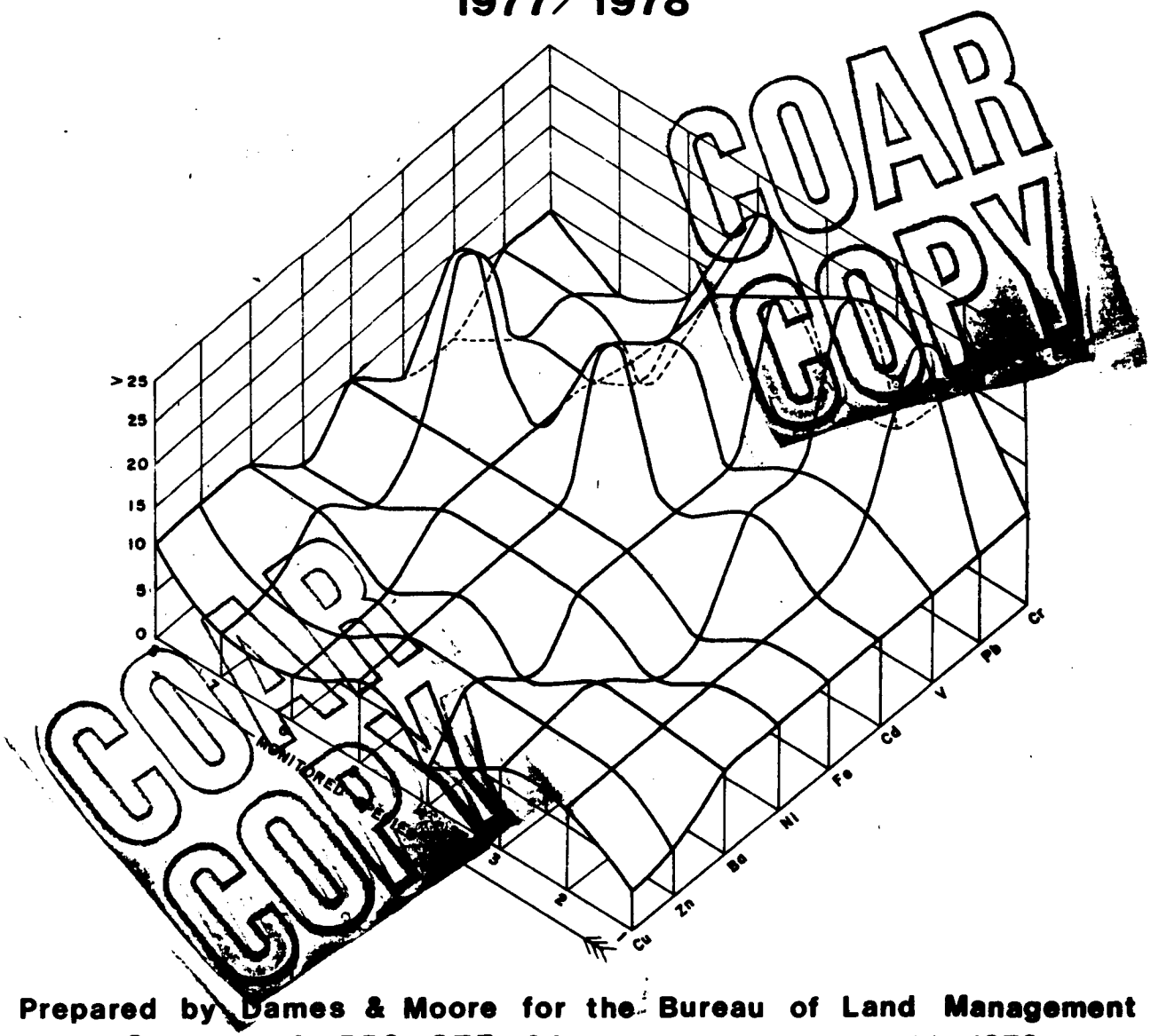
MAFLA

FINAL REPORT

THE MISSISSIPPI, ALABAMA, FLORIDA, OUTER CONTINENTAL SHELF BASELINE ENVIRONMENTAL SURVEY

1977/1978



Prepared by Dames & Moore for the Bureau of Land Management

Contract AA550-CT7-34 January 26, 1979

Volume II·A: Compendium of Work Element Reports

FINAL REPORT

MISSISSIPPI, ALABAMA, FLORIDA OUTER CONTINENTAL SHELF BASELINE ENVIRONMENTAL SURVEY; MAFLA, 1977/78 .

PREPARED FOR U.S. DEPARTMENT OF THE INTERIOR

BUREAU OF LAND MANAGEMENT

CONTRACT AA550-CT7-34

VOLUME II

COMPENDIUM OF WORK ELEMENT REPORTS

DAMES & MOORE JOB NO. 08699-008-88

NEW ORLEANS, LOUISIANA

JANUARY 26, 1979

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CHAPTER 1

INTRODUCTION

DAMES & MOORE
CONTRACT NO. AA550-CT7-34

INTRODUCTION

This second volume of Dames & Moore's final report, The Mississippi, Alabama, Florida, Outer Continental Shelf Baseline Environmental Survey, MAFLA, 1977/78, contains the Principal Investigators' (PI) final reports to Dames & Moore. These reports represent the PIs conclusions and opinions as independent contractors. Dames & Moore has edited these documents for content and format, and has incorporated suggestions from the Bureau of Land Management (BLM) with the authors' consent. This final set of Work Element Reports is continuous from Volume I in pagination, table and figure sequence.

The organization of Volume II, following this brief introduction, is as follows:

- Sedimentary Geology
- Sedimentary Chemistry
- Tissue Chemistry
- Benthic Biology
- Physical Oceanography
- Water Column Chemistry
- Plankton Biology

Chapter 25 on archived biological specimens reflects the disposition of samples as of January 15, 1979, by PIs in connection with BLM letter of September 29, 1978, 1513.51(110), AA550-CT7-34. Figure 104 and Table 26 are repeated here (from Volume I-A, Figure 1 and Table I) for reference, and references to Dames & Moore reports cited in this volume are also listed here.

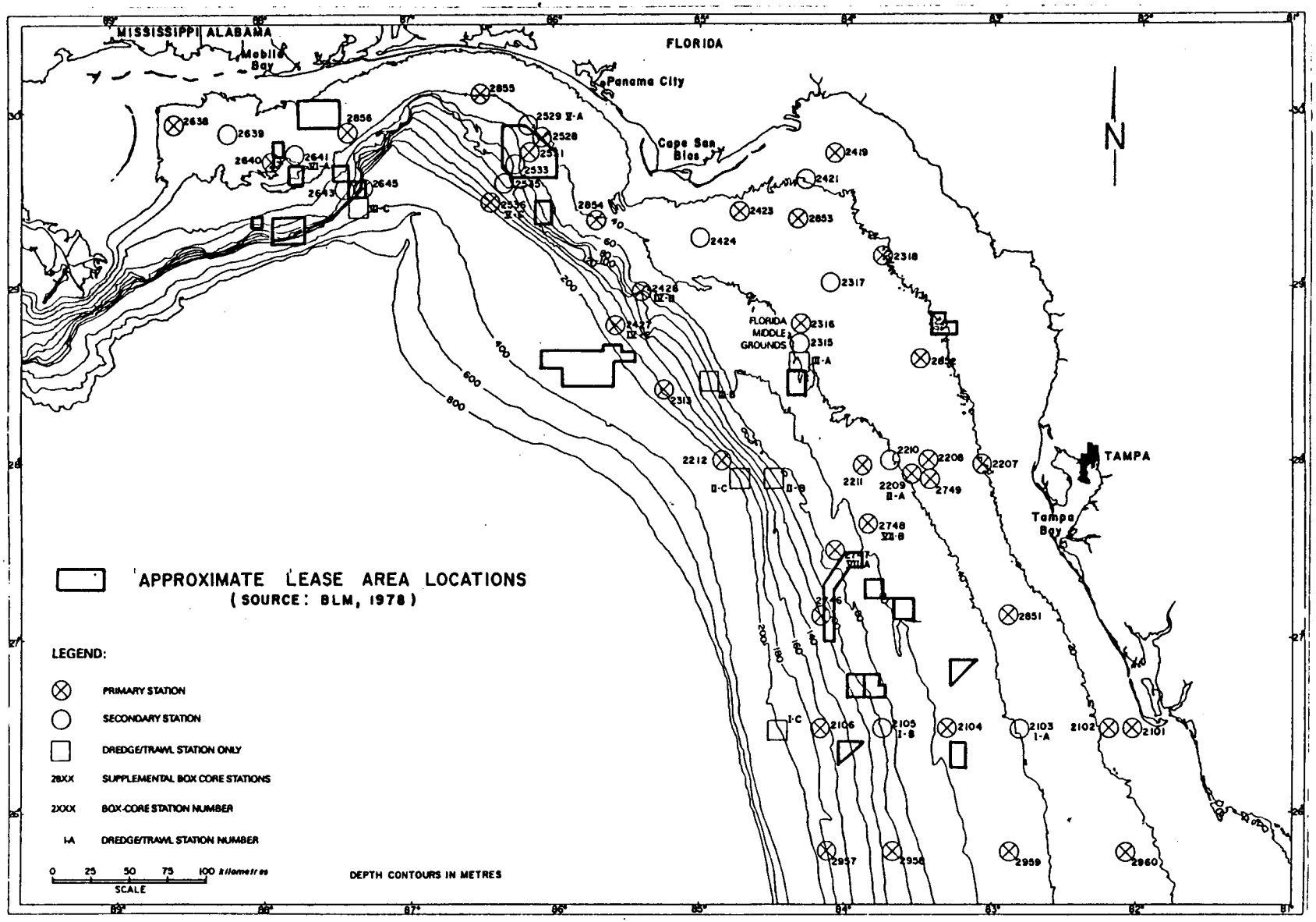

FIGURE 104

MAFLA PROPOSED AND ACTIVE LEASE AREAS AND 1977/1978 STATION LOCATIONS

TABLE 26

1977/78 MAFLA PROGRAM PARTICIPANTS

PRINCIPAL INVESTIGATORS	AFFILIATION	PROGRAM WORK ELEMENT
Dr. Wayne Bock	University of Miami	Foraminifera Taxonomy
Dr. Keith Cooksey	University of Miami	Biomass of Microrganisms (ATP)
Dr. Peter Betzer	University of South Florida	Water Column Trace Metals
Dr. Norman Blake	University of South Florida	Histopathology Macroinfauna Taxonomy/Molluscs
Dr. Kendall Carder	University of South Florida	Transmissometry (Water Clarity)
Dr. Larry Doyle	University of South Florida	Standard Sediment Parameters, Clay Mineralogy
Mr. John Caldwell/Dr. Frank Maturo	University of Florida	Zooplankton Taxonomy
Dr. Steve Bortone (with Dr. Robert Shipp)	University of West Florida	Demersal Fish Taxonomy
Dr. Sneed Collard	University of West Florida	Neuston Taxonomy
Dr. Richard Heard	University of Alabama Marine Lab	Macroinfauna Taxonomy/Crustaceans
Dr. Thomas Hopkins	University of Alabama	Macroepifauna Taxonomy
Dr. Susan Ivester	University of Alabama	Meiofauna Taxonomy
Dr. Robert Shipp (with Dr. Steve Bortone)	University of Alabama	Demersal Fish Taxonomy
Dr. Barry Vittor	Barry A. Vittor & Associates, Inc.	Macroinfauna Taxonomy/Polychaetes
Dr. Lela Jeffrey	Texas A&M University	Water Column Hydrocarbon and Organic Carbon
Dr. John Trefry	TerEco Corporation	Sediment Trace Metals
Dr. Robert Shokes	Science Applications, Inc.	Barium, Vanadium Chemistry
Dr. George Gould/Dr. Bud Moberg	Analytical Research Laboratories, Inc.	Hydrocarbon Chemistry/Benthos and Zooplankton; Trace Metal Chemistry, Macrofauna
Mr. Lee Fausak	Dames & Moore	Salinity, Temperature, Density
Dr. Harold Palmer	Dames & Moore	Technical Advisory Committee Chairman
Mr. Peter Feldhausen	Dames & Moore	Data Manager
Dr. Thomas Scanland	Dames & Moore	Program Manager

VOLUME II

CHAPTER 2

SURFICIAL SEDIMENT CHARACTERS AND CLAY MINERALOGY

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CONTRACT NO. AA550-CT7-34

SEDIMENTS OF MAFLA

by

LARRY J. DOYLE

and

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Report Submitted to Dames & Moore

1977-78 BLM MAFLA Contract Number AA550-CT7-34

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ABSTRACT

The MAFLA Continental margin is composed of two parts of opposing history and character. East of Cape San Blas lies the eastern limb of the Gulf Coast Geosyncline whose surface expression is a clastic sand sheet, called the MAFLA Sand Sheet grading westward into the muds of the Mississippi pro-delta. These sediments have a clay mineral suite dominated by smectite. East of Cape San Blas lies the West Florida margin, a sequence of carbonate and evaporitic rocks which has been cut off from a major clastic source since Jurassic time. The surface expression of this sequence is the West Florida Sand Sheet, predominantly a patchy veneer of shell hash, foraminifera, algal, and even oolitic sands. Kaolinite dominates the clay mineralogy. Seaward of the carbonate sands lies the West Florida Lime Mud facies, slope sediments mostly composed of planktonic foraminifera and coccoliths.

Inshore of the carbonate sands and separated from them by a zone of mixed composition lies a mature fine quartz sand, which also makes up the beaches of Southwest Florida. West Florida shelf quartz sands appear to have been deposited at lower sea level stands and to have sloshed back and forth in a longshore current system which changes seasonally from north to south.

Clay mineralogy of the MAFLA region shows distinct changes in composition over a period of a year in the benthos and over periods as short as a few hours in the water column. These changes reflect contribution from two distinct provenances. Benthic variation probably results from occasional intrusion of smectite laden Mississippi River or Loop Current water into the eastern zone. Water column variation may be the result of seiching of the Gulf or the pulsing movement of smectite laden western shelf water to the east.

Q-mode cluster analysis has produced groupings based upon all grain size and carbonate content data, which may be of considerable aid in interpretation of subtle relationships in benthic biologic and chemical detail.

INTRODUCTION

PURPOSE

This report presents the results of a four year investigation of the surface sediments of the eastern Gulf of Mexico continental shelf. In the first two years our approach consisted of sampling from two of the replicate box cores at each station and each season. During the final summer and year we altered our approach by collecting a large number of replicates at each of the relatively small number of stations in order to determine small scale variability.

In addition to sedimentologically characterizing the MAFLA margin, our task was to provide ancillary data for sediment chemistry and benthic biological studies. In order to realize these goals, each box-core subsample was analyzed for grain size and percent calcium carbonate, and selected samples were analyzed for total organic carbon and clay mineralogy. In addition, clay mineralogy of suspended sediments was determined for samples collected at four time series stations in the summer of 1976, fall of 1977, and winter of 1978.

Standard methodologies were used throughout in laboratory analysis. They are detailed in our third quarterly report (see Dames & Moore, 1978e), and summarized below. Along with determination of the standard statistical measures, such as mean and standard deviation, data were subjected to a number of multivariate tests by Peter Feldhausen and the Dames & Moore data management group in order to attempt to detail subtle groupings and relationships in the characteristics of the sediment samples which would in turn result in a more complete and sensitive understanding of the chemical/sediment and biological/sediment relationships. Theory and mechanics of the multivariate techniques utilized may be found in Volume II, Chapter 29.

LITERATURE SURVEY AND PREVIOUS WORK

Summarized by Martin (1976), the geology of the continental margin of the MAFLA region may be divided into two basic provinces. The transition zone between them trends southwest from Cape San Blas to the DeSoto Canyon. West of the transition lies the Gulf Coast Geosyncline which deepens to the west, attaining a thickness of over 30 kilometers. This great pile of clastic rocks, the accumulation of the Mississippi River system, is mostly Cenozoic in age and is underlain by Triasic-Jurassic salt measures which are the source beds for the numerous diapirs which characterize the area. East of the transition zone the nature of the rocks changes dramatically. The region has been cut off from major clastic provenance since Jurassic time, which in turn has led to the accumulation of over 4,600 metres of carbonates and evaporites, the former of which are still being slowly deposited. These rocks have been deposited behind a series of shelf edge algal reef dams which at various times in the geologic past have restricted circulation (Bryant et al., 1969; Pyle and Antoine, 1973; and Antoine et al., 1974). Pyle et al. (1977) have found vestiges of reef dams on the present shelf edge, but the original reefs, of the Albian/Aptian stages, have subsided over 1800 metres and now make up the Florida Escarpment.

SEDIMENT GRAIN SIZE ANALYSIS

Size analysis was performed on the top 10 cm of each box-core subsample. Approximately 15 g splits of each sample were wet sieved on a 63 μm screen; the fine fraction was collected in a 100 m graduated cylinder. The sand-and-gravel fraction was dried and then sieved through a nested set of standard 1 phi interval sieves from -1 phi (gravel) to 4 phi (very fine sand). The sand fraction caught on each sieve was weighed to the nearest gram. The pan fraction (<63 μm) sediments were added to contents of the graduated cylinder. Analysis of the finer-than-sand sediments was executed by standard pipette methods (Folk, 1974). A saturated calgon solution (10 mℓ) was added to the sediment in the cylinder to disperse the clay and prevent flocculation during sampling intervals. At least one pipette was taken from each sample; after correction was made for the added calgon weight, the total fine fraction weight was calculated. For those samples in which this weight exceeded ten percent of the total weight, a second pipette was taken so that both percent silt and percent clay could be determined. All full phi fractions were reported as weight percent of the total sample.

PERCENT CARBONATE OF SEDIMENTS

All box-core samples examined for grain size analysis were also analyzed for percent carbonate using standard acid-leaching, gas-displacement methods as described by Ireland (1971). Approximately 10 g of sediments were placed in a tared 250 mℓ beaker. Before treatment the beaker and dried sample were weighed together to the nearest 0.01g. Ten percent (10%) hydrochloric acid was added carefully so as to avoid frothing over the top of the beaker. After digestion was completed, the sample was rinsed twice with deionized water and the water was decanted each time following centrifugation. The insoluble residue was dried at 80 to 85°C overnight. The beaker and its contents were weighed, and the amount of insoluble residue remaining was calculated by subtraction of the preweighed beaker. The weight percent of carbonate was taken as the difference in weight between the untreated and treated sample and converted to a percent:

$$\% \, CaCO_3 = \frac{(\text{wgt untreated sample} - \text{wgt insoluble residue}) \times 100}{\text{wgt untreated sample}}$$

Results were reported as weight percent carbonate in a table.

TOTAL ORGANIC CARBON (TOC) IN SEDIMENTS

At least one sample from each box-coring station was analyzed for total organic carbon (TOC). After dissolution of the carbonate fraction following the method used by Ireland (1971) and described above, the insoluble resident was oven dried and weighed to the nearest 0.001 g. Approximately one gram of residue was placed into a Leco combustion crucible with like amounts of iron chip and copper metal accelerator. The crucible, with sample and accelerator, was set within an Angstrom Model 9000 Induction Furnace, and the contents were heated to incandescence. During combustion, organic carbon from the sample mixed with oxygen within the chamber forming carbon dioxide, CO_2. While maintaining a closed system, the gas was

piped to an Angstrom Model 7000 Carbomatic Carbon Analyzer which had been calibrated each day to known TOC standards. After analysis the instrument displayed a direct readout of percent carbon, and the data were recorded in tabular form.

CLAY MINERALOGY OF BENTHIC SEDIMENTS

One sediment subsample was taken from each box-coring station in the summer of 1977 for clay mineralogy analysis. Approximately 20 to 40 g of sediment were sampled from the uppermost 5 cm of each sub-core to ensure that enough clay would be available for analysis. The samples were disaggregated, wet-sieved to separate the coarse fractions, and centrifuged to remove salts. The clay was removed from the remainder of the fine fraction sediments by pipetting after settling, after which organic material was dissolved in hydrogen peroxide. The clay material slurry was placed on a glass slide, dried, and X-rayed on a Phillips Electronics (Norelco) X-ray generator with Wide Range Goniometer. The slides were X-rayed again after treatment with ethylene glycol vapor, and a third time of heating to 550°C. Identification of the major clay minerals was carried out using standard examination techniques s given by Griffin (1962) and Grim (1968). The clay species that were identified included smectite, illite, kaolinite, and mixed-layer clay, while other minerals that were searched for, but were rare or not present, were vermiculite and chlorite. Quantification was performed on the basal (001) peaks of each clay type identified from the glycolated slide. Relative proportions of the clays were estimated using peak height to calculate individual peak areas. The proportions of the areas were finally converted to percent clay present and recorded in tabular form.

SUSPENDED SEDIMENT CLAY MINERALOGY

The suspended particulates were collected on 0.45 μm pore-diameter Millipore filters. Each filter was placed in a centrifuge tube to which approximately 8 mℓ of filtered acetone was added; the tubes were shaken by hand until the filters completely dissolved. All tubes were centrifuged at 10,000 rpm for 20 min at a temperature of 3°C. The supernatent acetone was discarded, while special care was taken so that the sediment pellet was not disturbed. Acetone was again added to the tubes and each tube was then sonified using a Heat Systems-Ultrasonics, Inc., cell disrupter equipped with a microtip. Dilute HCl or H_2O_2 was added if the samples contained $CaCO_3$ or organic compounds which interfere with X-ray diffraction analysis. All the tubes were centrifuged, decanted, sonified, and centrifuged again giving a total of three washes in acetone. After the last acetone wash was poured off, 5-6 mℓ of deionized water were added. The tubes were sonified for 30 s to break down the pellets completely. The contents of each tube were vacuum filtered through silver filters (0.2 μm pore size) using a Millipore filtering apparatus. One millilitre was filtered at a time in order to minimize differential settling rates; no additional sample was added until the previous mℓ had passed through the filter. Care was taken so that the filters were not covered too thickly with the suspended sediment. With the sediments on silver filters, the samples were X-rayed at on a Rigaku "Miniflex" Model 2005 X-ray Diffractometer. Sediments indicating measurable amounts of clay present were treated with ethlene glycol fumes at 60 to 80°C for at least 12 h and were immediately X-rayed to

check for exapnsion of the smectite peak. A final heat treatment to 550°C for one hour followed by X-ray analysis for 3° to 15° was performed.

RESULTS AND DISCUSSION

TEXTURE AND CARBONATE CONTENT

The two parameters which are most diagnostic in describing the surface sediments are texture and carbonate content. Figure 105 is a map of the distribution of the fine fraction (<63 μ) in the sediments of the eastern Gulf shelf. Sand and a small amount of gravel normally make up the remainder of the sediment. Figure 106 shows the percent carbonate in the study area. Averages of all replicates from all sampling periods have been contoured to produce the figures.

Figure 105 shows that sands dominate the study area except for a large patch of sediments with an elevated amount of fines which lies to the west of Tampa Bay in the central shelf region. Highest values in the center of the patch exceed 60% fines. The 20% fine fraction contour lies well out on the shelf edge. Even upper slope sediments of the region contain up to 50% sand, almost entirely composed of the tests of planktonic foraminifera. The fine fraction increases rapidly west of Mobile Bay as the Mississippi Delta is approached and fine sediments also lie in the head of DeSoto Canyon. Although most of the shelf areas are dominated by sand sized sediments, Doyle and others (1977), based upon a series of samples at one-mile intervals across the shelf west of Tarpon Springs, have shown that patches of much finer sediment occur, probably related to shadow zones caused by local bathymetry.

While texturally the shelf sand sheets on both sides of Cape San Blas are similar, Figure 106 shows there is a major compositional break trending slightly east of south from the Cape. The low carbonate contours, which correspond to high quartz content, form a bulge out onto the shelf which marks the transition between western and eastern facies. The eastern portion is dominated by up to 90% carbonate components while the western portion is predominantly quartz sand. A band of quartz sand also lies inshore to the east of Cape San Blas and makes up the western beaches of the Florida peninsula. Perusal of Figure 106 shows a gradational transition between the nearshore quartz band and open shelf carbonate sediments, and the abrupt pinching of the quartz band at the southern limit of the study area.

SEDIMENT VARIABILITY

Deeper water, finer grained sediments in the study area are generally poorly sorted (σ1.0 - 2.0 ϕ) while those sands and muds lying on the shelf are generally very poorly sorted (σ 2.0 - 4.0 ϕ) according to Folk's (1965) classification. Only one station showed better sorting, Station 2856 which was moderately sorted (σ0.71 - 1.0 ϕ).

Another method for looking at intrastation variability, less traditional for sedimentologists, is to subject the data to canonical analysis. The theory and method are explained in detail in Volume II, Chapter 29 of

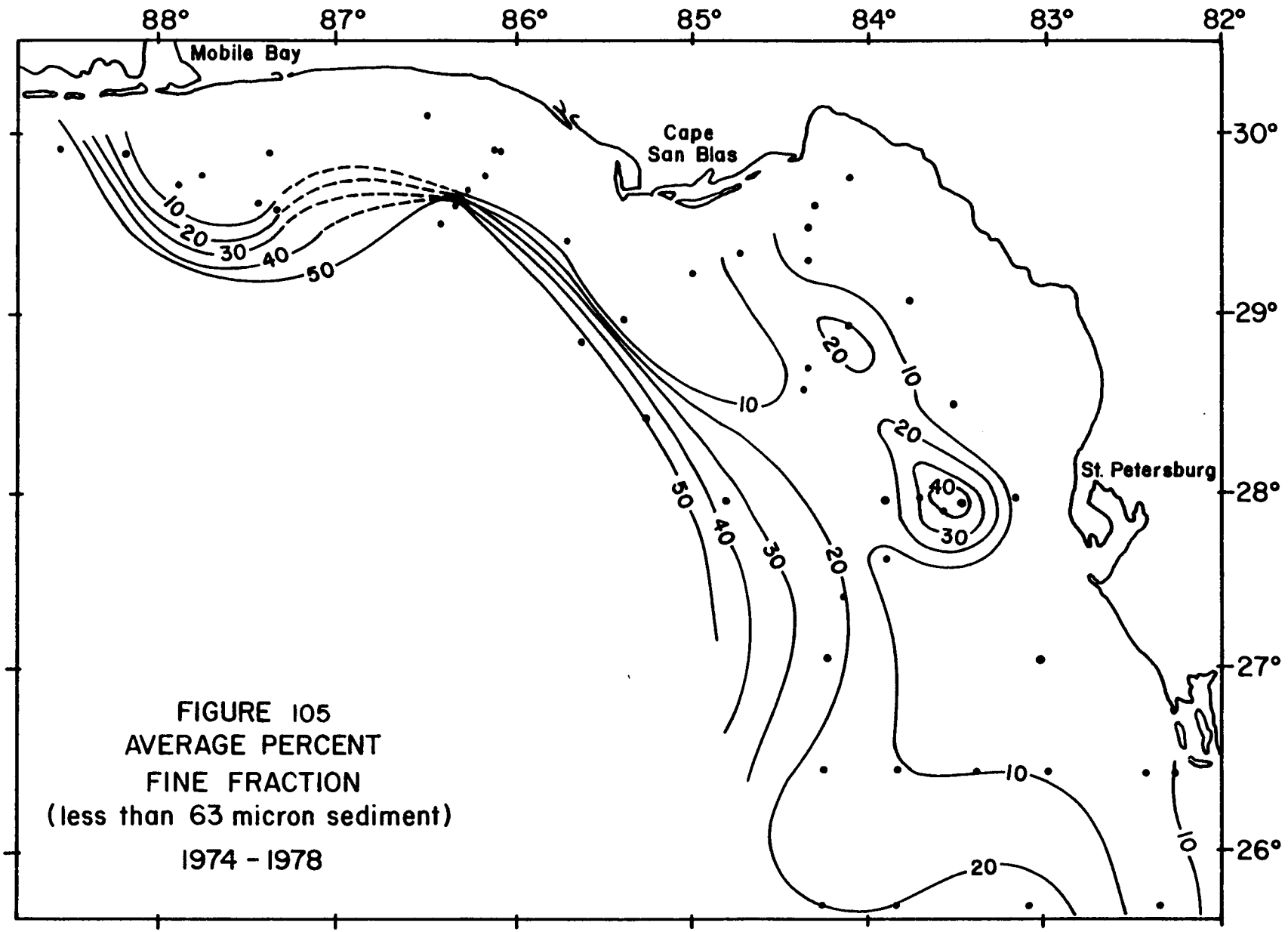


FIGURE 105
AVERAGE PERCENT
FINE FRACTION
(less than 63 micron sediment)
1974 - 1978

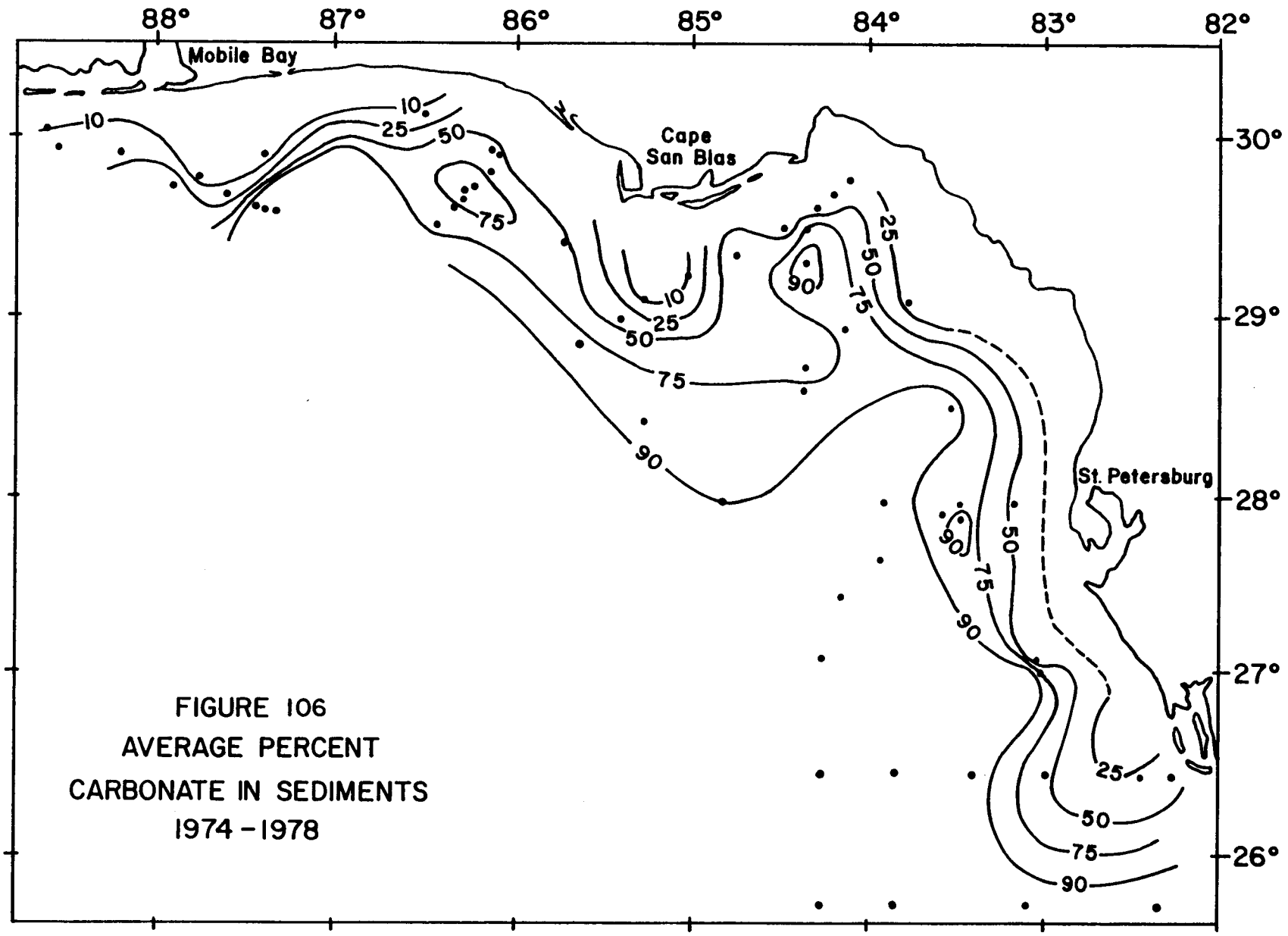


FIGURE 106
AVERAGE PERCENT
CARBONATE IN SEDIMENTS
1974 - 1978

this report. Here it is sufficient to say that the textural parameters in whole phi units are converted on the basis of component variability to a value which can be plotted on a system of X and Y coordinates. The coordinates for each replicate at each station are plotted as well as the centroid, the mean coordinates for each station. The spread of the replicate points from the centroid is a measure of intrastation variability. The strength of the method lies in utilizing all the data, not just a summary statistic such as mean or standard deviation.

Finer grained sediments were grouped most closely around their centroid, suggesting little within station variability, while the sandy shelf stations were more widely scattered about their centroids, and hence, more variable. Table 27 consists of replicates or outliers which showed extreme departure from their centroids. Asterisks identify those replicates whose sampling/location is displaced from the main grouping. Large displacement occurs in about one third of the outliers. Differences in sediment texture probably result from local, small scale bathymetric variation affecting currents transporting or eroding sediments. Variation is sufficient to warrant performing grain size analysis on each replicate upon which biological or chemical analysis will be performed.

TOTAL ORGANIC CARBON

Figure 107 shows the distribution of total organic carbon (TOC) in the sediments of the study area. Like Figures 105 and 106, contours are based upon station averages for all samplings. As is normally the case in marine sediments, total organic arbon content follows the grain size trends and increases with increases in the fine fraction. Values correspond with those of Emery and Uchupi (1972) for sandy shelf sediments.

BENTHIC CLAY MINERALOGY

Smectite and kaolinite are the predominant clay minerals in Eastern Gulf margin sediments. Illite is present in most samples ranging from trace amounts to about 16% and shows a non-systematic pattern of distribution within the study area. Mixed layer clays, and chlorite, are rare and scattered in benthic samples.

Distributions of the dominant clay minerals smectite and kaolinite are shown in Figures 108 and 109. Values are averaged for the summer of 1976, and the fall of 1977. Smectite, characteristic of the Mississippi drainage system, dominates west of Cape San Blas. Relative percentages of kaolinite increase toward the Cape. East of San Blas kaolinite becomes more important, and over large portions of the area is the dominant clay mineral. Kaolinite values are somewhat lower and smectite correspondingly higher than those reported by Huang et al. (1975) and by Huang (1977). This suggestion is variability in the benthic clay mineral suite is reinforced by apparent changes in relative percentages of kaolinite and smectite between summer 1976, and fall 1977, shown in Figures 110 and 111. Over most of the shelf, smectite decreased dramatically and regularly toward shore while kaolinite increased in relative amounts toward shore.

TABLE 27

SUMMARY RESULTS OF OUTLIER[1] ANALYSIS
SUMMER, 1976, DM-I, DM-II, DM-IV

S-'76	0007080160707	
	2207030160629	
	2211140160630	
	2529040160706	
	2862110160625	
	2863080160704*	
DM-I	2317010160702	
	2854030160707	
	2531070160707	
	2639060160709	
	2316060170830	
	2313120170821	
	2426060170901	
	2853110170901	
	2854060170902	
	2957150170820	
	2960050170819	
DM-II		2104090171116*
		2106010171115
		2209070171113*
		2640020171106
		2748100171115*
DM-IV		2207060180216
		2207100180216
		2316050180214*
		2316080180214*
		2426080180212*
		2645080180211*
		2747010180217
		2748010180217*
		2748080180217
		2959100180219*

[1]OUTLIERS: Those replicates that exhibit extreme departures from the centroid for the replicates at their station.

*Outliers whose sampling locations are displaced from the rest of the group.

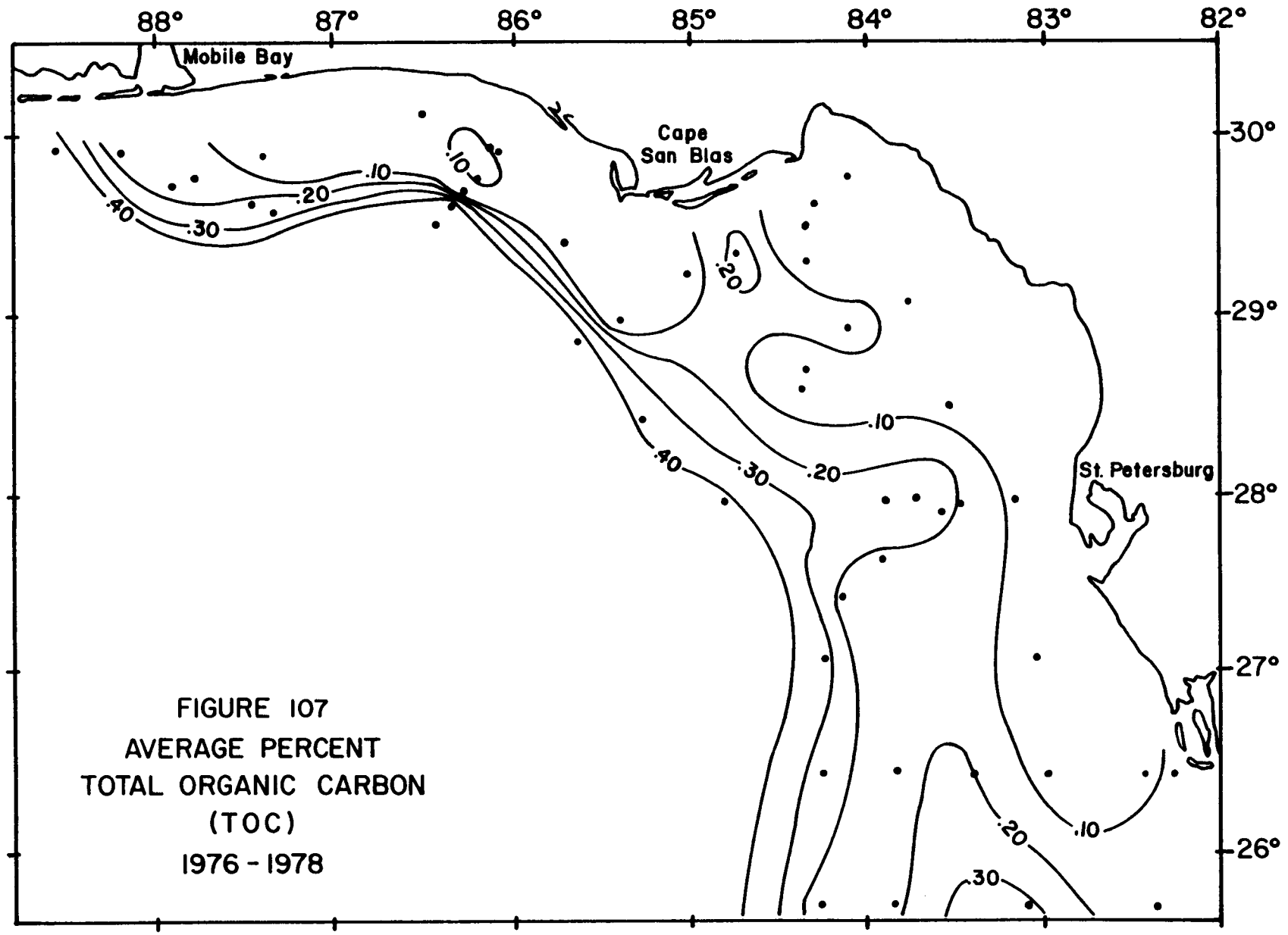


FIGURE 107
AVERAGE PERCENT
TOTAL ORGANIC CARBON
(TOC)
1976 - 1978

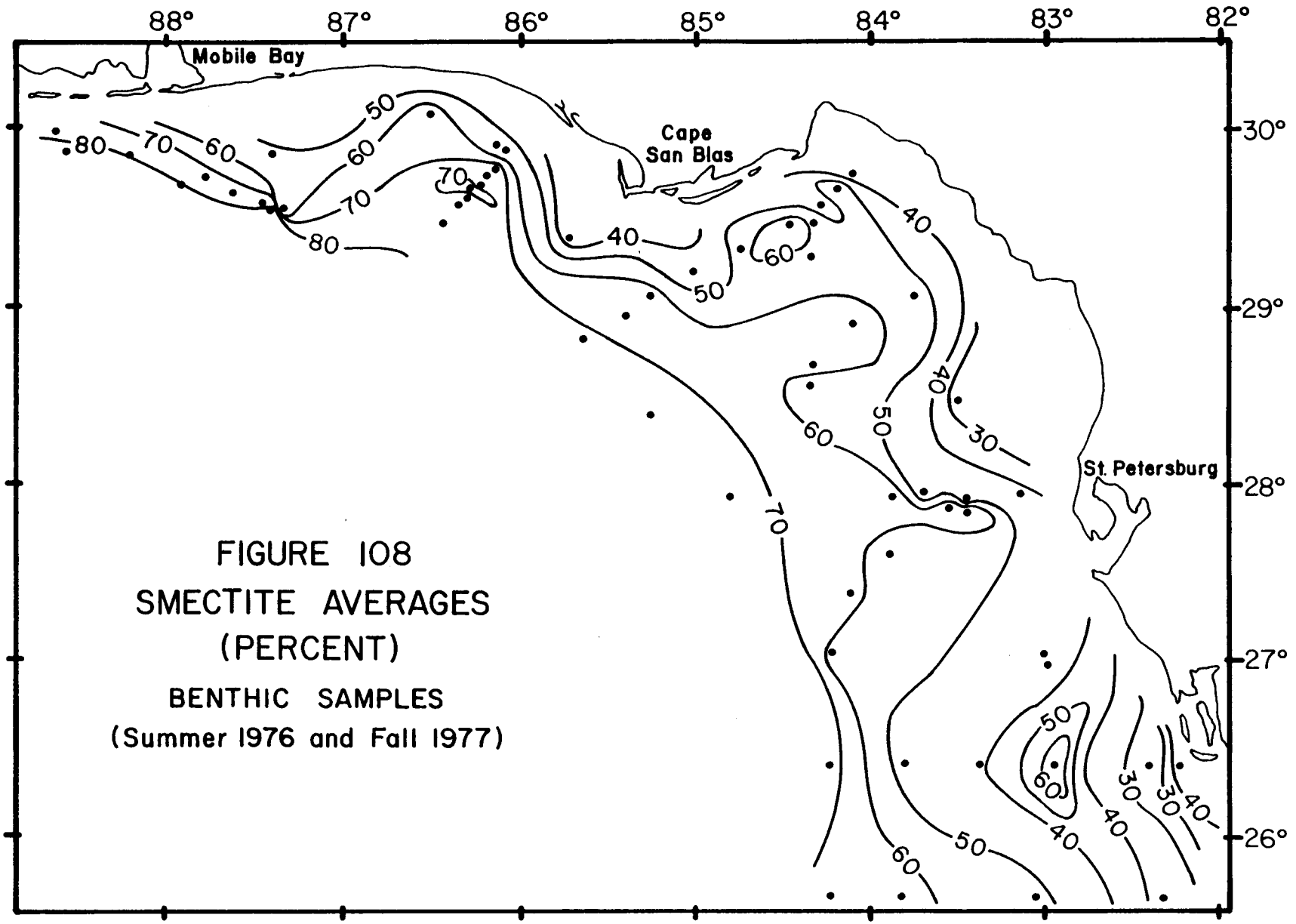


FIGURE 108
SMECTITE AVERAGES
(PERCENT)
BENTHIC SAMPLES
(Summer 1976 and Fall 1977)

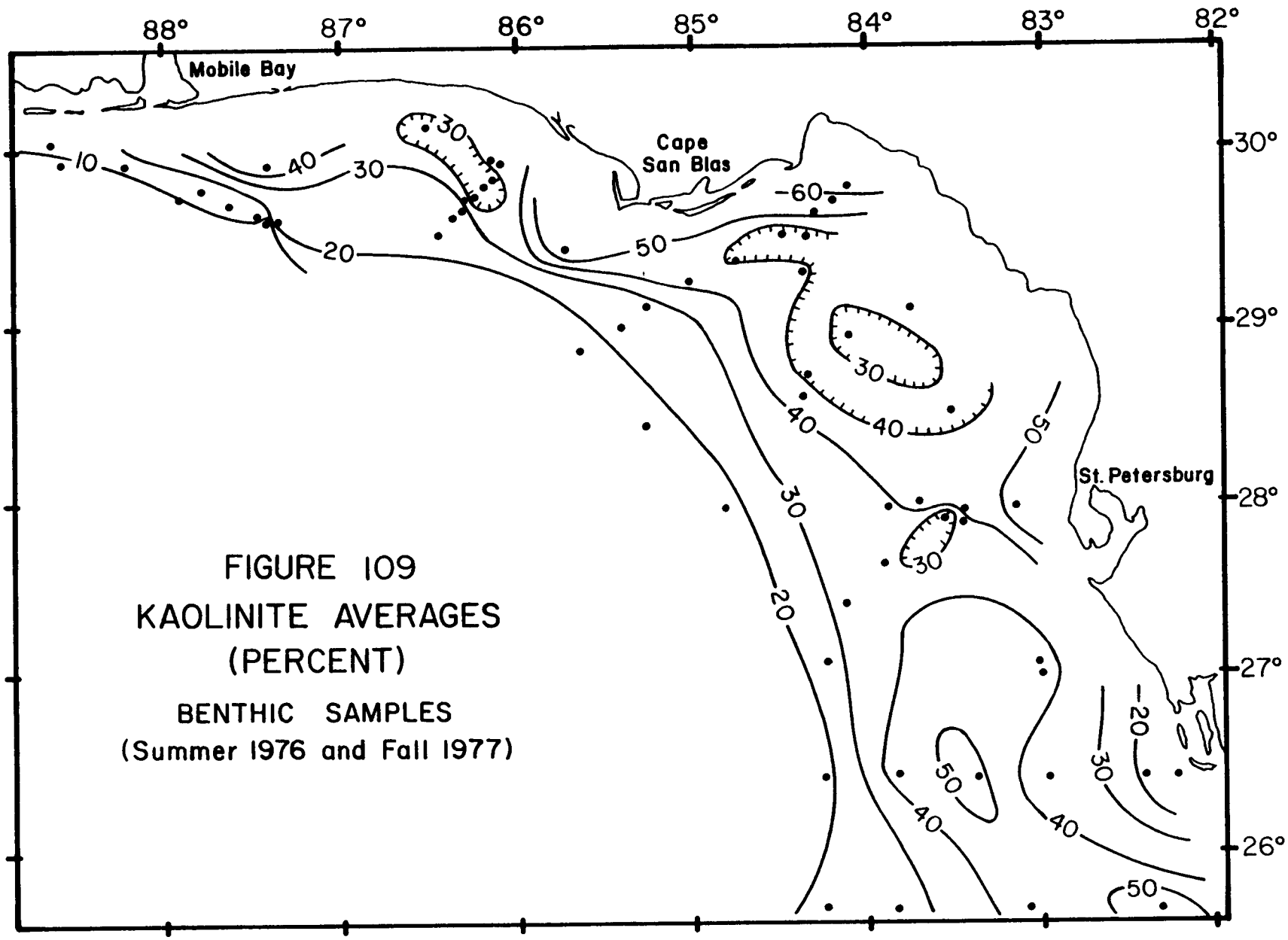


FIGURE 109
KAOLINITE AVERAGES
(PERCENT)

BENTHIC SAMPLES
(Summer 1976 and Fall 1977)

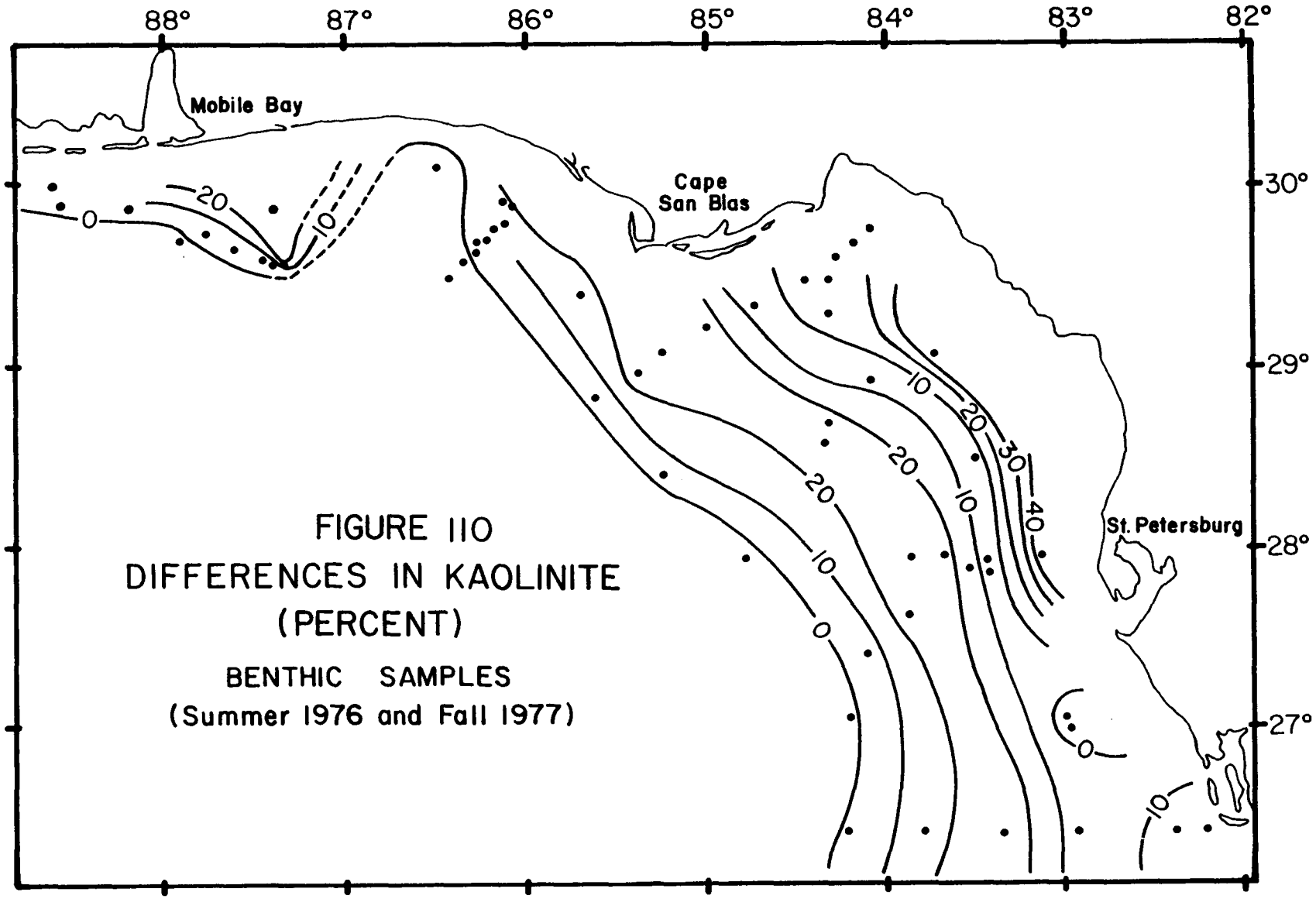
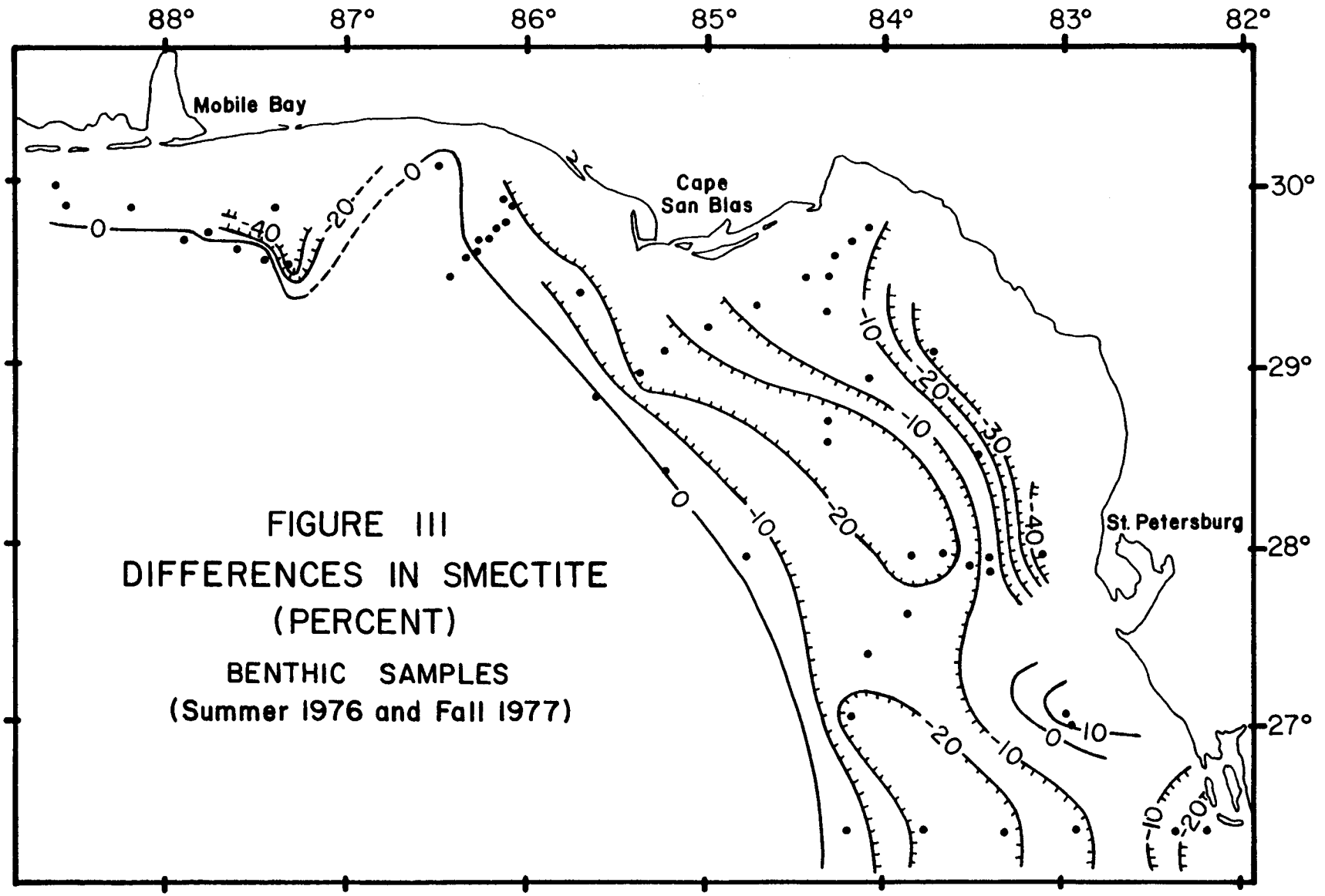


FIGURE 110
DIFFERENCES IN KAOLINITE
(PERCENT)
BENTHIC SAMPLES
(Summer 1976 and Fall 1977)


88°
87°
86°
85°
84°
83°
82°
30°
29°
28°
27°
Mobile Bay
Cape
San Blas
St. Petersburg
0
-10
-20
-30
-40
FIGURE III
DIFFERENCES IN SMECTITE
(PERCENT)
BENTHIC SAMPLES
(Summer 1976 and Fall 1977)

Significant variation in relative amounts of clay minerals in the benthic sediments over as short a period as one year is an exciting prospect which to our knowledge has never before been reported. Since clay mineralogy is a semi-quantitative method, differences in measurements must be judged conservatively, especially when conducted in different laboratories. Several factors support the veracity of the relative differences shown in Figures 110 and 111 however. Analyses for summer 1976 and fall 1977 samples were done in the same laboratory by the same personnel over a relatively short time period measured in months. Secondly, variations are not random nor are they either larger or smaller by a constant amount. They increase or decrease regularly toward shore. These factors indicate that the trends are probably real.

Several provenance areas feed sediments to the eastern Gulf margin. The Mississippi drainage basin is characterized by a clay mineral suite dominated by smectite (Griffen, 1962). Like the coastal plain of the southeastern United States to the north, smectite also dominates the clay mineralogy of those rivers which rise in the Tertiary rocks of peninsular Florida (Huang et al., 1975). With the possible exception of the Caloosahatchee River, which empties into Port Charlotte Harbor, where a bulge in smectite values is noticeable (Figure 105), these rivers contribute little to Gulf sediments. Kaolinite dominates the Appalachicola river system, while the Mobile River system has a mixed smectite/kaolinite suite. These latter two river systems must be the ultimate source of kaolinite in the eastern Gulf margin, a conclusion reinforced by Figure 112, which shows the crystallinity of kaolinite in the study area based upon basal reflector peak sharpness. Samples with sharp, well defined peaks are said to exhibit very good crystallinity, while broad low peaks are said to exhibit poor crystallinity. Based upon this rather subjective measure, kaolinite crystallinities are best in the northwestern part of the Gulf and decline to the south and east suggesting that the kaolinite source was to the north. Figure 113 shows the smectite crystallinity in the study area. A Mississippi source is apparent and the crystallinity generally declines away from the delta and to the south.

Seasonal or annual variation in kaolinite/smectite ratios on the west Florida shelf is probably the result of varying influence of Mississippi River water and the Loop Current which occasionally intrude upon the area. Since the shelf floor is subject to severe winnowing during major storms, smectite pulses in the benthos may be short lived.

SUSPENDED CLAY MINERALOGY

The suspended clay mineralogy suite is similar to that of the benthos with the addition of trace to minor amounts of talc which was present in the summer of 1976 samples. Talc disappeared in the fall of 1977 samples and was found in Station 2747 surface samples in February 1978. In the latter sample it was present in quantities from trace amounts to being the dominant constituent.

Variation in clay mineralogy was even more startling in some of the time series stations occupied in the fall of 1977 and the winter of 1978. Figures 114 and 115 show the variation in surface and bottom samples at

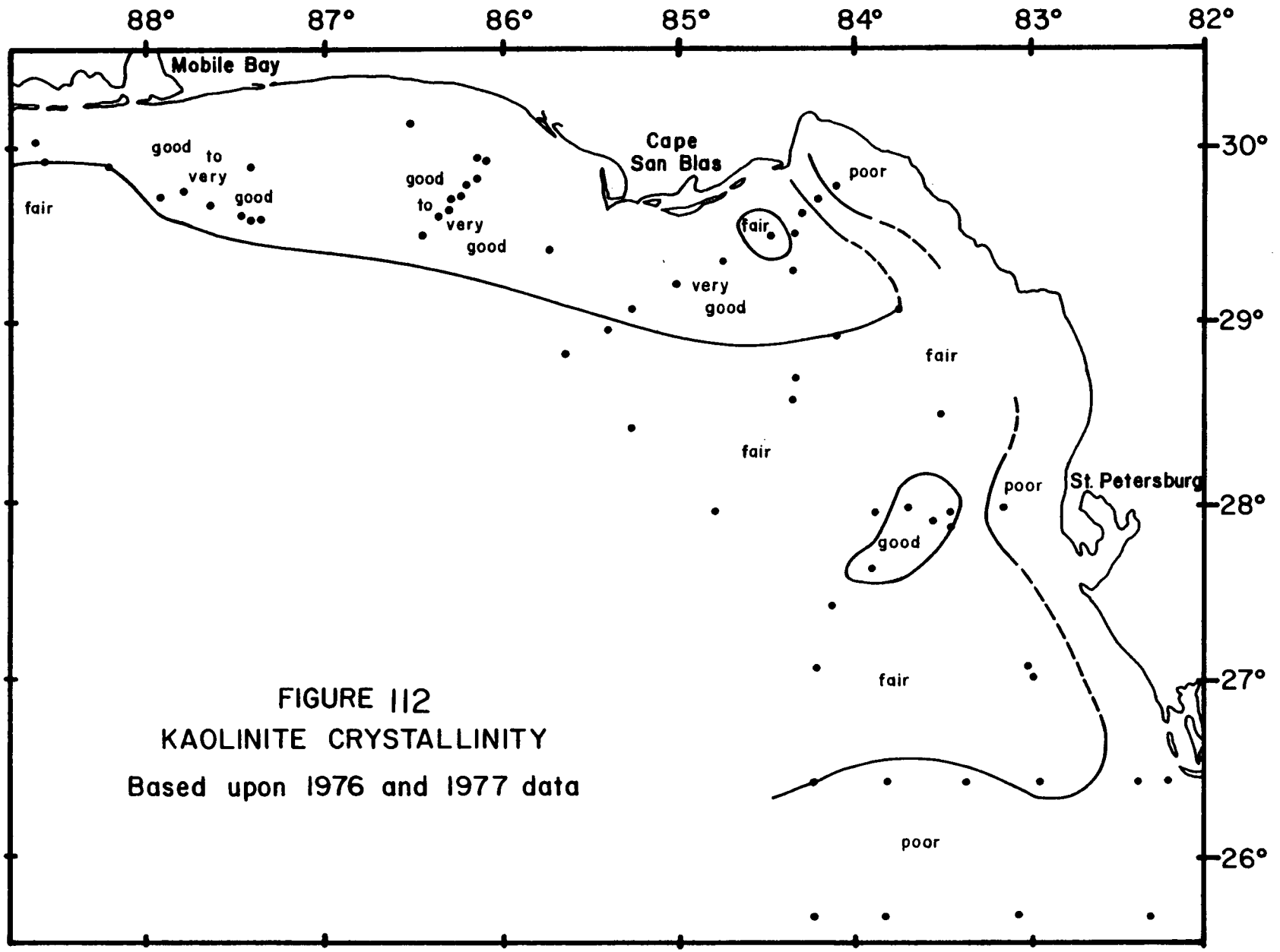


FIGURE 112
KAOLINITE CRYSTALLINITY
Based upon 1976 and 1977 data

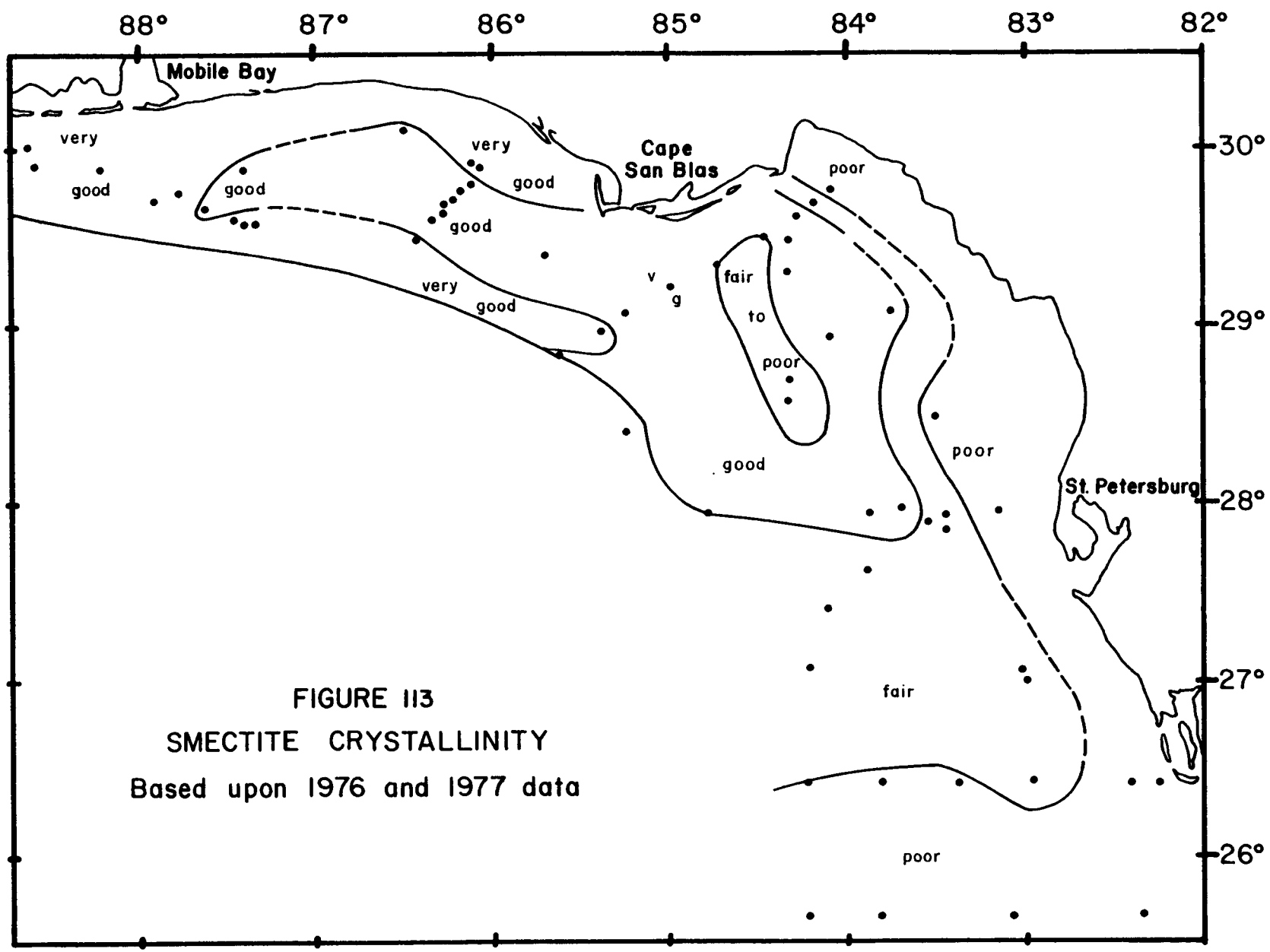


FIGURE 113

SMECTITE CRYSTALLINITY

Based upon 1976 and 1977 data

FIGURE 114

SUSPENDED CLAY MINERALOGY
(TOP)

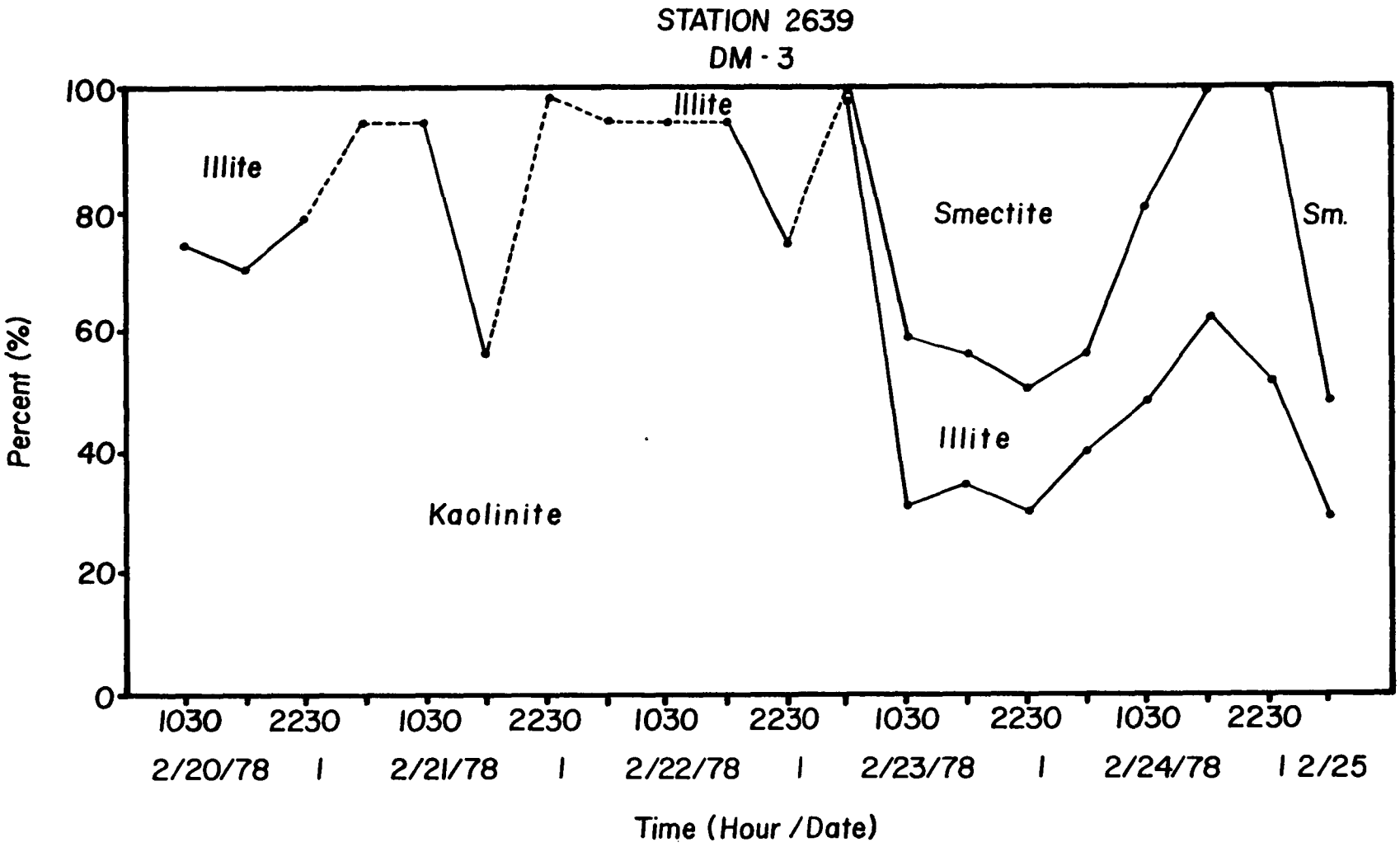
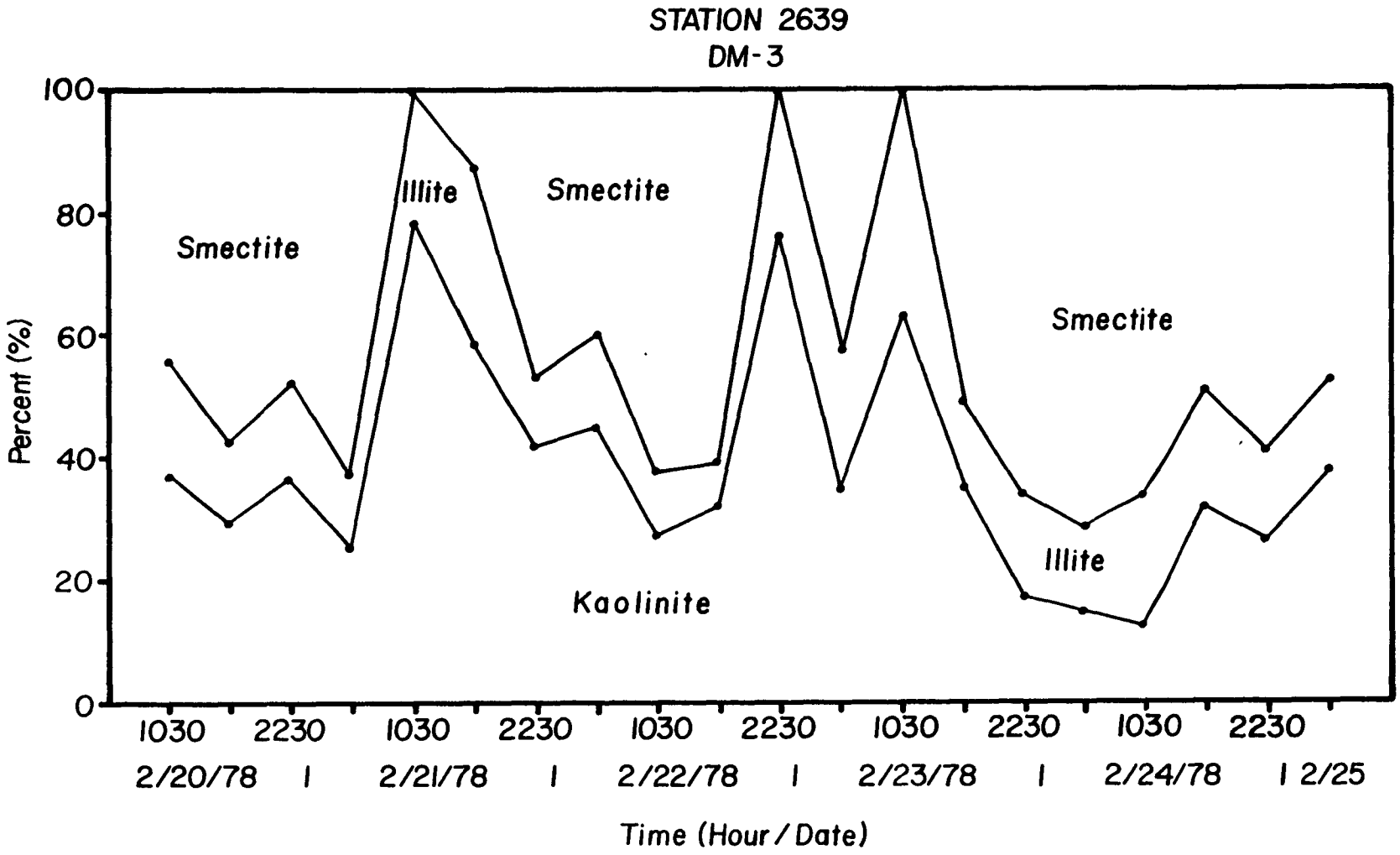


FIGURE 115

SUSPENDED CLAY MINERALOGY
(BOTTOM)



Station 2639, south of Mobile Bay over a five-day period from February 20 to 25, 1978. Both samples show regular and marked fluctuations of clay mineralogy. Bottom variations were the most spectacular with peaks of smectite and kaolinite alternating on about a 12-hour period.

Pulsations may be due to the passage of a sieche on a 12-hour cycle through the station, moving the same water mass first to the east then to the west, or to a periodic pumping of water laden with smectite from west to east (see Chapters 21 and 22 of this volume) and is correlative with transmissometry data in the water column. Surface fluctuations were subdued (Figure 114) and mineralogy differs from that of the bottom samples. Only illite and kaolinite were present in surface samples for the first three days of the time-series. A bolus of smectite rich sediment passed through on the 23rd of February, and was replaced by kaolinite and illite rich sediment on the 24th, to be in turn replaced by smectite-rich sediment on the 25th. To the authors' knowledge pulsations in mineralogy of the type shown in Figure 114 and 115 have not been previously reported. Fluctuations in mineralogy are not limited to the northwestern area. Station 2747 off Tampa Bay showed significant variation in mineral species over a 13-hour time period as shown in Figure 116.

EASTERN GULF SHELF-SURFACE SEDIMENT FACIES

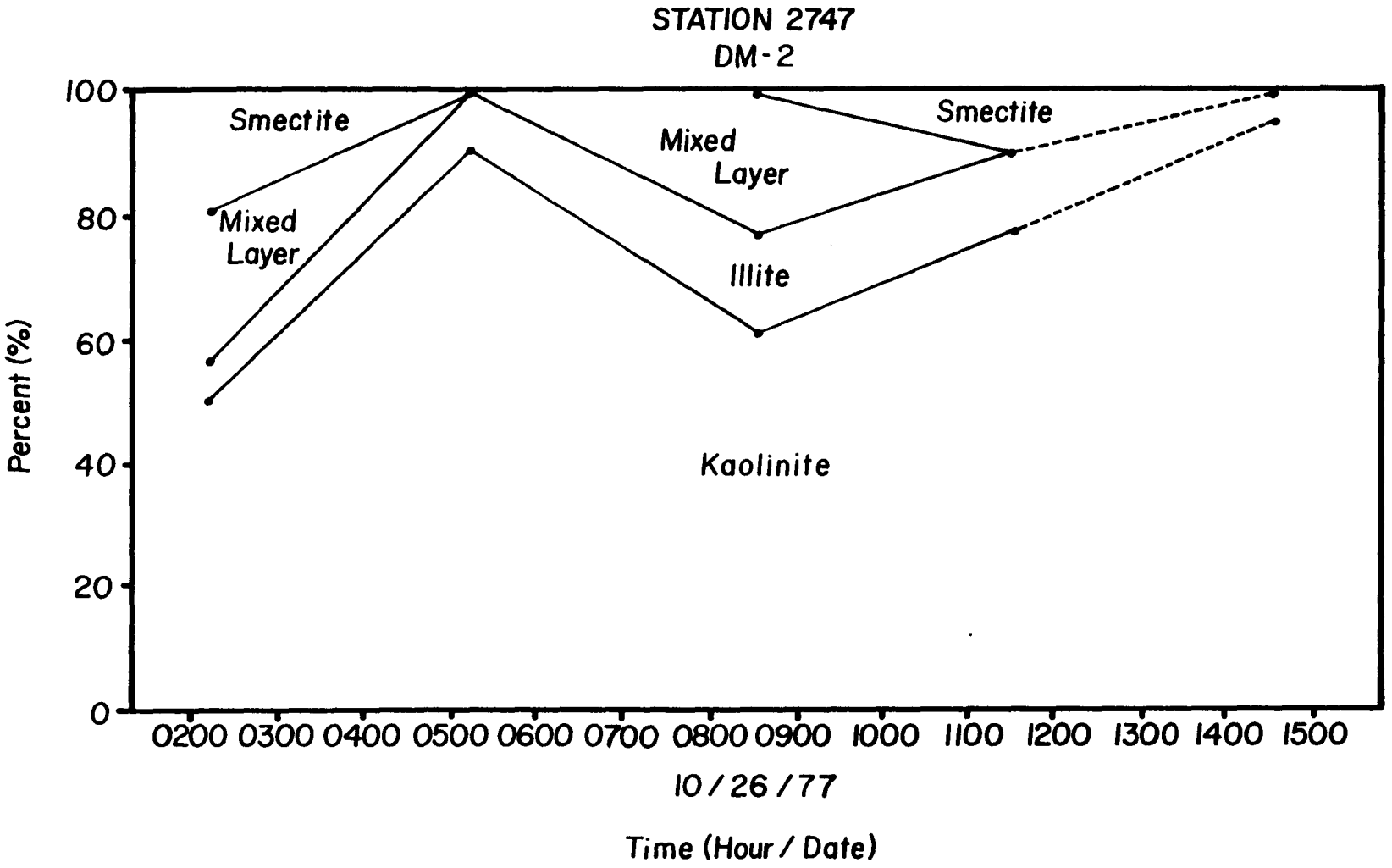
Present day expression of the surficial sediments of the eastern Gulf margin reflects that of the subsurface geology; that is, it may be roughly divided at Cape San Blas into a western region of clastics and an eastern region dominated by carbonates. Figure 117 shows the facies distribution of surface sediments in the study area.

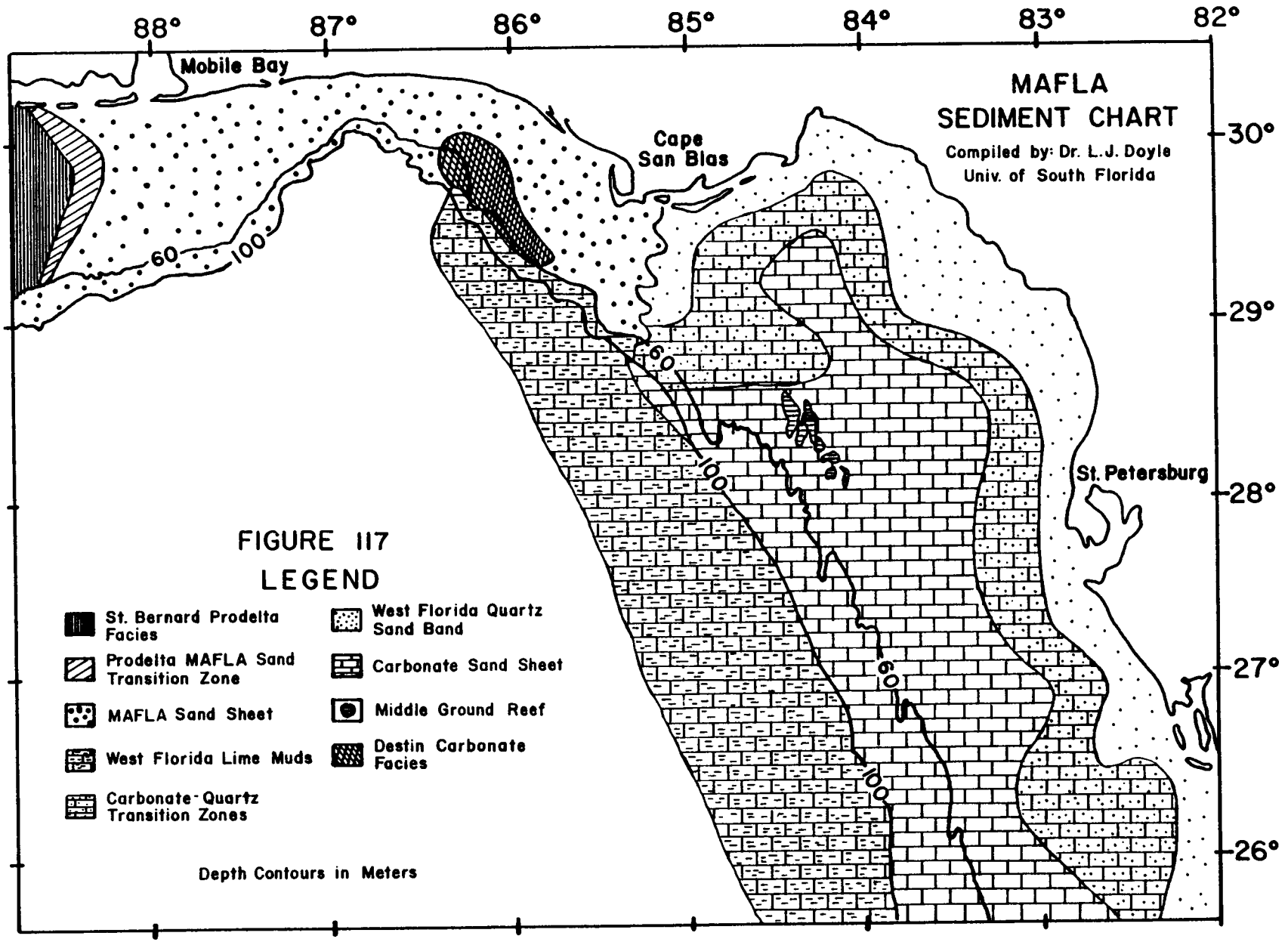
Since most of the load of the Mississippi River is delivered directly to the shelf edge or is carried west due to the distribution of major distributaries and the Coriolis force acting on the plume, sediments on the eastern margin of the delta change rapidly from the St. Bernard Prodelta facies (Ludwick, 1964) dominated by mud to an open shelf clastic facies, which we call the MAFLA sand sheet. Sediments within this sheet are quartz sands with carbonate percentages of generally less than 25%. Van Andel and Poole (1960), and Fairbank (1962) characterize the heavy mineral suite of the area encompassed by the MAFLA sand sheet as reflecting a southern Appalachian provenance. Kyanite and staurolite are diagnostic, with ilmenite, zircon, and tourmaline common. Hematite, pyroxenes, and amphiboles which dominate the Mississippi suite are present, suggesting some contribution from that river.

Within the MAFLA sand sheet adjacent to the eastern margin of DeSoto Canyon lies the rather geographically limited Destin Carbonate Facies with carbonate percentages over 75. Wanless (1977) shows this zone to be a combination of shell hash, lithothamnion algae, and foraminifera. Since the Loop Current turns to the east then south at the DeSoto Canyon, it may serve to block transport of clastic sediments into this zone resulting in the accumulation of carbonate sediments similar to those of the West Florida carbonate sand sheet.

FIGURE 116

SUSPENDED CLAY MINERALOGY
(BOTTOM)




88°
87°
86°
85°
84°
83°
82°
30°
29°
28°
27°
26°
Mobile Bay
Cape San Blas
St. Petersburg
MAFLA
SEDIMENT CHART
Compiled by: Dr. L.J. Doyle
Univ. of South Florida
60
100
60
100
60
100
FIGURE 117
LEGEND
St. Bernard Prodelta Facies
Prodelta MAFLA Sand Transition Zone
MAFLA Sand Sheet
West Florida Lime Muds
Carbonate-Quartz Transition Zones
West Florida Quartz Sand Band
Carbonate Sand Sheet
Middle Ground Reef
Destin Carbonate Facies
Depth Contours in Meters

East of Cape San Blas lies the West Florida shelf which may be divided mineralogically into two facies with a rather broad transition zone between (see Figure 117). A carbonate sand facies dominates the outer and middle shelf. Rather than being banded with regard to texture and carbonate constituents as described by Stewart and Gould (1955), sediments within it are of patchy distribution (Doyle et al., 1977; and Wanless, 1977). Carbonate content is arbitrarily placed at over 75%. Patches of shell hash, foraminifera, lithothamnion algae, and even oolites locally dominate (Stewart and Gould, 1955, and Wanless, 1977). As expected, detrital heavy minerals are essentially absent in the carbonate facies. Phosphorite associated with outcrops of probable Miocene Age is present in some locations.

Shoreward of the carbonate facies lies a transition zone shown in Figure 117 which includes ever increasing amounts of quartz to the east. The transition is gradational and the shoreward boundary is arbitrarily placed at 25% carbonate. Shoreward of the transition zone lies a quartz sand facies. This facies is a mature very fine to fine sand. The heavy mineral suite is characterized by the resistant minerals zircon, tourmaline, garnet, and staurolite (Fairbank, 1962). Significant for several reasons, the inshore quartz band also makes up west Florida's beaches.

The rivers of Florida carry little suspended load and even less bed load. The inshore band is bordered on the west and south by carbonates. Heavy mineral and clay mineral suites are distinct from the sediments to the west of Cape San Blas suggesting that there is little sediment exchange between the two. The question arises, that without a constant source for replenishment, why is the band still there? Why hasn't long shore drift removed the quartz to be replaced by carbonate sand? Northerly winds dominate during late fall and winter, while southerly winds predominate the rest of the year (Jordan, 1973). This alternating wind pattern leads to a southerly longshore drift in late fall and winter and a northerly drift during the remainder of the year. These two patterns balance so that there is essentially no net drift and sediments tend to slosh back and forth. The result is an exceedingly mature sediment.

Since quartz is not being fed to the system at present, it must be relict from an earlier time. It may be the result of quartz sands being brought down from the Tertiary clastic terraces of peninsular Florida during lowered stands of sea level or it may represent the surface of a partially drowned terrace. Since clay mineralogy of the shelf is dominated by kaolinite and the coastal plain sediments of peninsular Florida by smectite, the northern Appalachicola and Suwannee Rivers may have been the most significant provenance with original smectite being partially masked or winnowed.

Such a systems, bounded as it is by carbonates to seaward, should be an excellent place to test the theory espoused by Pilkey et al. (1972) which suggests that beach systems are fed from the adjacent continental shelf. Vibra-coring the transition zone might show whether the carbonates are encroaching over the quartz sand or not, thus supporting or weakening the offshore source argument.

Seaward of the carbonate sand facies lies the West Florida Lime Muds of Ludwick (1964). This facies lies on the continental slope. In many places it may contain large amounts of sand sized planktonic foraminifera. Clay minerals are dominated by smectite, probably the result of Loop Current transport, and fine grained carbonates, mostly of coccoliths, are also important.

CLUSTER ANALYSIS

Q-mode cluster analysis was run on the grain size and carbonate data. Since all size data and not just summary statistics are used to arrive at resultant groupings, cluster analysis should provide results which are sensitive, subtle and useful when compared with results of similar clustering techniques for chemical and biological data. Figure 118 shows Q-mode clustering for grain size along for all 60 stations all seasons and Figure 119 shows Q-mode clustering for grain size with carbonate for all 60 stations. All seasons' comparison of Figures 118 and 119 with Figure 117 shows that two quite different kinds of information have been generated. While Figure 117 shows the general geologic divisions of the continental shelf east of the Mississippi, the other two figures show similarities of groups of stations, individuals of which are often in quite different facies and are geographically widely separated. Figures 118 and 119 may be especially useful in interpretation of foraminiferal and benthic infauna assemblage distribution. Summary statistics of the subclusters shown in Figure 118 are presented in Table 28. Table 28 shows that the groupings do have distinct differences. It is presented only to build confidence in the group representations in Figure 118.

Q-mode cluster analysis was also performed on the primary stations for each seasonal sampling period from summer 1976 through winter 1978. Twenty-one of the primary stations showed no change in cluster group. The eight that changed group and corresponding changes in mean grain size are shown in Table 29. Variation could reflect seasonal fluctuation in grain size or may be the result of spread in sample location. Figure 120 shows the locations of all box-core replicates for one station for four sampling periods. Variation in groupings of box-core locations are such that any seasonal variations present in grain size could be masked.

CONCLUSIONS

1. Sediments of the eastern Gulf of Mexico continental margin may be divided into a number of facies which are the latest expressions of the history of the geologic column below. West of Cape San Blas lie the MAFLA sand sheet and the Mississippi Delta, the surface expression of the eastern limb of the Gulf Coast Geosyncline. These sediments get finer to the west and have Mississippi-type heavy mineral and clay mineral suites, the latter dominated by smectite. A patch of high carbonate sediments, possibly the result of winnowing and or blocking of clastic input by the Loop Current, lies on the outer shelf adjacent to the eastern rim of DeSoto Canyon.

2. East of Cape San Blas is found the West Florida Sand Sheet, the outer and middle portion of which is predominantly made up of carbonate

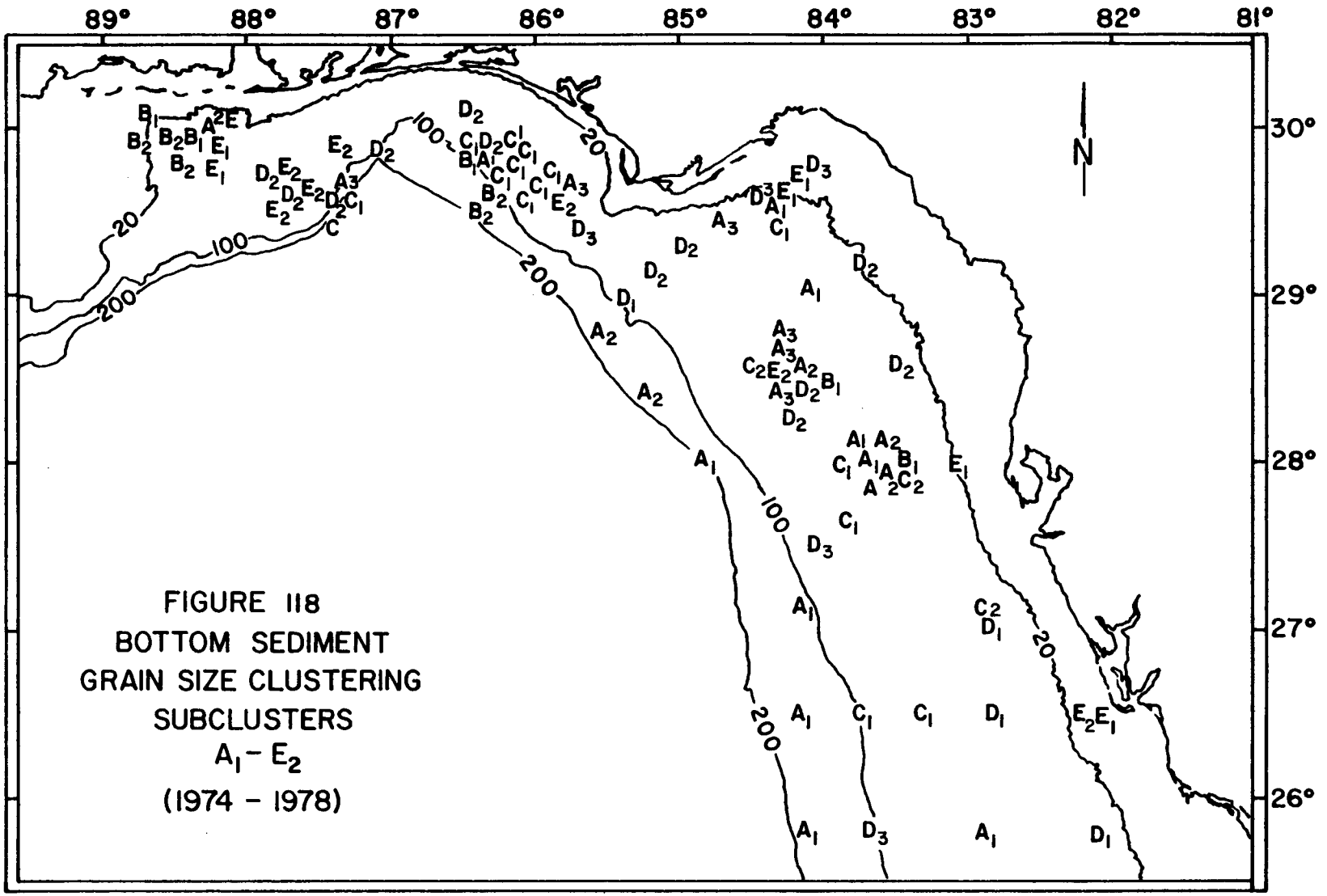


FIGURE 118
BOTTOM SEDIMENT
GRAIN SIZE CLUSTERING
SUBCLUSTERS
$A_1 - E_2$
(1974 - 1978)

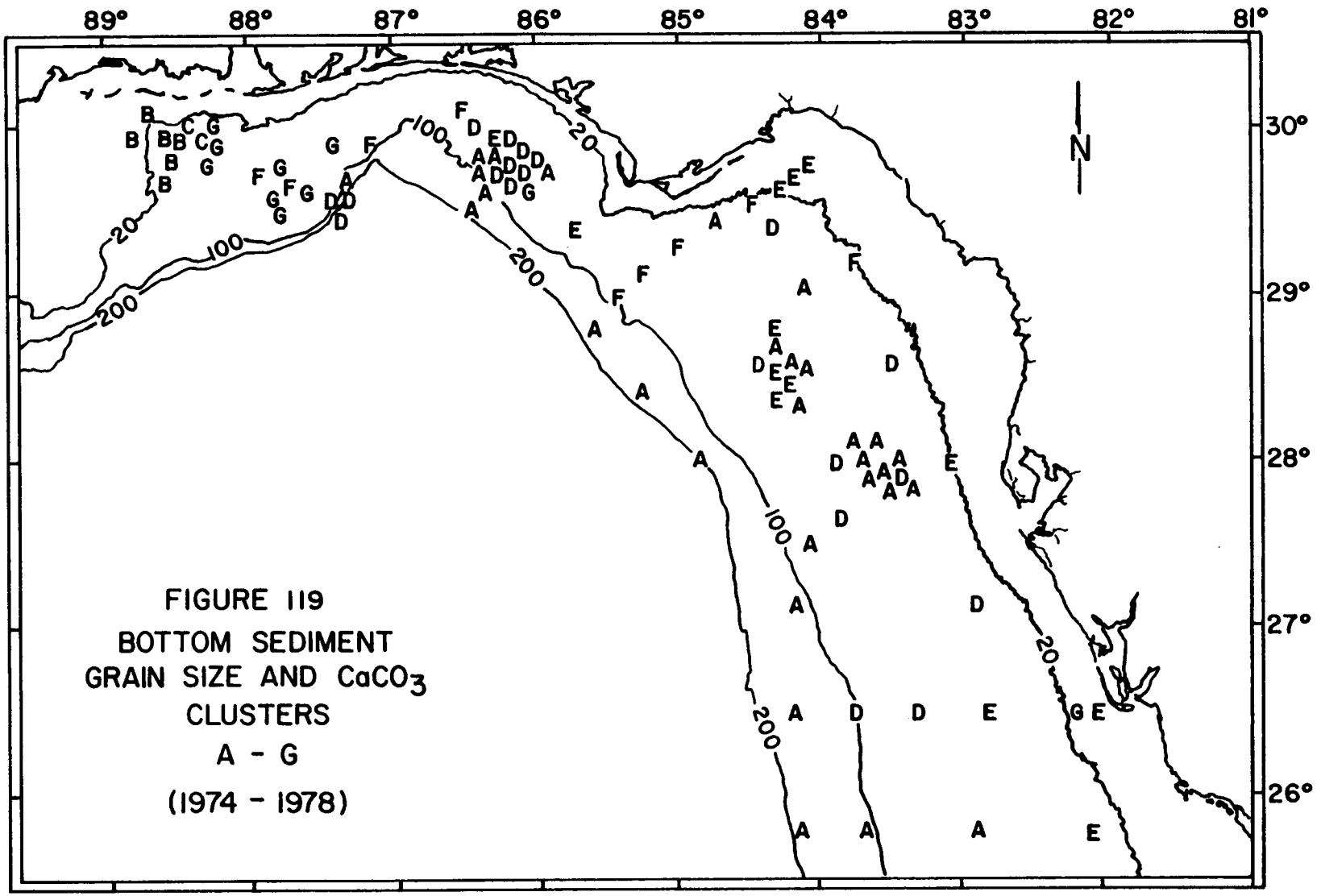


FIGURE 119
BOTTOM SEDIMENT
GRAIN SIZE AND $CaCO_3$
CLUSTERS
A - G
(1974 - 1978)

TABLE 28

GRAND STATION MEANS AND SEDIMENT TYPE OF 12 SUBCLUSTER GROUPS

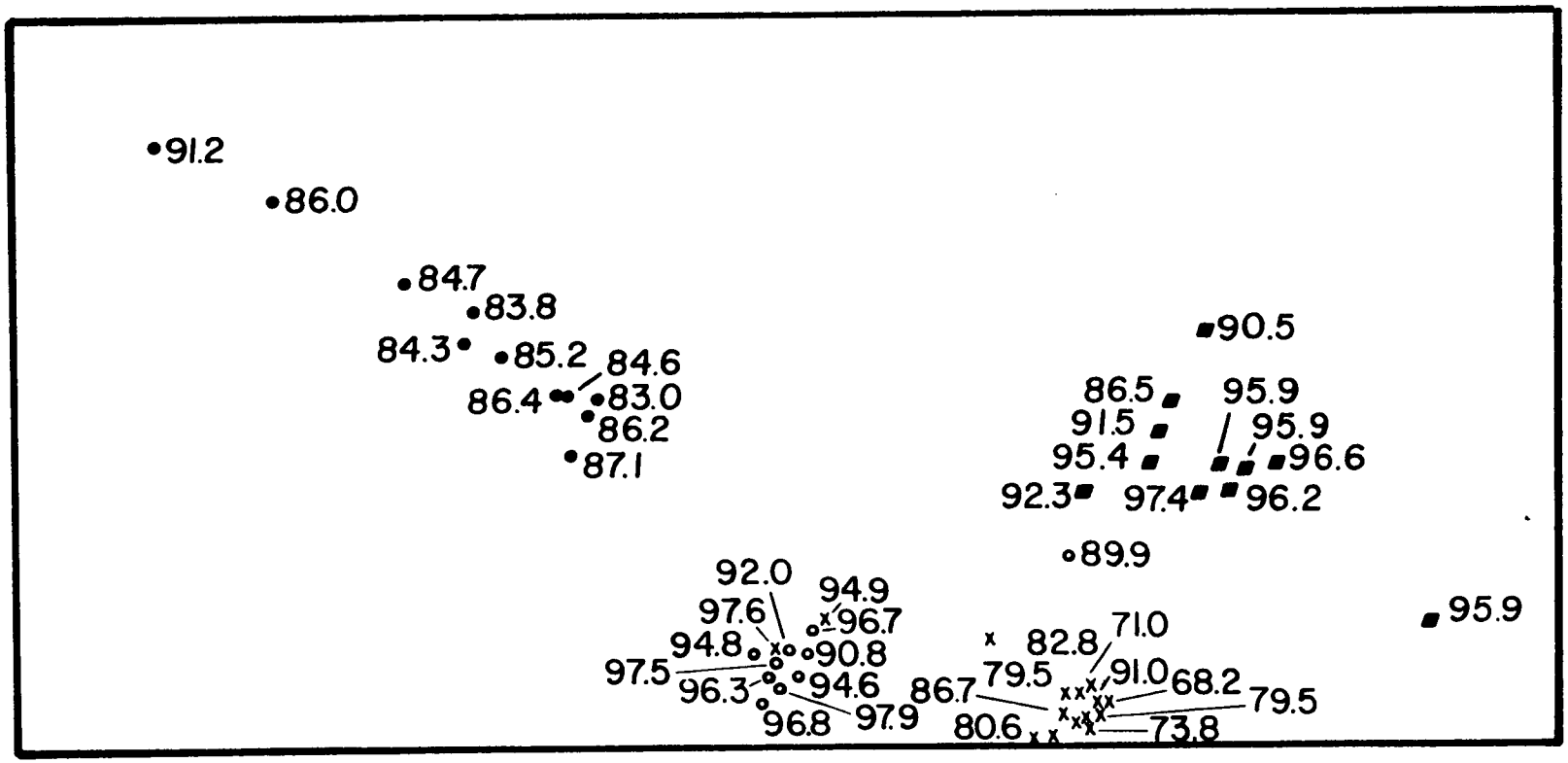
SHOWN IN FIGURE 118

SUBCLUSTER	X PHI	% SAND	S/F	$CaCO_3$	SED. TYPE
A_1	3.38	71.65	2.9	90.8	Silty, very fine sand
A_2	4.19	59.37	1.5	83.4	Clayey, sandy silt
A_3	2.18	71.80	5.1	73.7	Silty fine sand
B_1	5.08	39.21	0.7	48.0	Sandy silt
B_2	6.15	21.31	0.3	52.3	Clayey silt
C_1	0.88	83.63	17.9	84.0	Coarse sand
C_2	1.00	91.85	23.9	70.2	Medium-coarse sand
D_1	2.11	89.84	13.5	70.9	Fine sand
D_2	1.29	89.88	30.1	35.6	Medium sand
D_3	1.90	84.63	13.7	64.7	Medium-fine sand
E_1	2.98	87.75	10.0	40.4	Fine-very fine sand
E_2	2.29	93.50	34.2	14.5	Fine sand

TABLE 29

VARIATIONS IN MEAN PHI GRAIN SIZE AND CLUSTER GROUPING OF EIGHT PRIMARY STATIONS, 1976-1978

STATION	SUMMER 76	SUMMER 77	FALL 77	WINTER 78
	GROUP X	GROUP X	GROUP X	GROUP X
2102	F 2.47	F 2.25	E 1.79	F 2.47
2207	B 3.03	B 3.01	D 2.00	B 3.08
2208	A 4.66	A 4.70	C 1.05	A 4.65
2316	C 0.89	B 2.88	D 1.57	D 2.58
2419	- ----	E 1.62	B 2.70	C 1.17
2423	C 0.85	C 1.08	D 2.23	C 1.19
2640	D 1.72	C 1.20	E 1.07	C 0.59
2747	C 1.75	C 1.37	D 2.86	D 3.62



PERCENT SAND & GRAVEL

0 50 100
METERS

STATION 2316
CRUISES DM-1 & DM-2

FIGURE 120

CRUISE	SYM
DM-1	•
DM-2	▪
DM-4	x
S-76	o

sands, the surface expression of a thick section of carbonates and evaporites which have been accumulating since the Jurassic. Inshore of the carbonates lies a mature quartz sand surrounded by carbonates and cut off at Cape San Blas. Originally deposited at lower stands of sea level, it maintains itself by shifting north then south about equal distances under the pressure of seasonal variation in the wind induced longshore current system. A quartz/carbonate transition lies between the carbonate and quartz sands. Clay mineralogy is dominated by kaolinite, originating from north Florida River systems while the heavy mineral suite in the clastics has lost its Mississippi diagnostics and is composed of the most durable mineral species.

3. Variation within sand sheets are patchy both in texture and composition. Spacial variation masks any seasonal variation in texture which may be present.

4. Dominated by planktonic foraminifera and fine carbonate nannoplankton, a slope lime mud facies lies seaward of the West Florida Sand Sheet.

5. Clay mineralogy, however, shows distinct temporal variation over the course of a year in the bottom sediments and on a period of a few hours in the suspended sediments. These changes are the dramatic result of variations in transport of Mississippi contributed smectite past Mobile Bay either in pulses or by seiching, and the occasional intrusion of smectite-rich Mississippi or Loop Current water east of Cape San Blas.

6. Sediments of the MAFLA area have been grouped into a number of clusters by Q-mode analysis based upon all grain size data and carbonate content. These groupings have distinct sedimentologic characteristics and may be an effective tool for interpreting biologic and chemical data.

REFERENCES

Antoine, J.W., R.G. Martin, T.E. Pyle, and W.R. Bryant, 1974. Continental margins of the Gulf of Mexico, In Burk, C.A., and C.L. Drake, eds., The Geology of Continental Margins, Springer-Verlag, New York, p. 683-693.

Bryant, W.R., A.A. Meyerhoff, N.K. Brown, Jr., M.A. Furrer, T.E. Pyle, and J.W. Antoine, 1969. Escarpments, reef trends and diapiric structures, Eastern Gulf of Mexico. Am. Assoc. Petr. Geol. Bull. 53 (12): 2506-2542.

Doyle, L.J., B. Birdsall, G. Hayward, L. Lehman, S. Szydlik, and E. Warren III, 1977. Baseline monitoring studies, Mississippi, Alabama, Florida outer continental shelf, 1975-1976: Report to the Bureau of Land Management, Contract No. 08550-CT5-30, 14 p.

Emery, K.O., and E. Vchupi, 1972. Western North Atlantic Ocean: Am. Assoc. Petr. Geol. Memoir 17, 532 p.

Fairbank, N.C., 1962. Heavy minerals from the eastern Gulf of Mexico: Deep Sea Research, 9:307-338.

Folk, R.L., 1965. Petrology of Sedimentary Rocks, Hemphills, Austin, 152 p.

Grady, J.R., 1972. Reconnaissance Survey; Bottom sediments on the continental shelf, In Report of the National Marine Fisheries Service; Gulf Coastal Fisheries Center for fiscal years 1970 and 1971, p. 15-A.

Griffen, G.M., 1962. Regional clay mineral facies - products of weathering intensity in the northeastern Gulf of Mexico, Geol. Soc. Amer. Bull. 73:737-768.

Huang, W.H., L. Boyle, and Wen-An Chiou, 1975. Clay mineral studies of surface sediments from the shelf of the northeastern Gulf of Mexico, In Bailey, S.W., ed. Proceedings of 1975 Interna. Clay Conference Mexico, p. 55-70.

Huang, W.H., 1977. Baseline monitoring studies, Mississippi, Alabama, Florida outer continental shelf, 1975-1976: Report to the Bureau of Land Management, Contract No. 08550-CT 5-30, 14 p.

Jordan, C.L., 1973. The physical environment: Climate, In The Eastern Gulf of Mexico: SUSIO, St. Petersburg, p. IIA-1-IIA-22.

Ludwick, J.C., 1964. Sediments in the northeastern Gulf of Mexico, In Papers in Marine Geology, MacMillan Co., New York, p. 204-238.

Martin, R.G., 1976. Geologic framework of northern and eastern continental margins, Gulf of Mexico: in

Pilkey, O.H., and M. Field, 1972. Onshore transportation of continental shelf sediment: Atlantic southern United States, In Shelf Sediment Transport, Swift, D.J.P., D.B. Duane, and O.H. Pilkey, eds., Dowden, Hutchison and Ross, Inc., Stroudsburg, p. 429-447.

Pyle, T.E., V.J. Henry, M. Ball, J.C. McCarthy, R.J. Giles, and T.W. Neurauter, 1977. Baseline monitoring studies, Mississippi, Alabama, Florida outer continental shelf, 1975-1976: Report to the Bureau of Land Management, Contract No. 08550-CT5-30, 14 p.

Shepard, F.P., 1956. Marginal sediments of the Mississippi Delta, Am. Assoc. Petrol. Geol. Bull. 40(11):2537-2618.

Van Andel, T.H., and D.M. Poole, 1960. Sources of recent sediments in the Northern Gulf of Mexico, J. Sed. Petrol. 30:91-122.

Wanless, H., 1977. Baseline monitoring studies, Mississippi, Alabama, Florida outer continental shelf, 1975-1976: Report to the Bureau of Land Management, Contract No. 08550-CT5-30, 14 p.

VOLUME II

CHAPTER 3

BENTHIC SEDIMENT TRACE METALS

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CONTRACT NO. AA550-CT7-34

FINAL REPORT FOR

BLM MAFLA O.C.S. STUDY

"HEAVY METAL ANALYSIS OF BOTTOM SEDIMENT"

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COLLEGE STATION, TEXAS

SEPTEMBER 1978

ABSTRACT

During MAFLA 1977-78, 364 sediment samples were carefully collected for Cd, Cr, Cu, Fe, Ni, Pb and Zn analysis. All of the samples were analyzed after a 1 N HNO_3 leach; and metal content in 105 of these was determined after total dissolution.

Large variations in metal content are found throughout the MAFLA area, however, the overall means are quite low. Highest sediment metal content occurs in the fine-grained sediments of the Mississippi Delta and outer shelf areas whereas low values are found in shallow-water, nearshore sediments and in the $CaCO_3$-rich sediments of the West Florida shelf.

By leaching with 1 N HNO_3 about 60% of the total sediment metal load was removed. Near-complete removal was obtained from the carbonate-rich (clay-poor, quartz-poor) sediments of central shelf areas. Conversely, lower percent removal was generally found for very nearshore, noncarbonate sands and outer shelf clay containing sediments.

Statistical development of the MAFLA data and the use of Metal/Fe scatter plots have been used to explain the observed distribution of trace metals and predict the relative sensitivity of the area to anthropogenic metal input.

INTRODUCTION

Instances of trace metal pollution of inland and coastal areas are frequently reported in both the popular and scientific literature (Skei et al., 1972; Carmody et al., 1973, Holmes et al., 1974). Concern about the high toxicity of metals such as lead, cadmium and mercury arises from reports of hazards to health and life posed by metal pollution. Kobayashi (1970), for example, correlated the bone disease "itai-itai" with polluted rice paddies that had been irrigated by the cadmium-rich waters of Japan's Jintsu River. Patterson (1965) reported that the average American is suffering from "chronic lead insult" with a body burden of lead 100 times greater than natural levels.

"After the fact" identification of localized metal problems is most often a rather straightforward process. However, man has not yet demonstrated a proficiency in predicting the occurrence or extent of future instances of metal pollution. For this reason, it is advantageous to survey and understand the metal distribution in areas that have not yet been subjected to the activities of man, but may be at some future time. Such has been the case in our investigation of sediment trace metal content at proposed oil drilling sites in the MAFLA lease area.

The purpose of this study and the data presented herein is to provide a pre-drilling characterization of the patterns and geochemical significance of trace metals (TM) in MAFLA sediments. With this data base and future monitoring, we will be able to more logically predict sites which could be most affected by anthropogenic metal inputs and be able to clearly identify and trace these inputs before they become an environmental threat.

Previous work on MAFLA sediments (Holmes, 1973; Presley et al., 1975, 1976) shows the area to have extremely variable TM levels with highest concentrations near the Mississippi Delta and lowest values off the central Florida coast. However, the observed variability correlates well with fundamental sediment characteristics. Low metal values are found where $CaCO_3$ and quartz sand levels are greatest and higher metal concentrations occur where a significant fine-grained, clay component appears. No instances of metal pollution have been reported at any of the MAFLA sites.

Of the metals chosen for study (Ba, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn), some are associated with potential petroleum-related pollution whereas others represent some of the more toxic heavy metals often associated with the increased activities of man. Barium and Cr, for example, are common to drilling muds, whereas Ni and V have been shown to be present in large concentrations in some oils and tars (Yen, 1975). Lead, Cd and Zn, three potentially toxic metals, have been observed to be above natural levels near Gulf of Mexico industrial and populations centers (Trefry and Presley, 1976a, b; Hann and Slowey, 1972; and Holmes et al., 1974).

In continuing the MAFLA sediment TM program, the 1977-78 effort was almost four times greater than the combined previous work. Two additions were made to our program this year. First, sediment samples were leached with 1 N HNO_3 (in addition to total dissolution) to assess the "biological availability" of the various metals relative to the total metal content.

Second, Zn was added to the eight metals previously studied. The overall objectives of this year's study were (1) to continue and expand (areally) TM characterization of MAFLA-OCS sediments, (2) to identify regional sediment inhomogeneities and the consequences on tm concentrations via replicate samples, (3) to assess the "availability" of the various sediment metals when subjected to 1 N HNO_3, and (4) to continue development of our model for TM distribution in the MAFLA area (based on sediment mineralogy, particle size and provenance) and thus allow more rapid assessment of subtle perturbations. The previous years' work will also be considered in completing the above objectives.

METHODS

Detailed methodology for MAFLA sediment TM analyses was previously presented in our Third Quarterly Report (Dames & Moore, 1978e) and, hence, only a brief overview is given here. Throughout the entire sediment collection, preparation and analysis process, the utmost concern and care were given to minimizing possible sample contamination. Many reagent and procedural blanks, replicate samples, USGS standard rocks and laboratory environmental quality analyses were performed in this effort. Data quality is paramount to proper evaluation of observed trends.

Most of the sediment used for TM analysis was obtained by subsampling box cores with a 50 mℓ polyethylene syringe (~15 cm long) and storing the subcores in polystyrene vials and polyethylene bags. All equipment was scrupulously acid washed prior to use. Upon return to the laboratory, the sediment samples were freeze-dried and homogenized with a teflon policeman, sorting out >3 mm particles.

All samples were analyzed for trace metals after "partial digestion" in 1 N HNO_3. Two-gram portions of sediment were reacted with 1 mℓ aliquots of 1 N HNO_3 (redistilled in 50 mℓ polyethylene centrifuge tubes (tube was pre-cleaned in warm 1:1 HNO_3:H_2O for several nours and rinsed twice with distilled-deionized water). Acid additions were continued until the $CaCO_3$-HNO_3 reaction was complete. When more than 10 mℓ of 1 N HNO_3 were required, 1 mℓ aliquots of 2.5 N HNO_3 were introduced to complete the reaction. The final normality was adjusted to 1 with appropriate volumes of 2.5 N and/or 1 N HNO_3 and the mixture was shaken for two hours on a rotary shaker. The leachate was separated from the sediment residue by centriguation and the clear solution was sorted in an acid-washed polystyrene vial for analysis.

Total sediment dissolutions were carried out on ~1.5 g samples which were first treated as above, saving the Ca-rich decantate in a polystyrene vial. The residual sediment was dissolved in a teflon beaker (with cover) using HNO_3, HF and $HClO_4$. After the HF and $HClO_4$ reactions were complete, the resultant moist paste was dissolved in 1 mℓ of concentrated HNO_3, followed by small additions of ultra-pure water and finally the Ca-rich leachate. The solution was transferred to a 25 mℓ volumetric mixing cylinder and diluted to volume with distilled-deionized water. If the Ca-rich leachate is not removed prior to HF additions as outlined above, a vertually insoluble CaF_2 precipitate forms, coprecipitating Pb, Cd and fractions of the other elements.

Atomic absorption spectrophotometric (AAS) analysis of the sediment digests for Cu, Cr, Fe, Ni and Zn was carried out using a Perkin-Elmer 460 instrument equipped with a deuterium-arc background corrector. A second P-E 460 AAS with an HGA-2100 graphite furnace was used for detecting low levels of Cd and Pb present. Instrument specifications and details have been previously detailed. Method-of-additions (standard additions) analyses were used exclusively for Cd, Cr, Ni and Pb analyses and additions checks were made for each of the other elements.

Reproducibility in MAFLA sediment metal data was determined by replicate analysis of various samples and found to be a function of the levels encountered. For average and above average levels the following precisions were obtained: Cd, 12%; Cu, 5%; Cr, 7%; Fe, 4%; Ni, 9%; Pb, 10%; Zn, 4%. When very low levels were present, precisions for Cd and Pb were about 20%, Zn, 12%; Cr and Cu 5 to 10%, Fe, 5 to 8% and Ni about the same as above. Some of the variability on all these values is introduced by the lack of a powdering step in the ascribed methodology.

RESULTS AND DISCUSSION

Sediment trace metal concentrations in the MAFLA area are quite variable in response to a wide diversity in major element chemistry, mineralogy and grain size. As is expected, higher metal concentrations are found with significant quantities of fine-grained material, organic matter and Fe and Mn hydrous oxides, whereas lower concentrations are observed where sediments contain appreciable amounts of quartz, carbonate and coarse-grained particles. Highest sediment metal content in the MAFLA area occurs adjacent to the Mississippi Delta and in the more seaward sites of most transects. Low values are found in shallow water, nearshore sediments and in the $CaCO_3$-rich sediments of the West Florida shelf.

Table 30 shows that Stations 2638 (71% fine-grained particles, 0.8% TOC and 17% $CaCO_3$) and 2536 (73% fine-grained particles, 0.8% TOC and 71% $CaCO_3$) account for all observed maximum metal values, except Cd. These two sites represent both the Mississippi delta proximity and outer shelf components of the high metal group. Within this MAFLA sediment group, only Cd concentrations exceed crustal abundance levels. The other maximum values are below crustal averages; and the MAFLA area as a whole is quite depleted in TM relative to the continents.

As in the case of the maximum values, minimum metal concentrations are divided between just two stations (2318 and 2856). Interestingly, sediments from these two sites were low in the three descriptive sediment parameters considered, as shown below.

Station	$CaCO_3$ (%)	Fines (%)	TOC (%)
2318	11	2	0.06
2856	8	1	0.07

This trend of lowest metal values in sediments with low percent $CaCO_3$ and very low percent fines holds for Stations 2102, 2207, 2424, 2528, 2640 and

TABLE 30

RANGE OF TRACE METAL VALUES*
FOR MAFLA SEDIMENTS

	MAFLA SEDIMENTS				AVERAGE CRUSTAL ABUNDANCE[1]
	MAXIMUM (STATION NO.)		MINIMUM (STATION NO.)		
Cd	0.33	(2957)	0.01	(2856)	0.2
Cr	47	(2638)	2	(2856)	100
Cu	8	(2536)	0.3	(2318)	55
Fe	23,000	(2638)	420	(2856)	56,000
Ni	16	(2536)	0.4	(2318)	75
Pb	16	(2638)	0.6	(2318)	20
Zn	66	(2638)	0.8	(2102)	70
$CaCO_3$[2] (%)[3]	98	(2958)	6	(2641)	4.2% Ca
Fines[3] (%)	73	(2536)	1	(2856)	--
TOC[4] (%)	1.1	(2535)	<0.01	(2853,56)	--

[1]Taylor (1964) and Turekian and Wedepohl (1961)
[2]From grand station means
[3]Grain size <62 μm
[4]Total organic carbon

*All values as ppm

2641 (Table 31). Lowest metal values in the MAFLA region are therefore associated with the coarse-grained, quartz sand of these generally nearshore sites. A simple hierarchy of TM distribution based on sediment type for the MAFLA area may be extracted from Table 30 showing:

Clay >> $CaCO_3$ > Quartz sand, the important distinction, at this point, being that between carbonate and quartz sands.

Comparison of the TM content of MAFLA carbonates with noncarbonate sands (Table 32) shows the carbonates to have 3 to 5 times higher concentrations. For Cd, Cu, Ni and Zn, this trend is compatible with previous work, even though the absolute values of Graf (1960) and Turekian and Wedepohl (1961) given in Table 32 are consistently higher. Analytical difficulties with TM analysis of carbonates and quartz sands and the inhomogeneous character of even the most carefully screened samples do distort intercomparisons. Nevertheless, the scrupulously obtained MAFLA data do identify scavenging of measurable amounts of metals by carbonate-forming organisms and the paucity of TM in detrital noncarbonate sands. Certainly the carbonnate metal levels are significantly below crustal abundances (Tables 31 and 32 show generally 10 to 40 times less in carbonates), yet one exception, namely Cd, remains intriguing.

Exceptionally high Cd concentrations (~0.3 ppm) were consistently observed at recently added Station 2957 where sediments were 96% $CaCO_3$, 21% fines, and 0.2% TOC. A trend of high Cd in outer shelf sediments with high percentages of $CaCO_3$ (>90%) and fine-grained particles (>20%) is supported by data from Stations 2106, 2212, 2313 and 2958 (Table 31). Average total Cd levels in the eight sites with >90% $CaCO_3$ is 0.20 $\pm$ 0.05 ppm. This is significantly higher than the 0.12 $\pm$ 0.02 values for clay-rich sites 2535, 2536 and 2638. The observed Cd trend is nicely demonstrated with data from transects 27 and 29 in the following inset:

Station	Cd (ppm)	$CaCO_3$ (%)	Fines (%)
2746	0.17	96	36
2747	0.15	97	21
2748	0.11	97	9
2957	0.30	96	21
2958	0.23	98	20
2959	0.15	96	27
2960	0.08	98	5

Here, high $CaCO_3$ is found throughout, yet the percent fines decrease shoreward showing the high Cd values in the outer shelf sites. The wide range of Cd concentrations (0.30 to 0.08 ppm) over a narrow range of high carbonate levels (96 to 98%) is reassuring in light of the effort made to reduce matrix interference. One plausible explanation for this exciting trend of greatly enriched Cd levels in the outer shelf areas is through biological Cd uptake in nutrient-rich, productive waters of the southern MAFLA area. Cadmium uptake has specifically been noted in the waters of the California current (Martin et al., 1976) and may well have an analagous behavior in this area of the Gulf. One important aspect of this enrichment

TABLE 31

MAFLA SEDIMENT TRACE METAL SUMMARY (TOTAL DISSOLUTION)

STATION	N	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	$CaCO_3$ (%)	Fines[1] (%)
2101	2	0.05	8.6	0.70	1360	1.4	2.0	5.2	45	11
2102	3	0.03	5.4	0.34	660	0.9	1.0	1.5	30	4
2103	3	0.06	11.9	0.72	2070	2.0	1.8	3.0	58	10
2104	3	0.10	11.4	0.89	1050	2.0	1.2	5.0	97	10
2105	3	0.12	8.7	1.4	920	2.4	1.2	6.5	96	11
2106	2	0.21	11.2	2.8	4240	7.0	3.0	12.8	95	19
2207	3	0.13	7.0	0.50	900	0.6	2.2	2.7	48	8
2208	4	0.08	11.3	0.80	1710	2.3	2.4	4.9	86	50
		(±0.01)	(±1.1)	(±0.16)	(±720)	(±0.5)	(±0.5)	(±1.0)		
2209	2	0.09	11.5	0.94	1350	2.2	1.8	5.4	87	39
2210	2	0.09	13.1	0.92	1720	2.2	2.0	4.2	89	31
2211	1	0.14	15.1	1.1	2410	2.3	2.0	5.1	95	16
2212	4	0.18	17.4	4.2	9470	7.7	3.8	25.0	90	35
		(±0.02)	(±1.3)	(±0.2)	(±360)	(±0.7)	(±0.4)	(±0.5)		
2313	6	0.16	18.9	4.6	11500	9.0	4.1	26.9	85	50
		(±0.02)	(±1.0)	(±0.3)	(±1160)	(±0.8)	(±0.8)	(±2.6)		
2315	3	0.11	7.5	0.82	870	1.9	1.5	2.7	86	12
2316	3	0.07	7.8	0.68	1120	1.3	1.3	5.3	63	11
2317	2	0.12	11.2	0.69	2160	2.0	2.9	4.4	84	20
2318	1	-	7.0	0.26	370	0.4	0.6	5.1	11	2
2419	2	0.11	4.4	0.40	780	0.8	1.0	5.6	41	3
2421	1	0.09	9.2	0.92	680	1.9	2.2	14.4	48	9
2423	1	0.09	23.6	2.8	16200	6.8	5.8	17.3	72	14
2424	1	0.05	3.6	0.31	900	0.6	1.8	5.1	10	3
2426	2	0.08	12.2	0.88	4120	1.9	2.8	8.2	38	5
2427	1	0.13	24.1	5.9	16900	12.2	6.5	33.2	78	53
2528	2	0.06	7.8	0.55	2060	1.8	1.4	7.6	52	4
2529	2	0.12	15.0	1.1	5020	2.6	2.9	6.0	70	3
2531	1	0.19	16.3	0.91	5480	3.7	3.3	9.2	89	4
2533	3	0.17	18.5	1.2	5690	3.3	3.7	8.6	84	6
2535	1	0.12	33.9	7.1	10900	13.7	7.2	27.1	69	72
2536	3	0.15	33.0	8.1	13800	14.4	9.1	38.8	71	73
2638	2	0.10	38.5	7.4	22700	13.3	16.2	65.8	17	71
2639	1	0.07	17.2	3.0	9220	5.6	7.2	26.2	19	14
2640	3	0.05	6.1	1.1	6650	2.0	4.4	11.3	30	4
2641	2	0.06	9.9	1.6	4240	2.1	6.0	12.8	6	5
2643	3	0.17	17.6	2.7	13800	6.4	7.6	27.7	84	8
2645	1	0.16	13.9	2.6	11900	-	-	22.8	85	12
2746	3	0.17	11.9	2.5	1740	5.9	2.0	9.0	96	36
2747	3	0.15	14.9	1.3	1790	2.6	1.7	5.8	97	21
2748	2	0.11	18.4	0.85	3070	2.6	2.2	5.4	97	9
2851	1	0.05	17.9	1.0	3290	2.8	2.7	5.3	47	4
2852	1	0.10	11.8	0.54	1610	4.1	2.6	5.5	93	5
2853	1	0.10	9.9	0.98	2320	2.4	2.9	7.5	93	7
2854	1	0.06	16.5	1.4	6770	2.7	5.1	9.6	51	8
2855	1	0.03	3.0	0.33	860	0.5	1.4	2.5	11	2

TABLE 31 (CONTINUED)

STATION	N	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)	Pb (ppm)	Za (ppm)	$CaCO_3$ (%)	Fines[1] (%)
2856	1	0.01	2.4	0.44	420	0.9	1.1	2.3	8	1
2957	3	0.30	7.3	2.8	2100	6.7	2.6	10.2	96	21
2958	5	0.23 (±0.005)	8.0 (±0.4)	1.8 (±0.1)	1060 (±80)	3.5 (±0.2)	1.0 (±0.2)	6.2 (±0.5)	98	20
2959	3	0.15	13.5	1.1	2100	3.2	1.7	3.2	96	27
2960	1	0.08	24.6	0.48	2030	1.5	6.8	5.2	98	5

[1]Percent sediment with grain size <62 m.

TABLE 32

TRACE METAL CONTENT IN MAFLA CARBONATES AND NONCARBONATE SANDS

	Cd	Cr	Cu	Fe	Ni	Pb	Zn*
MAFLA Carbonates[1]	0.15	13	1.3	1900	3.4	2	6
MAFLA Qtz. sand[2]	0.03	4	0.3	600	0.7	1	2
Carbonate Rocks[3]	0.2 to 0.1	9	10	3800	12	8	26
Sandstones[4]	0.0X	35	X.	9800	2	7	16

[1]Samples with >90% $CaCO_3$

[2]Samples with <10% $CaCO_3$ and <10% fines

[3]Graf (1960) and Turekian and Wedepohl (1961)

[4]Turekian and Wedepohl (1961)

*All concentrations in ppm

is its probable natural occurrence, and thus Cd enrichment in such areas should certainly not immediately be construed as pollution.

Geographic variability in MAFLA sediment TM concentrations (total dissolution) is depicted in Figure 121 using Fe as an example. To a first approximation, the distribution of most of the other metals studied follows Fe well. Lowest Fe values in the noncarbonate sands of nearshore areas can be clearly identified as can the higher Fe levels found near the Mississippi Delta and along the seaward extensions of most transects. Along the central region of the vast carbonate-rich West Florida Shelf very low and uniform metal distribution is found.

The geochemical basis for the observed variability already has been alluded to and will be considered in more detail. But, what variability is encountered at a given site when sampled at different time intervals? Table 31 gives the means and standard deviations for samples analyzed more than three times during the 77/78 contract period. Data for high metal content sites 2212 and 2313 show that average variability for all elements was 7 and 10%, respectively. This is very close to the overall 7% analytical precision previously reported and one therefore cannot identify any seasonal or sampling artifacts at these sites. At Station 2208, where metal levels are significantly lower and sediments more inhomogeneously appearing, an average 20% variability was found, mostly due to consistently higher values from DM-II samples. From the triplicate sampling and total dissolution data from most other locations, the following overview is presented: (1) variability less than or approximately equal to the analytical precision at 2101, 2102, 2106, 2209, 2210, 2212, 2313, 2528, 2533, 2536, 2638, 2643 and 2958; (2) values generally less than twice the analytical precision at Stations 2104, 2208, 2426, 2746, 2747 and 2959; (3) significant variations in two or more metals at 2103, 2207, 2315, 2316, 2317, 2419, 2529 and 2640; and (4) only one data set for the remaining total metal population.

In addition to the total sediment metal concentrations presented above, an important facet of the TM program is identifying the potential "biological availability" of sediment metals. The ideal chemical treatment would use some analog of the digestive fluid of given benthic organisms. One can envision sophisticated treatments using enzymes or other organic chelators of metals or a simple system based on pH.

Gates and Travis (1969) note that white shrimp have internal pH levels greater than 5 whereas Barnard (1973) finds that pHs of 6 to 8 are characteristic of invertebrate guts, with special cases probably no lower than 4. Vertebrate digestive systems, on the other hand, are commonly at pHs of 3 or even less. Malo (1977) found 0.3 N HCl to be an appropriate leaching solution. We have opted for 1N HNO_3 because of the high $CaCO_3$ content of the MAFLA sediments which makes usage of very weak acids impractical (one would have to add a great deal of acid just to neutralize the $CaCO_3$). The results of the 1N HNO_3 leaching are summarized in Table 33.

These data (Table 33) are the produce of a 360-sample, 47-station effort with only the means and standard deviations at each site presented here. The overwhelming predominance of low values is till evident. Minimum

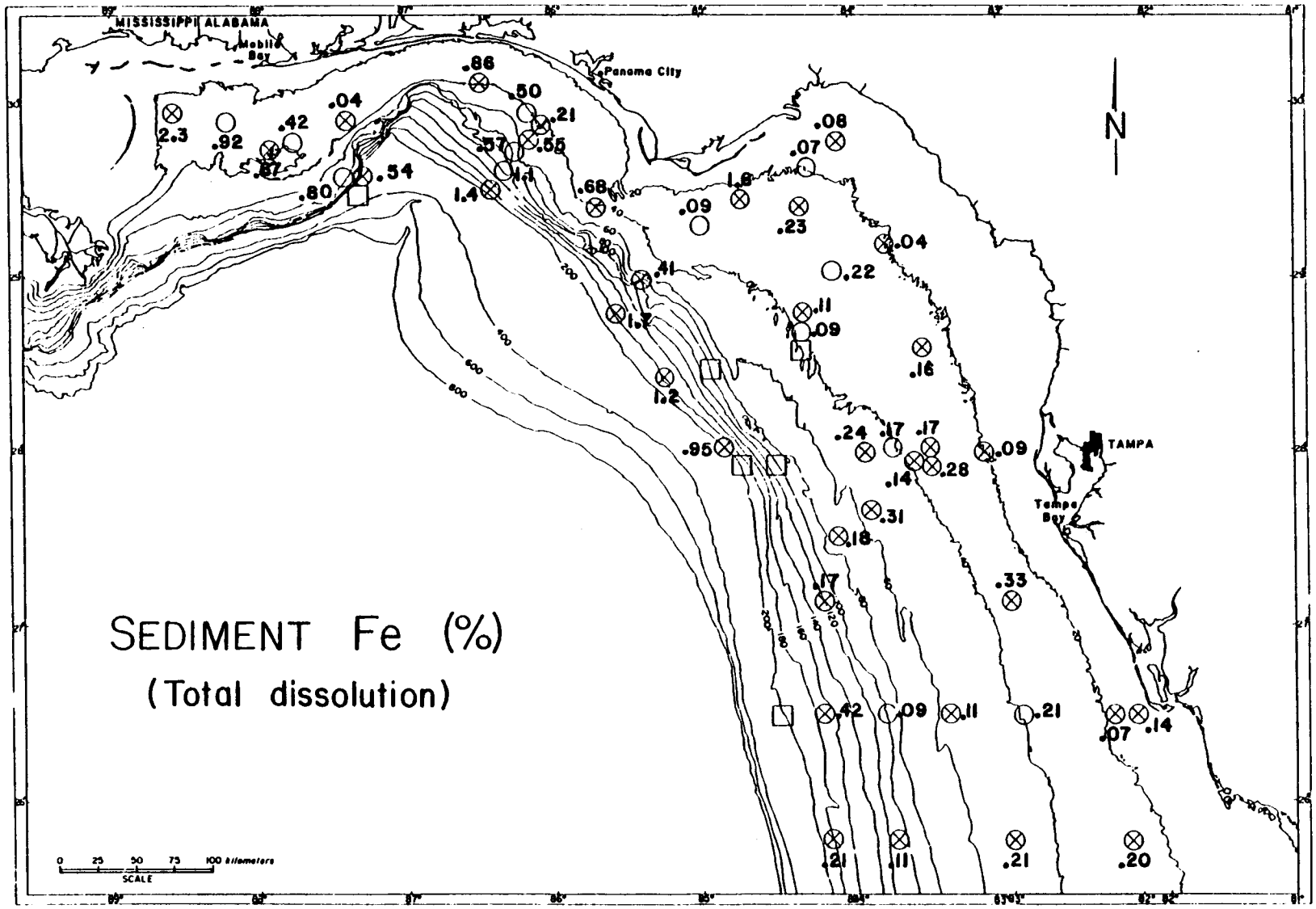

Figure 121 Geographic distribution of total Fe in MAFLA sediments.

TABLE 33

MAFLA SEDIMENT TRACE METAL SUMMARY
(1 N HNO_3 LEACH)

STATION N	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	ϕ	Sand Fine $CaCO_3$ (%) (%)
2101	0.04	3.5	0.45	700	0.6	1.1	1.2	3.0	8
9	(±0.005)	(±0.2)	(±0.02)	(±60)	(±0.1)	(±0.2)	(±0.3)	(±1.9)	45
2102	0.02	4.2	0.24	430	0.2	0.6	0.9	2.4	24
9	(±0.004)	(±0.6)	(±0.03)	(±110)	(±0.05)	(±0.2)	(±0.3)	(±1.3)	30
2103	0.04	9.1	0.39	1210	0.9	1.3	2.2	2.1	9
9	(±0.008)	(±1.4)	(±0.08)	(±200)	(±0.2)	(±0.2)	(±0.5)	(±1.9)	58
2104	0.09	9.4	0.44	680	1.5	1.0	2.5	1.7	9
9	(±0.01)	(±0.4)	(±0.05)	(±60)	(±0.3)	(±0.1)	(±0.7)	(±2.5)	97
2105	0.10	5.8	0.50	500	1.7	0.7	4.1	2.0	8
9	(±0.02)	(±0.4)	(±0.08)	(±120)	(±0.2)	(±0.2)	(±0.5)	(±2.6)	96
2106	0.18	7.5	0.95	1760	4.5	2.2	7.7	2.8	4
9	(±0.01)	(±0.3)	(±0.04)	(±80)	(±0.5)	(±0.2)	(±0.8)	(±2.5)	95
2207	0.11	4.3	0.29	326	0.3	0.9	1.4	2.9	11
9	(±0.01)	(±0.5)	(±0.05)	(±53)	(±0.2)	(±0.1)	(±0.4)	(±1.6)	48
2208	0.07	8.0	0.42	804	1.3	1.3	3.4	4.8	1
9	(±0.009)	(±1.1)	(±0.06)	(±340)	(±0.2)	(±0.3)	(±1.0)	(±2.3)	86
2209	0.08	8.6	0.47	830	1.4	1.3	3.0	4.2	2
9	(±0.005)	(±0.8)	(±0.04)	(±52)	(±0.2)	(±0.2)	(±0.4)	(±2.2)	87
2210	0.08	9.8	0.47	1250	1.6	1.5	3.8	3.6	2
9	(±0.007)	(±0.8)	(±0.07)	(±140)	(±0.2)	(±0.2)	(±0.6)	(±2.3)	89
2211	0.11	11.8	0.46	1450	1.7	1.5	4.2	1.4	5
9	(±0.01)	(±1.3)	(±0.14)	(±160)	(±0.3)	(±0.2)	(±1.4)	(±2.9)	95
2212	0.16	9.3	1.4	3080	4.9	2.8	15.0	4.1	2
9	(±0.02)	(±0.9)	(±0.13)	(±590)	(±0.6)	(±0.4)	(±2.5)	(±2.6)	90
2313	0.14	8.5	1.2	3110	4.7	3.0	14.3	4.8	1
8	(±0.009)	(±0.8)	(±0.08)	(±480)	(±0.2)	(±0.3)	(±1.6)	(±2.5)	85
2315	0.11	5.6	0.33	380	1.1	1.3	2.1	2.3	5
8	(±0.02)	(±1.6)	(±0.07)	(±170)	(±0.2)	(±0.2)	(±0.3)	(±3.8)	86
2316	0.04	4.7	0.36	378	0.5	1.2	1.5	2.4	8
8	(±0.01)	(±0.9)	(±0.07)	(±66)	(±0.3)	(±0.5)	(±0.6)	(±2.6)	63
2317	0.09	9.2	0.45	1320	1.0	2.1	2.2	3.4	4
8	(±0.008)	(±1.0)	(±0.06)	(±320)	(±0.4)	(±0.2)	(±0.7)	(±2.3)	84
2318	0.02	2.3	0.14	101	0.1	0.3	1.5	1.5	45
8	(±0.005)	(±0.3)	(±0.02)	(±36)	(±0)	(±0.1)	(±0.8)	(±1.2)	11
2419	0.05	3.1	0.19	468	0.1	1.1	2.5	1.8	33
8	(±0.007)	(±0.5)	(±0.05)	(±82)	(±0.04)	(±0.4)	(±0.7)	(±1.5)	41
2421	0.05	3.4	0.15	994	0.2	1.3	1.1	3.0	10
8	(±0.01)	(±1.4)	(±0.03)	(±180)	(±0.1)	(±1.3)	(±0.6)	(±1.5)	48
2423	0.07	10	0.77	10200	2.1	5.2	9.4	1.5	5
8	(±0.01)	(±1.1)	(±0.09)	(±2100)	(±0.5)	(±0.6)	(±2.6)	(±3.0)	72
2424	0.01	1.9	0.17	386	0.1	0.6	1.9	1.6	30
8	(±0.004)	(±0.2)	(±0.03)	(±73)	(±0)	(±0.1)	(±0.4)	(±1.3)	10

TABLE 33 (CONTINUED)

STATION N	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	ϕ	Sand/Fine $CaCO_3$ (%) (%)
2426	0.06	7.4	0.34	2470	0.9	1.5	4.5	1.8	20
8	(±0.02)	(±0.7)	(±0.08)	(±370)	(±0.2)	(±0.2)	(±1.7)	(±1.4)	38
2427	0.15	9.7	1.4	3560	4.9	3.5	15.9	4.8	0.9
8	(±0.01)	(±0.9)	(±0.1)	(±220)	(±0.4)	(±0.3)	(±5.4)	(±2.6)	78
2528	0.04	5.5	0.43	1470	0.52	1.5	2.6	0.5	20
6	(±0.004)	(±0.7)	(±0.12)	(±119)	(±0.37)	(±0.2)	(±0.5)	(±2.0)	52
2529	0.09	10.2	0.44	3900	1.4	2.3	3.8	0.5	34
8	(±0.02)	(±0.9)	(±0.07)	(±626)	(±0.27)	(±0.5)	(±0.5)	(±1.6)	70
2531	0.17	14.0	0.48	3500	1.8	2.9	6.7	0.6	21
8	±0.03)	(±1.2)	(±0.55)	(±908)	(±0.3)	(±0.2)	(±1.5)	(±1.7)	89
2533	0.16	17.2	0.49	3090	2.8	2.6	6.4	1.0	15
8	(±0.02)	(±3.8)	(±0.06)	(±332)	(±0.2)	(±0.4)	(±0.2)	(±1.9)	84
2535	0.11	9.9	2.0	3120	4.8	5.7	13	5.7	0.4
8	(±0.01)	(±1.0)	(±0.2)	(±293)	(±0.4)	(±0.8)	(±1.2)	(±2.2)	69
2536	0.14	9.4	2.6	3140	6.5	5.6	17	5.8	0.4
8	(±0.01)	(±0.4)	(±0.3)	(±157)	(±0.7)	(±0.8)	(±1.8)	(±2.5)	71
2638	0.04	4.2	3.9	5940	2.6	10.5	29.3	6.1	0.4
8	(±0.01)	(±0.9)	(±1.1)	(±1028)	(±0.5)	(±1.1)	(±4.0)	(±2.4)	17
2639	0.02	3.3	0.97	4220	1.3	6.0	12.3	3.2	6
8	(±0.005)	(±0.1)	(±0.14)	(±164)	(±0.2)	(±0.7)	(±0.6)	(±2.3)	19
2640	0.01	2.6	0.52	3800	0.78	2.9	8.4	1.1	21
8	(±0.005)	(±0.6)	(±0.17)	(±1346)	(±0.34)	(±0.9)	(±2.4)	(±1.9)	30
2641	0.02	1.8	0.51	954	0.13	2.3	6.1	2.6	18
8	(±0.005)	(±0.2)	(±0.07)	(±132)	(±0.07)	(±0.3)	(±0.8)	(±1.3)	6
2643	0.14	11.2	0.86	8040	3.7	6.2	16.4	1.3	10
8	(±0.01)	(±1.3)	(±0.16)	(±1341)	(±0.4)	(±0.4)	(±1.8)	(±2.0)	84
2645	0.14	6.9	1.5	5390	4.8	7.7	14.8	1.3	6
8	(±0.012)	(±0.4)	(±0.3)	(±544)	(±0.3)	(±1.2)	(±1.5)	(±2.9)	85
2746	0.16	7.9	0.88	1060	3.1	1.5	6.2	3.5	2
9	(±0.015)	(±0.6)	(±0.06)	(±86)	(±0.3)	(±0.2)	(±1.0)	(±2.7)	96
2747	0.13	15.1	0.50	1360	1.7	1.4	4.4	2.4	4
8	(±0.032)	(±2.4)	(±0.07)	(±163)	(±0.2)	(±0.2)	(±1.1)	(±2.6)	97
2748	0.10	12.6	0.39	2301	1.9	1.8	5.9	1.1	10
9	(±0.03)	(±2.5)	(±0.05)	(±275)	(±0.5)	(±0.2)	(±2.0)	(±2.1)	97
2957	0.26	4.2	1.2	920	4.6	1.7	7.0	2.8	4
8	(±0.03)	(±0.2)	(±0.04)	(±59)	(±0.5)	(±0.2)	(±1.1)	(±2.6)	96
2958	0.19	5.8	0.73	625	2.3	1.0	4.9	2.5	4
8	(±0.009)	(±0.5)	(±0.08)	(±29)	(±0.3)	(±0.1)	(±0.6)	(±2.7)	98
2959	0.09	9.8	0.53	1340	1.8	1.4	1.9	3.1	3
8	(±0.009)	(±1.0)	(±0.03)	(±192)	(±0.4)	(±0.2)	(±0.5)	(±2.6)	96
2960	0.03	19	0.31	1700	1.1	2.1	1.5	1.9	19
8	(±0.007)	(±2.4)	(±0.07)	(±66)	(±0.2)	(±0.1)	(±0.3)	(±1.4)	98

TABLE 34

RANGE OF TRACE METAL CONCENTRATIONS*
(1 HNO_3 LEACH) IN MAFLA SEDIMENTS

	MAXIMUM (STATION)		MINIMUM (STATION)	
Cd	0.26	(2957)	0.01	(2856)
Cr	19	(2960)	1.3	(2856)
Cu	3.9	(2638)	0.1	(2318)
Fe	8000	(2643)	100	(2318)
Ni	6.5	(2536)	>0.1	(2318, 2424, 2856)
Pb	10	(2639)	0.3	(2318)
Zn	29	(2638)	1	(2102)
	6.1	(2638)	0.5	(2528, 2529)
Sand/Fine	45	(2318)	0.4	(2535, 2536, 2638)
$CaCO_3$	98	(2958, 2960)	6	(2641)

*Concentration in ppm.

