TABLE 2-9

SAMPLE AND DATA COLLECTION SUMMARY:
IXTOC DAMAGE ASSESSMENT

YEAR	SOURCE	NUMBER OF SAMPLES			
		SEDIMENTS	SHRIMP	SORBENT PADS	BEACHED OILS
1974	STOCS* Data (pre-spill)	0	6		
1975	STOCS* Data (pre-spill)	18	8		
1976	STOCS* Data (pre-spill)	82	12		
1977	STOCS* Data (pre-spill)	37	15		
1979	RRT Samples (mid-spill)	99	65	9	30
1980	BLM Cruise Samples (post-spill)	44	51	0	23

*STOCS data are from the 12 primary stations only.

2.2.2 Sample Analysis

The analytical strategy for the chemical assessment consisted of three levels (Figure 2-2). In the first level, samples were extracted and analyzed by ultraviolet spectrofluorometry (UV/F) to screen them for the presence of petroleum. Those samples either suspected of containing petroleum or of interest due to time and position of the sampling were carried through to the next level, fused silica glass capillary gas chromatography flame ionization detection (FSCGC) and stable isotope analysis. These techniques were used to distinguish petroleum hydrocarbons from biogenic hydrocarbons and to identify the source of petroleum. Confirmation of the identity of the oil and measurement of low levels of aromatic hydrocarbons were both accomplished during the third phase when computer-assisted gas-chromatographic/mass spectrometry (GC/MS) was used. Additionally, capillary gas chromatography with sulfur-specific detection (Hall conductivity detector - S mode) was used to focus on the organic sulfur compounds. Nitrogen heterocyclic compounds were determined on a selected set of samples using gas chromatography/flame ionization detection (GC/FID) of the nitrogen compounds, following acidic extraction of the organic extract.

Four types of samples - sediments, tissues, beached oils, and sorbent pads - were analyzed within this study, each according to a slightly different analysis scheme. Each sample type required a unique initial processing/sample extraction protocol and followed its own analytical decision tree. Sorbent pads and oil samples contained oil and were immediately analyzed by Level 2 techniques, FSCGC and stable isotope analysis, without a Level 1 screening (Figure 2-7). Shrimp and sediment samples were first analyzed by the Level 1 technique, UV/F, and subsequently analyzed by Level 2 and Level 3 methods (Figures 2-8 and 2-9). Each step of the hierarchical analytical scheme is discussed below.

2.2.2.1 Sample Processing

The initial step of the chemical analysis was to extract the petroleum hydrocarbons from the sample matrix. This process was unique for the oils, sorbent pads, shrimp, and sediments. Subsequent analytical steps were nearly identical for all samples.

Oils

Two types of oil samples were received: tar and heavily oiled beach sediment . An aliquot of each tar sample was removed with a metal spatula, dissolved in dichloromethane, and dried using sodium sulfate. A measured aliquot (5 percent) of the dichloromethane (Baker resianalyzed) was weighed on a Cahn Model 26 electrobalance to determine the total lipid concentration.

One aliquot of the dichloromethane extract was removed to isolate the asphaltenes for stable isotope analysis. The volume of dichloromethane solvent containing about one gram of oil was transferred to a 50-ml centrifuge

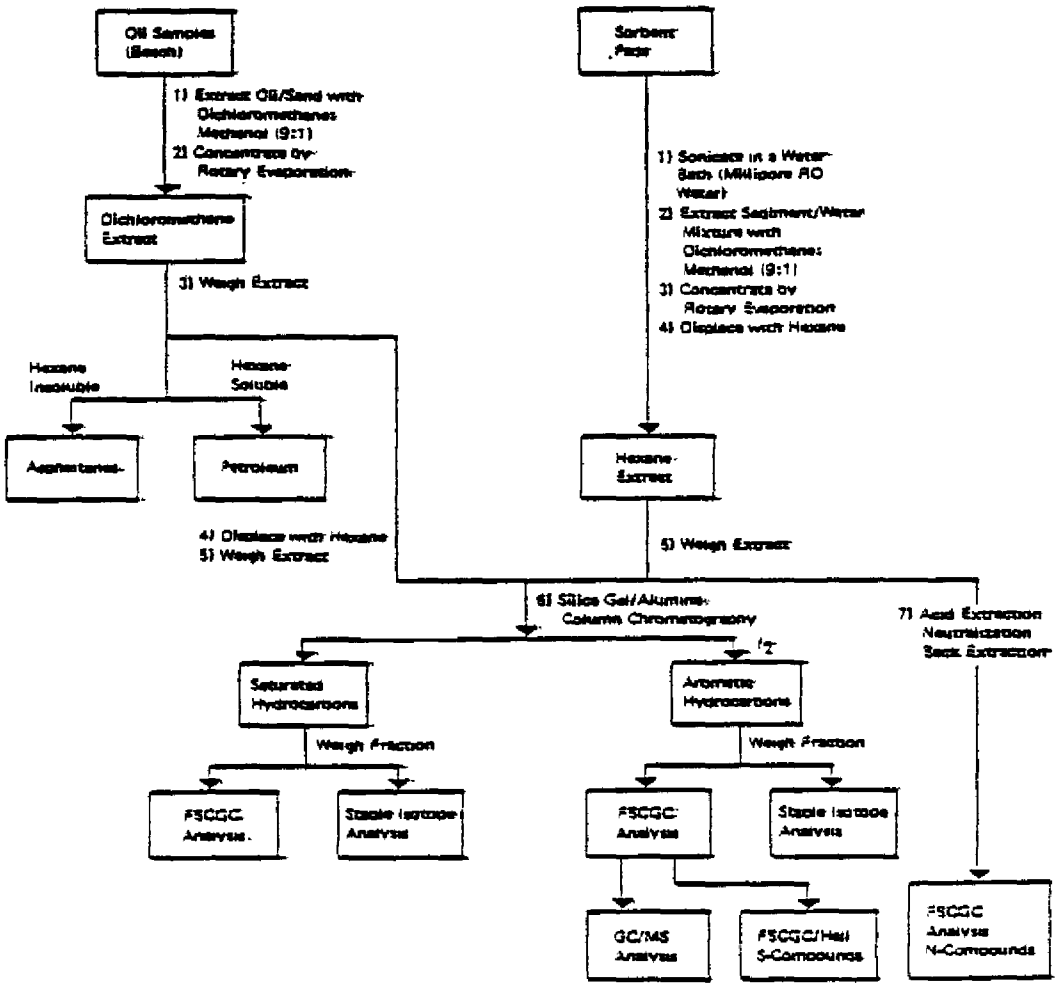

Figure 2—7. Analytical Scheme for Hydrocarbon Analysis for Sorbent Pads and Oil Samples.

