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Analysis of effluents and associated sediments and tissue for toxic organic compounds, 1987-1988 : final report to Virginia State Water Control Board

Robert Hale
Virginia Institute of Marine Science

Craig L. Smith
Virginia Institute of Marine Science

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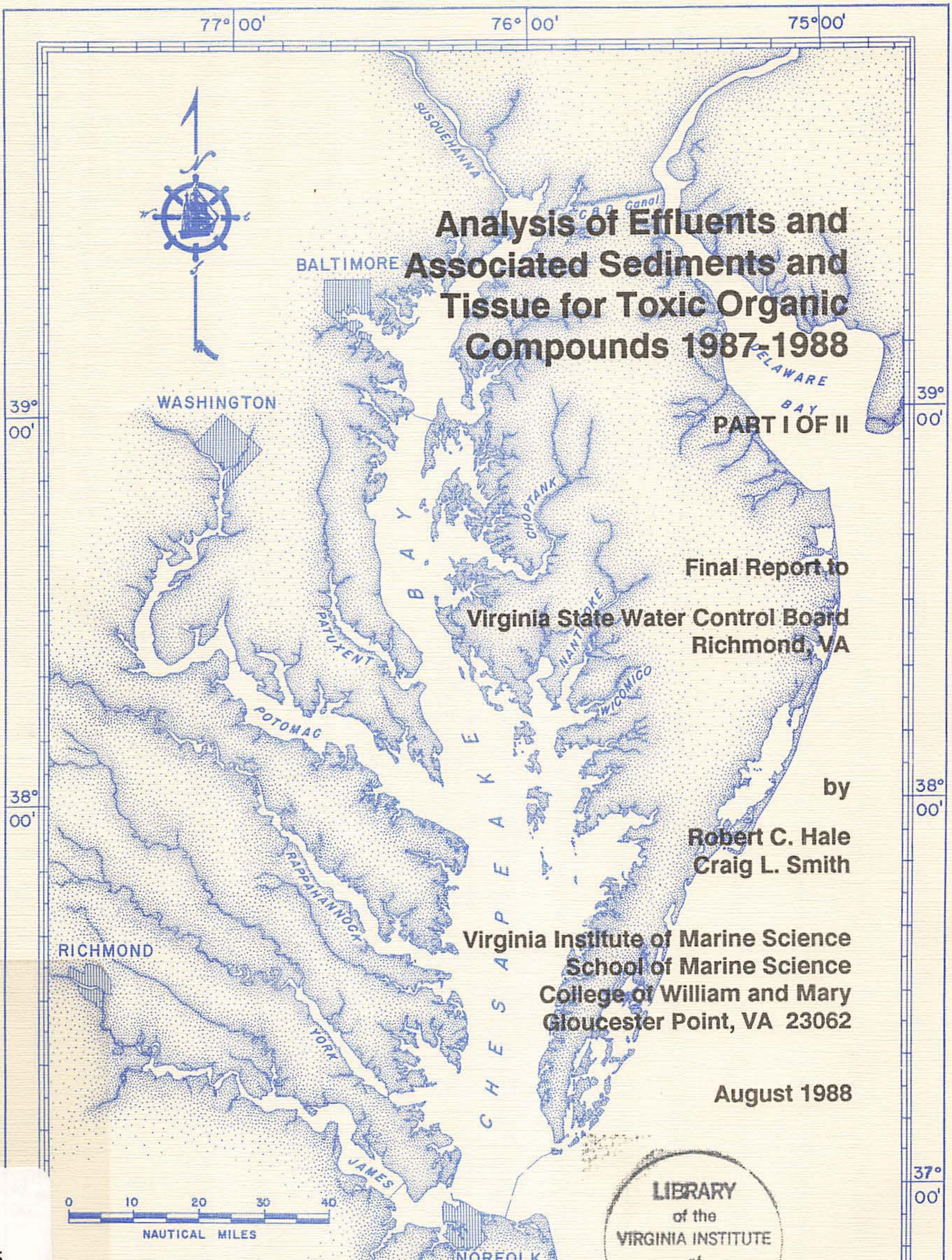

Analysis of Effluents and Associated Sediments and Tissue for Toxic Organic Compounds 1987-1988

PART I OF II

Final Report to

Virginia State Water Control Board
Richmond, VA

by

Robert C. Hale
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Virginia Institute of Marine Science
School of Marine Science
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SUMMARY

Effluent and sediment samples were collected from 30 point source discharge sites within tributaries to the Chesapeake Bay, and analyzed for the presence of toxic organic compounds. The facilities selected included: municipal treatment plants, oil refining and storage operations, shipyards, military bases, paper companies, electrical power generators and various other manufacturing enterprises. In addition to sediment, shellfish were collected from the receiving streams. Unfortunately, environmental conditions in the vicinity of many of the facilities were unsatisfactory for the long-term survival of shellfish. As a consequence their availability was limited.

Analytical procedures employed included: solvent extraction, size exclusion/polarity cleanup by liquid chromatography and high resolution gas chromatography. Detection of resolved components was accomplished with flame ionization and Hall electrolytic conductivity detectors. An aromatic retention index system aided in the compound identification process. Mass spectrometry was used to confirm identities. Data were collected and entered into a computerized toxics data base by retention indices, where available. The data base allows the tracking of compounds geographically and temporally. It also permits the updating of information when new data becomes available.

Effluents from a number of facilities were observed to contain appreciable concentrations of anthropogenic compounds. Petroleum derived hydrocarbons were major contributors. Polynuclear aromatic hydrocarbons (PAHs) as well as lower molecular weight benzenes, naphthalenes and phenols were detected. In several cases, high concentrations of nonylphenols were also reported. These compounds are thought to be derived from surfactants and detergents. Some effluents contained concentrations of toxic organics which exceeded the acute LC50 for aquatic organisms.

Nonylphenols were detected in sediments at several locations at very high concentrations. Due to the presence of heavy industry, all sediment samples collected near facilities located on the Elizabeth River were grossly contaminated by PAHs. Polychlorinated terphenyls (PCTs), structurally similar to PCBs, were detected in the vicinity of a Navy and a NASA facility at concentrations of 19,300 and 25,600 ug/kg, respectively. Literature information concerning the distribution and effects of PCTs in the aquatic environment are practically nonexistent. Two distinct formulations, differing in their degree of chlorination, were identified. Shellfish collected in the vicinity of NASA Langley contained 3920 ug/kg of PCTs. The shellfish were obtained from the Southwest Branch of the Back River, while the suspected source of the PCTs is located in the Northwest Branch. Therefore, it is probable that local indigenous shellfish, commercially exploited for human consumption, contain even higher burdens than reported here. Lower concentrations of PCTs (less than 1000 ug/kg) were detected in sediments from nine other sites located in the James, Elizabeth and Potomac River basins. Further research to determine the significance and distribution of these compounds is indicated.

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Acknowledgements

The authors wish to thank the individuals who contributed to the current report; in particular, George Vadas, Debbie Anderson and Patrice Mason for their efforts in sample collection/preparation and chromatography. Dr. John Greaves provided assistance in sample collection and negative CI GC/MS analysis. Phyllis Howard kept track of administrative details and Shirley Sterling provided assistance in the preparation of correspondence. Ellen Harvey maintained the instrumentation and performed much of the GC/MS analysis.

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Introduction

In recent years the Chesapeake Bay region has experienced rapid residential and commercial growth. The bay and contiguous waters have been exploited to a greater extent than at any previous time. Regional environmental conditions have correspondingly deteriorated. Episodes of low dissolved oxygen, algal blooms and decreases in biological diversity/productivity in the bay have been common. The influx of anthropogenic compounds to the ecological system is believed to have contributed to the development of many of the symptoms observed (O'Connor and Huggett 1988). Populations of commercial species, e.g. oysters and finfish, have decreased or been contaminated by toxicants to levels exceeding limits presumed safe for human consumption.

This report presents the results of the analysis of environmental samples collected from 30 sites located within tributaries of the Chesapeake Bay. It constitutes a continuation of a project aimed at characterizing deleterious releases of pollutants to the bay. A previous report (deFur and Smith 1987) was completed for the period 1985-1986 by VIMS for the VWCB, detailing analyses conducted during that interval.

The central strategy of the project is to identify facilities which are currently degrading the aquatic environment. Facilities examined included municipal treatment plants, industrial facilities and military bases. The source of the environmental insult may be a current wastestream or a reservoir of anthropogenic compounds, derived from previous discharges, in the sediments. Sediments function as both sinks and sources of xenobiotic chemicals. These substrates sorb hydrophobic contaminants and thus act as records of pollution events. Analysis of the surface sediment permits the recent environmental history of a given location to be determined.

To accomplish this strategy the effluents themselves, as well as sediments in the vicinity of the outfalls, have been collected and chemically characterized. In addition, shellfish were obtained near the sites and analyzed. These organisms function as excellent environmental monitors (Rice and White 1987). Unfortunately, indigenous specimens were not available at all sites, due to the presence of unsuitable substrates or other environmental conditions. Caged organisms were placed at two sites, sediment and effluents from which were examined in the 1985-1986 biennium, to monitor the bioaccumulation of xenobiotics.

The analytical techniques used were based on solvent extraction of the samples, followed by liquid chromatographic cleanup and fractionation. High resolution gas chromatography (GC), in concert with several selective and general detectors, was used to provide qualitative and quantitative information.

The GC techniques used are capable of detecting hundreds of compounds in a single sample. As a consequence, massive amounts of information are accumulated; which require the use of computers to record, manipulate and provide access to the data. Data systems are available to handle the output from GCs and to provide limited data manipulation, with the aid of specialized software and programs. However, previously, no mechanism was available to provide access to investigators and regulators not intimately connected with the analyses. In addition, the data needed to be organized such that it could be searched efficiently by parameters such as compound type, industry, geographical area and date of analysis. To provide this mechanism a computerized database was begun during the 1985-1986 biennium.

Development of the database retrieval capabilities continued during the 1987-1988 biennium to include faster data retrievals, eight-peak mass spectra for unknown and identified compounds, and the content of the database was expanded to include results of 1987-1988 biennium analyses.

Although many of the GC resolved compounds may be identified by their mass spectra and retention times, a great number remain unidentified due to a lack of adequate spectra, available reference standards or library spectra. An Aromatic Retention Index (ARI) system has been applied to the analysis of the environmental samples to aid in the identification process. This system allows the tracking of both identified and unidentified compounds, and is a prominent feature of the database retrieval system. Researchers may re-examine previously collected data and update compound identities as new data becomes available. The ARI system has been implemented for the nonpolar aromatic fraction, where its success has resulted in interest in expanding its application to the polar fractions. Compounds present in these fractions have not been as completely characterized as those in the nonpolar fraction. A Halogenated Retention Index (HRI) system was also instigated for the tracking of halogenated compounds. Halogenated compounds, e.g. PCBs, are of considerable interest due to their tendency to bioaccumulate and their potential for toxic effects. A more detailed description of this system is provided in the Methods section.

The sites examined during 1987-1988 are listed in Table 1. Their locations and supplemental sampling information are contained in Table 2. Figures 1 through 5 show the locations of these stations.

Table 1. Key to station abbreviations.

Abbrev.	Station Name	Outfall Number
AC	Allied Chesterfield (live box only)	-
AHC	Amerada Hess Corp.	001
AL	Alexandria STP	001
AY	Amoco Refinery Yorktown	101
AW	Atlantic Wood	002
CC	Chesapeake Corp.	001
CS	Colonna's Shipyard	005
DA	Dahlgren Naval Weapons Laboratory	004
FP	Fredericksburg POTW	001
HY	HRSD York River	001
JP	James River Paper	001
LA004	Langley NASA 004	004
LA009	Langley NASA 009	009
LAC	L.A. Clarke	001
LO	Lorton STP	001
LP	Lower Potomac STP	001
MM003	Metro Machine 003	003
MM016	Metro Machine 016	016
NB	Norshipco Berkley 015	015
NN017	Newport News Shipbuilding and Drydock 017	017
NN036	Newport News Shipbuilding and Drydock 036	036
NS020	Norfolk Naval Shipyard 020	020
PP	Portsmouth Pinner's Point STP	001
QU	Quantico Marine Corps	001
RP	Richmond STP (live box only)	-
RS	Reynolds Metals-South	001
SN052	Sewells Point 052	052
SN064	Sewells Point 064	064
SN066	Sewells Point 066	066
UC	Union Carbide-Linde	001
VPP	Virginia Power-Possum Point	005
VY	Virginia Power-Yorktown	001

Table 2

Outfall locations and sampling dates for 1987-1988 Toxics Initiative

Station Abbrev.	Outfall Latitude	Outfall Longitude	Effluent Sampling Date	Sediment Sampling Date	Availability of Indigenous Biota
AHC	36°46'06"N	76°18'06"W	04 Aug 1987	19 Oct 1987	
AL	38°47'39"N	77°03'36"W	11 Feb 1987	01 Sep 1987	
AW	36°48'27"N	76°17'42"W	15 Dec 1987	19 Oct 1987	
AY	37°13'36"N	76°26'18"W	10 Jun 1987	13 Jul 1987	C. virginica
CC	37°32'35"N	76°48'38"W	03 Dec 1987	13 Jul 1987	
CS	36°46'29"N	76°17'42"W	10 Sep 1987	19 Oct 1987	
DA	38°19'39"N	77°01'28"W	11 Mar 1987	31 Aug 1987	
FP	38°14'07"N	77°25'52"W	25 Jun 1987	31 Jul 1987	
HY	37°13'36"N	76°27'17"W	15 Mar 1987	13 Jul 1987	
JP	37°32'10"N	77°27'30"W	05 Aug 1986	08 Dec 1986	
LA004	37°05'00"N	76°20'26"W	06 Apr 1987	23 Jul 1987	C. virginica
LA009	37°05'37"N	76°22'42"W	06 Mar 1987	30 Jul 1987	
LAC	38°14'07"N	77°25'52"W	04 Jun 1987	31 Jul 1987	
LO	38°40'58"N	77°15'06"W	11 Feb 1987	01 Sep 1987	
LP	38°41'50"N	77°12'03"W	17 Mar 1987	01 Sep 1987	
MM003	36°50'19"N	76°17'20"W	21 Apr 1987	22 Jul 1987	
MM016	36°50'26"N	76°17'24"W	24 Aug 1987	19 Oct 1987	
NN017	36°59'09"N	76°26'30"W	05 Aug 1987	19 Oct 1987	
NN036	36°59'52"N	76°26'37"W	05 Aug 1987	19 Oct 1987	
NB	36°50'07"N	76°17'38"W	02 Sep 1987	19 Oct 1987	
NS020	36°50'29"N	76°16'05"W	04 Mar 1987	22 Jul 1987	
PP	36°51'20"N	76°19'09"W	06 May 1987	22 Jul 1987	C. virginica
QU	38°31'00"N	77°17'30"W	29 Jul 1987	01 Sep 1987	R. cuneata
RS	37°31'33"N	77°26'20"W	12 Aug 1986	08 Dec 1986	
SN052	36°57'13"N	76°18'02"W	27 May 1987	22 Jul 1987	M. mercenaria
SN064	36°56'59"N	76°17'53"W	27 May 1987	22 Jul 1987	
SN066	36°56'56"N	76°17'46"W	27 May 1987	22 Jul 1987	C. virginica
UC	37°05'35"N	76°23'30"W	16 Sep 1987	15 Oct 1987	
VPP	38°32'20"N	77°17'00"W	25 Jun 1987	01 Sep 1987	
VY	37°13'20"N	76°25'45"W	11 Jul 1986	11 Nov 1986	

