INVESTIGATIONS ON POLLUTANT ORGANIC CHEMICAL FLUXES IN THE HUDSON RARITAN ESTUARINE AND NEW YORK BIGHT COASTAL SYSTEMS

- FINAL REPORT -

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ABSTRACT

A detailed investigation of organic pollutant (polynuclear aromatic hydrocarbon-PAH, polychlorinated biphenyl-PCB and coprostanol - a sewage indicator) concentration, composition and distribution of suspended particulate matter in the Hudson River/Lower Bay/New York Bight system has been undertaken. Additionally, dredge spoil and sewage sludge waste deposits from the Bight have been size fractionated and analyzed in detail. Fused silica capillary gas chromatography and gas chromatographic mass spectrometry were employed for PAH, PCB and coprostanol determinations.

Key estuarine/shelf and benthic/water column organic chemistry flux mechanisms were revealed including Hudson River sediment resuspension and bottom water transport within the estuary, sewage effluent input to harbor/river surface waters followed by seaward transport, landward transport of resuspended Bight sediment, resuspension of PAH-rich dredge spoil and possible transport of sewage-associated organics down the Hudson Valley.

In addition, key sediment particle size/organic associations were revealed with dredge spoils (rich in pyrogenic PAH) and sewage sludge (rich in petroleum PAH) behaving dissimilarly with respect to these size/PAH/PCB associations.

PAH, PCB and coprostanol are decoupled in the water column particulates, probably due to differential solubility behavior of the three compound classes.

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David Fiest - Sampling design, field sampling, capillary GC (PCB).

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SECTION ONE

INTRODUCTION

All major population centers located adjacent to the coastal ocean will substantially influence the chemistry of adjacent marine waters and marine sediments by virtue of pollutant fluxes into the system. The mechanisms of pollutant introduction are numerous. In the case of the estuarine and continental shelf system of the Hudson/Raritan Rivers and New York Bight (Figures 1,2,3) the inputs can be broadly defined as continuous (i.e., riverine inputs) and intermittent (i.e., ocean dumping events). Continuous riverine inputs which couple to the shelf system by virtue of fluxes of pollutants through the Hudson River Estuary, actually are comprised of a myriad of point sources including sewage treatment plant effluents, resuspended contaminated sediments, stormwater runoff and inputs from shipping activities (Atwood et al., 1979; O'Conner and Stanford, 1979). Ocean dumping in the New York Bight results in the input of organic pollutants mainly from the disposal of contaminated dredge spoils from the outer and inner harbors and sewage sludges from various treatment plants in the metropolitan New York area.

Of the host of organic compounds introduced into the system through both riverine fluxes and ocean dumping events, the polynuclear aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) compound classes are of primary concern due to their well-documented toxic and carcinogenic properties. These classes along with the chlorinated pesticides are considered "major perceived

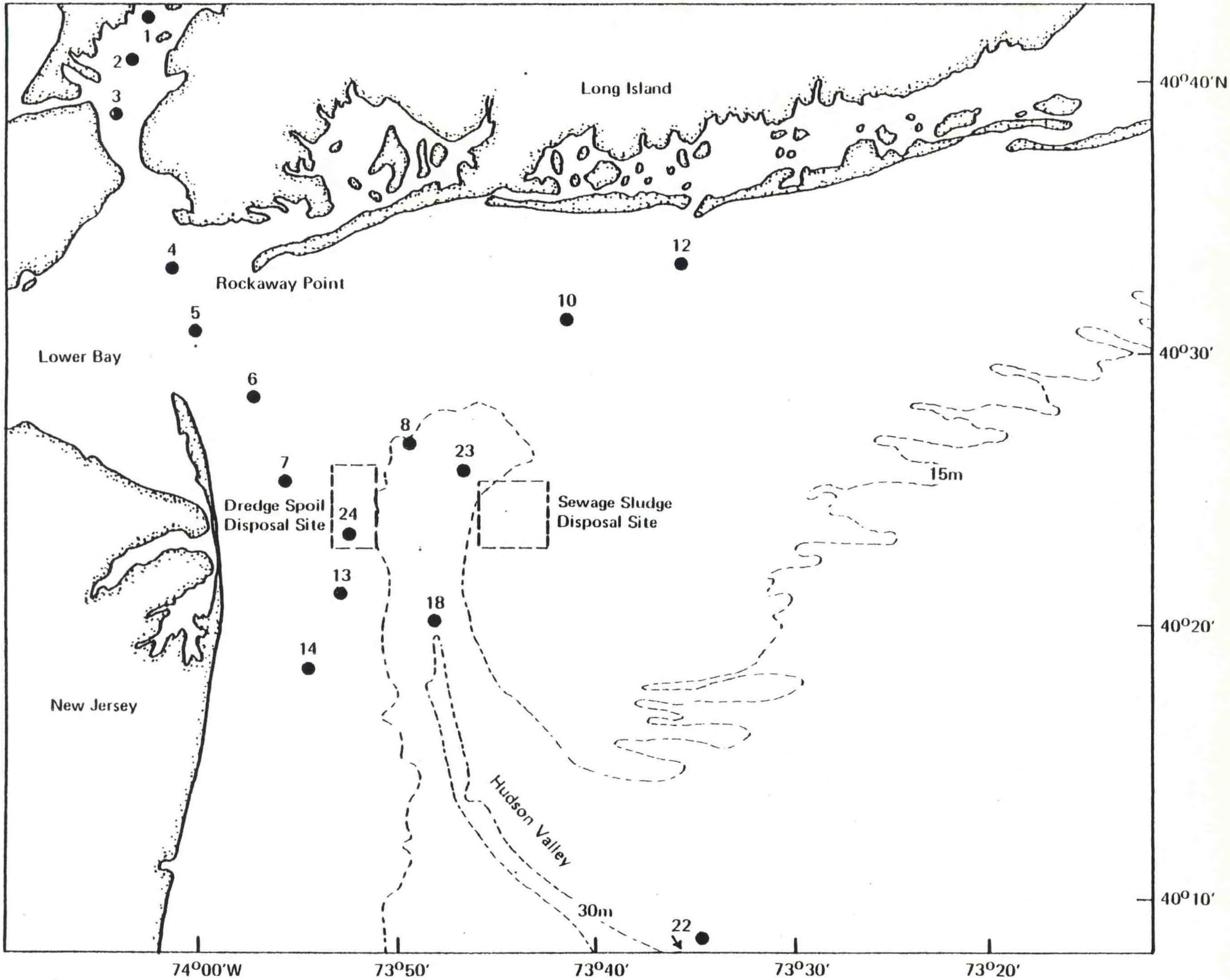


Figure 1. Location of Sampling Stations.

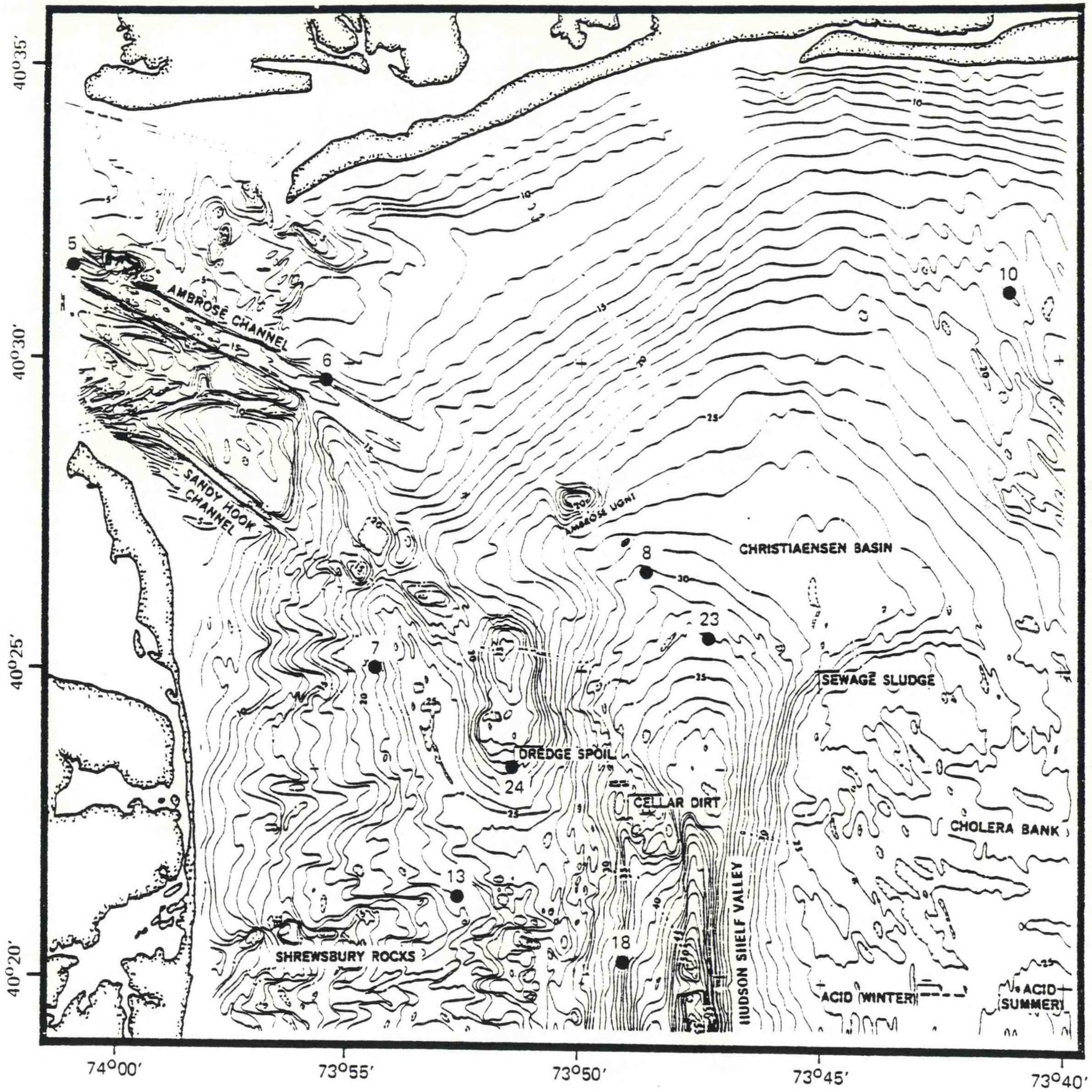


Figure 2. Detail of Bottom Topography in Heart of New York Bight Apex Sampling Region (Adapted from Freeland and Swift, 1978).

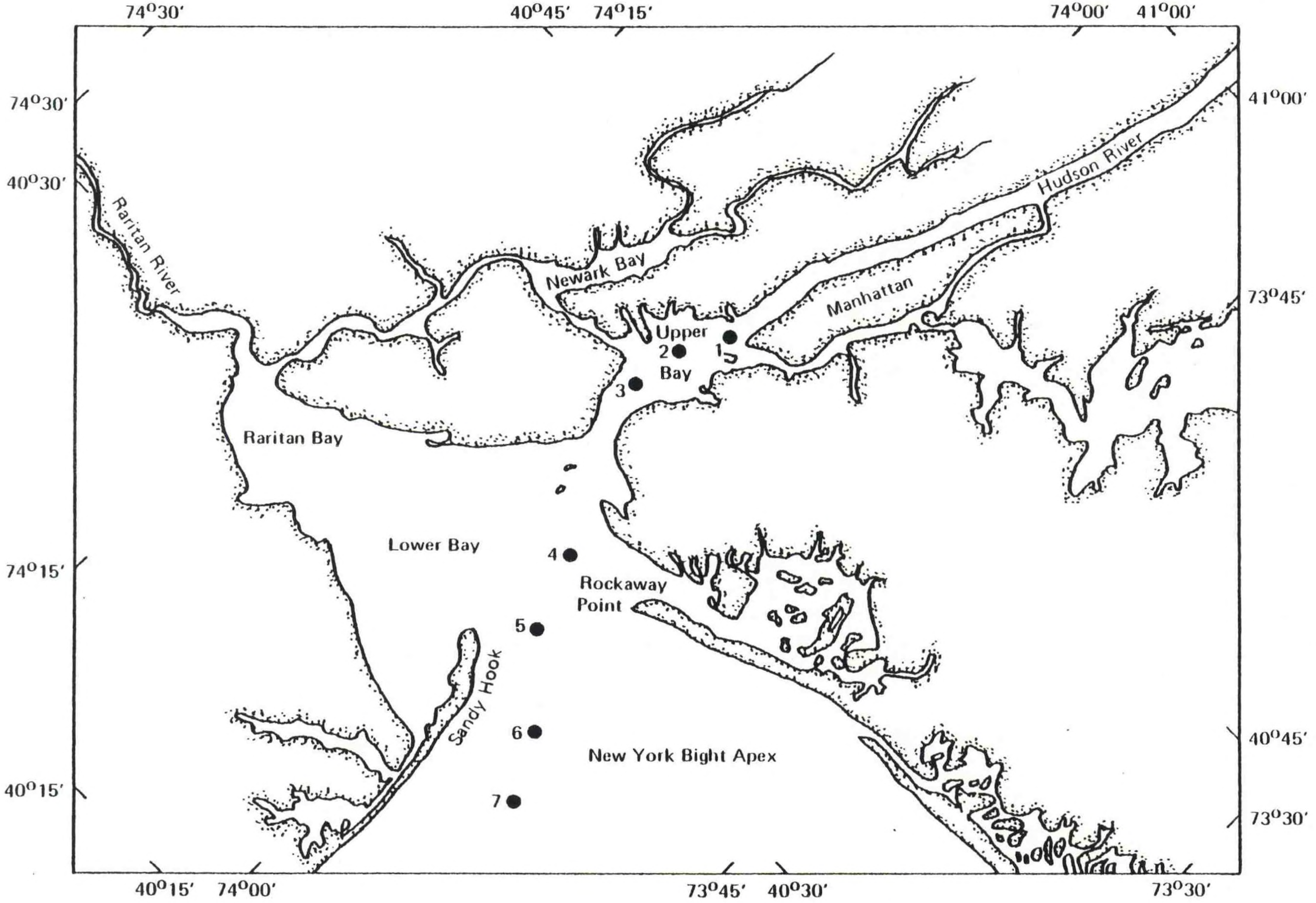


Figure 3. Detail of Sampling Stations within Bay/River System.

threats" to the "health" of the environment (O'Conner and Stanford, 1979) and have been the focus of numerous investigations in recent years concerning ambient levels of these compounds in Bight sediments (West and Hatcher, 1980; Boehm, 1980a; Laflamme and Hites, 1978; Farrington and Tripp, 1977; MacLeod et al., 1981), levels in sediments and suspended matter in the Hudson River (Bopp et al., 1981), levels in the Raritan Bay sediments and biota (Stainken and Rollwagen, 1979) and levels in biota from the Bight (Boehm 1980b; MacLeod et al., 1981; O'Connor, et al. 1981).

