## PRINCIPAL INVESTIGATORS FINAL REPORTS

BLM CONTRACT NO. 08550-CT5-30

VOLUME IV (X)



### HIGH MOLECULAR WEIGHT HYDROCARBONS IN MAFLA SEDIMENTS AND BENTHIC ALGAE AND RIG MONITORING SEDIMENTS

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#### EXECUTIVE SUMMARY

All of the first period MAFLA sediment samples were complete by the second quarter, and the samples from the third period were complete by the third period. The additional samples demonstrate the same distribution patterns as suggested in the first two quarterly reports and indicate good reproducibility in sampling and analysis. The Transect VI samples and all the deep water stations from Transects I-V are comprised chiefly of terrestrial hydrocarbons. Of lesser amounts in these samples are the low molecular weight hydrocarbons which produce a pattern much like weathered crude oil. Transects I-IV contain neither of these features but have a great abundance of a  $C_{25}$  branched-unsaturated moiety and a major <u>n</u>-alkane of <u>n</u>C<sub>17</sub> such as found in marine algae. Transect V sediments are intermediate in nature between the Transect VI and Transects I-IV sediments.

Thirty-six specimens of benthic algae from Transects I-VI have been analyzed, and 15 of these contain oil-like hydrocarbons. There are no clear patterns of pollution, i.e., no correlation of contaminated algae with contaminated sediments. The only discernible trend is found along Transect II where the percentage of polluted samples decreases from Period 1 to Period 3, but the few samples may cause a misleading trend. Algae showing no signs of pollution contain hydrocarbon distributions similar to that reported in the literature. A series of phytadienes, not reported before in algae, occurs in several algae. Their occurrence appears to be strictly due to biosynthesis.

All of the rig monitoring samples that have been received have

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been analyzed. All samples regardless of location or time of collection are incredibly similar in every respect. The aliphatic hydrocarbons are characterized by a large hump of unresolved complex material underlying a series composed mostly of <u>n</u>-alkanes in the high molecular weight range. These <u>n</u>-alkanes fall into a pattern that is distinctly terrestrial. The low molecular weight alkanes are distributed in a manner resembling very weathered crude oil. Also present in all samples is a complex of peaks between  $C_{20}$  and  $C_{22}$  alkanes which probably is similar to the  $C_{25}$  compound found in MAFLA sediments. Gravimetric and gas chromatographic data and cluster analysis reveal only minimal changes in samples due to drilling, but discriminant analysis confirms that the effects diminish quickly moving away from the rig.

The intercalibration results are very encouraging demonstrating very reproducible analyses within and among the hydrocarbon laboratories.

Additional comments may be found in the Addendum.

#### Status of Samples

Table 1 shows the status of samples we have received. Analysis is complete on all of the baseline sediment samples. Analyses are complete on all of the rig monitoring sediments. Of the 48 algal samples received the contracted analysis of 36 has been completed. In addition to the two intercalibration samples and several blanks analyzed during the first two quarters, seven intercalibration samples (including four American Petroleum Institute oils) have been exchanged, and analysis is complete.

#### I. MAFLA Study

A total of 43 sediment samples from the first sampling period of 1975-76 and 21 from the third sampling period have been analyzed. Chromatograms

# Sample Status Sheet

Kind of Sample	No. Samples Received	No. Samples Completed	No. Samples in Progress
Sediment - Period 1	42	42	0
- Period 2	0	0	0
- Period 3	21	21	0
- Rig Before	25	25	0
- Rig During	24	24	0
- Rig After	24	24	0
Algae - Period l	16	14	0
- Period 2	16	13	0
- Period 3	9	9	. 0
Intercalibration Samples	9	9	· 0

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of the aliphatic and aromatic hydrocarbons from the first period and third period may be found in appendices of the first, second and third quarterly reports. Gravimetric parameters for all the samples collected in 1975-76 are shown in Tables 2a-c and 3.

With no exceptions, the samples collected from the third period of 1975-76 support the evidence found in the first sampling period. These samples were chosen with three goal; in mind : (1) To sample stations unsuccessfully sampled in the first period, which coincidentally were station sites of 1974-75, (2) to verify some unusual characteristics of Gulf sediments, e.g., terrestrial hydrocarbons on the outermost shelf and (3) to do a random check for reproducibility. These aspects will be discussed in detail later. In general, the completion of the sediment samples confirms earlier conclusions that the Florida and E. Alabama shelf region contain hydrocarbons with no detectable source of terrestrial or petroleum hydrocarbons. The aliphatics predominantly are non-normal alkanes consisting of branchedcyclic-unsaturated complexes at Kovats Indices 1640, 2075-2150, 2500 and 3400 on FFAP. The Mississippi-W. Alabama and outermost shelf sediments are characterized by abundant high molecular weight n-alkanes of terrestrial distribution and lesser amounts of low molecular weight n-alkanes with a fairly uniform distribution typical of weathered petroleum.

#### Comparison of 1974 and 1975

Of the 21 stations sampled during the third period sampling of 1975-76, six samples were taken from stations corresponding to 1974-75 baseline stations. Of these six (from Stations #10, 14, 15, 31, 39 and 43), three samples (from Stations #10, 14 and 15) were collected from sites not successfully sampled in the first period of 1975-76. The 15 samples reported

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Tab	le 2 Gravimetri	c Data of Sediments,	, First Sampling	; Period
t (g)	Percent Carbonate	Percent Org. Carbon (Acidi- fied Basis)	Lipid Weight (g)	Aliphatic Weight (g)
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Table	2	Gravimetric	Data	of	Sediments.	First	Sampling	Period
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1   2052   94.1   1.96   0.20050     2   3432   34.1   0.19   0.20825     3   741   68.3   0.70   0.03588     4   1684   98.4   3.31/3.01   0.18158     5   2686   98.1   7.50   0.06612	0.00359 0.00311 0.00072	0.00324
2   3432   34.1   0.19   0.20825     3   741   68.3   0.70   0.03588     4   1684   98.4   3.31/3.01   0.18158     5   2686   98.1   7.50   0.06612	0.00311 0.00072	0 00354
3   741   68.3   0.70   0.03588     4   1684   98.4   3.31/3.01   0.18158     5   2686   98.1   7.50   0.06612	0.00072	0.00004
4   1684   98.4   3.31/3.01   0.18158     5   2686   98.1   7.50   0.06612		0.00050
<b>5</b> 2686 98.1 7.50 0.06612	0.00147	0.00278
	0.00073	0.00104
<b>6</b> 2516 96.5 7.20 0.16200	0.00220	0.00236
7 2625 47.6 0.40 0.13092	0.00364	0.00297
8 2683 86.2 2.00 0.35283	0.00398	0.00580
<b>9</b> 2730 · 86.0 1.86 0.36025	0.00311	0.00516
10	0100312	0100910
11 2404 97.2 6.82 0.24292	0.00189	0.00251
12 1941 92.9 4.80 0.20917	0.00239	0.00208
13 837 87.6 1.24 0.16417	0.00142	0.00110
15		
16 3093 79.6 0.60 0.15225	0.00190	0 00609
17 $2226$ $95.4$ $3.33$ $0.01200$	0.00127	0.00301
18     3908     10.9     0.07     0.05283	0.00127	0.00109
······································	0 00152	0.00139
20 $2303$ $71.1$ $0.32$ $0.04442$	0.00102	0.00131
21 $2243$ $53.6$ $0.40$ $0.08425$	0.00225	0.00242
<b>22</b> 2000 51.3 0.36 0.30800	0.00807	0.00339
23 1827 \$0.6 2.07 0.24442	0.00095	0.00350
24 1962 8.8 0.06 ' 0.02175	0.00083	0.00051
25 1502 11.5 0.05 0.01788	0.00079	0.C0063 ·
26 2416 61.2 0.57 0.12308	0.00128	0.00174
27     1579     80.5     2.96     0.19667	0.00244	0.00307

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Table 2a (Cont'd)

Station Dry Weight Number Sediment (g)		Percent Carbonate	Percent Org. Carbon (Acidi- fied Basis)	Lipid Weight (g)	Aliphatic Weight (g)	Aromatic Weight (g)
28 .	1351	65.0	0.40	0.10038	0.00132	0.00086
29	1780	77.9	0.68	0.12175	0.00131	0.00068
30	1274	75.7	0.48	0.05075	0.00072	0.00086
31	1746	92.1	1.96	0.09583	0.00120	0.00133
32	2159	80.7	0.87	0.05892	0.00158	0.00312
33	2610	44.0	0.34	0.12850	0.00125	0.00144
34	1834	93.4	2.42	0.03133	0.00105	0.00107
35	1065 .	73.7	4.10	0.51450	0.00350	0.00295
36	1289	74.4	4.05	0.54008	0.00516	0.00284
37 .	316	14.2	0.72	0.08850	0.00185	0.00252
38	1071	11.5	0.84	0.13825	0.00842	0.00573
39	2277	18.7	0.29	0.14875	0.00641	0.00394
40	3048	12.5	0.11	0.03963	0.00199	0.00195
41	1701	5.7	0.23	0.09833	0.00193	0.00232
42	1800	4.1	0.10	0.05958	0.00125	0.00122
43	1884	. 32.9	• 2.37	0.12800	0.00247	0.00218
44	1834	93.1	2.70	0.10942	0.00291	0.00261
45	1185	90.0	3.13	0.12750	0.00312	0.00288

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Station Number	Lipid Acid. Sed. (ppm)	Lipid Total Sed. (ppm)	Lipid Org. Carbon (%)	<u>Total HC</u> Lipid (%)	Aliph HC Arom HC
1	1645.	97.7	8.4	3.41	1.11
2	9211.	60.7	4.8	3.24	0.85
3	153.	48.4	2.2	4.24	0.90
4	6700.	105.0	5.4	2.12	0.75
5	1317.	24.6	1.8	2.75	0.75
6	1841.	64.4	2.6	1.80	0.93
7	95.2	49.9	2.4	5.05	1.22
8	951.	131.	4 - 8	2.77	0.69
9	943.	132.	5.1	2.29	0.60
· 11	3570.	101.	5.2	1.81	0.75
12	1514.	108.	3.2	2.13	1.15
13	1492.	185.	12.1	1.53	. 1.29
16	241.	49.2	4.0	5.25	0.31
17	117.	53.1	0.4	25.7	0.42
18	15.2	13.5	2.2	4.46	1.17
19	45.6	35.8	·3.0 °	3,21	1.10
20	55 6	19 3	1.7	5 34	0.81
. 21	80.9	37.6	2.0	5 60	0.01
22	155	320	8.8	3,72	2 38
23	689	134	3.4	1.82	0.27
24	12.2	11.1	3.2	6.16	1.63
25	13.4	11.9	. 2.7	7.94	1.26
26	13.1	50.9	2.3	2.45	0.74
27	638.	125.	2.2	2.80	0.80

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Table 2b

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Table 2b (Cont'd)

ation mber	Lipid Acid. Sed. (ppm)	Lipid Total Sed. (ppm)	Lipid Org. Carbon (%)	Total HC Lipid (%)	Aliph HC Arom HC
28	212.	74.3	5.3	2.17	1.53
29	310.	68.4	4.6,	1.64	1.92
30	164.	39.8	3.4	3.11	0.84
31	695.	54.9	3.5	2.64	0.90
32	141.	27.3	1.6	7.98	0.51
33	87 <b>.9</b>	49.2	2.6	2.09	0.87
34	259.	17.1	1.1	6.77	0.98
35	1840.	483.	4.5	1.25	1.19
36	1640.	42.	4.0	1.49	1.82
37	320.	276.	4.5	4.75	0.91
38	146	129.	1.7	10.24	1.47
39	80.3	65.3	2.8	6,96	1.63
40	14.9	13.0	1.4	9.94	· 1.02
41	61.3	57.8	2.7	4.32	0.83
42	34.5	33.0	3.4	4.15	1.02
43-	602.	68.0	2.5	3.90	1.29
44	265.	59 <b>.7</b>	3.2	5.04	1.11
45	1074.	108.	3.4	4.75	1.08

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Station Number	Aliph HC Acid. Sed. (ppm)	Aliph HC Tot. Scd. (ppm)	Aliph HC Org. Carbon (%)	Aliph HC Lipid (%)	Arom HC Acid. Sed. (ppm)	Arom HC Total Sed. (ppm)	Arom HC Org. Carbon (%)	Arom HC Lipid (%)
1	29.5	1.75	0.15	1.79	· 26.6	1.58	0 14	1.62
2	1.38	0.91	0.07	1.49	1.61	1.06	0.08	1.75
3	3.06	0.97	0.04	2.01	3.40	1.08	0.05	2.23
4	54.5	0.87 .	0.04	0.83	87.6	1.15	0.07	1.10
5	15.5	0.29	0.02	1.18	20.7	0.39	0.03	1.57
6	25.0	0.87	0.03	1.36	26.8	0.94	0.04	1.46
7	2.65	1.39	0.07	2.78	2.16	1.13	0.05	2.27
8	10.7	1.48	0.05	1.13	15.6	2.16	0.08	. 1.64
9	8.1	1.14	0.04	0.86	13.5	1.89	0.07	1.43
11	27.8	0.79	0.04	0.78.	36.9	1.04	0.05	1.03
12	17.3	1.23	0.04	1.14	15.1	1.07	0.03	0.99 -
13	12.9	1.6	0.10	0.86	10.0	1.24	0.08	0.67
16	3.01	0.61	0.05	1.25	9.65	1.97	0.16	4.0
17	12.4	0.57	0.04	10.6	29.4	1.35	0.09	25.1
. 18	0.36	0.32	0.05	2.40	0.31	0.28	0.05	2.06
	0.77	0.60	0.05	1.68	0 70	0 55	0.05	1 53
20 :	1.33	0.46	0.04	2.39	1.64	0.57	0.05	2 95
21	2,20	1.00	0.05	2.70	2.30	1,10	0.06	2.90
22	8.0	4.0	0.23	2.62	3.5	1.7	0.10	1.10
23	2.68	0,52	0.01	0.39	9.87	1.92	0.05	1.43
24	0.46	0.42	0.08	3.82	0.29	0.26	0.05	2.34
25	0.59	0.52	0.12	4.42	0.47	0.42	0.10	3.52
26	1.37	0.73	0.02	1.04	1.86	0.72	0.03	1.41
27	7.92	1.54	0.03	1.24	10.0	1.90	0.03	1.56
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Table 2c

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Station Number	Aliph HC Acid. Sed. (ppm)	Aliph HC Tot. Sed. (ppm)	Aliph HC Org. Carbon (%)	Aliph HC Lipid (%)	Arom HC Acid. Sed. (ppm)	Arom HC Total Sed. (ppm)	Arom HC Org. Carbon (%)	Arom HC Lipid (%)
28	2.79	0.98	0.07	1.31	1.82	0.64	0.05	0.86
29	3.33	0.74	0.05	108	1.73	0.38	0.03	0.56
30	2.32	0.56	0.05	1.42	2.77	0.67	0.06	1.69
31	8.70	0.69	0.04	1.25	9.60	0.76	0.05	1.39
32	3.79	0.73	0.04	2.68	7.49	1.44	0.09	5.30
33	0.86	0.48	0.03	0.97	0.99	0.55	0.03	1.12
34	8.68	0.57	0.04	3.35	8.86	0.58	0.04	3.42
35	12.5	3.29	0.03	0.68	10.5	2.77	0.02	0.57
36	15.6	4.00	0.04	0.96	8.61	2.20	0.02	0.53
37	7.17	6.15	0.09	2.23	8.13	7.21	0.11	
38	8.83	7.86	0.11	6.09	6.04	5.35	0.07	4.14
39	3.46	2.82	0.12	4.31	2.13	1.73	0.07	2.65
40	0.75	0.65	0.07	5.02	0.73	0.64	0.07	4.92
41	1.20	1.13	0.05	1.96	1.45	1.36	0.06	2.36
42	0.72	0.69	0.07	2.10	0.71	0.68	0.07	2.05 .
43	13.2	1.49	0.06	2.20	10.2	1.16	0.04	1.70
44	23.0	1.60	0.09	2.66	20.6	1.40	0.08	2.38
45	26.3	2.63	0.08	2.45	24.3	2.40	0.08	2.30

Table 2c (Cont'd)

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### Table 3

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### Gravimetric Data, 3rd Period Baseline Sediment Samples

tation	Dry Weight Sectorat (s)	% Carl	onate	% Organic (Acidifie	c Carbon ed Basis)	Lipid	Aliphatic	Aromat
unber	(Unacidified)	3rd Period	lst Period	3rd Period	lst Period	Weight (g)	Weight (g)	Weight
1	<u> </u>		<u> </u>				· · ·	
1	2874.	47.6	94.1	0.37	2.0	0.20650	0.00556	0.0030
4	1122.	97.5	98.4	0.8	· 3.2	0.12675	0.00093	0.0011
6	1565.	96.5	96.5	8.8	7.2	0.14850	0.00178	0.0013
7	2672.	51	47.6	0.24	0.40	0.19475	0.00279	0.0024
10	2073.	92.0	-	0.21	. <b>-</b>	0.09450	0.00149	0.0016
12	1477	92.3	92.9	5.5	4.8	0.16550	0.00168	0.0015
13	1918.	90.2	87.6.	4.3	1.2	0.12075	0.00258	0.0012
14	1957.	10.3	-	2.9	-	0.25200	0.00254	0.0033
15	2089.	96.1	-	4.6	-	0.13850	0.00163	0.0021
18	2841.	9.8	10.9	0.10	0.10	0.05350	0.00081	<b>0.0002</b>
24	2875.	· _	8.8	0.13	0.10	0.06475	0.00133	0.0012
25	2538.	14.7	11.5		0.10	0.04450	0.00093	0.0005
27 .	1540.	_	80.5	1.5	3.0	0.19275	0.00214	0.0015
31	2381.	-	92.1	2.6	2.0	0.11125	0.00079	0.0009
36	1296.	74.4	74.4	3.7	4.1	0.43000	0.00434	0.0032
37	173.1	-	14.2	-	0.72	0.04050	0.00106	0.0001
35	203.5	_	11.5	1.1	0.84	0.04125	0.00106	0.0010
39	2082	-	18.7		· 0.29	0.15975	0.00579	0.0034
43	1297.	-	32.9	<b>'2.1</b>	2.4	0.08175	0.00223	0.0011
44	2191		93.1	1.9	2.7	0.05000	0.00133	0.0011
45	1707.	85.0	90.0	2.0	3.1	0.19025	0.00348 .	0.0019

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earlier serve to show the constancy of hydrocarbon content in Gulf sediments. No alarming disparities were noticed then and none are noticed when comparing the 1974-75 and 1975-76 chromatograms of the remaining six.

Tables 2 and 3 show that the results of Stations #10, 14 and 15 fit neatly into the patterns found in the remainder of Transects II and III. At Station #10 (#57 in 1974-75) along Transect II the predominent peak is that cluster around Kovats Index 2075. The <u>n</u>-alkane component is insignificant compared to the 2075 peak; the high molecular weight material occurs in somewhat higher amounts in 1975-76 than 1974-75.

Stations #14 and 15 along Transect III (corresponding to #48 and #47 in 1974-75) are again dominated by the cluster of peaks at K.I. 2075 and another group around K.I. 2500. Odd <u>n</u>-alkane preference in high molecular weights (HMW) for #14 is approximately the same in both years; the odd/ even ratio in the low molecular weight (LMW) range is somewhat greater than one in both samples. Pristane/ $C_{17}$  and phytane/ $C_{18}$  ratios are unchanged over a time of one year at this station. Some very high molecular weight material appears in both years reducing the probability of contamination in the 1974 sampling period. In sample #15 the high molecular weight fraction is more pronounced in 1975-76 with other characteristics of 1974-75, i.e., pristane/ $C_{17}$ , phytane/ $C_{18}$  ratios and predominance of K.I. 2075, virtually the same.

The 1974-75 Station #31 was characterized by a gas chromatograph array containing a large peak at <u>ca</u> K.I. 2800. The two samplings in 1975-76 (also #31) do not show this peak. Several replicate analysis checks in our laboratory have produced an erratic peak in this region. We believe that

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it is most likely a laboratory contaminant, probably a phthalate ester. All three chromatograms contain an abundance of the K.I. 2075 peak with small amounts of <u>n</u>-alkanes. The H4W region of <u>n</u>-alkanes shows a notable odd/ even preference indicating the presence of some terrestrial material. With the possible exception of the extraneous peak at <u>ca</u> K.I. 2800 in 1974-75, the chromatograms are identical.

The sample from Station #39 in Transect VI has only a poorly resolved gas chromatogram from the 1974-75 sampling (Station #9); however the chromatograms from the first and third period samplings are quite similar. Again the H4W peaks are much greater than the LMW with a very high odd/even preference in this region. The peak complex at K.I. 2075 is in considerable quantities but not nearly as much as in the Florida samples.

The first and third period samples from Station #43 again do not have a chromatogram of suitable quality from the 1974-75 period (Station #17) but show striking similarities to each other and to the results found at Station #39.

Comparisons of first and third period samples

In addition to providing access to stations that were identical to stations sampled in 1974-75, the third period 1975-76 samples permitted resampling of areas which showed some unusual or questionable characteristics in the first period.

The chromatograms of Station #1 shown in Figure 1 demonstrate one of the peculiarities found in Transect I sediments, the presence of many peaks between  $C_{16}$  and  $C_{19}$  and a very large peak at K.I. 2500 which is probably not all  $C_{25}$ . The presence, in both, of large amounts of compounds above  $C_{31}$  provides sufficient proof that these peaks are not artifacts or laboratory contaminants.

The peak at <u>ca</u> K.I. 2500 also shows up at Station #4 where it is even larger.  $C_{17}$  is the largest <u>n</u>-alkane in both periods with the 2075 complex

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Figure 1. Aliphatic gas chromatograms (FFAP) of Station 1 aliphatics from period 1 (above) and period 3 (below) 1975-76.

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				- Sola	

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the dominant component in both chromatograms. The third period sample has the peak at K.I. 2850 that occurs so randomly that we can only assume that it is a contaminant.

The striking dissimilarity of Station #6 and the remaining Transect I sediments is again evidenced in the third period. The chromatograms are almost identical. The high predominance of HMW <u>n</u>-alkanes with a strong odd/even preference again suggests a terrestrial source of hydrocarbons on the outer edge of the shelf. The LMW <u>n</u>-alkanes have no dominant peak(s) and look reminiscent of the distribution of aliphatics from "polluted" Mississippi samples of 1974.

The abundance of unidentified peaks found in the first period at Station #7 were in evidence during the third period. A very large peak at ca K.I. 3400 appears to be characteristic of this station.

On the outer shelf of Transect II, Station #12 again displays an aliphatic distribution appearing to be of terrestrial origin. The HMW's have a very pronounced odd/even preference (see Figure 2), and the 2075 peak is greatly reduced compared to the samples nearer shore. Station #13, the outermost station of Transect III, also contains a HMW distribution characteristic of terrestrial organic matter in both first and third periods. Here the evidence of pollution is more pronounced than in Stations #12 and #6. Figure 3 demonstrates the even distribution of LMW <u>n</u>-alkanes supporting a suggested pollution origin. Considering the problem of reproducible sampling in 152 m of water, the chromatograms are remarkably similar.

The peak at 2075 and the group between 2500 and 2600 are strongly in evidence at Station #18 during both samplings. Not much <u>n</u>-alkanes are present in either sample.

Samples from Station #24 are remarkable in that the chromatograms are almost identical (see Figure 4). A peak which we have labeled phytane proves to be the remarkable feature of Station #25, being quite large in

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Figure 2. Aliphatic gas chromatograms (FFAP) of Station 12 aliphatics

from period 1 (above) and period 3 (below) 1975-76.

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Figure 3. Aliphatic gas chromatograms (FFAP) of Station 13 aliphatics from period 1 (above) and period 3 (below) 1975-76.

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Figure 4. Aliphatic gas chromatograms (FFAP) of Station 24 aliphatics from period 1 (above) and period 3 (below) 1975-76.

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both chromatograms.

As was apparent in the first period, Station #27 can be distinguished from the remaining transect by the absence of material other than <u>n</u>-alkanes in the LMW region. Figure 5 shows the similarity of the first and third period and points out the terrestrial nature of the HMW <u>n</u>-alkanes in this outer shelf sample.

Along Transect V similarities have been pointed out for Station #31 in an earlier discussion; Station #36 produced chromatograms in Figure 6 that also are quite similar. This station follows the trend of all deep water stations with only a slight odd/even dominance in the LMW <u>n</u>-alkanes and a shift to a very decided odd/even dominance in the HMW region implying terrestrial sources of input. Noted here is a suite of <u>n</u>-alkenes of <u>ca</u> one fifth the concentration of the corresponding <u>n</u>-alkanes.

The 2075 peak, still in evidence, is at about the same concentration level as C<sub>29</sub> in both periods at Station #36 but falls short of C<sub>29</sub> at Station #37, the shallowest station of Transect VI five miles off Pascagoula. The chromatograms from this station shown in Figure 7 show a distribution of aliphatic hydrocarbons very similar to all the deep water stations. The LMW <u>n</u>-alkanes seem to indicate some pollution; the HMW, <u>n</u>-alkanes reflect a terrestrial source so commonly seen in the Mississippi sediments with a dominance of C<sub>27</sub>, C<sub>29</sub> and C<sub>31</sub>. There is no noticeable difference in the samples collected during the two periods; neither was there any at Station #39 which looks very much like Station #37.

Stations #43, 44 and 45 on the outer shelf region of Transect VI produced chromatograms in the two sampling periods that are quite similar, and all three stations are similar to each other, to other Transect VI stations and all deep water transects. In Station #45, shown in Figure 8, can be seen the terrestrial signature in the HMW n-alkanes and the petro-

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Figure 5. Aliphatic gas chromatograms (FFAP) of Station 27 aliphatics from period 1 (above) and period 3 (below) 1975-76.

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Figure 6. Aliphatic gas chromatograms (FFAP) of Station 36 aliphatics

from period 1 (above) and period 3 (below) 1975-76.

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Figure 8. Aliphatic gas chromatograms (FFAP) of Station 45 aliphatics

from period 1 (above) and period 3 (below) 1975-76.



leum pollution in the LMW range. Here the  $C_{29}$  has decreased to somewhat less than the 2075 peak.

Some differences that were not evident in comparing the first and third period chromatograms can be seen by observing the data calculated in Table 4.

Though there is considerable difference in aliphatic weights at Stations #1, 13, 27 and 37 for the two collections, the <u>n</u>-alkane/aliphatic ratio remains virtually constant indicating that the difference is more likely due to sampling variability than contamination. This ratio is remarkably similar in all cases regardless of the absolute value of either component. Therefore this parameter is probably a safer one to use in assessing pollution being less subject to natural variability. In general, the ratios show less variability than gravimetric concentrations.

Station #4 is notable in that LMW <u>n</u>-alkanes are <u>ca</u> 75% higher compared to EAW material in the third period. However at Station #38 the ratio of LMM/HAW was four times higher in the third period. This probably resulted from laboratory losses at the low end since neighboring stations in both cases agree more favorably with the third period samples.

The odd/even ratios are fairly constant when comparing results of the first and third periods. The major exceptions occur at Stations #4 and 39 where the ratio among HMW <u>n</u>-alkanes is higher in the first period. This being a terrestrial component probably reflects the natural variability in sampling.

Surprisingly the <u>n</u>- alkane/ $C_{16}$  ratio does not vary significantly considering the high risk of loss of  $C_{16}$  by evaporation. Only at Station #12 where the value increases by ten-fold in the third period is evaporation a serious problem. Deviations are even slighter with the ratio of 15+17/ 2X16, Station #24 yielding the greatest difference in the two periods.

