MD. DEPARTMENT OF NATURAL RESOURCES
DRAFT FINAL REPORT ON
POLYNUCLEAR AROMATIC HYDROCARBONS
AND THE
CHESAPEAKE BAY

October 1986

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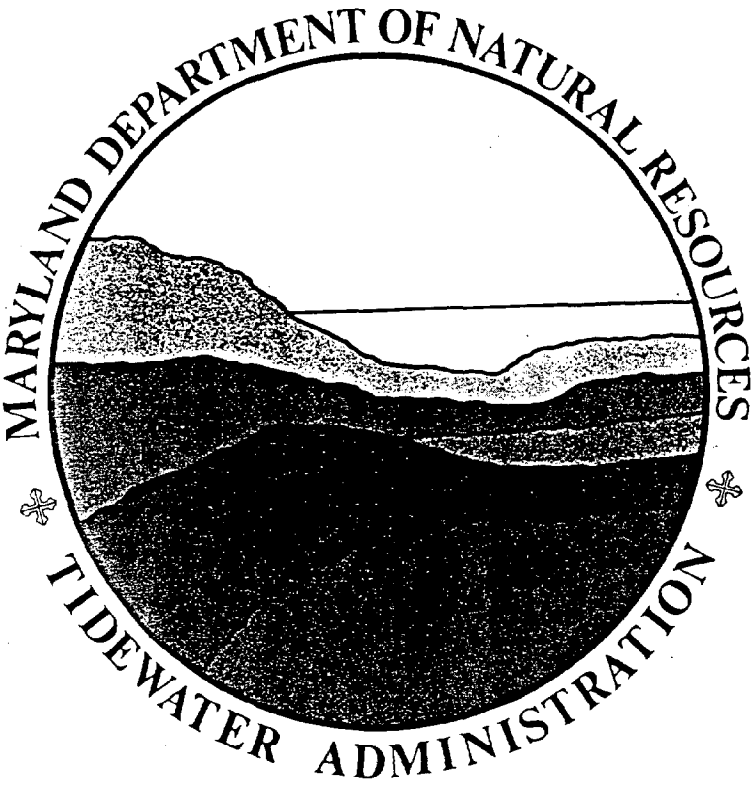

MARYLAND DEPARTMENT OF NATURAL RESOURCES

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FOREWORD

The Chesapeake Bay is a source of pride and abundant resources for the State of Maryland and its citizens. Responsible management and protection of those resources requires consistent, well-planned monitoring of water quality to identify and assess the effects of pollutants on aquatic plant and animal life.

The Maryland Department of Natural Resources is committed to the establishment of concrete knowledge about the types and sources of pollutants that are entering the Bay. The efforts of DNR in this regard are essential to an effective response to a pollution related emergency or imminent danger to any element of the Chesapeake Bay environment.

Torrey C. Brown, M. D.
Secretary
Department of Natural Resources

ABSTRACT

There are several research efforts underway to identify and assess the sources and effects of organic toxins in the Chesapeake Bay. As part of this effort, the Maryland Department of Natural Resources is committed to the detection and analysis of pollutant polynuclear aromatic hydrocarbons (PAH's) in the upper Bay area within the scope of its striped bass monitoring project.

Although research into the sources and effects of pollutant PAH's is in a preliminary phase, existing information about these compounds has provided a framework from which to develop study guidelines and goals that will lead to a better understanding with regard to the infusion of PAH's into the Chesapeake and their modes of action within the estuarine ecosystem. We know that PAH concentrations are abnormally high in some of the more developed areas of the Bay and that PAH exposure poses a potential danger to the Chesapeake's living resources and, ultimately, the human recipients of those resources. It is the extent of this threat and the mechanisms through which the potential harm is manifested that is not yet clear.

We are confident that the striped bass monitoring effort will produce information to help close the gap between general knowledge about PAH's and specific knowledge about PAH interactions in the Chesapeake Bay.

DNR is still awaiting 1986 field data on PAH concentrations in striped bass spawning reaches and in striped bass adult tissue and eggs. This data along with interpretation will be included in the final PAH report.

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ACKNOWLEDGEMENTS

Within the Maryland Department of Natural Resources, the Monitoring and Data Management Section of Tidewater Administration has prepared this draft report for submission to the National Oceanic and Atmospheric Administration under the terms of Grant No. NA-83-AA-H-CZ026. This grant provides substantial funding for the monitoring of PAH's in the Chesapeake Bay as part of NOAA's Coastal Energy Impact Program under its Office of Coastal Resource Management.

The text of this report was prepared by Julie Sobelman with technical input from Stephen Jordan, Chief of DNR's Monitoring and Data Management. We thank Candace Marsden for her textual and editorial assistance, and Linda Wall and Lorane Bruce for their typing assistance.

SUMMARY

The Chesapeake Bay has served man in a variety of ways for hundreds of years. It has and continues to provide recreational grounds for boating, fishing and hunting; water for industrial and agricultural uses; and a waterway for product transport. Anthropogenic activities, particularly those related to industry, have resulted in a significant chemical pollution problem caused, in part, by the release of polynuclear aromatic hydrocarbons into the Bay waters. A large portion of the PAH's that enter the Chesapeake are carried in sediments of the tributaries which feed into the Bay. Although the Bay can assimilate some of this material, most remains within the estuary. There is no doubt that the introduction of polynuclear aromatic hydrocarbons into the Chesapeake Bay poses a potential threat to the entire Bay ecosystem.

Initial steps in understanding the sources and mechanisms through which PAH's originate have been accomplished. PAH's have both natural and anthropogenic sources. Those that occur naturally in the aquatic environment are produced through the process of sedimentary diagenesis (the chemical and physical changes that take place in sediments during their conversion to rock), and biosynthesis (direct or indirect formation by aquatic microbes and plants).

Man-made PAH's are produced through pyrolysis at various temperatures in industrial heating processes. It is these pyrolytically produced PAH's, such as those generated during the combustion of fossil fuels, that have been found to account for the greatest contribution of PAH's to the aquatic environment.

Although the sources and structures of PAH's have been established, critical areas of concern remain unresolved. These areas have to do with the

extent and treatment of PAH contamination in the Bay and the impact of these contaminants on aquatic life and man.

Varying traces of PAH's have been detected in a broad range of aquatic organisms, and it has been determined that there is significant potential of bioaccumulation and magnification through food chains. Rates of uptake in aquatic materials and organisms are directly related to levels of concentration which have been found to be consistently higher in the urban and industrial areas of the Bay. Concentration levels are determined by the molecular and carbon makeup of naturally existing and pollutant PAH's in the water column. These structural makeups determine solubility and stability which, in turn, affect degree of concentration.

Just as there are considerable variations in both the sources and structures of PAH's, so too there are numerous routes by which these substances make their way into the aquatic environment. These include wastewater discharge and surface runoff, which account for proportionately large amounts of pollutant PAH's in the Bay, as well as casual spillage and atmospheric deposition.

Further experimental exploration is needed to determine, among other things, the mechanisms of PAH toxicity in the Chesapeake Bay through observation of PAH/PAH interaction and PAH reactions with other chemicals present in the water column. Testing of proposed treatment methods will aid in the discovery of legitimate anti-pollution procedures. Research of the early life stages of fish beginning with egg, larval and juvenile phases on through the entire life cycle will produce valuable information regarding the modes of PAH action and the effects of specific toxins on the reproduction of various

aquatic species. Finally, continued water and sediment monitoring is necessary to establish seasonal trends in PAH concentrations in the Bay. Current data is inadequate to draw any conclusions in this area.

Continued and extensive efforts in the areas noted are essential in light of the reciprocal relationship that exists between the Chesapeake Bay and the populace.

I. BACKGROUND

PAH Formation

Polynuclear Aromatic Hydrocarbons (PAH's) originate by one of three mechanisms: pyrolysis, sedimentary diagenesis or direct biosynthesis by microbes and plants. For each method of formation, there are different sources, reactions, and product PAH's.

Pyrolytic formation occurs when organic matter is expoosed to a broad range of high temperatures. Anthropogenic activities, such as the coking of coal and coal tar production, yield PAH's at temperatures from 1400-2000^{o}C. The scope of pyrolytic activity is so large, especially in urban and industrialized areas, that this mechanism appears to be the greatest contributor of pollutant PAH's to the aquatic environment.

Sedimentary diagenesis produces PAH's in fossil fuel sources such as petroleum, natural gas, minerals including idrialite and curtisite, and coal. Temperatures associated with these formation processes are low, probably less than 150^{o}C, with reactions occurring over long periods of time.

Biosynthesis of PAH's by microbes and plants is a controversial issue. Pigments in sea lilies and sea urchins contain PAH's which apparently are synthesized by the organisms (Blumer, 1976). There are data indicating that benzopyrene accumulates through bacterial synthesis in amounts of 2-6 ug/kg of dried material. Aliphatic and aromatic hydrocarbons produced by phytoplankton in the ocean may be as high as 3 tons/year (Andelman, 1970). Nonacosane, a PAH compound present in crude oil, is derived from terrigenous

plant material (Boehm, 1984). Neff (1979) reported data indicating that bacterial biosynthesis of benzo (a) pyrene and perylene may depend on growth medium. Specific substrates such as fatty acids may be necessary for bacteria to carry out PAH synthesis. Hase and Hites (1976) suggest that bacteria do not produce PAH's but bioaccumulate them from their environment. The possibility exists that blanks used in other experiments caused a lack of sensitivity and, therefore, apparent biosynthesis was actually an artifact.

All organic compounds containing carbon and hydrogen may serve as precursors of PAH. PAH such as benzo(a)pyrene could be formed from a simple C_2 unit being gradually built up by a series of free radical combinations. Most proposed mechanisms involve chain lengthening reactions followed by cyclization, possibly followed by degradation. For examples of pathways of PAH formation refer to Table 1 and Figure 1. Table 1 shows a variety of PAH's formed at various temperatures.

Structure Vs. Origin

Several relationships seem to exist between PAH origin and structure. By definition, PAH's consist of two or more fused benzene rings which may be arranged in linear, angular or cluster forms (Blumer, 1976). Of the three arrangements, those of the linear type, as found in naphthalene or anthracene, are the least stable. Greater stability is found in the cluster arrangement of compounds such as pyrene and benzopyrene. Phenanthrene is an example of an angular arrangement which, of the three, has the most stable ring organization. Overall stability in arrangement is relative to the amount of strain placed on the bond angles between carbon and hydrogen molecules found in

TABLE 1. Products from pyrolysis of malic acid, observed at various temperatures

	500°	600°	700°	800°	900°
Benzene	+	+	+	+	+
Toluene	+	+	+	+	+
Indene	+	+	+	+	+
Biphenyl			+	+	+
Naphthalene			+	+	+
Ethylbenzene } m-,p-Xylene }			+	+	+
Styrene } a-Styrene }			+	+	+
Dimethylnaphthalene					+
Acenaphthylene				+	+
Anthracene (Phenanthrene)				+	+
Fluorene				+	+
Pyrene					+
Chrysene					+
Phenol	+	+	+		
m-Cresol	+	+	+		
p-Cresol	+	+	+	+	
o-Cresol	+	+	+	+	
2,5-Xylenol		+	+	+	
Fumaric acid	+	+	+		
Succinic acid	+	+			+

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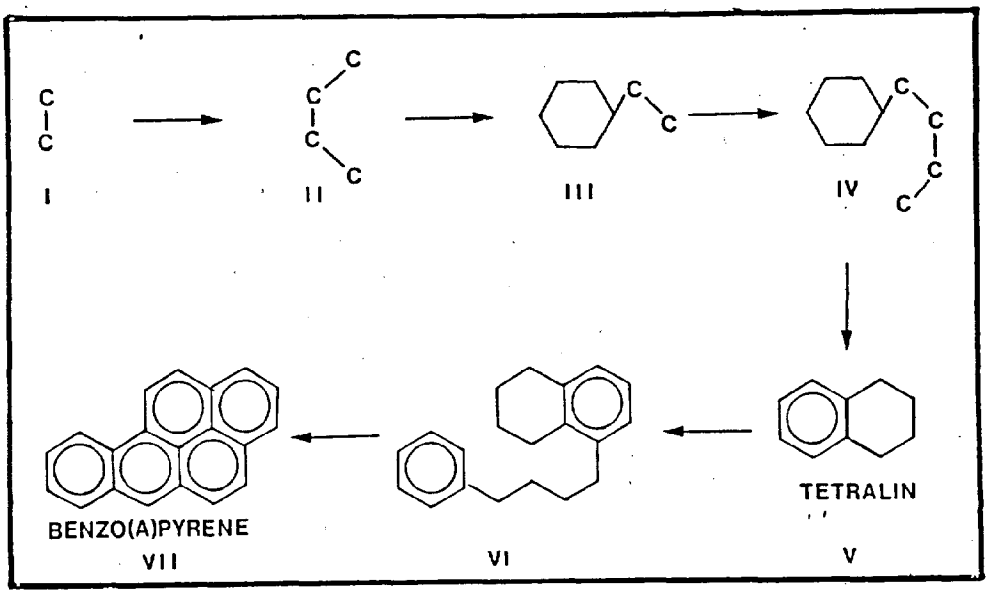


Figure 1. Proposed reaction scheme for PAH formation.

(from Crittenden, B. D. and Long, R. 1976. Copyright permission pending).

the benzene ring. If rings bind to each other in such a manner that is energetically difficult to maintain, the molecules will be more prone to find an arrangement of lesser stress.

In petroleum, PAH's consist of a homologous series of compounds in which the methyl and higher alkyl-substituted isomers significantly outnumber the parent hydrocarbons. Aromatic hydrocarbons from the combustion of fossil fuel or wood, however, contain certain predominant amounts of the parent hydrocarbon (Boehm, 1984). This relationship is probably related to differences in the formation temperatures for the two processes. Blumer (1976) noted that the abundance of side chains increases with decreasing temperatures of production and that the average number of five-member rings around an aromatic nucleus is greater in petroleum than in PAH's formed at higher temperatures. This observation was also noted in diesel engines where the total number of alkylated PAH's increases as the cylinder temperature decreases (Jensen, 1983).

Regardless of origin, lower molecular weight three- and four-ring structures are produced in greater quantities than five- and seven-ring PAH (Mix, 1984). Rings with no side chains (alkyl groups) are most common.

