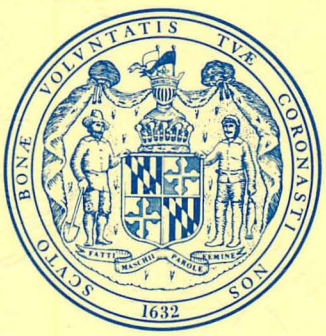
Department of Natural Resources
MARYLAND GEOLOGICAL SURVEY
Kenneth N. Weaver, Director

REPORT OF INVESTIGATIONS NO. 49

PHYSIOGRAPHIC DISTRIBUTION OF INTERSTITIAL WATERS IN CHESAPEAKE BAY

by

James M. Hill



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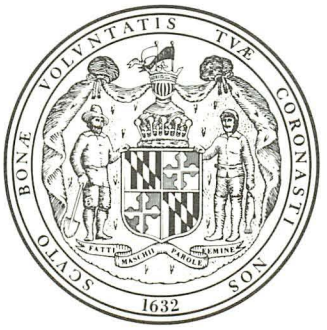

1988

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PHYSIOGRAPHIC DISTRIBUTION OF INTERSTITIAL WATERS IN CHESAPEAKE BAY

By

James M. Hill

ABSTRACT

The Chesapeake Bay can be divided into three major physiographic regions based on basin structure and sediment characteristics. These regions are:

1. The Northern Bay - a shallow region (ave. depth = 3m) dominated by fluvial inputs of freshwater and sediment;
2. The Middle Bay - characterized by a deep axial channel, stratified water column, and fine sediments, and;
3. The Southern Bay - a shallow region (ave. depth = 9m) composed of very coarse sediments (sand and silty sands).

Examination of the interstitial water compositions within each of these regions shows a strong relationship between the physical setting and the geochemical state of the sediment. Major relationships found are:

1. Northern Bay - pore water chemistry varies in response to variations in fluvial inputs, and dissolved total sulfide concentrations are below detection due to the large degree of dilution of seawater in this area;
2. Middle Bay - sediments highly sulfidic, in equilibrium with elemental sulfur. The composition of the pore waters is seasonally stable except at the transition between the Northern and Middle Bay where some fluvial influence is found, and;
3. Southern Bay - low carbon content of the sediment maintains low reaction rates thus metabolite levels are low and there is minimal depletion of sulfate.

ACKNOWLEDGEMENTS

This work has greatly benefited from the interaction with many individuals. I would like to specifically acknowledge: K. Weaver, E. Cleaves, and R. Kerhin of the Maryland Geological Survey for guidance and administrative support. R. Conkwright, J. Halka, P. Blakeslee, D. Wells, E.L. Hennessee, and R. Cuthbertson, of the Maryland Geological Survey, for valuable discussions and assistance in a myriad of ways. S. Jones for excellent secretarial support. O.P. Bricker III, formerly with the Maryland Geological Survey now with the United States Geological Survey in Reston Va., and G. Helz, at the University of Maryland, for critically reviewing the manuscript and for continual input into the research effort. Financial support was provided by the Department of Natural Resources.

INTRODUCTION

Particulate matter entering the Chesapeake Bay carries with it a variety of natural and anthropogenic substances such as nutrients, trace metals, trace organic compounds (e.g. herbicides, pesticides) and radionuclides. These substances may be associated with the particulate matter as part of the crystalline mineral lattice, as a coating on the detrital grains (usually hydrous iron and manganese oxides), adsorbed onto particulate organic matter and clays, or in organic coatings on detrital grains. A small portion of the loosely sorbed material and exchangeable ions are desorbed or exchanged when the particulate matter, which is primarily carried with fresh river water, mixes with the more saline waters of the estuary. The bulk of the material, however, travels with the suspended sediment to the site of deposition. During transport, this material is exposed to and tends toward equilibrium with an oxidizing environment. After the particulate matter and associated substances settle out they are exposed to very different biogeochemical conditions.

Bacterially mediated decomposition of organic material in the sediment consumes oxidants such as oxygen and sulfate ion and releases metabolites to the interstitial waters. This biological activity produces anoxic conditions in the sediment. Inorganic solid phases, particularly hydrous iron and manganese oxides react with the metabolites, are reduced and are mobilized into the interstitial waters. The direct result of these reactions is to increase the concentrations of dissolved components in the interstitial waters promoting a flux of dissolved chemical species across the sediment-water interface. The interstitial water composition and the flux across the sediment-water interface are controlled by the supply of organic and inorganic reactants, the rate of bacterially mediated decomposition of organic matter and the diagenetic reactions which remove certain chemical species from solution.

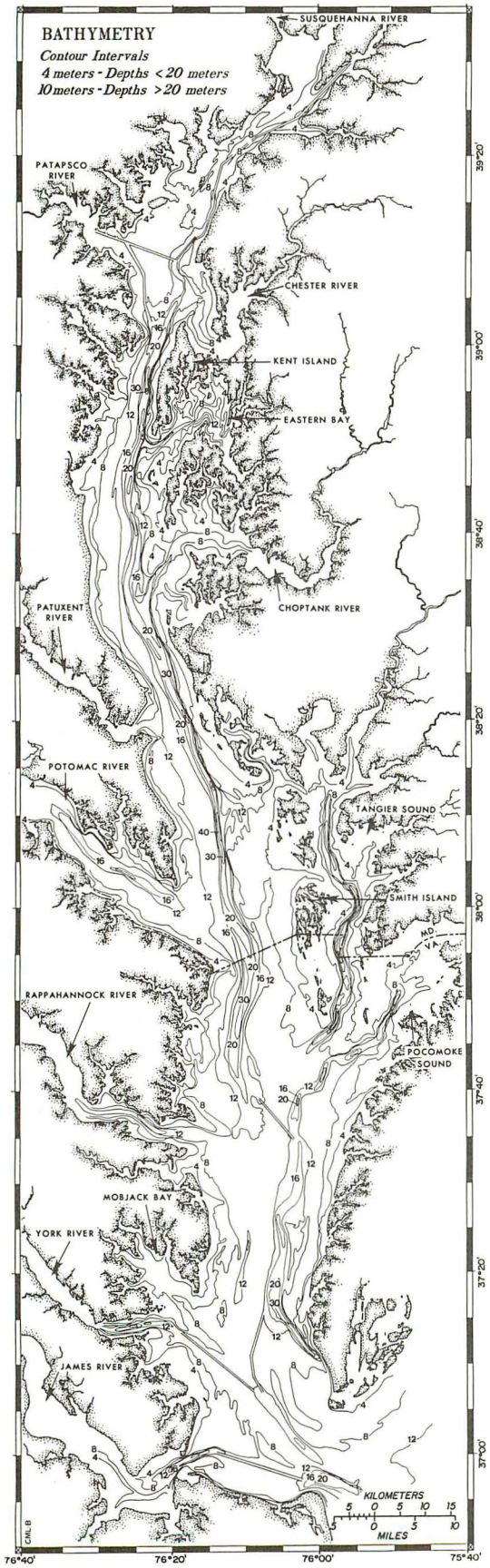
Benthic fluxes, i.e. the fluxes of material across the sediment-water interface, are important parts of the nutrient balance of many ecosystems, and may affect the quality of the benthic environment. Metals and other toxic substances may have direct acute or chronic effects on the benthic biota, or may accumulate in the biota and be transferred up the food chain to man. Evolving data on the biologic effects of trace metals (including radionuclides) coupled with increasing environmental burdens of these elements as a result of man's activities, makes it imperative that we thoroughly understand their behavior in natural systems. The determination and systematic investigation of the chemical environments which exist in the Bay are the first steps in a complex process of modeling the geochemical behavior of the Bay.

Bottom sediment contains the largest reservoir of nutrients and toxic substances in the estuarine system. Interstitial water is the vehicle through which the chemical contituents in the sediment are remobilized and transported. These waters are also the most sensitive indicator of the diagenetic reactions that occur during shallow burial, thus are a major key to interpreting the chemistry of the sedimentary environment.

This report presents an examination of the interstitial water chemistry in the Chesapeake Bay in the context of its physical and chemical setting. The interstitial water data used will be primarily taken from the compilation of Hill et al. (1985), and Tyree et al. (1981) with reference to the work of Bricker et al. (1977) and Reeburg (1969). Data on the physical and chemical framework, in which the pore water data will be referenced to, was collected synchronously as part of companion programs for the US EPA Chesapeake Bay project.

The reports of Byrne et al. (1982) and Kerhin et al. (1988) provide a description of the physical character of the Bay bottom sediments, in Virginia and Maryland portions, respectively. Data collected from the surficial sediments were: detailed grain size, visual and textural descriptions, water content, carbon and sulfur contents, and historic bathymetric change (to determine patterns of erosion and deposition). Surface samples were collected on a 1-kilometer grid in Maryland and a 1.6 kilometer grid in Virginia. Shallow cores (approximately 1 meter long) were also taken during three cruises, to provide physical characterization of the sediment at depth. These cores were taken in conjunction with cores taken for interstitial water chemistry (Hill et al., 1985; Tyree et al., 1981 a & b) and bethnic infaunal community analyses (Reinharz and O'Connell, 1981; Nilsen et al., 1980). The time of the year for each of the sampling cruises was selected to show the maximum seasonal variation of conditions.

Elemental composition of the sediment solids was determined on two hundred surficial samples and seventeen one-meter cores. These analyses were done in the studies of Sinex and Helz (1981), Helz et al., (1982), and Cantillo (1982). Also, sedimentation rates, measured by Pb^{210} techniques, were determined for the short cores. All of the shallow cores and most of the surficial samples were collected in cooperation with the aforementioned studies.



GEOGRAPHICAL SETTING

The Chesapeake Bay is the largest estuary in the United States. The Bay is situated within the Coastal Plain Province between the latitudes of 35° 55′ and 39° 35′. The main stem of the Bay is partitioned politically between the State of Maryland and the Commonwealth of Virginia (Figure 1). Population in the Bay region is concentrated in the urban areas of Baltimore, Maryland, Washington, D.C., and Norfolk, Virginia. Both Baltimore and Norfolk are major ports, which were developed to take advantage of the Bay as a natural waterway. Ships utilizing these ports enter the Bay either through its mouth, in the south, or via the Chesapeake and Delaware (C&D) Canal from the North. The C&D Canal links the Chesapeake Bay with the Delaware Bay.

GEOLOGICAL SETTING

The modern Chesapeake Bay was formed during the most recent post-glacial (Wisconsin) rise in sea level. This rise drowned the lower portion of the Susquehanna River drainage basin. The Bay is a long (≅300 km), narrow (≅5-50 km), shallow body of water which trends in a north-south direction. Its mean water depth is approximately 8 meters.

The main distinguishing feature of the Bay is a single, deep axial channel (Figure 1). Thalweg depths in this channel generally exceed 27 meters. The cross-sectionl profile of the channel is asymmetric; the western flank is formed by a relatively gentle, downward slope to the thalweg, while the eastern flank is quite steep. North and south of this channel are relatively uniform, shallow regions.

Figure 1. — Bathymetric map of the Chesapeake Bay with the major geographical features indicated.

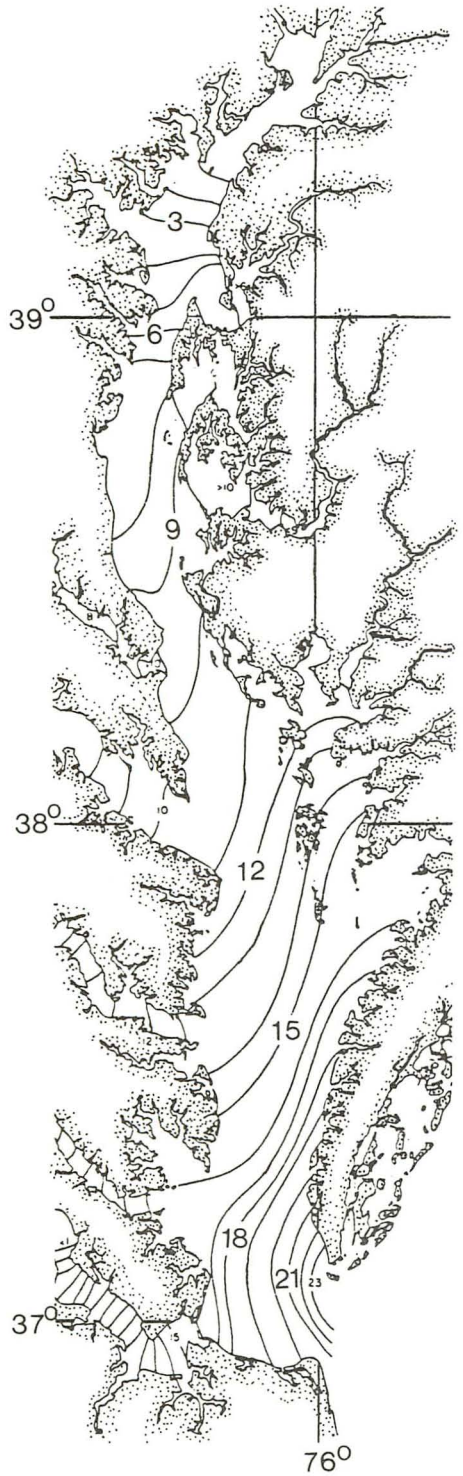


Figure 2. — Average Spring surface salinity of the main stem of Chesapeake Bay (adapted from Pritchard, 1971).

WATER COLUMN

The Chesapeake Bay is a partially mixed estuary (Pritchard, 1971). Mixing between the relatively fresh surface water and the denser, more saline bottom water occurs throughout the system. The Susquehanna River provides 60% of the total freshwater input to the Bay, with an average long-term discharge of 9.698×10^5 liters/sec (Lang and Grason, 1980). The other major tributaries are the Potomac River (3.225×10^5 liters/sec) and the James River (1.995×10^5 liters/sec). Residence time of freshwater in the Bay is approximately one year, assuming complete mixing and neglecting saltwater throughout.

The circulation of water in the Bay is controlled by freshwater inflow, density stratification, basin morphology, and the Coriolis force (Pritchard, 1971). Southward flowing freshwater travels predominantly along the western side of the basin (see Figure 2) Saline water entrained in this southward flow, by mixing, is removed from the Bay. The lost volume is replaced by the inflow of seawater which enters the system as bottom water at the mouth of the Bay. The more saline water travels northward along the eastern side of the basin where the flow eventually becomes trapped and directed by the main axial channel. A turbidity maximum occurs in the northern portion of the Bay, generally located north of the Bay Bridge.

The salinity of the Bay varies seasonally in response to the freshwater inputs. Figure 3(a-d) shows the average seasonal salinities of the water column down the axis of the Bay. Typically, the lowest salinities occur in the spring and the highest salinities occur in the fall.

