

1987

Organic Chemicals in Sediments from the Lower Chesapeake Bay

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**STATE OF THE CHESAPEAKE BAY
SECOND ANNUAL MONITORING REPORT**

COMPENDIUM

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April 1987

Prepared for the Chesapeake Bay Program
Monitoring Subcommittee
by
Chesapeake Research Consortium, Inc.
P. O. Box 1120
Gloucester Point, Virginia 23062
as
CRC Publication No. 125

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INTRODUCTION

The second report from the Chesapeake Bay Program Monitoring Subcommittee summarizes data collected from June 1984 through September 1985 at over 165 stations Bay-wide for the new coordinated monitoring program. This initial effort represents the baseline for a large, complex, and rapidly growing store of information.

This Compendium volume is intended to accompany the State of Chesapeake Bay summary report, amplifying the contribution of each group involved in this complex overall monitoring effort. Weaving these discrete and more technically oriented documents together has been the job of the summary report.

Like the summary report, this report is organized so the reader can follow discussion of the Bay's problems and progress in a logical sequence. First, the physical and chemical observations characterize the Bay system and its major tributaries. These physical and chemical characteristics underly the movement and transformation of materials we're concerned about in the water column.

Chapters on sediments and toxics discuss the current understanding of how materials enter and leave the sediments and outline the distribution of toxic materials we have been monitoring in the Bay.

In logical sequence, the chapters on living resources appear next, because we believe the Bay's living resources rely on the habitat quality, which is often limited by what is in the waters and sediments.

We follow the food chain: the phytoplankton, which synthesize nutrients into algal biomass; the zooplankton, which are primary consumers; and the benthic (bottom-dwelling) organisms and submerged aquatic vegetation that are also vital elements of the Bay's food base. Another step up the food chain brings us to fisheries and waterfowl.

Much interest has surrounded the Patuxent River, which served as a catalyst in focusing attention on many of the Bay's problems. As in the summary report, the Patuxent Story is developed as a case history.

This Compendium demands more of the reader than does its summary report, because the constituent chapters cover topics in greater technical detail. Still, these chapters are themselves simplifications, as we approximate an understanding of the Bay's complex systems. We hope this understanding will be broadened and deepened as monitoring progresses over its intended course of 10 to 15 years.

Organic Chemicals in Sediments from the Lower Chesapeake Bay

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Many of the toxic organic chemicals affecting the marine environment are hydrophobic and associate with sediments. Sediments can accumulate the substances over long intervals and store them after the original source of the toxic material has been eliminated. Contaminated sediments can provide small but damaging amounts of the toxicant to the overlying water for decades. For example, more than 10 years after the discovery of Kepone in the James River, Virginia, much of the James' fisheries is still closed because Kepone levels are above federal action levels.

Monitoring programs for detection of hazardous organic chemicals in aquatic systems often take advantage of the accumulating and storing capability of bottom sediments. Concentrations of the chemicals are usually higher in the sediments than in water, thus facilitating analytical detection and quantitation, and the sediments integrate over time. This latter property enhances the detection of intermittent discharges, which otherwise may go undetected if water samples are not collected during a discharge event.

In the late 1970s, the first comprehensive monitoring program for toxic organic chemicals in the Chesapeake Bay was undertaken in the mainstem. Previously, most of the monitoring efforts of Virginia and Maryland scientists had focused on the tributaries because the human population densities are greater and agricultural activities more extensive on the rivers. The Bay proper was largely ignored. Funding from Virginia and the first Chesapeake Bay Program allowed scientists to develop and use chemical analytical methodologies to quantify and track hundreds of organic compounds in Bay sediments. The first set of samples was taken in the

spring of 1979; the second in the fall of the same year. More samples were obtained in 1984 and 1985 with assistance from the second Chesapeake Bay program; findings of these studies are reported here.

SAMPLING

The sediment sampling locations are shown in Figure 1. Because one intent of the monitoring program was to determine the trace chemical content of the sediments, it was necessary to take precautions against contaminating the sample during collection. To achieve this, a stainless steel Smith-MacIntyre grab sampler was used. Before each sample was taken, the sampler was thoroughly rinsed with ambient water and then with "distilled in glass" methanol.

