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Toxic Substances

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PART III

TOXIC SUBSTANCES

by

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Technical Glossary

aerosol:	A colloidal solution in which a substance in which the other is dispersed, is a gas.
anoxic:	Total deprivation of oxygen.
anthropogenic:	Of human origin and development.
As	arsenic
bioecology:	The science that deals with the interrelations of communities of animals and plants with their environment.
Cd	cadmium
Ce	cesium
Co	cobalt
Cr	chromium
Cu	copper
diagenesis:	Physical and chemical changes occurring to sediments during and after the period of decomposition up until the time of consolidation.
dpm cm^{-2}	distintegrations per minute per square centimeter
Eh	oxidation-reduction potential
fall line:	Geographical line indicating the beginning of a plateau, usually marked by many waterfalls and rapids.
Fe	iron
ft^3/sec	cubic feet per second
Hg	mercury
interstitial:	Of, forming, or occurring in small or narrow spaces between things or parts.
lithology:	Science of rock structures.
loads:	Quantity of a constituent per unit per time.
Mn	manganese
Mo	molybdenum

mT	metric tons
Ni	nickel
oxic:	applied to a soil layer from which much of the silica that was combined with iron and alumina has been leached.
Pb	lead
ppt	parts per thousand
ps$^{=}$	expression of sulfur ion content
Sc	scandium
Sn	tin
synergism:	The property or condition of working together, such as muscles together effecting a certain motion, or of hormones, or medical substances.
Th	thorium
U	uranium
ug cm^{-2}	micrograms per centimeter
Zn	zinc

SECTION 1

INTRODUCTION

This part of the CBP Synthesis Report summarizes and integrates the research findings and recommendations of 13 projects of the Chesapeake Bay Toxic Substances Program performed between July 1978 and October 1981. The following sections describe research on potentially toxic substances, or toxicants, in water-sediments and selected biota. The subjects considered include a brief review of metals, their sources, distribution and behavior, and then a review of sources and distribution of organic chemicals. Finally, information concerning the significance of toxicants in the Bay and their pattern of enrichment is provided. Most information synthesized in this report can be traced to its origin in scientific project reports listed in Appendix A.

The last three decades have witnessed some disturbing changes in Chesapeake Bay. Some biotic components are less abundant than in the past and are below natural levels. Oyster reproduction has diminished throughout the Bay. Of particular concern is the virtual disappearance of rooted aquatic plants over a large portion of the Bay floor. Fish, such as shad and striped bass, once spawned in astronomical numbers; but in recent years, they have declined severely (Cronin 1977). Taken together, these changes are cause for concern.

An understanding of what is happening, and why, to grass, bass, shad, and oysters still eludes scientists, though toxic substances are strongly suspected to be at least partially responsible. The lessons learned from DDT and PCB contamination show that toxicants can cause substantial ecological damage, ranging from reproductive failure in fish and birds to inhibition of photosynthesis in phytoplankton. The outbreak of neurological illness with 52 deaths caused by mercury (Hg) poisoning of shellfish in Japan amplifies the fact that toxic contamination in seafood resources can reach humans. Release of Kepone into the James River in Virginia, resulted in closure of the estuary to fishing for years, with an enormous economic loss and a need for a large-scale, expensive cleanup. Chlorine, a widely used biocide in sewage treatment plants, is strongly suspected of causing massive fish kills in the James River in 1973 (Douglas 1979).

Toxic substances are usually defined as chemicals or chemical compounds that can poison living plants and animals, including humans, or impair physical or chemical processes. Two classes of toxic substances pose a threat to the Bay environment: inorganic and organic compounds. The inorganic materials are the metals. They can be produced and delivered to the Bay by natural processes as well as by human activities. Potentially toxic metals include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), tin (Sn), and zinc (Zn). Many of the organic compounds are products of human activities. However, a few polynuclear aromatic compounds (PNAs) can occur naturally, and thus augment the synthetic compounds. The main classes of organic compounds are pesticides, phthalate esters, polynuclear aromatic hydrocarbons, metalorganic compounds, alkyl-benzines, plasticisers, polychlorinated biphenyls (PCBs), and other halogenated hydrocarbon compounds.

Assessing the effects of toxic substances on biota has always been a difficult task. Effects range from rapid death, or acute toxicity, to gradual reductions in spawning success, or chronic toxicity. Months, or years of careful observations may be required to determine chronic effects for one chemical on one species. Effects of chemical mixtures on several species or a community are even more difficult to detect. The environment may also experience synergistic and antagonistic effects through exposure to two or more chemicals. In addition, toxic effects can be masked by wide fluctuations in natural conditions. In the laboratory, scientists have attempted to simulate effects of chemicals on the natural environment by subjecting single organisms, or a limited number of organisms, to toxicants, and observing the cause-and-effect relationships. But transfer of this information to interpret changes in entire faunal communities, with their wide variability within species, has achieved only limited success.

Because it is difficult to specify cause-and-effect relationships between toxicants and Bay resources, we attempted, during the Chesapeake Bay Program, to determine areas where levels of toxicants are high (above standards or threshold levels), and then relate these levels to known toxic effects. This evaluation will give us some insight into the existence of toxicity problems.

In summary, some trends recognized at the onset of the Program caused us to believe that the status of toxic substances in the Bay should be studied. These trends included: (1) decline of biotic components in the past three decades (Cronin et al. 1977); (2) increases in the number of potentially toxic chemicals being synthesized, produced, and used in the region (Huggett et al. 1977); (3) discharge of large amounts of potentially toxic substances (Brush 1974); (4) increase in population growth and industrial activity; (5) accumulation of toxicants in the sediments and biota, including commercial food species, many thousand-fold more than in ambient concentrations in the water (Huggett et al. 1974b, Huggett et al. 1977); and (6) carcinogenic nature of many organic compounds found in the Bay. At the same time the Bay is an important environmental resource for fisheries, wildlife, and recreation. Since controlling the threat of toxic substances to viable ecological resources requires new knowledge of their sources, distribution, and fate in the Bay ecosystem, we studied these factors.

Before the initiation of the CBP, information on metals and organic compounds was scarce. Data on the existence of metals were limited to the distribution and abundance of some trace metals in the northern Bay and several western tributaries. Likewise, available information on organic compounds consisted of levels of some chlorinated hydrocarbons (DDT, PCBs) and Kepone found in selected bivalves, fish, phytoplankton, and sediments of some parts of the Bay and tributaries. The CBP studies not only support and systematically expand this knowledge, but add information on sources of metals and organic compounds to the Bay, their behavior in the estuary, and impacts on resources.

Published information on potentially toxic metals in the Bay prior to the Chesapeake Bay Program, and from other studies, is summarized in Appendix B. Of note are studies of the Cu and Zn in oysters and sediments of the James and Rappahannock Rivers (Huggett et al. 1974a) that indicate differences in concentration gradients of the metals between sediments and oysters. Additionally, Carpenter et al. (1975) revealed marked temporal variations of the dissolved and suspended metals, Fe, Mn, and Zn, discharged over an annual cycle by the Susquehanna River. Our studies support these findings as discussed in Section 2. Villa and Johnson (1974) and Johnson and Villa (1976) reported high concentrations of metals in Baltimore Harbor and the Elizabeth River. By using a mass balance of metals for Northern Chesapeake Bay, Helz (1976) found that at least half of the Cd, Cr, Cu, and Pb input comes from human sources. Further assessment of contributions from human sources is presented in Section 2. Goldberg et al. (1978a), in a study of northern and central Chesapeake Bay, revealed anthropogenic fluxes of metal concentrations in upper parts of sediment cores. Since this study showed that sediment puts material into the system, we assessed sediments as a source. (See Section 2 for discussion of our results). The status of knowledge on biological effects of metals is presented by Frazier 1972, Cronin et al. 1974, Hansen et al. 1974, and Tsai et al. 1979. These studies indicate a biological toxicity problem that was cursorily studied by the CBP (see Section 6).

Prior information on synthetic organic compounds in the Bay is scant. Many synthetic compounds have been only newly created, with the necessary analytical instruments to detect them only recently developed. Of note (Appendix C) is the EPA National Estuarine Monitoring Program between 1965 and 1972, utilizing oysters (Munson and Huggett 1972). Additionally, Munson (1973) found that Chester River bed sediments, suspended sediment, and shellfish stocks contained chlorinated hydrocarbons derived from Chesapeake Bay. The Upper Bay Survey (Munson 1975) provided data on chlorinated hydrocarbon (PCBs, Chlordane, and DDT) sources and concentrations in suspended material and bed sediments as well as in shellfish and zooplankton. This study gave insights into routes and rates of transfer. Section 2 of this paper expands on this information. A consolidated listing of toxicants found in Chesapeake biota, water, and sediment, and a listing of toxicant data files is provided by CRC (1978). The intensive studies of Kepone in the James Estuary after 1975 provide detailed data for a single toxicant in a single tributary estuary. They cover studies of biota (Roberts and Bendl 1980, Huggett et al. 1980, Huggett and Bender 1980) and sediments (Trotman and Nichols 1978, Lunsford 1981, Nichols et al. 1979).

Brush's (1974) inventory of sewage treatment plants lists information on sources of toxicants. Additionally, the EPA-States National Pollutant Discharge Elimination System (NPDES), which began in 1973, contains extensive file data on metals and a few organic compounds discharged from point sources such as industrial effluents and sewage treatment plants.

In 1978 the CBP initiated research on toxic substances, aiming to provide new information and the data base necessary to manage toxic inputs to the Bay. It is the first comprehensive effort to address problems of potentially toxic substances in the Bay on a regional scale. Specifically, we attempted to:

- determine the present distribution and concentration of selected toxic substances in Bay sediments, water, and biota;
- assess the present input rates of potentially toxic substances to the Bay, their location, and composition;
- identify the major transport paths for toxic substances, their chemical behavior, and sites of accumulation; and

o determine the impacts of potentially toxic substances on the Bay ecosystem.

The chief studies were of four main types:

(1) Baseline Inventory
An assessment of the spatial distribution of sediments, biota, water characteristics, and toxic substances, (what toxic substances are present? where are they located?) and in what form or state (organic, inorganic, dissolved, particulate?) (Are they a problem?)

(2) Source Assessment
An identification of sources and estimation of the potential toxic inputs discharged by industry, sewage treatment plants, and the atmosphere.

(3) Behavior and Fate
An assessment of the mechanisms and routes of transport, sites of accumulation, chemical behavior, and likely biological impacts.

(4) Synthesis
A summary of research findings and integration of toxic substances with system components.

The program elements are interrelated scientifically by treating the Bay as a geochemical system with reservoirs. Sources, sinks, and pathways of material transports (such as air, water, and sediments) are the principal reservoirs inventoried; dissolved materials and biota are the main interacting components. As toxic substances are transferred between reservoirs and components, and from sources to sinks, they proceed along characteristic pathways, undergo transformation, and accumulate in viable and sedimentary constituents.

Research plans focused on toxic substances in the sediment reservoir, because toxicants have a great affinity for fine-grained sediment (which has a large surface area for sorption per unit mass). Levels in the water column may, in some cases, be important, but our work concentrated on sediment reservoirs because toxicants have a long residence time in sediments, build up to high concentrations, and are easily detected. Although toxic substances discharged in dissolved form can have a direct impact, their effect is believed to be short-lived because of rapid water movement and constant dilution. Consequently, sediments have a longer residence time in the Bay than dissolved substances. Thus, they can build up high concentrations of toxicants.

Growth of the region has increased the supply of sediment delivered to the Bay and, when combined with toxic substances, poses a significant problem to the Bay environment. Clearing land for agriculture and development has accelerated watershed erosion (Wolman 1967) and increased loads of suspended sediment (Schubel and Meade 1974). Suspended sediment creates turbidity which can decrease light penetration and adversely affect aquatic plants and primary production. As sediment fills channels and harbors, it creates a need for dredging and for disposal of contaminated sediment.

As in the previous part on nutrient enrichment, this section was written around several questions relevant to those interested in managing water quality of the Bay. The three basic questions addressed in this paper are:

Is there a toxic chemical problem in the Bay?
What is the distribution of toxic chemicals in the Bay?
What are the sources and loadings of pollutants of concern?

A more detailed list of these questions, with their answers, appears as the final section of this paper. The answers are drawn from the paper and serve as a summary of the technical material from a manager's perspective. They should concisely support Section 6, Conclusions and Research Needs.

SECTION 2

FINDINGS FROM STUDIES ON METALS

This chapter explains the results from CBP research on sources of metals to the Bay and their distribution and concentration in the estuary. The first part on sources discusses inputs of metals from industries and publicly owned treatment works (POTWs), the atmosphere, urban runoff, and three principal tributaries of Chesapeake Bay. The remaining sections summarize results from CBP studies on the concentration of metals in the Bay. Once in the estuary, the behavior of metals depends on how they respond to the Bay's chemical, biological, and physical processes. Some metals, for example, will become dissolved in the estuarine water. Others will associate with suspended matter, while certain amounts and types will be found in bottom sediments and interstitial water. This section deals with metals partitioned in all of their phases.

SOURCES

The CBP initiated studies to assess the input of metals from several major sources to the Bay. These sources are: industries and POTWs, atmospheric deposition, urban runoff, and three of the Bay's principal tributaries. Approximate loadings were computed for these sources to provide an estimate of the relative contributions each source makes.

Industries and POTWs Below the Fall Line

Rates of metal input from point sources in the Bay drainage basin were estimated for industries and POTWs below the fall line from data obtained between 1974 and 1980. Information from the National Enforcement Investigations Center (NEIC) of the U.S. Environmental Protection Agency (EPA) was used to place in priority the toxic dischargers from the approximately 5000 point source dischargers in the entire Chesapeake Bay basin. It was determined that there are 1000 major toxic dischargers, of which 122 are located below the fall line. For these 122 industries, loading estimates were computed for selected metals we found in relatively high concentrations in Bay sediments.

Concentration of metals in various industrial effluents was obtained from EPA effluent sampling data from Resources for the Future in the "Pollution Matrix Lookup Routine." Concentration values were assigned based on the industry's Standard Industrial Classification (SIC) code. The discharge rates for each industry were obtained from data collected for an EPA project referred to as the "Industrial Facilities Discharger File" (IFD). Loadings of metals in metric tons per year were computed by multiplying the effluent discharge rate (in millions of gallons per day [MGD]) by the concentration of the various metals milligrams per liter (mg/L), applying the appropriate conversion factors. However, when assigning effluent concentration values, the industries discharging cooling water were assigned concentrations representative of cooling water, not waste water. Those industries discharging cooling water and process

TABLE 1. POINT SOURCE LOADINGS OF METALS FROM INDUSTRIES[2] AND PUBLICLY OWNED TREATMENT WORKS (POTW'S)[1] IN COUNTIES BELOW THE FALL LINE FOR CR, CD, PB, CU, ZN, FE, IN METRIC TONS PER YEAR

	Metal											
	Cr		Cd		Pb		Cu		Zn		Fe	
	POTW	I[3]	POTW	I	POTW	I	POTW	I	POTW	I	POTW	I
Arundel	7.3	0.7	0.2	0.2	2.4	3.1	3.4	2.4	9.9	1.3	21.8	9.4
Baltimore		59.5		24.1		17.5		88.5		59.1		225.1
Baltimore City	78.9	47.2	1.8	142.3	25.5	9.9	37.1	20.7	106.8	45.5	234.4	1729.6
Calvert		3.8		-		8.9		1.9		-		-
Caroline		0.0		0.0		0.0		0.0		0.0		0.0
Cecil	0.6	0.0	0.0	0.0	0.2	0.0	0.3	0.0	0.9	0.0		0.0
Charles		0.0		0.0		0.0		0.0		0.0		0.0
Dorchester	4.9	0.6	0.1	0.1	1.6	0.2	2.3	0.4	6.6	0.4	14.4	-
Harford	2.2	0.8	0.1	0.2	0.7	0.1	1.0	0.6	2.9	0.6	6.5	-
Howard		0.0		0.0		0.0		0.0		0.0		0.0
Kent	0.2	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.3	0.0	0.7	-
Prince Georges	12.8	1.8	0.3	0.0	4.1	4.1	6.0	0.9	17.3	0.0	37.9	0.1
Saint Mary's	0.0	0.0	0.9	0.0	0.3	0.0	0.4	0.0	1.2	0.0	2.6	-
Wicomico	1.8	0.1	0.0	0.0	0.6	0.0	0.9	0.0	2.5	0.1	5.4	0.1
Alexandria City	10.2	2.2	0.2	-	3.3	5.1	4.8	1.1	13.7	-	30.2	-
Chesterfield	2.5	9.6	0.1	0.1	0.8	17.5	1.2	4.0	3.3	2.4	7.3	0.3
Henrico		1.1		0.0		0.4		0.2		1.9		0.0
Hopewell City	14.6	7.6	0.3	0.3	4.7	2.9	6.9	1.4	19.7	13.9	43.3	-
Louisa		22.7		-		53.0		11.4		-		-
Newport News City	12.8	9.6	0.3	3.9	4.2	2.7	6.0	13.9	17.4	9.3	38.1	36.7
Norfolk City	16.7	2.0	0.4	0.9	5.4	0.4	7.8	3.0	22.6	2.0	49.5	5.9
Northampton		0.0		0.0		0.2		0.0		0.0		0.7
Portsmouth City	5.2	14.4	0.1	5.9	1.7	3.1	2.5	20.8	7.0	14.9	15.5	-
Prince William	13.4	2.0	0.3	-	4.3	4.7	6.3	1.0	18.1	-	39.7	-
Richmond City	22.6	1.1	0.5	0.6	7.3	2.5	10.6	12.8	30.5	6.7	67.1	-
Spotsylvania	0.2	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.3	0.0	0.6	-
Westmoreland	0.3	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.4	0.1	0.9	0.2
Williamsburg City	2.3	0.1	0.1	0.0	0.7	0.0	1.1	0.0	3.1	0.1	6.8	-
York		12.1		0.2		18.7		4.5		8.9		-
TOTAL	199.5	199.1	5.7	178.8	68.1	155.0	98.9	189.6	284.4	167.3	624.6	2008.2

[1] POTW loadings were calculated for facilities where flows were 0.5 MGD.

[2] Loadings computed from approximately 122 industrial dischargers.

[3] I = Industry

waste water were assigned concentration values approximately 85 percent less than those industries in the same SIC code but discharging all process waste water.

Loadings from POTWs were computed by multiplying discharge flow rates (MGD), obtained from the EPA 1980 Needs Survey, by concentration values obtained from results of pilot-scale studies conducted by the EPA Municipal Environmental Research Laboratory (MERL) (Petrasek 1980). Discharge flow rates are compiled in the Needs Survey for use in Congressional allotment of construction grant funds to upgrade or expand existing POTWs.

Computation of loadings showed that discharge of metals is greatest in areas of high industrial activity and large population centers. With the exception of Fe, all of the metals listed in Table 1 have established criteria levels. These levels vary for each metal and for chronic versus acute toxicity. In localized areas, such as Baltimore Harbor and Elizabeth River, the quantities of metals discharged create situations with a strong potential for high aquatic toxicity. For example, in Baltimore Harbor, metals are discharged in moderate amounts; but because of low flushing rates (10 percent renewal rate) (Sinex and Helz, unpublished), these metals concentrate in Harbor waters. Although we have no data to demonstrate the severity of the problem in the water column, Sinex and Helz (unpublished) have shown from bottom sediment samples that the bulk of metals discharged in the Baltimore Harbor does, in fact, remain in the Harbor.

The distribution of metal loadings for POTWs and industries (Table 1) shows that discharges of Cd, Cr, Cu, Fe, and Zn from POTWs and industries in Baltimore County and Baltimore City far exceed those from other counties. Lead from POTWs in Baltimore City is higher than in other counties. Substantial inputs from POTWs are also noted for Cr, Fe, and Zn in Richmond City, Norfolk City, and Hopewell City. Lead is notably large in industrial discharge from Louisa County. Taken as a whole, industrial loadings are more than twice as large as treatment plant loadings.

Atmospheric Sources

Pollutants from the atmosphere can deposit directly as dryfall (dust) and as dissolved constitutents in precipitation (rain, snow, hail). Because we lacked data on the dryfall component of atmospheric deposition, no estimate of dryfall loading to the Bay is made in this section. However, Lazrus et al. (1970) and Davis and Galloway (1981) have done some work on dryfall atmospheric deposition of metals. Lazrus et al. (1970) showed that the deposition of metals from the atmosphere varies by a factor of three or less between North Carolina and Northern Virginia. Thus, the atmospheric deposition over the Bay is probably fairly uniform. Based on a residence time of 4.7 days for small aerosols (particles < 1 u) and a predominantly easterly air flow, Davis and Galloway (1981) revealed that atmospheric contaminants may reach the Bay from industrialized areas of the midwest. Deposits in industrialized areas, such as Baltimore, consist of heavy particulates that settle out rapidly, as well as small aerosols that rain out in the vicinity of the city. Thus, the concentration of metals in dryfall around Baltimore decreases with distance from the city (Baltimore Regional Planning Council, unpublished data), but such industrial centers constitute only a small percentage of the Bay's area.

CBP funded projects investigated atmospheric inputs to the Bay from precipitation. Two sources were used to evaluate atmospheric loads -- storm data from the Maryland Geological Survey and marsh cores. Data from the Maryland Geological Survey's sampling of six storm events from April to September 1981 were used to compute atmospheric loadings listed in Table 2. Because the areal variability of the deposition rate from each storm could not be determined at this time, we developed loading estimates that assume uniform concentrations over the entire Bay. Omitted from these estimates are dryfall loading rates and deposition that occur on the land surface in the drainage basins, eventually reaching the Bay or tributaries from surface runoff. Because of these limitations, the values presented in Table 2 are conservative estimates of total atmospheric deposition.

TABLE 2. ATMOSPHERIC INPUT OF SELECTED METALS FROM WETFALL TO CHESAPEAKE BAY AND TRIBUTARIES

Metals	Volume[1]-Weighted Concentration (ug/g)	Main Bay[2] (metric tons/ year)	Main Bay and Tributaries[3] (metric tons/ year)
Cd	0.23	2	3
Cu	2.20	16	28
Fe	6.85	50	87
Mn	1.77	13	22
Ni	1.95	14	25
Pb	2.66	19	34
Zn	65.20	467	825

[1] Based on sampling from six storm events. Data from Maryland Geological Survey (Conkwright et al. 1982).

[2] Surface area of Main Bay = 6,500 km^2.

[3] Surface area of Bay & Tributaries = 11,500 km^2.

Loadings computed using average annual precipitation of 1.1 meters.

Results from these studies show that quantities of metals entering Bay waters from atmospheric deposition are significant. The concentrations of metals in the atmosphere are proportional to the total mass of the metals released into the atmosphere from fossil fuel combustion, manufacturing processes, and many other anthropogenic and natural processes. The input of Zn, as shown in Table 2, is high because of its high emissions from fossil fuel combustion and other manufacturing processes like plating and cement production (Forstner and Wittman 1979). The total load of Zn from the atmosphere is at least double the amount from point source (Table 1). This suggests that some of the remote areas of the Bay, where anthropogenic contamination is assumed to be negligible are, in fact, areas receiving heavy inputs of metals, especially Zn. Other areas receiving high amounts of metals must also absorb elevated levels from the atmosphere, thereby worsening the problem.

Marsh deposits can record the atmospheric flux of trace metals deposited over time, thus providing another estimate of atmospheric input. The surface of the high marsh, Spartina patens, which is exposed to the atmosphere 95 percent of the time, retains most all atmospheric inputs. Although marsh cores from the Bay are scarce, McCaffrey and Thornson (1980) can estimate the atmospheric flux to the Bay from another core from Farm River Marsh, in Long Island Sound, Connecticut. In the Farm River Marsh core, all of the metals are assumed to have been deposited from the atmosphere. The concentration of these metals (Cu, Pb, and Zn) from the marsh samples was divided by the concentration of ^{210}Pb present in the sample. All of the ^{210}Pb in the marsh samples is assumed to have been deposited from the atmosphere (Helz et al. 1981). The metal to ^{210}Pb ratio from the marsh core is then assumed to be similar for the Helz cores, because the deposition rate between Long Island and the Bay is probably nearly the same. Therefore, by knowing ^{210}Pb concentrations in the Chesapeake cores, and applying the ratio from the marsh core, an estimate of the atmospheric contribution of these metals can be made.

In the northern Bay, core 4 (Table 3) shows that approximately 10 percent of the Cu (Cu/^{210}Pb Cu) and five percent of Zn (Zn/^{210}Pb Zn) is supplied from the atmosphere. However, in other cores from the central Bay (not shown) about 25 percent of the Cu and 13 percent of the Zn is of atmospheric origin. Consequently, the atmosphere becomes an important source in zones distant from sources of water pollution. When atmospheric and water pollution occur concurrently, the trend of "excess" metal over the background for the marsh, representing the atmospheric flux, is similar to those of Bay sediments as shown in Figure 1. Thus, atmospheric sources contribute to the increase of excess metals with time.

The trend, observed in Figure 1 for Zn in core 4 and in the Farm River marsh core, shows that Zn appears to be decreasing from a maximum value occurring around 1930 to 1940. The recent decrease could be due to an alteration in manufacturing processes or shifts in fossil fuel consumption (burning more oil instead of coal), thereby releasing less Zn to the atmosphere.

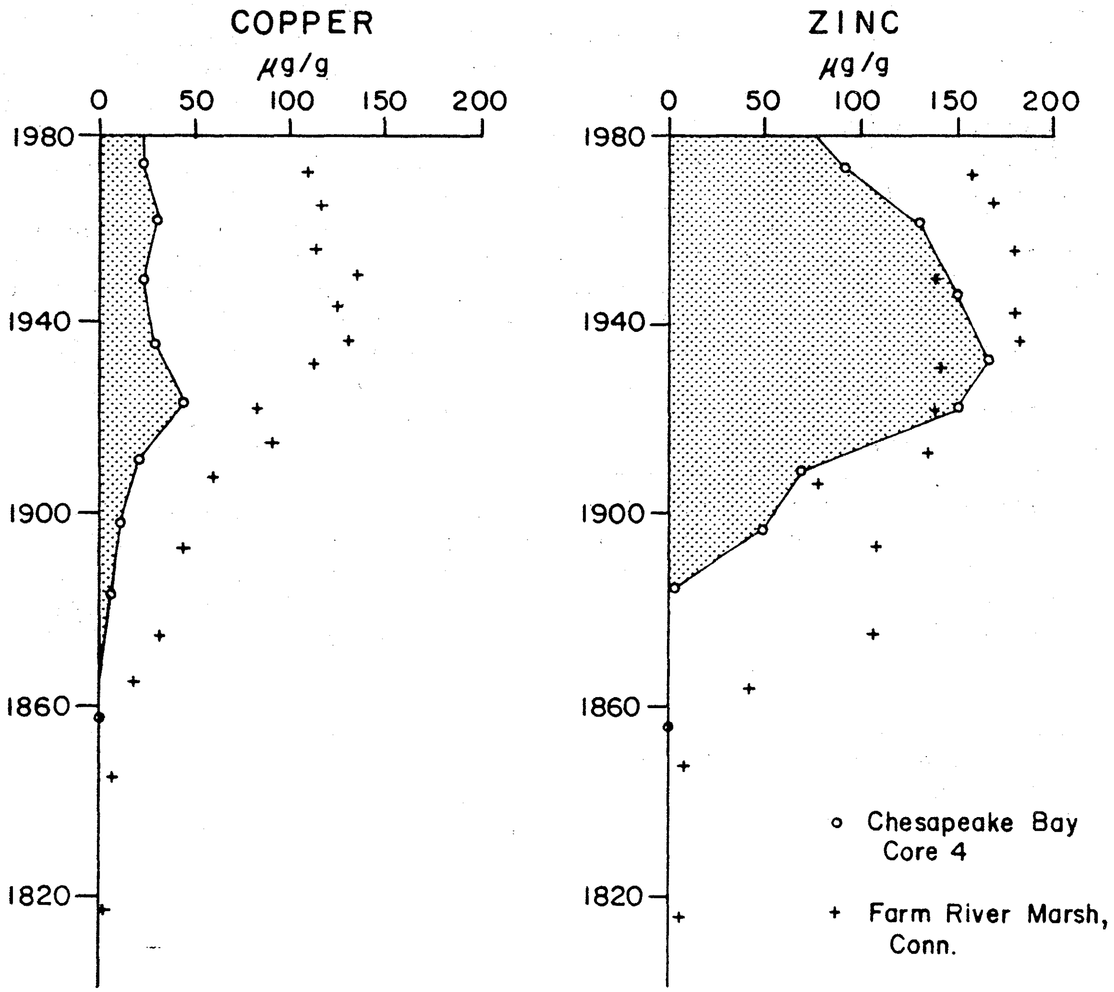

Figure 1. Graph of age versus metal content of Cu and Zn showing historical increase of "excess" metal concentration in Chesapeake Bay core 4 (Helz et al. 1981), by comparison to Farm River Marsh concentrations (McCaffrey and Thornson 1980).

TABLE 3. TOTAL EXCESS METALS IN CHESAPEAKE BAY CORES CONTRASTED WITH FARM RIVER MARSH

Core	^{210}Pb Standing Crop (dpm cm-2)[2]	Cu (ug cm-2)	Zn (ug cm-2)	Cu/^{210}Pb	Zn/^{210}Pb
4	7	793	3000	113	428
18	10.5	630	1500	60	142
60	10.0	644	1500	64	150
Farm River Marsh[1]				13	19

[1] From Benniger (1978).

[2] dpm cm^{-2} - decays per minute per square centimeter.

