SECTION THREE

CHEMICAL ASSESSMENT (STABLE ISOTOPES)

3.1 Introduction

The blowout of the Ixtoc I well in the Bay of Campeche, Gulf of Mexico, resulted in the largest release of oil in the history of the petroleum industry. From the initiation of the blowout on June 3, 1979 to its curtailment in March 1980, more than 0.5 million metric tons (530 million litres) of crude oil were released into the marine environment. From June to September of 1979 the oil moved in a northward direction and began impacting the coastal environments of Texas in August.

During the spill, the Department of Commerce (National Oceanic and Atmospheric Administration) funded a oceangraphic cruise (The Researcher/Pierce Ixtoc I Cruise) to obtain information regarding the chemical nature and physical behavior of the spill. As part of the program, Global Geochemistry Corporation was requested to explore the utility of stable isotopes in both the characterization and tracing of the oil. Based on some previous analyses of tracing beach tars to seepage sources it was felt that the stable isotope ratios (atomic composition) of the oil might serve as a mechanism for tracing the dispersed oil since when compared to the molecular analyses, the atomic composition of oils remained relatively constant with increased oil weathering. The approach of using both molecular distributions (GC and GC/MS) and isotope ratios have been used in the petroleum industry for correlating oils with their source and were found to complement and reinforce each other in differentiating sources and addressing the problems of migration and mixtures (Seifert, Molodowan, and Jones 1979). Similarly the atomic composition of tars and oiled sediments can serve as a tool either for screening samples for future detailed molecular analyses or for supporting conclusions drawn on the basis of the molecular results.

The initial investigations from the Researcher Cruise indicated that: (1) isotopic (atomic) change of the oil varied little with time when compared with the molecular analyses; (2) the carbon isotope ratio of the tars was similar to other oils found in the area; (3) the deuterium values of the tars were all similar to the value for the oil or heavier than -100 parts per thousand (ppt) (SMOW); (4) the sulfur content of the asphaltenes in mousse samples was lower and the corresponding isotope ratio heavier when compared to the tar samples, indicating selective weathering of the sulfur compounds during mousse formation (Sweeney, Haddad, and Kaplan 1980). Although carbon and sulfur isotopes have been used to correlate beach tars with seepage sources in Southern California (Hartman and Hammond, 1981), this initial study was the first attempt in using stable isotopes as means for tracing an oil spill. It was found that while an isotope measurement of a single element (eg. carbon) could point to multiple sources, a crossplot of two or more (hydrogen, carbon, sulfur) isotope ratios was quite useful in differentiating oils from the target spill.

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The previous work has been extended during this study to include analyses of oils, tars, and sediment extracts collected from the coastal areas off Texas in an attempt to identify those oils associated with the Ixtoc I spill and to assess its impact on the sedimentary and corresponding biological communities in the Gulf of Mexico.

The carbon isotopic composition of crude oils has received considerable attention in attempts to clarify the origin of oil deposits. Most of the early studies have been recently summarized by Deines (1980).

Most oils show $\delta^{13}C$ values in the range from -21 to -32 ppt. The frequency distribution shows a slow rise from -20 ppt, a suggestion of bimodality, to a strong maximum at -28 to -29 ppt and a very sharp drop in frequency towards lighter $\delta^{13}C$ values. If, in the frequency distribution of marine sediments, those deposited under special conditions and showing very heavy $\delta^{13}C$ values are for the moment ignored, there is a certain degree of similarity in shape between the $\delta^{13}C$ frequency distribution of the organic carbon from marine sediments and that of petroleum, with a shift of the petroleum $\delta^{13}C$ frequency distribution towards lighter $\delta^{13}C$ values by about 3 ppt. Compared to older sediments, petroleum shows again a similar frequency distribution, but it is also systematically displaced towards lighter isotopic compositions with respect to it. Hence, petroleum is on the average isotopically slightly lighter than the kerogen in sediments. In the few cases where it has been studied, it has been found that this holds true also for oil and supposed source rock. In comparison with coal it appears that in spite of a considerable overlap of the distributions, petroleum (mode -27 to 30 ppt) shows on the average lower $\delta^{13}C$ contents than coal (mode -23 to 26 ppt).

Although the carbon isotopic composition of all oils combined covers more than 10 ppt, it has been found that within a particular oil field the carbon isotopic composition variations can be much more restricted (less than 1 - 2 ppt). Hence, in combination with other oil characteristics $\delta^{13}C$ measurements may be used to characterize and correlate oils and can represent a useful tool to the explorationist. Likewise, $\delta^{13}C$ determinations may be of help to trace the source of major oil spills.