Several recent studies have addressed the short-term chemical perturbations in the water column during and immediately after sewage sludge disposal (Hatcher et al., 1978) and dredge spoil disposal (Boehm and Fiest, 1980) events. During dumping events physical and chemical fractionation of the dumped materials profoundly affect the seawater dissolved and particulate fraction chemistries. The dissolved plume remains above the thermocline (Hatcher et al., 1978) where it becomes subjected to dilution through mixing and advection. The particulate plumes rapidly penetrate the thermoclines (Hatcher et al., 1978; Boehm and Fiest, 1980) with the residual particulate plumes remaining detectable through PCB, PAH and coprostanol (a fecal steriod; Hatcher and McGillivary, 1979) measurements after 6 hours.

The present research investigation focuses on several questions relating to an assessment of the inputs of PAH and PCB compounds to New York Bight coastal waters.

1. What are the levels and detailed chemical nature of PAH and PCB compounds in suspended matter in the estuary?

2. What are the levels, areal distributions, and detailed chemical nature of PAH and PCB compounds in New York Bight surface, intermediate and bottom waters?

3. What is the relative importance of the waste deposits (spoils and sludge) as sources of PCB and PAH to the overlying waters through resuspension vis-a-vis estuarine/shelf fluxes of PAH and PCB bearing particulates (i.e., in non-dump situations)?

4. Can a combination of organic pollutant compound parameter measurements relate environmental chemical distributions to source material?

While information exists on the effects of dumping on the water column's organic chemistry, virtually no information pertaining to estuarine/shelf and benthic/water column fluxes of these important pollutants exists. The sampling and analytical designs of this research were geared towards addressing the questions outlined above and towards filling those informational gaps.

SECTION TWO

METHODS

2.1 Sampling

Samples of water column suspended particulates, sediments and sediment cores were obtained on two cruises of the R/V Kelez; KE-70/80-80 (7/28-8/5/80) and RP-28-KE-80 (8/9-8/25/81). Samples of surface sediments from the New York Bight sewage sludge dumpsite were obtained by R. Reid (NOAA/NMFS) on the first cruise. The main sampling activities centered on the latter cruise.

During this cruise a series of water column stations were occupied in the Bight (Figure 1,2) and in the outer and inner New York Harbor (Figure 3). The all-teflon NOAA underway-towed pumping system (UTPS) was used to pump water through a specially designed stainless steel filtration manifold located in the ship's wet laboratory. In-line precombusted (450° C) glass fiber (Gelman A/E, 142 mm diameter) filters were used to filter between 20 and 60 liters of seawater, depending on the suspended matter concentrations and hence when the filter clogged. The pumping rate through the filter was 3-4 liter/min. Samples were taken from surface water and intermediate or near bottom locations at each station (Table 1) for organic constituent studies. Separate samples were processed by scientists from University of Rhode Island for total suspended matter (TSM) measurements.

The sampling plan was designed to obtain suspended organics (1) in the estuary, (2) from a time series (one tidal cycle) at the entrance to the estuary, (3) in the

TABLE 1

DETAILS OF WATER SAMPLING LOCATIONS

STATION	LATITUDE	LONGITUDE	DEPTH (m)	DATE	TIME	APPROXIMATE BOTTOM DEPTH (m)
22	40°06.25'	73°32.95'	3,8,25	8-16-80	--	65
12	40°33.21'	73°35.67'	3	8-20-80	1540	11
10	40°31.24'	73°40.97'	3,12	8-20-80	2030	20
8	40°26.66'	73°48.63'	15,25	8-21-80	1000	30
13	40°21.38'	73°52.80'	5,16	8-21-80	1800	20
14	40°18.72'	73°53.00'	16	8-21-80	1950	23
4	40°34.55'	74°01.63'	3,5	8-22-80	1915 (start)	15
				8-23-80	0730 (finish)	
1	40°42.63'	74°01.63'	3,8	8-23-80	1105	15
2	40°40.97°	74°02.39'	3,8	8-23-80	1130	15
3	40°38.64'	74°03.58'	3	8-23-80	1215	15
5	40°31.55'	74°00.14'	3,14	8-23-80	1340	15
6	40°29.71'	73°55.58'	3,12	8-23-80	1440	16
7	40°25.25'	73°54.73'	3,10	8-23-80	1650	17
13	40°21.99'	73°52.47'	3	8-23-80	2000 (resampling)	21
24	40°23.50'	73°51.52'	3,10	8-24-80	1140	20
18	40°20.32'	73°48.87'	4,18,30	8-24-80	1430	36
23	40°25.94'	73°46.93'	3,28	8-24-80	1615	32

proximity of waste deposit locations in the Bight, and (4) along a series of transects radiating from the entrance to the estuary.

In addition to the particulate water column samples, sediment samples were taken using a Smith-MacIntyre grab sampler or alternatively by divers. Diver-obtained cores from the dredge spoil disposal site (Station 24) (Figure 2) were approximately 1 meter in length.

All samples (filters and sediments) were stored in non-contaminating containers and frozen at -20° C. They were shipped to our laboratories in this condition.

2.2 Analytical Methods

2.2.1 Processing of Filters

As all samples were to be used for PCB, PAH and steroid determinations, a single extraction processing/scheme was utilized to maximize the usefulness of a very small amount of extracted material. The method of choice involved sample extraction and silicic acid fractionation (column chromatography) into three fractions, f_1 (saturated hydrocarbons), f_2 (PAH and PCB) and f_3 (steroids).

Extraction was performed using the method of ambient-temperature shaking (Brown et al., 1980; Boehm et al., 1981) wherein the filter is thawed, cut into strips, and introduced into a screw-to teflon jar (∿250 ml). Distilled methanol is added first to dry (remove water) the filter. The filter/ solvent mixture is shaken for 4 hours. At that time the methanol/ water mixture is decanted and replaced with an azeotropic mixture of methylene chloride and methanol (9:1). Internal quantification standards are added at this point (deuterated phenanthrene, androstane). Extraction/shaking continues for an additional 16 hours at which time the extracts are combined in a separatory funnel, distilled water is added to the extracts and the organic (methylene chloride) phase obtained. The methylene chloride is concentrated, displaced with hexane and fractionated using silicic acid adsorption column chromatography.

2.2.2 Fractionation and Analysis

Saturated hydrocarbon (f_1), aromatic hydrocarbon/PCB (f_2) and polar (f_3) fractions are obtained through elution of the column by hexane (f_1), hexane-methylene chloride (60:40) (f_2), and methanol (f_3) respectively. Polynuclear aromatic hydrocarbons (PAH) from two to five rings were analyzed directly by fused silica glass capillary gas chromatographic mass spectrometry (GC^2/MS) using a Hewlett Packard Model 5985 GC/MS computer system. A 30 meter AA SE-52 fused silica capillary column was used in both GC^2 (glass capillary gas chromatography) and GC^2/MS analyses. The analytical conditions were as follows:

GC^2/MS

temperature program: 40-290° C @ 3° C/minute.
carrier flow: helium at 1 cc/min.
injection port: splitless "B" type, all glass, 250° C.
detection: mass spectrometer.
ionization voltage: 2200 eV.
scan rate: 40-400 amu; 1 scan every 1.5 seconds.

Parent ion (m^+) total ion currents were computer integrated and areas related to the area of the parent ion of the internal standard. Relative response factors were computed using quantitative standard mixtures and these factors were incorporated into the quantitation program. Quantification of aromatic hydrocarbons by GC^2/MS agrees with that obtained by GC^2 to within 20 percent.

F_2 fractions were also analyzed by GC^2 (electron capture detector) for PCB determinations. The technique of Ballschmiter and Zell (1980) was used. A mixed Aroclor standard (1016, 1242, 1248, 1254) (Figure 4) was analyzed by GC^2/MS to determine the number of chlorine substitutions on each resolved component. Subsequently the retention times of these identified compounds were compared to those of each eluting sample peak, definitive PCB isomeric family identifications made (dichloro, trichloro, tetrachloro, pentachloro, hexachloro, heptachloro), areas of each isomeric family summed and quantified relative to an external standard dilution curve of selected Cl_2 to Cl_7 isomers. Response factors were determined for each family for at least two individual compounds and averaged to arrive at a single factor for each isomeric family.

Capillary PCB quantifications based on individual components are more accurate than those based on Aroclor formulations (Ballschmniter and Zell, 1980; Krupcik et al., 1977; Albro et al., 1977; Duinker et al., 1980) and are far more revealing in terms of geochemical relationships.

F_3 (polar) fractions were analyzed for coprostanol and other sterol components using the method of Hatcher and McGillivary (1979). This method involves the silylation of

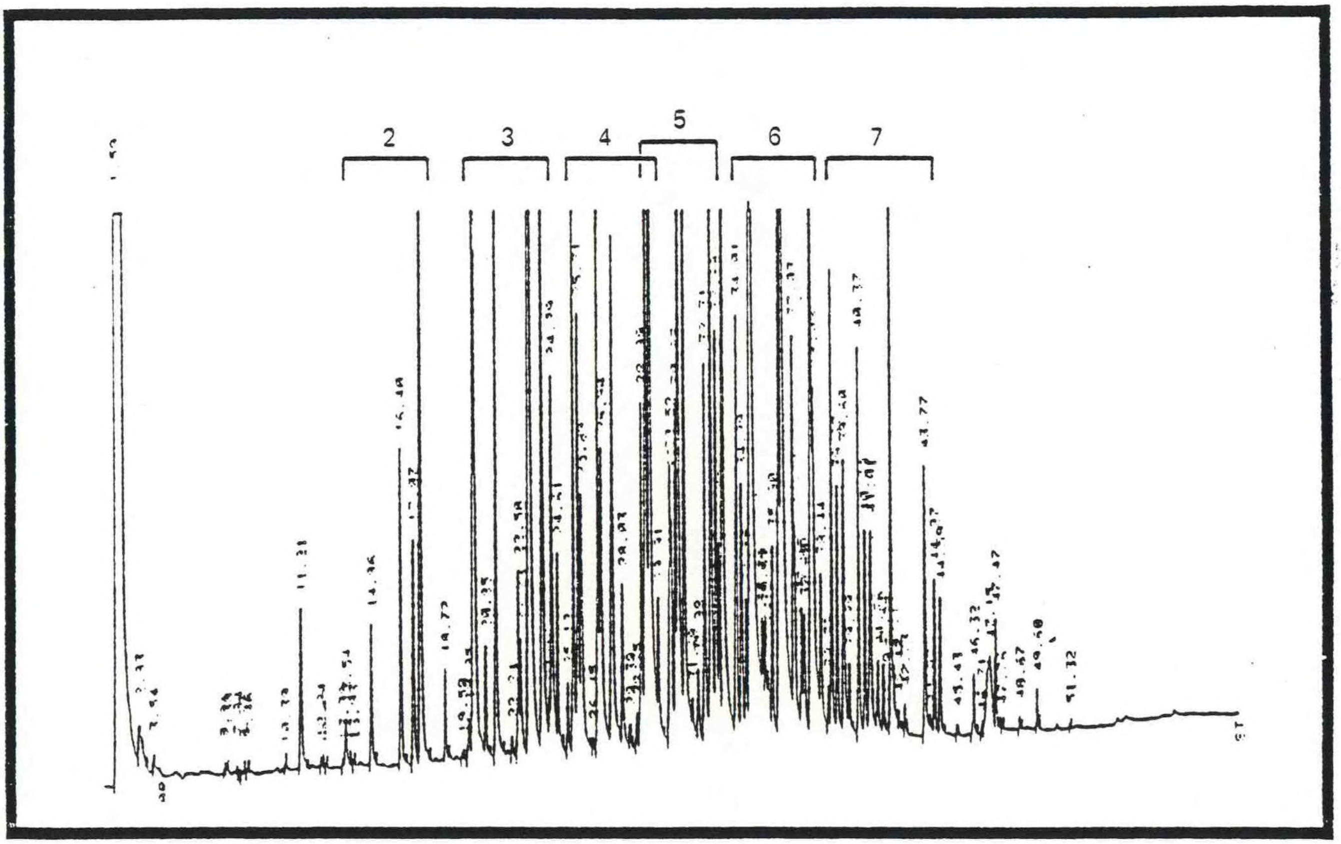


Figure 4. Glass Capillary Trace of Mixed Aroclor (1016, 1242, 1254, 1248) Standard (Numbers refer to number of chlorine atoms).

the dried f_3 eluate using N, O-bis (trimethyl silyl) acetamide in pyridine solution to form the trimethyl (TMS) ethers of the sterol compounds. The TMS ethers are then analyzed by GC^2 (flame ionization detection) and quantified relative to an external standard (cholestane) spiked to the injection solution prior to analysis. The identities of the TMS ethers were made by injecting silyated standard sterols onto the 30 m SE-30-AA fused silica column and by periodic sample coinjection.

2.2.3 Processing of Sediments

Sediments or sediment core fractions were wet sieved to obtain various size fractions for subsequent analysis. The sediment samples were wet sieved (distilled water washing) through a set of sieves, 1 mm, 250 μ and 66 μ mesh sizes. Material coarser than 1 mm was discarded. The sand fraction consisted of a combination of material trapped in the 250 μ and 66 μ sieve. Silt and clay were separated from each other through a combination of settling (silt) and centrifugation and flocculation (NaCl + HCl). The particle size of the clay was assumed to be <5 μ (Thompson and Eglinton, 1978). Each size fraction was weighed, dry weight determined on a small aliquot and extracted separately, using the ambient temperature shaking procedure (Brown et al., 1980; Boehm et al., 1981).

PAH (f_2), PCB (f_2), and steroidal (f_3) fractions were obtained as with the filter extracts and were analyzed by GC^2/MS, GC^2/ECD and GC^2/FID respectively.

SECTION THREE

RESULTS

3.1 Sediment (Waste Deposits) Size Fractions

Important quantitative and compositional differences are revealed when considering size fractions within sedimentary deposits (Thompson and Eglinton, 1978). In the present study significant chemical differences were observed in the (1) gross organic parameters, (2) the PAH levels, (3) PCB levels, and (4) Coprostanol levels in the dredge spoil core and in the sewage sludge deposit. These quantitative and qualitative differences are summarized in Tables 2, 3, and 4 and are discussed in detail below.

