

NEW YORK BIGHT BENTHIC  
SAMPLING SURVEY:  
COPROSTANOL, POLYCHLORINATED  
BIPHENYL AND POLYNUCLEAR  
AROMATIC HYDROCARBON MEASURE-  
MENTS IN SEDIMENTS

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1. Administrative Information

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ERCO (Energy Resources Co. Inc.),

1.3 Present Funding Level

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New York Bight Benthic Sampling Survey:  
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None

1.6 Reports or Publications

None at present

1.7 NEMP Work Monitor

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1.8 Duration of Work

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## 2. Objectives

The goal of this effort was to perform analytical measurements of the coprostanol and polychlorinated biphenyl (PCB) content of 40 surface sediment samples from the New York Bight and to analyze 10 selected samples for their polynuclear aromatic hydrocarbon (PAH) content.

The presence of coprostanol, a fecal steroid, has been utilized previously as an indicator of municipal sewage contamination in a given region (Hatcher and McGillivray, 1979; Hatcher et al., 1977; Escalona et al., 1980; Kanazawa and Teshima, 1978).

PCB compounds are ubiquitous contaminants of estuarine and near-shore sediment (e.g., Saylor et al., 1978; West and Hatcher, 1980) as are PAH (e.g., Windsor and Hites, 1979); these two categories of pollutants include both toxic and mutagenic compounds.

The organic chemical makeup of these sediments, along with the important support measurements of total organic carbon and grain size determinations, define the geochemical pollutant sources in the area and can thus be used to measure changes in the nature and quantity of these compounds with time.

## 3. Summary of Activities and Rationale

### 3.1 Sampling Activities

Forty (40) samples (100 g) of surface sediment from New York Bight were provided by NOAA/NMFS personnel for analysis. Samples were collected at those stations indicated in Section 6, Figure 6-1 and Table 6-1. Samples were collected during R/V George B. Kelez cruise no. KE-FRC-07/08-80, 28 July to 5 August 1980.

### 3.2 Analytical Methodology

All samples were processed (i.e., extracted and fractionated) according to the ball-mill tumbler method of Brown et al. (1979) as modified for the shaking table by Boehm et al. (1980) and adapted for coprostanol analysis using the method of Hatcher and McGillivray (1979). This latter method involves isolation of the  $f_3$ , or polar, fraction from a silica gel column in a methanol eluate followed by drying and silylation using N,O-bis (trimethyl silyl) acetamide in pyridine solution, to form the trimethyl silyl ethers of the alcoholic compounds (e.g., sterols).

The entire analytical scheme is illustrated in Figure 3-1. This scheme allows for simultaneous preparation of extract fractions for PCB and PAH analysis. PCB analyses were performed by electron capture gas chromatography (EC-GC), PAH analysis by glass capillary gas chromatography/mass spectrometry ( $GC^2/MS$ ), and sterol analysis by  $GC^2$ .

