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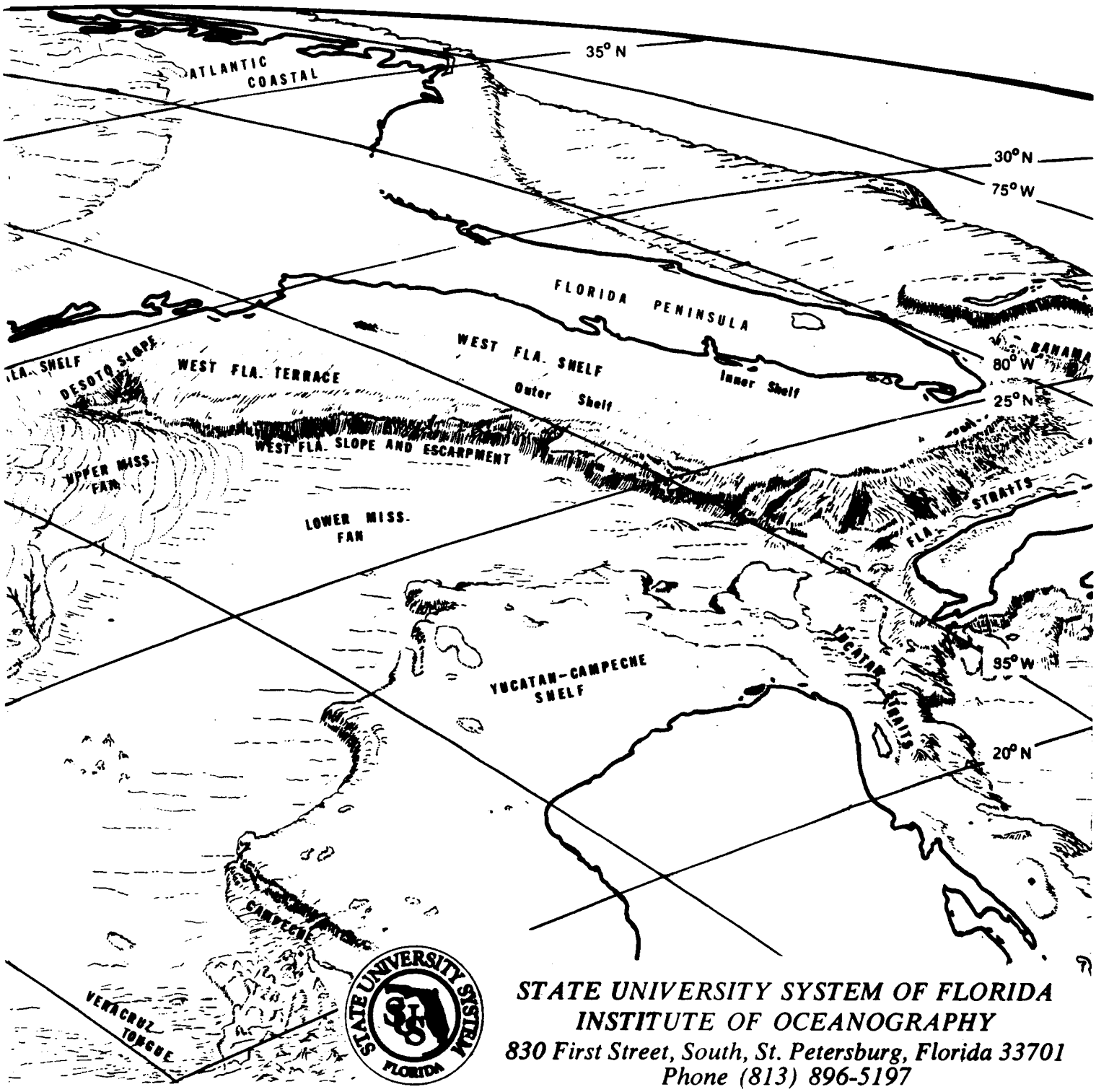
RIG MONITORING



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ASSESSMENT OF THE ENVIRONMENTAL IMPACT OF EXPLORATORY OIL DRILLING

A Report to the Bureau of Land Management

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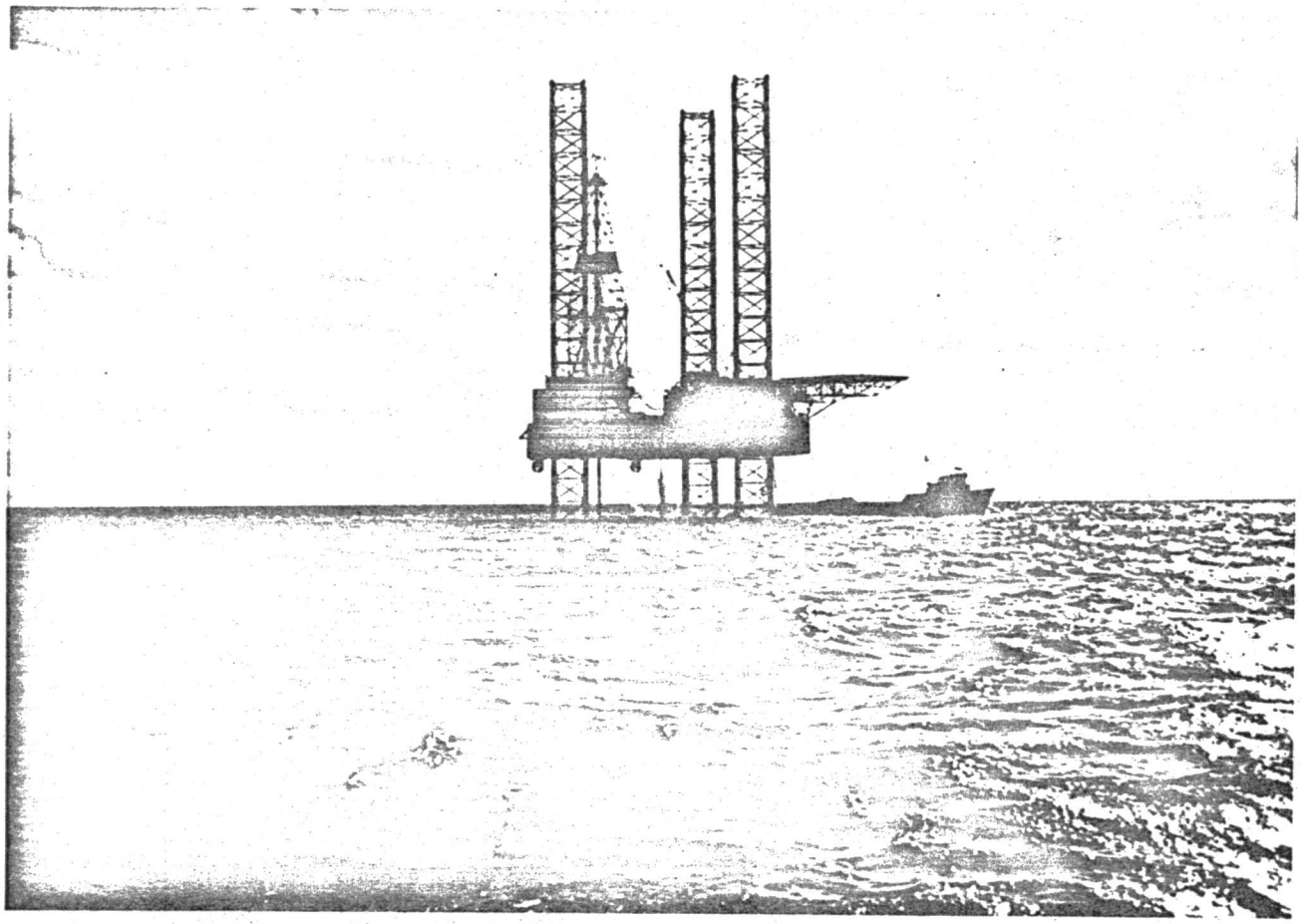

Figure 1. The exploratory drilling rig "Diamond M Gem."

ASSESSMENT OF THE ENVIRONMENTAL IMPACT OF EXPLORATORY OIL DRILLING

List of Projects

Management	State University System of Florida Institute of Oceanography (SUSIO)
Histopathology	University of South Florida
Standard Sediment Parameters	University of South Florida
Clay Mineralogy	University of South Florida
Dissolved Low Molecular Weight Hydrocarbons	University of South Florida
Trace Metals - Sediments	Texas A&M University
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INTRODUCTION

Numerous substances, including hydrocarbons, may be introduced into the marine environment from drilling rigs and production platforms during offshore petroleum and natural gas development. For instance, from a typical oil well (3048 m in depth), approximately 907,185 kg of drill cuttings alone are discharged before production commences and large volumes of drilling muds may be put over the side as well. Substantial quantities of brine (from formation waters) may also be discharged overboard, depending upon the geologic formation. Hydrocarbons may be released from minor spills and support activities; these are considered routine and unavoidable for practical reasons. In spite of the potentially large quantities of these introduced substances, there is little public information available on their fate and effects at the present time.

The studies discussed in this report were designed to provided a pre-, during-, and post-operational assessment of selected biological, chemical, and geological aspects of the environment in the immediate vicinity of an exploratory drill rig in a study area selected by the Bureau of Land Management. Originally this site specific study was to have been conducted in the eastern Gulf of Mexico. However, due to a lack of drilling acitivities in this area during the contractual period, this effort was relocated to the South Texas OCS area.

The actual site to be monitored was chosen on the basis of inquiries made by BLM to USGS regarding the location of tracts to be occupied, the specific drill site on the tract, and the schedule for occupation of that site. In addition, the experimental design took into consideration the following points:

1. Exploratory activity on a given site has a duration ranging from 15 to 90 days. Sampling was to be conducted in a comparable manner during the pre-, during-, and post-operations.

2. The rig that was monitored was temporary and not a permanent structure.

3. The site selected was located in the study area of the South Texas baseline effort.

4. The site was to be located in relatively shallow water depths (less than 36 m) which afforded a relative ease of access (particularly for diving operations).

The rig monitoring survey was centered on a drilling location near the north lease line of Mustang Island (Texas) Block 792. The location of the drilling rig was

Latitude: 27°37'13.87"N
Longitude: 96°57'55.17"W

METHODS

Field Operations

The vessels used were the R/V BELLOWS and the R/V TURSIOPS. Navigation during all phases of the work conducted in the vicinity of the rig near Mustang Island, Texas, is by the DECCA Hi-fix System. All stations except Master Stations 7 (during), and 1, 10 and 18 (after) were located or revisited within the accuracy of this equipment (±15 m). Master Stations 7 and 18 exceeded the limits by less than three meters and Master Stations 1 and 10 were approximately 91 m off position.

Navigation in the during phase of the "sniffer" operation was by ship's radar. This was used to maintain constant ranges of 100, 500 and 1000 m from the operating rig thus producing three concentric circles. Four to 12 samples were collected from each circle.

Sea Floor

Sampling was difficult for the divers because of the large amount of suspended particulate matter in the water column which reduced visibility to near zero and the existence of a definite nepheloid layer at the bottom. Visibility was so limited that the divers literally swam into the bottom without ever seeing it.

Sampling Pattern

As depicted in Figure 2, a sampling pattern was laid out in the form of a wheel with eight spokes; the drill site being the hub. Two of the spokes were oriented parallel to the bottom isobath; two of the other spokes were perpendicular to these. The remaining four spokes intersected each established quadrant at an angle of 45° thereby resulting in a total of eight radii (spokes).

One sampling point was established at the proposed drill site and additional points at distances of 100, 500 and 1000 m from the site along each spoke, thus producing twenty-five sampling points (twenty-four during rig operations). The inner "circle" had some variation in radius due to the physical conformation of the drill rig.

Geology

Standard Sediment Parameters and Clay Mineralogy

Two samples were collected from each station by a diver filling ten centimeter diameter x 0.5 m long PVC cores with sediment by scraping them horizontally along the bottom. The cores were then capped, brought to the surface, labelled and taped.

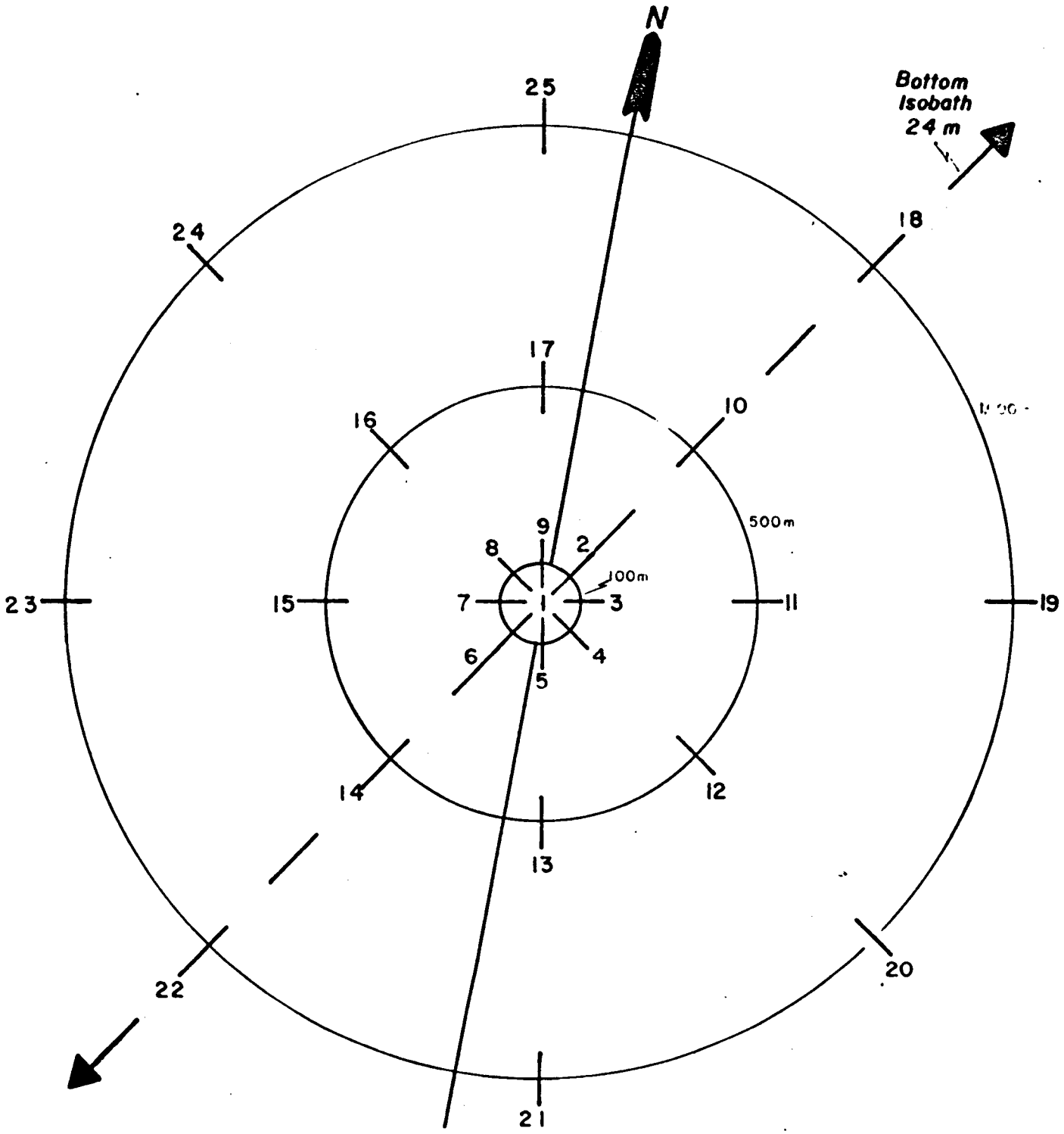


Figure 2. Station arrangement for rig monitoring.

Chemistry

Discrete sediment samples were collected by divers from each of the sampling points during the three phases of the survey. Samples for trace metal analysis were collected in acid-cleaned two centimeter diameter plastic tubes scraped horizontally along the bottom. The sediment filled cores were then capped, brought to the surface, labelled, taped and frozen. Hydrocarbon samples were collected in hexane-washed steel cans scraped horizontally across the bottom. The cans were closed while on the bottom, brought to the surface, the excess water drained off and then sealed and frozen. All samples were handled with extreme care to avoid contamination during collection, handling and storage.

The near zero bottom visibility precluded the efficient use of divers for the collection of macroepifaunal samples. A 9.1 m semi-balloon trawl was towed at a speed of three to six kilometers per hour on a course coincident with the arc described by the distance of the station from the hub to collect macroepifaunal samples from each of the sampling points for trace element and histopathological analyses. Tow duration was approximately five minutes. Additional macroepifaunal samples were removed for hydrocarbon analyses from 13 stations (12 in the during phase) located along the four quadrant spokes. No practical means exist to prevent exposure of trawl-collected organisms to possible surface hydrocarbon films. Other measures, however, such as the wearing of plastic gloves, an especially cleaned working area and pre-cleaned containers, were taken to minimize contamination. Epifaunal samples for trace metal analysis were placed in polyethylene bags and frozen until analysis. Epifaunal samples for hydrocarbon

analysis were placed in hexane-washed glass jars and frozen until analysis.

Biology

Foraminifera

One sample was collected at each station by a diver filling a ten centimeter x 0.5 m long PVC core with sediment by scraping it horizontally along the bottom. This core was then capped, brought to the surface, subsampled for foraminifera and the remainder of the core archived. The subsamples for foraminiferal analyses were collected in 2.5 cm diameter x 15 cm long tubes. Each of these was extruded and preserved in glutaraldehyde to allow for identification of living specimens by protoplasm content.

Histopathology

Samples were removed from each trawl for histopathologic examination. Each organism was numbered and placed in a plastic bag which was then immersed in Dietrich's fixative. The paucity of epifauna in the study site limited histopathological examination to specimens of only two species of nektonic shrimp.

Water Column

Chemistry

Dissolved Low Molecular Weight Hydrocarbons

A hydrocarbon "sniffer" survey for dissolved low molecular weight hydrocarbons in the vicinity of the drill rig was also made during the pre- and during phases of the investigation. Water was continuously sampled while the ship was underway; either through the ship's water sampling system (pre-phase) or by means of a towed tube and pump system (during phase). Under the operating conditions (ship's speed, sampling time and analysis

time, etc.) employed, the water sample obtained represents a composite sample obtained over a distance of about 213 m. (More details of this analysis system are given in the Analytical Methods section.)

Only the pre-drilling, dissolved, low molecular weight hydrocarbon values were determined at the Mustang Island site. Bad weather delayed ship operations so long that the rig was moved to a new location before the during "sniffer" sampling cruise could be performed. With the concurrence of COAR, the during "sniffer" operations were performed at a new rig location off Port O'Connor; the same rig was relocated to approximately 50 miles N.E. of the original location.

Analytical Methods

Geology

Standard Sediment Parameters

In the laboratory the samples were split. One aliquot was wet sieved through a 63 μm screen. An aliquot of sediments remaining in the screen was dried, weighed, and sieved for 15 min through 7.62 cm diameter sieves nested at one phi intervals. Another aliquot of sediment remaining in the 63 μm mesh was run through the rapid sediment analyzer. Percentage of silt and clay in the finer than sand sized sediment was determined by pipette analysis. The sand fraction was optically scanned in order to detect well cuttings and barite. Percentage of $CaCO_3$ was determined using standard acid digestion gasification techniques.