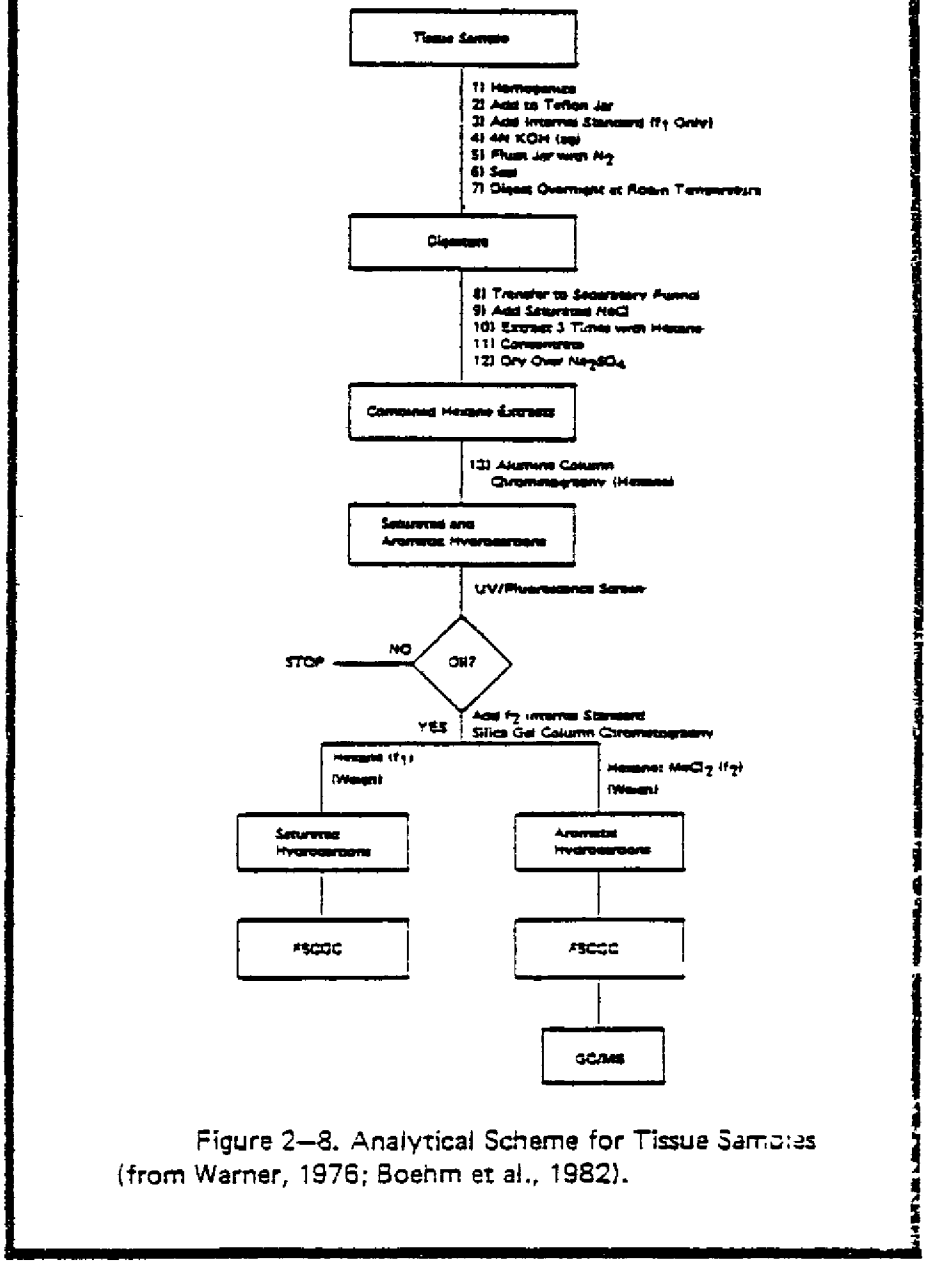

Figure 2–8. Analytical Scheme for Tissue Samples (from Warner, 1976; Boehm et al., 1982).