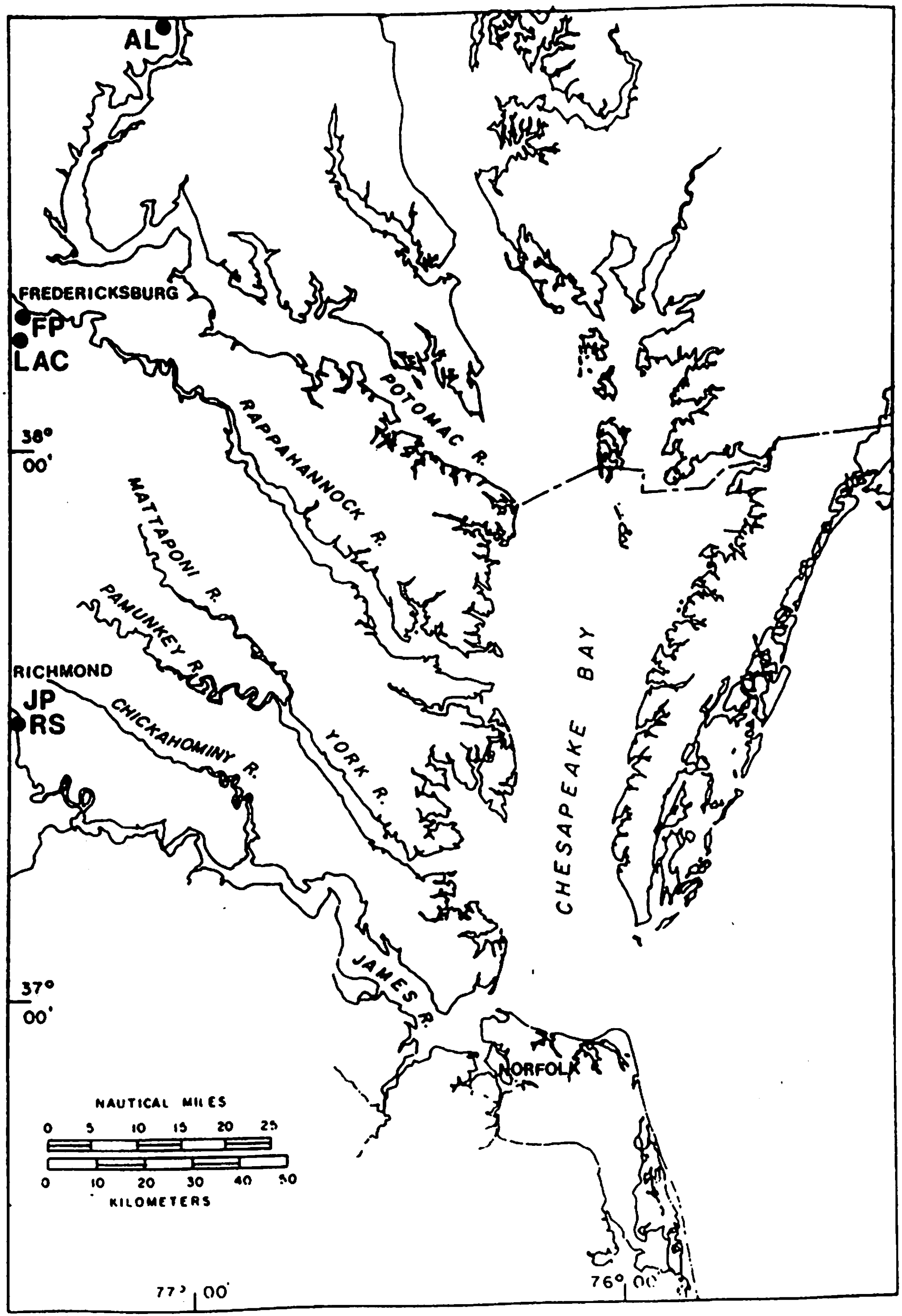

Figure 1. Map of the Chesapeake Bay and major tributaries. The approximate locations of stations JP and RS (Richmond), AL (Alexandria), and FP and LAC (Fredericksburg) are also provided.

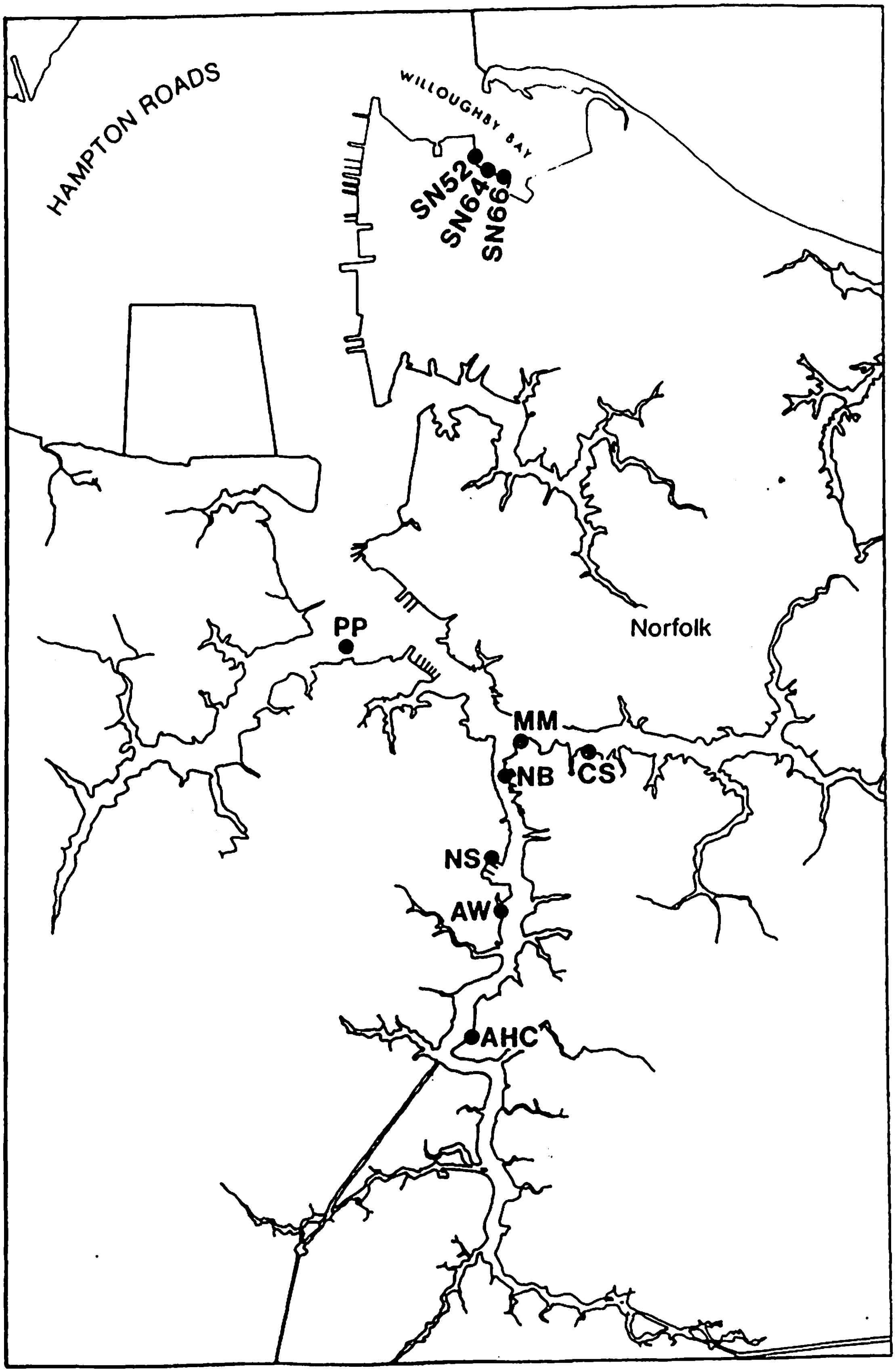

Figure 2. Map of the Elizabeth River, the southern section of Hampton Roads and Willoughby Bay. The approximate locations of stations AHC, AW, CS, MM, NB, NS, PP, SN52, SN64 and SN66 are included.

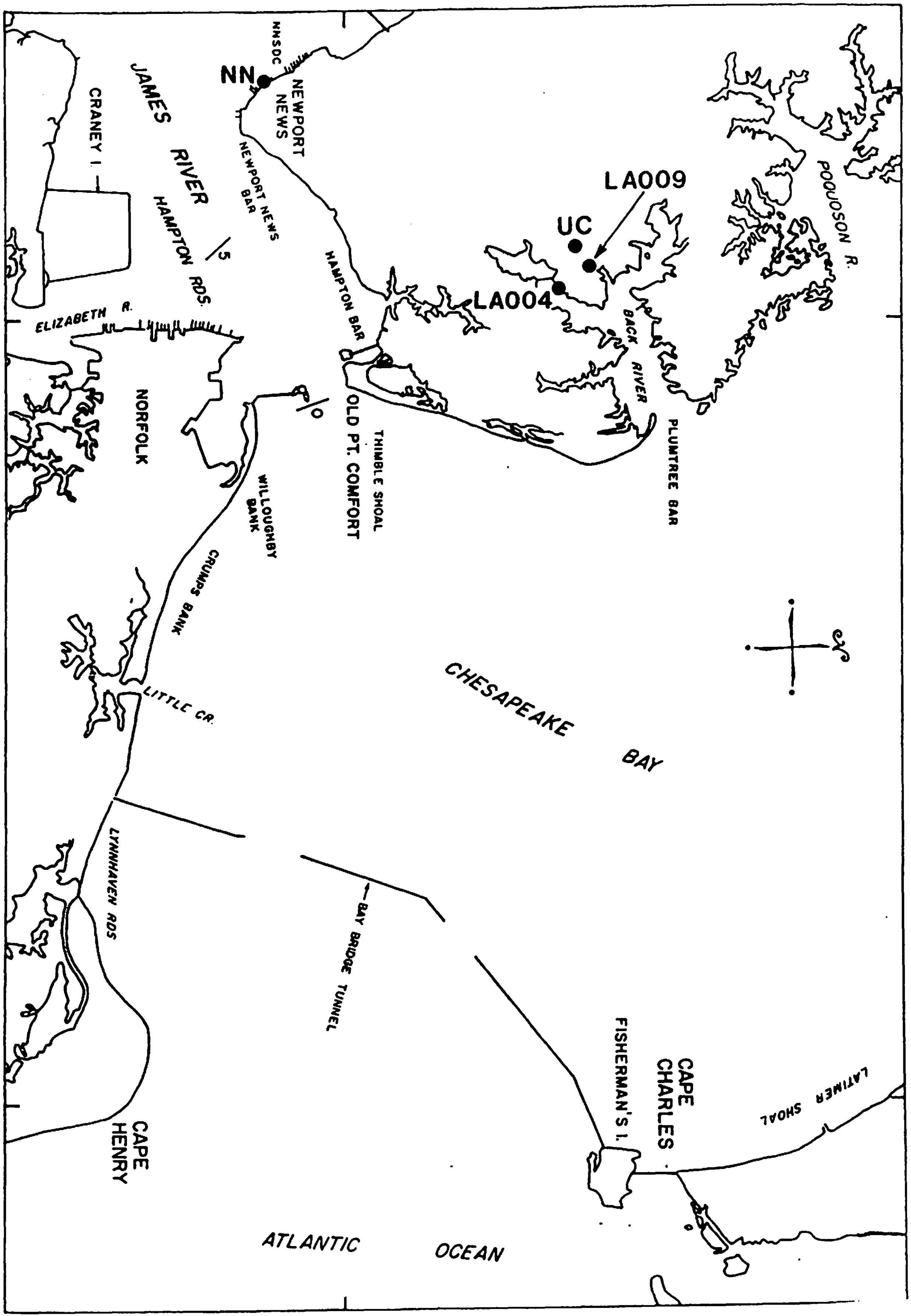

Figure 3. Map depicting the lower James River, mouth of the Chesapeake Bay and the Back River. Stations NN, LA004, LA009 and UC are also shown.

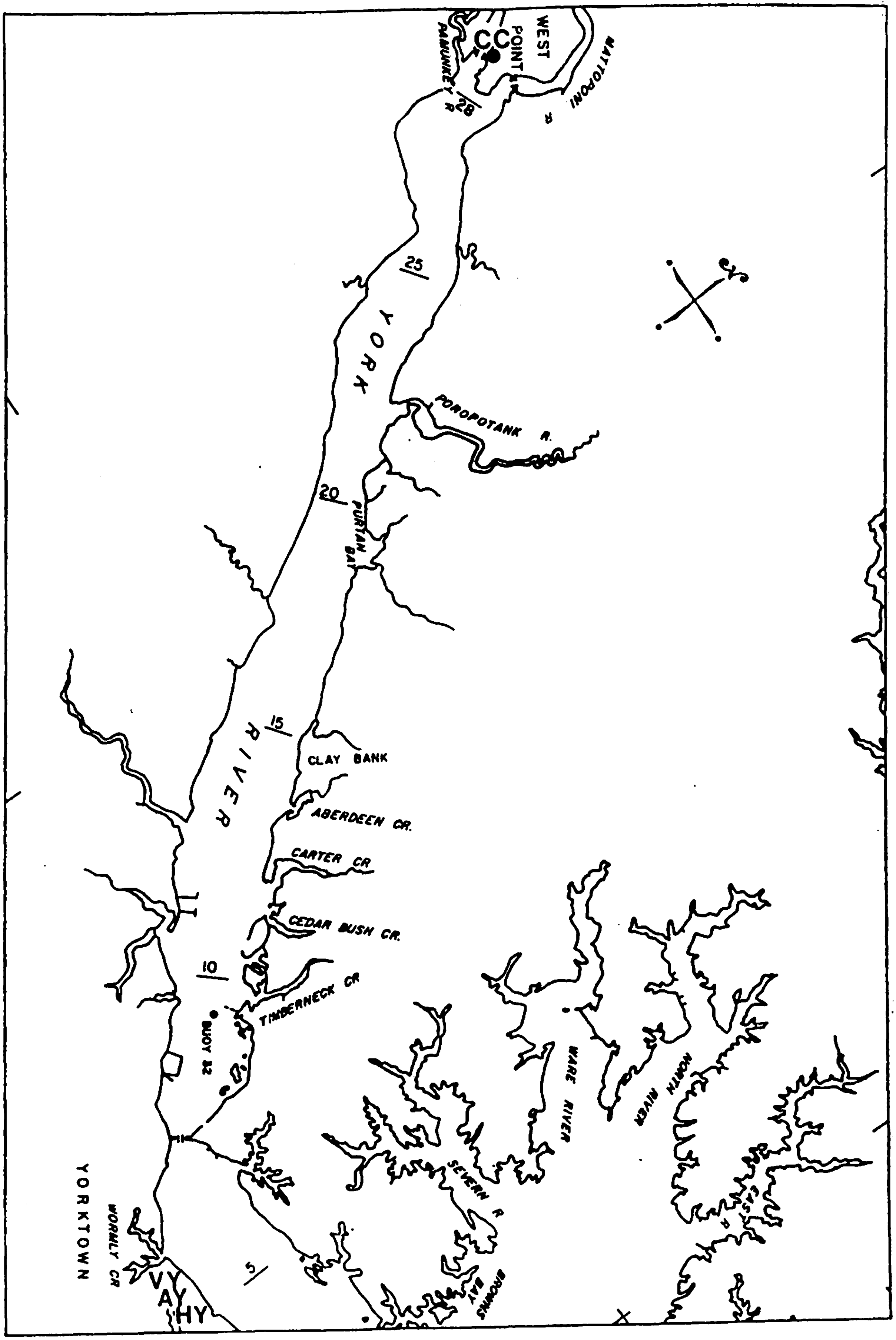

Figure 4. Map of the York River showing the locations of stations AY, HY, VY and CC.

