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# Gulf and Atlantic Survey for Selected Organic Pollutants in Finfish

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**16. ABSTRACT** This issue combines two reports prepared by the Energy Resources Co., Inc. The first report, "Gulf and Atlantic Survey for Selected Organic P1lutants in Finfish. 1: Gulf of Maine to Cape Hatteras," presents information on both finfish and benthic invertebrates. The secon report, "2: Chesapeake Bay to Port Isabel, Texas," presents information on finfish only. Selected finfish and benthic ecpfaunal samples were analyzed for levels of petroleum hydrocarbons, chlorinated hydrocarbons, and polynuclear aromatic hydrocarbons contained in edible flesh. 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 "not sports, (3) identify any pollution gradients that may exist from a potential source region through the study area, (4) utilize and evaluate a cost-effective multiphase 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. (Author extracted)

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II. CHESAPEAKE BAY TO PORT ISABEL, TEXAS

## FOREWORD

This issue of the *NOAA Technical Memorandum NMFS-F/NEC* series combines two reports prepared by the Energy Resources Co., Inc. (ERCO), under contract to the National Oceanic and Atmospheric Administration's (NOAA) National Marine Fisheries Service (NMFS). The contracts for both reports (i.e., NOAA Contract No. NA-80-FA-C-00046 and NOAA Contract No. NA-81-FA-C-00013) were awarded as part of NOAA's Northeast Monitoring Program, and were monitored by Dr. John B. Pearce, Chief of the Division of Environmental Assessment for NMFS's Northeast Fisheries Center.

The first report, "Gulf and Atlantic Survey for Selected Organic Pollutants in Finfish. I. Gulf of Maine to Cape Hatteras," presents information on both finfish and benthic invertebrates; it was submitted as a final report on 10 November 1980. The second report, "Gulf and Atlantic Survey for Selected Organic Pollutants in Finfish. II. Chesapeake Bay to Port Isabel, Texas," presents information on finfish only; it was submitted as a final report on 5 January 1982.

Both reports have been reprinted virtually as submitted; no substantive changes have been made. Some minimal format changes (i.e., title wording, section numbering, and text pagination) have been made to avoid confusion as a result of combining two separate reports. Both reports refer to specific trade names; such reference does not imply NOAA/NMFS endorsement.

Jon A. Gibson, Coordinator
*NOAA Technical Memorandum*
*NMFS-F/NEC* series

# GULF AND ATLANTIC SURVEY FOR SELECTED ORGANIC POLLUTANTS IN FINFISH

## I. GULF OF MAINE TO CAPE HATTERAS

## 1. 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 multiphase 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.

## 2. Summary of Activities and Rationale

### 2.1 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

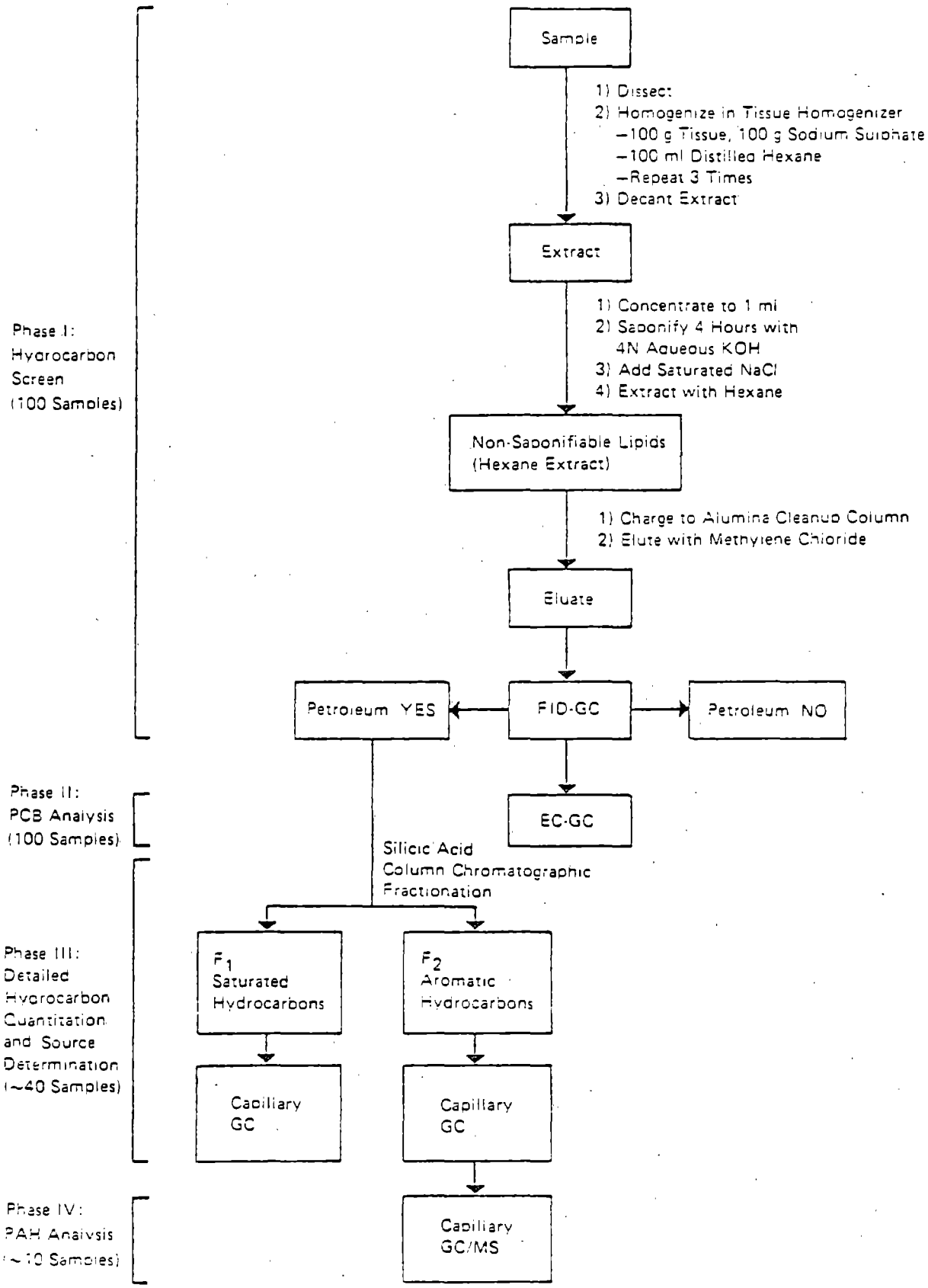


Figure 1. Proposed Multiphase Analytical Scheme.

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.

## 2.2 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 2-1.

### 2.2.1 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 2-1. 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.

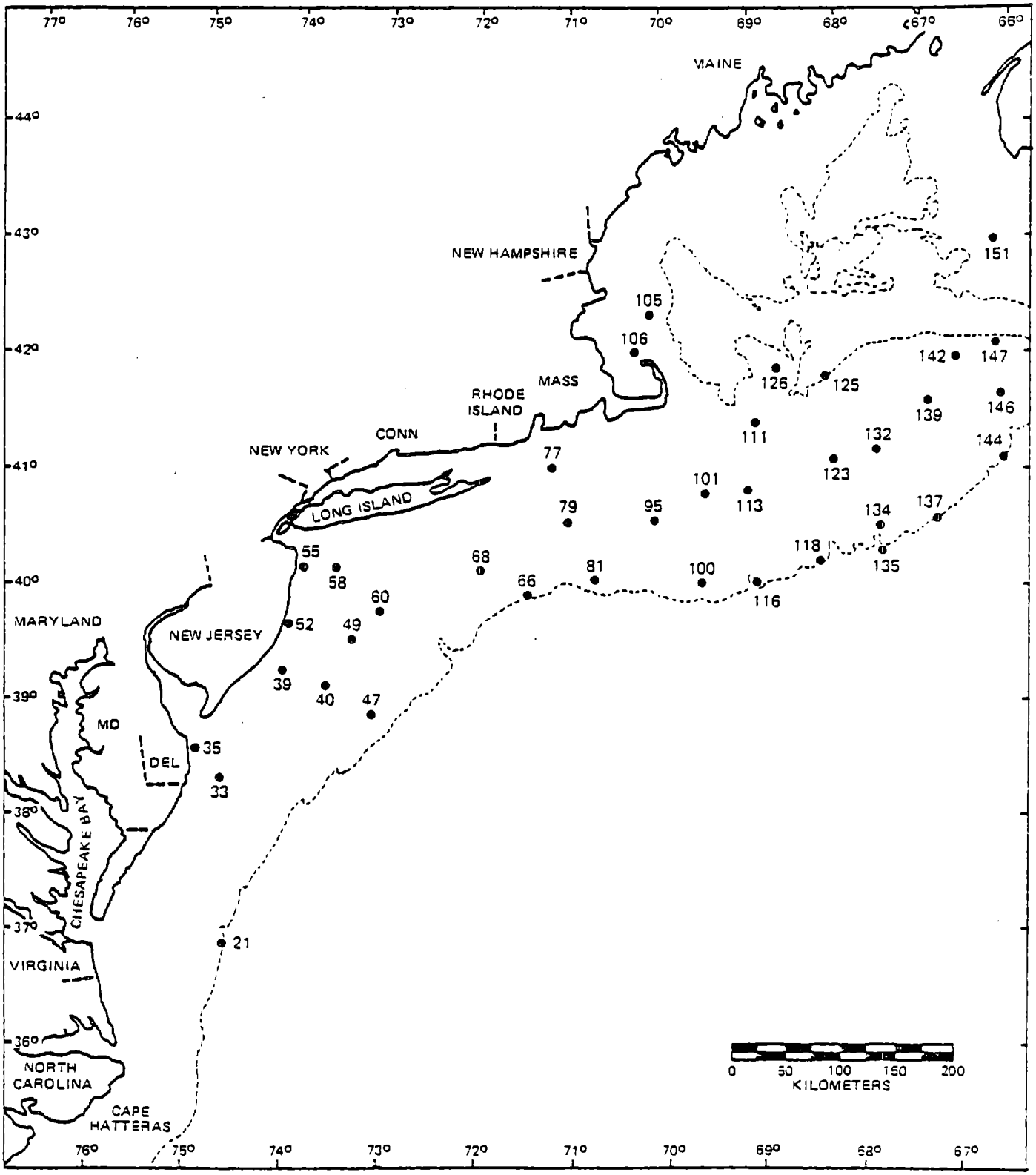


Figure 2. Map of Sampling Locations for Petroleum Hydrocarbon and PCB Analysis.

TABLE 2-1

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.

### 2.2.2 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.

### 2.2.3 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.

### 2.2.4 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.

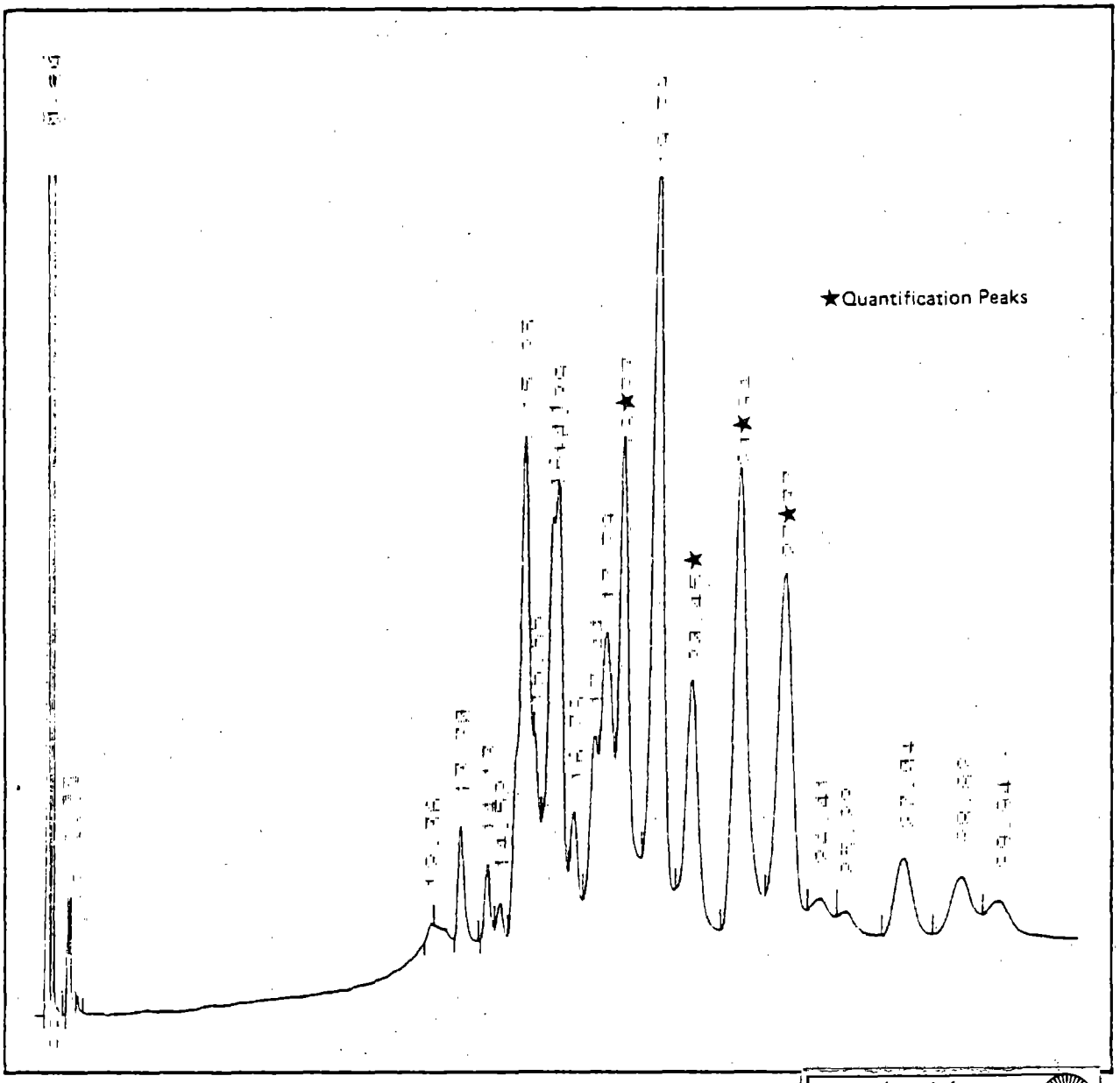




Figure 3. PCB Standard—Aroclor 1254.

## 3. Summary of Findings

Tabulations of the analytical results of this study are presented in Section 6, Tables 6-1 to 6-13, 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 $\sim \pm 0.2$).

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 $\Sigma$DDT 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.

### 3.1 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 $\mu$g/g ($\bar{X}_{PHC} = 27 \pm 29$) (see Section 6, Table 6-1). 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-$C_{13}$ to n-$C_{20}$ 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).

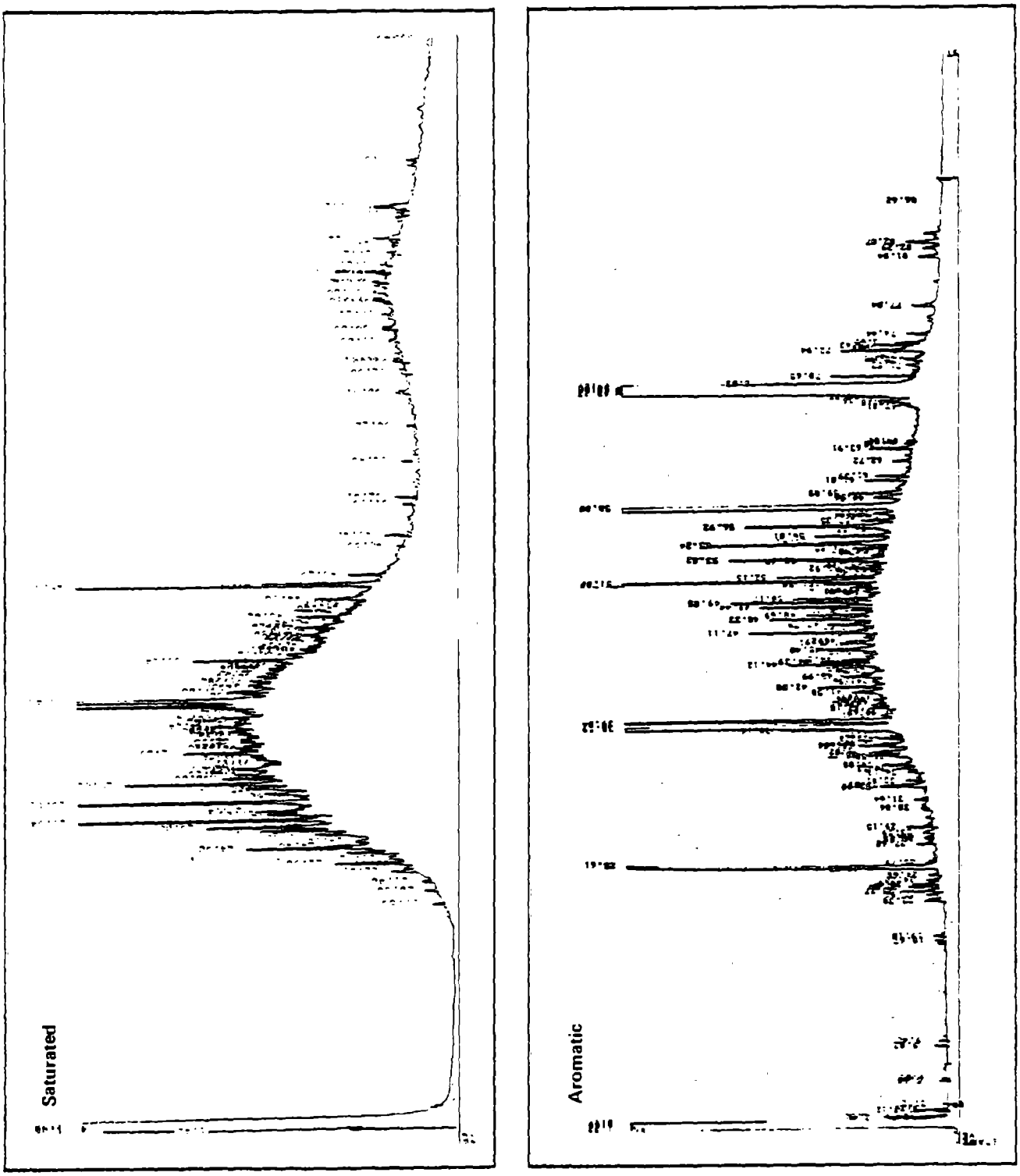


Figure 4. Petroleum Hydrocarbons in Silver Hake (Station 40).

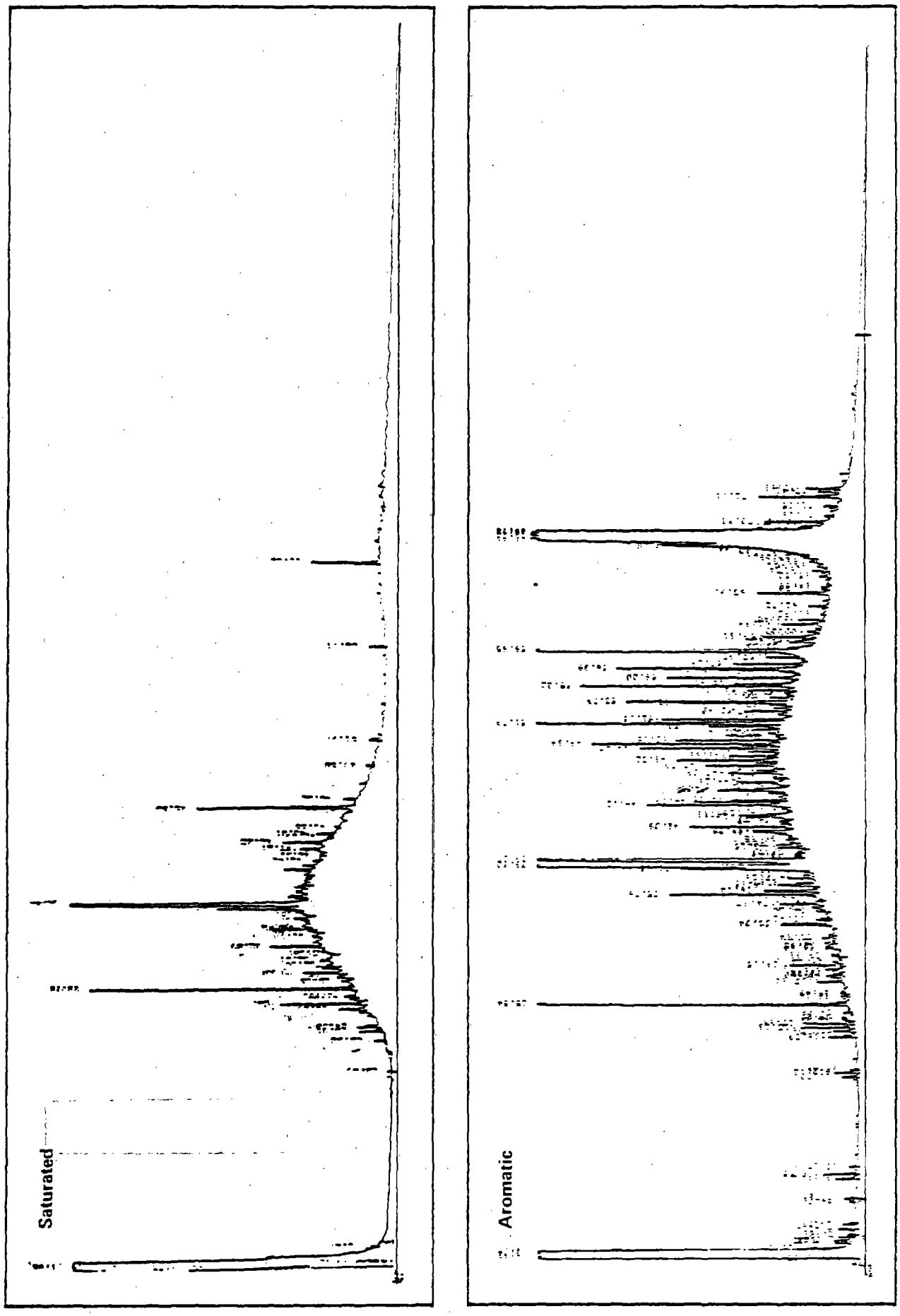


Figure 5. Petroleum Hydrocarbons in Silver Hake (Station 55).

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 3-1) 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.

### 3.2 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 3-1

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 = dibenzothiophenes
F = fluorenes
202 = fluoranthene + pyrene

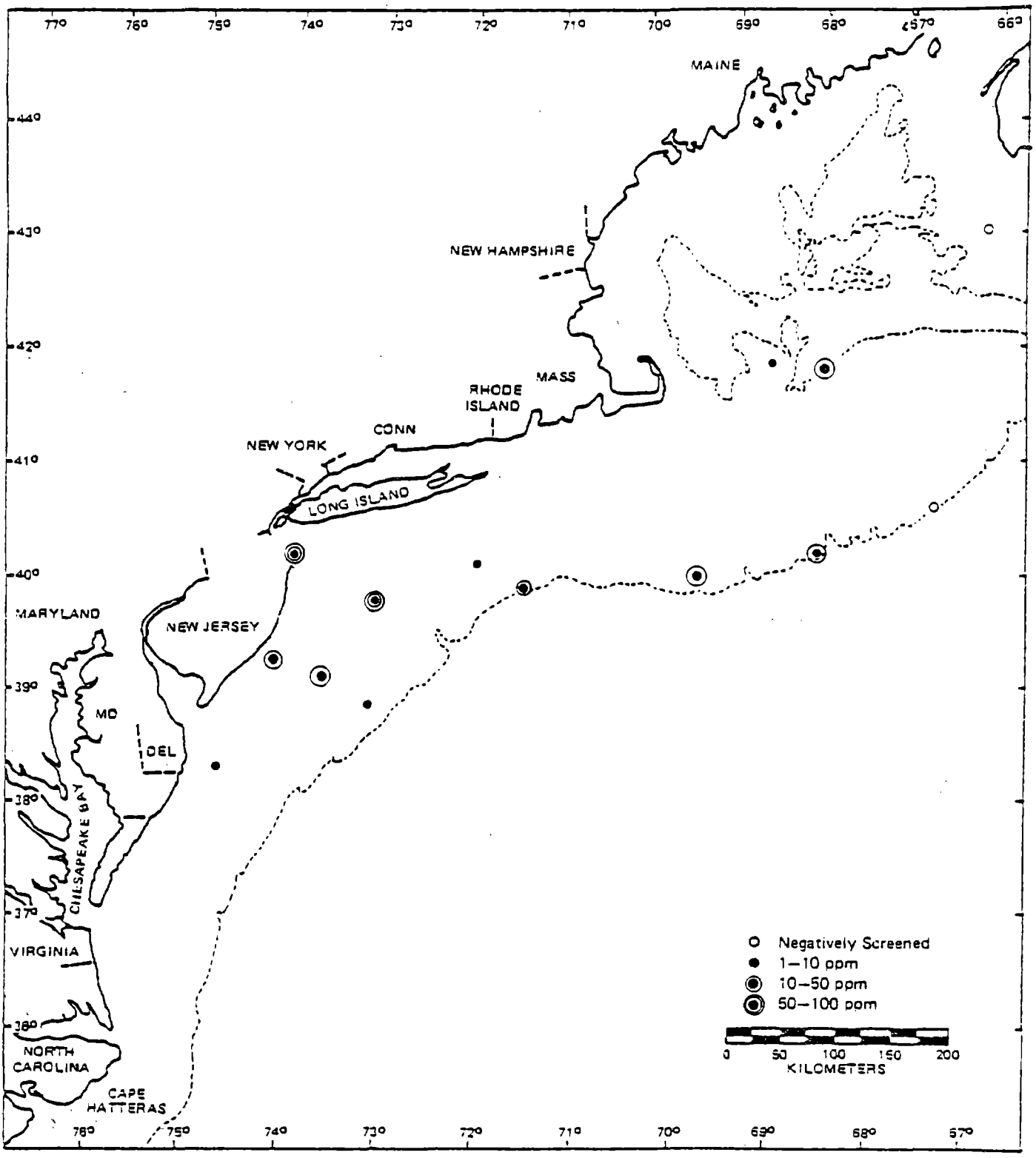


Figure 6. Silver Hake—Petroleum Hydrocarbons.

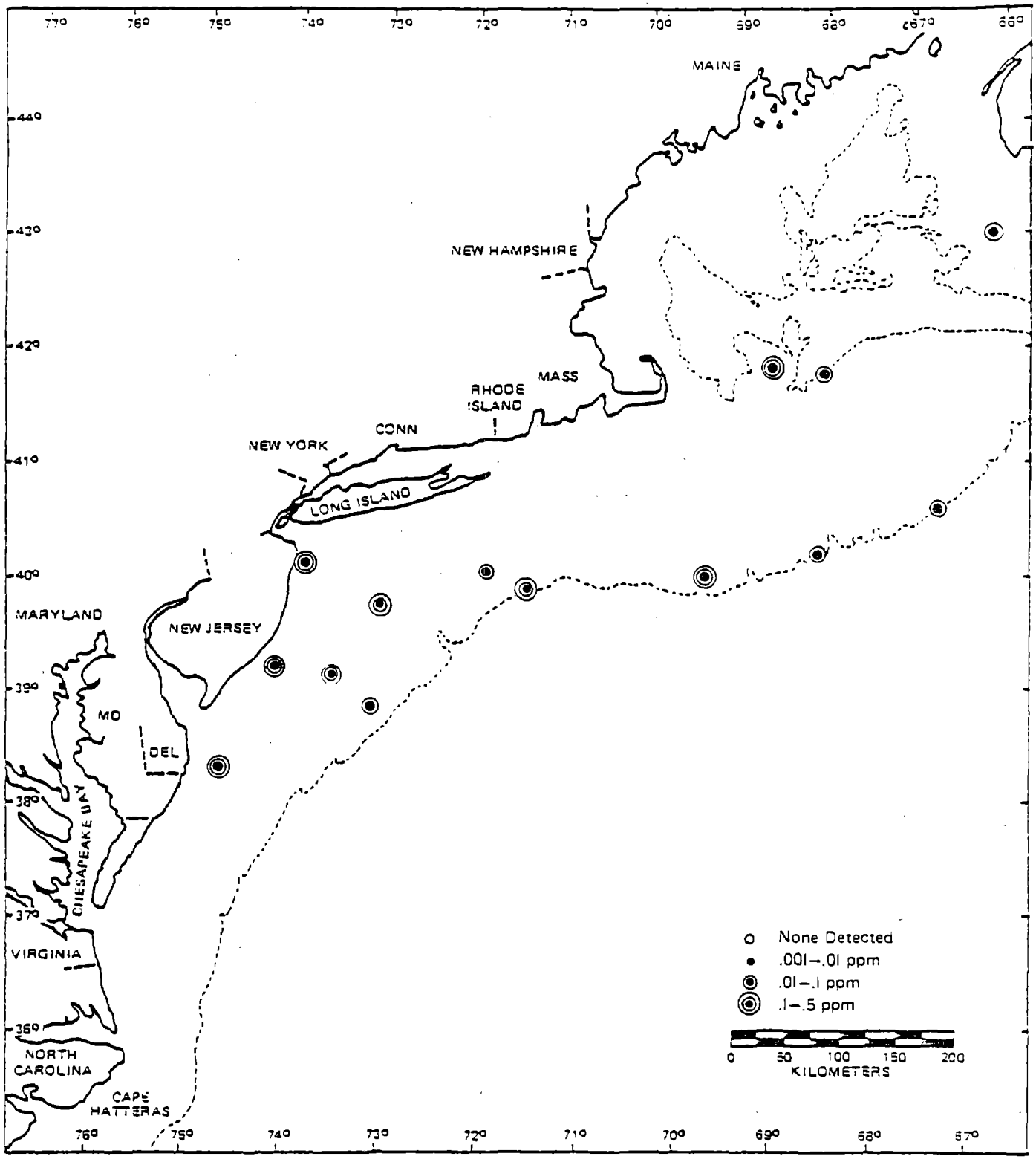


Figure 7. Silver Hake—PCB.

