6-1981

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September 1981

Abstract

This manuscript discusses the results of the first two and one half years of a three-year study designed to determine the present state of xenobiotic compounds in the Chesapeake Bay. It shows that polynuclear aromatic hydrocarbons are the most frequently encountered compounds and are the most abundant. Concentrations are highest in the Northern Bay with several sources implicated. During this study an apparent dumping of the pesticide, DDT, occurred. Either the quantity disposed of was small enough or the assimulation capacity was large enough that no adverse effects were noted. The detection by us of 6-phenyldodecane in bottom sediments of the Patapsco River and its detection in a nearby industrial outfall by the Monsanto Research Corporation shows that chemicals entering the River can be dispersed throughout the system and can enter the Chesapeake Bay.

Introduction

The Chesapeake Bay may be the most studied estuarine system in the world. Data on its fisheries go back to Captain John Smith at Jamestown Island in the early seventeenth century. A number of state and federal laboratories are still gathering data on the abundances, distributions and life histories of the Bay's flora and fauna. The early European settlers charted its waters with lead lines, and that task is still being updated using sophisticated electronic depth and positioning equipment including earth orbiting satellites. Wet chemical methods were used to determine trace metals in its sediments and biota, to be followed by atomic absorption spectrophotometry and activation analyses as these techniques became available.

Unfortunately, our knowledge of one class of chemicals in the Chesapeake has lagged behind; these are the synthetic or anthropogenic organic compounds (xenobiotics). This is partly because the analytical instrumentation necessary for such investigations has just recently been developed and is constantly being refined. Another reason is that many of these compounds have been synthesized only recently. In the last forty or so years, synthetic organic chemistry has presented us with a suite of compounds to do everything from controlling pests to replacing metals with plastics. Many of these substances reach the Chesapeake Bay via a variety of routes. Some of them can be toxic to the Bay's inhabitants. Therefore, the time has come to get an in-depth look at the present status of xenobiotics in the Chesapeake Bay to the limits of our current technology.

PREVIOUS WORK

The literature is almost void of studies pertaining to synthetic or anthropogenic organic compounds in the Chesapeake Bay proper. A few projects have been undertaken on chlorinated hydrocarbon pesticides or polychlorinated biphenyls (PCB's) in its estuaries.

Both the State of Maryland and the Commonwealth of Virginia were involved with the National Estuarine Monitoring Program which was federally funded under the direction of Dr. Philip Butler of the Environmental Protection Agency. The program originated in 1965 and continued until approximately 1970 in Maryland and 1972 in Virginia, utilizing the eastern oyster, Crassostrea virginica, as the sentinel organism wherever possible. In this program the DDT family of pesticides was sought in addition to dieldrin, aldrin, lindane heptachlor, heptachlor epoxide and, after about 1968, PCB's. During this period, 88 samples from Maryland's waters and 633 from Virginia's were analyzed. The data show that 81% of Maryland's samples and 91% of Virginia's contained DDT family residues. The highest value reported was 0.68 mg/kg (wet weight) from Virginia and 0.070 mg/kg (wet weight) from Maryland, with most falling between 0.01 and 0.10 mg/kg (Munson and Huggett, 1972).

Before 1968 there undoubtedly were unrecognized analytical interferences from PCB's. This resulted in overestimated DDT and DDT-derivative concentrations. After that date, PCB's were sought and quantatified separately. In Virginia, Aroclor 1242 was most common until 1970, when Aroclor 1254 became dominant. The highest values without exception occurred in the Elizabeth River, with concentrations approaching 2 mg/kg, wet weight in oysters.

Starting in 1972 and continuing for several years, the mollusks were replaced with yearling herbivorous and carnivorous fish sampled at six-month intervals. Analyses were no longer performed by the states but by a federal laboratory, and the list of compounds to be analyzed for was extended by adding atrazine, ethylenethiourea compounds, phenoxy herbicides and phthalates. The most commonly encountered pesticides were again DDT and its derivatives, but PCB's were often present (VIMS data).

A thesis by T.A. Barnard, Jr. (1971) investigated the role of an anadromous fish, the alewife, in transporting pesticides upriver or upbay during spawning. He found that the fish enter the Bay with approximately half of the level of DDT compounds that they contain after they enter the rivers. The concentrations in the ocean averaged 0.17 mg/kg while the means ranged from 0.28 to 0.35 mg/kg for fish on their spawning run in the James, Rappahannock and Potomac Rivers.

A study by Westinghouse Ocean Research Laboratory (funded by Westinghouse Electric and the State of Maryland) was started in 1971 to better understand the sources, methods of transport and sinks for chlorinated pesticides in a river system. Major emphasis was placed on the Chester River. The study showed that PCB's, chloradane and DDT pesticides were present and gave an insight into the routes and rates of transfer (Munson, 1973, 1975).

In 1976 a national study, Project Mussel Watch, was funded by EPA. It followed closely the design of Butlers' National Estuarine Monitoring Program of 1965-1972. Two of the sampling stations were located in the Chesapeake Bay near the mouth--one at Cape Charles (37°17,3'N, 76°01'W) and the other at Lynnhaven Bay (36 54.2'N, 76 05.3'W). At these stations, the eastern oyster was sampled on a yearly basis until 1978. These samples have been analyzed

for PCB's, the DDT family and a select group of polynuclear aromatic and aliphatic hydrocarbons. Most of the data are still unpublished and therefore unavailable for review. A few results were presented by Goldberg et al. (1978).

The impact of marinas on subestuaries relative to hydrocarbons was studied by Voudrias (1981). Three small subestuaries in or near the York River system were sampled. Two had marinas and one served as a control. He showed that boating activities as well as urbanization influenced the concentrations and the variety of such compounds in the sediments.

In 1978 the United States Geological Survey commenced a program of analyzing water and suspended sediments collected at the fall line of the three major tributaries entering the Bay. The object was to determine the input of a number of chemical substances into the estuaries by the riverine sources. Organic analyses were limited to pesticides, PCB's and herbicides. The results show that with a few exceptions levels in the suspended or solution phase were below the detection level of the analytical method (Lang and Grason, 1980).

From the above it can be seen that most of our knowledge concerning anthropogenic organic compounds in the Chesapeake is limited to biocides and PCB's. In 1979 the Chesapeake Bay Program of the United States Environmental Protection Agency approved and funded us to develop analytical methods and utilize them to determine as many of the xenobiotics as possible in the Bay, and in the Elizabeth River and Baltimore Harbor subestuaries.

We have completed the Bay portion and are now analyzing samples from Baltimore Harbor. While these are not yet completed, enough data have been generated to begin an assessment of the chemical state of this subestuary and its influence on the adjacent waters.

This manuscript is an attempt to summarize our findings. It would require literally hundreds of pages to present all of our data. Therefore, the reader is encouraged to refer to our final report to EPA on the first two years of effort (Bieri, et al., 1981).

METHODOLOGY

A. Sampling

A basic difficulty with any monitoring program which is intended to assess the state of a body as large as the Chesapeake Bay is in the selection of the sample type and sample location. Ideally, one would like to obtain and analyze enough "pieces" of the ecosystem so that any spacial and temporal abnormalities could be detected. Unfortunately, with time and financial constraints, the ideal case is not achievable. Therefore one must carefully select what and where to sample in order to be as efficient as possible and to still obtain data which reflect the state of the area being assessed. We selected bottom sediments and oysters. The former was chosen because of the usually high preference that synthetic organic compounds show for concentrating in and on sediment particles. Kepone in the James River is an example of this. While dissolved concentrations in the water were in the low parts per trillion range, Kepone levels in the bottom sediments were more than a thousand times higher. This propensity of synthetic organics for sediments yields two major advantages: (1) the compounds of interest are present in relatively high concentrations, thus making the analysis simpler and (2) the sediments accumulate the foreign materials over long periods of time thus integrating and making the detection of pulsed inputs more likely. Oysters were selected because they share the two advantages of sediments listed above as well as being organisms, thus serving as a link to the biota of the

Bay. They are also sessile. Being sessile is an important consideration in interpreting the data. Since the animal moves little (if at all), a compound detected in an oyster sample assures that the animal received it at the sampling location. This is not necessarily true for mobile organisms like fish or crabs.

Sample locations were then selected. We gave prime consideration to the areas of the Bay which were expected to contain fine grained sediments since these usually accumulate higher levels of synthetic organics than do more coarse ones under similar exposure. We also considered areas which would have the highest probability of reflecting man's activities. These included the mouths of the major tributaries and zones of high urban and industrial activities. The oyster sample locations were chosen as near as possible to the sediment sample locations. The locations are given in Figures 1 and 2. To get an indication of temporal trends, these stations were sampled twice during 1979, once in the spring and once in the fall.

B. Analytical Techniques

For the purposes of this document it is unnecessary to go into great detail on the analytical methodology. For those requiring more information, we refer to our report to EPA (Bieri, et al., 1981).

In brief, the methodology involves first freeze drying of the sample to remove moisture and thus providing better penetration of the extracting solvent into the sample matrix. This in turn allows for a higher extraction efficiency. The dried sample is then Soxhlet extracted with methylene chloride. After this step the extract, which contains not only the xenobiotics of interest but also many natural compounds, must be fractionated. There are two steps in the fractionation. The first utilizes Gel Permeation Chromatography

to remove high molecular weight compounds which are probably biogenic or natural. The remainder is then split into three parts by High Performance Liquid Chromatography. One fraction is aliphatic in nature, one is mainly aromatic and the third contains polar compounds.

The aromatic fraction has received the most study in our project since it is likely to contain most of the toxic xenobiotics. The polar fraction of samples from the Bay contained very few compounds which were at low concentration, so that little effort was expended on it. The aliphatic fraction was not extensively studied since these compounds are of relatively low toxicity. Indications of oil pollution can be obtained from aliphatics as well as from the aromatic compounds. Therefore, for the sake of efficiency, the aromatic fraction was the subject of the greatest effort.

After extraction and fractionation, the samples are analyzed by high performance glass capillary gas chromatography and gas chromatography-mass spectrometry, also using glass capillary columns.

The output from the gas chromatographs are electrical signals which are proportional to the amount of a compound going through the detector. The time required for a compound to reach the detector (retention time) is a function of the molecular structure of the compound. So, with the intensity of the signal and the time parameter, one obtains both quantitative and qualitative information regarding the compounds concentration and identity.

If one were looking for only a few compounds, such as PCB's and Kepone, then standard solutions of these could be analyzed and the resulting retention times and intensities compared to those of the sample. Our program, however, is looking for hundreds of compounds, many of which are not known to be present until detected. Therefore, standard solutions containing all compounds of interest are impossible. For this reason we have developed and

used a relative retention index based on unsubstituted polynuclear aromatic compounds. This index allows the computerization and storage of Gas Chromatographic data for all compounds detected, even though their identity may be unknown. Computer software can be written to compare the content of one sample with others. By knowing the relative retention time of a compound, the computer bank can be searched to determine which samples may contain the compound.

Unfortunately, gas chromatography alone is not sufficient to completely analyze samples as complex as those from the Chesapeake Bay. Gas Chromatography-Mass Spectrometry is required to determine a compound's identity based on the abundances and masses of the ion fragments which result when the compound is bombarded with electrons. As was the case with gas chromatography, the same relative retention index is used for gas chromatography-mass spectrometry.

We emphasize that this is a very brief summary of our analytical methodology. The methodology is not without problems and is still being refined. It has, however, been utilized to give the most complete picture of anthropogenic organic compounds in the Chesapeake Bay ever obtained.

RESULTS

A. Bay Sediments

Analyses of sediment samples collected during the spring and fall of 1979 revealed that over three hundred compounds were abundant enough to be either identified or given a surrogate name by assigning a relative retention time. In some samples, the complexity and abundance of compounds present were so great that many individual species at relatively low concentration undoubtedly were not detected. It is therefore probable that thousands of compounds were

present. An example is presented in Figure 3, which is a gas chromatogram showing individual peaks representing at least one compound superimposed on a background of peaks from numerous compounds that are lower in concentration thus forming what is commonly called an "unresolved complex mixture."

To give an indication of the distribution of organic compounds in bottom sediments in the Bay, Figures 4 and 5 are presented. These are histograms derived from samples collected in the spring and fall of 1979. Station numbers are indicated on the vertical axis (with their locations given in the chart to the left). The summed concentrations of chromatographically resolvable compounds eluting in the "aromatic" fraction is represented by the length of the bar on a logarithmetic scale. Both figures immediately convey the fact that the highest total concentrations are encountered in the northern portion of the Chesapeake Bay and that samples from Stations 2, 4, 6, 7, 10, 11 and 12 in the lower Bay are almost devoid of these compounds. With the exception of the fall sample from Station 9, only samples from locations 1, 3, 5 and 8 contained sums between one hundred and one thousand parts per billion. Stations 1, 3, 5 and 8 were located at the mouths of the Lynnhaven, James, York and Rappahannock Rivers respectively.

Unless the sedimentological character of these samples is taken into account, it is risky to assume that these distributions show that the Northern Bay and the river mouths have unnaturally high levels of organic compounds. As previously mentioned, fine grained sediments usually contain more of an organic compound than coarse ones. This can explain some of the anomalous distribution. In general, the sediment samples from the Northern Bay and the major river mouths contained a higher fraction of silt and clay

than did the other samples. Therefore, to normalize the concentrations of organics to the silt and clay content in the samples seems a reasonable approach to help account for the sedimentological effects. Normalized histograms are presented in Figures 6 and 7. There is no substantial change in the concentration sums in the Northern Bay with the exception of Station 27. In the lower Bay only Stations 1, 3, 9, 11 and 12 have visibly increased. At this time, without further analyses of samples collected within the subestuaries, it is impossible to determine whether organics in sediments collected near the major river mouths are high due to sediment grain size or unnaturally high inputs from upstream.

Normalizing the data from the Northern Bay did not substantially change the distribution pattern. With the exception of the fall Station 19 sample (this will be discussed later as there was an obvious introduction of pesticides and PCB's here between our samplings), there is an evident trend of increasing concentrations from just below the Potomac River to the mouth of Baltimore Harbor. North of Baltimore Harbor the concentration sums decrease and then increase to another maximum near the mouth of the Chesapeake and Delaware Canal. The most northern samples, Station 27--inside the mouth of the Susquehanna River--showed considerable variation between samplings. This variation was explained by the flow rates from the Susquehanna which were unusually high during the spring sampling and unusually low during the fall one. High flow scours the fine grained particles, but during low flows these materials deposit in the mouth. Therefore, it appears that the Susquehanna River is a source of organic compounds to the Northern Bay. During low flows they accumulate in or near the mouth; during high flows they are moved away. This source does not appear to explain the peak of concentration sums found near Baltimore Harbor, decreasing southward.

Up to this point the discussion has centered on the concentration sums of all resolvable components. While the total concentration sums allow a judgment of the quantities of organic compounds encountered in the Bay, Figures 8 and 9 give much more relevant information insofar as they represent the concentration sums of a group of compounds that contain many toxic, carcinogenic, mutagenic and teratogenic members, the polynuclear aromatics or PNA's. All of the PNA's whose concentrations have been summed in Figures 8 and 9 are unsubstituted and known to be generated in high temperature processes. As such, they are likely to be man-made pollutants (Youngblood and Blumer, 1975; Grimmer and Bohnke, 1972).

Although a "natural" origin in forest and prairie fires can be postulated (Youngblood and Blumer, 1975), their obvious preponderance in sediments near large population centers, industrial complexes and dense transportation networks must be taken as evidence of man-made input.

All the trends which were listed for Figures 4 through 7 generally also apply for the PNA's:

(a) The concentrations are higher in samples from the Northern Bay.

(b) In the Southern Bay, highest concentrations are found near river mouths.

(c) Concentrations tend to increase from the Potomac River to Baltimore Harbor.

(d) The Susquehanna River mouth sediments show considerable variability but can reach concentrations as high as one part per thousand.

Station histograms of several individual members of the PNA family are presented in Figures 10 through 23. Data displayed in these figures show even more clearly that a concentration maxima occurs in the Northern Bay in the vicinity of Baltimore Harbor and strongly suggest that this area is an important source.

The sediment samples collected at Station 19 were unusual in two aspects. One was a large increase in the overall concentration of organic compounds between the spring and fall samples; the other was a concurrent compositional change. The gas chromatogram for the fall sample was dominated by a very large peak that was identified (by mass spectrometry and retention) to be p,p'-DDT. o,p'-DDT is also present, but the derivatives, p,p'-DDE and o,p'-DDE, were not detected. Also present in abundance were polychlorinated biphenyls. Compared to the chlorinated hydrocarbons, the concentrations of PNA's were very small. This was the only sample collected in the Bay in which chlorinated hydrocarbons assumed such an overpowering presence. From the fact that p,p'-DDE and o,p'-DDE, compounds which DDT would degrade to over time, could not be found, one must conclude that a recent dumping operation had occurred. The relatively high PCB levels, not found in any of the other samples, point in the same direction.

In view of the drastic changes in the sample composition between the two cruises, this station and an area surrounding it were resampled about six and one-half months later (in cooperation with EPA, Annapolis). Analyses indicated p,p'-DDT to be present and at levels < 30 ppb.

The changes in sample composition and concentration occurring at Station 19 between the first and the second cruise are likely the result of the dumping of pesticides at high concentration in a container (such as a bag, carton or sheet-metal container) which in time eroded away or was disturbed in the sampling process, thus contaminating the area.

B. Oyster Samples

The gas chromatograms of oyster tissue extracts were much less complex than those of sediments, and the concentration of individual compounds was substantially lower than in sediments. The histograms in which the concentration representing the sum of all peaks are given as Figur s 24 and 25. It is obvious that there are no visible trends similar to those in the corresponding sediment histograms.

Many of the compounds present had structures we could not identify. 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 sum-histograms may not represent the pollutant content in oysters. Therefore a more meaningful approach may be to examine the number of compounds detected and their distributions rather than their sums. In all, there were 127 compounds tabulated. Oysters collected at the mouth of the James River contained 94 of these compounds. Oysters collected from Station 7 at Occohonnock Creek contained 27 and those from near Baltimore Harbor at Station 22 had 24. The oysters which contained the next most were from Station 20 at Holland Point with 23 compounds and Station 10 at Onancock Inlet with 19 compounds.

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 Station 3 at the mouth of the James River contained 29% of these. The next highest were from Station 22 near Baltimore Harbor with 24%. These were followed by Station 10 with 21%, Station 20 with 17%, and Station 7 with 14%. In summary, the following emerges:

(a) From abundance of compounds
James River > Occohonnock Creek > near Baltimore Harbor > Holland Point > Onancock Inlet

(b) From individual compound concentrations greater than 50 parts per billion
James River > near Baltimore Harbor > Onancock Inlet > Holland Point > Occohonnock Creek

In both cases the same five stations emerge as being the highest. Also, the James River station is highest in both, and the station nearest Baltimore Harbor is second in one and third in the other.