TABLE 35
SEDIMENT TRACE METAL DISTRIBUTIONS BY TRANSECT*

TRANSECT NO. OF SAMPLES	Cu	Cr	Cu	Fe	Ni	Pb	Zn
I	0.08	6.6	0.50	880	1.6	1.1	3.1
54	(±0.05)	(±2.4)	(±0.23)	(±480)	(±1.4)	(±0.5)	(±2.4)
	0.19	10.3	1.0	1960	5.5	2.4	8.9
	to	to	to	to	to	to	to
	0.02	3.2	0.19	270	0.2	0.3	0.5
II	0.10	8.6	0.60	1290	1.9	1.5	5.2
54	(±0.03)	(±2.5)	(±0.38)	(±930)	(±1.5)	(±0.6)	(±4.7)
	0.20	13.8	1.5	3880	5.6	3.4	17.7
	to	to	to	to	to	to	to
	0.06	3.9	0.21	270	<0.1	0.8	0.6
III	0.08	6.0	0.50	1060	1.5	1.6	4.6
40	(±0.05)	(±2.8)	(±0.38)	(±1150)	(±1.7)	(±1.0)	(±5.3)
	0.15	10.1	1.3	3620	5.0	3.4	16.5
	to	to	to	to	to	to	to
	0.01	2.0	0.11	60	<0.1	0.2	0.3
IV	0.07	6.0	0.53	3010	1.4	2.2	6.2
48	(±0.05)	(±3.3)	(±0.44)	(±3540)	(±1.8)	(±1.7)	(±5.9)
	0.16	11.6	1.7	13100	5.7	6.5	19.5
	to	to	to	to	to	to	to
	<0.01)	1.6	0.11	250	<0.1	0.4	0.6
V	0.12	10.9	1.0	3090	3.0	3.4	8.2
48	(±0.05)	(±4.0)	(±0.9)	(±890)	(±2.1)	(±1.7)	(±5.3)
	0.20	20.4	3.0	4710	7.0	7.0	19.4
	to	to	to	to	to	to	to
	0.03	4.4	0.22	1300	0.2	1.2	1.7
VI	0.06	5.0	1.4	4720	2.2	5.9	14.5
48	(±0.06)	(±3.3)	(±1.2)	(±2360)	(±1.7)	(±2.9)	(±7.8)
	0.16	13.0	5.5	9670	5.2	11.4	34.6
	to	to	to	to	to	to	to
	<0.01	1.6	0.27	860	<0.1	1.4	4.4
VII	0.13	11.8	0.59	1580	2.2	1.6	5.5
27	(±0.04)	(±3.6)	(±0.22)	(±580)	(±0.8)	(±0.2)	(±1.6)
	0.20	18.3	0.99	2790	3.9	2.0	7.6
	to	to	to	to	to	to	to
	0.04	7.4	0.33	950	1.0	1.2	2.5
VIII	0.05	6.9	0.34	1810	1.0	1.7	3.0
12	(±0.04)	(±4.2)	(±0.18)	(±2060)	(±0.7)	(±1.2)	(±1.7)
	0.12	11.6	0.66	6720	2.3	4.2	5.8
	to	to	to	to	to	to	to
	0.01	1.0	0.12	120	<0.1	0.2	0.3
IX	0.14	9.7	0.69	1150	2.4	1.6	3.9
32	(±0.09)	(±6.0)	(±0.33)	(±430)	(±1.4)	(±0.4)	(±2.4)
	0.29	21.7	1.2	1820	5.2	2.3	8.5
	to	to	to	to	to	to	to
	0.02	3.9	0.25	590	0.8	0.8	1.1

*Given as mean, standard deviation and range, all concentrations in ppm

metal concentrations (Table 34) are again found in the non-carbonate sands of Stations 2102, 2318, 2424, 2641, 2855 and 2856. In general, significantly less than half the total metal content was removed by 1 N HNO_3 from these chemically more resistant sediments. Maximum values (Table 34) for Cu, Pb and Zn at Station 2638, Cd at 2957, and Ni at 2536 are consistent with previously reported totals data (Table 30). The Cr maximum at Station 2960 results from ~80% leaching of this predominantly carbonate sample compared with less than 10% Cr removal from clay-rich Station 2638 sediment. A similar behavior is observed for Fe where ~60% of the total is leached from Station 2643 sediment and only 20-30% of the total is removed from higher iron-containing sediments at 2536 and 2638. These differences in percent removal are considered later in more detail.

Table 33 also gives a good review of the "in station" variability for 8 or 9 separate box cores taken during 3 to 4 different time periods. An average of 10% or less variability; i.e., (standard deviation/mean) X 100, for the seven elements studied was found at 15 of the MAFLA sediment stations (2101, 2104, 2106, 2209, 2313, 2427, 2533, 2535, 2536, 2639, 2643, 2645, 2746, 2957, and 2958). This low variability is in line with the analytical precision and thus no significatn seasonal or sampling artifacts can be discerned. These stations are predominantly from the outer shelf with a mean grain size of 3.2 phi relative to 2.3 for the remaining sites. Metal concentrations are also higher at those 15 stations, and thus, they are less affected by the poorer precision sometimes obtained with lower metal concentrations. With two exceptions (2421 and 2640) the remainder of the stations had concentration variations in the 10 to 20% range. At the 20% range, the explained variation is at the 95% confidence level for the standard deviations of the experimental precision. Frequently within the 10 to 20% variability population, one season will have a complete set of significantly higher or lower metal concentrations, indicative of differences in the sample collected and/or the effectiveness and variability of the 1 N HNO_3 leach. Furthermore no obvious station or seasonal trend for these larger variations is found. Although such deviations are somewhat disconcerting, the generally low metal levels and inherent sample inhomogeneity downplay this concern.

The important point in the above discussion concerns our ability to return to a given site at some later time and to quantitatively identify any perturbation in the sediment trace metal concentrations. From the data presented here, deviations from 1σ of the analytical precisions are significant at 15 sites and differences greater 2σ are meaningful at the remaining stations. This method of discerning changes is not overly satisfactory and another technique will be introduced presently. However, even at 2σ variations, the absolute concentration change is relatively small. For example, sediment with 3 ppm Cr would be considered deviant above 3.6 ppm and below 2.4 ppm. Such subtle variations would signal problems quickly since the ambient metal levels are so low.

Geographical distribution of the partial sediment metal data by transect (Table 35) re-emphasizes the highly diverse character of the MAFLA sediments. Transect VI, located off the Mississippi-Alabama coast in closest proximity to the Mississippi Delta, has the highest average concentrations of leachable Cu, Fe, Pb and Zn. This observation is a function of

the greater abundance of metal-bearing aluminosilicates in this region and is noted despite the low percent metal removal from these sediments with 1 N HNO_3. Two exceptions to this trend are the previously discussed high Cd values of Transect IX and the high Cr levels for Transect VII. Sediments from Transects VIII and I share the lowest metal averages by transect with the remarkable exception of very low leachable Cr for Transect VI.

A large range in metal values is also observed within each transect (Table 35) with the exception of the offshore VII group. Low values are generally found nearshore with the non-carbonate sands, and higher values are found seaward with the higher clay content samples. This variability stresses the importance of water depth to depositional environment and hence trace metal content.

With both total and partial sediment metal values for MAFLA 77/78, a third data set of "percent metal leached" may be created. Table 36 summarizes the means, standard deviations and range of percent removal found for each metal. The overall (7 element) removal was high at about 60% and is directly related to the high $CaCO_3$ content of the MAFLA sediments. Near-complete metal removal was obtained from the carbonate-rich (clay-poor, quartz-poor) sediments of the central shelf areas. Conversely, lower percent removal was generally found for very nearshore non-carbonate sands and outer shelf clay-containing samples.

Figure 122 depicts the percent removal trend discussed above. The figure was developed by setting boundaries at the extremes of percent removal (based on determined standard deviations, Table 36) for each element (Cd, $\leq\overline{50}$ and $\geq\overline{95}$%; Cr, $\leq\overline{40}$ and $\geq\overline{85}$; Cu, $\leq\overline{30}$ and $\geq\overline{60}$; Fe, $\leq\overline{35}$ and $\geq\overline{70}$; Ni, $\leq\overline{30}$ and $\geq\overline{75}$; Pb, $\leq\overline{50}$ and $\geq\overline{90}$; Zn, $\leq\overline{40}$ and $\geq\overline{75}$) and identifying those stations with values exceeding the chosen limits. Then, all stations with three or more exceptional values were marked on Figure 122, those with low percent removal with a black dot, those with high percent removal with a black triangle. The resultant trend (Figure 122) nicely points out the areas of low and high percent removal alluded to above. Further detail may be extracted from Figure 122 where the percent Fe removal at each station is also given. Iron data show the trend of lower percent removal in nearshore and outer shelf areas with a high leachable fraction in the more homogeneously carbonate sediments of the central shelf.

Statistical evaluation of the MAFLA trace metal data confirms most of the previously discussed trends and adds several new insights. Prior to mathematical treatment, data for each metal were normalized to a 0 to 1 range by:

$$x_i' = x_i/(x_i)_{max} \qquad (1)$$

where x_i' = normalized value

x_i = original metal concentration

$(x_i)_{max}$ = maximum value for a given metal.

TABLE 36

SUMMARY OF PERCENT OF TOTAL SEDIMENT METAL REMOVED WITH 1 N HNO_3

	MEAN ± STD. DEV. (%)	MAXIMUM (%) (STATION NO.)	MINIMUM (%) (STATION NO.)
Cd	76 ± 22	108	17
		(2313)	(2424, 2640)
Cr	62 ± 20	98	9
		(2747)	(2638)
Cu	45 ± 13	89	22
		(2528)	(2427)
Fe	53 ± 17	85	21
		(2317)	(2212)
Ni	53 ± 19	90	12
		(2210)	(2741)
Pb	70 ± 19	107	18
		(2528)	(2856)
Zn	58 ± 18	104	10
		(2421)	(2856)

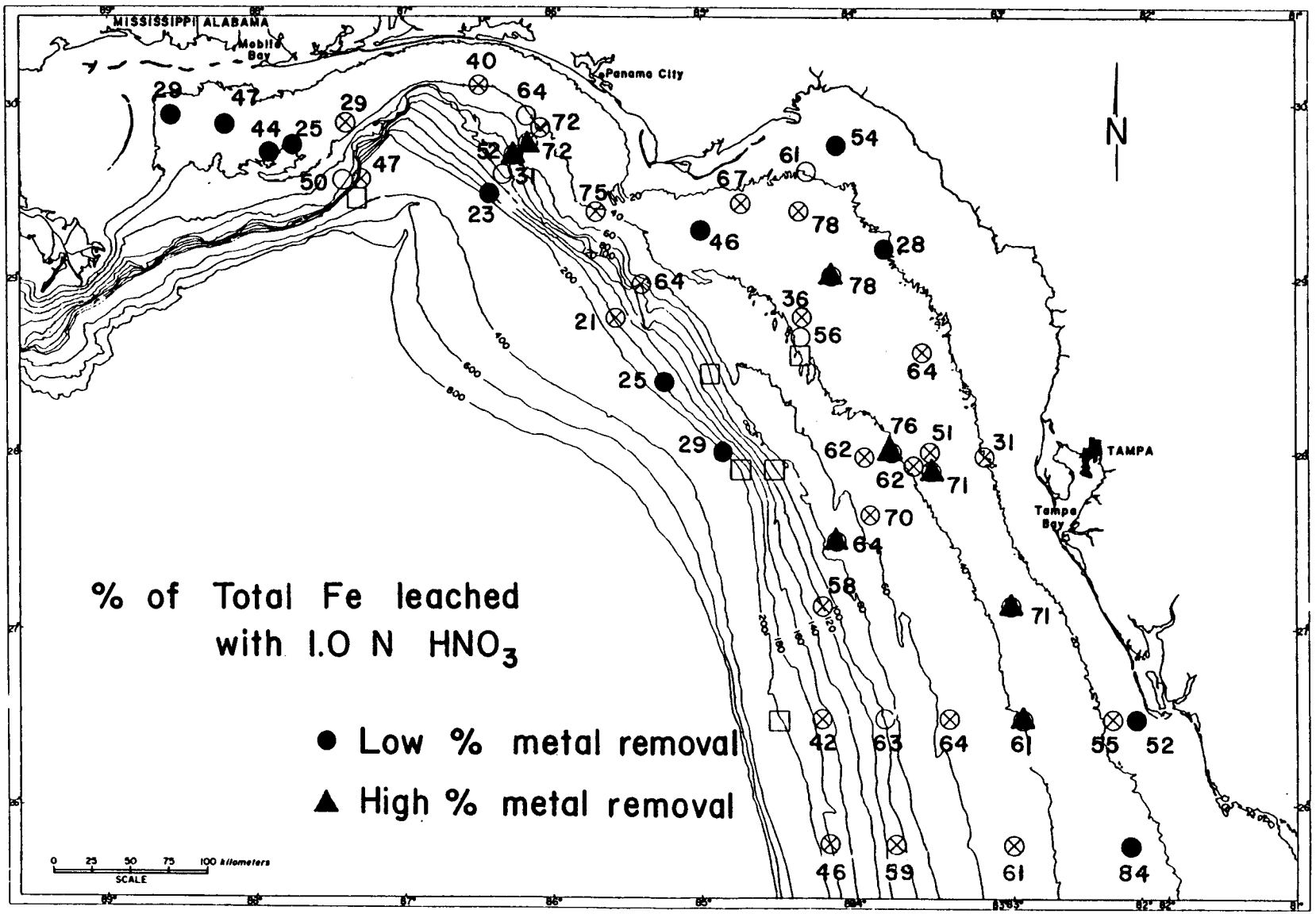

Figure 122 Regional trends for leachable Fe (and other metals) in MAFLA sediments.

This transformation equalizes the wide range in concentrations among metals (e.g., Fe_{max} = 13,000 ppm and Cd_{max} = 0.3 ppm) and thereby minimizes bias in resultant statistical calculations.

Initial data processing was carried out for just the 29 primary sediment stations. Table 37 gives the similarity matrix (Bray-Curtis Index) for the partial sediment trace metal data. The matrix shows the general interrelationship of leachable trace metals with Fe and each other. A significant covariance of metals with total organic carbon is also observed where as fine grained particle data (<16 μm in this instance) is less compatible since it includes both the carbonate and non-carbonate fractions. Barium behavior is somewhat contrary to the other metals with a high $CaCO_3$ similarity and a low TOC, Fe and <16 μm particle similarity. This occurs because the leachable Ba concentrations are surprisingly uniform despite large variations in total Ba and has interesting implications regarding the composition and distribution of leachable Ba (see Shokes, Volume II, Chapter 4).

Using principal components analysis (PCA), the leachable TM data were further evaluated. Figure 123 gives the Q-mode Wisconsin ordination (Bray-Curtis Index) with PC I plotted versus PC II for each of the 29 primary stations. The stations were initially divided along the sharp black line into two populations and subsequently groups into five smaller clusters. Each of the primary stations was then coded accordingly on Figure 124. Groups D and E clearly define the outer-shelf, finer-grained, higher metal-containing sediments. Groups A and B distinguish the non-carbonate sands and low metal-bearing sediments of nearshore areas (with the exception of borderline stations 2208, 2209 and 2104). Finally, Group C encompasses the $CaCO_3$-rich, metal-poor sediments of the central MAFLA shelf. This depiction of MAFLA sediment trace metal distribution is compatible with that presented in Figure 122.

Metal versus Fe scatter plots have previously been used to identify the "background" or "natural trends for the northwest Gulf of Mexico (Trefry and Presley, 1976a) and the MAFLA area (Presley et al., 1976). Figure 125 shows that the (total Zn)/(total Fe) relationship throughout the MAFLA area is quite good and serves as a useful predictor of "natural" Zn levels at a given site. Interestingly, the Zn/Fe slope of 20 x 10^{-4} for the entire MAFLA area is reasonably close to the value of 26 x 10^{-4} obtained by Trefry and Presley (1976b) for Mississippi Delta sediments. Variations in Zn concentration as estimated from Fe values in Figure 125 are <10 ppm at the 95% confidence level. This implies that a sediment sample from the MAFLA area which is analyzed for Fe may be used to predict the "natural" Zn concentration. Deviations from the prediction interval would then support an anthropogenic Zn source.

Metals other than Zn in the MAFLA region previously have been referenced to Fe (Presley et al., 1976) and the agreement between that work and the present is generally acceptable. Slope comparisons (x 10^{-4}) are as follows:

Cu, 3.8 (1976), 3.0 (1978); Pb, 4.3 (1976), 4.4 (1978); and Ni, 7.5 (1976), 5.7 (1978). Previous Cd data (1976) were predominantly below the detection limit encountered at that time.

TABLE 37

SIMILARITY MATRIX FOR TRACE METALS IN 1 N HNO_3 LEACH OF MAFLA SEDIMENTS

	Ba	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn	<16 m[1]	$CaCO_3$	TOC[2]
Ba	1.00											
Cd	0.66	1.00										
Cr	0.67	0.75	1.00									
Cu	-	-	-	1.00								
Fe	-	0.66	0.65	0.71	1.00							
Ni	0.65	0.79	0.64	0.62	0.70	1.00						
Pb	-	-	-	0.85	0.78	0.64	1.00					
V	0.60	0.70	0.74	0.68	0.76	0.69	0.74	1.00				
Zn	-	0.61	-	0.84	0.78	0.70	0.83	-	1.00			
<16 m	-	-	-	0.83	0.61	-	0.72	-	0.77	1.00		
$CaCO_3$	0.86	0.67	0.74	-	-	-	-	-	-	-	1.00	
TOC	-	0.68	0.67	0.75	0.69	0.70	0.71	0.75	0.77	-	-	1.00

[1]Grain-size fraction

[2]TOC = total organic carbon

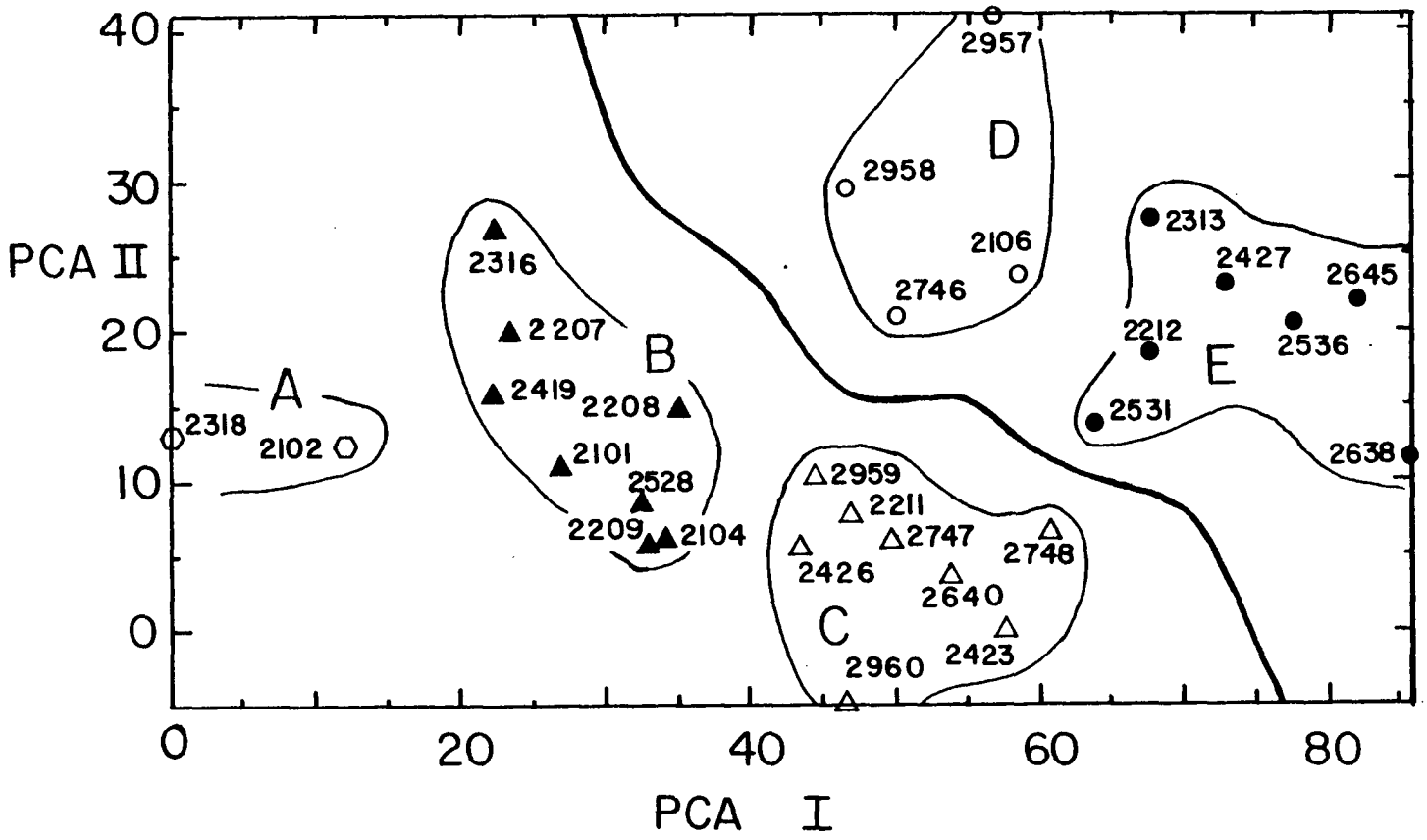

Figure 123 Ordination of MAFLA sites based on principal components analysis (PCA) of sediment trace metal data.

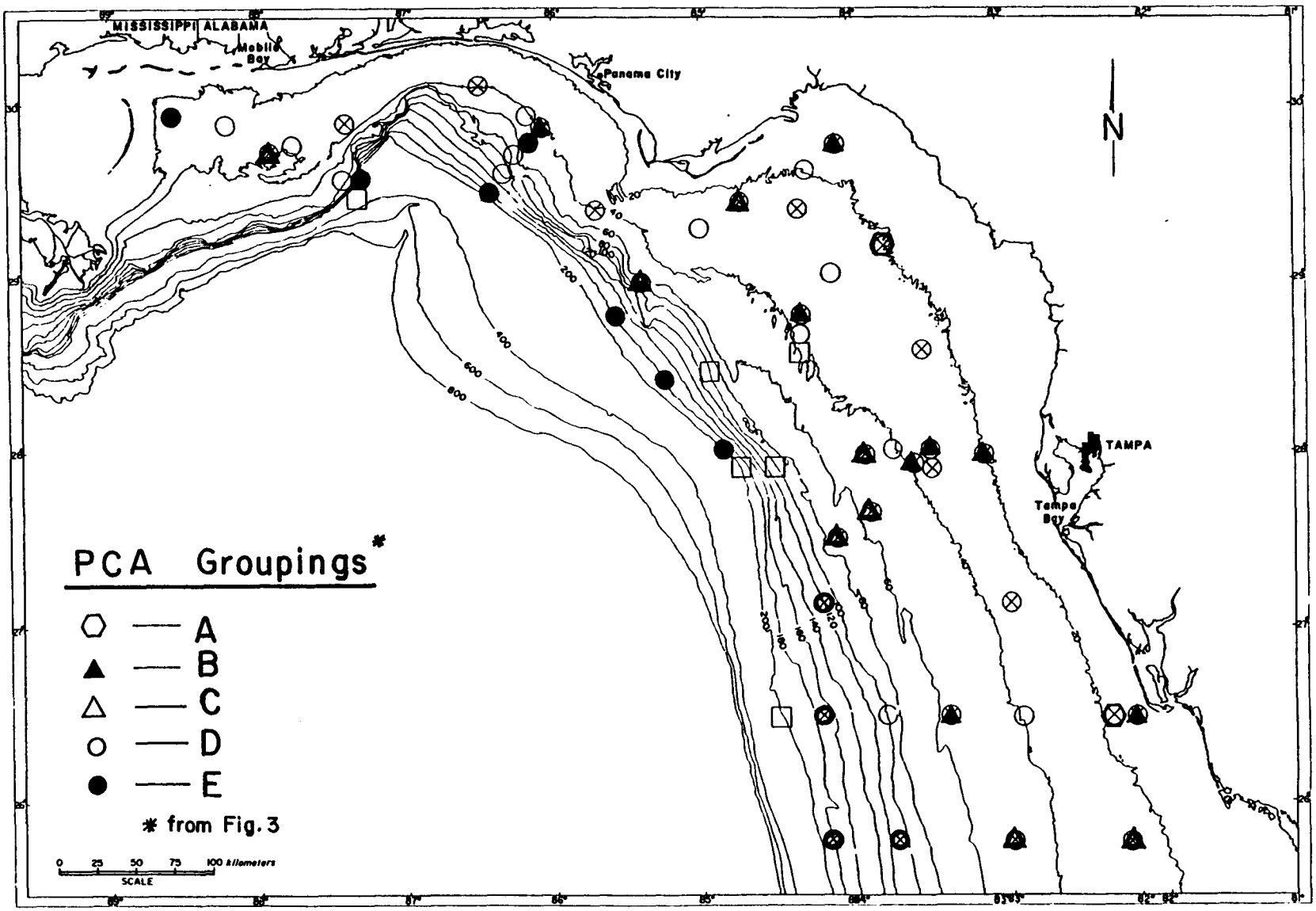

Figure 124 Geographic distribution of principal components analysis groups for MAFLA sediments.

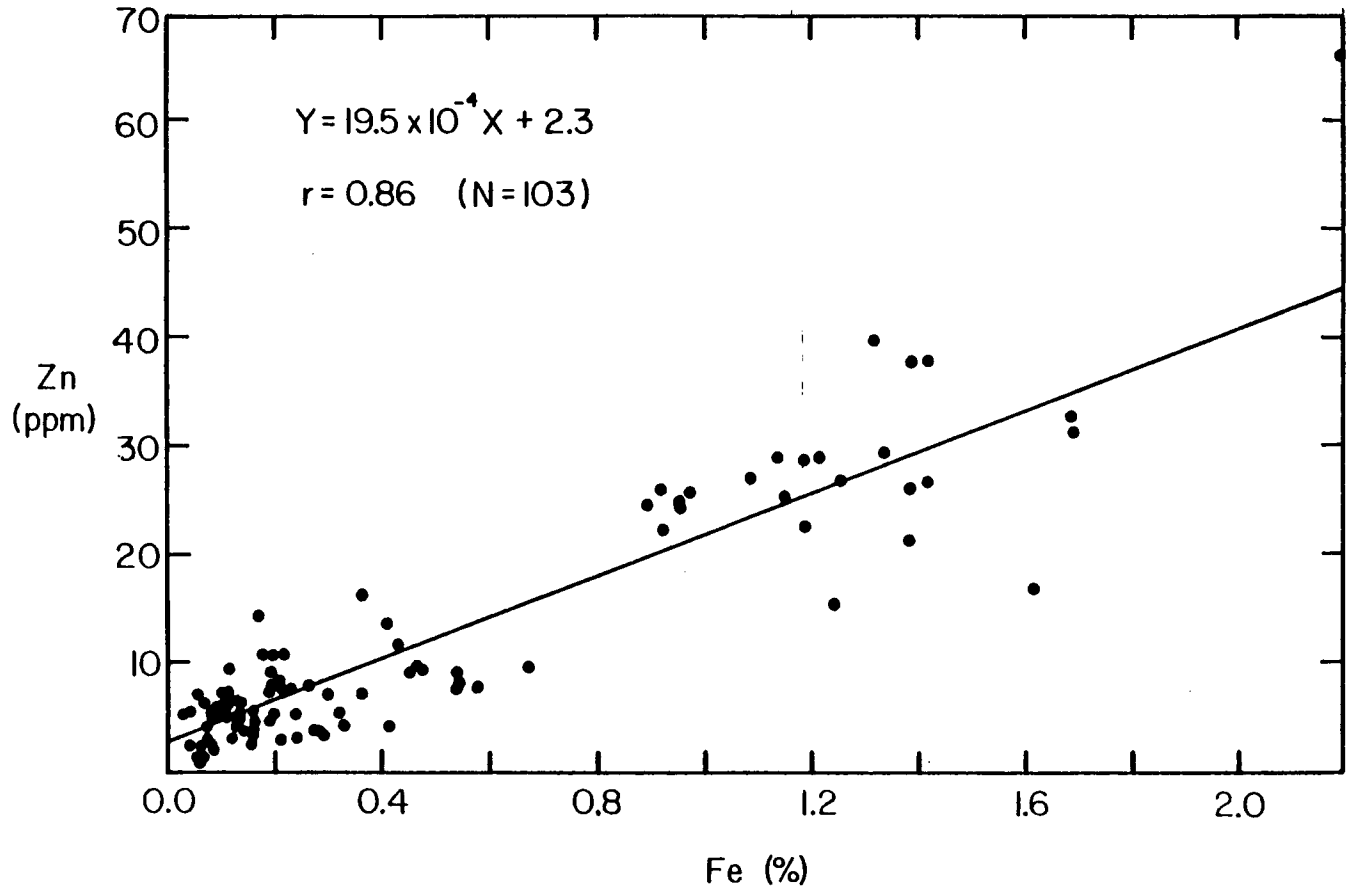

Figure 125 Zn vs Fe scatter plot (total concentrations) for MAFLA sediments.

Figure 126 uses the Metal/Fe relationship to consider leachable Pb and Fe concentrations. Note in this instance that the slope (7.9×10^{-4}) is almost double that found for total concentration. Lead, then, is removed at twice the level of Fe by 1 N HNO_3. For Cu, the leachable and total concentrations plotted versus Fe gave almost identical slopes of 3.2 and 3.0. Yet, for leachable Ni, two distinct trends appeared in the scatter plots, one for the higher concentration outer shelf sites and a second for the remaining lower Ni content sediments. Overall scatter in the leachable metal/Fe plots renders them less ueful for predicting metal concentrations at a given site, yet helps delineate relative removal percentages.

CONCLUSIONS

The distribution of total and 1 N HNO_3 leachable trace metals in MAFLA sediments has been diligently and extensively evaluated. Metal levels are, on the whole, lower than those expected for unpolluted sediments of similar mineralogical composition. Variations in metal concentrations within the MAFLA area are well explained by sediment composition. Highest sediment metal content occurs in the finer-grained sediments of the Mississippi Delta and outer shelf areas, whereas low values are found in shallow water, nearshore sediments and in the $CaCO_3$-rich sediments of the West Florida shelf.

Further delineation of the metal-poor sediments shows the nearshore, non-carbonate sands to have three to five times lower concentrations than the central shelf carbonates. Two instances of elevated metal levels were found. Cadmium levels are high in the vicinity of Station 2957 on the outer shelf of the southern transect and Pb concentration are enriched near the Mississippi Delta. The former observation is presented as a natural occurrence resulting from significant biological input whereas the latter is directly related to high Pb inputs by the Mississippi River (Trefry and Presley, 1976a,b).

Study of "in station" variability shows that with two exceptions (2421 and 2640) the observed metal concentrations generally varied by less than twice the analytical precision.

Sediment leaching with 1 N HNO_3 showed that, overall, 60% of the total metal load was removed. Near-complete removal was obtained from the carbonate-rich (clay-poor, quartz-poor) sediments of central shelf areas. Conversely, lower percent removal was generally found for very nearshore, non-carbonate sands and outer shelf, clay containing samples.

Metal versus Fe scatter plots were again used to identify natural metal levels in this diverse MAFLA area. Although the area now has no signs of significant metal pollution, the very low metal levels encountered can be easily perturbed. If pollutant metals are forced to associate with $CaCO_3$ particles (which may well be the case in much of the area) they will be readily available to the biota. These low levels thus present a real, but resolvable dilemma. The low metal concentrations will be easily perturbed by pollutant input from increased activity in the MAFLA area, yet the low levels and good data base now available allow quick detection of these perturbations before they become a problem.

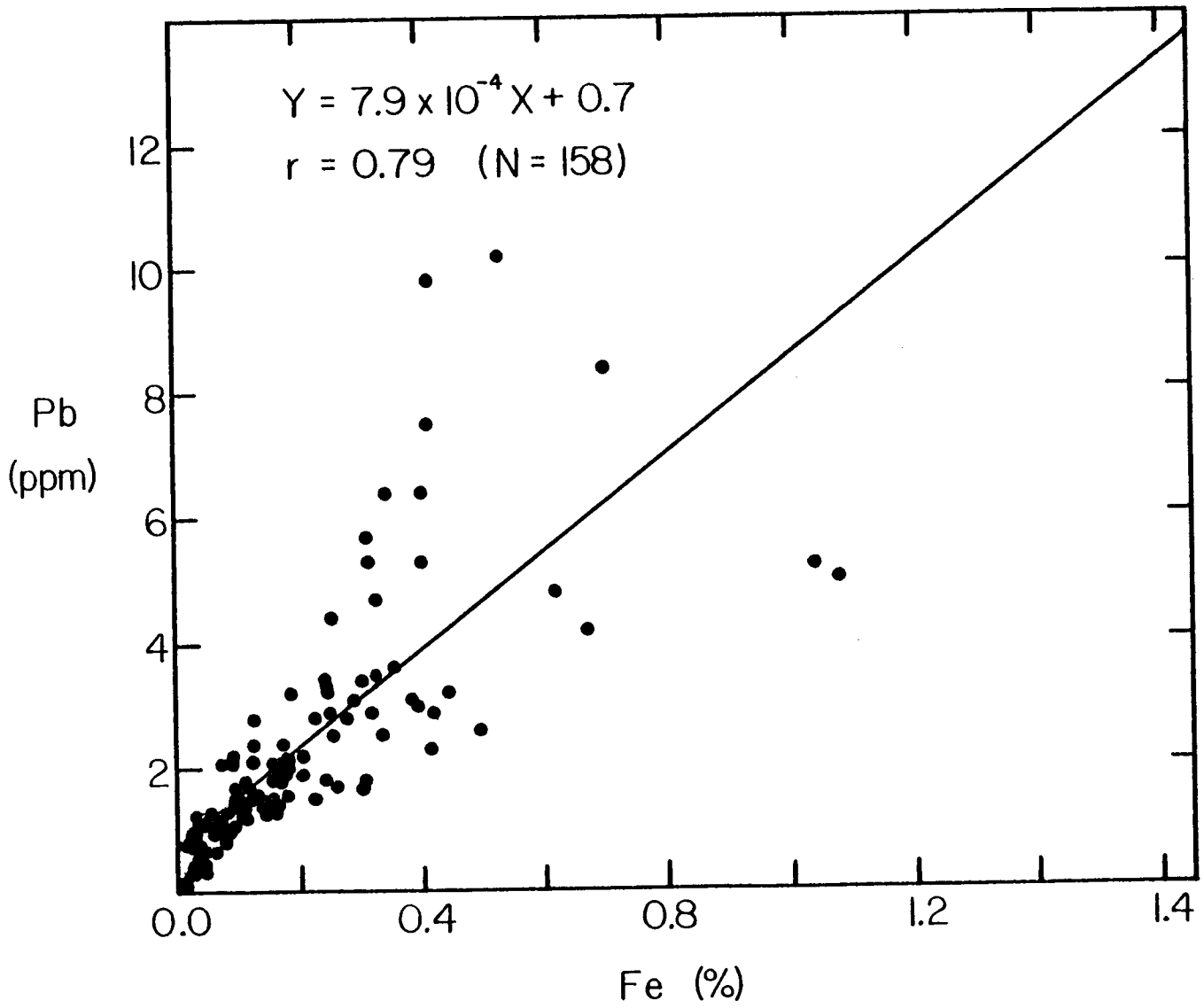

Figure 126 Pb vs Fe scatter plot (leachable concentrations) for MAFLA sediments.

REFERENCES

Bernard, E.A., 1973. Comparative biochemistry and physiology of digestion. In Prosser, C.L., ed., Comparative Animal Physiology, pp. 138-139.

Carmody, D.J., J.B. Pearce, and W.E. Yasso, 1973. Trace metals in sediments of New York Bight. Mar. Poll. Bull. 4:132-135.

Graf, D.L., 1960. Geochemistry of carbonate sediments and sedimentary carbonate rocks, Part III, Minor element distribution, Ill. Geol. Surv. Circ. 301, 71 p.

Hann, R.W., Jr., and J.F. Slowey, 1972. Sediment analysis - Galveston Bay, Env. Eng. Div. Texas A&M Univ. Tech. Rept. 24, 57 p.

Holmes, C.W., 1973. Distribution of selected elements in surficial marine sediments of the northern Gulf of Mexico continental shelf and slope, U.S. Geol. Surv. Prof. Paper 814, 7 p.

Holmes, C.W., E.A. Slade, and C.J. McLerran, 1974. Migration and redistribution of zinc and cadmium in marine estuarine system, Environ. Sci. Technol. 8:255-259.

Kobayashi, J., 1970. Relation between the "itai-itai" disease and the pollution of river water by cadmium from a mine, In Jenkins, S.H., ed., Adv. Water. Poll. Res. Proc. Int. Cong., San Francisco - Hawaii, 5th, Pergamon, Oxford, p. 25/1-8.

Malo, B., 1977. Partial extraction of metals from aquatic sediments, Environ. Sci. Technol. 11:277-281.

Martin, J.H., K.W. Bruland, and W.W. Broenkow, 1976. Cadmium transport in the California Current. In Windom, H.L., and R.A. Duce, eds., Marine Pollutant Transfer, D.C. Health and Co., Lexington, Mass., p. 159-184.

Patterson, C.C., 1965. Contaminated and natural lead environments of man, Arch. Environ. Health, 11:344-360.

Presley, B.J., C.W. Lindau, and J.H. Trefry, 1975. Sediment trace and heavy metal concentrations, In Final Report on the Baseline Environmental Survey of the MAFLA Lease Areas CY 1974, BLM Contract No. 08550-CT4-11, Vol. 3.

Presley, B.J., M.C. Dobson., R.F. Shokes., and J.H. Trefry, 1976. Heavy metal analyses of bottom sediment of the West Florida Shelf, In Final Report on Environmental Survey of MAFLA Lease Areas CY 1975.

Skei., J.M. N.B. Price, S.E. Calvert, and H. Holtedahl, 1972. The distribution of heavy metals in sediments of Serfjord, West Norway: Water, Air, Soil Pollut., L:452-461.

Taylor, S.R., 1964. Abundance of chemical elements in the continental crust: a new table, Geochim. Cosmochim. Acta. 28:1273-1285.

Trefry, J.H., and B.J. Presley, 1976a. Heavy metals in sediments from San Antonio Bay and the northwest Gulf of Mexico, Environ. Geol. 1:283-294.

Trefry, J.H., and B.J. Presley, 1976b. Heavy metal transport from the Mississippi River to the Gulf of Mexico. In Windom, H.L., and R.A. Duce, eds., Marine Pollutant Transfer, D.C. Heath, p. 39-76.

Turekian, K.K., and K.H. Wedepohl, 1961. Distribution of the elements in some major units of the earth's crust, Geol. Soc. Am. Bull. 72:175-192.

Yen, T.F., 1975. The Role of Trace Metals in Petroleum, Ann Arbor Sci. Pub. 221 p.

VOLUME II

CHAPTER 4

BENTHIC SEDIMENT BARIUM AND VANADIUM

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CHAPTER 4

BARIUM AND VANADIUM IN SURFICIAL SEDIMENTS

MAFLA BENCHMARK SURVEY, 1977-1978

FINAL REPORT

Robert F. Shokes (Co-Principal Investigator)
Nicholas Hansen
Adel Abusamara
John Reed (Co-Principal Investigator)

Science Applications, Inc.

La Jolla, California

September 11, 1978

Contract No. AA550-CT7-34

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ABSTRACT

For the first time in the four years of baseline survey in the MAFLA outer continental shelf, reliable concentration data for total and leachable (1 N HNO_3) sedimentary barium and vanadium have been obtained. In general, these two elements are distributed over the MAFLA geographical area as a result of the natural geochemical controls which supply and transport metals (and other materials) to the sea floor. On the areal scale surveyed in this program, no anthropogenic influences on the distribution of these two elements are apparent.

Vanadium trends coherently with the other transition metals assayed for in this program. The most striking trend is the contrast between the clay-rich, Mississippi River-derived sediments (high in vanadium) off Mobile and the carbonate-rich, biogenic sediments (low in vanadium) off the west coast of Florida. Except for a narrow band of almost pure quartz sediments (very low in vanadium) near-shore off the northwest Florida coast, these two sedimentary regimes act as end-members with other locations within the MAFLA area representing either variations or mixtures.

Barium is in general most closely related to sedimentary calcium carbonate content and, in contrast to vanadium and the other transition metals, shows no particular coherence to sediment grain size. Confounding this generalization, however, is that clay minerals which dominate in the western MAFLA sedimentary end-member are barium-enriched and carbonate depleted. The remarkably constant and low amounts of leachable barium found over the MAFLA area make it a potentially sensitive monitoring tool in future efforts to safeguard the marine environment from pervasive chemical insults during oil and gas production on the continental shelf.

INTRODUCTION

Of all the geochemical endeavors making up the MAFLA Baseline Studies since its beginning in 1973, the analysis of surficial benthic sediments for their trace heavy metal contents has yielded the most reliable and accurate description of ambient, pre-development conditions. This success has been due to two significant distinctions: (1) the distributions of metals in marine sediments are relatively independent of variation with time, regardless of the scale (especially true in environments which are relatively "pristine," which the MAFLA area has proven to be) and (2) the collection and analyses procedures utilized for sedimentary trace metals have not been plagued by the major problems of reliability, reproducibility and sensitivity characterizing to varying degrees the measurement of metal levels in other materials and of hydrocarbons in general.

With regard to this last claim, however, the determination of concentrations of barium, and vanadium to some degree, has been less successful than that of the other metals traditionally analyzed for the MAFLA program (cadmium, chromium, copper, iron, lead, manganese, zinc; Chapter 3). Because of the recognized insensitivity of atomic absorption spectrophotometry for barium and vanadium, these two elements have been determined by instrumental neutron activation analysis. However, because of the extremely low concentrations of these two elements in all but a few MAFLA area sediments, often magnified by the tremendous matrix interferences caused by the typically high calcium carbonate contents, the quantification of barium especially has been less than successful prior to the work reported herein (the 1977/78 study). Improved neutron activation techniques have finally enabled us to determine barium as low as the sub-ppm level, where previously the methodological detections limits were, at best, in the 30 to 50 ppm range.

In this Section, the results of measuring surficial sediment concentrations of barium and vanadium by neutron activation analysis are presented. Reference should be made to the discussion of other metals' distributions and sediment trace metal chemistry in general by Trefry in Chapter 3.

METHODS AND MATERIALS

The neutron activation analysis techniques utilized in this study are detailed in Shokes and Reed third quarterly MAFLA report, January 15-May 15, 1978, in Dames & Moore 1978e. The sediments subjected to partial digestion were analyzed for Ba with the Ba-139 procedure; the totally digested samples were analyzed using the Ba-131 (INAA) procedure. Vanadium was determined using the V-52 (INAA) analysis procedure. The method consists essentially of irradiating the samples for varying time periods in a Torga type reactor at the University of California, Irvine, and measuring activity levels with a spectrometer after given periods of time.

RESULTS AND DISCUSSIONS

Appendix 4-1 contains the seasonal station means of leachable and total barium and vanadium contents, as well as those for iron (from

Chapter 3) and grand station means of calcium carbonate, percent fines (silt plus clay; $\leq$ 62 μm) and total organic carbon. Figure 127 contains the sediment sampling station numbers and locations. Prior to the 1977/78 MAFLA study, sediments had been analyzed for total content of each metal. The addition of analyzing the amount of metal leachable with acid (in this case, 1 N HNO_3) was done to provide an indication of how much of a sediments metal content was particulate surface related. This interest stemmed from the expectation that any alterations in metal concentrations would be manifest in surface phases and also from the understanding that any metals (at natural levels or not) associated with particulate surfaces are more readily available to be cycled through the food chain than those imbedded in mineral matrices.

As can be quickly seen in Appendix 4-1, real seasonal variability in sedimentary metals is not apparent. What variations exist at some stations among seasons are almost totally related to sedimentary inhomogenieties which can be relatively large over a small geographical area, especially when course-grained quartz and carbonate materials dominate. Table 38 condenses Appendix 4-1 by presenting grand station means for the same parameters along with the variation among seasons as 1σ) and the mean leachable fraction (in percent).

It has been concluded (Presley et al., 1976) that no apparent alterations have been made to the metal burdens of MAFLA outer continental shelf sediments. Indeed, from the extensive set of metal data accumulated to this point, it can be said that trace heavy metal distributions throughout the MAFLA lease area are mineralogically controlled, reflecting the sources, the residence times in the water column and the depositional environments of the particles composing the sea bed.

The most quantitative mineralogical parameters available and, therefore, the ones we generally consider to be controlling the association of metals with sediments, are calcium carbonate and organic carbon contents along with the various parameters indicating particle grain size. In general, biogenic carbonate-rich sediments, which are common on the Florida shelf, are impoverished in heavy metals relative to the terrigenous (land-derived) clay minerals restricted to the northwest corner of the MAFLA area. Also, carbonate sediments tend to be more coarse than those of predominantly clay mineral composition and, with a less favorable surface area-to-volume ratio, are not as efficient at incorporating metals via surface-associated phenomena. Adding to this metal content bias is the trend toward higher organic carbon content with decreasing grain size, association with organic matter (e.g., through complexation) being another mechanism for imcorporation of metals into sediments.

The MAFLA lease area can be divided into several sedimentary provinces based upon the parameters just discussed. It can be shown that the distributions of trace metals (including barium and vanadium) can be explained with very little discrepancy by the segregation of these areas. It should be noted that barium is not a transition element as are the others analyzed on this program, and being a large Group II element it should exhibit a geochemical nature more coherent with that of calcium. The

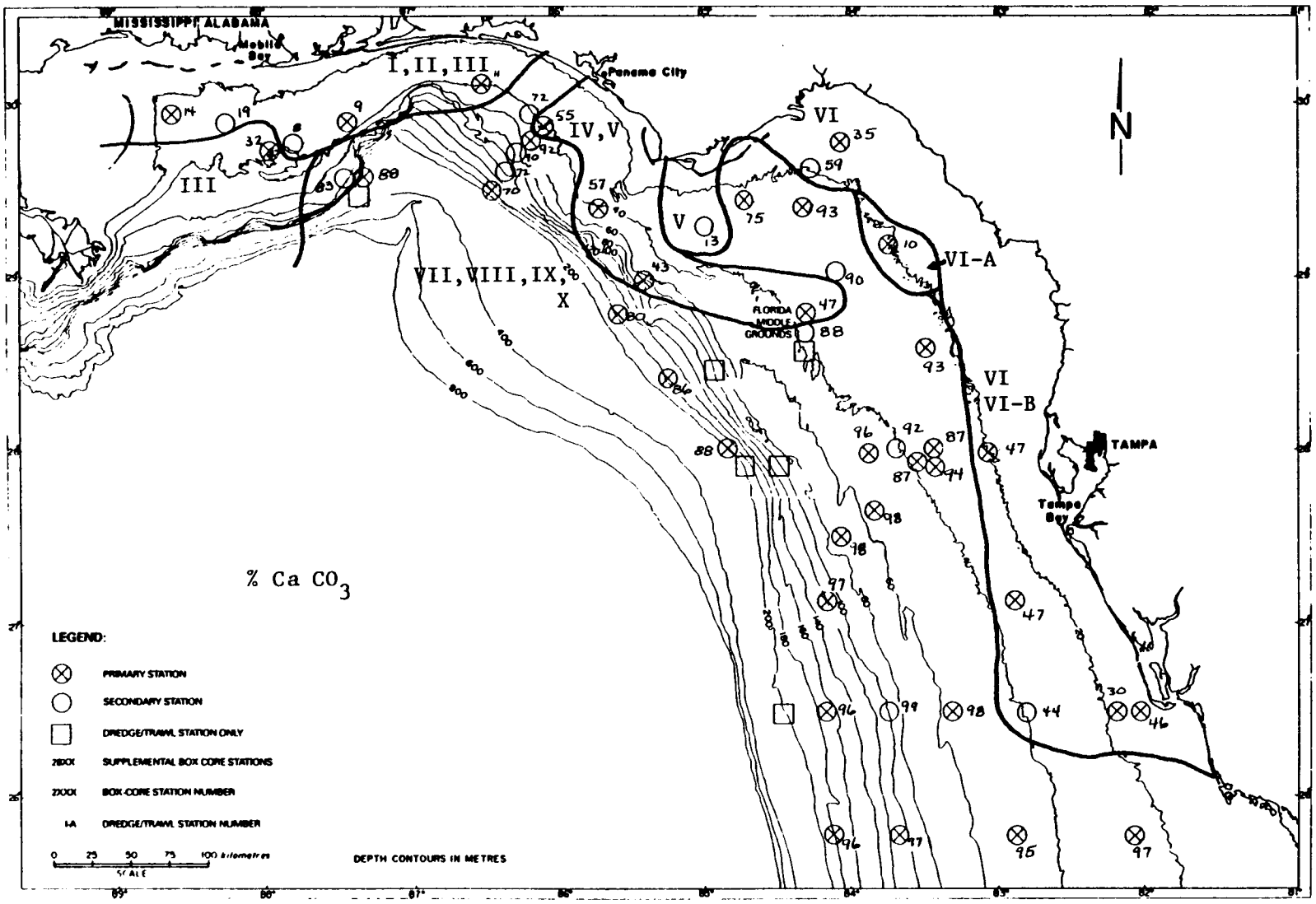


Figure 127. Sedimentary calcium carbonate ($CaCO_3$) distribution, MAFLA lease area. Roman numerals correspond to carbonate/texture groupings in Figure 130.

TABLE 38

GRAND STATION MEANS* OF LEACHABLE (-L)
AND TOTAL (-T) SEDIMENTARY BARIUM VANADIUM AND IRON

STATION	Ba-L	Ba-T	% L[1]	V-L	V-T	% L	Fe-L	Fe-T	% L	% CaCO3	%<62 μm	% TOC
2101	7.9±1.1	55	14	2.2±0.1	3.3	67	684±47	1360	50	46	9.5	0.11
2102	3.6±0.1	17	21	1.2±0.3	1.7	71	441±92	680	65	30	3.5	0.07
2103	7.9±2.1	24	33	1.7±0.5	3.5	49	1080±231	2073	52	44	6.5	0.09
2104	9.1±1.9	23	40	1.8±0.1	2.6	70	692±70	1047	66	98	9.7	0.16
2105	12.3±1.2	53	23	2.0±0.4	2.7	74	553±175	935	59	99	9.4	0.19
2106	12.3±0.6	21	59	2.8±0.1	6.0	47	1735±31	4235	41	96	19.2	0.28
2207	6.7±1.4	50	14	1.7±0.4	2.9	59	360±60	900	40	47	8.4	0.10
2208	10.1±1.6	46	22	1.7±0.5	4.5	38	929±514	1830	51	87	53.4	0.24
2209	10.3±1.2	49	21	2.0±0.3	4.3	47	805±31	1350	60	87	39.6	0.27
2210	13.0±1.0	37	36	2.1±0.7	4.2	50	1159±147	1715	68	92	29.2	0.27
2211	10.1±1.7	57	18	3.1±0.5	5.5	56	1388±188	2410	58	96	13.5	0.26
2212	10.4±2.3	25	42	2.0±0.6	7.0	29	2713±658	9373	29	88	33.0	0.41
2213	11.7±1.2	50	24	2.2±0.9	11.0	20	2760±485	11650	24	86	47.8	0.37
2315	10.1±1.7	47	21	1.1±0.6	2.3	49	506±243	873	58	88	7.8	0.10
2316	8.5±4.0	25	34	1.7±0.8	2.8	62	332±91	1060	31	47	14.3	0.13
2317	11.4±2.0	27	42	2.2±0.2	4.5	49	1407±564	2155	65	90	16.9	0.09
2318	2.3±0.4	5.9	39	0.7±0.2	1.3	54	95±11	370	26	10	2.3	0.05
2419	6.6±2.4	10.4	63	2.3±0.7	3.3	70	436±128	775	56	35	2.2	0.08
2421	8.0±0.2	25	32	2.1±0.2	5.4	39	1122±264	1680	67	59	9.1	0.10
2423	11.3±1.5	<70	>16	9.5±0.8	17.0	56	9140±2537	16200	56	75	13.9	0.25
2424	3.1±0.6	20	16	1.0±0.2	2.4	42	338±83	900	38	13	4.5	0.04
2426	7.4±4.0	47	16	1.8±0.2	5.1	35	2793±454	4125	68	43	5.1	0.08
2427	9.9±1.0	81	12	3.7±0.8	12.0	31	3557±310	16900	21	80	51.6	0.46

[1]Percent leachable
*Concentrations on $\mu g \cdot g^{-1}$ dry sediment (ppm)

TABLE 38 (CONTINUED)

STATION	Ba-L	Ba-T	% L	V-L	V-T	% L	Fe-L	Fe-T	% L	% CaCO3	%<62 μm	% TOC
2528	5.9±1.2	14	44	1.8±0.2	3.8	47	1517±78	2065	73	55	3.9	0.05
2529	8.0±1.8	18	44	2.6±0.9	10	26	3540±814	5020	71	72	3.8	0.08
2531	8.4±1.2	12	70	3.6±0.5	6.6	55	3663±743	5480	67	92	4.4	0.08
2533	8.5±4.4	17	50	3.1±0.8	8.5	36	2940±425	5690	52	90	5.0	0.08
2535	7.6±1.4	93	8	4.8±0.2	-	-	3103±331	10900	28	72	64.4	0.89
2536	8.2±0.8	82	10	4.4±0.4	31	14	3167±108	13767	23	70	74.0	0.71
2638	9.3±0.8	285	3	8.8±1.9	42	21	5737±1452	22700	25	14	72.8	0.64
2639	4.3±0.3	99	4	4.4±0.5	27	16	4113±154	9220	45	19	14.3	0.16
2640	2.4±0.7	44	5	1.9±0.8	8	23	2730±1654	6653	41	32	5.0	0.11
2641	1.8±0.3	63	3	2.0±0.2	14	14	1040±201	4245	24	8	4.6	0.17
2643	12.0±1.7	3.8	32	5.8±0.7	12	48	6903±1602	13833	50	83	5.7	0.25
2645	10.0±2.6	<45	>22	7.0±0.5	-	-	5007±786	11900	42	88	11.2	0.31
2746	9.2±4.9	18	51	2.8±0.5	4.3	66	1087±121	1745	62	97	39.1	0.32
2747	11	20	55	2.9±0.3	3.6	81	1110±209	1625	68	98	12.4	0.19
2748	12.5±2.1	18	69	3.1±0.5	4.0	78	2067±215	3120	66	98	6.8	0.20
2749	12	15	80	3.7	5.7	65	2010	2840	71	94	5.4	0.05
2851	9.8±4.6	41	24	2.7±1.4	5.9	46	1000	3290	30	47	4.3	0.05
2852	11.3±3.9	<42	>27	2.9±1.1	5.7	51	1260	1610	78	93	3.8	0.06
2853	11.6±4.9	47	25	3.7±1.6	4.5	82	-	2320	-	93	6.9	0.11
2854	4.6	83	6	4.3±0.2	11	39	6720	6770	99	57	6.5	0.14
2855	1.2±0.5	29	4	1.0±0.1	2.1	48	280	860	33	11	2.1	0.06
2856	1.3	29	4	0.6±0.3	1.5	40	220	420	52	9	0.8	0.05
2957	11.7±0.6	13	90	2.1±0.1	5.8	36	892±89	2070	43	96	21.7	0.22
2958	11.2±1.3	17	66	2.0±0.4	3.2	63	633±12	1060	60	97	20.8	0.17
2959	11.3	26	43	2.4±0.5	4.2	47	1293±302	2103	61	95	28.4	0.30
2960	10.5±2.2	11	95	3.2	-	-	1707±110	2030	84	97	6.2	0.14

difference in atomic (or ionic) size between barium and calcium, however, precludes total geochemical coherence.

Figures 127 through 129 map the distributions of calcium carbonate, silt plus clay sizes (i.e., weight percent of the sediment that is <62 μm in particle diameter; a measure of grain size in general), and total organic carbon in MAFLA sediments, and Figure 130 summarizes the combination of carbonate content and grain size (as fine, medium and coarse). In each case, inspection contours have been drawn and, although different patterns arise in each case, a general pattern begins to emerge as each is superimposed on the other.

Relative to the Roman numeral designations made in Figure 130, the MAFLA lease area can be described in terms of four distinct sedimentary areas and several other which are more complex zones of combined or mixed character. The northwest corner of the area (I and parts of II, III and VII) represents the clay mineral end-member being dominated by terrigenous materials from the Mississippi River. Here the sediments are generally high in fines, low in carbonate, high in organic content and high in metals.

The opposite end-member region relative to the previous discussions is the large section of latitudinally middle shelf off Florida (area X) which is controlled by the accumulation of planktonic debris and coral rubble of high carbonate, coarse size and low organic carbon (and low metal) contents. This area receives essentially no land-derived contribution to its sediments.

Two other fairly distinct areas are those designated by VI and IX in Figure 130. Area VI, especially its northern portion, is a sedimentary regime dominated by quartz sands of very little carbonate content but with coarse size character and very low organic carbon. These sediments have been found to be the lowest of all MAFLA substrates in metal content (both total and leachable).

Area IX is dominated by a finer-grained and higher organic content version of the biogenic carbonate sediments in the nearer-shore area X. these sediments are generally enriched in metals relative to those of X.

The geographically middle regions of the MAFLA area (IV, VIII, V, parts of III and II) represent the meeting zone between the clay mineral and biogenic carbonate end members and varied combinations of mineralogical geochemical composition are found.

Figure 131 (reproduced from Chapter 3) shows the distribution of total sedimentary iron over the MAFLA area with inspection contours showing general agreement with those of Figure 130. Iron can be considered an exemplary transition metal, indicative of the others measured in this study (except barium) with regard to geochemical association. From the discussion in Chapter 3 and the distribution of vanadium shown in Figure 132, we can see that this is the case. For barium (total), however, although some coherence with iron exists between the two end-member regions (Mississippi River provenance vs carbonate Florida shelf), the trends are significantly different (Figure 133).

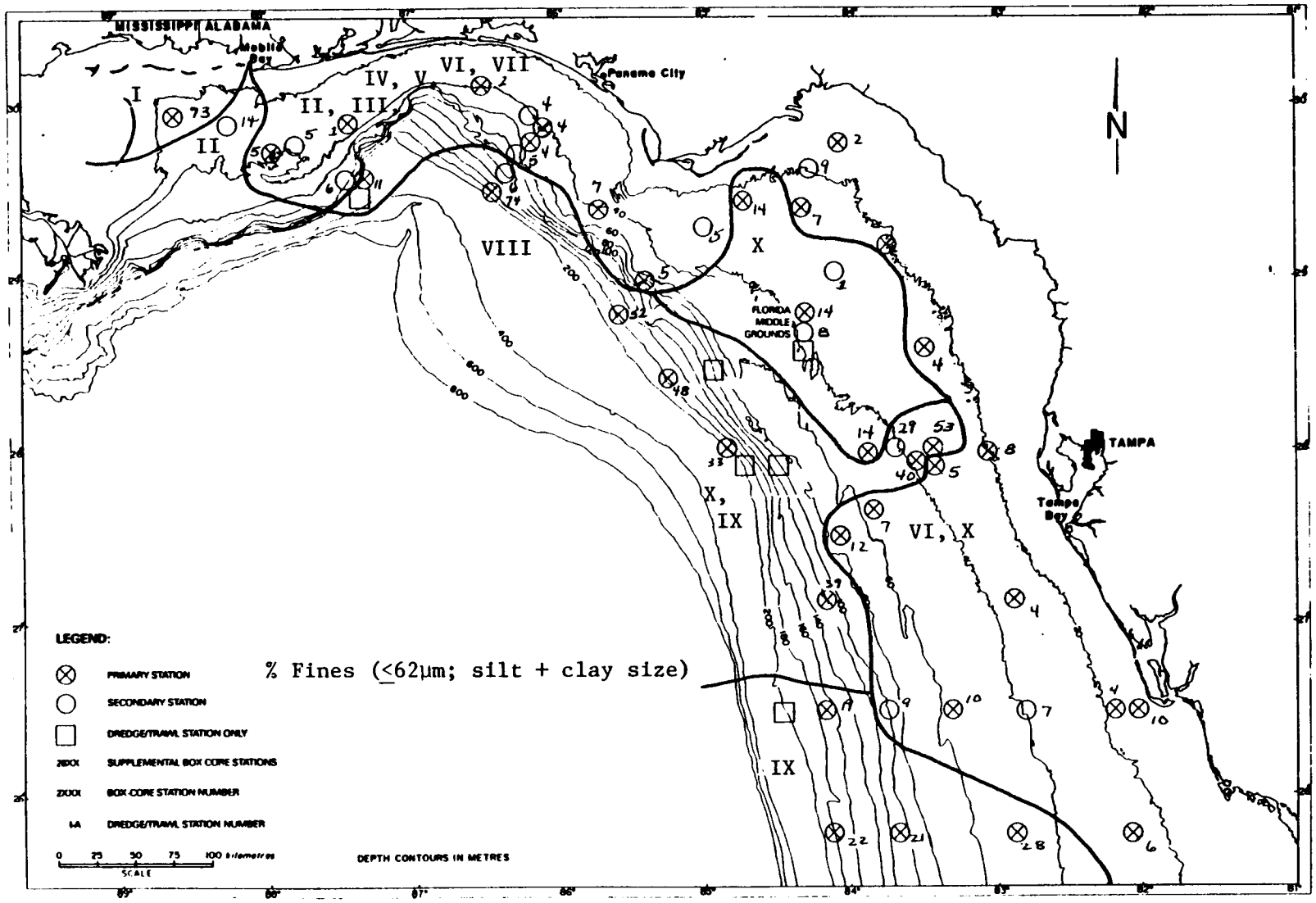


Figure 128. Sedimentary fraction of less than 62 µm particle size (% fines; silt + clay), MAFLA lease area. Roman numerals correspond to carbonate/texture groupings in Figure 130.

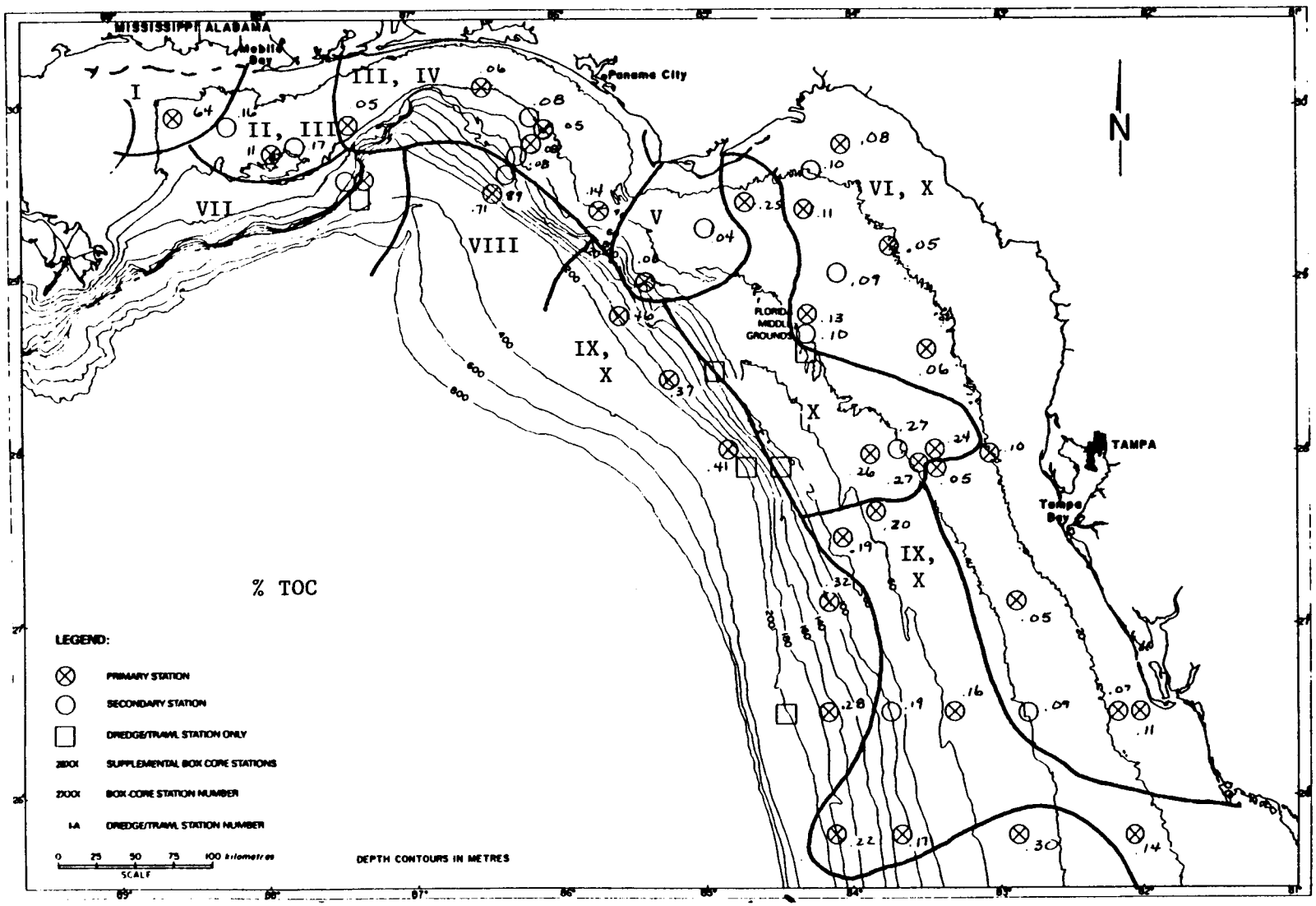
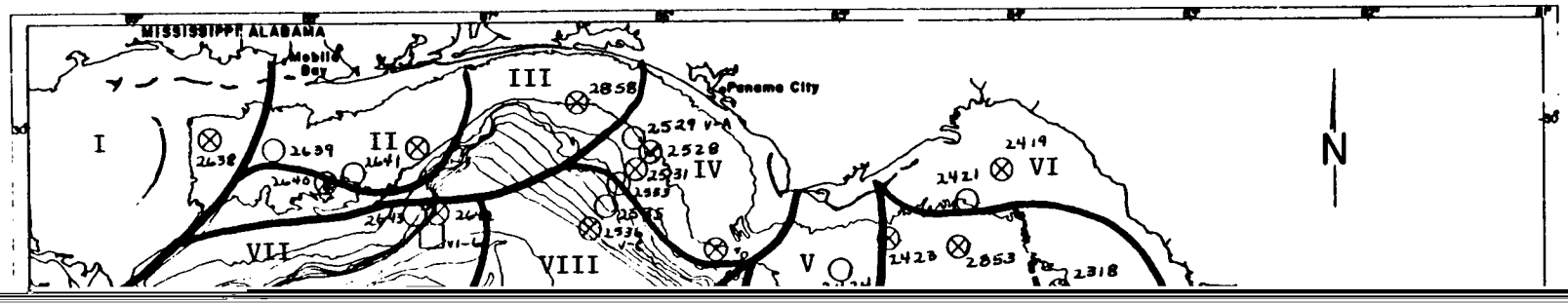


Figure 129. Total sedimentary organic carbon (TOC), MAFLA lease area. Roman numerals correspond to carbonate/texture groupings in Figure 130.


MISSISSIPPI ALABAMA
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Panama City
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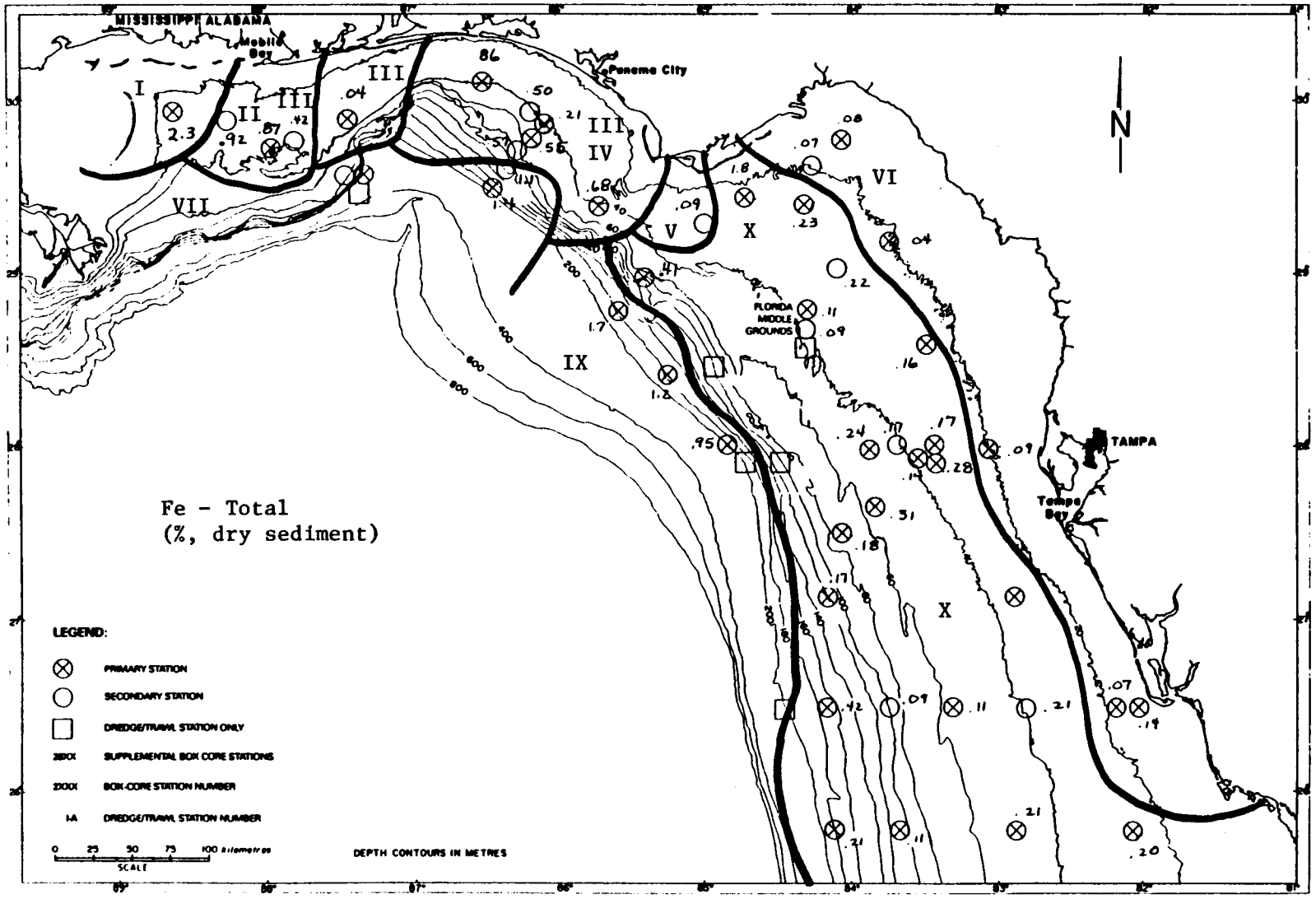

Figure 131. Total sedimentary iron content (% dry weight sediment) distribution, MAFLA lease area. Roman numerals correspond to carbonate texture groupings in Figure 130.

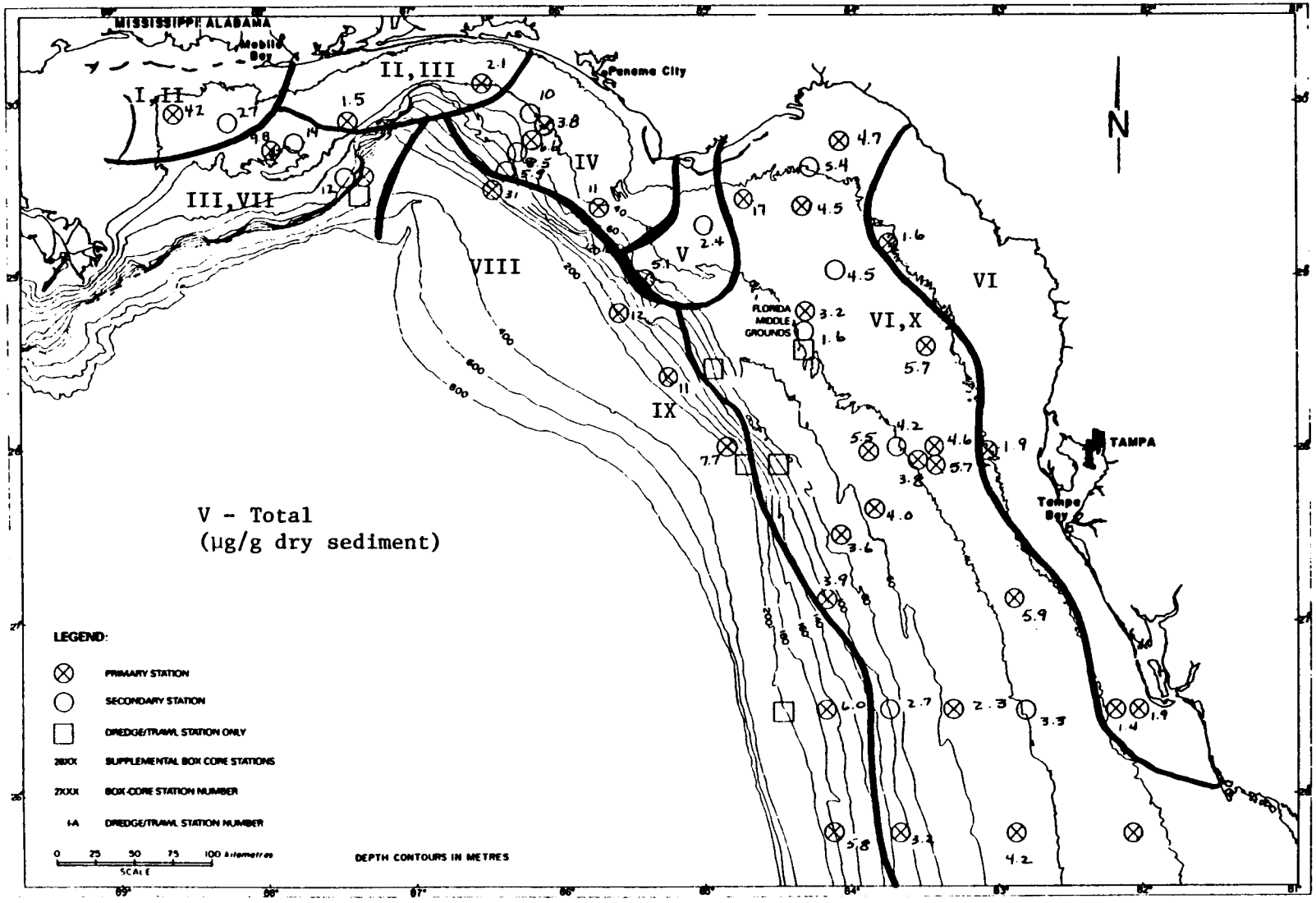

Figure 132. Total sedimentary vanadium content (µg/g dry sediment) distribution, MAFLA lease area. Roman numerals correspond to carbonate/texture groupings in Figure 130.

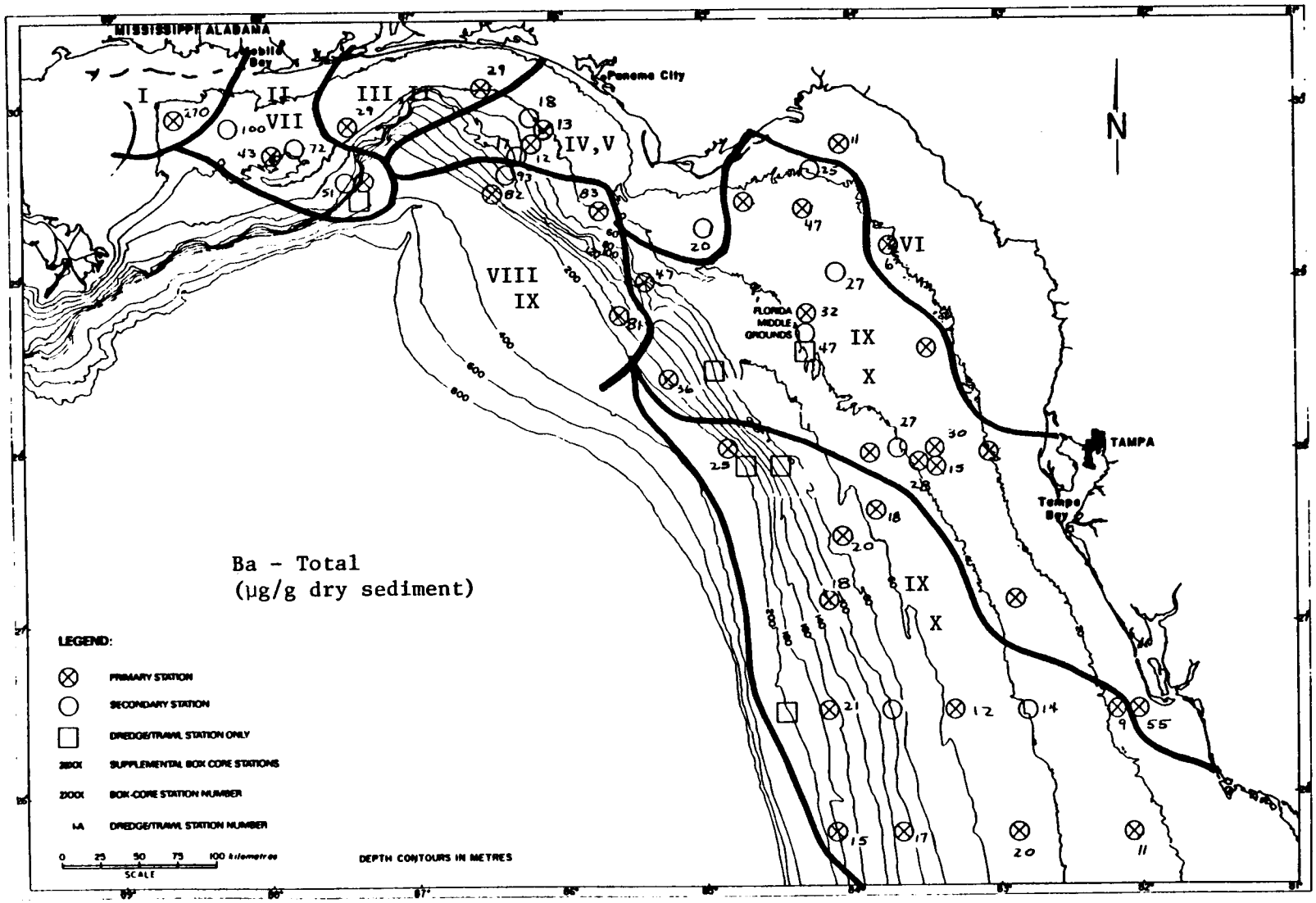

Figure 133. Total sedimentary barium content (µg/g dry sediment) distribution, MAFLA lease area. Roman numerals correspond to carbonate/texture groupings in Figure 130.

In general, it can be said that barium trends more or less positively with carbonate and decreasing grain size east of the areas influenced by terrigenous clay minerals, which happen to be mineralogically enriched in barium while low in carbonate. The net result is a substantially more complex distributional pattern for barium relative to iron and the other metals as can be seen in comparing Figure 133 with Figures 131 and 132.

The unique nature of barium relative to the other metals examined in this study becomes more apparent upon inspection of its leachable (1 N HNO_3) amount and fraction distributions. Although, as just described, the presence of clay minerals disrupts any positive trends between barium and calcium carbonate, clay mineral barium is mineral-related (as opposed to grain-size and/or organic matter related) and leaching the sediment with weak-to-moderate strength acid should not release it into solution. Table 38 (the Ba-L column) shows this quite dramatically to be the case with only a very narrow range of barium amounts being leachable relative to the large range of total barium amounts between sedimentary end members. As the similarity matrix (Table 39) shows, the result of analyzing leachable barium trends rather than total is that a clear barium-to-calcium carbonate relationship is established (S.I. = 0.86). The leachable amounts of the other metals, including vanadium, maintain their same strong similarities with grain size and organic carbon content that were established by total concentration distributions.

Figures 134 through 136 show the geographic distribution of leachable fractions (leachable divided by total concentrations) for iron, vanadium and barium, respectively. For iron and vanadium, the trends become much less distinguishable as the greater leaching power of 1 N HNO_3 on readily acid soluble carbonates compared to clay minerals and quartz sands tends to obliterate the clear dichotomy observed for leachable and total amounts. While the carbonates are low in metals, much of the mineral is dissolved in the leaching process releasing a large portion of what is present.

Quartz sands are also low in metals but most of what metal contents are assocaited with them are on surfaces. Therefore, even though little mineral dissolution takes place from the 1 N HNO_3, again a large portion of what metals are there is removed. The terrigenous clay minerals component of the sediments contains much higher leachabe amounts of metals but since the 1 N HNO_3-resistant minerals are also relatively enriched, the leachable fractions tend to be lower as the contribution from clays becomes greater.

Figure 136 substantiates the previous discussion for barium as the Mississippi River-influenced end member is characterized by very low leachable fractions. Essentially all (>90%) of the barium associated with clay minerals is bound into the acid-resistant phases. One potential ramification of this is that in the western MAFLA area, where oil production might eventually be most prolific (by virtue of the greater likelihood of its existence), leachable barium in sediments might prove to be particularly sensitive monitoring tool. Since the ambient, baseline leachable fractions are at the 3 to 5% level, small changes can conceivably be detected with great sensitivity.

TABLE 39

SIMILARITY MATRIX FOR TRACE METALS IN 1 N HNO_3 LEACH OF MAFLA SEDIMENTS

	Ba	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn	<16 μm[1]	$CaCO_3$	TOC[2]
Ba	1.00											
Cd	0.66	1.00										
Cr	0.67	0.75	1.00									
Cu	-	-	-	1.00								
Fe	-	0.66	0.65	0.71	1.00							
Ni	0.65	0.79	0.64	0.62	0.70	1.00						
Pb	-	-	-	0.85	0.78	0.64	1.00					
V	0.60	0.70	0.74	0.68	0.76	0.69	0.74	1.00				
Zn	-	0.61	-	0.84	0.78	0.70	0.83	-	1.00			
<16 m	-	-	-	0.83	0.61	-	0.72	-	0.77	1.00		
$CaCO_3$	0.86	0.67	0.74	-	-	-	-	-	-	-	1.00	
TOC	-	0.68	0.67	0.75	0.69	0.70	0.71	0.75	0.77	-	-	1.00

[1]Grain-size fraction

[2]TOC = total organic carbon

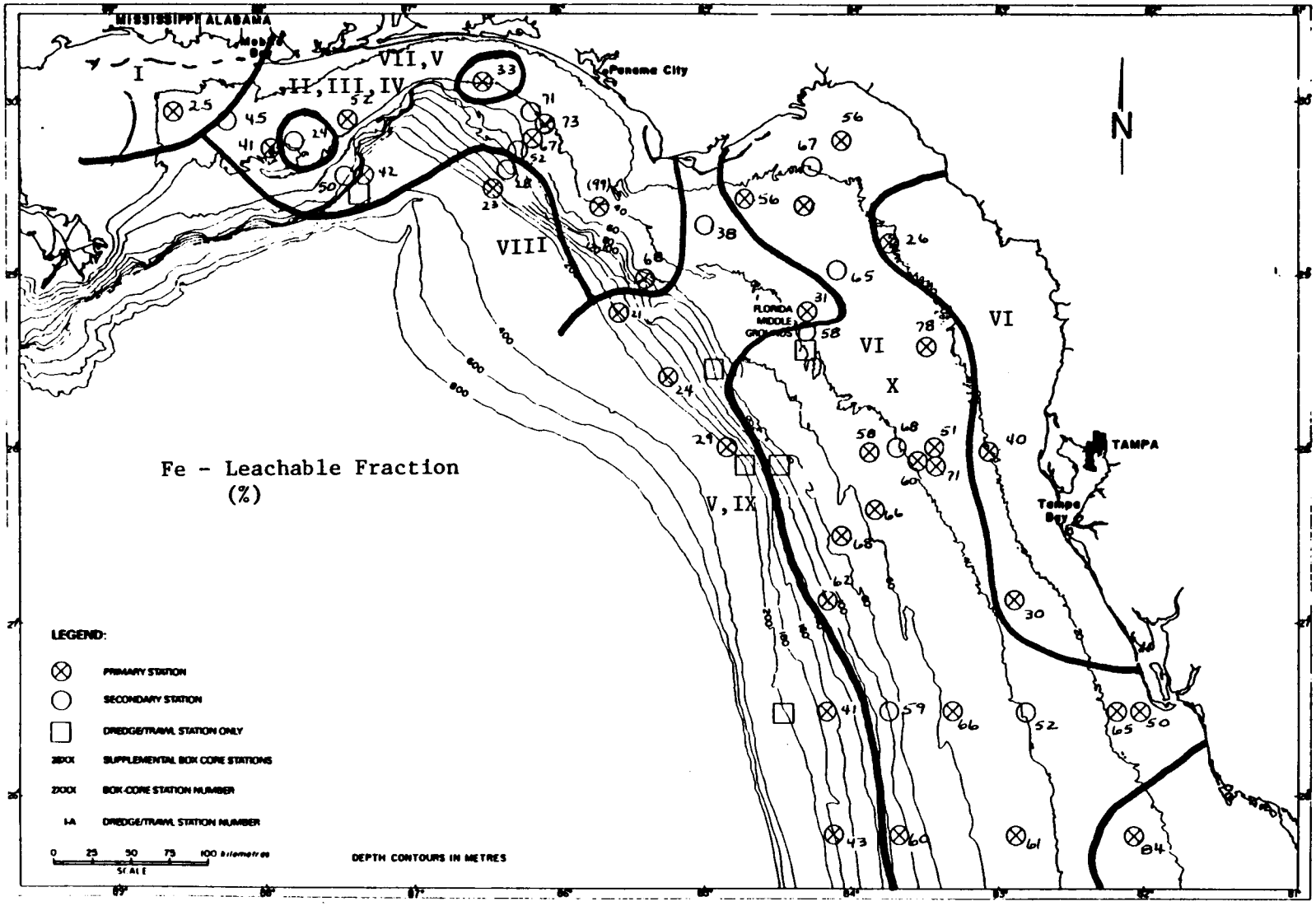

Figure 134. Leachable (1 N HNO_3) fraction of sedimentary iron (in %), MAFLA lease area. Roman numerals correspond to carbonate texture groupings in Figure 130.

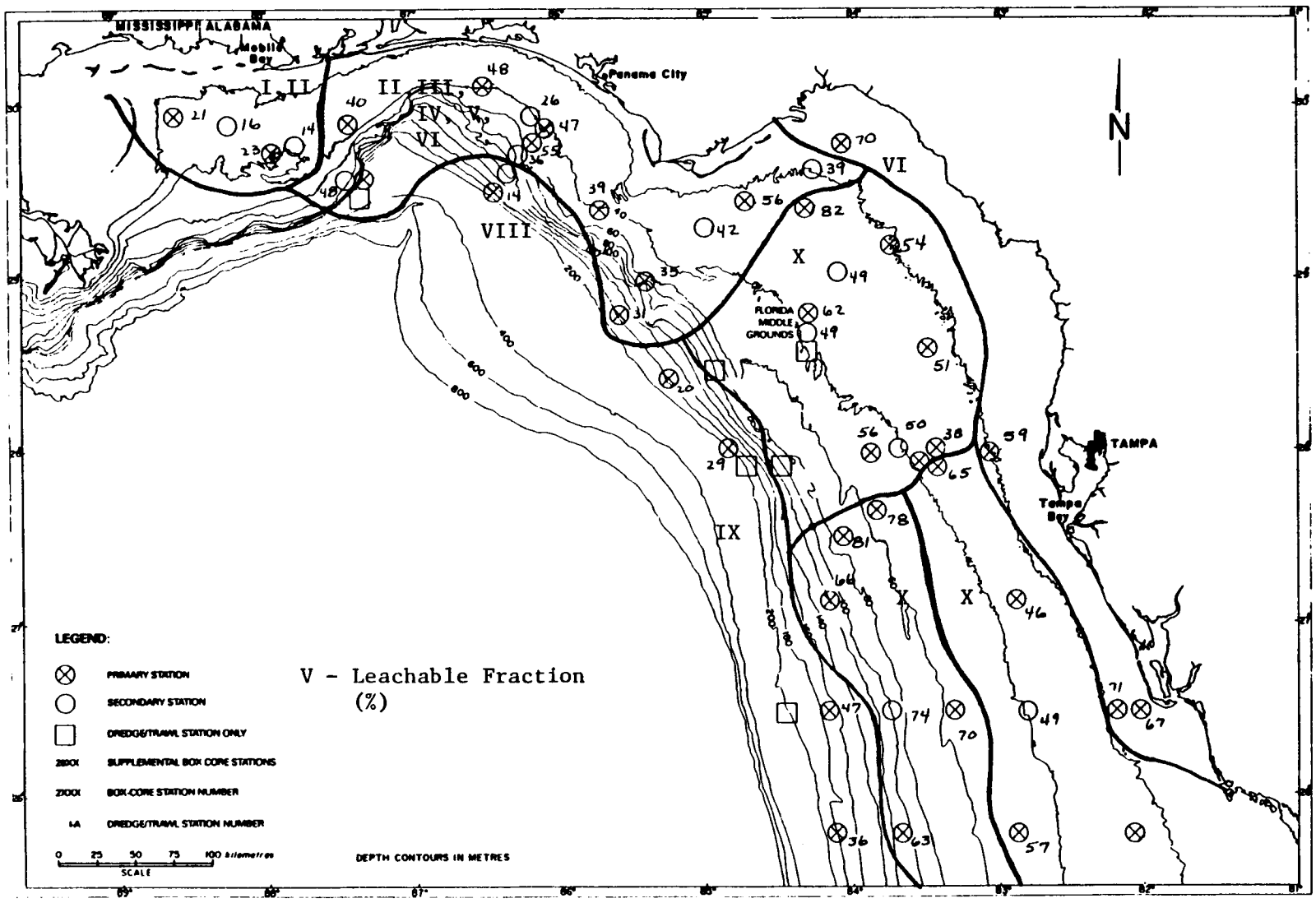

Figure 135. Leachable (1 N HNO_3) fraction of sedimentary vanadium (in %), MAFLA lease area. Roman numerals correspond to carbonate texture groupings in Figure 130.

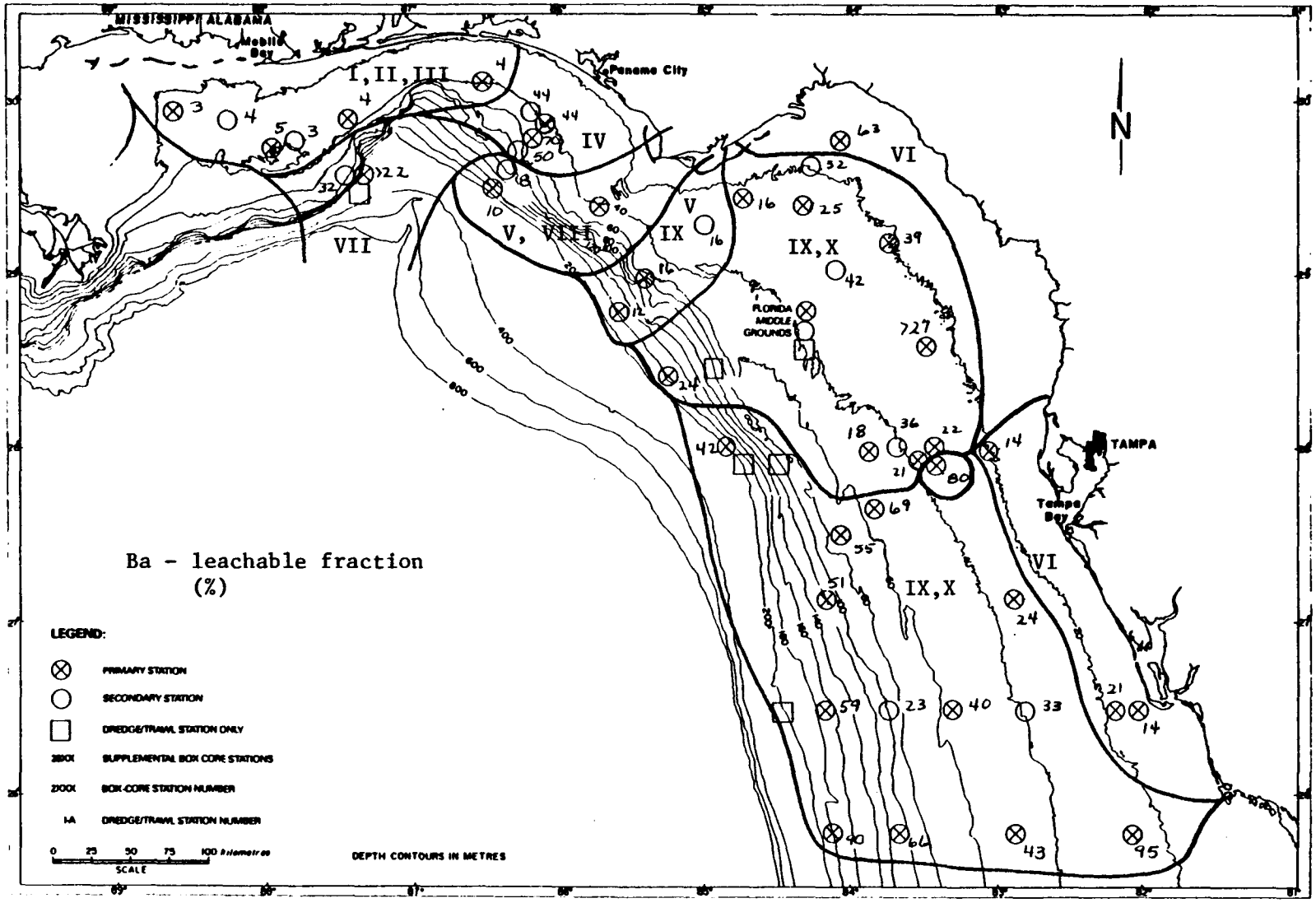

Figure 136. Leachable (1 N HNO_3) fraction of sedimentary barium (in %), MAFLA lease area. Roman numerals correspond to carbonate texture groupings in Figure 130.

CONCLUSIONS

Both vanadium and barium have been extensively characterized as to their sediment concentration (both total and 1 N HNO_3-leachable) distributions over the MAFLA outer continental shelf. Neither element appears to have had its sediment concentrations impacted by anthropogenic contributions; natural geochemical processes of supply and transport control the levels observed for each metal.

Vanadium is most closely related to mineralogy and grain-size character of the sediments of the MAFLA area with fine-grained, clay minerals having the highest concentrations, coarse-grained quartz sands having the lowest, and coarse-grained biogenic carbonates (the most wide-spread sediment type) having quite low concentrations. These trends are coherent with the rest of the transition metals (iron, copper, lead, etc.) discussed in Chapter 3.

Barium displays different mineralogical trends compared to the other metals. Within the large suite of biogenic sediment samples collected in this study from the Florida shelf, barium is more directly related to carbonate content than to grain size. However, the quartz-dominated terrigenous sediment of the near-shore northern Florida shelf and the clay mineral-rich muds off Mobile represent the most barium-depleted and barium-elevated sediments, respectively, as is the case for the other metals.

For all the metals except barium the amount leached with 1 N HNO_3 was quite variable but related to the total content in such a way that the leachable fractions spanned a relatively small range. For barium, however, the amount leached was relatively constant (and low) over the range of sediment types surveyed and the leachable fractions were somewhat more variable. This characteristic might enable the use of leachable barium as a monitoring parameter during future oil and gas production activities.

REFERENCES

Presley, B.J., M.C. Dobson, R.F. Shokes and J.H. Trefry, 1976. Final Report of Heavy Metal Analyses of Bottom Sediment, MAFLA Lease Area. To the Bureau of Land Management, Washington, D.C., via SUSIO, St. Petersburg, Florida.

APPENDIX 4-1

MEAN SEASONAL CONCENTRATIONS OF BARIUM AND VANADIUM IN THE 1 N HNO_3-LEACHABLE (L) AND TOTAL (T) OF MAFLA SURFICIAL SEDIMENTS. ALSO PRESENTED ARE AVERAGE TOTAL ORGANIC CARBON (TOC), CALCIUM CARBONATE ($CaCO_3$) AND WEIGHT FRACTION LESS THAN 62 μm IN PARTICLE SIZE. ALL METAL CONCENTRATIONS ARE IN $\mu g/g$ DRY WEIGHT SEDIMENT. SEASON KEY: -'76 = SUMMER 1976; -1 = SUMMER 1977; -2 = FALL 1977; -3 = WINTER 1978.

APPENDIX 4-1 (Continued)

S	Ba-'76	Ba-1	Ba-2	Ba-3	V-'76	V-1	V-2	V-3	Fe-'76	Fe-1	Fe-2	Fe-3	C/F/T*
2101	7.8[1]	7.4	6.9	9.4		2.1	2.3	2.1	712	630	710	700	46
	55[2]	<25			4.7	1.9			1350	620	1370		9.5
	13[3]				47	100			53		52		0.11
2102			3.5	3.7		1.5	1.2	1.0	463	340	520	270	30
	24			9.3	2.0			1.4	710			650	3.5
	15			40	65			71	65			42	0.07
2103		5.9	7.8	10		1.2	2.2	1.6	1310	810	970	1230	44
	34			14	3.6			3.3	1610		1650	2960	6.5
	20			71	47			48	81		59	42	0.09
2104		11	9.1	7.2		1.7	1.8	1.9	678	730	760	600	98
	33	<37		12	3.0	2.4		2.3	1060	1100		980	9.7
	30			60	60	71		83	64	66		61	0.16
2105		13	11	13		2.2	1.5	2.2	460	360	750	640	99
	53				2.7				790		1080		9.4
	23				73				58		69		0.19
2106		12	13	12		2.7	2.9	2.7	1770	1750	1700	1720	96
				21				6.0	4140			4330	19.2
				57				45	43			40	0.28
2207		7.9	7.0	5.2		2.0	1.2	1.8	298	320	420	400	47
	60			39	3.9			1.9	900				8.4
	13			13	41			95	33				0.10

[1]Leached fraction
[2]Total
[3]Leached/Total
*C = % $CaCO_3$; F = % sediment <62 μm; T = % TOC

APPENDIX 4-1 (Continued)

S	Ba-'76	Ba-1	Ba-2	Ba-3	V-'76	V-1	V-2	V-3	Fe-'76	Fe-1	Fe-2	Fe-3	C/F/T*
2208		8.2	11	11		2.1	1.2	1.9	705	560	1690	760	87
	61	30			4.5	4.6			1360	1350	2780		53.4
	18	27			36	46			52	41	61		0.24
2209		11	9.0	11		2.3	1.8	1.9	850	800	780	790	87
	70			28	4.8			3.8	1220			1480	39.6
	14			39	44			50	70			53	0.27
2210		12	14	(29)		1.3	2.7	2.3	1315	1010	1060	1250	92
	46			27	4.2				1610			1820	29.2
	28				53				82			69	0.27
2211		12	9.2	9.0		2.7	3.0	3.6	1500	1150	1330	1570	96
	57				5.5				2410				13.5
	18				56				62				0.26
2212		9.0	9.1	13		2.0	1.4	2.6	3370	2520	1880	3080	88
	<45			25	6.3			7.7	9640		8950	9530	33.0
					32				35		21	32	0.41
2313		11	11	13		1.9	3.2	1.4		3320	2500	2460	86
		63		36		10		11		11400		11900	47.8
				52		19		13		29		21	0.37
2315		9.4	12	8.9		1.5	1.4	0.5		780	420	318	88
		47		(10)		2.9		1.6		1220	800	600	7.8
		20				52		31		64	53	53	0.10
2316		7.2	5.3	13		1.3	1.2	2.6		360	230	405	47
		18		32		2.3		3.2		880		1240	14.3
		40		39		57		81		41		33	0.13
2317		12	13	9.2		2.1	2.5	2.1		1260	2030	930	90
		27				4.5				1480	2830		16.9
		44				47				85	72		0.09

APPENDIX 4-1 (Continued)

S	Ba-'76	Ba-1	Ba-2	Ba-3	V-'76	V-1	V-2	V-3	Fe-'76	Fe-1	Fe-2	Fe-3	C/F/T*
2318		1.9	2.6	2.4		0.9	0.6	0.6		104	98	82	10
		5.9				1.3				370			2.3
		35				69				28			0.05
2419		3.9	7.3	8.6		1.7	2.1	3.0		290	530	487	35
		7.8		13		1.9		4.7		450		1100	2.2
		50		66		89		64		64		44	0.08
2421		8.1	7.8	8.0		2.3	1.9	2.1		1030	1420	917	59
		25				5.4				1680			9.1
		32				43				61			0.10
2423		10	13	11		10		8.9		10800	6220	10400	75
		<70				17				16200			13.9
						59				67			0.25
2424		3.7	2.9	2.6		1.2	0.9	1.0		415	350	250	13
		20				2.4				900			4.5
		19				50				46			0.04
2426		12	5.8	(4.4)		1.9	1.6	(1.8)		3080	3030	2270	43
		46		47		5.1				4590		3660	5.1
		26				37				67		62	0.08
2427		9.2	9.5	11		3.8	4.5	2.9		3570	3240	3860	80
		81				12				16900			51.6
		11				32				15			0.46
2528		4.8	7.2	5.6		1.7	1.7	2.1		1540	1580	1430	55
		15		12		3.7		3.9		2000		2130	3.9
		32		47		46		54		77		67	0.05
2529		9.1	6.0	9.0		1.7	2.6	3.4		3890	2610	4120	72
		18				10				5860	4180		3.8
		51				17				49	62		0.08

APPENDIX 4-1 (Continued)

S	Ba-'76	Ba-1	Ba-2	Ba-3	V-'76	V-1	V-2	V-3	Fe-'76	Fe-1	Fe-2	Fe-3	C/F/T*
2531		7.0	9.2	8.9		4.0	3.8	3.1		3950	2820	4220	92
		12				6.6				5480			4.4
		58				61				72			0.08
2533		12	3.5	10		2.3	3.9	3.1		3170	2450	3200	90
		<49		17		8.5				5480	6110	5480	5.0
				59		27				58	40	58	0.08
2535		8.9	7.9	6.1		4.7	5.0	4.6		3420	2760	3130	72
		93				59				10900			67.4
		10								31			0.89
2536		9.1	7.6	7.9		4.9	4.1	4.3		3290	3090	3120	70
		82				31				13200	13900	14200	74.0
		11				16				25	22	22	0.71
2638		9.5	8.4	10		8.0	11	7.4		6060	4150	7000	14
	300			270		(14)		42		23400		22000	72.8
	3			4				18		26		32	0.64
2639		4.6	4.0	4.3		4.9	4.3	4.0		4290	4010	4040	19
	99					27				9220			14.3
	4					18				47			0.16
2640		1.6	2.8	2.8		1.1	2.0	2.7		1150	2590	4450	32
	44			43		6.1		9.8		2710	4750	12500	5.0
	5			7		18		28		42	55	36	0.11
2641		1.6	2.1	1.7		2.1	2.2	1.8		1270	950	900	8
	54			72		14				4830		3660	4.6
	4			2		15				26		25	0.17
2643		14	11	11		5.1	6.4	5.9		8730	5740	6240	83
	25			51		12				13400	13900	14200	5.7
				22		43				65	41	44	0.25

APPENDIX 4-1 (Continued)

S	Ba-'76	Ba-1	Ba-2	Ba-3	V-'76	V-1	V-2	V-3	Fe-'76	Fe-1	Fe-2	Fe-3	C/F/T*
2645		13	9.1	8.0		6.5	7.1	7.4		5620	4120	5280	88
	<45					(2.6)				11900			11.2
										47			0.31
2746		12	3.6	12		2.7	3.4	2.4		950	1180	1130	97
		17		18		4.6		3.9		1520		1970	39.1
		71		67		59		62		63		57	0.32
2747			11	11		3.1	2.6	2.9		1350	1010	970	98
				20				3.6			1980	1270	12.4
				55				81			51	76	0.19
2748			11	14		2.8	3.6	2.8		2050	1860	2290	98
				18				4.0			3120		6.8
				78				70			60		0.20
2749		12				3.7				2010			94
		15				5.7				2840			5.4
		80				65				71			0.05
2851	13	6.5			3.7	1.7				1000			47
	41				5.9				3290				4.3
	32				63				30				0.05
2852	8.5	14			3.6	2.1				1260			93
	<42				5.7				1610				3.8
					63				78				0.06
2853	8.1	15			2.5	4.8							93
	47				4.5				2320				6.9
	17				56								0.11
2854	4.6				4.4	4.1				6720			57
	83				11				6770				6.5
	6				40				99				0.14

APPENDIX 4-1 (Continued)

S	Ba-'76	Ba-1	Ba-2	Ba-3	V-'76	V-1	V-2	V-3	Fe-'76	Fe-1	Fe-2	Fe-3	C/F/T*
2855	1.5	0.8			1.0	0.9				280			11
	29				2.1				860				2.1
	5				48				33				0.06
2856	1.3	1.3			0.8	0.4				220			9
	29				1.5				420				0.8
	4				53				52				0.05
2957		12	12	11		2.0	2.2	2.0		937	790	950	96
		12		14		5.8				2170		1970	21.7
		75		79		34				43		48	0.22
2958		12	9.7	12			1.7	2.2		640	640	620	96
				17				3.2				1060	20.8
				71				69				58	0.17
2959		12	11	11		1.8	2.6	2.8		1370	960	1550	95
		32		20		(0.9)		4.2		2190	1650	2470	28.4
		38		55				67		63	58	63	0.30
2960		13	9.1	9.4		3.2	3.2	3.2		1820	1600	1700	97
				11								2030	6.2
				85								84	0.14

VOLUME II

CHAPTER 5

MACROEPIFAUNA AND DEMERSAL FISH TRACE METAL ANALYSES

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CONTRACT NO. AA550-CT7-34

ANALYSIS OF MARINE SAMPLES FROM THE OUTER CONTINENTAL SHELF OF MISSISSIPPI, ALABAMA, AND FLORIDA (MAFLA) FOR TRACE METALS IN DEMERSAL FISH AND MACROEPIFAUNA

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ABSTRACT

Demersal fish and macroepifaunal samples collected by Dames & Moore from the MAFLA area of the Gulf of Mexico were analyzed for trace metal content using methods approved by the Bureau of Land Management. Some unanticipated pooling of samples was necessary and a few samples could not be analyzed at all because of the small size of the specimens collected. A complete list of all samples received and an indication of how they were processed is appended to the report. Results appear to be comparable to those reported for earlier MAFLA studies. A detailed analysis and interpretation of the results, however, was not a contractual requirement and, thus, is not a part of this report. Replicate analyses of NBS standard material and the internal consistency of the results themselves indicate that the quality of the analytical results is high. No evidence of significant sample contamination in the laboratory was noted. Despite some early delays, the analyses were completed essentially on schedule.

INTRODUCTION

Analytical Research Laboratories, Inc. (ARLI) has completed work on its subcontract to Dames & Moore to perform trace metal (Cd, Cr, Cu, Fe, Ni, Pb, Zn) analyses on a portion of the samples collected by Dames & Moore on its Bureau of Land Management 1977/78 MAFLA Benchmark Survey (BLM Contract Number AA550-CT7-34). This final report includes a list of all samples received by ARLI for trace metal analysis since July 1977 and an indication of how each sample was processed. Some samples were processed individually, some samples were pooled before analysis, and a few were not analyzed due to lack of sufficient sample material.

The report also includes a brief description of the method used in analyzing the samples and a summary of the results. The evaluation and interpretation of the results are not included in this report. Responsibility for that task has been assigned to a committee appointed for the purpose.

METHODS

The methods used in this investigation are designed to meet the requirements prescribed in the Bureau of Land Management Solicitation Number AA550-RP7-10 modified as of June 30, 1977. Detailed descriptions of the analytical methods and the accompanying quality control practices were given earlier in our third quarterly report (Dames & Moore, 1978e). These items will be reviewed only briefly in this report.

ANALYTICAL METHODS

TISSUE PREPARATION

Demersal Fish

Tissue preparation is carried out in an enclosed clean bench using nitric acid-washed Pyrex glassware and utensils. The thawed specimen is washed, skinned, and 10 g sample of muscle tissue is transferred to a tared, nitric acid-washed breaker. After having been weighed to determine its wet weight, the sample is dried on the lyophilizer and weighed again to determine its dry weight.

Macroepifauna

Preparation of the macroepifaunal tissue is carried out in a manner similar to that used for the demersal fish. The type of sample material used varies with the kind of organism being sampled. Muscle tissue from the tail section composes the sample material for larger shrimp specimens, while one or more whole organism makes up the sample material for small shrimp and echinoderm specimens. Some starfish samples include only the arms of the specimen. Soft inner tissue makes up the sample material for shell fish and crabs.

ACID DIGESTION

One gram of dry tissue is digested in hot 70% nitric acid (Ultrex grade) and 30% hydrogen peroxide. The clear, yellow digestate is diluted with deionized water to a volume of 10 m in a polyethylene flask for analysis by atomic absorption. A procedural blank is prepared along with each batch of 10 to 30 samples by treating an empty beaker in the same way that the samples are treated.

ATOMIC ABSORPTION ANALYSIS

The metal concentrations of the digestate solutions are determined on a Perkin-Elmer Model 370 Atomic Absorption Spectrophotometer. The instrument is equipped with a deuterium arc background correcter and an HGA-2100 graphite furnace. The methods are taken from Analytical Methods for Atomic Absorption Spectrophotometry published by Perkin-Elmer in 1973 and updated to 1976. Methods using the graphite furnace are taken from Analytical Methods Using the HGA Graphite Furnace published by Perkin-Elmer in 1973 and updated to 1977.

The copper, iron, and zinc content of all samples is determined by using an air-acetylene flame to atomize these elements. Some of the macro-epifauna samples also have cadmium or chromium contents high enough to be measured in the flame mode. The cadmium and chromium content of most samples and the lead and nickel content of all samples were measured with the HGA-2100 Graphite Furnace. This method is used to determine elements present at concentrations too low to be measured effectively in the flame. In practice, the samples are analyzed in groups of 10 to 30. Absorbance values for each element in each sample are measured along with the absorbence values of the blanks and standards. When all these data have been collected for a given group of samples, they are entered into a computer along with the appropriate sample identifications, sample weight, standard solution concentrations, and dilution ratios. The computer has been programmed to establish standard concentration versus absorbence curves for each element and calculate the concentration of each element in the original sample of dry tissue.

INTERNAL QUALITY CONTROL

SAMPLE ACCOUNTABILITY

A description of each sample received at ARLI is recorded in a sample log book and a unique identificaton number is assigned to the sample. Using this number to identify the sample, permanent records are kept in laboratory notebooks of all operations, including weighings and other measurements involving the sample. Each record is dated and initialed by the individual performing the operation.

INSTRUMENT CALIBRATION

Calibration of the Perkin-Elmer Model 370 Atomic Absorption Spectrophotometer is accomplished through the use of standard solutions each containing 1,000 g m^{-1} of one of the seven metals to be reported, namely

Cadmium, chromium, copper, iron, lead, nickel, and zinc. The solutions are prepared by dissolving reagent grade metals in the appropriate acid, following the procedures recommended in Perkin-Elmer's Analytical Methods for Atomic Absorption Spectrophotometry, 1973 Edition with Supplements through 1976. These stock solutions are diluted to give solutions with absorbence values similar to those found in the samples. A standard calibration curve is then established relating absorbence and concentration for each metal as described above. The standards are run at the beginning of a series of analyses and repeated at intervals of 4 to 5 analyses when operating the graphite furnace.

Samples of the National Bureau of Standards Standard Reference Material 1577, Bovine Liver, have been analyzed to check the accuracy of the standard solutions and the precision of the methods. Results of a series of three analyses are given in Table 40. There is good agreement between the two sets of values, especially for the elements Cd, Cu, Fe, and Zn where the concentrations are at levels well above the detection limits for Atomic Absorption methods. The precision reported for these elements is also as good or better than that reported by NBS. The concentrations of the other two elements reported by NBS, Cr, and Pb, are so low that they are near the detection limits for these two metals. As a result, while the agreement with NBS values is still reasonably good, the precision of the measurements is not as good.

TRACE METAL PROCEDURAL BLANKS

Procedural blanks for trace metals analysis of demersal fish and macroepifaunal samples are prepared in an identical manner since the samples are analyzed in an identical manner. These samples are usually digested in groups of 15 to 30 samples. A procedural blank is prepared with each group of samples by adding to an empty beaker the same reagents that are added to the samples. The beaker is heated and cooled and otherwise treated in exactly the same manner as the samples in the group.

Average trace metal concentrations for 18 blanks are given in Table 41. The iron and lead concentrations are at least an order of magnitude smaller than those found in the samples. Cadmium, copper, and nickel levels in the samples are more variable, but for the most part are well above the blank levels. The chromium and lead concentrations in the samples are near the levels reported for the blanks.

Blank levels appear to be closely related to reagent lots. One lot of Ultrex grade nitric acid, for example, may be very "clean" with concentrations of the metals of interest well below specifications. While in the next lot of same reagent, several metals may be present in their maximum allowable concentrations.

MATERIALS

The nitric acid used in the trace metals analysis is J.T. Baker Ultrex Grade. Redistilled nitric acid supplied by the G. Frederick Smith Company of Columbus, Ohio shows blank levels equivalent to the Ultrex acid and is used in cleaning glassware and for digestion of some

TABLE 40

RESULTS OF TRACE METALS ANALYSIS
OF NBS BOVINE LIVER STANDARD

ELEMENT	BOVINE LIVER (NBS), ppm	BOVINE LIVER (ARLI)*, ppm
Cd	0.27 ± 0.04	0.34 ± 0.03
Cr	0.088 ± 0.012	0.06 ± 0.02
Cu	193.0 ± 10.0	184.0 ± 2.0
Fe	268.0 ± 8.0	263.0 ± 5.0
Ni	---	0.39 ± 0.07
Pb	0.34 ± 0.08	0.4 ± 0.1
Zn	130.0 ± 13.0	131.0 ± 2.0

*Average of 3 determinations + standard deviation

TABLE 41

BLANK LEVELS FOR TRACE METALS ANALYSES
(A Sample Weight of 1.00 g is Assumed)

ELEMENT	CONCENTRATION*, ppm	STANDARD DEVIATION, ppm
Cadmium	0.02	0.006
Chromium	0.16	0.09
Copper	0.24	0.15
Iron	1.51	0.72
Lead	0.2	0.07
Nickel	0.12	0.07
Zinc	0.8	0.30

*Average of 18 blanks

macroepifaunal samples. The 30% solution of hydrogen peroxide is reagent grade supplied in part by Mallinckrodt Chemical Company and in part by Fisher Scientific Company. Deionized water distilled in all-glass stills is used for diluting the digestate and in cleaning the glassware.

RESULTS

A total of 605 demersal fish and macroepifaunal samples for trace metals analysis have been received at ARLI from MAFLA Archives and Cruises DM I, DM II, and DM IV. Most of these samples were analyzed but some of them were pooled first in order to provide sufficient material for analysis. Some samples were not analyzed at all because the sample did not provide sufficient material. A complete list of these samples is given in Appendix 5-A along with an indication of the disposition of each sample. Table 42 summarizes the number of samples treated in each way. Note that only 69 samples were not analyzed. Of the remaining 536 samples, 108 were pooled to form 40 composite samples resulting in a further reduction in analyses completed.

Results of the analyses of individual samples were reported to the Data Processing Center at the New Orleans office of Dames & Moore as soon as they were completed. There the results were recorded on magnetic tape and will be on file at the National Oceanographic Data Center in Washington, D.C. Evaluation and interpretation of the results are to be done by a committee appointed for that purpose (see Chapter 6).

DISCUSSION

Since the generation of analytical data is the primary responsibility of ARLI in this project, it is appropriate to consider the quality of these data and to give some general impressions regarding the results. Some special problems will also be considered.

DATA QUALITY

The results of three determinations of the trace metals in the NBS Bovine Liver Standard were shown earlier in Table 40. The concentrations of six metals, cadmium, chromium, copper, iron, lead, and zinc measured at ARLI are in excellent agreement with the values reported for those metals by the National Bureau of Standards. The seventh metal, nickel, was not reported by NBS. The precision of these measurements, as indicated by the standard deviation, is as good or better than that reported by the NBS for the elements cadmium, copper, iron, and zinc. The concentrations of these elements are well above the detection limits for atomic absorption methods. The chromium and lead measurements shown less precision since their concentrations are approaching the detection limits of the instrument. Although the concentrations of the trace metals in the NBS standard is well above that found in many of the MAFLA samples, the same high degree of accuracy and precision seen in the NBS standard analyses can be expected in the MAFLA sample analyses.

TABLE 42

SUMMARY OF DISPOSITION OF MAFLA SAMPLES
RECEIVED AT ARLI FOR TRACE METALS ANALYSIS

SAMPLE TYPE	NUMBER SAMPLES RECEIVED	SMALL SAMPLES NOT ANALYZED	SMALL SAMPLES COMBINED	RESULTING POOLED SAMPLES	SAMPLES ANALYZED AND REPORTED
DEMERSAL FISH					
Archive	12	0	0	0	12
DM I	77	0	0	0	76*
DM II	77	19	2	1	57
DM IV	77	0	10	5	72
Subtotal	243	19	12	6	217
MACROEPIFAUNA					
Archive	108	20	0	0	88
DM I	148	27	96	34	59
DM II	54	2	0	0	52
DM IV	52	1	0	0	51
Subtotal	362	50	96	34	250
Total	605	69	108	40	467

*One sample lost during analysis

The MAFLA sample results themselves appear to bear out this expectation. The demersal fish samples, being nearly all of one species, show only minor variations from sample to sample for a given metal. On the other hand, the macroepifaunal samples, representing a variety of organisms, show wide variation in concentration of the various metals. Thus, we have similar metal contents for the similar demersal fish samples, but a variety of metal contents where these are a variety of macroepifaunal organisms.

REVIEW OF RESULTS

Although a detailed analysis and interpretation of the results is the work of the Trace Metals Committee, a preliminary survey indicates that the trace metal contents reported in this study are comparable to those reported in earlier MAFLA investigations. Values reported for demersal fish tend to be slightly lower, but of the same order of magnitude as earlier studies.

DEMERSAL FISH

These samples showed very low concentrations for all the metals reported. Cadmium, chromium, copper, nickel, and lead concentrations were almost always less than 1 ppm for archive samples as well as the DM cruises. Iron and zinc concentrations show wider variations, but very few samples exceed levels of 10 to 20 ppm.

MACROEPIFAUNA

These samples showed a wide range of values for the various metals. In this respect, the results resemble those reported in earlier MAFLA investigations. Despite the variations, there are some correlations that become evident in even a superficial survey. Many of the above-average zinc concentrations, for example, are found in a particular crustacean, Acanthocarpus alexandri. High cadmium levels are uniformly found in the mollusc, Spondylus americanus. A more detailed analysis of the data can be expected to reveal more complex relationships.

SPECIAL TOPICS

SAMPLE CONTAMINATION BY PARTICULATE FALLOUT

A series of tests designed to evaluate the risk of trace metals sample contamination from particulates in the laboratory atmosphere was carried out and reported during the month of September 1977. A copy of a complete report was included as Appendix H of the first quarterly report (Dames & Moore 1977c). This investigation involved exposing petri dishes containing 25 m of dilute nitric acid to the laboratory atmosphere for a period of one or four hours. Samples were collected both in the open laboratory and in the clean bench and hood where trace metal samples wuold actually be handled. These solutions were then analyzed by AAS. Results obtained showed trace metal levels that were lower in the clean bench and hood than in the open laboratory. But in all three locations, trace metal levels were quite low and of about the same order of magnitide as the precision that can be expected for AAS analyses. On the basis of these data, it was concluded that contamination would be minimal if the tissue

samples are prepared for acid digestion in the clean bench. This conclusion was strengthened by the recognition that the samples are exposed to the laboratory atmosphere for a much shorter time than the duration of the fall-out tests.

Results of sample analyses seem to support this conclusion. No evidence of gross contamination was observed. Many of the unusually high or low metal concentrations reported appear to be related to the type of organism analyzed.

UNDERSIZED SAMPLES

Some of the demersal fish and macroepifaunal samples received for trace metals analysis were too small to furnish sufficient tissue. The problem was most acute with the DM I samples, but was also present to some extent with the DM II and DM IV samples as well as with the archived samples from the summer of 1976. In order to understand how the problem arose and how it impacted the analytical process, it will be helpful to recall the sampling schedule for demersal fish and macroepifauna.

At one station, on each of seven transects of each of three benthic cruises, 11 specimens of demersal fish of species Syacium papillosum were collected. Each specimen was intended to supply 20 g of tissue for hydrocarbon analysis and 10 g of tissue for trace metals analysis. However, at ARLI, the specimens collected at some stations were found to be too small to furnish the necessary tissue for both analyses.

Because of the greater variety of organisms involved, the macroepifauna sampling schedule was somewhat more complex. Three different organisms were to be collected at each sampling station. On the summer 1977 (DM I) cruise, three separate specimens of each organism were to be collected and each individual specimen was to be analyzed for both hydrocarbons and trace metals. On the other two cruises, DM II and DM IV, several specimens of each organism could be pooled to make up the sample for that station. When the samples were received at ARLI, many of them, especially those from the DM I cruise, were too small to supply material for both hydrocarbon and trace metals analyses.

The Program Manager was informed of the problem in October 1977 and after a delay of more than a month seeking BLM approval, he directed that the following two-fold approach be followed in analyzing the undersized demersal fish and macroepifaunal samples. The first element of the approach would be to reduce the minimum sample size for hydrocarbon analysis from 20 to 10 g.

The second modification approved by the Program Manager set up an order of priority for sampling these undersized specimens. The tissue samples for both fish and macroepifauna were taken according to the following priorities.

a. When the specimen is large enough, separate tissue samples are taken for HMWHC and TM analyses.

b. When specimens are smaller, tissue from two or more specimens of the same species collected at the same station are pooled to provide sufficient material for both HMWHC analysis and TM analysis.

c. When the pooled tissue is insufficient for both analyses, HMWHC analysis is performed, if possible, and TM analysis is omitted.

d. When the pooled tissue is insufficient for HMWHC analysis, trace metals analysis only is performed.

e. When the pooled tissue is insufficient for either HMWCH or TM analysis, no further processing of the sample is done.

The approach gives some priority to hydrocarbon analysis and following it led to a 20% reduction in the number of trace metals analyses performed, as indicated in Table 42 (shown earlier).

Besides reducing the number of analyses, both hydrocarbon and trace metals, the undersized samples led to considerable additional paper work. This resulted because it was necessary to record which samples were pooled to form a composite and to assign a new identification number for each composite sample. The additional costs resulting from the reduction in sample numbers and the increased sample handling and record-keeping led to a modification of the total costs mid-way in the program.

Finally, the delay of over a month in seeking BLM approval of the plan for the undersized samples led to a schedule slippage which was not made up until the end of the trace metals program. A similar delay in the hydrocarbon program was never entirely overcome.

CONCLUSIONS

All but 69 of the 605 demersal fish and macroepifaunal samples received at ARLI for TM analysis have been analyzed by methods and procedures approved by the Bureau of Land Management. The 69 samples were not analyzed because of insufficient sample material. Of the 536 samples analyzed, 108 of them were pooled to form 40 composite samples since individual samples did not furnish sufficient material for individual analysis. Because some samples were not analyzed and some were pooled before analysis due to insufficient sample material, the number of reports submitted was reduced to 467.

The results appear to be comparable to those reported for earlier MAFLA studies. Detailed analysis and interpretation of the results is the task of the Trace Metals Committee.

The quality of the results is good as indicated by replicate analyses of NBS Standard material and by the internal consistency of the results

themselves. No evidence of gross pollution of samples by laboratory particulate fall-out was seen. This bears out the conclusion of preliminary studies in this matter.

The analyses were completed essentially on schedule. Some schedule slippage early in the program resulted from delays in securing BLM approval of the plan for processing undersized samples. This slippage was corrected by the end of the program.

REFERENCES

Anon., 1976. Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation, Norwalk, CT., Revised.

Anon., 1977. Analytical Methods Using the HGA Graphite Furnace, Perkin-Elmer Corporation, Norwalk, CT., Revised.

APPENDIX 5-1

INVENTORY AND STATUS OF MAFLA

SAMPLES FOR THE TRACE METALS ANALYSIS

CONTENTS

VOLUME II

CHAPTER 6

INTERPRETATION OF TISSUE TRACE METAL DATA

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INTRODUCTION

This report is a discussion of the trace metal (TM) analyses carried out by Analytical Research Laboratories, Inc. (ARLI) on demersal fish and macroepifauna collected in the MAFLA lease area. A complete listing of the results will be found in the Dames & Moore Data Tape. A detailed description of the analytical procedures can be found in the third quarterly report by ARLI (Dames & Moore, 1978e).

Seven metals were analyzed by atomic absorption spectroscopy: cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), and zinc (Zn). Two other metals, barium (Ba) and vanadium (V), were analyzed by neutron activation analysis, and are covered in the report by Shokes (Volume II, Chapters 4, 7, and 23). With the exception of Fe, all of the aforementioned metals can be considered toxic to varying degrees (Bowen, 1966). At the same time, Fe, Cu, and Zn are essential elements for most organisms (ibid.). Thus, the suite of metals selected by BLM for analysis contains elements whose augmented presence in the environment might prove detrimental, as well as elements which if withheld or made less "available," might also be of negative benefit to the local biological community.

Benthic biota are potentially valuable indicators of environmental perturbation because they both influence and are influenced by the interaction of two important oceanic geochemical reservoirs, the sediments and the water column. Geochemically important reactions largely take place at interfaces (Stumm and Morgan, 1970; Horne, 1978). In the benthic environment, the interface between water column and sediments is not a thin surface, but rather extends x cm below the surface in the "bioturbation" zone, and may be considered to extend upward into the near bottom nepheloid layer if it is present. In shallow areas where rooted macrophytes are found, the definition of an interface is further confused while at the same time increasing in surface area.

The inhabitants of the interface zone are thus subject to environmental changes which impact either the sediments and/or the water column, a situation which is most likely to occur in the event of OCS investigations for or procurement of oil and gas reserves. Changes in the water column might affect the coupling of the phytoplankton and zooplankton. This has been shown in the case of hydrocarbon release (Heinle and Vargo, 1977). This was followed by alterations in the benthic community (Grasle and Grasle, 1977). A restructuring of the benthic community would likely lead to a redistribution of TM in the various benthic biota reservoirs (Johnson, 1978). Thus, it is important in a benchmark study to not only document the TM content of benthic biota, but also to address the question of variability. The thrust of the subsequent discussion will be an attempt to deal with the variability of the 77-78 MAFLA biota TM data in a descriptive as well as a mechanistic sense.

RESULTS AND DISCUSSION

ANALYTICAL VARIABILITY

The first consideration is to determine how much of the observed variability of results is real or environmental, and how much can be ascribed to the analytical procedures. Unfortunately, the results presented here do not contain within them a convenient statistical basis for determining the variance. There are no sets of replicate analyses of the same sample material or matrix. The only replicate analyses were carried out on NBS-SRM (Standard Reference Material bovine liver), and on a series of procedural blanks. Because of the nature of the biota tissues analyzed, as well as probable real biological differences, consideration of the analytical uncertainty is different for the demersal fish samples and the macro-epifauna samples. Table 43 shows the comparison of NBS and ARLI results for analyses of NBS-SRM bovine liver along with an indication of about how much higher or lower the individual trace element concentrations of bovine liver are than the average MAFLA fish or epifaunal samples. Also included are the average and standard deviation of 18 procedural blank determinations based upon an assumed one gram sample. As can be seen, the estimate of actual uncertainty in the analytical results is somewhere between the CV% for bovine liver and the CV% as determined from the series of blanks, depending upon the sample size and the concentration in that sample. Table 44 lists the subjective compromise values for analytical uncertainty which have been used in this report. All error estimates are for one standard deviation.

TRACE METALS IN SYACIUM PAPILLOSUM

Figure 137 shows the weighted grand mean and weighted seasonal means for eight trace elements in the Dusky Flounder Syacium papillosum (skeletal muscle only). Barium and vanadium results are included in order to present a maximum comparison, but these elements will not be discussed in any detail here. Analyses for Pb are not included because >95% of the results were below the detection limit of 0.3 ppm (below 0.1 ppm in about 35% of the analyses).

One hundred ninety-three (193) specimens of Syacium were collected at 12 stations on cruises DM I, II, and IV. An additional 12 specimens of Monolene sessilicauda, another flounder, were obtained on one cruise. The chemical analyses of this species appear to coincide with Syacium and will not be discussed further. Seventy-two (72) fish analyses were carried out from seven stations in the winter, DM-IV; fifty-seven (57) from six stations in the fall, DM II; and sixty-four (64) from six stations in the summer, DM I.

The large number of replicate specimens collected at a variety of geographic locations in different seasons makes it possible to draw some conclusions about the TM distribution in this species and how it may relate to external environmental factors. This analysis is further aided by two fortuitous factors: the specimens analyzed for TMs were all large mature fish (130-170 mm) probably in their second year of growth (R. Shipp, personal communication). While these specimens were definitely biased toward the large side of the size frequency distribution (cf. histograms in

TABLE 43

COMPARISON OF ARLI AND NBS ANALYSES OF SRM BOVINE LIVER, AND COMPARISON OF TM'S IN BOVINE LIVER WITH LEVELS IN MAFLA FISH AND MACROEPIFAUNA SAMPLES

Element	NBS (ppm)*	ARLI (ppm)**	Liver (Fish)	Liver (Macroepifauna)	ARLI blank** n = 18
Cd	0.27 ± 0.04	0.34 ± 0.03 (9%)	~20	~0.5	0.02 ± 0.006 (30%)
Cr	0.088 ± 0.012	0.06 ± 0.02 (33%)	~0.3	~0.1	0.16 ± 0.09 (56%)
Cu	193 ± 10	184 ± 2 (1%)	~100	~20	0.24 ± 0.15 (62%)
Fe	268 ± 8	263 ± 5 (2%)	~30	~3	1.51 ± 0.72 (48%)
Ni	---	0.39 ± 0.07 (18%)	~1	~0.1	0.12 ± 0.07 (58%)
Pb	0.34 ± 0.08	0.4 ± 0.1 (25%)	~10	~1	0.2 ± 0.07 (35%)
Zn	130 ± 13	131 ± 2 (2%)	~10	~1	0.8 ± 0.3 (37%)

* Mean ± 1 S.D.

**Mean ± S.D. (C.V.%) (coefficient of variation)

TABLE 44

ESTIMATE OF COEFFICIENT OF VARIATION IN THE TRACE ANALYSIS OF MAFLA FISH AND MACROEPIFAUNA

Element	CV% for: Fish	Macroepifauna
Cd	30	10
Cr	50	35
Cu	10	10
Fe	10	5
Ni	15	20
Pb	-	25
Zn	5	5

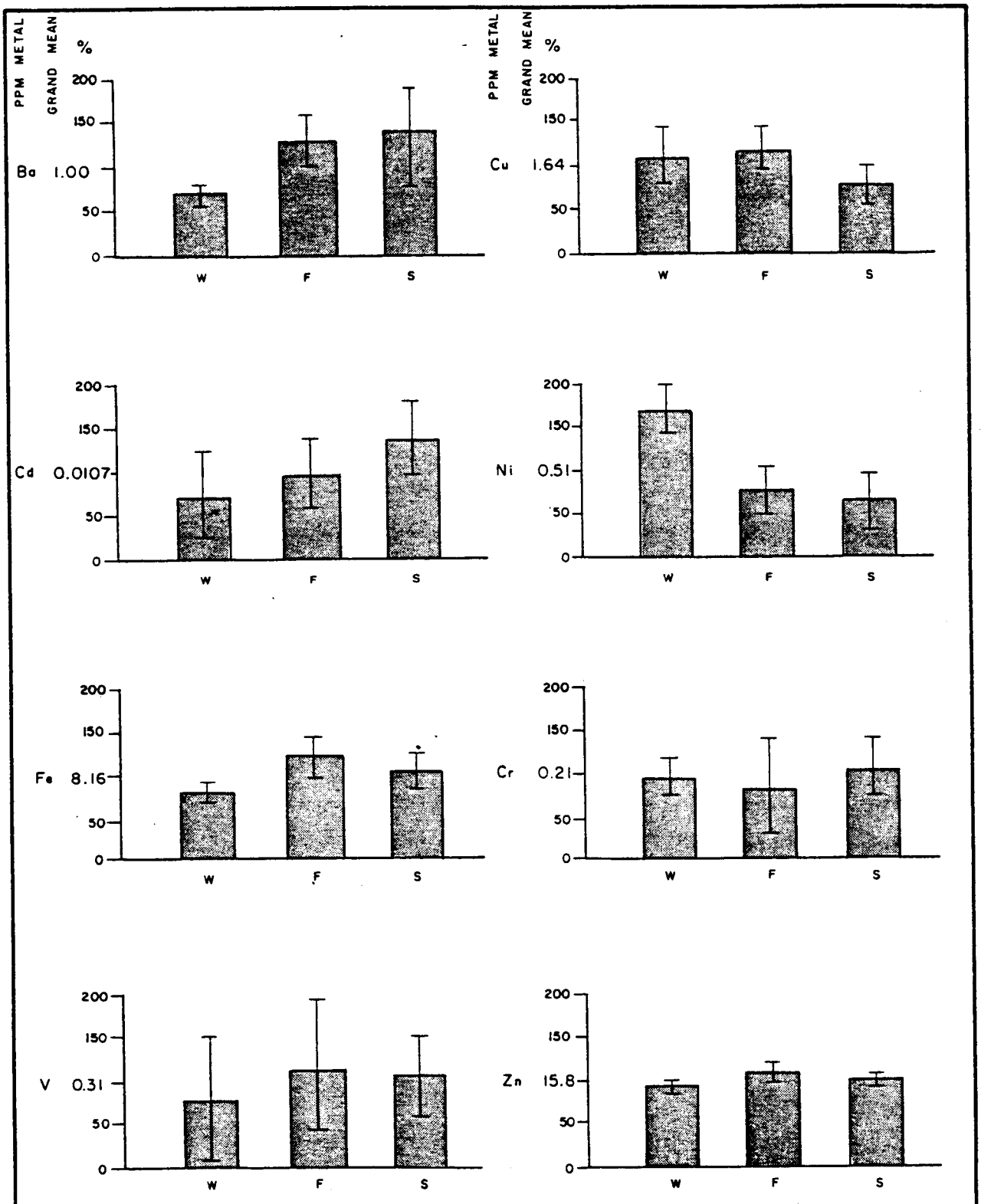


FIGURE 137

SEASONAL PLOTS FOR SYACIUM DM IV, II, I
TRACE METALS

Chapter 19), they eliminate some substantial portion of the variability in the results due to size differences. The other factor which helps in the interpretation of possible environmental effects on TM content is the small home range of the organism; probably this range is <10 km (R. Shipp, personal communication).

Cadmium in Syacium averaged 0.0107 ppm with a one-sigma coefficient of variation of about 45%. (About 30% to 40% of the Cd results were below detection limits (BDL) which varied from 0.006 to 0.02 ppm depending upon analysis conditions. In computing the weighted mean values, the BDL samples were assumed to have a value of 50% of the stated detection limit.) Thus, perhaps two-thirds of the observed variability is likely to be analytical in nature. In general, these results are about one order of magnitude (10x) lower than previous results for "flatfish" in the Gulf of Mexico (NMFS, 1975; Horowitz & Presley, 1977). As shown in Figure 137, there is a suggestion of a seasonal trend with Cd decreasing from summer, through fall, to winter. Some stations showed more seasonal variation than others. The maximum effects were shown at Stations 0005 and 2209 with >50% decline from fall 1977 to winter 1978.

Chromium averaged 0.21 ppm $\pm$ 0.07 (32%) with very little, if any, in the way of seasonal trends. The observed variation can be entirely accounted for on the basis of uncertainties inherent in the analytical procedures. The MAFLA samples are five times lower than NMFS (1975) compilations, and about 20 to 30 times lower than the results of Horowitz and Presley (1977).

Copper values for Syacium show good agreement with results cited in the two previous works, averaging 1.64 ppm $\pm$ 0.38 (23%). Figure 137 shows indications of a reverse seasonal trend with Cu being lowest in summer and highest in fall and winter. However, the variation is only about twice the analytical variation.

Iron in Syacium from the MAFLA area is about one-half that found in flatfish in the Western Gulf of Mexico (ibid.). The results presented here average 8.16 ppm $\pm$ 1.6 (19%), again with approximately one-half of the variability being analytical. Like Cd, Fe shows the lowest values in the winter, though the differences are not great (<20% cf. Figure 137).

Nickel averaged 0.51 ppm $\pm$ 0.14 (27%), lower than values cited by Horowitz & Presley (1977), but comparable to NMFS (1975) values. Over half the variation is analytical, but Ni shows one of the strongest seasonal trends. Like Cu, it is higher in winter than in fall and summer. Interestingly enough, Station 2209 shows the maximum seasonal effect with a five times increase from DM I to DM IV, a period of only about eight months.

Zinc shows the least variation of all the metals studied and it is ascribed the lowest analytical variation (5%). Average Zn values were 15.8 ppm $\pm$ 1.2 (8%) and agree well with the two cited references.

NATURAL VARIABILITY OF SYACIUM TRACE METAL CONTENT

As the previous section shows, something less than 50% of the variation in trace metal content of S. papillosum can be ascribed to natural causes. The natural variability is some complex function of size, diet, geography, season, and non-diet (or physical) water column inputs. All of these parameters appear to be confounded with the physiological state of Syacium as well as that of its diet organisms. We have some access to geographic and possible seasonal effects from the MAFLA samples owing to the large number of specimens collected. Possible non-diet effects might be related to sediment chemistry and the composition of the suspended particulates. Analyses of selected macroepifauna may provide some hint about changes in the composition of what Syacium eats. These latter data will be discussed in a subsequent section.

Seasonal variability in the Syacium trace metal data are indicated in Figure 137. Three types of trends are apparent, though in only two cases do the one-sigma error bars not overlap their neighbor. Ba, Cd, Fe, and V all show winter values which are smaller than those obtained in the summer. The trends for Ba (60% to 130% of mean value) and Cd (70% to 135%) are the most pronounced. Fe and V show slight maxima in fall instead of summer. The range of variation for Fe is quite small (82% of mean to 120% of mean) as is that of V (80% to 115%). Vanadium also has the highest uncertainty in the mean values by season.