3.1.1 Gross Organic Parameters

Included in these categories are total extractable organics, saturated hydrocarbons and aromatic hydrocarbons determined gravimetrically. Within the "aromatic" category are included the individual PAH and PCB levels reported in the next sections. On a dry weight basis the sewage sludge (sum of the size fractions = total, Table 2) material contains over four times as much extractable organic material, seven times as much saturated hydrocarbon material and almost five times as much aromatic material, as does the mud layer (4.5-9.0 cm) of the dredge spoil core. Thus in addition to differences in the organic composition of the sewage sludge and dredge spoil deposits, there are large concentration differences between the two materials as well. However, most relevant to geochemical behavior are the concentrations

TABLE 2

RESULTS OF THE ANALYSIS OF SEDIMENT SIZE FRACTIONS-GROSS PARAMETERS

SAMPLE	SIZE FRACTION	DRY WEIGHT (g)	TOTAL EX-TRACTABLE ORGANICS (ug/g)	TOTAL SATURATED HYDRO-CARBONS (ug/g)	TOTAL AROMATIC HYDRO-CARBONS (ug/g)
Dredge Spoil					
Top (sand layer 0-4.5 cm)	Sand	80.0	76.6	8.5	8.6
	Silt	2.5	5,070	1,110	628
	Total	82.5	227.9	41.9	27.4
Dredge Spoil					
Mud (layer 4.5-9 cm)	Sand	33.5	1,590	348	280
	Silt	6.8	7,180	996	922
	Clay	3.9	10,200	3,410	1,946
	Total	44.2	3,210	718	526
Sewage Sludge					
(0-5 cm)	Sand	7.4	6,130	3,590	1,750
	Silt	0.62	57,300	9,880	4,540
	Clay	0.50	79,500	16,000	11,400
	Total	8.5	14,193	4,787	2,525

TABLE 3

POLYNUCLEAR AROMATIC HYDROCARBONS IN WASTE DEPOSIT SIZE FRACTIONS

	DRY WEIGHT ANALYZED (g)	μg/g							P/A	BA/CH	F/PY	TOTAL PAH CONCENT. OF INDIVIDUAL SIZE FRACTIONS (μg/g)	TOTAL AMOUNT OF PAH IN SIZE FRACTION (μg)	TOTAL PAH CONCENT. OF ENTIRE SAMPLE (μg/g)
		N	F	DBT	P	FPY	BCH	BP						
Sewage Sludge														
Sand	7.4	11.	4.6	4.9	9.5	3.0	.6	1.8	6.1	-	1.01	35.4	261.9	-
Silt	0.6	70	15.0	16.2	21.9	4.7	1.5	1.0	8.2	.82	.90	130.3	78.2	-
Clay	0.5	18.	6.7	17.3	42.2	9.2	4.2	4.9	-	-	.72	102.5	51.3	-
Total	8.5	15.9	5.5	6.4	13.2	3.5	0.9	1.9						47.3
Dredge Spoil (Sand Layer -.0-4.5 cm)														
Sand	80.0	.006	.007	.017	.19	.53	.20	.30	4.7	1.03	1.18	1.25	100.	-
Silt	2.5	.21	.36	1.2	4.0	5.2	2.8	4.2	2.8	.88	.95	18.0	45.	-
Total	82.5	.01	.02	.05	.31	.67	.28	.42						1.8
Dredge (Mud Layer: 4.5-9 cm)														
Sand	33.5	1.5	.86	1.7	4.8	6.9	4.4	5.8	4.4	.91	.94	26.0	871	-
Silt	6.8	2.5	1.3	4.8	5.1	7.0	3.2	4.8	1.9	1.03	.98	28.7	195	-
Clay	3.9	6.0	1.3	2.3	6.8	7.8	3.1	5.4	1.4	1.02	1.08	32.7	127	-
Total	44.2	2.1	1.0	2.2	5.0	7.0	4.1	5.6						27.0

N = Napthalenes (C_o-C_5:m/e 128, 142 156, 170, 184, 198)
F = Fluorenes (C_o-C_3: m/e 166, 180, 194, 208)
DBT = Dibenzothiophenes (C_o-C_4: m/e 198, 212, 226, 240)
P = Phenanthrenes+anthracenes (C_o-C_4: m/e 178, 192, 206, 220, 234)
FPY = Fluoranthenes+pyrenes (C_o-C_2: m/e 202, 216, 220)
BCH = Benzanthracenes+chrysenes (C_o-C_3: m/e 228, 242, 256, 270)
BP = Benzopyrenes+benzofluoranthenes+perylenes (C_o-C_2: m/e 252, 266, 280)
P/A = Phenanthrene/anthracene
F/PY = Fluoranthene/pyrene
BA/CH = Benzanthracene/chrysene

increases, the associated absolute concentrations increase. The association of organic material with fine particles is dramatic. It is these particles that are most easily resuspended in the water column above. For example, in the top (0-4.5 cm) sandy layer of the dredge spoil deposit, ∼70 percent of all the organic material is associated with the 30 percent of fine material. Similarly, in the dredge spoil and sewage sludge mud layers, about 60 percent of the organics are associated with the 15 to 20 percent of fines.

The top (sandy) layer in the dredge spoil core (0-4.5 cm) has important similarities to the sand/silt fractions of the mud layer below with the concentrations of the silt-associated material similar in both layers. However the coarser (> 63 μ) fractions differ dramatically between the two dredge spoil layers, owing probably to two separate dredged material sources for the two core layers.

3.1.2 PAH Compounds

The salient points regarding the PAH concentrations, composition and size fraction dependence in the two waste deposit samples examined are presented in Table 3 and in Figures 5, 6, 7, and 8.

Sewage sludge is "rich" In PAH compounds (total 47.3 μg/g=ppm). This value is naturally much higher than "background" or non-waste deposit values determined in the New York Bight sediments (50-500 ppb; Boehm, 1980a). However, the actual sediment association of the PAH compounds is revealed in Table 3 and in Figure 5 where the PAH distributions in each sediment fraction are detailed.

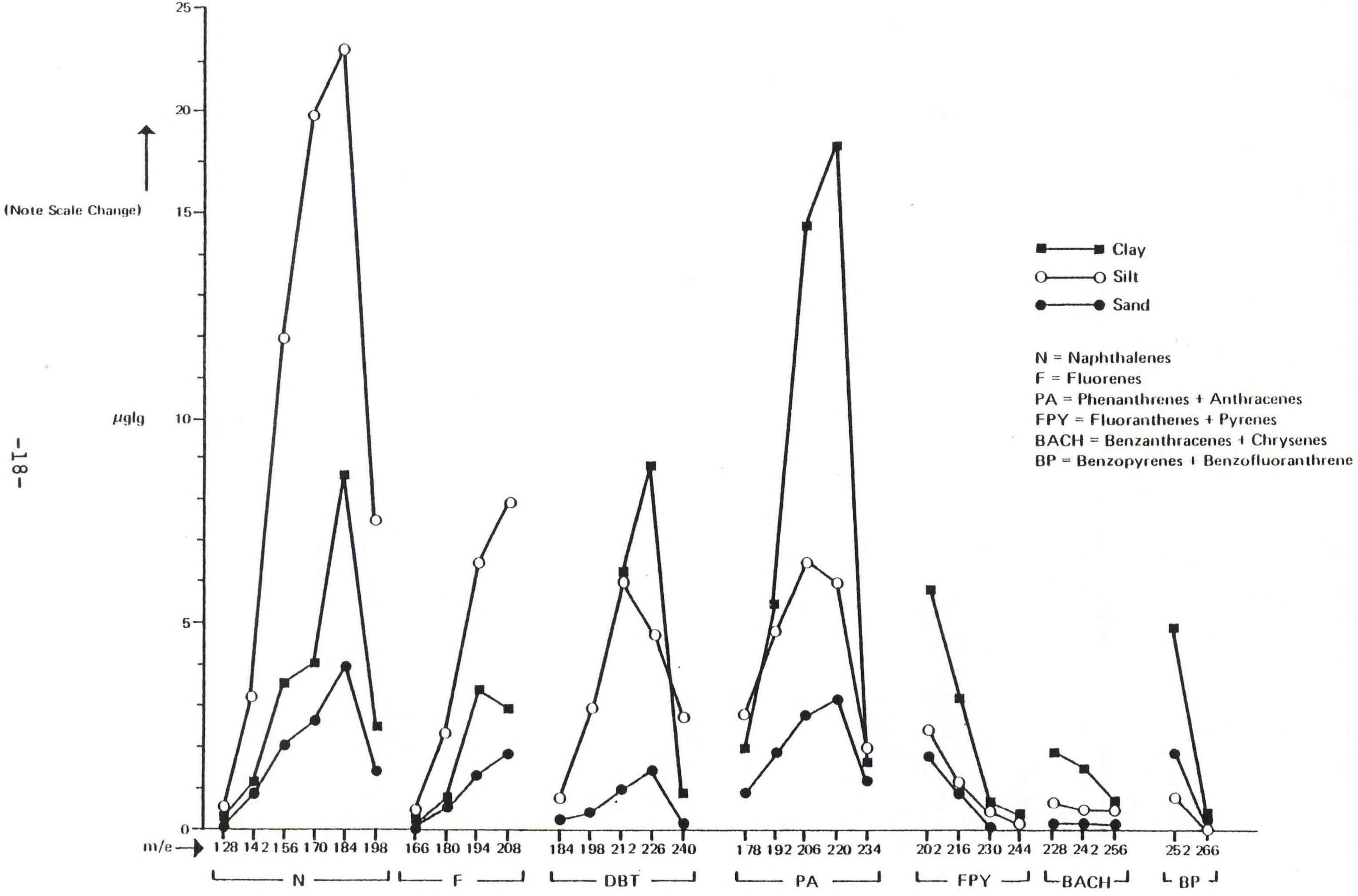


Figure 5. PAH Composition of Size Fractions of Sewage Sludge Waste Deposit.

For the most part, the naphthalene, fluorene and dibenzothiophene homologous compound series are generally attributable petroleum inputs, while the fluoranthene/pyrene benzanthracene/chrysene and benzopyrene series largely originate in pyrogenic combustion of fossil fuels (i.e., the high temperature combustion) (Brown and Weiss, 1978; Farrington, 1980; Lee et al., 1977). Sources of PAH material in marine samples can be generally attributed to either low temperature maturation (i.e., petroleum) or high temperature combustion (i.e., pyrogenic) sources based on the PAH alkyl homologue distribution curves (see Figure 9). These examine the relative content of parent (unsubstituted) PAH and alkyl homologues with a given molecular series (Youngblood and Blumer, 1975; Laflamme and Hites, 1978). The compound series which are detailed in Figures 5, 6, 7, and 8 are generally of two shapes representing the compositon of the parent (unsubstituted) and alkylated homologues. For example, as illustrated in Figure 9 A,B,C,, those series where the parent or unsubstituted compound dominates the homologous series of parent and alkylated PAH compounds are attributable to a pyrogenic source (Youngblood and Blumer, 1975). For those series where the alkylated members of the series dominate (Figure 9 D) the assemblage a low temperature source (i.e., petroleum or coal) is suggested (It is very difficult to attribute a particular pyrogenic assemblage to a particular combustion source (Laflamme and Hites, 1978), but petroleum and combustion sources are distinct). The phenanthrene series is a "swing" series in that compounds from the homologous series are prevalent in both petrogenic and pyrogenic sources. The parent compounds phenanthrene and anthracene are found in petroleum, coal (Tripp et al., 1981) and combustion sources (Lee et al., 1977). Alkylated phenanthrenes and anthracenes are present in both combustion and unburned fossil fuel sources. However, while the

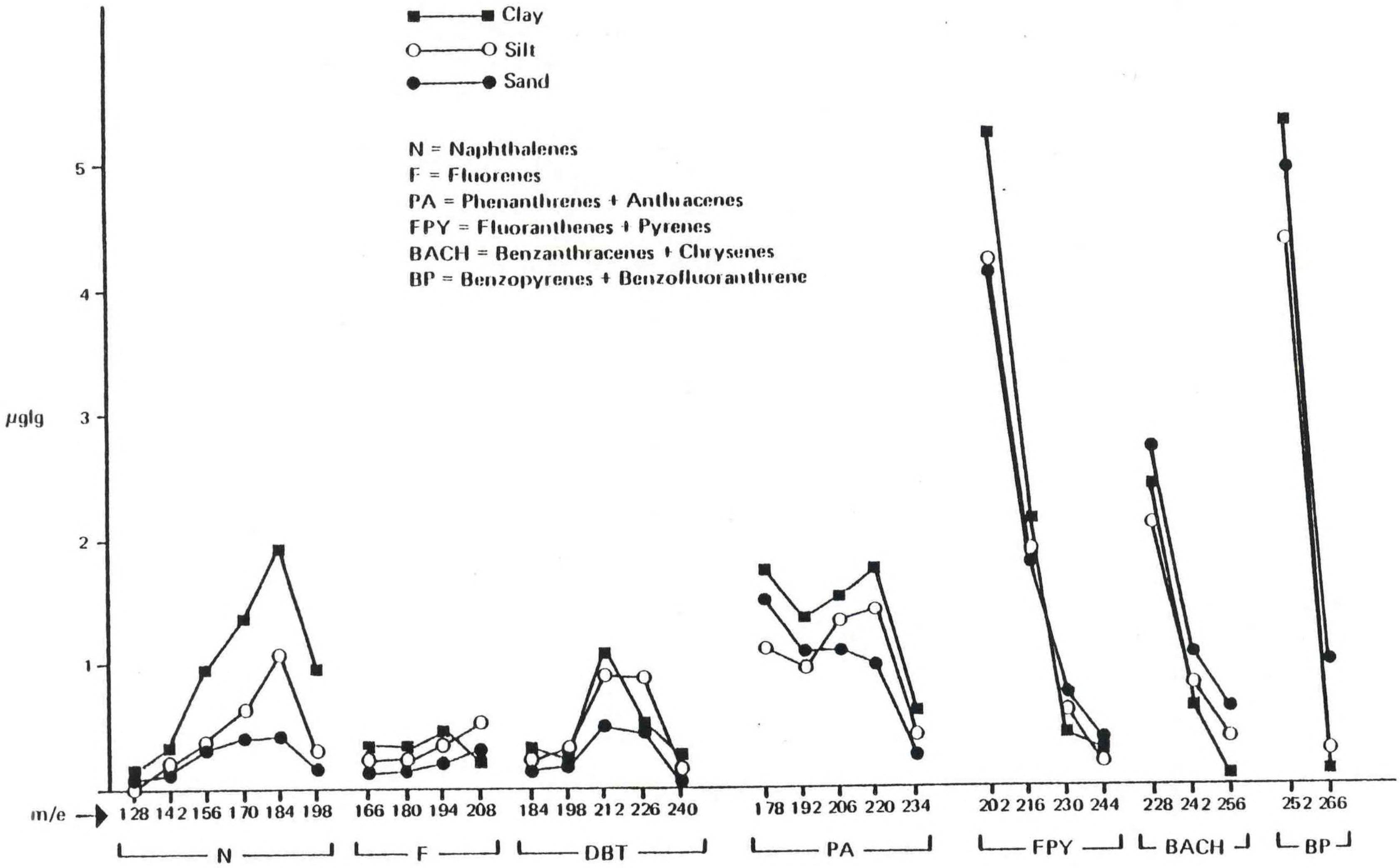


Figure 6. PAH Composition of Size Fractions of Dredge Spoil Core—Mud Layer (4.5—9cm).

