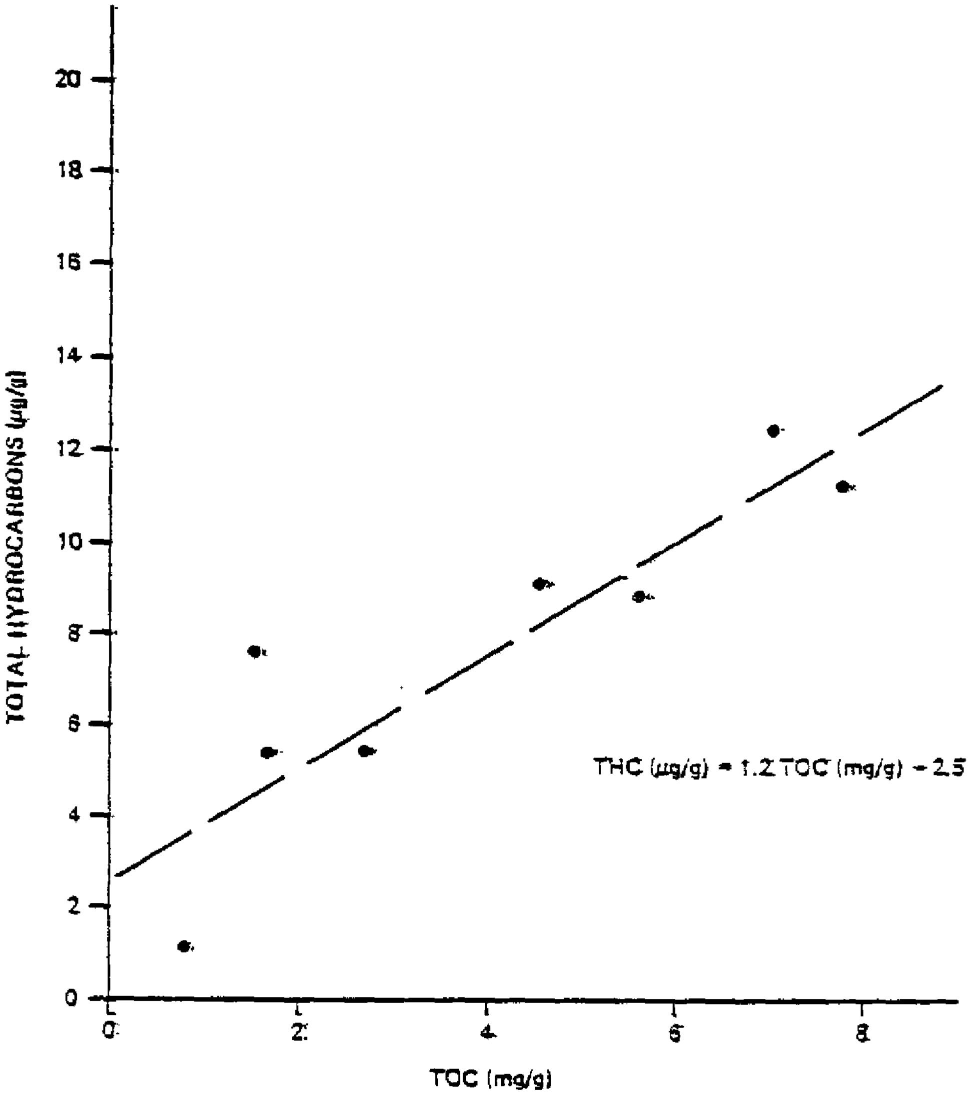

Figure 2–28. Total Hydrocarbon Concentrations in Sediments as a Function of TOC (1979).

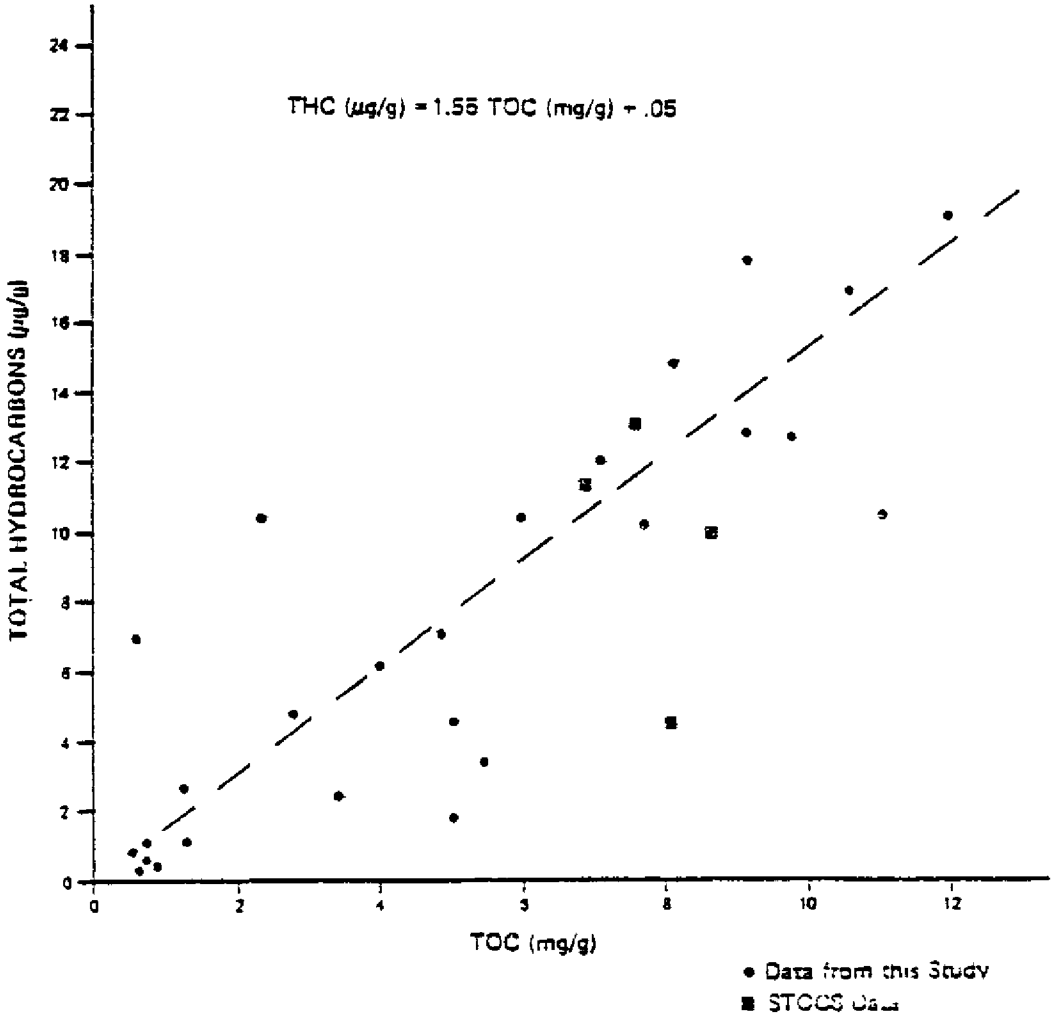

Figure 2–29. Total Hydrocarbon Concentrations in Sediments as a Function of TOC (1980).

