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# 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 n-alkane of $\mathrm{nC}_{17}$ 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
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 $\underline{n}$-alkanes in the high molecular weight range. These n-alkanes fall into a pattern that is distinctly terrestrial. The low molecular weight alkanes are distributed in a manner resembling very weatrered 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 197576 and 21 from the third sampling period have been analyzed. Chromatograms

Table 1
Sample Status Sheet
$\left.\begin{array}{ccccc}\text { Kind of Sample } & \begin{array}{c}\text { No. Samples } \\ \text { Received }\end{array} & & \begin{array}{c}\text { No. Samples } \\ \text { Completed }\end{array} & \end{array} \begin{array}{c}\text { No. Samples } \\ \text { in Progress }\end{array}\right)$
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 $2 a-c$ 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 hvdrocarbons. The aliphatics predominantly are non-normal alkanes consisting of branched-cyclic-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 197576, 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

Table 2 Gravimetric Data of Sediments, First Sampling Period

| Staたion :iumber | Iry Meisht <br> Sediment (g) | Percent Carbonate | ```Pcrcert Org. Carbon (Acidi- fied Basis)``` | $\begin{aligned} & \text { Lipid } \\ & \text { Weight (g) } \end{aligned}$ | Aliphatic <br> Weight (g) | Arcmatic <br> Weight (g) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 2052 | 94.1 | 1.96 | 0.20050 | 0.00359 | 0.00324 |
| 2 | 3432 | 3't. 1 | 0.19 | 0.20825 | 0.00311 | 0.00354 |
| 3 | 741 | 68.3 | 0.70 | 0.03588 | 0.00072 | 0.00050 |
| 4 | 1654 | 98.4 | 3.31/3.01 | 0.18158 | 0.00147 | 0.00278 |
| 5 | 2686 | 98.1 | 7.50 | 0.06612 | 0.00078 | 0.00204 |
| 6 | 2510 | 96.5 | 7.20 | 0.16200 | 0.00220 | C.00235 |
| 7 | 2525 | 47.6 | 0.40 | 0.13092 | 0.00364 | 0.00297 |
| 8 | 2688 | 8́. 2 | 2.00 | 0.35283 | 0.00398 | 0.00580 |
| 9 | 2730 | 86.0 | 1.86 | 0.36025 | 0.00311 | 0.00516 |
| 10 |  |  |  |  |  |  |
| 12 | 2404 | 97.2 | 6.82 | 0.24292 | 0.00189 | 0.00251 |
| 12 | 1941 | 92.9 | 4.80 | 0.20917 | 0.00239 | 0.00208 |
| 13 | 897 | 87.6 | 1.24 | 0.16417 | 0.00142 | 0.00110 |
| 14 |  |  | . . |  |  |  |
| 15 |  |  |  |  |  |  |
| :6 | 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 |
| 29 | 2531 | 21.6 | 0.15 | 0.09050 | 0.00152 | 0.00139 |
| 20 | 2303 | 71.1 | 0.32 | 0.04442 | 0.00106 | 0.00131 |
| . 21 | 2243 | 53.6 | 0.40 | 0.08425 | 0.00225 | 0.05242 |
| 22 | 2000 | 51.3 | 0.36 | 0.30800 | 0.00807 | 0.00339 |
| 23 | 1827 | 50.6 | 2.07 | 0.24442 | 0.00095 | 0.60350 |
| 24 | 1962 | 8.8 | 0.06 | 0.02175 | 0.00083 | 0.00051 |
| 25 | 1502 | 11.5 | 0.05 | 0.01788 | 0.00079 | 0.00063 |
| 26 | 2416 | 61.2 | 0.57 | 0.12308 | 0.00128 | 0.60174 |
| 27 | 1579 | 80.5 | 2.96 | 0.19667 | 0.00244 | 0.00307 |

Table 2a (Cont'd)


Table 2b

| Station Number | $\frac{\text { Lipid }}{\frac{\text { Acid. Sed. }}{(\mathrm{ppm})}}$ | $\frac{\text { Llpid }}{\frac{\text { Total }}{(\mathrm{ppm})} \text { Sed. }}$ | $\begin{aligned} & \frac{\text { Lipid }}{\text { Org. Carbon }} \\ & (\%) \end{aligned}$ | $\frac{\text { Total HC }}{\text { Lipid }}$ $(\%)$ | $\frac{\text { Aliph HC }}{\text { Arom } \mathrm{HC}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |
|  | 3570. | 101. | 5.2 | 1.81 | 0.75 |
| 12 | 1514. |  | 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 | 0.9 |
| 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 | 1.20 |
| 26 | 13.1 | 50.9 | 2.3 | 2.45 | 0.74 |
| 27 | 638. | 125. | 2.2 | 2.80 | 0.80 |

Table 2b (Cont'd)

| $\begin{aligned} & \text { ation } \\ & =j a r \end{aligned}$ | $\frac{\text { Lio1d }}{\substack{\text { Acid. } \\(p p m)}}$ | $\frac{\text { Lip1d }}{\frac{\text { Total Sed }}{(p p m)}}$ | $\frac{\text { Lipid }}{\text { Org. Carbon }}$ | $\frac{\text { motal } \mathrm{HC}}{\text { Lipid }}$ <br> (\%) | $\frac{\text { Alioh HC }}{\text { Arom HC }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 28 | 212. | 74.3 | 5.3 | 2.17 | 1.53 |
| 29 | 310. | 68.4 | 4.61 | 1.64 | 1.92 |
| 30 | 164. | 39.8 | 3.4 | 3.11 | 0.84 |
| 31 | 595. | 54.9 | 3.5 | 2.64 | 0.90 |
| 32 | 141. | 27.3 | 1.6 | 7.98 | 0.51 |
| 33 | 87.9 | 49.2 | 2.6 | 2.09 | 0.87 |
| 34 | 253. | 17.1 | 1.1 | 6.77 | 0.98 |
| 35 | 1840. | 483. | 4.5 | 1.25 | 1.19 |
| 35 | 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 | 57.3 | 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 | 255. | 59.7 | 3.2 | 5.04 | 1.11 |
| 45 | 1074. | 108. | 3.4 * | 4.75 | 1.05 |

Table 2c

| Station <br> Sumber | $\frac{\text { Aliph HC }}{\substack{\text { Acid. Sp } \\(p p m)}}$ | $\frac{\text { Aliph HC }}{\text { Tot. Scd. }} \underset{(\mathrm{ppm})}{ }$ | $\frac{\text { Aliph HC }}{\substack{\text { Org } \\(\%)}}$ | $\frac{\text { Aliph HC }}{\text { Lipid }}$ <br> (\%) | $\frac{\text { Arom HC }}{\underset{(\mathrm{ppm})}{\text { Acid.Sed. }}}$ | $\frac{\text { Arom } \mathrm{HC}}{\underset{\substack{\text { Total Spm })}}{\text { Sed. }} .}$ | $\frac{\text { Arom HC }}{\text { Org. Carbon }}$ <br> (\%) | $\frac{\text { Aror. HC }}{\text { Lipid }}$ <br> (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |
| 19 | 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 | 0.53 | 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 |


| Station siumber | $\frac{\text { Aliph HC }}{\substack{\text { Acid. Sed } \\(\mathrm{ppm})}}$ | $\frac{\text { Aliph HC }}{\substack{\text { Tot. Sed. } \\(p p m)}}$ | $\frac{\text { Aliph HC }}{\text { Org. Carbon }}$ <br> (\%) | $\frac{\text { Aliph HC }}{\text { Lipid }}$ <br> (\%) | $\frac{\text { Arom HC }}{\text { Acid. Sed. }}$ | $\frac{\text { Arom } H C}{\text { Total Sed. }}$ | $\frac{\text { Arom HC }}{\substack{\text { Org. Carbon } \\(\%)}}$ | $\frac{\text { Arom HC }}{\text { Lipid }}$ <br> (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 28 | 2.79 | 0.98 | 0.07 | 1.31 | 1.82 | 0.64 | 0.05 | 0.86 |
| 29 | 3.33 | 0.74 | 0.05 | 1.08 | 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 | 2.52 |
| 38 | 8.88 | 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 | 2.33 |
| 45 | 26.3 | 2.63 | 0.08 | 2.45 | 24.3 | 2.40 | 0.08 | 2.30 |

Table 3

Gravimetric Data, Ord Period Baseline Sediment Samples

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 \#lo, 14 and 15 fit neatly into the patterns found in the remainder of Transects II and III. At Station \#10 (\#57 in 1974-75) alo. g Transect II the predominent peak is that cluster around Kovats Index 2075. The n-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 n-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 \#l5 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 ca K.I. 2800. The two samplings in 197576 (also \#3l) do not show this peak. Several replicate analysis checks in our laboratory have produced an erratic peak in this region. We believe that
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 $\underline{n}$-alkanes. The $H \pi N$ region of $\underline{n}$-alkanes shows a notable odd/ even preference indicating the presence of some terrestrial material. With the possible exception of the extraneous peak at ca 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 HTW 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 \#l 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 comnounds above $C_{31}$ provides sufficient proof that these peaks are not artifacts or laboratory contaminants.

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

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

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 $\mathbb{H R W} \underline{n}$-alkanes with a strong odd/even preference again suggests a terrestrial source of hydrocarbons on the outer edge of the shelf. The LMW $\underline{n}$-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 \#T 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 FMW'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 FMW 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 n-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 n-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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-17-
$$

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

-21-

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

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 $\underline{n}$-alkanes in the LMW region. Figure 5 shows the similarity of the first and third period and points out the terrestrial nature of the HIW n-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 LMN n-alkanes and a shift to a very decided odd/even dominance in the HTW region implying terrestrial sources of input. Noted here is a suite of n-alkenes of ca one fifth the concentration of the corresponding n-alkanes.

The 2075 peak, still in evidence, is at about the same concentration level as $\mathrm{C}_{29}$ in both periods at Station \#36 but falls short of $\mathrm{C}_{2} 9$ 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 n-alkanes seem to indicate some pollution; the FMW, n-alkanes reflect a terrestrial source so commonly seen in the Mississippi sediments with a dominance of $\mathrm{C}_{27}, \mathrm{C}_{29}$ and $\mathrm{C}_{31}$. 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 $\underline{n}$-alkanes and the petro-

Figure 5. Aliphatic gas chromatograms (FFAP) of Station 27 aliphatics from period 1 (above) and period 3 (below) 1975-76.
-26-

Figure 6. Aliphatic gas chromatograms (FFAP) of Station 36 aliphatics from period 1 (above) and period 3 (below) 1975-76.

$\frac{\dot{7}}{\dagger}$
-28- -

Figure 7. Aliphatic gas chromatograms (FFAP) of Station 37 aliphatics from period 1 (above) and period 3 (below) 1975-76.


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.

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

Though there is considerable difference in aliphatic weights at Stations \#l, 13, 27 and 37 for the two collections, the n-alkane/aliphatic ratio remains virtually constant indicating that the difference is more lively due to sampling variability than contamination. This ratio is remartably 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 gereral, the ratios show less variability than gravimetric concentrations.

Station \#4 is rotable in that LMW n-alkanes are ca $75 \%$ higher compared to $2 \pi$ material in the third period. However at Station \#38 the ratio of LW/EN was four times higher in the third period. This probably resulted from lakoratory 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 n-alkanes is higher in the first period. This being a terrestrial component probably reflects the natural variability in sampling.

