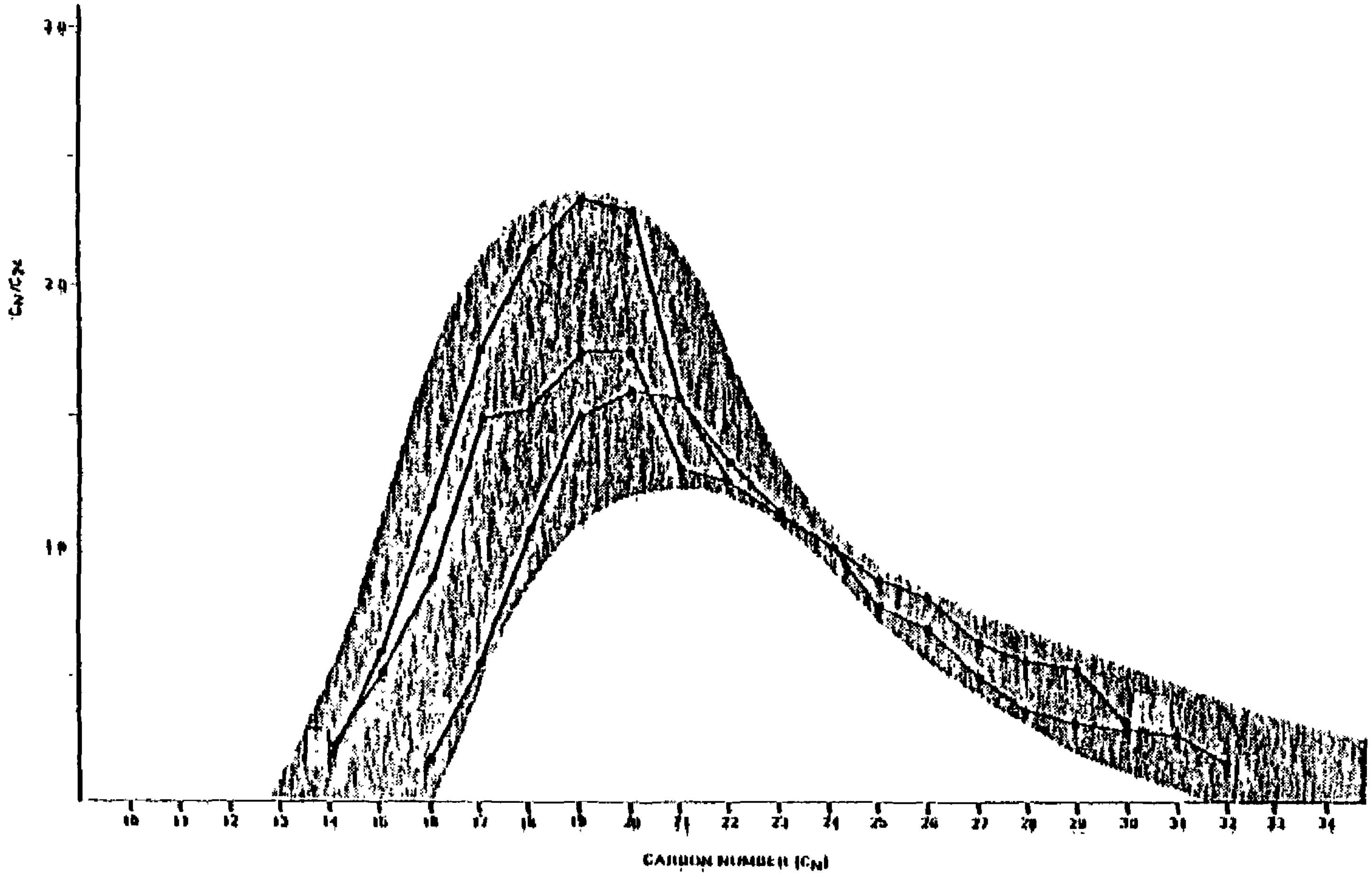

Figure 2-13. NAPA Plots Showing Range of Compositions of Weathered Ixtoc I Reference Oils.

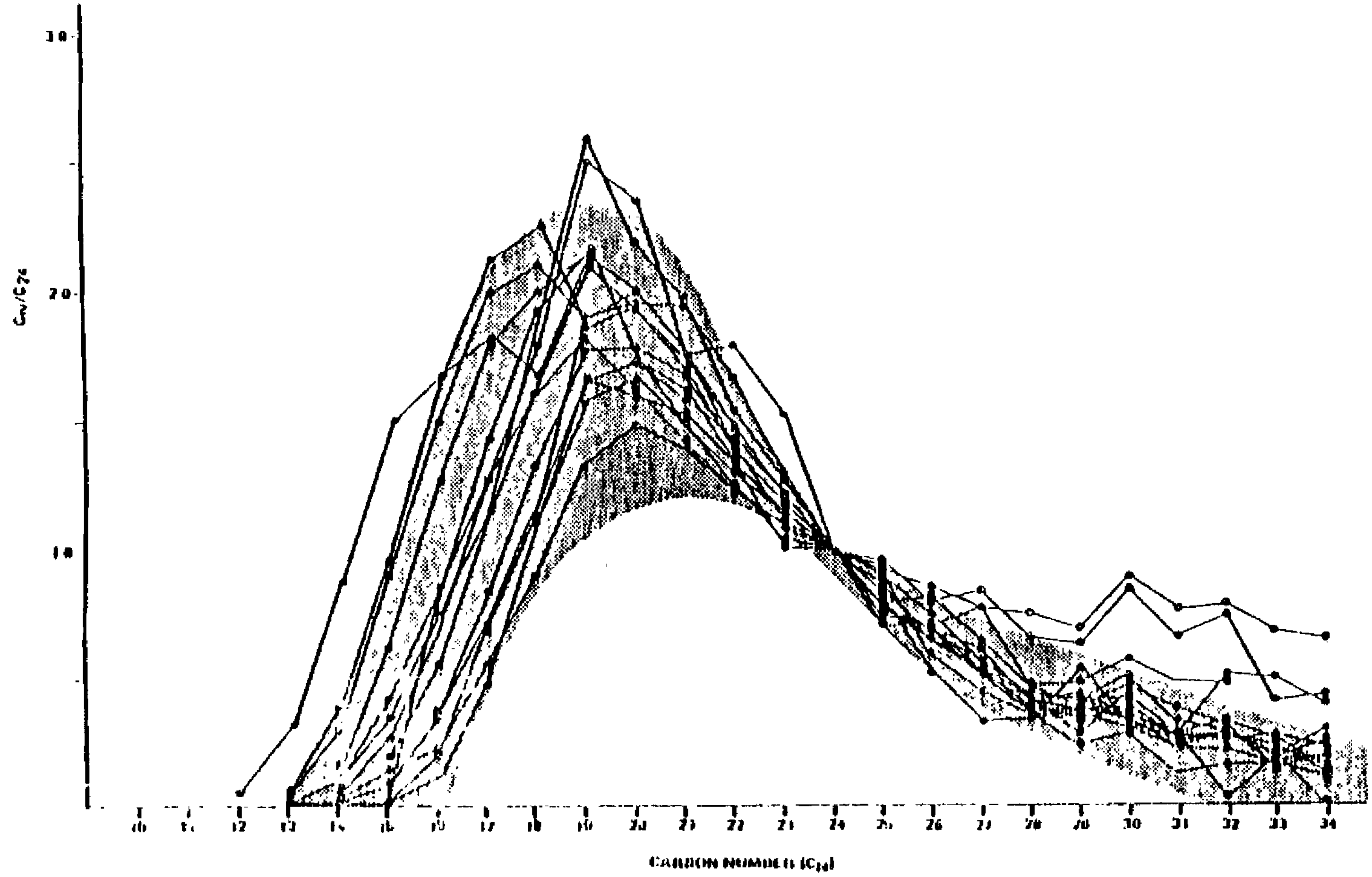

Figure 2-14. Composite NARA Plots of Ixtoc I - Related Oils/Tar.

