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NEMP-III-80-D-0045

GULF AND ATLANTIC SURVEY
(GAS I)

CAPE HATTERAS TO GULF OF MAINE SURVEY FOR SELECTED ORGANIC POLLUTANTS IN FINFISH AND BENTHIC ANIMALS

FINAL REPORT

NOAA CONTRACT NA-80-FA-C-00046

NOVEMBER 10, 1980

Submitted to:

National Oceanic and Atmospheric Administration
National Marine Fisheries Service
Northeast Fisheries Center
Sandy Hook, New Jersey 07732

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1. Administrative Information

1.1 Principal Investigator

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1.2 Organization

ERCO (Energy Resources Co. Inc.),
Environmental Sciences Division

1.3 Present (FY 80) funding

$40,000

1.4 Title of investigation

Gulf and Atlantic Survey (GAS I): Cape Hatteras to Gulf of Maine Survey for Selected Organic Pollutants in Finfish and Benthic Animals

1.5 NEMP cruises

None

1.6 Reports or publications produced

None at present

1.7 NEMP work unit monitor

Dr. John Pearce

1.8 Duration of work unit effort

15 August-1 November 1980

2. Objectives

Selected finfish and benthic epifaunal samples were analyzed for levels of petroleum hydrocarbons (PHC), chlorinated hydrocarbons (polychlorinated biphenyls [PCB], DDT compounds), and polynuclear aromatic hydrocarbons (PAH) contained in edible flesh (i.e., muscle). Samples were collected as part of the Gulf and Atlantic Survey (GAS I) sampling effort undertaken by National Marine Fisheries Service (NMFS) personnel.

The project's goals were to scrutinize a 100-sample subset for the above organic pollutants to (1) establish baseline levels of these compounds in the species examined, (2) identify potential pollutant "hot spots" in the Cape Hatteras to Gulf of Maine region, (3) identify any pollution gradients that may exist from a potential source region through the study area, (4) utilize and evaluate a cost-effective multi-phase analytical chemical approach to sample analysis and data acquisition, (5) evaluate possible sources of observed pollutant distributions within the specimens examined, and (6) make recommendations for future organic chemical monitoring strategies based on the observed results.

3. Summary of Activities and Rationale

3.1 Analytical Strategy

The analytical chemical goals of this investigation focused on four major questions which were linked together into an hierarchical analytical scheme in which the analytical complexity increased as the four successive levels were reached. The analytical questions (levels) were as follows:

1. Which samples contained the detectable levels of petroleum hydrocarbons (PHC)?

2. What are the levels of PCB and DDT compounds?

3. What are the concentations and sources of saturated (f_1) and aromatic (f_2) hydrocarbons in the samples?

4. What are the absolute concentrations of polynuclear aromatic hydrocarbons (PAH) in the tissues?

This sequential scheme (Figure 1) essentially screened a large number of fish samples by solvent extraction followed by rapid sample cleanup and rapid analysis. The initial cleanup was sufficient to yield the gross character of the hydrocarbon composition by glass capillary gas chromatography-flame ionization detector (GC^2/FID) and gross concentration levels of PCB compounds. Those samples containing hydrocarbon compositions resembling those of a possible petroleum origin (Reed et al., 1977; Farrington and

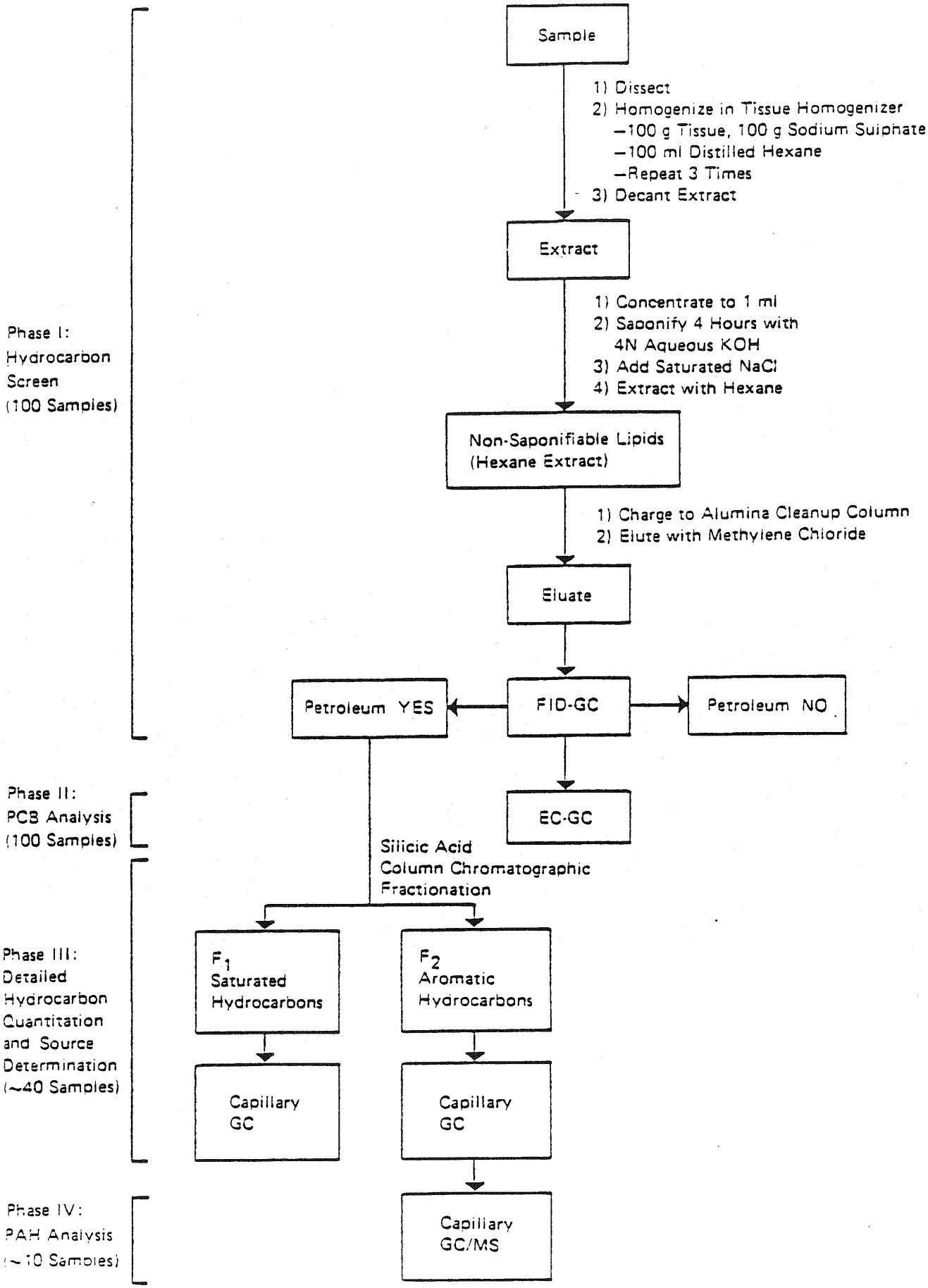


Figure 1. Proposed Multiphase Analytical Scheme.

Meyers, 1975) were subjected to adsorption chromatographic fractionation (silica gel column chromatography) to yield two hydrocarbon fractions. Both of these fractions were analyzed by GC^2. Of those samples fractionated and analyzed, a selected number of samples appearing to contain petroleum-type aromatic hydrocarbons and representative of the various species were further analyzed by glass capillary gas chromatographic mass spectrometry (GC^2/MS) to determine the identity and levels of the PAH compounds.

3.2 Methods and Materials

The detailed sample processing and analytical methods utilized in this study are presented in this section. Samples were obtained on the R.V. Albatross cruise no. AL-80-02, 27 February-5 April 1980, and a 100-sample subset chosen by NMFS scientists from those stations indicated in Figure 2 and Table 3-1.

3.2.1 Hydrocarbon Screening

This analytical task involved the processing (dissection, digestion, extraction, cleanup, analysis) of a large number (100) of fish samples as the first level analytical task. While the residue cleanup and analytical parts of this task were geared towards the rapid generation of information, the extraction techniques used were rigorous so as to allow for the use of the same extracts for quantitative analysis in later tasks. Extraction techniques are based on those of Warner (1976).

Samples consisted of from 1 to 10 individual specimens of those fish species shown in Table 3-1. Muscle tissue from each specimen was obtained, after removal of the surface skin, by dissection with solvent-rinsed stainless steel utensils. A total of approximately 100 g (wet weight) of tissue were thus obtained. A small aliquot of this tissue was obtained for dry weight determination. The tissues were introduced to 150 ml, 10 N aqueous KOH in a 500-ml Teflon jar. Internal quantification standards of saturate (androstane) and aromatic (fully deuterated anthracene, hexamethyl benzene, and 9-phenylanthracene) hydrocarbons were spiked to the aqueous digestion mixture. The jars were sealed with threaded Teflon lids and the mixture allowed to digest at room temperature (25° C) for 24 hours.

The digestate containing the saponified lipids and nonsaponifiable lipids (e.g., hydrocarbons) was transferred to a 1-liter separatory funnel where 75 ml saturated NaCl were added and the mixture extracted three times with 75 ml distilled hexane. The hexane extracts were isolated, combined, and centrifuged to remove any emulsions present. The extracts were concentrated to approximately 0.5 ml and were resaponified (1.0 ml aqueous 10 N KOH; 9.0 ml methanol) in a closed centrifuge tube at 100° C to complete the conversion of lipids to alcohols and fatty acid salts. The saponification mixture was then extracted with three 10-ml hexane portions which were dried over pre-extracted sodium sulphate and concentrated by rotary evaporation to 0.5 ml.

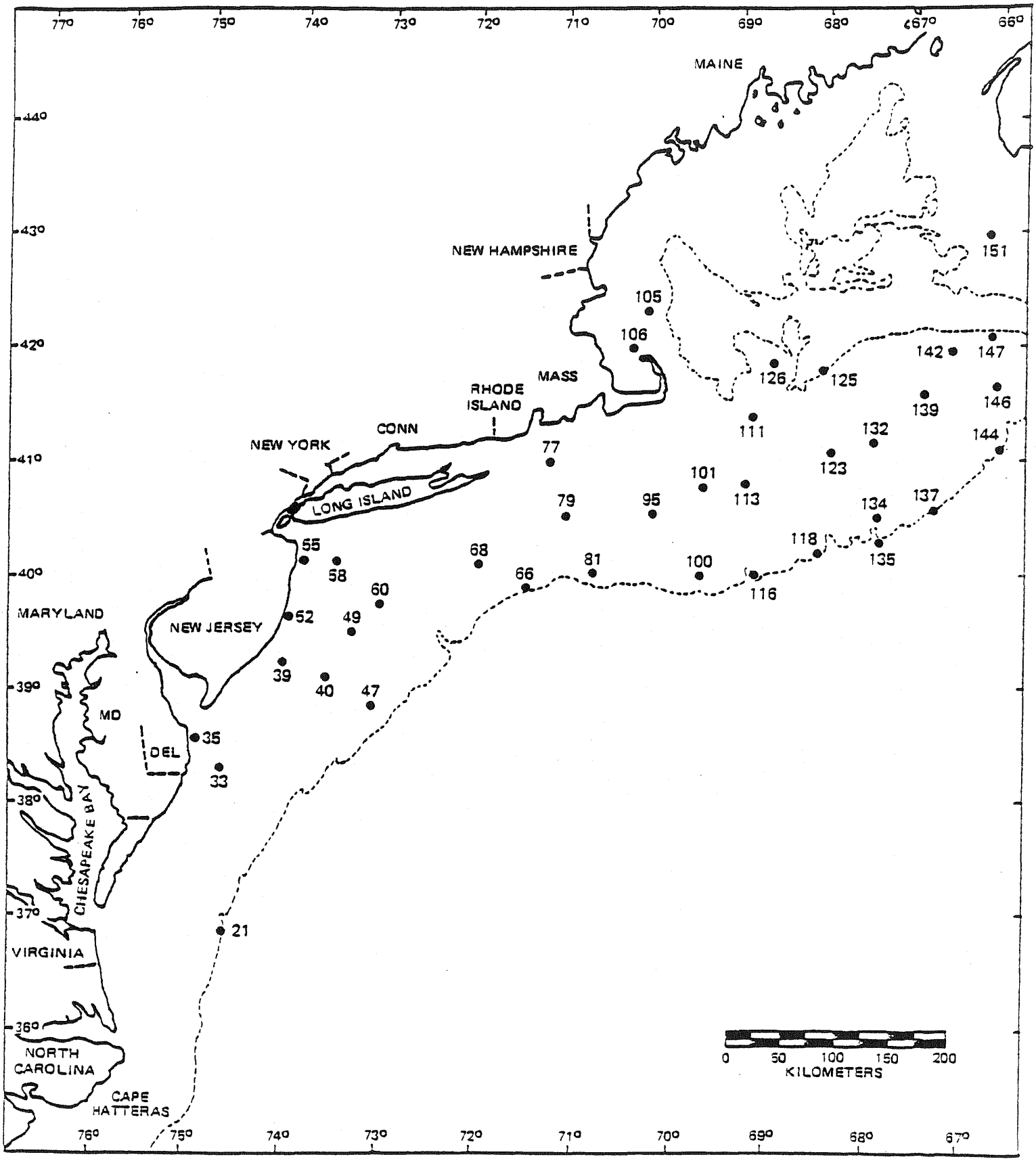


Figure 2. Map of Sampling Locations for Petroleum Hydrocarbon and PCB Analysis.

TABLE 3-1

SUMMARY OF FISH SPECIES ANALYZED

SPECIES	NO. OF STATIONS	STATION LOCATIONS
Silver Hake	14	33, 39, 40, 47, 55, 60, 66, 68, 100, 118, 125, 126, 137, 157
Red Hake	14	21, 33, 35, 47, 60, 66, 111, 116, 118, 125, 126, 135, 137, 157
Yellowtail Flounder	16	40, 49, 55, 58, 60, 68, 77, 79, 95, 101, 106, 123, 132, 139, 144, 146
Winter Flounder	13	52, 55, 58, 77, 95, 101, 105, 113, 123, 134, 139, 142, 157
Windowpane Flounder	8	33, 39, 40, 77, 79, 95, 101, 116
Four Spot Flounder	4	60, 100, 116, 118
Summer Flounder	1	81
American Dab	4	105, 106, 111, 125
Haddock	7	105, 111, 113, 123, 132, 139, 147
Cod	5	101, 105, 113, 123, 142
Skate	2	95, 116
Scallop	1	47
Rock Crab	1	35
Lobster	2	47, 79

A deactivated alumina column cleanup was employed to obtain an eluate suitable for GC^2 analysis. The 0.5-ml hexane extract containing the nonsaponifiable lipids was charged to a column of 6.5 g deactivated (7.5% water) alumina overlying 1 g of sodium sulphate in a 1-cm (i.d.) glass column. Twenty-five (25) ml of hexane are used to eluate a single fraction containing saturated and aromatic hydrocarbons and PCB compounds.

The single fraction was then analyzed by GC^2. An automatic sampler was used to inject 1 µl in the splitless mode into an HP 5840A reporting GC equipped with a 30 m SE-30 (0.25 mm i.d.) fused silica glass capillary column. Screening was achieved by temperature programming the column from 40° C to 275° C at 5°/min.

3.2.2 Chlorinated Hydrocarbons (PCB, DDE)

Chlorinated hydrocarbons were analyzed by electron capture gas chromatography using a ^{63}Ni EC detector (GC/ECD). An aliquot of the single hexane eluate was chromatographed using a 3% SP 2250 packed glass (1/4-in o.d.) column, temperature programmed from 130° C to 230° C at 8°/min and held at the upper temperature for 20 minutes. PCB and DDE were quantified using an external standard calibration curve. PCB compounds, measured as Aroclor 1254 (Figure 3) were quantified by measuring and averaging the areas of the four component peaks indicated and comparing to the standard curve.

As the saponification reaction will convert DDD and DDT to DDE, the "DDT family" or ΣDDT was measured as a single component, DDE.

3.2.3 Saturated and Aromatic Hydrocarbons

Those extracts of samples screened positively (i.e., containing indications of PHC content; Reed et al., 1977; Farrington and Meyers, 1975; Farrington et al., 1976; NAS, 1975) were fractionated by silica gel column chromatography (Boehm, 1980) and two fractions containing saturated (f_1) and aromatic (f_2) hydrocarbons were analyzed by GC^2 and quantified using the internal standard technique by which the areas of resolved and unresolved (UCM) components of the samples are compared to that of a known quantity of standard(s) spiked to the initial sample homogenate. Thirty-meter (30-m) fused silica SE-30 (J&W Scientific) capillary columns were used in the analysis.

3.2.4 PAH Analysis

Selected silica gel aromatic fractions (f_2) were analyzed by computerized GC^2/MS to determine the identity and quantities of PAH compounds in the tissues. The presence of aromatic hydrocarbons from 2 to 5 rings were examined by quantitative mass fragmentography.