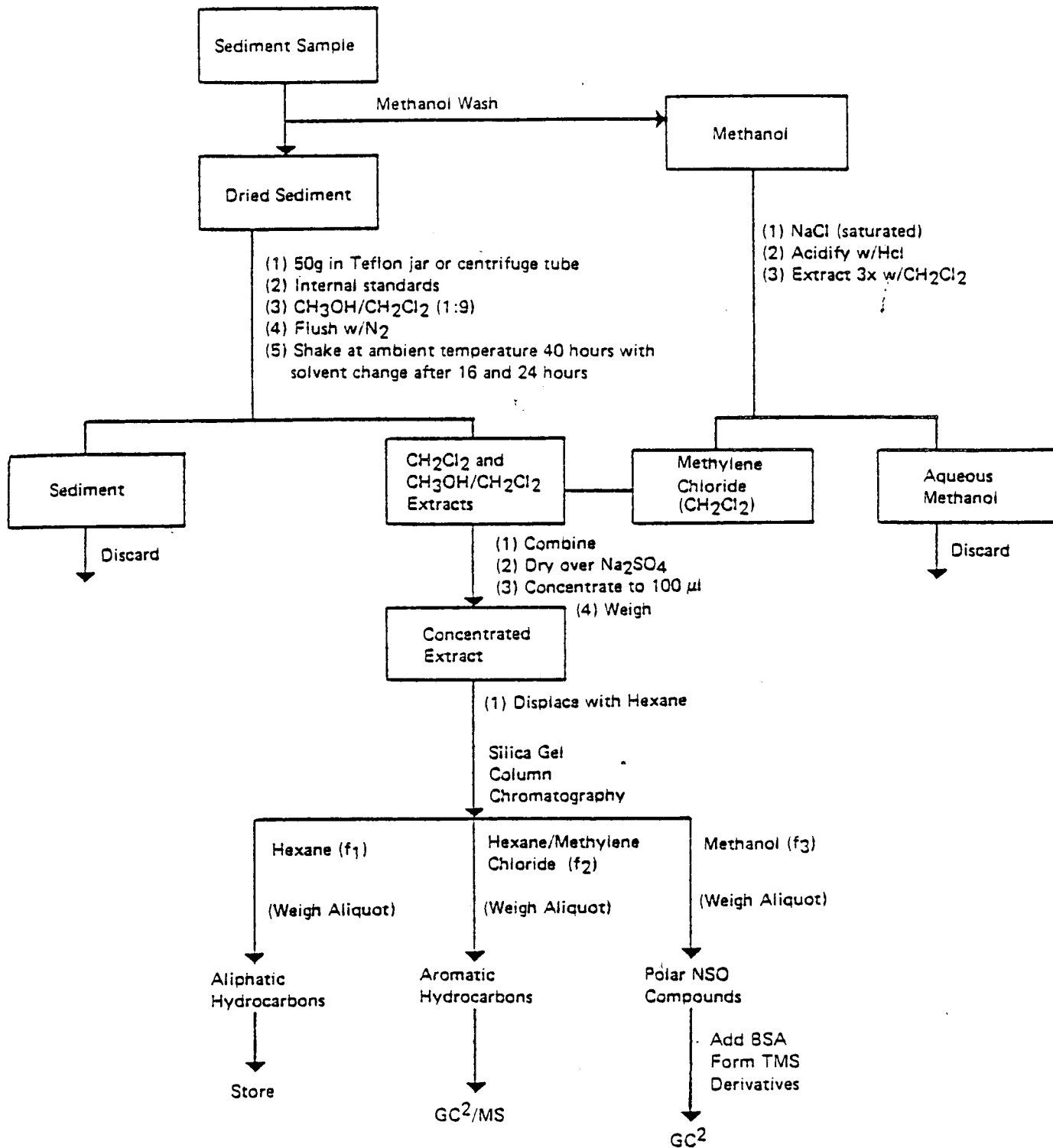


Figure 3.1. Analytical scheme for sediment samples.

#### 4. Summary of Findings

This section presents the absolute levels and distributions of PCB, coprostanol and PAH compounds in the sediment samples along with a presentation of several key parameter ratios and their use.

##### 4.1 Polychlorinated Biphenyls

PCB concentrations ranged from not detectable ( $< 0.1$  ng/g) to 160 ppb (=ng/g) at Station NYB-8 (Table 4-1). This range of values compares well with those of West and Hatcher (1980) from the New York Bight Apex ranging from 0.5 to 2,220 ppb. The 2,220 ppb value is associated with the sewage sludge dumpsite in the region (West and Hatcher, 1980). The comparable values here are from Stations 6 and 7 (55 and 32 ppb, respectively), which may indicate that the heart of the sludge deposit was not sampled. Most of the West and Hatcher values of surface sediments fall in the 0.5 to 360 ppb range. Station 55 from the Kelez survey, a sample from which was not analyzed, most closely approximates the location of the West and Hatcher (1980) maximum concentration.

Previously obtained results from this laboratory indicated that maximum PCB levels in sewage dumpsite samples were  $\sim 1,300$  ppb (Scott, Perry and Boehm, unpublished data).

The nature of the PCB composition most closely resembles an Aroclor 1016 distribution, consisting mainly of di- and trichlorobiphenyls, and to a lesser extent Aroclor 1254, consisting of tri-, tetra-, and pentachlorobiphenyls. The composition of a typical sample (NYB-8) is shown in Figure 4-1.

A contour map (Figure 4-2) illustrating PCB distributions in the study region indicates that two main sources dominate: (1) dredge spoil deposits and (2) sewage sludge. Surely direct transport out of the estuary of PCB material is occurring, but levels are low and sediment distributions caused by direct transport are masked by the greater influences of (1) and (2). Elevated concentrations are generally confined to two point sources as indicated except for some transport down the Hudson canyon (Station 13) and some apparent nearshore distribution along the New Jersey coast of an unknown nature.

##### 4.2 Coprostanol

The amounts of the fecal steroid coprostanol in the surface sediment (Table 4-1) ranged from not detectable ( $< 0.01$  ppm) to 11 ppm. Hatcher and McGillivray (1979) reported concentrations in the area from 0.06 to 5.2 ppm. The importance of sewage-derived organic matter relative to other inputs can be examined using the ratio of coprostanol to total measured sterols (=coprostanol + sitosterol + cholesterol + cholestanol). This

Table 4-1. Polychlorinated Biphenyl and Coprostanol Content of New York Bight Sediments.

Station	PCB (ppb)	Coprostanol (ppm)	Coprostanol/PCB	Coprostanol/Total Steroids
NYB 1	31	1.2	40	0.24
2	34	1.6	50	0.30
3	29	0.7	20	0.26
4	26	0.03	1	0.02
5	120	0.13	1	0.02
6	55	11	200	0.74
7	32	5.6	170	0.47
8	160	0.10	1	0.04
9	28	1.9	70	0.38
10	17	0.26	20	0.20
11	9.2	2.3	250	0.41
12	2.0	0.03	20	0.01
13	17	0.10	6	--
14	nd	0.07	--	0.02
15	nd	0.07	--	0.03
16	6.6	0.23	30	0.03
18	66	0.14	2	0.03
19	20	0.06	3	0.01
20	0.5	0.02	4	0.01
21	nd	0.07	--	0.06
22	0.7	0.31	400	0.25
24	1.4	0.01	7	--
25	0.4	0.01	30	0.02
26	nd	0.01	--	0.01
27	nd	nd	--	--
28	3.8	0.09	20	0.13
30	nd	0.29	--	--
31	nd	nd	--	--
33	4.0	0.04	10	0.03
34	nd	0.06	--	0.07
37	nd	0.01	--	0.04
38	nd	0.01	--	0.03
39	nd	0.15	--	0.12
40	71	0.13	2	0.02
41	1.0	0.01	10	0.07

Table 4-1 (Cont'd.)