Comparison of the compounds detected in the oysters with those found in the nearby sediments shows little correlation. In sediment samples the most abundant compounds were PNA's. With the exception of dibenzothiophene, fluoranthene, pyrene and benzo(e)pyrene, none were detected in oysters. This could be due to several reasons: (a) the compounds may not be biologically available to the oysters, (b) the oysters may depurate them very rapidly, (c) the oysters may metabolize them to other compounds which were not identified.

From this study it appears that oysters were not as useful as sediments to monitor the Bay for xenobiotics. This does not mean that with further refinements in methods or for special cases where selected groups of compounds are sought that this situation would remain.

C. Baltimore Harbor

The Patapsco River was sampled during the spring of 1981. In all, forty-one bottom sediments were collected for organic chemical analysis. With a few exceptions, the same protocol was followed as for the Chesapeake Bay samples. The samples were much more concentrated in organics than were those from outside the River. This resulted in the "flooding" of

chromatographic columns on numerous occasions and hence unpredictable separations. Flooding was corrected by reducing the amount of sample to be extracted. The equivalent sample size necessary for analysis was approximately one one-hundredth as that required for Bay samples.

The interpretation of data derived from the Patapsco River samples is not yet complete, but there are several notable aspects derived thus far. One is that the PNA's dominate the aromatic compounds present. This was also the situation for samples from the Chesapeake Bay proper. In some cases the concentrations were ten to twenty times higher than the highest found in the Bay, with the exception of the Bay Station 27 sampled in the fall of 1979 at the mouth of the Susquehanna River. Another aspect is that the distributions of the PNA's within the River are not uniform. This suggests that there are either point sources of PNA's or nonuniform water circulation and sediment type which causes the xenobiotics to accumulate more in specific areas. It is likely that a combination of these two factors is responsible for the distributions.

To convey a visual impression of the distributions, Figures 26 thru 29 are presented. Figure 26 represents the concentrations, normalized to silt and clay content, of one of the PNA's, benzo(a)pyrene, in the main channels of the Patapsco River. The length of a cylinder is proportional to the concentration found at that location. The longest represents a concentration of 1,400 parts per billion (ppb). It is obvious that there are several areas where relatively high levels exist. In an attempt to show that point sources may be, in part, responsible for the anomalous distributions, Figure 27 was constructed. It includes the same stations as in Figure 26, as well as ones located closer to shore and the closest one from the Bay, Station 23. In this case, the longest cylinder represents

a normalized benzo(a)pyrene concentration of 5,500 ppb. It appears that point sources contribute to the channel concentrations. The benzo(a)pyrene concentration in Bay sediments is depicted by the cylinder farthest to the right. The concentration here is about that of the station next closest within the Patapsco, 260 ppb vs 290 ppb, respectively. This suggests, but does not prove, that the peak of PNA's found in the Bay near the Patapsco River mouth could be the result of transport from the River.

Figures 28 and 29 convey essentially the same information as did Figures 26 and 27. The compound depicted in this case is the PNA, chrysene. The channel stations (Fig. 28) show that nonuniform concentrations exist and the addition of the near-shore stations (Fig. 29) support the conclusion that point sources may be partly responsible. Again, as with benzo(a)pyrene, the Bay station match those just within the mouth of the Patapsco. The longest cylinder in Figure 29 represents a normalized chrysene concentration of 7,900 ppb.

One sample from the Patapsco River gave a very anomalous gas chromatographic fingerprint which was dominated by an abundance of compounds with relatively low retention times and high concentrations (Fig. 30). The compounds were not PNA's. Mass spectrometric analysis and comparison with EPA-NIH Mass Spectral Data Base showed that they were composed of substituted benzenes. We then searched the mass spectrometry data files to see if these compounds were present at any other locations but had been hidden by more concentrated PNA's. The search showed that indeed several of the substituted benzenes were definitely present in other samples. Data from some other samples showed that they were either not present or were probably present. The basis for saying that they were probably present was that they had matching relative retention times and the required major ion fragments

generated by mass spectrometry, but there were additional fragments from other compounds eluting in the same region. Figure 31 shows the areas where a substituted benzene, 6-phenyldodecane, was searched for and either definitely detected, probably detected or not detected.

It is apparent that the compound has a widespread distribution within the Patapsco River and the data indicate that sediments within the Bay near the River probably contain it. The sample with the highest concentration was collected well upstream from the mouth of the River. It would be improper to assume, without source information, that the sample with the highest concentration was closest to where the compounds entered the system. For example, the highest concentrations of Kepone in the James River were found tens of kilometers downstream from the source.

Fortunately, another portion of the Chesapeake Bay Program focused on determining what organic and inorganic compounds were in effluents being discharged into the Bay and its tributaries. In this work, done by Monsanto Research Corporation under EPA Contract 68-02-3161, a number of effluents entering the Patapsco River were analyzed. Data generated by Monsanto showed that an effluent collected very near the sediment station which is given in Figure 30, contained substituted benzenes and specifically 6-phenyldodecane. Using this compound as a tracer, we must conclude that organic compounds can enter the Patapsco River from point sources to be transported throughout the River and probably into the Bay. The fact that 6-phenyldodecane was only "probably present" in the two eastern most samples (Figure 31) prevents our saying that this is definitely the case, but it is difficult to conceive of a mechanism which 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 which are less definitive than the others since they are in the Bay where more mixing and dispersion occurs and they are farthest from the source.

The PNA concentrations in the Bay which peak near the mouth of the Patapsco River, the much higher levels found within the River and the 6-phenyldodecane distribution form the basis for our argument that some of the xenobiotic compounds in the Northern Bay sediments come from the Patapsco River.

CONCLUSIONS

The data presented in this manuscript prove that the Chesapeake Bay contains polynuclear aromatic hydrocarbons in its sediments and in lesser amounts in its oysters. The question which must be answered is: are the concentrations the result of man's activity or are they natural from such sources as natural oil seeps or forrest fires? The distributions and abundances of the PNA's within the Bay and the Patapsco River leaves little doubt that man is in part responsible. Undoubtedly there is a natural background. For instance, samples collected from two rivers which should be relatively pristine, the Rhode and Ware Rivers, contained concentrations of chrysene ranging from 26 to 110 ppb and benzo(a)pyrene from 7 to 100 ppb. Perhaps these reflect the natural background. Yet with man's burning of fossil fuels which produces PNA's to be transported by winds far from their sources, even those levels are probably unnatural. The relatively high concentrations in the upper Bay are likely the result of airborne transport with subsequent rainout as well as waterborne transport from sources such as the Patapsco River.

With the increasing use of fossil 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/or teratogenic to mammals is enough cause for concern.

The Chesapeake Bay has, at least on one occasion, been the recipient of the direct disposal of pesticides. Fortunately the quantities were small enough and/or the assimulation capacity large enough that no long-term effects 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.

Finally, the importance of chemically monitoring effluents and sediments collected near the outfalls was shown. Perhaps more effort along these lines may help prevent future "Kepone episodes."

It is hoped that the data presented here will be of assistance to managers and decision makers concerned with the Chesapeake Bay and its tributaries.

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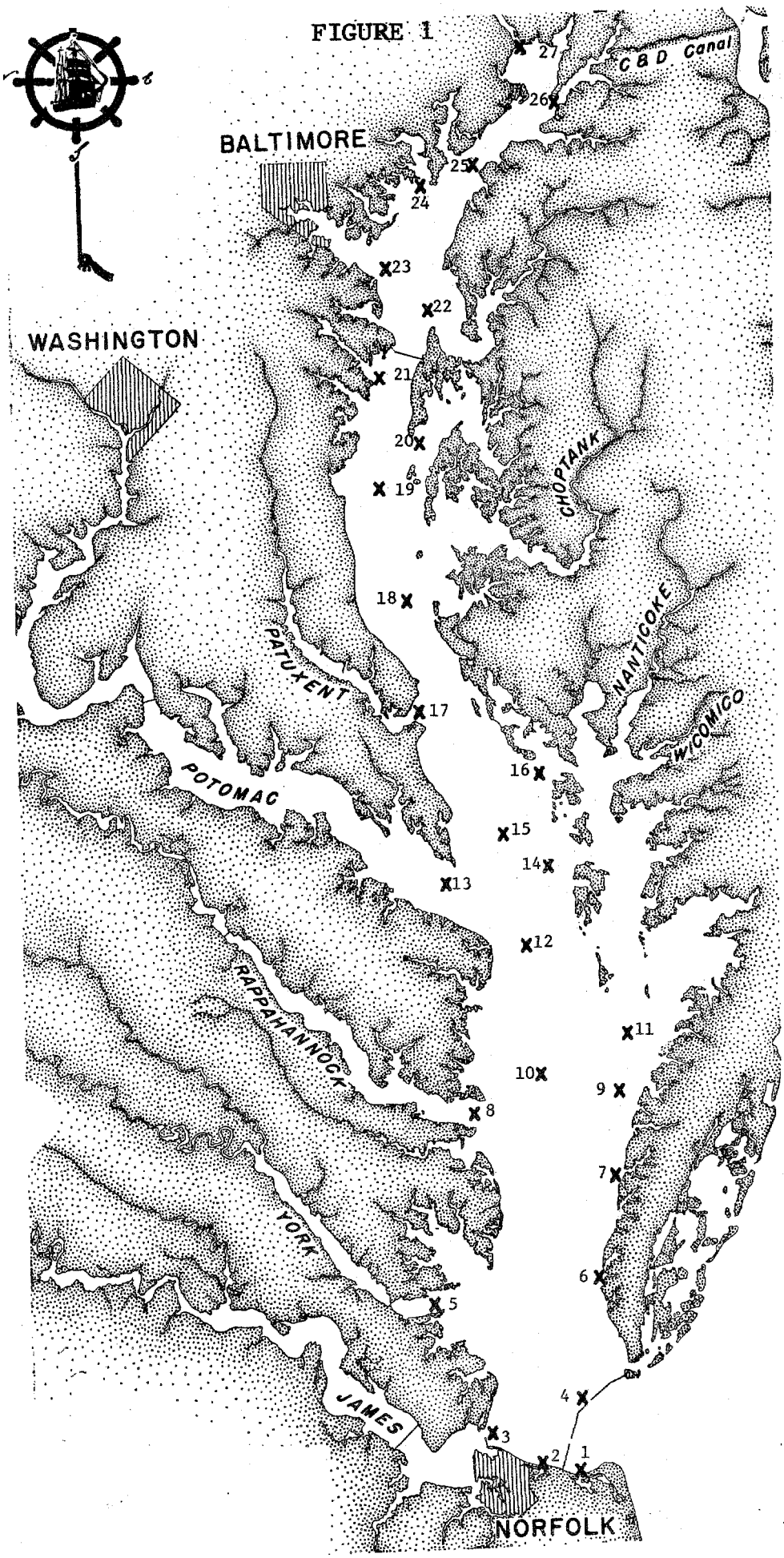
FIGURE 1

Chesapeake Bay Sediment Sample Locations.

FIGURE 1



Chesapeake Bay Sediment Sample Locations

Figure 1

FIGURE 2

Chesapeake Bay Oyster Sample Locations.

FIGURE 2

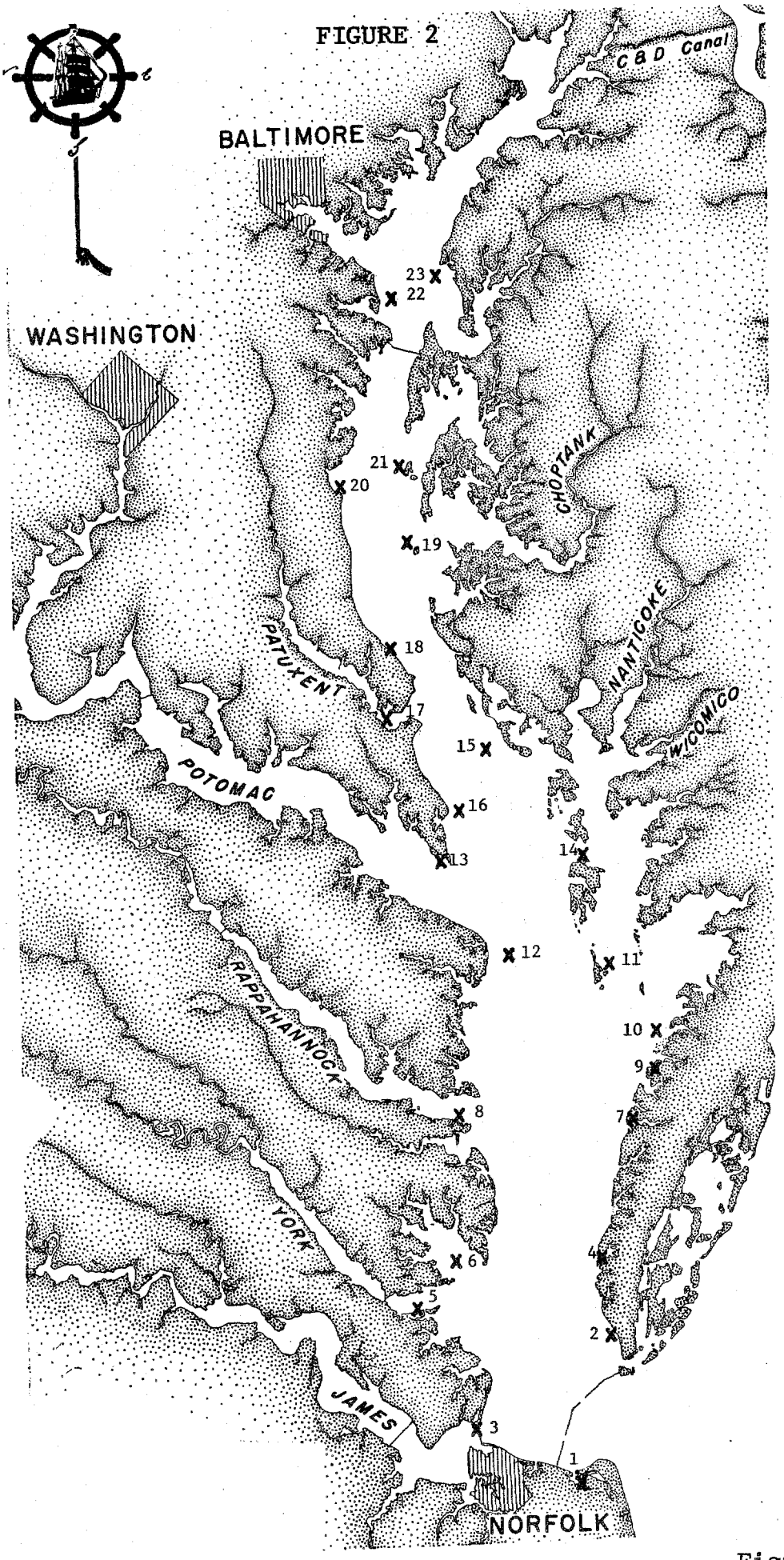
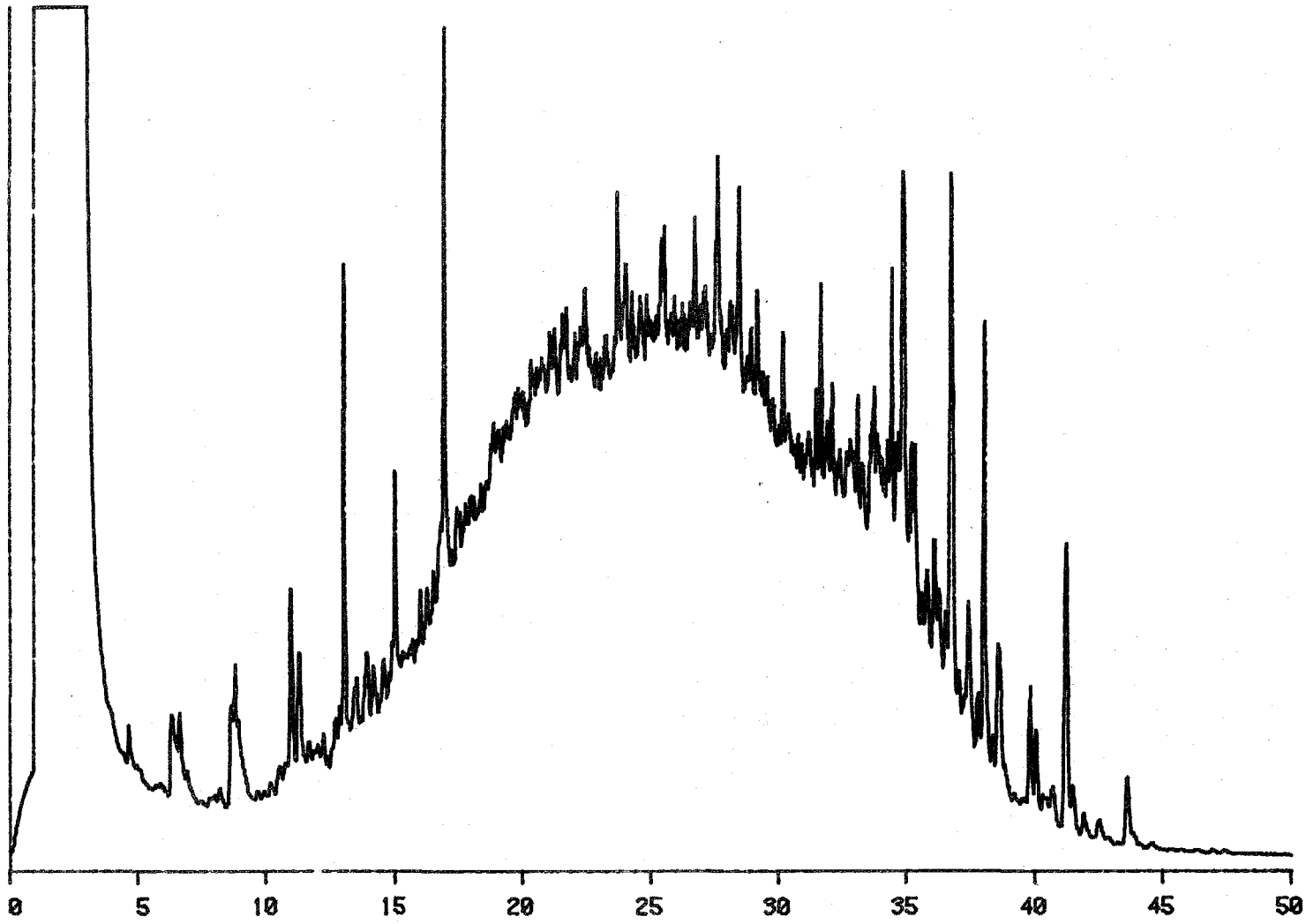


Figure 2

Chesapeake Bay Biota Sample Locations

FIGURE 3

Gas Chromatogram of Sediment Sample.



SAMPLE : 2-23SG3.1+BI RAW FILE : RP8SFR

PLOTTING TIME : 0 TO 50 MINS.

FIGURE 4

Sum of All Resolvable Peaks,
Sediment Samples, Spring 1979.