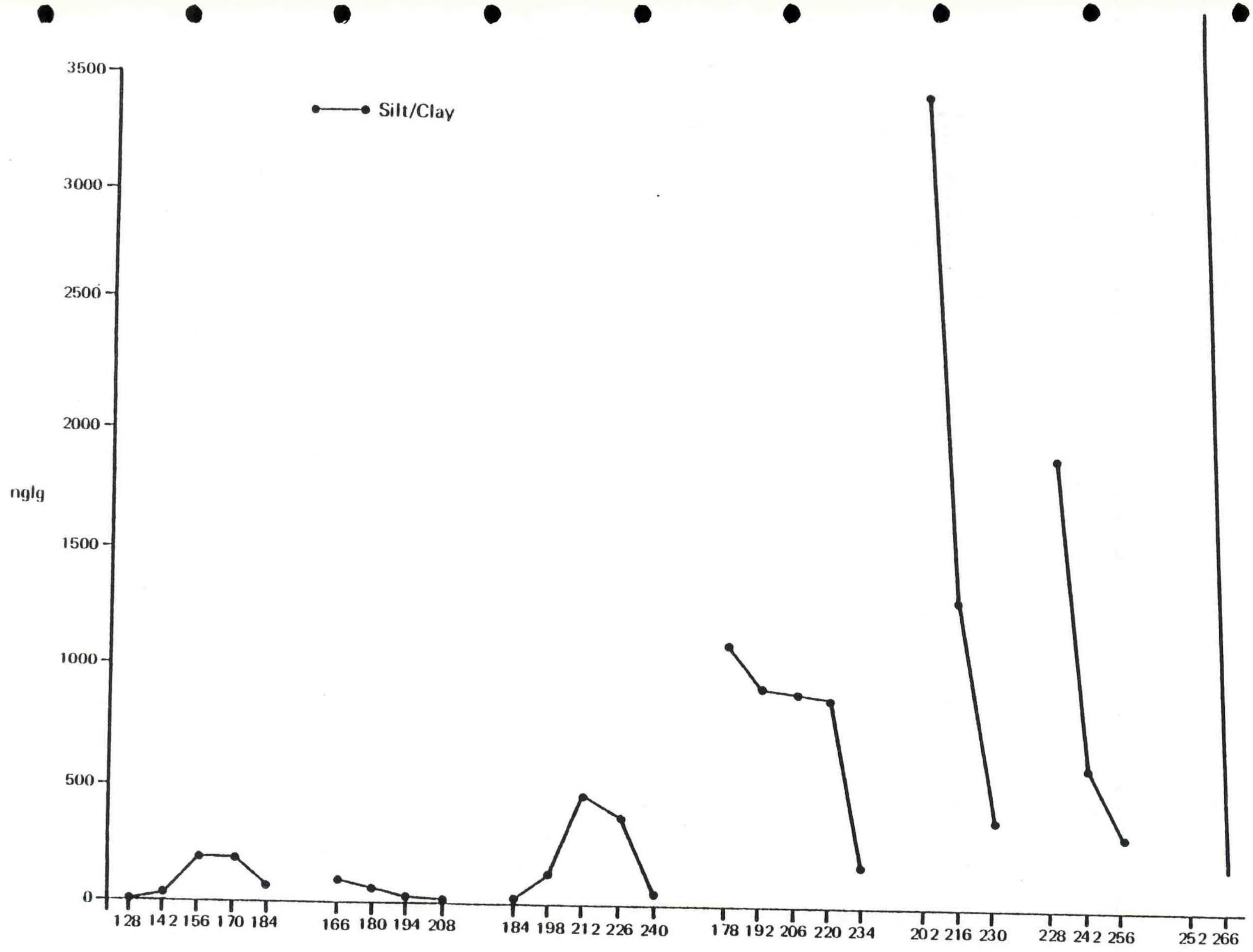


Figure 7. PAH Composition of Dredge Spoil Core–Sand Layer (0–4.5 cm)–Silt/Clay Size Fraction.

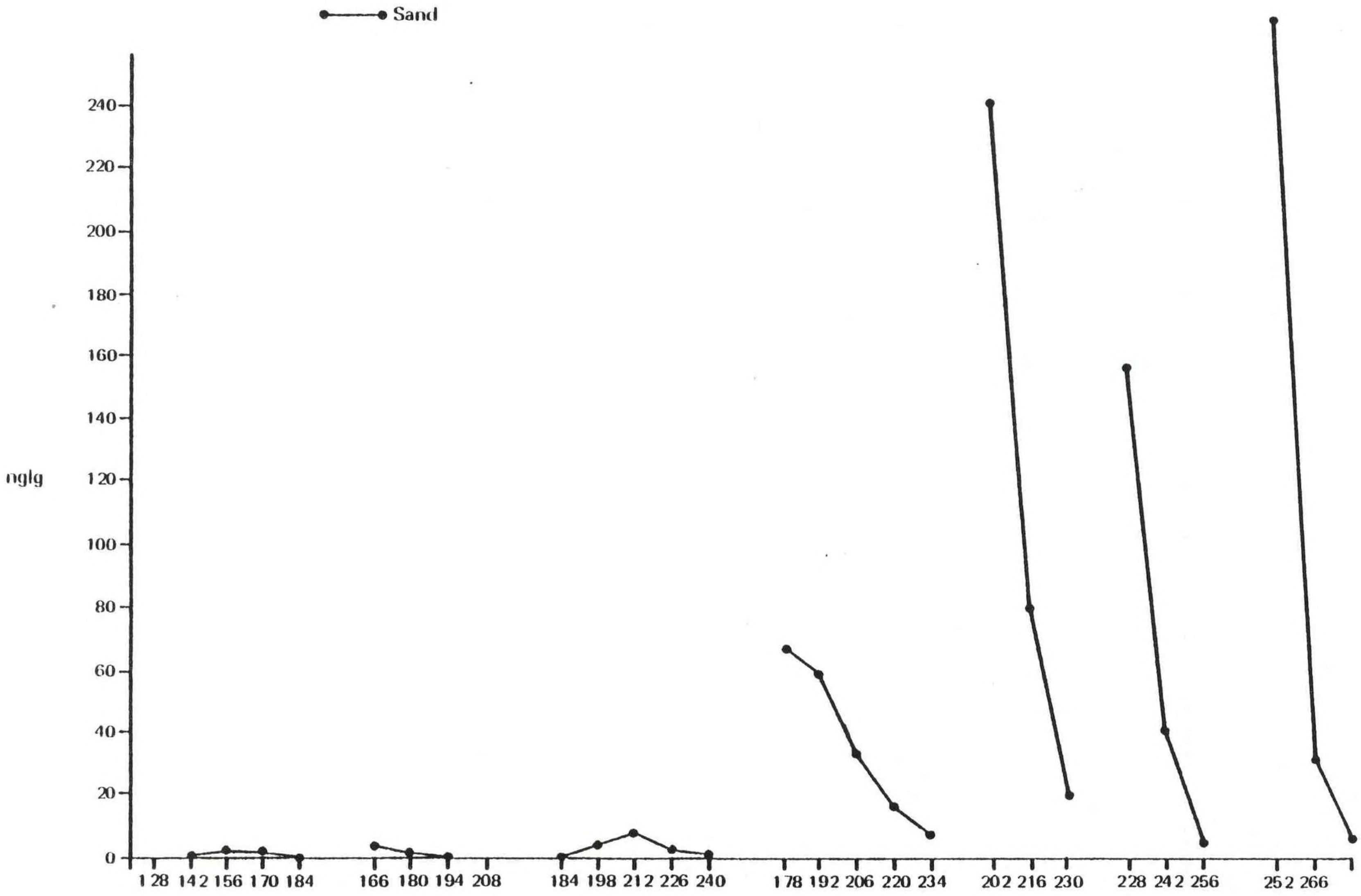
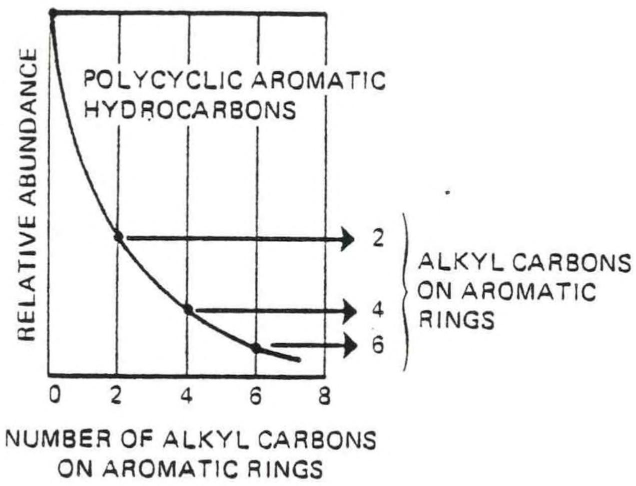
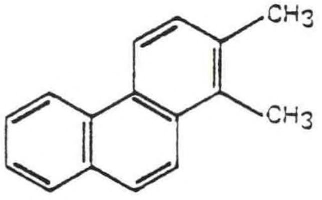


Figure 8. PAH Composition of Dredge Spoil Core—Sand Layer (0—4.5 cm)—Sand Size Fraction.



EXAMPLE: TWO ALKYL CARBONS ON PHENANTHRENE



(1, 10-DIMETHYLPHENANTHRENE)

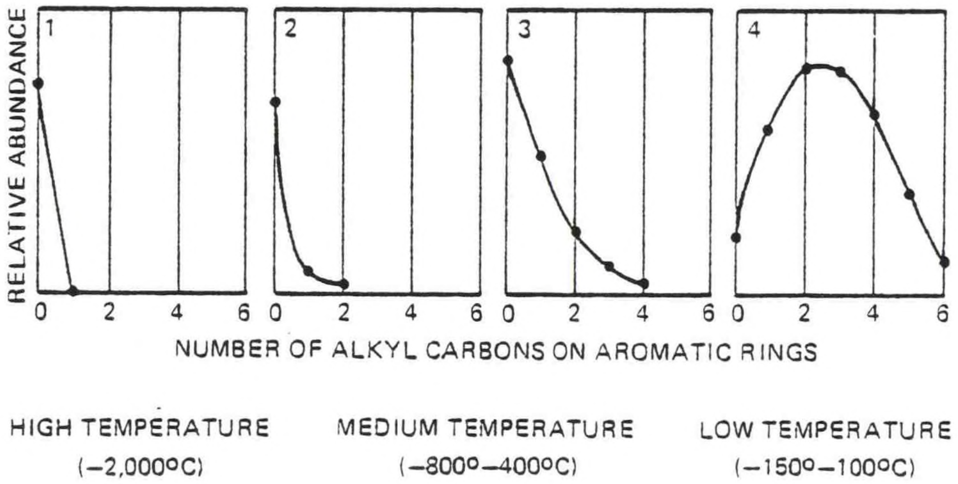


Figure 9. Idealized Alkyl Homologue Distribution Curves Showing that Number of Alkyl Carbons present on Side Chains of PAH Molecule is Function of Formation Temperature.

abundance of the higher (C_2-C_5) alkylated phenanthrenes/anthracenes decrease in combustion sources they increase in fossil fuel sources with maximum concentrations observed in the C_3-C_5 alkylated range.

Several important trends in the New York Bight waste deposits are noted. In the sewage sludge deposit (Figure 5) there are large PAH concentration differences between the three size fractions. These differences must be analyzed on a compound-series by series basis. For example, while the naphthalene and fluorene compound series are more strongly associated with the intermediate size particles (i.e., silt) concentrations of the dibenzothiophenes are roughly equivalent in the silt and clay size particles. Phenanthrenes are strongly associated with the fine clay particles. The pyrogenic compound series (i.e., the tetracyclic ($Z = -24$) and penta cyclic ($Z = -28$) PAH compounds) are found associated to a greater extent with clay than with either silt or sand. (The value of Z is derived for each aromatic series from the general molecular formula C_nH_{2n+Z}.)

The great abundance of naphthalenes, fluorenes and dibenzothiophenes in the entire sewage sludge sample along with the preponderance of alkylated phenanthrenes strongly suggest a dominant petroleum source for the sewage sludge PAH compounds. We estimate that 85 to 90 percent of PAH found in the sample originates in petroleum sources.

Dredge spoil PAH on the contrary are strongly linked to pyrogenic sources due to dominance of tetracyclic (the M/e 202 and 228 series; $Z = -22$ and -24) and pentacyclic (m/e=252 series; $Z = -28$) PAH compounds (Figures 6, 7, 8, Table 3). While the naphthalene and dibenzothiophene compound series in the clay and silt fractions of the spoil mud are significant, the single most abundant compounds are the parent (unsubstituted) fluoran thene, pyrene, chrysene, benzanthracene, benzofluoranthene, benzopyrene compounds indicating that pyrogenic sources for PAH are very important in these samples. Strong associatons of PAH with certain particle sizes are apparent only for the naphthalenes (with clay), less strongly indicated for the phenanthrenes,and not at all suggested by the data for the fluorenes, dibenzothiophrenes, and all of the pyrogenic series. The lack of particle size associations (Figure 6) observed for the M/e=202, 228 and 252 series is notable. Thus, the PAH/size associatons differ remarkably between the dredge spoil and the sewage sludge material.

The shape of the phenanthrene series (Figure 6) composition in all size fractions is interesting. The inflection at C_1 phenanthrene with a subsequent C_3 phenanthrene maximum for all size fractions strongly suggests a composite (pyrogenic and petrogenic) source of tricyclic ($Z = -18$) aromatics in this sample.

An examination of the PAH distribution of the sand layer (top 4.5 cm) of the core reveals additional source details (Figures 7 and 8). The PAH silt/clay associations are quite pronounced in this layer, where concen trations of PAH on silt/clay particles are an order of magnitude higher than corresponding sand associatons. The PAH-sand fraction in this sample (Figure 7) is almost entirely of a pyrogenic input with not only the tetra- and pentacyclic compounds overwhelmingly dominant, but with an almost "pure" pyrogenic source for the tricyclic PAH series. Virtually no petroleum (i.e., naphthalene, fluorene and dibenzothiophene series) is present. The minor amount of silt/clay material (3 percent of the top core layer) contains 93 percent of the PAH material. Also, small amounts of petroleum-related PAH are observed in the small amount of "fines" as exhibited by the naphthalene and dibenzothiophene series. An inflection in the phenanthrene curve of the silt fraction (Figure 7) indicates that the higher alkylated phenanthrenes of a petroleum origin have begun to affect the composition of the tricyclic PAH series.

The ratio of phenanthrene to anthracene (Table 3) in the various samples may indicate that the greater relative quantity of anthracene observed in the dredge spoil samples (i.e., lower P/A ratio) is due to the strongly pyrogenic PAH input to the dredge spoil material relative to the sewage sludge, the PAH of the latter, comprised of over 90 percent petroleum material. The other ratios presented in Table 3 do not vary between samples or within size fractions probably because all of the components in the BA/CH and F/PY ratios are primarily of pyrogenic origin.