Urban Runoff

As previously discussed, the deposition of airborne pollutants to the Bay's surface may be an important transport mechanism. Another pathway by which atmospheric pollutants enter the Bay is urban runoff. Some rainwater (and dust) deposited in urban areas eventually reaches the Bay. This transport is facilitated by the high percentage of paved surface area in urban regions. Flowing over the roads and other impervious and pervious surfaces, runoff accumulates certain metals in dissolved and particulate phases, notably Pb from the combustion of leaded gasoline, Zn from the abrasion of tires, and Cu and Cr from automobile brake shoes.

Although urban runoff is usually considered a nonpoint source, on a Bay-wide scale, loadings from the three major cities in the Bay area are of sufficient magnitude to represent major localized point sources. Table 4 shows annual loadings of metals from Baltimore, Hampton Roads, and Washington, DC runoff. Loadings were computed from data supplied by Hartigan (October 21, 1981, memorandum). Concentrations of metals in runoff were derived by averaging results from runoff data collected during the Metropolitan Washington NURP study and an early 208 monitoring study in the Occoquan River and Four Mile Run basins of Northern Virginia. Surface runoff volumes were obtained by assuming that soils are sandy loam and by computing values for the various land use categories based on 1967 hourly rainfall record (rain gage at Washington National Airport).

The loading values listed in Table 4 show that urban runoff is a significant source of metals. Metals exhibiting the highest loadings are Fe, Pb, and Zn. Iron is not considered a toxic metal; loading values are included only for comparison. The high Pb and Zn values reflect local sources of these metals such as automobile exhaust, incinerators, refuse, and other urban activities that generate dust, gases, and other noxious by-products. Since rain is the major component of runoff, the concentrations of metals in rain and other forms of precipitation will also cause high metal loadings in urban runoff.

TABLE 4 URBAN RUNOFF LOADINGS FROM THREE MAJOR METROPOLITAN AREAS OF CHESAPEAKE BAY (AREA VALUES IN METRIC TONS/YEAR)

Metro Area	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Baltimore	5	3	3	291	5	6	35	19
Norfolk/ Newport News/ Hampton	1	4	2	213	3	4	26	15
Washington, DC	1	4	4	473	7	10	50	29
Total	7	11	9	977	15	20	111	63

River Sources

An estimate of annual loadings of selected metals at the fall line of three rivers, the Susquehanna, Potomac, and James, was derived from samples collected approximately bi-weekly to monthly by the U.S. Geological Survey between October 1978 and April 1981 (Lang and Grason, unpublished). Loading values were computed, using one of the methods described below.

Prediction Model--

Various mathematical models were used to fit a relationship between concentration (C) and flow (Q) or loading rate (LR) and flow. The various models used were as follows: C versus Q, ln(C) versus Q, C versus ln(Q), ln(C) versus ln(Q), C/Q versus 1/Q, ln(C/Q) versus 1/Q, C/Q versus ln(1/Q), ln(C/Q) versus 1/Q, LR versus Q, ln(LR) versus Q, LR versus ln(Q), and ln(LR) versus ln(Q). A concentration and/or loading rate was then computed for each day, using the best model and observed daily flow rates. These daily loadings were then summed for the total annual loading.

Sum of Averages--

To obtain loadings using this method, a flow weighted, mean daily concentration was first calculated as follows:

$$C_{mean} = \frac{[(C_{inst})(Q_{inst})]}{Q_{inst}}$$

This value was then multiplied by mean daily flow to obtain a daily loading. Daily loadings for each month were then averaged to give an averge daily loading for that month. These averages were then multiplied by the number of days in the month to give a monthly loading.

The monthly loadings were averaged to give an average monthly loading. Where no samples were taken in a month, the monthly average was used for these months, and the monthly loadings were summed to give a yearly loading.

Mean or Median Value from Sampling Data Applied to Long-Term Mean Annual Flow--

This method involved using the mean or median value of the various parameters as reported by the USGS (Lang and Grason 1980) and the long-term mean annual flow to compute the loadings.

The loadings and the computation method used for each metal are listed in Table 5(a). The discharge flows for these years and the long-term mean annual flows are listed in Table 5(b). The flow rates for 1979 were significantly above normal for all three rivers and, for 1980, were somewhat less than normal except for the James which was approximately ten percent higher than the long-term mean annual flow. Therefore, the computed average loading for these years is probably slightly higher than normal.

TABLE 5(a). ESTIMATED AVERAGE ANNUAL LOADINGS FOR VARIOUS METALS FROM THE MAJOR TRIBUTARIES OF CHESAPEAKE BAY FOR 1979-1980 PERIOD* (VALUES IN METRIC TONS/YEAR) (FROM LANG AND GRASON 1980)

Parameter	Susquehanna @ Conowingo Dam		Potomac @ Chain Bridge		James @ Cartersville, VA		Totals
Al-D	6,509	(2)	1,724	(2)	2,631	(2)	10,864
Al-S	156,061	(2)	36,061	(2)	30,890	(2)	223,012
Al-T	161,618	(2)	37,626	(2)	33,884	(2)	233,128
As-T	82	(2)	13	(2)	20	(1)	115
Cd-T	65	(3)	4	(2)	6	(3)	75
Co-T	59	(2)	39	(1)	48	(2)	146
Cr-T	383	(3)	105	(1)	63	(3)	551
Cu-T	390	(2)	86	(1)	41	(1)	517
Fe-D	1,844	(1)	839	(2)	567	(1)	3,250
Fe-S	192,422	(2)	76,227	(2)	27,783	(1)	296,432
Hg-T	23	(2)	-		6	(2)	29
Mg-D	232	(2)	61	(1)	31	(2)	324
Mn-D	7,552	(2)	86	(3)	104	(2)	7,742
Mn-S	7,326	(2)	1,929	(3)	2,277	(2)	11,532
Mn-T	14,469	(2)	1,933	(3)	2,327	(2)	19,229
Ni-T	229	(1)	109	(1)	64	(1)	402
Pb-T	174	(3)	102	(3)	31	(3)	307
Zn-T	837	(1)	322	(1)	285	(1)	1,444

*Values listed represent the mean of 1979 and 1980 calender year loadings.

(1) Computed using a model
(2) Computed using sum of averages method
(3) Computed using the reported mean or median value applied against the long term mean annual flow

D - Dissolved
S - Suspended
T - Total

TABLE 5(b); ANNUAL AND LONG-TERM MEAN ANNUAL FLOWS FOR THE SUSQUEHANNA, POTOMAC, AND JAMES RIVERS[1]

	1979 Calendar Year (ft^3 sec^{-1})	1980 Calendar Year (ft^3 sec^{-1})	Long Term Average (ft^3 sec^{-1})
Susquehanna	52,200 (+34%)[2]	28,400 (-27%)	38,900
Potomac	20,400 (+79%)	11,000 (- 3%)	11,400
James	12,000 (+70%)	7,790 (+10%)	7,050

[1] Data from U.S. Geological Survey, unpublished

[2] Values in parenthesis represent the percent difference from the long-term mean annual flow.

Table 5(a) lists loading values for 13 metals of which several -- Al, Fe, Mg, Mn -- are not considered toxic. Some of these metals, such as Al and Fe, are contributed primarily from natural erosion processes and cannot indicate pollution. All of the metals in this list occur in crustal material and, therefore, are naturally found in rivers. This makes it difficult to determine the natural from the anthropogenic contributions, a subject more fully discussed in Section 4. It is important to mention, however, that even though some metals are contained in naturally-occurring soil and crustal material, the rate of this sediment entering the river may be dramatically enhanced by farming and other rural and urban activities.

Of importance to note in Table 5(a) are the high loadings for Cr, Cu, and Zn. These values reflect contributions from point and nonpoint sources, erosion, and other sources. Zinc values are particularly high and may be the direct result of the observed high concentrations of Zn in the precipiation that falls on these drainage basins. Of the three rivers, the Susquehanna produces the highest loadings, primarily because of the higher flows in this river.

Concentrations of total metal content in the rivers vary with total suspended material and with river flow. As shown in Figure 2, the concentration of suspended Fe at high inflow is more than 20 times the concentration at low inflow, and Mn is more than 15 times the concentration at low inflow. Some metals, like Mn, also exhibit seasonal changes in partitioning between dissolved particulate concentrations (Figure 2). Particulate Mn is more dominant than dissolved Mn in spring, summer, and fall--a trend associated with influx of decaying organic matter in winter (Carpenter 1975). Such changes in partitioning and the varying metal concentrations with sediment loads make determination of loading estimates difficult.

A comparison of the 1980 loadings on the Susquehanna River with values computed by Carpenter in 1965-1966 is presented in Table 5(c). These data show that loading values for Cd, Cu, Fe, and Zn are very similar. Manganese shows a slight increase, but Co and Ni show moderate to high decreases. The most notable change is the Cr loading that was

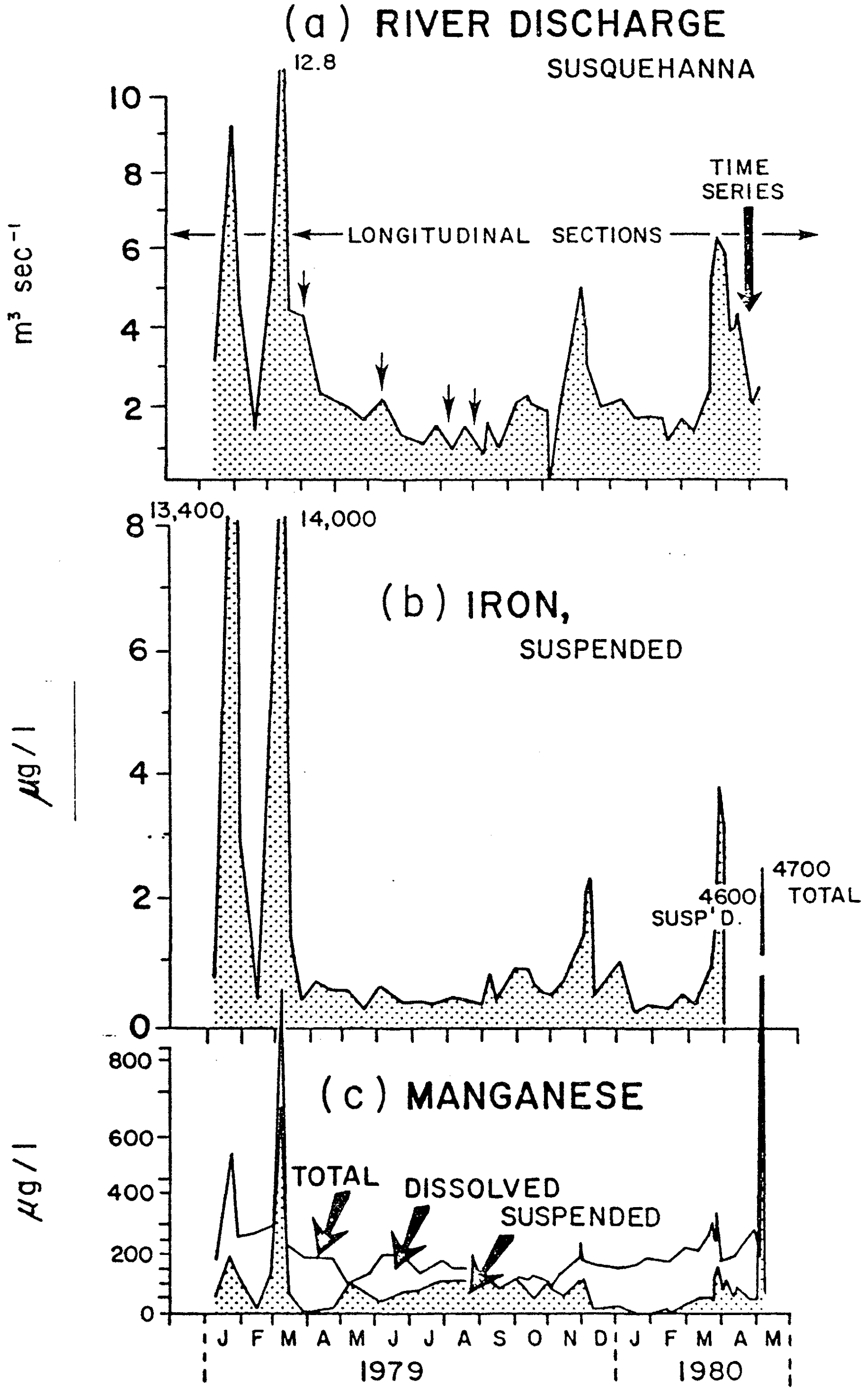

Figure 2. Temporal variations of: (a) Susquehanna River discharge at Conowingo Dam, and corresponding (b) Fe, and (c) Mn concentrations, dissolved, suspended, and total. Data from Lang and Grason (1980) based on instantaneous measurements and samples at peak inflows.

approximately 300 percent higher in the 1980 estimates than in the 1965-1966 estimates.

Comparison of the loadings from the three rivers in Table 5(a) indicates that the Susquehanna contributes a greater proportion of metals than the Potomac or James. To provide an estimate of the relative yield (or load per unit area) from these river basins, loading rate factors were computed by dividing the loadings listed in Table 4 by the area of the drainage basin above the fall line for each river system. These values are listed in Table 5(d). Generally, the Susquehanna appears to be no more enriched than the Potomac or James. Although certain metals are more enriched in one river system compared to the other two, the differences are significant for only several metals and may be largely explained by errors in sampling or loading computation.

TABLE 5(c). COMPARISON OF COMPUTED LOADINGS FOR THE SUSQUEHANNA RIVER WITH THOSE OF CARPENTER[1] (LOADINGS IN METRIC TONS/YEAR)

Metal	1980 Computed Loadings with Flow = 28,400 $ft^3\ sec^{-1}$	Annual Loadings Reported by Carpenter[2] Flow = 28,012 $ft^3\ sec^{-1}$	Percent Difference From Carpenter (%)
Cd	2	2	0
Co	20	90	-78
Cr	220	50	+340
Cu	106	100	+6
Fe	36,500	40,000	-9
Mn	6,100	5,000	+22
Ni	150	200	-25
Zn	570	600	-5

[1] Carpenter, J. H., W. L. Bradford, and V. Grant (1975).

[2] Sampled approximately one mile downstream from Conowingo dam every week for the period of April 1965 through August 1966.

Although rivers are a major source of metals, it is not known what proportion of these loadings enter the Bay. Monitoring on the Susquehanna generated loading values for the river just prior to discharge into the Bay, but the James, Potomac, and many other tributaries discharge into fresh water, tidal, and brackish-water reaches of substantial length.

Prior studies of eight Bay tributaries indicate that the bulk of suspended sediment is trapped within the tributaries--for example, in the Back River (Helz et al. 1975), the Chester (Palmer 1974), the Choptank (Yarbro 1981), the Patuxent (Keefe et al. 1976), the Rappahannock (Nichols 1977), and the James (Nichols 1972, O'Connor 1981). Entrapment of sediment is recorded either by direct measurements of suspended sediment transport, or by historical shoaling rates with an evaluation of these rates in relation to inputs of suspended sediment from different sources.

TABLE 5(d). METAL LOADING RATE FACTORS FOR THE SUSQUEHANNA, POTOMAC, AND JAMES RIVER DRAINAGE BASINS* (VALUES IN METRIC TONS/KM^2)

Metal	Susquehanna	Potomac	James
Al-D	240	149	420
Al-S	5,759	3,119	4,937
Al-T	5,964	5,255	5,415
As-T	3	1	3
Cd-T	2	1	1
Co-T	2	3	8
Cr-T	14	9	10
Cu-T	14	7	7
Fe-D	68	73	91
Fe-S	7,110	6,594	4,440
Hg-T	1		1
Mg-D	9	5	5
Mn-D	279	7	17
Mn-S	270	167	364
Mn-T	534	167	372
Ni-T	8	9	10
Pb-T	6	9	5
Zn-T	31	28	46
Basin Area (km^2)	27,100	11,560	6,257

* Values computed by dividing loadings listed in Table 5(a) by the area of the drainage basin above the USGS monitoring station.

The ability of these rivers to trap river-borne sediment was determined by calculating a capacity inflow ratio, using intertidal volume for capacity, and potential inflow (drainage area times annual precipitation) for inflow assuming all precipitation is runoff. As indicated in Table 6, tributary estuaries such as the Rappahannock and Choptank act as very efficient sediment traps. Therefore, if most of the sediment is trapped in the estuarine portion of these rivers, then the bulk of river-borne toxicants that are adsorbed to the sediment are also likely trapped. Despite the high efficiency of these rivers to trap sediment, some sediment will escape, especially during storms. At such times, these rivers and other similar areas should be monitored for exceptionally high levels of toxicants.

TABLE 6. DATA FOR CAPACITY/INFLOW RATIOS AND PERCENTAGE OF SUSPENDED SEDIMENT TRAPPED

System	Capacity/Inflow	Sed. Trapped	Source
Rappahannock	0.7	90%	Nichols (1977)
Choptank	2.0	92%	Yarbro (1981)
Susquehanna - Northern Chesapeake Bay	0.04	75%	Biggs (1970)

A summary of total metal influx to Chesapeake Bay and its tributaries from different natural and anthropogenic sources is presented in Table 7. The estimates are products of two quantities, average metal concentration and rate of discharge. Accuracy of the data varies with the number of measurements per unit time, seasonal variations in constituent composition, and many other factors. This table shows that the sum of industrial and municipal wastewater loadings (point sources) represents a major contribution of metals to the Bay. Rivers are the only other source that exceed the point sources. However, the loadings from rivers actually represent a combination of the other sources that discharge into these rivers above the point where loadings were estimated. That is, the river-loading estimates contain some fraction of anthropogenic and natural contributions and become a pathway for these sources. From the results shown in Table 5(d), it appears that the relative proportions of the metal sources in these river systems are fairly uniform. However, because point sources do contribute to some part of the river loadings and are also one of the major sources for the Bay, this suggests that for most metals, point sources are probably the major source to the Bay, with loadings from urban runoff and shoreline erosion significant for some metals.

The upper Bay and the upper reaches of the Potomac and James estuaries are critical areas for fish spawning and other biological activities. From our studies of metal concentrations in the Bay (discussed in Section 3 and Section 4), we know that the Northern Bay does exhibit elevated metal concentrations. Therefore, the Susquehanna River represents a major source of metals, causing the Northern Bay to have elevated concentrations.

DISTRIBUTION AND CONCENTRATION OF DISSOLVED METALS

Some of the metals, entering the Bay from any one of the sources previously discussed, will dissolve in the estuarine water. In this form, metal data are available for Cd, Ce, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sc, Th, U, and Zn in surface water and bottom water for one sampling cruise during June-July 1979 (Kingston et al. 1982).

Kingston's data show that a correlation exists between metal concentration and salinity for Cr, Mo, and U (Figure 3a, Figure 3b). Uranium and Mo concentrations increase linearly with increasing salinity and approach average seawater concentrations at the upper end of the

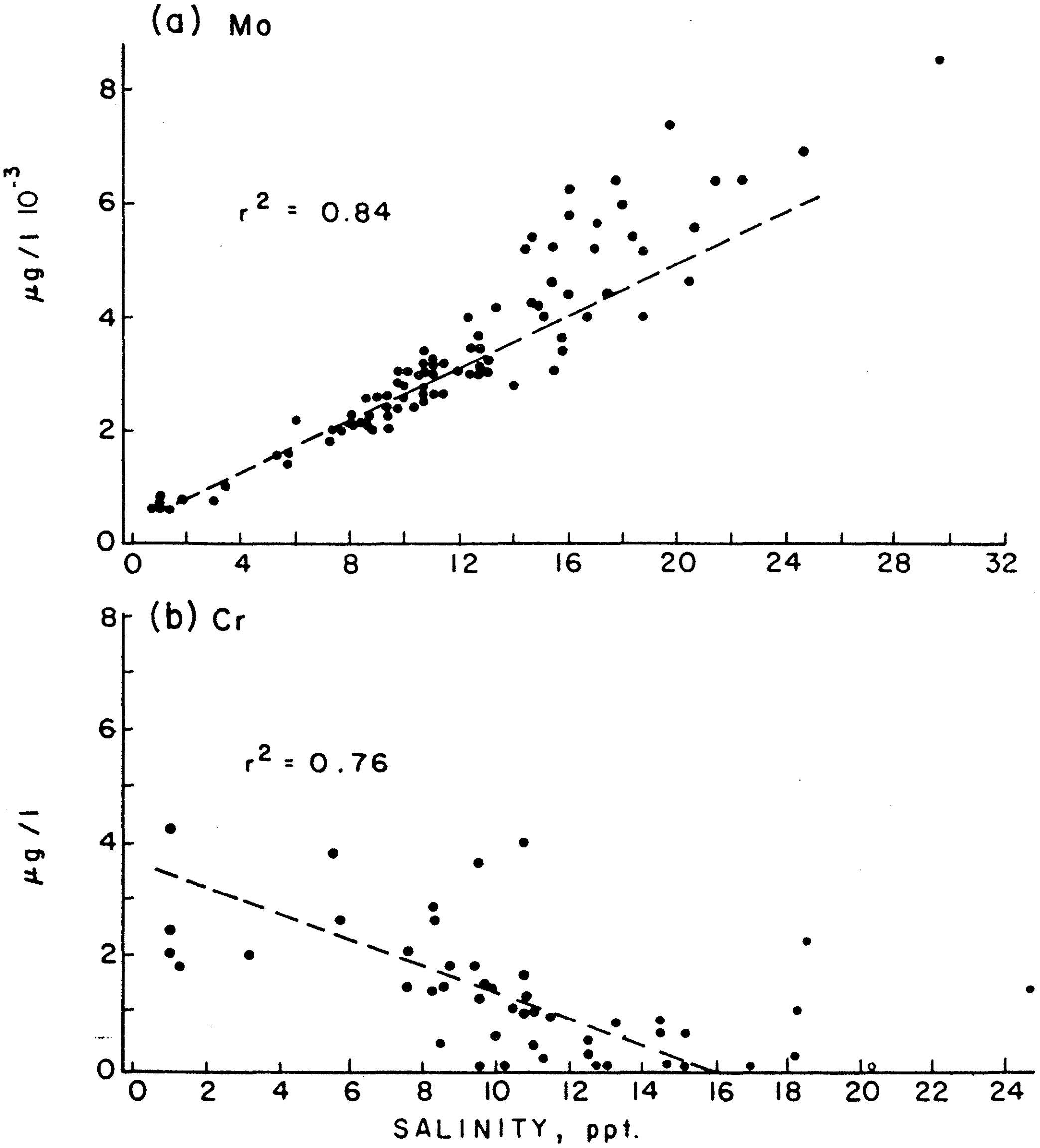

Figure 3. Plot of (a) dissolved Mo content versus salinity, and (b) dissolved Cr content versus salinity for samples from surface water along the Chesapeake Bay length, June-July, 1979. Data from Kingston (1982).

TABLE 7. LOADINGS OF METALS FROM THE MAJOR SOURCES AND PATHWAYS TO CHESAPEAKE BAY (VALUES IN METRIC TONS/YEAR)

Source	Cd	Cr	Cu	Fe	Pb	Zn
Industry	178 (66)[1]	200 (19)	190 (22)	2,006 (1)	155 (22)	167 (6)
Municipal Wastewater	6 (2)	200 (19)	99 (12)	625 (1)	68 (10)	284 (10)
Atmospheric	3 (1)	---	28 (3)	87 (1)	34 (5)	825 (29)
Urban Runoff	7 (2)	10 (1)	9 (1)	977 (1)	111 (16)	63 (2)
Rivers	75 (28)	551 (53)	517 (59)	199,682 (77)	307 (43)	1444 (50)
Shore Erosion	1 (1)	83 (8)	29 (3)	57,200 (22)	28 (4)	96 (3)

[1] Values in parenthesis represent percent of total loading

salinity range. This trend indicates that marine waters are the source of these metals, and that the concentration gradient is a result of dilution of marine water by river runoff. It also indicates that these metals are not significantly involved in chemical or biological processes in the Bay. By contrast, Cr concentrations decrease as salinity increases to a value approximating average seawater concentration at the upper end of the salinity range. This relationship indicates that river runoff is the major source of Cr, and that dilution by marine water controls dissolved Cr concentrations in the estuary. The scatter in the Cr data, however, is much greater (Figure 3b) than that for Mo, possibly indicating the influence of other processes in addition to dilution by marine waters.

All of the other dissolved metals investigated, Cd, Ce, Co, Cu, Ni, Pb, and Zn, are significantly affected by processes other than dilution. Therefore, plots of dissolved metal concentration versus salinity show little correlation. Cadmium, Cu, Ni, Sn, and Zn tend to decrease in concentration with increasing salinity, although there is much scatter in the data. Differences in metal concentrations in relation to salinity may arise from varying strength of sources (marine versus freshwater, or others), fluctuating chemical behavior (oxidizing versus reducing, salinity differences), hydrodynamic mixing patterns, and other factors.

Patterns of enrichment emerge from plots of the ratio of dissolved metal in surface water to dissolved metal in bottom water, versus salinity of the surface water (Figure 4). If surface waters are enriched (contain elevated concentrations) in a metal, the ratio is greater than one; if bottom waters are enriched, the ratio is less than one; if the surface and bottom concentrations are the same, the ratio is equal to one. For example, in Figure 4a, the dissolved-Cu-concentration-in-near-surface-water samples to dissolved-Cu-concentration-in-near-bottom-water ratios are mostly greater than one, and significantly greater than one in the 10 to 15

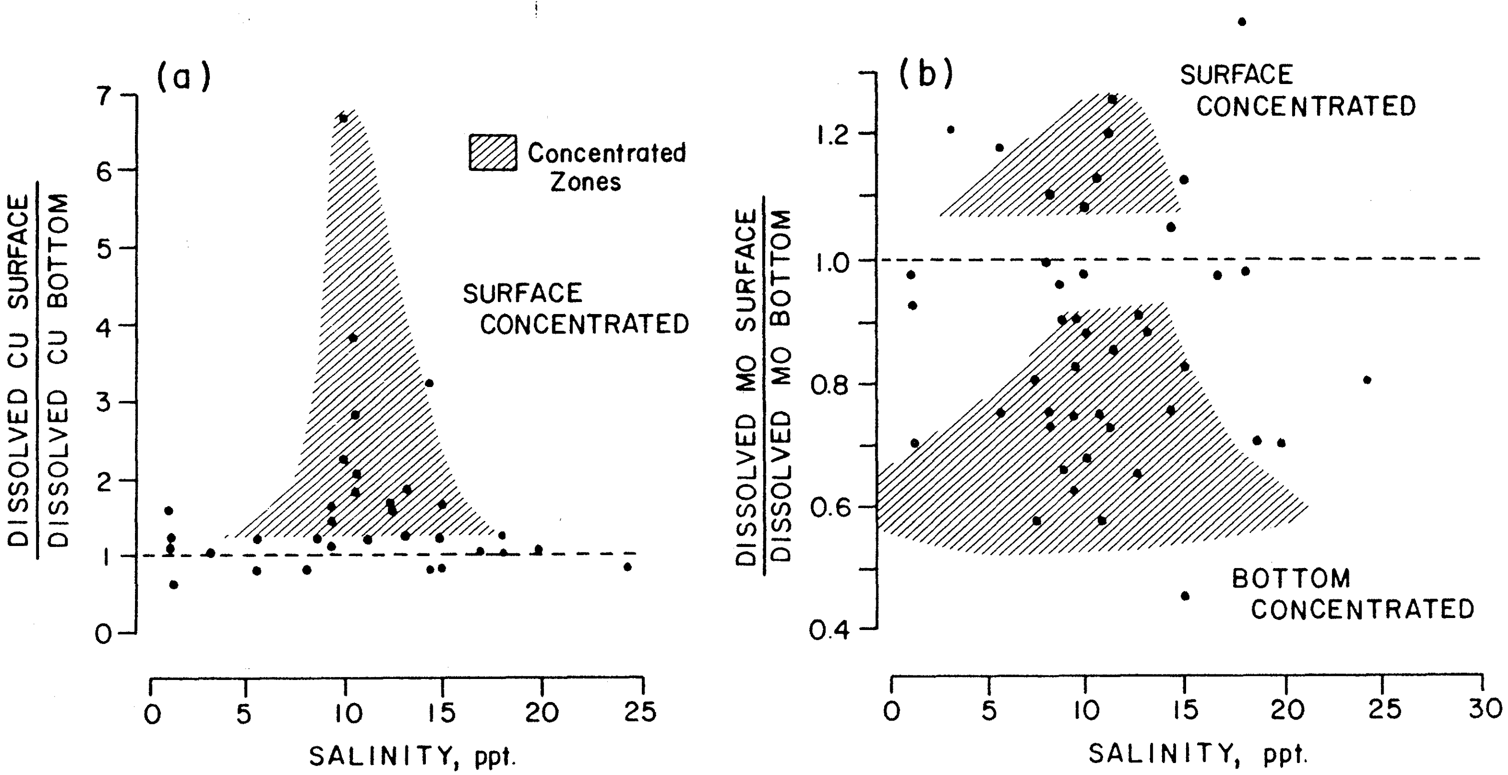

Figure 4.(a) Ratio of dissolved Cu concentration in surface water to dissolved Cu concentration in bottom water versus salinity, and (b) Ratio of dissolved Mo concentration in surface water to dissolved Mo concentration in bottom water versus salinity. Concentrated zones, shaded. Data from Kingston (1979).

ppt range of salinity values. This suggests that the mid-Bay (where salinities range from 10 to 15 ppt) has much higher Cu concentrations in the surface waters, relative to the bottom waters. Salinity indicates the relative position along the estuary where enrichment occurs. The term enrichment refers to the concentration of the metal in the surface water as a function of concentration in bottom water. This ratio does not indicate absolute concentration and cannot be used as an index of abnormal metal content.

