1) the relative importance of carrier-facilitated transport and endocytosis in metal uptake, (2) the nature of metal interactions with carrier molecules, (3) the type of particles transported by endocytosis, and (4) the effect of digestive processes on the form and transport of trace metals. Realistic studies of metal uptake cannot be conducted without a further understanding of the role of membrane-bound vesicles and synthesis of metal-specific binding proteins in that process. Development of geochemical models for predicting metal partitioning among sedimentary components may be within reach of a concentrated research effort (Luoma and Davis, 1983). However, methods for linking such models to biological data will also be necessary. Biochemical study of the processes controlling partitioning and direct methods of studying partitioning could aid in developing techniques for better estimating metal availability to deposit feeders. Biological studies of deposit feeding itself, and the exposure of suspension feeders to a variety of particle types, will be important, as will laboratory and field studies of the influence of different types of particles on metal uptake. Specific hypotheses concerning the availability of different types of sediment-bound metals may be developed from statistical studies. Laboratory tests of such hypotheses may, in turn, improve capabilities for predicting metal availability from particulates in nature. Such predictive capabilities could greatly improve the data base from which guidelines for the release of pollutants are established. However, a concentrated, focused, and interdisciplinary research effort will be necessary to accomplish that goal.

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CONCEPTS AND METHODS FOR CHARACTERIZING THE PHYSICAL PROPERTIES OF SEDIMENTS

By Tung-Ming Lai

INTRODUCTION

The impact on natural water systems of constituents contained in sediments has long been recognized (Jenne, 1968; Jones and Bowser, 1978; Feltz, 1980). Water, sediment, and biota are the main components of natural aquatic systems. These three components continually interact with each other and with their environment in a dynamic hydrologic and biologic system having unique physicochemical characteristics. Interrelationships of inorganic and organic constituents (including metals, nutrients, radionuclides, and synthetic organic chemicals) within this dynamic system are shown in figure 8. Sediments potentially serve as an important source of, and sink for, chemical constituents in the aquatic system.

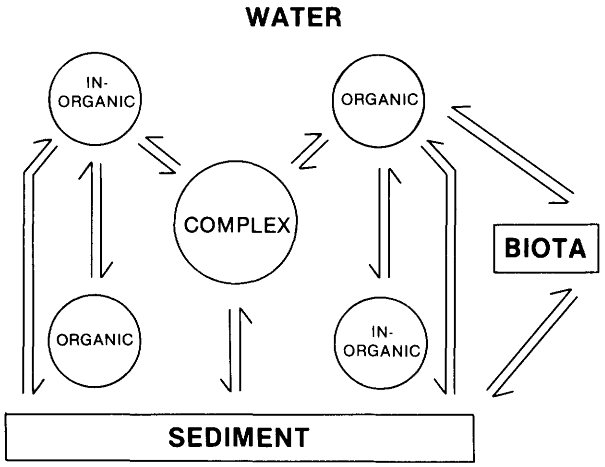

FIGURE 8.—Water-sediment-biota system.

Because sediments serve as a source or sink for chemical constituents, they may play a key role in the investigation of water-pollution sources and effects. A study of certain constituents in sediments can be of great benefit in many cases, as is illustrated in the following examples. An investigation of the distribution of mercury in the waters of Lake Ontario indicated no spatial relationship that would point toward a potential source. Determination of mercury in the sediments, however, revealed a pattern (Förstner and Wittmann, 1979) that led to the discovery that the Niagara River was the main source of mercury input into the lake. Sediment analysis can also be used to determine the level of enhancement of metals in aquatic systems due to atmospheric deposition. For example, determination of metals in sediment cores collected from Woodhull Lake, N.Y., were used to describe rates of atmospheric deposition over the last 30 years (Galloway and Likens, 1979). Both studies indicate that investigations of sediment can play an important role in the study of natural water systems.

The following reactions and processes are known to occur in aquatic systems: (1) precipitation, or coprecipitation, and dissolution, (2) oxidation and reduction, (3) adsorption and desorption, (4) ion exchange, (5) complexation, (6) biological growth and decay, and (7) sediment transport and deposition. The physical properties of sediments have a major effect on adsorption, desorption, ion exchange, transport, and deposition. These physical properties include particle size, surface area, specific gravity, bulk density, porosity, and surface charge. Recent developments in concepts and methods have advanced the measurement and interpretation of some of these properties. In this presentation, only these new concepts and methods are discussed.

COMPOSITION OF SEDIMENTS

The physicochemical properties of sediments are determined primarily by their mineralogical and chemical composition. If the composition is known, many of the properties of sediments can be predicted. Sediments contain both inorganic and organic phases. The inorganic phase generally can be classified as clay minerals, nonclay minerals, and amorphous or noncrystalline materials. Jones and Bowser (1978) pointed out that the mineralogical composition of sediments is seldom thoroughly investigated in studies of aquatic systems; thus a broad base of knowledge regarding the physicochemical behavior of sediments and their role in the chemistry of aquatic systems is generally lacking.

The clay-mineral concept has been well developed since Sterling Hendricks and Walter Kelley independently established that soil clays are primarily crystalline (as reviewed by Thomas, 1977). Clay minerals have high physicochemical activities that vary significantly according to the crystal structure. Nonclay minerals are not as reactive. They are referred to as the "backbone of sediments" because they mainly influence specific gravity and porosity. Nonclay minerals are also the primary source of heavy metals in natural aquatic systems, and their identification may be useful in the study of the origin of sediments.

Concerning the behavior of certain soil components, the emphasis of study has shifted over time. During the period 1930 to 1960, the emphasis was on characterization of clay minerals, and on interpretation of behavior in terms of crystal structure. Before this period, as influenced by the work of Sante Mattson (as discussed by Uehara and Gillman, 1981), soil scientists attempted to interpret soil behavior in terms of the colloid chemistry of mixtures of SiO_2, Al_2O_3, and Fe_2O_3. Unfortunately, Mattson's work was later neglected when the clay-mineral concept dominated soil-science research (Thomas, 1977).

Recent research developments (Thomas, 1977; Uehara and Gillman, 1981) have reaffirmed the importance of noncrystalline components in determining physicochemical behavior of soil particles. As a result, recent trends in research have emphasized these components (Wada and Harward, 1974; Schwertmann, 1978).

Amorphous materials occur mostly as surface coatings on soil particles. In most studies prior to 1970, these materials were systematically cleared from the surface in order to identify and study the mineral species. The possible role of the amorphous materials was largely discounted, even though the existence of a surface coating on freshly ground quartz was proposed by a number of workers in the British coal-mining industry as early as 1952 (Jones and Uehara, 1973). Later, Jenny and Grossenbacher (1963) pioneered the use of the electron microscope to study the root-soil boundary zone, revealing the presence of a mucilagenous coating on the surface of bentonite. Since then, several electron micrographs of amorphous coatings on mineral surfaces have been published (Jones and Uehara, 1973; Greenland and Mott, 1978).

Because of the high chemical activity of surface coatings (Jenne, 1968; Yariv and Cross, 1979; Davis, 1980), recent studies with sediments indicate that organic surface coatings partly mask chemical properties of the underlying solid (Neihof and Loeb, 1972; Kranck, 1975; Davis, 1980; Hunter, 1980). On the other hand, the significance of inorganic coatings, such as iron and manganese hydrous oxides on sediments in geochemical exploration, have also been recognized (Carpenter and others, 1975; Chao and Theobald, 1976). Several papers concerning the behavior and properties of surface coatings on minerals have recently appeared (Greenland and Mott, 1978; Förstner and Wittmann, 1979; Yariv and Cross, 1979).

PARTICLE SIZE

One of the fundamental properties affecting sediment transport and the transfer of chemical constituents between water and sediments is particle size. Size normally is expressed either as an effective or equivalent diameter or in terms of surface area (an aspect to be discussed later). Manual sieving and sedimentation are probably the most commonly used methods for particle size determination, although many automated or semiautomated particle-size analyzers recently have become available commercially (Allen, 1981). The common manual sieving and sedimentation methods are very time consuming. With more emphasis on water problems involving pollution and waste disposal, more particle size analyses will be required.