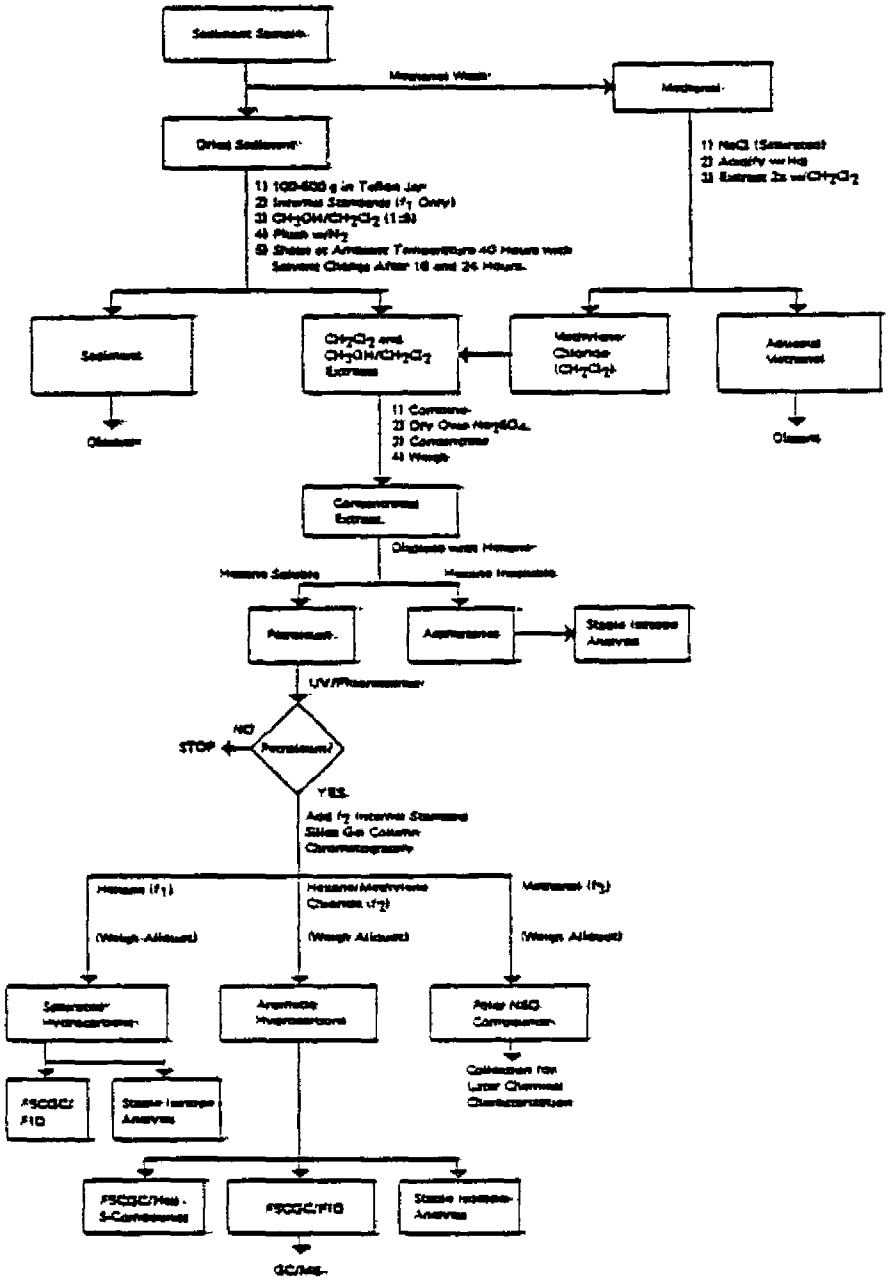

Figure 2–9. Analytical Scheme for Sediment Samples.

tube and concentrated to less than 1 ml under a stream of nitrogen. Thirty ml of hexane were added to precipitate the asphaltenes, which were isolated by centrifugation. The asphaltenes were washed with an additional 30 ml of hexane, then redissolved in dichloromethane.

A second aliquot of the dichloromethane extract was spiked with 10 ug each of androstane and d_{10}-phenanthrene and fractionated by silica gel/alumina column chromatography, after which each of the resulting saturated and aromatic hydrocarbon fractions was analyzed by FSCGC. The fractionation and FSCGC procedures are described in subsequent sections (2.2.2.3 and 2.2.2.4). Selected samples were analyzed by GC/MS and GC/Hall sulfur techniques (see Sections 2.2.2.5 and 2.2.2.6).

Heavily oiled beach sands were treated in a slightly different manner. Approximately 100 g of wet sediment was weighed into a 250-ml Teflon jar and dried by extracting three times with 100 ml of methanol. The methanol was transferred into a 500-ml separatory funnel containing 100 ml of water (Millipore RO), acidified to a pH of 2 with hydrochloric acid, and extracted three times with 30 ml of dichloromethane. The dry sediment was then extracted three times with 100 ml of dichloromethane:methanol (9:1) by shaking for a minimum of 8 hr for each extraction. All solvent extracts were combined, dried using sodium sulfate (Baker, precombusted at 400° C for 16 hr), and concentrated by rotary evaporation. At this point, aliquots were removed for precipitation of asphaltenes and column chromatography/FSCGC as for the tar samples.

Sorbent Pads

The sorbent pad samples were collected during the 1979 RRT program by placing a spun polymer pad in the cod end of a trawl net and doing an oblique tow. The pad collected oil and sediment suspended in the water column. Initial testing showed that rinsing an unused polymer pad with solvent partially dissolved the pads and produced significant quantities of interfering peaks in the gas chromatograms of the solvent. Consequently, an aqueous extraction of the pads in a sonic bath was used to [illegible] attached sediment and oil.

The sorbent pad was unfolded and placed into a solvent-rinsed metal ultrasonic water bath with 500 ml of water. Sonification for 5 to 15 minutes produced a suspension of sediment in water, which was siphoned with a Teflon tube and saved. The pad was then washed with an additional 500 ml of water. After washings were combined and allowed to settle for 16 hr, the aqueous phase was decanted into a separatory funnel, acidified with hydrochloric acid, and extracted three times with 30 ml of dichloromethane. The solid phase was transferred to a 250-ml Teflon jar and extracted with methanol and dichloromethane:methanol (9:1), using the procedure for the oiled beach sediments described above. Approximately 10 ug each of androstane and d_{10}-phenanthrene were added as internal standards.

The concentrated extract was fractionated by silica gel/alumina column chromatography into saturated and aromatic fractions, which were analyzed by an FSCGC (see Sections 2.2.2.3 and 2.2.2.4). The aromatic fractions of selected samples were analyzed by GC/MS (see Section 2.2.2.5).

Shrimp

Frozen shrimp samples were received in sealed glass jars. The species of the shrimp in the sample was confirmed by observing markings and shell characteristics.

The extraction and analytical procedure was based closely on that of Warner (1976) as revised by Boehm et al. (1982). The extraction and separation procedure follows.

Fifty to one hundred g (wet) of penaeid shrimp (a minimum of 12 individuals) were shelled, deheaded and minced with a sharp knife. A small aliquot of the tissue homogenate was taken for wet weight/dry weight determination. The remaining sample was transferred to a Teflon jar, and 50 ml of 4N KOH(aq) and 50 ml of methanol were added. Only a saturated internal standard (10 µg of androstane) was added at this time so as not to interfere with UV/F determinations. The mixture was flushed with nitrogen, sealed and allowed to digest at 60° C for 4 hr. The mixture was then transferred to a separatory funnel and extracted three times with 50 ml of hexane. The hexane was dried with sodium sulfate, concentrated, charged to an alumina cleanup column (12 g of 5% deactivated alumina), and eluted with 30 ml of dichloromethane. The dichloromethane was concentrated, displaced with hexane, charged to an alumina chromatography column (6.5 g of 7.5% deactivated alumina; 2 g Na_2SO_4) and eluted with 25 ml of hexane. The fraction was concentrated to 1 ml by rotary evaporation, at which time the extract was ready for UV/F analysis.

All extracts were analyzed by Level 1 UV/F (see Section 2.2.2.2). Selected samples were then fractionated by silica gel/alumina column chromatography into saturated and aromatic fractions which were analyzed by FSCGC (see Sections 2.2.2.3 and 2.2.2.4). The aromatic fractions of some of these samples were also analyzed by GC/MS (see Section 2.2.2.5) and/or FSCGC (Hall detector - S mode) (see Section 2.2.2.6). Prior to FSCGC and GC/MS analyses of aromatic fractions d_{10}-phenanthrene was added as a quantification standard. Aromatic compound concentrations, thus dervied, were corrected for method recoveries (60-80%).

Sediments

Sediment samples were received in sealed glass jars and polyethylene bags. Preliminary experiments showed that water leaches of the polyethylene bags contained few and insignificant levels of interfering peaks when analyzed by UV/fluorescence and fused silica capillary gas chromatography.

The extraction method for the sediment samples was based on those of Brown et al. (1979) and Boehm et al. (1981b).