Structure Vs. Activity

The chemical structure of PAH's lend to the many ways they interact both alone and with other substances in the environment. PAH's tend to be both hydrophobic and lipophylic in nature. In the aquatic environment, PAH's are relatively low in water solubility and readily available for uptake into fatty tissues of organisms, or binding to humic substrates.

Compounds of higher molecular weight persist longer than those of lower molecular weight (Hinga, 1980). The number of chemical bonds and the strength

of those bonds which need to be broken in order to separate or degrade the substance provides a possible explanation for this phenomenon. Phenanthrene and higher molecular weight alkylated naphthalenes are removed from sediments at a slower rate than lower molecular weight naphthalene and 2-3 carbon alkyl naphthalenes. Higher molecular weight compounds have a longer residence time than lower molecular weight compounds once incorporated into animal tissues (Farrington, 1980). In general, two- and three-ring PAH have been shown in laboratory studies to be acutely toxic to aquatic organisms (Mix, 1984).

Many authors allude to a correlative relationship between higher solubility of low molecular weight PAH and greater acute toxicity. So little is actually known, however, about the mechanisms of PAH toxicity that relationships of this type are more on the order of theoretical ideas than concrete facts. Table 2 lists some PAH's along with their relative solubilities and LC50 values. According to Mix (1984), all of the proven PAH carcinogens contain 4-6 rings.

Table 3 includes a number of PAH's along with their carcinogenic potency. Although some PAH's are carcinogenic by nature, others may be activated to a highly carcinogenic form in the presence of specific conditions. This may take place through a two-step oxidation process with the eventual formation of a dihydrodiol epoxide (Cassarett, 1980). Higher molecular weight polycyclic and heteroaromatic compounds possess the greatest potential for bioaccumulation, as well as carcinogenic and mutagenic effects in aquatic animals and man, and acute toxicity to aquatic organisms (Giesy, undated). One mechanism through which carcinogenicity or mutagenicity may be achieved is by direct binding of PAH to DNA. This could cause a crosslinkage of bases which may produce cancer or mutation (Josephson, 1984).

TABLE 2. Solubility and LC50 for several PAH's

Compound	Solubility observations mg/L	LC50(ppm) 96hr
Naphthalene	20 ± 2	3.8
2-6-Dimethylnapthalene	2.4 ± .5	2.6
Fluorene	.8 ± .2	1.0
Phenanthrene	.6 ± .1	.6
Fluoranthene	.1 ± .06	.5

LC50 values represented are for the marine polychaete (Neanthes araceodentata).

(Adapted from Neff, J. M., 1979.)

TABLE 3. Polynuclear aromatic hydrocarbons in the water environment

List of PAH compounds

Compound	Carcinogenic[a] potency	Empirical formula
anthracene	?	$C_{14}H_{10}$
alkylfluoranthene	?	
acenaphthylene		$C_{12}H_8$
alkylpyrene	?	
anthanthrene	-	$C_{22}H_{12}$
1,2-benzanthracene	+	$C_{18}H_{12}$
3,4-benzfluoranthene	++	$C_{20}H_{12}$
10,11-benzfluoranthene	++	$C_{20}H_{12}$
11,12-benzfluoranthene	-	$C_{20}H_{12}$
3,4-benzpyrene	+++	$C_{20}H_{12}$
1,2-benzpyrene	±	$C_{20}H_{12}$
1,12-benzperylene	-	$C_{22}H_{12}$
chrysene	+	$C_{18}H_{12}$
coronene	-	$C_{24}H_{12}$
1,2,5,6-dibenzanthracene	+++	$C_{22}H_{14}$
9,10-dimethyl-1,2-benzanthracene	(active)	$C_{20}H_{16}$
fluorenthene	-	$C_{16}H_{10}$
fluorene	-b	$C_{13}H_{10}$
indeno (1,2,3-cd)pyrene	+	$C_{22}H_{12}$
3-methylcholanthrene	(active)	$C_{21}H_{16}$
phenanthrene	?	$C_{14}H_{10}$
perylene	-	$C_{20}H_{12}$
pyrene	-	$C_{16}H_{10}$
triphenylene	-	$C_{18}H_{12}$

[a]Potency notation: +++, active; ++, moderate;+,weak;-,inactive;?, unknown. (Compounds labelled "active" are so listed by several authors). The notation is taken from Hoffman & Vynder (1962).

[b]Reference from Graf & Nowak (1966).

(from Andelman, J. B. et al. 1970, with permission of the publisher, World Health Organization)

II. PAH'S IN THE AQUATIC ENVIRONMENT

Routes of Entry and Distribution

The modes of PAH transport into the aquatic environment are as diverse as their sources and structure. The various routes of entry include wastewater discharge, surface runoff, casual spillage and atmospheric deposition. Different circumstances affect PAH entry into the water via various routes. Interms of relative quantity and distribution, spillage may release large amounts of PAH's into the water causing a local increase in PAH concentration in and around the area where the substance, usually oil or gas, has been spilled or has seeped out. Spillage may occur anywhere in the aquatic environment, from a boat docked near shore, to a drilling station in the middle of the ocean.

Both wastewater discharge and surface runoff make significant contributions to local PAH levels in rivers, estuaries, and coastal marine waters. Sources which contribute to these routes of entry are almost all anthropogenic, and are found largely in urban industrialized areas. Tables 4, 5 and 6 provide examples of PAH distribution from various routes of entry and land use areas. Higher PAH concentrations from discharge and runoff are due to an increase in sources which feed these routes of entry (Hamilton, 1984; Farrington, 1980). Weather conditions such as heavy rainfall may cause an increase in PAH's entering the aquatic environment via wastewater discharge, surface runoff and atmospheric deposition. Most of the aquatic PAH burden remains relatively close to the source of PAH deposition and concentrations can be expected to decrease approximately logarithmically with distance from the source (Neff,

TABLE 4. Estimated inputs of benzo[a]pyrene and total PAH to the aquatic environment from various sources

Sources	Input in metric tons/year	
	BaP	total PAH
Biosynthesis	25	2700
Petroleum spillage	20-30	170000
Domestic and industrial wastes	29	4400
Surface runoff from land	118	2940
Fallout and rainout from air	500	50000
Total input	697	230040

(from Neff, J. M. 1979, with permission of the publisher, Applied Science Publishers Ltd.)

TABLE 5. Input rate, million metric tons/year (mta)

Source	Probable Range	Best Estimate*
Natural Sources		
Marine Seeps	0.02 - 2.0	0.2
Sediment Erosion	0.005 - 0.5	0.05
Total Natural Sources	0.025 - 2.5	0.25
Offshore Production	0.04 - 0.06	0.05
Transportation		
Tanker Operations	0.4 - 1.5	0.7
Drydocking	0.02 - 0.05	0.03
Marine Terminals	0.01 - 0.03	0.02
Bilge and Fuel Oils	0.2 - 0.6	0.3
Tanker Accidents	0.3 - 0.4	0.4
Non-Tanker Accidents	0.02 - 0.04	0.02
Total Transportation	0.95 - 2.62	1.47
Atmosphere	0.05 - 0.5	0.3
Municipal and Industrial Wastes and Runoff		
Municipal Wastes	0.4 - 1.5	0.7
Refineries	0.06 - 0.6	0.1
Non-Refining Industrial Wastes	0.1 - 0.3	0.2
Urban Runoff	0.01 - 0.2	0.12
River Runoff	0.01 - 0.5	0.04
Ocean Dumping	0.005 - 0.02	0.02
Total Wastes & Runoff	0.585 - 3.12	1.18
TOTAL	1.7 - 8.8	3.2

(from Farrington, J. W. 1985)

TABLE 6. Chemical distribution of PAHs in urban runoff from four different land uses (mean percentage of sum of 14 quantified PAHs)

	Residential	Commercial	Industrial	Highway
naphthalene	0.2 ± 0.2	5.6 ± 9.9	1.8 ± 2.3	0.7 ± 0.7
2-methylnaphthalene	3.3 ± 5.4	3.0 ± 3.7	1.3 ± 1.2	1.2 ± 1.2
1-methylnaphthalene	2.1 ± 3.5	3.4 ± 4.7	1.1 ± 1.5	0.6 ± 0.8
biphenyl	0.4 ± 0.4	1.7 ± 2.9	0.2 ± 0.3	0.5 ± 0.8
2-ethylnaphthalene	0.02 ± 0.03	1.4 ± 2.4	1.3 ± 1.6	0.8 ± 1.1
fluorene	0.2 ± 0.3	1.3 ± 1.7	7.8 ± 11.5	2.9 ± 4.2
dibenzothiophene	0.2 ± 0.2	3.0 ± 5.2	3.3 ± 2.1	1.5 ± 2.3
phenanthrene	3.7 ± 3.0	12.4 ± 7.0	10.6 ± 6.3	15.8 ± 15.6
fluoranthene	33.6 ± 4.0	20.4 ± 7.9	21.5 ± 6.3	33.6 ± 2.2
pyrene	19.8 ± 5.6	16.5 ± 10.3	19.2 ± 12.3	19.3 ± 15.5
benz[a]anthracene	4.9 ± 1.9	4.8 ± 3.6	22.9 ± 22.2	8.7 ± 10.3
chrysene	7.7 ± 8.1	11.2 ± 14.9	1.6 ± 2.9	3.5 ± 6.0
benzo[e]pyrene	13.3 ± 12.8	5.8 ± 4.6	3.2 ± 4.6	3.8 ± 2.4
benzo[a]pyrene	10.9 ± 11.2	8.9 ± 11.4	5.6 ± 5.0	3.0 ± 2.9

(from Hoffman, E. J. et al. 1984. Copyright permission pending.)

1979). Weather conditions such as heavy rainfall may cause an increase in PAH's entering the aquatic environment via wastewater discharge, surface runoff and atmospheric deposition.

Atmospheric deposition is the primary means of PAH distribution and dispersion. Winds can carry PAH particulates for miles, depositing them in all reaches of the aquatic environment. PAH's from natural sources such as forest and prairie fires, along with those from industrial and exhaust emissions may be transported via this route.

Estimates of total PAH's entering the aquatic environment are variable, ranging from 230,000 metric tons/year (Neff, 1979), 3.2 million metric tons/year (NAS, 1985-from Farrington, 1985), to $1\text{-}10 \times 10^6$ tons/year (Calder, 1976) (Tables 4 & 5).

What happens to these compounds once they reach the water? Where do they go? PAH's are partitioned into different compartments in the aquatic environment. Relative concentrations are highest in sediments, intermediate in aquatic biota, and lowest in the water column (Neff, 1979).

PAH's In Sediments

Sediments seem to be the ultimate "sink" for PAH's. These settled materials contain insoluble particulates which enter the water column and are unavailable for uptake by biota. For example, PAH of pyrogenic origin pass through other components of the ecosystem and accumulate in sediments (Farrington, 1985). Sediments also contain particulates from the water column, including phytoplankton, detritus and zooplankton (Lee, 1978). Concentration of PAH is greater by a factor of 1,000 or more in sediments than in overlying water (Neff, 1979). PAH concentration in urban industrialized associated sediments are generally higher than those in sediments more remote from urban

areas. This divergence in PAH concentration levels for industrialized and non-industrialized regions is largely attributable to combustion processes. Estimates have revealed higher concentrations of 1 or more orders of magnitude in industrial areas (Farrington, 1985). Both Mix (1984) and Boehm (1984) have noted that combustion processes are the source of most, but not all, of the PAH incorporated into sediments.

Fine grained sediments such as silts and clays tend to contain higher concentrations of organic compounds than coarse sediments. Boehm (1984) noted higher concentrations of PAH in sediments with high silt/clay ratios. The organic carbon content of substrates such as sediments and soils seems to cause increased sorption of PAH. PAH's found in sediments with high silt/clay ratios, and high levels of organic carbon, are dominated by compounds from combustion (pyrogenic) sources.

Surface sediments seem to be more highly enriched in PAH than deeper sediments. Wakeham (1980) estimates that PAH concentration levels range by a factor 5-50 times higher in surface sediments than deeper layers. Recent increases in anthropogenic sources of input associated with human activities, and more widespread industrialization are the most probable explanations for this phenomenon. PAH in deeper layers is apparently derived from early diagenetic processes (Wakeham, 1980).

PAH's In The Water Column

The most important physical properties influencing PAH concentrations in the water column are their solubility and stability. In general, PAH solubilities can be related to their non-polar structure. An inverse relationship seems to exist between solubility and molecular weight; decreased solubility occurs as molecular weight increases (Rossi, 1978) (Neff, 1979).

PAH's appear to have even lower solubilities in seawater due to "salting out." Table 7 illustrates the relationship between salt concentration and solubility (Eganhouse, 1976). PAH-PAH interactions as well as PAH reactions with other chemicals in water affect overall solubility. Both naphthalene and phenanthrene work to enhance the solubility of acenapthylene, while biphenyl and phenanthrene together exhibit mutual solubility reduction (Neff, 1979). Micelles formed in the water by synthetic detergents increase PAH solubility (Andelman, 1970). The presence of surfactants in the range of 10-50 mg/l increase PAH solubility from 2-10 times as shown in laboratory studies; however, these surfactant concentrations are rare in natural waters (Andelman, 1974).

Another physical property of significance in the understanding of PAH/water interactions is the partition coefficient, which expresses the equilibrium concentration ratio of an organic liquid (e.g. octanol) and water. The partition coefficient may also be useful as a means to predict soil adsorption, lipophilic storage, biological uptake, and biomagnification (Chiou, 1977). A trend seems to exist between increasing molecular weight and higher partition coefficients, as seen in Table 8, which shows the octanol/water partition coefficients for several PAH's. This is in agreement with the relationship between increasing molecular weight and decreasing water solubility noted previously.