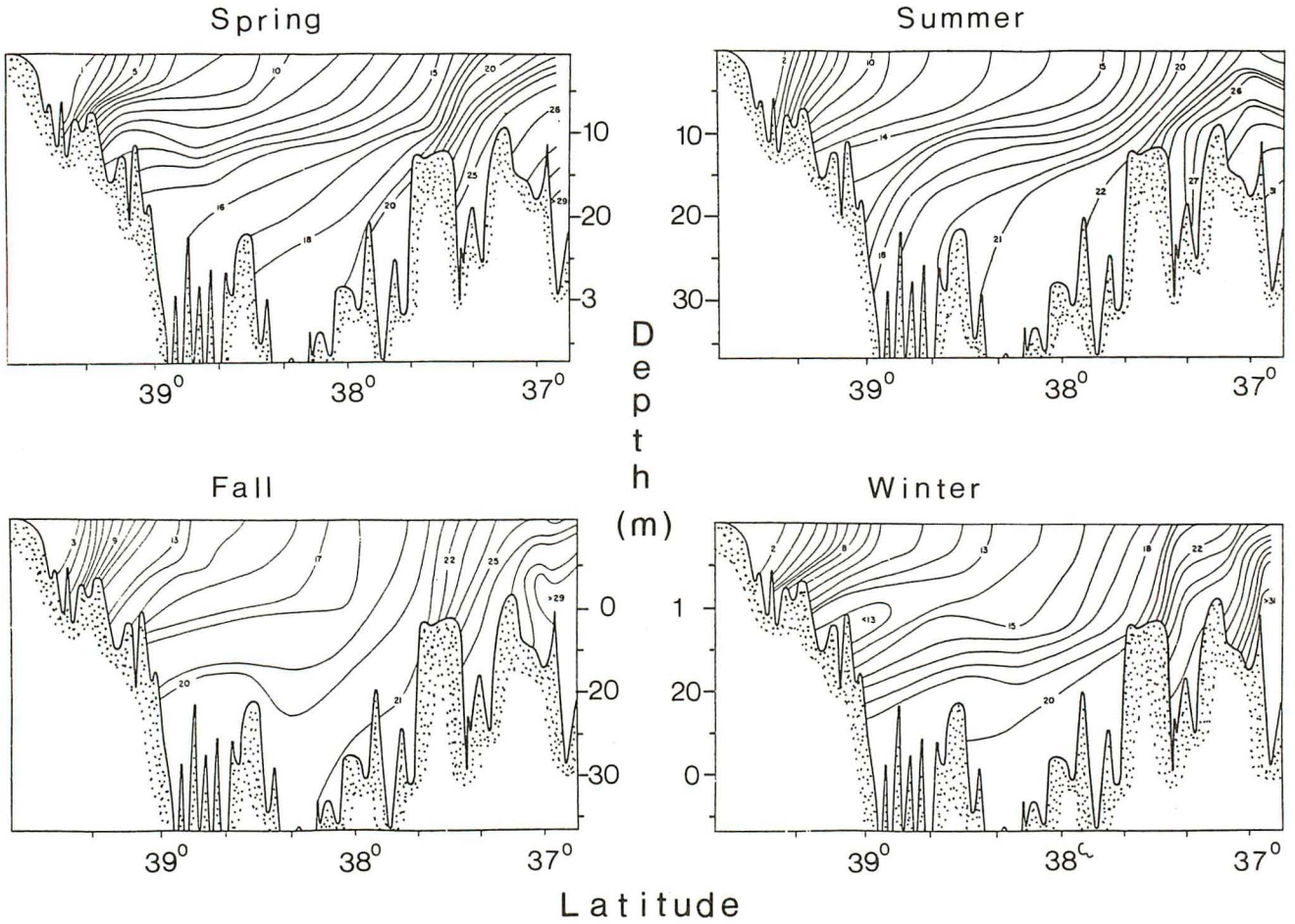


Figure 3. — Average seasonal salinity of the water column along the axis of the Chesapeake Bay (adapted from Pritchard, 1971).

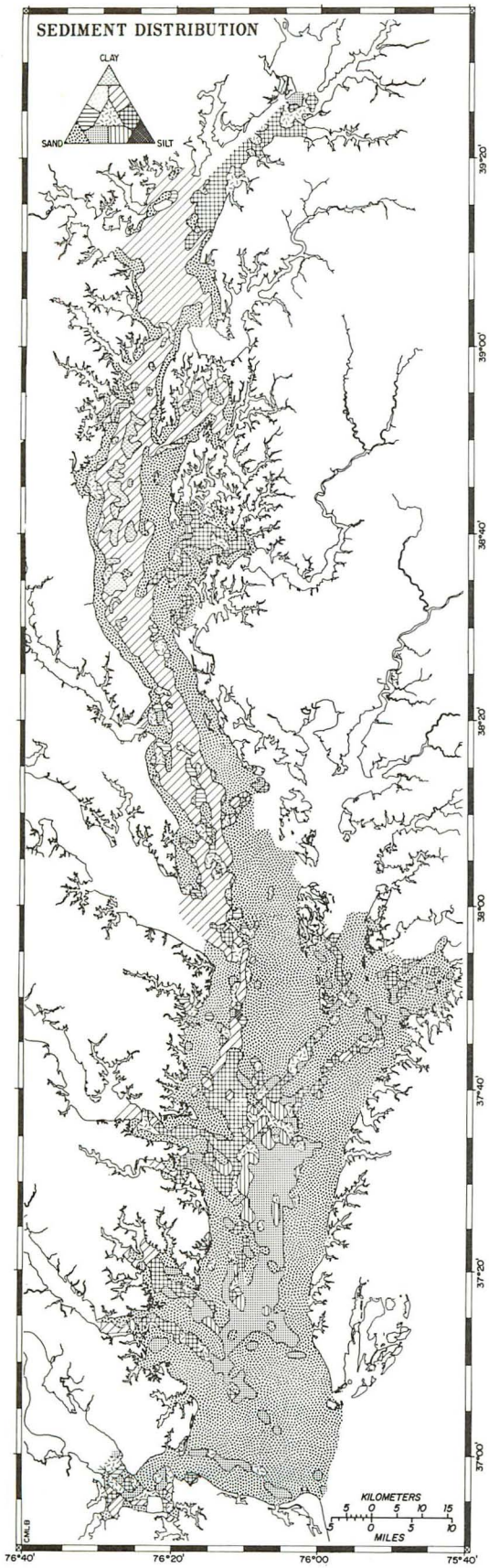


Figure 4. — Textures of surficial sediments based upon the classification scheme of Shepard (1954). Adapted from Byrne et al. (1982) and Kerhin et al. (1988).

SEDIMENT DISTRIBUTION

A sediment textural distribution map of the main stem Bay, based upon the data of Kerhin et al. (1988) and Byrne et al. (1982) and utilizing the ternary diagram and classification scheme of Shepard (1954), is presented in Figure 4.

This figure shows that sands, represented by the lower left corner of the ternary diagram, cover a much larger portion of the mainstem Bay than has been generally recognized. Over half of the bottom is composed of sediments in which sand sized particles constitute more than 75% of the grains by weight (Table I). The area represented by the lower left three fields of the ternary diagram, the sand, silty sands, and clayey sands in which sand sized particles comprise more than half of the grains, covers 66% of the mainstem Bay.

The bottom sediments in the deeper basins and axial channels largely consist of finer grained silts and clays (Figure 4). Throughout the Maryland portion of the Bay silty clays predominate with slightly coarser clayey silts occurring proximal to the Susquehanna River mouth. The finest grained clays are present only in the upper central portion of the Bay. The nearly continuous field of silty clays extends to south of the confluence with the Potomac River into Virginia where they grade into coarser clayey silts northeast of the Rappahannock River. South of the Rappahannock River sands and silty sands dominate the bottom sediments even in the deepest waters.

Within the dominant silty clay field, extending between the Bay Bridge and Rappahannock River, a wide variety of sediment types occurs in the deeper portions of the Bay (Figure 4). These include nearly all of the ten classes represented in the ternary diagram and have little if any relationship with water depth. Of particular note are the isolated pockets of sands and clayey sands which are located between the Patuxent and Potomac Rivers. These pockets occur in over 12 meters of water depth and are separated from nearshore sources.

In regard to geochemical consideration the classes can be grouped into two major categories; sediments containing greater than 25% clay (clay rich sediments) and those containing less than 25% clay (Quartzose sediments). The sand and silt size fractions of the Bay sediments are composed primarily of quartz, hence the name Quartzose. Quartz is inert in redox reactions, and virtually inert to most other lower temperature reactions. Consequently, the magnitude and rates of reactions occurring in these sediments would be expected to be low, but the areal extent of these sediments makes their contribution to the whole Bay significant (Hill and Halka, 1988). Clay-rich sediments are associated with high concentrations of carbon and other chemical species which are actively involved in the redox system in the sediment.

Table I. — Total areal extent covered by each Shepard's class within the main stem of Chesapeake Bay (Hill and Halka, 1988).

Sediment Type	Area (km^2)	% Area
Sandy Clay	67.9	1
Sand	3715.0	57
Silt	1.9	0
Clay	73.1	1
Sand-Silt-Clay	327.6	5
Clayey Sand	67.9	1
Clayey Silt	496.6	8
Silty Clay	1207.3	18
Silty Sand	546.8	8
Sandy Silt	87.0	1
	6526.6	

EROSION-DEPOSITION PATTERNS

The dynamics of sediment movement can be inferred by comparing corrected historic bathymetric records and determining changes with time. Areas of diminishing water depth indicate deposition, whereas areas of deepening indicate sediment removal, or erosion. Figure 5 shows the predominant trend within given areas of the Bay. There are five major areas of bathymetric change in the Bay; three depositional, one erosional, and one area of no apparent change. There is a great deal of complexity in each of these areas owing to localized processes such as slumping or dredging operations.

Sedimentation rates have been measured at 22 sites throughout the Bay using Pb^{210} isotopic techniques (Figure 6). Wide variations in the rates, for a given area, reflect the difficutly in the use of Pb^{210} rates. The assumptions, upon which Pb^{210} sedimentation rates are based are:

1) Measurements are limited to fine grained sediment, because Pb is associated with clay-sized material;
2) Sedimentation must be uniform through time;
3) The sediments cannot have been subjected to reworking;
4) The method is 'blind' to sediment erosion;
5) Pb is assumed free of diagenetic remobilization, and;
6) The measurements are applicable only to the site measured.

Generally, these constraints make extrapolation of Pb^{210} values over broad regions quite suspect in the Bay.

An alternate method of determining average changes in sediment thickness with time within large areas utilizes historic bathymetric changes, corrected for crustal warping

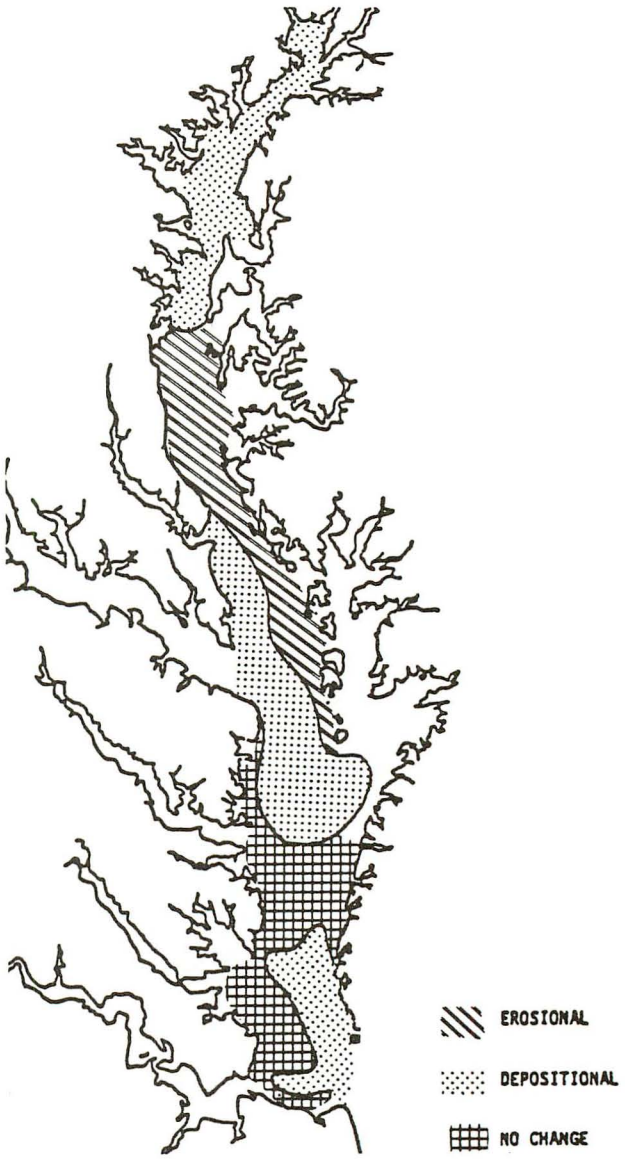
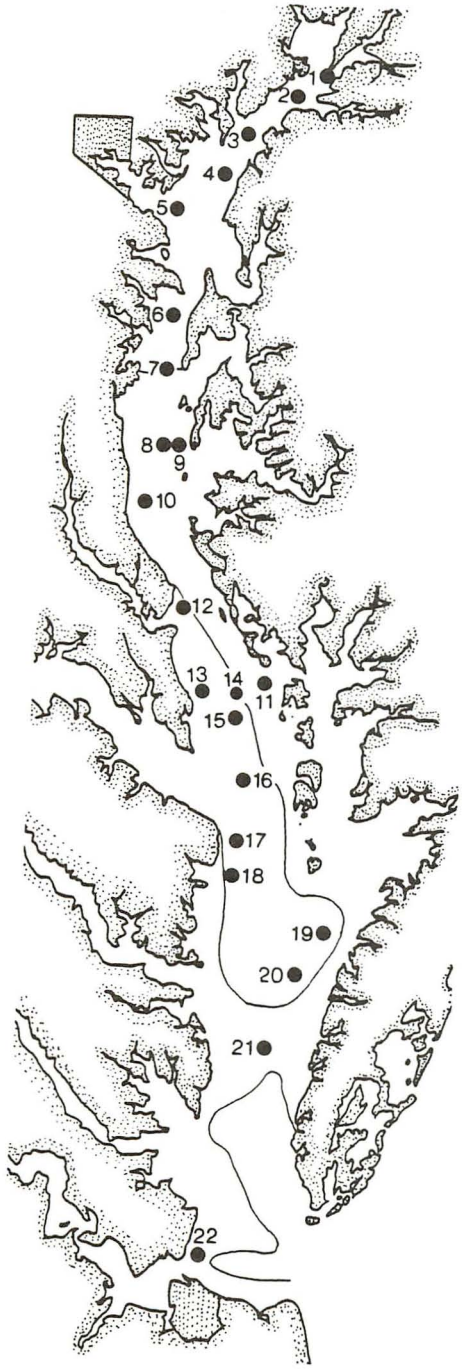


Figure 5. — Gross deposition-erosion patterns determined by comparison of historic bathymetric data (after Byrne et al. (1982), and Kerhin et al. (1988)).



Pb^{210} Sedimentation Rates (mm/yr)
Northern Depositional Area

Sta	Rate	Reference
1	2.0	1
2	4.5	2
3	3.1	1
4	80	3
5	8.7	1
6	30	3
	Middle Erosional Area	
7	17.9	1
8	.7	1
9	0.9-1.2	4
10	5	3
11	6.6	1
	Middle Depositional Area	
12	3.6	1
13	2.3	1
14	12.6	1
15	5.0	3
16	12.2	1
17	1.9	1
18	3	3
19	5.2	1
20	3.7	1
	Area of No Net Change	
21	2.3	1
22	3.8	1

References:

1 - Helz et al. (1982)
2 - Hirschberg and Schubel (1979)
3 - Goldberg et al. (1978)
4 - Schubel and Hirschberg (1977)

Figure 6. — Locations and sedimentation rates, determined using the Pb^{210} method, relative to the bathymetric deposition-erosion pattern of the Bay.