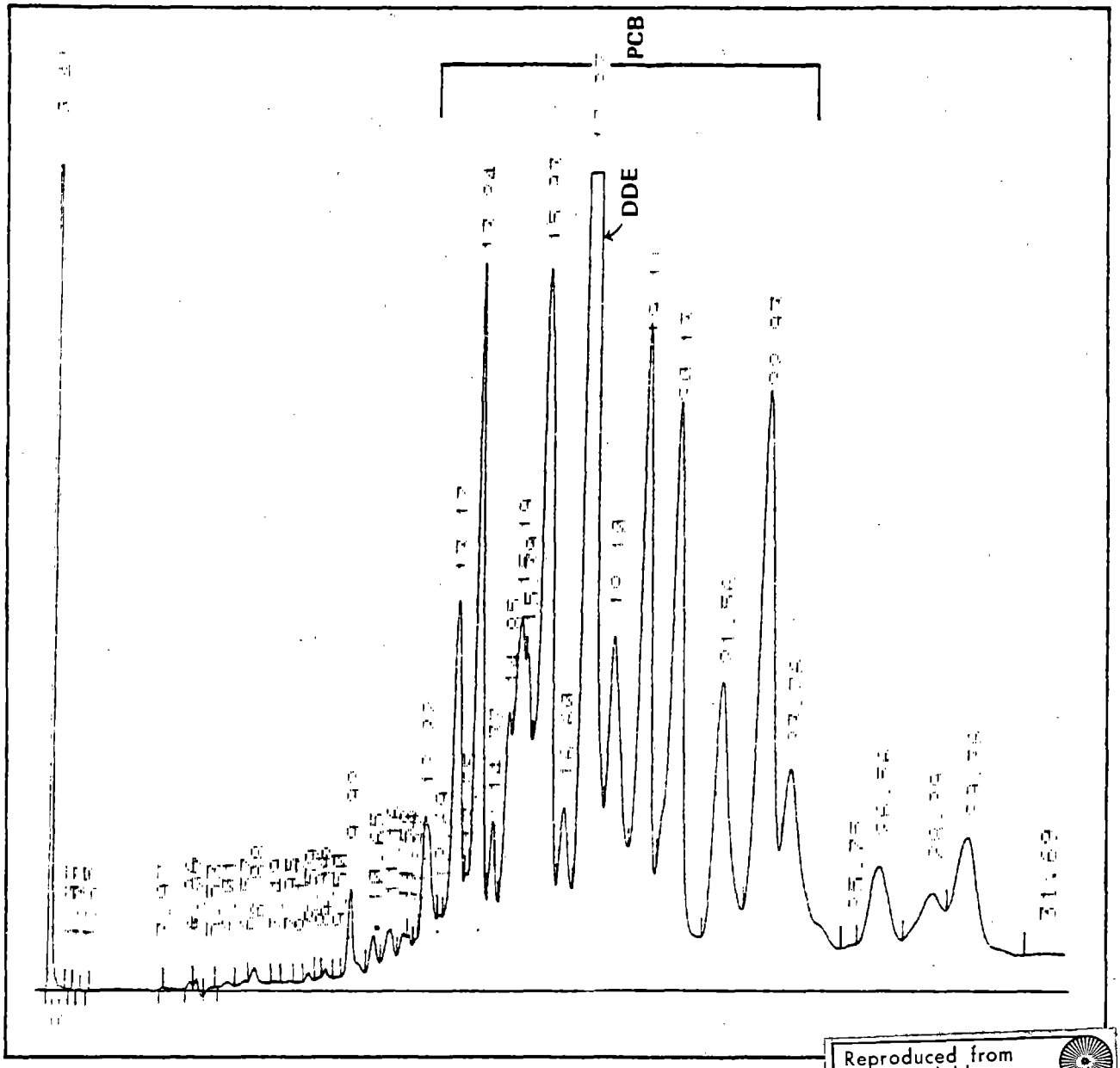




Figure 8. PCB and DDE in Silver Hake (Station 33).

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 6, Table 6-2) are quite low (PCB = mean 0.015 ± 0.015 g/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.

### 3.3 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 6, Table 6-3). 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 3-1).

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 compcunds for this species are indicated in Figures 13 and 14.

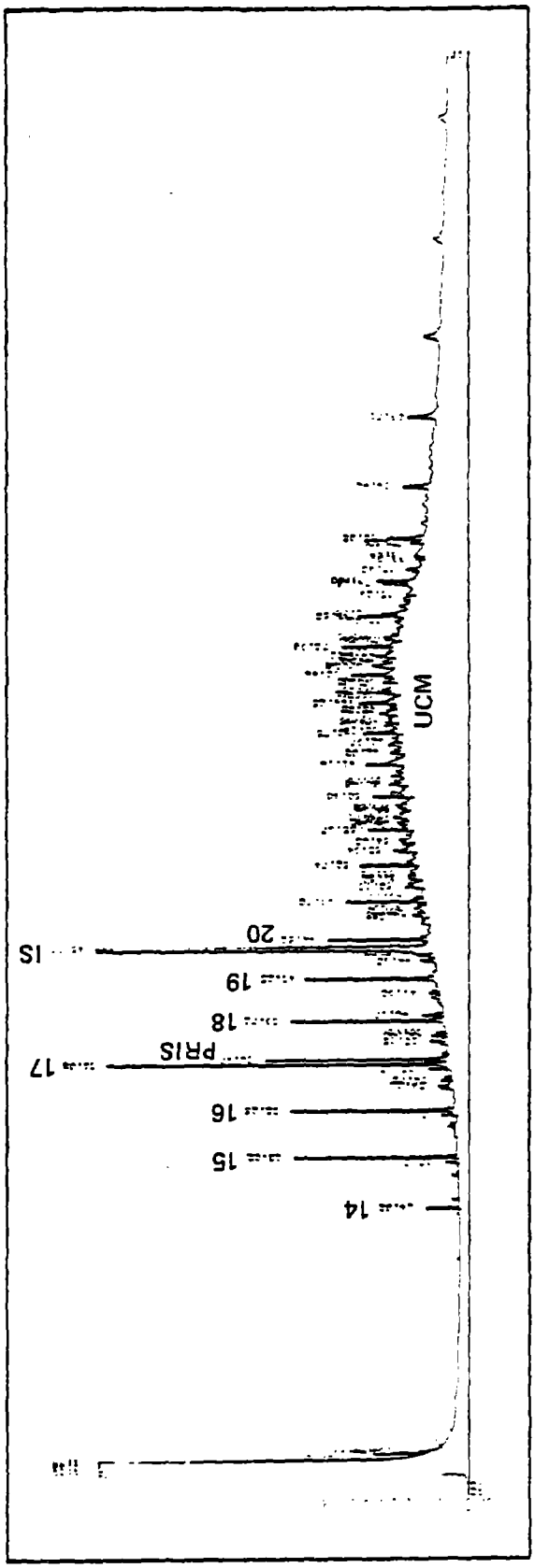


Figure 9. Saturated Hydrocarbon Fraction of Red Hake (Station 126).

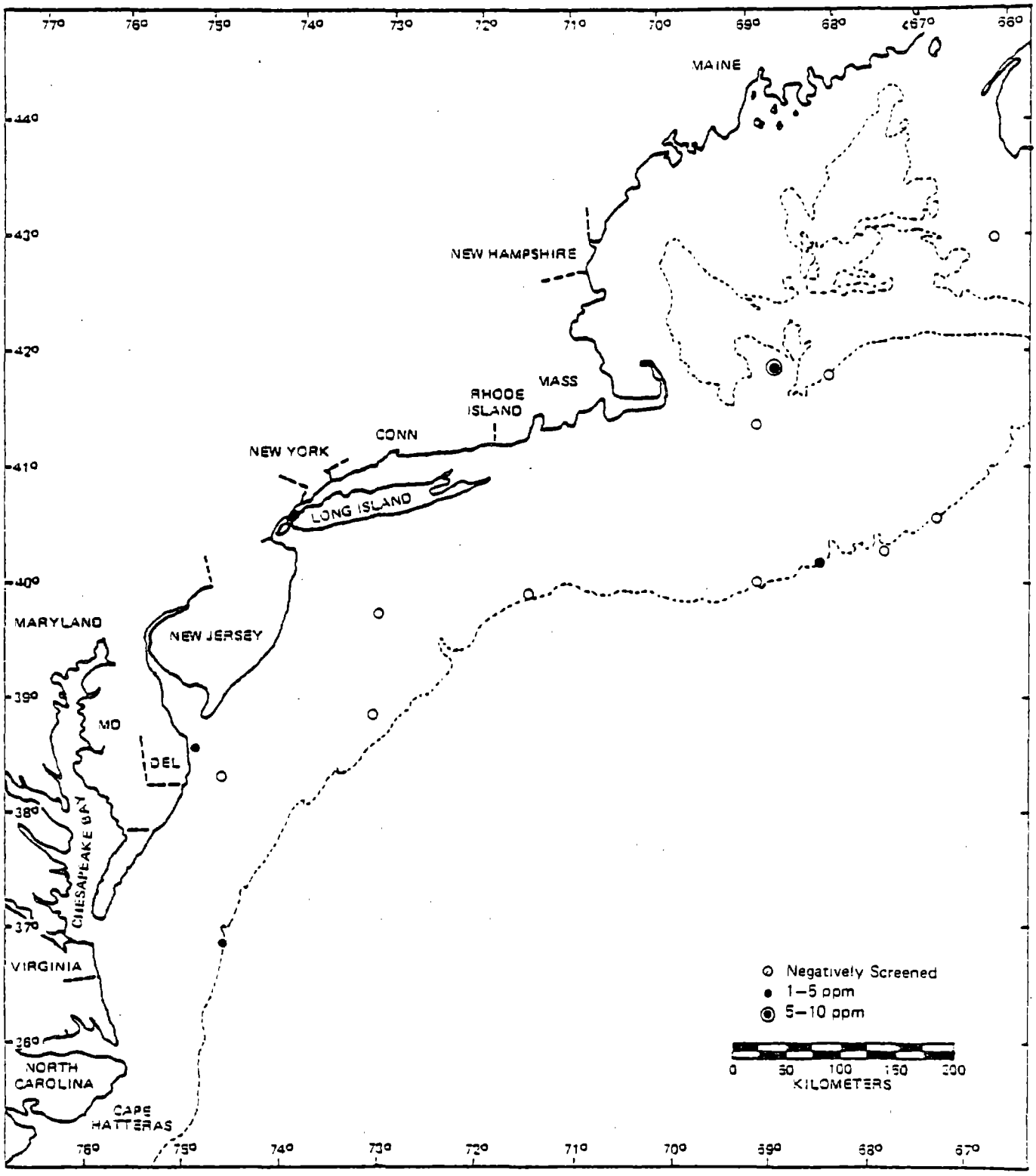


Figure 10. Red Hake—Petroleum Hydrocarbons.

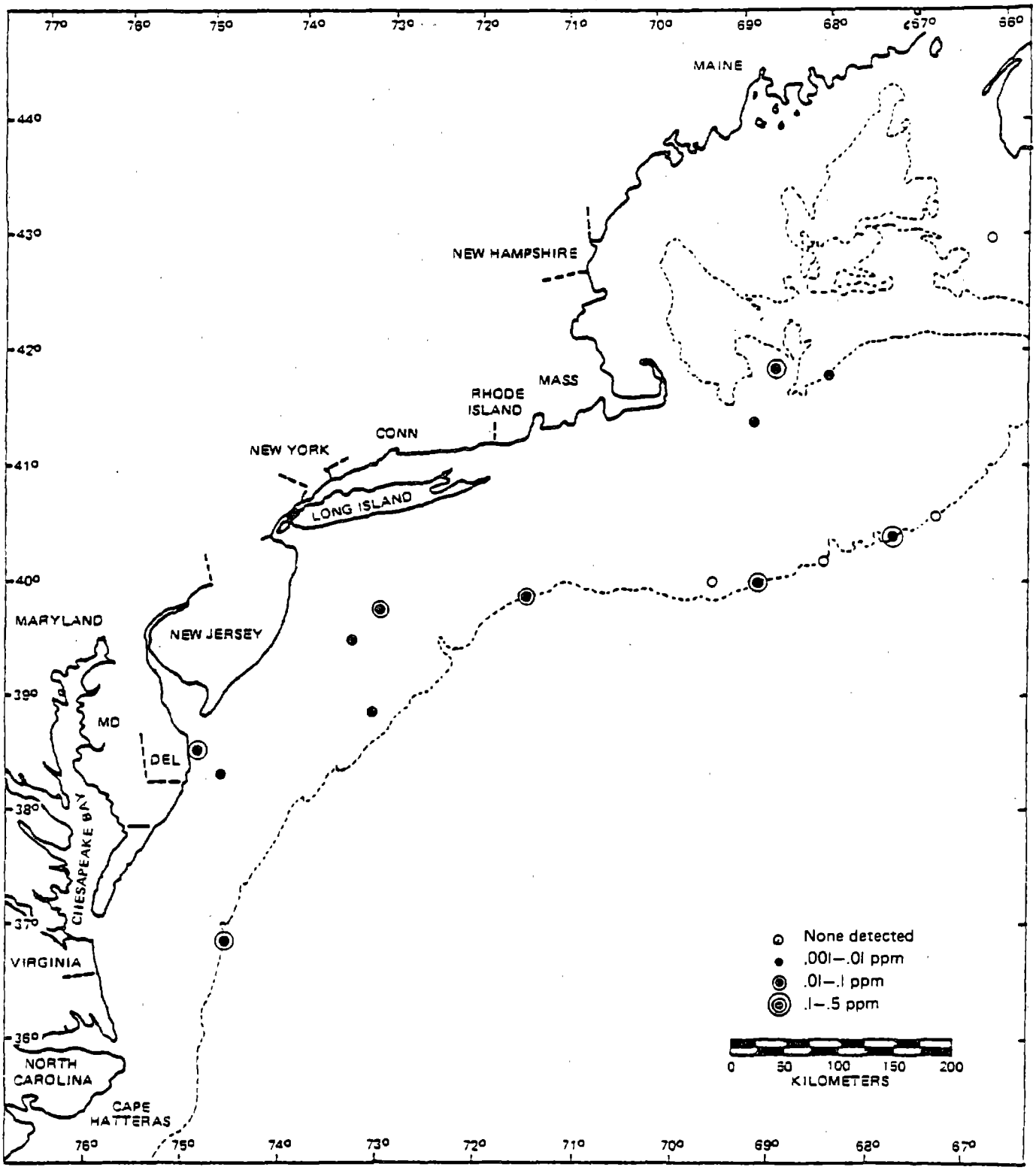


Figure 11. Red Hake–PCB.

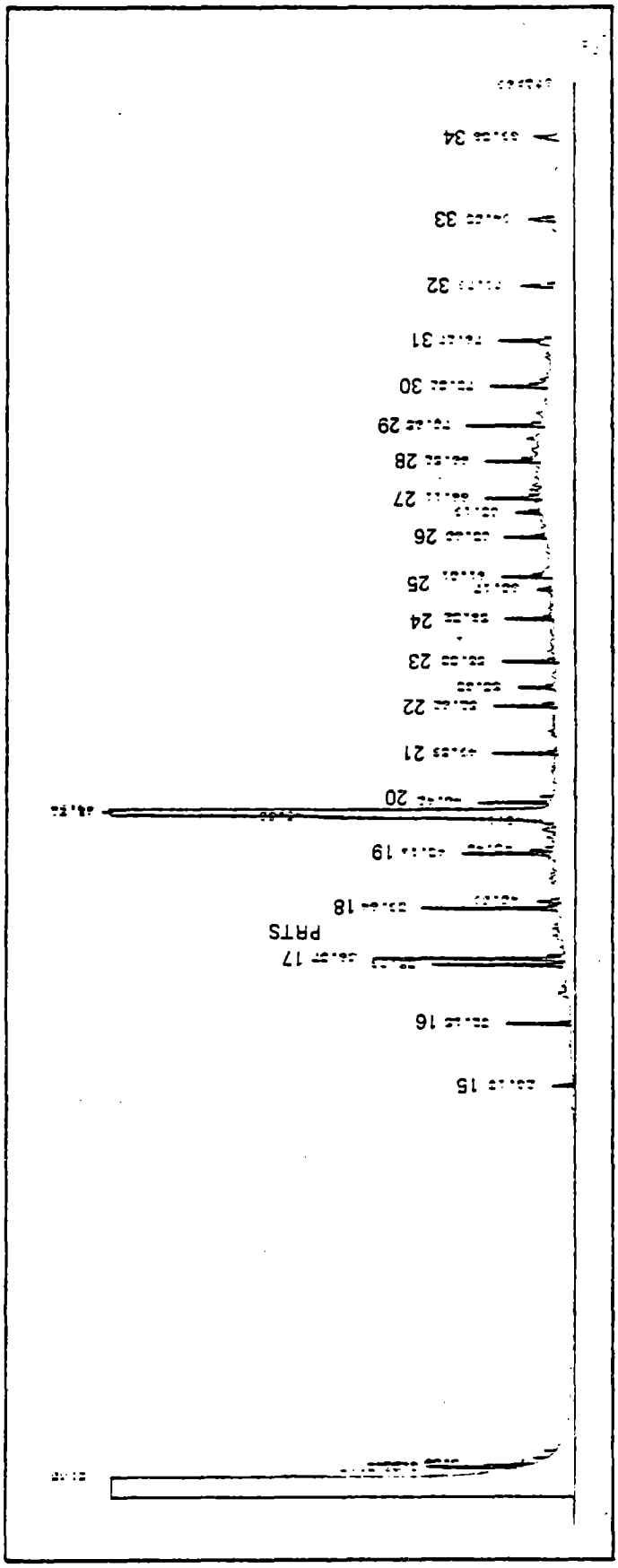


Figure 12. Saturated Petroleum Hydrocarbons in Yellowtail Flounder (Station 101).

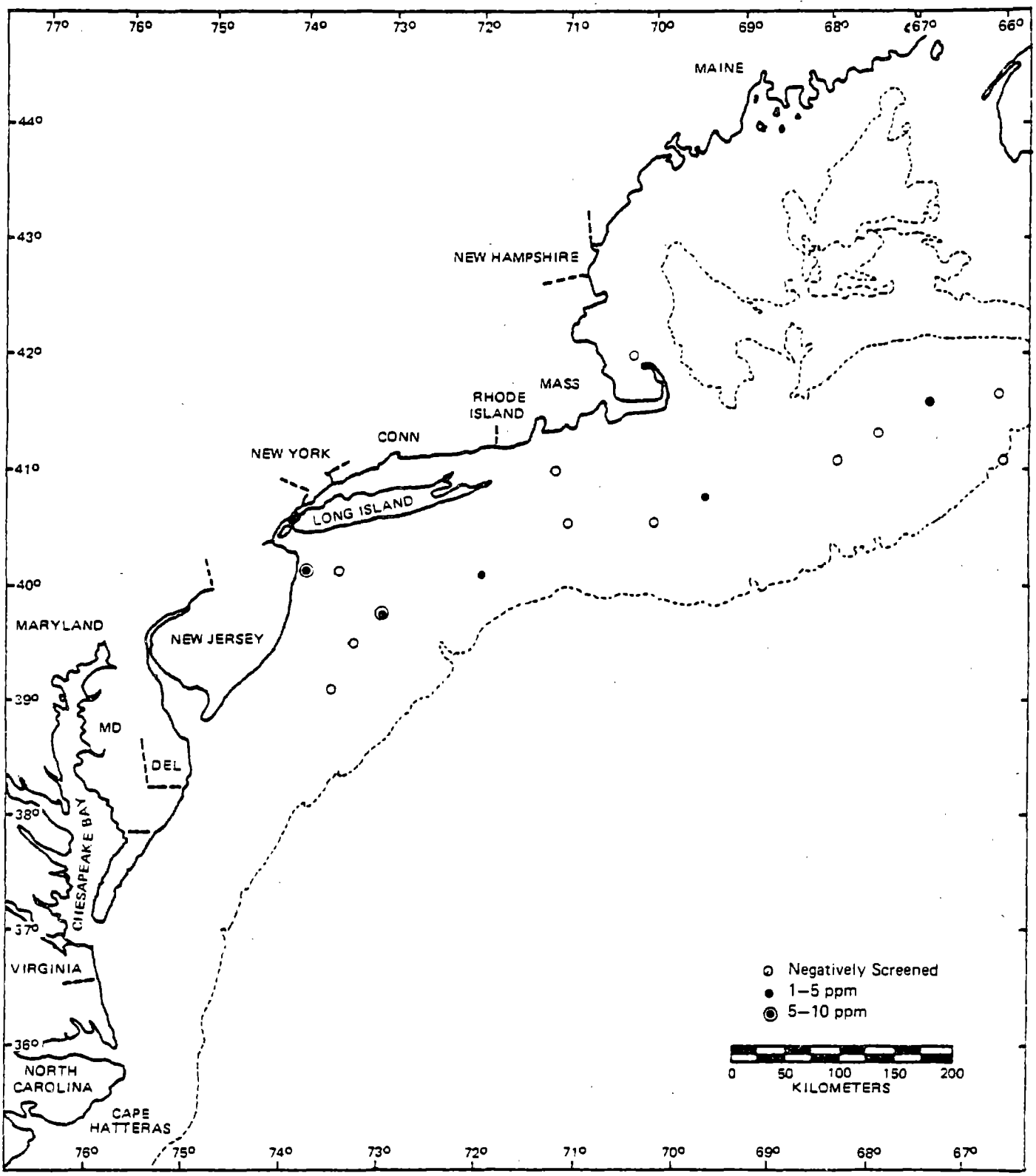


Figure 13. Yellowtail Flounder—Petroleum Hydrocarbons.

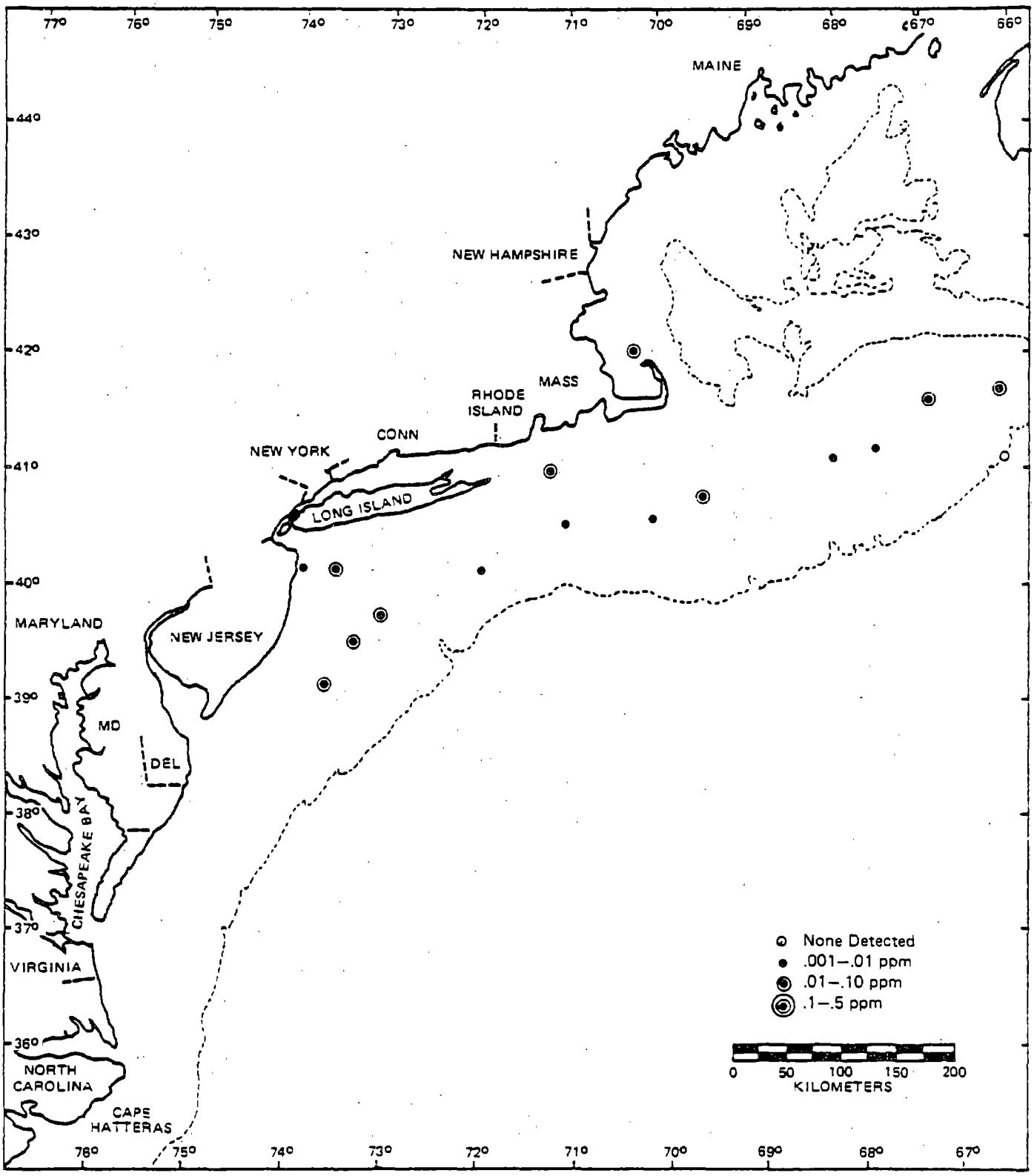


Figure 14. Yellowtail Flounder–PCB.

### 3.4 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 6, Table 6-4) 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 $\pm$ 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.

### 3.5 Windowpane Flounder

Where PHC compounds were present (38%; Stations 79, 95, 116), the absolute concentrations were low (see Section 6, Table 6-5) 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).

### 3.6 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 6, Table 6-6). Two of the seven samples showed slight indications of possible PHC compounds when screened, but little if

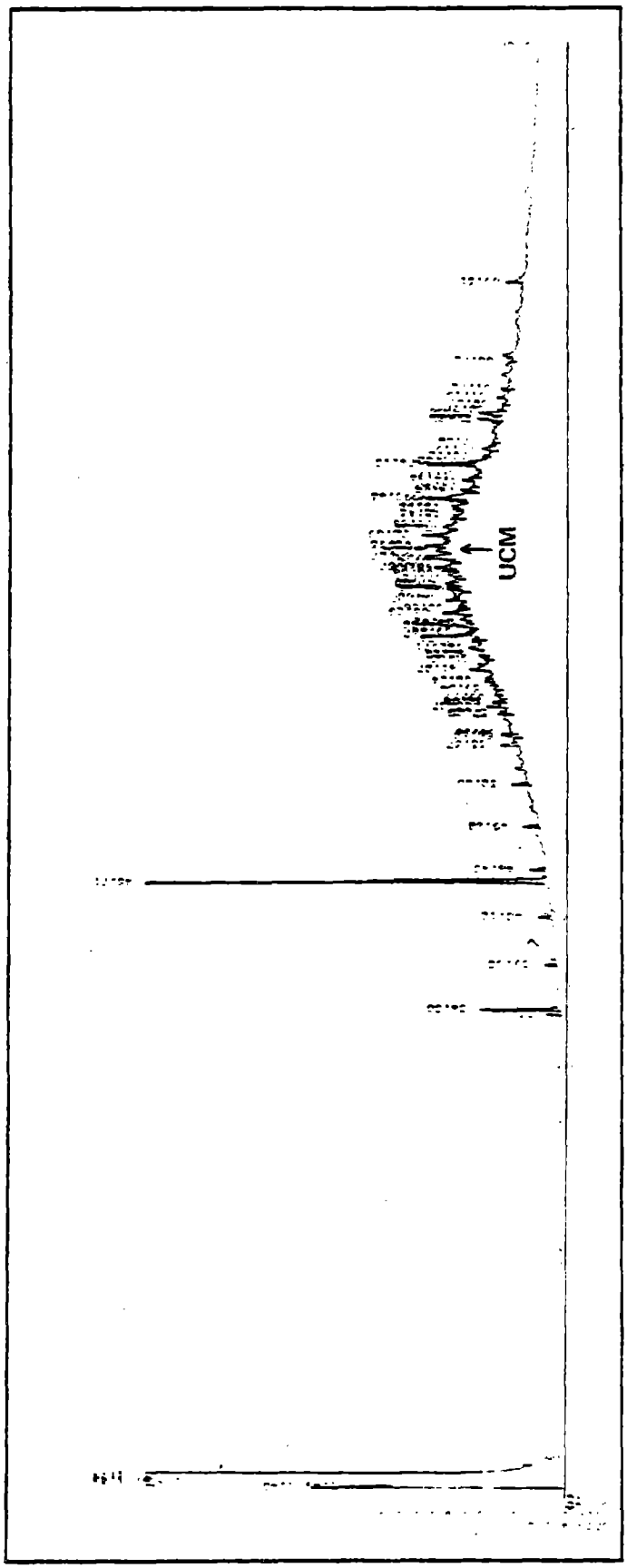


Figure 15. Saturated Petroleum Hydrocarbons in Winter Flounder (Station 139).

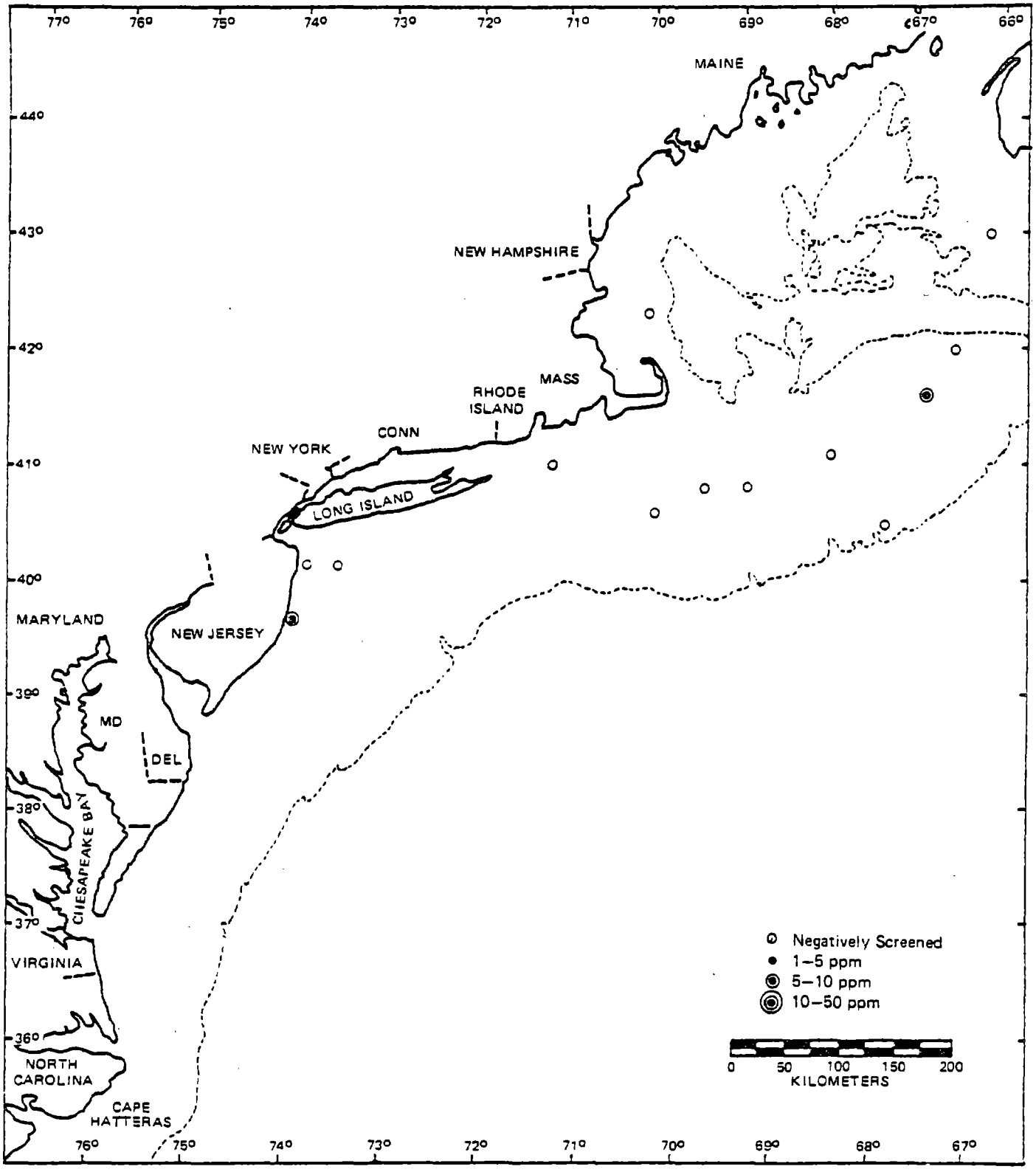


Figure 16. Winter Flounder—Petroleum Hydrocarbons.

