

TOXIC SUBSTANCES IN THE CHESAPEAKE BAY ESTUARY

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INTRODUCTION

The Chesapeake Bay is a geologically young estuarine system, born less than 10,000 years ago when the Atlantic Ocean, rising in response to meltwaters from receding Pleistocene glaciers, began to flood the valleys of the rivers draining the east coast of the North American continent. By approximately 3,000 years ago, tidal waters were beginning to encroach on the present mouth of the Susquehanna River at Havre de Grace and the estuarine geometry was probably quite similar to that which we observe today. The flooding process did not stop then, but the rate of sea level rise decreased. Even today, the flooding continues at approximately 1.6 mm/yr. in the Chesapeake Bay area (Nichols, 1972). This rate of sea level rise is larger than the world-wide average and reflects a local tectonic component in addition to that caused by the increase in volume of sea waters from melting ice caps.

Estuaries form a buffer zone between fresh water rivers and the sea. They behave as very efficient sediment traps for particulate material carried by the rivers and by the inflow of saline marine bottom waters through their mouths. The sediment that accumulates in estuaries is commonly a mixture of river borne terrestrial debris derived from

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weathering and erosion of the tributary watersheds and coastal marine sediment derived from the continental shelf (Mead, 1969; Hathaway, 1972). From a geologic perspective, estuaries are very ephemeral features, quickly filling with sediment from these sources. The lifespan of an estuary is a function of the rate of change in sea level vs. the rate of accumulation of sediment. In the Chesapeake Bay, the continuing rise of sea level partially compensates for the rate of accumulation of sediments and the net effect is a prolongation of the lifespan of the system. The estuary, however, is a dynamic system, undergoing continuous evolutionary changes which will ultimately lead to its destruction through infilling with sediment.

The Chesapeake Bay began to experience impacts, in addition to those caused by natural processes, from the time of first European settlement along its shores. Clearing of land for agriculture and development has greatly accelerated the rate of erosion in the adjacent land areas and increased the amount of sediment delivered to the estuary by its tributary rivers. Perhaps an even more serious impact is related to the tremendous technological advances that have been made through the years. Man has been exceedingly ingenious in synthesizing and producing a myriad of new chemical compounds, and in finding uses for an increasing variety of metals and, more recently, radionuclides. These substances enter the environment through waste discharges and other disposal practices, (e.g., industrial discharges, sewage effluents, land fills), by direct applications for specific purposes (e.g., herbicides, pesticides, fertilizers) and via atmospheric pathways (e.g., automotive exhausts, combustion of oil, coal and wood, incineration of refuse, fugitive dusts from storage or disposal sites, bomb testing). It is now clear that many of the substances that were either purposely or inadvertently released to the environment are

displaying unanticipated adverse affects on the biosphere. Historically, estuaries have been favored localities for siting industries, power plants and sewage treatment facilities. They provide an abundant supply of water for industrial processes and for cooling power plants, they are a convenient conduit for the disposal of a broad spectrum of wastes, and they provide direct accessibility to marine transportation of raw materials and finished products. As a consequence, estuaries have borne the brunt of man's activities. The Chesapeake Bay is no exception.

Two classes of materials, toxic substances and sediment, pose the greatest threat to the environmental well being of the estuarine system. These materials are intimately related in that many toxic substances, inorganic and organic, associate strongly with sediment via physico-chemical mechanisms. As a consequence, the sediment accumulating on the bottom is the largest reservoir of toxic materials in the estuary (Bricker and Troup, 1975).

Sediments

The sediments that accumulate in Chesapeake Bay are important for a number of reasons. From a physical standpoint, sediments tend to fill in channels and harbours and thus create a need for periodic dredging in order to maintain these facilities for their intended purpose. Dredging, in turn, requires disposal sites for placement of the material removed. Appropriate handling techniques and disposal site characteristics depend upon the chemical components and physical properties of the spoil. Suspended sediment creates turbidity which decreases the depth of light penetration and may also affect its spectral distribution. The decrease in intensity and shift in spectral qualities may adversely affect aquatic plants. Large concentrations of suspended sediment tend to clog the gills

and filtering apparatus of filter feeders causing impairment or death. Rapid sedimentation may cause burial and smothering of benthic fauna and flora.

