

SEDIMENTATION, DISPERSAL AND PARTITIONING
OF TRACE METALS IN COASTAL MISSISSIPPI-
ALABAMA ESTUARINE SEDIMENTS

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FINAL TECHNICAL REPORT

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Project Number R/ER-4
Final Report
Submitted to: Mississippi-Alabama SEA GRANT Consortium
Gulf Coast Research Laboratory
Ocean Springs, MS 39564

PURPOSE OF INVESTIGATION

The purpose of this investigation was to document the chemistry, mineralogy and lithology of the bottom sediments of Lake Borgne and Mississippi Sound. A second objective was to determine the manner by which various metals were site partitioned in these sediments. The latter is of particular importance because a number of recent studies have shown that, depending upon how a metal is actually incorporated in bottom sediments, it may be in a form that either (1) allows its later release back into the water column or (2) is present in a form that permits its extraction and subsequent incorporation into the tissues of bottom dwelling, filter-feeding organisms.

LOCATION

Mississippi Sound (see Fig. 1) is an elongated lagoon separated from the Gulf of Mexico by six barrier islands and, on the southwest, between Half Moon (Grand) Island and Isle au Pitre by marshy island remnants of the St. Bernard subdelta. The Sound has a length of 130 km, an average width of 15 km and encompasses a total area of approximately 1,400 square kilometers (Lake Borgne adds an additional 430 square kilometers). Four major estuaries are present along the northern margin of the Sound and include St. Louis Bay, Biloxi Bay, and the drowned valleys of the Pearl and Pascagoula Rivers. Pascagoula Harbor and Bayou Casotte are heavily industrialized and include ship building and refit facilities, bulk storage and handling facilities, offshore oil and gas support facilities, oil and gas storage and tank farms and seafood processing plants. The Sound receives fresh water from two major rivers (the Pearl and Pascagoula) and four smaller rivers (Tchoutacabouffa, Biloxi, Wolf and Jourdan). These rivers drain watershed areas totalling some 50,000 square kilometers and have an average combined flow rate of approximately 30,000 cfs. Other sources of

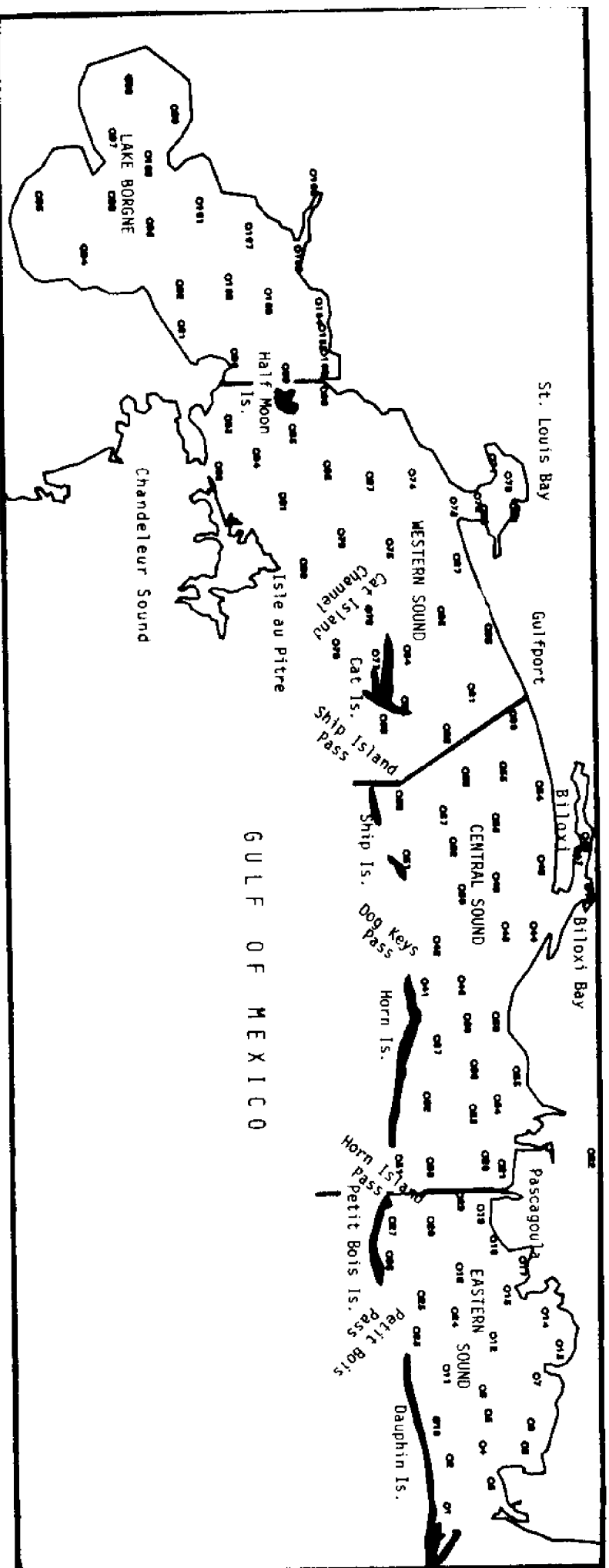


Fig. 1.-- Map of Mississippi Sound showing sample stations and physical subdivisions used in this report (Eastern Sound, Central Sound, Western Sound, and Lake Borgne).

fresh water inflow include water entering the eastern end of the Sound from Mobile Bay, via Pass aux Herons, and that flowing into Lake Borgne from Lake Pontchartrain.

METHODOLOGY

One-hundred nine cores, averaging $1\frac{1}{2}$ meters in length were collected at each of the sites shown on Figure 1. On-site measurements were also taken for surface and bottom pH, Eh, Salinity, Conductivity, temperature and dissolved oxygen. A portable glove box was used to provide a nitrogen environment in order to preserve a surface sediment sample for later site partitioning analysis. All samples were collected in 7 cm diameter, polycarbonate coring tubes. These were then returned to the laboratory, each day, and stored at 4° Celsius until processing was initiated.

Laboratory Analysis

Site Partitioning.-- Determination of the percentage of each metal present in:

(1) the pore water fraction, (2) the exchangeable phase, (3) the easily reducible phase, (4) the organic/sulfide phase, (5) the moderately reducible phase and (6) the residual (structurally coordinated) phase was carried out using the procedure outlined in the EPA "Redbook" (Plumb, 1981). All site partitioning analyses and analyses for total metal content of specific elements were carried out on a Perkin-Elmer, Model 460, Atomic Absorption Spectrophotometer equipped with Auto-sampler and HGA Graphite Furnace.

Clay Mineralogy.-- The mineralogy of the clay size fraction was determined by treating the clays according to the method recommended by Carroll (1970). All diffraction scans were run from 2 to 36 degrees, two-theta, using a Philips X-ray diffraction system equipped with a graphite, single crystal monochrometer. Clay mineral percentages were estimated from integrated peak height intensities with background corrections applied.

Carbon Analyses.-- Determinations were made for both the percent carbonate carbon and organic carbon using the Wood's Hole procedure developed by Hunt (1982, personal communication). A LECO Induction furnace equipped with automated sulphur titrator was used for each analysis.

Size Analysis.-- Size frequency distributions were calculated for each sample using a combination of hydrometer (Boyocous) and sieve analyses. Replicate analyses for some fine grained samples were run on a Sedigraph, Model 5000ET, X-ray particle analyzer. Statistical parameters were run using a program developed by the investigator (see Isphording, 1970) which calculates Inman, Folk and Ward and Moment Measure descriptors.

