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How Do Sediments Enter The Bay, Move Through The System, Remove And Store Chemicals, Or Release Them?

Maynard N. Nichols
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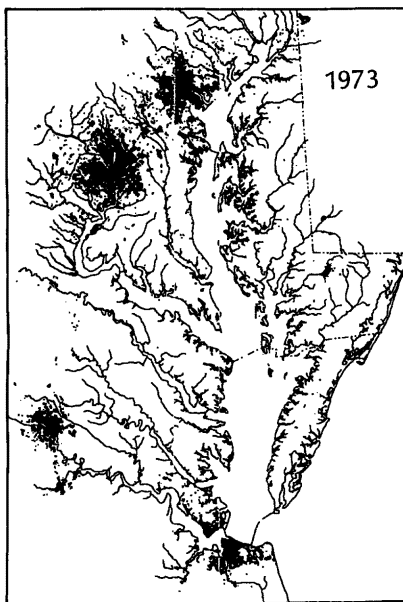
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TEN CRITICAL QUESTIONS FOR CHESAPEAKE BAY

IN RESEARCH AND RELATED MATTERS

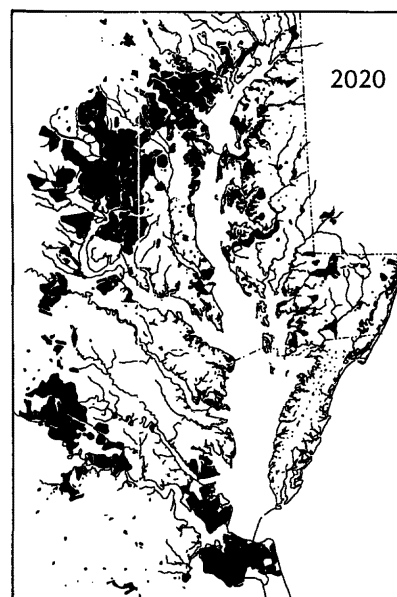
PEOPLE AND INDUSTRY



1. WHY HAVE FISH DECLINED?
2. WHAT ARE THE EFFECTS OF ENVIRONMENTAL CHANGES?
3. HOW SHOULD DREDGING BE DONE?
4. HOW DOES THE BAY SYSTEM FIT TOGETHER?
5. WHAT ARE THE SOURCES, FATE AND EFFECTS OF SEDIMENTS?

6. HOW SHOULD WE TEST THE BIOLOGICAL EFFECTS OF POLLUTANTS?
7. HOW MUST RESEARCH AND MONITORING BE INTEGRATED?
8. WHICH AREAS SHOULD BE PRESERVED FOR STUDY?
9. HOW SHOULD THE DATA BE MANAGED?
10. HOW CAN INFORMATION BE MADE MORE AVAILABLE?

PEOPLE AND INDUSTRY - ESTIMATED



CHESAPEAKE RESEARCH CONSORTIUM

OCTOBER 1983



**TEN CRITICAL QUESTIONS FOR
CHESAPEAKE BAY IN
RESEARCH AND RELATED MATTERS**

L. Eugene Cronin, Editor

**CHESAPEAKE RESEARCH CONSORTIUM
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The Johns Hopkins University
University of Maryland
Smithsonian Institution
Virginia Institute of Marine Science - The College of William & Mary**