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-32-

## Table 4

## Comparison of 1st Period with 3rd Period - Chromatographic Parameters 1975-1976

		pp	b dry wt. s	ed*	% Zn-alk	£C≤20		Odd/Even		Z <u>n</u> −alk	15+17	Pris/	Pris+Phy
S	Sample	Aliph	<u>n</u> -alk	Arom	Arom Zaliph		<u>C</u> <u>≺</u> 20	C <u>&gt;</u> 21	A11	<u>n-C16</u>	2×16	17	Z <u>n</u> -alk
, <b>#</b> 1	lst per 3rd per	736. 1021.	64. 87.	119. 110.	8.7 · 8.5	1.43 1.64	4.9 4.6	3.2 2.4	3.6 3.4	40.2 63.6	6.7 13.4	0.10	0.037 0.022
\$4	lst per 3rd per	<sup>·</sup> 129. 111.	15. 12.2	372. 108.	11.4 11.0	1.17 1.88	1.7 1.4	3.1 1.9	2.3 1.5	22. 30.4	2.0 3.8	0.22	0.03 0.09
<b>#</b> 6	lst per 3rd per	150. 174.	30. 39.1	68. 61.	19.1 22.5	0.17 0.16	1.5 1.2	3.9 2.8	3.8 2.7	133. 109.	1.5	0.70 0.57	0.027 0.024
<b>₽7</b>	, lst per 3rd per	561. 417.	68. 30.7	30. 151.	7.0 7.4	0.46 0.35	2.5 2.5	2.1	2.2 2.4	36.7 52.3	2.6 3.9	0.62 : 0.92	0.168 0.169
<b>#</b> 10	3rd per	297.	24.	73.	8.1	0.28	2.4	1.9	2.2	91.7	6.7	0.24	0.052
<b>#12</b>	lst per 3rd per	242. 217.	55. 58.	50. 104.	26. 27.0	0.19 0.09	1.0 1.4	4.0 2.9	2.5 3.1	15.4 166.	0.87 1.1	0.75 0.58	0.02 0.016
Ø13	lst per 3rd per	397. 197.	116. 54.8	88. 78.	29. 27.8	0.2 0.17	0.8	2.3 3.1	1.9 2.6	42.6 50.	1.1 1.1	0.45 0.63	0.028 0.032
#14	3rd per	518.	36.	171.	6.9	0.21	1.3	2.3	2.5	93.3	2.45	0.50	0.054
<b>₽15</b>	3rd per	234.	27.7	137.	11.8	0.64	2.1	3.1	2.4	25.	2.2	0.21	0.06
Ø18	lst per 3rd per	136. 130.	6. 9.	6. 40.	4. 6.8	_ 1.5	_ 3.9	 . 1.7	_ 2.6	40.	8.6	0.82	D.21
≨24	lst per 3rd per	120. 165.	14. 20.	37. · 35.	11.2 12.3	1.1 0.85	1.3 1.5	3.0 2.3	2.8 2.2	15. 40.	1.9 4.0	0.29 0.16	0.20 0.11

\*Measured gas chromatographically

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		PI	ob dry wt. s	ed*	% <u>∕</u> n−alk	C <u>∠</u> 20		Odd/Even	<u>≨ n</u> -alk 15+17		Pris/	Pris+Phy	
S	ample	Aliph	<u>n</u> -alk	Arom	E aliph	E aliph     C_221     C_20     C_221     All		<u>n-C16</u>	2x16	17	<u>En-alk</u>		
\$25	lst per 3rd per	142. 73.	31. 11.	15.	21.6 15.5	1.9	1.3	1.9 1.3	1.5	11.2 29.6	4.1	0.32	0.20
<b>∮</b> 27	lst per Grd per	295. 141.	105.	68. 55.	35.6	0.08	1.1 1.4	4.8 3.3	3.9 3.1	46.	0.9	0.59	0.04
#31	lst per 3rd per	122. 82.	26. 11.2	44. 36.	21. 14.	0.40 0.31	1.1 0.9	4.1 3.6	2.8	55. 44.8	3.2 1.7	0.21 0.41	0.04
<b>Ø</b> 36	lst per 3rd per	663. 446.	199. 112.	144. 293.	30.1 25.0	0.07	1.0 1.0	3.7 3.0	3.3	123. 108.	1.3 1.3	0.43 0.58	0.01
Ø37	lst per 3rd per	1700. 705.	1160. 320.	1280. 115.	67. 45.	0.02 0.19	1.5.	4.1 3.7	3.3 2.9	> 100 32.	1.9 1.1	0.77 · 0.57	0.01 0.04
<b>\$</b> 38	lst per 3rd per	700. 875.	481. 442.	313. 260.	68.5 51.0	0.06	1.1 1.1	3.0 2.9	2.8 2.5	113. 27.	1.3	0.83 0.76	0.02 0.05
<b>#</b> 39	lst per 3rd per	171. 260.	62. 65.	77. 145.	37. 25.	0.16 0.13	1.1 1.4	5.1 3.4	3.9 2.8	37. 61.	1.1 1.3	0.79 0.93	0.05
<u>\$</u> 43	lst per 3rd per	128. 197.	49. 40.	50. 40.	38. 20.	0.10 0.17	1.0	2.9 3.0	2.7 2.7	~100. 49.	1.5 1.2	0.51 0.71	0.03 0.03
\$44	lst per 3rd per	124. 83.	35. 27.	42. 33.	29. 33.	0.18 0.14	1.0 1.3	4.0 3.3	3.1 3.2	53. 95.	1.4 1.5	0.62 0.74	0.03
<b>#</b> 45	lst per 3rd per	232. 216.	100. 76.	94. 51.	43. 35.	0.09 0.16	1.3	2.7 2.7	2.5 2.7	87. 55.	1.4	0.44 0.63	0.03 0.02

Comparison of 1st Period with 3rd Period - Chromatographic Parameters 1975-1976

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\*Measured gas chromatographically

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Table 4

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These ratios must be treated cautiously since they can vary so much by variations in handling technique.

The ratio of pristane/ $C_{17}$  varies more than most parameters. However we recently have strong evidence that pristane does not even occur in most of the samples so we think very little should be made of these deviations until the compound we label as pristane has been positively identified.

#### Algae

All 36 algae collected during the three sampling cruises have been analyzed. Gas chromatograms and peak file data are contained in appendices of the second and third quarterly reports. Of the 36, 15 samples are contaminated to a greater or lesser degree with petroleum hydrocarbons. Tables 5a-c give the results confirming this evidence of pollution. All samples not designated as "polluted" have a very simple aliphatic hydrocarbon distribution dominated by the suite of <u>n</u>-alkanes from  $C_{15}$  to  $C_{23}$ . In this range  $C_{17}$  typically constitutes the majority of the <u>n</u>-alkanes. Also present in many of the specimens is a series of <u>n</u>-alkenes of oddcarbon number. In some cases a series of <u>n</u>-alkanes from  $C_{20}$ - $C_{33}$  with no odd/even preference occurs with little additional evidence of pollution. However, the 15 samples designated as polluted contain this series superimposed on a large unresolved envelope. This we consider sufficient evidence of petroleum pollution.

There are no overwhelming trends of pollution, i.e., pollution as a function of species, depth, proximity to polluted sediments or season of collection. The pollution seems to be of rather random occurrence. The third collection of algae does not clarify this condition noted in earlier collections. About the most that can be said for algal hydrocarbons

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## Table 5a

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## Benthic Algae 1975-1976. Chromatographic Parameters

•				PPY	1 Dry Wt. Hydroca	rbons
	Sample #	Location	Species	Aliph	Arom	<u>N</u> -all
RIOD 1						
Transect I				2 0	1.0	2 1
	12-2+2-0	25°25.5'N, 82°59.5'W	<u>Halimeda</u> sp.	3.8	1.0	2
	1A-A+B-7	26°25.5'N, 82°59.5'W	Rhodymenia sp.	34.0	11.J	27.
	14-4-5-8	26°25.5°N, 82°59.5°W	cystodictyon pavonium	. 08	0./	22
Transect I	I	•				
	IIA-A+B-1	27°50'N, 83°31'W	Laurencia corallopsis,			
			<u>Gracilaria</u> cylindrica +			
		•	<u>blodgettil</u>	38	12	25
	IIA-A+B-2	27°50'N, 83°31'W	<u>Gracilaria mammilaris</u>	171	8	12!
	IIA-A+B-3	27°50'N, 83°31'W	Eucheuma sp.	50	7	19
	C62-A-17	27°49'N, 55°90'W	<u>Caulerpa</u> sertularoides	153	11.5	95
Transect I	II					
	IIIA-A+E-2		Codium sp.	20.8	1.1	16
	⇒> 047-A-3	28°34'N, 84°20'12"W	Codium repens	50.5	1.1	38
	047-A-5	28°34'N, 84°20'12"W	Halimeda discoidea	96.2	6.7	83
	146-B-1	28°41'N, 84°24'W	Kallymenia perforata +			
		·	Dictyota dichotoma	143	14.0	13.
	147-B-5	28°40'N, 84°13'W	Halimeda discoidea	71.6	11.6	61
	247-A-2	28°36'16"N. 84°15'40"W	Codium repens	44	5	38
	251-E-25	23°33'N, 84°16'W	Halineda discoidea	31.0	4.3	26
		·				
RICD 2						
Transect I	I					
		27°50'N, 83°31'W	Halymenia sp.	42.8	5.7	40
	062-1-5	27°49'55"N, 83°31'10"W	Caulerpa sertularoides	30.6	11.5	. 19
	064-X-3	27°50'N, 83°25'W	Gracilaria blodgetti +			
			compressa	61.1	13.6	56
	064-8-3	27°50'N, 83°25'W	Gracilaria blodgetti	66.5	0.9	63

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## Table 5a

## Benthic Algae 1975-1976. Chromatographic Parameters

				PPM	Dry Wt. Hydroca	irbens
	Sample #	Location	Species	Aliph	Arom	<u>N</u> -alk
Transect III	<u>,                                    </u>					
	IIIA-A-10	28°29'N. 84°21'W	Caulerpa sp.	854	25.5	42
	047-A-5	28°34'N, 84°20'12"W	Helimeda discoidea	79.8	10.4	49
	146-B-14	28°41'N, 84°23'40"W	Dictyota dichotoma	327.	137	22
	147-A-2	28°38'18"N, 84°13'54"W	Halimeda discoidea	22	4 .	19
	151-A-3	28°32'07"N, 84°18'24"W	Laurencia intricata	20	50	15
	247-1-4	28°36'16"N, 84°15'40"W	Codium repuns	92.2	10.1	• 74
	251-A-3	28°32'40"N, 84°16'03"W	llalimeda discoidea	39.2	2.5	25
· •		·				
Transect IV					·	16
	IVA-A-6	29°04'N, 85°14'W	Codium sp.	33.0	2.0	10
Transact V	,					
110.0000	VA-A-12	29°50'N, 86°05.5'W	Pryssonnelia rubra	6.5	3.0	5.
<b>-</b>			,	<i>i</i>		
RIOD 3						
<u>Transect II</u>	YTA-4-17	27°50'N 83°31'W	Codium an	4.2	5.3	3.
	11 - 1 - 1 = 1 = 1	27°40'55"N 83°31'10"W	Codium dsthmocladium	4.4	3.3	3.
	052-8-1	27 49 55 N, 05 51 10 W	Fuchauma detforme	35 0	2.7	34
	004-7-9	27 JU N, US 25 W	Idencedina Isriorine	55.7	2	
Transect III						
	047-A-25	28°34'N, 84°20'12"W	Codium caroliniarum	30.5	3.5	18
	146-A-1	28°41'N, 84°23'40"W	Codium caroliniarum	SO.4	10.3	47
	147-A-2	28°38'18"N, 84°13'54"W	Halimeda discoidea	38.8	9.3	23
	151-A-1	28°32'07"N, 84°18'24"W	Codium caroliniarum	66.9	6.3	57
	247-A-27	28°36'16"N, 84°15'40"W	Codium caroliniarum	40.9	3.1	23
	251-A-10	28°32'40"N, 84°16'03"W	Codium caroliniarum	28.5	1.3	24
		• • •	and a second			•

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#### Table 5b

Benthic Algae 1975-1976. Chromatographic Parameters

Sample Ø	Series of hmw <u>n</u> -alk, CPI l	Unidentified series, K.I. 1712, 2117, 2320, 2524	Phytadienes 1928, 1957, 1984, 2011	Sample Polluted?
LA-A+3-6		No	No	No
IA-A+E-7	Yes, 1/12 of <u>n</u> -C17	No	Yes, 2 ppm	V. slightly, if at all
IA-A+B-S	Yes, 1/9 of n-C17	No	Yes, 1.3 ppm	V. slightly
IIA-A+B-1	Yes, 1/5 of n-C17	No	Yes, 8.5 ppm	Definitely
IIA-A+3-2	Yes, 1/10 of n-C17	No	Yes, 22.9 ppm	Yes
IIA-A+B-3	Yes, 1/15 of n-C17	No	Yes, 29 ppm	V. slightly, if at all
062-A-17	Yes, 1/9 of <u>n</u> -C17	Yes	No	Yes
IIIA-A+5-2	Yes. 1/7 of n-C17	Yes	No	Perhaps, slightly
047-A-3	No	No	No	No
047-6-5	tio	Yes	No	Ko
146-3-1	Yes, 1/25 of n-C17	No	No	V. slightly, if at all
147-5-5	Yes, 1 1/7 of n-C17	No	No	Yes, definitely
247-1-2	Yes, 1/50 of n-C17	No	Yes, 3.0 ppm	No
251-B-23	No -	Ycs	Yes, 1.5 ppm	No
114-4-12	$V_{cs.} 1/3 \text{ of } n=C17$	No	No	Үсв
062-A-5	No	Yes	No	No
064-4-3	Yes. 1/7 of n=C17	No	No	V. slightly, if at all
064-5-3	Yes, 1/50 of n-C17	No	Yes, 2 ppm	V. slightly, if at all
III3-A-10	Yes. 3/4 of n-C17	Yes	Yes, 740. ppm	Possibly
047-A-5	No -	Yes	Yes, 22.9 ppm	No
146-8-14	20	No	No	No Comment - Peak at 2064 (FFAP) = 72 ppr
147-A-2	No	Yes	No	No
151-A-3	No	No	No	No
247-A-4	Ycs, 1/16 of <u>n</u> -C17	No	Yes, 2.6 ppm	Very definitely (Lots of hmw unresolved material)
251-A-3	No	Yes	No	No

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	Ben	thic Algae 1975-1976. Chro	matographic Parameters	1 33 9
Sample #	Series of hmw . n-alk, CPI l	Unidentified series, K.I. 1712, 2117, 2320, 2524	Phytadicnes 1928, 1957, 1984, 2011	Sample Polluted?
IVA-A-6	Yes, 1/16 of <u>n</u> -C17	No	Yes, 14.5 ppm	V. slightly, if at all
V-A-A-12	No	No	. No	No .
IIA-A-17 062-A-1 064-A-9	Yes, 1/10 of <u>n</u> -Cl7 No No	No No No	No Yes, 0.5 ppm Yes, 0.3 ppm	No No No
047-A-25 146-A-1	No Yes (hard to measure)	No No	Ycs, 10 ppm Yes, 5 ppm	No Yes definitely (Lots of ! unresolved material)
147-A-2 151-A-1 247-A-27	No <sup>.</sup> No Yes, 1/12 of <u>n</u> -C17	Yes No No	No Yes, 3 ppm Yes, 2.5 ppm	No Yes definitely (Lets of 1
251-1-10	No	No	Yes, 1.8 ppm	unresolved material) No C22-C30

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Table 5b

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	,	,	В	enthic Algae	e 1975-1976.	Chromatographic	Parameters			Ŷ
Sample #	Pris+Phy/ <u>n</u> -alk	} Pris/ <u>n</u> -C17	Phy/ <u>n</u> -C18	Pris/ Phy	$\frac{n-alk}{n-Cl6}$	% <u>n</u> -alk/ Aliph	Odd/ Even	C10-C20 Odd/Even	C21-C31 Cdd/Even	C12-C20/ C21-C31
	0.228	0.013	0.0		247.	64.3	11.3	26.6	3.0	10.9
IA-A+B-7	0.002	C.0	0.0	-	630.	85.3	120.	150.	1.0	50.8
IA-A+B-S	0.0	0.0	0.0	-	173.	52.0	-	-	0.9	15.0
IIA-A÷B-1	0.017	0.005	2.5	0.3	167.	66.0	10.0	44.0	1.0	7.9
IIA-A+B-2	0.012	0.003	1.4	0.6	142.	76.0	-	-	0.9	11.5
IIA-A+S-3	0.005	0.003	0.5	1.1	351.	38.2	23.7	106.0	0.9	19.2
062 <del>,</del> A+17	0.001	0.003	0.0	-		61.7	15.5	19.5	2.0 .	37.2
IIIA-A+B-2	0.009	0.010	0.0		434.	77.5	6.6	9.8	1.4	19.8
047-A-3	0.002	0.002	0.0		690.	76.8	35.8	39.1	3.0	105.0
047-A-5	0.004	0.003	0.6	0.8	1170.	86.9	29.9	85.9	5.5	- 9.6
146-5-1	0.0	0.002	0.0	-		92.7	1	·	1.5	107.0
147-3-5	0.003	0.004	0.7	0.9	1150. <del>8</del>	6.2 5.0	78.0	1-478.2	<i>∕,</i> ∖, <b>3.</b> .0-	・ラこ
247-A-2	0.006	0.001	0.5	0.2	412.	85.9	44.5	73.0	0.8	103.0
251-B-25	0.001	0.002	0.0	-	.033	84.2	62.0	73.0	5.8	16.3
IIA-A-12	0.005	0.003	0.3	1.4	860.	94.2	52.0	60.0	1.0	16.5
Cé 2-à-5	0.0	0.0	0.0	_		64.4	55.0	63.5	2.8	14.4
C64-A-3	0.006	0.003	0.0	1.0	400.	92.3	41.0	46.3	1.6	13.7
034-2-3	0.002	0.002	C.O		805.	98.1	62.2	156.0	0.5	84.3
IIIA-A-10	0.031	0.040	0.2	1.8	53.5	5.1	3.2	7.4	1.1	· 4.2
047-A-5	0.001	0.001	0.0	-		61.6	9.8	11.9	7.1	12.2
146-8-14	0.002	0.101	0.0	-		67.1	245.0	262.0	0.8	103.0
147-A-2	0.004	0.004	-	-	4300.	86.1	35.7	78.1	7.4	10.5
151-A-3	<b>c.</b> 0	0.0	0.0	-	460.	68.1	72.0	72.0	-	32.4
247-A-4	0.004	0.002	0.0	0.45	560.	83.0	61.0	67.2	1.3	21.5
251-A-3	0.002	0.003	-		1090.	65.0	10.9	81.2	-	7.5

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Table 5c

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	В	F	I	Benthic Alga	e 1975-1976.	Chromatographic	Parameters			
Sample #	Pris+Phy/ <u>n</u> -alk	Pris/ <u>n</u> -Cl7	Phy/ <u>n</u> -C18	Pris/ Phy	<u>n</u> -alk/ n-Cl6	% <u>n</u> -alk/ Aliph	Odd/ Even	C10-C20 Odd/Even	C21-C31 Odd/Even	C12-C20/ C21-C31
IVA-A-6	0.003	0.004	0.0		2880.	51.8	21.0	40.2	1.5	50.0
VA-A-12	0.014	0.017	0.0		171.	81.8	14.9	28.0	1.3	18.4
IIA-A-17	0.014	0.017	-	-	201.	73.7	11.9	21.5	2.4	13.9
062-A-1 064-A-9	0.020	0.014	0.4	1.4	278. 1000.	77.0 94.0	17.4	36.3	1.3	15.2 v. large
047-A-25 145-A-1	0.002	0.002	0.0 0.0	-	630. 590.	60.2 59.0	44.9	41.8 45.9	1.7	74.0 28.4
147-A-2 151-A-1	0.003 0.001	0.004 0.001	0.0 0.0		571. 750.	61.2 85.0	23.9 45.4	61.1 60.7	4.7 0.5	7.8 52.7
247-A-27 251-A-10	0.007 , 0.001	0.005	0.3 0.0	1.4	338. 760.	57.6 · 85.0	23.7	51.3 75.0	0.9 2.4	12.6 44.0

Table 5c

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is that they sensitively do reflect petroleum pollution but at a very localized level.

Looking at pollution along the various sampling transects we see that two of the three algae from Transect I off Ft. Myers show a very slight degree of pollution though in neither of these is pristane and phytane even measurable.

Transect II contains samples all of which display signs of pollution in Period 1; three of four, in Period 2; and none, in Period 3. Only <u>Caulerpa sertularoides</u> was collected in more than one period and then not at the same location so conclusions based upon this seeming decline are at best speculative.

The percentage of samples from Transect III that demonstrate at least some degree of pollution remains about the same in all three sampling periods. Again only two species were sampled twice. In one instance, <u>Codium repens</u> from the first period shows no pollution but in the second period is very definitely polluted. The <u>Halimeda discoidea</u> from all three periods show no signs of pollution.

Transect IV and V were sampled only during the second period to yield one specimen each, neither of which contained abundant evidence of pollution.

#### Phytadienes

Blumer and Thomas (1965) have suggested that phytadienes present in some zooplankton are genuine but that they may occur as artifacts from any number of laboratory procedures commonly associated with hydrocarbon analysis. Since their precursor is assumed to be phytol, part of the chlorophyll molecule, their creation by saponification and/or adsorption chromatography would seem feasible in algal extracts. Blumer and Thomas

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(1965) report that the four phytadienes elute gas chromatographically from Carbowax between K.I. 1900 and 2000 and can be hydrogenated to phytane. This was the clue to our identification of phytadienes in the benthic algae. FFAP, being a modified Carbowax, we felt should give results similar to Carbowax.

A series of four peaks between <u>ca</u> K.I. 1900 and 2000 did occur in many algal samples as can be seen in Table 5b. Two of these samples were chosen to verify the natural occurrence of phytadienes in benthic algae. The samples were a <u>Caulerpa</u> sp. and a <u>Eucheuma</u> sp. The aliphatics and untreated lipid extracts were analyzed before and after hydrogenation with Adam's catalyst and yielded chromatograms shown in Figure 9a and b.

Additional identification of the phytadienes was provided by subjecting pure phytol to Activity I alumina and silica gel chromatography. Four peaks between X.I. 1900 and 2000 resulted in the hexane and benzene fractions. The total weight ratios were <u>ca</u> 30 ppm (total phytadienes/ phytol), a negligible amount when considering the amount of chlorophyll in algae. However the K.I.'s correspond exactly to those found in the algae. The quantitative results of this experiment are shown in Table 6 and demonstrate quite clearly that phytadienes do occur in algae and that phytol degradation during our laboratory analysis produces only very small if any amounts of phytadienes. Their presence in both polluted and non-polluted algae suggests that they are biosynthesized by certain algae and not by others.

#### Species Comparisons

Phytadienes are present in all <u>Colium</u> spp. collected. No great differences are noted in the overall characteristics of these specimens.  $C_{17}$  is the major <u>n</u>-alkane with some lesser amounts of  $C_{15}$  and pristane. Three of the Codium spp. have a look of pollution with weathered oil.

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## Table 6

## Phytadienes in Algal Extracts

Sample	Total µg of phytadienes	Total µg of phytane after hydrogenation
<u>Caulerpa</u> sp.		
IIIA-A-10 lipid <sup>2</sup>	74	208
IIIA-A-10 $alighatics^2$	288	301
Eucheuma sp.		
IIA-A+B-3 lipid <sup>2</sup>	193	247
IIA-A+B-3 aliphatics <sup>2</sup>	136	96
Phytol treated with		
alumina-silica gel <sup>3</sup>	22	12.6

<sup>1</sup>Phytadienes are the four compounds with K.I. <u>ca</u> 1921, 1949, 1977 and 2001.

 $^{2}$ Weights are calculated to represent the same initial weight of alga.

<sup>3</sup>Phytol treated was 50 times greater than would normally be found in the weight of algae analyzed for this experiment.



Figure 9a. Phytdienes in Algae. The FFAP gas chromatograms are of lipids before hydrogenation (upper left), after hydrogenation (lower left), aliphatics before hydrogenation (upper right), and after hydrogenation (lower right) taken from Cauleroa sp.



Figure 9b. Phytadienes in Algae. The FFAP gas: chromatograms are of lipids before hydrogenation (upper left), after hydrogenation (lower left), aliphatics before hydrogenation (upper right), and after hydrogenation (lower right) taken from <u>Euchema</u> sp.

Phytadienes occur only in the unidentified species of <u>Caulerpa</u>. All three however contain a homologous series of aliphatics just following  $C_{19}$ ,  $C_{21}$ ,  $C_{23}$  and  $C_{25}$  which themselves were in abundance.  $C_{17}$  is still the major peak.

The  $C_{17}$  peak is also the most abundant component of the <u>Gracilaria</u> spp. All four samples have phytadienes and contain a series of HMW <u>n</u>- alkanes with no odd/even preference.

As found in the <u>Caulerpa</u>, <u>Halimeda</u> sp. have the homologour series of compounds following the odd-C <u>n</u>-alkanes. Large components show up in all between K. I. 1900 and 2000 which definitely are the phytadienes in some cases. The order of abundance is  $C_{17}$   $C_{19}$   $C_{23}$   $C_{25} = C_{15} = C_{21}$ .

Euchema sp. is relatively simple compared to <u>Caulerpa</u> and <u>Halimeda</u>. Both contain phytadienes and have  $C_{17}$  as the major constituent.

Neither <u>Dictyota</u> sp. contain the phytadienes and as reported in the literature,  $C_{15}$  is the dominant aliphatic hydrocarbon.

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REFERENCE

[Blumer M. and Thomas D. (1965) <u>Science</u> <u>147</u>: 148-149.]

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#### II. RIG MONITORING SAMPLES

## METHODS AND MATERIALS

Bottom sediments were collected from a rig site off Mustang Island, Texas in three phases, the first in November, 1975 before construction of a rig, the second in January, 1976 during emplacement of a drilling rig and the third after the rig was in operation in March, 1976. Twenty five stations were established around the rig according to the description in Figure 1. The sediments from this area are at approximately 80 m in depth and are composed primarily of silty-clay material. Sediments are rather soupy in nature covered by a nepheloid layer of suspended material. Therefore obtaining precisely reproducible samples was impossible due to the difficulty of determining exactly what depth of penetration each sample represented. Surface sediments were collected by divers using plain tin pails as scoops and storage vessels. The pails were closed beneath the surface of the water and brought aboard ship. Excess water was drained off, and the samples were sealed and frozen until analyzed. Analysis of the samples followed that prescribed in the work statement.

#### Gravimetric Data

The gravimetric data for the rig samples are displayed in Tables 1-3. At first glance it would appear that there exists quite a diversity of samples in this 3.14 km<sup>2</sup> area. In some of the columns, e.g. % HC/Lipid, the range in the "before" samples covers over one order of magnitude. However, when comparing individual samples among the three groups of data it is seen that the same order of variability also exists.

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Figure 1. Rig sam

Rig sample station layout.

Station 1 is located at the rig site (Lat: 27°37'13.87" Long: 96°57'55.17") off Mustang Island, Texas. Stations 2-9 are located 100m from the center; 10-17, 500 meters from the center and 18-25, 1000 meters from the center. The "spoke" angles are 45°.

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## Table 1

Gravimetric Data of Rig Sediments Before Drilling

tion #	Sediment dry wt. (g)	Tot. Lipid Wt. (g)	Tot. Aliph. HC Wt. (g)	Tot. Arom. HC Wt. (g)	Lipid Wt. Tot. Sed. Wt. (ppm)	Z Tot. HC Wt. Lipid Wt.	Aliph. HC Wt. Arom. HC Wt.	Aliph. HC Tot. Sed. (ppm)	Z Aliph. HC Lipid	Arom. HC Tot. Sed. (ppm)	Z Arom. HC Lipid
-500102	151	0.015	0.0041	0.0022	99	42.0	1.86	27.1	27.3	14.6	. 14.7
-510201	235	0.050	0.0041	0.0005	212	9.20	8.20	1/.5	8.20	. 2.13	2.00
-510/01	222	0.050	0.0031	0.0012	155	14.2	1 06	16.5	0.20	7 /3	2.40 A 90
-510501	261	0.075	0.0047	0.0024	287	7 33	2 67	15 3	5 33	5 75	2 00
-510601	201	0.0950	0.0034	0.0022	392	5.89	1.55	14.05	3.57	9,09	2.32
-510701	332	0.080	0.0022	0.0016	241	4.75	1.37	6.63	2.75	4.82	2.00
-510801	335 -	0.100	0.0057	0.0022	• 299	7.90	2,59	17.0	5.70	6.57	2.20
-510901	423	0.150	0.0055	0.0029	355	5,60	1.90	13.0	3.66	6.85	1.93
	No Samp	1e Received	at #10							÷ •	•
-551101	185	0.080	0.0042	0.0019	432	7.63	2.21	22.7	5.25	10.3	2.37
-551201	143	0.105	0.0057	0.0024	734	7.71	2.38	39.8	5.43	16.8	2.29
-551301	147	0.055	0.0035	0.0022	374	10.3	1.59	23.8	6.36	14.9	4.00
-551401	195	0.010	0.0013	0.0007	51	20.0	1.86	6.66	13.0	3.59	7.00
-551501	391	0.12	0.0053	0.0039	307	7.66	1.36	13.5	4.40	9.97	3.25
-551601	287	0.065	0.0051	0.0019	. 226	10.7	2.68	24.4	7.84	6.62	2.92
-551701	387	0.055	0.0045	0.0019	142	11.6	2.37	11.6	8.18	4.91	3.45
-591801	217	0.045	0.0040	0.0013	207	11.7	3.08	18.4	8.80	5.99	2.88
-591901	205	0.070	0.0014	0.0005	341	2.71	2.80	6.83	2.00	2.44	0.71
-592001	92	0.085	0.0033	0.0018	923	6.00	1.83	35.9	3.88	19.6	2.12
-592101	152	0.090	0.0040	0.0028	592	7.50	1.43	26.3	4.44	18.4	3.11
-592201	271	0.045	0.0056	0.0033	166	19.7	1.70	20.6	12.4	12.7	7.33
-592301	197	0.070	0.0041	0.0020	355	8.71	2.05	20.8	5.86	10.2	2.86
-592401	374	0.115	0.0062	0.0009	307	6.17	6.89	16.6	5.39	2.41	0.78
-592501	. 222	0.085	0.0036	0.0022	· 383	6.82	1.64	16.2	4.24	9.90	2.59
-592301	180	0.060	0.0059	0.0024	333	13.8	<b>2.</b> 46	32.8	9.83	13.3	4.00