ANALYTICAL RESULTS

Introduction

In order to compare spatial differences, the area investigated was arbitrarily broken up into 4 "sub-regions". These are shown on Figure 1 and are defined as follows: Eastern Mississippi Sound - includes the area from the Dauphin Island bridge to Bayou Casotte channel; Central Mississippi Sound - from Bayou Casotte channel, west to the Gulfport, Mississippi channel; Western Mississippi Sound - from the Gulfport channel to Half Moon Island; Lake Borgne - includes the lake itself and the area eastward to Half Moon Island. The region defined as Eastern Mississippi Sound is the smallest, in terms of area (330 square kilometers), and is most influenced by depositional sources from Mobile Bay and inflow from Petit Bois Pass. No major rivers enter this portion of the Sound. Central Mississippi Sound, in contrast, encompasses some 510 square kilometers in area and is the primary depositional basin for the Biloxi, Tchoutacabouffa and Pascagoula Rivers. Other material is brought into this portion of the Sound by tidal currents operating through Horn Island Pass, Dog Keys Pass (between Ship and Horn Islands) and, to a lesser extent, the Ship Island Channel. Western Mississippi Sound is

the largest area (543 square kilometers) but is only, indirectly, influenced by riverine deposition. The Jourdan and Wolf Rivers empty into St. Louis Bay and this, in turn, discharges into the Sound. Other sediment sources include material carried eastward from the Pearl River, by longshore transport, and that brought into the sound by tidal currents operating through Cat Island Channel/South Pass and Ship Island Pass. The Lake Borgne region of the sound is unique, in many respects, both in terms of its physical parameters, mineralogy and chemistry. These aspects will be individually discussed later in the report but largely result from the restricted circulation in the lake and the influence of the discharge of the Pearl River and, to a lesser extent, material carried into Lake Borgne from Lake Pontchartrain through the Rigolets channel.

Sediments

A number of factors have acted to control sediment distribution within Mississippi Sound. These include the various rivers that empty into the Sound, reworking of older Pleistocene and Holocene sediments that form the barrier island chain, circulation patterns within the Sound, storm events and physico-chemical conditions existing at the time of deposition. Referring to the sediment map of the Sound (Fig. 2) it can be seen that the Lake Borgne area consists largely of clayey-silt and sand-silt-clay mixtures, using Shepard's (1954) classification. The predominance of silt is a direct reflection of material contributed from the Pearl River whereas clay-size sediment in the lake is derived from not only the Pearl River, but also reflects a Pontchartrain source and material brought into the lake from further east in the Sound by westward-flowing tidal currents. The small area of sandy-silt shown by the vertical bar-dotted pattern may represent remnant sediments from a former Mississippi River distributary source. A number of other sites are present in the Sound that reflect erosion from older, relict Pleistocene features. These include Deer Island at the mouth of Biloxi Bay, Round

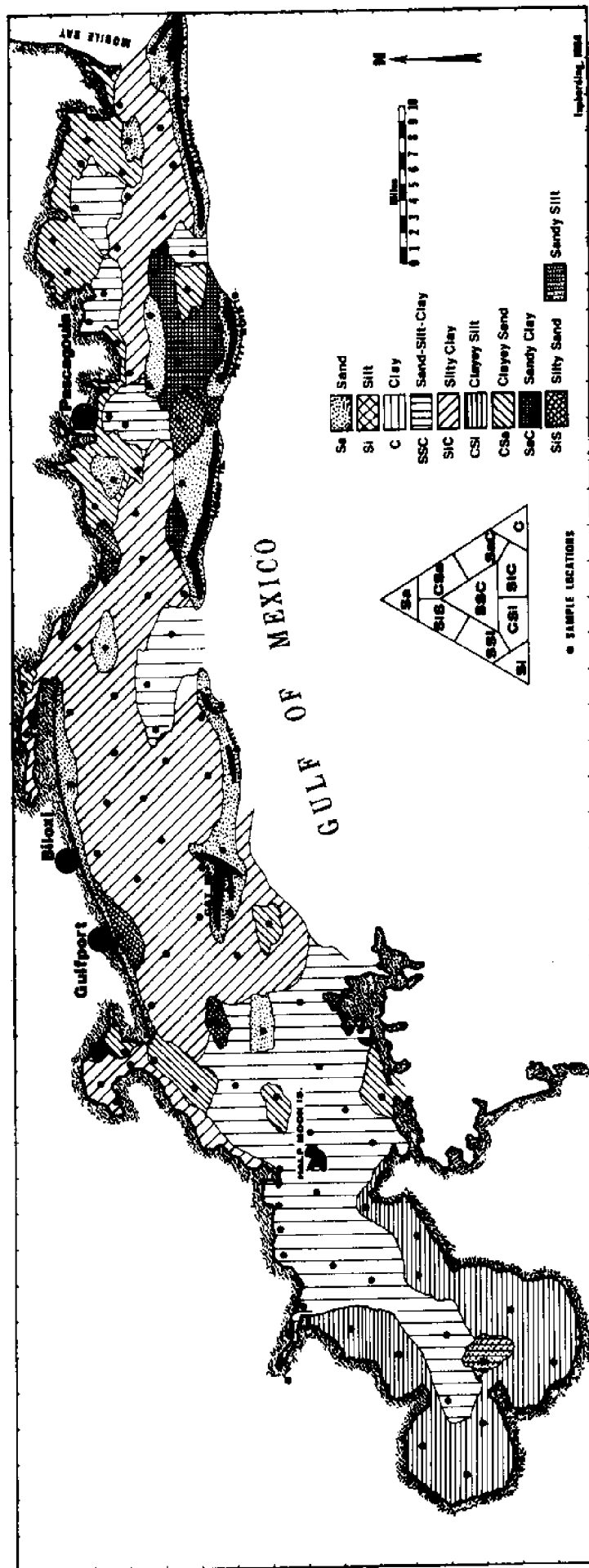


Fig. 2.-- Sediment map for Mississippi Sound and Lake Borgne.

Island, between Horn Island and Pascagoula, Grassy Island, west of Half Moon Island and several small islands located in Eastern Mississippi Sound. The dissimilarity of the Lake Borgne sediments with those of the remainder of the Sound may also be seen in Figure 3 which show plots of the sand-silt-clay components for all four regions. Western Mississippi Sound is less complex than the Central or Eastern Sound portions, in terms of its sediments, and can be seen to be dominated by sand-silt-clay mixtures and silty clays. Sands are present in the vicinity of the barrier islands, in the area of South Pass and in the beach areas between Gulfport and the mouth of Biloxi Bay. Much of these beach sands are "artificial" in that they have been transported to the sites by the State in order to maintain a sand beach for tourism purposes. Central Mississippi Sound is the most complex area, sedimentologically, as a result of the interaction of tidal currents, discharge from the Pascagoula River, reworking of barrier island deposits and older relict Pleistocene features (e.g., the Grand Batture Islands near the abandoned Escatawpa River delta). Clayey sediments (sandy clays, clayey sand, sand-silt-clay mixtures) are more common here because of flocculation that resulted when the Pascagoula River sediments entered the higher salinity waters of Mississippi Sound. The sediments of Eastern Mississippi Sound have a similar complexity however, in this case, the great preponderance of clay-size material has been derived by transport of material into the Sound from Mobile Bay through Pass aux Herons. That Mobile Bay can, and does, serve as an abundant source of clay-size sediment can be seen by comparing Figures 3 and 4. Mississippi Sound is similar to most other large bays in the northern Gulf in that sediments described as "pure clays" (i.e., greater than 75 percent clay) are chiefly lacking. This is largely a result of the stronger current action that takes place in the Sound which acts to remove, and carry seaward, significant amounts of clay-sized sediment. Restricted circulation patterns in Mobile Bay, however, combined with the relatively