Transformation and Degradation

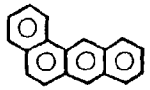
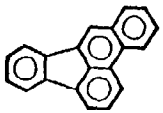
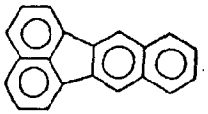
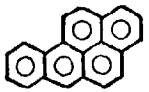
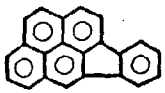
PAH's in the aquatic environment may be transformed or degraded through a variety of mechanisms. In the water column, photooxidation plays a major role in PAH transformation. Photooxidation is most effective for removal of high molecular weight PAH (Lee, 1978) for which transformation requires short

TABLE 7. Relationship between salt concentration (ppt) and solubility (mg/L)

	0 ppt	35 ppt
naphthalene	31.3 ± .4	22.0 ± .293
biphenyl	7.45 ± .1	4.76 ± .060
phenanthrene	1.07 ± .01	.71 ± .025

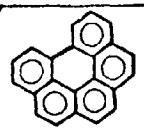
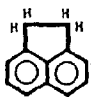
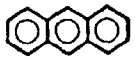
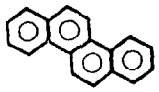
(from Eganhouse, R. P. and Calder, J. A. 1976. Copyright permission pending)

TABLE 8. Physical property data for 16 EPA priority PAH

Compound	Structure	Molecular Weight	Solubility in Water (25°C) mg/L	Log Octanol/Water Partition Coefficient	Biodegradability
Benzo-a-anthracene		228.3	.014	5.61	not significantly degraded
Benzo-b-fluoranthene		252.3	.0012	6.57	not available
Benzo-k-fluoranthene		252.3	.00055	6.84	not available
Benzo-a-pyrene		252.3	.0038	6.04	not available
Ideno-1,2,3-c,d-pyrene		276.3	.62	7.66	not available

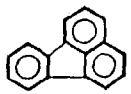
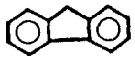
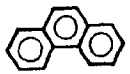
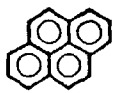
(continued)

TABLE 8 (continued)

Compound	Structure	Molecular Weight	Solubility in Water (25°C) mg/L	Log Octanol/Water Partition Coefficient	Biodegradability
Benzo-ghi-perylene		276	.00026	7.23	not available
Acenaphthene		154.2	3.42	4.33	significant degradation rapid adaptation
Acenaphthylene		152.2	3.93	4.07	significant degradation rapid adaptation
Anthracene		178.2	.073	4.45	significant degradation gradual adaptation
Chrysene		228.3	.002	5.61	not significantly degraded

(continued)

TABLE 8 (continued)

Compound	Structure	Molecular Weight	Solubility in Water (25°C) mg/L	Log Octanol/Water Partition Coefficient	Biodegradability
Fluoranthene		202.3	.26	5.33	significant degradation gradual adaptation
Fluorene		166.2	1.98	4.18	significant degradation gradual adaptation
Naphthalene		128.2	34.4	3.37	significant degradation rapid adaptation
Phenanthrene		178.2	1.29	4.46	significant degradation gradual adaptation
Pyrene		202	.14	5.32	significant degradation rapid adaptation

(Adapted from U. S. EPA Treatability Manual, EPA-600/2-82-001a, February 1983)

wavelengths of light capable of penetrating only a few meters. The photoreactivity of PAH adsorbed to the surface of particulates in the water column appears greater than those found in solution (Neff, 1979). Low molecular weight PAH's may be removed from the aquatic environment by evaporation from surface waters. Evaporation is considered to be one of the main routes of transformation for low molecular weight PAH (Lee, 1978).

Giesy (undated) found photolytic degradation to be the most important pathway of flux within channels studied both experimentally and in simulations. There appear to be discrepencies, however, between field and lab studies. Ultraviolet light from the sun, which was shown to degrade PAH in lab experiments, proved to be of minor importance to PAH degradation in field experiments.

Treatment of PAH Contamination

Ozonation,, chlorine disinfection and filtration are among the methods under consideration for treating PAH contamination. Ozonation has been found to be an effective treatment for the removal of PAH in water (Andelman, 1974). At 25°C and pH 7, half lives for pyrene, phenanthrene, and benzo(a)pyrene are .18, .44, and 1.00 seconds, respectively, at normal O_3 concentrations (10^{-4}M; Butkovic, 1983).

Chlorine disinfection is another method under consideration for PAH removal. However, there is evidence that some component(s) in waste water effluent may react with chlorine to yield more toxic compounds than were present in the original effluent (Pickering, 1983).

Filtration through activated carbon, followed by ozonation, is currently thought to be the most effective PAH removal method. Although these methods

may be impractical for widespread application, they may be useful in wastewater treatment, thereby alleviating one source of PAH to the natural environment.

III. INTERACTIONS BETWEEN PAH AND AQUATIC BIOTA

PAH's in Aquatic Biota

PAH's affect aquatic biota in a variety of ways. Their non-polar hydrophobic structure makes PAH's relatively high in lipid solubility which may allow for easier entry through cell membranes and collection in fatty tissues. As a method of measurement, concentrations of various organic compounds accumulated in fish are determined largely by fish lipid content (Chiou, 1985). PAH's have been found in a broad range of aquatic biota including bacteria, algae, phytoplankton, zooplankton, shellfish, and finfish. Thus, significant potential for bioaccumulation and magnification through food chains exists. Concentrations in organisms from polluted sites tend to be greater than those found in non-polluted sites. Mussels from environments containing higher PAH concentrations themselves showed higher PAH concentrations. Initial rates of hydrocarbon uptake in oysters is directly related to hydrocarbon concentrations up to at least 450 ug/l (Stegeman, 1973). Tables 9 and 10 give PAH concentration data for various marine organisms.

Aquatic animals contribute to PAH transformations in a variety of ways. One means of helping to eliminate PAH's from their environment is through physical mixing of buried oiled sediments which brings them to the sediment surface where there is greater chance of resuspension, solubilization, and more oxic conditions favorable to microbial attack. By pumping water through sediments, organisms may accelerate solubilization, allowing for removal of more soluble components, and may introduce oxygen into deeper sediments (Wakeham, 1980). Some marine fish have a detoxification system (mono-function

TABLE 9. Concentrations of selected PAH in the tissues of oysters, Crassostrea virginica, from the harbor of Norfolk, Virginia, USA

Compound	Approximate concentration (ug/kg wet weight)
Fluoranthene	600-1000
Pyrene	100-160
Chrysene	20-40
Benz[a]anthracene	<10
Benzo[k]fluoranthene	8-12
Benzo[a]pyrene	2-6
Benzo[e]pyrene	<20
Benzo[ghi]perylene	1-5

(from Neff, J. M. 1979, with permission of the publisher, Applied Science Publishers Ltd.)

TABLE 10. Summary of PAH hydrocarbons in marine tissues (ppb, wet weight)

	Location, lat., long.	Depth, m	Benz(a) anthracene	Benzo(a) pyrene	Pyrene	Methyl-pyrene	Other PAH's*	Dry Wt./ Wet Wt.
Summer flounder (Paralichthys dentatus)	37°53.5'N, 74°10.6'W	102	<1	<1	2	1	1.1-1.5	0.21
Scup (Stenotomus chrysops)	38°11.4'N, 74°09.1'W	66	<1	<1	2	<1	<1-<3	0.26
Black sea bass (Centropritus stricta)	38°33.2'N, 74°0.5.0'W	57	<1	<1	<1	<1	<0.1-<1	0.23
Butterfish (Paprilus triacanthus)	38°37.7'N, 74°18.5'W	39	<20	<5	<1	<2	<2-<13	0.29
Sea scallops (Placopeskin magellianicus)	38°47.0'N, 73°22.8'W	78	1.1	<1	4.1	2.7	<5-8.7	
Red hake (Arophysate chuss)	38°47.0'N, 73°22.8'W	78	0.3	<11	<5	<6	<2-9	

* Includes fluoranthene, chrysene, triphenylene, benzo(e)pyrene, and perylene

(from Brown, R. A. et al. 1979. Copyright permission pending).

oxidase) which renders PAH water-soluble. These soluble PAH are returned to the water via urine (Lee, 1972a). Crustaceans also seem to have the ability to metabolize and discharge petroleum hydrocarbons in a less dangerous form (Lee, 1976).

Microbial degradation also plays a major role in PAH transformation. Degradation of PAH's by microbial action seems to be more rapid near the surface than in deeper layers (Hinga, 1980; Floodgate, 1972). This mechanism works on both low and high molecular weight compounds but is a more predominant source of degradation in high molecular weight hydrocarbons after sedimentation (Lee, 1978). Degradation usually occurs during the stationary phase of bacterial growth.

Among the first scientists to study microbial degradation of PAH's was Zobell in 1946. His studies showed that microbes could degrade PAH's under both aerobic and anaerobic conditions, and that degradation by aerobes appears equally good at any oxygen concentration in the range of .1-20 or 30 mg/l. The temperature range for bacterial oxidation tends to vary. Zobell's experiments showed bacteria to be more active at 30-37°C than at 20°C, whereas Mitchell (1974) stated that decomposition occurs between a 5°C low and 25°C optimum.

Generally, the following rules seem to apply to PAH degradation regardless of mechanism: 1) PAH degrade faster in aqueous solutions than in pure organic solvents or crystalline form; and 2) higher temperatures, oxygen concentrations, and light intensities yield faster rates of degradation for certain PAH as do increased flow velocity and greater particle surface area (Andelman, 1970).

PAH Toxicity to Marine Organisms

Bacteria and PAH's interact on a variety of levels. Some may be involved with PAH synthesis or degradation, while others are themselves adversely affected by PAH's. In some bacterial strains PAH's decrease growth rate and maximum cell density. Inherent toxicity increases inversely with PAH solubility (Calder, 1976; Table 11).

Bacteria are only the beginning of a long list of organisms which exhibit toxic and other detrimental effects from exposure to PAH. PAH's may inhibit filtering ability in mussels (Lee, 1972b). DiSalvo (1975) discussed the fact that a potential mechanism of PAH release was in mussel eggs, which were found to be particularly enriched compared to total body burden. Studies have yet to be done to determine the effects of PAH on gestation.

In copepod populations, exposure to PAH's reduced the lifespan and egg production by 25% (Corner, 1975). Copepods, along with most other organisms, accumulate PAH's in "fatty tissues". Corner suggests that since lipid levels in copepods vary with season, so too may rates of hydrocarbon release. Here again exists a potential problem for offspring. Female copepods carrying eggs usually have higher lipid levels (possibly related to season of mating), thereby creating an environment for higher PAH levels which, in turn, could be transmitted to eggs. Again, it is not certain what effect this has upon gestation. Females initially exposed to PAH levels in excess of 1 mg/l become narcotized. Narcotization is reversible upon transfer to fresh seawater; however, mortality increases with increased length of exposure. Exposure to

TABLE 11. Effect of aromatic hydrocarbons on bacteria (Properties of hydrocarbons studied)

Hydrocarbons	Mol wt	(A) Solubility[a] (M)	(B) Δ %/ umole[b]	(C) Toxicity[c] index
Naphthalene	128.16	2.43×10^{-4}	0.4	97
2-Methylnaphthalene	142.19	1.73×10^{-4}	2.1	363
2,6-Dimethylnaphthalene	156.22	0.83×10^{-5}	12.8	106
Phenanthrene	178.22	0.66×10^{-5}	4.0	26
Pyrene	202.24	0.73×10^{-6}	170	124
Benzopyrene	252.3	0.30×10^{-7}	881	>26
2,3-Dihydroxynaphthalene	160.16	$>16.5 \times 10^{-4}$	.68	>1,120

[a] In distilled water at 25°C, 1 atm.

[b] Average Δ% (decrease in bacterial densities relative to controls) per umole of PAH.

[c] $C = AxB \times 10^6$.

(from Calder, J. A. et al. 1976, with permission of American Society for Microbiology. Author permission pending.)

TABLE 12. Effect of long-term, low-level exposure to ^{14}C-1-naphthalene on feeding and egg production of adult female Eurytemora sp.

		Control	Naphthalene concentration 10 ugl.$^{-1}$	50 ugl.$^{-1}$
Mortality during 10 days (%)		18	27	31
Ingestion rate (Isochrysis cells x 10^4 ingested female^{-1}24h^{-1})	x	3.39	3.40	4.33
	s	1.72	1.90	1.83
	n	10	10	10
Egg production (eggs female^{-1}24h^{-1})	x	2.83	3.07	3.39
	s	3.71	3.63	4.79
	n	10	10	10
Radioactivity in animal at end of 10 days exposure as naphthalene equivalents (ng female^{-1})	x	-	2.47	6.22
	s	-	0.33	1.69
	n	-	5	5

(x = mean, s = standard deviation, n = number of determinations).

(from Berdugo, V. 1977, with permission from Pergamon Journals, Inc. Author permission pending.)

TABLE 13. Toxicity of selected polynuclear aromatic hydrocarbons (PAH's) for Neanthes arenaceodentata. 96h TL_m values, 95% confidence limits, and corresponding slope functions were calculated by the method of Litchfield & Wilcoxon (1949). TL_m values are expressed as concentration (ppm) PAH initially present in test solution as determined by UV analysis. Values for chrysene, benzo(a)pyrene, and dibenzanthracene are not presented since these hydrocarbons were not lethal at the highest concentration tested (1ppm).

PAH	96 h TL_m	Confidence interval	Slope (TL_m/ppm)
Naphthalene	3.8	4.1-3.5	1.5
2,6-dimethylnaphthalene	2.6	2.9-2.3	1.4
2,3,6-trimethylnaphthalene	2.0	2.4-1.6	1.2
Fluorene	1.0	1.3-0.7	1.4
Phenanthrene	0.6	0.8-0.4	1.7
1-methylphenanthrene	0.3	0.4-0.2	1.1
Fluoranthene	0.5	0.7-0.3	1.2
Chrysene	-	-	-
Benzo(a) pyrene	-	-	-
Dibenzanthracene	-	-	-

*TL_m = median tolerance limits.

(from Rossi, S. S. 1978, with permission from Pergamon Journals, Inc. Author permission pending.)

concentrations of 1 mg/l naphthalene for 24 hours resulted in lower rates of egg production, fecundity and overall length of life (Berdugo, 1977; Table 12). Benzopyrene was found to be lethal to marine copepods (Calanus helgolandicus) at concentrations of 4 ppm (Lee, 1972).

Initial rates of hydrocarbon uptake in oysters are directly related to the hydrocarbon concentration of surrounding waters up to at least 450 ug/l. Oysters remained closed during exposure to concentrations of 900 ug/l. Some of the accumulated hydrocarbons in contaminated oysters were rapidly depleted upon transfer to clean seawater. The portion remaining was apparently retained in some stable compartment within the organism (Stegeman, 1973).

In the polychaete Neanthes arenaceodentata, toxicity appears to be related to both solubility and residence time in test solutions. A trend toward increasing toxicity with increasing molecular weight can be seen in the series naphthalene through fluoranthene (Rossi, 1978; Table 13).

