INVESTIGATION
ON THE SOURCE OF
BEACHED TAR SAMPLES

FINAL REPORT

CONTRACT AA851-CTO-71

CHANGE ORDER No.1 (8/30/82)

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Minerals Management Service
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1. INTRODUCTION

In the course of performing the "IXTOC Oil Spill Assessment" study (Contract AA851-CTO-71) for the Bureau of Land Management, a combination of analytical chemical methods was devised and utilized to obtain a chemical "fingerprint" of oil and tar samples to discern their sources. These methods combined molecular measurements - fused silica capillary (high-resolution) gas chromatography (FSCGC) and combined computer-assisted gas chromatographic mass spectrometry (FSCGC/MS) - with atomic measurements - the stable isotope ratios of carbon ($\delta^{13}C$), hydrogen (δ^2H), and sulfur ($\delta^{34}S$). FSCGC measurements, relying on n-alkane and branched alkane distributions, were added to the confirmatory FSCGC/MS measurement of alkylated phenanthrene (P) and alkylated dibenzothiophene (DBT) ratios and stable isotope measurements, in unbiodegraded oils and tars to match environmental samples with the Ixtoc I and Burmah Agate source materials. With increased biodegradation, FSCGC/MS and stable isotopes were the only useable methods for definitive source matching, as n-alkanes had been removed due to biodegradation. Biodegradation was not seen to affect the P:DBT ratios or the ratios of stable isotopes.

The appearance of large amounts of tar on certain islands and mainland beaches of Mississippi and Alabama during June/July 1982 prompted the MMS to submit four samples for source matching analysis (SMA) using the same techniques as used in the damage assessment study. This report summarizes the results of these analyses.

2. METHODS

2.1 Sampling

A series of 24 samples were shipped to ERCO's Marine
Organic Chemistry Laboratory. Four (4) of these were selected
in consultation with MMS personnel for SMA study (see Figure 1).

> Sample 1B Belle Fontaine Beach
> Spangs, MS (6/30/82)
>
> Sample 2B Gulf Shores Municipal Beach
> Gulf Shores, AL (6/30/82)
>
> Sample 3E Horn Island, MS (7/1/82)
>
> Sample 4F West Ship Island, MS (7/1/82)

2.2 Analytical Methods

Two types of oil samples were received: tar and heavily
oiled beach sediments. 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 extract
concentration.