Approximately 100 g of wet sediment was weighed into a 250-ml Teflon jar and dried by extracting three times with 100 ml of methanol. The methanol was transferred into a 500-ml separatory funnel containing 100 ml of water (Millipore RO), acidified to a pH of 2 with hydrochloric acid and extracted three times with 30 ml of dichloromethane. The dry sediment was then extracted three times with 100 ml of dichloromethane:methanol (9:1) by shaking for a minimum of 8 hr for each extraction. Approximately 10 µg of androstane was added as an internal standard. All solvent extracts were combined, dried using sodium sulfate and concentrated to 1 ml by rotary evaporation.

At this point, the dichloromethane was displaced with hexane to precipitate any polar and asphaltic compounds. The hexane was decanted and analyzed by UV/F (see Section 2.2.2.2), and the asphaltenes were redissolved in dichloromethane and stored at 4° C awaiting stable isotope analysis. Selected samples were fractionated by silica gel/alumina column chromatography into saturated and aromatic fractions, which were analyzed by FSCGC (see Sections 2.2.2.3 and 2.2.2.4) and stable isotope analysis (see Section 3.2). The aromatic fractions of some of these samples were analyzed by GC/MS (see Section 2.2.2.5). D_{10}-phenanthrene was added as a quantification standard prior to FSCGC and GC/MS analyses. Another subset of samples was analyzed by FSCGC (Hall-S-mode) to examine the organo-sulfur compound composition of the sediments (see Section 2.2.2.6).

2.2.2.2 UV Fluorescence Analysis

Although fixed excitation UV/fluorescence was called for in the original contract, the synchronous excitation/emission technique has been widely employed in recent years to examine the detailed fluorescent properties of environmental samples. The contract was modified to allow analysis of the shrimp and sediment samples by both fixed excitation and synchronous excitation/emission techniques. The purpose of the UV/F screening was to identify those samples containing elevated levels of petroleum suspected to be from the Ixtoc I blowout.

The fixed excitation technique was based on the method of the United States Coast Guard (1977). The sample was diluted to a working concentration range with hexane and transferred to a 10-mm square quartz cell for analysis. For the fixed excitation technique, the excitation monochromator was held at a constant wavelength (254 nm), while the emission monochromator was scanned from 250 to 500 nm. Instrumental conditions are listed in Table 2-10.

The synchronous excitation technique was based on the methods of Wakenam (1977) and Gordon and Keizer (1974). A measured aliquot of the sample extract was dissolved in a known volume of hexane. The intensity of the

TABLE 2-10

UV SPECTROFLUOROMETRY ANALYTICAL CONDITIONS

Instrument:	Farrand Mark I spectrofluorometer	
Features:	Corrected excitation Corrected emission	
Slits:		
Excitation:	2.5 nm	
Emission:	5.0 nm	
Scan speed:	50 nm/min	
Cell:	10 mm quartz	
Monochrometers:	Synchronous	Fixed
Excitation:	225-475 nm	254 nm
Emission:	250-500 nm	250-500 nm
Daily calibration:	API No. 2 fuel oil	
Quantification:	External standard	

fluorescence emission was measured from 250 to 500 nm while synchronously scanning the excitation monochrometer at a wavelength 25 nm smaller than the wavelength of the emission monochrometer. This technique measures aromatic hydrocarbons with a two- to five-ring aromatic structure (Lloyd, 1971).

The intensities of the fluorescence spectra were measured at several wavelengths (Table 2-11), which correspond to peak maxima present in an Ixtoc I reference oil sample. The fluorescence spectra were converted to relative concentration units by comparing the peak height at each wavelength to that of the appropriate No. 2 fuel oil standard curve. No. 2 fuel oil was used as the calibration standard as it yields a very reproducible and widely available standard. Since the exact composition of the fluorescent material in the shrimp and sediment samples was not uniform and not known, a single suitable calibration standard such as Ixtoc I could not be used.

2.2.2.3 Fractionation

Those sediment and shrimp samples chosen for Level 2 analyses and all of the oil and sorbent pad samples were fractionated by silica gel/alumina column chromatography prior to fused silica capillary gas chromatography. Column chromatography isolated the saturated and aromatic hydrocarbons from the total extract, thereby facilitating the identification and quantification of individual hydrocarbon compounds which were present in the sample extract.

The procedure was that of Boehm et al. (1982) and is summarized below.

The total extract was charged to a 100% activated silica gel/5% deactivated alumina/activated copper (11 g, 1 g, 2 g) chromatography column that was wet-packed in dichloromethane and prepared by eluting with 30 ml each of dichloromethane and hexane. The column was eluted with 18 ml of hexane followed by 21 ml of hexane:dichloromethane (1:1) to isolate the saturated (f_1) and unsaturated (f_2) hydrocarbons, respectively. After concentrating each fraction by rotary evaporation, the total gravimetric concentration was determined by weighing a measured aliquot on a Cahn Model 26 electrobalance.

2.2.2.4 Fused Silica Capillary Gas Chromatography

Fused silica capillary gas chromatography (FSCGC) analysis served to identify and quantify the petroleum hydrocarbon compounds present in the sample. The relative concentrations of individual compounds served to fingerprint the type of oil present, and the absolute concentrations served as a measure of the amount of oil present. The concentrations of certain compounds were also used to calculate indicator ratios that reveal the type of hydrocarbons present, i.e., biogenic or petroleum, and the weathering age of the petroleum.

Each fraction was analyzed by fused silica capillary gas chromatography on a Hewlett Packard 5840 gas chromatograph equipped with a splitless injection

TABLE 2-11

UV SPECTROFLUOROMETRY DATA OUTPUTS

Synchronous Excitation:	
Wavelengths (nm):	310, 356, 400, 437
Concentration units:	$\mu g \cdot g^{-1}$ dry weight #2 fuel oil equivalents
Fixed Excitation:	
Wavelengths (nm):	320, 355, 400, 437
Concentration units:	$\mu g \cdot g^{-1}$ dry weight #2 fuel oil equivalents

port and a flame ionization detector. Wall Coated Open Tabular fused silica columns (0.25 mm x 30 m, J&W Scientific) coated with SE30 and SE52 stationary phase were used to analyze the f_1 and f_2 from the column chromatography respectively. The instrumental conditions are listed in Table 2-12. Compounds were identified by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture that was analyzed daily. Concentrations were calculated by comparing the integrated areas of peaks with the area of the appropriate internal standard (androstane for the f_1, d_{10}-phenanthrene for the f_2). The total concentrations of saturated and aromatic hydrocarbons were determined by planimetering the unresolved area, converting it to integrator area units, adding it to the total resolved integrated area, and calculating a concentration using the internal standard method.