The main routes of entry to fish are through the gills and gut. Anthracene in concentrations of approximately 12 ug/l was acutely toxic to bluegill sunfish, due to a phototoxic mechanism (Giesy, undated). Fin erosion and liver neoplasms have been reported in fish from highly contaminated sediment areas (Malins, 1984).

IV. PAH'S AND THE CHESAPEAKE BAY

Bay Geographics

The Chesapeake Bay holds the distinction of being the largest estuary on the Atlantic Coast of the United States. It lies in the coastal plain region along the Atlantic seaboard between the states of Maryland and Virginia and is

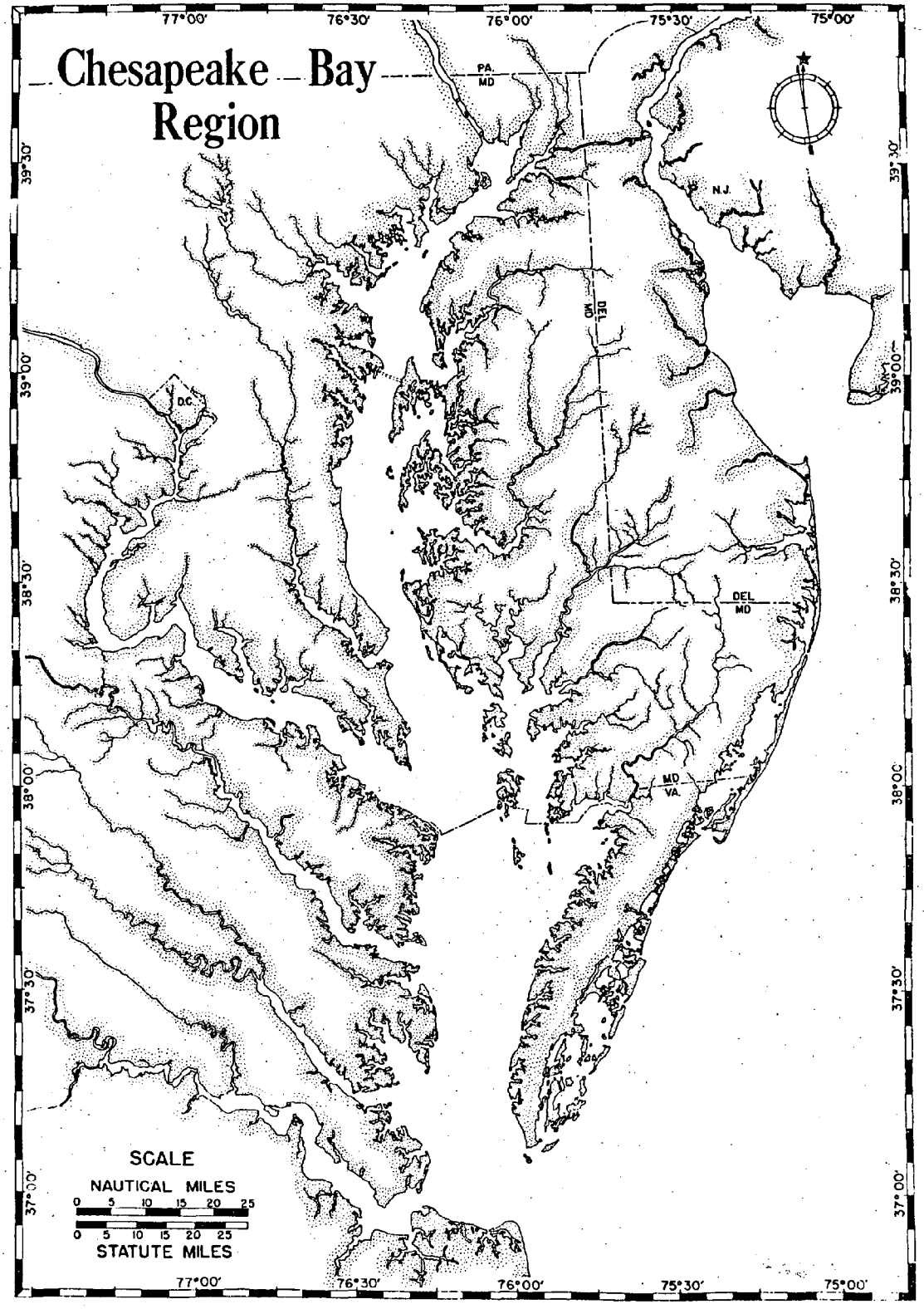


Figure 2. Physiographic map of Chesapeake Bay region.

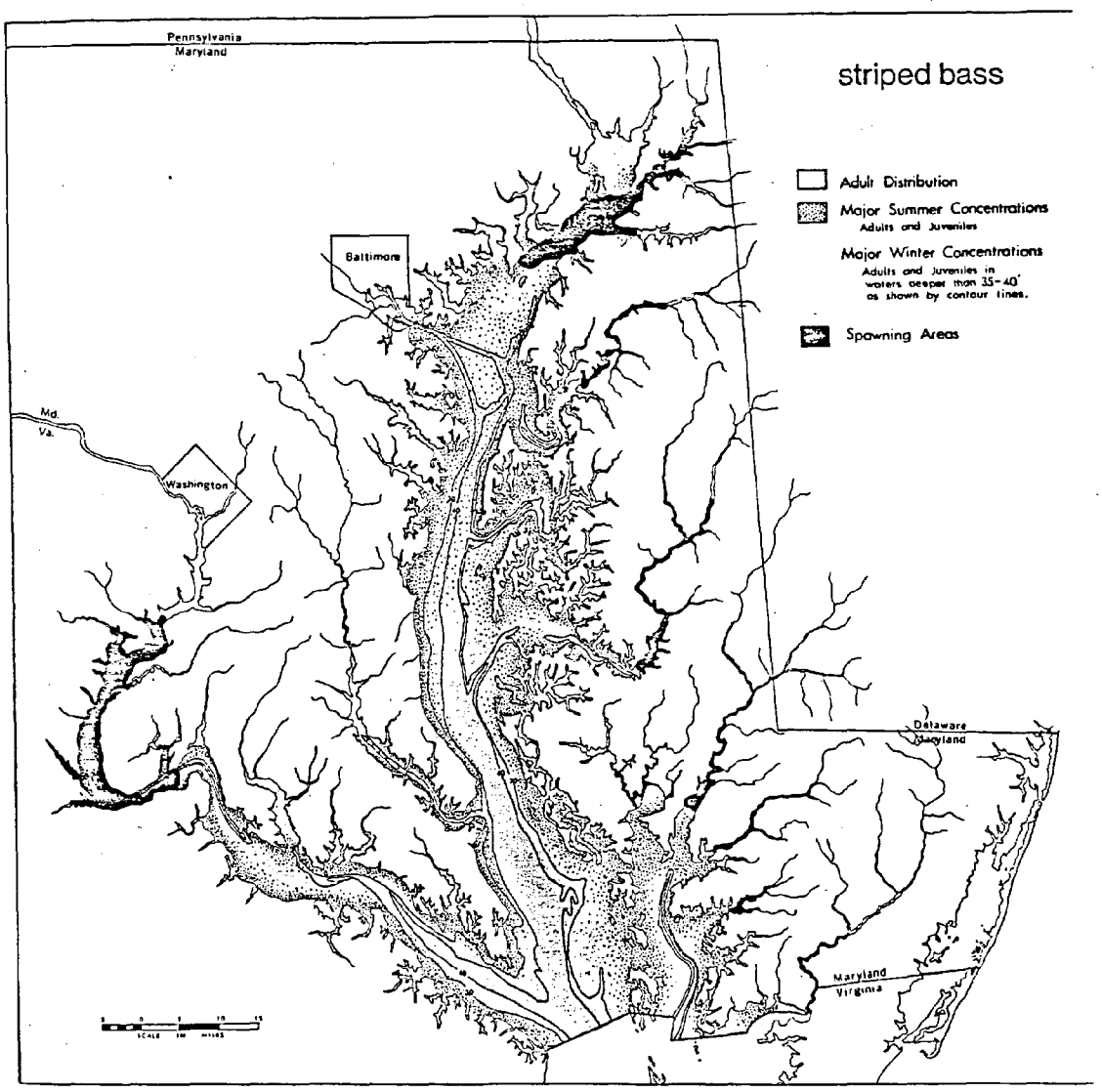


Figure 3. Striped Bass habitat and spawning reaches in the Chesapeake Bay.

(from The Chesapeake Bay in Maryland: An Atlas of Natural Resources, Johns Hopkins University Press, 1973. Copyright permission pending).

part of a drainage basin which includes Maryland, Delaware, Pennsylvania and portions of West Virginia and Virginia. Over 150 rivers, branches and tributaries flow into its waters. Figure 2 depicts the Chesapeake Bay region.

The estuary is a plentiful source of plant life, fish, and shellfish. There are approximately 326,000 acres of oyster bars and 250,000 acres of clam habitat in the Maryland portion of the Chesapeake. Figure 3 illustrates striped bass habitat and spawning reaches in the Maryland portion of the Chesapeake. The general distribution of oyster habitat along the Bay is shownin Figure 4. Besides the permanent biotic residents of the Chesapeake, the Bay area is a winter home for Canada geese and a spawning ground for many different types of marine organisms.

The land region around the northwest portion of the Chesapeake is highly developed, especially around the Potomac, Patapsco and portions of the Susquehanna River areas. Development along the eastern and southwestern shores is relatively sparse down to the southern tip of the Bay around Norfolk where another highly developed land area is found.

In and around the Chesapeake Bay region are petroleum and chemical industries, fossil fueled power plants (Figure 5), paper and paper pulp industries, fish processing industries, and iron smelting and refining. Much of the land in the lesser developed regions of the Bay is put to agricultural use.

PAH Studies in the Chesapeake

The Virginia Institute of Marine Science (VIMS) has, by far, done the most research on PAH's in the Chesapeake Bay region. Figures 6-9 are from a study conducted by VIMS showing PAH concentrations along the Chesapeake Bay. As

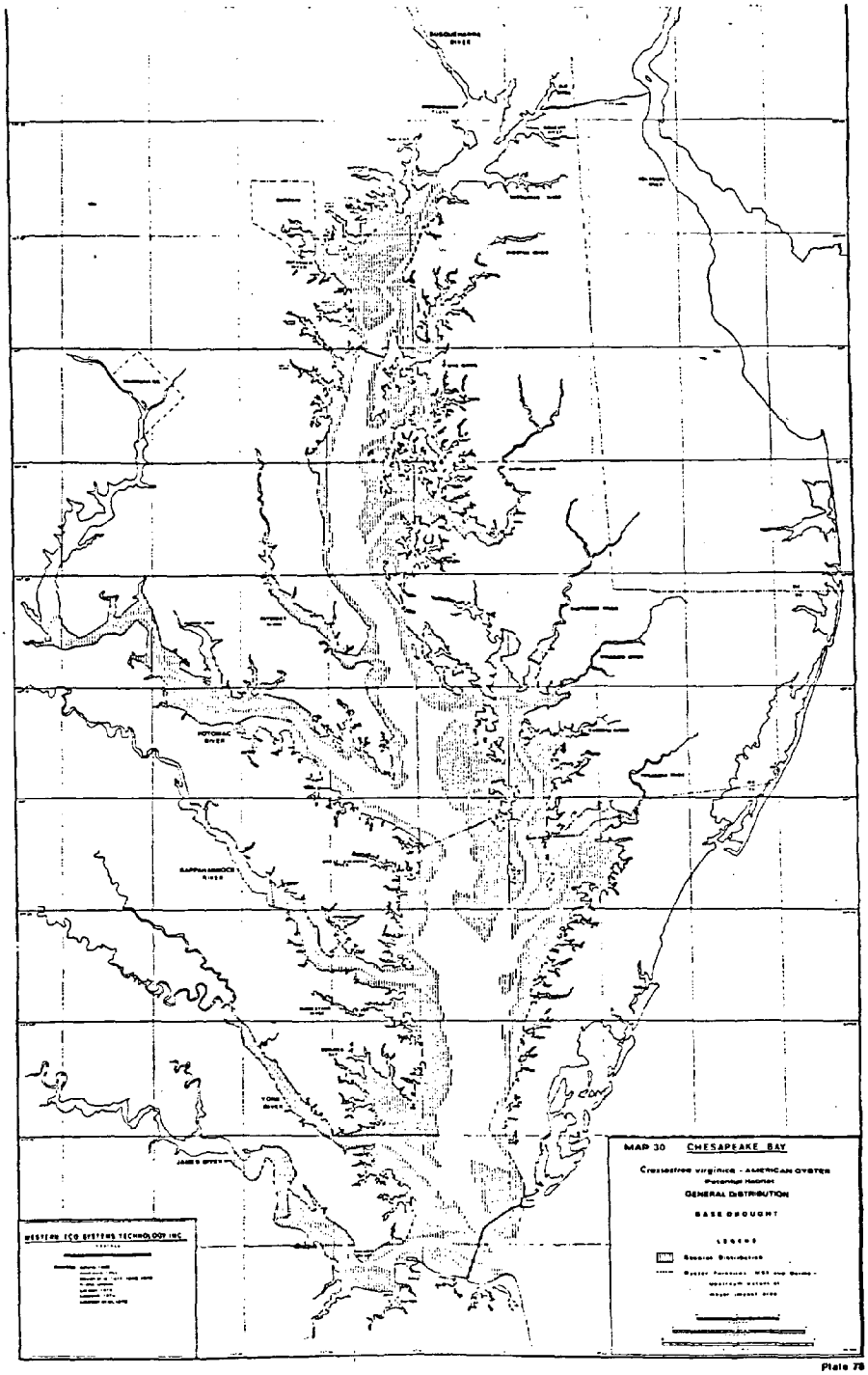
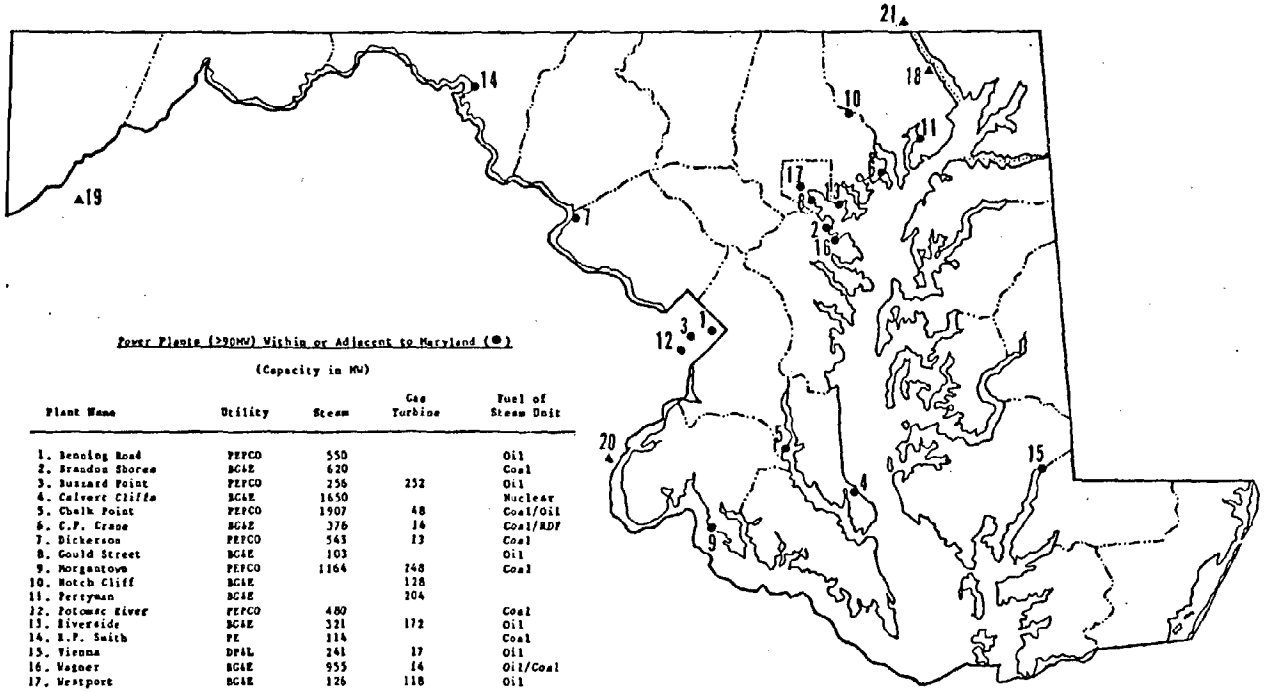