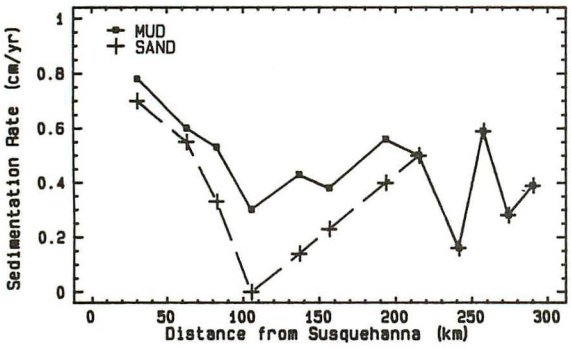


Figure 7. — Average sedimentation rates determined by the method of bathymetric comparison, calculated within twelve segments in the Bay. In the Maryland portion of the Bay, two rates per segment were calculated; a rate for muddy sediments (solid line), and a rate for sandy sediments (dashed line), Only one overall rate per segment was calculated in Virginia. (Hill and Halka, 1988).

and changes in sea level. Sedimentation rates determined by this method are shown for 12 geomorphic segments in Figure 7. Rates for both muddy and sandy sediments are given in Maryland and single rates are given in Virginia. The highest rate of nearly 0.8 cm/yr occurs in muddy sediments of the northern Bay adjacent to the Susquehanna River mouth. The rates decline southward from this high value to a minimum (approximately zero) in the upper middle Bay. Continuing south, rates rise again for both the muddy and sandy sediments to maxima of between 0.5 and 0.6 cm/yr. It is interesting to note that the shape of the curve is similar to that reported from radionuclide dating (Officer et al., 1984) with the minimum bathymetrically determined rate occurring approximately 60 km further up bay than the radiometrically determined minimum.

CARBON AND SULFUR DISTRIBUTIONS

Organic carbon is an important component of the estuarine system. Physically, it is a binder that aids in the agglomeration of suspended sediment (Zabawa, 1978). Chemically, organic carbon is the primary reduced chemical species which, through bacterial action, depletes the sediments of oxidized species thus producing the reduced, anoxic state of the system.

Figure 8a shows the carbon distribution in the main Bay in 1% (dry wt) contour intervals. The distribution of carbon in the sediment varies directly with the proportion of fine-grained material. Concentrations of carbon range from 0 to 5%, corresponding to Sand to Clay sediment types respectively. The major exception to this behavior is in the sediments found in the area north of the Bay Bridge. In this area reduced carbon concentrations are much higher, reaching concentrations of 10.5%. These high values have been attributed to sewage, coal, and/or terrestrial carbon input (Ryan, 1953; Folger, 1972 a & b; Goldberg et al., 1978; Helz et al., 1982; Spiker et al., 1982). Even though the precise origin of these anomalously high values is uncertain, it is clear that the nature of the carbon differs from the rest of the Bay. This is indicated by $\delta^{13}C$ values and C/N ratios which differ from values characteristic for marine sources (Hunt, 1966; Shimoyama and Ponnamperuma, 1975; Helz et al., 1982; Spiker et al., 1982).

Reduced sulfur found in sediments is a by-product of the oxidation of reduced carbon by SO_4^{2-} (Goldhaber and Kaplan, 1974). As such, sulfur concentrations are related to the concentrations of carbon in the sediment. This can be seen by comparing Figure 8a with Figure 8b. The major anomaly seen in the comparison is again found in the area north of the Bay Bridge. In this area carbon concentrations are quite high, but the concentrations of reduced sulfur are low. The low sulfur concentrations are due to the low availability of SO_4^{2-} in the water column. For a detailed description of sedimentary carbon and sulfur in the Bay refer to Hennessee et al. (1984), Hobbs (1983), and Hill (1987).

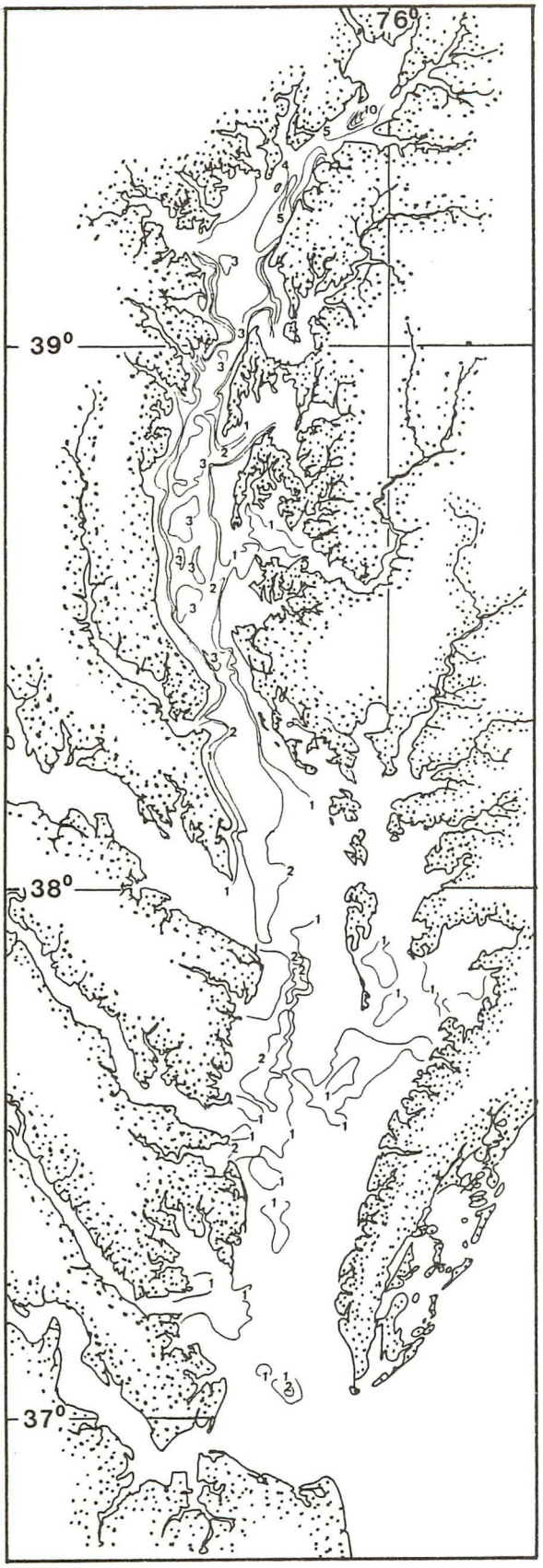


Figure 8a. — Organic carbon content of the surficial sediments of the Bay in 1% contour intervals.

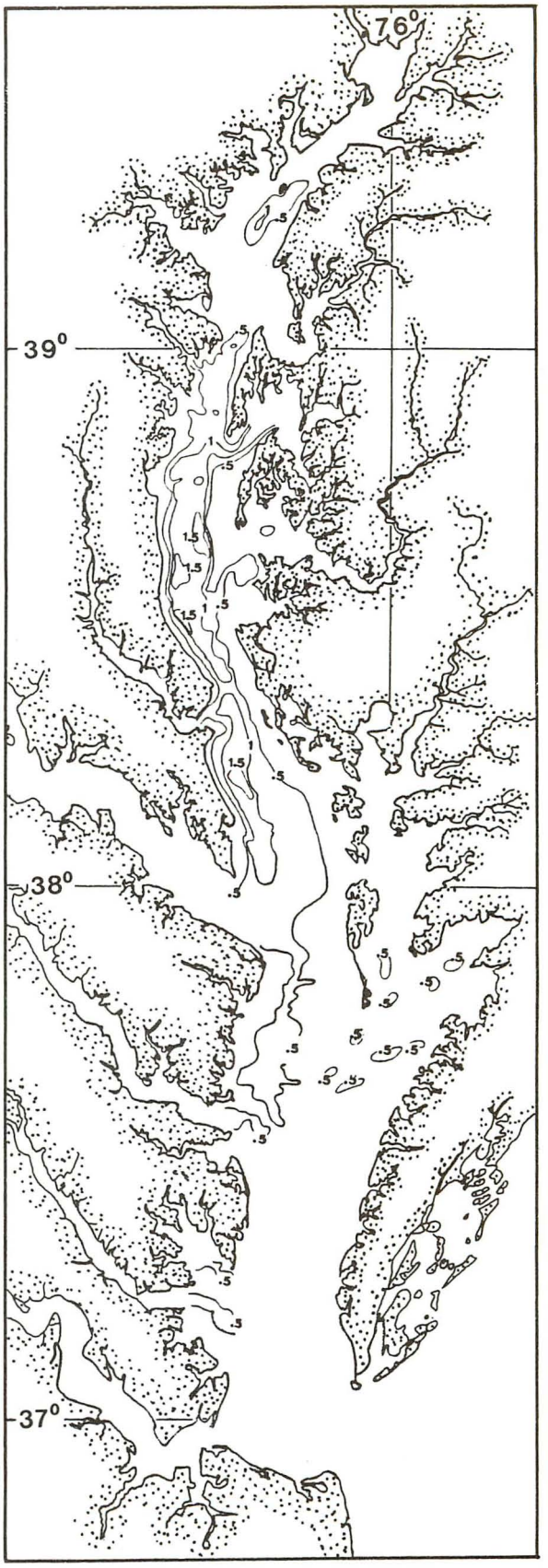


Figure 8b. — Sulfur content of the surficial sediments of the Bay in 0.5% contour intervals.

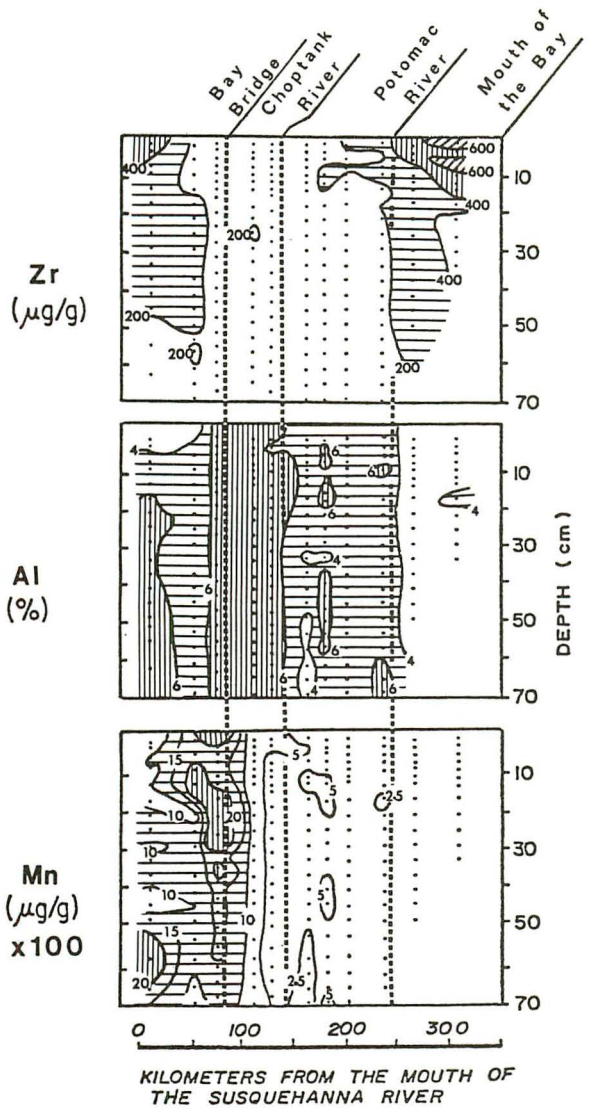


Figure 9. — Zr, Al, and Mn content of cores taken along an axial transect of the main stem of the Bay. Sediments were sampled from the sediment-water interface down 70 cm into the sediment. The dots on the figure represent depths at which the cores were sampled (modified from Cantillo, 1982).

TRACE METALS

Trace metals in environmental systems are important because of their affect on the health of plants, animals, and man (Bowen, 1966; Keith and Telliard, 1979; Forstner and Wittman, 1979), as indicators of sediment transport (Eaton et al., 1980), and their participation in redox processes (see Garrels and Christ, 1965). The first Baywide survey of the trace element composition of the bottom sediments was performed by Sinex and Helz (1981) and Sinex et. al. (1981). The samples analyzed were 200 surficial grab samples. Information on trace metal variation as a function of depth in the sediment was obtained by Cantillo (1982) on 17 one-meter long cores, taken throughout the main stem of the Bay. The pertinent results from these studies are listed below:

1) Trace element behavior in the sediments can be explained by a combination of three factors, or associations:
   a) Association with clay minerals - Al, Ga, Cr, and C;
   b) Association with heavy minerals - Ti, Zr, and the Rare Earth Elements, and;
   c) Association with oxyhydroxide grain coatings -Fe, Mn, Ni, Cu, Co.

   The areal extent of representatives of each of these major associations is shown in Figure 9. This figure presents north-south axial transects in the Bay. The data are taken from the core analyses (Cantillo, 1982), and show the concentrations of Zr, Al, and Mn in the sediments. Zr and Al would be expected to follow sediment distribution patterns. Zr should track coarse sediments, while Al should track fine-grain, clay mineral containing sediment; this is indeed the case. Mn, on the other hand, is associated with oxyhydroxide grain coatings which are chemical precipitates which form as a result of mixing freshwater with brackish water. The highest levels of Mn are found north of the Choptank River indicating the areal extent of the mixing and depositional processes dominated by the Susquehanna River.
2) The dominant source of trace metals is the Susquehanna River. The highest concentration of trace metals is within the area between the mouth of the Susquehanna River and the southern point marking the mouth of the Choptank River. (Note: this corresponds well with the bathymetric area of Susquehanna influence shown in Figure 5.)
3) Enrichment of trace metals diminshed southward towards the mouth of the Bay (Figure 10).
4) The possible input of material from the continental shelf is indicated by elevated Cr concentrations at the mouth of the Bay. The Cr is found in the $<63\mu$ size fractions and is thought to be associated with chlorite.

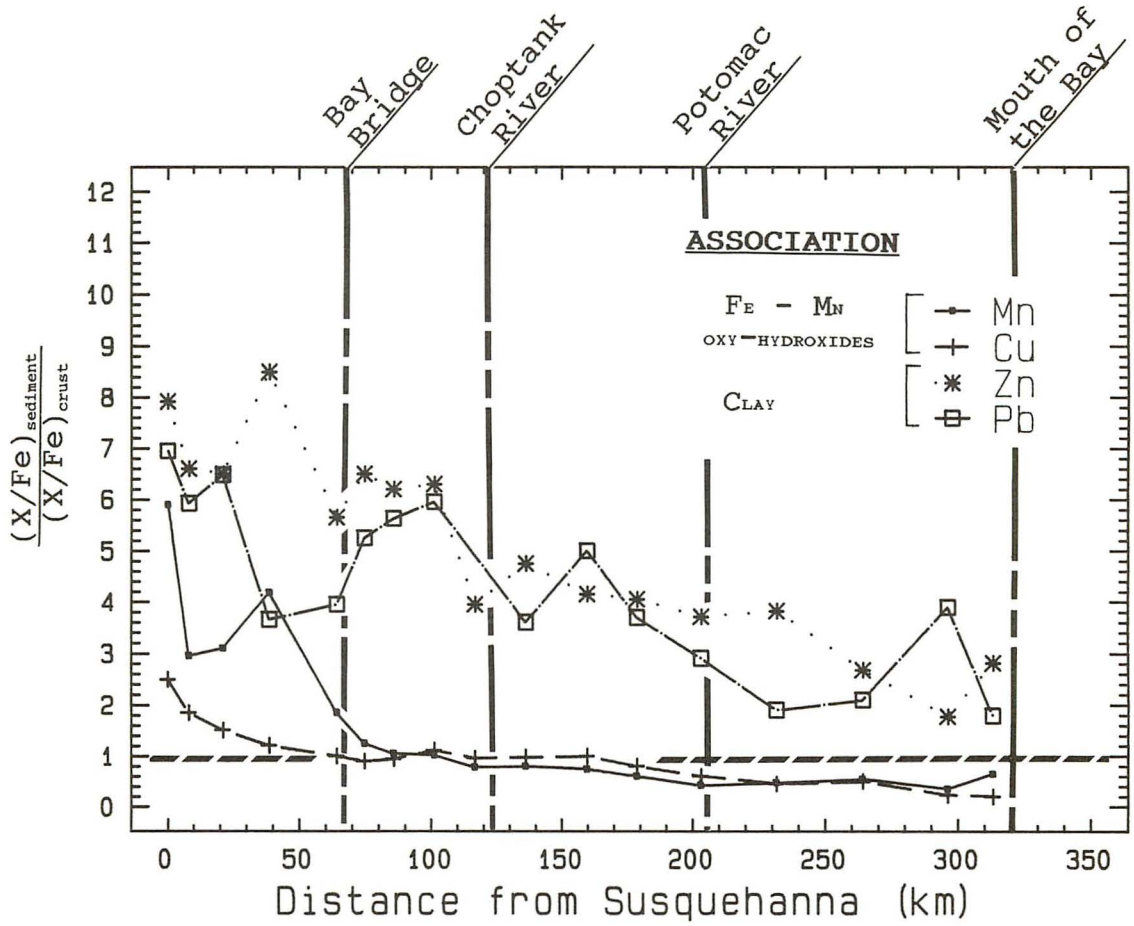


Figure 10.— Enrichment factors of Mn, Cu, Zn, and Pb in surface samples along the axis of the Bay. (modified from Sinex and Helz, 1981).