All available methods of size determination, including the current Water Resources Division procedure and the sophisticated commercial size analyzers, are based on different properties of the particle. It is not surprising, then, that a comparison between the pipet method and several size analyzers showed considerable differences (Pennington and Lewis, 1979; Welch and others, 1979). The purpose of particle-size analysis is to obtain a characterization of the sediment that relates to its behavior and properties. In a practical sense, the actual requirement is not to size the particles, but to define an index property that is size-dependent. The principles of current analyses are based on measuring different size-dependent criteria, such as x-ray attenuation, laser diffraction, fall velocity in a gravitational or centrifugal field, change in electrical resistance, and so forth (Allen, 1981). Therefore, in selecting a procedure or analyzer to be used, one must first consider the purpose of the information. The type of size analysis needed for studying and predicting sediment transport, water pollution, or waste disposal will not always be the same. Different analyzers should be developed or adapted according to the purposes of the information.

In the past, information on particle size has been used primarily in the study of sediment transport, and the commonly used methods for determination of particle-size distributions presumably are geared to that purpose. With more emphasis on water pollution and waste disposal, the relationship between physicochemical properties of sediments and the size fractions involved will have to be explored. This research will lead to better use of size-analysis methods and will improve knowledge about water pollution and waste disposal. For this purpose, a search for better ways to separate particle sizes for physical and (or) chemical characterization of each size fraction is also needed.

For many years, researchers in the Water Resources Division have been interested in the discrepancy between a particle-size distribution measured in the laboratory and that measured in natural waters (Sherman, 1953; Nordin, 1963). In this connection, from about 1950 to about 1970, Water Resources Division laboratories determined the size distribution in every tenth suspended sediment sample using native water without dispersants as part of a national program with the U.S. Department of Agriculture, Soil Conservation Service. The data were published in Water-Supply Papers (see, for example, U.S. Geological Survey, 1968).

When charged particles are dispersed in an electrolyte solution, an electrical double layer is associated with them. This double layer has an effect on viscosity, called an electroviscous effect. Through the efforts of several researchers, this effect has been established and can be measured. The well-known Stokes equation has been modified (Allen, 1981) as

$$v = \frac{(\rho_s - \rho_f)\, g r^2}{18\eta} - \frac{r\sigma E}{3\eta}, \tag{1}$$

where

v = fall velocity,
ρ_s = density of the solid (assumed to be spherical),
ρ_f = density of fluid,
g = acceleration due to gravity,
r = radius of sphere,
η = dynamic viscosity of fluid,
σ = surface charge per unit area, and
E = electrical field superimposed on the fluid.

This relationship has been confirmed by Pavlik and Sansone (1973) and Sansone and Civic (1975) using glass beads.

The fall velocity of particles in the fluid is the basis of size analysis by the sedimentation technique. Results published in Water-Supply Papers from 1950 to 1970, and in Nordin (1963) and Pavlik and Sansone (1973), indicate that the effects of dynamic viscosity and electroviscosity must be considered when the particle-size distribution in the natural water condition is studied.

Coagulation of primary particles is another important factor affecting size distribution in the natural condition. Results of research on coagulation or agglomeration of sediments have been well covered through 1970 by Meade (1972). Since then, many physicochemical studies or electron microscopic observations of sediment aggregates have been conducted (Biddle and Miles, 1972; Kranck, 1975; Feely, 1976; Sholkovitz, 1976; Zabawa, 1978; Chase, 1979). A general discussion of the theory and applications of coagulation has been presented by van Olphen (1977). Bulk density, porosity, surface area, and charge density of aggregates are changed during coagulation, compared with the primary particles. Therefore, coagulation may have a direct influence on sediment transport and pollutant transfer between water and sediments. In addition, pore fluids of sediments are affected by coagulation, and the chemistry of pore fluids is important in understanding natural aquatic systems (Jones and Bowser, 1978). Obviously, as far as the study of size distribution in natural water is concerned, one should first understand the formation and stability of aggregates. Organic matter, cations, oxides, microbes in the water, and the surface charge of particles are the dominant factors governing the process of coagulation. Because the current laboratory procedure is designed to measure primary particle-size distribution, suspended sediments must be well dispersed by systematic chemical and mechanical treatments. Apparently, to some degree, measured size distributions reflect the efficiency of the dispersion procedures used in the laboratories (R. H. Meade, U.S. Geological Survey, oral commun., 1981). Johnson (1974) pointed out that the conventional method of sediment-size analysis deliberately destroys the aggregate matter, resulting in an artifact. This problem is also discussed in the paper by Horowitz elsewhere in this circular. The discrepancy between size distributions measured in distilled water and those measured in native waters may be due primarily to the effects of coagulation and electroviscosity.

Study of sediment aggregates should be a high priority. As knowledge on the formation and stability of sediment aggregates in streams is gained, appropriate aggregate-size analyses may be adopted for certain streams under specific conditions. Given these circumstances, a size determination of aggregates rather than of primary particles may be a better approach to estimating "in-stream" size distributions in natural waters.

Particle shape may affect measured particle-size distribution because of its influence on fall velocity. Particle shape also influences such properties as the flowability of particles, porosity, and interaction with fluids. Effects of particle shape have been reviewed and discussed by Allen (1981).

SURFACE AREA

Surface area and particle size are interdependent. As mentioned previously, the size of particles may be expressed indirectly as surface area per unit mass (specific surface). Preference for the analysis of one parameter related to size over another may be due primarily to convenience or other circumstances, as discussed to a certain extent by Förstner and Wittmann (1979). Theoretically, one may use either value (size or surface area) to express experimental results. However, current methods of measuring size or surface area will yield a certain degree of deviation from actual values in the natural condition; therefore, size measured by a particular method may be found to relate better to certain properties of sediments in one case, and surface area in another case.

Although primary particles and aggregates may have the same apparent size, and even the same chemical and mineralogical compositions, their specific surface values may differ, as measured by an adsorption method. In another situation, one in which surface coatings of sediments are thicker on coarser particles (Gibbs, 1977), the effect of surface area on adsorption may dominate the size effect. In this case, a surface-area measurement would be more appropriate for evaluating certain properties of sediments. For instance, in a recent study of chromium accumulation in sediments of the Saco River, Maine, Mayer and others (1981) assessed the pollutant impact by textural normalization using sediment-surface area. In a study of chemical modeling of trace metals in fresh waters, Vuceta and Morgan (1978) showed that adsorption of metals is a function of surface area of hydrous oxides. Polychlorinated biphenyl (PCB) adsorption by sediments in Osaka Bay (Japan) was found to be controlled mainly by sediment-surface area (Hiraizumi and others, 1979).

Several ways of measuring surface areas are described in recent publications (van Olphen, 1977; Greenland and Mott, 1978; Allen, 1981). The most common and established method is based on the Brunauer, Emmett, and Taylor (BET) gas adsorption equation (Allen, 1981). In the past, most laboratories had their own homemade BET apparatus and the procedure was slow. Several BET devices are now commercially available and the procedure is simple and fast.

Use of these commercial BET devices will speed data acquisition on projects requiring surface-area measurements.

Each method has its limitation. The BET method can be used only with dried samples. Drying the sample may cause a change in surface area, as discussed by James and Parks (1982). Chemical changes in stored samples of aquatic humic substances, from either sediments or water, are inevitable (Gjessing, 1976). Chase (1979) noted that the use of fresh samples for the experiments was critical in his study of the settling behavior of natural aquatic particles. Several investigators have recognized that noncrystalline oxides vary in their surface character with drying (El-Swaify and Emerson, 1975; El-Swaify, 1976; Uehara and Gillman, 1981). Several methods exist that use adsorption of dyes or other organic compounds from solution for measuring surface area so that drying of samples is not necessary. One of these methods should be adopted for study of the effects of drying on surface area and, eventually, to establish a method for assessing the surface area of wet sediments.