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

Table 4
Compariaon of lat Period with 3rd Period - Chromatographic Parameters 1975-1976

| Sample |  | ppb dry wt. sed* |  |  | $\frac{\% \sum n-a l k}{2 a l i p h}$ | $\frac{\Sigma C \leq 20}{\Sigma C \geq 21}$ | Odd/Even |  |  | $\frac{\text { Zn-a1k }}{\underline{n} \text {-C16 }}$ | $\frac{15+17}{2 \times 16}$ | $\begin{gathered} \text { Pris/ } \\ 17 \end{gathered}$ | $\frac{\text { Prist?hy }}{\Sigma_{\underline{E}}-a i x}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\overline{\text { Allph }}$ | n-alk | Arom |  |  | $\bar{C} \leq 20$ | $C \geqslant 21$ | AII |  |  |  |  |
| \$1 | 1st per | 735. | 64. | 119. | 8.7 | 1.43 | 4.9 | 3.2 | 3.6 | 40.2 | 6.7 | 0.10 | 0.037 |
|  | 3rd per | 1021. | 87. | 110. | 8.5 | 1.6 .4 | 4.6 | 2.4 | 3.4 | 63.6 | 13.4 | 0.05 | 0.022 |
| 4 | 1st per | 129. | 15. | 372. | 11.4 | 1.17 | 1.7 | 3.1 | 2.3 | 22. | 2.0 | - | 0.03 |
|  | 3rd per | 111. | 12.2 | 108. | 11.0 | 1.88 | 1.4 | 1.9 | 1.5 | 30.4 | 3.8 | 0.22 | 0.09 |
| 06 | lst per | 150. | 30. | 68. | 19.1 | 0.17 | 1.5 | 3.9 | 3.8 | 133. | - | 0.70 | 0.027 |
|  | 3rd per | 174. | 39.1 . | 61. | 22.5 | 0.16 | 1.2 | 2.8 | 2.7 | 109. | 1.5 | 0.57 | 0.024 |
| 17 | 1st per | 561. | 68. | 30. | 7.0 | 0.46 | 2.5 | 2.1 | 2.2 | 36.7 | 2.6 | 0.62: | 0.168 |
|  | 3rd per | 417. | 30.7 | 151. | 7.4 | 0.35 | 2.5 | 2.1 | 2.4 | 52.3 | 3.9 | 0.92 | 0.169 |
| 410 | 3rd per | 297. | 24. | 73. | 8.1 | 0.28 | 2.4 | 1.9 | 2.2 | 91.7 | 6.7 | 0.24 | 0.052 |
| $\$ 12$ | 1 lst per | 242. | 55. | 50. | 26. | 0.19 | 1.0 | 4.0 | 2.5 | 15.4 | 0.87 | 0.75 | 0.02 |
|  | 3rd per | 217. | 58. | 104. | 27.0 | 0.09 | 1.4 | 2.9 | 3.1 | 166. | 1.1 | 0.58 | 0.016 |
| 013 | 1st per | 397. | 116. | 88. | 29. | 0.2 | 0.8 | 2.3 | 1.9 | 42.6 | 1.1 | 0.45 | 0.028 |
|  | 3rd per | 197. | 54.8 | 73. | 27.8 | 0.17 | 1.0 | 3.1 | 2.6 | 50. | 1.1 | 0.63 | 0.032 |
| 114 | 3rd per | $5: 8$. | 36. | 171. | 6.9 | 0.21 | 1.3 | 2.3 | 2.5 | 93.3 | 2.45 | 0.50 | 0.054 |
| 015 | 3rd per | 234. | 27.7 | 137. | 11.8 | 0.64 | 2.1 | 3.1 | 2.4 | 25. | 2.2 | 0.21 | 0.06 |
| 018 | lst per | 136. | 6. | 6. | 4. | - | - | - | - | - | - | 0.82 | - |
|  | 3rd per | 130. | 9. | 40. | 6.8 | 1.5 | 3.9 | 1.7 | 2.6 | 40. | 8.6 | 0.55 | 0.21 |
| \% 24 | $1 s t$ per | 120. | 14. | 37. | 11.2 | 1.1 | 1.3 | 3.0 | 2.8 | 15. | 1.9 | 0.29 | 0.20 |
|  | 3rd per | 165. | 20. | 35. | 12.3 | 0.85 | 1.5 | 2.3 | 2.2 | 40. | 4.0 | 0.16 | 0.12 |

*Measured gas chromatographically

Table 4
Comparison of list Period with 3rd Period - Chromatographic Parameters 1975-1976

*!measured gas chromatographically

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 n-alkanes from $C_{15}$ to $C_{23}$. In this range $C_{17}$ typically constitutes the majority of the $\underline{n}$-alkanes. Also present in many of the specimens is a series of $\underline{n}$-alkenes of oddcarbon number. In some cases a series of n-alkanes from $\mathrm{C}_{20^{-C}} \mathrm{C}_{33}$ 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 algre does not clarify this condition noted in earlier collections. About the most that can be said for algal hydrocarbons

Table 5a

Benthic Algae 1975-1976. Chromatographic Parameters


Table 5a

## Benthic Algae 1975-1976. Chromatographic Parameters



Table 5b
Benthic Algae 1975-1976. Chromatographic Paraneters


Table 5b
Benthic Algac 1975-1976. Chromatographic Parameters

| Sample | $\begin{aligned} & \text { Series of hmw } \\ & \text { n-alk, CPI } 1 \end{aligned}$ | $\begin{aligned} & \text { Unidentified } \\ & \text { series, K.I. } \\ & 1712,21 i 7, \\ & 2320,2524 \end{aligned}$ | $\begin{aligned} & \text { Phytadienes } \\ & 1928,1957, \\ & 1984,2011 \end{aligned}$ | Sample Polluted? |
| :---: | :---: | :---: | :---: | :---: |
| IVA-A-6 | Yes, 1/16 of n-C17 | No | Yes, 14.5 ppm | V. sifghtly, if at all |
| V-A-A-12 | No | No | No | No |
| İA-A-17 | Yes, 1/10. of $\underline{n}-\mathrm{Cl} 17$ | No | No | No |
| 062-A-1 | No | No | Yes, 0.5 ppm | No |
| 054-A-9 | No | No | Yes, 0.3 ррм | No |
| 04:- | So | No | Yes, 10 ppm | No |
| 145-A-1 | Yes (hard to measure) | No | Yes, 5 ppm | Yes definitely (Lots of 1 unresolved material) |
| 147-A-2 | No | Yes | No | No |
| 151- ${ }^{\text {- }} 1$ | No | No | Yes, 3 ppm | No |
| 24i-A-27 | Yes, 1/12 of n-C17 | No | Yes, 2.5 ppm | Yes definitely (Lets of unresolved material) |
| 25i-A-10 | so | No | Yes, 1.8 ppm | No C22-C30 |

Table 5c


Table 5c

| Sample ${ }^{\text {\% }}$ | $\begin{aligned} & \quad \begin{array}{l} \text { Pris+Phy/ } \\ \text { n-ali } \end{array} \end{aligned}$ | $\begin{gathered} E \\ \text { Pris/ } \\ \underline{n}-C 17 \end{gathered}$ | $\begin{aligned} & \text { Phy/ } \\ & \text { n-C18 } \end{aligned}$ | ic Als 1) Pris/ Phy | $\begin{gathered} 975-1976 \\ \frac{n-a 1 k /}{n-c 16} \end{gathered}$ | $\begin{gathered} \text { omatograph } \\ \% \frac{n^{\prime}-a 1 k /}{\hat{A} 11 p h} \end{gathered}$ | ranete <br> 1 odd/ <br> Even | $\begin{aligned} & \text { C10-C20 } \\ & \text { Odc/Even } \end{aligned}$ | $\begin{aligned} & \text { C21-C31 } \\ & \text { Odd/Even } \end{aligned}$ | $\begin{aligned} & \text { C12-C20/ } \\ & \text { C21-C31 } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |
| 11A-A-17 | 0.014 | 0.017 | - | - | 201. | 73.7 | 11.9 | 21.5 | 2.4 | 13.9 |
| 052-A-: | 0.020 | 0.014 | 0.4 | 1.4 | 278. | 77.0 | 17.4 | 36.3 | 1.3 | 15.2 |
| 054-A-9 | - | - | - | - | 1000. | 94.0 | - | - | - | v. large |
| 047-A-25 | 0.002 | 0.002 | 0.0 |  | 630. | 60.2 | 44.9 | 41.8 | 1.7 | 74.0 |
| 145-A-1 | 0.002 | 0.002 | 0.0 | - | 590. | 59.0 | - | 45.9 | - | 28.4 |
| 14i-A-2 | 0.003 | 0.004 | 0.0 |  | 571. | 61.2 | 23.9 | 61.1 | 4.7 | 7.8 |
| 151-8.1 | 0.021 | 0.001 | 0.0 |  | 759. | 85.0 | 45.4 | 60.7 | 0.5 | 52.7 |
| 247-A-27 | 0.007 | 0.005 | 0.3 | 1.4 | 338. | 57.6 | 23.7 | 51.3 | 0.9 | 12.6 |
| 251-A-10 | 0.001 | 0.002 | 0.0 | - | 760. | 85.0 | 50.0 | 75.0 | 2.4 | 44.0 |

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 Cauleroa sertularoides was collected in more than one period and then not at ti:e 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 pericas. Again only two species were sampled twice. In one instance, Codium repens from the first period shows no pollution but in the second period is very definitely polluted. The Halimeda discoidea 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
(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. FFAF, being a modified Carbowax, we felt should give results similar to Carbowax.

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

Additional idertification of the phytadienes was provided by subJecting pure phytol to Activity I alumina and silica gel chromatography. Four peaks between K.I. 1900 and 2000 resulted in the hexane and benzene fractions. The total weight ratios were ca 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 Colium spp. collected. No great differences are noted in the overall characteristics of these specimens. $C_{17}$ is the major $\underline{n}-a l k a n e$ with some lesser amounts of $C_{15}$ and pristane. Three of the Codium spp. have a look of pollution with weathered oil.

Table 6
Phytadienes in Algal Extracts

```
Sample
```

Total $\mu \mathrm{g}$ of ${ }_{1} \quad$ Total $\mu \mathrm{g}$ of phytane phytadienes ${ }^{1}$ after hydrogenation

Caulerpa sp.

| IIIA-A-10 lipid $^{2}$ | 74 | 208 |
| :--- | ---: | :--- |
| IIIA-A-10 aliphatics |  |  |

Eucheuma sp.

| IIA-A + B- 3 lipid $^{2}$ | 193 | 247 |
| :--- | ---: | ---: |
| IIA-A+B-3 aliphatics |  |  |
|  | 136 | 96 |

Phytol treated with
$\begin{array}{lll}\text { alumina-silica } \operatorname{gel}^{3} & 22 & 12.6\end{array}$

$2_{\text {Weights }}$ are calculated to represent the same initial weight of alga.
$3^{3}$ Phytol treated was 50 times greater than would normally be found in the weight of algae analyzed for this experiment.
-45-


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 riaht) token from Caulerda sp.


Figure 9b. Phytadienes in Algae. The FFAP gos chromatograms are of lipids before hydrogenation (upper left), after hydrogenation (lower left), aliphatics before hydrogenation (upper right), and ofter hydrogenation (lower right) token from Euchemo sp.

Phytadienes occur only in the unidentified species of Caulerpa. 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 Gracilaria srp. All four samples have phytadienes and contain a series of HMW n- alkanes with no odd/even preference.

As found in the Caulerpa, Halimeda sp. have the homologour series of compounds following the odd-C n-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 $C_{17} \quad C_{19} \quad C_{23} \quad C_{25}=C_{15}=C_{21}$.

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

Neither Dictyota sp. contain the phytadienes and as reported in the literature, $\mathrm{C}_{15}$ is the dominant aliphatic hydrocarbon.
$-48-$

RFFFRETINCE
[Blumer M. and Thomas D. (1965) Science 147: 148-149.]

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 l-3. At first glance it would appear that there exists quite a diversity of samples in this $3.14 \mathrm{~km}^{2}$ 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.

Figure 1. Rig sample station layout.
Station 1 is located at the rig site (Lat: $27^{\circ} 37^{\prime} 13.87^{\prime \prime}$
Long: $96^{\circ} 57^{\prime} 55.17^{\prime \prime}$ ) off Mustang. Island, Texas. Stations 2-9 are located 100 m from the center; $10-17,500$ meters from the center and $18-25,1000$ meters from the center. The "spoke" angles are $45^{\circ}$.