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tion #	Sediment dry wt. (g)	Tot. Lipid Wt. (g)	Tot. Aliph. HC Wt. (g)	Tot. Arom. HC Wt. (g)	Lipid Wt. Tot. Sed. Wt. (ppm)	Z Tot. HC Wt. Lipid Wt.	Aliph. HC Wt. Arom. HC Wt.	Aliph. HC Tot. Sed. (ppm)	Z Aliph. HC Lipid	Arom. HC Tot. Sed. (ppm)	Z <u>Arom. HC</u> Lipid
-510201	375	0.0250	0.0054	0.0003	67	22.8	18.0	14.4	21.6	0.800	1.20
-510301	300	0.175	0.0062	0.0023	583	4.86	2.69	20.7	3.54	7.66	1.31
-510401	386	0.205	0.0055	0.0021	531	3.71	2.62	14.3	2.68	5.44	1.02
-510501	441	0.0500	0.0064	0.0009	113	14.6	7.11	. 14.5	12.8	. 2.04	1.80
-510601	369	0.135	0.0078	0.0018	366	7.1	4.33	21.1	5.78	4.88	1.33
-510701	367	0.0950	0.0144	0.0102	259	25.8	1.41	39.2	15.2	27.79	10.7
-510801	416	0.0800	0.0077	0.0022	192	12.4	3.50	18.5	9.63	5.29	2.75
-510901	337	0.125	0.0090	0.0025	371	9.20	3.60	26.7	7.20	7.42 -	2.00
-551001	397	0.0850	0.0086	0.0031	214	13.8	2.77	21.6	10.12	7.808	3.65
-551101	404	0.1700	0.0044	0.0027	· 421	4.18	1.63	10.8	2.59	<b>6.</b> 68	1.59
-551201	260	0.0450	0.0027	0.0014	173	3.11	1.93	10.4	6.00	5.38	3.11
-551301	501	0.0500	0.0057	0.0014	100	14.2	4.07	13.77	11.4	2.79	2.80
-551401	510	0.160 .	0.0088	0.0034	314 .	7.63	2.59	17.2	5.50	6.67	2.13
-551501	494	0.110	0.0044	0.0016	223	. 5.45	2.75	8.91	4.00	3.24	1.45
-551601	424	0.0850	0.0043	0.0018	200 •	7.18	2.39	10.1	5.06	4.25	2.12
-551701	347	0.0450	0.0039	0.0020	130	13.1	1.95	11.2	8.70	5.76	4.44
-591801	368	0.100	0.0041	0.0023	272	6.40	1.78	11.1	4.10	6.25	2.30
-591901	315	0.0300	0.0049	0.0011	95	20.0	4.45	15.6	16.3	3.49	3.67
·592001	272	0.110	0.0078	0.0044	296	11.09	1.77	20.97	7.091	11.8	4.00
.592101	314	0.100	0.0064	0.0035	318	, <b>9.9</b>	1.83	20.38	6.40	· 11.5	3.5
-592201	387	0.0950	0.0076	0.0017	331	9.8	4.47	26.4	8.00	5.92	9.8
-592301	275	0.120	0.0046	0.0018	436	5.3	2.56	16.73	3.83	6.54	1.50
-592401	266	0.150	0.0074	0.0030	564	6.93	2.47	27.82	4.93	11.28	2.00
-592501	355	0.115	0.0068	0.0024	324	8.00	2.83	19.15	5.91	6.76	2.087

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## Gravimetric Data of Rig Sediments During Drilling

Table 2

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# Table 3

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## Gravimetric Data of Rig Sediments After Drilling

ation \$	Sediment dry wt. (g)	Tot. Lipid Wt. (g)	Tot. Aliph. HC Wt. (g)	Tot. Arom. HC Wt. (g)	Lipid Wt. Tot. Sed. Wt. (ppm)	7 Tot. HC Wt. Lipid Wt.	Aliph. HC Wt. Arom. HC Wt.	Aliph. HC Tot. Sed. (ppm)	X Aliph. HC Lipid	Arom. HC Tot. Sed. (ppm) .	Z Arom. HC Lipid
2-500101	386	0.0750	0.0088	0.0029	194	15.6	3.03	22.8	11.7	7.51	, 3.86
3-510201	287	0.0575	0.0072	0.0038	200	19.1	1.89	25.1	12.5	13.2	6.61
3-510301	308	0.040	0.0080	0.0030	130	27.5	2,67	25.9	2.0	9.74	7.50
3-510401	553	0.1350	0.0117	0.0064	244	13.4	1.83	21.2	8.67	11.6	4.74
3-510501	400	0.0750	0.0074	0.0025	188	13.2	2.96	18.5	9.87	6.25	3.33
3-510601	493.	0.140	0.0105	0.0050	284	· 11.1	2.1	30.4	7.5	· 10.1	3.57
3-510701	333	0.0150	0.0103	0.0023	450	84.0	4.48	<sup>.</sup> 30.9	68.0	6.91	15.3
3-510801	272	0.040	0.0081	0.0033	147	28.5	2.45	29.8	20.3	12.1	8.25
3-510901	315	0.0750	0.0061	0.0026	238	11.6	2.35	19.4	8.13	8.25	3.46
3-551001	355	0.1700	0.0055	0.0023	479	4.59	2.39	15.5	3.24	6.478	· 1.35
3-551101	469	0.1950	0.0083	0.0037	• 416	6.15	2.24	17.70	4.3	7.89 ·	1.90
3-551201	306	0.070	0.0055	0.0034	229	12.7	1.62	17.9	7.86	11.1	4.86
3-551301	301	0.105	0.0083	0.0033	349	11.0	2.52	27.6	7.90	10.9.	· 3.14
3-551401	364	0.1600	0.0070	0.0034	440	6.5	2.06	19.23	4.38	9.34	21.26
3-551501	215	0.0650	0.0052	0.0021	302	11.23	2.48	24.19	8.00	9.67	3.23
3-551601	378	0.1750	0.0094	0.0037	463	1.77	2.54	24.87	5.37	9.79	2.11
3-551701	589	0.130	0.0102	0.0058	221	12.3	1.76	17.3	7.85	9.85	4.46
3-591801	476	0.030	0.0030	0.0021	63	17.0	1.43	6.30	1.00	4.41	7.00
3-591901	302	0.0650	0.0052	0.0031	215	12.8	1.68	17.2	8.00	10.2	4.77
3-592001	364	0.050	0.0042	0.0014	137	2,59	3.0	11.5	. 8.4	3.85	2.80
3-592101	278	0.050	0.0046	0.0022	180	13.6	2.09	16.5	9.2	7.91	4.40
3-592201	286	0.0750	0.0053	0.0030	262	11.07	1.77	18.53	7.07	10.49	4.00
	No Samp	le Received	<b>at</b> #23		•						
3-592401	348	0.0800	0.0074	0.0039	230	19.0	1.90	21.26	9.25	11.21	4.87
3-592501	274	0.060	0.0054	0.0027	219	13.5	2.00	19.7	9.00	9.85	4.50
4-592401	379	0.1250	0.0095	0.0041	330	10.88	2.32	25.07	7.6	10.82	3.28

Table 3										
Gravimetric	Data	of	Rig	Sediments	After	Drilling				

ion #	Sediment dry wt. (g)	Tot. Lipid Wt. (g)	Tot. Aliph. HC Wt. (g)	Tot. Arom. HC Wt. (g)	Lipid Wt. Tot. Sed. Wt. (ppm)	Z Tot. HC Wt. Lipid Wt.	Aliph. HC Wt. Arom. HC Wt.	Aliph. HC Tot. Sed. (ppm)	Z Aliph. HC Lipid	Arom. HC Tot. Sed. (ppm)	X <u>Arom. HC</u> Lipid
500101	386	0.0750	0.0088	0.0029	194	15.6	3.03	22.8	11.7	7.51	• 3.86
510201	287	0.0575	0.0072	0.0038	200	19.1	1.89	25.1	12.5	13.2	6.61
510301	308	0.040	0.0080	0.0030	130	27.5	2,67	25.9	2.0	9.74	7.50
510401	553	0.1350	0.0117	0.0064	244	13.4	1.83	21.2	8.67	11.6	4.74
510501	400	0.0750	0.0074	0.0025	188	13.2	2.96	18.5	9.87	6.25	3.33
510601	493	0.140	0.0105	0.0050	284	· 11.1	2.1	30.4	7.5	· 10.1	3.57
510701	333	0.0150	0.0103	0.0023	450	84.0	4.48	30.9	68.0	6.91	15.3
510801	272	0.040	0.0081	0.0033	147	28.5	2.45	29.8	20.3	12.1	8.25
510901	315 .	0.0750	0.0061	0.0026	238	11.6	2.35	19.4	8.13	8.25	3.46
551001	355	0.1700	0.0055	0.0023	479	4.59	2.39	15.5	3.24	6.478	· 1.35
551101	469 <sup>°</sup>	0.1950	0.0083 ·	0.0037	• 416	6.15	2.24	17.70	4.3	7.89 •	1.90
551201	306	0.070	0.0055	0.0034	229	12.7	1.62	17.9	7.86	11.1	4.86
551301	301	0.105	0.0083	0.0033	349	11.0	2.52	27.6	7.90	10.9.	. 3.14
551401	364	0.1600	0.0070	0.0034	440	6.5	2.06	19.23	4.38	9.34	21.26
551501	215	0.0650	0.0052 ·	0.0021 ·	302	11.23	2,48	24.19	8.00	9.67	3.23
551601	378	0.1750	0.0094	0.0037	463	1.77	2.54	24.87	5.37	9.79	2.11
551701	589	0.130	0.0102	0.0058	221	12.3	1.76	17.3	7.85	9.85	4.46
591801	476	0.030	0.0030	0.0021	63	17.0.	1,43	6.30	1.00	4.41	7.00
591901	302	0.0650	0.0052	0.0031	. 215	· 12.8	1.68	17.2	8.00	10.2	4.77
592001	364	0.050	0.0042	0.0014	137	2.59	3.0	11.5	8.4	3.85	2.80
592101	278	0.050	0.0046	0.0022	180	13.6	2.09	16.5	9.2	7.91	4.40
592201	286	0.0750	0.0053	0.0030	262	11.07	1.77	18.53	7.07	10.49	4.00
	No Samp	le Received	<b>at</b> #23		•						
592401	348	0.0800	0.0074	0.0039	230	19.0	1.90	21.26	9.25	11.21	4.87
592501	274	0.060	0.0054	0.0027	219	13.5	2.00	19.7	9.00	9.85	4.50
592401	379	0.1250	0.0095	0.0041	330	10.88	2.32	25.07	7.6	10.82	3.28

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Indeed in most cases samples exhibiting extremes in gravimetric data do so in only one collection. Sample 1 is quite high in several parameters but only in the "before" phase. The aliphatic/aromatic ratio at Station #2 and aliphatic/sediment ratio at Station #12 are also isolated highs for these samples in the "before" collection. An extremely high value of aliphatic/lipid at Station #4 is also noted but only in the "during" phase. Station #7, oddly enough, contains highs and lows in the "during" and "after" phases but not reproducibly. Further, only in the "after" phase does Station #14 have the highest aromatic/ lipid and Station #16 the lowest hydrocarbon/lipid ratios. In view of this variability seen at specific stations, the stations show remarkable similarity in their gravimetric parameters and probably can be considered replicate samples. In looking at overall trends none of the parameters changes substantially with time so that based on this data no discernible effects can be traced to the drilling procedure.

Table 4 containing averages of percent carbonate and organic carbon again demonstrates the similarity of the samples with very little variation among the samples. The samples contain about the same amount of carbonate as the Transect VI MAFLA sediments. These rig samples differ primarily in that the lipid, organic carbon and total sediment are enriched in aliphatic hydrocarbons.

Correlation coefficients for the following hydrocarbon parameters <u>vs</u> percent clay and <u>vs</u> percent silt were calculated: aliphatics (ppb), aromatics (ppb), <u>n</u>-alkanes and percent organic C. Only at very low confidence limits are the correlations significant suggesting that the distributions of various components in the sediment are quite variable. The gravimetric data then do not reveal any real differences attributable to time of

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# Table 4

# Average Amounts of Carbonate and Organic Carbon for Rig Monitoring Samples

Cample #	<b>%</b> co <sup>=</sup> <sub>3</sub>	% Org. Carbon
Sample #	total sed.	Acid Basis
500101	17.2	1.02
510201	16.0	1.00
510301	13	.82
510401	12.2	.89
510501	12.6	.72
510601	15.5	
510701	14.0	.82
510801	16.4	.96
510901	17.6	.90
551001	17.8	- 86
551101	16.6	.87
551201	17.4	94
551301	17.9	
551401	18.8	.83 •
551501	18.9	77
551601	18.4	86
551701	17.2	.00
591801	17.2	. 02
591901	21.2	-32
592001	18.2	•75 68
592101	17.4	95
592201	17.5	• • • • • 8/
592301	16.0	• 04 • 81
592401	17.9	•01
592501	17.6	. 1 00

collection or activities in the area but only the natural variability of the sediment matrix.

Gas Chromatographic Data \_\_\_\_

Copies of peak files and gas chromatograms for all aliphatic and aromatic hydrocarbons extracted from rig sediment samples are contained in Appendix C. When looking at the chromatograms within any given group, the same basic characteristics are noticed whether observing the "before," "during" or "after" samples. A typical sample of aliphatic hydrocarbons is shown in Figure 2 with features pertinent to virtually all samples emphasized. All samples without exception contain a very large unresolved envelope of complex hydrocarbon material beneath a series of peaks consisting mostly of alkane material. This envelope peaks at <u>ca</u> the <u>n</u>-C<sub>20</sub> compound.

The resolved material of each chromatogram consists primarily of high molecular weight (HMW) <u>n</u>-alkanes with the decided odd/even ratio preference characteristic of terrestrial material. The large envelope may in itself indicate a past of oil pollution in this area. The diminished amounts of low molecular weight (IMW) <u>n</u>-alkanes with a slight odd/even preference do not give as clear evidence of pollution as does the Mississippi continental shelf area. Nevertheless a low level of oil pollution offers the simplest explanation of the envelope, odd/even ratio in IMW <u>n</u>-alkanes not much elevated above one and significant amounts of pristane and phytane.

Quite unusual are samples collected at Stations #13, 21 and 25 after drilling. At these stations the LMW <u>n</u>-alkanes are at the same level of concentration as the HMW <u>n</u>-alkanes. The odd/even preference appears unchanged but pristane and phytane levels are the same as in other

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Figure 2. Typical gas chromatogram of rig sediments.

This gas chromatogram of the aliphatics from Station #21 in the "after" phase typifies all of the samples. Note the strong odd/even (O/E) preference in the high molecular weight range of <u>n</u>-alkanes, the presence of a large unresolved envelope and the occurrence of two large branched-unsaturated-cyclic (?) compounds at Kovats Indices 2070 and 2140. The only atypical characteristic of this sample is pristane which in virtually all samples is <u>ca</u> 1.5x larger than  $C_{17}$ .



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samples. The only explanation we can offer is that these particular samples may have actually been taken closer to the sediment surface where unbranched LMW <u>n</u>-alkanes have not yet been preferentially consumed by bacteria. As found in the purely marine samples of the Florida shelf,  $C_{17}$  is the dominant component of the LMW <u>n</u>-alkanes of every sample probably indicating an algal source of hydrocarbons.

The complex of phytadienes noted in the algal samples in the MAFLA study are evident in all the rig samples but only in concentrations at or less than  $C_{19}$  or  $C_{20}$  (see Figure 2).

Present in concentrations exceeding  $C_{29}$  in a majority of samples is a complex of peaks occurring between  $C_{20}$  and  $C_{22}$ . The two major peaks in this group are those having Kovats Indices of 2070 and 2140. Table 5 compares the concentration of these two peaks to the major <u>m</u>-alkane in most samples,  $C_{29}$ . There are no relevant trends in the relative concentrations of these compounds. Their levels are high but quite variable. even in replicate samplings of individual stations. A peak eluting also at 2140 is a prominent component of the aromatic fractions of these samples. This fact suggests that the 2140 peak may be a polyunsaturated hydrocarbon eluting in both fractions. The 2070 peak does not appear in the aromatic fractions so may be similar to the 2070 peak in the Florida and Alabama shelf sediments which is tentatively a  $C_{25}$  brancheddiene. Comparisons of mass spectral data may clarify this situation.

The most distinguishing characteristic of the aromatics is the presence of the K.I. 2140 peak. As stated earlier this peak is probably a polyunsaturate since it also elutes partially in the aliphatic fraction. Gas chromatography and combined gas chromatography-mass

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# Table 5

	K	.I. 2070/C <sub>20</sub>	3	· K	K.I. 2140/C <sub>20</sub>				
Station	Before	During	After	Before	During	After			
<b>50</b> 0101	0.71		1.0	0.82		0.7			
<b>510</b> 201	1.2	0.61	2.1	2.6	1.2	2.3			
<b>510</b> 301	1.4	1.6	1.4	2.1	1.3	2.1			
510401	0.84	1.6	2.6	0.62	1.76	3.0			
<b>510</b> 501	1.0	1.5	0.85	1.5	1.8	1.2			
510601	1.2	1.8	1.4	2.7	2.0	1.1			
<b>510701</b>	0.6	0.63	0.64	2.1	0.76	0.57			
<b>510</b> 801	1.0	0.90	1.6	2.7	1.6	2.6			
<b>510</b> 901	0.64	0.81	1.5	0.50	0.99	2.4			
551001		0.83			0.34				
551101	1.4	0.59	2.5	1.9	0.31	2.9			
551201	2.0	0.43	1.5	2.5	0.26	1.9			
<b>551</b> 301	1.2	0.88	2.0	1.6	0.73	1.8			
551401	0.17	1.0	1.9	. 0.34	1.9	2.3			
<b>551</b> 501	0.69	2.8	0.95	0.062	2.9	1.2			
551601	0.65	4.8	1.8	1.2	1.2	1.9			
551701	0.32	1.8	1.8	0.48	2.0	2.6			
591801	0.39	0.53	3.0	0.64	1.3	3.2			
591901	0.67	0.24	2.0	0.83	.0.40	1.8			
592001	4.7	1.5	6.0	1.3	1.5	5.2			
<b>59</b> 2101	0.97	1.2	0.63	2.0	1.3	0.52 <sup>.</sup>			
592201	0.71	1.3	2.3	1.2	1.2	1.9			
<b>592301</b>	1.0	1.3		3.0	1.4				
592401	0.9	1.4	1.2	1.5	1.4	1.4			
<b>59</b> 2501	1.0	1.1	2.2	0.27	. 1.2	2.7			

# K.I. 2070-2140 Complex in Rig Samples

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spectrometry did not alone provide the ultimate identity of specific peaks (which probably are isomeric mixtures) of the MAFLA aromatic fractions. It has become apparent that these tools are limited in dealing with such immensely complex mixtures as found in the benzene eluates of sedimentary lipids. The most useful information in the future will probably be an extension of some of the work we reported in the BLM 1974-75 final report. Here the individual gas chromatography peaks were given some structural characteristics based on certain chemical reactions. Combining gas chromatography and gas chromatography-mass spectrometry with liquid chromatography, which could give information on the size of aromatic constituents, and spectrofluorometry, which could yield gross structural information for all components and precise identification of isomeric groups, will probably find use in solving the enigma of sedimentary aromatic hydrocarbons.

All that can be said for the benzene eluates is that there is a fair degree of uniformity of distribution of the aromatics over the low and high molecular weight range. Though chromatograms look very much different, examination of peak files reveals that most all of the peaks are recurrent and that most of the difference is due to variations at random, in concentration levels of the individual components. Some samples contain an unresolved envelope in the "before" samples but not later. Some very large high molecular weight peaks arise in isolated samples during all collections but with no systematic occurrence. Certainly there is nothing unique about the "after" sample aromatics or the others for that matter to indicate any sort of change in the chemical make-up of the sediments due to passage of time or man-induced effects.

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#### Gas Chromatographic Parameters

Some information that is not immediately apparent about gas chromatographic data becomes so when certain manipulations of the data are performed to describe the data for the sake of interpretations. The derived parameters in Tables 6-8 are those most often mentioned as serving to indicate the presence of oil pollution. Relative standard deviations are included in the tables as a measure of the natural variability of these parameters.

Scanning the means and standard deviations one is struck with the most remarkable similarity among the three groups of data. The parameters expressing concentration (ppb) are among those of highest variability (large relative standard deviations). These parameters encompass the entire range of the gas chromatogram which itself suffers quite high deviations at the lowest and highest molecular weight range. One or two contaminant peaks that may be authentic but unrelated to oil pollution can skew these parameters. Cut-off points in column chromatography, particilarly with regard to the aromatic hydrocarbons, are difficult to control with absolute assurance of reproducibility. What actually gets in each chromatographic fraction is quite variable. Unless large numbers of replicates are available, these parameters probably are not terribly useful in a baseline or monitoring study.

It might appear that the <u>n</u>-alkane  $C_{16}$  ratio is not very meaningful because of its large range and immense standard deviation. However it should be pointed out that  $C_{16}$  is very small in these samples, compared to the total <u>n</u>-alkanes with just slight changes resulting in dramatic changes in this ratio. Therefore a large change such as that encountered in the addition of LMW-rich oil probably would create an <u>n</u>-alkane/ $C_{16}$  value well outside the natural variability of this parameter. E.g. the three

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Table	6	۰.

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Rig Monitoring - Before Drilling - Chromatographic Parameters

	est.	dev ut a		PrictPhy	Pristana	Phytope	Printere		· (-11	Total	Cr20 odd	C>21 odd	C.: 20
Sample Ø	Aliph	<u>n-alk</u>	Arom	n-alk	C <sub>17</sub>	C <sub>18</sub>	Phytane	<u>n-C16</u>	Aliph	Even	even	even	<u>C_21</u>
451-500102SOX	1252	630	610	0.031	1 1	0 43	30	130	50	······	1 2		0.00
HS1-510201	3100.*	540.	520.	0.046	1.6	0.45	3 5	150	17 * .	1 9	1.5 .	4.0	0.15
HS1-510301	520.	161.	430	0.061	1.3	0.53	4.1	90	31	3.6	1 6	3.9	0.10
HS1-510401	1237.	530	740	0.022	1.4	0:82	3.7	330	43.	4.6	2 3	4.3	0.05
HS1-510501	2690.	690.	650.	0.036	1.4	0.75	3.8	150	26.	3.3	1.6	3.3	0.11
HS1-510602	1800.*	360.	370.	0.072	1.8	0.88	3.6	140	20.*	2.6	1.4	2.6	0.16
ES1-516701	. 320.	69.	66.	0.041	1.7	1.1	4.3	170	22.	2.6	1.7	2.4	0.12
251-510801	1300.	330.	490.	0.06	1.8	0.86	4.0	100	25.	2.8	1.8 .	2.5	0.15
¥S1-510901	770.	330.	570.	0.036	1.6	0.87	3.9	170	42.	2.7	1.3	2.9	0.11
HS1-551101	1360.	480.	290.	0.044	1.2	1.0	3.7	170	35.	3.9	1.9	4.0	0.12
HS1-551201	3500.	970.	1400.	0.04	1.8	0.77	4.6	220	28.	2.4	1.5	2.5	0.13
HS1-551301	1800.	650.	610.	0.048	1.1	0.49	3.8	120	36.	3.3	1.3	3.8	0.15
HS1-551401	930.	640.	190.	0.010	1.4	• 0.89	3.8	2700	68.	3.7	1.8	3.5	0.03
231-551501	920.	410.	.003	0.028	1.5	0.63	3.8	200	45.	3.2	1.2	3.5	0.11
HS1-551601SOX	1800.	420.	280.	0.028	1.3	1.1	· 3.0	200	23.	4.9	2.0	4.9	·0.10
1151-551701	770.	. 380.	300.	0.013	1.5	0.73	3.6	640	49.	4.0	1.6	3.8	0.05
HS1-591801	1300.	700.	310.	0.013	1.4	0.71	. 4.0	720	52.	4.2	2.1	3.9	0.05
HS1-591901SCX	340.	140.	72.	0.049	1.9	1.2	1.5	580	42.	4.1	1.5	4.1	0.11
HS1-592001	2600.	910.	510.	0.033	1.8	0.59	4.5	220	36.	2.6	1.2	2.3	0.10
ES1-392101 SOX	1800.	610.	1600.	0.05	· · 1.7	• 1.1	3.4	300	33.	3.7	2.0	3.6	0.14
HS1-592201SOX	1300.	570.	580.	0.031	1.5	0.87	3.2	190	44.	3.7	1.4	4.0	0.09
ES1-592301	1600.	520.	570.	0.036	1.6	0.71	3.6	230	32.	4.3	1.7	4.4	0.14
251-592401	· 530.**	120.	180.	0.055	1.3	0.83	3.5	240	22.**	3.0	2.4	2.8	0.15
HS1-592501	1200.**	480.	1300.	0.032	1.8	0.78	3.3	1000	38.**	3.0	1.4	2.9	0.11
HS2-592301	2200.	540.	480.	0.048	1.8	1.1	2.2	160	24.	3.9	1.4	4.0	0.15
Range	3500320.	97069.	160066.	0.072-0.01	0 1.9-1.1	1.2-0.43	4.6-1.5	<b>90-</b> 2700	6817.	4.9-1.9	2.4-1.2	4.9-1.7	0.12-0.03
Mean	1400.	480.	560.	0.038	1.5	0.81	3.7	370	36.	3.4	1.6	3.5 .	0.11
Standard													
Deviation	. 840.	230.	390.	0.016	0.24	0.20	0.6	530	12.	0.8	0.3	0.8	0.04
Mean ± 100x Std. De	v.					•							•
Mean	1400 <u>+</u> 60 <b>%</b>	480 <u>+</u> 48%	560 <u>+</u> 70 <b>%</b>	0.038+42%	1.5 <u>+</u> 16%	0.81 <u>+</u> 25%	3.7 <u>+</u> 16%	530+140%	- 36 <u>+</u> 33%	3.4+24%	1.6+19%	3.5+232	0.11+36%
Ranges, Means,	Std. deviat	ions, etc	. do not ir	nclude HS2-5	92301 valu	es ·					-	· –	-
** not includ SCX - Included	ing what app in calculat	ear to be ions, the	contaminar se samples	nt (phthalat were soxhle	es?) peaks tted								-64-

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Sample #	Aliph P	pb dry wt. <u>n</u> -alk	sed. Arom	<u>Pris+Phy</u> <u>n</u> -alk	Pristane Cl7	Phytane CI8	Pristane Phytane	<u>n-alk</u> n-Cl6	Z <u>n-alk</u> Aliph	Total <u>Odd</u> Even	C≤20 <u>odd</u> cven	C≥21 <u>odd</u> even	<u>C∠20</u> C∠21	_
ES2-500101	No Sam	ple Recei	lved											-
KS2-510201	750.	170.	42.	0.051	1.6	0.96	1.9	160.	23	2.2	1.1	2.4	0.20	
h52-510301	1709.	470.	390.	0.045	1.8	0.63	4.6	260.	27	1.7	1.5	1.7	• 0.20	
HS2-510401	1410.	430.	125.	0.051	1.7	0.60	4.2	120.	30	1.9	1.0	2.0	0.18	•
HS2-510501	860.	250.	74.	0.026	1.8	0.62	2.9	360.	29	2.0	1.2	2.1	0.15	
ES2-510601	1700.	330.	460.	0.060	1.3	0.70	2.1	54.	20	1.7	1.0	1.9	0.36	
HS2-510701	1400.	600.	1900.	0.024	0.73	0.65	1.2	280.	42	2.0	1.3	2.1	•0.27	
ES2-510801	1100.	240.	580.	0.041	1.6	0.59	3.6	130.	22	1.3	1.7	1.3	0.22	
HS2-510901	2200.	840.	240.	0.020	1.3	0.57	3.8	160.	37	3.9	1.5	3.9	0.099	
HS3-551091	900.	330.	280.	0.037	2.1 '	0.67	5.8	170.	34	3.1	1.3	3.0	0.14	
ES2-551101	790.	380.	320.	0.025	1.7	0.91	2.7	230.	48	2.8	1.3	2.9	0.12	
HS2-551201	890.	260.	35.	0.010	1.3	0.44	4.0	390.	30,	3.2	1.2	3.3	C.061	
HS2-551301	740.	380.	470.	0.0072	1.3	0.43	3.0	2300.	51	0.91	0.92	0.91	0.047	
HS2-551401	1400.	280.	260.	0.03	1.4	0.55	3.1	580.	20	1.7	0.78	1.7	0.11	
HS2-551501	1700.	240.	140.	0.032	1.6	0.74	2.9	1500.	14	3.0	1.4	2.9	0.14	
HS2-551601	420.	200.	290.	0.0097	1.5	0.60	4.1	51.	47	3.9	1.3	4.4	0.23	
HS2-551701	770.	200.	200.	0.023	1.4	1.2	2.1	64.	27	1.7	1.1	1.9	0.33	
KS2-591801	1100.	400.	150.	0.017	1.4	0.56	4.1	280.	36	2.9	1.1	3.0	0.098	
HS2-591901	970.	420.	330.	0.012	1.1	0.61	2.4	700.	42	3.9	1.1	4.2	0.071	
KS2-592001	1700.	570.	420.	0.019	1.2	0.61	4.2	950.	33	2.7	1.8	2.7	0.072	
ES2-592101	1400.	480.	530.	0.029	1.6	0.54	5.0	100.	35	2.6	1.4	2.9	0.14	
HS2-592201	1700	620.	270.	0.045	1.3	0.48	3.9	50.	. 36	4.8	1.2	3.2	0.25	
HS2-592301	1900.	770.	340.	0.044	1.4	0.51	• 4.2 ·	190.	41	2.0	1.6	2.0	0.16	
HS2-592401	2800.	710.	440.	0.040	1.7	0.52	5.5	67.	25	1.6	1.4	1.6	0.18	
HS2-592501	1500.	190.	300.	0.032	1.7	0.63	4.4	110.	36 -	2.1	1.3	2.2	0.13	
Range	420-2800	170-840	35-1900	0.0072-0.0600	0.073-2.1	0.43-1.2	1.2-5.8	50-23 <b>00</b>	14-48	1.3-4.8	0.78-1.8 `	0.91-4.4	0.061-0.3300	
Kean	1300	410	360	0.030	1.5	0.64	3.6	386	33	2.5	1.3	2.5	0.16	
Standard														
Deviation	550	190	360	0.015	0.28	0.17	1.2	530	9.6	0.96	0.24	0.89	0.082	•
Mean +						•								
100x Std.	Dev.												•	
Me	ean													Ň
•	1300 <u>+</u> 42%	410 <u>+</u> 46 <b>%</b>	360 <u>+</u> 100%	0.030 <u>+</u> 50%	1.5 <u>+</u> 19%	0.64 <u>+</u> 26%	3.6+33%	386 <u>+</u> 137%	33 <u>+</u> 29% ·	2.5 <u>+</u> 38%	1.3+18%	2.5+36%	0.10-21%	

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Table 7

Rig Monitoring - During Drilling - Chromatographic Parameters

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										Total			
	P	pb dry wt. s	ied.	Pris+Phy	Pristane	Phytane	Pristane	<u>n-alk</u>	7 n-alk	<u> 550</u>	C <u>≺</u> 20 <u>edd</u>	C <u>7</u> 21 <u>odd</u>	C <u></u> ≤20
Sample #	Aliph	<u>n</u> -alk	Arom	<u>n</u> -alk	C <sub>17</sub>	C18	Phytane	C16	Aliph	Even	even	even	<u> </u>
453-500101	740	200	144	0.039	1 4	0 / 9	2.0	100				• /	
HS3-510201	2100	290	100	0.020	1.4	0.40	3.0	190	39	2.3	0.98	2.4	· 0.14
253-510301	1700	720	200	0.024	1.5	0.03	2.4	200	30	. 1.0	1,2	1.0	0.12
HS3-510401	1300	430	200	0.020	1.4	0.75	2.0	500	41	1./	1.1	1.9 .	0.11
HS3-510501	600	320	02	0.024	1 2	0.00	2.0	420	53	2.2	1.2	2.2	0.12
HS3-510601	830	300	170	0.012	1.2	0.52	2.5	410	23	2.3	0.96	2.8	0.075
253-510701	1100	430	200	0.033	1.5	0.01	2.0	440	- 47		0.84	2.3	0.14
#53-510201	1700	910	200	0.0074	1 2	0.50	2.0	440	39	. 1./	0.80.	1.0	0.063
HS J= 510801	1700	350	460	0.015	1.2	0.53	3.2	200	24	0.70	1.2	0.00	0.10
N22-551001	No Semo	1. Beceived	200	0.020	1.1	0.70	4.2	TOD	39	2.1	1.1	2.1	0.15
NS3-551101	030	240	200	0 0 0 1 .	۰ e	o /o .		200	~~			• •	
NS3-551201	9/0	300	300	0.021	1.5	0.43	4.3	. 380	38	2.3	0.99	2.8	0.12
103-331201	1400	510	220	0.020	1.4	0.52	3.7	220	33	2.5	0.93	2.5	0.12
H22-51/01	1200	400	450	0.039	0.50	0.35	2.3	30	32	2.3	0.81	2.9	0.35
103-331401	200	490	270	0.020	1.3	0.51	.3.3	1330	41	2.5	1.0	2.5	.0.12
123-331301	910	430	130	0.022	1.2	0.54	3.0	170	49	3.4	1.2	2.8	0.14
R53-331001	1300	040	290	0.024	1.6	0.65	3.0	260	41	2.1	0.94	2.1	0.16
ES3-351701	1100	320	250	0.024	1.6	0.4/	5.0	350	29	2.9	1.0	3.0	0.12
253-591301	520	140	180	0.032	1.6	0.74	2.7	430	27	2.5	1.2	2.6	0.14
F23-241401	1100	370	250	0.036	1.3	0.60	3.6	130	35	3.2	1.3	3.4	0.17
ES3-592001	570	210	100	0.026	1.4	0.50	3.9	170	37	2.2	0.97	2.5	0.19
HS3-592101	910	430	260	0.018	<b>0.40</b>	0.35	1.8	61	47	2.4	1.1	2.5	0.20
HS3-592201	1400	610	290	0.017	1.4	0.45	4.6	330	. 43	2.9	1.1	3.0	• 0.10
253-592301	No Samp	le Received				•						,	
HS3-592401	1400	700	230	0.0080	1.5	0.41	5.4	780	50	2.8	0.89	2.8	0.052
HS3-592501	1300	500	340	0.055	0.42	0.39	1.9	18	39	2.0	1.1	2.5	0.54
XS4-592401	1400	620	230	0.016	. 1.5	0.52	3.8	450	46	2.8	0.96	2.9	0.088
Range	520-2100	140-910	92-480	0.0074-0.055	0.40-1.6	0.35-0.83	1.8-5.4	18-730	27-54	0.70-3.4	0.81-1.3	0.66-3.8	0.052-0.54
Mean	1100	470	250	0.024	1.3	0.54	3.3	280	40	2.3	1.0	2.5	0.15
Standard							٠					-	
Deviation	n 390	190	97	0.010	0.36	0.14	0.98	170	7.2	0.56	0.13	0.63	0.10
Mean +													
100x <u>Std</u>	. Dev.												
M	ean 1100+35 <b>%</b>	470+40%	250+39%	0.024+42%	1.3+28%	0.54+26%	3.3+30%	280+61%	40+18%	2.3+24%	1.0+13%	2.5+25%	0.15+67%

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## Table 8

Rig Monitoring - After Drilling + Chromatographic Parameters

samples in the "after" phase which have unusually large amounts of LMW <u>n</u>-alkanes at Stations #13, 21 and 25 have very low <u>n</u>-alkane  $C_{16}$  ratios.