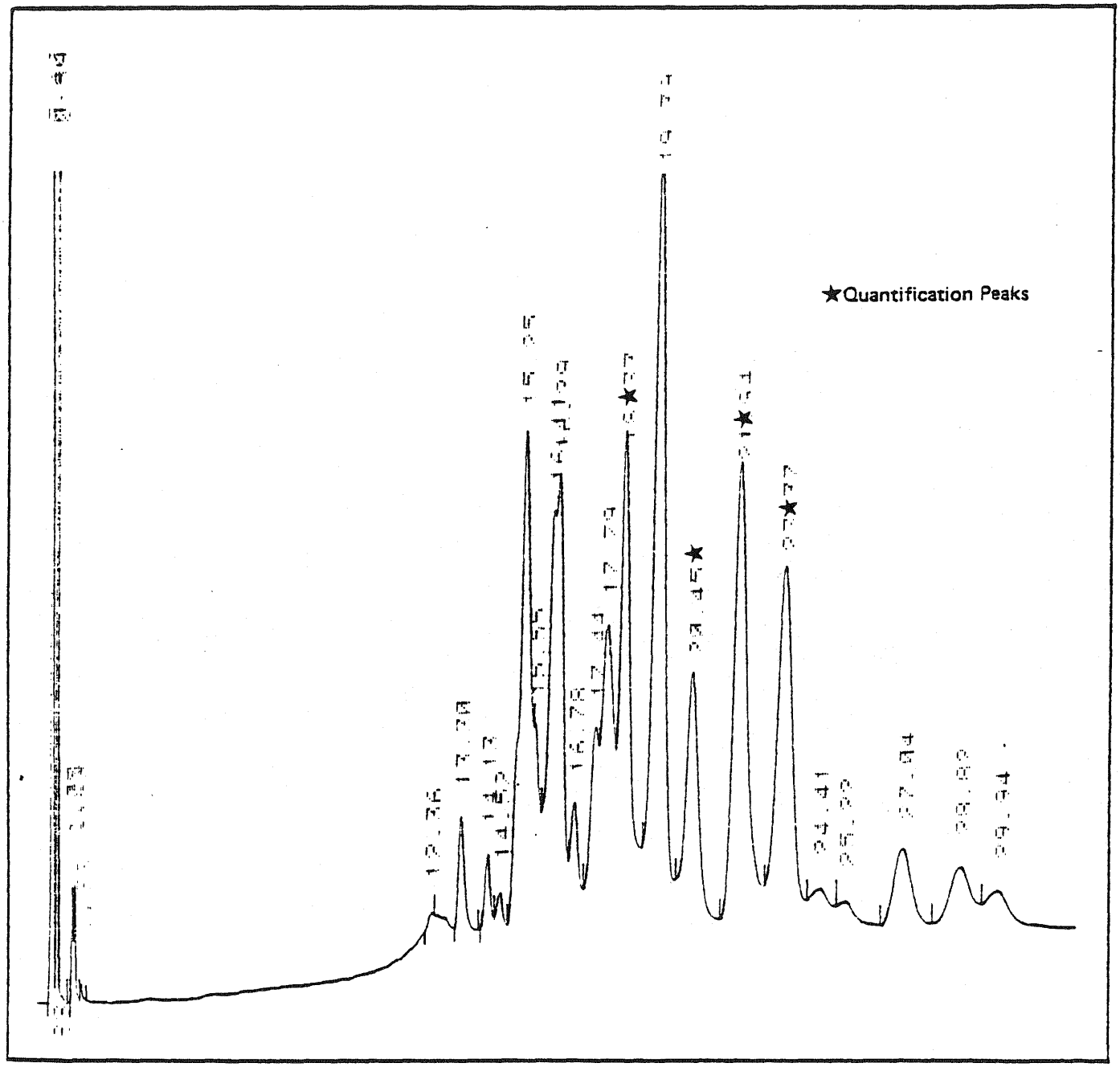


Figure 3. PCB Standard—Aroclor 1254.

4. Summary of Findings

Tabulations of the analytical results of this study are presented in Section 8, Tables 8-1 to 8-13, for each species. All quantitative results are reported on a dry weight basis. One can convert these data to a "fresh weight" (i.e., wet weight) basis by dividing by approximately a factor of five (dry weight/wet weight ~ 0.2).

The results of the petroleum hydrocarbon (PHC) screening are presented in these tables. Where screening results indicated a probable or possible presence of PHC compounds, the sample was fractionated and analyzed quantitatively by GC^2/FID. The combined GC^2/FID results (i.e., $f_1 + f_2$) are presented in the tables along with GC/ECD results for PCB and ΣDDT levels. GC^2/MS was performed on a set of samples selected for their likelihood of containing PAH compounds and/or to obtain a representative analytical set for most species.

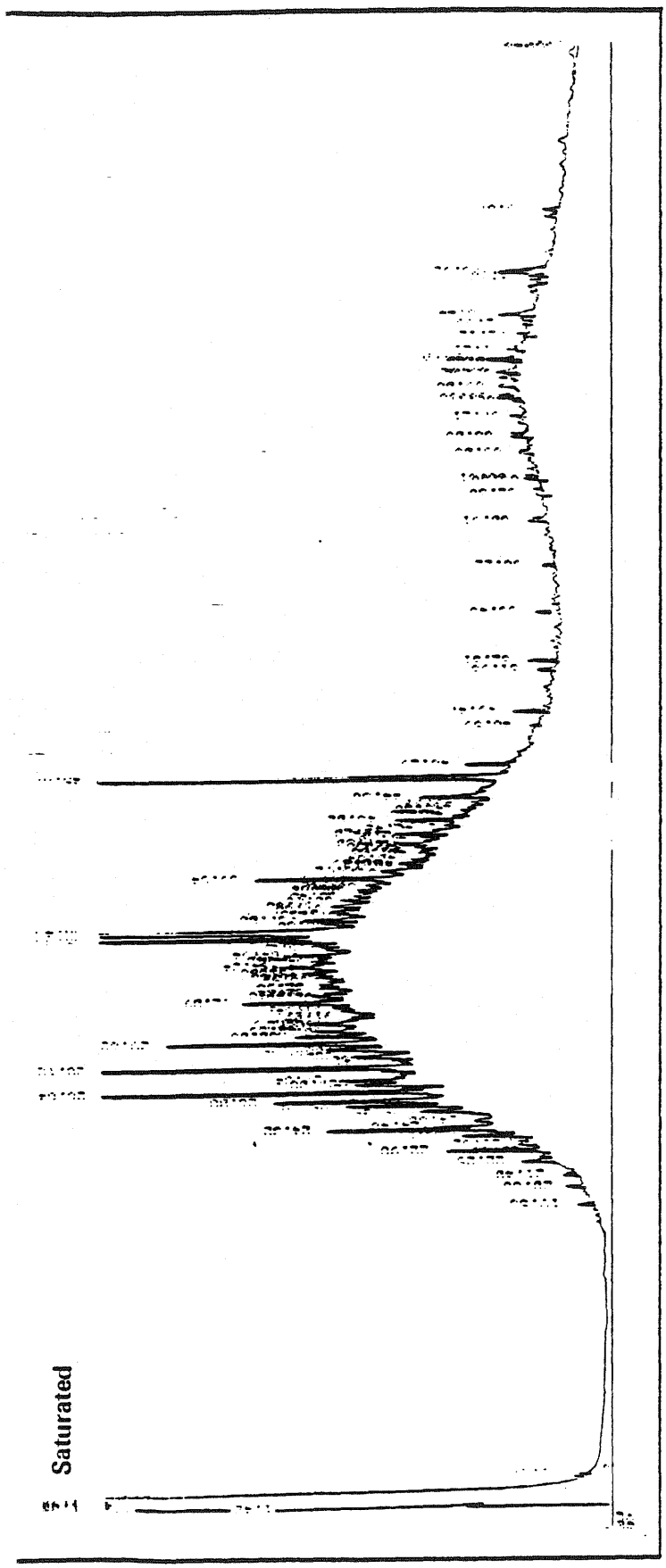
The remainder of this section of the report focuses on the analytical results for each species examined and on the geographical factors involved with each analytical set.

4.1 Silver Hake

Most samples of this species contained detectable levels of total petroleum hydrocarbons (i.e., >1.0 ppm). Concentrations ($f_1 + f_2$) ranged from 6 to 90 µg/g ($\bar{X}_{PHC} = 27 \pm 29$) (see Section 8, Table 8-1). The high incidence (86%) of petroleum hydrocarbon contamination of this species is unique among the various species analyzed.

Several representative gas chromatograms are shown in Figures 4 and 5. The qualitative hydrocarbon assemblage is nearly constant for all PHC-positive samples of this species. The GC^2 distributions illustrate a distribution of PHC compounds in the f_1 (saturate) fraction indicative of either or both of two sources of PHC material: (1) the residues of a crude oil, and (2) anthropogenic inputs of a terrigenous origin. Support for this source evaluation is as follows.

GC^2 traces of tissue samples taken from the Amoco Cadiz spill impact region a year after the spill are comprised of a very similar PHC boiling range distribution; a prominent unresolved complex mixture (UCM) in the $n\text{-}C_{13}$ to $n\text{-}C_{20}$ boiling range and a resolved peak distribution consisting of several prominent branched alkane and isoprenoid compounds. The organisms seem to retain a narrow distribution of the overall crude oil distribution (or alter the crude oil to yield the observed distribution). The f_2 (aromatic) distributions are "typical" of an altered crude oil distribution with the presence of prominent naphthalene, phenanthrene, and dibenzothiophene compound families (see GC/MS discussion below).



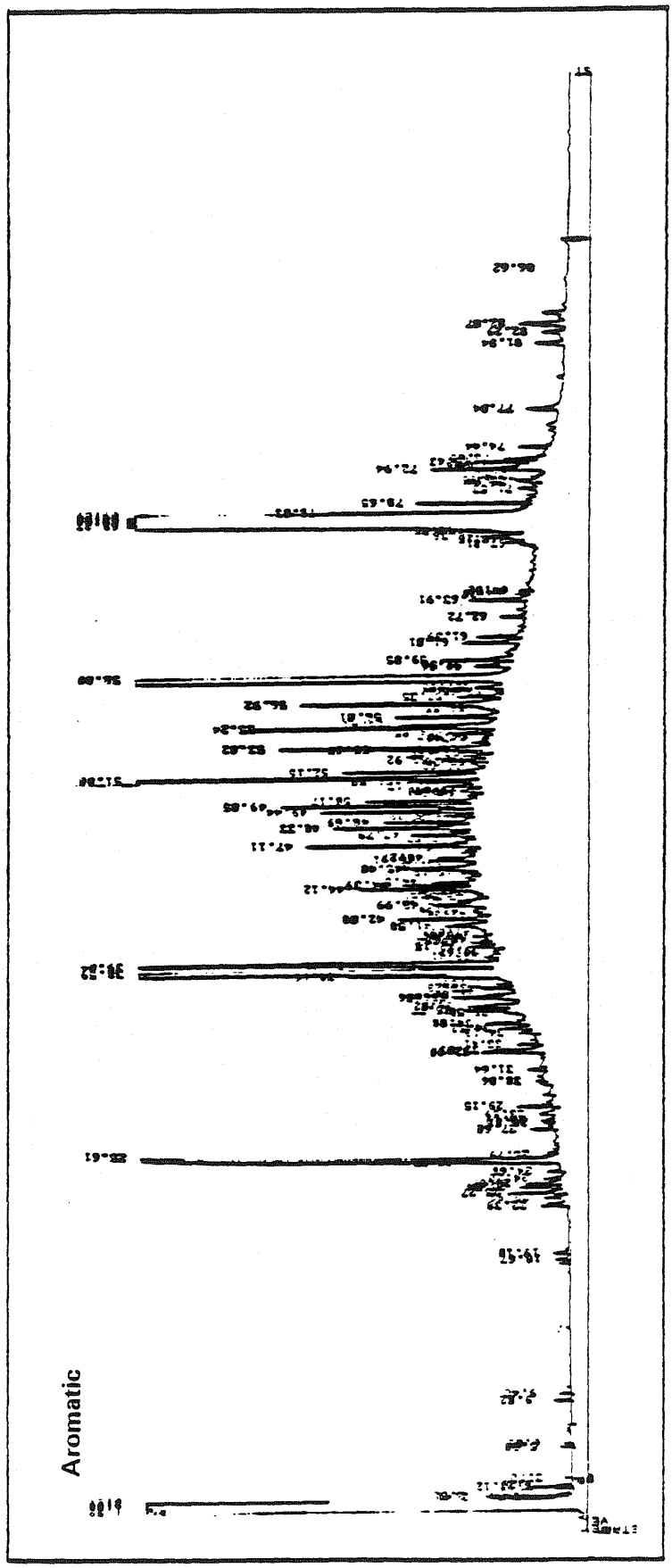


Figure 4. Petroleum Hydrocarbons in Silver Hake (Station 40).

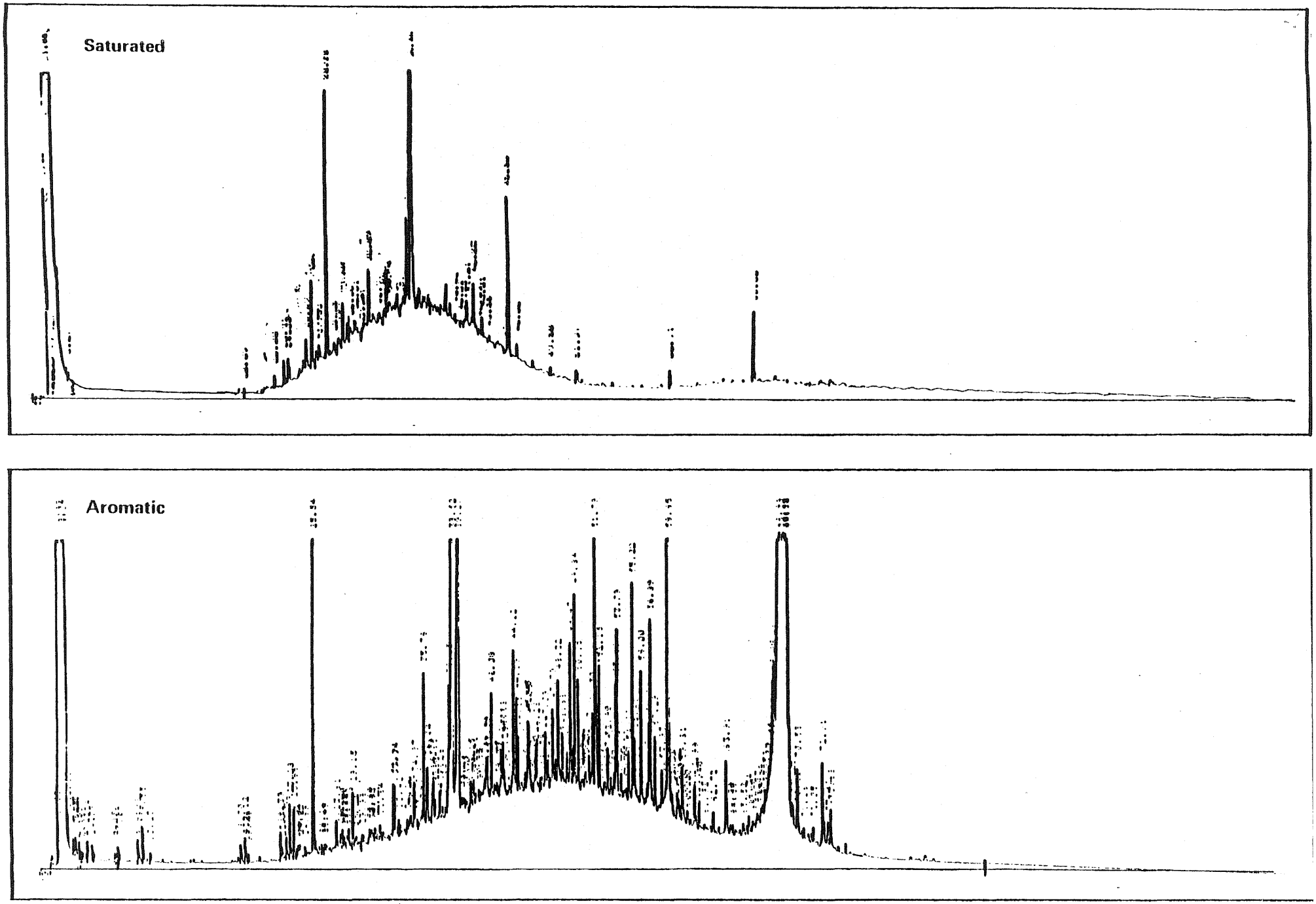


Figure 5. Petroleum Hydrocarbons in Silver Hake (Station 55).

The higher boiling or secondary source input observed in those samples containing higher levels of PHC compounds probably originates in material associated with pelagic tar balls (Boehm, 1980) and/or benthic PHC compounds (Boehm and Quinn, 1977).

The chromatographic distribution of hydrocarbon compounds (saturated and aromatic) were nearly identical to that previously reported (Boehm and Barak, 1979) for this species. Hydrocarbon concentrations, reported here in the range of 6 to 90 ppm (dry weight), were similar to those previously determined (10 to 40 ppm; Boehm and Barak, 1979).

Those samples scrutinized for their PAH content by GC/MS (Table 4-1) contain primarily compounds in the naphthalene (2 ring), phenanthrene (3 ring) and dibenzothiophene (3 ring, organosulfur) families. Compounds containing zero (parent compound) and one, two, three and four methyl substances were quantified individually and combined as a total "family" in all of the tables of results. PAH values obtained were similar to those reported previously (Boehm and Barak, 1979) for these species.