3.1.3 PCB

PCB concentrations in New York Bight and the adjacent estuary have been reported over a very wide range (Table 4; West and Hatcher, 1980; Boehm and Fiest, 1980; Boehm, 1980a; MacLeod et al., 1981; Bopp et al., 1981). Low resolution gas chromatography (electron capture) was used for all of these studies other than the present work and that of MacLeod et al., 1981. Capillary GC will yield more accurate quantitative data by virtue of the fact that most individual PCB components are resolved (Figure 10) quantified and reported either as isomer groupings (e.g., dichloro, trichloro, etc., biphenyls) rather than PCB formulations (e.g., Aroclor mixtures). In addition individual isomer determinations allow for PCB molecular distributions and hence, subtle compositonal variations between samples to be discerned.

TABLE 4

REPORTED PCB CONCENTRATIONS IN NEW YORK BIGHT SEDIMENTS

LOCATION	CONCENTRATION (ppm)	METHOD	REFERENCE
Hudson River	0.5-140	GC (packed column)	Bopp et al., 1981
Upper Bay	0.13	GC (capillary)	MacLeod et al., 1981
Lower Bay	0.7	GC (capillary)	MacLeod et al., 1981
Arthur Kill Region	2-3	GC (capillary)	MacLeod et al., 1981
Raritan Bay	0.4-0.5	GC (capillary)	MacLeod et al., 1981
Christiaensen Basin	1.3-1.5	GC (capillary)	MacLeod et al., 1981
	0.05-0.15	GC (packed)	Boehm, 1980a
	0.1-0.3	GC (packed)	West and Hatcher, 1980
New York Bight (non-dumpsite)	nd-.010	GC (packed)	Boehm, 1980a
	.002-.01	GC (packed)	West and Hatcher, 1981
Dredge Spoils	0.4-3.5	GC (packed)	MacLeod et al., 1981
	3.7-6.9	GC (packed)	Boehm and Fiest, 1980
Sewage Sludge	3.5	GC (packed)	Bopp et al., 1981
	6.4	GC (packed)	West and Hatcher, 1980
Sewage Sludge Deposit (New York Bight)	0.4	GC (capillary)	This study
	.06-0.2	GC (packed)	Boehm, 1980a
	1.5-2.2	GC (packed)	West and Hatcher, 1980
Dredge Spoil Deposit (New York Bight)	.003-.28	GC (capillary)	This study
	.03	GC (packed)	Boehm, 1980a
	0.4	GC (packed)	West and Hatcher, 1980

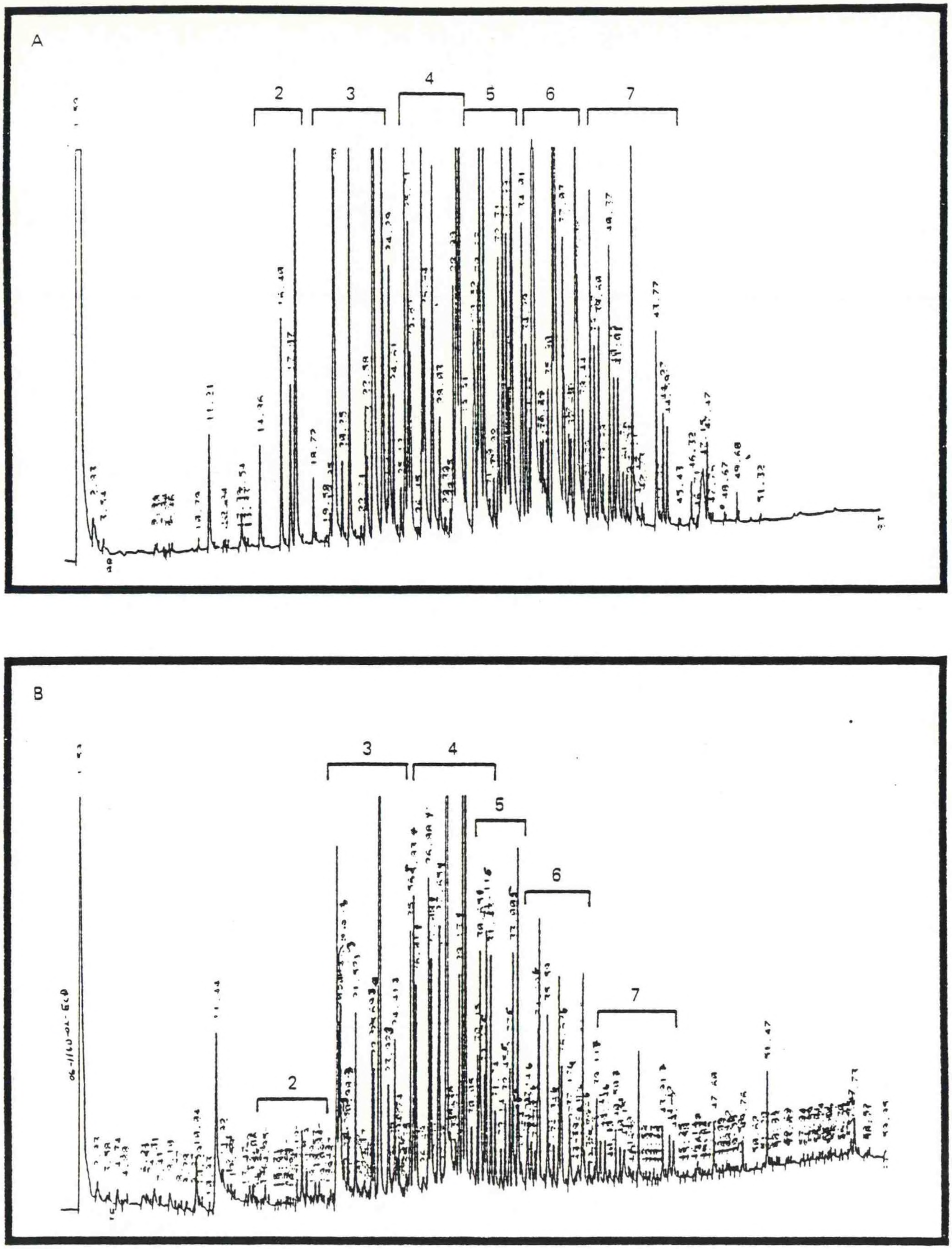


Figure 10. Capillary GC Traces of Mixed Aroclor PCB Standard (A) and Dredge Spoil—Clay Size Fraction (B) (2,3,4,5,6,7 represent number of chlorine atoms).

Such compositional information is shown in Table 5 and in Figures 11A, 11B and 11C for sewage sludge deposits, dredge spoil core (sand layer) and dredge spoil core (mud layer) respectively. Concentrations of PCB's within the sewage sludge deposit (overall 367 ppb) range from 208 ppb in the sand fraction, to 1450 ppb in the silt fraction. The clay fraction is of intermediate concentration (1370 ppb). Clearly a strong associaton of PCB with the finer sediment particles is evident although silt is "preferred" over clay. This association appears most pronounced for the tetrachloro and trichloro biphenyls (Table 5, Figure 11A) which are associated with both the silt and clay fractions albeit differentially with the two fractions. The higher chlorinated PCB are associated with the sand fraction to a greater relative extent (Figure 11A). These compositional details which clearly indicate both qualitative and quantitative fractionations within the sewage sludge bulk sediment are completely obscured when the overall composition is assessed (Figure 11A). In the latter case the pentachloro PCB's are most abundant followed closely by the tetrachloro PCB, a distribution commonly associated with an Arochlor 1254-type formulation.

A GC^2-ECD trace of a waste deposit PCB distribution (Figure 10B) indicates the isomeric complexity of a "typical" sample. Note the number of isomers which comprise each isomeric grouping (Table 6) of this sample fraction.

The overall concentration of PCB's in the mud layer of the dredge spoil core is about 75 percent (277 ppb) of the sewage sludge value (367 ppb). Again PCBs are seen to be associated with the fine fraction (i.e., clay=917 ppb) but now much more so with the clay than with silt. The compositional distribution does not vary with the size fractions

TABLE 5

POLYCHLORINATED BIPHENYLS IN WASTE DEPOSIT SIZE FRACTIONS

SEWAGE SLUDGE	DRY WEIGHT	DICHLORO-BIPHENYLS ng/g	TRICHLORO-BIPHENYLS ng/g	TETRACHLORO-BIPHENYLS ng/g	PENTACHLORO-BIPHENYLS ng/g	HEXACHLORO-BIPHENYLS ng/g	HEPTACHLORO-BIPHENYLS ng/g	TOTAL PCB AMOUNT ng	TOTAL PCB CONCENTRATION ng/g
Sand	7.4	13.0	26	31.8	86.6	36.7	14.0	1539	208.1
Silt	0.6	57.8	444	488	308	114	41.8	901	1454
Clay	0.5	72.9	140.1	600	371	138	43.8	683	1365
Total	8.5	19.8	62.3	98.6	120	48.4	17.8	3094	367.4
Dredge Spoil (Sand Layer)									
Sand	80.0	.2	0.8	1.2	3.4	5.6	2.4	1088	13.6
Silt	2.5	17.8	81.2	186	201	100	29.8	1540	61.6
Total	82.5	.73	3.2	6.8	9.4	8.5	3.2	2628	31.8
Dredge Spoil (Mud Layer)									
Sand	33.5	5.6	27.9	57.8	39.0	27.0	9.6	5591	167
Silt	6.8	18.6	67.3	163	130	56.2	16.0	3067	451
Clay	3.9	44	156	360	228	99.4	29.6	3576	917
Total	44.2	11	45.3	100.6	69.7	37.9	12.3	13234	276.7

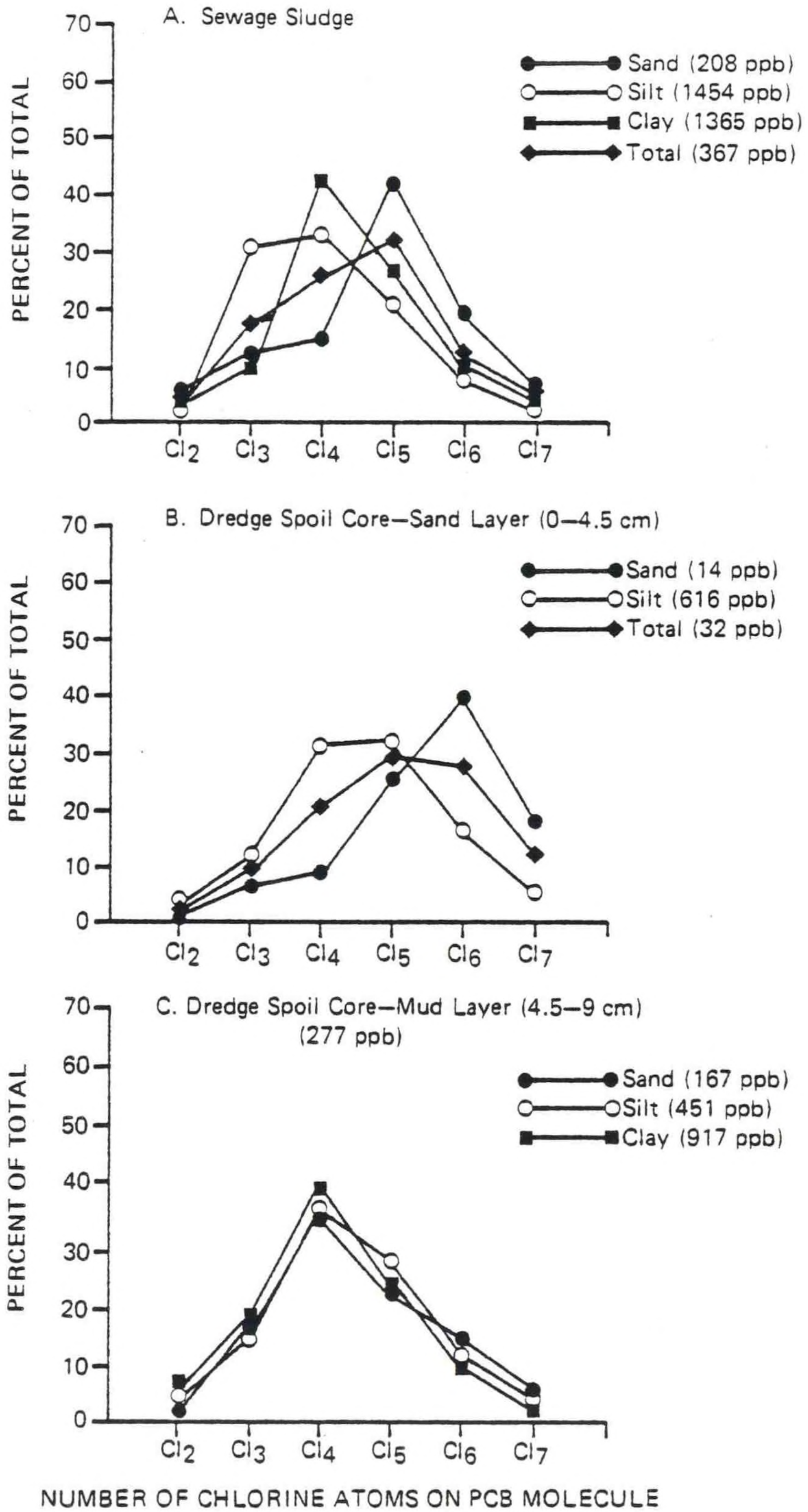


Figure 11. PCB Composition of Size Fractions of Waste Deposits.

TABLE 6

NUMBER OF PCB ISOMERS IN EACH ISOMETRIC GROUPING OF SEWAGE SLUDGE WASTE DEPOSIT

- CLAY FRACTION OF SEWAGE SLUDGE -

ISOMERIC GROUPING	NUMBER OF INDIVIDUAL ISOMERS	PERCENT OF TOTAL PCB
dichloro	4	5.3
trichloro	6	10.3
tetrachloro	9	43.9
pentachloro	9	27.2
hexachloro	11	10.1
heptachloro	4	3.2
	43	100.0

(Figure 11C). The compositions within the spoil size fractions are remarkably constant with the tetrachloro PCB isomers clearly dominant in all size fractions.

The top layer (sand) of the dredge spoil core differed substantially in PCB composition as well as concentration from the mud layer beneath possibly indicating multiple spoil sources. The overall layer contained 32 ppb of PCB, but with strong silt asociations present (Table 5). This material (silt) was dominated by pentachloro and tetrachloro isomers (Figure 11B) as contrasted from the sand fraction of this top layer which was largely dominated by the hexachlorobiphenyls. The overall composition (Figure 11B, Table 5) is dominated by the penta- and hexachlorobiphenyls.