As petroleum is a complex mixture of organic compounds part of the variability in the $\delta^{13}C$ values of petroleum might be related to carbon isotopic composition differences between the different chemical components of crude oil. There have been relatively few studies in which separated chemical compounds or compound groups have been analyzed. In some of these only very small $\delta^{13}C$ differences between petroleum fractions were observed, while in others, systematic trends in $\delta^{13}C$ variations were discovered. Asphaltenes, which contain the highest molecular weight molecules, and tars show a slight $\delta^{13}C$ enrichment with respect to the total oil; wax and paraffin, containing somewhat lower molecular weight molecules show a slight $\delta^{13}C$ depletion with respect to the total oil. For the gaseous components butane, propane, ethane and methane the $\delta^{13}C$ depletion increases with decreasing molecular weight. Another feature worth noting is that in most of the oils studied the saturates are systematically depleted in $\delta^{13}C$ with respect to the aromatic compounds.

Few D/H ratio measurements have been recorded for petroleum. Four

Middle East crude oils were measured by Schiegl and Vogel (1970) and they report an average δD value of -89 ppt. More recently, D/H measurements on fifteen Paleozoic oils from Michigan, U.S.A., yielded a δD range of -90 to -130 ppt (Brand et. al., 1980). In this latter study it was determined that the paraffin fraction was approximately 10 ppt lighter than the aromatic fraction.

In a very recent study, Yeh and Eptein (1981) report data of D/H and $\delta^{13}C$ for 114 petroleum samples and for several samples of related organic matter. δD of crude oil ranges from -85 to 181 ppt, $\delta^{13}C$ of crude oil ranges from -23.3 to -32.5 ppt. Variation in δD and $\delta^{13}C$ values of compound-grouped fractions of a crude oil is small, 3 and 1.1 ppt, respectively, and the difference in δD and $\delta^{13}C$ between oil and coeval wax is slight. Gas fractions are 53 - 70 and 22.6 - 23.2 ppt depleted in δD and $\delta^{13}C$, respectively, relative to the coexisting oil fractions. The δD and $\delta^{13}C$ values of the crude oils appear to be largely determined by the isotopic compositions of their organic precursors.

3.2 Methods and Approaches

Samples of tars and sediments were fractionated at ERCO into saturate and aromatic fractions and received by Global Geochemistry Corporation for sulfur, carbon, and hydrogen isotope analyses. For the majority of the sediments the saturate and aromatic fractions had to be combined to yield enough material for isotope measurement. Approximately one (1) milligram of sample was combusted at 900°C in the presence of cupric oxide and silver metal (Stump and Frazer, 1973). The produced CO_2 was purified and collected for isotope analysis. The water from combustion was converted to molecular hydrogen by reaction with uranium turnings at 800°C, collected on activated charcoal under liquid nitrogen, and transferred to a break-seal tube via a Toeplar pump.

Approximately 0.5 grams of the asphaltenes from the tar and oil samples were combusted in a Parr Bomb in 30 atmospheres of oxygen with the produced sulfate precipitated as $BaSO_4$ (Parr Instrument Company, 1965). Sulfur dioxide was prepared for isotopic analysis by direct combustion of the barium sulfate with quartz powder at 1200°C (Bailey and Smith, 1972).

The stable isotope ratios for carbon were determined on a Nuclide 3" - 60° RMS instrument, the hydrogen on Varian MAT 250, mass spectrometer, and the sulfur on Nuclide 6" - 60° RMS mass spectrometer. All isotopic data are expressed in the standard δ notation:

$$\delta x \text{ sample (ppt)} = \frac{R \text{ sample} - R \text{ standard}}{R \text{ standard}} \times 1000$$

where x represents the element and R the ratio of the rare to abundant isotope of that element. Values for carbon are relative to the Chicago Pee Dee Beleminite (PDB), those for hydrogen are referenced to standard mean ocean water (SMOW), and the sulfur isotopes are relative to the Canyon Diablo Troilite. Precision for carbon, hydrogen, and sulfur are 0.10 ppm, 1.0 ppm, and 0.3 ppm, respectively.

3.3 Results

The fractions of thirty-four oil and tar samples were analyzed for their C,H, and S isotope ratios and four sorbent pads for C and H isotope ratios (Table 3-1). Additionally, thirty-one sediment extracts were also analyzed for C and H isotope ratios to determine the extent of oil contamination in the coastal sediments (Table 3-2).

Both oil and sediment samples represent two collection periods during late 1979 and late 1980. All the sediment and tar samples were collected on the Southeast coast of Texas from Galveston Bay to the Mexican border. These collections included a suite of samples obtained when the *Burmah Agate* tanker spilled and burned its cargo during mid 1979. The *Burmah Agate* oil sample collection is designated as samples 9-15, and 23 and the sediments as 32, 33, and 34.