Station	PCB (ppm)	Coprostanol (ppm)	Coprostanol/ PCB	Coprostanol/ Total Steroids
42	7.2	0.01	1	0.005
43	nd	0.01	--	--
44	3.5	0.01	3	0.02
LIS 8	52	0.27	5	0.06
88	9.5	1.0	100	0.12

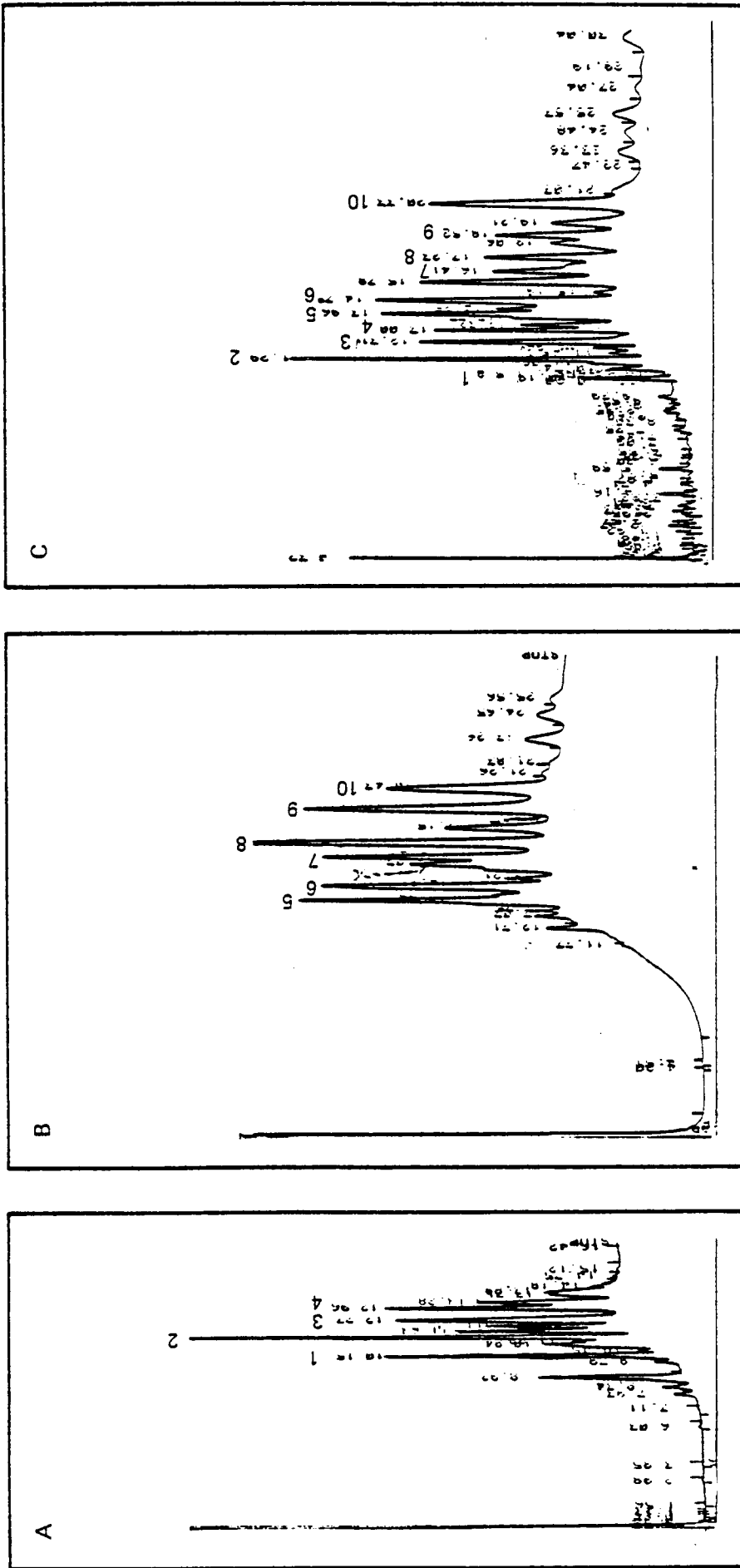


Figure 4.1. Electron capture gas chromatograms of PCB composition in surface sediment; A — Aroclor 1016 Standard; B — Aroclor 1254 Standard; C — representative sediment sample.