One aliquot of the dichloromethane extract was removed
to isolate the asphaltenes for stable isotope analysis ($\delta^{34}S$).
The volume of dichloromethane solvent containing about one
gram of oil was transferred to a 50-ml centrifuge tube and
concentrated to less than 1 ml under a stream of nitrogen.
Thirty ml of hexane were added to precipitate the asphal-
tenes, which were isolated by centrifugation. The asphal-
tenes were washed with an additional 30 ml of hexane, then
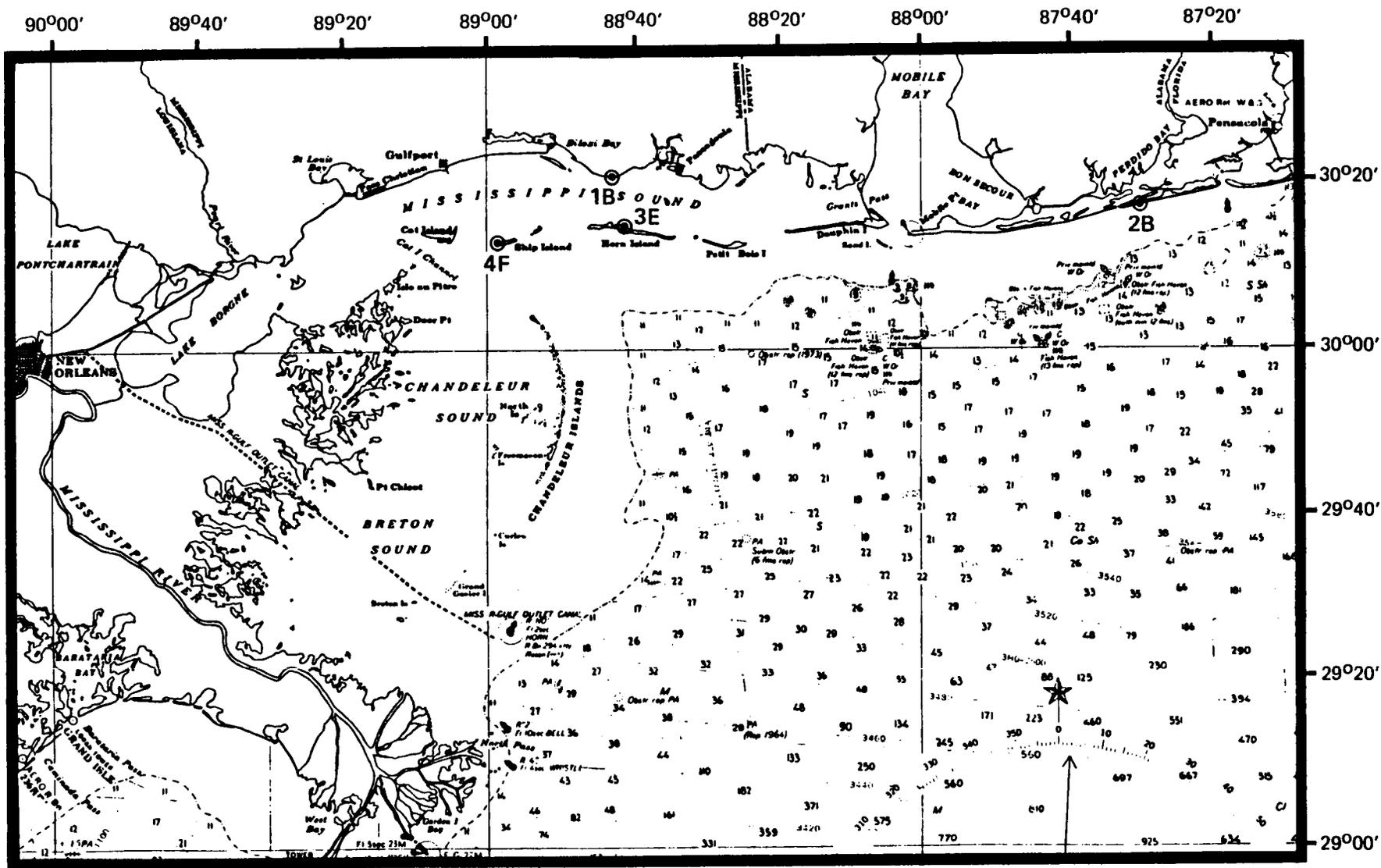redissolved in dichloromethane.

Figure 1. Location of Beached Oil/Tar Samples.

A second aliquot of the dichloromethane extract was spiked with 10 µg each of internal standards androstane and ortho-terphenyl 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 below. The samples were analyzed by FSCGC/MS as well. A combined saturated and aromatic hydrocarbon sample was subjected to $\delta^{13}C$ and δ^2H stable isotope analyses.

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.

2.2.1 Fractionation

The oil/tar samples were fractionated by silica gel/alumina column chromatography prior to FSCGC. 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 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 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 extent of weathering 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 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 2-1. Compounds were identified by comparing retention indices of peaks in the samples

Table 2-1. 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 o-terphenyl)

to retention indices of known compounds in a standard mixture that was analyzed daily.

The concentrations of n-alkanes and the isoprenoids pristane and phytane were calculated. 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.

2.2.3 Gas Chromatography/Mass Spectrometry

The aromatic hydrocarbon fractions (f_2) of the samples were analyzed by FSCGC/MS to verify the source of petroleum. 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 was analyzed for polynuclear aromatic hydrocarbons by FSCGC/MS. An aliquot of the fraction was analyzed using a Finnigan 4530 quadrupole 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 2-2.

Selected ion searches were used to obtain ion chromatograms for aromatic compounds with known retention indices and suspected to be present in the samples. 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

Table 2-2. Gas Chromatography/Mass Spectrometry Instrumental
Conditions

INSTRUMENT:	Finnigan MAT Model 4530 gas chromatograph/ mass spectrometer
FEATURES:	Data General NOVA 3 INCOS data system
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 (o-terphenyl) (response factors)

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response factors for each component were calculated from analyses of analytical standards, if available, or were extrapolated.