Figure 4. American oyster habitat in Chesapeake Bay region.
(from DNR Chesapeake Bay Low Freshwater Inflow Study Phase II Biota Assessment, May 1982)



Power Plants (>50MW) Within or Adjacent to Maryland (●)

(Capacity in MW)

Plant Name	Utility	Steam	Gas Turbine	Fuel of Steam Unit
1. Benning Road	PEPCO	550		Oil
2. Brandon Shores	BG&E	620		Coal
3. Buzzard Point	PEPCO	256	252	Oil
4. Calvert Cliffs	BG&E	1650		Nuclear
5. Chalk Point	PEPCO	1907	48	Coal/Oil
6. C.P. Crane	BG&E	376	14	Coal/RDF
7. Dickerson	PEPCO	543	13	Coal
8. Gould Street	BG&E	103		Oil
9. Morgantown	PEPCO	1164	748	Coal
10. Notch Cliff	BG&E		128	
11. Perryman	BG&E		104	
12. Potomac River	PEPCO	480		Coal
13. Riverside	BG&E	321	172	Oil
14. R.P. Smith	PE	114		Coal
15. Vienna	DP&L	241	17	Oil
16. Wagner	BG&E	955	14	Oil/Coal
17. Westport	BG&E	126	118	Oil

Plant Owned by Out-of-State Utilities (▲)

18. Conowingo	PECO	312		Hydro
19. Mount Storm	VEPCO	1695	16	Coal
20. Possum Point	VEPCO	1121	26	Coal
21. Peach Bottom	PECO	1800		Nuclear

Figure 5. **Frontispiece. Location of Power Plants in Maryland.**

(Power Plant Cumulative Environmental Impact Report for Maryland, Maryland DNR Power Plant Research Program, March 1986)

noted, there is a very strong correlation between heavy PAH concentration and high land development. The same is true for more industrialized regions of the Bay. Concentrations increase from the Potomac River North to Baltimore Harbor and again in the South near Norfolk, Virginia.

PAH contributors in the northern portion of the Bay are largely domestic sewage, as well as chemical and metal processing plant wastes. In the Norfolk area, especially in the Elizabeth River, the main source of PAH is attributed to now-abandoned wood treatment plants which used creosote (Bieri, 1983).

As mentioned before, sediments seem to house the majority of PAH's. The highest concentrations of organic chemicals in sediments found in the Chesapeake are in the Patapsco and Elizabeth Rivers. PAH concentrations are 1-90 ppm in the Patapsco and 1-over 100 ppm in the Elizabeth River (EPA, 1983).

Some of the problems caused by PAH contamination in the Patapsco and Elizabeth Rivers are changes in benthic community abundance, diversity and community structure. The two subject regions exhibit both low benthic diversity and abundance, and a dominant population of pollution-tolerant annelids, in comparison to non-polluted reference areas.

In a paper by Hargis (1984), results of a study were shown in which spot (Leiostomus xanthurus) were exposed separately to contaminated Elizabeth River sediments and non-contaminated James River sediments with PAH concentrations of 2,500 ppm and 1.2 ppm, respectively. Elizabeth River exposed fish showed: 1) penetrating integumental lesions within 8 days of exposure; 2) severe fin and gill erosion; and 3) severely reduced hematocrits. James River exposed fish showed none of these symptoms. In another study by Weeks (1984) Leiostomus xanthurus and Trinectes maculatus (hogchoker) were exposed to

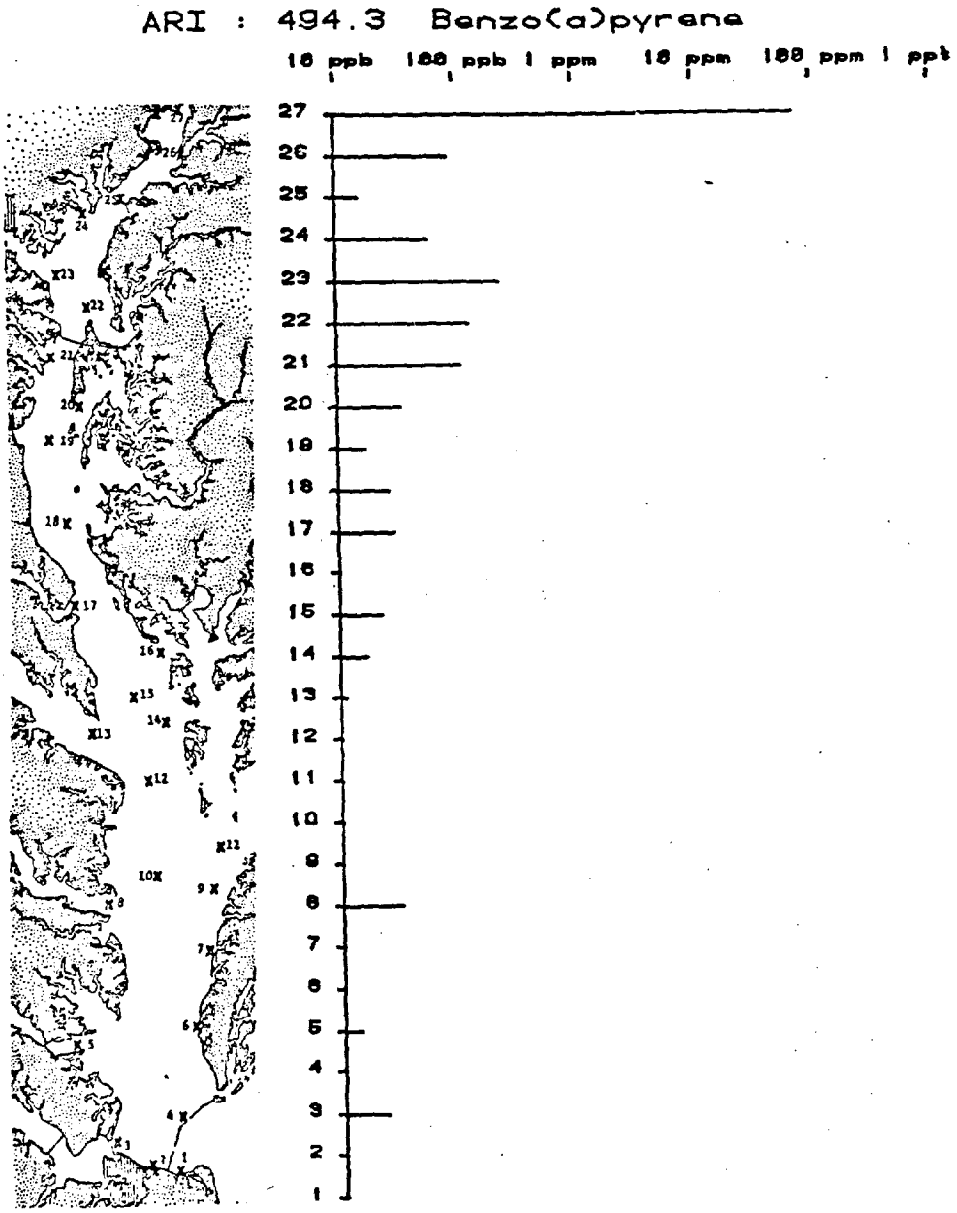


Figure 6. Benzo(a)pyrene in sediments, Fall 1979.

(from Bieri, R. H. et al. 1983)

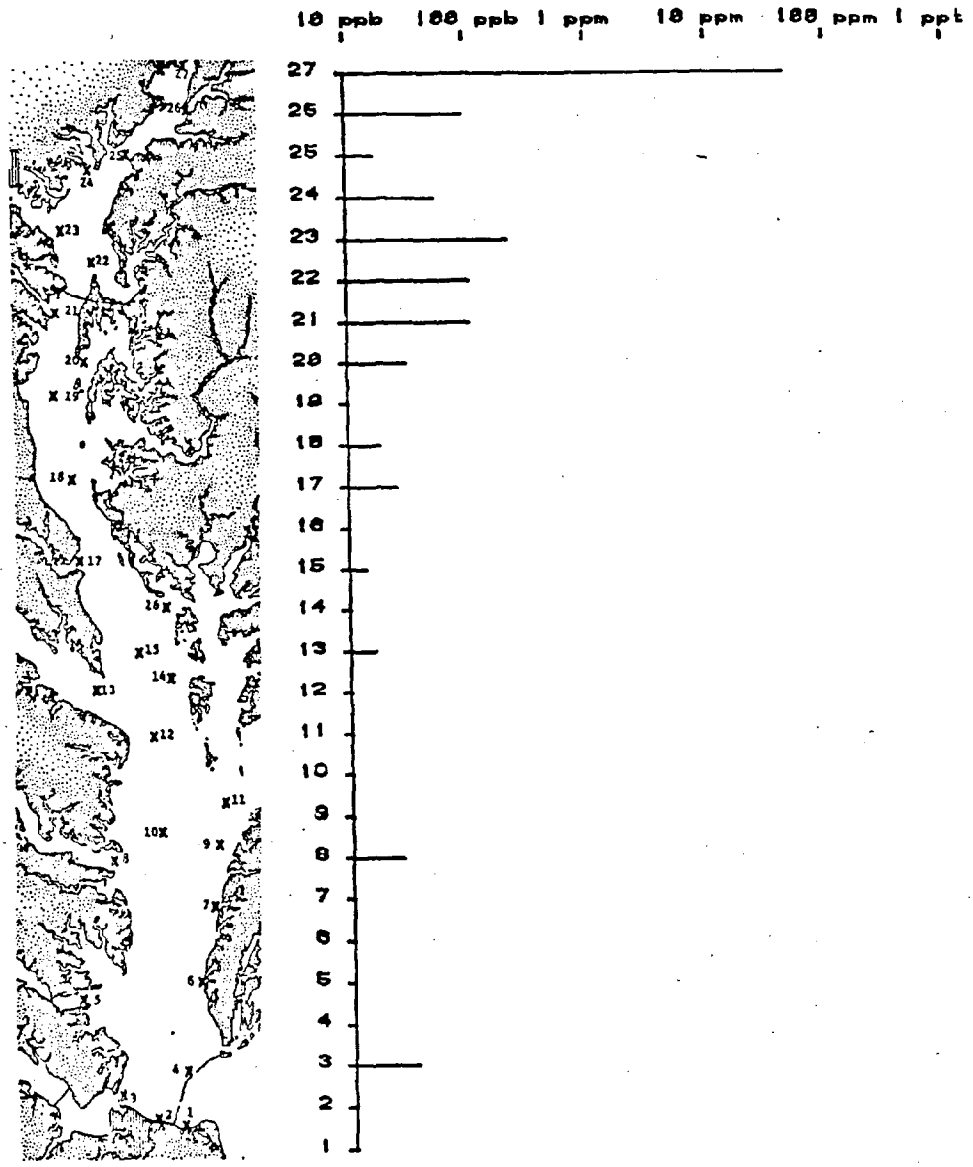


Figure 7. Benz(a)anthracene in sediments, Fall 1979.