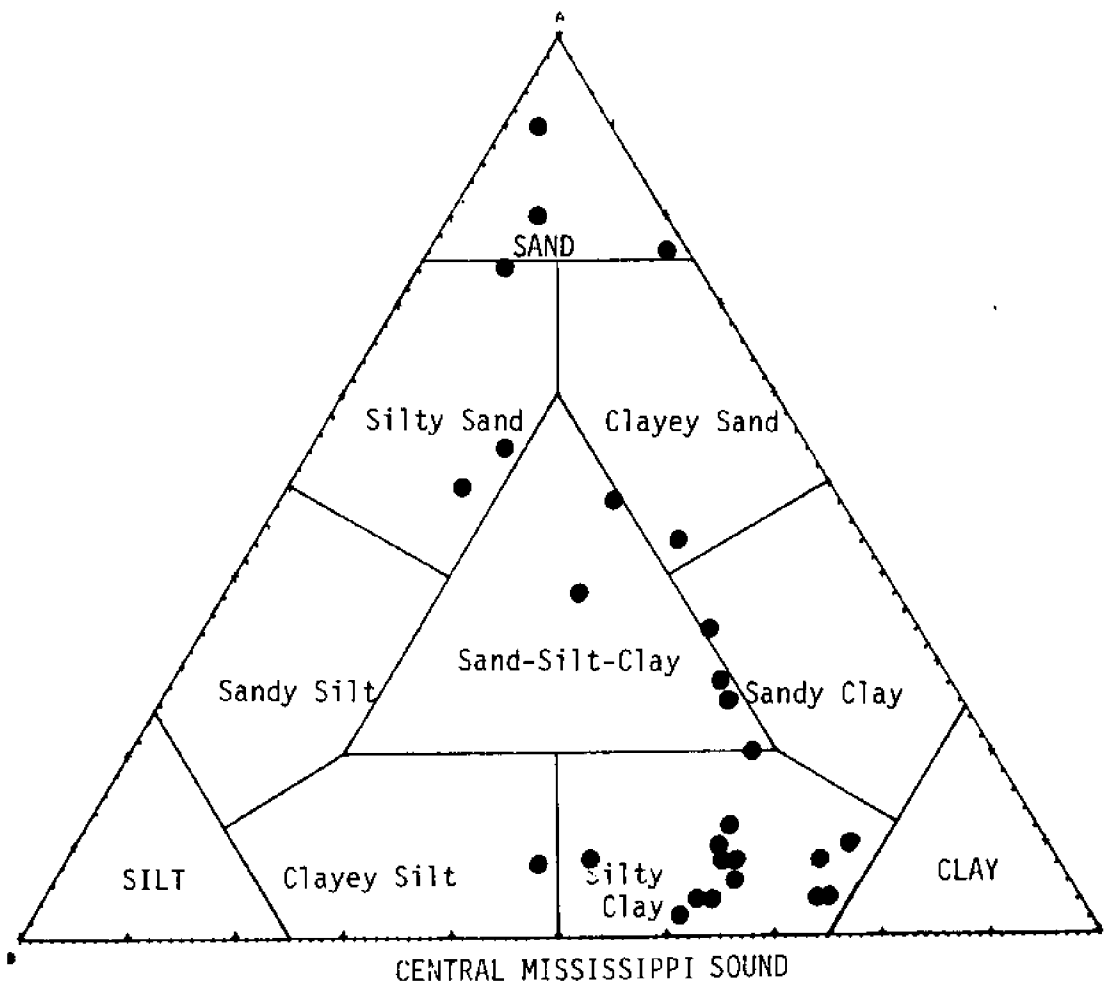
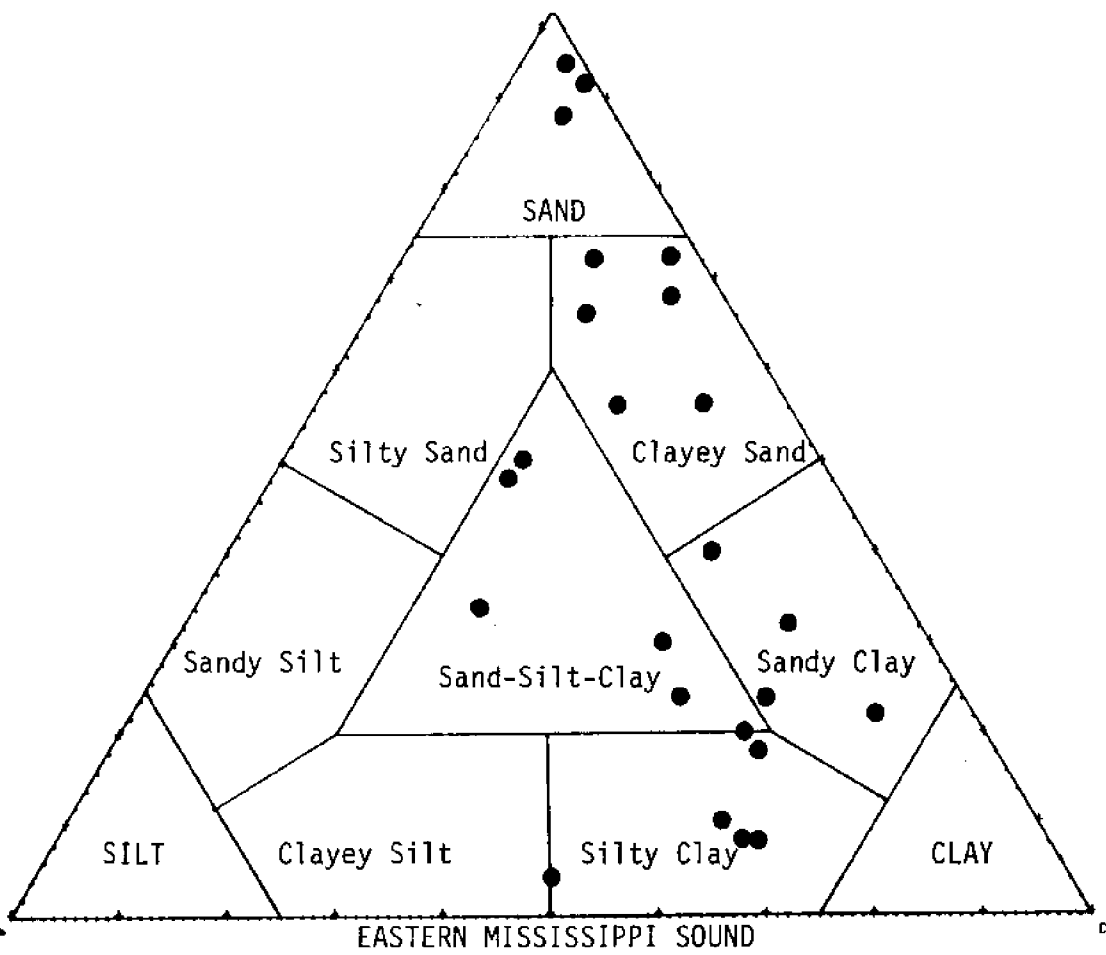


Fig. 3.-- Ternary diagrams for Mississippi Sound.