Table 1

## Gravimetric Data of Rig Sediments Before Drilling

| tion | Sediment dry wt. (g) | Tot. Lipid Wt. (g) | $\begin{aligned} & \text { Tot. Aliph. } \\ & \text { HC Wt. (g) } \end{aligned}$ | Tot. Arom. HC Wt. (g) | $\frac{\text { Lipid Wt. }}{\substack{\text { Tot. } \\(\mathrm{ppm})}}$ | $\frac{{ }^{\%}}{\text { Tot. HC Wt. }}$ | $\frac{\text { Alıph. HC Wt. }}{\text { Arom. HC Wt. }}$ | $\frac{\text { Allph. HC }}{\text { Tot. Sed. }}$ | $\frac{\text { ZAl1ph. } H C}{\text { Lipid }}$ | $\frac{\text { Arom. HC }}{\text { Tot. Sed. }} \begin{gathered} \text { (ppm) } \end{gathered}$ | $\frac{\text { Arom. HC }}{\text { Lipid }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| -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 | 17.5 | 8.20 | 2.13 | 1.00 |
| -510301 | 192 | 0.050 | 0.0031 | 0.0012 | 260 | 8.60 | 2.58 | 16.1 | 6.20 | - 6.25 | 2.40 |
| -510401 | 323 | 0.050 | 0.0047 | 0.0024 | 155 | 14.2 | 1.96 | 14.5 | 9.40 | 7.43 | 4.80 |
| -510501 | 261 | 0.075 | 0.0040 | 0.0015 | 287 | 7.33 | 2.67 | 15.3 | 5.33 | 5.75 | 2.00 |
| -510601 | 242 | 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 | $6.57^{\circ}$ | 2.20 |
| -510901 | 423 | 0.150 | 0.0055 | 0.0029 | 355 | 5.60 | 1.90 | 13.0 | 3.66 | 6.85 | 1.93 |
|  | No Sample | e 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 | . 2.46 | 32.8 | 9.83 | . 13.3 | 4.00 |

Table 2

## Gravimetric Data of Rig Sediments During Drilling



Table 3
Gravimetric Data of Rig Sediments After Drilling

| ation | ```Sediment dry wt. (g)``` | $\begin{gathered} \text { Tot. Lipid } \\ \text { Wt. (g) } \end{gathered}$ | Tot. Aliph. HC Wt. (8) | Tot. Arom. HC Wt. (g) | $\frac{\text { Lipid Wt. }}{\substack{\text { Tot. } \\(\mathrm{ppm})}}$ | $\frac{\text { Tot. }_{\text {\% }}^{\text {HC Wt. }}}{\text { Lipid Wt. }}$ | $\frac{\text { Aliph. HC Wt. }}{\text { Arom. HC Wt. }}$ | $\frac{\text { Aliph. HC }}{\substack{\text { Tot } \operatorname{Sed})}}$ | $\frac{\text { Z Aliph. HC }}{\text { Lipid }}$ | $\frac{\text { Arom. HC }}{\text { Tot. Sed. }} \begin{gathered} \text { (ppm) } \end{gathered}$ | $\frac{\stackrel{\%}{\%}}{\text { Arom. HC }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 | 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 Sample | e Received | at \#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


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 vs percent clay and vs percent silt were calculated: aliphatics (ppb), aromatics ( ppb ), n-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
-56-

Table 4
Average Amounts of Carbonate and Organic Carbon for Rig Monitoring Samples

collection or activities in the area but only the natural yariability 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 ca the $n-C_{29}$ compound.

The resolved material of each chromatogram consists primarily of high molecular weight (HMW) n-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) n-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 LMW n-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 $I M W$ n-alkanes are at the same level of concentration as the HMW n-alkanes. The odd/even preference appears unchanged but pristane and phytane levels are the same as in other

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 ( $0 / E$ ) preference in the high molecular weight range of $n$-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 ca $1.5 x$ larger than $C_{17}$.

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 n-alkanes have not yet been preferentially consumed by bacteria. As found in the purely marine samples of the Florida shelf, $\mathrm{C}_{17}$ is the dominant component of the LMW n-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 n-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

Table 5
K.I. 2070-2140 Complex in Rig Samples

| Station | K.I. $2070 / \mathrm{C}_{29}$ |  |  | K.I. $2140 / \mathrm{C}_{29}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Before | During | After | Before | During ${ }^{\text {g }}$ | After |
| 500101 | 0.71 |  | 1.0 | 0.82 |  | 0.7 |
| 510201 | 1.2 | 0.61 | 2.1 | 2.6 | 1.2 | 2.3 |
| 510301 | 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 |
| 510501 | 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 |
| 510701 | 0.6 | 0.63 | 0.64 | 2.1 | 0.76 | 0.57 |
| 510801 | 1.0 | 0.90 | 1.6 | 2.7 | 1.6 | 2.6 |
| 510901 | 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 |
| 551301 | 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 |
| 551501 | 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 |
| 592101 | 0.97 | 1.2 | 0.63 | 2.0 | 1.3 | 0.52 |
| 592201 | 0.71 | 1.3 | 2.3 | 1.2 | 1.2 | 1.9 |
| 592301 | 1.0 | 1.3 |  | 3.0 | 1.4 |  |
| 592401 | 0.9 | 1.4 | 1.2 | 1.5 | 1.4 | 1.4 |
| 592501 | 1.0 | 1.1 | 2.2 | 0.27 | 1.2 | 2.7 |

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.

## 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 n-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 n-alkanes with just slight changes resulting in dramatic changes in this ratio. Therefore a large change such as that encountered in the addition of $L M W-r i c h ~ o i l ~ p r o b a b l y ~ w o u l d ~ c r e a t e ~ a n ~ \underline{n}-a l k a n e / C_{16}$ value well outside the natural variability of this parameter. E.g. the three

Table 6
Ris Monitoring－Before Drilling－Chromatographic Parameters

| Sample | Allph ${ }^{\text {ppb }}$ | dry wt．$s$ n－alk | Arom | $\frac{P_{r i s}+P h y}{n-a l k}$ | $\frac{\text { Pristane }}{C_{17}}$ | $\frac{\text { Phytane }}{c_{18}}$ | $\frac{\text { Pristane }}{\text { Phytane }}$ | $\frac{n-a l k}{n-c I 6}$ | $\frac{\% n f a l k}{\text { Aliph }}$ | Total Odd Even | $c \leq 20 \frac{\text { sedd }}{\text { even }}$ | $C \geq 21 \frac{\mathrm{edd}}{\text { even }}$ | $\frac{C-20}{C=2!}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| HS1－500102 ${ }^{\text {SOX }}$ | 1252. | 630. | 610. | 0.031 | 1.1 | 0.43 | 3.9 | 130 | 50. | 4.3 | 1.3 | 4.6 | 0.09 |
| HSI－510201 | 3100．＊ | 540. | 520. | 0.046 | 1.6 | 0.88 | 3.5 | 150 | 17．＊ | 1.9 | 1.5 | 1.7 | 0.15 |
| YS 1－510301 | 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 |
| ：531－510501 | 2530. | 690. | 650. | 0.036 | 1.4 | 0.75 | 3.8 | 150 | 26. | 3.3 | 1.6 | 3.3 ． | 0.11 |
| п゙S：－512502 | 1200．＊ | 350. | 370. | 0.072 | 1.8 | 0.88 | 3.6 | 140 | 20．＊ | 2.6 | 1.4 | 2.6 | 0.16 |
| ES1－5iC701 | 320. | 69. | 66. | 0.041 | 1.7 | 1.1 | 4.3 | 170 | 22. | 2.6 | 1.7 | 2.4 | 0.12 |
| ごS1－510ço | 1300. | 330. | 490. | 0.06 | 1.8 | 0.86 | 4.0 | 100 | 25. | 2.8 | 1.8 | 2.5 | 0.15 |
| 2S：－510001 | 770. | 330. | 570. | 0.036 | 1.6 | 0.87 | 3.9 | 170 | 42. | 2.7 | 1.3 | 2.9 | 0.11 |
| 13S1－551101 | 1360. | 480. | 290. | 0.044 | 1.2 | 1.0 | 3.7 | 170 | 35. | 3.9 | 1.9 | 4.0 | 0.12 |
| HS1－55：201 | 3500. | 970. | 1400. | 0.04 | 1.8 | － 0.77 | 4.6 | 220 | 28. | 2.4 | 1.5 | 2.5 | 0.13 |
| H51－551321 | 1800. | 650. | 610. | 0.048 | 1.1 | 0.49 | 3.8 | 120 | 36. | 3.3 | 1.3 | 3.8 | 0.15 |
| 1．51－551401 | 930. | 640. | 190. | 0.010 | 1.4 | － 0.89 | 3.8 | 2700 | 68. | 3.7 | 1.8 | 3.5 | 0.03 |
| 1．3：－55：501 | 920. | 410. | 800. | 0.028 | 1.5 | 0.63 | 3.8 | 200 | 45. | 3.2 | 1.2 | 3.5 | 0.11 |
| HE1－5j1601SOX | 1800. | 420. | 280. | 0.028 | 1.3 | 1.1 | 3.0 | 200 | 23. | 4.9 | 2.0 | 4.9 | －0．10 |
| ： 5 1－551701 | 770. | 380. | 300. | 0.013 | 1.5 | 0.73 | 3.6 | 640 | 49. | 4.0 | 1.6 | 3.8 | 0.05 |
| ： $51-591301$ | 1300. | 700. | 310. | 0.013 | 1.4 | 0.71 | 4.0 | 720 | 52. | 4.2 | 2.1 | 3.9 | 0.05 |
| ！Si－59193⿺SCX | 340. | 140. | 72. | 0.049 | 1.9 | 1.2 | 1.5 | 580 | 42. | 4.1 | 1.5 | 4.1 | 0.12 |
| HS：－59200］ | 2600. | 910. | 510. | 0.033 | 1.8 | 0.59 | 4.5 | 220 | 36. | 2.6 | 1.2 | 2.3 | 0.10 |
| ES1－52210150X | 1860. | 610. | 1600. | 0.05 ． | 1.7 | － 1.1 | 3.4 | 300 | 33. | 3.7 | 2.0 | 3.6 | 0.14 |
| HS1－59220150X | 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 |
| بSS－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 | 2290. | 540. | 480. | 0.048 | 1.8 | 1.1 | 2.2 | 160 | 24. | 3.9 | 1.4 | 4.0 | 0.15 |
| Pange | 3500．－320． | 970．－69． | 1600．－66． | 0．072－0．010 | 1．9－1．1 | 1．2－0．43 | 4．6－1．5 | 90－2700 | 68．－17． | 4．9－1．9 | 2．4－1．2 | 4．9－1．7 | 0．28－0．03 |
| Yea： | 1400. | 480. | 560. | 0.038 | 1.5 | 0.81 | 3.7 | 370 | 36. | 3.4 | 1.6 | 3.5 | c．is |
| $\begin{aligned} & \text { Stanaa=d } \\ & \text { Deviation } \end{aligned}$ | $840 .$ | 230. | 390. | 0.016 | 0.24 | 0.20 | $0.6{ }^{\circ}$ | 530 | 12. | 0.8 | 0.3 | 0.8 | 0.04 |
| $\begin{aligned} & \text { Hear: } \pm \text { Std. Dev. } \\ & 100 \times \underset{\text { Span }}{ } \end{aligned}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Mean | $1400 \pm 60 \%$ | 480＋48\％ | 560＋70\％ | $0.038 \pm 42 \%$ | 1．5＋16\％ | $0.81 \pm 25 \%$ | $3.7 \pm 16 \%$ | 530＋140\％ | － $36 \pm 33 \%$ | 3．4＋24\％ | 1．6＋19\％ | $3.5 \pm 23 \%$ | $0.11 \pm 36 \%$ |
| Ranges，Means，Std．deviations，etc．do not include HS2－592301 values ＊＊not includirg what appear to be contaminant（phthalates？）peaks sca－Inciuced in caicuiations，these samples were soxhletted |  |  |  |  |  |  |  |  |  |  |  |  |  |

Table 7
Rig Monitoring - During Drilifing - Chromatographic Parametars


Table 8
Rig Monitoring - After Drilling + Chromatographic Parameters

samples in the "after" phase which have unusually large amounts of LMW n-alkanes at Stations \#13, 21 and 25 have very low n-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.

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 0m
B. after drilling sample at 0 m


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Figure 4. Cluster group plot of samples 100 m 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 100 m
B. all during drilling samples at 100m
C. all after drilling samples at 100 m


Figure 5. Cluster group plot of samples 500 m 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 500 m
B. all during drilling samples at 500 m
C. all after drilling samples at 500m


Figure 6. Cluster group plot of samples 1000 m 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 1000 m
B. all during drilling samples at 1000m
C. all after drilling samples at 1000 m


