TABLE 2-26

COMPARISON OF SELECTED AROMATIC COMPOUND CONCENTRATIONS WITH HISTORICAL DATA

(Concentration: $ng \cdot g^{-1}$)

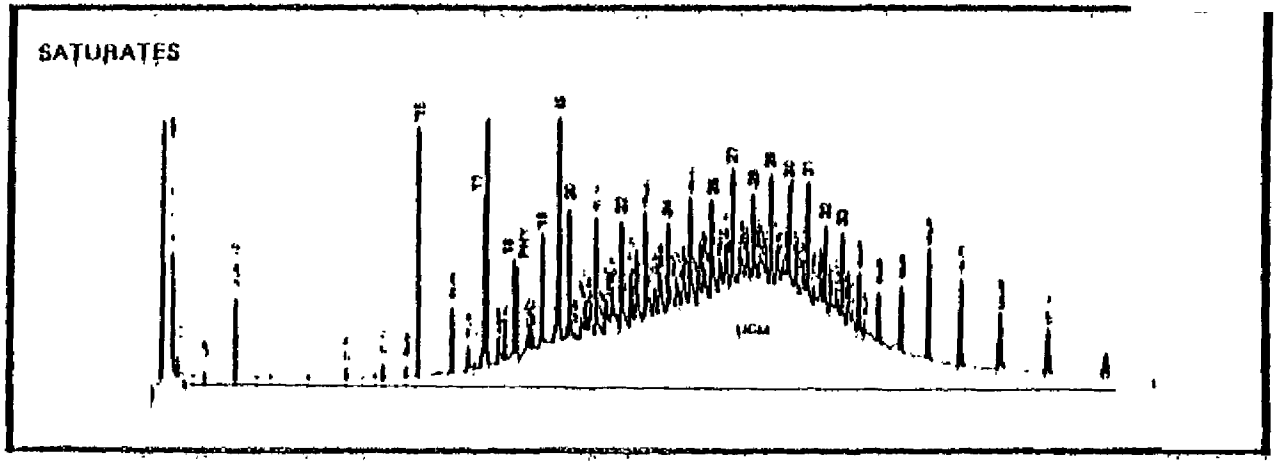
COMPOUND	STOCS STATION	1976 (1977) STUDY[a]	1979 STUDY	1980 STUDY
2-Methyl Naphthalene	M36	2.3	-	1.3
	S52	0.8 (Tr)	0.4	0.2
	S53	0.6	-	0.9
	N38	0.4	-	1.5
1-Methyl Naphthalene	M36	2.0	-	0.5
	S52	0.5 (Tr)	0.2	0.1
	S53	Tr	-	0.2
	N38	Tr	ND	ND
Fluoranthene	M36	7.0	-	17
	S52	3.2 (1.8)	1.3	1.6
	S53	1.9	-	7.3
	N38	4.9	15	4.9
Pyrene	M36	5.8	-	18.0
	S52	4.8 (2.9)	2.1	2.4
	S53	6.3	-	10
	N38	7.9	27	8.9
Chrysene	M36	5.5	-	11.0
	S52	4.9 (1.6)	1.0	0.1
	S53	2.0	-	3.7
	N38	5.3	9.6	2.4

[a]Laseter and Overton, undated.

TABLE 2-27

SORBENT PAD HYDROCARBON DATA SUMMARY

STATION	f_1 ($\mu g \cdot g^{-1}$)	f_2 ($\mu g \cdot g^{-1}$)	PRIS/ $n \cdot C_{17}$	PHY/ $n \cdot C_{18}$	PRIS/ PHY	CPI	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT	SOURCE
S27	177	108	2.8	1.5	2.4	1.2	7.30	0.66	0.26	oil
S15	165	107	3.5	2.1	7.2	2.5	-	-	-	oil/background
N26	125	79	1.7	0.5	5.1	8.0	-	-	-	background
N27	442	354	0.6	0.9	2.2	1.9	-	-	-	background/oil
S46	225	159	3.1	1.0	5.5	1.3	4.59	0.78	0.80	oil
M25	215	410	1.0	0.8	1.1	1.9	-	0.57	0.40	background/oil
M26	98	164	1.0	0.6	2.1	1.7	-	-	-	background
N20	140	74	5.0	0.5	9.4	1.8	-	-	-	background/oil
S21	86	64	0.8	0.9	3.1	1.3	2.83	0.62	0.74	oil
Range of Isaac I oils							.72-1.32	.41-.66	.49-.80	



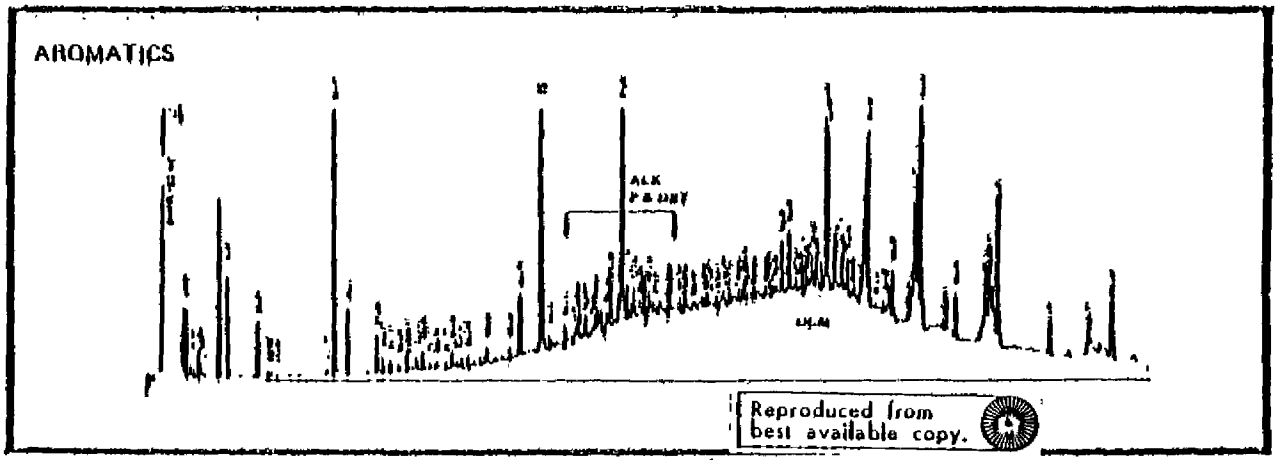
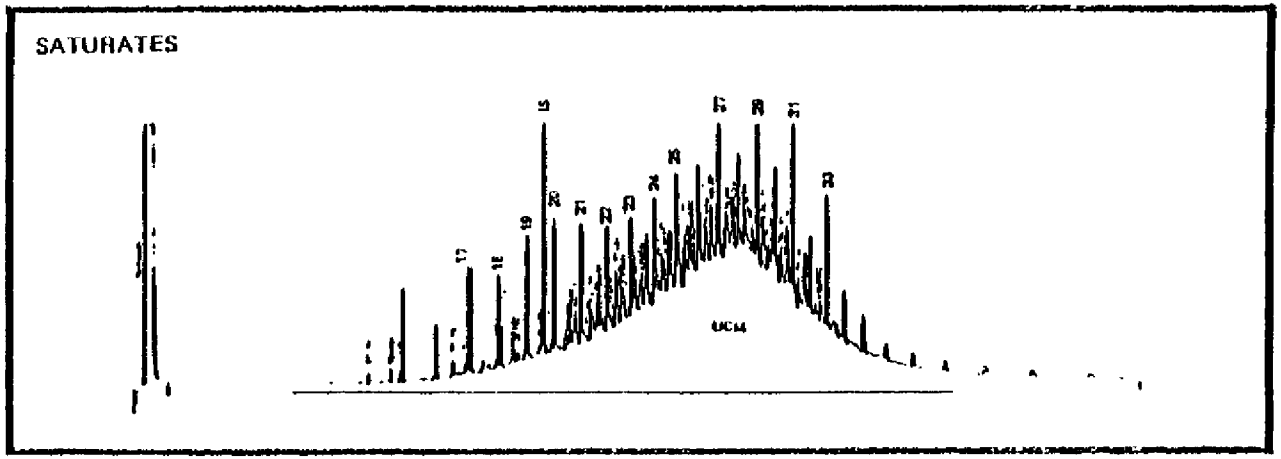


Figure 2—42. FSCGC Traces of Sorbent Pad Hydrocarbons—Station S46.



