Proceedings of a

Pollutant Transfer by Particulates Workshop

Old Dominion University Norfolk, Virginia
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Seattle, Washington
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U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
Office of Marine Pollution Assessment

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Pollutant Transfer by Particulates Workshop

Compiled and edited by
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Seattle, Washington
September 1982

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ABSTRACT

A workshop on Pollutant Transfer by particulates was held at the Center for Marine Studies, Old Dominion University, Norfolk, Va., on 19-21 January 1982. The workshop was sponsored and organized by the Office of Marine Pollution Assessment (OMPA) of the National Oceanic and Atmospheric Administration (NOAA) as a part of the implementation of its responsibilities mandated under Sections 201 (Ocean Dumping) and 202 (Long Range Effects) of the Marine Protection, Research and Sanctuaries Act, Public Law 92-532. The purpose of the workshop was to review the current understanding of the role of particulates in marine pollution transfer, and to identify key, tractable questions and problems. Central to the discussions was the concept of the particle as a pollutant "carrier". Emphasis was on the processes that govern the physical, chemical, and biological interactions between particulates and pollutants.

PREFACE

The overall goal of the OMPA program is to develop, integrate, and apply information required for technically based decisions on use of the marine environment with acceptable ecological, economic, and social consequences. To address this goal, three objectives have been defined:

1. Determine the ecological consequences of anthropogenic activities that pollute the marine environment.
2. Assess the consequences of marine-polluting activities in terms of ecological, economic, and social impacts.
3. Define management alternatives that will foster favorable or minimize adverse consequences of man's use of the marine environment.

All the objectives outlined above are being addressed in the broad sense, either by NOAA or by other agencies and institutions, but OMPA believes the current priority needs are principally in the development of management alternatives to reduce damage from specific activities, i.e., to find specific answers to specific problems.

Implementation of this program requires recognition of the need to apply current scientific knowledge of marine ecosystem processes to unresolved problems of how to predict the consequences that do or will result from polluting activities. The program emphasis is on developing the best marine environment management alternatives possible at any given time. Thus, in order to develop an effective, coherent program, it is essential that OMPA identify key, tractable questions and problems that must be addressed immediately. The Pollutant Transfer by Particulates Workshop was perceived by OMPA as being an effective mechanism for defining current research needs in a specific area of concern -- that of the role of particulates in mediating the impact of pollutants on a marine ecosystem.

R. E. Burns

L. W. Kimrey

PROCEEDINGS

OF

A POLLUTANT TRANSFER BY PARTICULATES WORKSHOP

Leal W. Kimrey and Robert E. Burns

> THE USEFULNESS OF OUR KNOWLEDGE
> IS MEASURED BY THE QUESTIONS
> WE CANNOT ANSWER
> --CYMRY--

INTRODUCTION

Suspended particulate matter may be defined as "small solid entities that are mixed with, but remain undissolved in the waters of an aquatic system." They are ubiquitous to the aquatic environment and come in a wide variety of sizes, shapes, and compositions. They are important environmental components, particularly where studies of marine pollutants are involved. Without particulate matter, the behavior of pollutants in the marine environment would be a relatively straightforward study of chemical processes. But particulate matter is present, and has an inordinate influence on the behavior of pollutants that enter the marine environment. Particulate matter can remove pollutants from the water column by adsorption or complexation, inhibit or facilitate contaminant availability to the biota of the ecosystem, transport contaminants from one area to another, and, with changing conditions, can release contaminants into the water column at great distances from the source. When deposited at the seafloor as sediments, particles may form a substrate that can accumulate and concentrate pollutants over a period of time, and then, either by natural or artificial mechanisms, reintroduce the pollutants back into the water column. In short, particulate matter in the marine environment is an extremely important factor in assessing marine pollution, and must receive a great deal more attention and respect as a pollutant "carrier" than has been the case in the past.

The purpose of this workshop was to elucidate the role of particulate-pollutant relationships in the marine environment, and to provide OMPA with a solid basis for the development of an effective research program in this area.

APPROACH

A "discussion paper", issued to all participants prior to the workshop, defined the principal areas for discussion:

Physical Processes: Physical processes are those processes that govern the transportation of suspended particulate matter from one point to another within a system and between systems, the deposition or dispersion of particulates within a system, or removal of the partiaculates from the system (i.e., permanent deposition).

Geochemical Processes: Geochemical processes are those processes that govern the reactions between particulates and dissolved materials. They include such phenomena as adsorption, complexation, precipitation, flocculation and dissolution. Of particular interest is the role of natural and anthropogenic organics in these processes.

Biochemical Processes; Biochemical processes are those processes in which the biota play an important role in altering the state of dissolved and particulate matter so as to make them more or less reactive, or more or less bioavailable through such mechanisms as biodegradation, bioturbation, fractionation, and transfer (e.g., via the food chain or as excreta).

The participants at the workshop were organized into three working groups; each group addressing one of the three topic areas defined above. The task of each group was to review its understanding of the role of the particulate as it pertained to the Group's area of expertise, and to identify key, tractable questions and problems. Central to the discussions was the concept of the particle as a pollutant transfer agent with emphasis on the "real world" processes that govern the interactions between particles, pollutants, and environment.

The three groups met separately, but not in vacuo. Each participant was furnished with Briefing Documents consisting of four "working papers" that provided an overview of the current understanding of pollutant-particle relationships, as well as more specific summaries of the recognized concerns in each of the three topic areas. Using the briefing documents as a starting point, each group was requested to develop a consensus of the perceived "gaps" and to develop testable hypotheses designed to address the identified "gaps". The Briefing Documents are Part II of this volume.

Defining the limits of our knowledge of the various processes as they occur in the real world of the marine environment also defines the limit of our ability to predict the probable effects of the growing number of polluting activities impinging upon the marine environment. However, simply defining the limits of our knowledge is not enough; we must also develop a coherent, efficient plan for the utilization of our limited research resources to address these deficiencies in our knowledge. It is toward this end that we requested each group to develop a set of testable hypotheses addressing the "gaps" in our knowledge. The Group Reports are Part I of this volume.

Summary:

The questions raised in the Briefing Document papers, and the large number of "testable" hypotheses developed by the Working Groups emphasizes the fact that while marine scientists have generated large quantities of data over the last two decades, they have produced very little information of practical use to marine environment managers. It is recognized that data production is necessary in developing an understanding of marine pollution problems. It is also recognized that the better we understand a problem, the greater the likelihood of developing a satisfactory solution. Current research efforts, including much of the research supported by OMPA, is directed toward obtaining a "better understanding" of "the problem"--whatever that "problem" may be. Society, however, is at a point where it is demanding not only solutions to current pollution problems, but the development of safegaurds against future polluting activities as well. Thus, the purpose of this workshop was to develop research objectives that would provide immediate, practical information that can be utilized by marine environment managers to address current and future polluting activities. We believe that the workshop was successful.

It was the original intent of OMPA to use the products of this workshop strictly as an internal planning aid. Therefore, no protocol was established for the preparation of the reports. To paraphrase Sergeant Friday, "We were only interested in the facts." However, the Briefing Documents, and the Group Reports are, we believe, of general interest to the marine scientific community at large. We present both essentially as received. We hope the next PTP Workshop, planned for early 1983, will be equally productive.

ACKNOWLEDGMENTS

The Office of Marine Pollution Assessment wishes to thank the Atlantic Oceanographic and Meterological Laboratories for their efforts in compiling the Briefing Documents; the authors--Jerry Schubel, Robert Young, Curtis Olsen, Norman Cutshall, Terry Nelsen, and Samuel Luoma for their contibutions to the Briefing Documents; the Chairmen--Robert Young (Physical Processes), Herb Curl, Jr. (Geochemical Processes), and Alan Mearns (Biochemical Processes) for their excellent direction of the deliberations of the Working Groups; Dr. Harris B. Stewart, Jr. and Staff, and Old Dominion University who were our gracious hosts; and a particular thanks to the members of the Working Groups whose interest and expertise contributed greatly to the success of the Workshop.

SUMMARY OF HYPOTHESES

PHYSICAL PROCESSES

The Physical Processes Worksing Group concentrated principally upon the sedimentation aspects, but also considered the interaction of chemical and biological factors. The hypotheses are ranked in order of priority as perceived by the group.

1. The most important factor in the resuspension of fine-grained cohesive sediment under specified flow conditions is the intensity and character of biological processing.

2. The temporal variation in suspended sediment concentration profiles at a given site can be modelled as an advection-diffusion process governed by a stress-driven resuspension term.

3. At a given site the resuspension rate is dependent on both turbulent shear stresses and mean bed shear stress.

4. Physicochemical flocculation is not a controlling mechanism for the deposition of suspended inorganic particles and associated particle-bound contaminants.

5. Fractionation of a suite of particle-associated contaminants from a single source is determined primarily by the reactivity of the contaminants rather than by physical sorting of the particles.

6. The accumulation of pollutants within a sedimentary body is proportional to the frequency and intensity of resuspension activity.

7. The importance of filter-feeding zooplankton in packaging inorganic fine suspended particles increases above some threshold with increasing particle concentration because the organism's efficiency in particle selectivity decreases.

GEOCHEMICAL PROCESSES

The Geochemical Processes Group limited its considerations to five major categories, and developed one or more hypotheses addressing each category. The hypotheses under each category were ranked from 1 to 3 (1 being highest) on the basis of relative importance and immediacy of need. The categories themselves were not ranked.

Category I. Nature and Properties of Particles

1. The flux of particles is primarily of abiotic origin.
   Importance: 1 Immediacy: 1

2. The residence time of particles in the water column is a

function of primary productivity.
Importance: 1 Immediacy: 1

3. The flux of biogenic particles is primarily the result of biological repackaging (i.e., fecal pellets).
Importance: 2 Immediacy: 2

Category II: Flocculation Processes in Estuaries

1. Flocculation of inorganic particles in the low and intermediate salinity regions of estuaries enhances the sedimentation and retention of pollutants.
Importance: 2 Immediacy: 2

Category III: Sorption and Desorption Processes

1. The distribution coefficient of a given contaminant is primarily dependent on suspended solids concentrations, surface characteristics, pH, Eh, salinity and dissolved organic ligand concentrations.
Importance: 1 Immediacy: 1

2. The amount of pollutants adsorbed is a function of surface area and composition of particles.
Importance: 1 Immediacy: 1

3. The adsorption and removal of reactive pollutants from the water column is a function of the average residence time of biogenic particles.
Importance: 1 Immediacy: 1

4. Rates of reaction between contaminants and particles are important in determining their partitioning in estuarine environments where major changes in water composition occur on time scales of the order of hours to days.
Importance: 1 Immediacy: 2

5. There are representative compounds (or elements) which may be identified for use in sorption/desorption studies.
Importance: 2 Immediacy: 1

6. Long contact times between contaminants and particles (2 months to years) result in reduced rates of desorption.
Importance: 2 Immediacy: 3

Category IV: Biologivally Mediated Processes

A. Biotransformation

1. The rate of biotransformation (alkylation, oxidation and reduction of organic and inorganic species in water and sediments) is proportional to local autotrophic and heterotrophic metabolism.
Importance: 2 Immediacy: 2

B. Bioturbation

1. The mean residence time of a particle-bound contaminant within the benthic mixed-layer determines the concentration of contaminants in the overlying water column, by resuspension or resolution.
Importance: 1 Immediacy: 2

Category V: Flux In/Out of Sediments

A. Particle Resuspension

1. The exchange of contaminants between water and resuspended particles is an important process for both pollutant removal from and pollutant release to the water column.
Importance: 1 Immediacy: 1

2. In the absence of net sediment accumulation, the net effect of particle resuspension and sediment mixing is to increase pollutant burdens in the sediments.
Importance: 3 Immediacy: 3

B. Dissolution

1. Diagenetic processes in sediments/interstitial water bring about the dissolution of particle-bound pollutants.
Importance: 1 Immediacy: 2

2. Diffusion, sediment mixing and resuspension, tidal pumping, and biologically induced irrigation reintroduce interstitial water pollutants to the overlying water column.
Importance: Immediacy: 2

Biochemical Processes

Those in the Biochemical Processes Group concentrated their efforts on developing a few major hypotheses that they believe could, when tested, make a difference in managing marine pollution and ocean waste disposal. The four areas addressed, residence time, accumulation and mobilization, transformations, and transport of pollutants, were considered to be equally in need of elucidation. A major hypothesis, together with sub-hypotheses as appropriate, were developed for each of these areas. In the following summary, the major hypothesis is listed first under each heading.

Residence Time

1. The euphotic zone residence time of a dissolved pollutant is inversely related to the rate of primary production.

2. The euphotic zone residence time of a pollutant is inversely related to the production of high-density fecal pellets and other excretions, i.e., it is related to water-column species composition.

3. The euphotic zone residence time of a pollutant is inversely

related to the ratio of diatom to dinoflagellate production.

Accumulation and Mobilization

1. Mobilization of pollutants from sediments to the water column is directly proportional to bioturbation rates in physically weak environments.

2. Mobilization of pollutants is inversely related to the number of sediment binding sites.

Transformations

1. Biodegradation of synthetic hydrocarbons and petroleum hydrocarbons is oxygen-limited in fine-sediment depositional environments. Conversely, in well-oxygenated environments, biochemical degradation is first substrate, and secondly nutrient-limited.

2. Carbon flow to food webs is a significant fate of petroleum hydrocarbons in areas of heavy input.

3, The degradation of chlorinated hydrocarbons (DDT's, PCB's, Kepone, mirex) in marine sediments and benthic communities is inconsequential in terms of their fate in contaminated environments.

4. The degradation of chlorinated hydrocarbons by marine animals is inconsequential with respect to the animals themselves as reservoirs, i.e., the half-life of chlorinated hydrocarbon burdens in marine animals is longer than their life-span.

Transport

1. Migratory animals that congregate are significant transport mechanisms for chlorinated hydrocarbon contamination of remote sites.

PART I

WORKING GROUP REPORTS

1. Report of Working Group on Physical Processes

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INTRODUCTION

One of the single most important physical parameters for the sedimentary system is the total length of time that a particle is available to interact with the biosphere. We have called this time period the removal time. We recognize that removal time will vary among classes of pollutants because neither pollutants nor particles are homogeneously distributed in the environment. Processes and their rates will, therefore, have varying degrees of effectiveness in eroding, transporting, depositing and ultimately removing pollutants.

To estimate removal time in a particular sedimentary system, we need to know the rate of supply of particles; the rate at which new particles are biologically processed; the rate, frequency and amount of resuspension; the rate at which particles are advected or diffused through the system; and the seasonality in these rates.

Removal time can be divided into two parts--the fraction of the time that the particle remains in the water column and the fraction of time that the particle is within the sediment and within the reach of benthic organisms or subject to resuspension. A polluted particle is considered removed when only extreme environmental events of very low frequency (i.e., one per 100 years) will reintroduce it to the environment because the frequency of biosedimentary interaction, in at least some coastal environments, approaches one per year (i.e., every particle is bioprocessed at least once per year).

Thus extreme environmental events, such as those resulting from 100-year storms or earthquakes, will in many cases remobilize vast quantities of polluted particles and govern the long-term dispersal patterns of associated pollutants. Much can be learned by studying processes that occur on a yearly or seasonal basis, but extreme events must be studied individually.

We focus here on physical processes occurring in the water column as well as on and within the bottom. In the spirit of lumping rather than splitting we have categorized these physical processes into those that affect resuspension rates and advection, and those that affect packaging (i.e., the way particles are combined together) as being of greatest importance to transport of polluted particles.

PACKAGING

Definition

Packaging can be defined as the agglomeration and aggregation of individual (primary) particles and of groups of particles into larger composite particles. Packaging occurs in the water column, and on and beneath the seafloor as a result of biological and physicochemical processes.

Filter-feeding organisms in the water column and on the seafloor package particles suspended in the water column. Deposit feeding-organisms package particles on and beneath the seafloor. Electrochemical flocculation of suspended *organic* particle has been shown to be important. Electrochemical flocculation of suspended inorganic particles *may* be important in the upper reaches of estuaries, particularly near the bottom, where salinities are low (3-5‰), where the concentrations of suspended particles are high (≥ 1,000 mg/ℓ) and where mixing is sufficiently intense to increase particle-particle collisions but not so strong as to disrupt composite particles once formed. The evidence for the importance of this process in sedimentation remains equivocal and the subject of debate.

Importance to OMPA

It is clear that packaging of fine particles into larger units is important in the dispersal and accumulation of fine particles and their associated contaminants in coastal waters, and in determining the interactive and removal times of fine particles. Packaging of particles within the water column increases their settling velocities and, therefore, decreases their residence times within the water column. Packaging plays a major role in determining the routes and rates of transport of fine particles and particle-bound contaminants and in determining their rates and patterns of accumulation.

Packaging in the water column, and particularly on the seafloor alters the texture and fabric of the bottom, its roughness, its bulk sediment properties, and as a result, the susceptibility of the bottom sediments to resuspension. Packaging on and below the seafloor may either increase or decrease the susceptibility of sediments to resuspension and, as a result, the transportation and mobilization of particle-bound contaminants and contaminants dissolved in the interstitial water. How benthic organisms alter the susceptibility of sediments to resuspension depends upon a number of factors, principal among them being the "kinds" of organisms doing the processing, and the rate of this reworking relative to the sedimentation rate.

While the implications of particle packaging within the water column are clear for questions of the particle transport of pollutants, the intensity of packaging and the relative importance of the several mechanisms of packaging in different coastal environments, particularly in estuaries, has not been demonstrated conclusively.

Hypotheses

1. Physiocochemical flocculation is not a controlling mechanism for the deposition of suspended *inorganic* particles and associated particle-bound contaminants.

   Rationale: The upper reaches of estuaries are characterized as areas of rapid sedimentation and as areas of elevated concentrations of particulate matter suspended in the water column. One of the mechanisms often stated as playing an important role in both cases is flocculation. If flocculation is an important sedimentation process for inorganic particles anywhere in nature, it is in the upper reaches of estuaries. According to laboratory studies, many of the necessary environmental conditions are "right" and flocculation should be important. But even here field evidence is equivocal and the subject of debate.

2. The importance of filter-feeding zooplankton in packaging inorganic fine suspended particles increases above some threshold with increasing particle concentration because the organisms' efficiency in particle selectivity decreases.

Rationale: Many filter-feeding organisms have very sophisticated mechanisms for selecting and sorting fine-suspended particles. Organisms may select and sort on the basis of particle size, settling velocity, composition, and a number of other particle properties. These mechanisms have been shown to be very effective in dilute suspensions of inorganic and organic particles such as those found in the open ocean and in most continental shelf waters where concentrations of total suspended matter rarely exceed a few milligrams per liter. It has not been demonstrated whether filter-feeding zooplankton can be selective in their feeding in areas where the concentrations of suspended matter are one to three orders of magnitude higher and where there is much more overlap in the size distribution of inorganic and organic components. Many filter-feeding zooplankton are abundant in such areas and may play an important role in removal of suspended matter--organic and inorganic--from the water column.

RESUSPENSION RATE

Definition

Resuspension rate is defined to be the instantaneous flux of material to the water column from the seabed. Resuspension rate will be dependent on both flow and bed properties. Among the bed properties that influence bed erodibility are bed composition; texture; bulk physical properties; and extent of bioprocessing. Important flow properties will be mean flow (averaged over varying time scales of interest) via bed stress and turbulent intensity level. Also influencing bed stress will be density stratification effects, hindered settling, bed morphology and roughness. Resuspension rates and erosion rates are sometimes used synonymously, though erosion rates in the geological context mean a longer term net flux of bed material. Resuspension rates are here considered to be inextricably coupled to resuspension processes, and they must be addressed simultaneously.

Very little has been done to date in measuring rates of erosion in contrast to more abundant measurements of threshold velocity for erosion. The literature provides two laboratory flume studies, only one of which is in a saline environment. Since sediments are disturbed and resettled in the flumes prior to erosion experiments, questions remain as to the representativeness of the experimental bed. The lack of in-situ measured or inferred resuspension rates is a critical missing element in making progress on the pollutant transfer problem.

Importance to OMPA

To have the capability of making quantitative estimates of resuspension rates is important to OMPA in the following ways. Resuspension rates

(1) determine the exposure levels of pelagic animals to contaminated sediment and by means of phase transformation, to dissolve pollutants;
(2) determine the rate of release of interstitial dissolved contaminants;
(3) along with sedimentation rate determine the vertical disposition and dilution of the pollutant and the exposure level of benthic infauna to pollutants;
(4) determine the degree to which particulates are diluted because of lateral transport.

Relation to Interaction Time of Particles

Knowledge of resuspension processes of fine-grained cohesive sediments is important because these processes influence the interaction time (τ_I) of particles with biota and dissolved pollutants in several ways. These include (1) reinjection of particles from the microenvironment of sediment/pore water to the macroenvironment of the water column. This change may profoundly affect sorption reactions and other chemical phenomena; (2) reinjection of pore water itself into the water column providing fresh sources of sorbable pollutants; and (3) complication of simple concepts of pollutant removal time by occasional reintroduction of particles and pore waters, which may have been removed from the "active" water column/sediment environment for months or years.

An interesting subset of τ_I is the determination, for particular classes of particles within the resuspension zone (or bottom nepheloid layer), of the probability of a given particle's being found in the water column or at rest on the seabed at any time. The importance of such a distinction depends on the difference in chemical reaction rates that characterize each state, and the difference in susceptibility to repackaging in each state.

Hypotheses

1. The most important factor in the resuspension of fine-grained cohesive sediment under specified flow conditions is the intensity and character of biological processing.

Rationale: Bed properties that affect erodibility include composition, bulk physical properties of the surface layer, sediment texture, and biological processing. We suggest that the last of these has the most influence. If it does, bottom areas with habitually low levels of bioturbation (due to periodic anoxic condition, for example) may be logical choices for dump sites on the basis of low biologic impact and low remobilization rates.

2. The accumulation of pollutants within a sedimentary body is proportional to the frequency and intensity of resuspension activity.

Rationale: The net transport of pollutants from the water column to the seafloor may be governed by the cycling of particles between these compartments. Removal of dispersed pollutants from the water column may thus be enhanced over areas of active resuspension.

3. Fractionation of a suite of particle-associated contaminants from a single source is determined primarily by the reactivity of the contaminants rather than by physical sorting of the particles.

Rationale: The distribution of particulate-associated pollutants in estuarine or coastal sediments is not normally geographically uniform. This areal fractionation may be a function of physical sorting of different particle types (and this different pollutants) during transport and/or different absorption-desorption reaction rates for different pollutants during resuspension/deposition transport cycles. Understanding the balance between these two processes will allow better prediction of the dispersal of particulate-associated pollutants after introduction to a specific site by planned or unintentional dumping.

4. The temporal variations in suspended sediment concentration profiles at a given site can be modeled as an advection-diffusion process governed by a stress-driven resuspension term.

Rationale: In order to generalize the measurements of in-situ erosion or to infer erosion rates through indirect measurements, a theoretical formulation must be given to the resuspension process. We suggest that as a start, an advection-diffusion model coupled to bed processes through a bed flux-erosion boundary condition is suitable to describe time variations of near-bed concentration under varying near-bottom flow conditions. Within such a framework, examination should also be given to the way in which erosion rates depend on or are independent of critical erosion stresses.

5. At a given site the resuspension rate is dependent on both turbulent shear stresses and mean bed shear stress.

Rationale: Bed stress is a time-averaged quantity which does not fully characterize flow at the bed. Detailed studies of boundary layer flow show that strong, intermittent events play a major role in the transfer of momentum near the bed, and it has been hypothesized that these intermittent events (bursts and sweeps) could mediate the resuspension process. For example, under declining tidal flow one might find that maximum resuspension lags maximum mean bed stress because of the intensification of turbulence in a decelerating flow. Examination of this hypothesis would establish whether bed stress alone is sufficient to parameterize the resuspension rate at a given site.

RECOMMENDATIONS

All of the above research tasks (hypotheses) are testable in a 2-to-3 year time frame with little or no need for development of new technology. We place highest priority on the study of the effect of sediment bioprocessing on erosion rates. Some work is in going on in this area, but we emphasize the need for progress.

Also of primary importance are the other boundary layer studies relating flow properties to bed properties. PTP models will require information on resuspension and transport rates. Models, per se, have not been discussed but are implicit in each working hypothesis. For example, several different theoretical models are available to describe suspended sediment concentrations in the boundary layer. None has been adequately tested in the field, but state-of-the-art is sufficient to make the required measurements of flow and sediment concentrations for several simple cases. Improvements and validation of transport models will allow us to predict what, if any, size-dependence the transport rates will exhibit under a given set of environmental conditions. This knowledge can be used to guide chemical and biological sampling and to establish boundary conditions for pollutant transport models.
We prioritize our working hypotheses as follows:

(1) Effects of bioprocessing on erosion rate.
(2) Testing of existing theoretical models of suspended sediment transport and erosion.
(3) Dependence of erosion rate on turbulent stresses as well as mean stress.
(4) Importance of physical flocculation to sedimentation.
(5) Dependence of geographical fractionation of pollutants on biochemical factors, not on physical sorting during transport.
(6) Enhancement of pollutant accumulation rates in sediments by high resuspension rates.,
(7) Biological packaging of inorganic particles as a function of particle concentration.

2. REPORT OF WORKING GROUP ON GEOCHEMICAL PROCESSES

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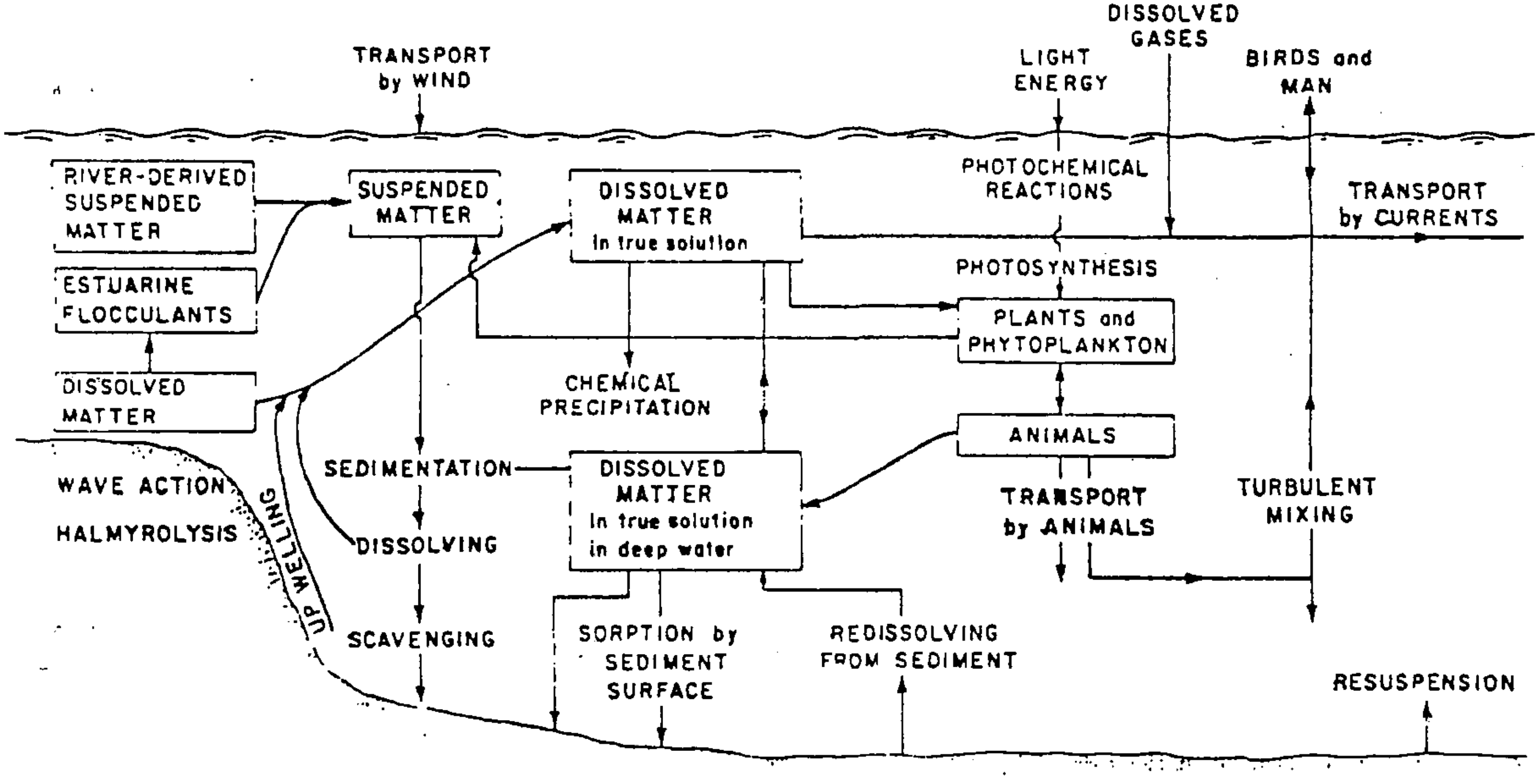
INTRODUCTION

It is generally accepted that most pollutants in marine estuarine systems are controlled by interaction with particulates. The particles may consist entirely of the pollutant itself or may provide a surface on which the pollutant adsorbs or desorbs. The particles themselves may be inorganic minerals and resistant to degradation or may be organic and less resistant or may be a combination of organic and inorganic, as in fecal pellets of grazing organisms. Particles with associated pollutants undergo a variety of transformations: formation, aggregation, dissolution, and biological alteration; and are transported by water currents and gravity. Particulate pollutants in sediments may be remobilized as resuspended particles. Interstitial waters in sediments may transport dissolved pollutants back into the water column.

An incomplete depiction of some of the major processes (and certainly not all their interactions) affecting pollutants in marine coastal waters is provided in Fig. 1. Pollutants may enter the estuary from rivers, surface runoff, wastewater discharge and atmospheric fallout. Once introduced, these compounds are dispersed, flocculated, or biologically modified, depending on their physicochemical properties and biological reactivity. Contaminants that are highly insoluble usually flocculate or become associated with organic-rich suspended particles. Because of their negative buoyancy, they are easily trapped and retained within estuarine systems. Either in the suspended state or while temporarily residing in near-surface sediments, theses materials become a food source for many detrital and pelagic organisms. The assimilative capacity of a marine system for pollutants thus depends on dispersive processes, the residence time of the water, and the presence of fine-grained sediments, as well as chemical/biological degradation processes that tend over the long term to detoxify the system.

Pollutants introduced into marine systems, and estuaries in particular, can undergo three fates other than chemical or biological degradation. They can persist where they were introduced if they are insoluble and currents are weak or introduction rates high. They can be widely dispersed and removed from the system if soluble (at some time) or currents are strong. They can be winnowed and redoposited, depending on the strength of the currents and the physical properties of the suspended particulates. One system of equations can be used to describe particle/water/organism partitioning, and another can describe the transport of the pollutant. There are three fates that constitute ultimate sinks for physical pollutant materials: transport out of the defined system laterally, burying in sediment vertically, and diagenesis.

Within the context of this multiplicity of processes affecting the behavior of pollutants in marine systems, it was the task of the Geochemical



Major biogeochemical and physical processes in estuarine and coastal waters

Figure 1. Conceptual model of major geochemical and physical processes.

Processes Working Group to consider the role of transformation processes affecting the distribution, concentration and potential toxicity of selected classes of pollutants. Transportation and biological transformations were included in our considerations if they affected or caused geochemical transformation.

PROCEDURES AND RESEARCH STRATEGY DEVELOPMENT

In order to organize our thinking we first developed a matrix of relevant interactive processes to show interrelationships among them. Each process pair (two boxes connected by arrows) was analyzed with respect to--

1. importance - a subjective sensitivity analysis;
2. quality and quantity of available information;
3. what hypotheses and tasks we could pose regarding important pairs;
4. what information was required by one task from other tasks to reach completion.

This analysis was the basis for proposed working hypotheses, rationales, and tasks. The Working Group noted the relative importance of each hypothesis to be tested (on a scale of one to three, with one the most important) and the temporal importance: how soon tasks needed to be initiated (on the same scale). We propose that a PERT chart be developed for all the tasks to show projected sequencing and that a research plan be developed thereby.

GEOCHEMICAL PROCESSES

I. Nature and Properties of Particles

Rationale: The central theme of pollutant removal from estuarine and coastal waters is that particles of different origin carry organic and inorganic pollutants to the sediments. Different pollutants react with their substrates to different extents, and the reactivities can be generalized by using equilibrium distribution coefficients (i.e.,K_D) or adsorption equilibrium constants (i.e., K). In order to determine these relationships, we need to know the type, composition, and source of adsorbing particles and their residence time in the water column, Experiments can be designed to study thes aspects.

Hypotheses:

Hypothesis #1 - The influx of particles is primarily of abiotic origin.

Processes Working Group to consider the role of transformation processes affecting the distribution, concentration and potential toxicity of selected classes of pollutants. Transportation and biological transformations were included in our considerations if they affected or caused geochemical transformation.

PROCEDURES AND RESEARCH STRATEGY DEVELOPMENT

In order to organize our thinking we first developed a matrix of relevant interactive processes to show interrelationships among them. Each process pair (two boxes connected by arrows) was analyzed with respect to--

1. importance - a subjective sensitivity analysis;
2. quality and quantity of available information;
3. what hypotheses and tasks we could pose regarding important pairs;
4. what information was required by one task from other tasks to reach completion.

This analysis was the basis for proposed working hypotheses, rationales, and tasks. The Working Group noted the relative importance of each hypothesis to be tested (on a scale of one to three, with one the most important) and the temporal importance: how soon tasks needed to be initiated (on the same scale). We propose that a PERT chart be developed for all the tasks to show projected sequencing and that a research plan be developed thereby.

GEOCHEMICAL PROCESSES

I. Nature and Properties of Particles

Rationale: The central theme of pollutant removal from estuarine and coastal waters is that particles of different origin carry organic and inorganic pollutants to the sediments. Different pollutants react with their substrates to different extents, and the reactivities can be generalized by using equilibrium distribution coefficients (i.e.,K_D) or adsorption equilibrium constants (i.e., K). In order to determine these relationships, we need to know the type, composition, and source of adsorbing particles and their residence time in the water column, Experiments can be designed to study thes aspects.

Hypotheses:

Hypothesis #1 - The influx of particles is primarily of abiotic origin.

Tasks:

1. Conduct major elemental analyses of composition on sediment trap samples and normalize the data to calculate the percentages of detrital and biogenic particles. The percentage of biogenic particles should be further sub-divided into organic matter, $CaCO_3$ and opal.

2. Use SEM-EDAX studies on sediment trap samples to identify morphology, size, and composition of fecal pellets.

3. Separate the nature of the biological and detrital fluxes by studying trap material at high and low productivity and as a function of water column depth.

Hypothesis #2 - The flux of biogenic particle is primarily the result of biological repackaging (i.e., fecal pellets).

Tasks:

1. Examine sediment trap samples for free versus pelletized planktonic debris. Do this as a time series to cover the period of initiation and from each source. At the same time, measure primary production rate and standing stock of zooplankton.

Hypothesis #3 - The residence time of particle in the water column is a function of primary productivity.

Tasks:

1. Compare sediment trap flux from base of photic zone with integrated measurements of primary productivity as a function of time.

2. Make detailed time study of the period of initiation and duration of primary and secondary production. The objective here is to quantify effects of fecal versus free flux.

3. Calculate residence time in the water column from measurements of reactive U-Th isotope series depletions (specifically ^{234}Th and ^{228}Th) and compare with estimates from trap flux.

Relative and Temporal Importance:

Hypothesis	Relative	Temporal
1	1	1
2	2	2
3	1	1

Time and Space Scales:

Daily to seasonal, strongly influenced by tidal and biological cycles. Ten meter, one dimensional to 10-km, two dimensional space scales (site dependent).

II. Flocculation Processes in Estuaries

Rationale: Flocculation is a complex physical-chemical reaction in which riverborne suspended solids and colloids coagulate into larger particles in the presence of the increased electrolyte concentrations. Flocculation of organic and inorganic particles in estuaries accounts for the uptake and sedimentation of 10-50% of the total dissolved Fe, P, Mn, Cu, Ni, and Zn in some estuaries. Since organic pollutants sorb rapidly onto particles in suspension, this process can be an effective means of concentrating these contaminants in estuarine sediments.

Hypothesis:

Flocculation of inorganic and organic particles in the low and intermediate salinity regions of estuaries enhances the sedimentation and retention of pollutants.

Tasks:

1. Determine the physical and chemical nature of flocculated materials as a function of salinity, temperature, pH, Eh, and river water major ion concentration in model estuaries.

2. Determine the stability constants for selected pollutant-flocculant complexes.

3. Determine kinetic rates of flocculation and rates of complexation with representative pollutants as a function of temperature, salinity, pH, and Eh in model estuaries.

4. Develop a conceptual and predictive numerical flocculation model for model estuaries which can be tested with selected field studies.

Relative and Temporal Importance:

Relative	Temporal
2	2

Time and Space Scales:

Seasonal, two- dimensional, site- specific in estuaries, vertical scale: meters; horizontal: kilometers.

III. Sorption and Desorption Processes:

Rationale: Interactions of contaminants on non-geological time scales as well as passive interactions with biota have been frequently described in terms of equilibrium partition coefficients. This approach has been of considerable value in making first-order estimates of contaminant behavior in freshwater and marine environments and should continue to be used in first-order quantitative models, but additional research is required to assess the applicability of the approach for specific classes of contaminants and for specific time and space scales.

Since many passive contaminant-particle reaction rates occur on time scales of the order of minutes to hours, the equilibrium approach will be valid only for time scales greater than several days. Thus the rapid changes occurring under some conditions in estuaries may not be amenable to such treatment at all. Additionally, values of partition coefficients are known to depend on concentrations of sorbing particles, salinity and concentrations of organic matter. In some cases the use of partition coefficients may be misleading because contaminant-particle transfer reactions are not truly reversible or are geochemically determined, and may depend on conditions of Eh, pH, dissolved oxygen, etc. Finally, as generally determined, partition coefficients describe the partitioning of a contaminant between water and particulate matter without regard to particle composition. Identification of the primary carriers of specific contaminants and the partitioning of contaminants among those carriers is an important step in quantitative modeling efforts.

Hypothesis #1: There are representative compounds (or elements) that may be identified for use in sorption/desorption studies.

Rationale: There are many thousands of contaminants (compounds or elements) that have been, and are continuing to be, introduced into the marine and fresh water environment. Clearly, most contaminants cannot be treated with any degree of thoroughness. Hence, a rational approach to the selection of model contaminants must be taken which optimizes their representativeness of classes of compounds (or elements) and which assures inclusion of substances posing the greatest environmental impact.

Tasks:

1. Examine existing particle-contaminant interaction (sorption) data to identify classes of contaminants having comparable interaction characteristics. Categories should include halogenated hydrocarbons, phthalic acid esters, organo-phosphate pesticides, trace metals, fossil hydrocarbons, polyaromatic hydrocarbons and radioactive elements.

Relative and Temporal Importance:

Relative	Temporal
2	1

Time and Space Scales:

Not applicable

Hypothesis #2: Rates of reaction between contaminants and particles are important in determining their partitioning in estuarine environments where major changes in water composition occur on time scales of the order of hours to days.

Rationale: Since many passive contaminant-particle reaction rates occur on time scales on the order of minutes to days, the equilibrium approach will be valid only for time scales greater than several days. Thus, in estuaries where rapid spatial and temporal changes may occur in water properties (pH, Eh, salinity gradients, tidal pumping), exchange of contaminants with particles will depend on reaction rates.

Tasks:

1. In field studies, determine the rate of sorption or desorption of selected contaminants using natural materials. Determine the effects of salinity, Eh, pH, dissolved organic carbon, and particle composition on such rates.

Temporal and Relative Importance:

Temporal	Relative
2	1

Time and Space Scales:

Minutes to days/estuarine environments; centimeters to meters.

Hypothesis #3: The distribution coefficient of a given contaminant is primarily dependent on suspended solids concentration, surface characteristics, pH, Eh, salinity and dissolved organic ligands.

Rationale: Interactions of contaminants on non-geological time scales as well as passive interactions with biota have been frequently described in terms of equilibrium partition coefficients. This approach has been of considerable value in making first- order estimates of contaminant behavior in freshwater and marine environments and should continue to be used in first-order quantitative models. Limits on the applicability of the concept are understood in a general way, but additional research is required to assess the applicability of the approach for specific classes of contaminants and for specific time and space scales. Values of the distribution (or partion) coefficients are known to be dependent on concentrations of sorbing particles, salinity, dissolved organic ligands, particle type, surface charateristics (area and presence of organic or metal hydroxide coatings).

Tasks:

1. Determine distribution (partition) coefficients for sorption and desorption of selected contaminants as a function of physical-chemical states. In some cases, complement field determinations with measurements under carefully controlled laboratory conditions. In such studies, solids concentration ranges should extend from concentrations

characteristic of dilute suspensions to concentrations approximating surface sediments. The nature and occurrence of both organic and metal hydroxide coatings on particles and particle surface area are of special importance. Determine the complexing ability of model and natural organic ligands and their effect on distribution coefficients. Examine pollutant adsorption onto specific particle phases (clay minerals, Fe/Mn oxides, fecal pellets, plankton, etc.).

Relative and Temporal Importance:

Relative	Temporal
1	1

Time and Space Scales:

Minutes to hours; estuarine and nearshore; centimeters to meters.

Hypothesis #4: The amount of pollutants adsorbed is a function of surface area and composition of particles.

Tasks:

1. Laboratory determination of K_{ADS} on natural sediment trap material with associated surface measurements ($m^2 g^{-1}$), and determinations of types of trapped particles (see Hypothesis #1). These studies should involve the determination of the total number of available sites (site m^{-2}) to establish K's independent of particle concentration. This will facilitate the general application of results.

Relative and Temporal Importance:

Relative	Temporal
1	1

Time and Space Scales:

Not applicable

Hypothesis #5: The adsorption and removal of reactive pollutants from the water column is a function of the average residence time of biogenic particles.

Tasks:

1. Experiments under controlled or simulated field conditions (MERL or smaller scale) in which reactive pollutant spikes are added to systems with different residence times of particles.

Relative and Temporal Importance:

Relative	Temporal
1	1

Time and Space Scales;

Hours to weeks; meter scale.

Hypothesis #6: Long contact times between contaminants and particles (2 months to years) result in reduced rates of desorption.

Rationale: Sorption and desorption processes are seldom truly reversible in nature. Often rates of desorption of contaminants are less than sorption rates, and the difference may be enhanced through prolonged contact between contaminants and particles. Desorption of contaminants from sediments resuspended following a period of quiescence of sufficient duration to allow migration of contaminants into particle interiors may be considerably less than expected on the basis of desorption rates determined from short term studies.

Tasks:

1. For selected contaminants determine the rate of desorption (and operationally defined distribution coefficients) as a function of contaminant-particle contact time.

2. Determine the rates of desorption of contaminants from sedimentary materials of various relatively well-determined ages.

Relative and Temporal Importance:

Relative	Temporal
2	3

Time and Space Scales:

Months to years to decades. Coastal marine/lacustrine environments.

IV. Biologically Mediated Processes

a. Biotransformation

Rationale: The oxidation state of many trace metals (e.g., Mn, Cr) is biologically mediated. The transformation of trace metals such as Hg, As, Se, S and halogens, into volatile, and some times highly toxic, organic molecules is accomplished both by microbial processes and autotrophic organisms. The rates of these transformations are proportional to the rate of carbon fixation.

Hypothesis #1: The rate of biotransformation (alkylation, oxidation and reduction of organic and inorganic species in water and sediments) is proportional to local autotrophic and heterotrophic metabolism.

Tasks:

1. Conduct laboratory and field experiments using chemostats and natural populations of organisms to determine species-specific incorporation of ions into identified organic molecules and the conditions under which this process occurs, and determine rate constants.

2. Determine the partitioning of substituted toxic compounds among water column, sediments and sediment-water interface.

3. Conduct laboratory experiments to measure transformation rates of substituted toxic compounds by benthic organisms.

4. Conduct a field study to measure flux (traps) and accumulation (cores) of organic carbon and selected compounds in areas of differing carbon fixation.

Relative and Temporal Importance:

Relative	Temporal
2	2

Time and Space Scales:

Hours to seasonal over centimeters to tens of kilometers.

b. Bioturbation

Rational: Particulate organic carbon flux and net sedimentation rate are critical parameters for the development and maintenance of a viable benthic community. The density and activity of this community will determine the thickness of the mixed (aerated) sediment layer and the rate of biochemical processes within the mixed layer. The combination of net sedimentation rate, mixing rate and mixed thickness determines the residence time of materials within the active sediments.

Worm tubes may be as important as epifaunal processes in the transfer of gases and other solutes from sediments to the overlying water column. They have a demonstrated role in gas transfer. In addition, tidal pumping of water in tubes, in particular, and sediments in general, may enhance the transfer of other solutes out of the sediments by advection with diffusive processes playing a secondary role, especially in coastal regions.

Bioturbation disturbs the sequence in which sediments are deposited and affects geochronological measurements using long-lived radioisotopes.

Hypothesis: The mean residence time of a particle-bound contaminant within the benthic-mixed layer determines the concentration of contaminants in the overlying water column, by resuspension or resolution.

Tasks:

1. Conduct laboratory experiments to measure the rates of mixing of a spiked tracer into the mixed layer for different sediment types by a variety of benthic organism densities.

2. Conduct field studies to measure the particle flux (traps) and sediment accumulation (net sedimentation rate and mixed depth from cores) at various sites selected for a range of sediment particle sizes, flux rates and densities of benthic organisms.

3. Conduct field studies to measure the vertical distribution in cores of particle bound radionuclides with half lifes are appropriate to the time scale of mixing.

4. Develop a numerical simulation model of mixing and burial.

5. Investigate gas transfer rates at the sediment/water interface. Expand those studies to include extensive work on the relationship between density of infauna and gas transfer rates. (The role of worm tubes in gas transfer is being investigated to a limited extent.)

6. Conduct studies on the role of tidal pumping, and its role in advective flushing of worm tubes in particular, as well as areal distributions of sediments due to decreasing pressure in benthic chambers.

7. Trace the degradation of know sediment organic pollutants at monthly intervals over a 2-year period as a function of sediment type, sedimentation rate, microbial activity or redox potential and sediment loading of pollutant.

Relative and Temporal Importance:

Relative	Temporal
1	2

Time and Space Scales:

Months to decades; centimeters vertical; tens of meters horizontal.

V. Flux In/Out of Sediments

a. Particle Resuspension

Rational: Pollutant scavenging from the water by resuspended particles with subsequent deposition may be an important mechanism for pollutant removal from estuarine and near -shore coastal waters. Diagenetic processes (decomposition, dissolution, reduction, etc.) frequently cause an increase in pollutant pore-water concentration relative to the overlying water column. This increase gives rise to a vertical concentration gradient which allows for the diffusive flux of pollutants out of the sediments (see Part b). Advective fluxes resulting from tidal pumping, or the reinjection of pore waters during a resuspension event may also release pollutants into the water column. Release of pollutants from resuspended particles may also occur as a result of desorption or partitioning into the water phase.

Hypotheses:

Hypothesis #1: The exchange of contaminants between water and resuspended particles is an important process for both pollutant removal from and pollutant release to the water column.

Tasks:

1. Determine the time scale and extent of surface sediment resuspension in estuarine and marine waters. This has been documented in estuarine systems on the basis of particle concentrations and current measurements over tidal cycles. In coastal systems, the extent of resuspended particles may be estimated from current meter - nephelometer - sediment trap arrays. Also, biogeochemical signatures may help distinguish resuspended particles from those that are riverborne or produced *in situ*, (e.g., differences in microbial communities on resuspended sediments relative to particles in the water column).

2. Determine the extent of resuspended-particle scavenging by comparing pollutant fluxes by means of *in situ* organics to pollutant fluxes estimated from radionuclide removal rates. ^{228}Th/^{228}Ra disequilibria indicate that reactive-pollutant (Th, Pu, PCB's) removal rates are on the order of 150 to 200 days in the open ocean, 50-100 days on the slope, 15-30 days on the shelf and 1-15 days in estuaries and bays. Measurements of pollutant fluxes by settling plankton and fecal material can be compared with pollutant fluxes estimated from radiometric methods to determine whether scavenging by resuspended particles is an important process in specific environments.

Relative and Temporal Importance:

Relative	Temporal
1	1

Time and Space Scales:

The rate, extent, and effects of sediment resuspension progressively increase as water depth decreases (marine shelf coastal estuarine). The role of particle resuspension in removing or releasing pollutants from and to the water column should be examined in all of the above environments.. Hours to days; centimeters to meters.

Hypothesis #2: In the absence of net sediment accumulation, the net effect of particle resuspension and sediment mixing is to increase pollutant burdens in the sediments.

Rationale: A combination of particle resuspension and sediment mixing exchanges pollutant-poor for pollutant-rich particles and thereby causes pollutant accumulation and increased burdens in areas where net accumulation of particles is absent or low.