2.3 Stable Isotopes

Samples of saturate and aromatic fractions of oils/tars were shipped by Global Geochemistry Corporation for sulfur, carbon, and hydrogen istotope analyses. Approximately one (1) milligram of sample was combusted at 900° C in the presence of cupric oxide and silver metal. 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 activate 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 $BaSO_4$. Sulfur dioxide was prepared for isotopic analysis by direct combustion of the barium sulfate with quartz powder at 1200° C.

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° FMS 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
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, sulfur are
0.10 ppm, 1.0 ppm, and 0.3 ppm, respectively.

3. RESULTS

3.1 FSCGC Analysis

Plots of n-alkane relative abundances (NARA) reveal possible similarities and differences of the four oil/tar samples in question with Ixtoc I and Burmah Agate sources. Note that, as in the Damage Assessment Study, the screened part of the Ixtoc I NARA plot (Figure 2) represents the compositional region wherein positively identified weathered Ixtoc I residues were previously found. The four samples do not fall within this compositional "window." All four samples did have substantial quantities of n-alkanes and other component ratios indicative of a (microbially) un-degraded oil (Table 3-1). Paired samples 1B and 2B are more similar to each other than they are to the other pair (3E and 4F, which are similar), or to Ixtoc/Burmah Agate oils. The 3E and 4F samples are much "fresher," containing sizeable quantities of the light ($<$n-C_{20}) n-alkanes. These oils also contain ratios of alkanes (Table 3-1) indicating similarity to each other. The 1B/2B pair is apparently cosourced as indicated by the FSCGC data although 2B is somewhat less weathered as indicated by the large amounts of n-alkanes less than n-C_{18} (see Figure 2).

The NARA plot of the unknowns is superimposed on the Burmah Agate group in Figure 3. The 3E and 4F samples are definitely different from the Burmah Agate oil while the 1B and 2B samples are possible matches. However, the n-C_{17}/ pristane ratio of the unweathered Burmah Agate oil is 0.97 as compared with a range of 2.23-2.36 for the 3E/4F pair thus indicating a non-match.
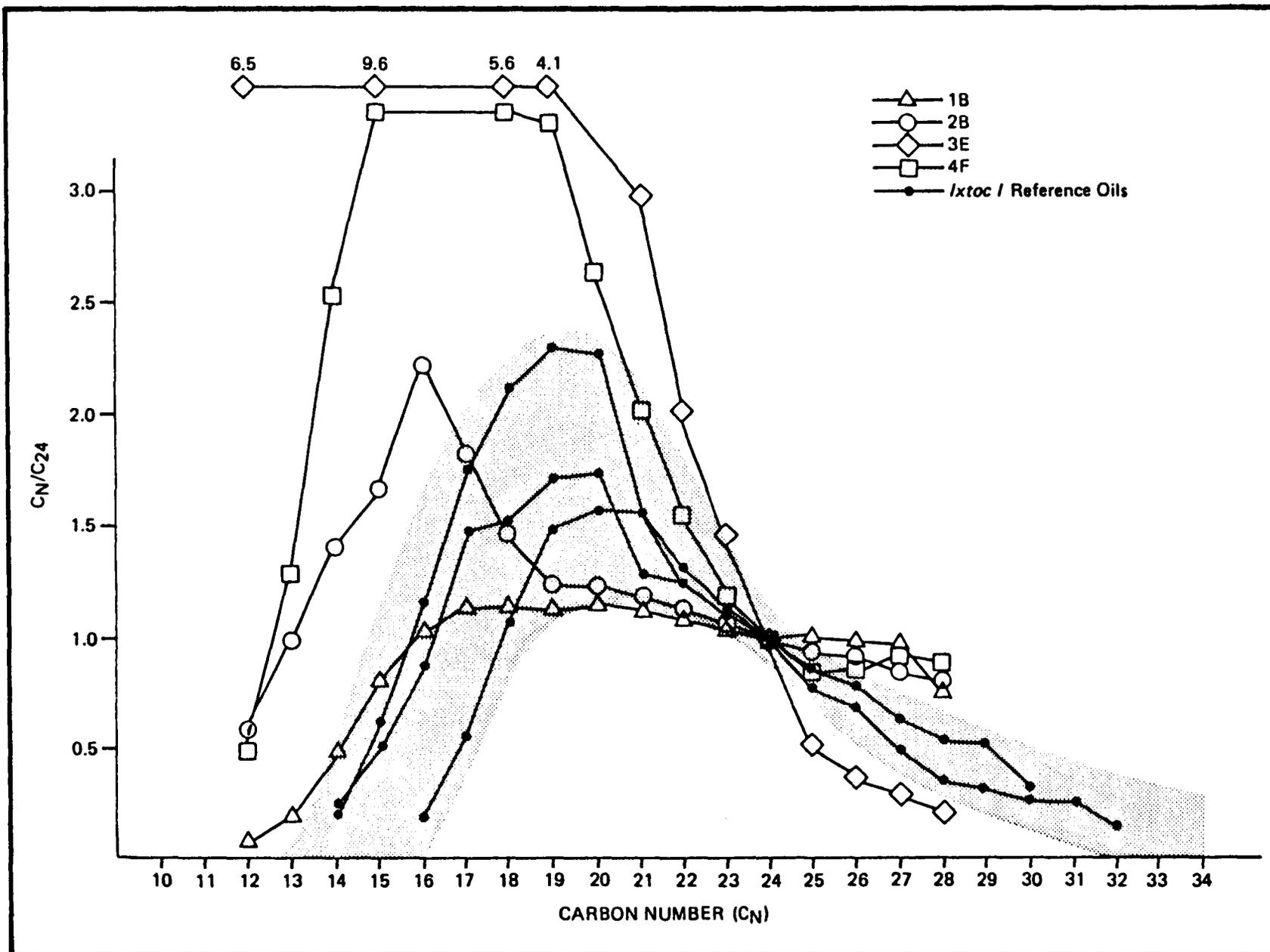
Figure 2. NARA plots showing range of compositions of weathered *Ixtoc I* reference oils and unknown samples.