Copper and nickel illustrate a seasonal variation which is directly opposite to the Ba-Cd group. Nickel is substantially high in winter than in summer (165% of mean to 65% of mean). While copper is less intense, minimum values are also observed in the summer.

Chromium and zinc show the least seasonal variation, and might be classified as having "neutral" trends.

The Ba and Cd trends of being low in winter may be realted to changes in the TM content of the food organisms, a subject which will be discussed later. Copper is an essential micronutrient and may show a buildup in body tissues owing to a decline in metabolic rate in winter if copper excretion biochemistry is more affected than copper intake. The chemistry of Ni is similar to Cu, which is about as good a clue to nickel biochemistry as is available. The "neutral" trends of Cr and Zn may be related to active internal concentration regulation. Such processes have been indicated for mulluscs (Sheldon Pratt, personal communication) in the case of zinc.

Geographic variation in these trace metal in fish data was addressed through a Bray-Curtis Q-mode cluster analysis. In this treatment Ba, Pb, and V are eliminated, so that the station similarities reflect only Cd, Cu, Cr, Fe, Ni, and Zn. Figure 138 shows the result of ordination in two dimensions. Nine of the stations fall into clusters indicated as B, C, and E. These designations are the same as those for the partial-digest trace metal in sediment clusters which, remarkably, plot in these same clusters. This suggests that the "available" TMs in sediments are somehow related to the TM content of Syacium muscle tissue.

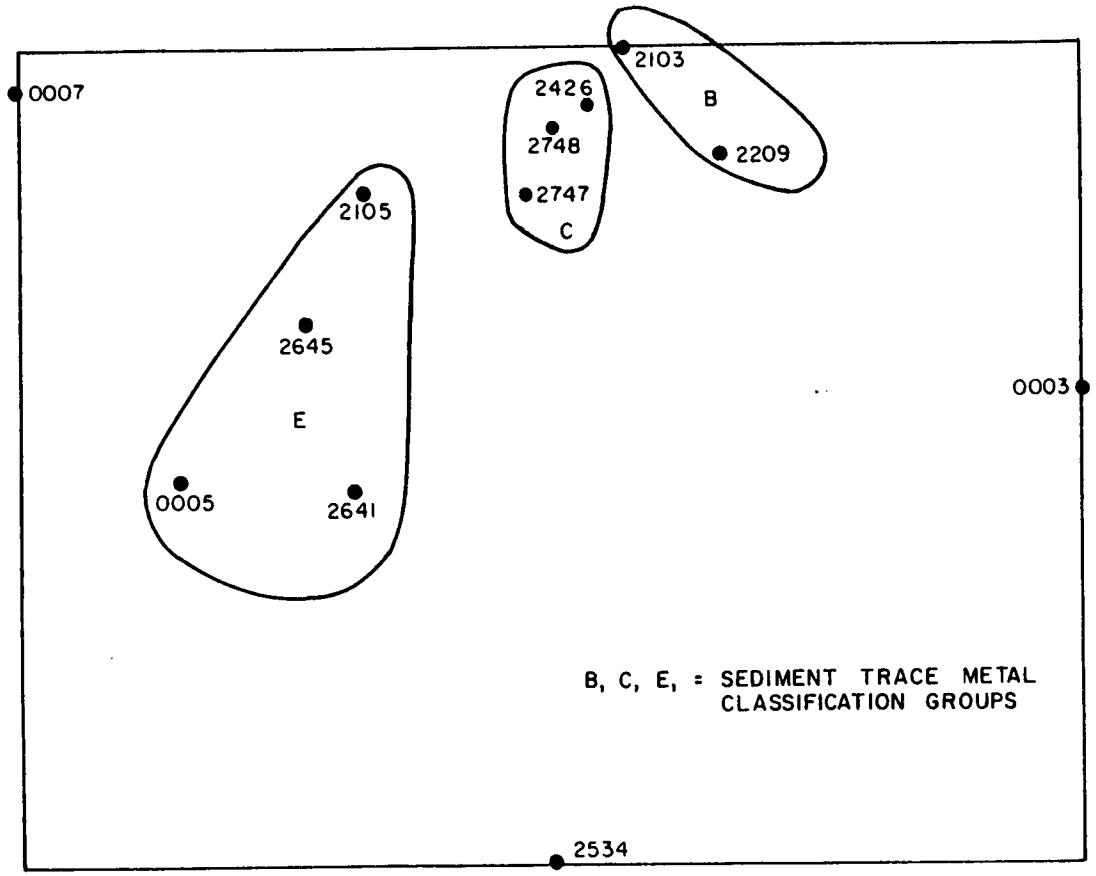


FIGURE 138

BRAY CURTIS Q MODE CLUSTER OF 6 TRACE METALS IN SYACIUM PLOTTED IN ORDINATION

A similar cluster analysis was attempted with the inclusion of Ba and V, but the resulting clusters did not bear such straightforward relationships to the partial-digest TM in sediment clusters. Apparently Ba and V in Syacium behave in a manner different from the other six metals studied.

When the individual metal mean concentrations in Syacium at each station are plotted against an X-axis Bray-Curtis ordination, the curves fall into two families. Figures 139 through 143 (for Cd, Ba, Fe, Cr, Zn) all show a positive slope with respect to the one-dimensional ordination of relative TM similarities between stations. (Note that both Ba and V were plotted on the station ordination derived by not including them.) Figures 144 and 145 for Cu and Ni show trends which are opposite to those of the Ba and Cd group. Figure 146 for V appears to be nondeterminate.

Thus, the geographic station clustering for metals in Syacium provides the same metal behavior groupings as did the seasonal variation plots; Ba and Cd low in winter with positive slope vs. station ordination, and Cu and Ni high in winter with negative slopes vs. station ordination. There is no obvious reason for this comparative grouping. The data are not available for Syacium in order to determine differences in seasonal TM behavior at different stations. However, the mean seasonal trends and the geographic clustering suggest that seasonal differences are geographically distributed.

TRACE METALS IN MAFLA MACROEPIFAUNA

Over 240 specimens comprising some 60 species of organisms were analyzed for Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Table 45 presents a summary of these data as mean values and includes the range. The groupings, which account for more than 95% of all MAFLA macroepifauna analyzed, are arranged in approximate order progressing up the food chain. The sponges are filter feeders, as are for the most part the clams and scallops. Snails are included in this second group in order to keep them with the rest of the molluscs even though they are scavengers. Shrimp are next, utilizing both filter feeding and deposit feeding. These are followed by sea urchins, sand dollars, and then the starfish, the last group being both deposit feeding and carniverous. The final group is made up of crabs and lobsters, which are predators who may also deposit-feed. The underlined names serve to identify the entire groupings as they may be used in subsequent discussion.

The TM data are also plotted by metal against the six groupings. These data are shown in Figures 147-149. An internal comparison of the data by generic grouping and an evaluation of the results relative to other TMs in biota studies follows here on an element-by-element basis.

Cadmium was less than 1 ppm, on average, in the sponges, shrimps, urchins and starfish. High concentrations were found in the clam group with a substantial contribution coming from the scallops Aequipecten (66 ppm) and Argopecten (9.4 ppm), as well as the clam Spondylus (15.7 ppm). Similar cadmium concentrations in molluscs were found in the previous MAFLA study (Betzer & Sims, 1976). In general, molluscs tend to be high in Cd with scallops being particularly good at concentrating this element (Segar et al., 1971).

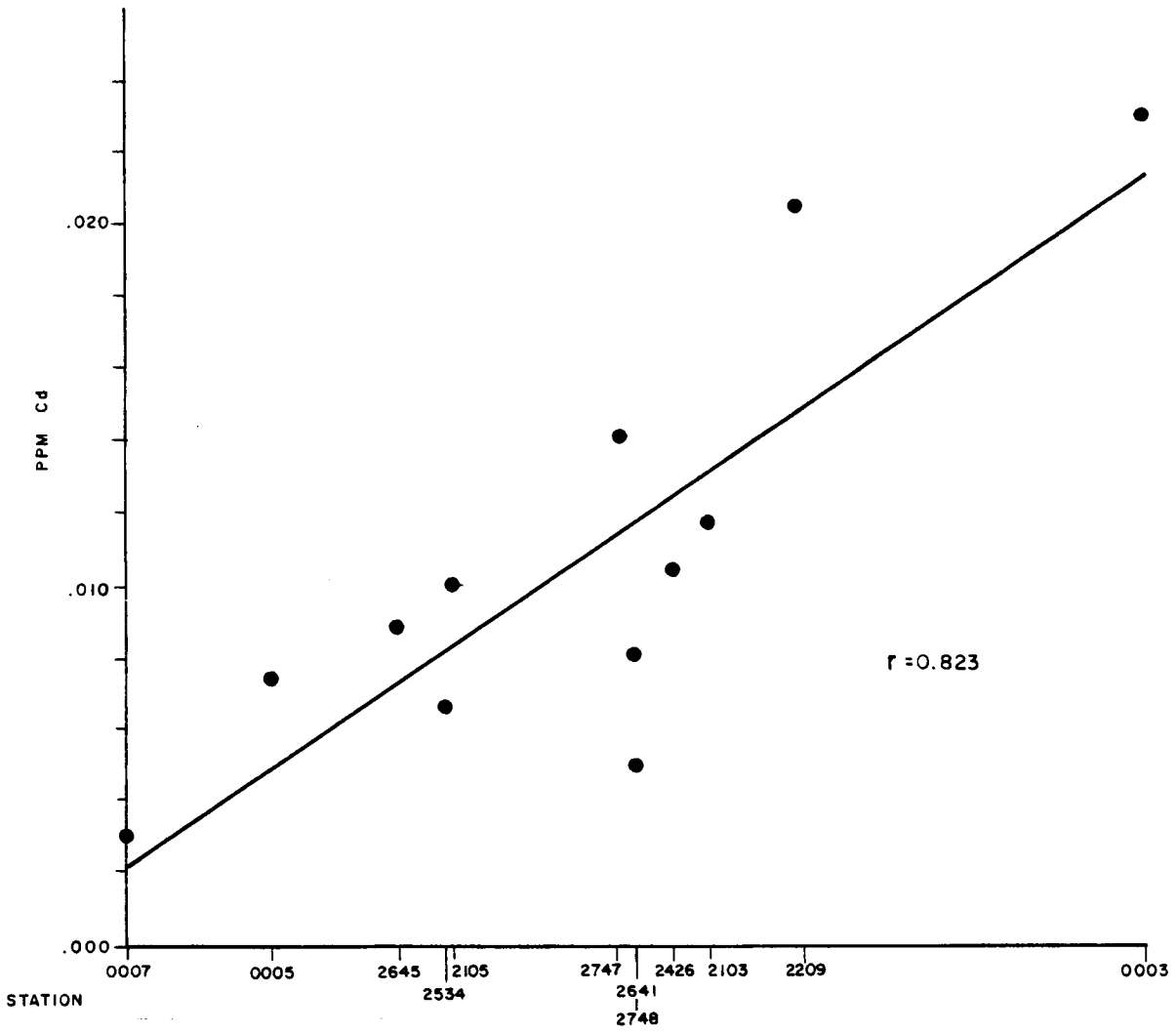


FIGURE 139

MEAN Cd IN SYACIUM VS STATION
BRAY CURTIS Q MODE

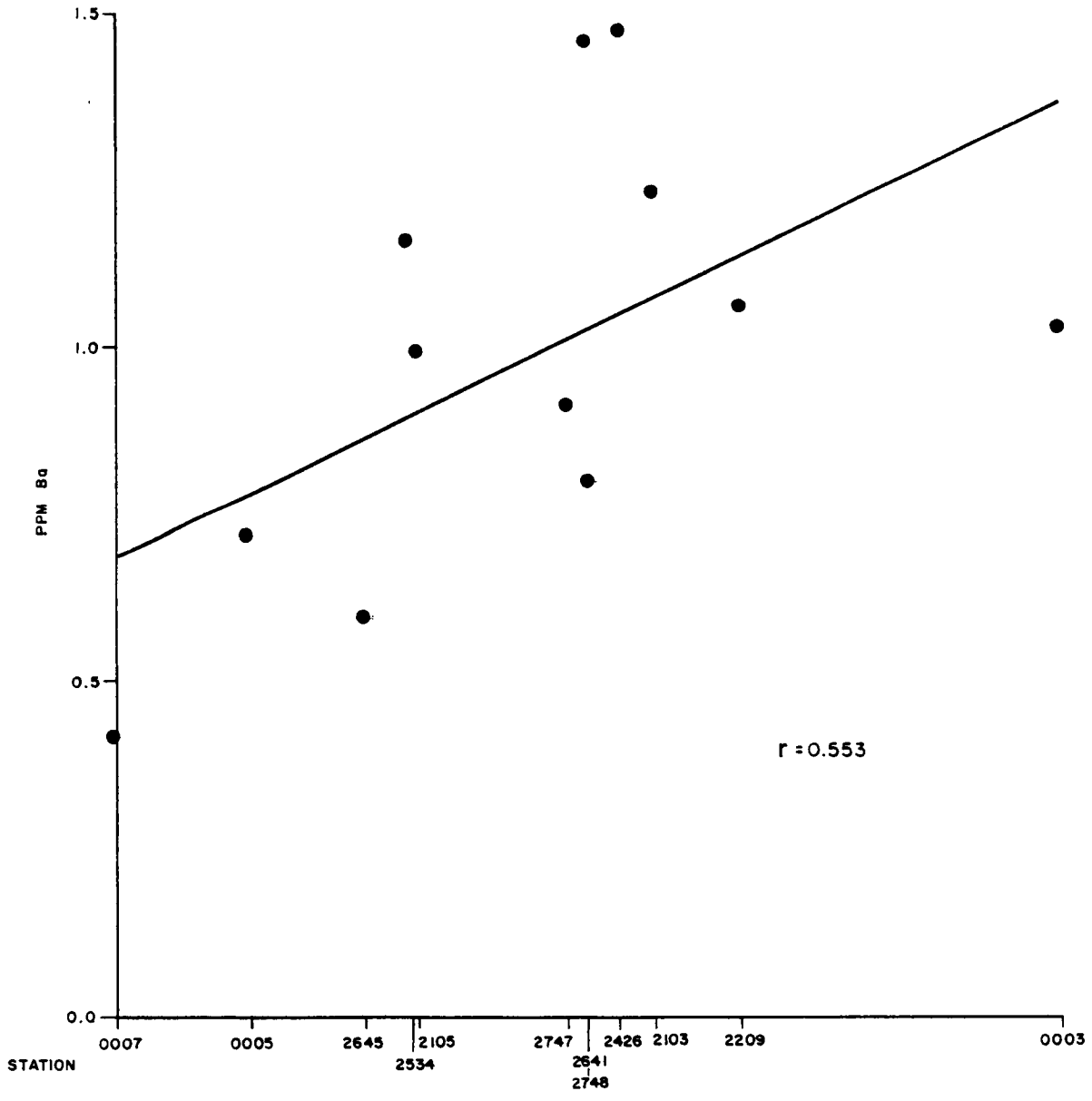


FIGURE 140

MEAN Ba IN SYACIUM VS STATION
BRAY CURTIS Q MODE

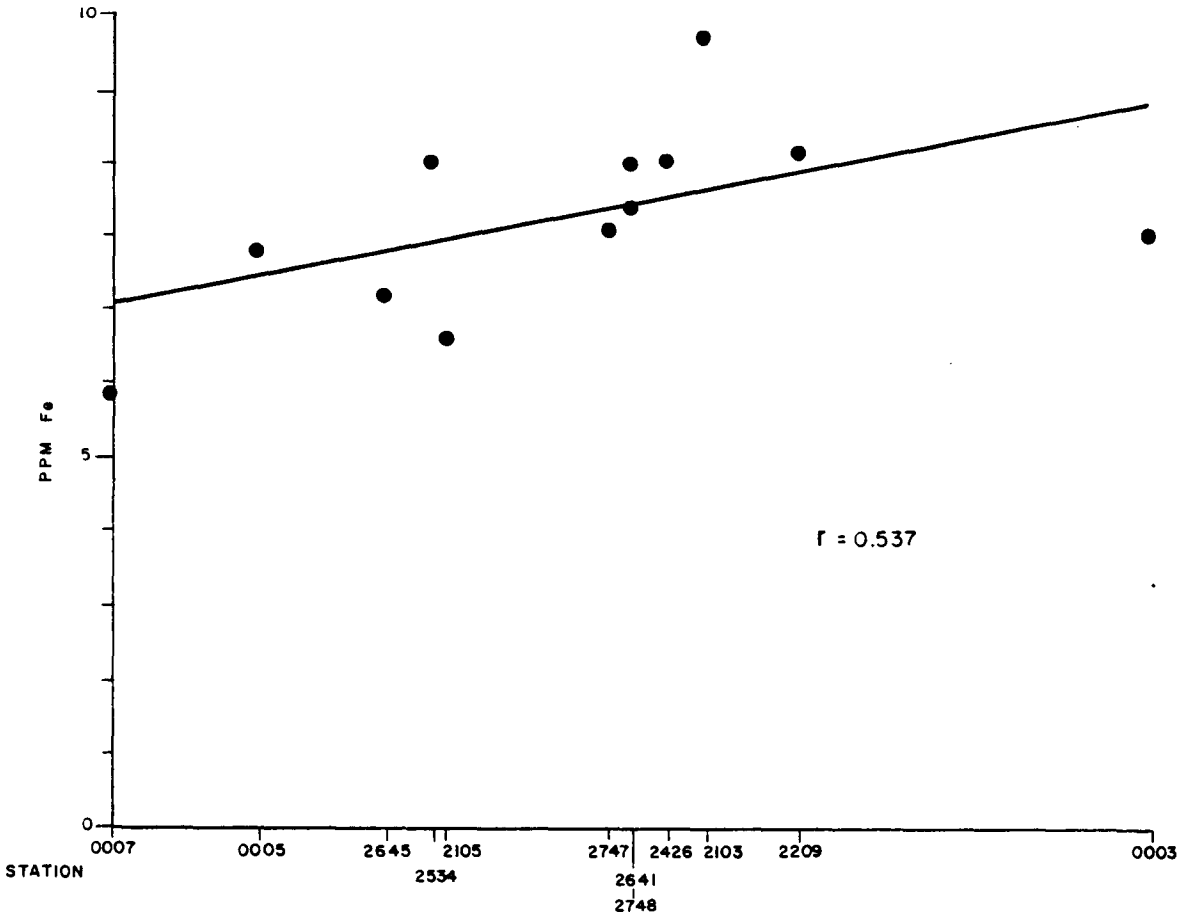


FIGURE 141

MEAN Fe IN SYACIUM VS STATION
BRAY CURTIS Q MODE

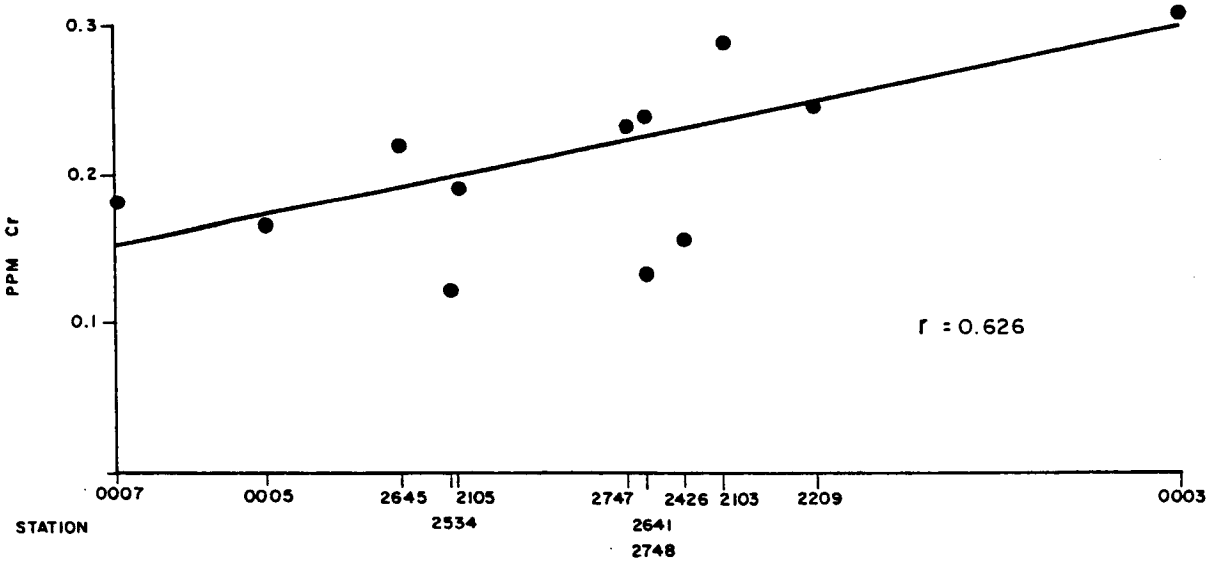


FIGURE 142

MEAN Cr IN SYACIUM VS STATION

BRAY CURTIS Q MODE

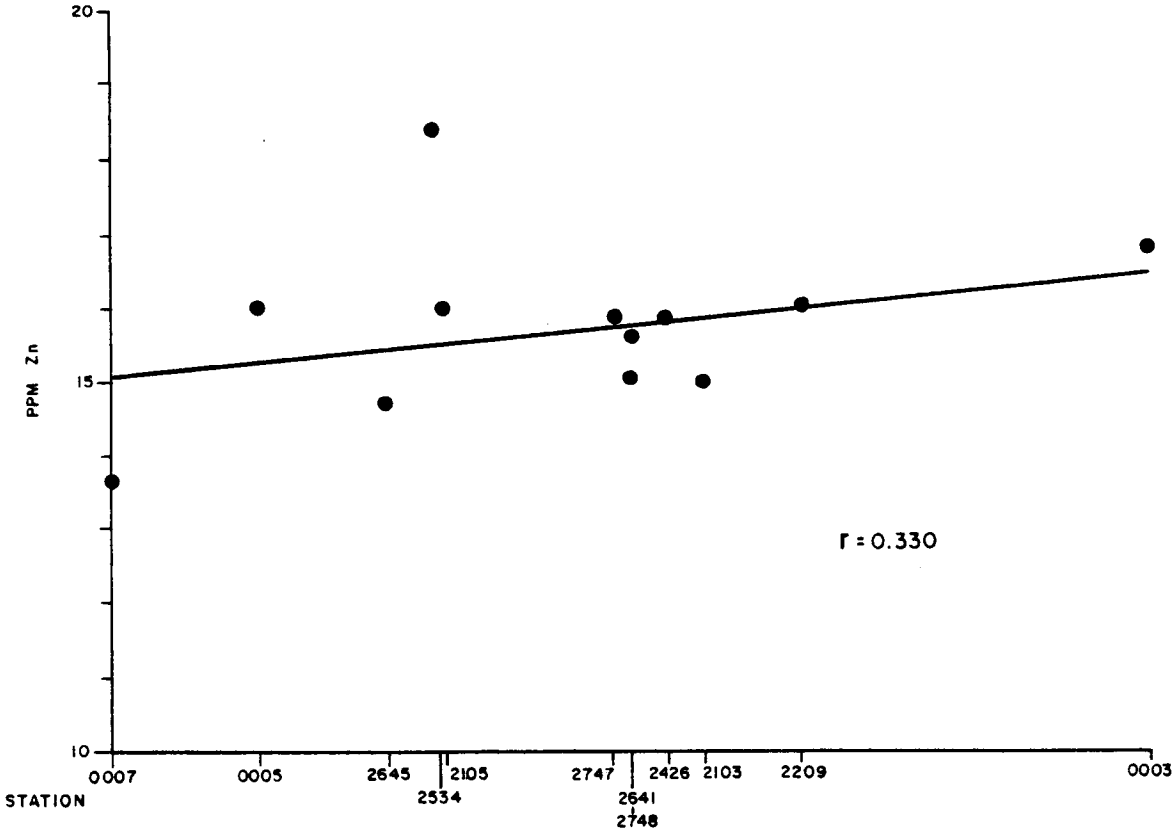


FIGURE 143

MEAN Zn IN SYACIUM VS STATION
BRAY CURTIS Q MODE

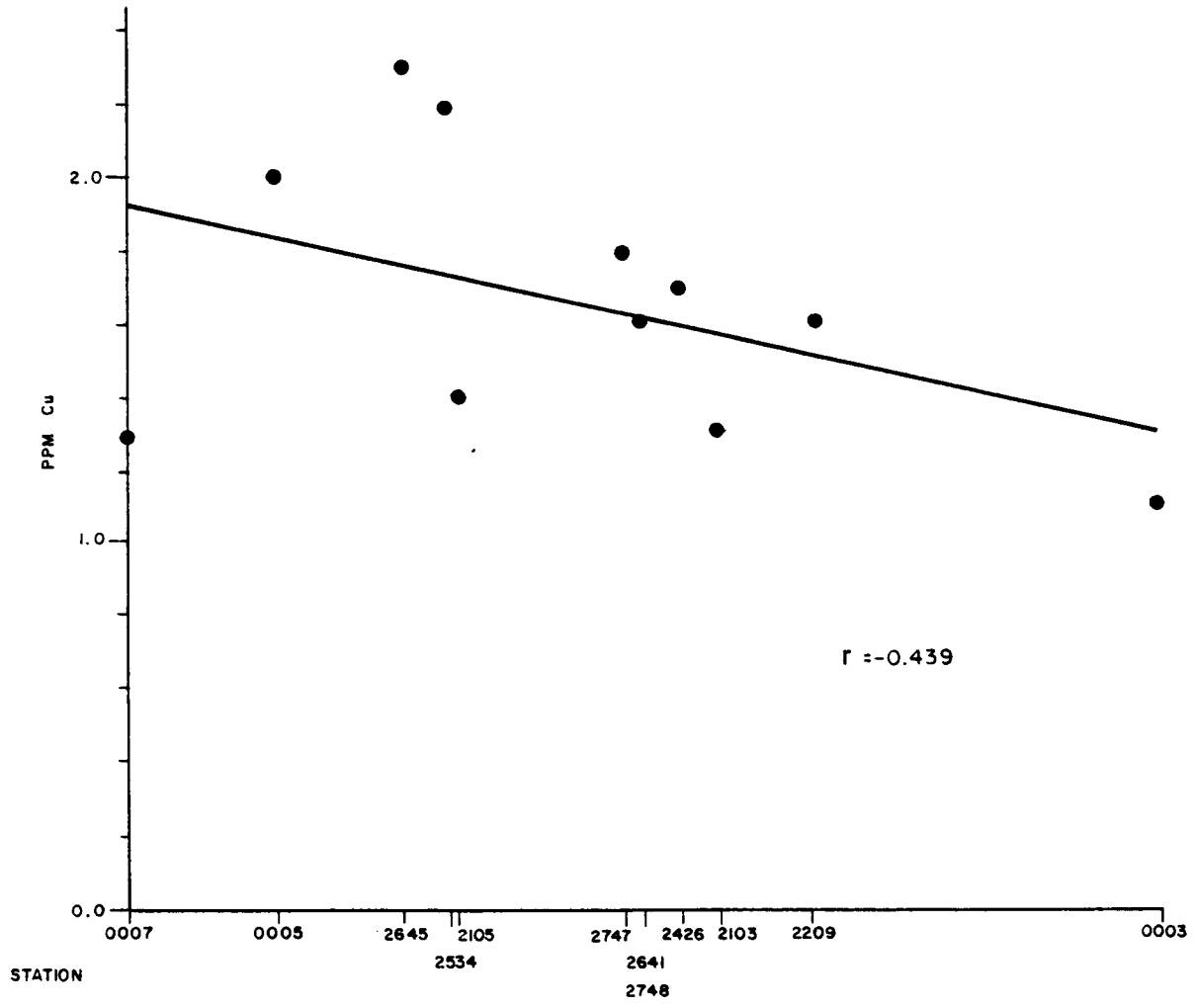


FIGURE 144

MEAN Cu IN SYACIUM VS STATION
BRAY CURTIS Q MODE

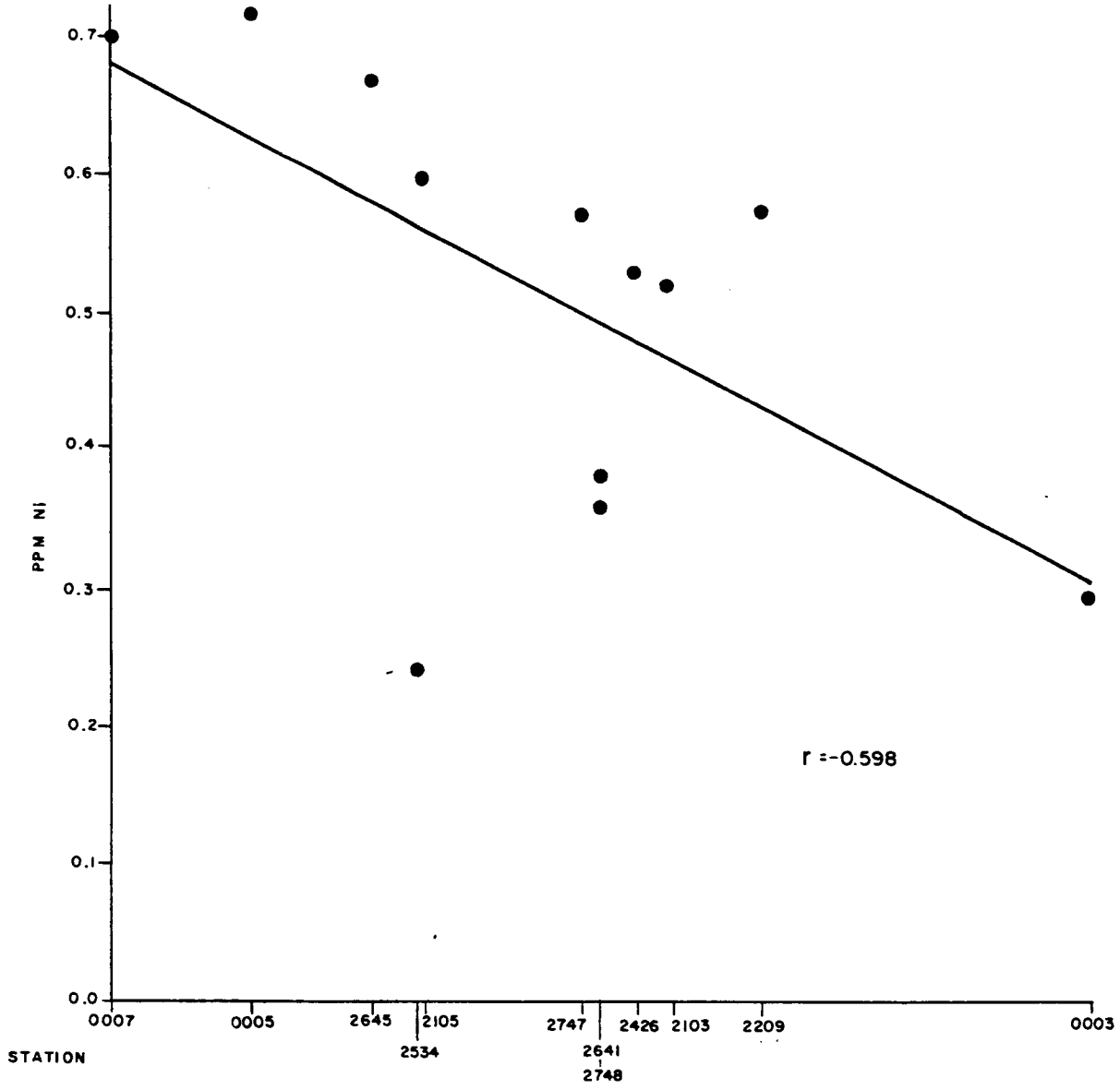


FIGURE 145

MEAN Ni IN SYACIUM VS STATION
BRAY CURTIS Q MODE

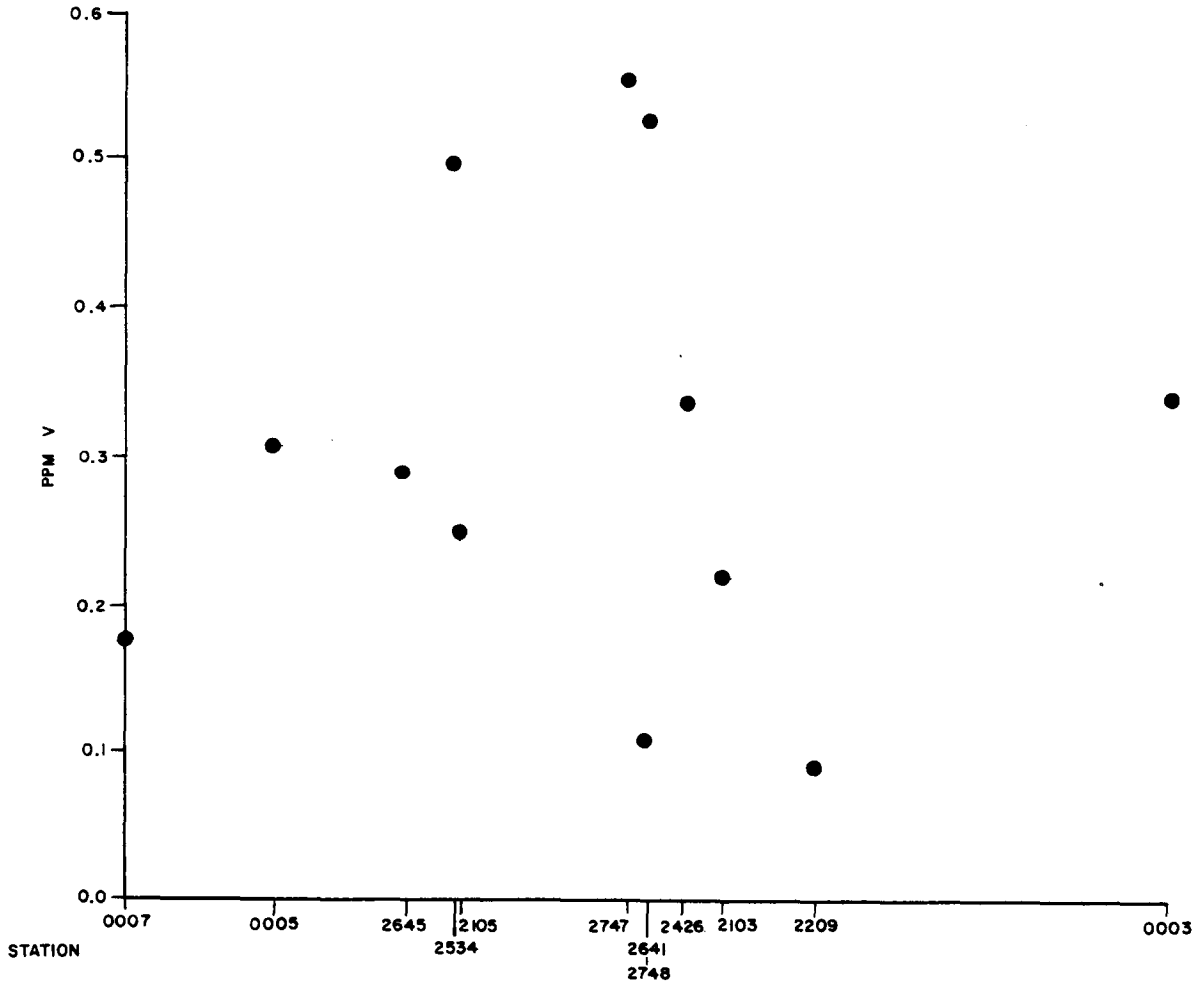


FIGURE 146

MEAN V IN SYACIUM VS STATION
BRAY CURTIS Q MODE

TABLE 45

MEAN, STANDARD DEVIATION, AND RANGE OF TRACE METAL CONCENTRATIONS FOUND IN VARIOUS GROUPS OF MAFLA MACROEPIFAUNA SPECIMENS

Sponges	0.82* ± 1.25	0.94 ± .75	5.7 ± 4.0	91.5 ± 92	9.7* ± 4.5	0.43 ± .33	14.0 ± 7.4
n = 28	0.02 - 3.8	0.42 - 2.7	1.2 - 13.3	34 - 314	0.2 - 13.9	0.00 -1.00	7.0 - 29.4
Clams	13.7[1] ± 7.2	3.4 ± 2.3	4.3[2] ± 1.05	90.1 ± 36.9	2.4* ± 2.2	0.83 ±1.18	163 ± 61
n = 18	0.36 - 18.4	0.36 - 6.5	3.6 - 5.7	10.4 - 110	0.6 - 5.5	0.2 - 3.4	39 - 205
Shrimp	0.42* ± .36	0.21 ± .19	32.5 ± 13.8	17.0 ± 17.4	0.81 ± 1.18	0.067 ± .001	48.6 ± 13.1
n = 45	0.06 - .88	0.04 - .51	22.8 - 60.0	3.4 - 51	0.1 - 3.3	0.0 - 0.3	39.3 - 74.6
Sea Urchins	0.56 ± .30	2.00 ± 1.07	5.57 ± 1.8	128 ± 89	0.51 ± 0.19	0.39 ± 0.37	14.7 ± 9.5
n = 48	0.065 - .94	.6 - 3.3	2.8 - 8.2	29 - 292	0.05 - 0.6	0.0 - 1.1	3.2 - 31.1
Starfish	0.99* ± 1.5	2.13 ± 1.49	8.03 ± 4.95	43 ± 16	0.48[3] ± 0.16	0.37 ± 0.16	37.7 ± 18
n = 38	0.54 - 5.0	0.4 - 4.9	4.6 - 19.6	16 - 65	0.2 0.6	0.22 - 0.70	11.3 - 66
Crabs	3.45[4] ± 5.0	0.83 ± 0.79	39.5 ± 42.6	50 ± 52	0.77 ± 0.32	0.18 ± 0.14	48* ± 34
n = 60	0.2 - 15.3	0.14 - 2.52	11 - 140	6.5 - 164	0.15 - 1.11	0.0 - 0.4	24 - 124

* reject one outlier

1 The scallop Aequipecten was excluded from the mean. Its [Cd] was >60 ppm.

2 The two snails Tugurium and Murex were excluded from the mean for Cu only.

3 Apparently a bimodal distribution. The three high species 4.3 (n=8), 10.8 (n=1), and 13.1 (n=1) were excluded from this mean.

4 There were two high outliers, Iliacantha and Scyllarus which could not be excluded on the basis of a Q test (Dean & Dixon, 1951).

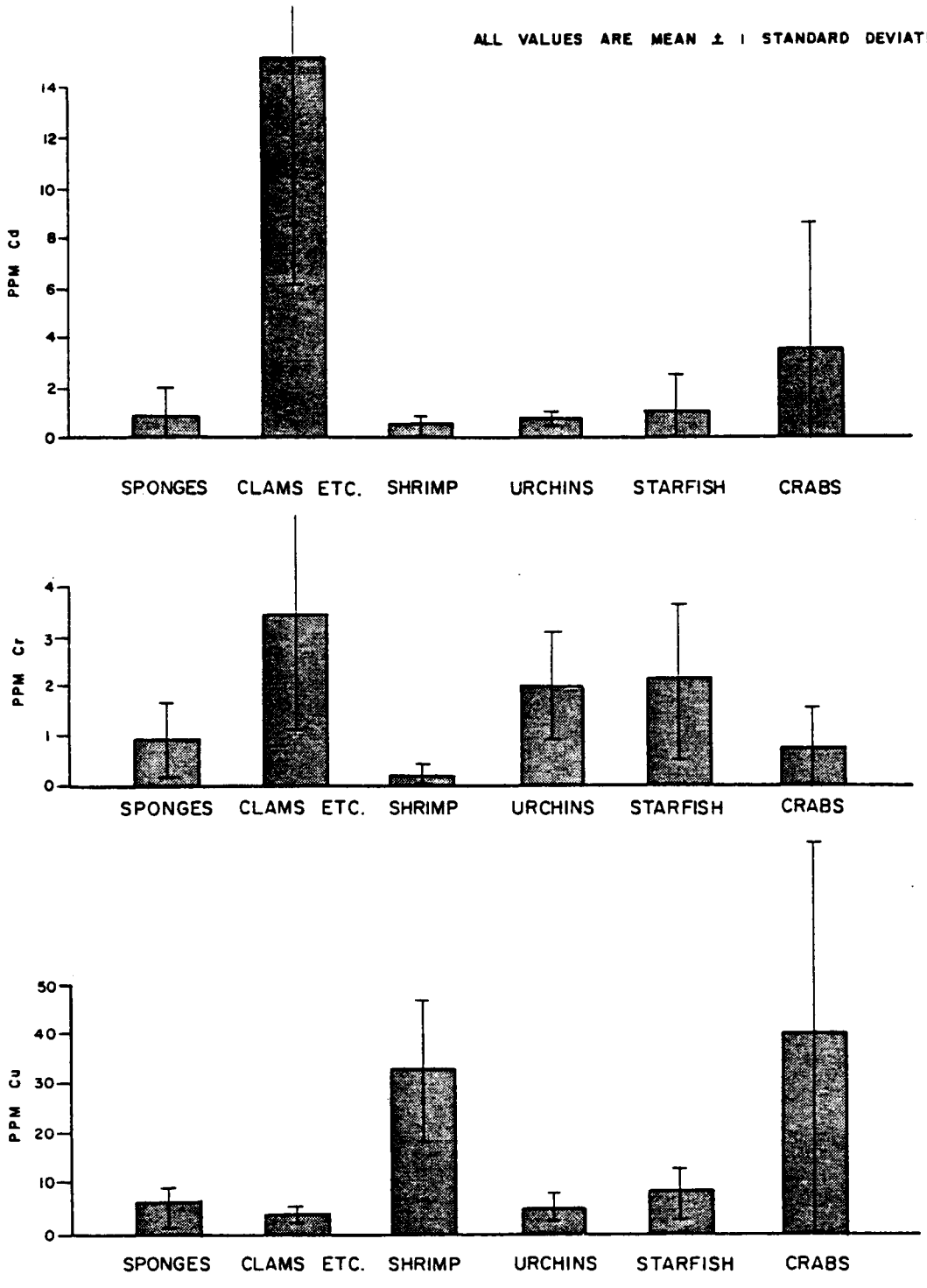


FIGURE 147

DISTRIBUTION OF TRACE METALS BY MAJOR TAXONOMIC GROUP
CADMIUM, CHROMIUM AND COPPER

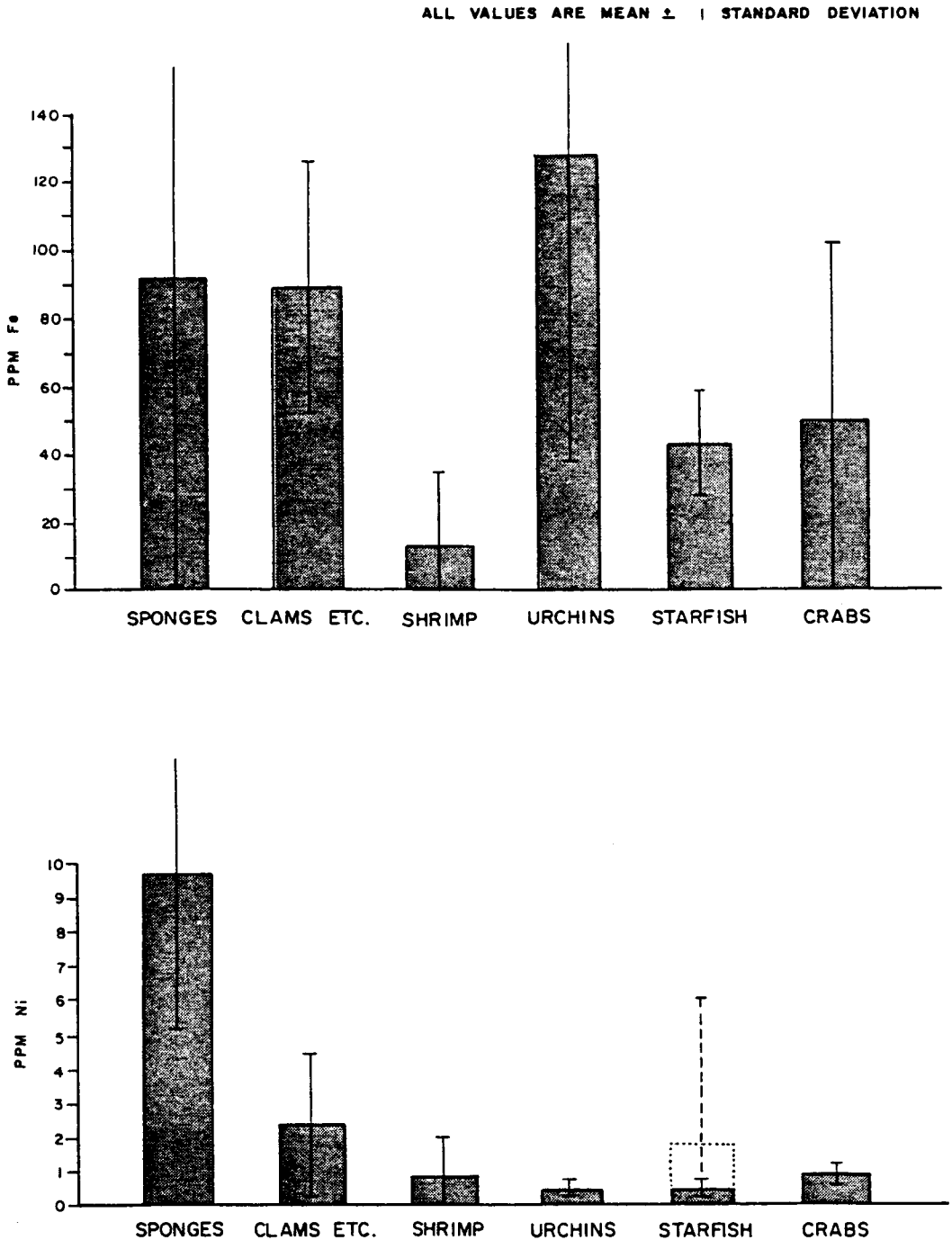


FIGURE 148

DISTRIBUTION OF TRACE METALS BY MAJOR TAXONOMIC GROUP
IRON AND NICKEL

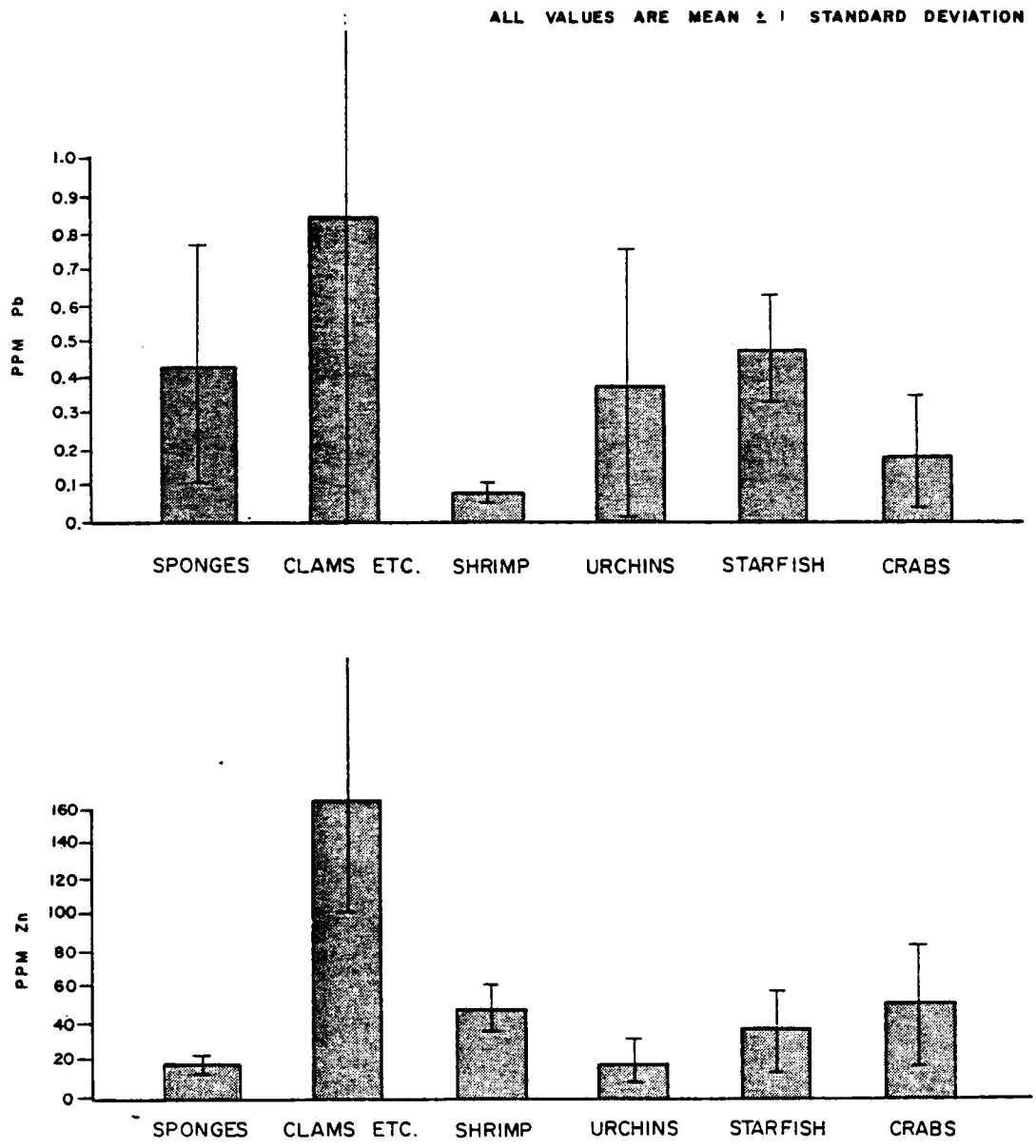


FIGURE 149

DISTRIBUTION OF TRACE METALS BY MAJOR TAXONOMIC GROUP
LEAD AND ZINC

The MAFLA (77-78) sponge samples are about a factor of three lower than those Cd concentrations found by Betzer & Sims (1976). The sea urchin class and the starfish have Cd values similar to the prior MAFLA samples (Betzer and Sims, 1976) and are in agreement with values of Segar et al. (1971). In the crustaceans, the present MAFLA values for shrimp are quite low, and in agreement with values of Horowitz and Presley (1977) and Shokes (1978). The crab group, on the other hand, shows distinctly higher Cd values, more like the previous MAFLA results of Betzer and Sims (1976). The crabs are generally higher up the food chain than are the shrimp which might account for the increase in the former group. The results of Betzer and Sims (ibid) included both shrimp and crabs and averaged 1.8 ppm Cd as compared to 2.1 ppm Cd in the present study if a weighted mean of shrimps and crabs is used.

The analyses for chromium range from a low of 0.2 ppm for the shrimp group to 3.4 ppm for the molluscs. Again, the sponges are lower than the previous MAFLA samples by about four times, whereas, the echinoderm groups are higher than the 1976 MAFLA samples by about three times. No comparisons with Segar et al. (1971) are possible as they found Cr to be below their detection limits in echinoderms. Thus, the present Cr values for MAFLA starfish, sea urchins, and sand dollars should be viewed with caution. They may be high by two to three times.

Chromium in the crustaceans and the molluscs shows comparable values to the 1976 MAFLA data with the molluscs being the group with the highest values though the results of Segar et al. (1971) are considerably lower (different species). Values for the shrimp are lower (5 to 10 times) than those of Horowitz and Presley (1977), but higher than those of Shokes (1978). As with the Cd, the crabs are higher than the other crustaceans examined. With the exception of the sponges, it appears that the 1977-1978 MAFLA maceoepifauna samples are higher in Cr than are other comparable specimens.

Copper results for the 1977-78 MAFLA project compared very well with the 1976 results reported by Betzer and Sims (1976). Naturally, the crustacean groups showed the highest values as copper is used in the blood as hemocyanin. The crabs Iliacantha (140 ppm) and Paguristes (122 ppm) had the highest values. Also note that the two species of snails, Murex beauii (62 ppm) and Tugurium caribaeum (35 ppm), were eliminated from the mean values computed for molluscs (Table 45). The results for Cu in shrimp agree well with Gulf of Mexico data of Horowitz and Presley (1977) and Shokes (1978). The mollusc (excluding snails) data and the echinoderm results are similar to values quoted by Segar et al. (1971), but slightly higher than the Southeast Atlantic data quoted by Windom & Betzer (1978).

Iron shows a wide range of values, being highest in sponges, molluscs and sea urchins. One sea urchin, Araeosoma violaceum (452 ppm) was eliminated from the computed means for this echinoderm group. Sea urchins seem to concentrate iron to a high extent. One species reported by Segar et al. (1971), Echinus esculentus, had a concentration of 22,000 ppm in the intestines, though other tissues were 1,000 times lower.

As in the 1976 MAFLA study, Fe was high in the sponges, though the present data are about 5 times lower than the results of Betzer & Sims (1976). Fe values in the molluscs, however, are virtually identical in the 1976 and 1977/78 studies. Values for Fe in the shrimp and crabs of the present study are lower by about 3 times than the 1976 data. The present data on shrimp are comparable to those of Horowitz and Presley (1977) and only slightly lower than results of Shokes (1978).

Nickel shows the same biota group trends for the 1976 MAFLA study and the 1977-78 study, that is, highest in sponges, next highest in the molluscs, and lower in all the other groups. However, in both the sponges and the clams, the 1977-78 data are about 5 times lower than the previous results and are in general agreement with data of Segar et al. (1971). The 1976 and 1977-78 results for Ni in crustaceans and echinoderms are in good agreement. In particular, the shrimp values are about one-half those reported by Horowitz and Presley (1977), but are about 5 to 10 times higher than the results of Shokes (1978).

The results for Pb are quite as variable as those for Fe, with a low mean of 0.07 ppm for the shrimp and a high mean of 0.83 ppm for the molluscs. With the exception of the molluscs, all of the 1977-78 lead data are 2 to 3 times lower than the 1976 data. The mollusc data for the two studies are virtually identical. The mollusc data of Segar et al. (1971) are quite variable, but also 2 to 5 times higher than the results reported here.

For shrimp, the 1977-78 MAFLA biota with the lowest Pb values, the results are lower than the data quoted by Windom and Betzer (1978) and much lower (10 to 30 times) than the results of Horowitz and Presley (1977). The data of Shokes (1978) are comparable to the present results. Again, the crabs, which are higher up the food chain than are the shrimp, show higher mean values for Pb.

Not many comparative data on Pb in echinoderms exist. All of the data of Segar et al. (1971) are higher by 2 to 5 times, while the data for Asterias forbesii (Windom and Betzer, 1978) are lower by about two times.

Zinc shows a relatively uniform distribution within the six groups of organisms presented here (15 ppm to 50 ppm) except for the mollusc group which averages over 160 ppm. This is the same general trend as the data of Segar et al. (1971). Molluscs apparently concentrate Zn and have some ability to regulate their internal concentrations independent of the substrate (S.D. Pratt, personal communication).

For shrimp, the zinc data are comparable to the other Gulf of Mexico studies by Horowitz and Presley (1977) and Shokes (1978). The Atlantic data in Windom and Betzer (1978) are somewhat higher.

For echinoderms, the present results compare well with Segar et al. (1971) and Windom and Betzer (1978). For the crabs, however, the Gulf of Mexico data are about 3 times lower than the Atlantic data of Windom and Betzer (1978).

INTERACTION OF SYACIUM WITH MACROEPIFAUNA, SEDIMENT, AND THE WATER COLUMN

All of the seasonal trends in individual TM content of Syacium shown in Figure 137 are significant at the 0.01 level. While the metal contents of individual replicate specimens appear not to be normally distributed, the test of the hypothesis that total winter means are different from total summer means is based upon the means of station means, making a "t" test valid. It is important to examine other MAFLA TM data for the macroepifauna, sediments and suspended particulates for clues to the causes of these seasonal variations.

For several of the metals examined, fairly rapid changes in Syacium muscle tissue apparently occur. For instance, Ni shows more than a two times change over approximately the three-month period between the fall sampling and the winter collections. In order to compare the different chemistries of the several metals, an estimate of the relative whole organism turnover time was computed for Ba, Cd, Fe, V, Cu, Ni, Cr, and Zn. The estimate is based upon the TM content of Syacium and the average concentrations in the pooled shrimp, a major food item in the Syacium diet (Topp and Hoff, 1972). Table 46 presents the results of this computation. The time period is purposely eliminated from the table in order to minimize misinterpretation of the estimated values. The comparative values are important in determining differences in chemistry. The estimates are normalized to the minimum value, Cd = 1.00.

Little is known about the actual chemical form of these elements as they exist in the muscle tissue of Syacium (or any other animal). It would seem, however, that they must be fairly free to migrate in and out of the tissue, or else the marked seasonal changes we observe could not be so pronounced. For elements with relatively low turnover times, like Cd and Cu, changes in the TM content of the Syacium diet might be an important factor. The longer residence time elements which show significant seasonality (e.g., Ba) must be relatively less biologically active in order to have sufficient time to change between seasons.

With shrimp comprising a significant portion of the Syacium diet, perhaps seasonal variation of TMs in the shrimp are important. Barium, cadmium, copper, and nickel, the metals which show the strongest seasonal trends in Syacium, were studied in detail in the MAFLA shrimp specimens. For Ba in Mesopenaeus tropicalis, Solenocera atlantidis, Sicyona brevirostris, Parapenaeus longirostris, and Penaeus setiferus (pooled) the winter values are one-half of the summer values. For Cd in this same group, the winter analyses average less than 60% of the summer values. Thus, for Cd and Ba, seasonal changes in the food Syacium eats certainly help to explain the observed seasonal trends for that fish.

On the other hand, changes in Cu and Ni in the aforementioned group of shrimp do not take place on a seasonal basis. Summer and winter averages for these metals are virtually identical, forcing a search for other explanations.

Body burdens of TMs in fish may be affected by direct interaction with the water column as well as diet and intake. Absorption through the

TABLE 46

ESTIMATED RELATIVE TURNOVER TIMES OF TRACE METALS IN SYACIUM, NORMALIZED TO Cd = 1.00

Element	Relative Turnover Time
Cd	1.0
Cu	1.9
V	7.7
Zn	12.3
Fe	18.3
Ni	23.6
Ba	36.4
Cr	38.2

gill tissues is a likely pathway, and may offer an explanation for the seasonality in copper content of Syacium. Data of Betzer (Chapter 22) show large increases in the near-bottom total suspended loads in the Florida Middle Grounds (Station 2315), off Panama City (Station 2528), and in the Mississippi-Mobile area (Station 2639). In addition, copper in the suspended particulates was 2 to 14 times higher than in the sediment samples (average 7 times increase). A similar but less pronounced trend was observed for Cd (average 2 times increase), with no change in the Pb distribution. Cr was also much higher in the near-bottom suspended particulates than in the sediments. Unfortunately, no data were obtained for Ni as all the results were below detection limits (BDL).

Thus, the higher values for Cu in Syacium in the winter versus the summer could be related to water column interactions, and storm resuspension of the fine surface sediment. If so, the mode of uptake of Cu must be quite different from that of Cr which was also enriched in the particulates. Such a difference in biological interactions is also suggested by the large difference in relative fish tissue residence times (Table 46) and the fact that Cr shows a relatively neutral seasonal variation in Syacium (Figure 137).

We have no ready explanation for the strong seasonality of Ni in the demersal fish analyzed here. Its coordination chemistry is much like that of Cu, its next door neighbor in the periodic table. Perhaps Cu and Ni behave in a similar fashion with respect to their biological chemistries. It would be of considerable interest to know the relative proportions of Cu and Ni that are removed from suspended particulates by a weak acid leach. Nickel might be highly "available."

Biogeochemical Relationships by Elements

Cadmium and zinc show very similar distributions within the six groups of biota plotted in Figures 147-149. This is not surprising in view of the fact that they belong to the same group in the periodic table (IIB). Such group relationships do not always hold, but in this case the strength of the trend of phylogenetic differences suggests that it might continue down the group to Hg.

The maximum Cd and Zn values occur for the molluscs, and the phylogenetic group with the second highest values are the crustaceans, principally the crabs. While the shrimp have relatively elevated Zn values, the Cd in shrimp is extremely low.

Two other heavy metals which exist primarily in the divalent state, Ba (Group IIA) and Pb (Group IVA), are also found in high concentrations in the molluscs. Lead shows its maximum values in this group, while Ba exhibits high values in only two of the MAFLA species, namely Tugurium and Argopecten. It would be of value in future studies to determine whether this trend of relatively high Ba, Cd, Pb, and Zn holds for other mollusc species.

Iron and nickel show a similarity in that they are highest in the filter feeders. Here we neglect the somewhat anomalous behavior of "iron

concentrating" by the sea urchins. Data of Betzer (Volume II, Chapter 22) for the concentration of metals in the suspended particulates in the MAFLA area show that in winter the suspended loads in the water column are highest. Further, the concentrations of Fe, Cu, Cr, and Cd in the winter samples of suspended particulates are higher than those in the surface sediments from which resuspension had taken place. It would seem that filter feeders would thus be presented with higher levels in the water column and might subsequently show seasonal trends.

Of course, possible seasonality of occurrence of these metals in the filter feeders would likely also be a function of the "availability" of the particulate TMs to the organisms. An indication of this parameter is given by the percent of total metal released to the aqueous phase by a weak acid leach. Again, data of Betzer (Volume II, Chapter 22) show that this is highly variable. For Stations 2737 and 2315, the concentration of metal in the weak-acid-soluble fraction averaged about 20% for Fe, 80% for Cu, and approximately 0% for Cr (many of the Cr data were based on BDL values). Thus, the "availability" and the mass which is resuspended into the water column to become available to filter feeders reach a compromise.

Unfortunately, the number of specimens of filter feeders collected, and the uneven seasonality of collection, make it impossible to establish seasonal trends in these biota. It would be important in future studies to get good seasonal data for sponges and molluscs, as these organisms could be quite valuable in examining water column/benthos interactions.

Biogeochemical Relationships by Taxa

The variability of results for TM analyses in the MAFLA macroepifauna samples is much greater than that for the demersal fish Syacium. Most of this variability cannot be ascribed to analytical variations (compare Tables 44 and 45) but is most likely "natural," i.e., dietary, geographic, seasonal, etc. Though data for individual species are too few, in most cases, to assess these variables, some indications can be seen through a principal component analysis of relative TM distributions by taxa.

Figure 150 shows the results of such an analysis for 37 species and the nine TMs analyzed in the MAFLA 1977/78 program. All species represented by single replicates only, as well as several species with internally anomalous or distorting individual metal contents, were excluded from the analysis. Table 47 lists the species in Figure 150 by identifying number.

Three major groupings of organisms can be identified by this technique: two groups of basically deposit feeders, A and C, and predators. Several filter feeders are scattered across the ordination. Also, three species of crabs are distributed outside the larger predator or deposit feeder groups.

Sponges 5 and 8 are each comprised of several specimens collected at the same set of stations in the summer of 1976. In a plot such as Figure 150, one would expect similar species (close taxonomic relationships) to lie close to each other. However, sessile filter feeders may more accurately reflect the average nature of the water column flowing over them. The average conditions in which sponges 5 and 8 lived were similar.

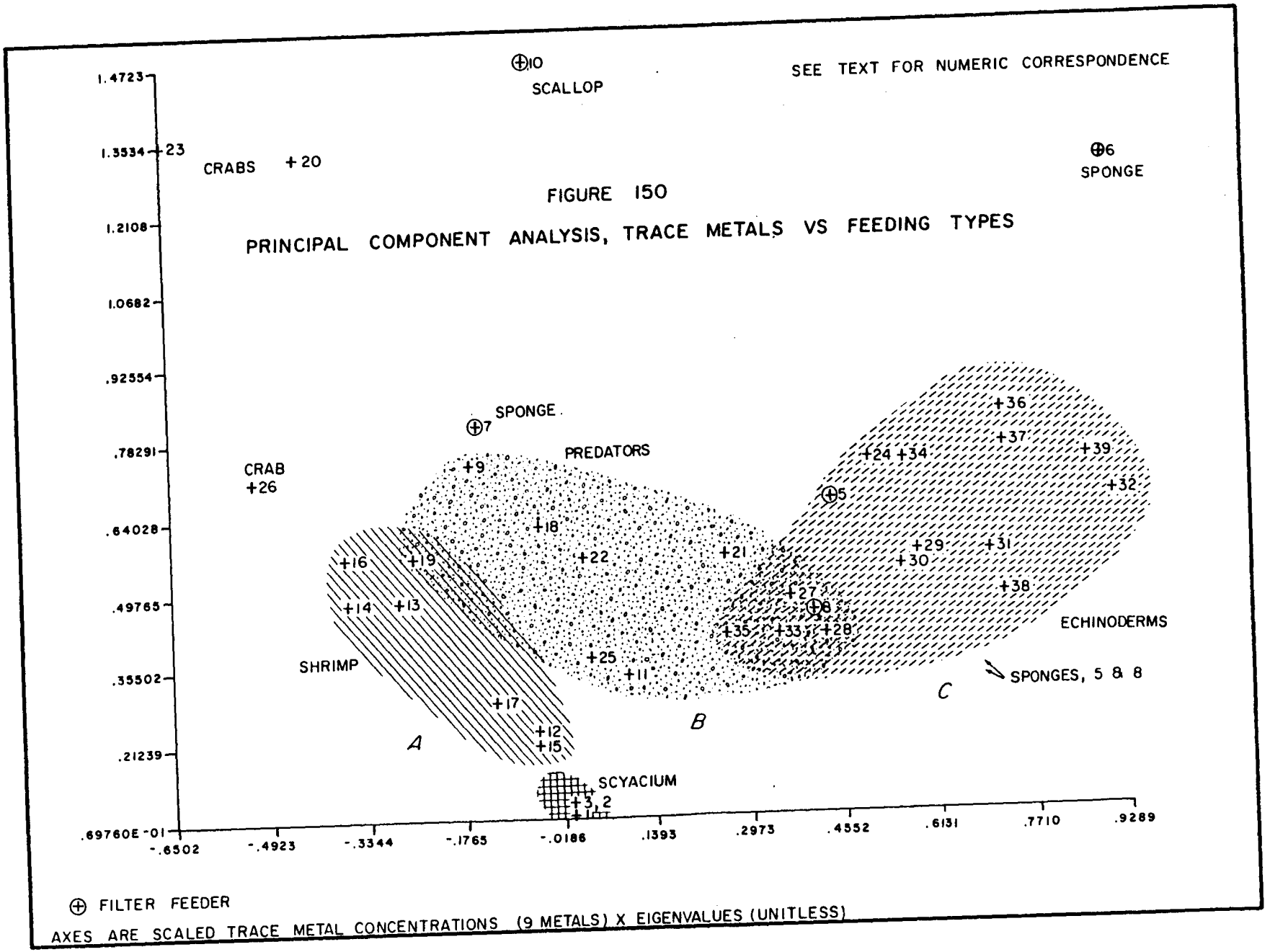


FIGURE 150

PRINCIPAL COMPONENT ANALYSIS, TRACE METALS VS FEEDING TYPES

⊕ FILTER FEEDER

AXES ARE SCALED TRACE METAL CONCENTRATIONS (9 METALS) X EIGENVALUES (UNITLESS)

TABLE 47

SPECIES USED IN THE CLUSTER ANALYSIS OF TRACE METALS BY TAXA (R-MODE)

No.		No.	
1	Syacium, winter 78	21	Munida irrasso
2	Syacium, fall 77	22	Acanthocarpus alexandri
3	Syacium, summer 77	23	Iliacantha subglobosa
4	Omitted	24	Stenorhynchus seticornis
5	Pseudoceratina crassa	25	Portunus spinicarpus
6	Haliclona urceola	26	Portunus spinimanus
7	Placaspongia carina	27	Luidia clathrata
8	Craniella	28	Astropecten duplicatus
9	Murex beauii	29	Astropecten nitidus
10	Aequipecten glyptus	30	Goniaster tesselatus
11	Loligo pealeii	31	Astroporpa annulata
12	Eucarida decopoda	32	Astrophyton muricatum
13	Penaeus aztecus	33	Eucidaris tribuloides
14	Penaeus duorarum	34	Stylocidaris affinis
15	Parapeneus longirostris	35	Arbacia punctulata
16	Sicyonia brevirostris	36	Lytechinus variegatus
17	Solenocera atlantidis	37	Clypeaster ravenelli
18	Mesopenaeus tropicalis	38	Encope michelini
19	Scyllarus chacei	39	Comactina echinoptera
20	Paguristes spinipes		

The two sponge specimens represented by 6 and 7 were also collected during the summer of 1976, but at widely differing locations. While the mean values were used for this analysis, inspection of individual Haliclona values collected at Stations 0005 and 2103 shows that the metal content of the specimen at Station 0005 was generally higher.

The deposit feeder Cluster C is made up primarily of echinoderms, although some of them are predators (27 and 28), hence, the overlap there is with Group B. Note that the deposit feeding crab, Stenorhynchus, is included in the "echinoderm" deposit feeding group. This species is from a group which would be expected to include deposit feeders. Some of the species in Group C are mixed deposit feeders and predators (24, 29, 30) but apparently more closely related to the deposit feeders than the predators.

The other deposit feeder group, Group A, is comprised completely of shrimp, and in general, this group has lower total TM contents than the echinoderm group. This can be seen by the comparison in Figures 147, 148 and 149, and the fact that in the cluster analysis, the shrimps are considerably more negative on the X-axis. Clearly there are distinct taxonomic differences between the two groups on the basis of TM distributions. What is not so clear is whether this separation results from different phylogenetic biochemistries, variations in the nature of the "deposit" feeding mechanism practiced by the two groups, or by subtle biases resulting from analytical or sampling errors. However, the tight taxa groupings and the relatively large number of organisms sampled over various geographic areas and seasons suggest true species differences.

A possible seasonal and/or geographic trend can be seen in the shrimp samples. Mesopenaeus tropicalis (#18) is taxonomically close to Solenocera atlantidis (#17), yet falls considerably outside the rest of the shrimp cluster. The five specimens of S. atlantidis were collected mainly in fall and winter off the Panama City area, whereas M. tropicalis was collected in summer off the Tampa Bay area. It is impossible from such small samples to determine whether season or geography are more important.

Other examples of such differences can be seen by comparing time and area of catch of some of the individuals falling outside the major groupings, but will not be dealt with further here. This approach, however, might well be utilized in future studies where larger numbers of specimens are collected.

Two additional aspects of Figure 150 should be noted before leaving the subject. The predator group, which includes crabs, a squid, a snail, a deposit feeder/predator lobster (#19), and two starfish at the echinoderm end, lies intermediate between the two deposit feeder groups. That is, it contains species with relatively higher TM content than the shrimp, but lower than the echinoderm group. This suggests that predators in Figure 150 are feeding more on the shrimp group than on the echinoderm group. This fits with the known behavior of the organisms in Group B.

Finally, Syacium papillosum is included in the cluster analysis as three entries, representing relative TM contents determined for three seasons. The data plot nearly one on top of the other, though the winter

data are slightly separated from the summer and the fall. Syacium is most nearly like the lower end of the shrimp group, and shrimp are known to be a major component of their diet (Topp and Hoff, 1972). Thus, seasonal variations in shrimp TM content and element distribution might be important factors in the observed seasonal variations in Syacium.

POTENTIAL INDICATOR ORGANISMS

The development of OCS areas for oil and gas reserves will result in the disruption of the benthic environment in local areas. Affects upon the water column may be more widespread because of its geographic movement through the area, sediment resuspension being carried downstream, etc. This means that monitoring efforts should include study of deposit feeding organisms and higher trophic levels which feed on them, as well as filter feeding organisms which interact more directly with the water column.

The results of the TM analyses of MAFLA biota presented here show that the Eastern Gulf of Mexico is, in general, a very "clean" area. None of the analyses show that the area has been subjected to heavy metal pollution. While low levels of TMs in the biota may make the analytical chemistry more difficult, they also make it easier to see a change, should the biota be impacted. The relatively pristine environment of the Eastern Gulf of Mexico should be viewed critically. This is an area where further studies of the nature of trace element distribution in the biota can be conducted without the effects of outside perturbations. The benchmark studies of the MAFLA area provide a sound basis for the development of further programs.

Table 48 gives a summary of how the TM results of the present study compare with other reported work. As can be seen, the results are about the same as, or are lower than, previous data.

Filter feeders, such as sponges and molluscs, could be used as integrators of water column effects. However, considerably more study of the seasonality in TM distributions needs to be undertaken. With respect to the water column, both molluscs and sponges should be used because of the apparent ability of the molluscs to concentrate some metals and not exchange them. This would be an advantage in comparing a chronically stressed location to a supposedly unstressed environment, but may be a disadvantage when attempting to document a "transitory" or one-time event. If sponges have a higher turnover time (shorter time constant in response to a change), they may be more useful in the latter type of monitoring.

Figure 151 shows a plot of the number of replicates required to "see" a stated percent difference between two samples of the clam Spondylus americanus. For all nine metals studied, a sample size of 20 is sufficient to see a 100% difference between two samples. The "clean" nature of the MAFLA area indicates that a 100% difference in trace element content of Spondylus could easily occur, and an impact resulting in such a difference might be small and could be seen quickly. It is doubtful that a 2 times change in the concentration of any of nine elements studied would be detrimental (or even noticed) by any of the organisms studied.

TABLE 48

SUMMARY OF MAFLA BIOTA TRACE METAL RESULTS
COMPARED TO OTHER DATA

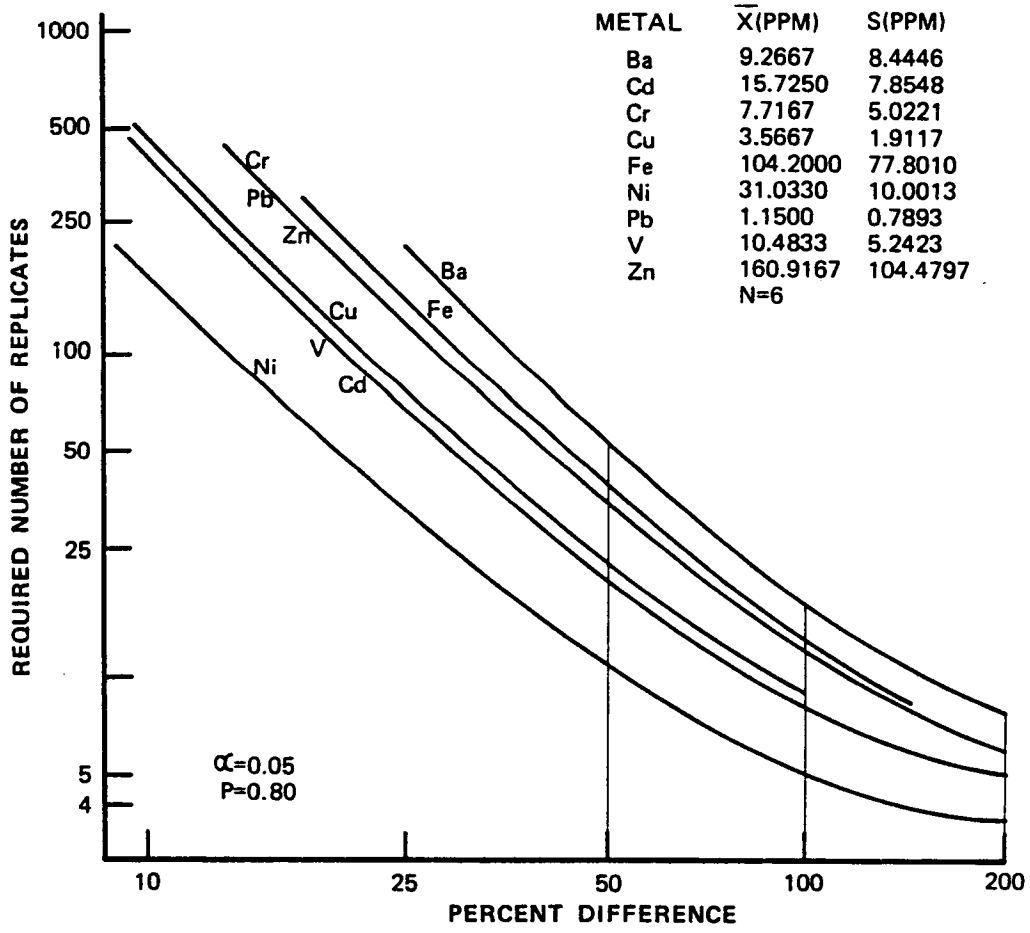
A. Trace Metals in Syacium

Cd -	about 10 x lower than previous
Cr -	5 x -10 x lower than previous
Cu -	about same
Fe -	about same
Ni -	about same
Zn -	about same
Pb -	lower than previous, but probably still too high*

B. Trace Metals in Macroepifauna

Cd -	about same, but 2x - 3x lower in sponges
Cr -	about same, but sponges low, some echinoderms high
Cu -	about same
Fe	about same, but 3x - 5x lower in sponges and crustaceans
Ni	about same, but 5x lower in filter feeders
Zn	about same
Pb	2x - 3x lower than 1976 MAFLA, but probably still too high*

* cf. results of Settle and Patterson (1976).



MINIMUM DETECTABLE DIFFERENCE (%)
BETWEEN TWO SAMPLES OF
SPONDYLUS AMERICANUS
5509070101
FIGURE 151

The second type of monitoring that should be considered is that of food chain increase or "bioconcentration." It would seem that the combination of a deposit feeding shrimp and the carnivore Syacium would be appropriate. Processes which affect the benthos directly (dumping, dredging, drilling, etc.) are likely to impact the deposit feeders. A change in these organisms is quite likely to be reflected further up the food chain, e.g., in the crabs, fish, and starfish.

The advantage of analyzing the demersal fish Syacium papillosum have been mentioned previously. The fact that they spawn over a very long time scale (Topp and Hoff, 1972) results in a wide spectrum of specimen sizes (and ages) at any one point in time (see Volume I, Marine Chemistry, this report). If there is any cumulative effect which overrides seasonal trends for a particular metal, such an age class mixture could be used to good advantage in monitoring.

Any one of the several shrimp studied here could be used in conjunction with Syacium for the deposit feeders/food chain monitoring. We happen to have the highest number of replicates for Sicyonia brevirostris. Figure 152 shows the required number of replicates to determine a stated particular TM difference between two samples. As with Spondylus, the number of replicates required to see a 100% difference is relatively small.

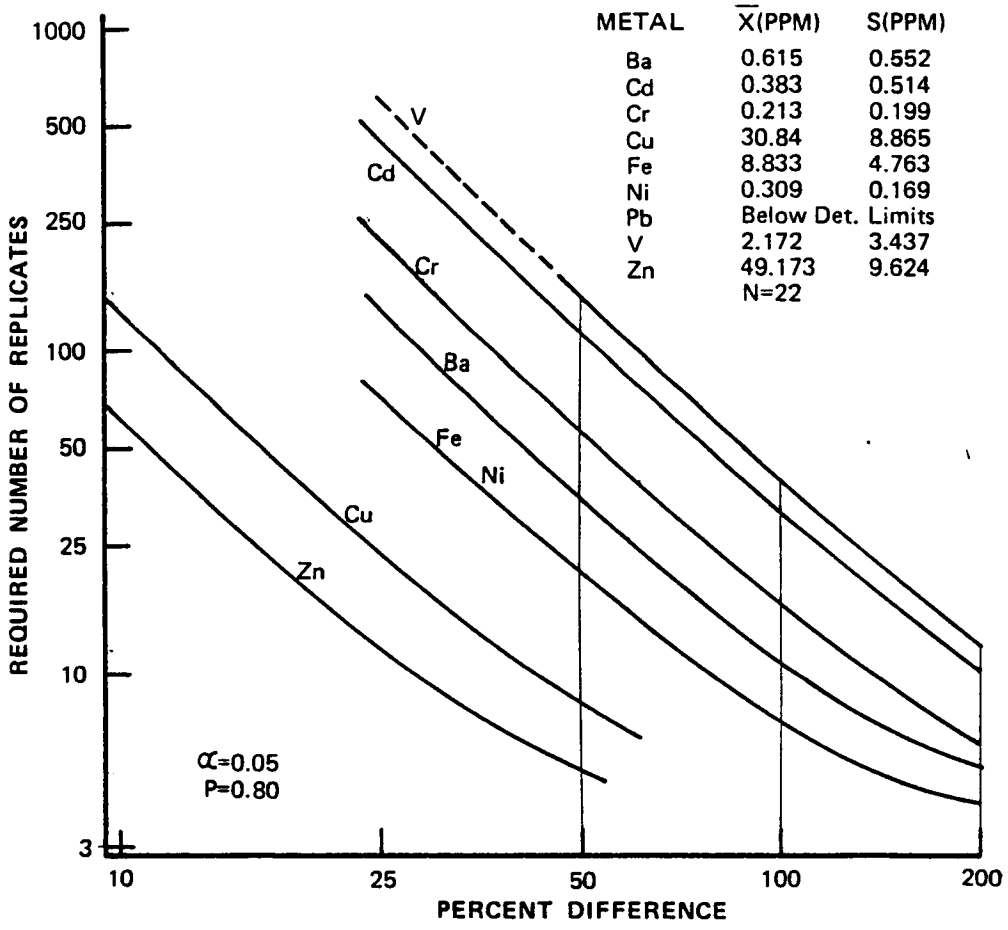
CONSIDERATIONS FOR FUTURE WORK

The data presented here, and their interpretation, point to several considerations in the design of future studies.

1. The natural variability of the results should be examined in more detail. In particular, more replication in the laboratory is required in order to document the analytical uncertainties. This should consist of at least triplicate analyses of a single specimen digest, and periodic (say 20% of samples) replicate digests of the same specimen. Analytical abilities to approach accuracy vary considerably from laboratory to laboratory. The work statement should recognize this and trade off some field data for time spent in documenting analytical uncertainties.

2. More detailed seasonal data are required for the several indicator species in particular, and for the macroepifauna in general. This should be done at different geographic locations. As things stand now, many possible geographic trends are obscured by or confounded with seasonal trends. Complete seasonal data are needed at several individual geographic locations. This might be accomplished by examining, in detail, the chemistry and biology at monthly intervals at only two or three stations. The extant MAFLA benchmark data are probably sufficient to extrapolate to the rest of the eastern Gulf of Mexico.

3. In terms of interpreting results from indicator organisms, we need considerably more study on the question of individual metal turnover time in the various species. We need to know the time constants for the "indicator organism" response in order to



MINIMUM DETECTABLE DIFFERENCE (%)
BETWEEN TWO SAMPLES OF
SICYONIA BREVIROSTRIS
6177030101

FIGURE 152

improve sampling strategy. Such data are also necessary in order to understand the role of the biota in coupling the water column to the benthos.

CONCLUSIONS

1. From examinations of the TM content of the demersal fish and the macroepifauna of the MAFLA OCS area, it is clear that the area represents a "clean" environment. There are no obvious indications of anthropogenic pollution impact.

2. The data set collected thus far, combined with many of the previous results, give us a reasonably good benchmark from which to work, either in more detailed mechanistic studies, or in the monitoring of OCS oil and gas reserve development.

3. The distribution of similarities in TM content within species of the macroepifauna make taxonomic and behavioral sense. Cluster analysis such as has been presented here can help to illucidate seasonal and geographic trends in data variability.

4. From all of the above considerations, there emerge several "indicators species" of filter feeders, deposit feeders, and predators which are potentially valuable for monitoring the effects of OCS activities which disrupt the marine environment. The species can be selected so as to efficiently address the question of water column/benthos/sediment interactions with regard to OCS development impact.

5. The clean environment of the MAFLA lease area is a resource that should be utilized for further mechanistic studies. It would seem a most advantageous area in which to examine the nature and dynamics of the biota mediation of water column/sediment interactions, and would provide a good comparison to similar coupling roles of the benthos in temperate climates.

REFERENCES

Betzer, P.R., et al., 1978. Volume II of this report, Chapter 22.

Betzer, S. and R. Sims, 1976. Environmental monitoring survey of the MAFLA lease area trace metals in benthic macrofauna (1975-1976), in SUSIO 1977, Baseline monitoring structure, Mississippi, Alabama, Florida Outer Continental Shelf, 1975-1976. Contract 08550-CT5-30.

Bowen, H.J.M., 1966. Trace Metals in Biochemistry, Academic press, N.Y.

Grasle, F. and Grasle, J., 1978. Year III MERL report to ERA, in press.

Heinle, D. and Vargo, S., 1978. ibid.

Horne, R.A., 1978. The Chemistry of Our Environment, Wiley Interscience, N.Y., 869 pp.

Horowitz, A. and Presley, B.J., 1977. Trace metal concentration and partitioning in zooplankton, neuston, and benthos from the South Texas Outer Continental Shelf, Arch. Env. Contamin 5(2): 241-255.

Johnson, D.L., 1978. Geochemical Cycling, presented at Dames & Moore fourth quarterly BLM PI's meeting - July 1978, Kenner, LA.

National Marine Fisheries Service, 1975. First interim report on micro-constituent resource survey, 146 pp.

Park, R.A., 1978. Paeoecoloy of Venericardia sensu lato (Pelecypoda) in the Atlantic and Gulf Coastal Province: An application of paleo-synecologic methods. J. Paleo. 42: 955-986.

Riley, J.P. and Segar, D., 1970. The distribution of the major and some minor elements in marine animals, I. Echinoderms and coelenterates. J. Mar. Biol. Assoc. U.K. 50: 721-730.

Segar, D. et al., 1971. The distribution of the major and some minor elements in marine animals, II. Molluscs. J. Mar. Biol. Assoc. U.K. 51: 131-136.

Shokes, R.F., et al., 1978. Geochemical baseline study of the Capline Offshore Brine Disposal Sites, February, 1978. SAI report No. SAI-78-854-LJ, 147 pp.

Stumm, W. and Morgan, J.J., 1970. Aquatic Chemistry, Wiley - Interscience, N.Y.

Topp, R.W. and Hoff, F.H., 1972. Memoirs of the Hourglass cruises, flat fishes. Volume IV, Part II. Fla. Dept. Nat. Resources. 135 pp.

Windom, H. and Betzer, P.R., 1978. Trace Metals. S.E. Atlantic BLM OCS synthesis report - preprint (Draft).

VOLUME II

CHAPTER 7

MACROEPIFAUNA AND DEMERSAL FISH BARIUM AND VANADIUM

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SAI
CONTRACT NO. AA550-CT7-34

BARIUM AND VANADIUM IN DEMERSAL FISH AND MACROEPIFAUNA

MAFLA BENCHMARK SURVEY, 1977-1978

FINAL REPORT

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Science Applications, Inc.
La Jolla, California
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ABSTRACT

For the first time since the inception of the MAFLA Lease Area baseline survey, reliable barium concentration data have been generated for biological specimens (demersal fish and macroepifauna) from the area. Also the vanadium data base for these samples has been substantially added to and comparison has been made between the previous atomic absorption-derived data (Betzer and Sims, 1976) and the currently used neutron activation techniques.

In the case of the Syacium papillosum, the only demersal fish sampled extensively, no geographical trends were found for either element, but barium tissue burdens do appear to be lower in the winter than in the summer. Also, there is less populational variability in tissue barium in the winter relative to the summer (and fall). Most likely this season trend, if real, is due to either change in average specimen maturity (or size), change in feeding habit, or some combination of the two. Vanadium does not show such a trend but cadmium does (Volume II, Chapter 3).

Macroepifauna demonstrated no observable seasonal or geographic trends. However, significant differences were found for both elements among the four major phylogenetic groups represented (sponges, echinoderms, crustaceans and molluscans) and more specifically among the feeding habit types represented (filter feeders vs deposit feeders vs grazers). As a phylum, echinoderms (starfish, urchins) contained the highest levels of both barium and vanadium while only select feeding types (especially deposit feeders) of crustaceans and molluscs exhibit barium and vanadium contents approaching those of echinoderms.

INTRODUCTION

As part of the effort to characterize demersal fish and macroepifauna from MAFLA (east Gulf of Mexico) lease area with respect to their trace heavy metal chemistry, barium and vanadium have been determined apart from the other elements (Chapters 5 and 6) by using neutron activation analysis techniques. The more traditional atomic absorption spectrophotometry methods do not have the necessary sensitivity to reliably detect these two metals. As a result, prior to the 1977/78 program, there have existed no comparable data (especially for barium) in tissues from eastern Gulf of Mexico organisms.

Barium and vanadium can potentially enter the marine environment through their associations with drilling and/or oil itself. Barium, as barite (barium sulfate), can be the dominant single material in drill muds and has been found dispersed in surface sediments in the vicinity of drilling operations (Presley et al., 1976; Patterson, unpublished data). Vanadium is known to occur in characteristic proportions in crude oil and has been found in concentrations as high as 300 ppm (Yen, 1975). The exact detrimental effects, if any, that either of these elements might have at either acute or chronic levels are unknown. However, it is thought that each in its own way might serve as a relatively sensitive indicator of the dispersal of oil development impacts once their ambient, predrilling baseline concentration distributions have been adequately determined.

This study has produced a substantial amount of data representing the distributional variations across lines of geographical, seasonal, phylogenetic and species-related changes. Unfortunately, for the sake of interpreting these variations, an important change--the natural bio-geochemical variation among individuals of a species--could not be controlled in most instances. Therefore, in only a few situations have enough members of any sample population been analyzed to allow the appending of statistical significance to any observable trends. All the data however, are to be considered useful as long as they are analytically reliable, since they provide documentation of ambient conditions somewhere within the boundaries of natural variation.

This report will focus on variations found in the demersal fish, Syacium papillosum, for barium and vanadium tissue burdens, and on geographical and phylogenetic differences among the five categories of macroepifauna collected. Chapters 5 and 6, which discuss the other trace heavy metals distributed in the organisms assayed, apply several rigorous statistical analyses to all the metals including barium and vanadium. Reference is made to those chapters for the appropriate discussions.

METHODS AND MATERIALS

The neutron activation analysis techniques utilized in this study are detailed in Shokes, R. and Reed, J., 3rd Quaterly MAFLA Report, January 15 - May 15, 1978 (Dames & Moore, 1978e).

RESULTS AND DISCUSSION

DEMERSAL FISH

The demersal fish Syacium papillosum (flounder or flatfish) was collected in replicates (approximately ten per station) at several locations during 1977-1978. In addition, one or two individuals from several of the same stations had been collected during the summer of 1976. All samples were of relatively large and uniform size (130-170 mm length) and enough were collected to allow meaningful statistical comparison.

In Chapters 5 and 6, the barium and vanadium data are evaluated statistically and reference is made to those areas of discussion. Mean barium and vanadium data are listed in Table 49 and shown geographically distributed in Figure 153. As can be seen in Figure 153, there apparently are no geographical trends in grand (all seasons) mean barium and vanadium tissue levels over the MAFLA area. However, when examining the seasonal means for each element an apparent trend does exist (Figures 154 and 155; Table 50). Along with cadmium (Chapter 6), barium tissue burdens (and to a lesser extent, those of vanadium) tend to decrease from summer, to fall, to winter.

There is a large amount of variability contained around each mean used as a data point in these trends, and this must be recognized. Given the proximity of the amounts of barium and vanadium found in these samples to the analytical detection limits, there certainly is a substantial analytical imprecision contained in these variations. However, analytical precision from replication (see Methods and Materials, third MAFLA quarterly report; Dames & Moore, 1978e) indicates that in the case of these two elements in Syacium, natural variability is the dominant component of variation among the data shown in Table 49 for the number of samples averaged from any one location and season (typically 10 to 11 individuals).

As discussed in the case of cadmium (Chapter 6), the barium tissue burden trend for Syacium in going from summer to winter is likely the result of changing food supply. Possibly an association can be made between this trend and the high barium contents of zooplankton, which dominated the Middle Ground waters in summer (1977), compared to phytoplankton, which dominated in winter (1978), although plankton are probably a full order removed from Syacium in the food chain. Also it is interesting to note from Table 50 that variation between station mean barium levels decreases from summer to winter (38 to 17%) implying less heterogeneity in the winter and, if the food source hypotheses is correct, it implies that Syacium have a more restricted and geographically uniform diet in the winter.

MACROEPIFAUNA

For the many epifaunal specimens analyzed for barium and vanadium contents, concentration means and ranges are presented by phyla and species in Table 51 and Appendix 7-1, respectively (demersal fish are included for relative comparison). Table 51 preserves the seasonality of collection and although some apparent differences stand out upon examining this data, causal seasonal control cannot be implicated.

TABLE 49

GEOGRAPHICAL AND SEASONAL VARIATIONS IN BARIUM AND VANADIUM CONTENTS IN Syacium papillosum
(concentrations in μg/g dry tissue)

SPECIES	STA #	# OF SAMPLES	BA	V	
		DM-1 (August-September 1977)			
Syacium papillosum	2748	11	0.67 to 2.70	0.12 to 2.10	Range
			1.45	0.53	Mean
			0.59	0.29	std. dev(1σ)
Syacium papillosum	0003	11	0.45 to 2.70	0.09 to 0.96	
			1.02	0.34	
			0.61	0.30	
Syacium papillosum	2105	10	0.65 to 2.20	0.09 to 0.54	
			1.31	0.26	
			0.55	0.13	
Syacium papillosum	2209	11	0.56 to 2.90	0.06 to 0.53	
			1.07	0.15	
			0.66	0.14	
Syacium papillosum	2426	11	<0.5 to 5.40	0.08 to 0.98	
			2.15	0.56	
			1.51	0.31	
Syacium papillosum	2641	11	0.37 to 1.30	0.05 to 0.59	
			0.71	0.15	
			0.26	0.15	

TABLE 49 (CONTINUED)

SPECIES	STA #	# OF SAMPLES	BA	V	
		DM-2 (November 1977)			
Syacium papillosum	0005	6	0.58 to 1.40	0.24 to 0.96	Range
			0.98	0.43	Mean
			0.28	0.11	1σ
Syacium papillosum	2103	9	0.11 to 2.10	0.06 to 0.72	
			1.23	0.22	
			0.77	0.21	
Syacium papillosum	2209	9	0.39 to 1.80	0.03 to 0.16	
			1.36	0.06	
			0.49	0.04	
Syacium papillosum	2426	8	0.39 to 2.30	0.07 to 0.81	
			1.60	0.28	
			0.68	0.24	
Syacium papillosum	2534	9	0.49 to 1.70	0.13 to 1.30	
			1.16	0.50	
			0.38	0.35	
Syacium papillosum	2641	10	0.48 to 1.50	0.05 to 0.09	
			0.91	0.07	
			0.36	0.02	
Syacium papillosum	2747	6	0.68 to 2.60	0.11 to 1.70	
			1.50	0.70	
			0.76	0.56	

TABLE 49 (CONTINUED)

SPECIES	STA #	# OF SAMPLES	BA	V	
		DM-4 (February 1978)			
Syacium papillosum	0005	10	0.18 to 1.20	0.03 to 0.83	Range
			0.56	0.26	Mean
			0.30	0.25	1σ
Syacium papillosum	0007	10	0.14 to 0.90	0.03 to 0.53	
			0.42	0.18	
			0.24	0.16	
Syacium papillosum	2105	11	0.38 to 1.40	0.00 to 1.00	
			0.68	0.24	
			0.29	0.29	
Syacium papillosum	2209	8	0.38 to 1.00	0.01 to 0.08	
			0.70	0.04	
			0.26	0.03	
Syacium papillosum	2426	11	0.19 to 1.70	0.04 to 0.34	
			0.70	0.15	
			0.49	0.08	
Syacium papillosum	2645	11	0.30 to 1.30	0.04 to 1.00	
			0.60	0.29	
			0.30	0.31	
Syacium papillosum	2747	11	<0.20 to 1.50	0.04 to 0.87	
			0.53	0.43	
			0.35	0.30	

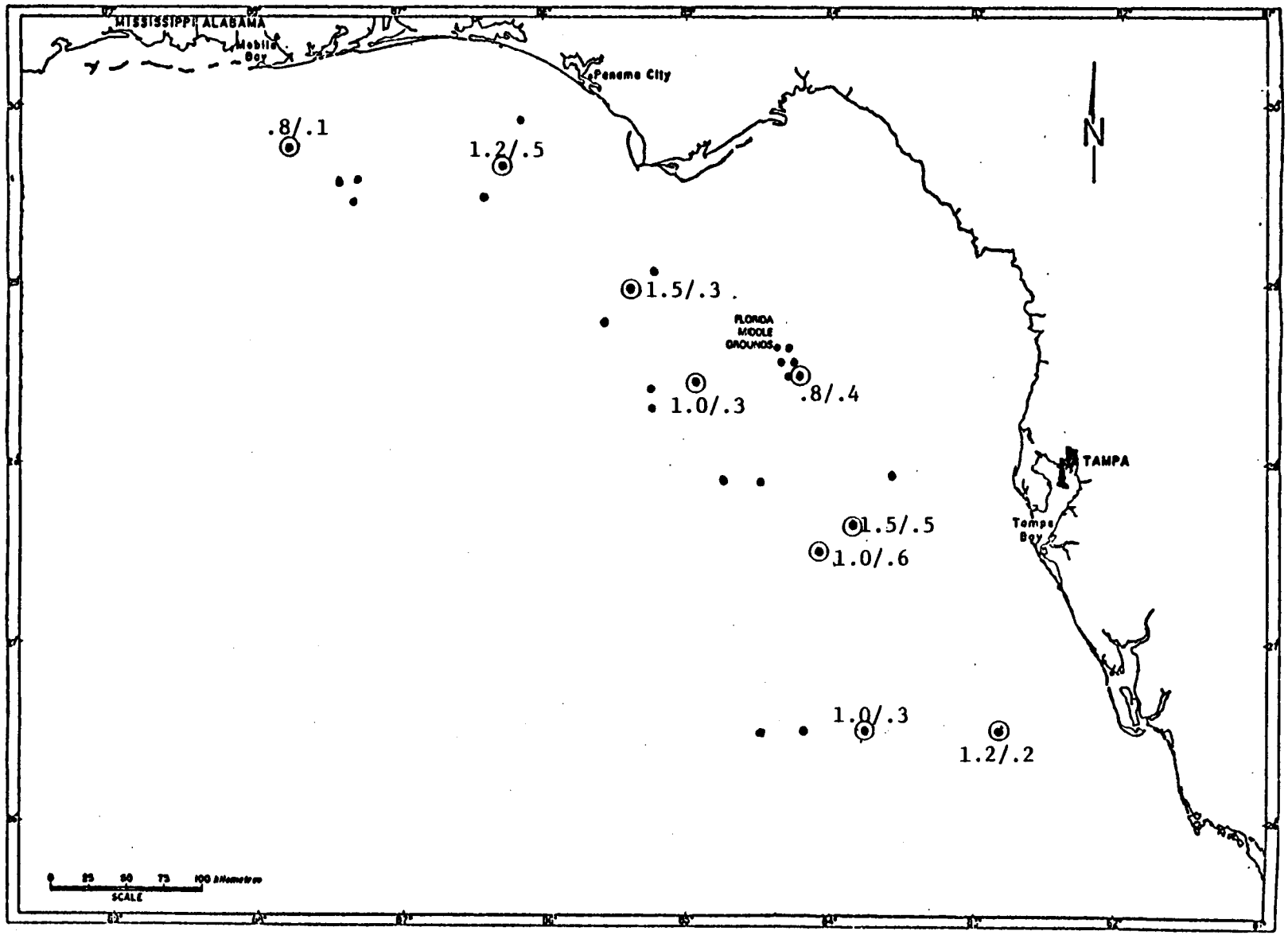

Figure 153 Distributions of barium and vanadium concentrations (µg/g dry tissue; means over the three 1977/78 sampling periods) in Sycaium papillosum (a demersal fish) -- MAFLA lease area.

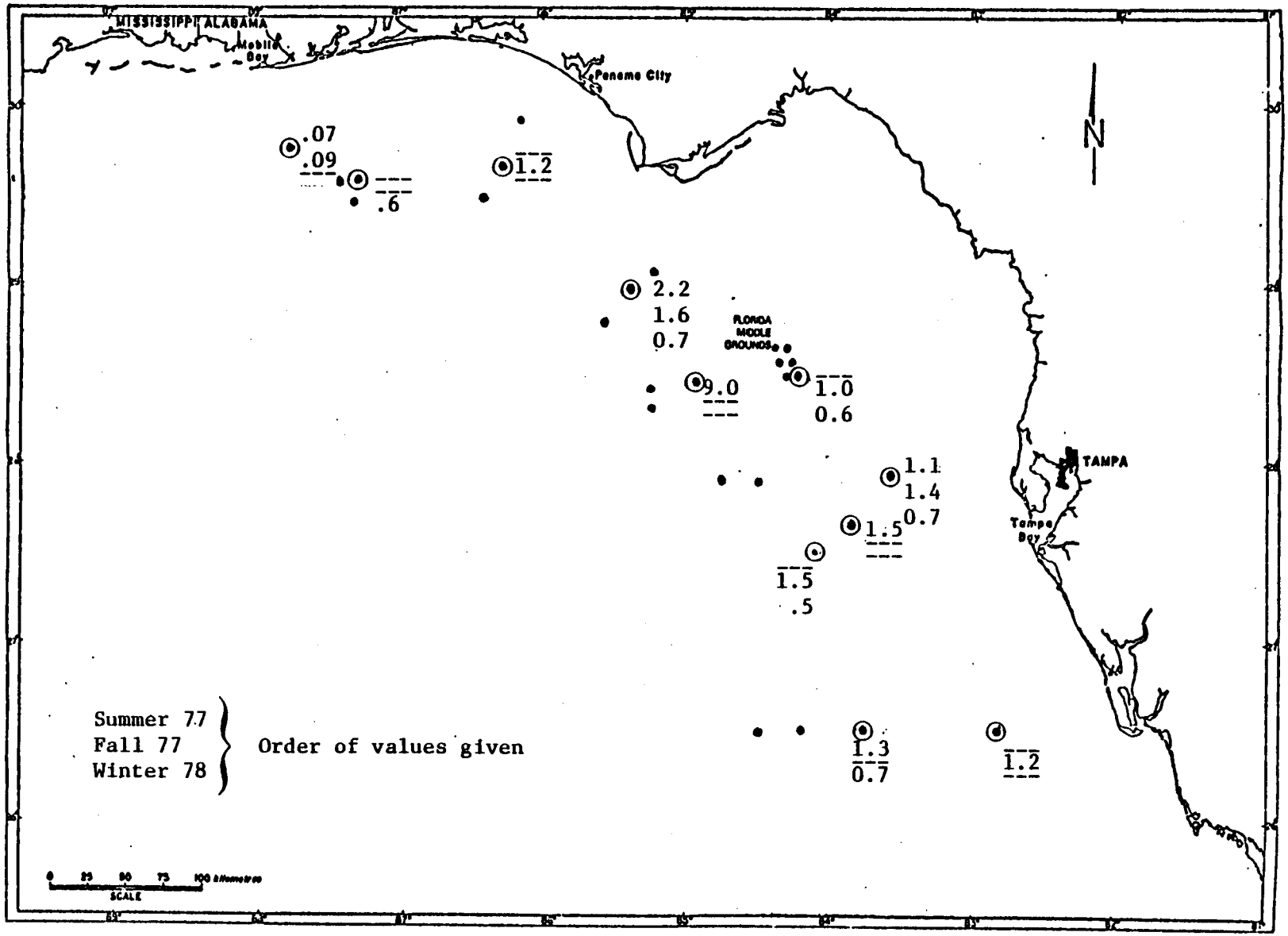

Figure 154 Seasonal and geographical distributions of barium (µg/g dry tissue; means of 6-11 individuals per season, per station) in Syacium papillosum -- MAFLA lease area.

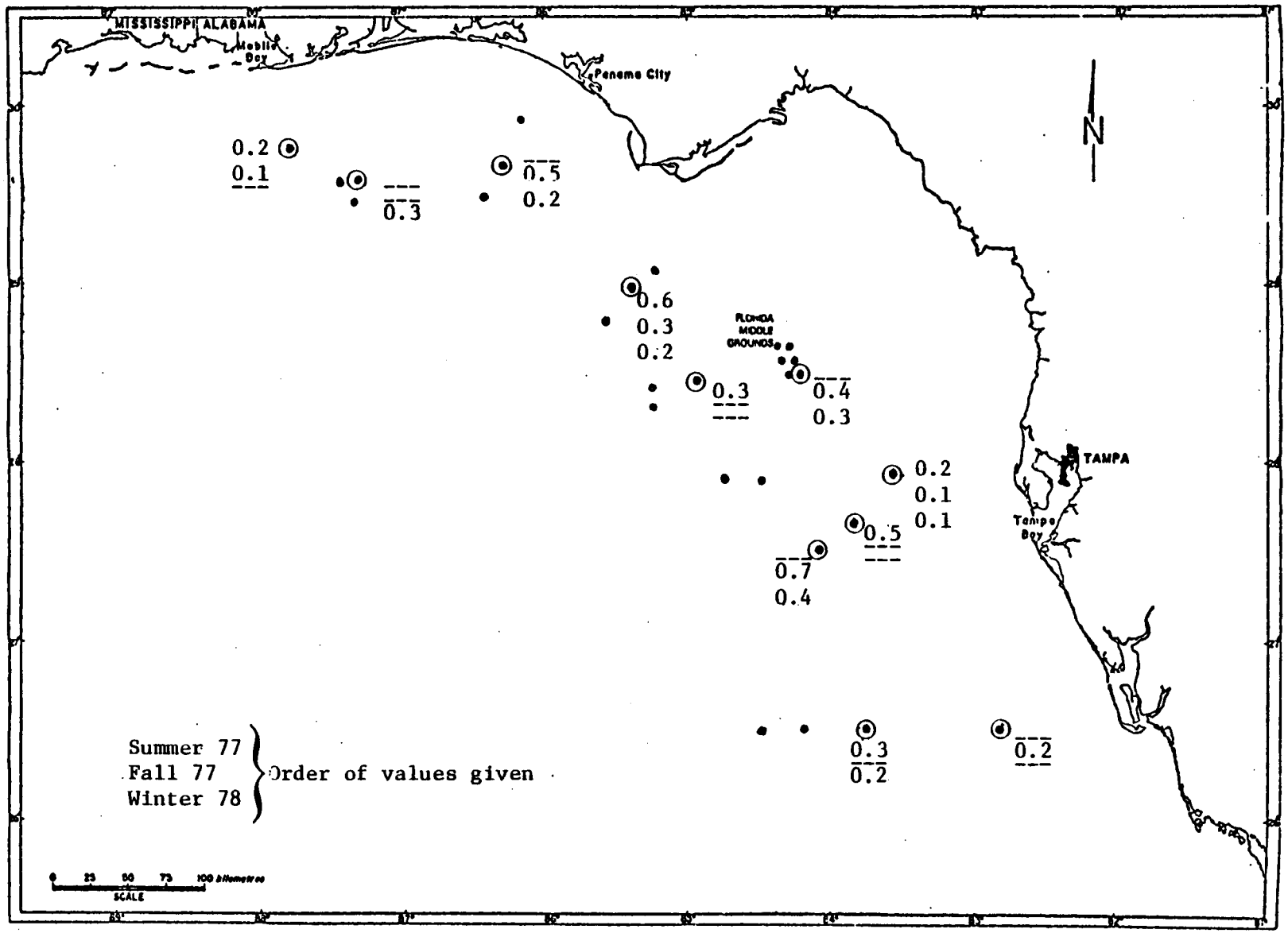

Figure 155 Seasonal and geographical distributions of vanadium (µg/g dry tissue; means of 6-11 individuals per station, per season) in Syacium papillosum -- MAFLA lease area.

TABLE 50

SEASONAL MEANS OF STATION MEANS FOR BARIUM AND VANADIUM CONCENTRATIONS
(μg/g dry tissue) in *Syacium papillosum*
(Variations Expressed as Coefficient of Variation (%))

SEASON	NO. OF STATIONS	Ba (+ %CV)	V (+ %CV)
Aug-Sep 1977	6	1.29 ± 38%	0.33 ± 55%
Nov 1977	7	1.25 ± 21%	0.32 ± 73%
Feb 1978	7	0.60 ± 17%	0.23 ± 51%

TABLE 51

PHYLOGENETIC MEANS, BY SEASON, OF BARIUM AND VANADIUM CONCENTRATIONS
(μg/g dry weight)

PHYLA (or organisms type)	SEASON	Ba (ppm ± 10)	V (ppm ± 10)
Sponges	Summer 76	3.26 ± 1.97	1.09 ± .43
	Summer 77	1.20 ± .71	.29 ± .18
	All seasons	2.57 ± 1.89	.82 ± .54
Molluscs	Summer 76	5.26 ± 4.56	5.84 ± 5.19
clams	Summer 77	.99 ± .91	.83 ± .07
scallops	All seasons	3.55 ± 4.01	3.83 ± 4.58
snails			
Crustaceans	Summer 76	2.12 ± 1.20	1.16 ± .85
shrimp	Summer 77	2.08 ± 1.25	.39 ± .21
crabs	Fall 77	1.60 ± 1.58	.48 ± .35
lobsters	Winter 78	.81 ± .37	.30 ± .27
	All seasons	1.43 ± 1.12	.55 ± .56
Echinoderms	Summer 76	6.86 ± 3.09	.80 ± .47
starfish	Summer 77	5.99 ± 3.90	.51 ± .24
sand dollars	Fall 77	7.01 ± 4.83	.67 ± .37
sea urchins	Winter 78	4.70 ± 0.67	.41 ± .21
	All seasons	6.32 ± 3.56	.62 ± .36
Demersal Fish	Summer 76	1.65 ± 1.11	.54 ± .52
	Summer 77	1.28 ± .90	.33 ± .29
	Fall 77	1.30 ± .65	.30 ± .34
	Winter 78	.60 ± .33	.24 ± .25
	All seasons	1.29 ± .70	.39 ± .30

From the echinoderm and crustacean data (Table 51) it can be seen that the former is uniformly enriched in barium relative to the phyla and is so in all its species (Appendix 7-1). This probably reflects the utilization of barium into exoskeleton building and possibly the inclusion of some amounts of hard parts in the analysis preparation of the echinoderms. This same elevation is not seen for vanadium in echinoderms.

Crustaceans, on the other hand, are relatively low in both barium and vanadium but the phlogenetic mean (Table 51) is elevated somewhat by the occurrence of a few species of unusually high barium (and to a lesser and more limited extent, vanadium). Examples are the arrow crab Stenorhynchus, the spider crab Acanthocarpus, the pelagic crab Portunis, the lobster-like crab Muniza, and the deposit-feeding shrimp Mesopenaeus. As discussed in Chapter 6, most of these species differences are related to feeding type and geographical location, especially with respect to substrate and other food source types.

Figures 156 through 158 plot the seasonal means of barium and vanadium in molluscs, echinoderms, and crustaceans, respectively, relative to geographical location. The elevation in barium and vanadium in molluscs from more nearshore Florida shelf stations (Figure 156) is probably due to collection of certain metal-enriched species at those locations. In that case, it is difficult to assess whether or not the differences are geographically or species controlled.

The high value of barium and low of vanadium for echinoderms (Figure 157) show no apparent geographical trend and represent, as mentioned, a fairly homogeneous grouping of species according to concentration. For the case of crustaceans (Figure 158), the ranges of means for both metals are sufficiently low, even though a few crustaceal species are elevated somewhat in barium, to forgo any implication of geographical trends.

Chapter 6 discusses the possible relationships between macroepifauna, fish and water column materials with respect to the trace metal (including barium and vanadium) chemistry of those phases.

In sponges and molluscs the only comparison that can be made is between summer 1976 and summer 1977. Although for both sampling periods there are differences in the barium and vanadium mean values, most likely these differences represent some artifact of sample size, sample storage, or some other interjection affecting the summer 1976 (BLM-4) samples.[1] For crustaceans and echinoderms (and demersal fish), for which data from all four collections are available, these variations are not evidenced and in fact from Table 51 no case can be made for systematic seasonal changes in epifaunal tissue loads with season.

[1]Actually the main difference in summer 76 and summer 77 sponge and mollusc concentrations can be seen in Appendix 7-1 as being due to collection of different species. All the sponges collected during 1976 have higher means of barium and vanadium than two different species collected during 1977. The same is true for molluscs except for one case in which Aequipectin glyptus was collected at both seasons and was found to be higher in both barium and vanadium in summer 76 relative to summer 77.

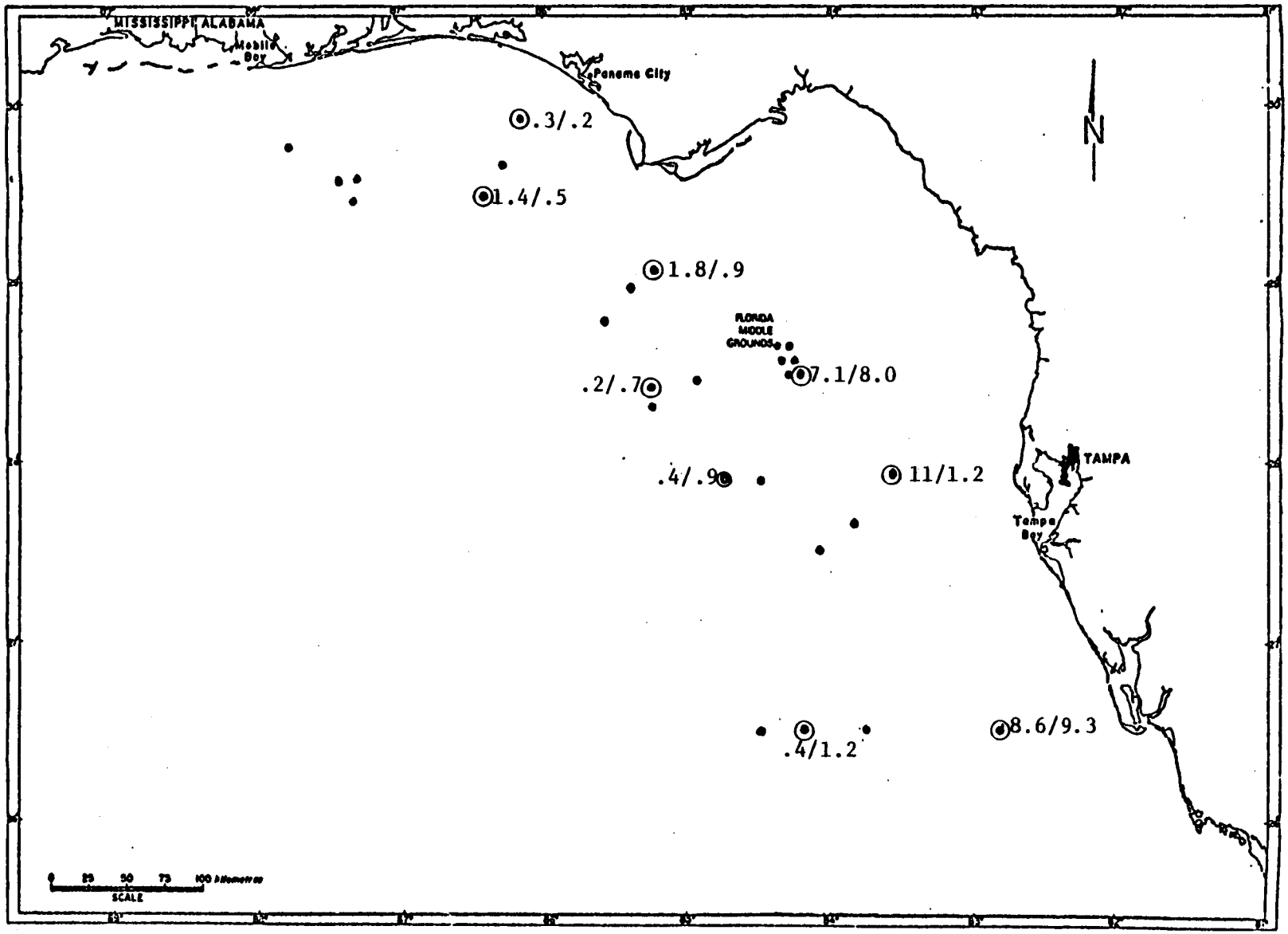

Figure 156 Distributions of barium and vanadium concentrations (µg/g dry tissue; means overall sampling periods) in molluscs -- MAFLA lease area.

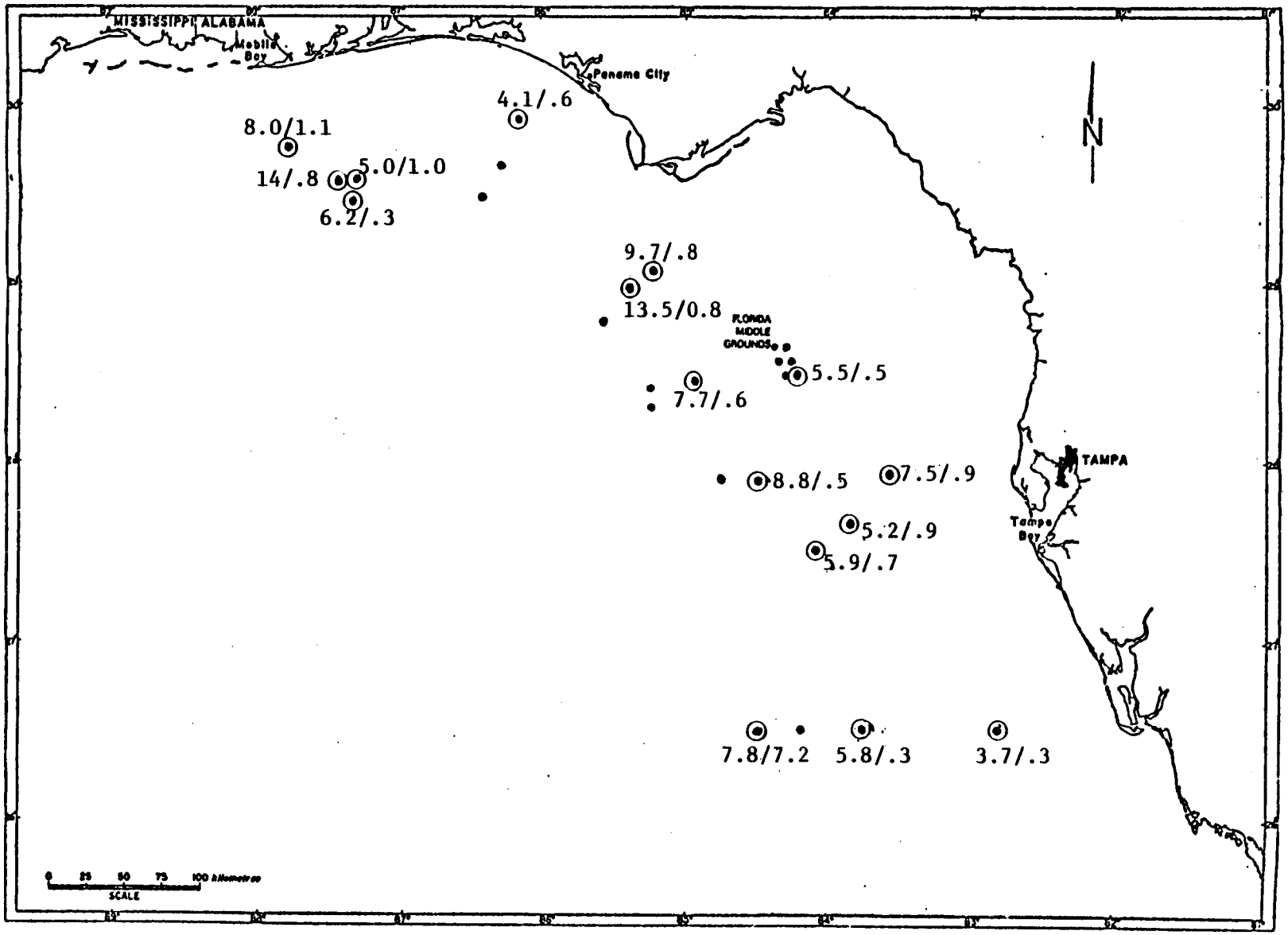

Figure 157 Distributions of barium and vanadium concentrations (µg/g dry tissue; means over all sampling periods) in echinoderms -- MAFLA lease area.

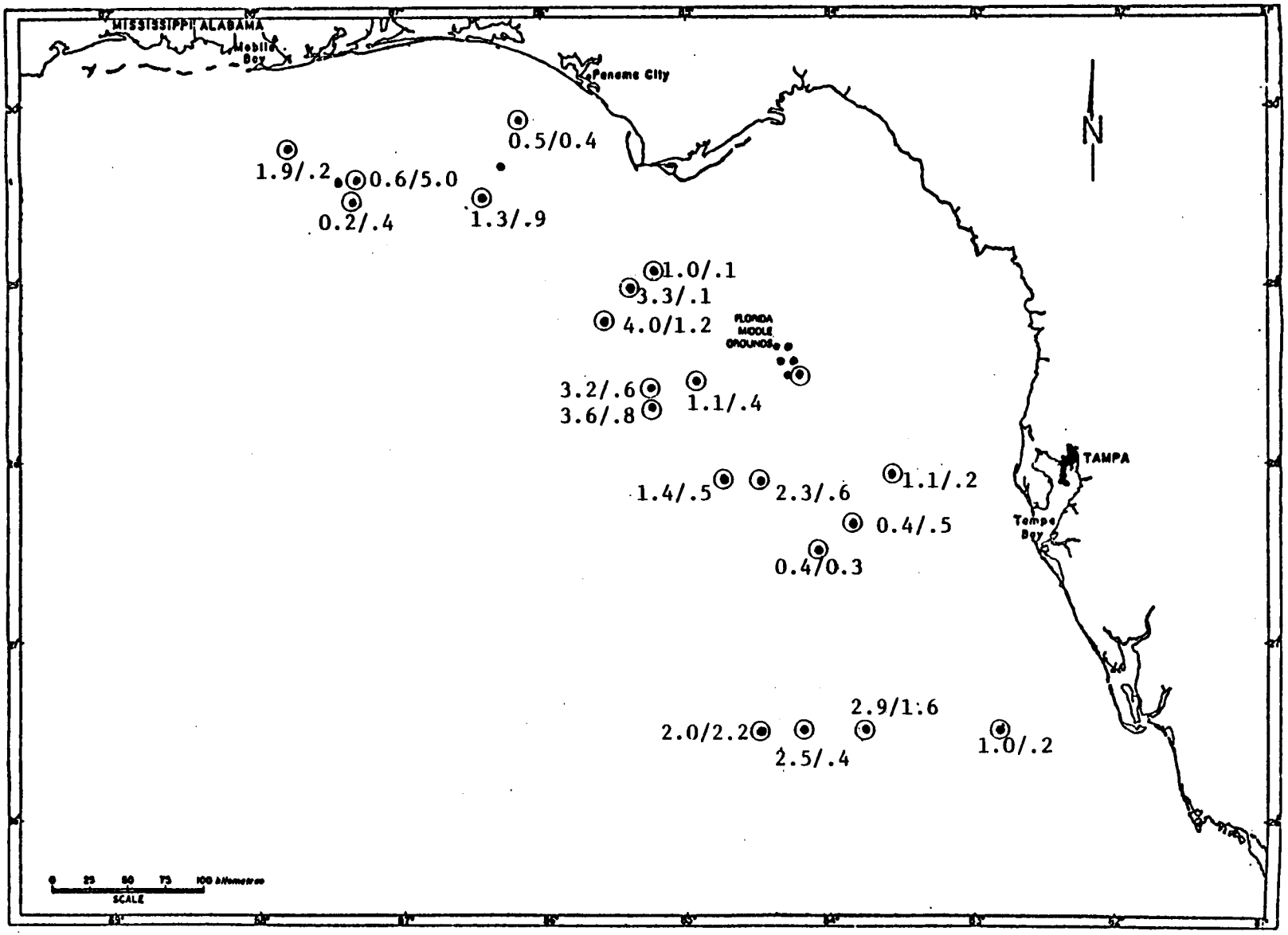

Figure 158 Distributions of barium and vanadium concentration (µg/g dry tissue; means over all sampling periods) in crustaceans -- MAFLA lease area.

CONCLUSIONS

Barium and vanadium tissue burdens have now been determined for MAFLA demersal fish and macroepifauna with the degree of reliability needed for environmental baseline data. Although the problems of populational variability were not directly approached by the sampling design employed, representative data for the species collected have been obtained for future comparison.

In general, the dominant fish sampled (Syacium papillosum) demonstrated no geographical trends for either barium or vanadium; however, an apparent decrease in barium was observed between summer 1977 and winter 1978 samples, indicating some effect of changing age (size) and/or changing feeding habits. Vanadium showed no seasonal variation.

The only observable trends for these two elements in the tissues of representative macroepifauna were among the major phyla groupings (sponges, echinoderms, molluscs, and crustaceans) and among different feeding habit types. In general, echinoderms exhibited elevated levels of both vanadium and barium relative to the other groups and deposit feeding crustaceans were enriched relative to other types within that group. No significant seasonal or geographic trends were observed.

REFERENCES

Betzer, S.B., and R.R. Sims, 1976. Environmental Monitoring Survey of the MAFLA Lease Area: Trace Metals in Benthic Macrofauna (1975-76). To the Bureau of Land Management, Washington, D.C., via SUSIO, St. Petersburg, Fla.

Presley, B.J., R.F. Shokes, J.H. Trefrey, and M.C. Dobson, 1976. Heavy Metal Analyses of Sediments from the MAFLA Rig Monitoring Study. To the Bureau of Land Management, Washington, D.C., via SUSIO, St. Petersburg, Fla.

Yen, T.F., 1975. The Role of Trace Metals in Petroleum. Ann Arbor Science (Ann Arbor, Michigan), 221 pp.

APPENDIX 7-1

INTRASPECIES VARIABILITY OF BARIUM AND VANADIUM AMONG THE DOMINANT MACROEPIFAUNA

(contentrations are in ppm dry weight)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
SPONGES				
BLM-4 (June-July 1976)				
Pseudoceratina crassa	7	Range	<0.64 to 1.60	0.33 to 1.40
		Mean	1.22	0.66
		2 Standard deviations	0.68	0.84
Halicolona rubens	2	Range	2.9 to 9.0	0.82 to 2.50
		Mean	5.95	1.66
		2 Standard deviations	8.62	2.38
Neofibularia noltangere oxeata	2	Range	1.4 to 4.7	0.76 to 1.60
		Mean	3.05	1.18
		2 Standard deviations	4.66	1.18
Cinachyia sp.	6	Range	1.50 to 3.70	0.24 to 2.70
		Mean	2.80	0.87
		2 Standard deviations	1.64	1.86
		Phylogenetic cruise mean	3.26 ±1.97	1.09 ±0.43
DM-1 (August-September 1977)				
Aegles dispar	2	Range	<0.70 to 2.7	0.27 to 0.55
		Mean	1.70	0.41
		2 Standard deviations	2.83	0.40
Placospongia carina	3	Range	0.23 to 1.10	0.06 to 0.35
		Mean	0.70	0.16
		2 Standard deviations	0.44	0.33
		Phylogenetic cruise mean	1.20 ±0.71	0.29 ±0.18
		Total phylogenetic mean	2.57 ±1.89	0.82 ±0.54

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
MOLLUSCS				
BLM (June-July 1976)				
Aequipectin glyptus	2	Range	3.10 to 9.60	2.68 to 11.00
scallop (bivalve mollusc)		Mean	6.35	6.80
		2 Standard deviations	9.20	11.88
Spondylus americanus	6	Range	2.50 to 23.00	4.60 to 17.00
rock oyster (bivalve mollusc)		Mean	9.17	10.48
		2 Standard deviations	17.02	10.48
Loligo pealeii	2	Range	0.15 to 0.34	0.15 to 0.30
squid (cephalopod)		Mean	0.25	0.23
		2 Standard deviations	0.26	0.22
		Phylogenetic cruise mean	5.26 ±4.56	5.84 ±5.19
DM-1 (August-September 1977)				
Murex beauii	3	Range	0.20 to 0.43	0.76 to 1.20
snail (gastropod)		Mean	0.34	0.88
		2 Standard deviations	0.24	0.55
Aequipectin glyptus	3	Range	1.40 to 2.00	0.49 to 0.93
scallop (bivalve mollusc)		Mean	1.63	0.78
		2 Standard deviations	1.64	0.50
		Phylogenetic cruise mean	0.99 ±0.91	0.83 ±0.07
		Total phylogenetic mean	3.55 ±4.01	3.83 ±4.58

APPENDIX 7-1 (CONTINUED

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
CRUSTACEANS				
BLM-4 (June-July 1976)				
Sicyionia brevirostris rock shrimp	5	Range	<0.40 to 1.50	0.07 to 0.14
		Mean	0.85	0.10
		2 Standard deviations	0.88	0.06
Mesopenaeus tropicalis shrimp	5	Range	0.30 to 3.40	0.30 to 5.20
		Mean	1.35	1.47
		2 Standard deviations	2.46	4.20
Acanthocarpus alexandri spider crab	2	Range	1.00 to 4.80	0.45 to 1.50
		Mean	2.90	0.98
		2 Standard deviations	5.38	1.48
Stenorhynchus seticornus arrow crab	6	Range	9.50 to 54.00	0.98 to 1.50
		Mean	23.58	2.41
		2 Standard deviations	32.14	2.98
Portunis spinicarpus swimming (pelagic) crab	8	Range	1.20 to 7.40	0.15 to 2.20
		Mean	3.36	0.85
		2 Standard deviations	4.24	1.23
		Phylogenetic cruise mean	2.12 ±1.20	1.16 ±0.85
DM I (August-September 1977)				
Sicyionia brevirostris rock shrimp	6	Range	<0.10 to 1.50	0.04 to 0.81
		Mean	0.81	0.31
		2 Standard deviations	1.11	0.61
Muniza irrasa lobster-like crab		Range	0.20 to 6.40	0.39 to 1.00
		Mean	3.30	0.70
		2 Standard deviations	8.77	0.86

APPENDIX 7-1 (CONTINUED

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
CRUSTACEANS				
Acanthocarpus alexandri spider crab	2	Range	<0.23 to <2.00	0.07 to 0.41
		Mean		0.24
		2 Standard deviations		0.48
Portunis spinicarpus swimming crab	6	Range	<0.10 to 5.00	0.19 to 0.43
		Mean	2.13	0.31
		2 Standard deviations	3.29	0.20
		Phylogenetic cruise mean	2.08 ±1.25	0.39 ±0.21
DM II (November 1977)				
Parapenaeus longirostris shrimp	4	Range	0.19 to 1.20	0.10 to 0.98
		Mean	0.55	0.42
		2 Standard deviations	0.89	0.80
Sicyonia brevirostris rock shrimp	4	Range	0.28 to 0.78	0.06 to 0.32
		Mean	0.41	0.19
		2 Standard deviations	0.49	0.27
Solenocera atlantidis shrimp	2	Range	0.24 to 0.59	0.65 to 1.50
		Mean	0.42	1.08
		2 Standard deviations	0.49	1.20
Acanthocarpus alexandri spider crab	4	Range	0.78 to 5.20	0.14 to 0.92
		Mean	2.97	0.42
		2 Standard deviations	4.60	0.70
Portunis spinicarpus swimming crab	6	Range	<0.10 to 8.30	0.05 to 0.55
		Mean	3.65	0.30
		2 Standard deviations	6.00	0.36
		Phylogenetic cruise mean	1.60 ±1.58	0.48 ±0.35

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
CRUSTACEANS (Cont.)				
DM IV (February 1978)				
Penaeus duorarum pink shrimp	2	Range	0.47 to <0.66	<0.02 to 0.05
		Mean	0.57	0.04
		2 Standard deviations	0.27	0.04
Panaeus longirostris shrimp	2	Range	<0.07 to <1.00	0.03 to 0.09
		Mean	0.85	0.06
		2 Standard deviations	0.42	0.08
Sicyonia brevirostris rock shrimp	8	Range	<0.03 to 0.07	<0.02 to 0.33
			0.47	0.09
		2 Standard deviations	0.26	0.20
Solenocera atlantidis shrimp	2	Range	0.40 to <0.60	0.17 to 0.74
		Mean	0.50	0.46
		2 Standard deviations	0.28	0.81
Scyllarus chacei rock lobster	2	Range	0.67 to <0.70	0.44 to 0.93
		Mean	0.69	0.69
		2 Standard deviations	0.04	0.69
Acanthocorpus alexandri spider crab	3	Range	<0.40 to 1.80	0.11 to 1.20
		Mean	1.20	0.63
		2 Standard deviations	1.44	1.09
Illacantha subglobosa spider crab	3	Range	1.20 to 2.30	1.30 to 7.60
		Mean	1.60	4.83
		2 Standard deviations	1.22	6.44

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
CRUSTACEANS (Cont.)				
DM IV (February 1978)				
Portunis spinicarpus	6	Range	<0.40 to 1.40	0.04 to 1.20
swimming crab		Mean	0.76	0.36
		2 Standard deviations	0.67	0.92
Portunis sp.	3	Range	<0.30 to <1.00	0.05 to 0.16
swimming crab		Mean	0.67	0.09
		2 Standard deviations	0.70	0.12
		Phylogenetic cruise mean	0.81 ±0.37	0.30 ±0.27
		Total phylogenetic mean	1.43 ±1.12	0.55 ±0.56
ECHINODERMS				
BLM-4 (June-July 1976)				
Astroporpa annulata	2	Range	6.20 to 8.80	0.29 to 0.56
brittle star (ophuiroid)		Mean	7.50	0.43
		2 Standard deviations	3.68	0.38
Astrophyton muricatum	2	Range	3.70 to 4.10	0.26 to 0.59
basket star (ophuiroid)		Mean	3.90	0.43
		2 Standard deviations	0.57	0.47
Stylocidaris affinis	4	Range	2.00 to 7.10	0.39 to 1.90
urchin (echinoid)		Mean	3.88	1.20
		2 Standard deviations	4.63	1.53
Lytechinus variegatus	3	Range	4.30 to 8.50	1.10 to 1.50
urchin (echinoid)		Mean	6.83	1.37
		2 Standard deviations	4.46	0.46
Clydeaster raveneli	4	Range	9.30 to 16.00	0.58 to 1.90
sand dollar (echinoid)		Mean	12.32	1.08
		2 Standard deviations	5.76	1.24

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
ECHINODERMS (Cont.)				
BLM-4 (June-July 1976)				
Encope michelini	2	Range	5.10 to 8.30	0.29 to 0.29
sand dollar		Mean	6.70	0.29
		2 Standard deviations	4.53	0.0
		Phylogenetic cruise mean	6.86 ±3.09	0.80 ±0.47
DM I (August-September 1977)				
Luidia clathrata	2	Range	3.10 to 3.70	<0.20 to 0.39
starfish (asteroid)		Mean	3.40	0.30
		2 Standard deviations	0.85	0.27
Astroporpa annulata	7	Range	3.30 to 7.00	0.19 to 0.59
brittle star (ophiuroid)		Mean	5.00	0.33
		2 Standard deviations	2.79	0.30
Eucidaris tribuloides		Range	3.10 to 5.10	<0.20 to 0.79
sea urchin		Mean	3.93	0.47
(echinoid)		2 Standard deviations	1.68	0.49
Stylocidaris affinis	2	Range	4.00 to 5.50	0.79 to 0.99
urchin		Mean	4.75	0.89
		2 Standard deviations	2.12	0.28
Clypeaster raveneli	8	Range	8.00 to 16.00	<0.30 to 0.99
sand dollar		Mean	12.88	0.56
		2 Standard deviations	5.06	0.50
		Phylogenetic cruise mean	5.99 ±3.90	0.51 ±0.24
DM II (November 1977)				
Luidia clathrata	3	Range	4.00 to 7.10	0.23 to 0.43
starfish (asteroid)		Mean	5.13	0.33
		2 Standard deviations	3.42	0.20

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
ECHINODERMS (Cont.)				
DM II (November 1977) (Cont)				
Astropecten duplicatus starfish (asteroid)	2	Range	6.70 to 7.90	0.31 to 0.32
		Mean	7.25	0.32
		2 Standard deviations	1.56	0.01
Astroporpa annulata brittle star	2	Range	3.70 to 2.50	0.34 to 0.25
		Mean	3.10	0.30
		2 Standard deviations	1.70	0.14
Eucidaris tribuloides urchin	2	Range	4.10 to 4.20	0.38 to 1.00
		Mean	4.15	0.69
		2 Standard deviations	0.14	0.88
Stylocidaris affinis urchin	3	Range	3.90 to 8.00	0.54 to 1.50
		Mean	5.30	0.89
		2 Standard deviations	4.68	1.06
Lytechinus variegatus urchin	2	Range	3.30 to 10.00	0.95 to 1.60
		Mean	6.65	1.28
		2 Standard deviations	9.48	0.92
Clypeaster raveneli sand dollar	4	Range	13.00 to 22.00	0.53 to 1.10
		Mean	17.50	0.86
		2 Standard deviations	8.41	0.48
		Phylogenetic cruise mean	7.01 $\pm$4.83	0.67 $\pm$0.37
DM IV (February 1978)				
Luidia clathrata starfish	2	Range	3.40 to 5.90	0.30 to 0.89
		Mean	4.65	0.60
		2 Standard deviations	3.54	0.83

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
ECHINODERMS (Cont)				
Astropecten nitidus starfish	2	Range	3.70 to 3.90	0.10 to 0.16
		Mean	3.80	0.13
		2 Standard deviations	0.28	0.08
Astroporpa annulata brittle star	3	Range	3.50 to 5.70	0.17 to 0.80
		Mean	4.93	0.39
		2 Standard deviations	2.48	0.72
Eucidaris tribuloides urchin	2	Range	4.90 to 5.90	0.43 to 0.62
		Mean	5.40	0.53
		2 Standard deviations	1.41	0.27
		Phylogenetic cruise mean	4.70 $\pm$0.67	0.41 $\pm$0.21
		Total phylogenetic mean	6.32 $\pm$3.56	0.62 $\pm$0.36
DEMERSAL FISH				
BLM-4 (June-July 1976)				
Syacium papillosum flounder	12	Range	1.30 to 5.90	<0.02 to 0.56
		Mean	2.43	0.17
		2 Standard deviations	2.39	0.30
Monolene sessilicauda	11	Range	0.26 to 2.60	0.12 to 2.10
		Mean	0.86	0.91
		2 Standard deviations	1.42	1.46
DM I (August-September 1977)				
Syacium flounder	65	Range	0.45 to 2.70	0.09 to 0.96
		Mean	1.28	0.33
		2 Standard deviations	1.80	0.57

APPENDIX 7-1 (CONTINUED)

SPECIES NAME	NUMBER OF SAMPLES ANALYZED		Ba	V
DEMERSAL FISH (Cont.)				
DM-I (August-September 1977) (Cont.)				
Syacium papillosum	57	Range	0.11 to 2.60	1.53 to 1.70
flounder		Mean	1.30	0.30
		2 Standard deviations	1.29	0.67
DM IV (February 1978)				
Syacium papillosum	72	Range	0.14 to 1.50	<0.01 to 1.00
flounder		Mean	0.60	0.24
		2 Standard deviations	0.66	0.50
		TOTAL Phylognetic Mean	1.29 ±0.70	0.39 ±0.30

VOLUME II

CHAPTER 8

SEDIMENT AND MACROFAUNAL TISSUE HYDROCARBON ANALYSES

DR. GEORGE GOULD
DR. BUD MOBERG
CONTRACT NO. AA550-CT7-34

ARLI Report Number 4850-F

ANALYSIS OF MARINE SAMPLES FROM THE OUTER CONTINENTAL SHELF OF MISSISSIPPI, ALABAMA, AND FLORIDA (MAFLA) FOR HIGH MOLECULAR WEIGHT HYDROCARBONS IN BENTHIC SAMPLES

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INTRODUCTION

Analytical Research Laboratories, Inc. (ARLI) has completed work on its subcontract with Dames & Moore to perform high molecular weight hydrocarbon (HMWHC) analyses on sediments, demersal fish, and macroepifaunal samples collected on each of three Benthic Cruises conducted during the summer and fall of 1977 and the winter of 1978. Also included in the subcontract work was a similar group of samples collected during the summer of 1976 and stored in freezers since that time. This work is performed for Dames & Moore on its Bureau of Land Management 1977/78 MAFLA Benchmark Survey (BLM Contract Number AA550-CT7-34). This final report includes a list of all benthic samples received at ARLI for HMWHC analyses in addition to those already listed in the trace metals report (Chapter 5). The list also indicates whether each sample was processed individually, or was pooled with one or more other samples before analysis, or was not analyzed because of its small size. The report also gives a brief description of the methods used in analyzing each type of sample, and a summary of the analytical results of these analyses. The responsibility for a detailed interpretation of the results has been assigned to the Hydrocarbon Committee and that topic is not included in this report.

METHODS

The methods used in this investigation are designed to meet the requirements prescribed in BLM Solicitation Number AA550-RP7-10, as modified June 30, 1977. The third quarterly report submitted to Dames & Moore by ARLI in June, 1978 (Dames & Moore, 1978e) should be consulted for a detailed description of the analytical methods and quality control practices used in processing these samples. Only a brief description of them is included in this report.

ANALYTICAL METHODS

Benthic Sediments

Sample Drying

Benthic sediment samples are shipped to ARLI frozen and packed in quart metal cases with friction-sealed lids. To begin processing, a can is allowed to stand at room temperature until the sediment has thawed sufficiently to permit transfer of 200 to 300 g of it to a clean beaker. The sediment is then refrozen before drying on a Virtis Model 10-145 lyophilizer. Drying times range from 24 to 48 hours.