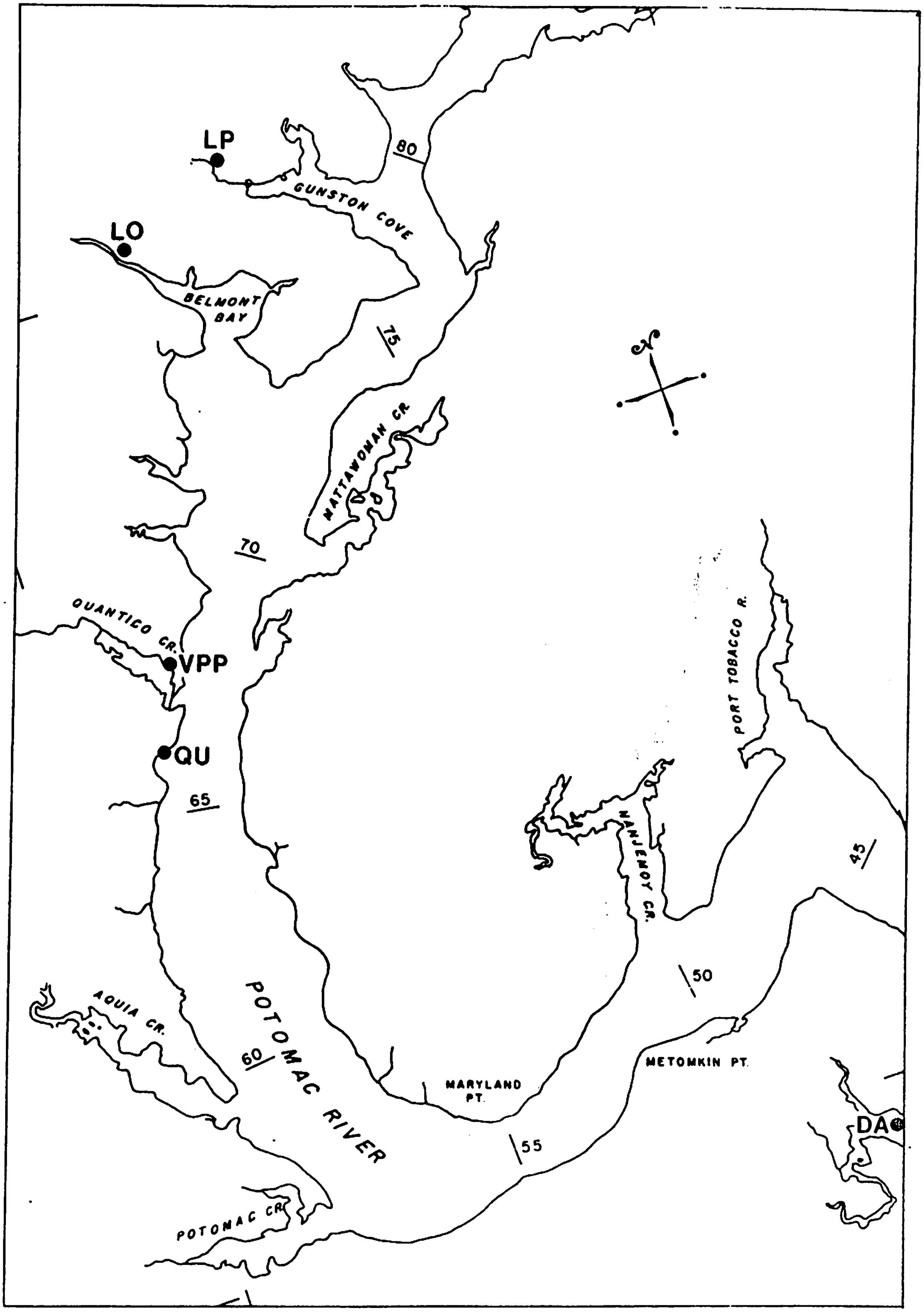

Figure 5. Map of the Potomac River depicting the locations of stations LP, LO, VPP, QU and DA.

Sampling

Effluent samples were collected by VWCB personnel in containers provided by VIMS. Samples were stored on ice and transported to the laboratory immediately following collection. Containers used were amber four liter glass bottles that previously had contained high purity "distilled-in-glass" organic solvents. Bottles were equipped with teflon lined caps.

Sediment samples were collected near the confluence of the outfall and the natural receiving stream. Samples collected by boat were obtained with a 0.1 m^2 stainless steel Smith-McIntyre grab. This type of grab obtains a sediment sample with minimal surface disturbance. The stainless steel construction of the sampler facilitates cleaning and obviates the need for lubrication, thus minimizing the potential for sample contamination. Prior to deployment, the grab was sequentially rinsed with water and methanol. The upper two centimeters of sediment from the grab sample were removed with a clean scoop and transferred to a precleaned glass jar equipped with a teflon seal. Alternatively, samples were collected directly with the scoop in accessible areas. Efforts were made to exclude large heterogeneous material, such as rocks and sticks, from the sediment samples. Immediately after collection, samples were placed on ice until transfer to the laboratory.

Glassware cleaning entailed an initial soap and water washing, followed by a thorough rinsing with deionized water and acetone and baking at $200^{\circ}C$

for 15 hours. After cooling, jars were sequentially solvent rinsed with acetone, toluene, methanol and dichloromethane (DCM) and sealed with previously rinsed teflon lids.

Upon return to the laboratory, each sample was mixed to ensure homogeneity. Fifty grams were removed for grain size analysis and 50 grams for metals analysis. The latter samples were forwarded to the VWCB. Approximately one kilogram of the remaining sediment was transferred to a shallow stainless steel tray, covered with aluminum foil, and frozen for subsequent lyophilization. The remainder of the wet sediment was archived frozen.

Indigenous bivalves, either clams or oysters, were present at six sites (AY, LA004, PP, QU, SN052 and SN066). Biota were collected using a standard steel framed dredge, towed behind the vessel. At the laboratory, the organisms were placed in mesh bags, suspended from a pier in the York River and allowed to purge their gut contents overnight. In addition to those shellfish collected by VIMS personnel, specimens were received from the VWCB. These latter organisms were obtained from live boxes which had been suspended in the vicinity of outfalls AC and RP. Effluent and sediment samples from these two sites had been previously examined (deFur and Smith 1987).

Specimens were subsequently washed, shucked and the meats homogenized in a Virtex mixer at 40,000 rpm. The homogenate was subsampled for metals analysis and the remainder was placed in a stainless steel tray, covered with aluminum foil and frozen prior to lyophilization.

Analytical Methods

A detailed description of the analytical methodology was provided in the report by deFur and Smith (1987); however some modifications have been made. Flow diagrams in Figures 6 through 8 depict the procedures used for the sample preparation. All solvents used were Burdick and Jackson "Distilled in Glass" grade.

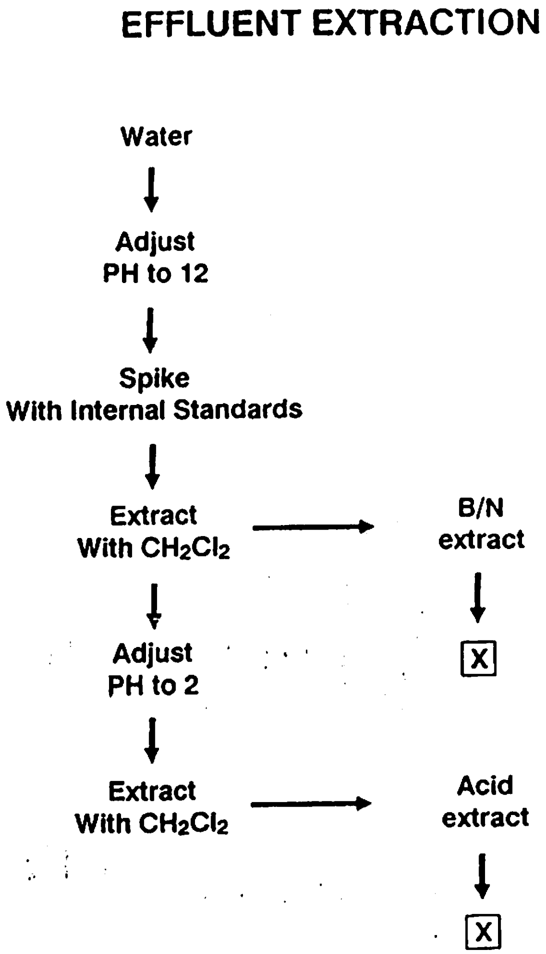
EFFLUENT EXTRACTION

Figure 6. Flowchart of water sample extraction procedures is depicted.

SEDIMENT AND TISSUE EXTRACTION

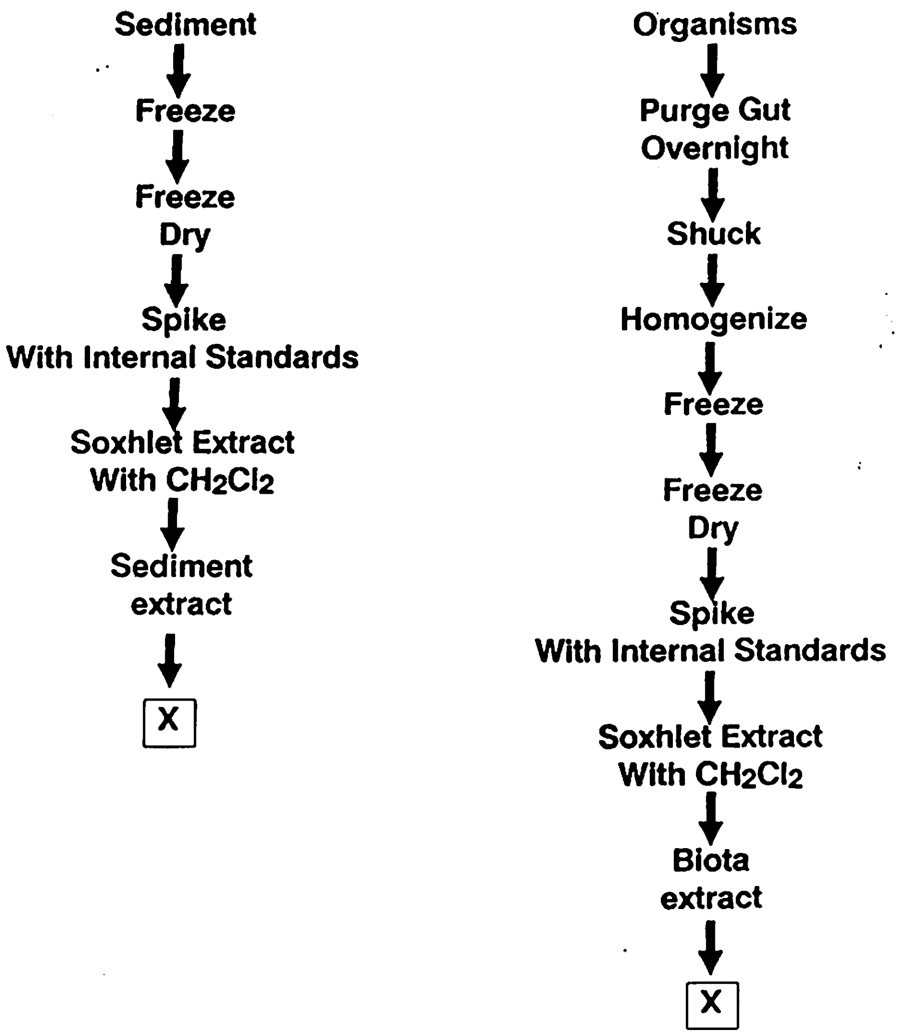

Figure 7. Flowchart of sediment and biota extraction procedures is depicted.

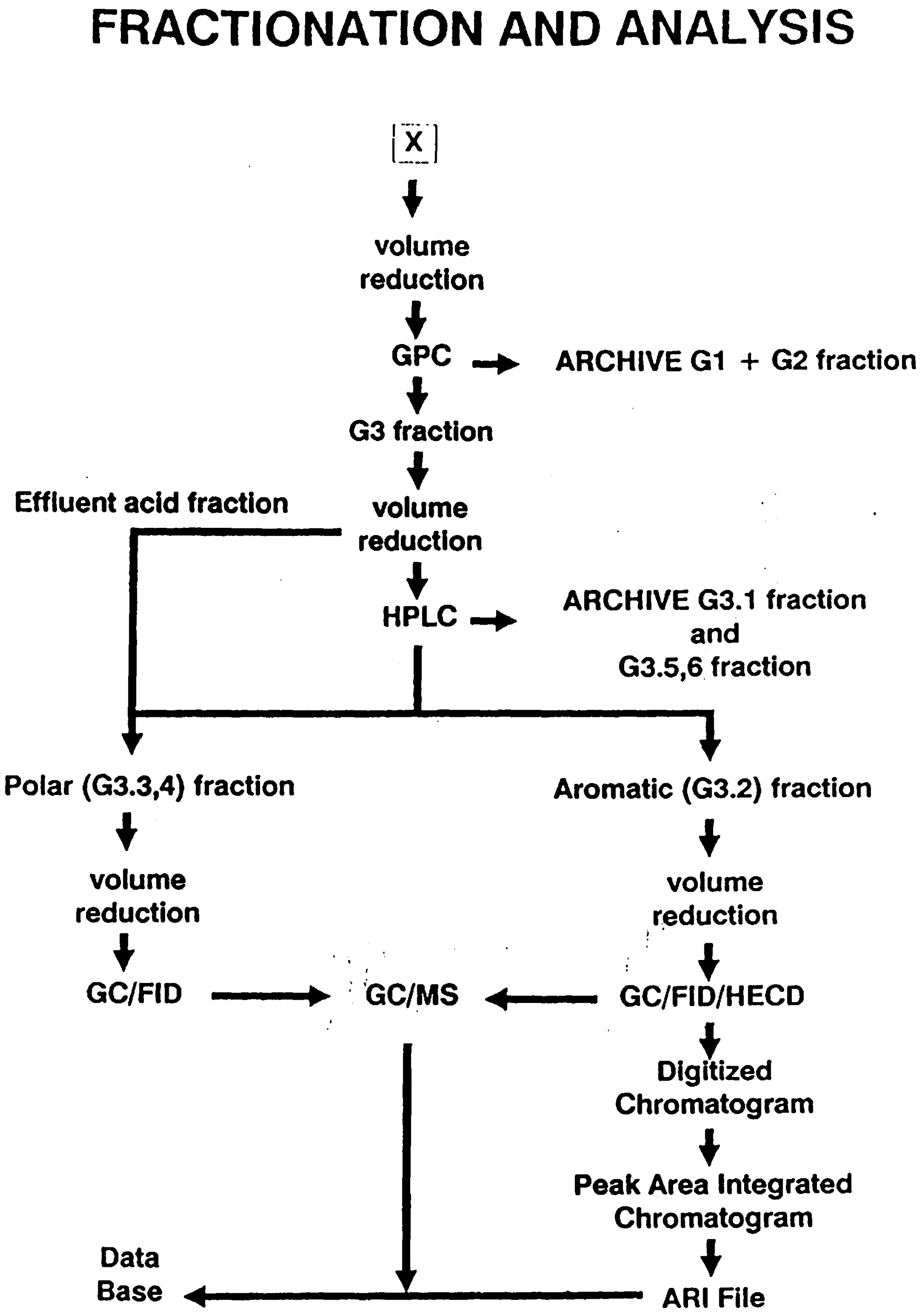

Figure 8. Flowchart of the extract fractionation and analysis procedures is depicted.

Effluent extraction

Extraction procedures used for the effluent samples were basically base/neutral/acid techniques. Since the purpose of the study was to determine the total amount of anthropogenic compounds discharged to the receiving stream, no filtering of the effluent was performed prior to analysis.

One liter aliquots of each effluent sample were transferred to two liter glass separatory funnels. An internal standard solution containing 1,1'-binaphthyl, 2,4,6-tribromophenol, perinaphthenone and decachlorobiphenyl was then added to the funnels. The volume of the spike added was adjusted according to the anticipated concentration of anthropogenics present. The pH values of the water samples were adjusted to approximately 12, using a pre-extracted 6N sodium hydroxide solution. Each sample was then sequentially extracted with three aliquots of DCM (initially 100 ml, followed by two 50 ml aliquots). Stable emulsions which formed were frozen and subsequently thawed to achieve separation. This procedure extracted basic and neutral compounds (B/N) from the water. The pH of the effluent sample was then adjusted to 2, with a pre-extracted 6N HCl solution, and re-extracted in a manner analogous to that described above. The resulting extract contained the acidic compounds. Both extracts from the effluent were reduced in volume using a rotary evaporator and transferred to separate graduated tubes. Further volume reduction was achieved under a gentle stream of purified nitrogen. The extract volumes were then adjusted to 6.0 ml, in preparation for additional sample cleanup.

Sediment extraction

Frozen sediment samples were lyophilized in a FTS Systems freeze drier. Shelf temperature was 15 °C. Chamber pressure was maintained at 400 microns of mercury with a nitrogen bleed system designed to eliminate pump oil backstreaming. Drying required 24 to 48 hours. Following lyophilization, each sample was thoroughly mixed, transferred to a glass soxhlet thimble and weighed. Thimbles were filled with 20 to 150 g of dried material. Smaller sample sizes were used for sediments exhibiting gross contamination, e.g. AW and LAC. The dried sediment was spiked with an internal standard containing 1,1'-binaphthyl, perinaphthenone and decachlorobiphenyl. Soxhlet extraction with DCM was continued for 48 hours. The resulting extract was reduced in volume on a rotary evaporator to 6.0 ml, as described previously for the effluent extracts.

Biota extraction

Frozen tissue homogenates were lyophilized under the same conditions as the sediment samples. Three to 13 grams of the dried material were placed in a glass soxhlet thimble, spiked with an internal standard containing 1,1'-binaphthyl, perinaphthenone and decachlorobiphenyl, and extracted for

48 hours with DCM. Sample size used was a function of tissue availability. The resulting extracts were reduced in volume to 6.0 ml prior to cleanup.

Cleanup and fractionation

Initial cleanup of the extracts was accomplished by gel permeation chromatography (GPC). The instrument employed was an ABC Laboratories Autoprep 1001. GPC separated large biogenic molecules from the lower molecular weight anthropogenics. A more detailed description of the theory is available in the previous report by deFur and Smith (1987). The resin used in this system was BioBeads SX-8, a polystyrene divinylbenzene copolymer. The column was 2.5 cm by 65 cm and was packed with 100 g of resin. The eluting solvent was DCM and the flow rate was 7.0 ml min^{-1}. A six port sample injection valve with a 5.3 ml sample loop controlled the sample introduction. Six ml of extract were injected for each sample. Elution volumes were calibrated by injecting a standard containing a range of target compounds and collecting and analyzing column effluent in small aliquots. It was determined from these calibration runs that the first 140 ml of effluent contained mostly biogenic compounds. This material was labeled the G1,2 fraction and archived. The following 70 ml contained the majority of the toxic anthropogenic compounds of interest and was labeled the G3 fraction.