Pigure 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 0 m
B. after drilling sample at 0m
C. all before drilling samples at 100m
D. all during drilling samples at 100 m
E. all after drilling samples at 100 m
F. all before drilling samples at 500m
G. all during drilling samples at 500m
H. all after drilling samples at 500m
I. all before drilling samples at 1000 m
J. all during drilling samples at 1000 m
K. 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 $100 \mathrm{~m}, 500 \mathrm{~m}$ 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 $100 \mathrm{~m}, 500 \mathrm{~m}$ 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 $/ \mathrm{C}_{18}$ 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
```

| Distance <br> from Rig | DF1 | DF2 | F Ratio |
| :---: | :---: | :---: | :---: |
| 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 entanced.

Gravimetric Data
API Oils
Intercalibration

|  | Total <br> Lipid | Total Aliphatics | Total Aromatics | Total <br> Polar Lipids | $\frac{\text { Aliphatics }}{\text { Total Lipid }}$ | $\frac{\text { Aromatics }}{\text { Total Lipid }}$ | $\frac{\text { Polar Lipid }}{\text { Total Lipid }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Venezuelan Crude 1st Determination | 0.3800 g | 0.0992 g | 0.2054 g | 0.0538 g | 26.1\% | 54.1\% | 14.2\% |
| Venezuelan Crude 2nd Determination | 0.6700 g | $0.1497 g$ | 0.4070 g | 0.1258g | 22.3\% | 60.7\% | 18.7\% |
| Venezuelan Crude 3rd Determination | 0.4100 g | 0.1178 g | 0.2700 g | 0.0449g | 28.7\% | 65.9\% | 10.9\% |
| \#2 Fuel Oil | 0.4800g | 0.3293 g | 0.1200 g | 0.0474 g | 68.6\% | 25.0\% | 9.88\% |
| lst Determination \#2 Fuel Oil | 0.5262 g | 0.3381 g | 0.1624 g | 0.0358 g | 64.3\% | 30.8\% | 6.80\% |
| 2nd Detemmination <br> \&2 Fuel Oil <br> 3rd Determination | 0.4600 g | 0.3149 g | 0.1177 g | 0.0092 g | 68.5\% | 25.6\% | 2.00\% |
| Louisiana Crude 1st Determination | 0.65738 | 0.4066 g | 0.1384 g | 0.0420 g | 61.8\% | 21.1\% | 6.39\% |
| Louisiana Crude 2nd Determination | 0.3900 g | 0.2468g | 0.0764 g | 0.0384 g | 63.3\% | 19.6\% | 9.84\% |
| Louisiana Crude 3rd Determination | 0.4500 g | 0.3075 g | 0.0947 g | 0.0487 g | 68.3\% | 21.0\% | 10.8\% |


|  | $\begin{aligned} & \text { Total } \\ & \text { Lipid } \end{aligned}$ | Total <br> Aliphatics | Total <br> Aromatics | $\begin{gathered} \text { Total } \\ \text { Polar Lipids } \end{gathered}$ | $\frac{\text { Aliphatics }}{\text { Total Lipid }}$ | $\frac{\text { Aromatics }}{\text { Total Lipid }}$ | $\frac{\text { Polar Lipid }}{\text { Total Lipid }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Kuwalt Crude <br> 1st Determination | 0.6236 g | 0.2470 g | 0.2207g | 0.0599 g | 39.6\% | 35.4\% | 9.61\% |
| Kuwait Crude <br> 2nd Determination | 0.4344 g | 0.1887 g | 0.1628 g | 0.0909 g | 43.4\% | 37.5\% | 20.9\% |
| Kuwait Crude <br> 3rd Determination | 0.4077 g | 0.1943 g | 0.1525g | 0.0634 g | 47.6\% | 37.4\% | 15.6\% |

Table 2
Gas Chromatographic Parameters of Intercalibration


## 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) n-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 n-alkanes, the $[\mathbb{W}$-alkanes are present in lower concentrations in 1975 samples. A loss of all LMW alkanes (including oristane and phytane) with some greater loss of the n-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.

## 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 ca. 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
unassociated terrestrial organic debris. Correlation coefficients of 0.3077 and 0.4912 for aliphatics and aromatics vs 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 vs 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 alrae displayed little if any correlation with the presence of petroleum residues in the nearby sediments. The tyoes 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
in some samples. The benthic faunal samples analyzed by Philip Meyers also tended to display rather random inclusion of pollutants, in apreement with the benthic alpae 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 $A 2$, occurring between the $C_{19}$ and $C_{20}$ n-alkanes. Though minor components, their significance should not be overlooked. In tinis figure it may also be noted that the ratio of phytane $/ C_{18}$ is rather hish. This oil polluting indicator might imply a history of oil pollution except the pristane $/ C_{17}$ and pristane/phytane ratios are small. Dhis phenomenon was noticed in 1974 , but no explanation was offered. It is auite 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 $/ C_{18}$ ratios in this or other areas of no other perceivable evidence of oil Dollutants. 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 chronatogram from 1974. The Transect VI-Station 41 is taken fron the same location but in 1975.


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.



## APPENDIX A

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

ALIPHATIC.S HYISADCARISONS






OLM SEOTRENT- MS1 510701
4/21/76
altimatics hydrocarbons
retention time

| kovals | micnocrams |
| :---: | :---: |
| 1338. | 0.02 |
| $14 \mathrm{C3}$. | 0.03 |
| 1460. | 0.01 |
| 1501. | 0.17 |
| 1572. | 0.13 |
| 1060. | 0.22 |
| $1624^{\circ}$ | 0.11 |
| 1632. | 0.16 |
| 1074. | 1.21 |
| 1699. | 0.12 |
| 1118. | 0.03 |
| 1754. | 0.25 |
| 1719. | 0.28 |
| 1799. | 0.26 |
| 1851. | 0.62 |
| 1ess. | 0.15 |
| 1849. | 0.10 |
| 1859. | 0.69 |
| 1923. | 0.63 |
| 1969. | 0.69 |
| 1906. | 0.51 |
| 1970. | 0.36 |
| 2060. | 0.76 |
| $2 \mathrm{cs3}$. | 7.68 |
| 20 es. | 0.31 |
| 2046. | 2.47 |
| 2108. | 3.63 |
| 2160. | 21.40 |
| 2162. | 2.50 |
| 2167. | 1.68 |
| 22 CO . | 1.39 |
| 2226. | 2.24 |
| 2260. | 0.19 |
| 2299. | 1.56 |
| 2369. | 0.46 |
| 2366. | 0.40 |
| 24c0. | 1.80 |
| 2407. | 0.13 |
| 2500. | 2.96 |
| 2520. | 0.51 |
| 2353. | 0.95 |
| 2599. | 2.35 |
| 2634. | 4.01 |
| 2076. | 0.69 3.35 |
| 2734. | 0.31 |
| 2164. | 0.51 |
| 2798. | 2.42 |
| 2847. | 2.53 |
| 2899. | 9.11 |
| 2459. | 1.e4 |
| 3032. | 0.18 |
| 3059. | 1.40 |
| 3138. | 4.14 |
| 3109. | 2.22 |
| 3192. | 0.50 |
| 3220. | 5.17 |
| 3235. | 0.92 |
| 3278. | 2.03 |
| 3269. | 11.30 |
|  | 12.50 |
|  | 3.78 |
|  | 7.43 |
|  | 2.13 6.24 |

















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## EXECUYIVE SUMMARY

Transmissonetry measurements have been performod at seasoral intervals alone four transects in the Eastern Gulf of Veyico, rancine from Clearwater, florida to Mobile Bay. In summer and early fall of $19 \%$ most areas excert the vicinity of the Mississippi Delta showed ciear waters having upwards of $80 \%$ light transmission (coefficient of attradution less than $\alpha=0.22$ or roughly $<.2 \mathrm{mg} / \mathrm{h}$ 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, $19^{\prime 7} 6$ ) shelf waters were turbjd over long periods, due to repeated resusperision of fine fractions of bottom sediments owing to storms. Inshore shelf waters were vertically vell mixed to a considerable degree. Transmissivities of $50-60 \%$ ( $\alpha=0.7-0.5$ or about $0.5 \mathrm{mg} / \ell$ 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 frequentily 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-botton water were related to temperature, salinity and density anomalies interpreted as contour currents, which were enhanced ty the forcing functicn of the violent storm.

## INTROUUCTION

Suspended matter studies of anelytical or optiad character are limjed in the Gulf of Kexico in gencral and in the eastern Gulf in particuiar (Manheim, et al., 1972; Carder and Schlomer, 1973, and references cited). Generally speakirig 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 $l \mathrm{mg} / \ell$ 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 easterm 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
measurements were added to the study plan in order to provide recional 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 (SFM), mineralogy, particulate orfanic carbon, hydrocarbons, trace netals, and primiry productivity.

IU $u$ ing the first sampling season late ncgotiations, 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 Wite in maintaining the equipment in functioning ordex and to thank Tom Pyle, Ted White, J. E. Alexander and M. Rinkel for their special efforts and cooperations with the transmissometry


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 nore 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 or 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.


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


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

## METHODS

As pointed out by Tyler, et al. (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 colunns. 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 $5500 \AA$ ( 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:

$$
\frac{I}{I_{o}}=e^{-\alpha x}, \text { or } \alpha=\ln \frac{I}{I_{0}} \text { where } x=\operatorname{lm}
$$



## \% 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 (pyonocline).

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

[^0]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, dependjng 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.


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

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 $200 \mathrm{mg} / \mathrm{l})$ 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

[^1]

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


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


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


Fie. 10. Transect II., Season III. Note break in time.


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

-20-

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 serjes 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-bottorn nepheloid layer, apparently resulting from Hurricane EIOISE, was found at station 1207. This layer may have had a slight, semi-diu:nel 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 colunn 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 measurenents, if sufficient calibration points of SPM measurements are available. The


Fig. 14. 24 hour time series. Season II (Sept, 1975).


Fig. 15. 24 hour time series. Season III (Jan.-Feb, 1976).
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 SM in surface water of the lMFIA area has been prepared for the September, 1975 period (Ficure 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 $\mu \mathrm{g} / 1$, based on transmissometry and data of Betzer (1976)

Some seasonal trends can be easily seen by comparing figures $4-8$ with 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 ncphcioid 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


Fig. 17. Transmissometry traces for sumner, fall, and winter, Station 1101, off Clearwater Fla. a 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.
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 eviden: 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-bottorn 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 $1.58 / \mathrm{m}=\alpha$ or roughly $2.2 \mathrm{mg} / \mathrm{l}$ (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
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 downard 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 $2 l$ 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 botton 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 plunes, 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

TEMPERATURE ( $\left.{ }^{\circ} \mathrm{C}\right)$