In the absence of sediments, however, the estuary would not be the fertile and productive environment that it is. Sediments form a substrate upon which rooted aquatic plants grow; they provide a habitat for burrowing benthic organisms; they are a source of nutrients for benthic flora and fauna. Sediments also carry with them metals derived from natural weathering and erosional processes and those introduced by man. Many of these metals are essential to maintain a healthy biota, but if present in excess are toxic. In addition, sediments are a vehicle for the transport and localization of a large number of the anthropogenic organic compounds that enter the aquatic environment (Olsen, 1979). Both inorganic and organic toxic substances have a great affinity for particulate matter of small size and large surface area. Sites of accumulation of sediments possessing these physical characteristics usually contain significantly higher concentration of metals and organic compounds than sites of accumulation of sediments of sand size or larger. Sediments thus play a major role in the transport and distribution of toxic materials in the estuary.

No systematic study of toxic materials in the Chesapeake Bay had been attempted until the Environmental Protection Agency Chesapeake Bay Program was initiated in 1975. In planning that program, it was concluded that any toxic substances discharged into the Bay and its tributaries could have direct impact during their residence time dissolved in the water, however, because of the rapid water movement and concomitant dilution, these effects would be short lived. The most serious potential problems were identified as those associated with toxic substances that accumulate in the sediment and/or biota. These substances have a much longer residence time in the

system and may also build up to very high concentrations through sediment sorption mechanisms or bioaccumulation. For these reasons, knowledge of the distribution, amount, and physical characteristics of the recent sediments in the Bay is fundamental to understanding the behavior and fate of toxic substances in the estuary. In addition to the physical characteristics, the content of organic carbon and sulphur play an important role in determining the oxidation/reduction state of the sediments after deposition. The water content correlates with the stability and ease of resuspension of the bottom and with the rate at which dissolved substances diffuse through the sediment. The mineralogy of the sediment provides information on the reactivity of the inorganic particulate constituents. These parameters together form the framework into which the chemical and biological pieces of the system fit.

The most basic data concerning sediments in the estuary are:

1. location in the system
2. morphology of deposits
3. physical characteristics
4. rate of addition to the system
5. sources
6. sites and rates of present accumulation

In Chesapeake Bay, geophysical methods have been used to examine the thickness and morphology of the bottom sediment (Maryland Geological Survey, Virginia Institute of Marine Science open file reports). These methods also provide information on some other sediment properties in that sand and shell layers can be differentiated from finer silty and muddy sediments.

The physical characteristics of the surface sediments (particle size

distribution, water content) have been determined for the entire Bay; on a 1 km grid in Maryland waters and on a 1.4 km grid in Virginia waters. In addition, these same properties have been determined on a selected suite of meter length cores collected between the Susquehanna River and the Virginia capes. Sediment, on the basis of particle size, displays a relatively systematic distribution pattern with sand occurring in the shallow shoreline areas and mud in the deeper mid-Bay regions. Between, there occurs a zone of mixing of these two sediment types (Byrne, 1980; Kerhin, 1980). This sediment work provides a description of the state of the system relative to sediments at the present time in history and it will serve as a valuable baseline against which future changes can be measured.

Three major sources contribute sediment to Chesapeake Bay; tributary rivers, shoreline erosion and marine inflow. The northern part of the Bay is dominated by sediment carried via the Susquehanna River; the southern Bay, by sediments transported by inflowing coastal marine waters; and the mid-Bay region, by sediments derived from shoreline erosion.

Each of the tributary rivers, with exception of the Susquehanna, is characterized by an estuarine segment in its lower reaches. A large part of the sediment carried by these rivers is trapped in their lower estuarine portions and never reaches the main Bay. As a consequence, infilling of the middle portion of the Bay is occurring at a slower rate than to the north or the south, with fine particle size sediment that escapes the tributary estuaries collecting in the deeper areas and coarse sediment derived from shoreline erosion accumulating in the shallow waters adjacent to the shorelines. The Susquehanna River debouches directly into the upper Bay and the bulk of the sediment it carries is deposited there. Sediments from the continental shelf, carried into the Bay in the saline bottom waters, dominate the southern segment of the Chesapeake Bay.