SURFACE CHARGE

Surfaces of sediment particles are electrically charged, whether the particles are of inorganic or organic origin. Surface charge is one of the principal properties involved in controlling ion exchange, ionic adsorption, and coagulation of sediments. These charges arise either from isomorphous lattice substitution in the crystal structure or from adsorption of potential-determining ions on the surface. When the charge arises from isomorphous substitution, it is permanent and constant; in the past, it has often been called permanent or pH-independent charge. When the charge develops from adsorption of potential-determining ions, which most commonly are protons (H^+) and hydroxyl ions (OH^-), the sign can be negative, zero, or positive, and the magnitude can vary. This has been called pH-dependent charge. The more general terms, variable charge and constant charge, are preferred because it has been found that other factors besides pH influence the charge (this is discussed later). Constant surface charge and variable surface charge particles behave differently; the clay-minerals tend to have a constant surface charge, and organic substances and colloidal hydrous oxide, which occur often as coatings, have variable surface charges (Uehara and Gillman, 1981).

According to the double-layer theory, surface charge density, σ, can be expressed by the following equation (see van Olphen, 1977, for details):

$$\sigma = \left(\frac{2n\epsilon kT}{\pi}\right)^{1/2} \text{Sinh} \left(\frac{ze\phi}{2kT}\right) \qquad (2)$$

where

n = concentration of the counter ion in the fluid,
ϵ = dielectric constant of the fluid,
k = Boltzmann constant,
T = temperature,
z = valence of the counter ion,
e = charge of an electron, and
ϕ = potential difference across the electrical double layer.

With a constant surface charge density, if electrolyte concentration (n), valence, or dielectric constant of the medium is increased, the double-layer potential difference (ϕ) must be concomitantly reduced. This results in a reduction in the distance that the double layer extends into the solution; as commonly expressed, the double layer is compressed.

Where H^+ and OH^- are the potential-determining ions on the surfaces of oxides and organic matter, the potential is governed by the H^+ or OH^- activity, that is, by pH in solution. Equation 2 can be modified as follows (see the derivation in the text of Uehara and Gillman, 1981)

$$\sigma = \left(\frac{2n\epsilon kT}{\pi}\right)^{1/2} \text{Sinh}\ 1.15\, z\,(\text{pH}_0\text{–pH}), \qquad (3)$$

where pH_0 is the pH at which the surface charge density is zero, commonly referred to as the "point of zero charge."

Surface charge can be obtained from standard potentiometric titration and ion-adsorption measurements. Other methods employ the electrokinetic (or zeta) potential, the potential in a glide plane of an electrolyte moving past a surface in a superimposed electrical field parallel to the surface (as in a capillary). The zeta potential is related to the potential drop across the diffuse outer portion of the electrical double layer.

Although the theoretical significance of zeta potential in the double-layer theory has been questioned, improved understanding of the electrokinetic phenomena of particles and of experimental devices has produced important developments in using the electrokinetic technique to study the surface charge density of sediments and minerals (Pravdic, 1970; Mackenzie, 1971; Dibbs, 1972; Horn and Onoda, 1977; Hunter, 1980; James and Parks, 1982; Tipping and Cooke, 1982). Since the concept of variable surface charge has only recently been developed, a better method for investigating the surface charge of sediments needs to be established.

Recent studies of surface charge have led to a better understanding of cation exchange capacity (CEC). Since 1850, when Thompson and Way (Thomas, 1977) discovered the cation-exchange reaction, CEC has been one of the important parameters used in the study of charged particles. More than 15 years ago, after completing a reconnaissance study of mineralogy and CEC of stream sediments, Kennedy (1965) pointed out that CEC must be considered in understanding the chemistry of streamwaters. Later, Malcolm and Kennedy (1970) conducted a further investigation of the variation of CEC with particle size in stream sediments. Glenn (1973) produced a more detailed study of CEC variation with particle size in Columbia River sediments. Today, as the problems of water pollution and waste disposal become more serious, an understanding of CEC becomes more necessary.

The CEC of a particle is the product of its charge density and specific surface. Until recently, the method of measuring CEC was based primarily on an assumed constant surface charge which was subsequently found to be an oversimplification. The surface charge density is currently viewed as having a constant component, and a variable component that is influenced by pH and electrolyte concentration (eq. 3). Gillman (1981) and Wada and Harada (1969) clearly demonstrated the electrolyte-concentration effect on CEC. On the basis of the current surface-charge concept, Mehlich (1981) and Gillman and Uehara (1980) recently proposed different procedures to measure constant surface charge CEC and variable surface charge CEC.

Virtually no soil or sediment material has an exclusively constant surface charge or variable surface charge; rather, it has mixtures of these two types. For practical purposes, Uehara and Gillman (1981) proposed that if 60 percent or more of a material's surface has a certain type of charge, it be so categorized. Accordingly, they estimated that, worldwide, 32 percent of soils have a constant surface charge, 29 percent have a variable surface charge, and 39 percent have a mixed surface charge. Information on the distribution of various types of surface charges in sediments from the United States is not available at the present time. Such information should be very useful.

RECOMMENDATIONS

As mentioned by Allan (1979), there are gaps in the existing knowledge of sediment chemistry. To quote Allan:

> The lack of published results in the role and significance of suspended loads on nutrient and contaminant transport in rivers is partly a result of historical disciplinary splits. Suspended sediment is mainly studied by engineers and sedimentologists concerned exclusively with engineering and physical aspects. The second group of professionals associated with suspended loads are water quality chemists (who are chemists by training rather than geochemists). Thus, they focus on the solution phase, the water, rather than the total medium which is a complex geochemical mixture of mineral-sediment, organic material and amorphous oxides.
>
> Only when he [the chemist] finds his activities involved with environmental management and protection does he have to become involved in contamination of rivers and then on the pathways of contaminant transport and thus with the suspended load phase. This dilemma between the water quality chemist focusing on solution chemistry and the sedimentologist engineer focusing on physical aspects of suspended load transport has left a vacuum of knowledge relevant to the chemical-contaminant transmission role of suspended sediment. Only in the last two years has this vacuum begun to be filled.

It seems clear, from the above statement and the literature reviewed recently, that to understand the behavior of sediments, more work is needed to fill the knowledge gaps in sediment chemistry. As far as the physical properties of sediments are concerned, the following studies are recommended:

1. Kennedy's early work (1965) should be continued and enlarged. Knowledge of the composition of sediments is the foundation for studying and predicting the behavior and properties of sediments. At a minimum, clay minerals, nonclay minerals, noncrystalline materials, and surface coat-

ings should be included in the study of composition. A nationwide sediment record of this sort could serve as a desk reference for professionals who deal with sediments.

2. Automation of procedures for the determination of particle size should be accelerated. When an adaptation of a size analyzer is investigated, the purpose of analysis and the principle of operation for that particular analyzer should be considered.
3. Differences between particle-size distributions measured in the laboratory and their distributions in natural waters should be investigated to improve current size-analysis procedures. Coagulation of particles is one of the important factors that should be evaluated. While the principle of sedimentation is involved in the size analysis, dynamic viscosity and electroviscosity are key factors as well.
4. Research on the chemical properties of sediments relating to size and surface area should be undertaken. Actual separation of particles according to size is required. Frequently, the effect of size on the adsorption and ion-exchange properties of particles is strongly influenced by the surface coating and the formation of aggregates. Appropriate studies will be helpful in understanding the relationships between surface properties and particle size of sediments.
5. Methods for measuring the surface area of sediments and the effect of drying the samples should be investigated.
6. Adsorption and coagulation, two processes governed primarily by the surface charge of particles, should be studied. A lack of information exists on the variable surface charge of sediments because the concept of and method for measuring this type of charge have been developed only recently. A few reports on modeling adsorption using surface charge have been reviewed and discussed by James and Parks (1982). Exploratory studies on the distribution of variable surface charge in sediments, and on the effect of this charge on adsorption and coagulation in various situations, are necessary for making decisions about the priority of further studies of this type of surface charge.
7. Better methods for measuring CEC according to the recently developed concept of surface charge should be developed. CEC is important in characterization of sediments and in modeling adsorption.