Tasks:

1. Natural (Pb-210, Be-7, Th-234) and anthropogenic (Cs-137, Cs-134, Co-60, Pu-239, 240) radionuclides, which have known histories of input to the system, can be used to determine particle accumulation rates and the extent that mixing and resuspension affect burdens.

Relative and Temporal Importance:

Relative	Temporal
3	3

Time and Space Scales:

Particle resuspension and sediment mixing will occur in all aquatic environments but will have their greatest influence in environments where the pollutant accumulation by net particle deposition is low. Hours to seasons; meters to 10^4 meters.

b. Dissolution

Rationale: In sediments, a higher solid/aqueous ratio, changes in redox conditions, microbial activity, and other early chemical diagenetic processes can create higher concentrations of a given pollutant in the interstitial water than in the overlying water column. These dissolved pollutants may then be directly available to benthic infauna and create a strong diffusion gradient toward the overlying water column. These processes all serve to return dissolved pollutants to the overlying water column and thereby re-expose organisms to pollutant loadings.

Hypotheses:

Hypothesis #1: Diagenetic processes in sediments/interstitial water bring about the dissolution of particle-bound pollutants.

Tasks:

1. Measure of selected organic pollutants in interstitial water (IW). Choose 2 to 3 "model" organics and measure IW concentrations as a function of sediment type, sedimentation rate, microbial activity or redox potential, and sediment loading of the pollutant.

2. Measure 2 to 3 "model" metals in IW as a function of the parameters listed above.

3. Trace the degradation of known sediment organic pollutants at monthly intervals over a 2 year period as a function of the variables listed above.

4. Measure/calculate inorganic pollutant speciation in IW as a function of the previous noted variables.

Relative and Temporal Importance:

Relative	Temporal
1	2

Time and Space Scales:

Pollutant dissolution in IW is important to many estuarine and coastal marine systems. Changes in IW concentrations occur on a seasonal (even monthly) basis.

Hypothesis #2: Diffusion, sediment mixing and resuspension, tidal pumping and biologically induced irrigation reintroduce IW pollutants to the overlying water column.

Tasks:

1. Measure fluxes of selected organic and inorganic pollutants between IW and the overlying water column, using benthic chambers. Compare these fluxes with those calculated from IW profiles and consider both as a function of sediment type, sedimentation rate, microbial activity or redox potential, and sediment loading of the pollutant.

Relative and Temporal Importance:

Relative	Temporal
1	2

Time and Space Scales:

Pollutant fluxes from IW are important in many estuarine and coastal marine systems. Releases are on a continuous time scale with significant changes in fluxes being seasonally variable. Centimeter on vertical axis and kilometers to tens of kilometers horizontally.

3. Report of Working Group on Biochemical Processes

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R. SPIES, W. SUNDA, and D. ATWOOD

> "It is not in the terrestrial experience continuously to inhale the young, eggs, sperm, and excreta of all our fellow creatures, . . . Although it may seem repulsive to us, it, nevertheless, is the way of marine life."
>
> John D. Isaacs
> 1915-1981

INTRODUCTION

A growing body of knowledge indicates that marine microbes, plants, and animals are intimately involved in determining the disposition and toxicity of particulate-bound contaminants such as certain metals, petroleum hydrocarbons, and synthetic organic chemicals. For example, it is now quite clear that in the deep ocean, many miles removed from the coastline or river plumes, plankton concentrate and partition metals such as copper, cadmium, and zinc among dissolved and particulate material. It is also generally accepted that the high levels of mercury, DDT, and PCB's in higher trophic level marine animals (tuna, swordfish, shark, and air breathing vertebrates) result partially, if not primarily, from food-chain transfer of these contaminants via lower trophic levels. Finally, more evidence is coming forth in support of the concept that benthic organisms are capable of both sequestering and mobilizing (to dissolved forms) trace chemicals deposited in surface sediments.

Despite this knowledge, biological processes such as bioturbation, bioaccumulation, biomagnification, metabolism, excretion, or migration are not given a great deal of importance in developing actual models, simulations, or field projections of the fates of contaminants. It is the consensus of this panel that existing information on biological processes is not being utilized adequately to help identify reasonable waste disposal strategies. Typically, such strategies and activities are developed from physical and chemical considerations only. Thus, either the biological/biochemical processes are relatively unimportant, or, as was the consensus of the panel, their importance has been overlooked, and thus, some of the current projections of pollutant fates are wrong--or are right for the wrong reasons.

This report summarizes a panel inquiry designed to develop workable principles about the role of organisms in the transport of pollutants. Our mission was to develop and support testable hypotheses relating to the influence of marine biological processes on the transport, fate, and form of pollutants in natural marine environments. In particular, we wished to propose hypotheses which, when tested, could make a difference in managing marine pollution and ocean waste disposal.

In the discussion immediately following, we describe how we brought focus to a relatively small number of processes and hypotheses. This is followed by a review of the hypotheses and their support, and by suggested strategies for testing them.

BACKGROUND

Seawater is both a solution of dissolved organic and inorganic substances, and an aqueous suspension of living and non-living particulate materials. In some areas of the ocean, and at certain depths, or during certain seasons or time of the day or night, the "suspension" is dominated by inanimate material; elsewhere, and at other times, the "suspension" is a mass of living organisms. In the latter situation, one must suppose that organisms are, indeed, important factors regulating the transport, fate, form, biological availability, and toxicity of pollutants.

Theoretically, marine organisms can influence the transport and fate of pollutants just as they influence the transport and fate of nutrients, dissolved and particulate carbon, sulfur and nitrogen, essential trace metals, and a host of natural organic chemicals. In fact, animal life in the sea can be said to be entirely dependent on the successful and continued production of small particles (mainly bacteria, phytoplankton, and detritus). But marine organisms are active in other ways that can influence the fate of pollutants. For instance, at the biochemical level, many organisms metabolize lipophilic petroleum hydrocarbons and synthetic chemicals to more soluble materials (Lee, 1981; Stegeman, 1981). Some are even capable of manufacturing halogenated hydrocarbons not unlike those associated with pesticides (Fenecal, 1981).

At the physiological level, marine organisms offer massive, specific surface areas, both passive and active, for the exchange of gases, cations and anions, produce various sorts of excreta including gametes, exoskeletons, and mucous materials (often in the form of complex webs, nets, and strands). And while many organisms are small and subject to the vagaries of transport by currents and winds, many others are capable of massive and frequent vertical and horizontal migrations that can, in a few hours, transport thousands of tons of material distances of up to a kilometer or more. Such migrations may reconcentrate acquired chemicals or disperse chemicals in locations far removed from their origin. Finally, benthic animals are capable of sequestering chemicals in the sea floor, and, in the process of feeding, burrowing, and reproduction, can mobilize contaminants from the sediments either directly, by "bulldozing," or indirectly, by changing the reduction potential of overlying and interstitial water or the "binding" character of the sediments themselves (Luoma, this report; Lee and Swartz, 1980).

Such processes are well documented in specific laboratory and field experiments, and presumably, these biologically-driven processes are underway wherever there is marine life. We are faced with this question, then: Under what conditions are each or any of these processes so important that they determine and direct the transport of pollutants in ways that significantly enhance or counter the actions of physical and chemical processes? In other words, defining these conditions defines which of the biological/biochemical processes should be studied, and when and where they should be studied.

As a first step, we have eliminated those areas where physical and geochemical factors dominate the interactive processes. These include inshore areas heavily influenced by strong waves, or by runoff and riverine discharges wherein strong currents, steep salinity gradients, and massive, constantly moving bedloads of suspended and settleable inorganic materials prevail (e.g., beaches, river mouths, major portions of river plumes, and tidally scoured passages).

The marine environments that we will be addressing include the relatively quiet waters of the deeper, low-latitude estuaries and embayments, the greater part of the coastal shelves, the deep ocean, and the physically active, but inorganically impoverished euphotic zone beyond the usual influence of runoff--in short, the "where" of our concern includes most of the world's oceanic environment that lies outside the direct influence of most urban and industrial areas.

The oceans constitute nearly three-fourths of the world's surface area, but have been little utilized for the direct disposal of anthropogenic wastes. The growing advocacy for use of this vast reservoir as a repository for the world's municipal and industrial wastes necessitates our developing an understanding of the processes involved in order to devise strategies and methodologies to mitigate potential harmful effects.

The processes of most importance, we believe, as those that enhance or inhibit the downward flux of pollutants to the sea floor or ocean depths, and those that could remobilize pollutants from the sea floor and return them to key organisms in the water column. Also of importance are those processes that markedly change the form and toxicity of contaminants while they are in biologically active waters (especially the euphotic zone), and those processes that return pollutants to shore or distribute them long distances to reconcentrate in special environments such as bird, turtle, and mammal breeding sites.

The panel has used the above rationale as the basis for selecting the most relevant processes, and developing hypotheses which, when tested, will yield results of practical use to marine management.

HYPOTHESES

Residence Time of Dissolved and Suspended Pollutants in the Photic Zone

Scientists and managers need to know if all offshore waters are equally capable of sequestering pollutants and wastes or, if they are not, how to identify those waters most amenable to sequestering the pollutants. In other words, is the residence time of a pollutant in offshore waters everywhere the same? If not, what controls the residence time?

To aid the panel in its deliberations, a conceptual model was developed of the major processes that influence the overall residence time of a contaminant in the oceans (Figure 1).

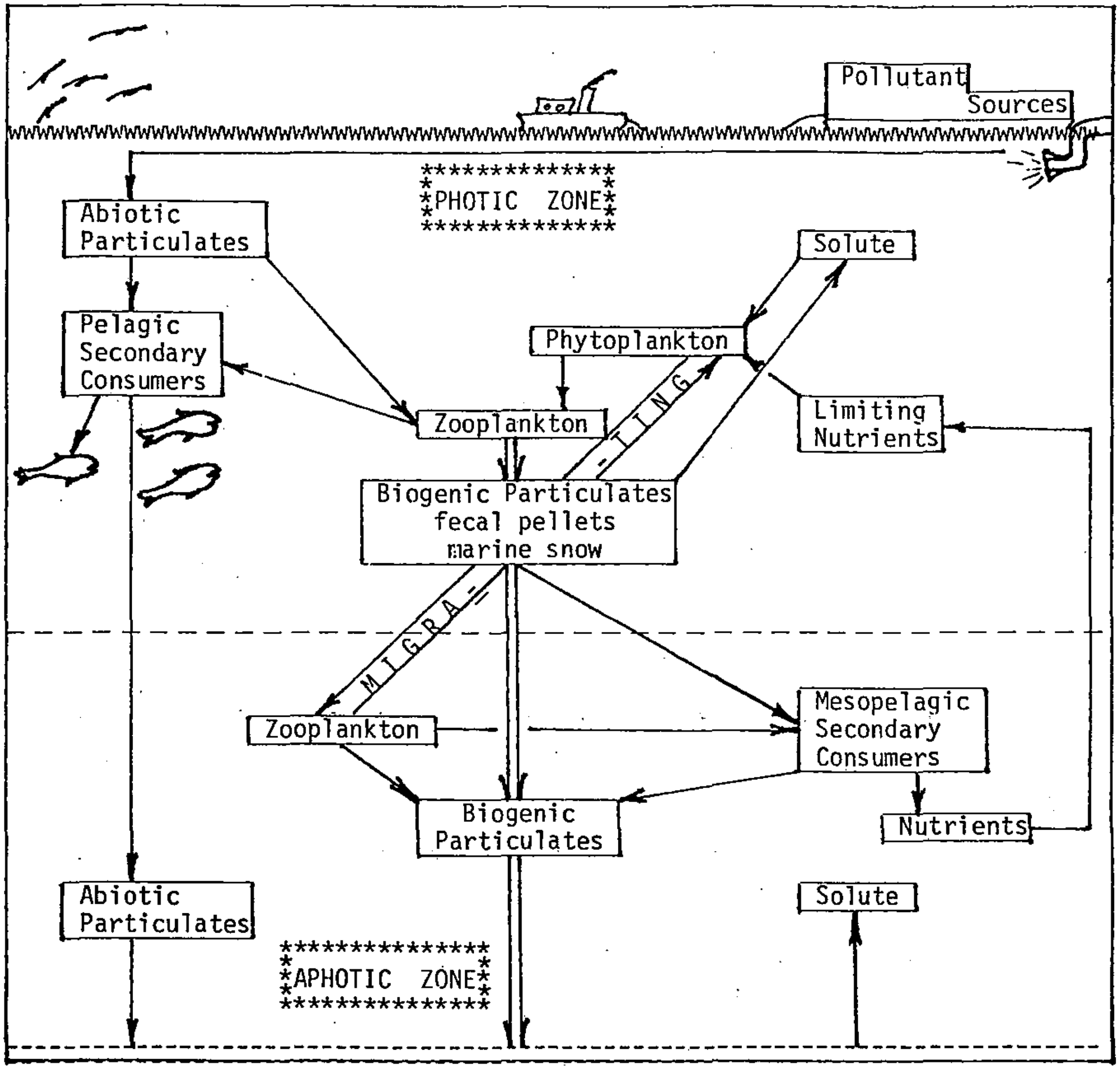

Figure 1. Conceptual model of underlying processes that determine the overall residence time of a contaminant in the coastal and offshore euphotic zone

The model identifies many pools (boxes) and rates (arrows), but we believe that only a few of these constitute the primary transport pathways for a number of pollutants. A control concept is that the primary removal mechanism in euphotic waters is the incorporation of pollutant solutes and particles into biogenic particles associated with zooplankton ingestion of phytoplankton, mucous products of other zooplankton (e.g., larvaceans and pteropods), and other organic and inorganic particulates. It is also recognized that the concentration of a given pollutant in solution and its affinity for uptake by the biota (particularly phytoplankton), its ingestion rate by zooplankton, and its incorporation (rate of "gut" transfer) into fecal particles of large enough size to have appreciable sinking rates (e.g., Small _et al._, 1979). The major driving force, however, is the rate of primary production since this will ultimately determine the rate of production of biogenic particles capable of downward vertical transport.

Hypothesis: _The euphotic-zone residence time of a dissolved pollutant is inversely related to the rate of primary production_.

Knauer _et al_. (1979) have shown that fluxes of C, N, and P from the euphotic zone into deep water are higher during periods of upwelling than during non-upwelling periods. These variations in flux appear to be strongly coupled to production within the euphotic zone (not below the euphotic zone).

As a first approximation, we assume that pollutants injected into euphotic zone waters will be removed to deep waters by the same processes that regulate C, N, and P. If so, then the residence time of these pollutants in the euphotic zone decreases with increased production and, specifically, primary production. A proposed relationship is shown in Figure 2.

The usefulness of this hypothesis as a diagnostic or predictive tool is related to the ability to quantify the following ancillary factors:

1. Rate of input contaminant.
2. Standing biomass in the area of concern.
3. Composition of biomass.
4. Affinity of a specific pollutant for uptake by biota.
5. Contaminant loading of excreta and other sinking detrital material (i.e., marine snow).

The rate of input is a controllable factor that can be adjusted to an optimum injection rate with respect to conditions dictated by the other four factors. The biomass (particularly phytoplankton) is amenable to reasonable quantification. Composition of the biomass will affect the transfer rate and is a factor that may change as a result of continued injection of a pollutant in a local area (a deepwater dumping site, for instance). Verification of the constancy of compositions would be a necessary adjunct to any prolonged waste disposal program. The affinity of a specific pollutant for uptake by the biota of concern can be established in the laboratory and verified in field experiments. Recent work, however, indicates that many species can adapt to continued pollutant insult by developing a tolerance for greater than normal body burdens of the pollutant. This could affect the removal rate if the zooplankton respond adversely. Zooplankton gut transfer efficiency determines the amount of contaminant contained in the fecal material. Conceivably, ingestion of phytoplankton having elevated levels of contaminant could result in even more efficient removal of the pollutant from the euphotic zone by increasing the load carried in the fecal pellet. On the other hand, the increased contaminant load could result in an inhibition of the grazing capability of the zooplankton with the consequent reduction in fecal product. This could then result in a less removal of the contaminant from the euphotic zone and a longer residence time in the water column.

We believe that the most important of these ancillary factors is the composition of flora and fauna and, in particular, the production of species that produce biogenic material with fast settling velocities (e.g., salps, Silver and Bruland, 1981; Copepods, Urrere and Knauer, 1981). It is also recognized that taxa dominance will also influence removal rate. Sunda and Lewis (1981) suggest that pollutants may be more effectively removed from the euphotic zone during diatom blooms than during dinoflagellate blooms, because of differences in uptake of the substance between the two algal taxa. It also seems probable that zooplankton grazing will be affected, depending upon the dominant algal species. Thus, we suggest two supplementary hypotheses:

> The euphotic zone residence time of a pollutant is inversely related to the production of high-density fecal pellets and excretions.

and

> The euphotic zone residence time of a pollutant is inversely related to the ratio of diatom to dinoflagellate production.

We thus conclude that an experiment is needed whereby known amounts of waste are injected into euphotic waters representing a range of production rates and in which variation in pollutant concentrations, primary production, species composition, fecal pellet production, and fecal pellet fallout rates are measured and the results subjected to statistical analyses designed to identify trends and sources of deviations due to the biological variables. Sediment traps can be deployed to capture fecal pellets and other biogenic debris to determine contaminant concentrations, downward fluxes, and, indirectly, sources. Confirmation of biogenic sources can be determined by visual methods (divers, UW-TV), indirectly from micro- and macro-plankton tows, or, possibly, by acoustic techniques. Direct samples will be needed to confirm species identifications and to determine ratios of prominent phytoplankters. Trace metals and chlorinated hydrocarbons could serve as the initial test contaminants.

Pollutant Accumulation and Mobilization on the Sea Floor

A long-term goal for ocean waste management should be to avoid the kinds of sediment accumulations that currently lead to contamination of harvestable resources and that affect the health of nearshore and benthic marine life. Obviously, conditions in the euphotic zone that maximize downward fluxes also maximize the chance of unacceptable sea floor accumulations of pollutants. For example, one possible objection to injecting wastes into the highly productive euphotic zone is that organically-complexed or linked pollutants may find their way into a benthic situation where sediments will be oxygen-depleted and have negative Eh. Such conditions could be conducive to rapid remobilization of metals to the water in a toxic (= ionic) form ("solute" of Figure 1.). Thus, we need more quantitative tools for predicting conditions that lead to pollutant remobilization and transport from the sea floor.

As indicated previously in Luoma (this report), and in Swartz and Lee (1980), much is known about the role of benthic organisms in sequestering and mobilizing pollutants from the sea floor. Now needed are quantitative tests of hypotheses about the actual importance of some of these processes in natural marine environments.

Hypothesis: Mobilization of pollutants from sediments to the water column is directly proportional to bioturbation rates in physically weak environments.

The assumed correlation between sediment pollutant loss and biological disturbance rates has never been conclusively tested in natural marine ecosystems. Laboratory and mesocosm experiments support the hypothesis, especially, in the case of worm tube construction and its ability to enhance metal transport from sediments to the water column (Luoma, this report).

The degree of bioturbation can be approximated by measuring benthic respiration coupled with documentation of community composition (e.g., abundance of tube-dwelling species, abundance of different feeding guilds of benthic organisms, and other measures of activity). Field experiments involving intentional pollutant exposure of sediments in calm waters are one approach to testing this.

Obviously, this simple hypothesis is subject to qualifications due to other processes. Especially notable are geochemical conditions of the sediments themselves. Accordingly, we offer a qualifying hypothesis to test:

Mobilization of pollutants is inversely related to the number of sediment binding sites.

It is now fairly well documented that metals most strongly bound to sediment components are least available to benthic deposit feeders. Conversely, where metal concentration/binding site ratios are high (e.g., in metal-contaminated sandy estuaries), bioavailability is often enhanced. Presumably, then, mobilization is also related (inversely) to the number of sediment binding sites.

An approach for determining the "number" of sediment binding sites requires laboratory development of methods. For example, it may be possible in the laboratory to make binding site density estimates of pure components such as Fe oxides, Mn oxides, and various other inorganic materials of defined surface areas, and of organic materials such as humic substances, lignins, cellulose, and bacteria. These properties can then be measured in the field and the number of potential binding sites computed. Promising areas for examination include operational extraction of monophosphorus iron oxide, concentration of Mn (total) and measurement of organic matrices using data on TOC, absorbance of humic substances, and bacterial counts or biomass (ATP). An alternative field approach is simply to compare contaminant concentrations in organisms from different sediment types over large concentration gradients.

Incidentally, this work is directly relevant to documenting the potential bioavailability of pollutants on particulates.

Pollutant Transformation by Marine Organisms

Marine organisms can biochemically convert petroleum hydrocarbons, synthetic hydrocarbons, and trace metals into compounds that may be toxic. It is assumed such transformation in invertebrates, fishes, birds, and mammals is an inconsequential factor in degradation of these contaminants (Swartz and Lee, 1980). Moreover, methylation of mercury does not occur at rates sufficient to significantly alter transport of mercury (Knauer, personal communication). In contrast, the ability of microorganisms to metabolize petroleum hydrocarbon and chlorinated hydrocarbons may alter or even control the fate of these materials in some ecosystems and under some conditions (Lee, 1988; Voll *et al.*, 1977; Sayler *et al.*, 1978), and these rates may be subject to control by man.

Several hypotheses could be of consequence if validated.

Hypothesis: *Biodegradation of petroleum hydrocarbons and chlorinated hydrocarbons is oxygen-limited in fine sediments. Conversely, in well-oxygenated environments, biochemical degradation is first substrate-, then nutrient-limited.*

Microbial degradation of petroleum hydrocarbons occurs at rates significant enough to be of interest in considering the fate of a variety of contaminated materials (sludges, dredge spoils, sewage effluent, oil itself). However, degradation of chlorinated hydrocarbons occurs at a fraction of oil (i.e., polycyclic aromatic hydrocarbon) degradation rates (Carey and Harvey, 1978). There is a paucity of information on *in situ* degradation rates, especially in sediments where microbial populations are orders of magnitude more concentrated than in water. There is some evidence that petroleum hydrocarbon degradation by microorganisms is nutrient-limited (Atlas and Bartha, 1972; Floodgate, 1973) and that nutrient additions to spilled oil speed degradation (Ward and Brock, 1976; Le Petit and N'Guyen, 1976; Dibble and Bartha, 1979). Degradation can also be limited by low oxygen, but it is not known generally how this may relate to nutrient levels and under what conditions either of these is limiting. This would be of consequence in anaerobic or anoxic basins and in sediments near large sewer and industrial outfalls, and dumpsites where bottom and interstitial waters harbor microbial and animal communities markedly different from those found elsewhere.

Even less is known about the factors controlling degradation of synthetic and chlorinated hydrocarbons. In the absence of a more detailed review, we offer that the same factors--substrate type, oxygen and nutrients--limit chlorinated hydrocarbon degradation by limiting the activity of microbes and abundant invertebrates.

To test this hypothesis in the field at existing contaminated sites, it is necessary to locate or purposely contaminate benthic ecosystems representing each geochemical state, and, over time, measure decreases in mass of parent compounds and the production of metabolites or degradation products. This requires use of advanced chemical methods (such as high pressure gas-liquid chromatography) and a unique experimental design (such as diver- or submersible-implanted experimental chambers).

Hypothesis: <u>Carbon flow to food webs is a significant fate of petroleum hydrocarbons in areas of heavy input</u>.

Spies <u>et</u> <u>al</u>., (1980) and Spies and Des Maras (in preparation) and others have determined that petroleum hydrocarbons provide significant sources of carbon to exposed food webs. The extent to which, or the processes involved are significant in the fate of the petroleum has yet to be determined or estimated.

One approach to testing this is to use sites chronically contaminated by petroleum hydrocarbons, and attempt to construct a budget for carbon entering primary consumers by using stable isotope shifts of carbon and sulfur.

Hypothesis: <u>The biological degradation of chlorinated hydrocarbons (DDT's, PCB's, Kepone, mirex) in marine sediments and benthic communities is negligible in terms of their eventual fate in contaminated environments</u>.

There is strong, but fragmentary, evidence that sedimentary reservoirs of DDT, PCB, Kepone, and other chlorinated hydrocarbons remain intact, and serve as sources for years. Yet, to our knowledge, no one has addressed this assumption, especially as it pertains to ruling out microbial or macrofaunal activity as unimportant in degradation of these contaminants.

Research to test this hypothesis might be done in concert with the tests for transformations by benthic ecosystems as noted above. In this case, antibiotics could be used to control microbial activity in experimental chambers implanted on the sea floor.

Hypothesis: <u>The degradation of chlorinated hydrocarbons by marine animals is inconsequential with respect to the animals themselves as reservoirs, i.e., the half-life of chlorinated hydrocarbon burdens in marine animals is longer than the animals life span</u>.

Evidence is confusing. Traditional laboratory studies suggest that once contaminated, marine vertebrates and invertebrates are extremely slow to metabolize or degrade these compounds. Yet there are situations where source control (e.g., DDT) has resulted in rapid one- to two-year declines in contamination of mussels and other organisms. There is new evidence that metabolites have not been adequately measured in the past and that they may be significant in regulating the total contaminant budget of individual animals. The residence times of chlorinated hydrocarbons in feral animals and populations and associated metabolic processes need to be conclusively identified and documented.

The test of this is, conceptually, relatively simple. Animals from contaminated sites can be transferred to clean sites and measured over time to determine changes in total mass of parent compounds and metabolites. There are obvious operational difficulties to be resolved in such a study.

Pollutant Transport by Populations

Many large marine animals, and large populations of small animals, such as herring and flatfish, migrate long distances, and congregate in high concentrations and large biomass to spawn or feed; other fish migrate vertically (e.g., Pererya *et al.*, 1969) Birds are also believed to be significant accumulators and transporters of oceanic material (Anderson *et al.*, 1980). Such organisms could be important vectors for pollutant transport to sites remote from and even "upstream" of pollutant sources.

Hypothesis: *Migratory animals that congregate are significant transport mechanisms for chlorinated hydrocarbon contamination of remote sites.*

Despite source control, marine birds and mammal populations off California and in the North Sea maintained high concentrations of mercury and chlorinated hydrocarbons in their tissues, and, apparently, in the tissues of organisms at breeding, feeding, and haulout sites remote from the sources (in part, Flegal *et al.*, 1981; and Risebrough *et al.*, 1980). Scientists also speculate that elsewhere, anadromous fishes are responsible for upstream migration of pesticides such as mirex. Flat fish may transport chlorinated hydrocarbons to distant sites (McDermott-Erlich *et al.*, 1977), but to our knowledge, the role of migratory animal populations as confirmed and important vectors of chlorinated hydrocarbons has not been explicitly tested in the sea.

One way to approach the problem would be to attempt a contaminant mass balance for a specific population of marine mammals or birds exposed to urban contamination with particular attention to cycling within the marine ecosystem adjacent to the population's major site of congregation.

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PART II

BRIEFING DOCUMENTS

INTRODUCTION TO BRIEFING DOCUMENTS

It is becoming increasingly clear that the study of sedimentation as a scientific discipline can serve national needs in several ways. At first, geologists investigated modern sedimentary processes in order to draw uniformitarian conclusions about ancient deposits in which oil might be found. Civil engineers were interested in sedimentary processes occurring on beaches and in harbors. Marine biologists studied organic particles, but saw little relation between their activities and those of geologists and engineers. Increasingly, however, we have been concerned with marine particles of all kinds as carriers of pollutants. Studies suggest that environmental pollution may be one of the important factors that will shape the future economic and social course of human society. Over the past decade we have seen many laws passed that set high standards for pollution control. More recently economic problems of global scale have intensified the debate over how to reconcile the conflicting requirements for development of resources and industries, versus the need to maintain a healthy environment. But whatever environmental standards we decide to set, whether stringent or lax, these standards must be based on a full understanding of environmental processes. Without such an understanding, we may fail to identify serious pollution problems or see problems in areas where none exists.

The study of particle sedimentation can make a major contribution here, because the partitioning ratio for most pollutants between the particulate and dissolved phases is very high--on the order of many thousands to one; hence, the study of pollutant dispersal becomes, to an important extent, a study of the behavior of sediment particles, the physics of their interaction with moving fluids, and the chemistry of their interaction with organisms.

The conceptual framework on which the following documents are based is a matrix, as seen in the figure below in which the state of the pollutant (attached to organisms, particles, or dissolved) is ranked against the environment in which the pollutant occurs (water column, resuspendable substrates, or state of permanent deposition). This volume is concerned with the interactions of the particulate states defined by this matrix with each other, and with adjacent states.

The first Briefing Document is concerned with the origin and behavior of fine particles in the coastal (beach-shelfbreak) marine environment. The second considers the adsorption and desorption of pollutants by particles. The third describes fluid particle interactions and the role of benthic boundary layer in mediating chemical processes. Document 4 describes the fole of particles in the transfer of pollutants to organisms.

All these documents were undertaken as a preparation for a workshop on pollutant transfer by particles held by the Office of Marine Pollution Assessment, NOAA, in January 1982.

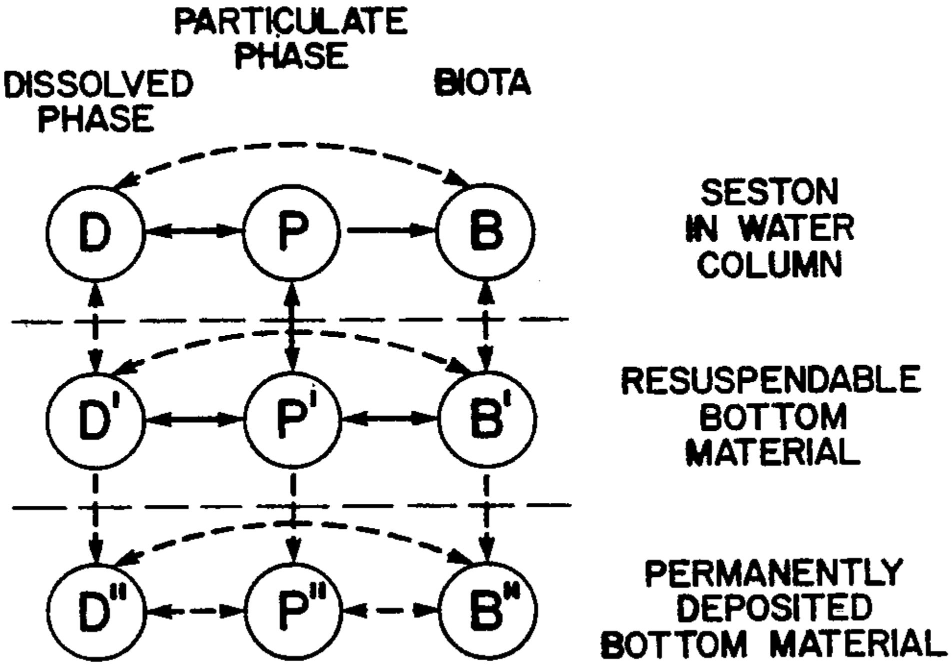

Figure 1. Pollutant states in the coastal ocean as defineed by phase and environment.

BRIEFING DOCUMENT 1
AN ECLECTIC LOOK AT FINE PARTICLES IN THE COASTAL OCEAN

CONTENTS

BRIEFING DOCUMENT 1

AN ECLECTIC LOOK AT FINE PARTICLES IN THE COASTAL OCEAN

J. Schubel

INTRODUCTION

The subject of this chapter is particles; particles in the Coastal Ocean. For the purposes of this discussion, we define the Coastal Ocean as extending roughly from the landward limit of sea salt penetration to the seaward edge of the continental shelf. The emphasis is on the inner part of this zone because that is where most of the particles--at least the inorganic particles--originate. It is also the part of the World Ocean upon which people have had their greatest impact on the inputs, distributions, accumulations and compositions of particulate matter; and it is the part of the World Ocean within which particles have their greatest effect upon the uses society wishes to make of the ocean.

For our purposes, a particle is any identifiable object having a definite geometric figure that occurs in nature. The stipulation that it be identifiable distinguishes it from the conceptual fluid particle of fluid dynamics. The stipulation that it occurs in nature means that we are concerned with the particle's natural mode of occurrence, particularly its size. Particles occur in nature in a wide range of sizes. We are concerned in this paper with those fine-grained particles whose primary mode of transport is as suspended load. These particles usually are silt and clay-sized particles, particles less than 62.5 m in size, although they may be sand-sized particles, particles 62.5 m to 2 mm in size, if the flow is turbulent or the particles are of low density.

The terms *suspended sediment*, *seston*, *suspended particulate matter*, *particulates*, *total suspended matter*, and *suspended solids* have been used more or less interchangeably to describe the total amount of solid particulate matter suspended within the liquid medium. *Turbidity* is a qualitative term used to describe the clarity of water.

Particles are added to the marine environment by rivers, by the atmosphere, by shore erosion, by biological activity, and by municipal and industrial discharges. The sources are thus external, internal, and marginal. The particles are organic, living and dead, and inorganic; naturally occurring and anthropogenic. People's activities have affected the flow of particles into the Coastal Ocean, their quantity, their composition, and their size distribution.

In this chapter we review some of the sources of fine particles to the Coastal Ocean and how people have affected those sources, the distributions of suspended sediment in the Coastal Ocean, some of the processes that control these distributions, and some of the effects of fine particles on environmental quality. Some research priorities are also outlined. This is not a comprehensive overview of particles in the Coastal Ocean. I have concentrated on some aspects of particles in the Coastal Ocean that are important and that deserve further attention.

SOME REPRESENTATIVE CONCENTRATIONS OF TOTAL SUSPENDED SOLIDS IN THE COASTAL OCEAN

Estuaries and Coastal Embayments

Concentrations of total suspended solids in estuaries and other coastal embayments typically range from a few milligrams per liter to a few hundreds of milligrams per liter, except in a few estuaries such as the Chang Jiang (Yangtze), the Huang Ho (Yellow) and the Ganges/Brahmaputra where concentrations often are in the thousands of milligrams per liter. The fraction accounted for by organic matter may range from near zero to more than 90% of the total concentration of suspended solids.

Meade (1972) and Drake (1976) provided summaries of "typical" concentrations of total suspended matter in estuaries; these and other data summarized in Table 1 are representative also of lagoons and other coastal embayments. In estuaries, the concentrations of total suspended solids are usually higher in the upper reaches than farther seaward, and are usually higher near the bottom than near the water surface, primarily because of the local resuspension of bottom sediments by tidal currents and wind waves. The variability is greatest near the bottom because of the alternative resuspension and deposition of sediments. Concentrations within the zone 1 m or so above the bottom may change by one or two orders of magnitude every few hours as a result of tidal scour and fill.

Most observations of the concentrations of suspended sediment in estuaries represent average, or typical, conditions. But in addition to these "normal" variations, marked fluctuations can result from catastrophic events such as floods and hurricanes. There are a number of excellent studies of the effects of floods on the sediment loads of rivers, but the only well-documented case study of the effects of a major flood on an estuarine system and its subsequent recovery is for Tropical Storm Agnes (June 1972) and the Chesapeake Bay (Davis 1977; Schubel 1974; Zabawa and Schubel 1974). During events, concentrations of total suspended sediment within the estuary may be increased several thousand-fold over those typical of average conditions; and the discharge to the ocean--even from large estuaries such as Chesapeake Bay--may be increased substantially (Schubel 1974; Schubel 1975).

Continental Shelf Waters

Concentrations of total suspended solids in continental shelf waters typically range from less than a tenth of a milligram per liter to a few milligrams per liter. In local areas off the mouth of major rivers such as the Huang Ho (Yellow) and Chang Jiang (Yangtze) concentrations may run as high as hundreds, or even thousands, of milligrams per liter. Concentrations are usually highest nearshore and decrease in an offshore direction. Within the water column, the concentration of suspended solids often shows a double maximum: one near the surface, the other near the bottom. Accumulations of organic matter along the pycnocline have been reported by a number of investigators. Except in nearshore areas and near the bottom, the organic fraciton is the major component, often accounting for more than 90% of the mass of total suspended solids.

Drake (1976) provided a useful summary of concentrations of suspended solids typical of continental shelf waters around the world. These data and others are summarized in Table 2. These concentrations are representative of typical, or average, conditions. During major floods of rivers that do not have large estuaries, concentrations of suspended sediment nearshore may exceed several thousand milligrams per liter (Drake et al. 1974; Chen Ji-Yu, personal communication, 1981). During hurricanes, and other periods of large wind waves, bottom sediments may be resuspended increasing concentrations of suspended sediment, particularly in shallow areas blanketed with fine-grained sediments. Concentrations produced by resuspension of bottom sediments normally fall to background levels within a day or two after passage of the storm (Rodolfo et al. 1971; Drake 1974; Meade et al. 1975), although they may persist for longer periods (Nelsen 1979).

Table 1. SUSPENDED SOLIDS STATISTICS FOR SELECTED ESTUARIES AND COASTAL WATERS

Estuary	Water Layer	Concentration (mg ℓ^{-1})	Composition (combustible organics)	Reference
Amazon	surface	20-200 at mouth with highest concentrations during high riverflow; 50-600 well upstream in river with highest concentrations during high riverflow	10-25%	Gibbs 1967, 1976, 1977; Milliman et al. 1975; Meade et al. 1979
Brahmaputra	near-bottom	100-500 at mouth		
	not specified	1170		Subrammanian and Dalavi 1978
Charleston Harbor	surface	32	28%	Federal Water Pollution Control Admin. 1966
	near-bottom	52	27%	
Chesapeake Bay	surface	10-100 in upper Bay and 1-5 in the lower Bay with highest concentrations during periods of high riverflow	20-90% (percent increases near mouth)	Schubel 1968; Schubel and Biggs 1969; Schubel et al. 1970
	near-bottom	10-500 at 1 m off bottom, with highest concentrations near periods of peak ebb and flood current speeds		
Columbia		8-40		Conomos 1969
Connecticut (upstream)	surface	2-100		Bohlen 1975
	bottom	2-100		
(mouth)	surface	8-100		
	bottom	10-200		
Congo		23		Gibbs 1967
Danube		350		Conway 1942

(Continued)

Table 1 (Continued)

Estuary	Water Layer	Concentration (mg ℓ$^{-1}$)	Composition (combustible organics)	Reference
Delaware Bay	surface	10-100	1-10%	Biggs et al. 1982
Ganges		1250		Subramanian and Dalavi 1978
Gironde	surface	200-1000		Allen et al. 1977
	bottom	1000-10,000		
Hudson		20-110 (31 average) with highest concentrations during high river flow	22%	Bokuniewicz et al. 1981; Olsen and Simpson 1981
Indus		68		Subramanian and Dalavi 1978
James	surface	22	29%	Brehmer and Haltiwanger 1966
	bottom	36	26%	
Long Island Sound	surface	4	40%	Riley 1959
(mouth)	surface	0.1-1.7		Benninger 1976
	bottom	0.4-1.9		
(eastern end)	surface	1-40		Bohlen 1975
	bottom	2.80		Bohlen 1975
Miramichi		0.5-100		Kranck 1981
Mississippi		250-670		Scrutan and Moore 1953; Conway 1942; Edwards et al. 1956
Narragansett	surface	1-5		Morton 1967
	bottom	1-5		
Pearl		200-300		Chen 1981 (pers. comm.)

Continued

Table 1 (Continued)

Estuary	Water Layer	Concentration (mg ℓ^{-1})	Composition (combustible organics)	Reference
Rappahannock	surface	20-40	27.6%	Nichols 1977
	mid-depth	20		
	bottom	40-80		
Rio de la Plata		16-514		Urien 1972; Strakhov 1967
Rio Grande		42,600		Livingstone 1963
San Francisco Bay	surface	15-20	3-30%	Conomos and Peterson 1977
	turbidity maximum	90		
St. Lawrence		10-230	10-40%	Gobeil et al. 1981; Silverberg and Sundby 1979; D'Anglejan and Smith 1973
Thames	surface	51-70	20-30%	Thames Survey Committee and the Water Pollution Research Lab 1964
	mid-depth	54-63		
	bottom	55-68		
Yangtze		500		Chen 1981 (pers. comm.)
Yellow		34,000		Chen 1981 (pers. comm.)
York	surface	10	35%	Patten et al. 1961, 1963, 1966
	bottom	35	21%	
Yukon		980		Strakhov 1967

Table 2. SUSPENDED PARTICULATES IN CONTINENTAL SHELF WATERS

Location	Depth	Concentration (mg ℓ^{-1})	Composition (combustible organics)	Reference
Argentina				
S. Argentine shelf	--	0.10-40.56	4.5-68%	Pierre and Siegel 1979
Brazil				
Off Amazon River				
Coastal waters salinity <10 $^{o}/oo$	--	>4	10-25%	Milliman et al. 1975
Brackish shelf waters		0.25-1.0	--	
Equatorial Atlantic Waters	--	0.10-0.25	50-80%	
China				
E. China Sea shelf to 50 km offshore	surface 1 m	260-1230	--	Yun and Wan unpubl.
Sierra Leone, Liberia				
W. African shelf	lower 20 m	(av.) 0.32	16-100%	McMaster et al. 1977
	upper 12 m	.0016-0.113		
Spanish Sahara				
W. African shelf	surface	0.25-1.0	75-100%	
	bottom	0.14	85%	Milliman 1977
United States				
East Coast				
Georges Bank	Feb.-Mar. surface	0.25-1.0	25-75%	Bothner et al. 1981
	near-bottom	0.25-1.0	25-50%	
	May surface	∿ 0.5	∿ 75%	
	near-bottom	0.25-1.0	50-75%	
	Aug. surface	0.25-0.50	75%	
	near-bottom	0.25-1.00	50-75%	
	Nov. surface	0.25-1.00	50-75%	
	near-bottom	0.1-4.2	25-75%	

Continued

Table 2 (Continued)

Location	Depth	Concentration (mg ℓ^{-1})	Composition (combustible organics)	Reference
Middle Atlantic Bight	surface 5-6 m	0.1-1.0 decreasing offshore	40-80%	Meade et al. 1975
	bottom 2-5 m	0.1-1.0 decreasing offshore	20-60%	
New York Bight	surface	0.1-0.2+	--	Biscaye and Olsen 1976
	bottom	0.05-0.6	--	
	bottom + 10 m	0.05-0.4	--	
New York Bight Apex	Sept. surface Oct.	0.3-3.2 decreasing offshore	30-50%	Drake 1977
	10 m	0.2-8.6	--	
	Nov. surface	0.7-4.8	--	
	10 m	0.6-12.1	--	
Off Hatteras Inlet	surface	1.4	41%	Manheim et al. 1970
Off Helana Is., SC	surface	2.4	24%	
Off Charleston, SC	surface	0.5	90%	
Shelf off Charleston	surface	0.4	58%	
Blake Plateau	subsurface	0.15-2.2	50-83%	
Cape Canaveral, FL	surface	0.25	--	Manheim et al. 1970
2 days after hurricane (1965)	surface	7.0	--	
Pacific Coast				
San Pedro, CA	bottom + 1 m	1-4	--	Karl 1980
Oregon	--	0.25-0.75 decreasing seaward	50-80%	McCave 1979

Continued

Table 2 (Continued)

Location	Depth	Concentration (mg ℓ^{-1})	Composition (combustible organics)	Reference
Alaska				
Norton Sound	surface and bottom nearly same in winter	1.3-8.4	--	Drake et al. 1979
	surface	0.7-1.5	15%	
	summer			
	lower 10 m	4.4	<5%	

TURBIDITY MAXIMA

A feature characteristic of estuaries, particularly of mixed estuaries, is the "turbidity maximum"--a zone in the upper reaches of the estuary in which the concentrations of suspended matter are higher than both those farther upstream in the river and those farther downstream in the estuary. The turbidity maximum is located near the upstream limit of sea salt penetration and tracks changes in this limit produced by alterations in river discharge. It migrates downstream during periods of high river discharge, and upstream during periods of low river discharge.

A number of mechanisms have been proposed to explain the formation and maintenance of these zones of apparently anomalously high concentrations of suspended matter and turbidity. These mechanisms include the flocculation of river-borne sediment (Luneburg 1939, Ippen 1966), the flocculation of river-borne sediment (Nelson 1959), and hydrodynamic process (e.g., Postma and Kalle 1955; Inglis and Allen 1957; Glangeaud 1938; Schubel 1968a; Nichols and Poor 1967; Allen 1973; Gallene 1974). Postma (1967) indicated that the strength of a turbidity maximum depends upon the strengths of the sediment sources at both ends--river and ocean--the settling velocities of the suspended sediment, and the strength of the estuarine circulation.

Studies of the Chesapeake Bay, Rappahannock, York, James, Thames, Elbe, Ems, Gironde, Savannah, San Joaquin/Sacramento, and Chang Jiang (Yangtze) estuaries, to select a few, have shown that the turbidity maximum in each of these estuaries is produced and sustained by the net non-tidal circulation and is located near the upstream limit of sea salt penetration in the lower layer. This limit corresponds to the "null zone," the region where the net upstream flow of the lower layer dissipates and upstream of which the residual flow is downstream at all depths.

The net non-tidal circulation leads to the formation of an effective "sediment trap" in the upper reaches of the estuary in the transition zone where the net non-tidal upstream flow of the lower layer dissipates until finally the net flow is downstream (seaward) at all depths. Many of the suspended particles that settle out of the seaward flowing upper layer into the lower layer are carried back upstream by its net non-tidal upstreamflow leading to an accumulation of sediment on the bottom and in the water column--the so-called turbidity maximum--near the head of the estuary.

Many of these particles are transported back into the upper layer by vertical mixing and the whole process is repeated many times before the particles are carried so far downstream that they ae not returned, or are deposited permanently.

Postma (1967) hypothesized that suspended particles within turbidity maxima should have a relatively narrow spectrum of particle sizes (settling velocities). Schubel (1968b, 1969, 1971a) pointed out that particles with settling velocities much greater than the mean vertical mixing velocity would be deposited, and once deposited, those particles with threshold velocities greater than the maximum current velocity would not be resuspended; others would be alternately resuspended and deposited. Particles with settling velocities much less than the mean vertical mixing velocity would be concentrated within the upper layer and would eventually be carried far downstream or out to sea by the net non-tidal seaward flow of the upper layer. Between these two "critical settling velocities" there would be a sub-set of particles which would be exchanged repeatedly between the upper and lower layers and which would be trapped effectively within the zone of the turbidity maximum. Schubel (1969) examined this hypothesis in the turbidity maximum of the upper Chesapeake Bay and demonstrated the effectiveness of the sorting mechanism.

Schubel (1969, 1971a) showed that the suspended particle population of the Chesapeake Bay's turbidity maximum is composed of two sub-populations; one, a natural background of suspended particles made up of particles in more or less continual suspension throughout the water column; the other, made up of particles alternately suspended and deposited by tidal scour and fill. Since the latter sub-population is superimposed upon the background sub-population, it cannot be observed directly. It must be determined by removing, by calculation, the background sub-population from the total particle population. Schubel (1971a) demonstrated that in the Chesapeake Bay's turbidity maximum the background sub-population of particles had a narrow, stable size distribution with a mean settling velocity of about 10^{-3} cm s^{-1}--the same order as the mean vertical mixing velocity. The sub-population of particles alternately suspended and deposited had a much broader, less stable particle size distribution. The mean settling velocity of these particles at 1.5 m above the bottom ranged from about 1×10^{-3} cm s^{-1} near times of slack water to more than 1×10^{-2} cm s^{-1} near times of maximum ebb and flood currents. Schubel (1971a) demonstrated through actual measurements that the range in the size distribution of particles suspended within the turbidity maxima varies as the estuarine dynamics change. Festa and Hansen's (1978) two-dimensional numerical model of turbidity maxima elucidated the connection between particle size (settling velocity) and estuarine circulation.

Models of suspended sediment transport and turbidity maxima have been developed by Ariathurai and Krone (1976) and Festa and Hansen (1978), and have been reviewed by Owen (1977). Festa and Hansen's (1978) steady-state, two-dimensional numerical model of turbidity maxima in partially mixed estuaries supports the hypothesis that estuarine dynamics are primarily responsible for their occurrence. Their model showed that the magnitude and location of the turbidity maximum depends upon the settling velocity of the sediment, the amount of sediment introduced by the river and the ocean, and the strength of the estuarine circulation.

SOURCES OF INORGANIC PARTICLES TO THE COASTAL OCEAN

Compared with the total amount of inorganic material discharged by rivers to the Coastal Ocean, the amounts introduced by the atmosphere, by shore erosion, and by industrial activities are relatively small. The latter sources may dominate locally, but their collective contribution to the total mass of new inorganic material added to the Coastal Ocean pales in comparison with that of rivers. In this section, we concentrate on the additions of fluvial sediments to the Coastal Ocean and on the partitioning of these sediments between estuaries and open coastal waters.

Fluvial Suspended Sediment Input to the Marine Environment

There are few independent estimates of the total discharge of suspended sediment by the world's rivers to the marine environment, and all these estimates are of the discharge to the coastal zone and not to the "ocean". Estimates range from 58 billion tons per year (Fournier 1960) to 13 billion tons per year with most estimates falling between 20 and 30 billion tons (Milliman 1980).