It is important to know what changes have occurred in the system in the past so that predictions can be made concerning future trends. In order to understand how the system has changed from past to present, and to identify impacts related to man's activities, we must rely on information recorded in the sediment. To interpret this record, we must first know the time interval represented by the record. Three independent methods for deciphering the time (rate) of sedimentation have been employed in the Chesapeake Bay: 1) comparison of historical bathymetric charts, 2) pollen biostratigraphy, and 3) Pb^{210} geochronology. Parts of the Bay have been surveyed bathymetrically at irregular time intervals beginning in 1846. Where these surveys overlap, the change in depth represents the amount of deposition (or erosion) that has occurred during the time between surveys (Maryland Geological Survey, Virginia Institute of Marine Science, open file reports). A second technique is based on pollen biostratigraphy, that is, the identification of specific time horizons in the sediment recognized by pollen distribution. For instance, the time of disappearance of American chestnut in the 1930's, in response to the chestnut blight, is recorded by the absence of chestnut pollen in sediments deposited after that time. Other identifiable horizons, both older and younger, have been recognized in Chesapeake Bay sediments and are valuable time markers in this system (Brush, 1980). A third technique employs the decay of a radioactive isotope of lead. Pb^{210} , a member of the U^{238} series, is continuously being added to the earth's surface environment. It adsorbs strongly onto sediment particles and is deposited with them wherever they accumulate. Once buried beneath the sediment-water interface, no additional Pb^{210} can be added, and that contained in the sediment

continues to decay at a constant rate (half life = 22.5 years). This permits the dating of sediments back to approximately 100-125 years B.P. (5 x half life) (Setlock and Helz, 1980). Each of these methods provides an estimate of the rate at which sediment has accumulated at the site sampled. In areas of the Bay where sedimentation rates have been determined by either two or all three of the above techniques, the correspondence is usually quite good. Using this information the age of a particular layer or bed of sediment can be dated by its depth beneath the surface. If a change in the concentration of any toxic substance is observed as a function of depth, the rate of loading of that substance can be inferred and projections made about future concentration trends. The time of introduction of various substances into the system can also be documented. Data about sedimentation rates are directly useful in planning dredge disposal sites, locating channels to provide minimum maintenance, and estimating the frequency and volumes of material that will have to be dredged in order to maintain harbours and channels in various parts of the system.

Toxic Substances

Along with knowledge of the distribution and physical characteristics of bottom sediments in the estuary, it is necessary to know the concentrations of the toxic substances they contain if these materials are to be effectively managed.

Two major classes of toxic materials are particularly important to the estuarine environment; metals and anthropogenic organic compounds. Metals are derived from natural weathering and erosion of the metalliferous Piedmont rocks underlying the watersheds of many of the Bay tributaries, and from man's activities. Most of the organic compounds of environmental concern are strictly the product of man's chemical ingenuity. These sub-

stances enter the system via direct discharges, in input from the tributaries, in non point source runoff, and through atmospheric pathways. The distribution of these materials in surface sediments (upper few centimeters) is a result of recent deposition and accumulation in the estuary. Dated cores provide information on how the concentrations of these materials have changed with time in the sediment. Because metal behavior is better understood and analytical methods for metals are more straightforward and less expensive than those for organic compounds, the data for metals in the estuarine environment is much more detailed than that for organic compounds. Emerging evidence over the past decade suggests, however, that synthetic organic compounds may be of greater concern than metals from the standpoint of environmental degradation of aquatic systems.

The similarity in behavior between metals and many organic pollutants with respect to sorption behavior on fine particle size sediment suggest that metals may be used as surrogates for predicting the transport and accumulation of many organic pollutants. A limited number of samples of surface sediment from the main stem of the Chesapeake Bay have been analyzed for organic compounds using glass capillary gas chromatography/mass spectrometry and corroborate this hypothesis. Preliminary inspection of both the metals data and the organics data show that the highest concentrations of these substances occur in samples from tributary mouths, suggesting that the tributaries act as sources of these materials to the main Bay (Huggett, 1980). Not surprisingly, the highest concentrations were observed at the mouths of the Susquehanna, Patapsco, and James Rivers.