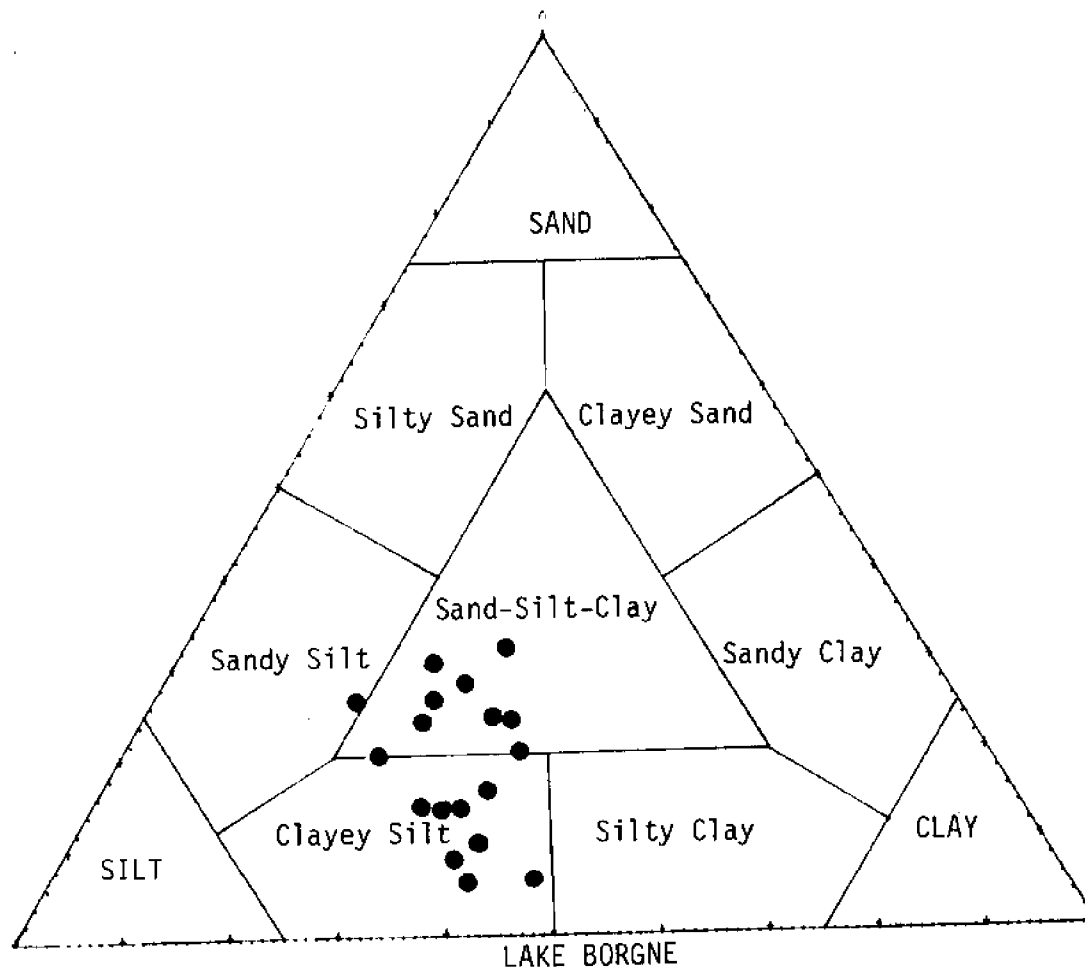
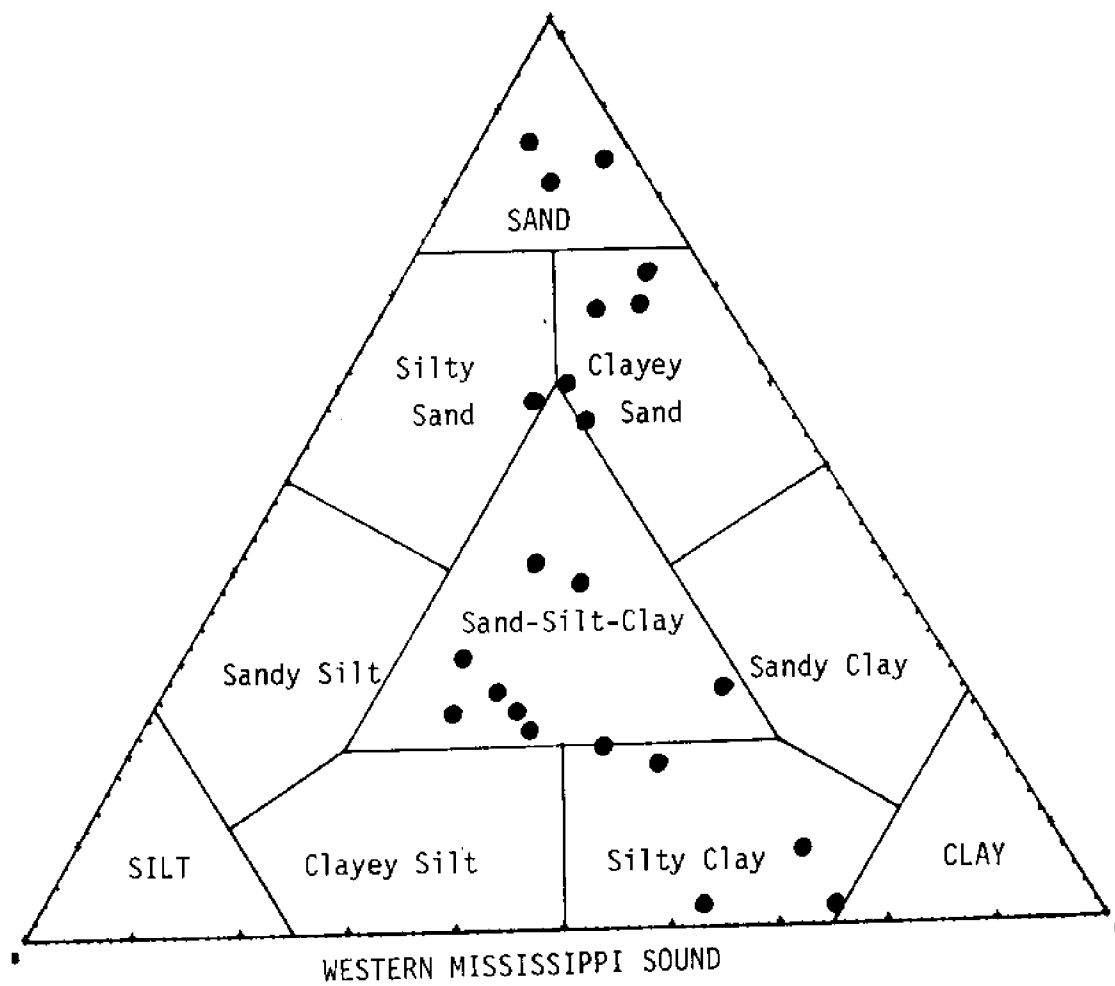