The most frequently quoted world summary is that of Holeman (1968) who estimated that the total discharge of suspended sediment by the world's rivers is about 18 billion tons per year, Table 3. More recently, Milliman (1980) put the total at 16 billion tons, but cautioned that his estimate could be off by as much as 50 percent.

Milliman (1980) pointed out a number of problems associated with such estimates.

1. Rivers with highest sediment loads (e.g., the Huang Ho, Yangtze, Ganges/Brahmaputra, Indus, and Amazon) are in developing countries and are poorly documented. Estimates of annual discharges by different investigators often vary by more than a factor of two. Often, measurements are made during dry seasons when river discharge and sediment loads are low. Improper sampling methods and techniques can lead to gross errors in estimating sediment concentrations and sediment discharges.

2. In the absence of adequate data, investigators often have used rating curves to estimate suspended sediment concentrations for different river discharges. Errors of at least 50% can be expected in sediment discharges based on rating curves.

Table 3a. Holeman's (1968) "Summary of Measured Annual Sediment Yields of Rivers to Oceans (tributaries deleted)". [Holeman's data have been converted to metric units].

Continent	Measured Drainage Area, km^2	Annual Suspended Sediment Discharge metric tons (1000 tons)	Tons km^{-2}
North America	6,383,416	547,899	85.8
South America	9,894,720	552,863	56.0
Africa	8,149,870	196,191	24.5
Australia	1,073,836	42,955	40.3
Europe	3,515,541	110,620	31.5
Asia	10,911,188	5,819,205	535.9
Total	39,928,571	7,269,733	Average 182 tons km^{-2}

Table 3b. Holeman's (1968) "Total Sediment Yield to Oceans Extrapolated from Above Data." [Holeman's data have been converted to metric units].

Continent	Total Area Draining to Oceans, km^2	Annual Suspended Sediment Discharge metric tons km^{-2}	10^9 metric tons
North America	20,719,920	85.8	1.78
South America	19,424,925	56.0	1.09
Africa	19,942,923	24.5	0.49
Australia	5,179,980	40.3	0.21
Europe	9,323,964	31.5	0.29
Asia	26,935,896	535.9	14.43
Total	101,527,608		18.29

Total suspended sediment discharge to oceans is about a billion metric tons a year.

3. In most estimates, bed load is ignored completely, even though in some rivers it may be of great importance.

4. Most measurements are made during average or typical periods. These "average" values of sediment discharge do not reflect catastrophic events such as extreme floods.

5. Average sediment loads of many rivers have been changed by man's activities.

6. A substantial portion of sediment carried by many rivers is stored temporarily along the river as channel deposits or permanently in levees or flood-plain deposits.

In his summary, Milliman (1980) pointed out that in spite of the paucity of data several conclusions can be drawn regarding the transfer of fluvial suspended sediment to the "ocean":

(1) Most major rivers have average suspended sediment concentrations between 100 and 1000 mg l^{-1}. Together the world's major rivers carry about 8 billion tons of sediment annually, nearly 50% of which comes from two Asian rivers--the Huang Ho (Yellow) and Ganges/Brahmaputra. Other Asian rivers including the Indus, Chang Jiang (Yangtze), Red and Mekong bring the figure to 75% of the total for the major rivers. In contrast, North American and European Rivers collectively contribute less than 7% of the total discharge of the world's major rivers.

(2) Rivers draining humid areas (e.g., Ganges/Brahmaputra) and desert areas (e.g., Colorado and Orange) tend to have very high suspended sediment concentrations; rivers draining low-lying areas, regardless of the latitude, have low concentrations. Lowest concentrations of suspended sediment are observed in rivers that empty into lakes before reaching the ocean (e.g., St. Lawrence and Congo).

(3) Perhaps a reasonable figure for the total discharge of suspended sedimentary rivers is 16 billion tons per year, assuming that small rivers collectively transport about the same as major rivers. The error in this estimate could, however, easily be 50%.

Milliman and Meade (in press) have prepared a new world-wide summary of the discharge of fluvial sediment to the coastal zone incorporating new data that have not been used in previous summaries. Meade (personal communication, November 1981) believes that the contribution of suspended sediment from the smaller rivers may have been underestimated substantially, particularly for those bordering the Pacific.

If the quantities of suspended particulates discharged by rivers are poorly known, even less is known about the composition of these materials. The composition of suspended particulate load of rivers is less well known than that of the dissolved load. According to a study of 20 major rivers (Martin and Meybeck 1978; 1979) the composition of fluvial suspended particulate matter depends on the ratio of mechanical erosion to chemical denudation, and on the weathering types. In temperate and arctic zones the composition of fluvial suspended matter reflects closely the composition of average fresh rocks, consisting mainly of rock debris and poorly weathered soil particles. In tropical zones, fluvial suspended matter originates mainly from highly developed soils and is strongly depleted in Ca, Na, and Mg and enriched in Al and Fe. For most rivers one is fortunate to know the percentage of the total load accounted for by combustible organic matter, let alone the mineralogy of the inorganic fraction and associated contaminant burdens.

Partitioning of Fluvial Sediments between Estuaries and Open Coastal Waters

There are few data on the partitioning of fluvial suspended sediment discharges between estuaries and coastal marshes on the one hand and the open continental margin and the deep sea floor on the other. Most of the estimates of partitioning that are available are for rivers with relatively small sediment discharges and large estuaries. Drake (1976) estimated that less than 10% of modern river-borne suspended sediment reaches the deep sea (basin and ocean ridge systems) and that most inorganic sediment is deposited on continental margins (including shelf, slope, and rise), or in marginal seas. There probably is general agreement that little fluvial sediment reaches the deep sea, but less agreement on the partitioning between the coastal zone and the shelf.

Nearly all of the sediment that reaches the Atlantic coastal zone of the United States is trapped in estuaries and coastal marshes (Meade 1969; 1972). Budget calculations indicate that virtually all of the fluvial sediment discharged into large east coast estuaries such as Long Island Sound (Bokuniewicz *et al.*, 1976) and Chesapeake Bay (Schubel and Carter 1976) must be deposited within their estuaries. In addition, sediments from the inner continental shelf and the ocean shoreline are carried into the lower reaches of estuaries along the east coast of the United States (Firek *et al*. 1977; Hathaway 1972; Meade 1969, 1972; Van Nieuwenhuise *et al*. 1978; Schubel and Carter 1976).

Along the southern Atlantic seaboard where the major rivers debouch into the ocean without flowing through large estuaries the identifiable river-borne sediment is restricted to a narrow zone near the coast (Bigham 1973; Meade 1980; Milliman *et al*. 1972). According to Meade (1972) the principal sink for river sediment in this area are the extensive marshes. Probably less than 5% of all river sediment discharged into tidal waters of the U. S. Atlantic seaboard is deposited on the floor of the continental shelf or the deep sea. The fate of suspended sediment discharged by other rivers with major estuaries is similar.

Most of the fluvial sediment discharged by the Parana-Uruguay River system which flows into the large estuary of the Rio de la Plata is entrapped within the estuary (Urien 1972). Duinker and Nolting (1976) reported tha 50% of the suspended sediment discharged by the Rhine River is deposited in the Wadden Sea, and Bewers and Yeats (1977) estimated that 93%

of the suspended sediment entering the Gulf of St. Lawrence is deposited within the marginal sea.

These rivers combined with all the world's other small to medium-sized rivers collectively account for only a relatively small percentage (<10%) of the world's total fluvial discharge of suspended sediment to the coastal zone. The bulk of the total (>75%) comes from a few large rivers that no longer have significant estuaries. The partitioning of the sediment discharged by these large rivers between their estuaries and the adjacent shelf is much different from partitioning by rivers that still have large estuaries. Probably more than 30% of the suspended sediment discharged by the Chang Jiang (Yangtze), for example, is deposited on the continental shelf (Chen Ji-Yu, personal communication, 1981), and more than 50% (perhaps as much as 90%) of the suspended sediment discharged by the Amazon is deposited on the adjacent continental margin (R. Meade, personal communication, 1981).

Data from the Mississippi indicate that more than 75% of its suspended sediment load near the river's mouth escapes the estuary and is deposited on the delta and in the Gulf of Mexico. For the Huang Ho (Yellow) River, more than 70% of its sediment load reaches the Yellow Sea (Chen Ji-Yu, personal communication, 1981).

Clearly, large estuaries are effective "filters" for removing suspended particles discharged into them by their tributary rivers. As the volume of an estuary decreases, its filtering efficiency for particulate matter decreases also, and at a more rapid rate than its volume. While all modern estuaries were formed at approximately the same time, the stages of filling vary markedly. Estuaries of rivers with large sediment discharges such as the Huang Ho (Yellow), Chang Jiang (Yangtze), and Atchafalaya all have been largely filled with sediments and have low filtering efficiencies relative to estuaries of rivers with smaller sediment inputs such as Chesapeake Bay, Long Island Sound, and the Rio de la Plata.

In summary, the best estimates of the total discharge of suspended sediment to the coastal zone place the value at 16 to 18 billion tons per year. New data may increase this estimate (Meade, personal communication, 1981). There are no world-wide estimates on what fraction of this total escapes estuaries and coastal marshes to reach the open shelf and slope and the deep sea floor. The author's own Mark Twain[1] estimate places the mass that escapes estuaries between 6 and 10 billion tons per year and rising. One would expect the fraction of fluvial sediment that reaches the sea to increase as estuaries are filled in.

MAN'S ACTIVITIES AND SEDIMENT INPUTS TO THE COASTAL OCEAN

Although sediment in the Coastal Ocean comes from many sources--including erosion of the margins and of the sea floor, and from biological productivity--the sources most affected by man are the rivers that carry sediment from upland areas into estuaries. This discussion focuses on the sediment loads of rivers which are increased by activities such as farming, mining, and urbanization, and which are decreased by activities such as construction of reservoirs and other protective works. A brief discussion is also presented of how an estuarine sedimentation pattern was affected by changing the freshwater input to that estuary.

People's activities have affected not only the amounts of suspended particulate matter added to the Coastal Ocean, but the size distribution and composition of these materials as well. There has been a shift to smaller particles and an increase in the amount of organic matter (Schubel 1976).

Man's Activities That Increase River Sediment Loads

Soil erosion is the ultimate source of most fluvial sediment. Ever since the first European settlers landed in North America, man has affected the amount of sediment in streams draining this region. The influence of man on sedimentation is especially well-documented in the Chesapeake Bay region, where clearing of forests and wasteful farming practices (especially those used in raising tobacco) contributed enormous loads of sediment to the rivers. Clear streams became muddy and once relatively deep harbors at the heads of a number of the tributaries were filled rapidly with sediment (Gottschalk 1945). The Potomac River, whose waters were already somewhat turbid but which were still suitable for municipal use in

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[1] Mark Twain once pointed out that "There is something fascinating about science. One gets such a wholesome return of conjecture out of such a trifling investment of fact."

1853, had become so muddy by 1905 that the city of Washington had to install its first filtration plant. A comparison of the 1792 and 1947 shorelines of the upper Potomac shows that large areas of the Potomac near Washington had been filled with sediments stripped from farmland farther upstream. The Lincoln and Jefferson Memorials now stand on what was described in 1711 as a harbor suitable for great merchant vessels. Even today, an average of about 2 million m^3 of sediment is deposited every year near the head of tide in the Potomac; not all of this sediment is the result of agriculture, as we shall see. There are other former seaport towns on the western shore of Chesapeake Bay where decaying docking facilities now are separated from navigable water by several kilometers of sediment-filled lowland.

Streams that drain modern day farmlands in many of the mid-Atlantic states carry about 10 times as much sediment as streams that drain equivalent areas of forest land. And this relationship is by no means unique. In the Coastal Plain of northern Mississippi, sediment yields from cultivated lands are 10 to 100 times the yields from equivalent areas of forested lands (Gottschalk 1945; Trimble 1974). In two other areas where studies have been made--the Tobacco River Valley of Michigan and the Willamette Valley of Oregon--streams draining farmland carry two to four times as much sediment as streams draining equal areas of forested land.

Mining is another activity that has increased the sediment loads of some rivers that flow into estuaries. San Francisco Bay, for example, contains nearly a billion cubic meters of sediment washed from the Sierra Nevada during the approximately 30 years of intensive hydraulic mining for gold in that Range. Even after the hydraulic processing was stopped in 1884, the mining debris continued to choke for many decades the valleys of the Sacramento River and some of its tributaries. Gradually, over the years, the debris was moved downriver to be deposited more permanently in the marshes and shallow areas surrounding San Francisco Bay. The mining debris released in only three decades is more than the total sediment from all other sources (including farmland) that the Sacramento River has carried in the twelve-and-a-half decades since 1850 (Gilbert 1917). It has been shown that this sediment had an important effect on San Francisco Bay; the tidal prism was decreased, and the flushing regime changed significantly.

The high soil erosion rates prevalent in many unglaciated areas during the 19th and early 20th centuries now have been reduced by soil conservation practices and by reversion of uplands to pastures and woodlands (Meade 1980). But the effects of the earlier higher erosion rates are still being experienced strongly downstream in the lower reaches of rivers and partiularly in their estuaries. "Much of the soil material that was eroded off the uplands since 1700 is stored on hillslopes and on the floor of stream valleys" (Meade 1980). Many alluvial valleys in the southern and middle-Atlantic Piedmont of the United States are lined with a layer of sediment a meter or more in thickness that has accumulated since European settlers arrived (Costa 1975). Since the time when upland erosion was curtailed by appropriate soil conservation practices, sediment has been supplied to streams from intermediate storage sites between the uplands and the river (Meade 1980; Meade and Trimble 1974; Trimble 1977). Trimble (1975) has estimated that more than 90% of the sediment eroded off the uplands of the southern Piedmont of the United States since 1700 still remains above the Fall line--the boundary between the Piedmont and the Atlantic Coastal Plain. The implication is that soil material removed during an erosional episode can be expected to be released from intermediate storage sites over a period of decades to centuries and move downstream as a wave.

In glaciated areas, the influence of man on soil erosion rates has been less marked than in unglaciated areas (Gordon 1979; Meade 1980; Williams and George 1968). In a study of the Connecticut River valley, Gordon (1979) found little evidence that sediment yields had changed since pre-colonial days.

Urbanization is the most recent of man's activities to contribute large amounts of sediment to streams. Sediment loads derived from land being cleared or filled for the building of houses, roads, and other facilities are best documented in the area between Washington, D.C., and Baltimore, Md. During periods when housing development, shopping centers, and highways are being built, the soil is disturbed and left exposed to wind and rain. The concentration of sediment in storm runoff from construction sites often is 100 to 1,000 times what it would be if the soil had been left in its natural vegetated state. Even though the soil is left exposed to erosion of this intensity for only a short time--a few years at most--the amount of land cleared for new housing and ancillary uses in the Washington-Baltimore area was so great in recent years the contribution of sediment has been significantly large. Harold Guy of the U.S. Geological Survey has estimated that the Potomac River receives about a million tons of sediment per year from streams that drain the metropolitan Washington area. This is about the same amount of sediment that the Potomac River brings into the Washington areas from all its other upland sources.

Another human activity that increases the sedimentation rates of estuaries is the discharge of dissolved phosphorus, nitrogen, and other plant nutrients into rivers and estuaries. Municipal sewage effluents, including effluents that have received secondary treatment--the highest degree of conventional treatment--contain high concentrations of nutrients. In some areas, agricultural runoff from fertilized croplands and animal feedlots also contributes nutrients to river waters and estuaries. These nutrients promote the growth of diatoms and other microscopic plants (phytoplankton) both in the rivers and in the estuaries that the rivers flow into. The mineral structures formed by many of these organisms persist after the organisms die and become part of the sediment loads of the rivers and the sedimentary deposits of the estuaries. The Army Corps of Engineers estimates, for example, that the diatom frustules produced in the Delaware River and Delaware Bay contribute about the same amount of sediment (1½ million tons per year) to the Delaware estuary as all other upland river sources. The effects of nutrient loading from municipal wastes on primary prouctivity are readily observable in the Potomac estuary, in Baltimore Harbor and the Back River estuary (Maryland), in Raritan Bay, in the Arthur Kill estuary, in the Hudson estuary, in the Delaware estuary, in San Francisco Bay, and in many other estuaries around the country. Stimulation of plant growth by nutrient-enriched runoff from agricultural areas is apparent in the upper Chesapeake Bay, the estuary of the Susquehanna River.

Man's Activities That Decrease River Sediment Loads

Reservoirs probably cause the most significant interruptions in the natural movement of sediment to estuaries by rivers. Reservoirs are built on rivers for a number of purposes: for hydroelectric power, for flood control, for water supply, and for recreation. Regardless of their purpose, reservoirs share in common the ability to trap sediment (Schubel and Meade

1977). Even small reservoirs can trap significant proportions of river sediment. For example, a reservoir that can hold only one percent of the annual inflow of river water is capable of trapping nearly half the river's total sediment load. A reservoir whose capacity is 10% of the annual river water inflow can trap about 85% of the incoming sediment (Meade 1976; Meade and Trimble 1974). Although a river will tend to erode its own bed downstream of a reservoir to partly compensate for sediment it has lost, the net effect of the reservoir is to decrease the overall amount of sediment carried by the river. In the larger river basins of Georgia and the Carolinas, the sediment loads delivered to the estuaries are now something like one-third of what they were about 1910, mainly because of the large number of reservoirs that have been built since then for hydroelectric power and, to a lesser extent, for flood control (Schubel and Meade 1977).

The trapping, however, cannot always be considered permanent, not even on time scales smaller than the life span of the reservoir. The sediment held behind some dams can be mobilized by extreme flood events (Meade 1980). Flooding of the Susquehanna River in Pennsylvania and Maryland following passage of Tropical Storm Agnes in June 1972 purged 10-20 years' accumulation of sediment from reservoirs of the lower river (Schubel 1974; Zabawa and Schubel 1974; Gross et al. 1978).

On some rivers, settling basins and reservoirs have been built specifically as sediment traps to improve the quality of water farther downstream. In 1951, three desilting basins were constructed on the Schuylkill River of Pennsylvania to remove the excessive sediment that resulted from anthracite coal mining in the upper river basin. The basins are dredged every few years, and the dredged material is placed far enough from the river to be out of reach of floods. As a result of these basins, the sediment load carried by the Schuylkill into the Delaware estuary has been reduced from nearly a million tons per year to about 200,000 tons per year. Return of cultivated lands to forests can significantly reduce sediment yields. In the last 50 years, the average suspended load of South African rivers has decreased by 50% largely because of the stabilization of river banks by introduced vegetation (Rooseboom 1978).

Net Effect of Man's Activities on Sources of Sediment

The net effect of man's activities no doubt has been an increase in the sediment supplied to most coastal marine environments, but we cannot say how much. Although reservoirs and other controls have reduced the sediment in rivers in recent years, they have only partly offset the influences that caused the increases in the first place.

Added to this is the fact that sediment takes decades to move through a river system. Much of the sediments released by past mistakes--such as poor mining practices and poor soil conservation practices associated with agriculture--are still in the river valleys in transit storage between their sources and the estuaries. Even if the active supply of sediment to rivers were completely checked today, many decades would pass before the sediment loads woud drop to their natural levels.

The fight against erosion has been more successful in developed countries than in developing countries because of better regulation of land use. But deterioration of water quality in coastal areas is a much more serious problem in developed--industrialized--countries than in most developing countries.

Man's Activities That Alter Estuarine Sedimentation Patterns

Man can alter dramatically the sedimentation patterns in an estuary by altering its estuarine circulation pattern. This can be achieved by changing its freshwater input or the geometry of its basin. The classic example of the effects of changing the freshwater input to an estuary is Charleston Harbor (Schubel 1971b; Kjerfve 1976). Prior to about 1940 the total freshwater input to Charleston Harbor was small ($\sim 3\ m^3\ s^{-1}$) and the estuarine circulation pattern was somewhere between that of a well-mixed (Type C) and a sectionally-homogeneous (Type D) estuary. There was a slow net seaward transport of water and finer-grained suspended sediment at all depths., and dredging requirements were small ($\approx 60{,}000\ m^3\ yr^{-1}$). In 1941 the freshwater inflow to the Harbor was increased significantly by the diversion of the Santee River into the Cooper River which flows into the Harbor. Freshwater input increased to about 425 $m^3\ s^{-1}$--nearly a 150-fold increase. In response to the increased freshwater inflow, the circulation in the Harbor was shifted to that of a partially mixed estuary with a characteristic two-layered flow pattern. There was a slow net upstream movement of water and fine-grained sediment in the lower layer. Dredging requirements jumped to 1.8 x 10^6 m^3 yr^{-1}. The increased input of suspended sediment (a fourfold increase) accounted for only a small fraction of the 30-fold increase in sedimentation in the upper reaches of the Harbor. The bulk of the shoaling was caused by the shift in the circulation pattern whcih produced a null zone and a turbidity maximum within the Harbor.

PARTICLE SIZE--AN IMPORTANT AND OFTEN ABUSED AND MISUSED MEASURE

One of the most important physical properties of a particle is its size. The size of a particle may be defined as any measure characteristic of the fineness of its subdivision, or as the representative dimension that best describes the degree of comminution of the particle.

The choice of a measure that best describes the size of a particle, particularly a fine-grained particle, is a vexing question. Measures are not limited to those with dimensions of length. Measures with dimensions of volume, velocity, and area are used, although the results are usually reported as "equivalent lengths."

The measure most commonly chosen is the "diameter" but the definitions of diameter are myriad. The diameter of a particle may be any straight line drawn through its center of mass and terminating at its boundaries. The term diameter is defined unequivocally only for spheres and circles. For these shapes, and only for these, are the concepts of "diameter" and "size" equivalent. For any irregular particle, there is an infinity of diameters whose distribution is continuous between some upper and lower bounds. If the "diameter" is to be a meaningful measure of the size of an irregular particle, it must be defined as some one of the possible statistics associated with the diameter distribution of that particle. The number and variety of statistical measures that might be constructed are strictly unlimited. A few that have obvious appeal as being computationally simple are geometric mean, the harmonic mean, and the arithmetic mean. At the simplest, the labor required to accumulate the diameter data for a particle directly and to calculate the statistical measure is inordinate. Attempts to size a sub-population of sedimentary particles--a sample--by these definitions have been reduced to triviality by the inordinately small sample size forced on the investigator. The only practical solution is to construct "equivalent diameters." Indeed, if one uses a method of size analysis other than the microscopic method, one has no choice in the matter.

Since this is the case, investigators should be careful to select a method of particle size analysis that measures the property related to particle size that is most important to the question being investigated, that is, a method that deals in the appropriate currency. All too frequently this is not the rationale used to select the method to determine particle size distributions of fine-grained sediments. Often a method is selected because the equipment is available readily, or the investigator has used it in the past, or it generates a lot of data with little thought or work. Useful reviews of the methods for determining the particle size distribution of fine-grained sediments have been provided by Swift *et al.* (1972) and McCave (1979).

McCave (1979) points out that the usual reasons for determining particle size distributions of sediments are (1) studies of sediment variations in relation to tidal dynamics and sediment budgets, (2) studies of particle dynamics--aggregation, disaggregation, flocculation, etc., (3) sediment tracing and provenance determination, and (4) determination of suspended organisms--changes in their numbers and population size characteristics. For any research on suspended sediment dynamics the most useful parameter is the *in situ* settling velocity distribution, but this is determined rarely. Research on dynamics of particle interaction and on the interactions of organisms with particles should involve *at least* some direct measurements of the particles being studied or measurements of images of those particles as well as measurements of the *in situ* settling velocity distribution. Research on tracing of fine-grained sediments requires a combination of techniques to assess the *in situ* size distribution (settling velocity distribution) and the size distribution (settling velocity distribution) of the primary--disagglomerated--particles.

Research on changes in the composition and size distribution of population of suspended organisms can be done best by a combination of electronic techniques that provide rapid determinations of the number and volume size distributions with visual observations.

There are surprisingly few studies in which size distributions of suspended particles have been related to physical processes. Some notable exceptions include the studies of Postma (1961) in the Wadden Sea, Allersma _et al_. (1967) in the Chao Phya, Schubel (1968b, 1969, 1971b) in Chesapeake Bay, Swift and Pirie (1970) in the Gulf of San Miguel, Owen (1971) in the Thames, Nelsen _et al_. (1978) and Nelsen (1981) in the New York Bight Apex, and Kitchen _et al_. (1975) off the Oregon coast.

PARTICLE AGGLOMERATION

Fine particles occur in the Coastal Ocean as individual units--primary particles-- and as composite particles--aggregates and agglomerates (Figs. 1-7). Aggregates and agglomerates are alike in being composite, but they differ in the nature of the forces that bind their components and in the strengths of those forces. Aggregates are bound tightly by intermolecular, intramolecular, or by atomic cohesive forces. They are stable under high speed mixing, ultrasonics, and indeed, under all customary handling and dispersion techniques. Agglomerates are bound by relatively weak forces including those arising from electrostatic fields, surface tension, and sticky organic matter. Because agglomerates are held together weakly, investigators interested in determining their _in situ_ size distributions must exercise great care during samping and analysis to ensure that agglomerates are neither formed nor destroyed. This continues to be a problem.

While the larges fraction of the total _number_ of suspended particles in the Coastal Ocean probably is accounted for by individual--primary--particles, the bulk of the total _volume_ and _mass_ of suspended particles probably is accounted for by composite particles. This is certainly true for deposited fine particles. Schubel (1971a) found that individual particles accounted for more than 90% of the total number of suspended particles in water samples from upper Chesapeake Bay, but that composite particles accounted for more than 90% of the total volume of suspended particles in these samples. Drake (1978) reported similar findings for the New York Bight. Deuser _et al_. (1981) reported that 85 to 90% of suspended particles in the ocean are primary particles of biogenic origin.

Figure 1. Photomicrograph of suspended matter from upper Chesapeake Bay collected on a Millipore filter.

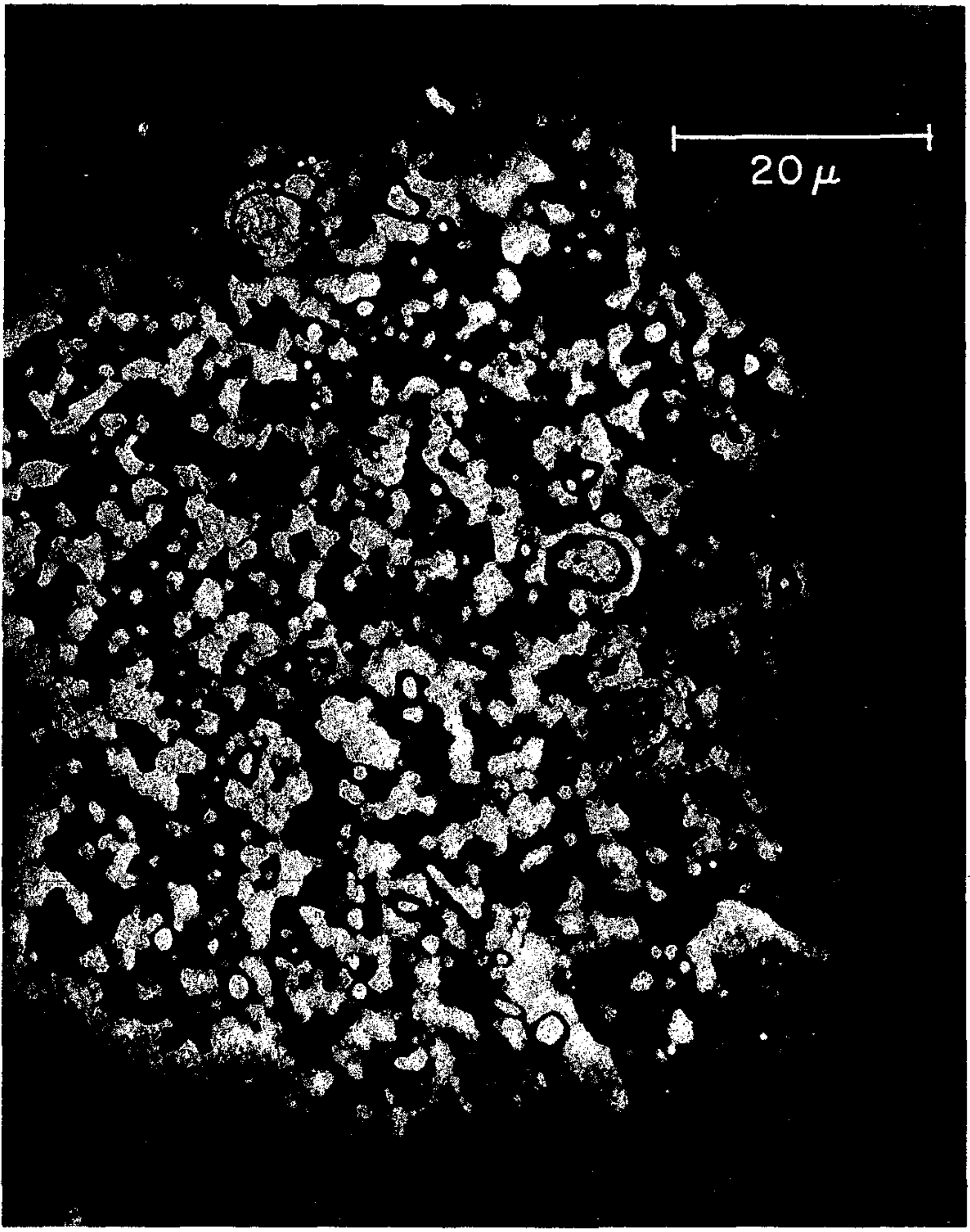

Figure 2. Photomicrograph of suspended matter from Chesapeake Bay collected on a Millipore filter.

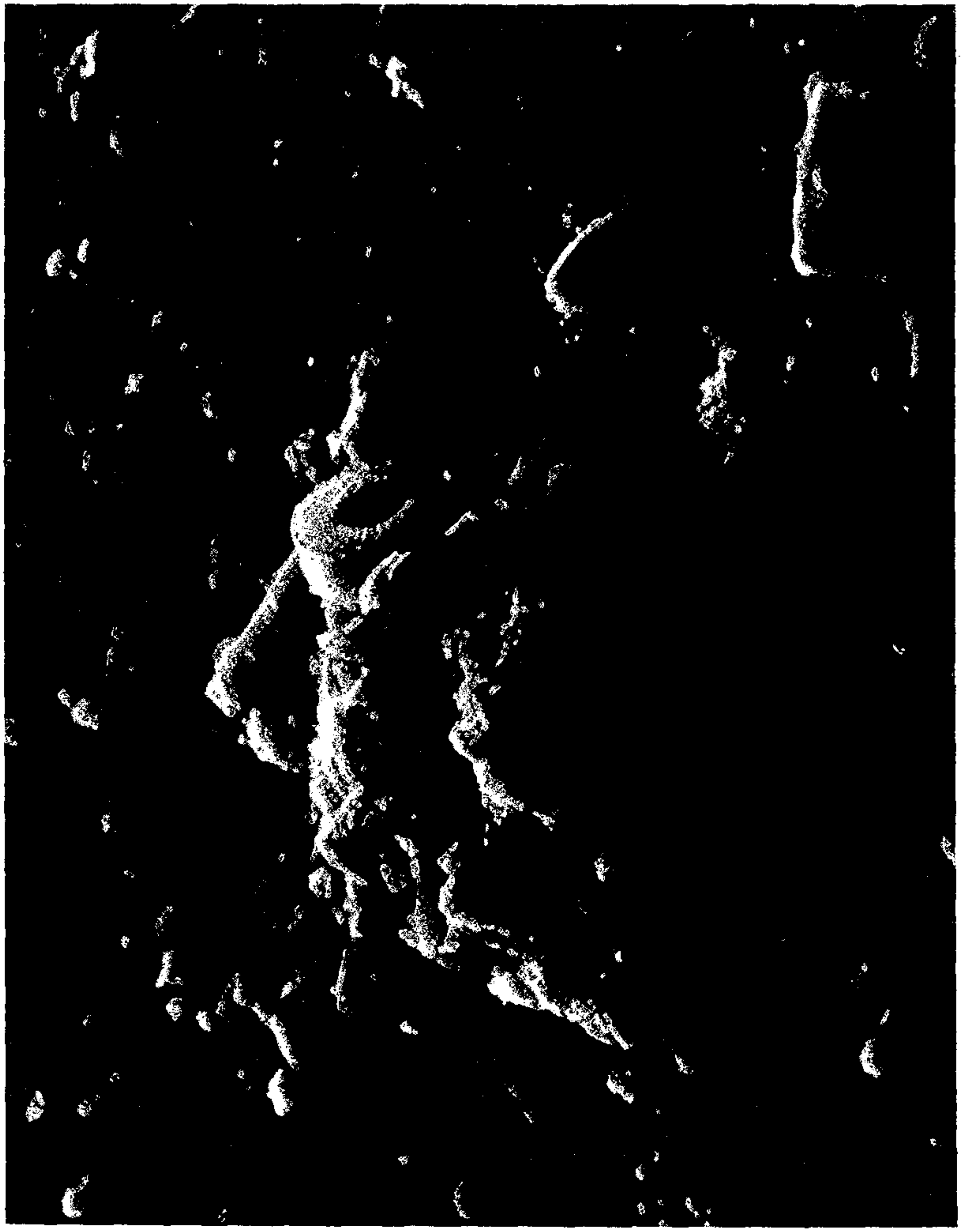

Figure 3. Scanning Electron Micrograph of suspended matter from upper Chesapeake Bay. Magnification about 4000x.

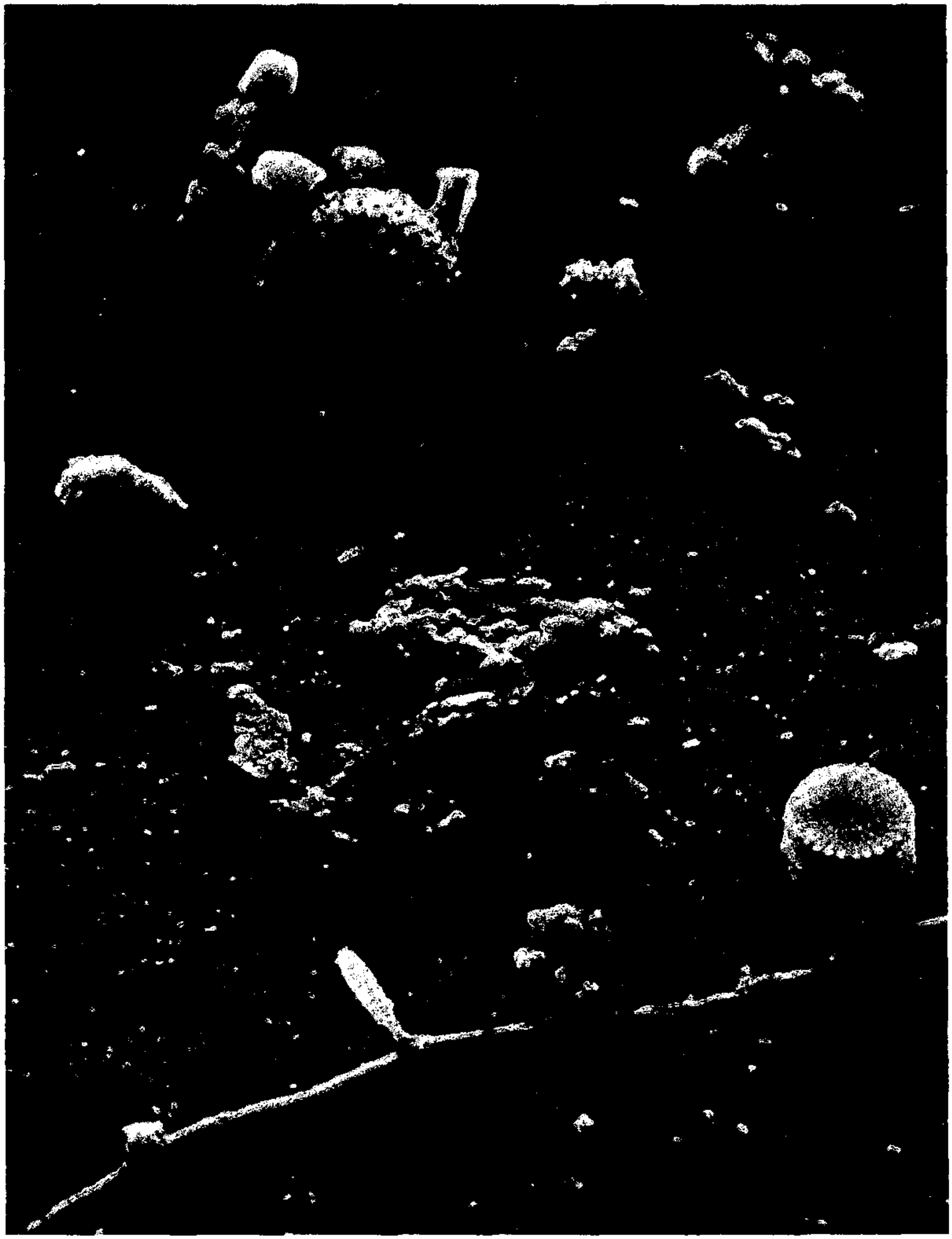

Figure 4. Scanning Electron Micrograph of suspended matter from Chesapeake Bay. Magnification ábout 5000x.

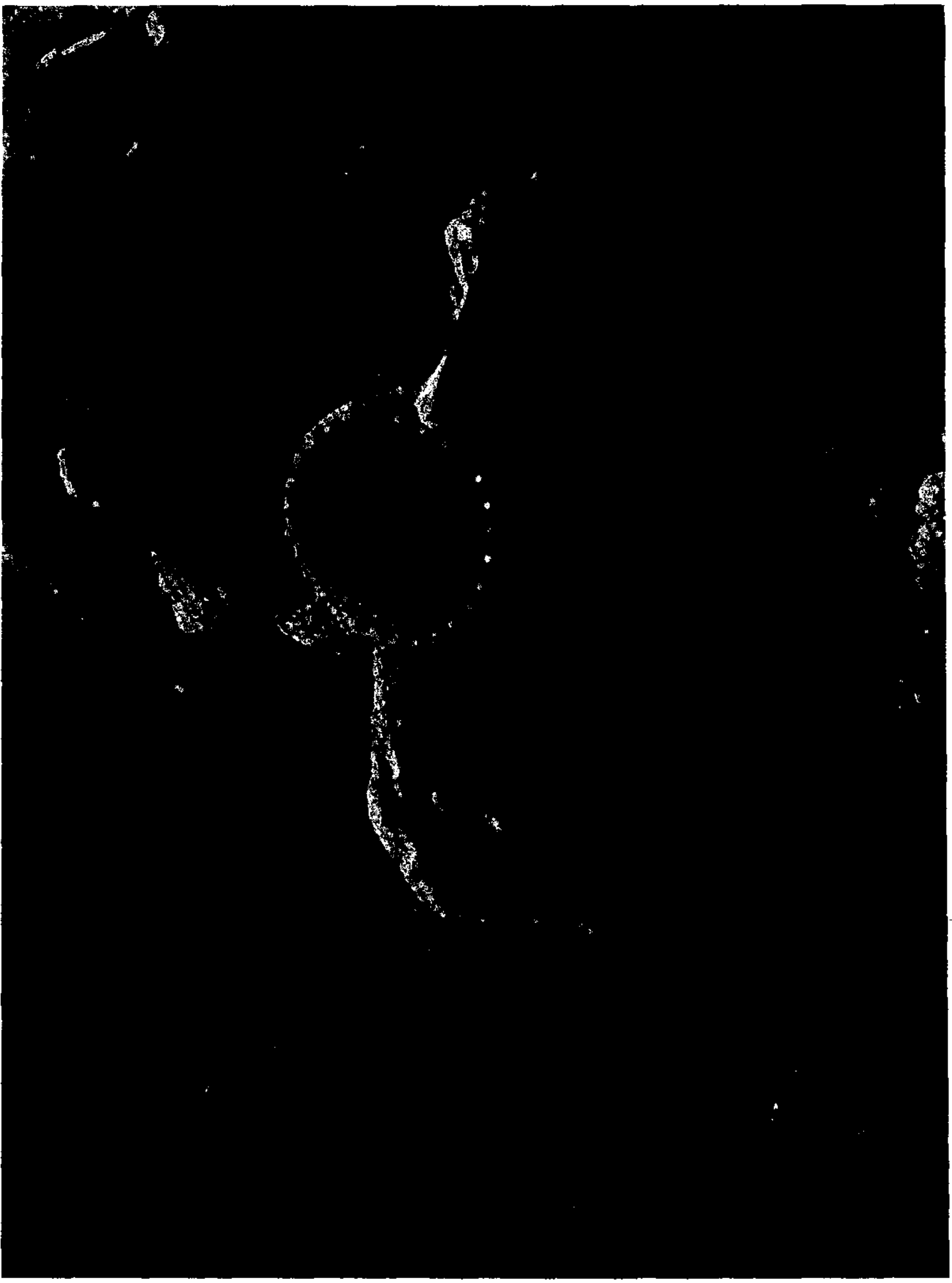

Figure 5. Scanning Electron Micrograph of suspended matter from Chesapeake Bay. Magnification about 4000x.

Figure 6. Photomicrograph of copepod and fecal pellet.

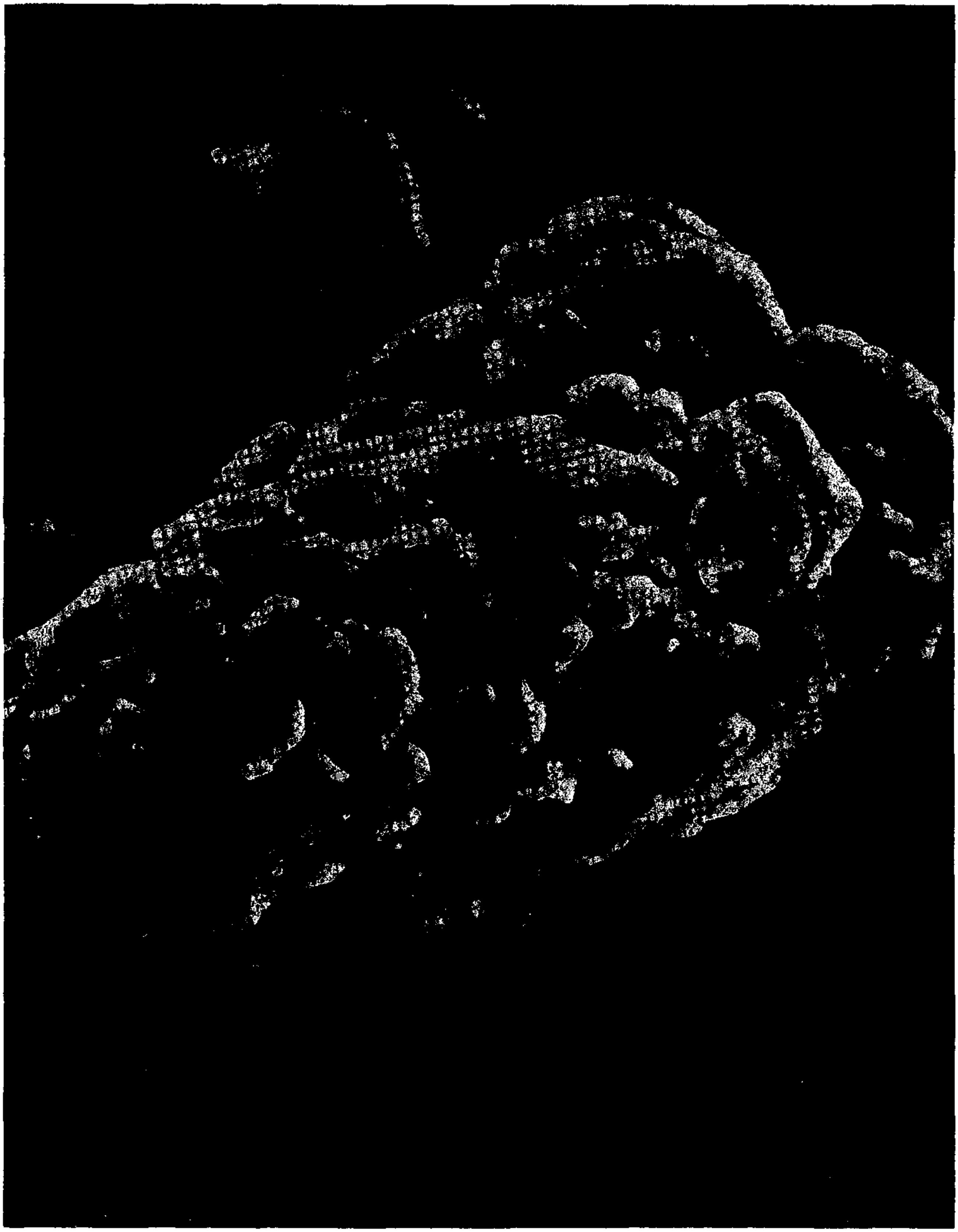

Figure 7. Scanning Electron Micrograph of well-formed fecal pellet collected from waters of Chesapeake Bay. Magnification about 3900x.

Natural particles may be agglomerated by electrochemical flocculation, by dissolved organic compounds, and by organisms. In this section we review briefly the evidence for the importance of agglomeration in nature by flocculation and by organisms in the Coastal Ocean. In 1969 Meade (1972) pointed out that we know from laboratory experiments that some dissolved organic compounds agglomerate clays and that others deagglomerate them; and that some organic compounds agglomerate clays at one concentration and deagglomerate them at another (Black et al., 1965; Bloomfield, 1956; Chang and Anderson, 1968; Lawson and Keilen, 1951; Morgan and Birkner, 1966; Ries and Meyers, 1968), but that we know virtually nothing about the effects of dissolved organic compounds on suspended matter found in estuaries. This statement is as true in 1981 as it was in 1969 and applies not only to estuaries but to the entire Coastal Ocean.

AGGLOMERATION BY ORGANISMS

Biological processing of fine-grained particulate matter in the water column and on the bottom can have profound effects on the transportation and accumulation of these particles. Establishing the importance of these effects in estuarine sedimentation has been long in coming. Organisms within the water column and on the bottom play a major role in agglomerating fine particles. The principal effect of filter-feeding planktonic and benthonic organisms is to bind small particles together as agglomerates--as feces and pseudofeces--increasing the settling velocities over those of their constituent individual particles and as a result increasing their sedimentation rate and decreasing their residence times in the water column. Settling rates of fecal pellets of a variety of zooplankton were measured at from 36 to 376 m d^{-1}, or from 0.04 to 0.4 cm s^{-1} (Smayda 1969).

There are few studies that have attempted to quantify the importance of filter feeders in coastal sedimentation, but in every case their apparent roles is impressive. Moore's (1936) early research in the Clyde Sea indicated that during the spring the flux of pellets from barnacles and euphausids was more than 47 g $m^{-2}day^{-1}$. Verwey (1952) suggested that Wadden Sea mussels could deposit as much as 150,000 metric tons of sediment each year and Haven and Morales-Alamo (1966) showed that small oysters in

Chesapeake Bay could deposit approximately 1.6 grams of sediment per individual per week.

Deposit-feeders and suspension-feeders are the most frequently encountered benthic invertebrates (Rhoads 1974). The feeding activities of these two trophic types are quantitatively important in changing bottom properties. According to Rhoads, deposit-feeders may feed at the sediment surface or at depth within the bottom. Feeding may be selective or non-selective regarding particle composition and size. Mobile deposit-feeders move laterally and vertically within the bottom, causing mixing and transport of particles as well as of interstitial water and dissolved gases. Transfer of detritus through the gut may result in particle agglomeration in the form of fecal pellets. Some sedentary deposit-feeders form dense populations of vertically-oriented tubes. If these worms feed at the lower ends of the tubes, massive transfer of sediment may take place from below the bottom to the sediment surface. These tubemats may also physically bind and stabilize the sea floor.

Suspension-feeders actively or passively entrap suspended seston on ciliated tentacles, mucus nets, and on ciliated and mucus-covered respiratory surfaces. Particles entrapped in mucus are sorted and moved to the mouth. Dense populations of suspension-feeders may effectively remove most suspended seston from the water column. This material will be egested as pellets and incorporated into the bottom. In studies of bottom sediments near Cape Cod, Johnson (1974) found that organic-mineral composite particles accounted for more than 40% (by number) of the total subpopulation of particles with diameters >5 µm. The degree of agglomeration was so high that Johnson concluded that nearly all the fine silt and clay size particles were incorporated into composite particles.

Bivalves initiate deposite of particles in the 1-3 µm range and consolidate suspended matter faster than detrital sedimentation alone (Haven and Morales-Alamo 1966). Oysters alone can process and deposit a mass of suspended material equal to that from the combined activity of filter-feeding zooplankton and gravitational settling in a 45 m column of water (Bernard 1974). These large quantities of biodeposits modify the physical and chemical characteristics of substrate sediments, allowing establishment of diverse groups.