A geographic dependence of the hydrocarbon concentration and compositional patterns, indicating a potential gradient from pollutant sources, appears to occur with increasing concentrations of PHC with proximity towards the inner New York Bight region (Figure 6).

The same is true for PCB levels. Figure 7 illustrates the PCB distributions in silver hake from the study region. Highest levels (0.1 to 0.5 ppm) are found in those fish from the New York Bight region. PCB levels in general are higher in this species than in any of the other finfish examined, although levels are two orders of magnitude below FDA "action level" of approximately 25 ppm (dry) (= 5 ppm fresh or wet weight).

DDT values measured as the sum of p,p' DDT and p,p' DDE and determined as a single p,p' DDE peak range from 0.002 to 0.073 ppm. The occurrence of DDE closely follows that of PCB compounds. A representative GC/ECD trace for this species shows an Aroclor 1254 PCB distribution and a prominent DDE peak (Figure 8).

The correspondence of PHC and chlorinated hydrocarbons is quite pronounced in this species, indicating a similar source(s) of these pollutants to silver hake.

4.2 Red Hake

The incidence of PHC compounds in red hake is far less than that in silver hake (26 versus 86%), as are the determined concentrations in those samples screened positively. PHC concentrations are low, ranging from 1 to

TABLE 4-1

POLYNUCLEAR AROMATIC HYDROCARBONS - CONTENT OF SELECTED SAMPLES

	STA-TION	TOTAL PHC (µg/g)	TOTAL N (ng/g)	TOTAL P (ng/g)	TOTAL DBT (ng/g)	TOTAL F (ng/g)	TOTAL 202 (ng/g)
Silver Hake	40	37.5	--	4.0	--	--	<0.1
Silver Hake	66	15.2	1.4	20.3	--	0.3	1.0
Silver Hake	100	17.5	10.4	14.5	10.9	1.0	1.5
Silver Hake	55	93.1	0.8	63.5	15.0	1.2	1.1
Silver Hake	60	75.0	3.4	2.8	--	--	1.3
Silver Hake	39	32.3	84.6	54.2	4.1	18.5	15.0
Yellowtail Flounder	55	6.5	2.0	53.8	14.4	7.4	1.8
Winter Flounder	55	ND	--	3.0	--	0.2	1.1
Haddock	123	2.0	12.1	14.5	3.4	--	--
Rock Crab	35	327	0.3	59.0	--	58.0	--

N = naphthalenes
P = phenanthrenes
DBT = bibenzothiophenes
F = fluorenes
202 = fluoranthene + pyrene

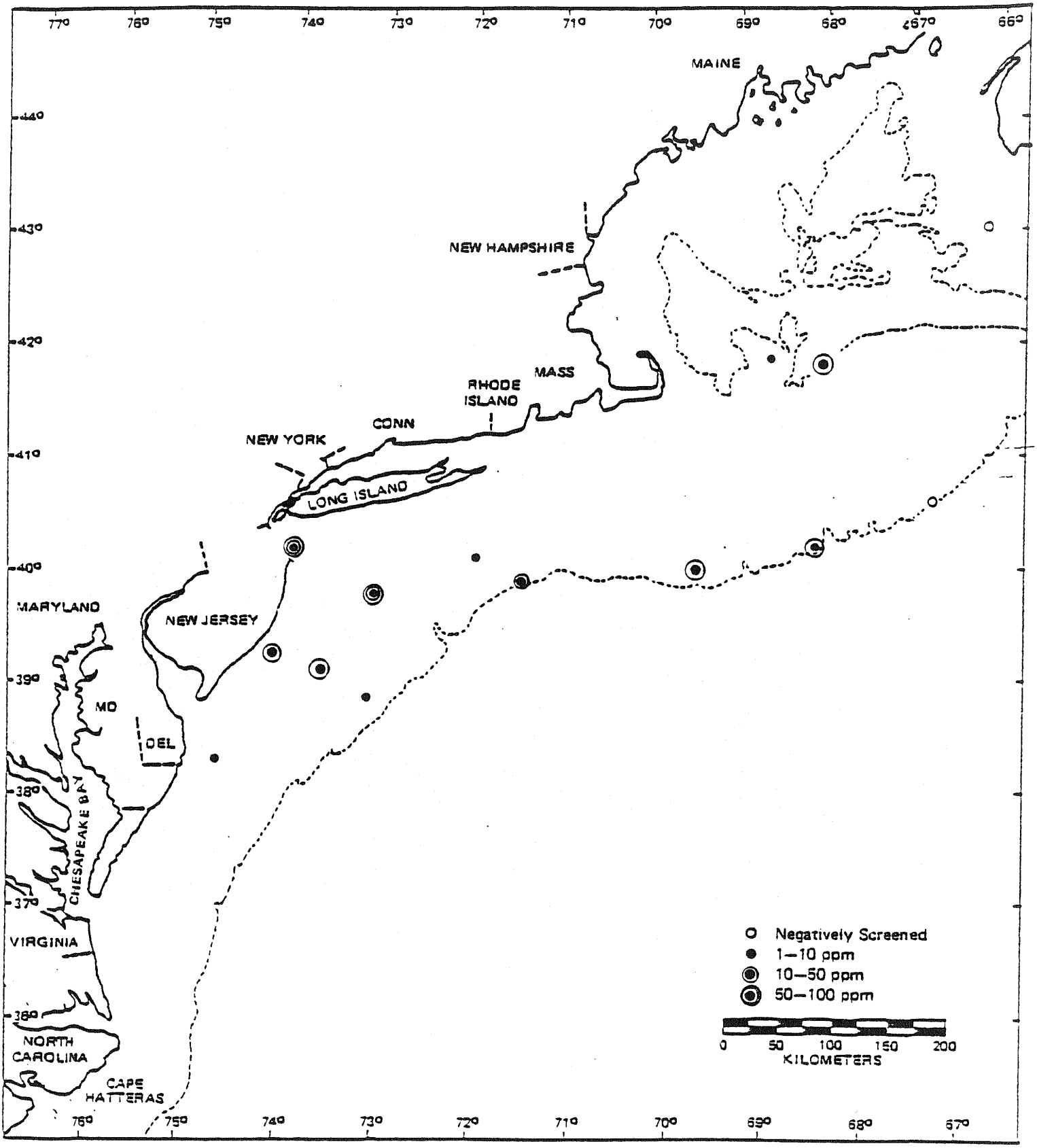


Figure 6. Silver Hake—Petroleum Hydrocarbons.

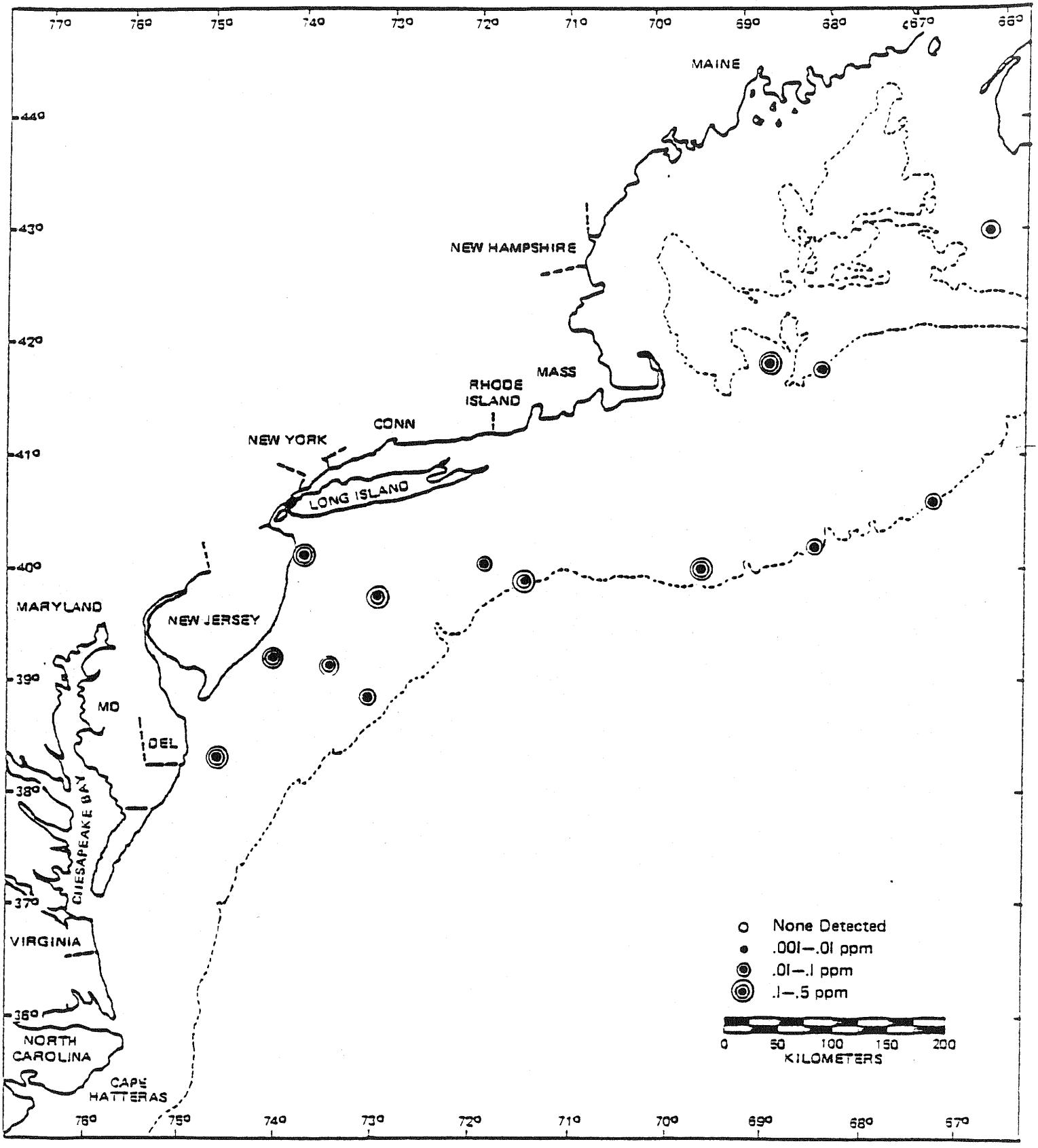


Figure 7. Silver Hake—PCB.

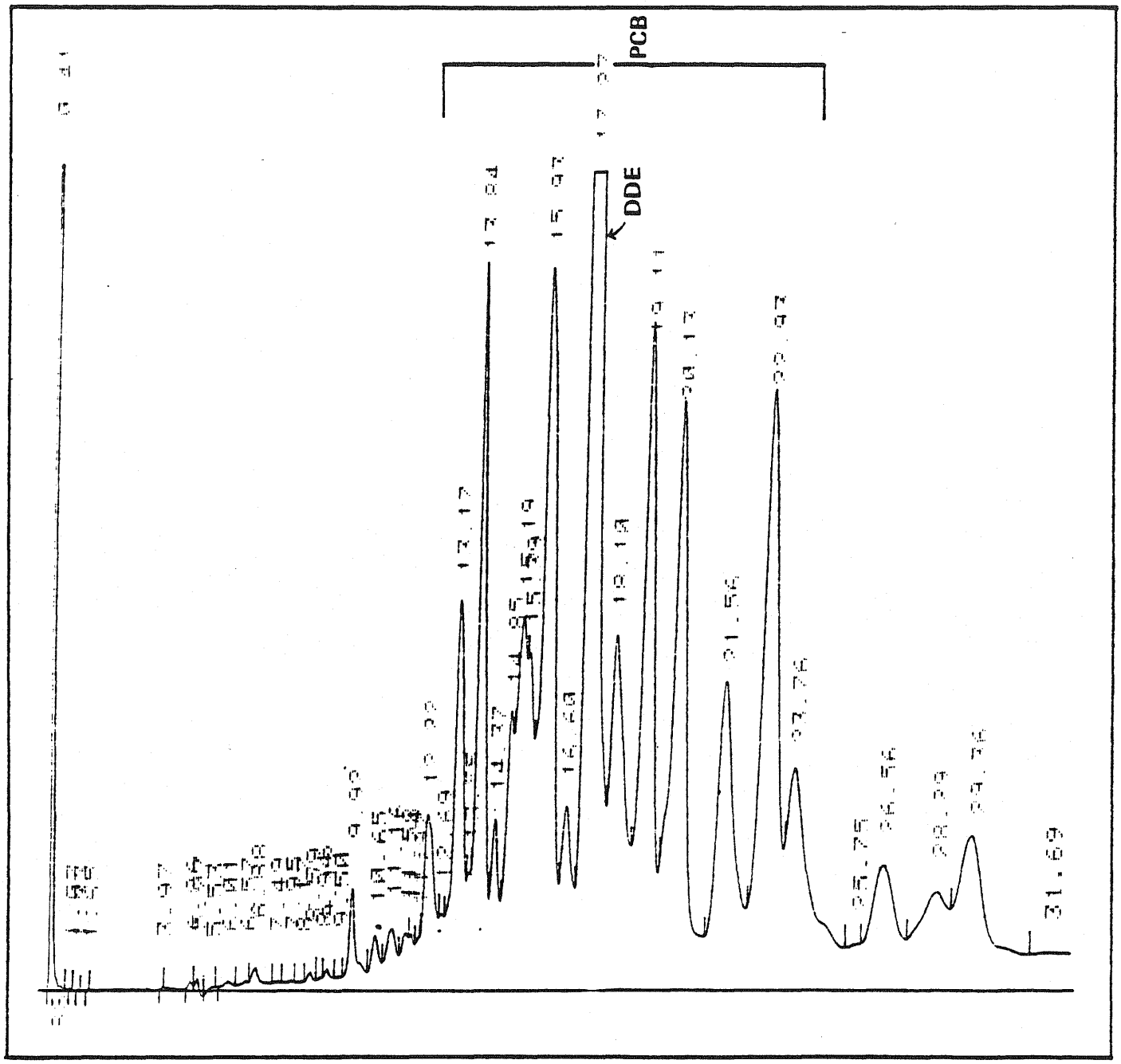


Figure 8. PCB and DDE in Silver Hake (Station 33).

5 µg/g. One sample (Station 126) contains a GC^2 distribution attributable to petroleum (Figure 9), although there appears to be very little if any indication of the presence of aromatic hydrocarbons from the f_2 trace (not shown). GC/MS was not performed on any red hake samples.

PCB and DDE concentrations (see Section 8, Table 8-2) are quite low (PCB = mean 0.015 ± 0.015 µg/g; median value = 0.01 µg/g; DDE = 0.004 ± 0.006 µg/g). Several samples containing the highest red hake PCB values (Station 66 = 0.032 ppm; Station 116 = 0.025 ppm) contain no detectable PHC compounds, thus indicating differential sources for these two classes of compounds for this species.

GC/ECD chromatograms for red hake consistently illustrate an Aroclor 1254 type distribution with a prominent DDE component peak.

The geographic distributions of PHC and PCB compounds indicate no regional "point source" pollutant forcing of contaminant concentrations in this species (Figures 10 and 11). Significant levels of PCB were not coincident with detectable PHC compounds, indicating, unlike the case for silver hake, that PCB and PHC sources are decoupled with respect to this species.

4.3 Yellowtail Flounder

One-third (31%) of the samples of this species contained evidence of PHC contamination but at very low levels (2 to 7 ppm) (see Section 8, Table 8-3). A typical GC^2/FID distribution of the saturated hydrocarbon fraction (Figure 12) indicates that small amounts of pelagic tar-like material contribute to the observed PHC distributions. Associated with this PHC distribution are PAH compounds (naphthalenes 2 ppb; phenanthrenes 54 ppb, dibenzothiophenes 14 ppb, fluorenes 7 ppb) as determined via a single GC/MS analysis (Table 4-1).

Nearly all (94%) of the samples contained detectable levels of PCB compounds (Aroclor 1254) ($\bar{X}$ = 0.018 ± 0.016 ppm) and lower levels of DDE (0.005 ± 0.009 ppm).

There appears to be little correspondence between PCB and PHC levels. Indeed for this species some of the highest PCB levels are found in those fish exhibiting no PHC compounds. The highest PHC value found at Station 55 corresponds with a low PCB value.

The PCB distribution appears similar to an Aroclor 1254 distribution, much like the situation for the other species examined.

Geographic distributions of PHC and PCB compounds for this species are indicated in Figures 13 and 14.