Fig. 3, cont. -9-

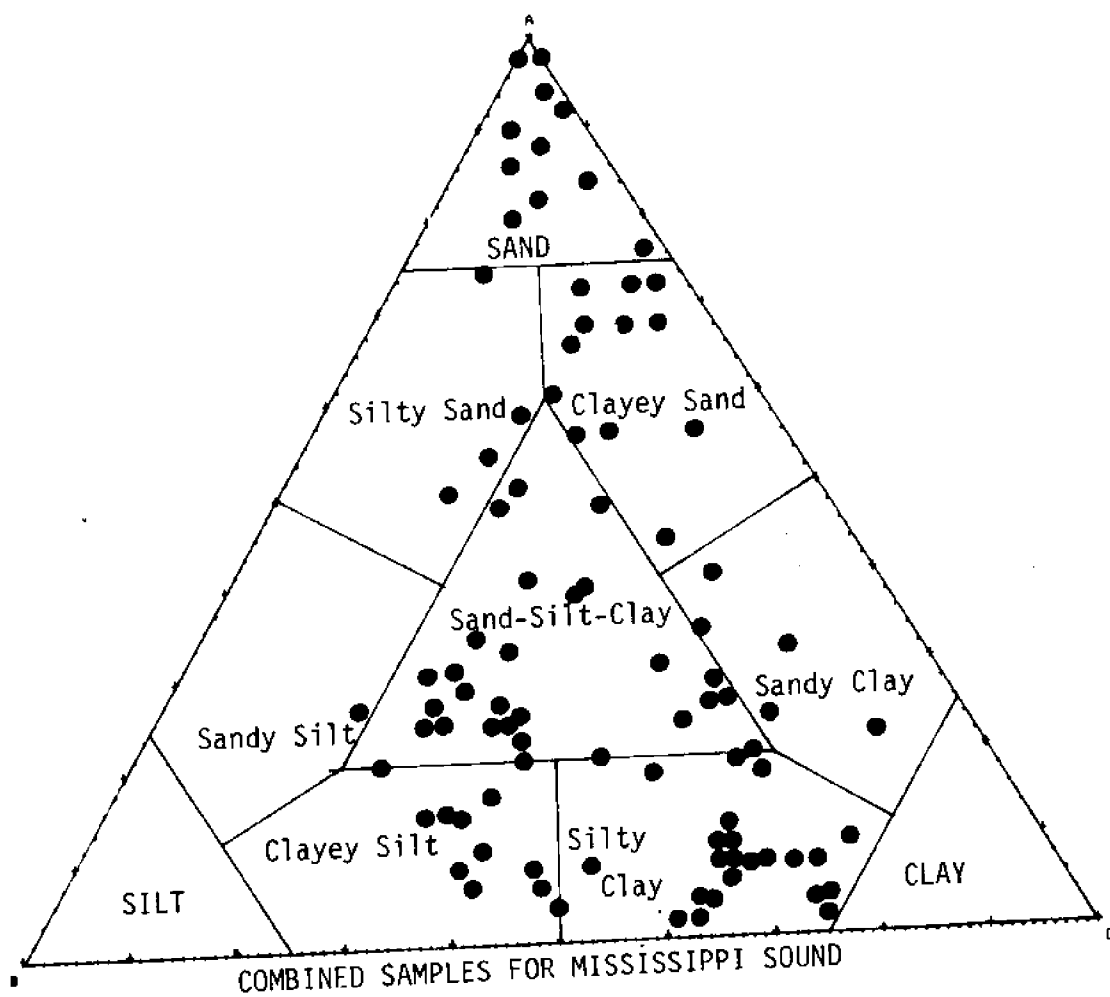
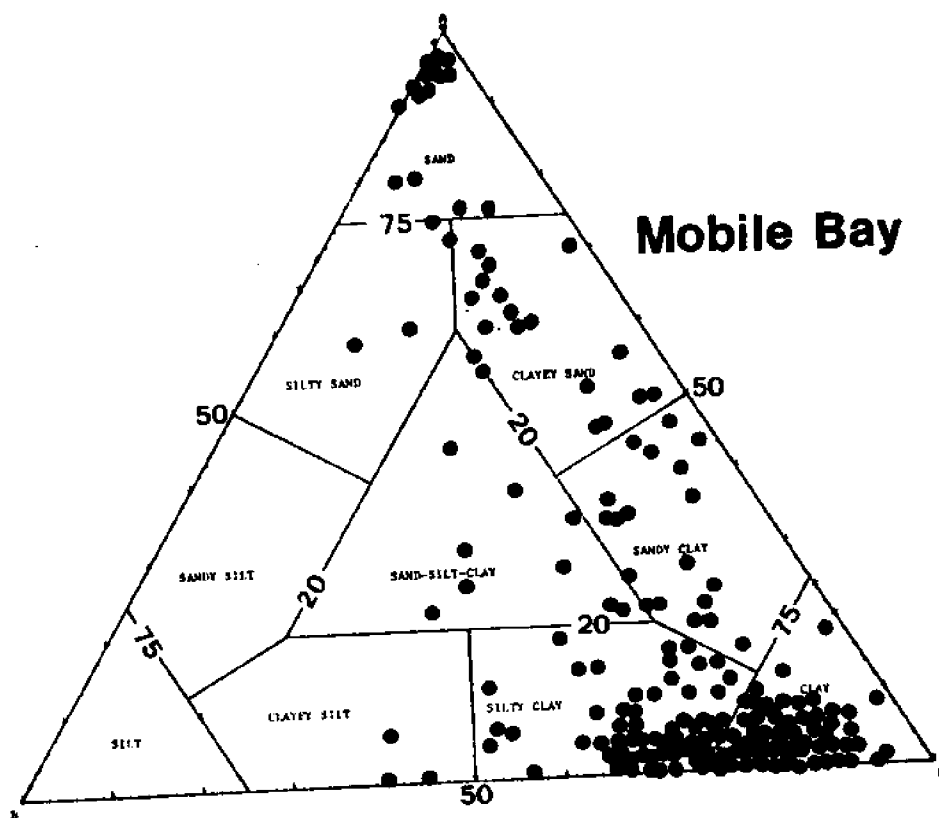
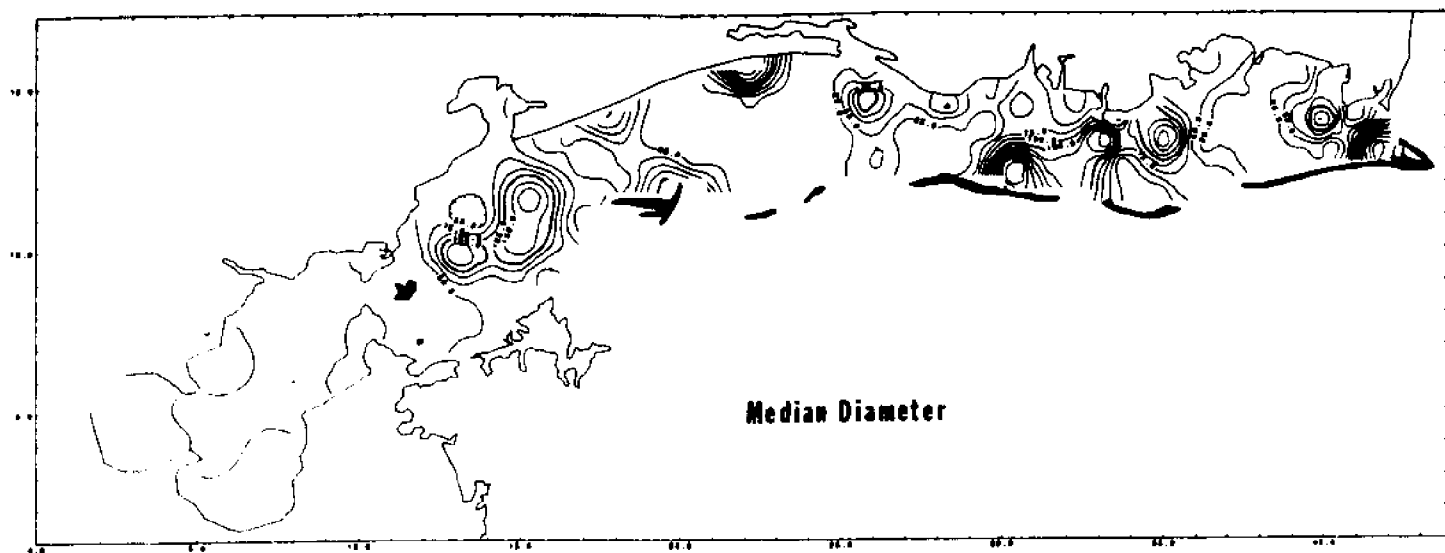
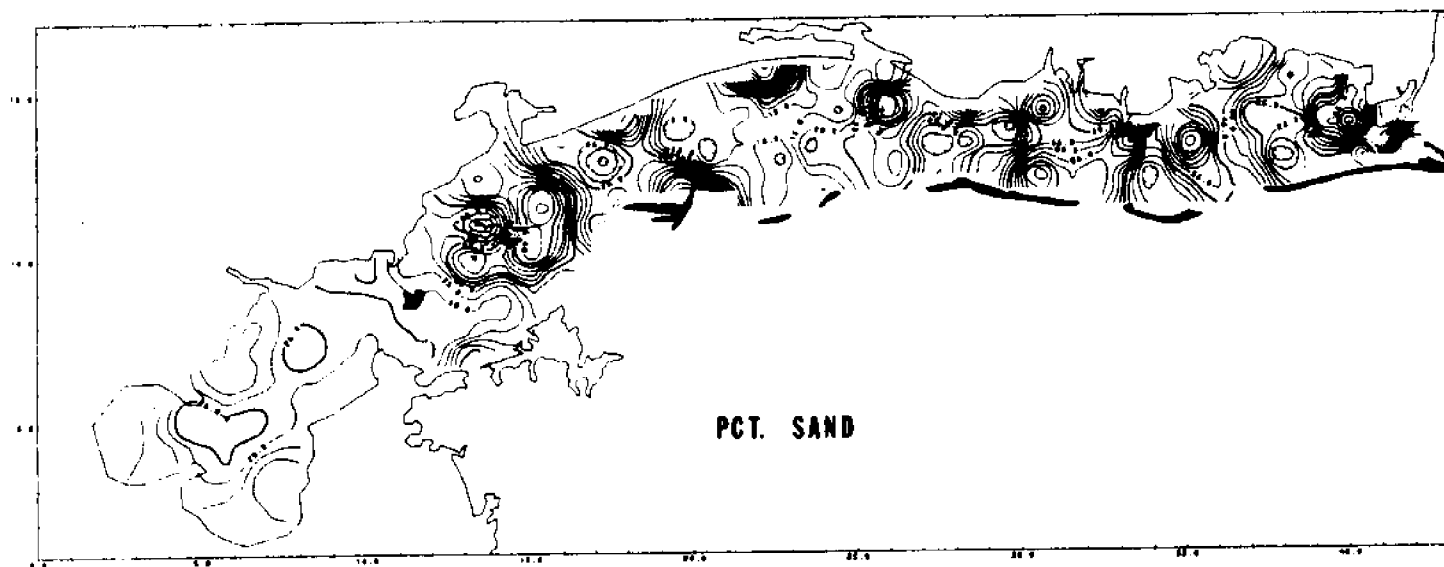