Surface deposit feeders move particles horizontally at the interface. Subsurface deposit feeders transport ingested particles vertically, and particles overlying the feeding zones fall down to fill the resulting voids (Aller 1977). If special classes of particles are transported in this way, inhomogeneities of various types, both vertical and horizontal, can be created in the sediment (Van Straaten 1952; Schafer 1962; Rhoads and Stanley 1965; Davis 1974). If feeding is nonselective, sediment is homogenized to the depth of feeding (Aller 1977).

According to Rhoads (1974), the specific effect of benthos on bottom stability is related to the processing of the interface by infaunal and epifaunal benthos. He considers two conditions: (1) mobile deposit-feeders produce pelletal surfaces and sediments with an open fabric which have high near-surface porosity, low compaction and cohesion, and a mud surface that is easily suspended; (2) sedentary deposit-feeders or suspension-feeders, especially tube-dwellers, bind the bottom by cementation of mud into tubes and by entrapping particles between tubes, so that a "tighter" fabric results with greater compaction and more cohesion.

When pellets or pellet aggregates are entrained, they move as a bed load because their settling velocities are high relative to critical entrainment velocities (Nowell et al. 1981). If the whole bed is suspended into the water column by wave action, the presence of fecal pellets can increase the effective settling velocity by two orders of magnitude (Haven and Morales-Alamo 1972). Benthic processing can either increase or decrease the erodibility of the bottom. Boyer (1980) determined that meiofaunal roughening of the bed can lower critical entrainment speed by up to 70% of that for an unprocessed bed, with an average reduction of 20-30%. Three days after the polychaete Heteromastus filiformes was introduced to mud, the critical erosion speed was increased by 80% relative to critical erosion speed required to entrain tube-free sediment (Rhoads, Yingst, and Ullman 1978). Nowell et al. (1981) found that very fine sand tracked by the 4 mm clam Transanella tantella reduced the critical entrainment velocity 20% from that of untracked sand.

Shear strengths are also affected by benthos. The shear strength within 20 cm of the anemone Cerianthus americanus increased from 10 g cm^{-2} to 19 g cm^{-2} in intensively burrowed mud in Buzzards Bay, Massachusetts. This phenomenon is poorly understood, although it may be the result of mucous films which in themselves can increase entrainment velocities by up to 60%.

Once a fine-grained sediment is deposited on the sea floor it may be reworked by deposit-feeders and resuspended, or it may be physically bound or agglutinated to the bottom by plants or invertebrates (Rhoads 1974). Figures 8 and 9 are schematic representations of this cycle.

Filter feeding zooplankton, which are more ubiquitous, may be even more important than the benthos in the agglomeration and deposition of particles although there are even fewer studies to document this. Schubel (1971b) and Schubel and Kana (1972) conducted preliminary experiments to determine the role of copepods in agglomerating fine-grained suspended matter in Chesapeake Bay. According to these investigators, a volume equivalent to that of the entire Chesapeake Bay is filtered by copepods and other zooplankton at least every few days.

Manheim et al. (1972) reported that suspended composite particles were common in the transitional zone between the turbid waters in the plume off the mouth of the Mississippi River and the clear waters of the Gulf of Mexico.

Agglomeration by Flocculation

Extensive theoretical discussions of flocculation are presented by Krone (1962, 1972, 1978) and by Verwey and Overbeek (1948). The process depends upon the fact that small particles have unbalanced charges near their boundaries. If immersed in a weak electrolyte such as dilute sea water, the particles attract ions to satisfy the charge imbalance and the attracted ionic layer in turn attracts a second outer layer of oppositely charged ions. The result is a double layer of ions clustered about the particle. The boundary charge depends upon the nature and concentration of electrolyte as well as on the nature of the particle; when this charge is above a critical value no flocculation occurs even if particle concentrations are as high as 150 g l^{-1} (Krumbein and Pettijohn 1938). However, an increase in electrolyte concentration decreases the boundary charge and causes particle attraction, provided the particles collide (Drake 1978). Flocculation depends upon two events--collision and cohesion. The particles must be brought together and once together, must stay together. The factors that determine the frequency of collision are the

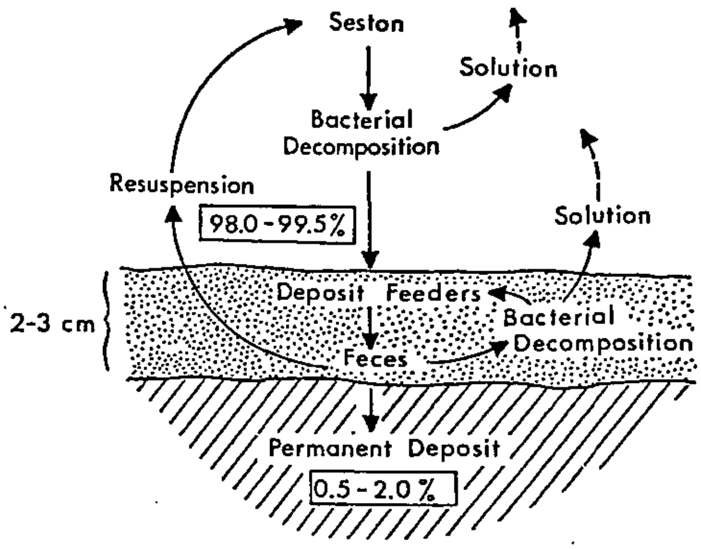

Figure 8. Resuspension cycle in Buzzards Bay, Mass.: approximately 98.0 to 99.5% of annual sediment influx to the bay floor is resuspended and cycled within the upper 2-3 cm thick, bioturbated surface (from Young, 1971).

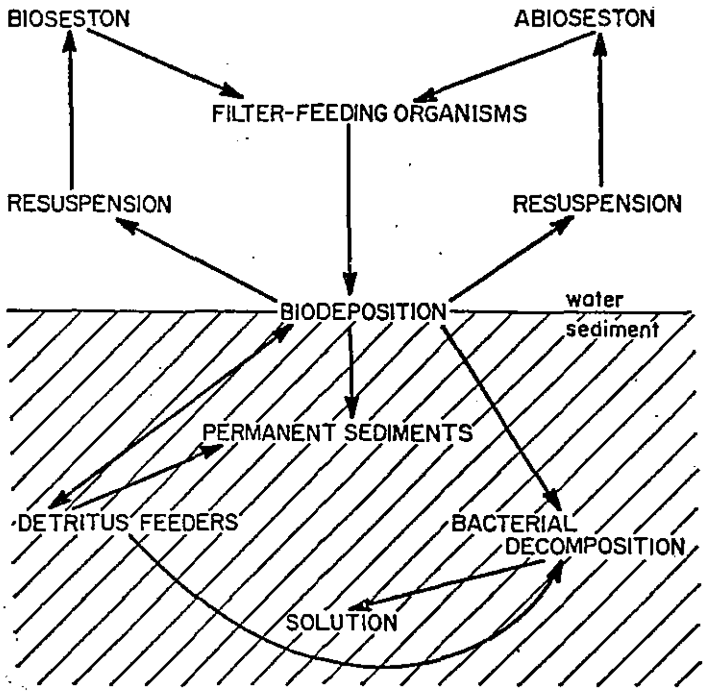

Figure 9. Theoretical estuarine biodeposition cycle (from Haven and Morales-Alamo, 1966).

concentration of particles, their sizes and settling velocities, and the agitation of the fluid. Increasing the concentration, increases the probability of collision. Increasing the agitation increases the probability of collision, but above some threshold it may disrupt agglomerates. A broad settling velocity distribution increases the probability of collision. Factors that influence the cohesion include the salinity of the water, the composition of the suspended particles, and the presence of organic coatings.

Increase in salinity at least up to a point, decreases repulsion of particles and enhances cohesion. Clay mineralogy is also a factor. Illite has a greater tendency to flocculate than kaolinite which in turn has a greater tendency to flocculate than montmorillonite. Organic coatings on clay particles are sticky and enhance cohesion.

Collision of suspended particles results from Brownian motion, velocity gradients (shears), turbulent mixing, and from differential settling. Krone (1978) showed that at 20°C the frequency of collision (per second) of uniformly-sized particles, assuming their viscous resistance to movement is described by Stokes' drag, is $5 \times 10^{-2}n$, where n is the number concentration of particles. Obviously, Brownian motion is important in producing collision only at high suspended sediment concentrations--greater than about 10 g l^{-1}. Concentrations of 10 g l^{-1} are typical of fluid muds, but extremely rare in estuaries except during floods. In more dilute suspensions fluid shear and differential particle settling result in collisions.

Krone's (1962) laboratory experiments indicate clearly the relationship between flocculation--as measured by the increase in particle settling velocity--and salinity, and the strong dependence of flocculation on particle concentration (Fig. 10). According to Krone, most flocculation occurs at chloride concentrations between 0 and 3 $^{o}/oo^{1}$, and increases above 3 $^{o}/oo$ in chlorinity usually have little effect on flocculation, except at very high suspended sediment concentrations. Similar results were found by a variety of researchers using natural riverine and estuarine muds from Australia (Rochford 1951), British Guinea (Postma 1967), and North Carolina (McCoy et al. 1963). The continued increase in settling velocity at very high suspended particle concentrations had been shown earlier by Grippenberg (1934) using suspensions of Baltic Sea mud at

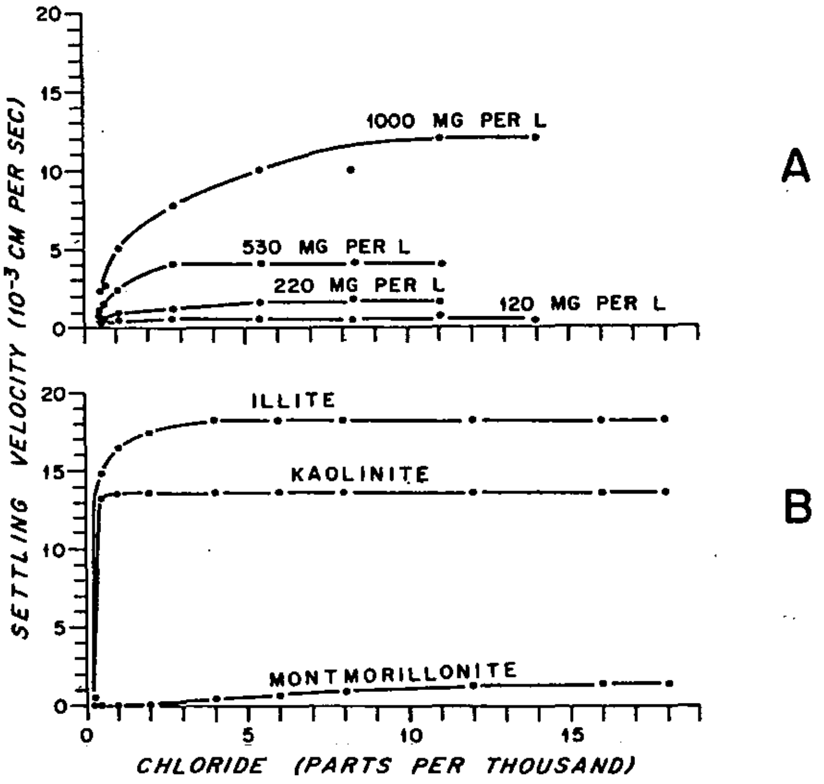

Figure 10. (A) Variation in clay particle settling rates with chlorinity and sediment concentration. Data based on Krone (1962); figure from Meade (1972).

(B) Settling rates of clay floccules with changing chlorinity. Data based on Whitehouse *et al.* (1960); figure from Meade (1972).

concentrations of about 9,500 to 10,500 mg l^{-1}. Whitehouse et al. (1960) found that for mono-suspensions of pure clay minerals, flocculation began abruptly at chlorinities of 1 to 2 ^{o}/oo. Chlorinity above 2 ^{o}/oo increased the flocculation of montmorillonite, but had no measurable effect on either illite or kalonite.

The often-quoted results of Whitehouse et al. (1960) shown in Fig. 10B for suspensions of pure clay minerals at a concentration of 2,000 mg l^{-1} differ substantially from those of Krone (1962) as far as the effects of concentration are concerned. Whitehouse et al. (1960) reported that the settling rate (flocculation) was not affected by the concentration of suspended sediment over a range of from 0 to 3,600 mg l^{-1}. The reasons for the marked differences between the results of Whitehouse et al. (1960) and Krone (1962) are obscure, but are probably related to different behavior of mono-suspensions of pure clays and suspensions of natural sediments which not only are a mixture of minerals, but also contain particulate organic matter; and many of the inorganic grains have sticky organic coatings. The natural sediments probably also have broader size distributions which may increase the probability of particle collisions through differential settling and, as a result, the rate of flocculation.

Flocculation can be demonstrated easily in the laboratory and in such a dramatic way that it has led many investigators to ascribe an important role to flocculation in coastal sedimentation, particularly in the upper reaches of estuaries. But the direct field evidence is less compelling. Direct field evidence for the importance of electrochemical mud flocculation in estuarine sedimentatino processes is sparse and inconclusive (Meade 1972; Schubel 1971). Schubel (1968) and Meade (1972) both have pointed out that available field evidence does not demonstrate that flocculation plays an important role in estuarine sedimentation processes, including the formation and maintenance of estuarine turbidity maxima--areas that should favor flocculation.

The only turbidity maximum for which a detailed microscopic examination of particles has been made is that of the upper Chesapeake Bay (Schubel 1968a, b; 1969; Schubel et al. 1978; Zabawa 1978). Schubel (1968a, b; 1969; 1971b) found that the Chesapeake Bay's turbidity maximum

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[1] A chlorinity of 3 ^{o}/oo corresponds to a salinity of about 5.5 ^{o}/oo.

is maintained by the estuarine circulation pattern which entraps fine suspended particles within this segment of the Bay and by the periodic resuspension of bottom sediments by tidal scour. He reported the presence of large numbers of composite particles, but indicated that most were organically-bound agglomerates.

Zabawa (1978) made detailed scanning electron microscopic examinations of suspended particles from the Chesapeake Bay's turbidity maximum, and used the microstructures of composite particles to infer the modes of particle agglomeration. According to Zabawa (1978) and Moon (1972), composite particles produced by organisms (fecal pellets and pseudo feces), composite particles produced by electrochemical flocculation, and composite particles produced by coagulation by dissolved molecules sorbed onto mineral surfaces each have distinctive microstructures. To ensure preservation of these microstructures great care is required in sampling, sample preparation, and in analysis. Critical point drying is essential to preserve microbial structures. Using this technique, Zabawa reported that in the background subpopulation of suspended particles--those particles present in more-or-less continual suspension (Schubel 1971a)--few of the agglomerates he observed had microstructures attributable to flocculation. He found in the subpopulation of particles alternately resuspended and deposited (Schubel 1971a) "relatively large numbers of mineral grains arranged in pelleted microstructures to which additional grains are attached in a floc mode."

According to Zabawa (1978), agglomeration by organisms (pelletization) was crucial for deposition of fine suspended particles..." but flocculation is still an important mechanism which agglomerates individual clay- and silt-sized mineral grains to pelleted sediments." Kranck (1974, 1981) also reported that flocculation does occur in zones of turbidity maxima. The important question is not whether it occurs, but whether it plays a significant role in sedimentation.

Another phenomenon often explained by flocculation is the rapid sedimentation of suspended material near times of slack water in estuaries with strong oscillatory tidal currents. Krone (1972) reported semi-tidal fluctuations of the concentration of suspended sediment in Savannah Harbor similar in pattern to those reported by Schubel et al. (1978) for Chesapeake Bay, but the magnitude of the variations reported by Krone were much greater--concentrations at 0.6 m above the bottom ranged from less than 25 mg l^{-1} near times of slack water to a maximum value of 3,300 mg l^{-1}. The striking feature of these variations was the rapid loss of material with decreasing flood current speed. Figure 11 shows a decrease in concentration from more than 1,500 mg l^{-1} to less than 50 mg l^{-1} in only about 2.5 hours. The rapid decrease in the concentration of suspended sediment with decreasing current speed coupled with textural analyses of bottom sediments led Krone (1972) to remark:

> "In every case, the suspended sediment concentration in the 8 ft. or so of water immediately above the bed fell rapidly to low values as the tidal currents near the bed approached slack. The fine particles found to comprise the shoal (more than half less than 2 microns [micrometers] diameter) would not have settled in so short a time if they were not aggregated to form clumps of appreciable size."

Krone (1972) calculated settling velocities from the observed changes in the concentration of suspended matter and found them to be 1.3 to 4.5 cm s^{-1}. These settling velocities are typical of those for fine to medium quartz sand.

Krone (1972) did not specify the time scale on which this "aggregation" took place, but it is implicit in his remarks that it occurred in the water column and that the time scale must have been a few hours, at most. Unfortunately, Krone did not make any observations of the particle size distributions of suspended sediment, and the analyses of bottom sediments have little diagnostic value because the samples apparently were disaggregated thoroughly before analyses. As Drake (1976) points out, it is unlikely that flocculation could account for such high settling velocities. Such settling velocities are more typical of the settling rates of fecal pellets (Smayda 1969; Schubel 1971a; Haven and Morales-Alamo 1972).

There is a considerable body of information (e.g., Rhoads 1963, Johnson 1974 and many others) showing that fine-grained sediments in estuaries usually have been thoroughly processed by a variety of organisms into agglomerates of much larger size. Conventional methods of preparing samples for particle size analysis are designed specifically to destroy

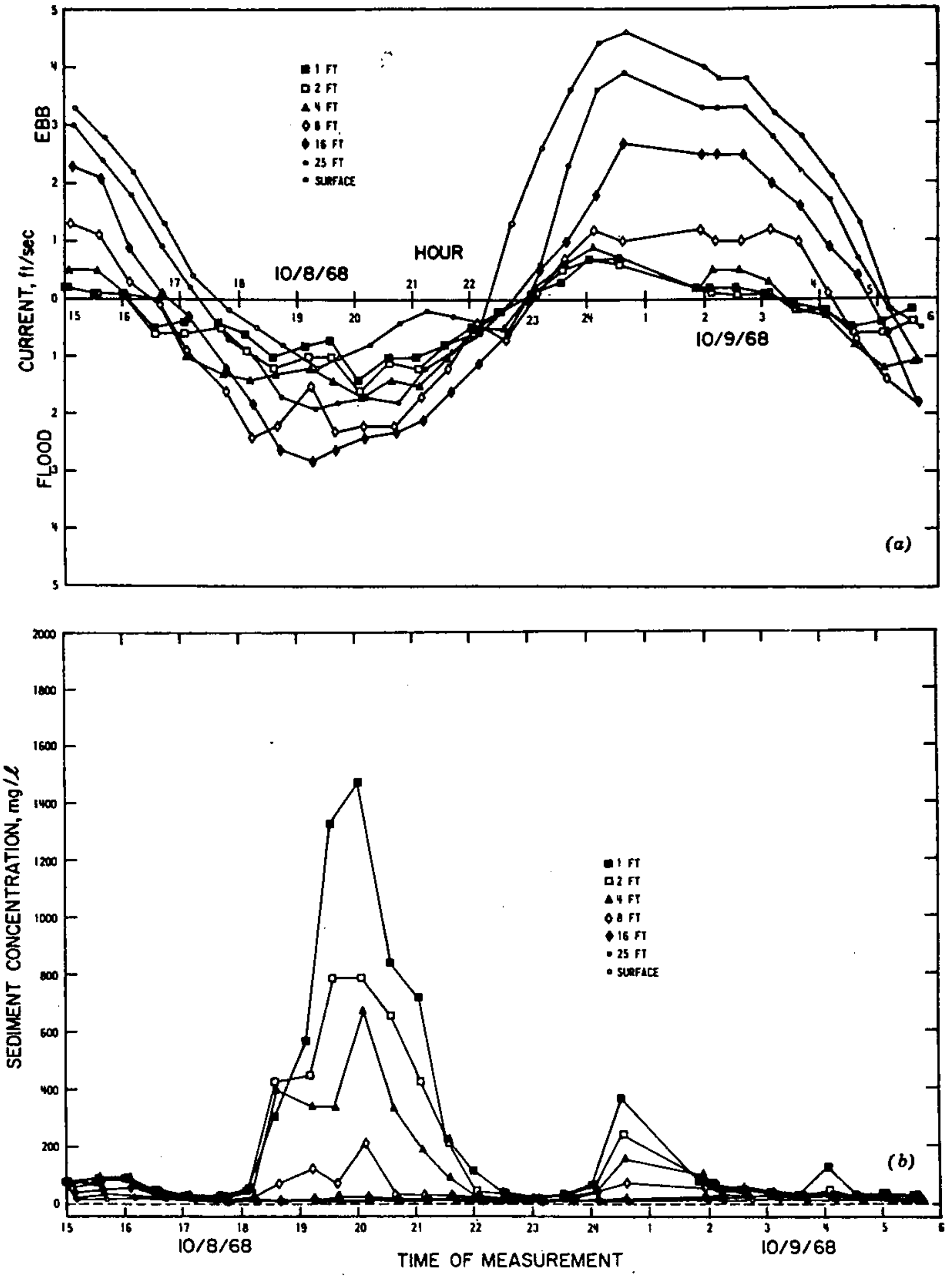

Figure 11. Currents and suspended solids at one location in Savannah Harbor. Sample levels are referenced to bottom. Note that flood and ebb currents are stronger at near-bottom and near-surface levels, respectively. From Krone (1972).

agglomerates to yield the size distribution of the primary particles (individual units) and of any aggregates (particles so tightly bound that they are stable under normal handling and dispersing techniques, including ultrasonication) that may be present. The results of such analyses are of little diagnostic value to investigators interested in estuarine sedimentation processes.

Schubel et al. (1978) examined a set of data in which the concentrations of suspended sediment (Schubel 1968a), the size distribution of the suspended sediment (Schubel 1969; Schubel 1971a) and the current speed were measured at a number of depths throughout the water column over a tidal cycle at a station in the turbidity maximum of the upper Chesapeake Bay. One of the questions these investigators addressed was "Can the marked and rapid decreases in the mass of total suspended sediment that occur in the water column between maximum current velocities--both ebb and flood--and slack water be accounted for by simple particle-by-particle settling? Or, do the data indicate that particle interactions signficantly increase the effective settling velocity and therefore play an important role in controlling sedimentation?"

The variations in current velocity and suspended sediment concentration analyzed by Schubel et al. (1978) are shown in Fig. 12. Schubel (1971) had previously reported size analyses of the "undisturbed" samples of suspended sediment collected at hourly intervals at 0.5 and 1.0 m above the bottom and of the "undisturbed" samples collected on alternate hours near the surface. He showed that at 0.5 m above the bottom the volume-weighted mean settling velocity ranged from 1 to 2 x 10^{-3} cm s^{-1} (Stokes' diameter 2.5 to 5 μ m) near times of slack water to 25 to 50 x 10^{-3} cm s^{-1} (Stokes' diameter 12 to 24 μ m) near times of maximum ebb and flood velocities. Schubel (1971a) selected methods of sampling and analysis to minimize both disruption of natural composite particles and formation of new ones.

Schubel et al. (1978) used these data to determine the vertical flux densities of total suspended sediment through a series of imaginary planes at depths of 2, 4, 6, 8 and 9 m (water depth 9.5 m). They showed that the flux densities varied markedly in magnitude and direction over a tidal cycle, and that the magnitude of these fluctuations increased near the bottom, Fig. 13. The total flux density was apportioned relatively

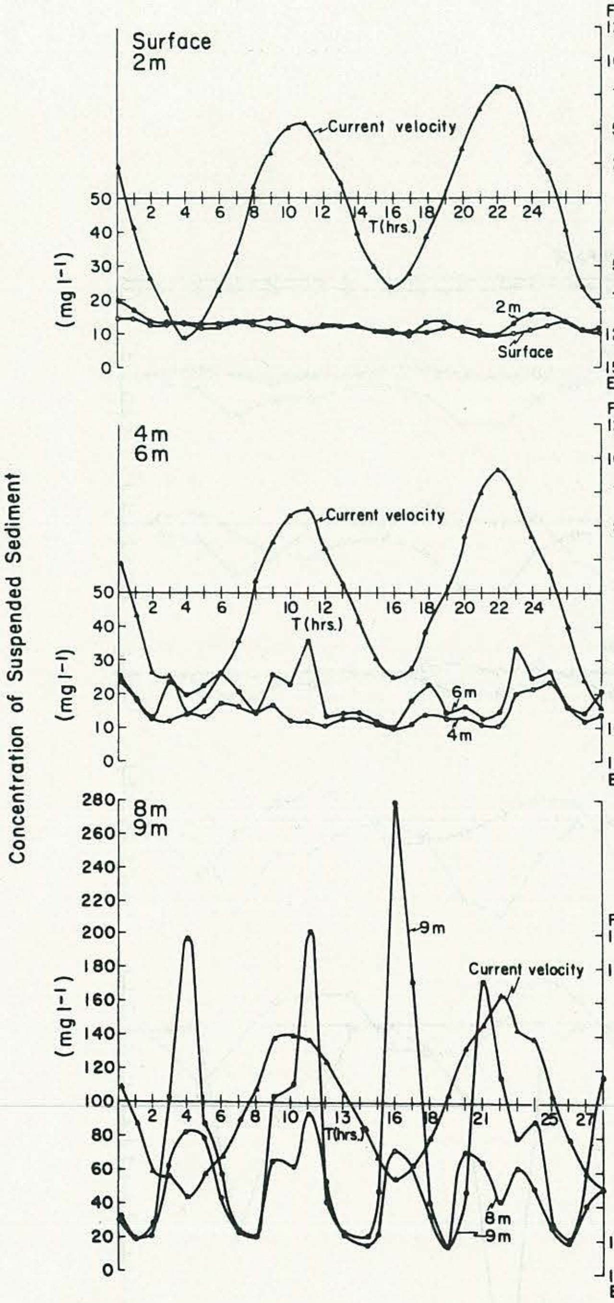

Figure 12. Variations of current velocity (cm/sec) and suspended sediment concentration (mg/liter) at station IIIC (9.5 m) over two tidal cycles. Based on hourly measurements at six depths.

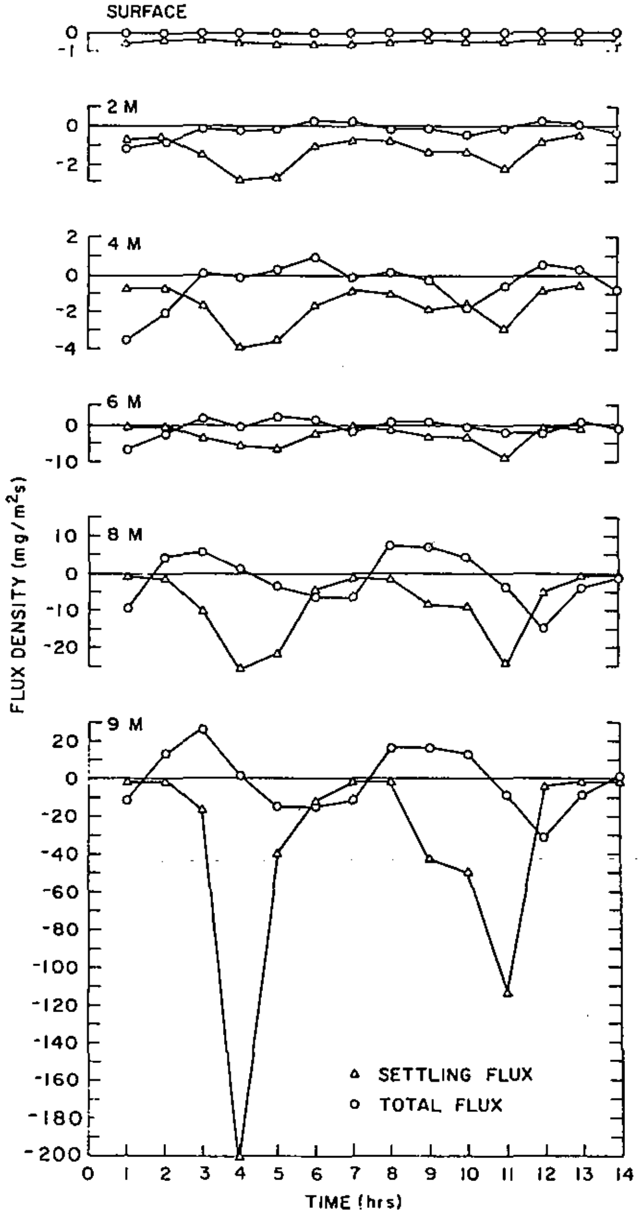

Figure 13. Vertical flux densities of total suspended sediment through imaginary horizontal planes at 0, 2, 4, 6, 8 (1.5 m above the bottom) and 9 m (0.5 m above the bottom), and settling flux densities of total suspended sediment through the same planes.

uniformly among particles with Stokes' diameters ranging from about 2 μm to 64 μm (Fig. 14). Smaller and larger particles contributed relatively little to the total flux density. According to Schubel et al. (1978), the flux density attributable directly to particle-by-particle settling according to Stokes' law was sufficiently large to account for the marked decreases in the mass of suspended sediment following peak concentrations and peak current speeds on both ebb and flood. They reported that "The mechanism of flocculation is therefore not required to explain the large semi-tidal variations of the concentration of suspended sediment in the lower part of the water column."

Schubel et al. (1978) reported that the relatively large fluctuations in concentration of suspended sediment they observed were caused by the alternate resuspension and deposition of bottom sediments. With increasing current speed on ebb and flood "more and larger particles are resuspended from the bottom... when the current begins to move these particles settle to the bottom without any measurable change in their state of agglomeration."

Other investigators have argued that flocculation is responsible for the rapid deposition of fluvial sediments discharged to the ocean during floods. Drake (1976) pointed out that circumstantial evidence indicated that physiocochemical flocculation was responsible for the nearly complete retention on the inner shelf of the large volume of fine silt and clay discharged by the Santa Clara River in 1969. During average years the Santa Clara River in southern California discharges about 69,000 tons of sediment (Curtis et al. 1973). During the 1969 flood the River discharged more than 50 x 10^6 tons of sediment (22 x 10^6 tons in one day), 25 to 35% of which was fine silt and clay, to the continental shelf near Santa Barbara, California. According to Drake (1976), "such rapid deposition is difficult to explain in any other way" than physiocochemical flocculation.

Some Conclusions

It is clear that the agglomeration is important in removing fine particles from suspension in the Coastal Ocean. It is clear also that agglomeration takes place by a variety of mechanisms. The relative importance of these several mechanisms to sedimentation processes in the

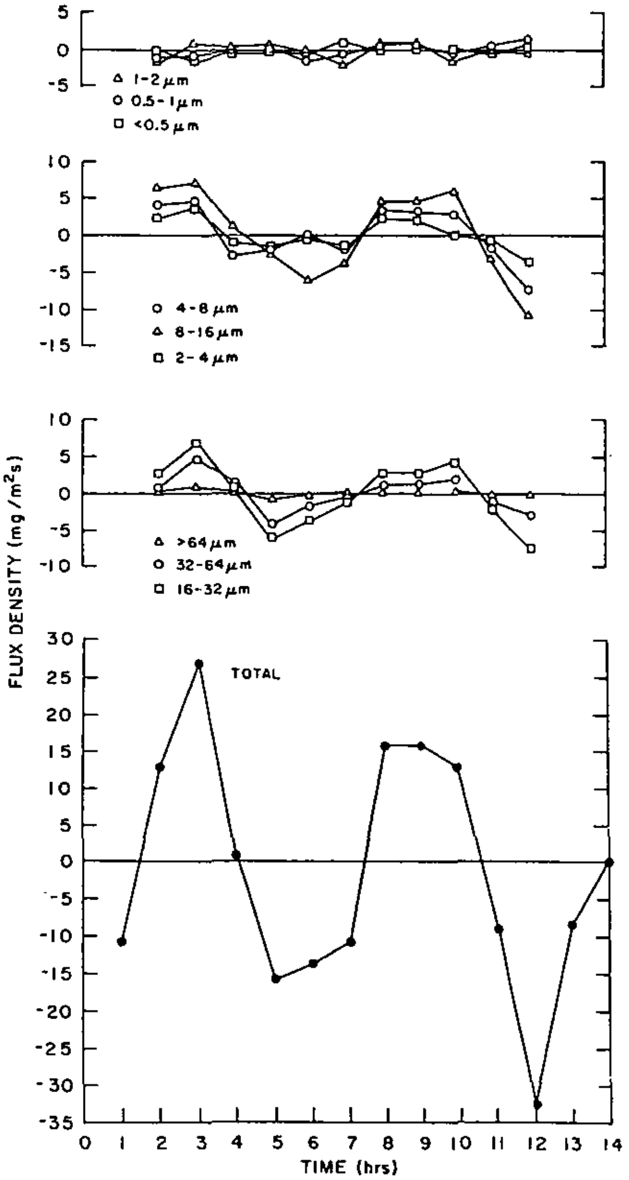

Figure 14. Partitioning of the flux density of total suspended sediment at 0.5 m above the bottom among various particle size classes.

Coastal Ocean is considerably less clear. Meade (1972) and Schubel (1968b, 1971a) concluded that the importance of electrochemical flocculation in controlling estuarine sedimentation had been exaggerated. Neither I nor Meade (personal communication, 1982) see any compelling reason to alter this conclusion on the basis of the research done in the past decade. It has been shown that flocculation occurs in estuaries. This has been done particularly well by Kranck (1981) and by Zabawa (1978). The importance of flocculation as a sedimentation process remains obscure, however.

In 1969 Meade (1972) wrote:

> "Before sediments can be flocculated and precipitated appreciably by inorganic salts in natural situations, several conditions must be met. The suspended sediment must contain a large portion of particles (such as clay minerals) whose surface electrochemical properties make them subject to flocculation. The concentration of suspended matter should be large, preferably measurable in grams rather than milligrams per liter. And the velocities of the water must be small enough to permit flocs to form and settle out of suspension. However, electrochemically sensitive materials such as clay minerals are not necessarily the most abundant constituents of the suspended matter in estuaries or inflowing rivers. Concentrations of suspended matter in inflowing river waters only infrequently exceed a few hundred milligrams per liter. And tidal velocities of estuarine waters are often great enough to prevent the deposition of fine sediment, no matter how flocculated it may be."

If flocculation is important in sedimentation in the Coastal Ocean, it must be where concentrations of suspended sediment are high: in the upper reaches of estuaries in zones of turbidity maxima, in fluid mud layers, in estuaries such as the Huang Ho (Yellow) and the Chang Jiang (Yangtze) where the concentrations of suspended sediment are particularly high (thousands to tens of thousands of mg l^{-1}), and in other estuaries during unusually high riverflow events when concentrations of suspended sediment are abnormally high. Even in these cases the evidence that flocculation plays an important sedimentological role is equivocal.

In the middle and lower reaches of most estuaries, and in waters overlying most of the continental shelf and slope, biological processing must account for most agglomeration. Concentrations of suspended particles are too low, except off a few major rivers such as the Huang Ho (Yellow) and Chang Jiang (Yangtze), for flocculation to be an important mechanism. Biological processing of suspended particles by filter-feeding zooplankton and benthos also may be an important mechanism of agglomeration in the upper reaches of estuaries, but for a different reason. In those regions the concentrations of suspended particles are high; so high that filter-feeders may be unable to select organic particles from inorganic particles effectively because the mean separation of particles is so small. They may be forced to do the selecting after ingestion. This hypothesis has not been bested.

FINE-GRAINED SEDIMENT AND ENVIRONMENTAL QUALITY

Fine-grained sediment can affect the quality of coastal environments in a variety of ways. Environmental quality is in large part a subjective measure. Quality is defined according to Webster as "any character or characteristic which may make an object good or bad, commendable or reprehensible." But good and bad are value judgments largely; good or bad for whom, for what purpose must be considered. People frequently measure the quality of the environment in terms of its capacity or suitability to accommodate those uses which they as individuals, or groups, believe are most important. If one is a shipper, a longshoreman, or a commercial seaman, channel depth and deep water at the piers may be the most diagnostic measure of the "quality" of a coastal environment. If one is a fisherman--commercial or recreational--"quality" may be measured best by fish landings. If one's primary use of coastal waters is for water-contact sports, the best indicators of environmental "quality" may be the turbidity of the water; the levels of bacteria, coliform, and enteric viruses; or perhaps the availability of marinas and other pleasure boat support facilities. And, if one values the coastal environment for its aesthetic character, perhaps the best criteria for assessing "quality" may be inaccessibility and preservation of pristine characteristics.

Regardless of the measure one chooses to assess environmental quality, the increased influxes of fine-grained particulate matter to the Coastal Ocean resulting from man's activities have been deleterious to many of society's uses of these environments, and have had a salutory effect on few, if any. This is true whether the particles are suspended in the water column or deposited on the bottom. It is probably not an exaggeration to say that fine-grained particulate matter has a greater effect on environmental quality than any other single factor. In this section we review briefly the effects of fine suspended particles on the milieu of the Coastal Ocean.

Direct Biological Effects

There exists an extensive literature dealing with the effects of suspended sediments on organisms in marine, brackish, and freshwater environments. An organism's response to sediment suspensions depends upon the organism's stage of development, the condition or health of the organism, the length of exposure, the composition and physical characteristics of the suspended material, and the presence of contaminants sorbed to the particles. It is possible to place the ecological effects of suspended solids in a number of categories:

(1) Mechanical or abrasive action (i.e., irritation of tissues, clogging of gills, reduced feeding effectiveness, etc.)
(2) Direct smothering
(3) Scouring
(4) Reduction in light penetration
(5) Availability as a surface for bacterial growth
(6) Adsorption and/or absorption of various chemicals
(7) Reduction in temperature fluctuations.

The effects of suspended matter on organisms may be direct, with the particles themselves bringing about the organism's response, or they may be indirect, with the presence of suspended material modifying the environment in such a way as to produce a response.

For phytoplankton the effect of increased turbidity on light penetration is of principal significance. The presence of suspended material in the water column alters the quantity and quality of light available to organisms. The amount of light penetrating to a given depth, d, can be expressed as

$$I_d = I_o e^{-kd} \quad ,$$

where I_o is the incident light and k is the coefficient of extinction (Parson and Takahashi 1977). The coefficient of extinction has two components, one due to absorption, the other to scattering.

To assess the effects of particulate matter on available light, we can look independently at its effects on absorbance and on scattering. Jones and Wills (1956) measured the attenuation coefficient of suspensions of mud in sea water, in estuary water, and in tap water (Fig. 15). The attenuation coefficient is essentially a measure of absorption, because the attenuation measurement includes only that small amount of forward scattering that occurs within the path of the beam.

From Fig. 15 it can be seen that suspensions of mud in tap water are linear, whereas in natural waters the function levels off. Jones and Wills attribute this behavior to the state of agglomeration of higher concentrations of particles in natural waters.

In Jerlov's (1976) discussion on marine optics, he notes that scattering has components of diffraction, refraction, and reflection. Inorganic materials tend to have high refractive indices, in the range of 1.15-1.20, whereas organic matter lies much closer to 1.0. In general, however, the effects of differences in composition tend to be overshadowed by the effects of particle size in determining the degree of scattering.

Both scattering and absorption caused by particulate matter show some degree of wavelength selectivity, although it is much more pronounced in the case of absorption. Jerlov gives some evidence for higher scattering in the red than in the blue. Others (Kullenberg 1969) have reported scattering to be dominant in the green. The difference may be attributable to angle of incidence. For absorbance, however, spectral selectivity is much stronger and indisputably occurs in the short wavelength region.

Light quantity and nutrient regimes are generally regarded as the two primary environmental variables that regulate photosynthetic production. In coastal waters, the interplay between these two parameters often manifests itself in the spring diatom bloom (Russel-Hunter 1970) where the dramatic increase in phytoplankton production is a result of increasing light intensity. Other studies (Garside et al. 1976; Mahoney and McLaughlin 1977) indicate that dense blooms of phytoplankton in Lower New York Bay also may be limited by light intensity.

Experiments conducted by Sherk et al. (1976) demonstrated the effects of fine suspended particles on the carbon assimilation rates of various phytoplankton cultures. Their results showed that for particulate concentrations (SiO_2) between 100 and 500 mg l^{-1}, reductions in carbon fixed were significant. At concentrations of 1000 mg l^{-1} most species tested showed a 90% reduction in photosynthetic activity. The authors pointed out that the range of concentrations used in their experiments are typical of those occurring during dredging and disposal operations (May 1973), (Masch and Espey 1967). Others (Wetzel and Van Tine 1981) have studied the effects of light levels on the submerged aquatic vegetation in Chesapeake Bay and concluded that light-energy distribution was a major environmental variable controlling the distribution, growth, and survival of submerged aquatic vegetation and that suspended sediment concentrations were a significant factor in determining light levels.

The ecological implications of increased suspended sediment loads, particularly in regard to species compositions and energy transfers between trophic levels, need to be investigated further. Studies have shown that some phytoplankton species are better adapted to lower light conditions than others (Jitts et al. 1964, Sorokin 1969, Halldal 1974) with the possibility existing for changes in species composition resulting from increased turbidity levels. Most studies of phytoplankton production as a function of light intensity have been conducted with single species cultures, so the possible effects of multi-species competition and resulting changes in species composition due to lower light levels are not fully understood. Any reduction in photosynthetic production caused by suspended particulates would reduce the amount of food available to the next trophic level, predominantly zooplankton. This could have serious consequences for the larval and juvenile stages of many important estuarine organisms.

In coastal and estuarine waters, crustaceans and the larval stages of many fish and invertebrate species are the dominant members of the zooplankton. Filter feeding, a primary mechanism by which many members of the zooplankton obtain their food, has been studied widely and the processes by which particles are selected are fairly well-understood (Hardy 1965, Rubenstein 1977, Fenchel 1980, Moore 1977). The concentration of suspended matter affects feeding efficiency and survival of zooplankton. For a given volume of water that a zooplankter must filter to obtain the food required to satisfy its nutritional needs, an increase in turbidity will tend to "dilute" the concentration of nutritious particles. Stated simply, with increased suspended matter above some threshold, a filter feeder must ingest and pass through its system more particles to obtain the same nutritive value--if the organism cannot select particles. This places a higher metabolic demand on the organism and may force it to draw on its own stored energy reserves. Under extreme conditions this store could be exhausted in which case the organism would die of starvation (Jermolajev 1958). As discussed earlier, photosynthetic production also is reduced under conditions of high turbidity, further decreasing the amount of available food.

The experimental evidence that high concentrations of suspended particulates adversely affect filter feeding organisms suggests that several possible mechanisms are at work. The idea that several species of common estuarine copepods feed nonselectively under conditions of high particle densities was put forward by Paffenhofer (1972) and further demonstrated by Sherk et al. (1976). This non-selective ingestion results in reduced consumption of food particles which, if substantial on a large scale, could lead to a serious break in the food chain (Sherk et al. 1976).

Because of the commercial importance of many species of benthos, particularly the bivalves, the effects of high suspended sediment concentrations on these organisms have been researched heavily. Pioneering work by Loosanoff and Tommers (1948), Loosanoff (1961), Davis (1960), and Davis and Hidu (1969), has demonstrated that there is a direct correlation between suspended sediment concentrations and certain metabolic processes such as feeding rate, shell movement, and water pumping activity. Concentrations of 100 mg l^{-1} of silt were found to significantly reduce the pumping rate in oysters (Loosanoff 1961). Hsiao (1950) reported that higher concentrations of suspended solids increased irregularity in respiratory and feeding movements of oysters, and that oysters died if covered by sediment for more than two days. Since food intake in filter-feeders is related directly to the water pumping rate, any reduction in pumping rate caused by increased suspended solids levels would tend to reduce the organism's ability to obtain food.

In addition to normal feeding and respiratory behavior, bivalves have a tendency to remove particles from suspension by gill-cleaning (often called the clearance function) and by the production of pseudofeces. Both of these processes place a high metabolic demand on the organism (Lund 1957). If large quantities of inorganic particulates are being ingested and excreted, the organism may literally starve to death trying to clear the surrounding waters (Winter 1972). Actual burial of benthic species by sediments has been widely studied as well. An organism's ability to survive varies from species to species, and is highly dependent upon the nature of the blanketing sediment (Saila et al. 1972, Shulenberger 1970).

Much recent research centers around the importance of resuspended bottom material as part of the food chain for benthic invertebrates (Rhoads et al. 1975). New evidence indicates that some level of resuspended bottom muds may stimulate growth rather than inhibit it.

The effects of suspended sediment on eggs and larvae of benthic organisms have also been widely researched. Loosanoff (1961) reported that silt concentrations of 250 mg l^{-1} had an effect on egg development, and that larval development of _Crassostrea virginica_ was affected at concentrations of 750 mg l^{-1}. Davis and Hidu (1969) concluded that the large particles present in silt were the main deleterious factor in oyster egg development, while the smaller particles appeared to be more important in hindering the development of clam eggs. Various authors have pointed to the potential beneficial effects of small (100 mg l^{-1}) concentrations of silt on the development of larval _Crassostrea_, possibly because of adsorptive processes which would tend to reduce availability of waste products and toxic substances, or because of slight mechanical stimulation of the gills (Davis 1960, Loosanoff and Davis 1963, Davis and Hidu 1969).

The literature dealing with the ecological effects of suspended sediment on fishes is quite extensive, and numerous research papers and literature reviews have appeared over the years (Van Oosten 1948; Wallen 1951; Cairns 1968; Rogers 1969; Sherk et al. 1970, 1974; O'Connor et al. 1977; Auld and Schubel 1978; Brinkhuis 1980). Studies have shown that there are both lethal and sublethal effects of suspended solids on estuarine fishes at concentrations typically found during extreme flooding, at industrial sites, and in the immediate vicinity of dredging and dredged material disposal operations (Sherk et al. 1972). Certain generalizations can be made on the basis of the literature cited above.

(1) Although different mechanisms come into play to produce mortality in fishes, the common cause of death is anoxia.

(2) Within a given species, juvenile forms tend to be more sensitive to suspended solids than adults.

(3) Bottom fishes that normally live near the sediment-water interface are more tolerant to high levels of suspended solids than pelagic and littoral forms.

(4) Particle size and shape are important deleterious factors. Generally, larger grain sizes, as well as angular and rough particles are more harmful than smaller, smoother particles.

(5) Fish possess behavioral and physiological mechanisms to help clear their gill surfaces from particulate coatings.

(6) Temperature and oxygen concentrations are very important in determining fishes' tolerance to suspended solids. Generally, species with low oxygen requirements were more tolerant to very heavy concentrations of suspended solids than species with high oxygen requirements.

Suspended Sediment and Dissolved Oxygen

Fine suspended particulate matter can affect the distribution of dissolved oxygen directly and indirectly. The oxygen demand of organic-rich, reduced sediments can produce a sag in the oxygen distribution. It has been reported, for example, that in the Arthur Kill (New York-New Jersey) resuspended dredged materials reduced oxygen levels in the water column to 16 to 83% of the levels observed on non-dredging days (Brown and Clark 1968). Other investigators (Frankenberg and Westerfield 1968, Odum 1970) reported that when surface sediments from Warsaw Sound (Georgia) were resuspended in estuarine waters they were capable of utilizing significant amounts of dissolved oxygen. According to Odum (1970), resuspended sediments could remove 533 times their own volume of oxygen from the water. No such effect was observed in the upper Chesapeake Bay (Biggs 1967), however, and studies of Louisiana marshes did not demonstrate any significant oxygen depletion as a result of dredging activities there

(Macklin 1962). In a comprehensive study of the water column effects of open-water pipeline disposal of fine-grained dredged materials, Schubel et al. (1968) found that the effects of the continuous discharge of fine-grained dredged materials through pipeline operations on dissolved oxygen were small, local, and transitory.

Since the concentration of suspended matter affects the transparency of water, increases of suspended sediment levels, particularly of fine-grained sediment, decrease the depth of the euphotic zone and therefore decrease the photosynthetic production of oxygen by photoplankton. Increased suspended sediment concentrations may also decrease the photosynthetic production of oxygen by rooted aquatic plants. Areas of the bottom formerly within the euphotic zone can be removed from it by increased turbidity levels, leading to the elimination of attached vegetation. Prior to about 1920, much of the bottom of the upper Potomac (Maryland-Virginia) outside of the main channel was covered with a dense growth of rooted plants (Cumming et al. 1916, Wolman 1971). During the 1920s, this vegetation almost completely disappeared, and lower oxygen levels were reported throughout this stretch of the Potomac river and estuary. The effects the disappearance of these plants had on the distribution of dissolved oxygen was counfounded by the effects of other significant environmental changes.

Sediments and Nutrients

Fine particles can act as a source or a sink for some nutrients. Nutrients can be sorbed onto fine-grained suspended particles or desorbed from them depending upon the nutrient and its specific form, and upon a variety of physicochemical conditions. These include salinity, pH, temperature, the size distribution and composition of the particles, and the concentration of nutrients in the water column. The processes are complex and the results often apparently conflicting.