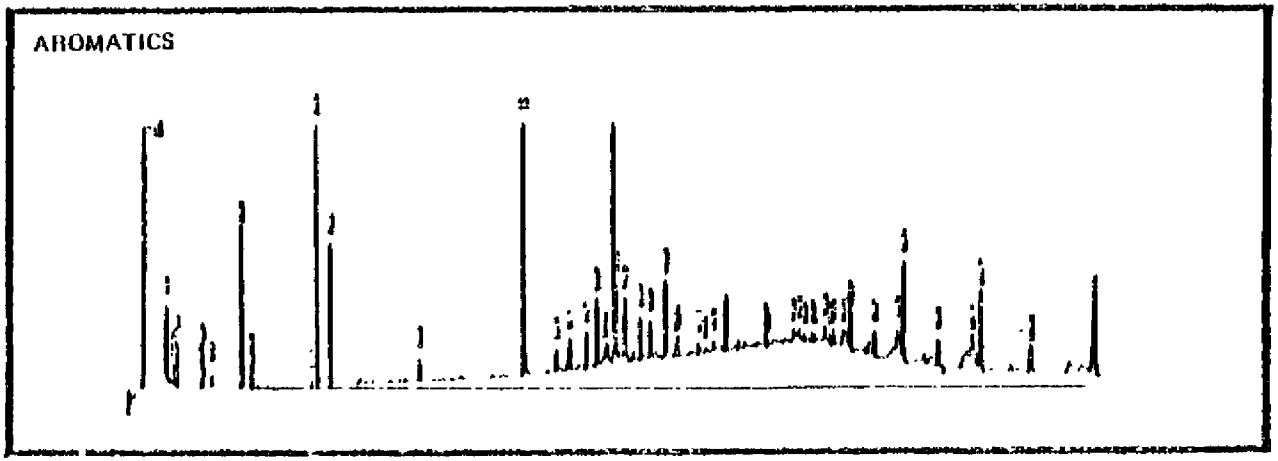


Figure 2–43. FSCGC Traces of Hydrocarbons in Sorbent Pad (Station M–26).

consistently exhibit oil residues in the FSCGC traces (e.g., Figure 2-42) while the "N" and "M" stations contain largely background hydrocarbon material. When n-alkane comparisons are used to match sorbent pad residues with Ixtoc oil (Figure 2-44), the mixed source inputs become apparent and the use of n-alkane source matching becomes difficult. Even in samples largely dominated by oil residues (see next section) the presence of disproportionate quantities of n-C_{15} and n-C_{17}, both of phytoplanktonic origin, and n-C_{25} through n-C_{29}, of terrigenous plant origin, overprints the petroleum fingerprint. By tradition, the use of pristane and phytane ratios, to each other and to the adjacent n-alkanes (Table 2-14) have been used to distinguish oil from biogenic material. While all four components are present in oil, initially with PRIS/PHY ~1 and PRIS/n-C_{17} and PHY/n-C_{18} both less than 1, inputs of n-C_{17} from phytoplankton and pristane from zooplankton obscure the ability of these ratios to establish the presence of weathered oil residues.

2.3.3.2 Aromatic Hydrocarbons by GC/MS

The examination of four representative sorbent pad samples by GC/MS yielded the aromatic data presented in Appendix 9.1. Levels of individual Group I (two and three rings) aromatics ranged from nd to 140 $ng \cdot g^{-1}$ with maximum concentrations for the alkylated phenanthrene and dibenzothiophene compounds. Sourcing of these apparent petrogenic residues by ratios of these alkylated compounds indicates a strong relation to Ixtoc oil in the C_2 and C_3 ratios (Table 2-27). Stable isotope data on the S21 and S46 samples confirm this probable identification.

Group II PAH levels in these samples are low (1-30 $ng \cdot g^{-1}$) indicating that the aromatic assemblage is not strongly petrogenic. Rather, taken together, the high Group I levels and low Group II levels indicate a strongly petrogenic source of the aromatic assemblage in the sorbent pad samples. This is quite a different result from that found for the surface sediments where the aromatic assemblage was found to be highly pyrogenic.

2.3.4 Petroleum Hydrocarbons in Macroepifauna (Penaeid Shrimp)

Seventy samples of penaeid shrimp obtained from the 1979 Western Gulf, Longhorn IV and dockside shrimp collections and forty-one 1980 samples were considered in this study (see Figure 2-5 and Table 2-4 for locations).

2.3.4.1 UV/F Screening

Solvent extracts of all samples were analyzed by synchronous and fixed-excitation UV/F to enable a selection of samples to be made for subsequent more detailed analysis. Several experiments were performed prior to the analysis of the entire sample set. These experiments explored: (1) the quenching of the spectral bands by the tissue extract matrix (high lipid content), (2) the threshold detection level of oil based on incremental oil additions to shrimp UV/F background, and (3) the additivity of spectral response.