Other parameters that include a wide molecular weight range show moderate standard deviations. Again substantial replication would be necessary when using these parameters. Perhaps the easiest parameters to use are those which cover only a narrow range of the gas chromatographic run. The ratios of pristane/ $C_{17}$ , phytane/ $C_{18}$ , pristane/phytane and the low and high odd/even are quite reproducible in all three samplings.

In a search for the affects of the rig emplacement no discernible differences are noticed when comparing the means of these 13 parameters. In comparing sample to sample from the various collections certain differences are seen in one or more parameters but it appears just to be random variations. A type of statistical plot which encompasses the weighted effects of all parameters was used in comparing stations among the three samplings. This cluster plot was originally used by D. F. Andrews (1972). The sinusoidal plot that results is responsive to all parameters used to create it. For the rig samples the 13 parameters used in Tables 6-8 were used and groups of plots are shown in Figures 3-7. Figures 3-6 are composed of means of parameters for samples at equal distances from the rig. All but Figure 3 have three lines depicting the before, during and after phases.

A drilling rig would be expected to exert the greatest effects at the rig site with rapidly decreasing effects with distance from the center. In a cluster plot a line must deviate a great deal from another before one can say there is a statistical basis for declaring

\* Andrews, D. F. 1972. Biometrics 28: 125-136.

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Figure 3. Cluster group plot of samples at rig site. These plots represent the combined effects of all 13 parameters in Tables 7-9. The two lines depict A. before drilling samples at Om B. after drilling sample at Om



RIG MONITORING
Figure 4. Cluster group plot of samples 100m from rig.
These plots represent the combined effects of all
13 parameters in Tables 7-9. The three lines shown depict the means of:
A. all before drilling samples at 100m
B. all during drilling samples at 100m
C. all after drilling samples at 100m



## Figure 5. Cluster group plot of samples 500m from rig.

These plots represent the combined effects of all 13 parameters in Tables 7-9. The three lines shown depict the means of:

A. all before drilling samples at 500m

B. all during drilling samples at 500m

C. all after drilling samples at 500m



RIG MONITORING

Figure 6. These plots represent the combined effects of all 13 parameters in Tables 7-9. The three lines shown depict the means of: all before drilling samples at 1000m A.

Cluster group plot of samples 1000m from rig.

all during drilling samples at 1000m Β.

all after drilling samples at 1000m C.



RIG MONITORING

Figure 7. Cluster group plot of all rig samples.

These plots represent the combined effects of all 13 parameters in Tables 7-9. The 11 lines shown depict the means of:

A. before drilling sample at Om

. B. after drilling sample at Om

all before drilling samples at 100m C. D. all during drilling samples at 100m Ε. all after drilling samples at 100m F. all before drilling samples at 500m G. all during drilling samples at 500m all after drilling samples at 500m H. all before drilling samples at 1000m I. J. all during drilling samples at 1000m ĸ. all after drilling samples at 1000m



a difference in the two samples. Figure 3, representing the rig site, shows just how little difference exists in the before and after phases of drilling based on oil-pollution indicators. Statistically these samples are very similar. Even more dramatic are the similarities seen in samples at 100 m, 500 m and 1000 m from the rig. Figure 7 demonstrates quite clearly that not only is there no clear difference due to drilling, there evidently is no major difference in any of the 1974 samples.

Another method of analyzing those data was tried to discern differences in the "before", "during" and "after" samples. Discriminant analysis (Veldman, 1967)\* was applied to the same data used to generate Figures 4-6. The F ratios which were found are shown in Table 9. At the 99.95% level (alpha = 0.0005) no significant difference exists among the three groups at 100 m, 500 m and 1000 m from the rig. However at the 99.9% level a significant difference does exist at the 100 m samples, i.e., there is 99.9% probability of a difference among the three groups. There is only 97.5% . assurance of a difference in the 500 m samples and only 75% assurance of a difference in the 1000 m samples. The probability of a difference then when comparing the "before", "during" and "after" samples increases as one approaches the rig site. Perhaps just as impressive is the fact that the parameters which consistently yield the most significant contribution to the discrimination of the groups are  $phytane/C_{18}$  and the LMW odd/even ratios. Therefore though the hydrocarbon data indicates only minimal changes in the area adjacent to the oil rig off Mustang Island, changes should be more pronounced in the area immediately surrounding the rig.

Veldman, Donald J. 1967. Fortran Programming for the Behavioral Sciences.
 Holt Rinehart and Winston, pp. 275-277.

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## Table 9

## Discriminant Analysis Data on Rig Monitoring Samples

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from Rig	DF1	DF2	<u>F Ratio</u>
100 meters	26	18	5.222
500 meters	24	14	2.908
1000 meters	26	20 ·	1.649

Note: The analysis was applied to the means of the 3 groups (before, during, and after) at each distance for 13 gas chromatographic parameters.

#### III. Intercalibration Studies

Contained in Appendix B are chromatograms and peak file data for the last of the intercalibration results for 1975-76. The results of the final intercalibration meeting held in June, 1976 are presented in a separate report. However we felt that this study also afforded us a means of determining the reproducibility of our methods.

Table 1 lists the gravimetric data from replicate analyses of Venezuelan Crude, Kuwait Crude, No. 2 Fuel Oil and So. Louisiana Crude. Considering the difficulty of weighing such volatile materials, the results are very reproducible. Surpassing this reproducibility however is the list of gas chromatography parameters contained in Table 2. In view of this degree of reproducibility the credibility and reliability of the hydrocarbon data from MAFLA and rig monitoring study are further enhanced.

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## Gravimetric Data

# API Oils

# Intercalibration

	Total Lipid	Total Aliphatics	Total Aromatics	Total Polar Lipids	<u>Aliphatics</u> Total Lipid	Aromatics Total Lipid	<u>Polar Lipid</u> Total Lipid	
Venezuelan Crude 1st Determination	0.3800g	0.0992g	0.2054g	0.0538g	26.1%	54.1%	14.2%	
Venezuelan Crude 2nd Determination	0.6700g	0.1497g	0.4070g	0.1258g	22.3%	60.7%	18.7%	
Venezuelan Crude 3rd Determination	0.4100g	0.1178g	0.2700g	0.0449g	28.7%	65.9%	10.9%	
#2 Fuel Oil 1st Determination	0.4800g	0.3293g	0.1200g	0.0474g	68.6%	25.0%	9.88% .	•
#2 Fuel Oil 2nd Determination	0.5262g	0.3381g	0.1624g	0.0358g	64.3%	30.8%	6.80%	
#2 Fuel Oil 3rd Determination	0.4600g	0.3149g	0.1177g	0.0092g	68.5%	25.6%	2.00%	
Louisiana Crude lst Determination	0.6573g	0.4066g	0.1384g	0.0420g	61.8%	21.1%	6.39%	
Louisiana Crude	0.3900g	0.2468g	0.0764g	0.0384g	63.3%	19.6%	9.84%	
Louisiana Crude 3rd Determination	0.4500g	0.3075g	0.0947g	0.0487g	68.3%	21.0%	10.8%	

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	Total Lipid	Total Aliphatics	Total Aromatics	Total Polar Lipids	<u>Aliphatics</u> Total Lipid	Aromatics Total Lipid	<u>Polar Lipid</u> Total Lipid
Kuwait Crude lst Determination	0.6236g	0.2470g	0.2207g	0.0599g	39.6%	35.4%	9.61%
Kuwait Crude 2nd Determination	0.4344g	0.1887g	0.1628g	0.0909g	43.4%	37.5%	20.9%
Kuwait Crude 3rd Determination	0.4077g	0.1943g	0.1525g	0.0634g	47.6%	37.4 <b>%</b>	15.6%

### Table 2

					<b>.</b>	<b>.</b>			<b>.</b>	Total	C <u>∕</u> 20	C <u>&gt;</u> 21	∽_20
	Aliph	t total oil <u>n</u> -alk	Arom	<u>n-alk</u>	C17	C18	Pristane Phytane	$\frac{n-alk}{Cl6}$	Z <u>n-alk</u> Aliph	<u>Udd</u> Even	Even	Even	_C <u>≻</u> 21
nezuelan Crude t Determination	20	13	114	0.10	0.65	0.39	1.6	17	. 64	1.1	0.85	1.2	1.4
nezuelan Crude d Determination	24	16	89	0.064	0.68	0.41	1.5	20	63	1.0	0.83	1.3	1.2
nezuelan Crude d Determination	27	16	129	0.065	0.66	0.39	1.6	19	59	0.96	0.83	1.2	1.3
Fuel Oil t Determination	97	50	220	0.083	0.55	0.28	 1.6	9.2	52	0.96	0.88	2.8	11
Fuel Oil d Determination	116	67	91	0.10	0.76	0.37	2.3	11	58	1.0	0.96	2.1	11
Fuel Oil d Determination	130	58	120	0.090	0.75	0.39	2.3	8.8	43	0.95	0.87	2.8	11
uisiana Crude t Determination	74	42	23	0.092	0.93	0.53	1.8	15	57	0.93	0.83	1.2	2.3
uisiana Crude d Determination	76	42	23	0.091	6.91	0.51	1.9	15	55	0.93	0.86	1.2	2.3
uisiana Crude d Determination	87	48	24	0.093	0.93	0.53	1.8	15	56	0.94	0.83	1.2	2.4
wait Crude t Determination	70	35	11	0.040	0.18	0.28	0.61	11 .	50	1.1	1.1	1.1	1.3
wait Crude d Determination	70	31	13	0.045	0.18	0.29	0.61	10	45	1.1	1.1	1.1	1.3
wait Crude d Determination	70	32	12	0.042	0.18	0.29	0.61	13	60	1.1	1.1	1.1	1.3

### Gas Chromatographic Parameters of Intercalibration

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#### Addendum

In light of further observations and data synthesis some comments not made in the main body of the report.

1. Comparison of 1974 and 1975

In comparing the 1974 to 1975 sampling programs, it was noted that the low molecular weight (LMW) <u>n</u>-alkanes in the sediments of the Mississippi shelf appear to be less pronounced in 1975 samples than in those collected in 1974. Figure Al clearly demonstrates that relative to the high molecular weight <u>n</u>-alkanes, the LAW <u>n</u>-alkanes are present in lower concentrations in 1975 samples. A loss of all LMW alkanes (including pristane and phytane) with some greater loss of the <u>n</u>-alkanes in the period 1974-75 indicates that the rate of supply of these hydrocarbons, probably petroleum derived, has decreased recently.

2. Seasonal effects

The only discernible seasonal effect in the hydrocarbon distributions of the northeastern Gulf was seen again in the pollutant hydrocarbons present in Mississippi and deep water stations. The six months interval between the summer and winter of 1975-76 in these deep water stations has resulted in a decrease in the LMW alkane suite that is indicative of petroleum input. The loss is much more noticeable in deep water stations and most likely is not due to a seasonal effect but to the time lapse and subsequent degradation of alkane hydrocarbons.

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#### 3. Aromatic hydrocarbons of NE Gulf sediments

The results of aromatic hydrocarbons are much more difficult to interpret than the aliphatic components. As seen in 1974, the aromatic fractions contain a good bit of polyunsaturated compounds. Chief among them is squalene (at <u>ca</u>. K.I. 3048) occurring at all stations. The source of the squalene has not been firmly established but was shown by John Calder and Philip Meyers to be found in some benthic organisms and, depending upon seasou, in the water column. The Texas oil rig sediments contain little evidence of marine input and no squalene. Therefore squalene probably reflects the input of oceanic organic material in the eastern Gulf. The Florida inner shelf is characterized by aromatics of very high boiling point (Anthracene and higher), whereas Mississippi shelf and deep water stations exhibit both low and high molecular weight aromatics. No apparent loss of the LMW aromatics (possibly of petroleum origin) was in evidence when comparing 1974 to 1975 samples. A more rigorous characterization of the aromatics will be necessary before more meaningful observations can be made.

#### 4. Outer shelf sediments

It was concluded that the hydrocarbons from the outer shelf sediments are a result of transport of organic matter from the Mississippi shelf area along the edge of the continental shelf. This theory was tested by determining carbon isotope ratios of acid-treated sediment. The results revealed an isotopic composition not much different from the marine deposits of the Florida inner shelf. Consequently the hydrocarbons (aliphatic and aromatic) must be transported by a mechanism entirely separate from the bulk of the organic matter. The hydrocarbons may be associated with the clay fraction which could penetrate further into the open ocean than the remaining

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unassociated terrestrial organic debris. Correlation coefficients of 0.3077 and 0.4912 for aliphatics and aromatics <u>vs</u> percent clay suggest significant correlations at the 98+% confidence level and a very likely association of hydrocarbons with clay. The transport of pollutant-clay complexes over great distances emphasizes the importance of oil spill prevention in areas of high run-off of clay rich materials.

#### 5. Correlations - Sediments

The lack of consistency of sampling scheme for sediments and water, makes correlations of these two masses of hydrocarbon data not possible. However, it should be noted that John Calder found, at times, two provinces of hydrocarbon distributions roughly coinciding with the two major sedimentary hydrocarbon regimes of the northeastern Gulf. Correlations of trace metals <u>vs</u> hydrocarbons provided no real information because no excess nickel or vanadium could be seen in the Mississippi sediments where hydrocarbons indicate obvious pollution. It is felt that the level of pollution seen in these sediments as determined by hydrocarbons (major constituents of oil) could not be seen by trace metal analysis. The levels of nickel and vanadium in oil probably require methods that can differentiate all the various sources of the metals.

#### 6. Correlations - Benthic Algae

Hydrocarbon pollutants in the benthic algae displayed little if any correlation with the presence of petroleum residues in the nearby sediments. The types of pollution seen in these two sample programs were distinguishable the algae containing mostly extremely weathered petroleum residues. The random nature of pollutant occurrence in the algae and its state of weathering may be the result of inclusion of asphaltic tar ball materials

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in some samples. The benthic faunal samples analyzed by Philip Meyers also tended to display rather random inclusion of pollutants, in agreement with the benthic algae recults.

The occurrence of the phytadiene complex in certain benthic algae may be more important than was at first realized. After looking at retention index data and results of hydrogenation of Florida inner shelf sediments it has become apparent that phytadienes also occur in these sediments. Their locations in chromatograms can be seen in Figure A2, occurring between the C19 and C<sub>20 n-alkanes. Though minor components, their significance should not</sub> be overlooked. In this figure it may also be noted that the ratio of phytane/C<sub>18</sub> is rather high. This oil polluting indicator might imply a history of oil pollution except the pristane/ $C_{17}$  and pristane/phytane ratios are small. This phenomenon was noticed in 1974, but no explanation was offered. It is quite conceivable that the abundance of phytadienes in the algae (and in the zooplankton) could serve as sources of phytadienes in recent sediments. This phytadiene material may in turn be reduced to phytane to yield high phytane/C18 ratios in this or other areas of no other perceivable evidence of oil pollutants. Extreme caution must therefore be used when such oil indicating parameters are interpreted.

Figure Al. Hydrocarbons from typical Mississippi shelf sediment. The Area IV-Station 12 is an aliphatic gas chromatogram from 1974. The Transect VI-Station 41 is taken from the same location but in 1975.



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Figure A2. Hydrocarbons from typical Florida shelf sediment.

1974 (left) and 1975 (right) gas chromatograms from a Florida inner shelf location. "X" denotes a series of phytadienes not resolved in the 1974 samples.



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## APPENDIX A

Gas chromatograms and quantitative peak files for 1975-76 rig monitoring aliphatic and aromatic hydrocarbons.



	SLM SECIPENT_ 4/21/76 LIPHATICS HYGRCC	1 M33 510; Aliphat: Arrows	201 ICS	4-2													n-																F
AETENTION TIME	*CVATS	PICACGRAPS		-76	·				  			l													-						-		-
1.75 2.13 2.45	1313. 1345.	0.01 0.12 0.00		#																									-				1 
2.63 3.07 3.54	1363. 1405. 2442. 1479.	C.13 0.26 0.58 0.CL		<u>,</u>							Bartistica	0	•	. <del></del>	(5)														Í				İ
6,29 6,61 6,61	1499. 1521. 1539.	1,83 0,34 0,35	•	0.3	-																											-	!
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| 34.31<br>35.10<br>36.59          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     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TIPE<br>1.71<br>2.71<br>3.65<br>4.63<br>4.63<br>4.63<br>5.22<br>5.63<br>5.64<br>5.64<br>6.68<br>5.24<br>6.68<br>7.37<br>E.08<br>5.64<br>6.68<br>5.60<br>10.55<br>10.55<br>10.55<br>10.55<br>10.67<br>13.65<br>13.65<br>14.02<br>13.65<br>14.03<br>13.65<br>14.02<br>13.65<br>14.52<br>14.52<br>14.52<br>15.70<br>15.73<br>15.70<br>15.73<br>15.70<br>15.73<br>15.70<br>16.61<br>17.34<br>17.44<br>17.46<br>17.46<br>17.35<br>15.70<br>16.65<br>14.73<br>15.73<br>15.70<br>15.73<br>15.73<br>15.70<br>16.63<br>17.35<br>15.70<br>16.65<br>14.52<br>15.73<br>15.70<br>15.73<br>15.73<br>15.70<br>16.63<br>17.46<br>17.36<br>17.46<br>17.36<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46<br>17.46 | ETENTICN TIPE         KOVATS           1.71         1336.           2.71         1336.           3.65         1435.           4.63         1457.           5.62         1531.           5.22         1555.           6.61         1531.           5.22         1555.           6.63         1669.           7.37         1669.           7.37         1669.           7.37         16649.           7.37         16641.           6.66         1775.           8.96         1736.           16.66         1775.           9.96         1745.           9.66         1843.           16.55         19001.           16.75         19022.           11.67         1948.           11.69         2055.           12.09         2051.           12.09         2051.           13.65         2104.           14.03         2160.           15.53         2208.           14.52         2163.           15.53         2208.           15.53         2208.           15.53 | ETENTICN TIPE         RDVATS         PICACGHAMS           1.71         1216.         0.05           2.71         1330.         0.02           3.65         1435.         0.12           4.63         1457.         0.07           5.65         1435.         0.12           4.63         1531.         0.07           5.72         1557.         0.12           5.64.         1600.         0.45           6.24         1625.         0.16           6.24         1625.         0.16           6.24         1649.         0.32           7.37         1641.         2.16           8.66         1775.         0.61           9.68         1843.         0.97           10.55         1901.         1.59           10.55         1902.         0.31           11.27         1946.         2.21           11.69         1975.         1.31           12.99         2021.         0.40           13.12         19         2055.         17.20           13.65         2164.         12.00         14.92           14.92         2196.         3.77 </td <td>ETELLICA TIPE         KOVATS         PICACGRAMS           1.71         1216.         0.05           2.71         1336.         0.02           3.17         1435.         0.12           4.65         1435.         0.12           4.65         1435.         0.12           5.61         1600.         0.63           5.62         1623.         0.12           5.63         1670.         0.63           6.24         1623.         0.16           6.64         1649.         0.32           7.33         1651.         2.16           8.66         1735.         0.61           6.76         1665.         0.72           16.75         1666.         0.73           11.27         1922.         0.73           11.27         1944.         2.21           11.44         1975.         1.34           12.66         2064.         7.10           13.65         2160.         12.10           14.77         2146.         22.80           15.53         2160.         12.10           14.29         2165.         12.10           15.53</td> <td>ETERATION TIME       KOVA15       MICACGAANS       T6         1.11       1336       0.05       4#       3         1.11       1394       0.05       4#       3         1.11       1394       0.05       4#       3       0:3         1.11       1394       0.05       4#       3       0:3       4#         1.11       1394       0.05       0.12       5       5       0.12       5         1.01       1531       0.012       0.05       0.12       5       5       6       1600       0.132       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7<td>ETERATION TIPE       KOVATS       PICACGAANS       76         1.71       1216       0.05       76         2.71       1336       0.02       44         2.71       1336       0.02       44         2.71       1336       0.02       44         2.71       1336       0.02       44         2.71       1336       0.02       44         2.71       1336       0.02       44         2.71       1337       0.012       0.05         2.72       1600       0.52       0.12         3.72       1601       0.12       0.12         3.71       1611       2.16       0.12         3.72       1601       0.12       1.59         1.702       1609       0.70       H.S.T.S.O.         1.71       1922       0.73       1.70         1.72       1974       2.21       1.71         1.72       1974       2.71       1.70         1.72       1975       0.40       1.71         1.73       1972       0.73       1.76         1.73       1974       2.71       1.76         1.74       1975</td><td>ETENTION VIPE       KOVATS       PICREGRAMS       76         1.71       1216       0.05       44         2.71       1330       0.05       44         3.45       1.455       0.12       5         4.53       1.455       0.12       5         5.45       1.555       0.12       5         5.45       1.555       0.12       5         5.45       1.500       0.452       5         5.45       1.500       0.452       5         5.45       1.500       0.452       5         6.42       1.520       0.462       5         7.53       1.501       0.42       5         7.53       1.502       0.462       7         10.464       1.775       0.48       45         4.64       1.775       0.48       45         4.64       1.775       0.48       45         4.64       1.755       1.33       5         10.45       1.620       1.43       5         11.47       1.922       0.70       1         11.47       1.922       0.70       1         11.47       1.922       1.</td><td>ETENTION TIPE       KOVATS       FIGACGAAMS       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       <tht< th=""> <tht< td=""><td>ETENTION TIPE       NOVA15       PICACGHAMS       T         1.11       1716       0.001       14         1.11       1716       0.001       33         1.11       1716       0.001       33         1.11       1716       0.001       33         1.11       1716       0.001       33         1.11       1716       0.001       33         1.11       1716       0.012       0.13         1.11       1716       0.012       0.13         1.11       1716       0.012       0.13         1.11       1716       0.13       0.13         1.11       1716       0.13       0.13         1.11       1716       0.13       0.13         1.11       1716       0.13       0.13         1.11       1116       0.13       0.13         1.11       1116       0.13       0.14         1.11       0.13       0.13       0.14         1.11       0.14       0.13       0.14         1.11       0.14       0.15       0.14         1.11       0.14       0.15       0.14         1.12       0.14</td><td>ETENTION TIPE       KOVAIS       PICAEGRAMS       <math>3^{\circ}</math> <math>76^{\circ}</math> /td><td></td><td>tetektick type     kDVA15     PICACGAAMS       1/1     111     0.05       1/1     111       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05</td><td></td><td></td><td></td><td>titalion tipe комала рідаєбана<br/>1.51 133 0.05<br/>1.51 td><td></td><td></td><td><math display="block">\frac{1}{10} + \frac{1}{10} </math></td><td>The life is a second second second second second second second second second second second second second second second second second second second 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      7.10           13.65         2160.         12.10           14.77         2146.         22.80           15.53         2160.         12.10           14.29         2165.         12.10           15.53 | ETERATION TIME       KOVA15       MICACGAANS       T6         1.11       1336       0.05       4#       3         1.11       1394       0.05       4#       3         1.11       1394       0.05       4#       3       0:3         1.11       1394       0.05       4#       3       0:3       4#         1.11       1394       0.05       0.12       5       5       0.12       5         1.01       1531       0.012       0.05       0.12       5       5       6       1600       0.132       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       7       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1.71         1.73       1972       0.73       1.76         1.73       1974       2.71       1.76         1.74       1975</td> <td>ETENTION VIPE       KOVATS       PICREGRAMS       76         1.71       1216       0.05       44         2.71       1330       0.05       44         3.45       1.455       0.12       5         4.53       1.455       0.12       5         5.45       1.555       0.12       5         5.45       1.555       0.12       5         5.45       1.500       0.452       5         5.45       1.500       0.452       5         5.45       1.500       0.452       5         6.42       1.520       0.462       5         7.53       1.501       0.42       5         7.53       1.502       0.462       7         10.464       1.775       0.48       45         4.64       1.775       0.48       45         4.64       1.775       0.48       45         4.64       1.755       1.33       5         10.45       1.620       1.43       5         11.47       1.922       0.70       1         11.47       1.922       0.70       1         11.47       1.922       1.</td> <td>ETENTION TIPE       KOVATS       FIGACGAAMS       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T   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0.14</td><td>ETENTION TIPE       KOVAIS       PICAEGRAMS       <math>3^{\circ}</math> <math>76^{\circ}</math> /td><td></td><td>tetektick type     kDVA15     PICACGAAMS       1/1     111     0.05       1/1     111       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/1     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05       1/2     0.05</td><td></td><td></td><td></td><td>titalion tipe комала рідаєбана<br/>1.51 133 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1601       0.12       1.59         1.702       1609       0.70       H.S.T.S.O.         1.71       1922       0.73       1.70         1.72       1974       2.21       1.71         1.72       1974       2.71       1.70         1.72       1975       0.40       1.71         1.73       1972       0.73       1.76         1.73       1974       2.71       1.76         1.74       1975 | ETENTION VIPE       KOVATS       PICREGRAMS       76         1.71       1216       0.05       44         2.71       1330       0.05       44         3.45       1.455       0.12       5         4.53       1.455       0.12       5         5.45       1.555       0.12       5         5.45       1.555       0.12       5         5.45       1.500       0.452       5         5.45       1.500       0.452       5         5.45       1.500       0.452       5         6.42       1.520       0.462       5         7.53       1.501       0.42       5         7.53       1.502       0.462       7         10.464       1.775       0.48       45         4.64       1.775       0.48       45         4.64       1.775       0.48       45         4.64       1.755       1.33       5         10.45       1.620       1.43       5         11.47       1.922       0.70       1         11.47       1.922       0.70       1         11.47       1.922       1. | ETENTION TIPE       KOVATS       FIGACGAAMS       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T       T      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# TRANSMISSOMETRY AND PARTICULATE MATTER DISTRIBUTION ON THE EASTERN GULF OF MEXICO SHELVES, MAFLA SURVEY, 1975-76

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#### EXECUTIVE SUMMARY

Transmissometry measurements have been performed at seasonal intervals along four transects in the Eastern Gulf of Mexico, ranging from Clearwater, Florida to Mobile Bay. In summer and early fall of 1975 most areas except the vicinity of the Mississippi Delta showed clear waters having upwards of 80% light transmission (coefficient of attenuation less than  $\alpha = 0.22$  or roughly <.2 mg/L total suspended matter) in the upper water columns. A few meters from bottom, however, more turbid layers characterized inshore waters.