The technical complexity and expense of analyzing estuarine samples for organic compounds led to the development of a strategy for maximizing the

output of data of the type that would be most useful to identify potential problems with these compounds. Instead of trying to identify each peak (compound) on GC/MS traces, the complete GC/MS output from each sample is stored on the computer. Subsequent sampling at the same localities using the same analytical procedures disclose changes in peak height (concentration) for the organic compounds. If there has been a significant increase in any peak from one sampling period to the next, the compound represented by that peak can be identified and evaluated with respect to its toxicity and potential impact on the system. Possible sources of the compound can be identified by concentration gradients provided by a more detailed sampling grid in that particular area of the Bay, and appropriate regulatory measure instituted. The chances of associating a particular compound with its source are increased by performing identical analytical work on industrial, municipal sewage treatment plant and power plant discharges into the Bay (Monsanto Research Corporation, 1980). By periodically analyzing effluent discharges, it may be possible to stop a potential toxic problem at a very early stage before the substance has been discharged into the environment in large quantities. The frequency of sampling, however, must be appropriate to correspond to changes in process or treatment in the plants. One serious drawback is that the direct discharge analysis may not detect some toxic substances present in very small concentrations, yet if these substances are strongly sorbed by sediment or bioaccumulated by organisms, they may build up to dangerously high levels in the environment. By emphasizing the sediment and biota sampling in the estuary, and supplementing this with periodic sampling of effluent discharges, it may be possible to manage toxic substances from point sources in a much more effective manner than is presently being done.

An up-to-date inventory of raw materials, processes and finished products from all dischargers into the estuary would aid greatly in assessing the loading of toxic materials in the Bay system.

Coupling the data on toxic substances in the sediment with the compositions and volumes of industrial discharges and the type of inventory data described above, it will be possible to identify those substances that accumulate in the environment and permit estimates of mass-balance budgets for specific toxic substances of concern. Combining this information with the distribution and physical characteristics of the sediment will disclose specific toxic substance-sediment associations. Extending this type of work to dated core samples will provide estimates of changes in loading of toxic substances with time.

Perhaps as important as knowledge of the identities and spatial distribution of toxic substances in the estuary is an understanding of how these substances behave in the environment. After deposition and burial in the bottom, sediments and associated toxic substances are exposed to an anoxic reducing environment. This leads to changes in speciation, desorption, dissolution and remobilization of many elements (Elderfield and Hepworth, 1975). Three major mechanisms lead to the re-introduction of these materials at the sediment surface and to the water column: 1) transport in the dissolved state in the interstitial water via diffusion and/or advection, 2) physical transport of sediment and interstitial water by benthic infauna (bioturbation, irrigation, ventilation), and 3) physical disturbance of the sediment by storms and by man's activities (dredging, propeller wash, etc.). Investigation of the metal and organic content of the sediment areally and with depth provides information which permits prediction of the chemical impacts of re-exposure of sediments at the surface. Sampling and analysis of interstitial waters provides a data base

from which flux of metals and nutrients into the water column can be calculated. Available data disclose that the sediment behaves as an important source of nutrients to the estuary (Maryland Geological Survey, open file reports). At certain times of the year, a significant flux of dissolved manganese and iron into the deep bottom waters is also observed. Data for other metals is not yet available. In addition to nutrient and metals flux calculations, the interstitial water chemistry provides critical information on the reactions that occur within the sediment and the composition of the aqueous environment in which the benthic infauna live.

Examination of the benthic fauna, particularly the infauna, is providing a picture of the distribution of organisms in the estuary as a function of salinity, sediment type, and depth beneath the sediment-water interface (Maryland Geological Survey, Virginia Institute of Marine Science, open file reports). These studies document the effects of the benthic communities on the disturbance and mixing of the sediment (bioturbation), the stabilization-destabilization of the bottom sediments relative to erosion and resuspension, and the role of burrows and other biogenic structures on physical and chemical processes occurring in the sediments. Benthic organisms are restricted in their mobility and therefore must adapt to any changes that occur in the local environment. For this reason, benthic organisms may be good early warning indicators of environmental degradation. Investigations in the main Bay have disclosed cycles of colonization and extermination of benthic fauna in the deep trough along the Eastern Shore, apparently in response to the yearly summer development of anoxia in the bottom waters (Reinharz and Diaz, 1980). Systematic examination of benthic communities Baywide, and particularly in the tributaries, may identify areas subject to environmental stress. These

areas would be prime targets for detailed investigations of the causes of the stress. The response of organisms; distribution, abundance, species diversity, histopathologic features, genetic effects and other biologic effects could be used as indicators of the state of health of the particular segment of the system in which the organisms live. The foundation for developing an assessment strategy based on biologic criteria is a thorough description of the estuarine benthic organism communities in conjunction with the physical and chemical characteristics of the environment in which they live.

