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Analyses of Hydrocarbons in BLM Sediment Intercalibration

Sample from Santa Barbara Basin and Spiked with

API South Louisiana Crude Oil.

A Preliminary Report.

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This is a preliminary report of BLM intercalibration sediment sample from Santa Barbara basin spiked with South Louisiana crude oil. We could not start analyses until early July due to delays in funding from ERDA and a research cruise in June. Thus, only two subsamples have been analyzed in a hurried manner. The procedure used is essentially that of Appendix I except the internal standards spiked at the time of extraction were androstane, $n\text{-C}_{20}$, and hexamethylbenzene.

Due to the high oil content of the sediment, the usual TLC procedure resulted in an overloaded plate. Thus, we found about 10% cross over of alkanes/cycloalkanes to the aromatic fraction. This report is prepared for the BLM Hydrocarbon Methodology Review Group meeting at U.C.L.A., July 26-28th, 1977.

The procedure described in Appendix I was developed by Professor James G. Quinn at the Graduate School of Oceanography, University of Rhode Island and in our laboratory for the analyses of MERL sediment samples. We gratefully acknowledge the assistance of Dr. Richard Bromund and Dr. Rene Schwarzenbach in obtaining the glass capillary GC data.

Table 1. Concentration of Non-Saponifiable Lipid Extract and Hydrocarbon Fractions from Silica Gel TLC.

	Subsample 1	Subsample 2
Dry Weight	18.4 g	23.3 g
% H ₂ O	56.2%	55.4%
Petroleum Ether Extract	3.73 mg/gdw	3.00 mg/gdw
Extract After Cu/Al ₂ O ₃ Column	2.17 mg/gdw	1.87 mg/gdw
Silica Gel TLC Fraction [*] (gravimetric)		
f1. Alkanes and Cycloalkanes	1.02 mg/gdw	0.79 mg/gdw
f2. Aromatics	<u>0.75 mg/gdw</u>	<u>0.65 mg/gdw</u>
Total f1 and f2	1.77 mg/gdw	1.44 mg/gdw
(FFAP GC FID)		
Total f1	1.05 mg/gdw	0.90 mg/gdw
UCM f1	0.90 mg/gdw	0.80 mg/gdw
Resolved Peaks f1	0.15 mg/gdw	0.10 mg/gdw
(SE-52 Glass Cap. GC FID)		
Total Integrated Peaks Supergrator 3.		
f1	0.331 mg/gdw	0.413 mg/gdw

Table 2. Concentrations of Most Abundant Hydrocarbons in BLM
 Intercalibration Sample Alkane-Cycloalkane Fraction:
 20 m x .35 mm (i.d.) SE-52 Glass Capillary GC
 Supergrator 3 Calculation (µg/gdw).

	Subsample 1		Subsample 2	
	I.S. n-C ₂₀	I.S. Androstane	I.S. n-C ₂₀	I.S. Androstane
n-C ₁₃	10.8	6.3	17.4	10.6
n-C ₁₄	20.9	12.1	28.9	17.5
Compound a	13.6	7.9	18.7	11.3
n-C ₁₅	23.2	13.4	32.2	19.5
n-C ₁₆	22.4	13.0	30.2	18.3
Compound b	16.8	9.7	16.6	10.0
n-C ₁₇	20.8	12.1	21.0	12.7
Pristane	9.3	5.4	14.6	8.9
n-C ₁₈	10.6	6.2	14.2	8.6
Phytane	6.7	3.9	5.6	3.4
n-C ₁₉	10.0	5.8	8.0	4.8
n-C ₂₀	7.6	4.4	6.0	3.6
n-C ₂₁	5.2	3.0	4.0	2.4
n-C ₂₂	3.5	2.0	3.1	1.9
n-C ₂₃	2.7	1.5	NC	NC
n-C ₂₄	2.2	1.3	NC	NC
n-C ₂₅	2.0	1.1	NC	NC
	188.3 µg/gdw	109.1 µg/gdw	220.5 µg/gdw	133.5 µg/gdw

Table 3. Concentrations of Most Abundant Hydrocarbons in BLM
Intercalibration Sample Alkane-Cycloalkane Fraction:
FFAP Packed GC Column, Hand Calculation ($\mu\text{g/gdw}$).

	Subsample 1		Subsample 2	
	I.S. n-C ₂₀	I.S. Androstane	I.S. n-C ₂₀	I.S. Androstane
n-C ₁₃	5.1	4.1	5.9	6.0
n-C ₁₄	8.5	6.9	9.3	9.5
Compound a	5.6	4.6	5.5	5.6
n-C ₁₅	10.4	8.5	10.4	10.6
n-C ₁₆	9.8	8.0	9.1	9.3
Compound b	3.9	3.2	3.7	3.7
n-C ₁₇	9.0	7.3	8.7	8.9
Pristane	6.1	5.0	6.0	6.1
n-C ₁₈	6.9	5.6	6.9	7.0
Phytane	2.9	2.4	2.8	2.9
n-C ₁₉	5.8	4.7	5.8	5.9
n-C ₂₀	4.3	3.5	4.4	4.5
n-C ₂₁	2.8	2.3	3.0	3.1
n-C ₂₂	2.5	2.0	2.3	2.3
n-C ₂₃	1.8	1.5	1.6	1.6
n-C ₂₄	<u>1.4</u>	<u>1.2</u>	<u>1.2</u>	<u>1.2</u>
	86.8 $\mu\text{g/gdw}$	70.8 $\mu\text{g/gdw}$	86.6 $\mu\text{g/gdw}$	88.2 $\mu\text{g/gdw}$

Table 4. Ratios to n-C₁₅ Calculated from Tables 2 and 3.