Clay Mineralogy

After the cores were cut, sediments from the topmost layers (10 cm) were taken and digested in water overnight. Clay fractions (<2 μm size) were completely separated from sediments by a superspeed centrifuge and

analyzed for clay mineral constituents in the sediments by X-ray diffraction. Two oriented clay slides were prepared for each sample by treatment with Mg-glycerated saturation and K-saturation, and were X-rayed following the procedure as described by Huang, et al. (1975), and Huang (1976). Relative percentages of clay minerals in the sediments were also estimated.

Chemistry

Trace Metals

Sediments

Samples were prepared for analysis by initially drying the entire aliquot (~50 g) of wet sediment at 105°C and then reducing it to a fine powder with a porcelain-lined Spex mixer-mill. Cadmium, chromium, copper, iron, lead, and nickel were determined by atomic absorption spectrophotometry after dissolution of the sediment. Barium and vanadium were determined by instrumental neutron activation analyses of the solid samples.

For total dissolution, 0.5-1.0 g of finely powdered sediment were heated in a muffle furnace at 350°C for eight hours to ash the organic matter present. After heating, the samples were transferred to teflon beakers and four milliliters of HF (48%) and one milliliter of $HClO_4$ were added. The acid-sediment mixture was heated to near dryness. A second acid mixture (four milliliters HF, one milliliter $HClO_4$) was then added and again heated to near dryness. The residue was redissolved in two milliliters of 16 N HNO_3 and diluted to 25 ml with deionized water.

Cadmium, chromium, copper, lead and nickel were determined by direct aspiration into a Jarrell-Ash model 810, two channel atomic absorption spectrophotometer. Iron was determined, after appropriate dilution, by the same technique. Background absorbance, due to molecular band absorption

and light scattering, was monitored, when necessary, by simultaneously measuring the absorbance of a non-specific line and the analytical line of the element of interest. Cadmium and chromium concentrations were also checked by flameless atomic absorption techniques using a Perkin-Elmer 306 atomic absorption spectrophotometer equipped with an HGA-2100 graphite atomizer and a deuterium background corrector.

Instrumental neutron activation analysis was used for vanadium determination. Initial preparation for neutron activation involved accurately weighing about 0.2 g of sediment, which had been dried at 105°C, into a small one gram capacity polyethylene vial. The vial was heat-sealed to prevent any loss of sample during the analysis. The marked, encapsulated samples were irradiated by the MW Triga reactor at the Texas A&M University Nuclear Science Center. Each sample was irradiated separately for two minutes. This process was facilitated by a pneumatic transport system which can rapidly transfer samples in and out of the reactor core. The sample vial was placed in a secondary polyethylene vial, together with an aluminum flux monitor, and transported to the core for the two minute time period.

After return of the sample and a one minute delay, the aluminum flux monitor was counted by a multichanneled pulse height analyzer. After an appropriate delay period (usually three to five minutes, so that the dead time was <30%) the irradiated sediment sample was placed on an Ortec Ge(Li) detector and counted using a separate GEOS Quanta 4096 channel multichannel pulse height analyzer. The analyzer was set for a gain of one KeV per channel and the 1434 KeV ^{52}V peak analyzed. After a five minute counting period, the spectrum was stored on magnetic tape.

Data reduction was done using the program HEVESY (Schlueter, 1972).

The program calculates peak intensities and converts these to concentration by comparison with appropriate USGS standard rocks (DTS-1 and AGV-1). Corrections were made for varying delay times, deadtimes and neutron fluxes.

Barium analysis was carried out on the same samples prepared for vanadium determination. The samples were irradiated for a 14 hr period in aluminum Swagelok tubes along with standards and blanks and set in a rotisserie in the reactor core. Once irradiated the samples require a period of two weeks to "cool" before they can be counted and at this time the samples were counted for two hours using an Ortec Ge(Li) detector and a Canberra model 8700, 1024 channel multichannel pulse height analyzer. The peak of interest is produced by xenon X-rays at 29 KeV and is recorded in channel 160. Subsequent to counting, the spectral data was stored on magnetic tape and reduced by the program HEVESY using USGS rocks standards W-1 and GSP-1 to calculate sample concentration.

USGS standard rocks were analyzed to determine the accuracy of these analyses. Agreement for replicate analyses was, overall, quite good with the results being consistently within ten percent of the published values. Quadruplicate dissolutions and analyses were made on separate sediment aliquots for five of the study samples. Precisions were calculated by dividing standard deviation by mean and were as follows: Cd, 35%; Cr, 15%; Cu, 5%; Fe, 5%; Pb, 8%; Ni, 15%, and V, 20%.

Organisms

Samples were received frozen in polyethylene bags and remained frozen until they could be prepared for analysis. Samples were thawed just prior to being prepared for freeze-drying. Preparation included dissections done in a clean room on plastic wrap or acrylic plastic "cutting

boards" using stainless steel scalpels, scissors and glass filled PTFE tweezers as required. At no point during the dissection did the preparer's fingers touch the tissue to be analyzed. All dissecting equipment was thoroughly rinsed with 1 N HNO_3 and deionized water between each sample and at the end of each sample preparation session, all equipment was thoroughly cleaned using a Na_2CO_3 solution, rinsed with 0.5 N HNO_3 and deionized water and stored in polyethylene bags until the next use. The acrylic boards were soaked in 0.5 N HNO_3 between each use.

Except when very large numbers of organisms were provided, all tissues from all individuals of the same species in each sample was pooled to make a single sample from which a representative aliquot was removed for analyses.

Shrimp samples (Penaeus setiferus, P. duorarum, Sicyonia sp., Trachypenaeus similis) were prepared by cutting off the head and thorax and removing the abdominal muscle by making a mid-ventral incision with scissors and peeling off the exoskeleton. The mid-ventral artery was removed from the surface of the muscle and the digestive tract excised by making a mid-dorsal incision. The muscle tissue was rinsed sparingly as necessary with deionized water to remove any remnants of the artery or digestive tract. Stomatopods (Squilla empusa, S. chydaea) were prepared similarly except that the gelatinous digestive gland adhering to the abdominal muscle was also removed. The starfish (Astropecten duplicatus) were small and were therefore prepared whole. Each individual was rinsed thoroughly with deionized water to remove any mud or other foreign material adhering to the exterior surfaces. The crabs (Callinectes sp., C. sapidus, Illiacantha sp.) were also prepared whole. The exterior was thoroughly rinsed and the dorsal carapace and

telson removed.

The tissue from each sample was placed in a tared plastic snap-cap vial and weighed immediately to determine wet weight. The samples were covered with parafilm and placed in a freezer. When a sufficient number of samples accumulated, all were freeze-dried for 24-96 hr to a constant weight. After removal from the freeze-dryer, the samples were reweighed to determine dry weight and the percentage of moisture in each sample was calculated. Samples were then stored in a desiccator until they could be analyzed.

All glassware used in digesting samples was cleaned with detergent, rinsed thoroughly with deionized water and soaked in 2-3 N HNO_3 between each use. Reagent blanks were determined on all chemicals prior to their use. Samples were digested by placing a 2-3 g dry weight aliquot in a spoutless, electrolytic style pyrex beaker and adding 4-5 ml of 70% HNO_3 (G. F. Smith Chemical Co. double redistilled) per gram of sample. The beaker was covered with a non-ribbed watchglass and allowed to sit overnight at room temperature. The mixture was then refluxed at low heat for 6-24 hr. One milliliter of $HClO_4$ acid (G. F. Smith Chemical Co.; double redistilled) was then added and the original watchglass replaced with a ribbed one. The heat was increased and the HNO_3 allowed to evaporate. At the first sign of white $HClO_4$ fumes a clean non-ribbed watchglass was placed on the beaker and the sample was allowed to reflux until it cleared completely. If the sample charred, 1-2 ml of HNO_3 was added. In those rare cases when the sample still did not clear an additional 1-2 ml of HNO_3 and 1 ml of $HClO_4$ were added and the refluxing was continued until complete clearing occurred and the sample reached near dryness. The contents of the beaker were rinsed with several

washings of 0.5 N HNO_3 into a screw-cap centrifuge tube and was diluted to a volume of approximately 25 ml. The tubes were weighed to determine the exact volume of acid added and were centrifuged to remove any suspended material. Concentrations were determined directly on this solution or on a further dilution of it.

All trace metal analyses were done by atomic absorption spectroscopy (AAS). Copper and iron were determined after appropriate dilution by direct aspiration into a Jarrell-Ash Model 810, two channel atomic absorption spectrophotometer (AAS). Non-specific or broad band molecular absorption was monitored, when necessary, by measuring simultaneously the absorbance of a non-specific line and the analytical line of the element of interest. Cadmium and vandium were determined using a Perkin-Elmer Model 306 AAS equipped with an HGA-2100 graphite furnace atomizer. Corrections for non-specific absorption were made by a deuterium arc background corrector. Initial analyses for Cr, Pb and Ni were done by flame atomization using the Jarrell-Ash AAS. However, due to the low levels of these elements in the organisms sampled, the bulk of the analyses was done by flameless atomization with the Perkin-Elmer AAS. The instrumental parameters used for both AAS were in accordance with the manufacturers' recommendations with only slight modifications. The sensitivity of V analysis was improved by first coating the graphite furnace tubes with pyrolytic carbon according to the method of Manning and Ediger (1976). The concentration of trace metals in the samples was calibrated using "Titrasol" standards prepared with dilute HNO_3.

At least ten percent of the samples in each of the seven separate digestions were procedural blanks. Also, in every digestion one or more samples in at least triplicate and two National Bureau of Standards (NBS)

reference materials were included to determine the accuracy and precision of our trace metals analyses. Table 1a compares our values from two reference materials with those published by the NBS. The only value which is significantly different from the NBS value is Fe in orchard leaves and we have no explanation for this difference. However, because our Fe value was so consistent from numerous digestions conducted under varying conditions over a considerable period of time, we feel that our number is probably accurate as well as precise. Table 1b lists the precision of our analyses for the seven metals studied as percent coefficient of variation. The precision is lower for Cd, Cr, Pb, Ni and V largely because of the low levels of these elements in the shrimp samples analyzed and because of the need to run Cd, Cr, Pb and Ni analyses at >1:10 dilution in order to minimize matrix interferences.

Hydrocarbons

High Molecular Weight

Sediments

The frozen sediment was allowed to thaw in a Buchner funnel and as much water as possible was filtered off. Approximately 100 g was removed and reserved for total organic and inorganic carbon analyses. Water removal was completed by addition of methanol to the filter cake. The filtrate was back extracted with hexane, and the hexane was retained for later addition to the sediment extract.

The water free sediment was extracted overnight with chloroform, then treated for 15 min with sonification and stirring. The sediment was filtered, and extracted two more times or until the extract was colorless. The extracted sediment sample was oven dried at 100°C to constant weight,

Table 1a. Accuracy of Trace Metals Analyses

Concentrations in µg/g dry weight ± one standard deviation

Sample No.	Number of Replicates Analyzed	Cd	Cr	Cu	Fe	Pb	Ni	V
Bovine Liver (NBS #1577	7	0.4±0.2	0.4±0.4	188±7	258±13	0.7±0.5	0.2±0.3	0.1±0.2
NBS Value (1 Oct 74)	-	0.27±0.04	*	193±10	270±20	0.34±0.08	*	*
Orchard Leaves (NBS #1571)	7	0.1±0.05	2.3±0.6	12±1	232±20	39±4	1.4±0.3	0.1±0.2
NBS Value (1 Oct 74)	-	0.11±0.02	2.6±0.2	12±1	300±20	45±3	1.3±0.2	*

* No NBS value available

Table 1b. Precision of Trace Metals Analyses

Percent Coefficient of Variation (C.V. = Standard Deviation/Mean x 100)

Sample	No.	Number of Replicates	Cd	Cr	Cu	Fe	Pb	Ni	V
4106	1	4	23	37	3	15	25	67	61
4511	1	4	0	5	5	23	10	38	*
4919	2	4	35	17	1	30	25	*	*
4106	4	4	45	41	4	7	37	*	56
4108	3	3	58	*	17	1	*	64	*
4921	8	3	64	*	3	4	13	85	*
4921	9	4	35	28	10	12	43	52	*
Average C.V.			37	26	6	13	26	61	58
Average concentrations of all replicates (ppm dry weight)			0.04	0.3	25	12	0.4	0.3	0.1

* All concentrations were "less than" values. No calculation of C.V. possible.

and weighed. All extracts (hexane and chloroform) were combined and reduced to a small volume in a rotary evaporator. Elemental sulfur was removed from the lipid extract by refluxing with activated copper wool after which the copper was washed with chloroform. The combined extracts were washed with acidified water (pH 4) several times (until the water remained clear) and then brought to dryness under nitrogen at room temperature.

Extracts were refluxed overnight in ten milliliters of 0.5 N KOH in methanol after which equal volumes of water were added. The nonsaponifiables were extracted three times with benzene (ten milliliters). The volume of nonsaponifiable extract was reduced to dryness under nitrogen, taken up in one milliliter of hexane, separated by column chromatography, and analyzed by gas chromatography. The primary column was a 2.2 mm I.D. x 2 m stainless steel Chromasorb Z, 80/100 mesh. Linear programming and flame ionization detectors were utilized and retention indices were computed based on known standards.

Organisms

Samples were thawed and then dried at 60°C to a constant weight. This usually required from 20-60 hr. The dried organism was then reduced to a granular powder in a mortar and pestle and/or a Virtis homogenizer. The homogenized powder was weighed and then sonicated for ten minutes at 60% power using an Artek Model 300 Dismembrator. The liquid used during sonication was the saponification mixture of 0.5 N methanolic KOH/benzene, 50/50.

A modification of this first step was necessary for hard coral samples because of the large amount of carbonate skeleton present. Thawed samples were broken into pieces with a hammer and chisel and decalcified with 3 N HCl.

Coral tissue was isolated from the dissolved skeleton by filtration using preweighed filters which were then dried at 60°C and weighed to obtain the weight of dry tissue. The filters plus the tissue were inserted into a flask for the sonication and saponification steps.

Samples were saponified in order to separate non-saponifiable lipids from total lipids and from total tissue. Refluxing for one hour in a mixture of 0.5 N methanolic KOH/benzene, 50/50, forms the potassium salts of saponifiable lipids and extracts the non-saponifiable lipids from the samples. The tissue residue was removed by filtration, and the liquid phase was transferred to a separatory funnel. Distilled water was added to partition the saponifiable and non-saponifiable lipids between the aqueous and organic phases, respectively. The organic phase was isolated, and the basic aqueous phase extracted twice with petroleum ether. These extracts were combined with the original organic phase and washed once with dilute aqueous HCl to remove trace amounts of non-lipid materials. The organic phase was concentrated on a rotary evaporator at 30°C, and the residue transferred to a pear-shaped flask. One gram of 5% deactivated alumina was added, and the solvents evaporated. The non-saponifiable lipids were thus adsorbed onto the alumina and ready for column chromatography. Resaponification and re-extraction of the tissue residue indicated that this procedure is 85-95% efficient.

The classes of lipids comprising the non-saponifiable fraction were separated by chromatography on a silica gel/alumina column. The column utilized in this study consists of two grams of five percent deactivated silica gel overlaid by two grams of five percent deactivated alumina in a nine millimeter inside diameter column. The column was packed in benzene

which was flushed out with multiple rinses of petroleum ether. This also effectively cleans the column packing material. Non-saponifiable lipids, adsorbed on one gram of alumina, were placed on the top of this column. Normal, branched, and cyclic alkanes and mono-alkanes were eluted from the column with ten milliliters of petroleum ether. Polyunsaturated hydrocarbons, aromatic hydrocarbons, and methyl ketones were eluted with 15 ml benzene. Fatty alcohols were eluted with 25 ml benzene/methanol, 90/10. Chromatography of test solutions showed that separation was quantitative and complete (Meyers, 1976). Solvents were evaporated and the residue stored at 0°C for further analysis.

Gas-liquid chromatography was performed on the petroleum ether and benzene fractions. Resolution of the various components comprising each fraction was achieved using both non-polar and polar columns. The non-polar column type was a 2.1 mm I.D. x 4 m 3% OV-101 on 80-100 mesh Chromosorb WHP column. The polar column was 2.1 mm I.D. x 2.5 m 10% SP-1000 on 80-100 mesh Supelcort column. Both columns were temperature-programmed. The OV-101 column programming rate was 4°C per minute from 150° to 325°C, and holding at 325°C for ten minutes, with a flow rate of 15 ml N_2/min. The SP-1000 column (equivalent to FFAP) was operated at 8°C/min from 150° to 250°C, holding the upper limit for 30 min. Columns were operated in dual differential mode to minimize baseline shifting due to column bleed. The instruments used in this study were a Hewlett-Packard 5710A Gas Chromatograph equipped with a Hewlett-Packard 3380A Integrator and a Hewlett-Packard 5830A Gas Chromatograph. Both instruments use hydrogen-air flame ionization detectors.

The overall best column for separation of petroleum-type hydrocarbons appears to be the packed OV-101 column (Meyers, 1976). It has good resolution

of isoprenoids and normal alkanes and also has more theoretical plates than the FFAP columns. For these reasons, most of the analytical data in this report are derived from chromatograms obtained from packed OV-101 columns. The isoprenoid ratios were obtained from FFAP chromatograms.

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

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

Low Molecular Weight

The hydrocarbon sniffer unit and auxiliary equipment, as originally received from the loaning institution (AMOCO), were in good condition but the unit was not capable of analyzing water samples for

specific hydrocarbons. It was therefore redesigned to permit gas chromatographic-like analyses for trace amounts of specific light hydrocarbons. The redesigned unit is shown in Figure 3.

The system was designed to permit the scrubbing collection of hydrocarbons from 10-50 ℓ of sea water or more, if necessary. Provision was also made for batch analysis of up to 250 ml of sea water using the system shown in Figure 4. This modification could be used if very high concentrations of hydrocarbons were encountered.

The water scrubbing section of the unit was retained from the old AMOCO equipment. Helium gas was used as part of the scrubbing gas and also as a carrier for the hydrocarbons removed from the water samples. The sample gas stream was passed through a drying tube and into a liquid nitrogen-cooled U-trap which collected all of the hydrocarbons. The trapped gases were then analyzed by a flame ionization detector (FID) (Perkin-Elmer) as they evolve from the heated U-trap. The analysis obtained was similar to a programmed temperature gas chromatographic analysis and a typical standard analysis pattern is shown in Figure 5.

The most serious problem encountered was an amplifier failure during a sea trial but this amplifier was replaced with a new solid state FET transistor input stage amplifier (Kiethley Model 414S), and after the Rust Rack recorder was replaced by a new integrating strip chart recorder (Linear Instruments Corp.) no other data collection problems were encountered.