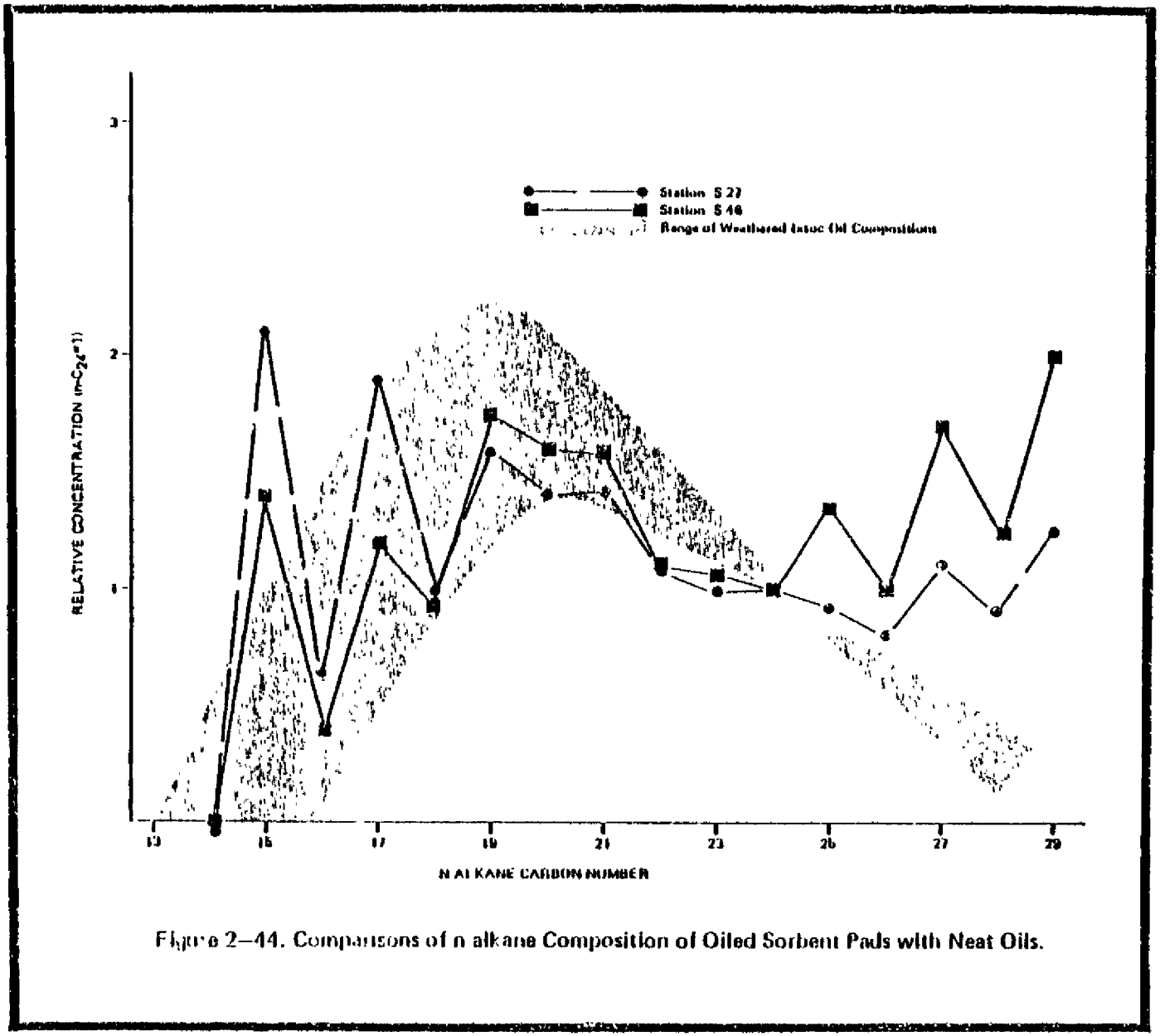


Figure 2–44. Comparisons of n alkane Composition of Oiled Sorbent Pads with Neat Oils.

This latter experiment proved most revealing. Incremental additions of Ixtoc oil were made to a shrimp extract to examine the qualitative changes in the synchronous UV/F spectra so as to facilitate the detection of Ixtoc oil residues in the tissues and to examine the additivity of this response. These incremental additions are shown in Figure 2-45. While the UV/F response of the two wavelengths monitored (312 and 350 nm) was additive, a substantial 312-nm background was observed. This 312-nm background had been noted before (Boehm and Fiest, 1980c) in shrimp from the Texas-Louisiana coasts, probably owing to a combination of biolipid fluorescence and background PHC levels. Although the additivity is apparent (Table 2-28), the incremental (nonquenched) response becomes roughly linear only at concentrations greater than ∿1.0 ppm. For a 20-µg (∿2 ppm) addition of oil to the observed background, the expected change, based on the sum of the "oil alone" UV/F trace and the "background" trace, was in reasonable agreement (11% @ 312 nm; 48% @ 350 nm) with that actually observed (Table 2-28).

Perhaps the more important part of this experiment was the appearance of the significant and variable 312-nm background. The 350-nm band is not a significant feature of the nonoiled shrimp, making the 350-nm band (and/or the 400-410 band if it appeared) more diagnostic for oil than consideration of the two-ringed (312-nm) band alone (Figure 2-45). The oil addition series reveals the significance of the 350-nm band. Also of importance at higher concentration levels is the nonquenched ratio of 312/350 nm. Background ratios were roughly 5-10 while the ratio in oil was 2. Thus as concentrations of oil increased to the 2-ppm level (Table 2-28) this ratio approaches the oil value. A summary of this ratio in the shrimp samples examined appears in Figure 2-46, which shows that by this criterion many shrimp samples exhibited the potential for recent oil additions. Many of those samples were chosen for additional analytical work by virtue of this ratio value and by virtue of a prominent 350-nm band (e.g., Figure 2-47).

Shrimp "No. 2 fuel oil equivalent" concentrations were calculated based on the 312-nm response in the synchronous mode and for both the 312- and 350-nm bands in the fixed excitation mode. Good agreement was achieved by comparison of synchronous and fixed-excitation quantification although, as previously stated, these values do not represent quantities of "oil" due to considerable 312-nm background.

2.3.4.2 FSCGC Analysis

Forty-six samples were chosen for further (FSCGC) analysis based on the UV/F results outlined above. Giam et al. (1980) have previously discussed the historical Penaeus aztecus data from the STOCS program and have noted seasonal hydrocarbon (n-alkane) compositional variations summarized in Figure 2-48. Based on their evaluation of the historical data, several data treatments seemed most appropriate for consideration in the mid- and post-spill samples, namely: (1) consideration of FSCGC compositional information (n-alkanes) and (2) aromatic hydrocarbon data (see next section 2.3.4.3), (both in view of the composition of the potential source materials).