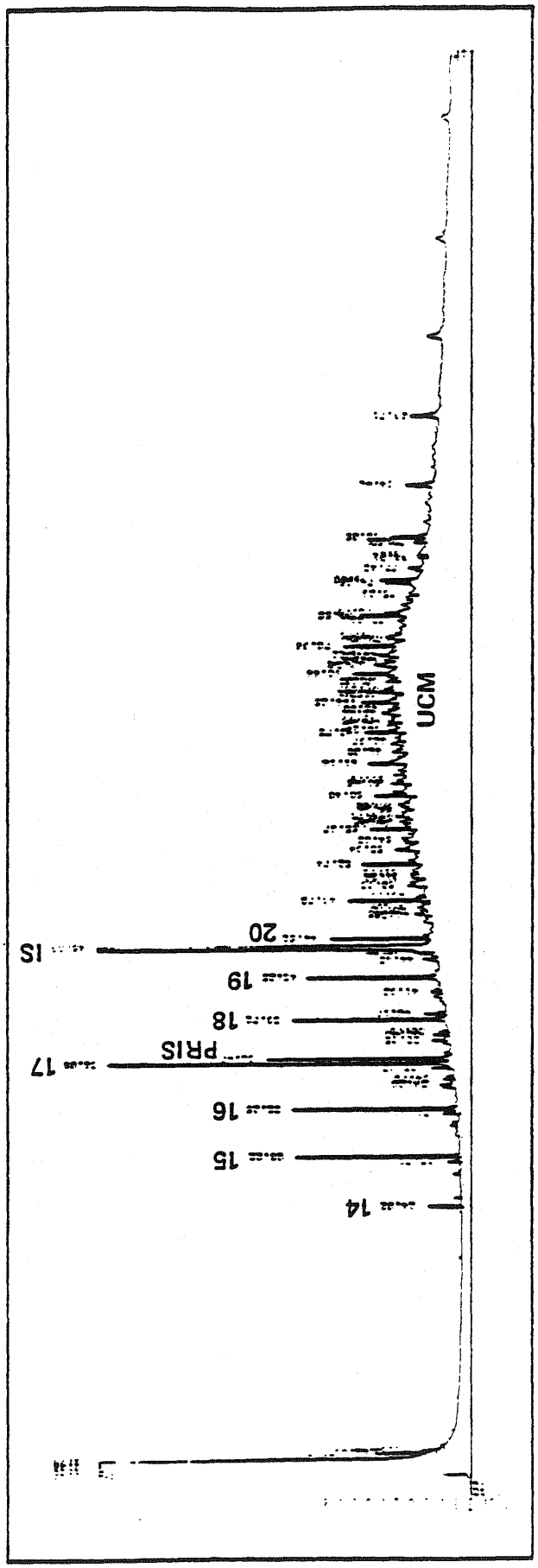


Figure 9. Saturated Hydrocarbon Fraction of Red Hake (Station 126).

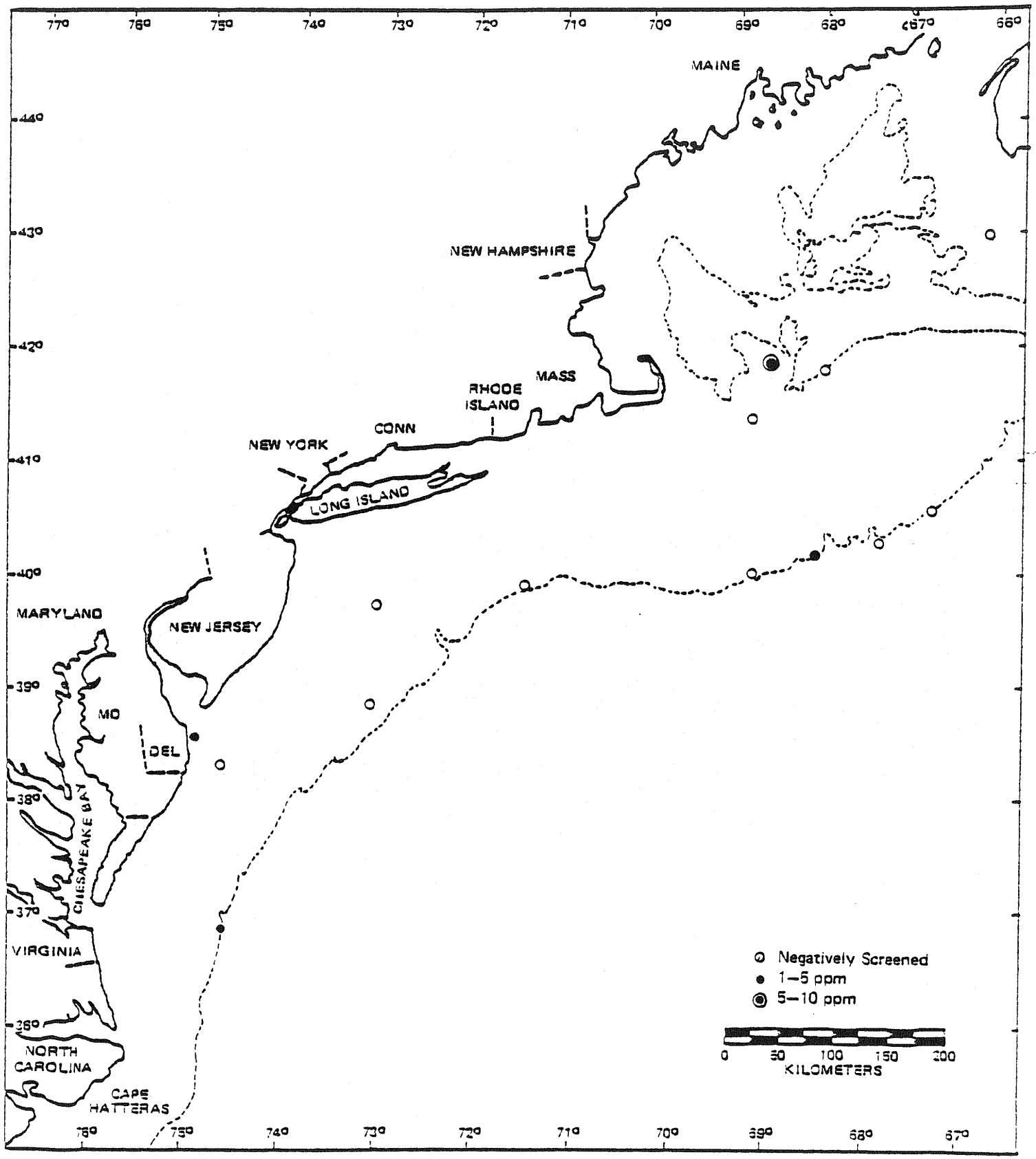


Figure 10. Red Hake—Petroleum Hydrocarbons.

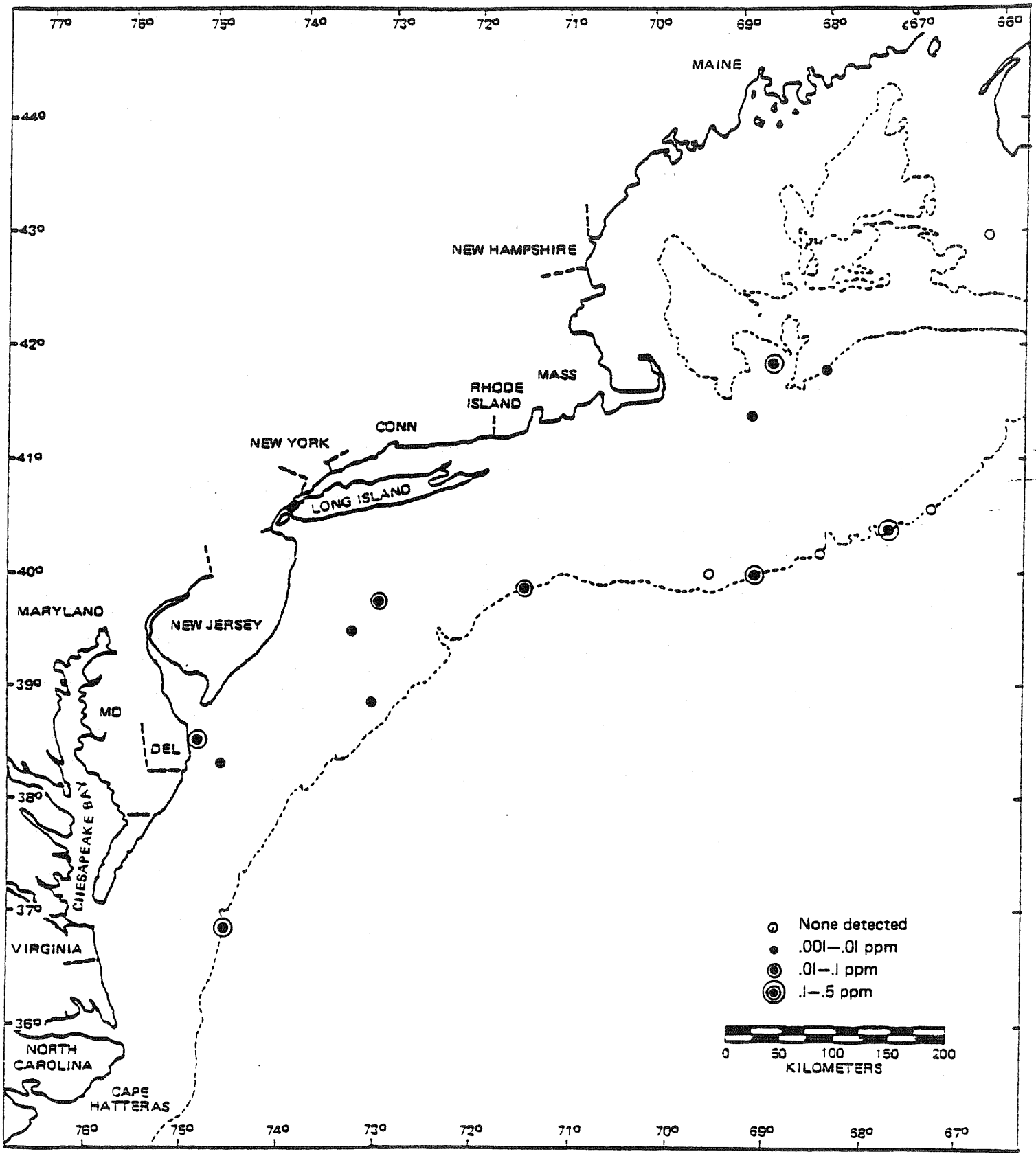


Figure 11. Red Hake—PCB.

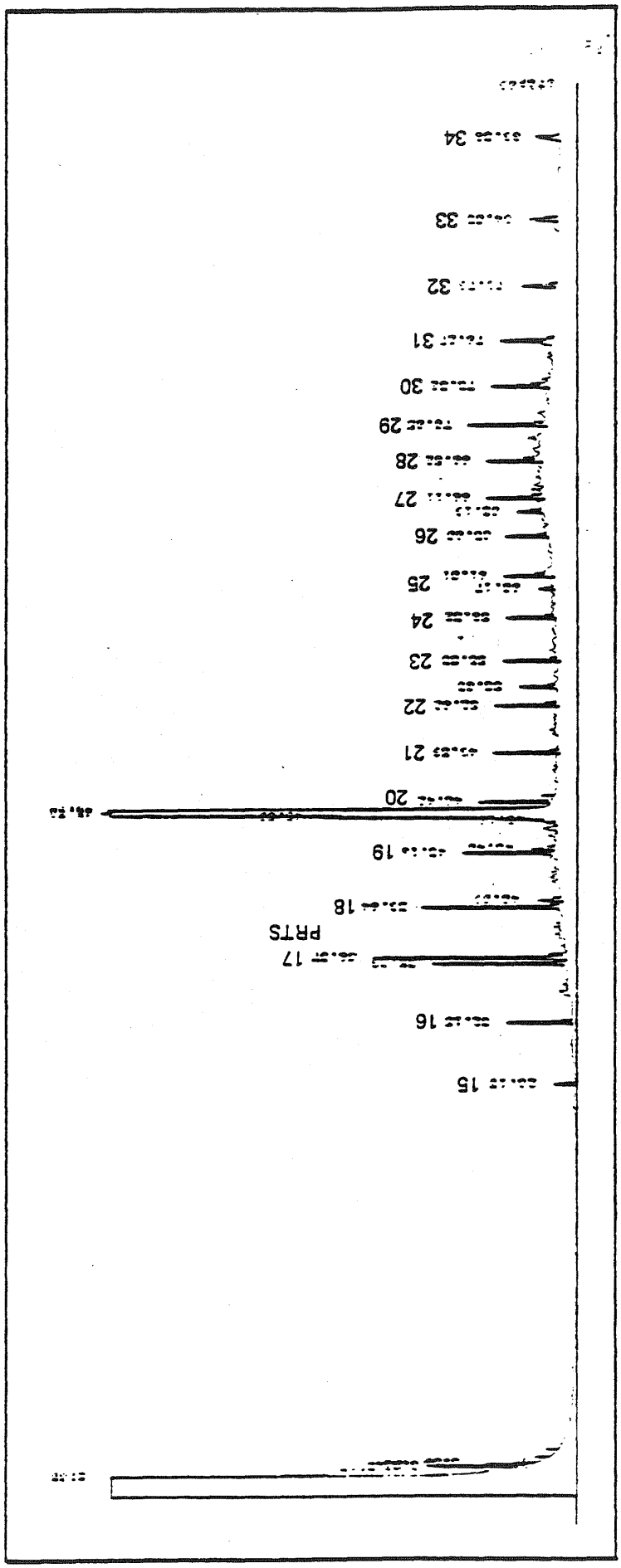


Figure 12. Saturated Petroleum Hydrocarbons in Yellowtail Flounder (Station 101).

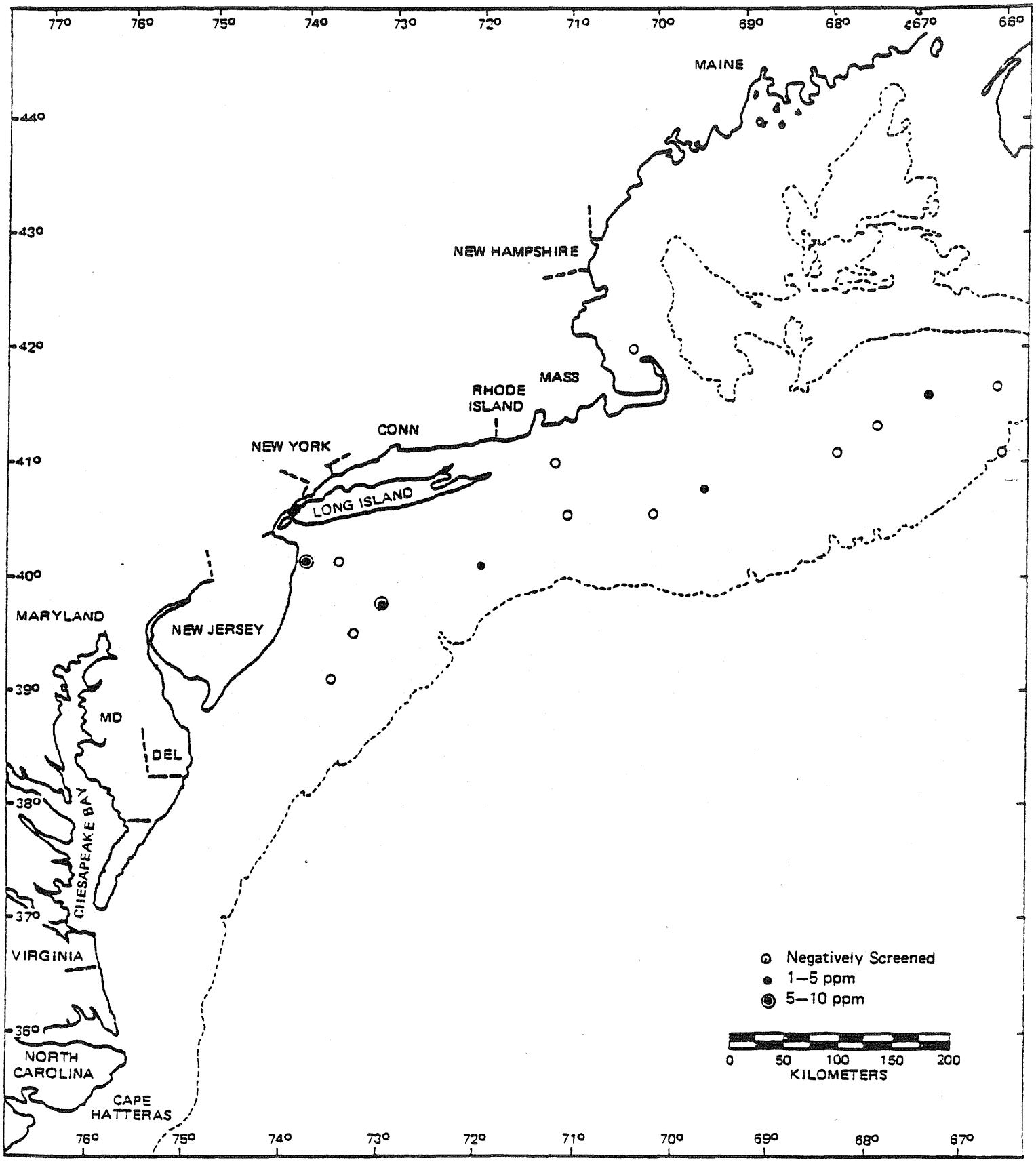


Figure 13. Yellowtail Flounder—Petroleum Hydrocarbons.