The analytical outputs from the FSCGC are listed in Tables 2-13, 2-14, and 2-15. The concentrations of n-alkanes and isoprenoids were reported on a dry weight basis. From these concentrations a series of key diagnostic parameters were calculated. These ratios are useful in establishing the source of the oil, the contribution of biogenic hydrocarbons, and the degree that the oil was weathered.

2.2.2.5 Gas Chromatography/Mass Spectrometry

Selected samples found to contain petroleum by the Level 2 analyses were analyzed by fused silica capillary gas chromatography/mass spectrometry (GC/MS) to verify the source of petroleum or to identify the petroleum source in samples for which the n-alkane fingerprint was weathered and therefore inconclusive. The concentrations of a series of polynuclear aromatic hydrocarbons, in particular the alkylated phenanthrenes and dibenzothiophenes, serve as a fingerprint of weathered petroleum.

The f_2 (aromatic fraction) from the silica gel/alumina column chromatography (see Section 2.2.2.3) was analyzed for polynuclear aromatic hydrocarbons by GC/MS. An aliquot of the fraction was analyzed using a Hewlett Packard 5985 instrument equipped with a 0.25 mm x 30 m SE52 fused silica capillary column (J&W Scientific), which was threaded directly into the ion source. Instrumental conditions are listed in Table 2-16.

Selected ion searches were used to obtain ion chromatograms for aromatic compounds with known retention indices and suspected to be present in the samples. If necessary the mass spectrum and retention time of an identified peak was retrieved and compared with an authentic standard or to a mass spectrum library to aid in identification of the compound. An in-house probability-based computer matching system, the HP 7920 multi-disc system containing EPA/NIH probability-based mass spectral libraries, was utilized for this purpose.

Concentrations of the identified compounds were determined by measuring peak areas of the appropriate peaks in the selected ion chromatograms and relating them to that of the internal standard. Relative response factors

TABLE 2-12

FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY/
FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS

Instrument:	Hewlett Packard 5840 gas chromatograph
Features:	Split/splitless capillary inlet system Microprocessor-controlled functions
Inlet:	Splitless
Detector:	Flame ionization
Column:	
f_1:	0.25 mm I.D. x 30 m SE30 fused silica (J&W Scientific)
f_2:	0.25 mm I.D. x 30 m SE52 fused silica (J&W Scientific)
Gases:	
Carrier:	Helium 2 ml/min
Make-up:	Helium 30 ml/min
Detector:	Air 240 ml/min
Temperatures:	
Injection port:	250° C
Detector:	300° C
Column oven:	40-290° C @ 3° C/min
Daily calibration:	Alkane/aromatic mixture
Quantification:	Internal standard (f_1 androstane, f_2 d_{10} phenanthrene)

TABLE 2-13

COMPOUNDS QUANTIFIED BY FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY

COMPOUND	ANALYTICAL TECHNIQUE	USE
Saturated hydrocarbons		
n-alkanes ($n\text{-}C_{10}$ to $n\text{-}C_{34}$)	Capillary GC	Weathering and source indicators, especially when ratios are derived
Isoprenoids (farnesane, pristane, phytane, 1650, 1380)	Capillary GC	Weathering indicator (marker compounds as a group in lightly weathered samples)

TABLE 2-14

FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY ANALYTICAL OUTPUTS
(KEY DIAGNOSTIC PARAMETERS)

VARIABLE	DEFINITION OR ABBREVIATION	UNITS
1. Sum of n-alkanes, C_{14}-C_{32}	N-alkanes (C14-C32)	$\mu g \cdot g^{-1}$
2. Pristane/phytane	Pr/Ph	-
3. Pristane/n-C_{17}	Pr/n-C17	-
4. Phytane/n-C_{18}	Ph/n-C18	-
5. (Pristane + phytane)/sum of n-alkanes		-
6. Sum of n-alkanes, C_{14} to C_{18}	SUM LOW	% of total n-alkanes
7. Sum of n-alkanes, C_{19} to C_{24}	SUM MID	% of total n-alkanes
8. Sum of n-alkanes, C_{25} to C_{32}	SUM HI	% of total n-alkanes
9. Average OEP of n-alkanes, C_{14} to C_{18}	OEP LOW	-
10. Average OEP of n-alkanes, C_{19} to C_{24}	OEP MID	-
11. Average OEP of n-alkanes, C_{25} to C_{32}	OEP HI	-
12. Average OEP of n-alkanes, C_{14} to C_{32}	AV. OEP	-
13. Average OEP of n-alkanes, C_{14} to C_{20}	OEP1	-
14. Average OEP of n-alkanes, C_{20} to C_{32}	OEP2	-
15. CPI of n-alkanes, C_{14} to C_{20}	CPI1	-
16. CPI of n-alkanes, C_{20} to C_{32}	CPI2	-
17. Alkane/isoprenoid ratio	ALK/ISO	-
18. Saturated hydrocarbon weathering ratio	SHWR	-
19. Aromatic weathering ratio (GC/MS)	AWR	-

TABLE 2-15

EXPLANATION OF PETROLEUM WEATHERING RATIOS

The Biodegradation Ratio (Alkane/Isoprenoid)

$$ALK/ISO_{14-18} = \frac{[1400] + [1500] + [1600] + [1700] + [1800]}{[1380] + [1470] + [1650] + [1708] + [1810]}$$

The ALK/ISO ratio approaches 0 as the n-alkanes are depleted.

The Saturated Hydrocarbon Weathering Ratio (SHWR)

$$SWHR = \frac{[\text{sum of n-alkanes from n-}C_{10} \text{ to n-}C_{25}]}{[\text{sum of n-alkanes from n-}C_{17} \text{ to n-}C_{25}]}$$

The SWHR approaches 1.0 as low-boiling saturated hydrocarbons (n-C_{10} to n-C_{17}) are lost by evaporation.

The Aromatic Weathering Ratio (AWR)

$$AWR = \frac{\text{Total naphthalenes + fluorenes + phenanthrenes + dibenzothiophenes}}{\text{Total phenanthrenes + dibenzothiophenes}}$$

The AWR approaches 1.0 as low-boiling aromatics are lost by evaporation and/or dissolution.