Figure 5a compares the ratio of dissolved metal concentration in surface water to dissolved metal concentration in bottom water, with the ratio of surface water salinity to bottom-water salinity. On these plots, a salinity ratio of one indicates there is no halocline and, therefore, little or no stratification. The data displayed in Figure 5 can be divided into four quadrants. For example, in Figure 5(b), the ratios of dissolved-Mo-concentrations-in-near-surface-water samples to dissolved-Mo-concentrations-in-near-bottom-water samples, appear to fall primarily in the bottom, left-hand quadrant. This indicates that Bay waters display a tendency for Mo concentrations to be higher in salty, bottom waters than surface waters. If the ratio exceeds one, the surface water is more saline; if the ratio is less than one, the bottom water is more saline. As in the previous graphs, a metal ratio greater than one indicates surface enrichment, whereas a ratio less than one indicates bottom enrichment.

Plots like those of figure 5b show that Cu, Ni, and Zn are strongly enriched in surface waters, particularly under conditions of strong halocline development. Under the same conditions, Co, Cr, and Mo are strongly enriched in bottom waters. Similar data show that Cd is enriched in low-salinity surface water. Cobalt shows enrichment in surface waters of salinity up to approximately eight ppt, and in bottom waters over the salinity range from eight to 15 ppt. Chromium is enriched in surface waters up to 15 ppt salinity and in bottom waters from eight to 20 ppt. Copper, Ni, and Zn are strongly enriched in surface waters from five to 18 ppt. Uranium is enriched in bottom waters in the range seven to 15 ppt.

Table 8 summarizes univariate statistics for near-bottom and near-surface dissolved metal concentrations throughout Chesapeake Bay as sampled and analyzed by Kingston et al. (1982). Because of the high precision and accuracy used in these analyses, the information in Table 8 represents data generated for the first time for several metals in Bay waters. These numbers, then, are "benchwork" values from which to compare future numbers, and can indicate potential increases or decreases in contaminated areas.

The NBS investigations (Kingston et al. 1982) analyzed particulate as well as the dissolved concentrations in the sample. This information provides better understanding of how the various metals partition between dissolved and adsorbed phases. Dissolved metal concentrations are very important, because this phase is completely biologically available. Therefore, some of the maximum values shown in Table 8 may be hazardous to aquatic life in Bay waters where these high concentrations are found.

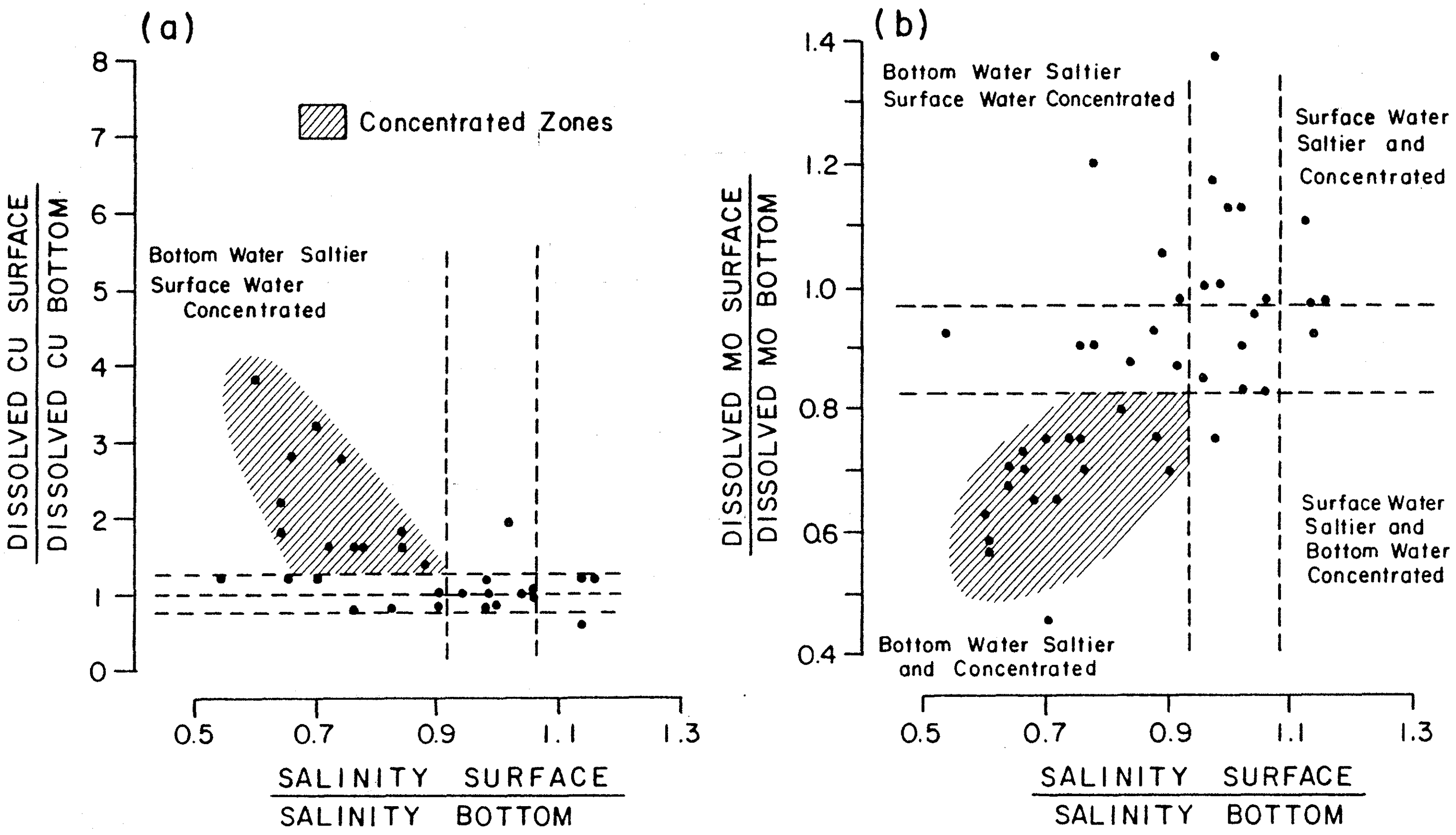

Figure 5. Plot of the ratio of (a) dissolved Cu concentration and (b) dissolved Mo concentration in surface water to bottom water versus the ratio of surface salinity to bottom salinity. Concentrated zones, shaded. Data from Kingston (1979).

TABLE 8. SUMMARY OF MEAN AND MEDIAN METAL CONCENTRATIONS AND RANGE OF BAY-WIDE VALUES (UG/L) (DATA FROM KINGSTON ET AL. 1982) CRUISE OF JUNE-JULY 1979.

	Dissolved			
	N*	Mean	Median	Range
Cd	45	0.05	0.04	0.007-0.101
Co	102	0.07	0.05	0.01-0.56
Cr	102	0.17	0.11	0-1.68
Cu	79	0.66	0.48	0.15-2.25
Fe	102	3.12	1.63	0.09-71.67
Mn	102	13.88	3.34	0-388
Mo	102	3.26	2.93	0.61-8.68
Ni	102	1.21	1.15	0.5-2.59
Pb	102	0.11	0.05	0-1.59
Sc	102	0.0006	0.0005	0.0002-0.002
Sn	9	0.86	0.86	0.31-1.61
Th	39	0.001	0.001	-
U	102	0.93	0.88	0.13-2.57
Zn	102	1.19	0.42	0-11.11

*N is number of samples treated.

DISTRIBUTION AND CONCENTRATIONS OF METALS IN SUSPENDED MATERIAL

Chesapeake Bay Program research has shown the distribution of metals in suspended material displays marked longitudinal and vertical gradients. Although concentrations were highly variable between samples and surveys, the mean metal content per gram of material exhibits distinct trends (Nichols et al. 1981). Content of the metals, As, Cd, Cu, Pb, Hg, Ni, Sn, and Zn, reached a maximum in near-surface suspended material of the central Bay, shown in Figures 6a, 6b, and 6c. Because this part of the Bay is an area of high biological activity, elevated levels of these metals could threaten biota there. The concentrations for these metals were higher than farther landward near major sources in the Susquehanna River mouth and Baltimore Harbor zone. Particularly high maxima or "hot spots" were observed for Cu and Cd (Figure 7 and Figure 8). The mean concentrations for Cu and Cd were five to 10 times greater than the Susquehanna River mouth. Secondary maxima occurred in the main Bay off Baltimore Harbor for surface concentrations of Cd, Mn, Ni, Pb, Sn, and Zn (Figure 7 and Figure 8). High levels of metals at these "hot spots" indicate areas of possible toxic impacts.

Metal concentrations were higher in surface and mid-depth suspended material than near the bottom, a trend resulting in stratified distributions. For example, Cu, Ni, Sn, and Zn concentrations were higher in surface than in near-bottom water in the same zone by a factor of two or more. Again, these results indicate where unnatural levels of metals can occur, with a consequence of increased risk of toxicity.

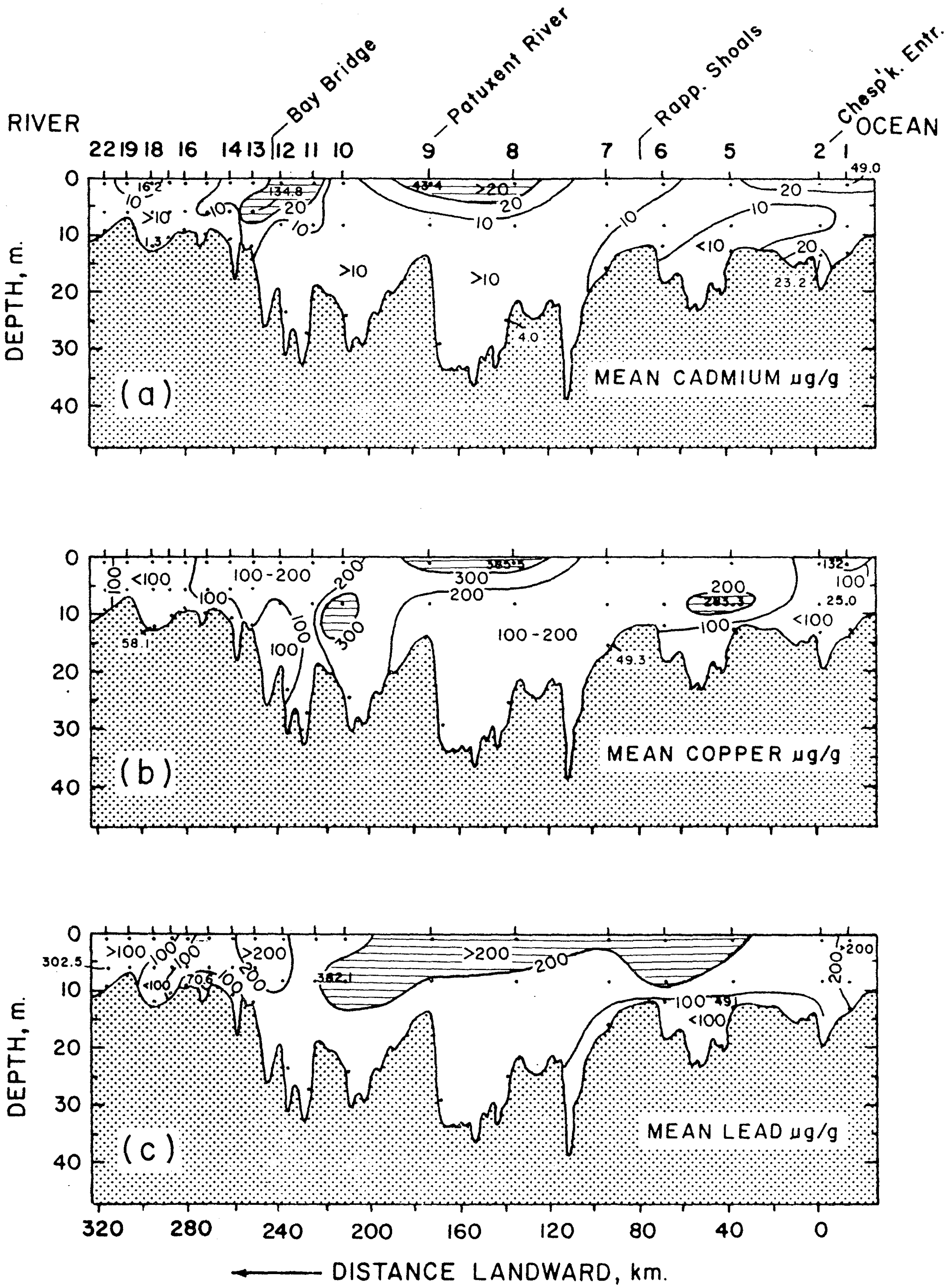

Figure 6. Longitudinal-depth distributions of mean metal concentration per gram of suspended material, along the axis of Chesapeake Bay, for (a) Cd, (b) Cu, and (c) Pb. Relatively high zones, shaded. Data from Nichols et al. (1981).

METALS IN SUSPENDED MATERIAL
SURFACE

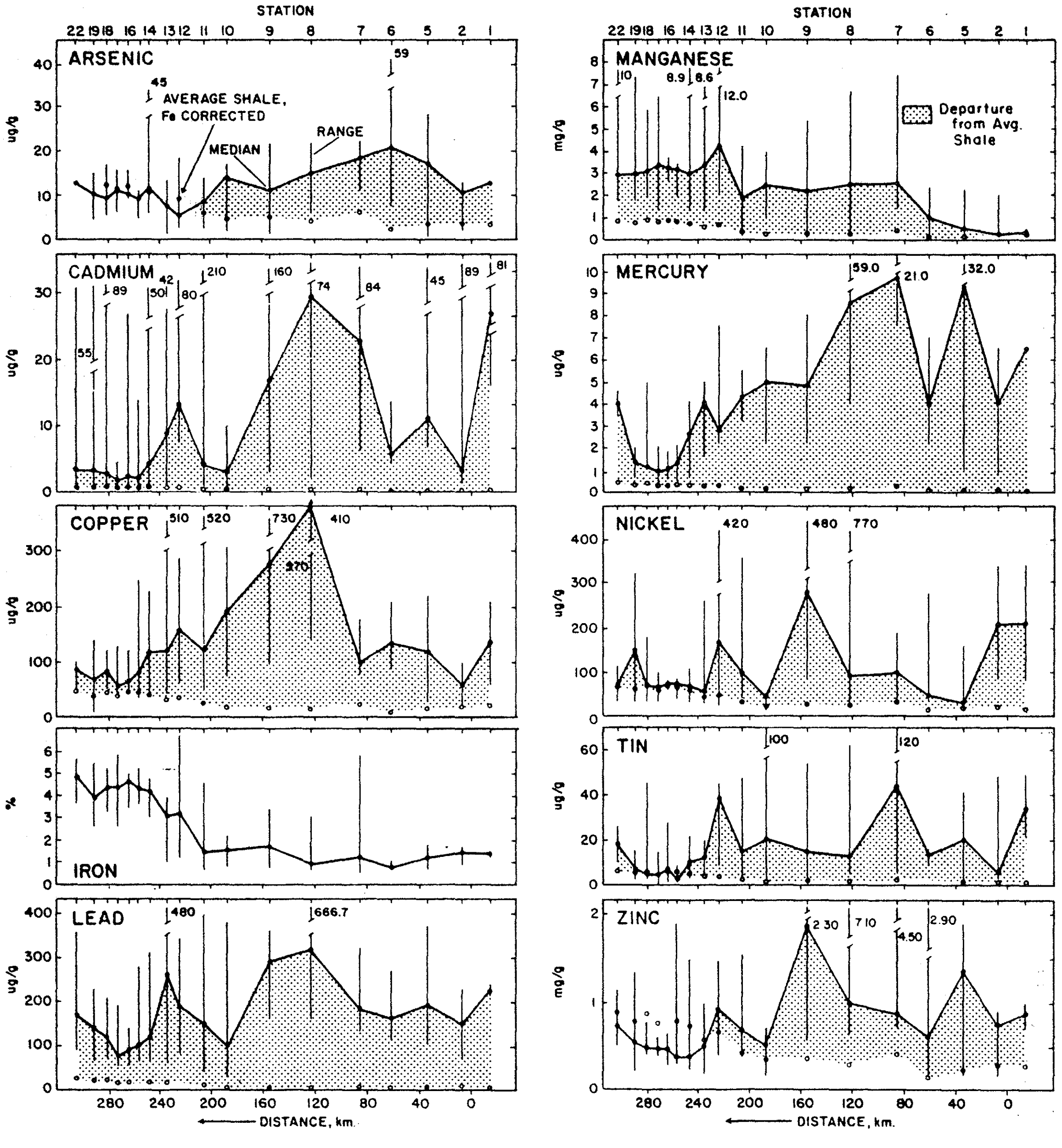

Figure 7. Distribution of metal content in surface suspended material with distance along the Bay axis. Median values and range of concentrations from all available observations of Nichols et al. (1981). Shaded zone indicates magnitude of departure between median values and mean values for Fe-corrected average shale, open circles.

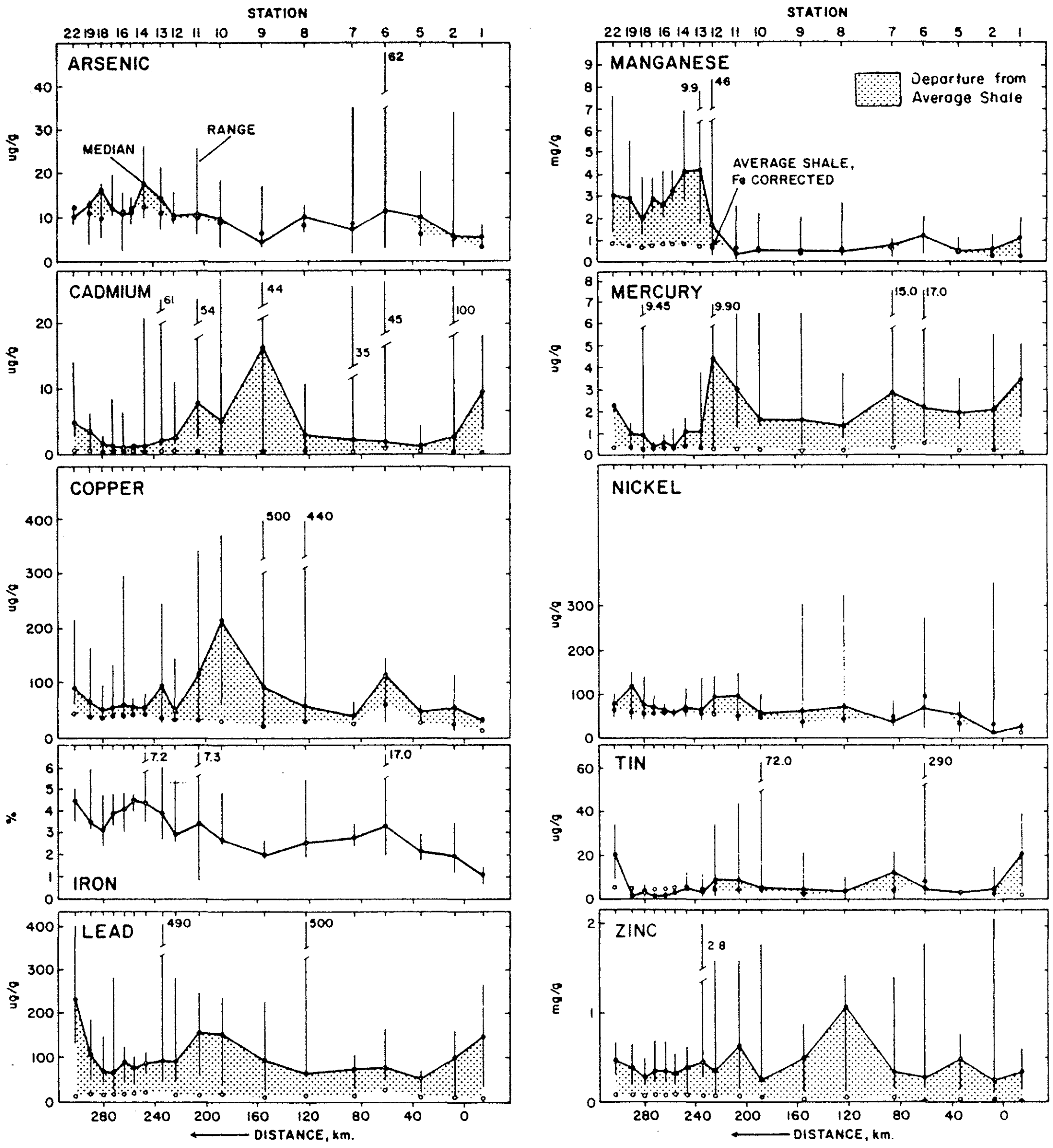
METALS IN SUSPENDED MATERIAL NEAR-BOTTOM

Figure 8. Distribution of metal content in near-bottom suspended material with distance along the Bay axis. Median values and range of concentrations from all available observations of Nichols et al. (1981). Shaded zone indicates magnitude of departure between median values and mean values for Fe-corrected average shale, open circles.

Concentrations of metals in suspended material changed with season. Seasonal changes were marked by a 10-fold increase in surface Cu concentrations between March to April and May to August (Nichols et al. 1981). Zinc was higher in March to April than at other times, whereas Pb was highest during June. Table 9(a) summarizes the mean metal concentrations and range of values at all sample depths throughout the Bay (Nichols et al. 1981). Table 9(b), from Kingston et al. (1982), supports these values.

TABLE 9(a). SUMMARY OF MEAN METAL CONCENTRATIONS AND RANGE OF BAY-WIDE VALUES, PER GRAM OF SUSPENDED MATERIAL, LEFT; AND WEIGHT PER VOLUME OF SUSPENDED MATERIAL, RIGHT (DATA FROM NICHOLS ET AL. 1981) FOR MORE THAN 550 SAMPLES AND 8 CRUISES ALONG THE BAY-LENGTH BETWEEN MONTHS OF MARCH AND SEPTEMBER 1979 AND 1980

Metal	Mean	Range	Metal	Mean	Range
As ug/g	13.00	0.55-100.00	As ug/L	0.32	0.006-5.00
Cd ug/g	14.16	0.12-790.00	Cd ug/L	0.14	0.003-3.80
Cu ug/g	127.96	9.90-570.00	Cu ug/L	1.84	0.068-17.00
Fe ug/g	3.11×10^7	$0.29-17 \times 10^7$	Fe mg/L	88×10^5	$1.0-1200 \times 10^5$
Hg ug/g	3.89	0.5-59.00	Hg ug/L	0.035	0.01-0.47
Mn ug/g	2880	80-46,000	Mn ug/L	65.13	0.48-1000.00
Ni ug/g	95.80	4.80-770.00	Ni ug/L	2.00	0.03-34.00
Pb ug/g	160.30	21.00-730.00	Pb ug/L	2.27	0.10-15.00
Sn ug/g	17.97	0.25-290.00	Sn ug/L	0.20	0.01-4.80
Zn mg/g	750	100-7100	Zn ug/L	11.02	0.55-94.00

TABLE 9(b). MEAN, MEDIAN, AND RANGE OF METAL CONTENT FOR ONE CRUISE ALONG THE BAY-LENGTH (JUNE-JULY 1979) (DATA FROM KINGSTON 1982)

ug/l	N*	Mean	Median	Range
Cd	51	0.018	0.008	0.001-0.11
Co	102	0.24	0.06	0.17-2.37
Cr	102	0.75	0.23	0-5.31
Cu	102	0.65	0.36	0.1-4.69
Fe	102	342.45	131.50	14-2911
Mn	102	38.16	19.20	1.2-349
Mo	12	0.08	0.03	0.01-0.25
Ni	102	0.57	0.27	0.03-5
Pb	96	0.75	0.23	0.01-7.3
Sc	102	0.11	0.04	0.003-0.93
Sn	-	-	-	-
Th	100	0.10	0.04	0.002-0.68
U	86	0.029	0.012	0.002-0.192
Zn	90	2.15	0.73	0-15.2

*N is number of samples treated.

Table 9c. • COMPARISON OF MEAN PARTICULATE, DISSOLVED AND TOTAL METAL CONTENT IN SURFACE AND BOTTOM WATER FOR STATIONS THROUGHOUT CHESAPEAKE BAY, JUNE-JULY 1979; DATA FROM KINGSTON (1982).

Metal	Surface Water				Bottom Water			
	Particulate	Dissolved	Total	D/T x 100	Particulate	Dissolved	Total	D/T x 100
Co	0.207	0.046	0.255	18	0.270	0.083	0.354	10%
Cr	0.622	0.133	0.756	17	0.877	0.199	1.077	18
Fe	264.600	1.619	266.200	1	420.300	4.634	424.900	1
Mo	0.060	2.974	2.278	99	0.097	3.551	2.648	97
Sc	0.086	0.001	0.087	0.1	0.134	0.001	0.135	0.4
Th	0.077	0.001	0.150	1.0	0.113	0.001	0.150	0.9
U	0.024	0.830	0.846	98	0.035	1.020	0.986	97
Zn	1.882	1.756	3.636	48	2.410	0.623	3.095	20
Cd	0.016	0.048	0.072	66	0.018	0.044	0.065	68
Cu	0.563	0.771	1.437	53	0.733	0.560	1.376	41
Mn	33.750	2.645	36.410	7	42.56	25.120	67.680	37
Pb	0.554	0.111	0.662	17	0.927	0.117	1.045	11
Ni	0.478	1.283	1.761	73	0.672	1.155	1.828	63

Concentrations of metals and other chemical constituents can be expressed in several ways, including concentration expressed as weight of the specific metal per unit weight of suspended material, and per unit volume of water. The expression used depends on the substance (water or sediment) being analyzed. Discussion of metal concentrations thus far has been based on concentrations expressed on a weight per weight basis. However, when metal distributions reported as weight per volume are examined, the metal concentrations are directly proportional to the concentration of total suspended material. Therefore, mean metal concentrations of As, Fe, Mn, Ni, Pb, Sn, and Zn were highest in the zone of the turbidity maximum where suspended sediment concentrations are highest (Nichols et al. 1981). Likewise, near-bottom metal concentrations of most metals were usually higher than surface concentrations, resulting in stratified distributions.

In addition to seasonal variations, metal concentrations were highly variable on short-time scales. For example, concentrations of Cu and Pb per gram of suspended material from the turbidity maximum zone of the northern Bay, varied more than two-fold over a tidal cycle. By contrast, Fe, Mn, and Zn varied within relatively narrow limits. These fluctuations are associted with large fluctuations of suspended material entering the Bay, and moderate fluctuations of particle size and organic content as tidal currents resuspended sediment from the bed. Such short-term (tidal) changes added to long-term (seasonal) variations produce wide ranges in metal content. These variations must be taken into account for planning metal samplings for monitoring and meaningful interpretation of data.

Despite the wide spatial and temporal variations of metal concentrations, many metals correlated statistically with each other, allowing the potential use of one or several as predictors. For example, from the VIMS cruise series (Nichols et al. 1981), Fe-Mn, Cu-Zn, and Ni-Zn, Ni-Fe, and Zn-Fe had $r > 0.80$. Many metals from the NBS cruise (Kingston et al. 1982) also correlated with each other: Co, Cr, Fe, Sc, Th, Zn, Cu, Mn, Pb, and Ni with $r > 0.90$. These associations reflect the affinity of metals for suspended material through adsorption or uptake, and show that many metals display similar behavior. Metals like Mo, U, and Cd did not correlate, however, because they tend to stay in solution. The similar behavior of these metals can be used to predict the occurrence of unknown concentrations when only one metal is known. Moreover, Fe was found useful as a surrogate element since it is naturally abundant. Iron also varies within relatively narrow limits throughout the Bay. Its use for normalizing enrichment factors is demonstrated in a separate section.

A comparison of the mean metal content of the dissolved fraction and the corresponding particulate fraction per volume of suspended material [Table 9(c)] reveals several significant trends. The ratio of dissolved to total metal content provides an index to the mobility of the metal, and thus its availability to biota. For example, Mo and U are dominately in dissolved form in both surface and bottom water, whereas Co, Fe, Mn, Pb, Sc, and Th are dominately in the particulate form. Note that Zn displays much higher percentages in surface water than in bottom water. Therefore, samples of surface water alone are not indicative of the dissolved Zn content in bottom water. By contrast, Mn (both particulate and dissolved) is much higher in bottom water than in surface water in summer. This trend probably reflects mobilization and release of Mn from central Bay sediments during summer anoxia. The index provides an indication of which metals organisms are exposed to in summer. Since dissolved metals generally have a shorter residence time in the Bay than particulate metals, the index further predicts that metals like Mo and U will likely escape the Bay whereas Co, Cr, Fe, Mn, and Sc are most likely retained in the estuary. The fate of other metals probably varies with natural biochemical and sedimentological processes native to the Bay.

DISTRIBUTION AND CONCENTRATION OF METALS IN BOTTOM SEDIMENTS

During the Bay Program, surface sediments were analyzed for As, Cd, Co, Cr, Fe, Hg, Mn, Ni, Pb, and Zn by Helz et al. (1981) and Nichols et al. (1981). All of these metals are more concentrated in the fine fraction (< 63 um) of bottom sediments than in bulk samples and show that the Susquehanna River is a major source of most metals. Figure 9 illustrates the Cu distribution in bulk and in < 63 um surface sediments of the Bay. Copper in the fine fraction decreases seaward from the Susquehanna mouth, indicating a river source. Copper also decreases eastward across the Bay, suggesting that seaward transport carries contaminated sediment seaward along the western shore. This pattern is consistent with the observed salinity pattern and net circulation of the Bay. An alternate cause of the western shore enrichment is the input from Baltimore Harbor and western shore tributaries.