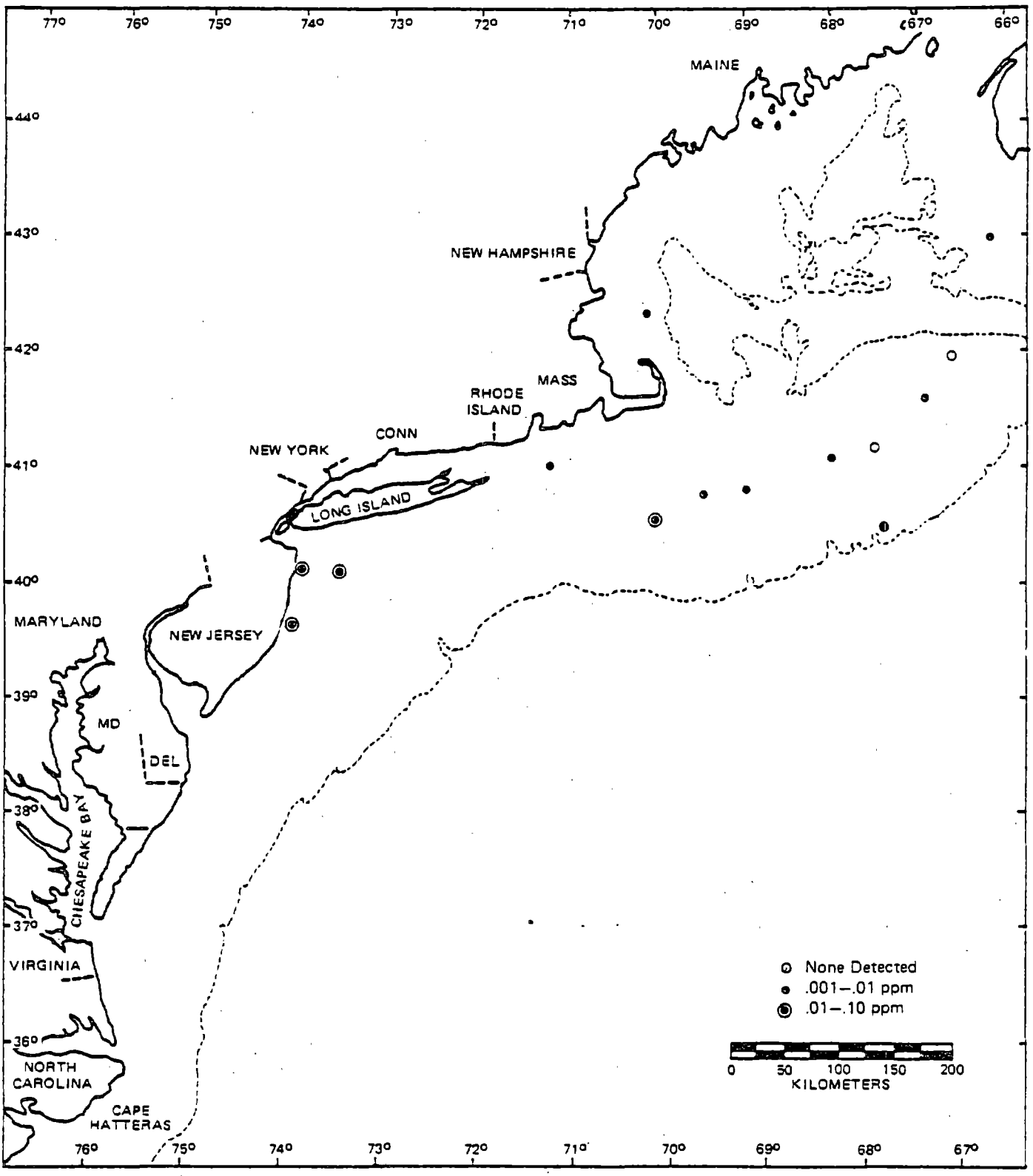


Figure 17. Winter Flounder—PCB.

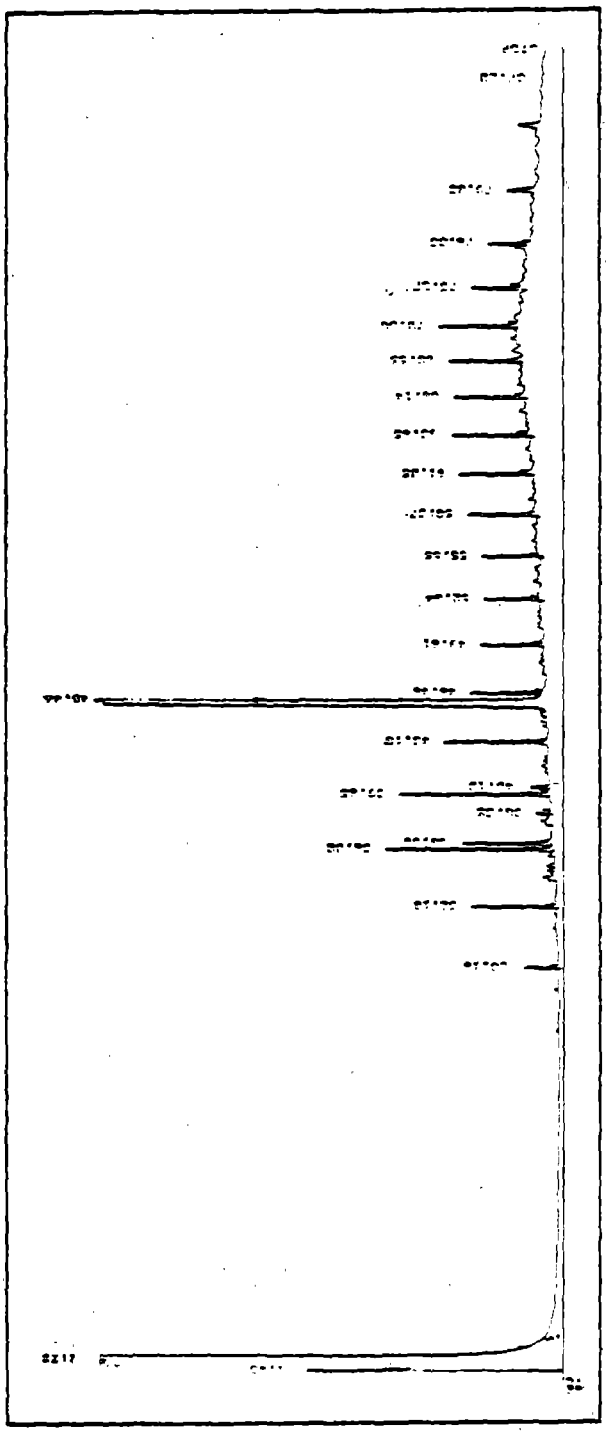

Figure 18. Saturated Petroleum Hydrocarbons in Windowpane Flounder (Station 79).

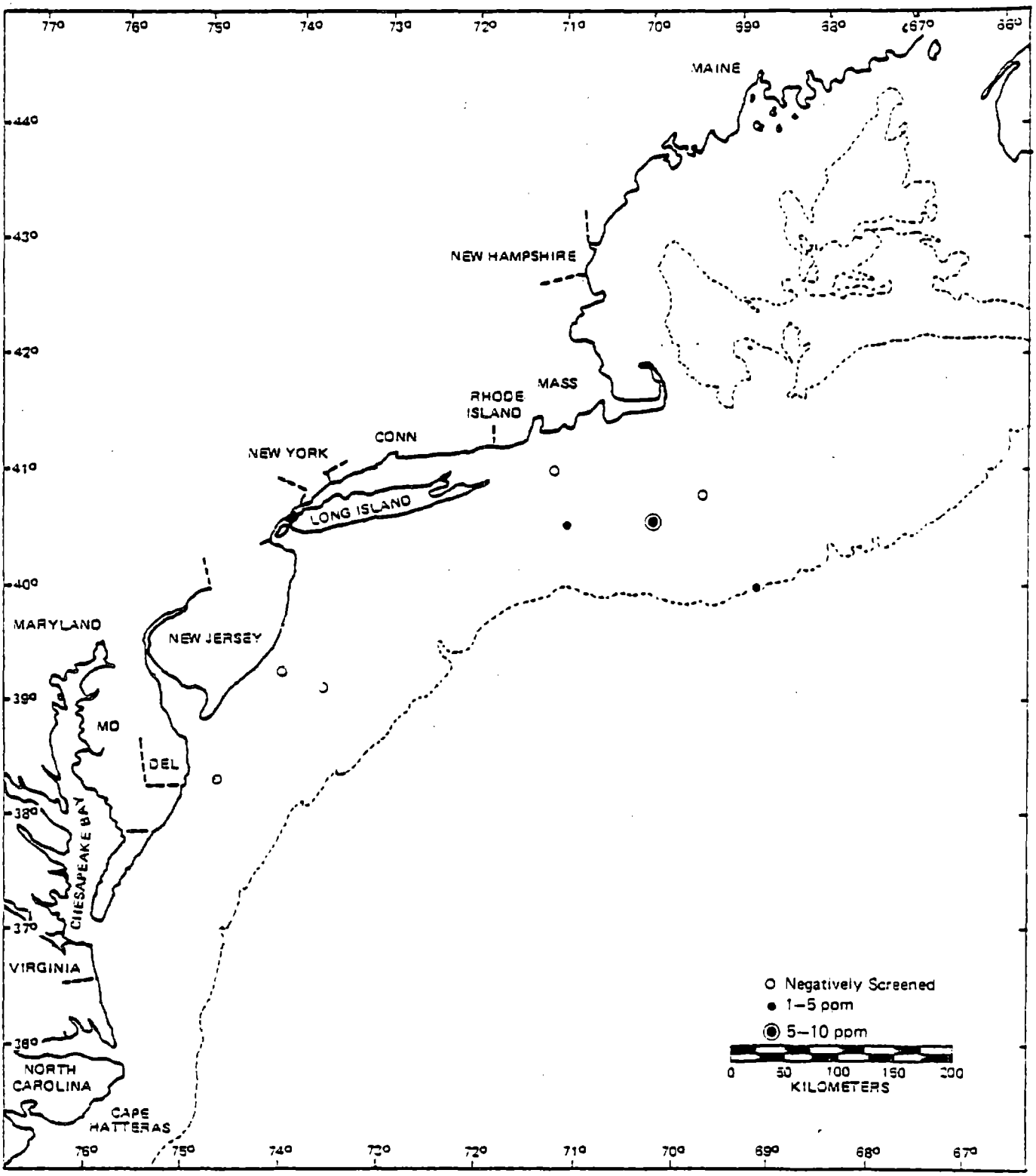


Figure 19. Windowpane Flounder—Petroleum Hydrocarbons.

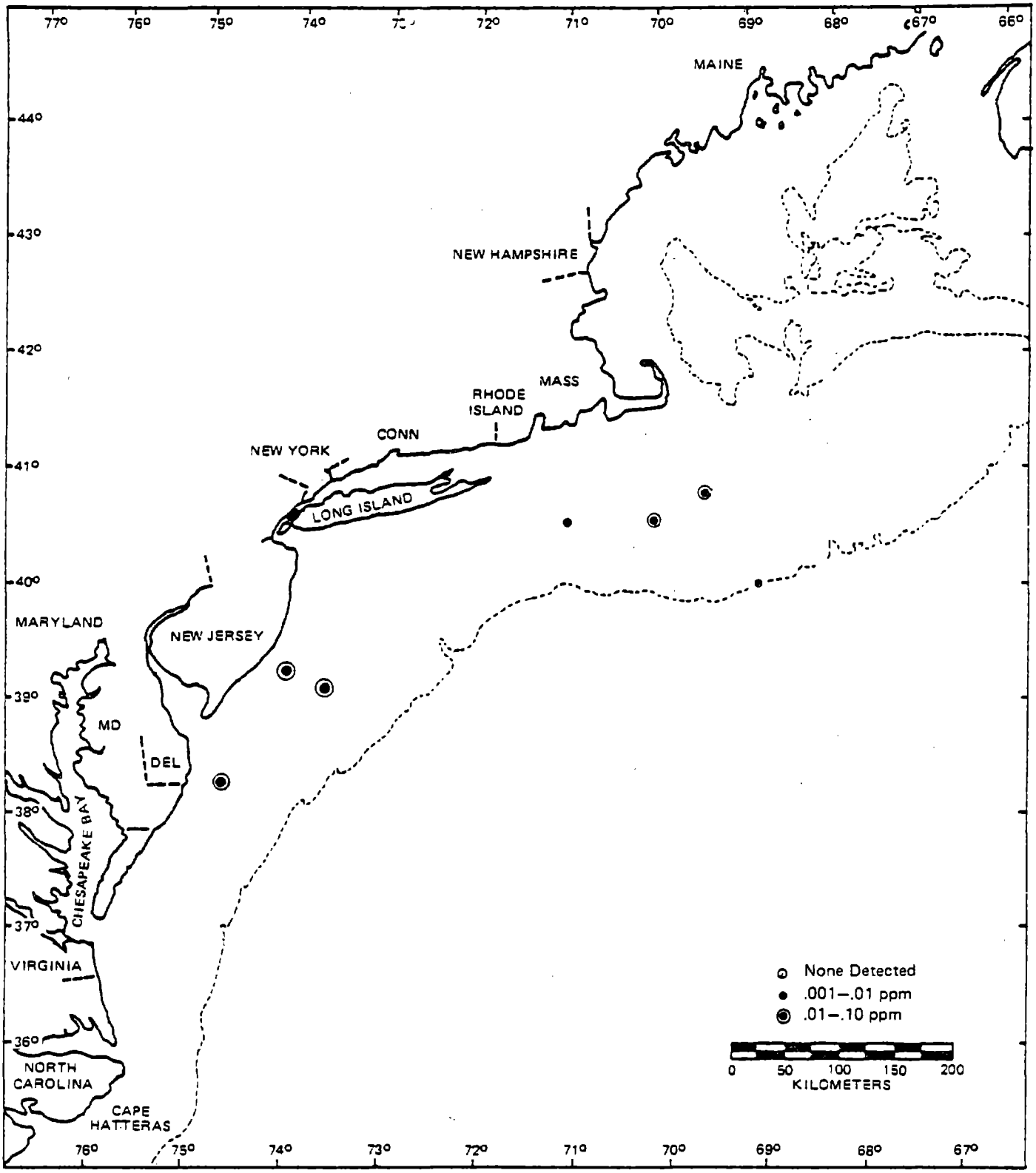


Figure 20. Windowpane Flounder—PCB.

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.

### 3.7 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 6, Table 6-7).

### 3.8 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 6, Table 6-7), 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.

### 3.9 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 6, Table 6-8).

### 3.10 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 3-1) were quite high: phenanthrenes 59 ppb; fluorenes 58 ppb.

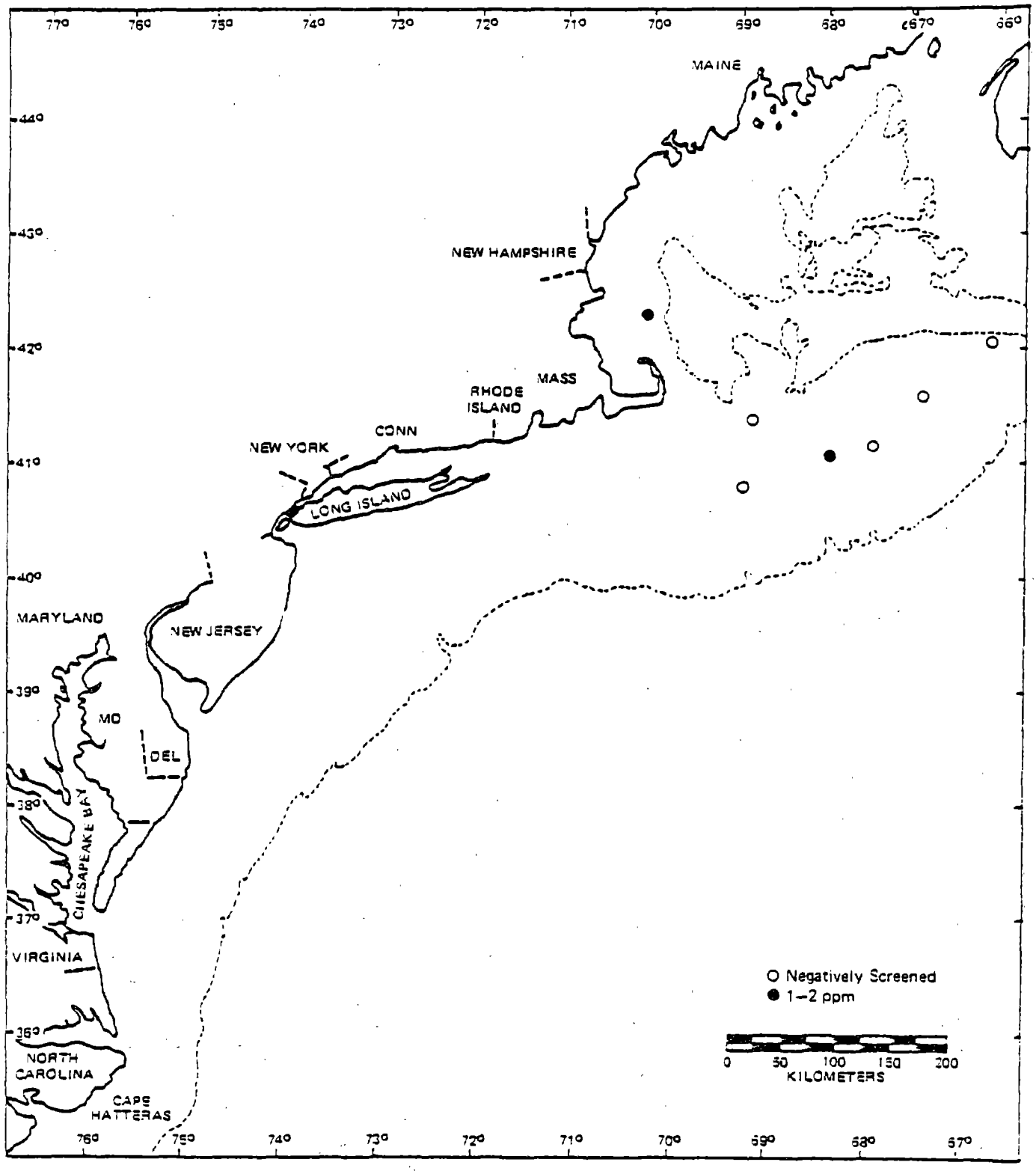


Figure 21. Haddock—Petroleum Hydrocarbons.

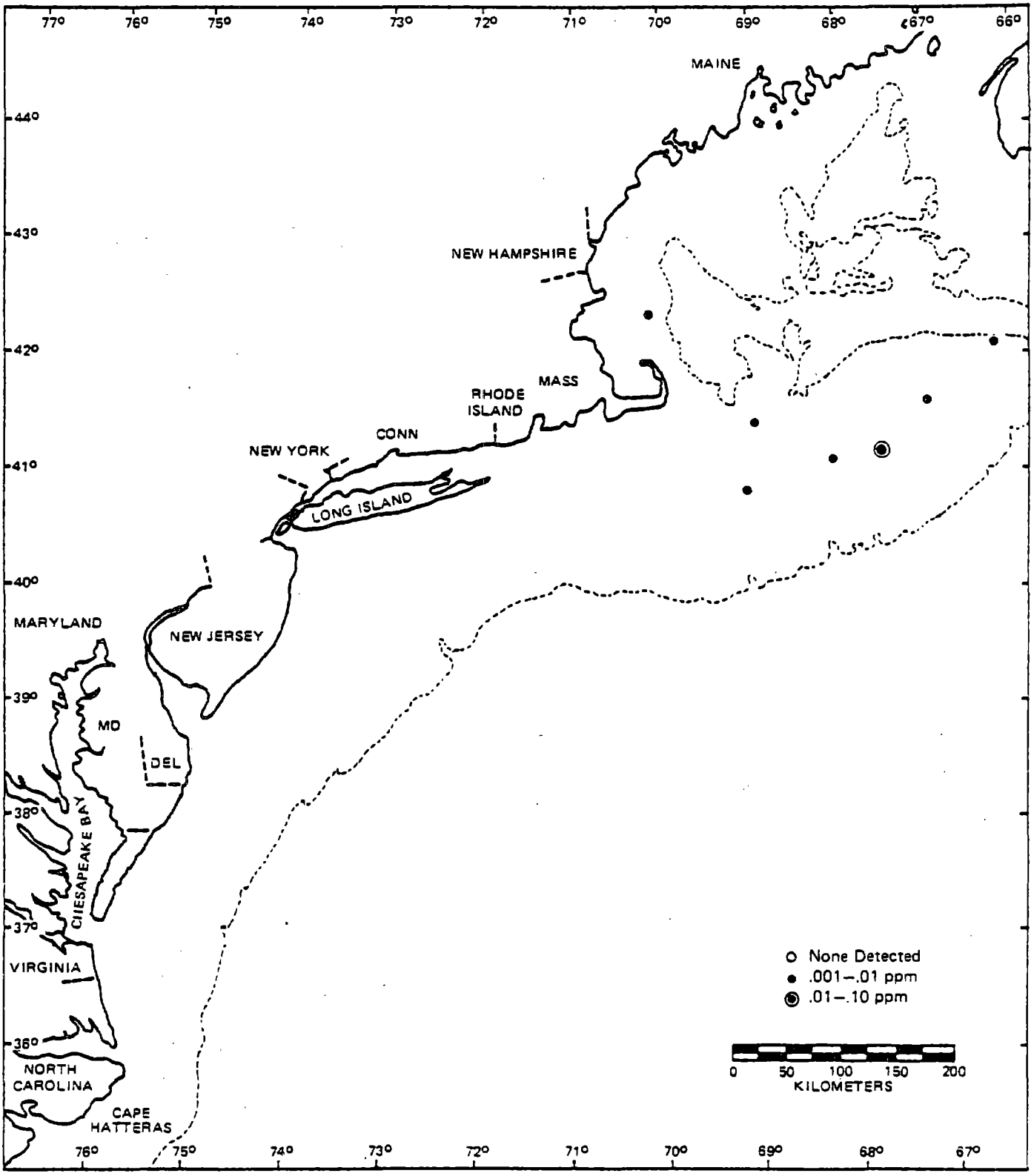


Figure 22. Haddock–PCB.

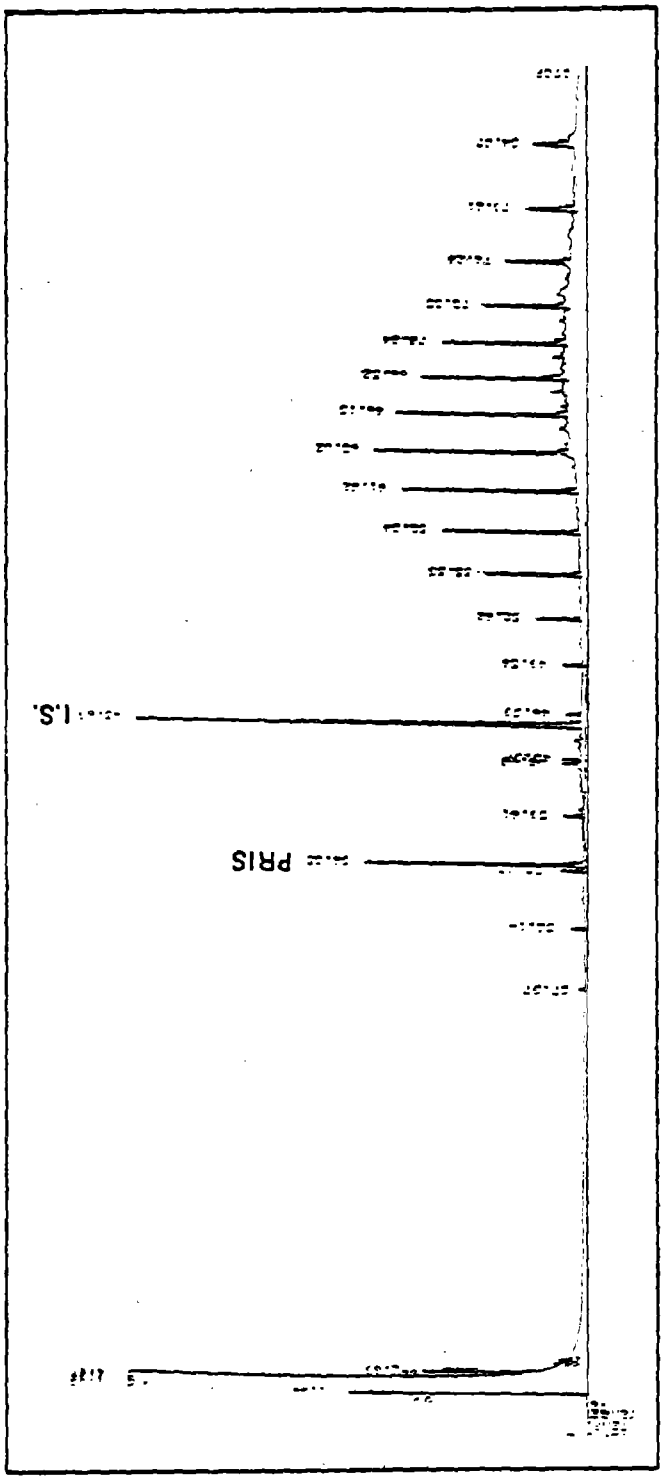


Figure 23. Saturated Petroleum Hydrocarbons in Four Spot Flounder (Station 100).

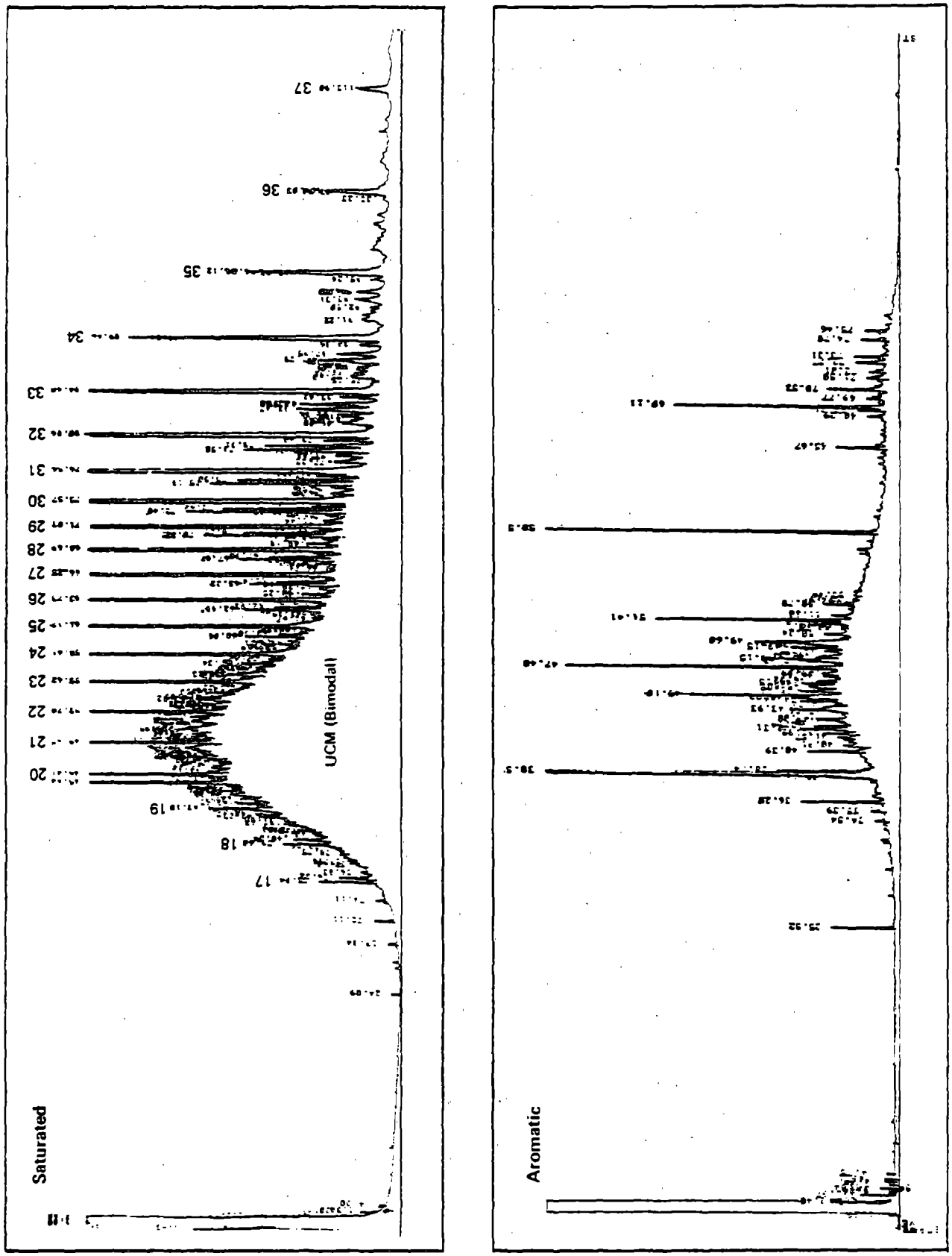


Figure 24. Petroleum Hydrocarbons in Rock Crab (Station 35).

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 6, Table 6-8). 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.

### 3.11 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.

### 3.12 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 $\Sigma$DDT) (See Section 6, Table 6-9).

## 4. 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 4-1. What can be said, though, is that levels reported here (Table 4-2) 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.