In winter (January and February, 1976) shelf waters were turbid over long periods, due to repeated resuspension of fine fractions of bottom sediments owing to storms. Inshore shelf waters were vertically well mixed to a considerable degree. Transmissivities of 50-60% ( $\alpha = 0.7-0.5$  or about 0.5 mg/% were common during this period. These data correspond to finding that particulate detritus resembled bottom sediments mineralogically during the winter period (Huang, 1976), and included appreciable carbonates at certain locations.

Turbidity distributions are frequently closely related to water mass structures and movements. A notable example was provided by phenomena observed on the Middle Ground a few days after Hurricane ELOISE (September 26, 1975). Sharply defined turbid boluses of near-bottom water were related to temperature, salinity and density anomalies interpreted as contour currents, which were enhanced by the forcing function of the violent storm.

### INTRODUCTION

Suspended matter studies of analytical or optical character are limited in the Gulf of Mexico in general and in the eastern Gulf in particular (Manheim, <u>et al.</u>, 1972; Carder and Schlemmer, 1973, and references cited). Generally speaking the data available prior to the current MAFLA Survey suggested that the waters in the Eastern Gulf shelf regions may be highly transparent, reaching tenths of 1 mg/l total suspended matter within only a few kilometers of shore. Greater turbidity has been noted on approaching the Mississippi Delta, around which sharp-edged, turbid plumes are characteristic. Storms are presumed to have significant influence on turbidity distribution, but details of their influence on the shelf regions of the eastern-Gulf have been unavailable. Carder and Schlemmer (1973) concluded that the suspended particle distribution above the slope and outer shelf of the eastern Gulf was highly dependent on the Loop current and associated eddies.

The first MAFLA Survey (1974 - 75) included total suspended matter, particulate organic carbon (POC), and other particulate measurements on discrete samples in five major oil lease tracts. These data implied the existence of very low turbidity regimes over much of the W. Florida shelf, but were puzzling in that they did not adequetely reflect the heavy turbidities in the Delta region, as confirmed at times by bottom photographs and divers' observations. Irregular spatial and temporal variability in turbidity was postulated to account for some discrepancies (Manheim, 1975).

In the following 1975 - 76 MAFLA Survey optical transmissometry

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measurements were added to the study plan in order to provide regional background information and vertical and spatial variability of particulate concentrations. These would aid in assessing the turbidity regime and interpreting the significance of other suspended solid measurements such as total suspended particulate matter (SPM), mineralogy, particulate organic carbon, hydrocarbons, trace metals, and primary productivity.

During the first sampling season late negotiations, and subsequently late arrival and failures of equipment supplied by manufacturers resulted in only small recovery of information. In season II profiles were obtained for roughly 80% of envisaged stations. For season III, despite problems, data were obtained for 100% of envisaged stations. The overwhelming bulk of data were obtained with a Hydro Products instrument. The method chosen for display of these data was that of sections of transmission (T %) based on depth profiles along transects were permitted by the distribution of water column and intermediate stations (Figure 1). Digital records of the data are also available (Appendix 1).

In addition to the optical information, a number of water samples were filtered through Millipore filters for the purpose of visually characterizing the types of particulate matter involved. Such data were useful in calibrating and relating the optical data to analytical measurements performed by other investigators, and to sediment transport processes on the shelf.

We wish to acknowledge the assistance of Mack Barber, Bill Jester, Harvey Mason, Tom Tyska and Ted White in maintaining the equipment in functioning order and to thank Tom Pyle, Ted White, J. E. Alexander and M. Rinkel for their special efforts and cooperations with the transmissometry

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Fig. 1. Location map of water column stations and transects.

program. Our thanks go to our colleagues in the MAFLA studies for making data available at early stages, and to J. L. Simon for his equipment loans.

The above features indicate that natural dispersal and sinking of spilled hydrocarbon slicks will be greater in winter by a factor of three or more than in summer. We should also expect tract metal content of particulate matter to be enriched in constituents characteristic of carbonate and ferrigenous particulate matter.

Taking turbidity distributions and other factors into account, we suggest that the talc reported by Huang represents an indicator of landderived matter of industrial origin. Extending interpretations of the turbidity distributions to measurements such as hydrocarbons and trace metals in particulate matter, we conclude that inshore samples (10 m below sea surface) were reasonably representative of the entire water column in winter, but not in summer. During the former period the particulate matter represents a fine, mobile fraction of local bottom sediments (surficial), whereas during the summer long-distance transport of fine (probably highly organic) particulates in the upper water column are characteristic. The features mentioned above are particularly well illustrated in Figure 4 and 9.

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Fig. 4. Transect I., Season I % Transmission

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Month Parts



## Fig. 9. Transect I., Season III. % Transmission

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#### METHODS

As pointed out by Tyler, <u>et al</u>. (1974) practical optical measurements of particulate matter have lagged behind the theoretical groundwork of Mie (1908), Hulbert (1945) and Van de Hulst (1957). However, the sensitivity and rapidity of optical measuring devices have promoted the use of transmissometers (alpha meters) and nephelometers (scatterance meters) for measuring distribution of suspensoids in water columns. A summary of information in this area is provided in Gibbs (1974) and Jerlov (1968).

The main optical data for the present study were collected during three sampling seasons 1975 - 76 by a Hydro Products Model 912 transmissometer having a 20 mm diameter beam collimated over a one meter path length, with peak photocell response at 5500 Å (550 nm). This unit was equipped with a 350 foot (approximately 100 m) cable. Readouts were obtained on deck each one to two meters for shallow stations, and at somewhat wider intervals for deeper stations.

A few measuremnts were obtained with a cableless Montedoro-Whitney unit originally intended as the primary unit, but whose self-contained chart recording system proved to be poorly designed and permitted only limited use of the instrument. Examples of traces from these instruments are shown in Figures 2 and 4.

For the present purposes the operation of the transmissometers is described by the equation:

$$\frac{I}{I_{o}} = e^{-\alpha x}, \text{ or } \alpha = \ln \frac{I}{I_{o}} \text{ where } x = \ln .$$

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% TRANSMISSION

Fig. 2. Transmissometry trace for Montedoro-Whitney instrument, Sta. 1412-1413, Sept. 9, 1975. The offset in the lines represents differences in down-up traces. Extra scale refers to approximate salinity, (halocline) values at the site. Note the turbid layer at the boundary between well-mixed shelf water above, and clear Gulf water below. This turbidity is probable organic matter collected at a strong density interface (pycnocline). The basic operational unit is % of transmission with respect to theoretically maximally transparent water (distilled water); i.e. for the reference solution itself,  $I/I_0 = 1.00$  or T = 100%. As a practical technique, before each station lowering the transmission of the instrument is checked with neutral density filters in air. Depending on the optical design of the instrument, air transmission may be higher (Montedoro-Whitney) or lower (Hydro Products) than in pure water. Raw data collected with the HP instrument were corrected on board utilizing the optical correction information, and assuming that a transmission of 92% in air corresponded to 100% transmission in pure water, according to manufacturer's data. Without special bulk filtration systems the purest distilled-deionized water available in the laboratory has a % transmission of approximately 90 - 92, whereas offshore waters in the Gulf reached values of 95%.

Further calibration has been performed to relate T and  $\alpha$  values to suspensoid concentrations determined by filtration and weighing techniques (Betzer, 1976). Although some preliminary calibrations were performed with artifically suspended materials such as kaolinite\*, comparison with measurements of suspended particulates from actual water under investigation provides more meaningful intercalibrations, and allows extrapolations and interpolations of analytical information over areas having similar particulate matter character. For such purposes  $\alpha$  is the preferred optical unit, since it has been demonstrated that for a given fluid medium and type of suspended particulate matter  $\alpha$  is proportional to particle mass (weight) per unit water volume over a wide range of concentrations. A

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<sup>\*</sup> See discussion of calibration of turbidity units in McCarthy <u>et</u>. <u>al</u>., (1975).

plot of  $\alpha$  against SPM for typical MAFLA waters is given for Leg II (September, 1975) in Figure 3.

Since all SPM data were obtained at 10 m, few of the high turbidity layers noted near bottom were sampled and particulate weights obtained. To give an indication of calibration for higher turbidity regions, data from layers in Hueneme Canyon, off Southern California (Drake, 1975) are plotted. These data are in reasonable agreement with information on terrigenous detritus from West African continental margin (Carder and Betzer, 1974). Offsets from the data of Drake reflect variable response of light attenuation to particle mass, depending on the proportion and kind of organic matter present and its degree of decomposition, the size, shape and refractive index of mineral matter and possible presence of colloidal and coloring matter (Gelbstoff) in waters. However, for the present purposes the chart provides an approximate guide to SPM magnitudes for the transmissometry distribution.

Aside from the Montedoro-Whitney instrument, chief problems occurred in matching cables to light source, systems instability owing to current leakage in cable connectors, gasket leaks in the light source housing, and other electrical system problems. When occurring, these problems were apparent and modifications were made before sampling was continued. With few exceptions, we feel that intra-trace values are reproducible to within the rounding of the data.

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Fig. 3. Calibration of transmissometry with total suspended matter (SPM). Shown in the plot of extinction coefficient (α) against SPM are data from MAFLA and from southern California (Drake et. al., 1974).

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#### RESULTS

#### Seasonal shelf transects

Available data for sampling season I (June - July, 1975) are given in Appendix 1. Data for sampling season II (September, 1975) are presented in the form of transects in Figures 4 - 8. The chief features noted are the strong vertical stratification and development of bottom nepheloid layers as in Figure 4, the clear offshore and Loop waters again noted in Transects I and IV, and the turbid bottom layers associated with Hurricane ELOISE in Transect II (Figure 5). Near-bottom filtered samples (1.7 & Niskin bottles) from the turbid\_layers in the Hurricane-influenced Transect II revealed dominance of fine carbonate particles, similar to bottom sediments in the general region. Unfortunately, special samples filtered from 1.7 & Niskin bottles for SPM analyses showed probably far too high values (approximately 200 mg/l) to be correlated with the transmissometry data.\* As expected, turbidity increased markedly toward Mobile Bay (Transect IV, Figure 8).

Data for sampling season III (January - February, 1976) are given in Transects I - IV in Figures 9 - 13. The greater vertical homogeneity of particle distributions in the nearshore water column is immediately obvious. The lack of synopticity during the winter sampling emphasizes the temporal nature of turbidity regions. One or two days' difference may result in a completely altered distribution pattern.

# Twenty-four hour transmissometer stations

To provide an initial estimate of the short-term temporal variability

\* See later discussion.



Fig. 5. Transect II., Season II. Zig-zag line denotes break in continuity; Sta. 1204 taken before Hurricane Eloise, other stations post Hurricane.



# Fig. 6. Transect I-II., Season II. % Transmission

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Fig. 7. Transect III., Season II. Montedoro-Whitney traces calibrated to match Hydro-Products through SPM-α adjustment.

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Fig. 8. Transect IV., Season II. % Transmission

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Fig. 11. Transect I-II., Season III. % Transmission



Fig. 12. Transect III., Season III. Note break in time.



Fig. 13. Transect IV., Season III.

of particle concentration in the water column, two 24 hr. time series stations were occupied during the fall and winter seasons: One at the Middle Grounds (1207) and one near the Mississippi Delta (1412). The temporal spacing of casts was about six hours.

Figure 14 depicts the fall time series for the two stations. A near-bottom nepheloid layer, apparently resulting from Hurricane ELOISE, was found at station 1207. This layer may have had a slight, semi-diu nal variation in its thickness. At station 1412 a relatively clear layer appears between turbid water at the surface and near-bottom. The surface water cleared up markedly with time, perhaps indicating the transport of turbid Mississippi plume water away from this station. Near-bottom turbidity remained constant, with only the layer thickness changing with time.

Figure 15 shows two winter sequences for the same stations. At station 1207 a nepheloid layer intensified and then faded during the 24 hr. period, but a much longer record is needed in order to consider whether periodic forcing functions could be responsible. The delta series (Station 1412) depicts a turbid water column with little variation in time.

#### Particulate matter distributions

Transmissivity measurements do not correlate uniquely with suspensate weights or particle counts in ocean waters, owing to the individual effects of particle size, shape, specific gravity, and refractive index. However, since particle properties normally vary transitionally for non-living particulates that make up the bulk of seston, it is possible to interpolate suspended matter by weight (SPM) values from the transmissivity measurements, if sufficient calibration points of SPM measurements are available. The

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Fig. 15. 24 hour time series. Season III (Jan.-Feb, 1976).

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errors involved in such interpolation appear for the present case not to exceed the fluctuations relating to time delays (sequentiality) in coverage of the stations.

Using SPM calibration of transmissivity data aided by visual inspection of filters, a map of SPM in surface water of the MAFLA area has been prepared for the September, 1975 period (Figure 16). The map clearly demonstrates progressive decrease in particulate concentrations with distance from shore, with an interesting, more homogeneous zone in the vicinity of the Middle Ground.



Fig. 16. Particulate distributions in surface waters of Eastern Gulf of Mexico shelves. Contours in  $\mu g/l$ , based on transmissometry and data of Betzer (1976)

#### DISCUSSION

## Seasonal relationships

Some seasonal trends can be easily seen by comparing Figures 4 - 8with Figures 9 - 13, respectively. In general the fall data reveal the effects of water column stratification with often quite clear-water (e.g. % T>85%) overlying near-bottom nephehoid layers resulting from interaction of currents with the bottom. The only exceptions to these general trends were observed in the shallower stations just prior to and after Hurricane ELOISE (Figure 5), where well-mixed, turbid water columns were found. The winter data reveal much more turbid, often well-mixed water columns having transmissivities never exceeding 55% for some of the shallower stations. In fact only at the stations over the slope were transmissivity values exceeding 90% found. As one would expect, the winter data appeared to have been strongly influenced by the lack of water column stability brought on by the succession of windy cold fronts passing through during this season. As a matter of incidental interest, a project to collect certain sponge species in shelf regions had to be delayed through the entire winter season until May (early spring season) owing to turbidity too great to permit divers to observe bottom fauna. Regular checks confirmed the absence of any significant periods of water clarity beyond the sampling cruise in question. Some typical profiles of attenuation coefficient may be seen in Figures 17 and 18.

# Turbidity distributions and their relation to water column structure and water mass movements

Many authors have reported the accumulation of particles at density interfaces, especially at the top of the pycnocline. Jerlov (1959) attributed

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Fig. 17. Transmissometry traces for summer, fall, and winter, Station 1101, off Clearwater Fla. α refers to attenuation coefficient. Included are the SPM values at 10 m depth.



# Fig. 18. Plot of attenuation coefficients for typical station during Jan-Feb., 1976.

α

this phenomenon to the reduced mixing at that point as well as the increase of water density with depth. Usually, the particles are predominantly organic, and large concentrations are likely to accumulate if the pycnocline starts in the euphotic zone (i.e., phytoplankton). With the establishment of a thermocline, particles are "trapped" and many phytoplankters are unable to migrate across the pycnocline (Bogorov, 1958; Raymont, 1963). This is evident in the sharp zone of increased turbidity at the halocline in Figure 2. To various degrees similar features have been observed elsewhere in the world ocean as indicated by studies in the Gulf of California (Kniefer and Austin, 1974), the Irish Sea (Heathershaw and Simpson, 1974), off Mission Beach, California (Ball and LaFond, 1964), and in the eastern Gulf of Mexico (Carder and Schlemmer, 1973).

A near-bottom nepheloid layer is indicative of turbulence in the bottom water. This turbulence is usually caused either by the shear induced by the bottom on an overlying current, or by the interaction of wave-induced water motion with the bottom. Figure 19 provides an example of a near-bottom nepheloid layer that has been induced at least in part by a bottom current. Notice that the temperature and salinity are homogeneous from the bottom to about five meters above the bottom. This region also contains the major portion of the turbid matter. The SPM values associated with the 24% transmission value near the bottom would correspond to  $1.58/m = \alpha$  or roughly 2.2 mg/l (see Figure 3).

The entire water column was quite turbid, indicating that particles were being mixed all the way to the surface. If this turbidity profile had been the direct result of wind alone, the water column would have been vertically homogeneous in temperature and salinity. Hence we conclude the

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profile was caused by a bottom current, perhaps in combination with wind waves.

Figure 20 provides an example of a well-mixed water column resulting from turbulence which was probably largely wave induced. Here the temperature and salinity values are uniform with depth, and the nephcloid layer extends all the way to the surface. Its turbidity is higher near the bottom since the upward mixing of particles is offset by downward settling. If a steady state existed for the particle concentrations at all depths, then a balance would have been established between the upward flux of particles caused by turbulent diffusion and the downward flux of particles caused by settling. This would have resulted in an exponential decrease in concentration of particles or  $\alpha$  (increase in percent transmission) with distance above the bottom for a given particle size, shape and density. Such a distribution approximates the shape of the transmissivity curve in Figure 20. For small, low-density particles the curve could become nearly uniform with depth, given sufficient turbulence. For larger, denser particles, a rapid decrease in concentration with distance above bottom would be expected.

The particle content of a water column is often indicative of its history. Figure 21 demonstrates a very well-defined, turbid, and well-mixed layer between 185 and 215 m. This layer appears to have been in contact with the bottom at some prior time. The per cent transmission minimum is not an instrumental effect since both down and up traces repeated the pattern.

The net result of such mechanisms as phytoplankton productivity, river plumes, and sediment erosion often results in particulate distribution patterns quite similar to those for salinity and/or temperature. For example, the % T patterns in Figure 22a parallel almost exactly the temperature trends

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Fig. 19. (Upper Figure) T<sup>o</sup>C, S(<sup>o</sup>/oo) and T(%) profiles for a wellmixed water column. S. T data courtesy M. Rinkel.



Fig. 20. (Lower Figure) T<sup>O</sup>C, S(<sup>O</sup>/oo) and T(%) profiles for a partly stratified water column.



Fig. 21. Vertical profile of Transmissivity (%), Salinity and temperature at Station 1311/1310, Fall sampling season. Note anomalous feature at about 200 m depth,

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Fig. 22. Transmissivity and temperature distributions for Station IV. Winter Cruise, 1976. Note time break indicated by zig-zag lines.

shown in Figure 22b. This apparently is the result of warm off-shore being also clear relative to Mississippi Delta water. Other such similarities exist between % T and temperature and/or salinity distributions as illustrated in the next section.

### Hurricane ELOISE and turbidity-water mass relationships

The eye of Hurricane ELOISE hit landfall at 0630 hours, September 23, 1975 just west of Panama City, Florida (Data of Naval Coastal Systems Laboratory). Transect II was traversed three days after the hurricane, with temperature, salinity and transmissometer measurements included in the sampling program. Some of the results are depicted in Figures 23a, 23b, and 23c, showing salinity,  $\sigma_t$  and per cent transmission sections, respectively.

The inshore waters were vertically well-mixed and turbid while extreme stratification occurred at station 1206/1207. A turbid lens of cold, saline water was found on the bottom. This lens was much more dense ( $\Delta \sigma_t = 1.2$ ) than the adjacent (seaward) water. Such dense water would normally be expected to flow downhill; however, if it had sufficient longshore momentum (induced by the Loop Current, for instance), the landward acceleration associated with its vertical vorticity component could cause it to become a contour current. Thus, in seeking deeper waters it would probably flow generally along the shelf, crossing depth contours obliquely. Similar lenses of low temperature and high salinity have been found on the west Florida shelf when hurricanes have not been present (SUSIO, 1975), but such lenses were not nearly so dense nor so isolated from the Loop Current as the one discussed above. Thus the hurricane appears to have enhanced a phenomenon which could be occurring each summer. The cool, saline nature of the water in question suggests that it was a remnant of Loop water which

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Fig. 23. Comparison of transmissivity and physical oceanographic parameters (σ<sub>t</sub> and S) Transect II, Fall season, immediately after Hurricane Eloise, Sept. 1975.

had been upwelled and stranded from the Loop Current, perhaps at some point near the De Soto Canyon. It then may have progressed as a contour current driven by its increased density.

The magnitude of the flow can be estimated to some extent by the fact that the transmission values of the lens had a minimum of about 39% T, corresponding to SPM values of about 1.5 mg/ $\ell$  (Figure 3). For such enrichment in particulate matter to occur in a region not overly populaded by fine sediments suggests that the currents involved may have exceeded one knot (54 cm/sec). Visual evidence of scour and rearrangement of bottom organisms by epifaunal investigations (T. E. Hopkins, oral communication) confirmed this concept. For comparison, nepheloid layers associated with the Guiana Current have been reported by one of us (K. L. C.) to have SPM values of 700  $\mu g/\ell$  resulting from erosion due to 35 - 40 cm/sec currents.

A subsequent time series took place at Station 1207 (Figure 14) where the turbid, dense lens reappeared about 12.5 hr after appearing at Station 1206 - 1207 (Figure 5). This trend is even more apparent in the STD data of M. Rinkel. This indicates that the core of the flow traveled 26 km in 12.5 hr or about 2 km/hr, or 56 cm/sec seaward, which would be only one component of the flow.

Such high water velocities are certainly compatible with the values of suspended particulate matter found in the nepheloid layer. Such currents are clearly capable of rearranging the distribution of fine sediments on the middle to outer shelf regions and transporting fine particles rather large distances.

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# Relationships to hydrocarbon and trace metal distributions in particulate matter, and other environmental implications

The seasonal patterns of turbidity distribution have been commented on earlier. These and regional patterns have critical bearing on interpretation of chemical measurements of particulate properties. During the winter (January - February, 1976) season wind-wave, top-to-bottom mixing was extensive in the inshore stations. Only approaching the outer shelf and slope did clearer water of the type noted closer to shore during summer and fall appear. Moreover, the rapidity with which new turbid distributions developed even within a few days, as demonstrated by reoccupations of stations, indicates that the sediments in question were of relatively local origin, and are probably fine mobile fractions stirred up from the bottom primarily by wave action. Data of Huang (1976 - this report) confirm this concept in that the mineralogy of the inshore suspensates strongly resembles the mineralogy of bottom sediments, and includes significant concentrates of carbonate minerals such as high and low magnesium carbonates and dolomite in given areas. Related observations were made by Hopkins (1976 - this report) in suggesting that the repeated effects of winter storms may exert a stronger erosive effect on the Middle Ground and its organisms than a few yearly events of hurricane force.

The significance of these observations is that during wind-agitated periods in winter, water samples in the middle of the water column probably represent the total water column quite representatively with respect to particulate matter and perhaps phytoplankton, chylorophyll and related measurements as well.

Not only does sampling water column particulates provide a

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representative sampling for the water column, but it offers a rapid integrated sample of fine bottom particulates for local areas during turbulent periods. Based on results from bottom sediment trace metal and particulate trace metal values in MAFLA baseline studies for 1974 - 75 (Presley, 1975; Betzer, 1975) we may presume that significant proportions of particulate trace metals for the winter season originate from the fine, mobile fraction of bottom sediments in inshore waters. It has not yet been possible to study hydrocarbon in particulates in detail for relationship to overall turbidity distribution; however, one would predict a significant relationship to detrital or degraded biogenic hydrocarbons derived from the fine mobile fraction of bottom sediments.

It is unfortunately not possible to estimate the percentage of particulate matter comprised by organic matter quantitatively, since comparison of SPM and POC shows POC values frequently exceeding SPM by considerable margins. Systematic errors in particulate determination virtually always occur on the high side; for this reason, and because the available SPM values agree well with transmissometry - SPM data from other areas, we conclude that the available particulate organic carbon (POC) data must be too high owing to some systematic factor.

For the summer-fall water column the picture is entirely different than the winter, owing to the significant transparency of the water column, and the strong vertical gradients in turbidity distributions. It is expected that at ten meters particulate organic carbon may well predominate over terrigenous or mineral detritus in these waters, and may be a result of long distance transport depending on physical oceanographic, meteoric and

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other conditions. A single sample at ten meters or any other arbitrary depth will not be representative of the water column. However, depending on shelf water depth and complexity of particulate distributions, two or three samples may provide adequate characterization of particulates, if sampling depths are chosen after preliminary examination of turbidity distributions. For example, in Transect I, Season II at least two samples, one in the clear water column and ong in the bottom nepheloid zone would be needed to determine end member composition of the suspensates, and permit estimation of intermediate values if needed. Similar arguments would apply for the Rig Monitoring, where turbidity additions could be complex depending on local currents and turbidity regimes.

The turbidity distributions also have implications for coagulation and removal of oil slicks from the column by coascervation, zooplankton sweeping, and aggregation of detrital particles with adsorbed oil and subsequent sinking to the bottom. Such removal should be two to ten fold greater during winter than during the summer well-stratified periods.

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# Appendix 1

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SAMPLE PERIOD III			

SI)	DEPTH(M)	* TYANS	HETWEEN STNS
M#32	2.00	77.00	· · ·
N 132	4.00	77.00	
M#32	6.00	77.00	
<del>~~**3?~~~</del>			
MA32	10.00	77.50	
4232	12.00	78.00	
1132	14.00	78.09	
· ***35	18.00	59.00	
M#32	<b>20.0</b> 0	65.00	
M#32	55•00	<b>63.00</b>	
	<u> </u>	7 7 0 0	
4 3 2	29.07	75.00	and the second second second second second second second second second second second second second second second
1.35		77.00	
		82.00	
N#32	45 00	81.00	
7436	50.00	81.00	
		77.00	
4.25	50.00	62.00	
Nr32	52.00		
			and a second second second second second second second second second second second second second second second

SID DEPTH(M) & TRANS HETWEEN STNS

-ME37		
M+37	S.00	85.00
1437	4.00	85.00
Mn 37	6.00	85.00
	fr. 1117	
M 4 3.7		
4837	15.00	87.00
M # 37	14.00	H7.00
-Mr.37	10.00	
MW37	18.00	87.00
M#37	20.00	87.00
M#37	- 26.00	86.00
	33.00	
Mw37	40.00	77.00
M#37	42.60	75.00
M#37	45.00	70.00

SID	DEFTH(M)	+ TRANS	HETVEEN STNS
N#35	2.00	54.00	
4435	4.00	54.50	
***35	6.00	54+59	
- <del>- M+35</del>			
<u>35</u>	<u>10.00</u>		······································
M#35	12.60	54.00	
M+ 35	14.00	54.00	
	10.00		
M#35	18.00	54.00	
4*35	50.00	53.50	
M 4 3,5	22.00	54.00	

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M#15	3.00	84.00	• • • • • • •
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<u></u>	12.00		and the second second second second second second second second second second second second second second second
	17.00	85.00	
<u>M#15</u> M#16	20.00	85.00	
Mals	30.00	85.00	
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	<u>50.00</u> 55.00	90.50	
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MW15 MW15	70,00	92.00	
M+15	75.00	94.00	
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<del>Mikfrig</del> Miafria	2 00	77.00	<u>1.304</u>
<b>WW0</b> P	4.00	73.00	
<u>M¥03</u>	<u> </u>	78.00	
		· = 4 • 0.0	
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Mir () -) Mir () -)	18.00	81.00	
MAGA	22.00	81.00	
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	<u></u>	81.00	
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	<del></del>		
4810	4.00	84.00	
M#10	5.00	87.00	
Ma10	10.07		
4-10	12.00	40.00	
	<u> </u>	<u>~</u>	
M#20	2.00	82.50	
M#20	4.00	82.50	
<u> </u>			
M 4 2 ()	12.00		
·····	14.00°	······································	
4420	18.00	23.00	
MW20	20.00	87.00	
A	<u> </u>		
1420 ···	30.00	. <u>d</u> 2• <u>2</u> 2	
	40.00	85.00	
M*50	55.00	79.00	
(15 N M	00.00	79.50	
<u>My20</u>	/5.00	85.00	
(15WN .	50.00	45.50	
N" (V ( 1) "	22.00	90.00	······································

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### DMSAG FILE 0221 OFF-STATION TRANSMISSOMETRY DATA SAMPLE PERIOD III

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S I D	DEPTH(M)	× 1-×ANS	BETHEEN STNS
MW12 MW12 MW12 MW12	2.00 4.00 5.00	87.00 87.00 87.00 87.00 87.00	1310-1311
4+12 M+12 M+12	<u> </u>	88.00 54.00 85.00 55.00	· · · · · · · · · · · · · · · · · · ·
N#12 N#12 N#12	15.00 19.00 20.00 25.00	89.00 89.00 89.00 89.00	
M+12 M+12	30.00 35.00 40.00 45.00	90.00 90.00 91.00 91.00	
51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m 51 m m	56.99 55.99 50.00 57.09	91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00     91.00	
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## OFF-STATION FRANSMISSUMFIRY DATA SAMPLE FERIOD III

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	10.00 12.00 14.00	75.50 75.00 79.00 01.50	
M#13 M#13	19.00 20.00 22.00	84.00 85.00 87.50	
	26.00 28.00 30.00	87.00 87.00 87.50 85.00	
M#18 M#18 M#18	34.00 36.00 37.00	77.00 75.50 75.00	

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## DMSAG FILE 0221 OFF-STATION FRANSMISSOMETRY DATA SAMPLE PERIOD III

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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	M#22	4.00	92.00	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	M 425	5.00	42.00	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	4422	8.00	81.00	
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mw24	4.00	82.00	
$w_{2}^{2}$ $4,00$ $54,00$ $4,24$ $19,03$ $44,00$ $4,24$ $12,00$ $85,00$ $4,24$ $12,00$ $84,00$ $4,24$ $12,00$ $84,00$ $4,24$ $12,00$ $83,00$ $4,24$ $12,00$ $83,00$ $4,24$ $22,00$ $42,00$ $4,24$ $22,00$ $42,00$ $4,24$ $22,00$ $42,00$ $4,24$ $22,00$ $42,00$ $4,24$ $22,00$ $42,00$ $4,25$ $2,00$ $74,00$ $4,25$ $2,00$ $74,00$ $4,25$ $4,00$ $74,00$ $4,25$ $4,00$ $74,00$ $4,25$ $4,00$ $74,00$ $4,25$ $12,00$ $73,00$ $4,25$ $12,00$ $73,00$ $4,25$ $12,00$ $73,00$ $4,25$ $20,00$ $52,00$ $4,25$ $20,00$ $52,00$ $4,25$ $23,00$ $55,00$ $4,25$	MAZA	6.00	85.00	
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	33124	13 <b>11.</b> 00	<del>5</del> 5.00	
4426 33.00 65.00				
	4125	33.00	65.00	

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H216 H216 H216	2.00	93.00 93.00	
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	10.00 11.00	47.10 47.10	
		97.00 97.00 	
	17.00 177.07 		
4515 H515	25.06	47.04 47.00 	
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4215 4215 4215	39,00 41,00 43,00	97.00 93.00 92.00	
<u>====15</u>	. 47. 30		

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DMSAG FILE 0221 OFF-STATION TRANSMISSOMETRY DATA SAMPLE FERIOD IT -----

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## Appendix 2

% Trans	-alpha	% Trans	-alpha	% Trans	-alpha
100	0	59	.528	19	1.661
99	.010	58	• 545	18	1.715
98	.020	57	.562	17	1.772
<b>7</b> 7	.030	56	.580	16	1.832
96	.041	55	.598	15	1.897
95	.050	54	.616	14	1.966
94	.062	53	.635	13	2.040
93	.073	52	.635	12	2.120
92	.083	51	.673	11	2.207
91	.094	50	•693	10	2.302
90	.105	49	.713	9	2.408
89	.116	48	.734	8	2.526
88	.128	47	.755	7	2.657
87	.139	46	.776	6	2.813
86	.150	45	.798	5	2.996
85	.162	44	.821	4	3.219
84	.174	43	.843	3	3.506
83	.186	42	.868	2	3.912
82	.198	41	.892	1	4.605
81	.211	. 40	.916		
80	• 223	39	.942		
79	• 236	38	.968		
78	• 248	37	•994		
77	.261	36	1.022		
76	• 274	35	1.050		
75	<b>. 28</b> 8	34	1.078		
74	.301	33	1.109		
73	.315	32	1.139		
72	• 328	31	1.171		
71	.342	30	1.204		
70	.357	29	1.238		
69	.371	28	1.272		
68	.386	27	1.309		
67	.400	26	1.347		
66	.415	25	1.386		
65	.431	24	1.427		
64	.446	23	1.470		
63	.462	22	1.514		
62	.478	21	1.561		
61	<b>.</b> 49 4	20	1.609		
60	.511				
# ANALYSIS OF ZOOPLANKTON FROM THE MAFLA OCS AREA

Frank J. Maturo

See John W. Caldwell

# MEIOFAUNA OF THE MAFLA AREA

Frank J. Maturo

See Michael R. Crezee

# BLM MAFLA DEMERSAL FISH SURVEY 1975-1976

Garry F. Mayer

See Stephen A. Bortone

# BLM MAFLA DEMERSAL FISH SURVEY 1975-1976

Garry F. Mayer

See Stephen A. Bortone

FINAL SUMMARY REPORT X-RADIOGRAPH AND RELIEF PEEL FINDINGS

University of South Florida, Department of Geology

Principal Investigator: Taylor V. Mayou

Associate Investigator Scott M. Huse

### INTRODUCTION

This is the third and final quarterly progress report describing work accomplished during the preceding quarter for the sediment studies portion of the environmental monitoring of the MAFLA lease area. This particular report is organized into three sections. The first section consists of a table which summarized all samples taken during the three cruises. Section two includes specific descriptions of all samples collected during sampling periods, I, II, and III, with regard to physical structures, biogenic structures, and degree of bioturbation (Table 1). Numerous stations were sampled twice during cruise III and, in these instances, it was the second set of data that was evaluated and incorporated in this report. Descriptions are based upon data provided by X-radiographs and relief peels. Section three is a concise final summary of the significance of-these findings.