Fig. 19. (Upper Figure) $\mathrm{T}^{\circ} \mathrm{C}, \mathrm{S}\left({ }^{\circ} / 00\right)$ and $\mathrm{T}(\%)$ profiles for a well, mixed water column. S. T data courtesy M. Rinkel.


Fig. 20. (Lower Figure) $T^{\circ} \mathrm{C}, \mathrm{S}(\% / 00)$ and $\mathrm{T}(\%)$ profiles for a partly stratiffed 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,


Fig. 22. 'Pransmissivity and tomperature distributions for Station IV. Winter Cruise, 1976. Note time break indicated by zig-zag lines.
shown in Figure 22b. This apparently is the resul.t 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 insltore 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 $\left(\Delta \sigma_{t}=1.2\right)$ 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


Fig. 23. Comparison of transmissivity and physical oceanographic parameters ( $\sigma_{t}$ and $S$ ) Transect II, Fall season, dmediately 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 procressed 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 $39 \% \mathrm{~T}$, corresponding to SPM values of about $1.5 \mathrm{mg} / \mathrm{l}$ (Figure 3). For such enrichment in particulate matter to occur in a region not overly popula' ed by fine sediments suggests that the currents involved may have exceeded one knot (54 $\mathrm{cm} / \mathrm{sec}$ ). 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 $700 \mu \mathrm{~g} / \ell$ resulting from erosion due to $35-40 \mathrm{~cm} / \mathrm{sec}$ 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 $2 \mathrm{~km} / \mathrm{hr}$, or $56 \mathrm{~cm} / \mathrm{sec}$ 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.

Relationships to rydrocarbon and trace metal distributions ir particulate matter, and other environmental implicatjons

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-acitated 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
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 MAFIA 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
other conditions. A single sample at ten meters or any other arbitrary depth will not be representative of the water colurn. 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 on 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 argunents 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


DMSAG FILE 0221


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1205

1206














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| MN19 | 36.00 | 75．50 |  |
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Appendix 2

| \% Trans | -alpha | \% Trans | -alpha | \% Trans | -alpha |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 100 | 0 | 57 | . 528 | 19 | 1.661 |
| 99 | . 010 | 58 | . 545 | 18 | 1.715 |
| 98 | . 020 | 57 | . 562 | 17 | 1.772 |
| 97 | . 030 | 56 | . 580 | 16 | 1.832 |
| 96 | . 041 | 55 | . 578 | 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 | . 633 | 10 | 2.302 |
| 90 | . 105 | 49 | . 713 | 9 | 2.408 |
| 87 | . 116 | 48 | . 734 | 8 | 2.526 |
| 88 | . 128 | 47 | . 755 | 7 | 2.653 |
| 87 | . 139 | 46 | . 776 | 6 | 2.813 |
| 86 | . 150 | 45 | . 798 | 5 | 2.996 |
| 85 | . 162 | 44 | . 821 | 4 | 3.217 |
| 84 | . 174 | 43 | . 843 | 3 | 3.506 |
| 83 | . 186 | 42 | . 868 | 2 | 3.712 |
| 82 | . 198 | 41 | . 892 | 1 | 4.605 |
| 81 | . 211 | 40 | . 916 |  |  |
| 80 | . 223 | 39 | . 942 |  |  |
| 77 | . 236 | 38 | . 968 |  |  |
| 78 | . 248 | 37 | . 994 |  |  |
| 77 | . 261 | 36 | 1.022 |  |  |
| 76 | . 274 | 35 | 1.050 |  |  |
| 75 | . 288 | 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 |  |  |
| 67 | . 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 | . 494 | 20 | 1.609 |  |  |
| 60 | . 511 |  |  |  |  |

# ANALYSIS OF ZOOPLANKTON FROM THE MAF'LA OCS AREA 

Frank J. Maturo
See John W. Caldwell

MEIOFAUNA OF THE MAFLA AREA

Frank J. Maturo

See Michael R. Crezee

BLM MAFIA DEMERSAL FISH SURVEY 1975-1976

Garry F. Mayer
See Stephen A. Bortone

BLM MAFIA DEMERSAL FISH SURVEY 1975-1976

Garry F. Mayer
See Stephen A. Bortone

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This is the third and final quarterly progress report describing work accomplished during the preceding quarter for the sediment studies portion of the environmontal monjtoring of the MAFIA 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. Scction three is a concise final summary of the significance of-these findings.
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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 I

Station Number

|  | Cruise 1 | Cruise 2 | Cruise 3 |
| :---: | :---: | :---: | :---: |
| 2101 | * | * | * |
| 2102 | * | * | * |
| 2103 |  | * | * |
| 2104 | * | * | * |
| 2105 | * | * | * |
| 2106 | * | * | * |
| 2207 | * | * | * |
| 2208 | * | * | * |
| 2209 | * | * | * |
| 2210 |  | * | * |
| 2211 | * | * | * |
| 2212 | * | * | * |
| 2313 | * | * | ** |
| 2314 |  |  | * |
| 2315 |  | * | * |
| 2316 | * | * | ** |
| 2317 | * | * | ** |
| 2318 | * | * | ** |
| 2419 | * | * | * |
| 2420 | * |  | ** |
| 2421 | * | * | * |
| 2422 |  | * | * |
| 2423 | * | * | ** |
| 2424 | * | * | * |
| 2425 | * | * | ** |
| 2426 | * | * | ** |
| 2427 | * | * | ** |
| 2528 | * | * | ** |
| 2529 | * | * | ** |
| 2530 | * | * | ** |
| 2531 | * | * | ** |
| 2532 | * | * | ** |
| 2533 | * |  | ** |
| 2534 |  | * | ** |
| 2535 | * | * | ** |
| 2536 | * | * | * |
| 2637 | * |  | * |
| 2638 |  | * | * |
| 2639 | * | * | * |
| 2640 | * | * | * |
| 2641 | * | * | * |
| 2642 | * | * | * |
| 2643 | * | * | * |
| 2644 | * | * | * |
| 2645 | * | * | * |

## Cruise I

2101-K
No physical structures; bioturbation index classification (B.I.C.) \#6.
2102-K
No physical structures; no distinctive biogenic structures; B.I.C. \#6.
2104-K
No physical structures; 1 lined burrow (probably callinasa) in the lower ]eft portion of the peel; BIC $\ddagger 6$.
2.105-K

No physical structures; 1 thickly lined arthropod burrow; BIC \#G.
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-K
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-K
No physical structures; BIC \#6.
2318-K
No physical structures; BIC $\$ 6$.
2419-K
No physical structures; 1 long Polychaete burrow; BIC \#6.
2420-K
Faint horizontal sandy lamimitions 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 非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 irreguiar 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-K
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
$\overline{\text { At } 12-22} \mathrm{~cm}$ 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 $\#$.
2536-K
No physical structures; 2 small polychaete burrows, top left; BIC $\# 6$.
2637-K
No physical structures; numerous small worm burrows near the sediment surface; BIC ${ }^{2} 6$.

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 $\# 6$.
$2644-\mathrm{K}$
No physical structures; BIC ${ }^{\text {F }} 6$.
2645-K
No physical structures; parts of two callinasa burrows are evident; BIC \#6.
Cruise II
2101-K
No physical structures; some Polychaete burrows at the sediment surface; BIC ${ }^{\prime \prime} 6$.

2102-K
No physical structures; BIC $\# 6$.
2103-K
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-K
Several horizontal shell layers; some small polychaete burrows; BIC $\# 4-5$.
2209-K
No physical structures; 1 living pelecypos at 9 cm depth with siphons partially visible; BIC ${ }^{\#} 6$.

2210-K
No physical structures; a few small polychaete burrows; BIC \#6.
2211-K
No physical structures; BIC \#6.

2212-K
Wavy-looking, silty laminations at a depth of 25 cm ; no distinctive biogenic structures; BIC \#4.

2313-K
No physical structures; some small, thin polychaete burrows; BIC \#6.
2315-K
Concentration of coarse shell hash material at 15 cm depth; BIC $\# 6$.
2316-K
No physical structures; no biogenic structures; BIC \#6; ship log note - 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 $2316-\mathrm{K}$ (I) and also is finer grained.

2317-K
No physical structures; BIC \#6; 2317-K (II) is finer-grained, less shelly, and better sorted than $2317-\mathrm{K}$ (I).

2318-K
She11 concentration at 3 cm depth; part of 1 burrow is evident and is attributed to a siphunculid which was found in the peel; BIC \#5-6.

2419-K
No physical structures; 1 long polychaete burrow; BIC \#6.
2421-K
No physical structures; some small polychaete burrows near the sediment surface; BIC \#6.

2422-K
No physical structures; 1 small worm tube in the lower left portion of the peel; BIC \#6. .

2423-K
No physical structures; 1 small polychaete burrow; BIC $\# 6$.
2424-K
No physical structures; BIC \#6; 2424-K (II) is coarser than $2424-\mathrm{K}$ (I) and contains more shell material.

2425-K
Upper 3. cm is slightly coarser than the underlying sediment with a fairly distinct boundary; 1 burrow which has been filled in with shell material is evident; BIC \#5-6.

2426-K
No physical structures; 2 small worm tubes near the center of the peel and 2 large callinasa burrows at the bottom of the peel, 19 cm depth; BIC \#6; $2426-\mathrm{K}$ (II) is slightly coarser than $2426-\mathrm{K}$ (I).

2427-K
At a depth of 29 cm , faint horizontal laminations are evident; no distinctive biogenic structures; BIC \#5.

2528-K
No physical structures; BIC \#6.
2529-K
No physical structures; BIC \#6.
2530-K
Some cross-bedded coarse carbonate material; no distinctive biogenic structures; BIC \$4.

2531-K
Faint horizontal layering with gradational boundarjes; no biogenic structures; BIC ${ }^{2} 5$.

2532-K
No physical structures; BIC $\# 6 ; 2532-\mathrm{K}$ (II) resembles the upper 12 cm of 2532-K (I) but does not exhibit the partially bioturbated horizontal laminae that $2532-\mathrm{K}$ (I) has.

2534-K

2535-K
No physical structures; BIC \#6.
$\frac{2536-K}{\text { No physical structures; BIC } \# 6 . ~}$
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 $\# 3-4 ; 2640-\mathrm{K}$ (II) is considerably finer-grained than $2640-\mathrm{K}$ (I) and contains much less shell hash.

2641-K
An inclined ("cross-bedded") thin shell concentration occurs near the sediment surface; 1 large worn tube at 18 cm depth; BIC \#5; 2641-K (II) contains much more shell material than $2641-\mathrm{K}$ ( I ) and is coarser grained.

2642-K
A near surface heavy mineral lamination; no biogenic structures; BIC \#5.
2643-K
No physical structures; BIC $\$ 6$.
2644-K
No physical structures; BIC $\$ 6$.

2645-K
No physical structures; BIC \#6.
Cruise III
2101-K
No physical structures; one well developed, long, shel1-1.ined, polychaete burrow; BIC $\# 6$.

2102-K
No physical structures; BIC \#6.
2103-K
No physical structures; BIC \#6.
2104-K
No physical structures; BIC \#6.
2105-K
No physical structures; BIC \#6.
2106-K
No physical structures; BIC \#6.
2207-K
No physical structures; BIC \#6.
2208-K
No physical structures; part of a polychaete burrow at a depth of 10 cm ; BIC \#6.

2209-K
No physical structures; BIC \#6.
2210-K
No physical structures; abundant bivalues; BIC \#6.
2211-K
No physical structures; BIC \#6. 2212-K
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 \#G.

2318-KR
Upper 8 cm is cross-bedded and underlain by 12 cm of totally bioturbated sediment; no distinctive biogenic structucs; 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 stractures; BIC \#6.
2426-KN
No physical structures; BIC \#6.
2427-KR

2528-KR
No physical structures; BIC ${ }^{2} 6$.
2529-KR
No physical structures; BIC \#6.
2530-KR
No physical structures; BIC $\# 6$.
2532-KR
No physical structures; BTC \#6.
2533-KR
No physical structures; BIC $\# 6$.
2534-K
No physical structures; BIC $\# 6$.
2535-KR
No physical structures; biogenic structures possible heart urchin traces; BIC $\# 6$.
2637-K
Very faint, nearly totally bioturbated horizontal mud laminations; numerous burrow ; BIC $\# 5$.