Zinc distribution in bulk and fine sediments is illustrated in Figure 10. Zinc values in the silt-clay fraction are highest in the Bay off of Baltimore Harbor and decrease both landward and seaward, suggesting that Baltimore Harbor is a source of Zn to the Bay. Two mechanisms may be responsible for metal transport from the Harbor in particulate form: the estuarine circulation and dredge spoil disposal. More than 4.6 million cubic meters of dredged material have been disposed in the Bay off the Harbor (Schubel and Williams 1976). However, from the metal distributions, it is not possible to identify the magnitude of either of these mechanisms. Tidal action may be partially responsible. However, we do not feel it is a dominate factor and believe the data suggest riverine sources. The bulk Zn distribution displays relatively high concentrations in the lower Bay off the Rappahannock mouth. The high clay content of these sediments is probably responsible for the elevated concentrations observed in bulk samples.

Chromium and Pb exhibit surface sediment distribution patterns similar to Zn with maximum concentrations occurring in the fine fraction off Baltimore Harbor. The distribution of the metals Mn, Fe, Co, and Ni mirror Cu distributions, with highest values found in the northern Bay and along the western shore. Metal to Fe ratios of bottom sediment decrease with distance seaward from the Susquehanna River, indicating the river is a major source of Mn, Ni, and Zn.

METALS IN INTERSTITIAL WATER

Until recently, the massive reservoir of materials contained in the bottom sediments of the Bay has largely been ignored as a potential source

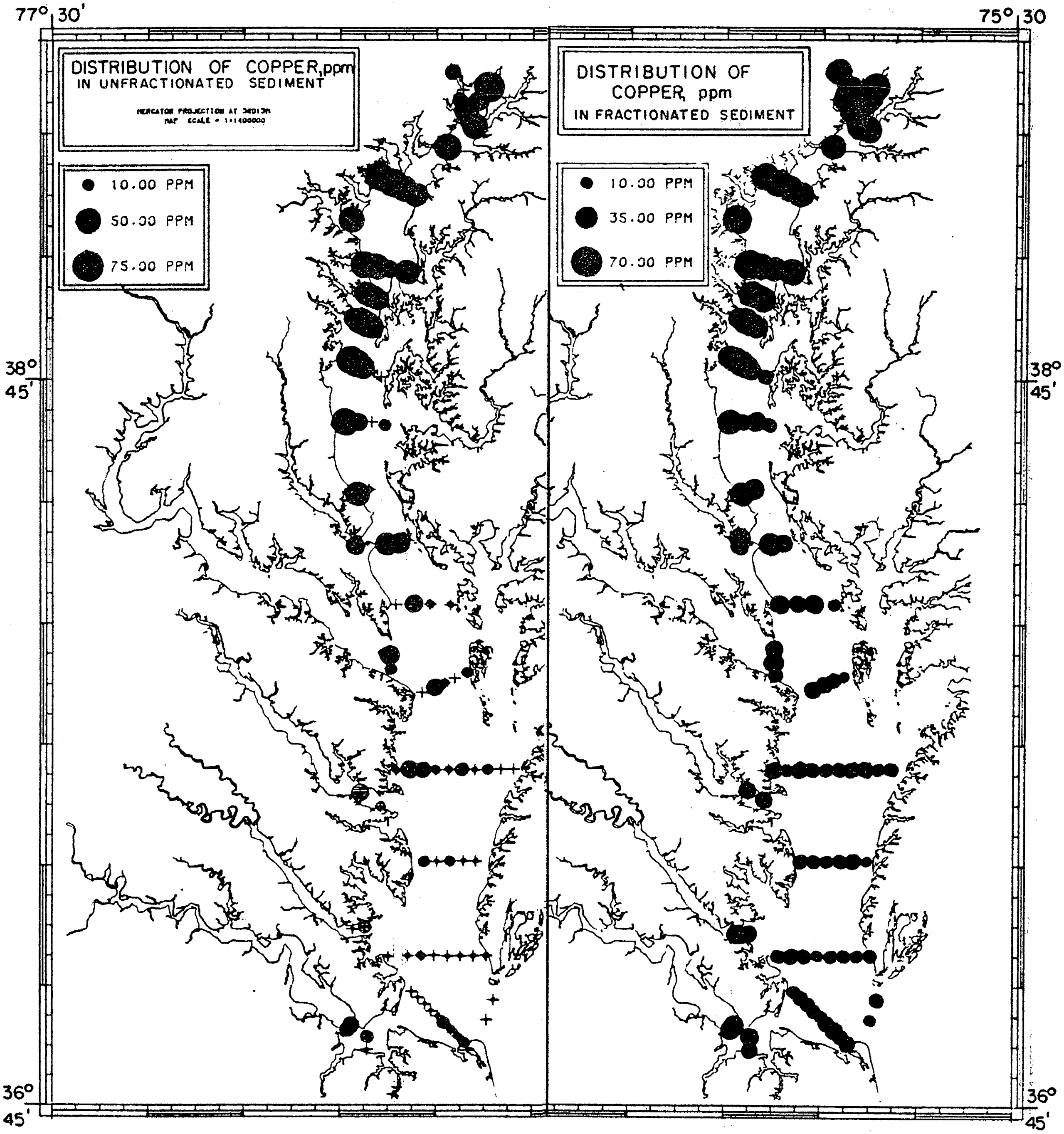

Figure 9. Distribution of Cu content in bottom sediments of (a) bulk bed sediment, unfractionated, and (b) the less than 63 u size fraction, fractionated. Data from Helz et al. (1981).

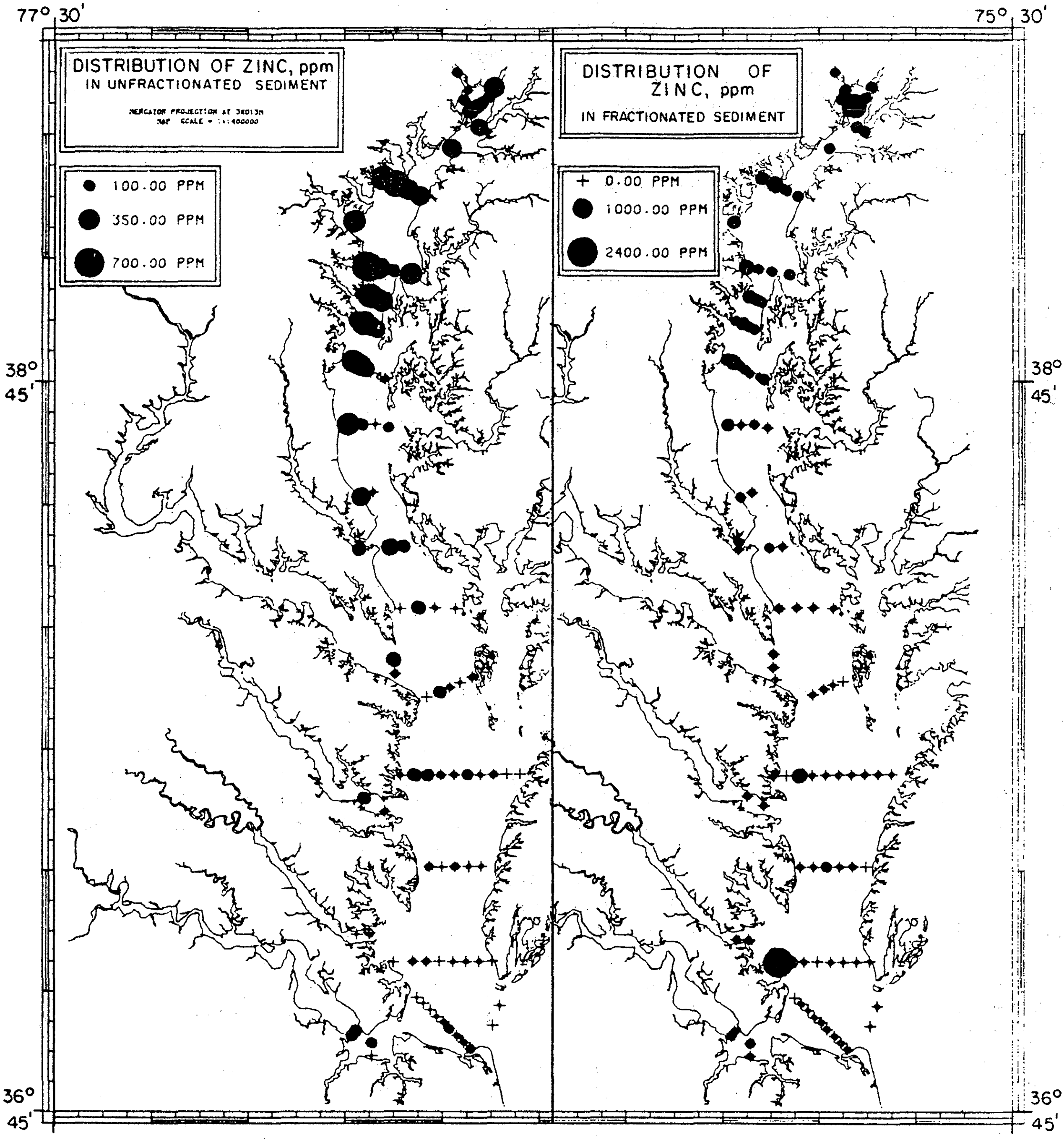

Figure 10. Distribution of Zn content in bottom sediments of (a) bulk sediment, and (b) the less than 63 u size fraction. Data from Helz et al. (1981).

of nutrients and trace elements. Previous investigations, Berner (1979) and Bricker and Troups (1975), show a substantial transfer of trace metals from the sediment to the water column. The principal vehicle for transporting this material from the sediment to the overlying water is the interstitial or pore water (water contained in the sediment). Many of the constituents of interstitial waters are derived from chemical reactions of water with the solid material of the sediment.

The constituents and parameters measured on 97 cores by Hill et al. (1981) and Tyree et al. (1981) are:

Na^+, K^+, NH_4^+, Ca^{++}, Mg^{++}, F^-, Cl^-, NO_3^-,

NO_2^-, $PO_4^=$, $SO_4^=$, $SO_3^=$, $HCO_3^=$, pH, $pS^=$, Eh,

Conductivity, Fe, Mn, and SiO_2.

A subset of these cores was analyzed for the trace metals Pb, Cd, Cu, and Zn. Figure 11 is a graphical presentation of some core data of a representative station.

The transport of dissolved constituents across the sediment-water interface proceeds in response to concentration differences. Constituents migrate from areas of high concentration to more dilute areas according to Fick's law (Lerman 1979). Generally, the concentration of nutrients (such as NH_4^+, $PO_4^=$, and HCO_3^-) and trace elements in the interstitial water exceeds the concentration in the overlying water column. Thus, the gradient predicts that these materials are transported from the sediment into the water column.

The chemical sedimentary environment controls the concentration of constituents in the interstitial water that, in turn, controls the transport of materials between the water column and sediment, and within the sediment. Three major chemical sedimentary environments have been identified for the main portion of the Bay: the northern Bay; the central Bay, including upper and lower parts; and the southern Bay, including two subsections (Figure 12). The chemical environments are classified according to a set of parameters, which influence and reflect the redox state of the sediment. These parameters are: major ionic composition of the interstitial water; organic carbon content of the sediment; reduced sulfur content of the sediment; degree of $SO_4^=$ reduction; Eh; and the concentrations of dissolved sulfide species, Fe, Mn, and NH_4^+. The three environments correspond to Berner's (1981) method of classification of sedimentary environments.

The northern Bay, as shown in Figure 12, is primarily characterized by: (1) ratios of the major ion concentrations that differ in comparison to ratios from marine-dominated environments, (2) high organic carbon content (five to six percent), (3) absence of dissolved sulfide species, (4) complete ($>$80 percent) reduction of available $SO_4^=$, and (5) the most positive Eh values in the Bay. The primary chracteristics of the central Bay environment are: (1) intermediate to high organic content (two to five percent), (2) high concentration of dissolved species, (3) variable degree of $SO_4^=$ reduction between cores, and (4) the most negative Eh in the Bay. The southern Bay characteristics are: (1) low organic carbon (zero to two percent), (2) essentially no $SO_4^=$ reduction ($\leq$20 percent),

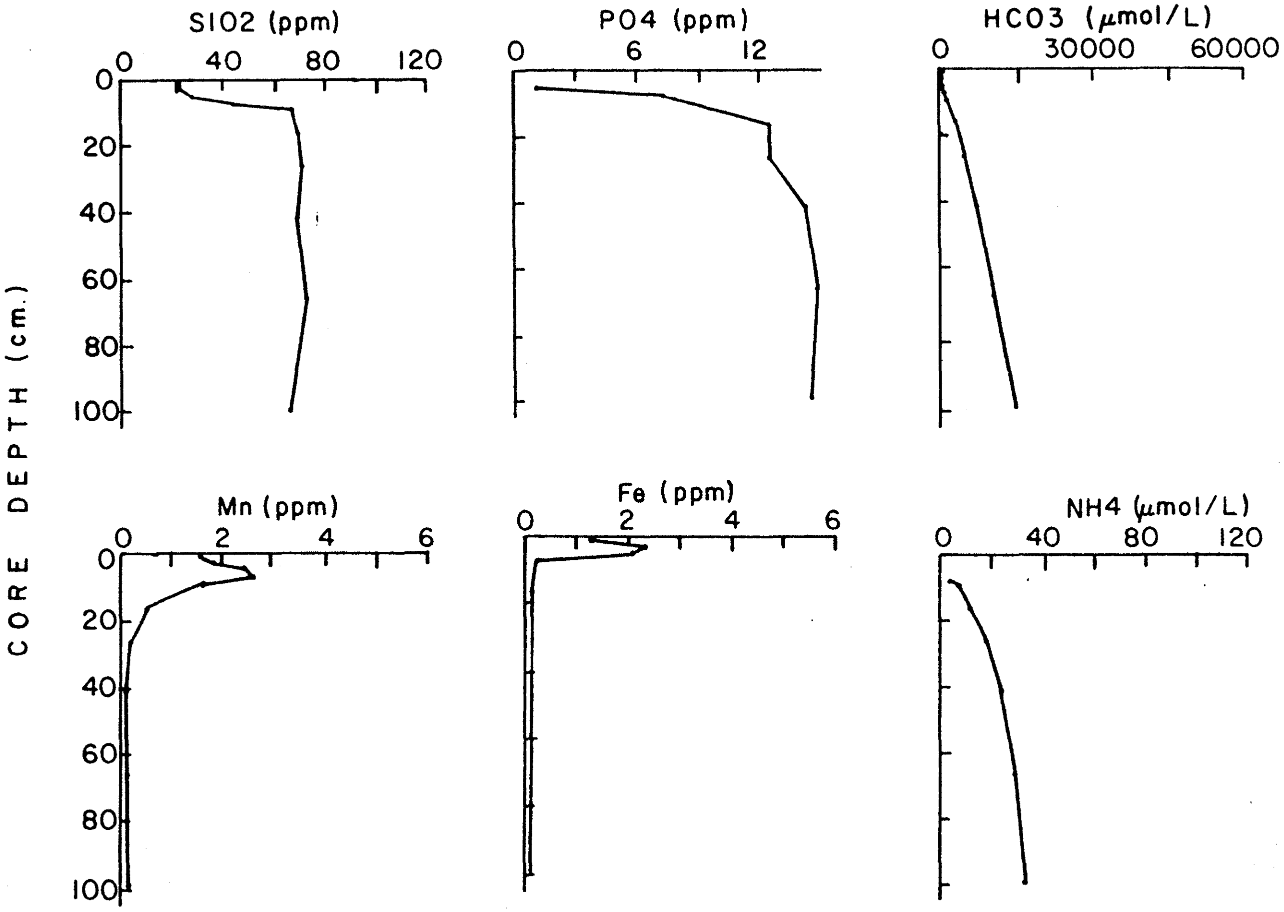

Figure 11. Vertical profiles of SiO_2, PO_4, HCD_3, Mn, Fe, and NH_4 in interstitial water composition for a station in central Chesapeake Bay, September-November, 1978. Data from Conkwight (1981) and Tyree et al. (1981).

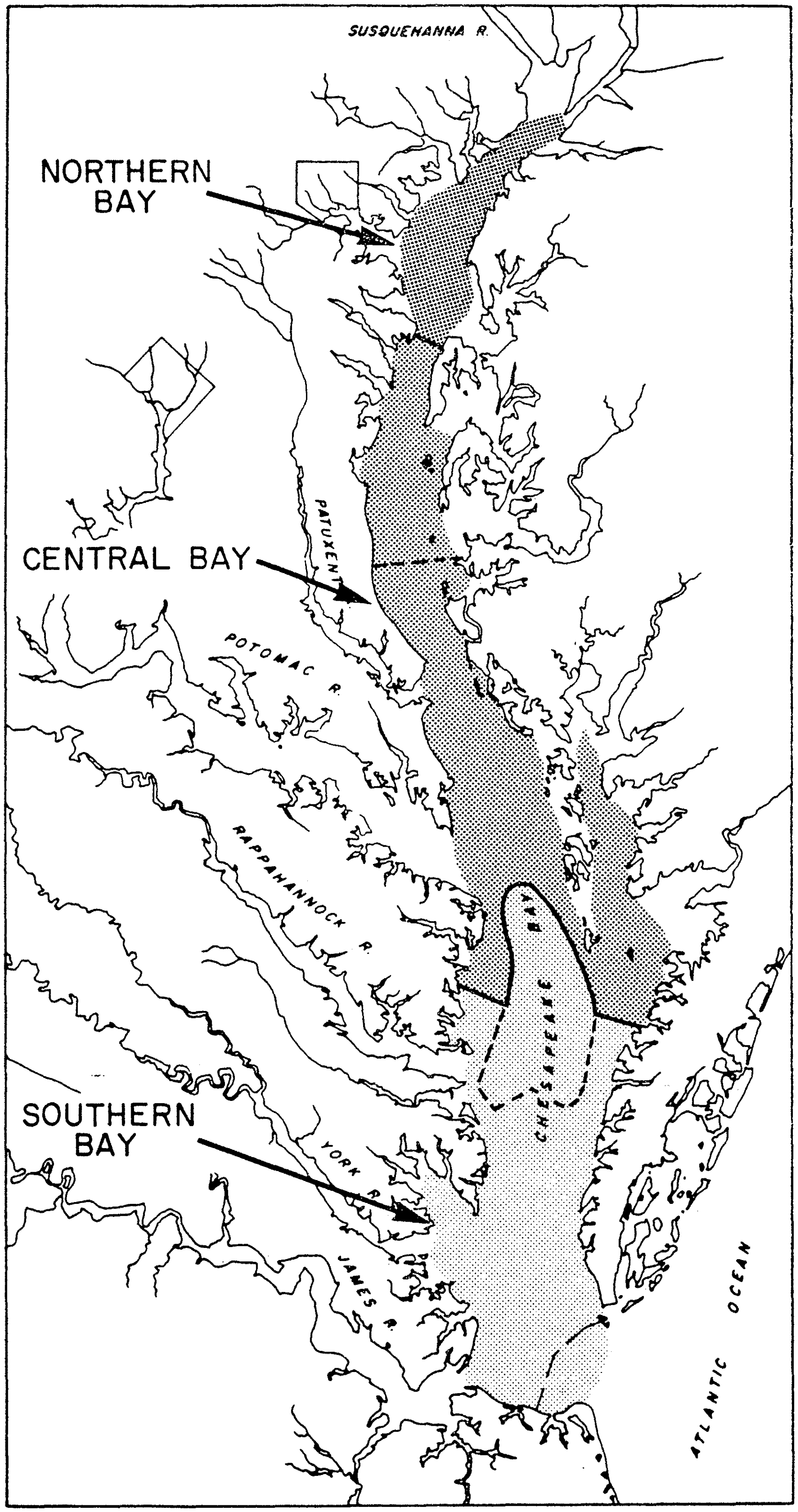

Figure 12. Distribution of chemical sedimentary environments in Chesapeake Bay, based on data of Hill and Conkwright (1981).

(3) very little detectable NH_4^+, and (4) and Eh more positive than the central Bay, but more negative than the northern Bay.

Estimates of the transport of material, with respect to the sediment-water interface, according to the three major chemical sedimentary environments, are presented in Table 10. The ranges include seasonal changes of temperature and salinity, which can markedly effect the chemical environment. The fluxes calculated from the concentration gradients generally indicate: (1) NH_4^+, HCO_3^-, and $PO_4^=$ are added to the overlying water column in the northern and central Bay; (2) Fe and Mn are transported to the overlying water column in the northern Bay, but stabilized in the sediments in the central and southern Bay; (3) sediments contribute sulfide (HS^-) to the overlying water of the central Bay, and (4) $PO_4^=$ is stabilized in the sediments of the southern Bay. The trace metal data indicate that the concentration of the metals in the interstitial water corresponds to the chemical sedimentary environments, but the concentration gradient profiles are too complicated for a simple Fick's law estimate.

TABLE 10 GENERAL ESTIMATED RANGES OF FLUXES DIVIDED ACCORDING TO CHEMICAL ENVIRONMENT, VALUES EXPRESSED AS u MOLS/M^2/DAY

	NH_4^+	Fe^{++}	Mn^{++}	HCO_3^-	$PO_4^=$	HS^-
Northern Bay	+ 50–+700	- 20–+70	-100–+60	+800–+3000	+ 30–+80	**
Central Bay	+200–+2000	-100– 0	- 60–+30	+100–+20,000	- 20–+70	+400–+30,000
Southern Bay	**	- 30–-10	-30–-10	*	-100–-20	*

** - Chemical species below detection limits in these areas
* - Core data did not fit the simplified model used to estimate the fluxes

Note: Positive flux values reflect transport into the overlying water column; conversely negative values reflect transport into the sediment.

SECTION 3

FINDINGS FROM STUDIES ON ORGANIC COMPOUNDS

The following chapter explains the results from CBP research on the distribution and concentration of organic compounds in Chesapeake Bay. Since polynuclear aromatic compounds (PNAs) constitute the largest proportion of toxic synthetic substances entering the Bay (and are also listed on EPA's Pollutant list), much of the CBP research focused on these compounds. Other organic compounds, including dieldrin, terpenoid, DDT, and other pesticides were detected. However, extensive, quantitative analyses were performed on PNAs. In this section, sources of PNAs to the Bay are discussed, followed by results of analyses on levels of organic compounds found in bottom sediments and oysters. The remainder of the chapter interprets these results and considers important factors affecting the distribution and abundance of organic compounds.

SOURCES

The major source of most of the organic compounds (PNAs) entering the Bay is the burning of fossil fuels, coal, oil, and wood. Sources from the Patapsco River also produce compounds made up of substituted benzenes. These compounds are also released in industrial processes such as coal liquefication and gasification (Bjoreth and Dennis 1979, Cooke and Dennis 1980). Simple substituted aromatic compounds are assembled at high temperatures (combustion gases) to produce PNA compounds, with different compounds dependent primarily on the combustion temperature and secondarily on the fuel source. As indicated by PNA analysis of old sediments deposited prior to human's use of fossil fuel, very few aromatic compounds were produced by organisms. Most PNA compounds produced by combustion differ from those in oil or in the complex polymeric network of coal in that combustion products are generally not substituted.

Specific sources of PNAs in the Bay region include vehicles burning gasoline and diesel oil, coal and oil fired power plants, coal and oil fired heating industrial plants, oil and wood home heating, and forest and refuse fires. PNA compounds can be transported from the locations of the sources to the Bay by air-borne particulates containing PNA (smoke and exhaust), airborne volatile PNAs, water-borne particulates (sediment) containing land runoff and river-borne PNAs, and compounds carried in solution by rivers and land runoff. Some small amounts of PNAs are produced in the Bay by the combustion of vessel fuels.

Within the Bay, large concentrations of PNAs were found at the mouths of rivers. Some small subestuaries, like the Elizabeth River and Baltimore Harbor, with very high industrial actvity and population density, can also produce high local PNA concentrations. PNA compounds are probably continuously increasing throughout the Bay, because these many sources repeatedly produce PNA that is stable over long periods in the Bay water and sediments. A final source of PNA to the Bay is long-range atmospheric transport by Northern Hemisphere air currents. Chesapeake Bay is receiving air-borne PNA in vapor and particulates introduced in other regions of the

United States or other Northern Hemisphere countries. Contributions to PNA concentrations in the Bay from such long-range sources are probably uniform from place to place, because the Bay and its watershed area (which together serve as a PNA collection basin) are small with respect to the areal extent of single air masses.

ORGANIC COMPOUNDS IN BOTTOM SEDIMENTS

Analyses of sediment samples collected for the Bay Program during the spring and fall of 1979 (Bieri et al. 1981) revealed that over 300 organic compounds were abundant enough to either be identified or given a surrogate name by assigning a relative retention time. Only a small percentage of these 300 is not toxic in certain amounts. In some samples, the complexity and abundance of compounds present were so great that many individual species at relatively low concentrations were undoubtedly not detected. It is, therefore, probable that thousands of compounds were present. An example is presented in Figure 13, which is an actual gas chromatogram showing individual peaks. These peaks represent at least one compound superimposed on a background of peaks from numerous compounds of lower concentrations. This is commonly called an unresolved complex mixture.

The distribution of organic compounds in bottom sediments (Figure 14) is presented as bar graphs representing summed concentrations on a logarithmic scale of chromatographically resolvable compounds eluting in the "aromatic" fraction. The figures show that the highest total concentrations are encountered in the northern portion of Chesapeake Bay. Furthermore, samples from Stations 2, 4, 6, 7, 10, 11, and 12 in the lower Bay are almost devoid of these compounds. However, with the exception of the fall 1979 sample from Station 9, samples from river mouth stations, numbers 1, 3, 5, and 8, contained substantial sums--between 100 and 1000 parts per billion (Figure 14).

To demonstrate that the northern Bay and the river mouths have unnaturally high levels of organic compounds, it is necessary to account for variations in sediment character. Fine-grained sediments usually contain higher organic concentrations than coarse sediments, and this can explain some of the anomalous distributions. In general, sediment samples from the northern Bay and the major river mouths contained a higher fraction of silt and clay than elsewhere. When the samples are normalized for silt and clay content the distributions (Figure 15) change in the concentration sums in the northern Bay with the exception of Station 27, Fall 1979. In the lower Bay, only Stations 1, 3, 9, 11 and 12 have increased. Without further analyses of samples collected within the subestuaries, it is impossible to determine whether high concentrations in sediments collected near the major river mouths were due to sediment grain size or unnaturally high inputs from upstream. Normalizing the northern Bay data did not substantially change the distribution pattern. With the exception of the fall Station 19 sample, there is a trend of increasing concentrations from below the Potomac River mouth toward the Baltimore Harbor mouth. North of Baltimore, the concentration sums decrease and then increase to another maximum toward the Susquehanna mouth. Inside the Susquehanna mouth (Station 27) samples showed considerable variation between spring and fall, differences that may arise from variations of

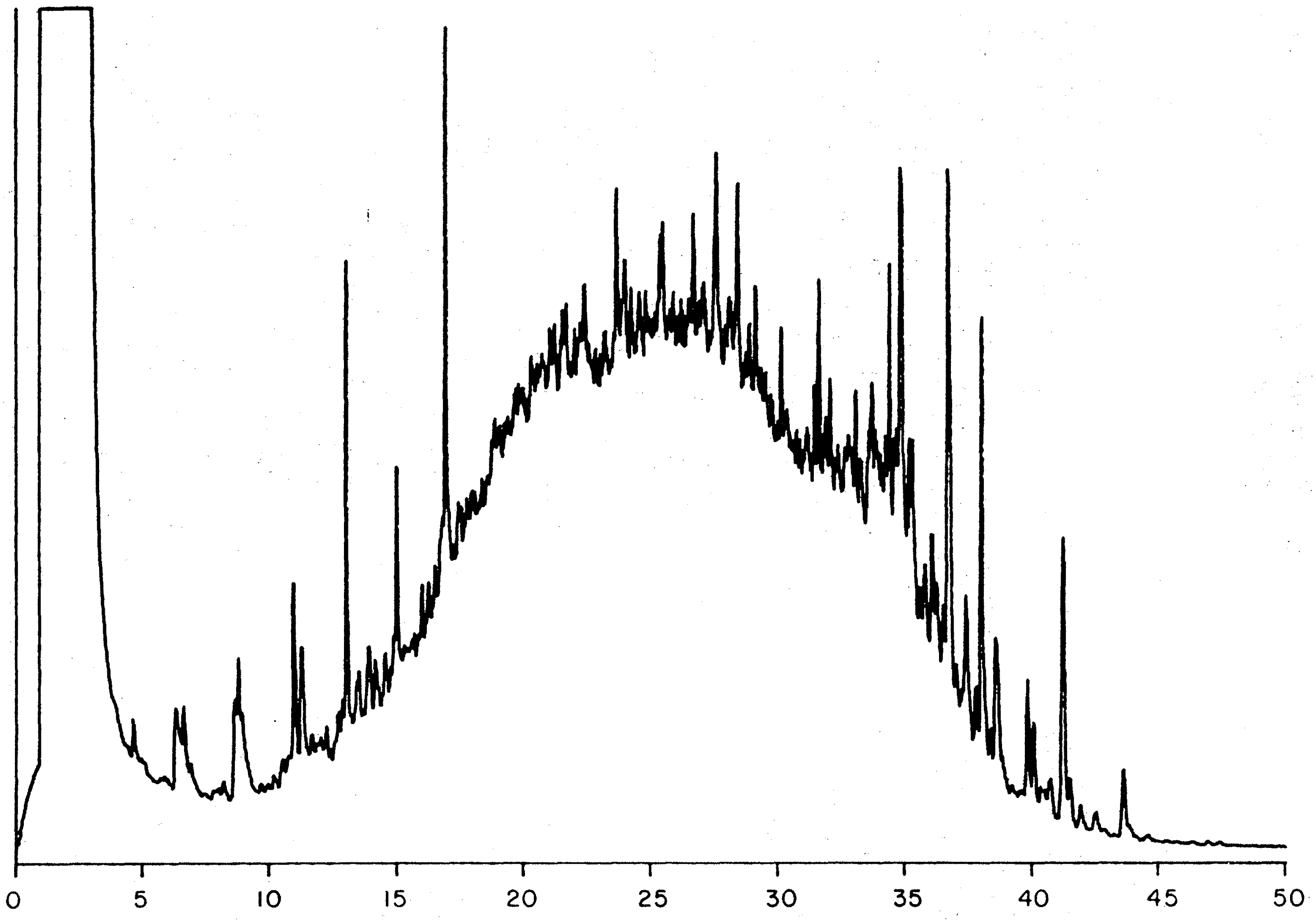

Figure 13. Typical gas chromatogram of a sediment sample. From Bieri et al. (1981).