# Table 1. Bioturbation Index Classification

•

Number	% of Bioturbation	Description
0	0%	No observable burrowing
1	1-4%	Rare sporadic burrows with little bioturbation
2	5-30%	Burrows common, with up to 1/3 of core bioturbated
3	31-60%	Abundant burrowing, up to 2/3 of core bioturbated
4	61-90%	Burrows very abundant with few primary layers visible
5	91-99%	Almost complete bioturbation, only occasional primary layers visible
6	100%	No observable primary layers

.

PART	Ι

Station Number

Samples Taken

•	Cruise 1	Cruise 2	Cruise 3
2101	*	*	*
2102	*	*	*
2102		*	*
2105	*	*	*
2104	*	*	*
2105	ż	*	*
2100	*	*	*
2207	*	*	*
2200	*	*	*
2209		*	*
2210	*	*	*
2211	*	*	*
2212	*	*	**
2010	~		*
2314		*	*
2315	*	*	***
2310	^ *	*	**
2317	· · · · · · · · · · · · · · · · · · ·	*	**
2310		*	*
2419	· •		**
2420	*	*	*
2421	^	*	*
2422	*	*	**
2423	*	*	*
2424	*	*	**
2425	* *	*	**
2420	*	*	**
2427	*	*	**
2520	*	*	**
2529	*	*	**
2530	*	*	**
2001	*	*	**
2002	4- 		* *
2000		*	**
2234	*	*	**
2333	*	*	*
2000	т. 	*	*
2037	^	*	*
2030	*		*
2639	*	۲. 2	*
2040	<del>بر</del> ب	÷	~ ~
2641	т Х	ت ۲	× J.
2642	*	۲ ۲	× بد
2643	×	× 	-L -
2644	*	×	× *
2645	*	*	*

### PART II

-4-

Cruise I 2101-К No physical structures; bioturbation index classification (B.I.C.) #6. 2102-К No physical structures; no distinctive biogenic structures; B.I.C. #6. 2104-K No physical structures; 1 lined burrow (probably callinasa) in the lower left portion of the peel; BIC #6. 2105-K No physical structures; 1 thickly lined arthropod burrow; BIC #6. 2106-K No physical structures; BIC #6. 2207-K No physical structures; numerous Polychaete burrows throughout; BIC #6. 2208-K Faint horizontal shell layering; some small Polychaete burrows; BIC 4-5. 2209-K Shell concentration layer at a depth of 19 cm; no distinctive biogenic structures; BIC 5-6. 2211-К No physical structures; BIC #6. 2212-K Shell concentration layer at a depth of 3 cm; possible heart urchin traces and small Polychaete burrows; BIC #5. 2313-K No physical structures; BIC #6. 2316-K No physical structures; BIC #6. 2317-К No physical structures; BIC #6. 2318-K No physical structures; BIC #6. 2419-к No physical structures; 1 long Polychaete burrow; BIC #6. 2420-K Faint horizontal sandy laminations in the upper 1 - 2 cm of sediment; a few small polychaete burrows; BiC #5-6. 2421-K

No physical structures: BIC #6.

# 2423-K No physical structures; BIC #6. 2424-K An apparent shell concentration at a depth of 12 cm; no distinctive biogenic structures; BIC #5. 2425-K Shell fragment concentration at 12 cm depth with gradational boundaries; no distinctive biogenic structures; BIC #5-6. 2526-K Upper 15 cm consists of relatively shelly, coarse, sediment which is underlain by a much finer grained muddy sand; the boundary of these units is irregular and both beds intermingle at the contact zone; no biogenic structures; BIC #5. 2427-K No physical structures; BIC #6. 2528-K No physical structures; BIC #6. 2529-К No physical structures; BIC #6. 2530-K Some cross-bedded, coarse, carbonate material; no distinctive biogenic structures; BIC #4. 2531-K No physical structures; 1 small Polychaete burrow; BIC #6. 2532-K At 12-22 cm depth, partially bioturbated horizontal mud laminations are evident; several worm burrows; BIC #3. 2533-K No physical structures; BIC #6. 2535-K No physical structures; BIC #6. 2536-K No physical structures; 2 small polychaete burrows, top left; BIC #6. 2637-К No physical structures; numerous small worm burrows near the sediment surface; BIC #6. 2638-K Faint silt laminations truncated by burrowing activity; #5. 2639-K

No physical structures; BIC #6.

2640-K At 10-14 cm depth, a wedge-shaped bed occurs which has a much higher shell content than the sediment above and below; no distinctive biogenic structures; BIC #4. 2641-K No physical structures; 1 small polychaete burrow, BIC #6. 2642-K Faint heavy mineral laminations; no distinctive biogenic structures; BIC #5. 2643-K No physical structures; BIC #6. 2644-K No physical structures; BIC #6. 2645-K No physical structures; parts of two callinasa burrows are evident; BIC #6. Cruise II 2101-К No physical structures; some Polychaete burrows at the sediment surface; BIC #6. 2102-К No physical structures; BIC #6. 2103-К No physical structures; BIC #6. 2104-K No physical structures; BIC #6. 2105-K No physical structures; 1 thickly lined arthropod burrow; BIC #6. 2106-K No physical structures; BIC #6. 2207-K No physical structures; several small polychaete burrows; BIC #6. 2208-к Several horizontal shell layers; some small polychaete burrows; BIC #4-5. 2209-К No physical structures; 1 living pelecypos at 9 cm depth with siphons partially visible; BIC #6. 2210-К No physical structures; a few small polychaete burrows; BIC #6. 2211-К

No physical structures; BIC #6.

-6-

2212-K Wavy-looking, silty laminations at a depth of 25 cm; no distinctive biogenic structures; BIC #4. 2313-К No physical structures; some small, thin polychaete burrows; BIC #6. Concentration of coarse shell hash material at 15 cm depth; BIC #6. No physical structures; no biogenic structures; BIC #6; ship log note - 2316-K 2317-К No physical structures; BIC #6; 2317-K (II) is finer-grained, less shelly, and Shell concentration at 3 cm depth; part of 1 burrow is evident and is attri-No physical structures; 1 long polychaete burrow; BIC #6. 2421-К No physical structures; 1 small worm tube in the lower left portion of the peel; 2423-K No physical structures; 1 small polychaete burrow; BIC #6. 2424-K No physical structures; BIC #6; 2424-K (II) is coarser than 2424-K (I) and 2425-К Upper 3. cm is slightly coarser than the underlying sediment with a fairly distinct 2426-к No physical structures; 2 small worm tubes near the center of the peel and 2427-K At a depth of 29 cm, faint horizontal laminations are evident; no distinctive

### 2315-K

### 2316-K

(II) was significantly different from the other nine box core samples taken at that station in that it was much more fine-grained, better sorted, and less shelly; This sample is not as shelly as 2316-K (I) and also is finer grained.

better sorted than 2317-K (I).

### 2318-K

buted to a siphunculid which was found in the peel; BIC #5-6.

### 2419-K

No physical structures; some small polychaete burrows near the sediment surface; BIC #6.

### 2422-K

BIC #6.

contains more shell material.

boundary; 1 burrow which has been filled in with shell material is evident; BIC #5-6.

2 large callinasa burrows at the bottom of the peel, 19 cm depth; BIC #6; 2426-K (II) is slightly coarser than 2426-K (I).

biogenic structures; BIC #5.

2528-K No physical structures; BIC #6. 2529-K No physical structures; BIC #6. `2530-к Some cross-bedded coarse carbonate material; no distinctive biogenic structures; BIC #4. 2531-К Faint horizontal layering with gradational boundaries; no biogenic structures; BIC #5. 2532-K No physical structures; BIC #6; 2532-K (II) resembles the upper 12 cm of 2532-K (I) but does not exhibit the partially bioturbated horizontal laminae that 2532-K (I) has. 2534-K No physical structures; BIC #6. 2535-K No physical structures; BIC #6. 2536-К No physical structures; BIC #6. 2637-K No physical structures; a few faint worm burrows; BIC \$6. 2638-K No physical structures; BIC #6. 2639-K No physical structures; BIC #6; 2639-K (I) contains coarser and more abundant shell material than 2639-K (II). 2640-K Several extremels thin cross-bedded laminae in the upper 5 cm; 1 very small worm tube at 14 cm depth; BIC #3-4; 2640-K (II) is considerably finer-grained than 2640-K (I) and contains much less shell hash. 2641-K An inclined ("cross-bedded") thin shell concentration occurs near the sediment surface; 1 large worm tube at 18 cm depth; BIC #5; 2641-K (II) contains much more shell material than 2641-K (I) and is coarser grained. 2642-к A near surface heavy mineral lamination; no biogenic structures; BIC #5. 2643-K No physical structures; BIC #6. 2644-K No physical structures; BIC #6.

-8-

2645-K No physical structures; BIC #6. Cruise III 2101-К No physical structures; one well developed, long, shell-lined, polychaete burrow; BIC #6. 2102-К No physical structures; BIC #6. 2103-К No physical structures; BIC #6. 2104-К No physical structures; BIC #6. 2105-K No physical structures; BIC #6. 2106-К No physical structures; BIC #6. 2207-К No physical structures; BIC #6. 2208-к No physical structures; part of a polychaete burrow at a depth of 10 cm; BIC #6. 2209-К No physical structures; BIC #6. 2210-К No physical structures; abundant bivalues; BIC #6. 2211-К No physical structures; BIC #6. 2212-К No physical structures; BIC #6. 2313-KR No physical structures; BIC #6. 2314-KR No physical structures; BIC #6. 2315-K No physical structures; BIC #6. 2316-KR No physical structures; BIC #6. 2317-KR No physical structures; BIC #6.

-9-

2318-KR Upper 8 cm is cross-bedded and underlain by 12 cm of totally bioturbated sediment; no distinctive biogenic structues; BIC 0 upper, lower BIC #6. 2419-K No physical structures; BIC #6. 2420-KR No physical structures; BIC #6. 2421-KR No physical structures; BIC #6. 2422-K Upper 6 cm are coarsely cross-laminated; underlain by bioturbated sediments; upper BIC 0-1, below BIC 6. 2423-KR No physical structures; BIC #6. 2424-K No physical structures; BIC #6. 2425-KR No physical structures; BIC #6. 2426-KR No physical structures; BIC #6. 2427-KR No Physical structures; BIC #6. 2528-KR No physical structures; BIC #6. 2529-KR No physical structures; BIC #6. 2530-KR No physical structures; BIC #6. 2532-KR No physical structures; BIC #6. 2533-KR No physical structures; BIC #6. 2534-к No physical structures; BIC #6. 2535-KR No physical structures; biogenic structures possible heart urchin traces; BIC #6. 2637-к Very faint, nearly totally bioturbated horizontal mud laminations; numerous burrow ; BIC #5.

-10-

<u>2638-K</u> No physical structures; abundant burrows; BIC #6.

<u>2639-K</u> No physical structures; BIC #6.

<u>2640-K</u> No physical structures; BIC #6.

 $\frac{2641-K}{No physical structures; BIC #6.$ 

 $\frac{2642-K}{No physical structures; BIC #6.$ 

<u>2643-K</u> No physical structures; BIC #6.

<u>2644-K</u> No physical structures; BIC #6.

<u>2645-K</u> No physical structures; no biogenic structures; BIC #6. .

### PART III

### FINAL SUMMARY REPORT

Major objectives of this portion of the <u>MAFLA</u> study were to identify and describe animal-sediment relationships and effect of benchic organisms on the sedimentary record. A total of 142 relief peels and 142 corresponding X-radiographs, collected during three sampling periods, has been described and examined for physical and biogenic sedimentary structures.

Analysis of relief peels and X-radiographs indicate a general lack of physically produced sedimentary structures. However, a few samples did exhibit physical sedimentary structures in the upper portion of the cores. For example, sample 2532-K (I) contained horizontal mud laminations and sample 2318-KR (III) showed distinctive cross-bedding. Lack of preserved physical sedimentary structures is attributed to the combined effects of a slow sediment accumulation rate and bioturbation infaunal organisms, i.e., polychaetes, bivalves, gastropods, ophiuroides, etc. Most commonly, samples were represented by a bioturbation index number of 6 (Table 1), that is, no observable primary layers. Samples which have been 100% bioturbated (#6) are commonly churned to such an extent that distinctive biogenic structures (Lebensspuren) are not visible. Isolated Lebensspuren were observed in a few samples in which the bioturbation index value was less than 6 (5-1). For example, the X-radiograph for station 2638-K (III) exhibits abundant burrows, some of which were probably produced by Arthropods along with small numerous, well-defined, polychaete burrows. Overall, the study area can be

characterized by a bioturbation index number of 6 regardless of depth, sediment type, etc. This statement is supported by Figures 1-2 and 3, which are maps indicating the distribution of bioturbation index numbers representing samples collected during the three cruises. Figures 4-9 contain photographs of the most representative relief peels and X-radiographs of stations along the 6 transects and also clearly support these findings.



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Figure I. Boxcore Cruise I, June-July, 1975

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Figure 2. Boxcore Cruise 2, September - October, 1975.



Figure 3. Boxcore Cruise 3, January – February, 1976.

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BLM TRANSECT I

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-17-

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Epoxy Relief Peel Station 2105

Figure 4b. Radiographs and Epoxy Relief Peels from Stations 2106 and 2105.



Epoxy Relief Peel Station 2103

Figure 4c. Radiographs and Epoxy Relief Peels from Stations 2104 and 2103.



Epoxy Relief Peel Station 2101

Figure 4d. Radiographs and Epoxy Relief Peels from Stations 2102 and 2101.

# BLM TRANSECT 2



-21-



Epoxy Relief Peel Station 2211

Figure 5b. Radiographs and Epoxy Relief Peels from Stations 2212 and 2211.



Figure 5c. Radiographs and Epoxy Relief Peels from Stations 2210 and 2209.



Radiograph Station 2207

Epoxy Relief Peel Station 2207

Figure 5d. Radiographs and Epoxy Relief Peels from Stations 2208 and 2207.



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Radiograph Station 2317

Epoxy Relief Peel Station 2317

Figure 6b. Radiographs and Epoxy Relief Peels from Stations 2318 and 2317.



Figure 6c. Radiograph and Epoxy Relief Peels from Station 2316.



Radiograph Station 2314

Epoxy Relief Peel Station 2314

Figure 6d. Radiographs and Epoxy Relief Peels from Stations 2315 and 2314.



Radiograph Station 2313

Epoxy Relief Peel Station 2313

Figure 6f. Fadiograph and Epoxy Relief Peel from Station 2313.





Epoxy Relief Peel Station 2426

Radiograph Station 2426

Figure 7b. Radiographs and Epoxy Relief Peels from Stations 2427 and 2426.



Epoxy Relief Peel Station 2424

Figure 7c. Radiographs and Epoxy Relief Peels from Stations 2425 and 2424.

Radiograph Station 2424


Epoxy Relief Peel Station 2422

Figure 7d. Radiographs and Epoxy Relief Peels from Stations 2423 and 2422.



Epoxy Relief Peel Station 2420

Figure 7e. Radiographs and Epoxy Relief Peels from Stations 2421 and 2420.



Epoxy Relief Peel Station 2419

Figure 7f. Radiograph and Epoxy Relief Peel from Station 2419.





Epoxy Relief Peel Station 2535

Figure 8b. Radiographs and Epoxy Relief Peels from Stations 2536 and 2535.



Epoxy Relief Peel Station 2533

Figure 8c. Radiographs and Epoxy Relief Peels from Stations 2534 and 2533.



Figure 8d. Radiograph and Epoxy Relief Peels from Stations 2532 and 2531.



Epoxy Relief Peel Station 2529

Figure 8e. Radiographs and Epoxy Relief Peels from Stations 2530 and 2529.



Radiograph Station 2528

Epoxy Relief Peel Station 2528

Figure 8f. Radiograph and Epoxy Relief Peel from Station 2528.

# BLM TRANSECT 6



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Geophysical Profile of Transect 6 with Station Locations plotted against Depth and Distance. Rectangular Figures represents percent Bioturbation at Stations during three sampling periods. 40



Figure 9b. Radiographs and Epoxy Relief Peels from Stations 2638 and 2637.



Epoxy Relief Peel Station 2640

Figure 9c. Radiographs and Epoxy Relief Peels from Stations 2638 and 2637.



Epoxy Relief Peel Station 2642

Figure 9d. Radiographs and Epoxy Relief Peels from Stations 2641 and 2642.



Epoxy Relief Peel Station 2644

Figure 9e. Radiographs and Epoxy Relief Peels from Stations 2643 and 2644.



Radiograph Station 2645

Epoxy Relief Peel Station 2645

Figure 9f. Radiograph and Epoxy Relief Peel from Station 2645.

HYDROCARBONS OF BENTHIC MACROFAUNA

University of Michigan, Department of Atmospheric and Oceanic Science

Principal Investigator: Philip A. Meyers

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# ABSTRACT

A total of 261 samples of benthic macroepifauna have had their hydrocarbon compositions determined. The organisms were collected over a tenmonth period from the MAFLA area of the Gulf of Mexico and over a fourmonth period off the Texas coast. A good representation of indigenous hydrocarbon contents of benthic populations of these areas has been obtained. Little or no evidence of petroleum contamination was detected, although the usefulness of hydrocarbon analyses in identifying such contamination is clearly demonstrated by certain of these samples.

#### INTRODUCTION

This investigation is intended to serve as a continuation of the accumulation of basic knowledge of hydrocarbon contents of benthic macroepifauna of the MAFLA-OCS area initiated under BLM Contract 08550-CT4-11 and extended by Contract 08550-CT5.43. The studies performed under these and the present contracts represent analysis of samples collected over a two-year period between May 1974 and March 1976, and provide an impressive data base upon which to build future investigations. In addition, the impact of drilling operations on offshore macrofauna was directly studied as a part of the 1975-76 contract.

Most published reports of hydrocarbon compositions of benthic macrofauna compare organisms living in areas believed to be polluted by petroleum hydrocarbons to similar organisms found in areas assumed free of pollution. Such studies have been reported by Blumer, <u>et al</u>. (1970) for the scallop <u>Aequipecten</u> <u>irradians</u>, by Farrington and Quinn (1973) for the clam <u>Mercenaria mercenaria</u>, by Stegeman and Teal (1973) for the oyster <u>Crassostrea virginica</u>, by Clark, <u>et al</u>. (1974) for the mussel <u>Mytilus edulis</u> and the oyster <u>Ostrea lurida</u>, and by Fossato and Siviero (1974) for the mussel <u>Mytilus galloprovincialis</u>. Burns and Teal (1973) report hydrocarbon compositions of the pelagic crab <u>Portunus sayi</u> and the pipefish <u>Syngnathus pelagicus</u> collected in the Sargasso Sea. Although this region is not obviously polluted, these organisms appear to have accumulated petroleum hydrocarbons.

Few published reports of hydrocarbon analyses of benthos from unpolluted areas are available. The alkane hydrocarbon contents of nine hard corals and one soft coral collected from locations in the Gulf of Mexico are presented by Pasby (1965). Additional analyses of benthic macrofauna are reported by Koons, et al. (1965), who list carbon preference indices

for the alkane content of eight Poriferans and three Cnidarians. The n-alkane composition of only one organism, the sponge <u>Terpios zeteki</u>, is given by these authors.

As part of BLM Contract 08550-CT4-11, the concentrations of total aliphatic and total unsaturated hydrocarbons were determined for 44 organisms collected from the MAFLA-OCS area. In 1975, an additional 24 organisms collected in 1974 were analyzed under contract 08550-CT5-43. Besides total concentrations, individual hydrocarbon components were identified and quantitated in the latter study. These data are reported by Meyers (1976). The present investigation utilized the same procedures as Meyers (1976). Thus, comparisons of data are possible.

#### PROCEDURES

The overall analytical procedure employed in this investigation is the same as that which was applied to hydrocarbon analyses of benthic macrofauna under BLM contract 08550-CT5-43 for MAFLA outer continental shelf monitoring. The hydrocarbon extraction and isolation portions of this procedure are basically unchanged from those used in contract 08550-CT4-11, although the initial phase is different and the final analytical steps and data workup are considerably more sophisticated.

The first step of the present scheme involves obtaining a dry weight of sample tissue; the 1974 procedure used a wet weight. Samples are thawed and then dried at 60°C to a constant weight. This usually requires from 20 to 60 hours. The dried organism is reduced to a granular powder with a mortar and pestle and/or a Virtis homogenizer. The homogenized powder is weighed and then sonicated for ten minutes at 60% power using an Artek Model 300 Dismembrator. The liquid used during sonication is the saponification mixture of 0.5 N methanolic KOH/benzene, 50/50.

A modification of this first step is necessary for hard coral samples because of the large amount of carbonate skeleton present. Thawed samples are broken into pieces with a hammer and chisel and decalcified with 3 N HCl. Coral tissue is isolated from the dissolved skeleton by filtration using preweighed filters which are then dried at 60°C and weighed to obtain the weight of dry tissue. The filters plus the tissue are inserted into a flask for the sonication and saponification steps.

Samples are saponified in order to separate non-saponifiable lipids from total lipids and from total tissue. Refluxing for one hour in a mixture of 0.5 N methanolic KOH/benzene, 50/50, forms the potassium salts of

saponifiable lipids and extracts the non-saponifiable lipids from the samples. The tissue residue is removed by filtration, and the liquid phase is transferred to a separatory funnel. Distilled water is added to partition the saponifiable and non-saponifiable lipids between the aqueous and organic phases, respectively. The organic phase is isolated, and the basic aqueous phase extracted twice with petroleum ether. These extracts are combined with the original organic phase and washed once with dilute aqueous HCl to remove trace amounts of non-lipid materials. The organic phase is concentrated on a rotary evaporator at 30°C, and the residue transferred to a pear-shaped flask. One gram of 5% deactivated alumina is added, and the solvents evaporated. The non-saponifiable lipids are now adsorbed onto the alumina and ready for column chromatography. Resaponification and re-extraction of the tissue residue indicates that this procedure is 85-95% efficient.

The classes of lipids comprising the non-saponifiable fraction are separated by chromatography on a silica gel/alumina column. The column utilized in this study consists of two g 5% deactivated silica gel overlaid by two g 5% deactivated alumina in a nine mm I. D. column. The column is packed in benzene which is flushed out with multiple rinses of pertroleum ether. This also effectively cleans the column packing material. Nonsaponifiable lipids, adsorbed on one g alumina, are placed on the top of this column. Normal, branched, and cyclic alkanes and mono-alkanes are eluted from the column with 10 ml petroleum ether. Polyunsaturated hydrocarbons, aromatic hydrocarbons, and methyl ketones are eluted with 15 ml benzene. Fatty alcohols are eluted with 25 ml benzene/methanol, 90/10. Chromatography of test solutions showed that separation is quantitative and complete (Meyers, 1976). Solvents are evaporated and the residue stored at 0°C for further analysis.

Gas-liquid chromatography is performed on the petroleum ether and benzene fractions as specified in contract 08550-CT5-30. Resolution of the various components comprising each fraction is achieved using non-polar and polar columns. The non-polar column type is a 2.1 mm I. D. x 4 m 3% OV-101 on 80-100 mesh Chromosorb WHP column. The polar column is 2.1 mm I. D. x 2.5 m 10% SP-1000 on 80-100 mesh Supelcort column. Both columns are temperature-programmed. The OV-101 column programming rate is 4°C per minute from 150 to 325°C, holding 325°C for ten minutes, with a flow rate of 15 ml N<sub>2</sub>/min. The SP-1000 column (equivalent to FFAP) is operated at 8°C/min from 150 to 250°C, holding the upper limit for 30 min. Columns are operated in dual differential mode to minimize baseline shifting due to column bleed. The instruments used in this study are a Hewlett-Packard 5710A Gas Chromatograph equipped with a Hewlett-Packard 3380A Integrator and a Hewlett-Packard 5830A Gas Chromatograph. Both instruments use hydrogen-air flame ionization detectors.

The overall best column for separation of petroleum-type hydrocarbons appears to be the packed OV-101 column (Meyers, 1976). It has good resolution of isoprenoids and normal alkanes and also has more theoretical plates than the FFAP columns. For these reasons, most of the analytical data in this report are derived from chromatograms obtained from packed OV-101 columns. The isoprenoid ratios are obtained from FFAP chromatograms.

Both of the gas chromatograph instruments present an electronically integrated printout of each sample giving retention time in minutes, integrator counts, and area percent for every peak in that sample. These data were punched onto IBM cards and entered into the University of Michigan Amdahl 470V/6 computer. A program was designed for the present study to convert the retention time and integrator count data into quantitative data

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for each hydrocarbon peak. Quantitation was effected using an internal quantitative standard of n-docosane added to the petroleum ether and benzene fractions after column chromatography and prior to gas chromatography. The computer program utilized the peak area of this standard, the dry weight of the organism, and the peak areas from the chromatograms to calculate the quantitative data and ratios required by contract 08550-CT5-30.

In order to permit broader application of data generated by this investigation and to detect and correct weaknesses in the analysis scheme, this laboratory participated in a Hydrocarbon Analysis Intercomparison Study. Other laboratories participating were at Florida State University and at Gulf Coast Research Laboratory. The results of the Intercomparison Study will be reported separately.

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#### RESULTS

A total of 261 analyses of hydrocarbon compositions of benthic macroepifauna were performed during 1975-76 under contract 08550.CT5-30. In the Baseline Monitoring portion of the contract, 183 samples were analyzed. An additional 78 samples were obtained from the Rig Monitoring study.

### Baseline Monitoring Samples

Samples were collected from eight dive stations and 18 dredge/trawl stations during three sampling periods. The collection periods were June-July 1975, September-October 1975, and February-March 1976. Of the organisms collected during these periods, 55 were analyzed from the first period, 64 from the second, and 64 from the third and final period. Lists of samples from each sampling period are presented in Appendix I. Representatives of many of the species in these lists had also been collected and analyzed during the earlier study in the MAFLA area.