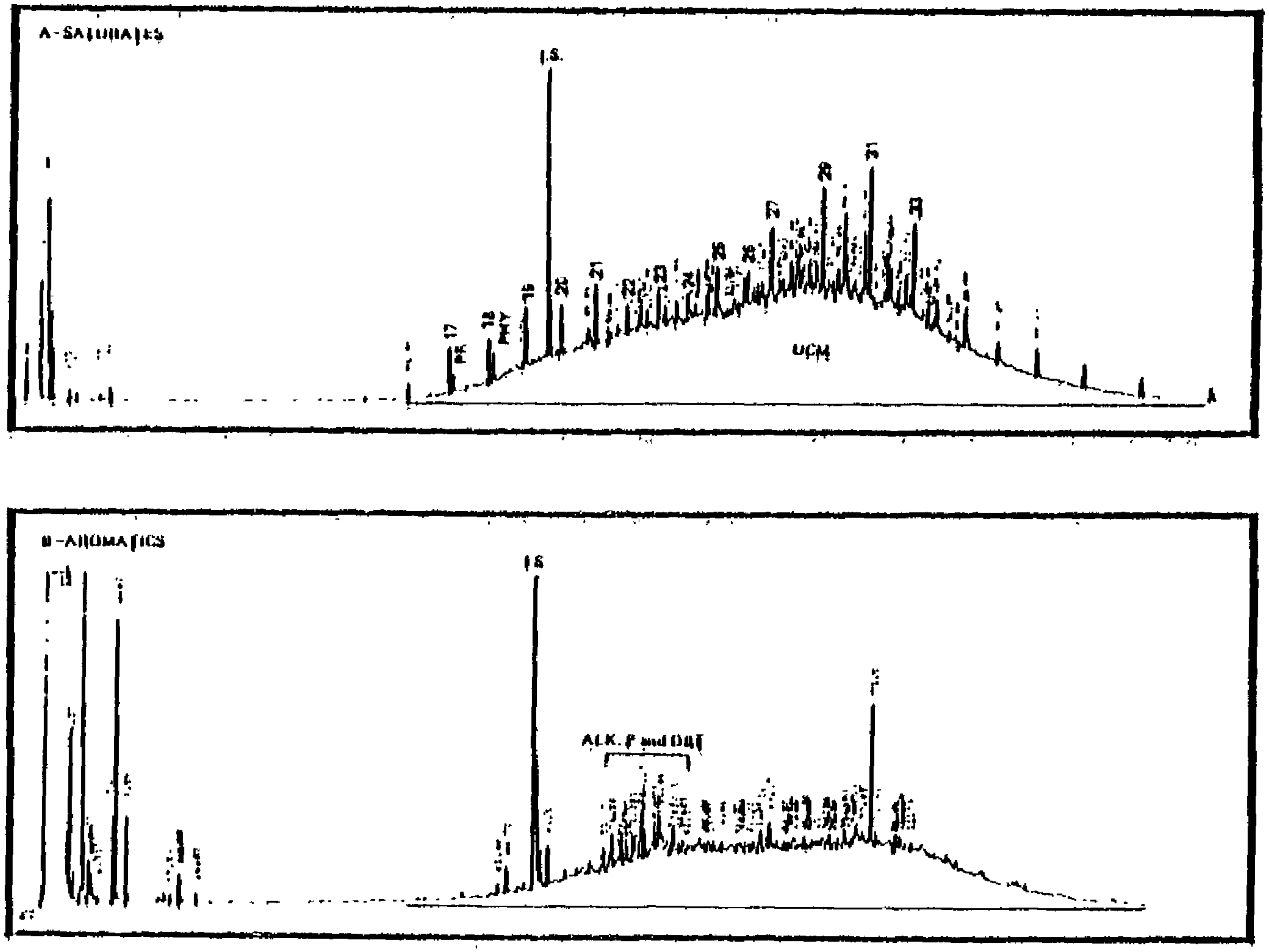

Figure 2–30. FSCGC Traces of Port Aransas Sediment Hydrocarbons.

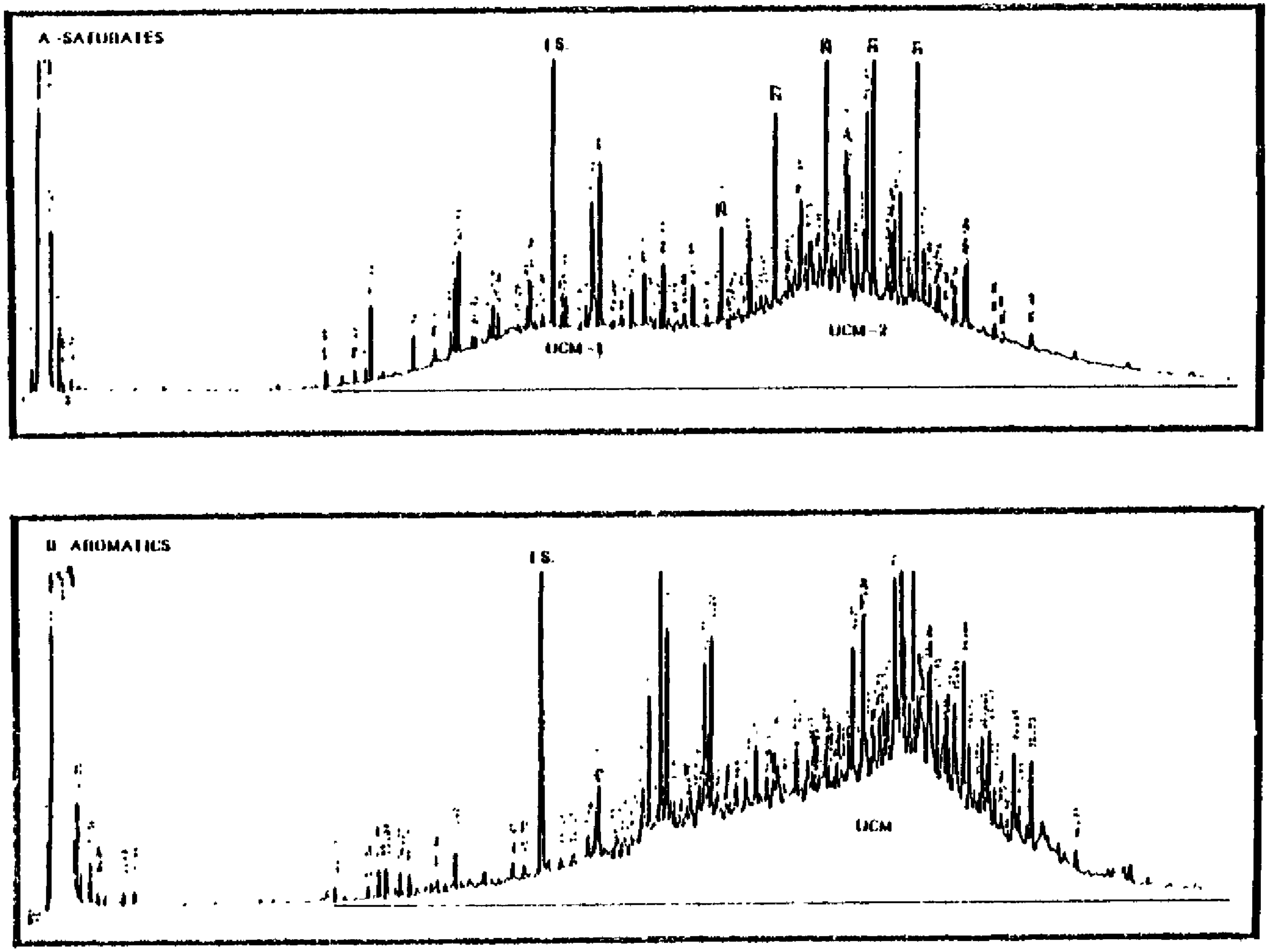

Figure 2-31 Typical South Texas OCS Hydrocarbon FSCGC Traces, (Station N—38, I—1, 1979).

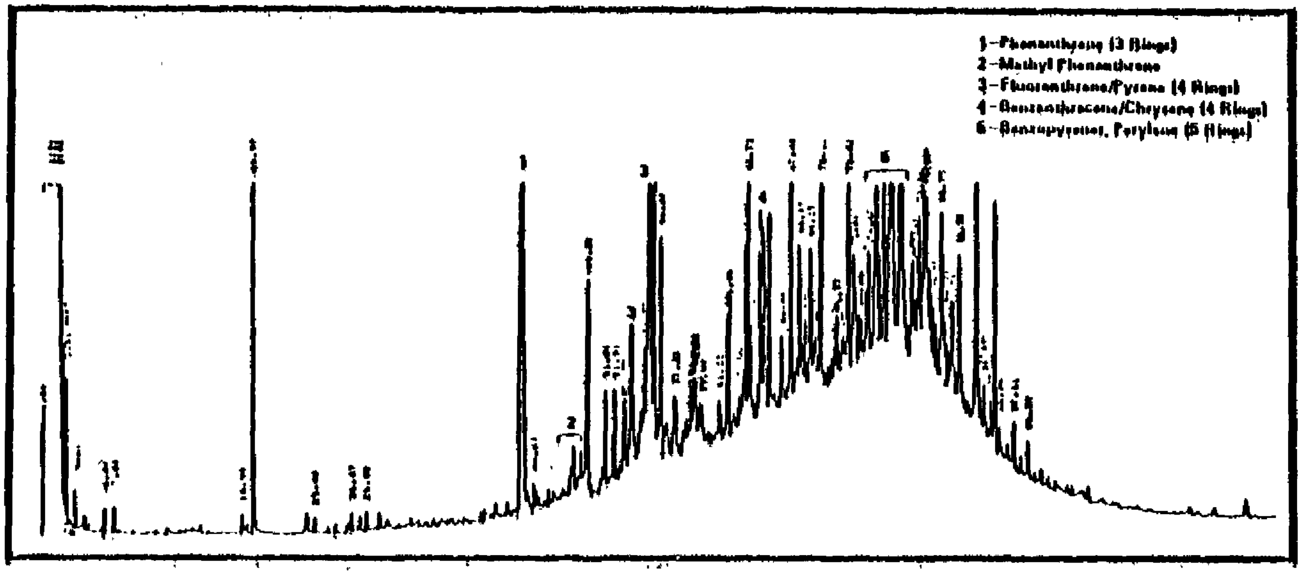

Figure 2–32. Capillary GC Trace of Aromatic Hydrocarbons in Texas OCS Intercalibration Sediment (Station II–2, M–36), Showing Pyrogenic PAH Inputs (See Section 2.3.2.3).

of petroleum-related hydrocarbons not attributable to either spill in question were detected by GC/MS analysis, as presented in Section 2.3.2.3.) Comparison of 1979 and 1980 FSCGC compositional data with the STOCS benchmark data (packed column GC) can be made through comparison of any or all of the parameter information derived from the FSCGC traces (see Table 2-14). However, most of these parameters rely heavily on the supposition that if oil were to impact the system, its n-alkane signature would be more or less intact. This is not the case as no obvious petrogenic n-alkane overprint of the sediment FSCGC traces was observed even in those samples in which petroleum was later detected (albeit not related to *Ixtoc*) through GC/MS analysis (see Section 2.3.2.3).