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SIMULATION OF TRANSPORT-RELATED PROPERTIES

By James P. Bennett

INTRODUCTION

Given a particular set of hydraulic parameters describing flow in a stream, sediment transport characteristics are primarily particle-size dependent. The sediments commonly found in streambeds are the sand sizes and coarser. Material of this size is called bed material. Bed material transport can be related directly to the hydraulics of the overlying flow and, conversely, to a certain extent, the hydraulic properties can be related to bed material particle size and other characteristics of the transport. A major portion of sediment transport literature is devoted to analyzing and enabling the prediction of bed material transport.

The term "wash load" is commonly applied to the transport of particles finer than sands, the premise being that a stream's capacity to transport silts and clays is not dependent on hydraulics but only on the amount of these materials supplied to the flowing stream. For upland streams flowing within banks at normal depth, the premise is probably valid. However, there are a number of important situations in which this wash load concept is an oversimplification.

The applicability of the classical bed material transport equations and wash load transport concepts to the prediction of the transport of the chemical constituents associated with sediments is limited because of the episodic nature of the major flood events that account for so much of the sediment transport of many streams and rivers. This is true because of a lack of understanding of and ability to quantify the diverse processes acting during these events. These processes cause the particles and the associated constituents to be deposited, stored for an indeterminate length of time, and later eroded and returned to transport.

This presentation discusses the characteristics of sediment particles that influence their transport, deposition, storage time, and resuspension. A conceptual framework for modeling these processes is presented and some existing models and case studies are discussed.

SUSPENDED-LOAD TRANSPORT

The primary characteristic determining the behavior of a particle or a group of particles in transport in a given hydraulic situation is the median fall velocity of the group of particles. The fall velocity of a particle is simply the terminal velocity achieved by the particle if it is allowed to fall indefinitely through a quiescent fluid, in this case, water. The terminal velocity or fall velocity is determined by the size of the particle, its density, its shape, and the water temperature. In fact, in sediment transport literature, the quoted diameter is usually the fall diameter. Specifically, this is the diameter of a sphere of equivalent specific gravity that would fall at the same velocity as that observed for the particle in question. Figure 9 shows the relationship between diameter and fall velocity for quartz spheres in water.

The behavior of a particle in a particular flow field is determined by the ratio of the particle fall

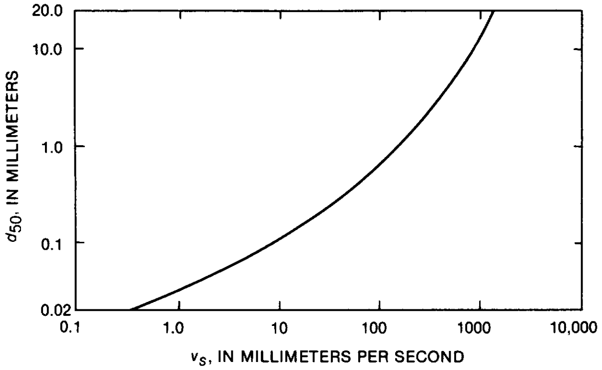

FIGURE 9.—Settling velocity (v_s) as a function of particle diameter (d_{50}) for quartz spheres. (Adapted from Graf, 1971.)

velocity to a velocity characteristic of the strength or state of development of the turbulence of the flow. If this ratio is large, as it would be, for example, for a stream with a bed consisting of cobbles or boulders, the particles will move only infrequently in the most extreme flood events, and then only in contact with other particles on the bed. If this ratio is small, as for silt or clay particles, the particles are almost continuously in motion at all stages of flow and are suspended nearly uniformly throughout the flow field.

Assuming steady, uniform flow, and assuming that the stream reach is long enough for an equilibrium suspended-sediment-concentration profile to have been achieved, the conservation of mass equation in the vertical direction may be written as follows (for more detail in the derivations that follow, see Graf, 1971):

$$v_s c + \epsilon_s \frac{dc}{dh} = 0, \tag{4}$$

where, as shown in figure 10, c is a suspended-sediment concentration, h is the distance above the streambed, v_s is the fall velocity of the sediment, and ϵ_s is the mass-transfer coefficient in the vertical direction, which is commonly assumed to be equal to the vertical momentum transfer coefficient, e. If the depthwise variation of the velocity is logarithmic, the average over the depth of the momentum transfer coefficient is

$$\epsilon_s = \epsilon \frac{\kappa \sqrt{g}\, U}{6\, C'} y. \tag{5}$$

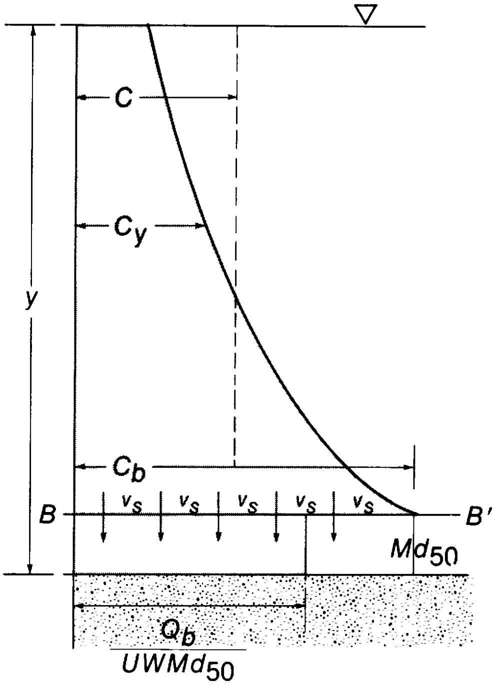

FIGURE 10.—Definition sketch of vertical transport processes. (After Bennett and Nordin, 1977.)

In this equation, κ is the von Carmer coefficient, usually around 0.4, g is the gravitional constant, C' is Chezy's coefficient, y is the total depth of flow, and U is the average stream velocity. If the concentration c_b can be determined at some elevation b above the bed, then equation 4 may be solved for any arbitrary elevation h above the streambed as

$$c(h) = c_b \exp \left[\frac{v_s}{\epsilon_s} (b-h) \right]. \tag{6}$$

Thus, the concentration of a particular size of suspended sediment decreases exponentially with increasing elevation above the streambed. As mentioned earlier, the rate of decrease is proportional to the ratio of the fall velocity to ϵ_s, a measure of the turbulent intensity. From equation 5, this measure (ϵ_s) is directly proportional to mean stream velocity. Note (from equation 6) that as fall velocity decreases, the amount of change of the concentration over depth also decreases. Consequently, the concentration profile becomes much more uniform. For example, there is seldom any detectable difference in concentration between water-sediment samples collected near the surface and those collected near the bed for silts and clays in well-developed upland streams.

As mean stream velocity approaches zero, ϵ_s of equation 5 also approaches zero and equation 6 becomes indeterminate. This simply means that the assumptions used in applying equation 4 have been violated and that the transient form of the equation should be used. In practical situations, however, this restriction is seldom applicable because ϵ_s does not decrease to zero even in large reservoirs and estuaries where wave action and other disturbing factors such as tidal currents maintain finite velocities.

In most sediment transport simulation situations, a one-dimensional expression in the direction of flow is desirable and consideration of the fluctuations or variations in the depthwise direction is undesirable. To obtain a depth-averaged equilibrium concentration, C, corresponding to the known concentration c_b at elevation b, equation 6 may be integrated over the height of the suspended load layer and divided by the height $(y-b)$:

$$C=\frac{\epsilon_s c_b}{v_s(y-b)}\left[1\text{-}\exp\left(\frac{v_s}{\epsilon_s}(b-y)\right)\right]. \tag{7}$$

This concentration, when multiplied by the discharge, defines the suspended load transport capacity or equilibrium suspended-load transport capacity that a flowing stream will achieve for a particular bed load transport rate given that the stream reach is long enough for the equilibrium condition to develop. When flow conditions are unsteady or nonuniform, transport conditions will adjust so as to attempt to reach capacity.