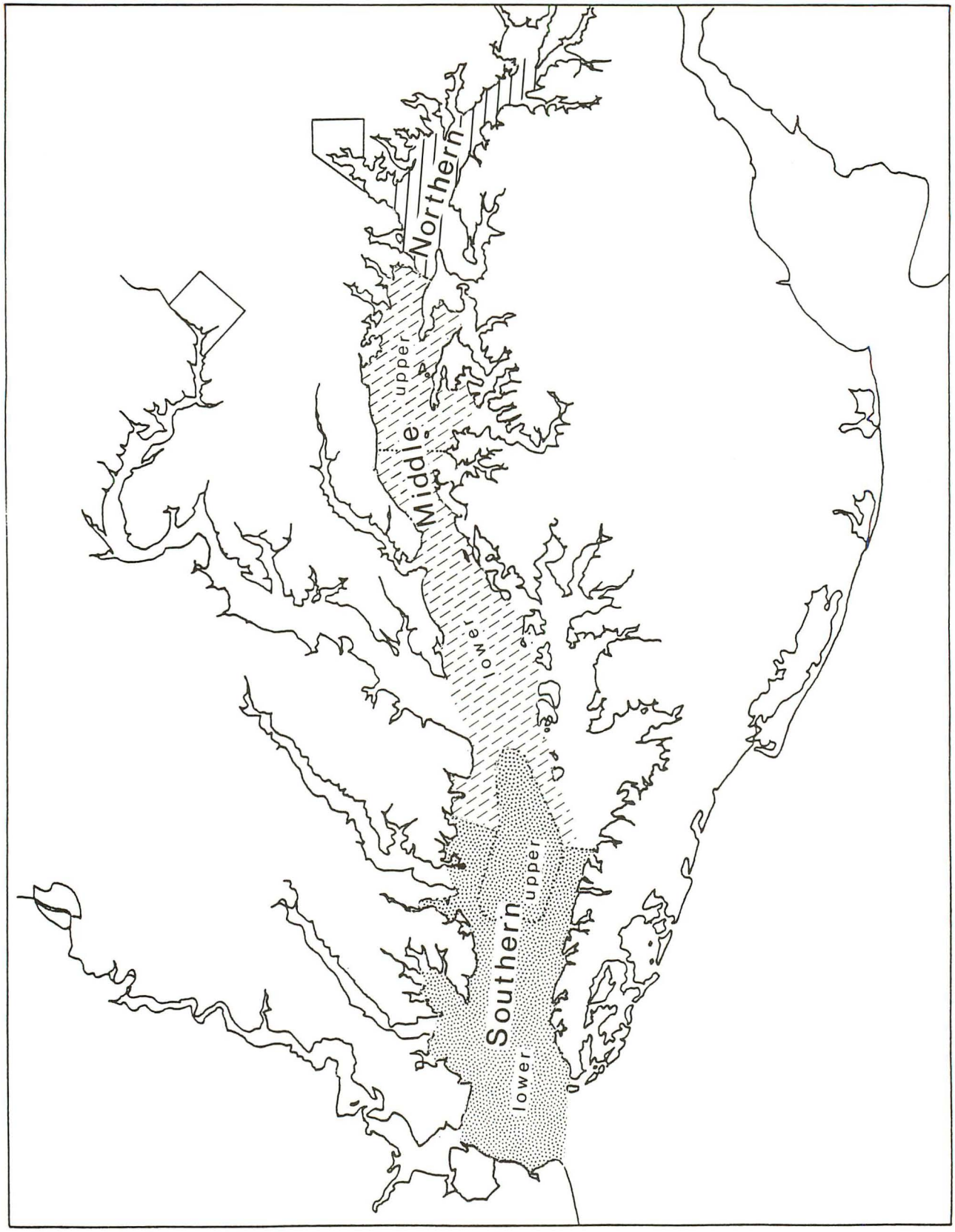


Figure 11. — Physiographic regions of the Bay.

PHYSIOGRAPHIC REGIONS OF THE BAY

The Bay can be divided into physiographic regions based on the preceding discussion. The distinctions which characterize the regions will be used in discussing the interstitial water chemistry of the Bay. These regions are shown in Figure 11; there are three major regions and two subregions. The major features of the regions are summarized in the following:

NORTHERN BAY

The Northern Bay region encompasses the area between the mouth of the Susquehanna River and the Bay Bridge. The water depths in this region are the shallowest in the Bay ranging from 0.6-7.0 meters. This region is dominated by freshwater and sediment inputs from the Susquehanna River.

The Susquehanna River supplies 60% of the freshwater input to the Bay, close to 90% north of the Potomac River, and is the major source of sediment to the Bay. The freshwater input maintains the low salinities (0-15 ppt) in this region, and produces large seasonal variations in salinity. Approximately 80% of the fluvial sediment load is deposited in this region. Consequently, this region has high depositional rates, and a sediment distribution pattern which follows the classical deltaic pattern of seaward fining (in the Northern Bay; Sand → Clayey Silt → Silty Clays). These sediments contain the highest concentrations of trace metals (with the highest enrichment factors) the highest concentration of organic carbon (3-10.5%; with a terrestrial component), and the lowest sulfur concentrations in the Bay.

MIDDLE BAY

The Middle Bay region is the area between the Bay Bridge and the mouth of the Potomac River. This region is dominated by the main axial channel (average thalweg depth >18 meters). The water column in this region (mean salinity 15-28 ppt) is stratified as a result of channeling the higher density saline water from the mouth of the Bay. As a result of stratification seasonally hypoxic/anoxic conditions are produced.

The sedimentation patterns in this region are quite complex owing to significant contribution of erosion of bottom sediments and input from the shoreline erosion. The sediments themselves are the finest in the Bay (Silty-Clays and Clay). Compositionally, the trace metal and organic carbon (2-4%) concentrations are intermediate between the Northern and Southern Bay, while the sulfur concentrations are the highest in the Bay.

The Middle Bay is divided, at the mouth of the Choptank River, into the Upper and Lower Middle Bay regions. The boundary, at the mouth of the Choptank, marks the southernmost extent of influence of the Susquehanna River evident in the sediment. This influence is shown in the depositional patterns and the trace metal distribution of the sediments (see Figures 5, 7, and 10).

SOUTHERN BAY

The Southern Bay is the region between the mouth of the Potomac River and the mouth of the Bay. Water depths in this region are shallow averaging approximately 9 meters. The deepest waters are found in the northern portion of the region, which is the shallowing southern end of the axial channel. Water circulation is dominated by marine/tidal influences, with salinities close to seawater.

This region is primarily depositional, with sediment supplied from the Middle Bay and from the Atlantic Ocean. Sediments, here, are the coarsest in the Bay; the predominant size classes are Silty-Sand and Sand. Trace metals, carbon and sulfur concentrations are the lowest found in the Bay.

In a similar manner to the Middle Bay, the Southern Bay is divided into sub-regions. The Upper Southern Bay is comprised of the shallowing southern end of the axial channel and the area encompassed by shoal complex off of the mouth of the Rappahannock River. Sediments in this subregion are the finest in size in the Southern Bay (Silty-Clays and Clayey-Silts). The composition of the sediments are intermediate between the Lower Middle Bay and the Lower Southern Bay; the Lower Southern Bay being composed almost entirely of Sand type sediments.

PHYSIOGRAPHIC DISTRIBUTION OF INTERSTITIAL WATER DATA

GENERAL CONSIDERATIONS

Interstitial waters are the fluids contained in the pore spaces of the solid sediments. It is the medium in which most of the reactions in the sediments occur and it is the transport vehicle for dissolved solids within the sediment and across the sediment water interface. Proceeding from the sediment-water interface down into the sediments, the environment of the sediment becomes increasingly isolated from the influences of environmental conditions of the water column. Shallow sediments are influenced by seasonal variations in temperature and water column composition (Figure 12). Bioturbation, advection, chemical and thermal diffusion from the water column are all significant processes in Shallow sediments. Deep sediments are insulated from these variations. These sediments are isothermal, maintaining the long term mean seasonal temperature. Transport of chemical species in deep sediment occurs in response to chemical reactions or flow of the pore waters. Chemical reactions either induce concentration gradients providing the drive for diffusive transport, or the reactions can produce gasses which due to their low densities bubble upward. Flow of water in the Deep sediments is the result either of compaction and dewatering, or groundwater flow. Composition of the interstitial waters are the results of many dynamic processes. The behavior of any individual chemical species at a given location in the Bay and a specified depth in the sediment can be understood by examining the influences which change the pore waters' concentration with time. Simply this can be expressed as follows:

$$\frac{dC(s)}{dt} = \text{Input } (s) - \text{Output } (s). \qquad (1)$$

Here, the change in concentration of a chemical species (s) with time, within a given location in the sediment, equals the rate at which s is added, or added to the location, minus the rate at which it is removed from the location. The chemical species can be added or removed by either transport/physi-

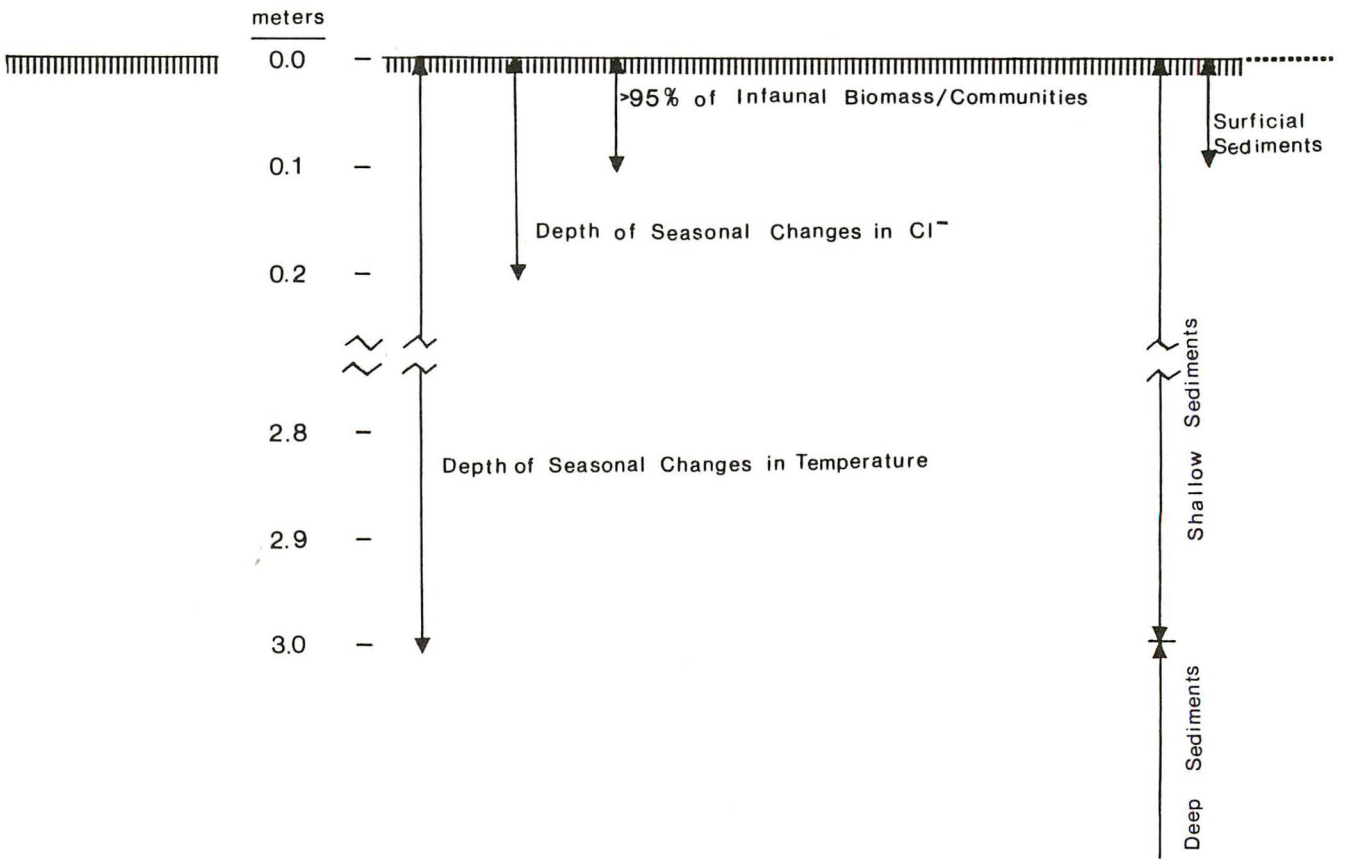


Figure 12. — Approximate depths at which major physical influences effect the muddy sediments of Chesapeake Bay.

cal processes or through chemical reaction. These processes can be incorporated into Equation (1) as follows:

$$\frac{dC(s)}{dt} = [I_R(s) + I_T(s)] - [O_R(s) + O_T(s)], \quad (2)$$

where: I and O - designate the rates of input and output respectively

$_R$ and $_T$ - indicate whether the fluxes are reaction ($_R$) or transport ($_T$) derived.

Separating Equation (2) into process related components yields:

$$\frac{dC(s)}{dt} = [I_R(s) - O_R(s)] + [I_T(s) - O_T(s)]. \quad (3)$$

From Equation (3) it can be seen that the concentration of any chemical species is the net result of fluxes of chemical reactions, and physical transport processes, and that the contribution of each of these processes can, in theory, be singled out.

Within the Bay, the degree of transport and the nature and extent of the chemical reactions which occur in the sediment can be substantially different when comparing spatially different locations. Locational variablity is the result of differences in sediment and water column composition, physical sedimentology, relationship to source, basin structure, and other conditions. The following sections discuss the major influences which effect the behavior of individual chemical species as they relate to the physiographic setting of the Bay.