SUM OF ALL PEAKS

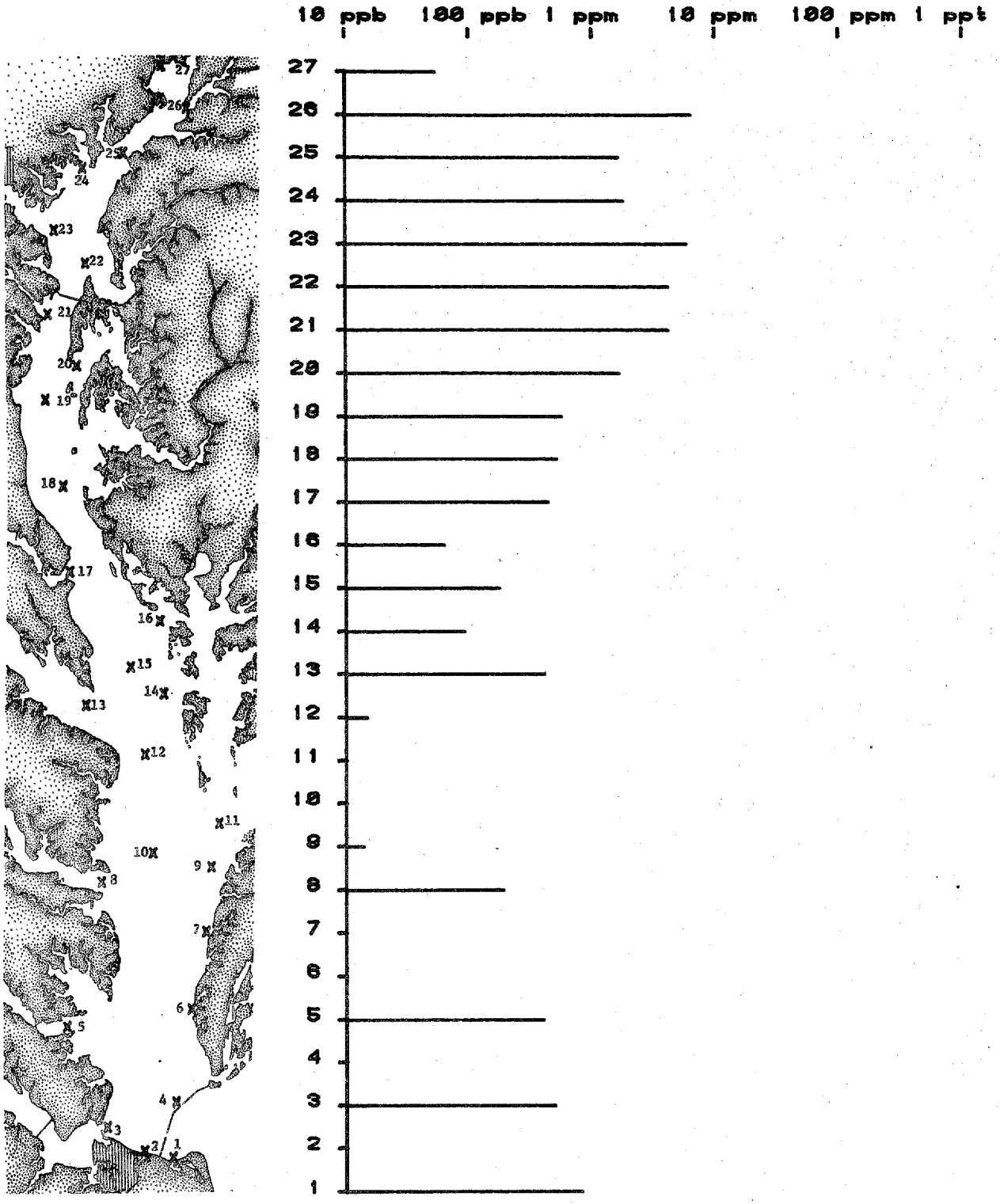


FIGURE 5

Sum of All Resolvable Peaks,
Sediment Samples, Fall 1979.

SUM OF ALL PEAKS

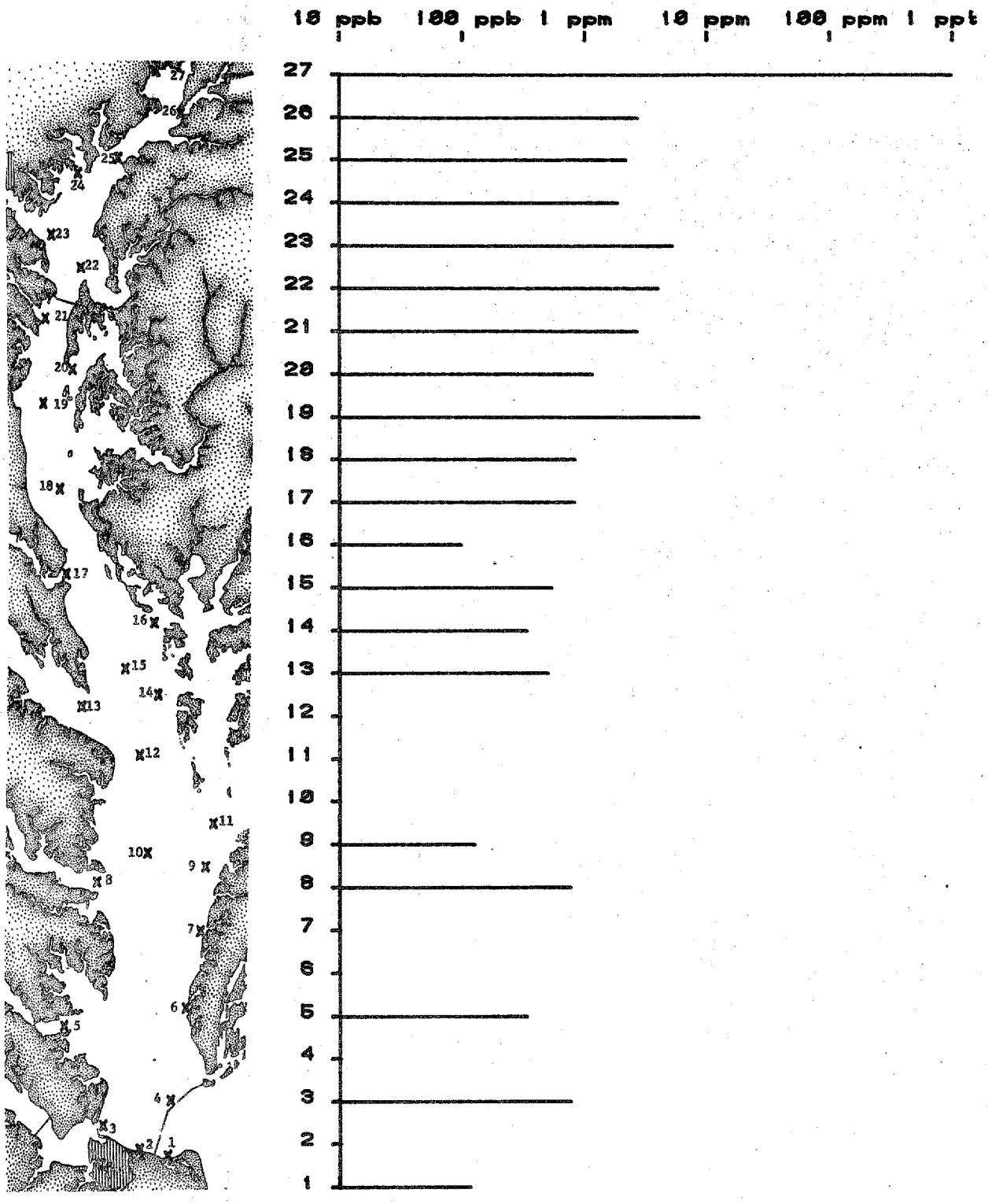


FIGURE 6

Sum of All Resolvable Peaks, Normalized to
Silt and Clay, Sediment Samples, Spring 1979.

TOTALS NORMALIZED TO SILT/CLAY

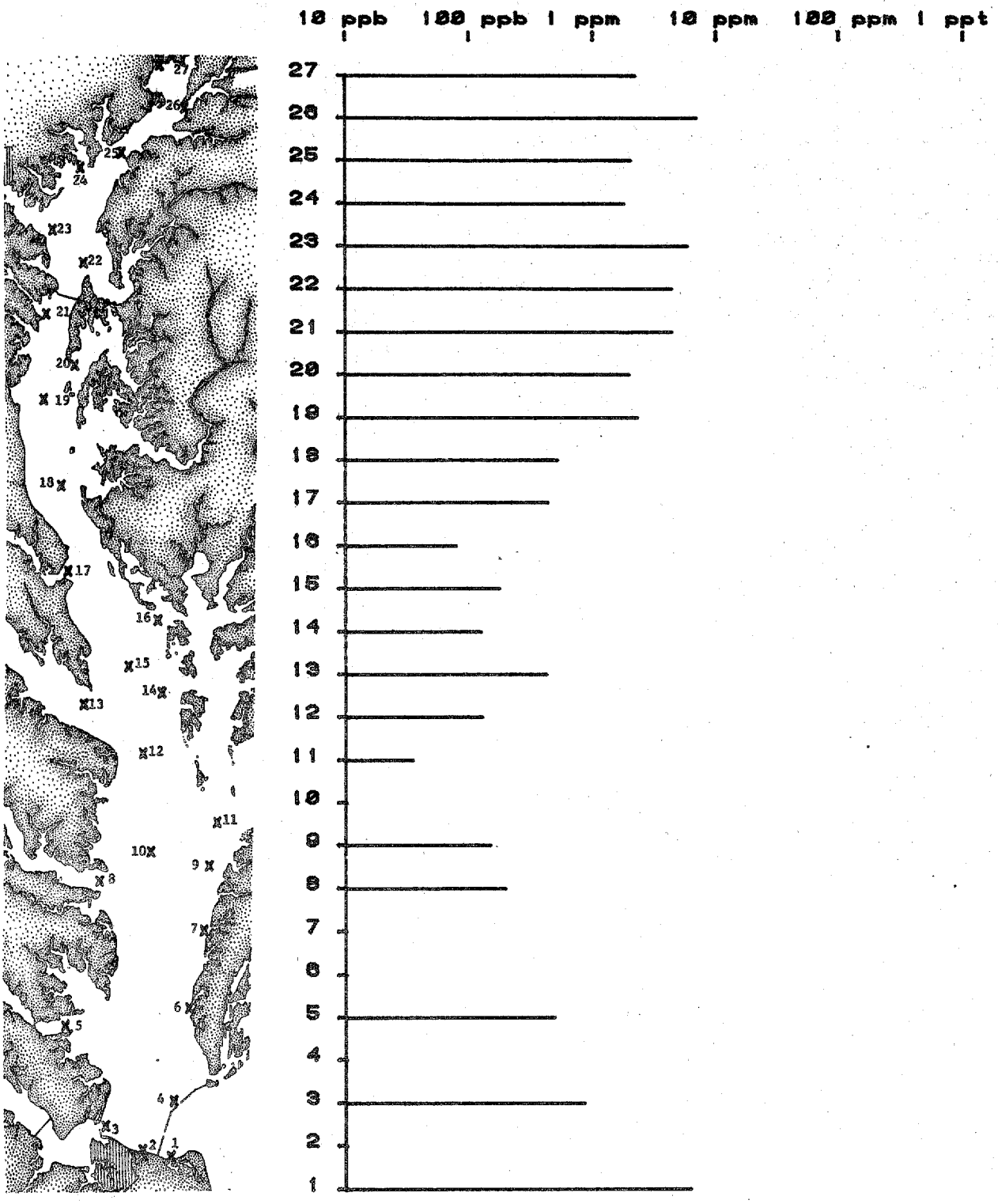


FIGURE 7

Sum of All Resolvable Peaks, Normalized to Silt and Clay, Sediment Samples, Fall 1979.

ARI : TOTALS NORMALIZED TO SILT/CLAY

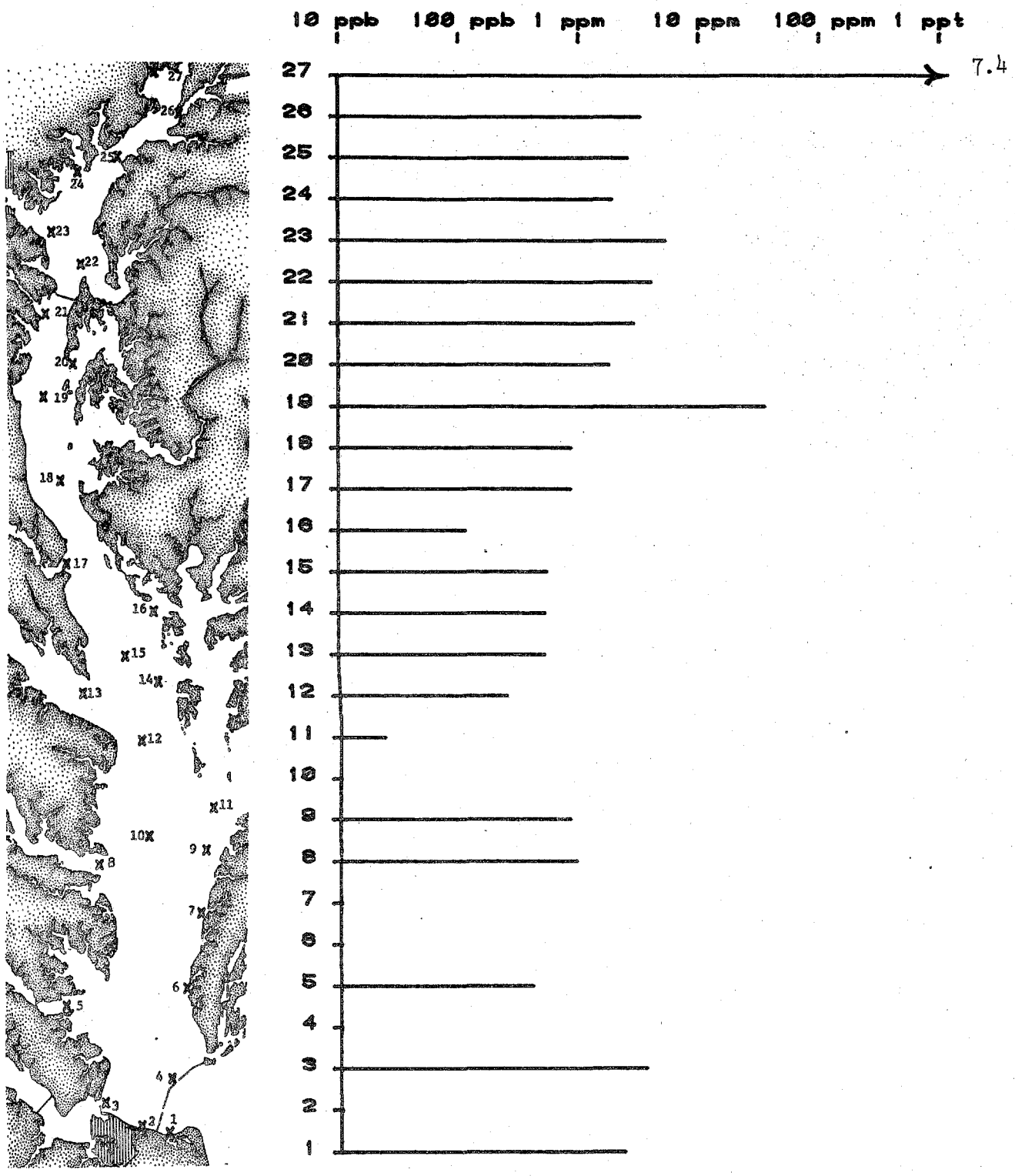


FIGURE 8

Sum of Pyrogenic Polynuclear Aromatic Hydrocarbons, Spring 1979.

SUM OF PYROGENIC PAH'S

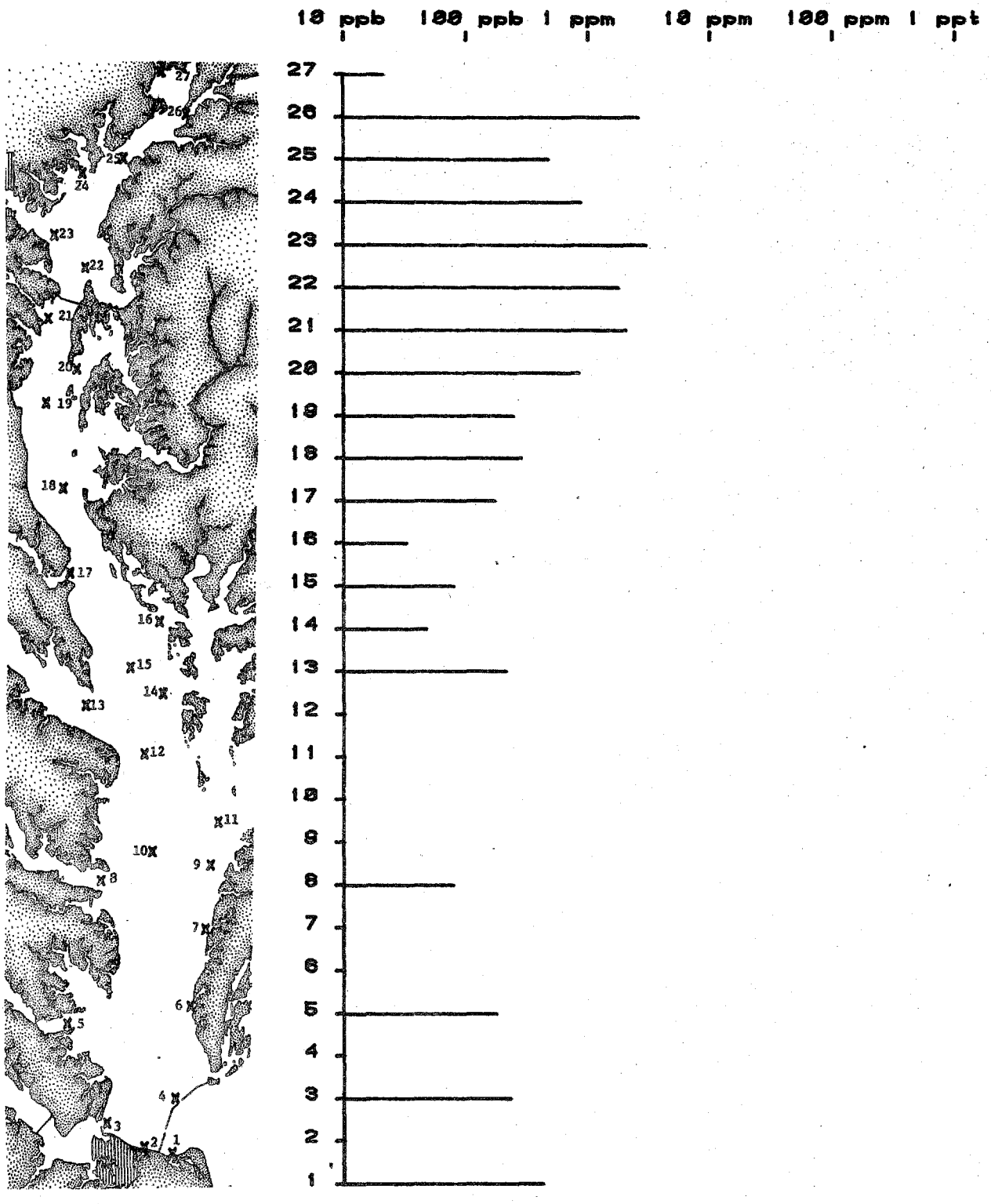


FIGURE 9

Sum of Pyrogenic Polynuclear Aromatic Hydrocarbons, Fall 1979.