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CRC Coordinating Committee

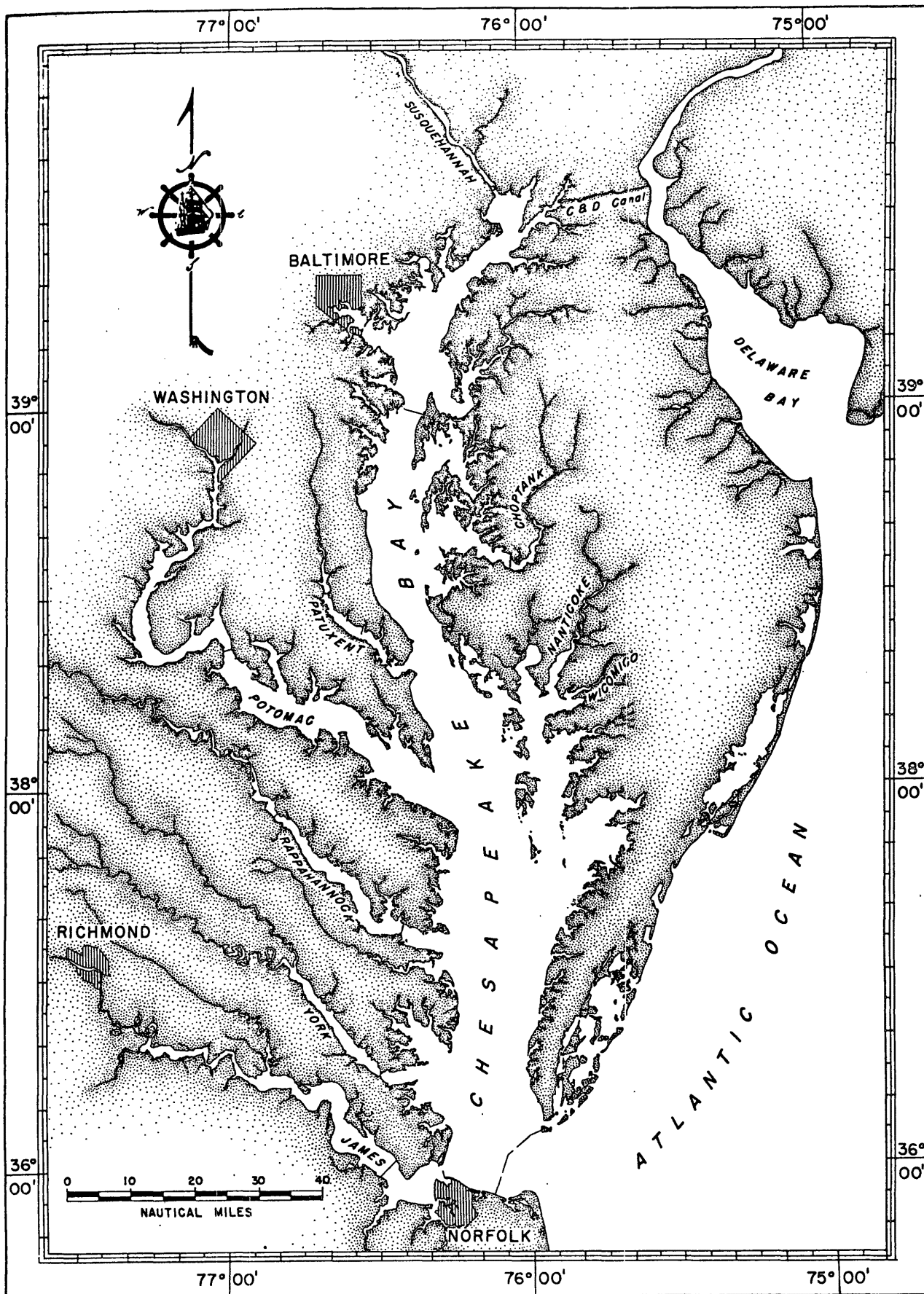
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Frontispiece - The Chesapeake Bay System

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HOW DO SEDIMENTS ENTER THE BAY, MOVE THROUGH THE SYSTEM, REMOVE AND STORE CHEMICALS, OR RELEASE THEM?

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INTRODUCTION

Escape of more than two million tons of sediment, 4,000 tons of man-made chemicals (e.g. Cd, Cu, Pb and Zn) and more than 300 types of synthetic organic compounds annually into the Bay, shoals shipping channels, reduces water quality and threatens biota. Where then do these enormous loads go? Are they mainly flushed into the sea or stored on the Bay floor? And what happens to chemicals attached to the sediments as they pass through different chemical regimes of the Bay? These are important questions facing scientists who aim to understand the cycling of sedimentary materials and to predict the fate of attached chemicals. These are also significant questions facing managers concerned with causative agents, regional attributes of receiving waters as well as locating disposal sites.

The importance of sediment transport in the Bay only occurs to many people when they read about disasters as storm flooding and catastrophic shore erosion. The consequences of sediment movement, however, are a continuing problem which costs more than 16 million dollars annually in channel dredging (Aurand and Mamantov, 1982). Additionally, large sums are spent on shore protection, on flood abatement works and on placement of polluted sediment. Moreover, uncertainties of environmental impacts have delayed some projects for years. The importance of chemicals is highlighted when we learn about accidental spills, of massive fish kills, and closure of an entire estuary to fishing, e.g. by Kepone contamination in the James Estuary. Few people are aware however, of the long-term subtle changes that may be taking place in the ecosystem as a consequence of sediment pollution or slow release of potentially toxic chemicals. Reportedly (EPA, 1982), oyster setting has failed in upper reaches of the Bay; fish as shad and striped bass that once spawned in astronomical numbers, have declined severely (Cronin, 1977). Few people are aware of the increasing number of chemicals being synthesized, produced and stockpiled in the region. Such large scale activity with concentrated mass of chemical substances increases the probability of accidental