3.1.3 Coprostanol

The absolute concentrations of the fecal steroid, coprostanol, in the dredge spoil and sewage sludge samples are presented in Table 7. The concentration of coprostanol is also presented relative to the major sterols and stanols of mixed planktonic/sewage (cholesterol, cholestanol) and planktonic (stigmasterol, β-sistosterol) origins (Figure 12). As seen in Table 7, both the absolute concentrations of coprostanol and the diagnostic ratio are higher in the sewage sludge. The ratio is invarient within the size fractions of each sample although the absolute coprostanol level is high on the fine fraction. The coprostanol concentration in the overall bulk sewage sludge is 94 ppm (420 ppm in the clay fraction) while it is only 2.7 ppm in the dredge spoil mud (12 ppm in the clay fraction).

TABLE 7

CONCENTRATIONS OF COPROSTANOL AND KEY DIAGNOSTIC RATIOS IN SEDIMENT SIZE FRACTIONS

	COPROSTANOL (µg)	COPROSTANOL CONCENTRATION (µg/g)	$\frac{\text{COPROSTANOL}}{\text{TOTAL STEROIDS}}$	$\frac{\text{COPROSTANOL}}{\text{PCB}}$
Dredge (Sand)				
Sand	5.5	0.07	.07	8.0
Silt	6.4	2.5	.03	7.2
Total	11.9	0.14		7.5
Dredge (Mud)				
Sand	42.2	1.3	.32	13.4
Silt	29.3	4.3	.39	12.5
Clay	47.7	12.2	.38	21.6
Total	119.2	2.7		15.3
Sewage				
Sand	438	60	.7	191
Silt	144	234	.6	179
Clay	216	423	.6	232
Total	796	94		232

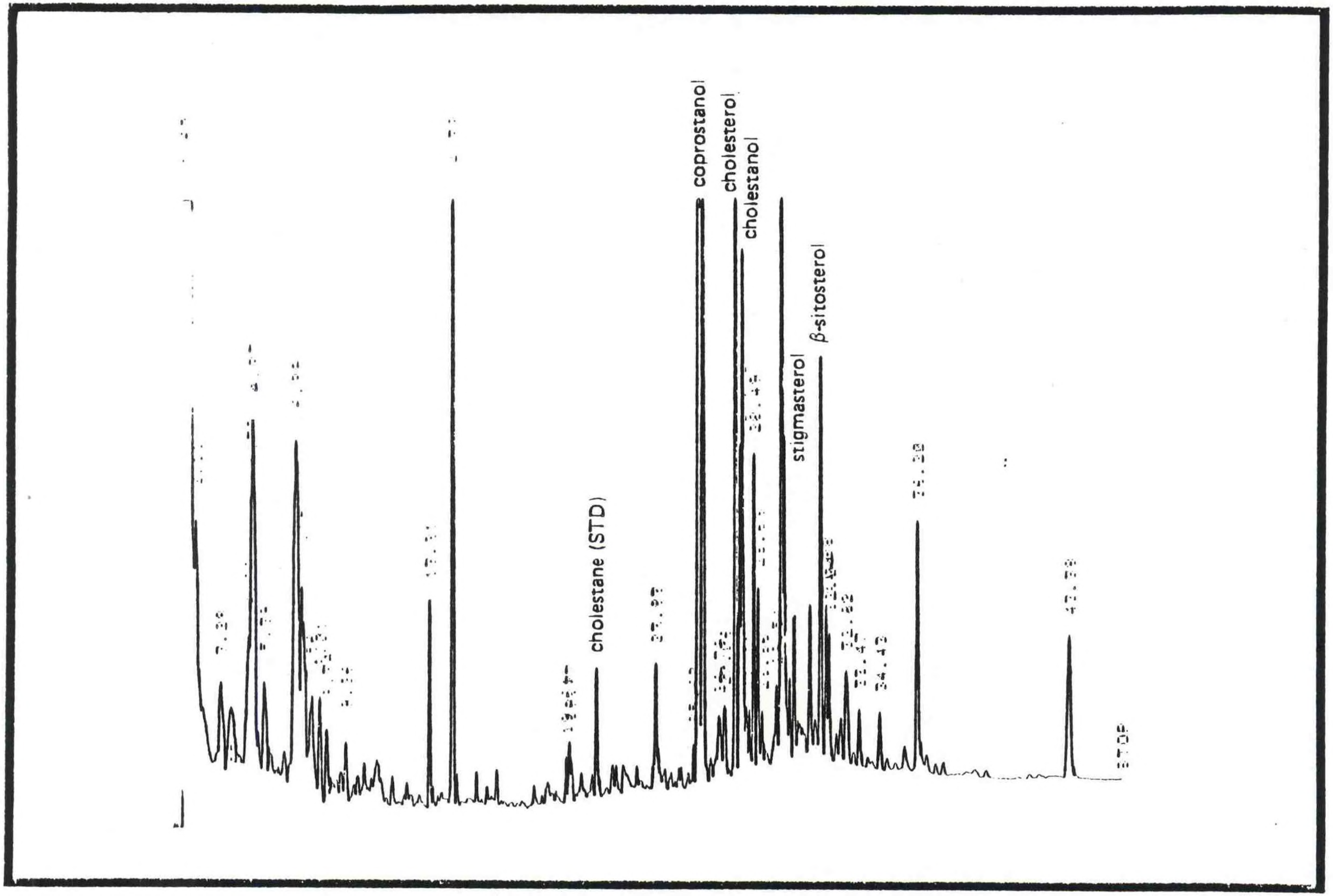


Figure 12. Capillary GC Trace of TMS Ethers of Sterols in Sewage Sludge—Clay Fraction.

The ratios of coprostanol/"total" steroids and coprostanol/ PCB have been considered before (Hatcher and McGillvary, 1979; Boehm, 1980a) and serve as key diagnostic ratios to discern the sources of sedimentary pollutants.

3.2 Water Column Particulates

3.2.1 PAH Compounds

Concentrations of PAH compounds in the suspended particulates ranged from non-detectable (< 0.5 ng/liter=part per trillion) to 370 ng/l in the study region including the upper and lower New York Bays, through the mouth of the estuary and out to the shelf break (Station 22). The mean total PAH concentrations from the entrance to the Bays (estuary) approach (Station 5) to the tip of Manhattan Island was 13 ng/l (±10.4 ng/l) (range nd -35 ng/l). At Stations 1 and 2 higher concentrations were observed in bottom water (8 meters) than in the surface (3 meters) in spite of the surface water's higher suspended load (2350 µg/kg surface; 1750 µg/kg bottom) concentration (Mukirji, personal communication). Concentrations decreased through the Narrows (Station 3) and remained low during the ebb tide at Station 4 (1-3 ng/l).

At Station 4 a time series of surface water particulate concentations were taken through one tidal cycle. Through the ebb part of the cycle and through the low slack water, PAH concentrations remained quite low (1-3 ng/l). However concentrations increased during the flood tide (8 ng/l) and peaked at high slack water (13 ng/l). Although not sampled, bottom waters may have had even higher concentrations during this peak in PAH concentrations. As important as as are the absolute concentrations are the PAH compositions observed during this time series. While the PAH in surface waters are comprised primarily of tricyclic (phenanthrenes, z= -18) and one tetracyclic (fluoranthene/ pyrene, z= -22) series PAH (Table 8), PAH material carried to this station from the seaward direction were richer in the heavier tetracyclic (benzanthracene/chrysene, z= -24) and pentacyclic (z=-28) PAH compounds. (Again the value of z is derived for each series from the general formula C_nH_{2n+Z}.) Note that the presence of tetra (z=-24) and pentacyclic (z=-28) PAH characterize both the particulates further in the estuary (Stations 1 and 2) as well as those just seaward of Station 4 (Stations 5 and 6). The PAH distributions at Station 4 and elsewhere in the study region reveal two basic PAH assemblages (i.e., source type) one comprised of the z=-18 and z=-22 series and that associated with z=-24 and z=-28 compound series (tetra and pentacyclic PAH). Station 5, just seaward of Station 4, and the "source" of suspended material for Station 4 during the flood tide contains the latter PAH source (which we will call the "heavy" PAH source). Outside of the River system (seaward of Rockaway Point) the "heavy" PAH were observed at only six other locations; midwater at Stations 6, 7, 18, 23 and 24. The existence of the heavy PAH did not necessarily covary with the total suspended matter load (Table 8).

Vertical stratification is tied into the PAH distributions. For example, while surface waters at Station 5 are more abundant in PAH (and PCB) compounds than in subsurface waters, the mid and bottom waters (mid and bottom waters are well mixed in the study region) contain elevated PAH levels, as well as the heavy PAH material at Stations 6, 7, 10 and 23. At Station 18 the mid water differs significantly from both surface and near bottom waters in both quantity and composion of PAH. Those observations suggest a patchiness for the PAH bearing particles in the New York Bight, but one that may be associated to resuspension phenonemna as will be discussed later.

3.2.2 PCB Compounds

PCBs in the particulate matter ranged in concentration from 50 picograms (10^{-12} gram)/liter (0.05 ng/l) at Station 22 out on the shelf to 3.53 ng/liter at Station 4 during flood tide. Although not measured, "dissolved" PCB will contain roughly an equivalent amount of PCB (Risebrough, 1978; DeLappe et al., 1980). These values are much lower than Bight "background values" previously reported elsewhere (Bopp et al., 1981; Hatcher et al., 1978) but are consistent with recent PCB values in coastal waters from coastal Massachusetts (New Bedford, Buzzards Bay; Risebrough, 1978) and California (DeLappe et al., 1980). Our background, or "normal" flux data are two to three orders of magnitude lower than those observed during dumping events involving sewage sludge (Hatcher et al., 1978) and dredge spoils (Boehm and Fiest, 1980) (20-60 ng/liter). Values off of the tip of Manhattan were highest near the bottom 1.4-2.2 ng/l which effectively decouples PCB values from total suspended matter levels which showed TSM to be higher in surface waters. PCB levels generally covary with PAH levels at Station 4, although slightly out of phase. However, PCB and PAH covariance is the exception rather and the rule for both in harbor waters and Bight/shelf waters. At Stations 7 and 10 where PAH levels are strikingly higher, only a modest increase in PCB levels is observed at Station 7 and none at Station 10. Also PCB values are low at Station 18 at the head of the Hudson Shelf Valley where PAH is elevated.

Stations 23 and 24 located adjacent to the sewage sludge and dredge spoil dumpsite show no striking PCB elevations although these samples contain moderately elevated PAH values. The compositional complexity of the particulate samples is illustrated in Figure 13.

The compositional profiles of particulate PCB's in the water column from several key stations are shown in Figures 14, 15, and 16. There appear to be three main PCB groupings best represented by the compositional plots shown in Figures 14A, 15B, and 16C. The first (Figure 14A) is the most frequently encountered PCB composition with a maximum of tetrachloro isomers. Note that although the PCB levels change markedly during the tidal cycle at Station 4 the PCB composition does not. The PCB behavior differs significantly from the PAH situation at Station 4, where heavy PAHs influence the station's PAH composition on the incoming tide. The second major PCB distribution (Figure 15B) was observed in the bottom waters of the inner Harbor region wherein trichlorobiphenyl isomers dominate and a slight bimodal distribution with a secondary maximum at the pentachloro-PCBs is seen. This distribution is linked to Hudson River resuspension in that the Hudson River sediments are impacted by Aroclor 1016 which has abundant tricholorobiphenyl isomers originating in an upriver industrial source (Bopp et al., 1980).

The third distribution is observed in several samples from the Bight (Figure 16C). This distribution is characteristic of bottom or intermediate waters at Stations 6, 7, and 24. This distribution is characterized by PCB constituent maxima in the pentachloro and tetrachlorobiphenyl region and may be associated with bottom sediment resuspension.

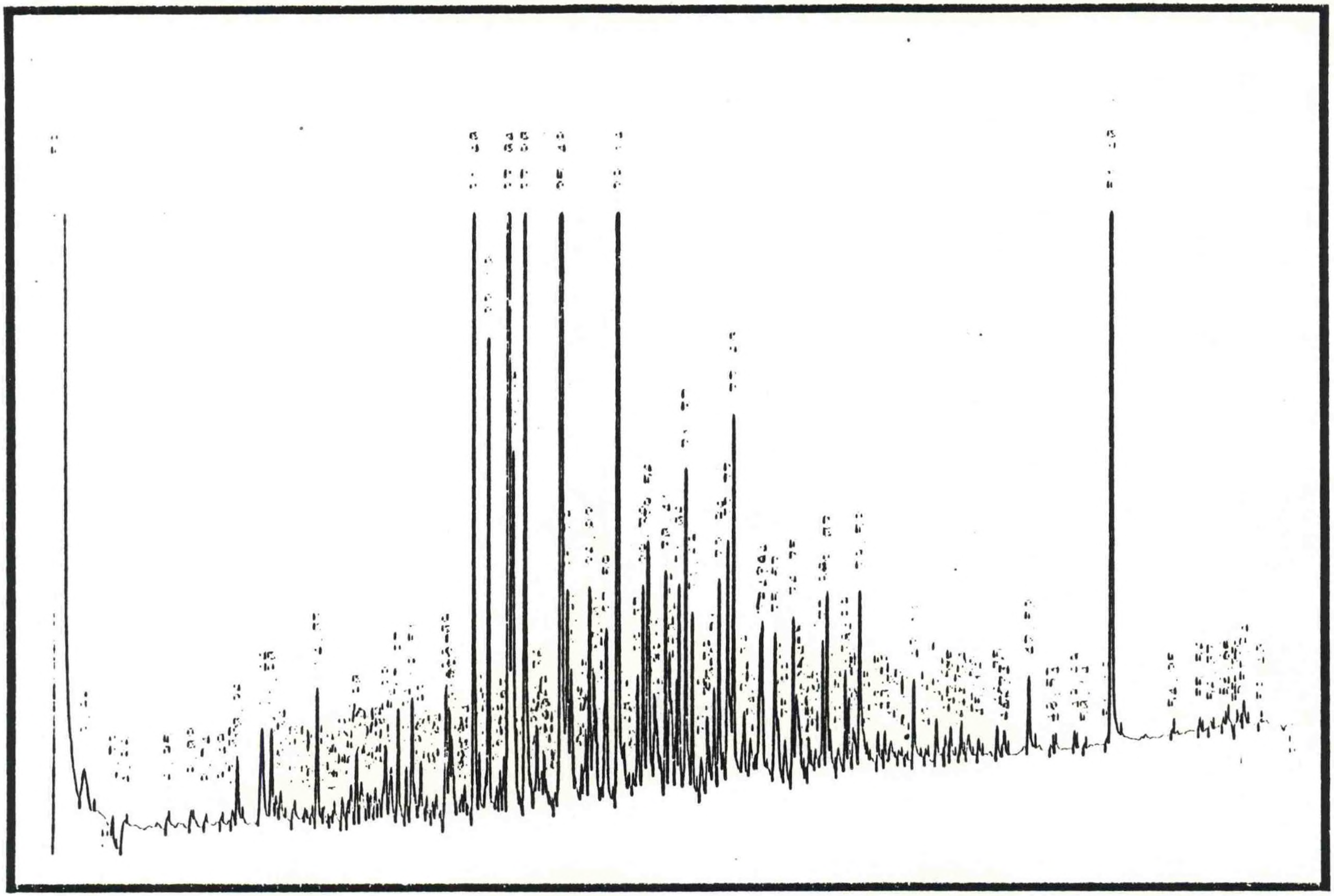


Figure 13. Capillary GC of PCB in Suspended Particulate Sample (Station 4, 3 meters flood tide; 3.1 ng/liter).