SUM OF PYROGENIC PAH'S

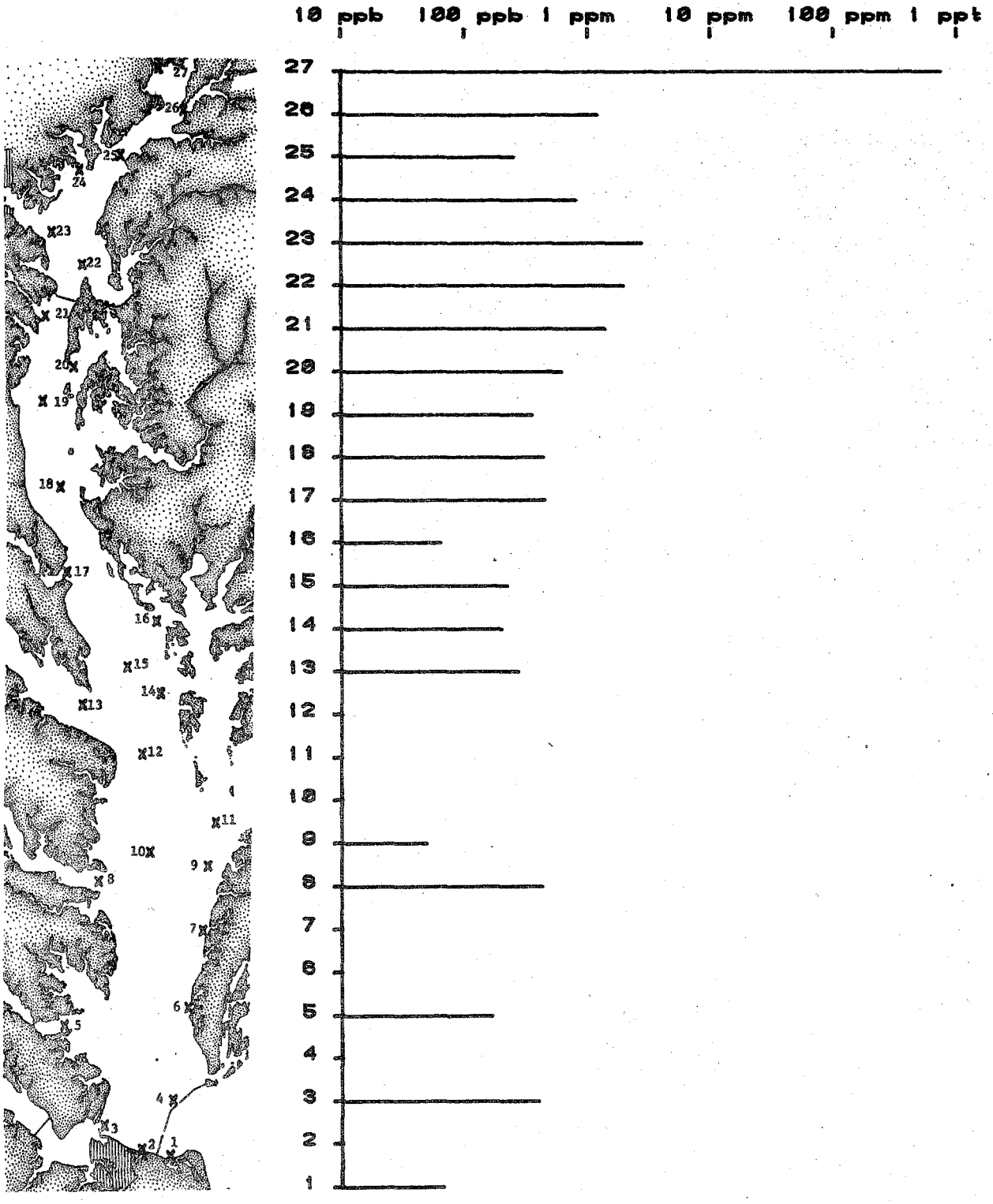


FIGURE 10

Phenanthrene in Sediments, Spring 1979.

ARI : 200 Phenanthrene

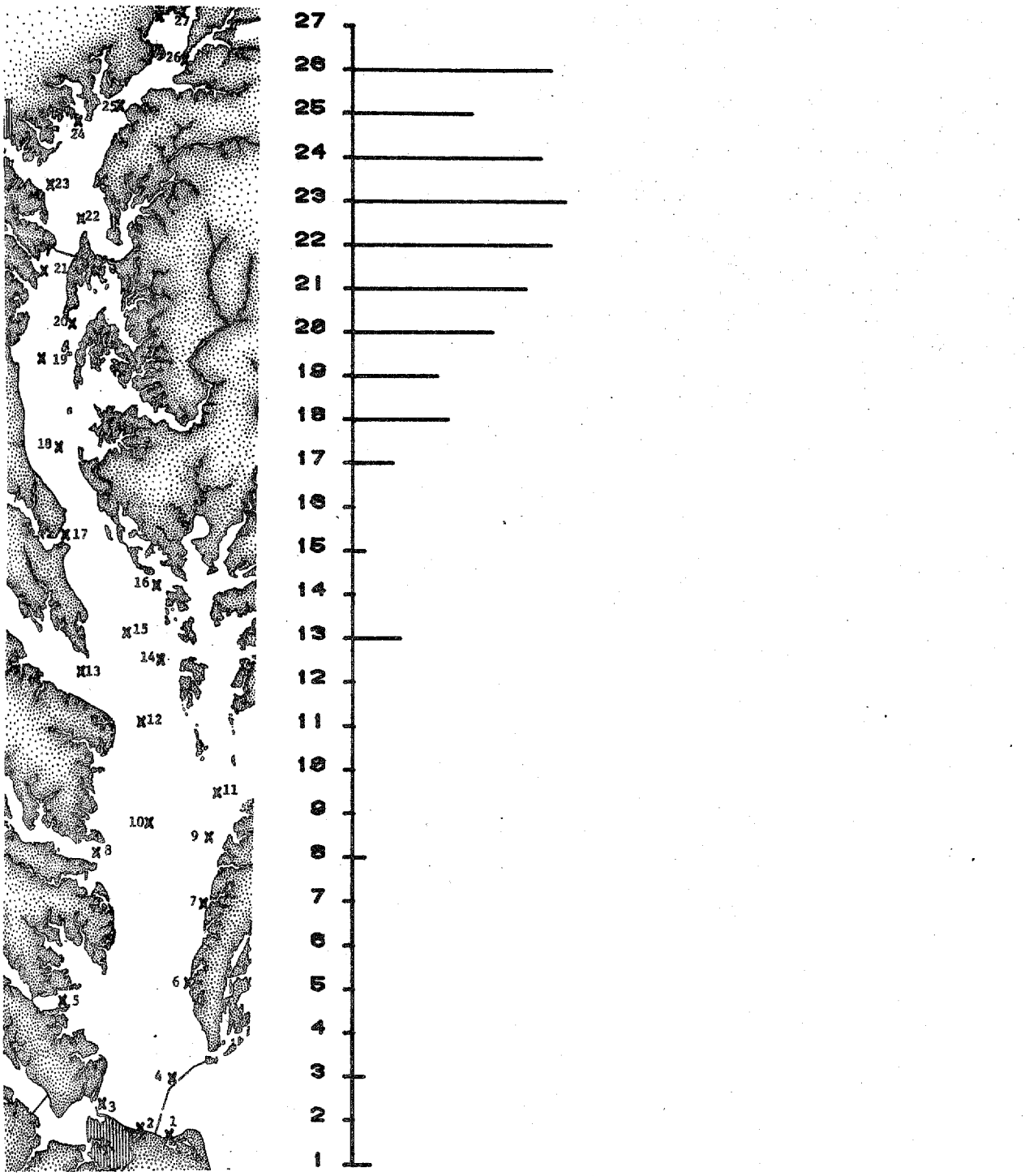
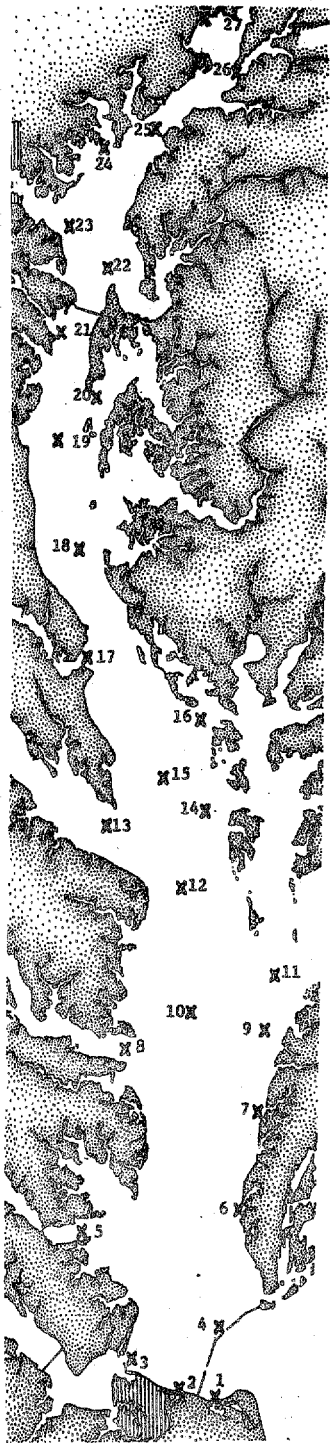


FIGURE 11

Phenanthrene in Sediments, Fall 1979.

ARI : 200 Phenanthrene



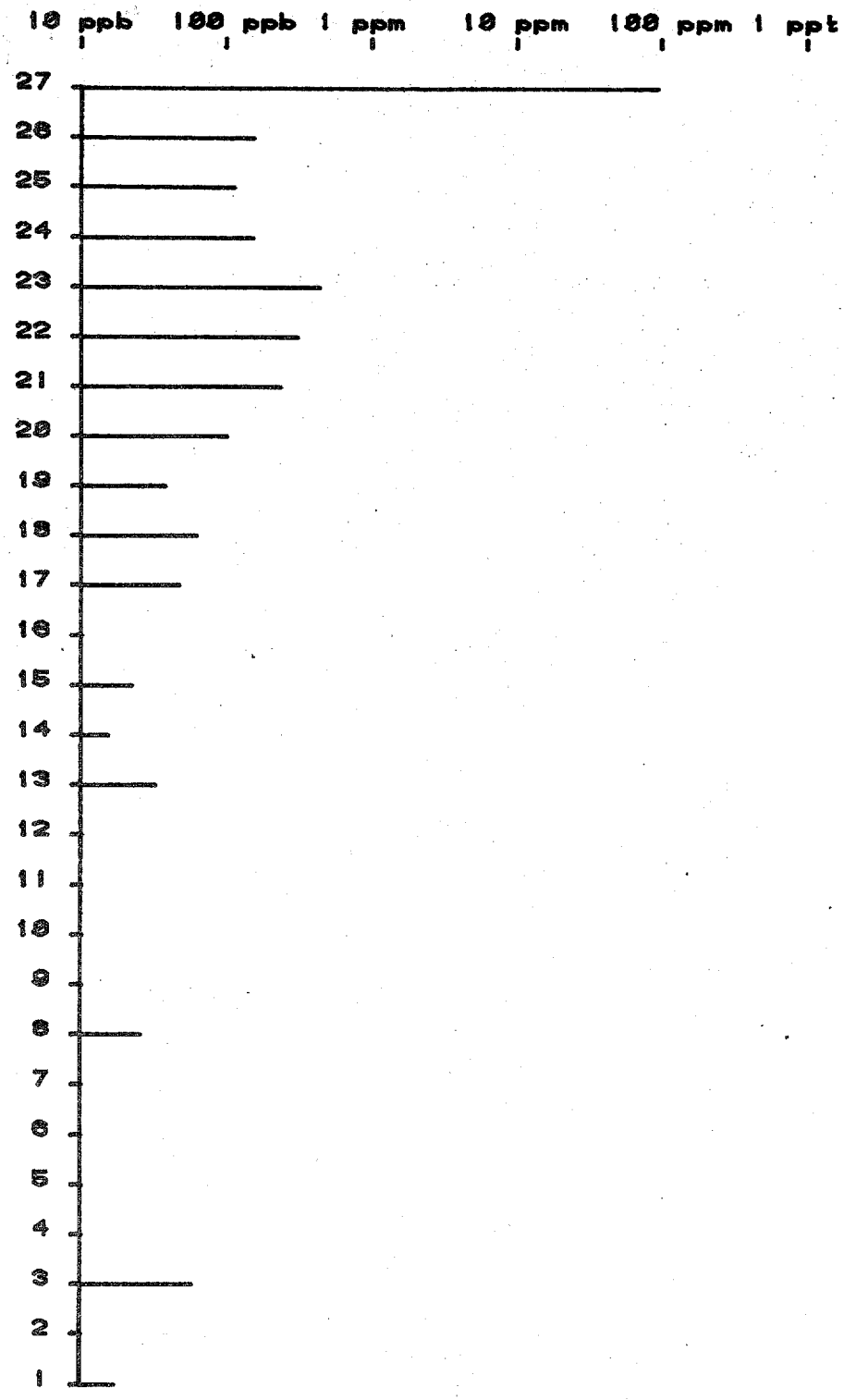


FIGURE 12

Fluoranthene in Sediments, Spring 1979.

ARI : 285.4 Fluoranthene

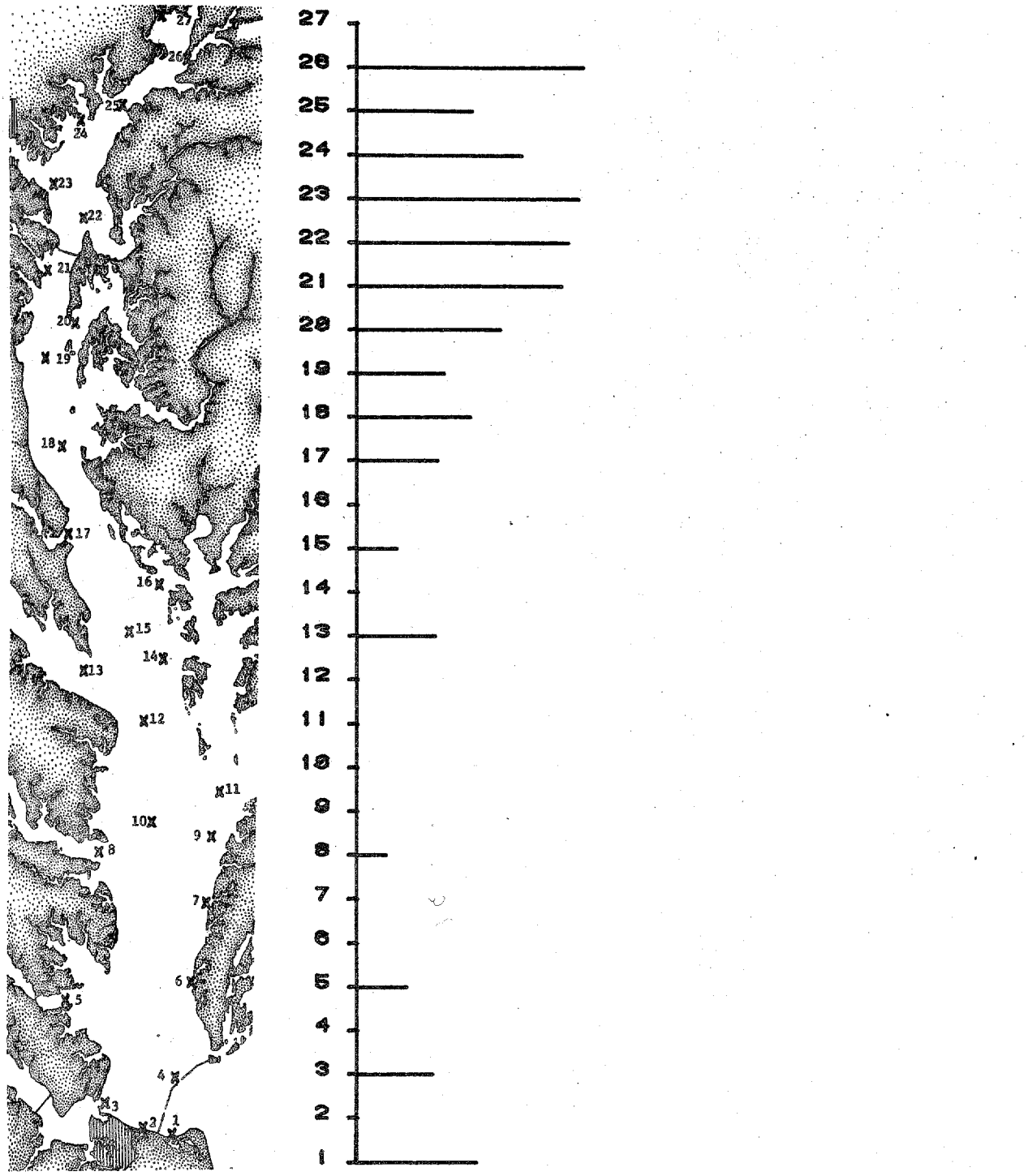
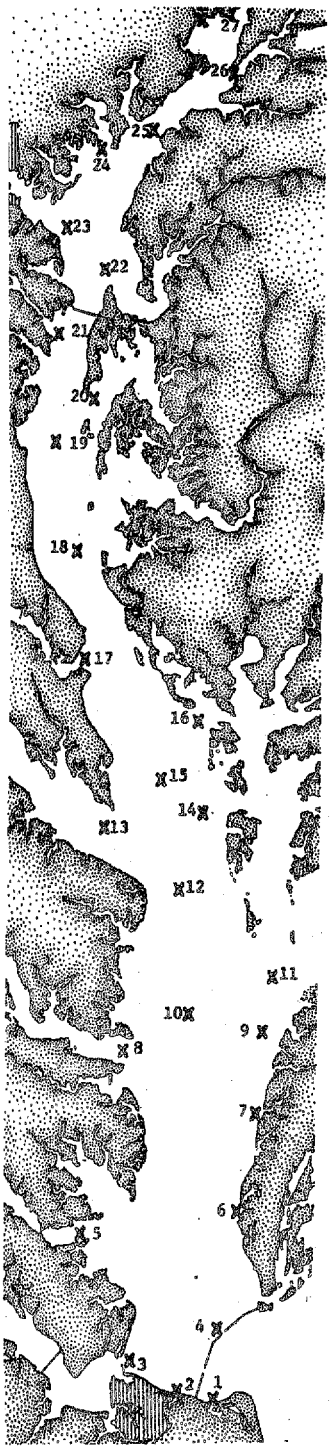


FIGURE 13

Fluoranthene in Sediments, Fall 1979.