spillage and a chemical crisis. Many of these substances, either metals or organic compounds, can affect biological productivity and be transferred up the food chain to man; some are known tetragens and carcinogens. In summary, the nature and magnitude of the problem reveal an urgent need to predict the transport of sedimentary materials and to understand the fate of attached chemicals. Obviously, there is a great deal of scope for improving waste disposal practices and for defining management alternatives if the scientific understanding can be increased.

RESEARCH PLAN

The broad goal of this research is to understand and predict the mode of entry, transport and fate of sedimentary materials and associated chemical contaminants in the Bay.

This broad goal is resolved into 5 attainable objectives or tasks.

1. To determine the sources, entry pathways and input rates of dissolved and particulate substances, natural and anthropogenic. Define the relative importance of different sources and pathways and establish whether the tributaries act as a source or a sink for sediment and chemicals from the Bay.
2. To determine the behavior of suspended particles as affected by aggregation or flocculation, biological packaging, fecal formation, water column mixing, organic material and particle reactivity.
3. To determine the changes in concentration, distribution and form of chemicals and sediment in the river-estuarine mixing zone, a zone of the turbidity maximum, and to decipher what processes account for the observed changes.
4. To determine the sediment-chemical interactions at the bottom boundary as affected by sediment resuspension, changing chemical regimes (e.g. Eh or pH) and biological activity.
5. To develop a conceptual and/or numerical model of sediment and chemical fluxes for predicting routes and rates of transport as affected by man-made modifications, e.g. prospective changes in chemical inputs, inflow diversions, or channel deepening.

A working model of sediment-chemical cycling routes and transformation in the Bay is presented in Figure 1. This provides a unifying scheme for linking the various objectives and tasks together.

PATHWAYS

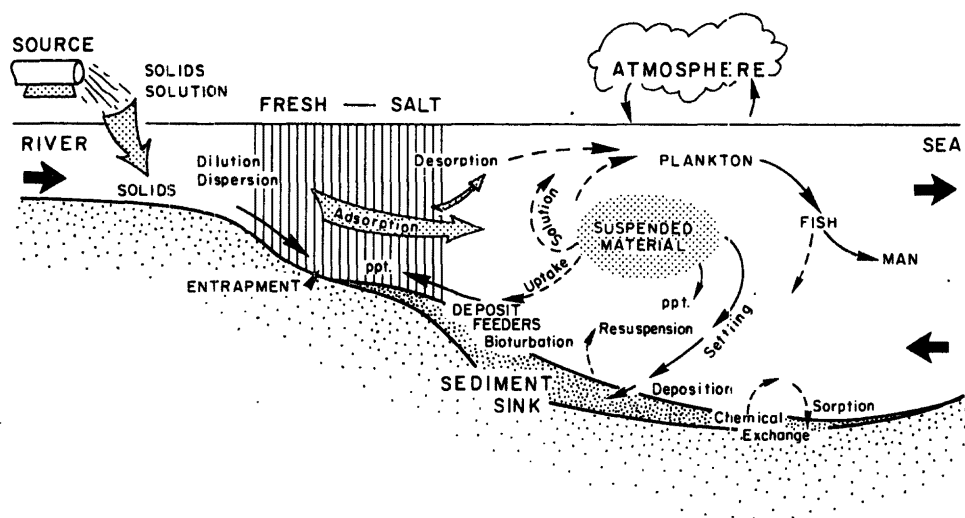


Figure 1. Schematic model of processes and cycling routes of chemicals along sedimentological and associated biological pathways. From Nichols (1982).

In this model sediments and chemicals as well as biota of the Bay are contained in three geochemical reservoirs: (1) the atmosphere, (2) water column and (3) bed sediments including pore water. The components are exchanged between reservoirs and can enter the Bay, along distinct pathways via the atmosphere, the bed or from adjacent systems, i.e. rivers, the sea, via landward transport or by direct discharge of effluents. The pathway that a chemical takes depends on its form, i.e. dissolved, particulate (solid) or biotic. Sediments are emphasized because most chemicals in estuaries exhibit strong interactions with fine sediment. Additionally, the sediments usually contain the major mass of chemicals. Therefore, predicting the fate of chemicals is to a large extent a problem of tracing fine sediment dispersal, understanding the behavior of particles and their interaction with chemicals and biota.