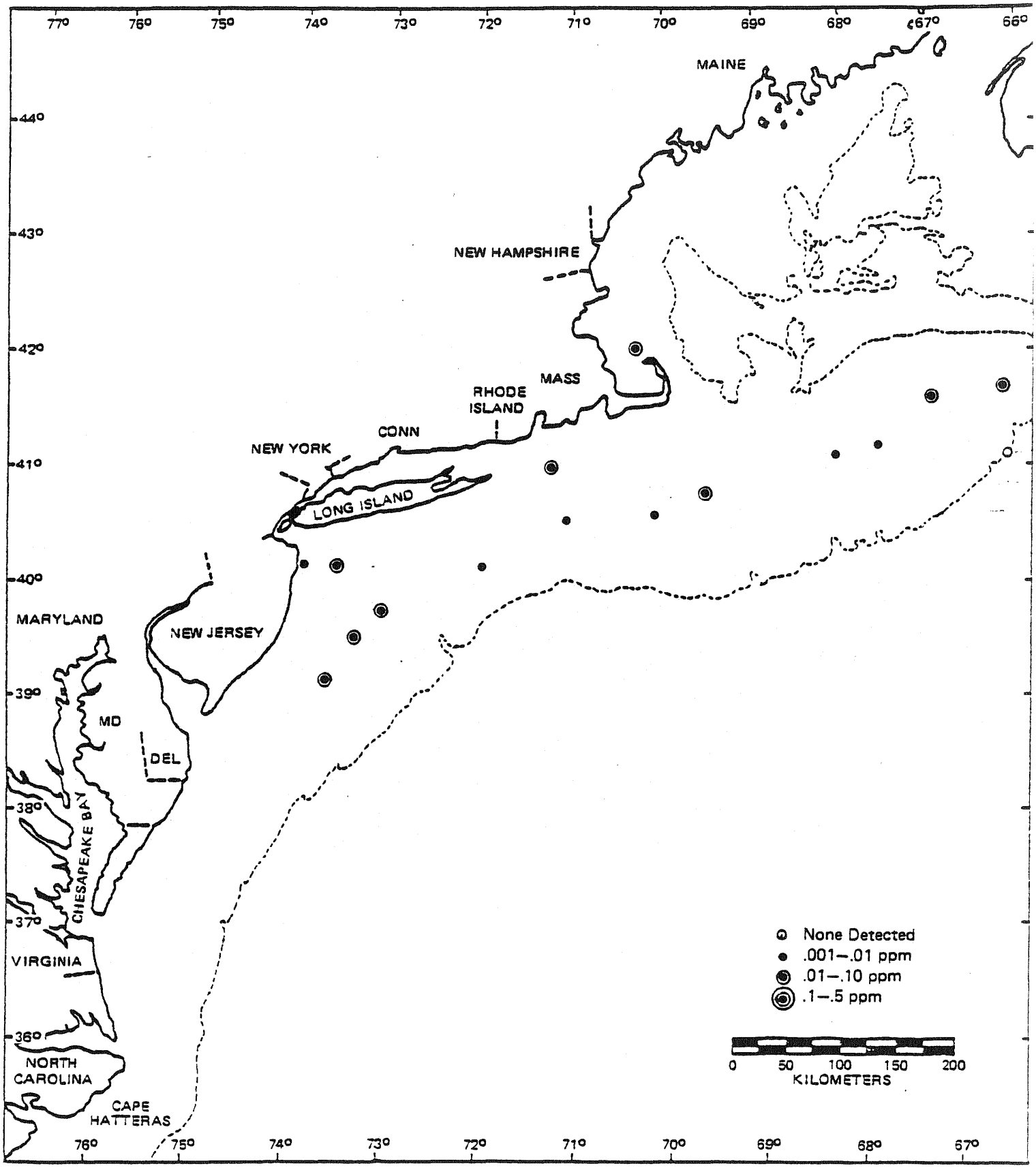


Figure 14. Yellowtail Flounder–PCB.

4.4 Winter Flounder

Boehm and Barak (1979) reported concentrations of hydrocarbons in this species ranging from 5 to 240 ppm (dry weight). However, the bulk of the hydrocarbons were of a biogenic origin. The petroleum hydrocarbon component of the total hydrocarbon number was about 2 to 20 ppm. Winter flounder examined in the present study were relatively free of petroleum contamination. Only 15% of the samples contained PHC compounds (Figure 15) in primarily degraded petroleum residues exhibiting mainly an unresolved complex mixture (or hump) of naphthenic hydrocarbons. This is quite unlike the distribution reported by Boehm and Barak (1979) which more resembled the tar-like distribution described in the previous section. PHC concentrations were more or less invariant (6 to 9 ppm) (see Section 8, Table 8-4) and significantly lower than previously reported.

PCB and DDE levels were quite low ($\bar{X}$ = 0.01 ± 0.01 µg/g; $\bar{X}$ = 0.002 ± 0.002 µg/g, respectively). An Aroclor 1254 type distribution is again typical. Again, the presence of chlorinated hydrocarbons and PHC appear independent of one another.

The areal distributions of both PHC and PCB compounds are presented in Figures 16 and 17. While the occurrence of PHC compounds in winter flounder seems not to be coupled with geographic pollutant point sources, elevated chlorinated hydrocarbons can be loosely ascribed to New York Bight sources.

4.5 Windowpane Flounder

Where PHC compounds were present (38%; Stations 79, 95, 116), the absolute concentrations were low (see Section 8, Table 8-5) and the source of these hydrocarbons again appeared to resemble paraffinic tar (Figure 18). Concentrations of PHC (1 to 5 ppm) are slightly lower than previously reported (Boehm and Barak, 1979) values of 2 to 20 ppm for the PHC component of the samples. However, the previously reported frequency of occurrence of PHC in this species was much higher, approximately 82%.

Quantities of PCB (Aroclor 1254) ranged from 0.004 to 0.086 µg/g and were found in all samples examined.

No evident New York Bight or other regional forcing or organic pollutant concentrations are apparent (see Figures 19 and 20).

4.6 Haddock

Similarly to that previously reported (Boehm and Barak, 1979), PHC concentrations are very low in haddock samples from the Georges Bank region (1 to 2 ppm) (see Section 8, Table 8-6). Two of the seven samples showed slight indications of possible PHC compounds when screened, but little if

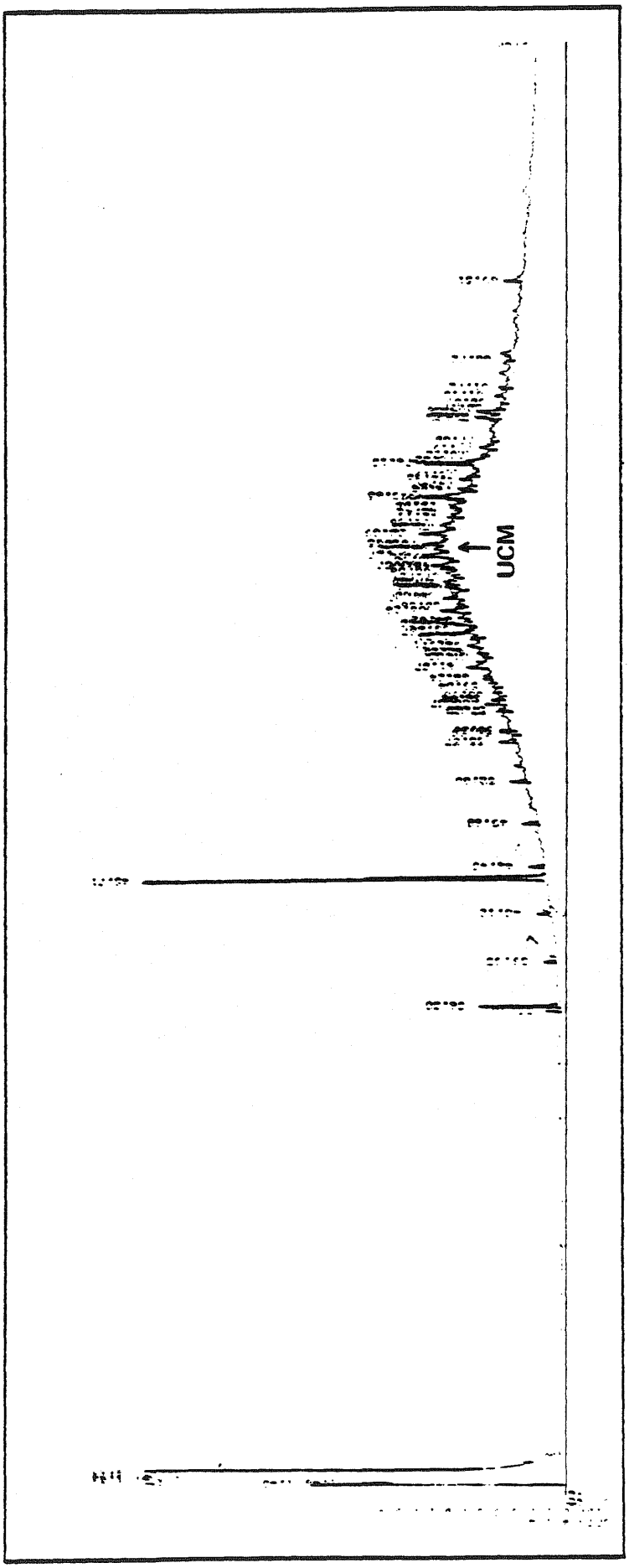


Figure 15. Saturated Petroleum Hydrocarbons in Winter Flounder (Station 139).

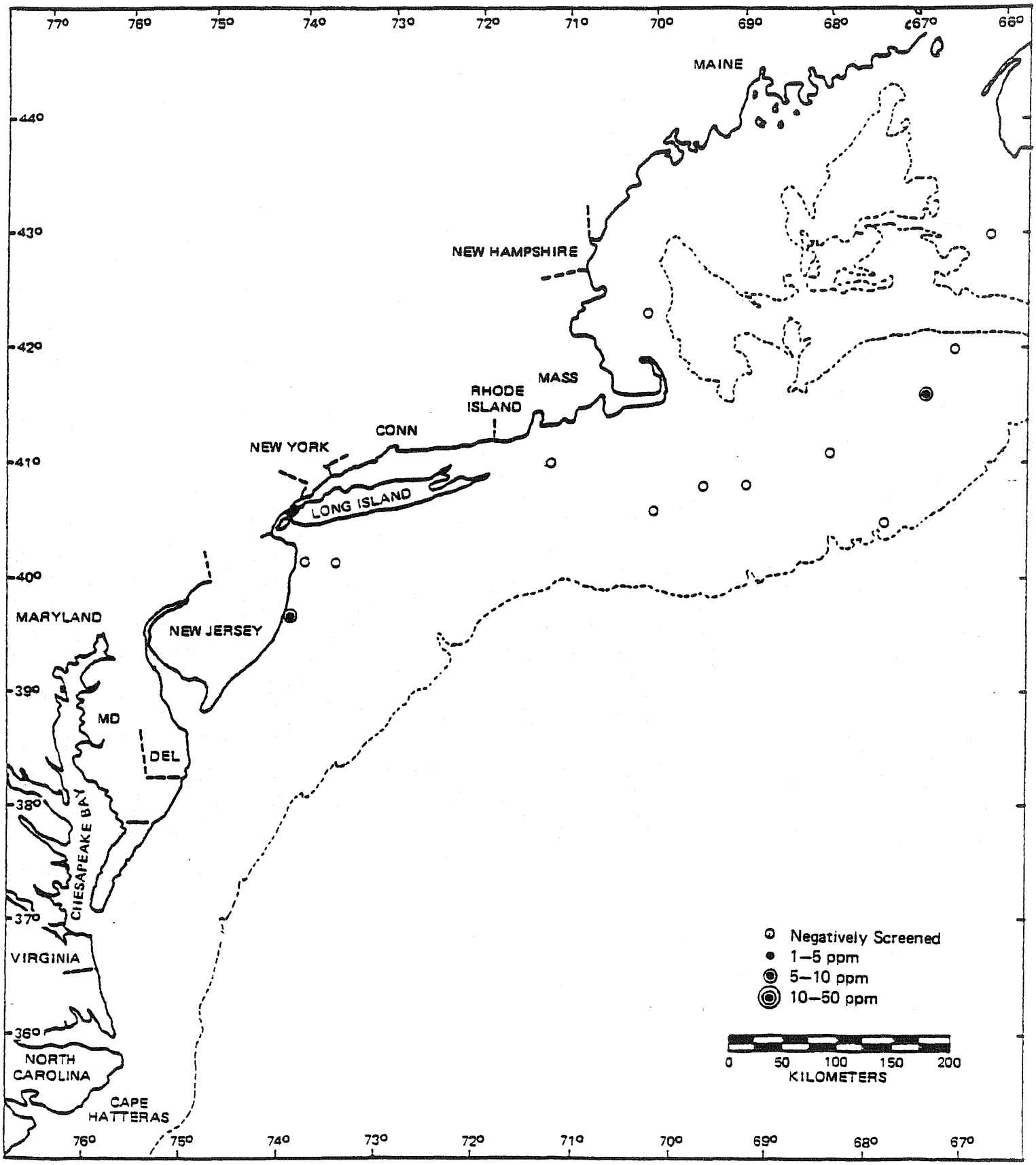


Figure 16. Winter Flounder—Petroleum Hydrocarbons.

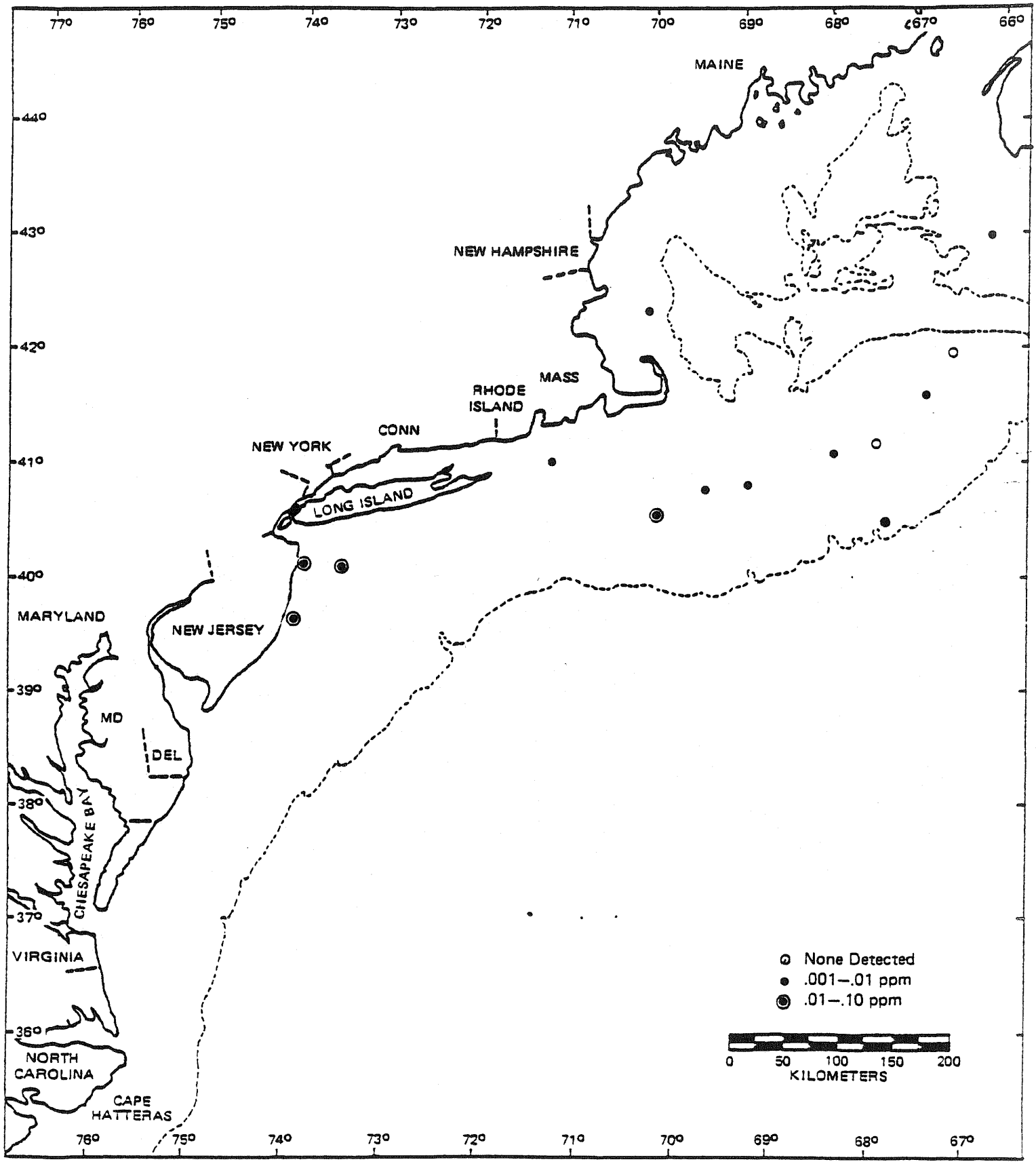


Figure 17. Winter Flounder—PCB.