Extraction of Sediments

A 100 to 200 g portion of dry sediment is extracted through 300 cycles on the Soxhlet extraction apparatus. With tentative approval of BLM, the methylene chloride: methanol (14:1) azeotrope was used as extraction solvent instead of the toluene: methanol azeotrope. Tests conducted at ARLI indicated that the two solvent mixtures produced similar results when used on two portions of the same sediment. Results of these tests and the reasons for the change are discussed later in this report.

After extraction, the sediment extract is reduced to a volume of 10 mℓ or less, using a rotary vacuum evaporator.

Sulfur Removal

If the extract solution darkens a strip of activated copper metal, the solution is treated to remove sulfur. Activated copper granules are added to the solution and allowed to stand for 30 min. or longer at room temperature. The extract is then removed from the copper by pipet and prepared for saponification.

Saponification

The extract solution, whether or not desulfurized, is combined with equal volumes of water and 0.5 N potassium hydroxide in methanol and refluxed for 4 hours. Saturated sodium chloride solution is then added and the mixture extracted three times with hexane. The organic fractions are combined, washed with water, and evaporated to dryness. The nonsaponifiable residue is then weighed to the nearest 0.1 mg.

Liquid-Solid Chromatography

A glass chromatographic column tube 10 mm in diameter is packed to a height of about 20 cm with activated silica gel (Davison, Grade 923). No more than 30 to 50 mg of nonsaponifiable extract is added to the column and two fractions are eluted. The first, or hexane, fraction contains mostly saturated hydrocarbons and is eluted with hexane. The second, or benzene, fraction is eluted with a mixture of 40% benzene in hexane and contains unsaturated and aromatic hydrocarbons. The fractions are evaporated under a stream of dry nitrogen and weighed to the nearest 0.1 mg.

Gas Chromatography

Analysis of each liquid chromatography fraction is carried out on one of three gas chromatographs: a Hewlett-Packard, Model 5730A, an ANTEK, Model 340 ALP, and a Hewlett-Packard, Model 5830A (GFE). All three instruments are equipped with dual flame ionization detectors (FID) and linear temperature programmers. The capillary columns are borosilicate glass, 30 m long by 0.25 mm I.D. The coating is OV-101. Helium at ~1 cc min^{-1} is used as the carrier with nitrogen as the make-up gas added just before the detector.

Each liquid chromatography fraction is dissolved in 10 μℓ of benzene, or more if the weight of the fraction is high enough to warrant additional dilution. A Hamilton 1 μℓ syringe is used to inject samples with volumes of 0.10 to 0.15 μℓ. With this small sample volume, no splitter is used at the head of the GC column.

The gas chromatograph is temperature programmed to recover normal hydrocarbons from n-C-14 to n-C-32. Solvent blanks are run daily and a short-cycle instrument blank is run between all sample injections.

The signal from the FID of the gas chromatograph is passed through a voltage-to-frequency (V/f) converter and recorded on magnetic tape with a conventional 4-track audio recorder. This taped signal provides long term storage of data that can be readily converted to "original" traces any time retrieval is convenient. The taped signal is passed through a V/f converter and the signal split between a strip chart recorder and an electronic integrator. The replayed strip chart record can be recorded at any chosen chart speed and the signals enhanced or suppressed as necessary in order to display all peaks on scale and of optimum size for visual study. The integrator output lists each peak by retention time and area. Integration distortion by this process in less than 1%.

Output from the integrator is in both printed tape and in ASCI-language punched-tape form. The latter integrator output is entered into a computer along with appropriate information about the type and amount of sample, response factor and retention times of standards. The computer then calculates the Kovat's Index and amount of material represented by each significant peak on the GC trace. The area on the GC trace representing the unresolved material is measured and entered into the computer to permit calculation of the amount of unresolved material. The computer is also programmed to calculate and print out the ratios and percentages of selected compounds in the two fractions specified by the BLM.

Gas Chromatographic/Mass Spectroscopic (GC/MS) Analysis

Paraffinic and aromatic fractions of sample extracts isolated and analyzed by gas chromatography may be further characterized by analysis on a computerized GC/MS system. At ARLI, this is done using the Finnigan Model 3200F GC/MS equipped with a 2300 INCOS computer.

The GC capillary column, operating conditions, temperature program, and sample size are the same as described above for GC analysis. In this case, however, the detector is a mass spectrometer analyzer, upstream of which is the helium separator. This latter consists of a Finnigan jet separator with a separation factor of about 20X. The Finnigan mass analyzer is a quadruple type operated at an electron energy of 70 eV, an emission current of 50 A, and an ion energy of 6 V. The electron multiplier is operated at 1,700 V at a setting of 44 A. These parameters are adjustable to permit compensation for changes in instrument sensitivity.

In the normal, temperature-programmed run, mass spectra are taken once every two seconds. Thus, about 2,500 scans or mass spectra are generated in a single GC/MS analysis. All of the data are retained in digital form in the computer on a magnetic disc.

The first step in the analysis of the data is the examination of the total ion trace or reconstructed ion chromatogram on the CRT terminal. This trace corresponds somewhat to the gas chromatogram obtained for the same extract. However, the mass spectrometer is less sensitive than the FID used in the gas chromatograph. As a result, chromatograms prepared on the two different instruments will be similar, but not directly comparable on the ordinate scale.

A background-corrected (enhanced) version of the total ion trace may also be prepared by the computer. On this corrected trace, peaks resulting from the sample are emphasized and peaks resulting from the instrumental background are eliminated. This simplifies the task of selecting the peaks that are to be examined in greater detail. A background-corrected mass spectrum can then be prepared for each peak designated by the operator.

Both total ion traces along with the selected mass spectra may be printed out on the Versatec line printer for manual search purposes. Assignments for the individual peaks may be requested through the terminal by asking for a library search. This consists of spectra matching with the National Bureau of Standards library which consists of mass spectra of 25,409 different compounds. The computer selects five or more, as instructed, of the best-fit candidates for the peak assignments. These are printed out in order of merit, together with data indicating purity and fit of the chosen mass spectra with the contents of the peak being explored. The "purity" parameter indicates the percentage of the mass spectral contributions of the assigned compound in the peak being analyzed while the "fit" relates to the statistical correlation between m/e values of the ions in the peak and those of the assigned compounds.

The next step in furthering the assignment is to compare the retention times of the selected compounds with the time at which the peak appeared. This hardens the selection, which can then be finalized by manually comparing the mass spectrum obtained for the peak studied with mass spectra published in the literature.

Demersal Fish

Tissue Preparation

Tissue preparation is carried out in an enclosed clean bench using clean, hexane-rinsed Pyrex glassware and utensils. The thawed specimen is washed, skinned, and a 20 g sample of muscle tissue is transferred to a tared, hexane-rinsed digestion flask. The flask is weighed again to determine the wet weight of the sample. The dry weight of the sample is calculated using the moisture content derived for the corresponding TMs sample which is prepared from the same specimen as the hydrocarbon sample. The TMs sample, however, is first dried on the lyophilizer, thus, permitting the calculation of moisture content for the tissue used in both types of determinations.

Digestion-Saponification

A 50 m portion of 0.5 N KOH in methanol is added to the flask containing the fish tissue for hydrocarbon analysis. The flask is attached to a condensor and refluxed for 4 hours (h) or until the tissue is well digested. An equal volume of water is then added and the mixture refluxed for an additional 4 h. At the end of that time, an equal volume of saturated NaCl solution is added to the mixture.

Extraction

The saponification mixture is next extracted with three 50 m portions of hexane. The extracts are combined, reduced in volume with a rotary vacuum evaporator or on a warm hot plate and transferred to a tared vial. The remaining solvent is evaporated under a stream of dry nitrogen on a warm hotplate. The vial is reweighed and the weight of nonsaponifiable extract is calculated.

Liquid Chromatography, Gas Chromatography, and GC/MS Analysis

These analytical procedures are carried out in the same manner as described above under Sediment Analysis.

Benthic Macroepifauna

Tissue Preparation

Preparation of the macroepifaunal tissue is carried out in a manner similar to that used for the demersal fish. The type of sample material used varies with the kind of organism being sampled. Muscle tissue from the tail section composes the sample material for larger shrimp specimens, while one or more whole organism makes up the sample material for small shrimp and echinoderm specimens. Some starfish samples include only the arms of the specimen. Soft inner tissue makes up the sample material for shellfish and crabs.

When the specimens furnished are too small or too few to provide sufficient sample material, the analysis cannot be performed. None of the coral specimens supplied could be analyzed because of insufficient sample weight.

Digestion-Saponification

From this point on, the macroepifaunal tissue is processed in the same manner as described above for demersal fish.

INTERNAL QUALITY CONTROL

Sample Accountability

A description of each sample received at ARLI is recorded in a sample log book and a unique identification number is assigned to the sample. Using this number to identify the sample, permanent records are kept in laboratory notebooks of all operations, including weighings and other measurements involving the sample. Each record is dated and initialed by the individual performing the operation.

Instrument Calibration

Gas Chromatograph

The computer-interfaced gas chromatograph system at ARLI is designed to classify the components of a sample mixture and to measure the amount

of each component in the mixture. Both of these operations require that the retention times and detector responses of the mixture components be compared with the retention times and responses of standards. Since retention times, especially, are very sensitive to GC operating conditions, such as carrier gas flow rates or aging of the column, standards must be run not only when a column is first installed in the gas chromatograph, but whenever carrier gas flow rates or other operating conditions are changed. Standards are run at ARLI daily.

Qualitative Standardization

The computerized GC system at ARLI is made up of three principal elements; the gas chromatograph itself, an Autolab System I electronic integrator (Spectra-Physics, Autolab Division, Santa Clara, California), and a computer.

A standard hydrocarbon mixture containing normal aliphatic hydrocarbons is first injected into the gas chromatograph. Retention times for each of the normal hydrocarbons are stored in the memory of the computer along with their corresponding Kovat's Indices. Another compound, either an aliphatic, such as pristane, an aromatic, such as anthracene, or a non-hydrocarbon such as methyl stearate, can then be injected into the GC and its retention time measured. Since this varies somewhat from day to day and because of instrumental reproductibility limitations, the computer has been programmed to compare the retention times of such reference compounds with corresponding values in memories. Correction factors can then be applied to the retention times of all compounds of known Kovat's Index stored in the computer memory. Then, when the retention times of complete GC traces are input, the computer furnishes the appropriate Kovat's Index and compound identifications for all constituents furnishing matches with the calibrated library. If there is no matching retention time in storage, the computer calculates a Kovat's Index for the compound by selecting the retention times of the three nearest normal hydrocarbons and their corresponding Kovat's Indices. A quadratic curve is then mathematically fitted through these three Kovat's Indices as a function of retention time. The computer then calculates a Kovat's Index for the new compound from the quadratic function. If the identity of the compound later becomes identified (in GC/MS operations) its retention time, name, and Kovat's Index can be stored in the computer memory and it becomes a new member of the library. A set of such reference data has been stored for use with the hexane fractions and another set for use with the benzene fractions.

Quantitative Standardization

Quantitative measurements in gas chromatography depend upon determination of a detector response factor that is applicable to the compound in question. The response factor for a particular compound is determined by injecting varying amounts of the compound into the GC and measuring the areas of the peaks produced on the GC trace by the various amounts injected. Ideally, response factors should be determined for each compound that makes up the mixture to be analyzed. The hydrocarbon mixtures analyzed in this project are too complex to make such a procedure practical.

In practice, response factors for the normal hydrocarbons are measured directly, using a standard solution containing three to eight or more components. These standard solutions are prepared at ARLI by dissolving in benzene a precisely weighed amount of each of the purified components. Then, a small, measured amount (0.1) of a standard solution is injected into a gas chromatograph, a strip chart record or GC trace is produced with a peak corresponding to each component in the standard. The area of each peak is measured electronically by the integrator system in arbitrary units or counts. Since the weight of each component of the standard can be calculated (concentration of component x injection volume), a Specific Response Factor for each component may be calculated by dividing the area of each peak produced by the weight of that component injected into the gas chromatograph.

Two factors must be taken into consideration in applying these Specific Response Factors to data from samples. In the first place, these Specific Response Factors vary somewhat from detector to detector and from day to day, due to small differences in detector systems, slight variations in gas flow rates and other operating parameters, gradual changes in the column itself, and the difficulty in reproducing small injection volumes. This day to day variation is compensated for by a daily injection of a standard on each detector, and a daily calculation to Specific Response Factors for each detector.

The second factor that must be considered in applying the Specific Response Factors to sample data is the relationship between the factors and carbon number of the compound producing the response. For the normal alkane hydrocarbons used in the standard solutions, the Specific Response Factors are constant and linear for carbon numbers between 14 and 18. As the carbon number increases beyond this value, the Specific Response Factors decrease markedly. Analysis of a series of Specific Response Factors collected over a period of several weeks shows that the data describe a bimodal function determined by the least squares method to be a horizontal straight line from n-C-14 to n-C-18 followed by a horizontal-axis semiparabola with the vertex at n-C-18 for the higher carbon number range. Further discussion of this relationship between response factors and carbon number was presented in the third quarterly report (Dames & Moore, 1978e).

Corrections for these two factors are made by means of a computer program, which takes as input the concentration of each component in the standard, the amount of standard njected into the gas chromatograph, and the area of each peak in the resulting chromatogram. The computer fits these data into the biomadal function described above and prints out two Fitting Constants (CTUG18 and CTUG30) that are characteristic of that particular standard relation, detector, and date. These two fitting constants are calculated daily for each detector. Since these values may fluctuate as much as 30% from day to day for a given detector, the values are averaged with those of the preceding five days. Variations in these six-day averages are between 5 and 10%. These average values are used in the quantitative evaluation of GC traces of sample extracts.

When a sample chromatogram is to be quantitatively evaluated, the two Fitting Constants for the date and detector corresponding to that of the

sample chromatogram are supplied to the computer along with the sample data. These two constants permit the computer to re-establish the proper standard function from which appropriate response factors may be calculated for each pak o the sample chromatogram. A more detailed explanation of the Specific Response Factor Correction Program was given in the third quarterly report (Dames & Moore, 1978e).

Gas Chromatograph/Mass Spectrograph

The three main requirements for insuring reliable performance of the GC/MS system are: (1) normal GC performance, (2) production of standard cracking patterns, and (3) acceptable instrumental sensitivity.

Gas Chromatograph Calibration

The GC/MS is calibrated for GC performance in essentially the same manner as described above for qualitative calibration of the gas chromatograph. The same standard solutions of normal aliphatic hydrocarbons are injected into the GC/MS to establish a correlation between the GC/MS scan numbers and the Kovat's Index system of identifying peaks in a GC trace.

Ion Abundance and Mass Calibrations

Because mass spectrometers tend to drift, cracking patterns are not entirely reproducible. To ensure that variations in cracking patterns are eliminated, mass and ion abundance calibrants are used daily on the ARLI GC/MS system. For calibrating mass numbers, FC-43, a fluorocarbon providing a variety of ions or mass markers over a broad molecular weight range is used. For tuning the instrument, so that the ratios of ions from the calibrant are correct, the compound normally used is decafluorotriphenylphosphine (DFTPP). An equivalent of 20 ng of this compound is injected into the GC/MS. The cracking pattern (mass spectrum) is then compared to the specifications promulgated by the U.S. Environmental Protection Agency and as they appear in Table IV of Eichelberger (1975).

Instrumental Sensitivity

The response of the GC/MS system to a fixed quantity of sensitivity calibrant will vary with the condition of the analyzer and other instrumental parameters. At ARLI, the GC/MS response is monitored daily through the use of a sensitivity calibrant specified by the U.S. Environmental Protection Agency, namely, 1,4-dichlorobutane. An equivalent of 20 ng of this material is injected daily and the integrated under-curve area for its GC peak is then recorded and compared with a Shewhart chart showing the average deviation for this parameter for the preceding dates.

Detectivity of the instrument is also determined periodically with methyl stearate. The manufacturer's specification is detection capability for 1 ng of this material. This is verified periodically by injecting 1 ng of this material and conducting a limited-ion search in the elution area.

Procedural Blanks

As a check on the purity of the solvents, the cleanliness of glassware and the care taken in handling the samples, a procedural blank is run at regular intervals. For the sediments, demersal fish, and macroepifauna, a blank is run with every 40 samples.

Sediment Procedural Blanks

A sediment procedural blank is prepared by freezing a small amount of distilled water in a clean beaker. After the beaker has been dried on the lyophilizer, extracting solvent is used to rinse the inside of the beaker. The rinsings are transferred to a Soxhlet extractor, a clean, empty extraction thimble is put into the apparatus, and the extraction process is carried out as if a sediment were being extracted. The extract solution is then processed in the same manner that a sediment extract would be. Although no sediment is used, a blank "sediment weight" of 100 g is assumed for purposes of calculating the results.

A total of 11 sediment procedural blanks were analyzed and the results reported to Dames & Moore. Table 52 summarizes the GC recoveries. Values shown there are at least an order of magnitude smaller than those reported for most of the sediments. One above-average blank, dated May 24, 1978, resulted from the use of an insufficiently cleaned extraction thimble. The level of hydrocarbons reported even for this highest blank is still well below that seen in most of the MAFLA sediment samples. The standard deviation seen in these blanks is typical of the sediment extraction and analysis process.

Demersal Fish and Macroepifaunal Procedural Blanks

The processing of these two types of samples is identical and their procedural blanks are run in the same way. A 25 mℓ portion of distilled water is poured into a clean glass dissecting tray. The tray is tilted from side to side so that the inner surfaces of the tray are thoroughly rinsed by the water. The tray is then tipped up so that the water collects in one end. A set of clean dissecting instruments, forceps, scissors, and knife is allowed to stand in the water for 15 min. or longer. The water is then poured into a digestion flask, methanolic potassium hydroxide solution is added, and the mixture is subjected to digestion, saponification, extraction, and the rest of the analytical process just as if it were a tissue sample. A dry tissue weight of 5 g was used for calculation purposes.

A total of 16 tissue procedural blanks was analyzed and the results reported to Dames & Moore. Table 53 summarizes the GC recoveries. Values shown there are very similar to, or only slightly less than, those reported for many of the demersal fish samples. Compared with the macroepifaunal samples, which exhibit a much broader range of hydrocarbon concentrations, the blanks vary from a level near the actual samples to an order of magnitude lower.

TABLE 52

MAFLA SEDIMENT PROCEDURAL BLANKS - GC RECOVERIES

ARLI ID#	Proc. Blank #	Date Started	Assumed Sample Weight,g.	GC Recoveries, $\mu g \cdot g^{-1}$ Hex.	Benz.	Total
Summer, 1976 (Archive)						
77066	2	8/11/77	100	0.026	0.036	0.062
77066	3	9/21/77	100	0.046	0.003	0.049
Summer, 1977 (DM I)						
97048	1	10/26/77	100	0.038	0.004	0.042
97048	2	11/01/77	100	0.008	0.018	0.026
97048	3	11/04/77	100	0.044	0.006	0.050
Fall, 1977 (DM II)						
117103	1R	12/12/77	100	0.009	0.015	0.024
117103	2	12/22/77	100	0.019	0.009	0.028
Winter, 1978 (DM IV)						
28073	1	3/06/78	100	0.029	0.020	0.049
28073	3	5/24/78	100	0.065	0.025	0.090
28073	4	6/01/78	100	0.022	0.000	0.022
28073	5	6/15/78	100	0.000	0.016	0.016
				Average ($\mu g \cdot g^{-1}$)		0.042
				Std. Dev. ($\mu g \cdot g^{-1}$)		0.021

TABLE 53

MAFLA TISSUE PROCEDURAL BLANKS - GC RECOVERIES

ARLI ID#	Proc. Blank #	Date Started	Assumed Sample Weight,g.	GC Recoveries, $\mu g \cdot g^{-1}$ Hex.	Benz.	Total
Summer, 1976 (Archive)						
Macroepifauna						
97077	1	11/21/77	5	0.00	0.84	0.84
97077	2	11/30/77	5	0.40	0.058	0.46
Summer, 1977 (DM I)						
Demersal Fish						
97044	1	10/25/77	5	0.00	0.00	0.00
Macroepifauna						
97047	1	11/21/77	5	0.00	0.22	0.22
97047	2	11/30/77	5	0.30	0.60	0.90
Fall, 1977 (DM II)						
Demersal Fish						
117104	1	12/07/77	5	1.0	0.33	1.3
117104	2	12/21/77	5	0.25	0.23	0.48
117104	3	1/09/78	5	0.30	0.15	0.45
Macroepifauna						
117106	1	12/27/77	5	1.0	0.84	1.8
Winter, 1978 (DM IV)						
Demersal Fish						
28052	1	2/14/78	5	0.95	0.083	1.0
28052	2	3/22/78	5	0.14	0.19	0.33
28052	3	4/08/78	5	0.26	0.37	0.63
28052	4	4/18/78	5	0.53	0.00	0.53
Winter, 1978 (DM IV)						
Macroepifauna						
28054	1	2/28/78	5	0.53	0.52	1.0
28054	2	3/09/78	5	0.24	0.42	0.66
28054	3	3/10/78	5	0.00	0.00	0.00
				Average ($\mu g \cdot g^{-1}$)		0.66
				Std. Dev. ($\mu g \cdot g^{-1}$)		0.47

Recovery Studies

Chromatography Recovery Tests

A standard solution of aliphatic hydrocarbons is prepared by dissolving in hexane weighed amounts of n-tetradecane, n-heptadecane, n-tetracosane, n-dotriacontane, and pristane. A similar standard solution of aromatic hydrocarbons is prepared by dissolving in benzene weighed amounts of 2,3-dimethylnaphthalene, anthracene, chrysene, and 1,3,5-triphenylbenzene. The concentration of each component in both solutions is within the range of 1 to 2 $mg \cdot m\ell^{-1}$.

The chromatography recovery tests are carried out by placing 0.5 $m\ell$ of each standard solution on a silica gel chromatography column which has been prepared in the same way that it would be for sample analysis. The standards are then eluted from the column in the usual way and the two fractions collected, dried, and injected into the gas chromatograph just as a sample would be. The amount of each component detected by the gas chromatograph is compared to the amount of that component placed on the silica gel column as a measure of the recovery efficiency of the LC/GC systems.

The results of a series of three of these tests are shown in Table 54. Recoveries are all at or above the 70% level expected by BLM, except for the low-boiling compounds, n-tetradecane and 2,3-dimethylnaphthalene. Loss of some of these relatively volatile compounds is nearly unavoidable during removal of the solvent from the liquid chromatography fractions.

Sample Spiking Program

Every fifth HMWHC sample is spiked with a mixture of n-tetracosane and chrysene. Sediment samples are spiked with 100 μg of each compound before extraction or with 20 μg of each before saponification or before liquid chromatography. Tissue samples are spiked with 20 μg of each compound either before digestion or before liquid chromatography. Spiking is done by using a 1 $m\ell$ glass syringe to measure the appropriate volume of a benzene solution containing the two spiking materials in a concentration of 100 $\mu g \cdot m\ell^{-1}$ for each compound. When a sediment is spiked before extraction, 0.5 $m\ell$ of spiking solution is added to each of the two thimbles containing the dried sediment. All other spikings are carried out by adding 0.2 $m\ell$ of spiking solution to the flask or beaker containing the extract to be spiked.

Spiking was carried out on 74 sediment samples, 41 demersal fish samples, and 30 macroepifaunal samples. Average recoveries are summarized in Table 55. No significant differences were noted in recoveries from samples spiked at different stages in the analytical process. Nor does there seem to be a significant difference between recoveries for sediments, demersal fish, and macroepifaunal samples. Recoveries of n-tetracosane in the hexane fractions show a weighted average of 87%, with the sediments showing slightly better recoveries than the tissue samples. On the other hand, recoveries of chrysene in the benzene fraction have a weighted average

TABLE 54

CHROMATOGRAPHY RECOVERY TEST RESULTS

Compound	Percent Recovered*	Standard Deviation,%
n-Tetradecane	38.	23.
n-Heptadecane	68.	9.
Pristane	76.	11.
n-Tetracosane	87.	16.
n-Dotriacontane	73.	20.
2,3-Dimethylnaphthalene	60.	9.
Anthracene	84.	4.
Chrysene	76.	13.
1,3,5-Triphenylbenzene	82.	14.

*Average of 3 tests

TABLE 55

HMWHC SPIKED SAMPLE SUMMARY

Sample Group	Number Spiked	Spike Recovery, % Average $n-C_{24}$	Average Chrysene	Standard Deviation $n-C_{24}$	Standard Deviation Chrysene
Sediment					
Archive	20	101	64	46	48
DM I	22	104	64	51	43
DM II	9	82	26	16	15
DM IV	23	85	75	45	49
Demersal Fish					
Archive	2	35	42	22	51
DM I	12	84	50	30	41
DM II	13	89	40	40	27
DM IV	14	68	54	40	32
Macroepifauna					
Archive	9	68	80	48	62
DM I	5	67	49	43	25
DM II	9	92	65	59	55
DM IV	7	91	64	31	24

of barely 60% with the demersal fish having slightly lower recoveries than the other two sample types.

These two compounds were selected as spiking materials on the basis of our experience with n-dotriacontane and naphthalene and anthracene as spiking materials. The n-dotracontane elutes near the end of the GC program where the specific response is not as good as it is earlier in the program. The choice of n-tetracosane, with its shorter retention time, was a good one and resulted in very good recoveries of the spike in the hexane, or aliphatic fraction. On the other hand, the choice of chrysene as a spiking compound was not so successful. It was selected because it was less volatile than naphthalene or anthracene and less likely to be lost during the evaporation steps in the analytical process. Unfortunately, chrysene proved to be very difficult to redissolve once the solvent was evaporated from it. Several small variations in technique were instituted in an effort to overcome this problem. A few drops of benzene were added to the hexane used to transfer the nonsaponifiable extract to the liquid chromatography column. Benzene was adopted as the gas chromatography sample injection solvent. Vials or beakers were warmed gently to encourage dissolving whenever solvent was added to a dry extract or fraction. These measures were not entirely successful and chrysene recoveries continued to average about 60%.

The standard deviations listed in the table indicate a variation of about 50% in recoveries of both aliphatic and aromatic spikes in all three types of samples. This range of recoveries apparently is the result of other factors besides the difficulty in dissolving the spiking materials. These factors include the day to day variations in the specific response of the gas chromatograph and the difficulty of reproducing the very small GC injection volumes (0.1 $\mu\ell$). The daily variation in response is a characteristic of gas chromatography and the daily injection of standards on each detector serves to minimize, if not eliminate, its effects on analyses. The very small sample size is more difficult to deal with. Capillary columns deteriorate very rapidly if too much solvent is used to inject the sample. An alternative to small sample volume injection is to inject a larger sample volume and use a splitter which permits only a small fixed percentage of the sample to enter the column. Our experience, however, indicates that the use of a splitter on a routine basis for large numbers of samples leads to a greater variation in recoveries than does the non-split injection of smaller samples. There was also some indication that the splitting ratios for higher-boiling, higher-molecular weight materials were often lower than for lower-molecular weight materials in the same GC run.

Despite its limitations, we have chosen the direct injection method and the $\pm$50% recoveries to which it leads because we believe it is the best option available at present. As new techniques and equipment are developed, the range of recoveries may be narrowed considerably. We believe that the direct injection method is presently the state-of-the-art for routine HMWHC analysis of large numbers of samples by quantitative capillary column gas chromatography.

Materials

The solvents used in the hydrocarbon extraction and analysis are Burdick and Jackson Distilled In Glass Solvents. They include benzene, hexane, methanol, methylene chloride, and toluene. Reagent-grade potassium hydroxide supplied by Fisher Scientific Company is used in preparing digestion and saponification reagents for the tissues and sediments. The silica gel used for liquid-solid chromatography is Davison Grade 923 manufactured by the Grace Chemical Company.

INTERLABORATORY CALIBRATION

In order to provide a basis for comparing HMWHC analyses performed at ARLI with similar analyses performed at other laboratories, a series of analyses were performed on the API Reference Oil, Kuwait Crude, in July and August, 1977. Four portions of the crude oil were analyzed by the same liquid chromatographic and gas chromatographic procedures used for analyzing samples. A report describing these analyses was submitted to Dames & Moore for interlaboratory comparison and will not be further discussed here.

RESULTS

A total of 976 sediment, demersal fish and macroepifauna samples for HMWHC analysis was received at ARLI. Some of these samples were collected in the summer of 1976 and were in freezer storage for a year before being analyzed. Most of the samples were collected on the three Dames & Moore Benthic Cruises, DM I, DM II, and DM IV, conducted during the summer 1977, fall-1977, and winter-1978. Analysis of most of these samples was completed, but the small size of some biological specimens necessitated some unanticipated pooling of samples before analysis. Some samples were not analyzed at all because of their small size. Appendices 8-A through 8-D list all the HMWHC samples that were not listed earlier in Appendix 5-A and give an indication of the disposition of each sample.

GAS CHROMATOGRAPHIC/FLAME IONIZATION DETECTOR ANALYSES

Individual reports of the results of the analysis of each sample were reported to the Data Processing Center at the New Orleans office of Dames & Moore. There, the results were recorded on magnetic tapes which will be placed on file at the National Oceanographic Data Center in Washington, D.C.

The format of the reports submitted for sediments, demersal fish, and macroepifaunal samples is identical. Appendix 8-E includes examples of reports for each of the three sample types. Each report includes three elements, namely, a cover page, computer printouts, and GC traces. The cover page includes information identifying the sample and lists gravimetric data for the sample, nonsaponifiable extract, and L.C. fractions.

The GC traces, one each for the hexane and the benzene fractions, are labeled with information identifying the sample, GC operating conditions, and the date of analysis. Several of the more prominent peaks are labeled with Kovat's Indices or other identifications to serve as references for

other peaks in the printout. The GC traces included in Appendix 8-E do not contain all the features just described, since they have been photoreduced. These same chromatograms are shown on the following pages as Figures 159-161 to illustrate graphically the results of ARLI's workmanship.

The computer printout for each fraction lists the peaks on the trace by their retention times and Kovat's Indices. Also listed is the concentration in the dry sample ($\mu g \cdot g^{-1}$) of the substance represented by each peak. The percentage of the compound in the particular fraction is listed and any specific identification is listed in the right-hand column whenever such identification is possible. Finally, the printout lists the total resolved material, the unresolved material, and their sum for the total recovery in each fraction. At the end of the benzene fraction report, the sum of the two recoveries is listed as the "TOTAL OIL" recovered from the sample.

The printout described above is included for both the hexane and the benzene fractions. In addition, the hexane fractio report includes a page listing the concentrations of the normal paraffins, the non-normal paraffin hydrocarbons, which are simply lumped together as "ISO-" compounds for each carbon number, and the isoprenoids, pristane and phytane. At the bottom of the page are listed certain percentages and ratios that are often useful in characterizing sediment or tissue extracts.

Table 56 shows the total number of each sample type received from each of the cruises and from archives and shows how the samples were processed. It can be seen that the undersized samples resulted in a 25% reduction in the number of analyses completed. The small samples also caused some delay in processing the samples while BLM approval was sought for an alternate plan for handling these small samples. As a result, completion of the analyses of these samples was approximately a month behind schedule.

GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC ANALYSIS

GC/MS analysis offers a means of identifying or confirming a tentative identification of a peak of particular interest on a gas chromatogram. A total of 33 GC/MS analyses have been completed on benthic samples. Table 57 summarizes the number of fractions that have been completed. Earlier samples were selected because of very busy chromatograms or chromatograms showing rather unusual fingerprints. These GC/MS files have been forwarded to Dames & Moore during the program.

In general, the reconstructed ion chromatogram (RIC) produced by the mass spectrometer is very similar to the GC curve. This is illustrated in Figure 162. In fact, the capillary column used for generating the RICs shows more separation between the isoprenoids, pristane and phytane, from n-C-17 and n-C-18 than the column used with the GC FID system and with adequate sensitivity for most of the samples selected. Brief comments on selected GC/MS runs are given below.

FIGURE 159

GC TRACES FOR SEDIMENT SAMPLE 97048-19

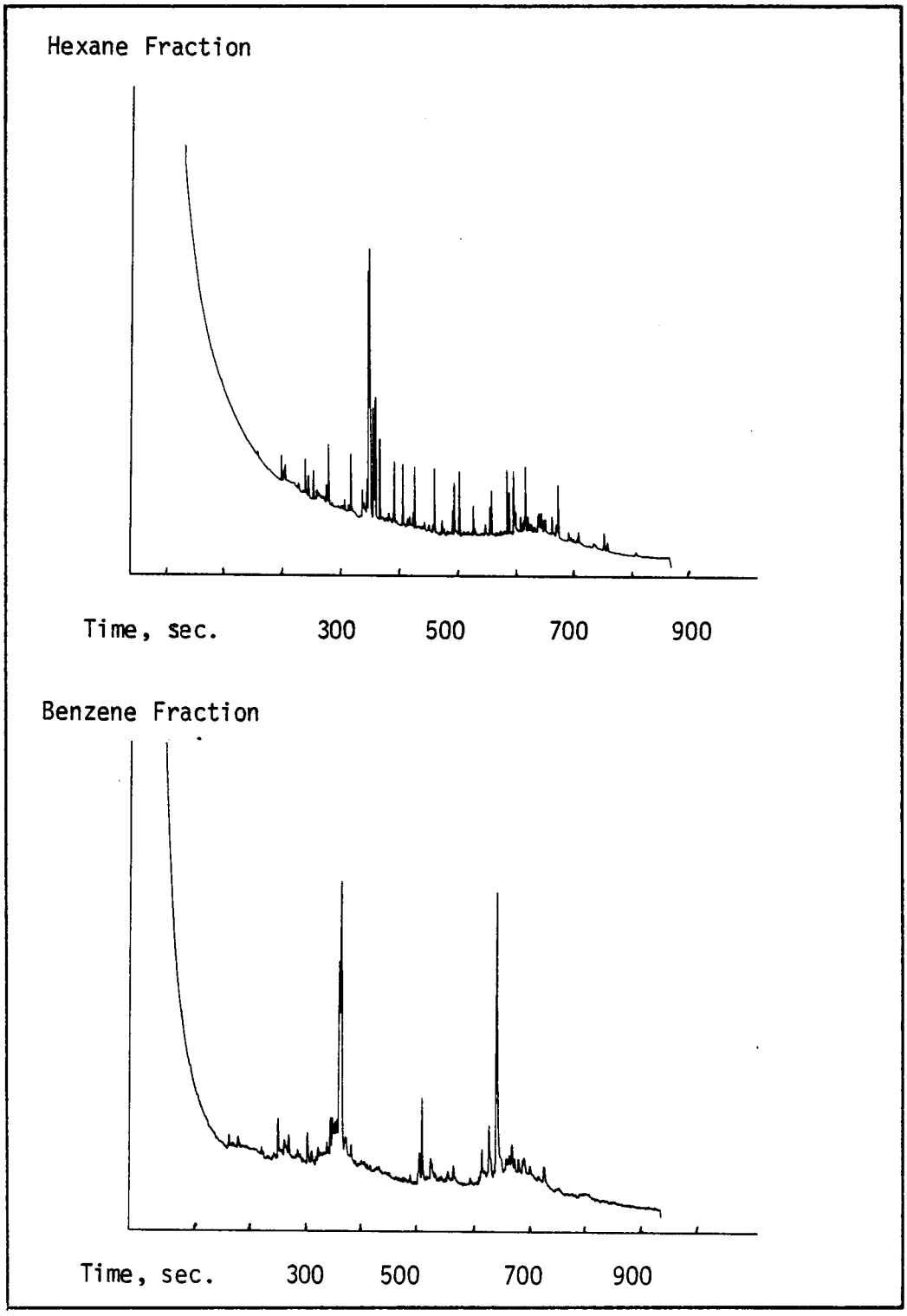


FIGURE 160

GC TRACES FOR DEMERSAL FISH SAMPLE 28052-63

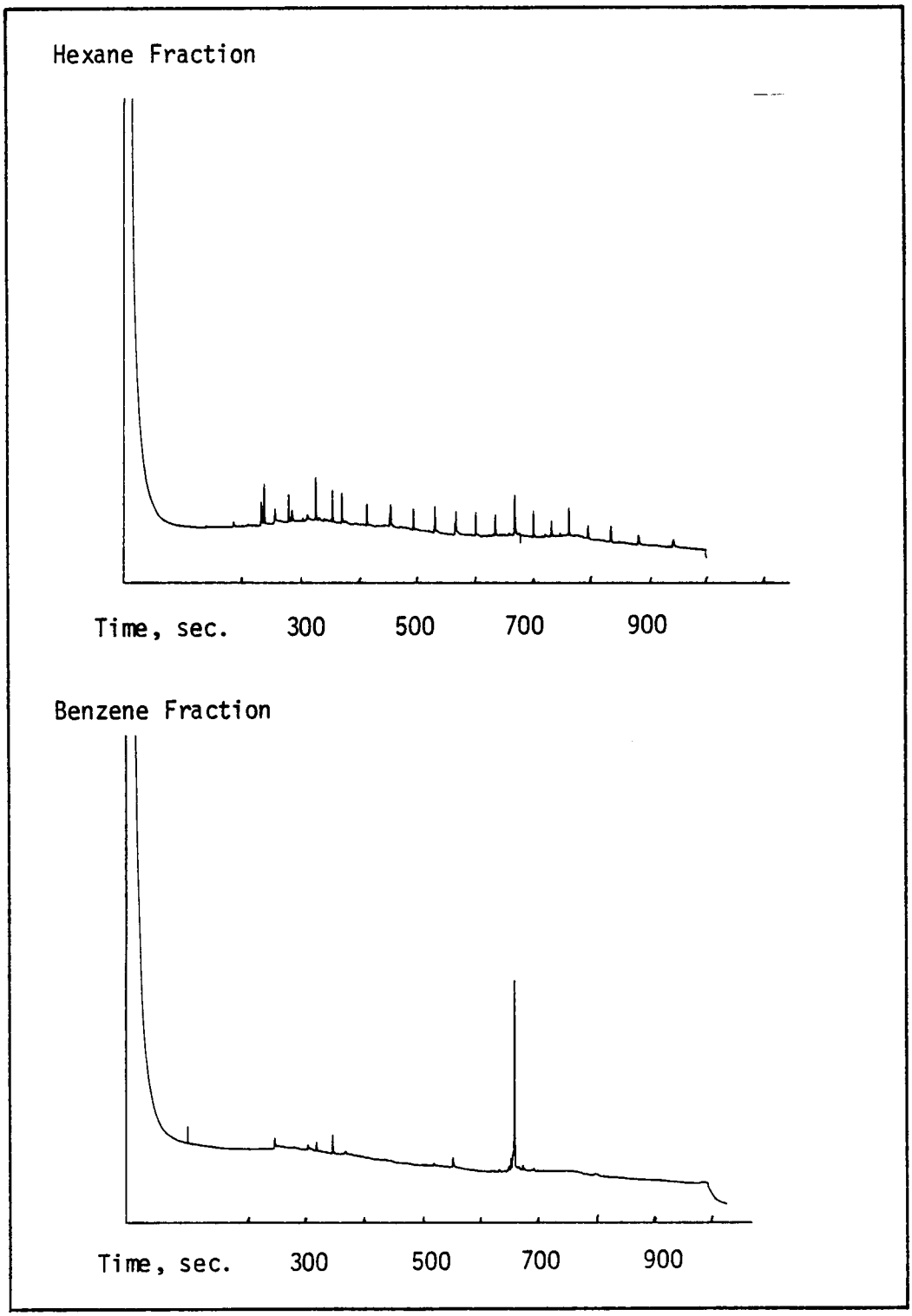


FIGURE 161

GC TRACES FOR MACROEPIFAUNAL SAMPLE 28054-42

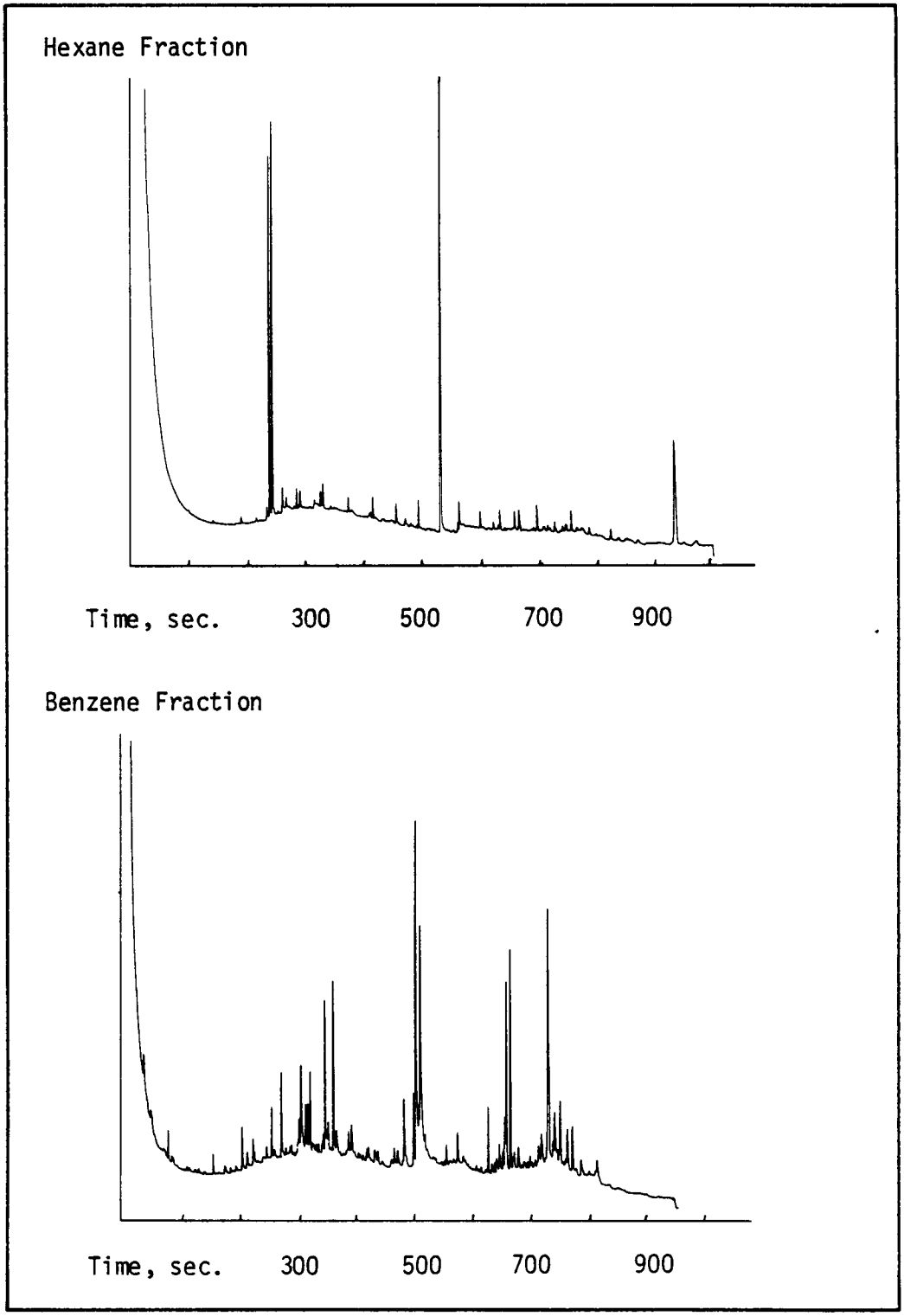


TABLE 56

SUMMARY OF DISPOSITION OF BENTHIC SAMPLES
RECEIVED AT ARLI FOR HMWHC ANALYSIS

	Number Samples Received	Small Samples not Analyzed	Small Samples Combined	Resulting Pooled Samples	Samples Analyzed and Reported
Demersal Fish					
Archive	12	0	0	0	12
DM I	82	3	29	6	55*
DM II	79	2	2	1	76
DM IV	77	0	10	5	72
Subtotal	250				215
Macroepifauna					
Archive	108	65	0	0	42*
DM I	148	77	65	22	28
DM II	54	8	0	0	46
DM IV	52	12	0	0	40
Subtotal	362				156
Sediments					
Archive	96	0	0	0	96
DM I	119	0	0	0	119
DM II	42	0	0	0	42
DM IV	107	0	0	0	107
Subtotal	364				364
Total	976	167	106	34	735

* One demersal fish and one macroepifaunal sample were lost during analysis.

TABLE 57

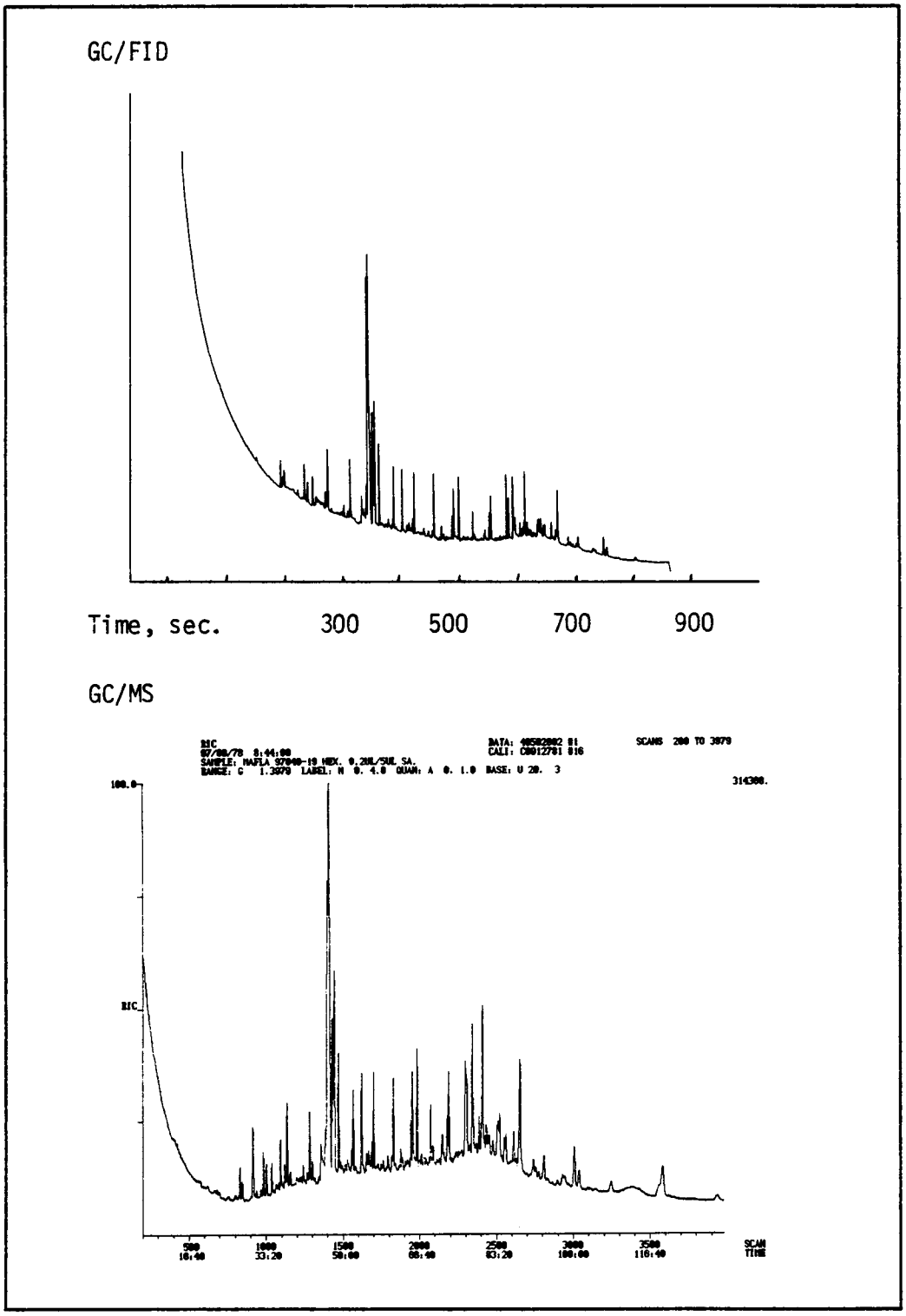
SUMMARY OF GC/MS ANALYSES COMPLETED ON BENTHIC SAMPLES

	Hexane Fraction	Benzene Fraction	Total
Sediments			
Summer, 1977 (DM I)	5	8	13
Fall, 1977 (DM II)	1	2	3
Winter, 1978 (DM IV)	0	2	2
			18
Demersal Fish			
Summer, 1977 (DM I)	4	0	4
Fall, 1977 (DM II)	0	1	1
			5
Macroepifauna			
Summer, 1976 (Archive)	0	1	1
Summer, 1977 (DM I)	1	3	4
Fall, 1977 (DM II)	1	0	1
Winter, 1978 (DM IV)	1	3	4
			10
Total			33

FIGURE 162

GC/FID AND GC/MS TRACES OF SEDIMENT

SAMPLE 97048-19, HEXANE FRACTION



Demersal Fish

The hexane fraction of sample No. 2426171770901-5, summer 1977, shows a trace of methyl naphthalene just prior to n-C-11, isobutyl phthalate following n-C-19 and a peak identified as octadecenyloxyethanol between n-C-28 and n-C-29. Other characteristics of the RIC are good separations of the pristane n-C-17 and phytane n-C-18 peaks and at least single isomers of even numbered hydrocarbons, i.e., i-C-24, i-C-26, i-C-28, etc.

The benzene fraction of sample No. 2103171671023-3, fall 1977, shows many early ketones and alcohols substituted benzenes and substituted naphthalenes. The major signal, indicated as scan 2544, approximately 84 minutes from the run start, appears to be a highly branched n-C-30 aliphatic hydrocarbon. An alternate identification for this peak is a branched hexadecatrienol. A search for polynuclear aromatics only showed a very weak response for chrysene.

Sample No. 2426171770901-1, a hexane fraction showed a predominance of polychloroflourohydrocarbons. This fish sample possibly reflects a serious marine contamination either from industrial dumping or terrestrial run-offs. Further studies of this animal or the general location where collected perhaps should be made. Without GC/MS, these peaks could be mistaken as aliphatic hydrocarbons or non-toxic esters that were of a natural origin.

Other demersal fish GC/MS scans are included in the cited submittal to Dames & Moore.

Macroepifauna

A benzene extract fraction of Placospongia carina, No. 21031870822-3 gave a GC/MS RIC very similar to the GC curve. The identities of the peaks are given on the RIC and in summary showed aromatics such as tetrahydro methylated naphthalenes, saturated and unsaturated substituted benzenes, small quantities of PCB's, a large number of aldehydes and alcohols between n-C-18 and n-C-28, and a significant response for benz(a) anthracene or chrysene. Phthalate esters were also found in significant quantities including a major response at scan 1861. This compound was identified as a butoxyethyl butyl ester phthalate. Cholestanol and ethoxycholestane were also significant peaks as expected.

A hexane fraction of MAFLA Sample No. 2426171580207-1, Portunus spinicarpus, (a crab) was analyzed by GC/MS. The large cluster of compounds between n-C-20 and n-C-25 appear to be a mixture composed of esters, aliphatic alcohols, acid amides, highly branched aliphatic hydrocarbons and the more common aliphatics with their isomers. The two principal peaks were aliphatic acid amides. The source of these amides is unknown and would be foreign to laboratory contamination. Tentative identifications were made for more than 35 compounds.

A number of other samples have been analyzed by GC/MS and the interpretive data together with their library searches are included with the data reported to Dames & Moore.

Sediments

The benzene fraction of a sediment sample No. 2536010870907 taken during the summer 1977 cruise contained a number of aromatics and oxygenated products as expected. While the concentrations of poly-nuclear aromatics are relatively low, their presence has significance. PCB's also appear as minor, but measurable, components of the sample. At least 30 components have probable assigned compositions that suggest natural petroleum contamination.

In contrast to the last sample, the benzene fraction of sediment No. 2427160870902 contained essentially all aldehydes, esters and alcohols. Some sesquiterpenes were found suggesting some potential as a petroleum source, but the information is inadequate for definitive conclusions.

Sample No. 2641010870908 produced a hexane GC/MS RIC curve that closely resembled the GC curve. Essentially, all of the minor peaks are aliphatic isomers and minor amounts of esters, probably from natural sources. The benzene fraction of sample No. 2210010880216 taken on the winter cruise of 1978 was processed through GC/MS. The chromatograms of GC and GC/MS were essentially the same. Identities of the RIC peaks suggested lower boiling esters of phthalic acid, substituted phenols, substituted pyrenes, many PCB fragments, azulenes (benzene rings joined with aliphatics), a number of higher molecular weight alcohols and esters and several aliphatic substituted poly-nuclear aromatics. The hydrocarbons suggest petroleum crudes as their origin while the alcohols, esters, and cyclic ethers would appear to be biogenetic in origin.

As mentioned earlier, Figure 162 shows the similarity between the gas chromatogram produced with an FID and the RIC produced by the GC/MS. Figure 162 is repeated as a figure in Appendix 8-E where it is accompanied by a list of some of the major compounds identified in the fraction by GC/MS.

DISCUSSION

Since the generation of analytical data is the primary responsibility of ARLI in this project, it is appropriate to consider the quality of these data and to give some general impressions regarding the results. Some special topics will also be considered in this section.

DATA QUALITY

Early in the Southern California Bight OCS Baseline Studies Program, efforts were made at ARLI and at the University of California at Los Angeles (Rohrback and Reed, 1975) to measure the analytical precision of the methods used for extracting and analyzing high molecular weight hydrocarbons in marine sediments. The studies indicated that the extracts from several aliquots of a homogenized sediment sample were qualitatively similar. The extracts show similar values for such ratios as odd-to-even ratios for normal hydrocarbons pristane to phytane, or resolved to unresolved. But the amount of material recovered varied considerably from aliquot to aliquot. The difficulty appears to lie in the preparation of analytically equivalent aliquots from nonhomogenous sediment. Similar problems exist with tissue samples taken from marine organisms, although mechanical homogenizing

equipment is much more effective with this type of sample than it is with sediments.

In the light of this experience and lacking any contractual provision for them, replicate analysis studies were not initially repeated as part of the MAFLA Program. In our third quarterly report, we reported good precision as measured by the Shewhart technique (USEPA, 1972) for measurement of the normal alkane odd-to-even ratios for 96 sediment samples. In this suite of samples, six replicate samples were collected at each of 16 stations. While good precision was seen in the measurement of the ratio mentioned above, the concentration of total hydrocarbons reported for each sediment, showed wide variation, even among sediment samples collected at the same station.

After analysis of all HMWHC samples had been completed, the Program Manager requested ARLI to perform a series of replicate analyses on two sediment and two demersal samples. After advising him of ARLI's conviction that such replicate studies reflect variations in the sample material as much as they measure precision of the analytical methods as explained above, the replicate analyses were completed. Results are summarized below.

Replicate Analysis of Sediments

Sediments collected from two stations, 2103 and 2212, during the summer of 1976 were selected for replicate analyses. Sediments were collected in gallon cans during this cruise and offered ample material for replicate studies. The sediments were allowed to thaw and were mixed thoroughly by hand before three subsamples were taken from each sediment. Each of these replicate samples was then freeze-dried, extracted, and analyzed exactly as described above in the section on methods. Complete reports on each sample have been submitted to Dames & Moore, but the GC recoveries are summarized in Table 58.

The results of analyses performed on the sediment from Station 2103 show good agreement among themselves and the total oil recovered shows a standard deviation of about 30%. Results from Station 2212 show excellent agreement between two analyses, but the third set of results is uniformly low. Because of the heterogeneous nature of the sediment sample, it is difficult to determine whether the low results were caused by losses during the analytical procedures, or were due to low hydrocarbon levels in that particular sediment subsample.

Replicate Analysis of Demersal Fish

Five specimens of demersal fish from Station 2747 were pooled to form one composite sample and four specimens from Station 2641 were pooled to form a second composite sample. These specimens were among some extra demersal fish samples shipped to ARLI after the summer 1977 cruise. Each of the pooled samples was divided into three subsamples. Each of these subsamples was then digested, extracted, and analyzed in the same way that demersal fish samples are processed. Complete reports on each sample have been submitted to Dames & Moore, but the GC recoveries are summarized in Table 59.

TABLE 58

REPLICATE ANALYSES OF SEDIMENTS

GC Recoveries Reported in $\mu g \cdot g^{-1}$

ARLI ID#	MAFLA Station Number	Hexane Recoveries			Benzene Recoveries			Total Oil
		Resolved	UCM*	Total	Resolved	UCM*	Total	
77066-15RA	2103	0.33	0.25	0.58	0.065	0.049	0.110	0.69
-15RB	"	0.16	0.19	0.35	0.023	0.002	0.025	0.37
-15RC	"	0.23	0.21	0.45	0.034	0.000	0.034	0.48
						Average		0.51
						Std. Dev.		0.16
77066-71RA	2212	0.26	0.018	0.28	0.010	0.0	0.010	0.29
-71RB	"	0.55	0.83	1.4	0.065	0.0	0.065	1.5
-71RC	"	0.49	0.79	1.3	0.090	0.0	0.090	1.4
						Average		1.06
						Std. Dev.		0.67

*UCM = Unresolved Complex Mixture

TABLE 59

REPLICATE ANALYSES OF DEMERSAL FISH

GC Recoveries Reported in $\mu g \cdot g^{-1}$

ARLI ID#	MAFLA Station Number	Hexane Recoveries			Benzene Recoveries			Total Oil
		Resolved	UCM*	Total	Resolved	UCM*	Total	
97044-83PA	2747	0.59	0.03	0.62	1.0	0.0	1.0	1.6
-83PB	"	0.41	0.0	0.41	2.0	0.68	2.7	3.1
-83PC	"	0.19	0.0	0.19	0.75	0.0	0.75	0.94
						Average		1.9
						Std. Dev.		1.1
97044-84PA	2641	0.84	0.0	0.84	1.1	0.66	1.8	2.6
-84PB	"	0.44	0.0	0.44	2.5	0.0	2.5	2.9
-84PC	"	0.48	0.0	0.48	2.2	0.0	2.2	2.7
						Average		2.6
						Std. Dev.		0.4

*UCM = Unresolved Complex Mixture

As was the case with the sediments, one set of replicate analyses (from Station 2641) produced results which are in excellent agreement and the total oil recovered has a standard deviation of about 15%. The other set of analyses shows a much greater variation and a standard deviation of more than 50%. As with the sediments, the significance of these results is difficult to evaluate because of the heterogeneous nature of the sample material.

REVIEW OF RESULTS

Detailed analyses and interpretation of the results of the high molecular weight hydrocarbon analyses is the responsibility of the Hydrocarbon Committee. However, some general impressions can be given here.

Sediment Analyses

The sediments from the archives and those from the three DM cruises appear to be typical marine sediments, free of any indication of gross petroleum pollution. Pristane and phytane are found in most samples along with normal heptadecane and normal octadecane. A complex of several peaks appears in the 2080 Kovat's Index region of the hexane fraction chromatogram. One of the peaks in this complex is often the dominant peak of hexane fraction chromatograms. Hexane fractions from a number of samples show significant amounts of the normal hydrocarbons, heptacosane, nonacosane, and hentriacontane which are indications of a terrestrial source of the sediment. The odd-to-even ratio in the normal paraffin hydrocarbons is greater than unity and the chromatogram of the hexane fraction shows a small to moderate amount of unresolved complex material. These characteristics are quite similar to those reported for MAFLA sediments in earlier investigations.

The amount of hydrocarbons extracted from these sediments is of the same order of magnitude as that reported in earlier MAFLA studies. The concentration of aliphatic hydrocarbons in these sediments, for example, is commonly in the 2 to 5 ppm range, with a few samples showing higher concentrations and many samples showing concentration of less than 1 ppm.

No pronounced differences have been observed between sediments from the archives or from any one of the three cruises of the current program. If there are differences, they may be revealed by a more detailed study of the data than we have been able to carry out.

Demersal Fish Analyses

The amount of lipid material extracted from the fish samples was generally quite small. Most of the liquid chromatography fractions weighed only about 0.1 mg or less. The most frequent and prominent peak in the chromatogram of the hexane fraction is due to normal heptadecane. This compound is accompanied by greater or lesser quantities of pristane. Phytane and some of the normal hydrocarbons appear in varying amounts in the different samples. A peak appearing at a Kovat's Index of 2815 in the aromatic fraction of many samples has been tentatively identified as squalene.

Macroepifaunal Analyses

The results of the analysis of the macroepifaunal samples resemble those of the demersal fish. The amount of lipid material recovered is small, pristane and normal heptadecane are present in most samples, and squalene is found in many aromatic fractions. Because of the variety of organisms included in this group of samples, there is a wide variation in occurrence and distribution of other hydrocarbons in these samples.

Highly colored extracts resulted from some of these samples, especially the sponge samples and some of the echinoderms. The hexane fraction produced in liquid chromatography of these colored extracts often contained a colored substance. A repetition of the chromatography did not always remove the color entirely. Extending the length of the digestion and saponification process was found to reduce this problem somewhat, but occasional repetition of the liquid chromatography was still necessary for a few samples.

SPECIAL TOPICS

Undersized Samples

Some of the demersal fish and macroepifaunal samples received for high molecular weight hydrocarbon analysis were too small to furnish sufficient tissue for analysis. The problem was most acute with the DM I samples, but was also present to some extent with the DM II and DM IV samples as well as with the archived samples from the summer of 1976. The origins of this problem, its impact on the TMs analysis, and the procedures adopted for handling the subsized samples are described in detail in the Trace Metals Report which forms Chapter 5 of this Final Report.

Table 56, shown earlier in this Benthic Hydrocarbon Report, indicates the impact on the Benthic Hydrocarbon Program. The number of macroepifaunal analysis completed was reduced by over 50% because of samples too small to analyze or which had to be pooled prior to analysis. A similar 15% decrease is seen in the demersal fish samples. These reductions led to additional sample-handling and record-keeping expenses which resulted in a modification of total costs mid-way in the program.

Finally, the delay of over a month while seeking BLM approval of the plan for the undersized samples led to a schedule slippage which was never entirely overcome. The large number of HMWHC analyses and a very tight schedule resulted in completion of anlayses about a month behind schedule.

Sediment Extracting Solvent

The toluene-methanol azeotrope prescribed by the BLM for sediment extraction has a boiling point of 63.5°F. On the other hand, the methylene chloride-methanol azeotrope boils at 39°C. This lower boiling solvent offers several advantages when used as a sediment extraction solvent. The lower temperature in the Soxhlet reservoir decreases the probability of decomposition or other reactions occurring in the extracted material. The lower boiling solvent can be heated with a hot water bath, thus, reducing

the temperature at the wall of the flask. Since the higher boiling toluene-methanol solvent must be heated with an electric heating mantle, a brown, insoluble material often coats the inside of the flask during extraction. In addition to this protection for the extract, the methylene chloride, with its lower flammability, offers added safety for the analyst.

Early in the program, a request was made through Dames & Moore for BLM approval of use of methylene chloride-methanol as a sediment-extracting solvent. Approval was given with the understanding that a series of duplicate extractions would be performed to show that the methylene chloride azeotrope was at least equivalent to the toluene azeotrope as an extraction solvent.

Nine sediment samples were extracted and analyzed twice, once using toluene-methanol as the extracting solvent, and once using methylene chloride-methanol. Reports of the individual analyses have been submitted to Dames & Moore, and the results are summarized in Tables 60 and 61. Examination of the results reveals no pronounced differences between the results of the two sets of analyses. In Table 60, for example, the amount of non-saponifiable material extracted from the sediment seems to be slightly larger for most of the samples extracted with methylene chloride. On the other hand, the same table indicates slightly higher LC and GC recoveries with the toluene solvent for many samples. However, the differences in nearly all cases are small and of about what would be expected for duplicate analyses of these sediments. As discussed earlier, the nonhomogeneous nature of marine sediments can easily result in variations of 60% or more in the amount of material recovered on the gas chromatograph. GC recoveries are also subject to variations approaching 50% as a result of the injection techniques used, as was explained above. All of the differences seen in Table 60 could easily be accounted for in terms of these two factors, variability in the sediments and in the analytical method. The various ratios listed in Table 61 show a similar scattering of small differences like those seen in Table 60. Both these tables show the type of results that would be expected from a series of duplicate analyses using the same extracting solvent throughout. They indicate that the methanol azeotrope of methylene chloride and the same azeotrope of toluene give comparable results for sediment extractions which are to be analyzed by the methods described earlier in this report.

Equipment on Loan From BLM

Equipment loaned to ARLI by BLM was quite helpful in expediting the processing of samples. A Hewlett-Packard Model 5830A Reporting Gas Chromatograph has been extremely useful in speeding up work in the gas chromatography laboratory. An automatic sampling attachment received with the instrument was not put into service for lack of the appropriate interfacing hardware which was not included with it. A Cahn Model 4400 Electrobalance has been used extensively for weighing the liquid chromatography fractions. Two Buchi-Brinkmann Model R Rotary Evaporators are used to reduce the volume of the extract solutions. An IEC Model HN-S centrifuge is used to aid in separating emulsions formed during the extraction process. The Virtis Model 45 Homogenizer arrived with a damaged and unusable sample-holding cup.

TABLE 60

EXTRACTION SOLVENT STUDY - LC & GC RECOVERIES

Data Expressed as $\mu g \cdot g^{-1}$ (dry basis)

			Liquid Chrom.		Gas Chrom.		
ARLI ID#	Solvent(1)	Nonsap. Extract	Hex. Frac.	Benz. Frac.	Hex. Frac.	Benz. Frac.	Total
77066-2	M	107	8	6	0.36	0.29	0.65
	T	59	4	3	0.38	0.15	0.53
77066-29	M	33	0	2	0.70	0.00	0.70
	T	58	2	0	1.1	0.092	1.2
77066-42	M	42	0	3	0.13	0.076	0.21
	T	39	0	3	0.74	0.12	0.86
97048-109	M	95	5	3	3.0	0.83	3.8
	T	81	7	7	3.1	0.50	3.6
97048-113	M	89	5	5	0.61	0.21	0.82
	T	62	9	7	1.9	1.5	3.4
117103-12	M	40	1	0	1.3	0.15	1.4
	T	43	2	3	0.077	0.16	0.24
117103-11	M	33	0	0	0.41	0.23	0.64
	T	45	4	1	0.58	0.35	0.93
117103-36	M	84	2	5	0.50	0.84	1.3
	T	79	7	10	0.12	0.063	0.18
117103-41	M	70	6	2	0.34	0.22	0.56
	T	46	7	4	0.39	0.064	0.45

(1) M = Methylene chloride:methanol azeotrope
T = Toluene:methanol azeothrope

TABLE 61

EXTRACTION SOLVENT STUDY - GC RATIOS

ARLI ID#	Solvent[1]	n-Alkanes, Odd / Even	Isoprenoid / n-Alkane	Pristane / Phytane	Pristane / n-C17	Phytane / n-C18	Alkanes, Branched / Normal
77066-2	M	1.6	0.42	0.43	0.69	4.0	0.66
	T	2.0	0.16	-	10.0	0.0	0.32
77066-29	M	1.7	1.4	0.19	0.35	6.7	4.5
	T	0.94	0.068	2.2	1.3	1.0	0.31
77066-42	M	2.5	0.71	13.	5.4	1.1	0.50
	T	2.7	0.0	0.0	0.0	0.0	0.55
97048-109	M	2.8	0.062	3.1	1.3	0.62	0.65
	T	2.3	0.021	1.7	0.99	0.62	1.2
97048-113	M	1.5	0.55	0.0	240.	0.0	0.58
	T	2.5	0.035	3.0	1.0	0.53	1.4
117103-12	M	1.9	0.077	2.3	0.30	0.47	0.61
	T	1.8	0.24	2.4	0.40	0.65	1.00
117103-36	M	2.3	0.15	5.0	2.0	0.88	0.56
	T	2.2	0.31	5.0	1.6	0.75	0.51
117103-41	M	1.4	0.31	4.1	1.5	0.66	0.26
	T	1.8	0.020	0.13	0.031	0.61	0.61
117103-11	M	1.4	0.075	1.1	0.36	0.35	0.68
	T	1.3	0.059	1.9	0.36	0.22	0.61

(1) M = Methylene chloride:methanol azeotrope
T = Toluene:methanol azeothrope

Delays in securing a replacement for this cup resulted in this instrument not being placed in service.

Most of the BLM equipment arrived at ARLI in need of minor repairs or without parts or accessories needed for operation. All, except the homogenizer, were quickly repaired and put into service. Our only regret is that the equipment could not have been made available earlier in the program. By the time the equipment was received in January and February, processing of the MAFLA samples was about 50% completed. Nevertheless, we are greatful that the equipment has been available for the latter part of the program.

CONCLUSION

A total of 976 benthic sediments, demersal fish, and macroepifaunal samples were received at ARLI for high molecular weight hydrocarbon analysis. Undersized specimens of the biological samples prevented the analysis of 167 samples, but 106 other small biological samples were pooled to form 34 composite samples. The number of benthic HMWHC analyses completed is 735. GC/MS analyses were performed on 33 liquid chromatography fractions to identify unusual peaks and to confirm identifications made by gas chromatography. The analysis of all these samples was performed using methods and procedures approved by the Bureau of Land Management.

The results appear to be comparable to those reported for earlier MAFLA studies. Detailed analysis and interpretation of the results is the responsiblity of the Hydrocarbon Committee.

Three replicate analyses performed on each of two sediment samples and on each of two demersal fish samples showed that the standard deviation for a set of three replicate analyses may vary from 15% to over 60%. Because of the difficulty of preparing analytically equivalent replicate samples of sediments or biological tissues, it cannot be determined whether the variation results from the nonhomogeneous nature of the sample material or from the analytical methods. Consequently, it is difficult to assign a numerical value for the precision of the methods.

Delays early in the program in connection with the undersized biological specimens resulted in a schedule slippage which was never entirely overcome. Nevertheless, except for some GC/MS analyses requested late in the program, all other analyses were completed within about a month of their scheduled completion date.

REFERENCES

Anon. 1976. Analytical Methods for Atomic Absorption Spectrophotometry. Perkin-Elmer Corporation, Norwalk, CT., Revised from 1973 edition.

Anon. 1977. Analytical Methods Using the HGA Graphite Furnace. Perkin-Elmer Corporation, Norwalk, CT., Revised 1973 edition.

Rohrback, B.G., and W.E. Reed, 1975. Evaluation of Extraction Techniques for Hydrocarbons in Marine Sediments. Institute of Geophysics and Planetary Physics, University of California at Los Angeles. Publication No. 1537.

VOLUME II

CHAPTER 9

INTERPRETATION OF TISSUE HYDROCARBON DATA

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INTRODUCTION

The composition and concentration of hydrocarbons in animal tissue depends on a variety of factors. Synthesis of hydrocarbons has been conclusively proven for a large number of algae, zooplanktons and bacteria. Synthesis of simple alkane structures, normal as well as branched, saturated and olefinic, is observed to be limited to one or a few characteristic compounds in any particular species. More complex hydrocarbon structures such as diploptene and hopane appear to be synthesized by some bacteria and blue-green algae. In higher life forms, the biosynthesis of hydrocarbons is more difficult to establish because of the incorporation of hydrocarbons from external sources. In this case, hydrocarbons may be acquired by partitioning into tissue directly from the water, or via ingested material. Unless detailed studies on a particular species have been carried out, it will in general be impossible to predict which of the two uptake mechanisms is more important. Where most of the uptake occurs from ingested material, additional difficulties in the interpretation of tissue levels are experienced, mainly due to the fact that the average composition and concentration of hydrocarbons in the ingested material remains unknown. Deposit feeders, for example, may be quite specific and selective in what they transport to their digestive system. Although we may know the mean hydrocarbon composition and individual concentrations of deposited material from surface sediment analyses, what eventually ends up in the digestive tract of a species may be substantially different from such means. Among different deposit-feeding species, one finds a whole range, from rather indiscriminate feeders to those that differentiate by size or by taste. An additional problem is that deposit feeders are known to be extremely heterogeneous. Thus, it can be expected that attempts to correlate hydrocarbon source characteristics with tissue concentrations of deposit feeders in general will not be too successful, and the situation is predictably even less favorable for species that not only filter feed, but in addition, are predators.

Slightly stronger correlations can in principle be expected for pure filter feeders, especially since much of the uptake must be from water. But even here many questions remain unanswered. While the partitioning mechanism is relatively well understood (Neely et al., 1974), the contribution of hydrocarbons from ingested material is not. Problems that remain to be investigated are: the extraction mechanisms and efficiencies for hydrocarbon absorbed to mineral particles and absorbed within cells. Also of interest may be the question, if and how bacteria contribute to the process of hydrocarbon uptake.

In fish, it is known that biomagnification occurs via partitioning mainly at the gills (Neely et al., 1974). If this were the major uptake mechanism, the tissue concentrations of individual hydrocarbons should reflect those in the water column. However, additional uptake does occur from material that has been ingested (Lee and Jonesheben, 1972) and problems similar to and incuding those mentioned for deposit and filter feeders are expected to interfere with trend predictions. Unless uptake by partitioning is dominating, hydrocarbon levels in fish can be expected to depend on:

- Dietary variability among individuals of the same species by its selection
- Dietary variability forced upon the animal by seasonal changes in food availability and food diversity
- Presence and species diversity of host bacteria
- Rate of hydrocarbon metabolism if tissue concentrations reflect a dynamic equilibrium between rate of hydrocarbon uptake and rate of removal by metabolic activity
- Changes in enzyme levels with hydrocarbon concentrations and season, and
- "Reverse" partitioning by exchanging of hydrocarbon (acquired via ingestion) at the gills with the water column.

Many experiments (Anderson et al., 1974; Lee and Benson, 1972; Lee and Jonesheben, 1972, Bieri et al., 1974) have shown conclusively that petroleum hydrocarbon in most marine animals cannot only be acquired, but that the reverse process, depuration, also occurs under laboratory and natural conditions. In a spill situation, Bieri and co-workers have concluded that the hydrocarbon concentrations in tissue are mainly related to hydrocarbon residence times in the environment, which in most cases are longer than the biological residence times. In any case, most hydrocarbons in animal tissue are transitory, and unless the concentration reach levels that are toxic (either acute or chronic) over the time of exposure, to the host species or to consumers of the host species there is little to be concerned about. Since chronic toxicities are difficult to establish and since accumulation effects via the food chain are not well understood, research into all aspects of petroleum hydrocarbon pollution is still actively pursued. It also is one of the major interests the BLM has in the MAFLA study.

While it seems simple enough to detect petroleum hydrocarbon in environmental samples, those familiar with the problem know it is not, with very few exceptions. Petroleum hydrocarbons are easily recognized in situations where fresh petroleum has been accumulated almost unmodified in water, and from where partitioning into tissue can occur. Also, where relatively shallow waters and highly turbulent conditions coincide with a fresh oil spill, practically unmodified oil can be incorporated into sediment from where it is available to macroepifauna. In tissues of indiscriminate deposit feeders and, if the sediment particles are coated with oil, also in bottom-dwelling filter feeders, tissue hydrocarbon extracts would be expected to be similar to the oil. More simply stated, where the spilled oil will have a dominating influence on tissue concentration and where weathering of the oil has not progressed too far, the presence of petroleum hydrocarbons would be hard to miss. At the other extreme, we are dealing with a situation where the petroleum has been dispersed, physically fractionated and biochemically and photochemically altered in its composition, long after being spilled. Only the most refractory hydrocarbons, to which the hopanes probably belong (Dastilling and Albert, 1977), survive and are being recycled. All the mechanisms mentioned above contribute to a steadily decreasing concentration. After sufficient time, the petroleum hydrocarbon level will drop below the level of natural hydrocarbons, and as time goes by, chances are good that petroleum hydrocarbons from other spills and at other stages of weathering are superimposed. Under such conditions,

no consistent set of criteria for the presence of petroleum can be found, cnd tissue hydrocarbon compositions from animal living in such an environment probably reflect mainly the total natural hydrocarbon input, plus what they are able to add by their own synthesis. What we see in the MAFLA samples is somewhere in between, and probably close to the lower extreme.

LIMITATIONS ON THE HYDROCARBON DATA

Before discussing the hydrocarbon data, it is necessary to mention certain limitations that apply to both qualitative and quantitative statements. The data in this report have been derived with methods prescribed in the BLM contract (AA550-CT7-34), and the total analytical effort is limited by available funding and time. Due to the extremely complex nature of the hydrocarbon fractions that are being analyzed, the generally very low concentration in the samples, the many steps involved in their extraction and separation, to mention just a few of the basic problems, sacrifices and comprimises have been necessary. Another important consideration in the design of the BLM studies was intra-comparability between data sets from different laboratories, which led to rigid procedural instructions for methodology. This rigidity also excludes subjectivity in certain operations. The calculation of GC peak areas, the translation of peak areas into concentrations and the calculation of a normalized retention parameter are typical examples of such an operation. It can be handled objectively, fast and reliably by computerized integrations. But the use of computers also has some shortcomings. A computerized integration lacks the pattern-recognition criteria and the sophistication to discriminate between real and false signals or to properly deconvolute fused peak groups. While it is an excellent instrument for the quantification of well-resolved chromatograms, it will produce a questionable output in the presence of partially-resolved peaks or superimposed peak groups. But even when it fails to make such numeric resolutions, it provides a printout that looks impeccable. For qualitative data, the assignment of compound names to retention indices by computer is another problem. It is well known that the retention index by itself is not a good parameter for the characterization of a compound. While it can be used as a first approximation, additional information such as can be obtained by mass spectrometry should always be used as a follow-up. This is particularly true for aromatic fractions, where systematic retention shifts relative to n-alkanes in different capillary columns are known to occur (Bieri et al., 1978).

Specific examples from the MAFLA data of problems described above in a general way, are discussed by the two fraction classes below.

Hexane Fraction

These fractions in general contain well resolved peaks, mainly n-alkanes. One exception is found in the region of n-C-17 which contains an unidentified compound eluting just past the pristane (clearly visible in some chromatograms of macroepifauna). In cases where the concentration of pristane is lower than the concentration of this unidentified compound, the latter would be labeled as pristane since it falls within the retention range of ± 5 units adopted in the ARLI computer program for compound

assignments. Similar problems can be expected to be present for other compounds. Without evidence from GC-MS (which came in too late to be included in this report) it clearly is difficult to identify the extent of this problem.

Quite common is the listing of a partially fused peak as a single peak, although the dendrograms clearly show that more than the one compound is present. As a consequence, listed concentrations, in absence of any comments about the fact that the one is looking at more than one compound, are misleading.

While the assignment of compound names in the hexane fraction may be correct most of the time, it is nevertheless important to keep such shortcomings in mind, in particular when interpreting the data.

Benzene Fraction

An inspection of computer printouts for all listed peaks in the benzene fraction of demersal fish immediately shows two problems: there is an almost monotonous distribution of Retention Indices (RI) from RI 1300 to 3200, and where compound assignments have been made, they cover a much wider range than in the hexane fraction. For example, all compounds eluting between RI 2800 and 2835 are identified as squalene. Chrysene spreads over a range between RI 2344 and 2374, and 3, 6 dimethyl phenanthrene over RI 1942 and 1961, etc. While the first observation suggests an almost continuous spectrum of retention indices, which in view of the known complexity of benzene fractions from tissue extracts is expected, the second observation increases the problem of providing a compound assignment that is worthy of any confidence. Here identification of individual peaks by GC-MS is an absolute necessity.

Since the dendrograms in addition are bare of any characteristic features that would at least provide some hints (e.g., characteristic groups of sources that can normally be recognized in petroleum fractions, the characteristic fingerprint of PNA's from pyrogenic inputs, etc.), and since there is evidence that peak assignments actually are wrong, it is not possible to include the benzene fraction in the discussion.

DISCUSSION AND RESULTS

The concentrations of hydrocarbons in tissues depends on many variables of which we know very little. In absence of such knowledge, multivariable statistical regression analysis cannot be applied to data sets of tissue concentrations. Any attempt to interpret hydrocarbon data is thus limited to the qualitative discussion of trends.

Several approaches to achieve this goal are possible. In general, one of the requirements that must be fulfilled is the availability of a good working hypothesis that allows the seemingly unrelated pieces of information to form distinct associations. In very complex situations, even such simple tasks may fail. It is our belief that an understanding of hydrocarbon concentrations in tissues of marine biota belong to the latter category. Some of the reasons have been given in the Introduction. There also is an

ambiguity in the form of data one chooses as a base for discussion: analog or digital, full or limited sets. While we have already mentioned that the data are not of the same quality as their analogs (the chromatograms) and that their information content has already been reduced, it is nevertheless the only way to handle the large amounts of data that were generated. In fact, in order to be manageable, the digital sets had to be further reduced by selecting the 10 largest peaks from the composition tables. Chromatograms, however, were consulted where a trend was suggested.

HYDROCARBONS IN DEMERSAL FISH

Demersal fish, Syacium papillosum, will be discussed first because they represent the largest data set. They are at the top of the food chain among all animals investigated. Syacium has a dietary preference for crustaceans. Complementary food sources consist of polychaetes, fish and sponges. With respect to hydrocarbons, an important factor is its adherence to a habitat of limited range: this fish appears to spend most of its life within a narrowly defined area (Dr. Robert Shipp, personal communication; also see Volume I-A, for a discussion of the biology of this species). From a knowledge of these factors, we can at least try to address some general questions of uptake. For example, if the uptake of hydrocarbons were mainly from the water, we would not expect to find a strong dependence of hydrocarbon composition on sampling location, since the hydrocarbon distribution in water is fairly homogeneous. On the other hand, if the hydrocarbons are mainly acquired via dietary input, the station dependence should be pronounced, not only because the species composition differs from locality to locality, but also because of a more pronounced relationship of the hydrocarbon composition of sediments with those of the ingested animals.

Before these questions can be approached, it is necessary to first determine which of the hydrocarbons are most commonly encountered in the 10 major peaks. Pooling of all samples (a total of 204) and searching by computer results in 2 compounds identified by their retention index as n-alkanes, and to branched alkanes or olefins. The frequency of each of these 26 compounds, the count and the retention index is found in Figure 163. The compound with RI 2800 has the highest frequency, with RI = 2200, 2000, 1700, and 2500 following. Seasonal subsets of the total fish sample (Figures 164-166) for the same compounds as in Figure 163 are quite similar, although some subtle differences are indicated. These histograms show what an inspection of individual chromatograms also suggests: that the presence of petroleum hydrocarbons in the MAFLA area is certainly not a common feature. If oil were abundantly present, than all n-alkanes should have about the same frequency, with perhaps a slight increase towards higher RI's to account for weathering. Pristane (RI = 1709) and phytane (RI = 1812) should not differ from n-C-17 or n-C-18.

The question of uptake-mode is addressed the same way by plotting the histograms for several stations (Figures 167-172). While the compound at RI = 2800 still dominates in all but one station (2209) other features change quite dramatically. In Station 2209, for instance, the histogram is dominated by n-C-17 and pristane, but in Stations 2105 and 0007 these two compounds have a relatively low frequency. Compounds n-C-25, n-C-22, and n-C-20 in Stations 2105, 2209, 2747, and 0005 relative to n-C-21 and n-C-23

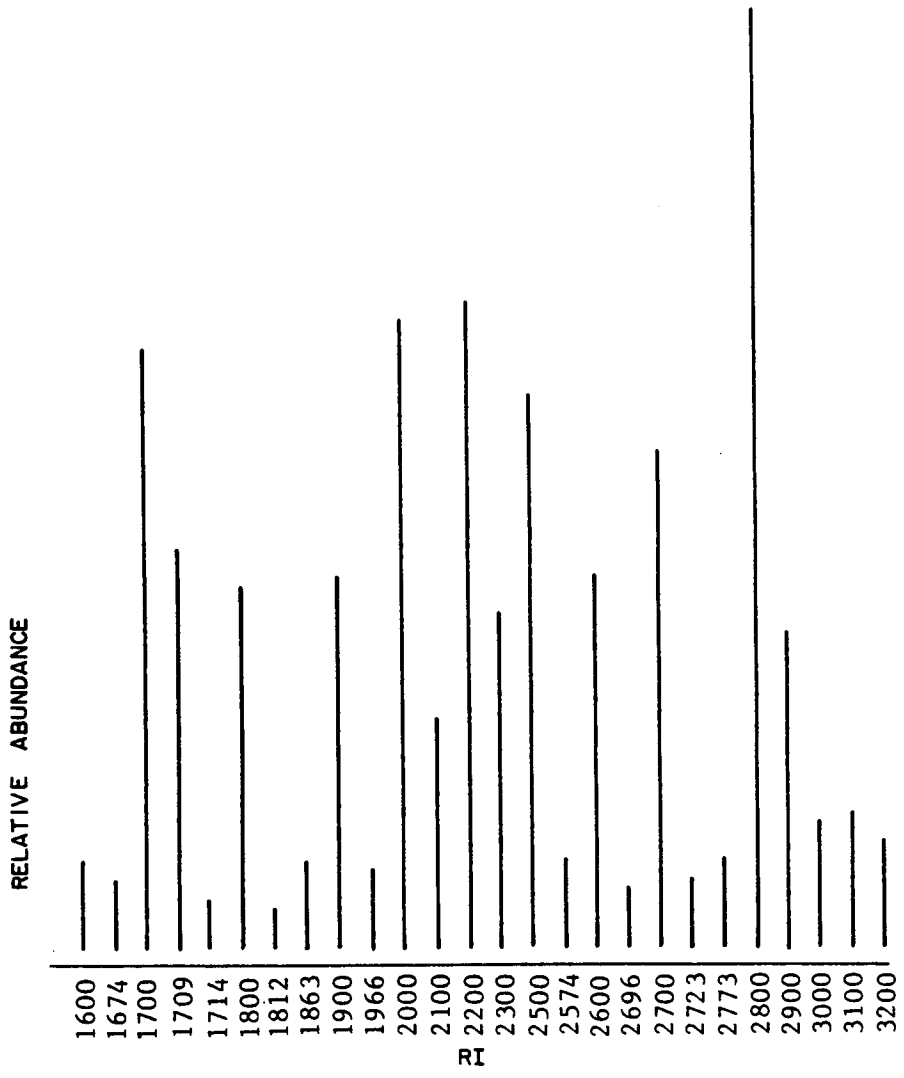


FIGURE 163

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
ALL SAMPLES POOLED

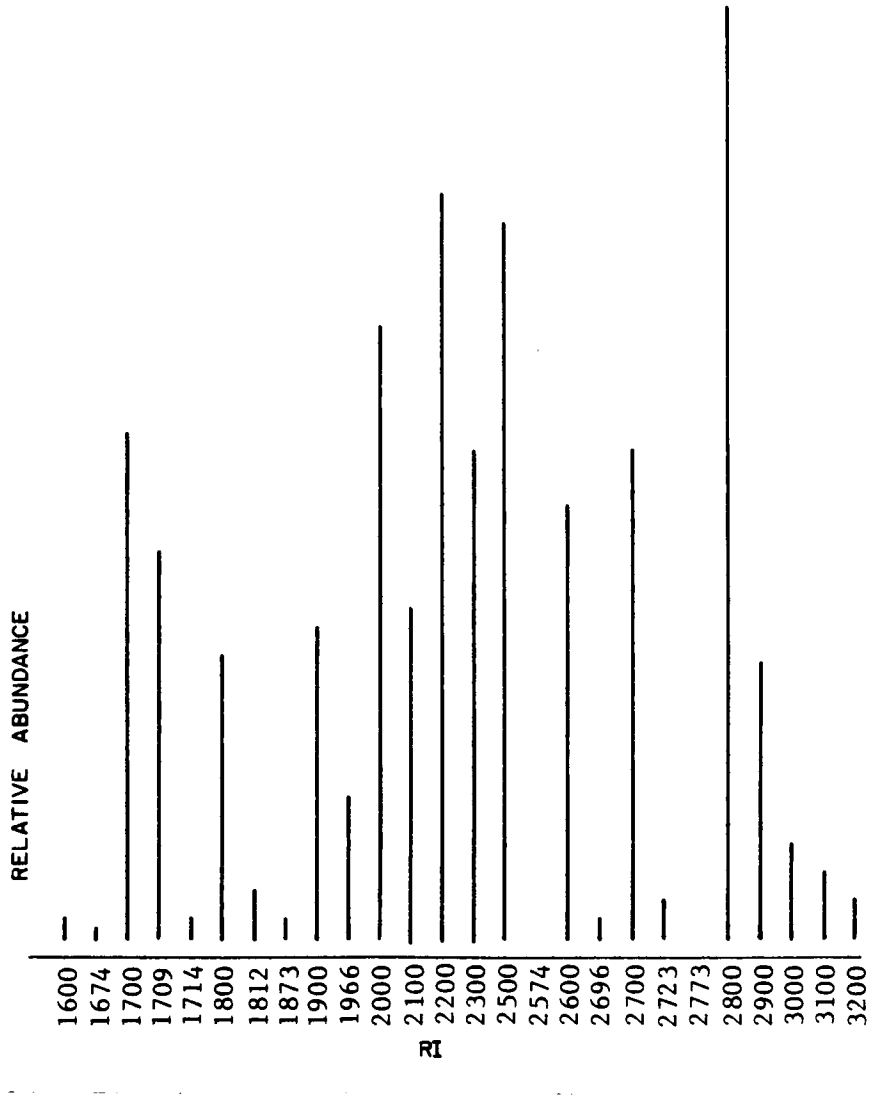


FIGURE 164

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
ALL STATIONS, YEAR 8, MONTH 2

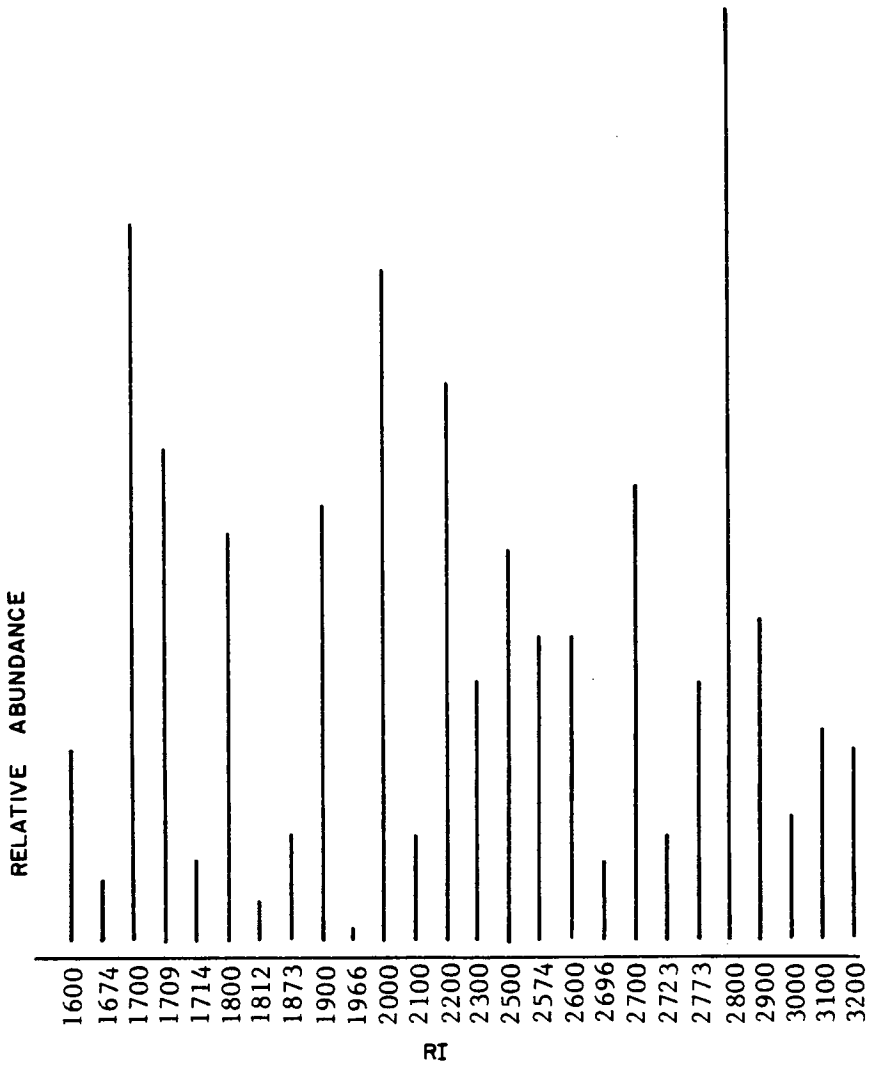


FIGURE 165

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
ALL STATIONS, YEAR 7, MONTH 10

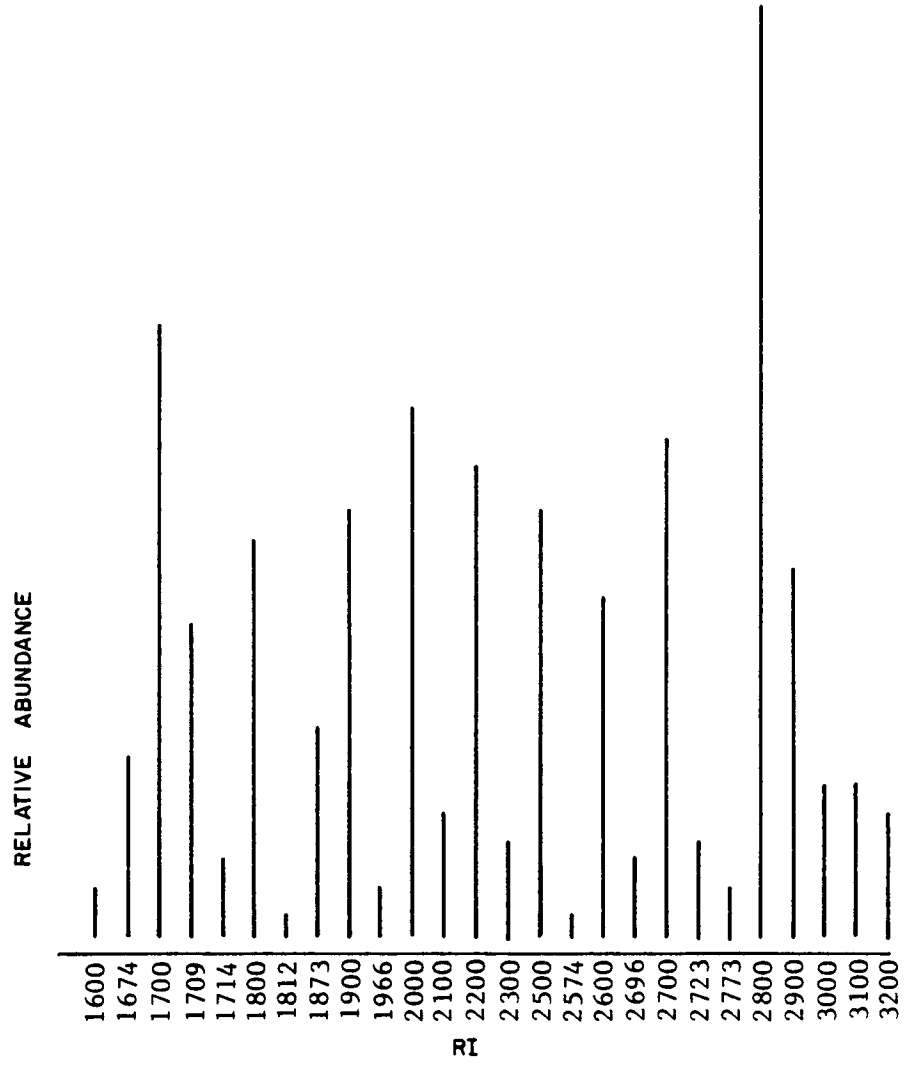


FIGURE 166

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

ALL STATIONS, YEAR 7, MONTH 8

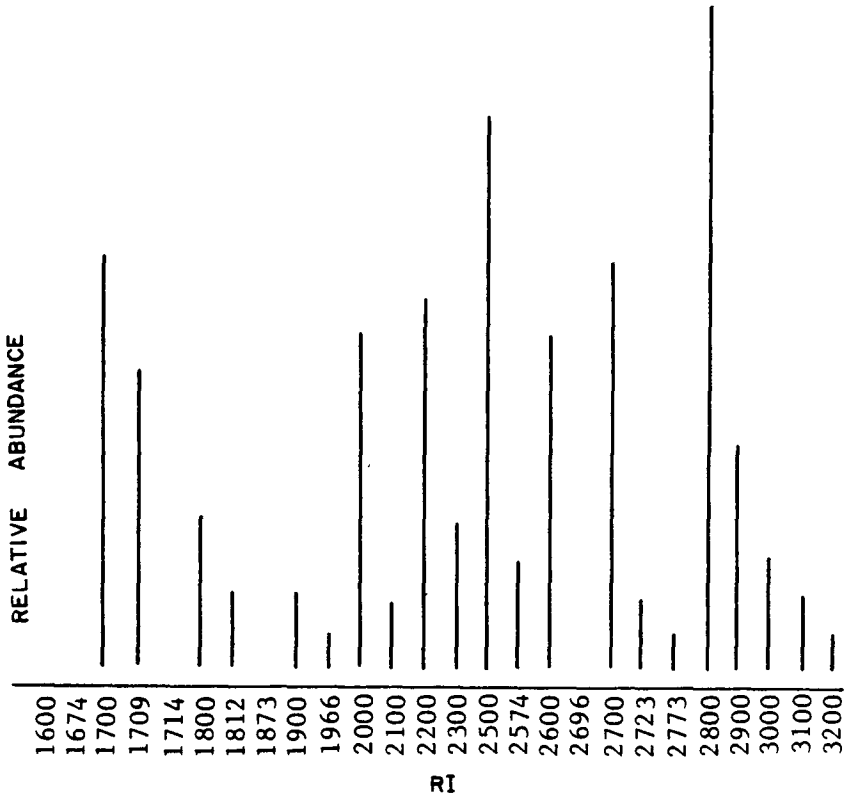


FIGURE 167

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 0005, ALL YEARS

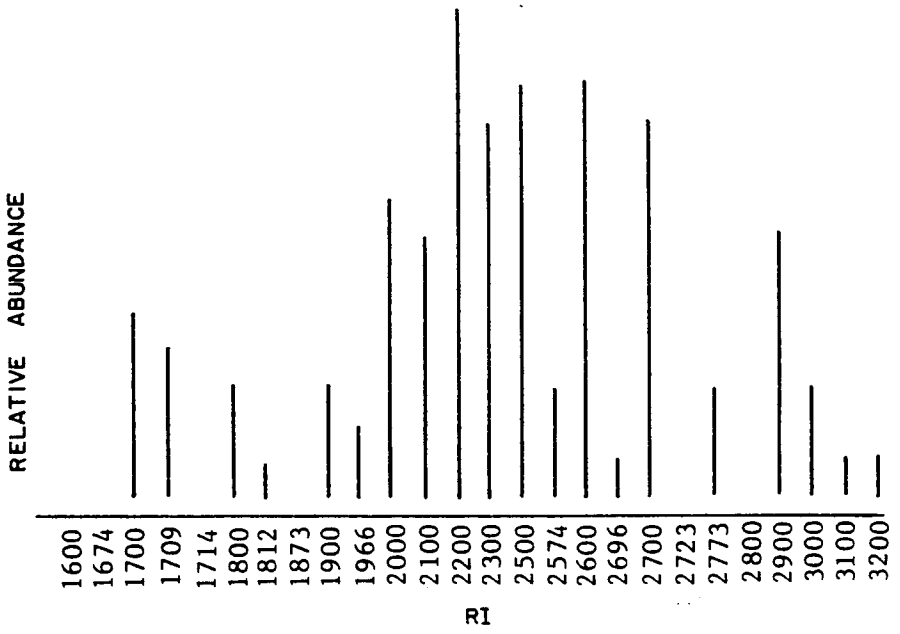


FIGURE 168

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 0007, ALL YEARS

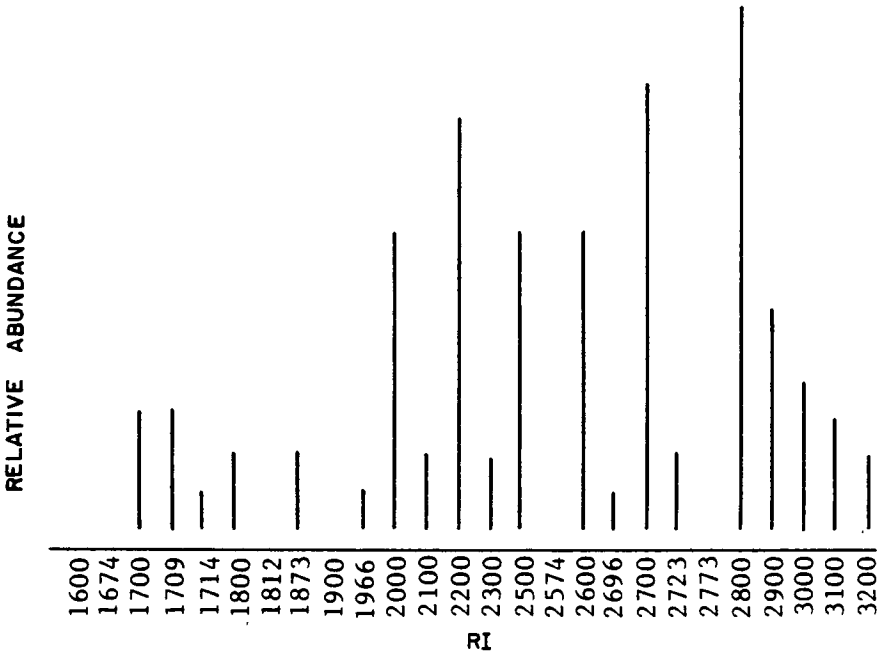


FIGURE 169

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 2105, ALL YEARS

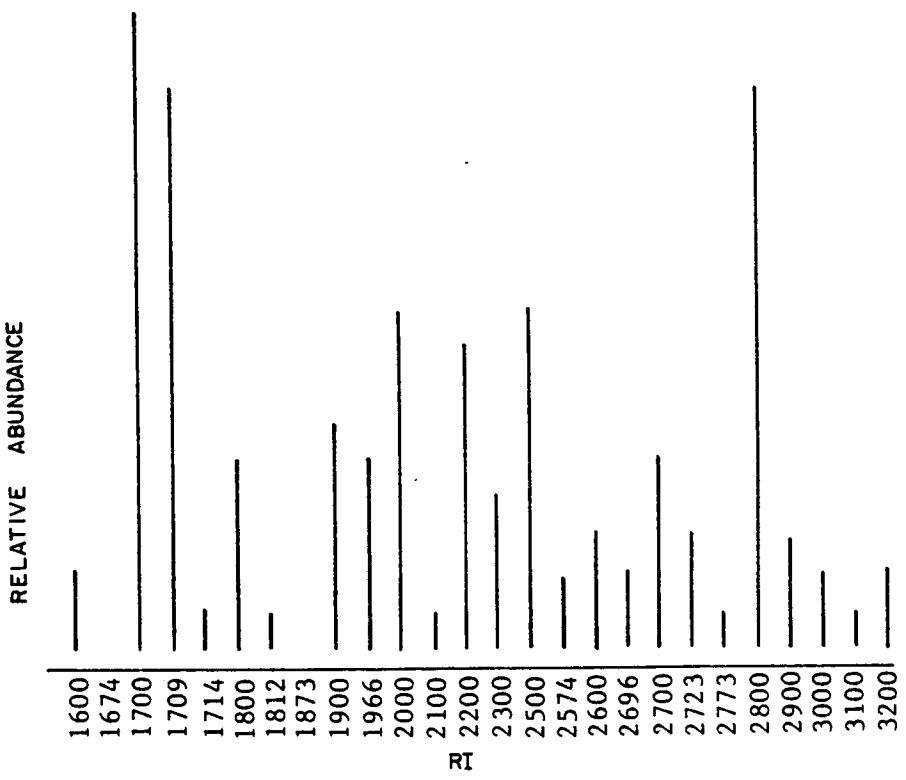


FIGURE 170

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 2209, ALL YEARS

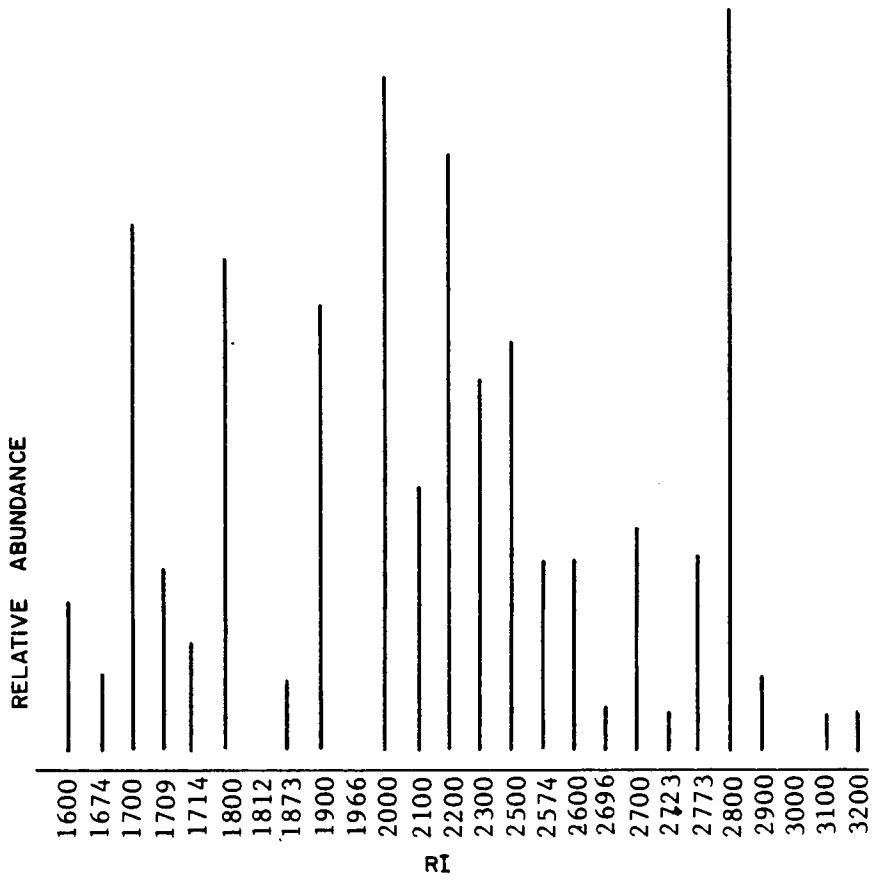


FIGURE 171

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 2426, ALL YEARS

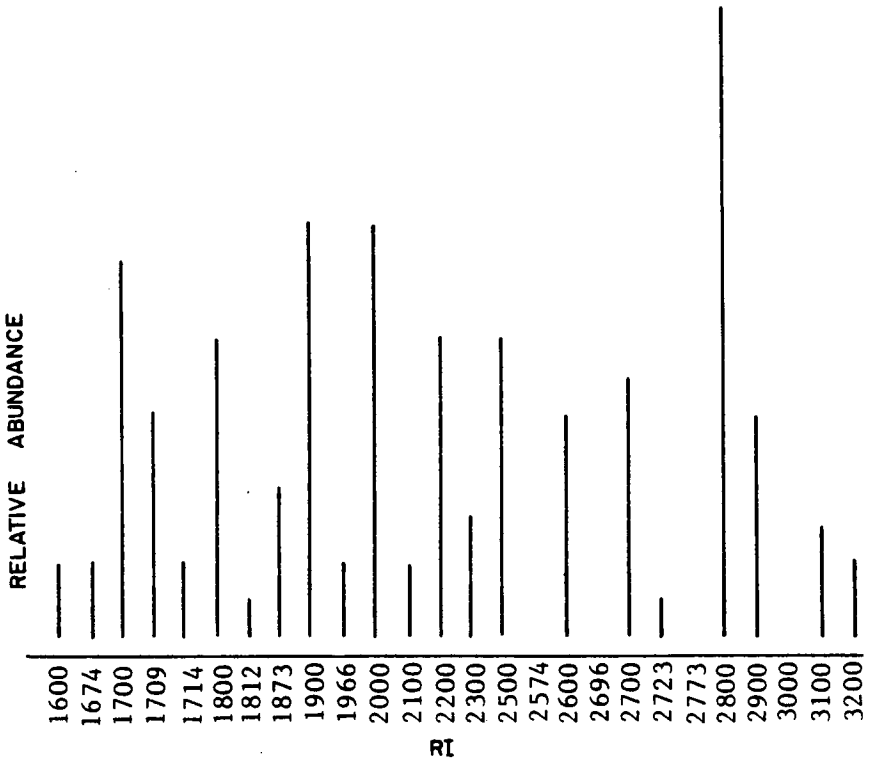


FIGURE 172

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 2747, ALL YEARS

stations into seasons (Figures 173-175L) even indicate the presence of seasonal changes within stations. In view of the rather small size of have substantially higher frequencies, but they are similar in Station 0007. All this would suggest that there indeed are substantial differences in the hydrocarbon composition with location. Further division of individual these data sets, however, we do not wish to emphasize those differences. Other inspections of all chromatograms, although difficult to judge because of the rather poor quality of some chromatograms, definitely lends some support to the reality of seasonal differences in individual stations. They also revealed the presence of a hump in some chromatograms, located between about RI = 1500 and 2100. It occurs most often in Station 0007, where it is accompanied quite regularly by a series of n-alkanes peaking at n-tetracosane (Figure 176). If both features are indicative of oil, they would have to come from different sources. The hump could be from a No. 2 fuel oil, but due to its irregular appearance in chromatograms of other stations is more likely to indicate a sample contamination problem than anything else. The series of n-alkanes probably indicates some pollution in the winter 78 samples. The presence of this oil, by the way, also shows up in Figure 176. The composition differences between different locations suggest strongly that Syacium papillosum accumulates most of its hydrocarbons from ingested material, since the food source composition also varies with stations. The same argument can also be made for differences between fall and winter. With the exception of Station 0007/ winter, evidence for the presence of petroleum in the MAFLA area is either absent or completely overpowered by hydrocarbons of non-petrolitic origin, in agreement with the conclusions based on interpretation of Figure 163. Biogenic hydrocarbons from autochthonous sources whose input is clearly indicated by the histograms are: n-C-17, pristane, n-C-18, and n-C-19. Always well represented are n-C-20, n-C-22, and especially n-C-28. Since they are also found as distinct peaks in some sediment samples (Figures 177 and 178), they may also have a biogenic origin. These three peaks are, however, also often encountered at low level in fish blanks. Intriguing are also n-C-21, n-C-23, and n-C-25. The first two, according to the local (samples from the same station) histograms, seem to be related: when the frequency of n-C-21 is low, the frequency of n-C-25 is also low, and vice versa. This would again point towards a biogenic origin, but their source is not known. The biogenic production of n-C-25 is again suggested by its presence as a dominant peak in a sediment sample (Figure 179) and its high variability in the histograms.

Although the origin of some of these compounds cannot be pinpointed, they certainly cannot derive from petroleum.

HYDROCARBONS IN MACROEPIFAUNA

It would be desirable to discuss the macroepifauna from two different aspects. One concerns the relation of their hydrocarbon composition with that of fish, the other would again be a search for a common denominator between food source and acquired tissue concentration. Since the fish have already suggested that uptake from the water column is probably small, partitioning will also be assumed to be of minor importance in macroepifauna.

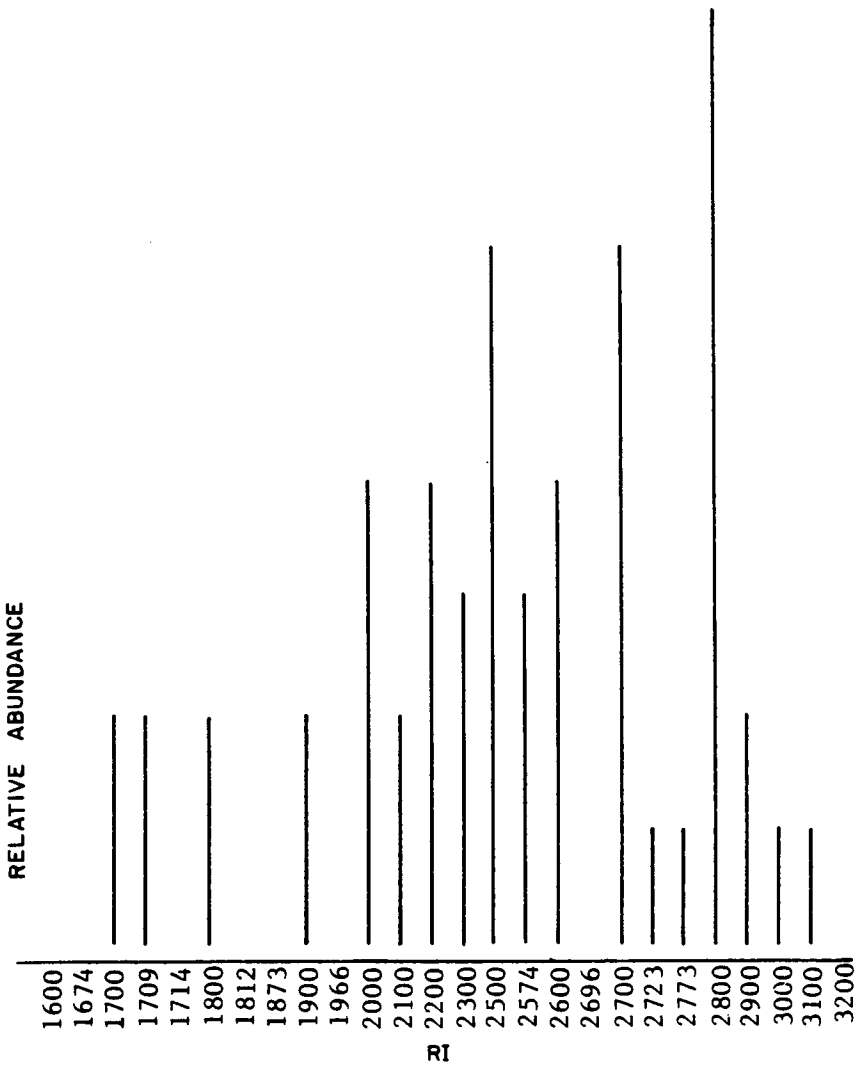


FIGURE 173

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 0005, YEAR 7, MONTH 10

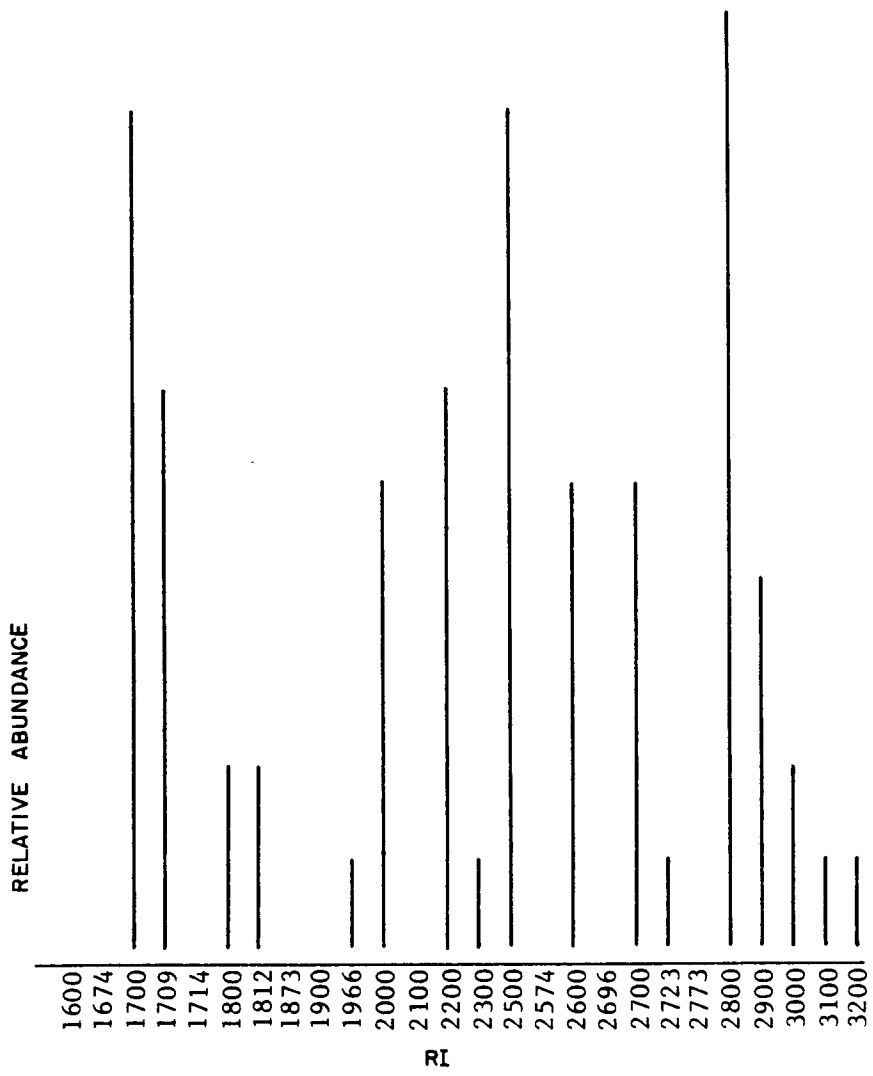


FIGURE 174

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 0005, YEAR 8, MONTH 2

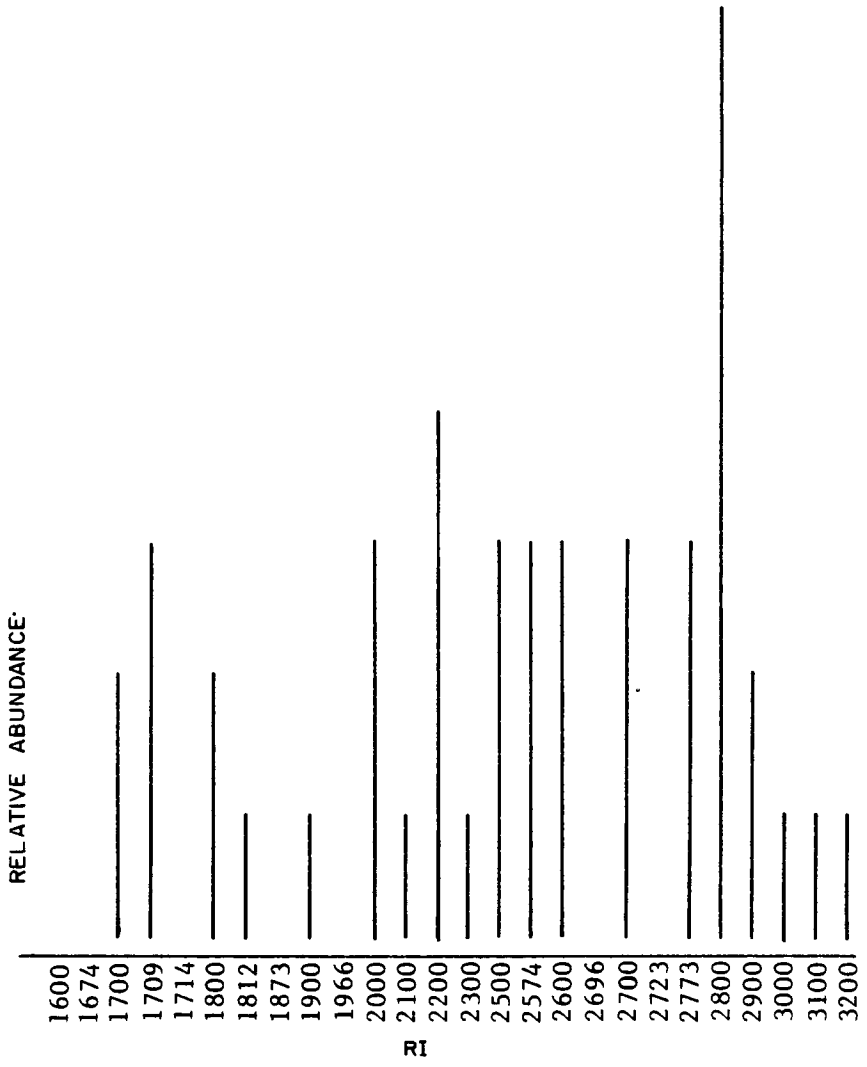


FIGURE 175

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 0007, YEAR 7, MONTH 10

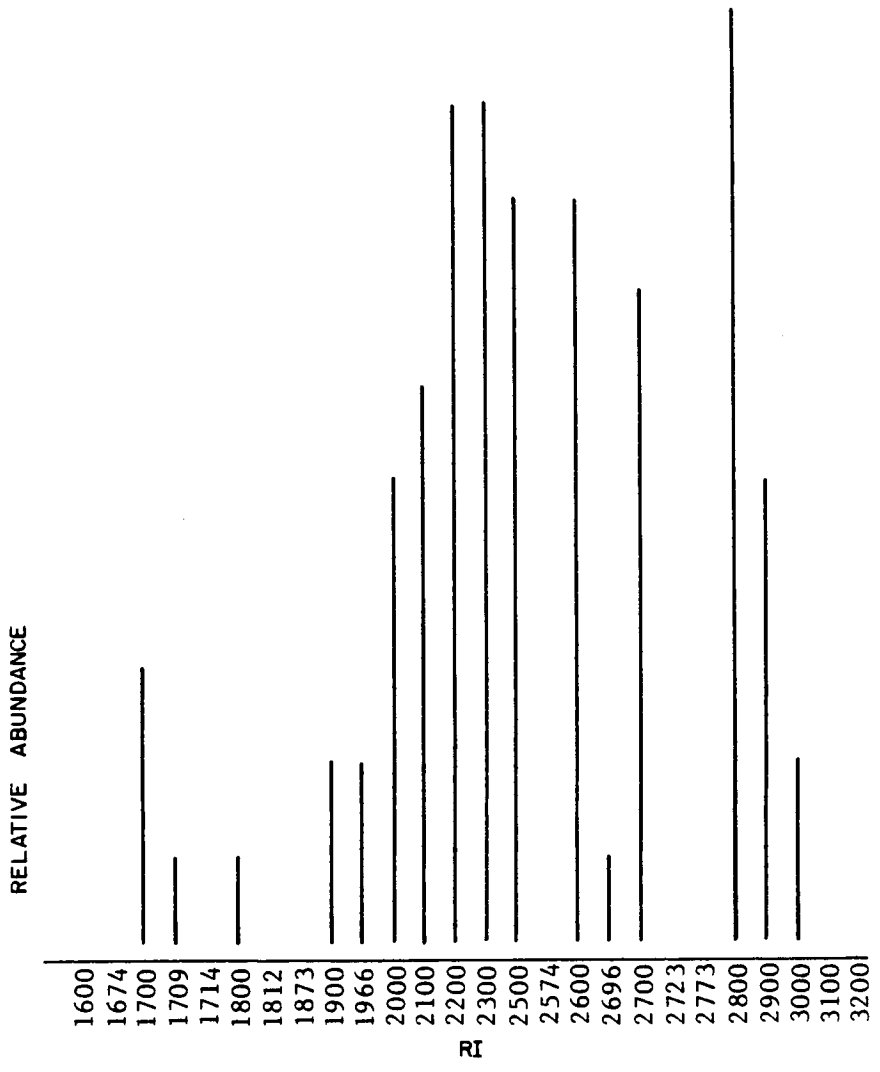


FIGURE 175A

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 0007, YEAR 8, MONTH 2

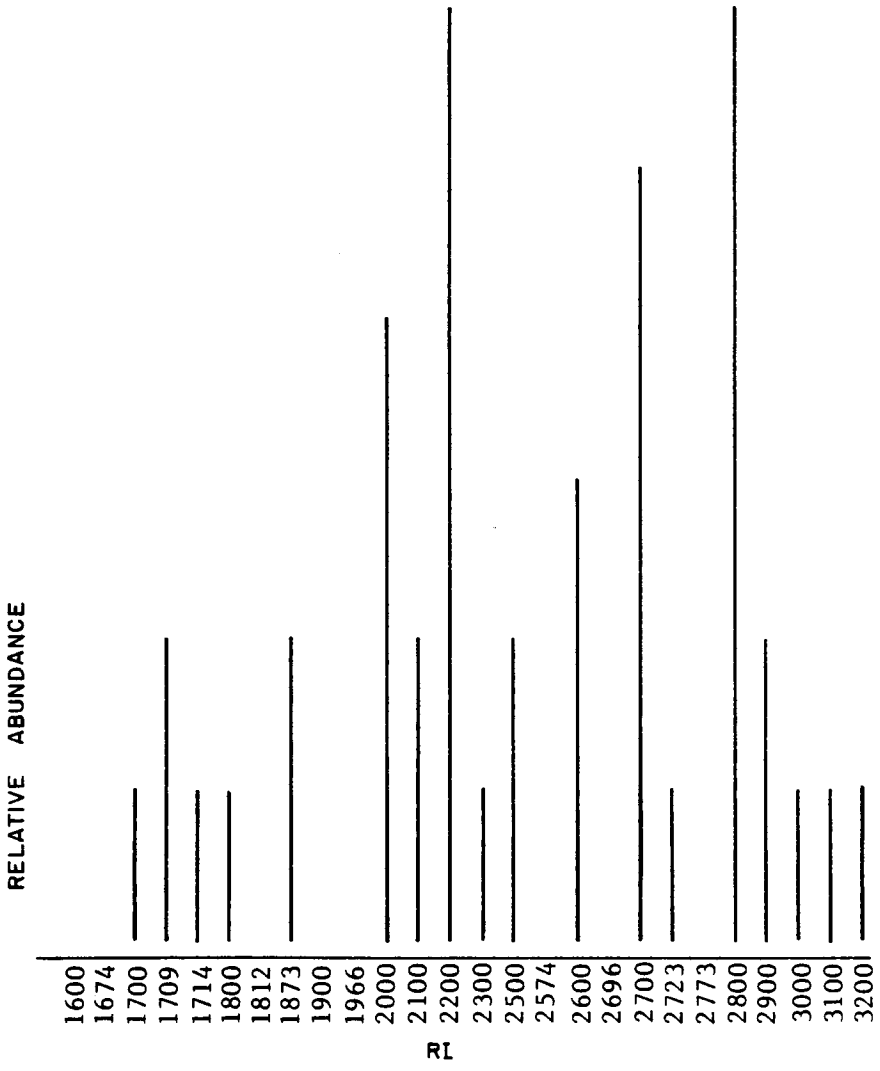


FIGURE 175B

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2105, YEAR 7, MONTH 8

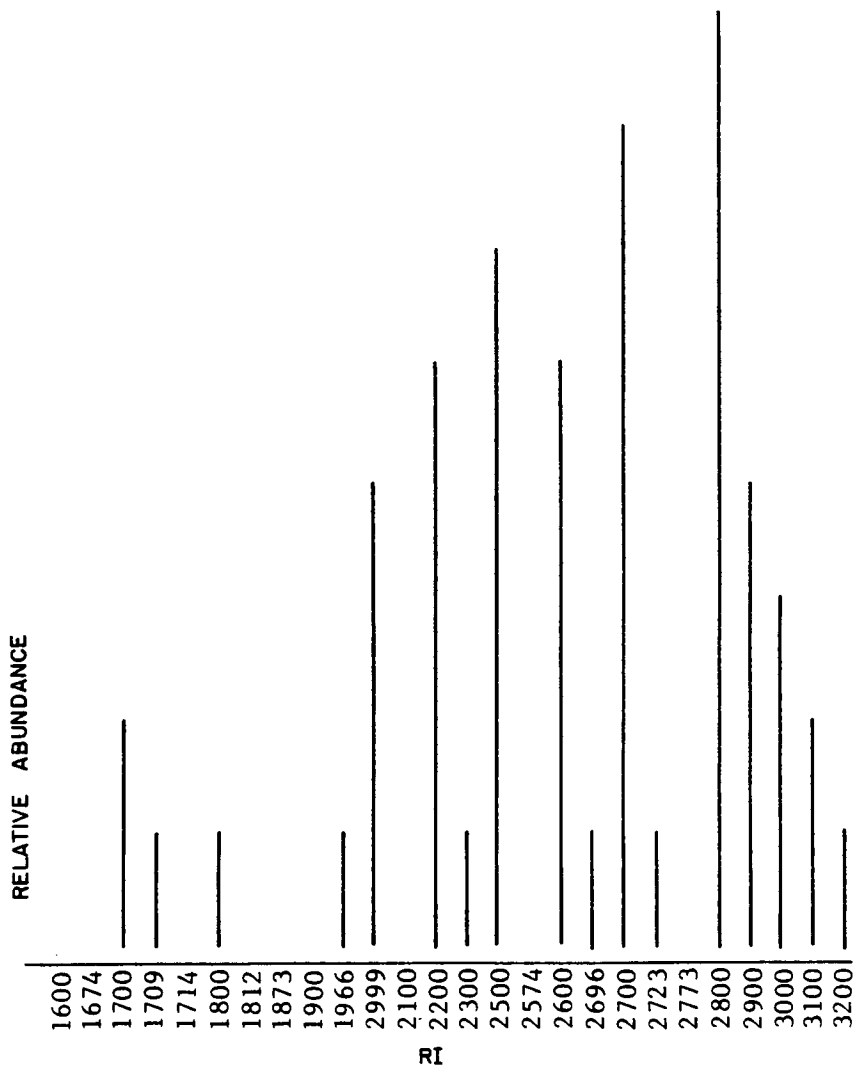


FIGURE 175C

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 2105, YEAR 8, MONTH 2

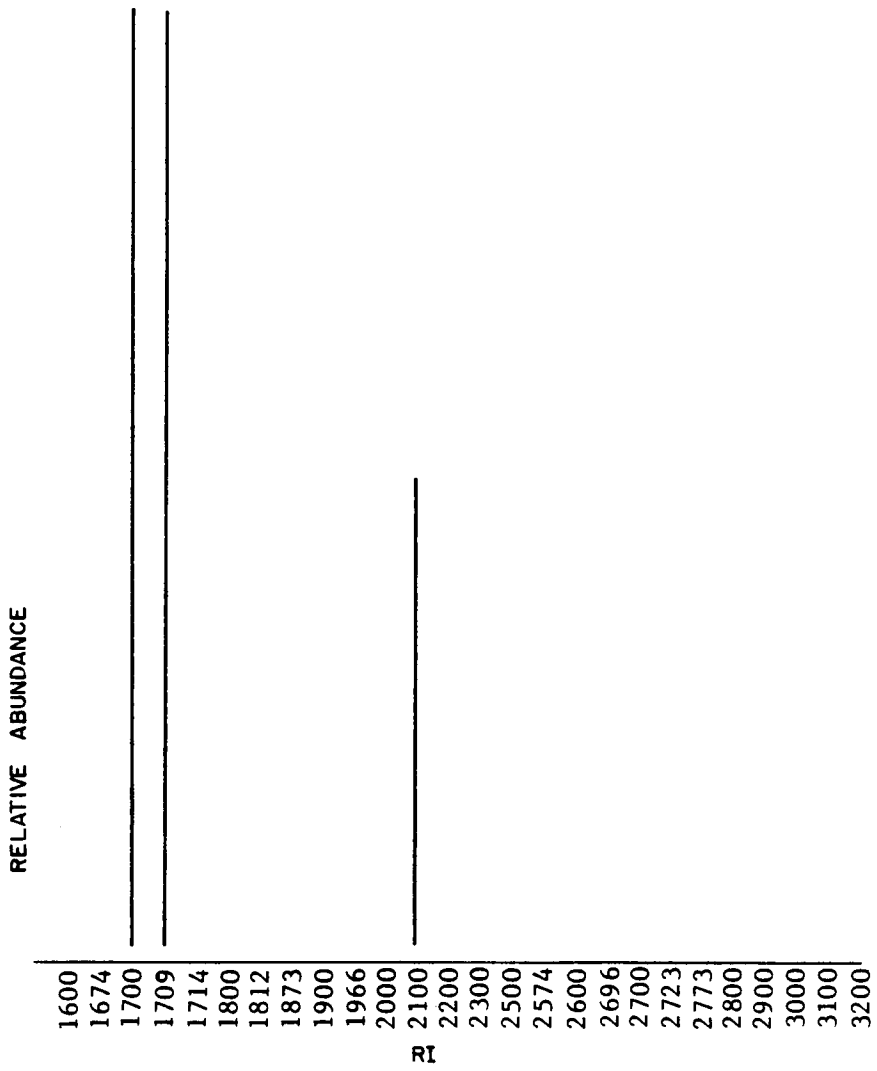


FIGURE 175D

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2209, YEAR 7, MONTH 8

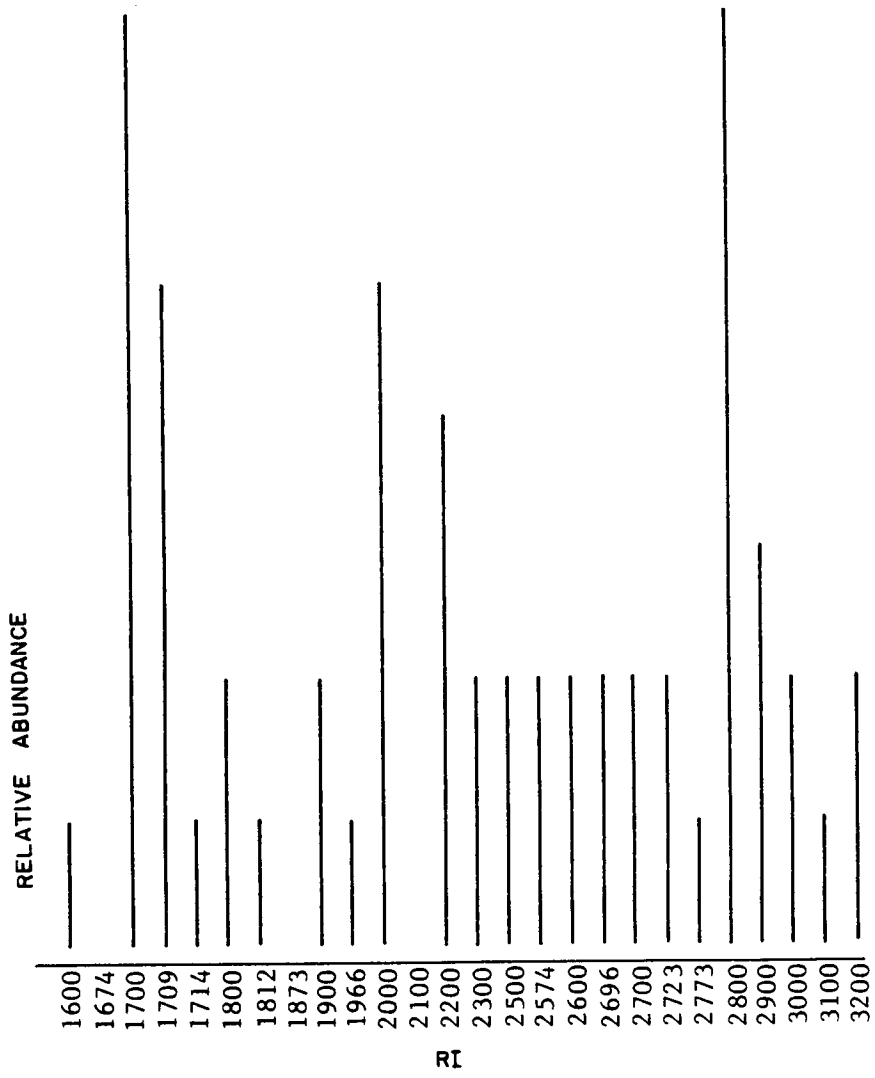


FIGURE 175E

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2209, YEAR 7, MONTH 10

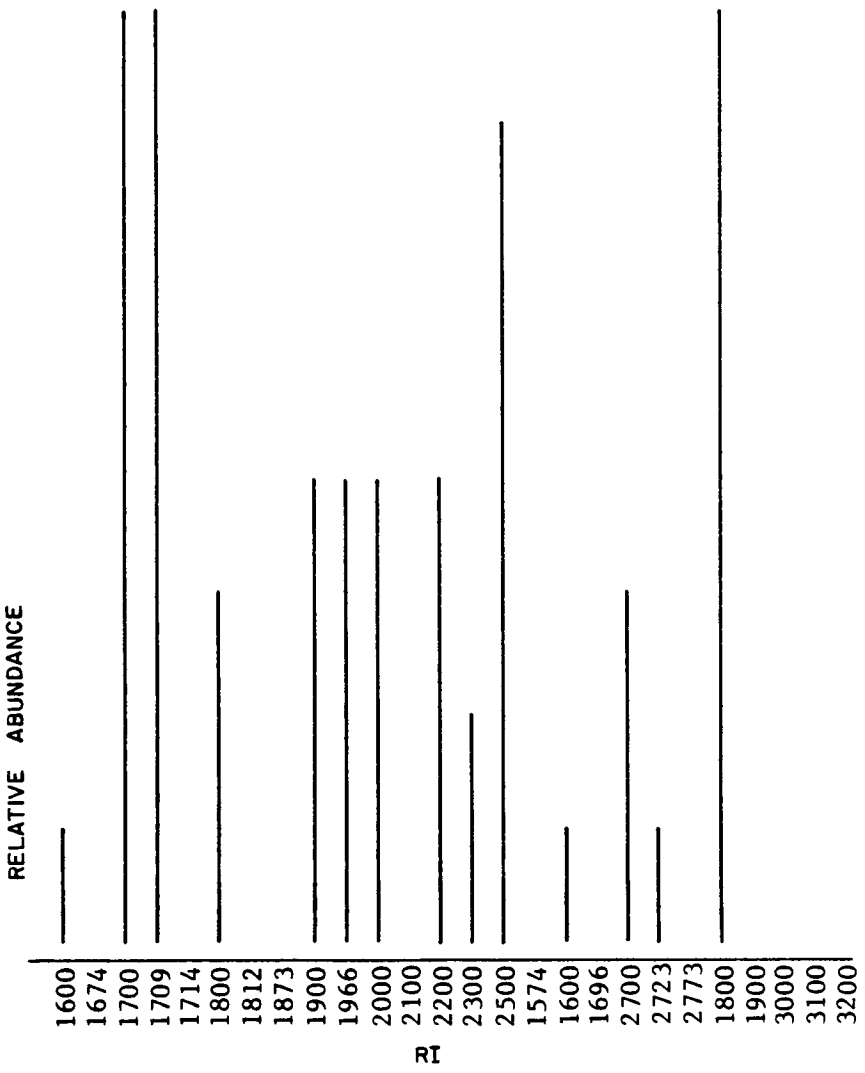


FIGURE 175F

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2209, YEAR 8, MONTH 2

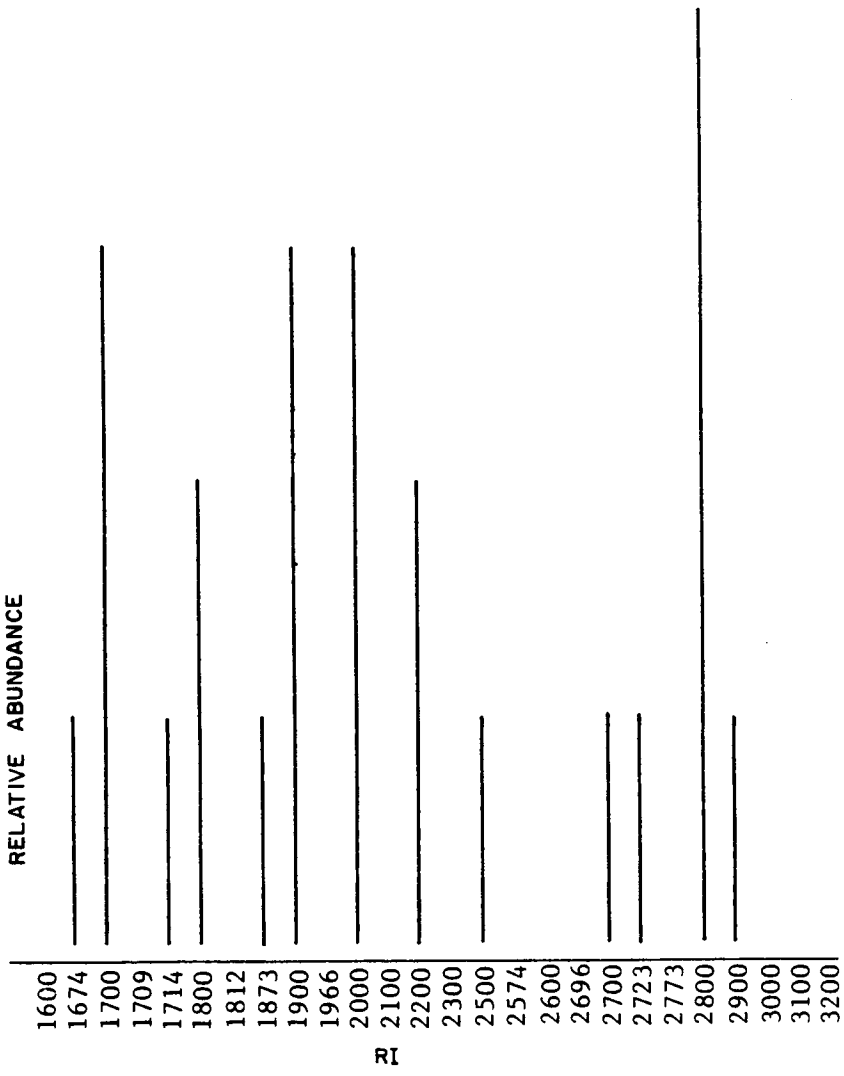


FIGURE 175G

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2426, YEAR 7, MONTH 8

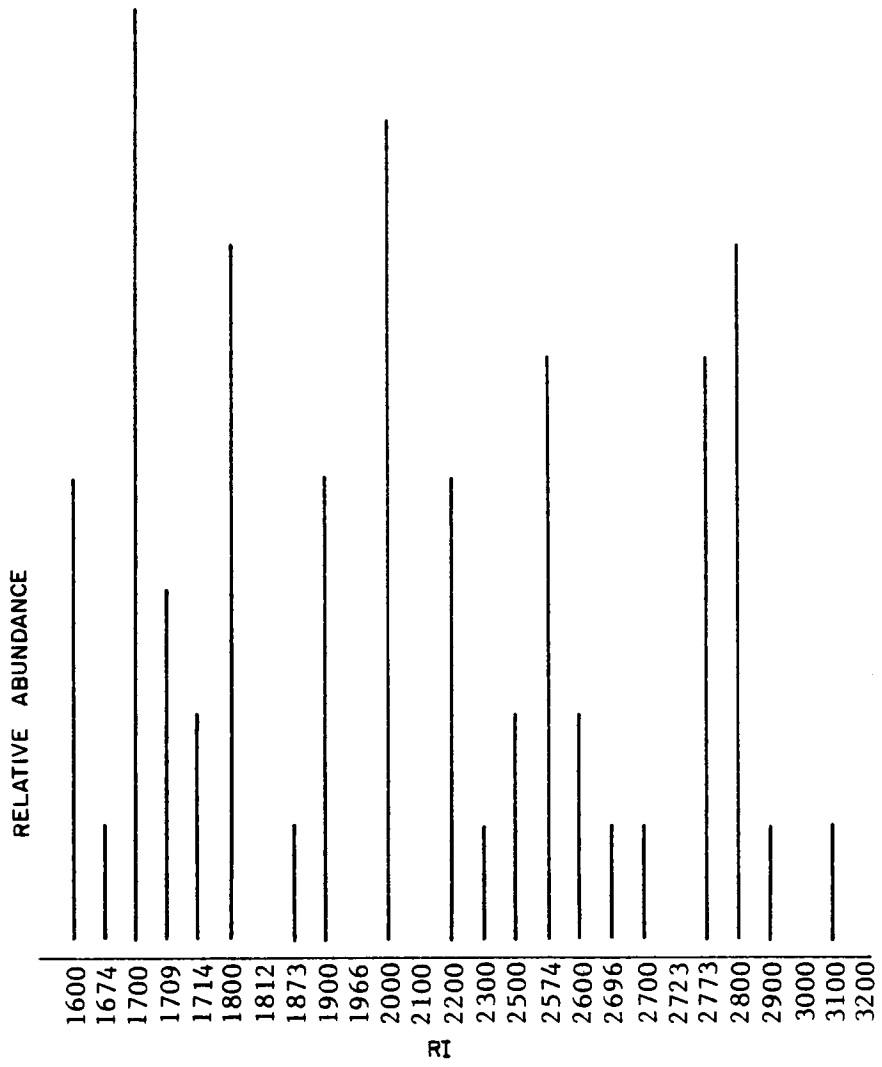


FIGURE 175H

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2426, YEAR 7, MONTH 10

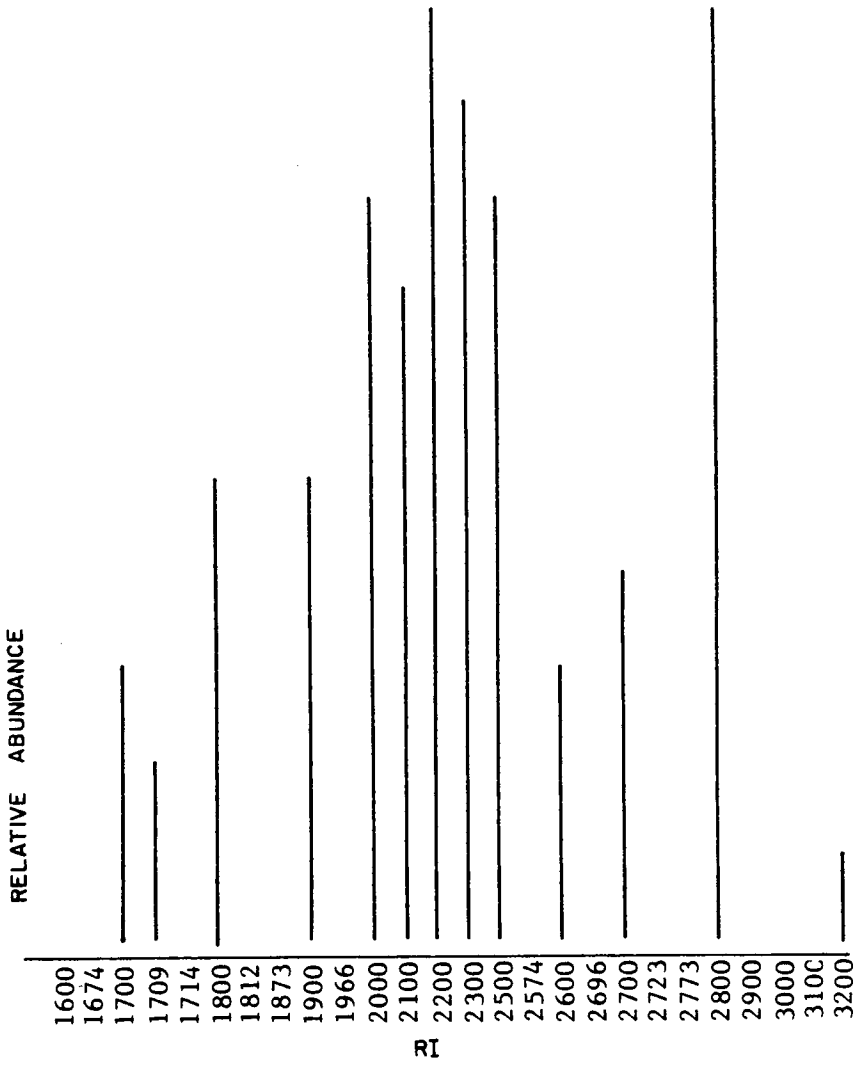


FIGURE 1751

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2426, YEAR 8, MONTH 2

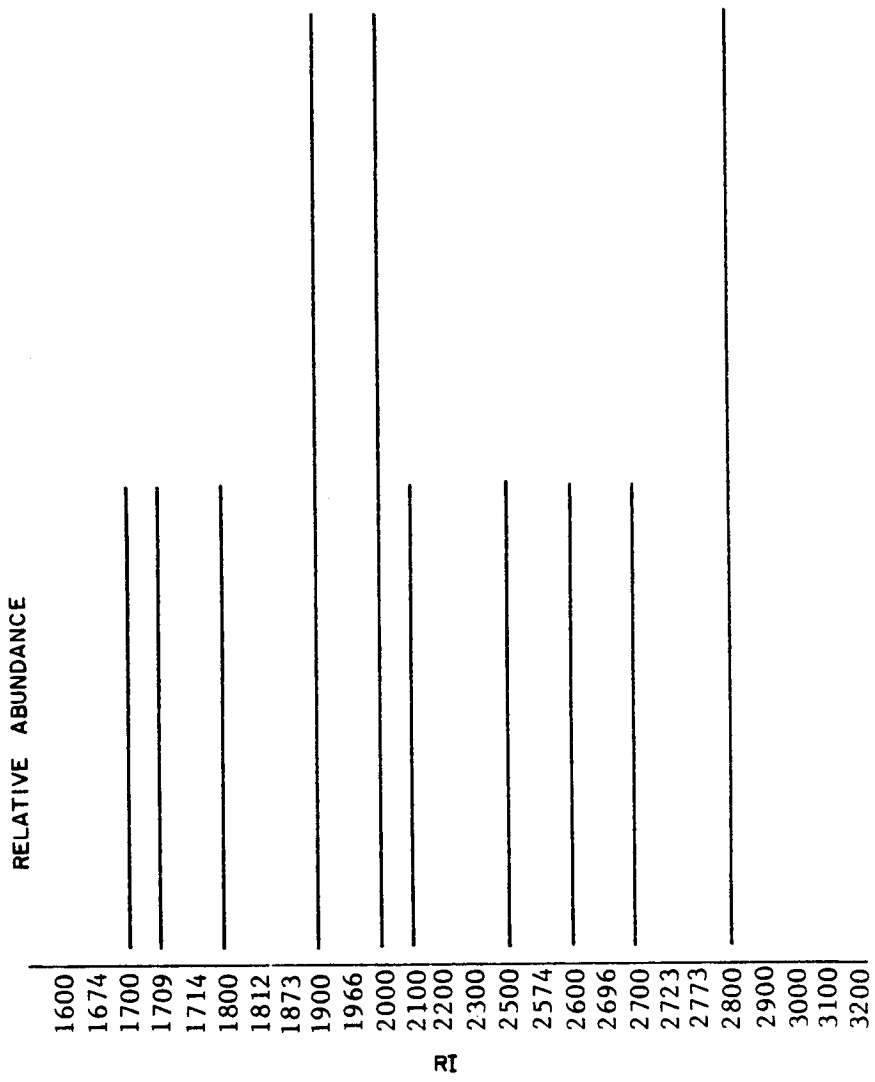


FIGURE 175J

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE

STATION 2747, YEAR 7, MONTH 8

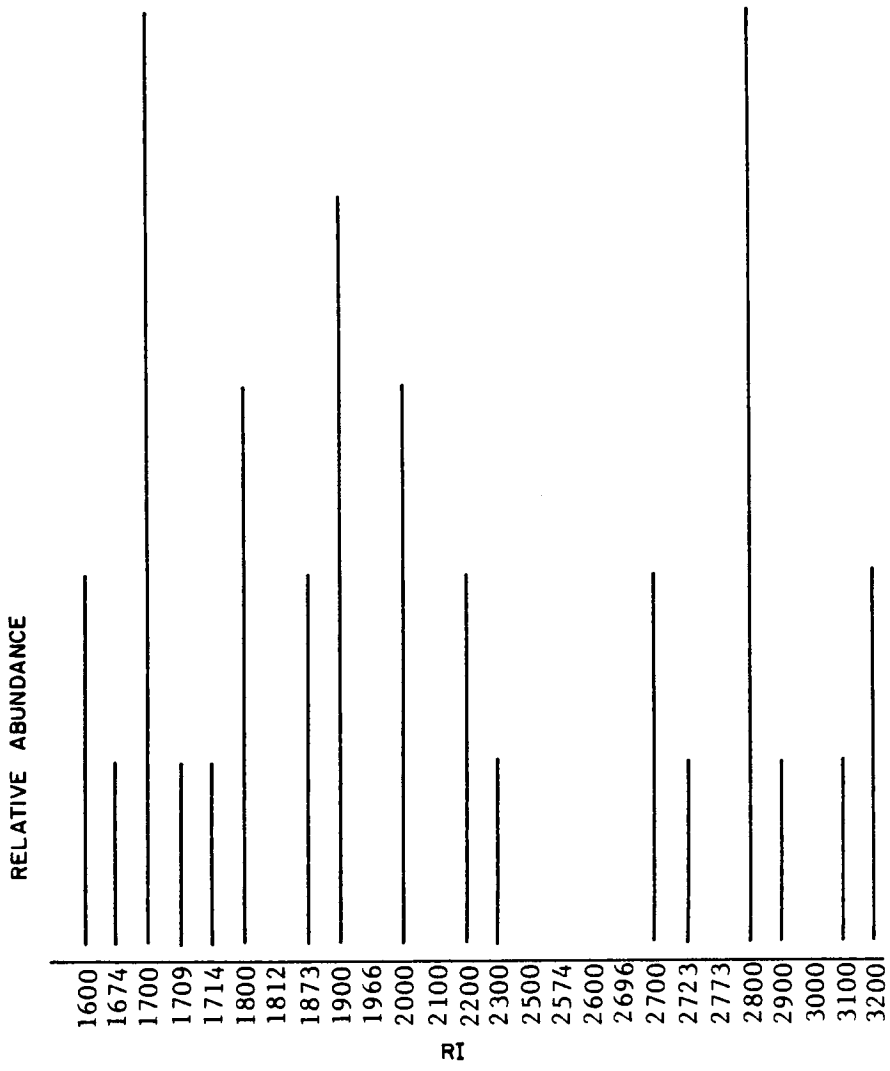


FIGURE 175K

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLE
STATION 2747, YEAR 7, MONTH 10