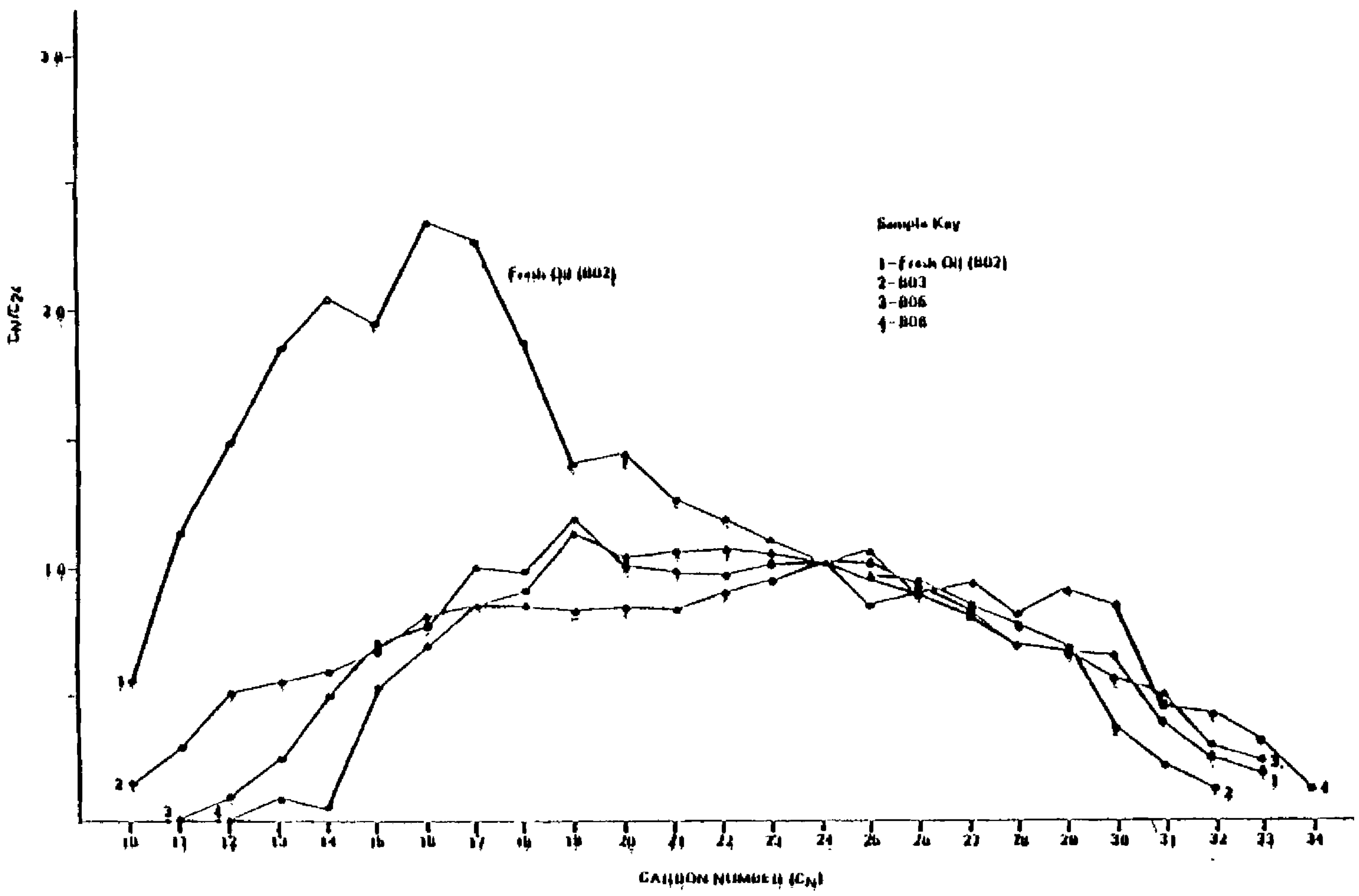

Figure 2-16. NARA Carbon Plots of Burmah Agate Related Oils in Various States of Weathering.

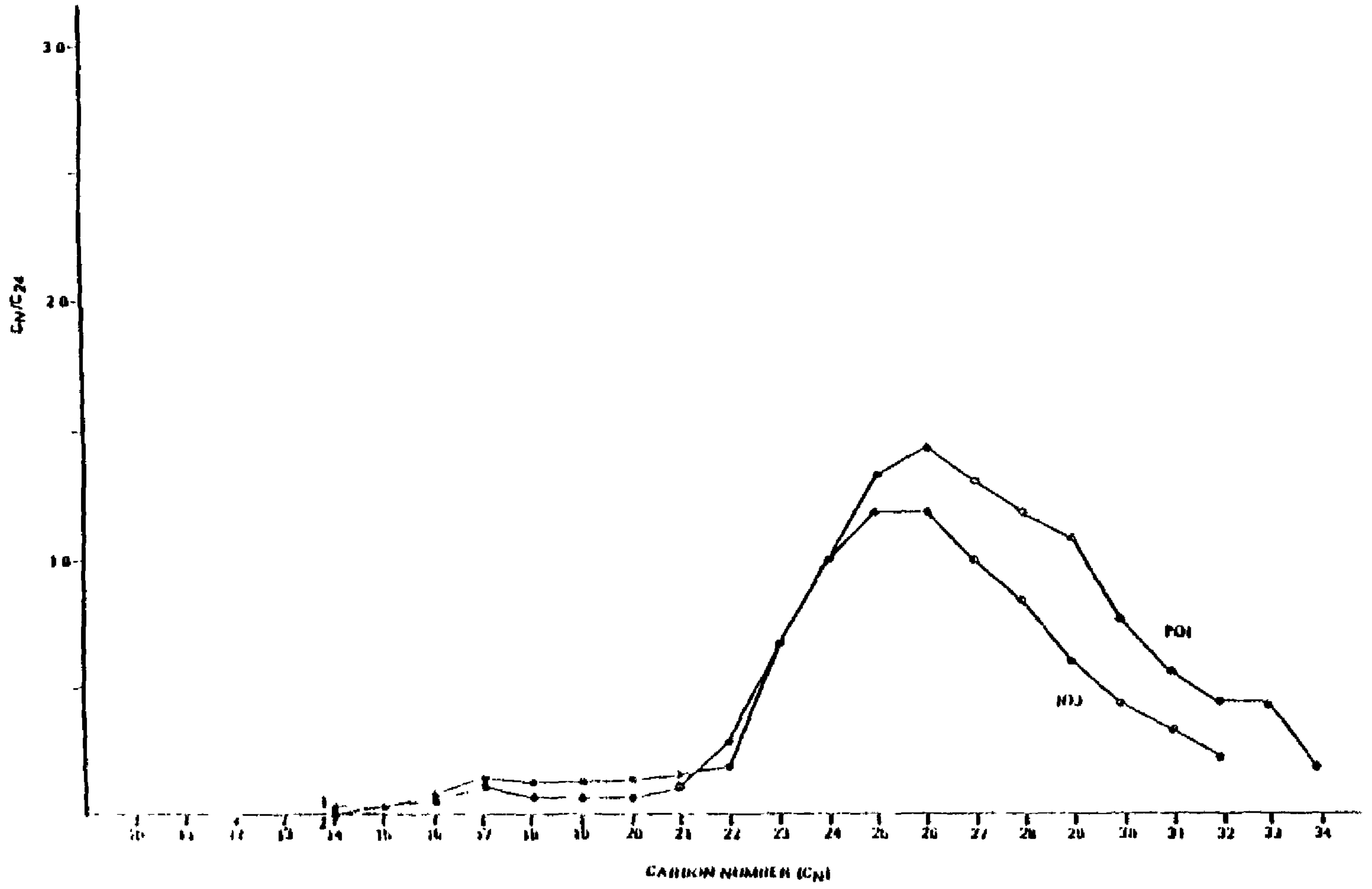

Figure 2 - 16. NARA Plots of Non-Spill Related Beach Tars.

The purpose of examining the aromatic content of environmental petroleum samples in the Texas Gulf Coast region is to decipher the origin of the oil. Petroleum samples analyzed as part of this phase of the program include Ixtoc I oil from the wellhead, weathered Ixtoc I oil near wellhead, floating oil collected at a distance from the wellhead (Hooper Collection), beached oil and tar (1979 and 1980), and Burmah Agate oil. The resultant quantitative aromatic data are presented in Appendix 9.1. The remainder of the investigation focuses on the Group I aromatic composition of the petroleum samples, because of their importance in identifying petroleum, and in establishing the presence of oil in environmental samples (Sections 2.2.3.3 and 2.2.5.2). Quantitative data on Group I aromatics in fresh and weathered Ixtoc and Burmah Agate oils are presented graphically in Figure 2-17 where the much greater relative abundance of these compounds in Burmah Agate oil is evident.

The recent presence of oil in the Texas Gulf Coast region is not necessarily indicative of an Ixtoc source. Other petroleum sources prevalent in the region (e.g., platform drilling discharges, tanker accidents and discharges) have produced small spillages, tar balls, etc. (Jeffrey et al., 1973; Geyer, 1981) and may confuse the evaluation of the impact of Ixtoc I to this environment. The Burmah Agate accident is of particular concern because the incident occurred near the area of the Ixtoc I oil contamination and oil spread to the Ixtoc impact region. The composition of Group I aromatics may be quite different for various petroleums. However, weathering may drastically alter the relative aromatic content of petroleum exposed to the environment, preferentially depleting lower molecular weight aromatics (e.g., Boehm et al., 1981a; Atlas et al., 1981). This is shown in Figure 2-17, where the relative petrogenic aromatic content of representative oil samples is depicted for selected fresh and weathered oils.

Overton et al. (1981) have suggested that a passive chemical tag may be useful in distinguishing different oils. Their suggestion involves comparing ratios of C_1, C_2, and C_3 alkyl phenanthrenes (m/e = 192, 206, 220) to the respective C_1, C_2, and C_3 alkyl dibenzothiophenes (m/e = 198, 212, 226). The relative quantities of each compound from a selected oil sample are shown in the GC/MS extracted-ion current profiles shown in Figures 2-18 and 2-19. A compilation of these ratios for the oil samples examined by GC/MS is presented in Table 2-18.