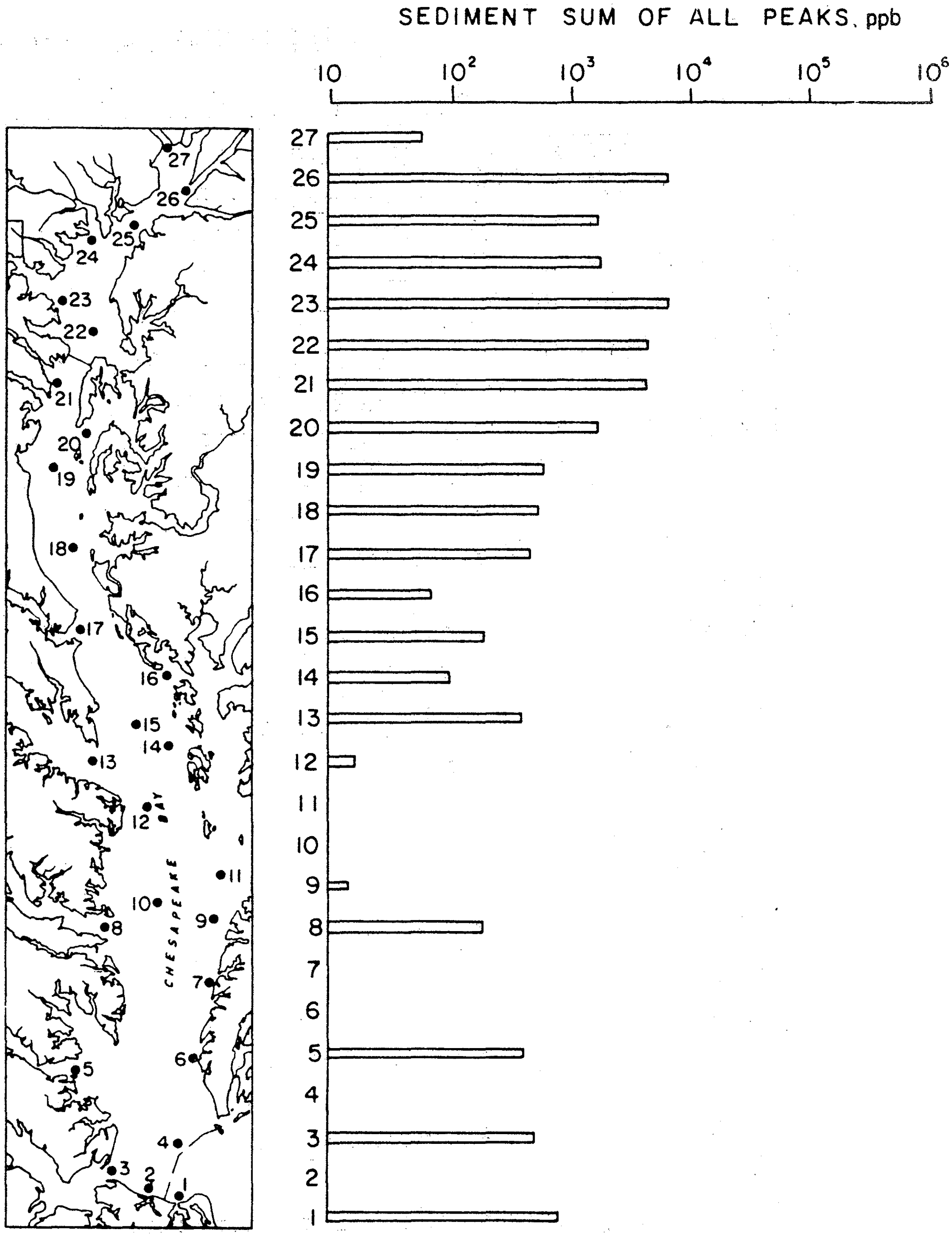

Figure 14. Chart of station locations and bar graph representing concentration sums of all resolvable peaks for organic compounds in sediments, spring samples 1979. Data from Bieri et al. (1981).

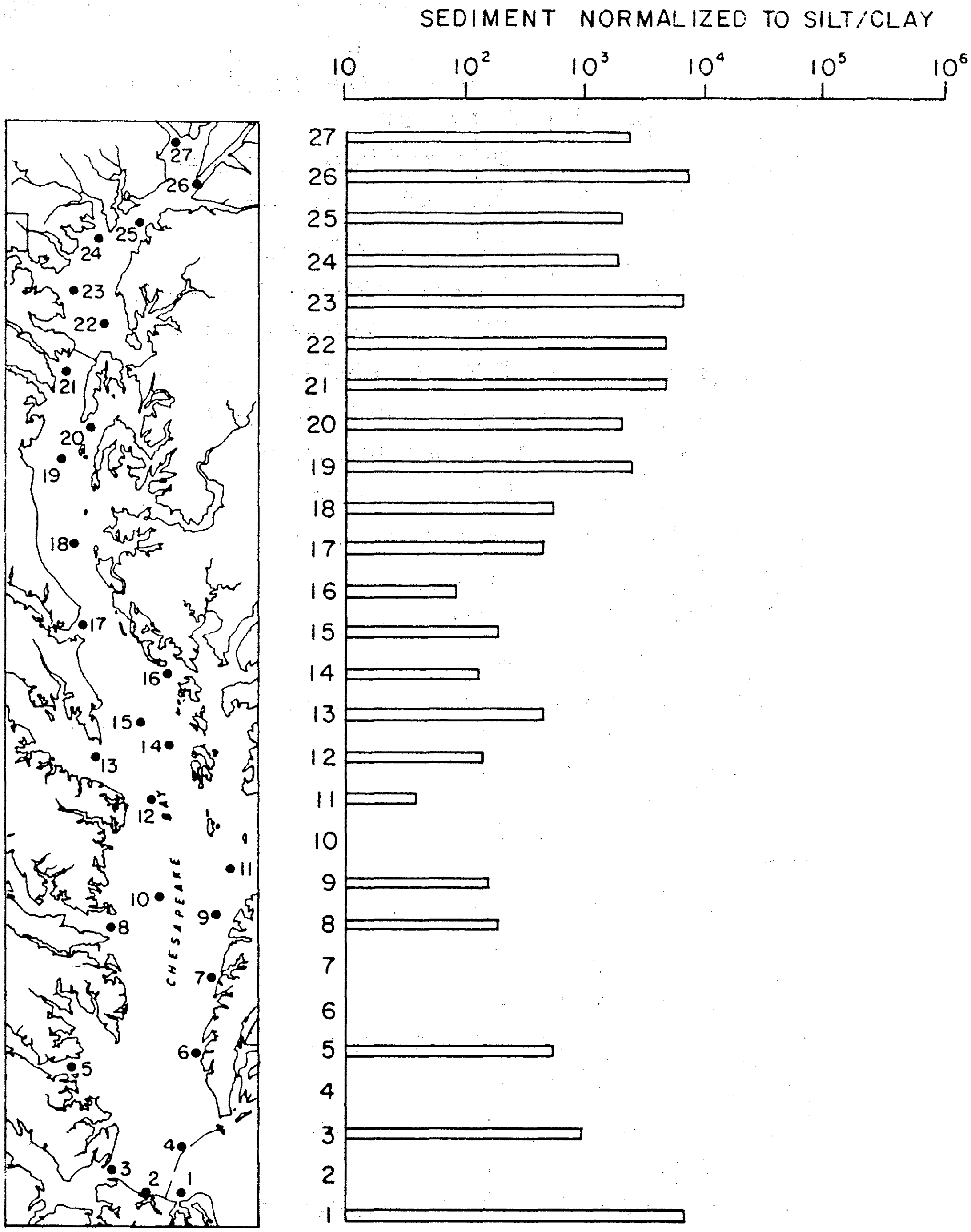

Figure 15. Chart of station locations and bar graph representing concentration sums (ppb) of all resolvable peaks for organic compounds after normalizing for silt and clay content. Spring samples, 1979. Data from Bieri et al. (1981).

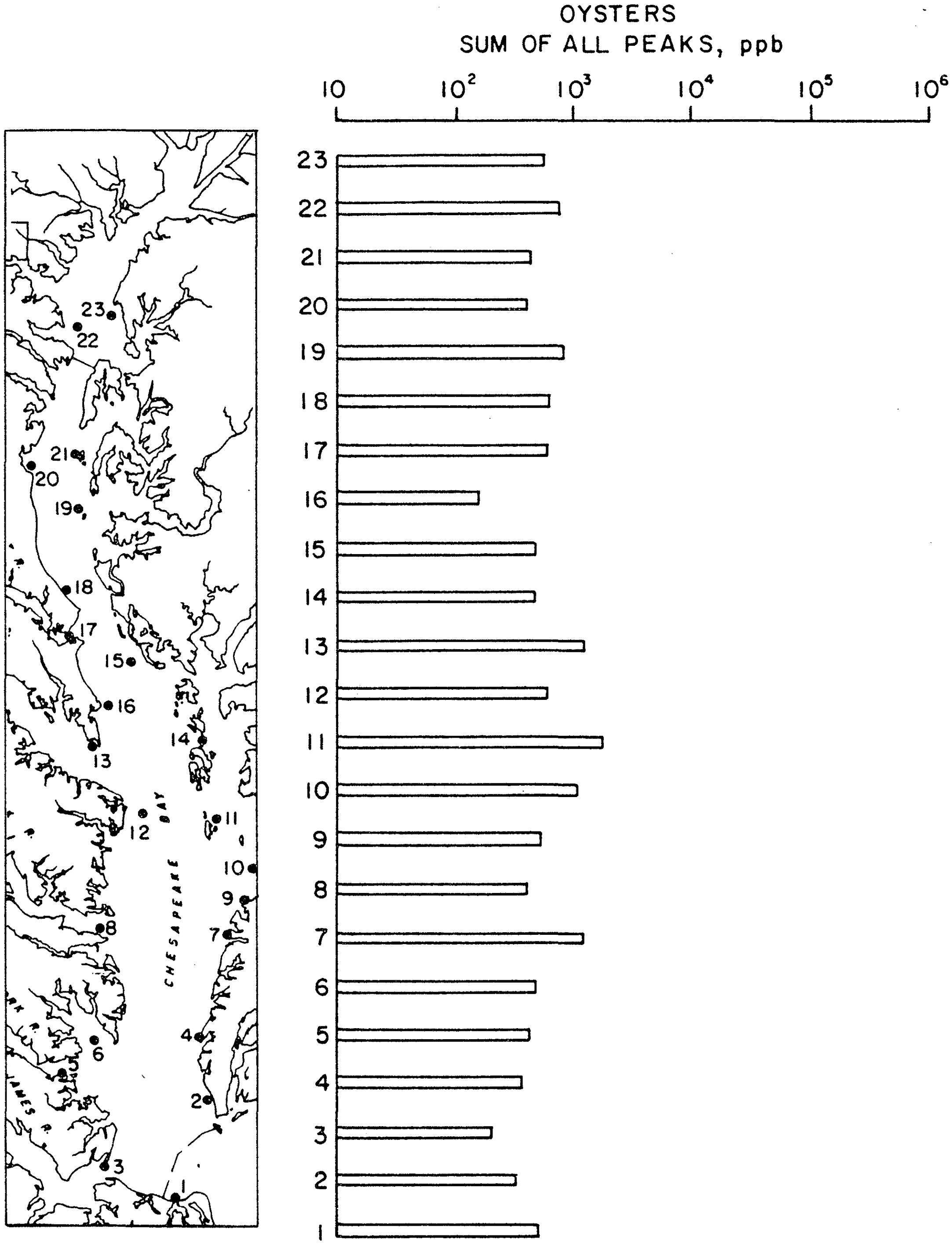

Figure 16. Chart of station locations and bar graphs representing concentration sums of all resolvable peaks for organic compounds in oysters, spring samples, 1979 (Bieri et al. 1981).

river flow that scour sediments during high spring flow and deposit sediment during low fall flow.

The trends for PNAs follow the trends for sums of all concentrations: (1) the concentrations are higher in samples from the northern Bay than in the southern Bay; (2) in the southern Bay, highest concentrations are found near river mouths; (3) concentrations tend to increase up the Bay from the Potomac River mouth toward Baltimore Harbor; and (4) the Susquehanna River mouth sediments show considerable variability, but can reach extreme concentrations. Data displayed for several individual members of the PNA family show even more clearly that a concentration maximum occurs in the northern Bay in the vicinity of Baltimore Harbor, suggesting that this area is an important source of PNA families (Bieri et al. 1981)

ORGANIC COMPOUNDS IN OYSTERS

In addition to sediments, oysters were also collected during the Bay Program and their tissue was analyzed for organic compounds. The gas chromatograms of oyster tissue extracts were much less complex than those of sediments, with the concentration of individual compounds substantially lower. The graphs for oysters (Figure 16) show no longitudinal trends like those in sediments (Bieri et al. 1981). In addition, methyl esters of fatty acids were present in most samples, as were some ketones. We hypothesize that many of these compounds have a biogenic or natural origin. Since they are often present in higher concentrations than identified pollutants, the summed concentrations may not represent a realistic pollutant content in oysters. Therefore, we examined the number of compounds detected and their distributions rather than their sums. Altogether, we identified 127 organic compounds. Oysters collected at the mouth of the James River contained 94 of these compounds. Oysters collected from Occohonnock Creek (Station 7) contained 27, and those from near Baltimore Harbor (Station 22) had 24. The oysters that contained the next highest numbers of compounds were from Holland Point (Station 20) with 23 compounds, and Onancock Inlet (Station 10) with 19 compounds. Although this analysis suggests that these areas have the highest contamination of organic compounds in oysters, there is no apparent reason why oysters from the Occohonnock Creek, Holland Point, and Onancock Inlet should compare to the James River and Baltimore Harbor, where sediment concentration of organic compounds is greatest. It is very likely that salinity or some other physical or chemical factor is influencing the levels of organic compounds in oysters.

If only the most concentrated compounds are considered, a similar pattern emerges. There were 42 compounds detected whose individual concentrations exceeded 50 ppb. The samples from the James River mouth (Station 3) contained 29 percent of these. The next highest were from Baltimore Harbor (Station 22) with 24 percent. These were followed by Station 10 with 21 percent, Station 20 with 17 percent, and Station 7 with 14 percent. In summary, the following sequence emerges from abundance of compounds: James River > Occohonnock Creek > near Baltimore Harbor > Holland Point > Onancock Inlet. For individual compound concentrations greater than 50 ppb: James River > near Baltimore Harbor > Onancock Inlet > Holland Point > Occohonnock Creek. In both cases the same five stations emerge as being the highest.

Although the presence of oysters in these locations indicates that numbers and levels of organic compounds in their tissue are probably not lethal, elevated concentrations can reach biota higher in the food web. Oysters and other invertebrates can store organic compounds in their tissue, passing on that amount to consumers. These organisms, in turn, may accumulate harmful levels.

Comparison of the compounds detected in the oysters with those found in nearby sediments showed little correlation (Bieri et al. 1981), indicating that oysters are not so useful as sediments to monitor the Bay for organic compounds. In sediment samples, the most abundant compounds were PNAs. With the exception of dibenzo-thiophene, fluoranthene, pyrene, and benzo(e)pyrene, none were detected in oysters. This could be due to the compounds not being biologically available to the oysters; or the oysters may depurate them very rapidly, or metabolize them to other compounds that were not identified.

ORGANIC COMPOUNDS IN BALTIMORE HARBOR

The CBP's sampling effort in Baltimore Harbor was identical to the work previously discussed for the main Bay. In addition, the CBP funded the Monsanto Research Corporation (MRC) to sample the major industrial and POTW dischargers in Baltimore Harbor. Together these two projects provided a mechanism by which the compounds found in Harbor sediments could be traced to possible sources in industrial and POTW effluents. Concentrations of the organic compounds in the Harbor sediments were generally much higher than those samples from the Bay. Additionally, many of the compounds found in the sediments were also detected in the point source dischargers.

Forty-one bottom sediments were collected from the Patapsco River and Baltimore Harbor during spring 1981 (Bieri et al. 1981). The PNAs dominate the aromatic compounds in the river as in samples from Chesapake Bay proper. In some cases, the concentrations were ten to twenty times higher than the highest found in the Bay. The concentrations of the PNAs within the river also vary drastically with location. This suggests that there are either point sources of PNAs or non-uniform water circulation and sediment type that cause the organic compounds to accumulate more in specific areas. It is likely that a combination of these two factors is responsible for the distributions.

Figure 17 represents the concentrations of one of the PNAs, [benzo(a)pyrene], normalized to silt and clay content, in the channel sediments from the Patapsco River. It is obvious that there are several areas where relatively high levels exist. Point sources may be partially responsible for the anomalously high concentrations that at one location reach 5.5 ppm. The benzo(a)pyrene concentration in Bay sediments is depicted by the cylinder farthest to the right. The concentration here is about equal to that of the station next closest within the Patapsco, 260 ppb versus 290 ppb, respectively. This suggests, but does not prove, that the peak of PNAs found in the Bay near the Patapsco River mouth could be the result of transport from the Patapsco.

One sample from the Patpasco River gave a very anomalous gas chromatographic fingerprint that was dominated by an abundance of compounds with relatively low rentention times and high concentrations. The

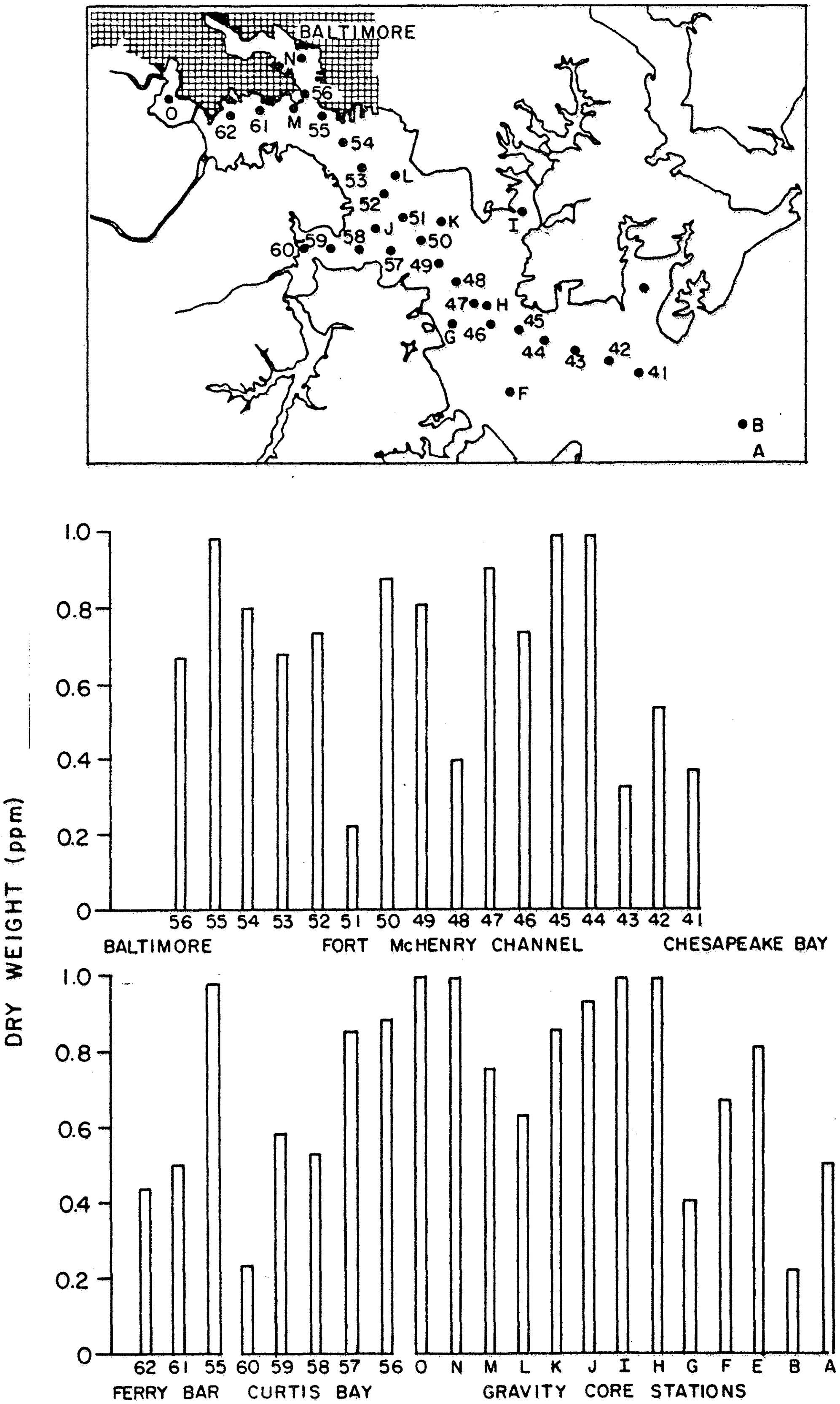

Figure 17. Distribution of PNA, benzo(a)pyrene in channel sediments from Baltimore Harbor and the Patapsco River. Relative concentration relates to height of column at each location.

compounds were not PNAs. Mass spectrometric analysis and comparison with EPA-NIH Mass Spectral Data Base showed that they were composed of substituted benzenes. The mass spectrometry data files were searched to see if these compounds were present at any other locations but had been hidden by more concentrated PNAs. The search showed that several of the substituted benzenes were either definitely present, probably present, or not present. The substituted benzene, 6-phenyldodecane, has a widespread distribution within the Patapsco River, and data indicate that sediments in the adjacent Bay also probably contain it. The sample with the highest concentration was collected landward from the river mouth.

Effluent sampling data generated by Monsanto Research Corporation (1981) showed that an effluent collected very near the sediment station contained substituted benzenes and, specifically, 6-phenylododecane. Using this compound as a tracer, we must conclude that organic compounds can enter the Patapsco River from point sources, travel throughout the river, and probably into the Bay. The fact that 6-phenyldodecane was only "probably present" in the two eastern most samples prevents stating that this is definitely the case, but it is difficult to conceive of a mechanism that would totally stop the eastward migration of the compound at the mouth of the River. It is not surprising that these two stations yield data that are less definitive than the others, because they are in the Bay where more mixing and dispersion occurs, and they are farthest from the source.

The methodology developed through the Bay Program for analyzing organic compounds within sediment of Chesapeake Bay has tremendous potential as an analytical tool for tracking known and unknown organic compounds in the system. The technique essentially generates a chromatographic "fingerprint" of the peaks found in the sample. These peaks are "tagged" by co-injecting relative retention markers and labeling each peak with a relative retention number. This becomes important when an unknown peak is found in a point source discharge and also in nearby sediment or resident fish tissue. This information allows one to "flag" potential problem compounds that may be building up or bioaccumulating in the Bay system. The technique was used in Phase II of the Monsanto Research Corporation Source Assessment Effluent Analysis and IMS sediment and oyster tissue analyses. A wealth of data on organic compounds is now available in the CBP data banks, and can be used for years, even decades to come.

In summary, the basis for our argument, stating that some of the organic compounds in the northern Bay sediments come from the Patapsco River, is that (1) PNA concentrations along the Bay rise near the Patapsco River mouth, (2) concentrations are much higher in the Patapsco River than in the Bay, and (3) the distribution of 6-phenylododecane is wide spread. Additional identification of compounds found in Harbor and Bay sediments and detected in the point source effluents has been done, but will not be discussed further in this paper.

CONCLUSIONS

Results from studies on organic compounds show that Chesapeake Bay contains many polynuclear aromatic hydrocarbons with lesser amounts in Bay oysters (Bieri et al. 1981). Because PNA compounds are fairly stable, they are transported by current flow and sediment motion to other locations in the Bay. In general, PNA compounds associate with sediment particles, partitioning in such a way that concentrations on sediment particles are much higher than in solution.

The influence of a local PNA source on PNA concentrations in the Bay will depend on the proximity of the source to the Bay, the magnitude of the source, the prevailing wind and water runoff patterns, and the characteristics of Bay sediments and current in the local region.

From this information, it can be expected that PNA concentrations in the Bay should be highest in areas of sedimentation near industrial regions, high population density areas, and power plant sites. Gradually, over a period of years, diffusion, advection, and sediment transport will spread PNA compounds over wider areas of the Bay. Although PNA transport from potential sources to sinks in the Bay can be described, quantitative measures of concentrations and transport rates are scant and inadequate.

The question which must be answered is: are the concentrations primarily the result of human activity or do they occur naturally from sources such as natural oil seeps or forest fires? The distribution and abundance of the PNAs within the Bay and the Patapsco River indicate that human activity is mainly responsible. The established origin of most unsubstituted PNAs (perylene is an exception) in high temperature reactions (Badger 1962, Schmelz and Hoffman 1976, Youngblood and Blumer 1975, Hase and Hites 1976) leaves little doubt about this fact. Since such pyrosynthesized PNAs can travel considerable distances (Lunde and Bjorseth 1977, Lunde et al. 1976), their occurrence is widespread. This may explain the presence of such PNAs in the relatively pristine areas of the Ware and Rhode Rivers, where chrysene concentrations range from 26 to 110 ppb, and benzo(a)pyrene from seven to 100 ppb. The majority of these PNAs, however, likely settle close to the source and, from there, reach the Bay by runoff and river transport.

With the increasing combustion of fossil and other carbonaceous fuels, it is likely that the PNA levels in the Bay will increase. Unfortunately, the toxicity data required to assess the resulting impact on the Bay's biota are inadequate. We do not know the toxicities of the individual components, much less the combinations, and we do not know if they are available to the biota. But the fact that many of them are carcinogenic, mutagenic, and teratogenic to mammals is enough cause for concern.

SECTION 4

PATTERNS OF TOXIC METAL ENRICHMENT

A limited, but important aspect of CBP research on metals in the Bay includes several studies on factors affecting their distribution and concentration. The dynamic nature of the Bay largely influences the behavior of metals and, consequently, their threat to the estuary. This section describes studies conducted on some of the behavioral aspects of metal inputs. It includes sections on processes affecting metal distribution; enrichment of metals above natural levels; historical trends in metal enrichment; and the important relationship between metals and sediment.

INTERPRETATION OF PROCESSES AFFECTING METAL DISTRIBUTIONS

Chemical substances like trace metals are continuously added to estuaries by inflowing tributary rivers, shoreline erosion, the coastal marine environment, the atmosphere, and the biosphere. Much of this material, dissolved and particulate, consists of the natural products of weathering, erosion processes, and of biological activity. In addition, anthropogenic products and wastes enter the estuary either directly in effluent discharges or by nonpoint source runoff. A large proportion of both the natural and anthropogenic material is intimately associated with sediments, particularly those of fine particle size and large surface area.

Suspended material is not only a reservoir for metals, but a vehicle that carries metals from their source to their depositional sink. It is an exchange medium for scavenging and removal of toxic metals from the water column. The metal distributions per liter of water show that the zone of the turbidity maximum is the most enriched (elevated above natural levels) part of the suspended material reservoir (Nichols et al. 1981). Additionally, time-series observations show that much material is resuspended from the bed, and that river-borne material is most likely trapped in the convergence of seaward-flowing river water and landward-flowing estuarine water. Enrichment is enhanced by small particle size (5-11u) of the material and by the relatively long residence time of particles in this zone.

In the central and lower Bay, metals borne on suspended material can be transported along two pathways, a hydrodynamic route, and a bioecologic route. The hydrodynamic route is revealed by dispersion patterns of metals in bottom sediments (Helz et al. 1981), whereby seaward transport from potential sources is indicated along the west side of the Bay. This route is in accord with the path of estuarine flow and the salinity regime. Landward transport through the lower Bay is indicated from metal distributions of Cr (Helz et al. 1981) that extend landward from the Bay mouth along the eastern side.

The relatively enriched metal content of central Bay surface water suggests that metals like Cd, Cu, Ni, and Pb follow a bioecological path. Because the enriched zone is generally an area of high suspended organic loads with more than 50 percent combustible organic material, it seems likely that the metals are assimilated from solution by phytoplankton or from suspension by zooplankton. Once in the food chain the metals can be further enriched (or bio-magnified) in fish or filter-feeding shellfish.