Nevertheless, as an academic exercise we have extracted data comparing n-alkane abundances in various boiling ranges (Tables 2-20, 2-21 and 2-22) and in total (Table 2-23), from available STOCS benchmark data and from the spill assessment data. Comparison of the n-alkane data through the various boiling ranges indicates that not only were a wide range of values found in the benchmark samples, but that almost always the 1979 and 1980 values fall within these ranges. The carbon preference index (CPI) and odd/even predominance (OEP) index, both measures of the contribution of petroleum alkanes to the background in the n-C_{25} to n-C_{32} region, are both consistently greater than 2.0 in all offshore sediment samples. CPI and OEP indices for petrogenic material are ∿1.0 indicating no odd or even carbon predominance. Thus CPI and OEP do not yield any indication of petroleum additions to the background, already dominated by terrigenous odd-carbon-number, high-molecular-weight alkanes.

Several typical saturated and aromatic hydrocarbon FSCGC traces are shown in Figures 2-30, 2-31, and 2-32. The saturated hydrocarbon traces reveal two major features: (1) a broad unresolved hump or unresolved complex mixture (UCM), and (2) a distribution of resolved components in the n-C_{22} to n-C_{32} range dominated by odd carbon chain n-alkanes, cyclic alkanes (naphthenes) and branched alkanes. The UCM is a characteristic chromatographic feature of weathered petroleum, urban air particulates, stormwater runoff, and the like (Farrington et al., 1976; Boehm, 1981), and is also a prominent feature observed in coastal marine sediments from many geographic regions. Its presence in sediments cannot be attributed to a particular spill without other evidence. Thus, in this case chronic anthropogenic inputs rather than recent spill inputs are responsible for the observed UCM. The odd chain n-alkanes are derived from waxy coatings on vascular land plants (Farrington et al., 1976).

The aromatic FSCGC traces also include unsaturated (olefinic) material as well. The trace shown in Figure 2-32 is typical of Gulf sediments (Gearing et al., 1976; Boehm and Fiest, 1980c) and consists mainly of (1) a UCM distribution related to chronic hydrocarbon inputs; (2) resolved olefinic material; and (3) polynuclear aromatic hydrocarbons (PAH) from a combustion (pyrogenic) source rather than a petroleum source (see Section 2.3.2.3 for a detailed discussion of PAH). Again, no traces of recent petroleum inputs can be seen. However, as will be seen, any recent low-level (ppb) inputs of petroleum will be detectable and identifiable in the aromatic fraction only

TABLE 2-20

SUMMARY OF "SUM LO" N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS[a]

	STOCS BASELINE DATA							DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{x}$(all)	RANGE (all)	1979	1980	CHANGE[b]
M35	0.0	0.008	-	0.119	0.014	0.035	0.0 -0.119	0.041	0.013	N
M36	-	0.010	-	0.088	0.012	0.037	0.01 -0.09	0.056	0.028	N
M37	0.048	0.130	-	0.089	-	0.089	0.05 -0.13	0.037	0.027	N
N38	0.006	0.037	-	0.089	0.027	0.040	0.01 -0.09	0.068	0	N
N39	0.016	0.0	-	0.014	0.009	0.010	0.0 -0.02	0.033	0.021	N
N40	0.013	0.002	-	0.026	-	0.014	0.002-0.03	0.041	0.023	N
S49	-	0.032	0.133	-	0.015	0.060	0.02 -0.13	0.034	0.032	N
S50	0.013	0.011	0.031	-	-	0.018	0.01 -0.03	0.021	0	N
S51	-	0.063	0.068	-	-	0.065	0.06 -0.06	0.064	0.020	N
S52	0.024	0.053	0.006	-	0.085	0.042	0.01 -0.08	0.038	0.045	N
S53	0.010	0.009	0.027	-	-	0.015	0.01 -0.03	0.039	0.015	N
S54	0.0	0.006	0.059	-	-	0.022	0.0 -0.06	0.089	0.045	N

[a] SUM LO = sum n-alkanes from n-C_{14} to n-C_{18}.

[b] Based on comparison of 1979, 1980 values with STOCS range of values; N indicates no change.

TABLE 2-21

SUMMARY OF "SUM MID" N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS[a]

	STOCS BASELINE DATA							DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{x}$(all)	RANGE(all)	1979	1980	CHANGE[b]
M35	0.06	0.03	-	0.09	0.04	0.055	0.03-0.09	0.290	0.050	(+)
M36	-	0.10	-	0.10	0.01	0.072	0.01-0.10	0.079	0.054	(N)
M37	0.02	0.52	-	0.11	-	0.286	0.02-0.52	0.151	0.115	(N)
N38	0.06	0.01	-	0.14	0.04	0.071	0.01-0.14	0.143	0.141	(N)
N39	0.13	0.002	-	0.02	0.01	0.017	0.002-0.13	0.094	0.078	(N)
N40	0.06	0.01	-	0.08	-	0.051	0.01-0.08	0.050	0.056	(N)
S49	-	0.04	0.26	-	0.07	0.124	0.04-0.26	0.029	0.158	(N)
S50	0.08	0.01	0.03	-	-	0.041	0.01-0.08	0.015	0.064	(N)
S51	-	0.14	0.15	-	-	0.146	0.14-0.15	0.103	0.093	(N)
S52	0.09	0.06	0.01	-	0.04	0.055	0.01-0.09	0.052	0.080	(N)
S53	0.05	0.02	0.02	-	-	0.031	0.02-0.05	0.047	0.034	(N)
S54	0.07	0.01	0.08	-	-	0.055	0.01-0.08	0.081	0.167	(+)

[a] SUM MID = sum n-alkanes from n-C_{19} to n-C_{24}.

[b] Based on comparison of 1979, 1980 values with STOCS range of values; (+) indicates value which falls higher than twice upper STOCS value, and N indicates no change.

TABLE 2-22

SUMMARY OF "SUM HI" N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS[a]

	STOCS BASELINE DATA							DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{x}$(all)	RANGE(all)	1979	1980	CHANGE[b]
M35	0.77	0.05	–	0.50	0.47	0.44	0.05–0.77	0.757	0.270	N
M36	–	0.20	–	0.45	0.16	0.27	0.16–0.45	0.482	0.193	N
M37	0.64	0.73	–	0.57	–	0.65	0.57–0.73	0.637	0.442	N
N38	0.39	0.07	–	0.80	0.07	0.42	0.07–0.80	0.455	0.633	N
N39	0.51	0.01	–	0.15	0.08	0.22	0.01–0.51	0.476	0.384	N
N40	0.09	0.03	–	0.29	–	0.14	0.03–0.29	0.194	0.338	N
S49	–	0.56	1.2	–	1.2	0.99	0.6 –1.2	0.022	0.590	N
S50	0.12	0.01	0.10	–	–	0.08	0.01–0.12	0.023	0.474	N
S51	–	0.92	0.97	–	–	0.93	0.92–0.97	0.457	0.377	N
S52	0.36	0.13	0.03	–	0.35	0.17	0.03–0.36	0.107	0.258	N
S53	0.13	0.02	0.08	–	–	0.08	0.02–0.13	0.155	0.112	N
S54	0.14	0.04	0.43	–	–	0.2	0.04–0.43	0.306	0.462	N

[a] SUM HI = sum n-alkanes from n-C_{25} to n-C_{32}.

[b] Based on comparison of 1979, 1980 values with STOCS range of values; (+) indicates value which falls higher than twice upper STOCS value, and N indicates no change.

TABLE 2-23

SUMMARY OF TOTAL N-ALKANE DATA ($ng \cdot g^{-1}$) AT 12 PRIMARY STATIONS

	STOCS BASELINE DATA								DAMAGE ASSESSMENT		
STATION	2/76	6/76	9/76	10/76	1977	$\bar{X}$(all)	RANGE (all)	$\bar{X}^a$	1979	1980	CHANGE[b]
M35	0.83	0.09	–	0.70	0.53	0.54	0.09–0.83	0.77	1.090	0.337	N
M36	–	0.31	–	0.64	0.19	0.38	0.19–0.64	0.64	0.617	0.274	N
M37	0.92	1.4	–	0.77	–	1.02	0.77–1.4	0.85	0.826	0.584	N
N38	0.46	0.18	–	1.0	0.14	0.45	0.18–1.0	0.53	0.666	0.774	N
N39	0.66	0.01	–	0.18	0.10	0.24	0.01–0.66	0.31	0.603	0.483	N
N40	0.16	0.04	–	0.39	–	0.20	0.04–0.39	0.27	0.285	0.417	N
S49	–	0.64	1.6	–	1.3	1.2	0.64–1.6	–	0.085	0.781	N
S50	0.22	0.03	0.16	–	–	0.14	0.03–0.22	0.22	0.060	0.538	N
S51	–	1.1	1.2	–	–	1.2	1.1 –1.2	–	0.623	0.490	N
S52	0.47	0.24	0.05	–	0.47	0.31	0.05–0.47	0.47	0.197	0.383	N
S53	0.19	0.45	0.13	–	–	0.26	0.13–0.45	0.19	0.242	0.161	N
S54	0.21	0.05	0.57	–	–	0.27	0.05–0.57	0.21	0.475	0.674	N

[a] Fall/winter values only.

[b] Based on comparison of 1979, 1980 values with STOCS range of values; (+) indicates value which falls higher than twice upper STOCS value, and N indicates no change.

through GC/MS investigation. On a grosser level (ppm), although petroleum parameters cannot be seen in the sediment through evaluation of the FSCGC traces, the combustion-related PAH are quite evident in most samples.