In Appendix II, tabulated data selected from computer printouts of hydrocarbon analyses of fauna from the three sampling periods are presented. Data from biologically related organisms are grouped together in each period. Certain aliphatic hydrocarbons in these samples could be identified by retention indices, but no unsaturated hydrocarbons were identified.

For the June-July period, the carbon preference index (CPI), or oddto-even ratio of n-alkanes, for all 55 samples ranges from 0.14 to 19.12 and averages 1.93±2.46. For the seven samples of Porifera, the mean is 1.66±1.06, and for the 14 Cnidaria it is 2.68±4.81. The 14 Echinodermata average 1.69±0.64, and the three Mollusca 1.59±0.51. The mean CPI for the 17 Arthropoda is 2.12±1.81. All the animals contained pristane, and over 90% contained phytane. The pristane/phytane ratio was usually between

one and three, although it reached a high of 247 in a squid (Loligo pealeii) whose aliphatic hydrocarbon content was more than 50% pristane. The ratio of total branched hydrocarbons to total n-alkanes was commonly between one and three, indicating that n-alkanes did not dominate hydrocarbon compositions. Concentrations of aliphatic hydrocarbons were usually between three and 10  $\mu$ g hydrocarbon per gram dry weight of organism. Unsaturated hydrocarbon concentrations were ten to 100 times larger.

The CPI of the 64 samples collected in the September-October period averages 2.98±3.15. The 16 Porifera have an average CPI of  $3.47\pm3.03$ , while the average of the ten Cnidaria is  $2.33\pm1.27$ . For the 13 samples of Echinodermata,  $2.64\pm2.54$  is the mean, and it is  $1.98\pm1.19$  for the six Mollusca. The mean of the 18 Arthropoda is  $3.43\pm4.50$ . Only 85% of the animals contained pristane, and slightly less than 70% contained phytane. Squid again had high pristane levels. As in the first period, n-alkanes did not dominate the aliphatic hydrocarbon fractions of these organisms. Branched-to-n-alkane ratios generally were between two and six. Total aliphatic hydrocarbon concentrations were usually between two and 50 µg/g dry weight, and total unsaturates ten to 100 times higher.

The CPI value of the 64 samples collected in the February-March period ranges from 0.18 to 30.97, with a mean of 4.84. For the 14 samples of Porifera, the mean is 7.01±8.06. For the 22 Cnidaria, it is 3.09±6.48. The 18 samples of echinoderms average 3.88, with a standard deviation of 4.20. The seven molluscs average 9.92±8.16, and the three arthropods 1.45±0.62. All but two of these samples contained pristane; this was usually at concentrations lower than those of n-heptadecane. In 24 of the samples having pristane, no phytane was present. Of these related isoprenoid hydrocarbons, pristane was usually dominant. The pristane/phytane

ratio was normally between one and three, although it reached a high of 39.4 in a sample of the squid <u>Loligo pealeii</u>. The hydrocarbon compositions of most of these animals was not dominated by n-alkanes; the ratio of saturated branched hydrocarbons to n-alkanes was usually between two to 'five. Total saturated hydrocarbon concentrations ranged from 0.2 to 200.8 micrograms per gram of dry tissue, and concentrations of unsaturated hydrocarbons were usually one to two orders of magnitude greater.

# Rig Monitoring Samples

Organisms were collected in the vicinity of a drilling platform located offshore of Mustang Island, Texas. Collection was done in December 1975 before the platform was present, in January 1976 during drilling operations, and in March 1976 after the platform had been moved away. A sampling grid consisting of four transects 90° apart and originating at the drilling site was employed. Samples were collected by trawl at distances of 100 m, 500 m, and 1000 m from the drilling site. Dive sampling was impossible because of extremely poor visibility close to the bottom.

At least two samples were collected at each of the twelve stations in the grid during each of the three sampling periods. During the March sampling, extra samples were collected at the four stations located 100 m from the drilling site. A total of 80 samples were obtained from the entire survey; 78 of these have been analyzed. They are distributed as 24 from each of the first two periods and 30 from the third period. Listings of samples analyzed for each of the three periods are presented in Appendix III.

Results of the hydrocarbon analyses of these samples are summarized in Appendix IV in tabulations similar to those of the MAFLA baseline monitoring samples. The odd-even preference of n-alkanes in the 23

arthropod samples collected in December averages  $1.77 \pm 0.95$ . In the January samples, this ratio is  $1.90 \pm 2.03$  for the 18 arthropods collected, and it is  $1.90 \pm 1.01$  for the 6 echinoderms. All of the 30 samples collected in March were arthropods. The odd-even preference for these samples was  $4.33 \pm 4.90$ . No systematic change was observed in the weight of total hydrocarbons in these animals over the three collection periods. Total saturated hydrocarbons ranged from 0.1 to 54.7 micrograms per gram of dry organism, while total unsaturated hydrocarbons ranged from 0.1 to 7970.8 micrograms per gram. As previously observed in MAFLA samples, unsaturated hydrocarbons were usually several orders of magnitude more abundant than saturated hydrocarbons.

# General Comments

Retention indices of saturated and unsaturated hydrocarbons from both the baseline and rig monitoring samples ranged from 1400 to 3500. Small amounts of hydrocarbons having higher retention indices were undoubtedly present, but their retention times became too great to warrant their measurement. The retention indices of the components comprising most of hydrocarbons in these samples were generally between 2000 and 3000. This was true for both saturated and unsaturated hydrocarbons. In some samples, pristane was also quite abundant. Its retention index is about 1708 on OV-101 columns and 1656 on FFAP columns.

#### DISCUSSION

Most of the 261 organisms analyzed in this study gave CPI values between one and three for their n-alkane hydrocarbons. This is generally considered to be low for biological samples. For example, plant waxes have CPI values greater than ten (Eglinton and Hamilton, 1963). However, similar low values have been reported for marine samples. Koons, et al. (1965) found numbers ranging from 1.0 to 1.4 for 11 samples of invertebrates, and Clark and Blumer (1967) determined values from 0.4 to 1.5 for algae and total plankton samples. The CPI values of 24 macroepifauna from the MAFLA area ranged from 0.20 to 5.26 and averaged 1.58±1.30 (Meyers, 1976). These data suggest that Carbon Preference Indices of marine biological samples may normally be lower than those derived from land organisms. Alternatively, these data may indicate a weakness of the CPI concept when applied to biological samples. As pointed out by Scalan and Smith (1970), CPI values of geological samples can become misleading when they are calculated over different ranges of n-alkanes. In the 261 samples of organisms in this study, an homologous series of n-alkanes was not commonly encountered. Therefore, the CPI values calculated for these samples were not necessarily based upon the same n-alkanes for all samples, and it is likely these values have less meaning than when this ratio is applied to geological samples.

Almost none of the chromatograms of either the saturated or unsaturated hydrocarbon fractions of the organisms analyzed in this study contained a complex, unresolved mixture of hydrocarbons. The presence of such a mixture is indicative of petroleum contamination (Blumer, <u>et al</u>., 1970; Burns and Teal, 1973). Therefore, few of these organisms give evidence of containing petroleum hydrocarbons, and their hydrocarbon compositions are judged to be representative of natural, biological hydrocarbons in these populations.

# Baseline Monitoring Samples

Inspection of the tabulated ratios in Appendix II reveals no discernible changes in either amounts or compositions of hydrocarbons in these samples over the ten-month interval covered by sampling operations. A similar lack of seasonal trend is obtained from comparison of chromatograms of individuals of a given species collected from the three sampling periods. If seasonal variations do occur in hydrocarbon compositions of benthic macrofauna from the MAFLA area, they must be relatively small and concealed by natural, intraspecific variability. No discernible differences in hydrocarbons could be detected between organisms collected from different MAFLA sampling stations. Although many of the samples contained more than one organism, it is felt that not enough replicates of a species were collected at a given location to allow a meaningful statistical comparison of geographical or seasonal influences on hydrocarbon compositons to be performed.

However, the 183 MAFLA area analyses do give a good representation of the hydrocarbon content of the benthic population. The broad and general characterization of this content indicates an absence of non-biogenic hydrocarbons. The organisms appear to be basically pristine. Natural hydrocarbon distributions appear to be relatively simple, with a small number of major components dominating. These components are different for different genera and phyla and may be useful in chemical taxonomic studies in the future. At present, however, few of these hydrocarbons have been identified.

One readily identifiable component of many of the hydrocarbon compositions is pristane. This isoprenoid hydrocarbon is present in most of the 183 samples and is a major component in all samples of the squid <u>Loligo</u> <u>pealeii</u>. The primary source of this hydrocarbon in marine organisms is believed to be from zooplankton which form it from phytol in their gut

passages (Avignan and Blumer, 1968). The high concentrations in <u>L</u>. <u>pealeii</u> indicate a diet containing large amounts of zooplankton and reflect the general refractory nature of hydrocarbons to metabolic alteration. These squid are therefore prime examples of bioaccumulation of hydrocarbons in the marine environment.

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#### CONCLUSIONS

- Based upon 261 hydrocarbon analyses, benthic macroepifauna sampled in this study from the Gulf of Mexico are largely free of petroleum hydrocarbon contamination.
- 2. Any seasonal and geographical variations in hydrocarbon compositions of these samples is masked by natural intraspecific variability.
- 3. As indicated by the build-up of pristane in squids, dietary hydrocarbons can accumulate within organisms. This implies that petroleum hydrocarbons, if ingested or otherwise taken up, can also accumulate within animals.
- 4. As shown by certain Rig Monitoring samples, patterns of hydrocarbons can clearly indicate petroleum contamination in organisms. This demonstrates the usefulness of hydrocarbon analysis of environmental samples.
- 5. If sufficiently large enough numbers of a species are collected, a representative hydrocarbon composition of that population can be obtained. This has been done for the Rig Monitoring samples.

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# Appendix I

Inventories of Analyses from MAFLA

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Baseline Monitoring Study

MAI	FLA	Monitoring	Samples	_	First	Sampling	Period,	1975	5-76	
Phylum Porifera							Lab No.	-	SUSIO	No.

Placospongia sp.	120	I - A - 1 (A+B-4)
Tethya sp.	117	III-251-1 (A-9)
	122	III-A-1 (C-5)
unidentified sponge	132	VI-B-1 (A-3)
unidentified sponge	138	V - A - 3 (A - 8)
	121	$T_{-B-2}$ (C-3)
	121	1 = 2 = (C = 7)
Phylum Chidaria	125	111-A-2 (C-7)
riyium ciridaria		
Class Anthozoa		
Madracis decactis	103	III-047-3 (A-13)
	112	III-146-4 (B-10)
	116	III-247-4 (B-8)
	146	III-151-3 (A-18)
	148	III-251-3 (B-5)
Porites divaricata	102	III-147-4 (A-13)
	109	III-047-2 (A-11)
Solenstrea byades	104	II - 64 - 4 (C-7)
<u> </u>	108	II-62-1 (A-11)
Class Hydrozoa		
Millepora alcicornis	110	III-146-5 (B-24)
	111	III-147-3 (A-12)
· .	145	III-151-2 (A-17)
	147	III-247-2 (A-15)
	149	III-251-4 (B-6)
Phylum Echinodermata	-	
Class Asteroidea	105	
<u>Clypeaster</u> sp.	125	1V-B-1 (C-5)
Luidia alternata	100	11-064-3 (A-22)
Class Echinoidea	1.01	** 0(0 0 (4 10)
Arbacia punctulata	101	11-062-2 (A-12)
Encope sp.	126	1V - A - 1 (A+B-4)
Moira sp.	143	V1-C-1 (C-4)
Stylodaris affinis	130	V1-B-2 (A-4)
Class Welsthursides	144	V-A-2 (A-2)
unidentified and encumber	127	X = 1 = (A - 1)
Class Ophiuroides	137	V-A-1 (A-1)
Actrophyton muricatum	0.0	TTT 1/6-6 (P-25)
Astrophyton muricatum	55 107	111-140-0 (B-23)
	107	111-047-7 (A-31)
	113	111-151-4 (A-33)
	155	111-251-5 (U-8)
ma to the second	157	111-247-5 (B-9)
Tropiometra sp.	119	1-B-1 (B-3)
Phylum Mollusca		
Class Cephalopoda		
Loligo nealeii	133	VI-C-3 (C-6)
Torres beaters	140	V = R = 3 (C = 5)
Class Pelecynoda	740	
Mercanaria campechiensis	156	V-B-1 (B-2)
		· · · · (·≃
### Phylum Arthropoda

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Class Crustacea		
Acanthocarpus alexandri	134	VI-C-2 (C-5)
and a second second second second second second second second second second second second second second second	135	IV-C-1 (C-4)
	141	V-C-1 (C-3)
Callidactylus asper	136	IV-C-2 (C-5)
	142	V-C-2 (C-4)
Portunus gibberi	131	II-A-1 (C-5)
Portunus spinicarpus	124	II-B-1 (C-3)
Portunus gibberi Portunus spinicarpus Sicyiona brevirostris	127	IV-B-2 (C-6)
	128	VI-A-1 (A-4)
	139	V-B-2 (C-4)
Sicyiona brevirostris	129	VI-A-3 (C-3)
Stenorhynchus seticornis	98	III-047-5 (A-49)
	105	III-146-3 (B-9)
	106	III-147-5 (C-5)
	114	III-247-3 (A-6)
	115	III-151-5 (A-34)
	118	III-251-2 (B-4)

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ΜΔΕΙΔ	Monitoring	Samples	 Second	Sampling	Period.	1975-76
PIAT LA	MONILOLING	Sampres	 Second	Sampring	reriou,	19/0-/0

Phylum Porifera	Lab No.	SUSIO No.	
Haliclona viridis	186	I-A-A-5	
Tethya sp.	152	III-047-1	(A-7)
*	158	II-064-1	(A-5)
	161	III-146-1	(B-8)
	163	III-147-1	(A-11)
	167	III-151-1	(A-12)
	174	III-251-1	(A-17)
	181	III-247-1	(A-6)
	191	II-A-A-3	
Verongia sp.	206	III-151-3	(A-16)
	207	III-147-3	(A-15)
unidentified sponge	188	I-B-A-6	
	192	II-B-C-6	
	193	III-B-C-9	
	194	V-A-A-7	
	195	VI-B-A-2	
Phylum Cnidaria			
Class Anthozoa			
<u>Cladocora</u> <u>debilis</u> (lost)	176	II-062-1	
<u>Madracis</u> <u>decactis</u>	184	III-247-2	(A-8)
	183	III-146-2	(B-10)
	198	III-A-3	(A-6)
Porites divaricata	175	111-047-2	(A-9)
	180	III-151-2	(A-14)
	182	III-251-2	(A-19)
<u>Solenastrea</u> hyades	177	II <b>-</b> 62-5	(A-30)
	178	II-64-3	(A-11)
	196	II-A-2	(A-6)
<u>Class Hydrozoa</u>			
<u>Millepora</u> alcicornis	179	III-147-4	(A-16)
Phylum Echinodermata			
<u>Class Asteroidea</u>	01.0	17T A A O	
Astropecten sp. Class Echinoidea	216	V1-A-A-3	
Arbacia punctulata	159	II-064-4	(B-7)
Lytechinus variegatus	153	II-062-4	(A-23)
Stylodaris affinis	210	V-A-A-5	
unidentified soft urchin	190	I-C-C-5	
Class Ophiuroidea			
Astrophyton muricatum	154	III-047-7	(A-41)
	162	III-146-7	(C-10)
	168	III <b>-</b> 151-6	(A-19)
	172	III-247-7	(B-22)
	170	III-251-7	(B-5)
Astroporpa annulata	200	III-B-A-2	
	217	VI-B-A-1	
Class Crinoidea			
unidentified crinoids	187	I-B-A-2	

Phylum Mollusca

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Class Cephalopoda			
Loligo pealeii	212	V-B-C-9	
	214	V-C-C-2	
	201	III-C-C-7	
·	208	IV-C-C-5	
Class Pelecypoda			
Mercanaria campechiensis	211	V-B-A-2	
Spondylus americanus	150	III-047-8 (A-4	2)
Phylum Arthropoda			
Class Crusterer			
<u>Acapthocarpus</u> alexandri	209	IV-C-C-6	
Acanchocarpus arexandri	207	V-C-C-1	
Colonna on	189	I-C-C-1	
<u>Lalappa</u> sp.	185	T-A-A-6	
rortanus spinicarpus	199		
	202		
	202	$VI_{-\Lambda-\Lambda-2}$	
	213	V = R + A - 2 $T V = R - \Delta - 1$	
Circiere hucuine strie	204	IV - D - A - 1 IV - A - A - 2	
Sicylona brevirostris	205	IV-R-R-2 IV-R-C-7	
	151		2
Stenorhynchus seticornis	160	TTT-146-5 (R-2	4)
	166	111-140-5 (b-2 111-147-5 (b-2	.JJ /51
	100	TTT 151 7 (A-2	.)) 10)
- · · · · · · · · · · · · · · · · · · ·	109	111-151-7 (A-5	
	1/1	111-247-6 (B-2	.0)
	1/3	111-251-6 (B-4	1) I
unidentified shrimp	197	11-0-0-5	
	218	VI-C-C-2	

	Analysis No.	SUSIO No.
Phylum Porifera		
Haliclone rubens	279	I-A-A-5
Tethya sp.	300	064-A-1
· Verongia longissima	280	I-A-A-4
Trachygellius cinachyra	306	247-A-20
Trachygellius cinachyra	307	147-A-15
Trachygellius cinachyra	314	151-A-22
Verongia sp.	299	247-A-7
unidentified sponges	278	VI-B-C-5
	277	V-A-A-2
	292	II-A-A-9
	293	I-B-A-3
	312	III-A-C-10
	313	II-B-A-4
	315	III-B-A-3
Phylum Cnidaria		
Class Anthozoa		
<u>Occulina</u> diffusa	309	062-A-3
<u>Madracis</u> <u>decactis</u>	334	147-A-18
<u>Madracis</u> <u>decactis</u>	327	III-A-C-9
<u>Madracis</u> <u>decactis</u>	340	151-A-25
<u>Madracis</u> <u>decactis</u>	357	146-A-22
<u>Madracis</u> <u>decactis</u>	358	251-A-6
Madracis decactis	359	047-A-9
<u>Madracis</u> <u>decactis</u>	298	247-A-22
Porites divaricata	316	247-A-25
Porites divaricata	332	14/-A-10
Porites divaricata	339	101-A-24
Porites divaricata	341	140-A-30 251 A 5
Porites divaricata	366	2JI - A - J
Porites divaricata	308	147 - A - 5
Solenastrea hyades	310	11 - A - A - 7 064 - 11
Solenastrea hyades	311	004 - R - 11 062 - R - 8
Class Wydrogoo	211	002-0-0
Millonora algigornia	317	247-4-24
Millepora alcicornis	333	147 - 4 - 17
Millopora algicornis	326	151-4-26
Millepora algicornis	361	146-A-21
Millepora alcicornis	369	047-A-6
Phylum Echinodermata		
Class Asteroidea		
Astropecten nitidus	350	IV-A-A-1
Clypeaster sp.	294	VI-A-C-3
Clypeaster raveneli	318	IV-B-A-2
Clypeaster raveneli	349	II-B-A-3
Astropecten sp.	301	I-C-A-2
Class Echinoidea		
Encope michelini	325	IV-A-A-2
Lytechinus variegatus	271	II-A-A-8
Lytechinus variegatus	272	062-A-7

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	Analysis No.	SUSIO No.
Lytechinus variegatus	273	062-A-7
Lytechinus variegatus	370	062-A-7
Stylocidaris affinis	274	V-A-A-3
Stylocidaris affinis	290	VI-B-C-4
unidentified urchin	324	I-C-A-1
unidentified urchin	288	VI-C-C-5
unidentified urchin	289	VI-C-C-6
Class Ophiuroidea		
Astrophyton muricatum	348	146-A-34
Astroporpa annulata	275	V-B-A-2
Astroporpa annulata	291	III-B-A-8
Astroporpa annulata	346	VI-B-C-3
Class Crinoidea		
Comactina echinoptera	319	I-B-A-3
Phylum Mollusca		
Class Cephalopoda		
<u>Loligo pealeii</u>	322	IV-C-C-2
Class Gastropoda		
<u>Murex beauii</u>	323	II-C-A-3
Class Pelecypoda		
Spondylus americanus	295	247-A-33
Spondylus americanus	296	147-A-19
Spondylus americanus	297	151-A-28
Spondylus americanus	351	047-A-33
Spondylus americanus	352	146-A-28
Phylum Arthropoda		
Class Crustacea		
Acanthocarpus alexandri	321	III-C-A-1
Hymenopenaeus tropicalis	347	II-C-A-4
Portunis spinicarpus	320	IV-B-A-3

### Appendix II

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Tabulations of Data from MAFLA Baseline

Monitoring Study

#### Summary Tabulation of Hydrocarbon Analyses - First Sampling Period

Sample Number	Analysis Number	Organism	Ä	<u>B</u>	<u>c</u>	D	E	F	G
I-A-1 (A+B-4)	120	Placospongia sp.	3.71	0.08	10.9	2.31	0.72	8.2	1103.5
III-251-1 (A-9)	117	Tethya sp.	1.20	2.09	59.5	2.01	0.41	33.7	2104.1
III-A-1 (C-5)	122	Tethya sp.	0.14	0.02	6.16	1.03	0.68	24.9	2034.4
VI-B-1 (A-3)	132	unidentified sponge	1.74	0.02	2.07	1.34	0.83	14.5	331.4
V-A-3 (A-8)	138	unidentified sponge	1.56	0.08	1.42	1.21	0.65	5.8	352.4
I-B-2 (C-3)	121	unidentified sponge	1.64	0.06	4.65	1.28	0.28	21.3	756.3
III-A-2 (C-7)	123	unidentified sponge	1.64	0.33	1.70	3.02	1.86	8.9	484.0
III-047-3 (A-13)	103	Madracis decactis	1.19	0.28	2.57	1.19	0.73	343.9	20079.8
III-146-4 (B-10)	112	Madracis decactis	1.18	0.03	1.44	1.02	0.63	209.7	2556.7
III-247-4 (B-8)	116	Madracis decactis	1.14	0.01	0.79	1.28	0.68	248.6	2049.7
III-151-3 (A-18)	146	Madracis decactis	19.12	0.11	2.22	0.00	0.52	69.9	2086.7
III-251-3 (B-5)	148	Madracis decactis	3.82	0.14	1.94	0.00	0.62	134.7	1252.7
III-147-4 (A-13)	102	Porites divaricata	1.06	0.03	0.57	1.38	0.57	191.6	3053 <b>.7</b>
III-047-2 (A-11)	109	Porites divaricata	1.44	0.05	0.82	1.57	0.60	66.5	1004.8
II-64-4 (C-7)	104	Solenastrea hyades	2.75	0.00	33.23	1.37	0.64	9089.4	7274.3
II-62-1 (A-11)	108	Solenastrea hyades	1.21	0.08	1.46	1.44	0.76	1820.5	10477.8
III-146-5 (B-24)	110	Millepora alcicornis	0.78	0.12	2.25	1.33	0.78	103.3	351.7
III-147-3 (A-12)	111	Millepora alcicornis	1.20	0.02	0.57	1.11	0.70	596.2	5173.9
III-151-2 (A-17)	145	Millepora alcicornis	1.47	0.06	1.72	0.89	0.45	1643,9	1793.7
III-247-2 (A-5)	147	Millepora alcicornis	0.81	1.22	2.68	13.98	4.28	757.0	1568.1
III-251-4 (B-6)	149	Millepora alcicornis	0.36	0.15	1.83	0.65	0.63	211.7	968.8
·IV-B-1 (C-5)	125	Clypeaster sp.	1.94	0.17	6.80	1.70	0.89	10.7	78.0
II-064-3 (A-22)	100	Luidia alternata	1.44	0.03	1.18	1.52	0.17	5.6	560.4
II-062-2 (A-12)	101	Arbacia punctulata	1.64	0.04	2.03	1.43	0.55	10.7	387.4
IV-A-1 (A+B-4)	126	Encope sp.	1.75	0.04	1.77	0.86	0.51	1.9	778.2
VI-C-1 (C-4)	143	Moira sp.	1.95	0.01	1.00	1.78	0.71	27.4	26.4
VI-B-2 (A-4)	130	Stylodaris affinis	2.01	0.01	1.99	2.25	0.58	4.8	259.0
V-A-2 (A-2)	144	Stylodaris affinis	0.52	0.01	0.82	1.03	0.45	4.3	120.5
V-A-1 (A-1)	137	unidentified sea cucumber	1.48	0.19	2.66	1.97	1.15	6.5	586.2
III-146-6 (B-25)	99	Astrophyton muricatum	1.90	0.36	2.31	9.36	2.89	10.8	1171.3
III-047-7 (A-51)	107	Astrophyton muricatum	0.38	0.01	0.72	1.59	0.65	17.7	379.3
III-151-4 (A-33)	113	Astrophyton muricatum	1.87	0.04	0.57	1.86	0.76	50.9	465.4
III-251-5 (C-8)	155	Astrophyton muricatum	2.39	0.03	0.74	2.22	0.61	1.5	296.6
III-247-5 (B-9)	157	Astrophyton muricatum	2.81	0.01	0.63	1.99	0.65	2.2	1756.3
I-B-1 (B-3)	119	Tropiometra sp.	1.54	0.11	2.46	1.20	0.73	9.4	220.2

	Analysis	<b>–</b> •	-		~	<b>D</b>		-	•
Sample Number	Number	Organism	<u>A</u>	B	<u>c</u>	Ð	E	<u>F</u>	<u>G</u>
VI-C-3 (C-6)	133	Loligo pealeii	1.94	1.67	2.16	247.37	40.68	7.0	2425.4
V-B-3 (C-5)	140	Loligo pealeii	1.00	0.78	1.72	2.11	1.35	3.6	2466.5
V-B-1 (B-2)	156	Mercanaria campechiensis	1.82	0.04	1.58	1.89	0.55	12.9	929.4
VI-C-2 (C-5)	134	Acanthocarpus alexandri	1.94	0.44	1.96	2.30	1,24	4.8	1113.4
IV-C-1 (C-4)	135	Acanthocarpus alexandri	1.59	0.19	0.81	1.62	0.86	1.4	771 <b>.3</b>
V-C-1 (C-3)	141	Acanthocarpus alexandri	1.93	0.18	1.56	0.73	1.00	5.2	838 <b>.9</b>
IV-C-2 (C-5)	136	Callidactylus asper	1.31	0.02	0.24	2.18	1.08	6.6	1926.1
V-C-2 (C-4)	142	Callidactylus asper	1.52	0.01	1.17	0.90	0.68	5.9	2381.4
II-A-1 (C-5)	131	Portunus gibberi	2.57	0.42	2.59	1.56	1.43	6.7	430.5
II-B-1 (C-3)	124	Portunus spinicarpus	1.20	0.34	1.79	3.72	1.64	7.4	2054.9
IV-B-2 (C-6)	127	Portunus spinicarpus	1.96	0.47	2.86	1.64	2.00	9.4	587.5
VI-A-1 (A-4)	128	Portunus spinicarpus	1.47	0.84	3.65	0.00	2.07	51.4	10940.4
V-B-2 (C-4)	139	Portunus spinicarpus	1.81	0.54	2.45	4.55	2.15	8.6	592 <b>.2</b>
VI-A-3 (C-3)	129	Sicyiona brevirostris	1.73	0.09	0.87	0.00	0.86	1.7	1031.4
III-047-5 (A <b>-49)</b>	98	Stenorhynchus seticornis	1.96	0.03	1.08	1.90	0.47	1.9	1648.9
III-146-3 (B-9)	105	Stenorhynchus seticornis	1.88	0.12	0.92	2.58	0.75	10.9	399 <b>.3</b>
III-147-5 (C-5)	106	Stenorhynchus seticornis	1.81	0.03	1.24	2.02	0.59	7.3	1310.7
III-247-3 (A-6)	114	Stenorhynchus seticornis	1.48	0.03	0.85	1.53	0.60	3.8	758.5
III-151-5 (A-34)	115	Stenorhynchus seticornis	1.02	0.05	1.09	1.15	0.65	17.1	2191.2
III-251-2 (B-4)	118	Stenorhynchus seticornis	1.27	0.03	0.78	1.56	0.56	31.2	1597.6

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A = odd/even ratio • B = isoprenoid/n-alkane ratio C = branched/n-alkane ratio D = pristane/phytane ratio E = Pristane/n-heptadecane ratio F = Total aliphatics; µgm/gm G = Total aromatics; µgm/gm