BED-LOAD TRANSPORT

The beds of many streams consist of a vertically homogeneous mixture of sand-size and coarser sediments. These beds can be visualized as non-Newtonian fluids such that their surfaces will become mobile in response to the shear force exerted by a fluid flowing above them, once a particular critical limiting shear stress level τ_c has been exceeded. The unit-width bed-load transport rate, q_b in this situation is

$$q_b=\chi\tau(\tau-\tau_c), \tag{8}$$

where τ is the shear stress of the fluid on the bottom and χ is an experimentally determined transport rate parameter. Both χ and τ_c are particle-size-dependent parameters that have been tabulated by Graf (1971) for a range of uniform sands.

Equation 8, known as the duBoys equation, is one of several in the critical-shear-stress class of bed load equations. It is one of the earliest bed load equations presented and is still one of the most widely used because of its simplicity and accuracy (especially for the coarser sand sizes).

This type of formulation is particularly appealing for purposes of modeling bed material transport because, with the addition of one further piece of information, it provides a means of relating bed and suspended load. The material in bed load transport is defined as those particles that move either continuously on the surface of the bed or saltating directly above it with frequent contact with the bed. If the thickness of the layer in which the bed load moves can be specified, and if it is assumed that the concentration of the particles moving in that layer is uniform, then this uniform concentration is also c_b, the concentration at the lower edge of the suspended load layer. Once the concentration at the lower edge of the suspended load layer is determined, then equations 6 and 7 describe the concentration profile and the average concentration for the suspended-load layer, respectively, assuming equilibrium transport conditions have been achieved.

Aside from the critical-shear-stress type of bed load transport equations represented by the duBoys equation, two other types of bed-load transport equations are discussed in the literature. The second group consists of equations in which unit bed-load discharge is related directly to unit water discharge. The third type consists of equations in which bed-load discharge is predicted on the basis of statistical considerations of lift forces on particles. All three types of equations are discussed in some detail by Graf (1971).

As can be inferred from the discussion above, definition of the bed-load layer thickness is arbitrary; thus, separation of transport into the two distinct entities of suspended-load and bed-load is somewhat artificial. Because of this and a variety of other reasons, there are a number of total-bed-material transport equations. The best known of these are probably Einstein's, a modified Einstein approach that incorporates measurements of the suspended load concentration and a method developed by Bagnold. These and other similar relationships are discussed by Graf (1971, chapter 9). These techniques are more sophisticated than the critical-shear-stress equations and tend to perform better than a bed-load equation in combination with the suspended-load transport relationship discussed earlier. However, because they do not make a distinction between a bed-load and suspended-load, they are not as useful or as general for simulation purposes as are the simpler relationships.

To this point, the discussion has concerned classical bed material transport concepts. The semiempirical bed-load equation and developments concerning the suspended-sediment concentration profile are applicable to uniform, steady flow in which equilibrium transport conditions have had adequate flow distance to develop. These concepts are applicable to streams having a relatively small range of bed material sizes (generally in the sand or gravel size ranges) and applicable only to a unit width of the stream. Discussion of geomorphological processes governing the evolution of stream valleys and the long-term adjustment of streams to changes in water discharge and supplied sediment load by adjusting channel widths, lengths, and slopes are beyond the scope of this paper. It is not possible either to deal with the short-term empirically observed tendencies of channels to adjust width and depth to changes in incoming water discharge, unit sediment discharge, size, and other variables such as temperature.

To gain an appreciation for the problems that may be encountered in dealing with as simple a phenomenon as unsteady flow, consider equation 8, in which, as discharge (or depth) increases, τ_c becomes negligible with respect to t so that the variation in the bed load discharge is a function of the square of the depth:

$$q_b \propto \tau^2 \alpha y^2. \tag{9}$$

Furthermore, from the Chezy equation (see Chow, 1959) stream velocity is a function of depth, as

$$q \propto y^{3/2}\ , \tag{10}$$

where q is the water discharge per unit of stream width.

Finally,

$$q_b \propto q^{4/3}\ , \tag{11}$$

which indicates that unit bed load transport is a nonlinear function of unit water discharge and indicates why most empirical regressions of bed load transport on water discharge plot best as linear relationships on double logarithmic coordinates. Such relationships generally show slopes near $\frac{4}{3}$.

In contrast to the shortcomings listed above, current understanding of processes is adequate to incorporate the type of response to unsteady flow described above into simulation routines. This is in fact done by using the duBoys relationship (eq. 8) to compute bed-load layer transport. The empirically observed interactions between bed-load transport parameters and resistance to flow can also be included. Furthermore, the suspended-load transport relationship has been specifically formulated to facilitate simulation of processes such as the deposition of fine materials from quiescent water, as in overbank flows.

DISPERSIVE CHARACTERISTICS OF SEDIMENT TRANSPORT

By nature, sediment transport is a very dispersive process. First, particles in suspension are subject to the same Fickian dispersion as are dissolved substances. Second, even the fine materials such as silts have a tendency to settle out during transport. The center of mass of the sediments is transported at a lower level in the flow than the center of mass of the water and, therefore, at a lower velocity. This causes the suspended material to lag behind and provides additional dispersion. Finally, the smaller bed material particles may, at times, travel suspended in the flow and virtually at the stream velocity, and at other times, in contact with the bed or bouncing along it.

These transport processes cause individual particles to move at an appreciably slower rate than the mean flow velocity. In addition, the beds of alluvial channels have a natural tendency to shape themselves into wavy translational forms in which, even in steady uniform flow, particles

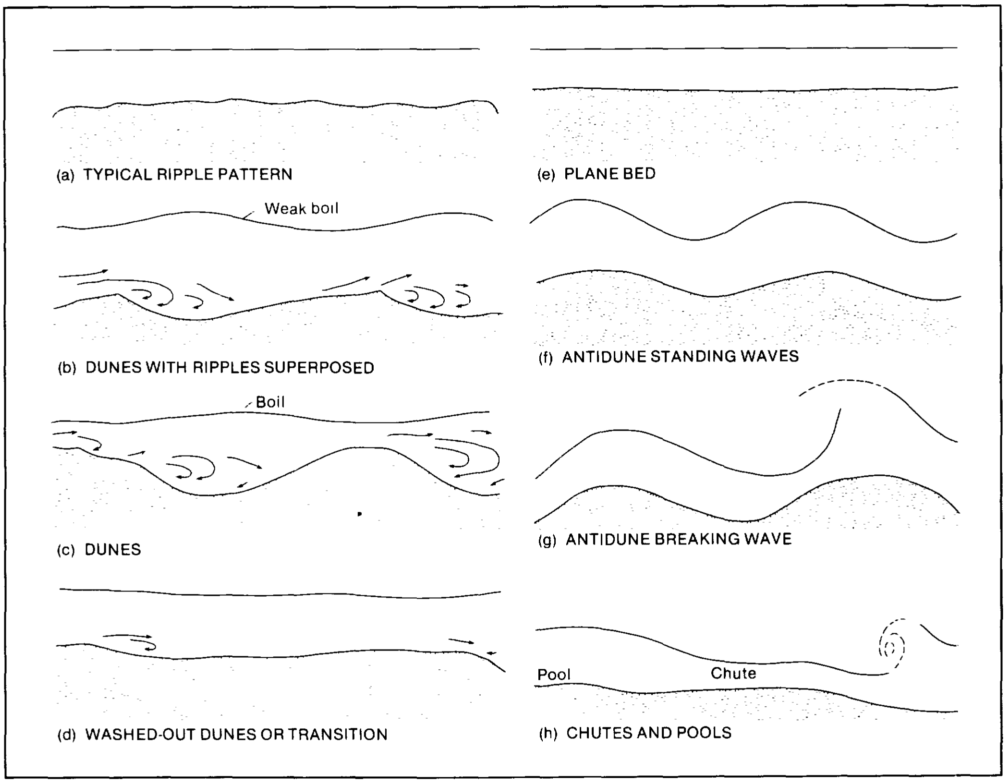

FIGURE 11.—Idealized diagram of the forms of bed roughness in an alluvial channel. (After Simons and others, 1965.)

may be buried for periods from hours to weeks. Moreover, during episodic events, when maximum sediment transport occurs and flow often goes over the channel's banks, both fine and coarse materials can be deposited and stored in such a fashion as to remain essentially in place for up to centuries before being returned to channel transport. The latter two illustrations are outside the realm of dispersive processes as concerns transport of dissolved constituents. With the possible exception of the erosion of flood-plain deposits, the foregoing processes can be dealt with satisfactorily in the realm of sediment transport simulation.