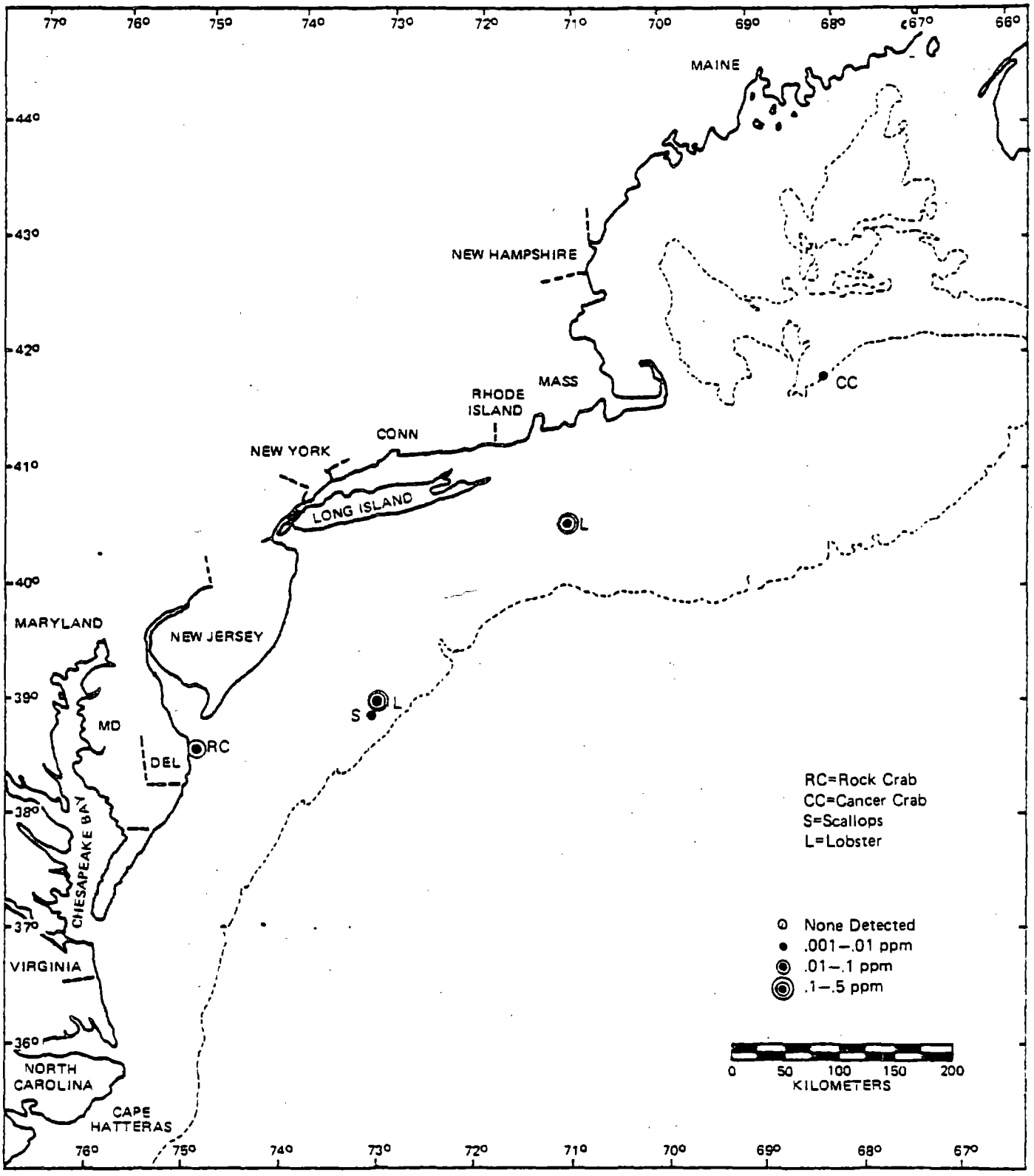


Figure 25 . Benthic Epifauna—PCB.

TABLE 4-1

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 4-1 (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 4-2

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 3, Table 3-1) 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 3, Table 3-1) 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 4-3. A summary of this study's findings is presented in Table 4-4. 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 4-4). 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 6, Tables 6-1 to 6-9. 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 4-3

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 4-4

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.

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. It is for this reason that in the GAS Ib study liver tissue, as well as muscle tissue, was analyzed for PHC, PCB, and EDDE contamination.

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/$\Sigma$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.

## 5. Summary of Data Acquired

The above-mentioned analytical scheme was applied to those samples previously inventoried in Section 2, Table 2-1. PAH determinations were made in those samples presented in Section 3, Table 3-1.

## 6. Data Appendices

Detailed analytical results are presented in Tables 6-1 through 6-9.

TABLE 6-1

ANALYTICAL SUMMARY - SILVER HAKE

| STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBON SCREEN | | PETROLEUM HYDORCARBONS (µg/g) | | CHLORINATED HYDROCARBONS (µg/g) | | |
|---|---|---|---|---|---|---|---|---|
| | | POSITIVE | NEGATIVE | RESOLVED | TOTAL | PCB | Σ DDT | PCB/Σ DDT |
| 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 6-2

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/<br>0.035 | 0.000/<br>0.011 | 3.2/<br>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 6-3

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 6-4

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 6-5

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 6-6

ANALYTICAL SUMMARY - HADDOCK

| STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBON SCREEN | | PETROLEUM HYDROCARBONS (µg/g) | | CHLORINATED HYDROCARBONS (µg/g) | |
|---|---|---|---|---|---|---|---|
| | | POSITIVE | NEGATIVE | RESOLVED | TOTAL | PCB | 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 6-7

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 6-8

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 6-9

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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# GULF AND ATLANTIC SURVEY FOR SELECTED ORGANIC POLLUTANTS IN FINFISH

## II. CHESAPEAKE BAY TO PORT ISABEL, TEXAS

## 1. Objectives

Information on the levels of organic pollutants in species of fish either presently or potentially of commercial importance is generally lacking. An informational gap relates to the influence that regional sources of pollution (e.g., drainage basins containing major population centers) have in affecting contaminant levels in both migratory and non-migratory fish populations.

In order to address these important questions, a specialized analytical program was used to quantify PHC, PAH, PCB, and DDT family concentrations in the muscle and livers of several species of fish collected by the National Marine Fisheries Service from the U.S. southeastern coastal and Gulf of Mexico regions. A hierarchical analytical approach in which progressively more sophisticated analytical techniques were used has allowed an initial rapid and informative screening of tissue samples and yet, at the most complex level, provides detailed information as to the composition and concentrations of organic contaminants in the coastal fish analyzed.

## 2. Summary of Activities and Rationale

### 2.1 Sampling Locations and Sample Distributions

The analytical chemical goals of this investigation were considered sequentially in the following four phases (Figure 1). Overall recoveries for PHC, PCB and DDT compounds averaged 80 percent. Samples were obtained on the R/V Albatross, cruise no. 80-01, February 1980, and the Oregon II, cruise no. 105, March 1980, by NMFS scientists, as shown in Table 2-1 and Figure 2.

#### 2.1.1 Phase 1: Hydrocarbon Screening

This analytical task involved the processing (dissection, digestion, extraction, cleanup, analysis) of 61 fish samples as the first level analytical task. A muscle and liver subsample was obtained from each sample (122 samples for analysis). While the residue cleanup and analytical parts of this task were geared towards the rapid generation of the qualitative PHC composition, 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), Boehm et al. (1981), and Boehm (1980).

Samples consisted of 1 to 32 individuals of the fish species shown in Table 2-1. Livers were excised from specimens with solvent-rinsed stainless steel utensils. A composite sample of up to 100 g of muscle tissue was then dissected by skinning and dissecting all or part of each fish comprising the sample. An aliquot of both liver and muscle tissue from each species of fish was reserved for a wet/dry weight determination. All solvents and KOH used

TABLE 2-1

SUMMARY OF FISH SPECIES ANALYZED

| SPECIES | # SAMPLES | STATIONS |
|---|---|---|
| Butterfish | | |
| unspeciated | 4 | 14, 13, 30, 31 |
| deepwater | 1 | 41 |
| gulf | 2 | 53,107 |
| Flounder | | |
| summer | 1 | 14 |
| broad | 2 | 31, 88 |
| shoal | 4 | 45, 140, 143 ,285 |
| gulf | 1 | 49, |
| blackbelly | 1 | 53 |
| 3-eye | 3 | 140, 53, 88 |
| windowpane | 1 | 15 |
| Lizardfish | | |
| unspeciated | 5 | 48, 49, 46, 33, 54 |
| offshore | 0 | |
| shortjaw | 1 | 53 |
| inshore | 4 | 256, 101, 130, 143 |
| largescale | 1 | 101 |
| Porgy | 4 | 54, 101, 256, 72 |
| Scad | | |
| unspeciated | 3 | 48, 49, 42 |
| round | 1 | 43 |
| rough | 4 | 107, 101, 140, 117 |
| Snapper | | |
| vermillion | 4 | 48, 42, 46, 43 |
| wenchman | 3 | 140, 88, 117 |
| Spot | 7 | 49, 107, 15, 43, 41, 30, 31 |
| Hake | 4 | 14, 41, 13, 53 |
| | 61 samples | |

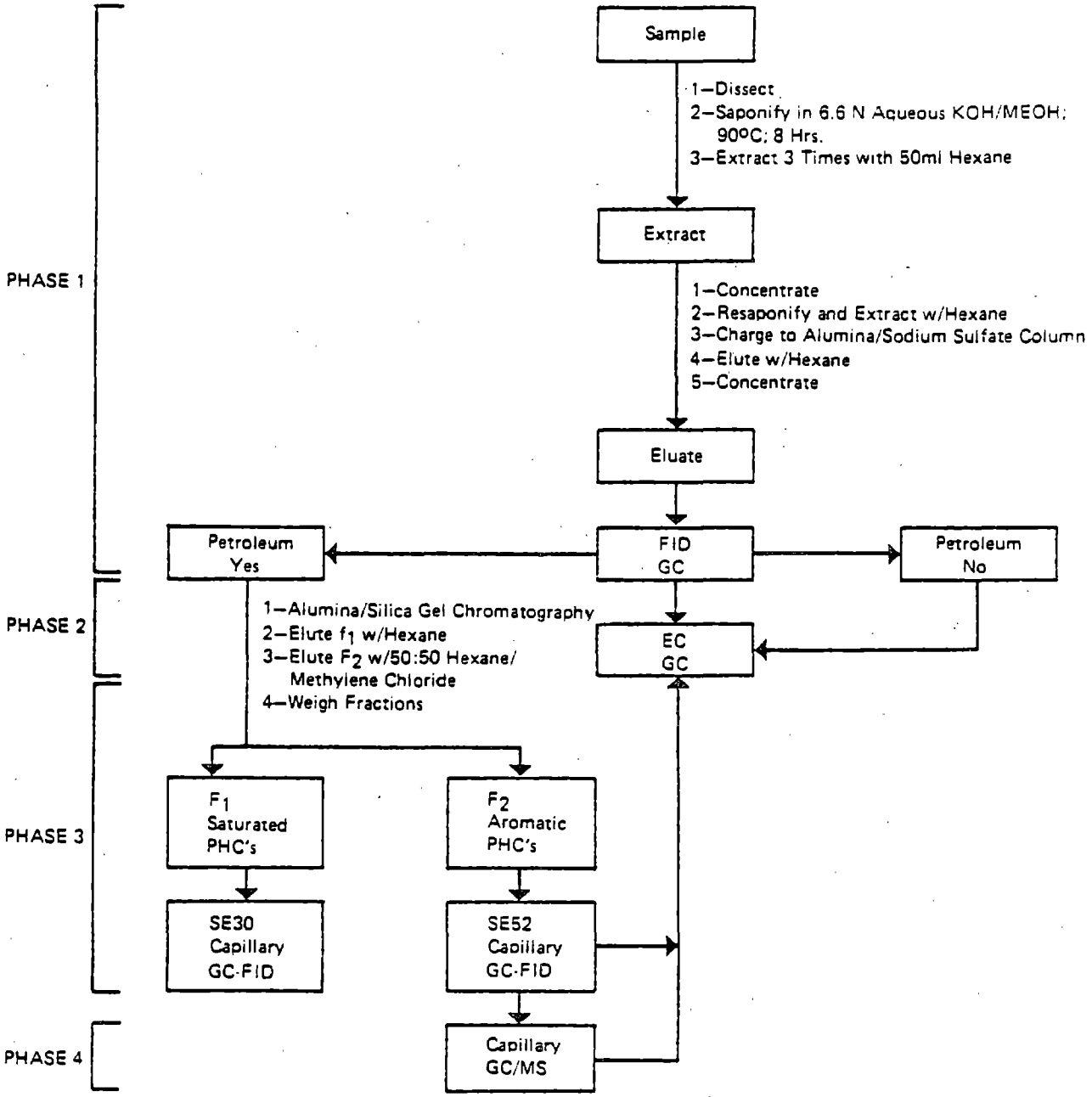


Figure 1. Multi-Phase Analytical Program.

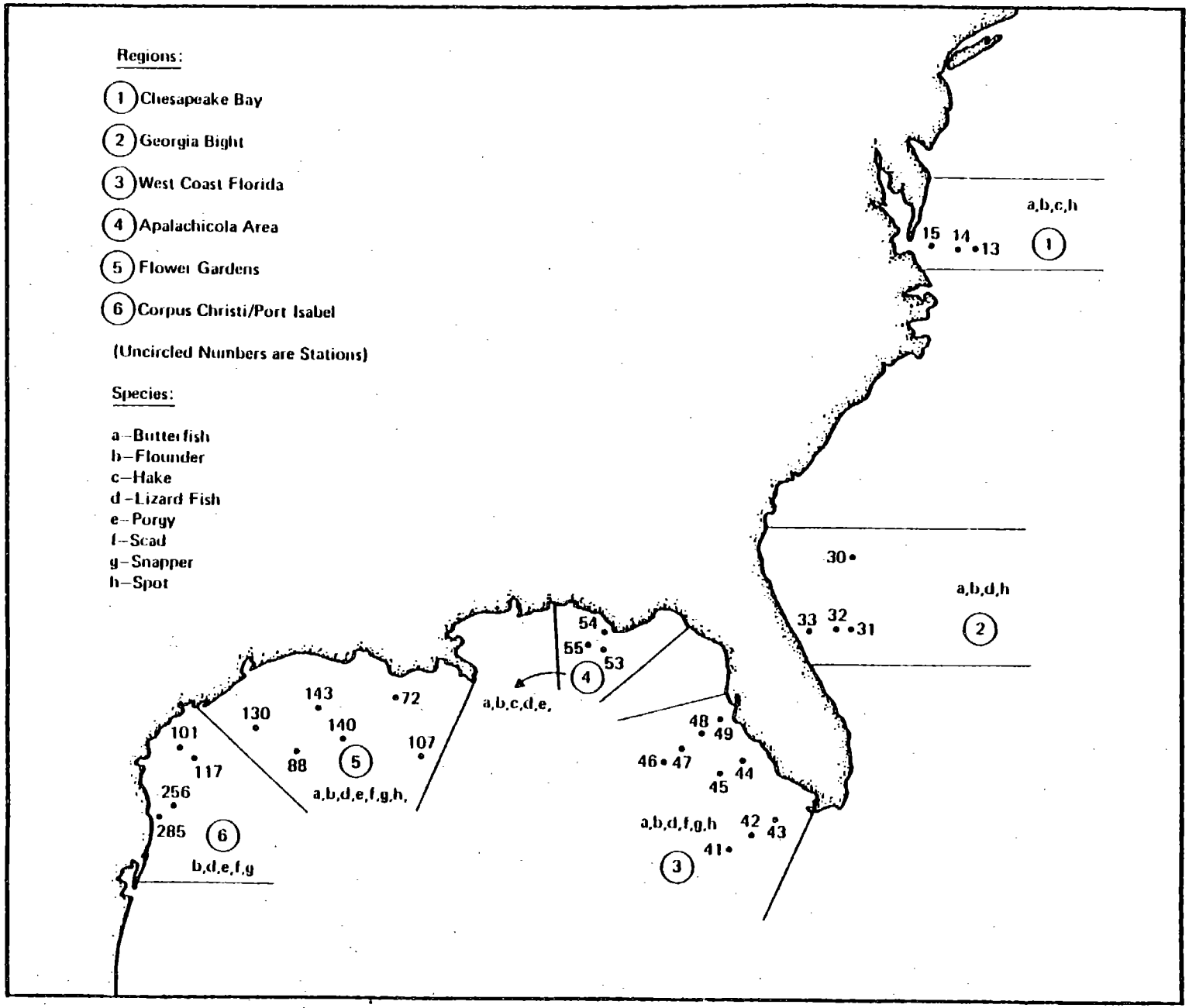


Figure 2. Sampling Locations and Distribution of Samples Selected for this Study.

were routinely checked for purity by GC prior to use. Ninety ml of 6.6N aqueous KOH in MeOH[1] and 5 µg of each internal quantification standard (deuterated naphthalene, androstane, deuterated phenanthrene and deuterated perylene) were added to all samples and blanks. Tissue was digested overnight (16 hr) at room temperature (25°C) in Teflon jars, sealed, and then heated in a water bath to 90°C, with frequent shaking, for approximately 8 hours.

The digestate containing saponified and nonsaponifiable lipids was then extracted three times with hexane, concentrated to 0.5 ml by rotary evaporation, and resaponified in 20 ml 1N aqueous KOH in MeOH for 2-4 hr at 90°C to complete the conversion of polar lipids to alcohols and fatty acid salts. The sample was next extracted three times with 15 ml hexane, and concentrated to 0.5 ml.

An alumina column cleanup was employed to obtain an eluate suitable for GC[2] analysis. The 0.5-ml hexane extract was charged to a column of 6.5 gm 7.5% deactivated alumina topped with sodium sulfate. Hexane (25 ml) was used to elute a single fraction ($f_1$ and $f_2$) containing saturated and aromatic hydrocarbons and PCB and DDT compounds.

The single fraction was then analyzed by GC[2] using a HP 5840 reporting gas chromatograph equipped with a glass lined splitless injection port, a flame ionization detector, and an HP 7671 automatic liquid sampler. Approximately 1 µl of sample was injected onto a 0.25 mm i.d. x 30 meter SE-30 fused silica capillary column (J&W Scientific), and the column oven was temperature-programmed from 40°C to 290°C at 3°/min. Chromatograms thus obtained were screened either positive or negative for petroleum-type hydrocarbons based on the following PHC-positive criteria: (1) presence of an unresolved complex mixture (UCM) eluting between n-$C_{13}$ to n-$C_{20}$, (2) suggestion of aromatic assemblages in the fine detail of the chromatogram, and (3) suggestion of a paraffinic tar by the presence of a smooth distribution of high molecular weight n-alkane peaks. Positively screened tissues were further fractionated in Phase 3.

### 2.1.2 Phase 2: Chlorinated Hydrocarbons (PCB, DDT)

Chlorinated hydrocarbons were analyzed by electron capture gas chromatography using a $^{63}Ni$ EC detector (GC/ECD). A 1.5% SP 2250/1.95% SP 2401 packed glass (0.25-in o.d.) column was temperature programmed from 130°C to 230°C at 8°/min and held at the upper temperature for 10 minutes. PCB and DDE were quantified using external standards of Aroclor mixtures and DDE. PCB compounds, measured against the best matching Aroclor, were quantified by adding the areas of the five component peaks indicated (e.g., Figure 3) and comparing this value to the same peak areas in the Aroclor standard. As the saponification reaction will convert DDD and DDT to DDE, the "DDT family" or ΣDDT was measured as a single component, DDE.

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[1]Liver tissues: 45 ml KOH in MeOH.

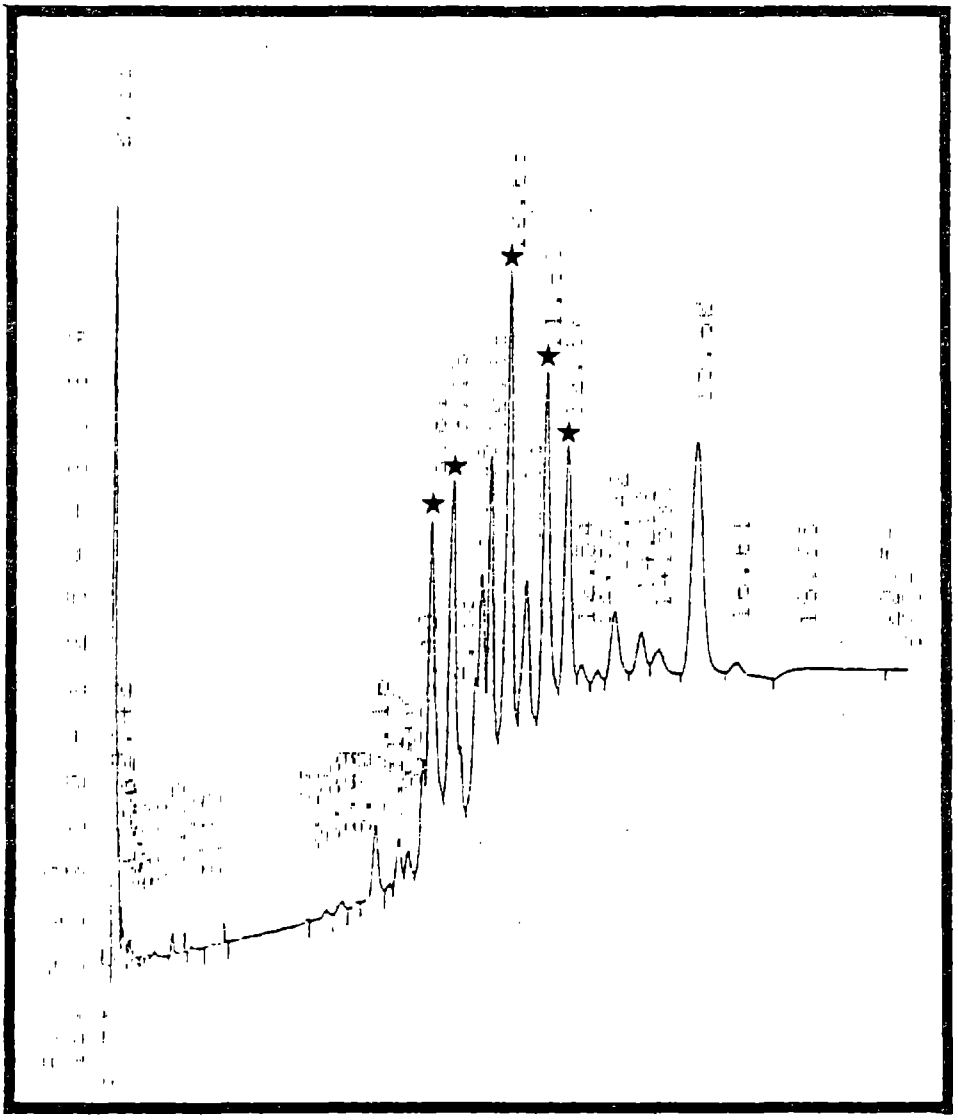


Figure 3. Aroclor 1254 Standard Mix, ( ★ = Quantification Peaks).

An aliquot of the hexane eluate from all negatively screened PHC samples from Phase 1 was analyzed by GC/ECD. Otherwise, an aliquot was taken for PCB/DDE analysis from the $f_2$ eluate of fractionated samples (Phase 3).

### 2.1.3 Phase 3: Saturated and Aromatic Hydrocarbons

Fifty-three extracts of tissue samples chosen from Phase 1 as probably containing PHCs were charged to a 11.0 gm silica gel column topped with 1 gm 5% deactivated alumina. Two fractions containing saturated $f_1$ compounds, eluted with 17 ml hexane, and unsaturated (aromatic and olefinic) $f_2$ compounds, eluted with 21 ml 50:50 hexane/$MeCl_2$, were collected. Fractions were concentrated, an aliquot weighed on a Cahn electrobalance, and approximately 10 µg of sample were applied to either an SE-30 ($f_1$) or SE-52 ($f_2$) 30-m fused silica capillary column run as for Phase 1. Data collected from the GC/FID was quantified by computer using the internal standards androstane ($f_1$) and deuterated phenanthrene ($f_2$) which were spiked to the initial tissue digestate.

The interpretation of the data on PHC concentrations was based on the following criteria. Those samples whose initial capcmmbxs GC chromatogram qualitatively suggested the presence of petroleum were further fractionated (approximately 40%). All tissues initially screened negative received no further quantitation of PHC or PAH. Those samples which were fractionated, and in which there was no unresolved complex mixture (UCM), a common indication of petrogenic contamination (Farrington et al., 1976) or in which the UCM was $\leq$30% of total ($f_1$ + $f_2$) hydrocarbons were also considered negative with respect to PHC. A positively screened tissue was one in which: 1) saturated $f_1$ fractions demonstrated (a) the presence of an UCM eluting between n-$C_{13}$ to n-$C_{20}$ and/or n-$C_{26}$ to n-$C_{34}$ (livers), usually $\geq$30% of total hydrocarbon for the $f_1$ fraction, and (b) an easily discernible n-alkane distribution between n-$C_{13}$ and n-$C_{20}$ suggestive of paraffinic tars; 2) unsaturated ($f_2$) fractions displayed some chromatographic fine detail suggestive of aromatic assemblages.

As a rule, aromatic resolved and unresolved concentrations were calculated for all samples after subtracting obvious biogenic inputs such as squalene from the computer-determined resolved peak areas. Alkanes were identified by their Kovat's indices. All UCMs were measured with a planimeter, and resolved and unresolved areas were converted to micrograms by comparing to the area of the internal standard. In the ensuing discussions, unless otherwise indicated, PHC concentrations are the sums of both $f_1$ and $f_2$ fractions.

### 2.1.4 Phase 4: PAH Analysis

Selected unsaturate fractions ($f_2$) were analyzed with a HP 5985 GC/MS computer system using GC conditions previously described (Boehm et al., 1981). The presence of aromatic hydrocarbons from two to five rings were identified by quantitative (internal standard = deuterated phenanthrene) single ion monitoring of major mass fragments. Samples were chosen to provide a range of species and geographic locations.

## 3. Summarization of Findings

### 3.1 Interspecies Variation

The following presentation will outline, by species, the information we have gathered concerning PHC, PAH, PCB, and DDT concentrations found in fish dissected for both muscle and liver analysis. Summaries of the incidence and concentrations of PHC and PCB/DDT compounds in µg/gm (ppm) and ng/gm (ppb) dry weight tissue are presented in Tables 3-1 and 3-2. Dry weight concentrations can be converted to fresh weight concentrations by dividing by 5. The information is also displayed graphically in Figures 4 and 5. Detailed analytical data are presented in Section 6, Tables A-1 to A-8.

#### 3.1.1 Butterfish

Seven samples of butterfish were analyzed from five different regions (Table A-1). Fractionated muscle tissues ranged from 20 ppm to 27 ppm (median = 23 ppm). These fish contained the next to highest concentrations of PHC found in muscle tissue, and the lowest concentration of PHC in the liver (Table 3-1, Figure 4). The saturated ($f_1$) fraction of a muscle sample from Region 3 (Figure 6) illustrates a large UCM between n-$C_{13}$ and n-$C_{20}$ and prominent n-alkanes distinctive of petroleum contamination. The unsaturated $f_2$ fraction contains a UCM also indicative of oil contamination. The large peak in the $f_2$ fraction at approximately 78 min is squalene, a large biogenic olefin. PAH determinations were obtainable only by GC/MS analysis (see Section 3.3).

The median PCB concentration found in butterfish muscle tissue was 80 ppb through the five different regions where butterfish were found (Table 3-2, Figure 5). Values ranged from none detectable (ND) to 120 ppb (Table A-1). The median concentration of PCBs in livers of this species was 100 ppb, with a range from ND to 1,020 ppb. No correlation of PCB and PHC data is found in either the muscle or liver tissues, probably owing to different sources for these compound classes. PCB values in the butterfish muscle suggest some regional dependence, with higher concentrations found in fish from Region 1. However, fluctuations in liver PCB and ΣDDT concentrations within regions do not support this observation.

TABLE 3-1

INCIDENCE OF PETROLEUM HYDROCARBONS (SPECIES VARIATION)

| SPECIES | # SAMPLES | % SCREENED POSITIVE | | CONCENTRATION OF PHC (µg/g DRY WT.)[a] | |
|---|---|---|---|---|---|
| | | MUSCLE | LIVER | MUSCLE | LIVER |
| Butterfish | 7 | 29 | 0 | 23 (20-27) | -- |
| Flounder | 13 | 15 | 23 | 5.0 (3.2-6.9) | 61 (47-235) |
| Lizardfish | 11 | 36 | 36 | 7.7 (5.9-12) | 325 (34-1,140) |
| Porgy | 4 | 75 | 50 | 5.8 (4.3-5.8) | 124 (103-146) |
| Scad | 8 | 38 | 25 | 12 (4.1-29) | 311 (136-486) |
| Snapper | 7 | 29 | 29 | 6.3 (5.7-7.6) | 152 (122-182) |
| Spot | 7 | 29 | 57 | 30 (22-38) | 316 (59-885) |
| Hake | 4 | 50 | 50 | 5.6 (5.0-6.1) | 158 (127-190) |

[a]Median values, followed by range.

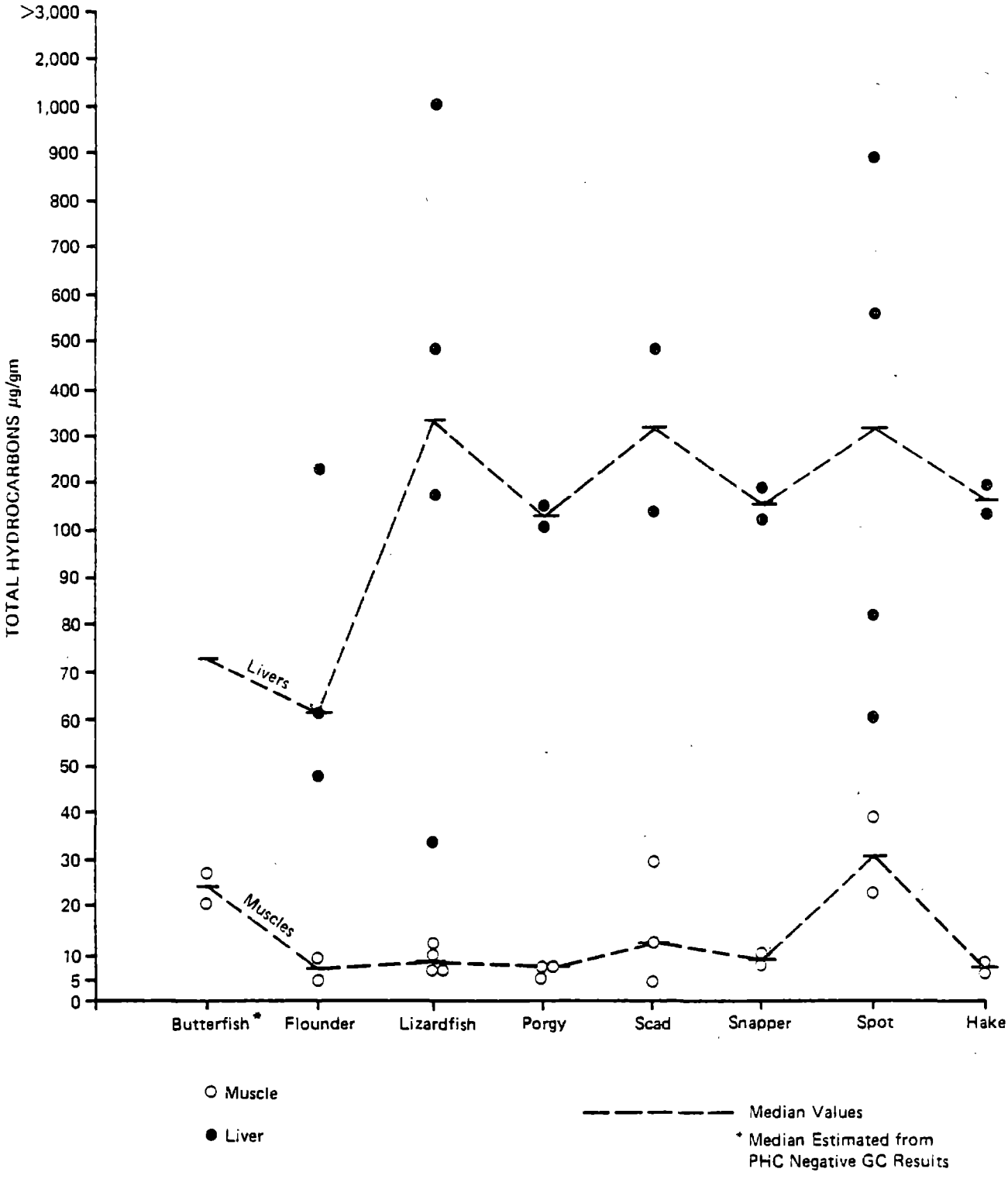



Figure 4. Petroleum Hydrocarbon Concentrations Graphed by Species.