The alkyl phenanthrene-alkyl dibenzothiophene ratios for the fresh wellhead Ixtoc I oil and the Ixtoc I oil floating in the vicinity of the wellhead are nearly identical. The C_2 and C_3 ratios for the beached Ixtoc oils and ing effects. This is most pronounced for the C_1 ratios of the beached and floating petroleum. The elevation of C_1 ratios is probably the first indication by this method that weathering processes are affecting the phenanthrene (P) and dibenzothiophene (DBT) aromatic compositions. Two of the three floating oil samples (7908-Q01-1001, 7908-Q03-1001) again show good C_2 and C_3 ratio correlations to the Ixtoc I oil, but C_1 ratios were also slightly elevated. Burmah Agate oil was also examined and found to be quite different from Ixtoc I oil Burmah Agate C_1 ratios were about five times greater than Ixtoc I, C_2 ratios about six times larger, and C_3 ratios about four times larger.

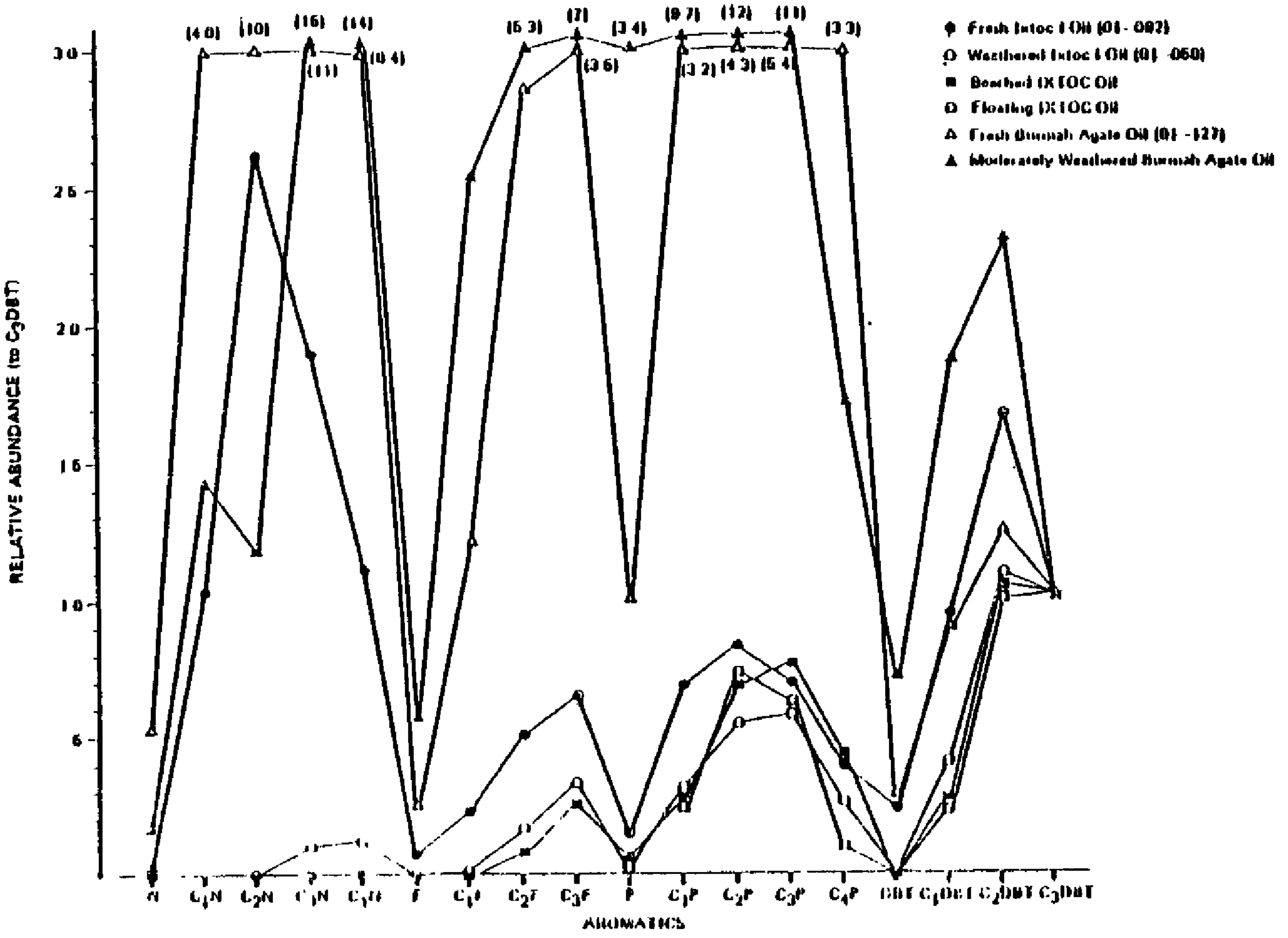

Figure 2–17. Group I Aromatics in Oils.

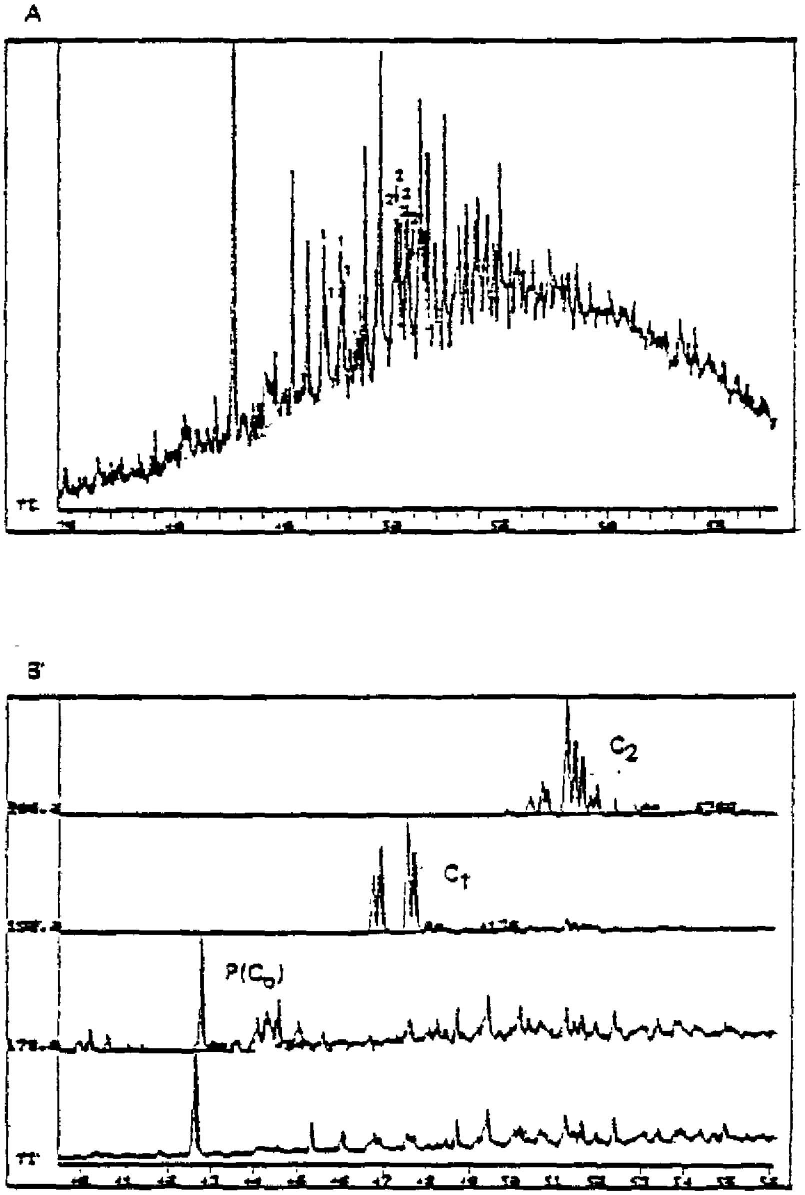

Figure 2–18. GC/MS Analysis of Oils. A = Total Ion Chromatogram, B = Phenanthrene Series Mass Chromatograms.