METAL ENRICHMENT

Both nonpoint and point sources contribute metals and many organic compounds to the Bay and tributaries from anthropogenic sources (Huggett et al. 1974b, Helz 1976, Brush 1974). These levels are superimposed on a background of natural concentrations. To assess the impact of human activity and control amounts reaching the Bay, it is critical to distinguish natural from anthropogenic levels.

Some organic compounds occur rarely, or not at all in nature, and their presence and concentration in sediments is direct evidence of anthropogenic input. The metals, however, occur both naturally and anthropogenically. For a given concentration of metal, there is no direct way to determine the portion that is natural and that which is anthropogenic. One method is to derive a ratio of the metal in question to a baseline metal also contained in the sample. The baseline metal should have no known anthropogenic source and should be naturally abundant so that no known pollution sources could significantly affect its concentration. The accuracy of this method can be verified by statistical tests. The precision would require comparison to known standards, which for this particular measurement, do not exist. Therefore, we cannot verify the precision and have not, at this time, determined the accuracy of this method.

Two metals, Al and Fe, were chosen to derive the ratios for determining anthropogenic levels of metals. Scandium was used by Kingston et al. (1982) in suspended sediment samples, because it is believed to have no anthropogenic sources. Aluminum and Fe were used in bottom sediments, and Fe was used in fluid mud samples. Concentrations of metals in these samples were normalized using Sc, Fe, or Al in ratios with concentrations of the metals in average crustal or shale material. For example, the ratio of Fe in average shale to Fe in Bay sediment and also to the concentration of metal in crustal material, yields an expected value for Bay sediment. The complete relation is:

$$EF = \frac{(X/Fe)\ \text{sediment sample}}{(X/Fe)\ \text{crust or shale}}$$

Where X/Fe is the ratio of the concentration of metal X to Fe in the sediment sample and in the crust.

The advantage of this geochemical baseline level is that it provides a standard for comparing data throughout the Bay. It assumes that the Chesapeake drainage basin is representative of average crust, and that a uniform crustal average exists throughout the region. Consequently, it does not account for local metal variations. Because the method is chemical, it is independent of sediment physical properties like particle size; it is affected, however, by compositional changes such as varying organic content within sediment.

Analyses show that enrichment factors in bed sediment for Cd, Co, Mn, Pb, and Zn are largely greater than two, and occasionally reach seven in the Baltimore-Susquehanna River area (Figure 18). For As, Cr, Cu, Hg, Ni,

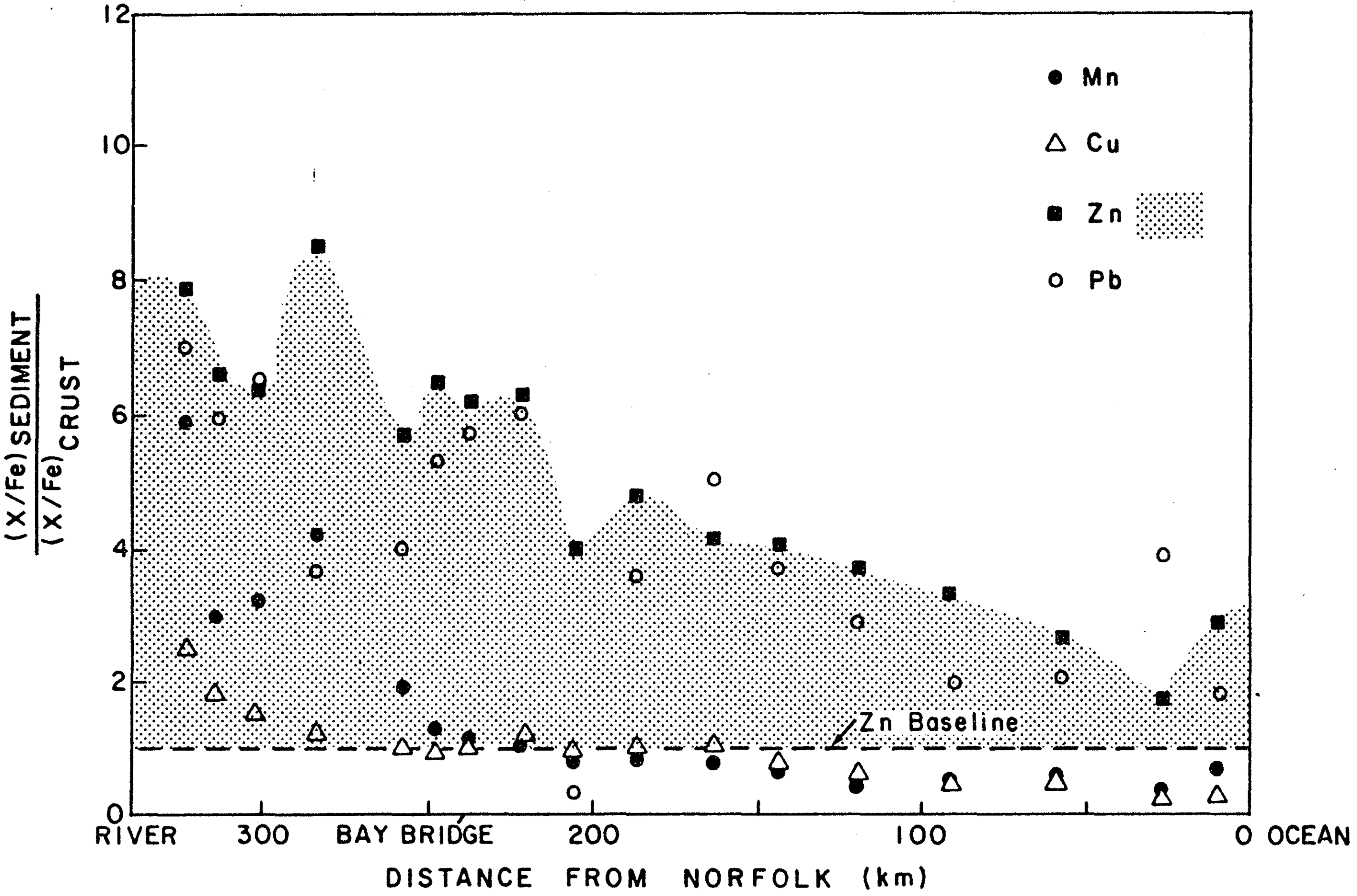

Figure 18. Longitudinal distribution of enrichment factors for Cu, Mn, Pb, and Zn in bed sediments along the length of Chesapeake Bay. Zn enrichment zones shaded. From Helz et al. 1981.

and Sn, factors are largely less than two or close to baseline factors throughout the Bay proper. Seaward of the Bay Bridge (Annapolis) factors generally diminish, but Cd, Pb, and Zn are greater than two. The longitudinal distribution of values does not display a maximum in the Bay near Baltimore, an expected increase if metals were emanating from Baltimore. Instead, the values mainly decrease from the Susquehanna River mouth, suggesting a river source (Helz et al. 1981). If the Susquehanna watershed is not naturally enriched compared to average crust, then the enrichment is affected by direct contamination from industrial and municipal sources or from acid mine drainage.

Bed sediments within the Patapsco River, Baltimore Harbor, are markedly enriched in Co, Cr and Zn (Sinex et al. 1981). Longitudinal distributions of enrichment factors, show that Cr increases with distance landward, and Zn is enriched throughout the Harbor. The Elizabeth River, Hampton Roads, is notably enriched in Zn with Zn/Al ratios of six to 25 (Sinex et al. 1981).

Enrichment factors for Cd, Cu, Pb, and Zn in surface suspended material of the central Bay are much greater than in bed sediments of the northern Bay. Metal/Fe ratios range from 10-118 for Cd, 12-27 for Cu, 37-51 for Pb, and 16-74 for Zn. The high enrichment factors in the central Bay are associated with high percentages of organic matter, probably produced by plankton metabolism. Additionally, the metal content of central Bay suspended material exceeds the content of oceanic phytoplankton more than nine times for Cd and Zn, and more than 19 times for Cu, Ni, and Pb.

Historic Metal Input Recorded in Sediments

Some sediments in the Bay reveal trends in metal enrichment. In sediments deposited in anoxic waters, no benthic macrofauna are present. Therefore, the sediments remain relatively undisturbed and may record the history and rate of change of metal influx. When a core of such sediments is analyzed for trace metals and dated by ^{210}Pb chronology, the vertical changes reveal variations in metal input. This approach assumes no diagenetic migration of metals through the length of the core. In oxic environments, however, burrowing activities of benthic organisms can disturb the record of sedimentary sequences, create an "artificial" ^{210}Pb distribution, and influence vertical trace metal distributions.

The vertical distribution of ^{210}Pb and metal concentrations (Helz et al. 1981) and the degree of bioturbation have been carefully examined for selected sediments of the Bay. Cores 4, 18, and 60 (Figure 19) exhibit exponential ^{210}Pb profiles, low ^{210}Pb depth-integrated concentrations, and low or moderate bioturbation. They also show no metal peaks and display a relatively uniform rock structure. In addition, core 4 has ^{137}Cs data that verify the ^{210}Pb sedimentation rate. Metal/aluminum ratios for the three cores, and ^{210}Pb chronology are presented in Figure 19. All three cores show Zn enrichment in the Zn/Al ratios near the core surface, with maximum enrichment occurring at about 1940 in core 40 and about 1960 in cores 18 and 60. The first appearance of excess concentrations is also temporally displaced down the Bay from 1890 in core 4, to 1920 in cores 18 and 60. If the source of this excess Zn is fluvial (or anthropogenic) and up-Bay, then it takes about 20 years for the metals to be transported 80 kilometers between core 4 and core 18, a nominal rate

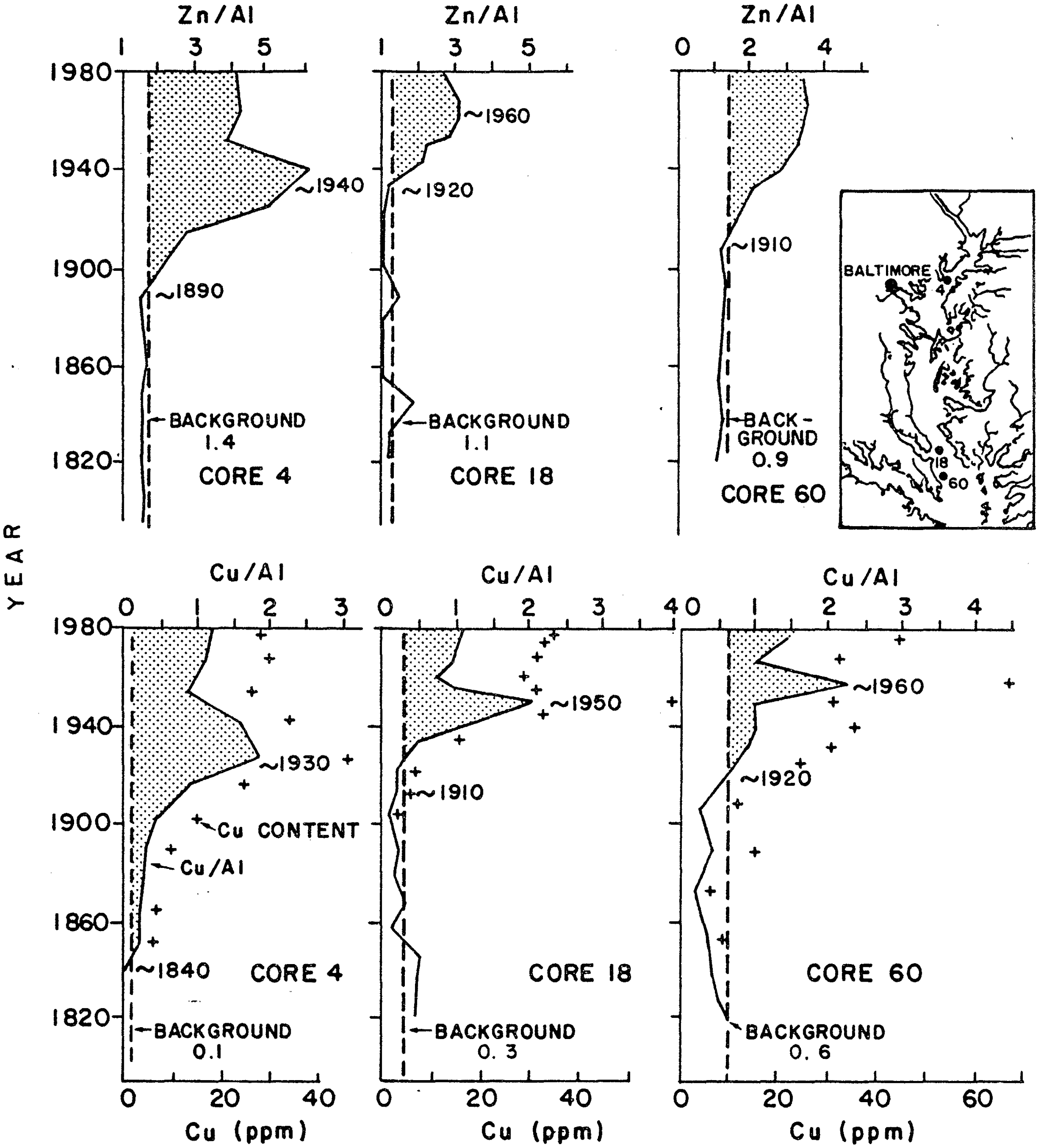

Figure 19. Metal/aluminum ratios, Zn/Al and Cu/Al, for three cores from northern and central Chesapeake Bay, cores 4, 18, and 60. Data from Helz et al. 1981. Dates in ^{210}Pb years; departure of metal/aluminum and metal/iron ratios from background in each core, shaded.

of four kilometers per year.

When interpreting concentration profiles from sediment core samples, we must be sure that the vertical concentration gradients are not a result of diagenetic processes that may alter the chemical environment within these sediments. Interstitial water data of Hill and Conkwright (1981) on oxidation-reduction (redox) potential and pH values were examined to provide an indication of the magnitude of the various chemical diagenetic processes in the sediment core samples. These data reveal no correlations between redox and pH, and metals, so we assume that the upward changes for the metal/aluminum ratios are not diagenetic; that is, there has been enrichment of trace metals with time. It is not now possible, and may never be, to assign a specific cause or source to these metal increases. However, we can speculate that human activity in the watershed and Bay has been sufficient to cause widespread perturbations. Deforestation for agriculture, mining, industrial pollution, the construction of three hydropower dams in the 1920s and 1930s, the construction of the sea-level Chesapeake and Delaware Canal, air pollution, domestic sewage, floods, and hurricanes probably all contribute to the changes observed.

Metal enrichment ratios in surface sediments vary in known geological patterns in the Baltimore-Susquehanna River zone as shown in Figure 18. The ratios increase near the surface of cores with time, matching those patterns in Figure 19. These results show that the northern Chesapeake sediments are experiencing important anthropogenic sources for Co, Cu, Ni, Pb, and Zn.

METAL - SEDIMENT RELATIONSHIPS

Analyses of metal concentrations and sediment characteristics performed during the CBP reveal a close association between metal content and certain sediment parameters. Ninety-six paired samples of surface sediments from the southern Bay metals and sediment parameters were subjected to stepwise regressions of metal content and sediment parameters. Every metal analyzed had a significant correlation with at least three independent variables (Table 11). Every metal had the highest correlation with percent silt and clay; metals in southern Bay sediments were dominantly associated with the fine particulate fraction. Over 30 years of research in other estuaries has consistently verified this finding (Forstner and Whittman 1979). Correlations with latitude represent axial variation and with longitude, lateral variation that, in turn, may reflect origins. These sources can be either up-bay or western-shore rivers, or an association with salinity that is higher seaward and along the eastern shore, than along the western shore. The regression equations are useful for predicting the metal content of bed sediments in the southern Bay when only sediment size analyses are available.

TABLE 11. RELATIONSHIP OF BULK CHEM ANALYSES OF METALS (HELZ ET AL. UNPUBLISHED) VERSUS SEDIMENT PARAMETERS (BYRNE ET AL. UNPUBLISHED) BY STEPWISE REGRESSION

Metal	R^2 [1]	Stepwise Regression Ranked Parameters[2]
Cd	.856	Silt, Clay, Latitude
Co	.763	Silt, Clay, Carbon, Latitude, Longitude
Cr	.885	Silt, Clay, Mean Size, Latitude, Longitude
Cu	.797	Silt, Clay, Mean Size, Longitude
Fe	.822	Silt, Clay, Mean Size, Carbon, Latitude, Longitude
Mn	.738	Silt, Clay, Carbon, Latitude, Longitude
Ni	.850	Silt, Clay, Carbon, Latitude, Longitude
Pb	.791	Silt, Clay, Carbon, Latitude, Longitude
Zn	.769	Silt, Clay, Mean Size, Carbon, Latitude, Longitude

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[1] Significant at .0001

[2] The parameters are percent silt, percent clay, mean size, percent organic carbon, percent sulfur, percent H_2O, Latitude, Longitude. Parameters were not ranked when they did not meet a 0.15 significance level.

SECTION 5

FINDINGS ON SEDIMENTS AND BIOTA

This section describes results of CBP research on aspects of sediment and biota that influence the fate and transport of metals in the Bay. The first part discusses physical and chemical characteristics of sediment, as well as patterns of sedimentation. The second half of the section describes the character of benthic animals in the Bay and how their activities influence the availability of toxic chemicals.

CHARACTER OF BED SEDIMENTS

Because of the close association between metals and sediment, the character of bottom sediment (including its texture, water content, carbon and sulphur content), and sedimentation rates were determined in detail (Kerhin et al. unpublished, Byrne et al. 1982, Carron 1979).

Information about the surface sediments was derived from more than 4000 samples collected on a 1.0 to 1.4 Km grid. Grain size of the sand fraction was analyzed by a Rapid Sediment Analyzer, and the clay and silt fractions were analyzed by settling and pippette withdrawal and a Coulter Electronic Counter. Total carbon and sulfur were analyzed in a LECO induction furnace equipped with a gasometric carbon analyzer and an automatic titrater. Water content was determined gravimetrically by weight loss on drying.

Texture

Sediment texture is characterized by its particle size, with sand the largest and clay the smallest component. Bay sediments are differentiated into 10 classes according to the percentages of sand (0.063-2mm), silt (0.004-0.063 mm), and clay (0.0006-0.004 mm), following Shepard (1954). Of the three end members, sand covers 57.4 percent of the total Bay surface area; silt and clay less than 2.2 percent, whereas the rest of the area consists of mixtures of sand, silt, and clay. Of the total sand area (3600 Km^2), 60 percent lies in Virginia. Sand, together with mixtures of sand, silty-clay, and sandy-silt types, cover 85 percent of the total Bay area, with nearly all the silty clay in Maryland and most silty sand in Virginia.

The distribution of sediment types in the Bay is controlled by the kind of material supplied and by the processes at the site of deposition. In the northern Bay, with the exception of the Susquehanna Flats, the predominate sediment type, silty clay, accumulates in the vicinity of a potential source, the Susquehanna River. As the Bay becomes wider seaward and the relative influence of river-derived sediment decreases, sand and clay eroded from banks and shores are the most abundant sediment. Sand accumulates in more energetic zones, for example, on shoals less than about six meters, and close to its shore source. Silty clay, by contrast, resides in deep water greater than about 10 meters, a less energetic zone of inhibited wave stirring on the bed. This fine-grained sediment includes river-borne as well as marine material, shore sediment, and some skeletal material produced in the central Bay itself. The basic pattern of sand on the shoals and silty clay at greater depths is interrupted by patches of mixed sediment, silty sand, clayey sand, and sand-silt-clay. A linear zone of clay at intermediate depths along the western side, between the South River and the Potomac represents a terrace exposure of old Coastal Plain formations. Similarly, a large zone of sand on shoals along the eastern side, between Bloodsworth-Smith and Tangier Islands, is probably relic sediment.

Sediments of the southern Bay are distinctly coarser than elsewhere. Silt predominates over clay and, therefore, zones of fine sediment in deep water are clayey-silt or sandy-silt. Sand resides on shoals less than 12 meters and in channels of the Bay entrance. Locally, deep channels greater than 20 meters that are scoured by currents are floored by coarse sand.

Water Content

Sediments with high clay and silt content have a correspondingly high water content and thus, potentially high toxicant content. The mean water content of surface samples expressed as percent of wet sediment by weight, range from 16 to 83 percent for Maryland (Kerhin et al. unpublished) and from 13 to 75 percent for Virginia (Byrne et al. unpublished). The mean of all samples in Maryland is 47.4 percent and 30 percent for Virginia. A plot of water content versus mud (clay and silt) content for Virginia sediments is shown in Figure 20. This graph shows a linear trend whereby water content increases with increasing mud content. A similar trend was revealed for Maryland except for clay samples from the relic terrace zone of the upper middle Bay, an area with relatively less water content for a given clay content. The high water content of fine sediment (greater than about 64 percent dry weight or equivalent to a density of 1.30 g/cm^3) defines fluid mud that is a sub-reservoir for toxicants.

Carbon and Sulfur

Organic carbon and sulfur affect the fate of toxicants in sediments by determining the redox state of the sediments after deposition. When organic matter and sulfate of seawater is reduced, hydrogen sulfide (H_2S) is produced, and metal sulfides (as Fe_2SO_4) are formed and concentrated in the sediment. Thus, they are more available to biota.

Organic carbon in bed sediments averages 2.2 percent dry weight for Maryland and 1.0 percent for Virginia. The bulk analyses of organic carbon include organic matter of plant and animal tissues as well as skeletal parts. Isolated high values reaching 10 percent in the northern Bay are attributed in part to bituminous coal particles. The organic carbon content shows a preference for fine sediment (Byrne et al. unpublished). Regression analyses indicate strongest associations with clay fractions. Consequently, organic carbon content is higher (greater than three percent) in the deep central Bay, where fine sediment accumulates, than in the nearshore zones of sandy sediment. Inner parts of tributary embayments like Mobjack Bay and Pocomoke Sound contain more than three percent organic carbon content. The distributions of organic carbon content reveal two main sources: the Susquehanna River for the northern Bay and primary production for the central Bay. Mid-Bay organic carbon levels are the

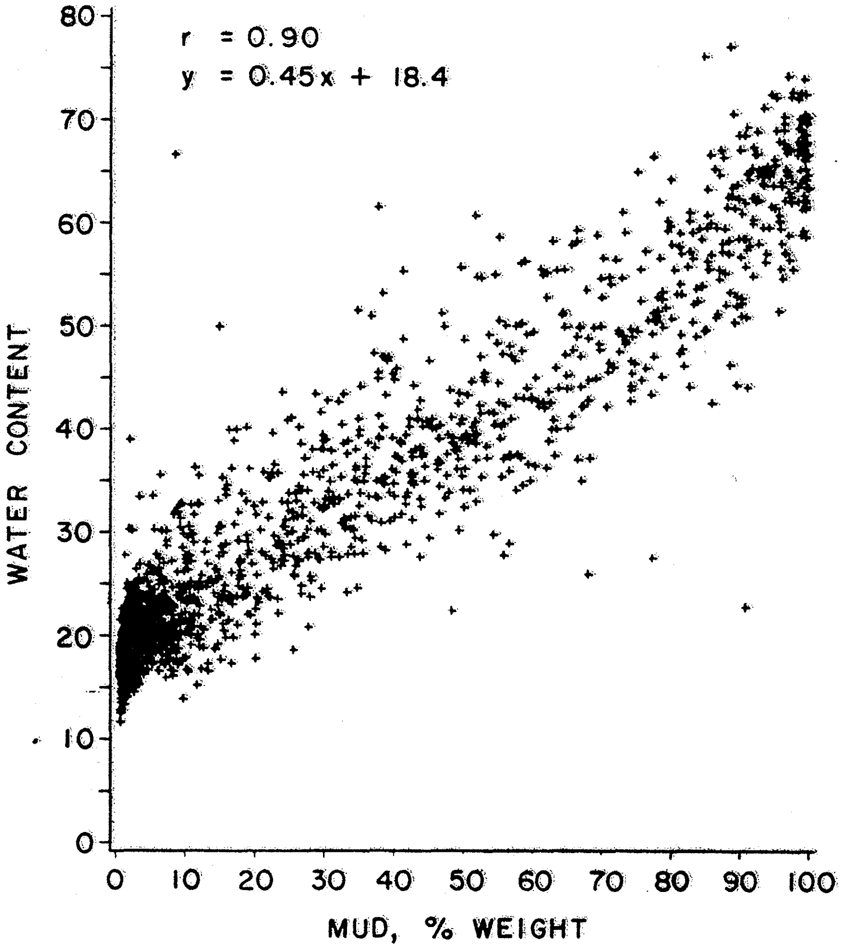

Figure 20. Relationship of percent water content to percent mud content for surface sediment samples from the Bay. Data from Byrne et al. (1982) and Kerhin et al. (1982).

SECTION 4

PATTERNS OF TOXIC METAL ENRICHMENT

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Chemical substances like trace metals are continuously added to estuaries by inflowing tributary rivers, shoreline erosion, the coastal marine environment, the atmosphere, and the biosphere. Much of this material, dissolved and particulate, consists of the natural products of weathering, erosion processes, and of biological activity. In addition, anthropogenic products and wastes enter the estuary either directly in effluent discharges or by nonpoint source runoff. A large proportion of both the natural and anthropogenic material is intimately associated with sediments, particularly those of fine particle size and large surface area.

Suspended material is not only a reservoir for metals, but a vehicle that carries metals from their source to their depositional sink. It is an exchange medium for scavenging and removal of toxic metals from the water column. The metal distributions per liter of water show that the zone of the turbidity maximum is the most enriched (elevated above natural levels) part of the suspended material reservoir (Nichols et al. 1981). Additionally, time-series observations show that much material is resuspended from the bed, and that river-borne material is most likely trapped in the convergence of seaward-flowing river water and landward-flowing estuarine water. Enrichment is enhanced by small particle size (5-11u) of the material and by the relatively long residence time of particles in this zone.

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METAL ENRICHMENT

Both nonpoint and point sources contribute metals and many organic compounds to the Bay and tributaries from anthropogenic sources (Huggett et al. 1974b, Helz 1976, Brush 1974). These levels are superimposed on a background of natural concentrations. To assess the impact of human activity and control amounts reaching the Bay, it is critical to distinguish natural from anthropogenic levels.

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The advantage of this geochemical baseline level is that it provides a standard for comparing data throughout the Bay. It assumes that the Chesapeake drainage basin is representative of average crust, and that a uniform crustal average exists throughout the region. Consequently, it does not account for local metal variations. Because the method is chemical, it is independent of sediment physical properties like particle size; it is affected, however, by compositional changes such as varying organic content within sediment.

Analyses show that enrichment factors in bed sediment for Cd, Co, Mn, Pb, and Zn are largely greater than two, and occasionally reach seven in the Baltimore-Susquehanna River area (Figure 18). For As, Cr, Cu, Hg, Ni, modern wave processes. The material eroded from the shore or inner shallows must be transported either laterally or channel-ward where it is deposited in deep, less energetic zones along the adjacent channel. The maximum shoaling rate in Virginia occurs in water depths of eight to 12 meters. For example, the clay terrace off Calvert County is largely erosional. It contains shoaling patches of sand along nearshore parts, suggesting offshore transport of eroded shore sand. Variable patterns on the "sand shield" around Tangier and Smith Islands, either slight deepening or shoaling in depths less than seven meters, indicate the constant reworking of sediments by wave action, local shoreline sources of sediment, migration of longshore bars, and relic sedimentary features. Other areas, like the steep eastern side of the main channel south of Core Point, have alternating patterns of shoaling and deepening that suggest slumping of the channel wall. This is confirmed by sub-bottom profiles that show slump scars at the slope break of the eastern channel wall and multiple sediment layers on the nearby channel floor.

The Chesapeake entrance and Bay floor, extending landward about 40 kilometers, is predominately shoaling (Figure 21). Most deposition occurs on elongate shoals; some occurs on flanks of the large Horseshoe Shoal, the main Chesapeake channel floor, and the lower part of old Plantation Flats. Most of the shoaling material is fine to very fine sand, probably derived from the Bay entrance on adjacent shores and inner shelf, and transported landward by the net residual bottom flow.

Toxicants may be expected to accumulate in areas of fine sediment shoaling. The rate of toxicant accumulation will vary from place to place in proportion to the shoaling rate (Figure 21). By contrast, deep channels where erosion is active, are poor places to dump waste materials because the currents would remove them. Areas in which the channel is stable or shoaling are the best sites for disposing waste materials.

BENTHIC ORGANISMS

Benthic organisms act with physical processes to either enhance or inhibit movement of toxic material. They can redistribute dissolved toxicants in interstitial water or mix contaminated sediment within the bed, as well as between the bed and overlying water. Through their feeding and burrowing activities, they can bury new surface sediment or expose older deposits. At the same time, their activity can stabilize surface sediments through binding or tube building. On the other hand, they can mobilize sediment by decreasing compaction and increasing water content. By feeding and filtering suspended sediment and by excretion, they produce fecal material and, in turn, promote sedimentation.

Character of Benthic Fauna

The distribution of benthic organisms in Chesapeake Bay has been documented in a number of studies (Boesch 1977a, 1977b; Holland et al. 1977; and Loi and Wilson 1979), most of which indicate that both physical (salinity, substrate type, depth) and biological (competition and predation) factors influence the distribution and abundance of the macrobenthos. The wide range of habitats sampled in this study affords the opportunity to make generalizations concerning species distribution on a Bay-wide basis. To avoid the confounding effects of seasonality on community structure, fall 1978 and summer 1979 collections were considered separately in a numerical classification analysis (Diaz and Schaffner 1981, Reihnarz and O'Connell 1981).