Simpson et al. (1980) reported for the lower Hudson estuary and Harbor that "Data for phosphate in the estuary during lowflow summer months and loading rates from sewage indicate that the water concentrations are primarily determined by physical transport away from the source area, and not by biological or chemical processes in the estuarine waters." They pointed out that similar conclusions could be drawn for other nutrients and for several trace metals and went on to state that "Thus, many materials which are clearly 'reactive' in estuarine waters can have quasi-conservative distributions as a function of salinity when supply rates are large and estuarine circulation is relatively strong."

In the Zaire estuary, desorption of phosphate from suspended material at salinities of about 7% was found to increase phosphate levels about twofold over those observed farther upstream in the river (van Bennekom et al. 1978). A phosphate maximum was also found in the Altamaha estuary (Pomeroy et al. 1972). Farther offshore in the deeper layers of the Zaire Canyon (van Bennekom et al. 1978) and in the coastal zone of Surinam (van Bennekom and Tijssen 1978) phosphate is adsorbed by suspended material. Some other nutrients exhibit conservative, or nearly conservative, behavior.

The distribution of reactive silicate during estuarine mixing shows only slight derivations from conservative behavior (van Bennekom and Solomons 1981). In the Zaire (Congo) estuary (van Bennekom et al. 1978) and in the Rhine estuary, the first influence of sea water causes an increase of 2-3% in the concentration of reactive silicate. In the Mississippi (Fanning and Pilson 1973) and in the Magdalena (Fanning and Maynard 1978) silicate exhibits conservative behavior, whereas a small inorganic precipitation (10-20%) has been reported for rivers with >230 μm reactive silicate (Liss 1976; Li Faxi 1980).

The mechanisms that control the exchanges of nutrients between the dissolved and particulate phases are poorly understood and deserve attention. In addition, there is a paucity of information on the pathways of nutrients from rivers to the ocean via estuaries, particularly in rivers with high sediment loads and high population densities. The output of nutrients from estuaries to the open ocean may be quite different from the input of nutrients to estuaries by rivers. The characteristics of the estuarine filter are poorly documented.

Sediment and Contaminants

Metals.--It is well-known that the fine particles concentrate a variety of pollutants including petroleum hydrocarbons, heavy metals, polychlorinated biphenyls and other chlorinated hydrocarbons, polynuclear aromatics, pesticides, and some radionuclides. In the water column, the bulk of each of these contaminants is associated usually with fine suspended particles, and therefore the distribution, transportation, and accumulation of these substances are determined primarily by the suspended sediment dispersal systems.

There is a considerable body of evidence that dissolved and colloidal iron are precipitated during estuarine mixing (e.g., Bewers and Yeats 1977, 1978; Boyle et al. 1974, 1977; Coonley et al. 1971; Subramanian and d'Angeljan 1976; and others). Most of the removal occurs at low salinities, and the principal mechanism appears to be the flocculation of mixed iron oxide/organic matter colloids of fluvial origin caused by the neutralization of charges on colloidal particles by sea water cations (Boyle et al. 1977). Aston and Chester (1973) showed that the rate of removal of dissolved iron is increased with increasing concentrations of suspended matter. Subramanian and d'Anglejan (1976) suggested that the removal of iron from solution in estuaries is enhanced within estuarine turbidity maxima. The opposite conclusion was reached by Gobeil et al. (1981) for the turbidity maximum of the St. Lawrence River estuary.

Aston and Chester (1973) demonstrated the importance of particulate matter to the processes of dissolved iron precipitation, and adsorption of other metals onto particles during mixing within estuaries and their subsequent deposition have been inferred by a large number of other investigators. Cranston and Buckley (1972) showed that in the LaHarve estuary (Nova Scotia) mercury was adsorbed onto fine suspended particles and that the distribution of mercury in the water column and in the bottom sediments depended primarily upon the fine sediment dispersal system. Mercury, however, also can be released from sediments as methylated mercury, which is formed by bacterial action and which is relatively soluble (Jensen and Jerrelove 1969).

While particulate matter may remove metals and other substances from solution, the removal may be only temporary. The metals may be released while the particles are still in suspension or after deposition. It has been demonstrated that iron can be introduced into the water column from estuarine sediments by release of enriched pore water during scouring or by early diagenetic release of ferrous irons by diffusion (Duinker et al. 1974; Murray and Gill 1978; Segar and Cantillo 1976; Yeats and Bewers 1976). The release of manganese from estuarine sediments is well-established (e.g., Yeats et al. 1979; Duinker et al. 1974). Observed distributions of dissolved manganese have been attributed to desorption of manganese from particulate matter by a number of investigators (Evans et al. 1977) and to sequestering of manganese by iron hydroxides and organic particulates (Bewers and Yeats 1979; Boyle et al. 1977; Scholkovitz 1978). While the precise roles played by suspended particulate matter in the cycling of manganese in estuaries are unclear, it is certain that suspended particles do play important roles in the distribution, transportation and fate of manganese.

The pictures for some other trace metals are even more confused. It is clear that particles play important roles in controlling the distribution of a number of metals, but the precise nature of these roles and how they are affected by changes in the milieu are unclear. Iron and manganese are not irreversibly bound; some other metals probably are.

PCBs and Kepone.--PCBs and other chlorinated hydrocarbons have high affinities for fine particulate matter. With partitioning coefficients of 10^3 to 10^5, the transportation, deposition, and ultimate fate of these compounds depend primarily upon the fine sediment dispersal system.

The distribution and transportation of PCBs in the Hudson River and Hudson River estuary have been described by Simpson et al. (1975), Simpson et al. (1976), Simpson et al. (1977), Bopp et al. (1979), and Olson et al. (1978a, 1978b). Huggett et al. (1979) and Cutshall et al. (1981) studied the movement and accumulation of Kepone, a chlorinated hydrocarbon pesticide, in the James River estuary. Since cessation of introduction of PCBs into the Hudson and Kepone into the James, the major reservoirs of these chlorinated hydrocarbons have been the sediments in the two systems. Removal and isolation of these contaminants from the ecosystem depend primarily upon the sites of accumulation and the rates of burial. Bopp et al. (1981) reported that PCB concentrations were considerably higher in dredged channels than in other areas. Since these channels must be maintained by dredging, safe disposal of these contaminated materials poses a problem. Burial of Kepone-contaminated sediments in the James has been more rapid than expected. In both estuaries, there continues to be controversy as to whether sediments contaminated heavily with chlorinated hydrocarbons should be dredged from the estuary and confined in specially constructed landfills, or whether they should be left in the estuary to be isolated naturally by burial beneath clean sediments.

Hiraizumi et al. (1979) examined the role of suspended matter in the transport of PCBs and concluded that more PCB accumulated on suspended sediments than on and in the plankton. They found the concentration on particles was inversely proportional to mean particle size and linearly related to specific surface area. The partitioning coefficients calculated by Hiraizumi et al. (1979) ranged from 0.2×10^5 to 3×10^6.

Turbidity and Aesthetics

Increases in the levels of suspended particulate matter also can have a significant effect on the aesthetics of the coastal environment. Above some threshold level, suspended matter is aesthetically displeasing and inhibits recreational use. This level is a function not only of the total concentration, but also of the size distribution and the composition of the material. A concentration of 100 mg l^{-1} of fine quartz sand does not have the same effect on water color, transparency, and other indices of water "quality" as does the same concentration of organic-rich silt and clay sized particles. Any "standards" for suspended matter, or "turbidity", must take this into account.

Individuals also have different aesthetic thresholds. It has been reported, for example, that when John Adams, a Democrat, was President of the United States, he swam in the upper Potomac near Washington, D.C. Abraham Lincoln, a Republican, not only did not swim in the upper Potomac, but remarked that the stench from it was so bad on some warm summer evenings when the wind was off the Potomac that he literally had to flee the White House. This would seem to indicate either that the "quality" of the upper Potomac had been seriously degraded by man's activities over the period of about 60 years separating their administrations; or as a Republican friend of mine points out, merely that" "A Democrat will swim in anything."

Some Conclusions

Fine-grained particles have an important effect on the quality of the Coastal Ocean, particularly in areas where concentrations of suspended sediment are high including estuaries and other coastal water bodies, and shelf waters off the mouths of major rivers. Since most contaminants that reach the Coastal Ocean enter by rivers, estuaries play a major role in determining the fates and effects of these contaminants.

Estuaries act as filters for the signals carried by rivers. The signals that emerge from estuaries are often modified substantially from those introduced by the rivers. The characteristics of the estuarine filter vary from one estuary to another and with time in any given estuary. The processes that determine the filter factors are understood poorly, but are functions of the estuarine circulation pattern, the ratio of the volume of the river discharge to the volume of the estuary, and the suspended load of the river. As pointed out elsewhere in this chapter, large estuaries are particularly effective filters for removing the suspended particles carried into them by their tributary rivers. As a result, they are also effective in removing substances that have a high affinity for particles.

As Lerman (1980) has pointed out "The role of the estuarine sediments as sources and sinks of various materials has so far received only little attention. We cannot precisely evaluate the contributions of coastal sediments to the open ocean."

Because of the major role fine sediments play in determining the quality of the Coastal Ocean and its living resources, much more attention should be directed at studying the sources, routes and rates of transport, fates, and effects of fine particles. Some research priorities are outlined in the next section.

SOME RESEARCH PRIORITIES

There are two quite different approaches to the study of fine particles. One deals with specific processes such as the physical mechanisms that control the deposition and erosion of mud, the formation of composite particles (agglomerates) by biological and physiochemical processes, and the reworking of sediments by benthic organisms and the consequent changes in the physical properties of the sediment. The other approach deals with the characterization of specific coastal environments as sedimentary systems.

Many studies of the first kind have been completed successfully; others are only beginning to be addressed. The prospects for resolving questions at this level are good so long as scientists find them exciting and reasonable support is provided through conventional funding mechanisms. But studies of the second kind--studies of coastal sedimentary systems--hardly have been considered. Where coastal sedimentary systems have been considered usually it has been in response to a crisis. One of the best examples of this is the work that led to the explanation of the formation of the mud deposits in the Thames and their relationship to maintenance dredging of the shipping channels to the London docks (Inglis and Allen 1957). Other examples are the study of the sedimentary system of the Hudson River estuary prompted by PCB contamination and the study of the sedimentary system of the James River estuary prompted by Kepone contamination.

One can learn a great deal about the mechanics of some sediment transport processes through laboratory flume experiments and through isolated, short-term field studies--through studies of the first kind. These studies, however, provide little insight into the long-term manifestations of sedimentation in the Coastal Ocean and the identification of the processes that control sedimentation in different parts of a coastal system. Attainment of this level of understanding--the level necessary for development of effective management strategies--requires a holistic approach; an approach that combines specific, short-term field and laboratory studies with system-wide studies.

Ideally, one would like to know for each important coastal environment: (1) the sources of sediment--their locations and strengths, (2) the character of the sediment introduced--its size distribution, composition, and associated contaminants, (3) the routes and rates of sediment transport--including the transient repositories, and (4) the sites of final accumulation and the losses to the deep sea. Schubel et al. (1978) outlined recommendations for research on the transportation and accumulation of fine-grained sediments in the estuarine environment and strategies to attack these problems. Much of that discussion is pertinent to all coastal water bodies.

Some of the specific kinds of studies of fine-grained particulate matter that should, in this author's opinion, be given a high priority are listed below. They are unranked.

(1) Studies to determine the fluvial inputs of suspended solids, both naturally occurring and anthropogenic, to important coastal systems.

(2) Studies to determine the routes and rates of movement of fine-grained materials in coastal systems, and the sites of accumulation.

(3) Studies to determine the discharge of suspended and bed loads to the ocean from major rivers and estuaries.

(4) Studies to assess man's impact on prevailing fine sediment dispersal processes, and to devise ways of ameliorating undesirable effects.

(5) Studies to characterize the composition, the chemical nature, and the reactivity of fine-grained suspended matter in a variety of coastal environments.

(6) Studies of fine suspended matter to determine the directions and rates of reactions involving nutrients, metals, halogenated hydrocarbons, and a variety of other contaminants as a function of environmental parameters.

(7) Studies of biologically-mediated reactions involving fine suspended particles.

(8) Studies to assess the role of climate on the inputs of dissolved and suspended loads of rivers to coastal waters.

(9) Studies to assess the relative importance of various agglomeration processes in controlling the size distribution of suspended particles in coastal waters, and the sedimentation (deposition) of fine particles in a variety of coastal environments.

(10) Studies to assess the importance of events (floods, hurricanes, tsunamis, etc.) in coastal sedimentation. Successful conduct of such studies will require the establishment of funding mechanisms capable of rapid response.

(11) Studies of the geochemical processes that control the composition of dissolved and suspended loads in rivers, estuaries, and open coastal waters.

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BRIEFING DOCUMENT 2

POLLUTANT-PARTICLE DYNAMICS IN GEOCHEMICAL CYCLES

CONTENTS

BRIEFING DOCUMENT 2

POLLUTANT-PARTICLE DYNAMICS IN GEOCHEMICAL CYCLES

C. R. Olsen, N. H. Cutshall, and T. A. Nelsen

INTRODUCTION

A wide variety of substances, with known or potential pollutant capacity, are transported into the marine environment from the continents by river discharge, ocean dumping or eolian processes. A few of these substances are relatively unreactive in the marine environment and consequently their transport pathways are conceptually straightforward and mediated by water mass movements. A much greater number of these substances, however, are highly reactive and have a strong affinity for association with fine-grained particles. The movement of these reactive pollutants, their removal from the water, and their accumulation in the sediment are thus governed to a great extent by sedimentary processes.

The dynamics of fine-grained particles and particle-associated pollutants in coastal marine environments are extremely complex because (1) intense short-term flow events are often more important to sediment transport than current flow which occurs on a regular basis during normal conditions; (2) fine particles often undergo numerous episodes of deposition and resuspension; and (3) numerous physical, chemical, and biological processes affect the fate of particles and reactive pollutants, especially in estuarine zones where freshwater mixes with seawater. As a result, transport calculations for particle-associated pollutants are much more difficult to make than those for dissolved substances.

During recent years there have been numerous studies measuring the distribution of contaminants in the environment. Most of these studies, however, merely report pollutant concentration data on particles, with little attention devoted to the biogeochemical cycles that affect the dynamics of particles and associated pollutants in estuarine, coastal and marine environments. Several of the input, removal, mixing, and regeneration processes involved in these geochemical cycles are schematically portrayed in Fig. 1. The extent to which the fate of a specific pollutant is affected by each of these processes depends upon the chemical form and concentration of the pollutant, as well as the chemical characteristics of the sorbing particle and the transporting medium. The particles involved in these cycles may be riverborne, airborne, resuspended from the bottom by currents and organisms, or generated within the water column by biological production, colloidal flocculation, or bioaggregation.

Most of the studies concerned with these processes have used geochemical signatures on particles to trace particle transport, differentiate particle sources, and quantify particle-pollutant fluxes. Such signatures can be metal/aluminum ratios (Eggiman et al., 1980; Sholkovitz and Price, 1980) or any adsorbed substance having a known source and history of input, such as radionuclides and synthetic organic compounds (Bopp, 1970; Olsen, 1979). Natural and anthropogenic radionuclides are particularly useful in that they can also serve as geochemical clocks to determine the rates of processes affecting particles and pollutants in aquatic environments (Pickering, 1969; Broecher et al., 1973; Patel et al., 1975; Robbins and Edgington, 1975; Aller and Cochran, 1976; Bacon et al., 1976; Simpson et al., 1976; Turekian, 1977a, 1977b; Goldberg et al., 1978; Lavelle et al., 1978; Olsen et al., 1978; Simpson et al., 1978; Li et al., 1979; Nittrouer et al., 1979; Olsen et al., 1980; Santschi et al., 1980; Benninger and Krishnaswami, 1981; and Cutshall et al., 1981) Quantitative estimates for the transfer rates associated with the processes illustrated in Fig. 1. are of prime importance for determining particle-pollutant fluxes, developing accurate particle-pollutant transport models, and predicting the fate of particles and their associated pollutants in the marine environment.

Pollutant Classification

Fig 2. diagrams a broad spectrum of substance with known or potential pollutant capacity. These substances are classified first as organic and inorganic; then each class is subdivided into groups. The groups are determined primarily by the chemical characteristics of the samples analyzed and the instrument with which the analyses are performed, for example, atomic adsorption spectrometry (heavy metals) alpha, beta, and

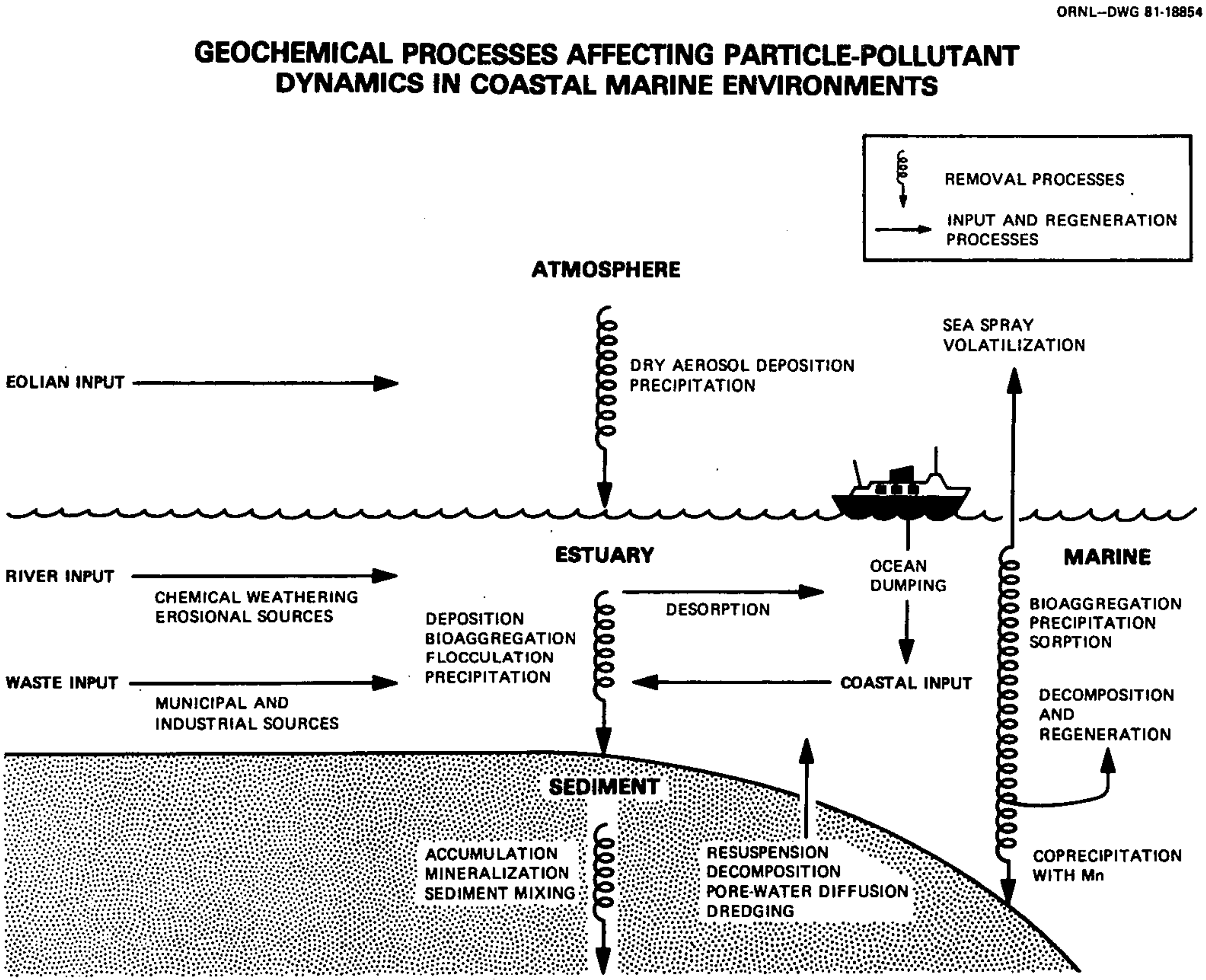

Figure 1. Schematic illustration of the biogeochemical processes which affect pollutant-particle dynamics.

gamma spectromety (radionuclides), gas chromatography (hydrocarbons), and mass, volume, and BOD measurements (municipal and industrial solid wastes).

The sources, chemical characteristics, and input histories of these pollutants into the marine environment have been extensively described in several publications (NAS, 1971; Goldberg, 1975; NAS 1975; Windom and Duce, 1976; NOAA, 1979; Farrington, 1980) and will not be reviewed here. We present a review and overview of the biogeochemical aspects of pollutant-particle associations and dynamics.

POLLUTANT-PARTICLE ASSOCIATIONS

Many chemically reactive pollutants, including synthetic organics, hydrocarbons, and some radionuclides and trace metals become appreciably associated with particles when discharged into turbid aquatic environments. This association may result from (1) ion-exchange, precipitation, or hydrophobic interactions with the particle surface; (2) coprecipitation with iron and manganese hydrous oxide coatings; (3) complexation with organic substances bound or aggregated with particles; (4) incorporation into mineral lattices, organisms, or fecal material; or (5) flocculation of colloidal organic and inorganic matter during river and seawater mixing (Sayre *et al.*, 1963; Jenne and Wahlberg, 1968; Saxby, 1969; Edzwald *et al.*, 1974; Burton, 1976; Sholkovitz, 1976; Boyle *et al.*, 1977; Gibbs, 1977; Turekian, 1977b; Gearing *et al.*, 1980). One of the most basic geochemical tools for assigning a quantitative value to this association is the distribution coefficient.

Distribution Coefficient

The distribution coefficient (K_d) is defined here as:

$$K_d = \frac{C_p}{C_w} \quad ,$$

where C_p is the concentration of a specific pollutant associated with a given weight of particles and C_w is the concentration of the pollutant in an equal weight of water. Ideally, this ratio is a measure of the equilibrium partitioning of a pollutant between dissolved and particulate phases. This distinction between "dissolved" and "particulate", however, is

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POLLUTANT CLASSES

ORGANIC

I. **PETROLEUM AND COAL HYDROCARBONS**
   - A. CRUDE OIL
     (ALKANES, CYCLOALKANES, AROMATICS)
   - B. REFINED PETROLEUM PRODUCTS
     (PETROL, KEROSENE, DIESEL, HEATING OILS, ASPHALTS)
   - C. COMBUSTION AND CONVERSION PRODUCTS
     (PAHs, CO_2, SYNFUELS AND BYPRODUCTS)

II. **SYNTHETIC ORGANICS**
   - A. HALOGENATED HYDROCARBONS
     (PCB's, DDT, KEPONE, MIREX, DIELDRIN, CHLORDANE, HEXACHLOROBENZENE, CHLOROFLUROCARBONS, TRICHLOROETHANE)
   - B. PHTHALIC ACID ESTER PLASTICIZERS
     (PVC, DEHP)
   - C. OTHERS
     (SURFACE ACTIVE AGENTS, ORGANOPHOSPHATE PESTICIDES, SYNTHETIC PYRETHRENOIDS)

III. **MUNICIPAL WASTES**
   - A. SEWAGE SLUDGE
   - B. NUTRIENTS
     (PHOSPHOROUS, NITROGEN, CARBON, SILICON)

IV. **BIOLOGICAL**
   - A. PATHOGENS
   - B. PLANKTON BLOOMS
     (DISSOLVED O_2 DEPLETION)

INORGANIC

I. **HEAVY METALS**
   - A. Cd, Hg, Pb*
   - B. Fe, Mn, Zn, Cu**
   - C. OTHERS

II. **RADIONUCLIDES**
   - A. TRANSURANICS
     (PLUTONIUM, AMERICIUM, CURIUM)
   - B. FISSION PRODUCTS
     (^{137}Cs, ^{90}Sr)
   - C. ACTIVATION PRODUCTS
     (^{60}Co, ^{54}Mn, ^{65}Zn, ^{51}Cr)
   - D. NATURAL
     (URANIUM-THORIUM DECAY SERIES)

III. **INORGANIC AND INDUSTRIAL WASTES**
   - A. DREDGE SPOILS
   - B. PROCESSING BYPRODUCTS
     (ACIDS, ASH)
   - C. SLAGS, MINE TAILINGS

*METALS MOST STUDIED IN TERMS OF POLLUTION AND TOXIC EFFECTS.
**METALS MOST STUDIED IN TERMS OF GEOCHEMICAL CYCLES.

Figure 2. A classification of substances with known or potential pollutant capacity.

generally operational (such as passage through a 0.45 um pore-size filter) and is one of the most important problems with using and determining distribution coefficients in natural water systems. In this respect, C_w includes not only pollutants in true solution, but also pollutants associated with dissolved and colloidal organic matter or sorbed onto particles small enough to pass through the filter, and C_p often includes pollutants which are sorbed from solution by the filter as well as those associated with particles trapped during the filtration.

Distribution coefficients for highly reactive pollutants, such as insecticides, polychlorinated biphenyls (PCBs), and plutonium are generally on the order of 10^5. Consequently, in an aqueous system having a suspended matter concentration of $\sim$10 mg/L (which is typical of near-shore coastal areas) approximately 50% of the mass of such pollutants will be sorbed into suspended particles and the other 50% will be "dissolved" in the water. In a system with a suspended matter concentration of $\sim$100 mg/L (such as the Mississippi River, Columbia River, and Hudson River during high flow), more than 90% of the mass of these pollutants will be transported in association with particles and the remaining 10% will be in the water. In shelf and slope waters, where suspended particle concentrations are on the order of 1 mg/L or less, much of the pollutant mass is transported with the water phase, but particulate phases play an important role in the removal of these pollutants from the water column and the bottom sediments are their major sink.

The distribution coefficient for a specific pollutant may vary depending on the chemical form and concentration of that pollutant. For example, plutonium may exist in at least two oxidation states, a reduced state (either III or IV) which is readily sorbed and strongly bound to particles and an oxidized state (either V or VI) which has a much greater tendency to remain in solution (Bondietti and Trabalka, 1980). Similarly, Bopp (1979) has shown that the lower chlorinated biphenyls (di- and Trichlorobiphenyls) have a lower distribution coefficient ($\sim 10^4$) relative to the higher chlorinated byphenyls (penta- and Hexachlorobiphenyls) which have a K_d value on the order of 10^5.

Variations in the distribution coefficient for a specific pollutant may also reflect changes in the physiochemical characteristics of the particulate and water phases. Fine-grained particles generally have a greater affinity for pollutants relative to coarser particles because they have greater surface areas (for binding sites and organic or manganese coatings) per unit weight and are enriched in layered aluminosilicate minerals (which contain more binding sites per unit area). In addition, coarser particles are generally enriched in quartz which is relatively nonreactive compared to organic and clay phases in natural waters. Studies on the sorption behavior of radiocesium have indicated that ^{137}Cs is strongly associated with K-rich, fine-grained particles (illite clays) in freshwater systems but remains in solution in marine waters because ^{137}Cs must compete with seawater cations (especially potassium) for binding sites on particle surfaces (Tamura and Jacobs, 1960; Rogowski and Tamura, 1970; Aston and Duursma, 1973; Hetherington and Jefferies, 1974; Patel et al., 1978).

Inorganic Flocculation and Ionic Sorption-Desorption

Inorganic flocculation is a complex physical-chemical reaction in which riverborne suspended colloids coagulate into larger particles in the presence of increased electrolyte concentrations. Inorganic colloids are electrically charged particles with large surface areas per unit mass. In fresh waters, repulsive charge effects tend to keep colloids apart but as the ionic strength of the water increases, as occurs during transport into an estuarine environment, interactions between the seawater ions and the charged colloids reduce the repulsive forces allowing flocculation into larger particles (Kranck, 1975).

Since the flocculation process depends on colloid collision and cohesion, the rate of flocculation is, therefore, influenced by the concentration and composition of the suspended matter, and the extent of turbulent mixing as well as the salinity (Meade, 1972). With adequate particle concentrations flocculation of most colloids is complete above a salinity of 4 p.p.t. (Dyer, 1972). Whitehouse et al. (1960) have shown that different clay minerals have different rates of flocculation (e.g., kaolinite has less surface charge and therefore flocculates more rapidly than illite) and Edzwald and O'Melia (1975) proposed that the distribution of clay minerals in recent sediments of the Pamlico Estuary (where kaolinite is found up stream of illite) is a result of their relative stabilities.

The colloid charge originates from unsatisfied or broken bonds at the crystal surface and from the substitution of structural cations in the mineral lattice by cations having a different valence state. The charge at the colloid surface may be positive (as in the case of aluminum hydroxide at high pH) or negative (as in the case of silica or clay minerals). the negative charge of clay minerals is usually attributed to substitution of $Mg^{+2}$for $Al^{+2}$and Al^{+3} for Si^{+4} without concomitant substitutions of OH^- for O^{-2}. To balance this negative charge, clay particles tend to sorb cations between their structural layers or at their surface. The surface-sorbed ions are subject to ion exchange. In this manner, ionic species of a wide variety of pollutant metals and radionuclides can become associated with colloidal particles in freshwater systems and may subsequently be flocculated and deposited, or desorbed, by ion exchange with seawater cations, as these particles are transported into the marine environment.

The adsorption-desorption characteristics of various metals and radionuclides on clay minerals in estuarine and coastal marine environments have been studied by many investigators (Aston and Duursma, 1973; Bothner and Carpenter, 1973; Murray and Murray, 1973; O'Connor and Kester, 1975; Murray and Fukai, 1975; Bourg and Filby, 1976; Duursma, 1976; James and MacNaughton, 1977; Bewers and Yeats, 1978; Frenet-Robin and Ottmann, 1978; and Parel et al., 1978). Most of these studies have involved laboratory experiments in particle composition and water characteristics. Patel et al. (1975) have indicated that pollutants sorbed by ion exchange exhibit a better relationship with sediment clay content than those sorbed by other processes. Tamura and Jacobs (1960) have indicated that illite has a particularly high affinity for ^{137}Cs as a result of cesium substitution for potassium in the clay mineral lattice. Cs-137 introduced into estuarine environments in fallout from atmospheric testing of nuclear weapons or in controlled releases from nuclear power facilities, apparently does not have enough time to become incorporated into the clay mineral lattice before ion exchange causes desorption in more saline environments (Reil, 1970; Jinks and Wrenn, 1976; Patel et al., 1978; Olsen et al., 1981a).

The desorption of several other metals, including Co, Ag, Mn, Zn, Cd, Hg, and ^{226}Ra has been noted in the estuarine environment (Kharkar et al., 1968; Evans and Cutshall, 1973; Lindberg et al., 1975; Graham et al., 1976; Evans et al., 1977; Li et al., 1977; and Bothner et al., 1980), In most of these cases, however, the "release" has been attributed to resuspension of sediments, decomposition of organics, or the cycling of reduced metal-hydroxides, rather that desorption from clay minerals. Hunter and Liss (1979) have suggested that organic and metal-hydroxide coating on colloidal particles may affect surface electrical properties, resulting in a suppression of coagulation rates and ion-exchange, This would agree with the findings of Gibbs (1977) and Trefry (1977) that metal-hydroxide coatings and organics are the major transport phases for sorbed metals and that only a small fraction of these metals are available for ion exchange. Consequently, processes involving organic flocculation-decomposition and Fe-Mn oxidation-reduction may overwhelm ion sorption and exchange on clay materials.

Organic Complexation and Flocculation

Dissolved and colloidal organics, which occur naturally in all aquatic systems, have a strong capacity for binding metals and other pollutants, and thus exert considerable control over the mobilization, transport, removal and accumulation of contaminants in the environment (Saxby, 1969; Schnitzer and Kahn, 1972; Rashid, 1974; Singer, 1974; Nissenbaum and Swain, 1976; Reuter and Perdue, 1977). Humic substances generally constitute about 60 to 80% of these dissolved organics. The remaining fraction is composed of polypeptides, polysaccharides, carbohydrates, proteinaceous matter, and free amino acids. Since these latter organic compounds are easily degradable and rapidly metabolized by microbial activity, their concentrations remain low in natural waters.

Chemically, river humic substances are complex and relatively stable polymers of amino acids, hexosamines, quinones, polycyclic aromatics, and oxygen-containing functional groups (Lindberg et al., 1975). The dominant functional groups are carboxyl (-COOH) and phenolic hydroxyl (-OH) groups but several amino ($-NH_2$) and sulfur-containing (thioether and thioketo) groups may also be available for complexation or chelation. Marine humic substances are somewhat less oxygenated than river humics and contain only about half the amount of carboxyls and phenolic groups, but contain more sulfur and nitrogen (Nissenbaum and Swaine, 1976). Schnitzer and Kahn (1972) have indicated that about 60% of the total weight of a fulvic acid molecule is in the functional groups.

The acidic character of these humic polymers (that is, the ability to give off H^+) allows them to exist in river water as negatively charged hydrophilic colloids and to interact with cations of heavy metals forming organic-metal complexes by ion exchange, surface adsorption or chelation (Reuter and Perdue, 1977) Ferric iron (Fe^{+3}) has the strongest affinity (stability constant) for complexing with humic polymers, whereas Hg^{+2} and Cu^{+2} are the most strongly associated of the divalent trace metal cations (Mantoura *et al.*, 1978; Sholkovitz, 1978). Mantoura *et al.* (1978) have found that the stabilities of the divalent metal-humic complexes follow the Irving-Williams order,

$$\mathrm{Hg,\ Cu > Zn \sim Ni > Pb > Co > Fe > Mn \sim Cd > Ca > Mg},$$

which is dependent on the orbital configurations of the electrons according to crystal field theory (Stumm and Morgan, 1970). Lees (1950) indicated that as many as 60 carbons may be associated with one copper ion in a saturated copper humic complex. Consequently, these organic-metal complexes are relatively stable in natural waters and can withstand large variations in pH even in the presence of large amounts of excess cations. Although the ability of humic substances to bind pollutant metals in the marine environment is undoubtedly affected by the presence of high concentrations of Ca and Mg (Stumm and Morgan, 1979); Mantoura *et al.*, 1978), the magnitude of this effect on specific metals is not well known (Reuter and Perdue, 1976). Slowey *et al.* (1967) found that the major portion of Cu in seawater is associated with organic matter, and several studies have shown strong correlations between metal and organic matter concentrations in coastal marine sediments (Calvert and Price, 1970; Bruland *et al.*, 1974; Jones and Jordan, 1979).

The hydrophilic nature of organic-metal complexes may cause an increase in the solubility and mobilization of a wide range of contaminants, including Cu, As, Pb, Hg, Cd, Co, Ag, Ni, Sn, Al, U, Th, and perhaps transuranic radionuclides that otherwise would not be readily transported in a solution phase (Saxby, 1969; Rashid, 1974; Picard and Felbeck, 1976; Sholkovitz, 1976; Nash *et al.*, 1981; Bondietti, in press). Although the ability of humic substances to reduce Fe (III) to Fe (II), leach minerals, and mobilize metals has been well documented in soils and peats, only recently have similar processes been identified in sediments. Preseley et al. (1972) indicated that humic substances can constitute between 40 and 70% of the organic matter in sediments and that organic complexes with metals, initially leached from silicates and metal oxides, may be responsible for the mobilization of Zn, Cu, and N, from sediments in Saanich Inlet.

In the major rivers of the United States, concentrations of humic substances may range as high as 100 mg/L but average about 10 mg/L (Reuter and Perdue, 1977). Concentrations of dissolved organic matter thus greatly exceed those of other dissolved trace elements or pollutants in river waters. As a result of their colloidal nature, humic substances and their complexed pollutants are rapidly flocculated from solution when river water mixes with seawater in an estuary (Sholkovitz, 1976). This flocculation process usually accounts for the removal of no more than about 10% of the dissolved organic matter but may result in almost total removal of dissolved iron (Boyle et al., 1979). This suggests that iron in some way may enhance the flocculation of humic substances. In addition, experimental studies have indicated that other metals and trace elements may be associated with these iron-rich flocs and may also be removed from solution. Experiments by Sholkovitz (1978) suggest almost total removal of dissolved Fe and P, 20 to 40% removal of Mn, Cu, Ni, and Al, and less than 10% removal for Co and Cd by the dissolved Fe-humic flocculation process.

Hydrophobic Associations with Surfaces

The solubility of a pollutant substance in a polar medium, such as water, is determined largely by its ability to interact electrochemically through hydrogen bonding or ion-dipole interactions. If the substance is nonpolar, that is uncharged and unable to engage in electrochemical interactions, it will probably have a very low solubility and a strong affinity for phase boundaries such as air-sea interface or the surface of particles. This tendency of nonpolar substances to adhere to one another or to phase boundaries in aqueous environments has been called hydrophobic bonding (Parks, 1975).

Many of the organic molecules in petroleum hydrocarbons (Farrington, 1980) and halogenated hydrocarbons (PCBs, DDT, DDE, chlordane, dieldren, kepone, and other commercially-produced toxic organic chemicals) are nonpolar or have nonpolar functional groups. In natural waters, these surface active organic compounds are readily sorbed with their hydrophobic (nonpolar) functional groups oriented away from the aqueous phase and any polarized chemical structure directed toward water. Typical water-particle distribution coefficients for halogenated hydrocarbons fall between 10^3 and 4×10^5 (Bopp, 1979) and consequently sediments are an important sink.

Another important chemical property of nonpolar organic pollutants is their affinity for other less-soluble organic phases. For example, the solubility of DDT in water is less than 10^{-4} g/L, whereas its solubility in vegetable oils, kerosene, and gasoline is approximately 10^2 g/L, and its solubility in benzene (another aromatic organic chemical) is approximately 10^3 g/L (NAS, 1971). The distribution coefficient of DDT between river oils and water is 1.5×10^6 (Hartung and Klingler, 1970). Consequently, there is a strong tendency for organic pollutants to become associated and accumulate with other organic phases, whether that be lipid or adipose tissue in organisms (Clayton et al., 1977), oils in sea surface films (Duce et al., 1972), dissolved or particulate humic substances in seawater (Boehm and Quinn, 1973; Pierce et al., 1974), or organic detritus in sediments (Bopp, 1979).

Sorption studies with nonpolar hydrocarbons have shown that the extent of sorption is directly related to particle surface area (increasing with decreasing particle size) and to the percentage of organic matter in particles (Hiraizumi et al., 1979; Pavlou and Dexter, 1979; Gearing et al., 1980). The extent of sorption can be modeled using a Freundlich isotherm that relates the amount of a substance sorbed (X) to the concentration of the substance in solution (c) and the mass of sorbing particles (m):

$$X/m = Kc^{1/n} ,$$

where K and n are constants that can be determined from the slope and intercept of the line connecting measured values of log (X/m) as a function of log (c).

At the air-sea interface organic compounds may adhere to form a coherent thin film. These films that may result from oil spills and discharges from industrial and municipal outfalls, as well as from natural causes, are often visible by their damping effect on capillary waves. Duce et al. (1972) found that concentrations of Pb, Fe, Ni, Cu, fatty acids, hydrocarbons, and halogenated hydrocarbons are enriched as much as 50 times in the top 100 to 150 um of Narragansett Bay relative to water 20 cm below the surface and suggested that the high metal concentrations reflect complexing with the surface-active organic substances. The extent that nonpolar hydrocarbons in this microlayer are aggregated into sinking particles, volatilized into the atmosphere, photochemically degraded, emulsified into the water, incorporated into organisms, or deposited as coating on eolian particles penetrating the sea surface is relatively unknown.

Biological Incorporation, Aggregation, and Cycling

Pollutant incorporation into biogenic particles, with subsequent organism migration, food chain transfer, or fecal pellet deposition, provides a rapid and ecologically important transport system in the marine environment. It has been well established that biological processes can concentrate nutrients, trace elements, and pollutants (Goldberg, 1957) and that biological cycles play an important role in controlling the distribution of these substances in the ocean (Turekian, 1968; Broecher, 1974; Brewer, 1975). Pollutant associations with organisms are a result of direct uptake from ingestion of sediment particles, organic-pollutant complexes or other contaminated food and passive sorption as water passes over gills, mucous layers, tests, or other exposed surfaces (Livingston, 1976). Bioassimilation varies depending on the chemistry of the incorporated pollutant. For example, hydrophobic chlorinated hydrocarbons (DDT and PCBs) are fat soluble and become associated with lipid tissues, whereas metals may complex with protein functional groups. Pollutants may be removed from the organism after assimilation by secretion or before assimilation by test molting or in the form of particulate fecal material.

Several investigators suggested that sinking biogenic particles (primarily fecal pellets) are important in removing nutrients, trace elements, and pollutants from surface sea waters and transporting them to greater depths in the ocean (Krishnaswami et al, 1976; Bishop, 1977; Lal, 1977). Bishop (1977) indicated that more than 98% of the mass flux through the upper 400 m in the equatorial Atlantic could be attributed to particles greater than 53 micrometers and Wiebe et al. (1976) found that even at depths between 2000 and 4000 m, fecal pellet fluxes were on the order of hundreds per square meter per day.

Harding and Phillips (1978) showed that phytoplankton can accumulate substantial amounts of PCBs from seawater. Elder and Fowler (1977) reported high concentrations of PCBs in fecal pellets from grazing zooplankton in the Liguran Sea, suggesting that sinking biogenic particles are important in transporting PCBs into the deep sea. Higgo et al.(1977) measured extremely high concentrations of plutonium in zooplankton fecal material and also suggested that pellets are an important vector in the vertical transport of plutonium in the ocean., Several other studies have indicated that biogenic particles may contain significant amounts of other trace elements and pollutants, including Cd, Ce, Nb, Zr, Po, Pb, Zn, Al, Fe, Mn, P, and petroleum hydrocarbons (Osterberg et al., 1963; Conover, 1971; Martin and Broenkow, 1975; Bacon et al., 1976; Grishnaswami and Sarin, 1976; Lal, 1977; and Bennett and Carpenter, 1979).

As these biogenic particles sink (following nutrient, trace element, and pollutant uptake in ocean surface waters), recycling of the organic matter occurs, leading to the regeneration of nutrients and to a release of some of the associated trace elements. This recycling (or oxidation of the organic matter) is most pronounced in the thermocline below the mixed layer (i.e., at oceanic depths between 400 and 800 m) and is identified by both a depletion in dissolved oxygen and by an increase in phosphate, silicate, and nitrate (Fig. 3.). Bacon et al. (1976) found that about 50% of the incorporated ^{210}Pb was regenerated in the water column as particulate organic material sank through the thermocline, whereas only about 5% of the ^{210}Pb associated with inorganic particles was recycled. Sclater et al. (1976), Boyle et al. 1977a, and Bruland (1980) demonstrated that the distributions of Cd, Ni, Zn, and to some extent Cu are strongly correlated with nutrient profiles in the ocean, indicating that the distributions of these metals are greatly influenced by biological cycling (Fig. 3.).

In shelf and coastal areas, where concentrations of suspended particles are considerably greater, the mass of pollutants incorporated into marine organisms and removed from the water by fecal pellets appears to be minor compared with the mass of pollutants removed by sorption onto

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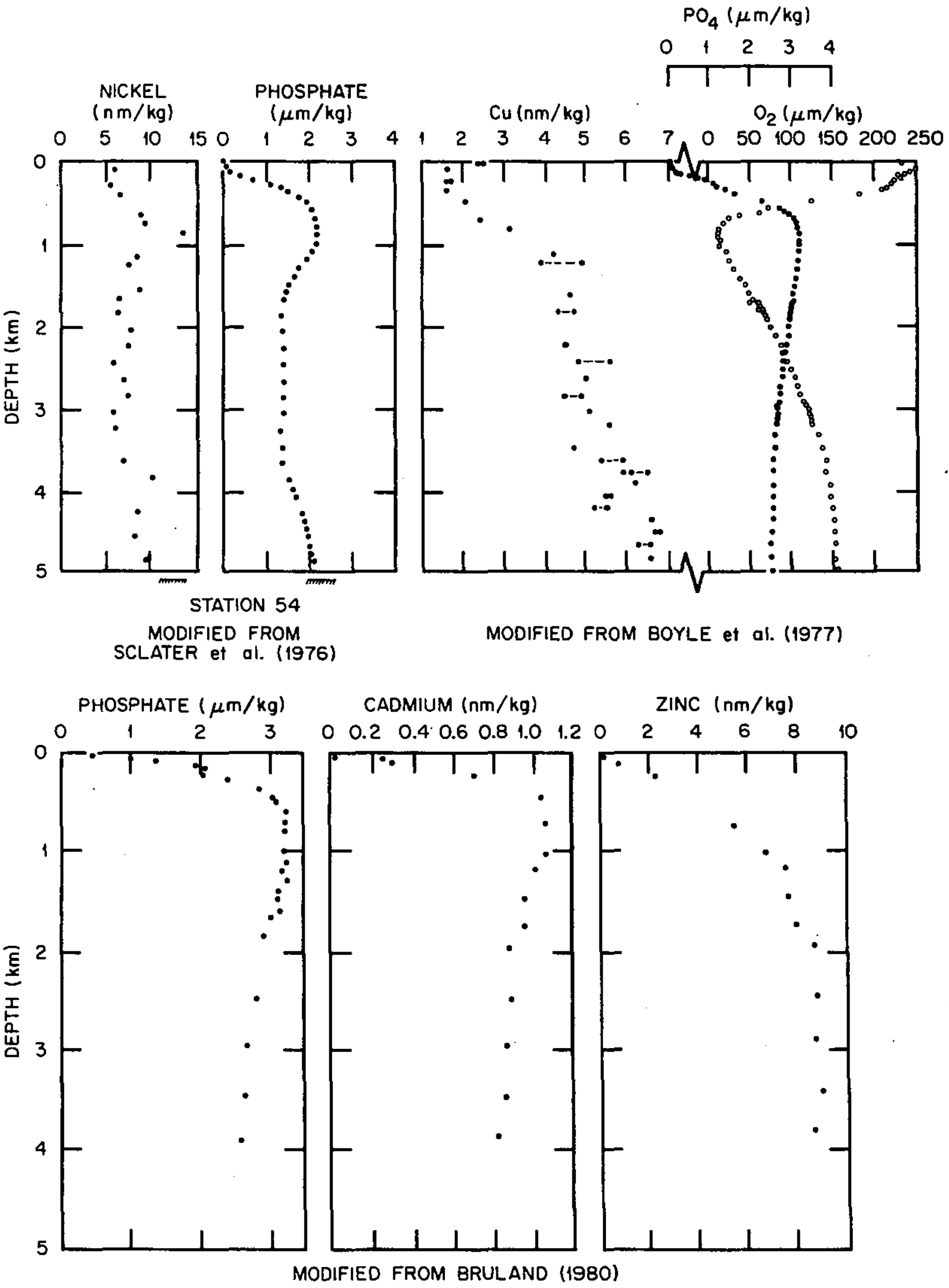

Figure 3. The distribution of dissolved Ni, Cu, and Zn and its correlation with nutrient (PO_4) and oxygen profiles in the ocean. These data indicate that the distribution of several metals is greatly influenced by biological cycling.

particles resuspended from the bottom (Li et al ., 1979). For example, Santschi et al. (1980) calculated that the removal rate of plutonium by zooplankton grazing in the waters of the New York Bight is 1.6×10^{-3} dpm cm^{-2} yr^{-1} (100 Bq cm^{-2} yr^{-1}, which is almost an order of magnitude less than the Pu removal rate ($7\text{-}14 \times 10^{-3}$ dpm cm^{-2} yr^{-1} or 420-840 Bq cm^{-1} yr^{-1}) calculated from ^{228}Th removal. This would agree with the laboratory results of Fisher et al. (1980) that live or dead marine plankton cells and glass beads accumulate Pu at similar rates, indicating that initial uptake was a passive phenomenon depending primarily on the concentration of particle surfaces.

Metal-Hydroxide Scavenging

Manganese, and to some extent iron, are important elements in geochemical cycles affecting pollutant-particle dynamics because (1) oxidation-reduction reactions are continually moving Mn and Fe in and out of solution, and (2) the precipitation-dissolution of Mn-Fe hydroxides is an effective mechanism for scavenging or remobilizing many elements and pollutants. Manganese and iron are readily liberated from host rocks during weathering, are quite soluble in their divalent (manganous of ferrous) form, and are, therefore, easily transported in water. In the presence of oxygen and a catalytic site (such as the surface of particles, colloids or preexisting Mn-Fe oxides), soluble divalent forms will oxidize and precipitate out of solution as hydrous Mn-Fe oxide coatings on particles or nodules.