CONSERVATIVE BEHAVIOR OF CHLORIDE (AND THE MAJOR SEAWATER IONS)

One of the major sources of dissolved species in the interstitial water is from the overlying water column. These species enter the sediment by being entrained in water trapped in the sediment as the sediment solids are deposited (advection), by mixing with the pore water by various mixing processes (such as bioturbation), and through diffusional transport. The major ion composition of the water column varies thoughout the length of the Bay, reflected in the down-Bay salinity gradient (see Figures 2 and 3). This gradient results from the mixing of fresh river water with saline ocean water. Both river water and seawater have distinct composition. The mixing behavior of the two waters can be approximated by a conservative mixing model which emulates the behavior for each of the major ions as a function of the chloride ion concentration (Figure 13). Chloride is used in the figure as the normalizing and indicative parameter because its behavior is strictly conservative within the water column and sediments; that is, there are no processes which remove Cl^- from the aqueous phase.

There are two features to note in Figure 13. First, at salinities less than approximately 2 ppt, the fluvial component has a significant effect on the ratios of the major ions to Cl^-; the water no longer appears as simply diluted seawater, i.e. constant ratios independent of Cl^- concentration. Secondly, the range of dissolved solids varies over two orders of magnitude in the Northern Bay.

Besides showing regional differences in water column composition, the conservative mixing model which produced Figure 13 can be used to show the presence of diagenetic processes. For example, Figure 14 plots the ratio of SO_4^{2-}/Cl^-; the points are data taken throughout the Bay, from samples collected at the surface to one meter downhole, and the solid line is the predicted conservative behavior. Clearly, SO_4^{2-} is being removed from the system as shown by the points below the curve; the process involved is anaerobic sulfate reduction.

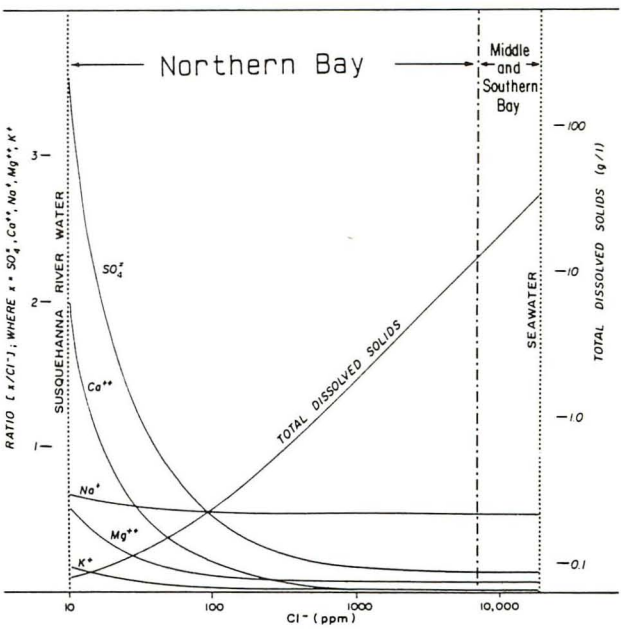


Figure 13. — Compositional behavior of Bay water as a result of the mixing of river water with sea water (Hill, 1984).

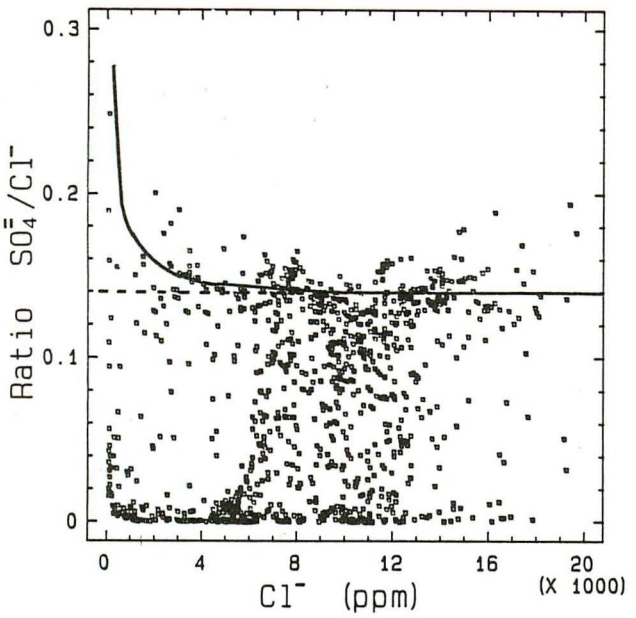


Figure 14. — Sulfate depletion in the pore waters of Bay sediments is shown by the measured ratios of SO_4^{2-}/Cl^- (dots) lower than the predicted ratio shown by the solid line (data from Tyree et al. 1981 a).

Eh (OXIDATION POTENTIAL)

The redox state of any portion of the sediment column represents a balance between the rate of supply of oxidants (electron acceptors) to the sediment and the rate at which the oxidant is utilized by reduced compounds (electron donors). The primary reduced compounds are complex organic compounds which have been derived from terrigenous detritus and land plants, and from the settling of dead planktonic assemblages. This organic matter is utilized by heterotrophic organisms, predominantly bacteria, as a food source. The organisms derive energy from the organic matter by mediating, or catalyzing, the reactions between the organic matter and the available oxidants.

There are several oxidants available for use by the bacteria. However, based on field observations (Froelich et al., 1979; Reeburg, 1969) and free energy considerations (Stumm and Morgan, 1981) there is a preferred sequence of oxidant utilization. This sequence arises due to the amount of energy released in the reaction; the greater the energy that a particular bacterium can liberate per mol of organic carbon, the more favored is that bacteria in competing for the food sources. The preferred oxidant sequence utilized by competing bacterial groups is:

$$O_2 > NO_3^- > MnO_2 > FeO(OH) >> SO_4^{2-} > CO_2$$

(CO_2 represents Internal Conversion or Fermentation)

All of these oxidants can be used within the sediment column in any region of the Bay. Figure 15 is an idealized core from the Bay. This figure lists the general physical features, color, oxidant used and associated metabolic redox reaction (organic matter is written as CH_2O). The actual depth interval over which the various reactions are dominant depends on the relative availability of oxidant and reduced carbon.

There are two physical settings where the strongest oxidants (O_2, NO_3^-, MnO_2, and FeO(OH) are used. In areas of the Bay where the carbon content of the sediment is high these strong oxidants are important in the water column, which is usually well aerated (saturated with O_2), the flocculent layer, a highly fluid material not incorporated in the sedimentary column (see Hill et al., 1985), and possibly the uppermost portion of the sediment column at the sediment-water interface. Within the sediment, this division appears as a distinct brown colored layer. The second setting where strong oxidants are dominant is in bottom sediments which are characterized by extremely low levels of reactive carbon, with the corresponding slow rates of bacterial decay. This condition is similar to the environment found in pelagic deep sea sediments. In the deep sea sediments the organic detritus, which has been incorporated into the sediment, has been exhaustively oxidized during its long exposure to the water column's oxic environment. Consequently, the deposited carbon is chemically refractory and is decomposed slowly. The slow decomposition allows for the deeper penetration of the stronger oxidants (Froelich et al., 1979). The Bay analog of this system would be found in the Quartzose sediments where the concentrations of carbon approach zero.

Sulfate is one of the primary oxidants in the shallow sediments of the Bay. Bacteria, such as *Desulfovibrio desulfuricans,* which reduce SO_4^{2-} are strict anaerobes; they cannot live in environments where oxidants stronger than SO_4^{2-} predominate. This is generally seen in the sediments as a sharp color contact, brown on the aerobic side and black on the anaerobic side. The black color is due to the precipitation of iron monosulfides (FeS), acid leachable sulfides (Berner, 1970), which results from sulfide generation (HS^-) during SO_4^{2-} reduction. The black color grades into a grey color going down-hole. This color change indicates the conversion of the FeS into pyrite (FeS_2). Throughout the sediment column where there is vigorous SO_4^{2-} reduction there is a strong odor of hydrogen sulfide. Sulfate reduction occurs thoughout the sedimentary environment of the Bay. This has been shown in Figure 14 which shows the observed ratio of SO_4^{2-}/Cl^- as a function of Cl^-.

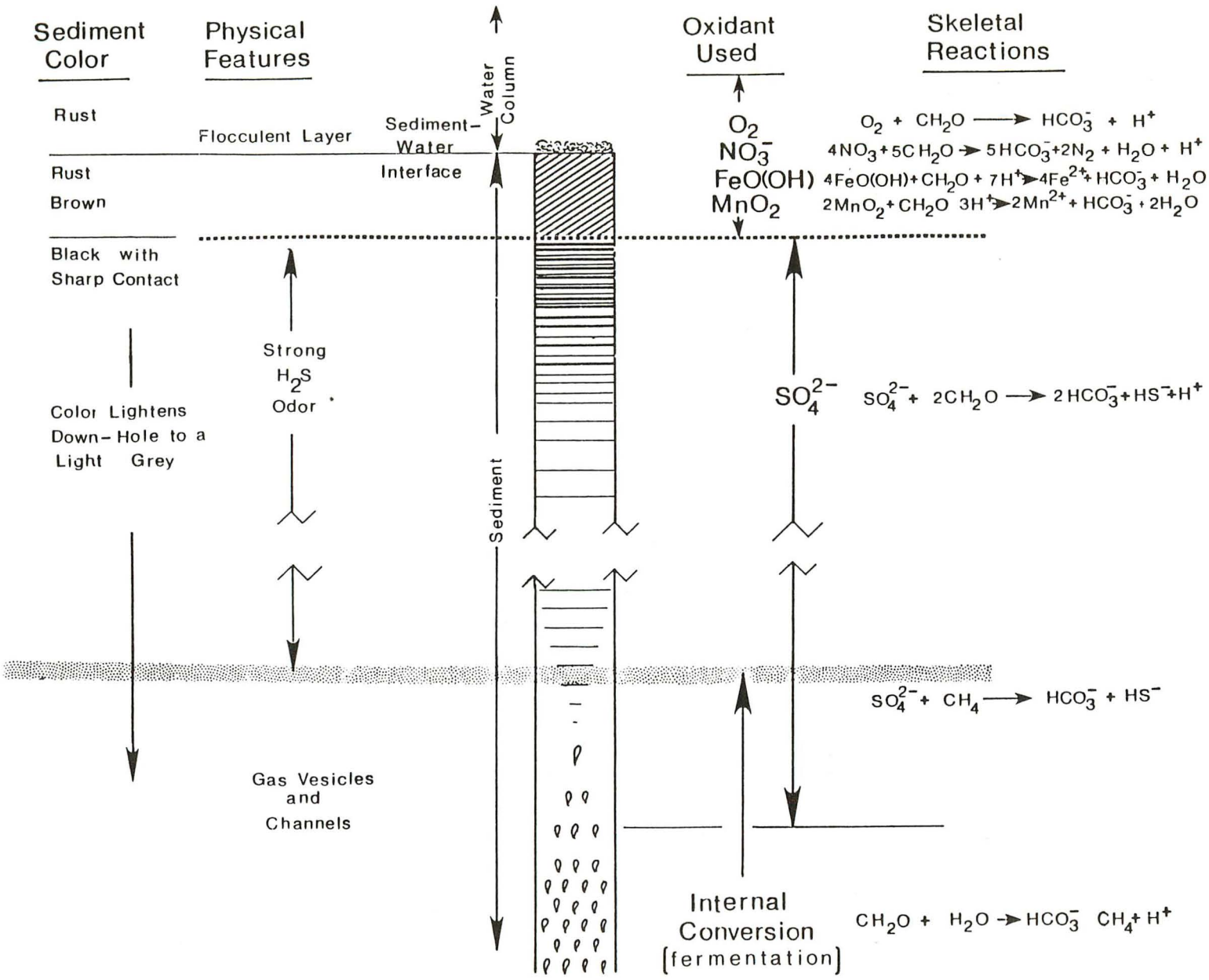


Figure 15. — Idealized core showing major physical features with corresponding bacterial metabolic reactions and oxidants used.

Once SO_4^{2-} is depleted the primary mode of organic matter decay is methanogenesis. Methanogenesis incorporates the processes by which methane (CH_4) is produced, i.e. CO_2 reduction or internal conversion. The bacteria in this environment derive energy from the organic matter by disproportionation; that is, the organic matter is the source for both the oxidant and reductant. Evidence of CH_4 production in the Bay is derived from limited direct measurements (Reeburg, 1969; Reeburg and Heggie, 1974) and by indirect evidence, seismic reflection data and observation of bubble and bubble channels in X-rays of cores (Halka et al., 1988). From this data, methanogenesis appears to be a wide-spread phenomenon throughout the Bay, particularly in the low salinity, carbon-rich (i.e. clay-containing) sediments.

Methanogenesis and SO_4^{2-} reduction are not mutually exclusive biological processes. Methane production can occur simultaneously with SO_4^{2-} reduction, after the SO_4^{2-} concentration has been reduced to lower levels. Also SO_4^{2-} reducers can utilize CH_4 as a food source (see for discussion and references Zehnder and Brock, 1980). The nature of the processes occurring at the transition between the sulfate reduction and methanogenesis are not clearly understood.

Eh is an equilibrium parameter which is commonly employed to indicate the overall redox state of natural systems, which result from the processes discussed above. It is defined as:

$$Eh = E^\circ + \frac{RT}{nF} \ln K \qquad (4)$$

Where: E° - is the half-cell potential of the measured reaction as referenced to the standard hydrogen electrode ($E^\circ_{H_2/H^+} \equiv O$)

R - the Gas Constant

T - absolute temperature (°K)

F - the Faraday constant

n - the number of electrons involved in the half-cell reaction

K - the reaction quotient of the oxidized species over the reduced.

When equilibrium exists in a system all of the redox reactions which are occuring have the same potential (i.e. $\Delta E = O$). Consequently, Eh has been used as an overall measure of the redox state of natural systems, and has been employed as a master variable for distinguishing geochemical environments (see Garrels and Christ, 1965). However, there are several practical difficulties in measuring Eh (see Hostettler, 1984). In spite of these major difficulties, Eh is useful as a simple measurement which gives information on the relative environment (Troup, 1974) and as a measure of on-going reactions involving electroactive species.

As a general indicator, the more positive the Eh, the more oxidizing the system and, conversely, the more negative the Eh potential, the more reducing the system. Figure 16 shows the normalized frequency distribution of Eh for each of the previously defined physiographic regions of the

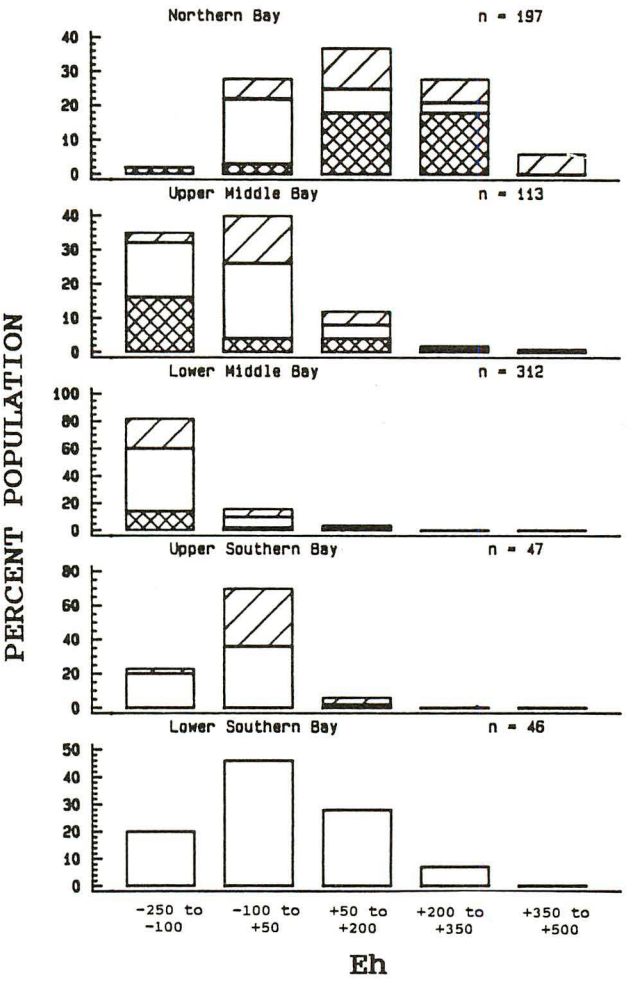


Figure 16. — Nomalized frequency distribution of Eh for each physiographic region in the Bay. The contribution of each cruise to the total distribution is given by the in-fill pattern: cross hatched - Cruise 1 (Fall 1978), blank - Cruise 2 (Summer 1979), and diagonal slashes - Cruise 3 (Winter 1980).