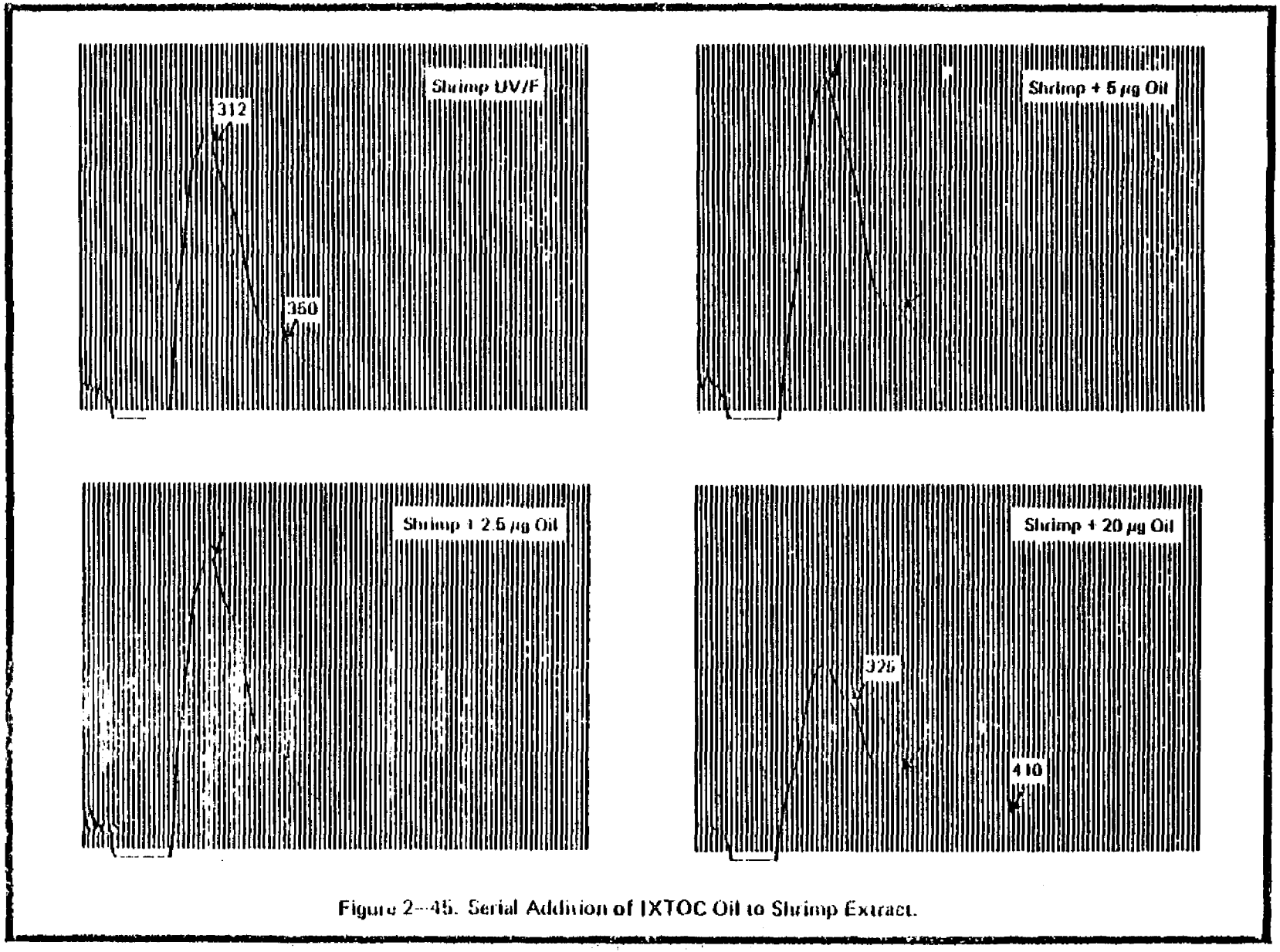


Figure 2--45. Serial Addition of IXTOC Oil to Shrimp Extract.

TABLE 2-28

UV/F RESPONSES TO INCREMENTAL ADDITIONS OF OIL TO A TISSUE EXTRACT

	WAVELENGTH (nm)			OIL ADDED (g)	APPROXIMATE OIL CONCENTRATION ($g \cdot g^{-1}$ dry weight)
	312	350	312/350		
1)	45.5	7.5	6.1	0	0
2)	47.5	8.5	5.9	1.0	0.1
3)	51	11.5	4.4	2.5	0.25
4)	59	15	3.9	5.0	0.5
5)	75	22	3.4	10.0	1.0
6)	103	53	1.9	20.0	2.0
1)	45.5	7.5		Background	
	64.4	28.1		Expected incremental change (20 g addition) (from oil UV/F trace)	
6-1)	57.5	45.5		Observed change	

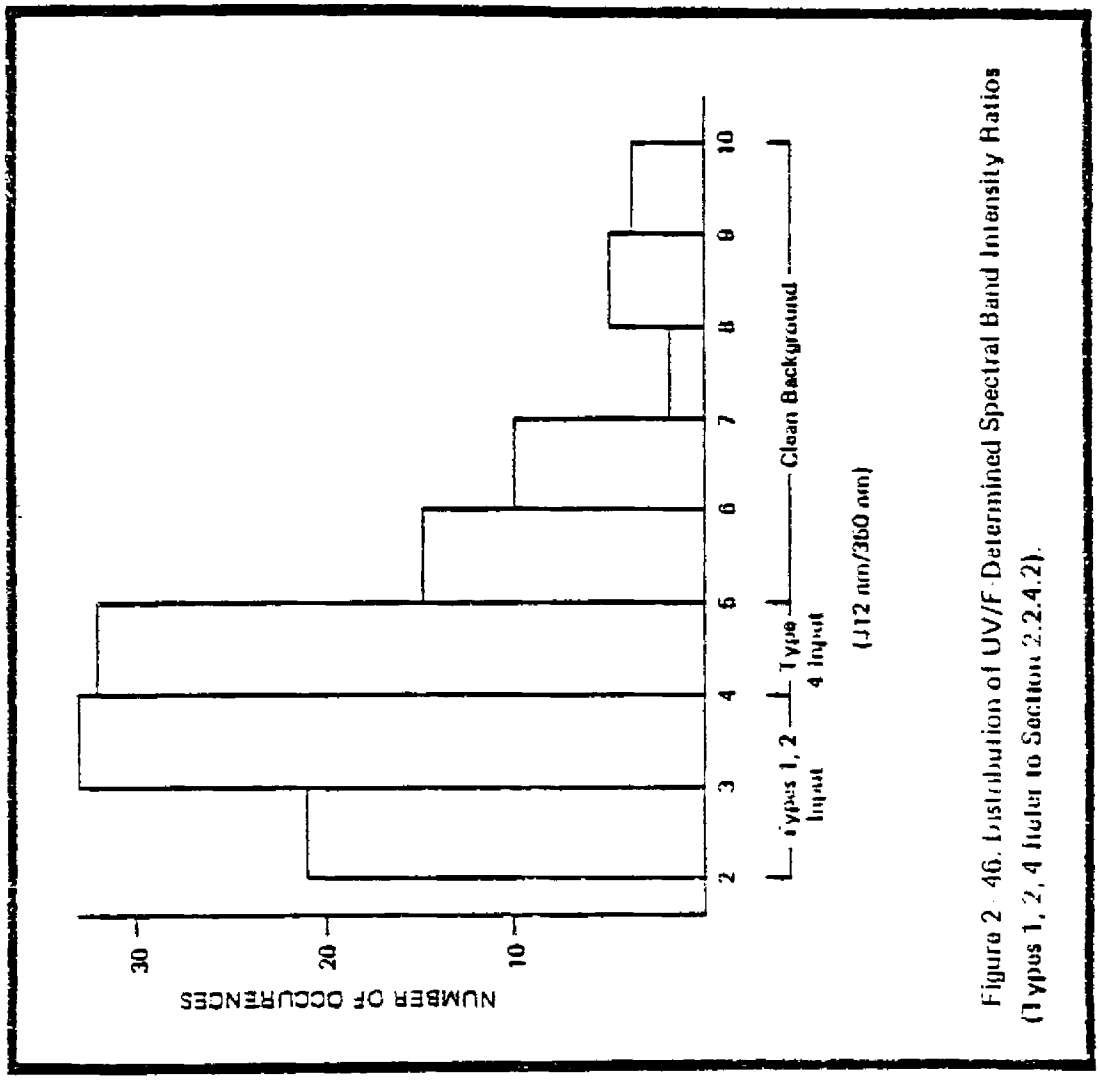


Figure 2 46. Distribution of UV/F-Determined Spectral Band Intensity Ratios (Types 1, 2, 4 Refer to Section 2.2.4.2).