Laboratory testing, redesign and construction were an interrelated part of this project. The experimental parameters of carrier gas flow rate, hydrogen gas and air feed rates to the detector, and sample gas flow rate had to be adjusted to obtain maximum sensitivity, maximum separation

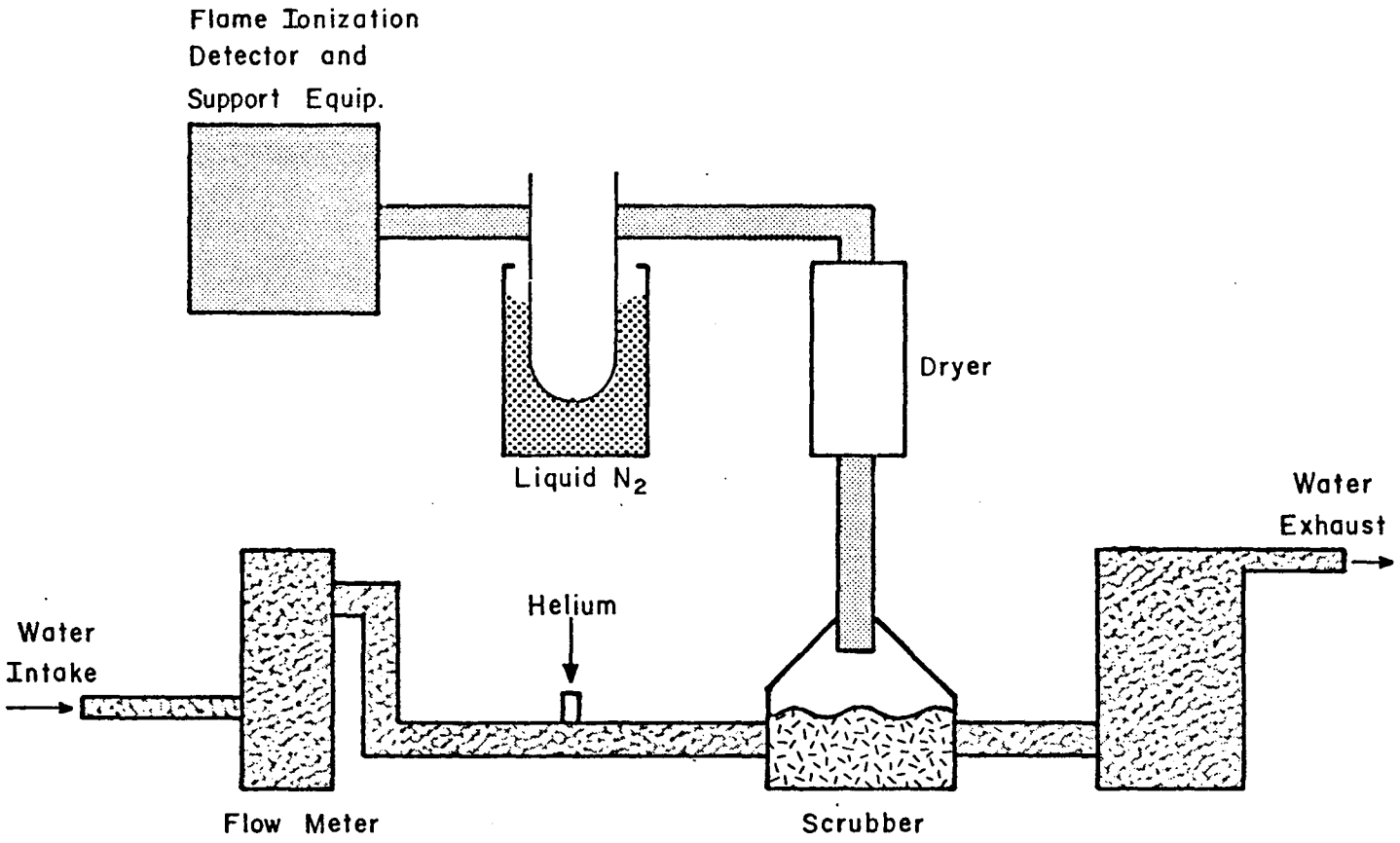


Figure 3. Schematic diagram of "sniffer" unit.

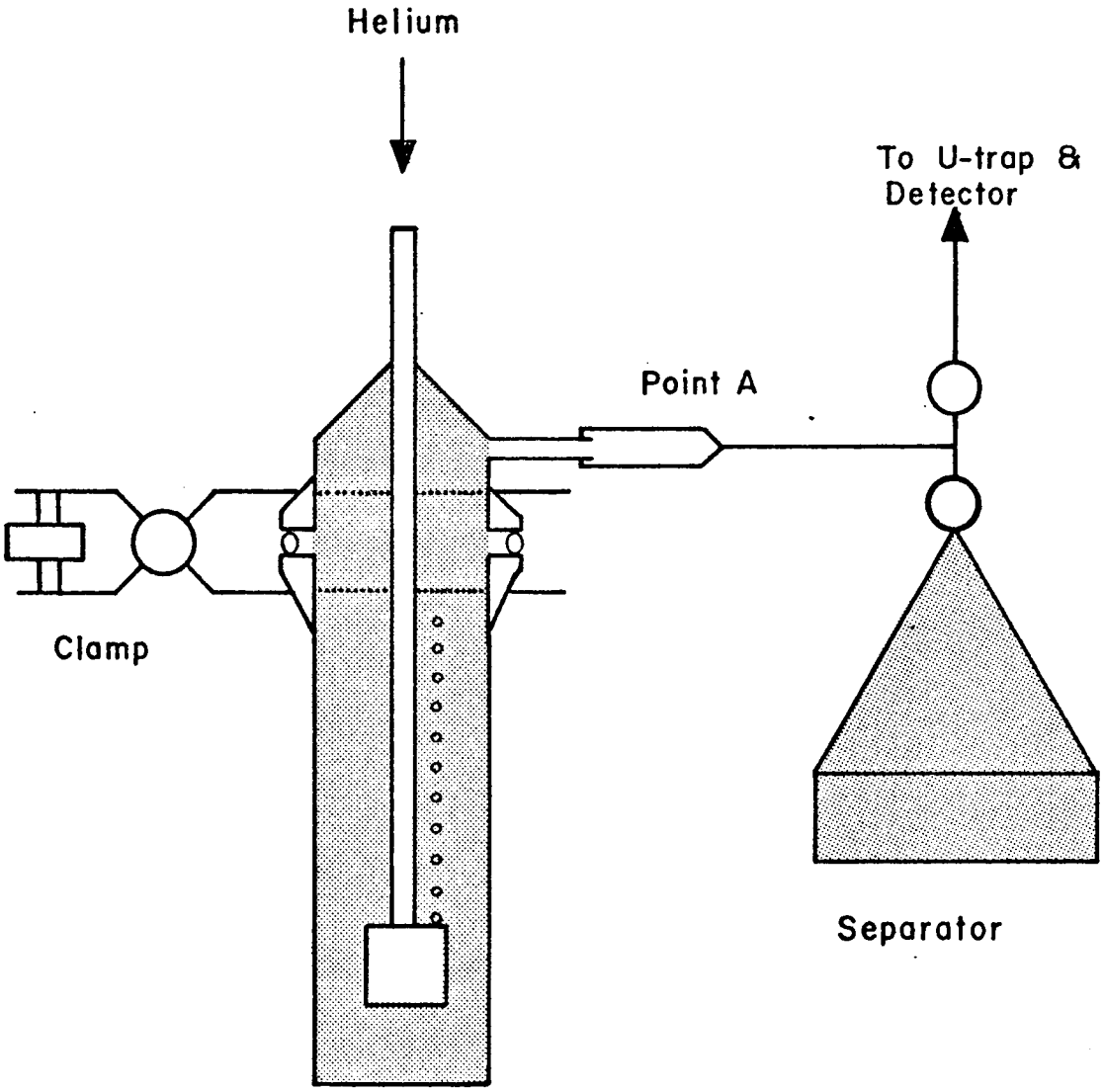


Figure 4. Batchwise water scrubbing system (connection to LHA unit).

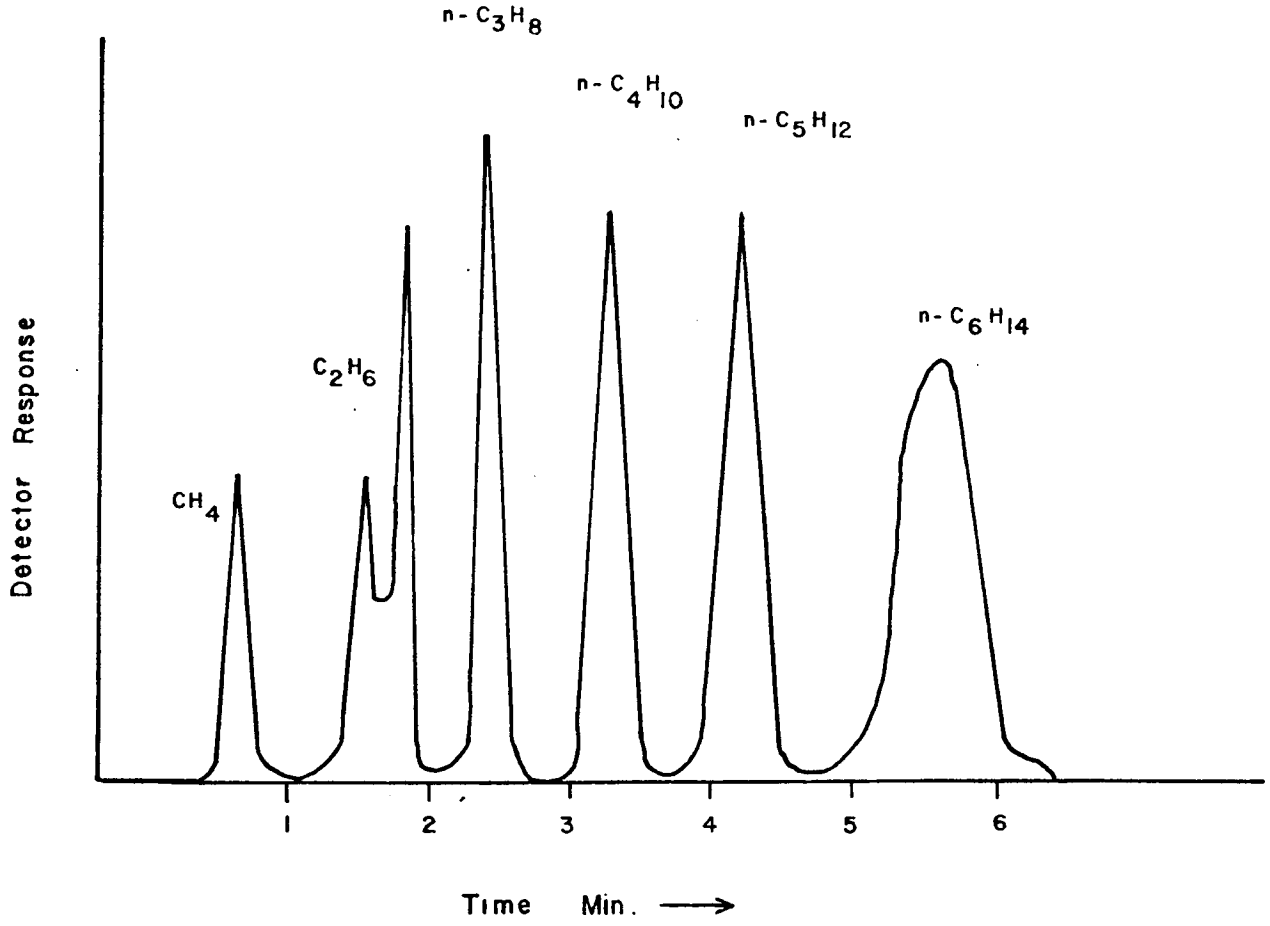


Figure 5. Typical "sniffer chromatogram" (standard sample).

of components and minimum separation time. This was done along the way as modifications were made in the equipment. Analysis time was reduced to less than five minutes per sample.

Standardization of the detector response was found to be easily accomplished using a standard 1000 ppm mix of C_1 to C_6 normal alkanes in nitrogen gas (Micricyl calibration gas, MG technical products, Kearny, N.J.). Samples of 20-500 µℓ were injected directly onto the liquid nitrogen cooled U-trap through an injection port. The limit of detection for hydrocarbons was found to be less than 0.1 nℓ/sample. This was well below the needed limit of detection for sea water analysis even when working at open ocean ambient concentrations (about 50 nℓ/ℓ).

The efficiency of the water scrubbing system was tested using a 100 ℓ hold tank. The efficiency had to be known to relate the standardized detector response to light hydrocarbon concentrations in water. The scrubbing factor was found to be an exponential expression and is discussed below. In the scrubbing efficiency experiments amounts of hydrocarbons were placed in 100 ℓ of water. The light hydrocarbon analyzer (LHA) continuously scrubbed these hydrocarbons from the tank as a function of time and returned the partially degassed water to the holding tank. Two minute collections were periodically acquired and analyzed. To assure that the scrubbing process was monitored as a continuous function of time, the pump was temporarily halted during the analysis cycle.

The scrubbing versus flow rate experiments were accomplished in an analogous manner. The instrument's flow gauge was calibrated in liters per minute of water flow and the scrubbing experiments were repeated at various flow rates and the results of these experiments indicated that control must be maintained over sample flow rate. Calibrations of the system for scrubbing factor upon which quantitative results depend must

be maintained over sample flow rate. Calibrations of the system for scrubbing factor upon which quantitative results depend must be made at the actual sampling flow rate. The k factor is not a highly sensitive function of flow rate, a ten percent change in sample flow rate will cause a ten percent change in results. Sample flow rate control was found to require careful observation of the flow meter during operation and occasional changing of filters in the sample pump system. Flow control during operations was maintained to within ±5% relative to the calibration flow rate. Since flow rate is the major source of error compared to others (temperature, calibrations, etc.), ±5% is a good estimate of the data precision of the system.

Scrubbing as a function of temperature experiments was done in the 100 ℓ Dewar tank. The temperature was adjusted before the analysis began and maintained by the addition of small amounts of ice. Low temperature experiments were terminated before any appreciable dilution error occurred. The results of these experiments showed that temperature has little effect on the k factor for methane over a wide range. Failure to calibrate at each operating temperature should result in errors on the order of two percent relative, and these errors are considered low and well within the precision limitations (±5%) of the instrument.

Biology

Foraminifera

After transport to the laboratory the samples were wet sieved through a 63 μm sieve to remove the finer sediment and retained wet for analysis. The retention of a wet sample allows for identification of

protoplasm content without the use of questionable staining techniques. After sieving, the amount of sediment greater than 63 µm was measured, 300 total specimens were picked and identified, the planktonic/benthonic ratios were determined, the percentage of living specimens was determined for each sample, and the number of total and living specimens was calculated per milliliter of sediment and per sample. In addition, after the 300 specimens were picked, counts and species identifications of additional living specimens were made from each sample until 300 living specimens were obtained. Percentages of live specimens were then determined for each species.

Histopathology

All individuals were fixed in Dietrich's fixative and returned to the laboratory for processing. All exoskeleton bearing organisms were placed in "D-Cal" for varying periods of time depending upon size. They were then cut into pieces not greater than 0.5 cm thick and washed in flowing tap water for 24 hr. All tissues were processed on an Autotechnicon using the 15 1/2 hr UC670-S29-Paraplast technique. Six-micron thick sections were prepared and stained with Harris hematoxylin-eosin.

RESULTS AND DISCUSSION

Geology

The clay mineralogy of the bottom sediments consisted predominantly of smectite followed by illite and kaolinite (Table 2). Only trace amounts of chlorite were found. Smectite levels did not vary significantly between the before and during, and during and after drilling phases. Illite levels measured in the during drilling phase were significantly

Table 2. Percentage weight of smectite, illite, kaolinite and chlorite in the clay mineral suite of the bottom sediments of the oil rig study site.

Drilling Phase	Smectite	Illite	Kaolinite	Chlorite
Before				
$\bar{X}$±1 S.D.	78.0±4.2	11.9±3.4	10.1±1.7	T
Range	65-86	7-23	7-14	-
During				
$\bar{X}$±1 S.D.	74.2±3.2	16.8±2.4	6.0±1.6	T
Range	71-84	11-21	4-12	-
After				
$\bar{X}$±1 S.D.	77.3±2.7	16.9±2.3	5.8±1.2	T
Range	71-81	13-21	3-8	-
t Tests				
Before vs during	0.812	-5.759*	8.344*	-
During vs after	-0.183	-0.190	0.684	-

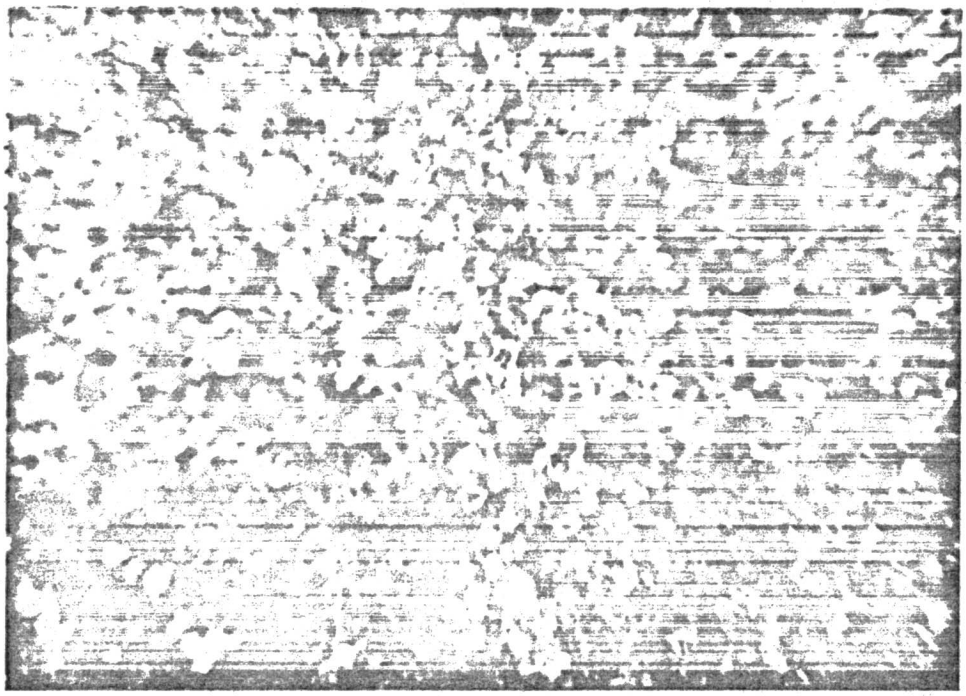
* Significant difference at $\alpha \leq 0.05$
T Trace amount

higher than those measured in the before drilling phase; after drilling levels were not significantly different from the during drilling levels. Changes in kaolinite levels were opposite to those for illite. Kaolinite levels measured in the during drilling phase were significantly less than those of the before drilling phase. Like illite, the after drilling levels of kaolinite were statistically similar to the during drilling levels.

Significant changes in the levels of sand, clay, silt and $CaCO_3$ occurred between the before and during drilling phases (Table 3). Sand, clay and $CaCO_3$ levels increased significantly and silt levels showed a significant decrease. Comparison of the during and after drilling levels shows that the clay and $CaCO_3$ levels decreased significantly between the during and after drilling phases and silt levels increased significantly. The after drilling levels of sand were not significantly different from the during drilling levels. In the during drilling phase drill cuttings (Figures 6a and b) were noted specifically at only four - 100 m periphery stations and one - 500 m periphery station in the during drilling phase. Drill cuttings were still observable at these same five stations in the after drilling phase but were notably less abundant.

Chemistry

The averaged gravimetric hydrocarbon data for the rig sediment samples are presented in Tables 4 and 5 for each of the three drilling phases. The large ranges and standard deviations demonstrate the high variability which occurred in the study site. Comparisons of before, during and after drilling values for individual stations showed that these variations were random and not associated with drilling activities or station location.