Bay. These distributions were constructed by using data from all samples in a region; surficial samples and samples collected between the sediment-water interface and one meter into the sediment, for all three main Bay cruises. Subdivisions within each bar interval are the relative contributions from each cruise, or season, to the overall distribution of a given region. The frequency distributions are normalized to the total number of samples analyzed within

a given region. This number is given at the top corner of each histogram. A similar graphical format will be used in discussion of the other parameters (NH_4^+, pS^{2-}, SO_4^{2-}, Fe and Mn). The boundary between oxic and anoxic environments is defined at an Eh of zero (Krumbein and Garrels, 1952; Jorgensen, 1977).

Some important trends in the distributions are apparent from Figure 16. The Northern Bay contains the most positive Eh of the sedimentary regions. Marked seasonal variations are indicated by the shifting of the relative contributions from each of the cruises (or seasons). Virtually all of the samples from the fall cruise (Cruise 1; Sept.-Oct. 1978) are within the +50 to +350mV intervals. This is in contrast to the summer cruise (Cruise 2; June-July 1979) in which the samples are more negative, ranging from -100 to +50mV. The samples from the winter cruise (Cruise 3; March 1980) are widely and relatively uniformly distributed over the broad range of -100 to +500mV.

The Middle Bay regions are characterized by negative Eh values, indicative of highly reducing conditions with measurable electro-active species (i.e. sulfide species). The Lower Middle Bay population is seasonally stable, with over 80% of the samples in the interval -250 to -100mV. The Upper Middle Bay is transitional between the Northern Bay and the Lower Middle Bay, as most Eh values are intermediate between the two bordering environments. The seasonal stability of the Upper Middle Bay is greater than that of the Northern Bay, but considerably less than that of the Lower Middle Bay.

The Eh potentials of the Southern Bay are intermediate between those of the Northern and Middle Bay environments. The trend generally indicates that the Upper Southern Bay is a region of chemical transition between the Lower Middle Bay and the Lower Southern Bay. The lack of seasonal data, which resulted from instrumental and sampling constraints, prevented assessment of the temporal variablility in these regions. An absence of data in this region also exists in the data set of Bricker et al. (1977).

The variability in Eh follows what would be expected due to the influence of the Susquehanna River. Fluvial input dominates the Northern Bay affecting both the composition and concentration of the overlying water (refer to the mixing model in the previous section). The effects of fluvial inputs lessens as one proceeds towards the mouth of the Bay. The processes influencing the measured Eh values will be discussed in the section which deals with dissolved sulfide.

AMMONIUM ION (NH_4^+)

Nitrogen is a component of sedimentary organic carbon. Based on the average planktonic composition, determined by Redfield et al. (1966), the composition of sedimentary organic matter can be written as:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4).$$

Under oxidizing (aerobic) conditions nitrogen is released primarily as nitrogen-oxygen compounds (such as N_2O) and nitrogen gas. Anaerobic decomposition produces ammonium (NH_4^+) as the predominant nitrogen metabolite.

Ammonium, produced by degradation reactions, is a useful indicator for the presence of anaerobic decomposition processes. It is not removed from solution by precipitation reactions in natural systems; however, the concentrations can be modulated by adsorption processes (Rosenfeld, 1979). Also, NH_4^+ is not chemically altered in systems with low O_2 availability (as is the case in the Bay sediments).

Figure 17 shows the population distribution of NH_4^+ concentrations. The dotted line in the figure is the generalized analytical detection limit for NH_4^+. There are two main features to note from Figure 17. The first is the similarity between the frequency distributions of the Northern and Middle Bay environments. These regions all have distributions with the same range and modal interval, approximately the same percent of samples below detection, and approximately the same seasonal spread of data. The general physical characteristics of the sediments, such as water content and grain size distributions, are similar in the Northern and Middle Bay. These properties strongly affect diffusional transport. Thus, if these properties are similar and the frequency distributions of the two areas are similar, it can be inferred that the rate of production of NH_4^+ in the two environments is equivalent. Bray (1973) noted that the amount of ammonia produced in the Northern and Upper Middle Bay could not be accounted for solely by sulfate reduction. He attributed the regeneration of nitrogen from the sediment to methanogenesis, basing this conjecture on the work of Reeburgh (1969). Additional confirmation of this can be seen in shallow seismic studies of the Bay (Halka et al., 1988).

The other, more striking, feature of Figure 17 is the virtual absence of measurable NH_4^+ in the Southern Bay. Based on Eh, the Southern Bay is more anoxic than the Northern Bay; thus NH_4^+ would be expected to be present. The absence of NH_4^+ can be explained if the rate of production of NH_4^+ is offset by loss of NH_4^+ from the sediment to the water column due to transport. Calculations based on diffusional transport, the slowest transport mode, using typical sediment characteristics for the Southern Bay and decomposition rates of organic matter in Bay sediments support this hypothesis (Hill, 1984).

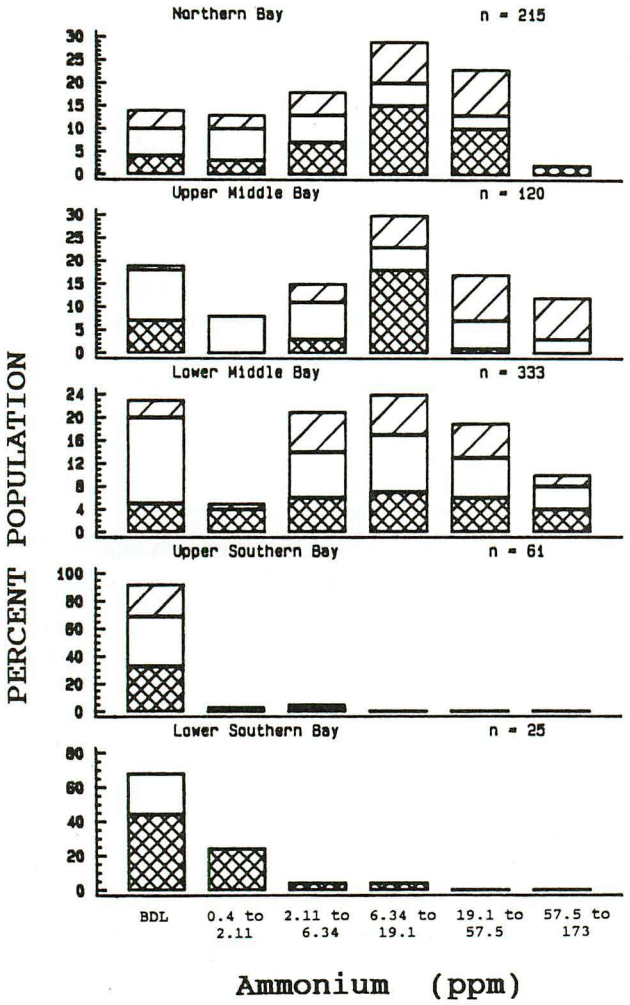


Figure 17. — Normalized frequency distribution of NH_4^+ for each physiographic region of the Bay. Note the concentration scale is logrithmic where 0.4 is the generalized detection limit and 173 ppm is the highest measured concentration [this format will be used in most of the other frequency distributions].

Southern Bay Problem

The ammonium ion data for the Southern Bay regions conflict with the data in the compilation of Bricker et al. (1977), whose cores from the Southern Bay contained detectable NH_4^+. This inconsistency between the two data sets highlights the difficulties of accurately assessing the interstitial water composition in the Southern Bay. These difficulties are primarily due to the limited success encountered when collecting gravity cores in sandy sediments, the dominant type of sediment in the Southern Bay. Thus, when sampling these areas, one must either accept whatever can be collected or seek out isolated pockets of fine-grained sediments. Either way, sampling is severely limited. This limitation is shown well by Hill et al., (1985), who present the details of collection and analysis that this work is based on. Coring attempts at 54 sites in the Southern Bay yielded only 15 cores suitable for interstitial water collection. Only seven cores were collected by Bricker et al. (1977); three of these represent seasonal replicates.

The data compiled by Bricker et al. (1977) reflect sediments of higher organic carbon content (Bricker, pers. comm.). These data are similar to the data distributions found for the Elizabeth River (see Hill et al., 1982). The Elizabeth River is part of the Norfolk Harbor complex, which has essentially no freshwater influx. The sediments of the river are finer grained than those of the main Southern Bay, with carbon contents of $\geqq 2\%$. Thus, Elizabeth River sediments are carbon-rich and located in high salinity water, the same setting as the cores of Bricker et al. (1977). The primary difference between the Elizabeth River data and the Bricker et al. (1977) data occurs in the concentrations of sulfide. The Elizabeth River data show lower concentrations of sulfide, most likely because of temperature differences in the sediment at the times the two sets of samples were collected. The Elizabeth River samples were collected in the early spring, the samples of Bricker et al. (1977) in the summer and fall. Therefore, the main Bay data set presented here for the Southern Bay is considered the more representative set. Though it must be kept in mind that this set is also biased towards the higher clay, carbon-rich sediments in these areas.

SULFATE

Sulfate (SO_4^{2-}) is one of the most important oxidants used in organic degradation reactions in the Bay system. Sulfate is an abundant oxidant in seawater having the oxidative capacity 200 times that of dissolved oxygen. Even within the freshwater of the Susquehanna River the oxidative capacity of SO_4^{2-} is comparable to dissolved oxygen. Within the water column of the Bay the mean SO_4^{2-} concentrations increase monotonically north to south, reflecting seawater dilution. Within the sediments SO_4^{2-} concentrations diminish with depth into the sediment as it is consumed by bacterial action. It would be expected that the depth to which the SO_4^{2-} penetrated into the sediment would reflect the availability of SO_4^{2-} from the water column. This is indeed the case as seen in Figure 18.

Aside from using the absolute SO_4^{2-} concentration as an indicator of oxidant availability, SO_4^{2-} used in conjunction with HCO_3^- concentrations can yield information on the bacterially mediated reactions which are at work. For example in simple SO_4^{2-} reduction 2 mols of HCO_3^- are produced for every mol of SO_4^{2-} consumed (i.e. $\Delta HCO_3^-/\Delta SO_4^{2-} = 2$). Three types of behavior in the ratio of $\Delta HCO_3^-/\Delta SO_4^{2-}$ might be expected from the equations in Figure 15. These are:

1) $\Delta HCO_3^-/\Delta SO_4^{2-} = 2$, simple sulfate reduction, where the sedimentary organic matter is the primary electron donor;
2) $\Delta HCO_3^-/\Delta SO_4^{2-} = 1$, where CH_4 is the primary electron donor in sulfate reduction, and;
3) $\Delta HCO_3^-/\Delta SO_4^{2-} >> 2$, where HCO_3^- produced is independent of the sulfate reduced (i.e. $\Delta SO_4^{2-} \approx 0$). This is the case where methanogenesis, or aerobic decomposition is occurring (only methanogenesis is important in the carbon-rich sediments).

Figure 19 shows the ratio of $\Delta HCO_3^-/\Delta SO_4^{2-}$ determined on selected cores down the main stem of the Bay. The ratio was determined by plotting HCO_3^- as a function of SO_4^{2-}, the slope of the resulting line, determined by a least-squares fit, is the ratio $\Delta HCO_3^-/\Delta SO_4^{2-}$. In the Northern Bay, the presence of methanogenic activity can be seen both in the extremely large value of the ratio in the deeper sediments, and the ratio of one (denoting CH_4 as an electron donor) in the shallower sediment. Cores from the Middle Bay fluctuate around a ratio of 2; data below 2 may indicate some influence of CH_4 transported from depth. The Southern Bay samples are not represented in the Figure because $\Delta SO_4^{2-} \cong 0$ due to transport processes not reaction control (this will be discussed later in this section).

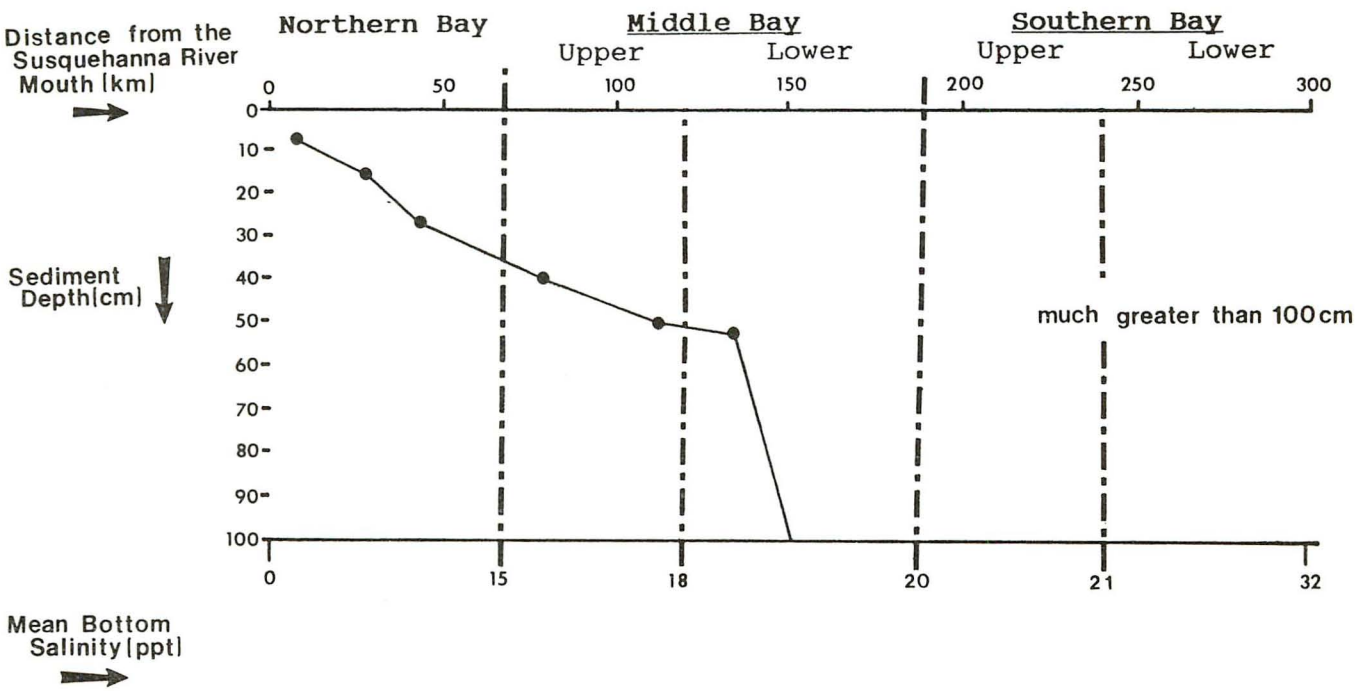


Figure 18. — The mean seasonal depth in the sediment where 90% of the available sulfate is depleted (less than 2mM). Data points indicate the center of areal segments in the Bay. Below the depth indicated methanogenesis should commence.