TABLE 2-16

GAS CHROMATOGRAPHY/MASS SPECTROMETRY INSTRUMENTAL CONDITIONS

INSTRUMENT:	Hewlett Packard 5985 gas chromatograph/mass spectrometer
FEATURES:	HP 5933 data system with 7900 and 7920 disc drives 5840 gas chromotograph
INLET:	Splitless
DETECTOR:	Mass spectrometer
SCAN RATE:	400 amu/sec (46–446 amu)
IONIZATION VOLTAGE:	70 eV
COLUMN:	0.25 mm i.d. x 30 m SE52 fused silica (J&W Scientific)
INTERFACE:	Direct insertion of column into source
CARRIER GAS:	Helium 2 ml/min
TEMPERATURES:	
INJECTION PORT:	250° C
TRANSFER LINE:	300° C
SOURCE:	250° C
GC OVEN:	40–290° C, 3° C/min (temperature program)
DAILY CALIBRATION:	PFTBA and DFTPP aromatic mixture
QUANTIFICATION:	Internal standard (d_{10}–phenanthrene) (response factors)

for each component were calculated from analyses of analytical standards, if available, or were extrapolated. The compounds reported from the GC/MS analyses are listed in Table 2-17.

2.2.2.6 Gas Chromatography/Hall Detector (Sulfur Mode)

Selected oil and sediment samples were analyzed by gas chromatography/ Hall detector (sulfur mode) to obtain a fingerprint of the sulfur compounds for petroleum source identification. The relative concentrations of a series of sulfur-containing polynuclear aromatic hydrocarbons were measured by this technique.

The f_2 (aromatic fraction) from the silica gel/alumina column chromatography (see Section 2.2.2.3) was analyzed for sulfur-containing aromatics by GC/Hall (sulfur mode). An aliquot of the fraction was analyzed using a Hewlett Packard 5850 gas chromatograph to which a Tracor 603 conductivity detector was coupled. The selector was operated in the sulfur mode. Compounds were identified by comparing the retention times of peaks in the sample with retention time of known compounds. Since the trace was used as a fingerprint, identification of every compound was not necessary and only relative concentrations were reported. A series of nine peaks corresponding to alkyldibenzothiophenes were reported.

2.2.2.7 Acid Extraction of Nitrogen-Containing Compounds

Selected oil samples were analyzed for nitrogen-containing aromatic compounds by using an acid extraction technique to isolate the compounds and FSCGC and GC/MS to identify the compounds.

The procedure for isolating the nitrogen-containing compounds was similar to that of Overton et al. (1980). In summary: an aliquot of the total extract of oil samples was dissolved in 20 ml of hexane and extracted three times with 20 ml of 3N hydrochloric acid. The acidic aqueous extract was back-extracted twice with 20 ml of hexane, made basic with 6N KOH and extracted three times with 20 ml each of dichloromethane. The combined dichloromethane extracts were dried with sodium sulfate, concentrated by rotary evaporation, and finally concentrated under a nitrogen stream. The extracts were analyzed by FSCGC and GC/MS using conditions described in Sections 2.2.2.4 and 2.2.2.5, respectively.

2.3 Results

The hydrocarbon compositions and concentrations of the environmental samples examined by a number of screening and definitive analytical techniques are presented in this section. First the chemical criteria for establishing the presence of oil in environmental samples of sediments and tissues are examined in detail through a suite of oil/tar samples and then

TABLE 2-17

GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYTICAL OUTPUTS

POLYNUCLEAR AROMATIC HYDROCARBONS
C_4 to C_6 Benzenes
Naphthalene
2-Methyl naphthalene
1-Methyl naphthalene
C_2 to C_4 Alkyl naphthalenes
Biphenyl
Acenaphthene
Fluorene
C_1 to C_3 Fluorenes
Phenanthrene
C_1 to C_4 Phenanthrenes
Dibenzothiophene
C_1 to C_3 Dibenzothiophene
Fluoranthene
Pyrene
C_1 Pyrene
Benzo(a)anthracene
Chrysene
C_1 Chrysene
Benzofluoranthene
Benzo(a)pyrene
Benzo(e)pyrene
Perylene

these criteria applied to the sediments and tissues. Although stable isotope results are incorporated to some extent in this section, the isotopic results are presented in greater detail in Section 3.

2.3.1 Oils and Tars

The source evaluation strategy for oils/tars focused on three primary analyses: (1) FSCGC of saturated hydrocarbons to derive n-alkane information, (2) GC/MS of aromatic hydrocarbons, and (3) stable isotope ($\delta^{13}C$, δD, $\delta^{34}S$) measurements of hydrocarbon and asphaltene fractions. The first two are discussed in this section, with a summary of all techniques. Details of the stable isotope analyses will be found in Section 3.

2.3.1.1 UV/F Analyses

In order to establish the UV/F pattern of a variety of weathered oil residues from both the Ixtoc and Burmah Agate spills, a variety of oil/tar samples were analyzed by UV/F. The range of the resultant spectra indicates that Ixtoc and Burmah Agate oils exhibit similar fluorescence patterns, the latter having a greater abundance of compounds that fluoresce in the 310-nm (two-ring) region. However, the overall spectral appearance of the two oils is the same. In highly weathered Ixtoc residues (e.g., sample 8012-T05-1001, a 1980 beach tar, Figure 2-10), the spectrum takes on a markedly different appearance with the two-ringed aromatics severely depleted relative to the 1979 oils. Thus a range of UV/F spectral types are possible in environmental samples.

2.3.1.2 Alkanes by FSCGC

A set of 40 samples of waterborne oil, beached oil/tar, and oil associated with organisms was selected for analyses based on several criteria: (1) the samples should cover the geographical range of both spill impact areas, (2) the samples should represent oil available to the ecosystem both in 1979 and 1980 (mid- and post-spill), and (3) the samples should represent both offshore oil and beached oil.

FSCGC analysis first focused on the n-alkane distribution in the samples. N-alkane distributions in samples exhibited various degrees of weathering. As oil weathers, the n-alkanes are subject to loss from the samples. In this spill the losses were mainly through evaporation, as losses due to biodegradation were negligible (Boehm and Fiest, 1980a; Atlas et al., 1980). Thus when FSCGC traces such as Figure 2-11a are transformed to n-alkane relative abundance (NARA) plots, the weathering of the oil can clearly be seen. For example, an Ixtoc weathering sequence (Figure 2-12; Boehm et al., 1981) dramatically shows progressive loss of n-alkanes less than $n\text{-}C_{23}$.