ARI : 285.4 Fluoranthene



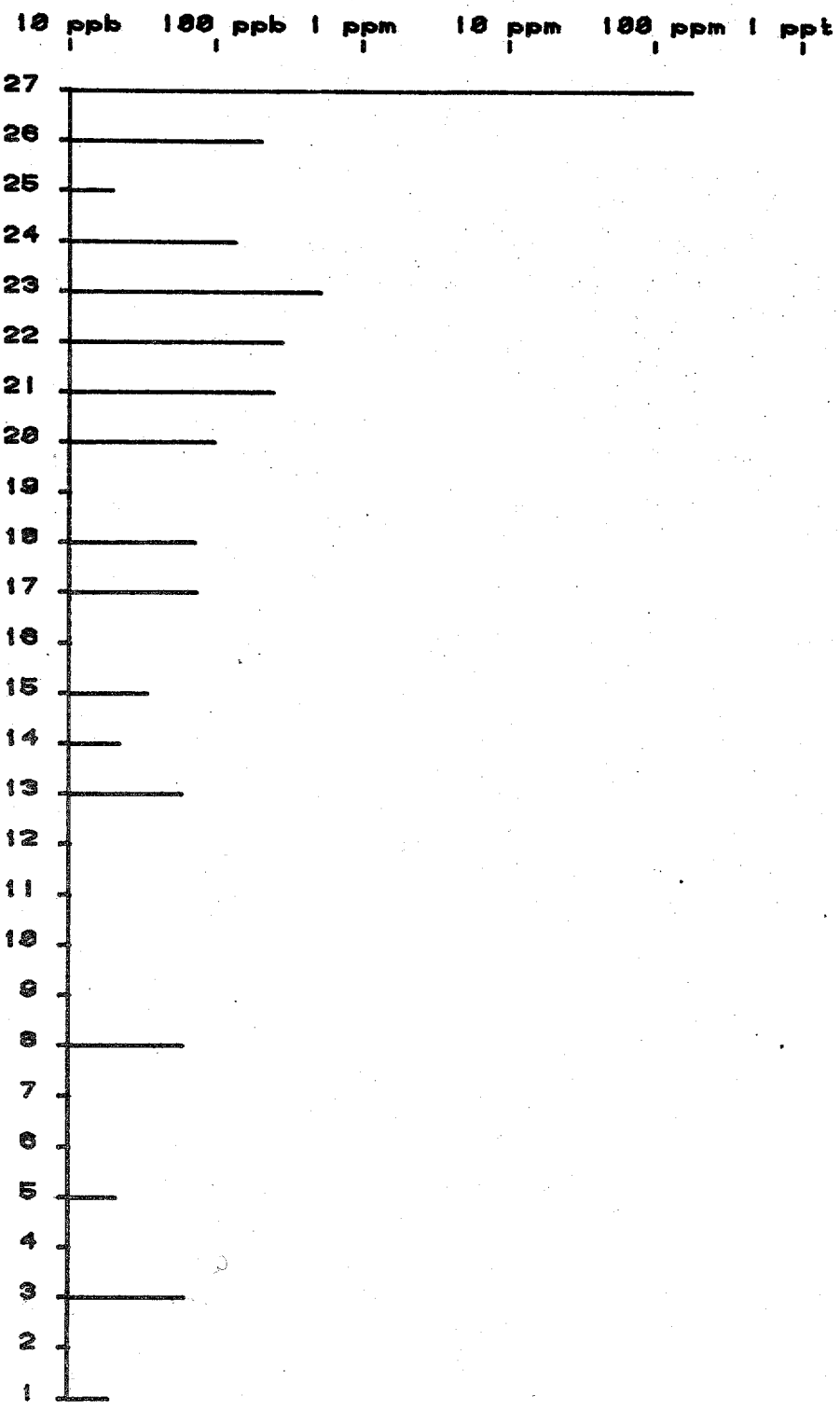


FIGURE 14

Pyrene in Sediments, Spring 1979.

ARI : 300 Pyrene

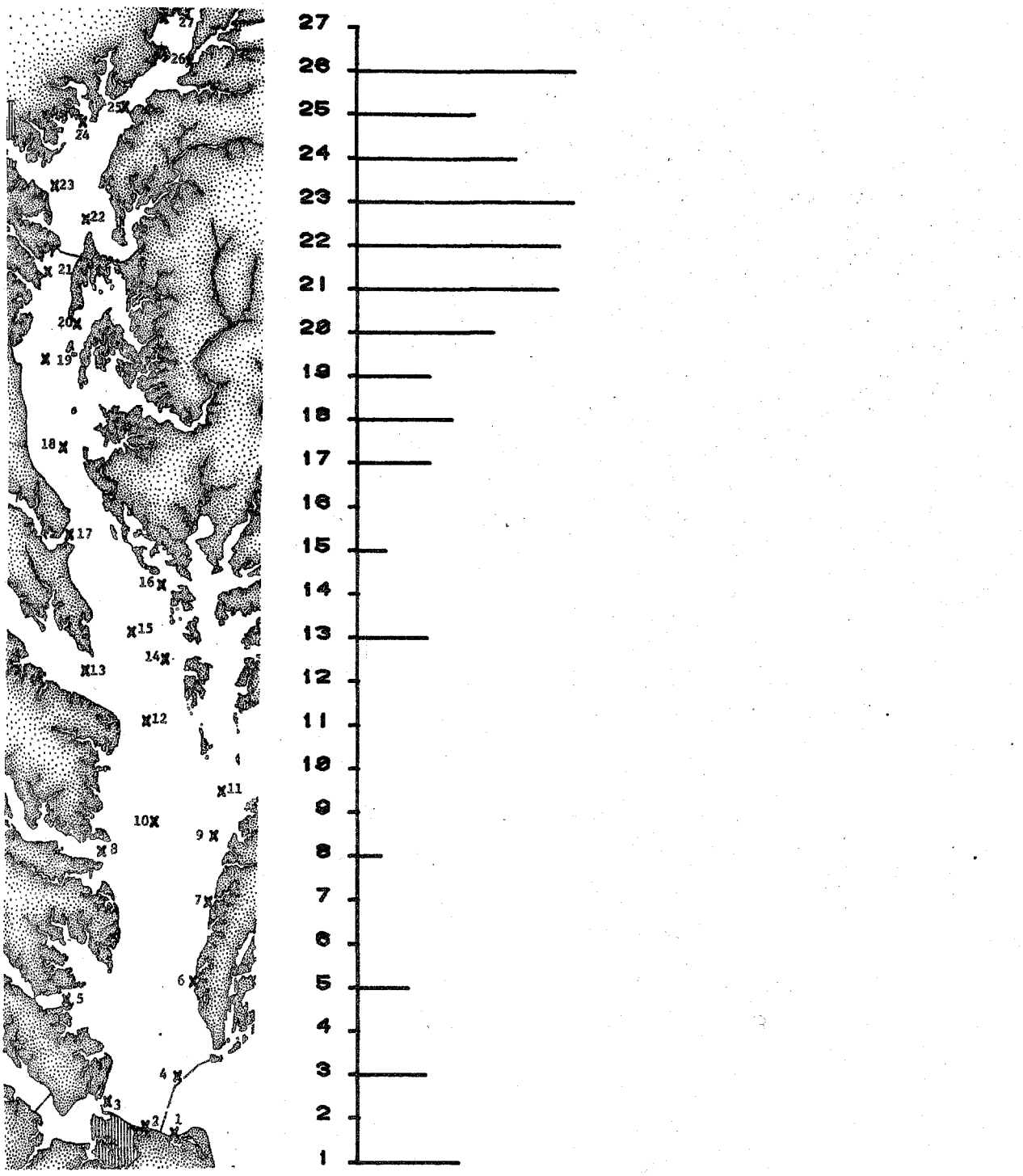


FIGURE 15

Pyrene in Sediments, Fall 1979.

ARI : 300 Pyrene

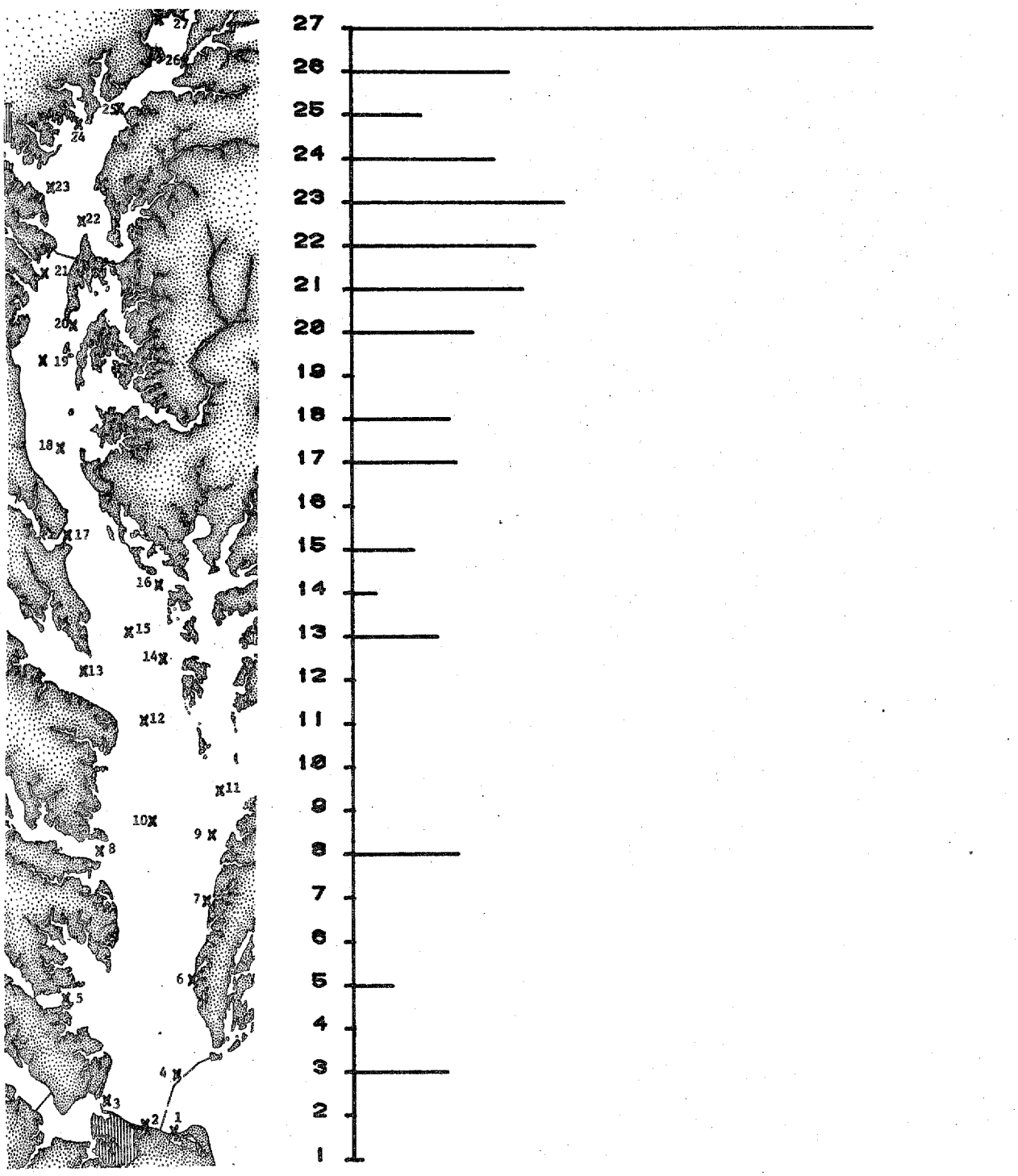


FIGURE 16

Benz(a)anthracene in Sediments, Spring 1979.

ARI : 397.1 Benz(a)anthracene

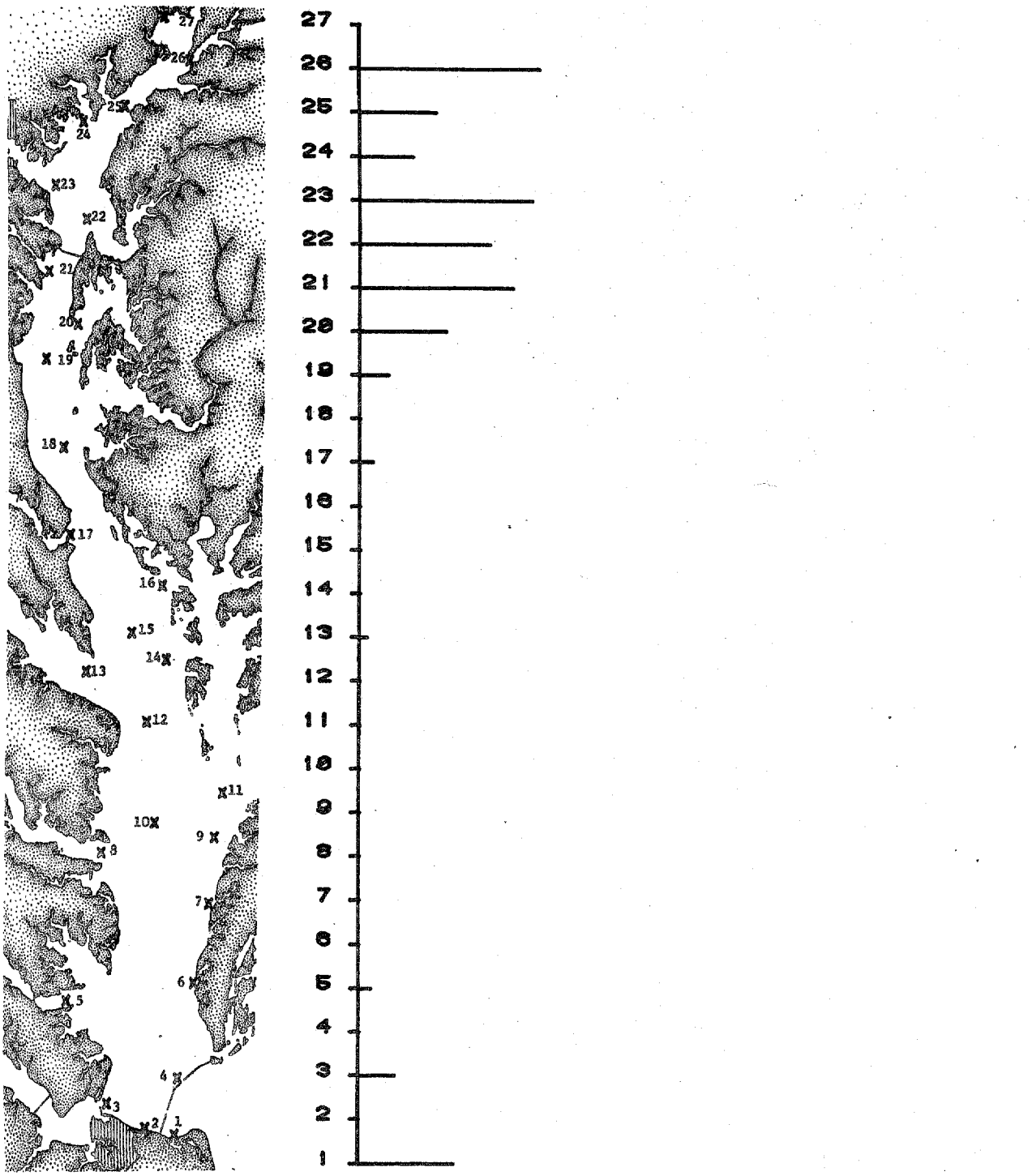


FIGURE 17

Benz(a)anthracene in Sediments, Fall 1979.

ARI : 397.1 Benz(a)anthracene

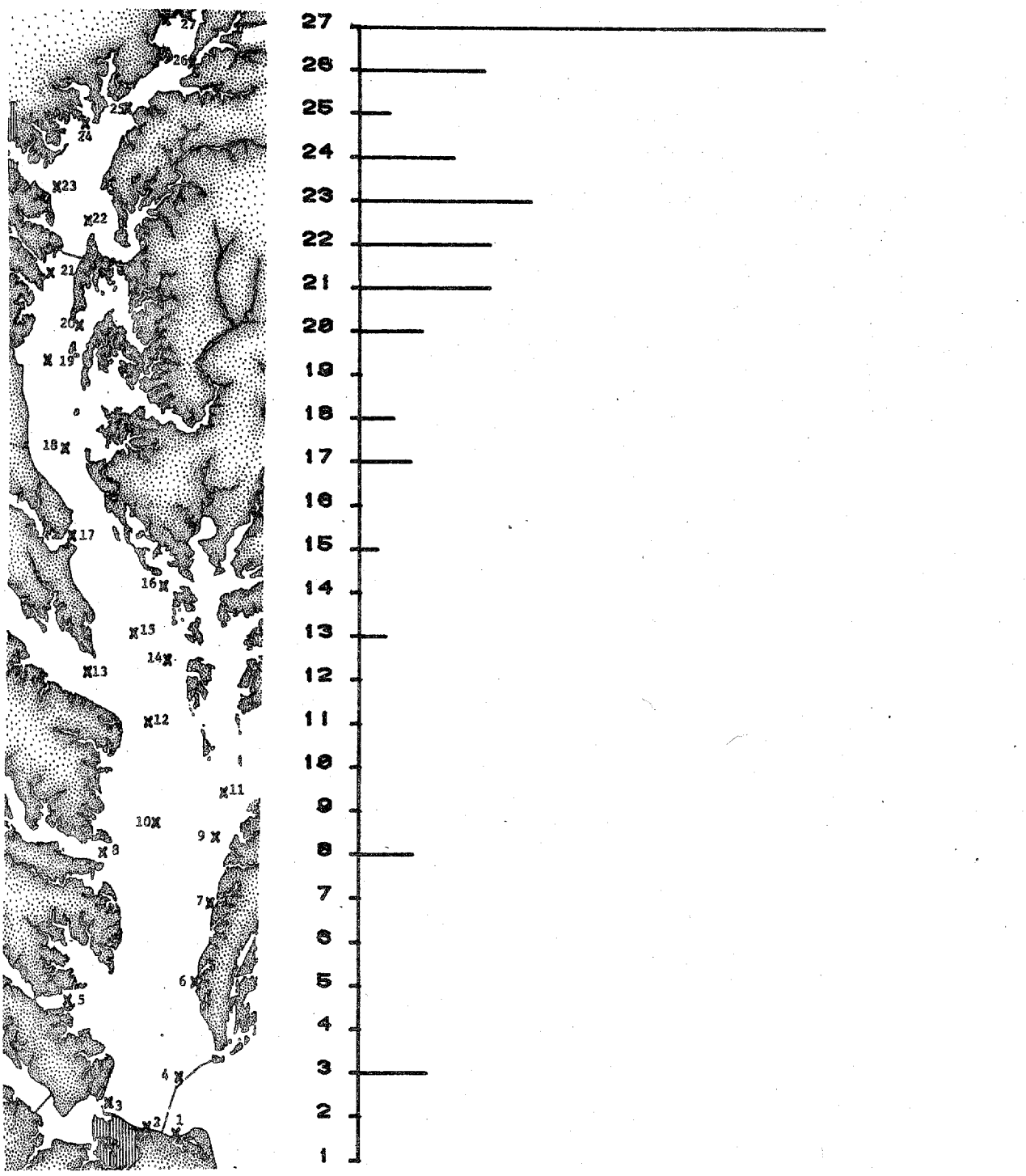


FIGURE 18

Chrysene in Sediments, Spring 1979.