The $\delta^{13}C$ values of the saturate hydrocarbons for the tar samples ranged between -27 ppt to -28 ppt (PDB). For the 1979 samples, the *Burmah Agate* collection of oils is generally heavier (greater δ^{13} content) than -27 ppt and the *Ixtoc I* oils are lighter than -27.5 ppt. The 1980 *Ixtoc I* oils are about 0.5 ppt heavier than those collected in 1979 (Figure 3-1 and 3-4). The deuterium values of the *Ixtoc I* saturates range between -80 and -100 ppt (SMOW) with the 1980 samples slightly heavier than those collected in 1979 (Figure 3-1). The deuterium values of the *Burmah Agate* saturates are about 20 ppt lighter than those related to *Ixtoc I*, ranging between -110 and -120 ppt (SMOW). Three samples from the *Burmah Agate* suite (1, 9, 14) have a deuterium content similar to the *Ixtoc I* samples.

The $\delta^{13}C$ values for the aromatic fractions of the *Burmah Agate* oils are heavier than the *Ixtoc I* samples by about 0.5 ppt; and the deuterium of the *Burmah Agate* tars is depleted by about 20 ppt relative to *Ixtoc I* samples (Figure 3-2).

A plot of the $\delta^{34}S$ values of the asphaltenes versus the $\delta^{13}C$ of the aromatic fraction indicates that the *Burmah Agate* related oils are isotopically heavier for both carbon and sulfur relative to samples suspected of being *Ixtoc I* sourced (Figure 3-3).

As indicated by the other isotope crossplots, a carbon vs. carbon plot of the saturate and aromatic fractions show the tars and oils separated into three groups: *Ixtoc I*, *Burmah Agate*, and unrelated sources (Figure 3-4). The separation of the groups is largely controlled by the $\delta^{13}C$ of the aromatic fraction.

The saturate fraction of four sorbent pads (samples 35 - 38, Table 3-1) was analyzed for its carbon and hydrogen isotope ratios. As the data indicate, samples 35 and 38 would fall in the *Ixtoc I* compositional "window" with the isotope ratios of samples 36 and 37 being much too heavy to be *Ixtoc I* sourced.

As previously mentioned, for a large number of the sediment samples,

Table 3.1

CARBON, HYDROGEN, AND SULFUR ISOTOPE DATA FOR THE TARS, OILS, AND SORBENT PADS.

		F_1		F_2		F_3	PROBABLE
GGC#	SAMPLE # (BLM)	$\delta^{13}C$	δD	$\delta^{13}C$	δD	$\delta^{34}S$	SOURCE
1	7911-P02-1001	-27.13	-96	-26.54	-91.7	3.82	Bur. Ag.
2	7912-P20-1001	-27.54	-83	-27.3	-93	-2.31	Ixtoc
3	7912-P24-1001	N.D.	N.D.	-27.33	-94.3	-2.54	Ixtoc
4	7911-P06-1001	-27.9	-95.1	-27.25	-87.9	-4.72	Ixtoc
5	7911-P09-1001	-27.83	-88.6	-27.12	-90.5	-.27	Ixtoc
6	7912-P12-1001	-27.84	-93.4	-27.29	-93.2	2.31	Ixtoc
7	7908-I4C-1001	-27.6	-94.4	-27.27	-92	-5.18	Ixtoc
8	7908-I5A-1001	-27.71	-92	-27.24	-90.1	-3.86	Ixtoc
9	7911-B04-1001	-27.85	-91.6	-26.85	N.D.	3.50	Bur. Ag.
10	7911-B02-1001	-27.43	N.D.	-26.54	-117.3	7.46	Bur. Ag.
11	7911-B02-1002	-27.37	-114.8	-26.62	-114.5	5.74	Bur. Ag.
12	7911-B07-1001	-27.38	-115	-26.31	-108	4.92	Bur. Ag.
13	7911-B03-1011	-27.27	-118	-26.28	-78	2.54	Bur. Ag.
14	7911-B01-1011	-27.29	-98	-26.47	-114	4.59	Bur. Ag.
15	7911-B04-1002	-27.76	-118	-26.53	-103	10.06	Bur. Ag.
16	8012-T01-1001	-27.26	-91	-27.07	-90	-3.79	Ixtoc
17	8012-T02-1001	-27.32	-100	-26.68	-90	-.70	Unknown
18	8012-T03-1001	-27.31	-92.4	-26.66	-87.5	.02	Unknown
19	8012-T04-1001	-27.18	-89	-26.91	N.D.	N.D.	Unknown
20	8012-T05-1001	-27.10	-90	-26.90	-94	-5.45	Ixtoc
21	7908-CM2-1001	-27.43	-83.8	-27.07	-91.4	-3.06	Ixtoc
22	7911-B05-1001	-27.40	-118	-25.87	-125	4.81	Unknown
23	7911-B06-1001	-27.46	-118	-26.47	-111	-4.13	Bur. Ag
24	7908-Q05-1001	-28.95	-108	-28.28	-112	3.11	Unknown
25	7908-CM1-1001	-27.46	-89	-27.06	-83	-2.21	Ixtoc
26	8004-E02-1001	-27.28	-86.9	-27.10	-73.2	-3.61	Ixtoc
27	8004-E03-1001	-27.41	-85.5	-27.08	-75.7	-.22	Ixtoc