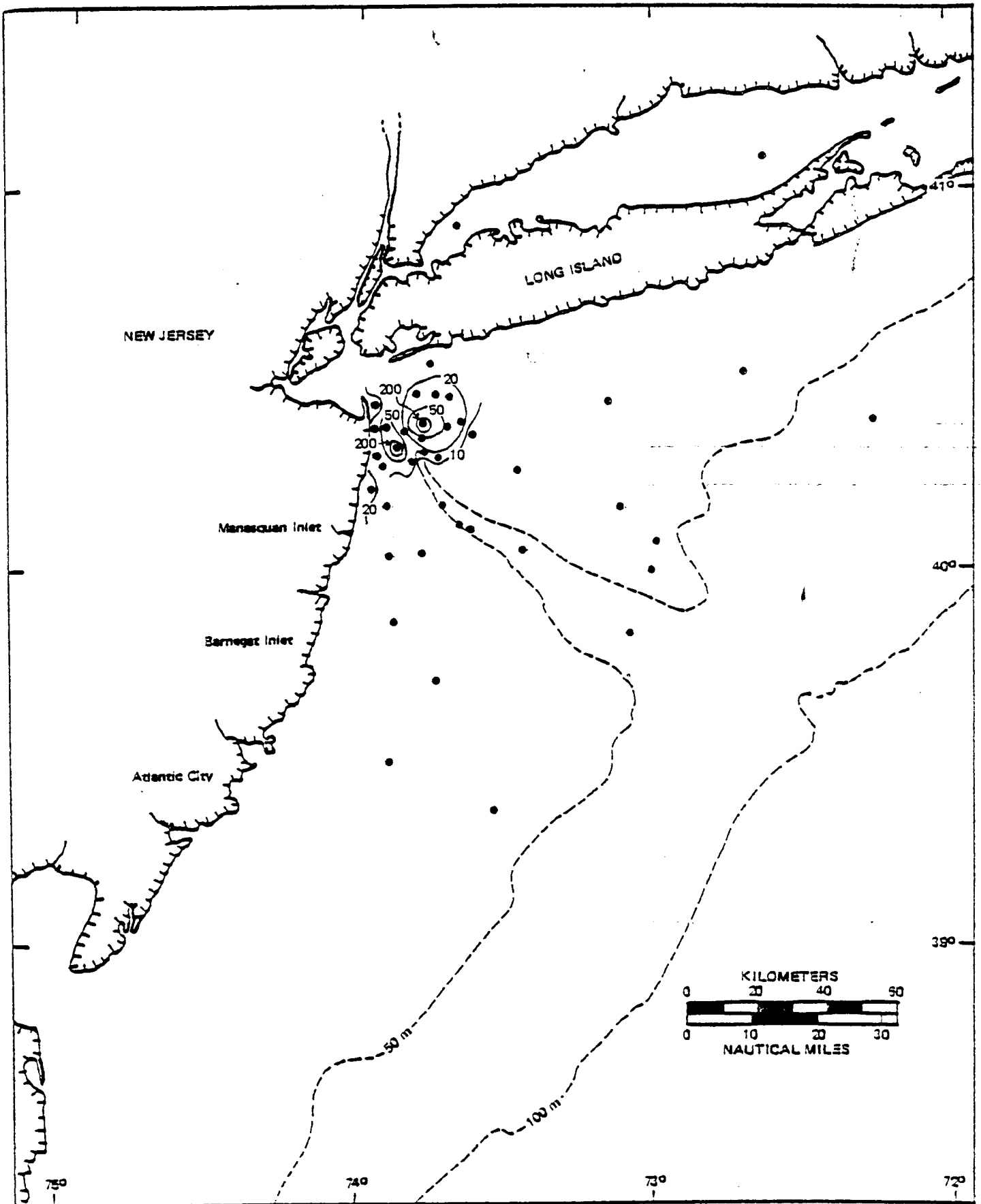


Figure 4.2. PCB concentration contours (concentrations in ppb).

ratio in sewage sludge is approximately 33% (Hatcher and McGillivray, 1979). Thus a scale of 0 to 33% should define the relative sewage versus other organic inputs to the sediments. The percentage of coprostanol in clean sands (e.g., stations 42, 12, 19, 20, and 26) from stations within the region is generally about 1%, indicating low inputs of sewage-derived organics, according to this scheme, while Stations 6 and 7 from the sewage dump site contain almost pure sewage.

Note that there appears to be a systematic analytical difference between our "percent coprostanol" scale and that of Hatcher and McGillivray (1979). Values reported here range from 0 to 74% coprostanol, thus establishing a 0-74 scale comparable to 0-33 of Hatcher and McGillivray (1979) for defining steroid inputs. The reason for this difference undoubtedly lies in the fact that "total steroids" for Hatcher and McGillivray included three other sterols, brassicasterol, campesterol, and stigmasterol.

However, the values reported in Table 4-1 do define a percent sewage input scale, assuming that the 74% value is that found in the sludge itself (not analyzed here).