(from Bieri, R. H. et al. 1983)

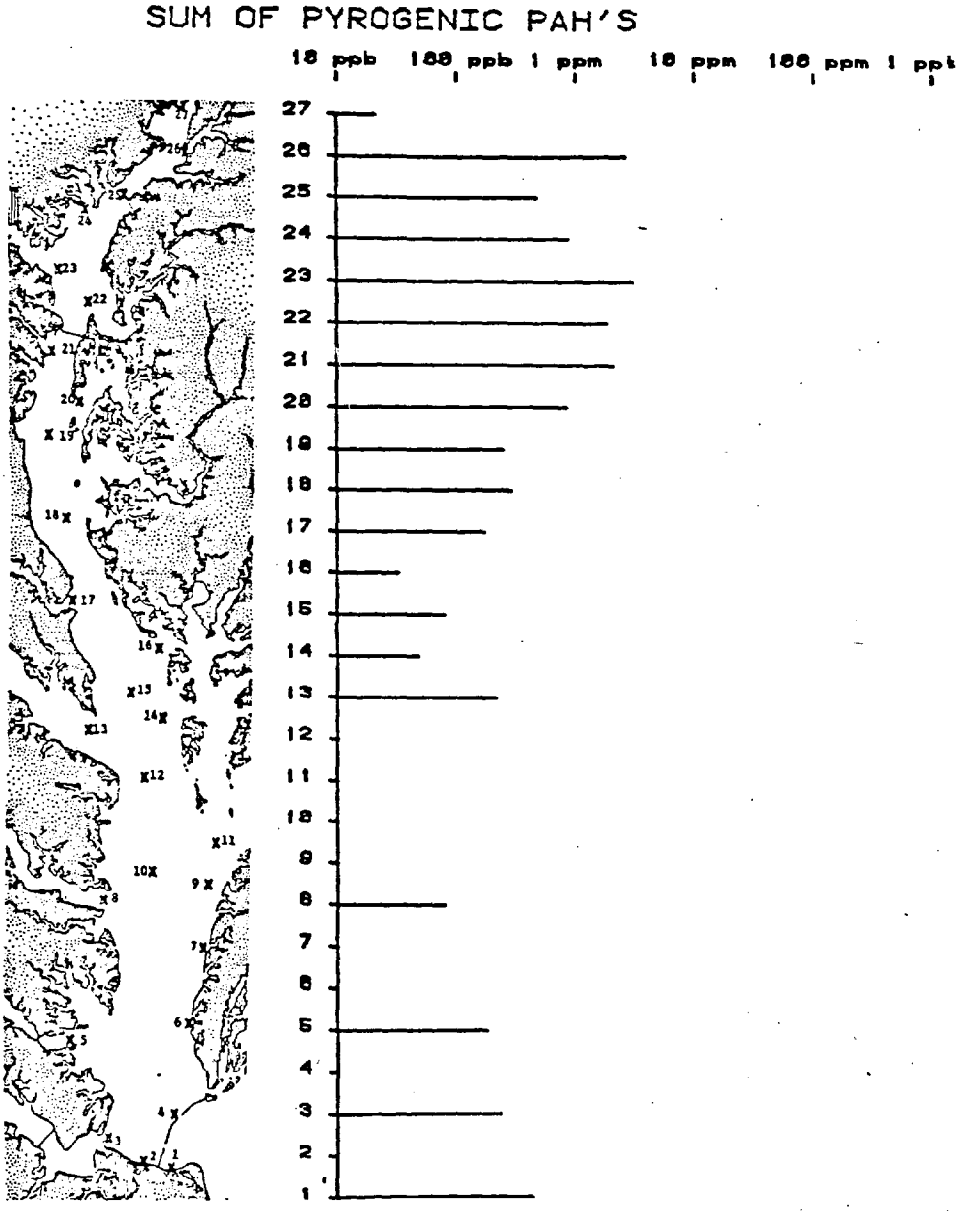


Figure 8. Sum of pyrogenic polynuclear aromatic hydrocarbons, Spring 1979.

(from Bieri, R. H. et al. 1983)

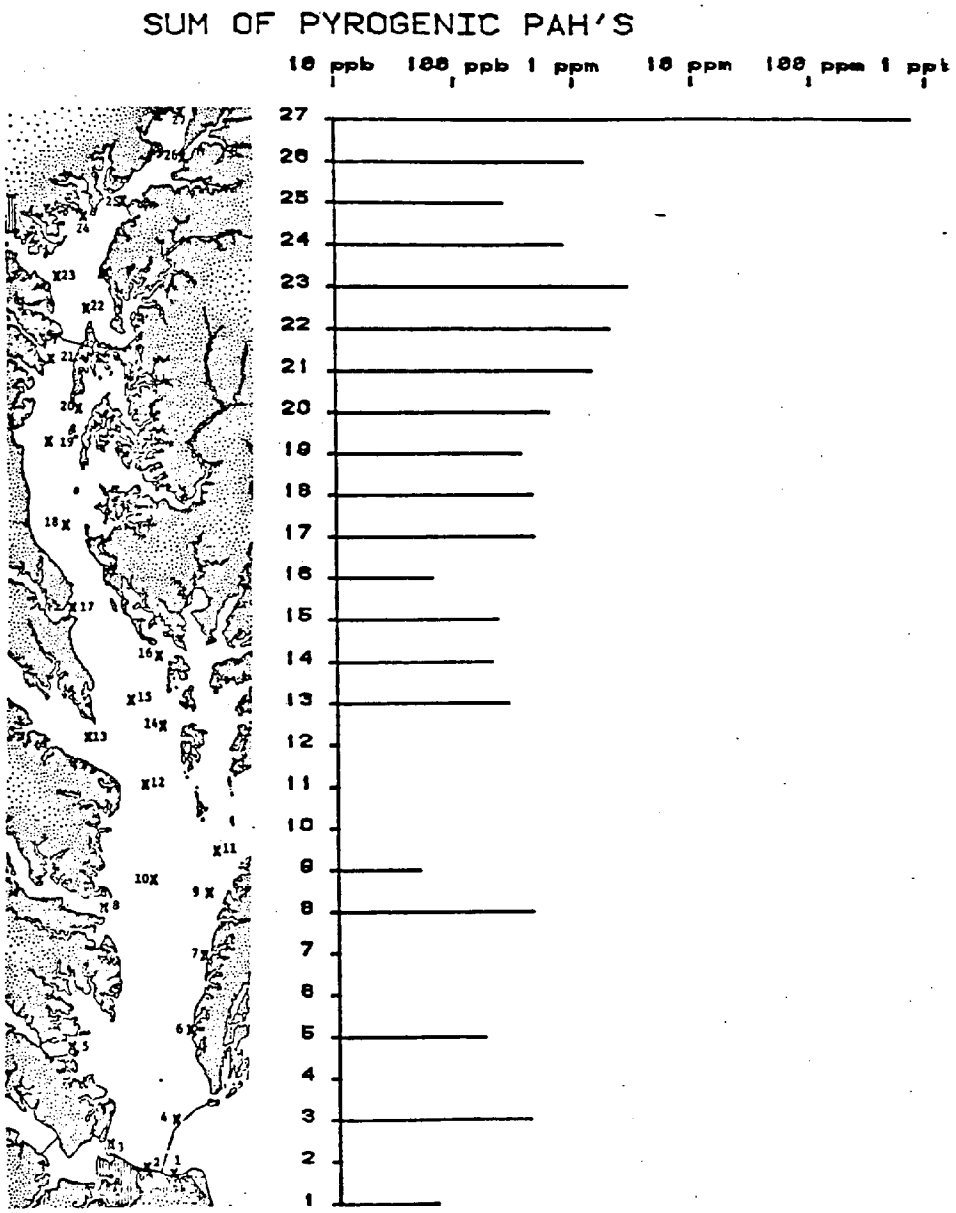


Figure 9. Sum of pyrogenic PAH's, Fall 1979.

(from Bieri, R. H. et al. 1983)

TABLE 14. PAH concentrations in sediment and water column samples around Hart and Miller Islands (August 1981)

Compound	Concentrations	
	Water column (ppb)	Sediments (ppm)
Naphthalene	<.04 - .05	<.0041 - .0098
Fluorene	<.04 - .12	.0061 - .207
Phenanthrene	<.04 - .07	.0061 - .0497
Anthracene	<.04 - .09	<.0007 - .0395
Fluoranthene	<.04 - .07	.0086 - .597
Pyrene	<.04 - .07	<.0098 - 1.429
Benzo(a)pyrene	<.04 - .07	<.0067 - 1.61
Benzo(a)anthracene	<.04	<.0098 - 1.69
Chrysene	<.04	<.0067 - .0923
Acenaphthylene	<.04	<.0040 - .0098

(Adapted from Chesapeake Research Consortium Data Report on Hart and Miller Islands, October 1982)

TABLE 15. PAH concentrations in crab and fish tissues from Hart and Miller Islands area (August 1981)

Compound	Organism	Concentration (ppb)
Naphthalene	Callinectes sapidus	<1.5 - 3.8
Fluorene	"	<3.0 - 10.6
Phenanthrene	"	<3.0 - 11.3
Anthracene	"	<3.0 - 12.1
Fluoranthene	"	<3.0 - 13.6
Pyrene	"	<3.0 - 15.2
Benzo(a)pyrene	"	2.3 - 9.8
Benzo(a)anthracene	"	<1.5 - 3.0
Chrysene	"	<1.5 - 15.2
Acenaphthylene	"	<3.0 - 9.8
Naphthalene	Morone americana	<1.5 - 33.3
Fluorene	"	<1.5 - 68.2
Phenanthrene	"	<1.5 - 68.2
Anthracene	"	<1.5 - 68.2
Fluoranthene	"	9.09 - 68.2
Pyrene	"	12.1 - 68.2
Benzo(a)pyrene	"	<1.5 - 68.2
Benzo(a)anthracene	"	<1.5 - 68.2
Chrysene	"	<1.5 - 68.2
Acenaphthylene	"	<1.5 - 68.2
Same As Above	Scolecolepides viridis	<403 - 4530
Naphthalene	Leiostomus xanthurus	<1.5 - 385
Fluorene	"	<1.5 - 385
Phenanthrene	"	<1.5 - 385
Anthracene	"	<1.5 - 385
Fluoranthene	"	5.3 - 385
Pyrene	"	5.3 - 385
Benzo(a)pyrene	"	<1.5 - 385
Benzo(a)anthracene	"	<1.5 - 385
Chrysene	"	<1.5 - 385
Acenaphthylene	"	<1.5 - 385

(Adapted from Chesapeake Research Consortium Data Report on Hart and Miller Islands, October 1982)

TABLE 16. PAH concentrations in Elk and Choptank Rivers and Baltimore Harbor (Maryland DNR Upper Bay survey)

Compound	Elk River		Choptank River	
	Seston	Sediment	Seston	Sediment
Acenaphthylene	.01 - .05	.008 - .01	.01	.02
Anthracene	.02 - .05	.001 - .03	.22	.02
Benzo(a)anthracene	.03 - .14	.004 - .04	.01 - .16	.10
Chrysene	.03 - .17	.01 - .04	.02 - .21	.12
Fluoranthene	.09 - .34	.05 - .19	.01 - .22	.31
Fluorene	.01 - .05	.01	-	-
Naphthalene	.07 - .15	.02 - .08	-	-
Phenanthrene	.09 - .19	.05 - .11	.02	.10
Pyrene	.10 - .33	.06 - .20	.02 - .29	.31

Baltimore Harbor Sediments
October 1983

Compound	Concentration (mg/kg)
Anthracene	.015 - .028
Benzo(a)anthracene	.027 - .087
Fluoranthene	.003 - .190
Phenanthrene	.016 - .053
Pyrene	.001 - .173

Elizabeth River conditions and Ware River controls. Elizabeth River exposed fish showed a marked reduction in macrophage phagocytosis compared to the control group; however, this activity returned to normal after fish were held in clean water for several weeks.

PAH concentration data is also available from a study conducted by the Chesapeake Research Consortium on Hart & Miller Island sediment, crab, fish and water column samples. This data is presented in Tables 14 and 15. This study confirmed findings from other studies in that PAH concentrations proved to be lower in the water column and higher in both biota and sediments. The highest overall concentrations from this data were found in Scolecolepides sp. This might have been due to higher lipid concentration, greater bioaccumulation, or the polychaete's inability to synthesize or degrade PAH's.

Table 16 contains data on PAH concentrations in the Elk and Choptank Rivers, and Baltimore Harbor sediments. These measurements were made by the Maryland Department of Natural Resources. Although PAH's were found in all of these areas, none were in concentrations as high as those in the the Elizabeth River region.

Water and sediment sampling data as presented do not cover an adequate span of time to draw any conclusions in terms of seasonal or long-term trends in PAH concentrations. Computer analyses of Maryland's DNR Elk and Choptank River sediment and seston studies show that concentrations were the same in both 1983 and 1984 in some cases, but in other instances, measurements fluctuated (Figures 10-13). It is important that this type of monitoring continue so that water quality trends concerning PAH's can be established.

Aside from the reported high PAH concentrations in the Patapsco and Elizabeth Rivers, data developed from studies in other regions of the Bay show