Once chemicals are attached to sediments through processes like adsorption, they follow hydrodynamic and sedimentologic pathways that have been active through geologic time. As shown in Figure 1, for example, river-borne sediments transported into freshwater reaches of the Bay are rapidly mixed and diluted with less contaminated sediments and further dispersed seaward by diffusion and advection. As suspended sediment and chemicals are flushed into the fresh-salt transition zone, or turbidity maximum, their seaward movement slows and they are partly trapped near the bottom in a convergence of seaward and landward currents. Material that stays in suspension for long periods, e.g. the less dense or clay size fraction, can move farther seaward through the upper estuarine layer. Material that settles, however, aided by aggregation, flocculation or biological packaging, can become entrained in the lower layer and accumulate landward in the convergence. Other materials accumulate in less energetic zones of the Bay floor after many cycles of deposition and tidal resuspension.

Superimposed on the hydrodynamic-sedimentological route, there are chemical, sedimentological and biological transformations. River-supplied chemical contaminants, for example, can precipitate in the fresh-salt transition while some dissolved chemicals can be adsorbed on particles and taken up by plankton. As a source of food, sediment and chemicals can enter bioecological paths via suspension feeders or fish and thence to man. Some transformations make chemical contaminants more susceptible to bioaccumulation whereas others make chemicals more refractory, and therefore less biologically available.

These possibilities suggest several geochemical processes and critical zones of the Bay that need special attention. Such elements are summarized in Figure 2 and are central focus of projects 2, 3 and 4.

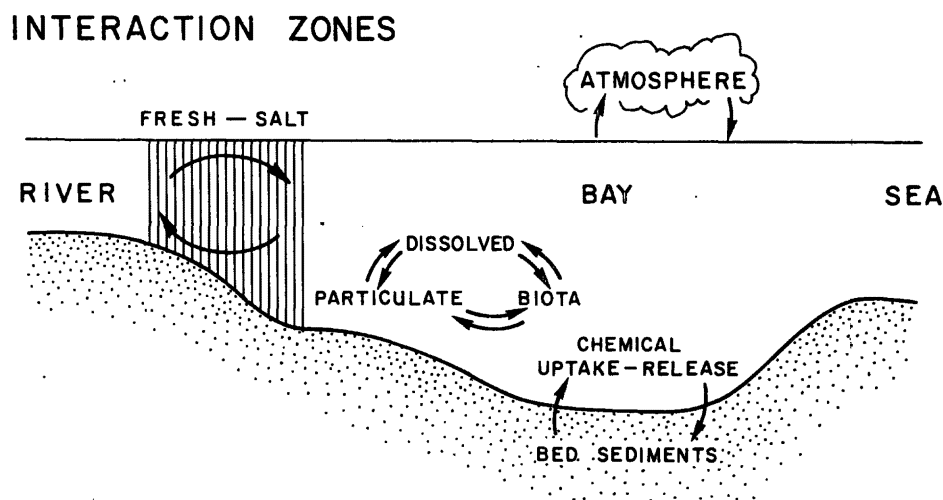


Figure 2. Critical zones of the Bay and important sediment-chemical transformations that need attention.

PROJECT 1. Sources and pathwaysObjective:

To determine the sources, entry pathways and input rates of dissolved and particulate substances, natural and anthropogenic. Define relative importance of different sources and pathways and establish whether the tributaries act as a source or a sink for sediment and chemicals from the Bay.

Approach:

Although the location of major sediment and chemical sources is partly known, the rates of influx are poorly known because they are so variable and chemical constituents can change form with season and with variations of inflow. Often only a small suite of chemicals are monitored and these constituents are not always meaningful. For example, trace chemicals are usually monitored on flow-weighted and composited solids samples, but scientists need to know how much is dissolved and how much is particulate. Likewise, "settleable solids" in sewage effluents and sludges are monitored without appropriate seawater dilutions; dilution can result in dissolution of some constituents and agglomeration and flocculation of others. Monitoring of influx should be accomplished at several key river stations, as well as major effluents, with particular attention to periods of high sediment influx and high chemical loading. In particular, the validity of data acquired should account for variability of concentrations and flux through a rigorous statistical sampling plan.