Community Composition

Of the animals sampled in the Bay, polychaete annelids were the most abundant and diverse taxonomic group, consisting of 23,797 individuals and 95 species. Crustaceans were second in abundance and diversity with 10,427 individuals and 48 species, and molluscs were third with 5,088 individuals and 43 species. Miscellaneous groups were represented by 310 individuals and 17 species.

Although the number of species did not change drastically from fall 1978 to summer 1979, a great disparity existed between the number of individuals and the relative composition of fauna collected. Some of this disparity is explained by an increase in the percentage of muddy stations sampled in the summer relative to the fall. More importantly, summer collections, particularly in the lower Bay, contained large numbers of juvenile polychaetes that were presumably recruited to the sediments during the spring. Low abundances in fall collections may result from the heavy predation pressure, by blue crabs and fish, exerted on these populations throughout the summer (Virnstein 1977).

Species Diversity

Mud habitats were generally less diverse and had fewer species than sand or mixed-sediment habitats. In some cases, these results related to the fact that stations were located in deep channels or sound areas where periodic oxygen depletion resulted in a depauperate fauna (Diaz and Schaffner 1981, Reinharz and O'Connell 1981).

Vertical Distribution

The majority of macrobenthic organisms, in all salinity regimes and sediment types, were found in the upper 10 centemeters of the sediment column. Generally, mixed or sandy sediments had the greatest percentage of deep-living organisms. Most of the organisms below 10 centimeters are annelids.

Bioturbation

Evidence from both the vertical distribution studies and x-radiography suggests that nearly all of the benthic communities in the Bay have the potential to move and mix sediments, which in turn can affect the fate and distribution of sediment-bound toxicants. The modifications of physical structure in sediments by organisms (bioturbation) fall into three categories: (1) the construction of tubes as dwelling structures, (2) the abandonment and subsequent filling-in of old tubes, and (3) general sediment disturbance and mixing from locomotion. Analyses of the degree of bioturbation as estimated from x-radiography of box cores indicate that levels of bioturbation and types of biogenic structures vary depending on both salinity regime and sediment type (see Reinharz et al. 1980, Nilson et al. 1980).

Sandy habitats in the Bay are generally restricted to the head and mouth of the Bay as well as to some areas along the eastern shore. Physical structures preserved in these regions include cross-bedding patterns and ripple lamination. In shallow, high energy regions of the upper Bay, some of these structures have been completely disrupted because of wave action. Sands in the lower Bay generally have a uniform bioturbated sediment fabric, reflecting movement and mixing by communities composed of a highly mobile fauna.

Mud habitats are most abundant in the lower salinity regimes of the Bay, north of the Rappahannock River. Physical structures dominate the muddy sediments of deep channels and holes at the mouths of major rivers. Stressful fluid mud substrate and periodic summer anoxia allow only the temporary settling of opportunistic species.

Muds in shallower regions are less likely to suffer anoxic conditions and have a more diverse fauna for mixing sediments. In all areas of the Bay, biogenic structural diversity is greatest in shallow mud habitats.

Bay-wide patterns in degree of bioturbation, based on x-rays of sediment cores, are summarized in Figure 22. Sediments are highly bioturbated (90-100 percent) throughout most of the Bay. Areas where bioturbation is low include the uppermost oligohaline reaches of the Bay, deep channels, sounds, and river mouths that are presumably subjected to periodic oxygen depletion and often characterized by fluid mud substrate.

Biological Sediment Mixing and Fate of Toxicants

Evidence from both the vertical distribution studies and x-radiography suggests that nearly all of the benthic communities in the Bay have the potential to move and mix sediments and, in turn, influence the fate and distribution of sediment-bound toxicants. Several studies (Rhoads 1963, Gordon 1966) have measured particle mixing rates of common marine invertebrates of shallow-water North Atlantic habitats and have found them to exceed annual sedimentation rates. Depending on local sedimentation rates, sediment-bound toxicants may be retained in the upper sediment layers as a result of biological activities.

Areas of high sedimentation rate (generally in the oligohaline salinity regime of the upper Bay [Figure 21] and in some channel areas) were generally found to have low levels of bioturbation. Thus, the fate of sediment-bound toxicants in these areas would probably be primarily controlled by non-biological physical factors such as storms. The fate of toxic materials in the mud habitats of the central and lower Bay, where bioturbation averages greater than 90 percent, would probably be influenced by biological mixing. The probability for retention of toxicants in surface-sediment layers in these habitats seems high because of the turnover of sediments by animals.

The effect of bioturbation on the vertical distribution of heavy metals in the sediment is revealed by depth distribution of radioactive lead. This isotope, 210 Pb, is delivered uniformly to the Bay from atmospheric sources. Once in the sediments, its concentration is proportional to the rate of sedimentation and time because it radioactively decays. The deeper

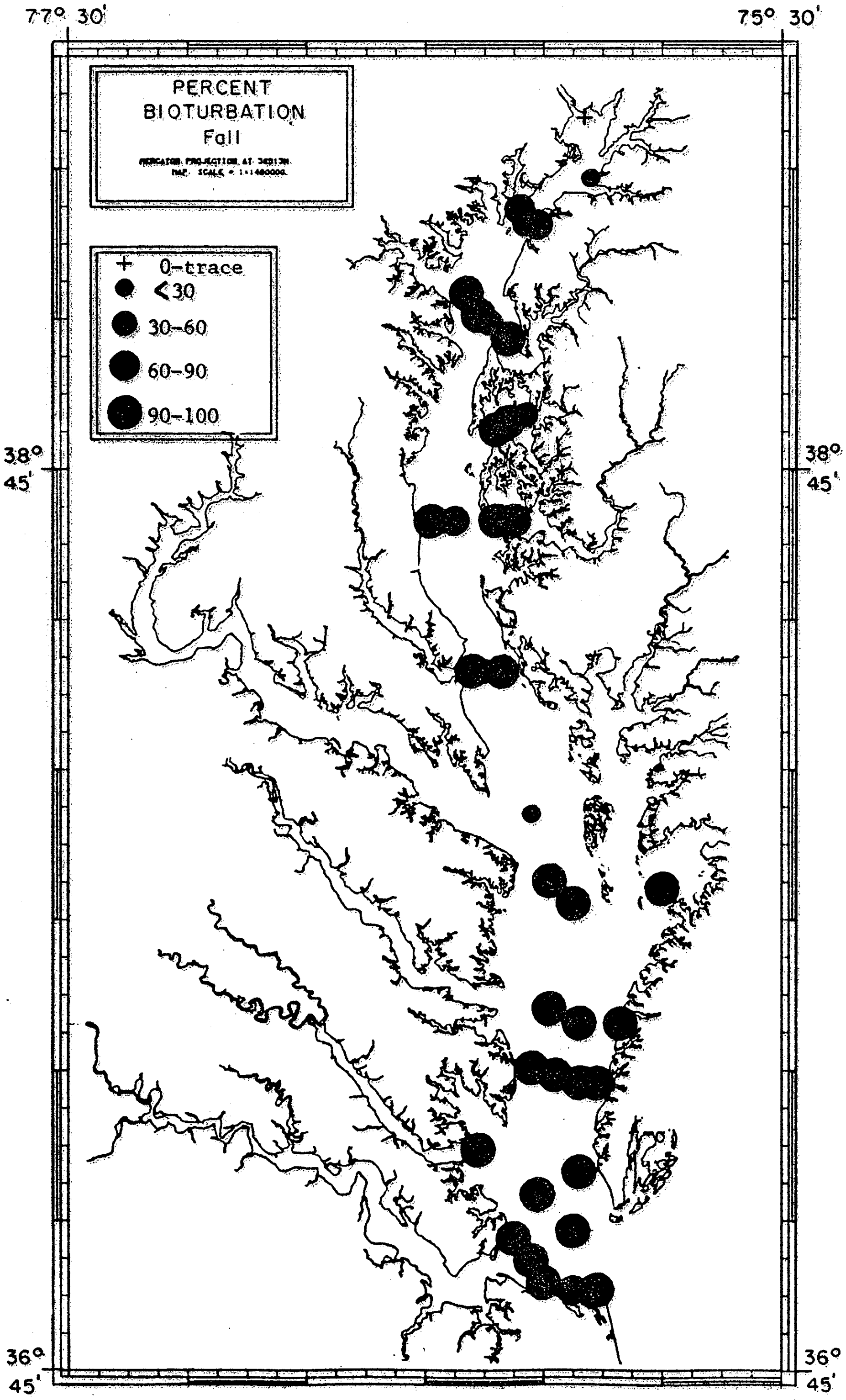

Figure 22. Distribution of percent bioturbation in sediments, fall 1978. Data from Diaz and Schaffner (1981), Reinharz and O'Connell (1981).

the sediment, the less ^{210}Pb (Helz et al. 1981). This is found to be the case in areas where there is little or no bioturbation; for example, in the deep muddy channels of the middle Bay. However, in areas of high bioturbation there is a zone of uniform ^{210}Pb concentration that corresponds to a biologically active zone where animals are mixing the sediments. Such areas were found in the upper and lower Bay where bioturbation caused mixing of sediments down to levels equivalent to 50 years of deposition. Therefore, in these areas toxicants are not likely to be buried.

SECTION 6

TOXIC SUBSTANCES AND BIOTA

An important question remaining in the CBP's investigation of toxic substances is whether or not levels found in the Bay are harmful to the many organisms living there. Although assessing the toxicity of metals and organic compounds was not part of the CBP's original scope of work, a limited evaluation of some metals and organic compounds was done. Further assessment of the problem is presented in the third CBP final report, Characterization of Chesapeake Bay (in progress). Specifically, the characterization report includes discussion of levels of organic compounds and metals in the water column and bed sediment, with a separate section on Kepone in the James River.

This section addresses toxicity studies done during the research portion of the Bay Program. It includes results from the CBP's exposure assessment, experiments on histopathology of a native bivalve, and bioassays of sediment and industrial effluent.

EXPOSURE ASSESSMENT

This discussion only addresses concentrations of toxic chemicals in the water column measured during the CBP Toxic Substances Program, and for which we have EPA criteria. The EPA Ambient Water Quality Criteria Documents (EPA 1980) for priority pollutants, lists the criteria values. These are expressed as the total recoverable concentration in the water column, including dissolved, plus the potentially biologically available fraction associated with suspended sediment. Assuming that any metal attributable to enrichment is potentially biologically available to biota, we can calculate the "available" concentration of that metal. Adding this to the concentration of dissolved metal produces a reasonable, and probably conservative, estimate of the total recoverable value.

Except for the Baltimore-Susquehanna River mouth zones, no metal exceeded the EPA criteria in the Bay proper. Above Baltimore, several stations barely exceeded the 24-hour average (chronic) criteria for Cd or Cu. The criteria violated are based on subtle chronic effects of sensitive species, the impact of which is not understood, and the calculated concentrations exceeded these criteria only marginally. These violations alone do not necessarily imply a serious ecological impact. Additionally, there is some evidence that organisms can acclimate to toxic substances, thereby lowering their sensitivity to those toxicants. On the other hand, there may be species that are more sensitive than the species tested. In addition, synergistic interactions may greatly increase the toxicity of a pollutant, thereby affecting the biota even at sub-criteria levels.

Although this assessment does not show immediate ecological impacts, the toxicity of some Bay sediment (see section on Sediment Bioassays) and the proximity of metal concentrations to EPA criteria values (recommended levels for water) indicate that north of Baltimore the Bay may border on toxic impacts. Additional loadings of toxic substances to these waters may, therefore, prove harmful to the biota.

TOXICITY STUDIES

Histopathology

Diaz et al. (1981) conducted preliminary studies on populations of the bivalve, Macoma balthica, to determine potential toxic effects. [See "Characterization of Chesapeake Bay" in progress for more complete analyses.] Macoma balthica is an infaunal species that burrows to 30 centimeters deep in soft mud. Although not a commercial species, Macoma was selected because it has varied feeding habits in both surface deposits and suspended material, and it is ubiquitous. Seven hundred and forty clams were analyzed for abnormalities from relatively contaminated sites of the Patapsco and Elizabeth Rivers and from relatively uncontaminated sites of the Rhode and Ware Rivers. Of the 740 clams examined, only 26 pathogenic cases, or 3.5 percent, were found (Table 12). No statistical relationship is evident between the pathogenic conditions and the river system in which the clams reside, indicating that the data do not reveal any adverse effects of sediment-associated contaminates.

Sediment Bioassays

Since many potential toxicants accumulate in the sediments at concentrations higher than in the water column, preliminary bioassays were performed on sediment from 70 sites throughout the Bay and selected tributaries including the Patapsco and Elizabeth Rivers. The infaunal amphipod Repoynius abronius, a species considered sensitive to sediment contamination, was collected from relatively uncontaminated sediment and water from Oregon. Repoynius abronius was placed in test sediment from the Bay, and in the relatively uncontaminated sediment for control, at the EPA Marine Science Center, Newport, Oregon. The samples were split and run in both quiet (non-stirred) and stirred, aerated, overlying water of 25 ppt salinity. The stirring action was induced to release interstitial water and obtain a common salinity in all samples. After ten days, the number of survivors were recorded from sieved samples.

The highest mortalities, greater than 90 percent, occurred in stirred and non-stirred samples from the upper reaches of the Patapsco and Elizabeth tributaries and from the northern Bay, particularly in the zone between Baltimore and the Susquehanna River mouth. As shown in sections III and IV, sediments from this zone are generally more enriched in metals and organic compounds than elsewhere. The results of these experiments conclude that toxicants may cause experimental mortality.

TABLE 12. SUMMARY OF HISTOLOGICAL ABNORMALITIES FOUND IN MACOMA BALTHICA CLAMS FROM UPPER AND LOWER BAY TRIBUTARIES (DATA REPRESENT NUMBER OF CLAMS WITH ABNORMALITIES; PARENTHESES INDICATE THE PERCENT OF TOTAL FROM THE RIVER)

	Total Clams Examined	Number of Pathogenic Cases			
		Dermo	Bacteria	Glandular Cysts	Total
Upper Bay					
Patapsco River	404	7(1.73)	1(0.25)	1(0.25)	9(2.23)
Rhode River	189	2(1.06)	1(0.53)	5(2.65)	8(4.23)
Lower Bay					
Elizabeth River	83	1(1.21)	0(0.0)	1(1.21)	2(2.41)
Ware River	64	2(3.12)	0(0.0)	5(7.81)	7(10.93)
Totals	740	12	2	12	26

Effluent Toxicity Tests

Of an estimated 5000 discharges in the Chesapeake region, approximately 1000 are considered to have the potential for discharging toxic material based on criteria established by the National Enforcement Investigation Center of the U.S. Environmental Protection Agency. As part of the CBP Source Assessment Program, effluent from fifty of these dischargers was sampled and characterized in terms of major chemical species (down to 1-10 ppm) and their potential toxic effect on biota as determined by bioassay tests. The selections were based on industries with the highest potential for toxicity (not known toxicity problems). The criteria for ranking the industries were based on flow rate of effluent and expected concentration of chemicals in the effluent. The bioassays were conducted to evaluate, or indicate toxicity of the effluent. The dischargers from which effluent was sampled during the Program are shown in Appendix E. This appendix also shows the many different bioassays performed and the experimental results. Values of results are expressed as percentages of diluted effluent that caused death for various species tested. The EC_{50}, LC_{50}, [or SC_{20}, EC_{50} (Effluent Concentration)] is the percentage of effluent that would inhibit growth by 50 percent. LC_{50} (lethal concentration) is the percentage of effluent that caused a 50 percent kill of the species. SC_{20} is the percentage of the effluent that stimulated growth by 20 percent. Bioassays were performed on fish, several invertebrates, bacteria, and seagrass. Table 13 shows the kinds of tests used.

TABLE 13. TESTS USED FOR MEASURING POTENTIAL TOXICITY OF INDUSTRIAL EFFLUENT

Organism	Test
Fathead minnow	96 hr. LC50
Sheepshead minnow	96 hr. EC50
Daphnia sp.	48 hr. LC50
Mysid shrimp	96 hr. LC50
Thalassia sp.	3-week EC50
Marine bacteria	EC50 Microtox

Results: Bioassays of Fathead minnows and Sheepshead minnows were tested at minimal, low, moderate, and high toxicity values (NT-75, 50-75, 25-49, and 0-24 respectively, Appendix F). Twenty percent of the effluents sampled exhibited moderate to high toxicity, whereas 80 percent exhibited minimal to low.

Invertebrate bioassays of *Daphnia* and mysid shrimp were tested at minimal, low, moderate, and high toxicity values, NT-75, 50-75, 25-49, and 0-24 respectively (Appendix G). With the results of these two bioassays combined, approximately 30 percent of the effluents sampled indicated moderate to high toxicity. In addition, the mysid shrimp appeared more susceptible than the *Daphnia* to the toxic substances found in the effluents.

A Marine Bacteria Bioluminescence Bioassay indicates that 50 percent of the effluent samples were moderate to highly toxic. However, a bioassay on *Thalassia* (Sea Grass) displayed little or no effect from the effluents (Appendix H).

Mutagenic and cytotoxic effects were tested by utilizing Salmonella/microsomal (Ames Test) spot tests and plate incorporation assays (not listed in Table 13). These were performed on filtrates and extracts of 10 effluent samples. No mutagenic response was observed in the pour-plate assay with the particulate recovered from sample filtration (Appendix I). A positive mutagenic response in sample A108 Filtrate I was observed using the plate assay. The spot test of effluent sample A104 Filtrate I showed an increase in revertants over the control, but no clear positive response.

The Chinese hamster ovary (CHO) mammalian cell cytotoxicity assays showed that effluent samples from A105, A106, A110 exhibited medium level toxicity for the sample as received; A100 showed low toxicity in samples A102, A103, A104, A106, A108, and A110 (Appendix J). Acetone extracts of the particulate showed low or very low toxicity ratings for samples A100, A103, A106, A107, A108, and A110. Samples A101 and A109 showed no toxicity for any of the three types of sample.

In summary, effluent bioassays on fish, invertebrates, and bacteria indicate that 20 to 50 percent of the effluents sampled had moderate to high toxicity. A greater risk of toxicity in the Bay is generally associated with high effluent toxicity.

SECTION 7

CONCLUSIONS, INTERPRETATIONS, AND MANAGEMENT IMPLICATIONS

The following abbreviated statements are organized to review the key observational findings (underlined) followed by an interpretation and management implication(s).

METALS

1. The Bay receives metals from human and natural sources through rivers, the atmosphere, and industry. The rivers are a dominant pathway for Cr, Cu, Fe, and Zn; industry is a dominant source of Cd, and the atmosphere is a significant pathway for Pb and Zn. Metal input to the main Bay is greatest from the Susquehanna River.

Metal input from rivers is relatively high because of large contributions from geologic weathering and soil erosion of fine sediment in the drainage basins. Additionally, rivers supply metals from municipal and industrial effluents and, indirectly, from atmospheric deposition on the drainage basin. The Susquehanna River is a strong pathway because of its relatively large water and sediment discharge.

The Susquehanna is the only river that discharges directly into the Bay. Main tributaries, like the James and Potomac, discharge into estuaries that entrap sediment and sediment-borne toxicants.

2. Bay water contains the metals, Mo and U, mainly in dissolved form ($>$ 90 percent of total metal), and they positively and linearly correlate with salinity. The metals Cd, Co, Cr, Cu, Ni, Pb, and Zn occur both in dissolved and particulate form (between 10 and 90 percent are dissolved), whereas more than 90 percent of the Fe, Mn, Sc, and Th occurs in particulate form.

Relatively high concentrations of Mo and U are probably controlled by alkalinity of Bay water and by dilution of seawater with river inflow. The concentrations of metals Cd, Co, Cr, Cu, Pb, Ni, and Zn are controlled by complex interactions of chemical solubility, sediment adsorption, and bioconcentration; Fe, Mn, Sc, and Th distributions are mainly a function of sediment adsorption-precipitation reactions. Metals in dissolved form are diluted, mixed, and flushed through the Bay and, therefore, their effects are short-lived. Metals in particulate form, however, have a longer residence time in the Bay and can build up to high concentrations through bioaccumulation and sediment adsorption.

The relevant management practice is to monitor and control metals discharge while taking into consideration the different solubilities, bioavailability, and adsorption properties of the different metals. Through consideration and understanding of these properties, one can better regulate the type, amount, and location of allowed discharges. As an example, dissolved metals are readily taken up by plankton, whereas particulate metals are likely consumed by suspension feeders or benthic filter feeders. Adverse effects, however, will vary with the chemistry of the metal and the response of the organism to the metals.

3. Concentrations of As, Cd, Cu, Hg, Ni, Pb, Sn, and Zn per gram of suspended material are maximal in near-surface suspended material of the central Bay. Enrichment factors range: Cd, 10-118; Cu, 12-27; Pb, 37-51; and Zn, 16-74. The percentage of organic matter in this zone is generally higher than elsewhere.

The association of a relatively high content of metals with organic matter in the same zone suggests that biological activity is the proximal cause of accumulation. The metals can be derived from multiple sources, natural or anthropogenic.

Control of bioaccumulations can be affected by changes in water quality that will reduce productivity. These changes include lower light, increased turbidity, lower nutrient input, and reduced mixing. However, some biota, such as phytoplankton, require certain metals, like Mn for photosynthesis. Other metals such as cupric ions, with extreme reactivities, interfere with uptake of essential metals. Because metals, sediments, and nutrients are interrelated, they need to be managed together. Piecemeal management of single components cannot succeed.

Most control measures have focused on near-field discharges and immediate effects. There is a need to manage for subtle changes and "far-field" effects. Processes leading to bioaccumulation and particle concentration in the turbidity maximum need to be taken into account in any effective management plan. Moreover, water, particulates, sediments, and biota should be managed as a dynamic system in which trace metals are continually being repartitioned.

4. Secondary maxima of Cd, Mn, Ni, Pb, Sn, and Zn concentrations per gram of suspended material are found in near-surface water of the Bay off the Patapsco River.

These secondary "hot spots" suggest that metals are derived in part from the Patapsco River and Baltimore Harbor via near-surface currents or, for another part, by periodic resuspension from old dredged material on the Bay floor.

The relevant management practice is to stabilize potential sources of contaminated sediment from the Harbor either by removing future dredged material from the system or by stabilizing the natural sediment through consolidation, dewatering, or grass cover.

5. Sediments from the northernmost part of the Bay floor are enriched relative to average crustal shale in Cd, Co, Cu, Mn, Ni, Pb, and Zn by factors of two to eight. Cd, Pb, and Zn are enriched throughout the main Bay by factors of two to six relative to average shale.

The Susquehanna River is a distinctive primary source of metals in bed sediments of the northernmost Bay. This is confirmed by similar enrichment factors and similar metal-Fe ratios in the river and northern Bay. The metals are sequestered in fine sediment and associated with river-borne organic material. Since enrichment factors diminish markedly with distance seaward from Kent Island, contaminated sediment is probably not transported seaward of the Patapsco mouth in quantity. This assumes diagenetic processes are not contributing significantly to the seaward reduction of enrichment. Instead, metals mainly accumulate in the turbidity maximum zone where suspended sediment is trapped. Once deposited, the metals can be resolubilized and, thus, released from contaminated sediment and potentially available to the biota.

Because the Bay system is complex, it requires a fairly sophisticated input of technical information about the system being managed. It should be managed with a scientific data base and a knowledge of processes affecting behavior transport and fate of potential toxics. Therefore, effective management decisions should be coupled to monitoring data and scientific knowledge of processes.

The new information on distribution of enriched bed sediment provides data with which to broadly classify potential dredged material. Such a classification provides input for decisions on dredged spoil management -- its best use, disposal techniques, or dumping sites.

6. The Bay floor is a major sink for metals and organic compounds. More than 60 percent of the total input of Fe, Mn, Ni, Pb, and Zn is retained in the bed sediments.

Bed sediments in the central and northern Bay are enriched with metals, (Cu, Pb, Zn) to depths of 14 to 26 cm, representing about 60 to 90 years of deposition. Metal enrichment reaches a peak between four and 18 cm (1930 and 1960) and diminishes toward the surface.

The enriched metal peaks in the northern Bay probably represent peak metal loading from a dominant source, the Susquehanna. The influx was first felt in the northern Bay and later in the central Bay. Zones of fast sedimentation are sensitive to contamination. When metals are buried deeper than the zone of active diagenesis, they may be effectively immobilized and thus unavailable to biota.

Since sediments record long-term changes in metal loading, they can provide an indication of future trends if the depositional flux is coupled to the input flux. Whereas analyses of water samples from contaminated zones may not detect some toxic chemicals in small amounts, sediments with toxic substances that are strongly sorbed can build up to levels and thus be readily detected.

7. Major transport pathways for metals follow either a hydrodynamic route or a bioecologic route. The principal sinks for toxics are located in near-source zones where fine sediment accumulates.

The hydrodynamic route through the northern Bay follows the pattern of estuarine circulation; that is, seaward through the river and upper estuarine layer, and landward through the lower layer. This route leads to entrapment of contaminated sediment near the inner limit of salty water close to its major source the Susquehanna River. Secondary sinks of accumulation occur in less energetic zones: the central Bay axial basin and inner reaches and mouths of tributaries that promote moderate to fast sedimentation and accumulation of fine sediment.

8. More than 300 organic compounds were detected in Bay sediments. Most were PNAs having anthropogenic sources, and many compounds are among EPA's priority pollutants.

The organic compounds tend to associate with fine suspended material in the water and accumulate on the Bay floor as the suspended material settles. Because of their polarity, some organic compounds may occur in dissolved form, but they are below the detection limit of most present-day instrumentation. Significant concentrations of priority pollutants are cause for concern about sources and effects on Bay ecology.

9. Concentrations of organic compounds in bed sediment are greatest in the northern Bay. Seaward from the Patapsco River, concentrations decrease to the Potomac River mouth. In the southern Bay, concentrations near tributary mouths are greater than elsewhere.

The Susquehanna River is a source of many organic compounds. The compounds are likely supplied from pollution sources and atmospheric deposition on the drainage basin, and they accumulate in the turbidity maximum zone where fine sediment is trapped. Accumulation at tributary mouths relates either to the accumulation of fine sediment or to sources of contamination in the tributaries.

If contaminates have distinctive point sources as industrial discharges they should be controlled pursuant to Federal and state policy.

10. Concentrations of organic compounds are higher and more variable in the Patapsco River than in the main Bay.

A Patapsco River source of organic compounds is indicated by the distribution of concentrations that are high in landward parts of the river. Additionally, they vary as the location of sources varies within the river. Most PNAs, however, are widespread, mixed, and lack specific sources. Part of the contaminated sediment is trapped within Baltimore Harbor and the Patapsco River, but some escapes to the Bay. This is revealed by the occurrence of a Patapsco derived compound, 6-phenylodecane, in the main Bay. Since concentrations diminish seaward from the river mouth and down Bay, dispersion of significant quantities is probably low.

11. More than 120 organic compounds were detected in oysters from the Bay. The compounds, methyl esters, fatty acids, and ketones, were present in most oysters, but PNA's were scarce.

The organic compounds in oysters may have a biogenic or natural origin. Because the composition in oysters differs from sediments, and has fewer PNAs, oysters are of lesser importance for general monitoring of organic compounds in the Bay. The oyster, however, can be useful for monitoring specific PNA compounds as benzo(a)pyyrene which is a suggested carcinogenic compound or an oyster metabolite.

12. Bay-wide bioassays reveal that sediments from inner reaches of the Patapsco and Elizabeth Rivers and from the northern-most Bay have a higher toxicity than elsewhere.

Effluent bioassays of fish, invertebrates, and bacteria indicate that 20 to 50 percent of the effluents sampled had moderate to high toxicity.

The occurrence of relatively high toxicity and low survival rate generally relates to zones of high metal content and high organic compounds in bed sediments close to major sources. We speculate that high sediment toxicity is produced by a combination of high metal content and high loads of organic compounds. It remains to be determined what acceptable levels of sediment pollution the Bay resources can endure. Generally, a greater risk of toxicity in the Bay is associated with high effluent toxicity, unless organisms can adapt to certain concentration levels.

SECTION 8

RESEARCH NEEDS

Chesapeake Bay is a very complex estuarine system, and our knowledge of hydrodynamic, sedimentological, and bio-ecological processes is limited. The data gained in this study point to gaps in our knowledge that deserve future research.

1. Inasmuch as results show that some sediment-associated toxicants occur outside major harbors (the Patapsco River and Hampton Roads) and seaward of Kent Island, it remains to be determined how much material presently escapes the harbors and northern-most Bay. Is the contaminated sediment outside the harbors a product of disposal activities or presently escaping near-source contamination zones? Do harbor contaminates contribute to up-Bay, or up-tributary, contamination zones by landward transport?

2. Since results show maximal particulate concentrations of abnormally high Cd, Cu, Pb, and Zn in surface waters of the central Bay, a location far from major sources, it remains to be determined how they get there. The distribution of metal in various states (dissolved, colloidal, particulate; organic or inorganic) must be determined together to demonstrate how the metals are partitioned on a seasonal basis. We must learn if metals stimulate production of organic matter like plankton or, by contrast, affect the health of organisms in the central Bay. And, does bio-accumulation and turnover make the metals more or less mobile?