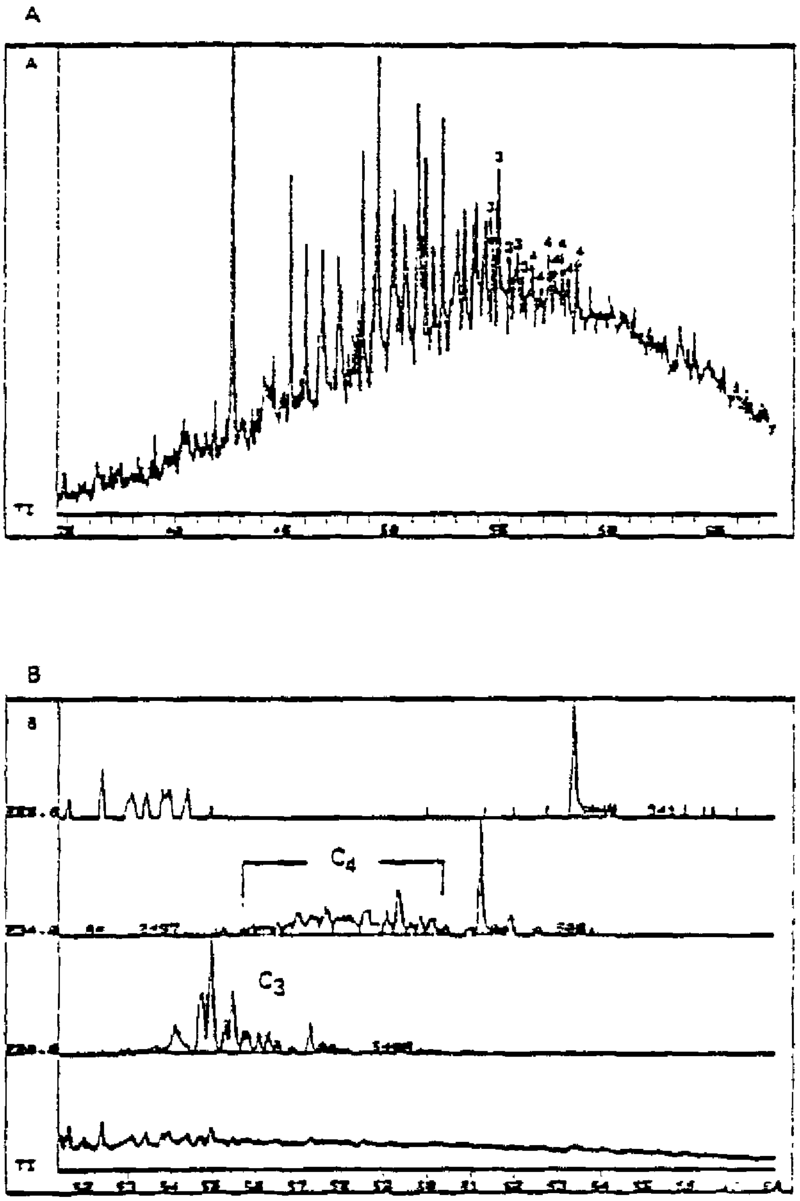

Figure 2–18. (Continued).GC/MS Analysis of Oils, A = Total Ion Chromatogram.
B = Phenanthrene Series Mass Chromatograms.

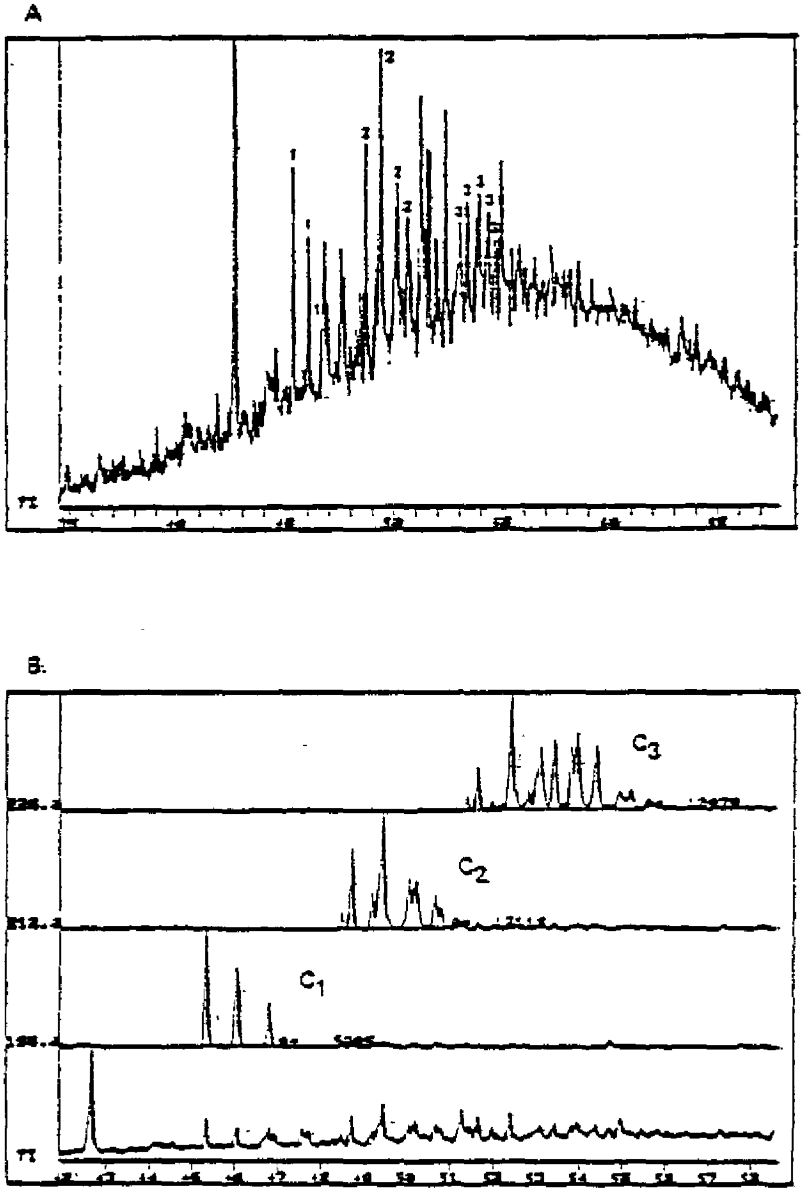

Figure 2—19. GC/MS Analysis of Oils, A=Total Ion Chromatogram, B=Dibenzothiophene Series Mass Chromatogram.

TABLE 2-18

PETROLEUM ALKYL PHENANTHRENE-ALKYL DIBENZOTHIOPHENE RATIOS

SAMPLE	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT
Ixtoc Collection			
Fresh Oil From Wellhead			
PIX-5-E050[a]	0.72	0.51	0.69
Weathered Ixtoc I Oil Near Wellhead			
Texas mousse flake[b]	0.89	0.43	0.59
Texas mousse[b]	0.73	0.41	0.49
PIX-5-B116[a]	0.82	0.48	0.69
PIX-17-E186[a]	0.89	0.48	0.58
Beached Ixtoc Oils and Tars[c]			
7908-I4C-1001	1.02	0.66	0.78
7911-P20-1001	1.18	0.64	0.76
7911-P06-1001	1.32	0.60	0.80
Overall Ixtoc (Range)			
	0.72-1.32	0.41-0.66	0.49-0.80
Burmah Agate Collection			
Floating Oil			
7911-B02-1001	3.56	3.41	5.36
7911-B02-1002	5.69	4.80	11.36
Beached Oil			
7911-B03-1001	5.06	5.11	11.02
Overall Burmah Agate (Range)			
	3.56-5.69	3.41-5.11	5.36-11.36

TABLE 2-18 (CONT.)

SAMPLE	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT
Identified Oils/Tars[d]			
Beached Oil/Tar (Ixtoc)			
7912-P12-1001	1.03	0.57	0.71
8004-E02-1001	0.65	0.47	0.66
8004-E05-1001	0.90	0.67	0.72
8012-T01-1001	1.41	0.49	0.68
8012-T02-1001	1.18	0.53	0.70
8012-T03-1001	1.65	0.56	0.60
8012-T05-1001	0.86	0.57	0.62
Beached Oil/Tar (Burmah Agate)			
7911-B04-7001	4.92	4.52	9.47
7911-B04-1002	5.68	3.67	6.15
Floating Oil (Ixtoc)			
7908-Q03-1001	1.06	0.62	0.63
7908-Q01-1001	2.20	0.62	0.69
Unidentified Oils/Tars			
Beached Oil/Tar			
7911-P02-1001	2.15	1.40	1.52
Floating Oil/Tar			
7908-Q02-1001	6.17	4.20	5.44

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[a] Data from *Researcher* cruise, September 1979 (Boehm and Fiest, 1980a).

[b] Data from Patton et al., 1981.

[c] Definitively identified by FSCGC and stable isotopes.

[d] Based on determined ranges of C_2 and C_3 ratios.

Based on the range of the C_2 and C_3 ratios, identifications of oil/tar samples are made in Table 2-19. Two samples definitely are not of either origin (P02 and Q02). Note that even the very highly weathered beached oil/tar collection (i.e., 8012-T series) is identifiable through the C_2 and C_3 ratios.

By incorporating the results of the alkyl phenanthrene-alkyl dibenzothiophene ratios with saturated hydrocarbon FSCGC data and carbon, hydrogen, and sulfur stable isotope data, the source of many of the oils can be determined (see Table 2-19). At least two matches are needed to assign a sample to a category. Results from stable isotope analyses are weighted more strongly than FSCGC results alone. Sulfur stable isotope data are tentatively used to overturn FSCGC results but C and H isotope data are overruled by a combination of FSCGC and GC/MS data (e.g., sample 8012-T03-1001).