Another approach is to characterize the composition of the sediments, e.g. by chemical ratios, and use the data on chemical ratios as indicators, or tracers, of different sources and their relative strengths of input. Anthropogenic sources can be characterized by metal concentration ratios, particle shape and size, carbon-nitrogen ratios, sulfur isotopes, and by lead isotopes. Fluvial and oceanic sources can be distinguished by carbon or strontium isotopes, and by clay minerals or micro-organisms.

It has been assumed that atmospheric deposition of chemicals is negligible. Recently, however, entry of anthropogenic chemicals via the atmosphere has been recognized as a significant pathway (EPA, 1982). Contaminates include particulate auto emissions, radionuclide fission products, insecticide dusts as DDT, and industrial combustion products. Atmospheric contributions are important in areas distant from significant water-borne sources and in areas of low sedimentation. Since atmospheric contaminants are readily entrapped in salt marshes, sediment cores from marshes should hold a record of chemical concentrations that reveal the history of atmospheric input and contamination. Once dated by ^{210}Pb or similar techniques, lower parts of the cores representing pre-industrial

Bay Sediments

deposits, can indicate natural concentrations, and thus serve as a baseline for determining anthropogenic concentrations usually from upper parts of the cores. Such trends can reveal the present status of contamination, e.g. are controls of emissions having an effect.

Regional rates of input integrated over long periods of time, can be monitored by sampling surface sediments in sinks or zones of relatively fast deposition. These zones, especially those having clay size sediment, are more sensitive to contamination than other zones, and thus provide an early warning of increasing loads from multiple sources. Zones of fast deposition are contaminated first; they also decontaminate first if discharge is stopped. Such zones can be located from the history of bathymetric changes and may include deeper parts of tributary mouths, the turbidity maximum, sides of deep basins and dead-end reentrants of shipping channels or anchorages. Freshwater areas near rivers should be avoided because they are subject to flooding and alternate scour and fill. Changes in surface sediment with time can be confirmed by analyzing sediments with depth in cores. Once normalized for particle size, by analyzing sediment fractions less than $16\ \mu$, a change in concentration as a function of depth implies a change in the rate of cumulative loading, though the sources may not be known. The advantage of this strategy is that it provides maximum data integrated over a time scale of days or months, from relatively few samples.

Scale:

Temporal changes can be revealed by sampling surface fluid mud 2 to 6 times per year depending on deposition rates. Because certain chemicals like trace metals associate with one another, key chemicals can be stored frozen for reference or used as future needs dictate or as instrumentation improves.

Feasibility:

Past efforts of Carpenter, et al. (1975) and of the U.S.G.S. (Lang, 1980) in monitoring rivers demonstrate the feasibility of monitoring rivers. However, frequency of sampling needs to be increased, especially during high inflows. Additionally, detection of many different kinds of organic compounds at low concentrations needs to be accomplished. For monitoring sinks, experience with Kepone (Nichols, 1981) shows that this approach is feasible and useful.

Due to the large variations of influx which can change seasonally along with changes of chemical ratios, this project is likely to take 3 to 5 years and require the concerted effort of hydrologists, chemists and sedimentologists from several organizations. Funding is the most severe constraint.

PROJECT 2. Particle behaviorObjective:

To determine the behavior of suspended sediment particles as affected by aggregation or flocculation, biological packaging, fecal formation, water column mixing, organic material and particle reactivity.

Approach:

Particle size and packaging of fine particles into larger units is a key feature controlling mass transfer of chemical constituents, their dispersal and accumulation. By aggregation and packaging in the water column, particles settle faster, thereby removing attached chemicals from the water column, cleansing the water and increasing sedimentation and burial rates. By rapid settling and packaging, chemicals can be retained near their source. Additionally, particle size governs the nature and rate at which processes proceed, like aggregation, dissolution and sorption. Details of how particles are packaged by physico-chemical or biological processes are quite complicated.

Much useful information on flocculation and settling behavior can be acquired by laboratory simulation of processes as demonstrated by Sholkovitz (1973). By controlling chemical gradients and the mixing rates of fresh and salty water, a much better understanding of particle-chemical behavior can be achieved than now exists from field observations; for example, just how do aggregates act and react chemically to store or release substances? And to what degree do different chemicals affect aggregate formation? Special studies should be directed along the lines in which aggregates can be formed: (1) by repetitive resuspension from the bed; (2) action of bubbles in the water column; (3) by reduction of ionic charge strength either in the medium or through adsorption; (4) by bonding of molecules adhering to the particle surfaces; (5) by enmeshment in Fe hydroxides or in mucus or fecal matter; and (6) by biological processing of filter-feeding, suspension feeding or deposit feeding organisms.