After GPC, the G3 fractions from the sediment, biota and effluent extracts were reduced in volume to 0.2 ml. The acid fraction of the effluent was not subjected to additional cleanup. Further fractionation of the biota and sediment extracts was based on polarity considerations. This step was accomplished with a Hewlett Packard 1084B high performance liquid chromatograph (HPLC). A Waters semi-preparative normal phase column (cyano-amino bonded to silica) was installed in the HPLC. An Alltech Applied Science guard column was directly connected to the semi-preparative column. A solvent gradient program was used to separate the components of the extracts into polarity classes. Hexane was used initially to separate the extremely non-polar constituents, e.g. aliphatics, from the more toxicologically important aromatics. This early eluting aliquot was labeled the G3.1 fraction. The addition of DCM (programing from 0% to 15% DCM) resulted in the elution of a slightly polar fraction (G3.2) containing the majority of the aromatic compounds of interest. For simplicity this will be designated as the aromatic fraction. A more polar fraction or G3.3/3.4 fraction, was collected during solvent programing from 15% to 100% DCM. This fraction will be designated the polar fraction during subsequent discussion of results. A highly polar fraction (G3.5/3.6) was also collected using methanol and acetonitrile as eluting solvents. The G3.5/3.6 fraction was dominated by fatty acids and other polar biogenic material and was not routinely analyzed. Compound classes which elute in the two HPLC fractions of interest are listed below:

Fraction	Compound Class
Aromatic	Polycyclic aromatic hydrocarbons (PAHs) Polychlorinated biphenyls (PCBs) DDT, DDE and DDD Mononitro PAHs
Polar	Cyano PAHs Ketones Amines Carbazoles Aldehydes Hydroxy PAHs Azaarenes Phenols

These two fractions were reduced to an appropriate volume and analyzed by GC.

Gas chromatography

The aromatic, polar and acid fractions (where appropriate) of the extracts were analyzed by GC using flame ionization detection (FID). The carrier gas used was helium. This work was performed on a Varian 3700 instrument under the following conditions:

injector temperature	300°C
detector temperature	300°C
initial column temperature	75°C
final column temperature	300°C
program rate	6°C min^{-1}
final hold time	5 min

Samples were coinjected with a toluene plug in the splitless mode. An initial isothermal hold was employed until elution of the solvent began, at which time temperature programing was initiated and the split was opened. Glass capillary columns were prepared in this laboratory using the method of Grob (Grob et al. 1982). Columns were coated with a 0.2 micron film of SE 52, a phenylmethyl silicone phase. Chromatographic data were recorded and analyzed on a Hewlett Packard 3354B laboratory data system.

An aromatic retention index (ARI) system (Bieri et al. 1978) was applied to the chromatographic analysis of the aromatic fractions. This approach allows the comparison of data obtained by different researchers over time. Basically, the retention time of each individual chromatographic peak is compared to those of two standards, the retention times of which encompass that of the compound of interest. The ARI value of the compound of interest is then determined by interpolation. The markers chosen encompass a range of molecular weights and are commonly found in extracts of sediment samples, precluding the necessity for coinjection. If particular marker compounds are not present in an individual sample, their retention times may be inferred from a standard mixture routinely injected at the beginning of each work day. The markers and the ARI scale utilized are given below.

Marker	Molecular Weight	ARI
naphthalene	128	1000
biphenyl	154	2000
phenanthrene	178	3000
pyrene	202	4000
chrysene	228	5000
perylene	252	6000
benzo(ghi)perylene	276	7000

The formula used to calculate the ARI values is given below:

$$ARI_x = \frac{T_x - T_{mp}}{T_{mf} - T_{mp}} \times 1000 + ARI_{mp}$$

ARI_x = ARI of peak x

T_x = retention time of peak x

T_{mp} = retention time of the last marker preceeding peak x

T_{mf} = retention time of the next marker following peak x

ARI_{mp} = ARI defined for the last marker preceeding x

The first three effluents received (VY, JP, RS) were quantitated using 1,1-binaphthyl as an internal standard for the aromatic fraction. Terphenyl was spiked into the remaining fractions prior to injection onto GC for quantitation purposes. All sediment and biota determinations were made on a dry weight basis.

After these samples were analyzed a more extensive system of standards was implemented. For the aromatic fraction, 1,1'-binaphthyl was retained as the internal standard. However, perinaphthenone was chosen as the internal standard for the polar fraction. Initially 2-bromocresol was investigated as a possible internal standard for the effluent acid fraction. However, recovery of 2-bromocresol was not reproducible due to its high volatility. Therefore, 2,4,6-tribromophenol was substituted for 2-bromocresol as the internal standard for the acid fraction of the effluents. This improvement was implemented after the MM003 effluent sample.

Analysis of the extracts for halogenated compounds was conducted with a Tracor 700A Hall Electrolytic Conductivity Detector (HECD) interfaced to a Varian 3300 GC. The GC contained a capillary column similar to that described previously. A halogenated compound retention index (HRI) system was devised for the identification of the compounds detected. The HRI standard consisted of the following markers:

Marker	Molecular Weight	HRI
2-chloronaphthalene	163	1000
alpha-BHC	291	2000
o,p'-DDD	320	3000
decachlorobiphenyl	499	4000

The theory behind the HRI is similar to that for the ARI system discussed previously. The HECD was operated in the halogen-selective mode and its sensitivity to these type of compounds is much greater than electron-impact MS. As a consequence, MS confirmation of minor constituents in the GC/HECD chromatograms was frequently not possible. Injections were made in the splitless mode. Decachlorobiphenyl was added to the samples prior to extraction and was used to monitor recovery of the chlorinated compounds during analysis. Investigations determined that variable amounts of decachlorobiphenyl eluted in the G3.1 fraction during HPLC fractionation. This occurred due to its low polarity. As a consequence, a methodology change was made for the effluent samples. The B/N fractions of effluents LAC, AY, VPP, FP, QU, NN017, NN036, AHC, MM016, NB015, CS, UC, CC and AW were analyzed by HECD prior to the HPLC step. Only one effluent, CC, was observed to contain significant concentrations of chlorinated compounds. Aromatic (G3.2) fractions of the sediment and biota extracts were routinely examined. Pentachlorobenzene, coinjected with the extracts, was used as the internal standard for all HECD determinations. The carrier gas used for the HECD analyses was hydrogen and GC conditions were as follows:

injector temperature	310°C
detector temperature	950°C
initial column temperature	90°C
initial hold time	4 min
final column temperature	315°C
program rate	4°C min^{-1}
final hold time	12 min

As previously mentioned, internal standards were added to all the samples prior to extraction. Therefore general sample losses, such as the 0.7 ml of extract lost during GPC injection, were taken into account. Losses of compounds possessing dissimilar physical properties (e.g. the volatile xylenes and naphthalene) could not be compensated for without the inclusion of multiple internal standards, greatly increasing the complexity of the analyses. The response of the FID is a function of the carbon content of the molecule in question. As a consequence, differences in relative response will be greater for heterocyclic compounds. Therefore, quantitation of polar compounds should be considered as semi-quantitative. However, responses of nonpolar aromatic hydrocarbons, such as those present in the aromatic fraction, are quite similar. Use of "ideal" internal standards, i.e. standards possessing response factors and chemical properties identical to the sample analytes would still result in discrepancies between actual environmental concentrations and calculated values. This effect would be due in part to differences in extraction efficiency between unbound or weakly bound standards, spiked into the sample, and more tightly bound matrix associated environmental contaminants.

A computerized ARI file, consisting of ARI values and corresponding peak identities, has been established. Data has been assembled from the analysis of authentic standards, as well as hundreds of actual environmental samples. Currently, the ARI system has only been extended to the aromatic fraction. Samples containing significant concentrations of compounds in the polar and acid fractions currently require individual analysis by gas chromatography/mass spectrometry (GC/MS).

Mass Spectrometry

Samples containing particularly complex or unusual chromatograms were subjected to GC/MS. A GC similar to that used for GC/HECD analyses was coupled to a DuPont 492B double focusing magnetic sector mass spectrometer using an open interface maintained at 350°C. This interface allows the detector end of the GC column to remain at atmospheric pressure and maintains the validity of the ARI system. The instrument was operated in the electron impact mode with an ionization energy of 70 eV and a source temperature of 300°C. Scan speed was 1 second per decade with a 1.5 sec reset, allowing one scan each 2.5 sec over the mass range from 45 to 450 amu. A spectrum validation test was performed using DFTPP at least once every ten samples. After collecting data on the GC/MS data system, the calibration of the instrument was verified by examining the spectrum of the internal standard in each run. If this was judged satisfactory, the spectra could be examined in detail. Mass spectra alone generally do not provide sufficient information to establish the position of substituent functional groups. Reference standards for all possible isomers are often not available. Therefore the use of generic descriptors, e.g. C3-naphthalene (where C3- refers to three carbons in the alkyl substituent), were sometimes necessary. Compounds, such as aliphatic acids, exhibit significant fragmentation. As a consequence information, such as molecular weight, could not always be determined due to the absence of a molecular ion.

Particle size analysis

Approximately 50 grams of wet sediment were removed for grain size analysis from each sediment sample. The analysis was performed by standard methods (Folk 1974). Samples were wet sieved. Particles above 2.0 mm were designated as gravel, while particles between 2.0 mm and 64 microns were denoted as sand. The fraction below 64 microns was further examined by pipette analysis. Settling rates of the particles in distilled water were used to determine percentages of silt (5.0 microns to 64 microns) and clay (below 5.0 microns) in the sediment samples.

Quality Assurance

Several steps were taken to ensure the accuracy and quality of the data generated. Quality control features included the consistent use of high quality solvents, exhaustive glassware cleaning procedures, daily standard mixture analysis, internal standard usage, and frequent blank runs. Quality assessment techniques included: the determination of surrogate/internal standard recoveries and the analysis of replicates, spiked blanks and samples.

Minimal problems were encountered in regards to contamination during the analyses. Blanks were generally free of extraneous peaks. The exception was the polar fraction. A series of peaks was observed and determined to be contributed by the hexane used during the HPLC fractionation step. These compounds were not detected in the neat solvent after 1000 fold concentration. However, when the hexane was mixed with DCM, and subsequently reduced in volume, the peaks appeared. This problem was mentioned in the previous report by deFur and Smith (1987). It was hypothesized, at that time, that the compounds were artifacts produced by exposure to UV radiation in the HPLC detector. Recent experiments showed that such exposure was not required. The artifacts were especially prevalent when older lots of solvent were used. Greater concentrations of artifacts were observed with other commercial brands of solvent. Therefore, attempts were made to use the freshest solvent available. Since the retention times of the artifacts were known, it was relatively simple to locate them and to disallow their contributions. The presence of artifacts associated with the use of DCM has been recently reported in the literature (Ibrahim et al. 1987).

As previously mentioned, internal standards were spiked into the samples, prior to extraction, to compensate for general analyte losses during sample workup. In addition, terphenyl was spiked into the fractionated extracts just prior to GC injection and the recoveries of the original internal standards evaluated. In this latter capacity the internal standards functioned as surrogate standards. Recoveries of these standards from the samples were generally quite good. Some low recoveries were observed in effluents when severe emulsions or extremely polluted samples, requiring significant dilution, were encountered. Recovery data were tabulated on QC forms for the effluents. This data is provided in Appendix I. Cumulative recovery acceptance intervals were calculated and updated for each five effluents analyzed. If recoveries for succeeding extracts fell outside these intervals, analyses were halted until the cause could be found. With the exception of the occurrences mentioned above, low recoveries were only encountered on a single occasion when the HPLC pneumatic injector failed, resulting in incomplete sample introduction. The unit was replaced with a Rheodyne 7125 manual injector and analyses then proceeded.

Effluent samples were extracted within seven days of collection and analyzed by GC within 40 days. Exceptions were several samples collected at the beginning of the biennium, which predated the implementation of the expanded QA program, and some early HECD analyses. These latter analyses were not performed on schedule, due to personnel changes which occurred during this period. Once these problems were resolved, analyses proceeded according to the schedule mandated by the QA agreement. The critical milestones for the effluent samples are presented with the recovery data in Appendix I.

Precision and accuracy demonstration

An initial one-time precision and accuracy demonstration was performed by spiking reagent water with known concentrations of several pesticides, polynuclear aromatic hydrocarbons (PAHs), phenols and non-priority pollutants. The results of this demonstration are given in Appendix II (Tables II-A through II-E). Data obtained were compared against EPA Method 625 Table 6 criteria (40 CFR Part 136) for the recovery of spiked standards from reagent water. The mean recoveries of only two compounds, naphthalene and 2,4-dichlorophenol, fell outside the ranges specified. The average recovery of naphthalene was 34.6% (compared with the criteria of 35.6%-120%) and was 129% for 2,4-dichlorophenol (compared with the criteria of 52.5%-122%). The additional sample manipulation involved in the VIMS methodology probably accounts for the lower recovery of the relatively volatile naphthalene. The polar nature of the phenols resulted in generally poorer chromatographic peak shape, and subsequent quantitation, than the aromatic hydrocarbons. In addition, the presence of electronegative substituents, e.g. oxygen and chlorine, reduced FID response. Incorporation of a response factor resulted in a proportional increase in any measurement error. Nonetheless, precision of the data surpassed the required criteria. Standard deviations of the measurements were generally one-third or less of those contained in Method 625, with the exception of the acid extractables which were comparable. A number of compounds were included which are not contained on the list of priority pollutants in Method 625. Mean recovery and standard deviation data are given for these compounds.

Matrix spike demonstration

A matrix spike demonstration was performed and the results are given in Tables III-A through III-D in Appendix III. An actual effluent sample, QU, was chosen and spiked with representative priority and nonpriority pollutants, similar to those used in the initial precision and accuracy demonstration. Intervals, corresponding to +/- two times the standard deviation of the mean recoveries (determined during the initial precision demonstration), are included for comparison. The matrix for the initial evaluation was preextracted laboratory water. Also included are the pertinent acceptance intervals given in Table 6 of Method 625 for matrix spike experiments. Method 625 provides an additional allowance for error when the EPA applied its reagent water spike criteria to matrix spike analyses. A corresponding allowance was not included in the VIMS intervals. This fact, in concert with the extremely low standard deviations determined for some compounds during the initial precision determinations, preclude the strict adherence to these criteria for the purposes of data acceptance. For example, the VIMS interval for fluoranthene, calculated using data from the reagent water spike exercise (n = 4), was only 89.4%-92.8%. The standard deviation for the percent recovery of this compound was 0.868.

Recoveries of spiked compounds were generally similar to those observed during the initial precision and accuracy demonstration, although some recoveries were slightly low. This was probably due to lower extraction efficiencies of the compounds from the more complex effluent matrix. Except for 2,4-dimethylphenol and 2,4-dichlorophenol, which were slightly high, all recoveries met pertinent EPA Method 625 criteria. The precision of this data was good, which suggests that the response factors used in these calculations may have been high.

QU sediment and biota replicates

To further demonstrate the reproducibility of the methodology, five replicates of the QU sediment and biota sample were analysed. The data generated from these exercises are presented in Appendix IV, Tables IV-A through IV-E. Mean, standard deviation and coefficient of variation data are provided. Considering the basic heterogeneity of the matrices, the coefficients of variation of the measurements were generally low. For the aromatic fractions of the sediment extracts the greatest variation in the recoveries occurred at the extremes of the volatility range, i.e. for the most and least volatile compounds. The coefficient of variation for the nonylphenols, contained in the sediment polar fraction, was quite high; due perhaps to the fact that these compounds exist as a mixture of several isomers and were quantitated as such. The chromatograms from the biota replicates were simpler than those derived from the sediments. No anthropogenics were detected in the polar fractions. The coefficients of variation were relatively low for compounds detected in the aromatic FID and HECD analyses.

Results

Data from the grain size analyses are presented in Table 3. Results of the chemical determinations performed on the various fractions of individual effluents, sediments and biota are presented in Appendix V. The tables for the aromatic fractions contain the ARIs, concentrations and probable compound identities. Only concentration and identity data are given for peaks in the polar and acid fractions. The level of confidence for the identifications are rated on a scale of 0-3. The confidence scale is defined as follows:

0) Compound identity unknown.