	Glass Capillary GC		FFAP	
	1	2	1	2
n-C ₁₃	.47	.54	.49	.57
n-C ₁₄	.90	.90	.82	.89
Compound a	.59	.58	.54	.53
n-C ₁₅	1.00	1.00	1.00	1.00
n-C ₁₆	.97	.94	.94	.88
Compound b	.72	.52	.38	.36
n-C ₁₇	.90	.65	.87	.84
Pristane	.40	.45	.59	.58
n-C ₁₈	.46	.44	.66	.66
Phytane	.29	.17	.28	.27
n-C ₁₉	.43	.25	.56	.56
n-C ₂₀	--	--	--	--
n-C ₂₁	.22	.12	.27	.29
n-C ₂₂	.15	.10	.24	.22
n-C ₂₃	.12	NC	.17	.15
n-C ₂₄	.09	NC	.13	.12
n-C ₂₅	.09	NC	NC	NC

Table 5. Concentrations of the Most Abundant Hydrocarbons in BLM Intercalibration Sample Aromatic Fraction* (µg/gdw).

	SE-52 Glass Capillary GC			FFAP Packed Column GC	
	Subsample 1		Subsample 2	Subsample 1	Subsample 2
	Injection a	Injection b			
C-1 Naphthalene	0.42	0.48	0.52	Not Calculated Peak Too Small on GCs Available at This Time.	
C-1 Naphthalene	0.32	0.33	0.48		
C-2 Naphthalene					
a	2.32	2.39	2.04	2.43	2.21
b	0.93	0.98	0.81	1.85	2.03
c	0.79	0.83	0.81	b and c not resolved	
DDE** by FID	2.9	1.9	1.3	4.0	2.4
DDE by EC Detector					
o,p DDE				0.52	0.45
p,p DDE				<u>2.41</u>	<u>2.10</u>
Total				2.93	2.55

* Analyses of this fraction are incomplete. GC-MS analysis shows many other aromatic compounds present in amounts approaching but not exceeding the concentrations given for the naphthalenes above.

** Any DDT family compounds present as DDT would have been converted to DDE by alkaline extraction method. Therefore, this represents total DDT + DDE present in sediment.

FIGURES

Gas chromatograms - glass capillary SE-52 20 meters 0.35 cm i.d. column. Sample of approximately 0.5 ul to 1.0 ul injected, splitless, cold injection split 10:1 after 30 sec., heated to 100°C after solvent elution, held for three minutes, then programmed at 3°C/min. 100°C to 230°C Carlo Erba GC. Attenuation x 16.

Figures 1 and 2. Duplicate subsamples extracted and carried through same procedure. Alkane/cycloalkane fraction. N-C₂₀ and androstane as internal standards.

Figures 3, 4, 5. Figures 3 and 4 are duplicate injections of the same subsample of aromatic fraction. Figure 5 is injection of the duplicate subsample of aromatic fraction. Note that there is carry over of alkane/cycloalkane fraction into the aromatic fraction due to overloading of TLC plate. Hexamethyl benzene is internal standard.

Figure 6. Aromatic hydrocarbon standard.

J.S.-1

Figure 1.

0.5-6 2101 Extra CS. F.

J.S - 2

Figure 2.

Archosart
11-50

Figure 3

Figure 4.

U.S.-2fe

Figure 5

3 C-1 Naphthalenes
3 C-2 Naphthalenes
Hexamethyl benzene

15

16

17

18

UNKOWN

arabutan

n-C20

105

from

naphthalene →

1-methyl naphthalene →

2-methyl benzene →

5,2,6 dimethyl naphthalene

1,2,3,4 naphthalene →

acronaphthalene

acronaphthalene

2,3,6 trimethyl naphthalene

fluorene

phenanthrene

1-methyl phenanthrene

pyrene

Figure 6.

OCEANUS 26 CRUISE REPORT

Oceanus 26: May 31 to June 4, 1977
Woods Hole to Woods Hole
J. M. Teal, Chief Scientist

Stations Occupied: Station H, 40°26' 73°48'
Station M, 40°17' 73°47'
Station L, 40°23' 73°37'

Sampling of near bottom water, sediment cores, epibenthos and infauna took place at each station listed above. An attempt was made to sample the same organisms at each station and to coordinate these species with other BLM-funded work (i.e. ERCO, Cambridge, Mass.). These stations were chosen because hydrocarbon data has been accumulated previously at these sites and because they represent three levels of contamination. We intend to reoccupy these sites in the future, and careful fixes were taken.