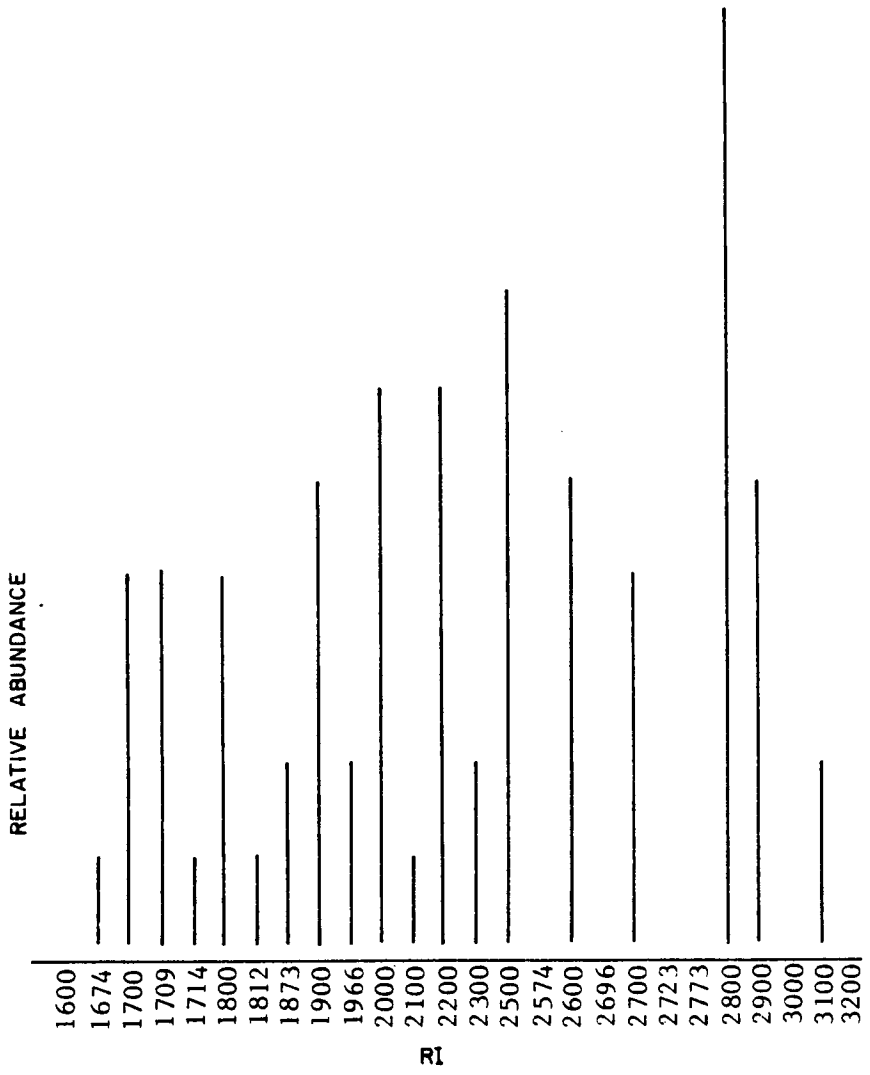


FIGURE 175L

HISTOGRAM: 10 MOST ABUNDANT COMPOUNDS FROM EACH SAMPLES

STATION 2747, YEAR 8, MONTH 2

FIGURE 176

UNRESOLVED HUMP AND REGULAR n-ALKANE SERIES INDICATIVE OF OIL CONTAMINATION IN SYACIUM PAPILLOSUM

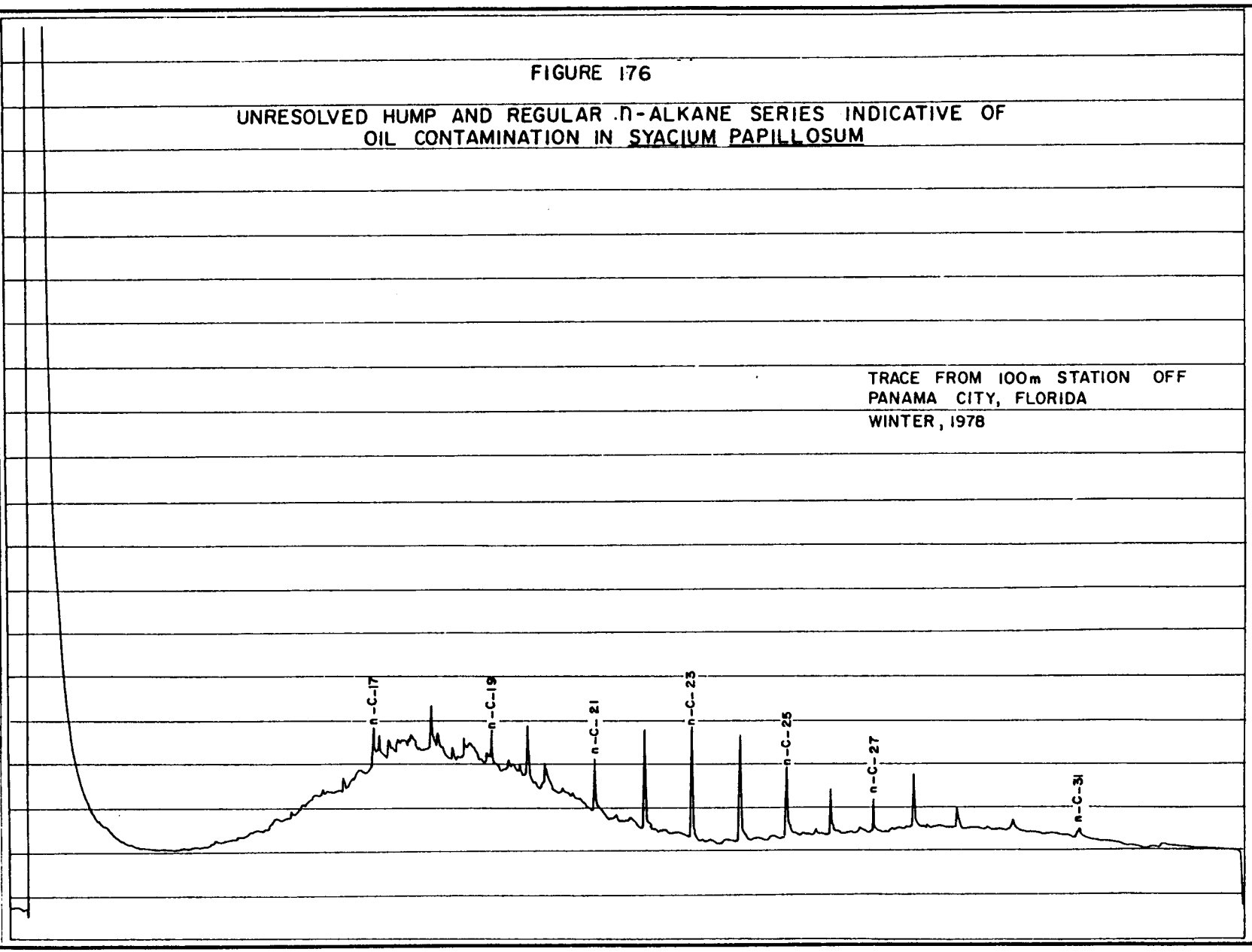


FIGURE 177

GC EXAMPLE OF POSSIBLE BIOGENIC PEAKS n-C-18, 20, 22
FROM SYACIUM PAPILLOSUM

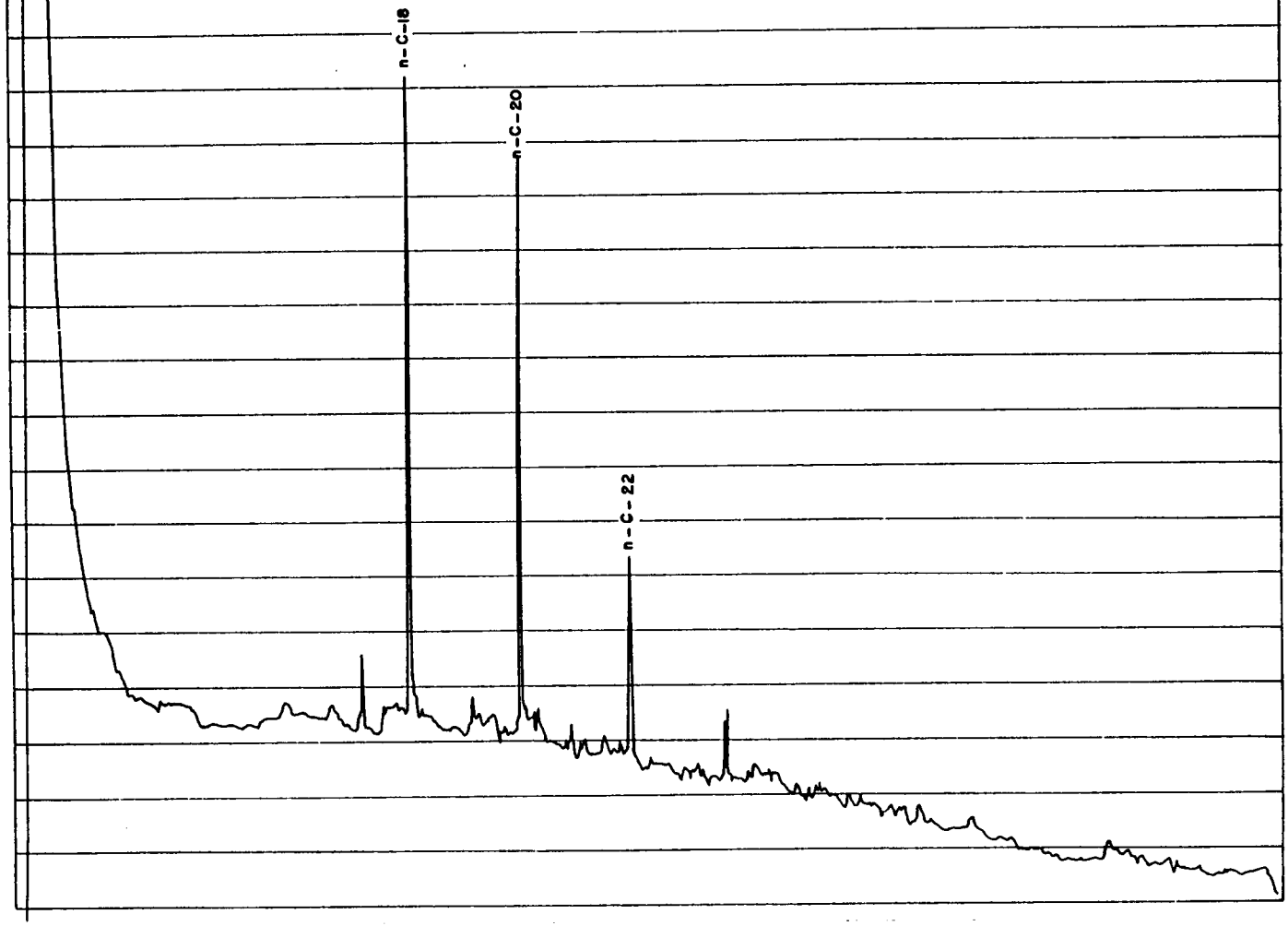
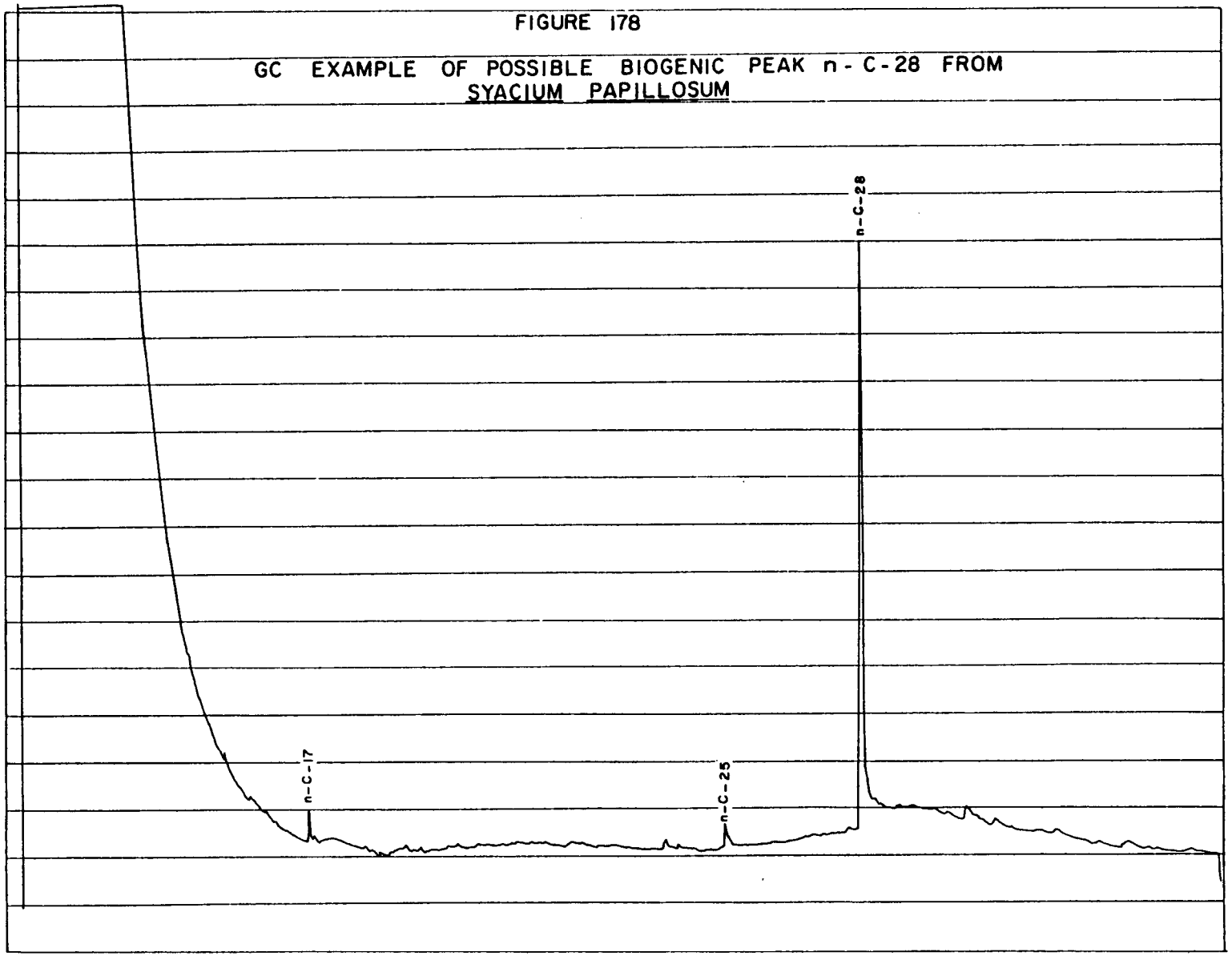


FIGURE 178

GC EXAMPLE OF POSSIBLE BIOGENIC PEAK n-C-28 FROM SYACIUM PAPILLOSUM



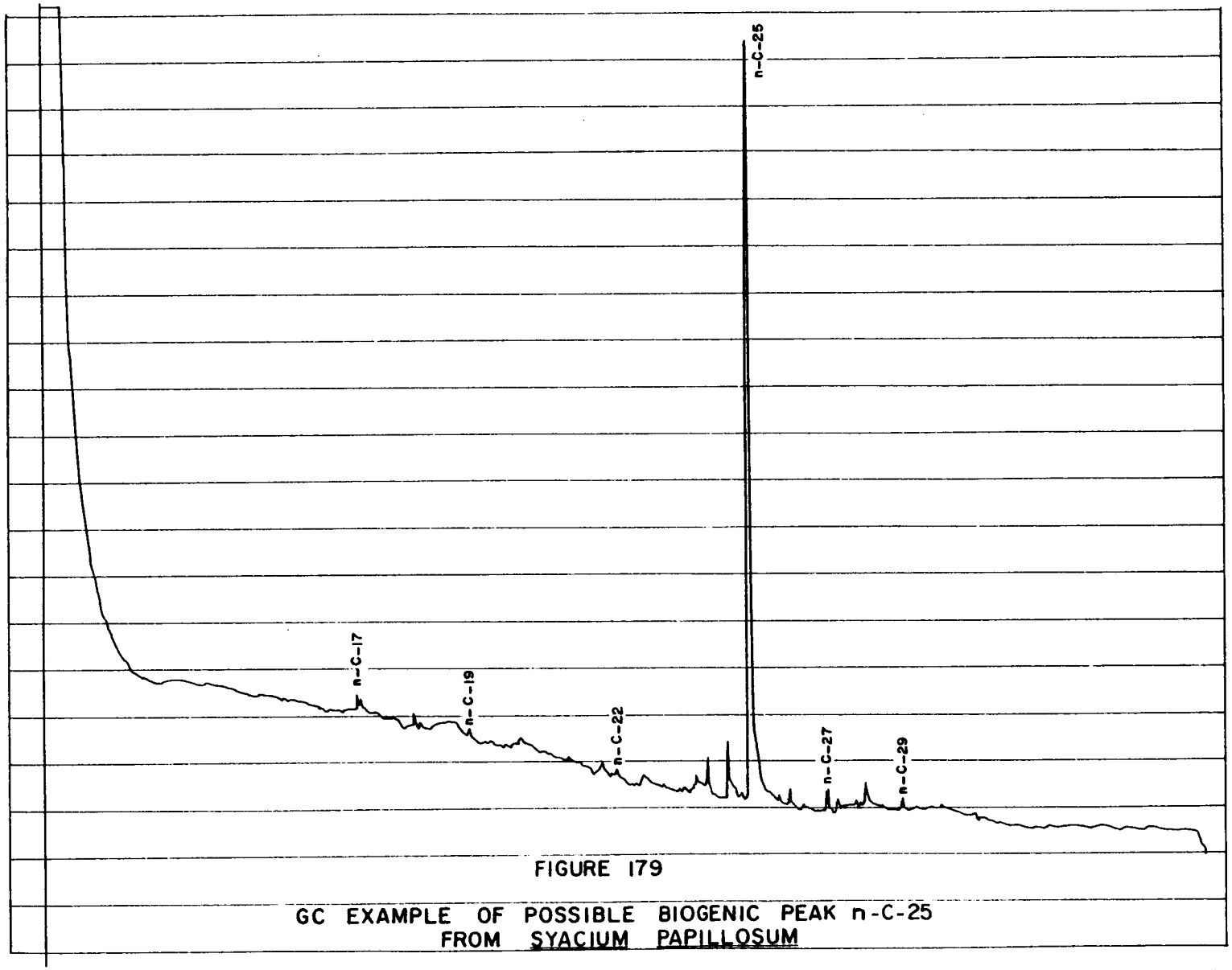


FIGURE 179

GC EXAMPLE OF POSSIBLE BIOGENIC PEAK n-C-25
FROM SYACIUM PAPILLOSUM

In an attempt to look into these two questions, several problems were encountered. In the macroepifauna data set, sample replication is much lower than in fish. Often there are just one or two analyses available. Thus, extensive pooling of data would be required to get some idea about their hydrocarbon composition. Pooling different species is a questionable procedure because each species can be assumed to relate to a given hydrocarbon input in its own characteristic way. It is well known that biological variability is a problem within single species. That is, given a well defined food source containing hydrocarbons, the composition and the concentrations of hydrocarbons incorporated in tissue of different individuals of the same species can be expected to be highly variable, especially at low hydrocarbon levels. If this variability is superimposed on the differences in uptake between different species, variability must be expected to increase. If variability in the food source is added, and that is what must be assumed to be the case in any natural environment, the results can be expected to be devastating.

This just about sums up what the macroepifauna data tells us. No matter how one tries to subdivide the data set, according to feeding habit, sediment type, order or area, there is very little present that is any way one looks at the data seems to make sense. The few features, observed in histograms based on the same chromatogram peaks as used in fish and based on the 10 largest peaks, in each chromatogram that may be worth mentioning are briefly discussed below.

In pure filter feeders, RI = 2800, 1700, 3200, and pristane have the highest frequency of occurrence. RI = 1800 and 2300 are absent. Most of the n-C-17 and pristane come from four species. All other compounds show an essentially flat distribution.

In the large group of mixed deposit feeders/predators, the only feature that is standing out is the peak at RI = 2800 and the low representation of those at RI = 2100 and 2300. N-C-17, pristane, the peaks with RI = 2000, 2200, 2500, and 2700 all have similar frequencies, about half of the frequency of RI = 2800. This is not too different from what is observed in the histograms from the total data set in fish (Figure 163). But it definitely is not something one wants to elaborate on.

Compared to fish, branched and olefinic compounds appear to be both more common and of higher variety than in fish. Not knowing what specific compound we are dealing with, little more can be said than that many of those compounds have not been encountered in the fish samples. But if they were olefinics, this would not be surprising.

As in fish, there is very little evidence for the presence of petroleum. This problem would most likely show up in the indiscriminate deposit feeders (Cypeaster ravenelli, Encope michelini) and maybe also in scallops (Aequipecten glyptus). Unfortunately, very few samples are available, but an inspection of their chromatograms does not suggest any petroleum pollution problem. Thus, in this aspect, the conclusion reached for fish does also apply to the macroepifauna.

HYDROCARBONS IN ZOOPLANKTON

The chromatograms of zooplankton extracts are distinguished by their uniformity. With only three exceptions, pristane is by far the most distinct peak, in concentrations as well as in frequency. Also common, but at lower concentration, is a partially resolved peak group centering approximately around RI = 2080. A very small amount of petroleum may be present in seven samples, mostly in winter collections. But conclusive evidence would have to come from the aromatic fraction.

An especially interesting feature is found in the difference between summer and winter collections: n-C-17 (and n-C-15 in three samples) is absent or present at low level only in all winter samples, but is a substantial peak in all except one sample (#6003302560725). N-C-19, on the other hand, is more prominent in the winter stations. It is likely that these peaks represent uptake from phytoplankton, while pristane is known to be biosynthesis, but this is not established. The hydrocarbon component due to uptake in the case of zooplankton is easy to recognize because much of their diet is limited directly or indirectly to phytoplankton and the hydrocarbon composition of this food source, although not investigated in this study, is known to be simple.

A very unusual chromatogram is shown in Figure 180, which is completely dominated by a peak at RI = 2500. It also contains a series of n-alkanes that could be due to a weathered oil, except that the unresolvable envelope, usually present in such weathered oil fractions, is absent. The origin of the peak at RI = 2500 is a puzzle that has been mentioned in the discussion of demersal fish (Figure 179).

REFERENCES

Anderson, J.W., J.M. Neff, B.A. Cox, H.E. Tatem and G.M. Hightower, 1974. The effects of oil on estuarine animals: toxicity, uptake and depuration, respiration. In Pollution and Physiology of Marine Organisms. Academic Press, New York, pp. 285-310.

Bieri, R.H.and V.C. Stamoudis, 1977. The fate of petroleum hydrocarbons from a No. 2 fuel oil spill in a semi-natural estuarine environment. In. D.A. Wolfe, ed. Fate and effect of petroleum hydrocarbons in marine organisms and ecosystems. Pergamon Press.

Bieri, R.H., V.C. Stamoudis and M.K. Cueman, 1977. Chemical investigations of two experiment oil spills in an estuarine ecosystem. Proc. Oil Spill Conference, New Orleans (API Publ. No. 4284, Washington D.C.) pp. 511-515.

Bieri, R.H., M.K. Cueman, and C.W. Su, 1978. In preparation.

Blumer, M., R.R.L. Guillard, and T. Chase, 1971. Hydrocarbons of marine phytoplankton. Marine Biology 8:183-189.

Dastillung, M. and P. Albrecht, 1976. Molecular test for oil pollution in surface sediments. Mar. Poll. Bull. 7:13-15.

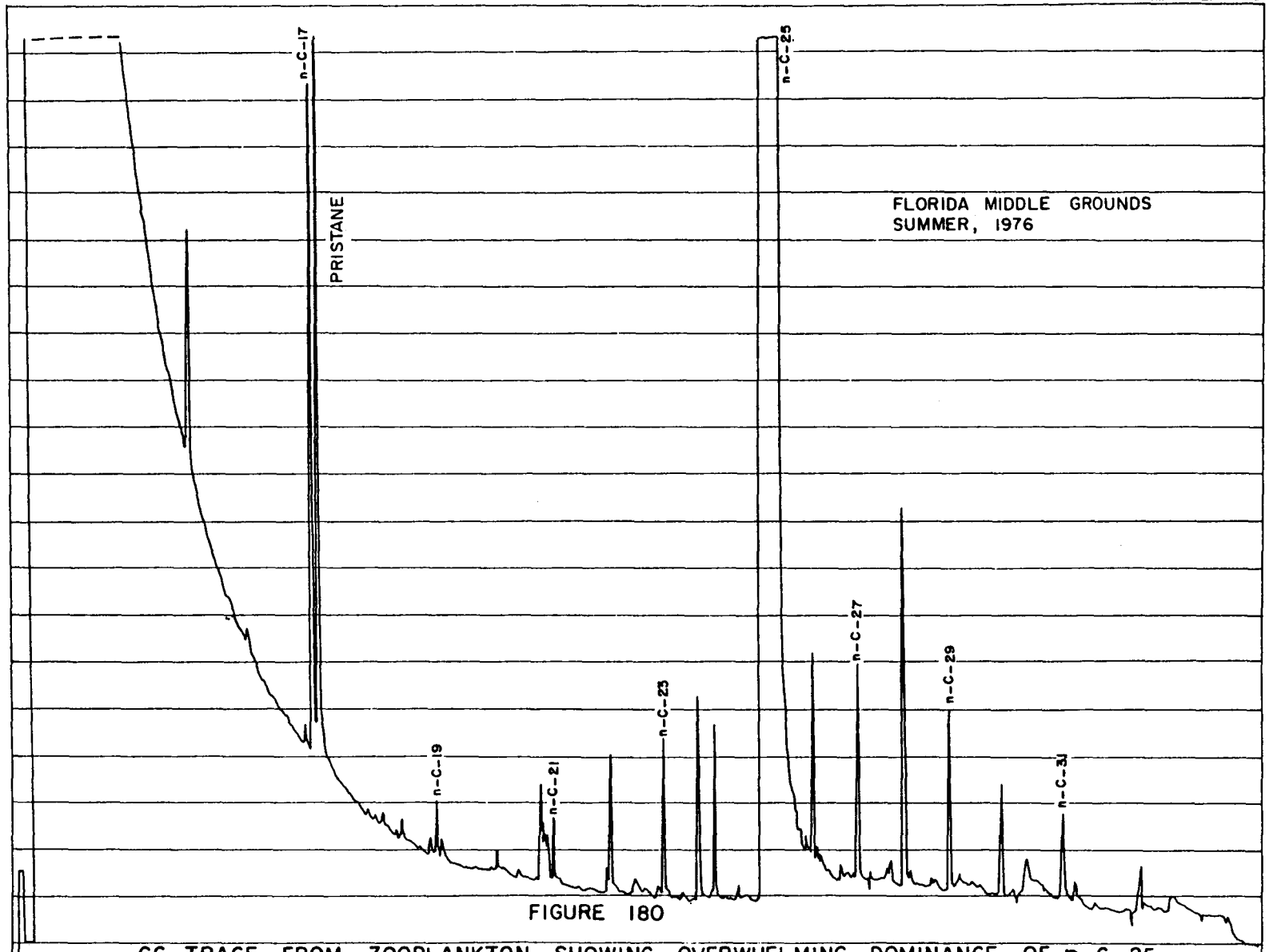


FIGURE 180

GC TRACE FROM ZOOPLANKTON SHOWING OVERWHELMING DOMINANCE OF n-C-25 AND n-ALKANE SERIES OF POTENTIAL OIL ORIGIN

de Rosa, M., A. Gambacorta, L. Minale, and J.D. Bu'Lock, 1973. Bacterial triterpenes (thermophyllics). Chem. Comm. 1971:619-620.

de Rosa, M., A. Gambacorta, L. Minale, and J.D. Bu'Lock, 1973. Isoprenoids of Bacillus acidocaldarius. Phytochem. 12:1117-1123.

Gelpi, E., H. Schneider, J. Mann, and J. Oro, 1970. Hydrocarbons of geochemical significance in microscopic algae. Phytochem. 9:603-612.

Han, J., E.D, McCarthy, M. Calvin, and M.H. Benn, 1968. Hydrocarbon constituents of the blue-green algae Nostoe musorum, Anacystis nidulans, Phormidium luridum, and Chlorogloea fritschii. J. Chem. Soc. (C): 2785-2791.

Lee, R.F., R. Sauerheber, and A.A. Benson, 1972. Petroleum hydrocarbons: uptake and discharge by the marine mussel Mytilus edulis. Science 177:344-346.

Lee, R.F., R. Sauerheber, and G.U. Dobbs, 1972. Uptake, metabolism and discharge of polyogelic aromatic hydrocarbons by marine fish. Mar. Bid. 17.201-208.

Neely, W.B., D.R. Branson and G.E. Blau, 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Envir. Sci. & Technol., 8, 1113-1115.

Oro, J., T.G. Tornabene, D.W. Nooner, and E. Gelpi, 1967. Aliphatic hydrocarbons and fatty acids of some marine and freshwater microorganisms. J. Bacteriol. 93:1811-1818.

Stegemen, J.J.and J.M. Teal, 1973, Accumulation, release and retention of petroleum hydrocarbons by the oyster Crassostrea virginica. Mar. Biol. 22:37-44.

Youngblood, W.W., M. Blumer, R.R.L. Guillard, and F. Fiore, 1971. Saturated and unsaturated hydrocarbons in marine benthic algae. Mar. Biol. 8:190-201.

VOLUME II

CHAPTER 10

INTERPRETATION OF SEDIMENT HYDROCARBON DATA

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INTRODUCTION

The hydrocarbon chemistry of marine surface sediments depicts both the short (weeks) and long (years) term histories of inputs of biogenic and anthropogenic hydrocarbon compounds to the benthic environment. A full description of the hydrocarbon chemistry of sediments of the MAFLA region starts with overall distribution of gross parameters (i.e., total alephatics or total aromatics) and continues with an evaluation of the relative contribution of individual hydrocarbon compounds and suites of hydrocarbon components which are diagnostic of input sources. Therefore, the hydrocarbon chemistry of surface sediments should actually be viewed as a composite discipline called biogeochemistry.

In this regard, it should be realized that a key consideration in interpreting the meaning of hydrocarbon distributions is how hydrocarbon parameters conary with other biogeochemical parameters such as total organic carbon (TOC), calcium carbonate and grain size and other chemical (elg., trace metal) parameters. Hydrocarbon distributions are either governed by their associations with natural processes (i.e., geochemical and biological sedimentation, fecal pellet transport, physical oceanographic forcing), or determined by pollution events in which case deviations from natural convariances (e.g., the hydrocarbon: organic carbon ratio in a given geochemical province) are keys to interpreting a data set.

The focus of this discussion will be an attempt at a quantitative and qualitative definition of geochemical "provinces" in the MAFLA study area. Once these areas are defined and relationships between variables in a given region evaluated, then three sets of questions can be addressed:

1. What are the sources of hydrocarbons in a given "province"
2. How are hydrocarbons normally transported into and through this "province"
3. What is the present state of the MAFLA benthic environment vis-a-vis petroleum contaminants in the sedimentary environment.

SOURCES OF SEDIMENTARY HYDROCARBONS (GENERAL)

There are three general classifications of hydrocarbons found in sedimentary environments:

1. Biogenic: produced by marine and terrestrial flora and fauna.
2. Anthropogenic: introduced directly (oil spills) or indirectly via aeolian or riverine input (sewage effluents, combustion of fuels-airborne, land surface drainage and runoff, etc.) through man's activities
3. Diagenetic: hydrocarbons altered or produced in the sediments through abiotic reactions.

A brief discussion of these various inputs is needed to set the stage for discussion of the MAFLA data.

HYDROCARBON SOURCE CLASSIFICATION

Well defined biochemical synthetic pathways yield discrete sets of hydrocarbon compounds. Pristane (2,6,10,14 tetramethyl penta decane) is the dominant aliphatic hydrocarbon in many marine zooplankters (Blumer et al., 1964). Penta decane and hepta decane (n-C-15 and n-C-17), normal alkanes, are produced by marine algae. The n-C-23 through n-C-31 n-alkanes show a strong odd carbon preference in vascular land plants and are delivered to OCS sediments via riverine and aeolian transport. Unresolved hydrocarbons, the so-called unresolved complex mixture (UCM), seen in gas chromatograms can be diagnostic of (1) degraded petroleum, (2) urban air particulates (3) recent (fresh) petroleum (4) land derived petrogenic compounds. Often when viewed in conjunction with the alkane distributions, the nature of the UCM can be better postulated.

A smooth alkane distribution (odd/even ratio = 1) overriding a UCM indicates recent petroleum inputs, while a UCM with a strong odd/even preference in the C-23 to C-31 range probably would indicate land derived material (e.g., sewage effluents) which has undergone degradation.

Olefinic compounds are present as a result of biogenic inputs. The polyunsaturated hydrocarbons heneicosa hexane (21:6) and squalene ($C_{30}H_{40}$) are present in sediments as a result of phytoplanktenic and animal biogenic inputs, respectively. Phytodienes are seen to be a result of zooplankton derived inputs and other olefinics are characteristic of benthic marine algae. A series of cycloalkenes, all having a C-25 backbone have been observed in marine sediments from many estuarine and OCS areas (Gearing et al., 1976; Boehm and Quinn, 1978; Keizen et al., 1978; Farrington and Tripp, 1975). Their origin is unknown and biogenic and diagentic sources have been postulated.

Aromatic hydrocarbon distributions have, in recent years, been shown to be quite useful in distinguishing between possible sources of anthropogenic materials. Youngblood and Blumer (1976), Laflamme and Hites (1978), Lee et al., (1977) among others have shown that in petroleum the alkyl substituted aromatic compounds predominate over the parent compound (e.g., alkyl naphthalenes over naphthalene), while pyrolytic sources (fuel combustion particulates, forest fires) exhibit a predominance of the parent compound (naphthalene, phenan threne, etc.) over the substituted homologs.

In this discussion an unambiguous petrogenic source for observed hydrocarbon distributions will be postulated if all of the following criteria are met:

1. A smooth n-alkane distribution over a broad molecular weight range; odd/even ratio = 1
2. The presence of pristane and phytane at roughly the same concentrations
3. The existence of an unresolved complex mixture; unimodal or bimodal

4a. Dominance of alkyl homologs of aromatic compounds per parent compounds denotes a recent petroleum input

4b. Predominance of unsubstituted parent aromatics denotes a pyrogenic input.

Pyrogenic sources for aromatic hydrocarbons dominate most OCS, polynuclear aromatic hydrocarbon distributions (Bieri et al., 1978; Laflamme and Hites, 1978; Boehm and Farrington, in preparation). Coastal sediments can yield aliphatic hydrocarbon profiles similar to crude or refined oils and at the same time exhibit an aromatic distribution in indecative of a pyrogenic source (Thompson and Eglinton, 1978a). The assumption here is that either (1) the pyrogenic sources dominate the aromatics (i.e., mask a petrogenic source) or that (2) the petrogenic aromatic fingerprint has been degraded or otherwise altered to yield a petrogenic pattern.

DISCUSSION OF RESULTS

GENERAL DISTRIBUTIONS OF HYDROCARBONS IN THE MAFLA REGION

Hydrocarbon distributions in the study region are to a first approximation defined by three source regions:

1. The Mississippi River suspended load and Mobile Bay inputs from the west carrying terrigenous biogenic and anthropogenic materials
2. Marine and some terrigenous biogenic material from the Florida Shelf and coastline, defined by several prominent individual compounds
3. The deep Florida Shelf (>40 metres) area influenced by both transport of fine grained smectites by the Gulf Loop current and deposition of terrigenous and marine biogenic compounds. (These regions are denoted as III, I, and II, respectively, on Figure 192, discussed below).

A consideration of the gross hydrocarbon parameters (i.e., total hexane or aliphatics and total benzene or aromatic/olefinics) is only useful when focusing on a specific region (I, II, or III) where source material is reasonably well defined. As indicated in Table 62 certain trends are seen between regions with respect to both gross and individual hydrocarbon parameters. Resolved aliphatics are more or less uniform between the three regions although the nature of the source material is grossly different between regions. Unresolved aliphatics are apparently greater in Region III on the average, due to the greater influence of detrital clay (smectite) in this region to which the aliphatic UCM is closely associated (Thompson and Eglinton, 1978). The resolved aromatic/olefinic fraction which is comprised mainly of olefinic hydrocarbons decreases from Region I through III. The influence of biogenic hydrocarbon input clearly decreases from the shallow Florida Shelf through the deep Florida Shelf, to the Mississippi-Alabama high smectite region. This is apparent in the trends for all marine biogenic compounds 2085, n-C-17 and pristane. In contrast the terrigenous n-alkane, n-C-29, increased from I to III indicating an increasing gradient in both smectite clay and terrigenous TOC originating in Region III. Presumably much of the TOC found in Region I is of marine origin.

An evaluation of trends in the hydrocarbon data as pertaining to trends in hydrocarbon pollution must be carried out in conjunction with

TABLE 62

GRAND STATION MEANS FOR SELECTED BIOGEOCHEMICAL PARAMETERS

	I	II	III
2900 (n-C-29)	0.012 ± 0.007	0.024 ± 0.012	0.048 ± 0.067
1700 (n-C-17)	0.011 ± 0.010	0.008 ± 0.003	0.006 ± 0.005
Pristane	0.012 ± 0.008	0.006 ± 0.004	0.005 ± 0.003
2085 ($C_{25}H_{44}$)	0.070 ± 0.053	0.043 ± 0.067	0.027 ± 0.016
Resolved Aliphatics	0.494 ± 0.294	0.441 ± 0.230	0.500 ± 0.466
Unresolved Aliphatics	0.418 ± 0.213	0.443 ± 0.324	0.622 ± 0.376
Resolved Aromatic/Olefinic	0.523 ± 0.998	0.231 ± 0.256	0.172 ± 0.130
Unresolved Aromatic/Olefinic	0.462 ± 0.552	0.278 ± 0.155	0.317 ± 0.210
Total Organic Carbon (TOC)	0.109 ± 0.085	0.231 ± 0.124	0.290 ± 0.309

scrutiny of the hydrocarbon composition. This is best illustrated by comparing two representative gas chromatograms (GC's) of hexane fractions from Regions II and I (Figures 181 and 182). The first chromatogram is from a sample from Station 2106. Its composition appears to consist of a composite of terrigenous n-alkanes C-21, C-23, C-25, C-29, and C-31, a large UCM, and n-alkanes (C-17 to C-28) perhaps associated with a petrogenic input. This chromatogram is more or less typical of the sediments from the deeper stations southeast of Cape San Blas (2106, 2957, 2746, 2212, 2313, 2427). The total hexane concentration (aliphatic hydrocarbons) is 0.3 $\mu g \cdot g$. The second chromatogram from Station 2419 consists almost entirely of biogenic inputs n-C-17 and pristane, the cycloalkene 2085, n-C-23, 25, 27, 29, and 31. No anthropogenic input is apparent yet the total concentration of this sample is about 0.6 $\mu g \cdot g^{-1}$ or twice that from 2106 where anthropogenic influence is readily apparent.

Therefore, sole considerations of total gross parameters obscure our primary objective; to define and quantify biogenic versus anthropogenic hydrocarbon distributions. The bulk of the following discussion will, therefore, focus on (1) qualitative aspects of the hydrocarbon composition; from gas chromatograms to infer sources of hydrocarbons; (2) concentrations of individual diagnostic hydrocarbon compounds; (3) relationships of hydrocarbon parameters to each other and to other non-hydrocarbon parameters.

GAS CHROMATOGRAPHIC CLASSIFICATION

Sediment hydrocarbon chemistry in the MAFLA region reflects a variety of source materials. The nature of the gas chromatographic fingerprint usually reflects a composite of sets of compounds associated with specific types of sources. The classification system presented in Table 63 is an attempt to relate these fingerprints between stations and at the same station over the course of the four sampling periods.

Class B - A representative GC trace illustrating primarily marine biogenic inputs is shown in Figure 183. The predominant features are the n-C-17 alkane, the 2085 cycloalkene ($C_{25}H_{44}$) and the isoprenoid, pristane.

Class T - This class is noted for the marked input of terrigenous n-alkanes (Figures 184 and 185); the odd chain n-alkanes from C-23 to C-31 originating mainly in the Mississippi drainage system but also from the Appalachicola and local terrigenous drainage.

Class U - Where a UCM is a main feature of the GC relative to other inputs, the sample is given this classification. Seldom existing as a class by itself, it is either unimodal (U) or bimodal (U2) as noted in Figures 186 and 187. A hydrocarbon fingerprint "TU" is most likely a composite of T compounds, associated with detrital plant remains in a silt size fraction, and a U assemblage most closely allied with a clay size fraction (Thompson and Eglenton, 1976b).

Class I - Represents an input of a smooth distribution of intermediate molecular weight alkanes (n-C-19 to n-C-25) which are prominent GC features (e.g., Figure 188). The odd/even ratio of these compounds is approximately equal to one and may represent a pelagic tar ball input.

FIGURE 181

GAS CHROMATOGRAM OF ALIPHATIC FRACTION
STATION 2106 - FALL 1977 (REGION II)

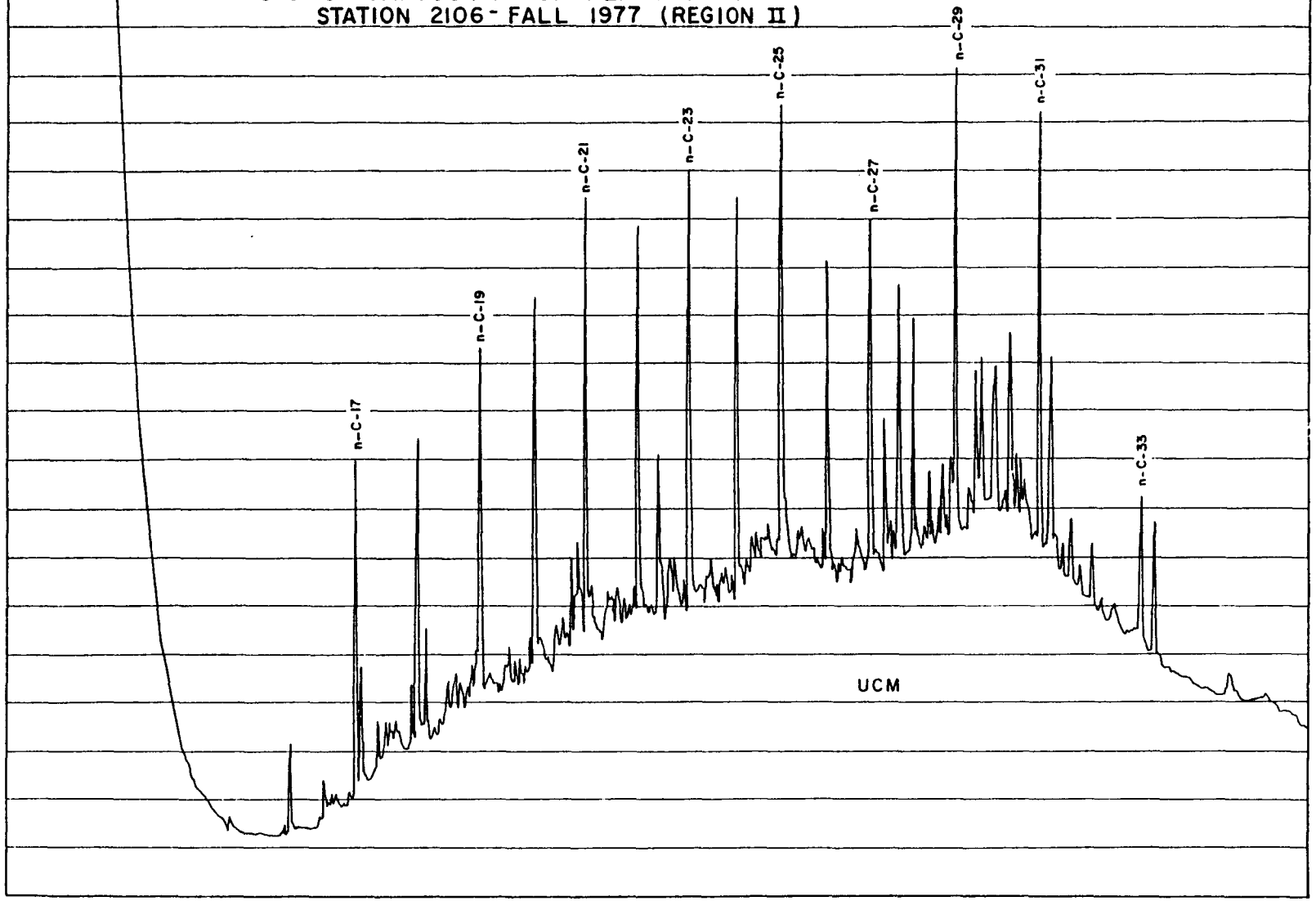


FIGURE 182

GAS CHROMATOGRAM OF ALIPHATIC FRACTION
STATION 2419 - FALL 1977 (REGION I)

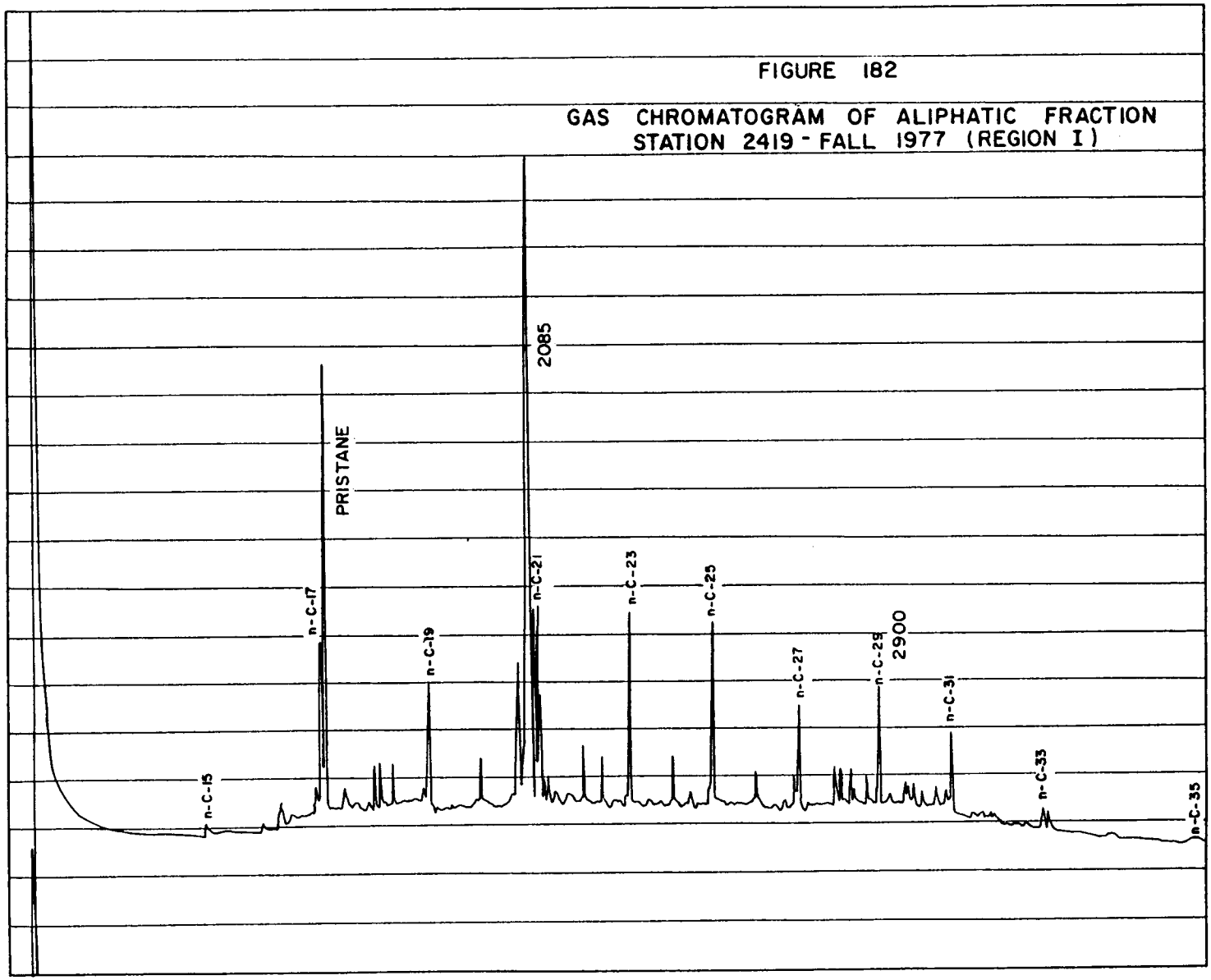


TABLE 63

CLASSIFICATION OF SURFACE SEDIMENT HYDROCARBONS AS TO SOURCE

Station Number	Summer 1976	Summer 1977	Fall 1977	Winter 1978
2101	BTU*	B	BU	-
2102	BT	B	B	-
2103	B	B	BT	-
2104	BT	BT	BU	-
2105	TULI*	TUL	B	BT
2106	TLU	TU	TUL*	-
2207	B	TB	B	BT
2208	BT	BT	B	BT
2209	B	B	B	BT
2210	BT	B	B	-
2211	ILTB	BT	B	-
2212	TL	TL	TUBL	TU2L
2313	-	TU	TUB	-
2315	-	BT	BTU	BILU*
2316	-	B	B	BT
2317	-	B	BU	BT
2318	-	BIU	B	B
2419	-	BTLU*	BT	BTLU*
2421	-	BT	B	BTLU*
2423	-	BTL	B	-
2424	-	BTU2L	B	BTLU*

B - Mainly marine biogenic (n-C-17 pristane, 2085 in hexane fraction)

T - Mainly terrigenous biogenic (n-C-23, n-C-25, n-C-17, n-C-29, n-C-31)

U - Unresolved complex mixture (UCM) a prominent feature (unimodal)

U2 - Bimodal UCM

I - Intermediate n-alkanes prominent (n-C-20 to n-C-24)

L - Lower n-alkanes (n-C-14 to n-C-22) prominent

* - Petrogenic source (L and U components prominent)

TABLE 63 (CONTINUED)

CLASSIFICATION OF SURFACE SEDIMENT HYDROCARBONS AS TO SOURCE

Station Number	Summer 1976	Summer 1977	Fall 1977	Winter 1978
2426	-	BT	TULB	LUBT*
2427	-	TUL	TU2L	LU*
2528	-	B	TUBL*	BUT*
2529	-	BTU	LUB*	LU*
2531	-	TUB	TU2BL*	LU*
2533	-	-	TU2BL	TLU
2535	-	TLB	TB	BU2T*
2536	-	TU2LB*	TUB	TU2BL*
2638	-	TU	TU	TU
2639	-	TUB	-	TU2BL*
2640	-	TU	TUBL	TUBL*
2641	-	TU2LB*	TU2BL*	TU2BL*
2643	-	TU*	TU	TU2BL*
2645	-	TUB	TU2L*	TU2BL*
2746	TU2L*	TU*	-	TU2BL*
2747	TU2LB	TULB	-	BTL
2748	TU2L*	TUL	-	BT
2749	-	B	-	-
2851	-	B	-	-
2852	L	B	-	-
2853	B	BL	-	-
2854	BTL	BL	-	-
2855	B	BL	-	-
2856	TUB	BTU	-	-
2957	-	TUL	TUL*	-
2958	-	BUL	TUL	-
2959	-	BTU2	-	-
2960	-	B	B	-

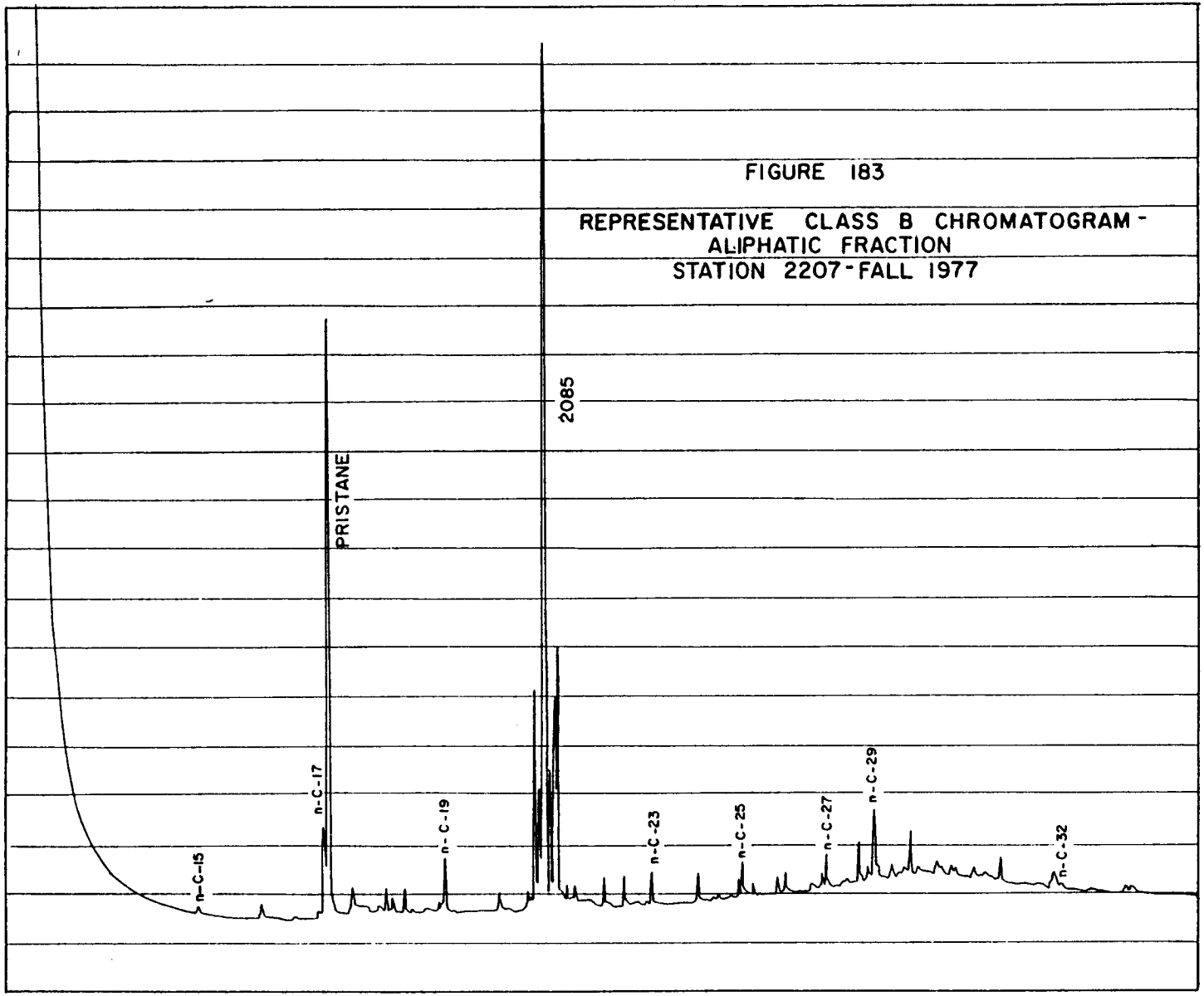


FIGURE 183

REPRESENTATIVE CLASS B CHROMATOGRAM - ALIPHATIC FRACTION
STATION 2207 - FALL 1977

FIGURE 184

REPRESENTATIVE CLASS T ALIPHATIC GAS CHROMATOGRAM
STATION 2638 - FALL 1977

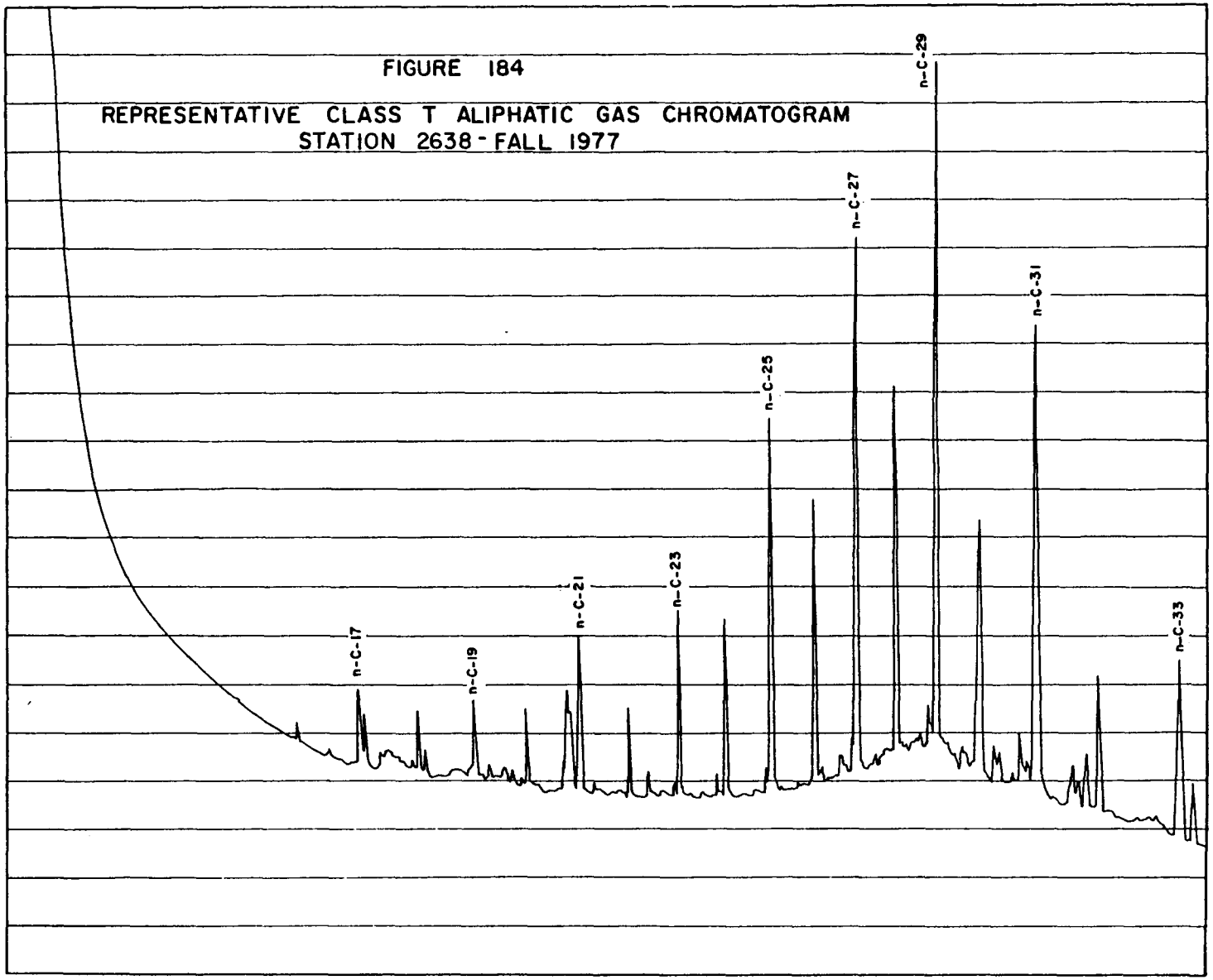


FIGURE 185

REPRESENTATIVE CLASS T GAS CHROMATOGRAM
STATION 2427 - SUMMER 1977 (TUL)

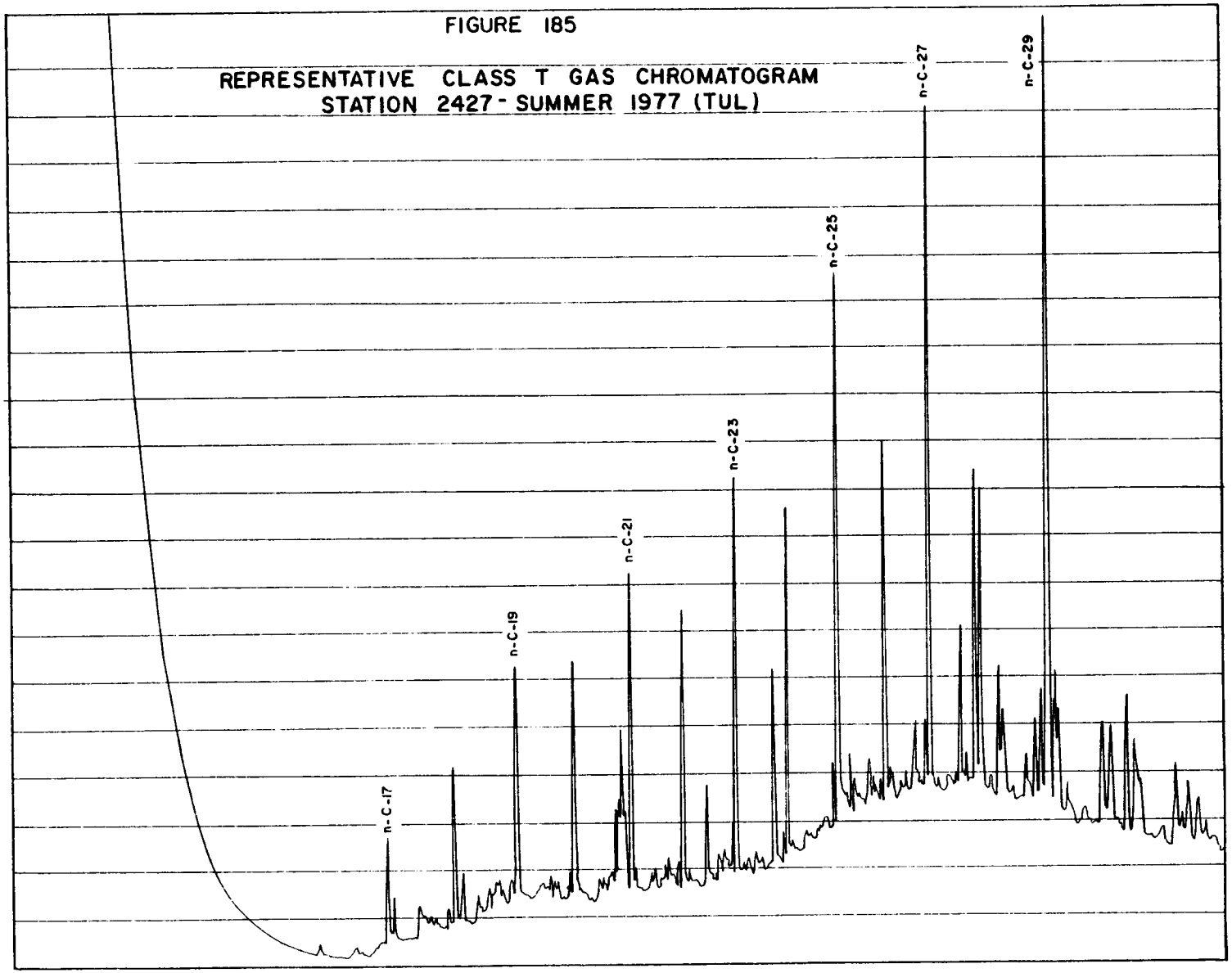
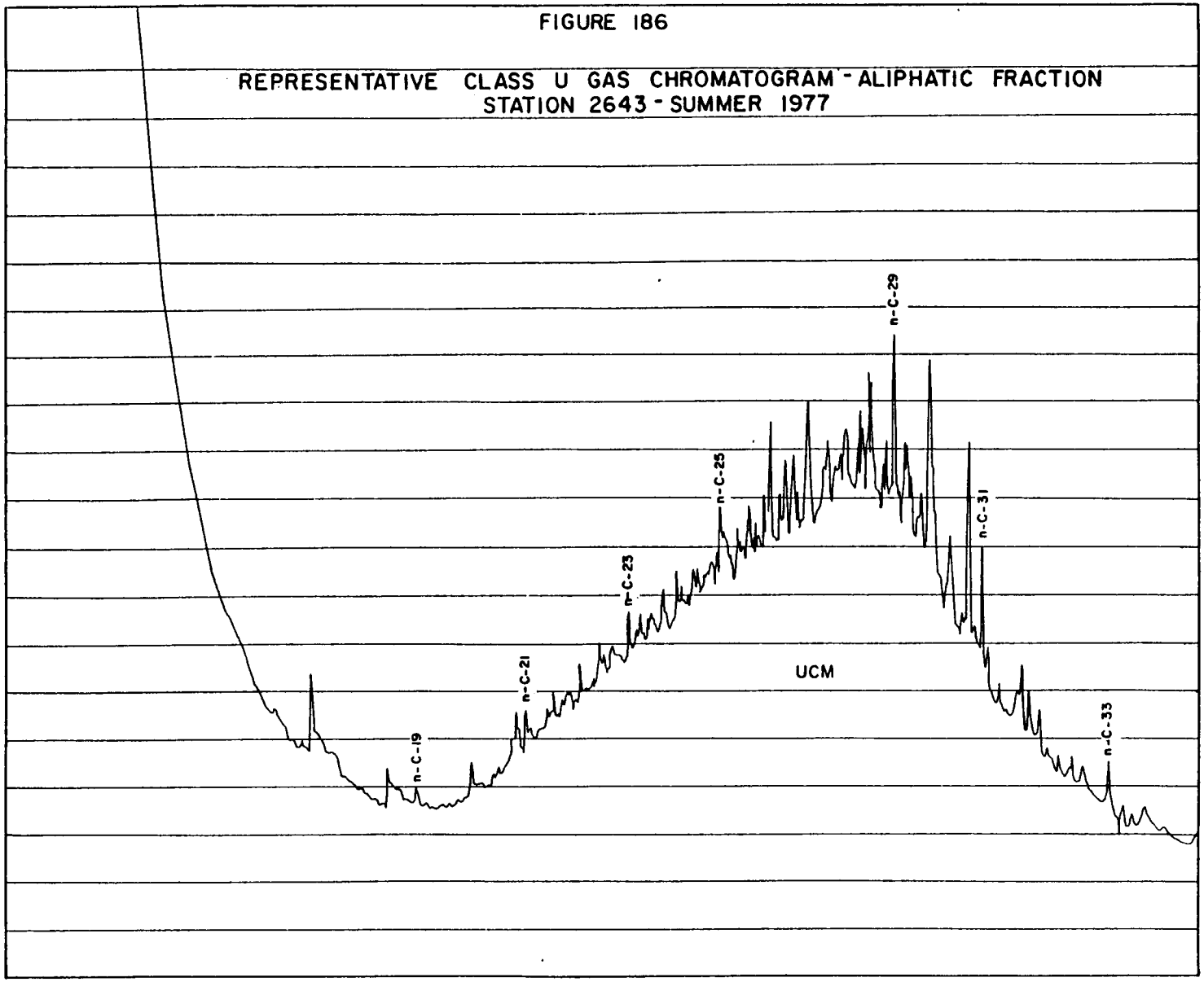


FIGURE 186

REPRESENTATIVE CLASS U GAS CHROMATOGRAM - ALIPHATIC FRACTION
STATION 2643 - SUMMER 1977



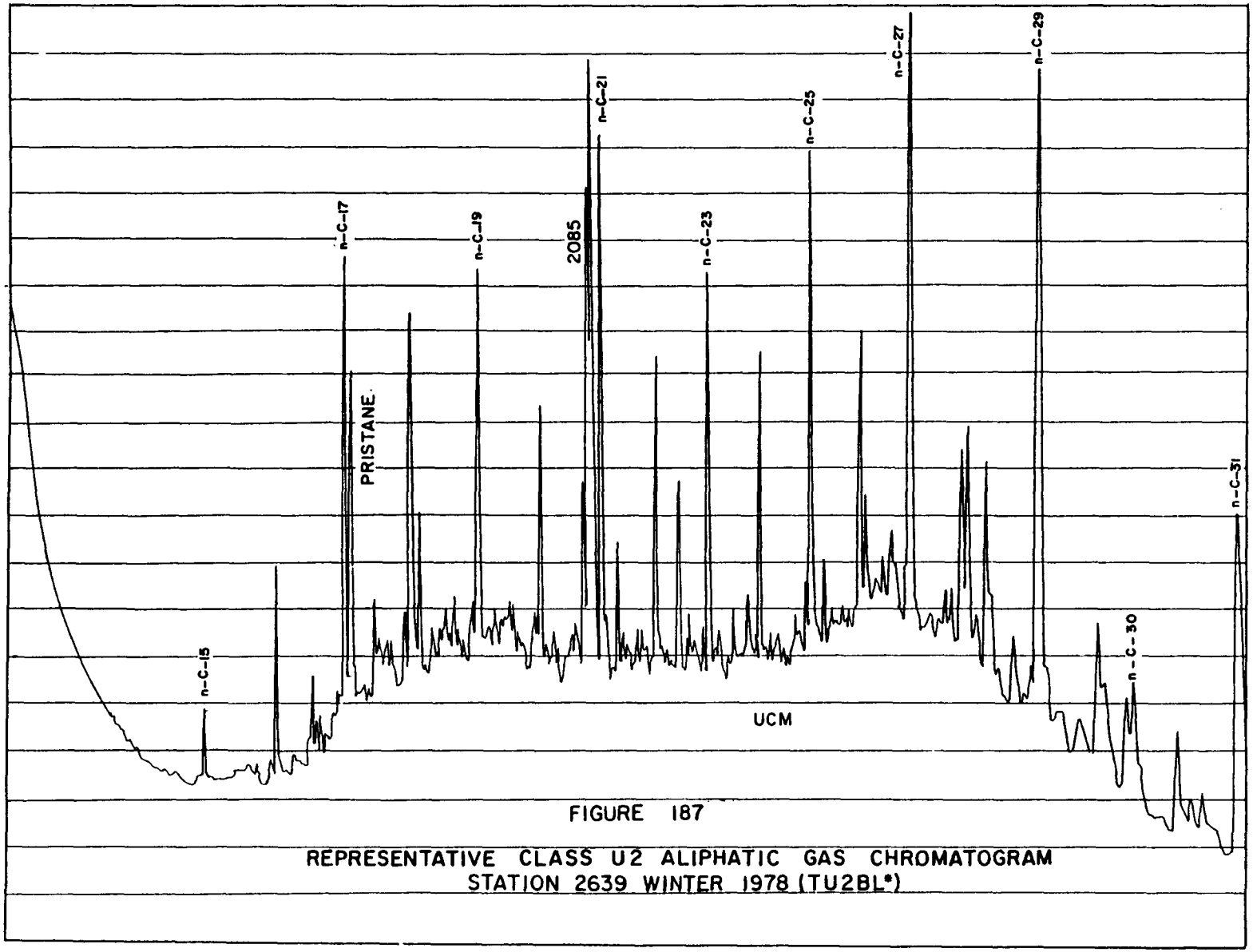
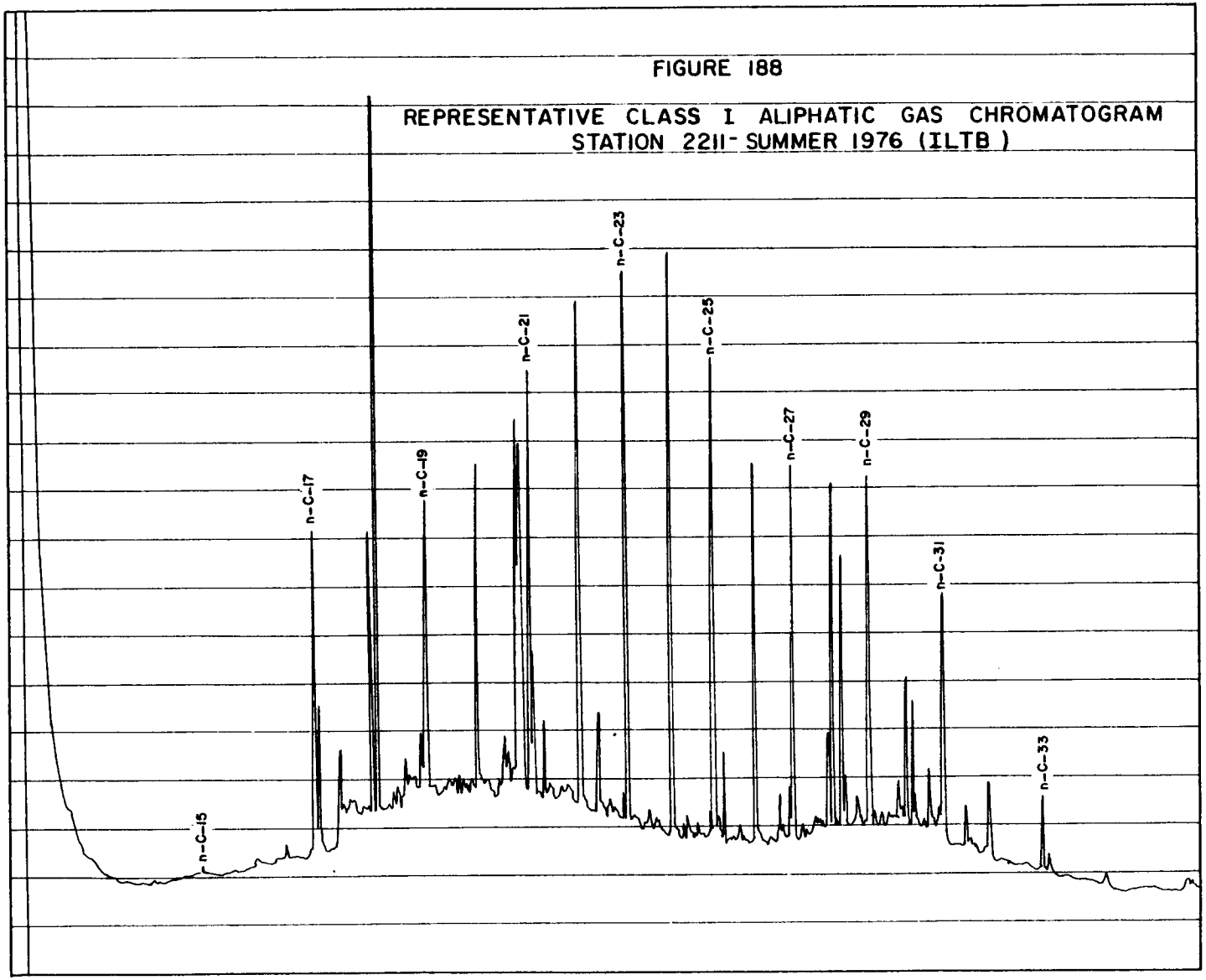


FIGURE 187

REPRESENTATIVE CLASS U2 ALIPHATIC GAS CHROMATOGRAM
STATION 2639 WINTER 1978 (TU2BL*)

FIGURE 188

REPRESENTATIVE CLASS I ALIPHATIC GAS CHROMATOGRAM
STATION 2211- SUMMER 1976 (ILTB)



Class L - Lower molecular weight (n-C-14 to n-C-20) n-alkane inputs, if significant, are denoted by Class L; for example Figure 189 consists mainly of these lower molecular weight n-alkanes paired with a large UCM. The designation LU or LU2 is often interpreted as indicating a petrogenic input (denoted in Table 62 by *) probably related to a light to medium petroleum distillate.

As an example of a complex composite pattern consisting of several inputs, consider Figure 187. This sample (Station 2639, winter 1978) is classified TU2BL* indicating terrigenous n-alkanes (T), biogenic olefins (1700 and 2085) (B), and n-C-16 to n-C-20 alkanes (L), overriding a bimodal (U2) UCM. The overall pattern suggests a composite of a petrogenic input (*) and inputs associated with a terrigenous biogenic input and some secondary anthropogenic source as indicated by the higher boiling UCM, which probably is associated with the smectite clays of the Mississippi River delta.

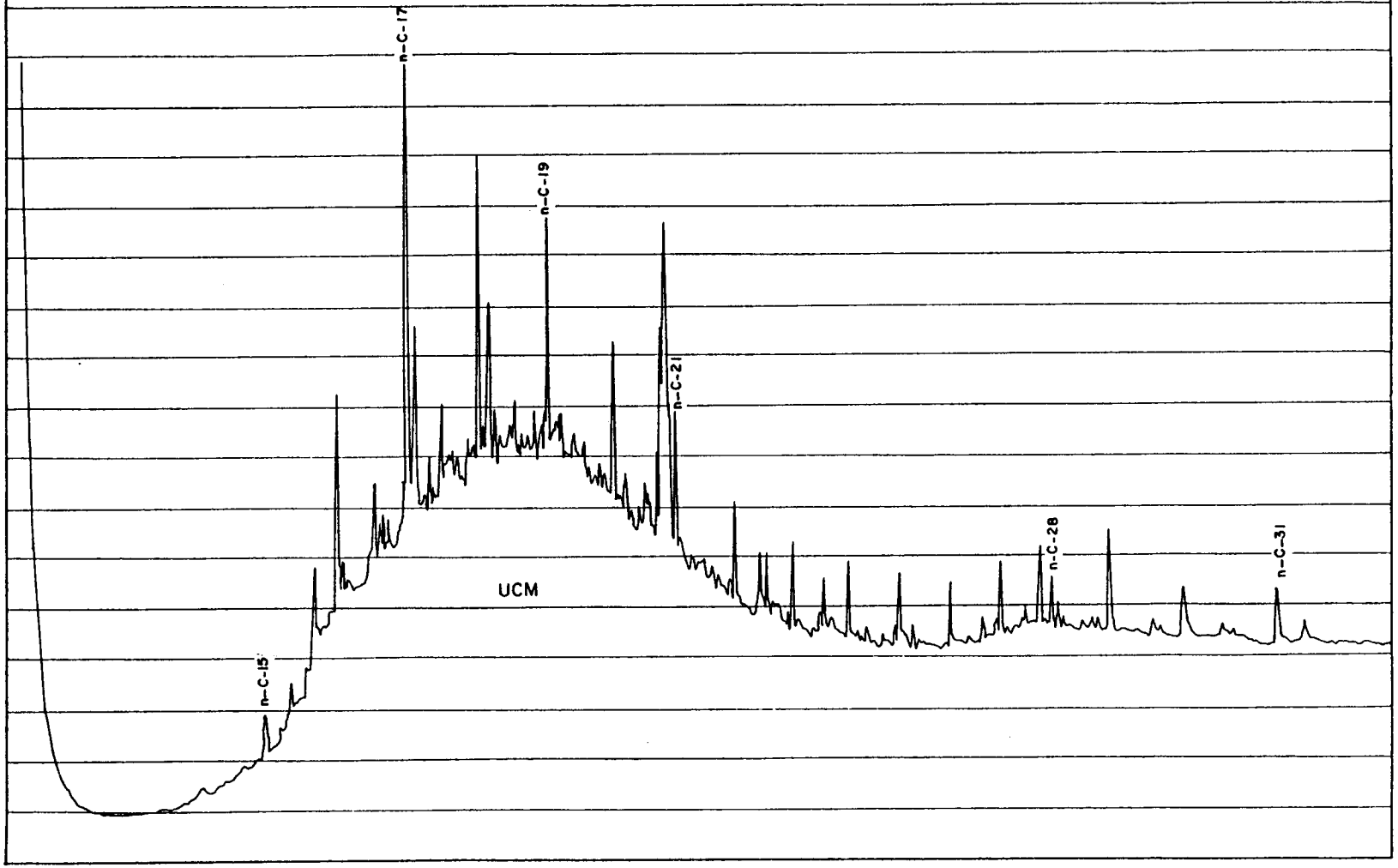
Inputs of hydrocarbons as defined by the above mentioned classification scheme, depend on both geographical location and the depth in a given region (Figure 190). Terrigenous biogenic components originate mainly in the west (i.e., Mississippi River area) and to a much smaller extent in the region around 2419, the Appalachicola River drainage area, also a main source of kaolinite clay. Marine biogenic and/or diagenetic compounds are the major chromatographic features in the west Florida lime muds and the carbonate sand sheet on the West Florida Shelf. Those sediments dominated by marine biogenic inputs are mainly confined to the mid-depth region (20-40 metres) west of Cape San Blas (see Figure 190).

The terrigenous compounds are often associated with a UCM having a boiling range also in the n-C-23 to n-C-31 range (max @ n-C-28). Introduction of a lower boiling UCM associated with n-C-14 to n-C-20 alkanes occurs sporadically at those stations indicated in Figure 191. The two anthropogenic assemblages, whose molecular weight ranges are defined by the bimodal UCM presumably have separate sources. However, both seen to originate in the west. Bimodal distributions of this sort have been noted by several researchers. Butler et al, (1973) showed that crude oil sludges from tanker washings exhibit this feature. Gearing et al., (1976) noted this feature in the previous MAFLA study. Thompson and Eglinton (1978b) observed this distribution in Severn Estuary sediments and attributed it to two anthropogenic inputs either from petroleum or from pyrolytic fuel combustion products. The earlier UCM with associated n-alkanes and a pristane/phytane ratio roughly equal to one has been observed in the water column (dissolved fraction) in the Gulf of Mexico Loop Current (Iliffe and Calder, 1973) as well as in other OCS regions (Boehm, 1978: North Atlantic; Barber et al., 1973: Eastern Atlantic).

Therefore, the presence of this assemblage in the water column and in the surface sediment indicates a water column-benthos coupling. As Figure 191 indicates, sediments west of Cape San Blas are impacted by this source most strikingly during the winter 1978 sampling period. High suspended loads during this season noted at Stations 2529 and 2639 may be responsible for the input of this petrogenic material to the sediment through:

FIGURE 189

REPRESENTATIVE CLASS L ALIPHATIC GAS CHROMATOGRAM
STATION 2426 WINTER 1978 (LUBT*)



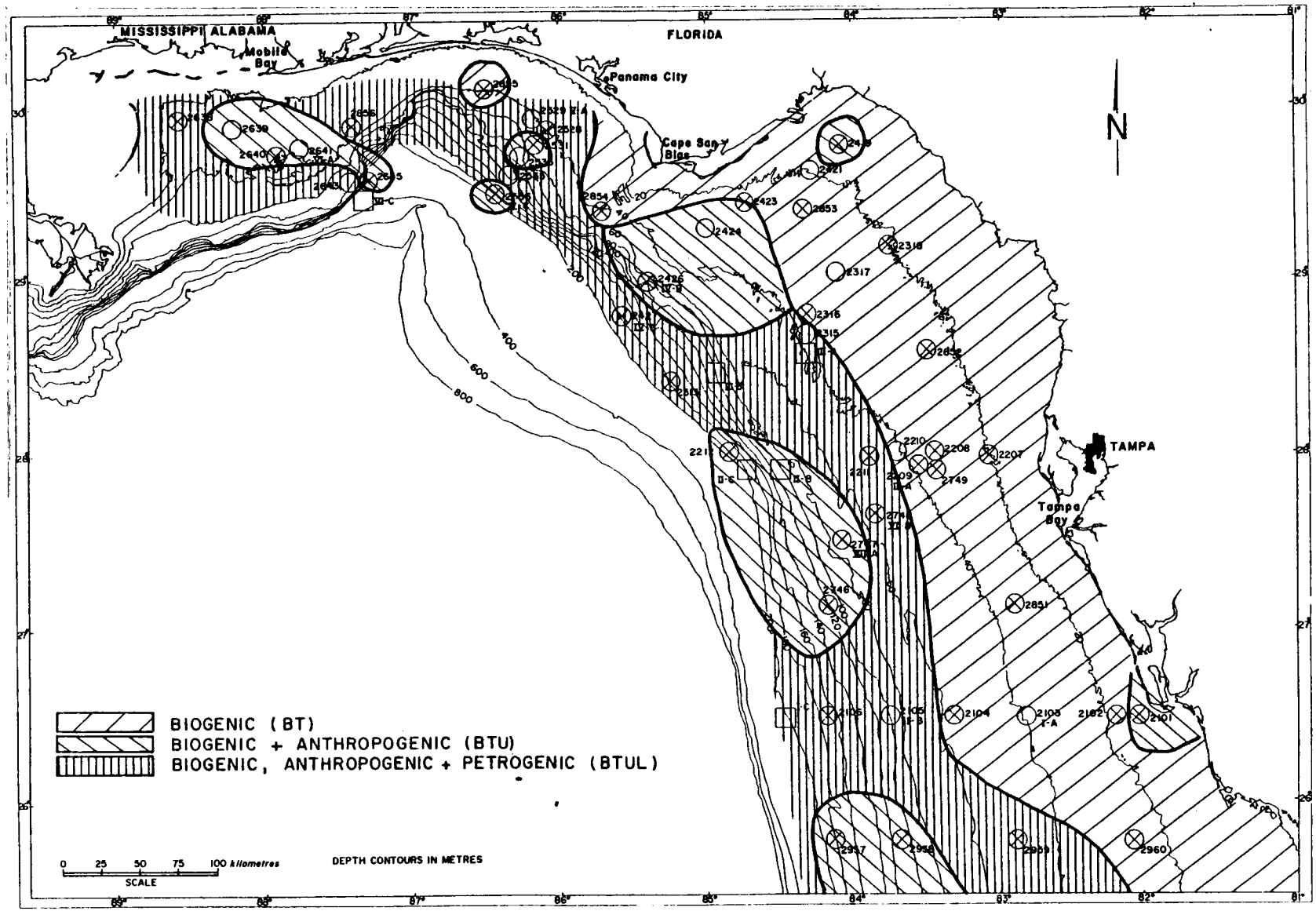


FIGURE 190

SOURCE DISTRIBUTION OF HYDROCARBONS IN MAFLA SURFACE SEDIMENTS

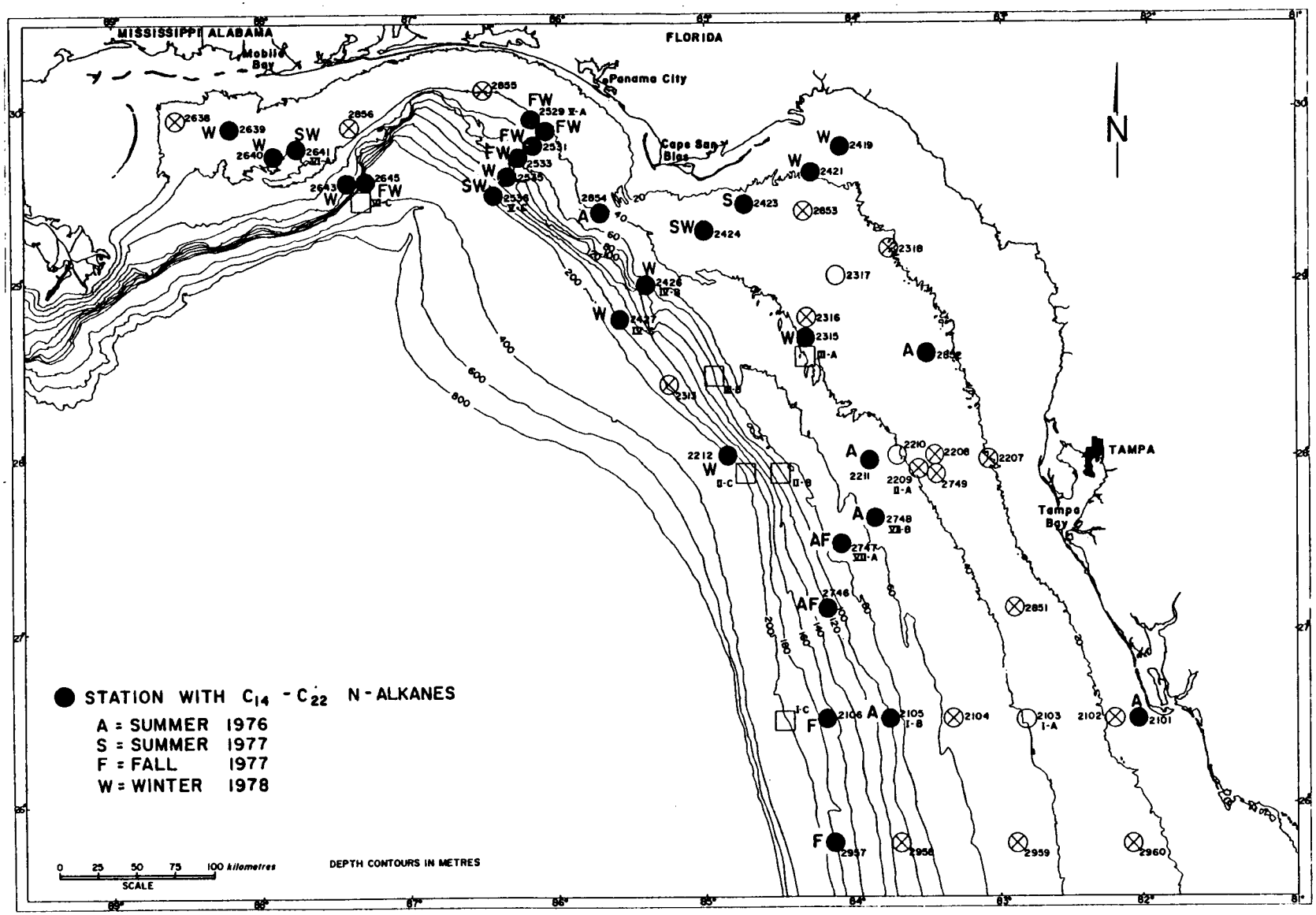


FIGURE 191

SEDIMENTS EXHIBITING LMW (C_{14} - C_{22}) n-ALKANE DISTRIBUTION WITH UCM

(1) Scavenging of the petrogenic material out of the water column,
(2) A direct input of polluted sediment from the Mississippi River drainage region.

It is concluded that the presence of this C-14 to C-22 resolved and unresolved assemblage in the sediment is related to Mississippi River/Loop Current suspended matter interaction.

CLASSIFICATION OF SOURCE MATERIAL BY TRANSECT

I - Transect I exhibits a direct correspondence of source material with increasing distance from shore, increasing TOC, and increasing percentage of fines. Stations 2102, 2103, and 2104 are dominated by marine and to a lesser extent terrigenous biogenic aliphatic compounds. At the steeper shelf break, Stations 2105 and 2106 exhibit a combination of terrigenous biogenics and a UCM associated with finer grained clays. Generally speaking, 2105 and 2106 are typical Florida Shelf stations having a water depth greater than 40 metres. Station 2101, closest to shore exhibits indications of anthropogenic inputs (i.e., UCM) during the summer 1976 and fall 1977 samplings, while exhibiting purely biogenic inputs in the summer of 1977. This may reflect a seasonal influence of input of sediment from the north (Tampa area).

II, III, VII - Stations along these three transects behave similarly with respect to source material. Stations at depths from roughly 20-40 metres are dominated by peak 2085 and to a smaller extent contain terrigenous biogenic n-alkanes. Other clear indications of marine biogenic sources are the presence of the isolated peaks, hepta decane (n-C-17) and pristane. The benzene (f_2) fraction of these sediments contains primarily olefinic hydrocarbons.

Samples taken from deeper waters show increased influence from terrigenous biogenic and anthropogenic sources of hydrocarbons originating in the west. Although marine biogenic inputs are still apparent, the hydrocarbon assemblage is dominated by a UCM, either unimodal or bimodal indicating one or two anthropogenic sources. Stations 2747, 2746, and 2212 exhibit bimodal UCM behavior during at least one of the sampling periods. The lower boiling UCM with a smooth distribution of n-alkanes and equivalent concentrations of pristane and phytane, on top of the UCM are taken to be of a relatively recent petrogenic origin. In addition GC/MS analysis of these stations reveals several triterpane compounds (hopanes) believed to originate in petroleum.

An examination of the benzene fraction (f_2) by GC/MS indicates the presence of aromatic hydrocarbons, phenanthrene, pyrene, and benzopyrene which probably are present in more abundant quantities than their alkylated hemologs indicating the dominance of a combustion source for the aromatics as opposed to a recent oil spillage.

IV - Transect IV appears to lie in a transitional zone with respect to all sediment geological and chemical characteristics. A water depth-hydrocarbon source criteria no longer holds. At different times during the

study one or all of these stations have yielded hydrocarbon patterns associated with petroleum inputs (Figures 187 and 191 and Table 63). The occurrence of abiogenic compounds at Station 2419 is probably related to its proximity to local inputs (as seen with 2101). However, the combined anthropogenic/biogenic nature of the aliphatic (f_1) chromatograms from Station 2424, 2426, 2427, and sporadically 2423 is most likely related to the anthropogenic source associated with the western end of the study area.

An examination of the temporal variability in the gas chromatographic character reveals that hydrocarbon sources can vary between primarily anthropogenic and biogenic during the study period at a given station (see Table 63). This may be due to the proximity of this transect, a boundary delineating two geochemical provinces influenced by (1) the Florida carbonates, in situ productivity and possibly Applachicola kaolinite, and (2) the Mississippi smectite clays associated with anthropogenc hydrocarbons.

V and VI - Clearly under the influence of the Mississippi silt/clay regime, stations along these transects are dominated by terrigenous and anthropogenic hydrocarbon inputs. The hexane (f_1) chromatograms are characterized by:

1. N-alkanes associated with terrestrial (vascular) plants
2. An unresolved complex mixture with a maximum detector response at n-C-28
3. The presence of triterpane compounds
4. The sporadic presence of a second UCM
5. The sporadic presence of n-C-16 to n-C-22 alkanes and equivalent concentrations of pristane and phytane
6. The presence of unsubstituted aromatic hydrocarbons.

The benzene (f_2) chromatograms are characterized by major amounts of olefinic hydrocarbons, a UCM, and lesser but significant amounts of aromatic hydrocarbons associated with a combustion source.

ASSOCIATION OF HYDROCARBONS WITH OTHER NON-HYDROCARBON PARAMETERS

Both the source of the hydrocarbon compounds and the quantity of the individual hydrocarbons as well as the UCM are closely allied to sedimentological parameters (i.e., silt/clay or smectite, $CaCO_3$ distributions) and to other chemical parameters (total organic carbon and selected trace metals). West of Cape San Blas, hydrocarbon distributions appear to be largely dominated by the smectite clays having their origin in the Mississippi River drainage system. Southeast of Cape San Blas onto the Florida Shelf, hydrocarbon source material and quantities appear to be largely dictated by TOC considerations. When smectite clay contours impinge on the shelf (e.g., at Station 2211, 2424, 2423) a terrigenous influence is imprinted on the hydrocarbon assemblage. Clayey material in turn influences TOC distributions markedly. Where Mississippi River clays are overwhelmed by $CaCO_3$ deposition, as occurs on much of the Florida Shelf (>90% $CaCO_3$) most of the TOC is presumably of recent marine origin and the hydrocarbons (n-C-17, 2085, etc.) reflect the dominance of marine versus terrigenous deposition.

In spite of the fact that the outer shelf sediments are also dominated by $CaCO_3$ (>85%) the small amounts of smectite clays in these sediments have a dramatic influence on the nature of the hydrocarbon chromatogram (Figure 181 vs. Figure 182).

TEMPORAL VARIATIONS

In spite of the minimal qualitative variations in surface sediment hydrocarbon chemistry, the noted exceptions being variations along Transect IV and the sporadic influence of the lower molecular weight resolved and unresolved assemblage associated with a petroleum source, significant quantitative variations occur throughout the study period.

Table 64 presents selected hydrocarbon parameters for three representative stations, averaged over the entire study period. Variations in gross parameters (i.e., total hexane and benzene) range from 5 to 100 fold. Single order of magnitude differences are common. Individual parameters (i.e., n-C-29 and n-C-17) varied usually by less than an order of magnitude and more commonly five fold. These differences clearly exceed the expected analytical variations presented on a comparative basis in Table 65 for triplicate analyses at two stations. Therefore, it may be concluded that both gross and individual parameters vary substantially with time. The minimum detectable difference indicating a pollutant input in any of these parameters will be on the order of a fraction of 10 to 100.

However, the ability to detect a change in hydrocarbon composition (i.e., qualitative GC patterns) associated with a petroleum input is much more sensitive than are the quantitative indications. For instance, even a small petrogenic input into many of the stations in Figure 183 designated BT, will be clearly noted as a radical difference associated with a change-over from a biogenic to an anthropogenic chromatogram will be noted. The usefulness of hydrocarbon chemistry as an indicator of petroleum input will be separately discussed.

QUANTITATIVE COMPARISONS WITH PREVIOUS MAFLA DATA

Data in Table 66 show comparisons of previously acquired MAFLA OCS hydrocarbon data with the present study. As can be seen, good agreement is seen in the gross hydrocarbon parameters between the two programs while data on individual component concentrations (e.g., n-C-29) often show wide discrepancies. This comparison might argue somewhat for the utility of the gross parameters (total hexane and benzene) in following the hydrocarbon character of the sediment over several years. However, as mentioned previously within the 1976-1978 program variations in individual components (e.g., n-C-29) are substantially smaller than those for the gross parameters. Methodology differences (packed vs. capillary columns) may account for discrepancies in n-C-29 data in Table 66.

OTHER QUANTITATIVE ASPECTS OF THE MAFLA DATA

In general gross quantitative aspects of the hydrocarbon data do not shed any light on whether sediments contain primarily biogenic or anthropogenic hydrocarbons. For instance, Figure 192 showing total aliphatic

TABLE 64

TEMPORAL VARIATIONS IN SELECTED HYDROCARBON PARAMETERS AT SELECTED STATIONS

Station 2101

Variable	Total Hexane	Total Benzene	2900	1700	2085	Pristane
Mean	1.12	0.71	0.018	0.022	0.116	0.023
Variance	1.27	0.31	<0.001	<0.001	<0.007	<0.001
Standard Deviation	1.13	0.56	0.014	0.024	0.085	0.019
Minimum	0.08	0.11	0.001	0.001	0.007	0.002
Maximum	3.70	1.87	0.040	0.08	0.28	0.054
Range	3.62	1.76	0.039	0.079	0.273	0.052

Station 2748

Mean	1.76	0.28	0.001	0.004	0.015	0.002
Variance	14.94	0.07	0.000	0.000	0.000	0.000
Standard Deviation	3.86	0.26	0.008	0.002	0.008	0.001
Minimum	0.08	0.08	0.005	0.001	0.004	0.001
Maximum	11.30	0.83	0.021	0.007	0.026	0.004
Range	11.21	0.75	0.016	0.006	0.022	0.003

Station 2638

Mean	2.89	0.97	0.24	0.01	0.044	0.011
Variance	4.03	0.45	0.02	0.00	0.002	0.000
Standard Deviation	2.00	0.67	0.13	0.006	0.099	0.005
Minimum	1.05	0.26	0.12	0.006	0.007	0.005
Maximum	6.90	2.03	0.53	0.021	0.120	0.018
Range	5.85	1.77	0.41	0.015	0.113	0.013

*all values in $\mu g.g^{-1}$

TABLE 65

ANALYTICAL PRECISION OF SEDIMENT HYDROCARBON MEASUREMENTS

Station 2212

Variable	Total Hexane	Total Benzene	2700	1700	2085	Pristane
Mean	0.91	0.055	0.037	0.003	0.020	0.002
Variance	0.20	0.001	0.000	0.000	0.000	0.000
Standard Deviation	0.55	0.04	0.018	0.002	0.006	<0.001
Minimum	0.28	0.01	0.017	0.002	0.013	0.001
Maximum	1.28	0.09	0.050	0.004	0.023	0.002
Range	1.00	0.08	0.033	0.003	0.010	0.001

Station 2103

Mean	0.46	0.056	0.007	0.004	0.031	0.006
Variance	0.009	0.001	0.000	0.000	0.000	0.000
Standard Deviation	0.11	0.046	0.003	0.005	0.016	0.004
Minimum	0.35	0.025	0.004	0.003	0.013	0.010
Maximum	0.58	0.11	0.009	0.001	0.046	0.002
Range	0.23	0.090	0.005	0.002	0.033	0.008

*all values in $\mu g.g^{-1}$

TABLE 66

COMPARISON OF D&M MAFLA DATA WITH SUSIO DATA
(REPRESENTATIVE PARAMETERS)

Station Number		Total Hexane	Total Benzene	2900
2101	A	1.75	1.58	0.0000
	B	1.12 ± 1.12	0.71 ± 0.56	0.018 ± 0.014
2102	A	0.91	1.06	0.0003
	B	0.89 ± 0.68	0.39 ± 0.25	0.01 ± 0.007
2103	A	0.97	1.08	0.0003
	B	0.97 ± 1.3	5.25 ± 12.4	0.008 ± 0.002
2105	A	0.29	0.39	0.0000
	B	0.40 ± 0.25	0.53 ± 0.98	0.015 ± 0.009
2207	A	1.39	1.13	0.0050
	B	0.50 ± 0.34	0.39 ± 0.38	0.012 ± 0.011
2209	A	1.14	1.89	0.0051
	B	1.65 ± 2.08	1.32 ± 1.93	0.026 ± 0.025
2211	A	0.79	1.04	0.0011
	B	0.58 ± 0.35	0.51 ± 0.22	0.013 ± 0.007
2212	A	1.23	1.07	0.001
	B	1.36 ± 1.22	0.47 ± 0.31	0.044 ± 0.029
2419	A	0.60	0.55	0.0035
	B	0.43 ± 0.29	0.26 ± 0.23	0.009 ± 0.002
2421	A	1.00	1.08	0.0001
	B	0.49 ± 0.37	0.34 ± 0.24	0.011 ± 0.009
2426	A	0.53	0.72	0.000
	B	0.45 ± 0.31	0.79 ± 1.68	0.017 ± 0.024

*all values in $\mu g.g^{-1}$

TABLE 66 (CONTINUED)

COMPARISON OF D&M MAFLA DATA WITH SUSIO DATA
(REPRESENTATIVE PARAMETERS)

Station Number		Total Hexane	Total Benzene	2900
2427	A	1.55	1.94	0.076
	B	1.89 ± 2.38	1.35 ± 2.59	0.052 ± 0.44
2638	A	2.82	5.35	0.0820
	B	2.89 ± 2.00	0.97 ± 0.67	0.24 ± 0.13
2645	A	2.63	2.43	0.0166
	B	1.24 ± 1.32	0.59 ± 0.54	0.047 ± 0.04

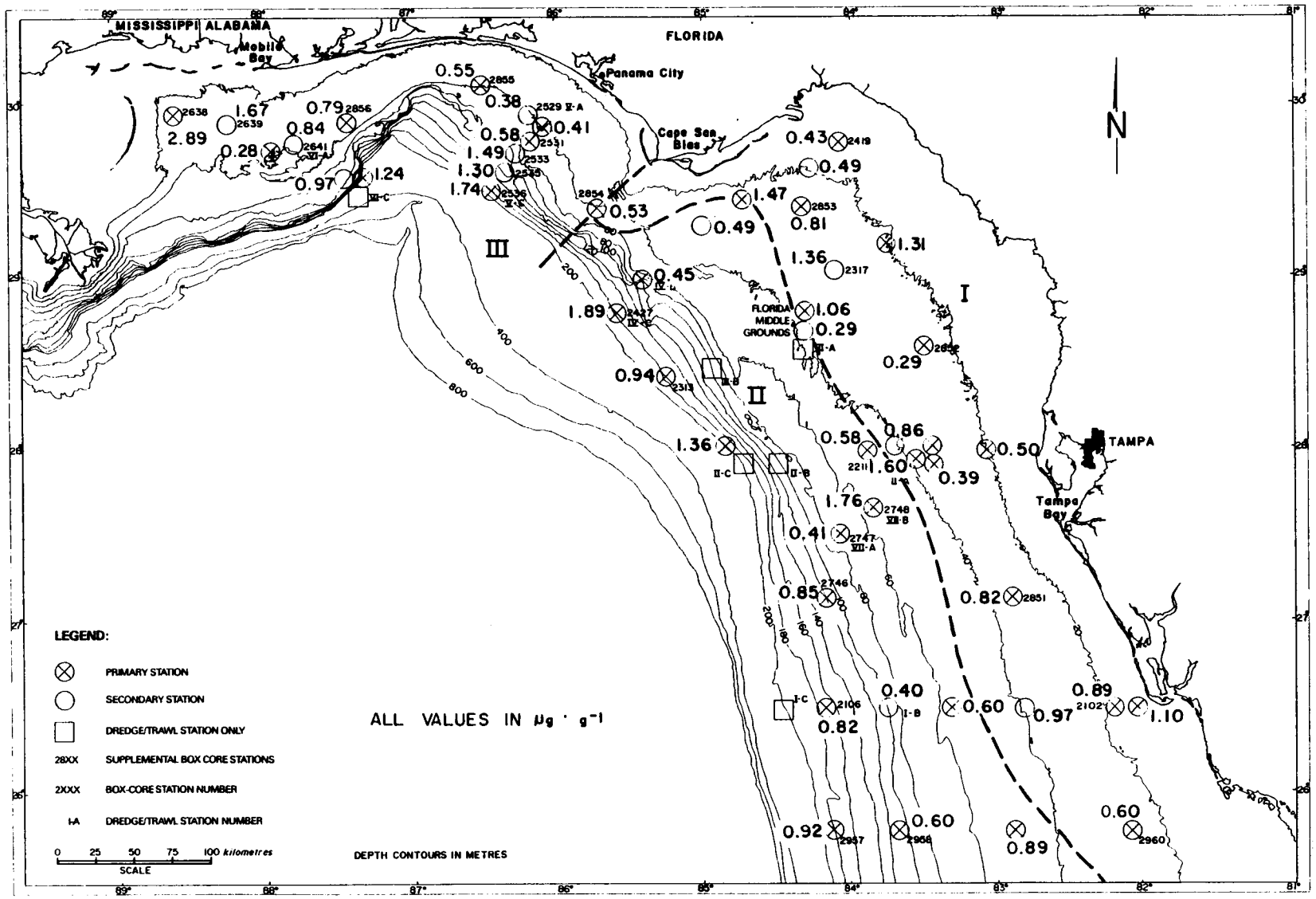


FIGURE 192

GRAND STATION MEANS - TOTAL HEXANE (ALIPHATIC) HYDROCARBONS WITH THREE BIOGEOCHEMICAL PROVINCES DELINEATED

hydrocarbons, is not useful when viewing the region in its entirety. However, it may be useful if the area is crudely subdivided into the regions defined in Figure 191. Regions I, II, and III are each roughly governed by the same sources and when the station means Figure 192 and Table 62 are viewed in the context of their temporal variability (e.g., Table 64) then concentrations within each region can be compared and post-development changes in these quantities can be evaluated statistically.

DISCUSSION OF HYDROCARBON PARAMETERS IN RELATION TO OTHER NON-CARBON PARAMETERS

Statistical analysis of selected gross and individual hydrocarbon and other biogeochemical parameters was performed using a cluster analysis based on the Bray-Curtis similarity index. Analyses were performed on individual geochemical regions (I, II, III) defined earlier.

Region I - The similarity matrix presented in Figure 193 indicates that the resolved hexane (R_H) fraction is related ($r^2 > 0.7$) to the distributions of n-C-29 (2900), and the cycloalkene 2085. The hypothesis that TOC in this region is largely biogenic is corroborated by the covariance of 2085 and somewhat 2900 with TOC. The association of n-C-17 with the benzene fraction may indicate that the aromatic/olefinic fraction is largely biogenic in Region I and that it is related to phytoplanktonic inputs rather than terrigenous sources. A similarity of particle size and hydrocarbon distributions is indicated with the silt size particles related to 2900 distributions. This trend is probably due to silt sized $CaCO_3$ fragments as $CaCO_3$ is most closely similar ($r^2 = 0.72$) to the silt size fraction in Region I.

Probably the most useful geochemical equation, defining a "normal" environment in Region I would be of the following types:

a. hydrocarbon parameters only
$R_H = C_1\ (2900) + C_2\ (2085) + C_3$

b. other parameters
$\%\ TOC = C_4\ (R_H) + C_5$
where R_H = resolved hexane; $C_1 - C_5$ are constants.

Deviations from a norm caused by a pollutant stress can be noted in changes in C_3 and C_55.

Region II - The similarity matrix of Region II, Figure 194, a transition region, shows that the strong association of 2900 and 2085 disappears. Now 2900 is related to both R_H and unresolved hexane (U_H) distributions in turn have become strongly similar to the distribution of TOC and fine grain size parameters as well as to the trace metals Cu, Pb, and Zn, and less strongly to Cd, Cr, Ni, V. The U_H originates in anthropogenic sources to the west (Mississippi) as presumably do the non-crustal trace metals. The link of hydrocarbons and trace metals is almost certain to be the smectite clays. The relationship of pristane to n-C-17 (1700) is interesting. No such similarity existed in Region I. They may convey in Region II (and very strongly in Region III) through their associationin the lower molecular

	TOC	MED SAND	FINE SAND	VERY FINE SAND	FINES (SILT & CLAY)	SILT	CLAY	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn	2900	1700	PRISTANE	2085	RES. HEXANE	UCM HEXANE	RES. BENZENE	UCM BENZENE	Ba	$CaCO_3$
2900	.67		.66	.71	.69	.74	.71			.65				.72					.73	(.81)	.69			.66	.65
1700																						(.72)	(.72)		
PRISTANE			.71																						
2085	(.74)				.76	.72	.60													(.76)					
RES. HEXANE	.66				.68	.73	.61							.62							.64				
UCM HEXANE		.72					.62		.66	.62	.65	.65	.65		.68										
RES. BENZENE																							.79		
UCM BENZENE																									

FIGURE 193

SIMILARITY MATRIX OF SELECTED HYDROCARBONS VS POTENTIAL DEPENDENT VARIABLES
REGION I

	TOC	MED SAND	FINE SAND	VERY FINE SAND	FINES (SILT & CLAY)	SILT	CLAY	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn	2900	1700	PRISTANE	2085	RES. HEXANE	UCM HEXANE	RES. BENZENE	UCM BENZENE	Ba	$CaCO_3$
2900	.72		.60	.68	.72	.69	.77		.64	.71		.66	.72		.80					.72	.75		.63		
1700			.69					.60	.62									.73						.71	.67
PRISTANE			.65																.64	.61					
2085																				.65					
RES. HEXANE			.62										.64		.60										
UCM HEXANE	.74			.67	.75	.72	.74	.63	.66	.73	.61	.68	.76	.64	.81								.64		
RES. BENZENE																									
UCM BENZENE	.69		.67	.64	.61		.69	.74	.71	.72		.70	.68		.69									.66	.62

FIGURE 194

SIMILARITY MATRIX OF SELECTED HYDROCARBONS VS POTENTIAL DEPENDENT VARIABLES
REGION II

weight petrogenic input (see Figure 189) which is prevalent in Regions II and III (Figure 190) and not in I. Resolved benzene (R_B) is not similar to any parameter considered in Figure 194 which may be ascribed to the increasing aliphatic anthropogenic sources in Region II despite a persistent biogenic source for the resolved benzene (olefinic) fraction.

Suitable geochemical equations defining Region II might be:

$$TOC = C_1\ (2900) + C_2\ (Pristane) + C_3$$

This equation was computed by a multiple linear regression analysis of hydrocarbon parameters on TOC. The following equation explains 92.5% of the variation in TOC in Region II:

$$TOC = 7.07\ (2900) - 14.54\ (Pristane) + 0.149$$

Measurement of n-C-29 and pristane concentrations can yield a TOC value which when compared to an independent TOC measurement can be used to evaluate the geochemical health of the region.

Region III - As Figure 195 shows, many of the hydrocarbon and non-hydrocarbon parameters in this region are related, by virtue of their proximity to the geochemical source for the entire region, the Mississippi River. The n-C-17 is even more strongly related to pristane indicating a covariance probably through a petrogenic input. Pb, V, Zn, and Cu are strongly similar to the hydrocarbon parameters by virtue of a common source. Peak 2085 is again related to other variables. A terrigenous source of 2085 (direct biogenic or diagenetic) is strongly suggested. Indeed the distributions of 2085 in all regions along transects perpendicular to the shore, show a decreasing concentration offshore. That is why 2085 does not figure strongly into the geochemical picture in Region II.

For the first time the distribution of R_B material is similar to other hydrocarbon parameters implying a major anthropogenic (mostly pyrogenic aromatics according to the few GC/MS analyses available) source for R_B in Region III.

In this region, multivariate regressions of TOC on hydrocarbon parameters indicate that TOC is very nicely (> 81%) predicted by a single compound, 2085. This is strikingly similar to the near-shore geochemical relationship noted by Boehm and Quinn (1978), at the mouth of the Narragansett Bay estuary when TOC and the same compound were strongly correlated and defined a geochemical province in which pollutant perturbations were easily noted by large inputs of TOC relative to 2085. Such a similar equation may be used in the Mississippi-Mobile Shelf region:

$$\%\ TOC = C_1\ (2085) + C_2$$

where $C_1 = 15.73$ and $C_2 = -0.134$.

	TOC	MED SAND	FINE SAND	VERY FINE SAND	FINES (SILT & CLAY)	SILT	CLAY	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn	2900	1700	PRISTANE	2085	RES. HEXANE	UCM HEXANE	RES. BENZENE	UCM BENZENE	Ba	$CaCO_3$
2900	.67			.62	.73	.66	.76			.81			.63	.60	.71			.66		.83		.74			
1700				.68							.64		.65	.65	.65			.85	.69	.64					
PRISTANE				.66			.66			.71	.67		.76	.74	.75				.74	.77	.65	.69			
2085	.74			.67	.72	.72	.69			.67	.62	.70	.70	.68	.67					.70			.62	.65	
RES. HEXANE	.72			.71	.72	.69	.76			.86	.62		.77	.73	.82						.66	.78			
UCM HEXANE							.64	.63	.65	.66	.68	.66	.76	.74	.75							.60	.75	.65	
RES. BENZENE				.67	.62		.66			.70			.67	.61	.68										
UCM BENZENE	.67					.63	.62			.61	.70	.71	.75	.72	.71									.62	

FIGURE 195

SIMILARITY MATRIX OF SELECTED HYDROCARBONS VS POTENTIAL DEPENDENT VARIABLES
REGION III

HYDROCARBON CHEMISTRY AS A MONITORING TOOL

Both qualitative and quantitative aspects of the MAFLA hydrocarbon data can be used to note changes due to pollutant inputs in the sediments. This can be accomplished through:

1. Qualitative aspects of the data through an evaluation of the sources of hydrocarbons through gas chromatographic evidence, by using a map such as Figure 190 and an approach to evaluating sources such as outlined previously.

2. Quantitative aspects of the data through a consideration of the expected concentration ranges of gross and individual hydrocarbon parameters, while appreciating the above discussed limitations on the use of gross parameters.

3. An evaluation of the quantities of alkyl substituted aromatics vs parent compounds as indicative of petrogenic vs pyrogenic sources.

4. Use of a set of geochemical equations which have been shown to generally predict TOC and hydrocarbon values in a given region. The TOC:hydrocarbon ratios in OCS sediments are grossly different from TOC:hydrocarbon ratios in oils. Therefore, these ratios may be sensitive indications of the biogeochemical health of the benthic environment.

Items 1 and 2 have been well defined by the MAFLA OCS programs. Item 3 needs more work in order to become a useful monitoring tool. This information exists in samples and in some cases on GC/MS tapes and needs to be fully evaluated. Item 4 is of potentially the most use and again this information is available in the MAFLA data base.

REFERENCES

Barbier, M., Joly D., Saliot A., Tourres D., 1973. Hydrocarbons from Seawater, Deep Sea Research, 20,305-314.

Bieri, R.H., Cueman, M.K., Smith C.L. and Su C-W, 1978. Polynuclear aromatic and polycyclic aliphatic hydrocarbons in sediments from the outer continental shelf, International Journal of environmental Analytical Chemistry (in press).

Blumer, M., Mullen, M.M. and Thomas, D.W., 1964. Pristane in the marine environment. Helglaenden Wiss. Meeresuntersuch 10, 187.

Boehm, P.D., 1978. The hydrocarbon chemistry of the North Atlantic OCS marine environment, in draft final report to the Bureau of Land Management. New England OCS Benchmark Program.

Boehm, P.D., and Farringon, J.W. (in preparation). Aromatic hydrocarbons from surface sediments of Georges Bank and Nantucket Shoals.

Boehm, P.D. and Quinn, J.G., 1978. Benthic hydrocarbons of Rhode Island Sound. Estuarine and Coastal Marine Science 6, 471-494.

Butler, J.N., Morris, B.F. and Sass, J., 1973. Pelagro Tar from Bermuda and the Sargasso Sea, Bermuda Biological Station Special Publication No. 10, Bermuda.

Farrington, J.W. and Tripp, B.W., 1975. A Comparison of Analysis Methods for Hydrocarbons on Surface Sediments, ACS Symposium Series No. 18. Marine Chemistry in the Coastal Environment, 267-284.

Farrington, J.W. and Tripp, B.W., 1977. Hydrocarbons in Western North Altantic Surface Sediments. Geochimica et Cosmochimica Acta 41, 1627-1641.

Gearing, P., Gearing J.N., Lytle, T.F., and Lytle, J.S., 1976. Hydrocarbons in 60 Northwest Gulf of Mexico Shelf Sediments: a preliminary survey. Geochimica et Cosmochemica Acta 40, 1005-1017.

Iliffe, Tim and Calder, J.A., 1974. Dissolved hydrocarbons on the eastern Gulf of Mexico Loop Current and Caribbean Sea. Deep Sea Research 21, 481-488.

Keizer, P.D., Dale, J., Garden, D.C., 1978. Hydrocarbons in surficial sediments from the Scotian Shelf. Geochimica et Cosmochimica Acta, 42, 105-172.

Laflemme, R.E. and Hites, R.A., 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochimica et Cosmochimica Acta, 42, 289-303.

Lee, M.L., Prado, G.P., Howard, J.B. and Hites, R.A., 1977. Source identification of urban airborne polycyclic aromatic hydrocarbons by GC/MS & HRMS, Biomedical Mass Spectrometry 4, 182-186.

Thompson, S. and Eglinton, G., 1975a. The fractionation of a recent sediment for organic geochemical analysis. Geochimica et Cosochimica Acta 42, 199-207.

Thompson, S. and Eglinton, G., 1978b. Composition and Sources of Pollutant Hydrocarbons in Severn Estuary. Marine Pollution Bulletin 9, 133-136.

Youngblood, W.W. and Blumer, M., 1975. Polycyclic aromatic hydrocarbons in the environment. Homologous series in soils & recent marine sediments Geochimica et Cosochimica Acta 39, 1301-1314.

VOLUME II

CHAPTER 11

SEDIMENT ATP

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ATP DETERMNATIONS IN THE MAFLA TRACT, 1977-1978

FINAL REPORT
TO
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TABLE OF CONTENTS

ABSTRACT

Three seasonal patterns of variation in sediment ATP levels have been found in the MAFLA area. These correspond to three distinct geographic areas, and relate to hydrographic and sediment calcium carbonate data for these areas. No correlations between ATP concentration and grain size or total organic carbon data could be found. The potential impact of oil drilling on the sediment microbial biomass is discussed.

INTRODUCTION

When Holm-Hansen and Booth (1966) first employed the bioluminescent techniques of Strehler (1957) for the determination of adenosine triphosphate (ATP) to oceanic water samples, a new and simple technique for microbial biomass estimations came into existence. Estimates of viable bacteria were 50 to 20,000 times those estimated by plate count techniques, but in the same order of magnitude as those made via direct count (Holm-Hansen and Booth, 1966). Of the latter two methods, the plate count was discredited since only organisms which grow on the media furnished would be counted, thus underestimating bacterial abundance, while direct count was too tedious and prone to investigator bias for routine use.

Upon examination of a variety of bacteria (Hamilton and Holm-Hansen, 1967), algae, and zooplankton (Holm-Hansen, 1973), the laboratory of Holm-Hansen proposed an empirical relationship that united the protista, plant, and animal kingdoms:

$$\text{ATP} \times 250 = \text{Living Organic Carbon}$$

Direct counts of such organisms in the field, when compared with ATP determinations (Holm-Hansen, 1969), corroborated the empirical relationship of Holm-Hansen between living organic carbon and ATP.

ASSUMPTIONS OF THE ASSAY

Certain assumptions are made in the estimation of living microbial biomass from ATP measurements:

1. ATP is ubiquitous to living material; it must not be found in dead cells or adsorbed onto detrital material.
2. The ATP to organic carbon ratio is constant.
3. Cellular ATP levels must not change with the environmental state or nutrient conditions of the cells.
4. The extraction procedure is efficient.
5. No significant changes in the ATP levels occur from the time of sampling to analysis.

Although No. 1 has not been refuted, Nos. 2 to 5 may depend on the method employed, and the nature or state of the material to be analyzed.

The ratio of carbon to ATP has been found to vary with culture phase for *Enterobacter aerogenes* from 110:1 to 42:1, and from 221:1 to 87:1 for another marine bacterium (Bancroft et al., 1976). ATP in *E. coli* K-12 has been shown to be either over-produced, under-produced, or in cyclic oscillation with respect to growth, depending on culture conditions (Cole et al., 1967).

The ratio of carbon to ATP in bivalve molluscs varies from 31.7 to 151.5, depending on species and tissue sampled. D.H. Karl (ASTM Meeting, Ft. Lauderdale, February 1978) claims that the 250:1 C:ATP ratio obtained by Holm-Hansen for a variety of organisms is an artifact of the hot Tris extraction employed, and that the true C:ATP ratio is far from constant. Finally, the volume of water filtered can affect ATP values, larger volumes underestimating true values by 10 to 50% (Sutcliffe et al., 1976). As can be seen, the measurements of ATP and the interpretation of ATP data is fraught with uncertainties.

CORRELATION OF ATP WITH OTHER WATER COLUMN PARAMETERS

Using ^{14}C-bicarbonate labelling of phytoplankton followed by autoradiography, Paerl and Williams (1976) found good correlation between the living carbon of phytoplankton and ATP levels in a variety of freshwater lakes, with variations no greater than +17% of the mean C:ATP ratio. Chlorophyll *a* and ATP seem to correlate well in the euphotic zone (Holm-Hansen, 1969; Paerl et al., 1976). The relationship between ATP and organic carbon is somewhat more complex. In vertical ocean profiles, large peaks in dissolved organic carbon (DOC) often coincide with large peaks in ATP (Karl et al., 1976). Particulate organic carbon (POC) peaks have also been shown to coincide with ATP and chlorophyll *a* peaks (Holm-Hansen, 1973). However, two profiles off the coast of California, one near a sewage outfall and the other outside the sewage plume, had similar DOC values, but large disparities in ATP values (Eppley et al., 1972).

In summary, ATP can give a relative indication of living biomass, which can often be correlated to other oceanographic parameters. However, conversion of ATP values to living organic carbon or bacterial cell numbers should be treated with reservation.

SEDIMENT ATP DETERMINATIONS

The measurements of ATP in the sediment has three additionl sources of error not encountered in water column determinations:

1. All the ATP may not be extracted. The efficiency of heat transfer drops markedly around sediment particles in boiling solvent extraction procedures (Karl, 1975). Once released from the cells, soluble ATP readily adsorbs to sediment particles (especially fines).

2. Sediment extraction procedures, often more severe than water column procedures, may degrade some of the ATP in the process.

3. The extraction procedure may release ions from the sediment which may interfere with the luciferase reaction, causing 'quenching' of the ATP-dependent, light-producing reaction (Karl, 1975).

The problem of releasing ATP from organisms intimately bound to a solid substrate into an assayable fluid is a major stumbling block in sediment ATP determinations, and several procedures have been developed over

the years. No extraction procedure is adequate for all sediment types. Boiling Tris buffer (Ernst, 1970), boiling bicarbonate solution buffered with Tris (Bancroft et al., 1976), cold sulfuric acid (Karl and La Rock, 1975), and cold sulfuric acid followed by charcoal column treatment (Hodson et al., 1976) have been employed. The heat extraction procedures suffer from the first problem mentioned above, while acid extraction is plagued by the third problem. The charcoal column method (Hodson et al., 1976) can overcome ionic interference, but quantitative recovery of ATP from the column and hydrolysis of ATP on the charcoal surface are additional problems with this method.

RESULTS OF OTHER SEDIMENT ATP DETERMINATIONS

Ernst (1970), one of the first to measure sediment ATP value, extracted sediment samples with boiling Tris buffer. Using 50 as a factor to convert ATP to living carbon, he found that living carbon was 0.13 to 1.6% of the total organic carbon (TOC) in the sediment.

Karl et al. (1976) measured ATP in sediments of the abyssal plain in the North Atlantic and found 2.5 ng ATP g^{-1} wet sediment, nearly three orders of magnitude greater than that in the overlying waters. This ATP maximum corresponded to a DOC peak in the sediment.

Sediment ATP values off the northwest coast of Africa ranged from 200-700 ng ATP $m\ell^{-1}$ wet sediment (Hodson et al., 1976).

Cadée and Hegeman (1977) measured ATP, primary productivity, TOC, and chlorophyll *a* over the seasons on a tidal flat in the Dutch Wadden Sea. They found a seasonal variation in ATP, with highest values in the early summer (June and July). For two out of five transects, the summer ATP peak correlatd with a TOC peak; for the other three, ATP peaks were not accompanied by peaks in TOC. When ATP values were converted to living organic carbon, these accounted for between 5.6 and 40% of the TOC.

La Rock (1976), in his final report on the ATP levels in the Gulf of Mexico, also found seasonal variations in ATP, with peak values in the fall. He found positive correlations between mean grain size and ATP levels for Transects I, II, III, and IV, but not for Transects V and VI. For the summer cruise data, an inverse relationship with organic carbon was proposed. Since the coefficient of determination is somewhat low (r^2 = 0.56), this may not have been a significant correlation. La Rock also found that the ATP values from Transects V and VI had little in common with the rest of the MAFLA stations.

In this report, we discuss the results of ATP analyses of sediment samples taken in the summer, fall, and winter of 1977-1978 in the MAFLA area. We have also included some interpretation of our findings and some speculation on the effect of the proposed drilling on the sediment microbial biomass in this area.

PROCEDURE

Detailed methods are described in the Procedure section of the third quarterly report to Dames & Moore (Dames & Moore, 1978e).

RESULTS

The ATP data for the benthic cruises DM-I, DM-II, and DM-VI appear in Figures 196, 197, and 198. Since Transect VIII was sampled only in DM-I, the ATP data from this transect appears separately in Figure 198. Figures 196 and 197 have been divided into four parts, each representing a transect. Each station illustrates three values, labelled A, B, and C, reprsenting DM-I, DM-II, and DM-IV, respectively. It should be noted that the values plotted are in ng $m\ell^{-1}$ sediment (and not ng g^{-1} sediment) to facilitate comparison between stations. Each sample was taken by a coring device with an opening of approximately 1 cm^2 in area and to a depth of 2 cm into the sediment (for detailed description, see third quarterly report). Thus, each ATP value corresponds to that of an identical volume of sediment (2 $m\ell$), which in turn corresponds to a fixed area of sea floor.

ATP values divided by wet weight have been calculated and have been employed when comparisons to other weight-normalized data were necessary. However, wet weights vary with the water content of the sediment, which may cloud ATP comparisons between fine and coarse sediment types.

The ATP values ranged from a maximum of 3,770 ng $m\ell^{-1}$ sediment (Station 2533, DM-II) to 23.6 ng $m\ell^{-1}$ (Station 2426, DM-I). Although no obvious patterns occurred in the data when a transect was viewed in isolation, a seasonal pattern appeared when the three cruises were viewed simultaneously (Figures 196 and 197). Transects V and VI (Figures 196(1) and 196(2)) had the highest ATP values in the fall (DM-II), with lower values in the summer and winter. This pattern could be observed at Stations 2427, 2424, 2423, and 2419 of Transect IV, and 2316 of Transect III (Figures 196(3) and 196(4)). However, the magnitude of the seasonal changes observed in Transects III and IV were significantly less ($\Delta\ ATP_{\bar{x}}$ = 506 ng $m\ell^{-1}$) compared to the average change observed in Transects V and VI ($\Delta\ ATP_{\bar{x}}$ = 998 ng $m\ell^{-1}$) sediment).

Most of Transects VII and IX and the Gulf-side stations of II and I (Figure 197(1-4)) showed the opposite of this pattern, with lowest values occurring in the fall, with higher values in summer and winter. A third seasonal pattern, characterized by ATP values increasing from summer through fall to a peak in the winter occurred in Stations 2317, 2318, 2207, 2209, 2101, and 2103. These stations are all located in the eastern portion of the MAFLA area, in 40 m or less of water. The geographic location of the stations possessing each particular seasonal pattern appears in Figure 199.

The stations that have the lowest ATP values in the fall (designated Type 3 seasonal variation in Figure 199) also seemed to have the highest calcium carbonate content (generally >95%). The exceptions to this are Stations 2210 (89%) and 2102 (23%). (Note: summer ATP value may not be accurate; see large standard deviation.)

The stations displaying the Type 2 seasonal variation (see Figure 199) had intermediate levels of calcium carbonate (50-90%). Finally, the northern stations, possessing peak ATP values in the fall, ranged from 6-90% $CaCO_3$.