Another intent of the program was to determine temporal and spatial trends in concentrations, should they exist. Because the sedimentation rate in the mainstem of the Bay is usually lower than in its tributaries, recently deposited contaminants likely would be present in the uppermost portion of the sediment column. Therefore, after the sampler was returned to the surface, only the top 2 cm of sediment was removed. These sediments were placed in cleaned glass jars with Teflon-lined lids for storage. The samples were immediately refrigerated and were transferred to the laboratory within eight hours of collection. To compensate for small-scale inhomogeneities in the bottom sediments, five separate samples were collected at each site on each sampling event. For analysis, equal subsamples from each of the five replicates were composited and mixed to produce a sample. The composite samples were stored at -4°C .

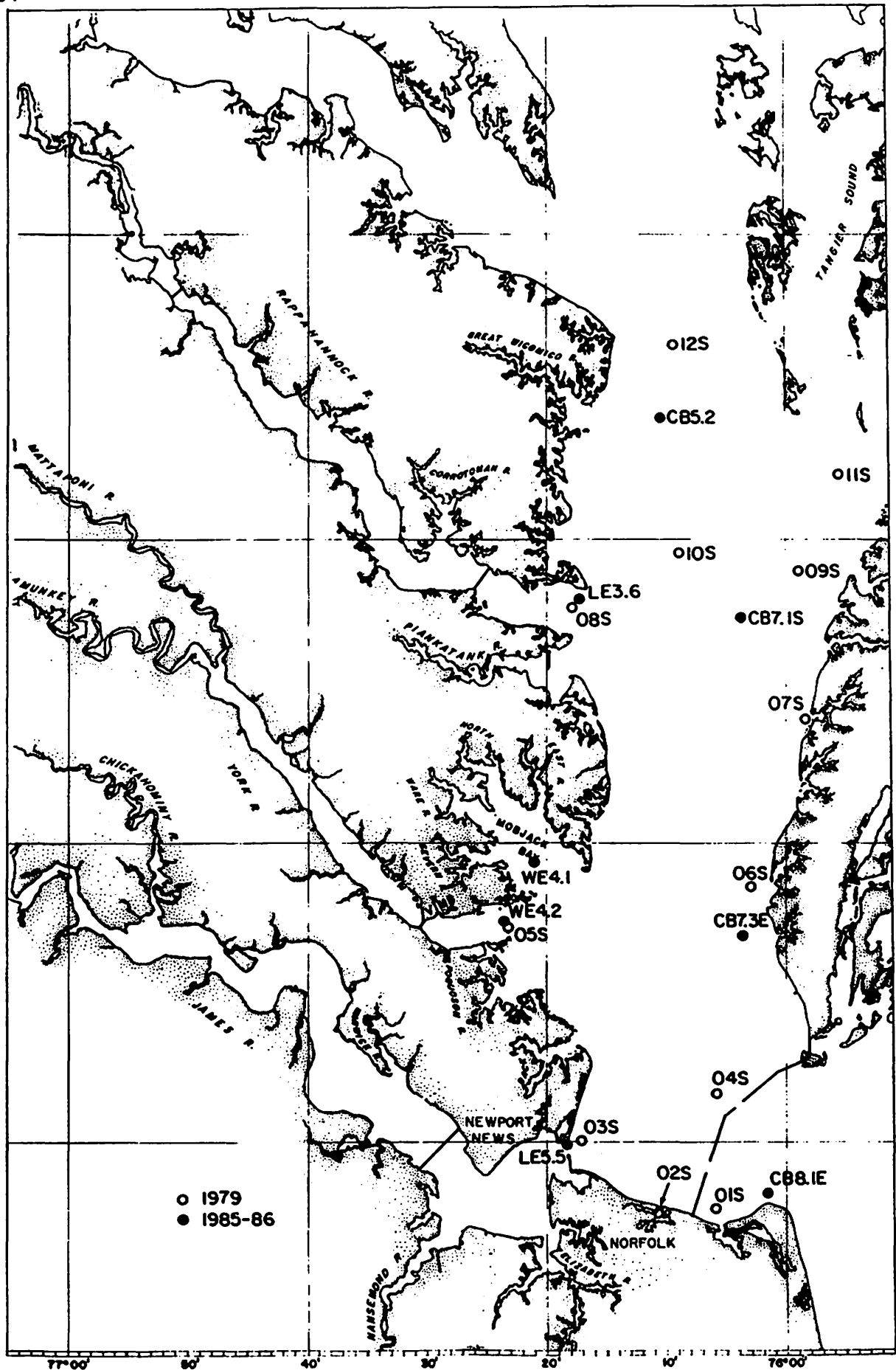


Table 1. Particle size distributions for bottom sediments collected in 1984 and 1985.

| Station | Sand and coarser (%) | | Silt (%) | | Clay (%) | |
|---------|----------------------|------|----------|------|----------|------|
| | 1984 | 1985 | 1984 | 1985 | 1984 | 1985 |
| CB 5.2 | 29.6 | 0.8 | 22.5 | 44.8 | 47.9 | 54.5 |
| CB 7.15 | 20.6 | 20.6 | 49.0 | 50.0 | 30.4 | 29.3 |
| LE 3.6 | 5.8 | 10.3 | 53.1 | 54.2 | 41.1 | 35.5 |
| WE 4.1 | 4.2 | 4.4 | 53.8 | 57.1 | 42.1 | 38.5 |
| WE 4.2 | 3.8 | 8.8 | 38.6 | 46.1 | 57.6 | 45.1 |
| CB 7.3E | 95.3 | 88.4 | 1.6 | 5.2 | 3.1 | 6.4 |
| LE 5.5 | 34.4 | 96.3 | 26.2 | 0.9 | 39.4 | 2.0 |
| CB 8.1E | 75.2 | 82.2 | 13.9 | 9.8 | 10.8 | 9.0 |

ANALYTICAL METHODOLOGY

The first step of the analytic procedure was to remove water by freeze drying. A known amount of 1,1'-binaphthyl was added to the dried samples, which allowed the analysts to compensate for varying extraction yields and losses. The samples were Soxhlet extracted with dichloromethane to separate organic chemicals from the sediments.