Samples collected at each station are listed below. Note that asterisk (*) denotes species found in at least two stations, double asterisks (**) denotes species found in all three stations.

Station L

Water: Triplicate 90 l near bottom water samples, filtered through glass fiber filters. Filters and filtered water brought home for analysis.

Sediment: Pooled sediment from three box cores, each core sectioned in 1 cm sections to 7 cm plus a single 7-10 cm bottom section. Clean, light-textured sand, poor penetration.

Organisms:	* Asterias spp.	Moon Snail
	** Cancer spp.	Sand Dollars
	Yellow Tail	** Polychaete Worms (several spp.)
	** Whiting	Mulina lateralis} } Clam
	* Ocean Pout	Artica islandica}
	* Sea Robin	
	* White Hake	
	* Winter Flounder	

Station M

Water: Triplicate 90 l water samples filtered. One filtered sample lost; duplicate water brought home for analysis.

Sediment: Pool sediment from two box cores, each core sectioned in 1 cm sections to 10 cm followed by 4 cm sections to 50 cm (total 20 sections). Replicates taken from each box and pooled. Sediment soft, black and sticky, with oxidized top layer, good cores.

Organisms:

* Asterias forbesi	* Homarus americanus
* Asterias vulgaris	* Nuclea proxima
** Cancer spp.	* Yoldia limatula
* White Hake	Sea Cucumber
* Ocean Pout	** Polychaete Worms (2 or 3 spp.)
* Squirrel Hake	Molpodia spp.
** Whiting	Anenome

Worm tubes very abundant at this station. Very fine sediment, difficult to wash.

Station H

Water: Triplicate 60 l water samples filtered, filters and filtered water brought home.

Sediment: Pool sediment from two good box cores, each core sectioned as at Station M (down to 42 cm). Mud is anaerobic with oxidized layer, but coarser than Station M.

Organisms:

** Cancer spp.	* Yoldia limulata
* Squirrel Hake	* Nuclea proxima
* Homarus americanus	** Polychaete Worms
* Winter Flounder	Clams, Unidentified
** Whiting	
Cunner	
* Sea Robin	

Worm tubes and much stringy debris found at this station.

Sample Processing

Water: Each 90 l sample was filtered directly from the pressurized sampling bottle through glass fiber filter(s) and approximately 60 l of the filtrate was saved. The filtrate was spiked with an internal standard, mixed well with CH_2Cl_2 and returned to the lab. The filters were stored frozen, and returned to the lab.

Sediment: The box cores were sectioned at once into glass jars and frozen. Each section (at every station) is a pooled sample from at least two cores. Samples will be stored frozen until analysis.

Organisms: Large organisms were picked from the trawl with forceps, identified, wrapped in rinsed aluminum foil and frozen whole. All samples will be stored frozen until analysis. Infauna which were sieved from mud were identified, stored in glass jars and frozen. A sample of sieving water was saved and will be analyzed as a possible contamination source.

**Analyses of Aromatic Hydrocarbons in Intertidal Sediments Resulting
from Two Spills of No. 2 Fuel Oil in Buzzards Bay, Massachusetts**

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Though there have been a number of studies of oil spills incorporated into coastal sediments (Blumer and Sass, 1972; Teal, 1972; Burns and Teal, 1971; NAS, 1975; Mayo *et al.*, 1978; Keizer *et al.*, 1978; among others), there is not much data as yet on the fate of the aromatic fractions of these oils in the environment. Previous studies have focussed on the fate of alkanes and cycloalkanes from the spilled oil (Blumer *et al.*, 1970; Blumer and Sass, 1972a,b; Burns and Teal, 1971). Yet aromatic hydrocarbons are major constituents of oil and generally considered to be the petroleum components which are the most damaging to organisms (Anderson, 1977; Rice *et al.*, 1977; NAS, 1975; Sanborn and Mallins, 1977; Roesijadi *et al.*, 1977). Thus, it is important to investigate the long term fate of fossil fuel aromatic hydrocarbons in surface sediments. If these compounds have a long residence time in surface sediments they might be released from sediments to organisms living in or on the sediments as well as in the overlying water column.

This study is a part of our ongoing efforts to understand the biogeochemistry of fossil fuel compounds in benthic ecosystems (Farrington and Teal, 1977; Farrington, 1977; Farrington and Tripp, 1977; Farrington *et al.*, 1977; Teal, 1976) and part of an overall effort to investigate the fate and effects of a No. 2 fuel oil spill in Buzzards Bay - The West Falmouth Oil Spill of 1969 (Blumer *et al.*, 1970; Blumer and Sass, 1972a,b,c; Burns and Teal, 1971; Krebs and Burns, 1977; Burns, 1976a,b; Sanders, 1978) and a more recent No. 2 Fuel Oil spill in Buzzards Bay in 1974 (Hampson and Mouhl, 1978). (Figure 1). We report here a study of the fate of some No. 2 fuel oil aromatic compounds in marsh sediments.