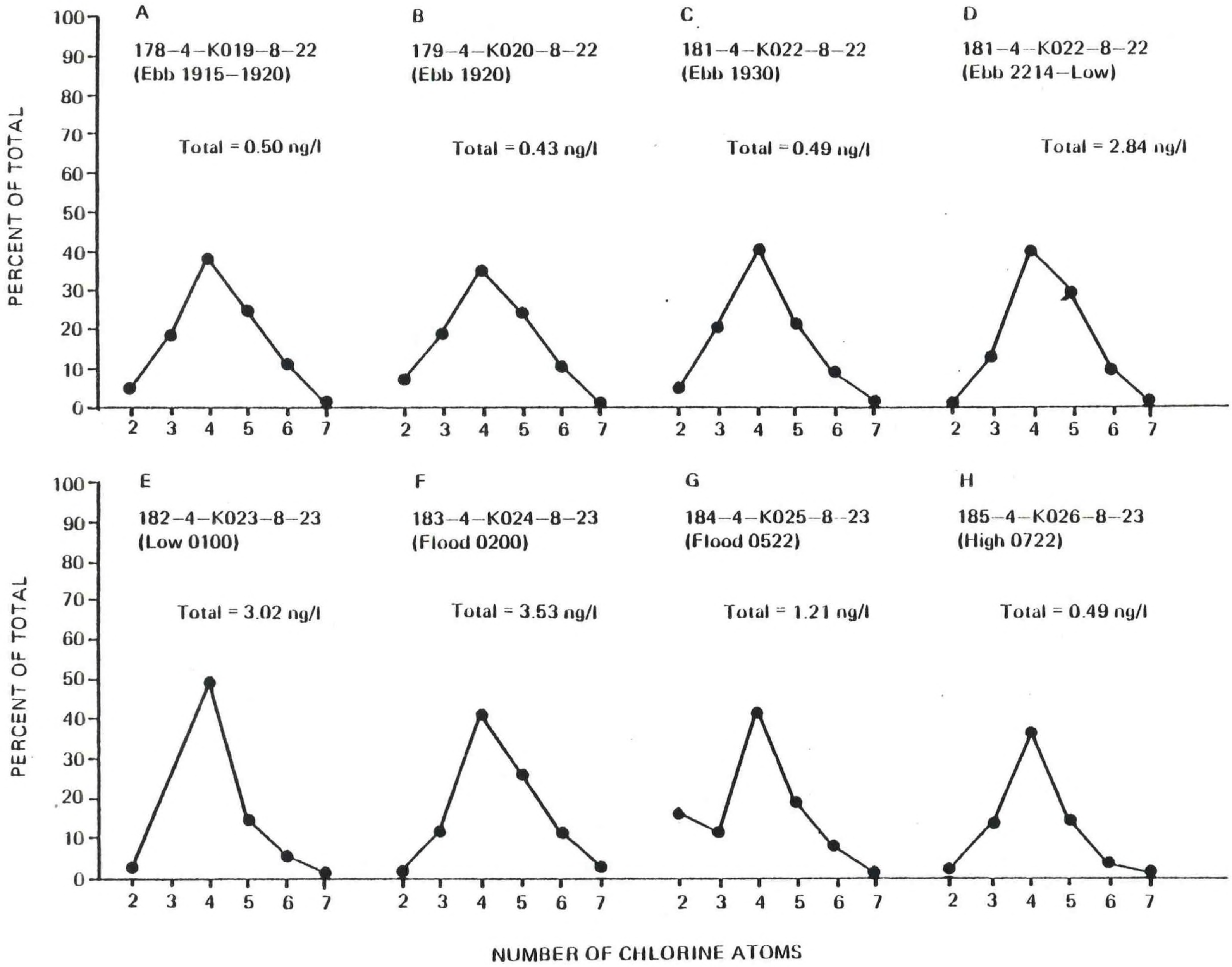


Figure 14. PCB Compositional Plots of Suspended Particulates at Station 4 Time Series.

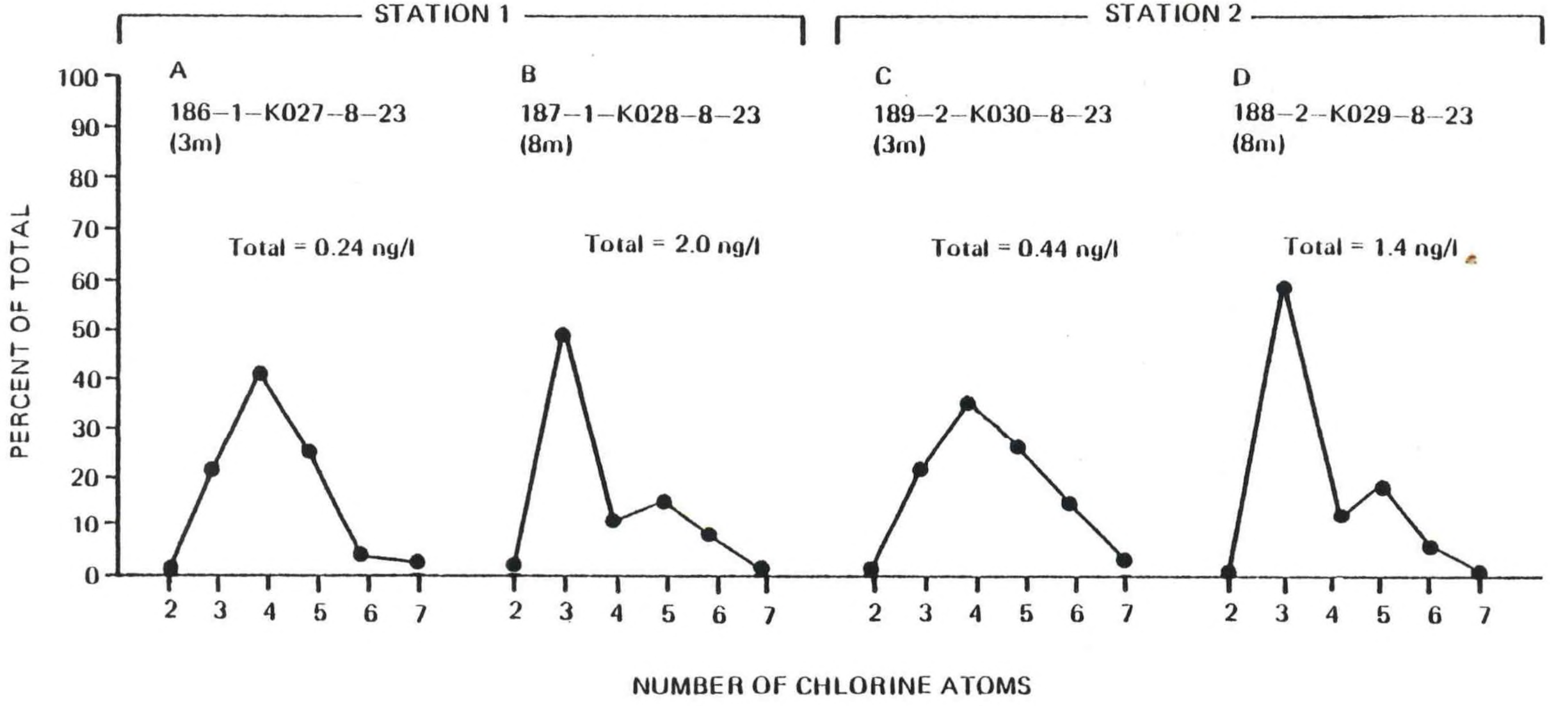


Figure 15. PCB Compositional Plots of Suspended Particulates of Inner Bay Samples (Stations 1 and 2).

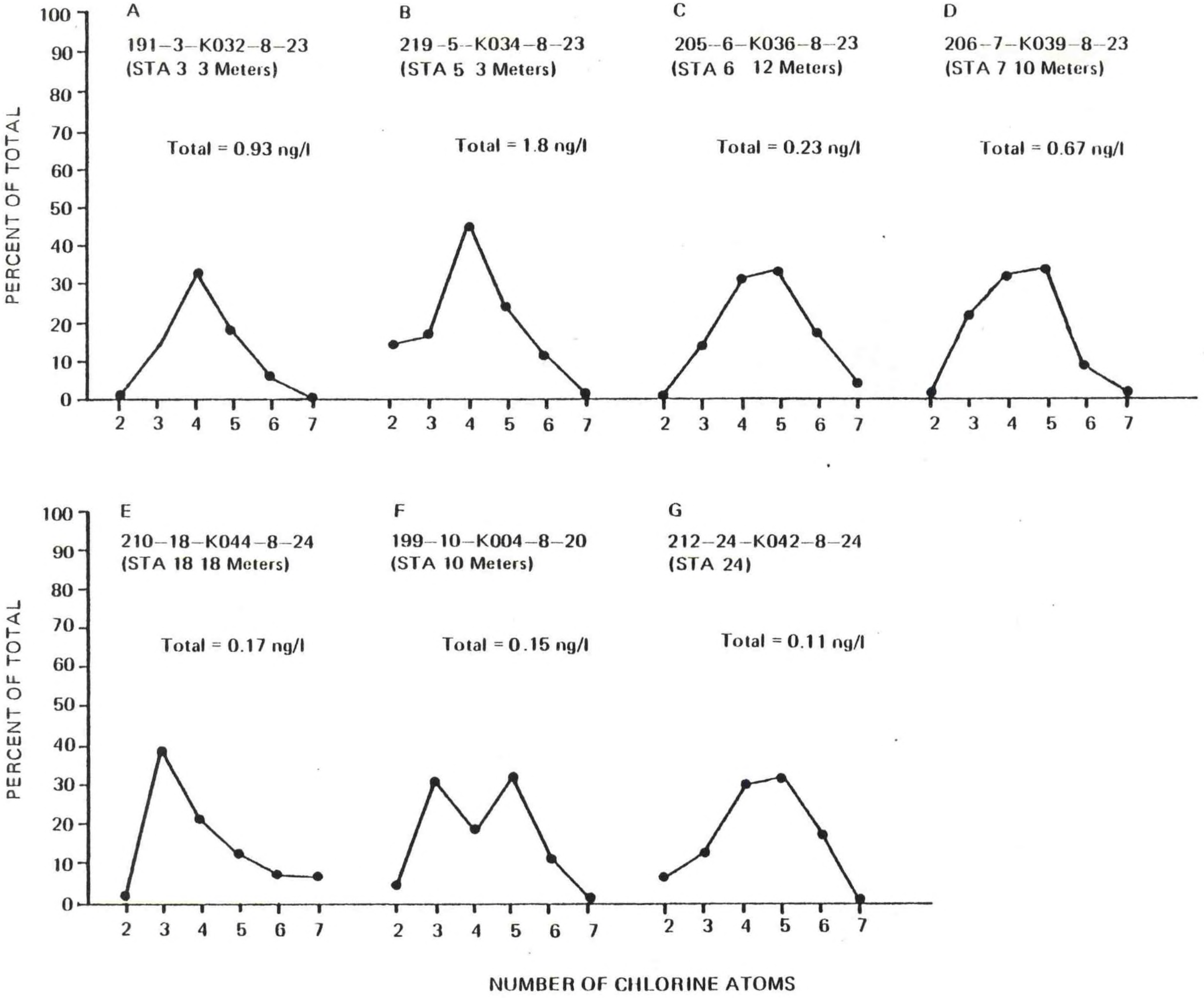


Figure 16. PCB Compositional Plots of Other Suspended Particulates.

3.2.3 Coprostanol

The concentrations of coprostanol within the estuarine system (i.e., landward of Rockaway Point) range from 50-200 ng/liter with maximum concentrations observed in the surface waters. Marked vertical water column differences can be seen especially at Station 5 (157 ng/l @ 3 m; 6 ng/l @ 14 m). Note that at this station there is good correspondence of PAH, PCB and coprostanol (i.e., all higher in surface waters). During the time series experiment at Station 4, again PCB and coprostanol exhibit reasonable covariance with PAH slightly out of phase. However, PCB and coprostanol values are completely decoupled in the waters of the inner estuary (Stations 1, 2) indicating the inner estuary sediment resuspension is not associated with sewage effluent material, the latter remaining in the surface waters and transported seaward in the surface waters as part of a classic two layer estuarine stratification: (i.e., brackish less dense riverine water flowing out on the surface.) The reason for the elevation of coprostanol at Station 13 is not entirely clear. However, it is a persistent feature. Station 13 was sampled twice over 3 days and the elevated coprostanol levels persisted. The PCB values were slightly elevated (0.2 ng/l) in two cases and moderately elevated (0.5 ng/l) in another case (Table 8). However, in only one sample were PAH compounds detected at all! Coprostanol and PCB levels covary more consistently than either with PAH, thus further suggesting complex interactions of sources and environmental behavior of organic-pollutant particulates.