When the GC/MS results are combined with FSCGC and isotope results, the overall results are definitive. The power of the aromatic ratios in confirming oil identifications, and in establishing identities if one of the other techniques is questionable, is evident (Table 2-19).

2.3.1.4 Aromatic Sulfur Compounds by Hall Detector

Analysis of oils by sulfur-specific GC detectors has previously been used in conjunction with GC-FID to fingerprint oils (ASTM 3328-78; USCG, 1977). However, no attempt at such an evaluation on heavily weathered oils has been documented.

Ten oil samples representing a range of Ixtoc and Burmah Agate samples were analyzed by this method. The FSCGC-Hall trace (e.g., Figure 2-20) offers much information on at least two homologous organo-sulfur compound series, the dibenzothiophenes (DBT) and naphtho-dibenzothiophenes (NDBT). In several samples a dibenzothiophene compound series is discerned but, as these compounds are relatively rapidly weathered from waterborne oils, source-matching using this compound series is limited to use in conjunction with a normalizing parameter (e.g., the alkylated phenanthrenes; Section 2.3.1.3).

Both the Ixtoc and Burmah Agate oils contain similar series of DBT and NDBT compounds. When graphed together to examine the compositional details of the DBT series (Figure 2-21), a wide range of compositions is observed. The methyl DBT (peaks C, D, and E) appears to fall into two groupings. Although the Burmah Agate oils appear relatively "rich" in methyl DBT, so does one Ixtoc residue. The other Ixtoc oils cluster fairly close to one another in the C, D and E compounds, but so do several residues not believed to be Ixtoc-related due to isotopic evidence. Much more scatter in the data appears in the relative compositional plots for the dimethyl dibenzothiophenes (peaks F-I).

Some heavily weathered samples do maintain their organic-sulfur profiles, in spite of a radical weathering of the n-alkane components. This was previously apparent in GC/MS studies.

TABLE 2-19

SUMMARY OF RESULTS OF OIL IDENTIFICATION PROCEDURES[a]

COLLECTION	ERCO ID	FSCGC RESULTS[b]	ISOTOPE RESULTS (C,H,S)[b]	GC/MS RESULTS[b]	OVERALL[b]
HOOPER	7908-Q01-1001	I	0	I	I
	7908-Q02-1001	0	0	0	0
	7908-Q03-1001	I	0	I	0?
	7908-Q04-1001	I	I	-	I
	7908-Q05-1001	W	0	-	0
ERNST	8004-E02-1001	I	I	I	I
	8004-E03-1001	0	I	-	I
	8004-E04-1001	I	I	-	I
	8004-E05-1001	W	I	I	I
	8004-E01-1001	I	I	-	I
STURTEVANT	7911-P02-1001	0	B	0	0
	7911-P17-1001	I	-	-	ID
	7911-P20-1001	I	I	I	I
	7911-P24-1001	I	I	-	I
	7911-P06-1001	I	I	I	I
	7911-P09-1001	I	I	-	I
	7912-P12-1001	I	I	I	I
RPI	7908-I4C-1001	I	I	I	I
	7908-I5A-1001	I	I	-	I
	7911-B11-1001	W	-	-	ID
	7909-I03-1001	0	-	-	ID
USCG	7911-B04-1001	B	B	B	B
	7911-B02-1001	B	B	B	B
	7911-B02-1002	B	B	B	B
	7911-B06-1001	B	B	-	B
	7911-B04-1002	B	B	B	B

TABLE 2-19 (CONT.)

COLLECTION	ERCO ID	FSCGC RESULTS[b]	ISOTOPE RESULTS (C,H,S)[b]	GC/MS RESULTS[b]	OVERALL[b]
BURMAH AGATE	7911-P01-1001	O	-	-	ID
	7911-B05-1001	B	B	-	B
	7911-P19-1001	O	-	-	ID
	7911-B07-1001	B	B	-	B
	7911-B03-1001	B	B	B	B
1980 BEACH SURVEY	8012-T01-1001	W	I	I	I
	8012-T02-1001	I	O	I	I
	8012-T03-1001	W	O	O	O
	8012-T04-1001	W	I	-	ID
	8012-T05-1001	W	I	I	I
	8012-T06-1001	W	-	-	ID
TURTLES	7908-CM2-1001	I	-	-	ID
	7908-CM1-1001	O	-	-	ID
USCG-COIL SAMPLE	155	I	-	-	I

[a] Refer to Appendix 9.1 for cross referencing and location of all samples.

[b] I - Ixtoc.
B - Burmah Agate.
O - Other source or questionable match.
W - Weathered Beyond Recognition.
ID - Insufficient data.

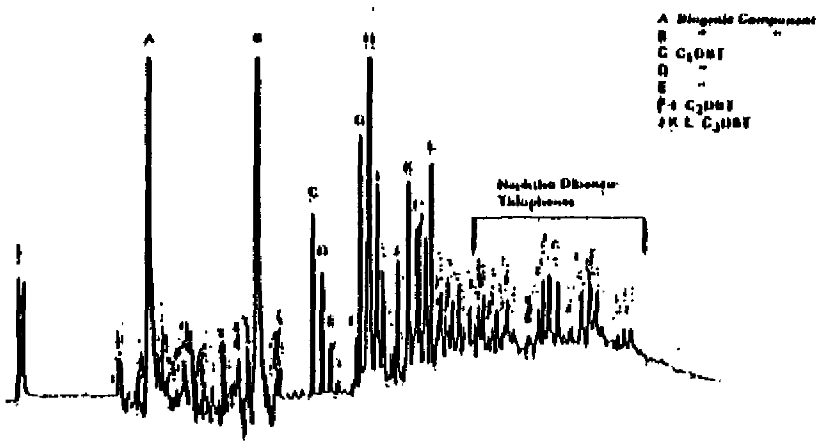


Figure 2–20. Capillary Hall Detector (S Mode) Trace of Beached IXTOC Oil (Letters Refer to Figure 2–21).

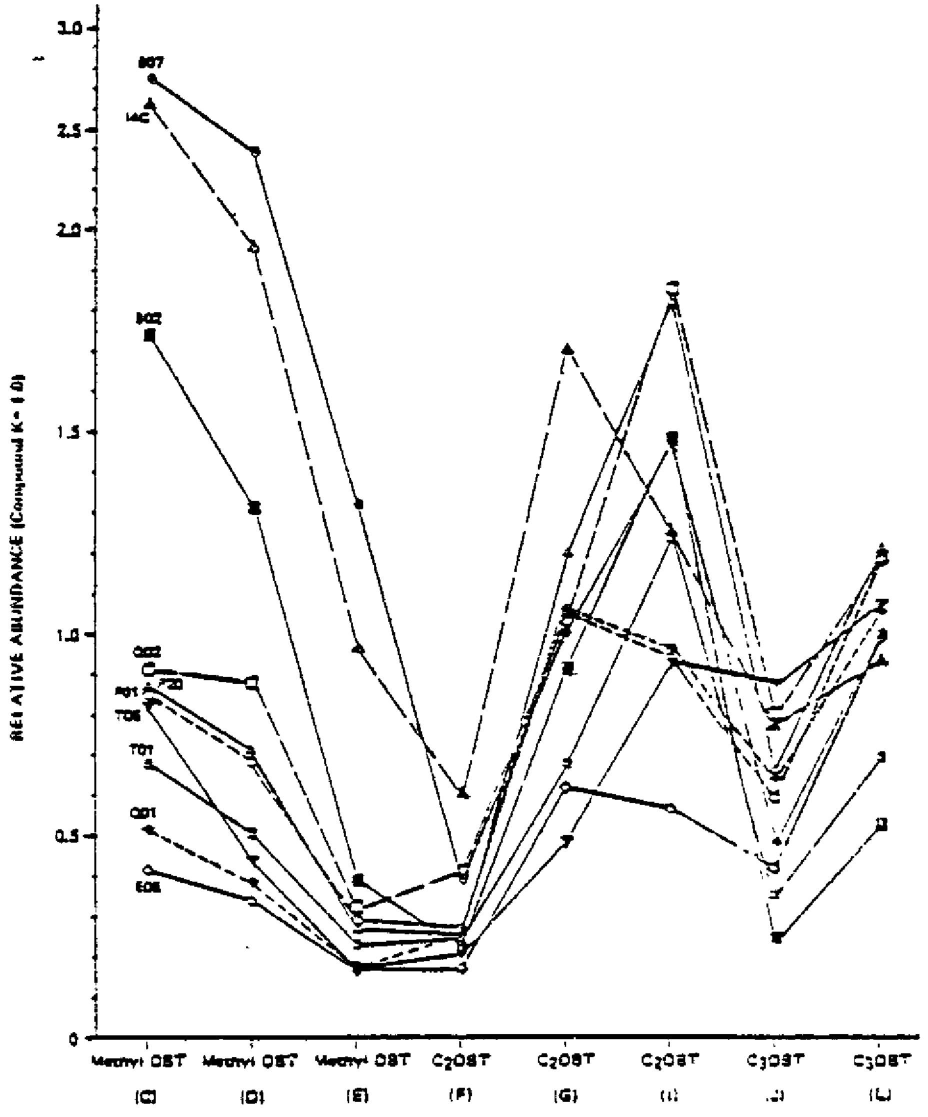


Figure 2–21. Compositional Plots of FSCGC–Hall (S Mode) Derived Information.