Methods

Cores of marsh sediments or intertidal mud flat sediments were obtained with a stainless steel coring device of 4 cm diameter and 120 cm length or by inserting plastic core liner tubes into the marsh sediments. In the latter case care was taken to remove the outside ring of sediment which was in contact with the liner in order to avoid contamination. The cores were sectioned and frozen at a temperature below 0°C until analysis one week to one year later. The methods of extraction and isolation of the hydrocarbons have been described in detail previously (Farrington and Tripp, 1975; Burns and Teal, 1971; Farrington *et al.*, 1976; Blumer and Sass, 1972a). Briefly, the sediments were extracted by Soxhlet extraction with methanol or benzene: methanol (1:1) or by alkaline (KOH) methanol; benzene digestion. The hydrocarbons plus some of the other lipids were partitioned into pentane, concentrated by rotary evaporation and then percolated through a copper column to remove sulfur. Two hydrocarbon fractions were collected by column chromatography through alumina (5% water) over silica (5% water). Fraction 1 was eluted with one column volume of pentane and contained primarily alkanes and cycloalkanes. Fraction 2 was eluted by one column volume of 10% benzene in pentane followed by one column volume of 20% benzene in pentane and contained primarily two and three ring aromatic compounds. Column eluates were concentrated by rotary evaporation at or below room temperature and aliquots were weighed on a Cahn electrobalance.

The aromatic compounds in fraction 2 were analyzed by gas chromatography on a .32 mm i.d. x 20 m glass capillary SE52 column installed in a Hewlett Packard Model 5710A gas chromatograph (g.c.) equipped with F.I.D.

and Model 18740A capillary column control split/splitless injector. Samples were injected using the splitless mode with column at 40°C and held at that temperature until the solvent peak eluted. Then the column was rapidly heated to 70°C and then immediately programmed at 2°/min. to 240°C. Gas flow rate was 2-3 ml/minute helium. Detector temperature was 250°C and injection port temperature was 200°C.

Quantitation was achieved by comparison of peak heights of compounds in samples with peak heights of an internal standard, hexamethyl benzene or by comparison with an external standard calibration plot of several aromatic hydrocarbon standards.

The aromatic compounds were also analyzed by GC-mass spectrometry on a Finnigan 1015 quadrupole mass spectrometer coupled to a Varian 1400 gas chromatograph equipped with a split/splitless injection. A 17 m x 0.32 mm i.d. SE 52 glass capillary column was installed in the system and operated as follows. Injection was at 40°C with 30 sec. in splitless mode, then rapidly brought to 70°C and programmed to 240°C at 4°/min. Helium carrier gas was at 14 psi. The mass spectrometry operating conditions were 20 eV, 500 ua, scan from 40-500 amu every three seconds. Mass fragmentographic quantitative analyses were obtained using the general procedure outlined in Farrington et al. (1977) except that the precision was only + 20% due to the small number of scans per peak resulting from the long scan time. Mass spectra for each peak selected for analysis were compared where possible with the API reference spectra (API, 1977) and compounds were identified in this manner. In many cases reference spectra were not available and compounds were tentatively identified by comparison of their spectra with known spectra for isomers or compounds with similar structure characteristics.

Results

Gravimetric Data

The concentrations of the f2 aromatic compounds in marsh sediments are given in Table 1. Note that the error associated with analysis of subsamples of marsh sediments from one location are given by the duplicates of three of the Winsor Cove samples. A factor of 2 or 3 variation is not uncommon due to the heterogeneity of the marsh sediment and the non-uniform distribution of the oil in these heterogenous sediments. The concentrations of the f2 aromatics in the Wild Harbor marsh sediments remained fairly constant over the time interval sampled. Unfortunately, we did not sample during the first one and one-half years after the spill and thus cannot directly compare the results with the first samples of the Winsor Cove marsh sediments which were taken shortly after the spill in that location.

At site 1 in the Winsor Cove marsh the concentrations of the f2 aromatics decreased by a factor of 5 between the October sampling just three days after the spill and the May 1975 sample taken about six months after the spill. A year later the concentrations at site 1 were the same as the May 1975 data. However, by June of 1977 the concentration had decreased again by a factor of ten. Curiously, the concentrations at Site G.H. increased by an order of magnitude during this same period. We cannot explain this except to hypothesize that site G.H. being near a small flowing stream might have received some additional oil input from sediments "upstream" or further up the tide zone. We think that all of the data in Table 1 can be explained by a combination of weathering of the oil in the sediment and mobilization of oil from other locations to the sites sampled, as we will explain later.

The concentrations of f2 aromatics normally present in the marsh sediments are given by the values for the control marsh samples at Chappaquoit and the lower sections of the marsh cores for site 1 in Winsor Cove. The analytical blank for these analyses is about one order of magnitude lower concentration than the control station values.