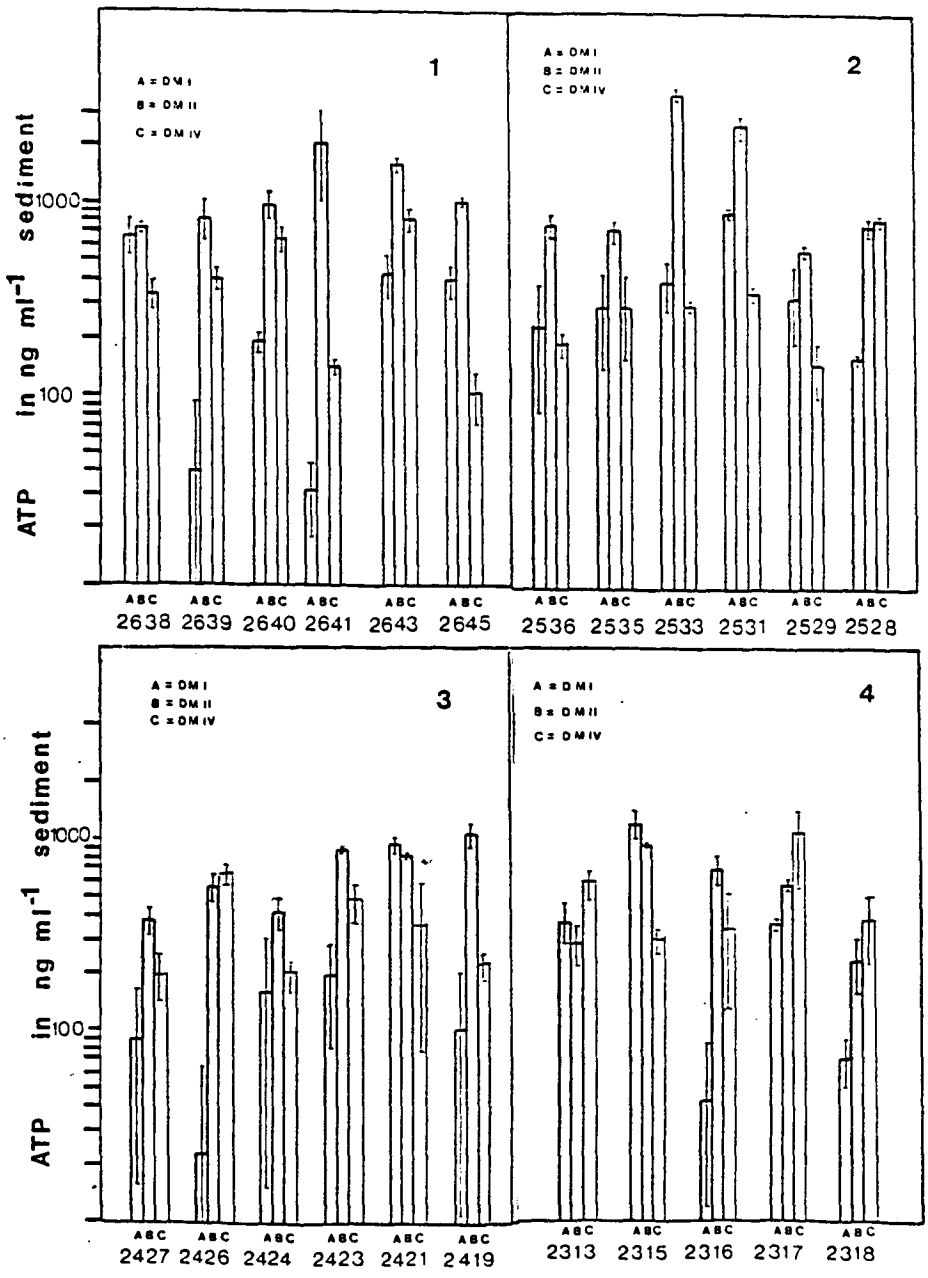

Figure 196 ATP content of the northern transects in the MAFLA area. Transects VI, V, IV, and III appear in (1), (2), (3), and (4) respectively.

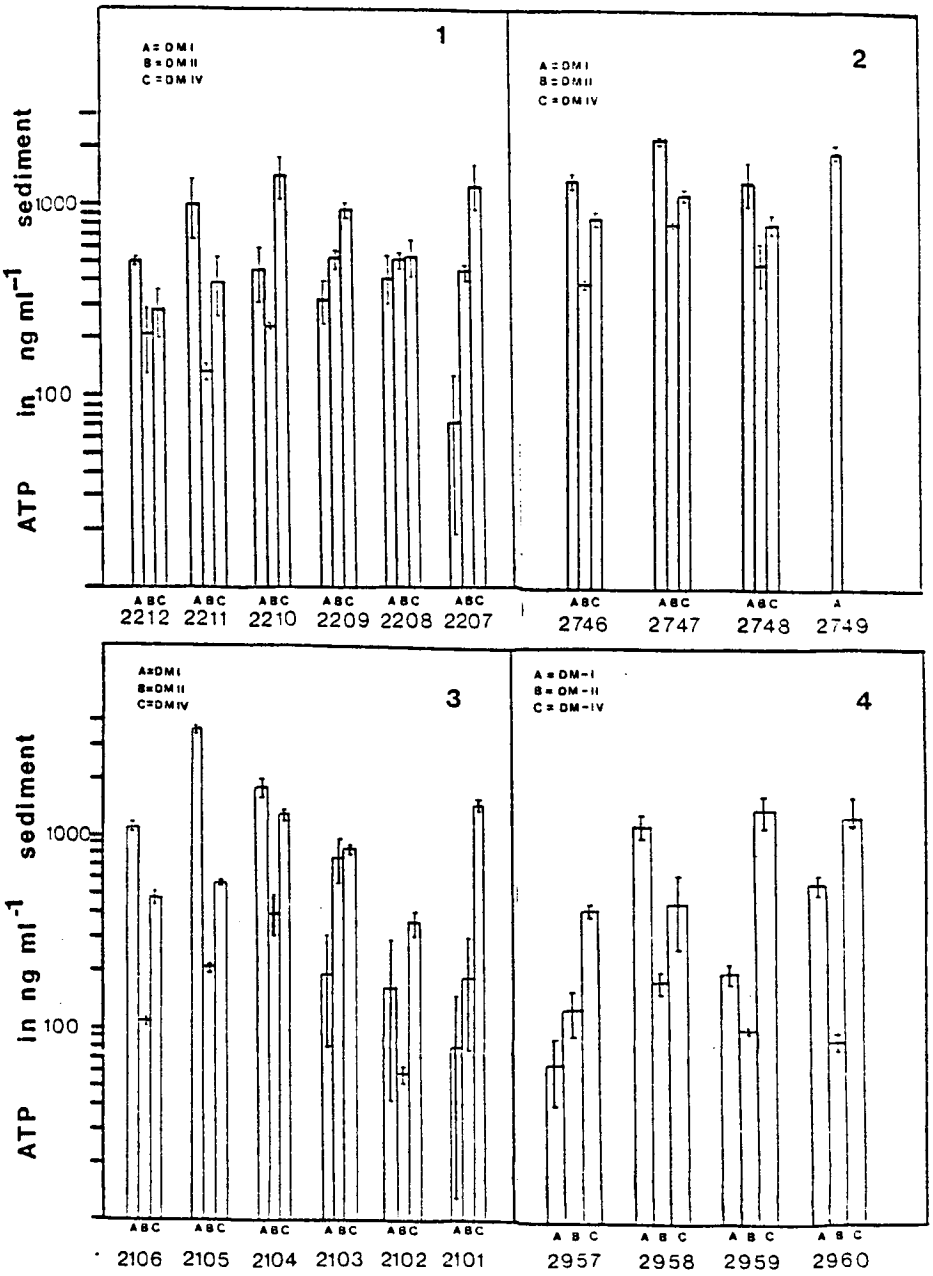

Figure 197 ATP content of the southern sections of the MAFLA tract. Transects II, VII, I, and IX appear in (1), (2), (3), and (4).

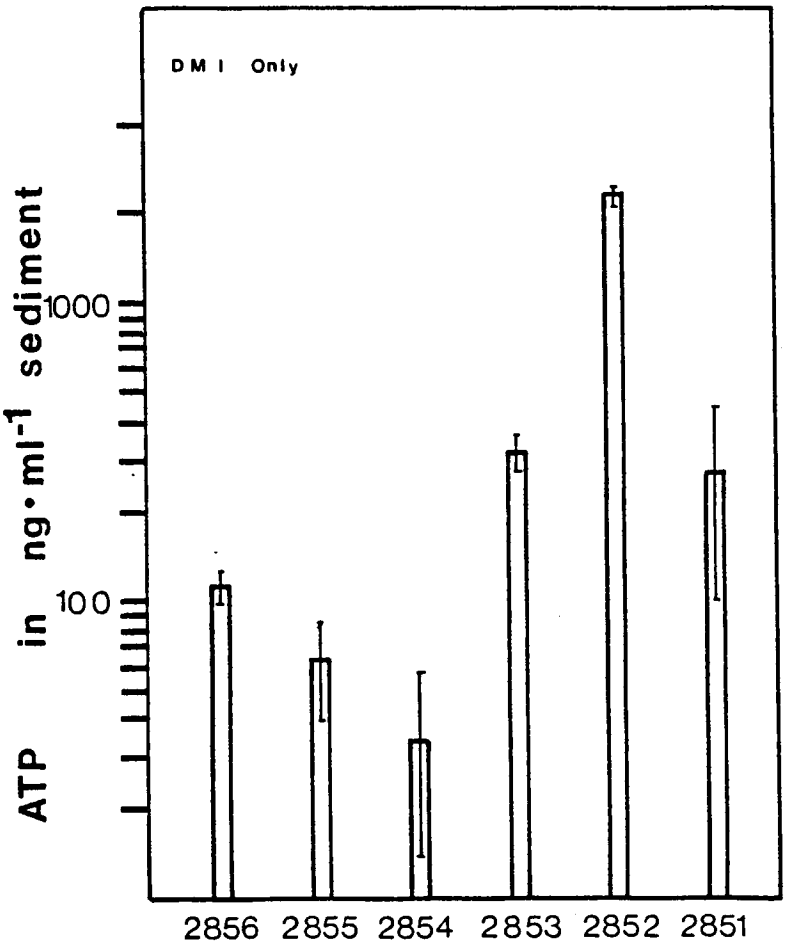

Figure 198 ATP content of Transect VIII.

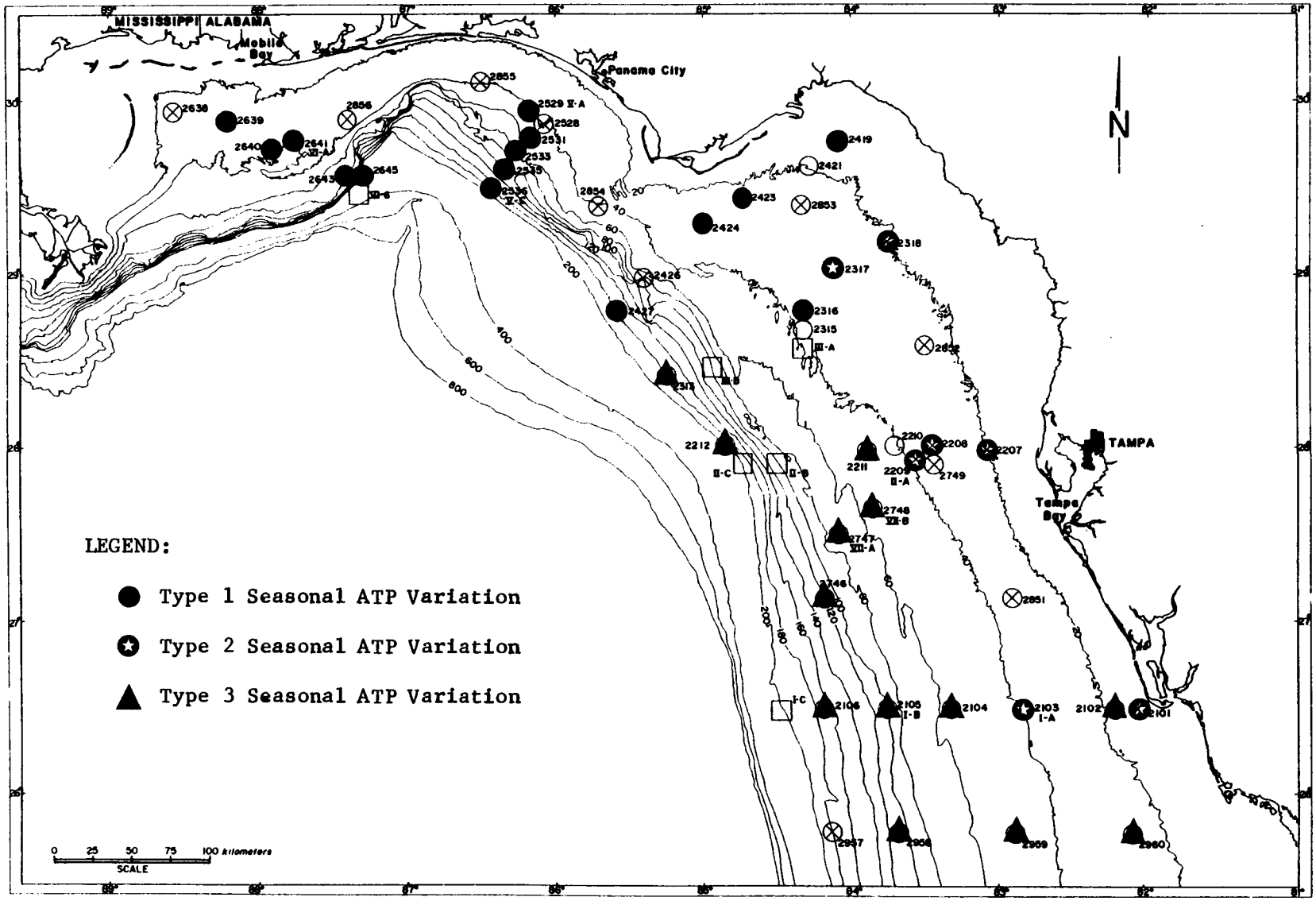

Fig.199 Geographic distribution of seasonal ATP variations

Transmissiometry data (K. Carder, fourth quarterly meeting of MAFLA program Principal Investigators, July 1978) indicated that low transmittance measurements occurred along the bottom, south and west of Station 2315, which was the same area of the Type 3 seasonal variation. These low transmittances were attributed to the intrusion of Loop Current water along the bottom on this portion of the shelf. Similarly, these stations (offshore stations of Transects I and IX) also showed an increase in temperature of bottom water from summer to winter, which is the opposite of all the other stations.* Mr. Lee Fausak (principal investigator for temperature and salinity data) provided a map of ΔT contours for bottom temperatures in the MAFLA area. The ΔT lines, though rough estimates, generally separated the three seasonal variation patterns in ATP geographically. The areas that possessed either a >15° or a 10-15° (in the north) seasonal change in temperature showed the Type 1 seasonal ATP variation. Those stations of the Type 2 seasonal ATP variation fitted into a small pocket of 10 to 15° temperature change in the south, while those of the third seasonal pattern occurred in the <5° or 5 to 10° seasonal variation area.

Correlations between ATP data and grain size parameters (i.e., mean grain size, percent fines, sand:fine ratio) were attempted with no success. Similarly, TOC values showed poor correlation with ATP data.

Questions of validity aside, ATP values have been converted to living organic carbon by the method of Holm-Hansen (1973). Percent living organic carbon was calculated by dividing by the TOC values of the MAFLA area. Percent living carbon ranged from 0.0032% to 5% of the total for Stations 2641 (DM-I) and 2531 (DM-II), respectively, with a grand mean of 0.25%.

DISCUSSION AND CONCLUSIONS

Three patterns of sesonal variation in sediment ATP levels have been found in the MAFLA tract, which correspond with three distinct geographic regions. The northernmost stations (Transects V and VI, and to a lesser extent, Transect IV) showed an ATP maximum in the fall, with lower values in summer and winter. The eastern stations (2101, 2103, 2207, 2208, 2209, 2318, 2317) showed a steady increase from summer lows to winter peak values in ATP. The southwest stations showed a minimum ATP value in the fall, with higher values in summer and winter.

The stations in the north (Transects V and VI) showed the greatest changes in bottom salinity over the seasons, as well as the greatest changes in bottom temperatures (>15°, or 10-15°). These stations are probably influenced strongly by freshwater input from Mobile Bay and numerous other bays adjacent to this area, and perhaps even the Mississippi River.

The eastern inshore stations showing the second type of seasonal variation were characterized by decreasing bottom water temperatures from summer to winter and increasing bottom salinities. Surface currents flowing northward in this area have been shown to increase in strength from summer to winter (Nowlin, 1971).

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*Salinity temperature data courtesy of Mr. Lee Fausak, Dames & Moore

The third area of seasonal ATP variation showed the least change in bottom temperatures for the seasons, with a slight increase from summer to winter.

Jones (1973) divided the MAFLA area into approximately three areas based on similar temperature-salinity characteristics. These have been shown to correspond well with geologic and bottom fauna regimes. The first is west of a line drawn south of Cape San Blas, including Transects V and VI. This area has been characterized as one with a complex eddy structure, caused by the mixture of low salinity water from the Mississippi River and Mobile Bay, with seasonal extensions of the Loop Current (Jones, 1973). The ATP data for this area in 1976 (La Rock, 1976) was unlike that of any other transect, characterized by unusually high values and lack of correlation with sediment or TOC parameters. The ATP data presented here showed this area to be characterized by extreme seasonal variations, the average change being 998 ng $m\ell^{-1}$ sediment.

The second area, east of a line drawn south from Cape San Blas and north of 28° north, encompassing the Florida Middle Grounds, is characterized by a simple salinity regime, increasing from shoreward out. Circulation is primarily a counter-clockwise gyre (Nowlin, 1971; BLM, 1978) that strengthens in the winter and weakens in the summer. This area encompasses Transects III and IV, which have shown a mixture of seasonal ATP patterns. The average seasonal change in ATP was 406 ng $m\ell^{-1}$ sediment, which was significantly less than that of V and VI ($0.005 < p < 0.01$).

The third area, from approximately 28° south to Cape Romano, is characterized by complex seasonal variations in circulation, influenced by intrusion of rings of the Loop Current (Jones, 1973). This area possessed the third type of seasonal ATP variation mentioned above.

La Rock (1976) found his ATP data of Transects I-IV to correlate well with mean grain size data. This correlation has not been found for any of the transects of DM-I, DM-II, or DM-IV. La Rock also found an inverse correlation between ATP and TOC, which we again did not find. Other investigators have found peak values in sediment ATP to correspond with DOC peaks (Karl et al., 1976), while seasonal studies have shown sediment ATP peaks do not correspond with TOC peaks (Cadee and Hegeman, 1977). The relationship between TOC and microbial biomass in the sediment is complex, and depends on the nutritive potential of the carbon and amount of oxygen available. Studies with decomposing Thalassia indicate that ATP is proportional to organic carbon content until only refractory carbon compounds are left (Knauer and Ayers, 1977). Although TOC has been measured in the MAFLA area sediments, there is no information on the type of carbon compounds these measurements represent.

EFFECT OF PROPOSED DRILLING ON SEDIMENT MICROBIAL BIOMASS

Since little data exists on the effect of drilling on sediment ATP levels, only speculations can be given here. However, sediment and water column ATP determinations could provide useful information on the effects of drilling on the quality of the environment, if coupled with other oceanographic parameters (i.e., chlorophyll a and primary productivity, etc.).

Bacteriocides in drilling fluids such as formaldehyde, glutaraldehyde, pentachlorophenol and others (BLM, 1977) would most likely cause drastic decreases in sediment ATP levels in the immediate vicinity of the drilling site. Since these are greatly diluted in relatively short distances (BLM, 1977), the effects would probably be local only. However, benthic diatoms are severely affected by pentachlorophenol concentrations as low as 5 μM (Chansang and Cooksey, unpublished observation).

The effect of petroleum hydrocarbon leakage or spillage on sediment ATP levels is difficult to predict. Evidence indicates that the greatest effect of oil spillage in sediments is to alter the compositions of the microbial population present. For example, following an oil spill on a beach in Narragansett Bay, Rhode Island, the total number of hydrocarbon degrading bacteria increased drastically from 4 to 16 days after the spill, and persisted at the higher level for at least one year (Pierce et al., 1975). However, the total number of heterotrophic microorganisms was not altered. Similarly, the study of a pristine and oil-polluted salt marsh in Louisiana indicated a higher ratio of hydrocarbon degrading microorganisms to total heterotrophs in the oil-polluted salt marsh, but did not show a significant difference in total numbers present (Hood et al., 1975). The polluted salt marsh had a higher bacterial diversity index as well.

From these studies one might conclude that the introduction of petroleum hydrocarbons into the sediment would have no effect on the total number of microorganisms present, and thus no effect on ATP levels. It would appear that a natural, self-purification would occur by selection for hydrocarbon-degrading bacteria. However, the plate count method for aerobic heterotrophs was used in both studies to estimate microbial populations. This procedure may not give an accurate indication of the autotrophic microbial population, thereby giving a distorted picture of the total of microbes present. The measurement of ATP, even with the uncertainties discussed earlier, would give a much more realistic indication of the total microbial biomass present.

Secondly, selection for hydrocarbon degrading bacteria was performed under aerobic conditions, since much of hydrocarbon breakdown (i.e., alkanes) is essentially an aerobic process. However, petroleum hydrocarbons seeping below the sediment surface interface would enter anaerobic conditions, beyond the reach of aerobic, hydrocarbon-degrading bacteria, and could therefore remain substantially unaltered for some period of time. Evidence from gas chromatographic analyses of Buzzard's Bay sediment extracts indicated that two years after an oil spill, much of the petroleum hydrocarbons in the 2.5 to 7.5 cm layer of sediment had not been degraded significantly (Blume and Sass, 1972). Thus the proposed microbial self-purification may only be limited to the upper, aerobic layers of the sediment.

SUMMARY

1. Three seasonal patterns of variation in sediment ATP levels have been found in the MAFLA area, and these correspond to distinct geographic areas.

2. Transects V and VI showed a pattern of extreme seasonal change, with highest ATP values occurring for DM-II sediment samples. This area was characterized by the greatest seasonal changes in bottom temperature and salinity, being influenced by the Mississippi River and Mobile Bay.

3. The eastern stations of Transects I, II, and III showed a pattern of increase in ATP levels from summer to winter. This area is believed to be influenced by a northward surface current that strengthens from summer to winter.

4. The western stations of Transects I, II, and all of VII and IX showed the opposite seasonal pattern of Transects VI and V, with a minimum in the fall. This area is believed to be influenced by the seasonal influx of rings of Loop Current water. Those stations also possessed very high calcium carbonate levels (> 95%).

5. No correlation could be found between ATP data and grain size parameters, or TOC values.

LITERATURE CITED

Ansell, A.D., 1977. The adenosine triphosphate content of some marine bivalve molluscs. J. Exp. Mar. Biol. Ecol. 28: 269-283.

Bancroft, K., E.A. Paul, and W.J. Wiebe, 1976. The extraction and measurement of adenosine triphosphate from marine sediments. Limnol. Oceanogr. 21: 473-479.

Blume, M. and J. Sass, 1972. Indigenous and petroleum derived hydrocarbons in a polluted sediment. Env. Pollut. 3: 92-94.

Bureau of Land Management, 1978. Draft environmental impact statement. Proposed 1978 Outer Continental Shelf Oil and Gas Lease Sale. OES Sale #65. U.S. Department of the Interior, Vol. 1. 233 p.

Cadee, G.C. and J. Hegeman, 1977. The distribution of primary production of the benthic microflora and accumulation of organic matter on a tidal flat area, Balgzand, Dutch Wadden Sea. Neth. J. Sea Res. 11: 24-41.

Cole, H.A., J.W.T. Wimpenny, and D.E. Hughes, 1967. The ATP pool in *Escherichia coli*. I. Measurement of the pool using a modified luciferase assay. Biochem. Biophys. Acta 143: 445-453.

Eppley, R.W., A.F. Carlucci, O. Holm-Hansen, D. Kiefer, J.J. McCarthy, and P.M. Williams, 1972. Evidence for eutrophication in the sea near southern California sewage outfalls - July 1970. California Mar. Res. Comm., CalCOFI Rept. 16: 74-83.

Ernst, W., 1970. ATP als indikator fÜr die biomasse mariner sedimente. Oecologia 5: 56-60..

Hamilton, R.D. and O. Holm-Hansen, 1967. ATP content of marine bacteria. Limnol. Oceanogr. 12: 319-324.

Hodson, R.E., O. Holm-Hansen, and F. Azam, 1976. Improved methodology for ATP detrminations in marine environments. Mar. Biol. 34: 134-149.

Holm-Hansen, O., 1969. Determination of microbial biomass in ocean profiles. Limnol. Oceanogr. 14: 740-747.

Holm-Hansen, O., 1973. Determination of total microbial biomass by measurement of adenosine triphosphate. pp. 73-89 in Stevenson, L.H. and R.R. Colwell, (Eds.), Estuarine Microbial Ecology. Columbia University of South Carolina Press.

Holm-Hansen, O. and C.R. Booth, 1968. The measurement of adenosine triphosphate in the ocean and its ecological significance. Limnol. Oceanogr. 11: 510-519.

Hood, M.A., W.S. Bishop, Jr., F.W. Bishop, S.P. Meyers, and T. Whelan III, 1975. Microbial indicators of oil rich salt marsh sediments. Appl. Microbiol. 30: 982-987.

Jones, J.I., 1973. Physical oceanography of the northeast Gulf of Mexico and Florida Continental Shelf area. In Jones, J.I., R.E. Ring, M.O. Rinkel, and R.E. Smith (Eds.), A Summary of Knowledge of the Eastern Gulf of Mexico. State University System of Florida, St. Petersburg.

Karl, D.M., 1975. Adenosine triphosphate in marine sediments: some comments on extraction methodology and measurement. pp. 360-393 In ATP Methodology Seminar, March 3-5, 1975. San Diego: SAI Technology Company.

Karl, D.M., and O. Holm-Hansen, 1976. Effects of luciferin concentration on the quantitative assay of ATP using crude luciferse preparations. Anal. Biochem. 75: 100-112..

Karl, D.M., and P.A. La Rock, 1975. Adenosine triphosphate measurements in soil and marine sediments. J. Fish. Res. Board Canada 32: 599-607.

Karl, D.M., and P.A. La Rock, J.W. Morse, and W. Sturges, 1976. Adenosine triphosphate in the North Atlantic Ocean and its relation to the oxygen minimum. Deep Sea Res. 22: 81-88.

Knauer, G.A. and A.V. Ayers, 1977. Changes in carbon, nitrogen, adenosine triphosphate, and chlorophyll a in decomposing Thalassia testudinum leaves. Limnol. Oceanogr. 22: 405-414.

La Rock, P.A., 1976. Adenosine triphosphate in the MAFLA tract area. Principal Investigators' Final Reports, BLM Contract No. 08550-CT5-30.

Nowlin, W.O., 1971. Water masses and general circulation in the Gulf of Mexico. Oceanology Intl. 6: 28-33.

Paerl, H.W., M.M. Tilzer, and C.R. Goldman, 1976. Chlorophyll a versus adenosine triphosphate as algal biomass indicators in lakes. J. Phycol. 12: 242-246.

Paerl, H.W., and N.J. Williams, 1976. The relation between adenosine triphosphate and microbial biomass in diverse aquatic ecosystems. Int. Rev. Gesamten. Hydrobiol. 61: 659-664.

Pierce, R.H., Jr., A.M. Cundell, and R.W. Traxler, 1975. Persistence and biodegradation of spilled residual fuel oil on an estuarine beach. Appl. Microbiol. 29: 646-652.

Sokolova, G.A and G.I. Karavaiko, 1968. Physiology and geochemical activity of Thiobacilli. Jerusalem: Israel Program for Scientific Translations. 283 pp.

Strehler, B.L. and W.D. McElroy, 1957. Assay of adenosine triphosphate. pp. 871-873 In Colowick, S.P. and N.D. Kaplan (Eds.), Methods in Enzymology, Vol. III. New York, Academic Press.

Sutcliffe, W.H., E.A. Orr, and O. Holm-Hansen, 1976. Difficulties with ATP measurements in inshore waters. Limnol. Oceanogr. 21: 145-149.

Walker, J.D., J.J. Calormis, T.L. Herbert, and R. R. Colwell, 1976. Petroleum hydrocarbons: degradation and growth-potential for Atlantic Ocean sediment bacteria. Mar. Biol. 34: 1-9.

Walker, J.D., R.R. Colwell, and L. Petrakis, 1975. Evaluation of petroleum-degrading potential from water and sediment. App. Microbiol. 30: 1036-1039.

VOLUME II

CHAPTER 12

BENTHIC FORAMINIFERA

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CONTRACT NO. AA550-C7-34

FORAMINIFERA OF THE MAFLA AREA

FINAL REPORT
TO
DAMES & MOORE

Wayne D. Bock

Rosenstiel School of Marine and Atmospheric Science
University of Miami

Contract No. AA550-CT7-34

TABLE OF CONTENTS

ABSTRACT

The environmental assessment program for 1977-1978 (BLM Contract No. AA550-CT7-34) was conducted along eight transects plus six supplementary stations. The work also included samples from the summer of 1976 collected from seven transects and six supplementary stations. The sampling sites ranged in depth from 33 to 200 m. Foraminniferal trends remained realtively constant seasonally even though abundances of major dominant species sometimes changed drastically. The abundances of living specimens in the southern transects were abnormally low during the fall and winter sampling periods. Comparisons of species composition and abundances with previous years' work are made.

Several trends exist among the forminifera of the MAFLA area. Diversity increases seaward in almost every transect. Living percentages increase with sediment grain size decrease. Living percentages increase with increasing depth and also increase northward and to the west. The upper limit of the depth habitat for Cassidulina curvata and C. subglobosa becomes shallower to the north. There is a narrow band of shifting sand bottom running parallel to the shore in Transects I, II, III, and IV containing attached foraminiferal faunas. Just to the west and seaward of this zone is another parallel band characterized by Planulina exorna. The shelf edge at approximately 200 m depth is characterized by Brizalina spp., Cassidulina spp., Cibicides concentricus, C. corpulentus, Planulina ariminensis, P. foveolata, Siphonina pulchra, Uvigerina flintii and U. peregrina. Deviations from these general trends are caused by local oceanographic conditions.

In the total populations there is a relict reef fauna running in an arcuate band from offshore Cape Romano, Florida to offshore Mobile, Alabama. The relict fauna is found in different depths along this band, and there is evidence that the Late Pleistocene or Early Holocene reef existed in shallower, warmer waters than are present in the same area today.

INTRODUCTION

PURPOSE

The MAFLA shelf, as an element of the OCS Environmental Benchmark Studies, can be characterized by dominant benthonic foraminiferal species contained in sediments collected by use of a box core from 30 primary, 18 secondary, and 6 supplementary stations. The presence of indicator species assures a method for monitoring sources of stress which may be placed on the environment. Monitoring changes in species composition of the fauna provides a method to note environmental change, and by comparing modern assemblages with those of the recent past in the subsurface it is possible to determine natural changes in the environment as opposed to man-made changes caused by the introduction of pollutants. The purpose of the foraminiferal investigation of the MAFLA program was to determine species composition of living and total populations and natural seasonal and annual variations in these populations.

LITERATURE SURVEY

The foraminiferal faunas from the northern part of the MAFLA area are well known with several excellent papers describing ecological habitats. In 1949, S.W. Lowman reported on foraminiferal faunas from surface samples along three profiles in the northern Gulf of Mexico. He also found abundant specimens of Amphistegina in an elongate band, subparallel to the shoreline, off the coast of the florida panhandle in about 70 m of water.

The stations along MAFLA Transect VI contain faunas similar to those described by Phleger (1954) from Mississippi Sound, from the eastern Mississippi Delta area (1955), and from the northern Gulf of Mexico (1960) and by Lankford (1959) from the east Mississippi Delta margin. Both authors established species characteristic of ecologic facies.

Parker (1954) reported on the distribution of the foraminifera in the northeastern Gulf of Mexico and found five faunal depth boundaries which she suggested were controlled by salinity and temperature. About 15 of the samples were located in the area covered by the MAFLA investigations, mostly in the northern and western part of the area.

Ludwick and Walton (1957) reported on 150 benthonic foraminiferal species contained in 41 sediment samples from an area in the northeastern Gulf of Mexico roughly covering an area from shore to the 200 m line, from the Mississippi Delta to Cape San Blas. They described both living and dead populations and found a nonindigenous West Indian assemblage that was abundant among the dead forms. Included were reef-type species most prominent among pinnacles on the shelf edge in 80 to 100 m of water.

Walton (1964), using several thousand sediment samples collected by Gulf Research and Development Company from the northeastern Gulf, east of the Mississippi Delta, made faunal analyses of the benthonic foraminiferal assemblages contained in the sediments. From this and existing data he outlined fourteen biofacies based on generic dominance, and also compiled frequency distribution charts for most of the dominant species.

Research on the southern part of the MAFLA area is sparse. In addition to the few samples reported on by Parker (1954), Bandy (1956), supplementing Parker's work, reported on the foraminiferal species in several West Florida bays and in sediment samples from transects across the West Florida Shelf. He described the ecological habitats of foraminifera in the shallow water bays and depth habitats of species in the waters of the shelf. Many of the benthonic species reported by Bandy are present in the southern part of the MAFLA area.

PREVIOUS WORK

The Bureau of Land Management has supported research in the MAFLA area since 1974. Foraminiferal investigations have been conducted under Contracts 08550-CT4-11 and 08550-CT5-30 to the State University System of Florida, Institute of Oceanography and subcontracted to the Rosenstiel School of Marine and Atmospheric Science, University of Miami. Bock (1976) charactrized the initial five MAFLA areas by doninant foraminiferal assemblages. The initial work was conducted within the lease areas and was limited to the mid-portions of the shelf. Subsequent investigations (1975-1976) were conducted along transects transversing the lease areas, but extending both into shallower and deeper waters. Bock (1976) described the foraminiferal faunas from these transects and compared the results with the findings of the 1974 survey.

METHODS AND MATERIALS

All sediment samples for foraminiferal analysis were collected and analyzed according to the method described in: Dames & Moore, 1978, Third Quarterly Progress Report, MAFLA Benchmark Survey, February-May, 1978, Appendix D, PI reports.

RESULTS

Frequency distributions for the benthonic foraminifera for the eight MAFLA transects plus six supplemental stations were determined for summer, 1976, and summer, fall, and winter, 1977-78. Major dominant species (abundance >5%) were used to characterize each station. Over 400 species of benthonic foraminifera were identified of which 51 occur in abundance over 5% in at least one station. Each of the eight transects and the six supplemental stations are regarded seprately.

Transect I (Stations 2101-2106) has species which are common to all the stations of the transect but Station 2106. However, each station has a distinctive character and can be considered separately. Station 2101 is characterized by Ammonia beccarii, Hanzawaia strattoni, Remaneica sp. A, Rosalina columbiensis and R. concinna. The presence of A. beccarii indicates stress and may be associated with high salinity values for all seasons. Station 2102 is characterized by H. strattoni, R. columbiensis, R. concinna, Asterigerina carinata, and Cibicides floridanus. This is typical of a shifting sand habitat although all but A. carinata are ubiquitous on the MAFLA shelf in depths less than 100 m. Station 2103 has the same species as 2102 plus Quinqueloculina lamarckiana and Planulina exorna. The latter is a mid-shelf indicator. Station 2104 has an identical fauna to

2103 but with the addition of Neoconorbina orbicularis as the most abundant species. This species is found in dominant abundance at only a few stations on the entire shelf and is noteworthy as having its maximum abundance at 2104. Station 2105 is characterized by: R columbiensis, Cibicides floridanus, and Cassidulina subglobosa. The latter is typically deeper in this southern part of the area, but occurs much shallower to the north. Station 2106 is characterized by Cibicides concentricus, C. floridanus, Planulina ariminensis, P. foveolata and Brizalina goessii. The last four are typical members of the 200 m fauna and their distribution is probably controlled by temperature and bottom type.

Transect II (Stations 2207-2212) can be divided into three zones. One zone is occupied by Station 2207 and is characterized by Asterigerina carinata, Cibicides floridanus, Hanzawaia strattoni, Rosalina columbiensis and R. concinna. All the species in these assemblages have numerous attached specimens and are associated with a shifting sand bottom. Stations 2208-2211 all have several common species and can be characterized by a single species, Planulina exorna, a mid-shelf indicator. Station 2211 differs from the rest in the group in having Neoconorbina orbicularis in abundance. Station 2212 contains specimens of the 200 m depth fauna: Brizalina lowmani, Cassidulina curvata, Cibicides concentricus, Planulina ariminensis, Siphonina pulchra and Planulina foveolata.

Transect III (Stations 2313-2318) can also be divided into three zones. Station 2313 has the same 200 m fauna as 2212. Stations 2315 and 2316 are in the Planulina exorna zone with some specimens of the reef indicator Amphistegina gibbosa. These stations are in the Florida Middle Grounds which contain living coral. The relict fauna is completely dominated by A. gibbosa. Stations 2317 and 2318 are completely dominated by attached specimens of the shifting sand community.

Transect IV (Stations 2419-2427) can also be divided into the same three zones with a possible subzone. Stations 2419, 2420, and 2421 belong to the shifting sand community. However, Station 2419 must be considered separately for some seasons. This station has the largest temperature range and some of the lowest salinity values and this is reflected by the presence of the stress-indicator species, Ammonia beccarii. Also, especially during the summer, the sediment must be stabilized by sea grass resulting in the presence of Archaias angulatus, which uses the sea grass for a preferred substrate although it can also survive on sediment. It cannot, however, tolerate low winter temperatures when its abundance drops to essentially zero. During summer and fall it is present in frequencies up to 17%. It never reaches dominance unless grass or algae is present. When it is rare or absent the fauna is a typical shifting sand community.

Stations 2422-2426 belong to the Planulina exorna zone. Station 2427 has a typical 200 m fauna.

Transect V (Stations 2528-2536) represents a mixture of zones. Stations 2528-2533 could be placed in the Planulina exorna mid-shelf zone. However, they are not mid-shelf and they have numerous representatives of much deeper water, especially Cassidulina curvata and C. subglobosa. The planktonic/benthonic ratios for these stations is also much too high for

the water depths. The whole transect must be affected by Loop Current water and maybe upwelling currents reproducing bottom conditions similar to deeper water. Station 2534 contains only three dominant species, Cassidulina curvata, C. subglobosa and Cibicides floridanus, all of which have rather wide depth ranges. Stations 2535 and 2536 contain the typical 200 m faunal assemblages. Both stations have sediment replete with fecal pellets. Station 2536 is the only station having Brizalina subaenariensis mexicana as a major dominant species. Stations 2529-2533 contain the relict reef fauna and also have living specimens of Amphistegina gibbosa, a reef indicator.

Transect VI (Stations 2637-2645) can be divided into three zones with some overlapping of zones. Stations 2637 and 2638 contain typical Mississippi Sound and deltaic species. Ammonia beccarii and Elphidium galvestonense are very abundant in Mississippi Sound and are usually associated with brackish water. Nonionella atlantica and N. opima are considered deltaic species by many and are thought to be affected by runoff. However, since bottom salinity measurements do not indicate brackish water the presence of these species, two of which are known stress indicators, must be explained by some other factor. It may be turbidity or low oxygen content. Stations 2639-2642 can be placed in the Planulina exorna mid-shelf zone with some overlapping of stress conditions indicated by the presence of A. beccarii. Stations 2643-2645 contain Amphistegina gibbosa and Lenticulina orbicularis, reef indicators, and the dead fauna belongs mainly to the relict reef fauna.

Transect VII (Stations 2746-2749) being a diagonal transect between Transects I and II has four distinct stations. Stations 2746 contains species of the 200 m fauna. It also has abundant specimens of Planorbulina mediterranensis, a species usully living at shallower depths. However, it is an attached species and could easily be transported downslope. There are always some shallow-water representatives in the deeper assemblages. Station 2747 also has large numbers of living specimens of species that should be living in shalower depths, Archaias angulatus and Peneroplis carinatus. The other dominant species are most ubiquitous and not limiting. Stations 2748 belongs to the Planulina exorna zone. Station 2749 belongs to the shifting sand zone.

Supplemental Stations 2851, 2852, 2853, and 2854 belong to the shifting sand zone. Stations 2855 and 2856 belong to the Planulina exorna zone.

Transect IX (Stations 2957-2960) has four distinct stations. Stations 2957 contains typical 200 m species. Station 2958 is very similar to Station 2747 and also contains abundant specimens of Planorbulina mediterranensis, which should be in shallower water. Station 2959 belongs to the Planulina exorna zone. Station 2960 belongs to the shifting sand zone.

DISCUSSION

Analysis of the foraminiferal faunas of the MAFLA area reveals three major foraminiferal zonations with several subzones. The zone of shifting sand bottom is characterized by Asterigerina carinata, Rosalina concinna, R. columbiensis, Cibicides floridanus and Hanzawaia strattoni. The major

indicator species is A. carinata. The other species in the assemblange are ubiquitous, but the only place they are found attached is in the zone of shifting sand bottom. Most of the foraminiferal specimens in this zone are attached to individual quartz grains, but some select shell fragments or anything of the right size and density. They use the grains as anchors to keep them on bottom in the shifting sand environment. The five species listed above are the most abundant, but over 20 speices have attached themselves to foreign objects in this zone. Some of the species, especially Asterigerina carinata, Rosalina concinna and Cancris sagra, have always been described as free-living. The stations with large percentages of attached forms are all in 10 to 30 m of water (see Figure 200) where current action shifts the sand bottom. The foraminifera are obviously using the quartz grains to which they are attached as anchors to allow them to exist in an environment which might otherwise prove hostile. The majority of the species attached in this zone are free-living at the other stations where they occur.

The Planulina exorna zone is the mid-shelf zone with medium to coarse sediment. Many species comprise the fauna of this zone, but all are restricted to the areal distribution of P. exorna. Individual specimens of P. exorna may exist outside the zone, but it is only found in abundances greater than 5% in the mid-shelf zone. A subzone exists withn this zone made up of only two stations where Neoconorbina orbicularis is the dominant species (Figure 200). A mixed zone of primarily the P. exorna assemblage and a 200 m faunal assemblage occurs in Transect V (Figure 200). Reasons for this were discussed above.

The 200 m depth zone is characterized by Brizalina goessii, B. lanceolata, B. lowmani, Cassidulina curvata, C. subglobosa, Cibicides concentricus, C. corpulentus, Planulina ariminensis, P. foveolata, Siphonina pulchra, Uvigerina flintii and U. peregrina. It concides with the shelf edge at roughly 200 m depth (Figure 200). A subzone characterized by Brizalina subaenariensis exists within this zone. All three zones parallel the shoreline.

One aspect which is invaluable in environmental monitoring is the presence of stress indicator species. Ammonia beccarii is represented in abundance only at Stations 2637, 2638, 2419, and 2101. It is a well known indicator, occurs over vast areas of the world ocean, and is well studied. It is considered here for its potential for indicating stress placed on the environment by activities associated with petroleum exploration and production. The fact that it occurs in every transect, although usually in very low frequencies, provides an ndicator speices for monitoring. With increasing stress placed on the environment, from whatever source, this species will increase in abundance as the normal fauna finds it more difficult to survive. It also provides a method for measuring recovery time from environmental contamination by recording the time necessary for an area to change from a fauna dominated by A. beccarii to that of its normal species composition. Other stress indicator species which are present in the MAFLA area are Nonion depressulum matagordanum and the various species of Elphidium.

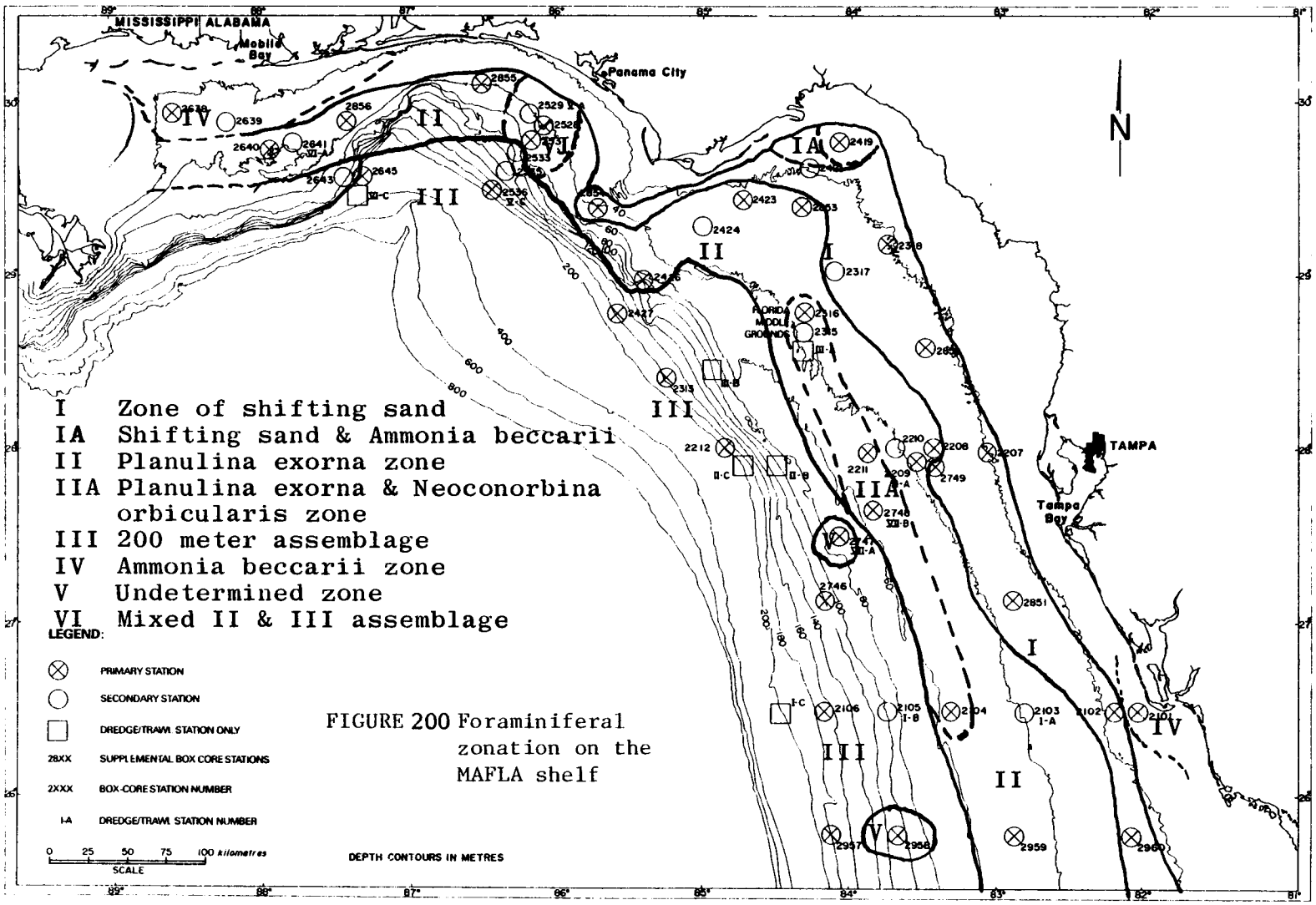

FIGURE 200 Foraminiferal zonation on the MAFLA shelf

BLM 77/78 MAFLA SURVEY STATION LOCATIONS

Although this report deals principally with the living fauna, it is worth examining the total fauna with regard to Amphistegina gibbosa. This species occurs live in abundance at different depths in different transects, always in association with coarse sediment. The genus is a worldwide reef indicator and most species belonging to it are always associated with reefs or high energy, hard substrates. The percentages of A. gibbosa in the total fauna are far greater than in the living fauna. Other reef species, at times abundant in the relict fauna, but rare in the living funa, are Archaias angulatus and Peneroplis proteus. The presence of A. angulatus in the relict fauna, its absence, or at least only a rare occurrence in the living fauna indicates a Late Pleistocene or Early Holocene reef, thriving at a time when the water temperatures were warmer than those of today. In the Gulf of Mexico-Caribbean region a prsent, A. angulatus is not able to survive in cool water temperatures (seiglie, 1968). Parker and Curray (1956) and Ludwick and Walton (1957) arrived at similar conclusions, the former based on the faunal evidence of mollusks, stony corals, and bryozoans. The distribution of the relict reef fauna is shown in Figure 201.

There are several faunal trends which are noticeable in the MAFLA area:

1) Diversity increases seaward in almost every transect. In general the more restricted waters of the shallow, nearshore areas, support a less diverse fauna than the deeper stations near the edge of the continental Shelf. This pattern can be disrupted, however, by coarse sediment, hard substrate areas such as the Florida Middle Ground located in Transect III where diversity may be less than on either the shoreward or seaward side.

2) Living percentages increase to the north and west, with the highest percentages being recorded in the areas immediately influenced by Mississippi runoff off the coast of Mississippi and Alabama. The percentages were higher in the first than in the subsequent years in this area, and this may be due to the greater amount of runoff in 1974. There were also much higher percentages of stress indicator species such as Ammonia beccarii in 1974.

3) The numbers of specimens increase with decreasing sediment size. This may simply be a result of physically more specimens in the smaller size fractions, but it may be that there is a greater source of nutrients and food supply available in the finer sediments, which would support a larger population.

A comparison of the living benthonic foraminiferal faunas in the MAFLA area from summer 1974 to winter 1978 indicates changes in species composition of the major dominant species. All the dominant species from 1974, 1975-76, are still present, but additional species have become dominant over the past two years. At the end of the winter sampling in 1976 there were 24 species occurring in abundances of 5% or greater at at least one station. At the end of the winter 1978 sampling period there were 51

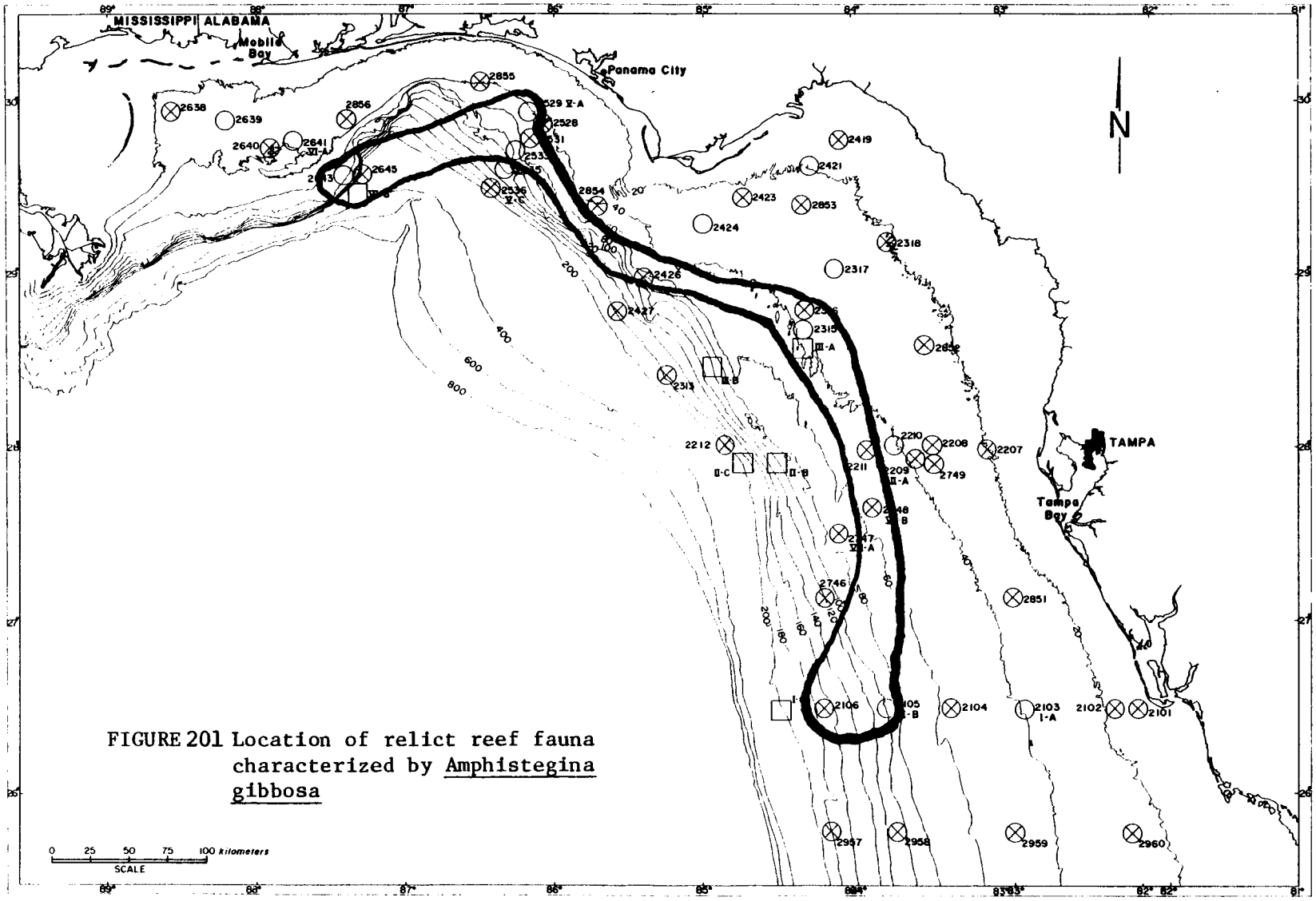

FIGURE 201 Location of relict reef fauna characterized by Amphistegina gibbosa

major dominant species. The increase in the number of species occurring in frequencies greater than 5% aparently is at the expense of the most abundant species, especially Hanzawaia strattoni. Abundances of this species have decreased drastically at certain stations. Percentages of living foraminifera have also decreased significantly since 1974. As reported at that time, there were many juveniles in the faunas which may have been the result of a seasonal bloom brought on by nutrients carried into the northwestern part of the area by runoff. Or the extremely cold winters of 1977 and 1978 may have affected the reproduction rates, especially in the southern part of the area where consistently low temperatures are less frequent. The greatest decrease in abundances was in Transects I, II, and III. The species abundances in Transects IV, V, and VI were variable, but within the same limits as noticed during 1975-76. They were noticeably down, of course, from the peaks of summer 1974.

CONCLUSIONS

The foraminiferal species characterizing the MAFLA shelf fall into three major zonations: 1) the shifting sand zone, 2) the Planulina exorna mid-shelf zone, and 3) the 200 m depth zone. The boundaries in most cases are quite clear, but in at least one transect, Transect V, there is overlapping of two zones. Subzones occur within major zones usually characterized by a single dominant species and usually occupying very few stations. These zonations are consistent for major dominant species and appear to be stable through time. Variations in the surface sediments and 12 to 15 cm level are no greater than variations between replicate samples.

It appears that sediment type is one controlling factor in benthonic foraminiferal distribution in all but Transect V, where circulation is exhibiting some control.

The presence of indicator species affords a method for determining environmental deterioration and reparation.

ACKNOWLEDGEMENTS

The author wishes to thank the Bureau of Land Management for providing research funds under Contract No. AA550-CT7-34 and Dames & Moore for subcontracting the foraminiferal program to the Rosenstiel School of Marine and Atmospheric Science, University of Miami, and making this research possible.

REFERENCES

Bandy, O.L., 1956. Ecology of foraminifera in northeastern Gulf of Mexico. U.S. Geol. Survey, Prof Paper 274-6: 125-204.

Bock, W.D., 1976. Distribution an significance of foraminifera in the MAFLA area. First Int. Symp. on Benthonic Foraminifera of continental Margins, Part A. Ecology and Biology. Maritime Sediments Spec. Publ. 1: 221-237.

Bock, W.D., 1976. Foraminifera of the MAFLA area. Final report to BLM, Contract No. 08550-CT5-30.

Lankford, R.R., 1959. Distribution and ecology of foraminifera from east Mississippi Delta margin. Bull. Amer. Assoc. Petroleum Geologists 43(9):2068-2099.

Lowman, S.W., 1949. Sedimentary facies in Gulf Coast. Bull. Amer. Assoc. Petroleum Geologists 33(12): 1939-1997.

Ludwick, J.C., and W.R. Walton, 1957. Shelf-edge calcareous prominances in northeastern Gulf of Mexico. Bull. Amer. Assoc. Petroleum Geologists 41(9): 2054-2101.

Parker, F.L., 1954. Distribution of the foraminifera in the northeastern Gulf of Mexico. Bull. Harvard Mus. Comp. Zool. 111(10) : 453-588.

Parker, R.H. and J.R. Curray, 1956. Fauna and bathymetry on banks on continental shelf northwest Gulf of Mexico. Bull. Amer. Assoc. Petroleum Geologists 40(10): 2428-2439.

Phleger, F.B., 1954. Ecology of foraminifera and associated microorganisms from Mississippi Sound and environs. Bull. Amer. Assoc. Petroleum Geologists 38(4): 584-647.

Phleger, F.B., 1955. Ecology of foraminifera in southeastern Mississippi Delta area. Bull. Amer. Assoc. Petroleum Geologists 39(5): 712-752.

Phleger, F.B., 1954. Sedimentary patterns of microfaunas in northern Gulf of Mexico. In Recent Sediment, Northwest Gulf of Mexico. Amer. Assoc. Petroleum Geologists: 267-381.

Seiglie, G.A., 1968. Relationships between the distribution of Amphistegina and the submerged Pleistocene reefs off western Puerto Rico. Tulane Stud. Geol. 6(4): 139-147.

Walton, W.R., 1964. Recent foraminiferal ecology and paleoecology. In Approaches to Paleoecology John Imbrie and Normal Newell (Eds.), New York, John Wiley and Sons, p. 151-237.

VOLUME II

CHAPTER 13

BENTHIC MEIOFAUNA

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CONTRACT NO. AA550-CT7-34

FINAL REPORT

ANALYSIS OF BENTHIC MEIOFAUNA FROM THE MAFLA/ EASTERN GULF OF MEXCIO

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ABSTRACT

Meiofauna density in the eastern Gulf of Mexico-MAFLA region are in the range for densities from other parts of the world. Marine free-living nematodes comprised 70.3% of all the meiofauna, copepods 14.2%, and polychaetes 4.5%. Density was highest in shallow inshore waters and decreased to lowest values in depths > 100 m. An inshore density depression is evident south of Mobile Bay where large river inputs apparently reduced meiofauna density. Meiofauna densities peak in moderate to high carbonate, medium to fine sands. Association patterns between taxa, between and within stations, and between seasons do not show any definite trends. Correlations between taxa and physical parameters are nonexistent or weak. This is due probably to the limited taxonomic identification. Thirty families of marine free-living nematodes were described from nine selected stations. All are indicative of sandy habitats. Some general reports are records for the North American continent.

INTRODUCTION

The term "meiobenthos" (meiofauna) was first coined by Mare (1942) to describe those benthic metazoans of intermediate size. These are smaller than those called "macrobenthos" but larger than those called "microbenthos." McIntyre (1964) asserts that there is no clear cut separation between the macro- and meiobenthos; the latter simply refers to those metazoans, which, because of their small size, can be most efficiently sampled by techniques differing from those used with larger organisms. The meiofauna are a very heterogeneous group including members in the psammon, endopelic, epibenthal and phytal modes of existence. Other authors (McIntyre, 1960; Muus, 1966) further break the meiofauna into 1) the temporary meiofauna, those spending only the larval part of their life in the meiofauna (usually larvae of macrofauna), and 2) the permanent meiofauna, including Rotifera, Gastrotricha, Nematoda, Archiannelida, Tardigrada, Copepoda, Ostracoda, Mystacocarida, Turbellaria, Oligochaeta, Polychaeta, Acarina, Gnathastomulida, Hydrozoa, Nemertina, Bryozoa, Gastropoda, Soelenogastres, Holothuroidea, Tunicata, Priapulida and Sipunculida. It is generally accepted that the term meiofauna refers to those metazoans which pass through a 500 μm mesh sieve but are retained on a 63 μm mesh sieve.

In recent years the increased interest in the meiofauna has produced an expanding volume of literature in many aspects of this field. However, examination of much of this literature shows it to be concentrated in the intertidal to shallow subtidal (Wieser, 1960; Coull, 1970; Tietjen, 1969) and the deep sea (Coull, et al., 1977). Quantitative estimates of the meiofauna of continental shelf areas, especially the Gulf of Mexico are rare. Traditionally, benthic research has centered on the macrofauna, probably due to their commercial value. This lack of data is all the more evident with the recognition of benthic ecologists of the significance of the smaller metazoans (Mills, 1975). Gerlach (1971, 1978) has suggested that the meiofauna may be responsible for five times the food supply of the macrofauna at any given place and time.

Meiofauna numbers and biomass vary greatly according to season, latitude, water depth, sediment characteristics, etc., but on the average one can expect to find densities of 10^6 m^{-2} and dry weight biomass of 1-2 g m^{-2} (extremes may reach densities of 10^9 m^{-2} and biomass of 11 g m^{-2}) (McIntyre, ND; Gerlach, 1978). Numbers and biomass decrease with increasing depths (1.18×10^7 m^{-2}, 11.2 g m^{-2}; McIntyre, ND). Values tend to be highest in detritally derived sediments and lowest in clean sands. Nematodes and harpacticoid copepods are usually the most abundant taxa. It is interesting to note that meiofauna are able to exist successfully in areas where macrofauna do poorly (i.e., exposed beaches) as well as in areas of rich macrofauna (McIntyre, 1968).

Distribution of meiofaunal taxa is closely related to sediment characteristics. In areas where the median grain diameter is below 125 μm burrowing meiofauna dominate. Interstitial groups such as gastrotichs are excluded from this habitat and conversely, Kinorhyncha (an endopelic taxon)

are excluded from the interstitial habitat (B.C. Coull, personal communication). In taxa with both interstitial and endopelic representatives, e.g., Nematoda, Copepoda, Turbellaria, there is usually a difference in morphology between organisms of the various habitats. Classically, interstitial forms are small and slender whereas burrowing forms are relatively large.

Most meiofauna are restricted to the upper levels of the sediments, generally above the reducing layer, although some function as true anaerobes (Fenchel and Riedl, 1970). Subtidally 90-95% of all meiofauna are located in the upper 7 cm and 60-70% in the upper 2 cm (Wieser, 1960; de Bovee and Soyer, 1974). Horizontally, meiofauna are known to exhibit patchiness in even apparently homogeneous sediments (Gray and Rieger, 1971; Gerlach, 1977; Lee et al; 1977).

Because of their small size and short generation times the meiofauna are probably more sensitive to, and, therefore better indicators of environmental stress than their macrobenthic counterparts (Fenchel, 1967; Coull, 1972; Marcotte and Coull, 1974; Pequegnat, 1975). Two basic problems, however, must be overcome before utilizing this assemblage. Firstly, the intrinsic spatial and temporal variation within the system must be established, and secondly, a level of taxonomic identifications vs. system completeness must be set. Depending upon the level identified (i.e., taxon, family, genus) one may be capable of describing only major taxonomic trends and associations rather than the ongoing community dynamics.

In the following I will describe the meiofaunal assemblages of the Mississippi-Alabama-Florida (MAFLA) region of the Gulf of Mexico and relate these assemblages to the available physical parameters. The interpretation of these data has been limited, from onset, by the level of taxonomic identification, i.e., taxon level for six of the most abundant groups and genus level for the Nematoda from only nine selected stations. A second problem in the interpretation of the data arose with the entire change of personnel (including PI) with the beginning of the 1977 program. Discrepancies in the data base between programs are evident and are most probably due to differences in methodology used and taxonomic interest of the Principal Investigators. Most of the interpretation that follows will, therefore, be based on samples from summer 1977, fall 1977, and winter 1978. Even with the small non-specific data base, some very evident and interesting trends have developed and with continued studies of material gathered during this program it is felt that significant contribution will be made in the study of meiofauna of the continental shelf.

MATERIALS AND METHODS

SHIPBOARD PROCESSING

Two quantitative samples were removed from each of three box-cores from the 30 primary stations during each of the three cruises and from the six supplemental stations during the summer cruise. Also one subsamples was taken from the single box-core at each of the 13 secondary stations during each of the three cruises.

Samples were removed using a 3.5-cm diameter lucite core pushed to a depth of 5 cm. The plug was placed in a labeled glass jar containing a measured volume of 10% isotonic magnesium chloride and rose bengal for 20 minutes. A measured volume of 15% buffered formalin in seawater was added to the jar to bring the final preservative concentration to 10%. The jars were sealed and additional labels placed on the outside with masking tape. During the summer and fall cruises (DM I, DM II) samples were taken from box-cores 1, 2, and 3. Due to length of time required for hydrocarbon analyses on box-core 1, a change was made on the winter cruise (DM IV) so that meiofaunal samples were taken from box-cores 2, 3, and 4 on the primary stations.

LABORATORY PROCESSING

A modified elutriation was used in which each sample was washed through 500 m and 63 m mesh sieves. The residue remaining on the 63 m sieve was washed from the sieve and treated as follows:

1. Make up elutriate sample to 200 mℓ
2. Divide into two ~100 mℓ portions (splits)
3. One technician to subdivide each split into four ~25 mℓ portions and proceed with the following
4. a) If there are less than 50 nematodes in the first 25 mℓ portion, count all nematodes and other taxa listed in number 5 in the entire sample
   b) If there are more than 50 nematodes in the first 25 mℓ portion, count all nematodes in this portion, disregard nematodes in remaining 75 mℓ, count and collect other taxa listed in number 5 in the entire sample (see instruction 6b).
5. Taxa to be counted and collected include:
   a. Nematodes
   b. Copepods
   c. Turbellarians
   d. Kinorhynchs
   e. Gastrotrichs
   f. Polychaetes
   g. Miscellaneous (cnidarians, ascidians, gnathostomulids, tardigrades, oligochaetes, mites, ostracods, nemerteans, priapulids, protozoa
6. Data analysis:
   a) Samples falling into category 5
   Numbers from each 100 mℓ split are added together and multiplied by 1.039 to give numbers · 10 cm^{-2} for each taxa.
   b) Samples falling into category 4b
   Nematodes counted from first 25 mℓ are multiplied by 4. The two independent "estimates" are added together for the two 100 mℓ portions to give an estimate of total nematodes. Numbers of other taxa added together from each split. Nematodes and other taxa are multiplied by 1.039 to give numbers · 10 cm^2. These samples are indicated

as estimated on data file. This indication is noted on permanent data file in event questions arise during data analysis/discussion.

All sorted specimens were placed in properly labeled one dram shell vials containing 10% buffered formalin or 70% ethyl alcohol with 15% glycerin depending on the taxa. The glycerin is added to prevent dessication during storage.

Data are reported as numbers of individuals per 10 cm^2 for the six higher taxa and for the miscellaneous group on the data file forms provided by Dames & Moore. Original data sheets with comments on specific taxa are retained by the principal investigator.

Nematodes from nine selected stations (2748, 2851, 2102, 2104, 2106, 2957, 2958, 2959, 2960) are being identified to genus level by Bruce E. Hopper. Slides containing 60-100 specimens per sample were prepared. For details refer to Dames & Moore, 1978e, Third Quarterly Progress Report, MAFLA Benchmark Survey, February-May, 1978 Appendix D.

STATISTICAL TREATMENT OF ESTIMATED SAMPLES

To determine the precision of the estimation technique, nine samples were first sorted using the estimation technique and then resorted with all nematodes being counted. The 95% confidence limits on means of estimates and means of counts were determined.

Results of the statistical treatment of the estimation technique show that at the 95% confidence level there is no difference between the mean estimates and the mean counts. All counts fit around a line $y = 1.2\ x$, however, no correction was attempted with the estimated data (Figure 202), since the data cannot be determined to be different.

ARCHIVED 1976 SAMPLES

Due to the compaction of many of the samples, the question of preservation of the others and the lack of time, the archived samples of meiofauna were not sorted.

DATA ANALYSIS

All values reported are converted to the standard meiofauna unit of number per 10 cm^2 (Hulings and Gray, 1971). R-mode (Harmon, 1967) and Q-mode (Cattell, 1965) factor analyses were run on each seasonal data set to discern if any association existed between the meiofauna on the taxon level or between the stations, based on taxonomic composition, respectively. Data used in these analyses had undergone square root transformation to reduce the effect of nematode abundance on the analyses. The similarity matrices were developed utilizing Bray-Curtis similarity coefficients

$$S = \frac{2C}{A+B}$$

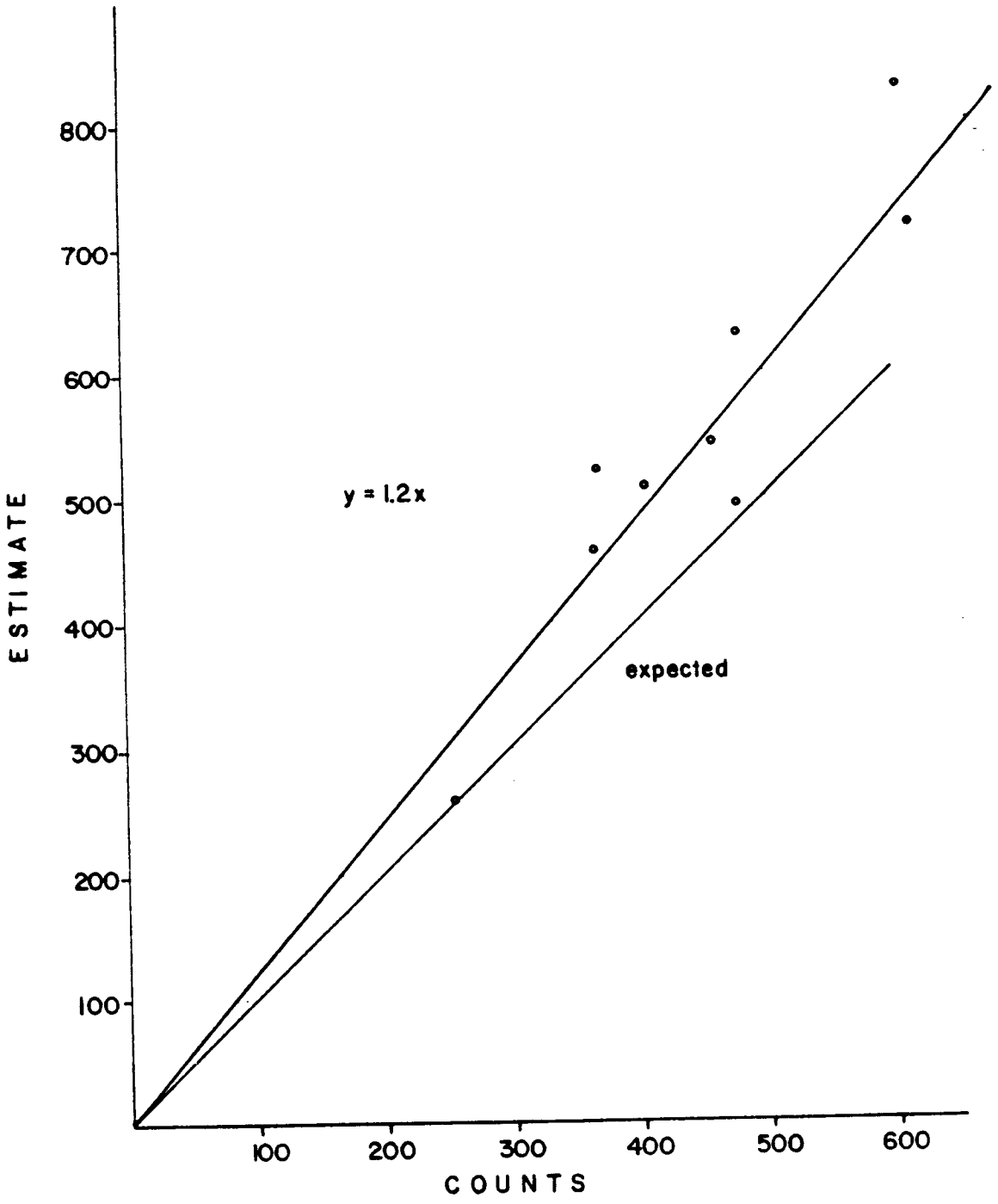

800
700
600
500
400
300
200
100
ESTIMATE
y = 1.2x
expected
100
200
300
400
500
600
COUNTS

Figure 202

where C is the number of species held in common between two stations, and A and B are the number of non-common species from any Stations A and B (Bray and Curtis, 1957).

Stepwise multiple regression (Davis, 1973) was run on meiofauna taxonomic data from summer, 1977 vs. depth, total organic content, calcium carbonate content and percent silt-clay to determine if there were any correlations between distribution and physical environment. This analysis was also run on the taxa in the Nematoda alone.

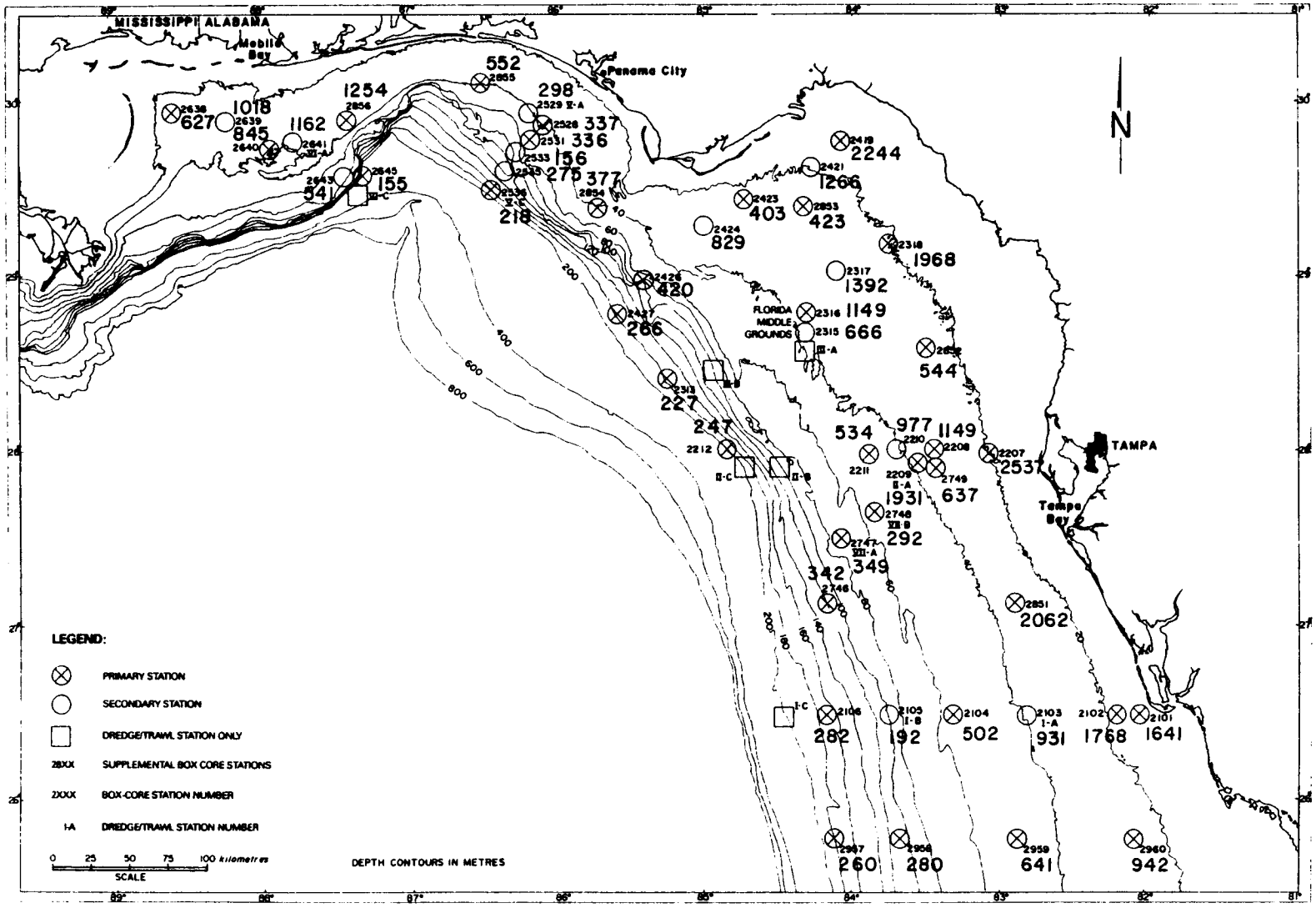
RESULTS

Marine free-living Nematoda was the dominant taxon encountered. Overall, nematodes comprised 70.3% of the total meiofauna. With the exception of Station 2530 (sampled 1975-1976 only) nematodes were the dominant form for all seasons, all years and all stations. Nematode abundance ranged from 29.6% (Station 2530-S75) to 98.6% (Station 2637-F75). Copepoda (> 95% harpacticoids) was the second most abundant taxon comprising 14.2% of the total meiofauna. In two instances (Station 2530, S75 and F75) they were more abundant than the nematodes. Copepod densities ranged from 0.3% (Station 2638-F75) to 51.8% (Station 2530-S75). Polychaeta was the third most abundant taxon sampled, representing 4.5% of the total abundance. In some cases, the Polychaeta were the second most abundant taxon. However, with lack of species identification it is not known whether these forms were members of the permanent meiofauna or represented "blooms" of temporary meiofauna. The Turbellaria and Gastrotricha were the fourth and fifth most abundant meiofauna taxa, 2.8% and 2.6%, respectively. At Station 2855 (S77) the gastrotrichs were the second most abundant taxa. Kinorhycha represented 0.8% of the total meiofauna abundance. Representatives of all remaining meiobenthic forms listed in the Introduction were encountered at some time during the study and collectively represented 4.8% of the total abundance.

Total meiofaunal density (all taxa; mean of replicate cores) ranged from 65 . 10 cm^{-2} (Station 2533-S77) to 3752 · 10 cm^{-2} (Station 2207-F75). Average station meiofauna densities for the entire study period ranged from 155 · 10 cm^{-2} (Station 2645) to 2537 · 10 cm^{-2} (Station 2207) (Figure 203). Meiofaunal densities are highest in shallow waters, < 40 m, mean value, 1200 • 10 cm^{-2}, and decrease significantly to depths of 100 m (mean value, 240 • 10 cm^{-2}). Total meiofauna densities, of course, reflect the density fluctuations of the major taxa and overall indicate highest densities in inner to mid-shelf areas in the region from 29°45'N to 26°50'N and the inner shelf area in the region from 87°20'W to 88°10'W (Figure 203). Meiofaunal densities peak in the moderate to high carbonate (30-85%), medium to fine sands (1.7-2.6 Ø median diameter) in less than 40 m depth.

Seasonal density peaks (Figure 204) do not reveal any of the expected relationships with latitude or depth. In fact, for most of the stations, the density peaks did not coincide from year to year. Density peaks are represented by the letter and year of the season in which they occurred.

Results of factor analyses run on data from 1975-76 and 1977-78 are shown in Figures 205 through 212. R-mode factor analyses for summer and fall 1975 and winter 1976, and summer and fall 1977 and winter 1978 are



BLM 77/78 MAFLA SURVEY STATION LOCATIONS

FIGURE 203 Meiofaunal densities, number per 10 cm^2.

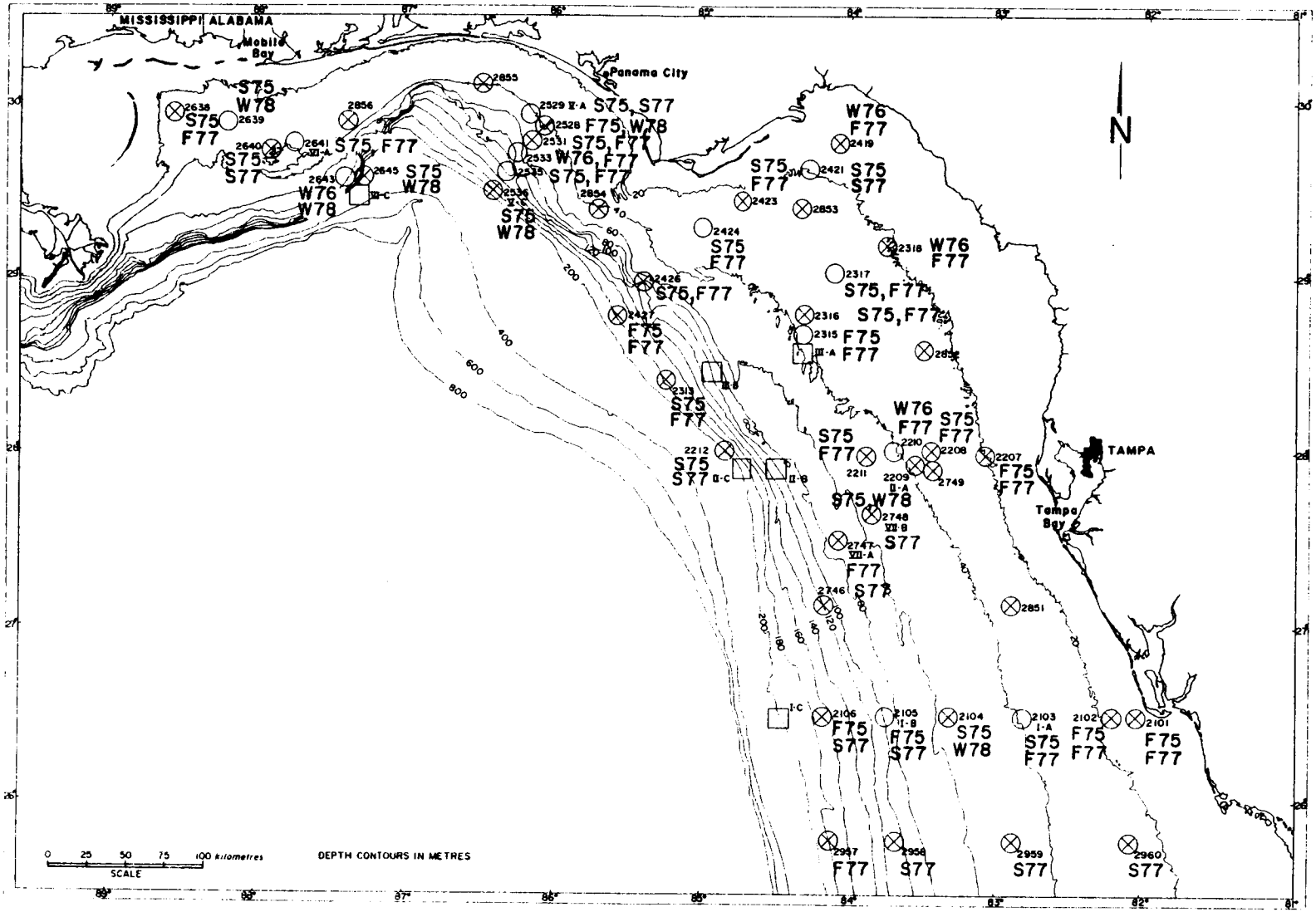


FIGURE 204 Time of maximum density.

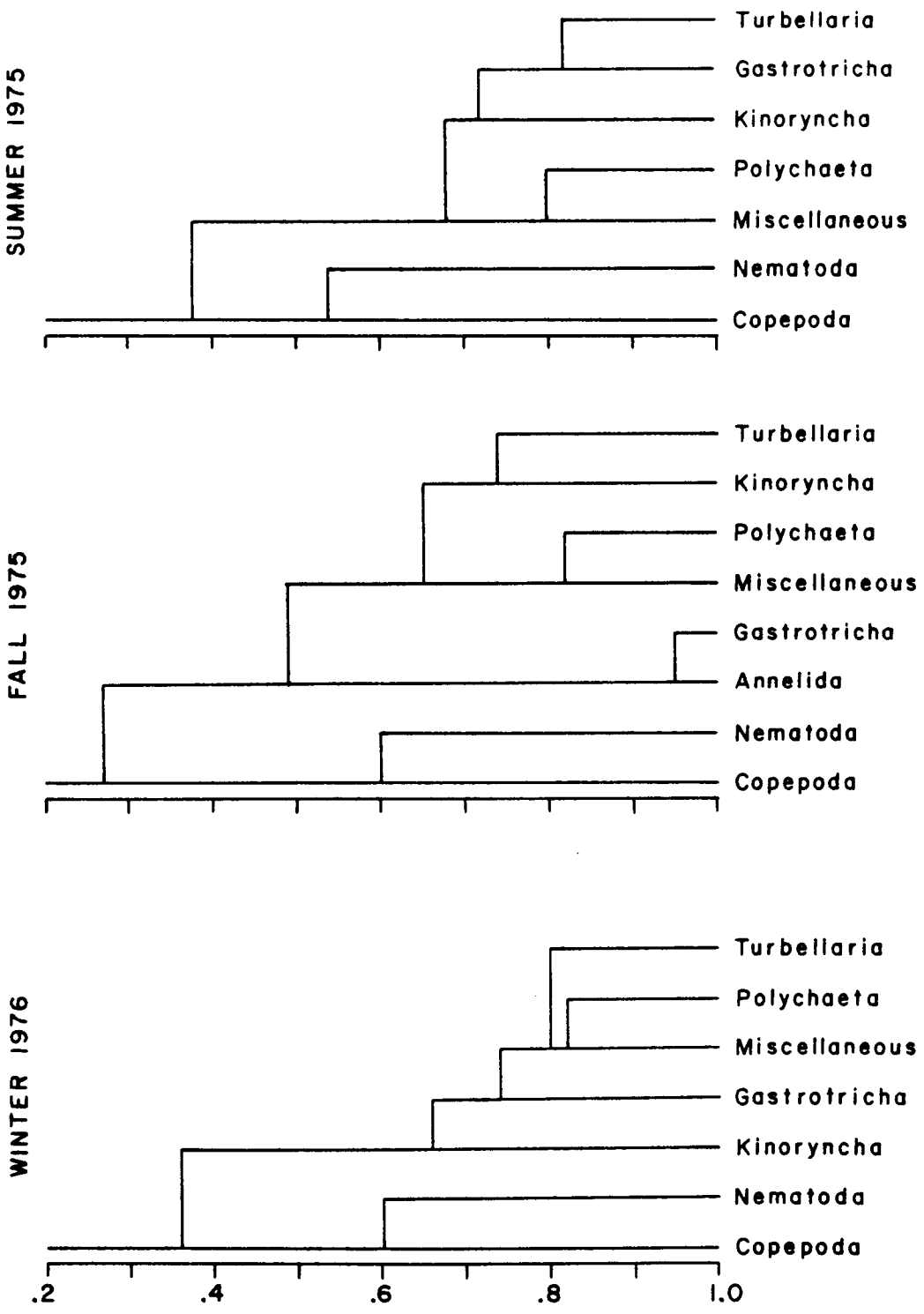


FIGURE 205 Similarity dendrograms - R-mode Factor Analysis

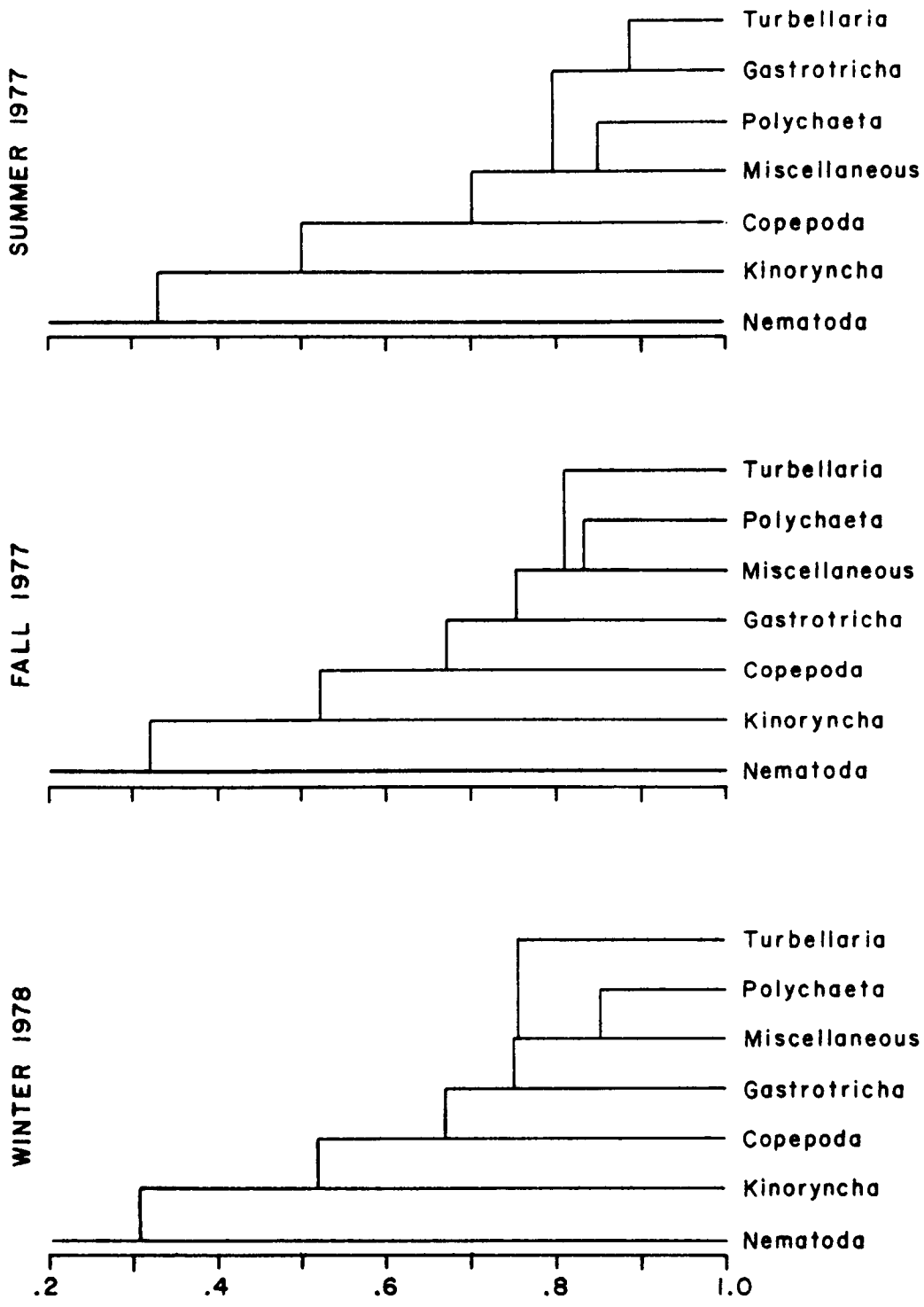


FIGURE 206 Similarity dendrograms - R-mode Factor Analysis

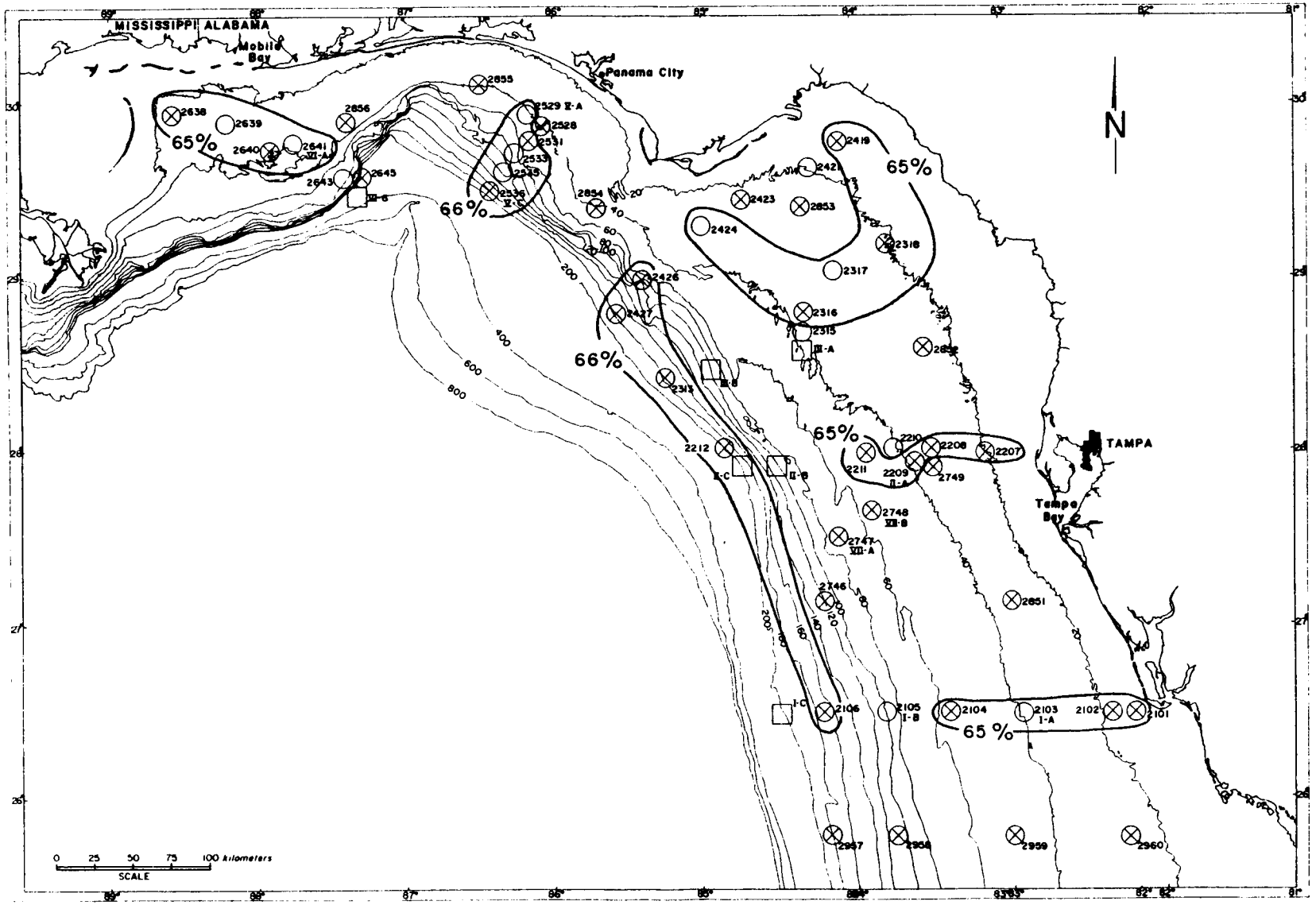


FIGURE 207 Q-mode Factor Analysis. Similarity between stations, Summer 1975.

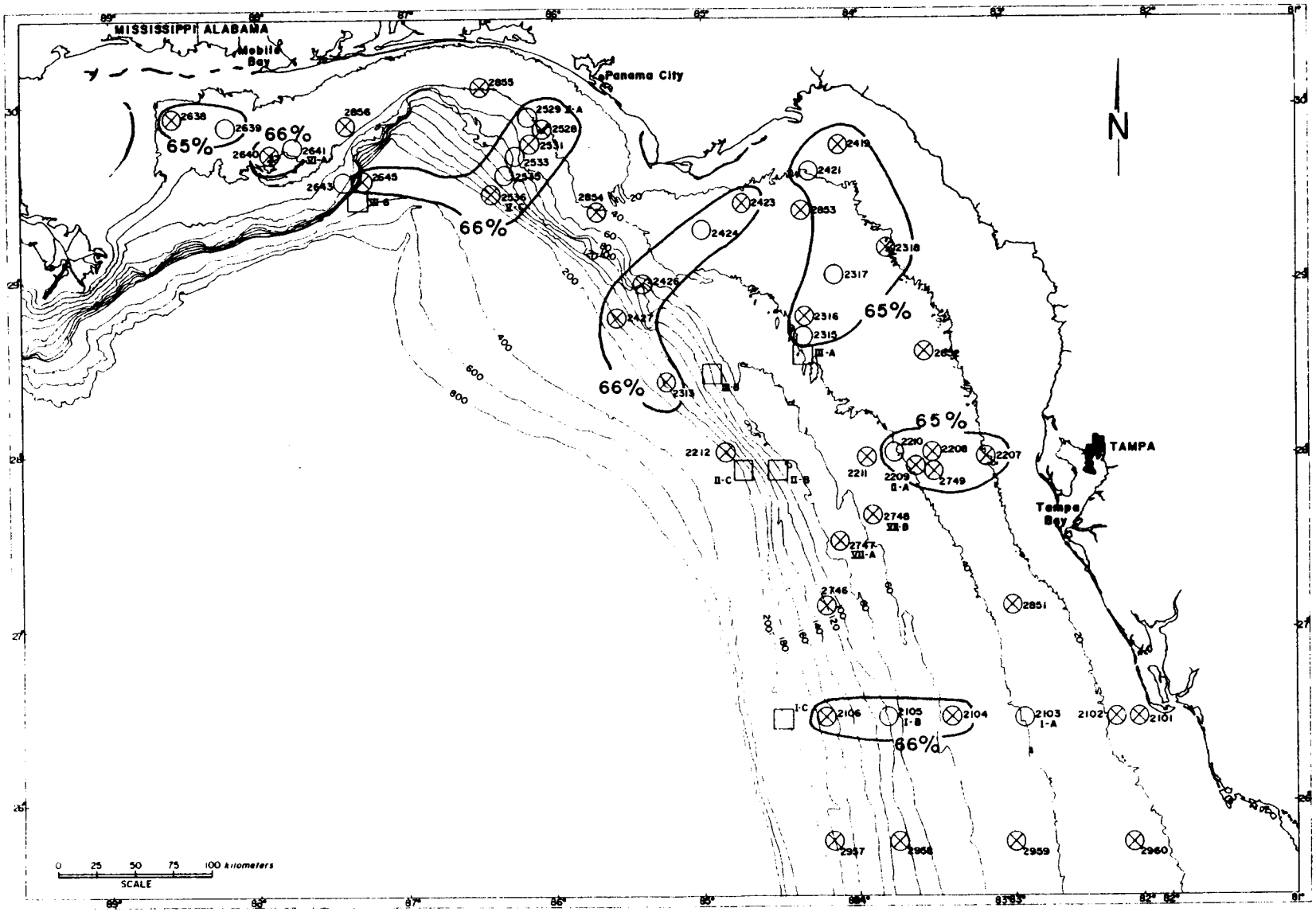


FIGURE 208 Q-mode Factor Analysis. Similarity between stations, Fall 1975.

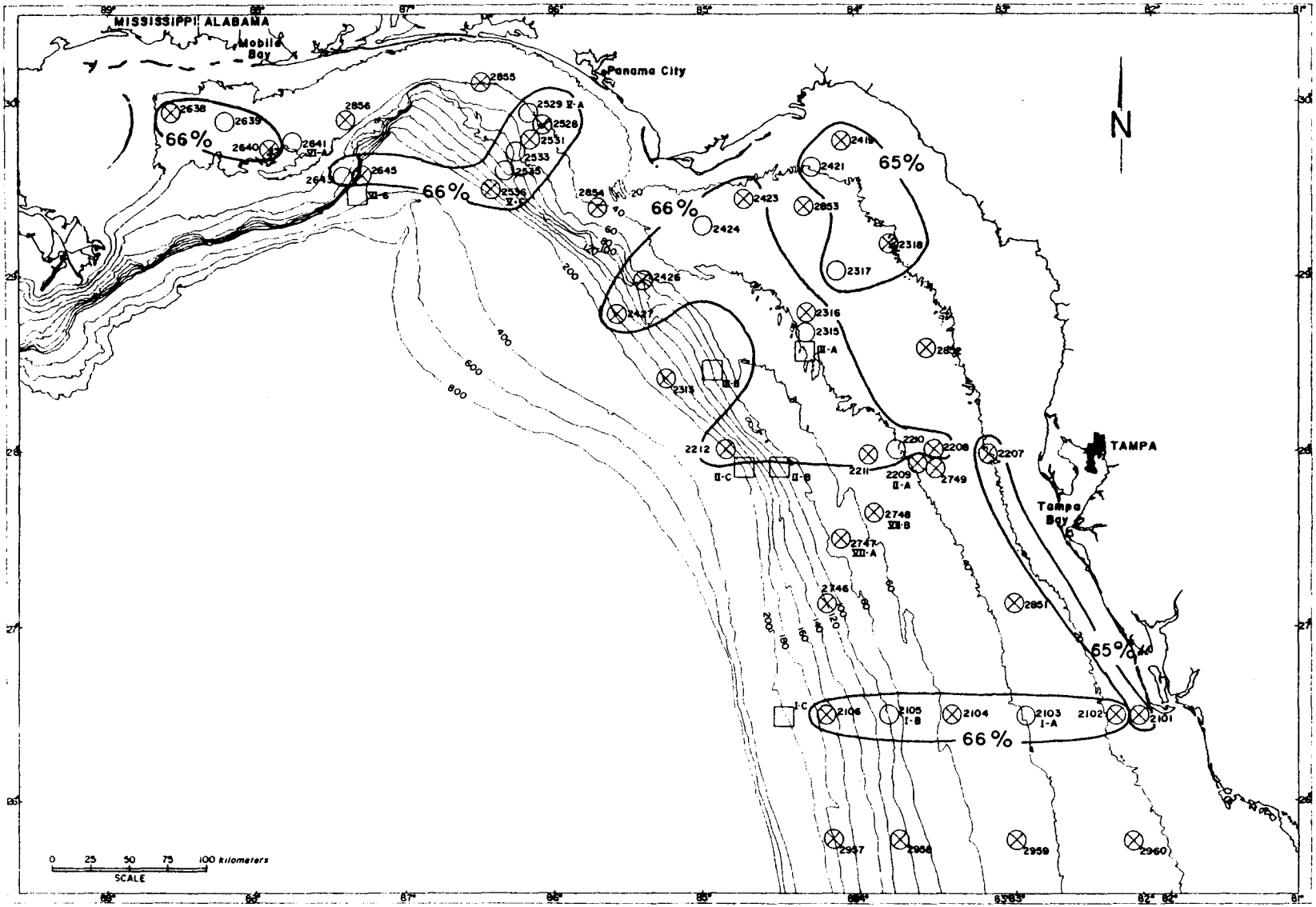


FIGURE 209 Q-mode Factor Analysis. Similarity between stations, Winter 1976.

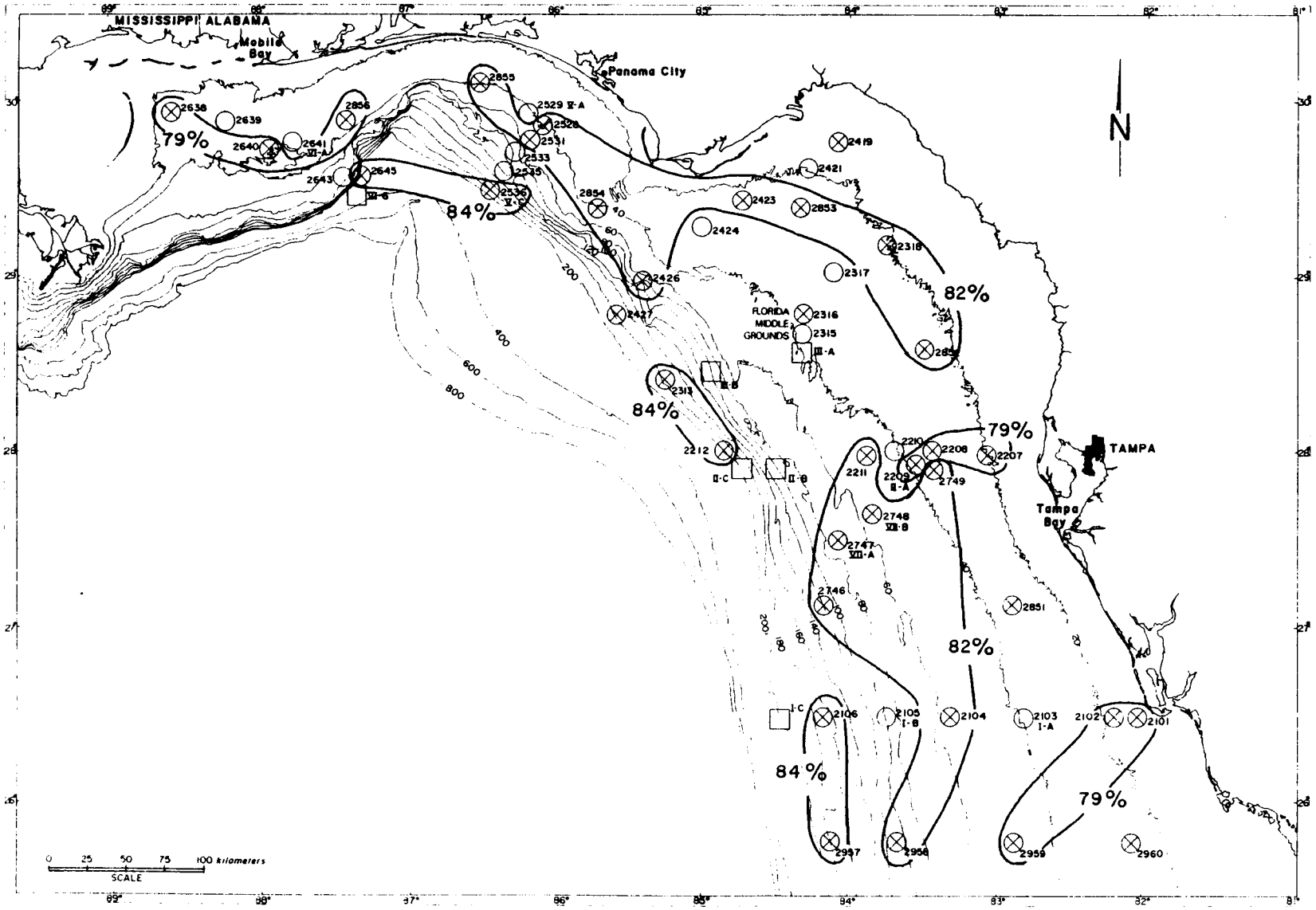


FIGURE 210 Q-mode Factor Analysis. Similarity between stations, Summer 1977.

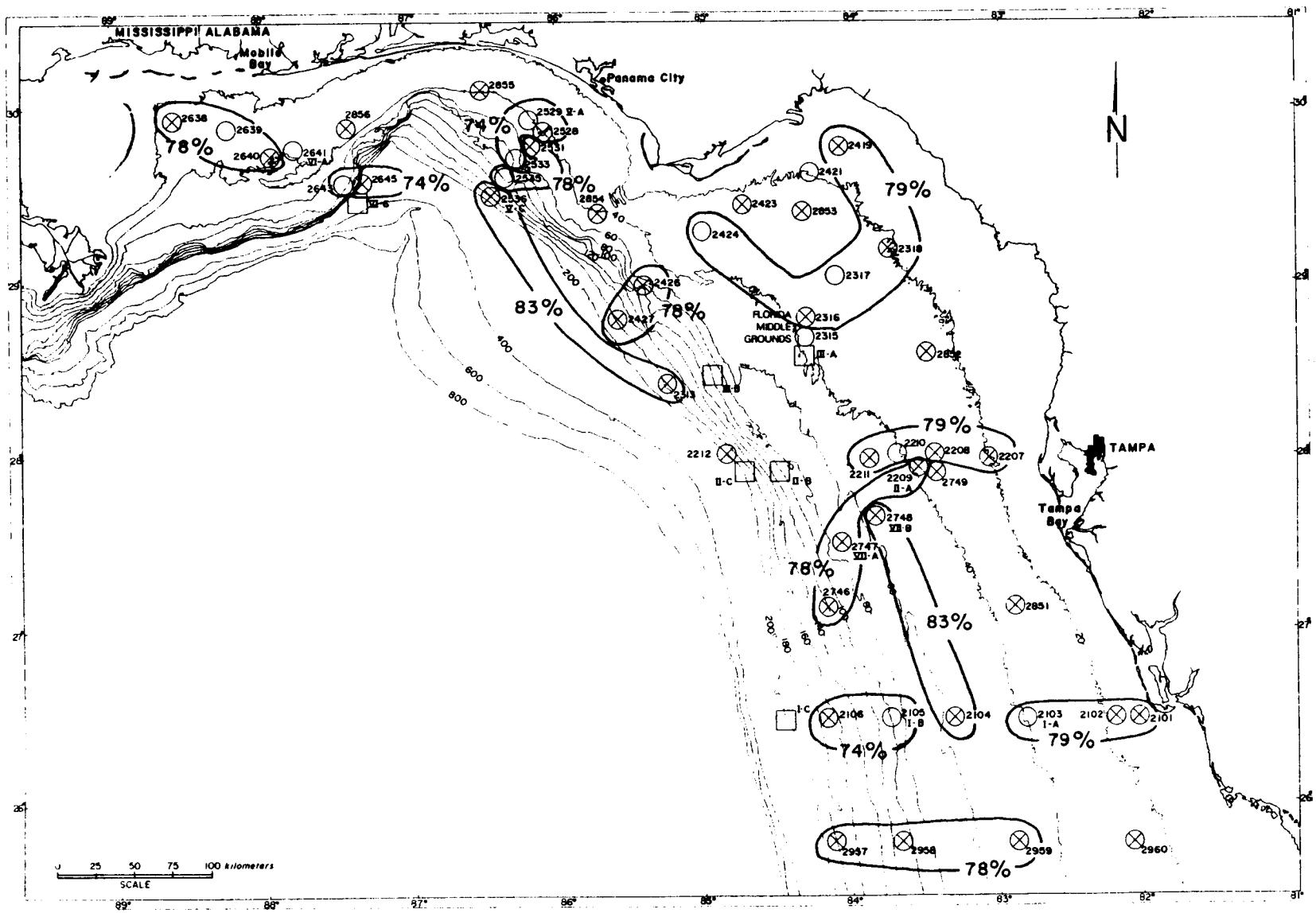


FIGURE 211 Q-mode Factor Analysis. Similarity between stations, Fall 1977.

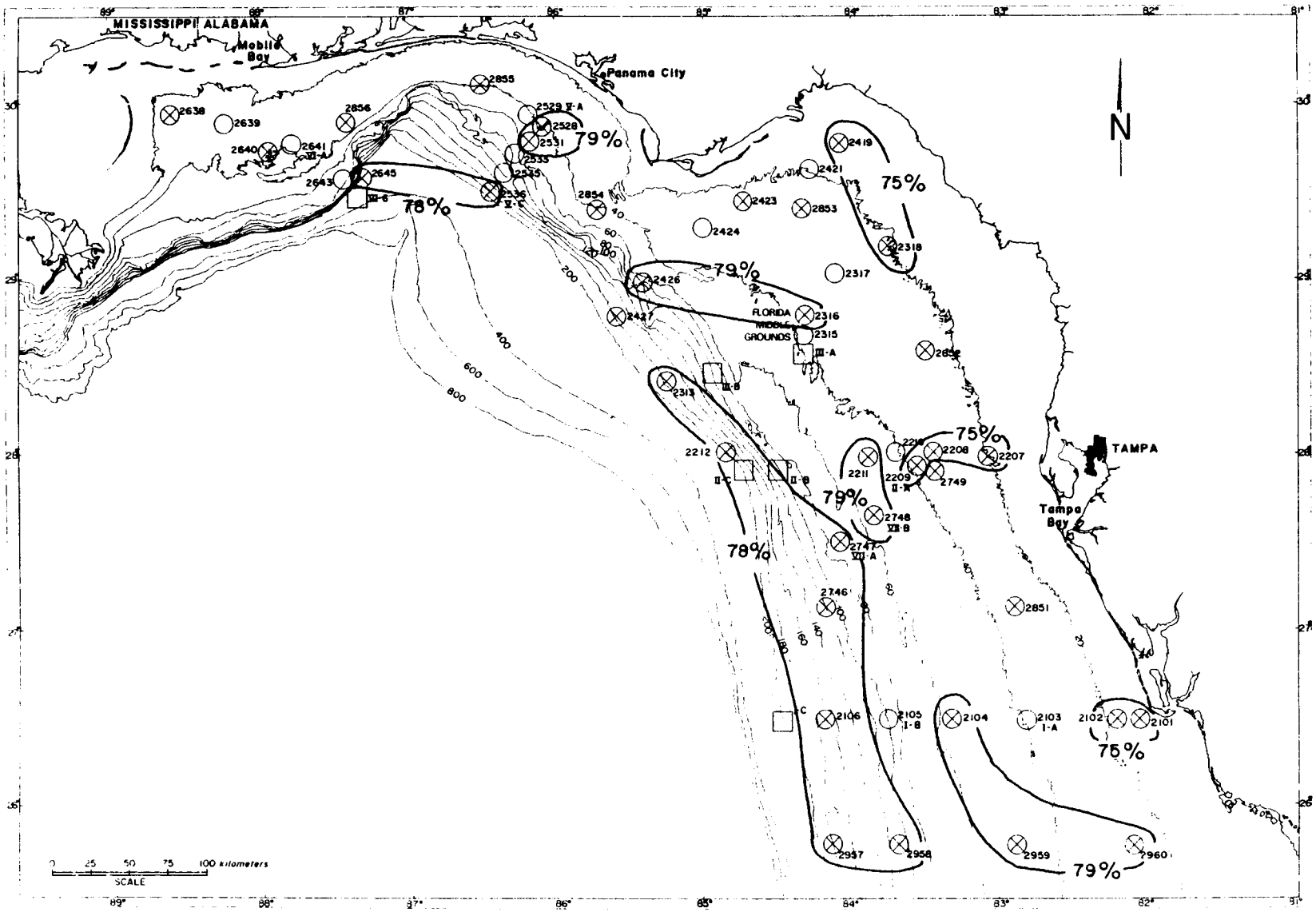


FIGURE 212 Q-mode Factor Analysis, Similarities between stations, Winter 1978.

shown in Figures 205 and 206, respectively. In Figure 205 the only apparent faunal associations are between the taxa Nematoda and Copepoda. In Figure 206 the faunal assemblages from fall 1977 and winter 1978 are remarkably similar. Comparing summer 1977 to the former two there appears to be some similarity in abundance and distribution of the taxa Copepoda, Kinorhyncha and Nematoda. However, the similarity between taxa with any one analysis should be taken with much reservation due to the level of taxonomic identification. Comparison of faunal associations between the data sets shows no trends of temporal similarity in overall community structure.

Figures 207-212 represent results of Q-mode factor analyses of each seasonal data set. Stations are grouped based on similarity of faunal assemblages. These groupings represent the greatest similarity between stations. Similarity between groupings is not represented due to complexity of graphing. Figures 207, 208, and 209 are markedly similar to each other with associations in Transect I, inshore stations north of Tampa Bay, inshore stations in Appalachee Bay, Transect V and stations west of Mobile Bay. Associations in the 1977-78 stations (Figures 210, 211, and 212) are much more variable on a seasonal basis. Some similarity is apparent between fall and winter in the regions of Transects IX, I, north of Tampa Bay and Appalachee Bay. Summer 1977, on the other hand, appears to have station associations much different from the others.

Comparing within seasons, in summer (Figures 207 and 210) there is some stability in station groupings, e.g., Mobile Bay stations and Tampa Bay stations. In fall (Figures 208 and 211) a great degree of stability exists between station groupings, but in winter (Figures 209 and 212) there is almost no basis for comparison.

Stepwise multiple regression on meiofauna taxa data obtained in summer 1977 was run against total organic carbon, percent calcium carbonate in sediments, percent silt-clay and depth. All meiofauna taxa showed negative correlations with depth. The Gastrotricha showed a slight positive correlation with percent calcium carbonate, TOC and percent silt-clay. The miscellaneous category also showed positive correlation with TOC and percent silt-clays.

Thirty families from seven orders of marine free-living nematodes were encountered in samples from the nine selected stations in three seasons (Appendix I). The majority of the species encountered belong to the orders Desmodorida and Chromadorida.

DISCUSSION

The total meiofaunal density values shown in Figure 203 are in the range of values for other continental shelf ecosystems. Tietjen (1971) found 352-849 organisms•10 cm^{-2} off the Carolinas, Wigley and McIntyre (1964) report 127-988 on the shelf of Southern New England and the South Atlantic Bight Program study reports 957•10 cm^{-2} (< 100 m) and 364 • 10 cm^{-2} in depths greater than 100 m (B.C. Coull, personal communication). The decrease in numbers off the shelf is consistent with other slope studies and the mean value of 249 • 10 cm^{-2} in water deeper than 100 m agrees with Wigley and McIntyre's (1964) values of 117-537, Tietjen's (1971)

values of 40-1174 and Coull et al.'s (1977) 217-1138 · 10 cm^{-2} on the slope off the Carolinas at 400 and 800 m.

The general decrease in total abundance with depth (Figure 203) was as predicted and known from other meiofaunal studies (Thiel, 1975). It is interesting to note that in areas of maximum freshwater discharge, i.e., Station 2638, the inshore densities are significantly lower than those in areas of reduced runoff (e.g., Stations 2419, 2101, 2107). It appears that the influence of Mobile Bay runoff, particularly silt-clay load, may be responsible for the depression in meiofauna abundance.

The lack of correlation between temperature and salinity distributions and food resource (measured as ATP and total organic content) with meiofaunal abundance is surprising. It is most intriguing that the stations with the greatest fluctuations in temperature and salinity (T. B. Scanland, personal communication). Station 2419 had salinities consistently below seasonal means and an 18.7°C temperature range yet had densities greater than 2,000 · 10 cm^{-2}. Stations 2318 and 2207 had temperature fluctuations of 17.1°C and 16.8°C, respectively. ATP measures indicate relatively high amounts of living microbial biomass but these values include the meiofauna themselves and total organic content of the sediments are low. These stations would represent what Valentine (1971) classified as unstable poor resource areas which theoretically should have low diversity and moderate to low population sizes. In these areas, sediment texture may be an overriding factor. Yet if this is true one would expect to find high abundance in areas of very fine sands - coarse silts and clays. This is not the case of these three stations, 2419 and 2318 are characterized by medium sands ($\bar{x}$ = 2.6 Ø).

The lack of seasonal reproductive patterns, except along Transect IX, is also surprising. This is probably due, however, to the few data points per station and the long time period between samples. The offshore delay in abundance pattern in Transect IX is as one would expect. Nothing, however, can be deduced concerning reproductive patterns.

Most meiofaunal studies have been able to correlate meiofaunal density and sediment granulometric correlates (Ivester, ms.). Only in one case, the Gastrotricha, did a positive correlation between taxa and sediment variables occur. The Gastrotricha are known to be most abundant in clean fine sands. The Kinorhyncha should have also shown significant correlation (all except one genus are endopels), but I suspect their low abundance precluded this correlation. The lack of correlation with other taxa again reverts to the level of identification. Since most of these taxa have both psammic and endopelic representatives, it would be impossible to correlate with specific sediment size classes unless we were using species level identifications.

Graphical interpretation using abundance data indicates there are interactions between various physical parameters, including sediment granulometry, controlling distribution of total meiofauna. In areas of similar salinity, temperature, calcium carbonate content, and depth (i.e., 2208, 2209, 2749), grain size appears to play a leading role. In areas of similar

salinity, temperature, calcium carbonate content, depth and grain size, some stations have similar abundance values (i.e., 2210 and 2209). This lack of correlation between density and sediment parameters is, I believe, a function of taxonomic identification level.

Examining closer the four stations mentioned above (i.e., 2211-2748 and 2210-2209) another problem with identification level arises. Even though very similar in total abundance, Stations 2211 and 2749 are very dissimilar in faunal composition with 73.8% nematodes-16.1% copepods and 47.8% nematodes-21.9% copepods, respectively. On the other hand, the dissimilar Stations 2210 and 2209 are very similar according to faunal composition with 84.4%-6.9% and 84.4%-9.4% nematodes and copepods, respectively.

Similarity analyses on faunal associations (1977-78, Figure 206) do not give much information because of the level of identification. That which is evident, i.e., the apparent association between The Turbellaria, Gastrotricha, Polychaeta and miscellaneous, should not be taken to mean they are positively correlated in some biological or physical sense. Instead, this reflects the data that mean abundance values for these taxa are similar. The entry of the Kinorhyncha at such low levels of similarity between the Copepoda and Nematoda and between the above mentioned groups is due to the dominance of these forms in the meiofaunal assemblage and dominance of Nematodes over copepods. The similarity between dendrograms for fall 1977 and winter 1978 shows that the composition of taxon abundance did not shift significantly as it did in the summer. Differences in structure in 1975-76 (Figure 205) and 1977-78 (Figure 206) are probably due to differences in methodology, and I do not feel comfortable discussing data I did not collect.

Q-mode factor analyses on taxa abundance reveal associations between and within stations on a seasonal basis. In all cases (Figures 207-212) spatial variation is most noticeable both within seasons and between seasons. Temporal variation is evident both between seasons and within seasons for different years. Overall, trends indicate some similarity among the stations on Transect I. However, variations in this similarity are not on a predictable basis. There is also some apparent similarity among the stations north of Tampa Bay, and in this case the similarity is on a somewhat semi-permanent/predictable basis. The stations around Appalachee Bay also show a semi-permanent, though variable association. By stretching one's imagination some resemblance is noted between summer 1975 and fall 1977 associations. It would be interesting to know the significance. of these similarities and how the unusually cold winters of 1976 and 1977 influenced these associations. The cold winters may also play a role in the disappearance of the association of stations south of Mobile Bay in the winter 1978. In general, greater stability of community composition is exhibited in the mid shelf and southern regions of the MAFLA region. This is probably due to 1) reduction of physical fluctuations felt in shallow shelf areas and 2) the larger number of meiofauna able to live in less than 100 m depth. Theoretically, however there should be a very stable population in the deeper areas. Even with some general trends evident, I would argue that clustering at the meiofauna taxon level is deceiving. To

accurately determine zonation and/or sediment correlates and meiofauna, it is imperative that identifications be made at the species level.

Since the Nematoda were the most abundant taxon they were singled out for more intense studies. Due to their large numbers, however, only representative forms from nine stations (2748, 2851, 2102, 2104, 2106, 2957, 2958, 2959, 2960) were identified to genus.

Densities of Nematoda ranged from a low of 18 · 10 cm^{-2} at Station 2535 (S77) to a high of 3220 · 10 cm^{-2} at Station 2209 (S75). Yearly average densities ranged from 81 · 10 cm^{-2} at 2533 to 2145 · 10 cm^{-2} at 2207. These densities are greater than those reported for the MAFLA area in 1974 (M.R. Crezee, personal communication).

These densities are comparable to the 157-593 nematodes · 10 cm^{-2} found in sandy areas off the Carolinas (50-100 m) (Tietjen, 1971). Shallow sand station nematode abundances are comparable to those of McIntyre and Murison (1973) on the coast of Scotland (6-7 m, 328-2172 · 10 cm^{-2}). Shallow mud stations are comparable to those of Wieser (1960) (328 · 10 cm^{-2}) in Buzzards Bay.

From the nine selected stations, 46 genera of marine free-living nematodes representing 30 families and 7 orders were identified.

The nematode fauna of the area sampled is very diverse and representative of a sand-inhabiting community. The Cyatholaimidae, Desmodoridae and a majority of the Monhysteridae found are indicative of sandy habitats but are present, to some degree, at all stations. Members of the Comesomatidae and the Linhomoeidae are indicative of muddy or silt-clay environments; they were present most abundantly at Stations 2106 and 2957 (especially certain species of Sabtieria and Terschellingia). Sabatieria hilarula which occurs in our sand habitats have long setae and are thus indicative of sand-inhabiting species. Tietjen (1977) finds over 25% of nematodes of the family Desmodoridae occupy fine to medium coarse sands.

Chromadoridae are normally found in association with algae. Their relative scarcity in the area sampled indicates a deficiency of algae.

The majority of the nematodes found are from the order Desmodorida and Chromadorida. The members of the order Enolopida were relatively scarce. This is to be expected since the members of this order are normally assumed to be of the omnivore-predator feeding group. It is not surprising, therefore, that this group is in lower numbers than the groups upon which it is presumed to feed.

Several of the genera of Nematoda reported in this study have not been previously recorded in North America. Ixonema is known only from Helgoland, Parallelocoilas and Peresiana are known only from the Mediterranean and Paratricoma from Indonesia (2 species) and the North Sea (2 species).

CONCLUSIONS

1. Marine free-living nematodes were the dominant taxon, harpacticoid copepods were second, and polychaetes were third.

2. Meiofaunal densities were highest in shallow inshore regions grading to lowest in depths greater than 100 m. Mean total meiofauna densities were 1200 • 10 cm^{-2} in depth less than 40 m, 443 • 10 cm^{-2} in depths to 100 m, and 249 • 10 cm^{-2} in depths greater than 100 m.

3. Total meiofaunal density is shown to decrease with depth.

4. There was a general lack of correlation between total meiofaunal densities or taxon densities with all physical parameters measured except depth.

5. No seasonal reproductive patterns were discerned.

6. Some very general interpretations were made concerning station similarity, particularly those of Transect IX, those inshore north of Tampa Bay, those in Appalachee Bay.

7. Nematodes of the orders Desmodorida and Chromadorida dominate the southern nematode assemblage.

8. The nematode assemblage identified is representative of sandy habitats.

9. Four genera of nematodes are reported for the first time on the North American continent.

REFERENCES

Bray, J.R. and J.T. Curtis, 1957. An ordination of the upland forest communities of southern Wisconsin. Ecol. Monagr., 27: 325-349.

de Bovee, F. and J. Soyer, 1974. Cycle annuel quantitative due Meiobenthos des vases terrigenes cotieres. Distribution verticale. Vie Milieu, 24 (1B): 141-157.

Cattell, R.B., 1965. Factor analysis, an introduction to essentials. Biometrics, 21: 190-215.

Coull, B.C., 1970. Shallow water meiobenthos of the Bermuda platform. Oecologia (Berl.), 4: 325-357.

_____, 1972. Species diversity and faunal affinities of meiofauna Copepoda in the deep sea. Mar. Biol., 14: 48-51.

_____, R.L. Ellison, J.W. Fleeger, R.P. Higgins, W.D. Hope, W.D. Hummon, R. M. Riger, W.E. Sterrer, H. Thiel, and J.H. Tietjen, 1977. Quantitative estimates of the meiofauna from the deep sea off North Carolina, USA. Mar. Biol., 39: 233-240.

Davis, J.C., 1973. Statistics and data analysis in geology. John Wiley & Sons, New York. 550 p.

Fenchel, T., 1967. The ecology of marine microbenthos. I. The quantitative importance of ciliates as compared with metazoans in various types of sediments. Ophelia, 4: 121-137.

_____, and R.J. Riedl, 1970. The sulfide system. A new biotic community underneath the oxidized layer of marine sand bottoms. Mar. Biol. 7: 255-268.

Gerlach, S.A., 1971. On the importance of marine meiofauna for benthos communities. Oecologia (Berl.), 6: 176-190.

_____, 1977. Attraction to decaying organisms as a possible cause for patchy distribution of nematodes in a Bermuda beach. Ophelia, 16: 151-165.

_____, 1978. Food chain relationships in subtidal silty sand marine sediments and the role of meiofauna in stimulating bacterial productivity. Oecologia (Berl.), 33: 55-69.

Gray, J.C. and R.M. Rieger, 1971. A quantitative study of the meiofauna of an exposed sandy beach, at Robin's Hood Bay, Yorkshire. J. Mar. Biol. Ass. U. K., 51: 1-20.

Harmon, H.H., 1967. Modern factor analysis, 2nd, ed. Univ. Chicago Press, Chicago. 47 p.

Hulings, N.C. and J.S. Gray (Eds.), 1971. A manual for the study of meiofauna. Smithson. Contr. Zool. 78, 1-83.

Lee, J.J., J.H. Tietjen, C. Mastropaolo, H. Rubin, 1977. Food quality and the heterogeneous spatial distribution of meiofauna. Helgolander Wiss. Meeresunters., 30: 272-282.

Marcotte, B.M. and B.C. Coull, 1974. Pollution, diversity and meiobenthic communities in the North Adriatic (Bay of Piran, Yugoslavia). Vie Milieu, 24 (213): 281-300.

Mare, M.F., 1942. A study of the marine benthic community with species reference to the micro-organisms. J. Mar. Biol. Ass. U. K., 25: 517-554.

McIntyre, A.D., 1964. Meiobenthos of sublittoral muds. J. Mar. Biol. Ass. U.S., 44: 665-674.

_____, 1968. The meiofauna and macrofauna of some tropical beaches. J. Zool., London, 156: 377-392.

_____, N/D. Meiobenthos. Proc. Challenger Society, 4 (3): 1-9.

_____, and D.J. Murison, 1973. The meiofauna of a flatfish nursery ground. J. Mar. Biol. Ass. U. K., 53: 93-118.

Mills, E.L., 1975. Benthic organisms and the structure of marine ecosystems. J. Fish. Res. Bd. Canada, 32 (9): 1657-1663.

Muus, B.J., 1967. The fauna of Danish estuaries and lagoons, Distribution and ecology of dominating species in the shallow reaches of the mesohaline zone. Medd. fra Danmarks Fisk. -og. Havunders., N.S., 5 (1): 3-316.

Pequegnat, W.E., 1975. Meiobenthos ecosystems as indicators of the effects of dredging. In: L. E. Cronin (ed.), Estuarine Research, Vol. 2., 00. 573-583. Academic Press, New York.

Theil, H., 1975. The size structure of the deep sea benthos. Int. Revue ges. Hydrobiol., 60: 575-606.

Tietjen, J.H., 1969. The ecology of shallow water meiobenthos in two New England estuaries. Oecologia (Berl.), 2: 251-291.

_____, 1971. Ecology and distribution of deep-sea meiobenthos off North Carolina. Deep-Sea Res., 18: 941-957.

_____, 1977. Population distribution and structure of the free-living nematodes of Long Island Sound. Mar. Biol., 43 (2): 123-137.

Valentine, J.W., 1971. Resource supply and species diversity patterns. Lethaia, 4: 51-61.

Wieser, W., 1960. Benthic studies in Buzzards Bay. II. The meiofauna. Limnol. Oceanogr., 5: 121-137.

Wigley, R. and A.D. McIntyre, 1964. Some quantitative comparisons of offshore meiobenthos and macrobenthos south of Martha's Vineyard. Limnol. Oceanog., 9: 485-493.

VOLUME II

CHAPTER 14

MACROINFAUNAL MOLLUSCS

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CONTRACT NO. AA550-CT7-34

INFAUNAL MACROMOLLUSCS OF THE EASTERN GULF OF MEXICO

BY

NORMAN J. BLAKE

Report Submitted to Dames & Moore

1977-78 BLM MAFLA Contract number AA550-CT7-34

TABLE OF CONTENTS

ABSTRACT

The macromolluscs of the Eastern Gulf of Mexico have been sampled over seven seasons from 1975 to 1978. A total of 322 taxa have been identified. The list includes both temperate and tropical species. In the northern sections of the Eastern Gulf of Mexico the molluscs are highly influened by the discharge of the Mississippi River and as a result the species richness and abundances are low; the species present are mostly deposit feeders which can survive the fine sediments. In the southern areas species richness and abundances increase although they were highly variable from one season to another and from one year to another.

A total of seven groups of stations resulted from cluster analysis. These groups appear to show a north-south linearity. Apparently the macromolluscan assemblages of the Eastern Gulf of Mexico are controlled not only by sediment and temperature but also by water depth.

INTRODUCTION

The macroinfauna (<500 m) of the Eastern Gulf of Mexico have been studied at intervals since the start of the Bureau of Land Management's MAFLA program in May, 1974. This portion of the study addresses the characterization of the macromolluscan assemblages of the MAFLA area. The number of stations, station location, and number of samples have not been consistent throughout the study; thus, this final report is based mainly upon those stations where 7-9 box-corer samples were taken during seven sampling periods from May, 1975 through February, 1978. Other data are discussed as needed for qualitative conclusions.

Infaunal studies of community structure have relied basically upon two approaches. The first approach utilizes the concept of diversity in which species richness, numbers of individuals, and distribution of individuals among species may be compared over time and space. The second approach is classification in which sampling stations may be grouped by their species composition and number of individuals belonging to each species, or in which species are grouped according to their distribution between sampling stations. Both approaches are utilized in the analysis of molluscan data resulting from this study. A detailed description of the methodologies may be found in Dames & Moore's data management report (Volume II, Chapter 29).

LITERATURE REVIEW

The Eastern Gulf of Mexico receives both temperate and tropical influences. During the summer months the Gulf Loop Current enters the Gulf of Mexico from the Caribbean through the Yucatan Straits and carries Caribbean water and fauna as far north as the Mississippi coastline (Maul, 1977). As the current loops south along the West Florida Shelf, eddies may break off from the current and affect the nearshore areas (Niiler, 1976). As a result of this phenomenon the shallow areas of the Eastern Gulf of Mexico as well as those areas receiving large estuarine influences have been thought to possess a temperate fauna, while at the shelf break more tropical assemblages have been thought to occur (Pully, 1952; Hedgpeth, 1953; Work, 1969). The Loop Current also may be responsible for the Caribbean coral assemblages of the Florida Middle Ground (Hopkins et al. 1977) and the Texas Flower Gardens (Bright and Pequegnat, 1974).

The infauna of the study area have been sampled on numerous occasions since the 1800's. The cruises of the S.S. Blake collected many molluscs in dredge hauls which were used by Agassiz (1888) for taxonomic descriptions. Cruises on the Albatross also made dredge hauls which were utilized by Dall (1889) for further molluscan descriptions. Later in the 1950's the Fish and Wildlife Service made numerous dredge hauls in the study area on the Oregon and Pelican (Bullis and Thompson, 1965) and from 1965 to 1967 the Florida Department of Natural Resources made dredge hauls of the infauna from the southern part of the study area at monthly intervals (Joyce and Williams, 1969). However, all of these studies have suffered because of the qualitative nature of the gear employed and because of the lack of precision navigational equipment. This study is the first time that the macromolluscan assemblages of the continental shelf of the eastern Gulf of Mexico have been

sampled quantitatively over repetitive seasons with the aid of precision navigation.

MATERIALS AND METHODS

The locations and depths of the macrobenthic infauna stations included in this report are indicated in Table 67. Sampling was conducted during seven seasons: Summer (June, 1975), Fall (September, 1975), Winter (January, 1975), Summer (June-July, 1976), Summer (August-September, 1977), Fall (November, 1977), and Winter (February, 1978).

Benthic samples were taken with a box-core measuring 21.3 x 30.5 cm. If an adequate sample could not be obtained with the box-core (at least 10 cm depth of sediment), samples were taken with a Smith-McIntyre grab for qualitative analysis only. Only those stations where nine replicate box-cores were taken are discussed here. Nine additional replicates were taken at six supplemental stations during the summer 1977 season to verify the biolithologic map contours.

The remaining top 15 cm of the sediment in the box-core to be used for macroinfauna (after any after required sub-samples had been removed) was sieved thorugh a 500 μm Nitex bag in a barrel containing seawater. The sediment and organisms remaining in the Nitex bag were washed into a pre-numbered cloth bag. Pertinent information such as cruise number, date, ship, collector, station number, station code, depth of sample, bag number(s), and field notes were recorded in a log book and on a waterproof label. After placing the label in the sample bag, it was tied shut and placed in a barrel of 15% $MgSO_4$ (14.5 kg, 32 lbs of Epsom Salts to 106 ℓ, 28 gallons of seawater) for a minimum of 30 minutes for narcotization. After relaxation, the bags were transferred to 10% neutral buffered formalin (9.5 ℓ, 2.5 gal of 37% formaldehyde, 2.3 kg, 5 lbs of borax, and 95 ℓ, 25 gal of seawater) for preservation and storage.

In the lab, the sample bags were transferred to a barrel containing a rose bangal dye solution for a minimum of 24 hours to stain the animal protoplasm. Each sample was then removed from the bag and washed gently through a 500 μm Wentworth sieve with tap water. After washing, the sample was floated with a saturated NaCl solution to remove the less dense organisms. The residual material was rough sorted on white enamel trays to remove any remaining organisms.

The organisms were separated into five groups (molluscs, polychaetes, crustaceans, echinoderms, and miscellaneous) with the aid of a dissecting microscope (7-40x) and stored in 70% ethanol (70 mℓ of 95% ethanol and 25 mℓ of water). Wet weight biomass determinations were made for each group to the nearest 0.1 mg. The molluscs were retained by Dr. Blake for subsequent identification and enumeration. The remaining groups were sent to the following specialists for identification: Dr. Vittor - polychaetes, Dr. Heard - crustaceans, Dr. Hopkins - echinoderms and miscellaneous organisms.

All molluscs were identified to the lowest practical taxonomic level. Key references for molluscan identification were Heath (1918), Henderson

TABLE 67

LOCATIONS AND DEPTHS OF PRIMARY STATIONS SAMPLED

DURING THE 1977/78 MAFLA PROGRAM

Station	Lat. N.	Long. W.	Depth (m)
2101	26°25'	82°15'	11
2102	26°25'	82°25'	18
2104	26°24'	83°22'	55
2105	26°25'	83°49'	99
2106	26°25'	84°14'	171
2207	27°56'	83°09'	21
2208	27°55'	83°27'	28
2209	27°52'	83°34'	32
2211	27°56'	83°53'	44
2212	27°56'	84°48'	142
2313	28°24'	83°14'	N/A
2316	28°42'	84°20'	33
2318	29°05'	83°45'	20
2419	29°47'	84°05'	11
2423	29°20'	84°44'	29
2426	28°57'	85°23'	85
2427	28°49'	85°37'	154
2528	29°54'	86°04'	36
2531	29°48'	86°09'	47
2536	29°30'	86°25'	181
2638	29°55'	88°33'	25
2640	29°43'	87°54'	35
2645	29°35'	87°20'	106
2746	27°03'	84°13'	122
2747	27°24'	84°07'	76
2748	27°40'	83°53'	53
2957	25°40'	84°15'	164
2958	25°40'	83°50'	110
2959	25°40'	83°05'	51
2960	25°40'	82°20'	26

(1920), Clench (1941-1972), Keene (1971), Kaas (1972), and Abbott (1974). Each species was assigned a numerical code based on the NOAA Taxonomic Code. Species lists and counts for each station were then transcribed to computer sheets and transmitted to Dames & Moore for key punching and data analysis.

RESULTS AND DISCUSSION

SPECIES OCCURRENCE

Samples collected from all stations during the seven sampling periods yielded 322 identifiable macromolluscan (<500 μm) taxa. The species included 148 gastorpods, 152 bivalves, 16 scaphapods, 7 polyplacophorans, 1 aplacophoran. The list contains some species which are basically temperate in geographical distribution as well as others which are basically subtropical to tropical in geographical distribution. Although little is known about the ecology of the vast majority of species identified, both filter feeders and deposit feeders are represented in the list. Since all individuals collected by the box-corer were identified to the lowest practical taxonomic level, the species list contains a limited number of epifaunal molluscs as well as infaunal molluscs.

Table 68 shows the eight molluscan species which occurred in 10% or more samples (i.e., in 17 or more of 167 samples). Of these, only three species (Tellina versicolor, Abra lioica, and Parvilucina multilineata) were found during all seven sampling periods at one or more stations.

The abundance of T. versicolor at the four stations where it was collected during all seven sampling periods is shown in Figure 213. All four stations were nearshore in less than 30 m of water. The sediment at the two most southern stations where the abundances were greater was medium sand with 30-40% $CaCO_3$. T. versicolor was the second most abundant species collected and occurred over broad areas of the MAFLA shelf study area, especially at sand stations in less than 90 m of water. Peaks in abundance generally occurred in the summer (Figure 213) indicating a spring or summer recruitment.

Parvilucina multilineata, the most abundant species collected, was found at two stations during all seven sampling periods. Its abundance is shown in Figure 214. Both stations are in less than 40 m of water and have medium (2101) to coarse (2209) sand sediments. P. multilineata was least abundant in winter at both stations and exhibited a substantial population increase at station 2101 in Fall 1977. Recruitment probably occurs in summer or fall.

Abra lioica was collected at four stations during all seven sampling periods. These stations were all the most distant from shore (deeper than 170 m) along each of the four southern transects (I, II, III, IV). The sediments at these stations consisted of medium sand with greater than 90% $CaCO_3$. As is characteristic of deep water species, seasonal fluctuations in abundance were small (Figure 215).