Depending on hydraulic parameters and on the characteristics of the material, sand channel streams are found with a variety of bottom configurations, as illustrated in figure 11. Among the earliest to recognize that the existence of these bed forms implied that bed material particle transport could be characterized as a random walk (or as an interrupted process consisting of a series of steps of finite length followed by periods of resting of variable duration) was Einstein (1950), who formulated some probabilistic laws governing the distributions of the step lengths and of the durations of the resting periods. He then used these laws as a basis for computing bed material transport. As a consequence of this mode of transport, the centroid of a cloud of marked, or tracer particles, introduced into a sand channel stream will move at a much slower rate than the mean velocity of the stream. The dispersion of this cloud of particles will be much greater than the dispersion of a corresponding cloud of neutrally buoyant particles or of a dissolved substance, and a small proportion of the marked particles will be present in the streambed long after the main cloud has passed downstream. For example, Sayre and Hubbell (1965), in the classical set of experiments conducted on the North Loup River in Nebraska, found the centroid of a cloud of tracer particles to be moving at a velocity of approximately 9×10^{-4} foot per second when the mean stream velocity was approximately 2.25 feet per second.

The median diameter of the bed material in the North Loup is 0.29 millimeter. For the hydraulic conditions in effect at the time of the experiment, the concentration in the suspended load layer averaged 380 milligrams per liter and the median diameter of the suspended material was approximately 0.15 millimeter. Under somewhat similar bed-form and stream-hydraulic conditions, N. S. Grigg (written commun., 1969) found the particles to be taking steps of approximately 2.5 feet with waiting periods in between on the order of 10 minutes. As the size of the features involved increases (such as when dealing with deposition on the lee slopes of point bars) or as the frequency of occurrence of the transporting flow conditions decreases, the length of the particle rest period and, hence, the residence time of the sediment, becomes longer. This is because the particles have a tendency to be deposited deeper in the stream channel under slower moving bed forms or in less accessible places such as in the banks or on the flood plain. For the usual case of in-bank flow, as the sizes of the particles decrease, the tendency for this type of behavior should become less and less apparent because the particles spend more time suspended in the flow and less time in contact with the bed. On the other hand, even under these hydraulic conditions, silts and sometimes clays can be deposited in the sheltered areas near the banks and on the lee sides of large bed forms and bars. As the discharge goes over the banks, greater amounts of fine particles can be deposited by simple settling from the fluid in sheltered areas and by being stranded as discharge decreases and floodwaters recede.

The storage of particles is further complicated by a process called armoring. An armored bed is one in which a single layer or a few layers of large particles cover extensive deposits of finer material and prevent them from being transported at discharges well above the critical limit for the buried material because the stream cannot transport the larger particles in the armoring layer. Armoring occurs when homogeneous deposits with a large size range are sorted by subsequent flows. The particles that can be moved at the existing transport capacity are winnowed out and the larger particles are left until a sufficient number of them have been collected so as to form the armor layer. The finer material (which often have highest concentrations of trace metals and organic substances, as discussed in other papers in this circular) is therefore protected from erosion and transport and its storage time is correspondingly increased.

DEPOSITION AND EROSION

In unsteady or nonequilibrium flow conditions, deposition from the suspended load can be calculated using a two-dimensional non-steady-state version of the continuity equation (eq. 4). However, the solution of such an equation is difficult and time consuming, and the resulting detail is not merited considering the other uncertainties involved in the simulation of the transport processes. As an alternative, deposition (assuming temporarily that there is no resuspension) from the suspended load layer can be adequately represented by the following equation (Bennett and Nordin, 1977):

$$\frac{\partial C}{\partial t}+U\frac{\partial C}{\partial x}=-\frac{v_s c_b}{(y-b)}, \qquad (12)$$

which is readily solvable by simple finite difference techniques. Note that in equation 12, C is the depth-averaged suspended-sediment concentration, x is longitudinal distance in the direction of stream flow, and the flux term on the right-hand side is obtained by multiplying the fall velocity of the sediment by its concentration at the bottom of the suspended load layer. Equation 12 is valid for bed material particles and silt-sized particles. In two extensive reviews, Partheniades (1971a, b) shows that rather than being governed by equation 12, the deposition of cohesive materials does not occur until the shear stress drops below a certain critical value, following which deposition is extremely rapid. Even though average conditions in most upland flows would indicate a negligible deposition of wash load, there are localized areas in most such flows where conditions are favorable for deposition of both silts and clays. In estuaries, the large cross-sectional area, the tidal currents causing the velocity to drop to zero, salinity gradients, and average circulation patterns all combine to create shoaling zones in which conditions are extremely favorable for deposition of fine material. In fact, many estuaries, such as the Potomac Estuary near Washington, D.C., are virtually perfect sediment traps (Bennett, 1983).

Partheniades (1971a) reports that the critical shear stress for erosion of a cohesive bed material is appreciably greater than the critical shear stress for deposition. He concludes that for channels with cohesive bed material, there will be erosion, deposition, or no bottom elevation changes but that erosion and deposition cannot occur simultaneously. Partheniades also reports that the rate of erosion is itself a function of shear stress; however, the processes are not generally well enough understood to relate the coefficients describing the rate of erosion to the properties of the sediments. Therefore, although the amount of cohesive sediment carried cannot be related to the flow properties (the transport capacity is effectively infinite), the rate of increase of the concentration can be related to flow properties when erosion is occurring. Partheniades' observations generally confirm the earlier statements regarding wash load, in particular concerning the cohesive material; that is, the transport rate is not a function of flow parameters but only a function of the amount of such material supplied by the watershed or upstream flow.

Whether or not there is transport of bed-material-sized particles, as has been pointed out, is also dependent on the magnitude of the shear stress at the bed. That is, below a certain critical value there is no movement and hence no transport of these particles. Above the critical shear stress, empirical observations have shown that the equilibrium rate of transport is approximately a quadratic function of bottom shear stress. Studies of the rate of erosion of bed material particles in prototype situations have not been documented to any extent, so the transport equations for this type of material are strictly applicable only for steady, uniform sediment transport at equilibrium conditions. However, analysis of the rate of erosion can be made by considering the transport capacity of the stream along with the continuity equation (eq. 4) for the bed material. Analysis of the physics of the transport processes in the bed load layer shows that in the absence of armoring, a good assumption is that the bed load transport rate closely approximates that for equilibrium steady flow conditions. In other words, it can be assumed that as stream hydraulics change in either space or time, the bed-load transport rate adjusts to these changing conditions virtually instantaneously. If the corresponding adjustments in suspended load transport can be determined, then total load transport from a segment of stream channel can be computed for a given time period. By application of a conservation of mass equation for the bed sediment to the stream segment, the rate of change of bed elevation from scour or fill can be determined. If the thickness of the bed-load layer is specified as a parameter M times the median diameter of the sediment d_{50} as shown in figure 10, then the necessary relationship between the bed-load and the suspended-load layers can be written as follows (Bennett and Nordin, 1977):

$$\frac{\partial c}{\partial t}+U\frac{\partial c}{\partial x}=\frac{v_s}{(y-b)}\left(\frac{\rho_s q_b}{\rho UMd_{50}}-c_b\right) \qquad (13)$$

where ρ is the density of water, ρ_s is the density of the sediment particles, and q_b is the bedload transport rate.