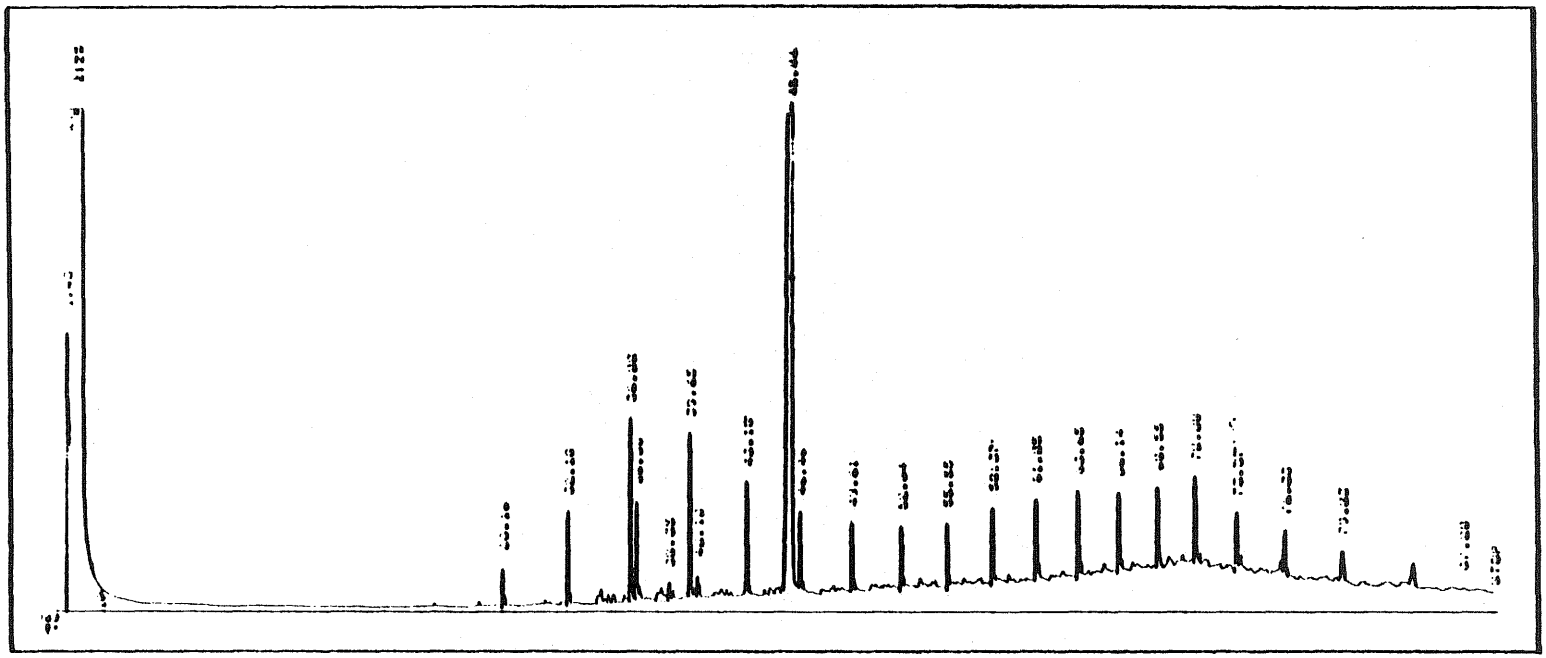


Figure 18. Saturated Petroleum Hydrocarbons in Windowpane Flounder (Station 79).

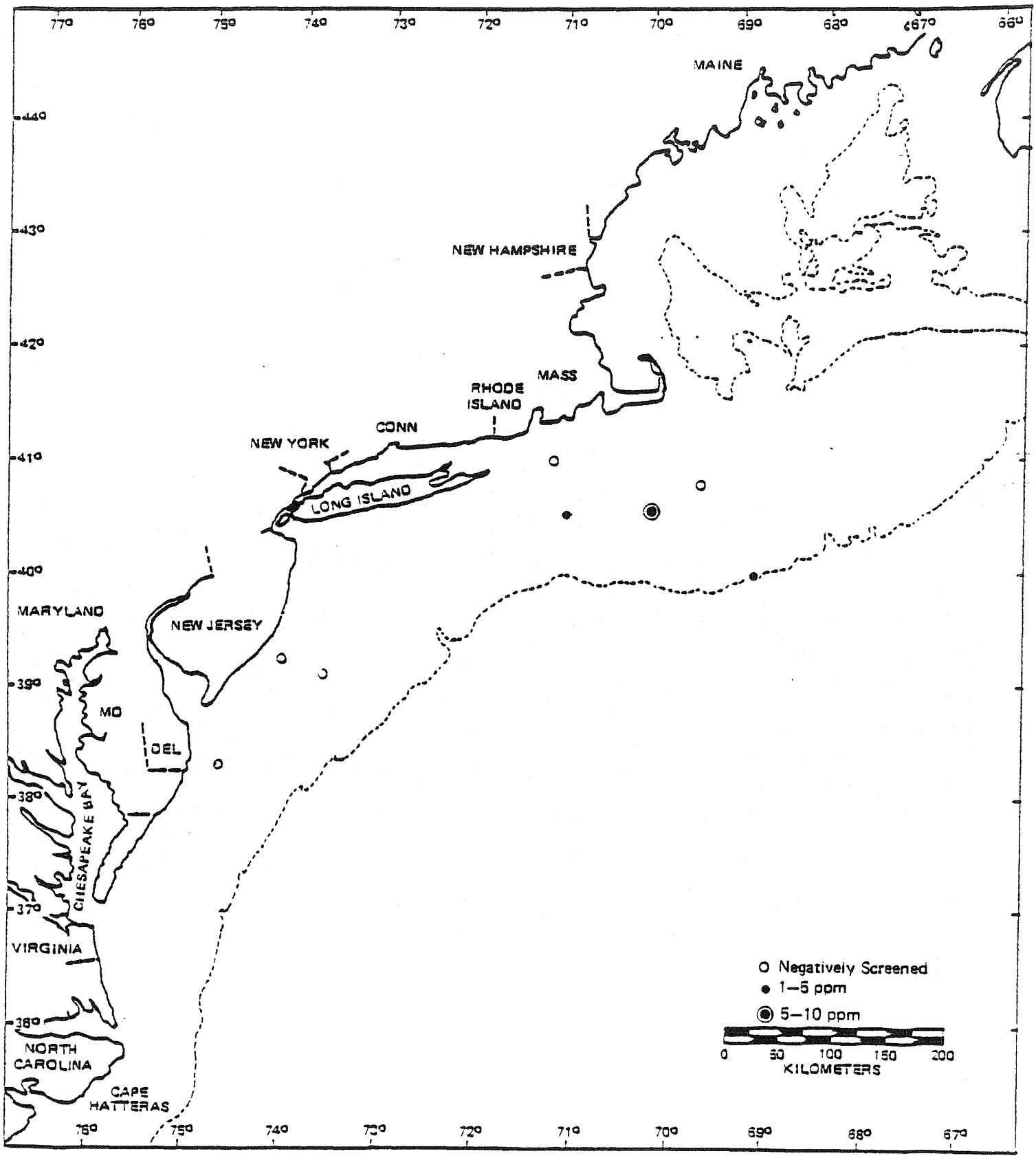


Figure 19. Windowpane Flounder—Petroleum Hydrocarbons.

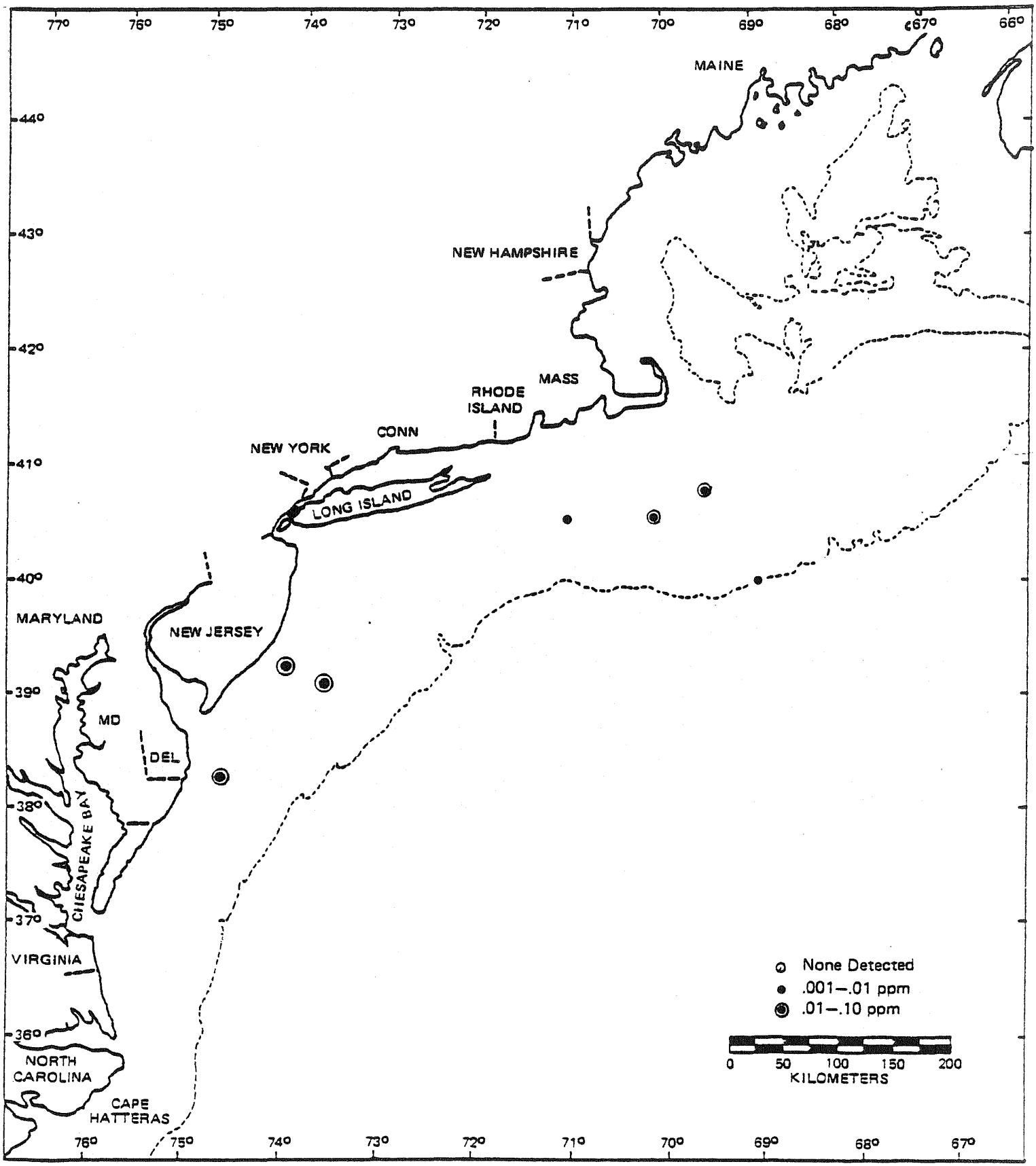


Figure 20. Windowpane Flounder—PCB.

any after fractionated and analyzed by GC^2. However, GC/MS analysis of the aromatic fraction from Station 123 reveals PAH compounds: naphthalenes 12 ppb, phenanthrenes 15 ppb, dibenzothiophenes 3 ppb. This illustrates that GC^2 alone is not sufficient to yield detailed information on small quantities of PAH compounds.

PCB concentrations are also very low (<0.005 ppm) except for one sample (Station 132) where levels reached 0.026 ppm. Notably, PHC and PCB compound occurrences are totally unrelated. As the areal coverage only includes the Georges Bank region (Figures 21 and 22) observed distributions cannot be related to any source.

4.7 Cod

None of the five cod samples analyzed exhibited any PHC compounds, but PCB were detected in four of the five. The highest concentration (0.018 ppm) of PCB was detected at Station 113 (see Section 8, Table 8-7).

4.8 Four Spot Flounder

Fifty percent (50%) of the four samples screened contained PHC compounds. The two samples after fractionation were determined to contain PHC levels from 2 to 6 ppm (see Section 8, Table 8-7), the higher of the two values occurring at Station 100 on the southern edge of Georges Bank. Pelagic, paraffinic tar appears to be the main contaminant source (Figure 23).

PCB ranged from 0.004 to 0.008 ppm and the DDE component was either not detected or was extremely low (approximately 0.002 ppm) in these fish.

4.9 Summer Flounder

The single summer flounder sample (two individuals) analyzed was from Station 81. It contained no PHC compounds but did contain PCB (0.014 ppm) and DDE (0.003 ppm) compounds (see Station 8, Table 8.8).

4.10 Rock Crab, Cancer Crab, Scallops, Lobsters

As a group these benthic epifauna contained no detectable hydrocarbons in the gross screening phase, except for the single rock crab sample from Station 35 at the mouth of Delaware Bay. This sample contained very large (327 ppm) levels of petroleum-derived hydrocarbons (Figure 24) and exhibited GC^2 profiles indicative of a mid-boiling, degraded distillate oil. Levels of GC/MS-determined PAH compounds (Table 4-1) were quite high: phenanthrenes 59 ppb; fluorenes 58 ppb.

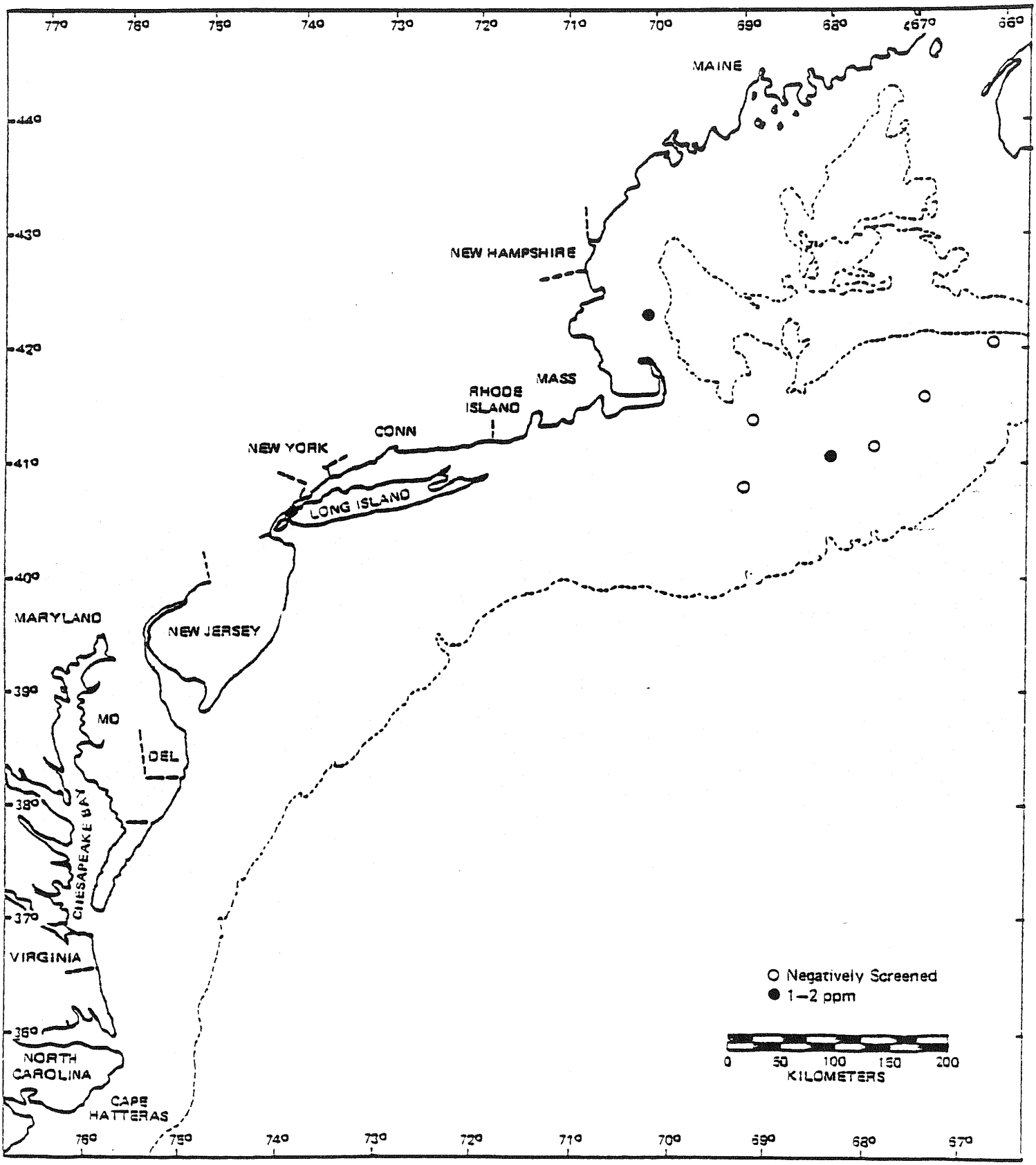


Figure 21. Haddock—Petroleum Hydrocarbons.