2.3.1.5 Azaarene Compounds

Ten oil samples were subjected to the acidic extraction, neutralization, solvent back-extraction scheme to isolate the basic organo-nitrogen heterocyclics. Most of the samples contained only small traces of these compounds made up mainly of the highly alkylated three-ringed acridine/phenanthridine series. GC/MS was used to examine these distributions (Figure 2-22). The predominant azaarenes in weathered Ixtoc and Burmah Agate oils show that these compounds (m/e 207, 211, 233) are more abundant in the Ixtoc oil than in the Burmah Agate oil but that little information of a source-matching nature can reliably be gained by azaarene evaluations due to the extremely low levels of these compounds.

2.3.2 Petroleum Hydrocarbons in the Benthic Substrate

One hundred and twenty-five samples were screened for the presence of petroleum residues by UV/F, and eighty-three were further subjected to detailed FSCGC (FID) analysis to quantify both the saturate (f_1) and aromatic (f_2) fractions. Of the 83 samples analyzed by FSCGC, 40 were analyzed by GC/MS to determine detailed aromatic hydrocarbon and sulfur heterocyclic compositions.

2.3.2.1 UV/F Screening

A serial addition of whole Ixtoc oil was added to a low-level sediment sample extract, to determine the ease of recognition of newly deposited oil residues in offshore sediments by UV/F. The data presented in Figure 2-23 indicate that Ixtoc oil can be seen at levels as low as 0.25 mg oil per ~100 grams of original sample (2.5 $ng \cdot g^{-1}$). However, there is a substantial amount of background fluorescence in many Gulf Coast samples (Boehm and Fiest, 1980c; Figure 2-24) similar in the overall UV/F spectrum to the oil. Therefore false positive or indeterminate UV/F screenings are quite probable occurrences, indicating that further, more detailed, discriminating analytical work is necessary to differentiate the background from small incremental oil additions.

Roughly half of the sediment samples screened were considered to be "petroleum-possible" samples. UV/F traces such as those shown in Figure 2-25 were commonly encountered. Samples were selected for further analysis based on the similarity of UV/F spectra to the spectra of weathered Ixtoc oil. Samples were also selected for overriding geographical considerations. UV/F results might not have indicated obvious oil, but sufficient historical data existed (i.e., the 12 primary STOCS stations) and thus pre- to post-spill comparisons could be made.

All sediment samples exhibited UV/F spectral maxima in the two, three and four aromatic compound bands (e.g. Figure 2-25). The perylene doublet (five rings) was a prominent feature of many of the offshore samples. In a

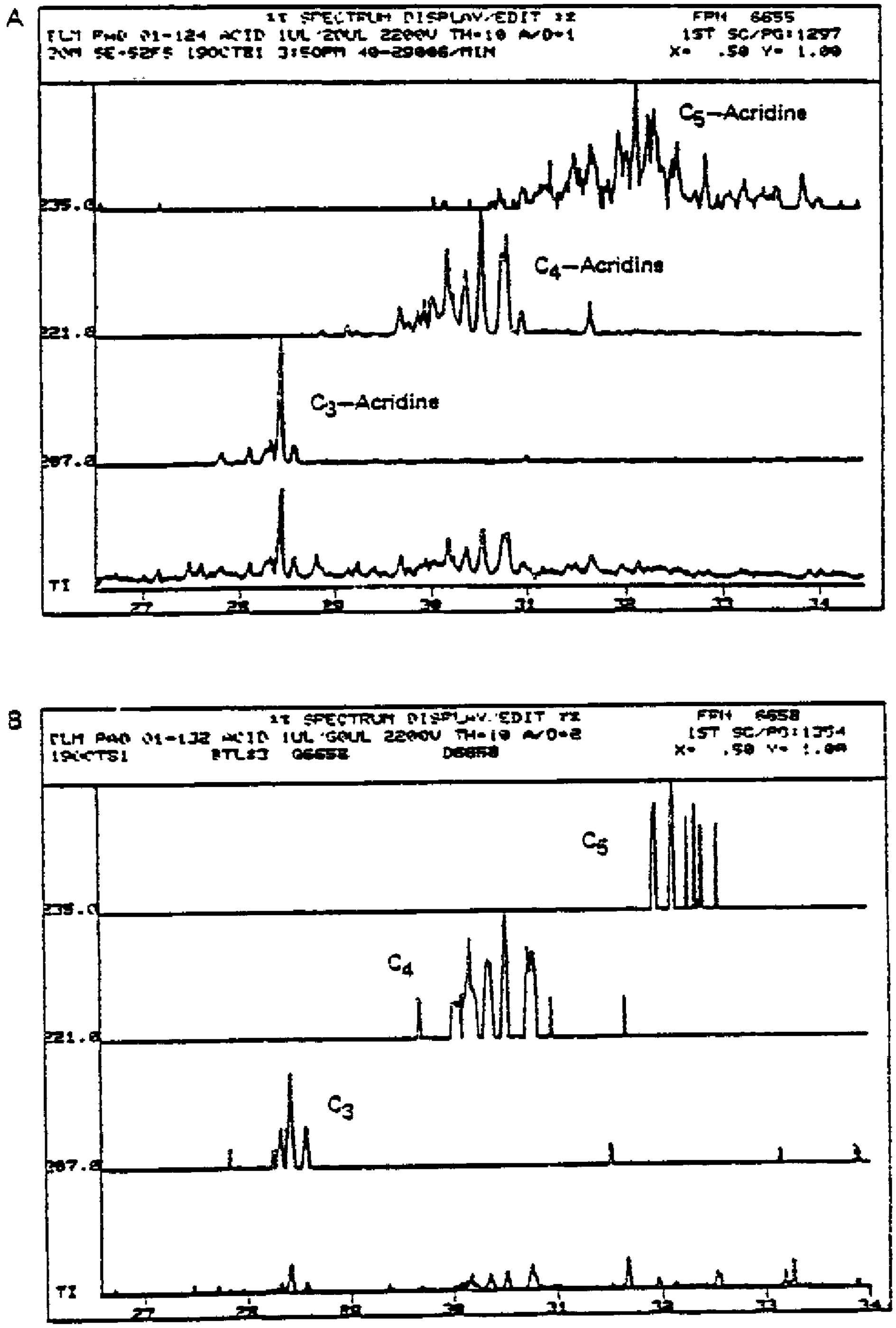


Figure 2—22. GC/MS Mass Chromatograms of Alkylated Acridine/Phenanthridine Compounds in Weathered Ixtoc I Oil (A) and Weathered Burmah Agate Oil (B).

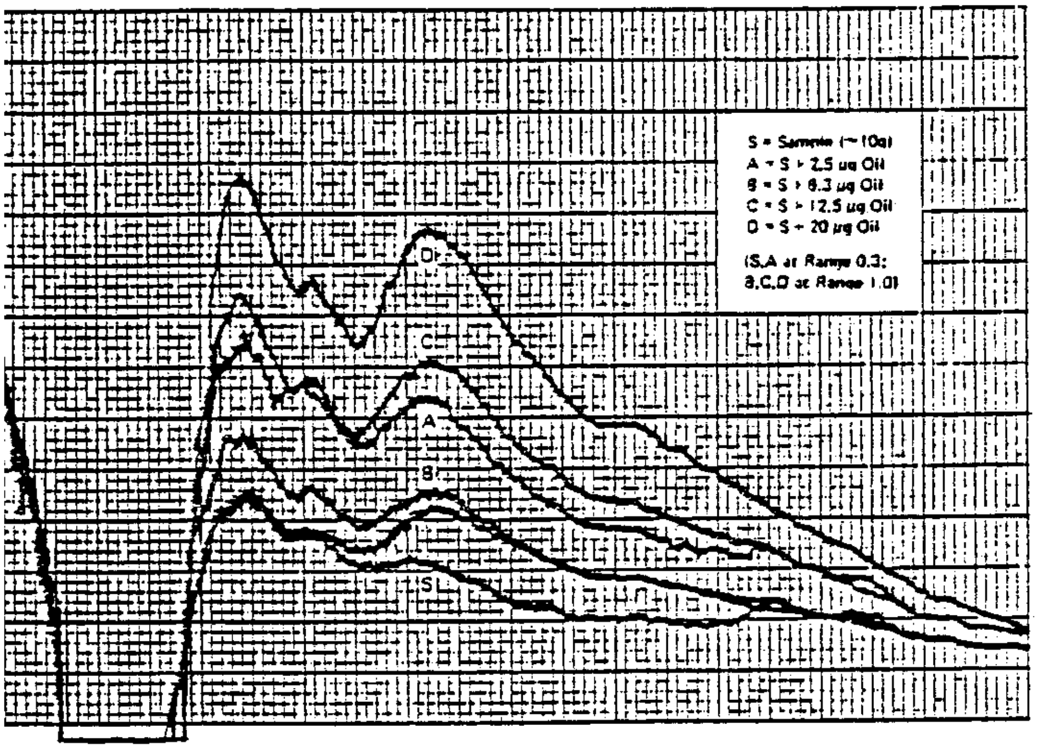


Figure 2–23. UV/F of Serial Addition of Ixtoc I Oil to Sediment.