Another potentially useful parameter is that of the ratio of coprostanol to PCB. PCB are, of course, found in both dredged material and sewage sludge. The absolute quantity of coprostanol in the sewage material itself is unknown. Coprostanol/PCB ratios in sediments in or near the sewage dump site (e.g., Stations 6,7) are ~200. Other stations apparently strongly influenced by sewage-related deposits are Stations NYB 11, 22, and 9. Station 22 contains low quantities of both PCB and coprostanol, but appears to be influenced by sewage. Several other samples (NYB 1, 2, 3, 10) are suspected to be influenced by sewage-derived organic matter by virtue of the elevated percent coprostanol measurement although less strongly implicated by the coprostanol/PCB ratio.

Of note is the fact that several other stations (NYB 4, 5, 8, 18; LIS 8) contain somewhat equivalent PCB concentrations to those influenced by sewage, but by virtue of low coprostanol/PCB and percent coprostanol values (Table 4-1) are linked with another source material; i.e., dredge spoil. The highest PCB concentration of 160 ppb is found in Station 8, in close proximity to the dredge spoil dumping area. Station 5, although seemingly close to the sewage material, is composed of primarily dredging material instead, by this criterion.

Clearly, analyses of both source material, sewage sludge and dredge spoil, are needed to firm up these diagnostic ratios.

Contours (Figure 4-3) of coprostanol concentrations in the sediment strongly suggest two sources or components of the coprostanol distribution: (1) the sewage sludge deposit, and (2) transport of sewage related organics directly from the New York Harbor area via resuspension and transport of outer and inner harbor material.

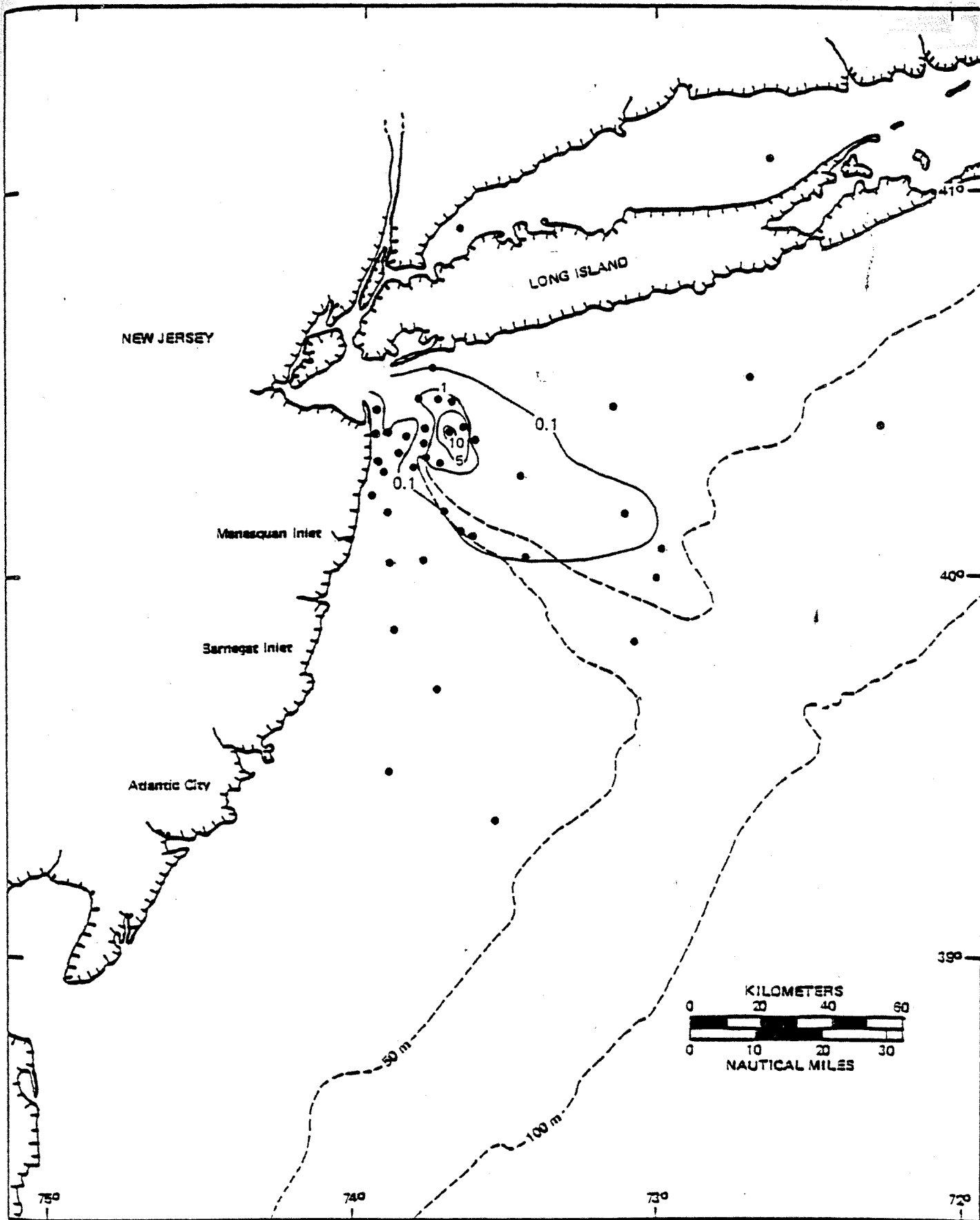


Figure 4.3. Concentration contour map of coprostanol levels in sediments (concentrations in ppm).