Because sediments contain naturally occurring or biogenic organic substances, "clean-up" steps are usually required to separate these from the anthropogenic compounds of interest. This separation was achieved with gel permeation chromatography. The extracts were then separated into aliphatic, aromatic, and polar fractions by subjecting each "cleaned" extract to high-performance liquid chromatography. The aromatic and polar fractions were analyzed by glass capillary gas chromatography and glass capillary gas chromatography-mass spectrometry.

A detailed description of the analytical methodology can be found in Bieri et al. (1981).

RESULTS

The ability of sediment to assimilate and store chemicals is related to the particle-size distributions in the sediments. Finer-grained sediments contain a relatively higher surface area per unit mass than do coarser grained ones. Therefore, all other factors being equal, surface-associated chemicals are more concentrated in finer grained sediments. In addition,

finer grained sediments will usually contain a higher proportion of naturally occurring organic matter. It follows that chemicals that partition to these natural organics would be more abundant in finer grained sediments.

Because of these factors, it is important to determine the particle size distribution in the sediment samples so that chemical concentrations found at one site can be compared with those at another. The particle size distributions for samples collected in 1984 and 1985 are shown in Table 1.

Hundreds of compounds were detected in some of the samples. Almost all of these were in the aromatic fraction. Table 2 lists some of the more abundant compounds for the four sampling periods. It should be noted that the stations sampled in 1984 and 1985 do not coincide exactly with those sampled in the 1979 program. Also, the analytical methodology was slightly modified after 1979 to resolve more compounds. Therefore, some caution is advised in comparing the 1979 data with those obtained later.

The concentrations of the total resolved aromatic fraction for all the sampling periods using data from the 1979 sample stations closest to those from 1984 and 1985 are given in Figure 2. It is important to reiterate the caution on comparing 1979 data with those from 1984 and 1985.