(a)

(b)

Figure 6. Sand fraction before (a) and after (b) drilling operation (Magnification: 20X).

Table 3. Percentage weight of sand, clay, silt and $CaCO_3$ in the bottom sediments of the oil rig study site.

Drilling Phase	Sand	Clay	Silt	$CaCO_3$
Before				
$\bar{X}$±1 S.D.	1.3±1.4	45.0±5.0	57.3±13.3	3.9±2.3
Range	0.5-7.9	31.6-51.5	45.0-98.0	0.8-9.3
During				
$\bar{X}$±1 S.D.	6.9±2.8	53.8±17.6	39.3±18.2	12.3±2.4
Range	4.1-17.3	38.0-93.6	1.3-55.7	8.5-17.9
After				
$\bar{X}$±1 S.D.	9.1±5.3	39.7±5.7	50.6±4.4	6.8±8.2
Range	4.1-26.8	27.0-48.3	36.6-57.9	1.4-43.5
t Tests ($\alpha \leq 0.05$)				
Before vs during	-8.964*	-2.292*	3.971*	-12.415*
During vs after	-1.750	3.800*	-3.031*	3.186*

* Significant difference at $\alpha \leq 0.05$

In looking at the overall trends none of the variables changed significantly with time so that based on these data no discernible effects were traced to the drilling procedure.

Table 4. Averaged (for all stations) gravimetric, aliphatic and aromatic hydrocarbon levels of rig sediments before, during and after drilling.

		Aliphatics, ppm	Aromatics, ppm
Before			
	$\bar{X}$±1 S.D.	18.2±9.1	9.0±5.0
	Range	4.8-39.9	2.1-19.6
During			
	$\bar{X}$±1 S.D.	17.9±7.3	7.0±5.6
	Range	8.9-39.2	0.8-27.8
After			
	$\bar{X}$±1 S.D.	20.6±5.5	9.2±2.3
	Range	6.3-30.9	3.8-13.2

Table 6 contains averages of percent carbonate and organic carbon and demonstrates the similarity among the samples with very little variation among the samples. The samples contained about the same amount of carbonate as the Transect VI MAFLA sediments. These rig samples differed primarily in that the lipid, organic carbon and total sediment were 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 carbon. Only at very low confidence limits are the correlations significant which suggests that the

Table 5. Averaged (for all stations) gravimetric data of rig sediments before, during and after drilling.

Drilling Phase	Lipid wt / Total sed wt (ppm)	Total HC wt / Lipid wt (%)	Aliph HC wt / Arom HC wt	Aliph HC wt / Total sed wt (ppm)	Aliph HC / Lipid (%)	Arom HC wt / Total sed wt (ppm)	Arom HC / Lipid (%)
Before							
$\bar{X}$±1 S.D.	327±192	10.6±7.8	2.5±1.6	19.1±8.6	7.2±5.0	9.0±5.0	3.4±2.8
Range	51-923	2.7-42.0	1.4-8.2	6.6-39.8	2.0-27.3	2.1-19.6	0.7-14.7
During							
$\bar{X}$±1 S.D.	287±147	10.3±5.9	3.6±3.3	17.9±7.1	7.8±4.7	6.9±5.2	3.0±2.4
Range	67-583	3.1-25.8	1.4-18.0	8.9-39.2	2.6-21.6	0.8-27.8	1.0-10.7
After							
$\bar{X}$±1 S.D.	264±113	15.6±15.6	2.3±0.6	20.9±5.8	10.3±12.6	9.2±2.3	5.4±4.3
Range	63-479	2.6-84.0	1.4-4.5	6.3-30.9	1.0-68.0	3.8-13.2	1.3-21.3

Table 6. Average amounts of carbonate and organic carbon for rig monitoring sediment samples.

Station	% $CO_3^=$ / Total sediment	% Organic Carbon Acid Basis
1	17.2	1.02
2	16.0	1.00
3	13	0.82
4	12.2	0.89
5	12.6	0.72
6	15.5	0.82
7	14.0	0.82
8	16.4	0.96
9	17.6	0.90
10	17.8	0.86
11	16.6	0.87
12	17.4	0.94
13	17.9	0.77
14	18.8	0.83
15	18.9	0.77
16	18.4	0.86
17	17.2	0.81
18	17.2	0.92
19	21.2	0.73
20	18.2	0.68
21	17.4	0.95
22	17.5	0.84
23	16.0	0.81
24	17.9	0.94
25	17.6	1.00
$\bar{X}$	16.8	0.86
S.D.	2.1	0.09

distributions of various components in the sediment were quite variable. The gravimetric data then do not reveal any real differences attributable to time of collection or activities in the area but only the natural variability of the sediment matrix.

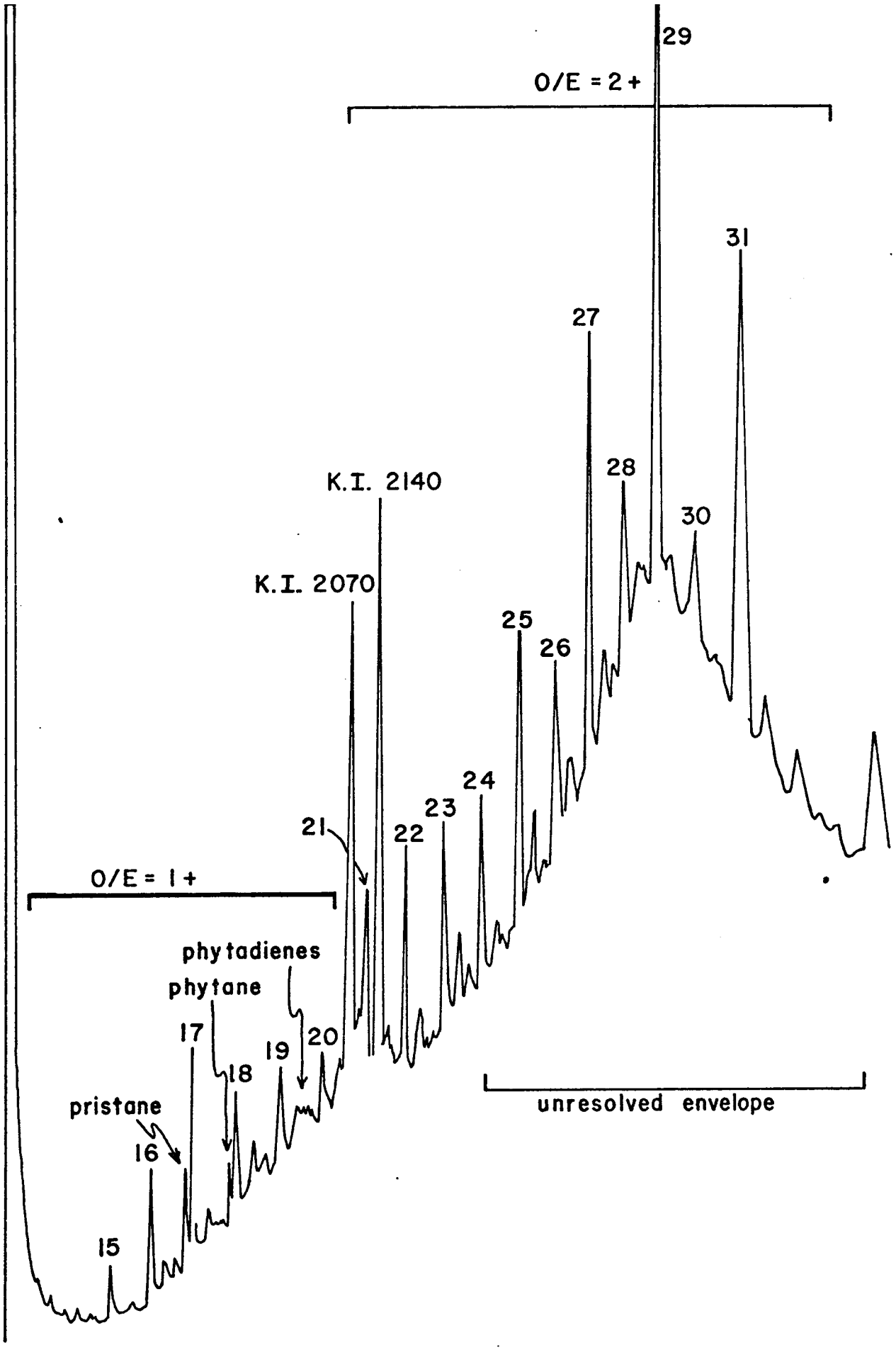
Examination of the gas chromatograms shows that for any given hydrocarbon group, the same basic characteristics are apparent in before, during or after samples. A typical sample of aliphatic hydrocarbons is shown in Figure 7 with features pertinent to virtually all samples emphasized. All samples without exception contained a very large unresolved envelope of complex hydrocarbon material beneath a series of peaks consisting mostly of alkane material. This envelope peaked at ca the n-C_{29} compound.

The resolved material of each chromatogram consisted primarily of high molecular weight (HMW) n-alkanes with the decided odd/even ratio preference characteristic of terrestrial material. The large envelope may be indicative of past oil pollution in this area. The diminished amounts of low molecular weight (LMW) 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 postulated 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.

As found in the samples of the Florida shelf, C_{17} was 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 is evident in all of the rig samples but only in concentrations at or less than C_{19} or C_{20}.

Figure 7. Typical gas chromatogram of rig sediments. This gas chromatogram of the aliphatics from Station No. 21 in the "after" phase typifies all of the samples. Note the strong odd/even (O/E) preference in the high molecular weight range of 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. 1.5X larger than C_{17}.


29
O/E = 2+
31
27
28
K.I. 2140
30
K.I. 2070
25
26
24
23
21
22
O/E = 1+
phytadienes
phytane
17
19
20
18
pristane
16
15
unresolved envelope

Present in concentrations exceeding C_{29} in a majority of samples was 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 7 compares the concentration of these two peaks to the major n-alkane in most samples, C_{29}. There were no relevant trends in the relative concentrations of these compounds. Their levels were high but quite variable even in replicate samplings of individual stations. A peak eluting also at K.I. 2140 was 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 did not appear in the aromatic fractions. This hydrocarbon may be similar to the one which occurred at the 2070 peak in the Florida and Alabama shelf sediments (tentatively identified as a C_{25} branched-diene).

The most distinguishing characteristic of the aromatics was the presence of the K.I. 2140 peak. As stated earlier this peak was probably a polyunsaturate since it also eluted partially in the aliphatic fraction.

All that can be said for the benzene eluates is that there was a fair degree of uniformity of distribution of the aromatics over the low and high molecular weight range. Though the chromatograms looked different an examination of peak files reveals that almost all of the peaks were recurrent and that most of the difference was due to random variations in concentration levels of the individual components. Some samples contained an unresolved envelope in the before phase but not in the later phases. Some very large high molecular weight peaks occurred in isolated samples during all collections but with no systematic trend or pattern. There was

Table 7. K.I. 2070-2140 complex in rig samples.

	K.I. 2070/C_{29}			K.I. 2140/C_{29}		
Station	Before	During	After	Before	During	After
1	0.71		1.0	0.82		0.7
2	1.2	0.61	2.1	2.6	1.2	2.3
3	1.4	1.6	1.4	2.1	1.3	2.1
4	0.84	1.6	2.6	0.62	1.76	3.0
5	1.0	1.5	0.85	1.5	1.8	1.2
6	1.2	1.8	1.4	2.7	2.0	1.1
7	0.6	0.63	0.64	2.1	0.76	0.57
8	1.0	0.90	1.6	2.7	1.6	2.6
9	0.64	0.81	1.5	0.50	0.99	2.4
10		0.83			0.34	
11	1.4	0.59	2.5	1.9	0.31	2.9
12	2.0	0.43	1.5	2.5	0.26	1.9
13	1.2	0.88	2.0	1.6	0.73	1.8
14	0.17	1.0	1.9	0.34	1.9	2.3
15	0.69	2.8	0.95	0.062	2.9	1.2
16	0.65	4.8	1.8	1.2	1.2	1.9
17	0.32	1.8	1.8	0.48	2.0	2.6
18	0.39	0.53	3.0	0.64	1.3	3.2
19	0.67	0.24	2.0	0.83	0.40	1.8
20	4.7	1.5	6.0	1.3	1.5	5.2
21	0.97	1.2	0.63	2.0	1.3	0.52
22	0.71	1.3	2.3	1.2	1.2	1.9
23	1.0	1.3		3.0	1.4	
24	0.9	1.4	1.2	1.5	1.4	1.4
25	1.0	1.1	2.2	0.27	1.2	2.7

nothing unique about the hydrocarbons of the after drilling phase which would indicate any sort of change in the chemical make-up of the sediments due to the drilling activities.

Some information that was not immediately apparent from the gas chromatographic data became more meaningful when certain manipulations of the data were performed to describe the data for interpretative purposes. The derived parameters in Tables 8a,b,c 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 the high degree of similarity among the three groups of data is apparent. 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 in itself displays 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, particularly with regard to the aromatic hydrocarbons, are difficult to control with absolute assurance of reproducibility and what actually gets in each chromatographic fraction is quite variable. Unless large numbers of replicates are available, these parameters may not be 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

Table 8a. Rig Monitoring - before drilling - chromatographic parameters.

Sample Number	ppb dry weight sediment			Pris + Phy	Pristane	Phytane	Pristane	n-Alkane	% n-Alk	Total odd	C≤20	C≥21	C<20
	Aliphatic	n-Alkane	Aromatic	n-Alkane	C_{17}	C_{18}	Phytane	n-C_{16}	Aliphatic	even	odd/even	odd/even	C≥21
HS1-500102SOX	1252.	630.	610.	0.031	1.1	0.43	3.9	130	50.	4.3	1.3	4.6	0.09
HS1-510201	3100.*	540.	520.	0.046	1.6	0.88	3.5	150	17.*	1.9	1.5	1.7	0.15
HS1-510301	520.	161.	430.	0.061	1.3	0.53	4.1	90	31.	3.6	1.6	3.9	0.10
HS1-510401	1237.	530	740.	0.022	1.4	0.82	3.7	330	43.	4.6	2.3	4.3	0.08
HS1-510501	2690.	690.	650.	0.036	1.4	0.75	3.8	150	26.	3.3	1.6	3.3	0.11
HS1-510602	1800.*	360.	370.	0.072	1.8	0.88	3.6	140	20.*	2.6	1.4	2.6	0.16
HS1-510701	320.	69.	66.	0.041	1.7	1.1	4.3	170	22.	2.6	1.7	2.4	0.12
HS1-510801	1300.	330.	490.	0.06	1.8	0.86	4.0	100	25.	2.8	1.8	2.5	0.15
HS1-510901	770.	330.	570.	0.036	1.6	0.87	3.9	170	42.	2.7	1.3	2.9	0.11
HS1-551101	1360.	480.	290.	0.044	1.2	1.0	3.7	170	35.	3.9	1.9	4.0	0.12
HS1-551201	3500.	970.	1400.	0.04	1.8	0.77	4.6	220	28.	2.4	1.5	2.5	0.13
HS1-551301	1800.	650.	610.	0.048	1.1	0.49	3.8	120	36.	3.3	1.3	3.8	0.18
HS1-551401	930.	640.	190.	0.010	1.4	0.89	3.8	2700	68.	3.7	1.8	3.8	0.03
HS1-551501	920.	410.	300.	0.028	1.5	0.63	3.8	200	45.	3.2	1.2	3.5	0.11
HS1-551601SOX	1800.	420.	280.	0.028	1.3	1.1	3.0	200	23.	4.9	2.0	4.9	0.10
HS10551701	770.	380.	300.	0.013	1.5	0.73	3.6	640	49.	4.0	1.6	3.8	0.05
HS1-591801	1300.	700.	310.	0.013	1.4	0.71	4.0	720	52.	4.2	2.1	3.9	0.05
HS1-591901	340.	140.	72.	0.049	1.9	1.2	1.5	580	42.	4.1	1.5	4.1	0.11
HS1-592001	2600.	910.	510.	0.033	1.8	0.59	4.5	220	36.	2.6	1.2	2.8	0.10
HS1-592101SOX	1800.	610.	1600.	0.05	1.7	1.1	3.4	300	33.	3.7	2.0	3.6	0.14
HS1-592201SOX	1300.	570.	580.	0.031	1.5	0.87	3.2	190	44.	3.7	1.4	4.0	0.09
HS1-592301	1600.	520.	570.	0.036	1.6	0.71	3.6	230	32.	4.3	1.7	4.4	0.14
HS1-592401	530.**	120.	180.	0.055	1.3	0.83	3.5	240	22.**	3.0	2.4	2.8	0.15
HS1-592501	1200.**	480.	1300.	0.032	1.8	0.78	3.3	1000	38.**	3.0	1.4	2.9	0.11
HS2-592301	2200.	540.	480.	0.048	1.8	1.1	2.2	160	24.	3.9	1.4	4.0	0.15
Range	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	0.18-0.03
Mean	1400.	480.	560.	0.038	1.5	0.81	3.7	370	36.	3.4	1.6	3.5	0.11
Std. Dev.	840	230	390	0.016	0.24	0.20	0.6	530	12.	0.8	0.3	0.8	0.04
Mean ± 100 x Std. Dev./Mean	1400±60%	480±48%	560±70%	0.038±42%	1.5±16%	0.81±25%	3.7±16%	530±140%	36±33%	3.4±24%	1.6±19%	3.5 23%	0.11±36%

Ranges, Means, Std. deviations, etc. do not include HS2-592301 values. *, ** not including what appear to be contaminant (phthalates?) peaks
SOX - Included in calculations, these samples were soxhletted.

Table 8b. Rig Monitoring - during drilling - chromatographic parameters.