3. Whereas the present research deals mainly with metals and organic compounds supplied to the Bay at more or less normal conditions, episodic events may control their distribution. Floods, hurricanes, and storms can produce exceptional conditions for massive resuspension and dispersal of sediment-borne metals. Observations are needed to study the impact of short-term events with respect to the following: How much sediment and toxicant are released or mobilized by an event compared to average conditions? What are the corresponding effects on marine resources? How long does it take to recover, decontaminate, or come to a new chemical equilibrium?

4. Synthesis results reveal that atmospheric inputs of potentially toxic material can compose a significant portion of the total toxic load. It appears that atmospheric inputs are relatively important in areas far from contamination sources, especially for metals like Cd, Cu, and Pb, and the organic compound like PNAs. We must determine, in detail, the magnitude and extent of atmospheric inputs relative to water-borne inputs. With increasing use of fossil fuels, are atmospheric imputs increasing the total toxicant input to the Bay despite controls on water-borne inputs? There is a need to determine if atmospheric inputs are from distant sources and homogeneous, affecting the entire Bay. Because atmospheric dry and wetfall collects on salt marshes, and the flux can be recorded by marsh deposits, attention should focus on high marsh sediments that reflect atmospheric influence. The historical record combined with monitoring should provide an early warning of increasing anthropogenic inputs from the atmosphere.

5. To ascertain the validity of data acquired, future efforts should account for variability of field sampling through a rigorous statistical sampling plan. This study reveals that the concentrations of metals and organic compounds can vary widely with location, especially in suspended material. Verifying results are needed to account for short-term tidal variations; fortnightly, neap-spring changes; and seasonal as well as non-periodic changes of episodic events.

6. Chesapeake Bay has, at least on one occasion, been the recipient of the direct disposal of pesticides like Kepone (Huggett et al. 1980). Fortunately, the quantities were small and the assimilation capacity large enough so that no adverse effects on the biota were noted. The disposal of such compounds in this manner was, and is, illegal. This indicates that laws alone are insufficient to protect the Bay and that chemical monitoring is necessary. The chemical monitoring of effluents and sediments collected near outfalls shows that more effort of this type is needed to prevent future "Kepone episodes" (Bieri et al. 1981). Key sinks in the Bay also require monitoring. Because some dissolved toxicants are difficult to detect in near-source zones, monitoring of peripheral sediment sinks having fast deposition can provide an early warning of increased loading. (For details see separate Monitoring Recommendations, Flemmer et al., unpublished)

In this study over 300 organic compounds were analyzed, but results indicate that "thousands of other compounds are present at low concentrations." Therefore, monitoring needs to account for a wide compositional range of organic compounds having low concentrations. These data are needed to establish valid baselines as well as to detect anomalous concentrations of pollutants before they build up. To guide State water pollution control authorities, an effluent toxicity characterization program is needed to screen industrial effluents for toxic chemicals and to determine their degree of toxicity, both acute and chronic.

7. Additional toxicity data are needed to evaluate impacts on the Bay's living resources and to formulate diagnostic criteria that are generally accepted. Little is known about the toxicity of individual components, and less is known about the toxicity of populations or communities. Most bioassays have examined acute effects; little is known about long-term chronic effects. Moreover, the Bay ecosystem is complex and dynamic, involving the interactions of physio-chemical parameters and biological components with time. We need to know if the toxicants found in the Bay are biologically available. Once organisms are exposed to toxicants, can they adapt to certain concentration levels? Most bioconcentrations have been treated as static levels in tissues of organisms. Some organisms, however, accumulate toxicants quickly, whereas others that metabolize slowly can accumulate toxicants slowly but to high levels. Therefore, bioaccumulation needs to be examined as a dynamic equilibrium determined by the metabolism rate.

8. A major problem for future research is determining the relative capacities of different parts of the Bay to assimilate toxicants. Although a numerical model can predict the distribution and resulting concentration of a given input and its residence time, toxicants are subject to

transformation and building up through biological and sedimentological processes. A single concentration level value applied to the entire Bay is not a universally valid criteria for control because it does not take into account the characteristics of the receiving segment. We need to know the relationship between the contaminate concentrations and their toxic effect on the biota in each receiving segment. This requires much better data and a greater understanding than now exists. In particular, we need to overcome the difficulties of: (1) making accurate measurements of diverse and potentially toxic compounds at very low concentrations; (2) measuring the toxicity effects of chemicals on organisms; and (3) making valid interpretations by comparing laboratory results and field observations.

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APPENDIX A

INVENTORY OF PROJECT DATA DISCUSSED IN THIS REPORT

Project Name	Organization/ Principal Investigator(s)	Sample Collection Dates	Spatial Description	Sample Type	Parameters	Analytical Methods
Toxic Point Source Assessment of Industrial Discharges to the Chesapeake Bay Basin	Monsanto Research Corp./ Rawlings	April, 1978- May, 1981	54 Point sources located near Baltimore and Hampton/ Richmond	Effluent	Bioassays, NPDES Parameters, metals organics	ICAP, GC, GC/MS, etc.
The Characterization of the Chesapeake Bay: Systematic Analysis of Toxic Trace Elements	National Bureau of Standards/ Kingston	June-July, 1979	51 Stations* Bay-wide	Near bottom & surface Water Column, Suspended and Dissolved	Metals	NAA, GFASS
Chesapeake Bay Sediment Trace Metals	University of Maryland/Helz	April, 1977- May, 1979	200 Surface Bed Sediment Samples Collected from 25 Traverses, Bay-wide	Dried sediment, Fine and Coarse Fractions	Metals	AAS
Chesapeake Bay Sediment Trace Metals	University of Maryland/Helz	Nov., 1978, May-June, 1979	17 Gravity Sediment Cores, Bay-wide, sampled every 2 cm.	Dried sediment	Metals	DCP
Chesapeake Bay Earth Science Study - Interstitial Water Chemistry	Maryland Geological Survey/ Bricker & Hill	Sept.-Oct., 1978, June-July, 1979, March, 1980	1 Meter Gravity* cores taken at 97 stations, Bay-wide	Pore Water samples at 10 depth intervals	Metals, pH, Eh, pS$^{=}$, conductivity, SiO_2	Electrode measurements, AAS

Project Name	Organization/ Principal Investigator(s)	Sample Collection Dates	Spatial Description	Sample Type	Parameters	Analytical Methods
Sediment Pore Water Chemistry	College of William & Mary/ Tyree	Sept.-Oct., 1978, June-July, 1979, March, 1980	1 Meter Gravity* cores taken at 97 stations, Bay-wide	Pore Water samples at 10 depth intervals	Major ions and nutrients	Ion chromatography
Investigation of Organic Pollutants in the Chesapeake Bay	Virginia Institute of Marine Science/Huggett & Beri	Spring and Fall, 1979	27 Stations, Bay wide	Bed sediment	Organic Compounds	GC, GC/MS
Investigation of Organic Pollutants in the Chesapeake Bay	Virginia Institute of Marine Science/Huggett	Spring & Fall, 1979	23 Stations Bay wide	Oyster tissue	Organic Compounds	GC, GC/MS
Chesapeake Bay Earth Science Study - Animal Sediment Relationship	Maryland Geological Survey/ Reinharz	Sept.-Nov., 1978, June-July, 1979	52 Stations* in northern Bay	Box cores, samples at 7 depth intervals	Biotic assessment, radiographs, grain size, salinity, temp.	
The Biogenic Structure of Chesapeake Bay Sediments	Virginia Institute of Marine Science/Boesch & Diaz	Sept., 1978, April, 1979, June, 1979	50 stations* in Bay below Md./Va. state line	Box cores, sampled at 7 depth intervals	Biotic assessment radiographs, grain size, salinity, temp.	
Fate, Transport & Transformation of Toxics: Significance of Suspended Sediment and Fluid Mud	Virginia Institute of Marine Science/Nichols	March-April, May, August, 1979; April May, 1980	Bay longitudinal and harbor transsects	Water column and fluid mud/bed sediment	Metals, temp., salinity, D.O., pH, solids, organic carbon, particle size	AAS, GFASS, etc.
Baseline Sediment Studies to Determine Distribution, Physical Properties, Sedimentation Budgets & Rates	Virginia Institute of Marine Science/Byrne	Nov. 1978-June 1979	2,018 stations in southern Bay (1.4 km grid)	Bed sediment	Particle size, % water, carbon, sulfur, sedimentation rate	

Project Name	Organization/ Principal Investigator(s)	Sample Collection Dates	Spatial Description	Sample Type	Parameters	Analytical Methods
Chesapeake Bay Earth Science Study-Sedimentology of the Chesapeake Bay	Maryland Geological Survey/ Kerhin	April, 1976-Oct. 1981	4,200 stations in northern Bay	Bed sediment (upper 8-10 cm)	Particle size, % water, carbon, sulfur, sedimentation rate	

* Samples for several projects collected at same locations.

NAA - Neutron Activation Analysis
GFASS - Graphite Furnace Atomic Absorption Spectroscopy
ASS - Atomic Absorption Spectroscopy
DCP - Direct Current Argon Plasma Emission Spectroscopy
GC - Gas Chromatograph
GC/MS - Gas Chromatograph/Mass Spectroscopy
ICAP - Inductively Coupled Argon Plasma

APPENDIX B

SUMMARY OF DATA SOUCES FOR TRACE METALS IN THE CHESAPEAKE BAY AND TRIBUTARIES

Area	Reference	Metals	Component
James, York, & Rappahannock Rivers	Huggett et al. (1971)	Hg	Bed Sediments
Potomac River	Pheiffer (1972)	Ag,Ba,Cd,Co,Cr, Cu,Fe,Li,Mn,Ni, Pb,Sr,V,Zn	Bed Sediments
James River	Huggett & Bender (1975)	Cu,Zn	Oysters & Bed Sediments
Northern Bay (1974)	Owens et al.	B,Ba,Ce,Cr,Mn,V Zn,Zr	Bed Sediments
Patapsco River & Balto. Harbor	Villa & Johnson (1974)	Cd,Cr,Cu,Hg,Mn,Ni Pb,Zn	Bed Sediments
Northern Bay (1974)	Sommer & Pyzik	Co,Cu,Ni,Pb,V	Bed Sediments
Northern Bay	Cronin (1974)	Fe,Mn,Zn	Bed Sediments
Northern Bay & Susquehanna	Carpenter	Co,Cr,Cu,Fe,Mn,Ni, (1975) Zn,Cd,Pb	Dissolved and Suspended Sediment
Central Bay	Matisoff (1975)	Fe,Mn	Interstitial Sediment & Water
Back River	Helz et al. (1975)	Cd,Cu,Fe,Mn,Pb,Zn	Bed Sediments
Northern Bay	Helz (1975)	Cd,Co,Cr,Cu,Pb,Fe Mn,Ni,Zn	Bed Sediments
Rappahannock River	Huggett et al. (1975)	Cu,Zn	Bed Sediments

(APPENDIX B, CONTINUED)

Area	Reference	Metals	Component
Northern Bay	Matisoff et al. (1975)		
Rhode River	Frazier (1976)	Cd,Cu,Fe,Mn,Zn	Bed Sediments
Elizabeth River	Johnson & Villa (1976)	Cd,Cr,Cu,Hg,Pb,Zn	Bed Sediments
Patuxent River	Ferri (1977)	Cd,Co,Cr,Cu,Fe, Mn,Ni,Pb,Zn	Bed Sediments
Northern Bay	Schubel and Hirschberg (1977)	Cr,Cu,Ni,Pb	Bed Sediments
Patapsco River & Balto.Harbor	EPA-440/5-77-015A	As,Cd,Cr,Cu,Hg, Mn,Ni,Pb,Zn	Bed Sediments
Northern Bay	Goldberg et al. (1978)	Ag,Al,Cd,Co,Cr,Cu, Fe,Mn,Ni,Pb,Zn,V	Bed Sediments
Northern Bay	Eaton et al. (1979)	Mn	Dissolved Bed Sediments
Northern Bay	Eaton (1980)	Fe,Ti,Zn	Suspended Sediments

APPENDIX C.

SUMMARY OF DATA FOR ORGANIC CHEMICALS IN CHESAPEAKE BAY AND TRIBUTARIES

Area	Reference	Organic Chemicals	Component
Chesapeake Bay & Selected Tribs.	Munson & Huggett (1972)	DDT compounds	Oysters
James, Rappahannock, & Potomac Rivers	Barnard (1971)	DDT compounds	Fish
Chester River	Munson (1973)	PCBs, Chloradane, DDT	Sediments Shellfish
Northern Bay	Munson (1975)	PCBs Chloradane DDT	Sediments Shellfish Zooplankton
Cape Charles, Lynnhaven Bay	Goldberg et al. (1978)	PCBs DDT compounds PNAs, DAHs	Oysters
James River	U.S. EPA (1978)	Kepone	Soil, water, Bed sediments
James River	Huggett (1980)	Kepone	Bed sediments & biota
James River	Huggett & Bender (1980)	Kepone	Biota, Bed sediments, Suspended sediments
James River	Lunsford (1980)	Kepone	Bed sediments
James River	Nichols & Gutshall (1981)	Kepone	Bed sediments

APPENDIX D

AREAL DISTRIBUTION OF SEDIMENT TYPE IN CHESAPEAKE BAY: FROM DATA OF KERHIN ET AL. (1982) AND BYRNE ET AL. (1982)

	Sand		Silt		Clay		Sand-Silt-Clay		Sandy Clay		Silty Clay		Clayey Silt		Sandy Silt		Silty Sand		Clayey Sand		Total Area
Bay Segment	km^2	%^{1}	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	km^2	%	
Northern	218.6	6.1	-	-	3.8	2.9	78.2	26.2	-	-	405.8	34.3	15.9	5.3	-	-	7.8	1.5	8.8	7.6	738.9
Upper Middle	630.9	17.5	-	-	126.3	97.1	61.1	20.4	2.5	100	447.5	37.8	52.4	17.4	-	-	41.8	7.8	32.9	28.4	1395.4
Lower Middle MD^3	590.7	16.4	-	-	-	-	57.3	19.2	-	-	282.0	23.8			4.5	4.7	-	-	53.4	46.0	987.9
VA	820.8	22.8	3.1	100	-	-	49.0	16.4	-	-	49.0	4.1	138.4	46.0	26.3	27.5	44.8	8.4	13.5	11.6	1144.9
Upper Southern	211.9	5.9	-	-	-	-	22.9	7.7	-	-	-	-	57.0	18.9	49.3	51.5	160.5	30.0	5.0	4.3	506.6
Central Southern	262.9	7.3	-	-	-	-	11.2	3.7	-	-	-	-	9.9	3.2	9.1	9.5	138.3	25.9	2.4	2.1	433.8
Lower Southern	864.9	24.0	-	-	-	-	19.2	6.4	-	-	-	-	27.5	9.1	6.5	6.8	140.6	26.3	-	-	1058.7
Sediment Type Totals	3600.7	57.4^2	3.1	0.1	130.1	2.1	298.9	4.8	2.5	0.1	1184.3	18.9	301.1	4.8	95.7	1.5	533.8	8.5	116.0	1.8	6266.2

* Exclusive of Choptank River and Eastern Bay and Tangier and Pocomoke Sounds in Maryland.
Exclusive of Pocomoke and Tangier Sounds, Mobjack Bay, and lower tributary areas of Rappahannock, Piankatank, York, and James Rivers.

[1] Percent of area for given sediment type by segment.

[2] Percent of area for given sediment type for entire Bay.

[3] Dividing line between Maryland and Virginia taken as latitude 37°55' (Smith Point).

APPENDIX E

SUMMARY OF CHESAPEAKE BAY TOXIC SOURCE ASSESSMENT AND BIOASSAY TESTS

Plant Name	S/C Code	Industry Type	Date of Sampl.	Fish Bioassay		Invertebrate Bioassay		Algal Bioassay						Marine Bacter.	Seagrass Thalassia	Cytotoxic Effect	
				Minnow 96 Hr. LC50	Sheepshead 96 Hr. LC50	Daphnia LC50 48NC	Mysid 96 Hr. LC50	Selenastrum EC50 4 day	SC20 4 day	SC20 4 day	EC50 14 day	Skeletonoma 96 Hr. EC50	96 Hr. SC20	Microtox		AMES	CHO
Pre-Phase I																	
1. Bethlehem Steel	3312	steel industry (021)	4/14/78				NT					38.4% 41.5%	NS				
2. Bethlehem Steel	3312	steel industry (1010)	4/14/78				100% (100% mortality)					30.5%	NS		NT		
3. Bethlehem Steel		steel industry (112B)	4/14/78				100%					NT	NS		NT		
4. E & R Creosote	2491	Wood Preserving	4/14/78				--					NT	NS		NT		
5. Va. Chemicals	2811 2819 2869	Chemical Manufacturer	4/27/78									NT	2.3%				
6. Chesapeake Corp.	2611 2621 2631	Pulp & Paper	5/3/78				NT					3.7%	NS				
7. Amoco	2911	Petroleum Refining	5/3/78				100% (100% mortality)					45%	7.5%				
8. Badische Corp.	2824 2299	Synthetic Fibers	7/7/79				50% (100% mortality)					8.2% 6.8%	NS		NT		
9. Allied Chemical	2821 2824	Synthetic Resins & Fibers	7/7/78				NT					NT	16.8%		NT		

PLANT NAME		INDUSTRY TYPE		FISH BIOASSAY		INVERTEBRATE BIOASSAY		ALGAL BIOASSAY						MARINE BACTER.	SEAGRASS THALASSIA	MUTAGENIC and CYTOTOXIC EFFECTS	
	S/C Code		Date of Sampl.	MIN-NOW 96 Hr LC50	SHEEPS-HEAD 96 Hr LC50	DAPHNIA LC50 48NC	MYSID 96 Hr LC50	SELENASTRUM EC50 4 day	SC20 4 day	SC20 4 da	EC50 14 da	SKELETONOMA 96 Hr EC50	96 Hr SC20	MICRO-TOX		AMES	CHO
10. Allied Chemical (cooling water)	2821 2824	Synthetic Resins & Fibers	8/5/18				NT					NT	NS		NT		
11. Hopewell, STP	4952	POTW, Secondary	9/28/78				50%					13.5% 7.5%	NS				
Phase I																	
1. Westvaco A100	2621 2631	Pulp & paper	11/26/78	NT		NT,NT	45.7%	62.1%	.04	NS	NT	NT	.07%			No response	Low
2. Badische Corp. A101	2824 2299	Synthetic Fibers	11/30/79	NT, NT	NT	94%, NT NT	NT 44.9%	45.6	1.96	NS,NS	11% 14%	18% 19.9%	1%			NR	NT
3. Crompton A102	227	Textile Dyeing	11/21/79	NT		NT, 66.8%	NT	NT	.01	39%	56-100%	NT	..53%			NR	Low
4. Amoco A103	2911	Petroleum Refining	12/1/79	NT	NT	45%, NT	NT,NT	NT	.05	7%	56-100%	11%, NT	.02			NR	NT
5. Aileen A104	221	Textile Dyeing	11/21/79	60%		77%, NT	46.4%	NT	.004	32-56%	NT	53.3%	.64%			NR	Low
6. Va. Fiber A105	2631	Pulp & paper	11/26/79	NT		NT, NT	NT	13.6%	NS	NS	61%	NT	.88%			NR	Low
7. Ches. Corp. A106	2611 2621 2631	Pulp & paper	11/30/79	NT, NT		NT, NT NT, NT	87.9%, NT	28.6% 43.4	.09 .02	NS, 57%	NT,NT	63.5% 42.4%	.73% .49%			NR,NR	Low,low
8. E. I. DuPont A107	2824 2299	Synthetic Resins & Fibers	11/20/79	NT		NT, NT	NT	NT	8%	8%	NT	NT	.04%			NR	NT
9. VOTAN A108	3111	Leather Tanning	11/20/79	60%		22%,44.4%		5.1	1	13%	32-56%	29.8%	1.03%			Positive	Low
10. Va. Chemicals A109	2811 2819 2869	Inorganic & Organic Chemicals	11/27/79	NT		6%,9.6%	NT	81.5	.4	NS	56%	44.3%	20%			NR	NT

PLANT NAME	S/C Code	INDUSTRY TYPE	Date of Sampl.	FISH BIOASSAY		INVERTEBRATE BIOASSAY		ALGAL BIOASSAY						MARINE BACTER.	SEAGRASS THALASSIA	MUTAGENIC and CYTOTOXIC EFFECTS	
				MIN-NOW 96 Hr LC50	SHEEPS-HEAD 96 Hr LC50	DAPHNIA LC50 48NC	MYSID 96 Hr LC50	SELENASTRUM EC50 4 day	SC20 4 day	SC20 4 da	EC50 14 da	SKELETONOMA 96 Hr EC50	96 Hr SC20	MICRO-TOX		AMES	CHO
Phase II																	
1. FMC Corp. B1295	2821 2879	Pesticides & Plasticides				1%	.69%	5.6%	.1%			3.57%	.1%				
2. Bethlehem Steel B1305	3312	Iron & Steel				NT	50.5%	NT	NS			53%	.32%				
3. Bethlehem Steel (Back Rvr. POTW) B1315	4952	Plant Intake Water				NT	27%	NT	.1%								
4. Bethlehem Steel B1365	3312	Coke Prod.				30.8%	NT	62%	.1%			49.5%	1.4%				
5. SCM Adrian Joyce B1435	2816	Inorganic Pigment				51.2%	13.3%	3.3%	NS								
Phase III																	
1. Badische A101	2824 2299	Synthetic Fibers	4/16/81	NT										NT			
2. Va. Chemicals A109	2811 2819 2869	Inorg. & Organ. Chem.	4/23/81	NT			24%							NT			
3. Atlantic Wood Preservers B112	2491	Wood Preserving	4/20/81	80%										30%			
4. Amer. Tobacco B111	2621	Tobacco Processing	4/9/81				NT										

PLANT NAME	S/C Code	INDUSTRY TYPE	Date of Sampl.	FISH BIOASSAY		INVERTEBRATE BIOASSAY		ALGAL BIOASSAY						MARINE BACTER.	SEAGRASS THALASSIA	MUTAGENIC and CYTOTOXIC EFFECTS	
				MIN-NOW 96 Hr LC50	SHEEPS-HEAD 96 Hr LC50	DAPHNIA LC50 48NC	MYSID 96 Hr LC50	SELENASTRUM EC50 4 day	SC20 4 day	SC20 4 da	EC50 14 da	SKELETONOMA 96 Hr EC50	96 Hr SC20	MICRO-TOX		AMES	CHO
5. E. I. DuPont - Spruance B113	2821 2829	Synthetic Resins & Fibers	4/7/81	NT										NT			
6. ICI Americas B117	3079	Poly-ester Film & Plastics	4/8/81	17.5%			NT							12%			
7. Phillip Morris B1240	2111	Tobacco Prods.	4/8/81				59%										
8. HRSD - Western Branch C150	4952	POTW	4/27/81	48%										5%			
9. VEPCO-Dutch Corp. C151		Elec-tric Power	4/13/81				56%										
0. Smith-Douglas Div. Borden Chem. C1530		Phos-phate Fert.	4/21/81		NT									NT			
11. Royster Co. C1540		Ammonia Fert.	4/30/81				5%										
12. HRSD - Boat Harbor 1550	4952	POTW	4/22/81				15%										
13. HRSD - Lamberts Point 1560	4952	POTW	4/28/81	24%										.7%			
14. Rich-mond STP 1580	4952	POTW	4/13/81				87%										

PLANT NAME	S/C Code	INDUSTRY TYPE	Date of Sampl.	FISH BIOASSAY MIN-NOW 96 Hr LC50	FISH BIOASSAY SHEEPS-HEAD 96 Hr LC50	INVERTEBRATE BIOASSAY DAPHNIA LC50 48NC	INVERTEBRATE BIOASSAY MYSID 96 Hr LC50	ALGAL BIOASSAY SELENASTRUM EC50 4 day	ALGAL BIOASSAY SELENASTRUM SC20 4 day	ALGAL BIOASSAY SC20 4 da	ALGAL BIOASSAY EC50 14 da	ALGAL BIOASSAY SKELETONOMA 96 Hr EC50	ALGAL BIOASSAY SKELETONOMA 96 Hr SC20	MARINE BACTER. MICRO-TOX	SEAGRASS THALASSIA	MUTAGENIC and CYTOTOXIC EFFECTS AMES	MUTAGENIC and CYTOTOXIC EFFECTS CHO
15. Smithfield Pack. C159		Meat Processing	5/4/81	42%										5%			
16. Sheller Globe C160		Fabricated Rubber	4/15/81	NT										NT			
17. Portsmouth STP C161	4952	POTW	4/29/81	97%			10%										
18. Hopewell Regional, STP C163		POTW	4/9/81	59%										56%			
19. HRSD, Williamsburg C164		POTW	4/14/81	7%										2%			
20. Amer. Recovery B142S	4963	Waste Neutralization					4%										
21. Allied Chem. C157	2821 2824		4/14/81				77%										
22. Patapsco, STP B141S	4952	POTW					3%										
23. Tennecox B133	2821	Plasticizers					41%										
24. SCM-Adrian Joyce B1435	2816	Inorg. Chems.					22%										
25. Allied Chem. C1695	2879						12%										
26. SCM - St.Helena B126S	2816	Inorg. Oxides					21%										

PLANT NAME	S/C Code	INDUSTRY TYPE	Date of Sampl.	FISH BIOASSAY		INVERTEBRATE BIOASSAY		ALGAL BIOASSAY						MARINE BACTER.*	SEAGRASS THALASSIA	MUTAGENIC and CYTOTOXIC EFFECTS	
				MIN-NOW 96 Hr LC50	SHEEPS-HEAD 96 Hr LC50	DAPHNIA LC50 48NC	MYSID 96 Hr LC50	SELENASTRUM EC50 4 day	SC20 4 day	SC20 4 da	EC50 14 da	SKELETONOMA 96 Hr EC50	96 Hr SC20	MICRO-TOX		AMES	CHO
27. Armco B1475	3312	Stainless Steel Mfg.					54%										
28. Eastern Stainless Steel B1495		Stainless Steel Mfg.					21%										

APPENDIX F

RESULTS OF FISH BIOASSAYS FOR EFFLUENT SAMPLES BY SPECIES

Toxicity Index	Fathead Minnow	Sheepshead Minnow	Totals
Minimal 75-NT^{2}*	14	3	17
Low	3		3
Moderate 25-49	2		2
High 0-24	3		3
Totals	22	3	25

^{*2} NT is not toxic; a 100% effluent concentration did not kill 50% of the test species.

APPENDIX G.

RESULTS OF INVERTEBRATE BIOASSAYS FOR EFFLUENT SAMPLES BY SPECIES

Toxicity Index	Daphnia (Magna)	Mysid Shrimp	Total
Minimal 75-NT^{2}*	9	18	27
Low 50-74	2	8	10
Moderate 25-49	2	4	6
High	2	11	13
Totals	15	41	56

*NT^{2} is not toxic; a 100% effluent concentration did not kill at least 50% of the test species.

APPENDIX H.

RESULTS OF BACTERIAL AND GRASS BIOASSAYS

Toxicity Index	Microtox (Marine Bacteria)	Thalassia (Sea Grass)
Minimal 75-NT	5	6
Low 50-74	1	
Moderate 25-49	1	
High	5	
	12	6

APPENDIX I.

RESULTS OF SALMONELLA/MICROSOMAL ASSAYS FOR MUTOGENICITY OF CHESAPEAKE BAY EFFLUENT SAMPLES

Plant Number/Sample	Spot Test	Plate Incorporation
Filtrate I*		
A101	(-) negative	(-) negative
A102	(-) negative	(-) negative
A103	(-) negative	(-) negative
A104	(-) inconclusive	(-) negative
A106	(-) negative	(-) negative
A107	(-) negative	(-) negative
A108	(-) negative	(+) positive
A109	(-) negative	(-) negative
Filtrate II**		
A100	0	-
A105	-	-
A110	-	-
Particulate *** - Acetone Extract		
A100	Not performed	negative
A101	Not performed	negative
A102	Not performed	negative
A103	Not performed	negative
A104	Not performed	negative
A105	Not performed	negative
A106	Not performed	negative
A107	Not performed	negative
A108	Not performed	negative
A109	Not performed	negative
A110	Not performed	negative

* Filtrate I - Filtrate from initial filtering through a .45 u filter.

** Filtrate II - Filtrate I passed through a 0.2 u filter.

*** Particulate - Material retained on polyester drain disc and a 5 u teflon filter.

APPENDIX J.

RESULTS OF MAMMALIAN CELL CLONAL ACUTE CYTOTOXICITY ASSAY

Neat Effluents Sterilized by Antibiotic Addition			Filtered Sterilized Effluents		Particulate Extract, Acetone Concentrate	
Sample Number	EC_{50},[a] pL/mL	Toxicity rating	EC_{50} pL/mL	Toxicity rating	EC_{50},[b] pL/mL	Toxicity rating
A100	150	L[c]	ND[d]		600	L
A101	ND		ND		ND	
A102	C[e]		200	L	ND	
A103	ND		200	L	700	VL[f]
A104	ND		250	L	ND	
A105	25	M[g]	ND		ND	
A106	45	M	200	L	300	L
A107	ND		ND		650	VL
A108	C		200		700	VL
A109	C		ND		ND	
A110	55	M	200		300	L

[a] Effective concentration at 50% killing

[b] Normalized to toxicity of particulate extracts recovered from 1,000 mL of neat sample.

[c] Low, 60-600 pL/mL.

[d] No toxicity found at highest concentration tested and with no contamination.

[e] Microbial contamination; toxicity not determined.

[f] Very low, 600PL/mL

[g] Moderate, 6-60PL/mL