DISCUSSION

No polar compounds were detected in any of the samples; discussion will focus on the aromatic compounds. The most abundant compounds detected

Figure 1 (facing page). Location of stations in the lower Chesapeake Bay sampled for organic chemicals in sediments in 1979 and in 1985-1986.

in all four surveys were polynuclear aromatic hydrocarbons (PAHs). PAHs produced during the combustion of carbonaceous fuels such as coal, oil, and wood are called pyrogenic; others are naturally derived. Finding that most PAHs detected in the four surveys were pyrogenic probably reflects a broad-scale, low-level input from the atmosphere as well as riverine sources.

The fraction of naturally derived PAHs was low (4-8%) at all stations. This finding agrees with a study of several Chesapeake Bay tributaries (deFur 1985) in which the percentage of natural compounds in surface sediments was observed to decrease with movement downriver in all cases. The reasons for this decrease are not known.

The spatial distribution of concentrations appears to reflect both the particle size distribution in the sediments and input from rivers. Coarser-grained sediments, such as those found at stations CB 8.1E and CB 7.3E, contained low PAH levels. An

exception to this general trend was for station LE 5.5 during the 1985 sampling. This station will be discussed below. The samples collected near river mouths were generally higher in PAH concentration than those further away, probably because the rivers deliver PAHs produced throughout their drainage basin.

There are too few stations to draw far-reaching conclusions about an area the size of the southern Chesapeake Bay, but some information may be gained by comparing the four samplings. Most stations showed a slight decrease in total concentration in 1985, but the changes were too small to be significant. As mentioned previously, the 1979 samples were not from the same sites as those collected later. The largest change was at station LE 5.5 in the Hampton Roads entrance, where total PAHs increased by a factor of approximately four. Qualitatively, this sample was similar to both the previous samples and the other stations in the present sampling, with all containing the array of pyrogenic

Table 2. Concentrations (mg/kg, or ppb) of compounds detected in sediments at stations LE 3.6, WE 4.2 and LE 5.5.

| Compound | Station LE 3.6 | | | | Station WE 4.2 | | | | Station LE 5.5 | | | |
|---------------------------|----------------|----|-----------|----|----------------|----|-----------|----|----------------|----|-----------|-----|
| | Spring 1979 | | Fall 1979 | | Spring 1979 | | Fall 1979 | | Spring 1979 | | Fall 1979 | |
| Phenanthrene | 10 | 24 | 28 | 29 | 5 | 8 | 26 | 32 | 11 | 47 | 22 | 100 |
| Fluoranthene | 16 | 59 | 63 | 56 | 26 | 16 | 54 | 58 | 29 | 52 | 51 | 410 |
| Pyrene | 12 | 58 | 64 | 55 | 21 | 18 | 49 | 67 | 34 | 46 | 40 | 380 |
| Benzo(a)-fluorene | 3 | 13 | 24 | 15 | 7 | 4 | 13 | 13 | 13 | 25 | 16 | 130 |
| Benzo(a)-anthracene | 5 | 30 | 29 | 16 | 12 | 9 | 28 | 17 | 18 | 30 | 21 | 140 |
| Chrysene/triphenylene | 7 | 39 | 44 | 29 | 18 | 16 | 39 | 34 | 37 | 47 | 35 | 170 |
| Benzo(j,b,k)fluoranthenes | | | | | -- | | -- | | -- | | -- | |
| Benzo(e)-pyrene | 5 | 2 | 27 | 17 | 2 | 11 | 25 | 17 | 2 | 1 | 23 | 93 |
| Benzo(a)-pyrene | 4 | 35 | 33 | 19 | 18 | 12 | 26 | 19 | 22 | 18 | 23 | 130 |
| Perylene | 11 | 39 | 46 | 21 | 21 | 22 | 44 | 34 | 26 | 8 | 42 | 36 |
| Benzo-(g,h,i)- | 3 | 17 | 28 | 12 | 15 | 8 | 31 | 23 | 15 | 6 | 18 | 46 |