The collection of six sediment samples from the Burmah Agate site were analyzed similarly by FSCGC. Hydrocarbon concentrations in these samples ($f_1 + f_2$) ranged from 8 to 75 ppm ($\bar{x} = 29.5 \pm 24.5$). The samples, which were not subjected to UV/F, contained large quantities of UCM material which account for most of the differences in concentration between these samples and those of the main study area. The total n-alkane concentrations in these samples fell well within those from further south, thus again illustrating the lack of usefulness of n-alkanes in spill assessments of this type. Three of the Burmah Agate sediment samples do contain aromatic residues of the Burmah Agate oil, as will be seen in the next section (Stations G02, G04 and G05). Stable isotope measurements (Section Three) confirm the presence of Burmah Agate oil residues in one of the samples and give ambiguous results on the others. Representative FSCGC traces (Figure 2-33) of a sediment sample from station G02 illustrates the large UCM (bimodal) in both f_1 and f_2 fractions but gives little indication of the source of the PHC residues.

Five samples taken further offshore in deeper water (see Figure 2-6) from the 1979 Antelope collection were analyzed by FSCGC as well. These samples ranged in PHC concentration from 8 to 15 ppm. No recent oil additions are evident from the FSCGC traces. An interesting group of compounds appears later in the f_2 GC trace. These are believed to be sterenes and triterpenes of a biogenic origin, although further GC/MS confirmation is needed.

The series of Researcher/Pierce samples from south of the study area (Figure 2-6) examined by FSCGC revealed levels of hydrocarbons in the 3-25 ppm range with concentrations increasing offshore. However, no relation to any spillage event was discerned in the FSCGC traces; normal geochemical inputs are responsible for the observed distributions.

2.3.2.3 Aromatic Hydrocarbons by GC/MS

All polynuclear aromatic hydrocarbons that were detected in the Ixtoc I oils were again sought in the sediment extracts. These data are presented in detail in Appendix 9.1. The concentrations of individual petroleum aromatic compounds (two and three rings) are most often in the low ppb range while the pyrogenic PAH are present at higher concentrations. Similar information is not available from the STOCS program.

In most of the sediment samples, significant amounts of alkylated phenanthrenes and alkylated dibenzothiophenes were not found. As these compounds are the major diagnostic molecular markers of crude oils, this finding rules out widespread Ixtoc I or Burmah Agate petrolem inputs to the sediments. In some cases only the mono- and dialkylated phenanthrenes and

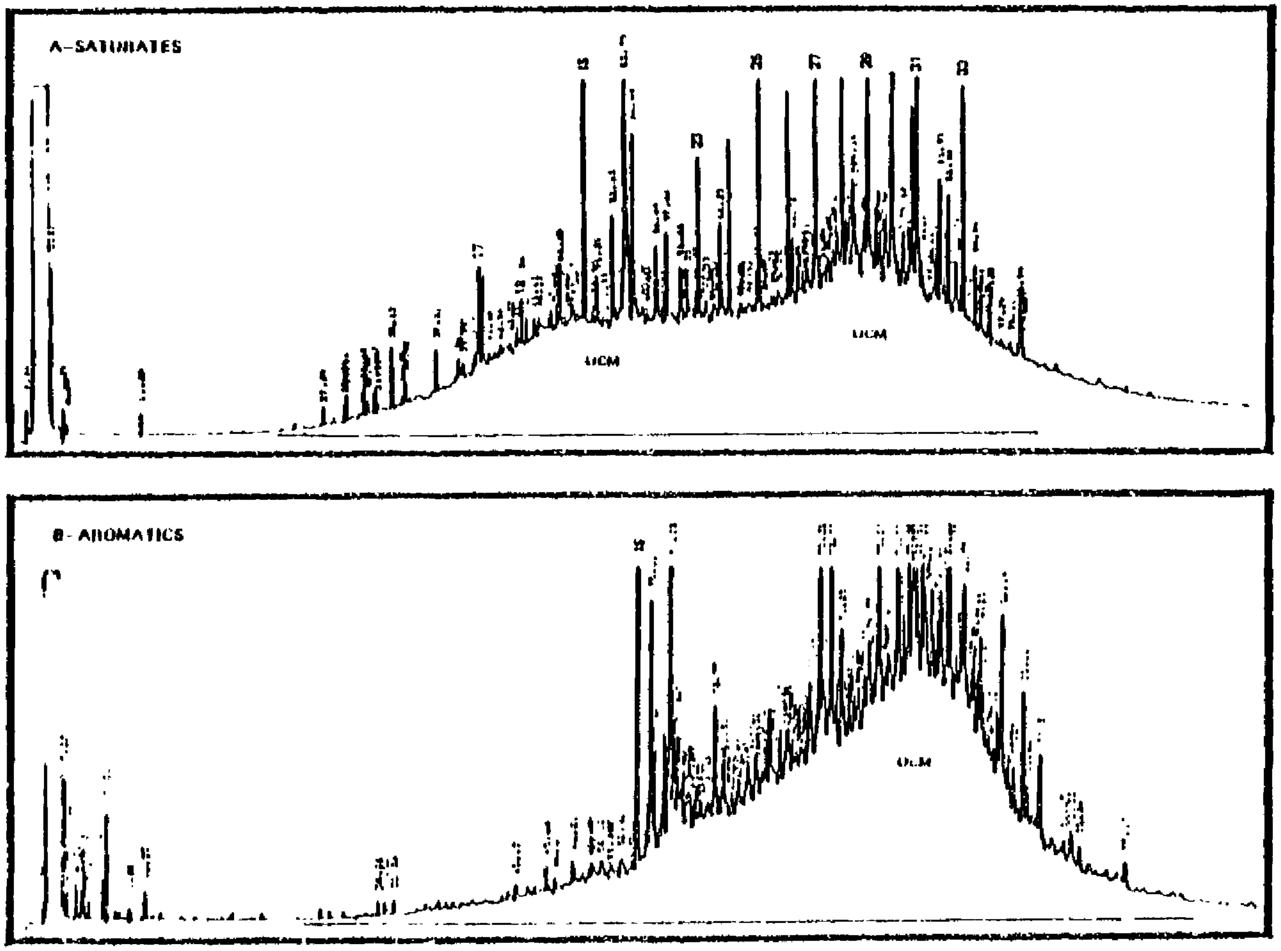

Figure 2–33. Representative FSCGC Traces of Durmah Agate Impact Area Sediments (Station G 02).

dibenzothiophenes were detected. In these cases, attempts to match these aromatic compounds with a source fail primarily because the C_1P/C_1DBT ratio is not reliable due to weathering effects (Table 2-24) and the presence of the C_3 homologs is essential to establish a match. The few sediments which did contain the complete series of alkyl phenanthrenes and alkyl dibenzothiophenes (e.g., NO_3, NO_4; Table 2-24) had C_1, C_2, and C_3 homologue ratios decidedly higher than either the Burmah Agate or Ixtoc I oils (see Table 2-24). The presence of these aromatics in these samples may be attributable to low levels of an unknown source of petroleum and to pyrolytic inputs. The high ratios of phenanthrenes to dibenzothiophenes are due to phenanthrene inputs attributable to combustion (i.e., pyrolytic inputs). Three sediment samples collected in the area of the Burmah Agate spill were found to contain petrogenic aromatics. C_2 and C_3 alkyl phenanthrene-alkyl dibenzothiophene ratios compare favorably with those values found for Burmah Agate oils. C_1 ratios were slightly higher for the sediment samples than the oil samples, which is probably attributable to weathering effects. One sediment sample shown to be contaminated with oil (Port Aransas sample - PA2) showed C_1, C_2, and C_3 alkyl phenanthrene-dibenzothiophene ratios nearly identical to those found for moderately weathered Ixtoc I oil. However, this sample is taken from a heavily used port area so attributing the aromatics in this sample to Ixtoc I oil has some uncertainty.

Significant quantities of nonalkylated PAH were found in many of the sediments. These compounds include phenanthrene (m/e = 178), pyrene (m/e = 202), fluoranthene (m/e = 202), benzanthracene and chrysene (m/e = 228), benzopyrene isomers (m/e = 252), and perylene (m/e = 252). Concentrations of phenanthrene ranged from <0.1 $ng \cdot g^{-1}$ to 25 $ng \cdot g^{-1}$, fluoranthene-pyrene from 0.1 $ng \cdot g^{-1}$ to 96 $ng \cdot g^{-1}$, benzo(a)anthracene-chrysene from <0.1 $ng \cdot g^{-1}$ to 44 $ng \cdot g^{-1}$, benzofluoranthene-benzo(a)pyrene-benzo(e)pyrene from <0.1 $ng \cdot g^{-1}$ to 91 $ng \cdot g^{-1}$ and for perylene from <0.1 $ng \cdot g^{-1}$ to 123 $ng \cdot g^{-1}$. The predominance of these nonalkylated PAH compounds suggests pyrogenic sources (e.g., combustion of fossil fuels), not petroleum contamination (Youngblood and Blumer, 1975). Their presence in these sediments is probably a result of atmospheric fallout and terrestrial runoff, part of the usual pollutant depositional environment of the region.