Whereas interactions of chemicals have been described in terms of equilibrium partitioning coefficients to obtain first-order estimates of contaminant behavior, additional research is needed to assess this approach for specific classes of chemicals and for specific time and space scales. In Bay water, the equilibrium approach may be valid only at time scales greater than days. Additionally, partitioning of a chemical between water and sediment can vary with particle composition. And the chemical-particle transfer reactions are not truly reversible but depend on changing conditions of Eh, pH or dissolved oxygen. The rate of

Bay Sediments

sorption or desorption of selected chemicals needs to be determined in both field and complement lab studies using natural materials to determine the effects of salinity, Eh, pH, dissolved organic carbon, particle composition and particle concentration. Attention should focus on the amount of chemical adsorbed per surface area, i.e. the total number of available sites independent of particle concentration. Since particle-chemical changes are often great across the fresh-salt transition and just above the bed, field studies should be directed to zones where horizontal and vertical gradients are sharp. Chemical concentrations in different size fractions and packages, organic and inorganic, need to be analyzed to determine the magnitude of sedimentological fractionation with time and with distance across the gradient zones.

Scale:

Field and laboratory studies will require concerted effort of a scientific team including sedimentologists and chemists over 4 to 8 years. Techniques must be developed, controls established and data analyzed to account for a wide range of particle and chemical variations at different time scales. Aspects of these studies should be linked to projects 3 and 4.

Feasibility:

Examination of particle aggregates in their natural state has been hampered by the technical means for collecting them because they are so fragile and easily distorted on mounting, drying and handling. A recent break-through by Gibbs, (1982) permits in situ examination by laser holography supplemented by computerized image analyzers for particle abundance. Most CRC institutions are capable of assembling such apparatus and of providing the essential supportive geochemical analyses for laboratory experiments. Adequate funding is the most severe constraint.

PROJECT 3. Fresh-salt interactions

Objective:

To determine the changes in concentration, distribution and form of chemicals and sediments in the river-estuarine mixing zone, a zone of the turbidity maximum, and to decipher what processes account for the observed changes.

Approach:

Because of the marked sedimentological and chemical changes that occur as river water mixes with estuarine water in the turbidity maximum zone, an integrated approach should focus on partitioning of chemical constituents between aqueous and solid phases as well as sedimentological fractionation (settling and sorting) of organic and inorganic suspended materials including sediments of different particle size and degrees of packaging. Field observations should be designed to deal with these individual forms of chemicals in vertical and horizontal gradients across the river-salt water transition zone, or turbidity maximum, at varying conditions of river inflow, pH, Eh and salinity stratification. The simultaneous measurement of dissolved and solid chemical concentrations enables processes to be distinguished. Additionally, chemical surrogates are needed to assist in accounting for the wide chemical variations as well as tracers of river-estuarine end-members, e.g. radium and barium. The removal or dissolution fate of chemical constituents in the solid phase, or of radionuclides, can be utilized as tracers of different river-estuarine end-members. Ratios of non-reactive chemical constituents in the solid phase, or radionuclides, can be utilized as tracers of different river-estuarine sources. It is of interest to determine whether the chemical changes relate to changes in the character of river water or to resuspension from the bed. To assist in identity of controlling processes, field observations should be supported by parallel laboratory experiments of chemical mixing and behavior such as those of Sholkovitz (1973) and Duniker (1976). When field observations are coupled to simultaneous hydrodynamic measurements, removal or additions of chemical constituents can be established by mass balance analyses. Humic substances should be characterized and quantified if possible, because of their relatively high concentration and possible functions as complexing agents for metal ions. This project would be enhanced by coordination with projects 1 (Sources and Pathways), 2 (Particle Behavior) and 3 (Bed Sediment-Water Interactions). As with other chemical research efforts, cross-calibration of analytical procedures is essential and suitable reference solutions for this purpose are a basic need.