Present Status of Toxics in the Chesapeake Bay

The past decade has witnessed disturbing changes in the ecosystem of the Chesapeake Bay. Among the more widely publicized of these have been the decline and virtual disappearance of rooted aquatic plants from much of the Bay, the steady decrease in the abundance of striped bass and oysters, the cessation of the spring shad runs in the upper Bay, poor yields of clams and fluctuating, but generally declining catches of crabs.

Individually, any one of these could be attributed to a biological cycle or some other natural phenomenon. Taken together, however, the implications are more ominous. It has been strongly suggested that toxic substances are responsible for the observed changes. Over the years, however, the Bay has been under increasing pressures from a variety of man's activities. The harvesting of shellfish and finfish by commercial watermen and sports fishermen has not been effectively regulated from the standpoint of preserving the resource. An expanding population on the shores of the Bay and in the watersheds of the Bay tributaries, has tremendously increased the volume of sewage effluent delivered to the estuary. Increasing need for energy has led to the siting of conventional and nuclear power plants on the shores of the Bay and along its tributary rivers. Continued indus-

trial development in the Bay area has burdened the estuary with increased volumes of chemically complex discharges. Clearing land for agriculture and for development has greatly increased the loads of suspended sediment carried to the estuary. Chemicals in runoff from agricultural areas and in storm drainage from city streets, parking lots and highways ultimately end up in the Bay. Only recently has it been recognized that many toxic substances, including metals and organic compounds, are transported atmospherically and enter the surface environment via precipitation and by dry fallout. The sources of these pollutants are often far removed from where they impact the earth's surface. Each of these insults takes its toll on the finite assimilative capacity and resilience of the estuarine environment. Cumulatively, they appear to have reached the stage at which they exceed the regenerative capacity of certain parts of the resource. In turn, this has led to the decline and/or disappearance of some of the more sensitive biota.

What can be done to halt the degradation and reverse these trends? The tendency in the past has been to look for a single cause of the problem, such as toxic substances or excess nutrients and, thus far, the search has been less than successful. The estuarine system is very complex and each of the diverse activities mentioned above has an impact on the system; some greater than others. We observe the net integrated effect of all of these factors acting in concert, and it is thus not surprising that no simple answers have been found. Only two areas of the Bay, the Elizabeth River and Baltimore Harbor, show serious environmental degradation that can be directly attributed to toxic substances (Villa and Johnson, 1974; Johnson and Villa 1976; Chu-fa Tsai et al, 1979). Even in these localities it is

not possible, at present, to identify the specific effects of individual toxic elements or compounds. Over most of the Bay the effects are much more subtle and no direct cause and effect relationships have yet been demonstrated.

Effective management of toxic substances in the estuarine environment requires regulation of the amount of each toxic substance delivered to the system from all sources in order to keep environmental concentrations below the level at which adverse impacts occur. This regulation must be based on a firm understanding of the behavior and fate of natural and anthropogenic toxic substances introduced into the system; the effects of these toxic substances on estuarine biota; the identification of the sources contributing toxic substances; and quantification of the load of each substance delivered by each source. At the present time, there is no comprehensive inventory of loadings to the system and there is only fragmentary information concerning the types and concentrations of toxic substances already in the environment. There is a moderate body of information relative to the behavior and fate of metals in the estuarine environment; however, similar information about toxic organic compounds is difficult or impossible to find. Perhaps the largest gap is in our understanding of the effects of toxic substances, both metals and organic compounds, on the estuarine biota.

The Environmental Protection Agency Chesapeake Bay Program has initiated a research effort to begin to address these questions; however, this research must be intensified and expanded if it is to provide the data necessary to develop an effective program for the management of toxic substances in the estuarine environment.

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