28	8004-E04-1001	-27.39	-83.4	-27.08	-86.8	-3.65	Ixtoc
29	8004-E05-1001	-27.29	-80.6	-27.97	-75.5	-3.24	Unknown
30	8004-E01-1001	-27.33	-81.4	-27.09	-81.8	-4.02	Ixtoc
31	7908-Q01-1001	-27.54	-80.8	-27.89	-78.5	1.86	Unknown
32	7908-Q02-1001	-27.47	-123.0	-24.94	-121.7	3.91	Unknown
33	7908-Q03-1001	-27.62	-79.0	-27.05	-74.7	3.67	Unknown
34	7908-Q04-1001	-27.06	-79.4	-27.63	78.2	-6.44	Unknown
35	7911-S46-1001	-27.39	-90	N.D.	N.D.	N.D.	Ixtoc
36	7911-M25-1001	-22.46	-45	N.D.	N.D.	N.D.	Unknown
37	7911-S27-1001	-23.86	-30	N.D.	N.D.	N.D.	Unknown
38	7911-S21-1001	-27.31	-99	N.D.	N.D.	N.D.	Ixtoc

N.D. Not Determined

Table 3-2

CARBON AND HYDROGEN ISOTOPES FOR THE SEDIMENT EXTRACTS

		SATURATE (F_1)		AROMATIC (F_2)	
GGC	BLM I.D.	$\delta^{13}C$	δD	$\delta^{13}C$	δD
1	7909-R25-6001*	-26.66**	--	--	--
2	7912-PA2-6001*	-25.96	-51	--	--
3	7912-M04-6001*	-25.37	--	--	--
4	7912-M14-6001*	-26.03	-0.2	--	--
5	7911-M21-6001*	-25.90	-26	--	--
6	7912-M05-6001	-27.01	-90	-23.17	--
7	7911-M35-6001*	-26.78	-75	--	--
8	7912-M37-6001	-19.82**	--	-20.74	-7
9	7911-S06-6001*	-24.15	--	--	--
10	7912-N39-6001*	-26.31	-34	--	--
11	7911-S53-6001*	-21.35**	+11	--	--
12	7912-N38-6001	-27.18	-58	-25.30	-63
13	7912-S51-6001*	-25.85	-30	--	--
14	7911-S53-6001*	-25.10	-21	--	--
16	8012-N39-6001*	-25.89	-30	--	--
17	8012-S52-6001*	-22.09**	-12	--	--
18	8012-S51-6001*	-27.13**	-70	-21.02	-28
20	8012-M36-6001	-26.92**	-75	-20.23	--
21	8012-S31-6001	-27.36**	-80	-23.45	--
22	8012-M35-6001	-23.57	--	-25.97	-75
23	8012-N38-6001*	-26.46	-34	--	--
25	7911-S52-6001	--	--	--	--
26	7911-S54-6001*	-20.67**	-67	--	--
27	7911-S50-6001*	-23.95	-56	--	--
28	7911-S31-6001*	-23.98	-28	--	--
29	7911-S26-6001*	-20.49**	-22	--	--

30	7911-S29-6001*	-24.76	-133	--	--
31	8012-N37-6001*	-26.89	-157	--	--
32	8012-G04-6001	-27.28	-101	-25.74	-107
33	8012-G05-6001	-25.90	-70	--	--
34	8012-G06-6001	-24.83	-58	-24.87	-62
35	7909-ANC-6001	-22.54	-55	-25.71	-60