2638-K
No physical structures; abundant burrows; BIC \#6.
2639-K
No physical structures; BIC \#6.
2640-K
No physical structures; BIC \#6.
2641-K
No physical structures; BIC \#6.
2642-K
No physical structures; EIC \#6.
2643-K
No physical structures; BIC \#6.
2644-K
No physical structures; BIC \#6.
2645-K
No physical structures; no biogenic structures; BIC \#6.

## PART III

## FINAL SUMMARY REPORT

Major objcctives of this portion of the MAFLA study were to identify and describe animal-sedinent relationships and effect of benthic organisms on the sedimentary record. A total of 142 relief peels and 142 correspond: ng 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 $2532-\mathrm{K}$ (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 $2638-\mathrm{K}$ (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.


Figure 1. Boxcore Cruise 1, June-July, 1975


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


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

## BLM TRANSECT I




Etoturbation at Stazions buring throe atmp Ah; ywo.


Radiograph Station 2106


Radiograph Station 2105


Epoxy Relief Peel Station 2106


Epoxy Relief Peel Station 2105

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


Radiograph Station 2104


Radiograph Station 2103


Epoxy Relief Peel Station 2104


Epoxy Relief Peel Station 2103

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


Radiograph Station 2101


Epoxy Relief Peel Station 2102


Epoxy Relief Peel Station 2101

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

## BLM TRANSECT 2

S431ヨW NI H1dヨ



61-99\% Bioturbated for 2 sampling periods
$100 \%$ Bioturbated for 1 sampling period


[^2]

Radiograph Station 2212


Radiograph Station 2211

Epoxy Relief Peel Station 2212


Epoxy Relief Peel Station 2211

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


Radiograph Station 2210


Radiograph Station 2209


Epoxy Relief Peel Station 2210


Epoxy Relief Peel Station 2209

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


Radiograph Station 2208


Radiograph Station 2207


Epoxy Relief Peel Station 2208


Epoxy Relief Peel Station 2207

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

## BLM TRANSECT 3


$100 \%$ Bioturbated for 3 samnling periods

Fipure
Geophysical Profile of Transect 3 with Station Locations plotted against Depth and Distance. Rectangular Figure represents percent Bioturbation at Stations duriris three sampling neriods. Suetion
231.4 was only sampled once.


Radiograph Station 2318


Radiograph Station 2317


Epoxy Relief Peel Station 2318


Epoxy Relief Peel Station 2317

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


Epoxy Relief Peel Station 2316
Epoxy Relief Peel Station 2316


Radiograph Station 2316

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


Radiograph Station 2315


Radiograph Station 2314

Epoxy Relief Peel Station 2315


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

## BLM TRANSECT 4





91-99\% Bioturbated for 1 sampling period
$100 \%$ Bioturbated for 2 campling periods
$100 \%$ Bioturbated for 3 sampiing periods


Radiograph Station 2427


Radiograph Station 2426


Epoxy Relief Peel Station 2427


Epoxy Relief Peel Station 2426

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


Radiograph Station 2424


Epoxy Relief Peel Station 2425


Epoxy Relief Peel Station 2424

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


Radiograph Station 2423


Radiograph Station 2422


Epoxy Relief Peel Station 2423


Epoxy Relief Peel Station 2422

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


Radiograph Station 2421


Radiograph Station 2420

Epoxy Relief Peel Station 2421


Epoxy Relief Peel Station 2420

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


Radiograph Station 2419


Epoxy Relief Peel Station 2419

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

BLM TRANSECT 5



Radiograph Station 2536


Radiograph Station 2535


Epoxy Relief Peel Station 2536


Epoxy Relief Peel Station 2535

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

-38 -


Radiograph Station 2534


Radiograph Station 2533

Epoxy Relief Peel Station 2534


Epoxy Relief Peel Station 2533

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


Epoxy Relief Peel Station 2532


Radiograph Station 2531


Epoxy Relief Peel Station 2531

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


Radiograph Station 2530


Radiograph Station 2529


Epoxy Relief Peel Station 2530


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


$\begin{array}{llllllll}5 & 0 & 5 & 10 & 15 & 20 & 25 & 30\end{array}$ Kilometers


[^3]$100 \%$ Bioturbated for 1 sampling period

91-99\% Bioturbated for 1 sampling period
$100 \%$ Bioturbated for 2 sampling periods

100\% Bioturbated for 3 sampling periods


Radiograph Station 2637
Epoxy Relief Peel Station 2637


Radiograph Station 2638

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


Radiograph Station 2639


Radiograph Station 2640


Epoxy Relief Peel Station 2637


Epoxy Relief Peel Station 2640

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


Radiograph Station 2641


Radiograph Station 2642


Epoxy Relief Peel Station 2641


Epoxy Relief Peel Station 2642

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


Radiograph Station 2643


Radiograph Station 2644


Epoxy Relief Peel Station 2643


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

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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 know1edge of hydrocarbon contents of benthic macroepifauna of the MAFLA-OCS area initiated under BIM Contract 08550-CT4-11 and extended by Contract $08550-C T 5.43$. The studies performed under these and the present contracts represent analysis of samples collected over a two-year period between Ylay 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, et al. (1970) for the scallop Aequipecten irradians, by Farrington and Quinn (1973) for the clam Mercenaria mercenaria, by Stegeman and Teal (1973) for the oyster Crassostrea virginica, by Clark, et al. (1974) for the mussel Mytilus edulis and the oyster Ostrea lurida, and by Fossato and Siviero (1974) for the mussel Mytilus galloprovincialis. Burns and Teal (1973) report hydrocarbon compositions of the pelagic crab Portunus sayi and the pipefish Syngnathus pelagicus collected in the Sargasso Sea. A1though 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 Terpios zeteki, is given by these authors.

As part of BLM Contract $08550-C T 4-11$, 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 jdentified 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 piase 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 $60^{\circ} \mathrm{C}$ 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 $\mathrm{KOH} /$ 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 NHCl . Coral tissue is isolated from the dissolved skeleton by filtration using preweighed filters which are then dried at $60^{\circ} \mathrm{C}$ 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 $\mathrm{KOH} /$ 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 funne1. 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 $H C 1$ to remove trace amounts of non-lipid materials. The organic phase is concentrated on a rotary evaporator at $30^{\circ} \mathrm{C}$, 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 $\mathrm{g} 5 \%$ 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 $0^{\circ} \mathrm{C}$ for further analysis.

Gas-liquid chromatography is performed on the petroleumether and benzene fractions as specified in contract 08550-Ci5-30. 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 $4 \mathrm{~m} 3 \%$ OV-101 on 80-100 mesh Chromosorb WHP column. The polar column is 2.1 mm I. D. $x 2.5 \mathrm{~m} 10 \% \mathrm{SP}-1000$ on $80-100$ mesh Supelcort column. Both columns are temperature-programmed. The OV-1.01 column programming rate is $4^{\circ} \mathrm{C}$ per minute from 150 to $325^{\circ} \mathrm{C}$, holding $325^{\circ} \mathrm{C}$ for ten minutes, with a flow rate of $15 \mathrm{ml} \mathrm{N}_{2} / \mathrm{min}$. The $\mathrm{SP}-1000$ column (equivalent to FFAP ) is operated at $8^{\circ} \mathrm{C} / \mathrm{min}$ from 150 to $250^{\circ} \mathrm{C}$, 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 HewlettPackard 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 $470 \mathrm{~V} / 6$ computer. A program was designed for the present study to convert the retention time and integrator count data into quantitative data
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 investigatio: 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.

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 JuneJuly 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 odd-to-even ratio of n-alkanes, for all 55 samples ranges from 0.14 to 19.12 and averages $1.93 \pm 2.46$. For the seven samples of Porifera, the mean is $1.66 \pm 1.06$, and for the 14 Cnidaria it is $2.68 \pm 4.81$. The 14 Echinodermata average $1.69 \pm 0.64$, and the three Mollusca $1.59 \pm 0.51$. The mean CPI for the 17 Arthropoda is $2.12 \pm 1.81$. 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 $10 \mu \mathrm{~g}$ 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 $2.98 \pm 3.15$. The 16 Porifera have an average CPI of $3.47 \pm 3.03$, while the average of the ten Cnidaria is $2.33 \pm 1.27$. For the 13 samples of Echinodermata, $2.64 \pm 2.54$ is the mean, and it is $1.98 \pm 1.19$ for the six Mollusca. The mean of the 18 Arthropoda is $3.43 \pm 4.50$. 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 $50 \mu \mathrm{~g} / \mathrm{g}$ 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 $7.01 \pm 8.06$. For the 22 Cnidaria, it is $3.09 \pm 6.48$. The 18 samples of echinoderms average 3.88 , with a standard deviation of 4.20. The seven molluscs average $9.92 \pm 8.16$, and the three arthropods 1.45 $\pm 0.62$. 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 Loligo pealeii. 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 $90^{\circ}$ apart and originating at the drilling site was employed. Samples were collected by trawl at distances of $100 \mathrm{~m}, 500 \mathrm{~m}$, 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 0V-101 columns and 1656 on FFAP columns.

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 $1.58 \pm 1.30$ (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, et al., 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.

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 Loligo pealeii. The primary source of this hydrocarbon in marine organisms is belleved to be from zooplankton which form it from phytol in their gut
passages (Avignan and Blumer, 1968). The high concentrations in L. pealeii. 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.

1. 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 Baseline Monitoring Study

MAFLA Monitoring Samples - First Sampling Period, 1975-76

| Phylum Porifera | Lab No. | SUSIO No. |
| :---: | :---: | :---: |
| Placospongia sp. | 120 | I-A-1 ( $\mathrm{A}+\mathrm{B}-4$ ) |
| Tethya sp. | 117 | III-251-1 (A-9) |
|  | 122 | III-A-1 (C-5) |
| unidentified sponge | 132 | VI-B-1 ( $\mathrm{A}-3$ ) |
|  | 138 | $\mathrm{V}-\mathrm{A}-3$ ( $\mathrm{A}-8)$ |
|  | 121 | I-B-2 (C-3) |
|  | 123 | III-A-2 (C-7) |
| Phylum Cnidaria |  |  |
| Class Anthozoa |  |  |
| Madracis decactis | 103 | III-047-3 ( $\mathrm{A}-13$ ) |
|  | 112 | III-146-4 ( $\mathrm{B}-10$ ) |
|  | 116 | III-247-4 (B-8) |
|  | 146 | III-151-3 ( $\mathrm{A}-18$ ) |
|  | 148 | III-251-3 (B-5) |