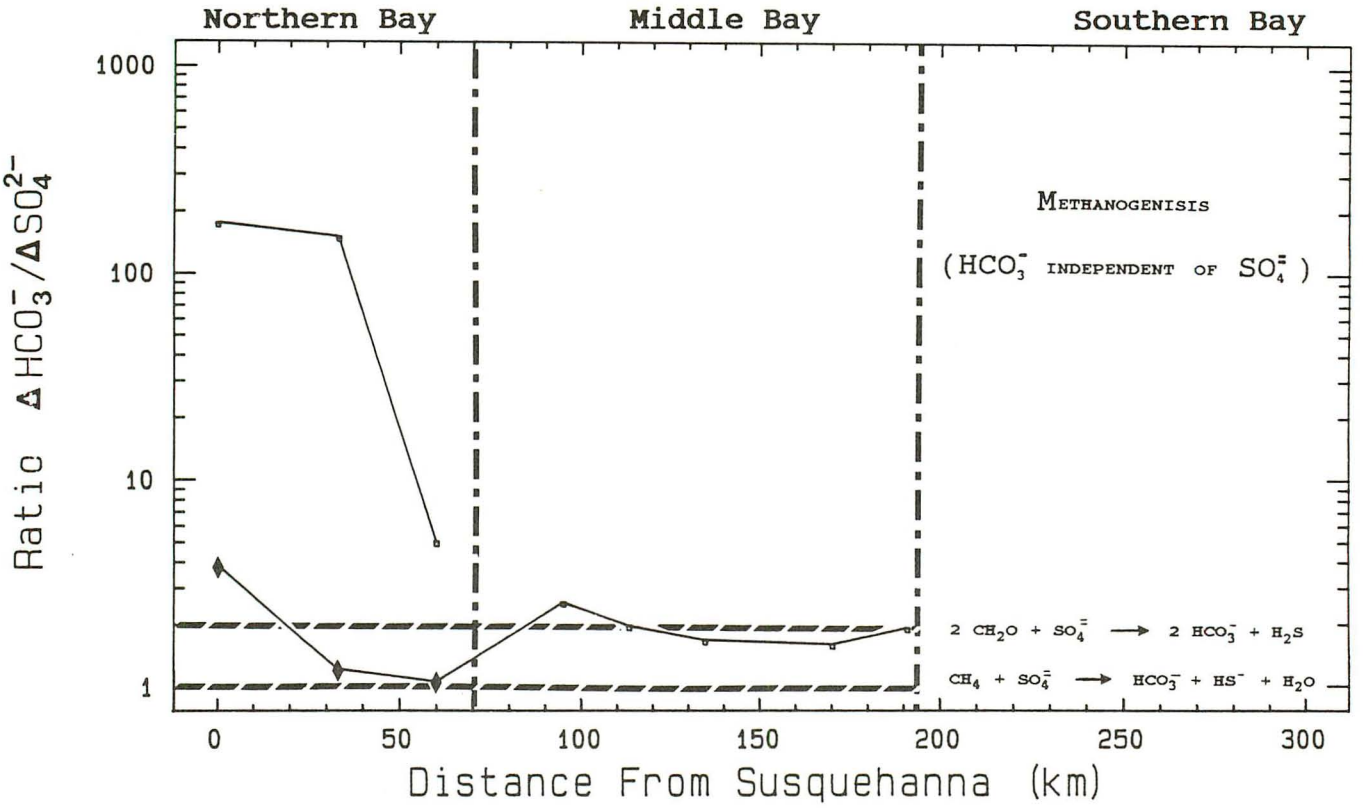


Figure 19.— Ratio of the change in bicarbonate to the change in sulfate concentration in selected cores down the axis of the Bay. The ratio is indicative of the dominant metabolic reactions occurring in the sediment. There were few cores taken in the Southern Bay and in these cores sulfate depletion is minimal, thus no ratio could be calculated.

Current work indicates that the biogeochemical processes at work in the sediment are more complex than the preceding discussion might imply. From seismic studies it appears that gas (assumed to be primarily CH_4) is entering the shallow sediments from the deep sediments often reaching the sediment-water interface (Halka et al., 1988). These gases are generated from sediments in Paleo-channels. These gases could strongly influence the geochemical processes and the distribution of benthic infauna in the Bay.

Percent SO_4^{2-} Reduced

In order to examine how SO_4^{2-} varies according to the physiographic regions, it is best to normalize the SO_4^{2-} concentration in the sediment to the predicted SO_4^{2-} concentration (Figure 13). By normalizing the SO_4^{2-} concentrations, the percent of the SO_4^{2-} removed by bacterial reduction can be calculated. The $\%SO_4^{2-}$ reduced is an indicator of the balance between the rate of supply of SO_4^{2-} and the rate of utilization of SO_4^{2-}. The percent SO_4^{2-} reduced is defined as follows:

$$\%SO_4^{2-}\text{Reduced} = \left[1 - \frac{(SO_4^{2-}/\ Cl^-)_m}{(SO_4^{2-}/\ Cl^-)_P}\right] \times 100 \qquad (3)$$

where • $(SO_4^{2-}/\ Cl^-)_m$; is the measured ratio of SO_4^{2-} to Cl^- in a sample

• $(SO_4^{2-}/\ Cl^-)_P$; is the predicted ratio of SO_4^{2-} to Cl^- in the sample, calculated by using a mixing model of sea water and Susquehanna River water, based on the Cl^- concentration of the water sample (see Figure 16).

The distribution of this parameter is shown in Figure 20. The percentage of SO_4^{2-} reduced in the Southern Bay is quite low (< 20%); very little of the SO_4^{2-} supplied from the water column is reduced. This is the result of the high sulfate concentrations in this region and the low rate of carbon oxidation. The data are consistent with the low NH_4^+ values observed in this area.

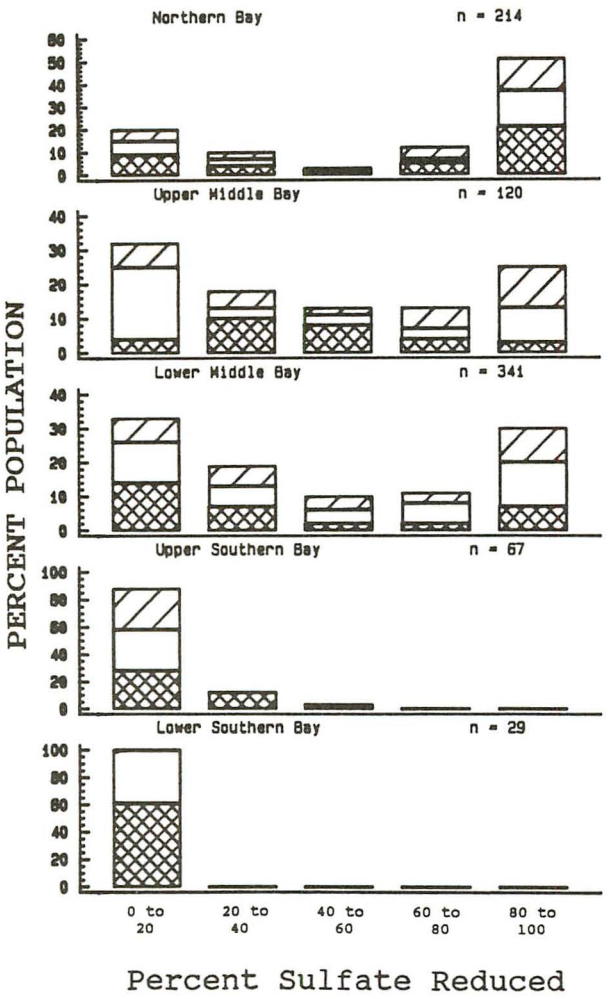


Figure 20. — Normalized frequency distribution of percent sulfate reduced for each physiographic region of the Bay.

The Lower Middle Bay varies from the Northern and Upper Middle Bay in that the population variations reflect core-to-core variability as well as down-hole changes. The behavior of the cores in this region indicates that, in terms of sulfate utilization, this area is transitional between the Upper Middle Bay and the Southern Bay regions. Cores from the Lower Middle Bay display sedimentological and compositional characteristics of both the Upper Middle Bay and the Southern Bay region.

All Northern Bay cores achieve SO_4^{2-} reduction between 80-100%. The spread of data is due to down-hole depletion of SO_4^{2-}. This depletion of SO_4^{2-} concentrations is produced by the rate of SO_4^{2-} reduction exceeding diffusional supply. The Upper Middle Bay exhibits the same behavior, but the depths at which $>$ 80% SO_4^{2-} reduction occurs is deeper in the cores. Consequently the distribution of samples is broader.

DISSOLVED SULFIDE

Sulfide, a catabolic by-product of SO_4^{2-} reduction, is expressed as pS^{2-} which is the negative common logarithm of the S^{2-} ion activity. The activity of the S^{2-} ion increases as the value of pS^{2-} decreases. Samples in which the pS^{2-} is greater than sixteen are below the calibrated range of the Ag_2S/ Ag electrode (Hill et al., 1985). Sulfide ion (S^{2-}) is one of three major dissolved sulfide species in natural waters, the others are H_2S and HS^-. The S^{2-} ion is discussed in this section because it is the species measured by the ion selective electrode, however the dominant species in the interstitial waters of the Bay is HS^-. The concentration of HS^- and H_2S can be determined by equilibrium calculations from the pH and the S^{2-} concentration (Garrels & Christ, 1965; Stumm and Morgan, 1981); total dissolved sulfide (S_T) is determined by summing the concentrations of H_2S, HS^-, and S^{2-}. Total sulfide concentrations have been used as indicators of chemical environment (Berner, 1981); $S_T \geqq 10^{-6}$M is sulfidic, $S_T < 10^{-6}$M is non-sulfidic. $S_T = 10^{-6}$M is equivalent to $pS^{2-} \approx 11$ at a pH of 8.

Figure 21 shows the distribution of pS^{2-} for the physiographic regions of the Bay. The absence of measureable S^{2-} in the Northern Bay region clearly separates the Northern Bay from the other two major sedimentary areas of the Bay. The lack of measurable S^{2-} in this environment is largely due to the low availability of sulfur (as SO_4^{2-} in the water column) and the high availability of dissolved Fe. The influence of low SO_4^{2-} concentrations in this region is discussed by Hill (1984), and Hennessee et al., (1984). Any S^{2-} produced in the Northern Bay is rapidly removed from solution via precipitation with the abundant dissolved Fe^{2+} in this environment (see the following section).

The Upper Middle Bay population of pS^{2-} shows a broad distribution in the data, indicating the transitional nature of this area. This region is transitional because it encompasses the average range of excursion of the boundary between first order (dependent only on carbon content) and second order (dependent on carbon and SO_4^{2-} concentrations) sulfate reduction (Hill, 1984 and 1987). First order sulfate reduction produces free sulfide species; whereas, second order reduction does not.

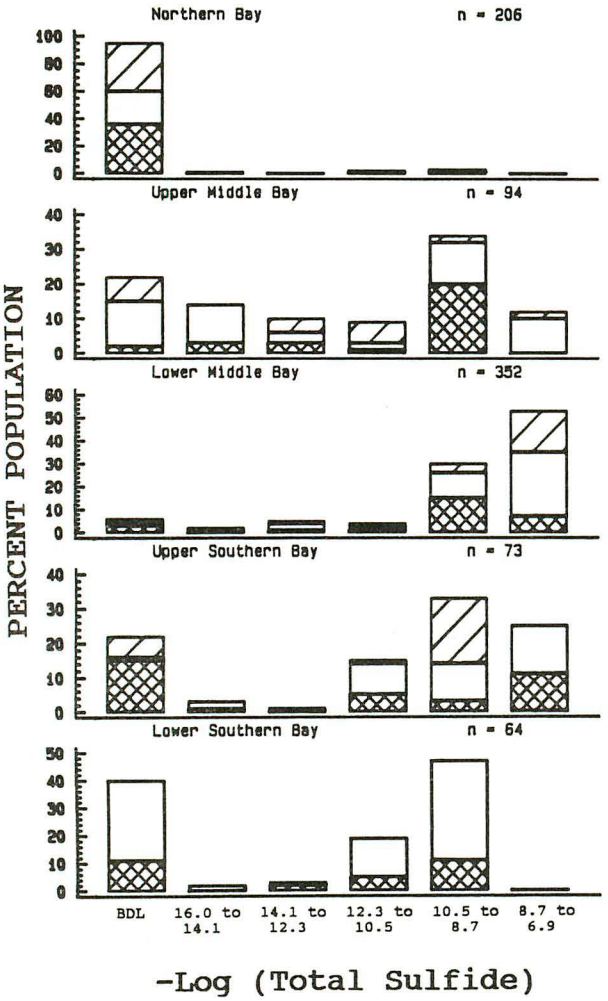


Figure 21. — Normalized frequency distribution of dissolved sulfide (pS^{2-}) for each physiographic region.

The location of the boundary varies due to the freshwater input from the Susquehanna. This variation is seasonal and results in spreading out the frequency distribution of sulfide. The influence of the Susquehanna River is more evident in the compilation of Bricker et al. (1977). In their data set, the Upper Middle Bay more strongly resembled the Northern Bay region, with over sixty percent of the samples containing sulfide concentrations below the analytical cut-off.

Most of the samples from the Middle and Southern Bay are 'Sulfidic' according to Berner's classification, (Berner, 1981), indicating that the sediments are anoxic, and that SO_4^{2-} reduction is indeed the major decomposition process in both the Middle and Southern Bay. The distribution of pS^{2-} data in these regions follows an antithetic trend with respect to Eh. This is expected because reduced sulfur species are the major electroactive species in the Bay sediments. Thus, the greater the concentration of sulfide (pS^{2-} decreasing), the more negative the value of Eh. The electrochemical half-cell measured by Eh is the sulfide/elemental sulfur (S°) couple. The presence of this half-cell has been noted in other estuarine and marine sediments (Berner, 1967). The half-cell reaction is written:

$$S^\circ + 2\bar{e} \rightleftarrows S^{2-} \qquad E^\circ_{S^\circ/S^{2-}} = 508 \text{ mv} \tag{6}$$

Both pS^{2-} and Eh were measured by electrochemical methods. The Nernst expression for each of these measurements is written as follows:

$$Eh = E^\circ_{S^\circ/S^{2-}} - \frac{RT}{2F} \ln (S^{2-}) \tag{7}$$

$$E(S^{2-}) = E^\circ_{Ag/Ag_2S} - \frac{RT}{2F} \ln (S^{2-}) \tag{8}$$

The difference (Δ; delta) between these two expressions is the difference in the electrochemical potential of the cells; the dependency on sulfide cancels out.

$$\Delta = E^\circ_{S^\circ/S^{2-}} - E^\circ_{Ag/Ag_2S} \tag{9}$$

Delta has three values depending on which sulfide species is considered but only the value of -227 mV for HS^- is significant at interstitial water pH values. The difference between the electrode measurements is presented in Figure 22 in the population distribution format.

The data can be grouped into three millivolt ranges, allowing for ± 25 mV uncertainty. The first range is +15 to -35 mV; empirically the data show that in very low salinity conditions, and in situations where active methanogenesis is occurring, delta is equal to zero; i.e. the sulfide electrode acts like the Pt electrode. In Figure 22, this indicates the influence of freshwater input from the Susquehanna. The influence is greatest in the Northern Bay and diminishes down-Bay with no influence seen in the Southern Bay (40% of the Northern Bay, 10% - Upper Middle, 1% - Lower Middle Bay and 0% of the Southern Bay samples).