**Small sample, data may not be reliable

*analysis of combined F_1 and F_2 fractions

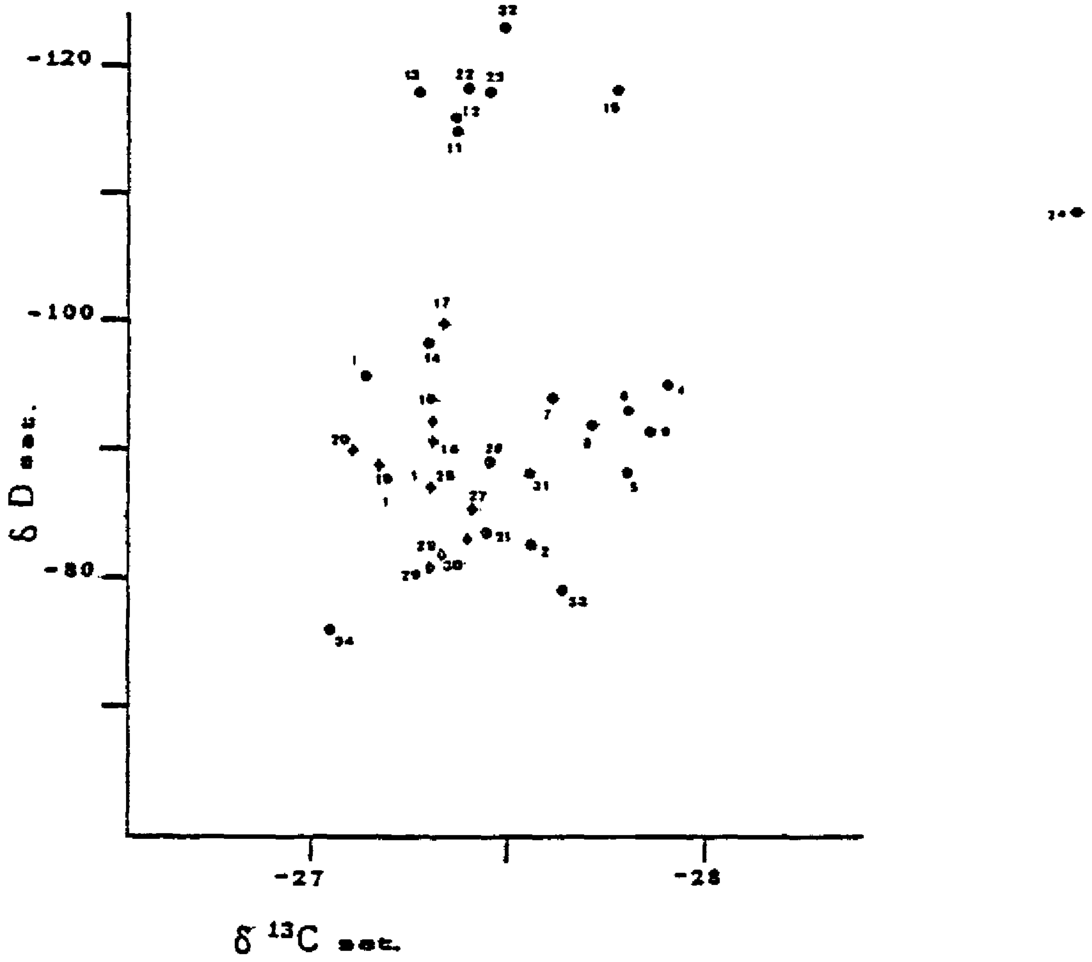

Figure 3—1. Carbon, Hydrogen, and Sulfur Isotope Data for the Tars, and Sorbent Pads (● 1979 Samples and ◆ are 1980 Samples).

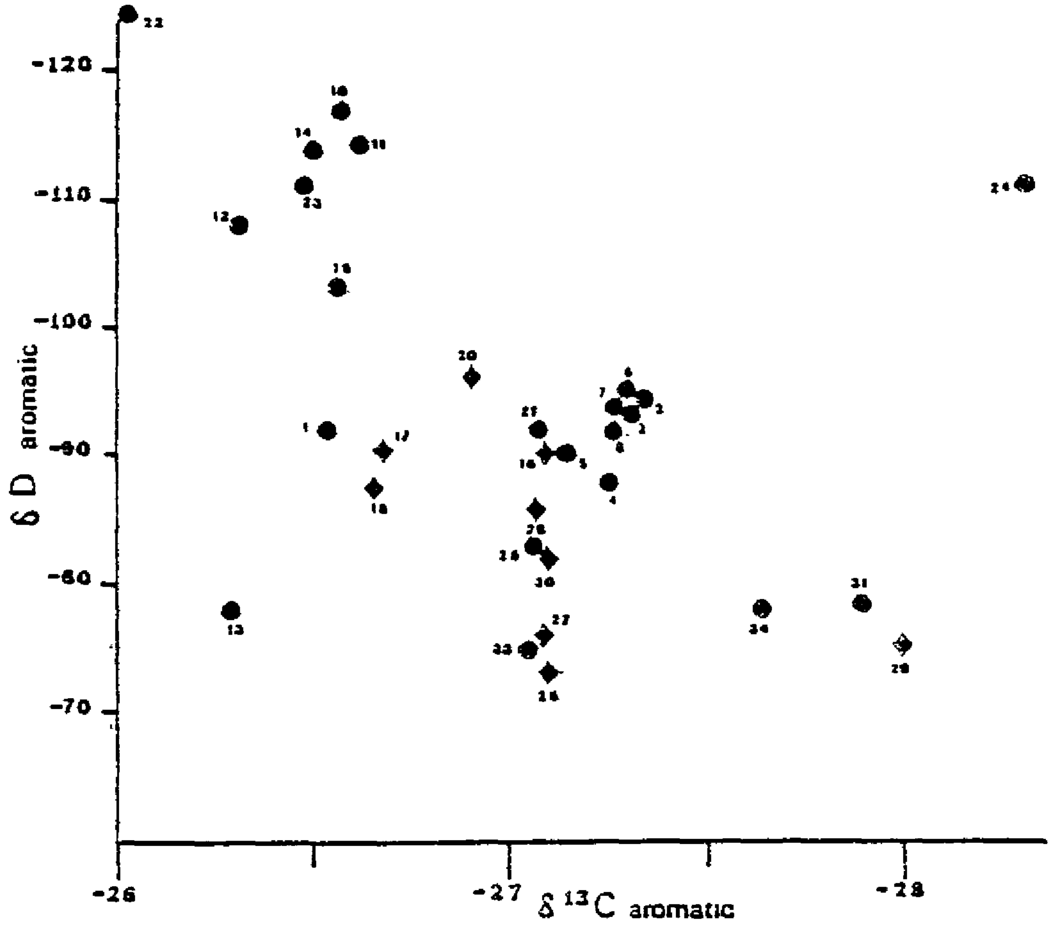

Figure 3-2. Carbon and Hydrogen Isotope Crossplot for the Aromatic Fraction of the Oil and Tar Samples (● 1979 Samples and ◆ Designates 1980 Collections).