Gas Capillary Gas Chromatography

Glass capillary gas chromatograms of representative samples are given in Figures 2, 3, and 4. For all figures of gas chromatograms the identity of numbered components as near as can be determined by GC-mass spectral data and retention indices of standard compounds are given in Table 2. Inspection of the chromatograms in Figure 2 clearly shows that between the initial spill at Wild Harbor and January 1971 there was removal of lighter molecular weight components at a faster rate than removal of the heavier molecular weight components. This decrease of lighter molecular weight components relative to the heavier components continues during the period January 1971 to July 1976. The dominance of the methyl naphthalenes (compounds 2 and 3) as the most abundant individual aromatics in the aromatic fraction of the fuel oil gives way to a dominance of C₂-naphthalenes by January 1971; C₃-naphthalenes by November 1972; and C₄-naphthalenes in September 1975.

Figures 2,
3, and 4
near here.

Chromatograms of aromatic compounds present at selected depths in marsh cores are given in Figure 3. Note that fuel oil aromatics are present at 10-15 cm in July 1973 and the methyl and dimethyl naphthalenes do not appear to be as depleted relative to the heavier molecular weight compounds as for November 1972 marsh surface sediments (Figure 2). The 45-50 cm core section chromatogram (Figure 3) shows an absence of fuel oil aromatics. The identity of the peaks in this chromatogram are not known at present but

they are probably aromatic hydrocarbons from pyrolytic sources (Youngblood and Blumer, 1975). The chromatograms of the July 1975 10-15 cm section (Figure 3) shows some fuel oil aromatics present. The lighter molecular weight components are reduced relative to the heavier molecular weight components when compared to the July 1973 analyses of the 10-15 cm core section from this location (Figure 3). Traces of fuel oil aromatics are also present in the 20-25 cm section of the July 1975 core. The lighter molecular weight components are present in *relatively* large amounts so that the chromatogram resembles that of the original oil (Figure 2). The trace amount of the sample prevents strict comparison with the original oil.

Chromatograms of the aromatics in the BOUCHARD Barge No. 65 No. 2 fuel oil and representative samples of marsh surface sediments are presented in Figure 4. In this series of samples we have captured the early stages of the processes governing the fate of the spilled oil in the sediments which we missed for the Wild Harbor samples. The sequence of decreasing relative abundance of the lighter molecular weight aromatics occurs over the two and one-half years sampled. However, the October, 1974 sample taken just three days after the spill contains a suite of aromatics almost identical in relative abundance with the original oil as determined by our analyses. Between October 1974 and May 1975 there was some depletion of the methyl naphthalenes and C_2 -naphthalenes relative to heavier molecular weight components. After that the pattern set by the Wild Harbor data is repeated as time progresses.

We have measured the concentrations of several of the classes of aromatics in the Winsor Cove marsh sediments using the G.C. and G.C.-M.S. data set. The total concentration of all the naphthalenes and phenanthrenes

measured decreases in concentration over the time interval sampled. The data normalized to C_3 -naphthalene concentration (Table 3) shows that over the first six months all the groups of compounds decreased in concentration at the same rate. However, from May 1975 to June 1977 these compounds had different rates of loss with the lighter molecular weight components decreasing at a faster rate. Concentrations of selected individual aromatic compounds from the Wild Harbor marsh show a similar picture over a longer time period (Table 4). The lighter compounds decrease throughout the 7 year period in both absolute and relative concentration. Intermediate weight compounds give indications of an increase in concentration during the middle of the study period followed by a decrease while the heaviest compounds increase relatively and absolutely in concentration throughout the seven years. Some of the variation is undoubtedly due to a combination of analytical and sampling error. But the picture for the listed compounds plus others is consistent enough to support the above description which must be explained by a combination of losses of the lighter fractions with concentration of the heavier by horizontal and vertical migration of the oil to the sampling site from other locations. The latter speculation is supported by the observations that the oiled sediments often release small oil slicks during tidal changes or when stepped on.

The data of Tables 1 and 4 are not incompatible. The individual compounds measured represent a small percentage of the total aromatics in the f2 fraction of sediment sampled a year or more after the spill. The C_2 - and C_3 -naphthalenes may well decrease in concentration while the total concentration of f2 remains fairly constant.

Glass Capillary-Gas Chromatographic-Mass Spectrometric Computer System Data

Computer reconstructed total ion chromatograms from the GC-MS analyses for three of the samples are given in Figure 5. Computer reconstructed selected ion plots of molecular ion m/e for phenanthrene, C_4 -naphthalenes, C_1 -phenanthrenes, C_5 -naphthalenes, C_2 -phenanthrenes, C_6 -naphthalenes, C_3 -phenanthrenes, and C_7 -naphthalenes are given in Figure 6. Such plots do not necessarily indicate the presence of these compounds. Rather they indicate whether or not these compounds are likely to be present as components of the sample and which mass spectra should be examined closely for evidence of these compounds. We inspected mass spectra of the peaks which were enhanced in these selected ion plots compared to total ion plots and where possible identified the compound or compounds present where the peak eluted. This approach allowed us to identify several of the compounds and tentatively identify several others. For example, we identified peak number 32 as dibenzothiophene and peaks 36 and 37 as methyldibenzothiophene based on a match of the mass spectra with spectra for those compounds given in the API reference spectra (API, 1977).