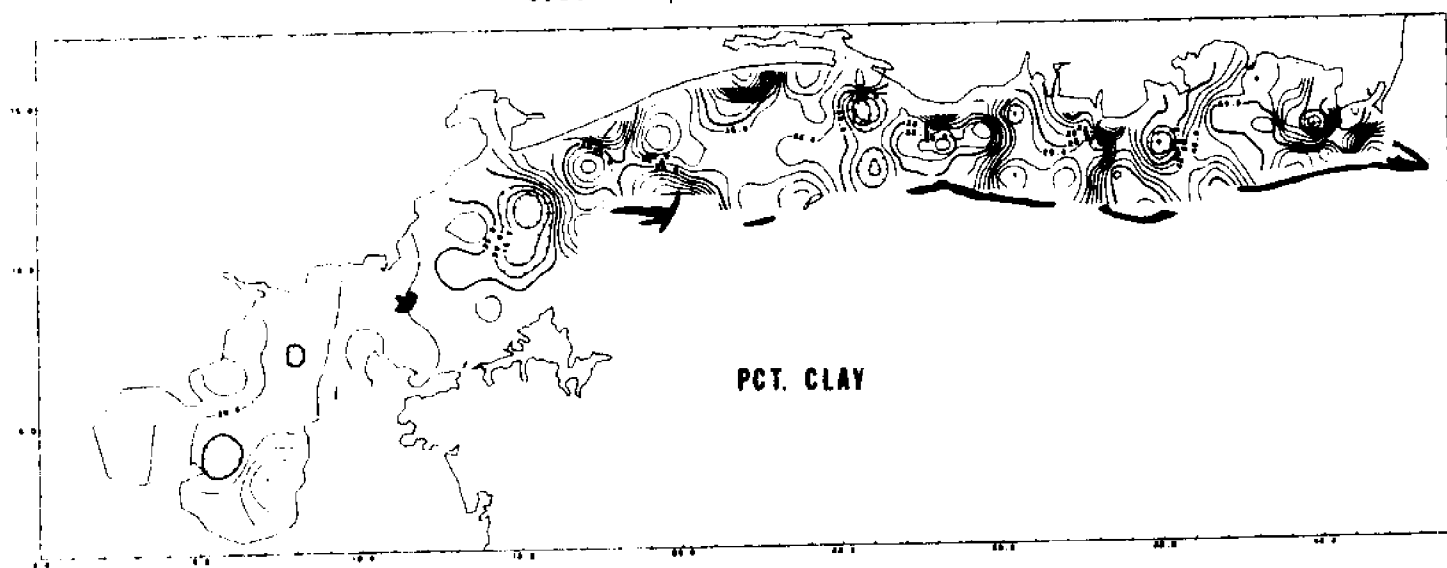
Fig. 4.-- Ternary diagrams comparing sediments from Mobile Bay and Mississippi Sound.



C.I. = 25 mm



C.I. = 5 percent



C.I. = 5 percent

Fig. 5.-- Median diameter, sand and clay percent maps for Mississippi Sound

narrow opening afforded to the Gulf of Mexico, have acted to "trap" large amounts of clay-size sediment within the bay (see Isphording and Lamb, 1979,1980).

Additional sediment textural information for Mississippi Sound is also presented in Figure 5. These diagrams show (from top to bottom) median diameter distribution (in mm), percentage of sand-sized (greater than 0.062 mm) material, and percentage of clay-size (less than 0.004 mm) material in the samples examined.

Chemical Analyses

Distribution maps for iron, aluminum, chromium, nickel, zinc, manganese, vanadium, copper and barium levels in the sediments of Mississippi Sound (in parts per million) are shown in Figure 6. Analyses for the individual metals were carried out by fusing the sediment sample in lithium metaborate and then dissolving in Spec-pure nitric acid. Replicate analyses were run on a number of samples and "spiking" was also carried out in order to insure reliability. Machine sensitivities and calibration standards were also compared with National Bureau of Standards Sample 1646 (Estuarine Sediment) as a further test for accuracy. The results obtained were in general agreement with other recently completed studies carried out in Mississippi Sound, in terms of order of magnitude observed (see O'Brien, 1980; GeoScience, Inc., 1983). Close agreement on samples collected near the Pascagoula Ship Channel was obtained when the results were compared with those published by Geoscience, Inc. (1983). Consistently lower values were found, however, when the samples analyzed in this study were compared with those of O'Brien (1980). The differences observed are summarized below:

		<u>This Study</u>	<u>O'Brien (1980)</u>
COPPER	Minimum	7	Minimum 5
	Maximum	50	Maximum 100
	Mean	10	Mean 37.5

		<u>This Study</u>		<u>O'Brien (1980)</u>
ZINC	Minimum	12	Minimum	15
	Maximum	149	Maximum	245
	Mean	74	Mean	108
COBALT	Minimum	0.2	Minimum	70
	Maximum	44	Maximum	200
	Mean	13	Mean	145
NICKEL	Minimum	2	Minimum	120
	Maximum	61	Maximum	400
	Mean	24	Mean	270
IRON	Minimum	179	Minimum	900
	Maximum	50,525	Maximum	13,600
	Mean	31,352	Mean	6,500

Because the general methodology used to carry out the metal analyses was the same for this investigation and that of O'Brien, the writer suspects that the differences observed may, at least in part, be traced to the fact that the NBS Standard for Estuarine Sediments was not available at the time O'Brien's work was carried out. Independent analyses performed on the same samples by Dr. George Flowers at Tulane University, using a Direct Current Plasma system were in very close agreement with the results obtained by the writer in his laboratory, using an Atomic Absorption spectrophotometer.

Further information on the overall distribution of metals in the bottom sediments of Mississippi Sound can be seen in Table 1, which lists minima, maxima and mean values for samples in Lake Borgne, Western Mississippi Sound, Central Mississippi Sound, and Eastern Mississippi Sound. Metal values for vanadium, zinc, iron, copper, cadmium, chromium and aluminum all averaged highest in Central Mississippi Sound, undoubtedly reflecting the heavy industrialization of this area. Barium values were observed to increase from east to west, culminating with an

VANADIUM				ZINC			
	Minimum	Maximum	Mean		Minimum	Maximum	Mean
Eastern Sound	2	157	76	Eastern Sound	12	145	71
Central Sound	17	144	88	Central Sound	23	148	81
Western Sound	1	125	75	Western Sound	26	149	68
Lake Borgne	65	105	82	Lake Borgne	40	89	65

NICKEL				CHROMIUM			
	Minimum	Maximum	Mean		Minimum	Maximum	Mean
Eastern Sound	6	57	21	Eastern Sound	25	85	54
Central Sound	2	45	21	Central Sound	24	82	59
Western Sound	10	57	28	Western Sound	24	80	57
Lake Borgne	6	61	29	Lake Borgne	45	72	59

IRON				MANGANESE			
	Minimum	Maximum	Mean		Minimum	Maximum	Mean
Eastern Sound	179	50,525	22,980	Eastern Sound	26	961	473
Central Sound	2,266	49,281	28,566	Central Sound	156	735	426
Western Sound	784	46,705	20,358	Western Sound	93	772	343
Lake Borgne	15,860	23,948	20,533	Lake Borgne	243	587	393

COPPER				COBALT			
	Minimum	Maximum	Mean		Minimum	Maximum	Mean
Eastern Sound	12	36	20	Eastern Sound	0.2	36	7
Central Sound	11	50	22	Central Sound	0.5	42	12
Western Sound	9	36	19	Western Sound	0.5	44	19
Lake Borgne	7	38	20	Lake Borgne	0.5	40	15