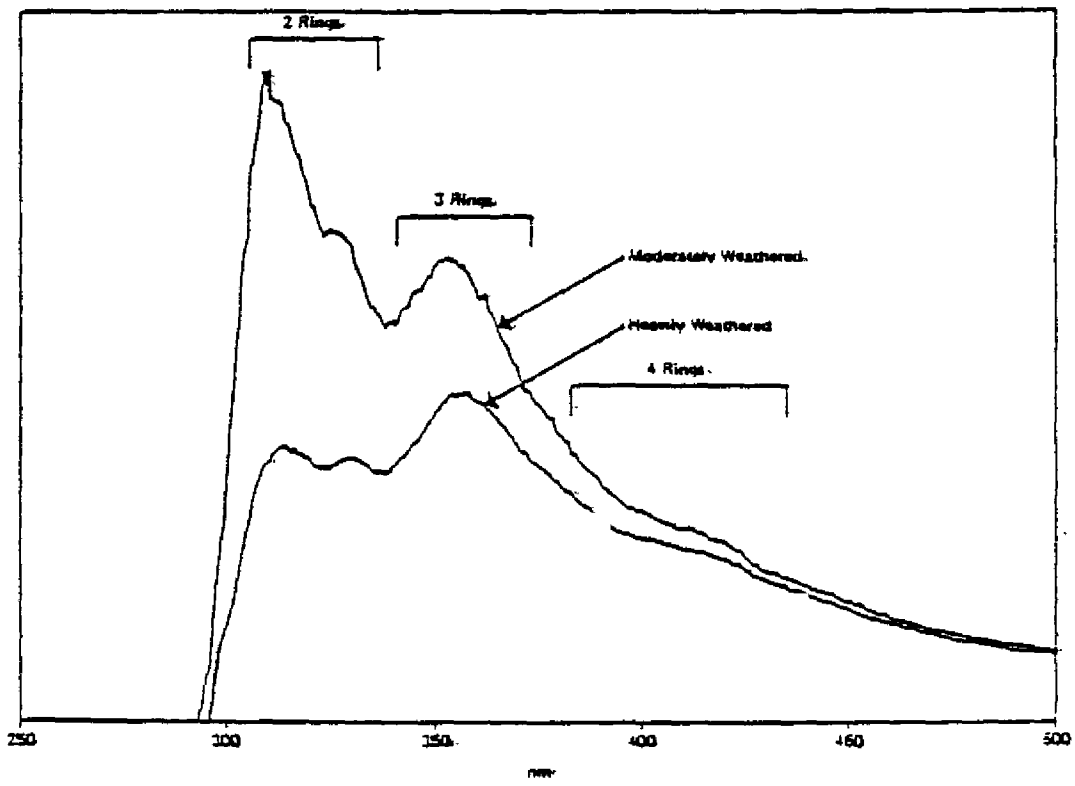

Figure 2–10. UV/F Synchronous Spectra of IXTOC Oils.

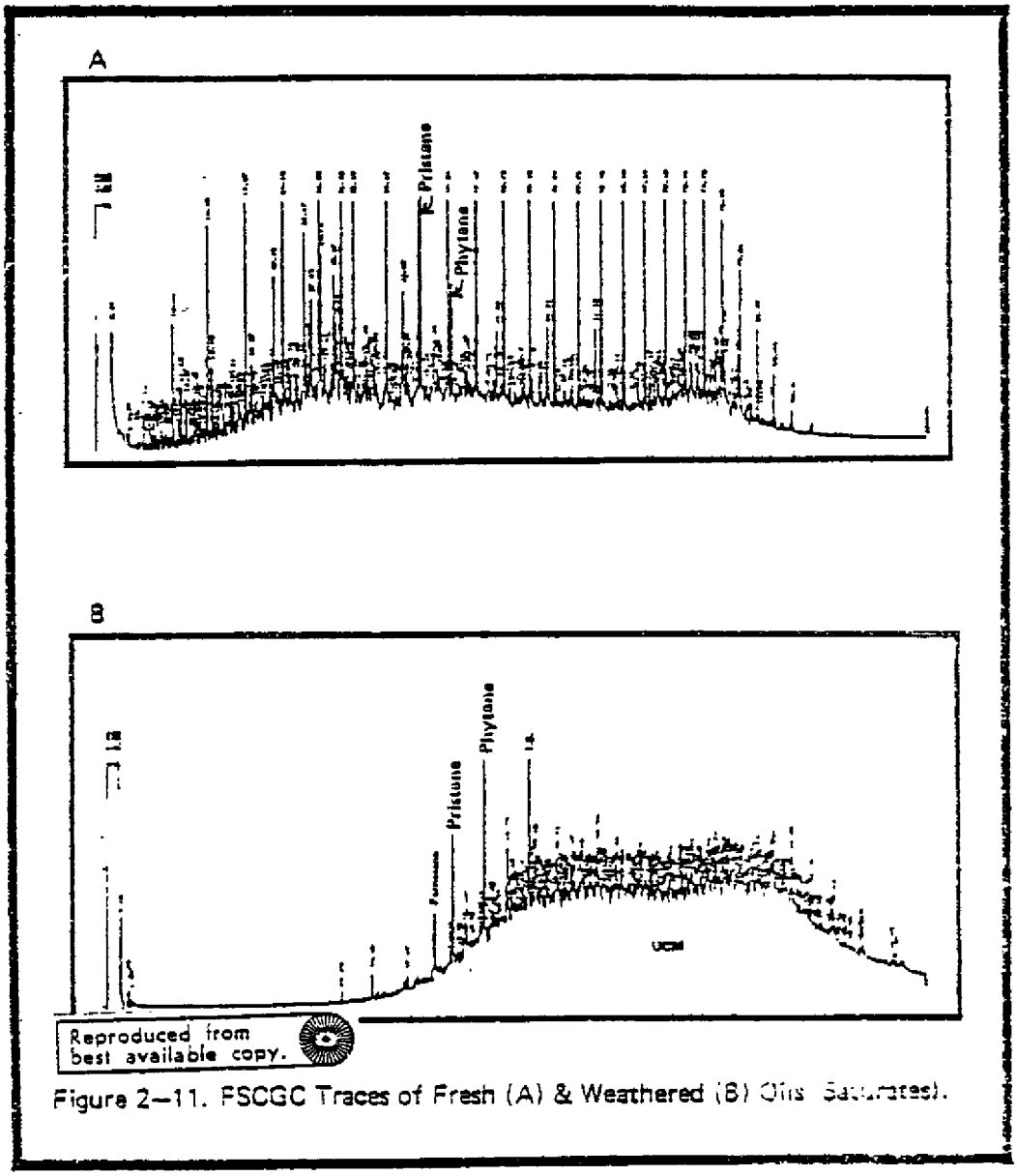

Figure 2—11. FSCGC Traces of Fresh (A) & Weathered (B) Oils (Saturates).