Sample Number	ppb Dry weight sediment Aliphatic	n-Alkane	Aromatic	Pris + Phy / n-Alkane	Pristane / C_{17}	Phytane / C_{18}	Pristane / Phytane	n-Alkane / n-C_{16}	% n-Alk / Aliphatic	Total odd / even	C<20 odd/even	C>21 odd/even	C<20 / C>21
HS2-500101	No sample received.												
HS2-510201	750.	170.	42.	0.051	1.6	0.96	1.9	160.	23	2.2	1.1	2.4	0.20
HS2-510301	1700.	470.	390.	0.045	1.8	0.63	4.6	260.	27	1.7	1.5	1.7	0.20
HS2-510401	1410.	430.	125.	0.051	1.7	0.60	4.2	120.	30	1.9	1.0	2.0	0.18
HS2-510501	860.	250.	74.	0.026	1.8	0.62	2.9	360.	29	2.0	1.2	2.1	0.15
HS2-510601	1700.	330.	460.	0.060	1.3	0.70	2.1	54.	20	1.7	1.0	1.9	0.36
HS2-510701	1400.	600.	1900.	0.024	0.73	0.65	1.2	280.	42	2.0	1.3	2.1	0.27
HS2-510801	1100.	240.	580.	0.041	1.6	0.59	3.6	130.	22	1.3	1.7	1.3	0.22
HS2-510901	2200.	840.	240.	0.020	1.3	0.57	3.8	160.	37	3.0	1.5	3.9	0.099
HS3-551001	900.	330.	280.	0.037	2.1	0.67	5.8	170.	34	3.1	1.3	3.0	0.14
HS2-551101	790.	380.	320.	0.025	1.7	0.91	2.7	230.	48	2.8	1.3	2.9	0.12
HS2-551201	890.	260.	35.	0.010	1.3	0.44	4.0	390.	30	3.2	1.2	3.3	0.061
HS2-551301	740.	380.	470.	0.0072	1.3	0.43	3.0	2300.	51	0.91	0.92	0.91	0.047
HS2-551401	1400.	280.	260.	0.03	1.4	0.55	3.1	580.	20	1.7	0.78	1.7	0.11
HS2-551501	1700.	240.	140.	0.032	1.6	0.74	2.9	1500.	14	3.0	1.4	2.9	0.14
HS2-551601	420.	200.	290.	0.0097	1.5	0.60	4.1	51.	47	3.9	1.3	4.4	0.23
HS2-551701	770.	200.	200.	0.023	1.4	1.2	2.1	64.	27	1.7	1.1	1.9	0.33
HS2-591801	1100.	400.	150.	0.017	1.4	0.56	4.1	280.	36	2.9	1.1	3.0	0.098
HS2-591901	970.	420.	330.	0.012	1.1	0.61	2.4	700.	42	3.9	1.1	4.2	0.071
HS2-592001	1700.	570.	420.	0.019	1.2	0.61	4.2	950.	33	2.7	1.8	2.7	0.072
HS2-592101	1400.	480.	530.	0.029	1.6	0.54	5.0	100.	35	2.6	1.4	2.9	0.14
HS2-592201	1700	620.	270.	0.045	1.3	0.48	3.9	50.	36	4.8	1.2	3.2	0.25
HS2-592301	1900.	770.	340.	0.044	1.4	0.51	4.2	190.	41	2.0	1.6	2.0	0.16
HS2-592401	2800.	710.	440.	0.040	1.7	0.52	5.5	67.	25	1.6	1.4	1.6	0.18
HS2-592501	1500.	190.	300.	0.032	1.7	0.63	4.4	110.	36	2.1	1.3	2.2	0.13
Range	420-2800	170-840	35-1900	0.0072-0.0600	0.073-2.1	0.43-1.2	1.2-5.8	50-2300	14-48	1.3-4.8	0.78-1.8	0.91-4.4	0.061-0.3300
Mean	1300	410	360	0.030	1.5	0.64	3.6	386	33	2.5	1.3	2.5	0.16
Std. Dev.	550	190	360	0.015	0.28	0.17	1.2	530	9.6	0.96	0.24	0.89	0.082
Mean ± 100 x Std. Dev./Mean	1300±42%	410±46%	360±100%	0.030±50%	1.5±19%	0.64±26%	3.6±33%	386±137%	33±29%	2.5±38%	1.3±18%	2.5±36%	0.16±51%

Table 8c. Rig Monitoring - after drilling - chromatographic parameters.

Sample Number	ppb Dry weight sediment Aliphatic	n-Alkane	Aromatic	Pris + Phy / n-Alkane	Pristane / C_{17}	Phytane / C_{18}	Pristane / Phytane	n-Alkane / n-C_{16}	% n-Alk / Aliphatic	Total odd / even	C<20 odd/even	C>21 odd/even	C<20 / C>21
HS3-500101	740	290	100	0.028	1.4	0.48	3.8	190	39	2.3	0.98	2.4	0.14
HS3-510201	2100	790	330	0.024	1.5	0.83	2.4	260	38	1.8	1.2	1.8	0.12
HS3-510301	1700	720	200	0.020	1.4	0.75	2.6	300	41	1.7	1.1	1.9	0.11
HS3-510401	1300	430	220	0.024	1.5	0.60	3.8	420	33	2.2	1.2	2.2	0.12
HS3-510501	600	320	92	0.012	1.2	0.52	2.5	410	53	2.8	0.96	2.8	0.075
HS3-510601	830	390	170	0.033	1.5	0.81	2.0	110	47	2.2	0.84	2.3	0.14
HS3-510701	1100	430	200	0.0074	0.92	0.38	3.6	440	39	1.7	0.86	1.6	0.063
HS3-510801	1700	910	480	0.013	1.2	0.53	3.2	260	54	0.70	1.2	0.66	0.10
HS3-510901	880	350	200	0.026	1.1	0.70	2.2	160	39	2.1	1.1	2.1	0.15
HS3-551001	No sample received												
HS3-551101	930	360	300	0.021	1.5	0.43	4.3	380	38	2.3	0.99	2.8	0.12
HS3-551201	940	310	220	0.020	1.4	0.52	3.7	220	33	2.5	0.93	2.5	0.12
HS3-551301	1400	460	480	0.039	0.50	0.35	2.3	30	32	2.3	0.81	2.9	0.35
HS3-551401	1200	490	270	0.020	1.3	0.51	3.3	330	41	2.5	1.0	2.5	0.12
HS3-551501	910	450	150	0.022	1.2	0.54	3.0	170	49	3.4	1.2	2.8	0.14
HS3-551601	1500	640	290	0.024	1.6	0.65	3.0	260	41	2.1	0.94	2.1	0.16
HS3-551701	1100	320	250	0.024	1.6	0.47	5.0	350	29	2.9	1.0	3.0	0.12
HS30591801	520	140	180	0.032	1.6	0.74	2.7	430	27	2.5	1.2	2.6	0.14
HS30591901	1100	370	250	0.036	1.3	0.60	3.6	130	35	3.2	1.3	3.4	0.17
HS3-592001	570	210	100	0.026	1.4	0.50	3.9	170	37	2.2	0.97	2.5	0.19
HS3-592101	910	430	260	0.018	0.40	0.35	1.8	61	47	2.4	1.1	2.5	0.20
HS3-592201	1400	610	290	0.017	1.4	0.45	4.6	330	43	2.9	1.1	3.0	0.10
HS3-592301	No sample received												
HS3-592401	1400	700	230	0.0080	1.5	0.41	5.4	780	50	2.8	0.89	2.8	0.052
HS3-592501	1300	500	340	0.055	0.42	0.39	1.9	18	39	2.0	1.1	2.5	0.54
HS4-592401	1400	620	230	0.016	1.5	0.52	3.8	450	46	2.8	0.96	2.9	0.088
Range	520-2100	140-910	92-480	0.0074-0.055	0.40-1.6	0.35-0.83	1.8-5.4	18-730	27-54	0.70-3.4	0.81-1.3	0.66-3.8	0.052-0.54
Mean	1100	470	250	0.024	1.3	0.54	3.3	280	40	2.3	1.0	2.5	0.15
Std. Dev.	390	190	97	0.010	0.36	0.14	0.98	170	7.2	0.56	0.13	0.63	0.10
Mean ± 100 x Std. Dev./Mean	1100±35%	470±40%	250±39%	0.024±42%	1.3±28%	0.54±26%	3.3±30%	280±61%	40±18%	2.3±24%	1.0±13%	2.5±25%	0.15±67%

should be pointed out that the C_{16} was 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 LMW-rich oil would probably create an n-alkane/C_{16} value well outside the natural variability of this parameter, e.g., the three samples in the after phase which had unusually large amounts of LMW n-alkanes at Stations No. 13, 21 and 25 had very low n-alkane C_{16} ratios.

Other parameters that included a wide molecular weight range showed 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 ratios were quite reproducible in all three samplings.

In a search for the effects of the rig emplacement no discernible differences were noticed when comparing the means of these 13 parameters. In comparing sample to sample from the various collections certain differences were seen in one or more parameters but these appeared 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 8a, b, and c were used and groups of plots are shown in Figures 8-12. Figures 8-11 are composed of means of parameters for samples at equal distances from the rig. All but Figures 8 and 12 have three lines depicting the before, during and after phases.

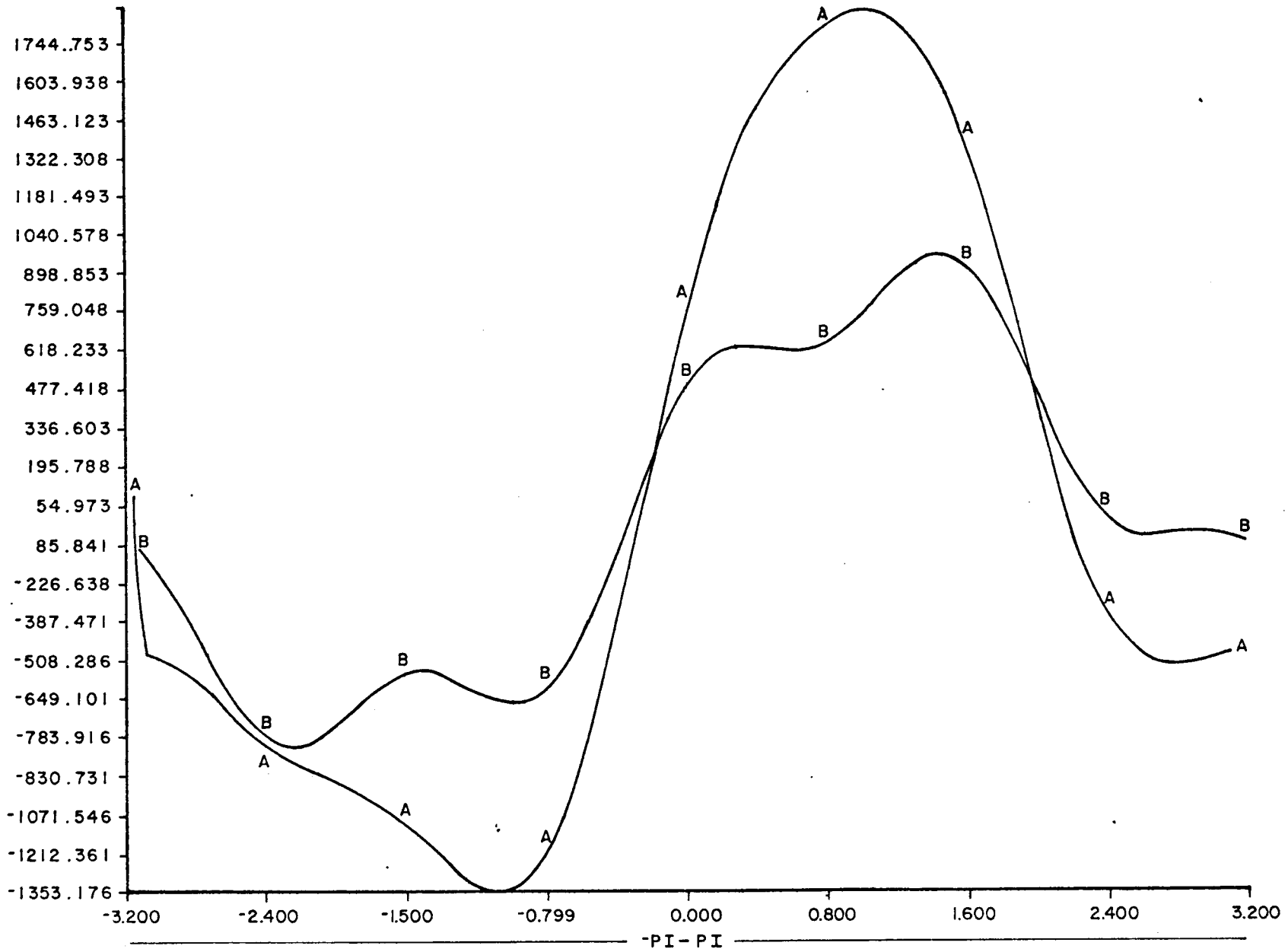


Figure 8. Cluster group plots of samples at rig site. Plots represent the combined effects of the 13 parameters in tables 8a-c. The two lines above depict the respective means of the before, during, and after samples.

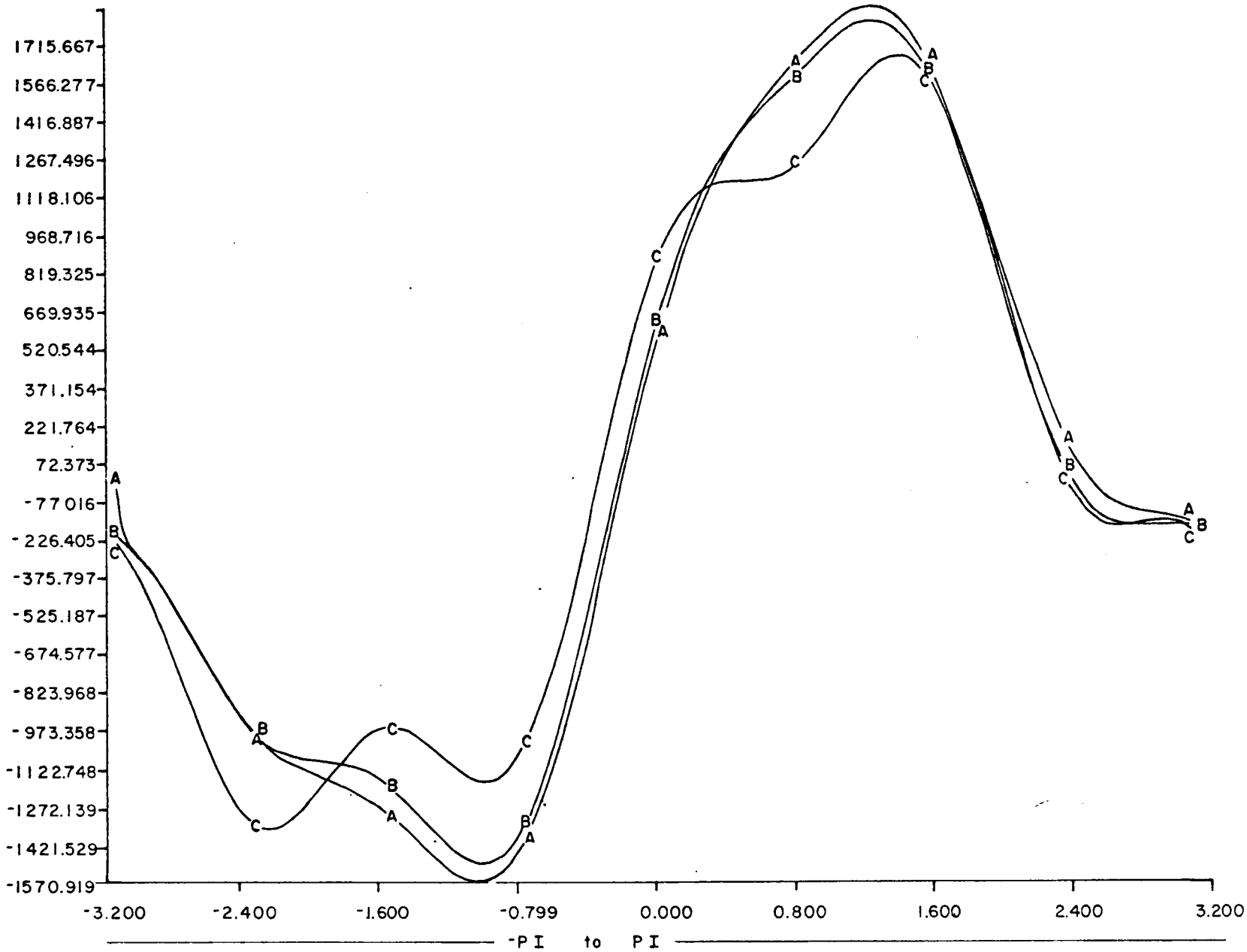


Figure 9. Cluster group plot of samples 100 m from the rig. Plots represent the combined effects of the 13 parameters in tables 8a-c. The three lines above depict the respective means of the before, during, and after sampling.

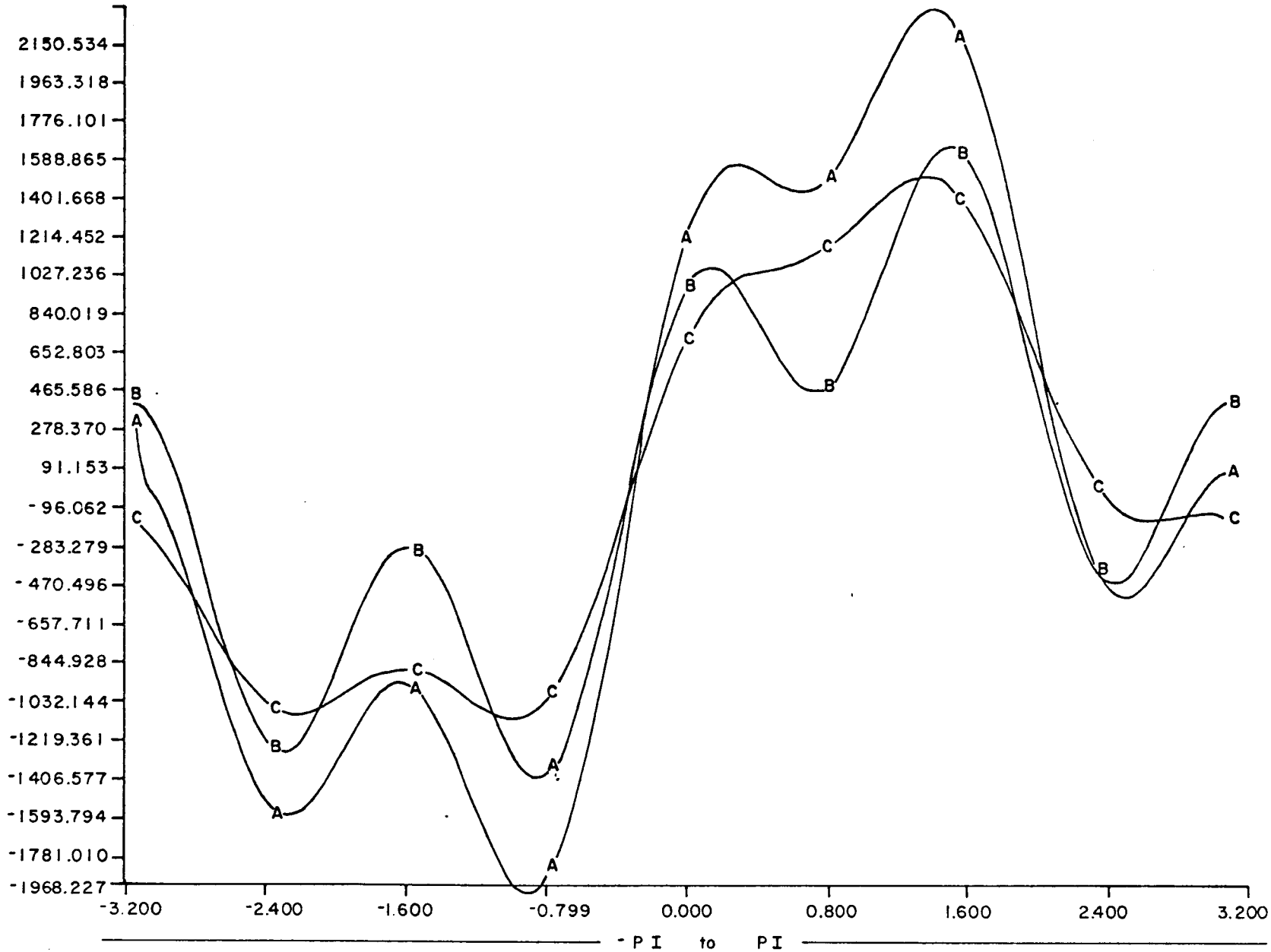


Figure 10. Cluster group plots for samples 500 m from the rig. Plots represent the combined effects of the 13 parameters in tables 8a-c. The three lines above depict the respective means of the before, during, and after samples.