TABLE 3-2

SUMMARY OF CHLORINATED HYDROCARBONS (PCB, ΣDDT)
(SPECIES VARIATION)

| | PCB (ng/g dry wt.)[a] | | ΣDDT (ng/g dry wt.)[a] | |
|---|---|---|---|---|
| SPECIES | MUSCLE | LIVER | MUSCLE | LIVER |
| Butterfish | 80 (ND-120) | 100 (ND-1,020) | 3 (1-62) | 16 (3-143) |
| Flounder | 30 (10-70) | 370 (40-980) | 5 (1-52) | 49 (1-294) |
| Lizardfish | 20 (10-80) | 310 (100-2,130) | 6 (ND-46) | 180 (51-1170) |
| Porgy | 78 (20-180) | 240 (30-420) | 12 (2-25) | 27 (10-53) |
| Scad | 30 (20-60) | 205 (60-11,400) | 6 (1-32) | 23 (9-1000) |
| Snapper | 20 (10-40) | 235 (70-1,420) | 11 (2-135) | 35 (18-288) |
| Spot | 30 (10-170) | 280 (50-1,230) | 5 (2-92) | 37 (2-267) |
| Hake | 70 (10-90) | 165 (40-410) | 16 (2-25) | 16 (9-128) |

[a]Median values, followed by range.

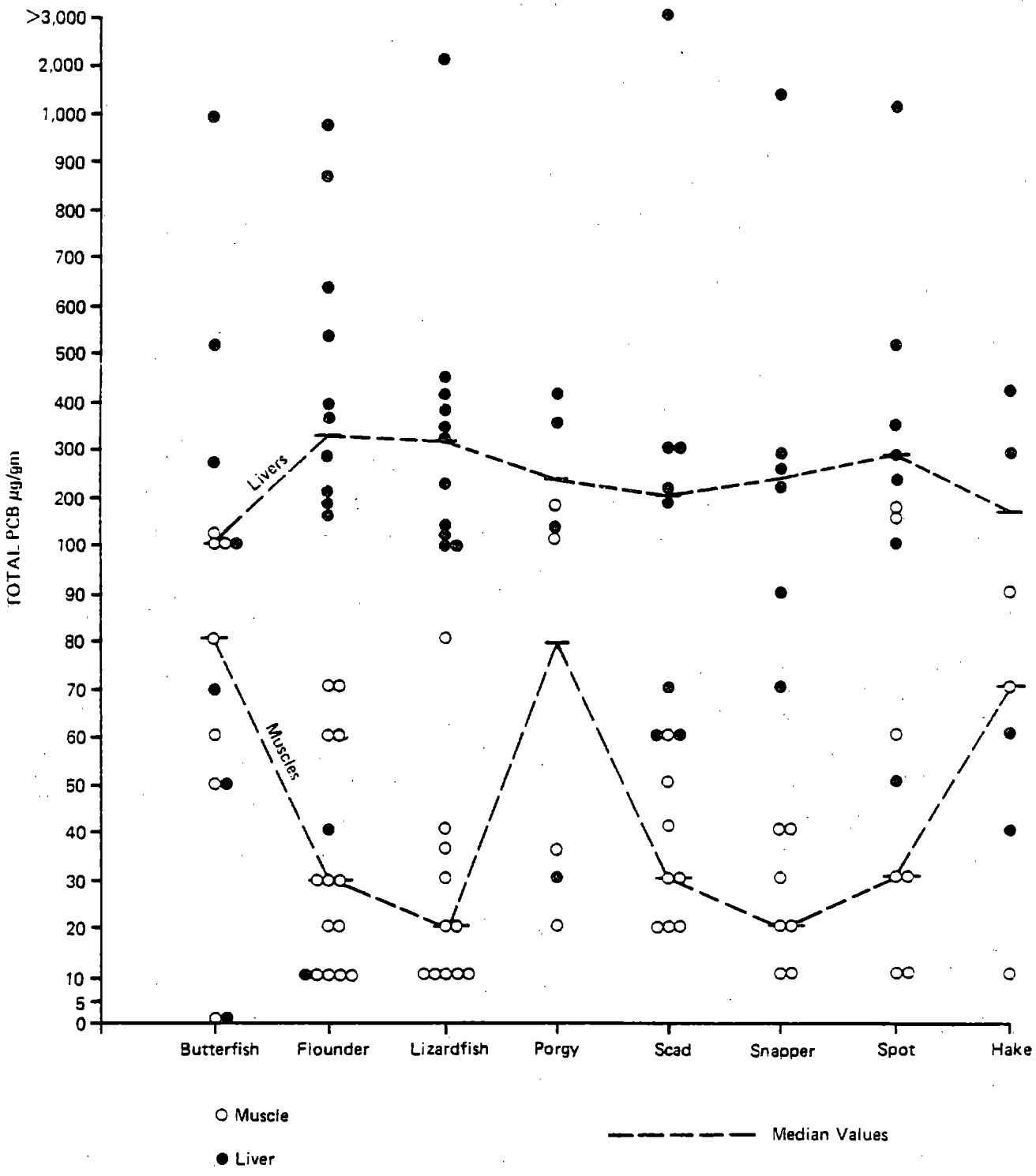
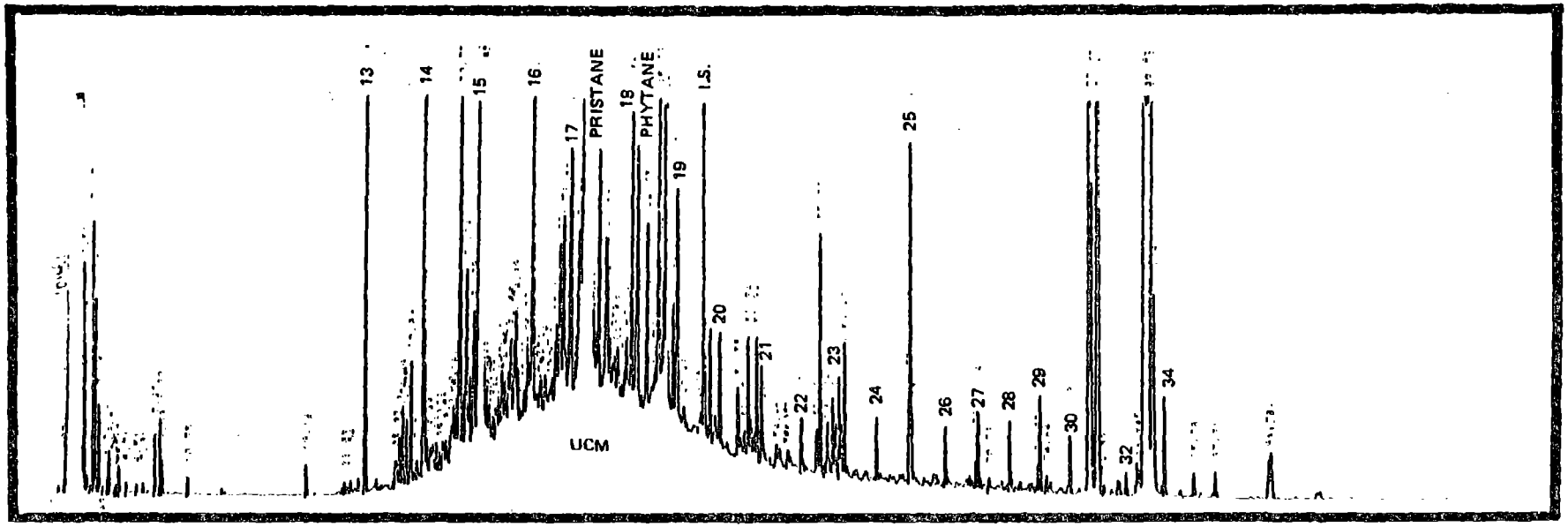
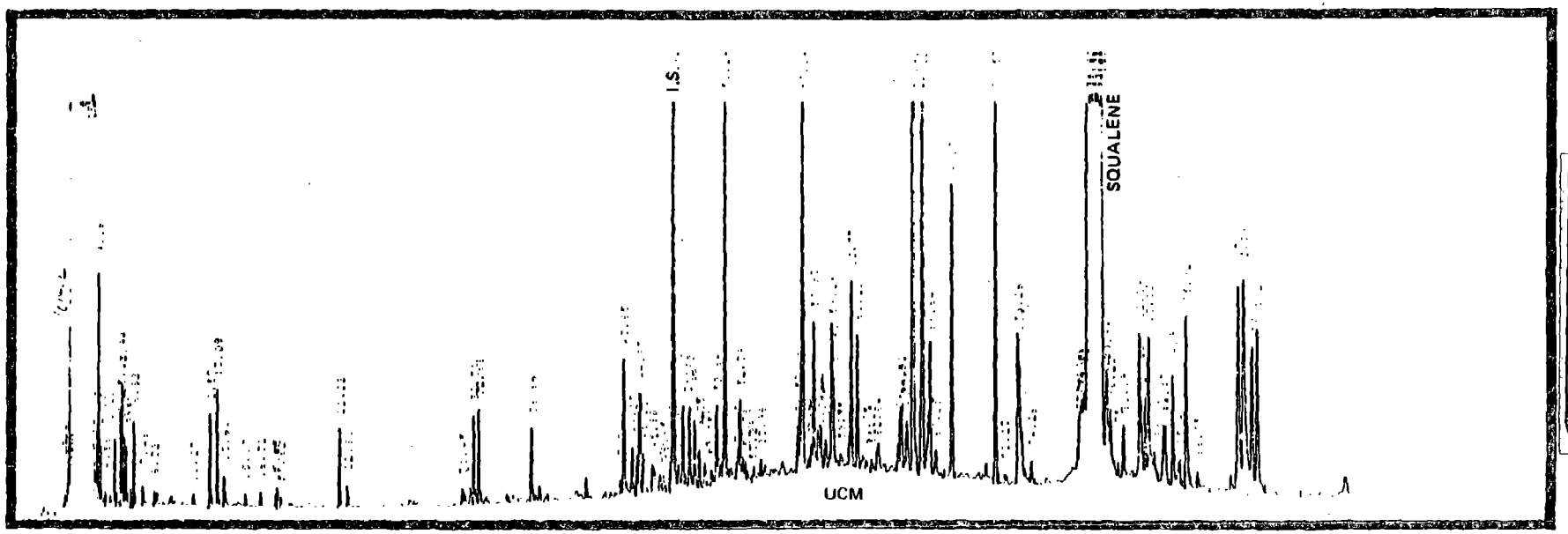



Figure 5. PCB Concentrations Graphed by Species.




BUTTERFISH MUSCLE–STN 41–SATURATED FRACTION




BUTTERFISH MUSCLE–STN 41–AROMATIC FRACTION

Figure 6. Representative Capillary GC Traces of Butterfish Hydrocarbons.

### 3.1.2 Flounder

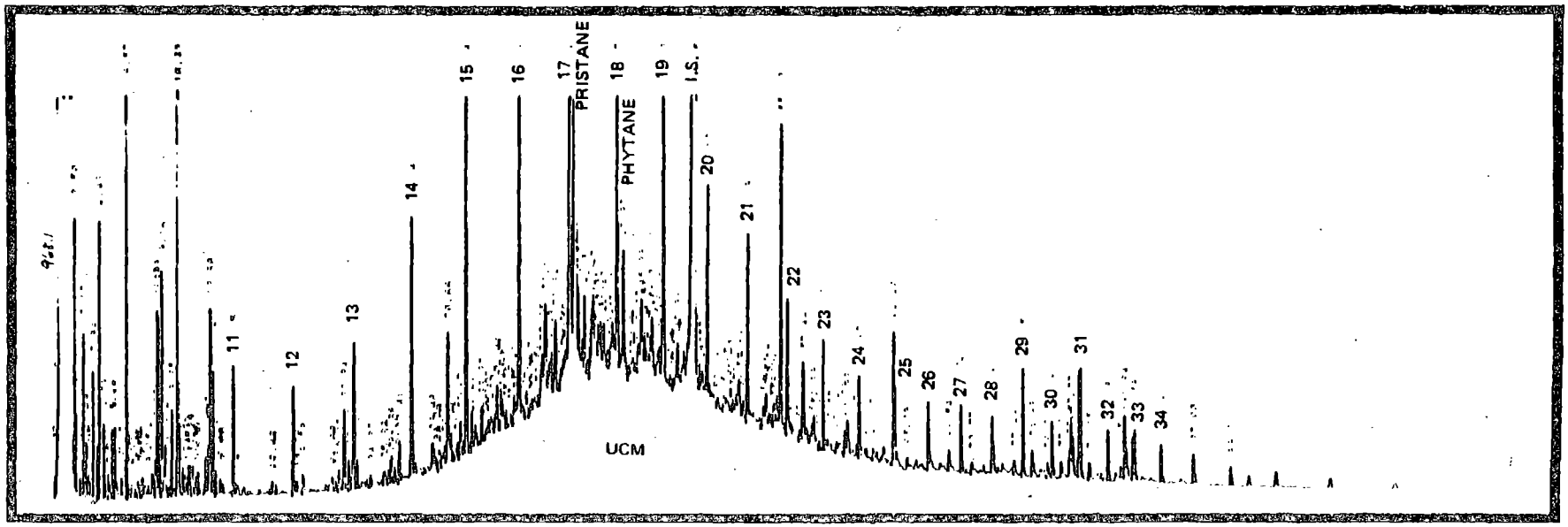
Thirteen samples of flounder (summer, broad, shoal, gulf, blackbelly, three-eye, or windowpane) were analyzed from the six different regions (Table A-2). Overall, flounder tissues contained the lowest amounts of PHC compounds in muscle or liver, of any of the species analyzed, ranging from 3.2 ppm to 6.9 ppm, with a median value of 5.0 ppm. Two separate samples were analyzed from Region 5 and demonstrate reasonable reproducibility: muscle PHCs were 1.2 and 1.0 ppm and liver PHCs were 61 and 119 ppm, respectively. The data from this species also demonstrate the importance of the resolved vs. unresolved composition of the chromatogram in determining petroleum contamination: the sample from Station 15 has a large %UCM but lower total hydrocarbon concentration than that from Station 53; hence fish at Station 15 are screened positive while hydrocarbons measured in fish from Station 53 (also 88 and 143) are assumed to be of biogenic origin. The same is also found in the liver samples.

Muscle and liver tissue $f_1$ fractions (Figure 7) display PHC-related UCMs, with the "typical" liver $GC^2$ trace easily distinguished by the second late-eluting UCM between n-$C_{26}$ and n-$C_{34}$ and prominent n-$C_{26}$ to n-$C_{33}$ alkanes. Both tissues contain a prominent n-alkane series representing petroleum-related contamination. Also labeled in Figure 7 are the branched alkanes, pristane and phytane. The $f_2$ fractions (Figure 8) also contain UCM material which, in some individuals of this species, can account for 70-75% of the total PHC for both the muscle and liver. Late-eluting peaks in the liver $f_2$ chromatogram (Figure 8) are large biogenic olefins which we found typical of this tissue. These were not included in quantifications.

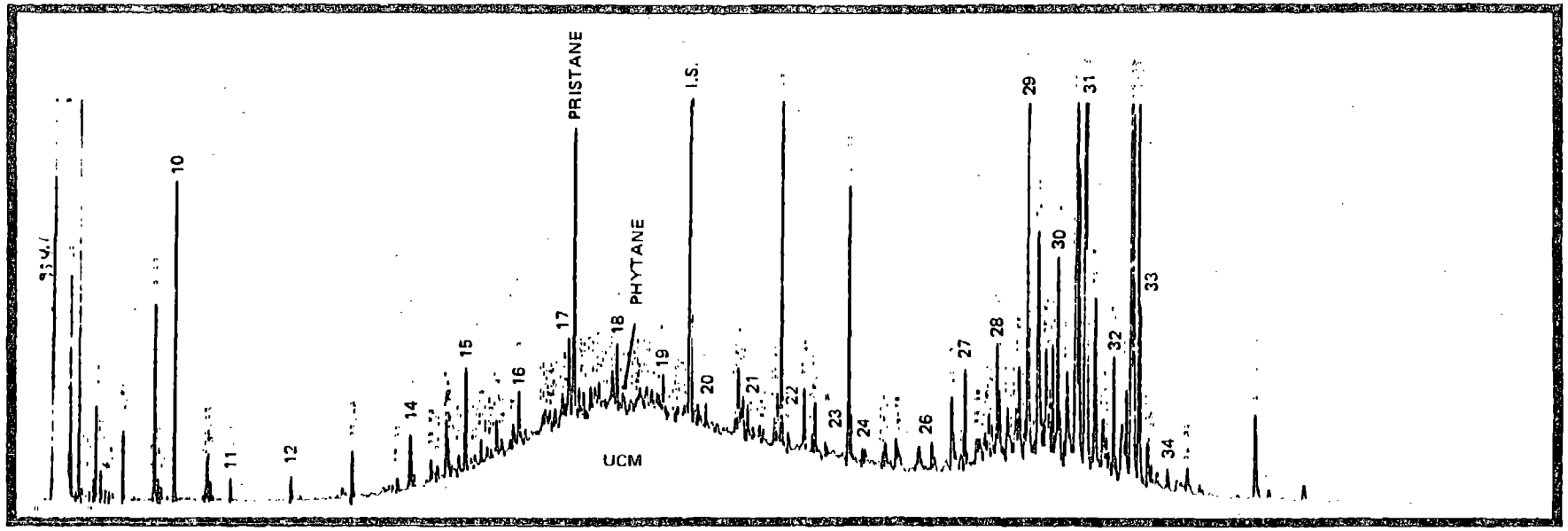
PCB concentrations found in flounder muscle tissue (Table 3-2, Figure 5) range from 10 to 70 ppb, with a median value of 30 ppb and, in liver tissue, are approximately 10 times higher (370 ppb). This species does not demonstrate a marked regional variation in PCB values of muscle tissue or livers. The two positively screened PHC tissues from Station 15 and 285 have high PCB values. Note that in this species, PHC-negative tissues also can contain significant concentrations of PCBs, and that there is no apparent relation between PHC and PCB concentrations in liver tissues in general.

### 3.1.3 Silver Hake

Two out of four hake samples (Table A-3), including both muscle and liver tissue, were screened positive for PHC compounds, containing a median value of 5.6 ppm. Liver tissue contained 158 ppm (190 and 127 ppm). The two samples are within reasonable agreement for both muscle and liver. Gas chromatograms are very similar to silver hake analyzed further north in the first GAS I study (Figures 9 and 10), although concentrations are lower in the southeast region (see Part I of this program). In the northeast region silver hake were singled out as the most pollution-impacted species. Such a designation seems unwarranted in the southeast-Gulf region. The

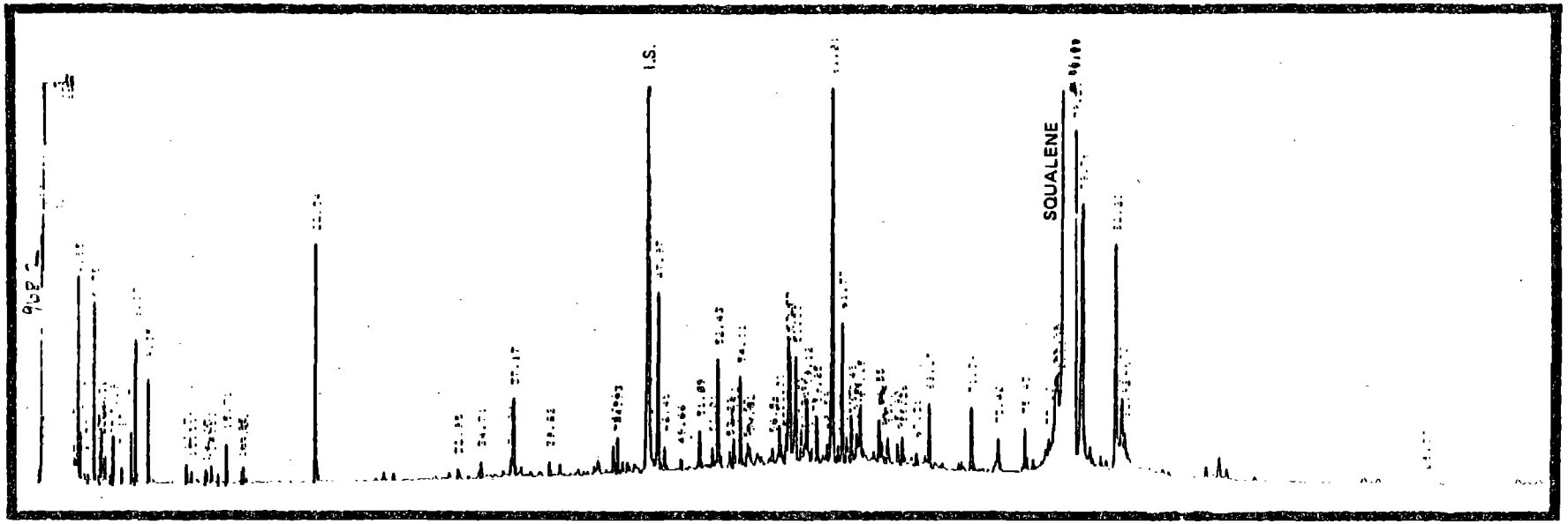



FLOUNDER MUSCLE–STN 15–SATURATED FRACTION

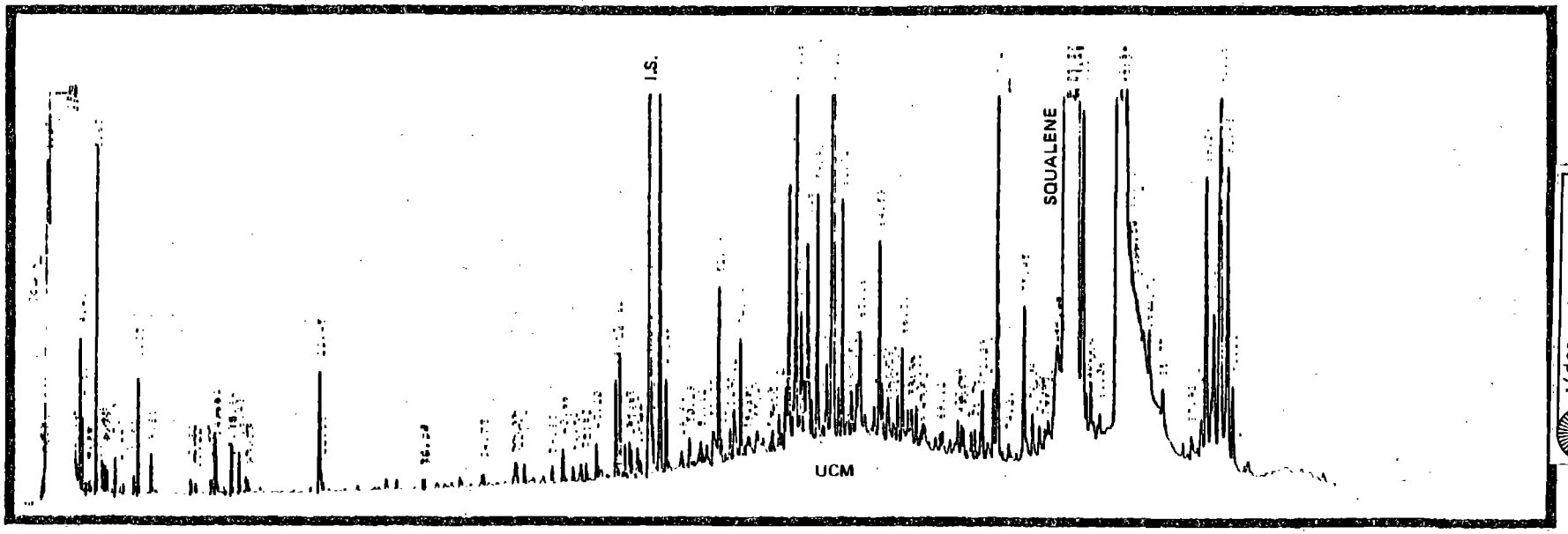



FLOUNDER LIVER–STN 15–SATURATED FRACTION

Figure 7. Representative Capillary GC Traces of Flounder Hydrocarbons.

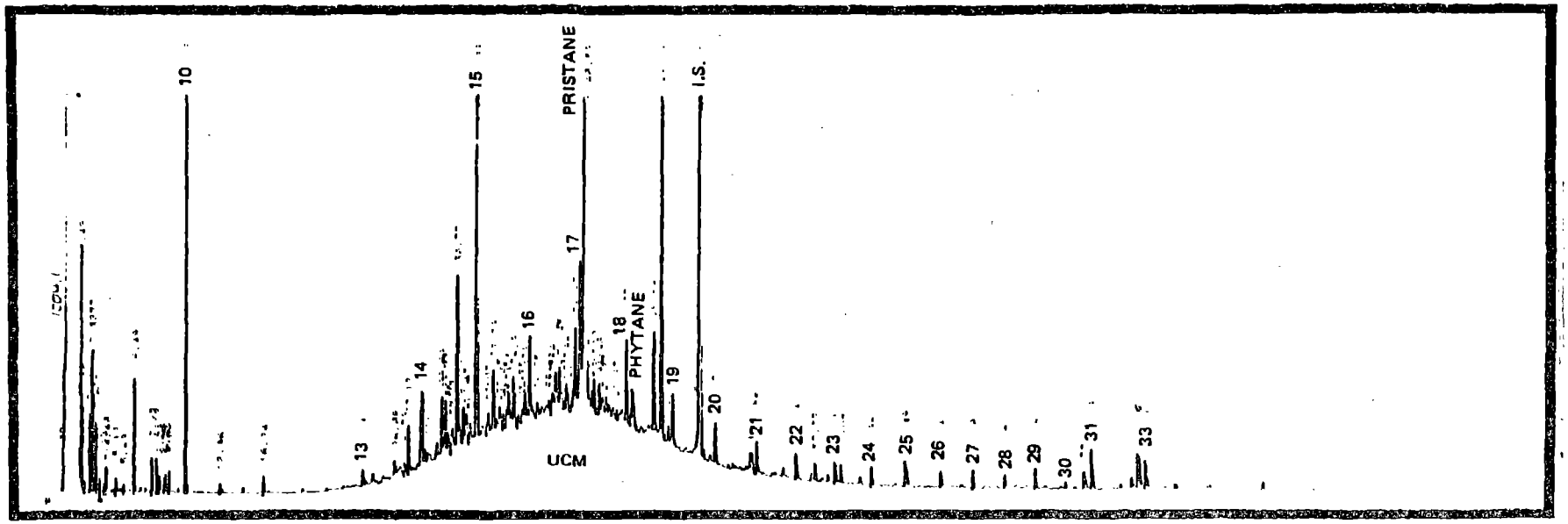



FLOUNDER MUSCLE–STN 15–AROMATIC FRACTION

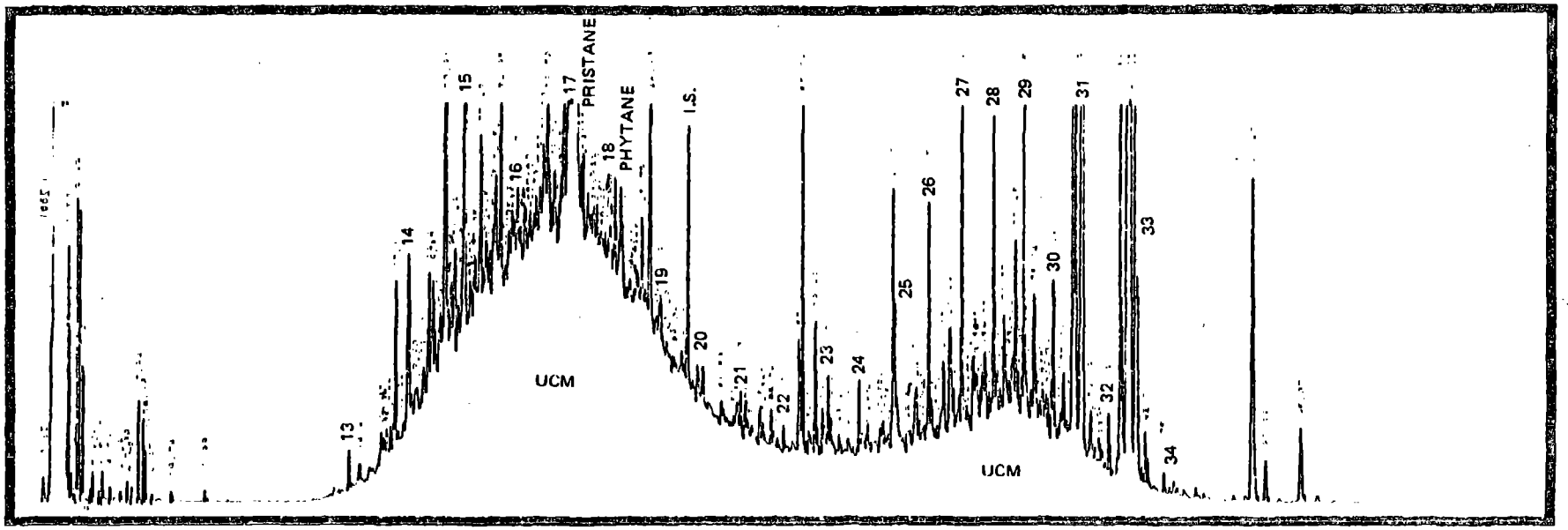



FLOUNDER LIVER–STN 15–AROMATIC FRACTION

Figure 8. Representative Capillary GC Traces of Flounder Hydrocarbons.