Figure 10. PAH's in Elk River Seston

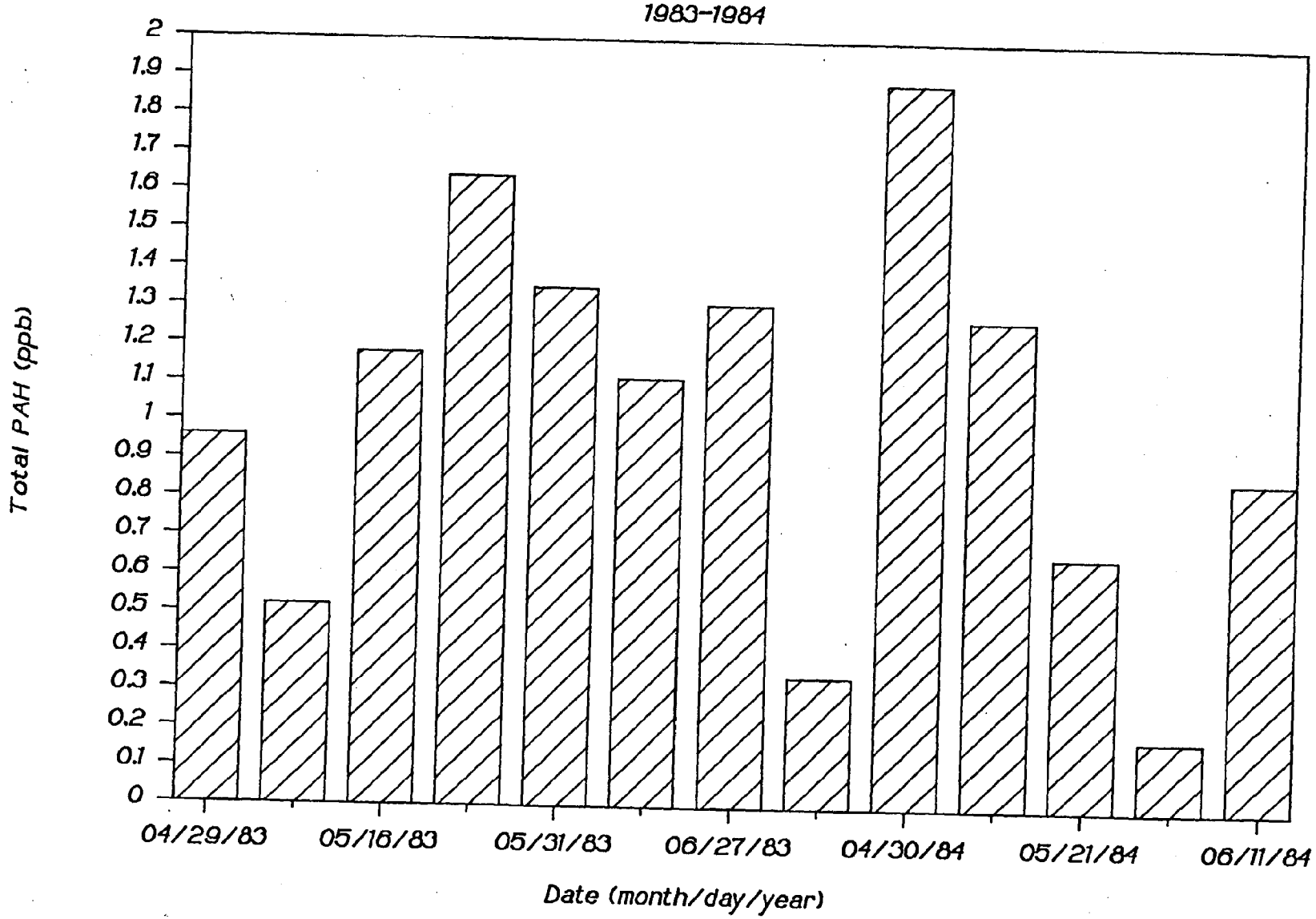


Figure 11. PAH's in Choptank River Seston; 1983–84

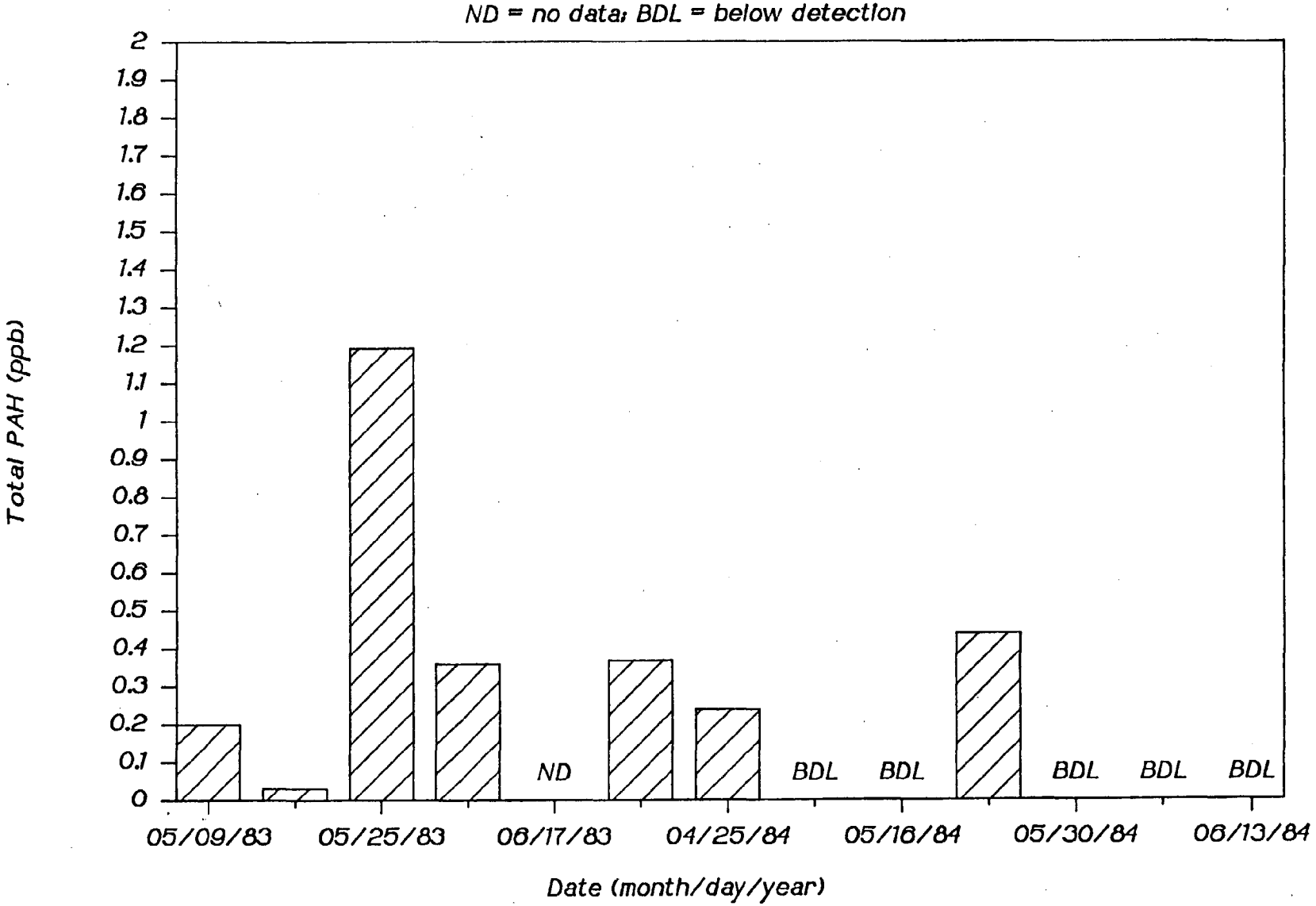


Figure 12. PAH's in Elk River Sediment

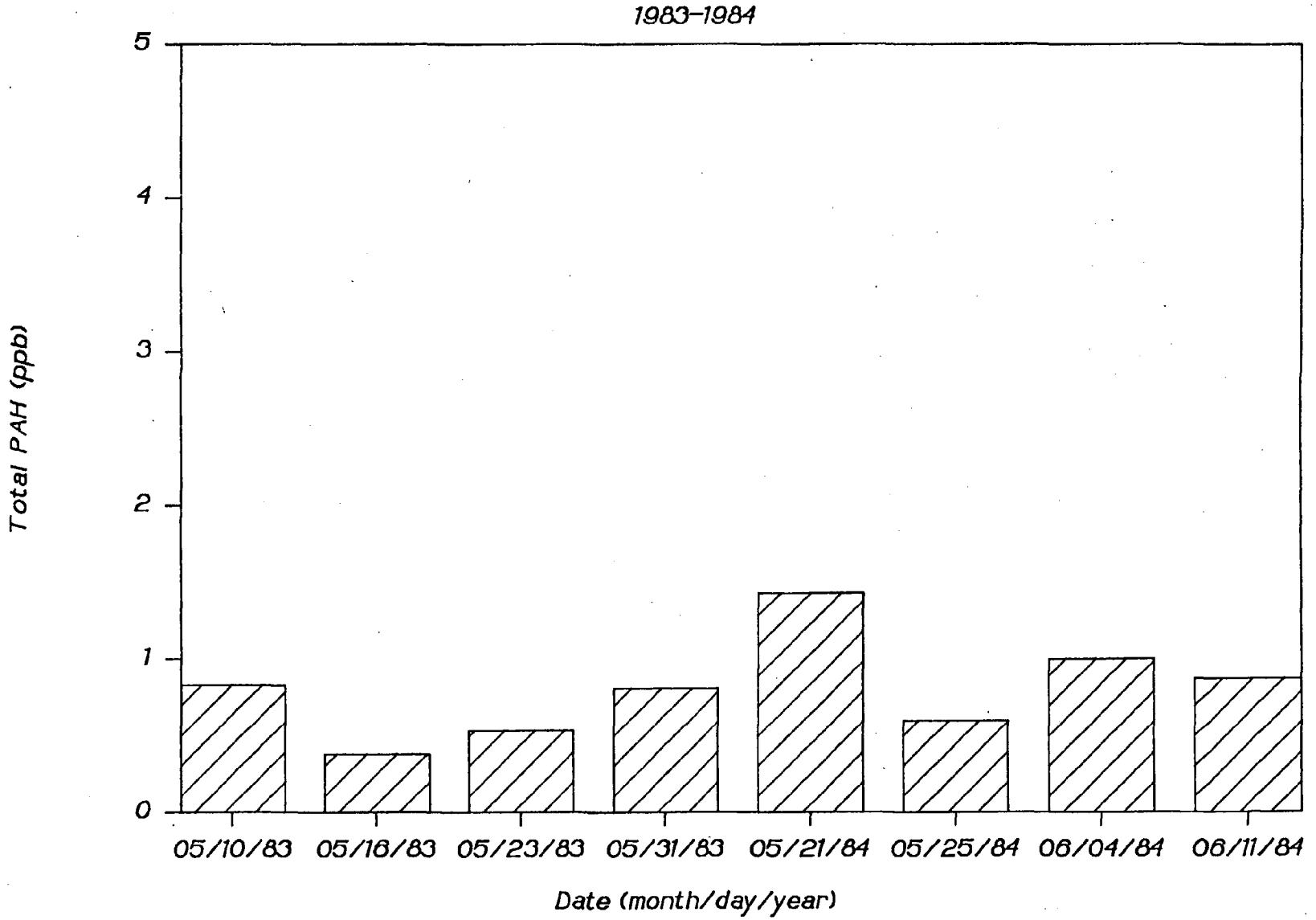


Figure 13. PAH's in Choptank River Sediment

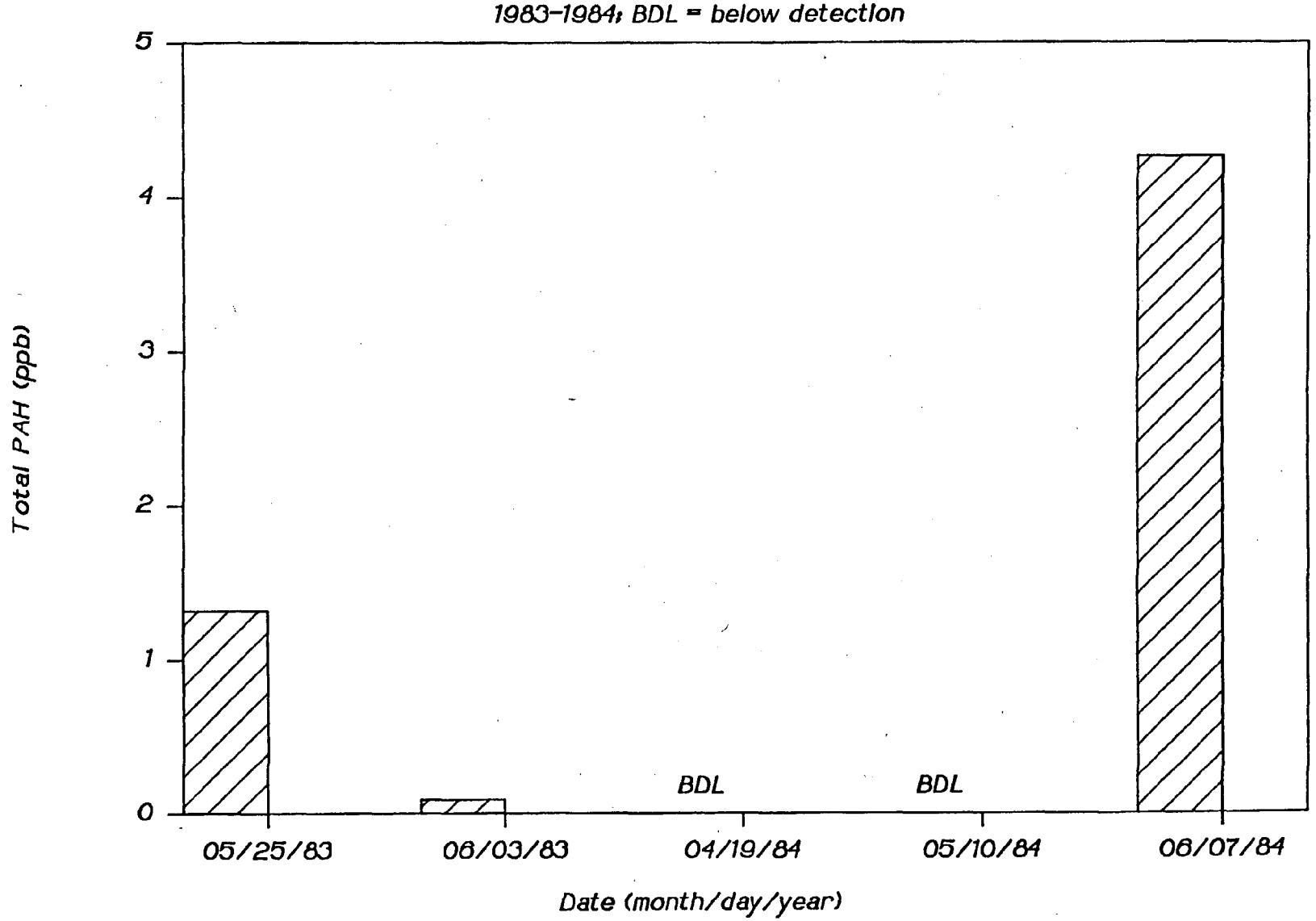


TABLE 17. PAH concentrations in rivers neighboring the Chesapeake region

	Benzo(a)pyrene Concentration ng/L	Total PAH
Monongahela River at Pittsburgh, Pa.	42-47	600-663
Ohio River at Huntington W. Va.	5.6	57.9
Delaware River at Philadelphia, Pa.	41.1	351.8

(Adapted from Neff, J. M. 1979)

TABLE 18. Most common PAH and PASH (sulfur-containing PAH's) found in striped bass adults, eggs, and young-of-year collected in 1981. Residues expressed in ng/g

Sample type	Location	Compound[a] 1	2	3	4	5	6	7	8
ADULT FEMALES	Nanticoke	16.2	12.8	98.7	96.9	16.6	—	20.2	8.5
	Choptank	16.0	13.3	106	111	37.7	—	—	5.1
	Hudson	18.9	19.7	72.5	54.5	21.1	7.6	2.4	12.5
	Savannah	17.2	13.5	36.2	43.8	10.6	—	6.3	—
	Santee	11.3	7.0	10.8	6.9	1.8	—	12.9	—
	St. John	13.4	—	—	13.3	—	—	—	8.4
	Brookneal Hatchery	15.3	2.8	12.3	13.5	—	—	3.2	—
EGGS	Nanticoke	12.0	—	89.4	—	19.3	—	—	—
	Choptank	11.6	3.9	83.8	—	44.7	—	1.5	—
	Hudson	10.4	5.3	60.3	6.7	122	—	—	—
	Savannah	26.6	6.2	18.2	—	22.4	—	—	—
	Santee	22.8	2.8	154	14.4	303	—	—	—
	St. John	10.8	—	12.2	—	—	—	—	—
	Brookneal Hatchery	4.7	—	1.8	4.6	—	—	4.7	—
YOUNG OF YEAR	Nanticoke	15.4	6.5	—	—	—	—	—	—
	Choptank	28.5	—	—	—	—	—	—	—
	Hudson	38.0	4.6	11.3	1.2	4.9	—	8.0	—
	Santee	19.3	2.7	2.3	—	—	1.8	—	—

a - Code for above compounds #'s 1-8:

1. Phenanthrene
2. Fluoranthene
3. Pyrene
4. Benzo[a]fluorene
5. Benzo[a]anthracene
6. Dibenzothiophene
7. Phenanthro[4,5-bcd]thiophene
8. Benzo[b]naphtho[2,1-d]thiophene

(from U. S. Dept. of Interior, Columbia National Fisheries Research Laboratory, Impacts of Contaminants on Early Life Stages of Striped Bass, Progress Report 1980-1983)

concentrations to be lower than those found to cause any of the toxic reactions discussed earlier in this paper. However, Table 17 shows both benzo(a)pyrene and total PAH concentrations from rivers in neighboring areas to be at least three orders of magnitude lower than in the Chesapeake Bay. Additionally, oyster tissues sampled from Norfolk, Virginia showed higher PAH concentrations than those noted for other sample locations.