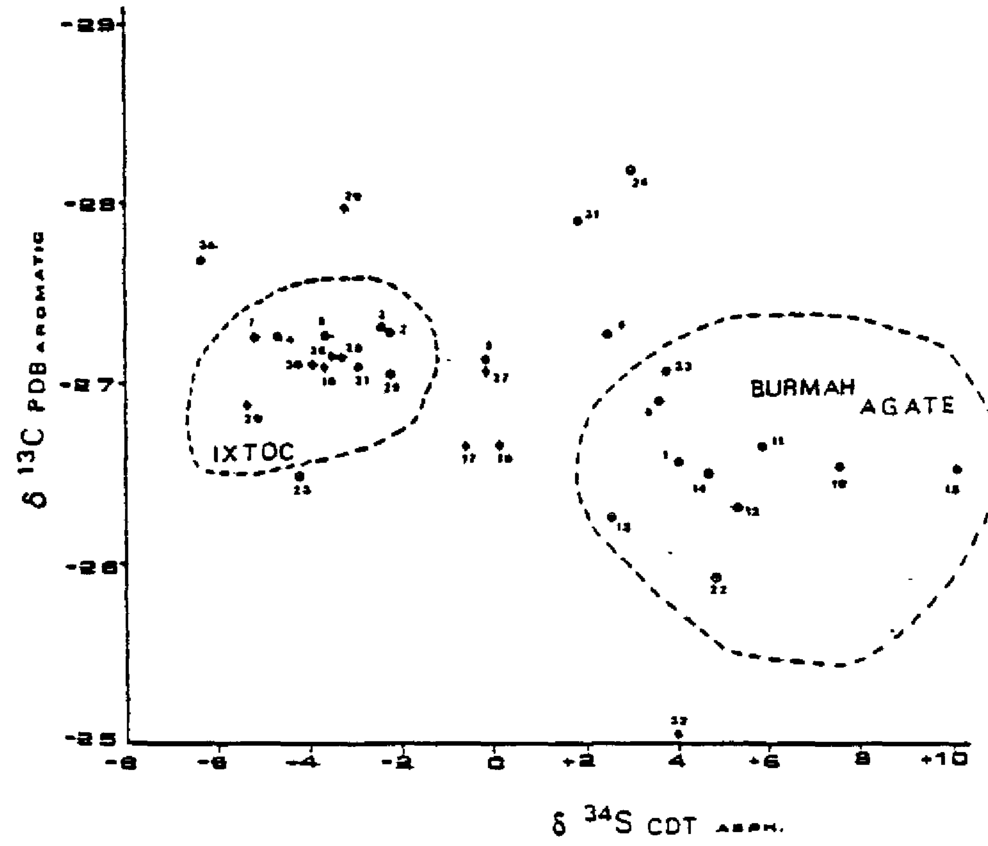

Figure 3—3. Crossplot of the Carbon Isotopes of the Aromatic Fraction Versus the $\delta^{34}S$ of the Asphaltenes from Tars and Samples (● 1979 Samples and ◆ Designates 1980 Samples).