Table 3-1. Alkane Parameters of Oil/Tar Samples

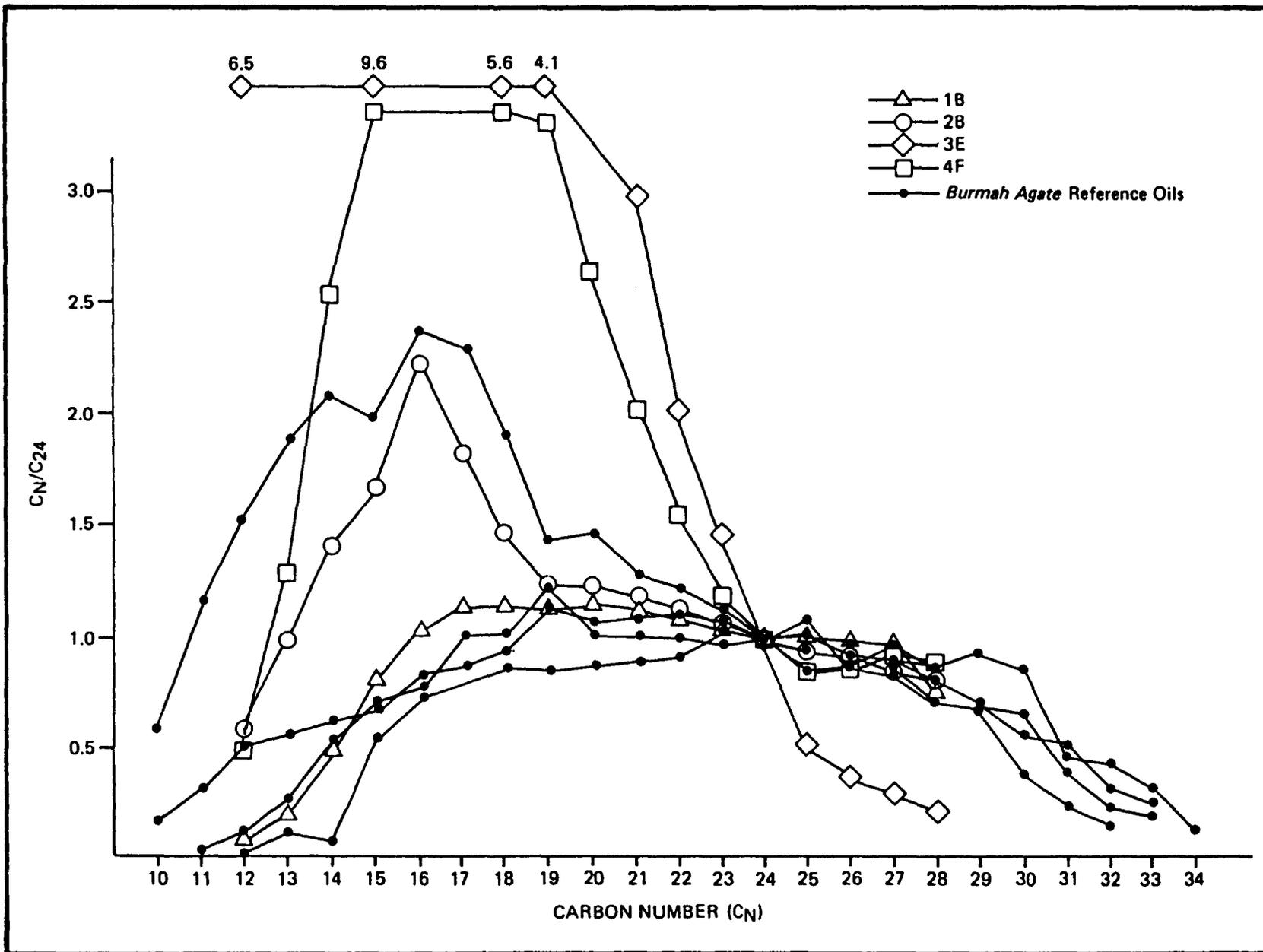| Sample	$n\text{-}C_{17}/$ Pristane	$n\text{-}C_{18}/$ Phytane	$n\text{-}C_{17}/$ $n\text{-}C_{18}$	Pristane/ Phytane	
Ixtoc I Reference	3.30	2.39	1.45	1.05	
1B	2.80	4.14	1.04	1.54	Group A
2B	3.26	4.08	1.18	1.48	
3E	2.23	1.77	1.20	0.96	Group B
4F	2.36	1.69	1.16	0.83	
Burmah Agate Reference	0.97	2.11	1.00	2.19	

Figure 3. NARA carbon plots of *Burmah Agate* related oils in various states of weathering and unknown samples.

3.2 Stable Isotopes

Stable isotope analytical results on the four samples
are presented in Table 3-2. The analyses were performed on
combined hydrocarbon fractions which does not allow for a
"fine-tuned" SMA between samples of similar isotopic com-
position. However, as can be seen from Table 3-2, neither
1B nor 2B matches even on a gross level with Ixtoc I or
Burmah Agate oils. The $\delta^{13}C$ of these samples is signifi-
cantly lighter (i.e., more negative) than either of the
reference oil collections. (Note that the reference oil
collections represent a series of fresh and weathered oils.
The stable isotopic compositions vary little with weathering.)
Samples 1B, 2B, 3E, and 4F are heavier in $\delta^{34}S$ than Ixtoc I
oil, and while the $\delta^{34}S$ values are similar to the Burmah
Agate oils, the lighter $\delta^{13}C$ of these unknown samples vir-
tually eliminates a positive source matching with either
reference collection. The δ^2H of 3E and 4F are different
(lighter; i.e., more negative) than 1B and 2B. From the
isotope data one can postulate that 1B and 2B are quite
similar, as are 3E and 4F thus implicating two separate oils
as having caused the observed beach fouling. This conclusion
is supported by FSCGC data as well.

3.3 FSCGC/MS (Aromatics)

As in the damage assessment study, the ratios of alkyl-
ated phenanthrenes to alkylated dibenzothiophenes are very
important SMA tools.