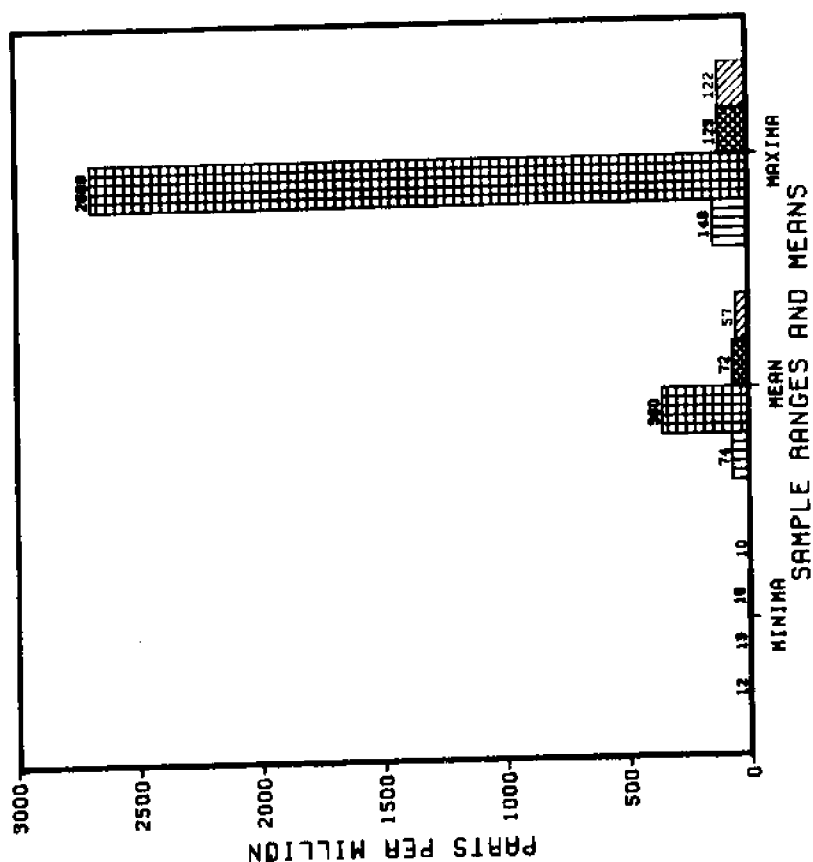
BARIUM				ALUMINUM			
	Minimum	Maximum	Mean		Minimum	Maximum	Mean
Eastern Sound	20	679	194	Eastern Sound	780	79,921	40,353
Central Sound	16	362	190	Central Sound	6,043	90,651	51,720
Western Sound	19	683	419	Western Sound	4,679	96,234	45,447
Lake Borgne	479	1,390	720	Lake Borgne	42,135	58,714	51,251

Table 1.-- Minimum, maximum and mean values (in parts per million) of metals in bottom sediments of Mississippi Sound.

average value of 720 ppm in Lake Borgne. Nickel, also, was found to increase in abundance from east to west. Manganese and Iron behaved opposite to this and were found in greatest abundance in the Central and Eastern Sound. Overall, however, the metal levels observed throughout the Sound (except for Barium) were comparable to other bays and estuaries in the northern Gulf Coast and well below those found in Mobile Bay, which remains the most heavily impacted site in the northern Gulf. This can be well seen in Fig. 6 which shows a comparison of minimum, maximum and mean values for several metals from Mississippi Sound, Mobile Bay, Perdido Bay and Apalachicola Bay. Mobile Bay is seen to exceed all other sites in both mean values and maximum values for all metals except barium.

Site Partitioning.-- Partitioning behavior for zinc, lead, copper, iron, nickel and vanadium is summarized in Figure 7. Three samples were selected for total partitioning and were treated according to the procedure referenced in the methodology section of this report. Sample MS-10 was collected near the west end of Dauphin Island; sample MS-45 from Biloxi Bay and sample MS-76 in Cat Island Channel. Reference to Figure 7 shows that zinc is largely found in the form of organic or organo-metallically chelated compounds in the Sound sediments. This phase, consistently, contained approximately 50 percent of the zinc whereas the reducible phases averaged about 25 percent and structurally-coordinated zinc was present in amounts of some 20 percent. The significance of this is simply that nearly 80 percent of the zinc in Mississippi Sound bottom sediments is potentially releasable, either into the water column under conditions that would alter the redox potential, or into the tissues of indigenous marine fauna, by digestive and metabolic processes. Similar behavior was also noted for lead, copper, and iron. Each of these elements was partitioned with a preponderance of the metal in non-structural sites. Only vanadium and nickel showed a significant amount of structural partitioning but even in these samples nearly 50 percent of the metal was potentially releasable. The

IRON



ZINC

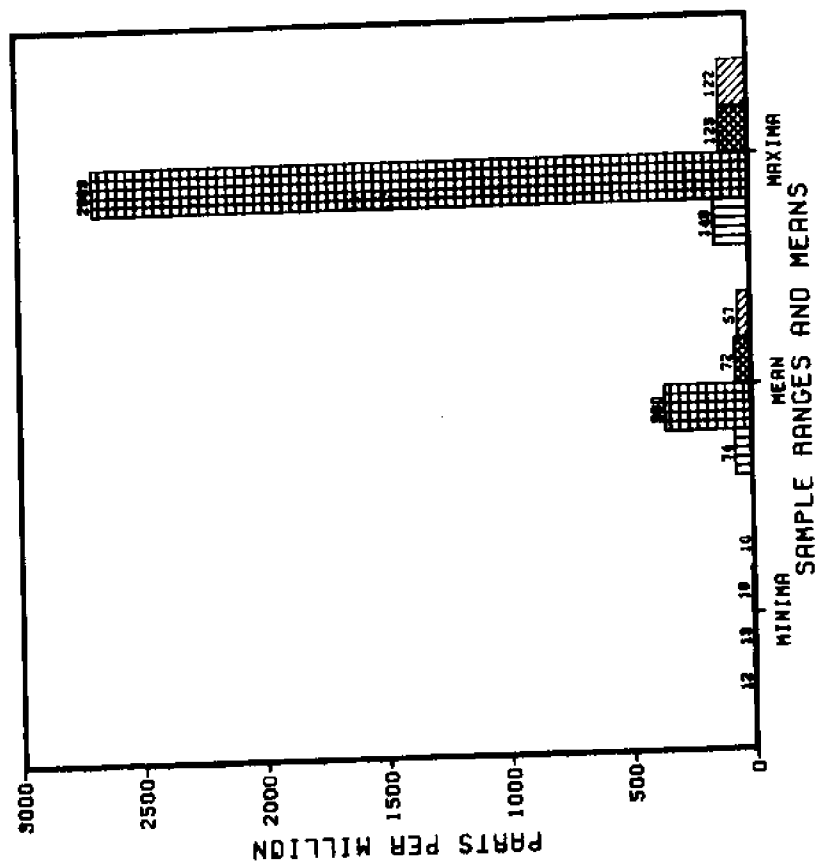
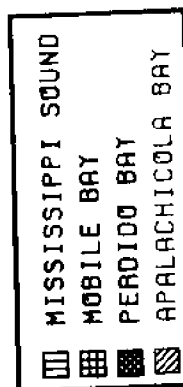
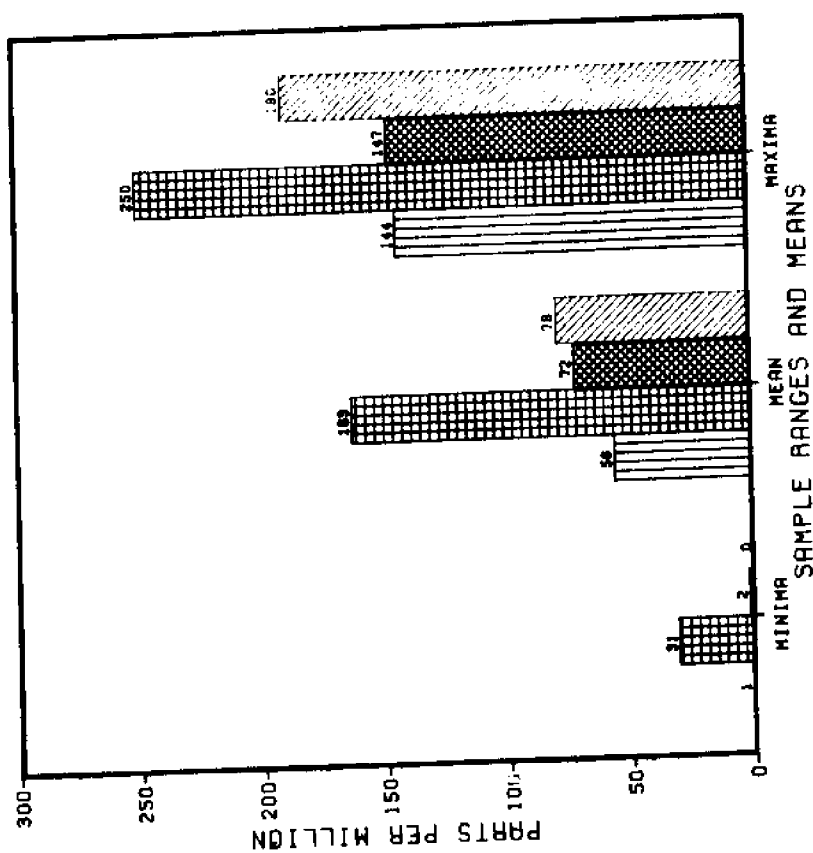


Fig. 6.-- Comparison of metals present in sediments (in ppm) for Mississippi Sound, Mobile Bay, Perdido Bay and Apalachicola Bay.