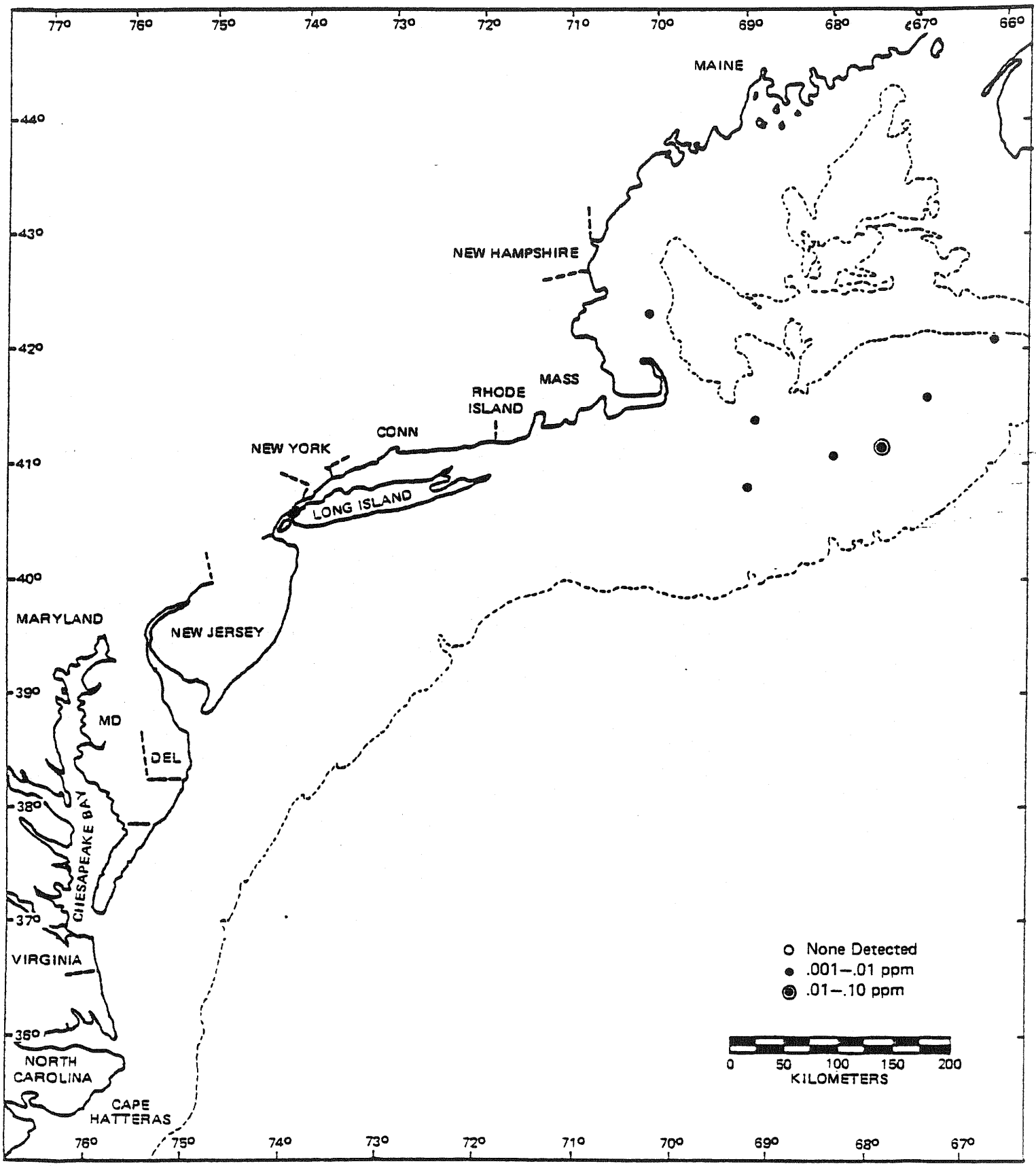


Figure 22. Haddock–PCB.

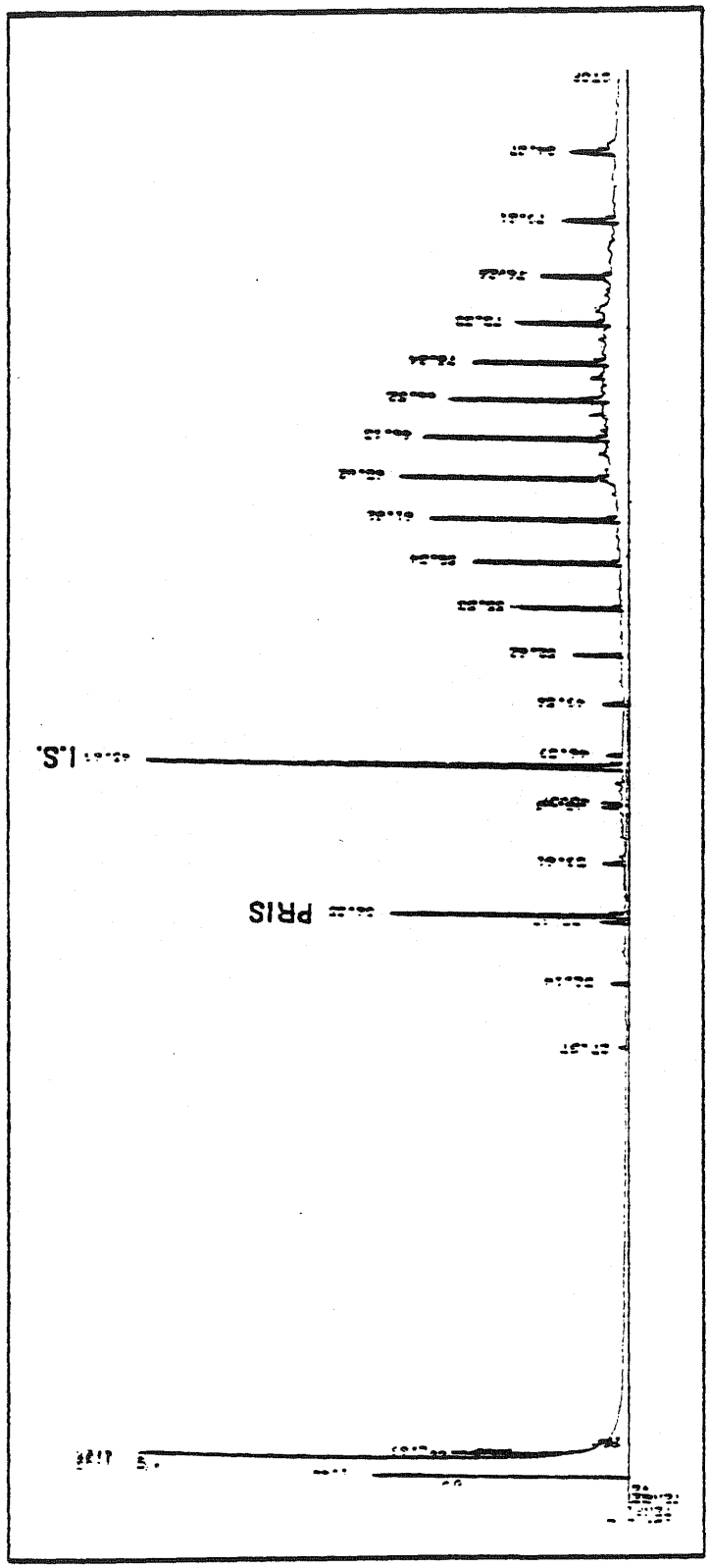
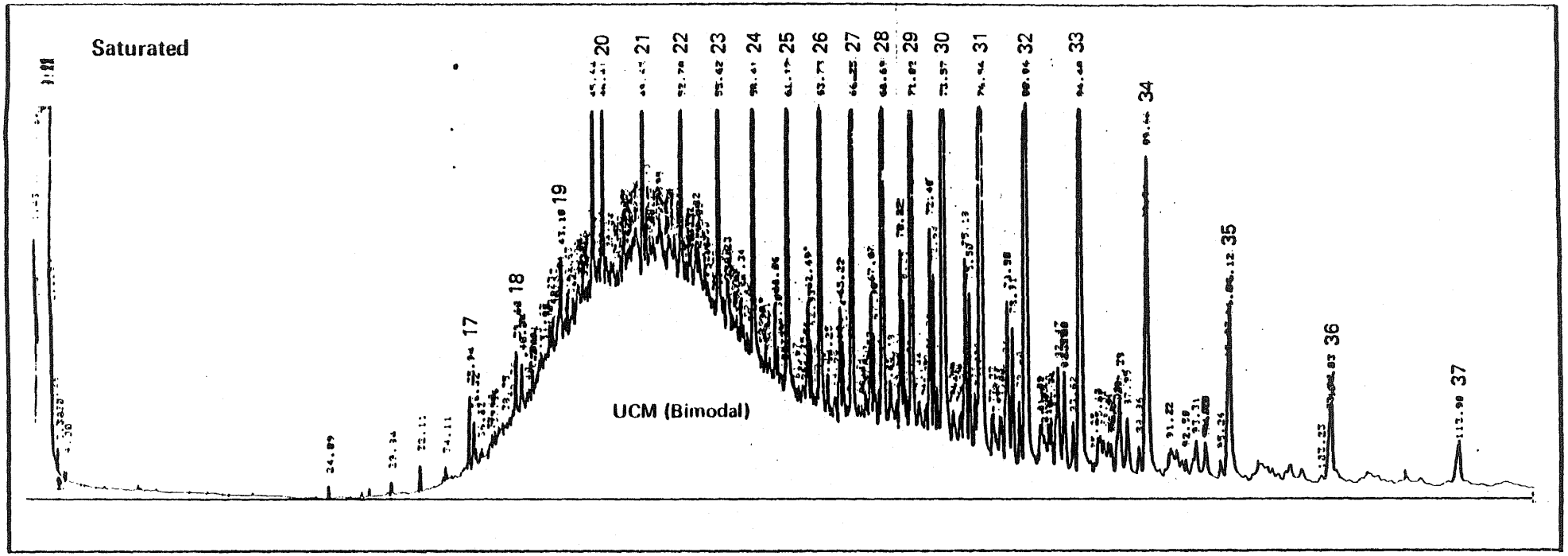


Figure 23. Saturated Petroleum Hydrocarbons in Four Spot Flounder (Station 100).



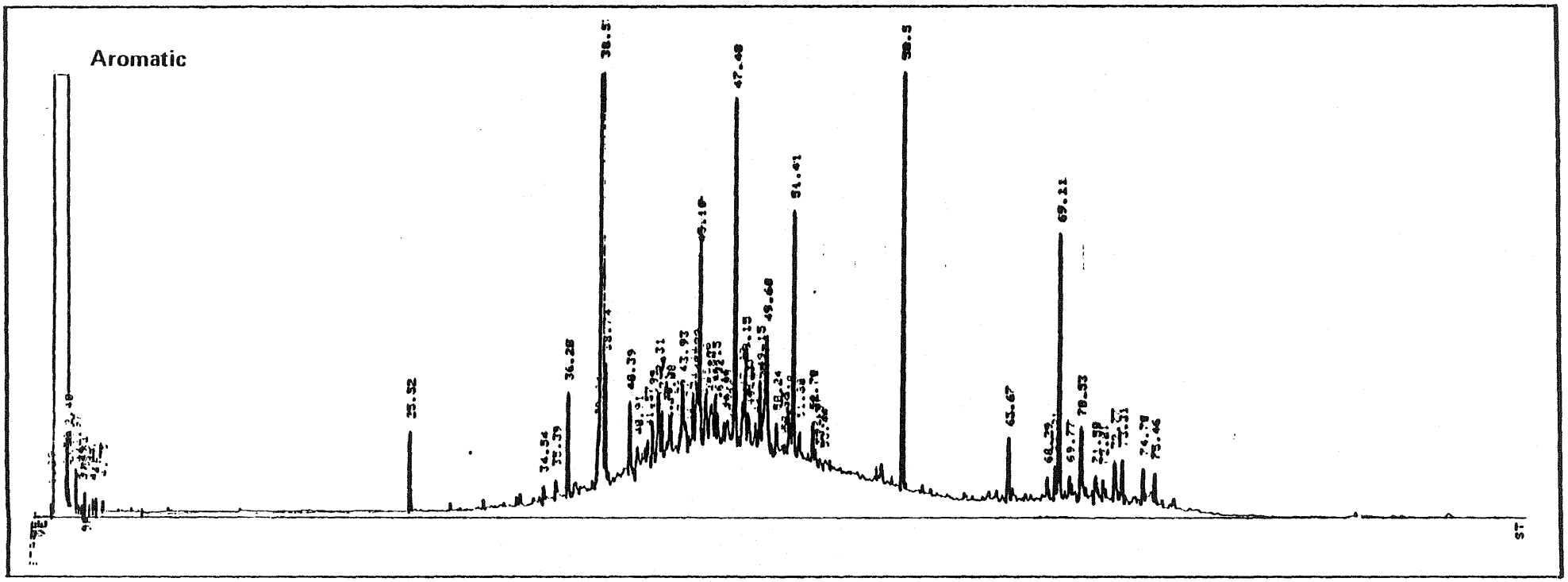


Figure 24. Petroleum Hydrocarbons in Rock Crab (Station 35)

PCB distributions were varied for these benthic epifaunal species with concentrations of PCB ranging from 0.001 ppm for scallops to 0.150 ppm for lobsters from Station 79 on the outer Rhode Island shelf (See Section 8, Table 8-8). In general, the lobsters contained high levels of PCB (and DDE) at both stations scrutinized (Stations 45 and 79). The rock crab also contained significant PCB and DDE levels.

Areal distributions of PCB are shown in Figure 25, which is inconclusive with regard to source(s) of these organic compounds.

4.11 Little Skate

Both little skate samples (Stations 95, 116) contained no PHC compounds and low levels (0.002 to 0.012 ppm) of PCB. The previous study of Boehm and Barak (1979) indicated that this species contained no or low (1 to 5 ppm) levels of PHC compounds.

4.12 American Dab

Of the four samples of this species analyzed, one contained small amounts of petroleum hydrocarbons (Station 106; 1.5 ppm). This sample also contained the highest quantities of the chlorinated hydrocarbons measured in this species (0.024 ppm PCB; 0.003 ppm ΣDDT) (See Section 8, Table 8-9).

5. Interpretation of Findings

Data on the concentrations of PHC compounds in fish are not plentiful. Recent studies include those of Boehm and Barak (1978, 1979), Pancirov and Brown (1977), Whittle et al. (1975), Mackie et al. (1974), and Parker et al. (1972). The lack of consistent analytical techniques and reporting formats somewhat impair one's ability to compare the various data shown in Table 5-1. What can be said, though, is that levels reported here (Table 5-2) are well within the range previously reported for the region of interest (Boehm and Barak, 1979) and lower than those PHC levels reported in fish samples along the coast (Boehm and Barak, 1978).

The sources (i.e., GC trace) of hydrocarbons in the PHC-positively screened samples ranged from pelagic tar (e.g., Figure 23) with a pronounced paraffinic GC pattern to a degraded petroleum residue in silver hake (e.g., Figure 4) very similar in appearance to residues in animal tisues a year after exposure to the Amoco Cadiz spill (Boehm and Neff, unpublished data). The PHC composition and concentrations in silver hake appear remarkably constant, with GC patterns previously reported (Boehm and Barak, 1979) identical to those observed here.

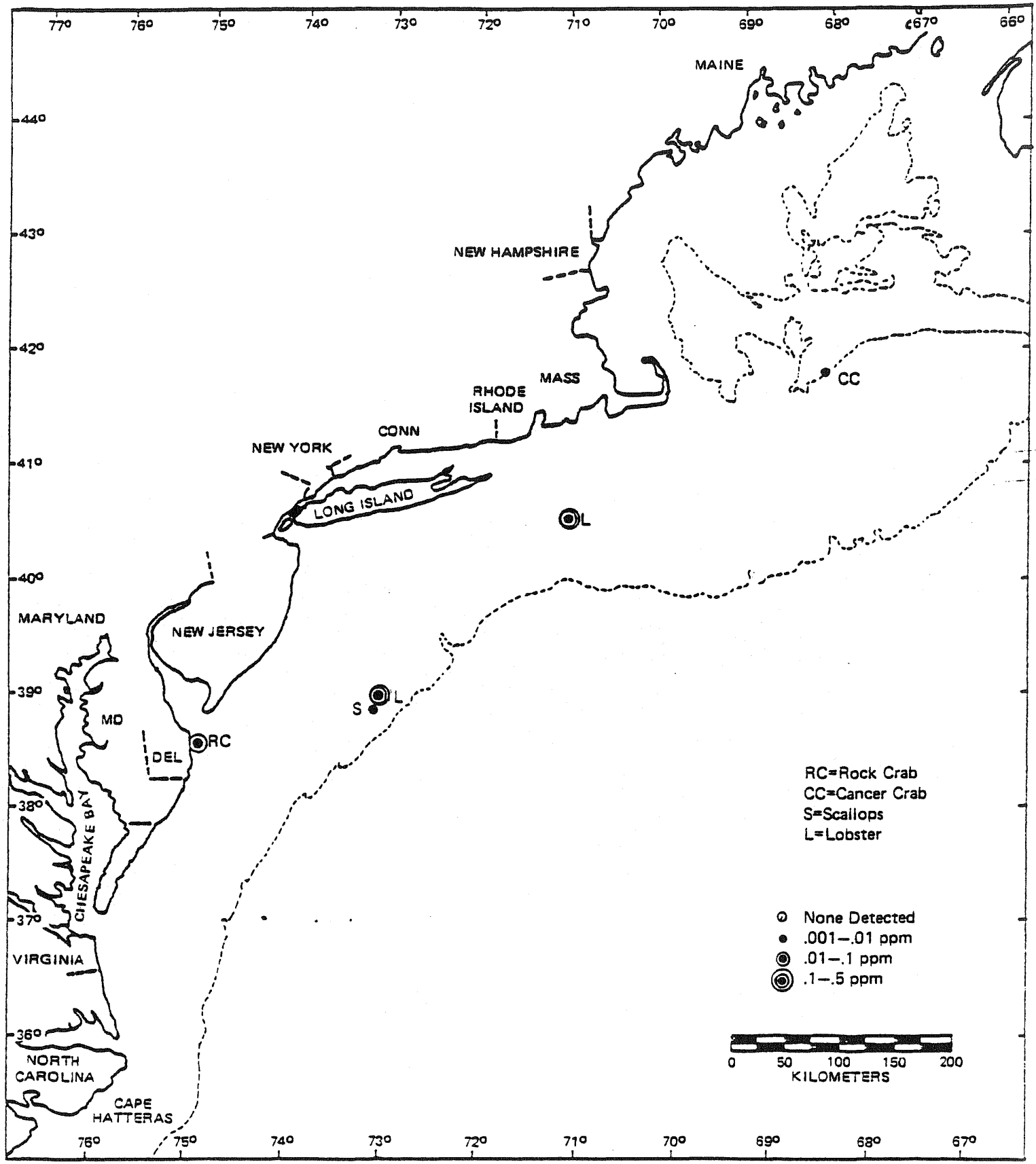


Figure 25 . Benthic Epifauna—PCB.