Oxidation is an electrochemical process involving the loss of electrons from a chemical element. Similarly, the gain of electrons by an element constitutes reduction, since both processes involve the exchange of electrons, the potential (Eh) of a specific medium of oxidation or reduction can be measured and expressed in terms of millivolts. The effects of Eh and pH on the equilibrium stability fields of iron and manganese are illustrated in Fig. 4. The shaded area represents the modest range of the Eh-pH conditions in soils and surface sediments (Jenne, 1968). In reducing environments (low pH or Eh), manganese and iron can occur as soluable manganous (Mn^{+2}) and ferrous (Fe^{+2}) ions. In oxidizing environments (high pH or Eh), manganese and iron form relatively insoluble oxides and hydroxides (Fig. 4.). With changes in the environmental Eh-pH conditions,

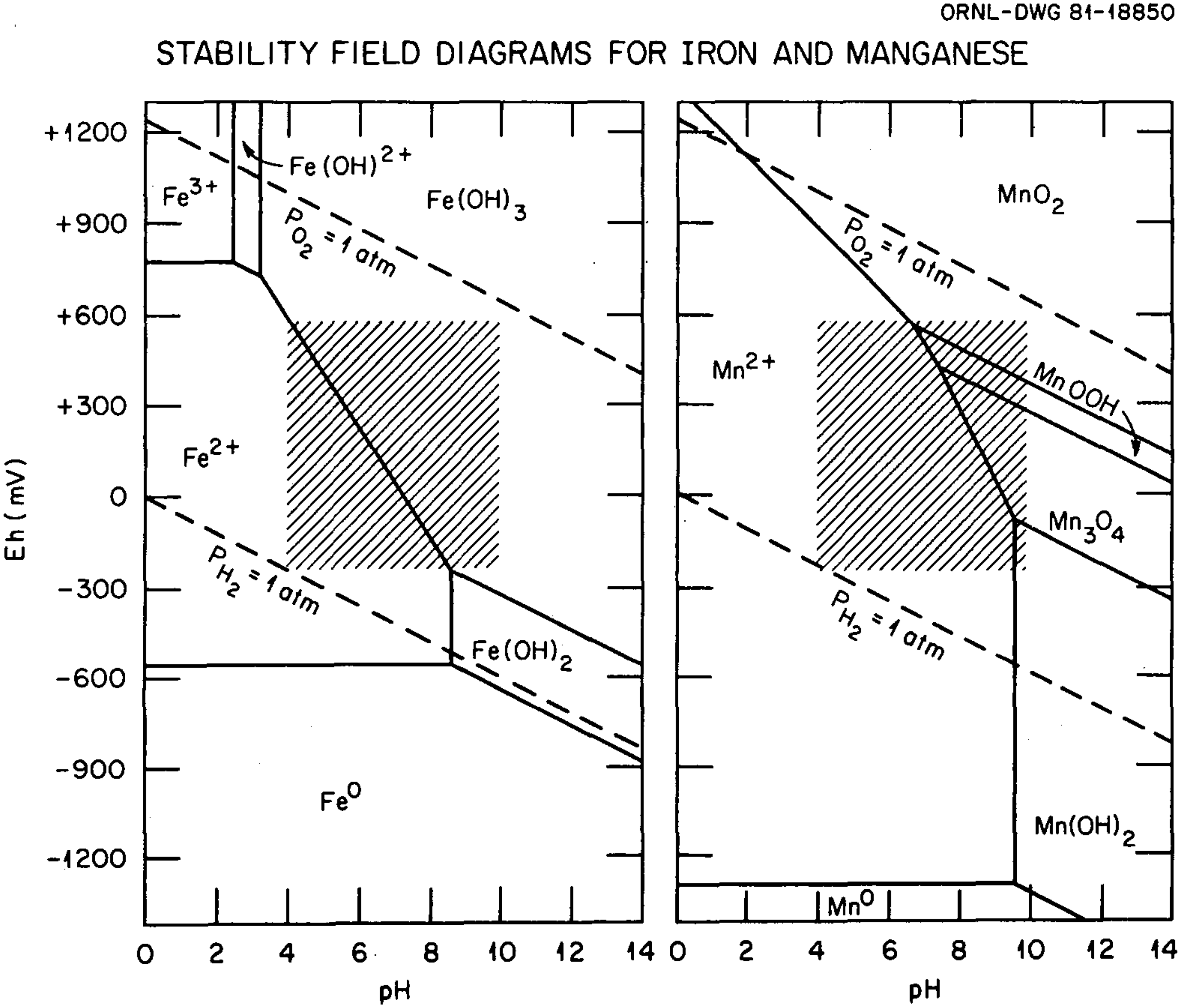

Figure 4. Eh versus pH stability field diagrams for iron and manganese ($a_{Fe,Mn} = 10^{-4}$ M; $pCO_2 = 0$; $P_{total} = 1$ atm; T = 25°C) as modified from Jenne (1968).

Mn and Fe can thus cycle between soluble and particulate phases. Such changes occur during transport from freshwater (pH ∿ 6.5) to seawater (pH 8) and after deposition from oxic water to anoxic sediments. For example, Evans et al. (1977) indicated that Mn may be reduced and released from estuarine sediments causing the concentration of dissolved Mn to increase in the water column. As this water is transported to the ocean, Mn is once again oxidized onto particles, giving rise to the elevated Mn concentration on coastal suspended matter. As the particles settle, particulate manganese may be transported back toward the river by estuarine circulation or deposited in shelf sediments where it may be reduced and recycled again.

Since freshly precipated Mn-Fe hydroxides act as efficient scavengers (by sorption or coprecipitation) for other metals, the cycling of these hydroxides may affect the dynamics of a wide variety of other elements and pollutants. Henne (1968), and Jenne and Wahlberg (1968) indicated that the ubiquitous occurrence of Mn-Fe as coatings, rather than discrete crystalline particles, allows Mn-Fe hydroxides to exert chemical controls on sorption that are far out of proportion to their concentrations and proposed that such coatings are the principal control for fixation of Zn, Cu, Ni, Co, radiocobalt, and plutonium in soils and freshwater sediments. Lewis (1977) showed that the precipitation of Mn-Fe hydroxides in the Susquehanna River system rapidly scavenges ^{210}Pb from solution, and Turekian (1977b) stresses the importance of Mn-Fe cycling in the removal of reactive metals from estuarine and coastal waters. In a classic study, Krauskopt (1956) indicated that adsorption by hydrated Mn-Fe oxides may be one of the most important mechanisms controlling the concentration of thirteen rare metals (An, Cu, Ni, Pb, Bi, Cd, Co, Hg, Ag, Cr, Mo, W, and V) in seawater. More recently, Spencer et al. (1981) suggested that the redox cycling of Mn and Fe hydroxides from reducing (organic-rich) sediments along the continental margins may cause these boundary areas to act as a sink for ^{210}Pb and other elements and thus exert considerable control on the minor element chemistry of the oceans.

Pollutant-Particle Transport

During recent years much attention has been devoted to the geochemical cycles that affect the dynamics of particles and associated pollutants in estuarine, coastal, and marine environments. The pioneering studies, in this respect, used radionuclides to trace water mixing (Bowen and Sugihara, 1960; Broecker, 1963; Osterberg _et al_., 1965), sediment transport (Sayre _et al_., 1963; Perkins _et al_., 1966; Pickering, 1969), and exchange processes between sediments and water (Aston and Duursma, 1973; Evans and Cutshall, 1973; Murray and Murray, 1973). In the Columbia River estuary, Perkins _et al_. (1966) found that (1) ^{46}Sc, ^{54}Mn, ^{58}Co, ^{59}Fe, ^{60}Co, ^{65}Zn, and ^{95}Zr-^{95}Nb were primarily associated with particulate phases, (2) ^{51}Cr, ^{106}Ru, ^{124}Sb, and ^{140}Ba were mainly in the dissolved phase, (3) the total radionuclide activity of the river increased when high flows resuspended bottom sediment, and (4) during this resuspension significant amounts of ^{46}Sc, ^{54}Mn, ^{58}Co, and ^{65}Zn were released.

In rivers such as the Mississippi, Yukon, and Amazon, where suspended-particle concentrations are high, Gibbs (1977) and Trefry (1977) showed that more than 90% of the total Fe, Mn, Co, Cu, Zn, Cr, and Ni loads are transported with particles. Sequential leaching studies have shown that most of these metals are in the crystal lattice of the particle (Fig. 5.) and that their input into the marine environment is a result of natural weathering processes. These lattice-bound metals do not appear to undergo any significant desorption from river particulates as they are transported across the freshwater-seawater interface (Trefry, 1977).

In more polluted rivers, however, appreciable quantities of Fe, Mn, Cu, Co, Ni, Zn, Pb,Cd, and Hg may be associated with metal-hydroxide coatings or organic phases (Presley _et al_., 1980). Metals associated with these phases can be released or remobilized from particles during organic decompositon or reduction of Mn-Fe hydroxide coatings. Such processes generally occur after the particles have been deposited rather than during their transport.

Hydrocarbons in water associate with suspended particulate matter in inverse proportion to their degree of aqueous solubility, with saturated

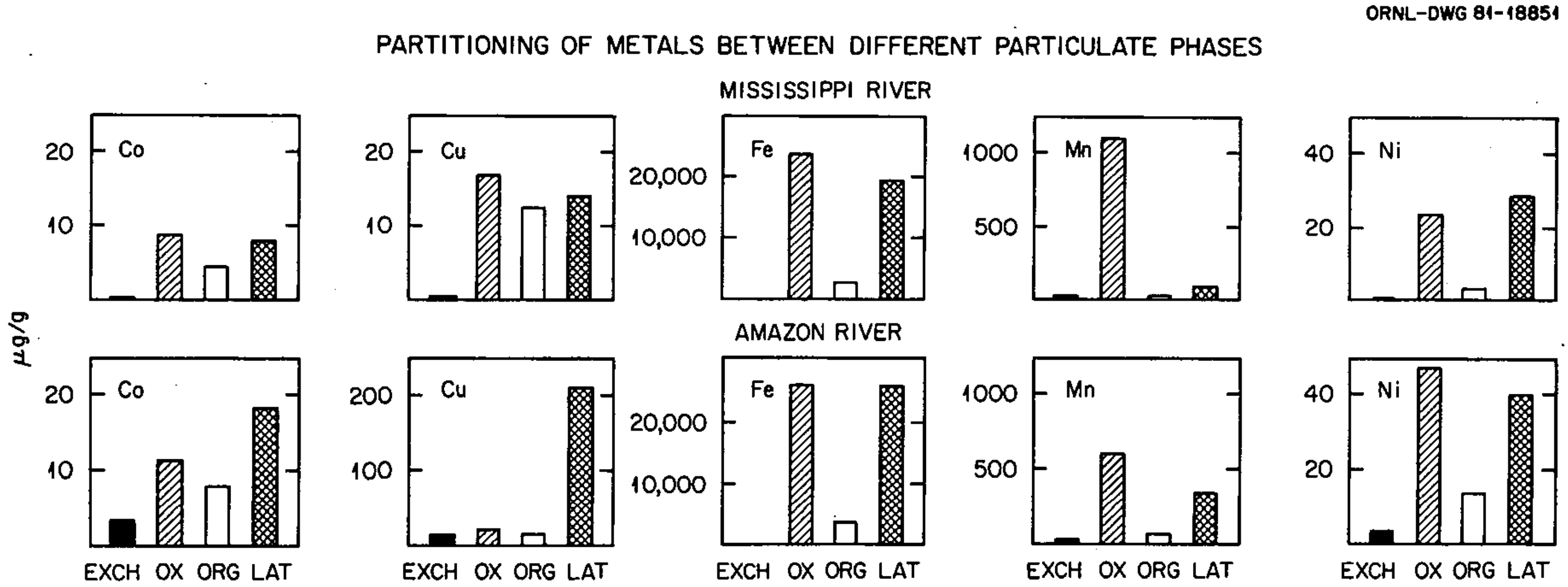

Figure 5. Distribution of trace metals between surface exchange, metal-hydroxide, organic and mineral lattice phases in the Mississippi and Amazon Rivers (modified from Presley et al., 1980).

hydrocarbons (n-alkanes) adsorbed preferentially over aromatics such as naphthalenes (Gearing et al., 1980). Studies in the Providence River, Narragansett Bay, and microcosm tanks of the Marine Ecosystems Research Laboratory have indicated that (1) approximately 90% of the saturated hydrocarbons are associated with suspended matter; (2) only about 10% of the aromatics are associated with suspended particles; (3) the particle-associated aromatics are skewed toward the higher molecular weight end with a depletion of benzenes and napthalenes relative to larger compounds; (4) as particle-associated hydrocarbons are transported down river, there is a loss of aromatic character due to solution in the water column; (5) the deposition of particle-associated hydrocarbons is the major transport pathway of oil to the sediments; and (6) microbial decay in the sediments causes a loss of saturated hydrocarbons leaving aromatics to predominate in deep sediments (Van Vleet and Quinn, 1977; Gearing et al., 1980).

Farrington (1980) indicated that the dumping of sewage sludge and dredge spoils is the primary source of hydrocarbons to shelf sediments in the New York Bight area. The extent to which dredge spoils and associated hydrocarbons are dispersed throughout this shelf area is still relatively unknown. Farrington and Tripp (1977) found, however, that the sediment concentration of petroleum and coal hydrocarbons decreases along the Hudson channel towards the edge of the shelf and suggested that the channel acts as a conduit or trap for hydrocarbon-contaminated particles. Hites et al (1980) also found anomalously high concentrations of combustion-generated polycyclic aromatic hydrocarbons (PAHs) in sediments of the Hudson Canyon. They suggest that the high concentrations reflect airborne movement of urban particulate matter to the ocean surface with subsequent particle transport to the canyon where accumulation occurs.

Although aerial transfer is also an important mechanism for the input of chlorinated hydrocarbons (PCBs and pesticides) into marine systems (Harvey and Steinhauer, 1976), once these compounds are in aquatic environments their dispersal and accumulation are primarily controlled by particle dynamics. Bopp et al. (1981) showed that the bulk transport of PCBs in the Hudson River estuary occurs during spring runoff or storm events that are characterized by high flow rates and suspended-matter concentrations. The highest concentrations of PCBs, DDT, and Kepone on

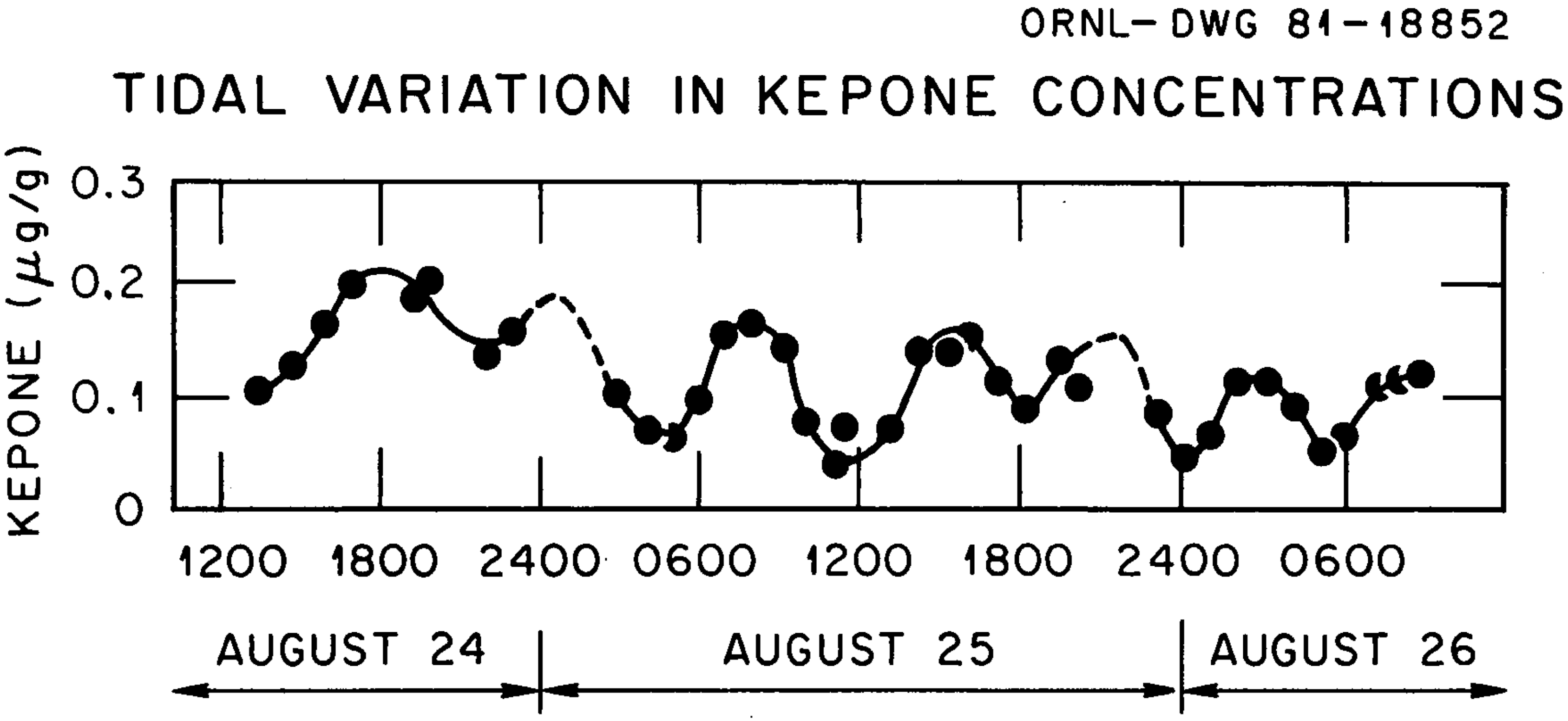

Figure 6. Tidal variations in the concentration of Kepone in suspended matter collected at one location in the James River estuary at 1 meter above the bottom. The maxima correspond to slack tides during which time mineral grains settle, leaving the water enriched with organic phases (taken from Huggett and Bender, 1980).

suspended matter, however, frequently occur during summer low-flow conditions and during slack tides. This is a result of the enhanced partitioning of chlorinated hydrocarbons to organic substance (Giam et al., 1976; Sayler, 1976; Hugget and Bender, 1980). These organic substances form a greater percentage of the total suspended-matter weight in the summer and during slack tides when inorganic particles settle out, leaving the water enriched in organics. Tidal variations in the concentration of Kepone in suspended matter at one location in the James River estuary were documented by Huggett and Bender (1980) and are illustrated in Fig. 6.

Studies in the Mississippi River also showed that variations in flow, current conditions, and biological activity can alter the composition (organic/inorganic ratio) of the suspended matter that, in turn, affects pollutant-particle associations and dynamics. An increase in the organic content of particulates (from less than 3% during high flow to 25 % during low flow) brought about a corresponding decrease in Al concentrations and an increase in particulate Mn, Zn, Cu, and Cd concentrations, indicating an association of these metals with organic substances (Trefry, 1977; Presley et al., 1980). In addition, Sholkovitz and Price (1980) showed that tidal and geographical increases in the P/Al, Si/Al, Ca/Al, Mn/Al, Mg/Al, and Ti/Al ratios of suspended matter in the Amazon may reflect increases in biogenic activity.

It is apparent from the above that significant temporal, vertical, and horizontal inhomogeneities can occur in the concentration and composition of suspended matter in estuaries and coastal marine environments, and consequently care must be taken to acquire representative samples for pollutant analyses. In general, bed loads tend to be overlooked in most sampling programs because the transport of most pollutants with the coarser bed load is probably less significant than transport with the finer suspended load (Carpenter,1976). In some cases, however, bed-load transport may be a major component of the total sediment transport, and if the bed sands are coated with Mn-Fe hydroxides or contain large quantities of organic-clay aggregates, pollutant transport with this load may be significant.

Pollutant-Particle Removal Rates

The disequilibrium between a highly reactive, short-lived radionuclide and its more soluble, longer-lived parent can be used to determine the rate at which biological, chemical, and physical process remove reactive pollutants from marine waters. In particular, two isotopes of thorium, ^{234}Th (half-life 24 d) and ^{228}Th (half-life 1.9 yr), have been used in this manner because they become rapidly associated with particles after their generation by radioactive decay of their more soluble parent nuclides (^{238}U and ^{228}Ra, respectively) in marine waters. If thorium were not rapidly removed from marine waters, it would exist in radioactive equilibrium with its parent; that is, the activity ratio of ^{228}Th/^{228}Ra, for example, would be approximately one. Actual ^{228}Th/^{228}Ra activity ratios average about 0.21 in open surface water, 0.016 in shelf surface water, and 0.010 in Narragansett Bay, indicating rapid ^{228}Th removal by settling particles in these waters (Broecker *et al.*, 1973; Li *et al.*, 1979; Santschi *et al.*, 1980).

This removal rate can be calculated from the model developed by Broecker *et al.* (1973):

$$\lambda_c = \frac{1-R\lambda}{R} t$$

where R is the measured ^{228}Th/^{228}Ra activity ratio, λ_t is the fraction removed per unit time. Frequently, the removal rate constant (λ_c) is expressed as the span of time required for the initial ^{228}Th activity in the water column to be reduced to one-half by settling particles. This half removal time (T_c) is related to the removal rate constant (λ_c) by the expression

$$T_c = \frac{\ln 2}{\lambda_c} \quad .$$

Li *et al.* (1979) showed that the half removal time of ^{228}Th (and by analogy other reactive pollutants such as plutonium) from surface waters by settling particles was about 185 ± 35 d in the open ocean, 70 ± 10 d on the slope, 28 ± 2 d in outer shelf waters, and 17 ± 1 d in inner shelf waters during the fall of 1974. In Narragansett Bay,Santschi et al. (1980) reported $^{228}Th/^{228}Ra$ activity ratios for Narragansett Bay ranging from 0.002 to 0.021 and corresponding half removal times ranging from 1.5 to 15 d. In addition, they determined that the settling velocities of Th-containing particles ranged between 1 and 11 m/d, that sediment resuspension was the main control on the removal behavior of thorium and that fast removal occurred when sediment resuspension was high.

Pollutant-Particle Accumulation

The large variations in pollutant accumulation patterns that occur in estuarine, coastal, and marine environments are primarily a result of variation in particle size, organic content, net deposition rates, and sediment mixing. The ability of fine particles and organic material to effectively scavenge pollutants from the water column has been discussed previously. This ability is enhanced by the fact that fine particles are more easily resuspended than coarser particles, remain in solution longer, and are swept across wide areas before coming to rest in an environment that is topographically or dynamically suited for fine-particle and associated pollutant accumulation. Such dynamically-suited places include the turbidity zone areas of estuaries (Hugget and Bender, 1980; Cutshall et al., 1981), behind dams or other objects that hinder flow (Olsen et al., 1981b), dredged or protected areas in harbors (Summerhayes et al., 1977; Olsen et al., 1978; Bopp, 1979), marsh or cove areas (Windom et al., 1976) or topographic lows on the shelf (Carmody et al., 1973; Farrington and Tripp, 1977; Freeland et al., 1979; Nittrouer et al., 1979; Olsen et al., 1980; and Bothner et al., 1981). Rates of net accumulation and sediment mixing may also be high in these localized areas, resulting in excessive pollutant inventories or burdens as well as higher pollutant concentrations relative to coarser-grained areas within the same environment.

Sayre et al. 1963 and Pickering (1969) showed that the distribution of radioactivity in the bottom sediments of the Columbia and Clinch Rivers, respectively, was primarily controlled by fine-particle accumulation. The distributions of trace metals and chlorinated hydrocarbons in the sediments on the Mississippi Delta and in the Gulf of Mexico was also governed primarily by sedimentary processes (Giam et al., 1976; Trefry, 1977). Hugget and Bender (1980) showed that the highest concentrations of Kepone

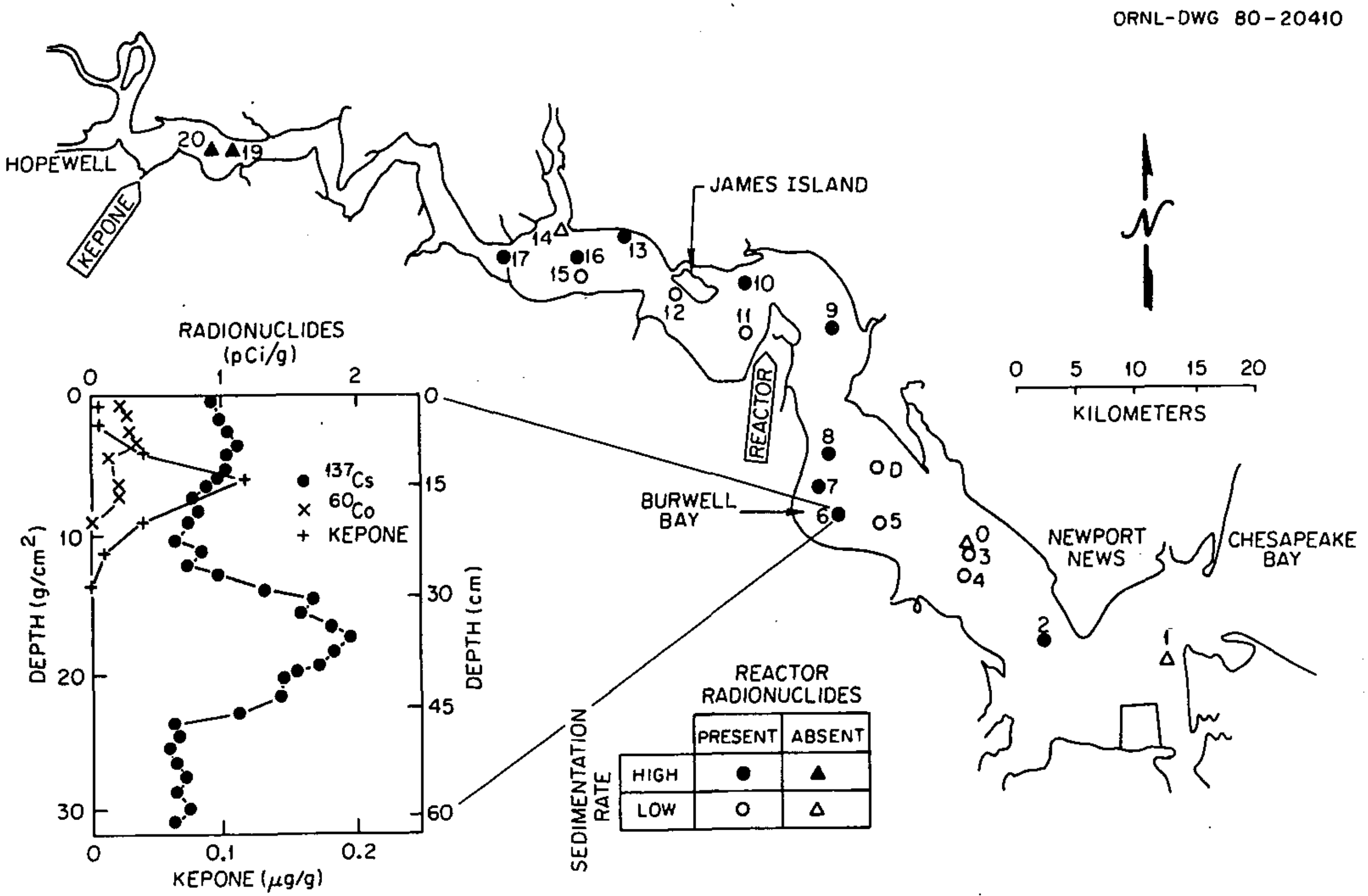

Figure 7. The distribution of ^{137}Cs, ^{60}Co and Kepone in a core collected in the James River estuary approximately 60 kilometers downstream from the Kepone source. These data indicate that estuarine sedimentary processes are causing rapid particle and Kepone accumulation in specific areas (taken from Cutshall et al., 1981).

in the sediments of the James River estuary were 15 to 60 km downstream from their source as a result of estuarine flow and the location of the turbidity maximum. Cutshall et al. (1981) showed that this area is also a zone of rapid sediment deposition (Fig. 7), and as a result Kepone contaminated sediments are rapidly being buried and diluted by uncontaminated particles. Similarly, Olsen (1979) showed that the major zone of reactor-released radionuclide accumulation in the Hudson estuary is not near the reactor site but is located more than 60 km downstream in New York's inner harbor where harbor dredging and estuarine processes are causing fine particles to accumulate at rates as high as 10 to 20 cm/yr. Particles and associated pollutants that escape an estuary appear to accumulate, with fine-grained material from other sources, in depressions along the shelf bottom (Olsen et al., 1980). These near-shore mud deposits, however, are suspended and dispersed by major storms (Harris, 1976; Freeland et al., 1979).

Physical or biological mixing of the sediments, in areas where net accumulation rates for particles are low, may also increase pollutant inventories or burdens and thus contribute to pollutant accumulation patterns. Aller et al. (1980) showed that in long Island Sound, where sedimentation rates are ∿ 0.1 cm/yr, ^{234}Th inventories can be increased in the sediments as mixing exchanges ^{234}Th-poor for ^{234}Th-rich particles of the overlying suspended material. Such a process may also be occurring in the large mud hole on the shelf off Massachusetts where Bothner et al. (1981) observed that the sediment accumulation rate is only 0.025 cm/yr but that the inventory of excess ^{210}Pb is twice as great as the atmospheric flux.

Understanding sedimentation rates in the marine environment is important for determining the ultimate fate of particles and associated pollutants as well as for ascertaining particle-pollutant fluxes and histories. Sedimentary cores represent a historical record of metal, radionuclide, and organic (both synthetic and natural) accumulation(Goldberg et al., 1977; 1978; 1979). Changes in the amounts and types of these pollutants are clearly evident with depth in the cores (Fig. 8.), due to both increased anthropogenic inputs and diagenetic reactions (reduction and mobilization, reduction and sulfide precipitation, and microbial degradation). Knowing the sedimentation rate, one can recognize preindustrial baseline distributions and date increases in contaminants that may suggest contaminant sources and transport paths (Carpenter, 1977). In addition, combining pollutant concentration analyses with radionuclide chronological data allows one to determine the rates of diagenetic processes that change pollutant distributions and calculate fluxes of pollutants to the sediments. Using such methods, Olsen (1979) has calculated that 45 ± 1.5 Mg of PCBs, 525 ± 175 Mg of zinc, and 405 ± 135 Mg of copper are annually accumulating with fine-grained sediments in the inner harbor area of New York, and ∿ 75% of the total zinc and ∿ 95% of the total copper burden are anthropogenic.

Pollutant-Particle Remobilization

As particles settle and accumulate, bacterial decomposition of organic matter (whether natural or anthropogenic) utilizes oxygen and recycles nutrients and other chemicals in biogenic detritus. In ocean waters, these metabolic processes primarily occur in, or just below, the thermocline, giving rise to a water layer depleted in oxygen but enriched in recycled nutrients and trace metals (Fig. 3.). In sediments, these biologically mediated reactions can change Eh-pH conditions which, in turn, can make some compounds, such as Mn, more soluble and other compounds, such as Cd, less soluble (Bender, 1976). Bacterial degradation of petroleum hydrocarbons, synthetic organics, or biogenic detritus may also form more soluble organic or organic-metal degradation products (such as methylmercury complexes) that are themselves harmful and that may escape from sediments to reenter aquatic food chains (deGroot, 1973).

The utilization of oxygen during organic matter decomposition can create anoxic conditions. Such conditions commonly occur in sediments but may also occur in the overlying waters where the bottom water is stagnant (fjords, for example) or where nutrient pollution has enhanced excessive phytoplankton growth. In anoxic sediments biologically mediated reactions may reduce carbon dioxide (CO_2) to methane (CH_4), nitrate (NO_3^{-2}) to ammonia (NH_3), sulfate (SO_4^{-2}) to hydrogen sulfide (H_2S), and some metals, such as iron and manganese, to more soluble divalent forms. As concentrations of dissolved metals, recycled nutrients, and other chemicals increase in sediment-pore waters, a vertical concentration gradient

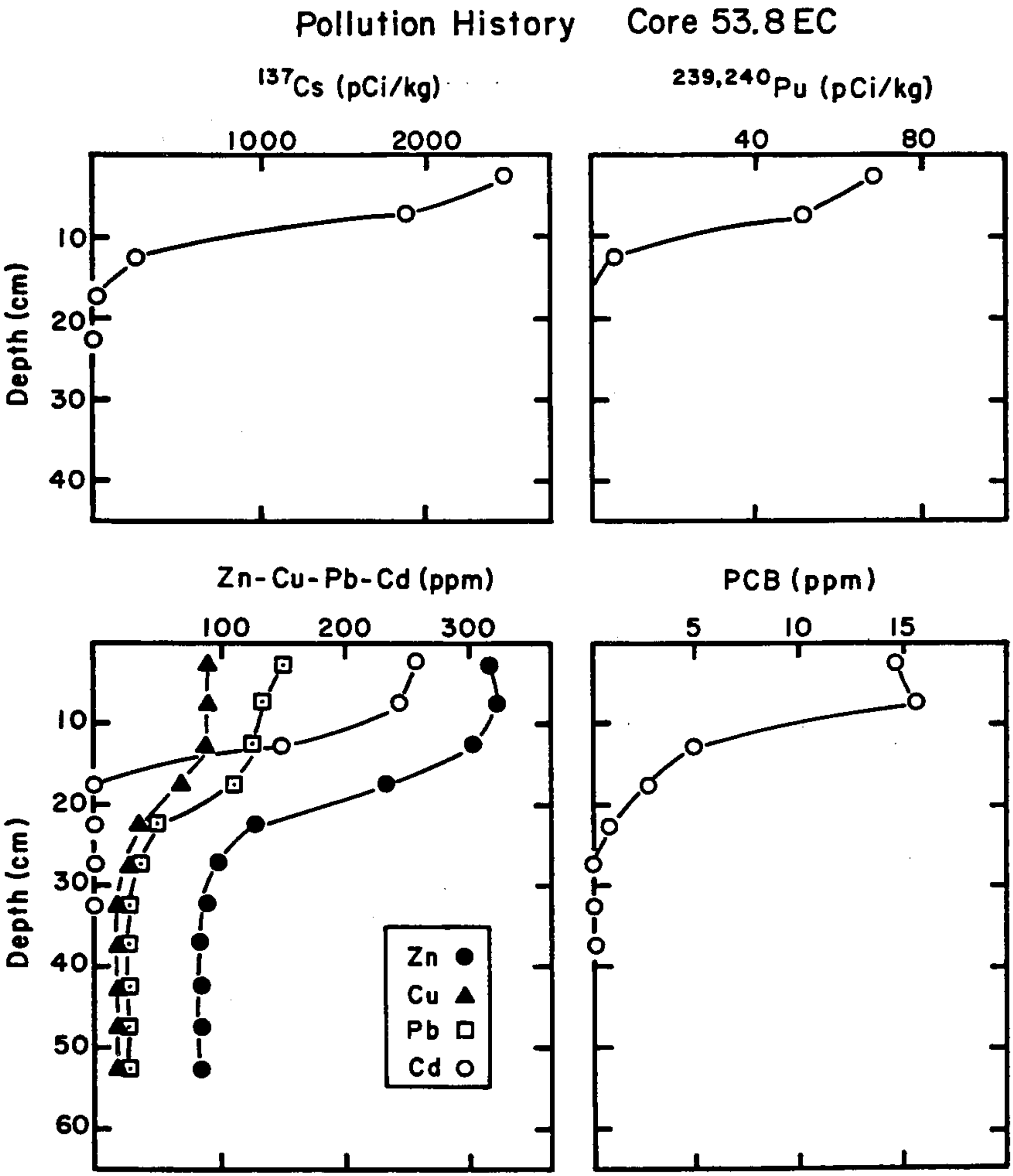

Figure 8. Vertical distributions of Cd, Cu, Zn, Pb, PCB's, ^{137}Cs and ^{239,240}Pu in the sediments of the Hudson River estuary. Despite the chemical's different properties and modes of input, their depth distributions are quite similar, attesting to the ability of fine particles to transport and accumulate a wide variety of reactive pollutants (taken from Olsen, 1979).

develops that allows for the diffusive remobilization of these substances out of the sediments and into the overlying water.

Work by Lynn and Bonatti (1969), Bender (1971), Bischoff and Sayles (1972) and Calvert and Price (1972) showed that solubilized Fe and Mn diffuses upward in sediment-pore waters and either reprecipitates in the more oxidizing sediments near the sediment-water interface or is released if reducing conditions persist too close to the interface. Although released iron is oxidized and removed from the water very quickly, the residence time of dissolved Mn^{+2} may be on the order of 2 to 10 days before oxidation and reprecipitation (Emerson et al., 1979). Graham et al. (1976) reported that the flux of dissolved manganese from the sediments to the overlying water in Narragansett Bay is about 1 to 2 $ug/cm^2/d$ and that manganese may undergo several cycles in and out of solution. Evans et al. (1977), Turekian (1977a) and Spencer et al. (1981) indicated that this redox cycling of manganese may play an important role in the sorption and/or release of other metals and pollutants. Olsen et al. (1981a) have shown that ^{60}Co may be released from New York harbor sediments in association with the release of reduced manganese, and Grieve and Fletcher (1977) showed that cycles of zinc in the Fraser River estuary correlate well with cycles of Fe and Mn.

In addition to diffusion, remobilization of pollutants across the sediment-water interface may also occur with sediment resuspension by currents (Bothner et al., 1980), bioturbation (Aller, 1978), or dredging operations (Lindberg and Harriss, 1977). For example, Lindberg and Harriss (1977) studied the mechanisms for mercury release from sediments in Mobile Bay and in the Florida Everglades. Under anaerobic and reducing conditions dissolved Hg (like Cd) may be immobilized by precipitation as an insoluble sulfide. Methylation of mercury into soluble complexes may occur, but concentrations of methylated mercury were so low in the sediment pore waters that the diffusive flux of this species was a relatively unimportant mechanism for Hg remobilization in these environments. Sediment resuspension by dredging, currents, and organisms, on the other hand, had a significant effect on Hg remobilization. Several other studies, including those of Perkins et al. (1966), Bothner et al. (1980, 1981), and Benninger and Krishnaswami (1981) also showed that sediment resuspension is a major mechanism for the remobilization of accumulated pollutants.

Finally, the dredging of estuary sediments and subsequent dumping of this dredged material in shelf waters was shown to be the primary mechanism responsible for the net transport of a wide range of particle-associated pollutants to the marine environment. Farrington (1980) estimated that 4 x 10^3 Mg of hydrocarbons (or ∿ 2% of the 1973 global discharge rate for production and drilling) are dumped each year into the New York Bight area. Bopp et al. (1981) estimated that 1.86 Mg of PCBs were also dumped into the New York Bight in association with dredge spoil disposal. Olsen et al. (1981a) showed that the Hudson estuary is an effective trap for plutonium and that harbor dredging is the primary mechanism by which riverborne plutonium is transferred to the shelf.

When dumped, pollutants can partition into a semifluid phase or a solid phase. The semifluid phase is typically retained in the water column for some period of time and may undergo advection from the dump site while the solid phase settles rapidly to the seabed (Joyce, 1979). In the New York Bight the dredge-spoil dump site covers an area of 35 km^2 and has a maximum height of about 14 m above the normal topography (Dayal et al., 1981). Fuhrmann and Dayal (in press) calculated that the rate of accumulation at the dump site ranges from 50 cm/yr near the apex of the deposit to 6 cm/yr at the periphery. Although no significant amounts of dissolved Zn, Cd, Cu, or Fe appear to be remobilized from the pore waters of this site, there is evidence of local resuspension and redistribution of fine particles and associated pollutants to the fringes of the dump site as a result of storms, tidal action, and the dump events (Dayal et al., 1981). Using acoustic profiling to trace individual dump events, Proni et al. (1976) demonstrated that there is an outward pulse along the bottom away from the dump event. This pulse was observed to reach velocities of 50 to60 cm/s providing a mechanism to erode and move particles and their associated pollutants away from the dump site.

SUMMARY AND NEEDED RESEARCH

Most of the reviewed studies concluded that many pollutants rapidly become associated with particles and that these particles are effectively trapped in the estuarine environment. This association may result from ionic sorption and flocculation (Edzwald et al., 1974) organic complexation and flocculation (Sholkovitz, 1976; Boyle et al., 1977b), hydrophobic interactions with particle surfaces (Parks, 1975), bioaggregation (Meade, 1972), or sorption and coprecipitation with Mn-Fe hydroxides (Krauskopf, 1956; Jennee, 1968). The net transport of particles and associated pollutants is downstream in the lower salinity surface layer of an estuary, but as these particles settle to the more saline bottom layer they may be transported back upstream and effectively trapped by estuarine circulation (Meade, 1972). Rates of particle-pollutant deposition in estuaries are generally high (Olsen, 1979), and particle-pollutant accumulation patterns are governed to a great extent by estuarine sedimentary processes. Although rapid burial in estuarine sediments provides a good mechanism for the removal of various pollutants from the system (Cutshall *et al.*, 1981), several processes, including sediment resuspension (Lindberg *et al.*, 1975; Bothner *et al.*, 1980), diffusion from anoxic sediments (Graham *et al*, 1976), and dredging-dumping operations (Dayal *et al.*, 1981) can reintroduce pollutants to marine waters.

Dissolved nutrients that may escape an estuary stimulate productivity in near-shore coastal waters and are rapidly removed by biological processes, frequently forming plankton plumes at the estuary mouth (Malone, 1976). Other reactive pollutants supplied to shelf waters by escape from the estuary, ocean dumping, or eolian transfer, will probably be removed within a month (Li *et al.*, 1979). Major removal mechanisms for pollutants in shelf waters include sorption onto resuspended sediments (Santschi *et al.*, 1980), incorporation into living organisms and sinking organic debris (fecal material and dead organisms), or boundary-layer scavenging in association with the redox cycling of Mn-Fe hydroxides (Bacon *et al.*, 1976; Spencer *et al.*, 1981). On the shelf, fine particles and associated pollutants accumulate in topographic lows such as depressions between sand waves (Freeland *et al.*, 1979; Olsen *et al.*, 1980), or in major morphological depressions such as basins (Trefry, 1977; Nittrouer, *et al.*, 1979; Dayal *et al.*, 1981), channels (Carmody *et al.*, 1973), or canyons (Farrington and Tripp, 1977). Net deposition, sediment mixing, and exchange with the overlying suspended matter cause these mud deposits to act as pollutatn sinks (Li *et al.*, 1979; Aller *et al.*, 1980; Bothner *et al.*, 1981; Benninger and Krishnaswami, 1981). The ultimate fate of this mobile pool, that is, what fraction is captured and buried in shelf sediments, what fraction is carried beyond the shelf to the open ocean, what fraction is returned to the estuary, and what fraction still resides in the mobile pool of particles and pollutants moving back and forth between the sediment and water column, is unknown. Consequently, our knowledge is still insufficient to predict how a specific pollutant will be transported through an estuary, across the shelf, and into the deep sea.

In light of the important role that particles play in the transfer and fate of pollutants, it is surprising that so little is known about the spatial and temporal variations in size, surface area, and resuspension of particulate matter in the marine environment. In particular, how do variations in freshwater flow, current regimes, biological activity, water stratification, and coastal morphology (resulting from changing tidal, meteorological, or seasonal conditions) affect particle characteristics and dynamics? What is the effect of activities like dredging and dumping on particle characteristics and dynamics? How do variations in salinity, temperature, pH, nutrient cycles, and metabolic processes affect particle characteristics and dynamics?

In addition, more fundamental research on the biogeochemical processes and mechanisms whereby pollutants are attached to or released from particles is needed to improve our predictive capabilities. Such research must consider selective association of specific pollutant types (Pb, Cd, Hg, PCBs, petroleum hydrocarbons, Pu, etc) with specific particle types (carbonates, clays, Mn-Fe hydroxides, detrital organics, in situ organics, humic functional groups, etc) and the effects of variations in salinity, temperature, pH, Eh, bacterial activity, etc., on particle-pollutant associations. Specifically, we need to know the quantitative distribution of each specific pollutant between particle types, the biogeochemical factors governing this distribution, and how that distribution would change given different chemical and environmental conditions.

Much of the previous work on particle-pollutant associations utilized bulk samples and bulk analytical techniques Such characterizations of the sample treated as whole (or in bulk) have advantages in that the data are of good analytical precision, are easily quantified, and can be used to observe statistical variations or correlation in pollutant or elemental abundances within and between different areas. More research, however, should be directed toward examining the surface morphology and surface chemical characteristics of discrete particles using scanning electron microscopy with an electron microprobe, ESCA, or EDXRF. Although it is more difficult to quantify results from these techniques, they have an advantage in that one can observe directly the nature of the particulate matter, associations of different particle types, chemical homogeneities along the surface which may result in large differences in chemical reactivity, and specific particle-pollutant associations (Nelsen, 1978)

Attention should also be given to the thermodynamical aspects of (1) pollutant solubility and fugacities (in the case of synthetic organics); (2) pollutant partition kinetics between particle, solution, and vapor phases; (3) complex speciations; (4) variations in solubility, fugacity, partition kinetics, and speciation with changing chemical and environmental conditions; and (5) the alteration of equilibrium by biochemical processes occurring in microenvironments, in organisms, and at interfaces. In all of the above cases, laboratory studies should complement field studies.

Finally, of prime importance in any predictive model is a quantitative understranding of the rates associated with the biogeochemical processes that affect pollutant-particle dynamics. These process-oriented transfer rates include input rates into the marine environment (river discharge, riverborne particle fluxes, eolian fluxes, pollutant input histories, and ocean dumping), exchange rates across the air-sea interface (aerosol deposition, sea spray, hydrocarbon volatilization, and gas exchange), transport rates in the water column (advection, diffusion, turbulent mixing, biological transfer, settling, degradation, and recycling), and transfer in and out of the sediments (accumulation, diagenesis, pore-water diffusion, sediment mixing, and resuspension). Quantitative values for the above transfer rates are necessary to determine particle-pollutant fluxes and to thus define how long a specific pollutant will persist in different parts of the marine environment. Only with such an understanding will it be possible to develop accurate pollutant transport models and to predict the fate of particles and their associated pollutants in the environment.

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BRIEFING DOCUMENT 3

MECHANISMS OF EROSION, DEPOSITION AND TRANSPORT OF COHESIVE SEDIMENTS IN THE BOUNDARY LAYER

CONTENTS

BRIEFING DOCUMENT 3

MECHANISMS OF EROSION, DEPOSITION, AND TRANSPORT OF COHESIVE SEDIMENTS IN THE BOUNDARY LAYER

Robert A. Young

INTRODUCTION

This chapter describes the past and present lines of research and our state of knowledge concerning the mechanics of erosion, transport, and deposition processes in the bottom boundary layer for cohesive sediments under the influence of marine currents and waves. Because of the strong adsorptive affinity of fine particles for many classes of metallic and organic pollutants, it is important to understand transport characteristics of cohesive sediments since they constitute a significant component in the marine food chain.

Incipient motion criteria and rates of transport of noncohesive marine sediments under steady currents and waves have been studied intensively for many decades. A reasonable body of theory and observation exists to model the main features of noncohesive sediment behavior (Graf, 1971; Yalin, 1977). Although the transport of fine-grained cohesive sediments has been studied for a like period, progress in our understanding has been much slower. A literature review by Einstein and Wiegel (1970) points out that most previous studies apply to freshwater where the effect of cohesion and flocculation is much reduced owing to the low concentrations of dissolved ions that cause interparticle attractions (e.g., Einsele et al., 1974).

Specifically, cohesion is the result of interparticle electrochemical attractions between clay mineral particles resulting from suppression of repelling surface charges when the particles are in a weak electrolyte such as seawater (van Olphen, 1963). A working definition of cohesion in marine sediments should also include the bonding of mineral particles with organic particles, the binding together of particles by the mucal secretions of organisms, and the modifications due to biogenic pelletization. Clay mineral cohesion and organic cohesion can, and probably do, coexist in most fine sediments on the shelf. There is little question that organic compounds are associated with clay minerals in marine sediments but the degree to which cohesive properties of these sediments are altered is not well understood.

The concentration and activity of cations such as Na^{+1} and Ca^{+2} in the sediment pore waters have also been shown to affect cohesion and erodibility of sediments (e.g., Sargunam et al., 1973; Mehta and Partheniades, 1973). However, changes in salinity and cation distribution in seawater are relatively small and well outside the range where such changes affect cohesion (Whitehouse et al., 1960; Hahn and Stumm, 1970).

Understanding of the fluid-particle interactions occurring during erosion, transport, and deposition is less developed than is desirable for adequate understanding of marine ecosystem dynamics. In this chapter, the relationships between chemical and biochemical processes and the mechanics of sediment transport will be described to the extent that they are known. It will be clear that this is a critical area of research which should recieve immediate attention.

EROSION AND DEPOSITION

Erosion Criteria

The threshold of sediment movement occurs when the frictional fluid forces in the boundary layer, represented by the bed shear stress, exceed the forces that hold the particle to the bed. For noncohesive particles, gravity acting through the submerged weight is the only force that must be overcome. Cohesive sediments are so fine-grained that their weight forces are negligible compared with the strength of their interparticle bonds.

Several studies have noted the need for inclusion of cohesive and adhesive parameters in erosion models (Young and Southard, 1978, Nowell et al., 1981). Cohesion appears to affect mainly erosion rates with marine muds eroding more slowly for a given bed shear stress than freshwater muds (Owen, 1977).