Scale:

This project could be performed in a relatively small fresh-salt transition zone of a tributary estuary, preferably where pollution is a problem. There is a need to select an estuary where physical influences are minimized so that chemical processes are easily evaluated, i.e. to emphasize the chemical behavior

associated with particular conditions. The problems are sufficiently complex to require a concerted effort of sedimentologists, hydrologists and chemists over a period of 3 to 6 years. Conventional chemical analyses and field equipment in common use by CRC institutions can be utilized; however, laboratory intercomparisons of chemical constituents are needed with particular attention to the wide variability of different constituents in estuarine waters. There is, however, a lack of procedures and specialized equipment for organic compounds. In particular, the lack of techniques for characterizing humic material precludes some desired analyses.

Feasibility:

Studies of metal variations in river-estuarine mixing zones by Boyle, et al. (1974), Duinker (1976), de Groot (1971), and Trefry (1976) demonstrate the importance and feasibility of the research approaches outlined above. Field observations and interpretation of results can be complicated by variations in the end-member concentrations, in the speciation of chemical constituents and by secondary sources within the study area. Because it is often difficult to distinguish between processes of exchange between water and suspended material and those of sediment-water interaction, this project should be closely coupled to projects 2 and 4.

PROJECT 4. Bed sediment-water interactions

Objective:

To determine the sediment-chemical interactions at the bottom boundary as affected by sediment resuspension, diagenetic releases and biological activity.

Approach:

Although the Bay floor is generally assumed to represent a sink or reservoir for suspended sediment and chemicals, it has recently been recognized (EPA, 1982) that the floor is dynamic and can also be an important source of suspended sediment. By repetitive current winnowing, erosion of the bed, sediment resuspension and changing chemical conditions, chemicals can be mixed, exchanged and released into overlying water. The nature of these changes is quite complicated. Different chemicals behave differently according to their reactivity, and the chemical regime of the water may shift rapidly as sediment is resuspended and exposed to alternate chemical conditions between the bed and water, e.g. from anoxic to oxic regimes. Consequently, a study must closely follow the progress

of partitioning between particulate and dissolved phases for individual chemical constituents of interest.

An integrated study of bed sediment-water interactions should include study of the nature and mechanisms of chemical mobilization from the sediments: (1) under varying conditions of resuspension and in turn, the chemical/particle interaction time, and (2) after burial just below the sediment-water interface. Resuspension will require a detailed hydrodynamic-sediment-chemical field study near the bed through time-series measurements in contrasting pH and reducing-oxidizing regimes. In many places the most important factor in resuspension may be the intensity and nature of biological packaging on the bed surface that deters erodibility. By contrast, intense bioturbation may enhance erodibility. After temporal and spatial variability is accounted for, processes can be traced by temporal and vertical trends in concentration, by flux calculations, mixing analyses and by supportive laboratory experiments under controlled conditions. Particle resuspension can be modeled as an advection-diffusion process driven by a stress term. It is desirable to couple resuspension measurements with pore water measurements although chemical changes in the latter probably occur at long-time scales. In the field, box cores should be taken and pore water extracted at intervals through upper parts of the cores. Analyses should not only include contaminants of interest but indicators of diagenetic activity, e.g. sulfate, alkalinity, Eh and pH. From the chemical concentration gradients, vertical fluxes can be calculated following methods of Berner (1971) and accounting for bioturbation, dissolution rates, adsorption, etc. following Schink, et al. (1975). Fluxes from the sediment can also be determined from "benthic chambers" placed over the sediments (Graham, et al., 1976) or by laboratory incubation of sediments (Fanning and Pilson, 1971). Additionally, stable chemicals should be employed, e.g. organic compounds or radionuclides, as surrogates to account for "departures" in the concentrations of mobilized constituents. An integrated study would allow study of a large number of chemicals as a function of salinity, depth, physical factors and chemical conditions.

Scale:

These problems are complex and require the effort of sedimentologists and chemists working closely together over a period of 4 to 8 years. Conventional chemical analyses and field equipment of CRC institutions can be utilized through special sampling tripods which need to be designed for near-bottom deployment.

Feasibility:

Recent efforts by Nichols (1982), Hill et al. (1981) and VIMS Kepone studies demonstrate the feasibility and value of field observations through chemical time-series. Because of high temporal variability, observations could be improved by a much greater frequency of sampling. Laboratory experiments such as those of Sholkovitz (1973) and Duniker (1976) show the advantages and limitations of an experimental approach. A major task is to seek authigenic phases within different zones of the bed sediments and to determine their relations to pore water compositions. Complications arise from effects of bioturbation, the fact that pore water chemistry of near-surface sediments can respond to changes in composition of the overlying water and from chemical changes caused by decomposition of organic matter.