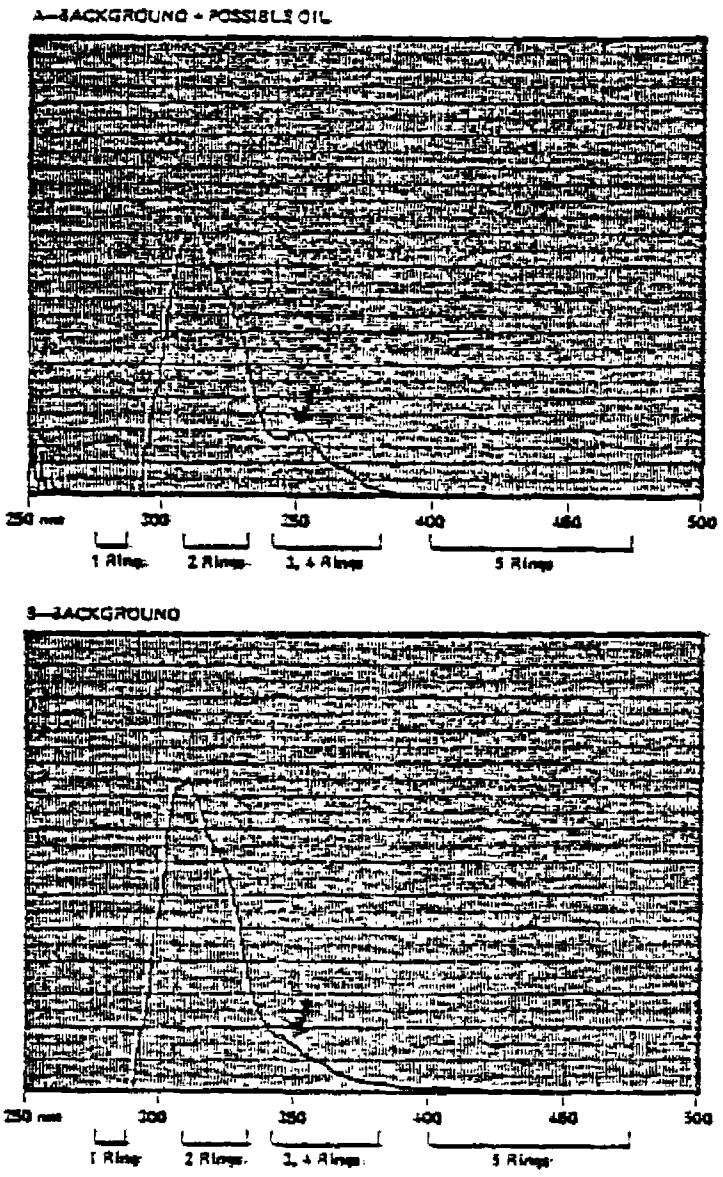


Figure 2—47. Representative Synchronous UV/F Spectra of Shrimp.

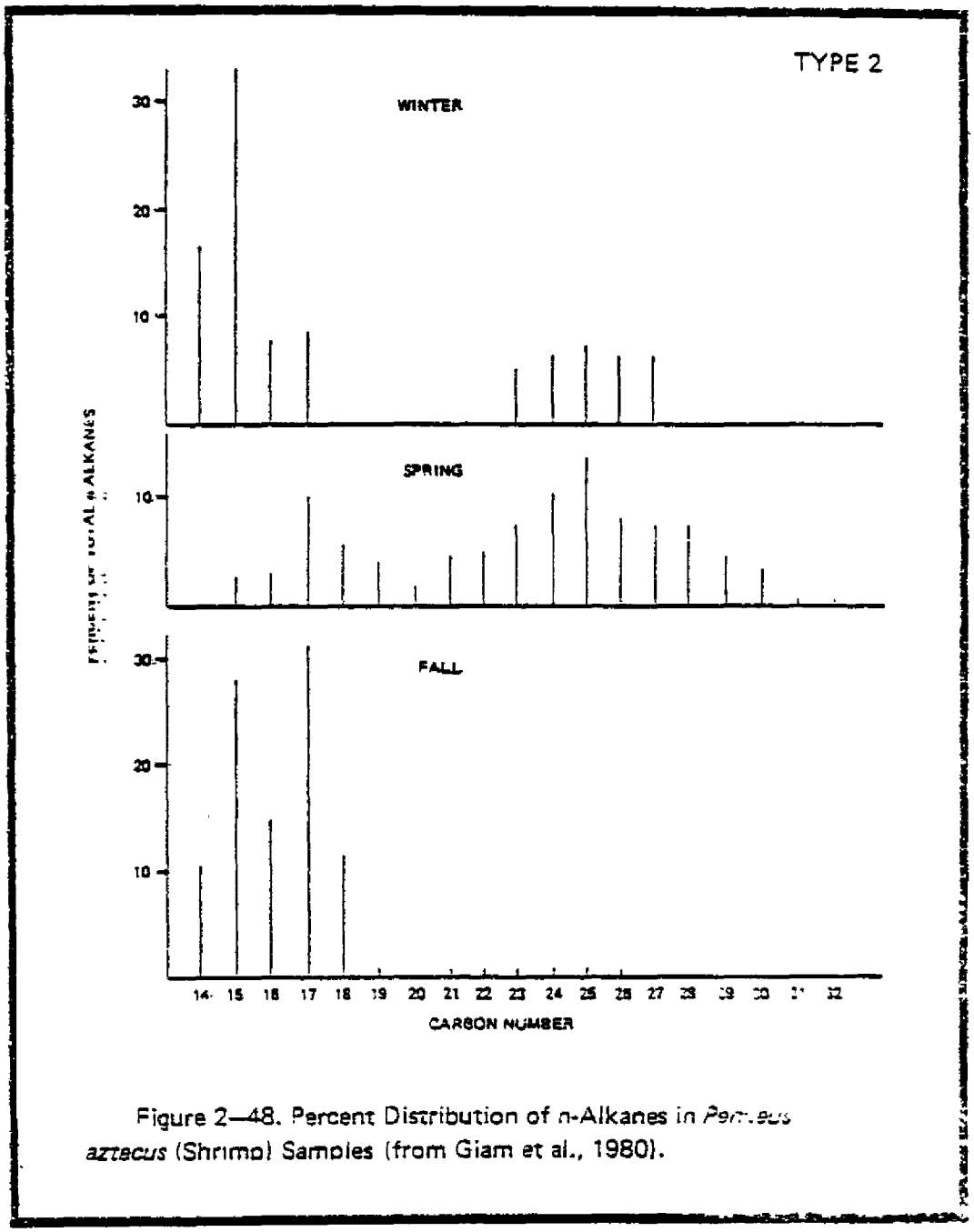


Figure 2—48. Percent Distribution of n-Alkanes in *Penaeus aztecus* (Shrimp) Samples (from Giam et al., 1980).

Parameters involving alkanes and alkane/isoprenoid relationships were considered to be inappropriate as diagnostic tools due to both the considerable biogenic hydrocarbon inputs to the shrimp (e.g., pristane, n-C_{17}, n-C_{15}) as well as the differential uptake of oil by marine organisms (Neff et al., 1976; Boehm et al., 1982) and pre-uptake weathering that one expects in this type of spill. Nevertheless if one compares the historical data on saturated hydrocarbons with mid- and post-spill data (Table 2-29), some differences in the parameter means are revealed. However, due to the wide variability in these data and due to the fact that almost none of the alkane variability can be ascribed to petroleum additions, we view this comparison of saturated hydrocarbon parameters to be inappropriate for this assessment study.

Four distinctly different compositional patterns were observed (Figures 2-48 and 2-49) based on the saturated hydrocarbon composition. A summary of the total hydrocarbon data, by FSCGC type, appears in Table 2-30. Detailed data appear in Appendix 9.1. Type 1 (Figure 2-50) is characteristic of a fresh oil and was found in one sample from 1979 (Sector W07, July 1979, in the northern part of the study area). This sample predates the observable movement of Ixtoc oil into the study area. The n-alkane pattern does not match Ixtoc oil nor does the aromatic hydrocarbon data (see next section). Several Type 2 samples associated with weathered oil (Figure 2-51) were found in 1979 from sector W06 (August and November 1979) and from sector W05 (December 1979). These residues, which are characterized by a prominent mid-boiling UCM and an overriding series of branched/isoprenoid hydrocarbons, are characteristic of assimilated petroleum residues subjected to weathering and differential uptake (Boehm et al., 1982). No definitive source can be associated with these residues from FSCGC data. Chromatogram types 3 and 4 are similar to those observed by Giam et al. (1980) (see Figure 2-49). Type 3 is characterized by a prominent series of high molecular weight n-alkanes usually without a significant underlying UCM. This distribution is commonly encountered in coastal animal populations (Boehm, 1980) and although its precise source is not known (though believed to be related to microbial activity), it is not petroleum-related. A similar pattern was ascribed to a seasonal dietary influence (Spring) by Giam et al. (1980).