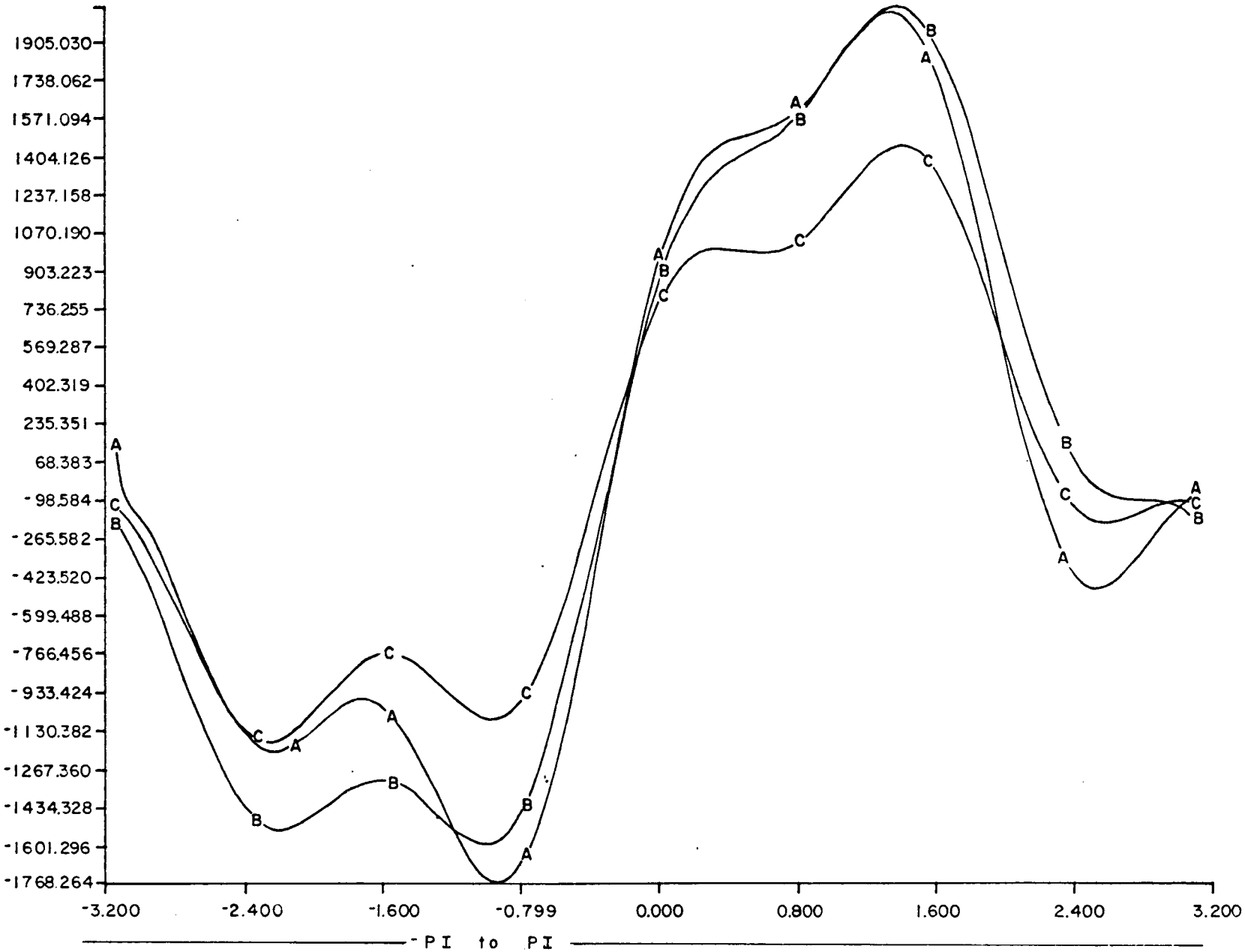


Figure 11. Cluster group plots of samples 1000 m from the rig. Plots represent the combined effects of the 13 parameters in tables 8a-c. The three lines above depict the respective means of before, during, and after samples.

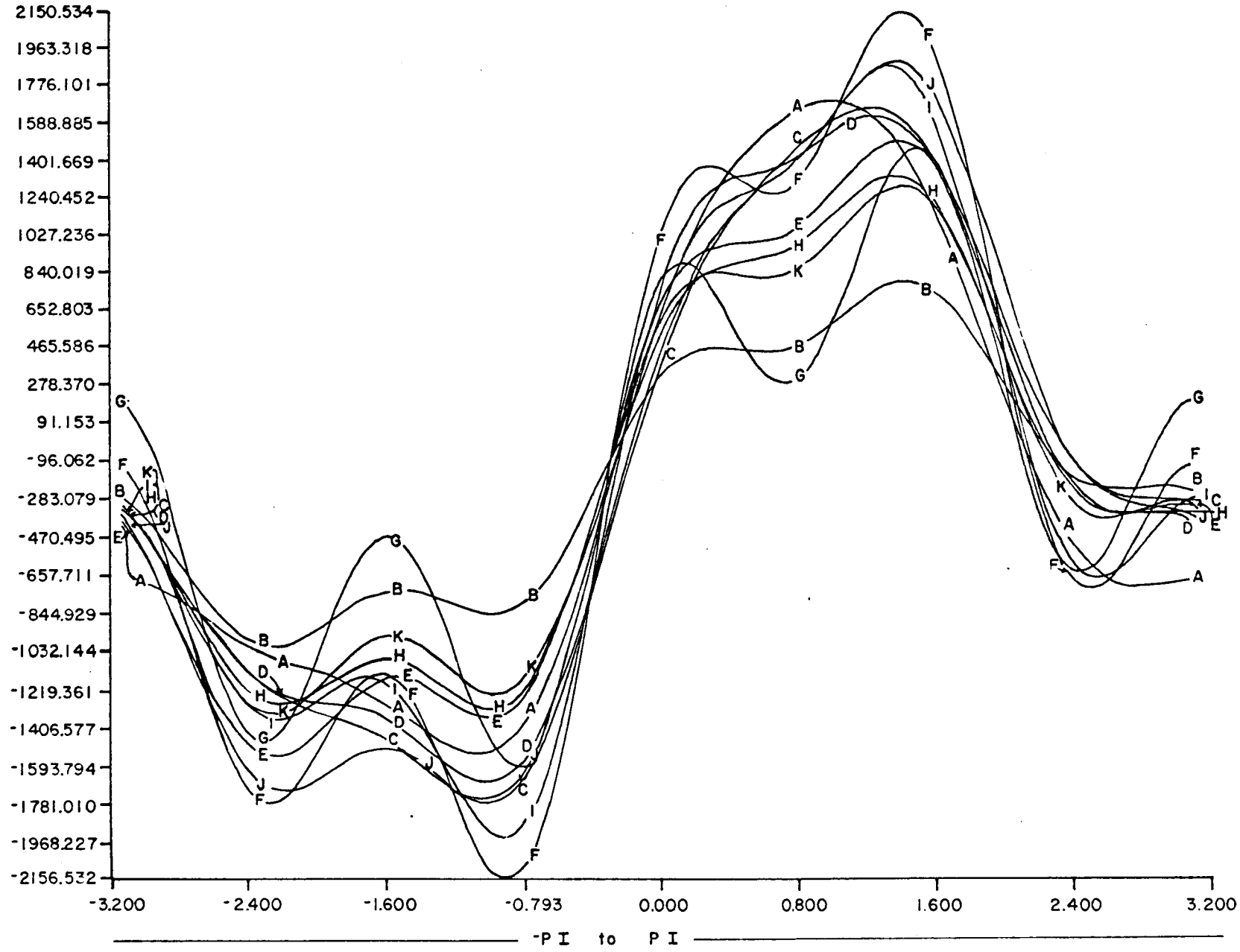


Figure 12. Cluster group plots of all rig samples. Plots represent the combined effects of the 13 parameters in tables 8a-c. The eleven lines above depict the respective means of before, during, and after drilling samples at the 0, 100, 500, and 1000 m respectively.

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 a difference in the two samples. Figure 8, representing the rig site, shows how little difference existed in the before and after phases of drilling based on oil pollution indicators. Statistically these samples were very similar. Even more dramatic are the similarities seen in samples taken at 100 m, 500 m and 1000 m from the rig. Figure 12 clearly demonstrates that not only was there no clear difference due to drilling, there evidently was no major difference in any of the 74 samples.

Another method of analyzing these 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 8-12. The F ratios which were found are shown in Table 9. At the 99.95% level ($\alpha = 0.0005$) no significant difference existed among the three groups at 100 m, 500 m and 1000 m from the rig. However at the 99.9% level a significant difference did 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 yielded the most significant contribution to the discrimination of the groups are phytane/C_{18} and the LMW odd/even ratios. There, though

the hydrocarbon data indicates only minimal changes occurres in the area adjacent to the oil rig off Mustang Island, changes should have been more pronounced in the area immediately surrounding the rig.

Table 9. Discriminant analysis data on rig monitoring samples.

Distance from Rig (m)	DF1	DF2	F Ratio
100	26	18	5.222
500	24	14	2.908
1000	26	20	1.649

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

Based on the various ratios reported, it appears that neither short-term seasonal nor drilling operations had any effect upon the hydrocarbon content of the organisms analyzed. This study suggests that the ratios reported have limited usefulness, especially in biological samples. There appear to be no significant inter- or intra- species differences in hydrocarbon concentrations in the biological samples. However, careful study of the chromatograms gives unmistakable evidence of contamination (probably No. 2 fuel oil) in two samples taken during the after period. Similarly, two samples from the during period may also be contaminated. This emphasizes the care that must be taken to prevent contamination; presumably these samples were contaminated when the trawl net came through a small surface film.

Only two species of epifauna were analyzed for hydrocarbon content in all three drilling phases. The two species, Penaeus setiferus and Trachypenaeus similis, are highly motile nektonic forms. The average aliphatic and aromatic hydrocarbon data for these species are presented in Table 10. The results of t tests ($\alpha \leq 0.05$) show that the T. similis samples analyzed from the after drilling phase were significantly higher in aromatic hydrocarbons than were the samples analyzed from the before and during phases.

Sediment and epifaunal samples were also analyzed for the following trace metals: Cd, Cr, Cu, Fe, Pb, Ni and V. Barium was also determined in the sediment samples.

The averaged trace metal concentrations in the sediments for each station during the three sampling operations are shown in Table 11. Inspection of these data (and also the raw data) reveals variations in the 74 samples. These variations were attributed to errors in analysis combined with minor mineralogical and textural differences between samples. The averaged data shown in the above table for both location and sampling period indicate standard deviations which are essentially those of analytical techniques alone. Nickel appears to have an observable change between the during and post sampling period; the standard deviations of the three sampling periods overlap however and these nickel changes are interpreted as being coincidental. Nickel is a particularly difficult element to analyze by atomic absorption, due to interferences by Al, Ca, and Fe all of which exist in high concentration in these sediments and to losses in small amounts of insoluble residue, which, at times, form during sample preparation.

Table 10. Average conccentrations of aliphatic and aromatic hydrocarbons in *Penaeus setiferus* and *Trachypenaeus similis* samples collected from the oil rig study site. Concentrations given in µg/g dry weight.

	Penaeus setiferus			*Trachypenaeus similis*		
Drilling phase	Samples Analyzed	Aliphatics	Aromatics	Samples Analyzed	Aliphatics	Aromatics
Before						
$\bar{X}$ 1 S.D.	12	5.2±8.0	2506.9±2036.1	7	4.6±4.4	867.3±330.1
Range		0.8-29.7	128.4-7970.8		0.4-11.3	475.7-1304.7
During						
$\bar{X}$ 1 S.D.	5	2.3±1.5	1404.6±704.0	7	11.1±21.4	958.3±399.7
Range		0.9-4.5	896.3-2621.3		0.5-54.7	591.6-1731.3
After						
$\bar{X}$ 1 S.D.	2	5.7±8.0	4674.6±1763.7	10	11.7±18.1	3271.3±1849.4
Range		0.07-11.4	3427.5-5921.7		0.2-46.8	964.0-6017.3
t tests ($\alpha \leq 0.05$)						
Before vs after		-0.014	-1.409		-1.003	-3.112*

* Significant difference at $\alpha \leq 0.05$.

Table 11. Rig monitoring study, surface sediment trace metal concentrations averaged at each station for all three sampling periods (TS1, TS2, TS3).

Station	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Pb (µg/g)	Ni (µg/g)	V (µg/g)
500101	955	0.05±0	52.4±8.1	13.5±0.5	3.12±0.04	20.1±3.0	26.9±1.1	75±24
510201	2,115	0.09±0.01	53.5±7.0	14.4±1.2	2.81±0.14	21.4±2.7	27.5±1.5	83±7
510301	798	0.06±0.01	52.6±7.1	13.9±0.8	2.92±0.26	21.0±1.8	23.1±1.8	86±4
510401	890	0.05±0.02	56.9±1.7	14.9±0.6	3.18±0.12	24.3±4.8	29.8±2.7	100±33
510501	654	0.10±0.01	49.2±8.8	12.8±2.5	2.75±0.36	20.6±1.8	25.6±3.5	83±15
510601	1,663	0.06±0.01	53.5± -	14.5±0.8	2.79±0.27	20.8±4.0	28.0±6.2	87±17
510701	872	0.04±0.01	47.2±9.5	12.9±1.6	2.70±0.43	18.9±3.4	26.5±7.1	83±15
510801	765	0.06±0.03	53.6±6.0	13.8±0.8	2.92±0.09	22.2±0.4	25.2±2.5	82±14
510901	1,604	0.05±0.01	55.4±3.9	14.5±0.6	2.95±0.06	21.3±1.8	27.8±4.6	87±17
551001	605	0.04±0.01	53.5±4.3	14.6±1.4	3.05±0.18	21.2±2.2	28.8±4.5	94±1
551101	550	0.09±0.02	52.8±2.9	14.3±1.4	2.91±0.30	20.2±2.6	26.6±2.3	82±11
551201	656	0.09±0.03	49.0±6.8	13.1±2.0	2.67±0.65	19.5±1.3	22.7±0.5	83±5
551301	618	0.05±0.02	51.6±6.5	14.5±1.1	2.90±0.19	22.0±1.2	26.9±0.3	83±8
551401	583	0.09±0.02	54.0±0.3	14.3±0.6	2.92±0.16	20.9±0.3	25.2±1.8	78±12
551501	581	0.08±0.03	51.9±6.7	14.5±0.9	3.02±0.16	20.1±1.0	24.9±1.1	82±4
551601	582	0.09±0.02	47.0±16.8	13.5±2.6	2.90±0.48	20.6±1.9	24.9±3.3	100±5
551701	614	0.06±0.02	50.2±2.1	13.9±0.5	2.76±0.04	19.7±1.5	26.2±1.2	69±18
591801	680	0.05±0.01	54.1±4.0	14.0±0.7	2.79±0.15	21.4±1.4	25.6±2.1	80±15
591901	655	0.10±0.01	54.1±6.9	14.2±0.6	2.92±0.14	20.7±3.1	27.6±5.3	97±6
592001	636	0.09±0.03	53.4±9.6	13.6±0.5	2.69±0.54	20.1±1.9	23.4±0	70±11
592101	640	0.05±0.01	51.9±12.1	14.1±0.5	3.06±0.17	21.5±2.4	26.8±4.0	103±6
592201	625	0.06±0.04	58.1±3.3	15.0±0.4	3.07±0.17	21.8±1.0	25.9±2.1	90±6
592301	554	0.06±0.01	51.7±17.1	13.9±2.3	3.02±0.25	22.3±3.8	25.6±6.2	83±18
592401	649	0.09±0.03	54.3±3.7	15.0±0.8	2.97±0.19	23.5±3.7	25.5±2.3	86±21
592501	647	0.05±0.01	52.8±5.2	14.1±2.0	2.86±0.33	21.1±0.7	26.1±6.2	94±19
Average of all stations		0.07±0.03 (n=74)	52.6±6.9 (n=73)	14.1±1.2 (n=74)	2.91±0.27 (n=74)	21.1±2.3 (n=74)	26.2±3.4 (n=69)	85±14 (n=71)

Table 11. Rig monitoring study, surface sediment trace metal concentrations averaged at each station for all three sampling periods (TS1, TS2, TS3) - continued.

Station	Ba (µg/g)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Pb (µg/g)	Ni (µg/g)	V (µg/g)
Trefry, 1974 (ave. NW GOM; hot HNO_3-HCl leach)	1.5	0.2	-	7.2		9.8	15.9	-
TS1 Average	575±95 (n=22)	0.07±0.02 (n=25)	49.5±7.8 (n=25)	14.0±1.2 (n= 25)	3.00±0.3 (n=25)	19.2±1.6 (n=25)	25.6±2.3 (n=25)	87±15 (n=24)
TS2 Average	1000±112 (n=22)	0.07±0.03 (n=25)	55.4±5.2 (n=25)	14.2±0.9 (n=25)	2.90±0.3 (n=25)	22.0±2.2 (n=25)	24.6±2.1 (n=25)	84±10 (n=24)
TS3 Average	1096±109 (n=16)	0.07±0.03 (n=24)	52.7±6.4 (n=22)	14.0±1.7 (n=24)	2.90±0.3 (n=24)	21.9±2.0 (n=23)	29.1±4.3 (n=19)	85±18 (n=23)

To further support these observations, Table 12 lists the metal/iron ratio for Cr, Cu, Pb, Ni and V (Cd is excluded due to its extremely low level and resulting higher degree of uncertainty). The data also indicate that no spatial trends exist in the metal concentrations.

As noted earlier, the only drilling effects detected were an incease in the abount of barium in the sediment and the presence of drill cuttings.

The barium data showed a marked increase in both the during and after drilling phases. Since barite (barium sulfate) is commonly used in drilling muds this finding is not unexpected. The amounts found were a function of both distance from the rig and tidal currents in the area. During drilling, the barium levels increased markedly near the rig (as much as eight-fold) at some stations. The distribution of barium demonstrates the influence of the local NE-SW tidal currents (Figures 13, 14 and 15). Barium levels also increased significantly but to a much smaller extent throughout the sampling area. Approximately three months after drilling was stopped and the rig had moved to another location, the "after-samples" were collected. Barium levels had returned to pre-rig levels in much of the area although a "core" of high levels still existed near the former drill site. This core was still distributed along a NE-SW axis but did not extend as far as the 500 m circle as it did during drilling (Figure 15).

The light hydrocarbon analyses ("sniffer") conducted prior to and during drilling indicated no significant change in these compounds. In most samples only methane was detected in significant amounts (100-?00 nℓ/ℓ). The "sniffer" unit was tested in the Corpus Christi ship channel during one of the "weather days" to verify that it was operating properly and high concentrations of hydrocarbons (up to C_6) were detected near refineries and

Table 12. Rig monitoring study, surface sediment metal/iron ratios.