TABLE 8

SUMMARY OF PARTICULATE WATER COLUMN DATA

			ng/l											
K	STATION	DEPTH (METERS)	N	P	m/e= 202	m/e= 228	m/e= 252	TOTAL PAH	(228+252) / (P+202)	PCB (ng/l)	COPROS. ng/l	COPROS. / STEROIDS	COPROS. / PCB	TSM (µg/kg)
27	1	3	nd	2	4	1	–	7	0.2	0.24	66	.25	275	2350
28	1	8	.3	3.4	6.3	3.0	3.1	16	0.6	2.24	56	.08	25	1750
30	2	3	nd	1.4	6.4	3.8	4.7	16	1.1	0.44	166	.24	377	
29	2	8	nd	8.7	11.7	7.8	7.6	35	0.8	1.35	27	.18	20	2511
31	3	3	no data							0.32	18	.26	56	2830
32	3	3	.5	.6	1.5	nd	nd	2.6	0	0.93	104	.22	119	
19	4 ebb	5	no data							0.50	56	.15	112	2320
20	4 ebb	3	nd	1.0	1.5	nd	nd	2.5	0	0.43	76	.11	177	
21	4 ebb	3	nd	0.4	0.5	nd	nd	0.9	0	0.49	79	.11	161	2440
22	4 ebb	5	nd	0.8	1.4	nd	nd	2.2	0	2.84	43	.17	15	2000
23	4 ebb (low)	5	no data							3.01	233	.24	77	
4	4 ebb (slack)	5	nd	1.0	3.2	1.5	2.3	8	0.9	3.53	127	.18	36	876
25	4 flood	5	no data							1.21	93	.36	78	
26	4 flood (high)	3	nd	1.5	4.3	3.6	3.4	13	1.2	0.49	47	.06	96	1240
34	5	3	nd	3.4	3.4	4.0	8.5	19	1.8	1.78	157	.13	88	
35	5	14	nd	1.0	2.1	nd	nd	3.1	0	0.12	6	.02	50	2900
36	6	3	nd	0.5	nd	nd	nd	0.5	0	0.11	5	.05	45	3000
37	6	12	3.5	4.8	4.4	2.2	2.3	17	0.5	0.22	–	–	–	1970
38	7	3	nd	6.7	nd	nd	nd	7	0	0.16	–	–	–	1621
39	7	10	nd	nd	21	150	200	370	13	0.67	83	.15	124	501
10	8	15	nd	1.1	nd	nd	nd	1	0	0.11	11	.04	100	350
11	8	25	nd	0.8	0.9	nd	nd	2	0	0.10	12	.05	120	563
4	10	3	nd	1.3	nd	nd	nd	1	0	0.15	1	.01	7	735
3	10	12	nd	27	40	19.0	25	110	0.5	0.11	1	.00	9	319
1	12	3	nd	nd	nd	nd	nd	nd	–	0.12	4	.01	33	
16	13	5	nd	nd	nd	nd	nd	nd	–	0.20	110	.28	550	545
17	13	16	nd	nd	nd	nd	nd	nd	–	0.20	125	.34	625	790
40	13	4	nd	2.2	1.2	0.4	nd	4	0.1	0.23	310	.41	1350	
43	18	4	nd	0.5	nd	nd	nd	0.5	0	0.08	5	.07	100	
44	18	18	nd	2.7	nd	7.3	8.0	18	5.7	0.17	20	.08	118	
45	18	18	nd	1.0	nd	2.4	3.3	6.7	5.7	0.15	26	.10	173	
46	18	30	nd	0.8	nd	nd	nd	0.8	0	0.14	36	.00	257	

N = m/e 128, 142, 156, 170
P = m/e 178, 192, 206, 220
nd = none detected = <0.5 ng/l
TSM = total suspended matter (Mukirji and Kester, unpublished data)

TABLE 8 (CONT.)

			ng/l										
K	STATION	DEPTH (METERS)	N	P	m/e= 202	m/e= 228	m/e= 252	TOTAL PAH	$\frac{(228+252)}{(P+202)}$	PCB	COPROS. ng/l	COPROS. STEROIDS	COPROS. PCB	TSM (µg/kg)
50	22	3	nd	nd	nd	nd	nd	nd	-	.06	1	.01	17	--
51	22	8				no data				.05	3	.01	60	--
52	22	25	5.8	3.7	0.7	nd	nd	10	0	-	2	.00	-	329
48	23 (sewage dump site)	28	nd	1.6	3.2	4.5	3.1	12.1	1.6	.11	6	.02	55	1881
42	24 (dredge dump site)	10	.6	1.0	3.2	1.2	2.0	8.0	0.8	.11	6	.08	55	790
41	24 (dredge dump site)	3				no data				.05	6	.03	120	--

Discussion

The process of piecing together the organic chemical data and relating PCB, PAH and coprostanol distributions to suspended particulate sources is one that must be undertaken with an awareness that while all of these chemical classes are constituents of all of the major pollutant sources to the estuarine/shelf system, their geochemical behavior and hence their areal distributions are not necessary coupled. This became apparent in the evaluation of the data sets in which there are many examples of elevation of one component class with minimal corresponding variance of another class.

Three notable examples of this concern chemical distributions at Stations 1 and 2, distributions at Station 13 and distributions at Station 10. In the first case we see markedly elevated PCB levels in bottom waters undoubtedly related to resuspension and downstream transport phenomena within the Hudson River system. The PCB composition is related to a non-sewage source and is linked to the chronic Hudson River PCB problem through the dominance of trichlorobiphenyl isomers (i.e., Aroclor 1016). The elevated PCB levels are accompanied by a modest PAH increase and virtually no coprostanol increase. Indeed the sewage input can be seen instead in the near surface water at Stations 1 and 2 where the PCB concentrations are lower, their composition maximum is in the tetrachlorobiphenyls (Figure 15) and where abundant coprostanol from sewage effluents is clearly observed (Table 8).

A significant increase in coprostanol levels at Station 13 (110-310 ng/l) was not accompanied by a concomitant PCB or PAH increase. The coprostanol to total steroid ratio initially suggests an input of particulate matter from the nearby dredge spoil deposit. However, the relatively minor PCB and PAH increases suggests that the origin of these coprostanol-rich water parcels may be from the estuarine surface waters where both the coprostanol/PCB and coprostanol/total steroid ratios approach the corresponding values observed at Station 13. The observation at Station 13 is of considerable interest as the elevated coprostanol levels were observed on two occasions separated by three days.

At Stations 10 and 7 marked elevations in PAH levels linked to the "heavy PAH" source(s) are either weakly linked (Station 7) or not at all linked (Station 10) to PCB or coprostanol levels. The set of values observed at Station 7, closer to the mouth of the river/harbor region suggests a mix of estuarine water (source of much of the coprostanol and PCB material) and an offshore source of "heavy" PAH perhaps from a dredge spoil source which exhibits "heavy" PAH profiles. The origin of PCB composition (Figure 16D) is not entirely clear but a composition of estuarine (tetrachlorobiphenyl-dominant source) and dredge spoil material (tetra- and pentachlorobiphenyl-dominant source) sources is not ruled out.

The origin of the "heavy" PAH distribution in the water column is strongly linked to resuspension of dredge spoil deposits through two pieces of information. Firstly, the bottom water (10 meter) particulate sample from Station 24, adjacent to the spoil disposal site contains moderately elevated levels of PAH in general and "heavy" PAH in particular. Such "heavy" PAH distributions are limited to only a few samples outside of the estuarine area (see Table 8) but notably impact intermediate depth water at Stations 7, approximately 4 nautical miles to the northwest of the dredge spoil dumpsite and Station 18, approximately

3.5 nm to the south-southeast (see Figure 2). Secondly, the PAH distributions in the dredge spoil deposit in all size fractions are characteristically dominated by pyrogenic PAH compounds (i.e., three-, four-, and five-ringed parent PAH compounds (Figure 7 and 8) as opposed to a largely petroleum derived sewage sludge PAH distribution.

Down-valley transport of organic chemical-bearing particulates from Station 23 in the Christaensen Basin to Station 22 further out on the shelf and in the Hudson Valley channel is suggested by the petrogenic nature of the PAH material at both stations (i.e., lighter two- and three-ringed PAH with some four-ringed influence, but no heavy PAH). The origin of this PAH material seems linked to sewage sludge by virtue of similarities in PAH compositional distributions. Coprostanol values are quite low, however, and PCB information is spotty. Thus, the postulation of down-valley transport of PAH is highly speculative at this point.

The particulate transport situation at the entrance to the estuarine/river area is quite complicated (Stations 4, 5, 6). The time series at Station 4 reveals that surface waters are profoundly influenced by the tidal movement of PCB- and PAH-rich particles from the seaward direction. If we look at the data from Station 5 at which both surface and bottom water particulates were obtained we see PCB and PAH-rich particles at the surface. Bottom waters are surprisingly low in PCBs and contain no heavy PAH. (Note that Station 5 was sampled during flood tide, approximately one hour prior to high tide). Thus landward transport of "heavy" PAH and abundant PAH material in surface waters is suggested. Station 4 data (Table 8) indicates that PCB and PAH concentration maxima are slightly out of phase with the maximum PCB levels occuring prior to the PAH maximum.

Unlike Stations 5, Station 6 particulates are richer in PCB and more notably PAH in the intermediate to bottom water. (Note that bottom water was not sampled at Station 4. Thus, no information on the chemical nature of bottom particles is available over a complete tidal cycle). At Stations 6 and 7, the midwater PAH increase outpaces the PCB increase. This is an indication that PCB material along with minor PAH associations is flushed out of the estuary in patchy distributions which "slosh" landward and seaward with the tides, but probably with a net movement seaward. Further offshore a PAH-rich pulse of suspended particulates is discerned. Stations 6 and 7 are closely linked by virtue of elevated mid-water (10 meters) PAH levels at 7 and elevated levels bottom waters at 6 (12 meters). The elevated PAH and PCB levels at Station 5 suggests a patchy distribution of material in surface waters at the estuary's entrance, probably of a mixed sewage effluent origin (high coprostanol at Station 3) and general Lower Bay/Raritan Bay inputs (high "heavy" PAH and PCB). The low Station 5 bottom water values are anomalous. The surface water's high PCB/coprostanol/PAH patch does not extend to Station 6, at which transport in subsurface waters appears to be landward with a Bight Apex origin for elevated "heavy" PAH observed in mud and bottom waters.

One should realize that the observatoins at all stations other than 4 and 13 where some time series information exists are essentially geochemical/oceanographic "snapshots." One envisions surface water and bottom water patches of organic pollutant-bearing particulates whose ultimate fate and transport is determined over several tidal cycles and which are highly dependent on the Bight circulation.

The covariance of PCB and PAH levels in the water column will tend to be strongest where suspended particulate densities are greatest (i.e., Stations 1 and 6) and where a common source for the two compound classes exists. A common source is inferred from data at Stations 4 and 5, but not from 1 or 2 or from 6. The situation at Stations 1 and 2 well within the harbor is clearly dominated by differential sewage effluent and resuspensed Hudson River sediment sources. However, the Station 6 and 7 situations are less clear. The data from those stations point to a loss of PCB from suspended particulates regardless of what the ultimate source of offshore suspended pollutants is. The solubility of the various compounds under consideration are presented in Table 9. Note that the PCB materials are more soluble in water than the benzanthracenes, chrysenes and benzopyrenes and more soluble than the other tetracyclic PAH (fluoranthene and pyrene) as well. PCBs do have a great affinity for solid surfaces with their adsorption strongly linked to the organic carbon content of adsorbing substances (Griffin and Chiang, 1980). Thus, non-recent (hours to days) resuspension of waste deposit material offshore followed by aqueous transport in areas of low suspended matter may result in the differential partitioning of PCB and PAH into the dissolved phase with dissolution affecting phenanthrene>PCB$\geq$ fluoranthene/pyrene>benzanthracene/chrysene>benzopyrenes. Apparent decoupling of PCB and "heavy" PAH may then be the result of transport away from an offshore source followed by selective PCB dissolution.

Chemical distributions within the size fractions of the two waste deposits are quite revealing and suggest differential potential chemical impact of resuspended size fractions of the sewage sludge but relatively little chemical differentiation between dredge spoil size particles. There is, however, little indication of PCB/PAH/coprostanol decoupling

TABLE 9

APPROXIMATE COMPOUND SOLUBILITIES

COMPOUND	SOLUBILITY (μg/l)	REFERENCE
PAH		
Phenanthrene (Z=-18)	∿1000	May, 1980
Fluoranthene (Z=-22)	∿ 220	May, 1980
Pyrene (Z=-22)	∿ 150	May, 1980
Benzanthracene (Z=-24)	∿ 10	May, 1980
Chrysene (Z=-24)	∿ 2	May, 1980
Benzopyrenes (Z=-28)	∿ 0.5	-- (inferred)
PCB		
Aroclor		
1016 (Cl_2,Cl_3,Cl_4)	906	
1242 (Cl_2,Cl_3,Cl_4,Cl_5)	703	Griffin and Chian (1980)
1221 (Cl_1,Cl_2,Cl_3)	3516	
1254 (Cl_3,Cl_4,Cl_5)	∿ 70	

Z derived from molecular formula C_nH_{2n+Z}

within the waste deposits as is suggested from the water column particulate data. The chemical/size fraction picture in sewage sludge is dominated by the strong petroleum PAH/silt association borne out by the presence of smaller aromatic hydrocarbon molecules (napthalenes and fluorenes) and the strong pyrogenic PAH/clay relationships borne out by the heavier PAH components. Dibenzothiophene appears to represent a transitional molecular family as nearly equal silt and clay associations are evident. Marked PCB size associations are observed in the sewage sludge as well, associations obscured by more commonly employed bulk sediment analyses (Figure 11).

The association of PCB and PAH compounds with size fractions within dredge spoil are entirely different from their behavior in sewage sludge. There is no PCB chemical preference (PCB) for a particular size fraction, concentrations associated with clay being greatest due to greater particle surface area. Furthermore, the PCB compositions of all size fractions within the dredge spoil mud are identical. The sand layer of the dredge spoil core exhibits some association of the heavier PCBs and the heavier PAH for the coarser (sand) fraction. The smaller amount of silt in this layer, however, is strongly linked to absolute PCB levels and to all petroleum inputs.

As stated by Freeland and Swift (1978) the regional fine sediment budget of the estuarine/New York Bight/shelf system is very complex. An exchange of suspended material between the "turbid water masses of the inner shelf, New York Harbor and associated bays . . ." occurs through every tidal cycle. Duedall et al. (1979) describes the tidal currents through the lower bay complex and estuary mouth as reaching 3 knots, quite sufficient for resuspending material in the mouth area and driving it landward or seaward depending on the tidal vector. Ocean dumping events do not have a profound lasting (>6-12 hours) effect on the region's suspended particulate organic chemistry as the bulk of the dumped material is rapidly sedimented. However, the long-term residence of fine particulates in the water column from ocean dumping events, hitherto undetected due to extreme patchiness or lack of instrumental sensitivity cannot be ruled out as impacting the trace organic chemistry of the Bight.

Storm-induced resuspension may play the dominant post-dumping role in introducing resuspended waste deposit sediments into the Bight water column. Indeed a substantial storm impacted the study area on 21 August, prior to much of the sampling. Thus the existence of "patches" of PAH-rich material with elevated PCB levels offshore may be attributable to storm-induced resuspension phenomena.

The fluxes of suspended organic chemical-bearing particulates thus may be summarized as follows:

1. In the New York Harbor/Hudson River area, PCB-rich sediment is resuspended and transported further down the estuary. There is no indication from our data that this material is transported unaltered out of the estuary.

2. Sewage effluent material is confined to surface layers in the inner harbor/river area and may be transported substantial distances seaward as part of a classical two-layer estuarine stratification system.

3. Resuspended particulates rich in PAH and PCB are transported from the inner Bight apex through the mouth of the estuary (Rockaway Point) during flood tide.

4. PAH-rich, PCB-depleted particulates resuspended from dredge spoil deposits are found in mid and bottom waters in patchy distributions in the Bight apex.

5. Resuspended sewage-associated particulates may be transported down the Hudson Valley in mid and bottom waters.

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