Figure 5
about here.

Figure 6
about here.

Unfortunately, we could not find reference spectra for most of the C_3 - C_5 naphthalenes and phenanthrenes nor were commercial standards available to us to generate reference spectra and gas chromatographic retention indices. Thus our identifications of several of the compounds in Table 2 are incomplete and tentative based on interpretation of the mass spectra.

The selected ion plots in Figure 6 illustrate the more rapid losses of the C_4 -naphthalenes, phenanthrene and methylphenanthrenes relative to the C_5 and C_6 naphthalenes and the C_2 phenanthrenes. It is also interesting to

note that the dibenzothiophene (peak 32, Figure 6) and methyl-dibenzothiophene (peaks 36, 37, Figure 6) concentrations decrease more slowly than the adjacent aromatic hydrocarbons, phenanthrenes and methylphenanthrenes (peaks 33, 38, 39, 40, and 41 respectively) when comparing the data from the original No. 2 fuel oil and the July 1972 sample. GC-MS selected ion plots for the Winsor Cove samples gave the same result.

Discussion

Two local marshes were contaminated by spilled No. 2 fuel oil at the same time of year, five years apart. Our investigations show that the aromatic compounds present in the spilled oil had similar fates. Lighter molecular weight compounds decreased in concentration more rapidly than heavier molecular weight compounds, e.g. naphthalene, C_1 - and C_2 -naphthalenes compared to phenanthrenes. By the end of the study periods, most of the aromatic compounds had decreased in absolute concentration. But the heaviest ones in Wild Harbor marsh actually were present in larger amounts than earlier in the study, although they may have been less concentrated than they were immediately after the spill since we have no data for that period. There is a wide variety of aromatic hydrocarbons present in marsh sediments at concentrations well above background six and one-half years after the spill of No. 2 fuel oil.

The most reasonable explanation of the decreasing concentrations of most of the aromatics is a combination of water solubilization or accommodation and transport from the sediments; evaporation; and perhaps microbial attack (Gibson, 1977). Water washing and/or evaporation could result in a more rapid removal of the lighter molecular weight compounds as they have

greater solubility and higher vapor pressure (McAuliffe, 1977; Boehm and Quinn, 1973; Eganhouse and Calder, 1976). The absolutely higher concentration of the heaviest compounds must be explained by a concentrating of the remaining oil in surface sediment from both depth in the peat and horizontally in the study area. Our samples came from a mid-tide region where marsh sedimentation is most rapid, while erosive processes are likely to be most active near high and low water (Owens, 1978) which could lead to just such a concentration.

The uniform decrease of aromatics from October 1974 to May 1975 for the Winsor Cove samples can be explained as follows. The marsh sediments were so saturated with oil as indicated by the high concentrations of aromatic hydrocarbons (Tables 1 and 3), that water washing removed the bulk oil without partitioning with the sediment. As the concentration of the oil was lowered, sediment-oil-water interactions became more important than the simpler water-oil interactions which first took place. By water-oil interaction we refer to interactions between the oil and the sum of seawater and its constituents including the macromolecular weight humic and fulvic materials which promote accommodations of some hydrocarbons into seawater (Boehm and Quinn, 1973). The relative importance of the solubilization, evaporation and microbial degradation of the aromatics cannot be discerned from our data. Oil slicks floating on the surface of the water as the tide came in were observed for several years after the spill in the absence of other disturbance of the mud. This demonstrates that water washing of oil out of the sediments did occur over that period of time.

Analyses of a few core sections from the Wild Harbor marsh showed that aromatics were incorporated below the upper 0-7 cm to a depth of 25 cm.

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Krebs and Burns (1977) in their studies of fiddler crabs (Uca) in the Wild Harbor marsh found that there was an inverse correlation between the amount of aromatics in the sediments and the size of the crab population. It is apparent from our data which comes from their "Station 1" that the lighter aromatics are responsible for most of the immediate and toxic effects. They have other stations where recovery has still not occurred but for which we do not as yet have detailed data on the aromatics. We do have the mud core data from 1975 which is not from their Station No. 1 which shows aromatics in relative concentrations much like that of the original oil, although the absolute concentration is very low. However, a small crab overwintering in the sediment would be in potential contact with that oil with its light aromatics for several months and the initial overwintering period is a time of principal mortality associated with oil. But all of the crabs, even those living in the areas where the population has built up again, are in long term contact with the heavily substituted naphthalenes and the phenanthrenes. Possible effects of these compounds has been, up to the present time, masked by the toxicity of the lighter fractions. We do not know to what extent these compounds are taken up by the animals. Further and more detailed studies are necessary to see whether the physiology and/or population structure will be affected by long exposure to these compounds.