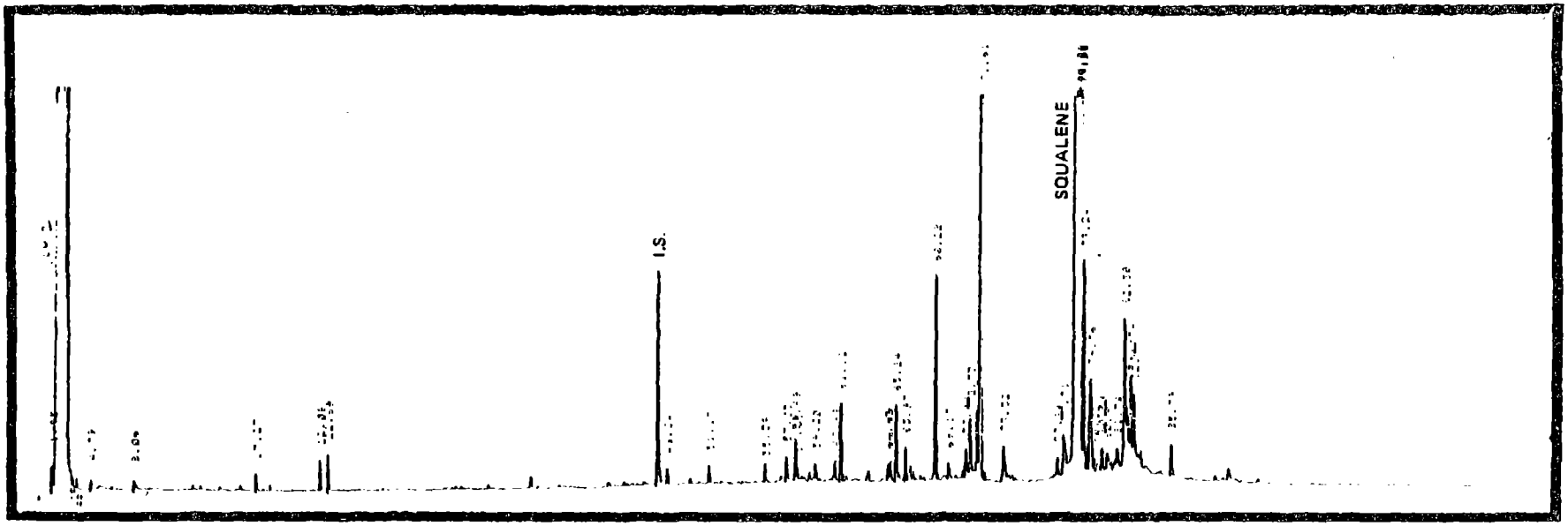



SILVER HAKE MUSCLE–STN 13–SATURATED FRACTION

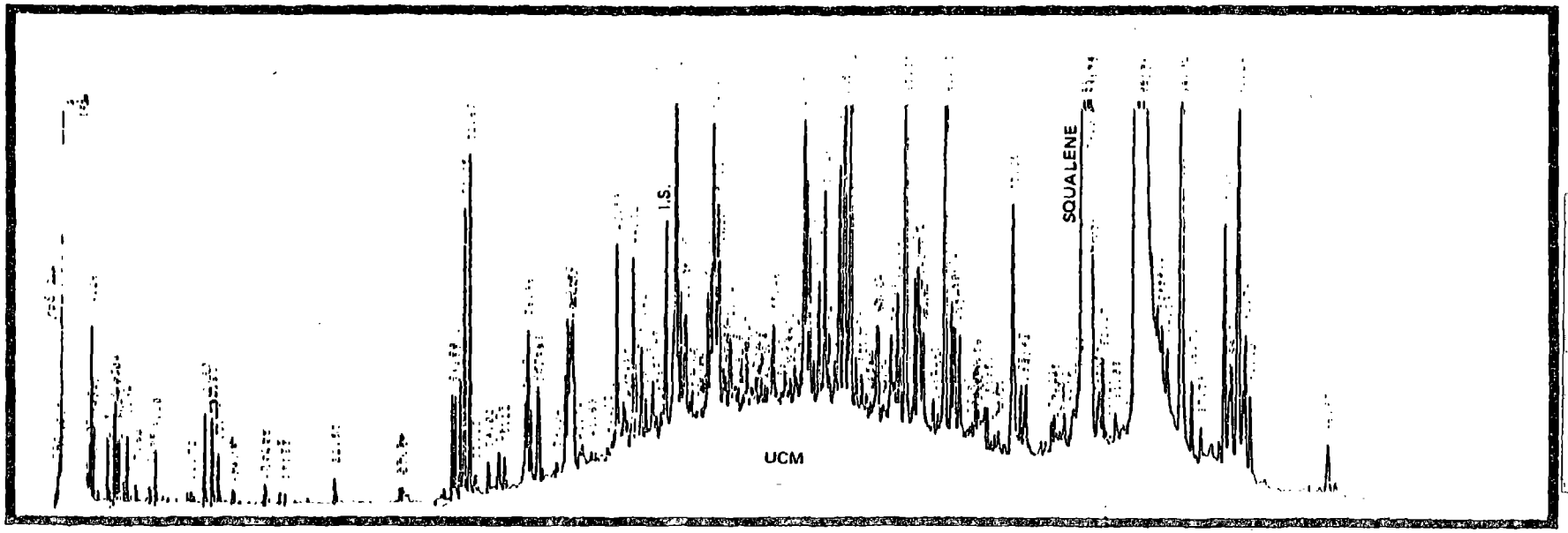



SILVER HAKE LIVER–STN 13–SATURATED FRACTION

Figure 9. Representative Capillary GC Traces of Silver Hake Hydrocarbons




SILVER HAKE MUSCLE–STN 13–AROMATIC FRACTION




SILVER HAKE LIVER–STN 13–AROMATIC FRACTION

Figure 10. Representative Capillary GC Traces of Silver Hake Hydrocarbons.

petrogenic nature of the $f_1$ fractions of both muscle and liver tissue is readily discernible. The large UCM and bimodal PHC distribution of the $f_1$ liver fraction is indicative of mixed sources of petrogenic and biogenic compounds, and is characteristic of many of the liver samples. $GC^2$ traces of the $f_2$ fractions of muscle and liver tissues show little indication of petroleum, perhaps due to biochemical metabolism of aromatic compounds as well as to the low absolute concentrations encountered.

The median PCB concentration in hake muscle was 70 ppb (Table 3-2) and in hake liver, 165 ppb. Both concentrations are mid-range of the eight species analyzed. No evidence of PCB/PHC coupling was found in the hake. Figure 11 illustrates a typical GC/ECD chromatogram of PCBs. Starred peaks were used for quantification. DDE is also labeled.

### 3.1.4 Lizardfish

Four of the 12 lizardfish samples were screened positive for both muscle and liver tissues (Table A-4). Muscle tissue PHC values were average, ranging from 5.9 ppm to 12 ppm (median = 7.7) throughout the four regions sampled. Liver tissues from each of the four fish samples show a wide concentration range of PHC (34-1140 ppm) with the highest median value, 325 ppm, determined for all species. As in earlier examples, $GC^2$ traces of $f_1$ muscle and liver samples (not shown) demonstrate the presence of PHC, with the n-alkanes and isoprenoids easily found in the $f_1$ fractions of muscle and liver. The $f_2$ fractions also contained large UCMs, indicative of exposure to anthropogenic hydrocarbon source(s).

Illustrated in Figure 12 is a packed column GC/ECD trace of a lizardfish muscle tissue; the starred PCB peaks correspond to those in the standard Aroclor 1254 formulation. The median PCB concentration for this species was 20 ppb in the muscle (range from 10 to 80 ppm) (Table A-4, Figure 5). In the liver, the median was 310 ppb with a range of 100-2,130 ppb. Although PHC-positive muscle and liver tissues also contain higher concentrations of PCB, the statistical sample size (n=4) is not large enough to conclusively establish this.

### 3.1.5. Porgy

Of the four porgy samples examined (Table A-5), three muscle tissues were screened positive, with a median value of 5.8 ppm. The two liver samples containing PHC averaged 124 ppm. Gas chromatograms generally support a petroleum-like contamination. A smooth n-alkane distribution ($n\text{-}C_{10}$ to $n\text{-}C_{34}$) is visible in $f_1$ fractions of positively-screened tissues. Porgies contained the third lowest concentrations of PHCs of the eight species analyzed, for both muscle and liver tissue.

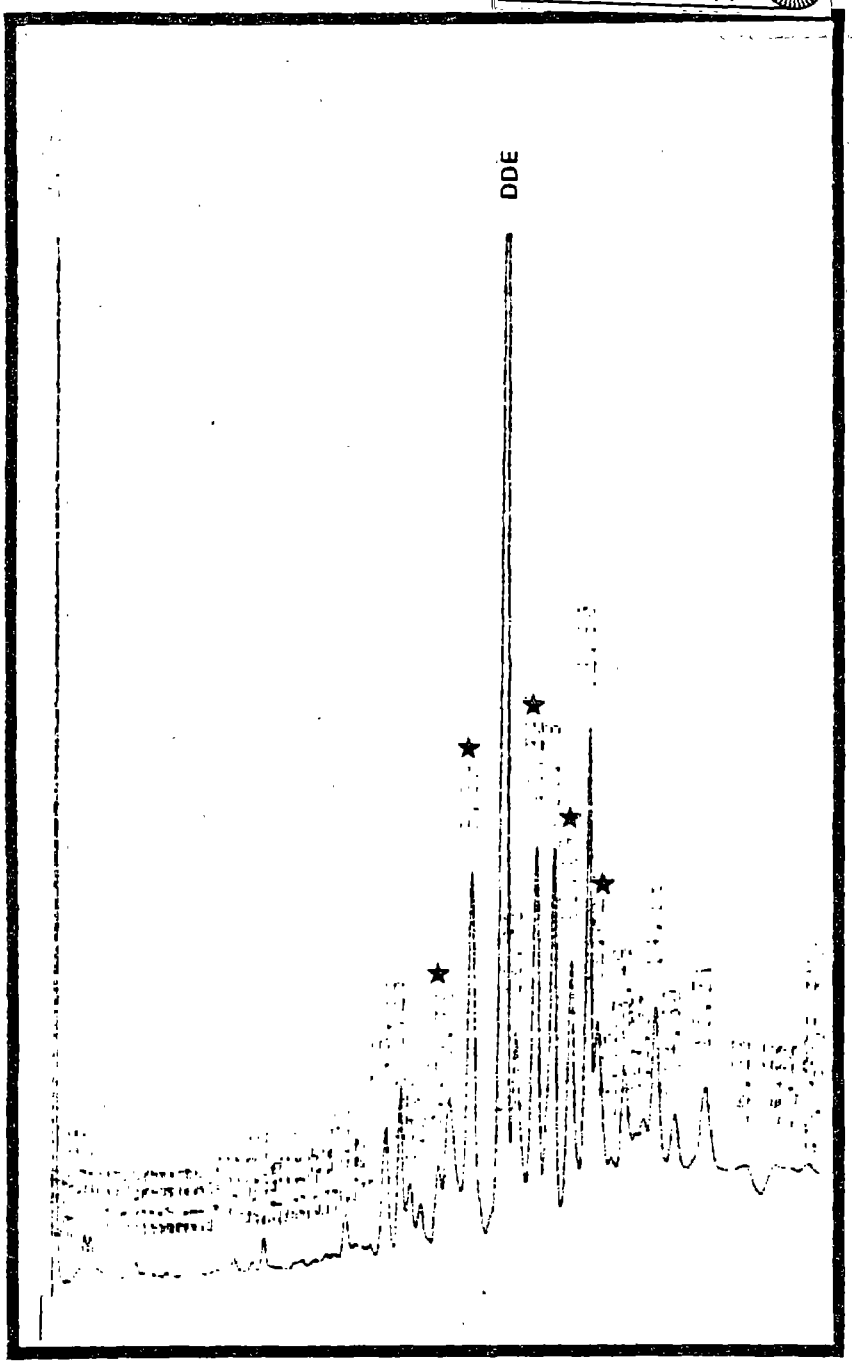



Figure 11. Representative GC/ECD Trace (Packed Column) of PCB's in a Hake Muscle Tissue from Region 1, Station 14. Starred Peaks Co-Elute with Aroclor 1254 Standard. Sample Contained 90 ng/g PCB.

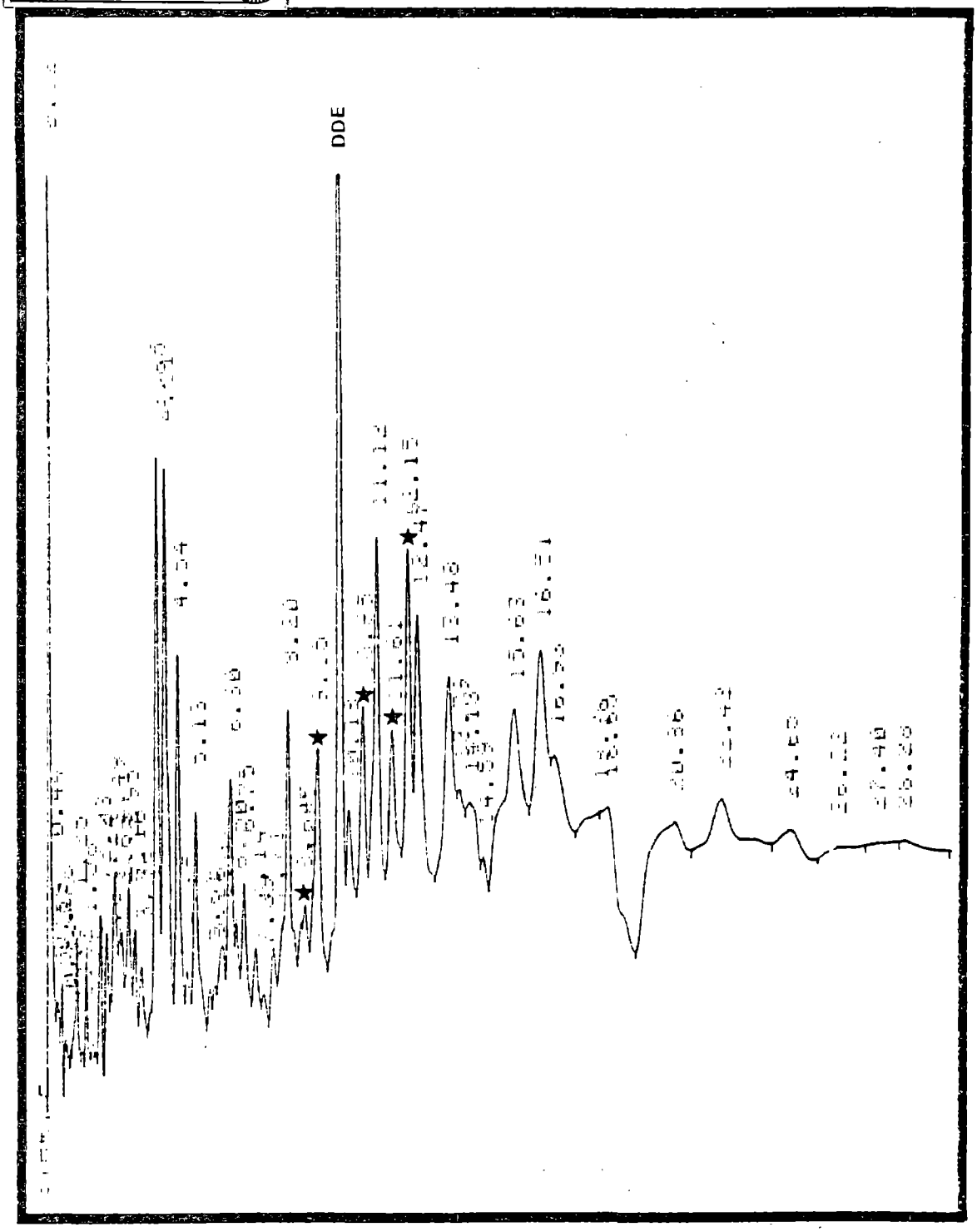



Figure 12. Representative GC/ECD Trace (Packed Column) of PCBs in a Lizardfish Muscle Tissue from Region 2, Station 33. Starred Peaks Co-elute with Aroclor 1254 Standard. Earlier Peaks do not Co-elute with any PCB Mixtures (e.g. Aroclor 1016 or 1242).

PCB concentrations in muscle tissues are among the highest found throughout the eight species analyzed (Table 3-2, Figure 5). The median muscle concentration was 78 ppb, with no evidence of regional variation or coupling to PHC values (Table A-5). The median liver value was 240 ppb, also with no correlation to PHCs or with regional variation.

### 3.1.6 Scad

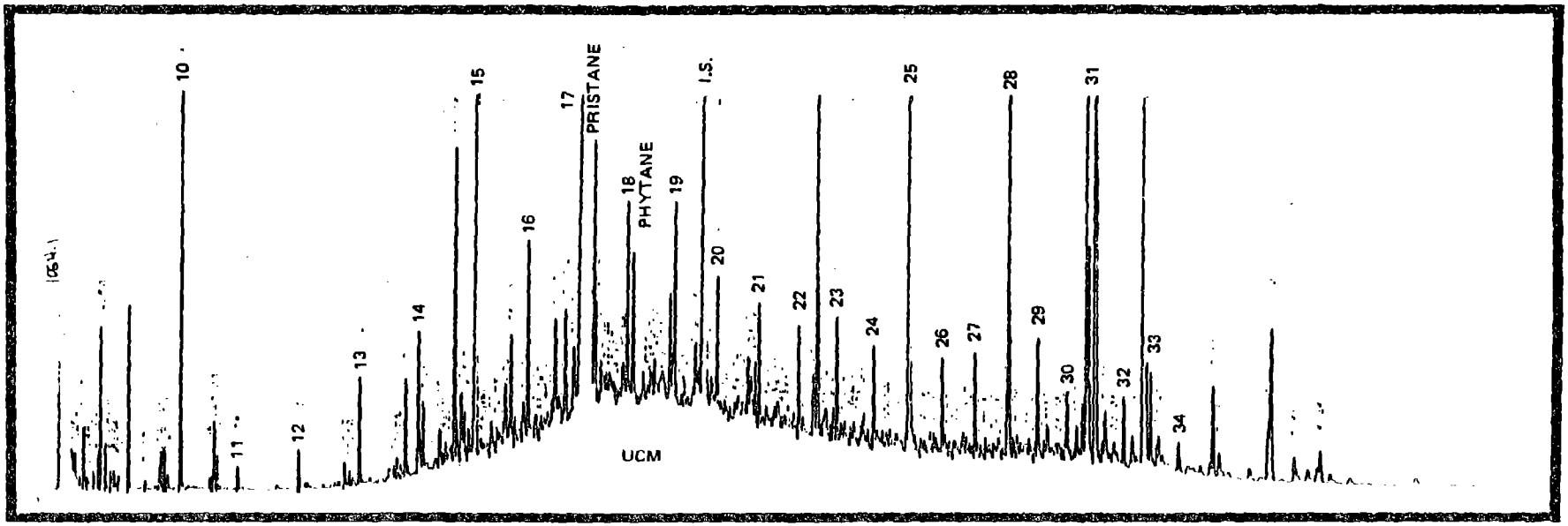
Seven scad samples were analyzed from three different regions (Table A-6). Scad tissues were among the three species containing the highest concentrations of PHC compounds in muscle or liver tissue (Table 3-1). The capillary GC traces illustrated (Figure 13) are of the $f_1$ muscle and liver samples screened positive from Region 6. Although the total concentration of PHC is low in the muscle, the petrogenic nature of the $f_1$ fraction is pronounced, with sizeable branched alkane peaks, including phytane, also evident. The large amount of pristane in both GC traces in Figure 13 is due to a biogenic origin. The liver chromatogram is very typical of this tissue, with a late UCM (eluting at n-$C_{26}$ to n-$C_{34}$) and high concentrations of n-alkanes n-$C_{26}$ to n-$C_{34}$. The total ($f_1$ + $f_2$) PHC measured in liver from different regions for this species ranged from 136 ppm to 486 ppm, with a median value of 311 ppm.

Scad muscle PCB concentrations do not demonstrate a strong regional variation, with a median of 30 ppb found in the samples from the three regions analyzed. Liver tissues show a much wider variation in PCB concentrations both within and throughout the regions analyzed, with a range from 60 to 11,400 ppb, and thereby also lacking in any regional dependence. PCB and PHC data trends are not related; the sample with the highest PCB concentration determined in this study (11,400 ppb, Station 101) was negatively screened for PHC, and contained average amounts (30 ppb) of PCB in the muscle.

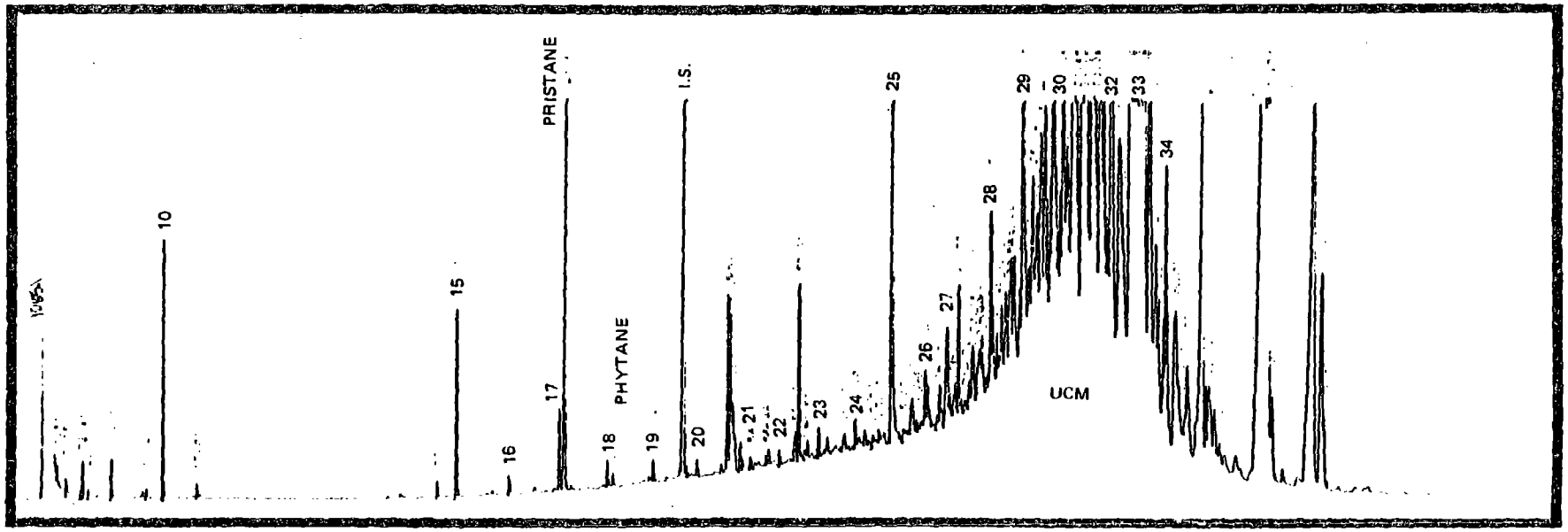
### 3.1.7 Snapper

PHC content measured in this species was about the median of the eight species analyzed, both for muscle and liver tissue (Table 3-1). Gas chromatograms are similar to those already illustrated. The n-alkanes, branched alkanes, and unresolved/resolved compositions all suggest a petrogenic input to those samples screened positive.

PCB concentrations found in snapper tissues for both muscle and liver are similar to the other species analyzed (Table 3-2): muscle - median value of 20 ppb, and liver - 235 ppb, demonstrating the commonly found 4-to-10-fold-higher PCB concentrations in the liver. A similar situation is found with PHC compound concentrations, but quantitation is difficult due to interference of biogenic compounds. PCB data, on the other hand,




SCAD MUSCLE–STN 117–SATURATED FRACTION




SCAD LIVER–STN 117–SATURATED FRACTION

Figure 13. Representative Capillary GC Traces of Scad Hydrocarbons.

can be more rigorously evaluated, as biogenic inputs are not a major factor in quantitation. One liver sample from Station 88, Region 5, has a high PCB value of 1,420 ppb, but a muscle value of 20 ppb (Table A-7), suggesting non-equilibrium distributions of PCB within the fish. Also, this sample was screened negative in both muscle and liver tissues for PHC. This species shows no evidence of coupling of PHC and PCB values.

### 3.1.8 Spot

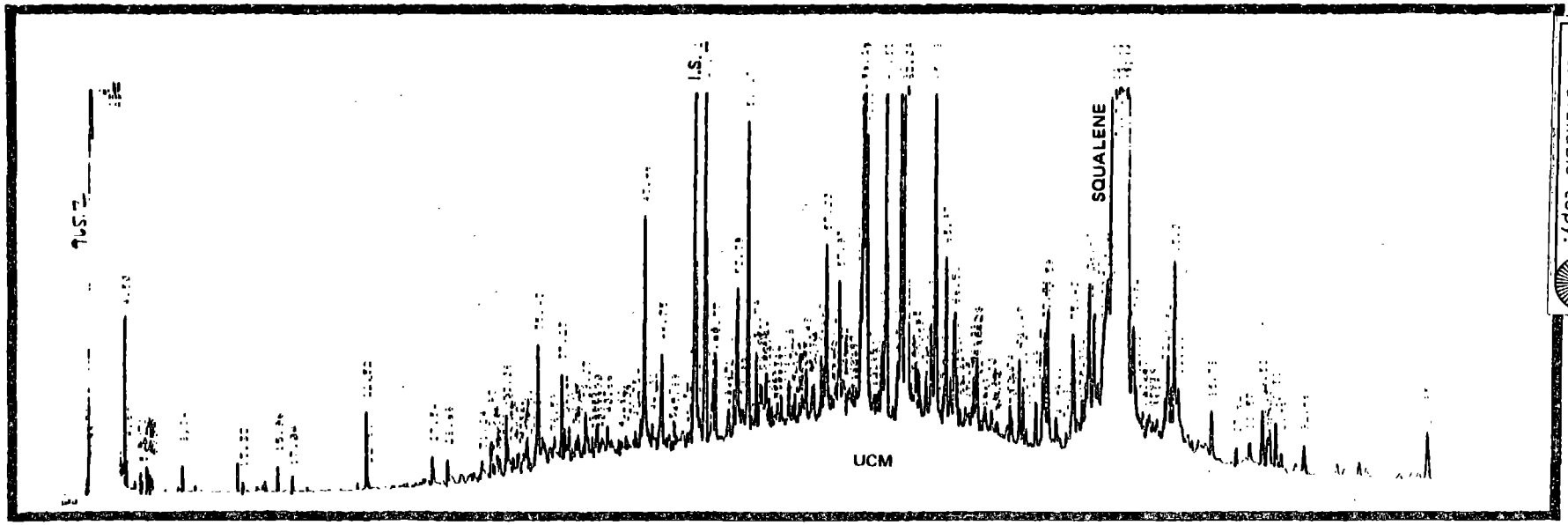
This species contained the highest PHC concentrations determined for muscle and the second highest concentrations in liver tissue of the eight species analyzed and, with the exception of one liver, was consistently the highest tissue in each of the four regions in which spot were found. Muscle tissue contained 30 ppm (range 22 ppm to 38 ppm; Table 3-1 and Figure 4). Liver tissue averaged 316 ppm (range of 59-885 ppm). Gas chromatograms of spot muscle and liver tissue from Region 5 (Figures 14 and 15) again illustrate prominent UCMs for $f_1$ and $f_2$ fractions and the n-alkane and branched alkanes of petroleum in liver and muscle $f_1$ fractions. Again, the liver has a late-boiling UCM, but little early-boiling UCM, as was seen for some other species (e.g., see Figure 9). The higher boiling n-alkanes were more pronounced in the liver than in muscle. Total PHC for this example was 22 ppm (muscle) and 59 ppm (liver).

This species, as with porgy, has moderate levels of PCB in muscle tissue (Table A-8). The median concentration is 30 ppb, with a range of 10 to 170 ppb. The median concentration of PCB in liver tissue was 280 ppb with a range from 14 to 1,230 ppb, with no apparent regional input. PCB values are decoupled from PHC concentrations, again suggesting a differential source input of organic contamination.

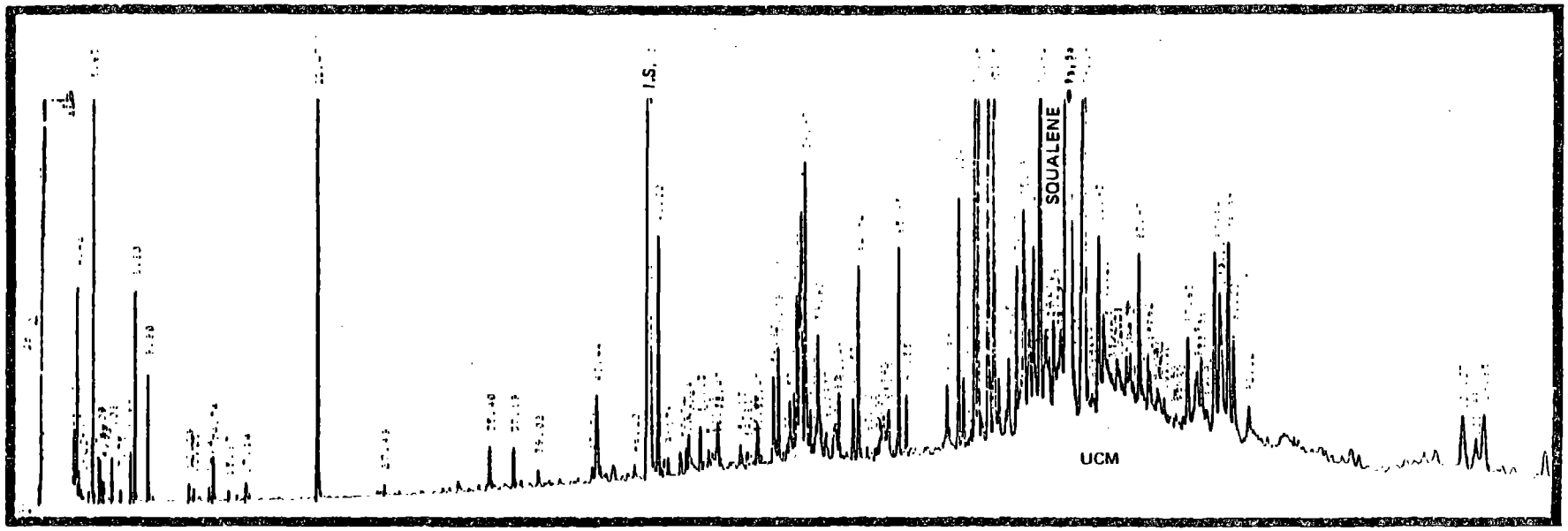
## 3.2 Regional Variations

The eight different species of fish have also been grouped into six different regions to assess regional variation of PHC (Figures 16, 17 and 18) and PCB (Figures 19, 20 and 21) values. The six regions investigated were Chesapeake Bay (1), Georgia Bight (2), Florida West Coast (3), Apalachicola area (4), Flower Gardens (5), and Corpus Christi/Port Isabel (6).

Regional trends of PHC have been evaluated in terms of median total PHC concentrations in the muscle or liver, and/or by the percentage of samples screened positive, Table 3-3. Regional gradients of PCBs have been viewed in terms of a median value, and a range of concentrations, Table 3-4.