| Porites divaricata | 102 | III-147-4 ( $\mathrm{A}-13$ ) |
|  | 109 | III-047-2 ( $\mathrm{A}-11$ ) |
| Solenstrea hyades | 104 | II-64-4 (C-7) |
|  | 108 | II-62-1 ( $\mathrm{A}-11$ ) |
| Class Hydrozoa |  |  |
| Millepora alcicornis | 110 | III-146-5 (B-24) |
| - | 111 | III-147-3 ( $\mathrm{A}-12$ ) |
|  | 145 | III-151-2 (A-17) |
| - | 147 | III-247-2 ( $\mathrm{A}-15$ ) |
|  | 149 | III-251-4 (B-6) |

Phylum Echinodermata
Class Asteroidea
Clypeaster sp.
Luidia alternata
Class Echinoidea
Arbacia punctulata
Encope sp.
101
Moira sp.
Stylodaris affinis
125
100
IV-B-1 (C-5)
II-064-3 (A-22)
II-062-2 (A-12)
IV-A-1 ( $\mathrm{A}+\mathrm{B}-4$ )
VI-C-1 (C-4)
VI-B-2 (A-4)
V-A-2 (A-2)
Class Holothuroidea
unidentified sea cucumber 137
Class Ophiuroidea

Astrophyton muricatum

Tropiometra sp.
Phylum Mollusca
Class Cephalopoda
Loligo pealeii
133
140
Class Pelecypoda
Mercanaria campechiensis

$$
\begin{aligned}
& \text { III-146-4 (B-10) } \\
& \text { III-247-4 (B-8) } \\
& \text { III-151-3 (A-18) } \\
& \text { III-251-3 (B-5) } \\
& \text { III-147-4 (A-13) } \\
& \text { III-047-2 (A-11) } \\
& \text { II-64-4 (C-7) } \\
& \text { III-146-5 (B-24) } \\
& \text { III-147-3 ( } \mathrm{A}-12 \text { ) } \\
& \text { III-151-2 (A-17) } \\
& \text { III-251-4 (B-6) }
\end{aligned}
$$

V-A-1 (A-1)
III-146-6 (B-25)
III-047-7 ( $\mathrm{A}-51$ )
III-151-4 (A-33)
III-251-5 (C-8)
III-247-5 (B-9)
I-B-1 (B-3)

VI-C-3 (C-6)
V-B-3 (C-5)
V-B-1 (B-2)

| Class Crustacea |  |  |  |
| :---: | :---: | :---: | :---: |
| Acanthocarpus alexandri | 134 | VI-C-2 ( | C-5) |
|  | 135 | IV-C-1 ( | C-4) |
|  | 141. | $\mathrm{V}-\mathrm{C}-1$ ( | 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) |
|  | 127 | IV-B-2 ( | C-6) |
|  | 128 | VI-A-1 ( | A-4) |
|  | 139 | $\mathrm{V}-\mathrm{B}-2$ ( | C-4) |
| Sicyiona brevirostris | 129 | VI-A-3 ( | (-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 | ( $\mathrm{A}-6$ ) |
|  | 115 | III-151-5 | (A-34) |
|  | 118 | III-251-2 | (B-4) |

MAFLA Monitoring Samples - Second Sampling Period, 1975-76

| 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 | ( $\mathrm{A}-5$ ) |
|  | 161 | III-146-1 | ( $\mathrm{B}-8$ ) |
|  | 163 | III-147-1 | ( $\mathrm{A}-11$ ) |
|  | 167 | III-151-1 | ( $\mathrm{A}-12$ ) |
|  | 174 | III-251-1 | ( $\mathrm{A}-17$ ) |
|  | 181 | III-247-1 | ( $A-6$ ) |
|  | 191 | II-A-A-3 |  |
| Verongia sp. | 206 | III-151-3 | $(A-16)$ |
|  | 207 | III-147-3 | ( $\mathrm{A}-15$ ) |
| unidentified sponge | 188 | I-B-A-6 |  |
|  | 192 | II-B-C-6 |  |
|  | 193 | III-B-C-9 |  |
|  | 194 | $\mathrm{V}-\mathrm{A}-\mathrm{A}-7$ |  |
|  | 195 | VI-B-A-2 |  |
| Phylum Cnidaria |  |  |  |
| Class Anthozoa |  |  |  |
| Cladocora debilis (lost) | 176 | II-062-1 |  |
| Madracis decactis | 184 | III-247-2 | ( $\mathrm{A}-8$ ) |
|  | 183 | III-146-2 | (B-10) |
| - | 198 | III-A-3 | ( $\mathrm{A}-6$ ) |
| Porites divaricata | 175 | III-047-2 | (A-9) |
|  | 180 | ITI-151-2 | (A-14) |
|  | 182 | III-251-2 | (A-19) |
| Solenastrea hyades | 177 | II-62-5 | (A-30) |
|  | 178 | II-64-3 | ( $\mathrm{A}-11$ ) |
|  | 196 | II-A-2 | ( $\mathrm{A}-6$ ) |
| Class Hydrozoa |  |  |  |
| Millepora alcicornis | 179 | III-147-4 | (A-16) |
| Phylum Echinodermata |  |  |  |
| Class Asteroidea |  |  |  |
| Astropecten sp. | 216 | VI-A-A-3 |  |
| Class Echinoidea |  |  |  |
| Arbacia punctulata | 159 | II-064-4 | ( $\mathrm{B}-7$ ) |
| Lytechinus variegatus | 153 | II-062-4 | (A-23) |
| Stylodaris affinis | 210 | V-A-A-5 |  |
| unidentified soft urchin | 190 | $\mathrm{I}-\mathrm{C}-\mathrm{C}-5$ |  |
| Class Ophiuroidea |  |  |  |
| Astrophyton muricatum | 154 | III-047-7 | (A-41) |
|  | 162 | III-146-7 | ( $\mathrm{C}-10$ ) |
|  | 168 | III-151-6 | ( $\mathrm{A}-19$ ) |
|  | 172 | III-247-7 | ( $\mathrm{B}-22$ ) |
|  | 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
Class Cephalopoda

Loligo pealeii
212
214
201 208
Class Pelecypoda
Mercanaria campechiensis Spondylus americanus

211
150
Phylum Arthropoda
Class Crustacea
$\begin{array}{ll}\text { Acanthocarpus alexandri } & 209 \\ 213\end{array}$
Calappa sp.
Portunus spinicarpus
Sicyiona brevirostris
Stenorhynchus seticornis
-
unidentified shrimp

189 185 199 202 215 204 203 205
151 160 166 169 171 173 197 218

$$
\begin{array}{r}
\mathrm{V}-\mathrm{B}-\mathrm{C}-9 \\
\mathrm{~V}-\mathrm{C}-\mathrm{C}-2 \\
\mathrm{III}-\mathrm{C}-\mathrm{C}-7 \\
\mathrm{IV}-\mathrm{C}-\mathrm{C}-5 \\
\mathrm{~V}-\mathrm{B}-\mathrm{A}-2 \\
\text { III-047-8 (A-42) }
\end{array}
$$

$$
\begin{array}{rr}
\text { IV-C-C-6 } \\
\mathrm{V}-\mathrm{C}-\mathrm{C}-1 \\
\text { I-C-C-1 } \\
\text { I-A-A-6 } \\
\text { III-A-C-7 } \\
\text { III-C-C-8 } & \\
\text { VI-A-A-2 } & \\
\text { IV-B-A-1 } & \\
\text { IV-A-A-2 } & \\
\text { IV-B-C-7 } & \\
\text { III-047-6 } & (\mathrm{A}-34) \\
\text { III-146-5 } & (\mathrm{B}-25) \\
\text { III-147-5 } & (\mathrm{A}-25) \\
\text { III-151-7 } & (\mathrm{A}-30) \\
\text { III-247-6 } & (\mathrm{B}-20) \\
\text { III-251-6 } & (\mathrm{B}-4) \\
\text { II-C-C-5 } & \\
\text { VI-C-C-2 } &
\end{array}
$$

MAFLA Monitoring Samples - Third Sampling Period 1975-76

|  | 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 |  |  |
| Occulina diffusa | 309 | 062-A-3 |
| Madracis decactis | 334 | 147-A-18 |
| Madracis decactis | 327 | III-A-C-9 |
| Madracis decactis | 340 | 151-A-25 |
| Madracis decactis | 357 | 146-A-22 |
| Madracis decactis | 358 | 251-A-6 |
| Madracis decactis | 359 | 047-A-9 |
| Madracis decactis | 298 | 247-A-22 |
| Porites divaricata | 316 | 247-A-25 |
| Porites divaricata | 332 | 147-A-16 |
| Porites divaricata | 339 | 151-A-24 |
| Porites divaricata | 341 | 146-A-36 |
| Porites divaricata | 360 | 251-A-5 |
| Porites divaricata | 366 | 047-A-3 |
| Solenastrea hyades | 308 | II-A-A-7 |
| Solenastrea hyades | 310 | 064-A-11 |
| Solenastrea hyades | 311 | 062-B-8 |
| Class Hydrozoa |  |  |
| Millepora alcicornis | 317 | 247-A-24 |
| Millepora alcicornis | 333 | 147-A -17 |
| Millepora alcicornis | 326 | 151-A-26 |
| Millepora alcicornis | 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 | $\mathrm{I}-\mathrm{C}-\mathrm{A}-2$ |
| Class Echinoidea |  |  |
| Encope michelini | 325 | IV-A-A-2 |
| Lytechinus variegatus | 271 | II-A-A-8 |
| Lytechinus variegatus | 272 | 062-A-7 |

Analysis No.
273
Lytechinus variegatus Lytechinus variegatus Stylocidaris affinis Stylocidaris affinis unidentified urchin unidentified urchin unidentified urchin
Class Ophiuroidea
Astrophyton muricatum 348
Astroporpa annulata 275
Astroporpa annulata 291
Astroporpa annulata 346
Class Crinoidea
Comactina echinoptera
319

322
323
Class Pelecypoda
Spondylus americanus
295
Spondylus americanus 296
Spondylus americanus 297
Spondylus americanus 351
Spondylus americanus 352
Phylum Arthropoda
Class Crustacea
Acanthocarpus alexandri
321
Hymenopenaeus tropicalis 347
Portunis spinicarpus

320

SUSIO No.
062-A-7
062-A-7
$\mathrm{V}-\mathrm{A}-\mathrm{A}-3$
VI-B-C-4
I-C-A-1
VI-C-C-5
VI-C-C-6
146-A-34
$\mathrm{V}-\mathrm{B}-\mathrm{A}-2$
III-B-A-8
VI-B-C-3
I-B-A-3

IV-C-C-2
II-C-A-3
247-A-33
147-A-19
151-A-28
047-A-33
146-A-28

III-C-A-1
II-C-A-4
IV-B-A-3

## Appendix II

Tabulations of Data from MAFLA Baseline
Monitoring Study

Summary Tabulation of Hydrocarbon Analyses - First Sampling Period

| Sample Number | Analysis Number | Organism | A | B | C | D | E | F | $\underline{G}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 ( $\mathrm{A}-3$ ) | 132 | unidentified sponge | 1.74 | 0.02 | 2.07 | 1.34 | 0.83 | 1.4 .5 | 331.4 |
| $V-A-3$ ( $\mathrm{A}-8$ ) | 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 ( $\mathrm{B}-10$ ) | 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 | 3053.7 |
| 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 | Solcnastrea 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 | Milluora alcicornis | 1.20 | 0.02 | 0.57 | 1.11 | 0.70 | 596.2 | 5173.9 |
| III-151-2 (A-17) | 145 | Mindopura 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 aloicornis | 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 |
| $V I-C-1 \quad(C-4)$ | 143 | Mnira sp. | 1.95 | 0.01 | 1.00 | 1.78 | 0.71 | 27.4 | 26.4 |
| $V I-B-2 \quad(A-4)$ | 130 | Stylodaris affinis | 2.01 | 0.01 | 1.99 | 2.25 | 0.58 | 4.8 | 259.0 |
| $V-A-2(A-2)$ | 144 | Stylodaris aftinis | 0.52 | 0.01 | 0.82 | 1.03 | 0.45 | 4.3 | 120.5 |
| V-A-1 ( $A-1$ ) | 137 | unidentificd sua 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 | Astromsyton muricatum | 2.81 | 0.01 | 0.63 | 1.99 | 0.65 | 2.2 | 1756.3 |
| I-B-1 ( $\mathrm{E}-3$ ) | 119 | Tropjometra sp. | 1.54 | 0.11 | 2.46 | 1.20 | 0.73 | 9.4 | 220.2 |


| Sample Number | Analysis Number | Organism | A | B | C | D | E | $\underline{F}$ | $\underline{\mathbf{G}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| VI-C-3 (C-6) | 133 | Loligo pealeii | 1.94 | 1.67 | 2.16 | 247.37 | 40.68 | 7.0 | 2425.4 |
| $\mathrm{V}-\mathrm{B}-3$ ( $\mathrm{C}-5$ ) | 140 | Loligo pealeii | 1.00 | 0.78 | 1.72 | 2.11 | 1.35 | 3.6 | 2466.5 |
| $\mathrm{V}-\mathrm{B}-1$ ( $\mathrm{B}-2)$ | 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 | 771.3 |
| $\mathrm{V}-\mathrm{C-1}$ ( $\mathrm{C}-3$ ) | 141 | Acanthocarpus alexandri | 1.93 | 0.18 | 1.56 | 0.73 | 1.00 | 5.2 | 838.9 |
| IV-C-2 (C-5) | 136 | Callidactylus asper | 1.31 | 0.02 | 0.24 | 2.18 | 1.08 | 6.6 | 1926.1 |
| $\mathrm{v}-\mathrm{C}-2$ (C-4) | 142 | Callidacty]us 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 | 7.00 | 9.4 | 587.5 |
| VI-A-1 ( $\mathrm{A}-4$ ) | 128 | Portunus spinicarpus | 1.47 | 0.84 | 3.65 | 0.00 | 2.07 | 51.4 | 10940.4 |
| $\mathrm{V}-\mathrm{B}-2$ (C-4) | 139 | Portunus spinicarpus | 1.81 | 0.54 | 2.45 | 4.55 | 2.15 | 8.6 | 592.2 |
| 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-49) | 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 | 399.3 |
| 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 ( $\mathrm{A}-34$ ) | 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 |

$A=$ odd/even ratio
B = isoprenoid/n-alkane ratio
$\mathrm{C}=\mathrm{branched} / \mathrm{n}$-alkane ratio
$\mathrm{D}=$ pristane/phytane ratio
$E=$ Pristane $/$ n-heptadecane ratio
$\mathbf{F}=$ Total aliphatics; $\mu \mathrm{gm} / \mathrm{gm}$
$\mathrm{G}=$ Total aromatics; $\mu \mathrm{gm} / \mathrm{gm}$

Sumary Tabulation of Hydrocarbon Analyges - Second Sampling Period

| Sample Number | Analysis No. | Organism | A | B | C | D | $\underline{E}$ | $\underline{F}$ | $\underline{\text { G }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I-A-A-5 | 186 | Hallciona Viridis | 1.50 | 0.03 | 6.66 | 0.0 | 0.0 | 5.7 | 286.6 |
| III-047-1 | 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 | Techya 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 |
| III-251-1 | 174 | Techya sp. |  |  |  |  |  | 0.4 | 184.1 |
| III-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 |
| 11I-151-3 | 206 | Verongia sp. | 4.89 | 0.58 | 211.8 | 0.0 | 0.35 | 13.7 | 272.7 |
| III-147-3 | 207 | Verongia sp. | 2.92 | 0.09 | 9.65 | 1.54 | 0.33 | 7.4 | 523.4 |
| 1-8-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 |
| $\mathrm{V}-\mathrm{A}-\mathrm{m}-7$ | 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 |
| III-247-2 | 184 | Madracis decactis | 4.74 | 0.02 | 6.63 | 0.0 | 0.15 | 259.4 | 1790.9 |
| III-146-2 | 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 |
| 11I-047-2 | 175 | Porites divaricata | 1.22 | 0.18 | 3.69 | 1.73 | 0.55 | 77.3 | 8089.9 |
| 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 |
| 11-62-5 | 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 | 1311.1 |
| 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 |
| 11-064-4 | 159 | Arbacta 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 |