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Sample Number	Analysis No.	Organism	Ă	B	<u>c</u>	D	E	<u>F</u>	<u>c</u>
I-A-A-5	186	Haliclona Viridis	1.50	0.03	6.66	0.0	0.0	5.7	286.6
III-047 <b>-1</b>	152	Tethya sp.	6.37	0.01	3.17	0.0	0.08	22.5	818.8
II-064-1	158	Tethya sp.	2.51	0.39	4.95	1.96	0.39	16.9	4649.8
III-146-1	161	Tethya sp.	7.65	0.03	9.15	0.0	0.15	18.7	1192.8
III-147-1	163	Tethya sp.	0.84	1.41	23.49	0.0	0.29	54.3	1036.4
III-151-1	167	Tethya sp.	1.61	1.99	22.5	0.0	0.40	5.4	1821.8
111-251-1	174	Tethya sp.						0.4	184.1
111-247-1	181	Tethya sp.	1.67	0.06	4.43	1.40	0.27	59.7	772.0
II-A-A-3	191	Tethya sp.	0.97	0.04	5.98	2.90	0.45	13.9	1173.7
III-151 <b>-3</b>	206	Verongia sp.	4.89	0.58	211.8	0.0	0.35	13.7	272.7
111-147-3	207	Verongia sp.	2.92	0.09	9.65	1.54	0.33	7.4	523.4
I-B-A-6	188	unid. sponge	2.36	0.06	8.79	2.29	0.69	44.6	184.7
II-B-C-6	192	unid. sponge	1.25	0.23	1.85	1.90	0.97	2.1	290.5
III-B-C-9	193	unid. sponge							140.3
V-A-A-7	194	unid. sponge	2.79	0.0	3.14	0.0	0.07	1.1	148.8
VI-B-A-2	195	unid. sponge	11.21	0.0	32.59	0.0	0.0	15.4	4180.8
111-247 <b>-2</b>	184	Madracis decactis	4.74	0.02	6.63	0.0	0.15	259.4	1790 <b>.9</b>
III-146 <b>-2</b>	183	Madracis decactis	3.34	0.0	5.58	0.0	0.32	842.0	12792.4
III-A-3	198	Madracis decactis	1.48	0.17	2.57	0.44	0.0	16.8	111.8
111-047-2	175	Porites divaricata	1.22	0.18	3.69	1.73	0.55	77.3	8089 <b>.9</b>
III-151-2	180	Porites divaricata	1.84	0.07	3.74	0.94	0.42	538.7	750.2
III-251-2	182	Porites divaricata	1.00	0.03	3.25	1.12	0.65	557.8	696.9
II-62-5	177	Solenastrea hyades	3.75	0.0	2.47	0.0	0.23	65.9	636.8
II-64-3	178	Solenastrea hyades	2.15	0.07	4.71	2.23	0.56	42.4	2570.6
II-A-2	196	Solenastrea hyades	1.07	0.07	1.34	0.0	0.0	41.9	1371.1
III-147-4	179	Millepora alcicornis	2.71	0.11	4.00	1.33	0.59	124.1	981.3
VI-A-A-3	216	Astropectin sp.	0.34	0.88	68.57	0.0	0.16	2.1	632.6
II-064-4	159	Arbacia punctulata	10.31	0.03	5.20	1.31	0.51	33.4	198.2
II-062-4	153	Lytechinus variegatus	1.96	0.05	4.22	1.72	0.44	5.4	213.7
V-A-A-5	210	Stylodaris affinis	3.34	0.04	0.98	2.03	0.39	1.1	50.2
I-C-C-5	190	unid. soft urchin	1.36	0.35	2.57	9.49	3.39	23.2	1130.8
III-047-7	154	Astrophyton muricatum	2.00	0.28	3.25	0.0	0.0	8.05	718.0
III-146-7	162	Astrophyton muricatum	1.97	0.02	1.52	2.55	0.40	2.7	347.8
III-151-6	168	Astrophyton muricatum	3.07	0.42	10.51	0.0	0.0	49.6	936.0
III-247-7	172	Astrophyton muricatum	2.06	0.02	2.76	2.39	0 39	12.2	477.9
111-251-7	170	Astrophyton muricatum	1.31	0.18	2.28	5.56	1.35	1.6	208.3

Summary Tabulation of Hydrocarbon Analyses - Second Sampling Period

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#### Summary Tabulation continued

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Sample Number	Analysis No.	Organism	<u>▲</u> .	B	<u>c</u>	<u>D</u>	<u>E</u>	<u>F</u>	G
111-B-A-2	200	Astroporpa annulata	0.59	0.01	1.77	1.95	0.40	11.3	483.6
VI-B-A-1	217	Astroporpa annulata	4.26	0.34	3.11	0.0	2.76	2.0	324.6
I-B-A-2	187	unid. crinoids	1.79	0.30	6.36	2.29	0.79	1.3	238.0
V-B-C-9	212	Loligo pealeii	3.73	0.56	2.45	6.58	2.19	2.2	6474.0
V-C-C-2	214	Loligo pealeii							
III-C-C-7	201	Loligo pealeii	1.42	0.0	10.02	8.45	2.13	14.0	7746.1
IV-C-C-5	208	Loligo pealeii	1.30	0.30	0.76	4.25	1.27	6.5	3094.4
V-B-A-2	211	Mercenaria campechiensis	0.82	0.16	1.01	1.80.	6.53	11.1	695.5
III-047 <b>-8</b>	150	Spondylus americanus	2.64	0.03	6.12	0.0	0.0	6.1	266.2
IV-C-C-6	209	Acanthocarpus alexandri	10.4	0.23	1.85	3.19	1.39	1.6	3031.7
V-C-C-1	213	Acanthocarpus alexandri	1.5	0.33	2.79	2.70	1.99	2.8	776.2
I-C-C-1	189	Calappa sp.	1.73	0.41	2.26	4.50	1.59	10.1	4097.9
I-A-A-6	185	Portunus spinicarpus	0.90	1.48	5.05	8.19	2.43	2.6	1386.9
III-A-C-7	199	Portunus spinicarpus	3.26	0.46	3.42	25.4	0.0	2.2	902.6
III-C-C-8	202	Portunus spinicarpus	3.86	0.67	3.46	9.64	1.36	1.1	565.9
VI-A-A-2	215	Portunus spinicarpus	0.70	0.18	3.11	0.0	1.10	5.1	754.1
IV-B-A-1	204	Portunus spinicarpus	1.82	0.60	4.12	13.88	4.07	4.0	1590.8
IV-A-A-2	203	Sicyiona brevirostris	4.02	0.0	45.50	8.09	2.33	2.9	755.2
IV-B-C-7	205	Sicyiona brevirostris	1.88	0.04	17.90	2.60	0.62	1.9	463.6
III-04 <b>7-6</b>	151	Stenorhynchus seticornis	1.50	0.14	1.12	1.68	0.61	4.8	697.3
III-146 <b>-</b> 5	160	Stenorhynchus seticornis	0.97	0.26	2.53	3.57	1.23	4.5	352.7
III-147 <b>-5</b>	166	Stenorhynchus seticornis	2.01	0.22	2.31	4.15	0.97	31.9	2094.6
III-151 <b>-</b> 7	169	Stenorhynchus seticornis	2.25	0.34	1.69	7.12	1.84	2.6	860.9
III-247-6	. 171	Stenorhynchus seticornis	2.58	0.16	1.48	46.57	0.60	4.1	1059.6
111-251-6	173	Stenorhynchus seticornis	2.03	0.16	0.82	2,85	0.70	3.1	493.8
II-C-C-5	197	unid. shrimp	1.20	0.22	1.44	0.0	0.0	10.3	5158.0
VI-C-C-2	218	unid. shrimp	19.18	0.93	8.66	1.97	1.44	1.0	729.6

A = odd/even ratio

B = isoprenoid/n-alkane ratio

C = branched/n-alkane ratio

D = pristane/phytane ratio

E = pristane/n-heptadecane ratio F = total aliphatics; μgm/gm G = total aromatics; μgm/gm

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	Analysis								
Sample No.	Number	Organism	A	B	<u>C</u>	D	E	F	G
T-A-A-5	279	Halicione rubens	0.86	0.87	2 30	1 42*	0.87*	6.3	196.9
064-A-1	300	Tethya sp	5 48	0.01	2.55	0 88*	0.33*	16.9	297.3
T-A-A-4	280	Verongia longissima	3 83	0 01	2.02	1 82*	0.24*	5 3	772.7*
247-A-20	306	Trachygelling cinachyra	16 57	0 01	5 36	0.0 *	0.15*	197	305.4
147-A-15	307	Trachygellius cinachyra	12 81	0.01	3.06	0.0 *	0.10*	16.7	488.1
151 - A - 22	314	Trachygellius cinachyra	1 45	0.01	1 70	0.0 *	0.39*	12.6	290.8
247-A-7	299	Verongia sp	3 02	0.03	2 68	1 08*	0.66*	10 0	314 6
VI-B-C-5	278	unidentified sponse	0.88	0.01	12 76	1 37*	1 12*	67 0	1159.4
V-A-A-2	277	unidentified sponge	8 67	0.01	1 12	0.0.*	0.09*	5.0	293.8
TT-A-A-9	292	unidentified sponge	3 87	0.06	1 77	0.57*	0.53*	51 3*	1106 1
T-B-A-3	293	unidentified sponge	3.07	0.00	1 73	1 26*	0.49*	11 3*	317 2
III-A-C-10	312	unidentified sponge	5.79	0.12	0.55	0.0 *	0.37*	1.4	42.8
II-B-A-4	313	unidentified sponge	1.60*	0.38*	5.08*	4.31*	0.99*	2.0*	42.7
III-B-A-3	315	unidentified sponge	30 00	0.03	4 52	0.0.*	1 07*	1.3	169.3*
	020		30100	0.00		0.0	2007	205	20000
062-A-3	309	Occulina diffusa	1.23	0.42	3.72	0.0 *	0.42*	13.5	225.7
147-A-18	334	Madracis decactis	1.69*	0.14*	9.70*	0.0 *	0.54*	48.0	783.9
III-A-C-9	327	Madracis decactis	1.30*	0.15*	2.47*	0.0 *	0.31*	1.5*	266.2
151-A-25	340	Madracis decactis	4.04	0.10	2.20	1.20*	0.61*	134.3	2140.1
146-A-22	357	Madracis decactis	2.58*	0.13*	5.22*	1.36*	0.40*	114.5	1166.2
251-A-6	358	Madracis decactis	0.84*	0.12*	21.87*	0.0 *	0.57*	200.8	2074.4
047-A-9	359	Madracis decactis	0.52*	0.07*	7.21*	0.0 *	0.56*	60.3*	2398.2
247-A-22	298	Madracis decactis	2.04	0.08	0.51	1.30*	0.31*	79.1*	546.2
247-A-25	316	Porites divaricata	1.34*	0.21*	3.05*	0.0 *	0.65*	9.3*	209.6
147-A-16	332	Porites divaricata	0.86*	0.06*	3.11	1.24*	0.57*	35.9*	86.1
151-A-24	339	Porites divaricata	0.47	0.51	1.31	1.10*	0.44*	6.7*	559.3
146-A-36	341	Porites divaricata	1.24*	0.16*	3.58*	1.64*	0.68*	10.9*	1052.8*
251-A-5	360	Porites divaricata	1.46	1.32	11.40	1.45*	0.74*	160.9*	1970.6
047-A-3	366	Porites divaricata	0.18	1.72	31.83	2.51*	0.75*	5.9	150.8
II-A-A-7	308	Solenastrea hyades	3.16	0.0	1.34	0.0 *	0.53*	15.2*	142.2
064-A-11	3 10	Solenastrea hyades	0.93	0.67	2.86	1.80*	0.53*	10.1	123.8
062-B-8	311	Solenastrea hyades	0.88*	1.74	4.88	1.29*	0.43*	6.4*	65.4
247-A-24	317	Millepora alcicornis	30.97	0.13	0.64	0.0 *	0.61*	10.6*	346.2 N
147-A-17	333	Millepora alcicornis	8.45	0.01	1.59	1.49*	0.69*	26.5*	129.0 ·
151-A-26	326	Millepora alcicornis	0.37	0.01	2.63	0.57*	0.57*	55.1	445.İ
146-A-21	361	Millepora alcicornis	0.72*	0.16*	11.17*	0.0 *	0.52*	38.4*	890.7

#### Summary Tabulation of Hydrocarbon Analyses - Third Monitoring Period

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047-A-6	369	Millepora alcicornis	2.78	0.11	5.12	2.28*	0.82*	5.8*	98.6
IV-A-A-1	350	Astropecten nitidus	4.47	1.68	10.69	3.93*	0.75*	0.6*	109.6
I-C-A-2	301	Astropecten sp.	0.39	0.55	35.79	0.0 *	0.67*	13.1	117.4
IV-B-A-2	318	Clypeaster raveneli	0.87	0.31	2.21	0.0 *	1.06*	2.7*	31.4
II-B-A-2	349	Clypeaster raveneli	0.34*	0.07*	1.30*	0.0 *	0.62*	0.2*	177.8
VI-A-C-3	294	Clypeaster sp.	1.94	0.17	2.10	1.64*	1.00*	7.3*	63.2
IV-A-A-2	325	Encope michelini	6.34	0.01	2.78	0.78*	0.64*	11.8	22.9*
II-A-A-8	271	Lytechinus variegatus							54.6*
062-A-7	272	Lytechinus variegatus							150.4*
062-A-7	273A	Lytechinus variegatus	0.0	1.66	3.08	0.0 *	0.0 *	0.2	8.0*
062-A-7	273B	Lytechinus variegatus	1.54	0.17	3.69	2.67*	0.55*	0.6	8.7
062-A-7	273C	Lytechinus variegatus	1.00	0.78	1.16	2.66*	0.50*	1.7*	8.6
062-A-7	370	Lytechinus variegatus							
V-A-A-3	274	Stylocidaris affinis	5.60	0.01	3.74	2.94*	0.49*	5.0	42.5
VI-B-C-4	290	Stylocidaris affinis	6.01	0.01	2.78	1.90*	0.91*	15.9	108.3
I-C-A-1	324	unidentified urchin	13.65	0.50	4.17	6.05*	2.50*	18.2	1034.8
VI-C-C-5	288	unidentified urchin	3.68	0.01	2.01	2.34*	0.94*	12.5	162.5
VI-C-C-6	289	unidentified urchin	2.44	0.01	3.96	1.87*	0.0 *	8.0	67.3
146-A-34	348	Astrophyton muricatum	1.39	0.44	1.67	1.28*	0.80*	6.9*	636.4
V-B-A-2	275	Astroporpa annulata	3.15	0.88	3.55	16.07*	5.92*	2.0	56.7
III-B-A-8	291	Astroporpa annulata	1.82	1.12	5.11	0.0 *	0.0 *	4.0	753.3
VI-B-C-3	346	Astroporpa annulata	0.55	0.39	2.82	6.41*	1.33*	1.7	270.4
I-B-A-3	319	Comactina echinoptera	14.61	0.01	1.25	0.0 *	1.01*	19.3	122.6
IV-C-C-2	322	Loligo pealeii	17.86	0.01	0.96	39.4*	9.4 *	13.4*	4011.6*
II-C-A-3	323	Murex beauii	23.98	0.03	1.30	1.85*	0.77*	129.8*	713.2
247-A-33	295	Spondylus americanus	3.41	0.01	13.49	0.0 *	0.41*	16.8	814.5*
147-A-19	296	Spondylus americanus	1.87	0.01	5.41	0.0 *	0.36*	15.9	253.7
151-A-28	297	Spondylus americanus	7.78	0.01	2.29	0.0 *	0.57*	11.6	485.2
047-A-33	351	Spondylus americanus	4.72	0.01	5.29	0.0 *	0.24*	12.8*	1169.7*
146-A-28	352	Spondylus americanus	9.80	0.01	2.69	2.00*	0.12*	7.0	1302.4*
III-C-A-1	321	Acanthocarpus alexandri	1.43*	0.18×	1.46*	4.12*	1.08*	0.8*	225.5
II-C-A-4	347	Hymenopenaeus tropicalis	0.85*	0.28*	1.50*	4.53*	1.12*	3.4*	763.3
IV-B-A-3	320	Portunis spinicarpus	2.08	0.11	8.78	0.0 *	4.03*	3.15	427.3

A = odd/even ratio

B = isoprenoid/n-alkane ratio

C = branched/n-alkane ratio

D = pristane/phytane ratio

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E = pristane/n-heptadecane ratio

F = total aliphatics, 'µgm/gm

 $G = total aromatics, \mu gm/gm$ 

\* FFAP column data

### Appendix III

### Inventories of Analyses from Rig Monitoring

Study

# Rig Monitoring Samples

# Predrilling Survey - December 1975

	Lab No	SUSIO No.
Dhulum Echinodormata		
Clean Astoroidon		
	228	4510 HE 2
Astropecten sp.	220	
Phylum Arthropoda		
Class Crustacea		
Callinectes sapidus	219	4918 HE 2
Penaeus setiferus	231	4108 HE 1
	232	4924 HE 1
	234	4918 HE 1
	235	4514 HE 1
	236	4920 HE 1
	237	4104 HE 1
	238	4102 HE 1
	239	4512 HE 2
	240	4510 HE 1
	241	4106 HE 1
	242	4516 HE 1
	243	4922 HE 1
Trachypenaeus similis	221	4104 HE 2
	222	4516 HE 2
	224	4514 HE 2
	225	4512 HE 1
	226	4102 HE 2
	227	4924 HE 2
	229	4108 HE 2
	230	4106 HE 2
Squilla sp. A	233	4922 HE 2
	223	4920 HE 2

	Lab No.	SUSIO No.
Phylum Echinodermata		
Class Asteroidea		
Astropecten duplicatus	257	4516 HE 4
	260	4922 HE 4
	261	4512 HE 3
	264	4510 HE 3
	266	4918 HE 4
	267	4920 HE 3
Phylum Arthropoda		
Penaeus setiferus	246	4918 HE 3
rendedo beerrerab	248	4104 HE 3
	251	4510 HE 4
	255	4924 HE 4
	258	4102 HE 3
Trachypenaeus similis	250	4924 HE 3
Ildenypendeds Similis	252	4512 HE 4
	254	4922 HE 3
·	259	4108 HE 4
<b>`</b>	262	4920 HE 4
	265	4514 HE 3
	268	4106 HE 4
Squilla sp. A.	247	4106 HE 3
<u>oquitta</u> sp. n.	249	4104 HE 4
	253	4514 HE 4
	256	4516 HE 3
	263	4108 HE 3
	269	4102 HE 4
	20)	

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### Drilling Operation Survey - January 1976

## Postdrilling Survey - March 1976

Phylum Arthropoda	353	
	353	
Class Crustacea	353	
Penaeus setiferus		4510 HE 5
	354	4515 HE
	367	4516 HE 5
Penaeus duorarum	337	4106 HE 7
	338	4108 HE 8
	344	4516 HE 6
	345	4922 HE 5
	355	4918 HE 5
	356	4924 HE 5
<u>Trachypenaeus</u> similis	283	4924 HE 6
	284	4510 HE 6
	285	4514 HE 5
	286	4512 HE 6
	302	4102 HE 6
	303	4104 HE 7
	304	4106 HE 6
•	305	4922 HE 6
	330	4918 HE 6
	331	4920 HE 5
	335	4108 HE 6
<u>Squilla chydea</u>	328	4108 HE 7
	329	4514 HE 6
	336	4104 HE 6
	342	4102 HE 7
	343	4512 HE 5
Squilla empusa	362	4104 HE 5
	363	4106 HE 5
	364	4108 HE 9
	365	4920 HE 6
	368	4102 HE 5

### Appendix IV

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### Tabulations of Data from Rig Monitoring

Study

Sample	Analysis								
Number	No.	Organism	<u>A</u>	<u>B</u>	<u>c</u>	D	E	<u>F</u>	G
	220		1 16	0.04	2 45	1 05+	0 39*	2.8*	128.4
4510 HE2	228	Astropecten sp.	5 16	1 60	6.63	1.95*	0.97*	11.7	409.1
4918 HE2	219	Callinectes sapidus	3.10	1.00	2 40	2 05*	0.57*	8.2*	3447.2
4108 HEL	231	Penaeus setiferus	1.70	0.03	2.40	1 25+	0.57*	2.6*	1987 5
4924 HE1	232	Penaeus setiferus	1.52	0.13	1.02	1.33^ 2.75+	0.33*	1.6	314 0
4918 HE1	234	Penaeus setiferus	1.34	0.26	1.12	2.75*	0.70*	20.7+	2522 0
4514 HE1	235	<u>Penaeus setiferus</u>	2.41	1.29	221.57	1.28*	0.91*	29.7*	1077 0
4920 HEl	236	<u>Penaeus</u> setiferus	0.68	0.48	4.79	0.78*	0.36*	1.0*	12//.2
4104 HE1	237	<u>Penaeus setiferus</u>	1.99	0.09	1.76	1.30*	0.60*	1.4	1354.8
4102 HE1	238	<u>Penaeus</u> <u>setiferus</u>	1.74	0.04	1.37	0.81*	0.70*	1.6*	1062.2
4512 HE2	239A	Penaeus setiferus	1.21	0.13	2.98	2.09*	1.11*	6.4*	2665.3
4512 HE2	239B	Penaeus setiferus	0.88	0.16	2.34	1.88*	0.77*	4.2*	1994.0
4510 HE1	240	Penaeus setiferus	1.33	0.06	1.01	1.82*	0.64*	2.5	939.6
4106 HE1	241	Penaeus setiferus	1.26	0.03	1.48	1.67*	0.52*	2.9	3538.1
4516 HE1	242	Penaeus setiferus							
4922 HE1	243	Penaeus setiferus	1.45	0.04	1.68	0	0.49*	0.8	7970.8
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4104 HF2	221	Trachypenaeus similis	2.22	0.01	2.32	0	0	1.7	674.3
4104 HE2 4516 HE2	221	Trachypenaeus similis	1.05	0.08	6.22	0	0	0.4	785.6
4516 HE2	222	Trachypenaeus similis	1.05	0.00	••==				
4J14 NE4	224	Trachypenaeus similis	2 23	0.03	1 37	2.36*	0.44*	2.5	726.6
4512 HEI	225	Trachypenaeus similis	1 07	0.05	3 25	0	0.32*	0.8	1236.7
4102 HEZ	~220	Trachypenaeus similis	1.97	0 02	2.07	1 57*	0.57*	6.4	1304 7
4924 HE2	227	Trachypenaeus similis	1.20	0.02	2.07	1.1.24	0.57*	0.7	475 7
4108 HE2	229	<u>Trachypenaeus similis</u>	0.82	0.03	1.01	1.4/*	0.00*	9.3^	4/5./
4106 HE2	230	<u>Trachypenaeus</u> similis	2.79	0.05	4.73	2.01*	0./1*	11.3*	n.d.
(020 1152	222	Couille op A	2 61	0 10	6 81	2 55	0.53	2.3*	840.3
4920 HE2	223	Squilla Sp. A	1 20	0.10	1 10	2.00	1 16*	2.0	1244.7
4922 HE2	233	Squilla sp. A	T• 20	0.05	1.10	2.75	T + T Ov	2.0	1644.1

#### Summary Tabulation of Hydrocarbon Analyses - Predrilling Rig Monitoring

A = odd/even ratio

B = isoprenoid/n-alkane ratio

C = branched/n-alkane ratio

D = pristane/phytane ratio

E = pristane/n-heptadecane ratio

F = total aliphatics, µgm/gm

 $G = total aromatics, \mu gm/gm$ 

\* FFAP column data

Sample No.	Analysis Number	Organism	A	<u>B</u> ,	<u>c</u>	<u>D</u>	E	F	G
4516 HE4	257	Astropecten duplicatus	3.44	0.01	5.95	1.68*	0.39*	15.1	563.6
4922 HE4	260	Astropecten duplicatus	1.32	0.51	5.73	1.78*	0.57*	2.3	241.8
4512 HE3	261	Astropecten duplicatus	2.05	0.01	2,60	1.40*	0.45*	3.1*	200.4
4510 HE3	264	Astropecten duplicatus	2.65	0.91	8.50	0.0	0.55*	2.1	0.1
4918 HE4	266	Astropecten duplicatus	1.16	0.02	1.05	1.89*	0.54*	7.2	401.6
4920 HE3	267	Astropecten duplicatus	0.79	0.01	2.20	0.0	0.55*	1.5	237.5
4918 HE3	246	Penaeus setiferus	0.06	0.03	3.38	2.13*	0.77*	3.4*	1393.5*
4104 HE3	248	Penaeus setiferus	2.15	0.01	1.11	2.11*	0.70*	1.6*	2621.3*
4510 HE4	251	Penaeus setiferus	1.84	0.60	8.05	2.62*	0.84*	1.3	1037.0*
4924 HE4	255	Penaeus setiferus	0.94	0.29	12.30	3.14*	1.11*	4.5	896.3
4102 HE3	258	Penaeus setiferus	1.51	0.01	1.04	2.08*	0.80*	0.9	1075.1*
4924 HE3	250	Trachypenaeus similis	1.51	0.01	0.49	2.87*	0.96*	0.5*	737.4
4512 HE4	252	Trachypenaeus similis	1.28	0.08	1.31	3.19*	0.90*	3.9	915.0
4922 HE3	254	Trachypenaeus similis	9.52	0.01	1.70	1.85*	0.69*	4.9*	605.3
4108 HE4	259	Trachypenaeus similis	1.07	0.36	1.85	3.22*	1.30*	1.1	943.4*
4920 HE4	262	Trachypenaeus similis							1184.1
4514 HE3	265	Trachypenaeus similis	1.13	0.16	1.38	1.34*	1.02*	54.7*	591.6
4106 HE4	268	Trachypenaeus similis	1.48	0.48	2.10	3.49*	1.15*	1.6	1731.3*
4106 HE3	247	Squilla sp. "A"	1.89	0.09	1.00	2.21*	0.80*	1.7	878.9
4104 HE4	249	Squilla sp. "A"	1.16	0.15	0.58	1.73*	0.86*	4.8	1250.3*
4514 HE4	253	Squilla sp. "A"	1.57	0.13	0.83	1.43*	1.05*	30.0*	236.7*
4516 HE3	256	Squilla sp. "A"	1.96	0.01	1.27	1.79*	0.64*	2.8*	233.4
4108 HE3	263	Squilla sp. "A"	2.14	0.25	1.44	2.12*	0.75*	2.8	762.4
4102 HE4	269	Squilla sp. "A"	1.08	0.60	12.17	3.20*	2.44*	0.3	190.7

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Summary Tabulation of Hydrocarbon Analyses - Drilling Phase Rig Monitoring

A = odd/even ratio

B = isoprenoid/n-alkane ratio

C = branched/n-alkane ratio

D = pristane/phytane ratio

E = pristane/n-heptadecane ratio

F = total aliphatics, ugm/gm

G = total unsaturates,  $\mu gm/gm$ 

\* Data obtained from FFAP column

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Sample No.	Analysis Number	Organism	A	B	<u>c</u>	D	E	F	G
4510 HE5	353	Penaeus setiferus	2.17	0.01	1.90	0*	0.66*	11.4*	3427.5
4515 HE	354	Penaeus setiferus							
4516 HE5	367	Penaeus setiferus	0.46	0.35	12.69	0*	3.44*	0.07	5921.7
4106 HE7	337	Penaeus duoraroum	2.75	0.17	1.29	2.59*	1.40*	2.1	1302.1*
4108 HE8	338	Penaeus duoraroum	14.15	0.31	1.58	4.06*	2.57*	1.3	1583.7*
4516 HE6	344	Penaeus duoraroum							
4922 HE5	345	Penaeus duoraroum	12.52	0.70	8.36	3.38*	1.97*	2.8*	3299.3*
4918 HE5	355	Penaeus duoraroum	2.51	0.63	6.34	4.10*	1.84*	2.2	403.4
4924 HE5	356	Penaeus duoraroum	3.27	0.37	3.75	2.79*	1.96*	5.6*	940.6
4924 HE6	283	Trachypenaeus similis	1.17	0.01	1.83	1.15*	0.98*	46.8*	5890.8*
4510 HE6	284	Trachypenaeus similis	0.78	0.67	2.70	1.11*	1.01*	45.0*	6017.3*
4514 HE5	285	Trachypenaeus similis	2.16	0.01	5.13	2.50*	0.59*	5.4	4941.1*
4512 HE6	286	Trachypenaeus similis							
4102 HE6	302	Trachypenaeus similis	2.78	0.24	5.57	0*	1.12*	4.9	3883.5
4104 HE7	303	Trachypenaeus similis	8.19	0.09*	1.08*	0*	0.71*	0.2*	964.0
4106 HE6	304	Trachypenaeus similis	2.11	0.16	1.83	0*	1.30*	3.3	2287 <b>.8*</b>
4922 HE6	305	Trachypenaeus similis	1.62	0.30	4.32	0*	1.20*	6.0*	1119.9
4918 HE6	330	Trachypenaeus similis	1.89	0.01	2.29	4.73*	1.74*	1.8	3032.2*
4920 HE5	331	Trachypenaeus similis	0.99	0.19	1.35	4.30*	1.15*	1.9*	1896.3*
4108 HE6	335	Trachypenaeus similis	5.33	0.29	2.62	3.00*	1.42*	1.7*	2680.6*
4108 HE7	328	Squilla chydea	1.92	0.03	1.10	4.29*	1.07*	1.1*	1198.5
4514 HE6	329	Squilla chydea	1.58	0.17	2.14	5.24*	1.07*	1.7*	626.6
4104 HE6	336	Squilla chydea	3.44	0.28	3.92	1.76*	0.80*	3.3*	2019.9
4102 HE7	342	Squilla chydea	15.23	1.07	12.86	2.87*	0.98*	2.0	1899.4
4512 HE5	343	Squilla chydea	18.10	0.08	2.15	4.63*	0.75*	8.0	2042.0
4104 HE4	362	Squilla empusa	1.42*	0.26*	8.07*	2.43*	0.61*	2.2*	1938.3*
4106 HE5	363	Squilla empusa	6.03	2.04	22.80	3.11*	0.65*	2.3	4557.1
4108 HE9	364	Squilla empusa	1.43*	0.17*	9.9()*	1.27*	0.35*	3.0*	637.9
4920 HE6	365	Squilla empusa	1.53	0.32	5.71	1.24*	0.47*	5.0*	2405.1
4102 HE5	368	Squilla empusa	1.26	0.01	7.23	1.50*	0.71*	6.2*	478.7

#### Summary Tabulation of Hydrocarbon Analyses - Post Drilling Rig Monitoring

A = odd/even ratio

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B = isoprenoid/n-alkane ratio

C = branched/n-alkane ratio

 $F = total aliphatics, \mu gm/gm$ 

G = total unsaturates, µgm/gm

D = pristane/phtane ratio

\* Data obtained from FFAP column

E = pristane/n-heptadecane ratio

#### Appendix V

Recommendations for further studies:

 Collect and analyze sufficient replicates of each species of organism to allow meaningful statistical analysis of the data and to give a representative hydrocarbon composition of each species.

2. Determine seasonal variations, if any, in hydrocarbon compositions of organisms.

3. Identify by GC-MS the important biological hydrocarbons present in organisms.

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#### Appendix VI

Works in progress:

1. "Effect of drilling operations on the hydrocarbon content of crustaceans", to be presented at and published in the proceedings of the Symposium on the Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms, Seattle, November 10-12, 1976.

(No other works are in progress, although more are certain to be done. The investigators are frankly overwhelmed at present by the mountain of data generated by this project!)