The second range is -185 to -235 mV, the range for elemental sulfur. Most of the data falls within this range, however the distribution of data is broad in the Northern and Southern Bay regions. The Northern Bay distribution of data is bimodal reflecting freshwater input and elemental sulfur equilibrium. The data between these two values of delta result from equilibrium with polysulfide species (Boulegue, 1975). The Southern Bay data is spread to the more negative values of delta; this will be discussed in the next range. Equilibrium with elemental sulfur is the major influence controlling delta, with over 90% of the samples in this

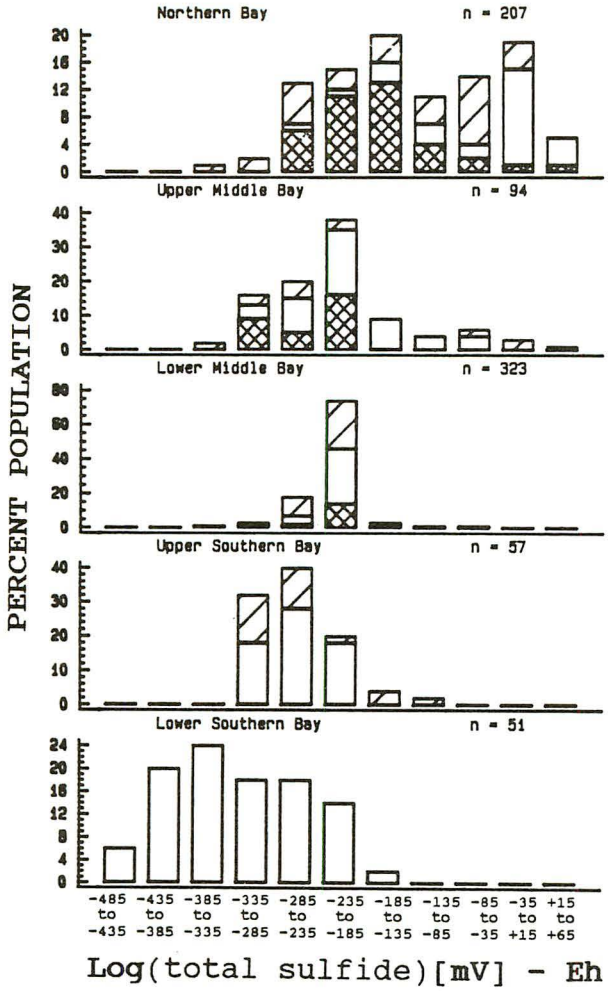


Figure 22. — Normalized frequency distribution of delta (Δ), the difference between the sulfide electrode measurement (mV) and Eh, for each physiographic region.

range. This is important not only to reactions which require elemental sulfur (e.g. pyrite formation), but also it indicates the geochemical stability of the system. The redox state of the system is buffered to some extent by elemental sulfur.

The third range consists of samples with delta more negative than -285 mV. Samples which fall into this range have Eh values more positive than the sulfide concentrations should produce. The Eh readings of these samples generally drift, indicating very low concentrations of electroactive species. These samples are found predominantly in the Southern Bay; 33% of the Upper Southern Bay samples and ≅ 68% of the Lower Southern Bay. These values are consistent with the slow rate of SO_4^{2-} reduction in these regions, as indicated by the $\%SO_4^{2-}$ reduced and the concentration of NH_4^+. Sediments in these regions are relatively the least buffered with respect to the redox state of the sediment.

TOTAL DISSOLVED IRON (Fe) AND MANGANESE (Mn)

Diagenetic reduction of grain coatings and other solid phases in the sediment are the sole source of dissolved Fe and Mn in sedimentary environments. This reduction can occur either as a primary process, where the oxidized solid metal oxy-hydroxides are used as the terminal electron acceptor in the decay of organic matter, or the reduction can occur due to reaction with reduced metabolites (such as S^{2-}). Once in the aqueous phase, the concentrations of Fe and Mn are modulated by reactions with the by-products of the bacterial action to produce authigenic minerals. The predominant anions which bind the metal ions are S^{2-}, PO_4^{3-}, and CO_3^{2-}. Generally, the solubilities of the PO_4^{3-} and CO_3^{2-} compounds greatly exceed the solubility of the S^{2-} compounds; the preference of mineral formation is $S^{2-} >> CO_3^{2-} > PO_4^{3-}$. This is reflected in Figures 23 a & b, in that as sulfide species increase, Fe and Mn concentrations decrease.

The Northern Bay is 'free' of dissolved sulfide; thus, the solubility of iron and manganese is controlled by PO_4^{3-} and CO_3^{2-} (Bray, 1973; Holdren, 1977). Because of this, most of the samples have high metal concentrations, the highest in the Bay. It is interesting to note that, in the same samples where high metal concentrations are measured, the Eh values indicate oxic conditions. At the pH of these waters and the measured Eh values, the measured dissolved metal concentrations could not exist (Garrels and Christ, 1965), they should precipitate as metal oxy-hydroxides. This discrepancy demonstrates that Eh alone is not a good indicator of environmental conditions.

The Upper Middle Bay follows the Northern Bay in the size of the population with high metal concentrations. Sulfide is present in this environment to a variable extent, with the resulting effects of shifting the population towards the detection limit. The remaining regions of the Bay are dominated by the sulfide species concentrations. This is shown in the antithetic behavior of the metals to sulfide (compare Figures 23 a & b with Figure 21).

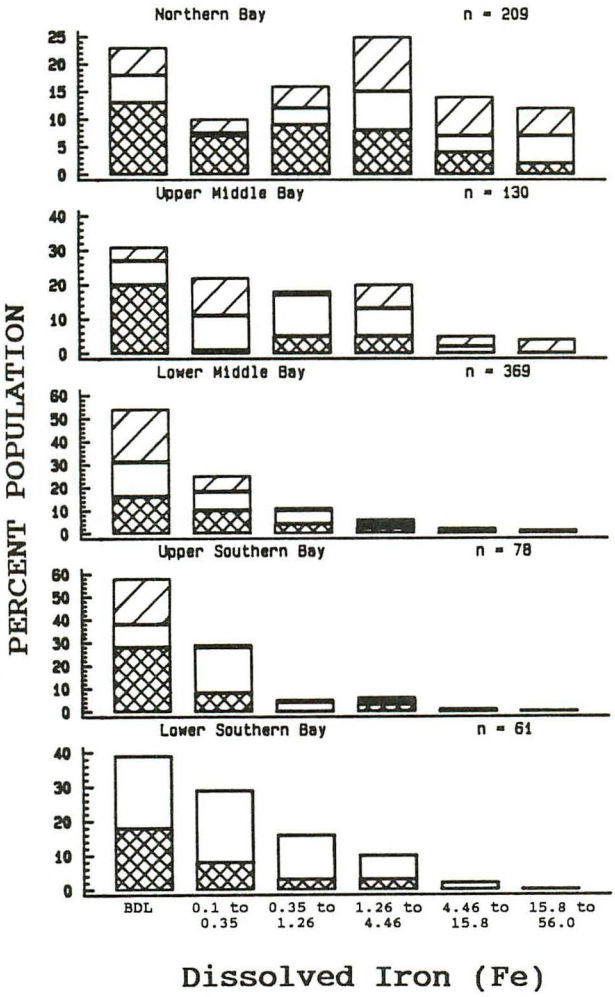


Figure 23a. — Normalized frequency of total dissolved iron (ppm) for each physiographic region of the Bay.

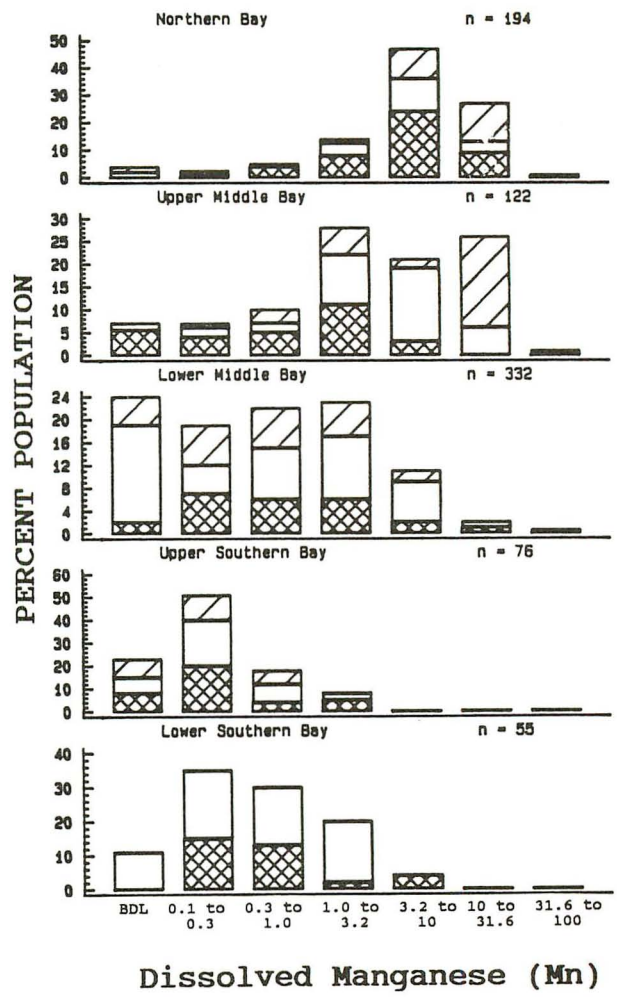


Figure 23b. — Normalized frequency distribution of total dissolved manganese (ppm) for each physiographic region of the Bay.

SUMMARY OF THE BEHAVIOR OF PORE WATER CHEMISTRY WITHIN PHYSIOGRAPHIC REGIONS

NORTHERN BAY

The distinguishing physiographic feature of the Northern Bay is the dominant influence of the Susquehanna River. Fluvial inputs strongly effect the distribution and composition both of the water column and the sediments. Within the pore waters of the Northern Bay this effect can be directly seen in the overall low concentrations of dissolved major seawater ions and their high degree of seasonal variability. The dilution of seawater by the Susquehanna strongly influences the biogeochemical reactions in the sediments.

The primary diagenetic reactions occurring in the sediment are bacterially mediated organic degradation reactions. The concentrations of organic carbon in the Northern Bay region are the highest in the Bay. Bacterial degradation of the organic matter is highly active, comparable to the Middle Bay, and more active than the Southern Bay; this is based on the seasonally stable distribution of NH_4^+ (Figure 17). The Northern Bay region is distinct from the Middle and Southern Bay in that no measureable sulfide is produced. The lack of sulfide is the result of low SO_4^{2-} concentrations in the water column, and is not indicative of the absence of SO_4^{2-} reduction. Sulfate reduction occurs thoughout the Northern Bay region based on $\%SO_4^{2-}$ reduced (Figures 18 and 20), but it is not the sole reaction. Methanogenesis is also important (Figures 18 and 19) in the shallow sediments of this region.

Secondary diagenetic reactions, that is reactions which utilize the metabolites of organic degradation reactions, are also strongly influenced by the Susquehanna River input. A good example of this can be seen in the behavior of Fe and Mn. In the Middle and Southern Bay where S^{2-} is abundant the concentration of Fe and Mn is controlled by equilibrium metal sulfides, and the levels are quite low. In the Northern Bay, minerals containing PO_4^{3-} and CO_3^{2-} are the controlling phases, and the solubilities of these compounds are the highest found in the Bay.

The Northern Bay region would be classified as an anoxic non-sulfidic (methanic) environment according to Berner (1981). However, the Northern Bay does not clearly follow the criteria proposed by Berner (Hill, 1984 and 1988).

MIDDLE BAY

The main physiographic feature which defines the length of the Middle Bay region is the main axial channel. Sedimentation patterns are complex owing to a variety of sediment sources; the Susquehanna River, shoreline erosion, and erosion of bottom sediments. Circulation is controlled to a large extent by the axial channel, which traps northward flowing saline water. This region is divided into two sub-regions; the Upper Middle Bay which encompasses the southernmost extent of the Susquehanna River's influence, and the Lower Middle Bay.

Lower Middle Bay

The chemical compositions of the pore waters in this sub-region are the most seasonally stable of any region in the Bay. This stability is the result of the high carbon content of the sediment coupled with the relatively constant water column composition from the channelled saline water. The resultant conditions promote vigorous sulfate-reduction, which in turn, produce high concentrations of NH_4^+ and the highest concentrations of dissolved sulfide species found in the Bay. The effect of the high concentration of dissolved sulfides is two-fold: first, the sulfides are in equilibrium with elemental sulfur producing a redox buffer (shown by the seasonal stability of Eh; Figure 16), and; secondly the high total sulfide concentrations limit the solubility of Fe and Mn (and presumably other chalcophilic elements), thus producing the lowest concentrations of these metals found in the Bay.

Upper Middle Bay

The Upper Middle Bay region is transitional between the Northern Bay and the Lower Middle Bay. The biogeochemical conditions in this sub-region oscillate depending upon the flow conditions of the Susquehanna River. As a result the pore water chemistry of this region shows broad, seasonally dependent distributions of S^{2-}, Fe and Mn, and Eh. There are seasonal variations shown by the major ions, in regard to concentration and composition, but significantly lower variations than in the Northern Bay.

Middle Bay Classification

It is difficult to classify this region of the Bay because of its dynamic nature. The Lower Middle Bay falls into the classification of anoxic sulfidic. However, the conditions in the Upper Middle Bay oscillate between anoxic sulfidic and anoxic non-sulfidic (methanic).

SOUTHERN BAY

The principal physiographic characteristic of the Southern Bay is the large spatial extent of coarse (quartzose) sediment. These sediments have low concentrations of trace metals, sulfur and organic carbon. The rate of bacterial action is strongly dependent both on the nature and concentration of organic matter. The Southern Bay sediments are only capable of supporting minimal bacterial action; this is shown in the $\%SO_4^{2-}$ reduced (which is near zero) and in the amount of NH_4^+ retained in the sediment. The evidence that bacterial action is occurring is most strongly found in the presence of dissolved sulfide species throughout this region.

The Southern Bay region is divided into two sub-regions based mainly on differences in grainsize; the Upper Southern Bay contains the finest sediment in this region. In regard to pore water chemistry there is little difference between the two sub-regions. The differences show gradation of compositional behavior between the Lower Middle Bay and the Lower Southern Bay.

The Southern Bay region is classified as anoxic sulfidic.

Table II. Summary of the Interstitial water data for the physiographic regions of Chesapeake Bay

	Northern Bay	Upper Middle Bay	Lower Middle Bay	Upper Southern Bay	Lower Southern Bay
Cl^{-*}	Seasonably variable. Influenced by Susquehannna-	Relative composition constant$^+$	Constant$^+$	Constant$^+$	Constant$^+$
Eh	most positive (seasonally variable)	Transitional (seasonally variable)	most negative (seasonally stable)	Intermediate	Intermediate
NH_4^+	High (similar distributions each season)	High (similar distributions each season)	High (similar distributions each season)	Below detection	Below detection
$\%SO_4^{2-}$ reduced	All cores >80%	All cores >80%	Variable	Most cores < 20%	All cores < 20%
pS^{2-}	Below Detection	Broad Transitional distributions	Highest S^{2-} concentrations	High S^{2-} concentrations	Intermediate
Fe & Mn	Highest concentrations	High (Transitional)	Low	Low	Intermediate

* Cl^- used as representative of major ion content

\+ Constancy refers to the ratio of the major ions to Cl^-, not to the absolute concentration (or salinity).

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