Type 4 distributions have been observed by Giam et al. (1980) in winter samples from the STOCS area. It includes samples having bimodal n-alkane distributions usually over a minor-to-moderate bimodal UCM, with or without a slight odd-carbon predominance in the n-C_{25} to n-C_{33} region (i.e., of sedimentary origin). These samples are influenced by a chronic petroleum input or inputs, but are not related to any recent oil spills.

Most of the recent petroleum inputs seen in the samples result in PHC concentrations between 15 and 40 ppm compared with background values from 0.2 to 8 ppm. The incidence of recent PHC additions, including fresh and weathered oils, is confined to the northern part of the study area (sectors W05 [n=1], W06 [n=3], and W07 [n=1] in 1979, and sectors W07 [n=2], X10 [n=1], Z03 [n=1], and Y04 [n=1] in 1980). Note that the W sectors (Figure 2-6) are well outside of the STOCS study area (X03,04; Y03,04, Z03,04). Thus the W sectors and X10 sector could very well have been influenced by other

TABLE 2-29

COMPARISON OF SATURATED HYDROCARBON PARAMETERS IN PENAEID SHRIMP SAMPLES (Penaeus aztecus)

		TOTAL ALKANES (µg/l)	SUM OF ALKANES (%)			PRISTANE / PHYTANE	PRISTANE / C_{17}	PHYTANE / C_{18}	CPI_{14-20}	CPI_{20-32}
			C_{14} - C_{18}	C_{19} - C_{24}	C_{25} - C_{32}					
1975-1977	STOCS	0.14±0.28 (48)	39.7±7.2 (34)	9.1±12.7 (34)	51.1±39.1 (34)	44.0±58.0 (2)	2.0±1.7 (17)	0.2±0.1 (2)	1.6±0.6 (5)	6.8±10.1 (22)
Damage Assessment	1979	1.09±2.62 (15)	34.46±22.21 (15)	23.76±19.49 (15)	39.78±23.01 (15)	4.15±2.26 (11)	1.25±0.89 (15)	0.38±0.39 (15)	1.27±0.72 (15)	1.57±0.46 (15)
	1980	0.86±1.51 (17)	29.8±19.9 (17)	41.3±29.0 (17)	28.9±17.7 (17)	4.06±2.26 (9)	0.76±0.45 (16)	0.23±0.32 (16)	1.36±0.56 (17)	2.6±3.14 (17)

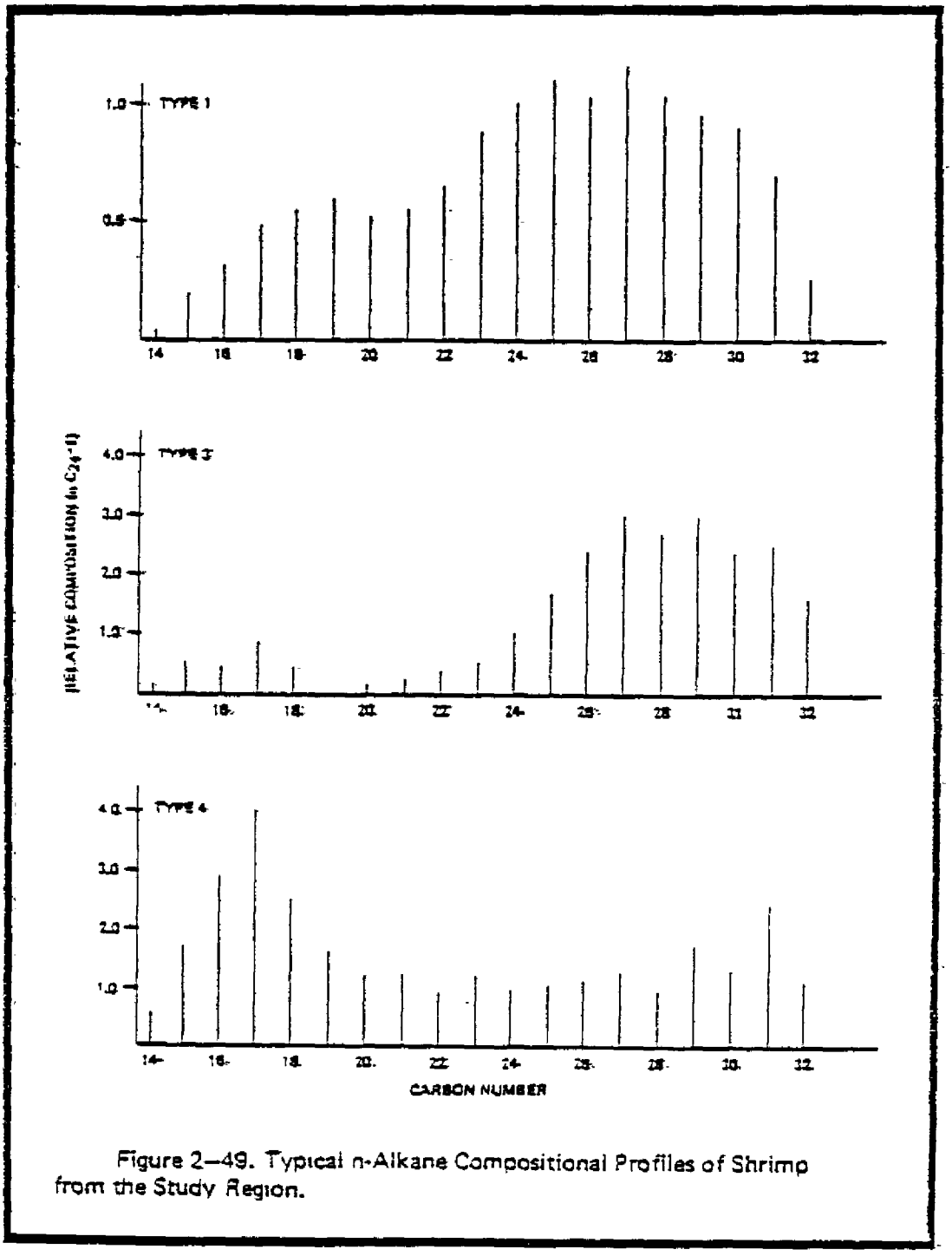


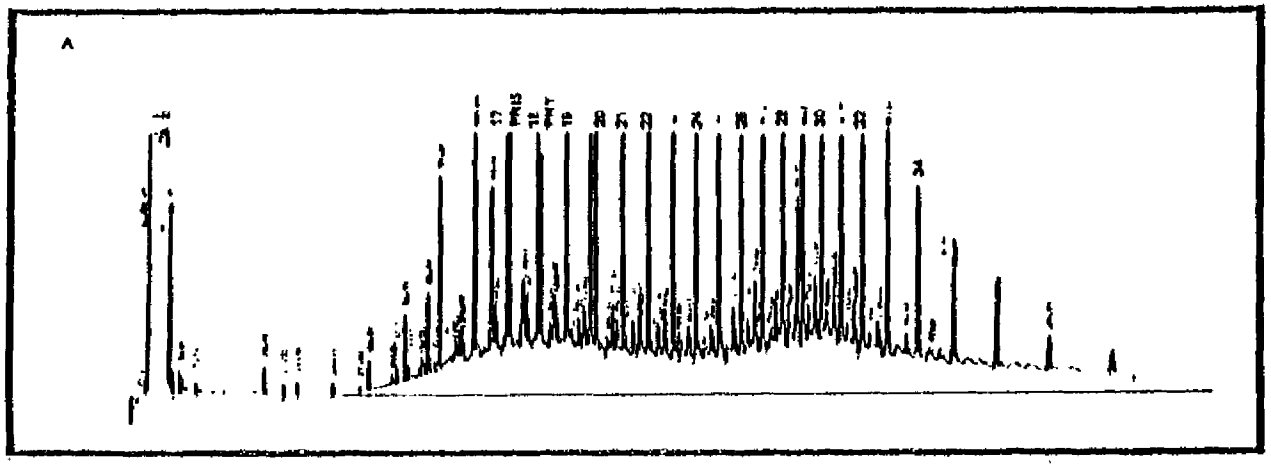
Figure 2–49. Typical n-Alkane Compositional Profiles of Shrimp from the Study Region.