1) Compound identity inferred by virtue of coincidence of its ARI with that of a known compound, or by interpretation of mass spectrum, or by partial match with the library mass spectrum of a compound. Compounds whose identities are strongly indicated, but for which the positions of the constituents are not known, are included in this category.

2) Compound mass spectrum closely matches library spectrum, or actual spectrum of a known compound, and isomeric composition is known.

3) Compound has a mass spectrum and ARI identical to an authentic standard.

Table 4 summarizes the total concentration of resolved compounds detected in the B/N aromatic, B/N polar and acid fractions of the effluent extracts. Contributions due to standards, extraneous contaminants and biogenic material have been removed. Table 5 summarizes the results for the sediment samples and Table 6 presents the results of analyses of indigenous shellfish. The results of the two live-box studies are discussed separately in the appropriate station summaries. Table 7 presents information concerning the occurrence of anthropogenic compounds in the effluents and their association with sediments and biota collected in proximity to the outfalls.

Table 3. Results of the grain size analyses of the sediments. Data are expressed on a dry weight basis.

Site	% Clay	% Silt	% Sand	% Gravel
AHC	3.1	0.8	92.9	3.2
AL	6.7	6.6	65.7	21.0
AW	42.7	45.7	11.6	0.0
AY	66.6	32.9	0.5	0.0
CC	46.2	19.9	33.0	0.9
CS	57.9	39.1	2.9	0.0
DA	5.5	3.2	91.2	0.0
FP	15.9	19.7	61.7	2.7
HY	39.7	28.5	31.8	0.0
JP	2.7	4.5	92.3	0.5
LA004	7.2	7.0	71.6	14.2
LA009	14.0	12.1	69.2	4.7
LAC	10.8	7.5	57.4	24.3
LO	24.1	48.4	21.7	5.8
LP	2.1	1.9	92.1	3.9
MM003	16.5	9.1	72.5	1.9
MM016	57.0	24.7	18.3	0.0
NB015	45.1	16.2	38.7	0.0
NN017	64.9	32.9	2.2	0.0
NN036	64.5	34.5	1.0	0.0
NS020	21.7	55.5	22.4	0.4
PP	34.8	27.3	36.7	1.2
QU	26.0	39.9	33.4	0.6
RS	2.2	3.0	92.4	2.3
SN052	3.3	2.1	94.0	0.6
SN064	2.4	0.8	95.8	1.0
SN066	11.7	7.6	64.7	16.0
UC	33.1	38.2	27.3	1.4
VPP	10.2	15.6	73.0	1.2
VY	13.0	8.9	78.1	0.0

Table 4. Total concentration in ug/l and number of resolved GC peaks detected by FID in the effluent samples analyzed. Only the CC effluent exhibited significant levels of halogenated compounds; the results of the GC/HECD analyses are discussed further in the text.

	B/N Aromatic Fraction		B/N Polar Fraction		Acid Fraction		Total Extractables	
	Conc.	# Peaks	Conc.	# Peaks	Conc.	# Peaks	Conc.	# Peaks
AHC	64.5	40	60.0	21	1050	24	1170	85
AL	4.5	13	11.0	5	<0.1	0	15.5	18
AW	124	78	13.0	3	140	3	277	84
AY	3.8	12	<0.1	0	<0.1	0	3.8	12
CC	167	149	18.0	14	391	12	576	175
CS	2040	137	356	30	4150	13	6546	180
DA	<0.1	0	<0.1	0	18.0	3	18	3
FP	1.8	5	<0.1	0	68.0	8	69.8	13
HY	0.3	2	<0.1	0	9.0	6	9.3	8
JP	<0.1	1	<0.1	0	<0.1	0	<0.1	1
LA004	11300	49	10.0	6	16.0	9	11300	64
LA009	18.2	4	2.0	2	22.0	10	42.2	16
LAC	184	59	82.9	14	303	21	570	94
LO	0.5	4	<0.1	0	<0.1	0	0.5	4
LP	0.7	7	<0.1	0	15.0	12	15.7	19
MM003	<0.1	0	<0.1	0	<0.1	0	<0.1	0
MM016	3610	96	7370	21	472	4	11500	121
NB015	18.0	24	<0.1	0	<0.1	0	18	24
NN017	0.6	2	<0.1	0	<0.1	0	0.6	2
NN036	0.2	2	<0.1	0	<0.1	0	0.2	2
NS020	6.5	18	8.0	10	<0.1	0	14.5	28
PP	20.0	50	85.0	21	919	13	1020	84
QU	0.2	2	<0.1	0	<0.1	0	0.2	2
RS	21.2	46	61.6	5	<0.1	0	82.8	51
SN052	0.1	1	<0.1	0	<0.1	0	0.1	1
SN064	16.1	64	<0.1	0	9.8	5	25.9	69
SN066	15.5	18	8.8	3	4.1	2	28.4	23
UC	25.6	38	1.0	1	6230	2	6260	41
VPP	0.2	1	<0.1	0	<0.1	0	0.2	1
VY	0.7	6	<0.1	0	<0.1	0	0.7	6

Table 5. Total concentration in ug/kg (dry weight basis) and number of GC peaks detected in the sediment samples. Results of the GC/FID analysis of the aromatic and polar fractions of the sediment, as well as the HECD analysis of the aromatic fraction, are presented.

	FID Analysis Aromatic Fraction		FID Analysis Polar Fraction		HECD Analysis Aromatic Fraction	
	Conc.	# Peaks	Conc.	# Peaks	Conc.	# Peaks
AHC	155000	107	8210	19	9.0	3
AL	5580	61	3840	22	148	74
AW	449000	115	147000	39	413	16
AY	4500	95	48	3	<0.1	0
CC	3050	119	13	1	12.0	11
CS	153000	134	4310	18	272	31
DA	1650	57	41	5	11.0	2
FP	983	72	<1	0	1.0	1
HY	1540	78	<1	0	3.0	4
JP	6100	130	132	12	16.3	46
LA004	90700	90	4290	14	135	4
LA009	76600	99	103000	28	10100[1]	64
LAC	835000	105	40100	9	61.0	6
LO	1250	50	440	23	34.0	21
LP	1150	52	141	18	<0.1	0
MM016	24300	120	111	24	74.0	24
MM003	43100	78	1250	11	9.0	2
NB015	54100	144	898	21	304	41
NN017	15600	104	389	26	250	46
NN036	6570	77	90	11	<0.1	0
NS020	34200	185	1620	14	190	48
PP	10200	131	5430	21	69.0	39
QU	9860	111	200	20	1680	14
RS	15900	125	109	3	<0.1	0
SN052	1030	78	21	7	2.7	6
SN064	474	20	141	19	10.6	16
SN066	170000	99	2960	27	4220[2]	37
UC	8980	109	2060	15	13.0	4
VPP	2090	72	13	4	5.0	5
VY	1090	143	<1	0	0.5	5

[1] This value was determined by routine GC/HECD analysis. Procedures were optimized for the PCTs and this sample re-analyzed. Utilizing response factors, a concentration of 25,600 ug/kg of Aroclor 5432 was determined in the sediment sample. See text for further details.

[2] A concentration of 19,300 ug/kg of Aroclor 5460 was determined in the sediment after procedural modifications. See text for further details.

Table 6. Total concentration in ug/kg (dry weight) and number of resolved GC peaks detected in the indigenous biota samples analyzed.

	FID Analysis Aromatic Fraction		FID Analysis Polar Fraction		HECD Analysis Aromatic Fraction	
	Conc.	# Peaks	Conc.	# Peaks	Conc.	# Peaks
AY	1490	10	ND	0	60.0	5
LA004	1620	19	ND	0	1370[1]	56
PP	2200	59	ND	0	186	15
QU	1250	13	ND	0	2320	39
SN052	315	14	ND	0	14.0	4
SN066	1754	44	ND	0	394	25

[1] This value was determined by routine GC/HECD analysis. Procedures were optimized for the PCTs and this sample re-analyzed. Utilizing response factors, a concentration of 3920 ug/kg of Aroclor 5432 was determined present in the tissues. See text for further details.

Table 7. Association between anthropogenic compounds detected in the effluent with sediments and biota collected near the outfalls. NA = Biota not available at this location.

Station	Compounds Detected in Effluent	Effluent Associated Compounds Detected in Sediment	Biota
AHC	Yes	Yes	NA
AL	Yes	Yes	NA
AW	Yes	Yes	NA
AY	Yes	Yes	Yes
CC	Yes	Yes	NA
CS	Yes	Yes	NA
DA	Yes	No	NA
FP	Yes	No	NA
HY	Yes	No	NA
JP	No	-	-
LA004	Yes	Yes	No[1]
LA009	Yes	Yes	NA[2]
LAC	Yes	Yes	NA
LO	Yes	Yes	NA
LP	Yes	Yes	NA
MM003	No	-	-
MM016	Yes	Yes	NA
NB015	Yes	Yes	NA
NN017	Yes	No	NA
NN036	Yes	No	NA
NS020	Yes	Yes	NA
PP	Yes	Yes	Yes
QU	Yes	Yes	No[3]
RS	Yes	Yes	NA
SN052	Yes	No	No[4]
SN064	Yes	Yes	NA
SN066	Yes	Yes	Yes
UC	Yes	Yes	NA
VPP	Yes	No	NA
VY	Yes	Yes	NA

[1] Chemically related compounds were detected in biota. Effluent at the time of collection consisted of relatively volatile constituents.

[2] Biota collected at LA004 possessed PCTs which were detected in sediments in the immediate vicinity of the LA009 outfall.

[3] PCBs and DDD were detected in both sediments and biota at this site.

[4] Compounds detected in this biota sample were similar to those detected in nearby SN64 sediment and effluent.

Individual Station Summaries

Alexandria STP

The Alexandria STP is located in northern Virginia near the Alexandria/Fairfax County line. The discharge canal passes under I-95 and enters Hunting Creek in the Potomac River Basin. The sediment sample was taken at the confluence of the canal with the creek and consisted of 87% sand and gravel. The area in the immediate vicinity of the sampling location was heavily vegetated and access was gained from I-95. The general locale is quite well developed with major highways, businesses and multiple unit housing developments present. The GC/FID analysis of the aromatic fraction of the effluent detected 4.5 ug/1 of material. About 3.1 ug/1 of this total were identified as PAHs (six compounds) and 1.4 ug/1 were unidentified (seven compounds). The compounds detected were of relatively high volatility. No halogenated compounds were detected by HECD in the B/N aromatic fraction. The B/N polar fraction contained alicyclic and terpenoid alcohols at 11.0 ug/1. These compounds are probably natural products or derived from same. No acidic compounds were detected.

The sediment aromatic fraction contained approximately 5600 ug/kg of PAHs. Nonsubstituted PAHs were the major contributors. Forty-four identified and 17 unknown compounds were reported. Major components were the PAHs. Volatile aromatics such as naphthalenes were also present. A number of halogenated compounds, including PCBs and chlorinated pesticides, were detected at a concentration of 148 ug/kg. The polar fraction contained a complex series of nonylphenols and related analogs at a concentration of 3600 ug/kg. Carbazole and benzocarbazoles at a concentration of about 100 ug/kg were also present. These compounds are present in fossil fuels (Southworth et al. 1979).

The sediment data suggests that deposition of anthropogenics was significant at this site in the past. Episodic events, not detected by the composite effluent sampling, might also have occurred. The most noteworthy observation was the presence of the high concentrations of alkylphenols in the sediments, probably derived from detergents.

Allied Chemical Chesterfield Live Box Study

An eight week live box study using transplanted clams (Rangia cuneata) was performed near the Allied Chemical Chesterfield facility on the James River by the SWCB. Effluent and sediment had been collected and analysed by VIMS in 1986 from this site. Clams were collected and analyzed after residing on-site for two, four and eight weeks. In addition, specimens were sampled at the initiation of the study to determine contaminant baselines for the clams. Results of the GC/FID analysis of the aromatic fraction are given below. Unresolved complex mixtures were present in all composites analysed, including Week 0. PAHs were the predominant compounds detected. The aromatic fractions were also analyzed by the HECD. Constituents identified by GC/HECD/HRI included PCBs, DDD, DDE, nonachlor, dieldrin and chlordane. No anthropogenic compounds were detected in the polar fraction.

FID Analysis the Aromatic Fraction

Sample	Concentration (ug/kg)	Number of Compounds
Week 0	1840	24
Week 2	3650	62
Week 4	965	7
Week 8	2530	46

HECD Analysis of the Aromatic Fraction

Sample	Concentration (ug/kg)	Number of Compounds
Week 0	166	12
Week 2	838	40
Week 4	227	15
Week 8	752	34

Concentrations of compounds in the clams did not consistently increase over the course of the eight week study. A decrease was observed at the Week 4 sampling for both halogenated and nonhalogenated compounds. Biological heterogeneity may have contributed to these observations or the fluctuation may be attributable to actual changes in environmental exposure to anthropogenics. It is worthwhile to note that the background clams analysed (Week 0) contained significant concentrations of material. The major compounds detected in the sediments and effluent from this facility in 1986 were biphenyl and diphenyl ether. These latter compounds were also detected in an effluent sample from LA009 in the present study. Diphenyl ether has been reported to be used in heat transfer fluids (Verschueren 1983). Biphenyl was reported in the Week 2 biota composite at a concentration of 26 ug/kg.

Amerada Hess Corporation

The Amerada Hess facility is located on the southern branch of the Elizabeth River. The receiving basin is the James River. The facility is used for bulk fuel storage and distribution. The effluent collected was from an oil/water separator. The B/N aromatic fraction of the effluent contained about 64.5 ug/l of PAHs. The major component reported was naphthalene at 19.0 ug/l. Light aromatics constituted a major portion of the residue. The polar fraction contained alkylphenols and carbazole at 8.0 and 27.0 ug/l, respectively. The C4-phenols probably originated directly from petroleum, while the nonylphenols are most likely derived from detergent use. No halogenated compounds were detected by GC/HECD in the B/N fraction. The acid extract contained 740 ug/l of C2 and C3-phenols. Phenylphenols and methylnaphthols were reported present at 110 ug/l. In addition, pentachlorophenol at a concentration of 38.0 ug/l and bromacil at 8.0 ug/l were detected. Bromacil is a herbicide generally used to control grasses and broad leaf weeds. It has an acute oral LD50 of 5200 mg/kg in rats (Verschueren 1983). Pentachlorophenol has been used as a general pesticide and a wood preservative. It has toxicities to aquatic organisms on the order of 200 ug/l (Verschueren 1983). Twenty-four compounds were detected in the acid fraction.

The sediment collected near the outfall consisted of 93% sand. It possessed a visible oil sheen. The aromatic fraction of the sediment extract contained 107 GC resolved compounds at a concentration of about 155,000 ug/kg. Petroleum derived aromatics dominated. Trace concentrations of halogenated compounds were detected. Compounds reported in the polar fraction included carbazoles and azaarenes at a total concentration of 8200 ug/kg. These nitrogen containing compounds are constituents of fossil fuel products.

Atlantic Wood Industries

The Atlantic Wood Industries, Inc. Portsmouth plant is located on the southern branch of the Elizabeth River. The facility is involved in creosoting operations. The effluent sampled consisted of stormwater runoff from the plant. The B/N aromatic fraction of the effluent was reported to contain 78 resolved compounds at a concentration of 124 ug/l. A total of 44 PAHs were identified by MS or ARI at a cumulative concentration of 106 ug/l. The B/N fraction contained no halogenated compounds. The B/N polar fraction of the effluent contained quinolines and carbazole at a total concentration of 13.0 ug/l. The acid extract contained 135 ug/l of pentachlorophenol and 5.0 ug/l of tetrachlorophenols. Pentachlorophenol is used as a wood preservative. An area on the Atlantic Wood site map has been designated "Penta Storage". The concentration of pentachlorophenol in the effluent is similar to the LC50 for aquatic organisms (Verschueren 1983).

The sediment sample collected consisted of 88% clay and silt and exhibited an oily sheen. During sampling, turbulence caused by the boat resulted in the resuspension of oily material in the near shore water, visible evidence of the high level of contamination. The FID analysis of the aromatic fraction of the sediment detected 449,000 ug/kg of material. A total of 54 compounds were identified as PAHs and 62 unidentified peaks were present. About 413 ug/kg of halogenated compounds, identified by HRI as PCBs, were detected in the aromatic fraction of the sediments. The polar fraction of the sediment extract contained about 147,000 ug/kg of material, attributable for the most part to nitrogen substituted PAHs.