Concentration profiles of each of the pyrogenic PAH are mapped in Figures 2-34 to 2-38. In each survey the quantities of pyrogenic PAH were greater in offshore (>25 m depth) than in near-shore (<25 m depth) samples. This seems to correlate well with total organic carbon (TOC) data derived for many of the sediments. This is demonstrated in Figures 2-39 to 2-41 where TOC values have been compared with representative pyrogenic PAH (benz[a]-anthracene-chrysene, fluoranthene, pyrene, perylene) from the 1980 survey. The reason for this is that near-shore sediments typically contain coarser sediment particles than do deep-sea sediments. Concentrations of lipids are usually higher in finer-grained sedimentary material (Thompson and Eglinton, 1978) found in depositional environments. These areas are also better suited for net deposition of fine-grained pyrogenic residues (i.e., soot).

TABLE 2-24

GC/MS-DETERMINED SEDIMENT ALKYL PHENANTHRENE/ ALKYL DIBENZOTHIOPHENE RATIOS

STATION	YEAR	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT	SOURCE[a]
<u>STOCS Stations</u>:					
S53	1979	8.00	2.50	0.73	P/U
N39	1979	22.5	8.67	20.0	P/U
S51	1980	12.5	5.80	-	P/U
S52	1980	5.18	4.60	-	P/U
N40	1980	21.0	4.50	-	P/U
S49	1980	19.8	8.00	-	P/U
N03	1980	15.7	5.74	2.43	P/U
N04	1980	30.2	8.59	5.68	P/U
<u>Burmah Agate Stations</u>:					
G04	1980	9.75	6.23	9.58	BA
G02	1980	7.78	3.70	3.26	BA
G05	1980	8.65	3.40	5.75	BA
<u>Port Aransas</u>:					
PA2	1979	1.50	0.53	0.72	I
Range of <u>Ixtoc</u> Oils:		0.72-1.32	0.41-0.66	0.43-0.80	
Range of <u>Burmah Agate</u> Oils:		3.56-5.09	3.41-5.11	5.36-11.36	

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[a] P/U = combined source of pyrolytic combustion aromatics and lesser amounts of unidentified chronic petroleum source.

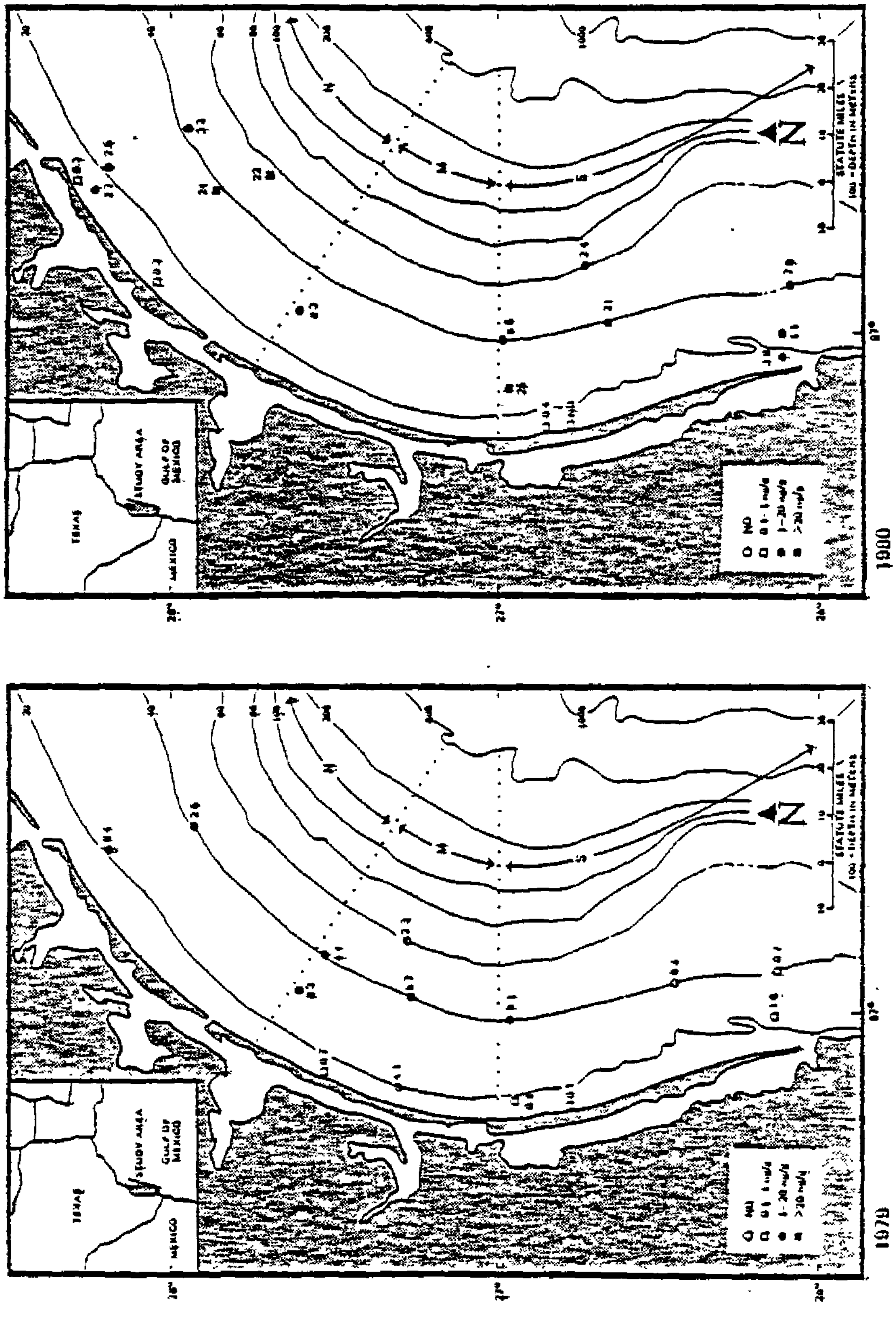


Figure 2–34. Phenanthrene Concentrations in Sediments (ng/g).

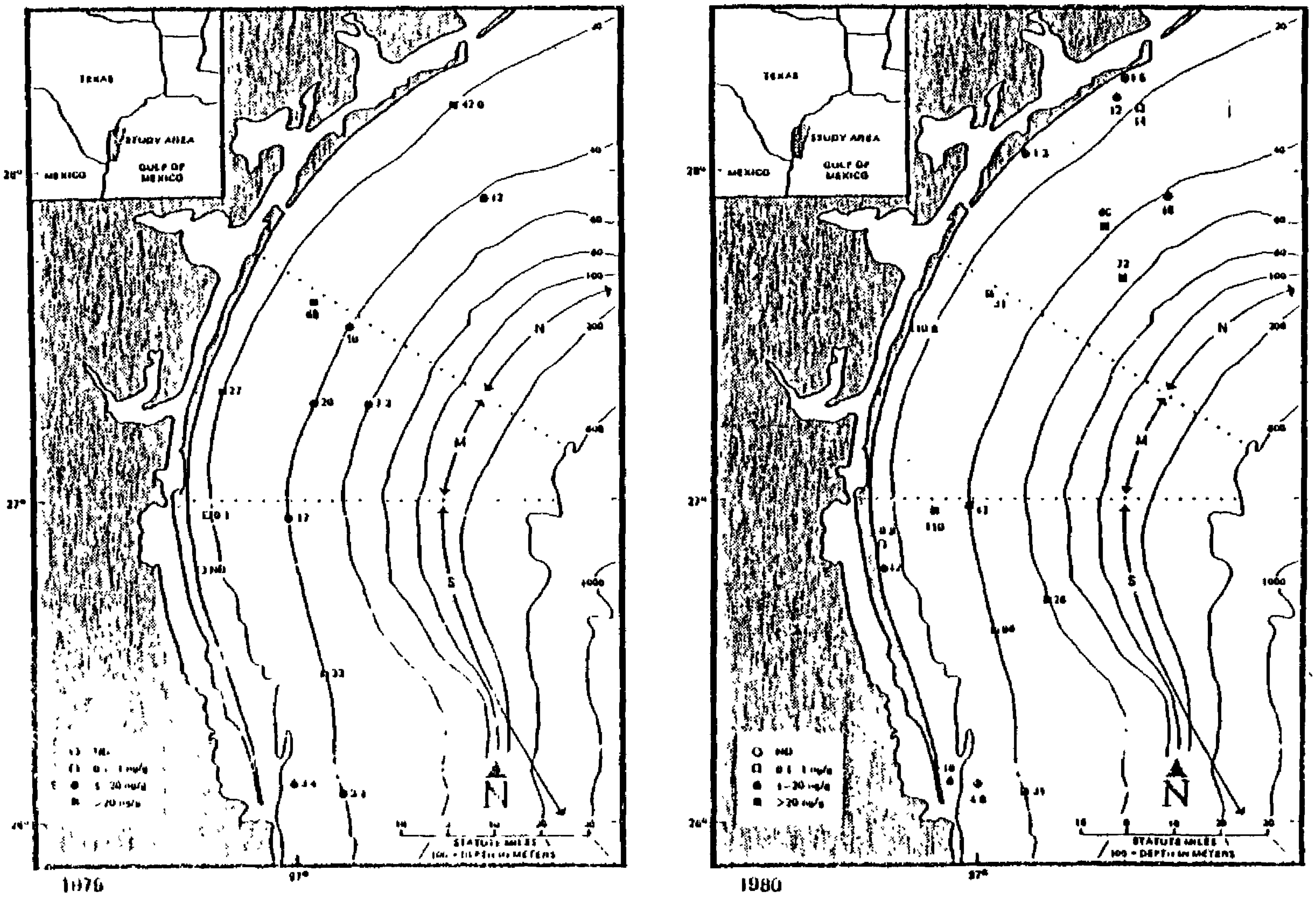


Figure 2–35. Fluoranthene/Pyrene Concentrations in Sediments (ng/g).