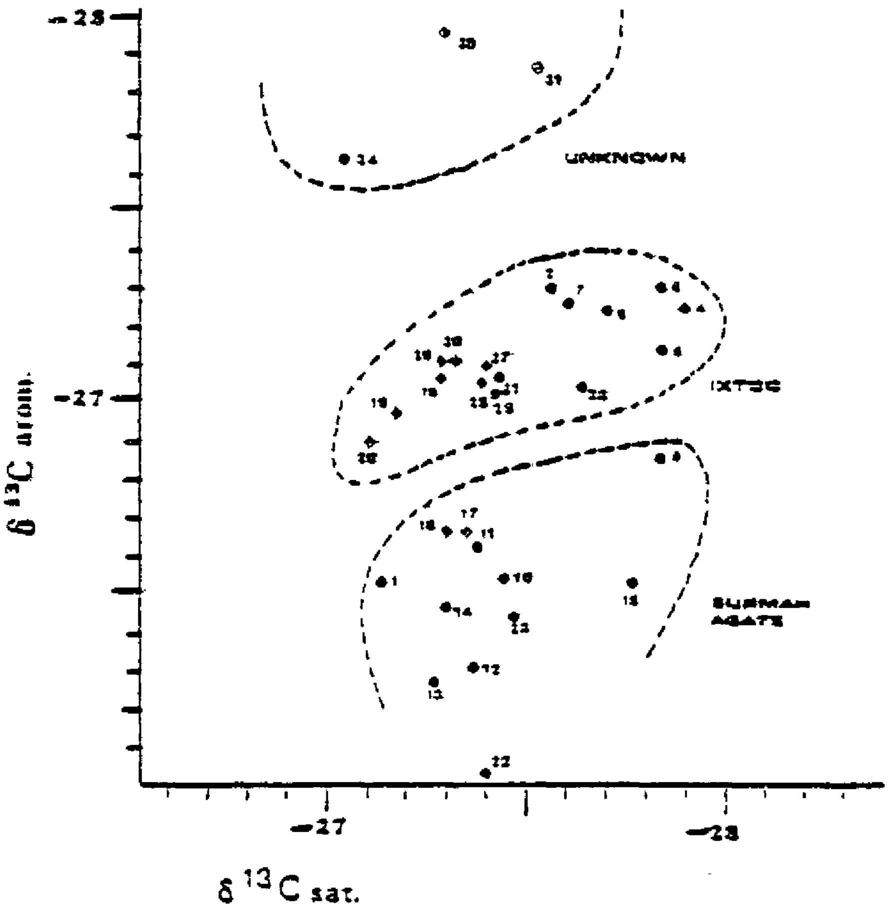

Figure 3—4. Crossplot of the $\delta^{13}C$ for the Saturate and Aromatic Fraction for the Tars and Oils (● 1979 Samples, ◆ 1980 Samples).

the saturate and aromatic fractions were combined to yield sufficient material for isotope analyses. The data for these samples are listed in Table 3-2 and illustrated in Figure 3-5.

Even with the combination of fractions some samples were so small that the isotope values obtained may not be accurate. These samples are indicated in Table 3-2 and were excluded in the plot of the data (Figure 3-5).

While general trends are difficult to establish for the sediments as a whole, paired comparisons of 1979 with 1980 collections can be made for certain stations. For both Stations S51 and S31 the 1980 samples are isotopically lighter, suggesting a greater degree of petroleum contamination in the 1980 collection. For Station M35, the isotope data of the 1979 sample represents both aromatic and saturate fractions; whereas, for the 1980 collection, only the aromatic fraction was measured. Since the deuterium values are similar, the data probably indicate that either little change or a slight decrease in the degree of contamination has occurred during 1980, even though the $\delta^{13}C$ value is approximately 1 ppt lighter for the 1979 collection. The isotopic data for Station N-39 are isotopically heavier for the 1980 sample indicating that a small decrease in the level of sediment petroleum has occurred with time. The same trend appears to have taken place for Station N-38, although, as in most cases, the comparison is between a saturate fraction for the 1979 sample and combined fractions for the 1980 sample.

The sediments collected from the Burmah Agate stations (32, 33, 34) show a progressive increase in the ^{13}C and deuterium content of the saturate fraction with increased distance from "source", corresponding to a decrease in contamination in a southwest direction.

3.4 Discussion

In this investigation, the carbon and hydrogen isotope ratios of hydrocarbon fractions from collected tars and sediments were determined along with the sulfur isotope ratios of the tar and oil asphaltenes. In using isotope crossplots, oils sourced from the Ixtoc I can be easily differentiated from other sources such as the Burmah Agate samples. For those oils suspected of being Ixtoc I sourced, the samples collected in 1980 are isotopically heavier than those collected a year earlier. Whereas this fractionation may result from increased weathering which selectively removes the lighter isotope, compositional variation of the source oil can not be discounted. In the earlier work on Ixtoc I (Sweeney, Haddad, and Kaplan 1980), the carbon isotopes of a certain fraction of the tars collected near the wellhead were isotopically heavier than the oil by about 0.5 ppt indicating either compositional variation in the source or rapid differential weathering.

Due to the difficulty in obtaining adequate sample sizes for the sediment hydrocarbons, detailed temporal and spatial analysis was not possible. As a result of the small samples, many of the isotope measurements had to be performed on combined saturate and aromatic fractions. Data comparisons based on these various fractions may therefore not be as rigorous as would be desired. Nevertheless, those samples