Amoco Yorktown

The Amoco Refinery in question is located near the mouth of the York River, at Yorktown. The outfall is located in the York River proper. The composite effluent received was treated process wastewater. The B/N aromatic fraction of the effluent contained 12 compounds at a cumulative concentration of only 3.8 ug/1. No compounds were detected in the B/N polar fraction. No halogenated compounds were detected by the HECD in the B/N fraction. No individual compounds were detected in the acid extract of the effluent. However, an unresolved complex mixture was present; these are observed when the GC column is unable to resolve the individual compounds present.

Sediment, collected in the area of the outfall, consisted of greater than 99% clay and silt. The FID detected 4500 ug/kg of 95 resolved compounds in the aromatic fraction of the sediment extract. Forty-seven compounds were identified, consisting mostly of alkyl substituted and nonsubstituted PAHs. Three benzocarbazole isomers were detected in the polar fraction at a concentration of 48 ug/kg. No halogenated compounds were detected by HECD in the sediments.

Indigenous oysters (Crassostrea virginica) were collected near the refinery outfall. The aromatic fraction of the extract contained 10 compounds at a concentration of 1490 ug/kg. The four compounds identified were high molecular weight PAHs, probably derived from pyrolysis of fossil fuels or degradation of natural products. No anthropogenic compounds were detected in the polar fraction. PCBs and BHC were detected by the GC/HECD/HRI analysis in the aromatic fraction of the sediment at a total concentration of 60.0 ug/kg.

Chesapeake Corporation

The Chesapeake Corporation operates a paper mill at the confluence of the Pamunkey and York River in West Point. The major product of the facility is kraft paper, although some bleached products are produced. The effluent examined consisted of process water. At the time of sampling Chesapeake Corporation was periodically exceeding their permit limit for the discharge of suspended solids. The effluent collected was exceedingly complex, due in part to the great number of wood derived compounds present. The B/N aromatic fraction contained 149 compounds at a cumulative concentration of 167 ug/1, most of which were not identified. A number were characterized as steroid derivatives by MS. These compounds were probably derived from wood pulp. The resolved compounds were superimposed on an unresolved complex mixture. Only 18.0 ug/1 of material were detected by FID in the polar B/N fraction of the effluent and included two chlorinated compounds and a trimethoxybenzene. The B/N aromatic fraction of the effluent extract contained 48 halogenated compounds at a total concentration of 71.5 ug/1. Chesapeake was the only effluent observed to contain significant concentrations of halogenated compounds. Some of the peaks were reported to be PCB congeners by the HRI. It is likely these are actually chlorinated natural products derived from the bleaching process which exhibit HRI similar to PCB congeners. The acid extract contained 391 ug/1 of 12 resolved compounds. Seven of these compounds were characterized as steroidal in composition by MS. The acid extract also possessed an unresolved complex mixture.

A sediment sample was collected near the effluent discharge point in the Pamunkey River. It consisted of about 66% clay and silt and 33% sand.

A plume was visible in the Pamunkey River at the outfall location at the time of collection. The aromatic fraction contained 119 compounds at an estimated concentration of 3050 ug/kg, superimposed on an unresolved complex mixture envelope. Carbazole at 13 ug/kg was the only compound detected in the polar fraction. The HECD reported the presence of only 12.0 ug/kg of halogenated material in the aromatic fraction of the sediments. Retention time data suggested that these were PCBs.

Colonna's Shipyard

Colonna's Shipyard is located on the eastern branch of the Elizabeth River. The sediment sample was collected in the vicinity of ongoing ship repair operations and consisted of 97% clay and silt. The B/N aromatic fraction of the effluent was heavily contaminated by petroleum hydrocarbons; approximately 2040 ug/l of material were reported to be present by GC/FID analysis. A total of 137 compounds were separated by the GC column. Seventy-three compounds at a concentration of about 1700 ug/l were identified, consisting predominantly of PAHs. The B/N polar fraction contained 356 ug/l of polar compounds consisting of C2 to C4-phenols, carbazole and methylcarbazoles. The presence of these compounds is indicative of petroleum contamination. The effluent contained less than 0.1 ug/l of halogenated compounds in the B/N fraction. The acid extract contained 4150 ug/l of predominantly C2 and C3-phenols. This effluent is expected to be acutely toxic to aquatic organisms.

The aromatic sediment extract contained 134 compounds at a cumulative concentration of 153,000 ug/kg, superimposed on an unresolved complex mixture. Of these compounds, 59 were identified as PAHs and contributed the bulk of the contamination. The polar fraction contained 4310 ug/kg of 18 nitrogen substituted PAHs. The HECD detected the probable presence of PCBs, chlordane, nonachlor, dieldrin, DDE, DDD and DDT at a concentration of 272 ug/kg in the aromatic fraction.

Dahlgren Naval Weapons Laboratory

The receiving stream for the Dahlgren outfall is the Machodoc Creek, which subsequently enters the Potomac River basin. The effluent consisted of stormwater and drainage from equipment cleaning, repair shops and paint spraying operations. The B/N fractions were devoid of contamination, as determined by FID. The HECD analysis of the B/N aromatic fraction of the effluent was also negative. The acid extract was reported to contain 18.0 ug/l of aliphatic acids.

FID analysis of the aromatic fraction of the sediment resulted in the detection of 1650 ug/kg of 57 compounds, mostly unsubstituted PAHs. Only 41 ug/kg were reported by FID in the polar fraction. These compounds consisted of carbazole and benzocarbazoles. HECD analysis of the aromatic fraction reported the presence of 2.0 and 9.0 ug/kg of DDE and DDD, respectively. The sediment collected consisted of 91% sand.

Fredericksburg STP

The Fredericksburg STP discharges to the Rappahannock River. The B/N aromatic fraction of the effluent contained 1.8 ug/1 of material. No compounds were detected in the B/N polar fraction by FID or in the B/N aromatic fraction by HECD. The acid extract contained 68.0 ug/1, consisting predominantly of aliphatic acids.

The sediment sample exhibited only 983 ug/kg of 72 resolved compounds. These were predominantly unsubstituted PAHs, with some contribution from alkylated PAHs. No polar compounds were reported by the FID in the polar fraction. The HECD analysis indicated that the aromatic fraction contained only 1.0 ug/kg of halogenated compounds. The sediment consisted of 62% sand and 36% finer material.

Hampton Roads Sewerage District York River POTW

The Hampton Roads Sewerage District York River POTW outfall discharges in association with the Virginia Power Yorktown outfall. The B/N aromatic fraction of the effluent contained 0.3 ug/l of material, as determined by the FID. The FID did not detect the presence of any significant contamination in the polar fraction. No halogenated compounds were detected by the GC/HECD in the B/N aromatic fraction. The FID reported 9.0 ug/l of aliphatic acids in the effluent acid extract.

The FID analysis of the aromatic fraction of the sediment extract revealed the presence of 1540 ug/kg of 78 discrete compounds. Unsubstituted PAHs predominated. No polar compounds were detected in the sediments by FID and minor levels of halogenated compounds were reported by the HECD in the aromatic fraction. The sediment consisted of similar percentages of clay, silt and sand.

James River Paper Company

The James River Paper Company discharges to the James River in Richmond. The effluent sample received consisted of noncontact cooling water. The presence of minimal levels of contamination were determined by the FID analysis of the B/N aromatic and polar fractions and the acid extract. The HECD failed to detect appreciable concentrations of halogenated compounds in the B/N fraction.

The sediment aromatic fraction contained about 6100 ug/kg of 130 GC resolved compounds. Although major contributors were unsubstituted PAHs, a number of alkylated naphthalenes, indicative of petroleum contamination, were present. About 132 ug/kg of 12 compounds, predominantly carbazoles and benzocarbazoles, were detected by GC/FID in the polar fraction. The GC/HECD detected the presence of a number of chlorinated pesticides and biphenyls, but at a cumulative concentration of only 16.3 ug/kg. The sediment itself was quite coarse and consisted of 92% sand.

NASA Langley Research Center Outfall 004

The NASA Langley Research Center is located in Hampton and is involved in aerospace research. The receiving stream for Outfall 004 is the Southwest Branch of the Back River. Langley Air Force Base is adjacent to the NASA facility. The effluent sample received was described as originating from cooling tower blowdown. However, the outfall site, at the time of the sediment sampling, was surrounded by an oil boom. Infiltration of contaminated groundwater has been mentioned (C. Lunsford, VWCB, personal communication) as a possible source of the petroleum contamination observed. The B/N aromatic fraction was the most heavily contaminated of the 30 effluents examined. It contained 49 resolvable compounds at an estimated concentration of 11,300 ug/l. The aromatic fraction was dominated by alkylated benzenes and naphthalenes, indicative of a light petroleum based fuel. In contrast, GC/FID analysis of the B/N polar reported only 10.0 ug/l and HECD analysis of the B/N aromatic fraction failed to detect any compounds. The FID analysis of the acid fraction contained 16.0 ug/l of several phenol and benzoic acid derivatives. This effluent is expected to be acutely toxic to aquatic organisms.

The sediment sample collected was also heavily contaminated. It was quite coarse in composition, containing 72% sand and 14% gravel. Ninety compounds were resolved at a cumulative concentration of 90,700 ug/kg. The domination by volatile aromatics was not as pronounced as in the case of the effluent. PAHs were the major constituents detected by FID. The polar fraction contained 14 resolved compounds including nonylphenols, carbazole and benzocarbazoles. The concentration of these peaks was 4290 ug/kg. A total of 135 ug/kg of halogenated compounds were detected at this site by the HECD. HRI data suggested that the major constituents were PCBs and DDD.

Oysters (C. virginica) were collected several hundred feet from shore in the Southwest Branch of the Back River. The outfall itself was located on the shoreline. The aromatic fraction of the biota extract contained 19 resolved compounds. The PAHs phenanthrene, fluoranthene, pyrene and chrysene were present at 440 ug/kg. Polychlorinated terphenyls (PCTs), chemically similar to PCBs, were identified in the tissues of the oysters collected. Thirteen PCTs and a PCB were reported by GC/FID at about 1100 ug/kg and 44 ug/kg, respectively. No polar anthropogenics were detected in the polar fraction. A total of 1370 ug/kg of halogenated compounds was calculated for the aromatic fraction by routine HECD analysis. The majority of these peaks were not identified by the retention library, since the PCTs had not been previously reported to occur in the Chesapeake Bay. Thus they were not entered into the HRI data base. Refinement of the analytical procedures and the application of response factors resulted in an improved estimate for the quantity of PCTs present. Using these techniques, a PCT concentration of 3920 ug/kg (dry weight) was calculated for the oysters collected. The GC/HECD pattern was similar to that of Aroclor 5432. These PCTs were not found in significant concentrations in the sediments at the LA004 outfall.

NASA Langley Research Center Outfall 009

NASA Langley Research Center Outfall 009 is described as being derived from an oil/water separator. The outfall discharges to Tabb's Creek which enters the Northwest Branch of the Back River and eventually the Chesapeake Bay. The B/N aromatic fraction of the effluent extract was reported to contain 18.2 ug/l of GC resolved compounds. The major components were biphenyl and diphenyl ether. The concentration of diphenyl ether is similar to that reported to taint seafood (Verschueren 1983). The recovery of diphenyl ether from spiked reagent water and wastewater was approximately 50% in laboratory experiments. Possible sources of these compounds are heat transfer fluids. Only 2.0 ug/l of material were detected in the B/N polar fraction by GC/FID. Initially no halogenated compounds were detected in the aromatic fraction by HECD. However, after concentrating the extract ten fold a complex mixture of halogenated compounds was observed. The components observed eluted prior to those of Aroclor 1254, Aroclor 5432 or Aroclor 5460. Due to differences in the relative water solubilities of the different PCB and PCT congeners, some alterations of their retention patterns is expected. Efforts are ongoing to identify these compounds. Ten compounds, at a cumulative concentration of 22 ug/l, were detected by FID in the acid extract of the effluent. Compounds identified included cresol and C4-phenol, C4-tetrahydrofuran and aliphatic acids.

The sediment collected at this location was heavily contaminated with several classes of compounds. It was relatively coarse, consisting of 69% sand. The aromatic fraction of the extract contained 99 compounds at a total concentration of 76,600 ug/kg, according to the FID analysis. Eighty-one of these compounds were identified. The single largest contributor, diphenyl ether, was present at a concentration of 11,000 ug/kg. This compound was also detected in the effluent. About 12,000 ug/kg of the total were nonylphenols or related compounds and 2500 ug/kg corresponded to PCBs. PCTs similar to those detected in biota samples from LA004 were present at a concentration of about 9300 ug/kg, as determined by GC/FID. PAHs constituted greater than 42,000 ug/kg of the remaining material in the aromatic fraction. The polar fraction contained even higher concentrations of anthropogenics. Twenty eight compounds at a total concentration of 103,000 ug/kg were detected by FID. Cumylphenols composed the majority of this material. These compounds have been reported to be used as intermediates in resins, insecticides and lubricants (Verschueren 1983). In addition, nonylphenols, thought to be derived from detergents were detected. Carbazole and benzocarbazoles were minor contributors. The GC/HECD analysis of the aromatic fraction provided additional evidence of the high concentration of halogenated compounds present. This analysis detected the presence of 10,100 ug/kg of halogenated compounds. This value is similar to the 12,000 ug/kg of PCBs and PCTs detected by GC/FID and subsequently identified by GC/MS. The analytical procedures were refined to maximize the recovery of the PCTs, response factors calculated and the sediment reanalyzed. A concentration of 25,600 ug/kg of Aroclor 5432 was subsequently determined present in the LA009 sediment.

L.A. Clark and Sons, Inc.

L.A. Clark and Sons, Inc. is a timber creosoting operation located south of Fredericksburg. The receiving stream is the Massaponax Creek which empties into the Rappahannock River. Groundwater monitoring wells were observed in place at the site. The effluent collected consisted of surface drainage and boiler blowdown. The B/N aromatic fraction of the effluent contained 59 resolved compounds at a concentration of 184 ug/l. Unsubstituted PAHs and methylnaphthalenes predominated. The polar B/N fraction contained 14 compounds at a concentration of 82.9 ug/l. These compounds appear to be methylcarbazoles and benzoquinolines, based on the retention times of the constituents and the facility involved. No halogenated compounds were detected in the B/N fraction by HECD. The acid extract of the effluent contained 21 compounds at a total concentration of 303 ug/l. The major components were C2 and C3-phenols, naphthoic acids and other oxygenated aromatics.

The sediment sample was collected at the confluence of a drainage ditch with the creek. It consisted of 82% sand and gravel. Bales of hay had been placed in the ditch at several points beween the facility and the creek to adsorb hydrocarbons. The creek area itself exhibited signs of severe contamination. The banks of the stream were marked by hydrocarbon deposits and several discarded metal barrels were observed partially buried nearby. The sediment sample exhibited an oily sheen, as did the creek water upon disturbance of the sediment. The aromatic fraction of the extract contained 105 resolved compounds at a cumulative concentration of 835,000 ug/kg. The LAC sample was the most highly contaminated sediment of the 30 analyzed in the present study. Creosote derived materials predominated. For example, phenanthrene, fluoranthene and pyrene contributed 330,000 ug/kg or 39% of the total sediment burden. The polar fraction contained 40,100 ug/kg of material. Carbazole was present at 28,100 ug/kg. Methyl carbazole, benzocarbazoles and an azaarene of molecular weight 203 were also identified. Only 61.0 ug/kg of halogenated compounds, consisting mostly of PCBs, were detected by the HECD/HRI system in the aromatic fraction.

Lorton STP

The Lorton STP is located in Fairfax County near Occoquan. The outfall discharges into the Mills Branch, which passes through the Occoquon Regional Park prior to emptying into the Occoquan River. At this point a mud flat has formed in the Occoquan River. Inspection of the Mills Branch itself revealed the presence of large quantities of filamentous organisms growing on the rocks therein. Only 0.5 ug/l of aromatics were detected in the B/N aromatic fraction of the effluent. No compounds were detected in the B/N polar or acid fractions by FID. The HECD analysis did not detect the presence of any halogenated compounds in the B/N aromatic fraction.

A sediment sample was collected in the vicinity of the bar. The grain size distribution of this material was 48% silt, 24% clay and 22% sand. The aromatic fraction of the extract contained 50 compounds at a concentration of about 1250 ug/kg. The polar fraction contained nonylphenols and related compounds at a concentration of 420 ug/kg and 21 ug/kg of carbazole and benzocarbazoles. The HECD analysis reported the presence of chlordane, nonachlor, DDE, DDD and PCBs at a cumulative concentration of about 34.0 ug/kg in the sediment.