PROJECT 5. Modeling transport systemsObjective:

To develop a conceptual model of sediment and chemical flux for predicting routes and rates of transport as affected by man-made modifications, e.g. prospective changes in chemical inputs, inflow diversions or channel deepening.

Approach:

A central focus and reasonable end-product for this research topic is development of a model in semi-quantitative form. A model not only assists scientists and managers in organizing diverse data but assists in communicating information about complicated phenomena. A conceptual framework also reveals gaps where future data needs to be acquired and thus can provide a motivating force for stimulating new studies.

An initial effort could be built on the concept of mass balance and likely pathways of input, e.g. Figures 1 and 3. It could build on existing mass balance models or sediment budgets for the Bay, e.g. Biggs (1970), Schubel (1976), and tributaries, e.g. Yarbrow, et al. (1982) and proceed to contaminants like toxic metals, synthetic organic compounds or radionuclides. The model could also incorporate a small number of rate-associated parameters that characterize an estuarine transport system. Plausible parameters could include: (1) rate of sediment/chemical supply, (2) amount of sediment/chemical in suspension, and in temporary or permanent storage, (3) the rate of transport and residence time in the water column,

Bay Sediments

and (4) the final fractionation of materials between entrapment in estuarine deposits and escape to the ocean. For special studies the model could be segmented according to zones of chemical interaction, e.g. as fresh-salt mixing zone, estuary-shelf exchange zone, bed-water column exchange (Fig. 2); as well as by geographic segments, e.g. single tributaries and tributary-Bay.

Ultimately, the conceptual model of transport should be integrated with ecosystem models to incorporate biological functions as well as effects of man and assessment of pollution (see Topic Paper of Ulanowicz). The search for emergent properties, which are discoverable only when the whole system is considered, is a great challenge of estuarine science today.

Feasibility:

Only a modest investment is needed in compiling and analyzing existing sediment data and commonly analyzed data on chemical constituents. A great deal could be accomplished in 1 to 2 years in better known tributaries as the Patuxent and James. At least two to three years of concerted effort by workers in several CRC institutions will be required for Bay-wide treatment. It must be appreciated that temporal variations in source inputs can result in bias of budgets and of sediment/chemical fluxes.

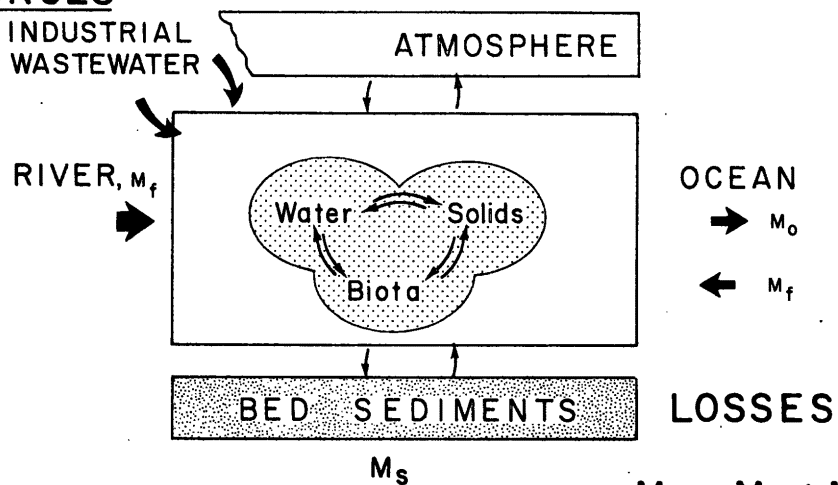
Value:

A model is useful to compare different sedimentary regimes and to discover the range of different conditions or processes controlling an estuary's classification. The effort is designed to produce not only a better understanding of transport mechanisms, but to raise our level of knowledge of those sedimentary processes that characterize estuarine systems. This level of understanding is not only required to enhance student comprehension, but it is required for effective management of estuaries since many of the most serious and persistent environmental problems in estuaries are associated directly, or indirectly, with transport of fine sediment.

APPROACH

SOURCES

- INDUSTRIAL
- WASTEWATER



$$M_f = M_s + M_o$$

MASS BALANCE

Figure 3. Schematic diagram illustrating a plausible framework for mass balance modeling of anthropogenic chemicals with main entry routes and exports, arrows; and interactions within the system, double arrows.

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