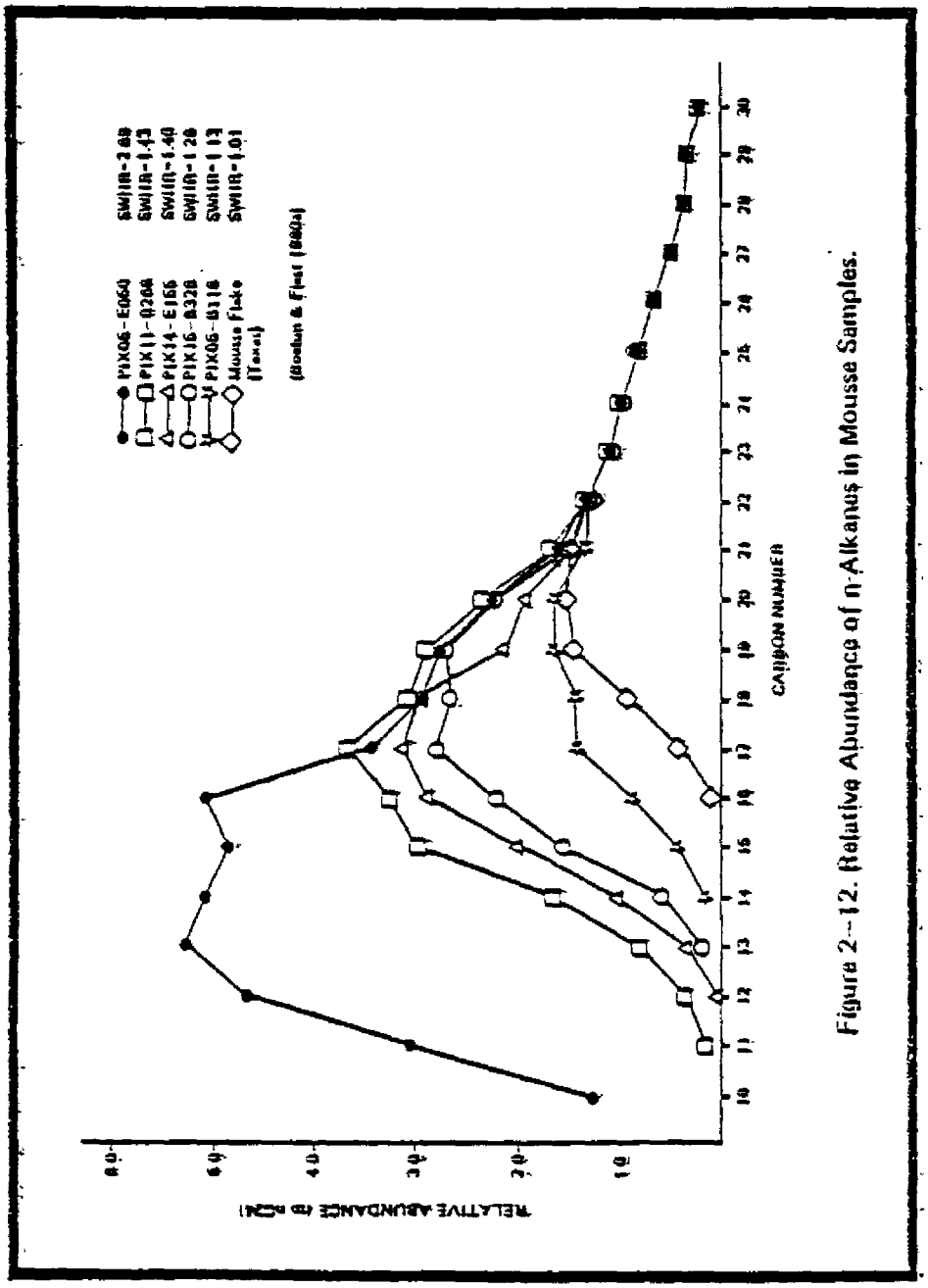

Figure 2-12. Relative Abundance of n-Alkanes in Mousse Samples.

In order to "bracket" the possible Ixtoc compositions on the NARA plots, three samples were selected as representative of three possible weathered Ixtoc residues. The three samples chosen were obtained during the Researcher/Pierce cruise (Boehm and Fiest, 1980a) to the wellhead and during the Longhorn IV cruise off the Texas coast in August 1979 as large patches of Ixtoc mousse (water-in-oil emulsion) entered Texas waters (Patton et al., 1981). These samples then served as reference oils to the 1979 oil/tar collections. Any oil/tar alkane compositions falling into the compositional window illustrated in Figure 2-13 were judged to be Ixtoc-probable oils.

A series of oil samples whose compositions fall within this window are shown in Figure 2-14. In contrast, two other compositions were observed. The first consists of fresh and weathered Burmah Agate oils (Figure 2-15) and the second of two paraffinic beach tars associated with neither spilled oil (Figure 2-16).

Although all of the 1979 oil/tar samples exhibited n-alkane components, thus allowing the evaluation presented above, the 1980 beach tar collection consisted of highly weathered, n-alkane depleted petroleum residues (e.g., Figure 2-11b). These isoprenoid-dominant FSCGC traces, the product of microbial weathering, precluded n-alkane source evaluation. In these cases other source evaluation techniques were required (GC/MS of aromatics; stable isotopes analysis).

2.3.1.3 Aromatic Hydrocarbons in Oils/Tars by GC/MS

For this study the aromatic hydrocarbon composition of petroleum has been classified into two groups: (1) two- and three-ring aromatics and their alkyl homologues, and dibenzothiophene (a sulfur heterocycle) and its alkyl homologues, and (2) four- and five-ring aromatics. The first group of aromatic compounds is dominant in fossil fuel aromatic compositions, especially the alkyl homologues of naphthalene, fluorene, phenanthrene, and dibenzothiophene, and therefore these compounds can be termed petrogenic aromatics. The second group consists of fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzofluoranthene, benzopyrenes, perylene, and their methyl homologues. These compounds, if present in petroleum, are usually present at lower concentration levels than the first group. These polynuclear aromatic hydrocarbon (PAH) compounds are ubiquitous in the geosphere, but their presence in the environment is usually attributable to pyrogenic sources (combustion of fossil fuels; Laflamme and Hites, 1978) rather than to petroleum itself.

Phenanthrene and anthracene, both three-ringed parent (unsubstituted) compounds, are found in both groups. However, alkylated members of these homologous series are more abundant than the parent compounds in petroleum, while the parent compound is more abundant in pyrogenic PAH assemblages. Thus, the abundances of alkylated phenanthrenes/anthracenes relative to the parent compounds are keys to the determination of the presence of petroleum. As petroleum weathers, the alkylated dibenzothiophenes and alkylated phenanthrenes become prominent residuals and become key diagnostic parameters for identifying oils (Boehm et al., 1981; Overton et al., 1981).