The threshold bed shear stress for erosion, τ_e, for noncohesive sediments is typically obtained from a Shields (1936) diagram which plots non-dimensionalized bed shear stress, θ_T, against the grain Reynolds number, (Figure 1). Shields's results were based on data from particles $>$100 μm in diameter. More recent work on cohesionless silts $<$ 100 μm (White, 1970; Mantz, 1977) has modified the shape of the

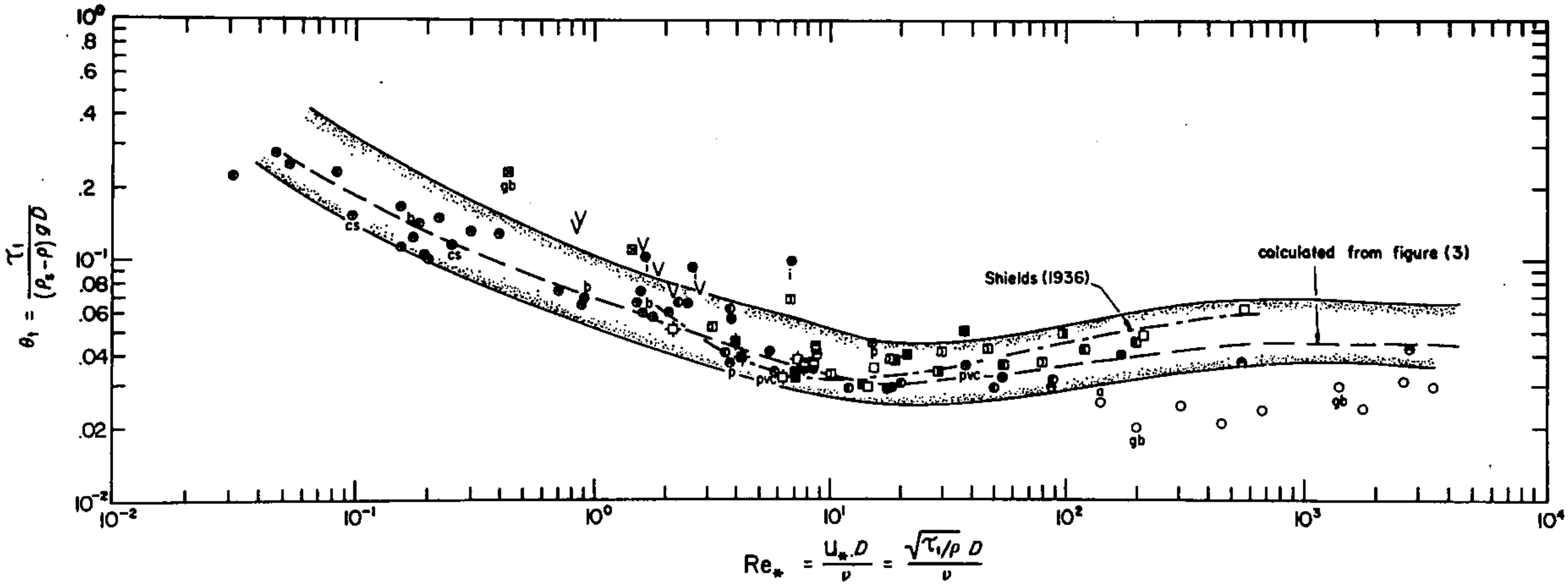

Figure 1. Shields diagram showing dimensionless shear stress θ_T required to erode flat-bedded noncohesive sands with grain Reynolds number Re_* (after Miller et al., 1977).

curve for fine sediments, showing θ_T to be much less than originally calculated by Shields on purely theoretical grounds. Figure 2 shows that these data smoothly join the previous data on threshold for sands and gravels (Miller et al., 1977).

The above experiments on fine cohesionless sediments were apparently aimed at understanding transport of azoic freshwater sediments where intergrain attractions are reduced. Salt water cohesion, adhesion between mineral particles and organic detritus, and biogenic modifications to the sediments once deposited significantly alter their resistance to erosion. However, it has been found that at least some fecal pellets produced by marine invertebrates behave like noncohesive sediments, and threshold conditions for their erosion can be determined using Shields's criteria (Figure 2). Organic detritus (leaf, stem and roots of marsh grasses), nominally of silt and sand sizes, also follow Shields's criteria (Fisher el al., 1979).

Sediment Physical Properties.--Many physical properties are related to cohesion and hence to erosion resistance. No single relationship has been found general enough for application under all flow conditions or for all types of sediments (Graf, 1971; Raudkivi, 1976).

Water Content.--Several investigators have shown good correlations between erosion velocities and the bulk water content of cohesive sediments (Postma, 1962, 1967; Southard et al., 1971; Lonsdale and Southard, 1974; Fukuda and Lick, 1980). However, Figure 3 shows that erosion velocities at a given water content vary widely among these studies (Southard, 1974), presumably because of differences in such factors as mineralogy, grain-size distribution, organic binding, age of the sediment, and methods used in preparing the beds for study (i.e., bed fabric).

Mineralogy.--Studies by Einselle et al. (1974) and Fukuda and Lick (1980) among others have demonstrated that mineralogy of the fine fraction influences erodibility in freshwater cohesive sediments. However, most studies cited here give incomplete information on composition, making comparisons between studies difficult. In those studies where composition was given in detail, other factors such as organic composition and content or bed preparation methods were unspecified and presumably have differed, again making comparisons difficult.

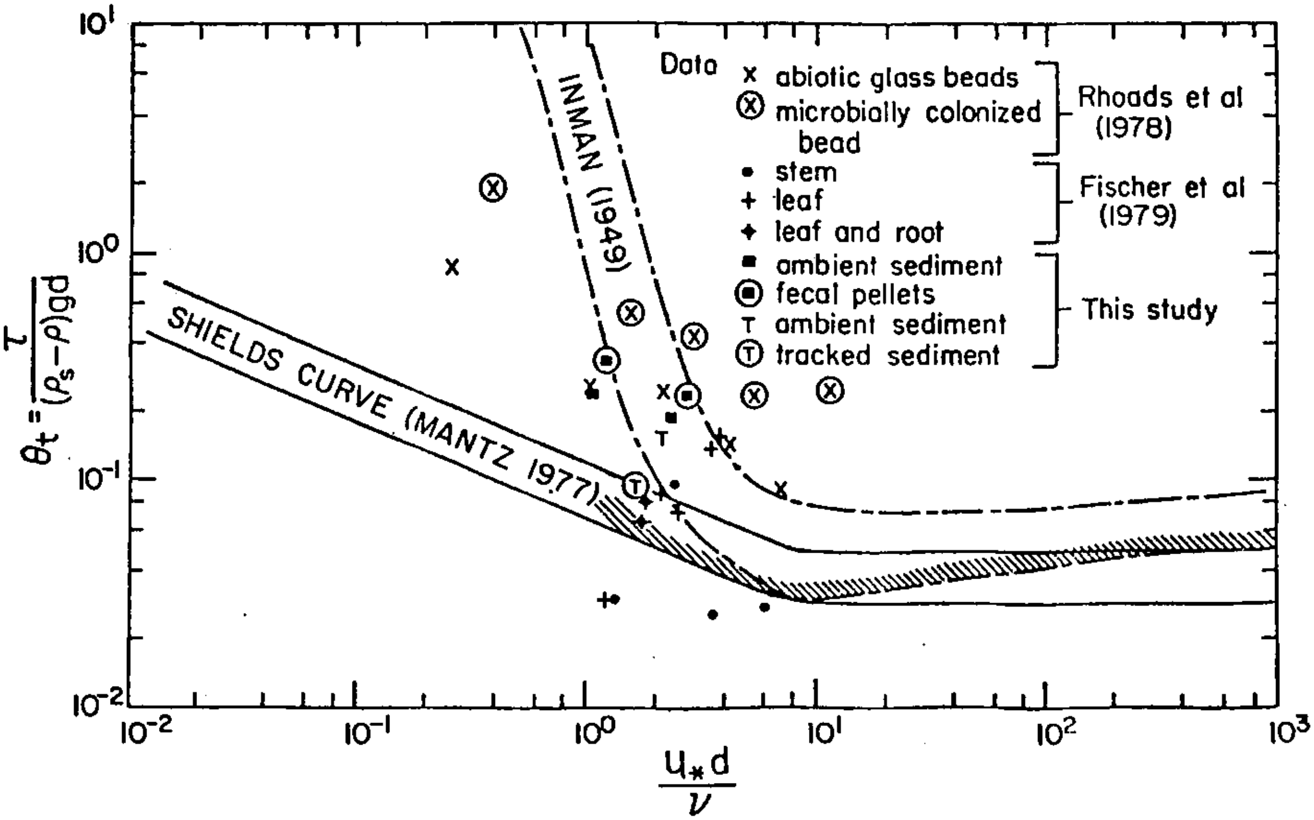

Figure 2. Shields diagram showing curves suggested by Inman et al. (1949) and Mantz (1977) for noncohesive silts and sands, biogenically modified slightly cohesive muds (Rhoads et al., 1978) and sands (Nowell et al., 1981) and a variety of organic detritus (Fisher et al., 1979). The hatched curve is the best-fitting curve suggested by Miller et al. (1977). From Figure 1.

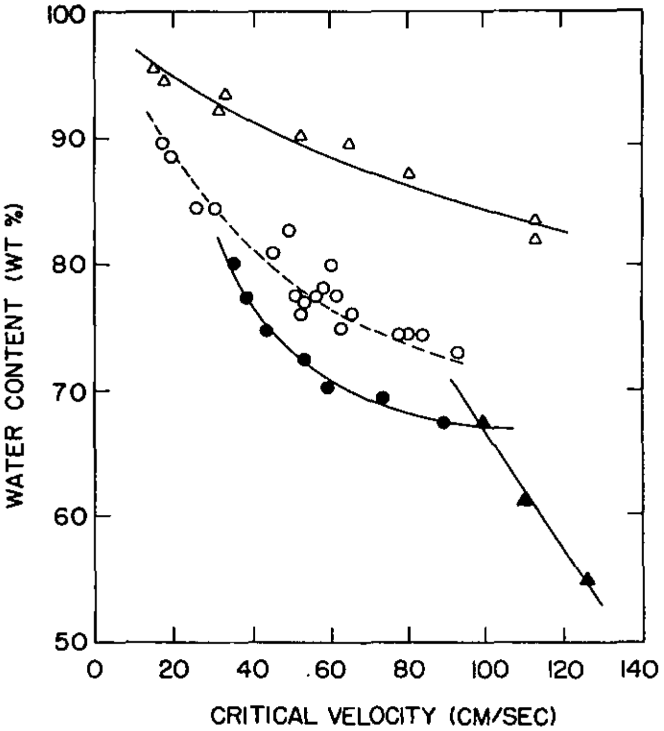

Figure 3. Erosion velocity of marine muds as a function of water content (from Southard, 1974). The different symbols indicate deep sea red clays (solid circles and triangles), and calcareous ooze with 25% clay minerals (open circles).

Age of Bed.--Some experiments have implicitly tested the hypothesis that age of the deposit affects erodibility. With aging comes changes in other factors such as water content (Figure 3; Southard et al., 1971; Young and Southard, 1978; Creutzberg and Postma, 1979) and possible changes in organic content or microbial activity, all of which affect cohesion and erosion resistance. There is also evidence that under some conditions the aging of the sediments does not affect erodibility (Partheniades, 1965). Age of the bed is therefore not a sufficient predictor of erosion.

Organic Content.--Little quantitative information exists relating organic composition or concentration to erodibility. The burrowing, feeding and pelletizing activities of larger organisms in coastal sediments is often quite vigorous, resulting in complete turnover or disturbance of the upper few tens of centimeters in periods of days or weeks (Rhoads, 1970). Fecal or other pelletized sediment (sediment-organic aggregates which are much lower in bulk density than their constituent particles) can be eroded at velocities much lower than the unpelletized muds surrounding them (Rhoads, 1970). Mucal secretions from molluscs and microbes are thought to bind sediments and increase cohesiveness (Rhoads et al., 1978). The effect of binding by organic detritus was examined by Young and Southard (1978) who demonstrated that erosion velocity increases with organic content (Figure 4). However, organic content as a parameter does not differentiate between living and non-living fractions, and made no distinction among various forms of biogenic bed modification. Effects of living benthic invertebrates on sediment transport are described in a later section.

Bingham Yield Strength.--The force required to break bonds between aggregates of cohesive particles is defined as the Bingham yield strength, τ_y. Krone (1963) has proposed a model that describes an ordered hierarchy of aggregate sizes and structures, proceeding from the lowest order represented by individual aggregates in equilibrium with the stresses generated in the surrounding turbulent fluid. Individual aggregates consist of cohesively bound particles. The next highest order of aggregate consists of two lowest-order aggregates, which have formed a cohesive bond having a strength somewhat less than the interparticle bonds in the lowest-order aggregates. Aggregates quickly lose their identity after deposition and compaction in the first few millimeters of the bed, but the

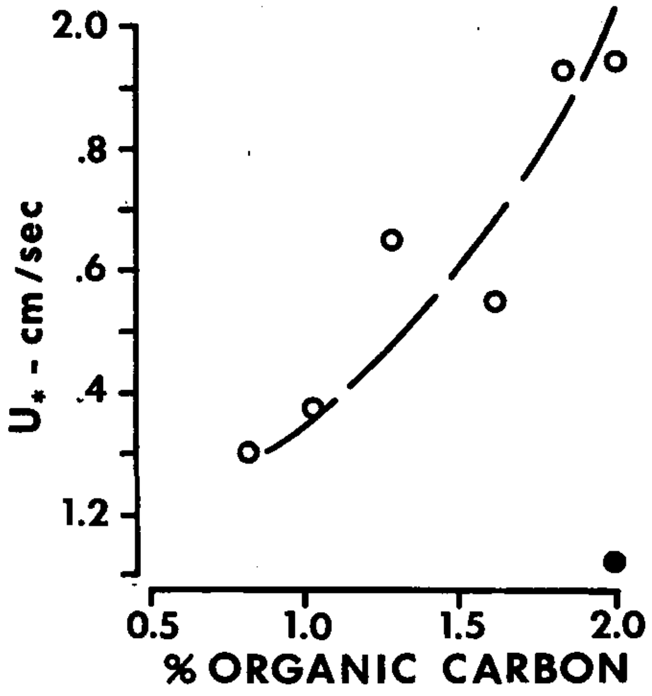

Figure 4. Laboratory flume experiments on threshold shear velocity u_* as a function of total organic content of a flat-bedded marine mud (from Young and Southard, 1978).

surface layer of a freshly deposited unreworked bed probably consists of these aggregates.

The yield strength, τ_y , of a suspension of aggregates has been studied by Krone (1963) and Migniot (1968) by forcing suspensions of aggregated sediments through a narrow capillary tube at various driving pressures. The rate of shearing turbulent flow in the tube at a given pressure is proportional to the shear stress necessary to break down bonds between various orders of aggregates. These experiments (Migniot, 1968, 1977) indicate that τ_y is well correlated with the critical shear velocity for erosion, $u_{*c} = (\tau/\rho)^{1/2}$ (Figure 5). Migniot's (1968) experiments included a variety of estuarine and marine sediments, but the results apply mainly to freshly deposited beds. Since these pioneering experiments there have been no further widely published accounts of the use of τ_y as an erosion parameter in the field. Lambermont and Lebon (1978) modeled cohesive sediments as visco-elastic solids and were able to use the empirical results of Migniot (1968) to develop a set of equations relating τ_y to u_* as a function of the sediment density distribution in the first few centimeters of the bed. Again, this model has received little attention, which is not consistent with its apparent ease of application to a number of marine sediment transport problems.

Field and Laboratory Measurements: Erosional Shear Stress

It is thought by many workers that erosion resistance changes rapidly with depth in the bed (Einstein and Krone, 1962; Partheniades, 1965; Migniot, 1968, Lambermont and Lebon, 1978; Young and Southard, 1978). While erosion rates at high excess shear stress may be large initially, they are observed to decrease rapidly to constant values in laboratory flume studies (Partheniades, 1965). This is interpreted as evidence for removal of aggregate layers whose shear strength is of the same order as the erosional shear stress, τ_e. In the laboratory, erosion depths were several centimeters over periods of several tens of hours. Thus, an argument is made for an increase in the cohesive strength between the sediment surface layer and the layers within a few centimeters of the surface.

Most sampling techniques (e.g., coring, grab sampling, dredging) mechanically disturb the sediment to such an extent that previous

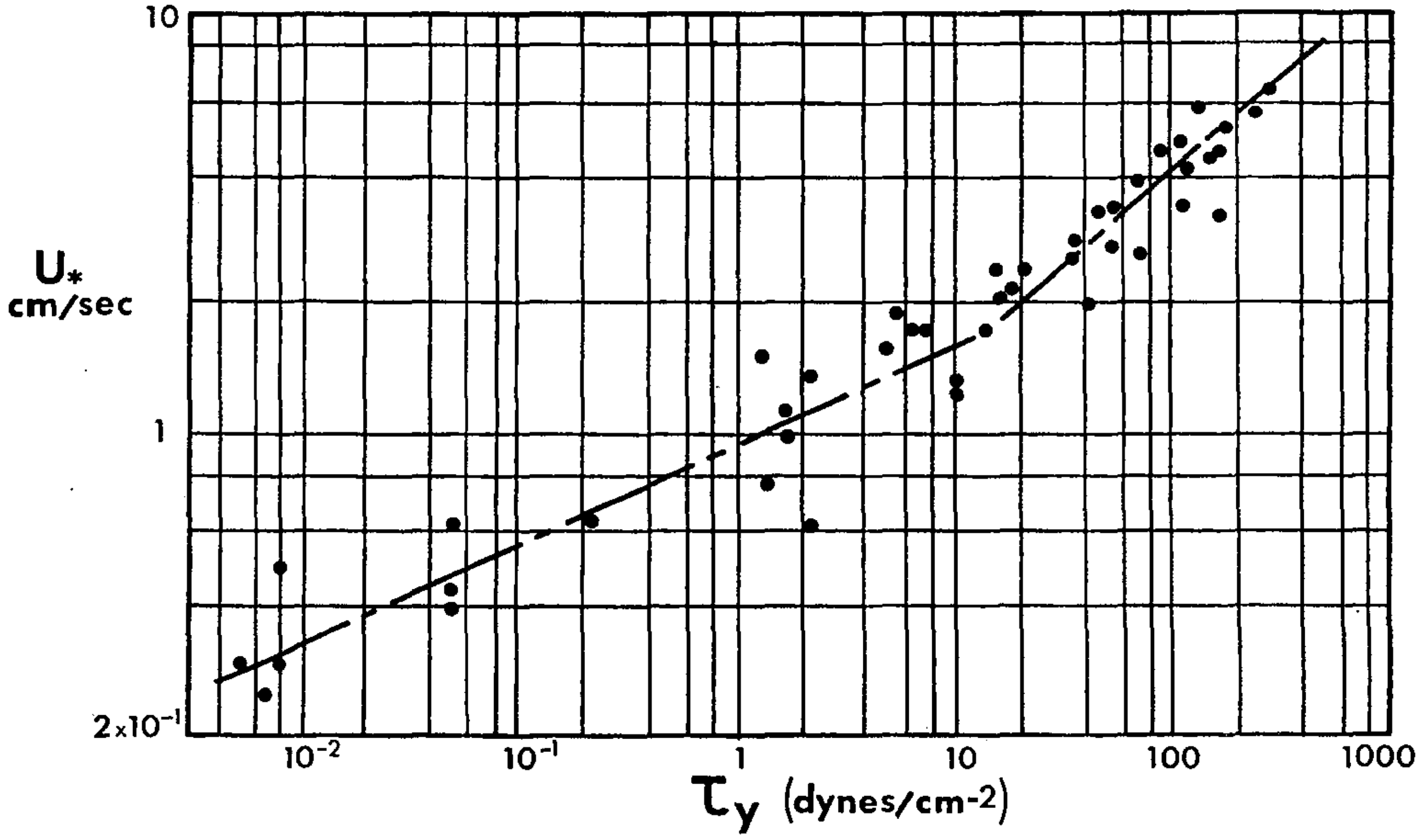

Figure 5. Threshod shear velocity for erosion versus the yield strength of the aggregated bed material (from Migniot, 1968).

structures and cohesive bonding are seriously altered. Even careful box-coring of the sediments cannot guarantee preservation of the in situ cohesive strength because of post-sampling changes in temperature and microbial activity (see following section on Organism-Sediment Interaction). In any case, there is no sediment parameter easily measured in situ and characterizing the bed surface that can be used to determine the effects of sampling on the sediment. Until such time as adequate methods are devised to reproduce a cohesive sediment bed in vitro as it exists in situ, other means must be found to compare laboratory and field studies.

An empirical comparison is possible by using the same erosion testing device on the seafloor as it is used in the laboratory. Neumann et al. (1970) described a simple flume channel placed directly on the seafloor to determine modes of erosion on algal-bound carbonate sediments. Pierce et al. (1970) made comparisons of the relative erodability of riverine and brackish water muds in the field and laboratory using a portable circular flume channel placed over the sediments in the field. The same sediments were brought to the laboratory, reconstituted by mixing and deposition, and re-eroded. Little difference was found between their erodibility in the field and in the laboratory.

Young and Southard (1978) used a seagoing flume with a straight channel to study mud erosion in a coastal marine environment. It was possible to estimate τ_e and u_* in this flume and make meaningful comparisons of these values with those obtained from laboratory flumes and measured in the tidal boundary layer. Erosional u_* values were found to be generally greater by as much as a factor of two in the laboratory flume. Reworking of the sediments by the ambient molluscan infauna greatly decreased the τ_e values in the laboratory after long reworking times, making them comparable with those measured in the field. Large variability in τ_e was observed between closely spaced sites in the field.

Temporal and spatial scaling of the boundary layer flow is a serious drawback in flume studies. Potentially affected are such important factors as turbulence intensity, concentration gradient effects on erosion (see below), and the rate of change in the mean flow of the flume. Improvements in technique and measurement instrumentation should remove some of these objections, while still retaining the speed and efficiency of the seagoing flume experiments.

Effect of Suspended Sediments.--Although the presence of suspended fine particles has been observed to reduce drag and alter the momentum exchange processes and velocity profiles in marine boundary layers (Gust and Walger, 1976), the effect on erosion is not clear. Partheniades (1965) found that erosion rates in a laboratory flume were not affected by variations in suspended load. Instead, he proposed that in open-channel flows a linear increase in concentration and depth of erosion would occur with time, completely independent of suspended load concentration, or

$$dC/dt = (1/d)\ M\ (\tau/\tau_e - 1), \quad \tau > \tau_e$$

Here, C is the depth average concentration of suspended load, d is the average water depth, τ_e is the critical bed shear stress for erosion, and M is an erodibility constant characteristic of the sediment (Partheniades, 1965). The obvious drawback in making practical use of this relationship is that it requires empirical (and therefore site-specific) detemination of M. This normally entails an in situ measurement, possibly of the sort yielded by the in situ flume experiments described above. It also appears to contradict the arguments advanced by Partheniades (1965), Lambermont and Lebon (1977) and others that erosion resistance increases with depth in the bed, which requires that erosion rates decrease with time for constant fluid discharge. Erosional roughening of the bed surface may help to produce higher local levels of turbulent shearing stresses at the bed and support the erosion of subsurface layers of more cohesive sediments. The exact mechanisms and modes of cohesive sediment erosion need more careful study before much more than empirical models of erosion can be advanced.

Deposition Criteria

Settling velocity and concentration of suspended particles are two of the main variables influencing deposition. At high concentrations, particles and their wakes interfere with each other, altering their settling speed and producing a condition called hindered settling. Settling velocities, w_s, of cohesive aggregates can be less in high concentration suspensions than in low concentration suspensions (Graf, 1971; Lavelle and Thacker, 1978), although the opposite effect has also been observed (Owen, 1977). Still-water values of w_s are usually used as an approximation to in situ values. Since the size and density of the settling aggregates depends on their structure under ambient conditions, values of w_s determined on reconstituted sediments under laboratory conditions are poor approximations to those in situ. A recent study by Ludwick and Domurat (1982) offers substantial insight into settling behavior of particles under turbulent flow conditions. Particles in the Stokes settling range ($\lesssim$ 2-10 μm) are generally unafffected by turbulence whereas empirical and theoretical studies indicate that settling rates for larger particles decrease as a function of concentration. Owen (1971) has measured w_s empirically for estuarine suspended sediments using the water sampling bottle in which the sample was initially obtained as a settling tube. If such work is done at sea, ship motion must somehow be prevented from shaking the tube during the analysis, and this seems to be the most difficult problem to overcome. Other techniques to determine w_s are under development and include use of a laser camera to photograph and produce holographic images of aggregates in rapid succession as they settle in the sea. Reconstruction of the holograms can provide a two-dimensional picture of the settling aggregate (Carder and Steward, 1980); distance traveled vertically per time interval between pictures gives w_s and will allow study of aggregate structures.

Threshold for Deposition.--Several workers (Einstein and Krone, 1962; Partheniades and Kennedy, 1966) have presented experimental evidence that critical depositional shear stress, τ_d , is less than the critical erosional stress τ_e or $\tau_d < \tau_e$. This difference apparently exists because interaggregate bonding in the bed surface layer is somewhat stronger than the bonds formed by aggregates momentarily contacting the bed during initial stages of deposition.

McCave (1970) suggests that for flows of low shear stress over smooth bottoms, suspended sediment that settles through the turbulent outer part of the boundary layer becomes entrapped in the sublayer flowing directly adjacent to the bed surface, the viscous sublayer. The sublayer is less turbulent or even laminar (Caldwell and Chriss, 1979), thus allowing fine particles with slow settling speeds to settle to the bed and deposit. Other boundary layer models and observations (Kline et al., 1967; Gordon and Witting, 1977) suggest that periodic disruptions of the sublayer occur where low velocity fluid is ejected from the sublayer and high velocity fluid from the outer layer is entrained. Sediment particles presumably take part in the process and thus apply to McCave's model.

Rate of Deposition.--McCave and Swift (1976) present a discussion of deposition rates in a marine boundary layer in which the earlier studies of Einstein and Krone (1962), Odd and Owen (1972), and Krone (1976) are summarized to express the mass rate of deposition as

$$dm/dt = -C\, w_s\, (1 - \tau/\tau_d), \quad \tau < \tau_d \quad .$$

This indicates that mass deposition is a function of the mean concentration of suspended particles, particle settling velocity and the deficit in shear stress below τ_d.

The existence of a single shear stress below which all deposition occurs applies only to suspensions of uniform size and w_s. Most real suspended sediments have a range of size, w_s, and hence τ_d values associated with them. This is reflected in the experiments of Partheniades and Kennedy (1967) who found that not all suspended particles were deposited when $\tau < \tau_d$ for the average particle size present. They also observed that greater deposition occurred in the clay-sized fraction of the suspended load than in the coarser silt fraction. From this they infer that the bonding strength and size of the aggregated particles may exert more control on deposition rate than does w_s. The influence of concentration and mineral or organic composition was not investigated.

Creation or destruction of aggregates in the turbulent boundary layer is also a possibility discussed by Einstein and Krone (1962). Greater concentrations nearer the bed and an increase in internal shearing rates as the velocity gradient increases will increase the rate of collisions between aggregates and modify their size distributions. Feely (1976) has recently found evidence for generation of larger aggregates from smaller ones in the nepheloid layer in the Gulf of Mexico. If the size and w_s distributions of the aggregates are a function of shearing in the boundary layer, deposition rates may differ considerably among boundary layer flows of different turbulent intensities.

Fine particles in the sea form aggregates either through flocculation or bioaggregation. The bulk density, shape and hydraulic behavior of aggregates have been the subject of much discussion, but only recently has detailed study begun. Kranck (1973, 1975) showed that aggregates from mineral-rich waters were composed of unsorted mixtures of particle sizes and that medium and coarse silts often occurred as single particles. Her later work showed that the modal size of the aggregates was related to the modal size of the disaggregated particles. When aggregates settle into the turbulent bottom boundary layer, they are subjected to shearing forces which may disrupt their structures and thus influence their settling velocity.

SUSPENDED SEDIMENT TRANSPORT

Several theories have been advanced to describe the distribution of suspended sediment in a turbulent boundary layer. All assume that the profiles can be described by the sediment diffusion equation and the Prandtl-von Karman boundary layer equations for steady flow. Vertical diffusion is parameterized by distance from the wall. All existing suspended sediment theories have at least one empirical coefficient, a near-bottom reference concentration usually located at the boundary between the bedload and suspended load layers. One of these theories (Smith, 1977, Smith and McLean, 1977a,b) is described in detail since it incorporates many of the recent ideas on modeling of suspended load. Although their model is meant to apply to steady river flows over mesoscale bedforms, it could ultimately be adopted for use in shelf sediment transport problems when more is known of the diffusivity due to interactions between the shelf mean flow and the wave-induced oscillatory flows (Smith, 1977; Grant and Madsen, 1978).

Other models (Taylor and Dyer, 1977; Soulsby and Dyer, 1981) have since been proposed for unidirectional flow which account for both bedload and suspended load transport over ripples and sand waves. One of these (Taylor and Dyer, 1978) concludes that stratification effects due to near-bottom suspended sediments are small in some cases, but all models need further verification for shelf sediment transport under combined wave and current flows, and for transport of cohesive sediments.

Diffusion Models.--Rouse (1938) is credited with first applying the sediment diffusion equation in a boundary layer. He assumed steady uniform flow and low concentrations. His solution results in a simple balance between particles settling under gravity and the vertical diffusion of particles under the influence of turbulence, or

$$w_s C + \varepsilon \, dC/dz = 0$$

where C is volumetric sediment concentration (fraction of unit volume occupied by sediment) at height z above bottom, and ε is a vertical diffusion coefficient for the sediment. An exact solution of this equation depends on how ε is expressed. Most workers agree that ε is dependent on z and shearing in the flow, but the exact form of that dependence differs among flow situations. Near the bed where $z \to 0$, the value of C(z) becomes infinite for all reasonable models of ε . Physically, the value of C(z) should not exceed unity.

By taking account of the volume occupied by the particles, Hunt (1954, 1969) was able to formulate a more general treatment of the diffusion equation, yielding solutions that have a finite value as z 0. In his later work, Hunt extended his results to suspensions having n size fractions by assuming that the sediment and water diffusion coefficients were equal, and that all sizes of sediment diffuse similarly. Hunt's equation is

$$\varepsilon \, \partial C_r/\partial z + C_r \left\{ w_r - \left(\sum^n w_r \, C_r \right) \right\} = 0 \quad ,$$

$$r = 1,2,3,\ldots n$$

where C_r and w_r are the concentration and settling speed for size fraction r. This set of equations also has solutions dependent on the distribution of ε.

In the constant stress region near the bed depends on friction and turbulence generated at the bed and distance from the wall, or $\varepsilon = \lambda z u_*$, where λ is an empirical constant (Hunt, 1969). Other workers have used the form $\varepsilon = k u_* z$ where k = 0.4 is von Karman's constant (Rouse, 1938), for the constant stress portion of the boundary layer. Other forms for the distribution of ε are described in Graf (1971), but in steady flow near the bed the effect on C is small. Hunt's λ can be thought to include von Karman's k and an additional factor β which is the proportionality constant between the water and sediment diffusivities. The value of β is thought to be near unity for fine sediments, and slightly less for coarser sediments.

The solution to Hunt's equations, corresponding to the constant stress region, is

$$C_r(z) = \frac{C_r(\alpha)\,[z/z(\alpha)]^{-\gamma_r}}{1 - \left[\Sigma C_i(\alpha)\,\{1 - (z/z(\alpha))^{-\gamma_i}\}\right]}$$

$r = 1,2,3...n$

$i = 1,2,3...n$

where $\gamma = w_r/\lambda u_*$ and α is a reference height above bottom. The above distribution of C_r can be summed over all r to obtain total concentration at any level z, or for the entire boundary layer. If velocity distribution u(z) in the boundary layer is also known or can be modeled, then the total transport is given by

$$\int_{\alpha}^{z_n} u(z)\; C(z)\; dz.$$

Agreement of Hunt's model with laboratory flume observations of suspended sand profiles is good (Figure 6). One problem inherent in the above model for suspended load distribution is the determination of particle concentration at the reference level . This requires at least one measurement of concentration close to the bed. Such measurements are difficult to obtain in practice.

Smith and McLean (1977a) assume that the size distribution at $z = \alpha$ is linearly related to the distribution in the bed. Their model also assumes that u_* is known for times when near-bed concentrations are large. In fact, neither theoretical nor empirical knowledge of the dependence of u_* on suspended load is adequate. While Hunt's assumption of equal diffusivity for particles and fluid is approximately correct for fine particles, Chien (1954) showed in laboratory experiments that for coarse particles the observed value of the exponent γ in Hunt's equation was smaller than expected by assuming $\gamma = w_s/ku_*$. A change in w_s due to the

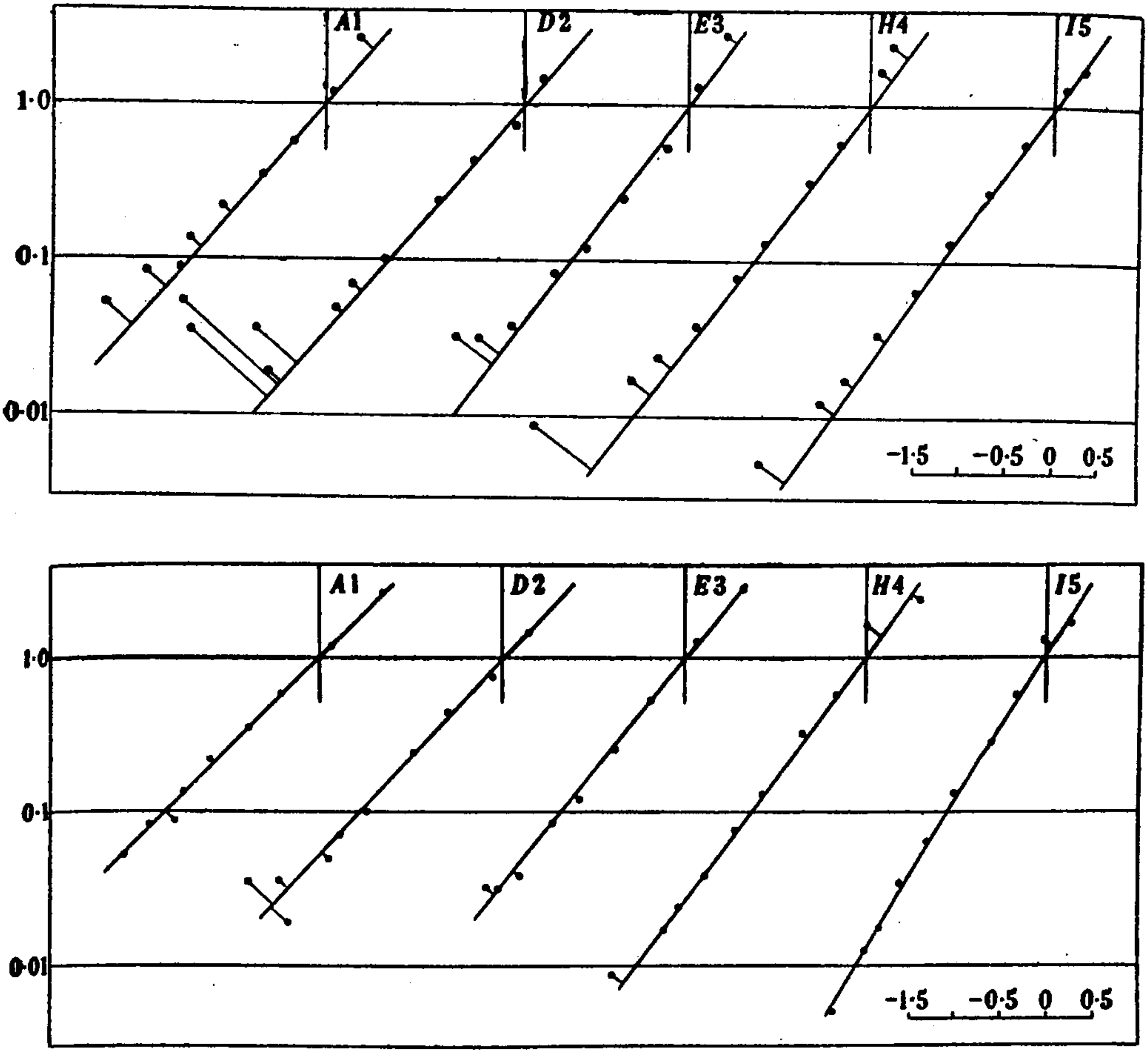

Figure 6. Suspended sediment profiles (lines) calculated from the models by Rouse (1938) (upper) and Hunt (1954) (lower) for monomodal grain size distributions plotted against concentrations (dots) from a series of laboratory flume experiments (from Hunt, 1954). The vertical axis is iverted such that $z_o = 1$ and non-dimensional height above bottom increases downward. The horizontal azis is $\ell n\ (C/C_o)$.

concentration-induced stratification may also serve to explain this observation (Smith and McLean, 1977b). It should be noted that the above results apply to noncohesive sediments. Other processes, described below, influence the settling behavior of cohesive fine sediments.

Boundary layer sediment transport theory (Yalin, 1977) indicates that total shear stress at the bed is a combination of form drag due to bedforms and skin friction due to the sediment particles. It is important to be able to separate these effects since sediment transport is proportional to the magnitude of the local shear stress. Recently, Smith and McLean (1977a, 1977b) have proposed a model for flow over bedforms which includes the effects of form drag and skin friction and the effect of flow stratification due to suspension and bedload. It is assumed that the flow can be divided into a series of internal boundary layers each due to successively larger classes of bed roughness and bedforms. The velocity and stress distributions in each layer (denoted by subscript n below) are given by the classical Prandtl-von Karman velocity profile equation for hydraulically rough boundary layer flow:

$$[u(z)/(u_*)]_n = (1/k)\ \ln(z/z_o)_n$$

where z_o is the point just above the rough bed where the mean flow velocity goes to zero, and k and u_* are as before. The height z_o is physically related to the bed roughness and possibly to the thickness of the bedload layer (W. Grant, personal communication). In the inner layer next to the bed, z_o is best related to excess shear stress, suspension-induced stratification, and bed grain diameter. In the outer layers the value of z_o, deduced from the velocity profile, includes form drag effects from the bedforms. In these layers z_o is also assumed to depend on the excess shear stress and on the bedform height and spacing.

Assuming that $(u_*)_n = (u_*)_{n+1}$ at the interface between the layers allows a solution of the equations by an iterative process which evalutes z_o and ε in the adjacent layers. Simultaneous solution of the suspended sediment profile, using an approach similar to Hunt's with $(u*)^n$ determined as above and assuming that a size distribution similar to that in the underlying sediments exists at $z = \alpha$, allows calculation of the verticle distribution of the sediments by size and concentration. Smith and McLean

(1977b) were able to obtain suspended sediment samples from a height of 10 cm above bottom that were in generally fair agreement with their predictions.

FLOW, SEDIMENT, AND ORGANISM INTERACTION

General

In this section the effects of organisms on sediment erodibility are discussed. Biogenic modification of the fine sediments is common on the shelf and may also be important at abyssal depths (Heezen and Hollister, 1971). Such effects are often overlooked, largely because of the lack of suitable observations.

Types of biogenic activity that modify sediment and flow include lateral and vertical burrowing, deposit feeding, and filter feeding from near-bottom suspensions. Each type of feeding and associated metabolic activity has an effect on the physical properties relating to cohesion and hence to sediment erodibility. It is important to note that existing suspended and bedload models (Yalin, 1977; Smith, 1977) do not include the effects of biogenic modification.

Biologic mediation of sediment transport seems most important in determining erosion threshold velocities and rates of erosion; it seems least important during active transport. Deposition rates may also be biologically mediated but other sediment and flow variables are likely to be of equal importance.

Modification of Sediment Properties

Cohesive binding of sediments can arise through interparticle attractions or through organic glueing. Creation of tubes by worms and the mucal trails left by gastropods or bivalves are examples of mucal binding. Byproducts of bacterial metabolism include mucal slimes which can bind surface layers of sediments and increase erosion resistance. Rhoad *et al.* (1978) report increases of 25-40% in the critical erosion velocities in flat beds of silt and sand-sized silica beads over periods of 3-15 days after bacterial cultures were introduced into the sediments. Microbial degradation of organic detritus is ubiquitous in the marine environment.

Pelletization of sediments by deposit-feeding polychaete worms and bivalves serves two functions. While bulk density of the sediment is reduced owing to increased porosity and bulk water content, the settling velocity of pellets may be significantly less than for a mineral grain of similar size (Rhoads, 1974; Haven and Morales-Alamo, 1972; Rhoads, 1973). Deposit feeders are thought to be more important than suspension feeders in pelletizing surface sediments. The presence of one type of organism usually signifies the absence of the other (amensalism). In some marine muds fecal pellets can form 100% of the bed surface deposit in the first 1-2 cm of the surface layer (Rhoads, 1970; Rhoads and Young, 1970).

Water Content.--Bioturbation, or the reworking of sediments by burrowing or deposit-feeding organisms increases the porosity and bulk water content (Rhoads, 1970, 1974). Increase in water content is one factor responsible for decreasing erosion velocity (Postma, 1967) but only if organic binding is negligible.

Biogenic Effect on Flow

Bed Roughness.--It has long been recognized that fecal pellet production and grazing increase the hydrodynamic roughness felt by the boundary layer (Rhoads, 1970). The increase in roughness is accompanied by a decrease in the critical erosion velocity. Trenches plowed by surface grazers, protruding worm tubes, and fecal mounds also increase the local roughness causing increased near-bottom turbulence and an increase in resuspension. Laboratory and field experiments have demonstrated these effects qualitatively (Rhoads, 1970, Young and Southard, 1978; Nowell *et al*., 1981).

Nowell *et al*. (1981) observed an increase in the bed shear stress for erosion in a laboratory flume when sediments were pelletized and built into mounds. Rhoad's previous observations indicated a decrease in erosional velocity for pelletized sediments created by a different group of infauna in a shallow marine embayment. Nowell *et al*. (1981) also observed that the tracks and feeding trenches left by grazers were less easily eroded than surrounding sediments, presumably because of mucal binding. This was also observed by Young and Southard (1978) who noted that the walls and levees of the trenches were eroded at lesser velocities than the floors of the tracks.

As with other types of bed roughness the aerial density of the biogenic surface features determines to some extent whether they will induce erosion or deposition on the bed. At low densities individual mounds or worm tubes accelerate the low flow and can cause scour. At high densities these same roughness types may induce deposition by providing sheltered microenvironments with lower turbulence levels and lesser velocities. This is analogous to the suggestion by Einstein (1962) that coarse particles in a finer matrix tend to shield the finer particle from resuspension by turbulent eddies larger in scale than the spaces between the coarse grains.

Clearly, more work is needed to fully understand and quantify the effects of biogenic modification. One goal of such research must be to determine if biogenic effects are species specific and what the range of such effects are in determining the erodibility of the sediments.

Suspended Load and Biodeposition.--As noted above, biogenic roughening of the bed surface may decrease the threshold velocity required for erosion. These same roughness elements may act as initial sites of deposition, also described above. Deposits on the lee side of erosion resistant mounds or worm tubes, or lee drifts, are formed by much the same mechanism. While the flow is accelerated on the upstream face of the mound, so long as the local bed shear stress is below the critical value, no erosion takes place. If the flow is carrying a suspended load, deposition is induced in the lee of the mound where the local velocity is reduced because of formation of a local adverse pressure gradient.

It has long been assumed that ejection of sediments into the boundary layer by benthic invertebrates could constitute a significant source for suspended sediments (Heezen and Hollister, 1971). Settling velocities of fecal pellets generally compare with those of quartz silt or sand (Haven and Morales-Alamo, 1972; Nowell et al., 1981). Ejection of fecal material can contribute to the suspended load but only when settling velocities of the pellets are small. More typically, pellets are found deposited around the burrow openings, skewed in the direction of the prevailing current. The mounds can be either more or less resistant to erosion than surrounding sediments, depending on the strength of the mucal binding and to some extent on the grain size of ingested particles (Nowell et al., 1981). Size shape, bulk density and strength of fecal pellets seem species specific (Kraeuter and Haven, 1970) so no broad generalities on their erodibility are possible at present.

MODELING

Most models of transport deal with some aspect of the erosion or deposition process, and not with regional transport. Because the understanding and modeling of erosion processes is still in an early state of development, it is not surprising that application to regional problems produces results that only roughly correspond to regional sedimentation patterns. However, in many cases, mapping of trends or qualitative results is sufficient since the understanding of pollutant-particle interactions is also in an early stage (Olausson and Cato, 1980).

The most critical flow parameter for sediment erosion (bed shear stress) is difficult to obtain by direct measurement because it involves observations or models of the velocity profile or turbulence very close to the bed (Taylor and Dyer, 1977). Hence, boundary layer models must first be developed that take into account the many complicating factors such as non-planar topography (Smith and McLean, 1977), accelerating flow (Soulsby and Dyer, 1981), wave-current interactions (Smith, 1977; Grant and Madsen, 1977), biogenic disturbances (Nowell et al., 1981; Jumars et al., 1981), suspended-sediment induced stratification (Smith and McLean, 1977; Soulsby and Dyer, 1981), and cohesion of fine sediments (Owen, 1977).

Even if adequately tested boundary layer models were available they would need to be coupled with regional circulation and/or interior flow models (Allen, 1980; Winant, 1981; Weatherly, 1978) which are also under development.

Some progress has been achieved recently in shelf modeling because of the acquisition of long-term observations of shelf flows in the New York Bight (Mayer et al., 1979; Han and Mayer, in press). However, the nature of the current observations (Savonius rotors for the most part) precludes the inclusion of wave and wave-current effects, and the resulting regional models describing bedload transport in the New York Bight (Vincent et al., 1981; Clarke et al., 1981) lack quantitative accuracy although they do reflect observed regional trends.

Numerical engineering models of transport under simple conditions are somewhat more successful (Odd and Owen, 1972) but usually expensive and not generally applicable.

Needs for future modeling research include further basic research in turbulence, boundary layers under waves, current and combined flows, and on the description of suspended and bedload transport processes, particularly in the presence of topographic or biogenic disturbances. Field work requires complex and expensive measurements over long time periods, but must be undertaken to verify boundary layer models.

POLLUTANT TRANSPORT AND BOUNDARY LAYER INTERACTION

Several recent reviews have discussed the interaction of dissolved trace metals and organic pollutants in estuaries and nearshore marine environments (Olausson and Cato, 1980; Burton and Liss, 1976). Duinker (1980) in particular has pointed out the complex relationships among the mineral particles, organic detritus and dissolved metals and organics. One major conclusion reached by Duinker is that only trace metals that form strong anionic complexes are likely to be discharged from the estuary in dissolved form. Particles play the dominant role in transport of trace metals through adsorption.

Dissolved trace metals and synthetic organics are two pollutant groups perceived as most threatening to humans. Because these substances are only slightly soluble in seawater they tend to become adsorbed onto fine-grained mineral particles (< 62 μm) and organics detritus. Adsorbtion reactions are relatively fast (minutes to hours). Thus, physical processes that resuspend or introduce fine particles into the ocean waters can be classified according to the length of time the process tends to keep the particles in suspension or at the sediment-water interface.

Physical processes that tend to produce deposits of fine particles are often mediated by infaunal activity, and sediment is reworked more or less continuously by the biota during non-storm periods. This serves several functions, the first of which is to homogenize the distribution of particles and hence pollutants in the reworked zone. Secondly, reworking tends to keep the surface layer well oxygenated, thus maintaining aerobic diagenetic reductions of organic detritus by bacteria. Diagenesis also releases some pollutants into the pore fluids where they may be released back into overlying waters either by diffusion or by erosion processes. Erosion processes affecting the reintroduction of particles and dissolved pollutants include aperiodic high-energy events (storms, high-velocity tidal flows), and low-energy events such as weak tidal and wind-driven waves and currents and injection of fecal pellets and pseudo-feces by infaunal organisms. Burrowing and grazing activities may also tend to destabilize fine sediments and make them susceptible to low-energy erosion processes.

Once resuspended, fine particles, with their characteristic low-density aggregate structures, will only slowly settle to the bottom. Thus, resuspended particles will apparently have adequate time to scavenge dissolved pollutants from the water before being redeposited. So long as erosion affects only the surface mixed layer, a short-term, quasi-equilibrium between bed particles and dissolved pollutants in the overlying waters can be postulated.

This short-term equilibrium can be disturbed by introduction of particles and pore waters from below the mixed layer, throughput of particles and dissolved pollutants from outside the area, which have different compositions or concentrations, or by rapid deposition and burial of the surface sediments beyond the recovery depth of the infauna.