TABLE 2-30

SUMMARY OF QUANTITATIVE PENAEUS AZTECUS DATA BY FSCGC TYPE
($\mu g \cdot g^{-1}$)

COMPOSITIONAL TYPE[a]	YEAR	
	1979	1980
1	37 (n=1)	none
2	16.1 ± 5.1 (n=5)	20.9 ± 8.7 (n=4)
3	5.9 ± 1.6 (n=4)	7.5 ± 5.5 (n=4)
4	4.4 ± 2.0 (n=6)	2.0 ± 0.9 (n=14)
5 (clean)	2.2 ± 1.3 (n=4)	2.0 ± 1.3 (n=4)

[a]Type refers to Figure 2-49.



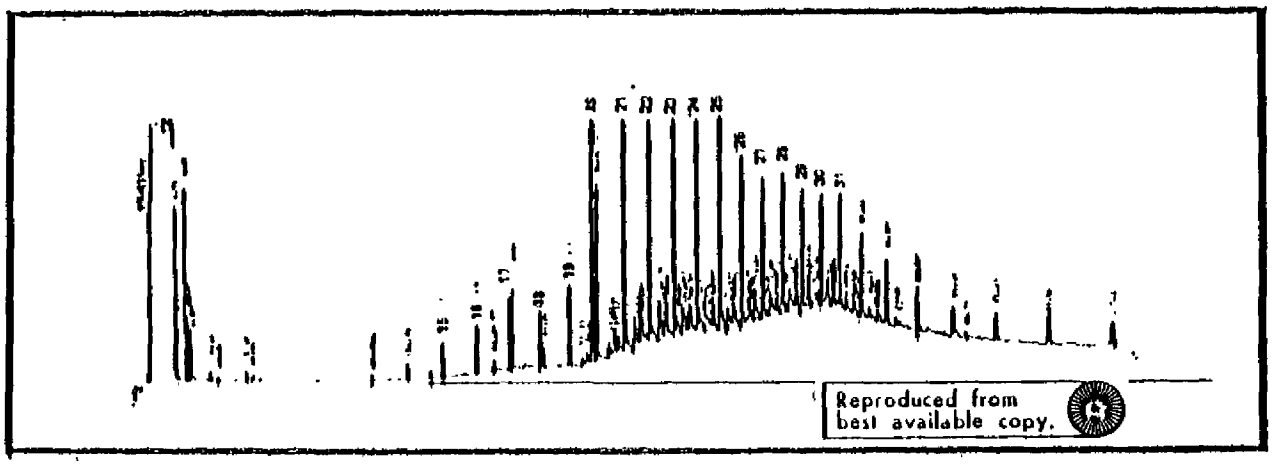


Figure 2–60. Type I FSCGC Saturated Hydrocarbon Traces (Oil) of Shrimp Samples (A–Station W–07; August 1979, B–Station S–15; December 1980).

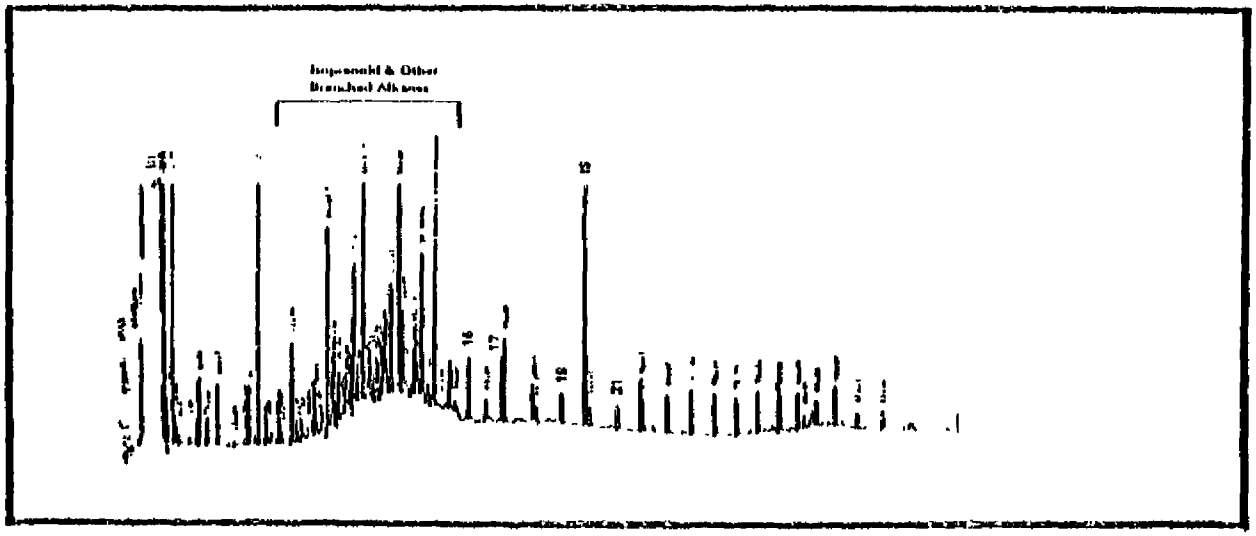


Figure 2–51. Type 2 FSCGC Saturated Hydrocarbon Pattern (Weathered Oil) in Shrimp.

inputs to the region, including industrial activities near Galveston and the Mississippi River inputs, as well as a myriad of point sources (e.g., drill rigs, tanker discharges, etc.). As will be demonstrated in the next section, only one of the aromatic hydrocarbon residue assemblages can be ascribed to Ixtoc spill input and not to Burmah Agate oil.

Additionally, if only the samples from the STOCS region are considered, most (15 of 20 = 75%) of the 1980 samples analyzed by FSCGC fall into Type 4 composition, as do nearly all (6 of 7 = 86%) of the 1979 FSCGC samples. Thus the Giam et al. (1980) winter GC-type (Figure 2-48) was the predominant FSCGC type observed here. However, Giam et al. (1980) report little if any UCM material, while many of the 1979 and 1980 Type 4 samples contained unimodal or bimodal UCM. We believe these UCM distributions are chronic additions to the biota rather than spill related, as we have seen these UCM distributions in tissues from the Western Gulf previously (Boehm and Fiest, 1980c). PAH compounds (see next section) accompany these chronic pollutant UCMs and account for many of the UV/F 312/350 ratios in the 4 to 5 aromatic ring range previously noted.