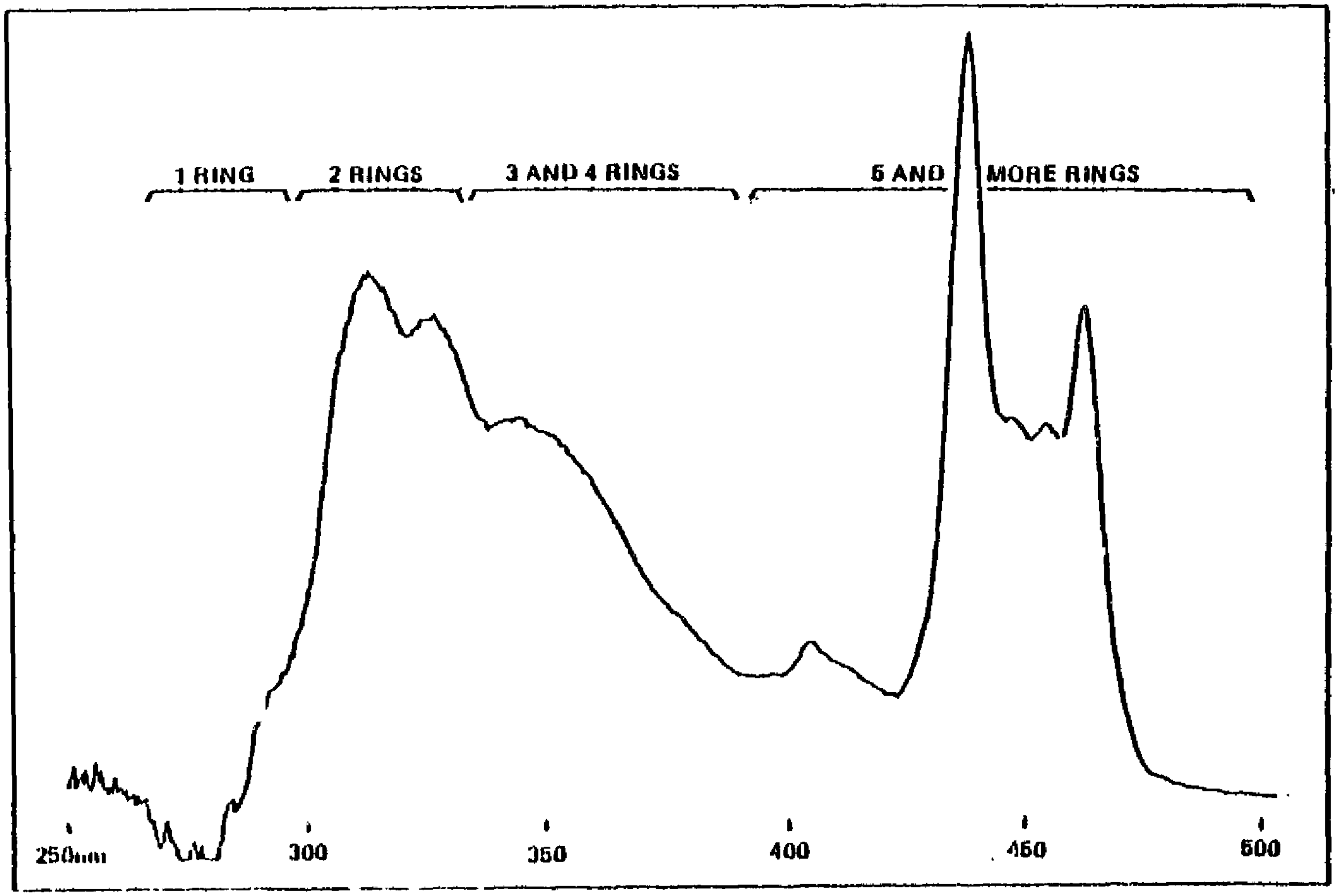
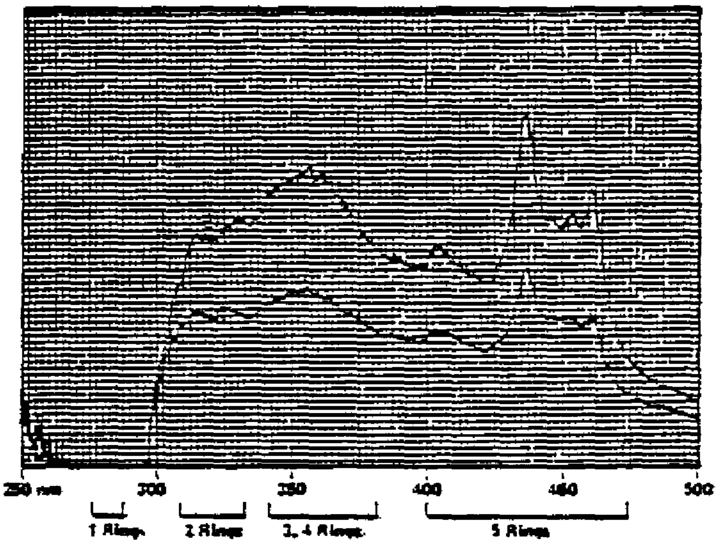


Figure 2-24. Synchronous Spectrofluorometry Spectrum of Gulf of Mexico Sediment Extract Showing the Resolution of Ring Classes and Perylene in the Right-Hand Side of the Spectrum.



B—IXTOC OIL

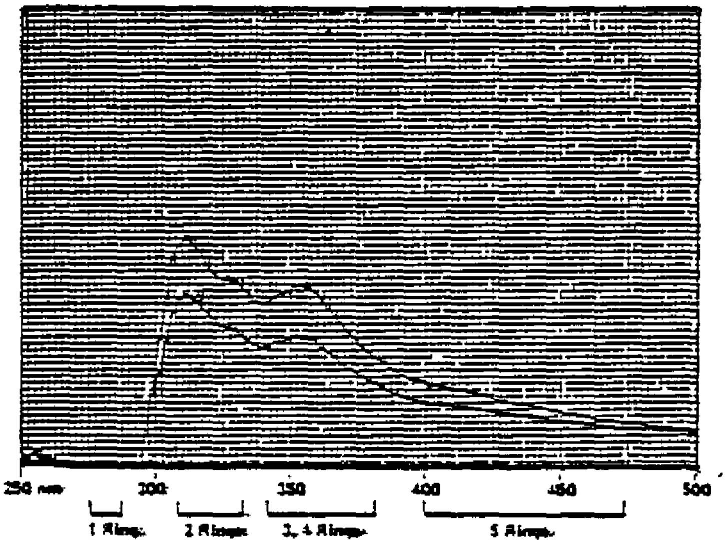


Figure 2—25. Sychronous UV/F Spectra of Sediment Sample Showing Typical Gulf of Mexico Background (A) Mixed with Possible Oil Contamination.

sample such as that shown in Figure 2-25a small incremental additions of oil would be difficult to discern from the fluorescent background characteristic of many Gulf coast sediments (Boehm and Fiest, 1980c).

2.3.2.2 FSCGC Analysis

On those samples selected for further analysis, FSCGC was used to obtain quantitative results on the gross saturated and aromatic fractions, and to obtain quantitative information on individual components (n-alkanes, isoprenoid alkanes), component groupings, and component ratios. Those parameters quantified and stored in the data base are shown in Table 2-14. Most of these parameters were available in the 1975-1977 STOCS data and were calculated here in anticipation of data comparisons.

Summaries of the total hydrocarbon levels observed in the sediments as determined from FSCGC traces are presented in Figures 2-26 and 2-27.

Concentrations fell into the 0.5-20 ppm range throughout the study area. In general, the hydrocarbon concentrations determined were directly related to the total organic carbon (TOC) content of the sediment and, at least on the gross (ppm) level, had no connection with *Ixtoc I* or *Burmah Agate* petroleum additions. For the most part PHC levels in sediments seem to be dictated by the geochemical ratio of PHC/TOC $\sim$0.006 (or 0.6%) throughout the study region. PHC versus TOC plots have been previously employed as diagnostic tools for looking at hydrocarbon sources (Boehm and Fiest, 1980c; Boehm, 1978). In nearshore nonpolluted sedimentary environments subjected to background inputs of PHC (i.e., chronic inputs) the PHC/TOC ratio will remain relatively constant if similar sources dictate the hydrocarbon geochemistry of the sediment. If oil from a spill should impact a sampling site, a proportionately greater amount of PHC will be added to the sediment as the PHC/TOC ratio in oils is very large ($\geq$ 0.5). Thus small additions of oil, on the order of 10 ppm, should easily be detected via PHC/TOC plots such as those shown in Figures 2-28 and 2-29.