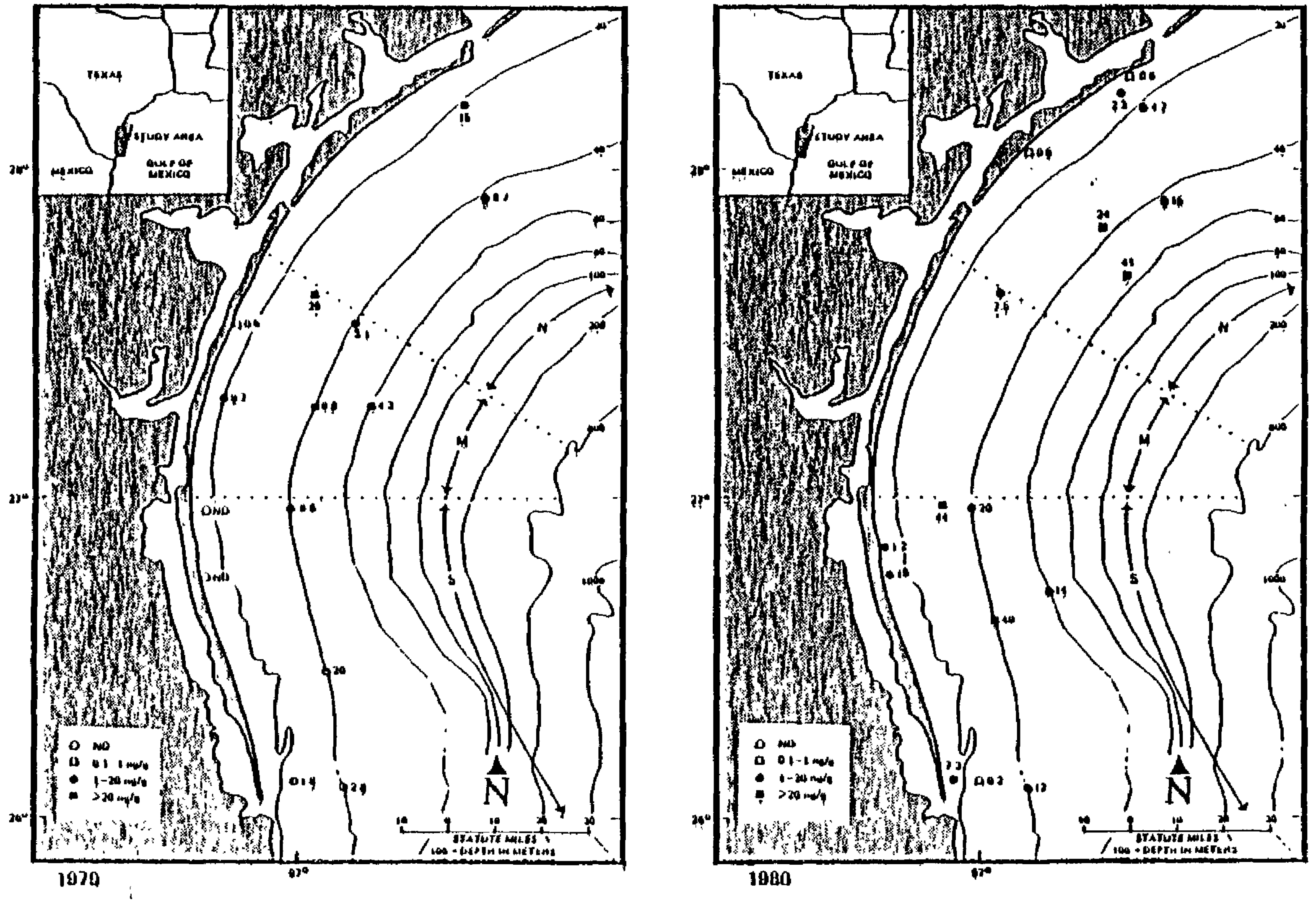


Figure 2-36. Benzanthracene/Chrysene Concentration in Sediments (ng/g).

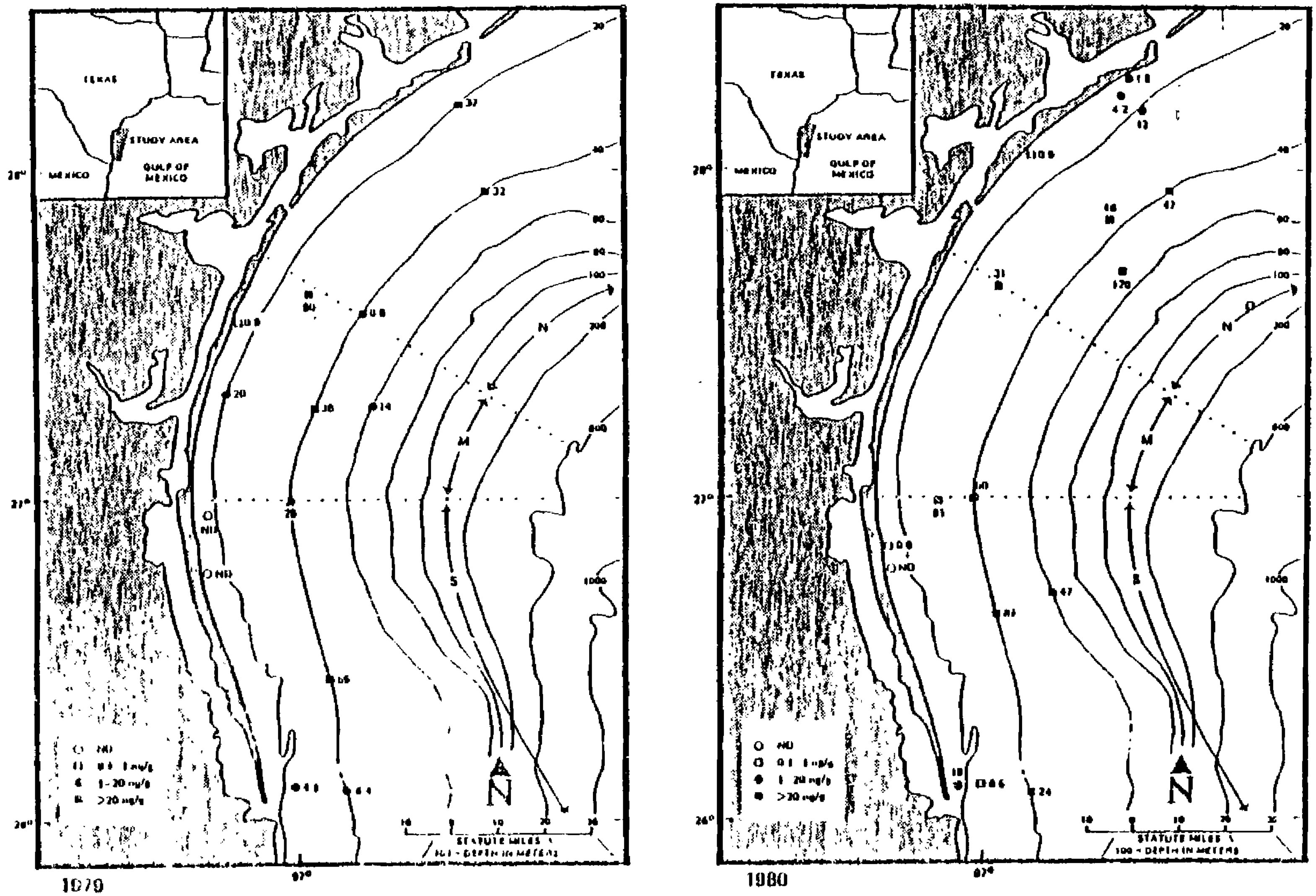
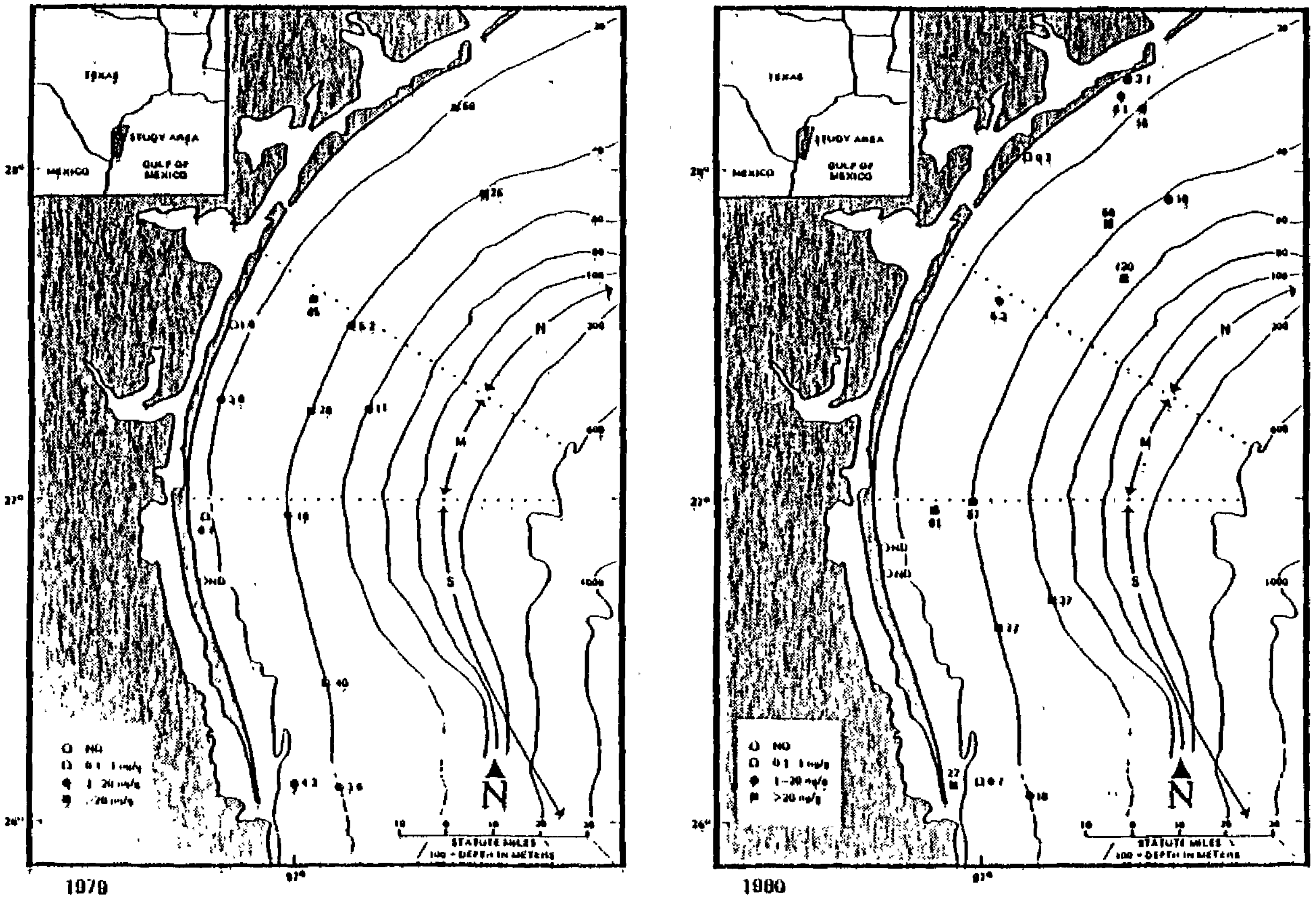