ARI : 400 Chrysene

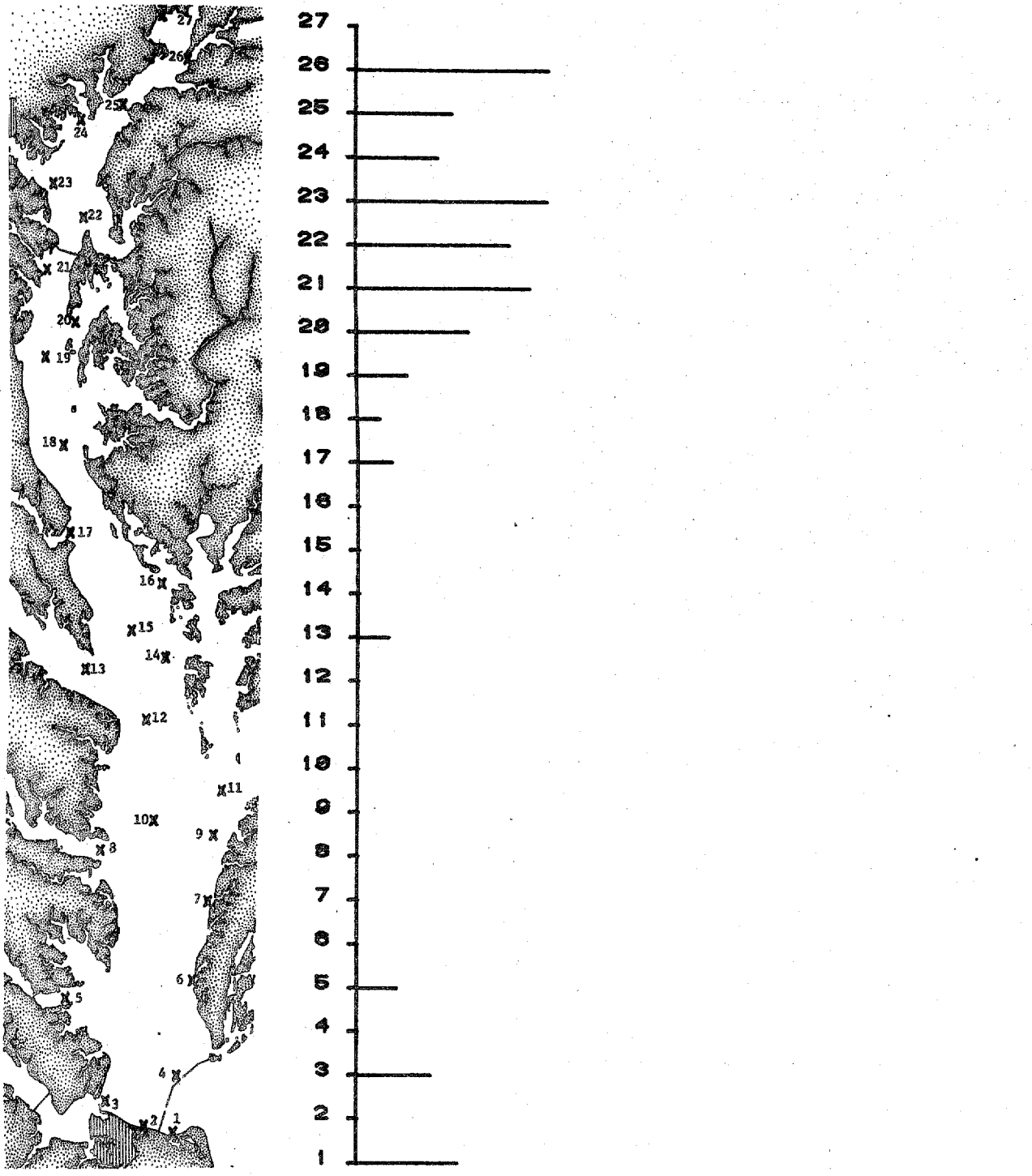
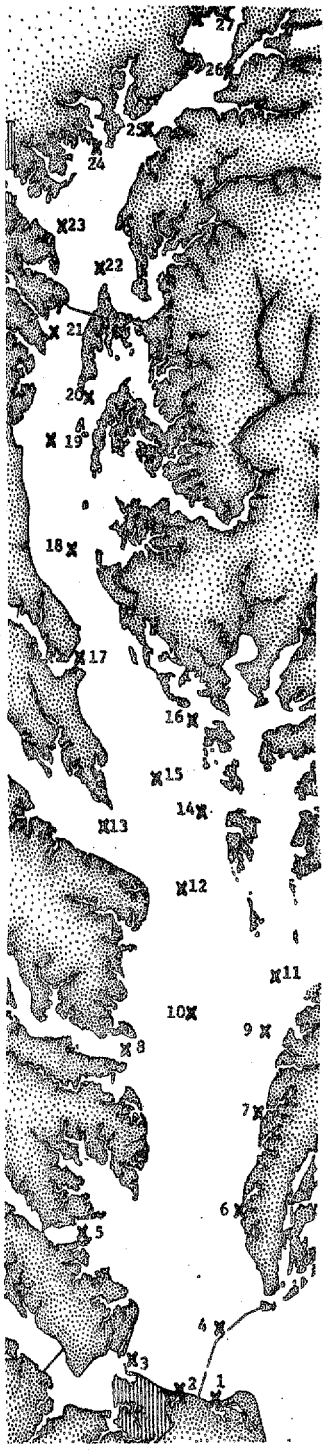


FIGURE 19

Chrysene in Sediments, Fall 1979.

ARI : 400 Chrysene



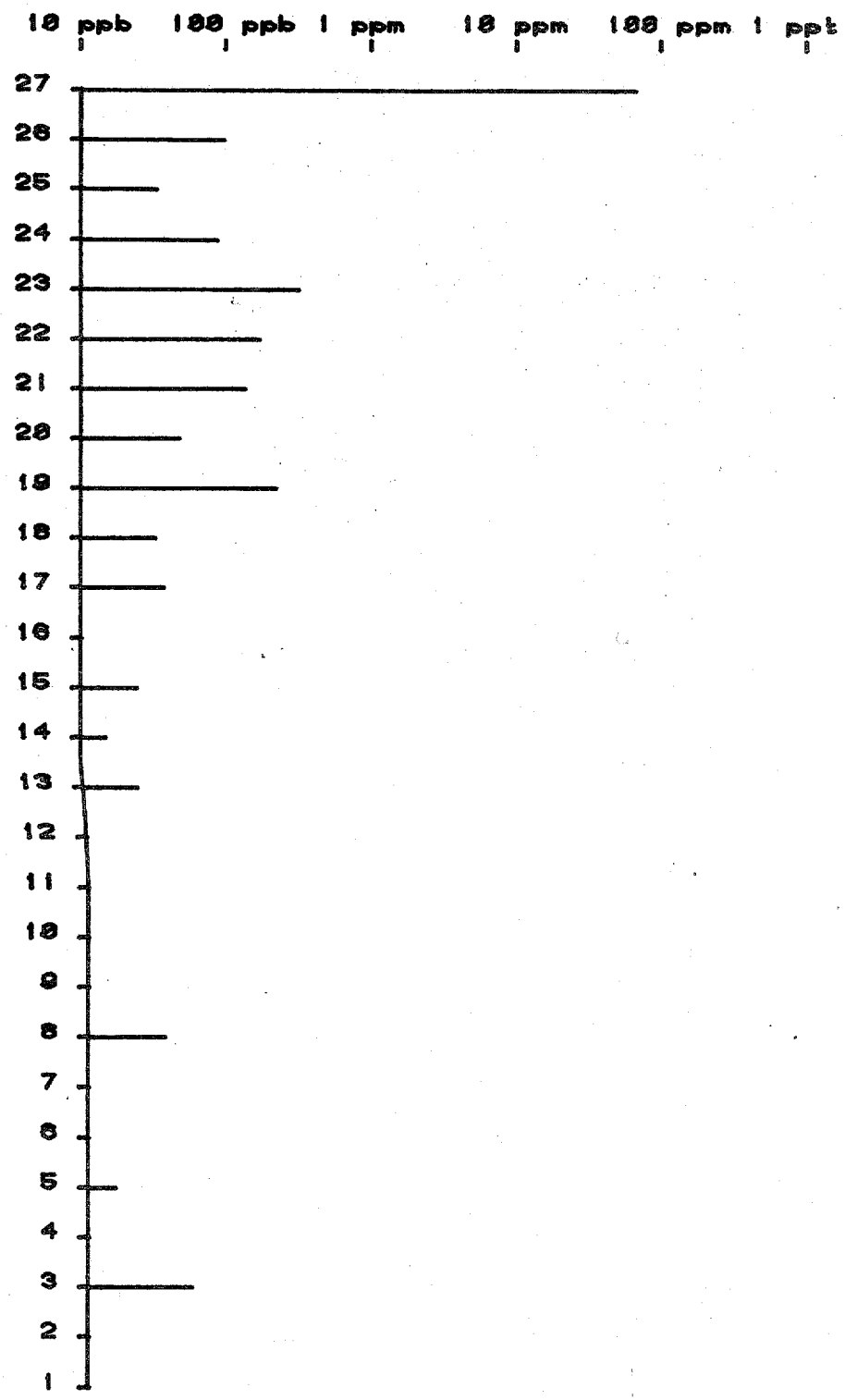


FIGURE 20

Benzo(a)pyrene in Sediments, Spring 1979.

ARI : 494.3 Benzo(a)pyrene

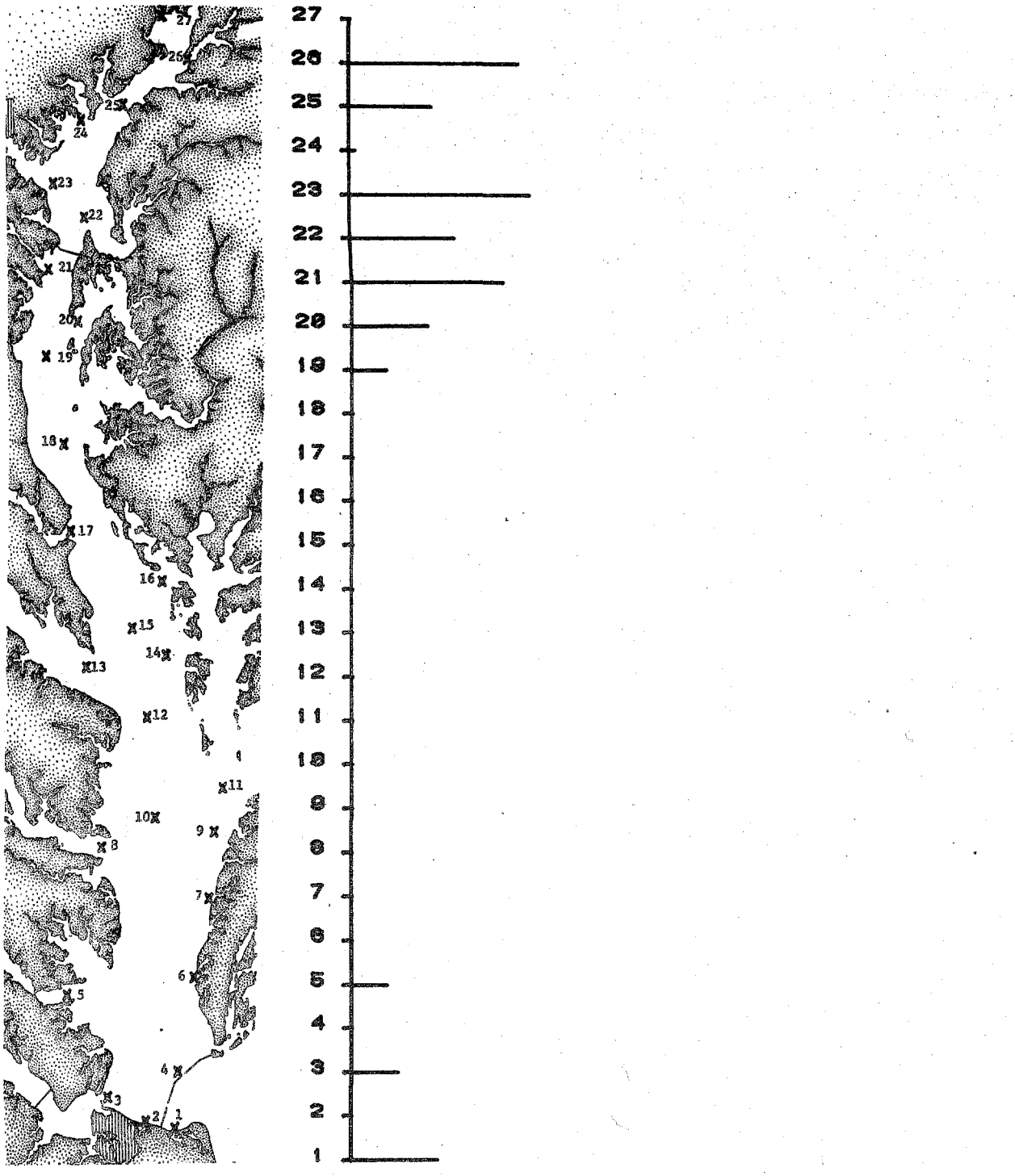


FIGURE 21

Benzo(a)pyrene in Sediments, Fall 1979.

ARI : 494.3 Benzo(a)pyrene

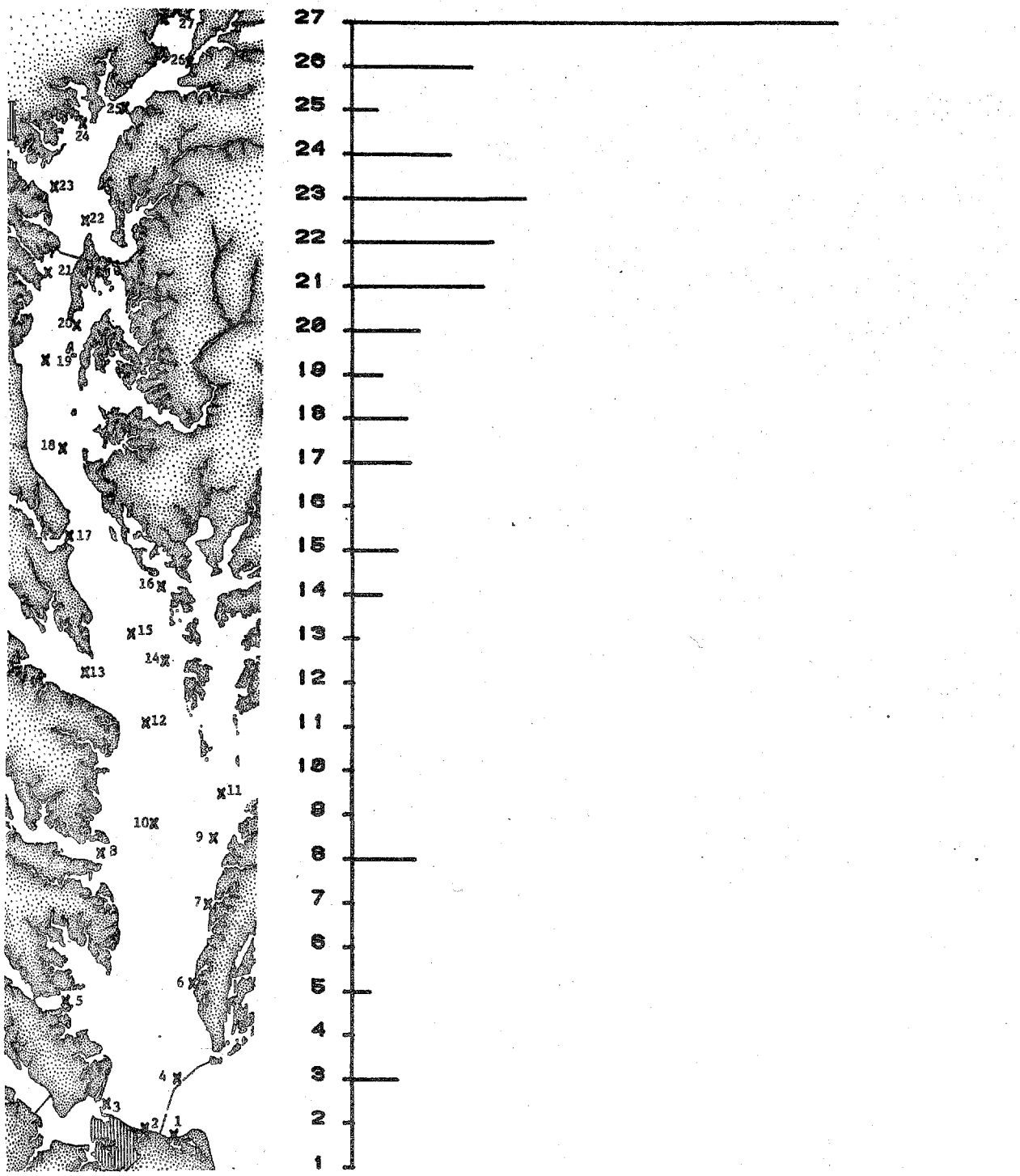


FIGURE 22

Benzo(ghi)perylene in Sediments, Spring 1979.