### 4.3 Polynuclear Aromatic Hydrocarbons (PAH)

PAH compounds are widely distributed in the study region (Table 4-2). PAH compound levels are greatest in the LIS 8 sample and, in the New York Bight, are greatest at NYB 1: LIS 8>NYB 6>NYB 9>NYB 4>LIS 88=NYB 8>NYB 14 = NYB 15>NYB 31>NYB 26. Concentrations are quite patchy in the inner Bight region and decrease away from the Bight apex along the Hudson Canyon. Concentrations are lowest on the shelf on either side of the apex (NYB 26 and 31). Concentrations of total PAH compounds at LIS 8 compare with the extremely high value found in Charles River (Massachusetts) sediment (Windsor and Hites, 1979).

To our knowledge these data represent the most detailed and analytically comprehensive set of PAH data in New York Bight sediments.

Precise sources of PAH compounds to the sediments are difficult to discern. However, a mixed source represented by petroleum material (most likely originating from New York Harbor and transported offshore) and combustion products (either through storm water runoff or direct fallout of airborne particulates) seems most likely. Petroleum sources are indicated by a high amount of alkylated ( $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ) naphthalenes, phenanthrenes, fluorenes, and dibenzothiophenes relative to the parent (unsubstituted) compounds (i.e.,  $C_0$ ) (Youngblood and Blumer, 1975). Combustion sources are indicated by an equal or larger amount of  $C_0$  compounds relative to  $C_1$  and  $C_2$  plus large relative quantities of the larger PAH compounds (fluoranthene and pyrene [4 rings], benzofluoranthene and the benzopyrenes [5 rings]). Several of the samples contain significant levels of anthracene, known to be abundant in combustion products of coal (Lee et al., 1977). Recent studies by Tripp et al. (1981) indicate that PAH compounds from petroleum may be difficult to distinguish from those from uncombusted coal, thus complicating the source evaluation of PAH to these sediment samples.

TABLE 4-2  
POLYNUCLEAR HYDROCARBON CONTENT OF NEW YORK BIGHT SEDIMENTS (10<sup>-9</sup> g/g = ppb)

COMPOUND	STATION												
	2637 NYB-4	7508 NYB-6	2466 NYB-7	2468 NYB-9	2832 NYB-14	7756 NYB-15	2874 NYB-26	2365 NYB-31	3067 LIS-8	3117 LIS-88	LOMERA <sup>a</sup> BAY	CHRIS <sup>a</sup> BAY	OUTER <sup>a</sup> BIGHT
Naphthalene (N)	26	25	17	43	<1	1.1	<1	<1	110	10	-	-	-
C <sub>1</sub> N	120	84	87	88	1.4	2.2	<1	1.2	230	16	-	-	-
C <sub>2</sub> N	360	220	200	190	3.9	3.6	<1	<1	510	24	5	200	-
C <sub>3</sub> N	460	250	180	170	4.2	4.0	<1	1.1	600	35	10	100	-
C <sub>4</sub> N	600	210	170	170	1.2	1.1	<1	<1	270	19	-	9	-
Total N	1,566	789	654	661	10.7	12.0	<5	<5	1,720	104	-	-	-
Dibenzothiophene (DBT)	51	84	6	21	<1	<1	ND	ND	250	17	-	-	-
C <sub>1</sub> DBT	62	180	21	71	<1	1.4	<1	<1	440	22	1	30	-
C <sub>2</sub> DBT	150	310	36	140	2	1.2	ND	<1	630	35	1	20	-
C <sub>3</sub> DBT	130	260	30	360	1	12	2.2	6	800	230	1	20	-
Total DBT	393	834	93	592	4	14.6	3	8	2,120	304	-	-	-
Acenaphthene	26	20	52	27	<1	<1	ND	<1	33	4	-	40	-
Biphenyl	7.1	48	4	24	<1	<1	ND	<1	210	5	-	-	-
Anthracene	200	80	4	25	1	<1	ND	<1	900	10	-	-	-
Fluorene (F)	41	75	7	34	1.3	1.2	<1	1.2	420	17	-	40	<1
C <sub>1</sub> F	86	150	18	49	1.7	<1	ND	ND	300	14	-	-	-
C <sub>2</sub> F	320	210	53	120	2.6	1.0	ND	ND	410	21	1	-	-
C <sub>3</sub> F	440	220	42	180	<1	ND	ND	ND	800	24	10	-	-
Total F	887	655	120	383	5.6	2.2	<1	1.2	1,930	76	-	-	-

TABLE 4-2 (CONT.)