Figure 2--37. Benzofluoranthene / Benzo (a)Pyrene / Benzo(e)Pyrene Concentrations in Sediments (ng/g).



1979

1980

Figure 2—38. Perylene Concentrations in Sediments (ng/g).

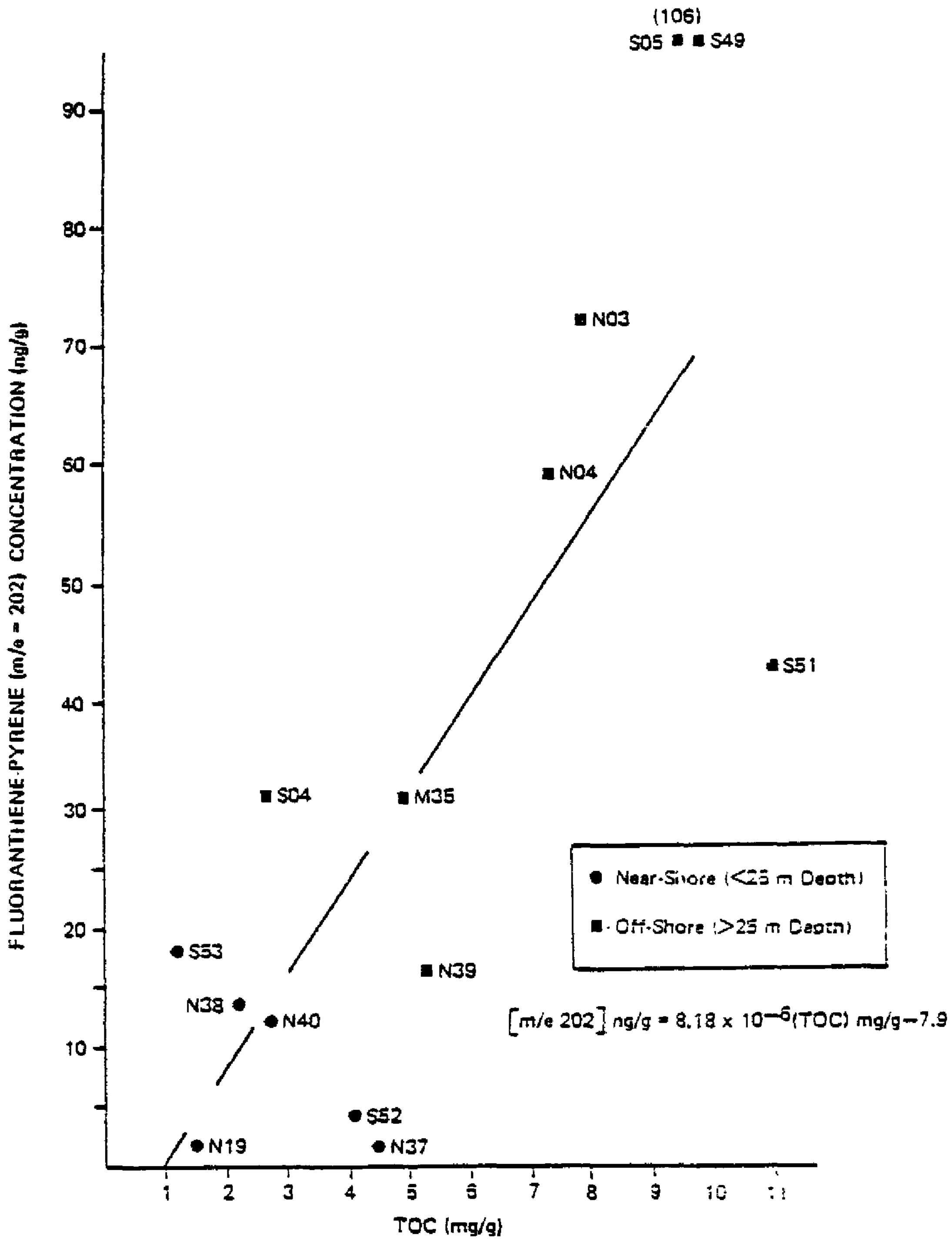


Figure 2—39. Fluoranthene, Pyrene Concentrations in Sediments as a Function of TOC (1980 Data).

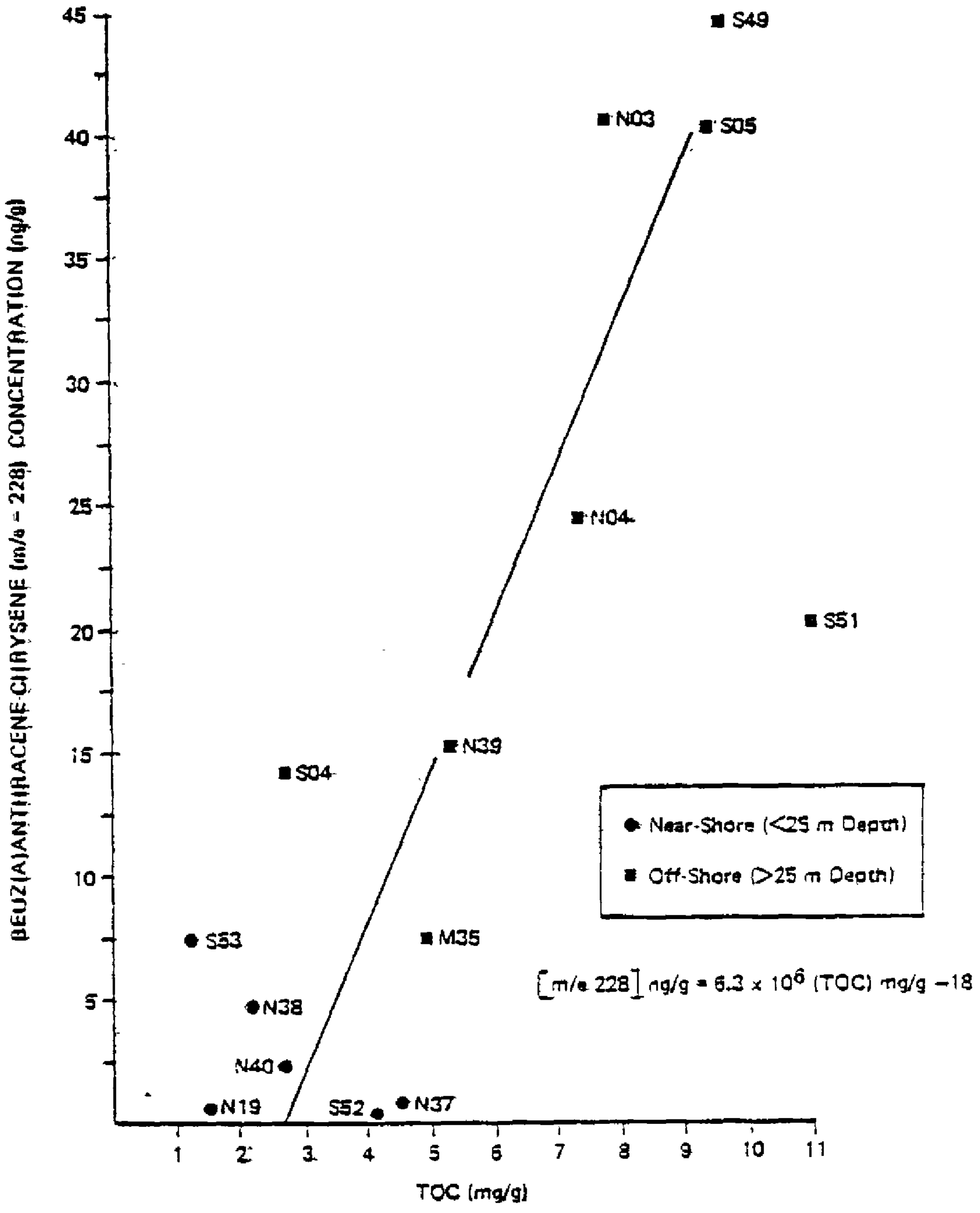


Figure 2—40. Benzanthracene, Chrysene Concentrations in Sediments as a Function of TOC (1980 Data).