Several 1979 and 1980 samples appear to be atypical of the regions' geochemical makeup (i.e., fall off the regression) and thus should be evaluated further for the presence of oil. This was accomplished by evaluating FSCGC traces and derived parameters to differentiate new petroleum additions from the 0.5-20 ppm background. FSCGC traces were scrutinized for weathered but nonbiodegraded oil, as biodegraded oil was found in 1980 samples from the south Texas beaches (Figure 2-11b), and for indications of local inputs such as source material from the Port Aransas Channel area (Figure 2-30).

Sediment samples from the study area subjected to FSCGC analysis and scrutinized for any gas chromatographic indication of recent oil (e.g., Figures 2-31, and 2-32) failed to produce any trace of spill-derived oil. Indications of weathered oil inputs were noted in the *Burmah Agate* sediment collection and will be discussed below. In addition, low levels

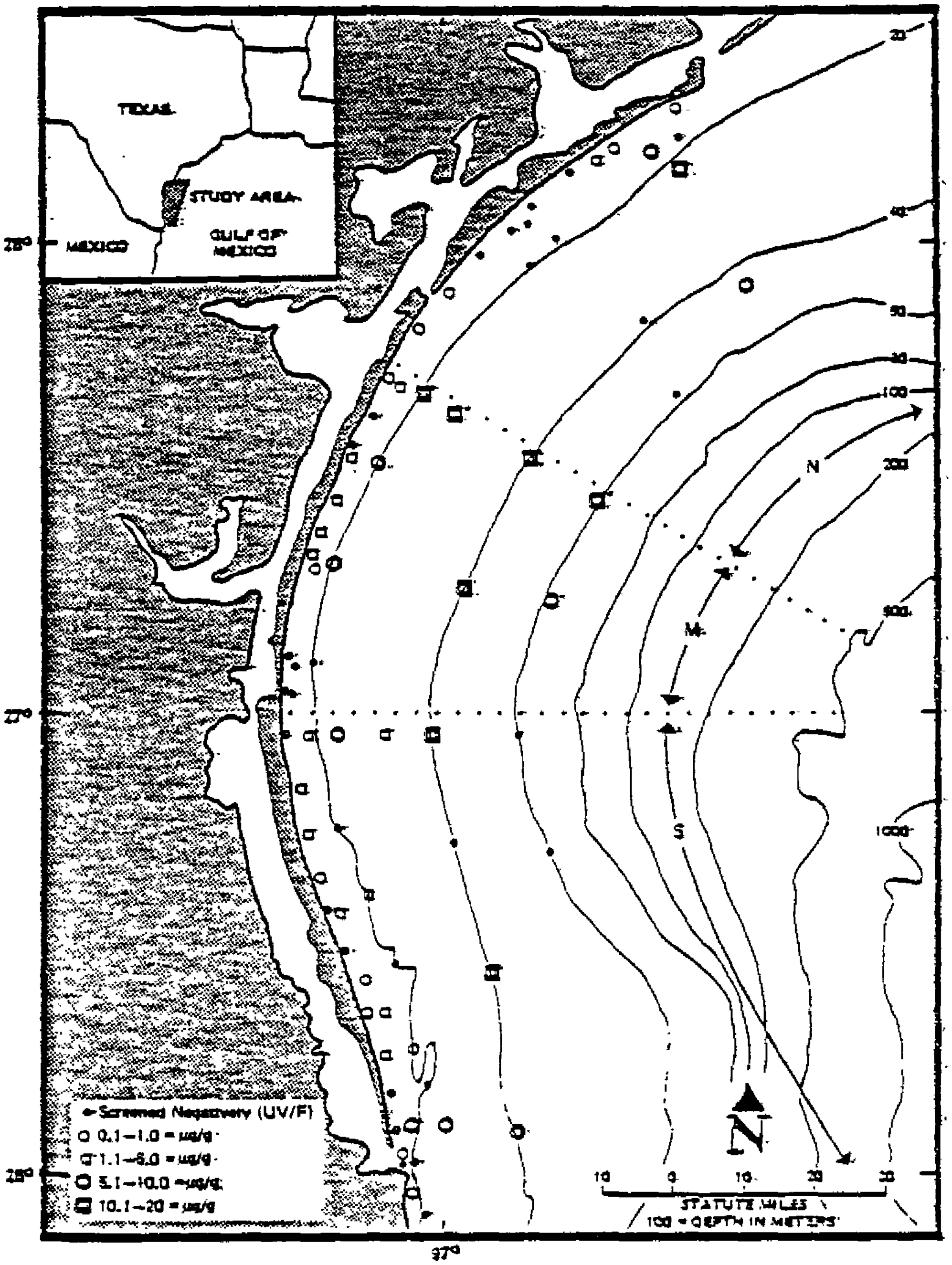


Figure 2–26. Total Hydrocarbons (1979) in Sediments (by FSCGC).

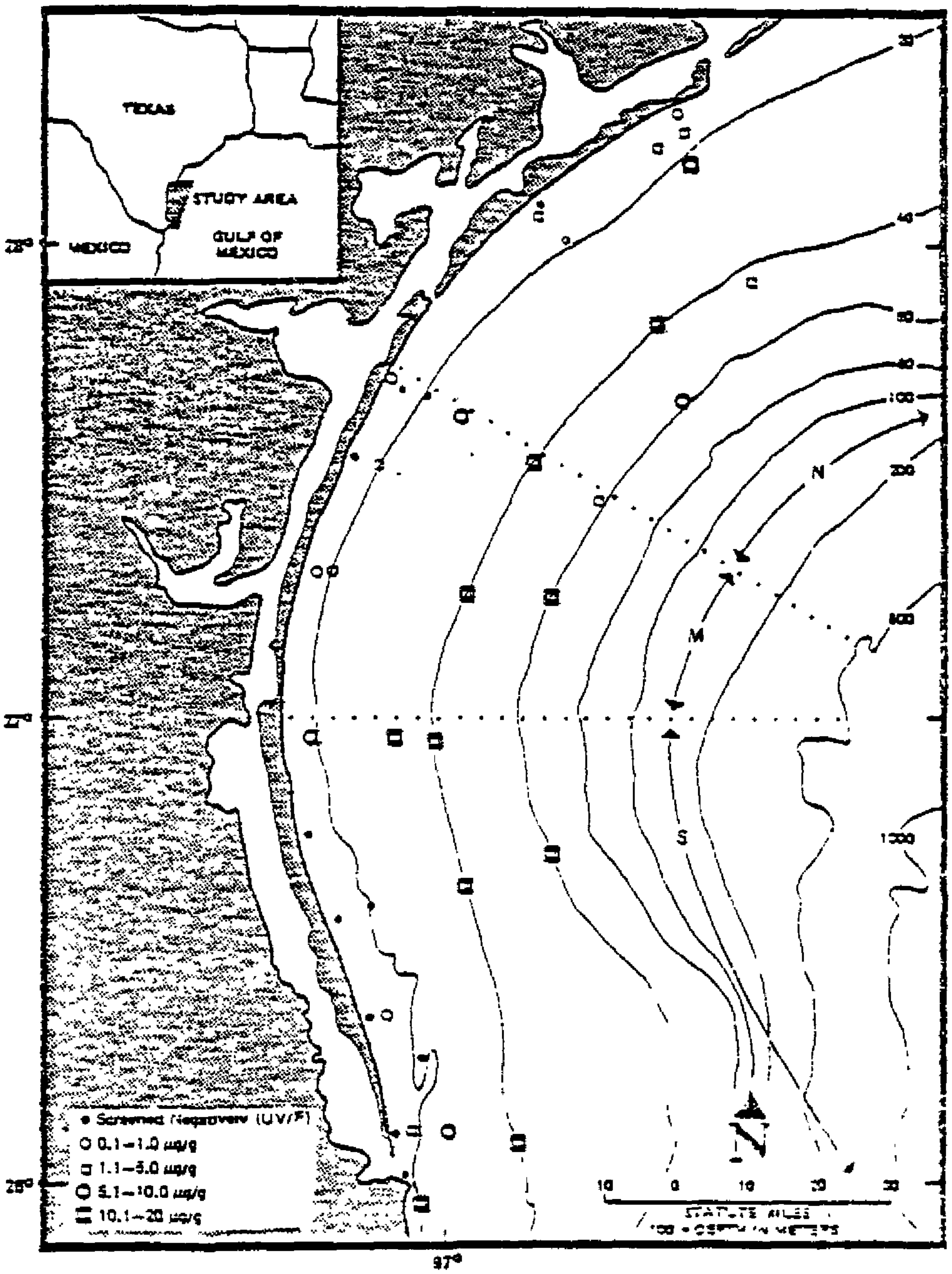


Figure 2–27. Total Hydrocarbons (1980) in Sediments (by FSCGC).