Our data also bear on the question of the origin of aromatic hydrocarbons in marsh and subtidal surface sediments not polluted by oil spills. Measurements by Giger and Blumer (1974), Youngblood and Blumer (1975), Farrington et al. (1977), Hites et al. (1977), LaFlamme and Hites (1978), Grimmer and Boehnke (1975), among others, all indicated the presence of aromatic hydrocarbons from pyrolytic sources in soils and surface sediments

in marshes, lakes, and oceanic areas. Several of these investigations reported depth distributions of these compounds which indicated that a historical record of increasing input of these compounds to sediments had occurred over the past 100 years as a result of increased burning of fossil fuels and release of pyrolytically formed aromatics to the environment. There was a slight but unlikely possibility that some biogeochemical processes acting on chronically spilled oil (Farrington et al., 1977) incorporated into sediments would change the distribution of aromatics found in petroleum (Youngblood and Blumer, 1975; LaFlamme and Hites, 1978) to the distinctive distribution of aromatics resulting from pyrolysis and that chronic small oil spills accounted for increased concentrations in some locations. This would require an enhancement of the parent aromatics relative to the alkyl-substituted aromatics once the oil was spilled. For example, phenanthrene would have to increase relative to C_1 -, C_3 -phenanthrenes. As is readily seen by inspection of the data in Tables 3 and 4, and Figures 2, 4, 5, and 6 this does not occur in the marsh sediments, after six and one-half years of biogeochemical weathering. We think that the Wild Harbor data is the longest recorded field test data available which demonstrates conclusively that conversion of aromatic distributions from spilled oils to that of a pyrolytic source distribution does not occur once oil is spilled to the environment, confirming the projections based on physical, chemical, and geochemical principals (Hase and Hites, 1976; Farrington et al., 1977; LaFlamme and Hites, 1978).

Our analyses also demonstrate the advances which are now possible in understanding the fate of petroleum compounds in marine ecosystems. The routine application of glass capillary gas chromatography and coupled glass

capillary gas chromatography-mass spectrometer-computer systems provides a capability to resolve, quantify, and identify aromatic compounds which differ only by the position of substitution of the same alkyl groups on the parent ring system. Hundreds of compounds can be simultaneously analyzed by these techniques. Limitations to progress in the full utilization to this potential, based on our own experience, are the lack of reference spectra for many of the compounds resolved by glass capillary GC coupled with a lack of commercially available standards to remedy this situation. In addition, most commercially available GC-mass spectrometer-computer systems lack a powerful enough computer to routinely and rapidly process combined GC retention index, mass spectral matching, and quantitative mass fragmentographic or GC detector integration data. All these limitations seem manageable in the short term. Ecologists and geochemists can look forward to very useful analytical data for studies of the fate and effect of petroleum compounds, other organic pollutants, and naturally occurring biologically and geochemically active organic compounds in marine ecosystems.

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Table 1. Concentrations of Aromatic Compounds in Marsh Sediments -
West Falmouth Oil Spill September 1969 Wild Harbor Station:
and BOUCHARD Barge No. 65 Oil Spill October 1974 -
Winsor Cove Stations.

West Falmouth Spill Wild Harbor Station		BOUCHARD Barge No. 65 Spill Winsor Cove Station	
Sampling Date	Conc. mg/gdw ¹	Sampling Date	Conc. mg/gdw
January 1971		<u>Site 1</u>	
0-7 cm	1.21	October 1974	
November 1972		0-6 cm a	20.6
0-7 cm	2.14	0-6 cm b	11.4
November 1973		14-18 cm a	0.12
0-7 cm	3.28	14-18 cm b	0.24
September 1975		May 1975	
0-7 cm	1.09	0-5 cm	4.6
July 1976		15-20 cm	0.05
0-7 cm	1.63	May 1976	
<u>Control Site Chappaquoit Marsh</u>		0-6 cm	5.1
May 1975		25-29 cm	0.06
0-6 cm	0.04	45-49 cm	0.06
July 1977		June 1977	0.32
0-6 cm	0.02	<u>Site G.H.</u>	
		May 1975	
		0-6 cm	0.37
		July 1977	
		0-6 cm a	3.04
		0-6 cm b	1.31

¹Gravimetric determination mg/g dry weight of sediment.

FIGURE LEGENDS

- Figure 1. Chart of locations of Wild Harbor and Winsor Cove in Buzzards Bay, Massachusetts.
- Figure 2. Gas chromatograms of aromatics from marsh surface sediments, Wild Harbor.^{1,2}
- Figure 3. Gas chromatograms of aromatic compounds from marsh surface sediments, Winsor Cove.³
- Figure 4. Gas chromatograms of aromatic compounds from marsh core sections, Wild Harbor.⁴
- Figure 5. Computer reconstructed total ion plot of g.c.-m.s. Analyses of aromatic compounds of marsh surface sediments, Wild Harbor.⁵
- Figure 6. Computer reconstructed selected ion plot of g.c.-m.s. analyses of aromatic compounds in marsh surface sediment, Wild Harbor.^{6,7}

¹SE-52 glass capillary column.