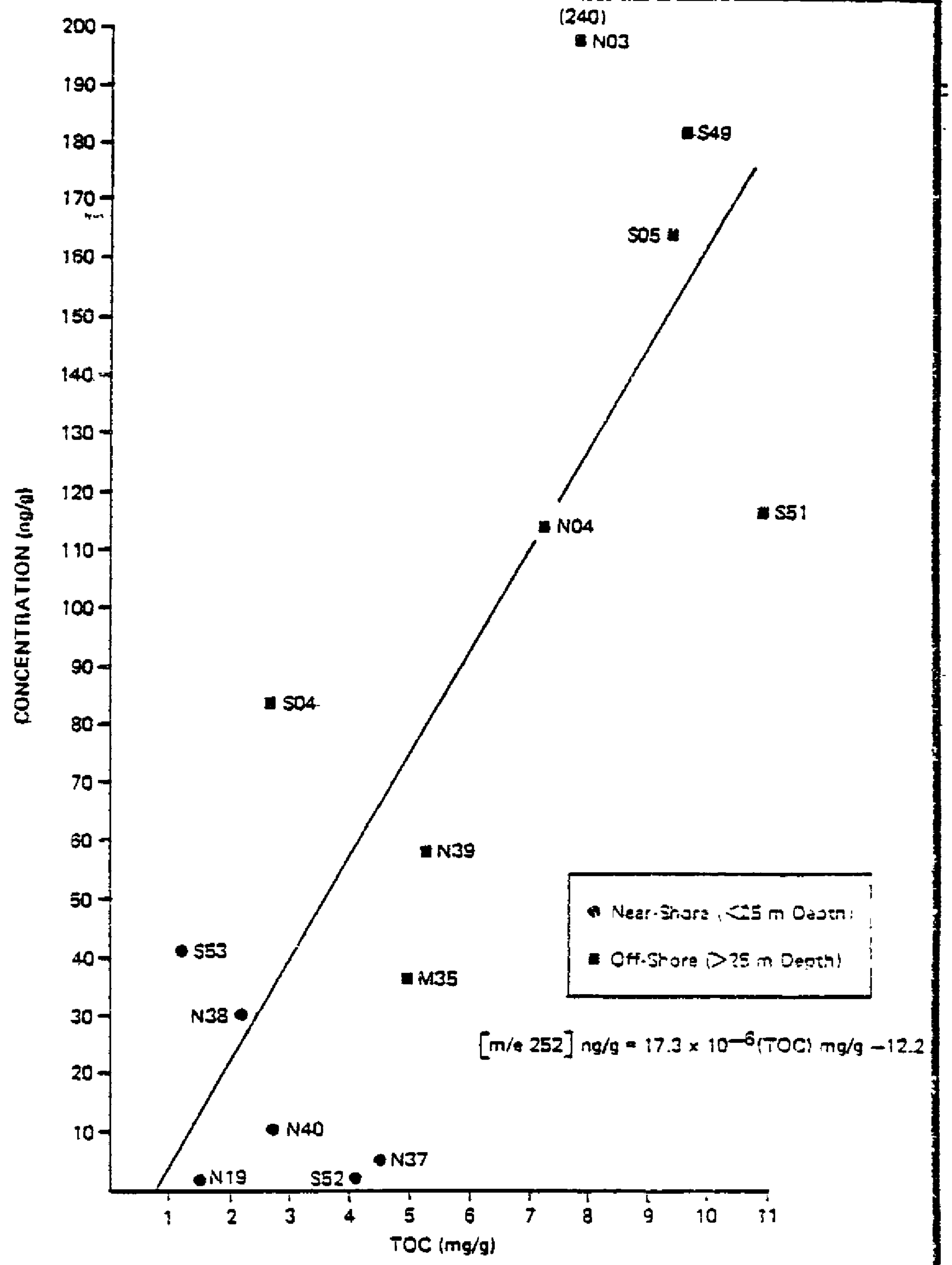


Figure 2—41. Benzofluoranthrene, Benzopyrene, Perylene Concentrations in Sediments as a Function of TOC (1980 Data).

A comparison of pyrogenic PAH concentrations has been made for coinciding 1979 and 1980 survey sites (Table 2-25). Although quantities were generally comparable, at sites N38, M35, and S52, 1979 PAH concentrations were higher by as much as two to three times the levels found in the 1980 samples. At sites N39, S51, and S31, 1980 values were slightly higher than 1979 values. Only at site S54 were values substantially different, with some concentrations being 10 times greater in the 1980 survey. An overall impression of these comparisons is that pyrogenic PAH levels have been fairly stable over a 1-year period, with no dramatic impact or degradation of these compounds apparent. Variations found can be explained by normal geochemical variability. For example the TOC levels at Station S54 increased from 4.7 to 10.6 and the total PHC levels from 9.8 to 17.5 between 1979 and 1980. As pyrogenic PAH would be associated with fine soot-like particles, this large TOC increase (6 $mg \cdot g^{-1}$) could have presumably included small amounts of soot-bearing PAH at the 50-100 $ng \cdot g^{-1}$ level. If one considers historical data available from Laseter and Overton (undated) (Table 2-26) then a remarkable stability in PAH levels is seen. These data are unique in that they not only combine temporal geochemical information but interlaboratory-derived results as well.

The precision of the GC/MS analyses on two subsamples of a sediment sample from Station S04 is excellent (coefficients of variation for individual PAH $\leq$20%), thus precluding analytical variability or subsampling variability in accounting for seasonal PAH changes (see Section 2.2.5).

2.3.3 Petroleum Hydrocarbons in Sorbent Pads

2.3.3.1 FSCGC Analysis

The sorbent pad samples captured a nonquantitative sample of subsurface particulate material potentially including suspended sediment and particulate oil residues. The aim of this sampling was to obtain subsurface oil residues and recently deposited (and then resuspended) particulate matter.

As much of the material in the samples was (possibly resuspended) sediment, concentrations of PHC were calculated on a dry-weight-of-sediment basis and are presented in Table 2-27. As indicated by the CPI values and as seen in the FSCGC traces (e.g., Figures 2-42 and 2-43), the sample obtained is most often a mixture of relatively recent petroleum input and background material. CPI values range from 1.2 to 8.0. Hydrocarbons in those samples having CPI values between 1.0 and 1.5 have been classified as primarily oil-derived. Terrigenous plant material and chronic anthropogenic input to the samples will increase the CPI. For example, the sample taken at Station N26 is predominantly background geochemical material.

The FSCGC traces indicate that the sorbent pads are significantly different from the surficial sediments in composition. The pads are in most cases characterized by a petroleum-related hydrocarbon assemblage combined with a sedimentary source, the latter signified by the terrigenous odd-carbon chain n-alkane (n-C_{23} to n-C_{33}) distribution. It is significant to note that the sorbent pad samples from the southern sector ("S" stations)

TABLE 2-25

COMPARISON OF PYROGENIC PAH AT STATIONS SAMPLED IN BOTH FROM THE 1979 AND 1980 SURVEYS

		CONCENTRATIONS ($ng \cdot g^{-1}$)				
SITE	SURVEY	PHEN.	FLUOR.-PYR.	BENZ.-CHRY.	BENZO PYRENES	PERYLENE
N38	1979	8.4	42.0	15.2	36.9	59.2
	1980	2.5	13.8	4.7	12.5	16.5
N39	1979	2.5	12.2	8.7	31.9	24.7
	1980	3.3	15.9	15.3	47.5	10.0
M35	1979	8.3	68.3	28.9	90.2	84.9
	1980	8.3	30.8	7.5	30.5	5.3
S51	1979	5.1	17.1	9.6	29.0	16.0
	1980	6.6	42.9	20.2	59.5	57.1
S31	1979	0.1	ND	ND	ND	ND
	1980	ND	11.6	19.4	ND	ND
S52	1979	1.0	3.4	1.6	4.1	4.3
	1980	1.1	4.0	0.2	0.5	0.7
S54	1979	0.7	3.1	2.0	6.4	3.6
	1980	7.8	31.3	11.8	23.6	17.8

PHEN = Phenanthrene
FLUOR = Fluoranthrene
PYR = Pyrene
BENZ = Benzanthracene
CHRY = Chrysene