COMPOUND	STATION													OUTER <sup>a</sup> BIGHT
	2637 NYB-4	7508 NYB-6	2466 NYB-7	2468 NYB-9	2832 NYB-14	7756 NYB-15	2874 NYB-26	2365 NYB-31	3067 LIS-8	3117 LIS-88	LOMER <sup>a</sup> BAY	CHRIS <sup>a</sup> BAY		
Phenanthrene (P)	510	820	53	280	15	16	4.1	10	3,500	170	-	-	<1	
C <sub>1</sub> P	740	980	150	290	14	13	3.5	8	2,460	170	1	300	-	
C <sub>2</sub> P	870	800	150	350	11	10	1.6	ND	2,000	150	2	100	-	
C <sub>3</sub> P	1,080	620	120	410	6.2	4.1	-	ND	1,400	120	2	-	-	
C <sub>4</sub> P	350	210	10	400	4.8	4.2	<1	3	1,200	110	-	20	-	
Total P	3,550	3,430	483	1,730	51.0	47.3	9.2	21	10,500	720	-	-	-	
Fluoranthene	260	1,100	67	370	26	28	6.7	18	5,700	410	-	-	-	
Pyrene	300	1,200	64	410	20	25	7.2	15	6,200	370	-	-	-	
Benzanthracene	130	800	38	320	14	15	3.8	8	4,200	220	-	-	-	
Chrysene	130	600	52	290	21	20	4.4	10	3,000	337	-	-	-	
Benzo(luoranthene	170	1,300	80	1,100	55	90	8.5	19	5,800	850	-	-	-	
Benzo(e)pyrene	74	590	25	270	19	22	3.0	6.6	2,200	360	-	-	-	
Benzo(a)pyrene	100	720	31	240	20	18	3.5	8.3	2,300	300	-	-	-	
Perylene	21	180	9	100	10	10	1.5	2.3	570	150	-	-	-	
TOTAL PAH	7,800	19,500	1,800	9,900	300	300	60	100	62,000	4,100	-	-	-	

<sup>a</sup>From Macleod et al., 1980.

## 5. Interpretation of Findings

The PCB, coprostanol and PAH data sets represent a powerful set of data with which one can monitor changes in both absolute levels and sources of pollutants to the New York Bight. The major sources of these pollutants are easily distinguishable from each other through consideration of the key parameter ratio of coprostanol/PCB and coprostanol/total steroids and potentially through ratios of these chemical components to total organic carbon content of the sediment. PAH concentrations and composition vary as well, with the highest concentrations of total PAH associated with sewage sludge deposits. The main difference between PAH compositions in sewage versus dredge spoils are the greater relative quantities of four- and five-ringed pyrogenic (combustion-related) aromatic hydrocarbons in the former. Those stations associated more with sewage sludge (e.g., Stations 7 and 9) exhibit this pyrogenic source of PAH (Table 4-2).

Thus while the organic pollutant assemblage is quite complex in this region, compound groupings fall roughly, but notably, into monitorable source functions, as was seen in Sections 4.2, 4.2, and 4.3.

While most of the organic pollutants related to ocean-dumping activities are restricted to the Bight Apex and to the Christiaensen Basin in particular, movement of those PCB and PAH and coprostanol compounds out onto the continental shelf (e.g., Stations 28, 33) was detected as was transport of coprostanol and PAH compounds seaward within the Hudson Canyon (Stations 14, 15). The absence of detectable (>0.1 ppb) PCB levels in sediments at Stations 14 and 15 is unexplained.

The relationship of levels of PCB and PAH reported here in the benthic substrate with those in benthic organisms is unknown at present, and the two data sets must be co-interpreted. However, Boehm (1980) has explored levels of these compounds in species of finfish and have determined that those silver hake and flounder species obtained in the Bight area do contain higher levels of these pollutants. PCB compositions, though, are different, with most resembling Aroclor 1254 in fish but composed of both 1016 and 1254-type formulations in the sediment. Resuspension of bottom sediment and movement in the water column, thus directly impacting finfish, or resuspension followed by uptake by the prey of the finfish could result in loss of the more soluble 1016 prior to PCB accumulation by finfish.

The sources and transport of polluted sediment, uptake by benthic organisms and final assimilation by higher trophic levels (finfish) all merit both further, more detailed organic biogeochemical study and most importantly coincident data interpretation and synthesis so as to best understand the "biogeochemical system" and hence focus upon the best strategy of monitoring of chemical change in this stressed environment.

6. Inventory of Data

Table 6-1 presents the identity of those sediment samples analyzed and the nature of the analyses performed on each sample.

The locations of the samples are indicated in Figure 6-1.



Table 6-1. Summary of Sediment Samples Analyzed for Organic Contaminants.