²See Table 2 for identity of numbered peaks.

³See Figure 2 for explanation.

⁴See Figure 2 for explanation.

⁵See text for details of analyses conditions.

⁶See text for details of analyses conditions.

⁷Same analyses as given in Figure 5, except for different data plot.

Table 2. Compounds List for Figures 2-6.

Peak No.	Compound	Identification by:
1	naphthalene	g.c. and m.s.a.
2	2-methylnaphthalene	g.c. and m.s.a.
3	1-methylnaphthalene	g.c. and m.s.a.
4-9	C ₂ -naphthalenes	m.s.a.
10-17	C ₃ -naphthalenes	m.s.a.
18	C ₄ -naphthalene	m.s.a.
19	tetrahydrophenanthrene	m.s.
20-29	C ₄ -naphthalene	m.s.
30	C ₄ -naphthalene + C ₁ -fluorene	m.s.
31	C ₄ -naphthalene	m.s.
32	Dibenzothiophene	m.s.a.
33	phenanthrene	g.c. and m.s.a.
35	C ₂ -fluorene	m.s.
36	methyldibenzothiophene	m.s.a.
37	methyldibenzothiophene	m.s.a.
38	methylphenanthrene	m.s.a.
39	methylphenanthrene	m.s.
40	methylphenanthrene	m.s.
41	methylphenanthrene	g.c. and m.s.
42-44	C ₆ -naphthalenes	m.s.
45-50	C ₂ phenanthrenes	m.s.
51-54	C ₇ -naphthalenes	m.s.
55	C ₃ -phenanthrene	m.s.
56	C ₃ -phenanthrene + trace of C ₃ -phenanthrenes	m.s.
57-58	C ₃ -phenanthrenes	m.s.

g.c. - gas chromatography retention indices

m.s. - mass spectral interpretation

m.s.a. - mass spectra match with API reference spectra.

Table 3. Concentrations of Naphthalenes and Phenanthrenes
in Winsor Cove Marsh Surface Sediments 0-6 cm
($\mu\text{g/g}$ dry wt.)

Compounds	October 1974	May 1975	June 1977
naphthalene	9.2	0.63	0.11
C ₁ -naphthalenes	370	41	1.2
C ₂ -naphthalenes	1380	260	15
C ₃ -naphthalenes	3040	590	33
C ₁ -phenanthrenes	500	97	15
C ₂ -phenanthrenes	480	96	27

Amounts of Naphthalenes and Phenanthrenes in Surface Sediments
from Winsor Cove, Normalized to C₃ Naphthalenes

Compounds	October 1974	May 1975	June 1977
C ₁ -naphthalenes	.12	.07	.04
C ₂ -naphthalenes	.45	.44	.45
C ₃ -naphthalenes	1.00	1.00	1.00
C ₁ -phenanthrenes	.16	.16	.46
C ₂ -phenanthrenes	.16	.16	.82

Table 4. Concentrations of Selected Aromatic Hydrocarbons in Wild Harbor Marsh Sediments.
($\mu\text{g/g}$ dry weight)^a

Compound	January 1971	November 1972	November 1973	September 1975	July 1976
C ₂ -naphthalene (# 6)	23.4	8.6	3.2	0.9	T
C ₃ -naphthalene (#13)	20.3	16.2	19.8	2.7	.45
C ₄ -naphthalene (#25)	5.4	5.9	14.9	6.8	1.4
C ₁ -phenanthrene (#38)	NM	8.6	15.8	7.2	0.9
C ₂ -phenanthrene (#47)	NM	5.0	23.0	23.0	7.2
C ₃ -phenanthrene (#57)		7.4	9.2	8.2	14.4

a) Total estimated error from analytical measurement and sediment subsample heterogeneity is ± 20 to 30%.

Concentrations of Selected Aromatics Normalized to C₃ Naphthalene

Compound	September 1969	January 1971	November 1972	November 1973	September 1975	July 1976
C ₂ -naphthalene (# 6)	1.4	1.2	.53	.16	.33	T
C ₃ -naphthalene (#13)	1.0	1.0	1.0	1.0	1.0	1.0
C ₄ -naphthalene (#25)	.21	.27	.36	.75	2.5	3.1
C ₁ -phenanthrene (#38)	.32	NM	.53	.80	2.7	2.0
C ₂ -phenanthrene (#47)	.32	NM	.31	1.2	8.5	16
C ₃ -phenanthrene (#57)	.06	NM	.46	.46	3.0	32

NM = not measured.

SEDIMENT CORES

JULY 1973
10-15 cm

JULY 1973
45-50 cm

JULY 1975
10-15 cm

JULY 1975
20-25 cm

SURFACE SEDIMENT

FUEL OIL
SEPT. 1969

JAN. 1971

NOV. 1972

NOV. 1973

SEPT. 1975

JULY 1976

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