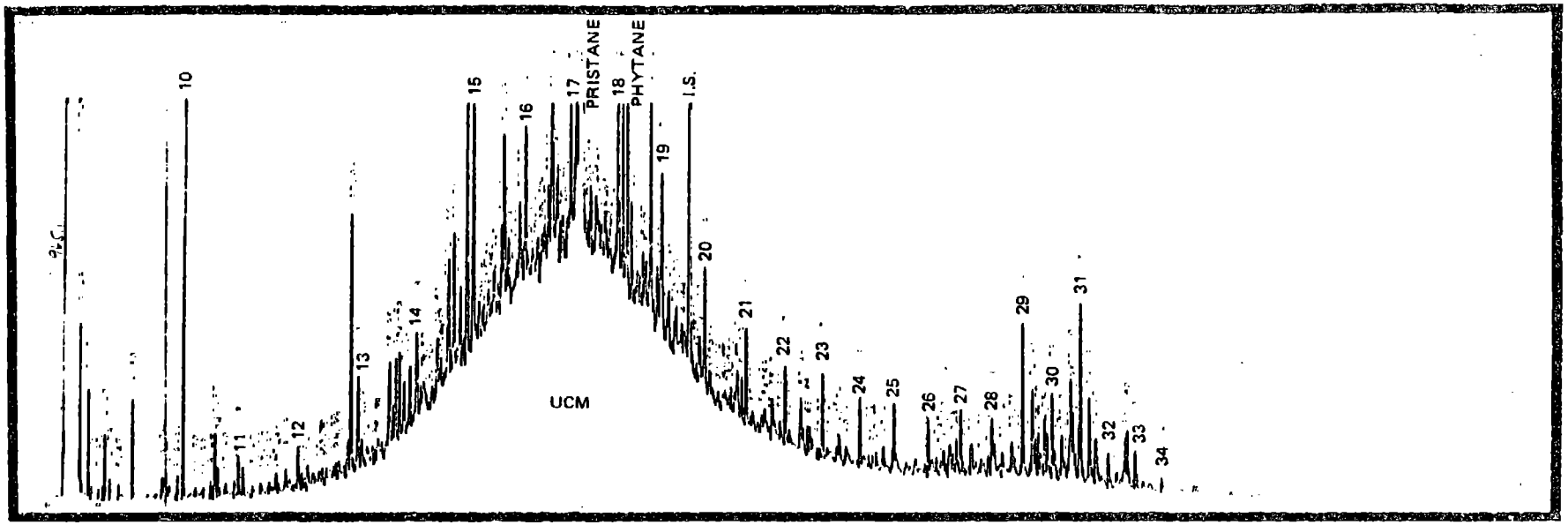



SPOT MUSCLE–STN 107–AROMATIC FRACTION

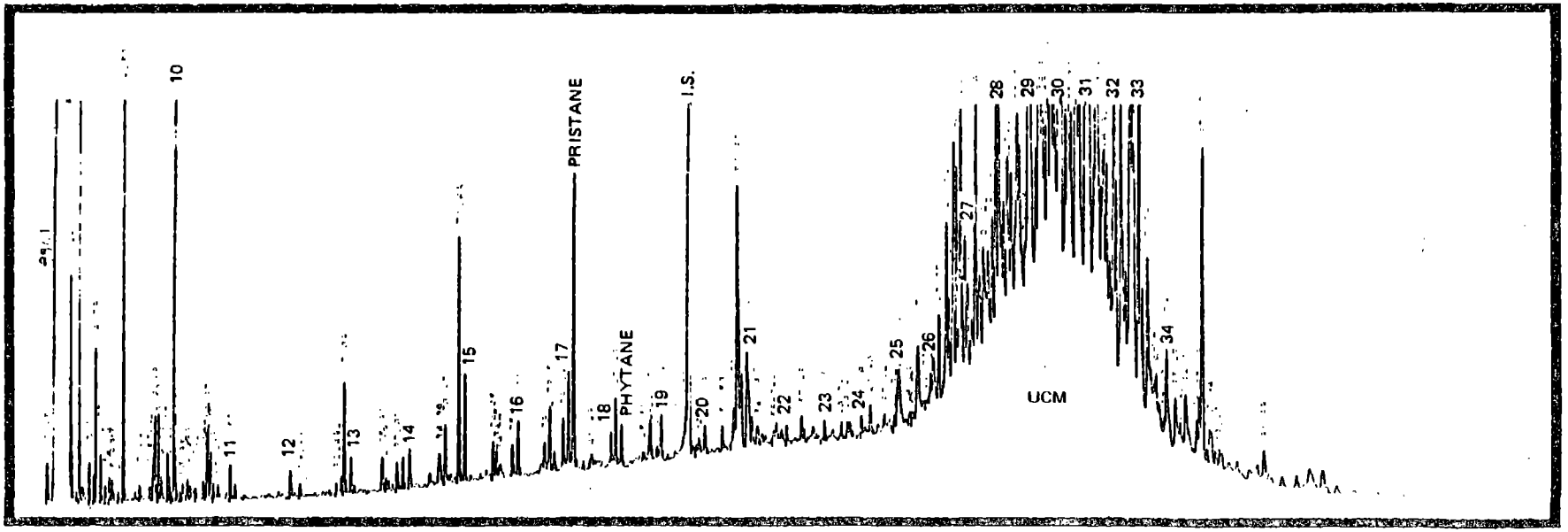



SPOT LIVER–STN 107–AROMATIC FRACTION

Figure 14. Representative Capillary GC Traces of Spot Hydrocarbons.




SPOT MUSCLE–STN 107–SATURATED FRACTION




SPOT LIVER–STN107–SATURATED FRACTION

Figure 15. Representative Capillary GC Traces of Spot Hydrocarbons.

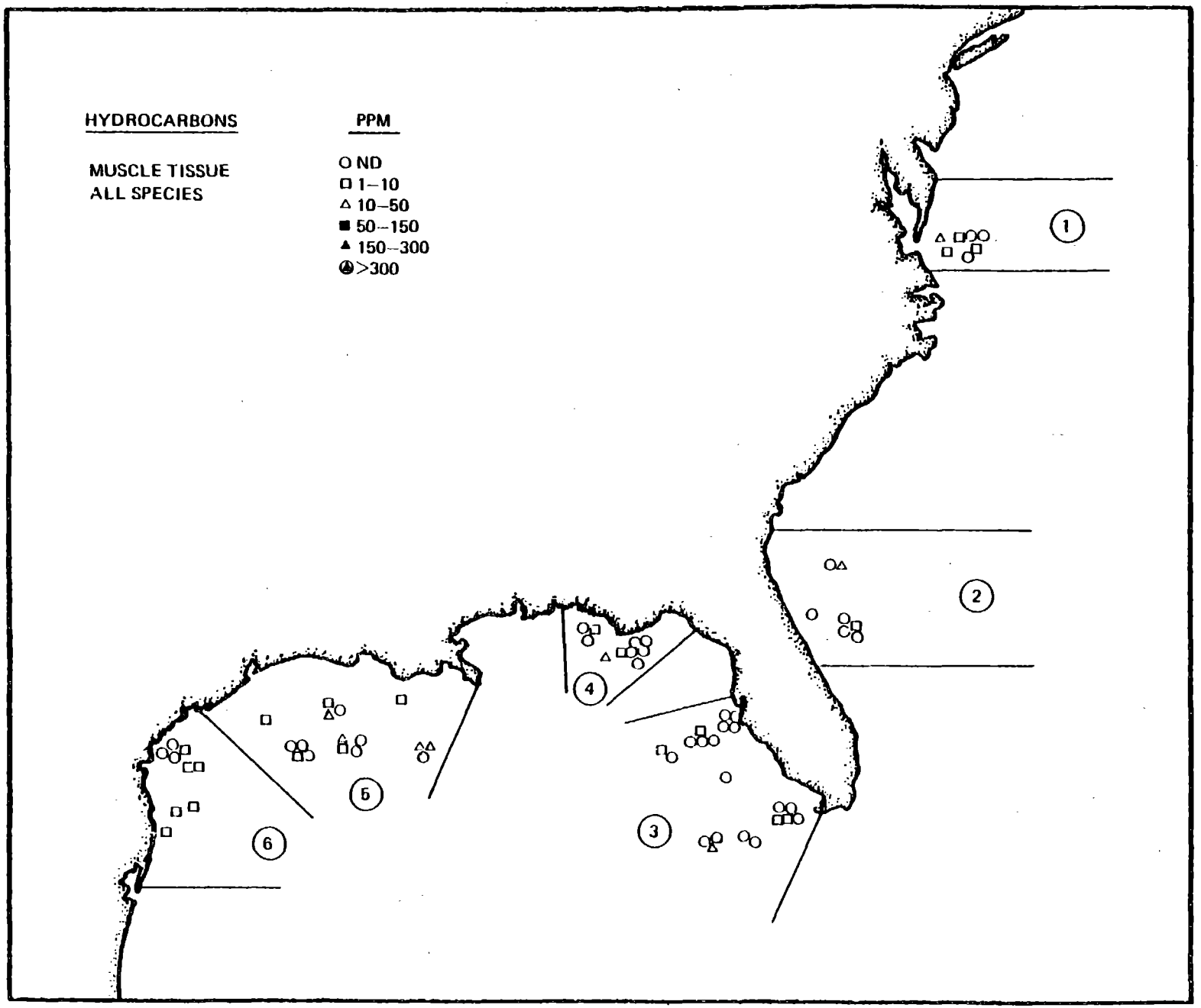



Figure 16. Regional Distribution of Hydrocarbons in Fish Muscle Tissues.

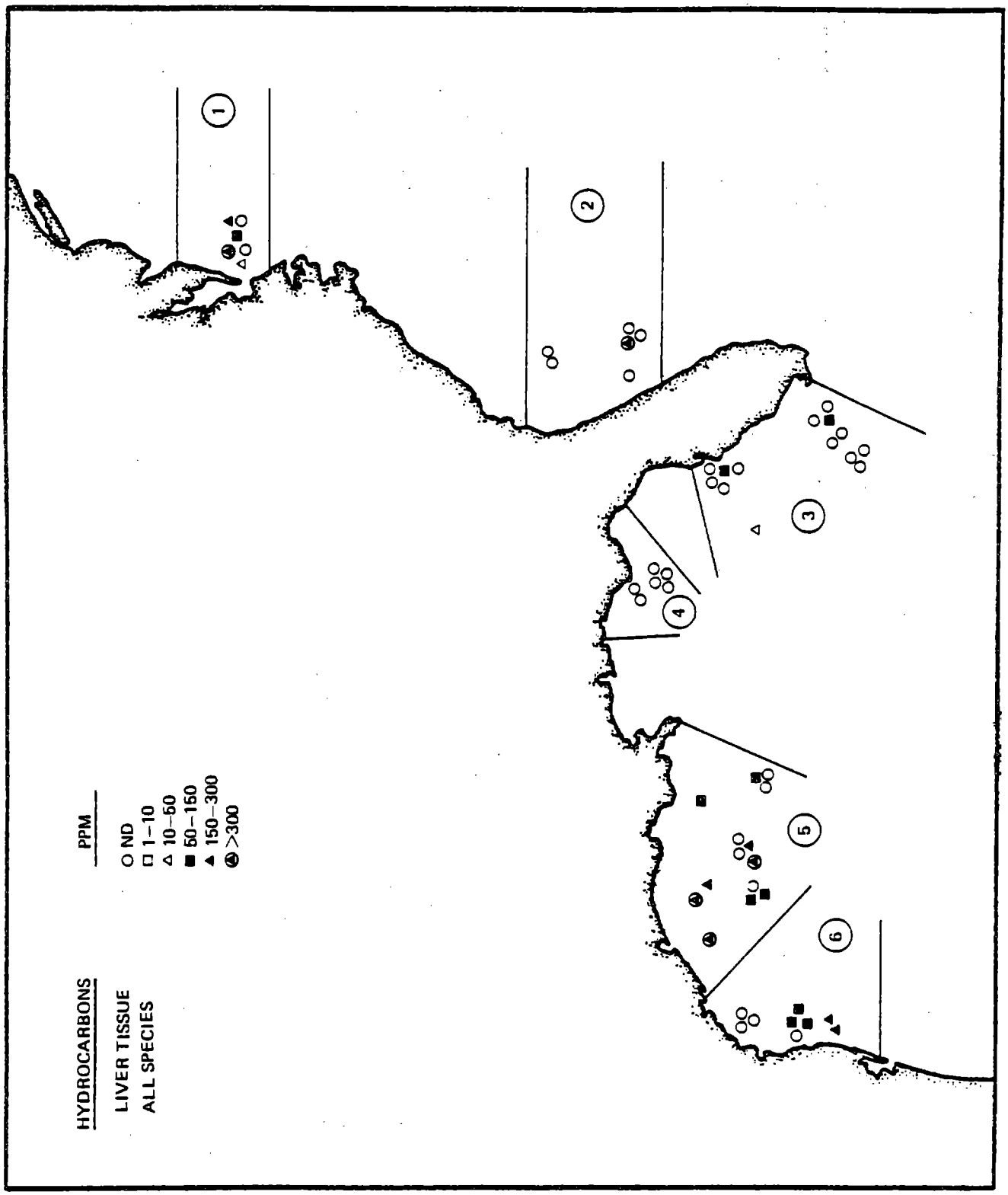



Figure 17. Regional Distribution of Hydrocarbons in Fish Liver Tissues.

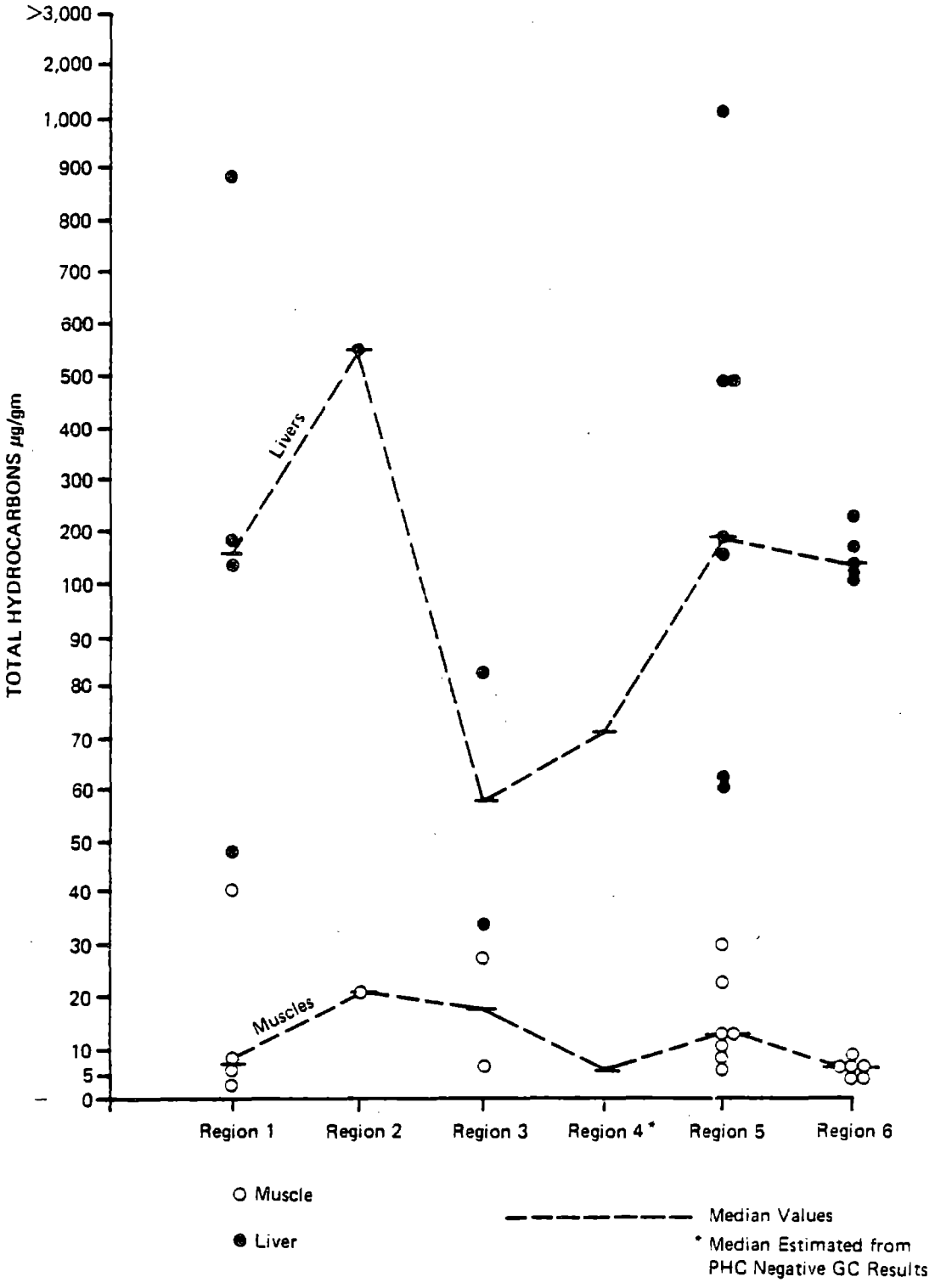



Figure 18. PHC Concentrations Graphed by Regions.

TABLE 3-3

INCIDENCE OF PETROLEUM HYDROCARBONS (REGIONAL VARIATIONS)

| REGION | NO. OF SAMPLES | % SCREENED POSITIVE | | PHC (µg/g DRY WT.) | | | |
|---|---|---|---|---|---|---|---|
| | | | | MUSCLE | | LIVER | |
| | | MUSCLE | LIVER | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] |
| 1. Chesapeake Bay | | | | | | | |
| a. Butterfish | 2 | 0 | 0 | - | | - | |
| b. Hake | 2 | 100 | 100 | 5.5 | 5.0-6.1 | 158 | 127-190 |
| c. Flounder | 2 | 50 | 50 | 3.2 | | 47 | |
| d. Spot | 1 | 100 | 100 | 38 | | 885 | |
| All species | 7 | 66 | 66 | 5.5 | 6.1-39 | 158 | 47-885 |
| 2. Georgia Bight | | | | | | | |
| a. Butterfish | 2 | 50 | 0 | 20 | | - | |
| b. Flounder | 1 | 0 | 0 | - | | - | |
| c. Lizardfish | 1 | 0 | 0 | - | | - | |
| d. Spot | 2 | 0 | 50 | - | | 551 | |
| All species | 6 | 17 | 17 | 20 | | 551 | |
| 3. Florida West Coast | | | | | | | |
| a. Butterfish | 1 | 100 | 0 | 27 | | - | |
| b. Flounder | 2 | 0 | 0 | - | | - | |
| c. Lizardfish | 3 | 33 | 33 | 6.0 | | 34 | |
| d. Hake | 1 | 0 | 0 | - | | - | |
| e. Scad | 4 | 0 | 0 | - | | - | |
| f. Snapper | 4 | 0 | 0 | - | | - | |
| g. Spot | 3 | 0 | 33 | - | | 82 | |
| All species | 18 | 11 | 13 | 16 | 6.0-27 | 58 | 34-82 |

[a]If available.

TABLE 3-3 (Continued)

| REGION | NO. OF SAMPLES | % SCREENED POSITIVE | | PHC (µg/g DRY WT.) | | | |
|---|---|---|---|---|---|---|---|
| | | | | MUSCLE | | LIVER | |
| | | MUSCLE | LIVER | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] |
| 4. Apalachicola Area | | | | | | | |
| a. Butterfish | 1 | 0 | 0 | - | | - | |
| b. Flounder | 2 | 0 | 0 | - | | - | |
| c. Lizardfish | 2 | 0 | 0 | - | | - | |
| d. Porgy | 1 | 0 | 0 | - | | - | |
| e. Hake | 1 | 0 | 0 | - | | - | |
| All species | 7 | 0 | 0 | 0 | | - | |
| 5. Flower Gardens | | | | | | | |
| a. Butterfish | 1 | 0 | 0 | - | | - | |
| b. Flounder | 5 | 0 | 20 | - | | 61 | |
| c. Lizardfish | 2 | 100 | 100 | 11 | 9.4-12 | 811 | 480-1,143 |
| d. Porgy | 1 | 100 | 100 | 5.8 | | 146 | |
| e. Scad | 2 | 100 | 50 | 20 | 12-29 | 486 | |
| f. Snapper | 2 | 50 | 50 | 7.0 | | 182 | |
| g. Spot | 1 | 100 | 100 | 22 | | 59 | |
| All species | 14 | 50 | 50 | 12 | 5.8-29 | 182 | 59-1,143 |
| 6. Corpus Christi/ Port Isabel | | | | | | | |
| a. Flounder | 1 | 100 | 100 | 6.9 | | 235 | |
| b. Lizardfish | 3 | 33 | 33 | 5.9 | | 170 | |
| c. Porgy | 2 | 100 | 50 | 5.0 | 4.3-5.8 | 103 | |
| d. Scad | 2 | 50 | 50 | 4.1 | | 136 | |
| e. Snapper | 1 | 100 | 100 | 5.7 | | 122 | |
| All species | 9 | 67 | 56 | 5.8 | 4.1-6.9 | 134 | 103-235 |

[a]If available.

TABLE 3-4

INCIDENCE OF POLYCHLORINATED BIPHENYLS AND DDT (REGIONAL VARIATIONS)

| REGION | NO. OF SAMPLES | PCB, DRY WEIGHT (µg/g) | | | | ΣDDT, DRY WEIGHT (µg/g) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | MUSCLE | | LIVER | | MUSCLE | | LIVER | |
| | | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] |
| 1. Chesapeake Bay | | | | | | | | | |
| a. Butterfish | 2 | 110 | 100-120 | 535 | 50-1,020 | 31 | 27-35 | 76 | 10-143 |
| b. Hake | 2 | 80 | 70-90 | 50 | 40-60 | 20 | 16-25 | 12 | 9-16 |
| c. Flounder | 2 | 35 | 10-60 | 365 | 90-640 | 29 | 2-52 | 108 | 19-197 |
| d. Spot | 1 | 10 | | 350 | | 2 | | 59 | |
| All species | 7 | 70 | 10-120 | 90 | 40-1,020 | 24 | 2-52 | 19 | 9-197 |
| 2. Georgia Bight | | | | | | | | | |
| a. Butterfish | 2 | 70 | 60-80 | 185 | 100-270 | 47 | 33-62 | 31 | 16-46 |
| b. Flounder | 1 | 30 | | 400 | | 1 | | 166 | |
| c. Lizardfish | 1 | 16 | | 100 | | 2 | | 59 | |
| d. Spot | 2 | 190 | 10-170 | 280 | 50-510 | 23 | 7-20 | 26 | 2-50 |
| All species | 6 | 45 | 10-170 | 185 | 50-510 | 14 | 1-62 | 48 | 2-166 |

[a]If available.

[b]One tissue not analyzed for PBC, DDT.

TABLE 3-4 (Continued)

| REGION | NO. OF SAMPLES | PCB, DRY WEIGHT (µg/g) | | | | ΣDDT, DRY WEIGHT (µg/g) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | MUSCLE | | LIVER | | MUSCLE | | LIVER | |
| | | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] |
| 3. Florida West Coast | | | | | | | | | |
| a. Butterfish | 1 | 50 | | 520 | | 48 | | 87 | |
| b. Flounder | 2 | 10 | 10-10 | 40[b] | | 1.5 | 1-2 | 10[b] | |
| c. Lizardfish | 3 | 10 | 10-10 | 120 | 100-420 | 3 | 2-13 | 180 | 51-274 |
| d. Hake | 1 | 10 | | 410 | | 2 | | 128 | |
| e. Scad | 4 | 30 | 20-50 | 65 | 60-190 | 4 | ND-14 | 22 | 9-44 |
| f. Snapper | 4 | 15 | 10-30 | 90 | 70-220[b] | 6 | 2-19 | 20 | 18-40[b] |
| g. Spot | 3 | 60 | 30-160 | 280 | 240-1,230 | 5 | 2-92 | 48 | 37-267 |
| All species | 18 | 20 | 10-160 | 155 | 40-1,230 | 3 | 1-92 | 40 | 9-267 |
| 4. Apalachicola Area | | | | | | | | | |
| a. Butterfish | 1 | ND | | ND | | 1 | | 3 | |
| b. Flounder | 2 | 46 | 30-50 | 920 | 860-980 | 13 | 7-20 | 164 | 49-279 |
| c. Lizardfish | 2 | 15 | 10-20 | 220 | 130-310 | 26 | 6-46 | 206 | 81-331 |
| d. Porgy | 1 | 20 | | 30 | | 2 | | 10 | |
| e. Hake | 1 | -[b] | | 290 | | -[b] | | | |
| All species | 7 | 20 | ND-50 | 290 | ND-980 | 6 | 1-46 | 65 | 3-331 |

[a]If available. (ND = none detected)

[b]One tissue not analyzed for PBC, DDT.

TABLE 3-4 (Continued)

| REGION | NO. OF SAMPLES | PCB, DRY WEIGHT (µg/g) | | | | ΣDDT, DRY WEIGHT (µg/g) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | MUSCLE | | LIVER | | MUSCLE | | LIVER | |
| | | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] | MEDIAN | RANGE[a] |
| 5. Flower Gardens | | | | | | | | | |
| a. Butterfish | 1 | 100 | | 70 | | 15 | | 7 | |
| b. Flounder | 5 | 20 | 10-70 | 330 | 10-540 | 5 | 3-12 | 32 | 1-96 |
| c. Lizardfish | 2 | 33 | 30-36 | 385 | 320-450 | 11 | 5-17 | 232 | 111-353 |
| d. Porgy | 1 | 180 | | 420 | | 12 | | 35 | |
| e. Scad | 2 | 40 | 20-60 | 300 | 300-300 | 3.5 | 1-6 | 10 | 1-20 |
| f. Snapper | 2 | 30 | 20-40 | 835 | 250-1,420 | 30 | | 162 | 135-353 |
| g. Spot | 1 | 30 | | 100 | | 4 | | 6 | |
| All species | 14 | 30 | 10-180 | 300 | 70-1,420 | 5 | 1-30 | 32 | 1-189 |
| 6. Corpus Christi/Port Isabel | | | | | | | | | |
| a. Flounder | 1 | 70 | | 210 | | 8 | | 294 | |
| b. Lizardfish | 3 | 40 | 20-80 | 350 | 230-2,130 | 10 | ND-18 | 367 | 76-1,170 |
| c. Scad | 2 | 30 | 30-30 | NA[b] | 220-11,400 | 23 | 14-32 | NA[b] | 65-1,000 |
| d. Snapper | 1 | 40 | | 290 | | 24 | | 288 | |
| All species | 9 | 40 | 20-120 | 290 | 130-11,400 | 16 | ND-32 | 288 | 19-1,170 |

[a]If available.
[b]NA = not available.

### 3.2.1 Petroleum Hydrocarbons

Of the six regions analyzed, Region 1, Chesapeake Bay, and Region 6, Corpus Christi/Port Isabel, had the highest percentage of muscle and liver tissues screened positive (approximately 66%). No samples of either muscle or liver tissues in Region 4 were screened positive; one out of six samples (17%) in the Georgia Bight, Region 2, was screened positive (spot tissue), and approximately 12% of samples off the Florida West Coast were screened positive. Fifty percent of the samples analyzed from Region 5, the Flower Gardens, showed evidence of petroleum assimilation. Figures 16 and 17 display this information geographically.

Table 3-3 presents the above data. It can be seen that muscle PHC concentrations vary from 5.5 ppm to 20 ppm from region to region, and that liver values range from 58-551 ppm (Figure 18). No simple correlation is apparent between measured PHC liver concentrations, muscle concentrations, and the percentage of fish screened positive in each region. Flounder is the only species found in all six regions. Spot consistently contains the highest or second highest muscle or liver concentrations of PHC wherever the fish is found (Figure 4).

### 3.2.2 Chlorinated Hydrocarbons, PCB and ΣDDT

We have not found any consistent regional variation in PCB concentrations of muscle tissues, either as the median value of PCB in each region, or in any significant inter-regional variation in the range of PCB concentrations (Table 3-4), except in Region 4. Liver tissue, although varying between a median value of 155 ppb from Region 3 to 300 ppb in Region 5, also does not support any apparent PCB concentration gradients. Ranges are similar from one area to the next, with Figures 19, 20 and 21 geographically displaying this information. Easily noted between these two figures is the order of magnitude increase in concentrations found in liver tissues versus muscle tissues.

## 3.3 Polynuclear Aromatic Hydrocarbon (PAH) Results

Sixteen samples of muscle or liver tissues were selected for detailed analysis by capillary GC/MS. Concentrations of compounds in the naphthalene (2 ring), phenanthrene (3 ring), dibenzothiophene (2 aromatic rings, 1 heterocyclic saturated ring), and fluorene (2 aromatic rings, 1 saturated ring) families, and the compounds fluoranthene and pyrene (m/e = 202), are presented for each tissue in Table 3-5. "Families" include zero- (the parent compound), one-, two-, three-, and four-methyl substituted components.

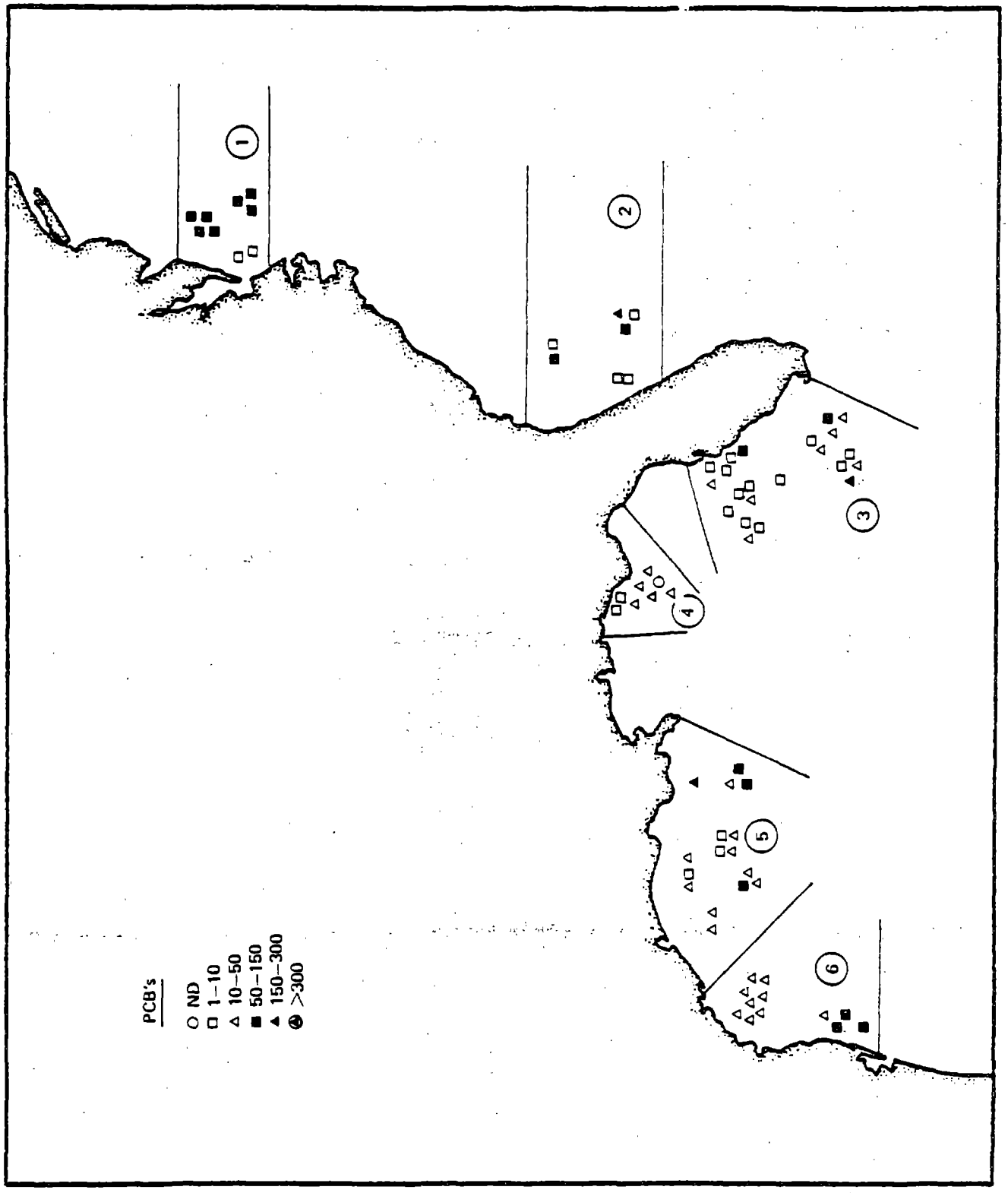



Figure 19. Regional Distribution of PCB Concentrations in Fish Muscle.