Station	Analysis		
	Coprostanol	PCB	PAH
NYB: 1	X	X	
2	X	X	
3	X	X	
4	X	X	X
5	X	X	
6	X	X	X
7	X	X	X
8	X	X	
9	X	X	X
10	X	X	
11	X	X	
12	X	X	
13	X	X	
14	X	X	X
15	X	X	X
16	X	X	
18	X	X	
19	X	X	
20	X	X	
21	X	X	
22	X	X	
24	X	X	
25	X	X	
26	X	X	X
27	X	X	
28	X	X	
30	X	X	
31	X	X	X
33	X	X	
34	X	X	
37	X	X	
38	X	X	
39	X	X	
40	X	X	
41	X	X	
42	X	X	
43	X	X	
44	X	X	
LIS: 8	X	X	X
88	X	X	X

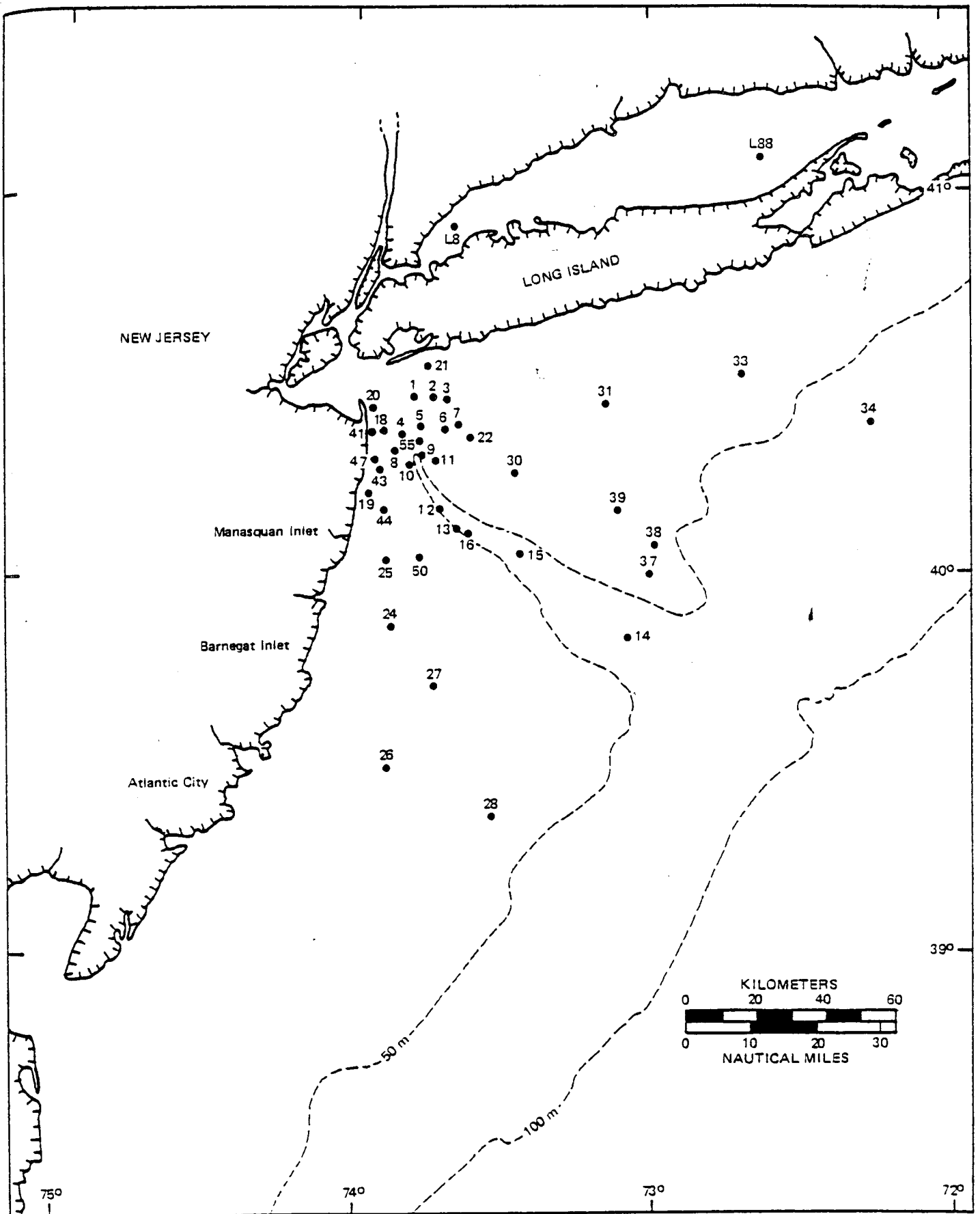


Figure 6.1. Location of samples selected for analysis.

## 7. Statement of Problems

There are several areas for improvement of both the caliber and interpretability of the generated data which would aid greatly in future monitoring work.

The first pertains to source materials and refining our ability to discern the identity of the specific pollutant source in the various samples. Simply stated, samples of dredge spoil(s) and sewage sludge(s) should be obtained for analysis for PCB, coprostanol and PAH compounds to establish not only absolute levels but, perhaps more importantly, the ratio of the various compounds to one another.

Secondly, total organic carbon and grain size measurements should be provided prior to the interpretation of the organic chemistry data, as these parameters are essential for interpretation of geochemical distributions.

Thirdly, PCB measurements should be broken down into specific chlorinated hydrocarbons, i.e., monochloro-, dichloro-, trichloro-, tetrachloro-, pentachloro-, and hexachlorobiphenyls, instead of Aroclor formulations. Such work, involving high-resolution GC<sup>2</sup> and GC<sup>2</sup>/MS, would greatly fine-tune the PCB distribution on the same level of sophistication as the PAH compounds. Thus the ability to monitor changes in absolute concentrations and sources of PCB would be greatly enhanced.

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