ARI : 600 Benzo(ghi)perylene

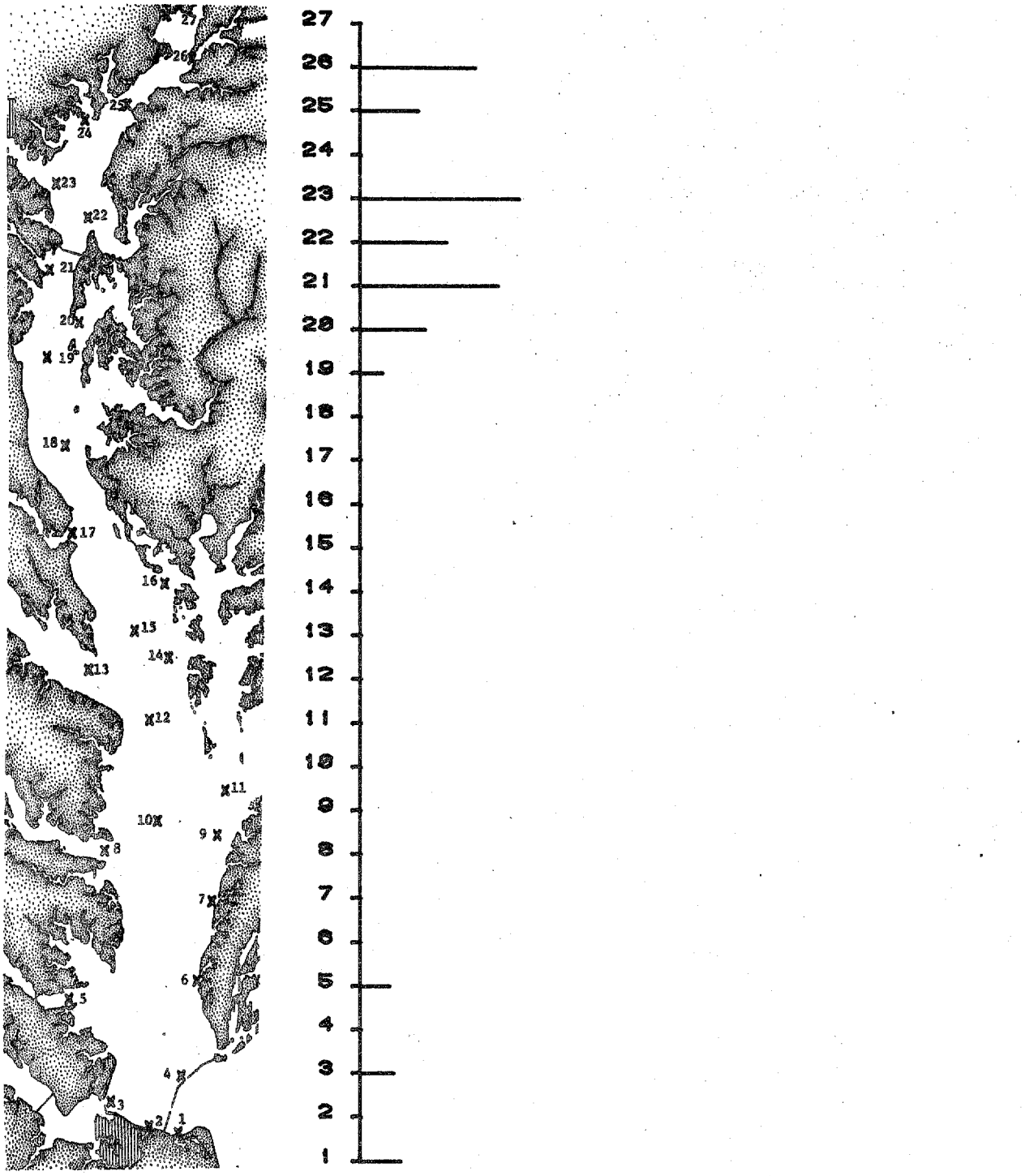


FIGURE 23

Benzo(ghi)perylene in Sediments, Fall 1979.

ARI : 600 Benzo(ghi)perylene

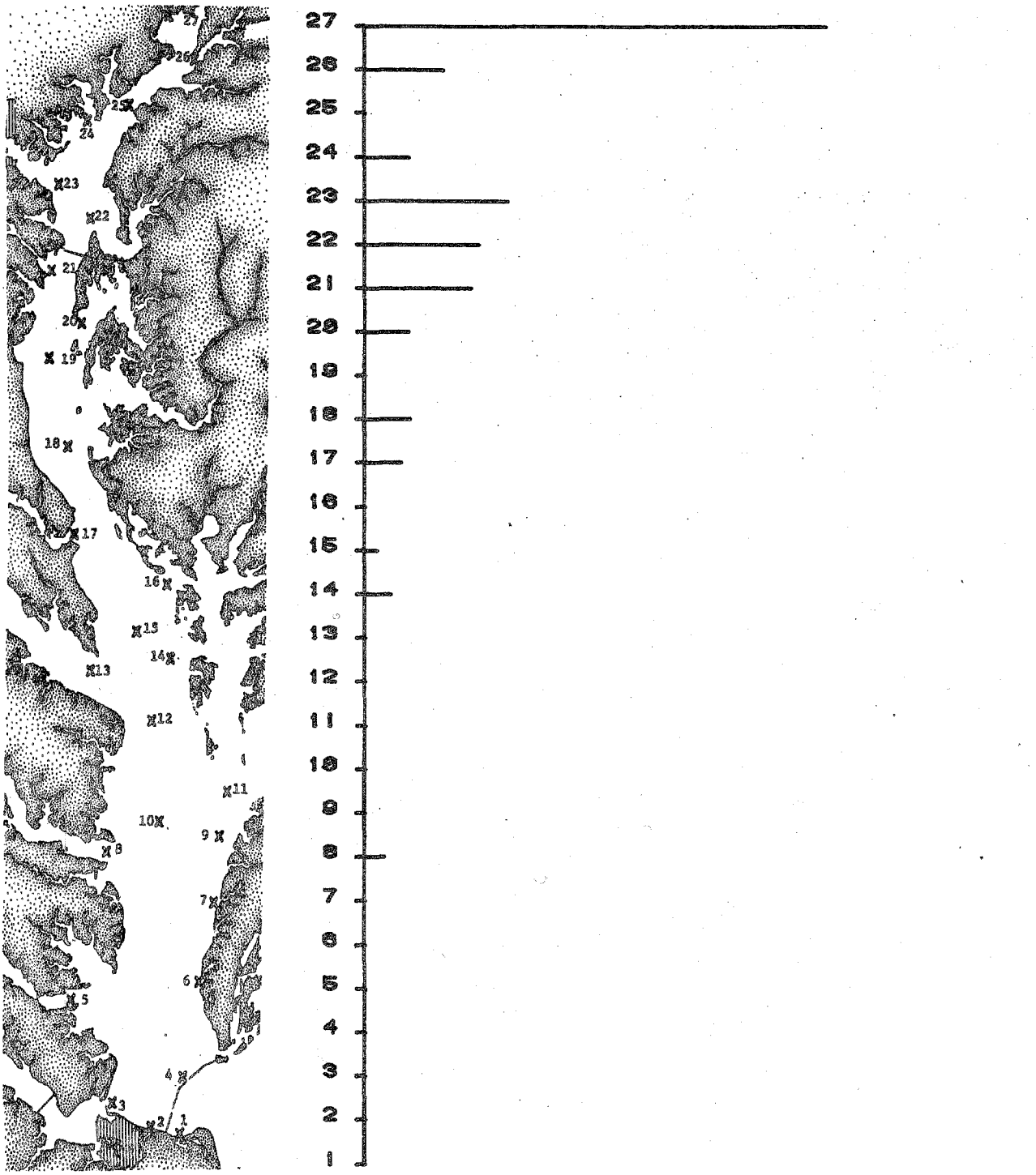


FIGURE 24

Sum of All Resolvable Peaks in Oysters, Spring 1979.

SUM OF ALL PEAKS

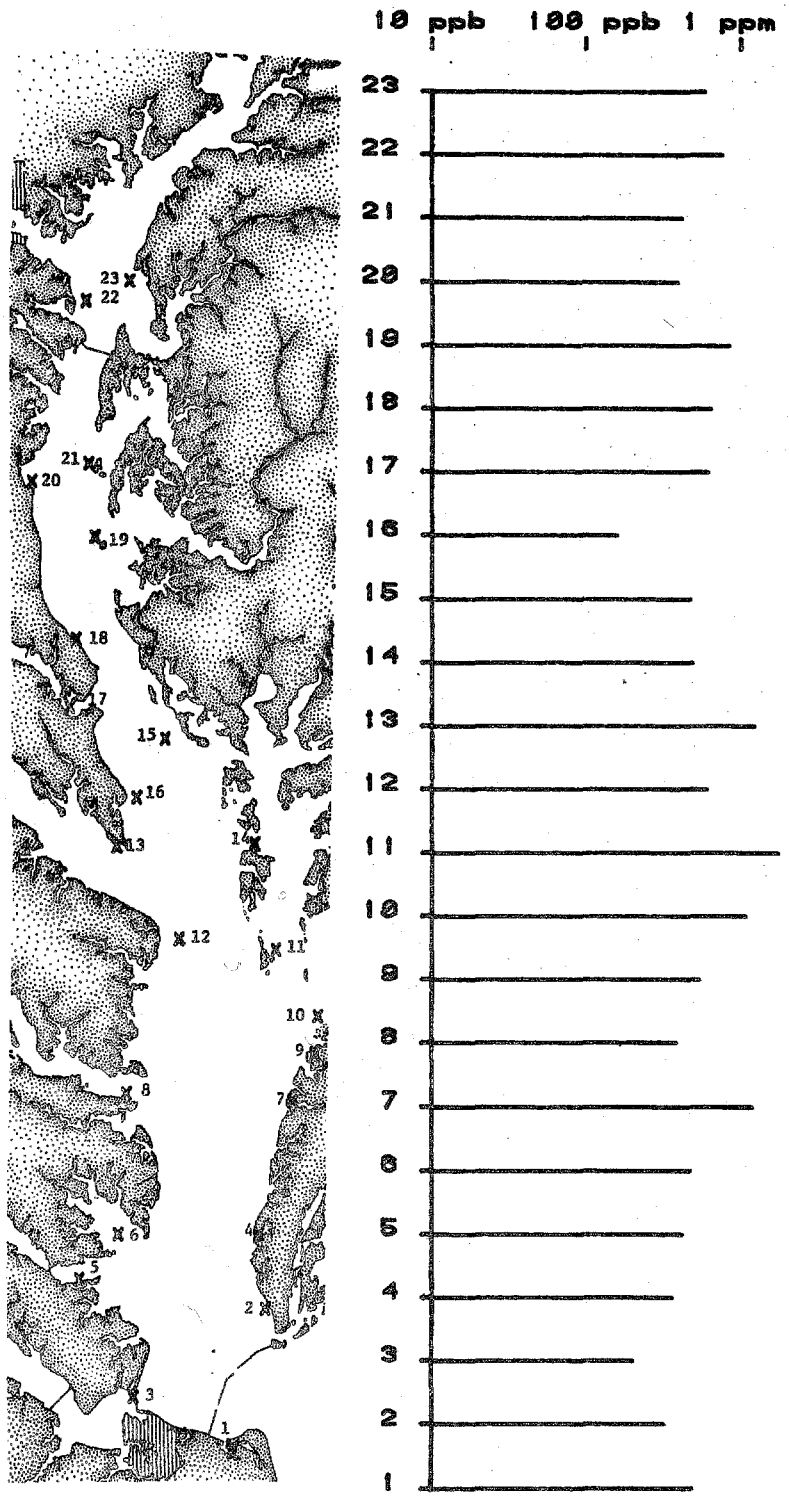


FIGURE 25

Sum of All Resolvable Peaks in Oysters, Fall 1979.

SUM OF ALL PEAKS

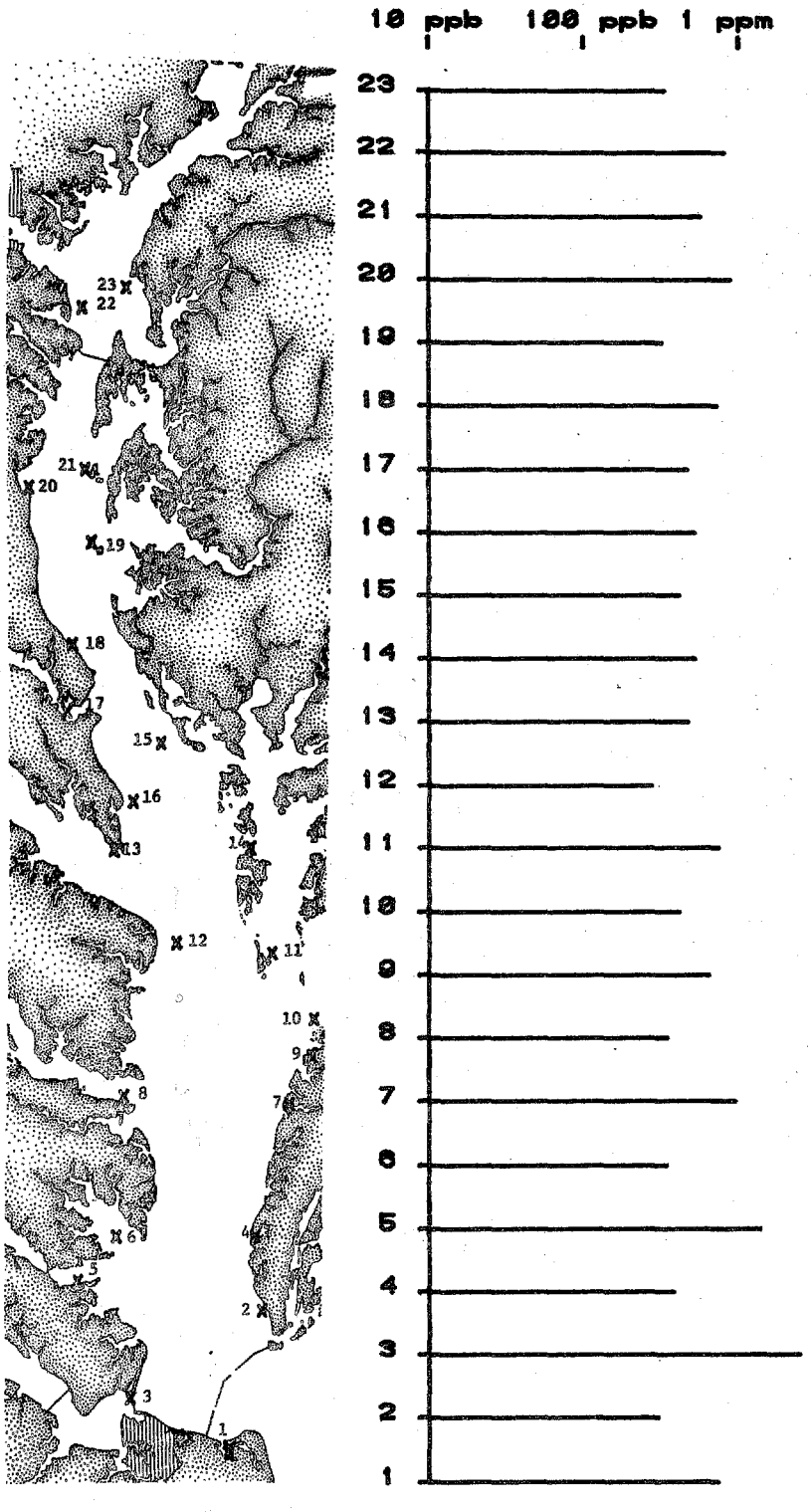


FIGURE 26

Benzo(a)pyrene in Channel Sediments
From the Patapsco River, 1981.

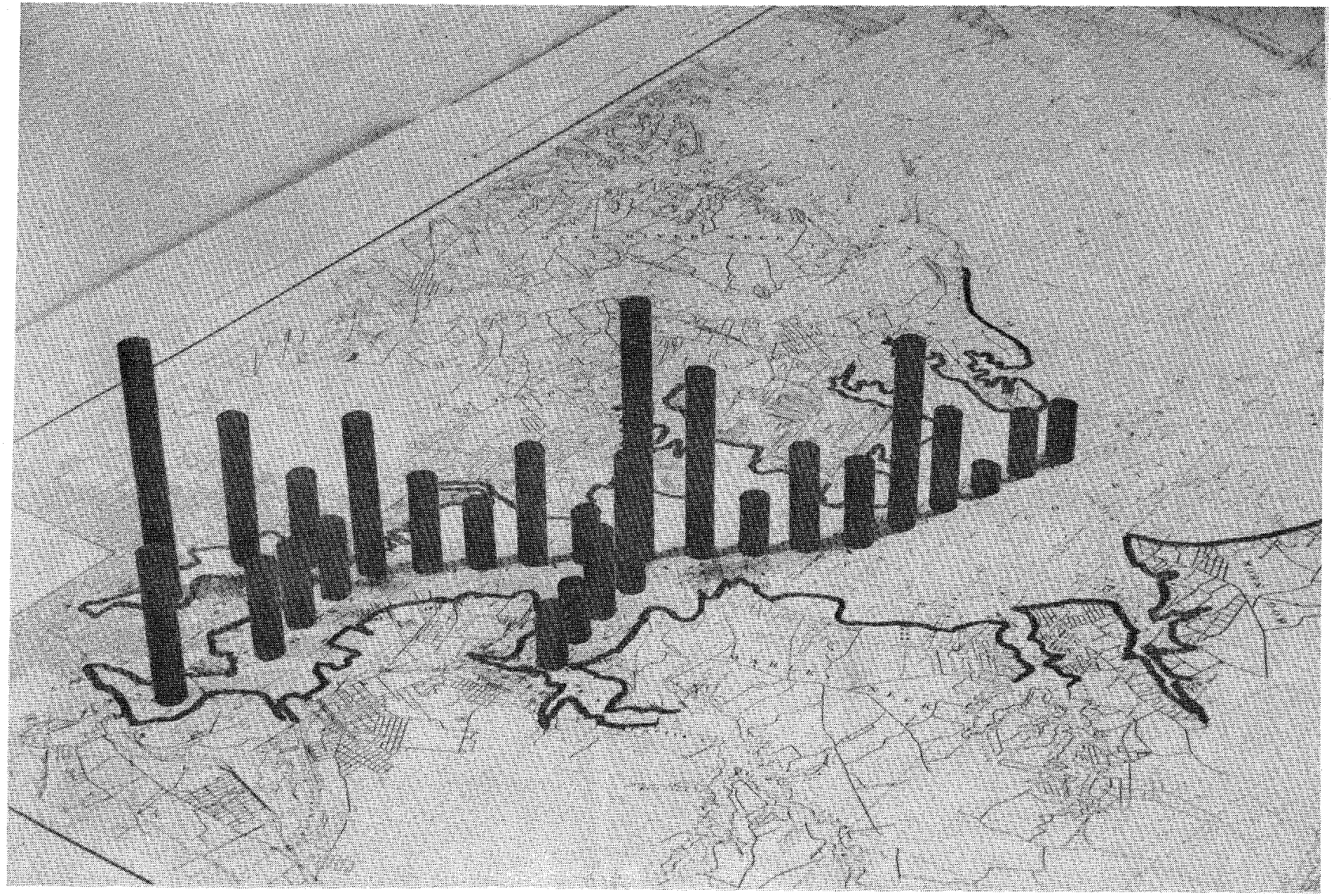


FIGURE 27

Benzo(a)pyrene in Channel and Nearshore Sediments From the Patapsco River, 1981.