Station	Sample Set	Ba/Fe ($\times 10^4$)	Cr/Fe ($\times 10^4$)	Cu/Fe ($\times 10^4$)	Fe (%)	Pb/Fe ($\times 10^4$)	Ni/Fe ($\times 10^4$)	V/Fe ($\times 10^4$)
500101	TS1	181	18.8	4.2	3.09	5.8	8.9	18.8
	TS2	-	14.8	4.4	3.15	7.1	8.3	29.2
	TS3	524	-	-	-	-	-	-
	Average	352	16.8±2.8	4.3±0.1	3.12±0.04	6.4±0.9	8.6±0.4	29.2
510201	TS1	199	17.3	5.1	2.67	6.9	10.9	31.5
	TS2	1,464	21.2	5.6	2.82	8.4	9.3	26.6
	TS3	572	18.4	4.7	2.95	7.4	9.2	30.2
	Average	745	19.0±2.0	5.1±0.5	2.81±0.14	7.6±0.8	9.8±1.0	29.4±2.5
510301	TS1	163	17.5	4.2	3.21	6.0	6.8	28.4
	TS2	291	20.2	5.2	2.83	7.5	8.6	29.7
	TS3	366	16.3	4.9	2.72	8.4	(13.9)	30.5
	Average	273	18.0±2.0	4.8±0.5	2.92±0.26	7.3±1.2	7.7±1.3	29.5±1.1
510401	TS1	154	17.8	4.5	3.16	6.6	8.5	27.5
	TS3	391	17.8	4.5	3.31	9.0	9.6	23.0
	TS3	-	18.1	5.0	3.08	7.3	10.0	44.5
	Average	273	17.9±0.2	4.7±0.3	3.18±0.12	7.6±1.2	9.4±0.8	31.7±11.3
510501	TS1	227	15.9	4.6	3.07	6.4	9.2	26.4
	TS2	217	20.5	5.1	2.81	8.1	9.5	35.9
	TS3	-	17.0	4.2	2.36	8.2	9.2	29.2
	Average	222	17.8±2.4	4.6±0.5	2.75±0.36	7.6±1.0	9.3±0.2	30.5±4.9
510601	TS1	211	21.6	5.9	2.48	6.9	10.7	42.3
	TS2	445	18.5	4.7	2.90	7.0	7.9	29.7
	TS3	1,062	-	5.1	2.99	8.4	11.6	23.8
	Average	573	20.1±2.2	5.2±0.6	2.79±0.27	7.4±0.8	10.1±1.9	31.9±9.5

Table 12. Continued.

Station	Sample Set	Ba/Fe ($\times 10^4$)	Cr/Fe ($\times 10^4$)	Cu/Fe ($\times 10^4$)	Fe (%)	Pb/Fe ($\times 10^4$)	Ni/Fe ($\times 10^4$)	V/Fe ($\times 10^4$)
510701	TS1	359	17.2	5.1	2.22	6.8	9.7	32.0
	TS2	312	18.9	4.7	3.03	7.0	7.7	33.0
	TS3	-	16.1	4.6	2.86	7.2	12.1	27.6
	Average	336	17.4±1.4	4.8±0.3	2.70±0.43	7.0±0.2	9.8±2.2	30.9±2.9
510801	TS1	252	20.7	4.6	2.90	7.6	8.8	23.5
	TS2	264	16.0	4.9	3.02	7.5	7.5	27.5
	TS3	-	18.4	4.7	2.85	7.7	9.7	33.7
	Average	258	18.4±2.4	4.7±0.2	2.92±0.09	7.6±0.1	8.7±1.1	28.2±5.1
510901	TS1	183	20.1	5.2	2.91	6.7	9.2	36.8
	TS2	375	19.4	5.0	2.93	7.9	8.1	27.0
	TS3	1,053	16.9	4.6	3.02	7.1	10.9	25.2
	Average	537	18.8±1.7	4.9±0.3	2.95±0.06	7.2±0.6	9.4±1.4	29.7±6.2
551001	TS1	148	17.2	5.0	3.26	6.2	7.9	29.1
	TS2	203	16.5	4.7	2.94	8.1	8.5	-
	TS3	251	18.9	4.6	2.95	6.6	11.2	31.5
	Average	201	17.5±1.2	4.8±0.2	3.05±0.18	7.0±1.0	9.2±1.8	30.3±1.7
551101	TS1	164	16.3	4.9	3.14	5.6	9.2	26.8
	TS2	194	18.6	4.9	3.02	7.5	8.1	23.2
	TS3	-	19.9	4.9	2.57	7.9	10.3	35.4
	Average	179	18.3±1.8	4.9	2.91±0.30	7.0±1.2	9.2±1.1	28.5±6.3
551201	TS1	-	16.4	4.3	3.41	6.1	6.6	22.9
	TS2	273	20.3	5.7	2.40	7.6	9.7	34.2
	TS3	-	19.2	4.9	2.20	8.8	10.1	40.0
	Average	273	18.6±2.0	5.0±0.7	2.67±0.65	7.5±1.4	8.8±1.9	32.4±8.7

Table 12. Continued.

Station	Sample Set	Ba/Fe (x 10^4)	Cr/Fe (x 10^4)	Cu/Fe (x 10^4)	Fe (%)	Pb/Fe (x 10^4)	Ni/Fe (x 10^4)	V/Fe (x 10^4)
551301	TS1	179	14.4	5.1	3.12	6.7	8.7	28.2
	TS2	242	18.7	4.9	2.80	7.8	9.5	30.7
	TS3	-	20.7	5.1	2.79	8.3	9.7	26.5
	Average	211	17.9±3.2	5.0±0.1	2.90±0.19	7.6±0.8	9.3±0.5	28.5±2.1
551401	TS1	182	17.3	4.6	3.11	6.7	8.5	25.1
	TS2	-	18.9	4.8	2.84	7.5	8.4	31.7
	TS3	213	19.3	5.3	2.82	7.3	(13.1)	23.4
	Average	198	18.5±1.1	4.9±0.4	2.92±0.16	7.2±0.4	8.5±0.1	26.7±4.4
551501	TS1	196	14.0	4.4	3.16	6.0	8.1	27.2
	TS2	205	19.9	4.9	2.85	7.1	8.5	28.4
	TS3	178	17.9	5.1	3.05	6.9	(14.1)	25.6
	Average	193	17.3±3.0	4.8±0.4	3.02±0.16	6.7±0.6	8.3±0.2	27.1±1.4
551601	TS1	173	11.7	4.7	3.01	6.5	8.8	34.9
	TS2	193	19.9	4.7	3.32	6.8	8.2	28.6
	TS3	-	16.6	4.5	2.38	8.2	8.9	-
	Average	183	18.3±2.3	4.6±0.1	2.90±0.48	7.2±0.9	8.6±0.4	31.8±4.5
551701	TS1	193	17.7	5.0	2.80	6.8	9.5	28.2
	TS2	199	17.8	4.9	2.73	6.8	9.1	29.3
	TS3	277	19.1	5.2	2.75	7.8	9.9	17.8
	Average	223	18.2±0.8	5.0±0.2	2.76±0.04	7.1±0.6	9.5±0.4	28.8±0.8
591801	TS1	248	19.0	5.1	2.62	7.6	9.3	26.0
	TS2	244	19.8	5.1	2.91	7.4	8.4	26.1
	TS3	-	19.2	4.9	2.85	8.0	9.8	34.0
	Average	246	19.3±0.4	5.0±0.1	2.79±0.14	7.7±0.3	9.2±0.7	28.7±4.6

Table 12. Continued.

Station	Sample Set	Ba/Fe ($\times 10^4$)	Cr/Fe ($\times 10^4$)	Cu/Fe ($\times 10^4$)	Fe (%)	Pb/Fe ($\times 10^4$)	Ni/Fe ($\times 10^4$)	V/Fe ($\times 10^4$)
591901	TS1	192	16.8	5.1	2.75	6.4	9.5	33.8
	TS2	267	19.5	4.5	3.00	6.9	7.7	34.7
	TS3	211	19.3	4.9	3.00	7.9	11.2	31.7
	Average	223	18.5±1.5	4.8±0.3	2.92±0.14	7.1±0.8	9.5±1.8	33.4±1.5
592001	TS1	266	20.7	6.3	2.08	8.7	11.3	32.2
	TS2	250	17.9	4.5	3.10	6.6	7.6	26.5
	TS3	207	21.4	4.8	2.89	7.5	(13.2)	21.1
	Average	241	20.0±1.9	5.2±1.0	2.69±0.54	7.6±1.1	9.5±2.6	26.6±5.6
592101	TS1	230	(13.2)	4.8	2.87	6.5	9.1	38.0
	TS2	225	19.2	4.5	3.12	7.3	7.4	32.1
	TS3	174	18.1	4.6	3.20	7.2	9.4	30.9
	Average	210	18.7±0.8	4.6±0.2	3.06±0.17	7.0±0.4	8.7±1.2	33.7±3.8
592201	TS1	173	16.7	4.7	3.25	6.4	7.6	30.2
	TS2	239	19.6	5.0	3.04	7.4	8.2	28.0
	TS3	202	20.8	5.0	2.91	7.6	9.7	29.6
	Average	205	19.0±2.1	4.9±0.2	3.07±0.17	7.1±0.6	8.5±1.1	29.3±1.1
592301	TS1	191	(11.8)	4.1	2.73	6.6	7.3	-
	TS2	186	19.8	4.8	3.19	7.3	7.8	21.9
	TS3	176	19.0	4.9	3.14	8.1	10.3	30.3
	Average	184	19.4±0.4	4.6±0.4	3.02±0.25	7.3±0.8	8.5±1.6	26.1±5.9
592401	TS1	-	17.4	5.2	2.89	7.0	9.4	38.1
	TS2	198	18.1	4.5	3.19	7.2	7.5	24.1
	TS3	236	19.3	5.6	2.83	(9.7)	(13.1)	25.1
	Average	217	18.3±1.0	5.1±0.6	2.97±0.19	7.1±0.1	8.5±1.3	29.1±7.8

Table 12. Continued.

Station	Sample Set	Ba/Fe ($\times 10^4$)	Cr/Fe ($\times 10^4$)	Cu/Fe ($\times 10^4$)	Fe (%)	Pb/Fe ($\times 10^4$)	Ni/Fe ($\times 10^4$)	V/Fe ($\times 10^4$)
592501	TS1	-	17.7	4.7	3.17	6.4	7.7	31.9
	TS2	284	18.6	4.7	2.52	8.3	8.3	29.0
	TS3	199	19.1	5.3	2.90	7.5	11.4	37.2
	Average	242	18.5±0.7	4.9±0.4	2.86±0.33	7.4±1.0	9.1±2.0	32.7±4.2
Average of all stations		280	18.4±1.7 (n=70)	4.9±0.4 (n=74)	2.91±0.27 (n=74)	7.3±0.7 (n=73)	9.1±1.2 (n=69)	29.8±4.8 (n=69)
Trefry, 1974 (ave. N.W. GOM; hot HNO_3-HCl leach)				4.8 *T/P=0.98	1.5 *T/P=0.52	6.5 *T/P=0.89	10.6 *T/P=1.16	
TS1 Average		192	16.5±1.6	4.7±0.4	3.0±0.3	6.4±0.7	8.9±1.2	30.0±5.5
TS2 Average		345	19.1±1.7	4.9±0.3	2.9±0.2	7.6±0.7	8.5±0.7	28.8±3.7
TS3 Average		361	18.2±1.7	4.8±0.4	2.9±0.3	7.6±0.8	10.2±1.0	29.8±6.1

* T/P = the ratio of Trefry's values to the values of this report.

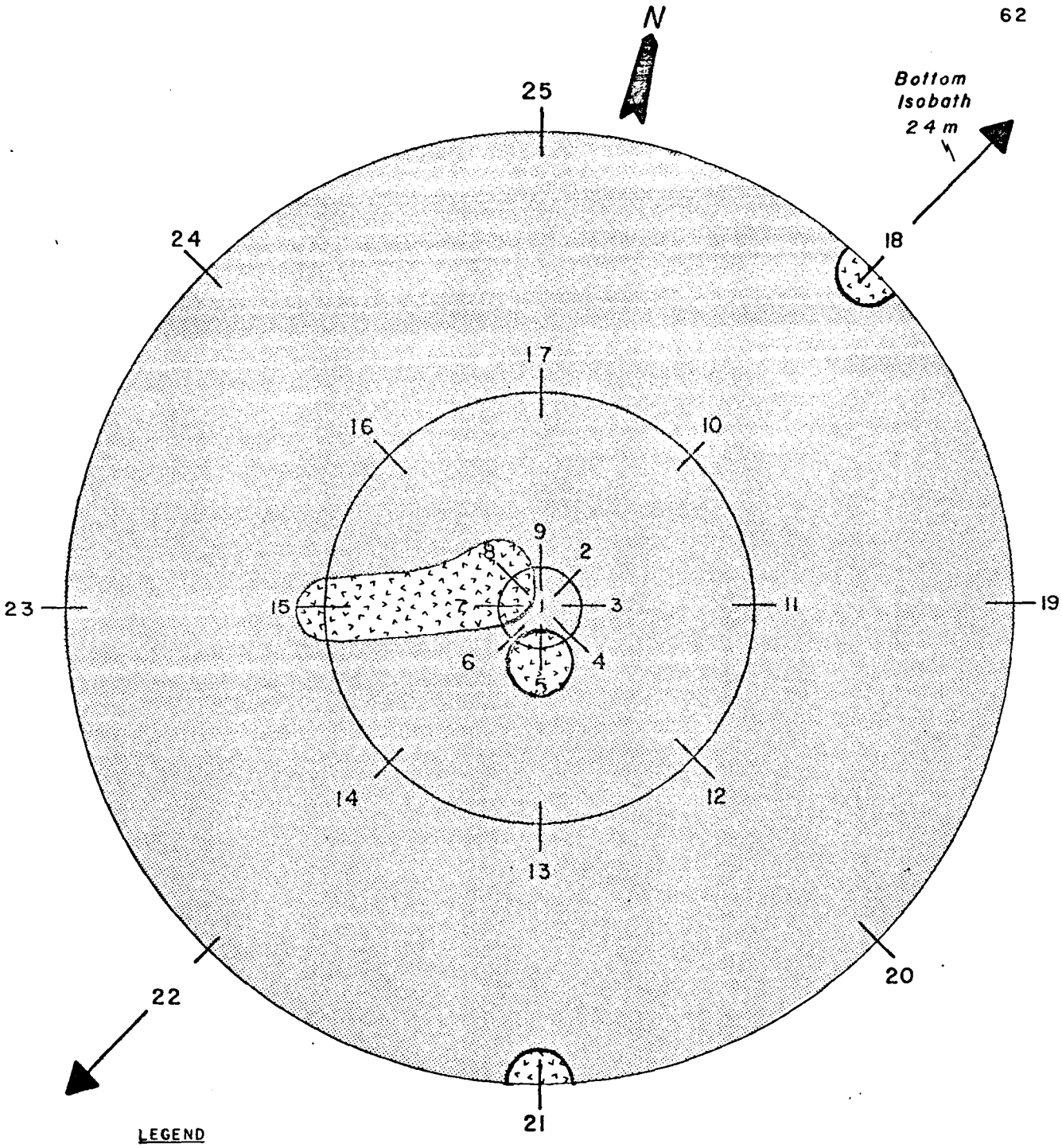


Figure 7.
Distribution of Barium pre-drilling.

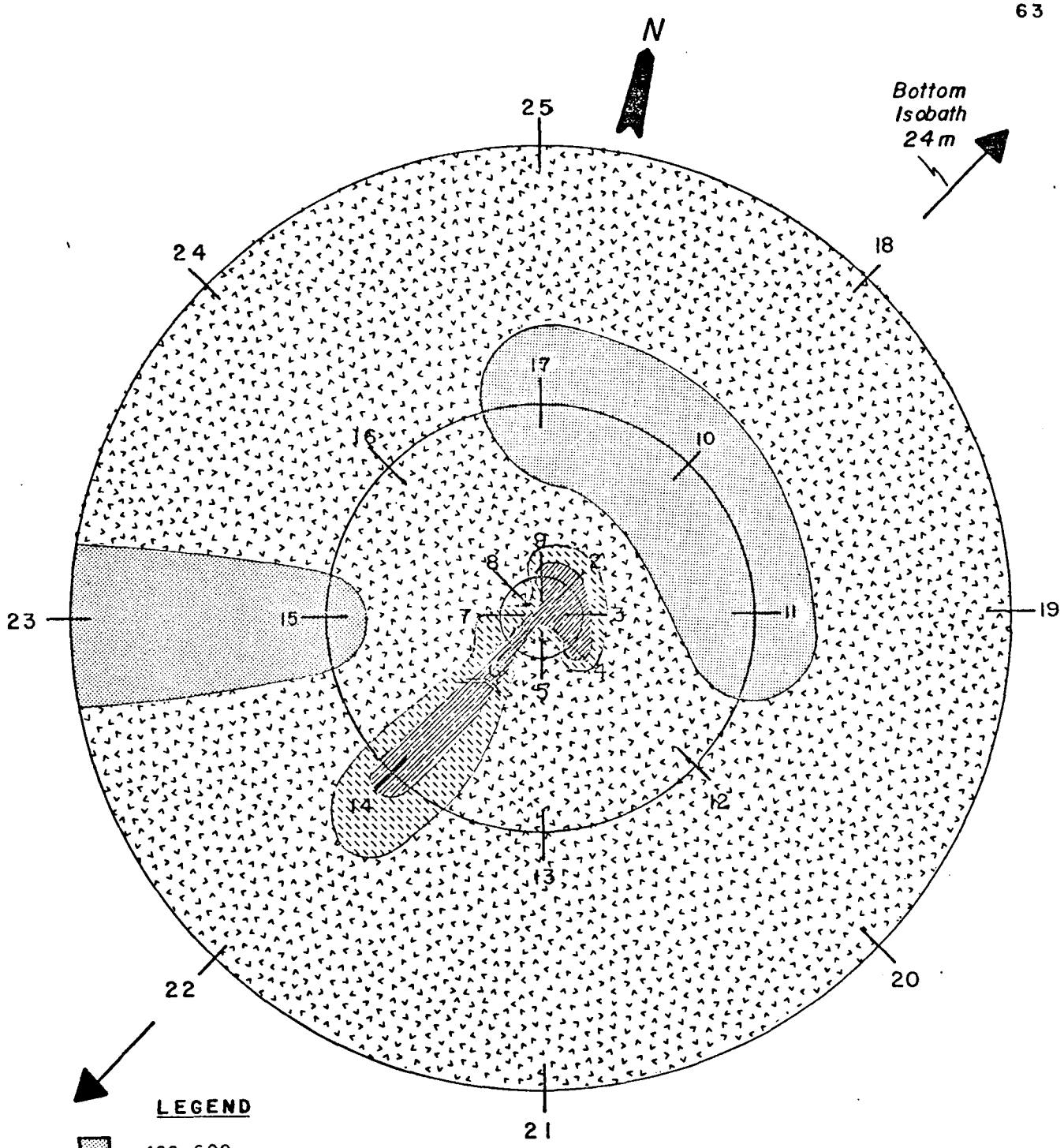


Figure 8.
Distribution of Barium during drilling.