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BRIEFING DOCUMENT 4

TRANSPORT OF TRACE ELEMENTS FROM PARTICULATES TO BIOTA

CONTENTS

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TRANSPORT OF TRACE ELEMENTS FROM PARTICULATES TO BIOTA

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 margin between the required concentration and the toxic concentration is very narrow. Recent research (e.g., Sunda and Guillard, 1976; Engel and Sunda, 1979) has verified earlier speculation that many aquatic organisms may 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 margin 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 generally to avoid the geochemical forms of trace metals that are most abundant, employing the geochemical complexity of metal reactions in aquatic environments to buffer potential toxic effects of those metals.

Because many biological systems exist on the margin of metal toxicity, the physical and geochemical redistribution of toxic metals in aquatic environments by human activities has a strong potential to disrupt aquatic ecosystems. Predicting (or even proving) such an impact is difficult, however. A major reason for this difficulty is our poor understanding of the geochemical selectivity of the organisms involved. To predict, or understand, impacts we obviously must focus our study on how human activities affect the distribution of metals to those geochemical forms of trace metals that are available to biota.

Metals concentrate in suspended and 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. In this review we consider the biological and geochemical processes that 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 since chemical reactions within the water itself will ultimately influence the availability of such metals, and uptake of metals from solution is a broad subject beyond the purview of this report.

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 is also dependent upon the biochemical transport and fate of the metal (e.g., detoxification or luxury uptake have both been documented). Thus, bioaccumulation is the most direct measure of bioavailability, although measurement of a response is sometimes more practical. I will not discuss the processes that could uncouple response from uptake. 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, 1976; reviewed by 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. Those 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 not always attained. Positive correlations between size, or age, and concentrations of some metals have been observed in fish (Cutshall, et al., 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 life-long, net metal accumulation (Cross et al., 1973). Recent studies point to mechanisms that might explain how life-long metal accumulation could occur in enriched environments coincident with metal fluxes, which 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; and the other involves the synthesis of metal-specific binding proteins.

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

Metal-specific binding proteins (metallothionein-like proteins) have also been observed in aquatic organisms (e.g., Brown and Parson, 1978;

Engel and Fowler, 1979). Synthesis of such proteins is induced by metal exposure. Paradoxically, in mammals, metal uptake is also 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 (Bryan, 1976; Noel-Lambot, et al., 1980). An on-going 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 that enhance metal accumulation may cause overestimation of availability under some circumstances. In contrast, unpublished work (F. L. Harrison, Lawrence Livermore Laboratory, personal communication) suggest 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; they may thus underestimate important components of uptake. In long-term experiments, the important influences of growth (e.g., 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 (Fowler and Benayoun, 1976; Benayoun, et al., 1974; Fowler, et al., 1978), perhaps reflecting differences in growth rates of animals in different circumstances (Farmer, et al., 1979; Fowler and Benayoun, 1974), but certainly affecting conclusions concerning metal availability. Similarly, starved animals may accumulate metals more rapidly than feeding animals (Cross, et al., 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.

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, 1976a). Zinc uptake by the crab Caranus maenus occurs at a slower rate at low concentrations (less than 100 ug/l) than at higher concentrations, implying a regulation of uptake below some critical environmental level (Bryan, 1976). Similarly, Zn concentrations in the polychaete Nereis diversicolor show little variation over wide ranges in environmental levels of Zn (Bryan and Hummerstone, 1973), also suggesting efficient regulation. However, at least 40% 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 (e.g., muscle), but not in others (e.g., liver). Some regulation of Cu in some molluscan bivalves might also occur (Bryan, 1976), but does not totally uncouple Cu uptake from Cu exposure. The uptake of non-essential metals such as Pb, Cd, Ag, and Hg most certainly is determined by exposure concentrations (for a comprehensive review see Bryan, 1976). 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. 1). 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 by diffusion, rather than an energy-dependent, active transport process (Coombs, 1980). Facilitated diffusion is a common mode of membrane

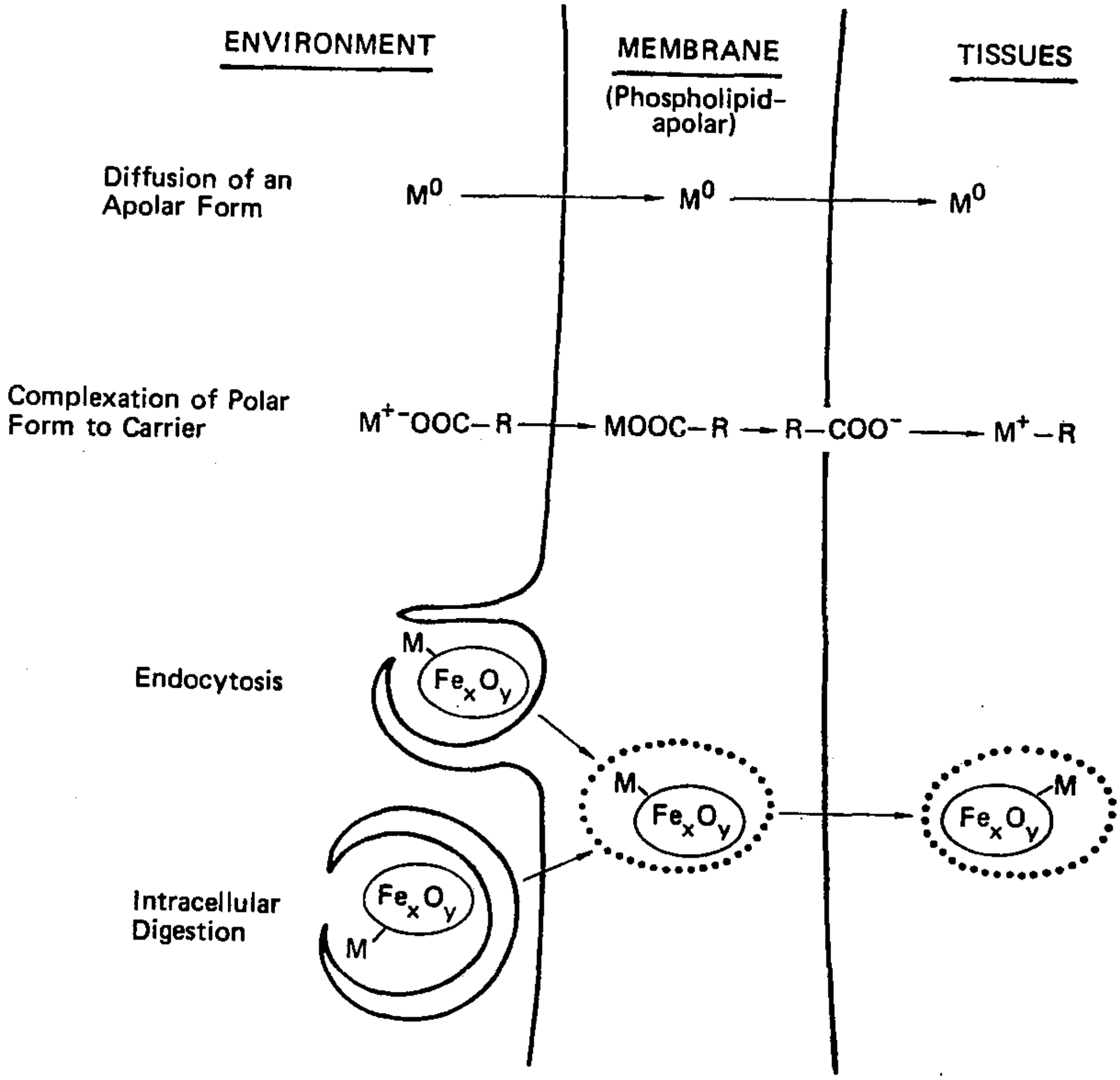


Figure 1. A simplified schematic characterization of the environmental interface of an organism, illustrating mechanisms of transport of metals (M) into biological tissues.

transport (Neame and Richards, 1972). The substance to be transported first complexes with a carrier molecule on the external surface of the membrane, 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 (Coombs, 1980; Lunde, 1974).

Metals occur as strongly bound complexes within tissues (Chou, et al., 1978). Rapid complexation to strong, slowly exchanging ligands could maintain a sufficient diffusion gradient to allow the degree of bioconcentration characteristic of most metals (Luoma, 1974; Luoma, 1977a). This process (termed Donnan equilibrium) 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 by diffusion. Reduced polarity (and 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, the most likely reason tha octanol:water partitioning coefficients are such useful indicators (Neely, et al., 1974) of the bioavailability of synthetic and petroleum-based trace organic substances is their relationship to membrane solubility (Riley, et al., 1981). However, low polarity forms of many metals are likely to be rare, and if mechanisms other than diffusion through the lipid membrane are involved in uptake, the octanol:water partitioning is not likely to be a good predictor of the bioavailability of all metals.

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 rate of reaction of Cr (III) with organic ligands is 3 to 12 orders of magnitude slower than are the reaction rates of other metals (Sutin, 1966), perhaps explaining the low availabiltiy 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 finite. 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-situ) was similarly characterized by saturable kinetics during influx. Antagonism of uptake should also occur between metals transported by the same carrier at concentrations sufficient to saturate carrier sites. Such antagonistic interactions are common among metals.

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, 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 (Murphy, et al., 1976; McKnight and Morel, 1980). Because of their unique capability for transporting siderochrome-bound Fe (presumably with carriers specific for the molecule), blue-green algae may dominate other types of phytoplankton in Fe-limited environments (Murphy, et al., 1976). Carrier systems for cobalamine and siderochrome-Fe have developed in response to specific nutritional needs, however, which are probably exceptional among metals.

Other possible mechanisms of carrier-facilitated metal uptake include (1) transport by carriers specific for nutritionally essential cations; (2) non-specific 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 membrane; (3) transport of metals complexed with essential nutrients (e.g., amino acids or proteins) on carriers specific for the nutrient; or (4) transport of nutritionally nonessential 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 et al., 1979) suggest that little uptake occurs through alternative four. However, little is known about the relative importance of the first three modes of uptake in aquatic organisms, despite their importance in determining what forms of metals are biologically available.

Uptake by passive diffusion of polar metals through nonpolar membranes could occur through 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 non-specific uptake mechanism.

Metal uptake by endocytosis has been documented, at least in molluscs. 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 (e.g., Fig. 1--Coombs, 1980). Alternatively, specific amoebocytes and/or digestive vesicles may engulf metals outside the cell membrane (e.g., in the lumen of the digestive tract) then move back into the tissues carrying their particulate burden. Digestion by engulfment within vesicles (termed intracellular digestion) is common in many invertebrates, constituting a major fraction of the digestion accomplished by molluscan 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 et al. (1977). Vesicles rich in Cu, Zn and Pb, similar to those observed by George et al. (1977) during endocytosis, have been reported in scallops (George, et al., 1979). 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, et al., 1977). However, the quantitative contribution of endocytosis to metal uptake has not been established.

Digestive processes will also play a role in determining metal uptake from food and ingested water. Enzymatic cleavage of proteins could facilitate metal assimilation if metal were transported with amino acids. pH is probably the most important factor in the digestive tract, however.

low pH is uncommon in the digestive tract of lower-trophic level invertebrates. pH 5 is the lowest observed in the digestive tract of suspension feeders such as oysters (Owen, 1966). The digestive pH of most deposit feeding organisms is closer to 6-7. Alkaline conditions have been observed to accompany digestion is some polychaetes. Little is known about conditions inside digestive vesicles or amoebocytes in the many species of invertebrates which employ intracellular digestions. Rigorous pH conditions, longer digestive times, and great digestive efficiency might be expected in upper trophic level, and air-breathing organisms (since the latter must rely upon food for their Ca). High concentrations of some metals (e.g., Hg) occur in large predatory fish, and in air-breathing animals linked to aquatic food chains. However, the biomagnification that would be expected through several trophic levels if rigorous digestion were the cause of such concentrations has not been observed in careful studies (reviewed in Bryan, 1979). It seems more likely that such factors as longer generation times in higher trophic level species (Bryan, 1979), the specific characteristics of metals such as Hg, and perhaps transformations of metals by bacteria in the gut of some species may be involved where high concentrations coincide with high trophic level.

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, while 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 the interaction was synergistic at pH 5.4 and above.

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

VECTORS OF TRANSPORT

The vectors of metal transport to organisms are food and water (Fig. 2). 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 of exposure; (2) the rate of exposure; and (3) specific geochemical and physiological reactions that determine the proportion of the total metal 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. We will consider the food vector in this review.

Food

The high concentrations of metals in the food of most organisms, relative to water, intuitively suggests 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 comparison of metal uptake from food and from solution at distribution ratios characteristic of nature seems the most obvious method of comparing vectors of uptake. However, the results of such experiments are seldom quantitative, and have not yielded consistent conclusions. For example, the uptake of Pb from spiked food and freshwater by rainbow trout

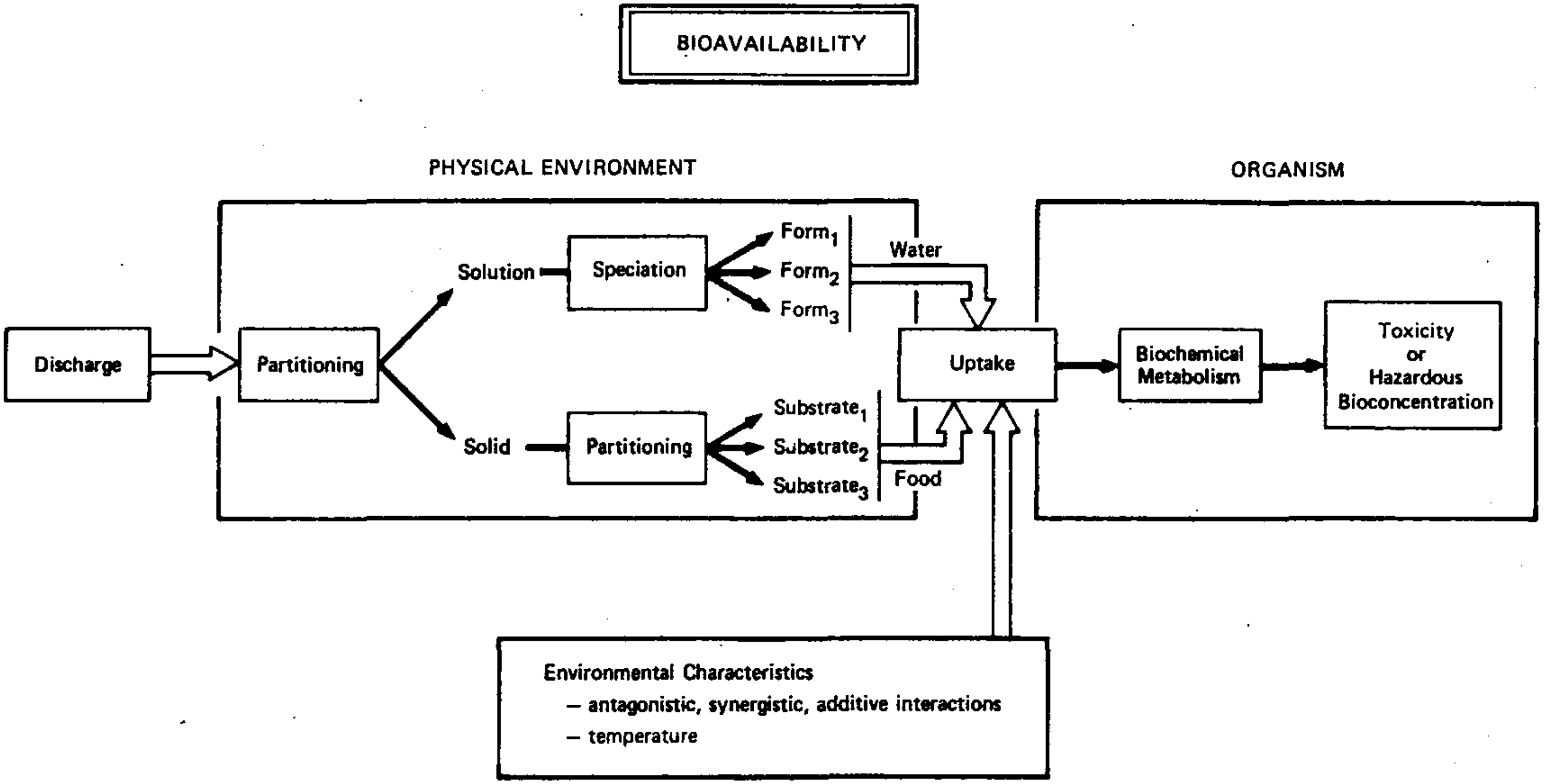


Figure 2. A simplified schematic illustration of the various processes that affect the availability of trace contaminants to organisms.

did not exdeed uptake from solution alone (Hodson, et al., 1978). Similar results were observed with freshwater isopods (Brown, 1977), although some excess uptake from food was observed in Pb-tolerant isoposds. In contrast, in long-term studies, abalone fed (ad libitum) Pb-contaminated brown algae accumulated substantial concentrations of Pb (Stewart and Schulz-Baldes, 1979).

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 et al. (1975) showed no greater uptake of Zn from food and solution than from solution alone 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 (Littorian 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 (Hartman, 1978; Phillips and Buhler, 1978; Spinelli and Mahnken, 1976). Singh and Ferns (1978) observed no difference in uptake of Mn, Co, Cu and Cd in trout fed metal contaminated activated sludge or trout fed commercial pellets. Some uptake of Cr and Pb was observed from the sludge, and substantial uptake of Zn and Ni.

All such experiments may underestimate the contribution of food to metal uptake. 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, et al., 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 is dependent upon 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 rates of water transport across the gills of organisms, 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 (1973 a, 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 et al. (1975) showed that biological pools of Zn may occur which do not exchange with ^{65}Zn in either food or solution, negating the basis of Pentreath's conclusions. In other approaches, the assimilation efficiency of metals from food were determined in short-term experiments, 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, i.e., less than 20% (e.g., Sick and Baptist, 1979; Jennings and Rainbow, 1979; Pentreath, 1973a; Kerfoot and Jacobs, 1976). The bulk of the ingested metal passes through the organism unassimilated and is excreted in feces (Boothe and Knauer, 1972; Small, et al., 1972; Benayoun, et al., 1974). Despite the inefficiencies of uptake, calculations have suggested food could be the dominant source of Zn to macrozooplankton (euphausiids--Small, et al., 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 euphausiid zooplankton (Benayoun, et al., 1974), Cr to oysters (Preston, 1971), Hg to mussels (Fowler, et al., 1978) and As to both snails (Littorin littoralis--Klump, 1980) and Lobster (Cooney and Benson, 1980). In contrast, calculations by Sick and Baptist (1979) suggested 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 upon poorly known values for uptake from solution alone, estimates of assimilation efficiencies that may be unreliable (Amiard and Amiard-Triquet, 1977), and a 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, et al., 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), as is contamination of "external organs" (e.g., mantle, gills) in molluscs (Amiard, 1978). In contrast, exposure to metals in food appears to result in greater metal accumulation in digestive organs and muscle in most species (e.g., Tenore, et al., 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 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 is bound to a medium-sized (12,000 dalton) protein in the mid-gut gland of crabs (C. maenus) exposed to Cd in food than in those exposed to solute Cd (Jennings, et al., 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, et al., 1979). Different tissue distributions and biochemical distributions could suggest differences in the predominant form of metal transported in 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 through different vectors. If efflux rates are slower than when uptake is from solution, the 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, 1979). Perhaps more intriguing are recent results which suggest that after a period of delay, synthesis of metal-specific binding proteins may occur in aquatic organisms exposed to sublethal metal enrichment (F. Harrison, LLL, personal communication). This could lead to an apparent attainment of equlibrium, followed by a resumption of uptake. Such kinetics were observed in Cd uptake from food and water by both mosquito fish (Gambusia affinis--Williams and Giesy, 1978), and zooplankton (Sick and Baptist, 1979). If equilibrium between metals in solutions and surface tissues occurs relatively rapidly, and if long-term exposure to metal enrichment in food eventually induces a stimulation of metal uptake in internal tissues (through growth of a pool of conservative binding sites), then uptake from food could be insignificant in short-term exposures characteristic of laboratory situations, but quite significant over the lifetime of an organism in nature. Obviously, a better understanding of the role of metal-specific binding proteins in metal uptake is a necessary prerequisite to testing such a specualtive hypothesis.

Experimental comparisons of metal uptake from food and solution, mass-balance models of the biological fate of metals, and indirect indications from the tissue distributions of metals in organisms in nature, all suggest that food is a significant vector for the uptake of at least some metals by some organisms. None of these studies allows a reliable quantitative estimate of the contribution of food, however. Basic methodological difficulties contribute to the uncertainties of such estimates. Even without these difficulties, however, estimates would be tenuous. Most organisms ingest a variety of food-types, which are not always well-defined. Furthermore, differences in metal availability appear to occur among foods. 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, et al., 1976). Demersal marine fish (P. platessa) accumulated towfold more ^{65}Zn from synthetic foods (gelatin or starch) than from ^{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% when the animals were fed synthetic food or tissue homogenates, but were only 20% in animals fed live carp labeled "in vivo".

Metal availability may also differ among prey species. For example, plaice feed upon 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 mixtue of foodtypes 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 methyl-mercury from the polychaetes N. diversicolor and A. marina exceeded retention observed when the fish were fed Methylmercury-enriched shrimp or mussel (Pentreath, 1976b). Sick and Baptist (1979) observed up to 5½ times greater uptake of Cd when copepods (P. coronatus were 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 as 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, et al., 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 by pike was more efficient from prey exposed to high concentrations of Hg for short periods than from 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 (e.g., Luoma, 1977a). Similarly, Merlini, *et al*. (1976) first fed snails freshly labeled with ^{65}Zn to fish, 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 porportionately more slowly exchanging Zn in the second group of snails than in the first. Zn uptake by the fish from the first group of snails was more efficient than uptake 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.

SEDIMENT

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, in press, for comprehensive review). First, concentrations of sediment-bound metals are strongly dependent upon 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 oxyhydroxides, manganese oxides, organic materials (viable and non-viable), and to a lesser extent, clays and carbonates (Jenne, 1979; Luoma and Davis, in press). 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 nutrition. 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; Whitlach, 1974; Bubnova, 1972; Self and Jumars, 1978), although particle-size selectivity may differ among species. For example, the clam, Macoma balthica, digests various types of particles less than 80 um in size (Yong, 1949). The average particle size in the digestive gland of Macoma inquinta is 10 um, while particles in the gut of Macoma secta average 300 um (Reid and Reid, 1969). The more selective feeder, Pectinaria gouldii (a polychaete worm), ingests particles > 75 um, and < 25 um, but employs no detectable chemical selection (Whitlach, 1974). "Selective" suspension-feeding organisms also may inadvertently ingest a variety of metal-binding substrates when heavy concentrations of re-suspended materials are mixed with phytoplankton in the water column, or may employ some suspended sediment as an essential source of nutrition.

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, in press). 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; but in general, the most influential effects on availability to most benthic animals occur within 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 coprecipitation, adsorption, or ion exchange phenomena. 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

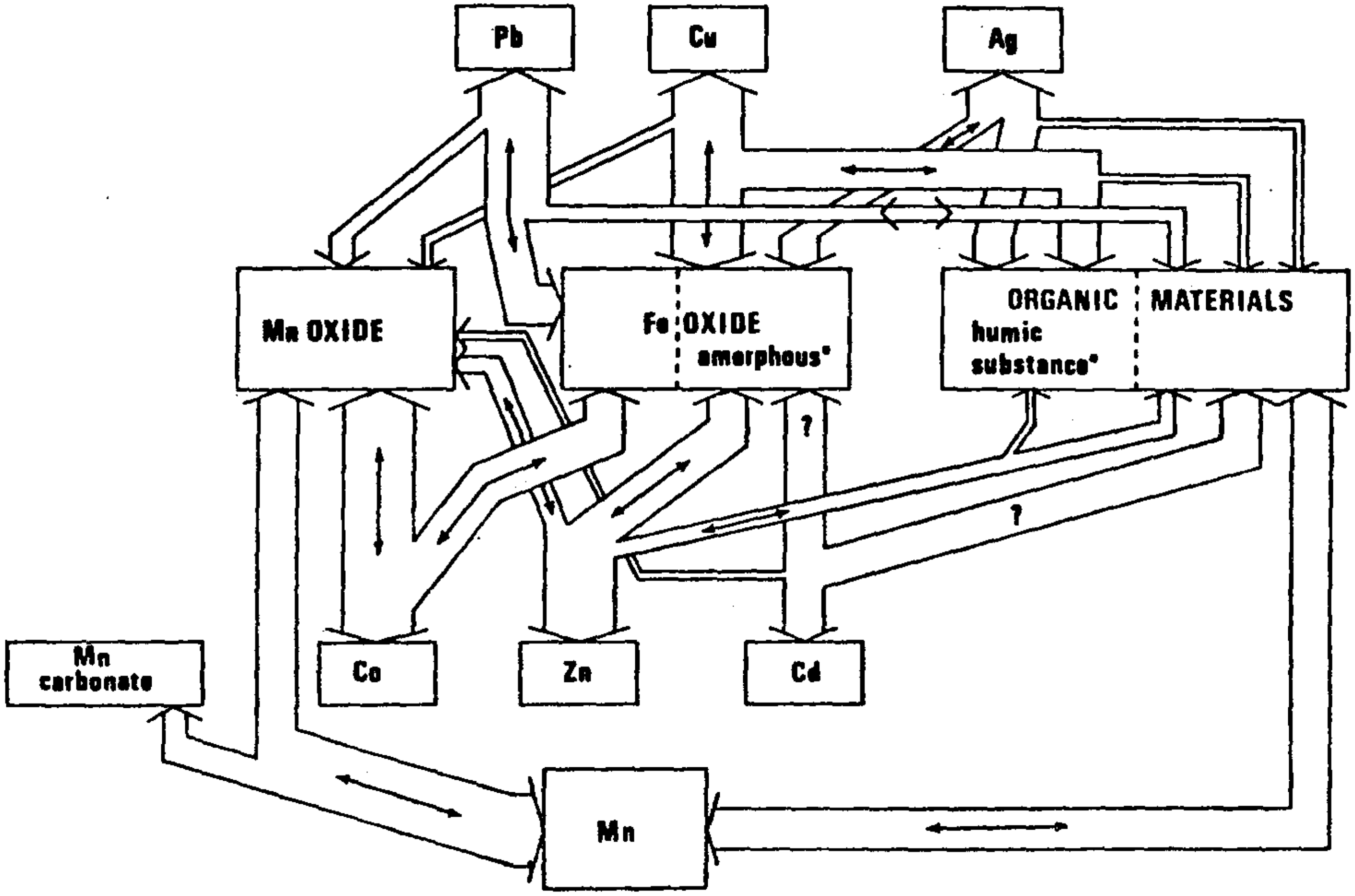
(4) the concentrations of other metal ions that may compete with trace metals for the available binding sites (e.g., Ca^{2+}, Mg^{2+}).

Because substrate concentrations may vary dramatically with space and time in some environments (e.g., Luoma and Bryan, 1981), the kinetics of metal redistributions among substrates may also play a role in determining metal partitioning (i.e., all systems may not be 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 has also been observed, generating complex, aggregated particles in which these two substrates are intermixed (Sholkovitz, 1976). Although manganese concentrations do not correlate well with the abundance of fine particles in sediments, manganese oxides may also occur in aggregate particles. Sunby *et al.* (1981) demonstrated that 80% of the manganese in near-bottom suspended sediments occurred as "weak enrichments ($<$ 1%) on a background of other wise undistinguished particles". Manganese was also observed as a stronger enrichment (1-20%) in 10-20 um-size 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 oxide coatings, organic coatings and minute, but discrete manganese 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 (Hunter, 1980; Davis and Leckie, 1978). For example, different types of model particles rapidly take on a common surface charge, different from their surface charges in artificial freshwater or artifical seawater, when immersed in natural seawater(Niehof and Loeb, 1972). Adsorption coating of particles by both viable (Corpe, 1975) and non-viable organic materials (Davis, 1980; Davis and Gloor, in press; Tipping , 1981) has been observed. Balistrieri et al. (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 the properties of oxide surfaces. Coatings of suspended particles with adsorbed organic particulates derived from biological processes, e.g., 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, in press). In general, differences in binding intensity among metals suggest that partitioning among substrates will be metal-specific (Fig. 3). 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, in press), The myriad of 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 non-specific (Guy, et al., 1978; Luoma and Jenne, 1976b). Methods for mathematically modeling metal partitioning in sediments, analogous to speciation models of metals in solution may offer some hope for estimating partitioning, but are not fully developed (Luoma and Davis, in press). Qualitative, indirect methods, such as statistical correlations (Luoma and Bryan, 1981) or studies with well-defined model sediments (e.g., Oakley, et al., 1980, 1981) can be used



*Operationally-defined

Figure 3. 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, 1981).

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). (1) 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 will be governed by this distribution coefficient. The sediment-water distribution observed in a closed laboratory experiment 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 (affecting bioavability 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. (2) Since 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 (Flegal and Martin, 1977; Elwood _et al_., 1976). (3) Redistribution of metals among different binding components may occur if changes in sediment chemistry occur (Oakley _et al_., 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 demonstrating that fish accumulate Hg (Jernelov, 1970; Gillespie, 1972) and other metals (Delisle _et al_., 1975) in a closed sediment-water system, did not differentiate the vector of uptake. Similarly, experiments showing that metal uptake differed among different types of sediments (Chipman _et al_., 1968; Beasley and Fowler, 1976; Phelps, 1979; Pesch, 1979) may have reflected differences in distribution coefficients rather than actual differences in availability from different ingestd sediments. Renfro and Benayoun (1976) compared uptake from organic materials and Fe oxides labeled with ^{65}Zn, ^{109}Cd and ^{110m}Ag when each was mixed with sediments from the Mediterranean Sea and fed to a polychaete (N. diversicolor). Only small differences were observed between treatments. However, no controls on metal redistribution among particle-types, or between particle and solution were established. Substantial uptake of ^{109}Cd from sediments by the polychaete Neries japonica (Ueda et al., 1976) was demonstrated, but the kinetics of uptake (Luoma and Jenne, 1976a) suggested that undigested sediments were an important component of the ^{109}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 ingestinon of either nuclide by the worms was evident. Harrison et al. (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 fish physically separated from sediment by nylon mesh. No control of undigested stomach or intestinal content was established in either of the whole-body analyses employed in the latter two studies, however.

In studies with deposit-feeding clams, Luoma and Jenne (1976a, 1977) separated the vectors of ^{100m}Ag, ^{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 oxides, manganese 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 as much as 1000-fold (Fig 4). Differences in availabiltiy among sediment types differed among metals. Since experiments with all metals were conducted simultaneously, a common biological control

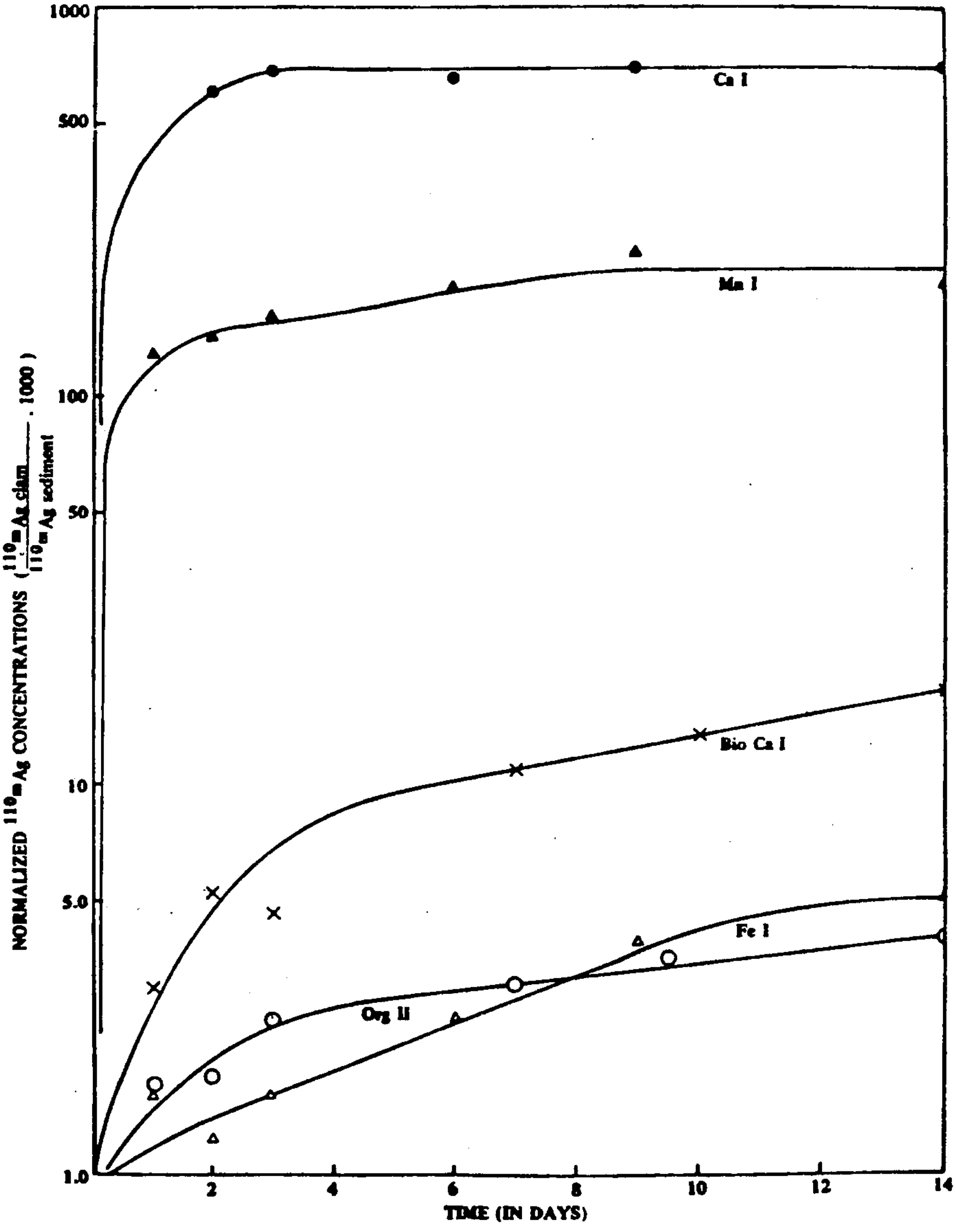


Figure 4. Differences in uptake of ^{110m}Ag when different types of well-defined sediments were ingested by the deposit-feeding clam Macoma balthica. Sediment types are amorphous iron oxides (Fe), decaying marsh grass fragments (org), manganese oxides (Mn), crushed bivalve shells (BioCa), and calcium carbonate (Ca) (from Luoma and Jenne, 1977).

(e.g., 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 et al. (1970), Halcrow et al. (1973), Valiela et al. (1974), Hugget et al. (1975), Luoma (1977b), and Schell and Nevessi (1977). The poor correlations between metal concentrations in benthic organisms and sediments could mean that metals in benthos are not derived from sediments, or sources coupled to sediments. However, they could also result from statistical problems in the comparison or from an influence of variables other than metal concentrations in sediment upon 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 are dependent primarily upon phytoplankton for food (e.g., oysters, mussels, and some species of clams), or herbivorous grazing animals, would not necessarily correlate with metal concentrations in sediments, even if food were the primary vector of metal uptake. For example, concentrations of most metals in grazing snails follow concentrations in algae, but not in sediments, where sediments and algae are not correlated (Bryan and

Hummerstone, 1977; Young, 1975). Even among deposit-feeding organisms, differences in food sources may affect metal exposure. For example, Phelps (1967) and Phelps _et al_. (1969) reported consistent differences in Zn concentrations among benthic polychaetes from different feeding guilds (surface feeders _vs_. subsurface feeders; selective _vs_. non-selective 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 _et al_. (1980) found that Cd and Zn concentrations in the polychaete _Arenicol 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 all the metals except Cu (Fig. 5a). 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 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 concentration in the environment.

Sediments need not be the only source of metal exposure for benthic organisms. 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 upon exposure alone are

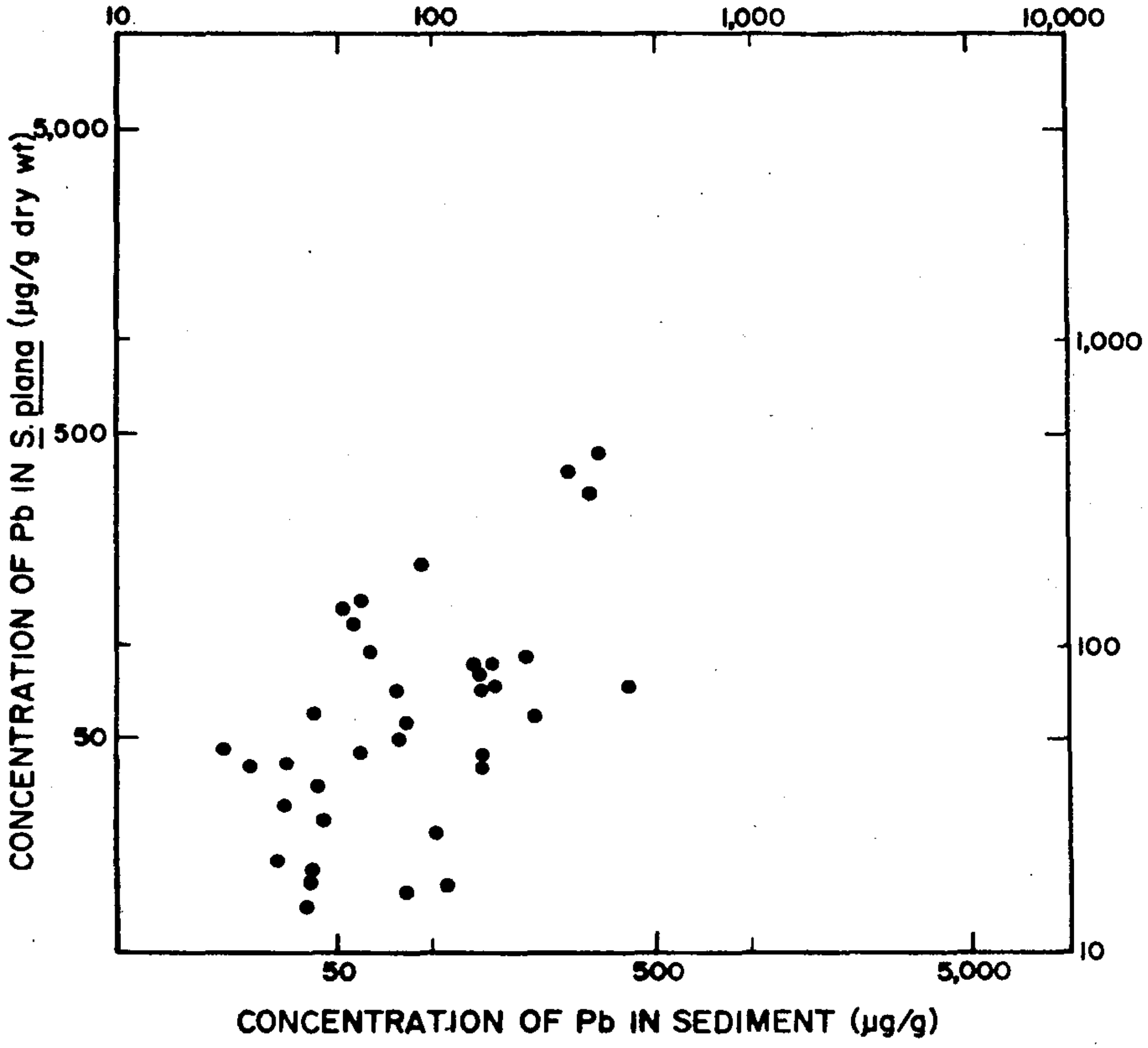


Figure 5a. Correlation of Pb in surficial estuarine sediments with Pb in the deposit-feeding bivalve Scrobicularia plana. r = 0.69 for power function fit. Data from 17 estuaries (from Luoma and Bryan, 1978).

evident. For example, Bryan and Hummerstone (1977) observed differences in Ag and Cu concentrations in S. plana from two estuaries that 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. Sediment analyses 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 surface sediments were an accurate indicator of Cu discharge from the plant, and the total exposure of M. balthica to Cu. Comparisons of five 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, the clams showed large fluctuations in Cu concentrations that could not be explained by changes in exposure. Again, a general dependence upon exposure was evident, but other variables were also obviously important in controlling bioaccumulation.

Employing the broad data set described earlier, Luoma and Bryan (1978), 1979; in press) 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 the 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 inter-metal 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 Sterritt and Lester, 1980). Various extractable fractions of metals in aquatic sediments have been described as biologically available (e.g., 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 that 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 auto-correlations occurred among independent variables.

The multiple regression calculations showed that 70-80% 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 1). 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, and Zn. The best correlations were obtained with 1N ammonium acetate for Zn (as reported in many soil studies--Sterritt and Lester, 1980) and 1N 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 exceptions of Cd, metal concentrations in sediment (extractable or total) explained 37-72% of the variation in the deposit feeders.

Concentrations of binding substrates in sediments explained 8-49% of the variation in metal concentrations in S. plana and N. diversicolor. Concentrations of Pb in S. plana were very closely correlated ($R^2 = 0.99$) with Pb/Fe in sediments (where Fe was measured by HCl extraction, Fig. 5b). Langston (1980) also reported a strong correlation of As in S. plana with As/Fe ratios in surface sediment, and Bryan (unpublished data) observed similar results for Cr. Luoma and Bryan (1978) suggested that the

TABLE 1

Percentage of the total variation in concentrations of Ag, Cd, Co, Cu, Pb and Zn in two deposit feeders (*Scrobicularia plana* - a bivalve; and *Nereis diversicolor* - a polychaete) from 17 estuaries explained by statistical correlation (multiple regression) with: (1) metals in sediment (extractant giving best correlation is in parentheses); (2) binding substrates indicative of metal partitioning (substrates which correlate significantly are in parentheses, along with the sign of the slope of the relationship); (3) metal in seaweed, which is indicative of biologically available metal (metal and sign of slope are in parentheses). This table is from a paper by S. N. Luoma and G. W. Bryan, which is in press in *Estuarine, Coastal and Shelf Science*.

		Percentage Variation Explained by Independent Variables			
Species	Metal	Metal in Sediment Extract	Metal Binding Substrate Concentrations	Fucus	Other Metals In Sediment
Scrobicularia	Pb[a]	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[b]	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 ($\overset{+}{\text{Mn}}$, $\overset{-}{\text{TOC}}$, $\overset{+}{\text{CO}}_3$)	16	0
	Cu	No relation	10 ($\overset{-}{\text{TOC}}$ or $\overset{-}{\text{Fe}}$)	?	16 ($\overset{+}{\text{Ag}}$)
Nereis	Cu	72 ($\overset{+}{\text{HNO}}_3$)	7 ($\overset{+}{\text{Mn}}$)	?	8 ($\overset{-}{\text{Pb}}$)
	Co	66 ($\overset{+}{\text{HCl}}$)	0	4	5 ($\overset{-}{\text{Ag}}$)
	Pb	54 ($\overset{+}{\text{HNO}}_3$)	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 ($\overset{-}{\text{CO}}_3$, $\overset{+}{\text{Mn}}$, $\overset{-}{\text{TOC}}$)	15	0
	Zn[c]	weak relation - regulation by organism			

[a] Luoma and Bryan, 1978; [b] Luoma and Bryan, 1979; [c] Bryan and Hummerstone, 1973a.

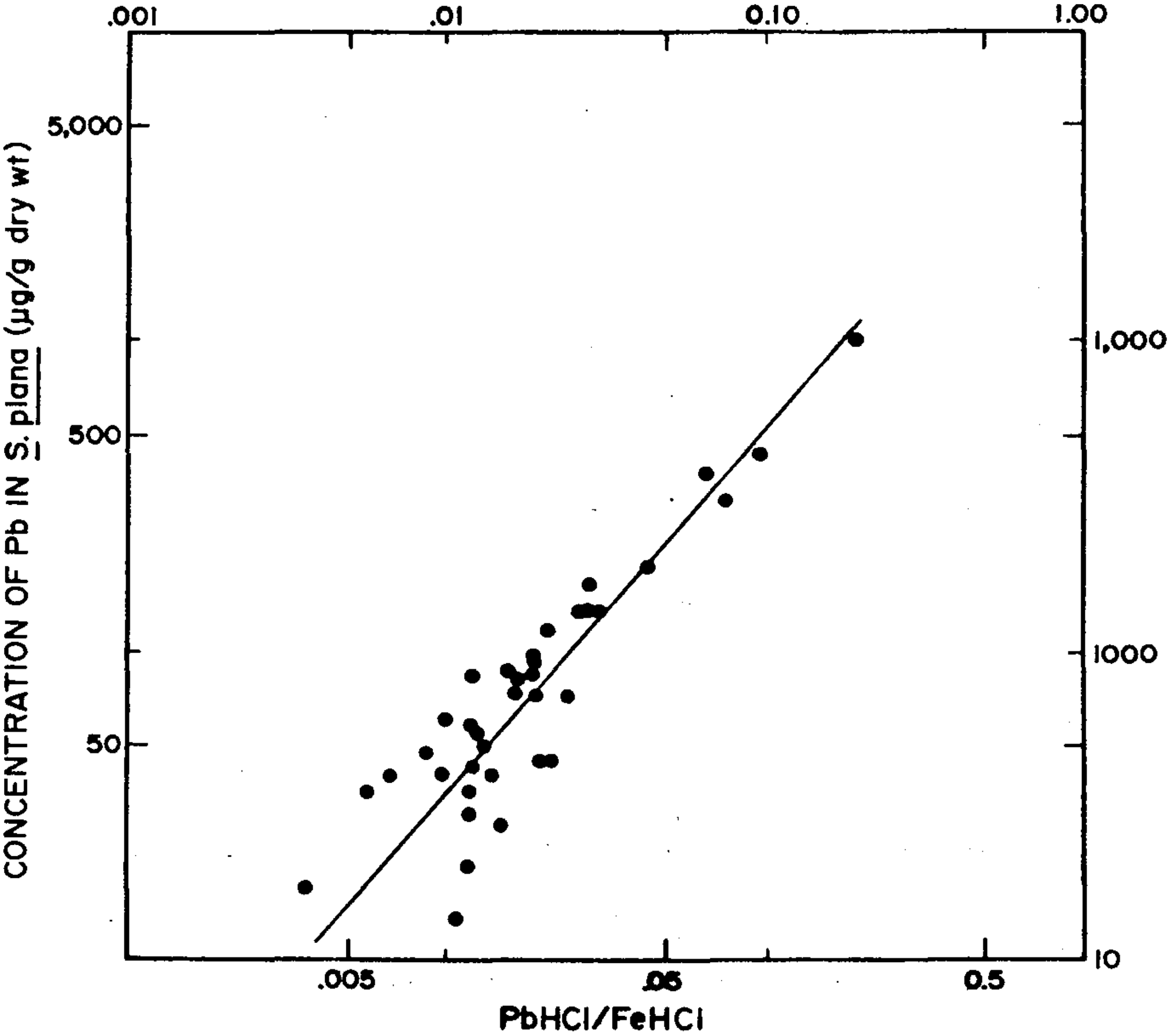


Figure 5b. Correlation of Pb in *S. plana* with ratio of Pb/Fe (both extracted by 1N HCl) in surficial estuarine sediments. r = 0. Data from 17 estuaries (from Luoma and Bryan, 1978).

availability of Pb was enhanced at low concentrations of Fe in sediment because less Pb was strongly bound to iron oxides as the Pb/Fe ratio in sediments increased. However, competitive inhibition of Pb uptake by Fe was also possible. Whatever the cause, the ratios Pb/Fe, As/Fe and Cr/Fe in sediments were accurate predictors of Pb, As and Cr 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 predicitve capabilities of the regressions were not as strong as observed with Pb, As and Cr. 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^{o}), but not Cu and Pb to marsh plants (Gambrell et al., 1977). Strong reducing conditions cause a substantial decline in the availability of Cd to marsh plants (Gambrell et al., 1977). Unpublished data from the study of Luoma and Bryan also suggest that Cd was of lower availability in highly anoxic mudflats (e.g., inner Poole Harbor). The availability of Cu to the polychaete Neanthes arenaceodentata also is less from subsurface than from surface sediments (Pesch, 1979), presumably because of differences in redox potential. In contrast, certain types of reducing conditions enchanced the bioavailability of Cu to the clams S. plana and M. balthica (Luoma and Bryan, in press). Exceptionally high concentrations of Cu were observed in these animals in seven anoxic mudflats, and during an unusual period of anoxia on 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.

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 unresolved; however, knowledge of (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 is essential in determining the physicochemical forms of metals that are available for transport into biological tissues. Realistic studies of metal uptake cannot be conducted without further understanding 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, 1982). However, methods for linking such models to biological data will also be necessary. Geochemical 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 efort will be necessary to accomplish that goal.

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