TABLE 5-1

PETROLEUM HYDROCARBONS IN FISH

ORGANISM	LOCATION	HYDROCARBON TYPE SUBCLASS OR CLASS	METHOD OF ANALYSIS	HYDROCARBON CONTENT (µg/g wet wt.)	REFERENCE
Cod (muscle)	British Isles	n-Paraffins	GC	0.005-0.03	Whittle et al. (1975)
Cod (muscle)	British Isles	n-Paraffins	GC	0.1-0.3	Whittle et al. (1975)
Flounder	Gulf of Mexico	n-Paraffins	GC	8.7	Parker et al. (1972)
Hake	Scotland	n-Paraffins	GC	6.0	Mackie et al. (1974)
Windowpane Flounder	Georges Bank	Saturates and Aromatics (f_1 & f_2)	GC	0.2-6*	Boehm and Barak (1979)
Winter Flounder	Georges Bank	Saturates and Aromatics (f_1 and f_2)	GC	1-10*	Boehm and Barak (1979)
Winter Flounder	Rhode Island Coast	Saturates and Aromatics (f_1 and f_2)	GC	5-50*	Boehm and Barak (1978)
Skate	Georges Bank	Saturates and Aromatics (f_1 and f_2)	GC	0.2-1*	Boehm and Barak (1979)
Silver Hake	Georges Bank	Saturates and Aromatics (f_1 and f_2)	GC	1-10*	Boehm and Barak (1979)
Haddock	Georges Bank	Saturates and Aromatics (f_1 and f_2)	GC	0.2-1*	Boehm and Barak (1979)

TABLE 5-1 (CONT.)

ORGANISM	LOCATION	HYDROCARBON TYPE SUBCLASS OR CLASS	METHOD OF ANALYSIS	HYDROCARBON CONTENT (µg/g wet wt.)	REFERENCE
Cod	Georges Bank	Saturates and Aromatics (f_1 and f_2)	GC	0.5-2*	Boehm and Barak (1979)
Yellowtail Flounder	Georges Bank	Saturates and Aromatics (f_1 and f_2)	GC	0.1-2*	Boehm and Barak (1979)
Yellowtail Flounder	Rhode Island Coast	Saturates and Aromatics (f_1 and f_2)	GC	5-50*	Boehm and Barak (1978)

*Values converted to wet weight basis for comparison.

TABLE 5-2

INCIDENCE OF THE PRESENCE OF PHC COMPOUNDS

SPECIES	NO. OF SAMPLES	PERCENT OCCUR-RENCE	CONCEN-TRATION (µg/g dry wt.)	CONCEN-TRATION* (µg/g wet wt.)
Silver Hake	14	86	6-90	1.2-18
Red Hake	14	29	1-5	0.2-1
Yellowtail Flounder	16	45	2-7	0.4-1
Winter Flounder	13	15	6-9	1.2-1.8
Windowpane Flounder	8	38	1-5	0.2-1
Four Spot Flounder	4	50	2-6	0.4-1.2
Summer Flounder	1	25	1	0.2
American Dab	4	25	1-2	0.2-0.4
Haddock	7	0	--	--
Cod	5	0	--	--
Skate	2	0	--	--
Scallop	1	0	--	--
Rock Crab	1	100	327	66
Lobster	2	0	--	--

*Dry weight basis ÷ 5.

PAH levels (see Section 4, Table 4-1) are also similar to those previously reported and indicate a combined source of PAH compounds; petroleum where naphthalene and fluorene compounds dominate and pyrogenic (combustion sources), where m/e = 202 compounds are significant and where parent aromatics (e.g., phenanthrene) are more abundant than the alkylated members of an homologous series (e.g., methyl phenanthrenes) as is the case with most of those samples (see Section 4, Table 4-1) subjected to GC/MS.

Therefore, it is encouraging to observe that when viewed against previous data sets, PHC levels fall into previously established ranges. This bodes well for future monitoring efforts. Of the finfish examined for PHC levels, silver hake, yellowtail flounder, and possibly winter and/or windowpane flounder appear to be good candidates for pollutant chemical monitoring as these species all exhibit tendencies to acquire low levels of PHC compounds, with the PHC sources being distinguishable and therefore monitorable.

PCB and DDE compounds are more widespread than the PHC compounds and, although present in very low levels, behave independently of PHC distributions. Recent literature values for PCB levels in fish are presented in Table 5-3. A summary of this study's findings is presented in Table 5-4. Values are well within the range of other reported values, tending towards the low end of the range. The ratio of PCB to ΣDDT compounds was computed for each species (Table 5-4). The species means of this ratio for the finfish fall in a narrow range - 3-6, perhaps indicative of a singular source material having a chlorinated pollutant composition reflecting this ratio. Monitoring this ratio might then indicate if a new chlorinated hydrocarbon source affects subsequent tissue measurements.

The baseline data amassed here will be most useful for monitoring future changes in pollutant loadings in these important fish species. Not enough information has been gathered as part of this study to monitor important benthic species in the same fashion. Indeed, benthic species will accumulate these pollutants to a greater degree than the finfish due to the former's conduct with the pollutant sink, i.e., the benthos.

Although silver hake appears to be forced by a New York Bight PHC and PCB source, the situation is less clear for the other species. It is probably more appropriate to designate regional means for petroleum and chlorinated hydrocarbon levels around which valid expected statistical variations can be bracketed, as was done in Section 8, Tables 8-1 to 8-9. The migratory behavior of fish require this treatment of the data. It would be much more appropriate to evaluate environmental change with regards to organic pollutant monitoring in terms of these regional means. Perhaps subregional (e.g., New York Bight, Chesapeake, Georges Bank) means could be established if a more intensive sampling and/or analytical program were pursued.

Finally, the analytical protocol used here proved to be useful for rapid, cost-effective screening and easily converted to the more sophisticated and revealing technique of capillary GC/MS.

TABLE 5-3

PCB COMPOUNDS IN FISH

ORGANISM	RANGE OF PCB LEVELS (µg/g dry wt.)	REFERENCE	LOCATION
Red Hake	0.07-0.40	Unpublished data	East Coast, United States
Flounder	0.07-0.35	Unpublished data	East Coast, United States
Mullet	2-3.7	Amico et al. (1979)	Mediterranean Sea
Mullet	Trace-0.4	Basturk et al. (1980)	Mediterranean Sea
Tuna	0.09-0.4	Amico et al. (1979)	Mediterranean Sea
Groundfish (Cod, Catfish, Flounder, Halibut, Haddock, Cod, Pollack, Redfish, Snapper, Rockfish, Skate, Sole, Plaice)	0.35 (mean of 141 samples)	Graham (1974)	East and West Coasts, Canada
Pelagic - Estuarine (Alewife, Capelin, Dogfish, Herring, Salmon, Smelt, Swordfish, Tuna)	2.0 (mean of 73 samples)	Graham (1974)	East and West Coasts, Canada
Sole	0.05-2.0	McDermott et al. (1974)	West Coast-Southern California

TABLE 5-4

INCIDENCE OF THE PRESENCE OF PCB COMPOUNDS

SPECIES	NO. OF SAMPLES	PERCENT OCCUR-RENCE	CONCENTRATION (µg/g dry weight)	MEAN PCB/ΣDDT
Silver Hake	14	100	0.025-0.457	5.1
Red Hake	14	93	0.002-0.042	3.3
Yellowtail Flounder	16	94	0.002-0.052	4.8
Winter Flounder	13	85	0.002-0.031	5.6
Windowpane Flounder	8	100	0.004-0.086	5.0
Four Spot Flounder	4	100	0.004-0.008	4.5
Summer Flounder	1	100	0.014	4.7
American Dab	4	100	0.001-0.024	5.5
Haddock	7	100	0.001-0.026	-
Cod	5	80	0.002-0.018	2.8
Skate	2	100	0.002-0.012	6
Scallop	1	100	0.001	-
Rock Crab	1	100	0.043	1.7
Lobster	2	100	0.1-0.15	3.5

*Dry weight basis.

6. Summary of Data Acquired

The above-mentioned analytical scheme was applied to those samples previously inventoried in Section 3, Table 3-1. PAH determinations were made in those samples presented in Section 4, Table 4-1.

7. Statement of Problems

Trace organic pollutants measured here in muscle tissue are more likely to accumulate in organs such as the liver and kidney to much higher levels than observed here. While it may be more appropriate in terms of considerations of human consumption to monitor muscle tissue, if chemical measurements are to be linked to biochemical or physiological change, analysis of the accumulator organs is required.

Furthermore, while the concept of PHC monitoring seems rational, only certain components of the broad PHC class of compounds are considered "toxic" or "mutagenic," i.e., the PAH compounds. Significantly more effort and emphasis should in the future be placed on GC/MS analysis of PAH compounds, perhaps using sample extracts obtained here and also in future studies.

The final "problem" or recommendation pertain to evaluating sources of observed pollutants. In order to fully evaluate how fish acquire pollutants and what are the likely future paths of uptake of PHC, PCB, and PAH (compounds), the chemical composition and an evaluation of the key chemical ratios (e.g., PCB/ DDT) in suspected sources (water column particulates, surface sediment, prey, etc.) should supplement fish monitoring studies. This combined evaluation of observed pollutant levels and sources of pollutants are the roots of a true monitoring program addressing contaminant levels in commercially important fish.

8. Data Appendices

Detailed analytical results are presented in Tables 8-1 through 8-9.

TABLE 8-1

ANALYTICAL SUMMARY - SILVER HAKE

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
33	10	X		4.0	9.0	0.149	0.036	4.1
39	6	X		9.0	32.3	0.284	0.075	3.8
40	12	X		10.0	37.5	0.157	0.047	3.3
47	5	X		2.3	6.5	0.076	0.015	5.1
55	11	X		19.7	93.1	0.457	0.073	6.3
60	10	X		21.4	75.0	0.215	0.063	3.4
66	8	X		6.2	15.2	0.203	0.030	6.8
68	10	X		2.9	3.0	0.025	0.003	8.0
100	7	X		6.0	17.5	0.319	0.038	8.4
118	8	X		4.3	15.7	0.035	0.010	3.5
125	6	X		2.5	10.4	0.079	0.002	4.0
126	10	X		4.2	6.0	0.100	0.026	4.0
137	3		X			0.031	0.016	2.0
157	4		X			0.017	0.002	8.5
					$\bar{X}$ = 26.8 ± 28.9	$\bar{X}$ = 0.15 ± 0.13	$\bar{X}$ = 0.031 ± 0.026	$\bar{X}$ = 5.1 ± 2.1

TABLE 8-2

ANALYTICAL SUMMARY - RED HAKE

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
21	6	X		1.6	1.6	0.042	0.023	1.8
33	15		X			0.006	0.006	1.0
35	12	X		1.6	2.0	0.013	0.004	3.3
47	10		X			0.007	ND	--
60	10		X			0.010	0.004	2.5
66	6		X			0.032	ND	--
111	3		X			0.002	ND	--
116	10		X			0.019/ 0.035	0.000/ 0.011	3.2/ 3.2
118	8	X		1.0	1.0	0.007	0.001	7
125	8		X			0.004	0.001	4
126	7	X		2.9	5.4	0.035	0.008	4.4
135	9		X			0.016	0.007	2.3
137	6		X			0.003	ND	--
157			X			ND	ND	--
					$\bar{X}$ = 7.5 ± 1.7	$\bar{X}$ = 0.015 ± 0.013	$\bar{X}$ = 0.005 ± 0.006	$\bar{X}$ = 3.3 ± 1.8

TABLE 8-3

ANALYTICAL SUMMARY - YELLOWTAIL FLOUNDER

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
40	7		X			0.037	0.011	3.4
49	6		X			0.028	0.039	0.8
55	7	X		4.5	6.5	0.007	0.001	7.0
58	8		X			0.039	0.006	6.5
60	6	X		1.3	4.0	0.033	0.007	4.7
68	2	X		2.1	2.1	0.008	0.002	4.0
77	5		X			0.011	0.002	5.5
79	8		X			0.008	0.002	4.0
95	8		X			0.003	ND	5.5
101	3	X		2.4	3.7	0.025	0.005	4.0
106	8		X			0.003	ND	--
123	4		X			0.002	ND	5.0
132	5		X			0.002	ND	--
139	5	X		2.0	3.7	0.015	0.002	--
144	3		X			ND	ND	7.5
146			X			0.052/ 0.002	ND/ ND	--/ --
					$\bar{X}$ = 4.0 ± 1.7	$\bar{X}$ = 0.018 ± 0.017	$\bar{X}$ = 0.005 ± 0.009	$\bar{X}$ = 4.8 ± 7.0

TABLE 8-4

ANALYTICAL SUMMARY - WINTER FLOUNDER

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
52	8	X		1.0	6.2	0.025	0.004	6.3
55			X			0.031	0.003	10.0
58			X			0.024	0.003	8.0
95			X			0.021	0.002	10.5
77	8		X			0.006	0.002	3.0
101	6		X			0.005	0.007	0.7
105	2		X			0.006	ND	-
113	4		X			0.004	0.005	0.8
123	5		X			ND	ND	-
134	1		X			0.004	ND	-
139	4	X		1.4	8.7	0.005	ND	-
142	1		X			ND	ND	-
157	1		X			0.002	ND	-
					$\bar{X}$ = 5.5	$\bar{X}$ = 0.01 ± 0.01	$\bar{X}$ = 0.002 ± 0.002	$\bar{X}$ = 5.6 ± 4.2

TABLE 8-5

ANALYTICAL SUMMARY - WINDOWPANE FLOUNDER

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
33	9		X			0.015	0.007	2.1
39	8		X			0.023	0.006	3.8
40	9		X			0.018	0.004	4.5
77	6		X			0.014	0.002	7.0
79	8	X		1.0	1.7	0.004	ND	--
95	8	X		6.2	6.5	0.086	0.011	7.8
101	6		X			0.018	0.033	6.0
116	2	X		1.8	4.8	0.004	0.001	4.0
					$\bar{X}$ = 4.2 ± 2.3	$\bar{X}$ = 0.02 ± 0.02	$\bar{X}$ = 0.004 ± 0.003	X = 5.0 ± 2.0

TABLE 8-6

ANALYTICAL SUMMARY - HADDOCK

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDROCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)	
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	ΣPCB	ΣDDT
105	11	X		1.0	1.0	0.004	ND
111	5		X			0.004	0.002
113	5		X			0.002	ND
123	4	X		2.0	2.0	0.004	0.001
132	1		X			0.026	0.002
139	4		X			0.001	ND
147	6		X			0.003	ND
					$\bar{X}$ = 1.5	$\bar{X}$ = 0.006 ± 0.008	

TABLE 8-7

ANALYTICAL SUMMARY - COD AND FOUR SPOT FLOUNDER

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
				COD				
101	3		X			ND	ND	--
105	6		X			0.003	0.004	0.75
113	3		X			0.018	0.005	3.6
123	3		X			0.003/ 0.005	0.001	4.0
142	3		X			0.002	ND	--
						$\bar{X}$ = 0.005 ± 0.002		
				FOUR SPOT FLOUNDER				
60	9		X			0.004	ND	--
116	10		X			0.005	0.001	5
118	10	X		1.7	1.8	0.008	0.002	4
100	1	X		3.3	5.7	0.004	ND	--
						$\bar{X}$ = 0.005		

TABLE 8-8

ANALYTICAL SUMMARY - OTHER SPECIES

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
				SUMMER FLOUNDER				
81	2		X			0.014	0.003	4.7
				LITTLE SKATE				
95	9		X			0.012	0.002	6
116	2		X			0.002	ND	--
				ROCK CRAB				
35	12	X		77	327	0.043	0.025	1.7
				CANCER CRAB				
125	4		X			0.002	ND	--
				SCALLOPS				
47	5		X			0.001	ND	--
				LOBSTER				
47	6		X			0.095	0.024	4
49	3		X			0.150	0.050	3

TABLE 8-9

ANALYTICAL SUMMARY - AMERICAN DAB

STATION	NO. OF INDIVIDUALS	PETROLEUM HYDROCARBON SCREEN		PETROLEUM HYDORCARBONS (µg/g)		CHLORINATED HYDROCARBONS (µg/g)		
		POSITIVE	NEGATIVE	RESOLVED	TOTAL	PCB	ΣDDT	PCB/ΣDDT
105	2		X			0.005	0.001	5
106	5	X		1.0	1.5	0.024	0.003	8
111	9		X			0.007	0.002	3.5
125	9		X			0.001	ND	
						$\bar{X}$ = 0.004 ± 0.01	$\bar{X}$ = 0.002	$\bar{X}$ = 5.5 ± 2.3

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