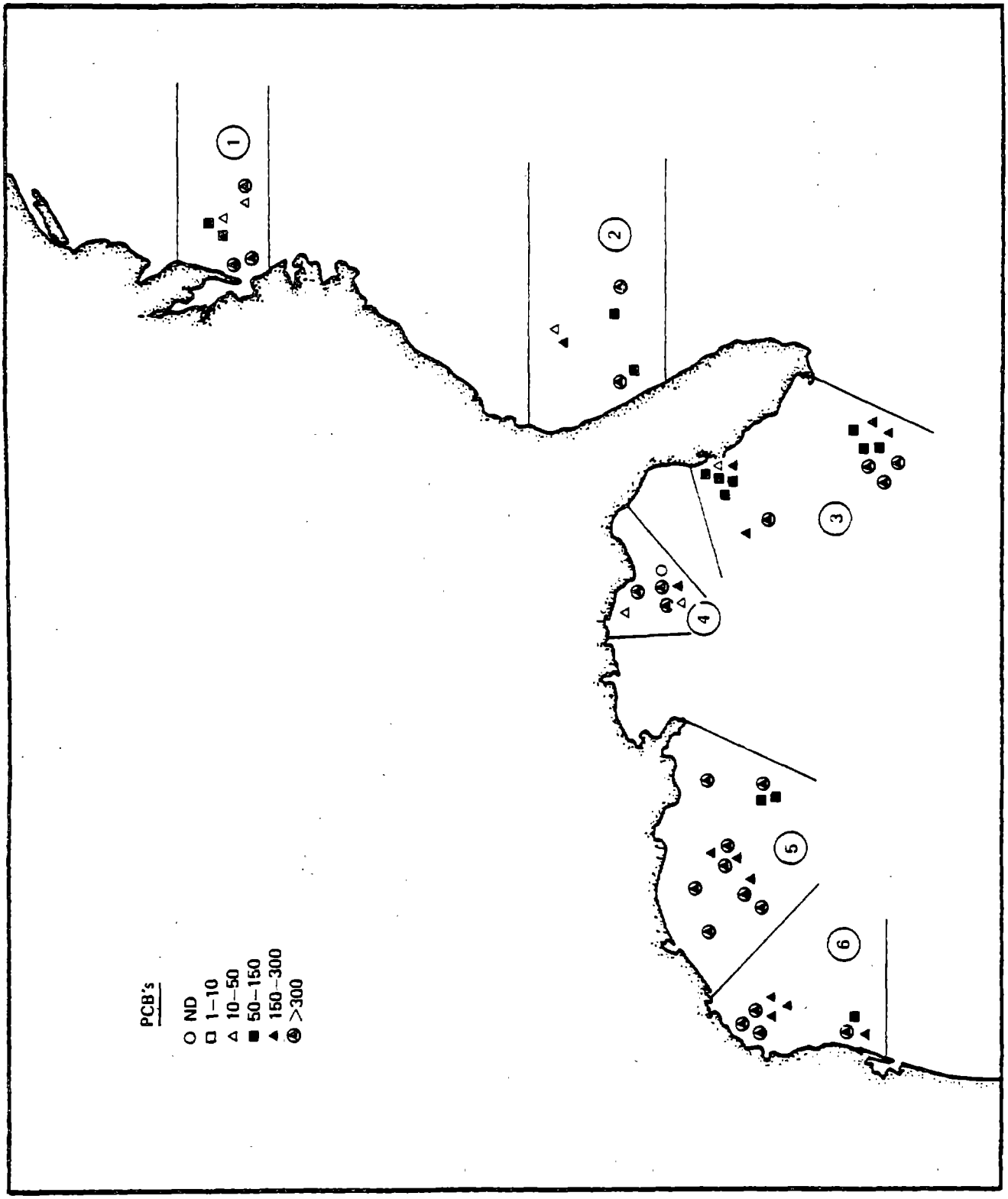



Figure 20. Regional Distribution of PCB Concentration in Fish Livers.

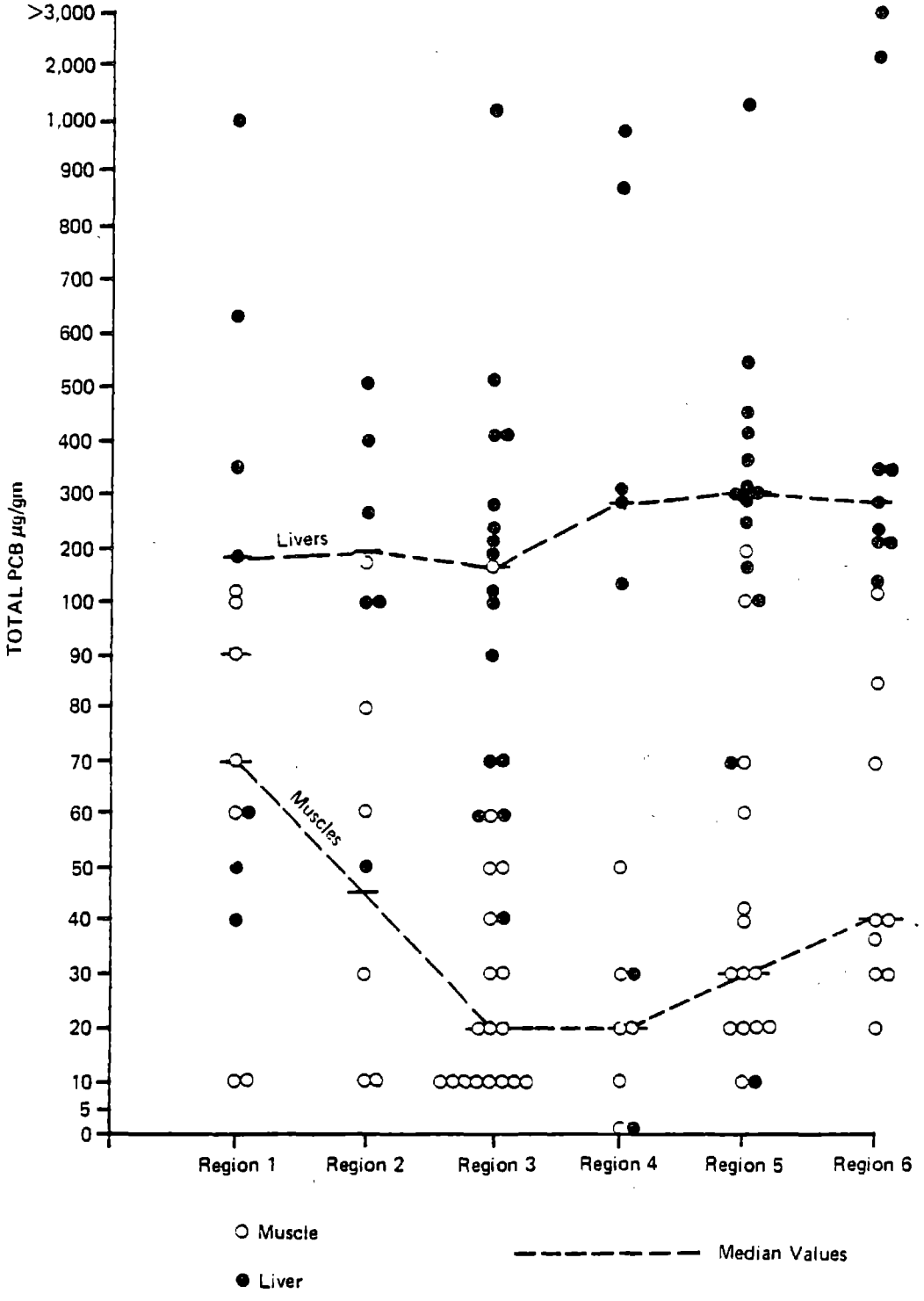



Figure 21. PCB Concentrations Graphed by Regions.

TABLE 3-5

POLYNUCLEAR AROMATIC HYDROCARBONS - CONTENTS OF SELECTED SAMPLES[a]

| SPECIES | STATION | TISSUE | TOTAL PHC | INDIVIDUAL NAPTHALENES | | | | | TOTAL N | INDIVIDUAL PHENANTHRENES | | | | | TOTAL P | TOTAL DBT | TOTAL F | TOTAL 202 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | PARENT | $C_1$ | $C_2$ | $C_3$ | $C_4$ | | PARENT | $C_1$ | $C_2$ | $C_3$ | $C_4$ | | | | |
| Flounder | 14 | Muscle | 3.2 | - | 0.7 | - | - | - | 0.7 | 4.1 | - | - | - | - | 4.1 | - | - | 3.7 |
| | 53 | Muscle | 5.3(-) | - | - | - | 0.3 | - | 0.3 | 3.1 | 1.1 | - | 0.6 | - | 4.8 | 2.9 | 0.06 | 1.3 |
| | 143 | Muscle | 1.0(-) | 1.1 | 1.2 | 1.2 | - | - | 3.5 | 6.4 | - | 1.0 | - | - | 7.4 | 0.6 | 0.1 | 0.5 |
| Lizard-fish | 130 | Muscle | 9.4 | - | - | 0.5 | 1.1 | 0.4 | 2.0 | 3.2 | 3.1 | 0.6 | - | 0.9 | 7.8 | 2.2 | 0.2 | 3.7 |
| Hake | 13 | Liver | 190 | 62 | - | - | - | - | 62 | 92 | - | - | - | - | 92 | - | - | 4.5 |
| | 14 | Muscle | 5.0 | 0.1 | 0.1 | 1.3 | 1.4 | 2.3 | 5.2 | 2.7 | 1.4 | 0.7 | - | - | 4.8 | 1.6 | 0.8 | 1.5 |
| | 14 | Liver | 127 | 64 | 54 | 35 | - | - | 153 | 35 | - | - | - | - | 35 | 6.8 | 8.5 | - |
| Porgy | 54 | Muscle | 5.2(-) | - | 0.3 | 1.0 | 1.7 | 0.4 | 3.4 | 3.1 | - | 0.3 | - | - | 3.4 | 0.5 | 0.4 | 1.9 |
| Scad | 107 | Muscle | 29 | 2.2 | 3.2 | 2.6 | 1.4 | 0.1 | 9.5 | 3.1 | - | - | - | - | 3.1 | 0.6 | 0.6 | 1.0 |
| | 140 | Muscle | 12 | 3.7 | - | - | - | - | 3.7 | 2.1 | - | - | - | 3.7 | 5.8 | - | - | - |
| Spot | 107 | Muscle | 22 | 1.5 | 7.5 | 52 | 43 | 29 | 133 | 8.0 | 3.6 | 0.9 | - | - | 12.5 | 6.1 | 6.5 | 3.6 |
| | 15 | Muscle | 38 | 4.8 | - | - | - | - | 4.8 | 13 | - | - | - | - | 13 | - | - | - |
| | 15 | Liver | 885 | 263 | 313 | - | 146 | - | 722 | 141 | 39 | - | - | - | 180 | - | - | - |

[a]All values are in ng/g (ppb) except for total PHC values, which are in µg/g (ppm).

Key:
N = napthalenes; P = phenanthrenes; DBT = dibenzothiophenes; F = fluorenes; 202 = fluoranthenes and pyrene.
Bracketed tissues are from the same station sample; (-) = negatively screened.

Individual concentrations of the naphthalene and phenanthrene alkylated families are tabulated to illustrate the degree of alkylation. The amount of alkylation indicates the relative abundance of petroleum versus combustion sources for the PAH. Petroleum contains substantial alkylated PAH while combustion sources are more abundant in the parent compound. Therefore, a higher abundance of alkylated compounds is indicative of petroleum assimilation in fish tissues.

As compared to the northern half of this study (Boehm, 1980-Part I of this program), naphthalenes, dibenzothiophenes, and 202 family compounds are of similar concentrations. Phenanthrenes and fluorenes, though, are lower than previously determined. As can be seen, the values of PAH compounds in liver tissues are an order of magnitude greater than in corresponding muscle tissues, following the observed pattern for PHC concentrations in general. Note that the three samples (flounders, Stations 53 and 143, and porgy, Station 54), which were screened negative for PHC (criteria listed in Section 2), still contain similar low concentrations of PAH compounds. Hence, PAH distributions are somewhat independent of gross PHC diagnostics ($GC^2$/FID) with low-level tissue burdens probably being ubiquitous in coastal fish populations.

## 4. Interpretation of Findings

Inputs of PHC, PAH, PCB, and DDT to marine fish populations in the U.S. southeastern and Gulf coasts have been successfully monitored in this study. Utilizing a sequential, progressively more complex analytical scheme, we have screened a large number of fish muscle and liver tissues, in an effort to establish ambient levels of organic pollutants on the Atlantic coast and in the Gulf of Mexico. These data have also been assessed regionally so as to define, if possible, any geographic point source contaminants or concentration gradients.

Two of the fish species studied here, silver hake and flounder, were monitored in the earlier GAS I study, covering the North Atlantic from Maine to Cape Hatteras. Table 4-1 provides a summary of PHC compounds in these fish, as well as data from other studies. Values for both species are within the lower range of those fish analyzed in the northern half of this study (Boehm, 1980), and off of Georges Bank (Boehm and Barak, 1979).

Most of the concentration data presented in Table 4-1 are for muscle tissue. In this study, we have also investigated the PHC burden in fish livers. Capillary GC chromatograms presented earlier (Figures 13 and 15), demonstrate a characteristic GC pattern of n-alkanes (large n-$C_{26}$ to n-$C_{34}$ peaks) and a late-boiling UCM. The source of this distibution is not apparent from this study but is probably related to biochemical synthesis and/or modification of assimilated PHC residues. Sample GC traces occasionally demonstrate a bimodal UCM, the earlier unresolved compounds eluting between n-$C_{13}$ and n-$C_{20}$, a typical range indicative of petroleum

TABLE 4-1

PETROLEUM HYDROCARBONS IN FISH

| SPECIES | LOCATION | PHC TOTAL (µg/g DRY WT.)[a] | REFERENCE |
|---|---|---|---|
| Hake | GAS I | | |
| Muscle | | 5.0-6.1 | This study |
| Liver | | 128-190 | This study |
| Flounder | GAS I | | |
| Muscle | | 1.0-6.9 | This study |
| Liver | | 47-235 | This study |
| Hake | GAS I | 1-90 | Boehm (1980) |
| Flounder | GAS I | 1-9 | Boehm (1980) |
| American Dab | GAS I | 1-2 | Boehm (1980) |
| Haddock | GAS I | ND | Boehm (1980) |
| Cod | GAS I | ND | Boehm (1980) |
| Hake | Georges Bank | 5-50 | Boehm & Barak (1979) |
| Flounder | Georges Bank | 1-50 | Boehm & Barak (1979) |
| Haddock | Georges Bank | 1-5 | Boehm & Barak (1979) |
| Cod | Georges Bank | 1-10 | Boehm & Barak (1979) |
| Flounder | Rhode Island Coast | 25-250 | Boehm & Barak (1978) |
| Hake | Scotland | 30[b] | Mackie et al. (1974) |
| Flounder | Gulf of Mexico | 43[b] | Parker et al. (1972) |
| Cod | British Isles | 0.025-1.5[b] | Whittle et al. (1975) |

[a]ND = none detected.

[b]Represents n-paraffins only, values converted to dry weight for comparison.

distillate contamination (Fig. 9). The second, late UCM may be biogenic, with only the earlier UCM representative of a recent petrogenic input. Therefore, liver samples with early eluting UCMs and a smooth distribution of n-alkane peaks between n-$C_{13}$ and n-$C_{20}$ should be considered to be PHC-positive. Some chromatograms support this theory (Figure 15), in that a pronounced late UCM is present, but only small n-alkane peaks are visible when compared to the respective muscle tissue. This analysis, though, may be overly simplistic. Consider that the liver operates as the primary detoxification organ in the fish, and so contains specific metabolic pathways not found in other tissues. High boiling n-alkanes, and compounds comprising the late UCM could be preferentially collected in liver tissues. PAH analysis of specific aromatics in liver tissue supports this observation by showing a 10-fold increase in naphthalenes and phenanthrenes in this organ over muscle tissue. Note that the liver samples investigated do not necessarily contain high levels of dibenzothiophenes, fluorenes, or mass 202 compounds as compared to muscle, also suggesting a preferential accumulation of certain petrogenic contaminants in this tissue or selective metabolism of certain PAH compound types. The liver consistently contains an average 10-fold increase in concentrations of PHC, PCB, and PAH and demonstrated much greater variability in concentration as compared to muscle.

It is encouraging to see that muscle concentrations of PCB and petrogenic-related compounds fall within ranges established by other studies. This reproducibility of measurement over the last 10 years (covered in Tables 4-1 and 4-2) supports the validity and continuance of the PHC monitoring of coastal fish and waters. Consistency of PHC and PCB concentrations found in the broad range of species now monitored encourages the use of fish in general as good candidates for pollutant chemical monitoring.

This study has been unable to clearly define any regional forcing of PHC or PCB concentrations in any of the eight species of fish. The hydrocarbon data do not provide a complete enough survey of each region to identify petrogenic concentration gradients. PCB data, although more complete, also do not demonstrate any clear regional variation, although for both PHC and PCB compounds, individual samples at particular stations clearly show evidence of elevated PHC and PCB levels in the respective $GC^2$/FID and GC/ECD traces. The fact that high PHC or PCB concentrations are not found in the same sample or at the same station well illustrates the general decoupling of PHCs and PCBs in this survey.

It has been suggested (Nisbet and Sarofinn, 1972) that the ratio of ΣDDT to PCB may provide an interpretable measurement of organic contamination in various organisms, independent of that organism's position in the food chain, and hence the known bioaccumulation of chlorinated hydrocarbons. PCBs determined for this study fall within range of PCBs determined both in the northern half of this study and in earlier studies (Table 4-2). PCB/ΣDDT ratios range from 4 to ∿10 with no apparent species preference, a similar result as was obtained in the northern half of this study (Boehm, 1980).

TABLE 4-2

PCB COMPOUNDS IN FISH

| SPECIES | LOCATION | PCB (ng/g DRY WT.)[a] | REFERENCE |
|---|---|---|---|
| Hake | GAS I (Southeast/Gulf) | | |
| Muscle | | 16-90 | This study |
| Liver | | 40-410 | This study |
| Flounder | GAS I (Southeast/Gulf) | | |
| Muscle | | 10-70 | This study |
| Liver | | 40-980 | This study |
| Hake | GAS I (Northeast) | 2-457 | Boehm (1980) |
| Flounder | GAS I (Northeast) | 2-86 | Boehm (1980) |
| American Dab | GAS I (Northeast) | 1-24 | Boehm (1980) |
| Haddock | GAS I (Northeast) | 1-26 | Boehm (1980) |
| Cod | GAS I (Northeast) | 2-18 | Boehm (1980) |
| Hake | East Coast, United States | 70-400 | Unpublished data |
| Flounder | East Coast, United States | 70-350 | Unpublished data |
| Mullet | Mediterranean Sea | 2,000-3,500 | Amico et al. (1979) |
| Mullet | Mediterranean Sea | Trace-400 | Basturk et al. (1980) |
| Tuna | Mediterranean Sea | 90-400 | Amico et al. (1979) |
| Sole | West Coast, Southern California | 50-2,000 | McDermott et al. (1974) |

Monitoring this ratio, then, may reflect the introduction of new chlorinated hdyrocarbons, either PCB or ΣDDT, into the environment or the migration of fish populations into high PCB or ΣDDT areas.

In conclusion, the baseline data accumulated in this study, together with earlier results from Maine to Cape Hatteras, will be indispensible for accurate, consistent monitoring of the Atlantic coastal waters and the Gulf of Mexico. The analytical method presented here has proven capable of providing rapid yet detailed information on pollutants measured in biological species. A larger, more complete sampling of the coastline, with perhaps an added Sephadex cleanup of $f_2$ fractions, will greatly aid the investigator's abilities to clearly define organic pollutants and regional concentration gradients.

This study has further expanded the information gathered in last year's GAS Ia study (see part I of this volume). The inclusion of liver tissues in the monitoring program has provided both new information and new questions as to the extent of petroleum and PCB contamination in coastal fish. Further investigation is needed to define metabolic mechanisms and possible preferential accumulation and distribution of petrogenic compound or metabolites in the liver vs. the muscle. The possible correlation between tissue lipid content, species variation in lipid content and the accumulated PHCs and PCBs can be explored. The ratio of liver to muscle contamination may provide information on exposure patterns, should compound distribution in the tissue be time dependent. Also, the inclusion of an alternate clean-up step involving Sephadex LH-20 (Ramos and Prohaska; 1981) will remove biogenic olefins which interfere with accurate quantification of the aromatic fraction or unfractionated tissues originally screened. The above information will greatly aid the interpretation of data as accumulated in this study.

To better identify any regional or species variance in PHC or PCB concentrations, a more complete sampling of each species in each region is greatly needed. This study did not provide sufficient samples to statistically demonstrate regional or species trends. Continued monitoring of both muscle and liver tissue is strongly recommended so as to increase the data base for the Atlantic and Gulf Coasts and to identify regional trends.

## 5. Summary of Data Acquired

The above mentioned analytical scheme was applied to those samples previously inventoried in Section 2, Table 2-1. PAH determinations were made in those samples presented in Section 3, Table 3-5.

## 6. Data Appendices

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

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TABLE A-1

ANALYTICAL SUMMARY - BUTTERFISH

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 13 | 5 | X | | | 100 | 35 | 2.9 |
| | 14 | 5 | X | | | 120 | 27 | 4.4 |
| | 30 | 20 | | 13 | 20 | 80 | 62 | 1.3 |
| | 31 | 20 | X | | | 60 | 33 | 1.8 |
| | 41 | 8 | | 13 | 27 | 50 | 48 | 1.0 |
| | 53 | 3 | X | (17) | (17) | ND | 1 | - |
| | 107 | 22 | X | | | 100 | 15 | 6.7 |
| Liver | 13 | | X | | | 1,020 | 143 | 7.1 |
| | 14 | | X | | | 50 | 10 | 5.0 |
| | 30 | | X | | | 270 | 46 | 5.9 |
| | 31 | | X | | | 100 | 16 | 6.3 |
| | 41 | | X | | | 520 | 87 | 6.0 |
| | 53 | | X | (72) | (72) | ND | 3 | - |
| | 107 | | X | | | 70 | 7 | 10 |

()negatively screened sample

TABLE A-2

ANALYTICAL SUMMARY - FLOUNDER

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 14 | 10 | X | | | 60 | 52 | 1.2 |
| | 15[a] | 4 | | 0.8 | 3.2 | 10 | 1.0 | 10. |
| | 31 | 4 | X | | | 30 | 1.0 | 30. |
| | 45 | 8 | X | | | 10 | 2.0 | 5.0 |
| | 49 | 2 | X | | | 10 | 1.0 | 10 |
| | 53[a] | 1 | X | (3.0) | (5.3) | 60 | 20 | 3.0 |
| | 53 | 1 | X | | | 30 | 7.0 | 4.3 |
| | 88 | 2 | X | (1.2) | (1.2) | 70 | 12 | 5.8 |
| | 88 | 19 | X | | | 20 | 6.0 | 3.3 |
| | 140 | 14 | X | | | 10 | 5.0 | 2.0 |
| | 140 | 8 | X | | | 20 | 5.0 | 4.0 |
| | 143[a] | 3 | X | (1.0) | (1.0) | 30 | 3.0 | 10 |
| | 285 | 24 | | 2.5 | 6.9 | 70 | 8.0 | 8.8 |

[a]GC/MS.
()negatively screened sample

TABLE A-2 (CONT.)

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Liver | 14 | | X | | | 190 | 19 | 10 |
| | 15 | | | 11 | 47 | 640 | 197 | 3.2 |
| | 31 | | X | | | 400 | 166 | 2.4 |
| | 45 | | X | | | [b] | - | - |
| | 49 | | X | | | 40 | 10 | 4.0 |
| | 53 | | X | | | 980 | 279 | 3.5 |
| | 53 | | X | | | 860 | 49 | 17.5 |
| | 88 | | | 23 | 61 | 540 | 96 | 5.6 |
| | 88 | | X | | | 290 | 70 | 4.1 |
| | 140 | | X | | | 370 | 29 | 12.8 |
| | 140 | | X | | | 170 | 32 | 5.3 |
| | 143[a] | | X | (63) | (119) | 10 | 1.0 | 10 |
| | 285 | | | 78 | 235 | 210 | 294 | 0.7 |

[a]GC/MS.

[b]Liver tissue not further analyzed.

TABLE A-3

ANALYTICAL SUMMARY - HAKE

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 13 | 10 | | 2.5 | 6.1 | 70 | 25 | 2.8 |
| | 14[a] | 6 | | 2.0 | 5.0 | 90 | 16 | 5.6 |
| | 41 | 2 | X | | | 10 | 2 | 5.0 |
| | 53 | 1 | X | | | [b] | - | - |
| Liver | 13[a] | | | 55 | 190 | 40 | 16 | 2.5 |
| | 14[a] | | | 38 | 127 | 60 | 9 | 6.7 |
| | 41 | | X | | | 410 | 128 | 3.2 |
| | 53 | | X | | | 290 | 2 | 145 |

[a]GC/MS.

[b]Muscle tissue not further analyzed.

TABLE A-4

ANALYTICAL SUMMARY - LIZARDFISH

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | POSITIVE | | | | |
| | | | NEGATIVE | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 33 | 10 | X | | | 10 | 2 | 5.0 |
| | 46 | 16 | | 3.0 | 6.0 | 10 | 13 | 0.8 |
| | 48 | 6 | X | | | 10 | 2 | 5.0 |
| | 49 | 15 | X | | | 10 | 3 | 3.3 |
| | 53 | 6 | X | | | 20 | 46 | 0.4 |
| | 54 | 4 | X | | | 10 | 6 | 1.7 |
| | 130[a] | 13 | | 4.2 | 9.4 | 30 | 5 | 6.0 |
| | 143 | 13 | | 5.2 | 12 | 36 | 24 | 1.5 |
| | 101 | 12 | X | | | 40 | 10 | 4.0 |
| | 101 | 32 | X | | | 20 | ND | - |
| | 256 | 13 | | 3.8 | 5.9 | 80 | 18 | 4.4 |

[a]GC/MS.

TABLE A-4 (CONT.)

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | POSITIVE | | | | |
| | | | NEGATIVE | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Liver | 33 | | X | | | 100 | 59 | 1.7 |
| | 46 | | | 17 | 34 | 420 | 51 | 8.2 |
| | 48 | | X | | | 120 | 274 | 0.4 |
| | 49 | | X | | | 100 | 180 | 0.6 |
| | 53 | | X | | | 130 | 81 | 1.6 |
| | 54 | | X | | | 310 | 331 | 0.9 |
| | 130[a] | | | 278 | 1,140 | 450 | 111 | 4.1 |
| | 143 | | | 146 | 480 | 320 | 353 | 0.9 |
| | 101 | | X | | | 230 | 76 | 3.0 |
| | 101 | | X | | | 350 | 1,170 | 0.3 |
| | 256 | | | 74 | 170 | 2,130 | 367 | 5.8 |

[a]GC/MS.

TABLE A-5

ANALYTICAL SUMMARY - PORGY

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 54[a] | 26 | X | (3.8) | (5.2) | 20 | 2 | 10 |
| | 72 | 32 | | 1.8 | 5.8 | 180 | 12 | 15.0 |
| | 101 | 21 | | 1.6 | 4.3 | 120 | 25 | 4.8 |
| | 256 | 22 | | 3.0 | 5.8 | 36 | 12 | 3.0 |
| Liver | 54 | | X | | | 30 | 10 | 3.0 |
| | 72 | | | 39 | 146 | 420 | 35 | 12.0 |
| | 101 | | | 37 | 103 | 350 | 53 | 6.6 |
| | 256 | | X | | | 130 | 19 | 6.8 |

[a]GC/MS.
()negatively screened sample

TABLE A-6

ANALYTICAL SUMMARY - SCAD

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 42 | 19 | X | | | 20 | 14 | 1.4 |
| | 43 | 25 | X | (5.7) | (5.7) | 41 | 6 | 6.8 |
| | 48 | 21 | X | | | 20 | ND | - |
| | 49 | 23 | X | | | 50 | 2 | 25 |
| | 107[a] | 2 | | 8.3 | 29 | 60 | 6 | 10 |
| | 140[a] | 15 | | 6.0 | 12 | 20 | 1 | 20 |
| | 101 | 3 | X | | | 30 | 14 | 2.1 |
| | 117 | 11 | | 2.3 | 4.1 | 30 | 32 | 0.9 |
| Liver | 42 | | X | | | 60 | 19 | 3.2 |
| | 43 | | X | (51) | (93) | 190 | 26 | 7.3 |
| | 48 | | X | | | 60 | 9 | 6.7 |
| | 49 | | X | | | 70 | 44 | 1.6 |
| | 107 | | X | | | 300 | 20 | 15 |
| | 140 | | | 208 | 486 | 300 | 53 | 5.7 |
| | 101 | | X | | | 11,400 | 1,000 | 11.4 |
| | 117 | | | 68 | 136 | 220 | 65 | 3.4 |

[a]GC/MS.
()negatively screened sample

TABLE A-7

ANALYTICAL SUMMARY - SNAPPER

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 42 | 17 | X | | | 10 | 12 | 0.8 |
| | 43 | 9 | X | (4.0) | (4.8) | 30 | 3 | 10 |
| | 46 | 2 | X | | | 20 | 9 | 2.2 |
| | 48 | 14 | X | | | 10 | 2 | 5 |
| | 88 | 13 | X | | | 20 | 6 | 3.3 |
| | 140 | 10 | | 3.6 | 7.0 | 40 | 30 | 1.3 |
| | 117 | 10 | | 3.1 | 5.7 | 40 | 24 | 1.7 |
| Liver | 42 | | X | | | 70 | 20 | 3.5 |
| | 43 | | X | | | 90 | 18 | 5.0 |
| | 46 | | X | | | 220 | 40 | 5.5 |
| | 48 | | X | | | b | - | - |
| | 88 | | X | (41) | (95) | 1,420 | 135 | 10.5 |
| | 140 | | | 73 | 182 | 250 | 189 | 1.3 |
| | 117 | | | 50 | 122 | 290 | 288 | 1.0 |

[b]Liver not further analyzed.
()negatively screened sample

TABLE A-8

ANALYTICAL SUMMARY - SPOT

| TISSUE TYPE | STATION | NO. OF INDIVIDUALS | PETROLEUM HYDROCARBONS (µg/g [ppm]) | | | CHLORINATED HYDROCARBONS (ng/g [ppb]) | | |
|---|---|---|---|---|---|---|---|---|
| | | | NEGATIVE | POSITIVE | | | | |
| | | | | RESOLVED | TOTAL | PCB | ΣDDT | PCB/ΣDDT |
| Muscle | 15a | 26 | | 3.5 | 38 | 10 | 2 | 5.0 |
| | 30 | 13 | X | | | 10 | 7 | 1.4 |
| | 31 | 14 | X | (2.7) | (4.0) | 170 | 20 | 8.5 |
| | 41 | 2 | X | | | 160 | 92 | 1.7 |
| | 43 | 2 | X | | | 30 | 5 | 6.0 |
| | 49 | 14 | X | | | 60 | 2 | 30 |
| | 107[a] | 10 | | 3.3 | 22 | 30 | 4 | 7.5 |
| Liver | 15[a] | | | 133 | 885 | 350 | 59 | 5.9 |
| | 30 | | X | | | 50 | 2 | 25 |
| | 31 | | | 258 | 551 | 510 | 50 | 10.2 |
| | 41 | | X | | | 1,230 | 267 | 4.6 |
| | 43 | | X | | | 240 | 48 | 5.0 |
| | 49 | | | 25 | 82 | 280 | 37 | 7.6 |
| | 107 | | | 14 | 59 | 100 | 6 | 17 |

[a]GC/MS.
()negatively screened sample