In deriving this equation, the additional assumption is made that the flux or rate of transport across the line B–B' of figure 10 is proportional to the difference in concentrations in the two zones immediately on either side of the line. The proportionality constant $v_s/(y-b)$ is the same as derived from the flux rate considerations leading to equation 12. If the parameter M is known, equation 13 provides a means of determining this equilibrium suspended sediment concentration for a particular bed-load layer transport rate. Unpublished preliminary analysis of flume data (obtained by the author in 1983) indicates that M generally lies in the range of from 10 to 100.

BED ELEVATION AND COMPOSITION ACCOUNTING—SCOUR, FILL, AND ARMORING

Beyond the bed-load transport equation (eq. 8) and the suspended-load continuity equation (eq. 13), the remaining component necessary to construct a conceptual sediment transport model is the bed-load continuity equation, which may be written

$$\eta\frac{\partial Z_b}{\partial t}+\frac{\partial q_b}{\partial x}=-v_s\left(\frac{\rho_s \rho_b}{\rho UMd_{50}}-c_b\right) \qquad (14)$$

and is expressed here for a unit width of streambed. As can be seen from the definition sketch of figure 12, Z_b is bed elevation, x is distance in the stream-wise or flow direction, and h is the solids ratio of the material in the bed. Figure 12 indicates that one other piece of information is necessary to simulate the behavior of natural channels, the width of channel bed, W, over which the processes of scour and fill (erosion and deposition) are active. At present, this information is obtained by observation; perhaps in the future it will be possible to predict W using equations similar to the regime equations discussed in the sediment transport literature.

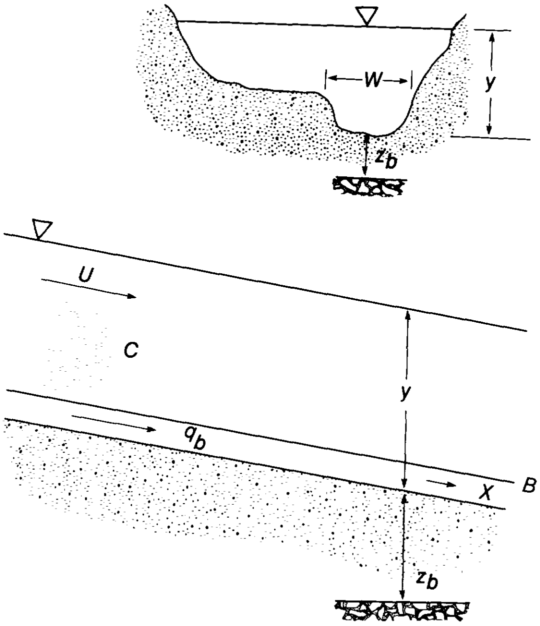

FIGURE 12.—Definition sketch for bed elevation accounting. (After Bennett and Nordin, 1977.)

For a stream having only a very small range of sizes in the streambed, the equations already given are sufficient for incorporation in a computer program for transport modeling. However, most streams have a greater range of sediment sizes in the bed material so that it is necessary to model the transport of a number of different sizes simultaneously by applying these equations repetitively. This procedure requires a streambed composition accounting component. The accounting is accomplished conceptually using two or three layers depending on whether net erosion or net deposition has occurred at the cross section during the simulation time. Each layer is assumed to be homogeneous within itself and to have the same solids ratio as that of the original bed.

As illustrated in figure 13, the upper layer of the bed is called the active layer. Its thickness is specified by a parameter, N, times the d_{50} of the largest size used in simulation. The active layer is always present and its thickness is constant over the simulation time. The composition of the active layer at each cross section is a function of time, and it incorporates the cumulative effects of selective scour and deposition.

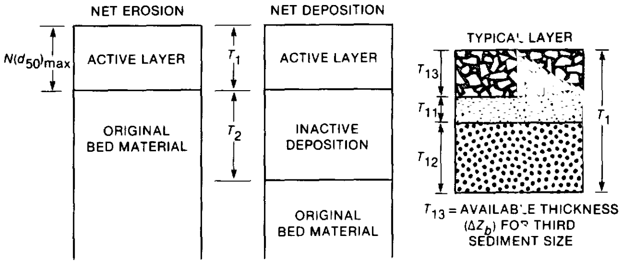

FIGURE 13.—Bed composition accounting procedures. (After Bennett and Nordin, 1977.)

Bed armoring is simulated by limiting erosion of a particular size of material in a time step to the amount of that size available in the active layer. If bed shear stress at a particular stream cross section is too low to transport any size present in the active layer, the bed is armored and no erosion can occur until the bed shear stress exceeds the critical value for the smallest size present in the active layer. If, for a particular size, the transport capacity as given by equation 8 is such that equation 14 predicts erosion of more material of that size than is present in the active layer, only the amount present is eroded, and the transport is termed "availability-limited" in that size. If there is enough present in the active layer to allow the erosion postulated by equation 14, transport is termed "capacity-limited" for that size at that cross section. In the first situation, the cross section is static, and in the latter two it is degrading. Capacity-limited transport also occurs when there is deposition of a particular size at a cross section. If there is net deposition at the cross section, the bed is aggrading.

Conceptually, the active layer represents the bed-material layer that can be worked or "sorted through" by the action of the flowing water in time step Δt to supply the volume of material necessary for erosion. The thickness of the layer must have some relation to the height and rate of movement of bed forms in the channel. The parameter N is related to Δt; the larger Δt, the larger N must be to yield the same predictions. From consideration of bed-form mechanics, this relationship is reasonable because, in a stream, a greater depth of bed can be sorted in a longer time period.

At a cross section when simulation starts, the bed composition and bed elevation are specified. The composition is assumed to be homogeneous over the active width of channel and to extend downward indefinitely, or, if clearcut individual layers are present, the compositions and elevations of the layers can be specified and considered in the scheme discussed below with little modification.

When the deposition of a certain thickness of a particular size fraction occurs during simulation, this material is added to the active layer. An equal thickness of the active layer is added to a second layer, the inactive deposition layer shown in figure 13. The size composition of the inactive deposition layer is recomputed assuming it to be homogeneous and considering the size composition of the active layer. The thickness of the inactive deposition layer is also updated. The size composition of the active layer is then recomputed, considering the size fraction and thickness of the layer of material deposited. The local elevation of channel bottom is then updated by adding to it the thickness of the material deposited divided by bed porosity (volume of solids deposited divided by active width and by porosity). This process is repeated for each size fraction.

If equation 14 predicts erosion of a particular size class of material from the bed, the reverse of the above procedure is followed. The required thickness is removed from the active layer, if available. The same thickness of material is added to the active layer from the layer below it. The composition of the active layer and the bed elevation are updated, considering the size class of material removed and the composition of the layer below. If the layer below the active layer is inactive deposition, its thickness must also be updated. Provision is also made for destroying the inactive deposition layer and adding material to the active layer from original bed material if necessary.

If there is erosion and transport is availability-limited, only the available amount of material is removed from the active layer. The updating process is the same as described above. Following updating, new values of q_b and the downstream suspended sediment concentration are computed to satisfy continuity.

SIMULATION OF SEDIMENT TRANSPORT, SCOUR, AND FILL

Incorporation of the conceptual components described above into a computerized simulation package is discussed by Bennett and Nordin (1977). Although the details of computation and the decision processes may vary somewhat, any sediment transport, scour, and fill simulation package requires inclusion of these same basic components. To run such a simulation model, initial-condition requirements for flow computation are cross-section geometry and absolute elevation, velocity, and depth. For sediment transport, initial-condition requirements are active width and bed size composition. Boundary-condition requirements for flow computation are time histories of inflow water discharge, and downstream stage or a downstream stage-discharge rating curve. For sediment transport, the requirements are time histories of inflowing suspended-load and bed-load discharge by size class.