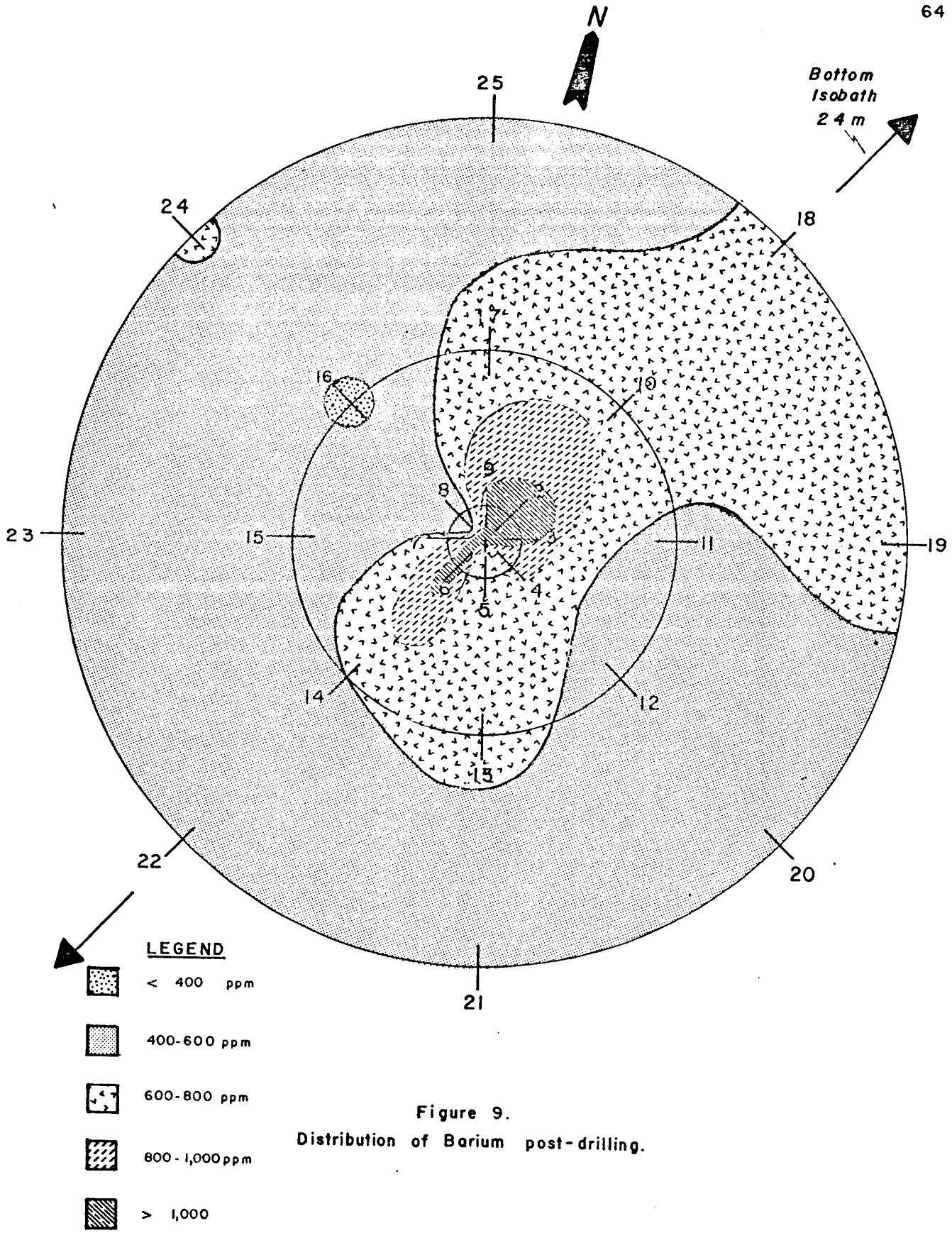


Figure 9.
Distribution of Barium post-drilling.

decreased markedly toward the open waters of the Gulf.

Table 13 shows the average metal concentration in individual species before, during and after rig operations. A total of 148 out of the 153 samples received were analyzed for Cd, Cr, Cu, Fe, Pb, Ni and V. Five stomatopod samples were inadvertently allowed to thaw for an excessive period ot time and could not be analyzed. These values are generally low and are comparable to levels in organisms from other "clean" areas. The rig monitoring site is in close proximity to Station 1 on Transect II of the BLM South Texas Outer Continental Shelf Baseline Study (27°40'N, 96°59'W, depth 22 m). The values for shrimp reported here agree well with those levels found in shrimp collected from baseline Station 1/II at three different times during 1975 (Presley, et al., 1976).

Since only a few samples of crabs and the shrimp Sicyonia were collected their values are not included in this summary table. The decrease in Cr, Pb and, to a lesser extent, in Ni levels from before through post drilling is most likely a reflection of the change from flame to flameless AAS techniques during the analysis of these samples than to any real process occurring in the environment. Cadmium, Cu and V showed significant intraspecific variation among the three phases for any of the species analyzed. Due to the severe matrix effects resulting from the high Ca concentration in Astropecten and crab samples, the Fe data especially, for these samples should, be viewed cautiously.

Iron was the only element which showed considerable and significant intraspecific change between the three phases of this study. For P. setiferus the during Fe concentration was significantly different from the levels

Table 13. Average trace metal concentrations in individual species before (Phase 1), during (Phase 2) and after (Phase 3) rig operation. Average concentration in ppm dry weight ± one standard deviation.

ganism	Phase	Number of Samples Analyzed	Cd	Cr	Cu	Fe	Pb	Ni	V
naeus	1	20	0.04±0.04	1.4±0.5	26±5	10±6	0.7±0.3	0.3±0.3	0.2±0.1
setiferus	2	8	0.05±0.02	0.6±0.2	28±4	20±9	0.4±0.4	0.2±0.1	0.4±0.2
	3	10	0.03±0.02	0.1±0.04	22±3	7±4	0.2±0.1	0.3±0.2	<0.1
naeus	1	None available.							
duorarum	2	None available.							
	3	10	0.05±0.03	<0.1	21±3	5.1±1.8	0.14±0.05	0.13±0.05	<0.1
achypenaeus	1	13	0.03±0.03	1.0±0.5	23±3	31±34	0.9±0.2	0.4±0.3	0.3±0.2
similis	2	11	0.04±0.06	0.7±0.4	25±3	57±24	0.6±0.4	0.5±0.4	0.4±0.1
	3	20	0.03±0.02	0.2±0.1	19±3	23±20	0.1±0.04	0.5±1.3	<0.1
dilla	1	4	1.6±0.4	0.8±0.3	64±12	36±8	1.2±0.7	0.9±0.3	0.6±0.1
empusa	2	None available.							
	3	12	1.4±0.7	0.4±0.7	76±12	15±4	0.2±0.1	1.7±0.7	0.3±0.1
dilla	1	None available.							
chydea	2	12	1.9±0.7	1.6±2.1	81±11	103±60	1.4±1.1	1.3±0.4	0.6±0.3
	3	7	0.8±0.5	0.5±0.6	92±12	30±11	0.2±0.05	1.9±1.7	0.5±0.2
tropecten	1	2	0.55±0.07	0.6±0	9.4±2.3	440±90	9.6±3.4	3.0±1.3	0.8±0.5
duplicatus	2	8	0.2±0.1	<0.4	5.4±1.8	432±93	5.3±4.1	1.0±1.0	2.7±1.0
	3	2	0.5±0.1	0.6±0	12±4	252±30	0.6±0.4	1.6±0.9	1.1±0.1

for the pre-, or post drilling operation as judged by a "t-test" for two population means (Sokal and Rohlf, 1969). The during Fe concentration was also significantly different ($\alpha<0.01$) from the post drilling level for T. similis and S. chydaea. For S. empusa the pre- Fe concentration was significantly ($\alpha<0.01$) different from that of the post drilling operation. Plotting the Fe values for various species according to station location showed no spatial localization of significantly different Fe values among the phases. Organisms containing higher Fe levels in the during phase were scattered over the entire rig monitoring study area and were not clustered around the rig site. Surface sediment iron concentrations in the vicinity of the rig were measured as part of a separate segment of this study (Presley and Dobson, 1976). No significant change in the sediment Fe concentration among the three phases was observed.

The increase in organismal Fe concentration observed in the during phase of this study could be the result of drilling operations at the site or a physiological response by the organisms to some other change in the environment (e.g., storm activity) coincident with but unrelated to the presence of the rig. The data presented here are insufficient to establish the cause of the observed changes. The effect which the observed increase in body Fe would have on the organisms themselves is uncertain.

Biology

The foraminiferal community composition indicated a "stressed environment" prior to initiation of rig installation and operations. Only four species occurred consistently in abundances over one percent. The stress indicator species, Ammonia beccarii, completely dominated

every sample and composed from 55-80% of the living fauna and somewhat less of the total (live + dead) fauna. The other three major dominant species, in order of abundance, were Elphidium galvestonense, Buliminella cf. B. bassendorfensis and Nonionella atlantica; these species are also indicators of environmental stress. Species abundance was low and ranged from eight-18 species per sample. Specimen abundance was also unusually low for the fine grain sediments of the rig site (less than 63 μm in diameter) and was generally less than 100 specimens per one milliliter of sediment. An additional indication of stressed conditions was the small size of the individuals (usually less than 125 μm).

Drilling activities further increased the stress on the foraminifera populations of the site area. Total and live specimen abundances of samples collected during drilling activities were significantly less (t tests, $\alpha \leq 0.05$) than those in the pre- drilling samples (Table 14). The greatest effect on specimen abundances occurred along the 100 m periphery but adverse effects were demonstrated all the way out to the 1000 m periphery. Stations 2, 3, 10, 17 and 19 had the greatest degree of change, and all are located northeast of the rig suggesting bottom currents may have carried rig-associated materials to the northeast. The percentage contribution of the stress indicator species, Ammonia beccarii, to the total specimen abundance increased at all but three stations during the drilling phase (Table 15).

Post drilling samples displayed a partial recovery when compared to the pre- drilling conditions. Total and live specimen abundances were significantly higher than during drilling levels. The percentage contribution of Ammonia beccarii to specimen abundances decreased at all but

Table 14. Foraminiferal abundance and per cent living - Mustang Island Rig Monitoring area.

	TOTAL/SAMPLE			LIVE/SAMPLE			% LIVE		
SAMPLE #	F1	F2	F3	F1	F2	F3	F1	F2	F3
500102	11248	----	8438	658	----	532	5.8	----	6.3
510201	3485	1029	2267	2259	379	815	64.8	36.8	36.0
510301	3308	267	1721	2833	195	1142	85.6	76.0	66.4
510401	800	353	578	360	236	303	45.0	66.9	52.4
510501	1034	655	806	591	348	452	57.2	53.1	37.6
510601	827	2057	2535	488	1263	1518	59.0	61.4	59.9
510701	1051	306	527	348	109	163	33.1	35.6	30.9
510801	1205	415	601	466	155	245	38.7	37.3	40.8
510901	10000	497	742	2008	294	393	20.1	59.2	53.0
551001	3000	878	1898	1200	189	689	40.0	21.5	36.3
551101	1800	497	1136	274	185	215	15.2	37.3	18.9
551201	2400	800	1648	848	493	693	35.3	61.6	42.1
551301	1149	339	724	234	60	182	20.4	25.6	25.1
551401	1974	870	1376	726	299	549	36.3	41.2	39.9
551501	1200	796	973	600	411	508	50.0	51.6	52.2
551601	2764	810	1775	1032	326	626	37.3	40.3	35.3
551701	725	200	525	231	74	153	31.9	36.9	29.1
591801	600	380	490	193	134	162	32.2	35.2	33.1
591901	1200	354	774	701	213	453	58.4	60.3	58.5
592001	1054	465	765	432	205	317	41.0	44.1	41.4
592101	1187	751	951	514	342	430	43.3	45.6	45.2
592201	1406	1054	1262	450	351	401	32.0	33.3	31.8
592301	4800	4080	4440	2480	2158	2348	51.9	52.9	52.9
592401	527	295	397	145	92	122	27.5	31.2	30.7
592501	616	761	596	225	288	255	36.5	37.8	42.8

F1 = November 1975
F2 = January 1976
F3 = March 1976

Table 15. Percent distribution of one of the major living dominant foraminiferal species - Mustang Island rig monitoring area.

Ammonia beccarii

Sta. No.	001	102	103	104	105	106	107	108	109	510	511	512	513	514	515	516	517	918	919	920	921	922	923	924	925
F1	55.3	69.0	60.0	61.0	73.0	73.7	73.3	62.3	75.0	70.7	87.6	64.7	66.7	67.0	83.6	68.0	78.8	80.8	74.3	83.0	72.0	84.7	75.0	73.1	73.3
F2		68.0	83.1	86.0	83.0	79.0	74.3	80.0	84.7	64.0	86.5	83.0	71.7	75.6	84.0	71.0	81.1	82.1	75.1	84.9	73.7	88.0	77.0	73.9	74.7
F3	58.3	68.0	65.3	64.3	78.3	76.3	71.8	76.3	79.3	75.0	87.0	75.0	64.8	71.3	84.0	69.7	83.0	82.1	77.3	85.7	76.3	86.7	76.3	72.1	74.5

F1 - November, 1975; F2 - January, 1976; F3 - March, 1976

five stations.

The bottom composition throughout the area consisted of soft sediments and only motile macroinvertebrates were present. Only two species of Penaeid shrimp were collected in sufficient quantities for histopathological analysis. A total of 150 specimens of Trachypenaeus similis (25 pre-, 25 during and 100 post drilling) and 98 specimens of Penaeus setiferus (46 pre-, 52 during and 0 post drilling) were analyzed for evidence of histopathology.

Tissue sections examined included the cornea, carapace, muscle, hepatopancreas, kidney and gonad. Pathology, excluding parasites which were observed in a few of the individuals, was not detected in any of the before, during or after samples. These observations are not surprising since the shrimp probably move in and out of the area and the same population was not repeatedly sampled. The abundance of P. setiferus in the post drilling phase was so low that sufficient samples were available for trace metal and hydrocarbon analyses only.

CONCLUSIONS

The significant changes observed in the monitored variables of this study cannot, in toto, be attributed to the drilling operations of the oil rig. Environmental effects directly attributable to drilling activities were the presence of obvious drill cuttings, the increased barium levels in the bottom sediments and the added stress on the already depaupered foraminiferal populations. The other significant changes which occurred may be attributable to the high storm activity in the study site region prior to and during drilling operations. Storm surge could cause resuspension

of the bottom sediment and conceivably alter its textural and compositional characteristics. On the other hand, the influx of drilling muds into the study site may have significantly influenced the bottom sediment texture and composition beyond that of drill cuttings and increased barium levels. Unfortunately, the specific composition of the drilling muds utilized is unknown. The lack of either localization of these changes in the immediate vicinity of the rig or a definite gradational trend moving outwards from the rig to the 1000 m periphery of the study site makes even a tentative interpretation impossible.

The increased iron levels of the epifauna are likewise difficult to assess, as is the increased aromatic hydrocarbon levels in T. similis. Increased iron levels in zooplankton and suspended particulate matter in the MAFLA study tract occurred in the winter when unstable water conditions and storm activity resuspended high amounts of bottom sediments into the water column.

The pre-drilling conditions in the rig site suggest an initially stressed environment. This contention is supported by the high turbidity, depaupered foraminiferal populations and the paucity of macro-epifauna. It is recommended that further oil rig monitoring studies be situated in less stressful and more biologically diverse environments so that potential perturbational effects of oil drilling activities can be better assessed both quantitatively and qualitatively. Normally the effects of acute changes in the environment can be detected biologically when short-term studies are being employed. Therefore, to detect the more subtle chronic effects, long-term studies using sessile organisms should be conducted. These remarks also apply to the hydrocarbon and trace metal

analyses presented previously.

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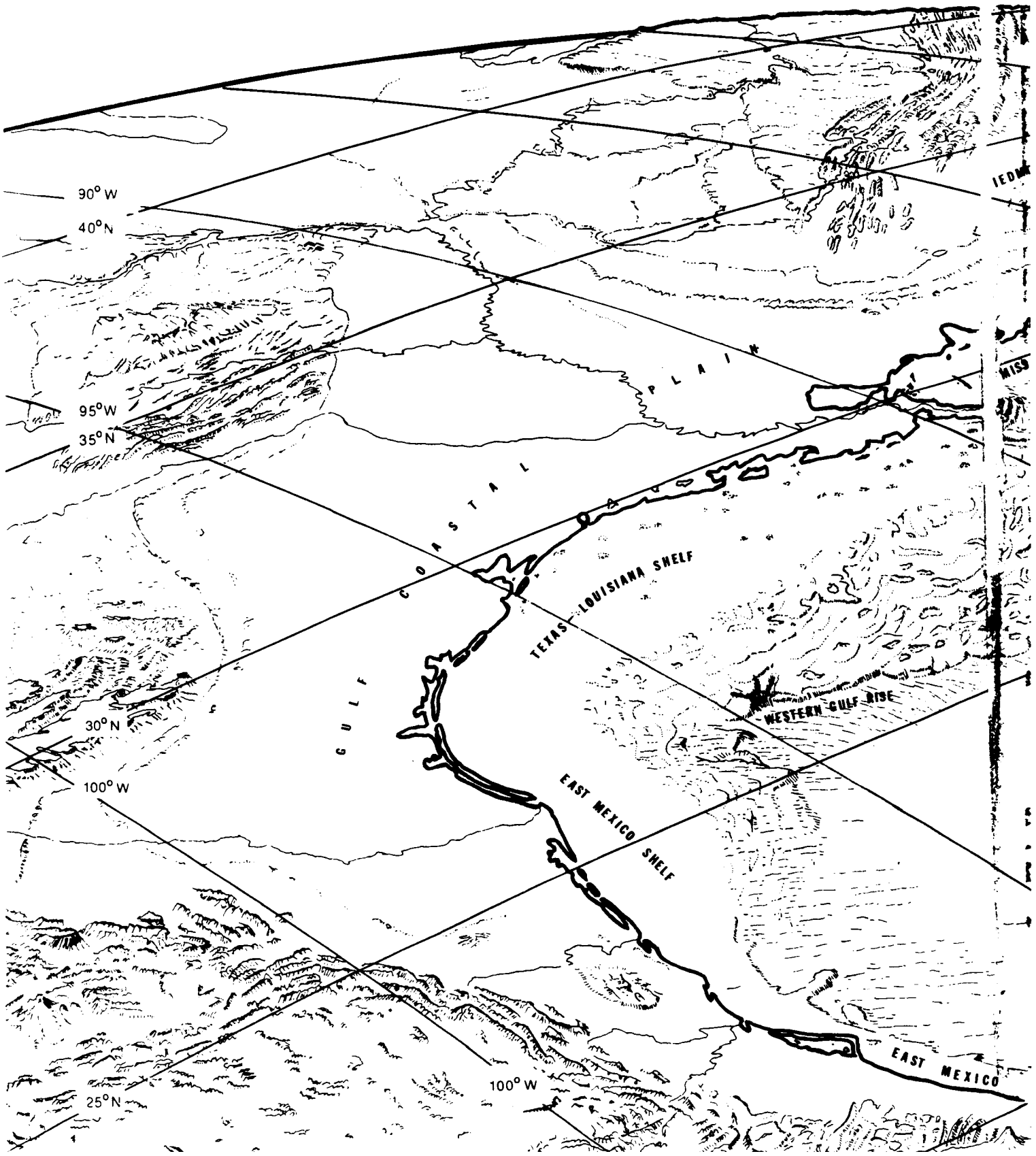
90° W
40° N
95° W
35° N
30° N
100° W
25° N
100° W
GULF COASTAL PLAIN
TEXAS-LOUISIANA SHELF
WESTERN GULF RISE
EAST MEXICO SHELF
EAST MEXICO