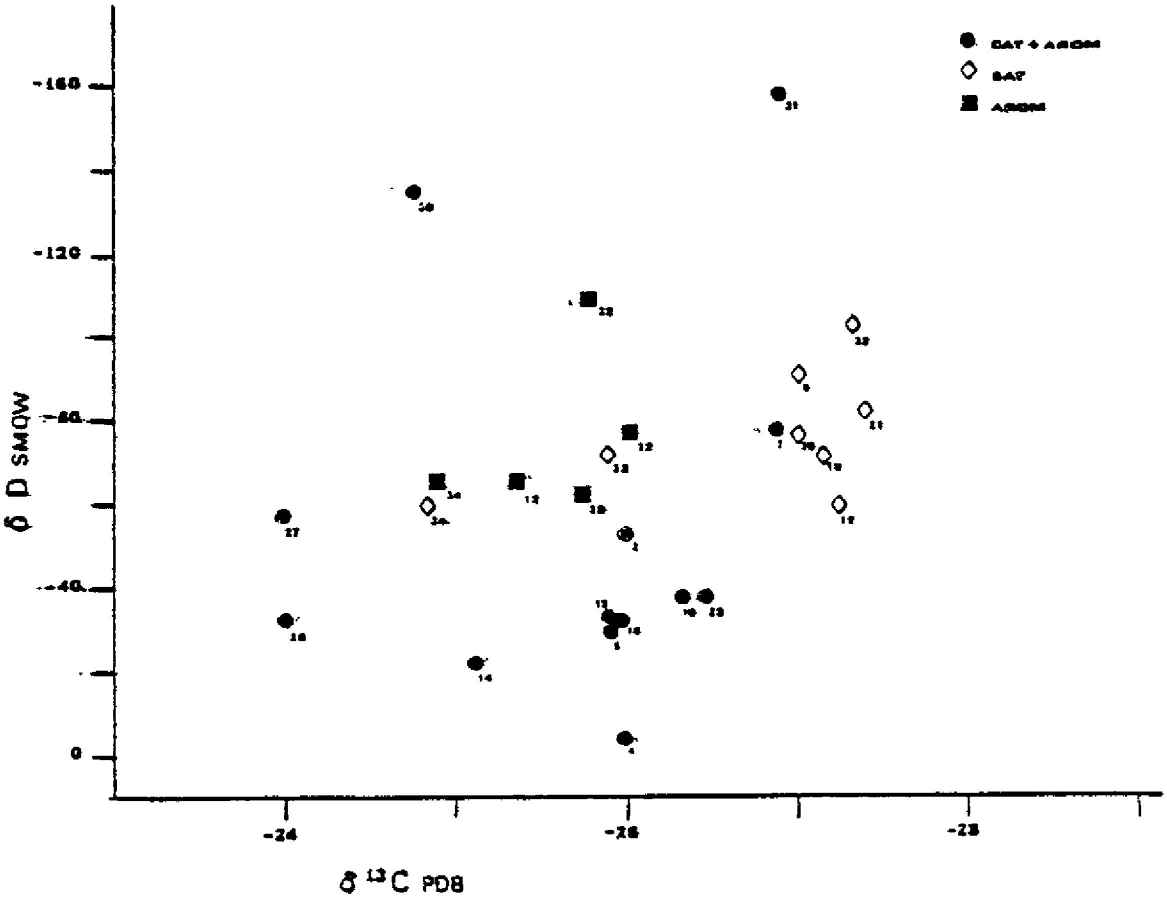

Figure 3—5. Carbon and Hydrogen Isotope Plot for the Sediments Extracts.

displaying $\delta^{13}C$ values lighter than -26 ppt and deuterium lighter than -60 ppt (SMOW) appear to be contaminated with petroleum-sourced material. This is readily apparent in viewing the *Burmah Agate* transect (sample 32, 33, 34).

3.5 Conclusion

The isotope ratios of carbon, hydrogen, and sulfur are useful in differentiating oils from various sources. Even upon extensive weathering which effects large changes in the molecular composition, the atomic ratios remain remarkably constant. In this study most of the tars could be definitively grouped into either *Ixtoc I*, *Burmah Agate*, or unrelated with a few tars possibly being mixtures.

The isotopic results from the sediment extracts are not as easily explained as those from the tars. The analyses (and consequent interpretation) was hampered by inadequate sample size. Furthermore, a baseline knowledge of the hydrocarbon isotope ratios of sediments was not available, so that determining the level of contamination in a system with differing degrees of terrestrial, pelagic, and anthropogenic deposition is difficult. However, in those samples which had adequate material for valid comparisons to be made, the temporal change in the "degree" of contamination could be assessed.

It has been demonstrated in this study and previous work that stable isotope analyses are a useful tool in sourcing an oil from seepage as well as a spill. In either case at least two isotope ratios are required for resolving oil populations. Relative to molecular distributions, the atomic ratios of oils vary little with the degradation experienced during a spill situation. In the case of widespread dispersal in areas of seepage or industrial development, stable isotope ratios can be a relatively low cost method of screening an oil, tar, or mousse sample for its probable source.

In areas such as the Gulf of Mexico where the retention capacity of the sediments maybe low (i.e. coarse grained sediments) larger extractions need to be performed to yield sufficient material for analyses. Also, in shallow waters where both bioturbation and/or storm activity can rapidly bury or remove the fine particles of sedimented oil, stable isotope as well as molecular analyses may serve little utility in damage assessment efforts. In these "high energy" environments, chemical tracing techniques may be useful only if the time between the event and sediment sampling are relatively short.