Lower Potomac STP

The Lower Potomac STP is located near Fort Belvoir and discharges to the Pohick Creek. The creek then empties into the Potomac River. The B/N aromatic fraction contained 0.7 ug/1 of aromatic material according to the GC/FID analysis. No compounds were detected in the B/N polar fraction. The acid fraction contained 12 compounds at a cumulative concentration of 15.0 ug/1. Aliphatic acids were major contributors. No halogenated compounds were detected by the HECD.

The sediment was collected from Pohick Creek at the point of discharge. The sample consisted of 92% sand. The creek water at this location was quite clear. Fifty-two compounds at a concentration of 1150 ug/kg were detected in the aromatic fraction at this site. Pyrogenic PAHs predominated. The polar fraction contained a total of 141 ug/kg of nonylphenols and related compounds, carbazole and benzocarbazoles. No halogenated compounds were detected by the HECD in the aromatic fraction of the sediment extract.

Metro Machine Outfall 003

This site was adjacent to the floating drydock area. No significant concentrations of compounds were present in the effluent sample received, as determined by either GC/FID or HECD.

Several welding rods and other debris were recovered with the sediment sample at this site. The sediment itself consisted of 73% sand. Seventy-eight aromatic compounds, at a cumulative concentration of 43,100 ug/kg, were detected in the aromatic fraction. An order of magnitude greater concentration, 1250 ug/kg, of polar constituents were detected in the sediment at MM003 than MM016, despite their proximity. However, the major constituents were similar, nonyl phenols and carbazoles. These former compounds are probably derived from detergents or de-emulsifiers, while the latter are constituents of fossil fuels. Only 9.0 ug/kg of PCBs were reported by GC/HECD analysis in the sediment aromatic fraction, which is much less than that detected at MM016.

Metro Machine Outfall 016

The Metro Machine Corp. Outfall 016 originates from an oil/water separator. The separator itself consisted of the tank from an oil tank truck and was quite ineffective in removing toxic organics, based on the results of the effluent analysis. The company is involved in shipbuilding and repair. The receiving stream is the eastern branch of the Elizabeth River which empties into the James River. The B/N aromatic fraction of the extract contained 96 resolved compounds at a concentration of 3610 ug/l. An unresolved complex mixture consisting of relatively volatile aromatics was observed. The composition was dominated by volatile alkyl benzenes and naphthalenes. The B/N polar fraction from this sample was the most contaminated of the 30 effluents examined. Alkyl phenols, particularly the nonylphenols, were major constituents. As noted previously, the nonylphenols are probably derived from detergents or similar products. The C3 and C4-phenols are constituents of petroleum. The total concentration of these compounds was 7370 ug/l, exceeding the next closest site in terms of B/N polar constituents by more than an order of magnitude. The acid extract of the effluent contained several additional C3 and C4-phenols at a total concentration of 472 ug/l. The acid extract had to be back extracted, in order to remove aliphatics which carried over from the initial B/N extraction. This was further evidence of the inefficiency of the oil/water separator used at this site. Halogenated compounds were present at only 0.2 ug/l in the B/N fraction. The effluent is expected to be acutely toxic to aquatic organisms.

The sediment collected contained 120 compounds in the aromatic fraction at a total concentration of 24,300 ug/kg. Significant concentrations of petroleum derived compounds were detected. An unresolved complex mixture was also observed. The polar fraction of the sediment contained a number of nonylphenols and related compounds at 53 ug/kg, in concert with several nitrogen containing aromatics at a total concentration of 58 ug/kg. Approximately 74.0 ug/kg of halogenated compounds were detected in the aromatic fraction of the sediment extract. These peaks were identified by HRI data as PCBs, chlordanes, nonachlor, DDD and DDE. Considering the depth of the water at the sampling location, 35 feet, it is likely that much of the material in the effluent is dispersed over a relatively wide area. The sediment at MM016 was relatively fine, consisting of 57% clay, 25% silt and 18% sand.

Norfolk Shipbuilding and Drydock Corp. Berkeley Outfall 015

The Norfolk Shipbuilding and Drydock Corp. is located on the southern branch of the Elizabeth River and is engaged in shipbuilding and repair operations. The effluent examined was obtained from the drydock "Titan". The B/N aromatic fraction contained 24 aromatics at a total concentration of 18.0 ug/l. The compounds detected generally contained three or more aromatic rings. No compounds were detected in the B/N polar or acid extract by FID, nor were any compounds reported present by the HECD analysis of the B/N extract.

The aromatic fraction of the sediment extract contained 144 compounds at a cumulative concentration of 54,100 ug/kg. Significant concentrations of naphthalenes, as well as higher molecular weight PAHs, were detected. An unresolved complex mixture was also observed in the aromatic fraction. The polar fraction exhibited 898 ug/kg of nonylphenols and nitrogen substituted aromatics; derived from detergents and fossil fuels, respectively. Carbazole was present at 200 ug/kg. The sediment also exhibited 304 ug/kg of halogenated compounds in the aromatic fraction. PCBs were identified by the HRI system as the predominant halogenated constituents. The sediment examined contained 45% clay, 16% silt and 39% sand.

Newport News Shipbuilding and Drydock Outfall 017

The Newport News Shipbuilding and Drydock Corp. is located on the James River. It is engaged in shipbuilding and repair operations. Outfall 017 was derived from drainage from drydocks 1 and 2. The B/N aromatic fraction of the effluent contained only 0.6 ug/1 of aromatic hydrocarbons. No compounds were detected in the B/N polar or the acid extract by FID. Only 0.3 ug/1 of halogenated compounds were detected by HECD in the B/N extract.

The sediment aromatic fraction examined contained 104 compounds at a total concentration of about 15,600 ug/kg. Alkyl substituted naphthalenes and high molecular weight PAHs dominated. The polar fraction contained 389 ug/kg of nonylphenols, carbazoles and other nitrogen substituted PAHs. The HECD analysis reported the presence of 250 ug/kg of halogenated compounds. The HRI system identified the majority of these peaks as PCBs. The sediment itself was fine in composition, consisting of 98% clay and silt.

Newport News Shipbuilding and Drydock Outfall 036

The effluent in question consisted of drainage from Shipway #12. As in the case of NN017, the effluent examined contained minimal chromatographable material in any of the fractions analyzed.

The sediment aromatic fraction contained 77 resolved compounds at a concentration of 6570 ug/kg. Typical PAHs and naphthalenes dominated. Only 90 ug/kg of polar constituents were detected in the polar fraction. These compounds consisted of the nitrogen substituted aromatics. No halogenated compounds were detected in the aromatic fraction by the HECD. The sediment was 99% fine clay and silt.

Norfolk Naval Shipyard Outfall 020

The Norfolk Naval Shipyard is involved in shipbuilding and repair and is located on the Elizabeth River in the James River Basin. The B/N aromatic fraction of the effluent contained 18 compounds at a concentration of 6.5 ug/l. Volatile alkyl naphthalenes were major constituents. The B/N polar fraction contained 8.0 ug/l of nonylphenols and related compounds. No acid extractables or halogenated compounds were detected.

The aromatic fraction of the sediment contained 185 compounds at a total concentration of 34,200 ug/kg. PAHs dominated. An unresolved complex mixture was observed in the chromatogram of the aromatic fraction. The polar fraction contained 14 compounds at a total concentration of 1620 ug/kg. Carbazole was present at a concentration of 520 ug/kg, while benzoquinolines, methylcarbazole and azaarenes contributed the bulk of the remainder. Nonylphenols were not present at significant concentrations. The GC/HECD analysis detected the presence of 190 ug/kg of halogenated compounds. PCBs and chlorinated pesticides were identified as major constituents according to the HRI system. The sediment consisted of 56% silt, 22% of clay and 22% sand.

Portsmouth Pinner's Point STP

Portsmouth Pinner's Point STP is located on the Elizabeth River. The B/N aromatic fraction of the effluent contained 20.0 ug/l of 49 compounds. The majority of the compounds were alkylated naphthalenes, biphenyls, fluorenes and phenanthrenes. The B/N polar fraction contained 85.0 ug/l of a variety of phenolics. A relatively high concentration of aliphatic and aromatic acids, 919 ug/l, were present in the acid extract. No significant peaks were detected in the aromatic fraction by HECD.

The aromatic fraction of the sediment contained 131 aromatics at a total concentration of 10,200 ug/kg. The polar fraction contained 5430 ug/kg, consisting mostly of nonylphenols. Carbazole and benzocarbazoles contributed 166 ug/kg to the total. Approximately 69.0 ug/kg of PCBs and chlorinated pesticides were detected by the HECD. Identification was accomplished by the HRI system. The sediment consisted of similar percentages of clay, silt and sand.

Oysters (C. virginica) were available near the outfall. Fifty-nine compounds were detected at a cumulative concentration of 2200 ug/kg. The compounds identified consisted of PAHs. This fraction contained an unresolved complex mixture. No polar anthropogenic compounds were detected in the polar fraction. Fifteen halogenated compounds, at a total concentration of 186 ug/kg, were reported to be present in the aromatic fraction by the HECD. PCBs, chlordane, nonachlor, DDE and DDD were identified by the HRI system.

U.S. Marine Corps Base STP-Quantico

The Quantico Marine Base STP effluent flows into Cedar Run and then into the Potomac River. The effluent contained only 0.2 ug/l of aromatics in the B/N aromatic fraction. No compounds were detected in either the B/N polar or the acid extract by GC/FID. Only 0.1 ug/l of halogenated material was reported by the HECD in the B/N extract.

The aromatic fraction of the sediment extract contained 111 compounds at a concentration of 9860 ug/kg. Total DDD at a concentration of 870 ug/kg and DDE at 52 ug/kg were detected. The polar fraction contained nonylphenols, carbazole and benzocarbazoles at a concentration of 200 ug/kg. The GC/HECD analysis detected 105 ug/kg of DDE and 970 ug/kg of DDD in the aromatic fraction of the sediment. The HECD also reported the presence of 78 ug/kg of DDT. PCBs, at a concentration of 530 ug/kg, were also detected by the HECD/HRI analysis. The sediment was collected from a location near the shoreline. Therefore, it is feasible that the pesticide contamination observed arose from application on adjacent land areas, rather than from the STP. The sediment sample consisted of similar percentages of clay, silt and sand.

Indigenous clams (<u>R. cuneata</u>) were collected near the outfall site. Thirteen compounds, at a total concentration of 1250 ug/kg were reported in the aromatic fraction by FID. The major peak consisted of DDD at a concentration of 240 ug/kg. Nine PCB congeners were reported at a cumulative concentration of 780 ug/kg. No anthropogenics were detected in the polar fraction. Thirty-nine halogenated compounds, at a cumulative concentration of 2320 ug/kg, were reported present in the aromatic fraction by the HECD. Thirty of the peaks, representing 1800 ug/kg of the total, were identified as PCB congeners by the HRI system. DDD, DDE and DDT were detected at 230 ug/kg, 220 ug/kg and 20 ug/kg, respectively. Chlordanes and nonachlor were reported at 31 ug/kg.

Richmond POTW Live Box Study

A live box study using (<u>R. cuneata</u>) was conducted by the SWCB near the Richmond POTW, located on the James River. Unfortunately, the study was terminated prematurely on two separate occasions due to the loss of the boxes. As a consequence, two sets of data are presented, obtained from Week 0 and Week 2 composites. Data for the GC/FID and GC/HECD analyses of the aromatic fractions are given below. No significant anthropogenic peaks were observed in the polar fractions.

GC/FID Analysis of Live Box Aromatic Fractions

Sample	Concentration (ug/kg)	Number of Compounds
Week 0A	3670	105
Week 2A	6860	90
Week 0B	980	21
Week 2B	7350	68

GC/HECD Analysis of Live Box Aromatic Fractions

Sample	Concentration (ug/kg)	Number of Compounds
Week 0A	644	22
Week 2A	90	4

Week 0B	126	9
Week 2B	264	14

Sediment and effluent from the Richmond POTW were analyzed in 1985. The effluent contained no significant concentrations of anthropogenic material. The aromatic fraction of the sediment contained typical PAHs. The polar polar fraction contained nonylphenols, indole and methylated indoles. The Week 2 live box biota composites exhibited elevated levels of PAHs and naphthalenes compared with Week 0 clams. The halogenated compounds did not exhibit a consistent pattern of accumulation. Major halogenated compounds identified by the GC/HECD/HRI analysis included PCBs, chlordanes, nonachlor, DDE and dieldrin.

Reynolds Metals Co.-South Plant

The Reynolds Metals Co. operates a facility on the James River in Richmond. The effluent sampled originated from an oil/water separator. The B/N aromatic fraction contained 46 compounds at a concentration of 21.2 ug/l. Major components were alkylated naphthalenes and PAHs, representative of the light ends of petroleum. The polar fraction contained 61.6 ug/l of two aliphatic alcohols and two C3-quinolines. No compounds were detected in the acid extract. No halogenated compounds were detected by the HECD in the B/N aromatic extract.

The sediment aromatic fraction contained 125 compounds at a total concentration of 15,900 ug/kg. PAHs and naphthalene derivatives predominated. The polar fraction contained carbazole and two benzocarbazole isomers at a concentration of 109 ug/kg. No halogenated compounds were detected by the HECD in the aromatic fraction of the sediment sample. The sediment itself was coarse and contained 92% sand.

Sewells Point Naval Complex-Outfall 052

The Sewells Point Naval Complex is located on Willoughby Bay which adjoins the James River in Norfolk. The effluent received consisted of cooling water, stormwater and avionics shop waste. This effluent was essentially devoid of contaminants in the fractions examined. The B/N aromatic fraction was examined by GC/HECD.

The sediment aromatic fraction contained 78 compounds at a concentration of 1030 ug/kg. Constituents were generally higher molecular weight PAHs. The low molecular weight compounds, e.g. the naphthalenes, were absent. Low concentrations of nonylphenols and benzocarbazoles were detected in the polar fraction. Only 2.7 ug/kg of halogenated compounds were detected in the aromatic fraction of the sediments. These were tentatively identified by their HRI as PCBs and DDD. The sediment was 94% sand.

Indigenous clams (Mercenaria mercenaria) were collected near the outfall. The aromatic fraction contained 14 compounds at a cumulative concentration of 315 ug/kg. PAHs dominated. No anthropogenic compounds were detected in the polar fraction. Four PCB congeners were reported at a total concentration of 14.0 ug/kg by the HECD/HRI analysis.

Sewells Point Naval Complex-Outfall 64

This effluent was reported to be derived from operations similar to those at Outfall 052. The B/N aromatic contained 64 compounds at a concentration of 16.1 ug/l. Naphthalene derivatives and higher molecular weight PAHs were detected. An unresolved complex mixture was observed in the chromatogram. No compounds were detected in the polar fraction. Cresol and several aliphatic acids were reported to be present at a concentration of 9.8 ug/l in the acid extract. No halogenated compounds were detected in the B/N aromatic fraction.

The aromatic fraction of the sediments contained only 20 compounds at a concentration of 474 ug/kg. This constituted the lowest level observed in the sediments examined in the present study. The polar fraction contained 141 ug/kg. Nonylphenols and related compounds were the major species observed. Carbazole and benzocarbazoles were also detected at a total concentration of 10 ug/kg. The GC/HECD/HRI analysis reported the presence of PCBs, chlordanes, DDD and DDE at a concentration of 10.6 ug/kg. The sediment collected was coarse and consisted of 96% sand.

Sewells Point Naval Complex-Outfall 066

The effluent at Outfall 066 was reportedly derived from cooling water, stormwater and process wastewater. All three Sewells Point outfalls were within several hundred yards of each other. Eighteen compounds were reported at a total concentration of 15.5 ug/l in the B/N aromatic fraction. Major components were naphthalene derivatives and higher molecular weight PAHs. The B/N polar fraction contained 8.8 ug/l. An alkyl phenol was the major component present. Cresol and an alkylbenzoic acid were reported present in the acid extract at 4.1 ug/l. No halogenated compounds were detected in the B/N aromatic fraction of the effluent.

Ninety-nine compounds, at a concentration of 170,000 ug/kg were detected in the aromatic fraction of the sediment. This concentration is more than two orders of magnitude more than that reported at SN52 or SN64. PAHs were major constituents. PCBs were also detected by GC/MS and GC/FID at a concentration of 3400 ug/kg. The polar fraction contained significant numbers of compounds. Twenty-seven compounds were reported present at a concentration of 2960 ug/kg. Included in this total were nonylphenols, alkylated carbazoles and benzocarbazoles, and several azaarenes. As previously noted, the aromatic fraction of the sediment contained PCBs. The concentration of PCBs was estimated at 4200 ug/kg by the HECD analysis. In addition to the PCBs, a mixture of PCTs were also detected. This PCT mixture consisted of a highly chlorinated series, similar to Aroclor 5460. The concentration of these was determined to be 19,300 ug/kg after methodology modifications. The presence of the PCBs and PCTs may be linked to the avionics work that has occurred near this site. The sediment sample itself was coarse in composition. It consisted of 65% sand and 16% gravel.