| II I-047-7 | 154 | Astrophyton muricatum | 2.00 | 0.28 | 3.25 | 0.0 | 0.0 | 8.05 | 718.0 |
| II 1-146-7 | 162 | Astrophyton muricatum | 1.97 | 0.02 | 1.52 | 2.55 | 0.40 | 2.7 | 347.8 |
| LII-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 | 039 | 12.2 | 477.9 |
| III-251-7 | 170 | Astrophyion muricatum | 1.31 | 0.18 | 2.28 | 5.56 | 1.35 | 1.6 | 208.3 |

## Surmary Tabulation continued page two

| Sample Number | Analysis No. | Organiem | A | B | C | D | $\underline{E}$ | F | G |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| III-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 |
| $\mathrm{V}-\mathrm{B}-\mathrm{C}-9$ | 212 | Loligo pealeit | 3.73 | 0.56 | 2.45 | 6.58 | 2.19 | 2.2 | 6474.0 |
| V-C-C-2 | 214 | Loligo pealeif |  |  |  |  |  |  |  |
| III-C-C-7 | 201 | Loligo pealeti | 1.42 | 0.0 | 10.02 | 8.45 | 2.13 | 14.0 | 7746.1 |
| IV-C-C-5 | 208 | Loligo pealeit | 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 | ${ }^{\circ} 0.53$ | 11.1 | 695.5 |
| III-047-8 | 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 |
| $\mathrm{I}-\mathrm{C}-\mathrm{C}-1$ | 189 | Calappa sp. | 1.73 | 0.41 | 2.26 | 4.50 | 1.59 | 10.1 | 4097.9 |
| I-A-A-6 | 185 | Porrumus spinicarpus | 0.90 | 1.48 | 5.05 | 8.19 | 2.43 | 2.6 | 1386.9 |
| II I-A-C-7 | 199 | Portunus spinicarpus | 3.26 | 0.46 | 3.42 | 25.4 | 0.0 | 2.2 | 902.6 |
| II I-C-C-8 | 202 | Portunus spinicarpus | 3.86 | 0.67 | 3.46 | 9.64 | 1.36 | 1.1 | 565.9 |
| VI-A- ${ }^{\text {- }}$ - | 215 | Portunus spinicarpus | 0.70 | 0.18 | 3.11 | 0.0 | 1.10 | 5.1 | 754.1 |
| IV-B-A-1 | 204 | Porcunus spinlcarpus | 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-047-6 | 151 | Stenorhynclius scticornis | 1.50 | 0.14 | 1.12 | 1.68 | 0.61 | 4.8 | 697.3 |
| III-146-5 | 160 | Stenorhynchits seticornis | 0.97 | 0.26 | 2.53 | 3.57 | 1.23 | 4.5 | 352.7 |
| III-147-5 | 166 | Stenorlynclits seticornis | 2.01 | 0.22 | 2.31 | 4.15 | 0.97 | 31.9 | 2094.6 |
| III-151-7 | 169 | Stenorhynchus seticornis | 2.25 | 0.34 | 1.69 | 7.12 | 1.84 | 2.6 | 860.9 |
| II 1-247-6 | 171 | Stenorhynclus seclcornis | 2.58 | 0.16 | 1.48 | 46.57 | 0.60 | 4.1 | 1059.6 |
| III-251-6 | 173 | Stenorhynchus seticornis | 2.03 | 0.16 | 0.82 | 2.85 | 0.70 | 3.1 | 493.8 |
| II-C-C-S | 197 | unid. shrimp | 1.20 | 0.22 | 1.44 | 0.0 | 0.0 | 10.3 | 5158.0 |
| $\mathrm{VI}-\mathrm{C}-\mathrm{C}-2$ | 218 | unid. shrimp | 19.18 | 0.93 | 8.66 | 1.97 | 1.44 | 1.0 | 729.6 |

[^4]Summary Tabulation of Hydrocarbon Analyses - Third Monitoring Period

| Sample No. | Analysis Number | Organism | A | B | C | D | E | F | G |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I-A-A-5 | 279 | Halicione rubens | 0.86 | 0.87 | 2.39 | 1.42* | 0.87* | 6.3 | 196.9 |
| 064-A-1 | 300 | Tethya sp. | 5.48 | 0.01 | 2.62 | 0.88* | 0.33* | 16.9 | 297.3 |
| I-A-A-4 | 280 | Verongia longissima | 3.83 | 0.01 | 2.09 | 1.82* | 0.24* | 5.3 | 772.7* |
| 247-A-20 | 306 | Trachygellius cinachyra | 16.57 | 0.01 | 5.36 | 0.0 * | 0.15* | 19.7 | 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 | 0.03 | 1.70 | 0.0 * | 0.39* | 12.6 | 290.8 |
| 247-A-7 | 299 | Verongia sp. | 3.02 | 0.01 | 2.68 | 1.08* | 0.66* | 10.0 | 314.6 |
| VI-B-C-5 | 278 | unidentified sponge | 0.88 | 0.04 | 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 |
| II-A-A-9 | 292 | unidentified sponge | 3.87 | 0.06 | 1.77 | 0.57* | 0.53* | 51.3* | 1106.1 |
| I-B-A-3 | 293 | unidentified sponge | 3.29 | 0.14 | 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* |
| 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 | 310 | 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 |
| 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 | 445.1 |
| 146-A-21 | 361 | Millepora alcicornis | 0.72* | 0.16* | 11.17* | 0.0 * | 0.52\% | 38.4* | 890.7 |


| 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 | Iytechinus variegatus | 1.54 | 0.17 | 3.69 | 2.67* | 0.55* | 0.6 | 8.7 |
| 062-A-7 | 273 C | 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 |
| $\mathrm{V}-\mathrm{B}-\mathrm{A}-2$ | 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 beauli | 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* | 4.1.* | 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 |
| $\mathrm{A}=$ odd/even ratio |  |  |  |  |  |  |  |  |  |
| $B=$ isoprenoid/n-alkane ratio |  |  |  |  |  |  |  |  |  |
| $\mathrm{C}=\mathrm{branched} / \mathrm{n}$-alkane ratio . |  |  |  |  |  |  |  |  |  |
| $D=$ pristane/phytane ratio |  |  |  |  |  |  |  |  |  |
| $E=$ pristane/n-heptadecane ratio |  |  |  |  |  |  |  |  |  |
| $\mathrm{F}=$ total aliphatics, ${ }^{\prime} \mu \mathrm{gm} / \mathrm{gm}$ |  |  |  |  |  |  |  |  |  |
| $\mathrm{G}=$ total aromatics, $\mu \mathrm{gm} / \mathrm{gm}$ |  |  |  |  |  |  |  |  |  |
| * ffar col | data |  |  |  |  |  |  |  |  |

Appendix III

Inventories of Analyses from Rig Monitoring Study

|  | Lab No. | SUSIO No. |
| :---: | :---: | :---: |
| Phylum Echinodermata Class Asteroidea Astropecten sp. | 228 | 4510 HE 2 |
| 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 I |
|  | 241 | 4106 HE 1 |
| . | 242 | 4516 HE 1 |
|  | 243 | 4922 HE 1 |
| Trachypenaeus similis | 221 | 4104 HE 2 |
| Irachypenaeus | 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 |

Rig Monitoring Samples
Dri11ing Operation Survey - January 1976

|  | Lab No, | SUSTO 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 |  |  |
| Class Crustacea |  |  |
| Penaeus setiferus | 246 | 4918 HE 3 |
|  | 248 | 4104 HE 3 |
|  | 251 | 4510 HE 4 |
|  | 255 | 4924 HE 4 |
|  | 258 | 4102 HE 3 |
| Trachypenaeus similis | 250 | 4924 HE 3 |
|  | 252 | 4512 HE 4 |
| - | 254 | 4922 HE 3 |
|  | 259 | 4108 HE 4 |
| $\cdots$ | 262 | 4920 HE 4 |
|  | 265 | 4514 HE 3 |
|  | 268 | 4106 HE 4 |
| Squilla sp. A. | 247 | 4106 HE 3 |
|  | 249 | 4104 HE 4 |
|  | 253 | 4514 HE 4 |
|  | 256 | 4516 HE 3 |
|  | 263 | 4108 HE 3 |
|  | 269 | 4102 HE 4 |

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Rig Monitoring Samples Postdrilling Survey - March 1976
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|  | Lab No. | SUSIO No. |
| :---: | :---: | :---: |
| Phylum Arthropoda |  |  |
| Class Crustacea |  |  |
| Penaeus setiferus | 353 | 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 |
| Trachypenaeus 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 |
| Squilla chydea | 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 |

35. 

Appendix IV

Tabulations of Data from Rig Monitoring Study

Summary Tabulation of Hydrocarbon Analyses - Predrilling Rig Monitoring

| Sample <br> Number | Analysis No. | Organism | A | B | C | D | E | F | $\underline{G}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4510 HE2 | 228 | Astropecten sp. | 1.16 | 0.04 | 2.45 | 1.95* | 0.39* | 2.8* | 128.4 |
| 4918 HE2 | 219 | Callinectes sapidus | 5.16 | 1.60 | 6.63 | 3.44* | 0.97* | 11.7 | 409.1 |
| 4108 HE1 | 231 | Penaeus setiferus | 1.70 | 0.03 | 2.40 | 2.05* | 0.57* | 8.2* | 3447.2 |
| 4924 HE1 | 232 | Penaeus setiferus | 1.52 | 0.13 | 1.62 | 1.35* | 0.53* | 2.6* | 1987.5 |
| 4918 HE1 | 234 | Penaeus setiferus | 1.34 | 0.26 | 1.12 | 2.75* | 0.70 * | 1.6 | 314.0 |
| 4514 HE1 | 235 | Penaeus setiferus | 2.41 | 1.29 | 221.57 | 1.28* | 0.91* | 29.7* | 3532.0 |
| 4920 HEl | 236 | Penaeus setiferus | 0.68 | 0.48 | 4.79 | 0.78* | $0.36 *$ | 1.0* | 1277.2 |
| 4104 HEl | 237 | Penaeus setiferus | 1.99 | 0.09 | 1.76 | 1.30* | 0.60* | 1.4 | 1354.8 |
| 4102 HEl | 238 | Penaeus setiferus | 1.74 | 0.04 | 1.37 | 0.81* | 0.70* | 1.6* | 1062.2 |
| 4512 HE 2 | 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 HEL | 240 | Penaeus setiferus | 1.33 | 0.06 | 1.01 | 1.82* | 0.64* | 2.5 | 939.6 |
| 4106 HEl | 241 | Penaeus setiferus | 1.26 | 0.03 | 1.48 | 1.67* | 0.52* | 2.9 | 3538.1 |
| 4516 HEL | 242 | Penaeus setiferus |  |  |  |  |  |  |  |
| 4922 HEl | 243 | Penaeus setiferus | 1.45 | 0.04 | 1.68 | 0 | 0.49* | 0.8 | 7970.8 |
| 4104 HE2 | 221 | Trachypenaeus similis | 2.22 | 0.01 | 2.32 | 0 | 0 | 1.7 | 674.3 |
| 4516 HE2 | 222 | Trachypenaeus similis | 1.05 | 0.08 | 6.22 | 0 | 0 | 0.4 | 785.6 |
| 4514 HE 2 | 224 | Trachypenaeus similis |  |  |  |  |  |  |  |
| 4512 HEL | 225 | Trachypenaeus similis | 2.23 | 0.03 | 1.37 | 2.36* | 0.44* | 2.5 | 726.6 |
| 4102 HE2 | 226 | Trachypenaeus similis | 1.97 | 0 | 3.25 | 0 | 0.32* | 0.8 | 1236.7 |
| 4924 HE2 | 227 | Trachypenaeus similis | 1.26 | 0.02 | 2.07 | ].57* | 0.57* | 6.4 | 1304.7 |
| 4108 HE2 | 229 | Trachypenaeus similis | 0.82 | 0.03 | 1.01 | 1.47* | $0.60 *$ | 9.3* | 475.7 |
| 4106 HE2 | 230 | Trachypenaeus similis | 2.79 | 0.05 | 4.73 | 2.01* | 0.71* | 11.3* | n.d. |
| 4920 HE2 | 223 | Squilla sp. A | 2.61 | 0.10 | 6.81 | 2.55 | 0.53 | 2.3* | 840.3 |
| 4922 HE2 | 233 | Squilla sp. A | 1.38 | 0.05 | 1.10 | 2.95* | 1.16* | 2.0 | 1244.7 |
| A $=$ odd/even ratio |  |  |  |  |  |  |  |  |  |
| $B=$ isoprenoid/n-alkane ratio |  |  |  |  |  |  |  |  |  |
| $C=\mathrm{branched} / \mathrm{n}-\mathrm{alkane}$ ratio |  |  |  |  |  |  |  |  |  |
| $D=$ pristane/phytane ratio |  |  |  |  |  |  |  |  |  |
| $E=$ pristane/n-heptadecane ratio |  |  |  |  |  |  |  |  |  |
| $F=$ total aliphatics, $\mu \mathrm{gm} / \mathrm{gm}$ |  |  |  |  |  |  |  |  |  |
| $\mathrm{G}=$ total aromatics, $\mu \mathrm{gm} / \mathrm{gm}$ |  |  |  |  |  |  |  |  |  |
| * FFAP column data |  |  |  |  |  |  |  |  |  |

$G=$ total aromatics, $\mu \mathrm{gm} / \mathrm{gm}$
fFAP column data

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

| Sample No. | Analysis Number | Organism | A | B 1 | C | D | 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 HE 3 | 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 | Squilia 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 |

$A=$ odd/even ratio
$B=$ isoprenoid/n-alkane ratio
$\mathrm{C}=\mathrm{branched} / \mathrm{n}$-alkane ratio
$D=$ pristane/phytane ratio
$E=$ pristane/n-heptadecane ratio
$F=$ rotal aliphatics, $\mu \mathrm{gm} / \mathrm{gm}$

Data obtained from frap columa

Summary Tabulation of Hydrocarbon Analyses - Post Drilling Rig Monitoring

| Sample No. | Analysis Number | Organism | A | B | C | D | E | E | $\underline{G}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 | 2287.8* |
| 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 HE 9 | 364 | Squilla empusa | 1. 4 3* | 0.17* | 9.90 * | 1.27* | 1).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 |
| $\mathrm{A}=$ odd/even ratio |  |  | $E=$ pristane/n-heptadecane ratio |  |  |  |  |  |  |
| $B=$ isoprenoid/n-alkane ratio |  |  | $\mathrm{F}=$ total aliphatics, $\mu \mathrm{gm} / \mathrm{gm}$ |  |  |  |  |  |  |
| $\mathrm{C}=\mathrm{branched} / \mathrm{n}$-alkane ratio |  |  | $\mathrm{G}=$ total unsaturates, $\mathrm{Hgm} / \mathrm{gm}$ |  |  |  |  |  |  |
| $\mathrm{D}=$ pristane/phtane ratio |  |  | * Data obtained from FFAP column |  |  |  |  |  |  |

## Appendix V

Recommendations for further studies:

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

## 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!)


[^0]:    * See discussion of calibration of turbidity units in McCarthy et. al., (1975).

[^1]:    * See later discussion.

[^2]:    Fisure . Geophysical Profile of Transect 2 with Station Iocations plotted ageinst Depth and Distance. Rectengular Figures rerresent percent Bioturbation at Stations durinc three sampling periods.

[^3]:    1-90\% Bioturbated for 2 sampling periods

[^4]:    $A=$ odd/even ratio
    $B=1$ soprenoid/n-alkane ratio
    $C=$ branched/n-alkane ratio
    $D=$ pristane/phytane ratio
    E = pristane/n-heptadecane ratio
    F = total aliphatics; $1 \mathrm{gm} / \mathrm{gm}$
    $C=$ total aromatics; $\mu \mathrm{gm} / \mathrm{gm}$