TABLE 68

MOLLUSCAN SPECIES WHICH OCCURRED IN AT LEAST 10%

OF THE 167 SAMPLINGS OF PRIMARY STATIONS

Species	No. of Stations	Percent Occurrence	Number of Individuals
Diplodonta sp.	28	16.8	143
Crassinella martiniciensis	26	15.6	161
Abra lioica	25	15.0	373
Amygdalum papyrium	22	13.2	60
Solemya occidentalis	20	12.0	353
Tellina versicolor	20	12.0	1,534
Thyasira sp.	17	10.0	81
Parvilucina multilinata	17	10.0	2,714

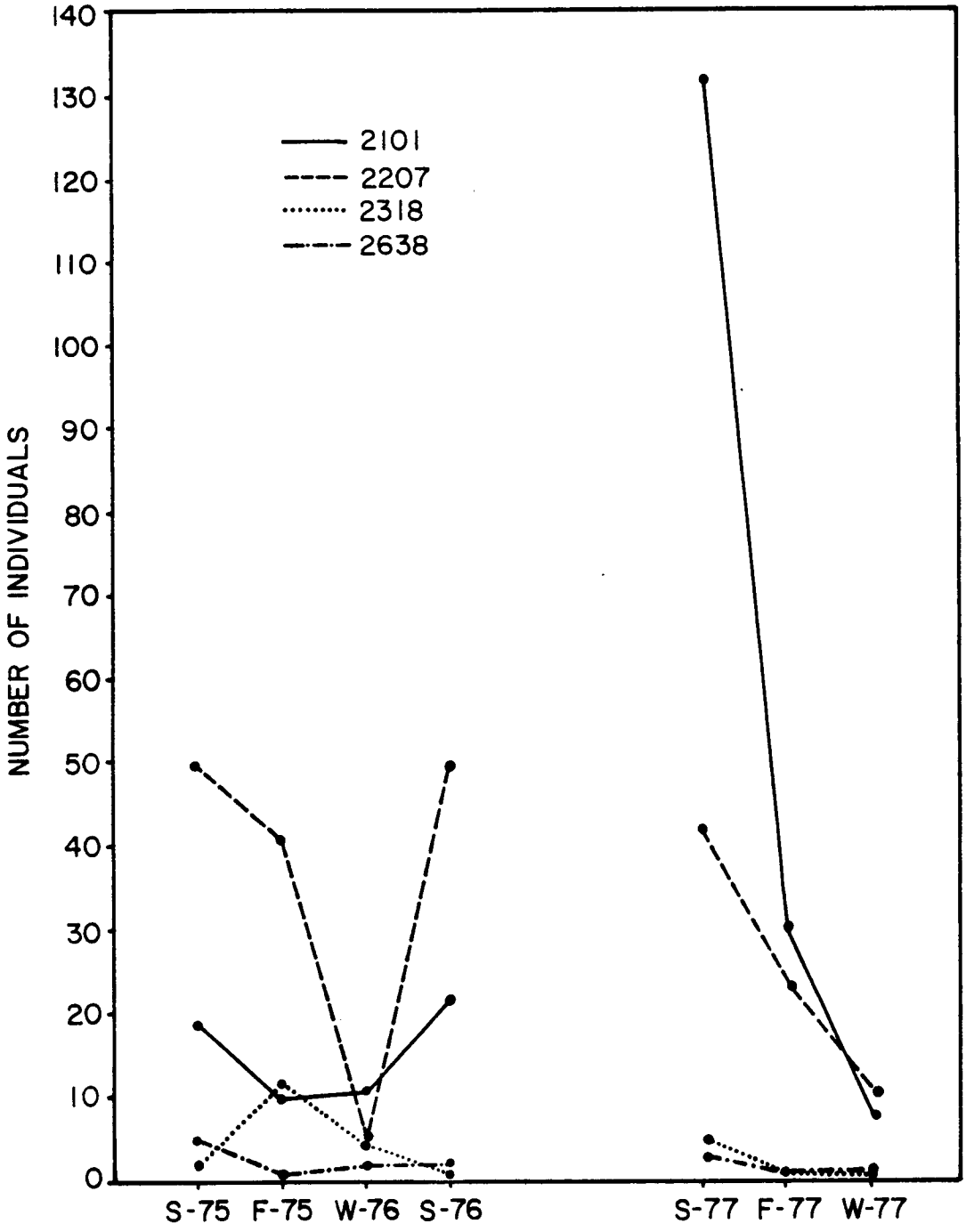

FIGURE 213 NUMBER OF INDIVIDUALS OF TELLINA VERSICOLOR COLLECTED AT 4 PRIMARY STATIONS DURING 7 SAMPLING PERIODS.

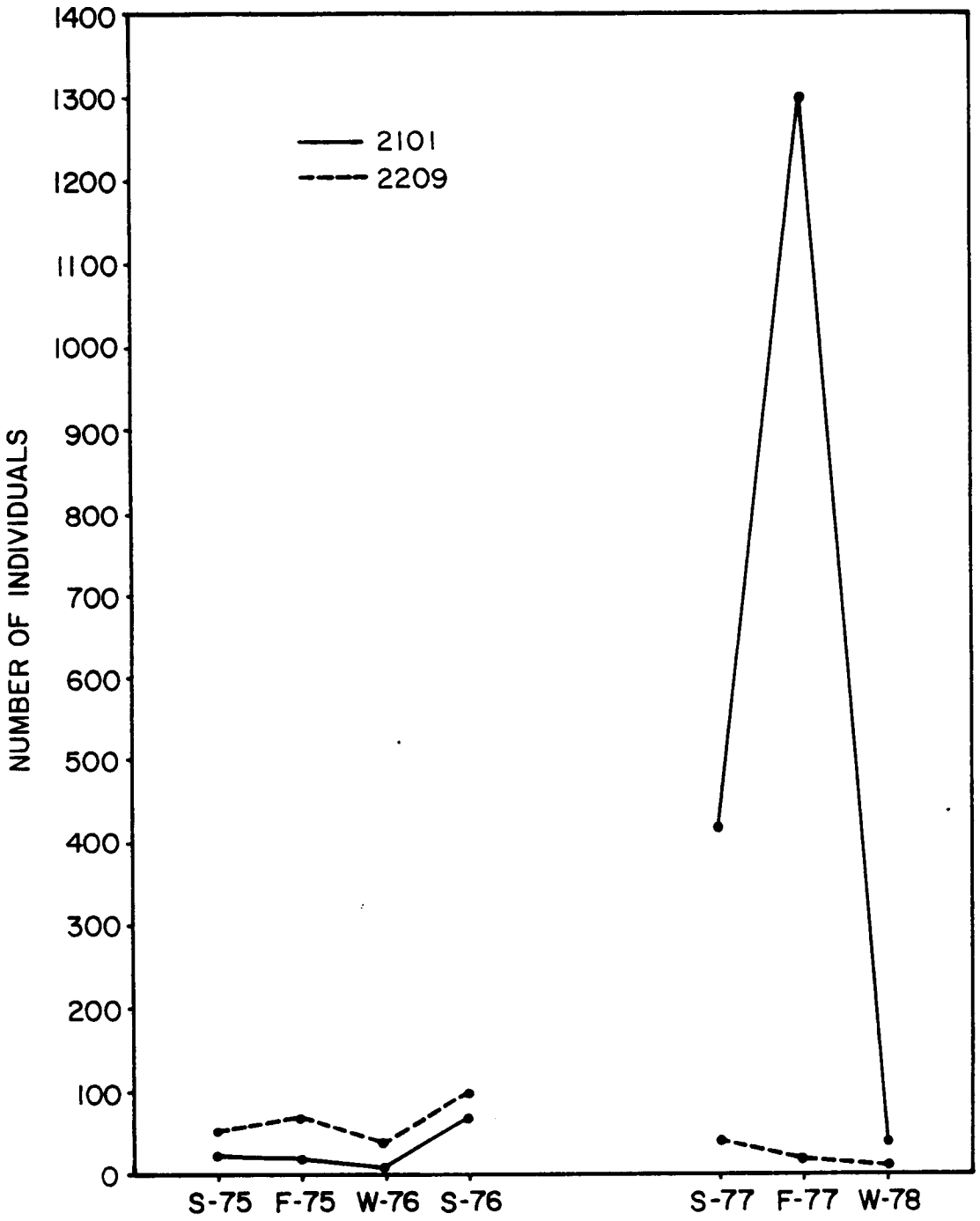

FIGURE 214 NUMBER OF INDIVIDUALS OF PARVILUCINA MULTILINEATA COLLECTED AT 2 PRIMARY STATIONS DURING 7 SAMPLING PERIODS.

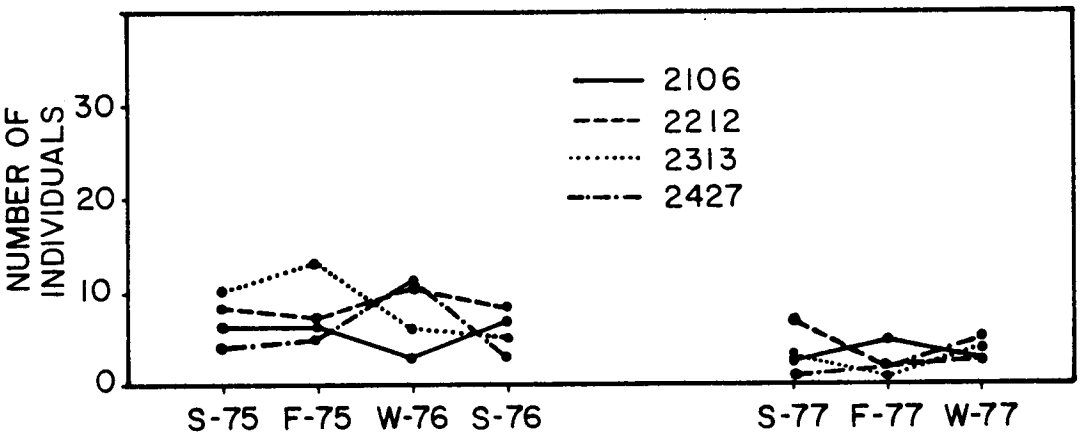

FIGURE 215 NUMBER OF INDIVIDUALS OF ABRA LIOICA COLLECTED AT 4 PRIMARY STATIONS DURING 7 SAMPLING PERIODS.

SPECIES DIVERSITY

Species richness (S), abundance (n), Shannon-Wiener diversity (H'), and evenness (J') are given in Tables 69 through 72. Only primary stations which were sampled at least three times during the seven sampling periods (June 1975, September 1975, January 1976, June-July 1976, August-September 1977, November 1977, and February 1978) were considered. Seasonal (i.e., Summer, Fall, Winter) differences in H' for 6 transects during 1975-76 and 1977-78 are presented in Figures 216 and 217. Annual variations in species richness and H' for the three summer sampling periods are presented in Figures 217 through 221.

Species richness generally decreased from south to north, and with increasing depth along each transect. Fewer species were collected along transects I, II, & III in 1977-78 than during the 1975-76 sampling period. This trend was not apparent for the more northern transects (i.e., IV, V, and VI). Annual changes in species richness during the summer sampling periods were most variable at the shallow stations (less than 55 m). It is possible that the winter of 1976, which was notably severe and which was not sampled, contributed to the loss of species.

Total numbers of individuals collected during the seven sampling periods have been averaged by collecting season, and are presented in Figures 222 through 224. Along transect I, station 2101 by far exhibited maximum abundance, especially during the fall season. Many of these individuals were small or juveniles and probably represent a recruitment from spring or summer spawning. As with species richness there is a general decrease in abundances with an increase in depth and with increase in latitude.

Shannon-Wiener diversity (H') ranged from 0.00 to 3.09 in 1975-76 and from 0.00 to 2.88 in 1977-78. H' generally declined from south to north and with increasing depth along each transect. However, the decrease in H' was not always progressive as some of the highest values occurred in the mid-depth range (29-55 m). These stations were usually characterized by a high species richness, a low abundance, and a high degree of evenness. Species richness was often relatively high at the shallower stations whereas it was generally lower at the deeper stations. Consequently, H' was high at the shallow (11-28 m) and mid-depth (29-55 m) stations and lower at the deeper stations (85-192 m). Annual variations in H' were most apparent at the shallow stations of the two most southern transects (Figures 216 and 217). In general, annual variations in H' followed closely the annual changes in species richness.

Stations showing the lowest diversity were near the shelf break or at the two most northern transects. On the northern transects the molluscs are obviously influenced by the Mississippi River. Large amounts of fine sediments are carried by the river and are deposited on the delta (Doyle, Chapter 2). Turbidity remains relatively high throughout the year and storms may resuspend the fines. As a result of this harsh environment populations of molluscs remain small and only a few species of deposit feeding bivalves survive the conditions. Any environmental perturbation is likely to destroy the assemblage and large seasonal fluctuations as well as

TABLE 69

NUMBER OF SPECIES COLLECTED AT PRIMARY STATIONS

DURING THE SEVEN SAMPLING PERIODS

	SEASONS						
Stations	Sum-75	Fall-75	Wint-76	Sum-76	Sum-77	Fall-77	Wint-78
2960	-	-	-	-	19	11	9
2959	-	-	-	-	25	16	3
2958	-	-	-	-	13	6	5
2957	-	-	-	-	12	3	2
2101	35	22	30	38	31	18	15
2102	17	23	25	16	11	22	7
2104	27	31	26	39	12	15	14
2106	8	12	5	12	7	3	3
2207	38	24	19	30	18	16	7
2208	19	18	19	25	15	-	5
2209	23	21	17	23	14	8	5
2211	24	22	23	35	24	14	10
2212	8	7	7	6	7	4	4
2318	8	26	7	9	10	11	4
2316	19	19	27	9	11	14	15
2313	4	2	5	1	3	1	3
2419	12	15	4	0	13	8	7
2423	13	19	6	6	9	5	6
2426	4	3	8	1	8	1	5
2427	1	1	4	1	1	1	1
2528	6	10	11	7	20	19	18
2531	6	9	5	9	7	7	9
2536	3	1	3	1	0	0	1
2638	7	2	4	3	5	4	3
2640	8	10	7	9	12	8	6
2645	4	0	0	4	1	4	7
2746	-	-	-	10	12	4	5
2747	-	-	-	22	12	6	9
2748	-	-	-	22	14	20	16

TABLE 70

NUMBER OF INDIVIDUALS COLLECTED AT PRIMARY STATIONS

DURING THE SEVEN SAMPLING PERIODS

	SEASONS						
Stations	Sum-75	Fall-75	Wint-76	Sum-76	Sum-77	Fall-77	Wint-78
2960	-	-	-	-	151	49	51
2959	-	-	-	-	99	44	3
2958	-	-	-	-	27	11	6
2957	-	-	-	-	24	7	2
2101	140	199	192	365	715	1476	73
2102	67	144	166	52	99	132	13
2104	48	75	62	86	18	19	27
2106	20	33	18	43	11	7	5
2207	146	163	74	226	112	54	20
2208	164	210	124	649	241	-	17
2209	177	219	105	256	165	30	14
2211	55	47	44	112	42	24	26
2212	25	19	23	17	15	5	6
2318	13	95	25	14	16	24	4
2316	59	51	88	16	15	22	28
2313	14	14	12	5	5	1	6
2419	52	64	20	0	39	12	16
2423	23	42	8	14	16	10	6
2426	7	4	14	1	10	3	12
2427	4	5	14	3	1	2	5
2528	14	11	16	11	49	63	29
2531	7	17	8	12	11	18	18
2536	3	1	3	1	0	0	2
2638	35	3	12	5	7	6	4
2640	45	26	13	26	31	21	9
2645	6	0	0	7	5	4	8
2746	-	-	-	33	23	5	6
2747	-	-	-	40	18	14	14
2748	-	-	-	79	23	35	27

TABLE 71

SHANNON-WIENER INDICES (H') AT PRIMARY STATIONS

FOR THE SEVEN SAMPLING PERIODS

	SEASONS						
Stations	Sum-75	Fall-75	Wint-76	Sum-76	Sum-77	Fall-77	Wint-78
2960	-	-	-	-	1.46	1.17	1.29
2959	-	-	-	-	2.77	2.28	1.10
2958	-	-	-	-	2.42	1.67	1.56
2957	-	-	-	-	1.88	0.80	0.69
2101	2.90	2.10	2.55	2.47	1.50	0.56	1.87
2102	2.27	1.69	2.19	2.06	1.26	1.99	1.69
2104	3.09	3.00	2.95	3.39	2.35	2.63	2.24
2106	1.71	2.16	1.43	1.54	1.85	0.80	0.95
2207	2.77	1.94	2.16	2.08	1.69	2.04	1.44
2208	2.01	1.64	2.41	2.01	1.61	-	1.36
2209	2.16	2.03	2.11	2.09	1.84	1.53	1.40
2211	2.69	2.86	2.96	2.79	2.88	2.43	1.74
2212	1.90	1.66	1.54	1.50	1.62	1.33	1.24
2318	1.93	2.76	1.36	2.07	2.06	2.03	1.39
2316	1.96	2.47	2.84	2.01	2.17	2.45	2.29
2313	0.90	0.26	1.31	0.00	0.95	0.00	0.87
2419	1.46	2.02	0.71	0.00	1.92	1.98	1.75
2423	2.45	2.47	1.67	1.35	2.05	1.47	1.79
2426	1.15	1.04	1.97	0.00	1.97	0.00	1.47
2427	0.00	0.00	0.75	0.00	0.00	0.00	0.00
2528	1.54	2.27	2.18	1.80	2.74	2.36	2.72
2531	1.75	2.02	1.39	2.09	1.85	1.89	2.11
2536	1.10	0.00	1.10	0.00	0.00	0.00	0.00
2638	1.11	0.64	0.98	1.05	1.48	1.24	1.04
2640	1.19	1.74	1.73	2.02	2.36	1.39	1.74
2645	1.24	0.00	0.00	1.35	0.00	1.39	1.91
2746	-	-	-	0.83	0.87	0.90	0.93
2747	-	-	-	2.77	2.37	1.47	2.04
2748	-	-	-	2.12	2.43	2.82	2.54

TABLE 72

EVENNESS (J') VALUES FOR PRIMARY STATIONS DURING THE SEVEN SAMPLING PERIODS

	SEASONS						
Stations	Sum-75	Fall-75	Wint-76	Sum-76	Sum-77	Fall-77	Wint-78
2960	-	-	-	-	.49	.49	.59
2959	-	-	-	-	.86	.82	1.00
2958	-	-	-	-	.94	.93	.97
2957	-	-	-	-	.76	.72	1.00
2101	.82	.68	.75	.68	.44	.20	.69
2102	.80	.54	.68	.74	.53	.64	.87
2104	.94	.87	.91	.92	.95	.97	.85
2106	.82	.87	.89	.62	.95	.72	.86
2207	.76	.61	.73	.61	.58	.73	.74
2208	.68	.57	.82	.63	.60	-	.85
2209	.69	.67	.74	.67	.70	.74	.87
2211	.85	.93	.94	.78	.90	.92	.76
2212	.91	.85	.79	.84	.83	.96	.90
2318	.93	.85	.70	.94	.90	.84	1.00
2316	.67	.84	.86	.91	.91	.93	.85
2313	.65	.37	.82	.84	.86	.96	.79
2419	.59	.74	.51	.94	.75	.95	.90
2423	.96	.84	.93	.75	.93	.91	1.00
2426	.83	.95	.95	.94	.95	1.00	.91
2427	.83	.95	.54	.94	.95	1.00	.91
2528	.86	.99	.91	.92	.91	.80	.94
2531	.98	.92	.86	.95	.95	.97	.96
2536	1.00	.95	1.00	.92	.95	.97	.96
2638	.57	.92	.71	.96	.92	.90	.95
2640	.57	.76	.89	.92	.95	.67	.97
2645	.90	.89	.92	.98	.95	1.00	.98
2746	-	-	-	.84	.86	.96	.97
2747	-	-	-	.90	.95	.82	.93
2748	-	-	-	.69	.92	.94	.92

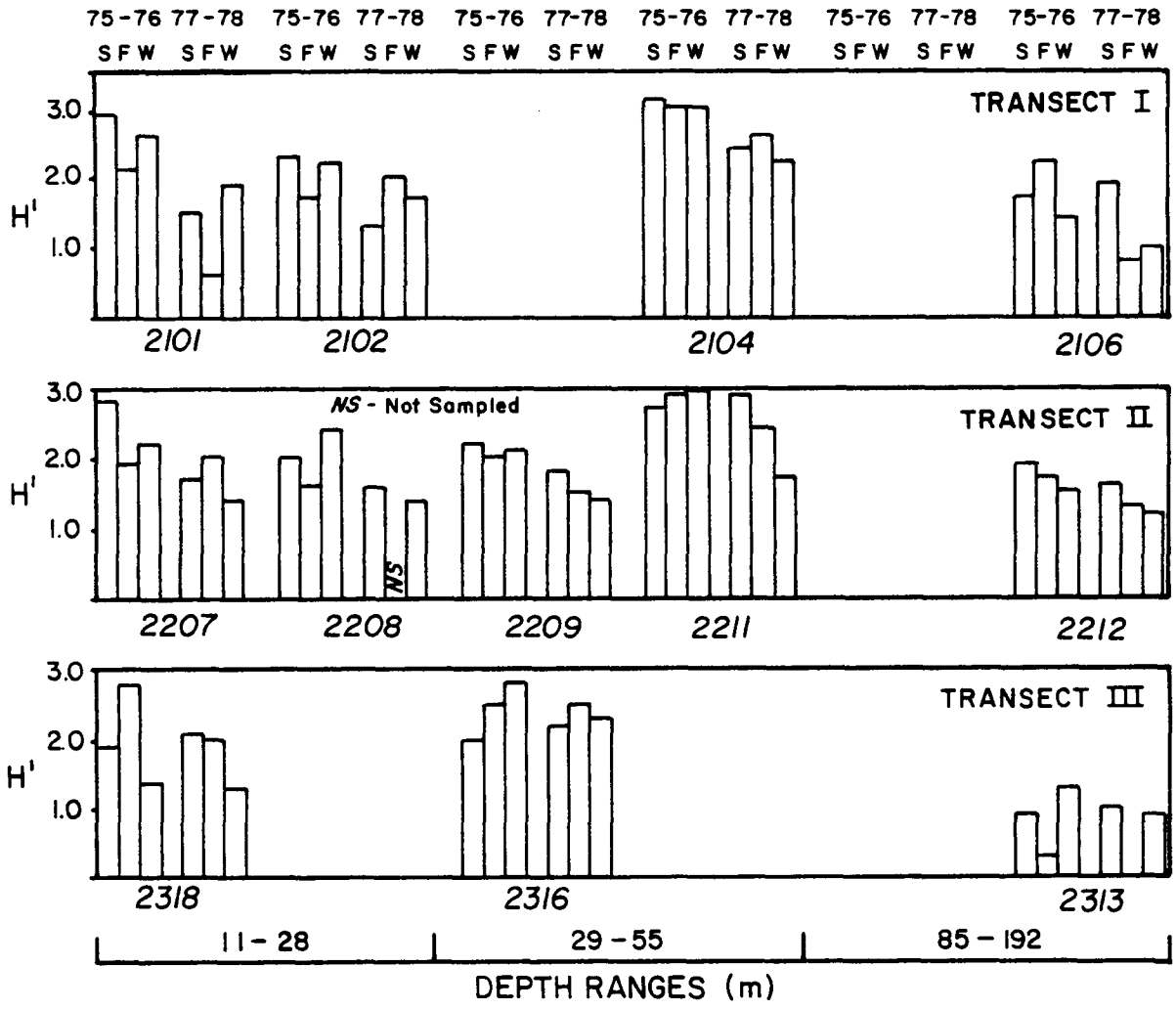

FIGURE 216 SHANNON - WIENER INDICES FOR PRIMARY STATIONS ALONG TRANSECTS I, II AND III.

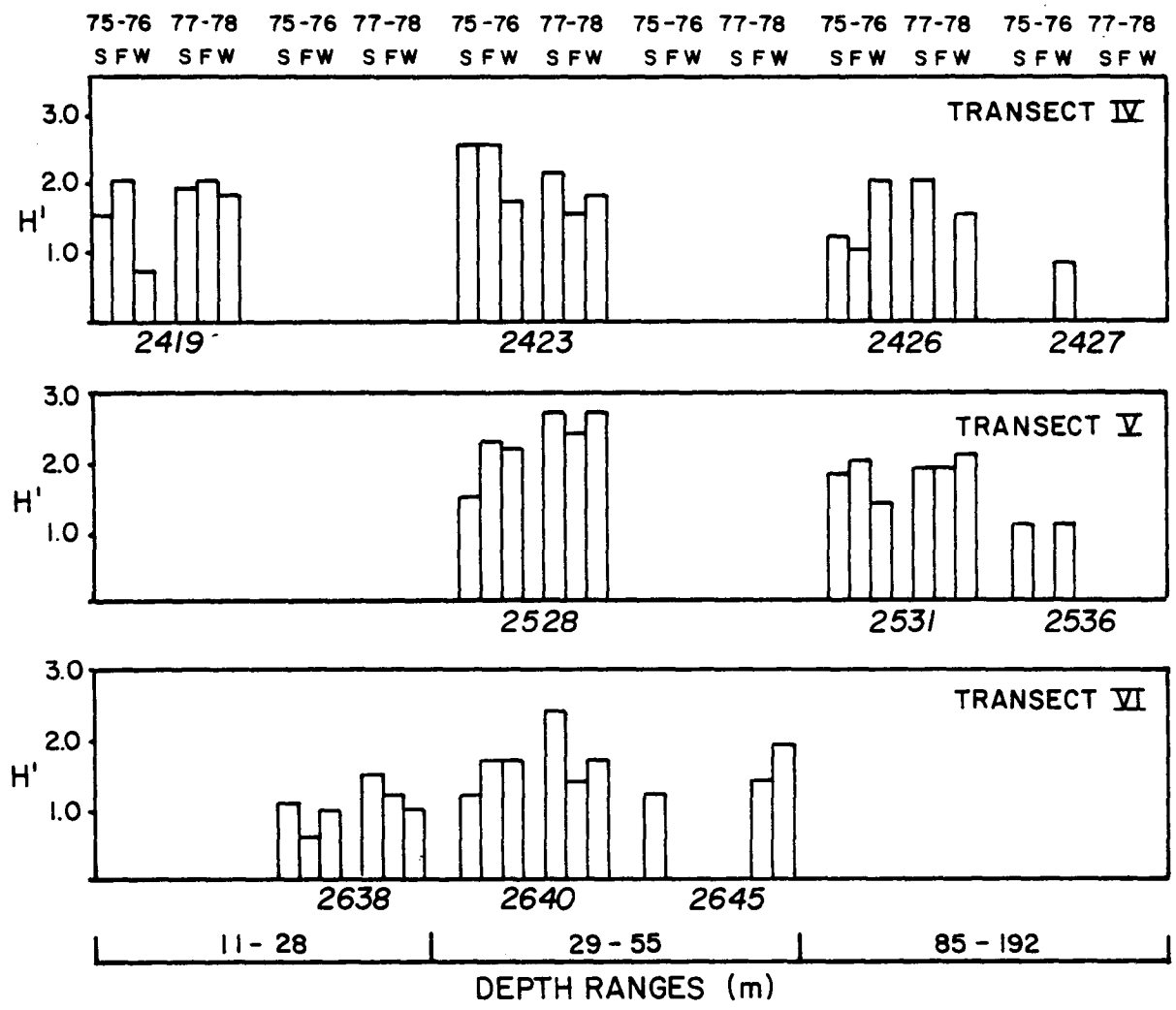

FIGURE 217 SHANNON-WIENER INDICES FOR PRIMARY STATIONS ALONG TRANSECTS IV, V AND VI.

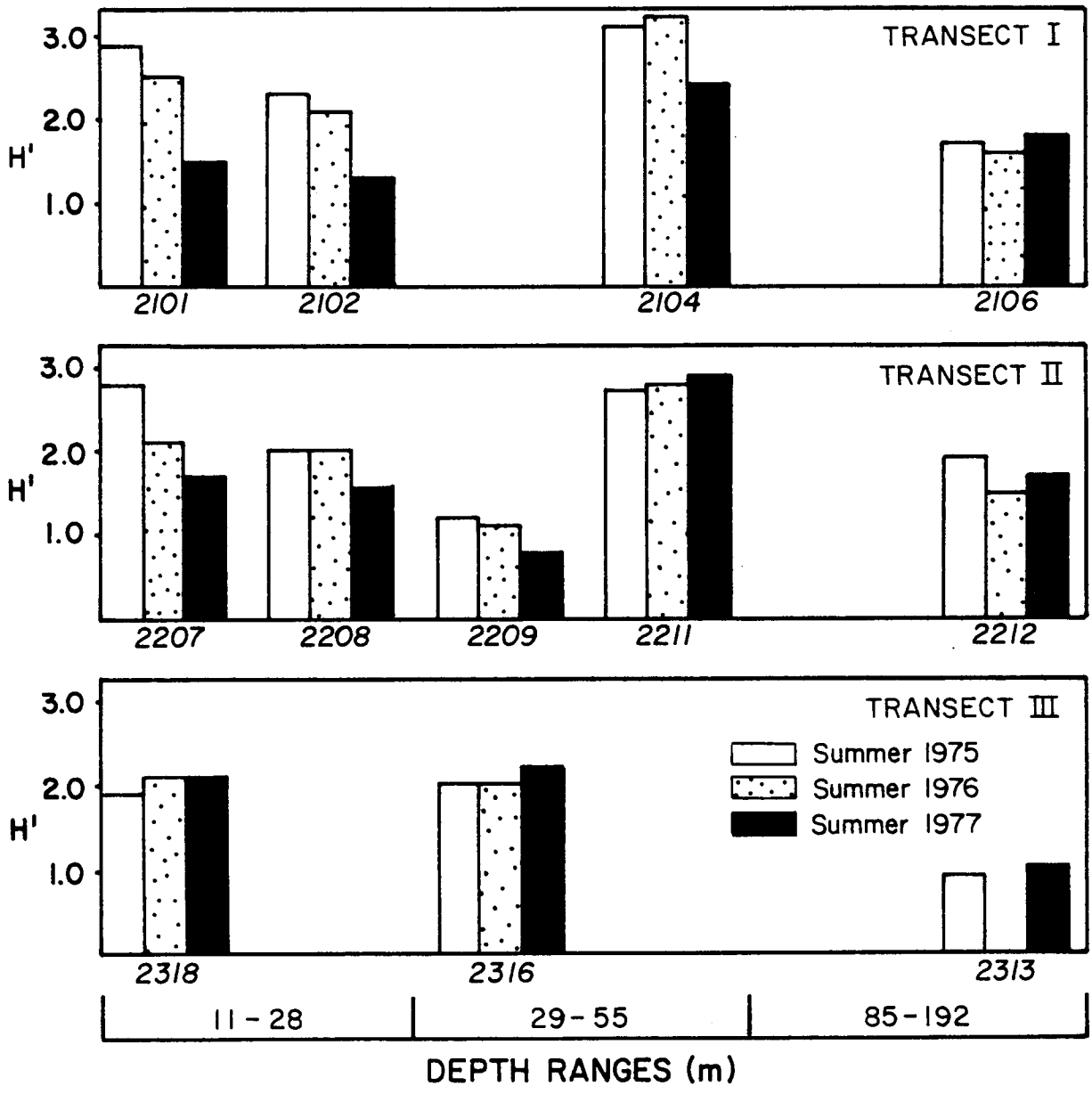

FIGURE 218 SHANNON-WIENER INDICES FOR PRIMARY STATIONS ALONG TRANSECTS I, II AND III SAMPLED DURING 3 SUMMER SEASONS.

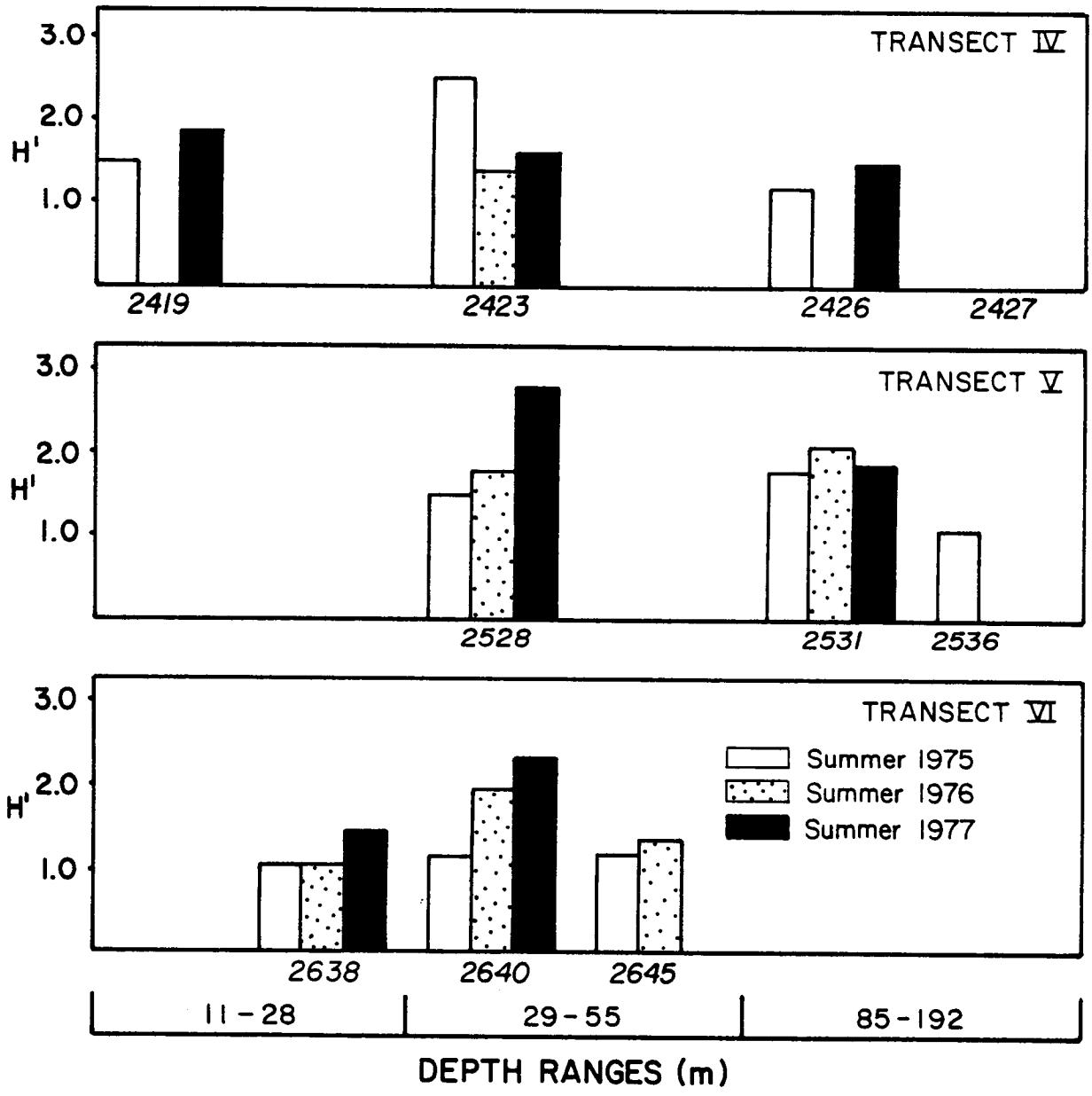

FIGURE 219 SHANNON-WIENER INDICES FOR PRIMARY STATIONS ALONG TRANSECTS IV, V AND VI SAMPLED DURING 3 SUMMER SEASONS.

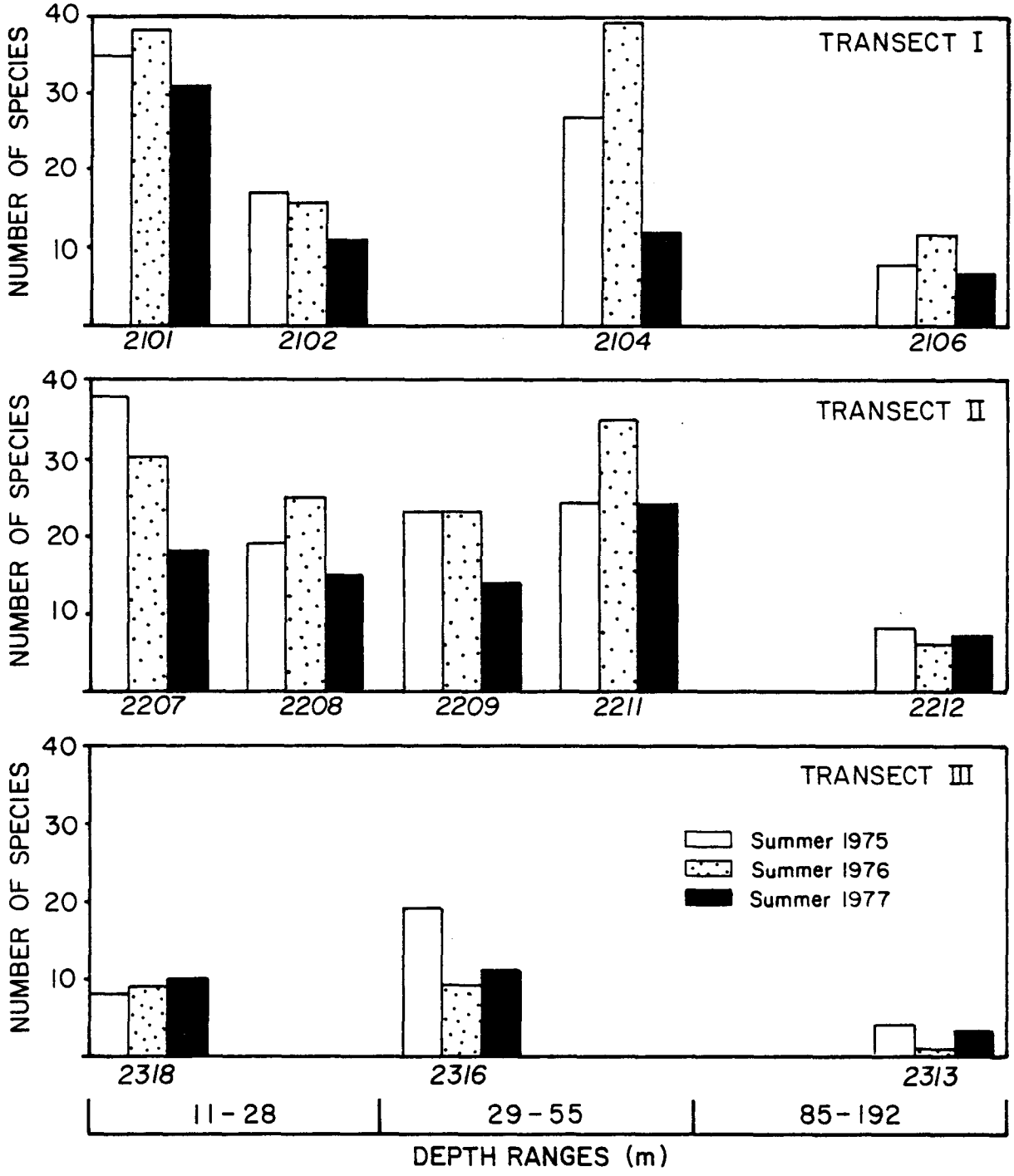

FIGURE 220 NUMBER OF SPECIES FOR PRIMARY STATIONS ALONG TRANSECTS I, II AND III SAMPLED DURING 3 SUMMER SEASONS.

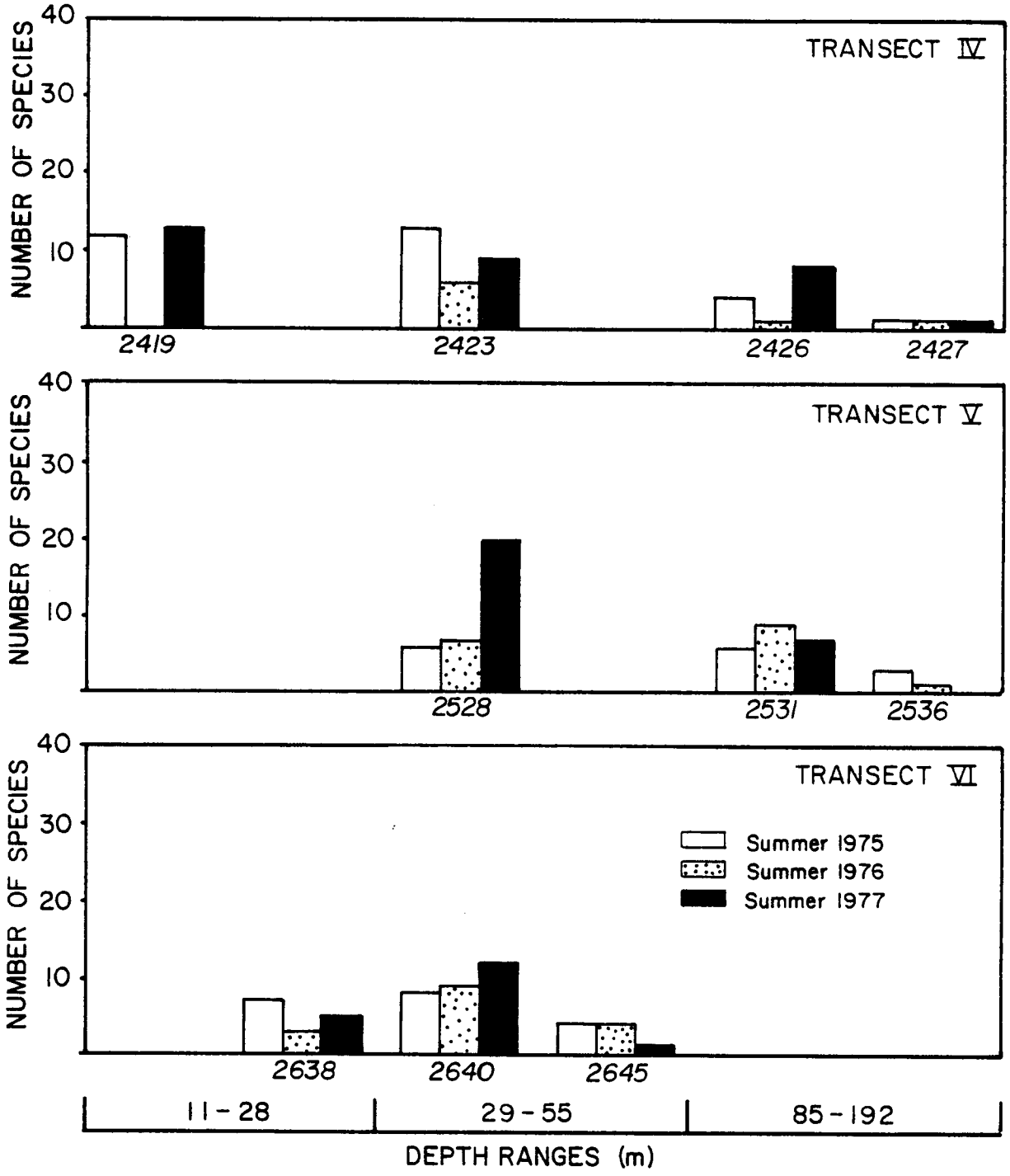

FIGURE 221 NUMBER OF SPECIES FOR PRIMARY STATIONS ALONG TRANSECTS IV, V AND VI SAMPLED DURING 3 SUMMER SEASONS.

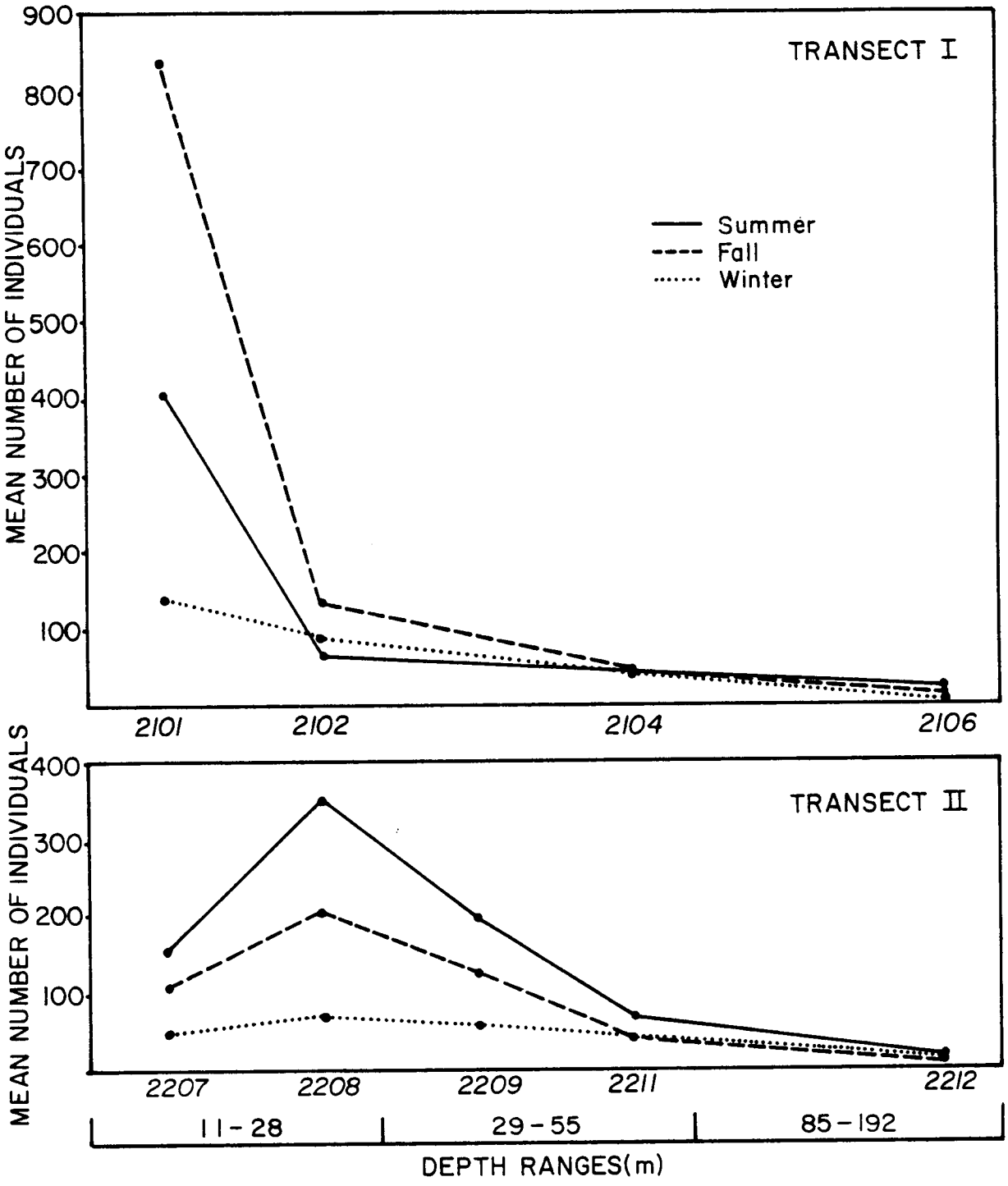

FIGURE 222 MEAN NUMBER OF INDIVIDUALS COLLECTED SEASONALLY ALONG TRANSECTS I AND II.

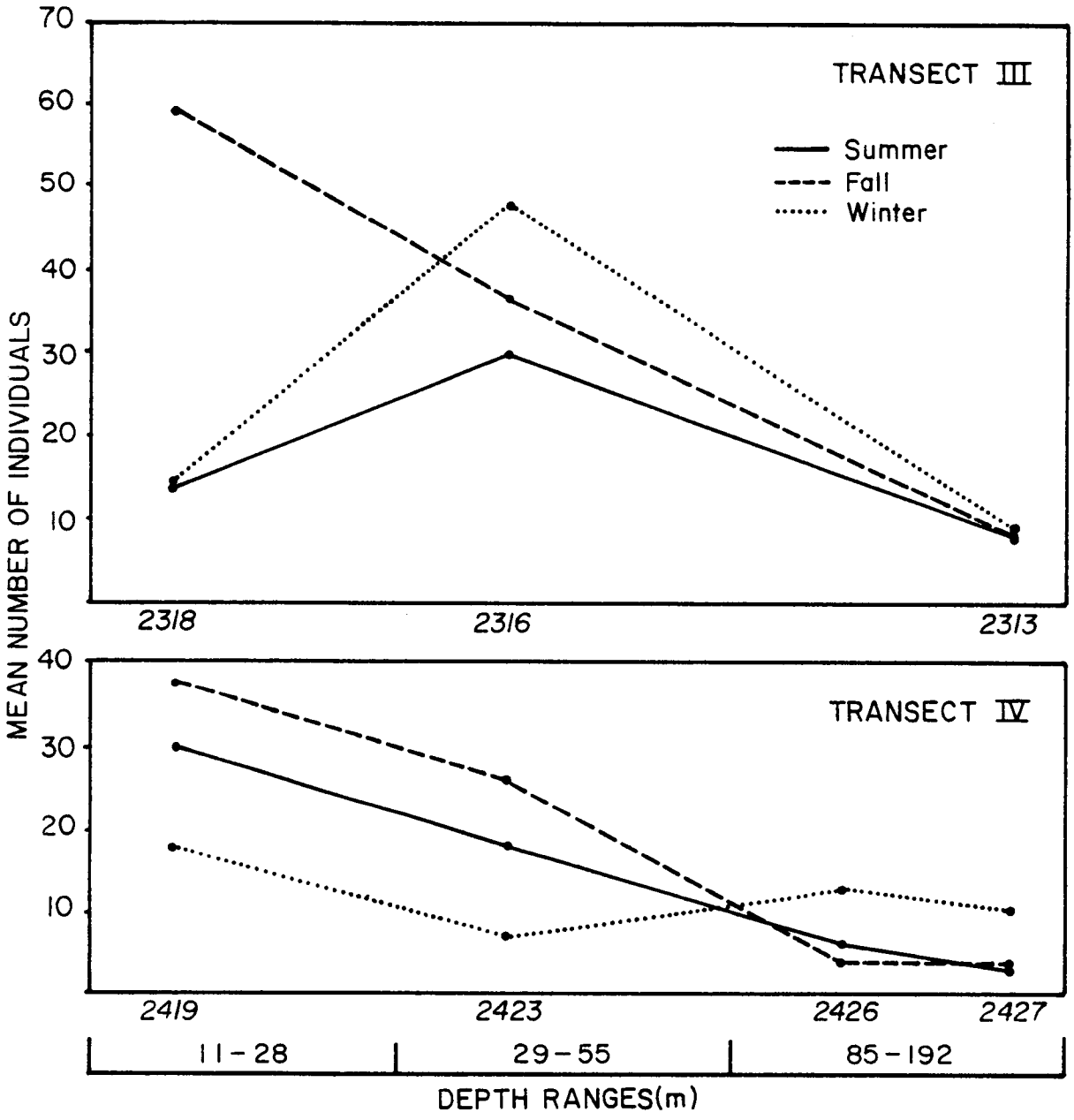

FIGURE 223 MEAN NUMBER OF INDIVIDUALS COLLECTED SEASONALLY ALONG TRANSECTS III AND IV.

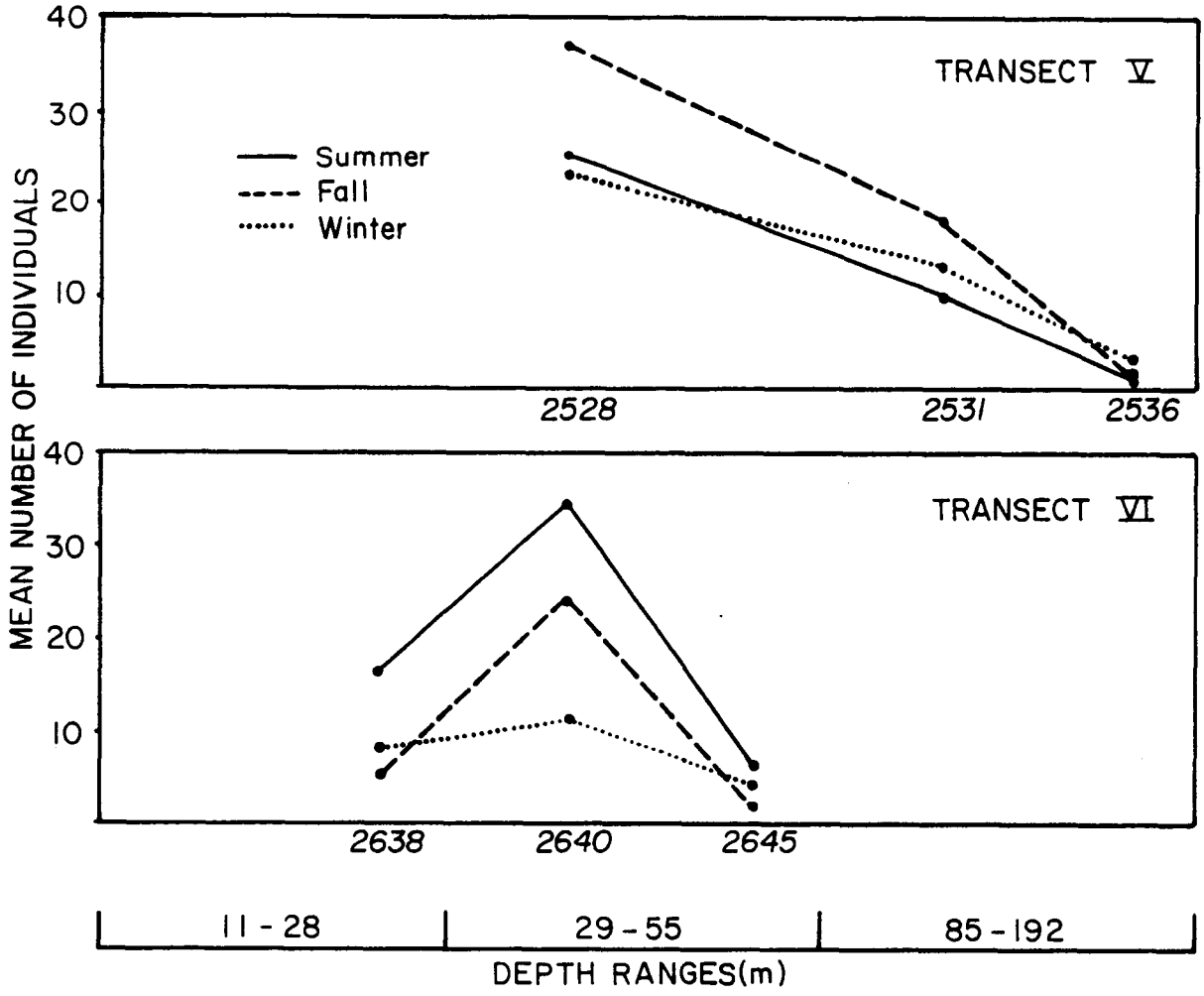

FIGURE 224 MEAN NUMBER OF INDIVIDUALS COLLECTED SEASONALLY ALONG TRANSECTS V AND VI .

yearly fluctuations are apparent. Measures of diversity or affinity on molluscan assemblages in the northern two transects are consequently of little value.

Although the stations on the southern transects have a greater number of individuals, they are still characterized by fewer individuals than are reported for more temperate areas (Popham and Ellis, 1971; Boesch, 1972). Even these more southern stations may be affected by adverse weather conditions since there is some indication that some stations, especially 2959, showed a large drop in individuals as well as species from the winter to the summer sampling during 1978.

CLASSIFICATION

The classification techniques employed by the Dames & Moore Data Management group failed to show consistently strong associations either in the R-mode or the Q-mode. This may result from the fact that all seven sampling seasons were lumped for one R-mode and one Q-mode analysis.

The results indicate that the species composition and abundance either between stations or within a station is highly variable especially for the nearshore southern station which possessed a relatively high species richness. Station 2208 showed only 18% similarity between summer 1976 and summer 1977. Although between-sampling similarities remained generally low for most of the nearshore southern stations, some stations such as 2101 and 2209 showed similarities of 45-75% from one sampling to another, although in the case of 2101 the high similarity was between winter 1976 and summer 1975. Based upon this analysis, the nearshore stations of the southern two transects show little consistency either between year or between seasons. This might be expected considering the large number of relatively rare species which compose the assemblages at these stations.

The deep and more northern stations which possess fewer species exhibited greater similarities ranging from 38-77%. At these stations there was little variability in species composition or abundance from either one season to another or from one year to another. In spite of the lack of strong within and between-stations similarities, seven groups (Figure 225) of stations can be discerned over the West Florida shelf and slope. Species associations resulting from R-mode analysis were not easily discerned for each of these groups of stations. However, each group possesses species which, although they vary in abundance, are common if not dominant to each station in the group. These species are shown in Table 73.

The groups tend to show a north-south trend lining up on relatively specific depth contours. It should be noted that group VI, which is circular rather than linear, still maintains the depth contour specificity since in the Big Bend area of the West Florida shelf depth contours change very slowly over broad areas. Undoubtedly sediment patterns which may in turn be related partly to depth contours and energy boundaries play a role in the species associations which are observed but analysis of these correlations has not been possible within the time of receipt of analyzed mollusc data and the due date of the final report.

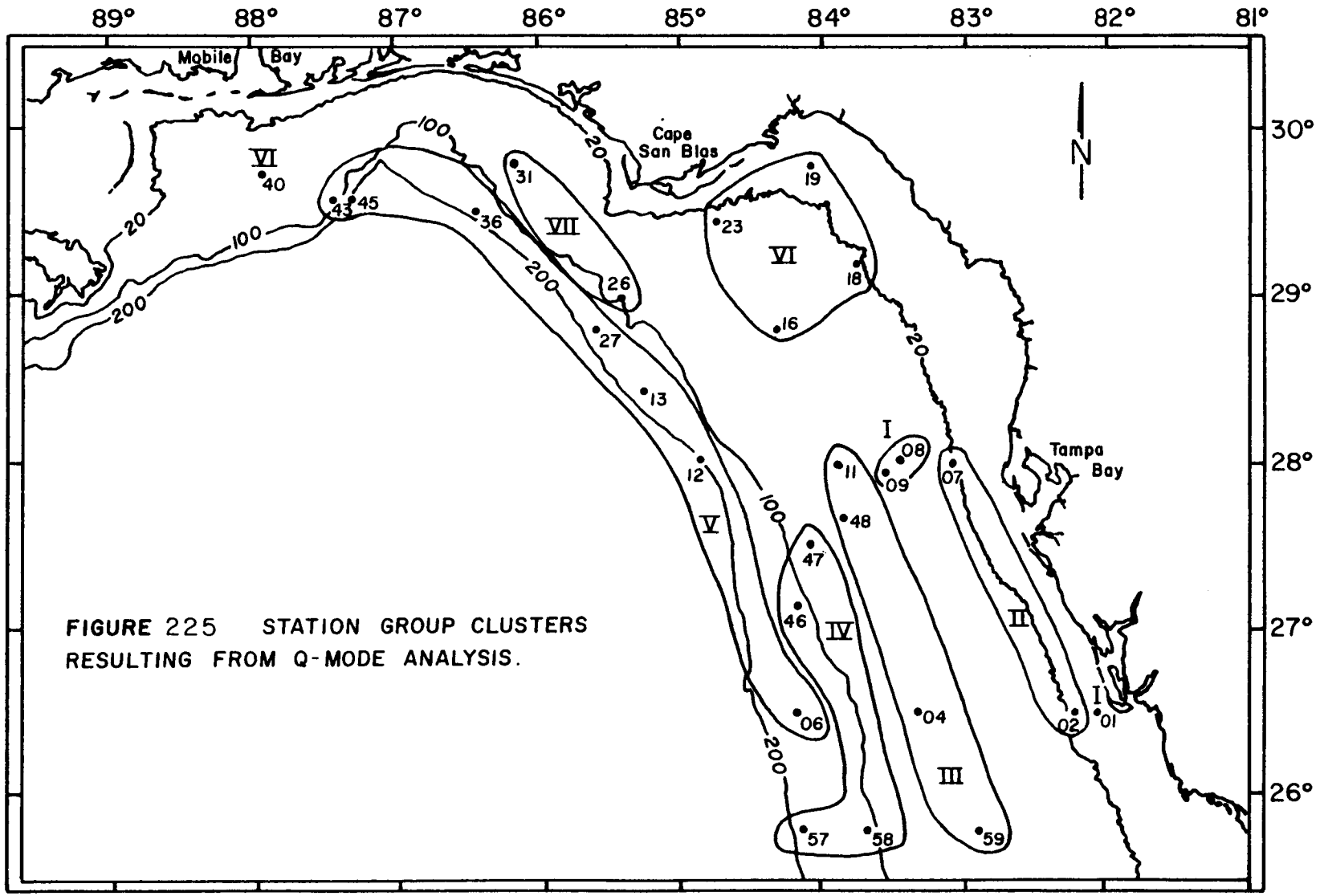

FIGURE 225 STATION GROUP CLUSTERS RESULTING FROM Q-MODE ANALYSIS.

TABLE 73

DOMINANT SPECIES ASSOCIATED WITH THE SEVEN GROUPS OF STATIONS RESULTING FROM Q-MODE ANALYSIS

GROUP I

Parvilucina multilineata

Tellina versicolor

Caecum bipatitum

GROUP II

Parvilucina multilineata

Tellina versicolor

Varicorbula operculata

GROUP III

Caecum cubitatum

Corbula dietziana

GROUP IV

Gouldia cerina

Corbula dietziana

Tellina versicolor

GROUP V

Abra lioica

GROUP VI

Tellina versicolor

Crassinella martinicensis

GROUP VII

weak group

highly unfaithful species

CONCLUSIONS

1. Both temperature and tropical species of molluscs are found in the eastern Gulf of Mexico. More temperate species are found in the northern nearshore regions while tropical forms appear in the southern regions, particularly those areas highly influenced by the Loop Current.

2. Tellina versicolor, Abra lioica, and Parvilucina multilineata occur over broad areas of the west Florida Shelf and are the only species which were found at any station or stations during all seven sampling seasons.

3. Species richness generally decreased from south to north and with increasing depth.

4. Abundances of individuals, although highly variable, also showed a general decrease from south to north and with increasing depth.

5. Maximum numbers of individuals generally occur during the fall seasons indicating a spring or summer spawning.

6. Cluster analysis yielded seven discernible station clusters which basically follow a north-south linearity following specific depth contours.

REFERENCES

Abbott, R. T., 1974. "American Seashells," 2nd ed. 663 pp. 24 pls. Van Nostrand Reinhold New York.

Agassiz, A., 1888. Three cruises of the United States Coast and Geodetic Survey Steamer Blake. Vol. 1. Bull. Museum Comparitive Zoology 14:1-314.

Boesch, D. F., 1973. Classification and community structure of macrobenthos in the Hampton Roads area, Virginia, Mar. Biol. 21:226-244.

Bright, T. J. and L. H. Pequegnat, Eds., 1974. "Biota of the West Flower Garden Bank." 435 pp. Gulf Publishing Co., Houston, Texas.

Bullis, H. R. and J. R. Thompson, 1965. Collections by the exploratory fishing vessels Oregon, Silver Bay, Combat, and Pelican made during 1956-1960 in the southwestern north Atlantic. U. S. Fish Wildl. Serv. Spec. Sci. Rep. No. 510:130 pp.

Clench, W. J., 1923. The marine shells of Sanibel, Florida. Nautilus, 37:52-56.

Dall, W. H., 1889. Report on the Mollusca ("Blake") II Gastropoda and Scaphapoda. Bull. Mus. Comp. Zool. Harvard, 18:1-492.

Heath, H., 1918. Solenogastres from the eastern coast of North America. Memoirs of the Museum of Comparative Zoology at Harvard College. Vol. 45(2):186-261. pls. 1-14.

Hedgpeth, J., 1953. An introduction to the zoogeography of the north western Gulf of Mexico with reference to the invertebrate fauna. Publ. Inst. Nar. Sci. Univ. Tex. 3:107-224.

Henderson, J. B., 1920. A monograph of the east American scaphopod mollusks. Bull. III U.S. Nat. Mus. p. 1-177 pls. 1-20.

Joyce, E. A., Jr., and J. Williams, 1969. Memoirs of the Hourglass cruises: rationale and pertinent data. Florida Department of Natural Resources Marine Research Laboratory 1(1):50 pp.

Kaas, P., 1972. Polyplacophora of the Caribbean region. Studies on the Fauna of Curacao and other Caribbean Islands, 141:1-162.

Keene, A. M., 1971. Sea Shells of Tropical West America, 2 ed. Stanford University Press, Stanford, California. 1064 pp.

Maul, G. A., 1977. The annual cycle of the Gulf Loop Current. Part I: Observations during a one-year series. Journal of Marine Research, 35(1):29-47.

Niiler, P. P., 1976. Observations of low-frequency currents on the West Florida Continental Shelf. Memoires Societe Royale des Sciences de Liege, 10:331-558.

Popham, J. D. and D. V. Ellis, 1971. A comparison of traditional, cluster and Zurich-Montpellier analyses of infaunal pelecypod associations from two adjacent sediment beds. Mar. Biol., 8:260-266.

Pulley, T. E., 1952. "A zoogeographic study based on the Bivalves of the Gulf of Mexico." 215 pp. Unpublished. Doctor thesis, Harvard University.

VOLUME II

CHAPTER 15

MACROINFAUNAL POLYCHAETES

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CONTRACT NO. AA550-CT7-34

ABUNDANCE, DIVERSITY, AND DISTRIBUTION OF BENTHIC POLYCHAETOUS ANNELIDS IN THE EASTERN GULF OF MEXICO

BY

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DAUPHIN ISLAND, ALABAMA

SEPTEMBER 1978

SUBMITTED IN FULFILLMENT OF

CONTRACT NUMBER AA550-CT7-34

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ABSTRACT

Polychaetous annelids were sampled at 107 sites on the Continental Shelf of the eastern Gulf of Mexico during the period June, 1975 through February, 1978. Approximately 195,400 individual polychaetes were identified and counted. These represented 60 families and 1,056 taxa. Wet weight biomass, individual abundance, and diversity varied with respect to sediment type, season, latitude and salinity. Average biomass values ranged from 39.04 to 306.53 $mg \cdot 0.06^{-2}$ m at deep stations, and from 392.02 to 2226.06 $mg \cdot 0.06^{-2}$ m at depths less than 100 m. Southern stations had generally higher standing crops. Polychaete abundance showed similar patterns, as expected. Species richness and diversity, however, were higher north of Cape San Blas, Florida and in shallow water habitats. Coarse sediments supported more polychaete individuals and species than either medium or fine sediments, although differences are small between coarse and medium sediment benthos. Polychaete assemblages appear to be arranged with respect to the same environmental parameters. Disjunct distributions of some groups are related to salinity and substrate preferences. Polychaete taxonomy and zoogeography are discussed.

INTRODUCTION

Polychaetous annelids are recognized as one of the most important components of soft bottom macroinfauna. As relatively immotile members of the benthos, they are good indicators of the impacts of environmental perturbation. The effects of such habitat changes have been studied by many investigators, including McNulty (1961, 1970), Godcharles (1971), O'Connor (1972), and others. Most such studies in the Gulf of Mexico have been related to dredging impacts in shallow waters and estuaries. These include work by Taylor and Saloman (1968), Taylor (1972), Lackey et al. (1973), Vittor (1974), Markey (1975), and others. However, none of the earlier work in the Gulf of Mexico has provided ecological information adequate to establish either large-scale patterns of distribution and abundance, or probable impacts of natural or man-induced changes on the Outer Continental Shelf (OCS).

Existing information on the systematics of polychaetes in the Gulf is also limited. Since the early work of Ehlers (1887) there have been a number of reports on polychaetes from estuarine and offshore waters. More recent papers on Gulf polychaetes taconomy include studies by Hartman (1951, 1954), Bault (1969), Foster (1969), Harper (1970), Taylor (1971), Kritzler (1973), and Vittor (1976). In addition, Perkins and Savage (1975) prepared a checklist of Gulf and Caribbean species. Vittor et al. (In Press) have also developed a checklist of Gulf species, but have based it on original data and collections produced by the MAFLA baseline environmental program. Fortunately, the taxonomy of polychaetes from similar (Carolinian) ecological provinces is better known. Guides for North Carolina (Hartman, 1945; Day, 1973; Gardiner, 1975), the United States east coast (Pettibone, 1963), and California (Hartman, 1968) are adequate to identify perhaps half of the polychaetes of the Gulf of Mexico. Many other papers provide descriptions which contribute to identification of Gulf polychaetes.

Benthic polychaete populations and assemblages serve increasingly as indicators of environmental quality. Studies by Boesch et al. (1974), for example, document the extent to which pollutants may disrupt marine ecosystems. Grassle and Grassle (1974), on the other hand, describe the natural variability of polychaete populations in high-stress environments. Impacts of oil spills (as at West Falmouth) on the marine environment have been described by Sanders et al. (1972) and include significant changes in polychaete assemblages.

Classification of polychaete assemblages has been described by several workers including Boesch (1973) in Virginia, Hessler and Jumars (1974) in the Central North Pacific, Nichols (1970) in Puget Sound, Washington and others. Most have correlated the abundance and diversity of polychaetes with sediment characteristics such as particle size distribution and organic content. Jumars and Fauchald (1977) have also described community structure in terms of feeding behavior and trophic function in the benthos.

The 1974/78 MAFLA benthic program has provided the opportunity to describe the polychaete assemblages in the eastern Gulf of Mexico and to

relate the abundance and diversity of these animals to such habitat characteristics as mean sediment particle size, carbonate and organic carbon content, geographic location, and season.

The purpose of the MAFLA benthic polychaete program was to contribute to our knowledge of the benthos in areas leased for oil exploration and development, in order to establish a baseline against which future habitat changes could be evaluated. This paper describes the results of these studies, and provides insight into the use of polychaete assemblages as predictive and analytical tools in measuring the impacts of offshore petroleum exploration and development.

MATERIALS AND METHODS

BENTHIC SAMPLING

Macroinfauna samples were collected eight times during the period 1974/78: June, 1974 (S-74); June, 1975 (S-75); September, 1975 (F-75); February, 1976 (W-76); June, 1976 (S-76); August, 1977 (S-77); November, 1977 (F-77); and February, 1978 (W-78). With a few exceptions noted below, these samples were taken with a box-core which removed a sediment plug measuring 21.3 x 30.5 cm in surface area and varying in depth from 15 to 43.2 cm. Where the corer could not penetrate at least 15 cm into the bottom (e.g., at Station 2851) a grab or dredge was used to obtain qualitative samples.

The following stepwise procedure was used in handling and processing each sample upon its arrival on deck:

1. Subsamples were taken for sediment characterization and any other required analyses;

2. Sediment depth in the box-core was measured;

3. Sediment was removed from box, to a depth of 15 cm, and placed in 0.5 mm mesh screen bags;

4. Samples were washed to remove most silt;

5. Sediment was funneled into cotton cloth sample bags, with label;

6. Sample bags were immersed in 15% $MgSO_4$ for 30 minutes to narcotize organisms;

7. Sample bags were transferred to 10% buffered formalin and stored on deck in sealed 200 ℓ (55 gal) steel drums.

Macroinfauna samples were transported to the laboratory for sorting and subsequent analysis described below.

SORTING

The procedures detailed below appear to be the most time-efficient and yet specimen-protective which can be accomplished given the volume of material to be processed.

1. Sediment from one bag was placed in a 19 ℓ (5 gal) plastic bucket equipped with a water inflow at the bottom and a spout near the top. The bucket rested on a platform which can be tipped in order to drain water and suspended material through the spout.

2. The sample was first stained for 10 minutes with approximately 25 mℓ of 1% Rose bengal solution.

3. The sample was then "floated" for two to five times, depending on the amount of material present. Organisms and debris which were suspended by a moderate water inflow were caught on a 0.5 mm mesh screen and carefully rinsed into a labelled 120 cc (4 oz) jar containing 70% ethanol.

4. Coarse material, free of silt and clay, was placed in a plastic bucket with the 120 cc jar, and carried into the sorting laboratory.

5. Approximately 100 mℓ aliquots of this coarse material were examined at a time under magnifying lights. The sediment was placed in 25 x 40 cm white enamal trays, covered with tap water, and carefully picked over for all remaining macroinfauna. Molluscs and echinoderms were most abundant in this recovery process, since most arthropods and polychaetes are readily suspended and removed during the floating step.

6. All macroinfauna were placed in 70% ethanol for subsequent anlaysis.

7. Fine-sorting was accomplished using a research-quality dissecting microscope. As specimens were identified to the appropriate taxon (Polychaeta, Arthropoda, Mollusca, Echinodermata, other), they were placed in glass vials containing 70% ethanol.

BIOMASS

Biomass was measured for each group separated during fine-sorting. This process was extremely error prone due to weight loss during weighing. Consequently, quick, accurate measurement was essential. Specimens were removed from their vial onto filter paper, carefully blotted dry, placed in a pre-weighed glass Petri dish, and weighed on a semi-micro balance accurate to $\pm$ 0.01 mg. They were immediately returned to their vial, and placed in the appropriate group container. Groups to be identified by other investigators were transferred periodically, via courier, counter-to-counter air shipment, or personal delivery (e.g., to Drs. Hopkins and Heard, both of whom also work in laboratories on Dauphin Island, Alabama.

POLYCHAETE IDENTIFICATION

The first step in polychaete identification involved family-level separation under a dissecting microscope. Family representatives were then examined under dissecting and compound microscopes in order to count and identify each individual to genus and species levels.

A taxonomic key and reprint file was used to establish polychaete identifications as accurately as feasible. Several pubished keys, and a set of keys to the Polychaeta developed by Barry A. Vittor & Associates, were critical to this process. Confirmation or correction of species identifications was accomplished by extended visits to the U.S. National Museum, and through collaboration with other polychaete taxonomists.

Representatives of each species identified were deposited in a voucher collection in the laboratory of Barry A. Vittor & Associates. These specimens were placed in separate vials for each particular box-core represented.

All polychaetes not placed in the voucher collection were returned to their original vial, or were returned to the jar containing family-level vials. All materials have been stored for future reference.

RESULTS

BIOMASS

Polychaete wet weight biomass data are tabulated in Appendix A for all stations sampled during 1975/78. Although the variability of the data precludes sophisticated analysis, some patterns are still visible. Table 74 summarizes standing crop data, arranged with respect to water depth and geographical location. In general, polychaete biomass levels were greatest during the summer and winter seasons. For example, stations along Transects V and VI supported average standing crops of 387.78 mg.0.07 m^{-2} core and 426.67 mg.0.07 m^{-2} core, respectively during June, 1975 (S-75). Corresponding values during September, 1975 (F-75) were 136.67 and 192.22, respectively. Increases to over 75% of S-75 levels were observed during February, 1976 (W-76). These differences were tested using nonparametric analysis of variance and were found to be significant ($p < 0.01$).

Seasonal changes apparent during the F-75 sampling program coincided with the passage of hurricane Eloise over Transect V. However, the greatest decreases in biomass occurred in deep waters (>100 m) south of Cape San Blas.

In fact, deep water samples (e.g., 2106, 2212, 2313, 2427, 2536, 2645, 2747) generally contained lower polychaete biomass than those shallower than 100 m. Combined deep station biomass levels averaged less than 15% of combined shallow stations. Division of each depth category into north/south components indicated that seasonal standing crop levels fluctuate most in deep water regardless of latitude. Fall declines, however, were most pronounced among southern deep-water stations.

TABLE 74

COMPARISONS OF PRIMARY STATIONS WITH RESPECT TO

BENTHIC POLYCHAETE BIOMASS

	SAMPLE PERIOD						
LOCATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
BIOMASS:							
Deep/Comb.	306.53	39.04	106.00	57.65	102.82	72.92	87.89
Shallow/Comb.	2226.06	392.02	535.72	519.56	588.21	402.09	503.11
Deep/North	221.60	66.94	120.20	30.36	70.12	142.94	50.02
Deep/South	349.00	25.09	98.90	68.57	112.16	52.24	98.71
Shallow/North	542.22	294.65	340.43	361.35	585.86	515.02	443.57
Shallow/South	2787.33	424.48	600.81	568.24	588.80	371.73	517.99

Biomass is expressed as $mg \cdot 0.06m^{-2}$ box core. Deep stations are defined as those at depths greater than 100 m, while north stations are those above Cape San Blas, Florida.

Unusually high biomass levels were reported for several S-75 stations (2101 in particular). These extremes were found to be the result of inclusion of fish in infaunal analyses. Vertebrates were omitted from subsequent samples analyses. Data for 1974 were not available for discussion in this report.

POLYCHAETE ABUNDANCE

Appendix B summarizes the total abundance of polychaetes at MAFLA stations sampled during the period 1975/78. Over 195,000 polychaetes were identified, counted, and archived during the MAFLA program. Table 75 provides a summary of these data with respect to water depth and latitude. As expected, deep stations were characterized by lower polychaete abundance. Shallow water population densities ranged from four to eight times higher, regardless of season. Maximum abundance occurred during 1976 and 1977 summer months at shallow stations, but during the winter months of both years at deep stations. Seasonal changes in deep water were highlighted by estimation of deep/north and deep/south averages. Although 1975/76 shallow water stations exhibited a similar trend, this pattern broke down during 1977/78.

The relationships between sediments and polychaete abundance are illustrated in Tables 76 and 77. Sediment groups in Table 76 were clustered on the basis of mean particle size grand station means for all stations sampled during the 1974/78 MAFLA program. Sediment classifications were defined using the Wentworth grain size scale. Stations occurring within each sediment cluster were averaged for mean numbers of individuals for all sample periods (excluding 1974).

Polychaete abundance was lowest in fine sediments containing moderate amounts of calcium carbonate ($CaCO_3$). Highest population levels occurred in medium sand mixed with shell hash and calcareous coral rubble (as occurred at most Transect IV and V stations). Coarsest sediments also supported high densities of worms. However, the correlations between polychaete abundance, mean particle size and $CaCO_3$ were not significant ($p > 0.10$).

Table 77 summarizes data for primary stations only (1975 through 1978). Sediment groupings for these stations do not correlate well with polychaete abundance. Highest abundance occurred in medium sand containing moderate amounts of $CaCO_3$, but also in coarse coralline rubble. Lowest densities were found among stations characterized by very fine sediments.

NUMBER OF SPECIES

The abundance of benthic polychaete taxa for the period June, 1975 through February, 1978 is tabulated in Appendix C. These data suggest general patterns which correlate with trends described for both biomass and individual abundance. Over 1,050 taxa were counted during the MAFLA program. Perhaps one-third of these represent incomplete identification of other species. Table 78 summarizes comparisons of species abundance and station depth and latitude. The average number of taxa in deep water habitats ranged from 39 to 54, and from 72 to 98 in shallow waters.

TABLE 75

COMPARISONS OF BENTHIC POLYCHAETE ABUNDANCE AT PARIMARY STATIONS

LOCATION	SAMPLE PERIOD S-75	F-75	W-76	S-76	S-77	F-77	W-78
INDIVIDUAL ABUNDANCE:							
Deep/Comb.	123	165	226	135	190	175	218
Shallow/Comb.	769	888	922	1105	1375	1069	754
Deep/North	162	239	362	150	187	232	246
Deep/South	101	128	156	127	190	158	210
Shallow/North	551	800	838	707	1734	2194	1170
Shallow/South	842	917	950	1304	1285	723	650

Abundance is expressed as mean number of individuals$\cdot 0.58 m^{-2}$. Deep stations occur in depths greater than 100 m, while north stations are those above Cape San Blas, Florida.

TABLE 76

SUMMARY OF BENTHIC POLYCHAETE AND SEDIMENT DATA FOR THE 1974/78 STUDY PERIOD BY SEDIMENT GROUPS

Sediment Group	Classification	Mean Particle Size (Ø)	Percent $CaCO_3$	No.of Species	No. of Individ.	H'
A1	Medium	3.38	88.9	56	372	3.20
A2	Medium	4.20	79.0	42	487	3.14
A3	Medium	2.18	67.9	123	1327	3.84
B	Fine	5.51	50.8	38	274	2.94
C	Coarse	0.90	79.9	98	838	3.80
C	Coarse	1.68	42.3	84	759	3.46
E	Medium	2.64	30.2	77	984	3.27

Sediments were grouped by cluster analysis based on mean particle size. Polychaete data exclude 1974 analyses.

TABLE 77

SUMMARY OF BENTHIC POLYCHAETE AND SEDIMENT DATA FOR PRIMARY STATIONS, 1975-78

Sediment Group	Classification	Mean Particle Size (Ø)	Percent $CaCO_3$	No. of Species	No. of Individ.	H'
I	Medium	2.74	38.0	71	1128	3.28
II	Medium	2.67	75.7	69	480	3.24
III	Coarse	1.53	31.2	80	767	3.49
IV	Coarse	1.14	77.5	107	1109	3.79
V	Fine	4.94	70.1	42	366	3.09

Sediments were grouped by cluster analysis based on mean particle size.

TABLE 78

MEAN NUMBER OF BENTHIC POLYCHAETE TAXA AT PRIMARY STATIONS

	SAMPLE PERIOD						
LOCATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
SPECIES NUMBER:							
Deep/Comb.	42*	39	54	39	44	44	50
Shallow/Comb.	77	72	83	98	98	87	89
Deep/North	52	48	72	56	42	61	64
Deep/South	38	34	45	30	45	39	46
Shallow/North	76	72	93	92	118	102	116
Shallow/South	77	72	80	101	93	82	82

*numbers $\cdot 0.59 m^{-2}$

Deep stations occur at depths greater than 100 m, while North stations are those above Cape San Blas, Florida.

Northern deep stations contained more species than southern stations. A similar pattern existed among shallow water stations, but was less conclusive. Seasonal trends were also somewhat confused. In general, however, the number of species declined during the fall and reached a peak during summer and winter months.

Species number correlated better with mean sediment size (Tables 76 and 77). Both sediment cluster analyses indicated that the number of species increases as sediment particle size decreases, although $CaCO_3$ concentrations also affect polychaete diversity to some extent. The greatest numbers of species were found in coralline rubble sediments typical of the northern portions of the West Florida Shelf. Medium to coarse foraminiferal sands found along the eastern slope of the De Soto Canyon (e.g., 2645) supported fewer species despite a favorable combination of particle size and $CaCO_3$.

SPECIES DIVERSITY

Shannon-Wiener (H') species diversity data for 1976/78 are provided in Appendix D. Earlier data were not available for inclusion in this paper. The data show a remarkable uniformity despite a range from 0.50 to 4.41. Extremely low values appeared at secondary stations represented by only one 0.06 m^2 box core. High diversities were observed at stations characterized by mixed sand and silt (e.g., 2211, 2316, 2645). In general, stations at which very high individual abundance was found exhibited only moderate diversity. Table 79 summarizes average diversities among deep and shallow stations. Shallow habitats had generally higher species diversities with little seasonal change. Highest average H' values occurred during the winter (W-78) regardless of depth. However, deep stations experienced greater fluctuation from summer to winter. Southern deep stations appeared to account for most of this variation, while northern deep water sites were quite uniform except during S-77. The opposite pattern was observed among shallow water stations: shallow northern sites exhibited greater seasonal changes.

Tables 76 and 77 summarize the relationships between sediment type and diversity. There appeared to be a negative correlation between grand station mean particle size (Table 76) and H', so that lowest diversity occurred in sediments with the greatest mean phi. Highest species diversities were observed in sediments consisting of coarse coralline rubble and medium sand composed of foraminifera tests. These patterns are generally reflected with H' (Table 77) and also compare favorably with polychaete abundance and species abundance trends.

POLYCHAETE CLUSTER ANALYSIS

Seasonal benthic polychaete data were subjected to Bray-Curtis similarity analysis and stations clustered to identify major assemblages. This analysis was based on a total 254 species, including surface deposit feeders, burrowing deposit feeders, and carnivores. Forms that were considered to be filter feeders, errantiate epibenthic and encrusting species were excluded from this treatment. Also omitted were taxa which could not be determined to be distinct species (e.g., families or indeterminable taxa). Figure 226 depicts the results of clustring of similarity values.

TABLE 79

MEAN SHANNON-WIENER SPECIES DIVERSITY (H') AT PRIMARY STATIONS

DURING 1976/78

LOCATION	SAMPLE PERIOD S-76	S-77	F-77	W-78
SPECIES DIVERSITY (H'):				
Deep/Comb.	3.24	3.18	3.11	3.53
Shallow/Comb.	3.24	3.44	3.36	3.53
Deep/North	3.64	3.13	3.63	3.67
Deep/South	3.04	3.20	2.96	3.49
Shallow/North	3.69	3.49	3.16	3.78
Shallow/South	3.02	3.42	3.42	3.46

$\overline{H'}$ is calculated using natural logarithms of p_i.

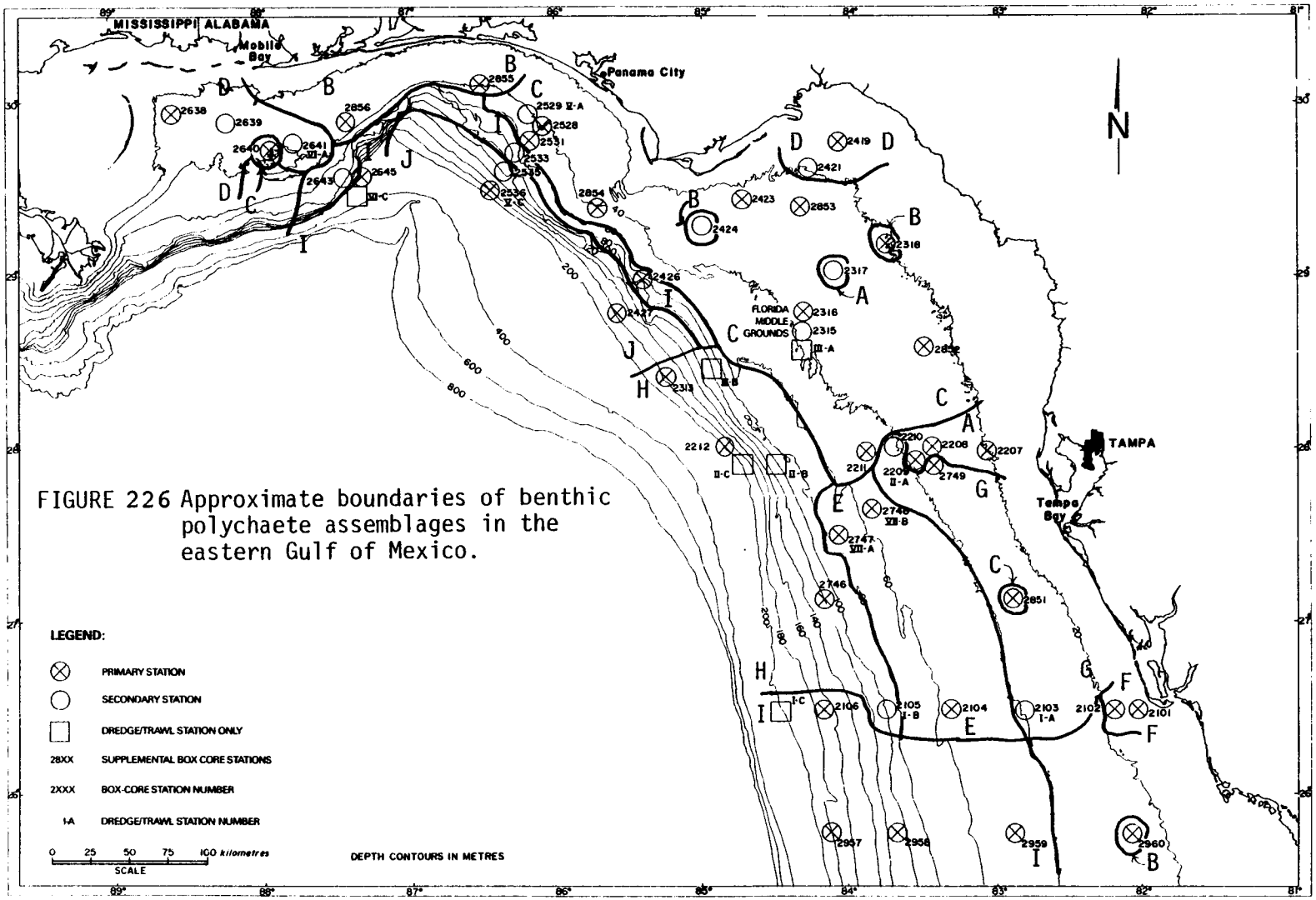

FIGURE 226 Approximate boundaries of benthic polychaete assemblages in the eastern Gulf of Mexico.

BLM 77/78 MAFLA SURVEY STATION LOCATIONS

The four seasons for which similarities were generated (1976/78) have been combined to produce Figure 226. Assemblage distributions were also based in part on sediment cluster analysis. Approximately ten polychaete groups have been defined in the MAFLA study area. Appendix E summarizes the dominant taxa in each assemblage. Several patterns in their distributions deserve description here. Groups A, B and C occur on medium to coarse bottoms, with patchy distributions dependent on suitable substrate. In general, these assemblages appear to be limited to depths less than 60 m. Assemblage D occurs in shallow water also, but is further restricted to medium to fine sediments subjected to periodic brackish conditions. Group F also occurs in brackish waters, but has only moderate affinities with the more northern group D. Groups E, G, H, and I exist in varied sediments ranging from fine to coarse. E and G appear to be limited to shallow waters offshore from Tampa Bay, while H and I are found on the outer edges of the Continental Shelf. Assemblage I is particularly widespread at depths greater than 60 m. It is interesting that this group is found on both sides of the De Soto Canyon, in coarse foraminiferal sands, but also occurs in medium sands typical of the OCS off Charlotte Harbor, Florida. Group J is limited in distribution to fine limestone muds in deep waters at the edge of the West Florida Shelf off Cape San Blas, Florida.

Statistical analysis has not yet been performed to correlate polychaete and sediment clustering. However, Table 80 represents the similarities between sediment clusters based on both $CaCO_3$ and mean particle size and polychaete clusters based on 254 species. Similarity values were calculated as the Bray-Curtis index of percent overlap in occurrence of stations in sediment and polychaete groups. Good correlations existed between polychaete groups F, G, H, and J, and their corresponding sediment (habitat) types. Fair correlations were found between groups A and D and their corresponding sediment groups. Little similarity existed between the remaining polychaete and sediment clusters.

DISCUSSION

ANIMAL-SEDIMENT RELATIONSHIPS

Temperate and tropical benthic environments include many species with pelagic larval stages. Settling larvae constantly invade benthic communities during seasonal recruitment periods, but community boundaries still are rather distinct. According to Thorson (1957), the appearance of boundaries between tropical and subtropical benthic fauna results from selectivity of settling larvae. Sediments as well as salinity/temperature regimes affect the ability of species to settle and persist in the benthos.

Many authors have discussed the relationships between the infauna and sediment and hydrographic characteristics of their environment. Sanders (1956, 1958) described patterns of infaunal abundance and diversity in Buzzards Bay (New England). He reported that deposit feeders dominate mud (fine) sediments, while filter feeders dominate sand (medium and coarse) substrates. Unstable sediments were described as being worked continually by deposit feeders, which prohibited the growth and survival of filter feeders and/or such sessile forms as Owenia fusiformis. Where tubicolous forms are able to become established, sediments may be stabilized and thus

TABLE 80

BRAY-CURTIS SIMILARITY MATRIX SHOWING OVERLAP BETWEEN CLUSTERING FOR POLYCHAETES AND SEDIMENTS

	POLYCHAETE GROUP									
SEDIMENT GROUP	A	B	C	D	E	F	G	H	I	J
I	0	0	0	0.33	0	0	0	0	0	0
II	0	0.25	0	0.50	0	0	0	0	0	0
III	0	0.29	0.14	0	0	0	0	0	0	0
IV	0	0	0.47	0	0	0	0	0	0.15	0
V	0	0.29	0	0	0	0	0	0	0.20	0
VI	0.22	0	0	0.40	0	0.57	0	0	0	0
VIA	0	0.33	0	0	0	0	0	0	0	0
VIB	0	0	0	0	0	0	0.67	0	0	0
VII	0	0	0	0	0	0	0	0	0.40	0
VIII	0	0	0	0	0	0	0	0	0	0.80
IX	0	0	0	0	0	0	0	0.50	0.50	0.18
X	0.29	0.09	0.48	0	0.30	0	0.11	0.10	0	0

Sediment clusters were based on $CaCO_3$ and mean particle size

favor establishment of non-deposit feeders. Rhoads and Young (1970) corroborated these successional patterns in their studies of Cape Cod Bay. They reported that tube mats tended to bind otherwise loose sediments and form a more solid substrate suitable for colonization by epifauna.

MAFLA polychaete assemblages also reflect these relationships. Unstable mud bottoms occur on the Mississippi-Alabama Shelf (in the vicinity of Mobile Bay), and in deep water off Cape San Blas, Florida. Other such areas have low species richness as well as individual abundance. More stable bottoms occur in deep water along the west slope of the De Soto Canyon and support a highly diverse polychaete fauna.

Similar patterns were found by Boesch (1972) in Virginia. He reported that polychaete assemblages were associated with three general sediment types: mud, muddy sand, and sand. Ubiquitous species were also present and did not appear to be associated with particular groups. Species diversity was highest in muddy sand and sand bottoms, largely as a result of increased species richness. Although the same general trend was observed in the present study of the eastern Gulf of Mexico, there are many irregularities introduced by hydrography and sediment chemistry ($CaCO_3$ content in particular). Polychaetes are most diverse in areas characterized by calcareous rubble substrates.

Sediment particle size distribution affects polychaete community structure in several ways including substrate stability (discussed above) and food availability. It may be stated generally that species diversity increases as productivity increases, if all other factors are equal (Connell and Orias, 1964). This appears to be true in some areas of the eastern Gulf of Mexico: stations 2638 and 2536 occupy fine unstable sediments. However, diversity at the former is much higher as a result of a greater influx of estuarine derived organic detritus. Similar comparisons may be drawn between shallow stations on the Mississippi-Alabama Shelf and those off Charlotte Harbor, Florida (Transects 1 and 9), with diversities being in the latter area.

Hessler and Jumars (1974) have shown that low productivity may not preclude high species diversity in the deep sea benthos. Abyssal depths experience very little environmental fluctuation, hence allow development of biologically-accommodated, high-diversity communities despite low productivity. The MAFLA study area did not include sites that may be considered very stable hydrographically, so their conclusions cannot be tested on the basis of this study.

SEASONAL EFFECTS

That temporal changes in hydrography and substrate elicit infaunal community changes has been well documented by several authors (Sanders, 1958; Lie, 1968; Boesch, 1972; and others). Most of these seasonal differences can be attributed to changes in larval recruitment or to food availability. Species abundance and richness in the MAFLA area exhibit seasonal patterns that suggest that both factors play an important role in benthic community structure. Individual and species abundance decrease somewhat during the winter. Heavy recruitment of polychaetes occurs during early

summer and results in very high abundance. Subsequent mortality of marginally adapted polychaetes is indicated by fall season declines in both individual abundance and species richness. Causes for this mortality are not known, but may involve storm activity, decreased temperature, or predation. Those species which persist appear to increase in numbers and size. Their success is doubtless related in part to reduced competition for food and space after the fall season decline.

Seasonal storms such as hurricanes may result in catastrophic polychaete mortality. Hurricane Eloise passed over Transect 5 during the fall, 1975 sample period. Substrate perturbations were reported to at least 50 m depth (L. Doyle, personal communication). However, it is not possible to draw a direct correlation between drastically reduced standing crop and abundance after the storm since similar changes occurred on the West Florida Shelf off Tampa Bay. On the other hand, a significant increase in polychaete abundance and biomass was observed during February despite a series of extremely severe winter storms. The implication of this recolonization is that benthic polychaete populations do recruit juveniles even in the fall (and possible the winter). Thus, habitat perturbations which decimate benthic standing crop may not have long-lasting impacts on the benthos. This is not to suggest that radical chemical and physical changes in the benthos will not have long-term effects, but rather that the MAFLA benthic environment is dynamic with respect to both physical and biological attributes.

TAXONOMY AND ZOOGEOGRAPHY

The polychaetes identified during the MAFLA program represent 60 families and 1,056 taxa. Seven families (Acrocirridae, Fauveliopsidae, Hartmaniellidae, Lacydoniidae, Pholoididae, Questidae, and Saccocirridae) have not previously been reported from the Gulf of Mexico/Caribbean region (see Perkins and Savage, 1975). Most records of the species collected represent range extension, largely as a result of a paucity of previous sample material from this area. At least 50 species identified here are new to science.

Hartman (1951) included 158 species and 36 families in her study of littoral polychaetes in the Gulf. Of these, 15 species were previously undescribed. Perkins and Savage (1975) reported the occurrence of 55 families of benthic polychaetes in the Gulf and Caribbean based on an extensive literature review plus examination of Hourglass Cruise samples from the West Florida Shelf off Tampa Bay. They included 247 papers in their review, while over 500 references (published and unpublished) have been used in the present study to establish polychaete identities for the MAFLA area alone. The complexity of the taxonomy of these animals is reflected in the fact that only 75% of the taxa enumerated represent valid species, and we have been able to verify the identities of less than 75% of these. The 300 or so invalid taxa include damaged specimens and unconfirmed or incomplete identifications. Nonverified names include especially those taxa not represented in the U.S. National Museum and species new to science. A total of 177 species have been accessioned by the U. S. National Museum and are listed in Appendix F.

Despite the magnitude of this taxonomy problem, some patterns of polychaete distribution can be discussed. As stated earlier, species distributions are related primarily to sediment type and secondarily to salinity and food availability. Coarse sand and rubble sediments are populated heavily by syllids, glycerids, goniadids, spionids, and paraonids. These sediments are generally well aerated and contain abundant food. The polychaetes typical of these habitats include all trophic categories (filter feeders, deposit feeders, carnivores), although surface deposit feeders and carnivores are especially important.

Fine sediments (e.g., 2638, 2419, 2536) are inhabited primarily by burrowing deposit feeders such as the lumbrinerids, cirratulids, opheliids, and some spionids. Also important in these areas are tube-dwelling forms including the maldanids and chaetopterids. Sediments in these areas can be characterized as unstable, poorly aerated, and containing abundant organic material.

Medium sand substrates contain a highly diverse polychaete assemblage which includes all feeding types. A rather even balance exists between carnivores, surface deposit feeders, and burrowing deposit feeders. Filter feeders occur in abundance in those particular areas where suitable firm substrate exists.

Disjunct distributions occur among many species, as suggested by Figure 226. Ninoe nigripes, for example, is found at station 2535 on the east side of the De Soto Canyon, and at many sites on the Mississippi-Alabama Shelf. The De Soto Canyon also appears to interrupt the distributions of Cossura sp. A, Paraprionospio pinnata, Asychis carolinae, and Synelmis albini. Congeneric species also show distribution differences. These include Asychis carolinae and A. elongata, Chone duneri and C. filicaudata, Prionospio cristata and P. cirrobranchiata, Lumbrineris cruzensis and L. cf. crassidentata, Magelona pettiboneae and M. sp. A, and many others. These congeners overlap somewhat but generally separate near Cape San Blas, Florida. The possible causes for this pattern include the change from quartz to calcareous sediment, the impact of the De Soto Canyon on mass circulation, and differences in stream discharge. More comprehensive statistical treatment of the data is necessary for resolution of the effects of these factors on polychaete assemblages.

The eastern Gulf of Mexico supports a polychaete fauna which includes approximately 17% cosmopolitan species, 25% Caribbean species, 28% Carolinian species, and perhaps 30% endemic species. The systematics of the last group must be better established before the biogeography of Gulf polychaetes can be compared accurately with other regions. It would be premature to conclude that the eastern Gulf represents a unique biogeographic province at this time.

CONCLUSIONS

Analysis of benthic polychaetous annelids in the MAFLA area leads to several major conclusions, summarized as follows:

1. Polychaete standing crop (biomass), individual abundance, and species richness are negatively correlated with mean particle size (as phi). That is, each of these community measures decrease as sediments increase in fineness.

2. Seasonal changes in polychaete abundance and diversity are repeated from one year to the next, with the extent of fluctuations related to storm intensity. Abundance generally declines during the fall, while species diversity increases from summer to winter.

3. Deep water habitats support a less abundant and less diverse polychaete fauna, regardless of geographical location. However, highest abundance occurs during the winter at deep stations but during the summer at shallow sites.

4. Benthic habitats north of Cape San Blas, Florida support higher numbers of species regardless of depth, but also show greater seasonal fluctuation in species diversity.

5. Ten polychaete assemblages are defined for the MAFLA study area. They correlate well with cluster analysis of sediments, except where sediments consist of a wide variety of materials (shell hash, sand, rubble). Assemblages are also defined in part by water depth, salinity, and latitude.

REFERENCES

Bault, E. I., 1969. A study of the distribution and zoogeography of the polychaetous annelids of the Continental Shelf in the northeastern Gulf of Mexico. M.S. Thesis, Florida State University. 113 pp.

Boesch, D. F., 1972. Species diversity of marine macrobenthos in the Virginia area. Chesapeake Science. 13:206-211.

Boesch, D. F., 1973. Classification and community structure of macrobenthos in the Hampton Roads area, Virginia. Mar. Biol. 21:226-244.

Boesch, D. F., C. H. Herschner, and J. H. Milgram, 1974. Oil spills and the Marine Environment, pp. 1-106. Ballinger Publish. Co., Cambridge, Mass.

Connell, J. H. and E. Orias, 1964. The ecological regulation of species diversity. Amer. Natur. 98:399-414.

Day, J. H., 1973. New Polychaeta from Beaufort with a key to all species recorded from North Carolina. NOAA Tech. Rep. NMFS Circ. - 375. 140 pp.

Ehlers, E., 1887. Report on the annelids of the dredging expedition of the U. S. Coast Survey Steamer "Blake." Mem. Mus. Comp. Zool., Harvard Univ. 15:1-335.

Foster, M., 1969. New species of Spionidae (Polychaeta) from the Gulf of Mexico and Caribbean Sea, with a partial revision of the genus Prionospio. Proc. Biol. Soc. Wash. 82:381-400.

Gardiner, S.L., 1975. Errant polychaete annelids from North Carolina. J. Elisha Mitchell Sci. Soc. 91(3):77-220.

Godcharles, M.F., 1971. A study of effects of a commercial dredge on benthic communities in estuarine areas. Fla. Dept. Nat. Resources Mar. Res. Lab., Tech. Ser. No. 64. 51 pp.

Grassle, J.F. and J.P. Grassle, 1974. Opportunistic life histories and genetic systems in marine benthic polychaetes. J. Mar. Res. 32(2): 253-284.

Harper, D.E., 1970. Ecological studies of selected level-bottom macro-invertebrates of Galveston, Texas. Ph.D. Dissertation, Texas A&M University. 300 pp.

Hartman, O., 1945. The marine annelids of North Carolina. Duke Univ. Mar. Sta. Bull. 2:1-54.

Hartman, O., 1951. The littoral marine annelids of the Gulf of Mexico. Publ. Inst. Mar. Sci., Univ. Tex. 2:7-124.

Hartman, O., 1954. Polychaetous annelids of the Gulf of Mexico, pp. 413-417. In: P. S. Galtsoff (ed). Gulf of Mexico, its origin, waters and marine life. U.S. Fish Wildl-Serv., Fish. Bull. 89.

Hartman, O., 1968. Atlas of the polychaetous annelids of California. Allan Hancock Found. Los Angeles, Calif. (2 Vol.).

Hessler, R.P. and P.A. Jumars, 1974. Abyssal community analysis from replicate box-cores in the central North Pacific. Deep-Sea Research. 21:185-209.

Jumars, P.A. and R. Fauchald, 1977. Between community contrasts in successful polychaete feeding strategies. pp. 1-20, In: B. C. Coull (ed). The Ecology of Marine Benthos. Baruch Library in Marine Science, No. 6 Univ. So. Carolina Press. Columbia, S.C.

Kritzler, H., 1973. Diversity, biomass and systematics of the benthic polychaete biocenoses of a selected estuary and an offshore platform. Project report to Gulf Universities Research Consortium, Offshore Ecology Investigation. 14 pp.

Lackey, J.B., T.W. Duncan Jr., J.L. Fox, J.W. Markey, and J.H. Sullivan, Jr., 1973. A study of the effects of maintenance dredging in Mobile Bay, Alabama on selected biological parameters. Contract Report. U. S. Army Corps of Engineers, Mobile District, Mobile, Alabama. 54 pp.

Lie, U., 1968. A quantitative study of benthic infauna in Puget Sound, Washington, U.S.A., in 1963-64. Fisk Dir. Skr. (Ser. Havunders). 14:229-556.

Markey, J. W., 1975. A study on the effects of maintenance dredging on selected ecological parameters in the Gulfport Ship Channel, Gulfport, Mississippi. Contract Report. U. S. Army Corps of Engineers, Mobile District, Mobile, Alabama. 321 pp.

McNulty, J. K., 1961. Ecological effects of sewage pollution in Biscayne Bay, Florida: sediments and distribution of benthic and fouling macro-organisms. Bull. Mar. Sci. Gulf Caribb. 11:394-447.

_____, 1970. Effect of abatement of domestic sewage on the benthos, volumes of zooplankton, and the fouling organisms of Biscayne Bay, Florida. Stud. Trop. Oceanogr. (Miami), No. 9, 107 pp.

Nichols, F. H., 1970. Benthic polychaete assemblages and their relationship to the sediment in Port Madison, Washington. Mar. Biol. 6:48-57.

O'Connor, J. S., 1972. The benthic macrofauna of Moriches Bay, New York. Biol. Bull. 142:84-102.

Perkins, T. H. and T. Savage, 1975. A bibliography and checklist of polychaetous annelids of Florida, the Gulf of Mexico, and the Caribbean Region. Fla. Mar. Res. Publ. No. 14. 62 pp.

Pettibone, M. H., 1963. Marine polychaete worms of the New England region. I. Aphroditidae through Trochonchaetidae. Bull. U.S. Nat. Mus. 227: 1-356.

Rhoads, D. K. and D. C. Young, 1970. The influence of deposit-feeding organisms on sediment stability and community trophic structure. J. Mar. Res. 28:150-178.

Sanders, H. L., 1956. Oceanography of Long Island Sound, 1952-54. X. Biology of Marine bottom communities. Bull. Bingham Oceanogr. Coll. 15:345-414.

_____, 1958. Benthic studies in Buzzards Bay. I. Animal-sediment relationships. Limnol. Oceanogr. 3:245-258.

Sanders, H. L., J. F. Grassle, and G. R. Hampson, 1972. The West Falmouth oil spill. I. Biology. National Technical Information Service. Springfield, Va. 49 pp.

Taylor, J. L., 1971. Polychaetous annelids and benthic environments in Tampa Bay, Florida. Doctoral dissertation, Univ. Fla. 1332 pp.

Taylor, J. L. and C. H. Saloman, 1968. Some effects of hydraulic dredging and coastal development in Boca Ciega Bay, Florida. Fish. Bull. 67(2):213-241.

Thorson, G., 1957. Bottom communities. pp. 461-543 in J. W. Hedgpeth, (ed.), Treatise on Marine Ecology and Paleoecology. Vol. I. Waverly Press, Baltimore.

Vittor, B. A., 1974. Effects of channel dredging on biota of a shallow Alabama estuary. J. Mar. Sci. Ala. 2(3):111-134.

Vittor, B. A., 1976. Abundance and diversity of polychaetous annelids on the Alabama-Mississippi near Continental Shelf. Proc. Fla. Acad. Sci. Unpublished report. 17 pp.

Vittor, B. A., G. R. Gaston, P. G. Johnson and J. M. Uebelacker, In Press. Annotated checklist of polychaetes from the northeastern Gulf of Mexico, MAFLA program. Northeastern Gulf Science.

APPENDIX A

Average benthic macroinfaunal biomass for MAFLA stations sampled during the period June, 1975 through February, 1978. Station sample area was 0.58 m^2 except for 1977/78 secondary stations (*), at which one 0.06 m^2 box core was collected. Data expressed as wet weight in milligrams per 0.06 m^2.

	SAMPLE PERIOD						
STATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
2101	12746.78	693.19	1130.94	744.22	705.68	962.69	1695.32
2102	2238.78	519.68	370.77	351.22	358.77	361.19	249.81
2103*	9494.33	627.10	329.22	488.71	369.40	57.70	1002.00
2104	2407.22	189.32	212.30	357.76	401.34	252.44	431.16
2105*	905.22	36.93	28.40	94.52	64.80	41.80	79.10
2106	852.11	17.38	12.40	31.91	47.96	48.27	103.36
2207	8859.56	550.77	870.77	1192.74	1230.07	421.83	885.01
2208	2593.56	79.29	183.60	142.54	783.33	ND	204.87
2209	2736.89	178.80	333.71	388.56	493.61	128.73	385.61
2210*	6970.00	194.28	282.14	283.77	510.00	40.60	451.20
2211	2635.33	400.63	515.94	861.54	1079.09	536.28	917.81
2212	354.11	18.66	54.21	65.52	98.38	20.19	169.64
2313	41.17	49.34	18.81	4.69	14.98	24.87	101.13
2314	2362.35	26741.75	241.98				
2315*	4691.15	681.17	773.38	ND	591.54	1077.83	1798.60
2316	734.20	431.66	669.82	413.60	570.63	480.45	727.90
2317*	356.53	634.23	377.79	588.59	587.25	158.23	267.16
2318	84.08	362.06	242.60	100.65	188.75	224.95	260.56
2419	167.00	314.02	289.12	ND	419.16	317.88	292.17
2420	443.03	416.49	532.00	394.38			
2421*	564.88	863.88	458.39	229.48	495.60	279.12	114.41
2422	1403.94	811.88	3866.40	610.17			
2423	804.31	1335.82	2136.13	1911.90	509.10	527.58	561.22
2424*	367.20	757.59	773.52	169.00	224.27	133.80	173.31
2425	487.88	738.90	824.63	229.80			
2426	75.60	38.46	254.17	18.11	92.43	50.25	36.67
2427	148.62	14.98	310.19	102.19	109.74	96.69	84.73
2528	894.49	481.90	320.63	398.69	1144.37	1037.77	855.96
2529*	441.22	186.20	292.40	553.91	249.46	268.47	254.94
2530	497.94	194.54	452.73	467.00			
2531	373.63	256.71	484.36	443.11	561.22	388.33	388.01
2532	230.12	47.47	442.30	537.66			
2533*	375.59	28.84	250.50	108.33	41.54	23.06	96.70
2534	198.02	20.40	ND	75.60			
2535*	364.92	2.92	67.49	61.92	2.79	34.66	34.62
2536	110.33	16.10	49.98	16.94	10.41	158.21	44.58
2637	520.53	101.74	68.68	279.97			
2638	300.98	105.56	73.34	43.79	143.02	191.07	76.33
2639*	847.26	248.89	577.99	429.47	576.55	397.05	600.03
2640	599.80	334.44	483.38	559.81	494.82	442.91	453.97
2641*	265.39	225.56	285.58	278.22	255.09	199.67	111.70
2642	249.03	286.67	157.11	219.36			
2643*	464.47	141.11	137.23	54.46	165.45	59.00	95.45
2644	370.74	166.67	321.22	75.59			
2645	332.88	117.78	190.43	43.78	129.83	127.66	55.45
2746				138.52	134.01	99.33	174.70
2747				338.78	419.09	243.62	338.37
2748				565.46	582.00	270.34	629.46
2749				2319.70	609.10		

	SAMPLE PERIOD						
STATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
2851				394.39	727.95		
2852				820.81	1725.50		
2853				322.48	674.05		
2854				780.38	728.36		
2855				135.41	177.45		
2856				70.99	208.71		
2957					74.84	19.99	15.87
2958					305.26	56.32	41.52
2959					521.54	317.64	147.93
2960					1066.18	583.72	523.97

ND = No Data Available

APPENDIX B

Number of polychaete species per 0.58 m^2 sample area during the period June, 1975 through February, 1978. Station sample area was 0.06 m^2 at 1977/78 secondary stations (*).

	SAMPLE PERIOD						
STATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
2101	56	73	80	-	76	-	58
2102	34	51	56	-	59	-	32
2103*	109	65	125	-	14	10	39
2104	94	122	95	-	78	43	117
2105*	55	56	82	-	2	4	15
2106	53	34	69	-	20	20	63
2207	68	67	94	95	123	136	56
2208	40	45	49	57	86	-	38
2209	57	49	60	97	92	58	43
2210*	61	70	67	97	50	19	23
2211	113	110	95	206	175	154	145
2212	34	45	42	78	52	41	48
2313	29	24	40	24	40	65	40
2315*	104	117	94	-	38	86	70
2316	123	119	145	148	131	155	129
2317*	146	74	116	76	50	46	29
2318	91	54	53	117	85	98	67
2419	74	55	60	-	92	57	101
2420	112	87	104	80	-	-	-
2421*	100	74	86	82	12	52	26
2422	113	59	142	174	-	-	-
2423	126	82	113	138	140	97	122
2424*	101	84	84	68	27	44	25
2425	132	104	102	124	-	-	-
2426	52	39	61	31	44	48	64
2427	29	34	31	26	32	22	43
2528	100	92	127	120	171	156	173
2529*	100	79	93	108	62	33	56
2530	87	119	103	100	-	-	-
2531	98	89	103	103	122	100	128
2532	75	84	94	112	-	-	-
2533*	51	104	90	66	16	14	21
2534	-	-	-	72	-	-	-
2535*	21	32	44	28	2	3	7
2536	31	33	36	41	15	33	40
2637	26	34	44	-	-	-	-
2638	30	29	43	32	37	44	33
2639*	69	68	93	74	25	35	31
2640	77	76	99	112	141	107	132
2641*	85	62	75	73	26	30	24
2642	81	65	86	-	-	-	-
2643*	65	61	93	52	35	31	16
2644	71	72	88	-	-	-	-
2645	74	65	107	71	68	89	87

	SAMPLE PERIOD						
STATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
2746	-	-	-	21	46	21	56
2747	-	-	-	22	52	21	73
2748	-	-	-	-	56	27	138
2749	-	-	-	-	37	-	-
2851	-	-	-	103	55	-	-
2852	-	-	-	170	121	-	-
2853	-	-	-	-	143	-	-
2854	-	-	-	-	120	-	-
2855	-	-	-	86	78	-	-
2856	-	-	-	-	68	-	-
2957	-	-	-	-	54	44	32
2958	-	-	-	-	72	58	44
2959	-	-	-	-	101	84	51
2960	-	-	-	-	92	98	82

APPENDIX C

Total benthic polychaete abundance for MAFLA stations sampled during the period June, 1975 through February, 1978. Station sample area was 0.58 m^2 except for 1977/78 secondary stations (*), at which one 0.06 m^2 box core was collected.

	SAMPLE PERIOD						
STATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
2101	518	845	1558	-	865	-	379
2102	788	645	646	-	458	-	152
2103*	1767	400	2076	-	24	30	76
2104	760	474	781	-	428	233	930
2105*	158	261	325	-	5	5	27
2106	156	120	222	-	48	48	134
2207	1187	1843	2195	2483	3421	1778	484
2208	431	501	749	752	939	-	309
2209	1076	1333	2136	-	2865	837	263
2210*	996	866	662	2372	176	36	49
2211	1062	1586	645	2049	1972	1029	1326
2212	129	256	251	327	270	147	138
2313	63	53	90	43	85	291	91
2315*	1006	1049	1296	-	71	286	547
2316	1259	1187	998	1023	1285	1208	702
2317*	1355	1206	744	1552	118	88	81
2318	881	1090	761	1069	848	1071	1020
2419	589	486	330	-	1583	415	1139
2470	1014	727	544	1582	-	-	-
2471*	1013	860	672	888	23	123	56
2422	775	647	1209	2414	-	-	-
2423	1324	799	900	2884	3053	1181	1470
2424*	1090	691	347	477	53	119	33
2425	1078	1030	377	1809	-	-	-
2426	228	216	203	115	199	187	303
2427	55	82	69	67	70	65	112
2528	445	1012	1169	754	3257	6488	1558
2529*	673	956	869	1082	224	74	173
2530	609	1230	779	679	-	-	-
2531	622	1140	524	923	1453	688	1217
2532	336	938	438	971	-	-	-
2533*	160	974	488	230	23	21	41
2534	-	-	-	245	-	-	-
2535 *	41	275	124	97	2	3	14
2636	52	118	83	94	19	84	94
2637	97	287	345	-	-	-	-
2638	165	152	224	164	317	356	336
2639*	390	795	1049	770	55	65	52
2640	743	894	1437	988	1907	1243	1571
2641*	395	1240	631	1535	96	89	55
2642	391	703	509	-	-	-	-
2643*	262	402	359	196	106	65	37
2644	321	531	370	-	-	-	-
2545	281	360	640	207	355	380	397
2746	-	-	-	71	181	100	210
2747	-	-	-	54	394	81	204
2748	-	-	-	-	751	67	931

	SAMPLE PERIOD						
STATION	S-75	F-75	W-76	S-76	S-77	F-77	W-78
2749	-	-	-	-	191	-	-
2851	-	-	-	748	440	-	-
2852	-	-	-	1592	887	-	-
2853	-	-	-	-	1108	-	-
2854	-	-	-	-	931	-	-
2855	-	-	-	539	380	-	-
2856	-	-	-	-	481	-	-
2957	-	-	-	-	243	159	90
2958	-	-	-	-	437	298	171
2959	-	-	-	-	867	510	289
2960	-	-	-	-	633	798	499

APPENDIX D

Benthic polychaete Shannon-Wiener species diversity for MAFLA stations sampled during the period June 1975 through February 1978. H' estimates were based on 0.58 m^2 sample areas except for 1977/78 secondary stations (*), at which one 0.06 m^2 box core was collected.

	SAMPLE PERIOD			
STATION	S-76	S-77	F-77	W-77
2101		3.51		3.34
2102		3.35		2.81
2103*		2.48	1.87	3.32
2104		3.74	3.26	4.03
2105*		0.50	1.33	2.48
2106		2.55	2.70	3.79
2207	3.07	3.25	3.74	3.18
2208	3.00	3.46		2.68
2209		2.85	2.97	3.01
2210*	2.64	3.48	2.62	2.84
2211	4.26	4.14	4.30	4.00
2212	3.63	3.41	3.09	3.48
2313	3.02	3.48	3.59	3.37
2315*		3.25	3.57	2.76
2316	4.27	3.68	4.19	4.23
2317*	3.33	3.52	3.57	2.94
2318	3.91	3.56	3.63	2.90
2419		3.31	3.03	3.14
2420	2.92			
2421*	3.42	2.38	3.63	2.99
2422	4.05			
2423	3.71	3.63	3.81	3.79
2424*	3.44	3.09	3.24	3.12
2425	3.61			
2426	2.74	2.68	3.00	3.51
2427	2.89	3.18	2.67	3.48
2528	4.14	3.58	2.75	4.33
2529*	3.67	3.60	3.32	3.68
2530	3.82			
2531	3.92	3.94	3.93	4.09
2532	3.72			
2533*	3.62	2.60	2.49	2.87
2534	3.78			
1535*	2.86	0.69	1.10	1.75
2636	3.38	2.62	3.24	3.34
2637				
2638	2.74	2.51	2.55	2.77
2639*	3.49	2.84	3.28	3.29
2640	3.95	3.93	3.39	3.92
2641*	3.06	2.68	2.90	2.95
2642				
2643*	3.56	3.15	3.14	2.56
2644				
2645	3.91	3.64	4.02	4.00
2746	2.62	3.17	2.26	3.35
2747	2.88	3.11	2.11	3.65

	SAMPLE PERIOD			
STATION	S-76	S-77	F-77	W-77
2748		3.04	3.03	4.20
2749		3.12		
2851	3.91	3.31		
2852	4.41	3.86		
2853		4.28		
2854		4.21		
2855	3.68	3.82		
2856			3.35	
2957		3.51	3.30	3.12
2958		3.08	3.12	2.19
2959		3.79	3.59	3.18
2960		3.67	3.86	3.76

APPENDIX E

Dominant polychaete species within major assemblages in the MAFLA study area. Dominant forms are those which include the three most abundant taxa at each station in each assemblage.

POLYCHAETE ASSEMBLAGE	DOMINANT SPECIES
A	Paraprionospio pinnata
	Prionospio cristata
	Prionospio fallax
	Prionospio steenstrupi
	Aricidea catherinae
	Paraonis gracilis
	Magelona pettiboneae
	Mediomastus californiensis
	Fabricia sabella
B	Parapionosyllis longicirrata
	Nereis riisei
	Nephtys sp. A
	Lumbrineris cf. crassidentata
	Lumbrineris cruzensis
	Spiophanes bombyx
	Aricidea catherinae
	Aricidea wassi
	Paradoneis lyra
	Armandia maculata
C	Bhawania goodei
	Synelmis albini
	Exogone dispar
	Sphaerosyllis pirifera
	Typosyllis hyalina
	Aglaophamus verrilli
	Glycera capitata
	Goniadella sp. A
	Goniadides carolinae
	Eunice vittata
	Onuphis nebulosa
	Lumbrineris cf. crassidentata
	Prionospio cristata
	Spionphanes bombyx
	Aricidea catherinae
	Cirrophorus lyriformis
	Paradoneis lyra
	Fabricia sabella
	Jasmineira caudata
	Filograna implexa
D	Synelmis albini
	Neanthes micromma
	Goniadides carolinae
	Lumbrineris cf. crassidentata
	Prionospio cristata
	Mediomastus californiensis

POLYCHAETE ASSEMBLAGE	DOMINANT SPECIES
E	*Pseudoeurythoe paucibranchiata* *Synelmis albini* *Pisione remota* *Ceratonereis mirabilis* *Goniada maculata* *Onuphis pallidula* *Spionphanes bombyx* *Fabricia* sp. A
F	*Exogone dispar* *Aglaophamus verrilli* *Nephtys picta* *Lumbrineris cruzensis* *Prionospio fallax* *Aricidea taylori* *Mediomastus californiensis* *Owenia fusiformis*
G	*Prionospio cristata* *Paraonis gracilis* *Tharyx annulosus* *Fabricia sabella*
H	*Sthenelais boa* *Synelmis albini* *Prionospio cirrobranchiata* *Aricidea neosuecica* *Paraonis gracilis* *Chone filicaudata*
I	*Synelmis albini* *Sphaerosyllis pirifera* *Ceratocephale* sp. A *Aglaophamus verrilli* *Onuphis pallidula* *Lumbrineris cruzensis* *Prionospio cirrobranchiata* *Spiophanes bombyx* *Aricidea catherinae* *Paraonis gracilis* *Mediomastus califoriensis*
J	*Paralacydonia paradoxa* *Apoprionospio pygmaea* *Ophelina cylindricaudata* *Tharyx marioni*

APPENDIX F

MAFLA benthic polychaete species accessioned into the U.S. National Museum (Smithsonian Institution).

FAMILY	USNM NO.	SPECIES	NO. SPEC.	I.D.
POLYNOIDAE	55796	Harmothoe spinifera (Ehlers)	1	JMU
	55797	Subdyte pellucida (Ehlers)	1	JMU
POLYODONTIDAE	55798	Euarche tubifex Ehlers	1	PGJ
	55799	Polyodontes lupinus (Stimpson)	1	JMU
EULEPETHIDAE	55800	Grubeulepis mexicana (Berkeley & Berkeley)	1	BAV
	55801	Mexieulepis weberi (Horst)	1	JMU
SIGALIONIDAE	56154	Ehlersileanira incisa Grube	1	JMU
	56148	Pholoe minuta Fabircius	1	JMU
	56146	Psammolyce ctenidophora Day	1	JMU
	55802	Sigalion arenicola Verrill	1	JMU
	56153	Stehenelais boa (Johnston)	1	JMU
	56147	Sthenelais limicola (Ehler)	1	JMU
PHOLOIDIDAE	56152	Pholoides dorsipapillata (Marenzeller)	6	PGJ
CHRYSOPETALIDAE				
	55803	Paleonotus heteroseta Hartman	39	JMU
PISIONIDAE	55804	Pisione romota (Southern)	5	PGJ
AMPHINOMIDAE	55805	Chloeia viridis Schmarda	1	GRG
	55806	Eurythoe complanata (Pallas)	1	JMU
	56133	Paramphinome pulchella Sars	1	JMU
	55807	Pseudoeurythoe ambigua (Monro)	1	PGJ
EUPHROSINIDAE	55808	Euphrosine triloba Ehlers	1	PGJ
PHYLLODOCIDAE	56121	Eteone heteropoda Hartman	1	HK
	56122	Eteone lactea Claparede	1	JMU
	56123	Eulalia bilineata (Johnston)	2	JMU
	56124	Eulalia macroceros (Grube)	1	PGJ
	56125	Eulalia sanguinea Oersted	1	JMU
	56126	Mystides borealis Theel	2	JMU
	56127	Paranaitis polynoides (Moore)	1	JMU
	56128	Phyllodoce castanea (Marenzeller)	1	JMU
	56129	Phyllodoce longipes (Kinberg)	3	JMU
	56130	Phyllodoce madeirensis (Langerhans)	1	JMU
	56131	Phyllodoce mucosa Oersted	1	JMU
	56132	Phyllodoce arenae Webster	1	JMU
PARALACYDONIDAE				
	55809	Paralacydonia paradoxa Fauvel	2	JMU
HESIONIDAE	55810	Gyptis brevipalpa (Hartmann-Schroeder)	1	JMU
	55811	Podarke obscura Verrill	6	JMU

FAMILY	USNM NO.	SPECIES	NO. SPEC.	I.D.
PILARGIDAE	55812	Ancistrosyllis carolinensis Gardiner	1	JMU
	55813	Ancistrosyllis hartmanae Pettibone	1	JMU
	55814	Ancistrosyllis jonesi Pettibone	1	JMU
	55815	Sigambra bassi (Hartman)	1	JMU
	55816	Synelmis albini (Langerhans)	1	JMU
SYLLIDAE	55817	Autolytus dentalius Imajima	1	PGJ
	55818	Branchiosyllis exilis (Gravier)	2	PGJ
	55819	Exogone dispar (Webster)	1	PGJ
	55820	Exogone hebes (Webster & Benedict)	1	HK
	55821	Exogone lourei Berkeley & Berkeley	2	PGJ
	55822	Haplosyllis spongicola (Grube)	44	PGJ
	55823	Parapionosyllis longicirrata (Web. & Benedict)	1	PGJ
	55824	Pionosyllis uraga Imajima	1	JMU
	55825	Syllis (Typosyllis) alternata Moore	1	PGJ
	55826	Syllis (Typosyllis) amica Quatrefages	2	PGJ
	55827	Syllis (Ehlersia) cornuta Rathke	1	JMU
	55828	Syllis (Ehlersia) ferrugina (Langerhans)	1	PGJ
	55829	Syllis gracilia Grube	1	PGJ
	55830	Syllis (Typosyllis) hyalina Grube	1	PGJ
	55831	Syllis (Typosyllis) regulata carolinae Day	1	JMU
	55832	Syllis (Typosyllis) variegata Grube	2	PGJ
	55833	Sphaerosyllis erinaceus Claparede	2	JMU
	55834	Sphaerosyllis hystrix Claparede	3	PGJ
	55835	Sphaerosyllis pirifera Claparede	4	PGH
	55836	Trypanosyllis coeliaca Claparede	1	PGJ
	55837	Trypanosyllis vittigera Ehlers	1	PGJ
	55838	Trypanosyllis zebra Grube	1	JMU
NEREIDAE	55839	Ceratocephale oculata Banse	1	JMU
	55840	Ceratonereis irritabilis (Webster)	1	JMU
	55841	Ceratonereis mirabilis Kinberg	2	JMU
	55842	Laeonereis culveri (Webster)	1	BAV
	55843	Nereis (Neanthes) acuminata Ehlers	10	JMU
	55844	Nereis grayi Pettibone	1	JMU
	55845	Nereis (Neanthes) micromma Harper	1	JMU
	55852	Nereis riisei Grube	1	JMU
	55853	Platynereis dumerilii (Aud & Milne-Edwards)	1	JMU
	56149	Rullierinereis mexicana (Treadwell)	1	JMU
NEPHTYIDAE	55854	Aglaophamus verrilli (McIntosh)	1	GRG
	55855	Nephtys incisa Malmgren	2	JMU
	55856	Nephtys picta Ehlers	2	JMU
	55857	Nephtys squamosa Ehlers	2	PGJ
SPHAERODORIDAE	55858	Sphaerodoridium claparedii Greeff	1	PGJ

FAMILY	USNM NO.	SPECIES	NO. SPEC.	I.D.
SPIONIDAE	55889	Aonides mayaguezensis Foster	7	PGJ
	55890	Dispio uncinata Hartman	1	JMU
	55891	Laonice cirrata (Sars)	7	PGJ
	55892	Malacoceros vanderhorsti (Augener)	1	PGJ
	55893	Microspio pigmentata (Reish)	1	PGJ
	55894	Paraprionospio pinnata (Ehlers)	2	JMU
	55895	Polydora caulleryi Mesnil	1+	PGJ
	55971	Polydora ligni Webster	2	PGJ
	55972	Polydora socialis (Schmarda)	1	JMU
	55973	Polydora websteri Hartman	6	PGJ
	55988	Prionospio cirrifera Wirens	4	PGJ
	55989	Prionospio cirrobranchiata Day	5	PGJ
	55990	Prionospio cristata Foster	3	JMU
	55991	Prionospio fallax Söderström	1	JMU
	55992	Prionospio steenstrupi Malmgren	4	GRG
	55974	Scolelepis squamata (Muller)	4	GRG
	55975	Spio pettibonae Foster	3	JMU
	55976	Spiophanes berkeleyorum Pettibone	1	BGJ
	55977	Spiophanes bombyx (Claparede)	3	GRG
	55978	Spiophanes wigleyi Pettibone	4	GRG
QUESTIDAE	55888	Questa caudicirra Hartman	2	JMU
UNKNOWN FAMILY				
	55979	Aberranta enigmatica Hartman	1	PGJ
CIRRATULIDAE	55980	Chaetozone gayheadia Hartman	1	JMU
	55981	Chaetozone setosa Malmgren	4	JMU
	55982	Tharyx annulosa Hartman	1	BAV
	55983	Tharyx marioni (St. Joseph)	1	JMU
COSSURIDAE	55984	Cossura delta Reish	2	JMU
FLABELLIGERIDAE	55985	Pherusa inflata (Treadwell)	1	PGJ
	55986	Piromis eruca (Claparede)	1	JMU
SCALIBREGMIDAE	55987	Hyboscolex longiseta Schmarda	1	GRG
OPHELIIDAE	55993	Armandia agilis (Andrews)	1	BAV
	55994	Armandia maculata (Webster)	2	JMU
	56151	Ophelina acuminata Orested	1	JMU
	56150	Ophelia denticulata Verrill	1	JMU
	55995	Travisia hobsonae Santos	2	JMU
STERNASPIDAE	56027	Sternaspis scutata Renier	1	PGJ

FAMILY	USNM NO.	SPECIES	NO. SPEC.	I.D.
GLYCERIDAE	55859	Glycera americana Leidy	1	PGJ
	55860	Glycera oxycephala Ehlers	1	JMU
	55861	Glycera tesselata Grube	1	PGJ
GONIADIDAE	55862	Glycinde nordmanni (Malmgren)	1	HK
	55863	Goniada littorea Hartman	7	JMU
	55864	Goniada maculata Oersted	1	JMU
	55865	Goniada teres Treadwell	1	PGJ
ONUPHIDAE	55872	Diopatra cuprea (Bosc)	2	JMU
	55873	Diopatra tridentata Hartman	2	JMU
	56143	Onuphis eremita Aud. & Miln-Edwds)	1	JRL
	55874	Onuphis pallidula (Hartman)	3	JMU
	56142	Rhamphobrachium agassizii Ehlers	1	JRL
EUNICIDAE	55866	Eunice antennata (Savigny)	1	JMU
	55867	Eunice filamentosa Grube	1	GRG
	56145	Eunice (Nicidion) cariboea Grube	1	JMU
	55868	Eunice vittata (delle Chiaje)	1	JMU
	55869	Lysidice ninetta Aud. & Miln-Edwards	1	JRL
	56144	Marphysa mortenseni Monro	1	JMU
	55870	Marphysa sanguinea (Montagu)	1	BAV
	55871	Nematonereis unicornis (Grube)	1	JMU
LUMBRINERIDAE	55875	Lumbrinerides acuta (Verrill)	1	PGJ
	56140	Lumbrineris albidentata Ehlers	1	PGJ
	55876	Lumbrineriopsis paradoxa (St. JOseph)	1	PGJ
	55877	Lumbrineris occinea (Renier)	1	JMU
	55878	Lumbrineris erecta Moore	1	BAV
	55879	Lumbrineris inflata Moore	1	JMU
	55880	Lumbrineris januarii (Grube)	1	PGJ
	56141	Lumbrineris januarii (Grube)	1	JMU
	55881	Ninoe nigripes Verrill	1	JMU
ARABELLIDAE	55882	Arabella mutans (Chamberlin)	1	JMU
	55883	Drilonereis longa Webster	1	JMU
LYSARETIDAE	55884	Lysarete brasiliensis Kinberg	1	JMU
DORVILLEIDAE	55835	Dorvillea sociabilis (Webster)	2	PGJ
	55886	Protodorvillea kefersteini (McIntosh)	4	PGJ
	56139	Schistomeringos rudolphi (delle Chiaje)	1	PGJ
			1	PGJ
ORBINIIDAE	55887	Scoloplos rubra (Webster)	1	PGJ

FAMILY	USNM NO.	SPECIES	NO. SPEC.	I.D.
CAPITELLIDAE	56137	Leiocapitella glabra Hartman	1	GRG
	56028	Leiochrides pallidior (Chamberlin)	1	PGJ
	56029	Mediomastus californiensis Hartman	6	PGJ
	56138	Notomastus americanus Day	1	PGJ
	56030	Notomastus hemipodus Hartman	1	JMU
	56031	Notomastus latericeus Sars	1	PGJ
MALDANIDAE	56032	Clymenella torquata (Leidy)	1	PGJ
OWENIIDAE	56033	Owenia fusiformis delle Chiaje	4	BAV
AMPHARETIDAE	56134	Ampharete acutifrons (Grube)	14	PGJ
	56135	Amphicteis scaphobranchiata Moore	2	JMU
	56034	Isolda pulchella Muller	1	JMU
	56136	Melinna cristata (Sars)	1	JMU
TEREBELLIDAE	56035	Amaeana accraensis (Augener)	2	PGJ
	56036	Amaeana trilobata (Sars)	3	PGJ
	56037	Loimia medusa (Savigny)	1	PGJ
	56038	Pista cristata (Muller)	1	PGJ
	56039	Polycirrus carolinensis Day	1	PGJ
	56040	Thelepus setosa (Quatrefages)	1	PGJ
TRICHOBRANCHIDAE				
	56041	Terebellides stroemi Sars	1	PGJ
	56042	Trichobranchus glacialis Malmgren	1	PGJ
SERPULIDAE	56043	Filograna implexa Berkeley	45	PGJ
	56044	Crucigera websteri Benedict	2	PGJ
	56045	Hydroides crucigera Morch	1	PGJ
	56046	Hydroides microtis Morch	1	PGJ
	56047	Hydroides protulicola Benedict	1	PGJ
	56048	Pseudovermilia holcopleura ten Hove	2	PGJ
	56049	Pseudovermilia occidentalis (McIntosh)	4+	GRG

APPENDIX G

Recommendations for further studies.

Recommendations for further study include both site specific data analysis and additional systematic analysis of the Polychaeta.

DATA ANALYSIS

Intra-station variability should be addressed through further data analysis. Plots already exist for individual box cores, but there has been insufficient time for evaluation of station homogeneity. This analysis should include correlations between individual core sediment size, polychaete abundance, species richness, and diversity. It is likely that some areas (e.g., coarse substrates on the West Florida Shelf) will display extreme heterogeneity within stations. The implications are serious, since any future analysis of oil effects on these sites must adequately address natural benthic variability.

TAXONOMY

A major deficiency in taxonomic treatment of the polychaetes is lack of a comprehensive and applicable guide to the Gulf of Mexico. Over 500 references have been used to identify species in the MAFLA area, and more information appears each year. A unified, concise key to the species in the MAFLA study area will be essential to accurate identification of species by workers not having access to our taxonomic library. Such a guide would include over 700 species among 60 families.

VOLUME II

CHAPTER 16

MACROINFAUNAL CRUSTACEANS

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CONTRACT NO. AA550-CT7-34

MACROARTHROPODS FROM THE MAFLA BOX CORE PROGRAM

(SUMMER 1977-WINTER 1978)

FINAL REPORT

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BY

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ABSTRACT

Under BLM Contract No. AA550-CT7-34, the macroarthropod samples from the 1977-1978 MAFLA box-core program were fine-sorted and identified. Of the 10,584 specimens collected, 9,014 were identified to species level. Nine major groups, Pycnogonida (3 spp.), Nebaliacea (2 spp.), Stomatopoda (8 spp.), Mysidacea (5 spp.), Cumacea (28 spp.), Tanaidacea (9 spp.), Isopoda (47 spp.), Amphipoda (129 spp.), and Decapoda (134 spp.), represented 88 families, 225 genera, and 360 species. Decapods and amphipods comprised 72% of the number of species with the latter making up approximately 50% of the total number of specifically identified specimens (4,468). Tanaids ranked second in number of specimens (1,445), but they were represented by only 9 species. Decapods ranked third (1,371), isopods fourth (1,113), and cumaceans fifth (428). The remaining four groups together made up less than 8% of the total specimens. Important infaunal species from each of the five large groups were documented based on the total number of specimens and the number of different station occurrences. Approximately 30% of the 360 species identified appear to be new to science. Amphipods and cumaceans rank highest in this category. Difficulties in drawing conclusions about zoogeographical affinities, diversity and evenness indices, and seasonal abundance are briefly discussed. Three appendices contain reference tables, recommendations for further studies, and a brief statement of the problems encountered during the study.

INTRODUCTION

PURPOSE

The purpose of this study was to fine-sort and identify the macroarthropod fractions from 779 MAFLA box-core samples collected by Dames & Moore for the Bureau of Land Management under Contract No. AA 550-CT7-34. The distribution patterns and species diversity were to be determined and compared. This involved the processing of approximately 9000 specimens representing over 350 arthropod species.

LITERATURE SURVEY AND PREVIOUS WORK

Relatively little work has been published on the benthic invertebrate fauna of the shelf of the eastern Gulf of Mexico (Collard and D' Asaro, 1973; Lyons and Collard, 1974). Most of the previous taxonomic work on the macrocrustacean fauna of this region resulted from the qualitative and largely epibenthic collections made by the research vessels U.S.S. Albatross and U.S.S. Blake over three-quarters of a century ago. During the past 25 years, as part of a program developed by the Department of the Interior and currently being sponsored by the Department of Commerce, a number of macrocrustaceans have been collected in conjunction with studies of the commercial fisheries in the Gulf region. However, with the exception of the stomatopods and the large, commercially important decapods, relatively little taxonomic work has resulted from that program, since most of the collections were made with large mesh trawls that generally do not capture the smaller macrocrustacean groups. Excluding the current BLM shelf monitoring program, the most recent and extensive epibenthic and benthic collections of macrocrustaceans were made by the Florida Department of Natural Resources' "Project Hourglass," in an extensive two-year survey of the western Florida shelf between Tampa Bay and Fort Myers. Several monographis dealing with macrocrustaceans collected during that project have been or are in the process of being published (Lyons, 1970; Camp, 1973; Cobb et al., 1973; Menzies and Kruczynski, in review).

Most of the published reports covering the macrocrustaceans occurring in the eastern Gulf of Mexico have dealt with decapods (see Coutiere, 1909; Rathbun, 1918, 1925, 1930, 1931, 1937; Provenzano, 1959; Wass, 1955; Chace, 1942, 1969, 1972; Cobb, 1971, 1973; Cobb et al., 1973; Lyons, 1970). The stomatopod crustaceans are probably the most completely known group of benthic macrocrustaceans in the northwestern Atlantic as a result of the excellent taxonomic and systematic monograph by Manning (1969). Since Manning's monograph, Camp (1971, 1973) has published two reports dealing with the mantis shrimps collected in the "Project Hourglass" study.

There have been very few taxonomic reports dealing with the benthic peracarideans from the Mississippi-Alabama-West Florida continental shelf region. The taxonomic literature on the benthic Amphipoda occurring on the continental shelf of this region is restricted to two short papers by Pearse (1908, 1913) and several records by Shoemaker (1926, 1945 a,b) and

Mills (1965). In an extensive study of the Amphipoda of the western Gulf, Culpepper, and Pequegnat (1969) have studied several epifaunal species off Panama City, Florida. McKinney (1977) reported 140 different species of gammaridean amphipods, 23 of which were undescribed.

The Mysidacea, which are generally considered planktonic and/or epibenthic, have several genera that are infaunal (i.e., Gastrosaccus and Bowmaniella). The available information on mysids occurring in the shelf waters of the Gulf was summarized by Tattersal (1952). Richardson (1905) has listed and diagnosed several species of isopods and tanaids from the Gulf of Mexico in her monograph on the American members of these two groups. Currently a monograph by Menzies and Kruczynski on the Isopoda collected by "Project Hourglass" is being prepared for publication (David Camp, personal communication). Most information on the Order Cumacea of the open Gulf was presented by Calman (1912). The remaining taxonomic publications on macrocrustaceans from the eastern Gulf of Mexico have dealt primarily with inshore or estuarine species (i.e., Shoemaker, 1934, 1941, 1947; Tabb and Manning, 1961; Croker, 1968; Rouse, 1970; Bowman, 1964; Molenock, 1969; Brattegard, 1969, 1970a,b; Lyons et al., 1971; Watling, 1977; Barnard and Gray, 1969; Myer, 1970; Wartz and Romback, 1955; Thomas, 1976).

METHODS AND MATERIALS

INITIAL PROCEDURES

Arthropod samples collected under BLM Contract No. AA550-CT7-34 were received from rough sorting centers (Dr. Vittor's and Dr. Blake's laboratories) and replicates for each station were logged and checked against the shipping invoice. Samples were placed in 4 cm petri dishes. Using a high-quality dissecting scope with a magnification range of 10X to 50X the arthropods were sorted into major taxa or groups (Amphipoda, Isopoda, Cumacea, Tanidacea, Mysidacea, Nebalacea, Decapoda, Stomatopoda, Ostracoda, Pycnogonida, and "others").