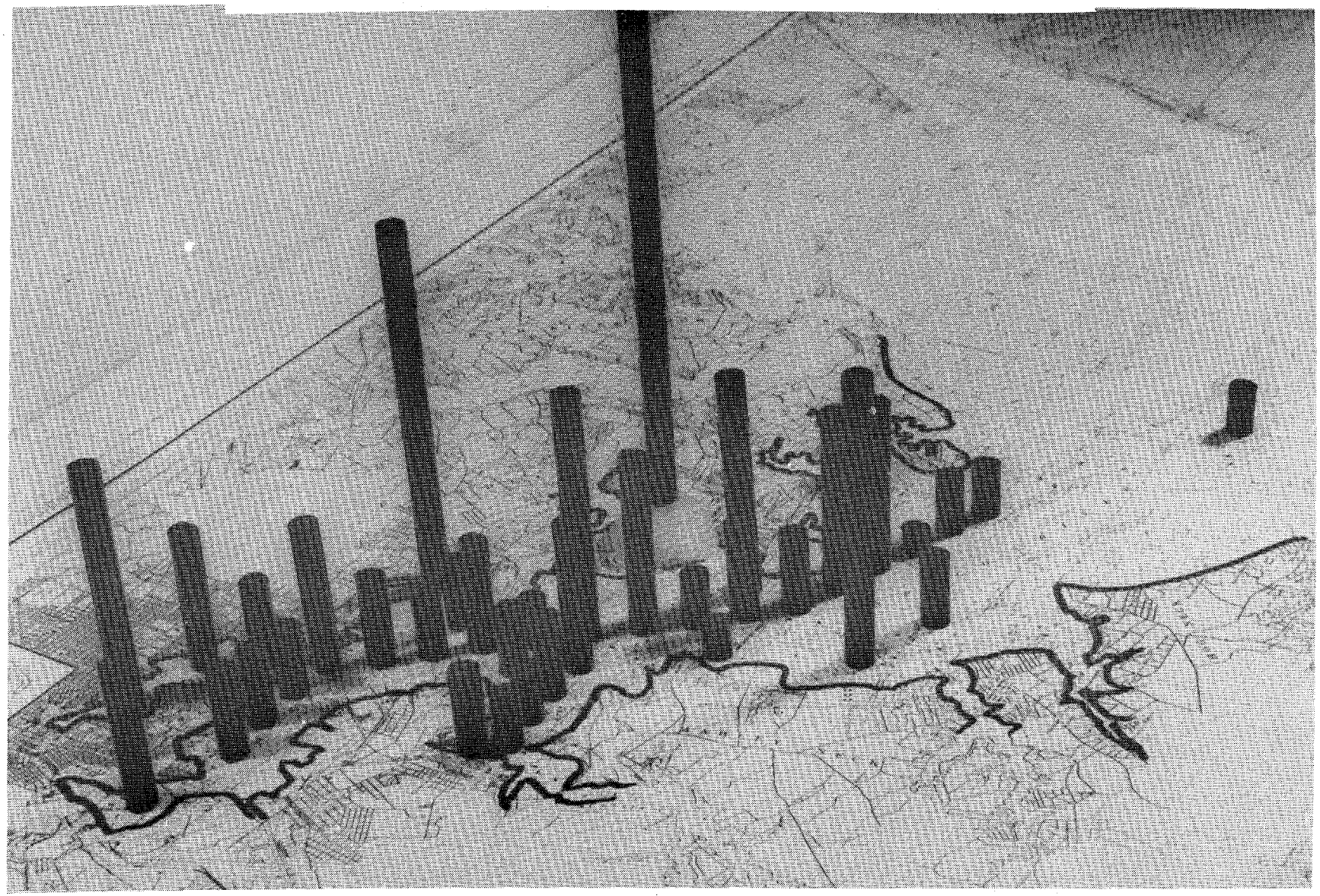


FIGURE 28

Chrysene in Channel Sediments
From the Patapsco River, 1981.

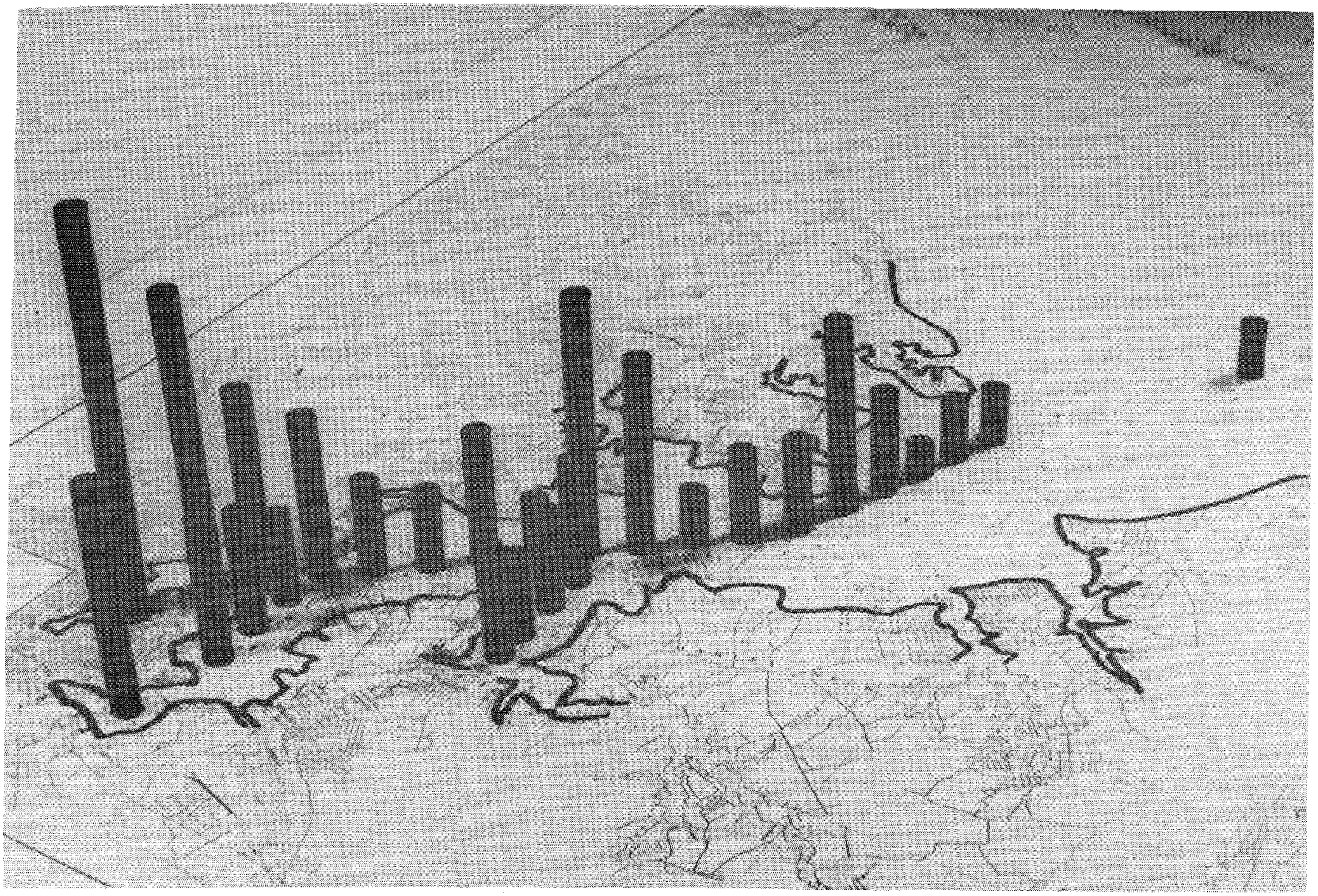


FIGURE 29

Chrysene in Channel and Nearshore
Sediments From the Patapsco River, 1981.

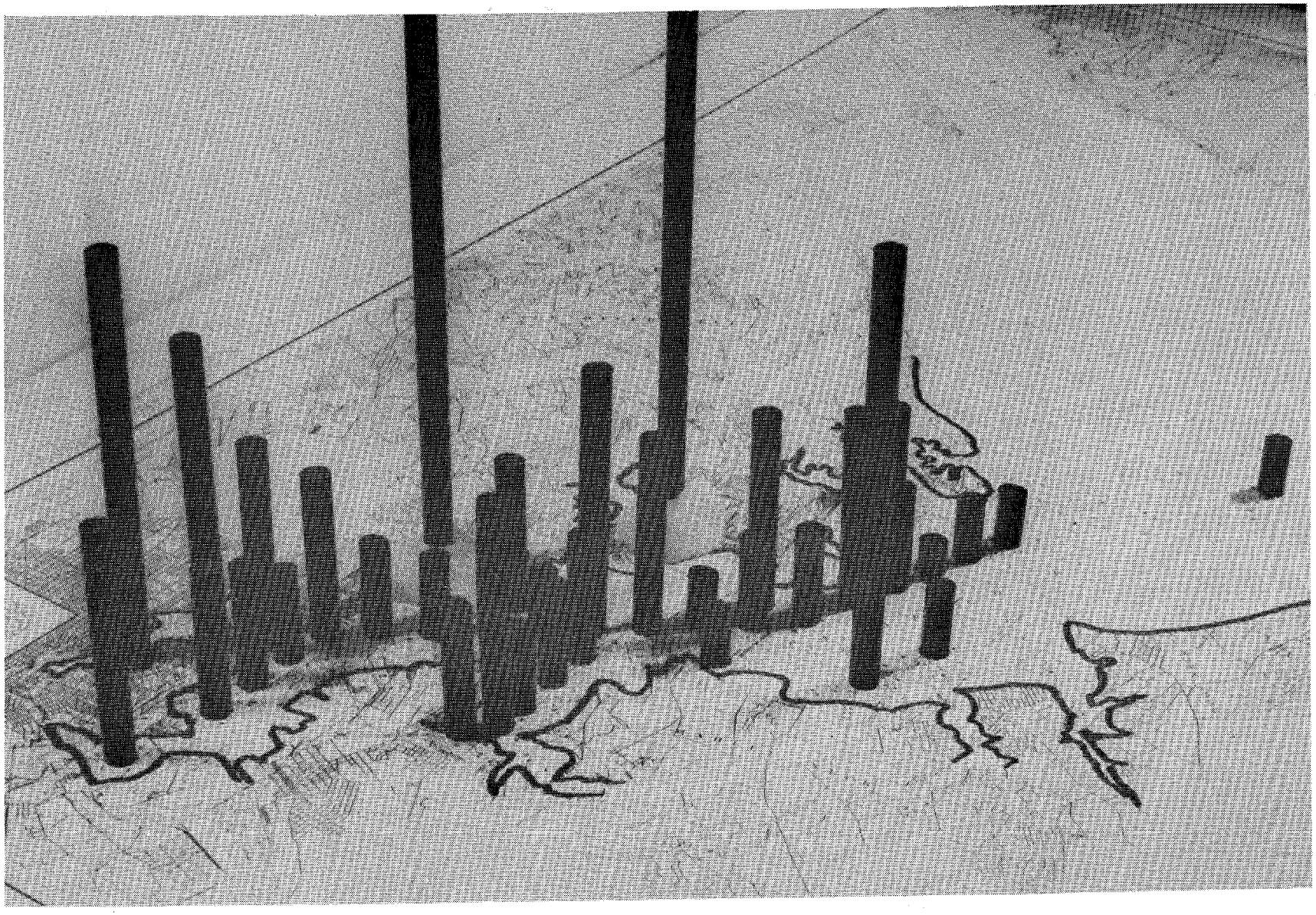
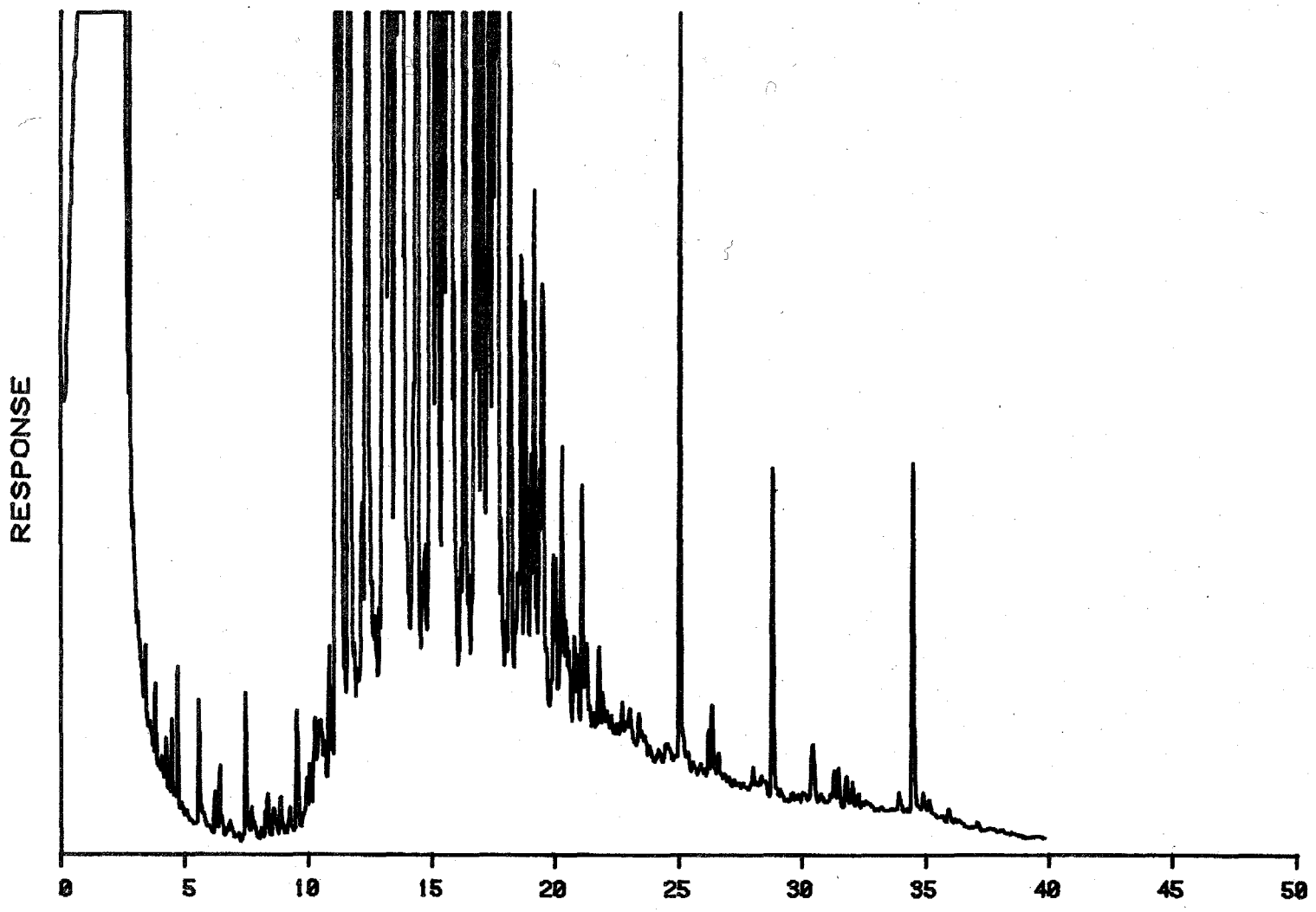


FIGURE 30

Gas Chromatogram of Sediment Sample
with Substituted Benzenes.



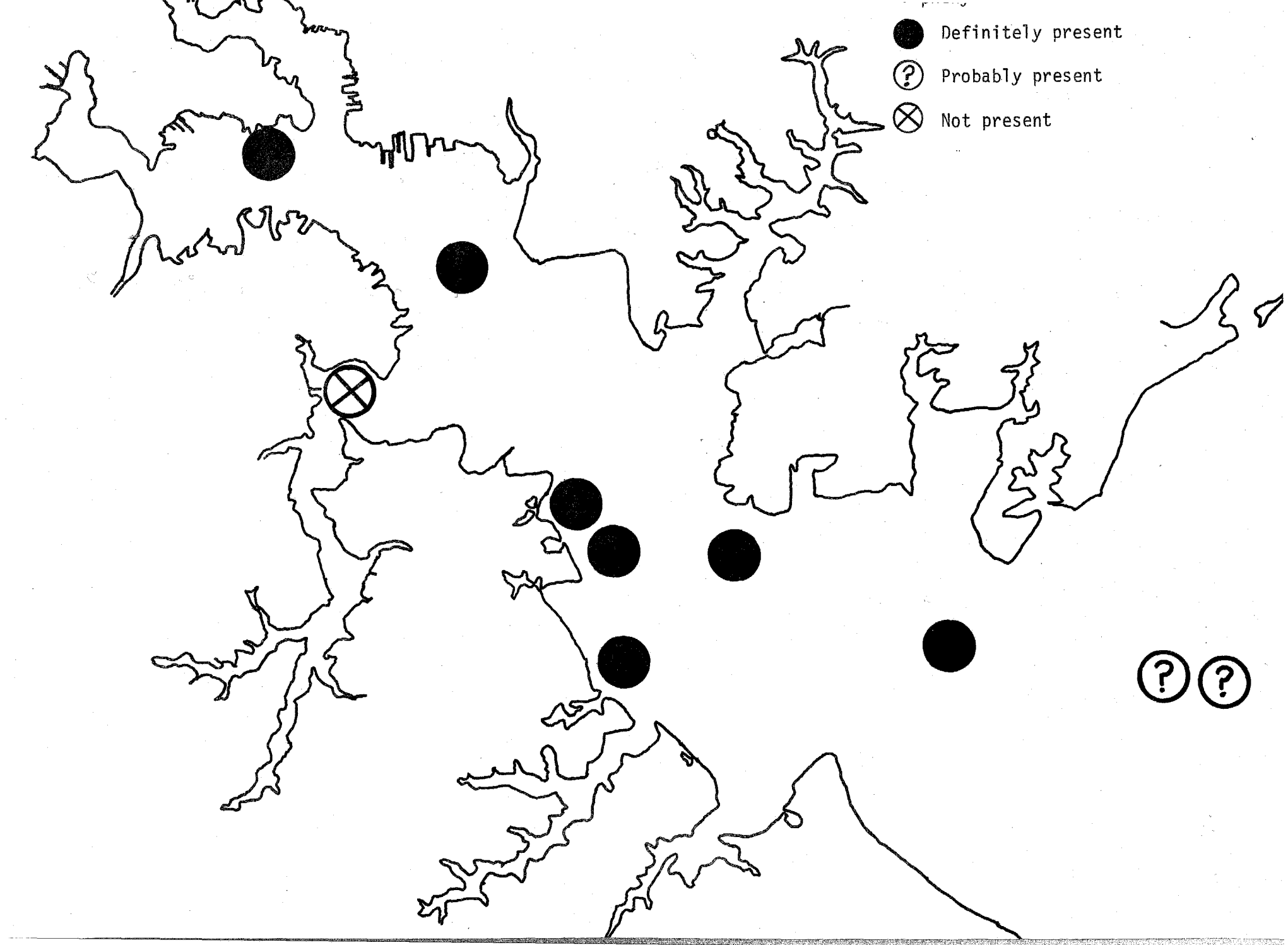
RAW FILE: H04SFR

SCALE FACTOR: .14

PLOT SPEED: 2

FIGURE 31

Locations in the Patapsco River Where 6-phenyldodecane was Either Definitely Present, Probably Present or Absent.


Definitely present
Probably present
Not present