For the flow component, the parameter available to fit the model to particular field situations is the Chezy discharge coefficient, C' or Manning's n. In the Bennett-Nordin (1977) model, the parameters are the duBoys characteristic sediment coefficient, χ, critical shear stress, τ_c, and M, which governs the thickness of the bed load zone. The parameter M indirectly governs the ratio of suspended-sediment discharge to bed-load discharge. The armoring parameter is N, which governs the thickness of the active layer and thus determines the amount of material available for erosion during a particular time step. Other models use similar parameters. Until sufficient experience has been gained concerning the variability of these parameters in field situations, it is extremely important that any model be carefully calibrated before prediction is attempted.

In modeling simultaneous transport of sediment and attached chemical constituents, a number of options are available, depending on the type of association of the constituent with the sediment particles and the number of constituents to be transported; the simplest case would be for a constituent or small group of constituents firmly attached to the particles (or the particles themselves) and negligibly soluble in water. If the constituents are strongly sorbed, the constituents-plus-particles are, in effect, another class of sediment, the erosion, transport, deposition, and storage of which can be computed separately in the framework already discussed. The only modification necessary would be to ensure that all particles of the same size are considered when restrictions involving transport capacity are applied and that all particles of the same size are represented proportionately when erosion or deposition takes place.

In the more general case, however, both dissolved and particulate-borne constituents, as well as the laws governing changes in phase between them, must be considered. Furthermore, the additional complication of several constituents being able to associate with each sediment particle simultaneously, and to react with each other, must also be accounted for. In this situation, during each time step Δt, transport of the dissolved phases and the sediment sizes would be computed according to the physical laws presented above. Following this, but still in the same time step, the constituents would be transferred to or from the sediments and reacted together according to the pertinent chemical equilibrium relationships. The final result would be the concentrations of the constituents and sediment sizes in the water as well as the concentrations of the constituents on the sediment particles (in the suspended-load layer, the bed-load layer, and the bottom). In this formulation, all particles of a particular size present in a particular layer of a segment of stream would contain equal concentrations of constituents. There would be no partitioning of a particular size by type of constituent; however, the type of transport discussed in the paragraph above could be incorporated in this latter scheme for a limited number of permanently contaminated particles by specifying them to be a slightly different size and by inhibiting transfer to the dissolved phase.

It is beyond the scope of this section to formulate a model for transfer between the dissolved and particulate phases; however, some mechanism similar to the Michaelis-Menton kinetics of ecological modeling might be most appropriate. This would allow both transfers in either direction and limitations due to saturation of the sediment particles or to lack of sediment without unduly complicating the mathematics or the computer programming.

SEDIMENT TRANSPORT MODEL CASE STUDIES

Bennett and Nordin (1977) used the model discussed above to simulate the behavior of the East Fork River in Wyoming during a snowmelt runoff period in the spring of 1975. The river in the study reach is about 60 feet wide and, at bankfull stage, averages about 4 feet deep. The slope of the stream is 0.007, and the streambed is composed of sand and gravel. The only transport mode of importance is bed load, and the observed d_{50} of the sediment moving was approximately 1 millimeter. Katzer and Bennett (1980) applied the same model to a 50-day period during the spring of 1978 along a 10.5-mile reach of the east fork of the Carson River in Nevada. The section of the east fork of the Carson simulated extends over a distance where the stream emerges from the Sierra Nevada and moves into the Carson River valley. Over the length of the channel simulated, the slope changes from approximately 0.004 to approximately 0.0008, average channel widths vary from about 140 to 80 feet, and bed material d_{50} varies from 11 to 0.35 millimeters. During the model calibration period, 60,000 tons of sediment were transported into the study reach and only 14,000 tons were transported out, so this length of the Carson River is aggrading rapidly. At various points in the channel reach being simulated, bed elevation changes were as much as ±2 feet. Again, the suspended-load component was not a significant enough part of the total load to allow evaluation of the model's capability to adequately simulate this process. However, both of the studies provided a test of the ability of a sediment transport model to simulate bed material transport, scour, and fill. One major conclusion that can be reached from both studies is that the modification process for both bed elevation changes and composition changes is extremely slow, and detailed data collection needs to be carried on for a considerable length of time to enable satisfactory model calibration and evaluation of the performance of the model in a particular situation.

Jennings and Land (1977) compared the effects of 50 years of simulated sediment-laden flow for two different channelization alternatives to a no-action alternative for the Atchafalaya River basin in Louisiana. They used a modified version of the U.S. Army Corps of Engineers (1977) HEC-6 program, which is designed to simulate scour and deposition in rivers and reservoirs. The model treats input flood hydrographs as a series of stepwise steady flows so that flow can be computed by the step-backwater technique. The model uses either of the total load relationships developed by Laursen (1958), or Toffaleti's (1969) modified Einstein technique. It can simulate the transport of clay, four sizes of silt, and five sizes each of sand and gravel. A modified critical-shear-stress relationship is used to decide whether or not particles of a particular size will be mobile at the surface of the bed. For a particular discharge, the thickness of the active surface layer is determined by first computing the smallest particle size present that will be immobile just on the surface of the bed at the prevailing water discharge. The thickness of the active layer is then set to provide a volume such that when all particles smaller than this size are eroded, the bed will be armored just by those that remain. Only the material present in that layer can be eroded until the layer is disturbed by a larger discharge. The modification of HEC-6 used by Jennings and Land (1977) permits deposition in two overbank channels. The Atchafalaya River carries flood-flows diverted from the Mississippi River and as such would be expected to be carrying sediment appreciably in excess of its transport capacity. As might be expected, all alternatives showed an appreciable deposition in both the channel and in the overbank sections. At the higher discharges, the least influence on inundated area and the smallest amount of deposition was caused by the larger channelization alternative. HEC-6 is not set up to simulate transport of sediment-borne or dissolved chemical constituents.

Onishi (1981) presents one of the few discussions in the literature of a joint study of sediment and constituent transport. Onishi's model is two-dimensional in the horizontal plane and uses the finite element technique to solve the conservation-of-mass equations for the sediments and constituents. However, in an analysis of Kepone transport in the James River Estuary in Virginia, it is applied in the one-dimensional sense because of lack of a suitable two-dimensional flow specification. The model uses three transport components, one each for sediment, dissolved constituents, and particulate-associated constituents. The sediment transport component will accept transport of three sizes (apparently sand, silt, and clay). It uses a critical-shear-stress type of relation similar to the one discussed earlier for total load transport, and apparently always simulates transport of bed material at capacity for the hydraulic conditions existing at a particular point in the flow field. The model also uses erosion and deposition criteria and source-sink terms similar to those discussed previously for the cohesive material. The model contains a bed elevation accounting component and conceptualizes the bed to be made up of a number of different layers. An armoring capability similar to the one discussed earlier is incorporated through restriction of erosion from any layer below the top layer until all material has been eroded from that layer and transported out. It is not clear from Onishi's (1981) discussion how the model keeps track of the constituent composition of the various bed layers. The second component routes the dissolved constituents in a way similar to most other models of this type. The third component routes particulate-associated constituents as though they were dissolved and uses benthic source-sink terms derived directly from the sediment transport component. This component apparently assumes that there is always enough sediment available to provide a vehicle for transporting the constituent in question. This is acceptable in the case of the James River study because Kepone is strongly associated with the clays and organics present and was present at less than detectable concentrations in the water phase, and because enough clays and other organic substances were always available for the Kepone to be sorbed to them.

However, as explained earlier in this section, in situations in which the amounts of sediments are limited or the ability for the sediments to sorb constituents from the water phase is limited, this would not be acceptable.

Despite the fact that concentrations of Kepone in the water were below analytical detection, Onishi (1981) concludes that more than five times as much of the material is transported in the dissolved phase as in the particulate phase. Because simulation times are short and calibration data are sparse, it is difficult to judge the performance of the constituent transport components of the model. Its performance in predicting sediment transport is comparable to the models discussed earlier.

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