The FSCGC/MS-determined ratios are presented in Table 3-3.
The C_2 and C_3 ratios of the Ixtoc I and Burmah Agate oils
are plotted in Figure 4. Two definite groupings based on

Table 3-2. Stable isotope analysis of oil/tar samples

Sample	$\delta^{13}C^a$	$\delta^{34}S^b$	δ^2H^a
Ixtoc I	(-27)	-6 to -2	(-90 to -95)
Burmah Agate	(-27)	+2 to +10	(-110 to -120)
1B	-28.47	+11.68[c] +12.00[c]	-79
2B	-28.39[c] -28.34[c]	+11.78	-82
3E	-28.41	+4.99	-105
4F	-29.54	+6.89	-155

[a]Combined saturated (f_1) and aromatic (f_2) fractions.
[b]Asphalentene fraction.
[c]Replicate analyses.

Table 3-3. Alkyl phenanthrene to alkyl dibenzothiphene ratios

Sample	C_1P/C_1DBT	C_2P/C_2DBT	C_3P/C_3DBT
Ixtoc I	0.72-1.32	0.41-0.66	0.49-0.80
Burmah Agate	3.56-5.69	3.41-5.11	5.36-11.36
1B	0.63	0.47	0.57
2B	0.37	0.67	0.63
3E	7.0	11.0	10.3
4F	>10.0	27.9	29.6

[a]Combined saturated (f_1) and aromatic (f_2) fractions.
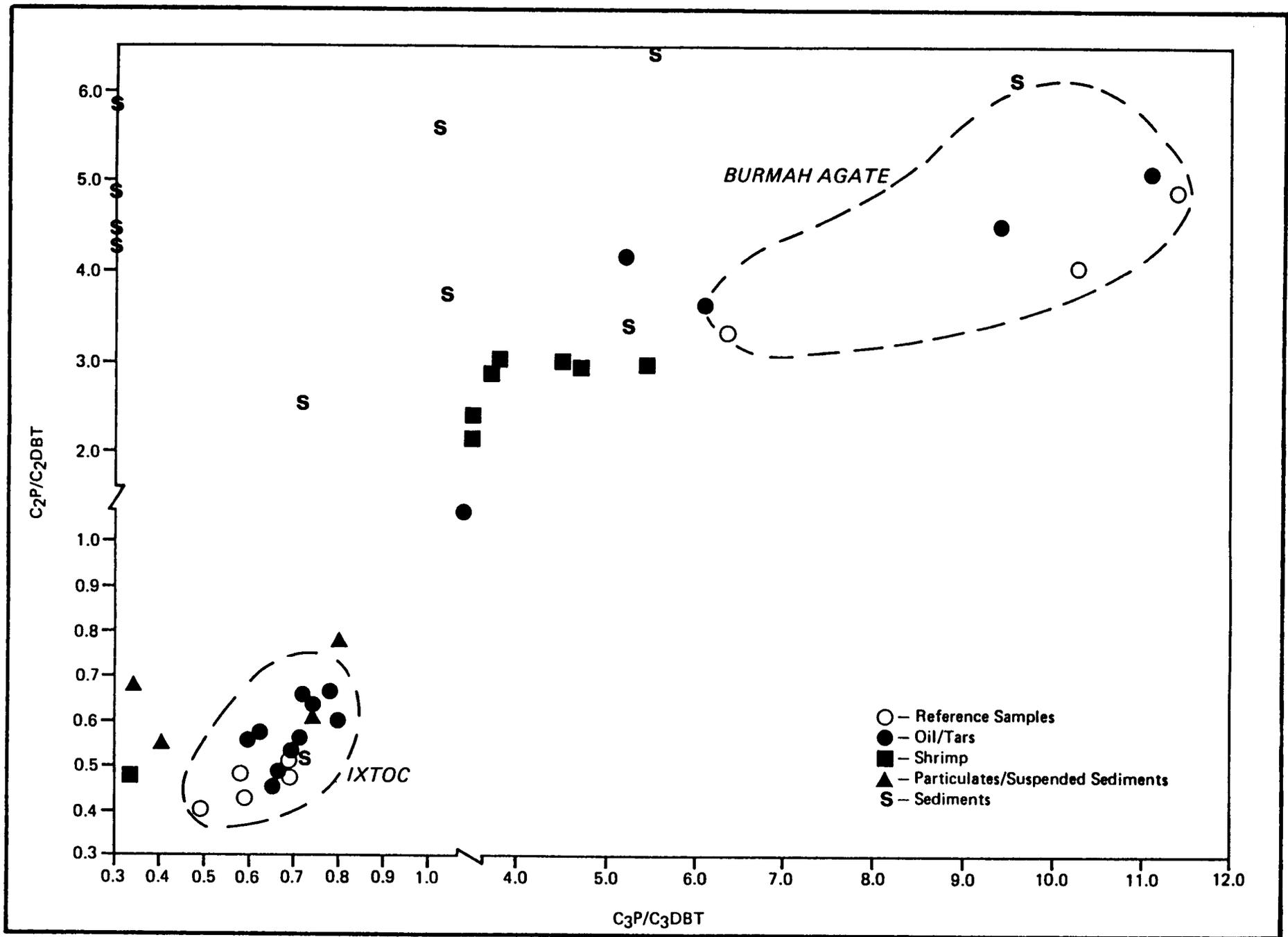[b]Asphalentene fraction.
[c]Replicate analyses.