2.3.4.3 Aromatic Hydrocarbons in Shrimp by GC/MS

To assess the impact of the Ixtoc I incident on the Texas Gulf Coast marine ecosystem, the aromatic hydrocarbon content of seventeen shrimp samples was determined by GC/MS. Although aromatic hydrocarbons are known chemical carcinogens, their effects on marine ecosystems are presently unknown (King, 1977). Hence, any data pertaining to the aromatic content of marine organisms exposed to a petroleum contaminated environment are of importance. The petrogenic (Group I) aromatic and pyrogenic PAH (Group II) content of the shrimp analyzed in this study is presented in Appendix 9.1 and summarized in Table 2-31.

Most samples contained only minimal amounts of four- and five-ringed aromatic compounds (pyrogenic PAH). Fluoranthene and pyrene were the only prevalent aromatics, usually present at concentrations of 1 to 5 $ng \cdot g^{-1}$. In only two samples (one at Station W05 and one at Station W06) were all the Group II aromatics present.

The petrogenic aromatic content of shrimp was used to determine whether petroleum hydrocarbons had been incorporated into this part of the Texas OCS ecosystem. In particular, alkyl phenanthrene-alkyl dibenzothiophene ratios were again examined to define the level of contamination and a possible source, as was done for sediments (see Section 2.3.3.3). Using this criterion, eleven of seventeen shrimp samples were found to have significant quantities of petrogenic aromatics which would suggest petroleum hydrocarbon uptake. A summary of the alkylated phenanthrene-dibenzothiophene ratios is presented in Table 2-31. The ratios for the Ixtoc I oil and Burmah Agate oil are presented elsewhere (see Section 2.3.1.3). In only one shrimp sample do the ratios compare favorably to those of the Ixtoc I oil (Station W06, September 1970). For all other samples the ratios, although generally similar to each other,

TABLE 2-31

ALKYL PHENANTHRENE-ALKYL DIBENZOTHIOPHENE RATIOS IN SHRIMP SAMPLES

STATION	DATE	TOTAL AROMATICS ($ng \cdot g^{-1}$) GROUP 1	GROUP 2	C_1P/C_1DBT	C_1P/C_2DBT	C_3P/C_3DBT
W05	DEC. 1979	380	55	3.15	2.86	5.78
W06	AUG. 1979	70	2	not enough aromatics present to calculate		
W06	SEPT. 1979	110	7	1.18	0.48	0.34
W06	NOV. 1979	710	55	3.00	3.03	4.51
W06	NOV. 1979	200	6	3.95	—	—
W07	SEPT. 1979	220	14	3.02	2.91	4.68
W07	OCT. 1979	450	2	3.12	3.06	2.00
W07	JAN. 1980	10	2	not enough aromatics present to calculate		
Y04	OCT. 1979	120	9	4.06	3.00	1.88
Y04	NOV. 1979	130	8	not enough aromatics present to calculate		
X07	SEPT. 1979	10	ND	not enough aromatics present to calculate		
G03	DEC. 1980	20	2	not enough aromatics present to calculate		
S46	DEC. 1980	50	3	7.64	5.11	—
M04	DEC. 1980	10	1	not enough aromatics present to calculate		
M05	DEC. 1980	20	1	4.33	1.50	—
M24	DEC. 1980	50	5	6.10	2.43	1.33
M36	DEC. 1980	50	5	6.25	2.17	2.67

are quite different than either the Ixtoc I or Burmah Agate ratios. This may be explained as being the result of preferential uptake of certain aromatics, preferential metabolism of certain aromatics, or uptake of petroleum from an unknown source. Petrogenic aromatics are in the shrimp tissues prior to either spill impact (Station W06, August 1979) and the elevated P/DBT ratios are characteristic of the shrimp prior to the Burmah Agate spill.

The petrogenic aromatics are far more abundant in the shrimp than the pyrogenic PAH, thus completely decoupling the shrimp from the surface sediment hydrocarbon composition, but perhaps not from the petroleum-aromatic-rich material found in the water column in the sorbent pad samples.

2.3.5 Quality Control Program

To ensure the quality of data generated during an analytical program of this type, two forms of quality control were employed: internal and external. The former involves: (1) monitoring the levels of the compounds of concern (PHC and PAH) in procedural blanks; (2) the daily calibration of instruments, calculation of response factors, and monitoring of column performance; and (3) routine analysis of sample splits (duplicates). The results of these duplicate analyses are presented in Tables 2-32 and 2-33. Additionally, "blind" spiked samples (PAH) were analyzed by the GC/MS facility periodically during this study and results always fell within ±12 percent of actual value.

This program was unique in that the successful completion of five major "external" quality control elements were required prior to and during the program. Three intercalibration exercises using actual environmental samples (one performed in duplicate) and an on-site working evaluation were undertaken. The pertinent results of the Duwamish II sediment, the Texas IRM, and the EPA Megamussel (twice during the program) are shown in Tables 2-34, 2-35, and 2-36. The first successful analysis of the Duwamish II sediment sample for a complex array of PAH and alkane components was accomplished by ERCO under this contract. The source of the discrepancies in the Texas IRM sample are not known, although sample heterogeneity as well as errors in either of the two participating laboratories are possibilities. The other results show excellent agreement between the two participating laboratories (NOAA/NAF and ERCO) and with other premier laboratories, and are better than previously accomplished in other published studies (e.g., MacLeod et al., 1981; Hilpert et al., 1978; Wise et al., 1980; Farrington, 1978).

Additionally, a team of analytical chemists from J&W Scientific and NOAA/NAF were dispatched to ERCO to evaluate our performance and to exchange information. The results of this visit plus those of the intercalibration exercises indicated that "state-of-the-art" analyses were being employed successfully in this program (Calder, 1981).

TABLE 2-32

PRECISION OF SATURATED HYDROCARBON MEASUREMENTS

Compound (Parameter) ($\mu g \cdot g^{-1}$)	STATION G03			STATION M26			STATION S04		
	1	2	3	1	2	3	1	2	3
Total alkanes	0.26	0.37	0.36	0.01	0.02	0.03	1.5	1.2	0.9
Sum low	0.01	0.01	0.01	0.003	0.003	0.006	0.003	0.002	0.001
Sum mid	0.06	0.05	0.03	0.002	0.006	0.003	0.14	0.18	0.10
Sum high	0.19	0.31	0.32	0.005	0.011	0.016	1.4	1.0	0.8
n-C_{17}	0.005	0.004	0.005	0.001	0.001	0.001	0.003	0.008	nd
Pristane	0.005	0.004	0.004	nd	nd	nd	nd	0.003	nd
n-C_{29}	0.031	0.035	0.033	0.001	0.001	0.002	0.11	0.16	0.12
n-C_{29}	0.039	0.092	0.087	0.002	0.003	0.004	0.17	0.24	0.23
Total hydrocarbons	6.9	9.4	9.4	1.1 0	0.28	0.75	10.4	15.0	13.6

TABLE 2-33

PRECISION OF AROMATIC HYDROCARBON MEASUREMENTS (STATION S04)

COMPOUND	CONCENTRATION ($ng \cdot g^{-1}$)	
	Rep 1	Rep 2
Naphthalene	ND	1.1
2-methyl naphthalene	ND	0.4
1-methyl naphthalene	ND	0.1
Phenanthrene	2.4	2.8
Methyl phenanthrene	5.2	6.3
Dimethyl naphthalene	3.3	5.8
Fluoranthene	9.5	12.2
Pyrene	16.1	18.5
Benzanthracene	5.6	7.2
Chrysene	8.6	7.8
Benzofluoranthene	28.1	21.9
Benzo(e)pyrene	10.9	9.1
Benzo(a)pyrene	8.4	6.4
Perylene	37.1	31.1