PAH's and Chesapeake Biota

Information derived from these studies should stimulate marked concern for the Chesapeake Bay and the biota which inhabits it. Special attention should be given to the effects of PAH's on recruitment of various biotic species in the Bay. As a general rule, eggs, larvae and juveniles are the most sensitive life stages. In the Chesapeake, freshwater spawners including alewife, catfish, shad, striped bass, and both white and yellow perch release their eggs in the fluvial or tide-fresh reaches of the bay system. Such reaches tend to be the first exposed to the toxic chemicals and suspended sediments from the rivers feeding the Bay (EPA, 1983).

Figure 3 shows approximate boundaries of striped bass spawning reaches within the Chesapeake. Many of these reaches fall in the northern and western portions of the Bay where PAH concentrations are highest. Concentrations of PAH's found in adult female striped bass, eggs and young of the year are presented in Table 18 (Columbia National Fisheries Research Lab). It is possible that adult females excrete PAH through their eggs, as noted in other species, or that the PAH's are taken up by the eggs at a later time.

Apart from localized effects in severely contaminated coastal and estuarine zones, it is difficult to determine the overall stresses and impacts a chemical pollutant may have on a given species or aquatic biota in general. Not only is

there the problem of deciding whether the chemical in question is acting on its own or in concert with another chemical or physical property, but organisms may be lost or damaged indirectly by the toxin acting on another trophic level. Bearing this in mind, one can easily see how PAH's could pose an enormous threat to the Chesapeake Bay as well as to other ecosystems.

Approaches to PAH Studies

A variety of approaches have been adopted in the study of PAH's. Initial work usually consists of water column and sediment analysis of an area in question to determine the types and quantities of particular PAH compounds. In areas where there have been found to be high levels of chemical pollutants, such as the Elizabeth River, sediments can be brought into laboratory tanks and used to monitor biotic reactions. In many cases "artificially" derived PAH's are used for experimental studies, so that concentrations can be metered out at desired time intervals and in desired quantities. Both of these methods are equally important; the first to determine effects of existing conditions, and the second to determine various hazard limits and modes of action. In cases of chemicals such as PAH where such a wide range of interactions come into play, simulation models are often used to evaluate various components of an ecosystem and the combined effects of each of these components.

Chesapeake Bay Monitoring

Organic chemical monitoring efforts are currently underway in the Chesapeake Bay within the scope of EPA's Chesapeake Bay Program. Regular monitoring of the Bay mainstem is conducted by the Maryland Office of Environmental Programs and the Virginia State Water Control Board. PAH's are

among hundreds of organic toxics targeted for sediment content analysis. DNR has also measured PAH concentrations as part of its striped bass spawning season monitoring.

Of the twenty-six organic pollutants detected in sediments and biota during the course of the 1984-85 upper Bay monitoring period, PAH's were the most prominent. Contamination levels ranged from 10,000 ppb in Baltimore Harbor to less than 1 ppb at the mouth of the Potomac River. PAH concentrations were particularly high around urban areas. According to the 1986 State of the Bay Report (in press), a majority of these PAH's were produced by the combustion of carbonaceous fuels.

Virginia's analysis of organic chemical content in lower Bay sediment samples revealed a predominant abundance of PAH compounds. Although PAH concentrations were not excessively high, only 4-8 percent were naturally derived. At the entrance to Hampton Roads, however, total PAH's increased in 1985 from 1984 by a factor of 4.

Although there is presently no known direct threat to human health with regard to the unnaturally high PAH levels that have been found to exist in some parts of the Bay, the effects of long-term, low dose PAH exposure upon organisms is not well understood. There is concern that these toxic organic compounds may cause an imbalance in species due to reduced fish reproduction, deformities, abnormal behavior or disease. There is also concern that PAH's can be accumulated by organisms that reach the family dinner table.

It is recognized that a number of ecological processes impact PAH concentration levels. However, the natural variability of contaminants in the Bay system, seasonal cycling of pollutants within sediments and the pathways by

which those toxics go from sediment to the Bay's living resources are not fully understood. These ambiguities warrant continued benthic surveillance.

Several general conclusions have come out of the 1984-85 Chesapeake Bay Program: 1) bioaccumulation seems to depend on both the organic content and grain size of sediment; 2) occurrences of non-cancerous lesions in croaker from the Chesapeake could be correlated with sediment concentrations of total PAH's.

DNR Striped Bass Sampling (1983-85)

Striped bass larvae and water quality samples were collected and analyzed for metals and organics once a week at one location in the Upper Bay and one location in the Choptank River. These samples were centrifuged in the field for recovery of particulates and dissolved fractions. Organic chemical analysis was performed on recovered particulates and filtered water. Figure 14 shows the collection and analysis scheme for metals and organic chemicals. Table 19 indicates detection limits for selected organic contaminants analyzed by EPA, and Table 20 shows the methods used for organics.

Sediments were taken in the vicinity of Elk Neck State Park for the Upper Bay and Dover Bridge for the Choptank River. Analysis focused on metals and organics as well as organic matter. Figure 15 shows sediment analyses procedures.

1986 Study Design and Methods for DNR Striped Bass Monitoring

Composite water samples were collected from surface, mid depth and bottom at 18 stations using a bilge pump and hose. Subsamples of the composites were

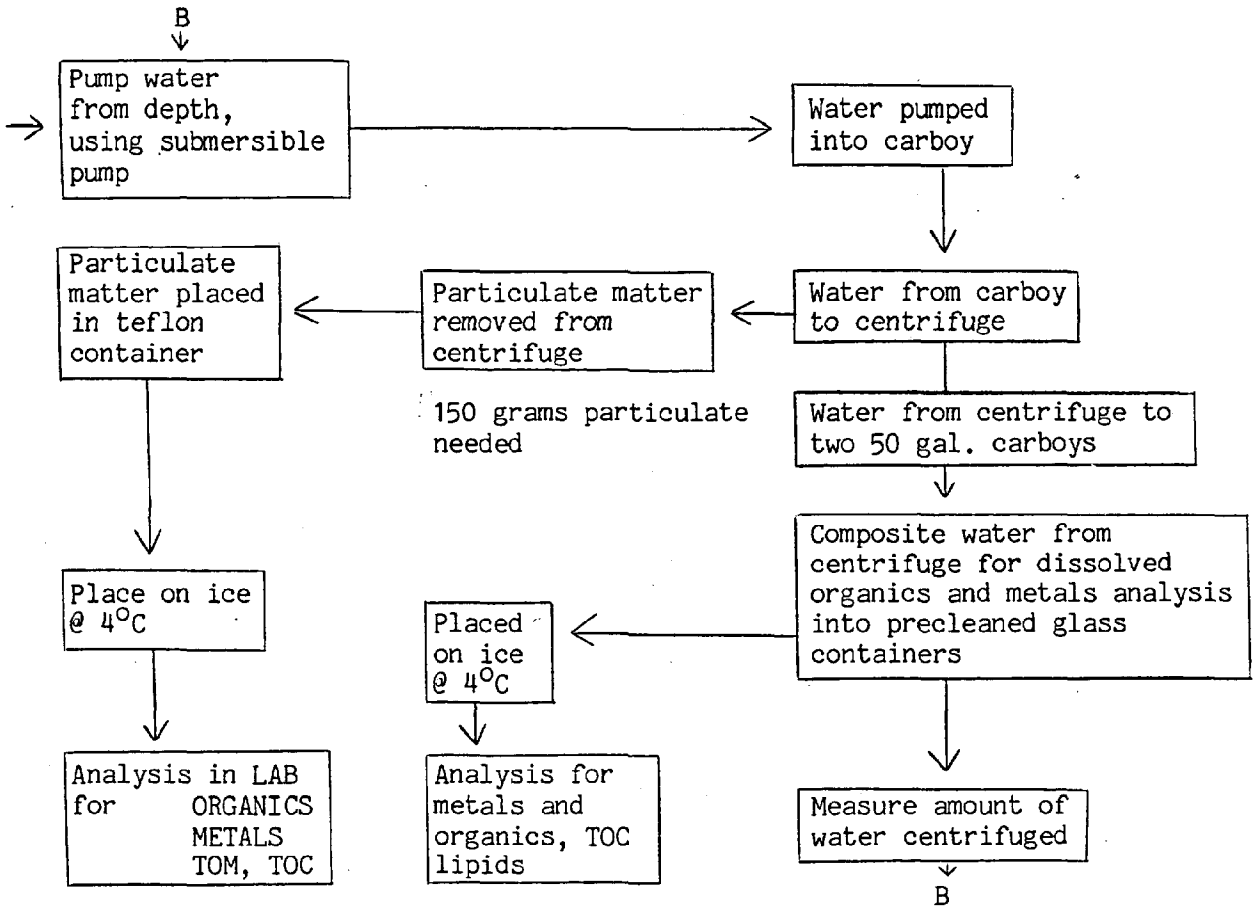


Figure 14. Sampling procedure for metals and organics.

TABLE 19. Detection limits for selected organic contaminants to be analyzed by EPA, CRL

Aldrin	.33 - 0.2	ppt
a - BHC	.23 - 0.14	ppt
b - BHC	.33 - 0.26	ppt
d - BHC	.43 - 0.26	ppt
g - BHC	.23 - 0.14	ppt
Chlordane	4.3 - 2.6	ppt
DDD	1.3 - 0.8	ppt
DDE	0.67 - 0.41	ppt
DDT	1.67 - 1.0	ppt
Dieldrin	0.67 - 0.4	ppt
Endrin	1.0 - 0.6	ppt
Heptachlor	0.23 - 0.14	ppt
Heptachlor-Epoxide	0.43 - 0.26	ppt
PCB 1242	5.5 - 3.32	ppt
1254	9.0 - 5.4	ppt
1260	16.67 - 10.7	ppt
Atrazine	5.67 - 3.4	ppt
Linuron	10.0 - 6.0	ppt
2-4-D	10.0 - 6.0	ppt
2-4-5-T	10.0 - 6.0	ppt

TABLE 20. List of methods for organics

PAH's	GC/MS Method 625: Rev 3.1 DB-5 capillary column Ext. Organic Screen Fed. Reg. December 3, 1979.
	Pesticides Capillary - ECD
	Method 608: Modified with DB-5 cap. column Fed. Reg. December 3, 1979.
Linuron	APLC, JAOC vol. 59, No. 5, 1976, p. 1066.
Triazines	GC Triazine Analysis in water and wastes Fed. Reg. 38, No. 75, 11/28/73.
Phenoxy Acid Herbicides	Fed. Reg. 38, No. 75, 11/28/73.

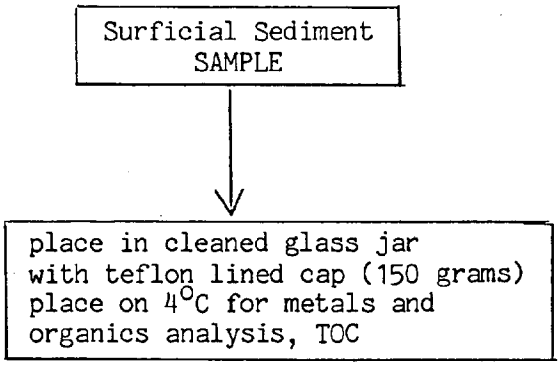


Figure 15. Sediment analyses procedures.

placed in pre-washed and fired glass jugs (with teflon cap liners) and frozen for PAH analysis. These samples were thawed, filtered and analyzed, using gas chromatography, for the sixteen PAH's selected by EPA as priority pollutants.

Eight fixed monitoring stations in the Upper Chesapeake Bay region were sampled twice a week. Four fixed stations were sampled in the Choptank River with sampling occurring once a week. There were also 2 movable stations per system in the Nanticoke, Potomac and Choptank Rivers. These station locations varied depending on where striped bass larvae were found. Sample collection occurred once a week.

Daily composite samples were also collected at two bioassay locations; one in the Upper Bay region at Elk Neck State Park, and the other in the Choptank River at Ganey's Wharf. Standard EPA analytical methods were used for identification of PAH's from samples taken from the above-mentioned striped bass monitoring sites.

DNR is still awaiting the results of these analyses. When available, the results will be reported in DNR's final report on PAH's in the Chesapeake Bay.

Future Needs

Notwithstanding the recent implementation of intensive research efforts concerning the effects of PAH's, there seems to be a large gap in the work devoted to early life stages among fish, particularly in the Chesapeake Bay region. This is where efforts should be focused in order to obtain conclusive evidence regarding biotic reactions to PAH exposure.

It is important to determine the chemical impact of PAH's on the egg, larval, and juvenile stages on through the rest of the life cycle. Abnormal effects should be noted on both an apparent observational level and a molecular

level to help determine a given PAH's mode of action. Another important and necessary study involves the observation of reproductive success of fish who have been exposed to a given toxin throughout their life cycle in order to ascertain potential alteration in reproductive ability. If species experience a significant reduction in population or cease to exist altogether, it is too often the case that not only is one group adversely affected; so are all its preditors, prey or competitors along the food web.

Before we start losing aquatic life to PAH pollutants, every effort should be made to project their possible impact and implement the appropriate procedures to relieve the Bay of their burden.

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