Indigenous oysters (C. virginica) were available at this site. Forty-four compounds were detected in the aromatic fraction at a concentration of 1750 ug/kg. Six PCB congeners were detected by GC/MS and quantitated at 210 ug/kg by GC/FID. The remaining compounds consisted of 19 PAHs and 19 unidentified compounds. An unresolved complex mixture was observed in the chromatogram of the aromatic fraction. No anthropogenic compounds were present in the polar fraction. The GC/HECD analysis of the tissue detected the presence of 394 ug/kg of halogenated compounds. Twenty PCB congeners, at a cumulative concentration of 340 ug/kg, were identified by the HRI system. Chlordane, nonachlor, DDE and DDD were also found at a total concentration of about 46 ug/kg. Only minor peaks eluted at retention times similar to those exhibited by Aroclor 5460 in the oyster extracts.

Union Carbide Corporation-Linde Division

The Union Carbide Corporation operates a facility which discharges to Wythe Creek. This creek then enters Tide Mill Creek, which in turn flows into the Back River. The plant produces industrial gases. The effluent sample analyzed was derived from an oil/water separator. The facility is near the Langley Research Center. The B/N aromatic fraction of the effluent contained 38 compounds at a concentration of 25.6 ug/l. PAHs exhibiting a range of boiling points were observed. Only 1.0 ug/l of material was detected by GC/FID in the B/N polar fraction. The acid extract contained two tolyltriazole isomers at a concentration of 6230 ug/l. These compounds are common in industrial corrosion inhibitors, such as that added to cooling water used at the Union Carbide plant. The concentration determined for the UC effluent was the highest of any of the acid extracts examined in this study. Only 0.2 ug/l of halogenated compounds were detected in the B/N fraction by the HECD.

The sediment sample was collected from a ditch at the rear of the fenced plantsite and consisted of similar percentages of clay, silt and sand. The aromatic fraction contained 109 compounds at a concentration of 8980 ug/kg. The major components identified were PAHs. The chromatogram of the sediment aromatic fraction exhibited an unresolved complex mixture. The polar fraction contained a number of nonylphenols and related compounds, as well as two benzocarbazole isomers. The total concentration of compounds in this fraction was estimated at 2060 ug/kg. The major component present had a mass spectrum similar to dimethylphenanthroline. This compound is also known as neocuproine. This compound is reported to be used in the spectrophotometric determination of copper (Winholz et al. 1983). It was present at a concentration of about 1400 ug/kg. The HECD reported the presence of 13.0 ug/kg of halogenated compounds. Chlordanes and nonachlor were identified by HRI.

Virginia Power Possum Point-Outfall 005

The Virginia Power Possum Point facility discharges to Quantico Creek, which subsequently empties into the Potomac. The plant is involved in the commercial generation of electrical power. The effluent sampled was derived from an ash pond. The B/N and acid extracts of the effluent contained insignificant amounts of material. No halogenated compounds were detected.

The sediment aromatic fraction contained 72 compounds at a concentration of 2090 ug/kg. Small amounts of naphthalene derivatives were present, in addition to larger concentrations of higher molecular weight PAHs. The polar fraction contained carbazole and three benzocarbazole isomers at a total concentration of 13 ug/kg. Only 5.0 ug/kg of total halogenated material, identified as DDD, DDE and PCBs by retention indices, were detected by the GC/HECD in the aromatic fraction. The sediment consisted of 73% sand.

Virginia Power Yorktown-Outfall 001

The Virginia Power Yorktown facility discharges to the York River. The outfall examined was reported to be derived from a condenser cooling canal. About 0.7 ug/1 of PAHs were detected in the B/N aromatic fraction. No compounds were detected by GC/FID in the B/N polar or acid extracts. The GC/HECD analysis did not detect the presence of any halogenated compounds in the B/N aromatic fraction of the effluent.

The aromatic fraction of the sediment extract contained 143 compounds. However, the total concentration of these was only 1090 ug/kg. PAHs and alkylnaphthalenes predominated. No compounds were detected in the polar fraction. About 0.5 ug/kg of halogenated compounds were detected by the HECD analysis of the aromatic fraction. The sediment collected was coarse and consisted of 78% sand.

Discussion

Several types of facilities were examined during the 1987-1988 biennium including: sewage treatment plants (6); paper companies (2); creosoting operations (2); oil refineries and storage facilities (2); military reservations and federal research installations (8); civilian ship building and repair operations (6); metal products and compressed gas producers (2); and electrical power generaters (2). Effluents from these sources were derived from a variety of sources such as oil/water separators, cooling and process water, treated sewage, floor drainage and surface runoff.

Effluents from sewage treatment facilities generally contained low concentrations of chromatographable material. Unlike most effluents, the major components were observed in the acid fractions and consisted of aliphatic acids and alcohols. These compounds are probably related to the bacterial oxidation of wastes, are relatively nontoxic and exhibit a low bioaccumulation tendency. The effluent sample from Pinner's Point STP contained approximately an order of magnitude more extractable material than the other five STPs examined. The Pinner's Point facility is a primary treatment plant (C. Lunsford, VWCB, personal communication). The sediment collected near the PP outfall exhibited high concentrations of anthropogenic material. However, PP is located on the Elizabeth River, major sections of which have been heavily contaminated by the resident heavy industry. Sediments from the vicinity of the Fredericksburg STP and Hampton Roads Sewerage District York River POTW outfalls possessed relatively low burdens of anthropogenic compounds, approximately 1000 ug/kg. The Lorton and Lower Potomac STP sediment burdens were relatively low, but exhibited considerable polar fraction contamination. The major constituents were nonylphenols. Alexandria STP exhibited intermediate contamination, most of which was again due to polar compounds. Nonyl phenols, derived from surfactants (Giger et al. 1984) were the major contributors. McLeese et al. (1981) reported LC50 values for shrimp and salmon of 300 and 190 ug/l in water, respectively. Considering the toxicity of these compounds and their presence at high concentrations, their environmental significance merits additional attention.

Two paper company facilities, Chesapeake Corporation (West Point) and James River Paper Company (Richmond), were examined. Paper mills have been observed to discharge toxic materials to the environment (Oikari and Nakari 1982). The effluent from CC contained significant levels of material in all fractions. Several chlorinated compounds were detected in the B/N extract. These compounds were probably formed during the pulp bleaching process (Carlberg et al. 1987). In light of the heavy contribution of material from this facility to the Pamunkey and York rivers, a more detailed examination of the effluent is warranted. The JP effluent sample received was relatively low in contaminants. Sediments from both sites contained intermediate concentrations of extractable material. Neighboring Richmond industries may have contributed to the burden of PAHs observed in the sediments near JP. The CC sediment contained significant amounts of steroidal material, probably derived from the mill itself. In addition to the inherent chemical toxicity of the waste, deleterious effects may also be expressed via a reduction in the ambient oxygen level of the receiving stream by virtue of the waste's high biological oxygen demand.

The Amoco Yorktown (AY) and Amerada Hess Corporation (AHC) facilities examined are involved in various facets of the petroleum industry. AY effluent contained minor levels of contamination. The water sample from AHC contained significant concentrations of petroleum hydrocarbons. Sediments from the vicinity of AHC, located in the Elizabeth River upstream from the major shipyards, were heavily contaminated with anthropogenic materials. An unsuccessful attempt was made to dredge for shellfish at this location, the sediment retrieved contained a heavy layer of oil. AY sediments contained intermediate levels of aromatics, indicating contamination of the environment. Shellfish obtained near AY possessed some PAH contamination.

Effluent from the two power generating facilities examined, Virginia Power Yorktown and Possum Point, exhibited low level contamination. Sediments from these locales contained modest amounts of anthropogenics.

Atlantic Wood and L.A. Clarke and Sons, creosoting operations, are major contributors of PAHs to the environment. The influence of these type of facilities has been noted previously (Bieri et al. 1986; Merrill and Wade 1985). Borthwick and Patrick (1982) reported a LC50 value for marine-grade creosote of 18 ug/l for mysids. AW is located on the Elizabeth River, while LAC is located near Fredericksburg. Significant concentrations of aromatics were detected in the effluents. The sediment samples collected from these sites were the most contaminated examined in the present study. Not only were PAHs present at high concentrations, but also heterocyclic compounds, e.g. carbazoles, which exhibit greater mobility in the aquatic milieu. Data concerning the distribution of these type of compounds in the marine environment is limited (Pereira et al. 1987; Furlong and Carpenter 1982).

Effluents from five outfalls associated with US Navy installations were examined. The Dahlgren Weapons Laboratory (Potomac River Basin) effluent and sediment contained minimal contamination. The Norfolk Naval Shipyard effluent exhibited moderate levels of pollutants. The sediment at this location was heavily laden with PAHs, but is located in an area of the Elizabeth River which is ubiquitously contaminated with this type of compound (Bieri et al. 1986). Three outfalls at the Sewells Point Naval Complex were also sampled. Moderate concentrations of anthropogenics were detected in the SN64 and SN66 effluents. Sediments at SN52 and SN64 contained low levels of contamination. SN66, however, was heavily impacted by PAHs. In addition, an unusual suite of chemicals, PCTs, were detected. The mixture observed resembled that of Aroclor 5460, a heavily chlorinated formulation. The retention times of these compounds exceeded that of decachlorobiphenyl, the final HRI standard. Therefore, no retention indices were generated. The length of the chromatographic run had to be extended to elute all PCT congeners. The formulation was identified by GC/HECD retention pattern and negative chemical ionization mass spectrometry (Greaves and Hale 1988). The concentration of this material was 19,300 ug/kg. Information on the distribution and effects of these compounds in the aquatic environment is virtually nonexistent. The concentration detected at SN66 represents one of the highest levels reported in either the terrestrial or aquatic environments. A review article by Jensen and Jorgensen (1983) states that the total production of PCTs from 1959-1972 was about 50,000 metric tons. The sole US producer was Monsanto. Manufacture of PCTs in the US ceased in 1972, although some references claim production in the US continued for several years thereafter (e.g. Clement Associates, Inc. 1977). PCTs were imported into the US after production by Monsanto was reported to have ceased (Jensen and Jorgensen 1983). PCTs have been used in plasticizers, hydraulic fluids, paints, sealants, fire retardants and waxes in the investment casting industry. PCTs have also been used in electrical equipment. The SN outfalls have been reported to drain avionics workshops.

Chemically, PCTs resemble PCBs. Therefore, it is expected that they will behave toxicologically in a similar manner. Reported effects have included hyperplasia, dysplasia and hepatocellular carcinomas (Jensen and Jorgensen 1983). The US EPA has not enacted specific regulations banning the use of PCTs (T. O'Bryan, US EPA, personal communication), although they may have been effectively regulated by the fact that most PCT formulations were contaminated by regulated PCBs. Shellfish were collected by VIMS in the vicinity of SN66. Although PCBs were detected in this sample, the concentration of PCTs was very low. Aroclor 5460 was detected at low concentrations (less than one ppm) in sediment samples collected at several shipyards (NB, CS, MM016, and MN17), military installations (SN052, SN064), STPs (PP, AL) and a paper company (JP).

Two outfalls from the NASA Langley facility were examined. LA004 was heavily contaminated by petroleum hydrocarbons. The source of this material may be infiltration of spilled fuel into the effluent, as it passes through the adjoining Air Force facility. The compounds detected consisted predominately of light aromatics. Shellfish collected in the Southwest Branch of the Back River exhibited relatively low bioaccumulation of these compounds. However, they did exhibit high concentrations of PCTs. The congener distribution matched that of Aroclor 5432. No conclusive reports of this PCT formulation being detected in the aquatic environment have been uncovered in the literature. Only low concentrations of halogenated compounds, identified as PCBs by their HRI, were present in the sediments at LA004. A second outfall, LA009 located on Tabbs Creek, was also examined. The effluent contained 16 ug/l of diphenyl ether. NASA Langley (V.W. Wessel, personal communication) has been unable to account for the presence of this compound in the effluent. Sediment collected near the outfall contained high concentrations of diphenyl ether, PAHs, nonylphenols and PCTs. The PCTs detected (25,600 ug/kg) were similar to those observed in the shellfish collected from the Southwest Branch. Thus, either the PCTs are quite mobile or an additional source(s) of these compounds is present in the vicinity. NASA has not been able to account for the presence of the PCTs at LA009.

An outfall on the Quantico Marine Corps Base was also examined. The STP effluent contained low concentrations of aromatic compounds. However, elevated levels of PAHs and DDT derivatives were detected in the sediment. Shellfish collected from the vicinity also exhibited elevated concentrations of DDT metabolites.

Six civilian shipyards were examined. Effluent from Colonna's Shipyard contained high levels of petroleum derived polar and nonpolar aromatics. Two Metro Machine Corporation effluent samples were collected and analyzed. One of these, MM016 derived from an oil/water separator, was heavily contaminated with petroleum constituents. In addition nonylphenols, perhaps added to the separator in the form of a de-emulsifier, were detected at a concentration exceeding the acute LC50 of this material. Modest levels of aromatics were detected in the Norfolk Shipbuilding and Drydock Corporation-Berkley effluent. NB, CS and the MM outfalls are located on the Elizabeth River. As mentioned, the sediments of the Elizabeth are, as a rule, heavily contaminated with PAHs. The two NN outfalls, located on the James River, were observed to contain modest concentrations of aromatics. The associated sediments exhibited elevated levels of PAHs.

The effluent from the Reynolds Metal Company-South Plant, an aluminum products manufacturer located on the James River in Richmond, contained a moderate amount of nonpolar and polar compounds. The majority of the compounds were petroleum related. James River sediments, in the Richmond locale, contained moderate levels of PAH contamination. Other local industries in the area probably contributed to the sediment burdens of the river.

The Union Carbide Corporation-Linde Division facility examined produces specialty gases. High concentrations of a common anti-corrosion additive and modest amounts of PAHs were detected in its effluent. In addition neocuproine, a compound used in the assay of aqueous copper levels was tentatively identified at high levels in the sediment near the discharge point. UC currently employs an in-situ copper electrode to assay cooling water corrosivity (B.C. Bean Jr., personal communication).

In regards to the analytical procedures employed, several improvements have been made. For example, internal standards for each of the various polarity fractions were introduced. The analysis of the acid fraction was streamlined. Analysis of extracts for halogenated compounds using a selective detector (HECD) was initiated. A more complete QA evaluation of the methodology was performed. Some additional work would, however, be valuable including: a substitute internal standard for decachlorobiphenyl should be evaluated, due to the behavior of this compound during HPLC fractionation; an aromatic retention index system for the polar compounds should be established; an evaluation of continuous liquid/liquid extractors should be made, since serious emulsions were often a problem during separatory funnel extraction of the effluent samples; an investigation of the effectiveness of an initial methanol extraction of the sediment to remove water and polar compounds, in place of lyophilization, should be undertaken (this would reduce the capital costs associated with the analysis and perhaps increase recoveries).

Monitoring of effluent streams has determined that several industries are presently disposing of significant amounts of toxic chemicals directly to the aquatic environment. Since sediments act as repositories of these chemicals, the analysis of this matrix allowed a time averaged measure of a facility's waste disposal practices. The chemical analysis of all outfalls is not feasible in a program such as that undertaken. Sediments not only provide a time averaged measure of the depositional history at a site, but also are capable of incorporating anthropogenics from nearby outfalls as well. A good association between contaminated effluents and sediments was observed, as shown in Table 7. Sediments act as a source of pollutants, in addition to functioning as a sink. Therefore, determination of the status of the sediments themselves, irregardless of any current waste streams, is of ecological significance. Difficulty was encountered obtaining shellfish from the majority of the stations selected (see Table 7), due to undesireable substrate type in concert with the high concentrations of pollutants present at many sites. This limited the applicability of the biological indicator to some degree. However, some successes were noted, e.g. the PCTs in LA004 shellfish.

The outfall categories exhibiting the most contaminated effluents included creosoting operations, shipyards and federal facilities. Petroleum hydrocarbons and PAHs were major components. Low levels of PAHs are ubiquitous in the sediments. Locales remote from significant industrialization generally contained less than 2000 ug/kg (dry weight basis). Impacted sediments contained up to 835,000 ug/kg of PAHs. PCTs were detected at high concentrations at locations in the Back River and Willoughby Bay. Despite the probable environmental consequences of PCTs, they have been largely overlooked by investigators. Nonylphenols, cumylphenols, diphenyl ether and nitrogen heterocyclics (e.g. carbazoles) were detected at high concentrations at several locations. Additional research is needed to ascertain the environmental significance of these compounds.

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