Figure 4. Plot of alkylated phenanthrene (P) and dibenzothiophene (DBT) ratios of oil and other sample types indicating source groupings (from *Damage Assessment Study*).

these ratios define the Ixtoc I and Burmah Agate oils. A
series of other unidentified oils (from the Damage Assessment
Study) fall mid-way in composition between these definite
sources.

The unknown samples group into at least two categories.
The results from Table 3-3 show that 1B and 2B are again
quite similar to each other and, on the GC/MS basis, similar
to Ixtoc I, as they fall in the Ixtoc I compositional terri-
tory in Figure 4. The 3E and 4F samples are again quite
different from 1B and 2B. Sample 4F appears to differ from
3E on the basis of data in Table 3-3. This difference is
supported by the δ^2H isotope data as well.

4. CONCLUSIONS

The combination of methods used in this study has been
and continues to be a powerful set of complementary and
interactive measurements used in SMA studies.

FSCGC-generated NARA plots indicate a relationship
between the 1B, Belle Fontaine Beach (Miss.) and 2B, Gulf
Shores Beach (Ala.) samples but no relationship to either
Ixtoc I or Burmah Agate oils. The similarity of these two
samples to each other and dissimilarity to any known oil is
borne out by the stable isotope and FSCGC/MS data as well.

NARA plots and other FSCGC data of the 3E, Horn Island
(Miss.) and 4F, West Ship Island (Miss.) samples indicate a
similar alkane distribution and a possible similarity to
Ixtoc I oil. However the $\delta^{13}C$, $\delta^{34}S$, $\delta^{2}H$ for these samples
are very different from those for Ixtoc I oil. FSCGC/MS do
not differentiate between the 1B/2B pair and the Ixtoc I oil
(Table 3-3). However, the stable isotope evidence clearly
indicates a "no-match." These samples (1B and 2B) are,
however, similar to each other in all chemical (molecular
and atomic) properties. Differences in FSCGC/MS data and
differences in $\delta^{13}C$ and $\delta^{2}H$ between the 3E and 4F samples
suggests that these oils are not related to each other.

Thus at least two and probably three unknown sources of
oil/tar have appeared to impact the islands and beaches along
the Mississippi and Alabama coasts. All three methods of
analysis, FSCGC, stable isotope analysis, and GC/MS aromatic
analyses based on P/DBT ratios have proven essential to
arriving at these conclusions. The $\delta^{13}C$ proved quite useful

in separating these unknown samples from either the _Ixtoc I_ or _Burmah Agate_ sources. However, in many cases, differences based on $\delta^{13}C$ alone are not definitive and the results from the other methods are essential as quality control checks on the data and as necessary parts of the SMA methodology.

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Minerals Revenue Management** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.