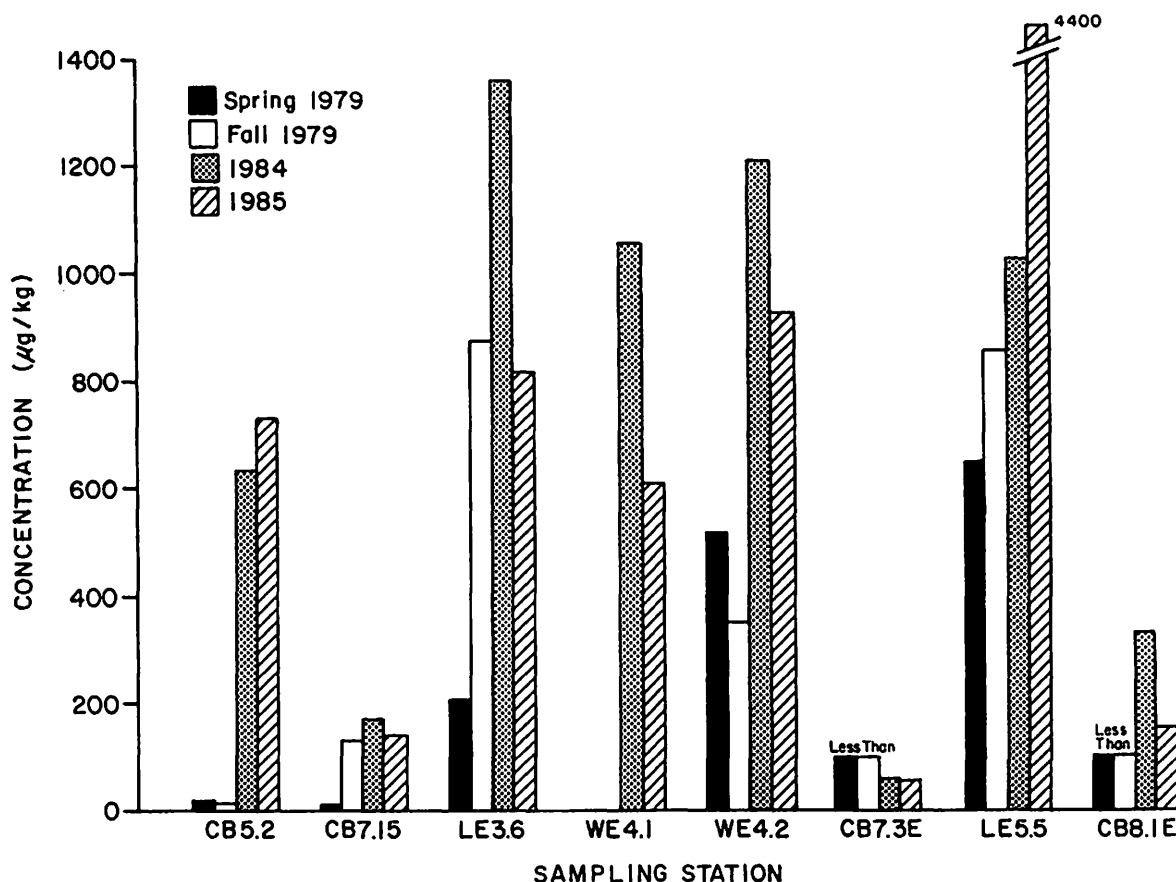


Figure 2. Concentrations of total resolved aromatic fraction in bottom sediments from the Chesapeake Bay.

PAHs referred to earlier. As transport of sediment and associated pollutants is dependent upon such variables as river flow, rainfall, dredging activities, and weather-induced circulation, the organic content of estuarine sediments may be highly variable over time. Recent flooding in the James River may have contributed large amounts of PAHs from there, as the observed total was similar to totals found in the upper James River in previous studies (Smith et al. 1985). The available data suggest that the increase in aromatic content from 1984 to 1985 should not be viewed as more than a natural fluctuation in sediment concentration.

Although PAH concentrations varied slightly between samplings, the variations were not large, and total PAH content at all stations was not

excessively high. It is very likely that the differences were not significant.

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