The presence or absence of various major taxa was recorded on a "Rough Sorting Check Sheet." Using fine forceps each group was placed in fresh 70% ethanol in a separate vial with a label giving its station, replicate number and month/year of collection (e.g., "2101-04, 2/78"). Small specimens, which made up most of the samples, were placed in quarter-dram or half-dram shell vials, and stoppered with sponge rubber plugs. Depending on their sizes, larger specimens, such as decapods and stomatopods, were placed in snap-cap Wheaton vials or small jars.

The groups designated as "other" refer to non-arthropod fractions (e.g., polychaetes, echinoderms, etc.) which are occasionally found entangled with arthropod specimens. These non-arthropod fractions were returned to Dr. Vittor's laboratory for reintegration into their respective groups.

The amphipod, cumacean, decapod, stomatopod, nebaliacean and pycnogonid specimens were retained for identification at the Dauphin Island Sea Lab. The vials containing isopods, tanaids, and mysids were prepared

for shipment to consultants specializing in these groups. The tanaids and mysids were hand-delivered to consultants John Ogle (tanaids) and Ken Stuck (mysids) at the Gulf Coast Research Laboratory, Ocean Springs, Mississippi. The isopods were usually sent by first class registered mail to William Kruczynski at Florida A&M University, Tallahassee, Florida, or hand-delivered. When mailed, the isopods were split into relatively small lots (20-30 vials/lot). If the consultants returned the specimens by mail they were instructed to use this same mailing procedure. A log sheet for each lot, indicating the stations and replicate numbers in which the group was represented, accompanied each shipment, and a copy was retained for our records. When shipment by mail was made to a consultant, he was informed of it by phone or letter within one or two days of the mailing date. The same mailing procedures were used for sending smaller lots of the other groups to specialists for confirmation of our identifications. All consultants were sent Data Recording Sheets for recording their identifications.

IDENTIFICATION PROCEDURES

The identification procedures for the arthropod groups processed by PI and his associates and technical staff at the Dauphin Island Sea Lab varied slightly with each group according to its size and diversity. The procedures are as follows.

The amphipods, nebaliaceans, cumaceans, and pycnogonids were counted, and preliminary identifications were made in 4 cm petri dishes using a research-quality dissecting scope at magnifications of 25x to 50x. Those specimens that required dissection or examination under higher magnification were transferred to a drop of glycerine on a microscope slide. When necessary, fine-tipped forceps and small gauge insect pins (mounted on Q-tip wood handles) were used. When the specimens were ready for high magnification examination (100-1000x) under a compound microscope, a size 0 cover-slide was placed over the glycerine mount. After examination, the specimens and their dissected parts were returned to their vials and stored in fresh 70% ethanol.

Identifications and numbers of individuals were recorded on our "Lab Data Sheet." The amphipod specimens for which identifications were still uncertain or questionable were separated into jars to be sent to E.L. Bousfield or Larry McKinney for confirmation or reidentification.

The decapods were further fine-sorted to generic groups before final identifications to species were made. In most cases, the decapods could be identified with a dissecting scope, but occasionally gonopods or other body parts had be to examine under a compound microscope. This was accomplished using the glycerine slide mount procedure described for the smaller arthropod groups.

FINAL PROCEDURES

After identification of the specimens in each sample was completed, the data sheets on which they were recorded were given to the data management clerk. Specific designations were placed on 3 x 5 index cards and

given a number representing phylum, order, family, genus and species based on the NOAA Code format or Dames & Moore File Taxa of New Taxonomic I.D.'s not in the NOAA Code. The number was representative of all specimens of that particular designation. Following this procedure, all identifications according to the number were transferred to Dames & Moore File 723 data sheets. Photocopies of these data sheets were made and originals were then sent to Dames & Moore data management group for statistical treatment. The data were analyzed to determine species diversity, species evenness, relative abundance, and other seasonal variables.

RESULTS

GENERAL

Of the 842 box-core samples collected under BLM Contract No. AA550-CT7-34 by Dames & Moore during summer 1977 to winter 1978, 779 (or 92.5%) contained arthropid fractions representing 360 species and 10,584 specimens, 9,014 of which were identified to species level. There were 1,570 damaged specimens or fragments that could be identified only to genus, family or order. Of the 315 samples from summer 1977, 294 (or 93.3%) had arthropod fractions representing 262 species and 4,441 specimens. Of the 265 samples from fall 1977, 257 (or 97.0%) had arthropod fractions representing 244 species and 3,061 specimens. Of the 262 samples from winter 1977, 228 (or 87.0%) had arthropod fractions representing 164 species and 1,512 specimens.

Nine major groups of macroarthropods were encountered in the box-core samples examined. These groups were Pycnogonida, Nebaliacea, Stomatopoda, Mysidacea, Cumacea, Tanaidacea, Isopoda, Amphipoda, and Decapoda. Table A-1 (Appendix A) lists these nine groups giving the number and percentage of species and specimens found seasonally in each group. All numbers referring to specimens in the text and tables, except for Table A-2 or unless otherwise stated, are based on the 9,014 specifically identified specimens. Except for the summer 1977 samples, in which a larger number of decapod species occurred, amphipods were more diverse and occurred in much larger numbers than did the other groups. Decapods had the largest over-all number of different species. Amphipods were next with 129 different species being represented. Together these two groups alone accounted for over 72% of the number of species (134). Amphipods comprised nearly 50% of all the specimens collected, followed by decapods, tanaids and isopods. The remaining five groups, the cumaceans, nebaliaceans, mysids, stomatopods and pycnogonids, made up less than 8% of the total number of specimens.

Table A-2 gives a systematic listing of the higher order groups of known malacostracan crustaceans with the number of species of each group represented in each group from MAFLA box-core samples. Table A-3 is a list of the 360 species identified during this study. The number of different taxa and specimens for each station by season is given in Tables A-3 and A-4, respectively.

Table A-5 is a list of the most commonly occurring and numerous species of the Orders Isopoda, Decapoda, and Tanaidacea. They are ranked seasonally by number of specimens and number of station occurrences.

A number of statistical tests were performed using the total number of specimens and taxa for each station for summer 1977, fall 1977 and winter 1978. Table A-6 presents the data obtained for the primary stations that were sampled for all three seasons. Seasonal comparisons using the Shannon-Weiner Diversity Index and an index of evenness (Number of Moves) are presented. The primary stations were analyzed also for similarities, and grouped. The groups of stations are listed in Table A-7 for each season. The patterns of similar stations are shown in Figures 227, 228, and 229.

Figure 227 is a plot of the pattern formed by groups of similar stations in summer 1977. Zone 1 consists of stations with a higher percentage of near-shore or shallow-water fauna. Zone V is an area with a lower percentage of near-shore fauna. The similarities existing among the stations in each group appear to be related to the depth of water. Only one group (IV) has a northern limit.

Figure 228 is a plot of patterns formed in fall 1977. The zones are still oriented north-south and are apparently related to depth of water. The only real difference from the plot of groups in summer is that there appears to be less homogeneity among stations in the fall.

The plot for winter 1978, Figure 229, shows a change from summer and fall patterns. There are six zones, as in the fall, but the zones apparently show more of the effect of temperature. The zones still follow the coastline, showing a relationship to depth of water, but zones II and III have northern limits, and zone V is disjunct.

DECAPODA

Members of the order Decapoda ranked highest in number of different species (134). These species represented 28 families and 80 genera. They ranked third in total number of specimens, making up 15.2% of the number of total specimens identified (see Table A-1). The most numerous and commonly occurring decapods were the fourteen species listed in Table A-5; eight species of caridean shrimps, three of galatheids, two of brachyuran crabs, and one species of macruran mud shrimp. These 14 species accounted for 64.5% of the 1,371 specimens identified. One species, Automate evermanni, which was widely distributed throughout the study area, along represented 27.7% of the decapods identified. With the exception of the macruran mud shrimps and pinnotheid crabs, most of the species complement those collected by Dr. Hopkins' MAFLA dredge-trawl study (see Chapter 17 of this report). Approximately 75% of the 30 species of mud shrimps and pinnotherid crabs appear to be new species.

AMPHIPODA

Members of the order Amphipoda made up nearly 49.6% of the total macrocrustacean specimens identified during this study. In the MAFLA box-core samples, this group was represented by 28 families and 84 genera.

Most of the infaunal species belong to the families Ampeliscidae, Haustoriidae, Phoxocephalidae, and Lysianassidae. Less than 40% of the

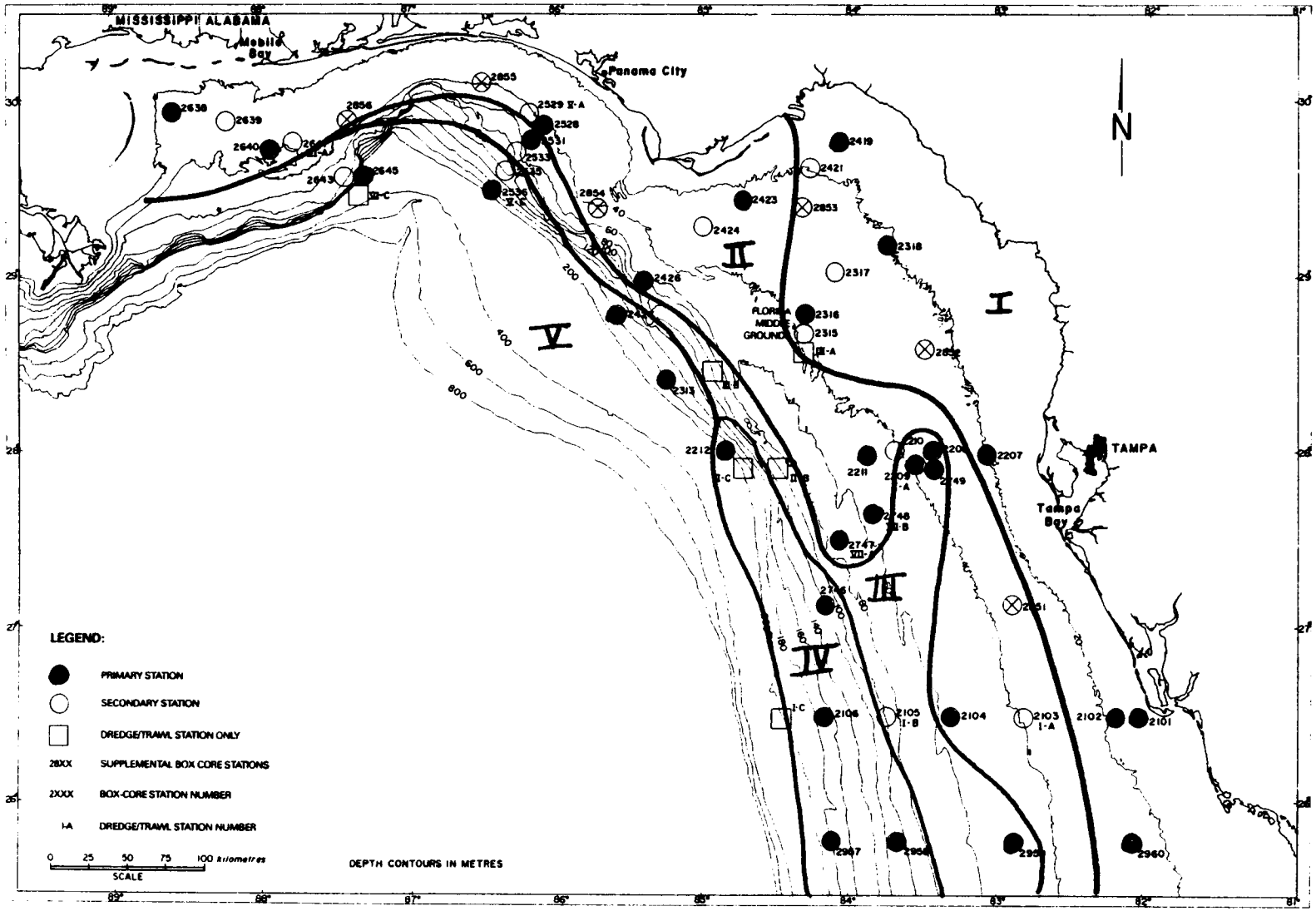

FIGURE 227
ZONES OF SIMILARITY FOR SUMMER 1977

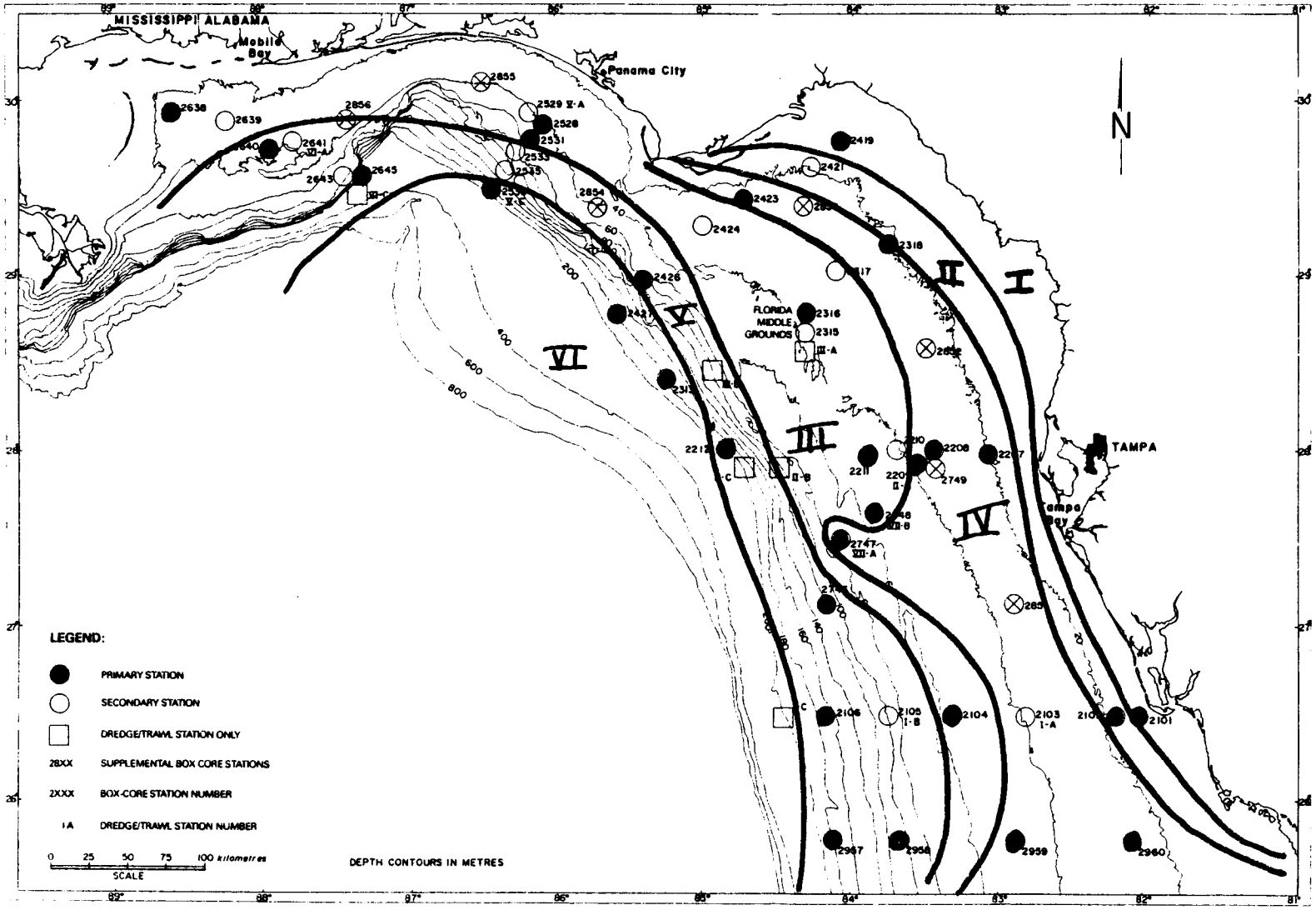

FIGURE 228
ZONES OF SIMILARITY FOR FALL 1977

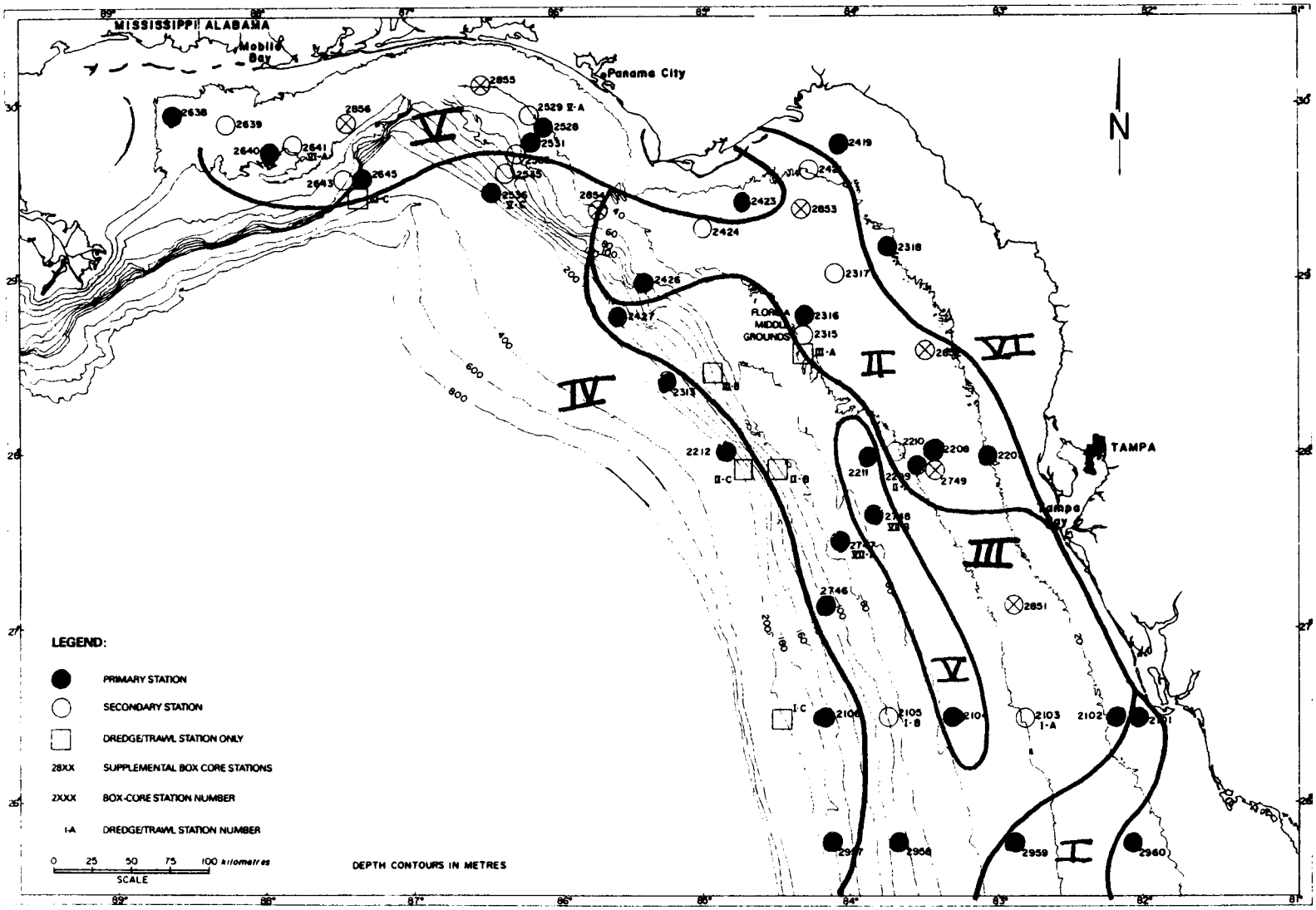

FIGURE 229
ZONES OF SIMILARITY FOR WINTER 1978

species were infaunal. Six of the most common and widely distributed species of amphipods are listed in Table A-5, along with the number of specimens and number of occurrences for each season.

Approximately 60 of the 129 species appear to be new to science. Over 90% are new records for the eastern Gulf of Mexico.

ISOPODA

In the MAFLA box-core samples, isopods were represented by 47 species belonging to 16 families and 34 genera. The more frequently occurring and numerous species were the infaunal anthurids; Xenanthura brevitelson, Apanthura magnifica, and Horoloanthura irpex. Together they constituted 60.3% of all the specimens of isopods identified. Table A-5 lists these and other species that occurred at five or more stations or were represented by more than 10 specimens.

A number of new species were collected during this study; however, many of these will be described in a forthcoming monograph on the eastern Gulf species by William Kruczynski and the late Robert Menzies (William Kruczynski, personal communication).

TANAIDACEA

The tanaids were represented by only nine species; however, they ranked second after the amphipods with 1,454 specimens (see Table A-1). Leptochelia sp. B may be synonymous with L. foresteri; however, the remaining eight species appear to be undescribed (John Ogle, personal communication). Three species, Apseudes sp. B, Leptochelia sp. A, and Kalliapseudes sp. A, were numerous and distributed throughout the MAFLA study area (see Table A-5). Two species, Apseudes sp. D and Leiopid sp. A, both from deep stations, were only represented by a single specimen each.

CUMACEA

Cumaceans occurred throughout the study area in small numbers. A total of 428 specimens representing four families, eight genera, and 28 species were identified. Only two species were collected from any one station during all three seasonal sampling periods: Campylaspis sp. B at station 2960, and Cyclaspis sp. G at station 2209. Excluding these two species, only 11 other species occurred in two of the three seasonal sampling periods. Table A-5 gives the most common species. Only five (or possibly six) of the 28 species appear to be described.

MYSIDACEA

The mysid shrimps or "opossum shrimp" were uncommon in the box-core samples. Only five species totaling 37 specimens were collected. Bowmaniella portoricensis, a burrowing form, was the most commonly occurring species and was represented by 13 specimens.

STOMATOPODA

Thirty-three mantis shrimps belonging to eight species and to three families were collected. Platysquilla horologii, considered a rare species, (David Camp, personal communication) was the most common species. It occurred at three of the southern stations. Twelve specimens were collected during summer 1977 and fall 1977.

NEBALIACEA

Two species of Nebalia representing 87 specimens were collected. Nebalia sp. A occurred at more than five stations and made up over 90% of the specimens.

PYCNOGONIDA

The chelicerate class Pycnogonida represented the only non-crustacean arthropods collected during the study. There were three species belonging to three genera and two families. They made up less than 1% of the specimens collected and only 1.1% of the species in this study. The single specimen of Anoplodactylus sp. A may represent an undescribed species (Allen Childs, personal communication).

DISCUSSION

The arthropod fractions from the 1977-1978 MAFLA box-coring program under BLM Contract No. AA 550-CT7-34 represent the most extensive collection of infaunal crustaceans ever made in the eastern Gulf of Mexico. Of the 360 species encountered during this study, nearly one-third probably represent undescribed species.

The stomatopods, mysids, pycnogonids, and decapods are relatively well known from the eastern Gulf; however, as a result of the MAFLA programs, new species in these groups (except the mysids) are still being found. The amphipods, cumaceans, tanaidaceans, nebaliaceans, and to a certain degree, the isopods, are poorly known from this area as well as from the adjacent southeast Atlantic coast and the Caribbean area.

Because of the lack of taxonomic and zoogeographical information for the eastern Gulf and adjacent regions, it is difficult to make valid comparisons for many of the arthropod groups. There appear to be some similarities between the eastern Gulf amphipod fauna and the western Gulf amphipod assemblages described and documented by McKinney (1977). McKinney pointed out the similarity between the northeastern Pacific amphipoda and those he studied in the western Gulf. A number of species collected during the MAFLA study appear to be Gulf cognates of the eastern Pacific species, especially those belonging to the families Synopiidae, Photidae, Melitidae, Ampeliscidae, and Aoridae. Mills (1965) discussed the zoogeography of the genus Ampelisca and mentioned a number of Gulf of Mexico records for the genus. He also pointed out the similarities between the northeastern Pacific species and the Gulf forms. The zoogeographical affinities of the Gulf tanaidaceans and cumaceans are more obscure and should be studied in

more detail. A cumacean collected from the MAFLA study area and currently being described by the PI and an associate, shows a close affinity to two southeastern Pacific species. The decapods from this study appear to be in part an extension of Caribbean fauna; however, one new species of Callianassa from the MAFLA area is most closely related to the Mediterranean species Callianassa acanthus. Many taxonomic and systematic studies must be completed before a basic understanding of the faunal assemblages of the eastern Gulf and adjacent regions can be attained.

Because of the heterogenous character of many of the bottoms that were sampled, the diversity and evenness indices may be misleading. For some stations the replicates were very different, but when all replicates were pooled for statistical treatment, the evenness indices in some cases were misleading. Statistical treatment of each replicate may help clarify this situation.

The noticeable seasonal drop in the number of species (S,294, F,262, W,164) and the number of specimens collected (S,4441, F,3061, S,1512) during the winter sampling was surprising (see Table A-1). In estuarine and nearshore areas, amphipod populations often increase in number and diversity during the winter. The dramatic drop for all crustaceans during winter 1978 may indicate an increase in predation by bottom fishes or a normal or abnormal die-off triggered by winter conditions. There are no seasonal data available for the arthropod fractions of the 1975-1976 MAFLA box-coring program. When these stored samples from this earlier study are identified and tabulated, it will be interesting to compare the seasonal changes in arthropod population of the two years.

CONCLUSION

The macroarthropods collected from the 1977-1978 MAFLA box-coring study, Contract No. AA550-CT7-34, constitute the best collection of infaunal crustaceans from the eastern Gulf of Mexico. The collection contains a large number of undescribed species, and because of this fact, it is difficult at this time to make any definite statement on the zoogeographical affinities of the various crustacean groups and subgroups from the study.

It is also difficult to interpret the diversity and evenness indices obtained because of the heterogenous bottom types occurring in the MAFLA study area. A comparative statistical analysis of each replicate at stations where relatively large numbers of arthropods occurred (i.e., more than 200.0.6 m^{-2}) would be useful.

The dramatic decrease (33%) in the total number of species and the over 50% reduction in the total number of specimens during the winter of 1978 compared to the fall of 1977 warrants further clarification. A comparison with the unsorted macroarthropod fractions from the 1975-1976 MAFLA box-coring study would be useful.

REFERENCES

Barnard, J. L. and W. S. Gray, 1969. Biogeographic relationships of the Salton Sea amphipod: Gammarus mucronatus. Say. Bull. So. Calif. Acad. Sci. 68(1):1-9.

Bowman, T. E., 1964. Mysidopsis almyra, a new estuarine mysid crustacean from Louisiana and Florida. Tulane Stud. Zool. 12(1):15-18.

Brattegard, T., 1969. Marine biological investigations in the Bahamas 10. In: Mysidacea from the Shallow Water in the Bahamas and Southern Florida, Part 1. Sarsia 39:17-106.

Brattegard, T., 1970. Marine biological investigations in the Bahamas 11. In: Mysidacea from the Shallow Water in the Bahamas and Southern Florida, Part 2. Sarsia 41:1-35.

Brattegard, T., 1970. Mysidacea from the shallow water in the Caribbean Sea. Sarsia 43:111-154.

Calman, W. T., 1912. The Crustacea of the order Cumacea in the collection of the United States National Museum. Proc. U. S. Nat. Mus. 41:603-676.

Camp, D. K., 1971. Platysquilla horologii (Stomatopoda, Lysiosquillidae), a new species from the Gulf of Mexico, with an emendation of the generic definition. Proc. Biol. Soc. Wash. 84(15):119-127.

Camp, D. K., 1973. Stomatopod Crustacea: Memoirs of the Hourglass Cruises. Fla. Dept. Nat. Resour. Mar. Res. Lab. Vol. 3, Part 2. 100 p.

Chace, F. A., 1942. Six new species of decapod and stomatopd Crustacea from the Gulf of Mexico. Proc. New England Zool. Club 19:79-92.

Chace, F. A., Jr., 1969. A new genus and fine new species of shrimps (Decapoda, Palemonidae, Pontonininae) from the Western Atlantic. Crustaceana 16(3):251-272.

Chace, F. A., Jr., 1972. The shrimps of the Smithsonian-Bredin Caribbean Expeditions with a summary of the West Indian shallow-water species (Crustacea: Decapoda: Natantia). Smith. Contrib. Zool. 98:179 pp.

Cobb, S. P., 1971. A new species of Sicyonia (Decapoda: Penaeidae) from the Gulf of Mexico with notes on S. stimpsoni Bouvier. Crustaceana 20(1):104-112.

Cobb, S. P., 1973. Fabia tellina, a new species of commensal crab (Decapoda, Pinnotheridae) from the northeastern Gulf of Mexico. Crustaceana 25(1):70-74.

Cobb, S. P., C. R. Futch, and D. K. Camp, 1973. The rock shrimp, Sicyonia brevirostris Stimpson, 1871 (Decapoda: Penaeidae): Memoirs of the Hourglass Cruises. Fla. Dept. Nat. Resour. Mar. Res. Lab. 3(1):38 p.

Collard, S. B. and D'Asaro, 1973. Benthic invertebrates of the eastern Gulf of Mexico. In: A summary of knowledge of the eastern Gulf of Mexico. (III-G-1-27) State Univ. System Fla. Inst. Oceanogr., St. Petersburg, Fla.

Croker, R. A., 1968. Distribution and abundance of some intertidal sand beach amphipods accompanying the passage of two hurricanes. Chesapeake Sci. 9(3):157-162.

Culpepper, T. J. and W. E. Pequegnat, 1969. Taxonomic and ecological study of selected benthonic gammarid crustaceans from the northeastern Gulf of Mexico. Texas A&M Univ., Dept. Oceanogr. Tech. Rept. Ref. 69-3T. 102 p.

Lyons, W. G. and S. B. Collard, 1974. Benthic invertebrate communities of the eastern Gulf of Mexico. In: p. 157-166 Proc. Mar. Inv. Impl. Offshore Drilling, Eastern Gulf of Mexico. State Univ. System Fla. Inst. Oceanogr., St. Petersburg, Fla.

Manning, R. B., 1969. Stomatopod crustacea of the Western Atlantic. Stud. Trop. Oceanogr., Miami 8:vii + 380 pp.

Manning, R. B. and F. A. Chace, Jr., 1975. Shrimps of the family Processidae (Crustacea, Decapoda, Caridea) from the northwestern Atlantic. Smith. Contrib. Zool. 89:41 pp.

McKinney, L. D., 1977. The origin and distribution of shallow water gammaridean Amphipoda in the Gulf of Mexico and Caribbean Sea with notes on their ecology. Dissertation submitted to the Graduate College of Texas A&M University.

Mills, E. L., 1965. The zoogeography of North Atlantic and North Pacific ampeliscid amphipod crustaceans. Sys. Zool. 14(2):119-130.

Molenock, J., 1969. Mysidopsis bahia, a new species of mysid (Crustacea: Mysidacea) from Galveston Bay, Texas. Tulane Stud. Zool. Bot. 15(3):113-116.

Myers, A. A., 1970. Taxonomic studies on the genus Grandidierella Coutiere (Crustacea: Amphipoda) with a description of G. dentimera, sp. nov. Bull. Mar. Sci. 20(1):135-147.

Pearse, A. S., 1908. Descriptions of four new species of amphipodous crustacea from the Gulf of Mexico. Proc. U. S. Nat. Mus. 34(1594): 27-32.

Pearse, A. S., 1913. Notes on certain amphipods from the Gulf of Mexico, with descriptions of new genera and new species. Proc. U. S. Nat. Mus. 43(1936):369-379.

Provenzano, A. J., 1959. The shallow-water hermit crabs of Florida. Bull. Mar. Sci. Gulf & Carib., 9(4):349-420.

Rathbun, M. J., 1918. The grapsoid crabs of America. U. S. Nat. Mus. Bull. 97, pp. i-xxii, 1-461, pls. 1-161, 172 text-figs.

Rathbun, M. J., 1925. The spider crabs of America. U. S. Nat. Mus. Bull. 129, pp. i-xx, 1-613, 283 pls., 152 text-figs.

Rathbun, M. J., 1930. The canceroid crabs of America of the families Euryalidae, Portunidae, Atelecyclidae, Canceridae and Xanthidae. U. S. Nat. Mus., pp. i-xvi, 1-609, pls. 1-230, 85 text-figs.

Rathbun, M. J., 1931. Two new crabs from the Gulf of Mexico. Proc. Biol. Soc. Wash. 44:71-72.

Rathbun, M. J., 1937. The oxystomatous and allied crabs of America. U. S. Nat. Mus. Bull. 166, pp. i-vi, 1-278, 86 pls. 47 text-figs.

Richardson, H., 1905. A monograph on the isopods of North America. Bull. U. S. Nat. Mus. 54:1-727.

Rouse, W. L., 1969(1970). Littoral Crustacea from southwest Florida. Quart. Jour. Fla. Acad. Sci. 32(2):127-152.

Shoemaker, C. R. Amphipods of the family Bateidae in the collection of the United States National Museum. Proc. U. S. Nat. Mus. 68(2626): 1-26.

Shoemaker, C. R., 1943. A new amphipod of the genus Corophium from Florida. Charleston Museum Leaflet No. 18, pp. 3-7.

Shoemaker, C. R., 1945a. The amphipod genus Photis on the east coast of North America. Charleston Museum Leaflet No. 22, pp. 1-17, Figs. 1-5.

Shoemaker, C. R., 1945b. The amphipod genus Unciola on the east coast of North America. Amer. Midl. Nat., 34:446-465, 9 figs.

Shoemaker, C. R., 1947. Further notes on the amphipod genus Corophium on the east coast of America. J. Wash. Acad. Sci., 32(2):47-63.

Tabb, D. C., and R. Manning, 1961. A checklist of the flora and fauna of northern Florida Bay and adjacent brackish waters of the Florida Mainland collected during the period July 1957 through September 1960. Bull. Mar. Sci. Gulf. and Carib. 11(4):552-649.

Tattersall, W. M., 1951. A review of the Mysidacea of the United States National Museum. U. S. Nat. Mus. Bull. 201:292 p.

Thomas, J. D., 1976. A survey of gammarid amphipods of the Barataria Bay, Louisiana Region. Contrib. Mar. Sci. 20:87-100.

Wass, M. L., 1955. The decapod crustaceans of Aligator Harbor and adjacent inshore areas of northwestern Florida. Quart. Jour. Fla. Acad. Sci. 18(3):129-176.

Watling, L., 1977. Two new genera and a new subfamily of Bodotriidae (Crustacea: Cumacea) from eastern North America. Proc. Biol. Soc. Wash. 89(52): 593-598.

Wurtz, C. S. and S. S. Romback, 1955. The invertebrate fauna of some Gulf coast rivers. Proc. Nat. Acad. Sci. Phil. 107: 167-206.

APPENDIX A

SAMPLE AND ANALYSIS INVENTORIES AND DATA TABULATION

TABLE A-1

NUMBER AND PERCENT OF SPECIES AND NUMBER AND PERCENT OF INDIVIDUALS FOR MAJOR GROUPS BY SEASON*

	Summer '77				Fall '77				Winter '77				Total	
	No. Species	% Total Species	No. Indiv.	% Total Indiv.	No. Species	% Total Species	No. Indiv.	% Total Indiv.	No. Species	% Total Species	No. Indiv.	% Total Indiv.	No. Indiv.	% Total Indiv.
Pycnogonida	3	1.1	15	0.3	1	0.4	6	0.2	1	0.6	2	0.1	23	0.3
Nebaliacea	2	0.8	52	1.2	2	0.8	31	1.0	2	1.2	4	0.3	87	1.0
Stomatopoda	5	1.9	17	0.4	5	2.0	12	0.4	2	1.2	4	0.3	33	0.4
Mysidacea	5	1.9	27	0.6	3	1.2	8	0.3	2	1.2	2	0.1	37	0.4
Cumacea	23	8.8	214	4.8	22	9.0	181	5.9	12	7.3	33	2.2	428	4.7
Tanaidacea	6	2.3	768	17.3	9	3.7	551	17.9	5	3.0	135	8.9	1454	16.1
Isopoda	32	12.2	545	12.3	27	11.1	375	12.1	21	12.8	193	12.8	1113	12.3
Amphipoda	91	34.7	2191	49.3	96	39.4	438	47.0	67	40.9	839	55.5	4468	49.6
Decapoda	95	36.3	612	13.8	79	32.4	459	15.0	52	31.8	300	19.8	1371	15.2
Total	262		4441		244		3061		164		1512		9014	

*Based on specimens identified to specific level

TABLE A-2

A SYSTEMATIC LISTING AFTER WATERMAN AND CHACE (1960) OF HIGHER MACROCRUSTACEANS WITH THE NUMBER OCCURRING IN BOX-CORES OF 1977-1978 MAFLA STUDY

Systematic Listing	Number of Species
Class Crustacea	360
Subclass Malacostraca	360
Series Phyllocarida	2
Order Leptostraca (=Nebaliacea)	2
Series Eumalocostraca	358
Superorder Syncarida*	0
Order Anaspidacea*	0
Order Bathynellacea*	0
Superorder Hoplocarida	8
Order Stomatopoda	8
Superorder Peracarida	218
Order Thermosbaenacea*	0
Order Spelaeogriphacea*	0
Order Mysidacea	5
Suborder Lophogastrida	0
Suborder Mysida	5
Order Cumacea	28
Order Tanaidacea	9
Order Isopoda	47
Suborder Gnathidea	6
Suborder Anthuridea	19
Suborder Flabellifera	12
Suborder Valvifera	4
Suborder Asellota	5
Suborder Phreatoicidea	0
Suborder Epicaridea	1
Suborder Oniscoidea*	0
Order Amphipoda	129
Suborder Gammaridea	125
Suborder Hyperiida	0
Suborder Caprellidea	4
Suborder Ingolfiellidea	0
Superorder Eucarida	134
Order Euphausiacea	0
Order Decapoda	134
Suborder Natantia	27
Section Penaeidea	3
Section Caridea	24
Section Stenopodidea	0
Suborder Reptantia	107
Section Macrura	20
Superfamily Eryonidea	0
Superfamily Scyllaridea	0
Superfamily Nephropsidea	0
Superfamily Thalassinidea	20

Section Anomura	16
Superfamily Coenobitoidea	0
Superfamily Paguroidea	7
Superfamily Galatheoidea	7
Superfamily Hippoidea	2
Section Brachyura	71
Subsection Gymnopleura	4
Subsection Dromiacea	3
Subsection Oxystomata	15
Subsection Brachygnatha	49
Superfamily Brachyrhyncha	27
Superfamily Oxyrhyncha	22

*Freshwater groups

TABLE A-3

TAXONOMIC LISTING OF MACROARTHROPODS
FROM MAFLA BOX-CORE SAMPLES
SUMMER '77 TO WINTER '78

Pycnogonida
- Achelia sawyeri
- Anoplodactylus sp. A
- Ascorhynchus pyrginospinum

Nebaliacea
- Nebalia sp. A
- Nebalia sp. B

Stomatopoda
- Acanthosquilla cf. biminiensis
- Eurysquilla plumata
- Gonodactylus bredini
- Meiosquilla quadridens
- Meiosquilla schmitti
- Odontodactylus brevirostris
- Platysquilla horologii
- Squilla deceptrix

Mysidacea
- Anchialina typica
- Bathymysis renoculata
- Bowmaniella sp. A
- Bowmaniella portoricensis
- Mysidopsis furca

Cumacea
- Campylaspis sp. A
- Campylaspis sp. B
- Campylaspis sp. C
- Campylaspis sp. D
- Campylaspis sp. F
- Campylaspis sp. H
- Cumella garrityi
- Cumella sp. A
- Cumella sp. B
- Cumella sp. C
- Cumella sp. D
- Cumella sp. E
- Cumella sp. F
- Cumella sp. G
- Cyclaspis sp.B
- Cyclaspis sp. C
- Cyclaspis sp. D
- Cyclaspis sp. F
- Cyclaspis sp. G
- Cyclaspis sp. H
- Eudorella ? sp. B
- Leucon sp. A
- Oxyurostylis salinoi
- Oxyurostylis smithi
- Sympodomma sp. A
- Vaunthompsonia minor
- Vaunthompsonia sp. B
- Vaunthompsonia sp. C

Tanaidacea
- Apseudes sp. A
- Apseudes sp. B
- Apseudes sp. C
- Apseudes sp. D
- Kalliapseudes sp. A
- Leiopid Genus A sp. A
- Leptochelia sp. A
- Leptochelia sp. B
- Leptochelia sp. C

Isopoda
- Accalathura crenulata
- Anthurid Genus B sp. A
- Anthurid Genus C sp. A
- Anthurid Genus D sp. A
- Anthurid Genus E sp. A
- Anthurid Genus F sp. A
- Anthurid Genus G sp. A
- Anthurid Genus H sp. A
- Apanthura cephalous
- Apanthura magnifica
- Apanthura sp. A
- Apanthura sp. B
- Apanthura sp. C
- Apanthura sp. D
- Arcturella bispinata
- Arcturella spinata
- Astacilla sp. A
- Carpius floridensis
- Cirolana gracilis
- Cirolana parva
- Cirolana polita
- Conilera sp. A
- Bathygnathia sp. A

Eurydice convexa
Eurydice littoralis
Eurydice piperata
Gnathia cf. crenulatifrons
Gnathia floridensis
Gnathia pranzia
Gnathia sp. B
Gnathid Genus A sp. A
Horoloanthura irpex
Jaeropsis rathbunae
Mesanthura floridensis
Munna sp. A
Nalicora rapax
Pananthura formosa
Paracerceis caudata
Ptilanthura tricarina
Rocinela signata
Serolis mgrayi
Sphaeroma sp. A
Stenetrium cf. minocule
Stenetrium occidentale
Tropedotea lyonsi
Xenanthura brevitelson

Amphipoda

Acanthohaustorius millsi
Acanthohaustorius sp. A
Acanthohaustorius sp. B
Acanthosquilla cf. biminiensis
Acanthosquillia cf. biminiensis
Ampelisca abdita
Ampelisca agassizi
Ampelisca cristata microdentata
Ampelisca schellenbergi
Ampelisca sp. A
Ampelisca sp. B
Ampelisca vadorum
Ampelisca venetiensis
Ampelisca verrilli
Amphideutopus sp. A
Amphilochus sp. A
Ampithoe sp. A
Anamixis n. sp. A
Argissa hamatipes
Batea sp. A
Byblis sp. A
Caprella penantis
Carinobatea carinata
Carinobatea monocuspis
Carinobatea sp. A
Ceradocus sp. A
Ceradocus sp. B
Cerapus tubularis
Chevalia mexicana
Colomastix sp. A
Corophium sp.
Corophium sp. B
Cymadusa sp. A
Dulichia ? sp. A
Elasmopus sp. A
Elasmopus sp. B
Erichthonius brasiliensis
Erichthonius rubricornis
Erichthonius sp. A
Eriopisa sp. A
Gammaropsis sp. A
Garosyrrhoe sp. A
Gitana ? sp. A
Gitanopsis sp. A
Haploops sp. A
Harpinia sp. A
Harpinia sp. B
Hemiproto sp. A
Heterophilias cf. seclusus
Heterophoxus sp. A
Hippomedon sp. A
Hippomedon sp. B
Idunella sp. A
Iphimedia sp. A
Jerbarnia sp. A
Lembos cf. tigrinus
Lembos ovalipes
Lembos smithi
Lembos unicornis
Leptocheirus sp. A
Leucothoe sp. A
Leucothoe sp. B
Leucothoides pottsi
Liljeborgia sp. A
Liljeborgia sp. B
Listriella barnardi
Listriella sp. A
Listriella sp. B
Listriella sp. C
Listriella sp. D
Luconacia incerta
Lysianassid Genus A sp. A
Lysianassid Genus A sp. B
Lysianopsis sp. A
Lysianopsis sp. B
Maera sp. A

Maera sp. B
Maera sp. C
Maera sp. D
Maera sp. E
Maera sp. F
Maera sp. G
Mandibulophoxus sp. A
Melita appendiculata
Melitid Genus A sp. A
Metaphoxus ? sp. A
Microdeutopus myersi
Microdeutopus sp. A
Microjassa sp. A
Monoculodes cf. nyei
Oediceros sp. A
Orchomene ? sp. A
Parametopella sp. A
Paraphoxus sp. A
Parelasmopus sp. A
Photid Genus A
Photid Genus A sp. A
Photid Genus B sp. A
Photis pugnator
Photis sp. A
Photis sp. B
Photis sp. C
Phtisica marina
Platyischnopus sp. A
Podocerid Genus A sp. A
Podoceropsis sp. A
Podocerus sp. A
Pontogeneia longleyi
Protohadzia sp. A
Protohadzia sp. B
Protohaustorius sp. A
Pseudohaustorius sp. A
Rudilemboides naglei
Rudilemboides sp. A
Seba sp. A
Stenothoe sp. A
Synchelidium americanum
Synchelidium sp. A
Synopia ultramorina
Syrrhoe ? sp. A
Syrrhoites sp. A
Tabzizius sp. A
Tiron sp. A
Tiron tropakis
Trichophoxus cf. epistomus
Trichophoxus floridanus
Unciola sp. A
Unciola sp. C
Westwoodilla sp.

Decapoda
Natantia
Alpheus armatus
Alpheus floridanus
Alpheus normanni

Alpheopsis sp. A
Automate evermanni
Hippolyte sp. A.
Leptochela bermudensis
Leptochela carinata
Leptochela papulata
Leptochela serratorbita
Metapenaeopsis goodei
Neopontonides beaufortensis
Ogyrides yaquiensis
Pandalid sp. A
Periclimenes americanus
Periclimenes iridescens
Periclimenes maxillulidens
Processa bermudensis
Processa hemphilli
Processa vicina
Salmoneus ? sp. A
Sicyonia brevirostris
Sicyonia laevigata
Synalpheus agelas
Synalpheus townsendi
Thor amboinensis
Trachycaris restrictus
Macrura
Calastacus hissutimana?
Calastacus ? oxypleura
Calastacus sp. A
Calastacus sp. B
Calastacus sp. C
Callianassa atlantica
Callianassa cf. batei
Callianassa cf. fragilis
Callianassa cf. longiventris
Callianassa marginata
Callianassa cf. minima
Callianassa sp. A
Callianassa sp. B
Callianassa sp. C
Callianassa sp. D
Callianassa sp. E
Anomura
Albunea gibbesii
Albunea paretii
Euceramus praelongus
Galathea rostrata
Labidochirus sp. A

Munida beanii
Munida beanii?
Munida evermanni
Munida flinti
Munida pusilla
Paguristes sp. A
Pagurus brandii
Pagurus carolinensis
Pagurus corallinus
Pylopagurus sp. A
Pylopagurus sp. B

Brachyura

Acanthocarpus alexandri
Aepinus septemspinosus
Arachnopsis filipes
Batrachonotus fragosus
Callidactylus asper
Chasmocarcinus cylindricus
Clythocerus cf. stimpsoni
Clythocerus granulatus
Clythocerus perpusillus
Clythocerus stimpsoni
Collodes leptocheles
Collodes trispinosus
Cryptopodia concava
Cyclodorippe antennaria
Dissodactylus sp. A
Dromidia antillensis
Ebalia cariosa
Ebalia cf. hancockii
Ebalia cf. stimpsoni
Ebalia stimpsoni
Ethusa mascarone americana
Euprognatha rastellifera marthae

Eurypanopeus cf. dissimilus
Euryplax nitida
Goneplax hirsuta
Goneplax tridentata
Hemus cristulipes
Hepatus sp. A
Heterocrypta granulata
Hypoconcha arcuata
Hypoconcha spinosissima
Iliacantha sparsa?
Inachoides forceps
Leptodius agassizii
Lithadia cadaverosa
Lobopilumnus agassizii
Macrocoeloma camptocerum
Macrocoeloma septemspinosum
Melybia thalamita
Mesorhoea cf. sexpinosa
Mesorhoea sexpinosa
Micropanope cf. sculptipes
Mithrax acuticornis

Mocosoa crebipunctata
Osachila semilevis
Osachila tuberosa
Palicus alternata
Parapinnixa hendersoni
Parthenope agona
Pilumnus floridanus
Pilumnus sayi
Pinnixa sp. A
Pinnixa sp. B
Pinnixa sp. C
Pinnixa sp. D
Pinnixa sp. E
Pinnixa sp. F
Pinnixa sp. G
Pinnotheres sp. A
Pitho iherminieri
Podochela gracilipes
Portunus ordwayi
Portunus spinicarpus
Prionoplacinae sp. A
Ranilia constricta
Ranilia muricata
Raninoides loevis
Solenolambrus tenellus
Speloeophorus pontifer
Speocarcinus cf. carolinesis
Speocarcinus lobatus
Stenocionops furcata
Symethis variolosa

Additional Macrura:

Metaconaxus sp. A
Metaconaxus sp. B
Metaconaxus sp. C
Upogebia sp. A

TABLE A-4

NUMBER OF TAXA FOR EACH SEASON

STATION NUMBER	SUMMER '77	FALL '77	WINTER '78
2101	31	49	15
2102	16	18	2
2103*	10	4	9
2104	36	37	53
2105*	4	5	4
2106	23	18	13
2179?	-	-	1
2207	67	42	18
2208	28	-	21
2209	34	38	16
2210*	9	9	5
2211	53	61	36
2212	14	18	13
2313	7	15	2
2315*	18	17	14
2316	50	45	26
2317	8	17	-
2318	41	38	7
2419	59	49	20
2421*	10	19	4
2423	51	53	32
2424	12	9	2
2426	20	28	23
2427	5	17	15
2429	2	0	0
2528	84	74	57
2529*	4	7	6
2531	37	39	22
2533*	4	8	9
2536	5	10	7
2638	9	10	10
2639*	4	3	3
2640	58	24	30
2641*	6	4	4
2643	4	5	1
2645	21	12	24
2646	27	19	15
2747	58	24	21
2748	38	51	57
2749	2	-	-
2851**	20	-	-
2852**	27	-	-
2853**	39	-	-
2854**	43	-	-
2855**	27	-	-
2856**	34	-	-
2957	22	21	5
2958	40	22	14
2959	4	35	8
2660	48	34	18

*Secondary Stations

**Supplemental Stations

TABLE A-5

RANKING OF SPECIES IN ORDER OF NUMBER OF SPECIMENS AND NUMBER OF STATION OCCURRENCES FOR ALL STATIONS*AND FOR PRIMARY STATIONS** BY SEASON

ISOPODA

Summer 1977

Species	No. Specimens *	**	Species	No. Occurrences *	**
Xenanthura brevitelson	125	115	Xenanthura brevitelson	20	14
Apanthura magnifica	119	118	Horoloanthura irpex	18	15
Horoloanthura irpex	99	94	Apanthura magnifica	16	15
Mesanthura floridensis	23	19	Eurydice littoralis	9	7
Cirolana gracilis	23	14	Eurydice piperata	9	8
Pananthura formosa	22	22	Cirolana gracilis	8	7
Accalathura crenulata	16	15	Accalathura crenulata	7	6
Eurydice littoralis	15	13	Mesanthura floridensis	7	5
Ptilanthura tricarina	6	12	Ptilanthura tricarina	7	7
Tropedotea lyonsi	12	5	Serolis mgrayi	6	6
Eurydice piperata	11	9	Tropedotea lysonsi	6	4
Apanthura sp. A	11	2	Apanthura sp. A	2	1
Serolis mgrayi	6	6	Pananthura formosa	2	2

Fall 1977

	*	**		*	**
Xenanthura brevitelson	95	92	Xenanthura brevitelson	20	17
Apanthura magnifica	69	66	Apanthura magnifica	13	10
Horoloanthura irpex	50	49	Horoloanthura irpex	12	11
Cirolana parva	35	35	Cirolana gracilis	7	7
Cirolana gracilis	20	20	Cirolana piperata	6	5
Eurydice littoralis	18	5	Eurydice littoralis	5	5
Mesanthura floridensis	11	10	Mesoanthura floridensis	5	4
Cirolana piperata	6	5	Cirolana polita	5	5
Cirolana polita	5	5	Cirolana parva	2	2

Winter 1978

	*	**		*	**
Xenanthura brevitelson	46	41	Apanthura magnifica	16	14
Horoloanthura irpex	35	34	Horoloanthura irpex	13	12
Apanthura magnifica	33	30	Xenanthura brevitelson	13	9
Eurydice littoralis	18	17	Eurydice littoralis	7	6
Stenetrium cf. minocule	17	1	Accalathura crenulata	5	4
Accalathura crenulata	7	6	Stenetrium cf. minocule	2	1

DECAPODA

Summer 1977

	*	**		*	**
Automate evermanni	153	133	Automate evermanni	24	18
Callianassa marginata	58	58	Alpheus normanni	9	7
Micropanope sculptipes	55	46	Micropanope sculptipes	9	6
Processa hemphilli	24	20	Callianassa marginata	7	7
Galathea rostrata	20	15	Leptochela papulata	7	6
Alpheus normanni	15	9	Processa hiamphilla	7	5
Processa berbudensis	15	15	Alpheus floridanus	5	5
Leptochela papulata	14	13	Munida pusilla	5	5
Munida pusilla	14	14	Processa bermudensis	3	3
Alpheus floridanus	11	11	Leptochela serratorbita	3	3
Leptochela serratorbita	10	10	Galathea rostrata	3	2

Fall 1977

	*	**			
Automate evermanni	133	122	Automate evermanni	27	22
Processa bermudensis	33	33	Leptochela papulata	9	9
Munida beanii	29	29	Callianassa marginata	7	7
Callianassa marginata	25	25	Ebalia stimpsoni	6	6
Synalpheus townsendi	19	18	Alpheus normanni	5	5
Galathea rostrata	18	18	Munida beanii	5	5
Leptochela papulata	14	14	Processa bermudensis	5	5
Micropanope sculptipes	13	13	Micropanope sculptipes	4	4
Alpheus normanni	8	8	Synalpheus townsendi	3	2
Ebalia stimpsoni	8	8	Galathea rostrata	2	2

Winter 1978

	*	**			
Automate evermanni	98	90	Automate evermanni	22	17
Callianassa marginata	32	31	Micropanope sculptipes	9	8
Micropanope sculptipes	24	23	Leptochela papulata	8	7
Alpheus normanni	19	19	Alpheus normanni	7	7
Munida beanii	13	13	Callianassa marginata	7	6
Leptochela papulata	11	10	Munida beanii	4	4

TANAIDACEA

Summer 1977

	*	**		*	**
Apseudes sp. B	287	231	Leptochelia sp. A	28	20
Leptochelia sp. A	212	182	Apseudes sp. B	22	14
Kalliapseudes sp. A	113	106	Apseudes sp. A	16	14
Apseudes sp. A	105	96	Kalliapseudes sp. A	11	9
Leptochelia sp. B	44	44	Leptochelia sp. B	4	4
Apseudes sp. C	7	6	Apseudes sp. C	3	2
Leptochelia sp. C	0	0	Leptochelia sp. C	0	0
Apseudes sp. D	0	0	Apseudes sp. D	0	0
Leiopid sp. A	0	0	Leiopid sp. A	0	0

Fall 1977

	*	**		*	**
Leptochelia sp. A	218	214	Apseudes sp. B	22	17
Apseudes sp. B	172	161	Leptochelia sp. A	20	16
Kalliapseudes sp. A	104	102	Kalliapseudes sp. A	104	102
Apseudes sp. A	23	22	Apseudes sp. A	9	8
Leptochelia sp. B	15	15	Apseudes sp. C	5	4
Apseudes sp. C	13	12	Leptochelia sp. B	2	2
Leptochelia sp. C	4	4	Leptochelia sp. C	1	1
Apseudes sp. D	1	1	Apseudes sp. D	1	1
Leiopid sp. A	1 1	1	Leiopid sp. A	1	1

Winter 1978

	*	**		*	**
Apseudes sp. B	70	62	Apseudes sp. B	15	10
Leptochelia sp. A	34	34	Leptochelia sp. A	12	12
Kalliapseudes sp. A	17	17	Kalliapseudes sp. A	5	5
Apseudes sp. A	9	9	Apseudes sp. A	6	6
Apseudes sp. C	5	5	Apseudes sp. C	3	3
Leptochelia sp. B	0	0	Leptochelia sp. B	0	0
Leptochelia sp. C	0	0	Leptochelia sp. C	0	0
Apseudes sp. D	0	0	Apseudes sp. D	0	0
Leiopid sp. A	0	0	Leiopid sp. A	0	0

AMPHIPODA

Summer 1977

	*	**		*	**
Ampelisca agassizi	151	124	Lysianopsis sp. A	18	12
Trichophoxus floridanus	86	29	Ampelisca afassizi	13	9
Lysianopsis sp. A	61	46	Ampelisca cristata mic.	13	9
Ampelisca verrilli	51	40	Synchelidium americanum	11	8
Ampelisca cristata mic.	41	25	Trichophoxus floridanus	10	7
Synchelidium americanum	37	31	Ampelisca verrilli	9	7

Fall 1977

Ampelisca agassizi	229	221	Ampelisca agassizi	20	17
Ampelisca verrilli	75	53	Ampelisca verrilli	17	13
Lysianopsis sp. A	32	30	Trichophoxus floridanus	9	6
Trichophoxus floridanus	28	24	Ampelisca cristata mic.	[illegible]	7
Ampelisca cristata mic.	26	26	Synchelidium americanum	9	9
Synchelidium americanum	26	23	Lysianopsis sp. A	7	8

Winter 1978

A. agassizi	219	201	A. agassizi	15	14
A. verrilli	53	48	A. verrilli	14	13
T. floridanus	16	15	T. floridanus	7	6
A. cristata mic.	15	15	Lysianopsis sp. A	6	6
Lysianopsis sp. A	8	8	A. cristata	5	5
S. americanum	8	6	S. americanum	4	3

CUMACEA

Summer 1977

Cyclaspis sp. G	39	37	Campylaspis sp. B	12	8
Campylaspis sp. B	35	24	Cumella sp. A	11	10
Cumella sp. A	26	25	Cyclaspis sp. G	8	7
Campylaspis sp. D	14	12	Campylaspis sp. D	8	7
Campylaspis sp. F	14	14	Cumella sp. C	5	3
Cyclaspis sp. C	12	8	Cyclaspis sp. C	5	3
Cumella sp. C	99	7	Cyclaspis sp. D	5	4

Fall 1977

	*	**		*	*
Cumella sp. A	49	45	Campylaspis sp. B	10	8
Campylaspis sp. B	27	25	Cyclaspis sp. G	9	7
Cyclaspis sp. G	18	16	Cumella sp. C	8	6
Cumella sp. C	14	14	Cumella sp. A	7	5
Cyclaspis sp. B	13	13	Oxyurostylis smithi	6	6
Oxyurostylis smithi	11	11	Cyclaspis sp. B	6	6

Winter 1977

Campylaspis sp. B	15	15	Campylaspis sp. B	5	5
Cyclaspis sp. B	4	3	Cyclaspis sp. B	4	3

TABLE A-6

NUMBER OF INDIVIDUAL SPECIMENS AT EACH STATION

STATION NUMBER	SUMMER '77	FALL '77	WINTER '78	ALL SEASONS
2101	83	160	29	272
2102	31	35	2	68
2103*	16	4	10	30
2104	100	161	134	395
2105*	4	5	5	14
2106	41	33	22	96
2207	381	179	36	596
2208	113	-	51	164
2209	134	296	200	630
2210*	11	17	25	53
2211	256	205	90	551
2212	17	20	28	65
2313	9	18	3	30
2315*	70	28	48	146
2316	148	103	64	315
2317	12	25	0	37
2318	114	296	8	418
2419	231	323	41	595
2421*	11	34	5	50
2423	166	192	88	446
2424*	24	14	2	40
2426	60	58	58	176
2427	6	22	18	46
2429	3	-	-	3
2528	480	299	205	984
2529*	5	9	9	23
2531	113	141	46	300
2533*	6	10	10	26
2535*	0	2	3	5
2536	6	18	16	40
2638	202	44	61	307
2639*	4	3	10	17
2640	443	61	70	574
2641*	11	5	4	20
2643*	4	5	4	13
2645	37	22	29	88
2746	57	60	43	160
2747	226	56	45	327
2748	225	290	153	668
2749	2	-	-	2
2851**	43	-	-	43
2852**	68	-	-	68
2853**	98	-	-	98
2854**	181	-	-	181
2855**	80	-	-	80
2856**	294	-	-	294

STATION NUMBER	SUMMER '77	FALL '77	WINTER '78	ALL SEASONS
2957	36	34	7	77
2958	73	50	17	140
2959	92	166	11	269
2960	364	98	83	545
Total for primary stations	4249	3440	1658	9347
Total for secondary stations*	178	161	132	471
Total for supplemental stns. **	764	-	-	764
Total for all stations	5191	3601	1790	10582

TABLE A-7

PRIMARY STATIONS LISTED IN GROUPS OF SIMILARITY BY SEASON

Group or Zone	Summer '77	Group or Zone	Fall '77	Group or Zone	Winter '78
I	2101	I	2101	I	2101
	2207		2419		2959
	2419				
	2960	II	2102	II	2207
	2316		2318		2208
	2318				2209
	2102	III	2104		2316
			2211		2426
II	2104		2748		
	2211		2528	III	2427
	2748		2316		2746
	2747		2531		2747
	2423				2102
	2528	IV	2207		
	2426		2423	IV	2106
	2640		2209		2212
			2960		2536
III	2208		2747		
	2209		2959	V	2104
	2959		2640		2748
	2531				2528
		V	2106		2211
IV	2106		2957		2423
	2957		2958		2645
	2746		2426		2531
	2958		2746		2640
	2212		2645		
				VI	2318
V	2313	VI	2313		2419
	2645		2536		2960
Misc.	2536	Misc.	2212	Misc.	2313
	2427		2427		2958
					2957

TABLE A-8

DIVERSITY AND EVENNESS FOR PRIMARY STATIONS

Station	Summer			Fall			Winter		
	No. Indiv.	SWI*	NM**	No. Indiv.	SWI	NM	No. Indiv.	SWI	NM
2101	48	2.89	154	140	3.10	1425	23	2.21	41
2102	16	2.19	20	24	2.50	47	2	0.69	0
2104	88	2.83	515	144	2.30	1188	112	3.27	1069
2106	34	2.78	76	28	2.49	57	16	1.75	19
2207	303	3.22	4220	162	2.95	1393	33	2.27	100
2209	119	2.28	975	226	1.63	2097	196	1.06	1021
2211	224	2.68	2722	160	3.04	1720	68	2.57	438
2212	10	2.03	6	13	1.95	13	25	1.73	55
2313	8	1.39	6	13	2.31	10	3	0.00	0
2316	118	3.24	1101	92	3.23	758	51	2.60	222
2317	9	1.43	7	21	2.45	40	-	-	-
2318	99	3.23	706	251	2.12	2401	8	1.73	4
2419	168	3.30	1977	301	2.54	3743	31	2.05	85
2423	146	3.33	1550	164	3.30	1566	76	2.59	463
2426	59	2.47	260	40	2.42	148	44	2.39	143
2427	6	1.57	2	16	2.18	24	13	2.35	9
2528	439	3.55	9554	7	1.48	4	157	3.30	1730
2531	95	2.92	602	123	2.53	1143	37	2.65	120
2536	5	1.33	2	16	1.56	24	16	1.67	22
2638	198	0.48	354	7	1.32	83	57	1.04	131
2640	358	2.72	5510	48	2.51	196	53	2.93	277
2645	30	2.23	69	16	1.84	14	23	2.63	45
2746	42	2.49	189	39	1.59	114	40	1.75	139
2747	194	2.52	2465	52	2.55	229	40	2.11	156
2748	203	2.53	1892	266	2.661	3315	130	3.33	1430
2957	23	2.32	42	31	2.68	77	5	0.95	2
2958	53	2.91	296	47	2.39	210	9	1.89	5
2959	76	2.57	560	143	2.00	1259	9	1.68	7
2960	325	2.25	4492	96	2.98	735	80	1.70	399

* Shannon-Wiener Diversity Index
** Number of Moves (Fager Index)

APPENDIX B

RECOMMENDATIONS FOR FURTHER STUDY

RECOMMENDATIONS FOR FURTHER STUDY

(1) Fine-sorting and identification of the arthropod fractions from the 1974 and 1975-76 MAFLA box-coring study for comparison with the data from the 1977-1978 study.

(2) Concentrate ecological studies such as the MAFLA to smaller areas to facilitate better and more complete sampling and more concentrated analyses. The data gained from such studies would form the basis for evaluating the ecological conditions of oil-lease areas in terms of seasonal variation, community structure and other ecological factors.

(3) Food studies on the bottom fishes from oil lease areas are strongly recommended.

APPENDIX C

PROBLEMS ENCOUNTERED

PROBLEMS ENCOUNTERED

The main problem encountered in the identification of macroarthropods from the 1977-1978 MAFLA box-coring study was the improper fixation and preservation of specimens. Samples often contained badly deteriorated specimens that were sometimes badly fragmented also. Such specimens were very difficult to identify and often required extra time. In many cases such specimens could only be identified to family or order.

A procedure such as the following should be used to insure the collection of all specimens without damage, including small, fragile specimens. The specimens should be "floated off" onto a sieve by placing the box-core sample in a large bucket with a spout and washing the sample with a moderate amount of water from a deck hose. Light-bodied animals are then displaced from the sediment and floated out of the bucket spout with the overflowing water and are not damaged. This procedure requires approximately the same amount of time at the collection stage, and will reduce rough sorting time at the labs by about half. It will also preserve many of the more fragile specimens that are otherwise too mangled for identification.

VOLUME II

CHAPTER 17

MACROEPIFAUNA

DR. THOMAS HOPKINS
UNIVERSITY OF ALABAMA
CONTRACT NO. AA550-CT7-34

FINAL REPORT

CHARACTERIZATION OF THE MACROEPIFAUNAL ASSEMBLAGES IN THE MAFLA OCS

BY

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CONTRACT NUMBER AA550-CT7-34

SEPTEMBER 1978

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ABSTRACT

Macroepifaunal invertebrates were collected by dredging and trawling at 19 localities in the MAFLA tract of the eastern Gulf of Mexico over three seasons in 1977-1978. In addition, archived samples, from 20 dredge/trawl and 6 dive stations, were also analyzed. Results report a species list of 51 coelenterates, 260 molluscs, 250 decapod crustaceans, 15 stomatopod crustaceans, 9 Pycnogonida, and 95 Echinodermata to the generic rank and below; 26 Families of the Polychaeta are reported. Molluscs were found to be good potential indicators of seasonality and decapod crustaceans and echinoderms may be good indicators of substrate at certain depths. Faunal assemblages are stronger along contour gradients and species numbers decrease with depth. Each station appears to have a characteristic assemblage which probably relates to such factors as annual temperature and substrate. There is continuing evidence that the MAFLA macroepifauna has its greatest affinities with West Indian stocks.

INTRODUCTION

PURPOSE

The authority and rationale for the conduct of this study is spelled out in the BLM's contract document AA550-RP7-10. This contract document also delineates the sampling design, seasonal regimen, and levels of taxonomic analysis. The contractor (Dames & Moore) and subcontractor (University of Alabama, Birmingham) have not deviated in any significant way from the requirements stipulated by the BLM for the conduct of this study.

LITERATURE SURVEY

Fortunately for this study, the literature on benthic invertebrates of the eastern Gulf of Mexico has been very carefully reviewed by Collard and D'Asaro (1973) and an alternate interpretation composed by Lyons and Collard (1974). Work subsequent to the above will be discussed under "Previous Work" below. Taxonomic source papers are listed by taxa under "References" in this report.

For the purpose of setting a stage of understanding the BLM's contractual results from data collected during 1974-1976, and to set a stage for the basis of describing results, developing a discussion, and drawing conclusions, it is worthwhile to understand the conclusions reached by Collard and D'Asaro (1973) and Lyons and Collard (1974).

Collard and D'Asaro (op. cit.) review the major factors which affect the distribution and abundance of invertebrates and then use these data to synthesize summarial accounts of invertebrate communities illustrated by habitat diagrams. They are very careful to point out that at the time of their synthesis the eastern shelf had not been thoroughly studied and all syntheses may suffer from the inadequacy of sampling efforts, the antiquity of the taxonomic efforts along with improper reporting of ranges by previous reviewers. The authors propose the existence of three communities which would be expected to be found in the MAFLA tract covered by the BLM study rationale. These would be (a) Shallow Shelf Communities: Carolinian affinities whose depth range was generally stated to be 10 to 50 meters in depth, (b) Deep Shelf Communities: West Indian affinities in depth from 30 to 200 meters and (c) Slope Communities which are in depths greater than 130 meters. In considering each of these communities the authors recognized the importance of substrate, e.g., rock vs. sand and hard vs. mud, respectively.

Lyons and Collard (1974) re-evaluated the existing published data and used the unpublished observations from the Florida Department of Natural Resources "Hourglass Project" cruises to divide the MAFLA tract into (1) the "Mississippi-Alabama Shelf" to the west of Cape San Blas and (b) the "West Florida Shelf" to the east and south of Cape San Blas. Within the Mississippi-Alabama Shelf these authors indicate the paucity of good collecting data by the lack of comparative definition in their depth or habitat categories as compared to the West Florida Shelf where they delineate five (5) clear cut mean estimated depth zones which are in response to and may vary in response to geological and hydrographic factors. For the purposes of our information their "Middle Shelf I (30-60 m)," "Middle Shelf II

(30-60 m)," "Middle Shelf II (60-140 m)" and "Deep Shelf (140-200 m)" are categories which correspond to depth regimes examined in this contract and in previous BLM efforts.

PREVIOUS WORK

In the context of this report, "previous work" is defined as those articles or reports which were not reviewed by Collard and D'Asaro (1973) or Lyons and Collard (1974). Hopkins (1974a) calls attention to the tropical nature of the Florida Middle Ground with depths around 30-40 meters; this depth is in Collard and D'Asaro's "Shallow Shelf - Carolinian Affinity" zone and provides a supportive role for the Lyons and Collard discussion. Hopkins (1974b) reports on data collected at 30 stations in the MAFLA tract. These stations were in depth zones which correspond to Collard and D'Asaro's "Shallow Shelf - Carolinian Affinity" and Lyons and Collard "Middle Shelf I (30-60 m)" east of Cape San Blas and "Deeper Areas" west of Cape San Blas. The reporting approach emphasized (a) the division of the MAFLA tract into five (5) sectors, two (2) east and south of Cape San Blas and three (3) west of Cape San Blas, and (b) Biotope (substrate variability) in these sectors. Important results of this effort are (1) the discovery that there is a very rich and diverse fauna west of Cape San Blas, (2) there is a distinct paucity of macroepifaunal habitats in the western extremity of Lyons and Collard's Mississippi-Alabama Shelf Zone, and (3) there is a great deal of habitat (substrate variability) in four (4) of the five (5) sectors examined by diving and dredging. Hopkins (1976) reports on seasonal dredging and trawling at 18 stations (6 in each of the three depth zones "20, 50 and 100 fathoms") along with data from six (6) diving stations in the Florida Middle Ground. Based on the data collected and a limited faunal analysis it was suggetsed that a Middle Shelf I (30-60 m) epifaunal assemblage might be developed around 2 molluscs, 7 decapod crustaceans, 1 stomatopod crustacean, 1 octocoral, and 5 echinoderms. The Middle Shelf II (60-140 m) epifaunal assemblage was constructed around 2 molluscs, 3 decapod crustaceans, 1 octocoral, and 3 echinoderms. The deep shelf (140-200 m) epifaunal assemblage consisted of two molluscs and 6 decapod crustaceans. In addition, a special assemblage was created for the Florida Middle Ground area. This faunal assemblage was by far the strongest and most cohesive. It involved molluscs, decapod crustaceans, echinoderms, octocorallians, sponges, polychaete worms, and coelenterates. It should be noted in passing that this assemblage was not specifically designated by either Collard and D'Asaro (1973) or Lyons and Collard (1974). Its existence is further substantiated by Hopkins et al., 1977a, 1977b; Grimm and Hopkins, 1977; Shaw and Hopkins, 1977; Vittor and Johnson, 1977.

Returning to the results of the dredge/trawling efforts, whereas it is clear that there are a few animals which represent the designated depth zone for the two sectors, it must be realized that the numbers of species in each group are only a small percentage of the total species at that station. This in spite of the evidence from Bray-Curtiss analysis which most assuredly indicates that there are stronger links with depth than there was with either substrate or regional sector. In summary, a review of the data would suggest that if a pattern exists it was obscured by a paucity of consistent species occurrence at a given station. This work has also contributed to new range records and a better understanding of the habitat

diversity in the MAFLA sector (Shaw, Heard and Hopkins 1977; Williams, Shaw and Hopkins, 1977 and Appendix concerning "Works in Progress").

Cairns (1977a, 1977b) gives a new insight into the zoogeography and depth distribution of ahermatypic corals in the Gulf of Mexico and provides further support to the zoogeographic discussions of Hopkins et al, (1977a, b).

MATERIALS AND METHODS

INTRODUCTION

The biological materials used in this study were collected by diving, dredging and trawling in June-July 1976 and dredging and trawling during August-November 1977 and January-February 1978. Stations where materials were collected are displayed in Figure 230. Specifics on materials are discussed below.

MATERIALS

Taxonomic effort at the family level has been accomplished throughout for Coelenterata: Octocorallia; Coelenterata: Scleractinia; Annelida: Polychaeta; Mollusca; Crustacea: Decapoda, Stomatopoda; Pycnogonida: Echinodermata. In the vast majority of cases, however, identification was taken to the species level and verified through the use of the U.S.N.M. collections and recognized workers in selected fields.

We have archived whole samples of Porifera and Chordata: Tunicata because of the difficulty in proper preservation in the field and the state of the art in the taxonomy of these groups. Since polychaetes were most likely infaunal, they were carried to the family level only.

Field collections were rough sorted to group on board the collecting vessel and then depending on the group, amount of material, or contingencies they were in some cases anesthetized, frozen, preserved in alcohol or preserved in 5% formalin. Upon return to the laboratory, all materials were fine sorted, preservative changed, catalogued, and archived. Identification processing was aided by Wild M-5, M-5A, and M-20 microscopes. Literature which was used to a substantial degree in the course of this study is listed by taxonomic group under references.

METHODS

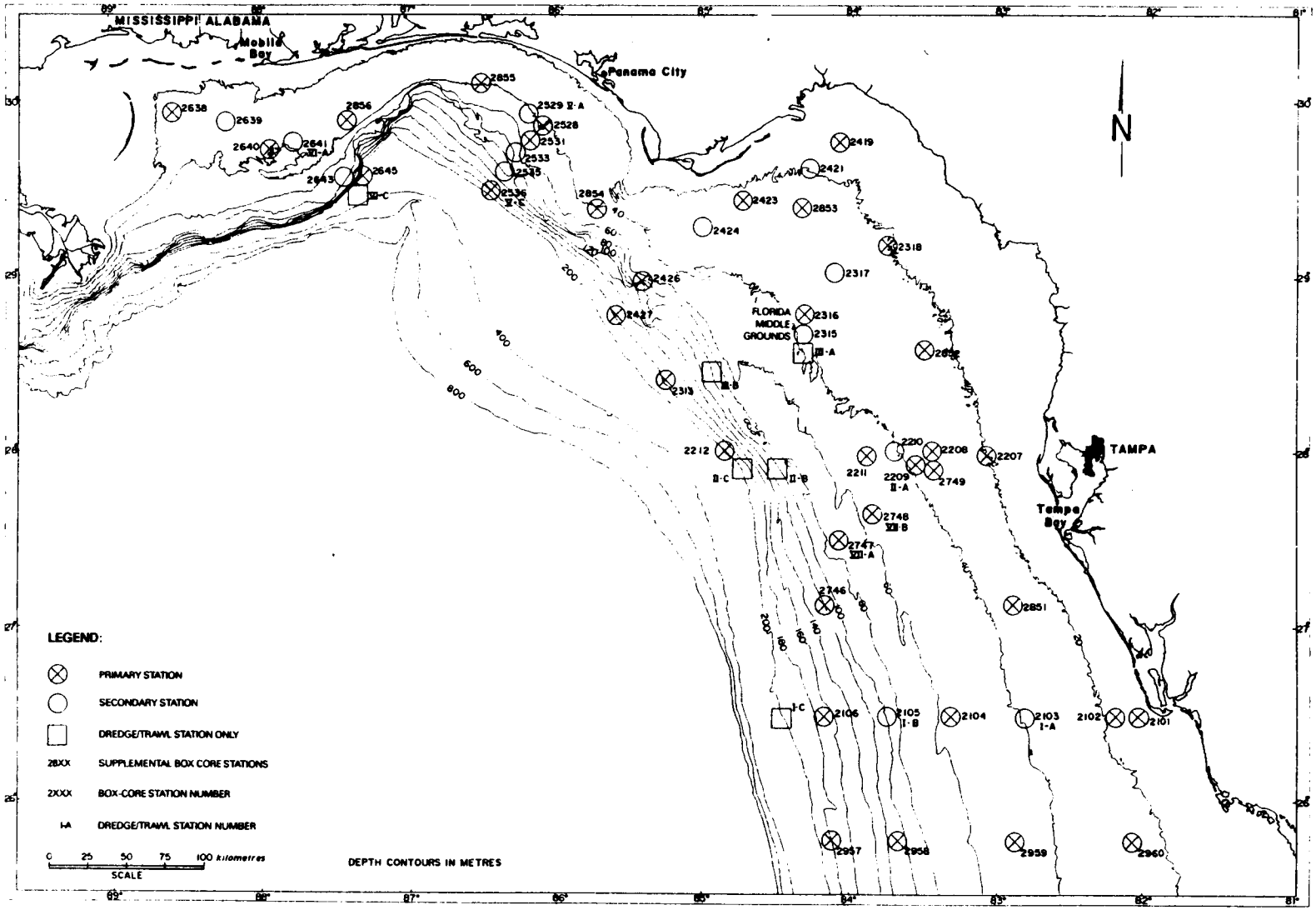
Diving

Macroepifauna was collected by divers using open-circuit SCUBA by hand and by hand net during the summer of 1976.

Trawling

Macroepifauna was collected by semi-balloon trawl during all four periods (summer 1976, summer 1977, fall 1977), and winter 1978). The specifics on trawling methods are covered elsewhere in this volume by Shipp

Figure 230



BLM 77/78 MAFLA SURVEY STATION LOCATIONS

(Chapter 19). As for trawl sorting, once the net was emptied onto a pre-cleaned sorting tray, (1.2 x 2.4 m) samples for chemistry and histopathology were removed first, followed by fish, and then macroepifauna which was rough sorted to group.

Dredging

Dredging was conducted through the use of a Capetown Dredge. I have not found a specific literature reference for this tool and consequently it is described hereunder. The shape is basically trapezoidal (Figure 231). The mouth has a pair of long blade-like slightly ellipsoid sides and a pair of shorter (33 cm) straight sides. The distance between the ellipses at their widest parts is 40.6 cm and the distance between the 33 cm sides is 96.5 cm. Because the ellipsoid sides become slightly flattened during use, the mouth could be approximated to be a rectangle of the dimensions 33 x 100 cm. The dredge is 121.9 cm deep and tapers to a rectangular end measuring 15.2 cm x 50.8 cm. The frame is constructed of angular steel and covered by expanded metal with a mesh size approximating 1 x 2 cm. The short sides were fitted with towing loops to which is shackled a 182.9 cm chain with a swivel placed at the tow point (91.5 cm from either side of the tow point to the towing loops).

The dredge was fitted with a basket with a rectangular mouth measuring 22.9 c 68.6 cm x 66.0 cm deep. The smaller rectangular end measures 11.4 cm x 49.5 cm. The basket is constructed of light weight angular iron and covered by 1.3 x 1.3 cm vinyl clad hardware cloth. The basket is removable.

The Capetown dredge is not a quantitative collecting device and due to the changing nature of substrates, towing speeds, towing time, current and wind sets it may not be a repetitive sampler. It is, however, an excellent survey tool for this kind of study. Its usefulness and ruggedness is heartily endorsed.

The dredge was usually towed with a 4:1 wire angle on parallel tracks passing by the Decca station buoy. On each tract the "start time" was equivalent to the time that the wire reached its ultimate allocated length and the "stop time" was that time marked when the winch began its first turn to wind the cable in.

On deck, the dredge was emptied onto the 1.2 x 2.4 m sorting tray and "picking the catch" proceeded as under trawling above. The Chief Scientist or biological watch leader made notes on substrate type and general dredge yield for each tow at each station.

Archived materials of interest to the U.S.N.M. will be transmitted by voucher invoice. All other materials will be deposited in the invertebrate repository at the Dauphin Island Sea Lab.

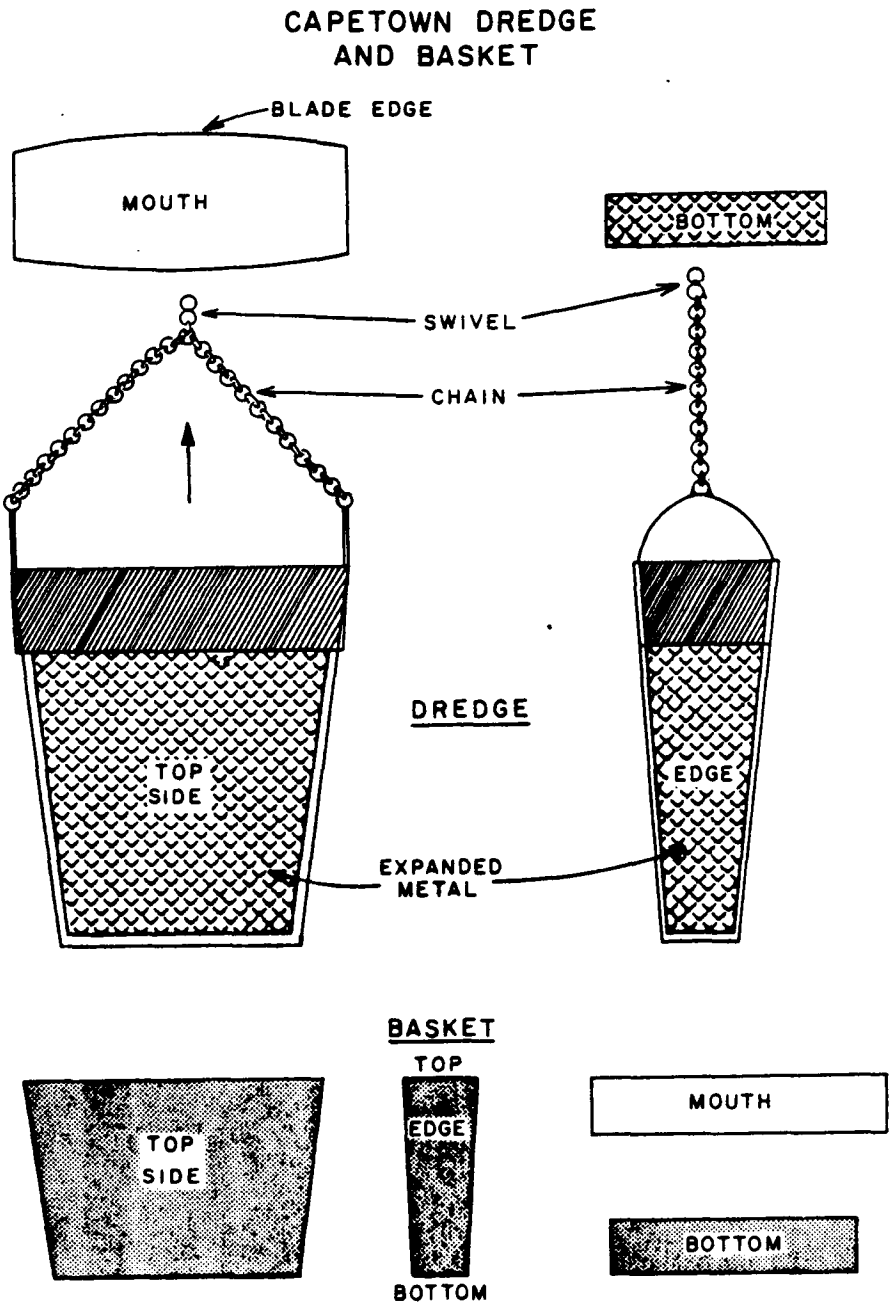

CAPETOWN DREDGE
AND BASKET
BLADE EDGE
MOUTH
BOTTOM
SWIVEL
CHAIN
DREDGE
TOP
SIDE
EDGE
EXPANDED
METAL
BASKET
TOP
TOP
SIDE
EDGE
MOUTH
BOTTOM
BOTTOM

FIGURE 231

RESULTS

OVERVIEW

The 1977-1978 Dames & Moore MAFLA epifaunal effort very closely parallels the stations occupation by this investigator during the 1975-1976 SUSIO effort. There are differences, however, which deal primarily with stations deleted (40 meters on transect IV; 100 meters on transect V; 200 meters on transect VI), or stations relocated (40 meters on transects II and III; 100 meters on transect VI) which were approved by the BLM. In addition, other major differences in the 1975-1976 program was the fact that numbers of individuals were not counted, the seasons were more distinct, and cruise tracks were less contiguous, not to mention, of course, that this investigator and his team were dredging into virtually univestigated habitats. We were very inexperienced with the diversity of macroepifauna and its perplexities. Nonetheless, we plowed new ground in elucidating species groups and depth assemblages. It was expected that we would not see many surprises in the 1977-1978 effort. Such has not been the case; we have encountered (a) species not recorded in the 1975-1976 effort, (b) range extensions, and (c) individuals new to science at both the species and generic level. Categories (a) and (b) are germane to virtually all the major groups we consider herein. In short, the results of this effort have greatly surpassed our expectations and we have an expanded knowledge of macroepifaunal form abundance and occurrence in the MAFLA tract.

COELENTERATES

We recorded 51 species of combined millepore, octocorals, and sclera-ctinian coelenterates. Most of the new additions are from the ahermatypic coral group and provide new range extensions of West Indian forms into the eastern Gulf. Notable range extensions are Madracis asperula, Oculina tenella, and Dendrophyllia cornucopia to the northern gulf, and Dasmosmilia lymoni and Asterosmilia prolifera to the middle gulf. Balanophyllia floridana and Paracyathus pulchellus were the most abundant ahermatypic corals in terms of number of individuals and frequency of occurrence (219 and 150 individuals; 18 and 11 stations occupied respectively). These two species are well distributed in the 60-200 meter range over the entire MAFLA tract.

Caryophyllia berteriana and C. horologium are interesting aherma-types in that both are limited to Transects I and II, but C. berteriana is also apparently limited along the 200 meter contour. This pattern was generally observed in the 1975-1976 effort.

POLYCHAETA

We recorded representatives of 26 families of the class Polychaeta (Annelida). Since they were worked only to the family level, we can conclude little. The families Amphinomidae, Eunicidae, Nereidae, Polynoidae, Sabellidae, Serpulidae, and Terebellidae were the most ubiquitous in terms of total stations and depth ranges. In contrast, the families Arabellidae, Capitellidae, Glyceridae, Lumbrinereidae, Maldanidae, and Ophelidae showed

the most restricted abundance and depth range (generally along the 40 meter contour) (see Vitter, this volume, Chapter 10).

MOLLUSCA

Molluscs are a very excellent group of macroepifauna to work with because of their relative stability taxonomically and ease with which they can be handled. The 1977-1978 effort produced the following additional records: 4 families, 15 genera, 7 subgenera, and 49 species. This amounts to about 260 molluscs beyond the generic rank.

Table 81 displays abundance data which should be useful in any future monitoring effort.

Table 82 displays some very interesting data on seasonality. In can be seen that the number of individuals decreases both with depth and season, as does the mean number of species/station.

DECAPOD CRUSTACEA

The Decapod Crustacea are another area where we have added significant knowledge to occurrence and abundance of maroepifauna in the food chain.

Within the Natantia (swimming forms) we have recorded a gain of 22 families, 14 genera, and 39 species; we did not encounter 2 species of Lysmata that we expected to find. The most ubiquitous shrimps were the penaeids: Mesopenaeus tropicalis, Parapenaeus longirostris, Sicyonia brevi rostris, Solenocera atlantidis, and Synalpheus townsendi.

Within the Reptantia-Macrura (crawling forms) we have added 1 family, 1 genus and 3 species. Among the Anomura, however, we have again made significant gains by elucidating new range records for galatheid and hermit crabs (5+ hermits and 12 galatheids). Turning to the Brachyura we are able to report 12 additional members of the Majidae (spider crabs) and 25 additional specis from other brachyurous families. Of noteworthy consequence is the discovery that there may well be two species of Stenorhynchus which is one of the most ubiquitous of the Brachyura. This taxa was used extensively for histopathology.

In summation our Decapod Crustacea now total about 250 identifiable species from dredging and trawling compared to 134 in 1975-1976. (That is a net gain of 100+!).

STOMATOPODA

As in the case of the Decapod Crustacea, we have had significant gains with this order of crustaceans. Of the 15 species I report from this effort, the data represents a gain of two families, 7 genera, and 9 species. We failed to collect only 1 species encountered in the 1975-1976 program. Much of the stomatopod data is new to science; among carcinologists this is astounding.

TABLE 81

CHARACTERISTIC MACROEPIFAUNAL MOLLUSCS

SPECIES	STATIONS	INDIVIDUALS
Loligo pealeii	52	1188
Doryteuthis pleii	30	431
Murex cabritii	30	67
Laevicardium pictum	29	102
Xenophora conchyliophora	28	83
Chlamys benedicti	25	83
Octopus vulgaris	24	41
Vermicularia spirata	23	799
Turritella exoleta	23	101
Dentalium lagueatum	21	70
Aequipecten muscosus	21	57
Amygdalum papyria	21	64
Turritella actopora	20	46
Murex beauii	19	78
Hiatella arctica	18	51
Nemocardium tinctum	18	51
Murex florifer dilectus	17	32
Pecten ravebeku	14	39
Crepidula plana	14	60
Plicatula gibbosa	13	72
Barbatia candida	13	102
Tugurium caribaeum	13	57
Vermicularia knorrii	13	309
Argopecten gibbus	12	312
Chama macerophylla	11	45

Molluscan species which occurred in any form at >10 stations with >25 individuals.

TABLE 82

MOLLUSCAN SEASONALITY

SEASON	~$\bar{X}$ DEPTH (m)	TOTAL INDIVIDUALS	$\bar{X}$ NO. SPECIES/ STATION	$\bar{X}$ NO. IND./ SPECIES/STATION
Summer 1977	40	1,272	34	37[a]
	100	496	25	19
	200	349	8	43[a]
Total	-	2,134		
Fall 1977	40	586	26	22[b]
	100	288	17	16
	200	50	3	17
Total	-	924		
Winter 1978	40	409	24	17
	100	140	12	17
	200	92	4	23
Total	-	641		

[a]Shows influence of Loligo pealeii at 2209 and 2313 and II-C.

[b]Shows influence of Dortheuthis pleii at 2641.

PYCNOGONIDA

We did not treat the Pcynogonida (Sea Spiders) in the 1975-1976 effort; however, we have concluded that they may have several representatives which are indicator species of faunal assemblages. This effort yields 5 families, 7 genera and 9 species; two species are new to science.

ECHINODERMATA

The echinoderms are perhaps the least taxonomically well established of the faunal groups considered. Experts in the field *per se* have specific interests and are few and far between; the literature is antiquated for several classes (Ophiaroidea; Holothuroidea). We have made significant gains in this area, however, in virtually all classes and we should be able to recognize about 95 echinoderms at the species level in the MAFLA tract. This is up from the 61 recorded in the 1975-1976 data. Gains were made in four of the five classes; however, gains in the Ophiuroidea and Holothuroidea may not be truly macroepifaunal gains.

The echinoderms may be the single best substrate and depth contour indicator group as they reveal some very interesting specific replacement patterns. They are probably not good indicators of seasonality, however, *Clypeaster* sp. could be used as a good growth indicator at a station by year class.

DISCUSSION

THE BACKGROUND

As indicated in the introduction, the state of our conceptual thoughts on macroepifaunal communities in the MAFLA trait is based on (a) synthetic reviews, and (b) collections/reports from two (2) previous BLM MAFLA efforts. The salient features of those reviews, collections, and reports can be summarized by these elements which will be discussed subsequent to their alphabetical listing.

A. Faunal assemblages exist in the eastern Gulf and are associated with depth contours; this situation may not hold true in the north central Gulf (Lyons and Collard, 1974). These faunal assemblages may vary with substrate in a given depth zone (Collard and D'Asaro, 1973; Hopkins, 1974b). Faunal assemblages may be grouped along depth contours with greater affinity than by substrate or geographic locale (Hopkins, 1976).

B. The macroepifauna of the eastern Gulf of Mexico have a large number of members with an affinity to the Caribbean Sea (Collard and D'Asaro, 1973; Hopkins, 1974a, Hopkins et al., 1977a, 1977b).

FAUNAL ASSEMBLAGES

We have taken two approaches to the analysis of faunal assemblages. Although both approaches use cluster analyses, one approach (Jaccard) uses only presence/absence; however, the other Sorenson/Bray-Curtis uses abundance

data. The fauna selected for input met one or more of these criteria: (a) they were always abundant at a given station (individual station persistence) or (b) they were present at 10 or more stations one or more of four sampling efforts. Faunal assemblages as I presently view them are shown in Tables 83 to 85.

The Jaccard approach very clearly groups stations along depth contours of 30-60 meters, 60-120 meters, and 120-200 meters not unlike the suggestion of Lyons and Collard (1974). It goes further, however, and refines this picture by extending these assemblages to the Mississippi-Alabama shelf. These data support the preliminary findings of Hopkins (1976) and lay to rest any caveat expressed about that region by Lyons and Collard (1974).

The Sorenson/Bray-Curtis approach very closely follows the Jaccard results with the exception that the one station (2747) lying in the 60-80 meter interval falls into the 30-60 meter grouping. I am not sure of the significance of this event other than to flag the idea that transitional or ecotone stations do exist in the MAFLA tract. We have not, heretofore, acknowledged the advent of this possibility.

Within the faunal assemblages we must recognize the effect of substrate at each contour interval. The Florida Middle Ground is a documented example in the 30-60 meter zone but less dramatic examples can be seen (a) at a given station at the same depth and (b) at two distant stations in the same contour interval. Stations 2103 and 2209/2749 are good examples of (a). From the standpoint of dredge and trawls tows, there are entirely different substrates/macroepifaunal communities (BIOTOPES, Hopkins, 1974b) existing over very short distances (0.5 kilometer) with no ecotone. Examples are coarse sand/shell rubble/sponge associations giving away suddenly to less coarse sand/no shell rubble/no sponges such as we find at 2103 or the situation at 2209/2749 where intermittent hard bottom/shell rubble gives away very suddenly to fine sand. In the case of (b) a comparison of I-C with 2313, 2427 and 2536 is in order and echinoderms show the relationship to substrate differences. I-C and II-C seem to have very firm bottoms as compared to 2313, 2427 and 2536. Not only that, they have some different characteristic fauna for which substrate is the best explanation. Araesoma biolaceum is a "collapsible test" echinoid and lives on firm substrates in the Caribbean; Brissopsis elongata and Schizaster orbignyonus are "heart urchins" and can be considered to be burrowers in soft fines. Dredge collected materials support this observation (Table 85).

Another observation about the effect of substrata is found along the 100 meter contour. Since not all the stations we dredged (II-B, III-B, and V-B) were box-cored at the same locality, we cannot use empirical data. Nonetheless, observations of the amount, size, and extent of either algae-cemented modules or fragment rock lead us to believe that there is a significant difference in the hard bottom generally along this contour. A dramatic example is a comparison of 2105 with III-B; suffice to say their substrates are different and their echinoderm faunas are remarkably distinct.

TABLE 83

30 TO 60 METRE CONTOUR REPRESENTATIVE MACROEPIFAUNA

Transect:	I-A	VII-A	VII-B	II-A	III-A	V-A	VI-A
Molluscs							
Vermicularia knorrii	P	P	P	P	P	P	
Vermicularia spirata	P	C		P		C	P
Modulus modulus		P	P	P	P		
Xenophora conchyliophora	P	P	P	P	P		
Murex cabritii	P	P		C	P	P	
Chlamys benedicti	C	P	C	P	P	P	
Pecten ravenelli	P		P	P	C	P	
Acquipecten muscosus		P	C	P	P	P	P
Argopecten gibbus	P		P	C	P	P	P
Laevicardium pictum	P	P	C	C	P	P	P
Octopus vulgaris	P	P	P	P	P	P	
Pycnogonida							
Anoplodactylus lentus		P	P	P		P	P
Decapod Crustacea							
Metapenaeopsis goodei	P	P	C	P	C	P	
Sicyonia brevirostris	P	P	C	C	P	C	C
Solenocera atlantidis	P	P	C	C	P	P	P
Alpheus normanni	P	P	P		C	P	
SynalAheus townsendi	C	P	P	P	P	P	P
Scyllarus chacei	P	P	C	P	P	C	P
Pylopagurus coralinus	P	C	C	P	P	C	P
Pachycheles rugimanus	C	P	P	P	P	P	
Dromidia antillensis	C	P	C	P	P	P	
Stenocionops furcata	P	P	P	P	P	P	
Parthenope fraterculus			P	P	P	C	P
Portunus spinicarpus	P	C	P	P	P	P	C
Portunus spinimanus	P	P	C	P	P	P	P
Carpoporus papulosus		P	P	P	P	P	
Palicus alternata	P	P	C	P	P	C	P
Echinoderms							
Luidia alternata	P		P	P	P	C	P
Luidia clathrata	P	P	P	C	P	C	C
Astropectan duplicatus	P		C	C	P		P
Goniaster tesselatus		P	C		P	P	P
Ophiolepis elegans	P		C	P	P	C	C
Ophiothrix angulata	C	P	C		C	P	
Eucidaris tribuloides	P		C	P	C	C	P
Arbacia punctulata	C		P	P	P	P	P
Lytechinus variegatus	P		C	P	C	P	P

P = present only

C = occurring during most sampling periods in abundances greater than rare for that species

TABLE 84

90 TO 110 METRE CONTOUR REPRESENTATIVE MACROEPIFAUNA

TRANSECT	I	II	III	IV	VI
COELENTERATES					
Bebryce grandis	P	P	C	P	P
Paracyathus pulchellus		C	P	P	C
Balanophyllia floridana		P	P	C	P
MOLLUSCS					
Loligo pealeii	P	P	P	P	P
DECAPOD CRUSTACEA					
Mesopenaeus tropicalis	P	P	P	P	C
Synalpheus townsendi	C	P	P	P	
Dromidia antillensis	C	P	P	P	
Calappa angusta	P	P		P	P
Iliacantha subglobosa	C	P	P	P	
Portunus spinicarpus	C	C	C	C	P
ECHINODERMS					
Luidia elegans		P	P	P	P
Anthenoides piercei		P	P	P	P
Astroporpa annulata	P	P	C	P	P
Stylocidaris affinis		P	P	P	C
Clypeaster ravenelli		P	P	C	P
Comactinia meridionalis	C				P

P = present only
C = occurring during most sampling periods in abundances greater than rare for that species

TABLE 85

180 TO 200 METRE CONTOUR REPRESENTATIVE MACROEPIFAUNA

	TRANSECT				
	I	II	III	IV	V
COELENTERATES					
Caryophyllia berteriana	C	P			
Flabellum fragile		C	P		
Balanophyllia floridana		C	C		
MOLLUSCS					
Turgurium caribaeum	C	P	P	P	P
Murex beauii	C	C	C	P	P
Aequipecten glyptus	P	P	P	P	C
Loligo pealeii	P	C	C	P	C
DECAPOD CRUSTACEA					
Parapenaeus longirostris	P	P	P	C	C
Calappa angusta	C				
Acanthocarpus alexandri		P	C	P	C
Myropsis quinquespinosa	P	C	P	C	P
Pyromaia arachna	P	P	P	P	P
Portunus spinicarpus	P	P	C	P	P
Goneplax hirsuta	P	C	P	P	P
STOMATOPOD CRUSTACEA					
Squilla heptacantha	P	P	P	P	
ECHINODERMS					
Astropecten cingulatus	C	P	P	P	P
Pectinaster mixtus	C				
Ophiura acervata	P				
Araeosoma violaceum	C				

P = present only
C = occurring during most sampling periods in abundances greater than rare for that species

ZOOGEOGRAPHY

I do not wish to delve into serious discussion about the origins, continued recruitment, or developing endemism in the eastern Gulf of Mexico. Hopkins et al. (1977b) and Cairns (1977a, b) are already providing satisfactory evidence that this may be the case regardless of the contour interval. What I do wish to point out is that (a) the newly collected specimens indicate a far greater number of undescribed examples than we previously thought, and (b) the newly collected specimens are giving us new collecting and range records for species whose origins are strictly Caribbean. I have also wondered about the diversity and tropicality of the fauna of the Panama City embayment (Station 2528/2529). Data from 1974 onward reveal that this area has a rich macroepifaunal assemblage; bottom studies indicate diverse substrates (hard bottom outcrops, shell rubble/coarse sand, and areas of almost pure shell rubble). With substrates of this kind available, it remains only for the intrusion of warm "Loop Current" waters to frequent the area, and bring in invertebrate larvae for colonization. Such seems to be the case for it is far more diverse and contiguous with the Florida Shelf than Lyons and Collard (1974) had speculated. The amount of spillover to the western side of the De Soto Canyon is large in the 30-60 meter zone, but greater at the 60-100 meter zone.

CONCLUSIONS

1. Comparison of the archived 1976 (Summer), and the recently collected 1977 (Summer, Fall) and 1978 (Winter) species lists to the list compiled for 1974 (Summer), 1975 (Summer, Fall) and 1976 (Winter) effort leads to the conclusion that we may not yet have a good understanding of the true nature of macroepifaunal distribution. Certainly, it is better now than it has ever been.

2. Using presence and abundance data is very important in determining (a) seasonality, and (b) macroepifaunal assemblages associated with substrate or depth contour.

3. Molluscs in particular may be good indicators of seasonality; Decapod Crustacea and Echinoderms may be good indicators of substrate; Ahermatypic Corals, Molluscs, Pycnogonids, Decapod and Stomatopod Crustacea, and Echinoderms are all good taxa for contouring faunal assemblages.

4. Faunal assemblages are stronger along contour gradients (40, 100 and 200 meter) than they are between gradients (40 vs. 100 meter). It must be noted, however, that specific studies of intergrade contour stations (45-50 and 65-70 meters) show shifting affinities depending on the analytical approach used.

5. Each station does have a faunal assemblage reasonably characteristic of the station and the assemblage probably relates to obvious physical factors such as substrate and annual temperature variation on the bottom. Its continuity will depend on water masses which probably originate in the Caribbean Sea.

REFERENCES

GENERAL/INTRODUCTORY

Cairns, S. D., 1977a. Stony corals. I. Caryophyllinia and Dendrophyllina (Anthozoa: Scleractinia). Memoirs of the Hourglass Cruises 3(4), 29 pp., 2 pls.

Cairns, S. D., 1977b. A checklist of the Ahermatypic Scleractinia of the Gulf of Mexico, with the Description of a New Species. Gulf Res. Rpts., 6(1), 9-15, 1 pl.

Collard, S. B. and C. N. D'Asaro, 1973. Benthic invertebrates of the eastern Gulf of Mexico. Pp. III G 1-27 in J. I. Jones et al. eds., A Summary of Knowledge of the eastern Gulf of Mexico. State Univ. at Fla. Inst. of Ocean., St. Petersburg, Fla.

Grimm, D. E. and T. S. Hopkins, 1977. Preliminary characteriztion of the Octocorallian and Scleractinian diversity at the Florida Middle Ground. Proc. Third Intl. Coral Reef Symp., Vol. 1, 135-141. Miami, Fla.

Hopkins, T. S., 1974a. Observation of the Florida Middle Ground through the use of open circuit SCUBA. pp. 227-228 in R. E. Smith, Ed. of Marine Environmental Implications of Offshore Drilling in the Eastern Gulf of Mexico. State Univ. of Fla. Inst. of Ocean., St. Petersburg, Fla.

Hopkins, T. S., 1974b. Final Report; "In situ and dredging studies on epifauna and flora at 30 stations in the MAFLA area of eastern Gulf of Mexico," Contract No. 08550-Ct4-11, Bureau of Land Management, Department of the Interior.

Hopkins, T. S., 1976. Final Report: "Epifaunal and Epifloral Benthic Communities in the MAFLA year 02 lease area," Contract No. 08550-Ct5-30, Bureau of Land Management, Department of the Interior.

Hopkins, T. S., D. R. Blizzard, S. A. Brawley, S. A. Earle, D. E. Grimm, D. K. Gilbert, P. E. Johnson, E. H. Livingston, C. H. Lutz, J. K. Shaw, and B. B. Shaw, 1977A. Proc. Third Intl. Coral Reef Symp., Vol. 1, 31-37. Miami, Fla.

Hopkins, T.S., D. R. Blizzard, and D. K. Gilbert, 1977B. The molluscan fauna of the Florida Middlegrounds with comments on its zoogeographical affinities. N.E. Gulf Sci., 1(1), 39-47.

Lyons, W. G. and S. B. Collard, 1974. Benthic invertebrate communities of the eastern Gulf of Mexico. pp. 157-165. In R. E. Smith, Ed., Proc. Marine Environmental Implications of Offshore Drilling in the Eastern Gulf of Mexico. State Univ. of Fla. Inst. of Ocean., St. Petersburg, Fla.

Shaw, J. K. and T. S. Hopkins, 1977. The distribution of the family Hapalocarinidae (Decapoda, Brachyura) on the Florida Middle Grounds with a description of Pseudocryptochirus hypostequs new species. Proc. Third Intl. Coral Reef Symp., Vol. 1, 177-183. Miami, Fla.

Shaw, J. K., R. W. Heard, Jr. and T. S. Hopkins, 1977. Notes on the biology of the Pontoniine shrimp, Lipkebe holthuisi Chace, with a description of the male. Proc. Biol. Soc. Wash., 90(2), 284-290.

Vittor, B. A. and P. G. Johnson, 1977. Polychaete abundance, diversity and trophic role in coral reef communities at Grand Bahama Island and the Florida Middle Ground. Proc. Third Intl. Coral Reef Symp., Vol. 1, 163-168. Miami, Fla.

Williams, A. B., J. K. Shaw, and T. S. Hopkins, 1977. Stilbomastax, a new genus spider crab (Majidae: Tychinae) from the West Indies region with notes on American relatives. Proc. Biol. Soc. Wash., 90(4) 884-893.

COELENTERATES

Almy, C. C., Jr. and C. Carriors-Torres, 1963. Shallow-water stony corals of Puerto Rico. Caribbean J. Sci. 3:133-162.

Bayer, F. M., 1961. The shallow-water octocorallia of the West Indian region. Martinus Nijhoff Publisher. 373 pp., 27 pls.

Cairns, S. D., 1977a. Stony corals. I. Cayophyllinia and Dendrophyllina (Anthozoa: Scleractinia). Memoirs of the Hourglass Cruises 3(4), 29 pp., 2 pls.

Cairns, S. D., 1977b. A checklist of the Ahermatypic Scleractinia of the Gulf of Mexico, with the Description of a New Species. Gulf Res. Rpts., 6(1), 9-15, 1 pl.

Cairns, S. D., 1977c. Guide to the commoner shallow-water gorgonians of Florida, The Gulf of Mexico, and the Caribbean Region. Univ. of Miami Sea Grant Field Series #6. 74 pp.

Cairns, S. D., 1977d. A review of the recent species of Balanophyllia (Anthozoa: Scleractinia) in the western Atlantic, with descriptions of four new species. Proc. Biol. Soc. Wash. 90(1):132-148.

Deichmann, E., 1936. The Alcyonaria of the Western part of the Atlantic Ocean. Men. Mus. Comp. Zool. LIII:1-317.

Deichmann, E. and F. M. Bayer, 1959. The lemon-colored plexaurids from the West Indies and Brazil. Breviora 115:1-12,5 pls.

Kinzie, R. III, 1970. The ecology of the gorgonians (Cnidaria, Octocorallia) Ph.D. Yale Univ. 107 pp.

Lang, J. 1970. Interspecific aggression within the scleractinian reef corals. Ph.D. Yale Univ. 80 pp.

Pourtales, L. F. de, 1971. Deep-sea corals. Illustrated catalogue of the Mus. Comp. Zool. 1-93.

Rannefeld, J. W., 1972. The stony corals of Enmedia reef off Veracruz, Mexico. Ms. Thesis Texas A & M Univ. 103 pp.

Roos, P. J., 1964. The distribution of reef corals in Curacao. Studies on the Curacao and other Caribbean Islands: No. 81:51.

Smith, F. G., 1972. Atlantic reef corals. Univ. of Miami Press. 164 pp.

Squires, D. F., 1958. Stony corals from the vicinity of Bimini, Bahamas, British West Indies. Bull. Amer. Mus. Nat. Hist. 115 (4):221-262. 42 pls.

Vaughan, T. W., 1900. The stony corals of the Puerto Rican waters. Bull. U.S. Fish. Comm. 2:291-320, 38 pls.

Vaughan, T. W., and J. W. Wells, 1943. Revision of the suborders, families and genera of the Scleractinia. Geol. Soc. of America Special Papers 44:1-363.

Wells, J. W., 1972. Some shallow water ahermatypic corals from Bermuda. Postilla 156:1-9.

CRUSTACEA

GALATHEIDAE

Benedict, J. E., 1902. Descriptions of a new genus and forty-six new species of crustaceans of the family Galatheidae with a list of the known Marine species. Proc. U. S. Nat. Mus. 26(1311):243-334.

Chace, F. A., Jr., 1942. Reports on the scientific results of the Atlantis expeditions to the West Indies, under the joint auspices of the University of Havana and Harvard University. The Anomuran Crustacea I. Galatheidea. Torreia 11:1-106.

Pequegnat, W. E. and L. H. Pequegnat, 1970. Deep-sea anomurans of superfamily Galatheoidea with descriptions of two new species. Cont. on the Biology of the Gulf of Mexico. 1:125-170.

Tirmizi, N. M., 1966. Crustacea: Galatheidae Sci. Reports. John Murray Expeditions 11(2):169-234. Figs. 1-40.

PAGURIDAE & DIOGENIDAE

Benedict, J. E., 1900. The anomuran collections made by the Fish Hawk Expedition to Puerto Rico Bull. U. S. Fish Comm. 20(2):129-148.

Biffar, T. A. and A. J. Provenzano, Jr., 1972. A reexamination of Dardanus venosus and D. imperator with a description of a new species of Dardanus from the western Atlantic. Bull. Mar. Sci. 22(4):777-805.

Biffar, T. A. and A. J. Provenzano, Jr., 1972. A reexamination of Dardanus venosus and D. imperator with a description of a new species of Dardanus from the western Atlantic. Bull. Mar. Sci. 22(4):777-805.

Forest, J. and M. de Saint Laurent, 1961. Campagne de la "Calypso" au large des cotes atlantiques de l'Amerique due Sud (1961-1962). I. 6. Crust. Decapodes:Paguereides. Ann. Inst. Ocean. 45(2):49-169, 1 pl.

Hart, J. F. L., 1971. New distribution records of reptant decapod crustacea, including description of three new species of Pagurus, from the waters adjacent to British Columba. J. Fish. Res. Bd. Canada 28:1527-1544.

Holthuis, L. B., 1959. The crustacea decapoda of Suriname. Zool. Verh 44:130-162.

McLaughlin, P. A., 1974. The hermit crabs (Crustacea Decapoda, Paguridae) of Northwestern North America. Zoologische Verhandelingess #130.

McLaughlin, P. A., 1975. On the identy of Pagurus brevidactylus with the description of a new species of Pagurus from the Western Atlantic. Bull. Mar. Sci. 25(3):359-376.

McLaughlin, P. A. and A. J. Provenzano, 1974. Hermit crabs of the genus Paguristes from the Western Atlantic. Pt. I. The Paguristes tortugae complex with notes on variation. Bull. Mar. Sci. 24(1):156-234.

McLaughlin, P. A. and A. J. Provenzano, 1974. Hermit crabs of the genus Paguristes from the Western Atlantic. Pt. II. Descriptions of six new species. Bull. Mar. Sci. 24(4):885-938.

Provenzano, A. J., Jr. 1961. Pagurid crabs (Decapoda Anomura) from St. John, Virgin Islands, with descriptions of three new species. Crustaceana 3(2):151-166.

Provenzano, A. J., Jr. 1965. Two new West Indian hermit crabs of the genus Paguristes. Bull. M ar. Sci. 15(3): 726-736.

Provenzano, A. J., Jr. 1959. The shallow-water hermit crabs of Florida. Bull. Mar. Science Gulf and Carib. 9(4): 349-420.

Wass, M. L., 1963. New species of hermit crabs (Decapoda, Paguridae) from the Western Atlantic. Crust. 6:133-157.

Williams, A. B., 1965. Marine Decapod crustaceans of the Carolinas. Fish. Bull. 65(1):1-298.

SHRIMPS

Able, L. C., 1971. A new species of Periclimenaeus Borradaile, 1915 (Crustacea Decapoda: Palaemonidae) from the northeastern Gulf of Mexico. Tulane Studies Zool. and Botany 17(2):38-40.

Biffar, T. A., 1971. The genus Callianassa (Crustacea: Decapoda: Thalassinidea) in South Florida, with keys to the Western Atlantic Species. Bull. Mar. Sci. 21(3):637-715.

Bouvier, El L., 1925. Les Macrouces Marcheurs. Part XLVII. Memoirs Mus. Comp. Zool. Harvard 47(5):397-472, 11 pls.

Burkenroad, M. D., 1934. Littoral Penaeidae chiefly from Bingham Oceanographic collection: with a revision of Penaeopsis and descriptions of two new genera and eleven new American species. Bull. Bingham Ocean. Collection 4(7):1-109.

Burkenroad, M. D., 1945. Status of th name Sicyonia with a note on Sicyonia typica and descriptions of two new species. Arkiv. for Zoologi. 37(9):1-10.

Chase, F. A., 1969. A new genus and five new species of shrimps (Decapoda, Palaemonidae, Pontoniinae) from the western Atlantic. Crustaceana 16(3):251-272.

Chase, F. A., 1970. A new shrimp of the genus Lysmata (Decapoda: Hippolytidae) from the western Atlantic. Crustaceana 19(1):59-66.

Chase, F. A., 1972. The shrimps of the Smithsonian-Bredin Caribbean Expedition with a summary of the West Indian shallow-water species (Crustacea: Decapoda: Natantia). Smithsonian Cont. Zool. 98:1-179.

Chase, F. A., Jr., 1976. Shrimps of the Pasiphaeid genus Leptochela with descriptions of three new species. Smith. Cont. Zool. 222:1-51.

Chase, F. A., and S. L. H. Fuller, 1971. A new shrimp of the genus Gnathophyllum (Decapoda: Caridea) from Puerto Rico. Proc. Biol. Soc. Wash. 83(44):493-504.

Cobb, S. P., 1971. A new species of Sicyonia (Decapoda: Penaeidae) from the western Atlantic with notes on S. stimpsoni Bouvier. Crust. 22: 104-112.

Coutiere, H., 1899. Sur Guelgues Alpheidae des cotes Americaines. Ann. Des. Sci. Nat. 9:356-358.

Gurney, R., 1943. Notes on Periclimenes americanus and the growth of the cheliped in this and other Palaemonid prawn. Ann. Mag. Nat. Hist. Ger. II, X:495-504.

Holthuis, L. B., 1946. The decapoda macrura of the Snellius Expedition. I. The Stenopodidae, Nephropsidae, Scyllaridae and Palinuridae. Temminckia VII:1-178, 10 pls.

Holthuis, L. B., 1951. A general revision of the Palaemonidae (Crustacea: Decapoda: Natantia) of the Americas. I. The subfamilies Urythynchinae and Pontoniinae. Allan Hancock Found. Occ. Papers. 11:1-332.

Holthuis, L. B., 1952. A general revision of the Palaemonidae (Crustacea: Decapoda: Natantia) of the Americas. II. The subfamily Palaemoninae. Allan Hancock Found. Occ. Papers. 12:1-396.

Holthuis, L. B., 1955. The recent genera of caridean and stenopodidea shrimps (Class Crustacea, Order Decapoda, Supersection Natantia) with keys for their determination. Zool. Verh. 26: 1-157.

Holthuis, L. B. and J. Eibi-Eibesfeldt, 1964. A new species of the genus Periclemenes from Bermuda. (Crustacea: Decapoda: Palaemonidae). Sends. Biol. 45(2):185-192.

Lunz, G. R., Jr., 1945. Carolina shrimps of the genus Eusicyonia. The Charleston Museum Leaflet #20.

Manning, R. B., 1963. The east American species of Gnathophyllum (Decapoda: Caridea), with the descripton of a new species. Crust. 5(1):47-63

Manning, R. B. and F. A. Chace, 1971. Shrimps of the family Processidae (Crustacea: Decapoda: Caridea) from the northwestern Atlantic. Smithsonian Cont. Zool. 89:1-41.

Milne-Edwards, A. and E. L. Bouvier, 1909. Les Peneides et Stenopides. Part XLIV. Mem. Mus. Comp. Zool. at Harvard College. 27(3):177-274, 9 pls.

Perez Farfante, I., 1967. A new species and two new subspecies of shrimp of the genus Penaeus from the western Atlantic. Proc. Biol. Soc. Wash. 80:83-99.

Perez Farfante, I., 1969. Western Atlantic shrimps of the genus Penaeus. Fish Bull. Fish Wildlife Service 67(3):461-591.

Perez Farfante, I., 1971. Western Atlantic shrimps of the genus Metapenaeipsis, with descriptions of three new species (Crustacea: Decapoda: Penaeidae). Smithsonian Coutr. Zool. 79:1-37.

Perez Farfante, I., 1977. American Solenocerid shrimps of the genera Hymenopenaeus, Haliporoides, Pleoticus, Madrepenaeus new genus, and Mesopenaeus new genus. Fish. Bull. 75(2):261-346.

Perez Farfante, I. and H. R. Bullis, Jr., 1973. Western Atlantic shrimps of the genus Solenocera with description of a new species (Crustacea: Decapoda: Penaeidae). Smith. Cont. Zool. 153:1-33.

Schmitt, W. L., 1935. Crustacea Macrura and Anomura of Puerto Rico and the Virgin Islands. pp. 125-227, 255-262; 80 figs. New York: New York Academy of Sciences.

Squires, H. J., 1977. A new species of Axiopsis (Axiopsis) (Thalassinidae, Axiidae) from the Columbia. Can. J. Zool. 55(11):1885-1891.

Williams, A. B., 1965. A new genus and species of snapping shrimp (Decapoda: Alpheidae) from the southeastern United States. Crustaceans 9(2): 192-198.

Williams, A. B., 1965. Marine decapod crustaceans of the Carolinas. Fish Bull. 65(1):1-298.

BRACHYURA AND MISCELLANEOUS

Guinot, D., 1958. Sur une collection de Decopodes Brachyoures de l'ile Mayotte. II. Xanthidae. Bul. Mus. Nat. Hist. 30:84-93, 175-183, 276-284.

Guinot, D., 1966. Recherches preliminaries sur les groupments naturels chez les crustaces Decapodes Brachyoures. Bull. Mus. Nat. Hist. 38:744-762, 828-845.

Guinot, D., 1967. Recherches preliminaries sur les groupments naturels chez les crustaces Decapodes Brachyoures. Bull. Mus. Nat. Hist. 39:345-374, 540-563, 695-727.

Guinot, D., 1968. Recherches preliminaries sur les groupments naturels chez les crustaces Decapodes Brachyoures. Bull. Mus. Nat. Hist. 40:149-166, 320-334.

Guinot, D., 1969. Recherches preliminaries sur les groupments naturels chez les crustaces Decapodes Brachyoures. Bull. Mus. Nat. Hist. 41:241-265, 507-528, 688-724.

Guinot, D., 1969. Recherches preliminaries sur les groupments naturels chez les crustaces Decapodes Brachyoures. Bull. Mus. Nat. Hist. 42:1063-1090.

Haig, J. , 1956. The Galatheidea (Crustacea Anomura) of the Allan Hancock Atlantic Expedition with a review of the Porcellanidae of the Western Atlantic. Allan Hancock Atlantic Expedition Report No. 8.

Holthuis, L. B., 1960. Notes on American Albuneidae (Crustacea:Decapoda: Anomura) with the description of a new genus and species. Konikl. Nederl. Adademie van Weternschappen-Amsterdam, Proc. Series C. 64(1): 21-36.

Lyons, W. G., 1970. Scyllarid lobsters. Mem. of the Hourglass Cruises 1(4):1-73.

Milne-Edwards, A. and E. L. Bouvier, 1902. Les Dromiaces et Oxystomes. Part XXXIX. Mem. Comp. Mus. Zool. of Harvard. 27(1):1-127, 25 pl.

Milne-Edwards, A. and E. L. Bouvier, 1923. Les Porcellanides et Des Brachyures. Mem. Comp. Mus. Zool. of Harvard. 47(4):1-395, 12 pls.

Monod, T. 1956. Hippidea et Brachyura ouest-africains. Mem de l'Institute Francais d'Afreque Noire 45(1-4).

Rathbun, M. J., 1901. The brachyura and macrura of Puerto Rico. Bull. Fish. Comm. 1900, 20(2):3-127.

Rathbun, M. J., 1918. The Grapsoid crabs of America. U. S. National Museum Bulletin #97.

Rathbun, M. J., 1930. The Cancroid crabs of America of the Family Eurgalidae, Portunidae, Atelecyclidae, Cancridae and Xanthidae. U. S. National Museum Bull. #152.

Rathbun, M. J., 1937. The Oxystomatous and allied crabs of America. U.S. Natinal Museum Bulletin #166.

Williams, A. B., 1974. Marine Flora and Fauna of the Northeastern United States Crustacea: Decapoda. NOAA Tech. Report NMFS CIRC-389.

POLYCHAETES

Fauchauld, K., 1977. Polychaete worms. Nat. Hist. Mus. L. A. County.

Hartman, O., 1951. Littoral Marine Annelids of the Gulf of Mexico. Publ. Inst. Mar. Sci. Univ. Texas 7(1):1-124.

Vittor, B. A., Key to the polychaetes. Unpublished 11 pp.

MOLLUSCS

Abbott, R. T., 1974. American Seashells, Van Nostrand Reinhold Co., New York, New York, 663 pp.

Andrews, J., 1971. Seashells of the Texas Coast, Univ. of Texas Press, Austin, Texas, 298 pp.

Bright, T. J. and L. H. Pequegnat, 1974 (eds). Biota of the West Florida Garden Bank, Gulf Publ. Co., Houston, Texas, 435 pp.

Clench, W. J. and R. D. Turner, 1950. The Western Atlantic Marine Mollusks Described by C. B. Adams. Occasional papers on mollusks, June 26, 1950. #(15):233-404.

Clench, W. J., (1975 Facsimile), Monographs of the Marine Mollusks of the Western Atlantic, Johnsonia Vol. II Numbers 19-32.

Clench, W. J., ed., 1960-1970. Johnsonia monographs of the Marine Molluscs of the Western Atlantic. IV(40-48).

Dall, W. H., 1889. "Report on the Mollusca ("Blake") II Gastropoda and Scaphopoda," Bull. Mus. Comp. Zool. Harvard. 18:1-492.

Henderson, J. B., 1920. "A Monograph of the East American Scaphopod Mol lusks," Smithsonian Instit. M.S. Nat. Museum Bulleita III.

Lipka, D. A., 1974. Biota of the West Flower Garden Bank Mollusks, in Bright, T. J. and L. H. Pequegnat, 1974 (eds.) Biota of the West Flower Garden Bank, Gulf Publ. Co., Houston, Texas, 435 pp.

Marcus, E. and E. Marcus, 1967. American Opisthobranch Mollusks, Stud. Trop. Oceanogr. Miami 6:VIII +256 pp.

Perry, L. M. and J. S. Schwengel, 1955. Marine Shells of the Western Coast of Florida, 318 pp., Paleontol. Res. Inst.

Vander Spoel, S., 1976. Pseudothecosomata, Gymnosomata and Heteropoda (Gastropoda), Bohn, Scheltema, and Holkema Utrecht, 484 pp.

Valentine, J. W., 1966. "Numerical analysis of marine molluscan ranges on the extratropical northeastern Pacific shelf," Limnol. Oceanogr. 11:198-211.

Valentine, J. W., 1973. "The Provincial Level," Chapter 8, pp. 337-371 in Evolutionary Paleoecology of the Marine Biosphere, Prentice-Hall Inc., Englewood Clifts, New Jersey.

Verrill, A. E., 1881. "The Cephalopods of the Northeastern Coast of America Part II. The smaller cephalopods, including the squids and the octopi, with other allied forms," Conn. Acad. Sci. Trans. 5:259-446.

Warmke, G. L., and R. T. Abbott, 1961. Caribbean Seashells, Livingston Publ. Co., Narberth, Pa., X + 346 pp., 34 figs. 44 pls.

Work, R. C., 1969. "Systematics, Ecology and Distribution of the Molluska of Los Roques, Venezuela," Inst. of Mar. and Atm. Sci., Univ. of Miami Bull. Mar. Sci. 19(3):614-711.

ECHINODERMATA

Agassiz, A., 1878. "Echine" in "Reports on the Dredging operations of the U. S. Coast Survey Str. 'Blake'." Bull. Mus. Comp. Zool. V(9): 181-194. 5 pls.

Clark, A. H., 1954. Echinoderms (other than Holothurians) of the Gulf of Mexico. Fish. Bull. 89, 55:373-379.

Clark, H. L., 1901. The echinoderms of Puerto Rico. Bull. U. S. Fish Comm., ii:233-263. Plates XIV-XVII.

Clark, H. L., 1933. A Handbook of the Littoral Echinoderms of Puerto Rico and other West Indian Islands. New York Acad. Sci. Survey Puerto Rico and the Virgin Islands. 16 pt. 1, pp. 1-147.

Clark, H. L, 1941. "The Echinoderms." Reports on the Scientific Results of the Atlantis Expeditions to the West Indies Under the Joint Auspices of the University of Havana and Harvard University. Memorias de la Sociedad Cubana de Historia Natural "Felipe Poey," XV(1):1-154, 10 pls.

Deichmann, E., 1954. The holothurians of the Gulf of Mexico. Fish. Bull 89, 55:381-410. 3 figs.

Downey, M. E., 1973. Starfishes from the Caribbean and the Gulf of Mexico. Smithsonian Contr. Zool., 126:1-158, 48 pls.

Fell, H. B., 1960. Synoptic Keys to the Genera of Ophiuroidea. Zool. Publ. Victoria Univ. of Wellington, N.Z. 26:1-44.

Lyman, T., 1878. "Ophiurans" in "Reports on the Dredging Operations of the U.S. Coast Survey Str. 'Blake'." Bull. Mus. Comp. Zool. V(9): 217-235. 3 pls.

Phelan, T., 1970. A field guide to the Cidaroid Echinoids of the Northwestern Atlantic Ocean, Gulf of Mexico, and the Caribbean Sea. Smithsonian Contr. Zool. 40:1-67, 22 pls.

Phelan, T. F., 1972. Comments on the echinoid genus Encope and a new subgenus. Proc. Biol. Soc. Wash., 85(8), 109-130.

Serafy, D. K., 1970. A new species of Clypeaster from the Gulf and Caribbean and a key to the species in the tropical Northwestern Atlantic (Echinodermata:Echinoidea). Bull. Mar. Sci., 20(3):662-677.

Thomas, L. P., 1962. The Shallow Water Amphiurid Brittle Stars (Echinodermata, Ophiuoidea) of Florida. Bull. Mar. Sci. Gulf and Carib., 12(4):623-694. 23 figs.

Thomas, L. P., 1966. A Revision of the Tropical American Species of Amphipholis (Echinodermata: Ophiuroidea). Bull. Mar. Sci., 16(4):827-833.

Thomas, L. P., 1967. The Systematic Position of Amphilimna (Echinodermata: Ophiuroidea). Proc. Biol. Soc. Wash. 80:123-230.

Thomas, L. P., 1973. Western Atlantic Brittlestars of the Genus Ophionereis. Bull. Mar. Sci., 23(3):585-599.

Thomas, L. P., 1975. The Ophiacanthid Genus Amphilimna (Ophiuroidea: Echinodermata). Proc. Biol. Soc. Wash., 88(14):127-140.

Verrill, A. E., 1899. Report on the ophiuroidea collected by the Bahama expedition in 1893. Bull. Lab. Nat. Hist. State Univ. of Iowa, V(1):1-86. 8 pls.

Ziesenhenne, F. C., 1955. A Review of the Genus Ophioderma M & T. In Essays in the natural sciences in honor of Captain Allan Hancock: 185-201. Univ. Sou. Calif. Press.

APPENDIX A

APPENDIX A

SUMMARY STATION ANALYSIS/DATA TABULATION

STATION NO.	$\bar{X}$ DEPTH METRES	NO SPECIES	DIVERSITY INDICES SIMPSON	SHANNON WIENER	SWI LN(S)	SED. PROVINCE
2103 (IA)	42	216	0.97	4.34	0.80	VI-B
2105 (IB)	96	142	0.84	3.28	0.66	X
0004 (I-C)	183	70	0.79	2.67	0.62	IX
2747 (VII-A)	74	165	0.96	3.96	0.78	X
2748 (VII-B)	54	210	0.93	3.97	0.73	X
2749	30	98	0.95	3.75	0.80	X
2209 (II-A)	33	142	0.95	3.57	0.71	X
0001 (II-B)	109	115	0.96	3.97	0.83	IX/X
0002 (II-C)	182	54	0.70	2.23	0.55	IX
0005 (III-A)	43	173	0.97	4.28	0.81	X
0003 (III-B)	85	153	0.93	3.87	0.76	IX
2313 (III-C)	181	48	0.84	2.49	0.64	IX
2426 (IV-B)	79	128	0.82	2.74	0.55	V
2427 (IV-C)	177	43	0.96	3.36	0.88	IX
2529 V-A	39	184	0.94	3.99	0.75	II
0007 V-B	80	60	0.87	2.81	0.68	II/VII
2536 V-C	173	47	0.89	2.75	0.70	VIII
2641 VI-A	39	129	0.90	3.21	0.65	II
2645 VI-B	110	130	0.94	3.70	0.75	VIII

COMPARISON AND INVENTORY OF ARCHIVED ALGAE, FMG, 1976

TAXON	Sink	047	146	147	151	247	251
RHODOPHYTA							
Agardhinula browneae						X	
Amphiroa rigida				X			
Amphiroa sp.			X	X		X	
Botryocladia occidentalis		X	X	X	X	X	X
Ceramium sp.					X		
Champia parvula		X	X		X	X	
C. salicornioides	X					X	
Cryptonemia crenulata				X			
Chrysymenia enteromorpha		X	X	X		X	
C. halymenioides		X	X	X	X	X	
Chysemenia sp.					X		
Coelarthrum albertsii			X	X	X	X	
Dasya sp.					X	X	
Dudresmaya crassa		X	X	X		X	
Eucheume isiforme				X	X	X	
Fauchea sp.			X	X		X	
Galaxaura obtusata	X	X	X	X	X	X	X
Gelidium crinale			X				

TAXON	SINK	047	146	147	151	247	251
Goniolithium sp.			X	X	X	X	
Gracilaria blodgettii						X	
Gracilaria cylindrica		X				X	
G. mammillaris	X	X	X	X		X	
Griffithsia globuliferax							
Halymenia agardhii	X	X				X	
H. duchassaignii						X	
H. floresia	X				X	X	
H. hancockii		X		X			
H. vinacea		X	X			X	
Halymenia sp.				X	X	X	
Hypnea spinella			X				
Halymenia pseudofloresia						X	
Herposiphomia sp.					X		
Hypoglossum involvens		X					X
Jania capillacea			X	X	X	X	
Kallymenia perforata	X	X	X	X		X	
Laurencia intricata	X	X	X	X	X	X	
Liagora ceranoides		X	X	X	X	X	
Lithothamnion mesomorphum		X	X	X	X	X	

TAXON	SINK	047	146	147	151	247	251
Lithothamnion sp.		X		X	X		
Lomentaria sp.						X	
Nemastoma gelatinosum				X	X	X	
Peyssoniella sp. A						X	X
Peyssoniella sp. B		X	X	X	X		
Peyssonniela sp. C							
Peyssonniela rubra				X		X	X
Polysiphonia binneyi	X					X	
Phodymenia occidentalis				X		X	X
Sciania complanata		X	X	X			
Solieria ramossissuma						X	
S. tenera		X				X	X
Spermothamnion sp.					X		

51 Species Rhodophyta

Totals By Station:

Sink	9
047	20
146	21
147	26
151	21
247	36
251	6

TAXON	SINK	047	146	147	151	247	251
PHAEOPHYTA							
Cladosyphon occidentalis	X					X	
Colpomenia sinuosa	X		X		X	X	X
Dictyota bartayresii		X	X	X	X		
D. ciliolata			X			X	
D. dichotoma	X		X	X	X	X	X
D. divaricata	X		X		X	X	
Giffordia sp.							
Lobophora variegata					X		
Padina sp.					X		
Rosenvingea intricata		X				X	
Sargassum fluifons		X				X	
S. matans			X	X			
S. filipendula						X	
Sargassum sp.						X	
Spatoglossum schroederi					X		
Sphacelaria sp.							

	SINK	047	146	147	151	247	251
Sporochnus bolleanus	X	X				X	

17 Species Phaeophyta

Totals By Station

047	5
146	4
147	6
151	7
247	10
251	2

TAXON	SINK	047	146	147	151	247	251
CHLOROPHYTA							
Anadyomene stellata		X	X	X	X		X
Avrainvillea levis	X	X	X		X	X	
A. migricans							X
Caulerpa microphysa					X	X	X
C. racemosa					X	X	
Caulerpa M. sp.						X	
Codium carglinianum		X	X	X	X	X	X
C. intertextum		X	X	X	X	X	X
C. isthmocladum	X	X	X	X	X	X	
Codium m. sp. A		X	X	X	X	X	X
Codium m. sp. B	X	X			X	X	X
Derbesia sp.			X				X
Enteromorpha sp.		X					
Enodesmis venticellata		X		X	X	X	
Halimeda discoidea	X	X	X	X	X	X	X
Microdictyon boergesenii							X
Pseudocodium sp.		X			X	X	

TAXON	SINK	047	146	147	151	247	251
Struvea elegans					X		
S. pulcherruma			X			X	X
Udotea cyathiformis	X						
U. flabellum		X	X	X	X	X	
Valonia macrophysa	X	X	X	X	X	X	X

22 Species Chloraphyta

Totals By Station

Sink	6
047	13
146	11
147	9
151	15
247	15
251	12

COMPARISON AND INVENTORY OF ARCHIVED ALGAE, DREDGING/TRAWLING, 1976

RHODOPHYTA	2103	2209	IIIA	IVA	VA	2748	2747
Agardhinula browneae	X		X				
Botryocladia occidentalis		x	x				
Botryocladia pyrifera					X		
Chondria sp.	X						
Chrysemenia enteromorpha	X	X	X				
Dasya pedicellata	X						
Goniolithon sp.	X	X	X	X			
Gracillaria blodgetti		X					
G. cylindrica	X	X				X	
Gracilaria sp.		X					
Gymnothamnion						X	
Holymenia bermudensis							X
H. floresia	X		X				
H. hancocki			X				
H. vinacea			X				
Halymenia sp.		X	X			X	
Laurencia intricata	X				X		
Lithothamnion sp. A	X	X			X		
Lithothamnion sp. B						X	
Lithothamnion mesomorphum		X			X		

RHODOPHYTA (CONT.)	2103	2209	IIIA	IVA	VA	2748	2747
Peyssoniela sp. A						X	
Peyssoniela sp. B	X	X			X		
Polysiphonia binneyi			X			X	
Rhadophyllis gracilarioides	X						
Rhodymenia occidentalis	X	X	X	X	X	X	X
Solieria tenera	X		X			X	

Total Species 26

Totals By Station

2103 = 13 IVA = 2 2748 = 8
2209 = 11 VA = 6
IIIA = 11 2747 = 2

PHAEOPHYTA	2103	IIA	IIIA	IVA	VA	2747	2748
Cladosiphon occidentalis		X					
Colpomenia sinuosa		X					
Dictyota bartayresii			X				
D. ciliolata		X					
D. dichotoma		X					X
Giffordia sp.		X					
Lobophora variegata		X	X				
Padina sp. A			X				
Rosenvingea intricata	X		X				
Sargassum natans	X	X	X	X		X	
Sporochmus bolleanus	X	X	X		X		

Total Species 11

Total Species By Station

2103 = 3 IVA = 1 2748 = 1
IIA = 8 VA = 1
IIIA = 6 2747 = 1

CHLOROPHYTA	2103	2209	IIIA	IVA	VA	2747	2748
Caulerpa ashmeadii		X	X				X
C. ollivierii	X		X				
C. sertularioides	X	X					X
Caulerpa n. sp. B			X				
Cladophora sp.				X			
Codium carolinianum		X	X				
C. isthmodladum	X	X	X	X	X		
Codium n. sp. B	X	X	X	X			
Cystodictyon pavonium	X						
Derbesia sp.							X
Halimeda discoidea	X						
H. opuntia	X	X	X	X	X		X
Microdictyon boergesenii		X					X
Neomeris sp.		X					

CHLOROPHYTA (CONT.)	2103	2209	IIIA	IVA	VA	2747	2748
Pseudocodium sp.	X	X	X				X
Struvea pulcherrima		X	X			X	X
Udotea cyathiformis	X						
U. flabellum		X	X				
Valonia macrophysa			X				

Total Species = 19

Total By Station

2103 = 9

2209 = 11

IIIA = 11

IVA = 4

VA = 2

2747 = 1

2748 = 7

RECOMMENDATIONS FOR FURTHER STUDY

DATA ANALYSIS

There is a serious need for PI's with large data bases to be able to edit, correct, and refine their data bases so that the data files are more reliable.

FIELD EFFORTS

Field efforts in pursuit of macroepifauna characterization should concentrate on (a) the ecotone concept, (b) the refinement of the macro-epifauna and its relation to substrate along the 100 meter contour, and (c) should employ 5 or more tows per station utilizing the Capetown Dredge and Trawl over two distinct seasons, summer vs. winter. A station should be defined as an area 2 kilometers on a side, and Loran C is more than adequate for navigational repeatability from season to season.

From a management point of view, (c) above should be used in new lease areas as opposed to a continued monitoring effort over the whole MAFLA trait.

PROBLEMS ENCOUNTERED

STATE OF THE SCIENCE - SYSTEMATICS

We felt we had a good handle on what we would find based on our species list and museum collection from previous effort. Bear in mind, we had no contractual obligation to go below family--either in 1975-76 or now. At any event, we were wrong in our estimate of what we would find, and we had difficulty resolving so many new taxa. As might be expected, the personnel and collections of the USNM were invaluable as were several other university scientists who were specialists with certain groups. Even so, this approach is not without shortcomings. A museum, like a library, does not always have what you want when you want! Specimens thought to be at the USNM are (a) on loan, (b) misplaced, or (c) were lost and not replaced. This effort will help fill gaps.

THE NOAA CODE

Conversion of all taxa to NOAA Code was and is an excellent practice. However, NODC was not ready to service our time schedule and, in point of fact, I'm not sure they knew or cared what the BLM had written in the RFP. The fact is that NOAA coding time was an overwhelming time "sink" and we were totally unprepared for the difficulties we would encounter. Needless to say, and the problem was not created solely at Dames & Moore, there are errors in the NOAA Code format even now. NODC just won't prioritize making coding corrections in their own program, and they are using some obsolete taxonomic terms and omitting certain entry points at others. At the user end (here), it has created huge snarls in data processing, not to meniton time delays.

THE TIME FRAME

The time frames for taxonomic identification, about (90 days), is realistic; however, the time frame for data transcription, processing, correcting, editing, plotting, studying, interpreting and writing is not realistic. There are too much data to sift through, and, in fact, it is too much for a computer to handle. This is a common misconception. The BLM needs reports on certain time schedules; I have no problem with that, but it's a sham and a shame to have to prepare a final report on a data base that has not been edited to the 99% level and to be forced to write from superficial impressions rather than careful analytical thought.

The BLM could rectify this problem at not too great an expense, and they should. In this matter, I am greatly concerned because it is the major shortcoming of at least this OCS program.

WORKS IN PROGRESS

The occurrence of Meticonaxius microps (Decapoda: Axiidae) in the Eastern Gulf of Mexico.

The occurrence of Zygopa michaelis (Decapoda: Albuneidae) in the Eastern Gulf of Mexico.

Notes on Caridean shrimps new to the Eastern Gulf of Mexico.

Notes on Upogebia operculata (Decapoda: Upogebiidae) from the Eastern Gulf of Mexico.

New host records of Pontonia margarita and range extension of its parasitic isopod, Bopyrina pontoncae.

Description of a new genus and species of Sysiosquillidae (Stomatopoda) from the Eastern Gulf of Mexico.

Description of a new species of Eurycyde (Pycnogonida: Ammotheidae) from the Northwestern Atlantic and the Gulf of Mexico.

Color notes on Pantomus parvulus (Decapoda: Pandalidae).

Description of Synalpheus aegeles (Decapoda: Alpheidae) from the sponge, Aegeles dispar in the Western Atlantic and the Gulf of Mexico.

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The Department of the Interior Mission

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

The Minerals Management Service Mission

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

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

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