VANADIUM



NICKEL

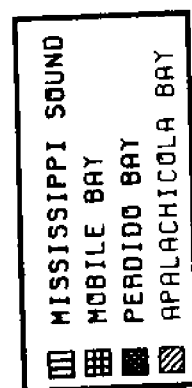
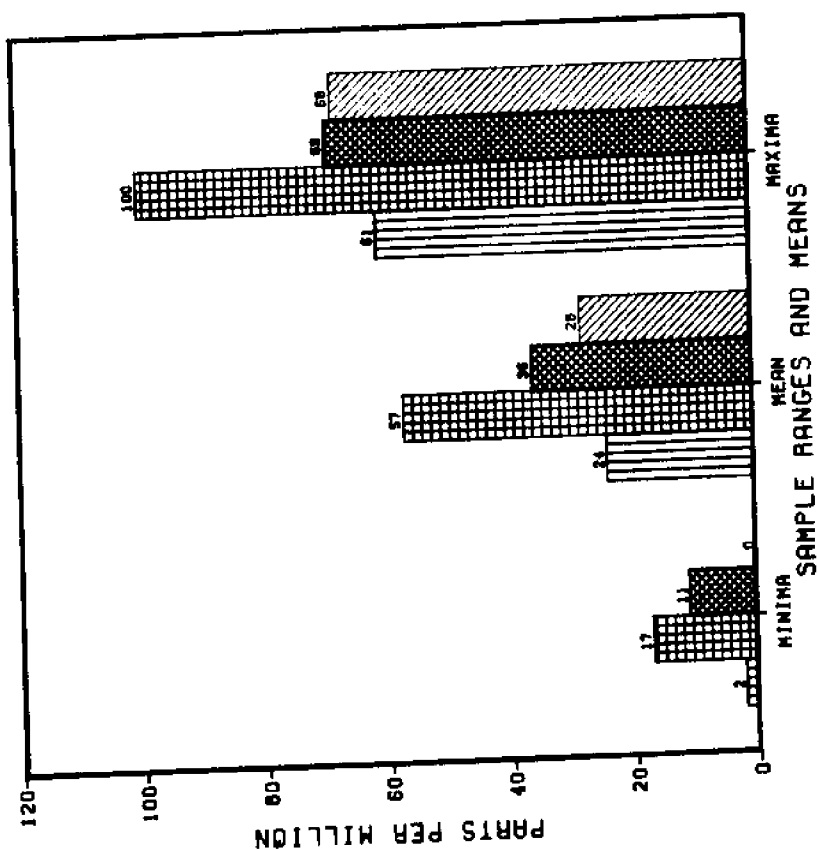
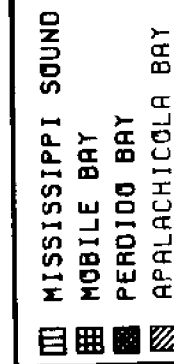
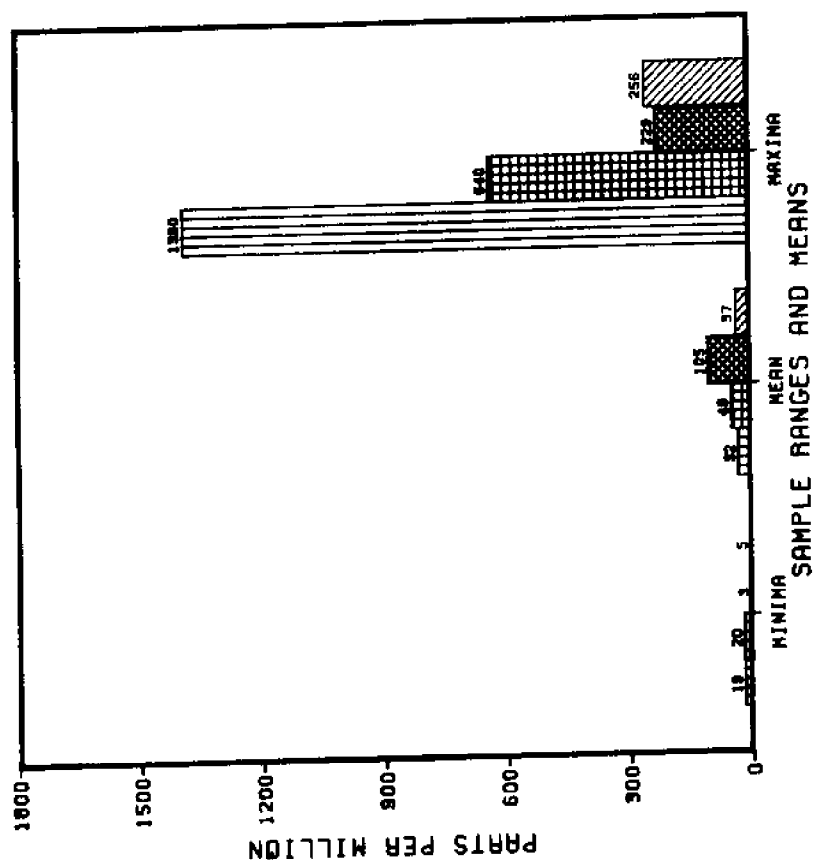


Fig. 6.-- cont.

BARIUM



CHROMIUM

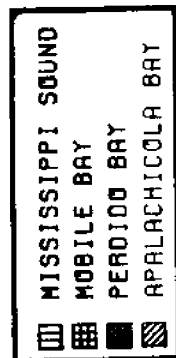
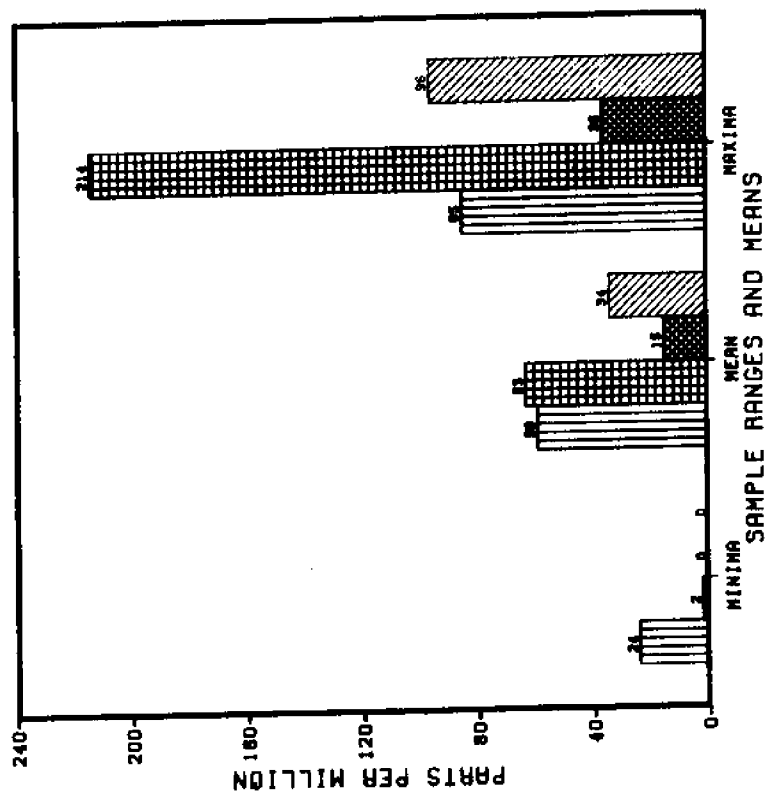


Fig. 6.-- cont.

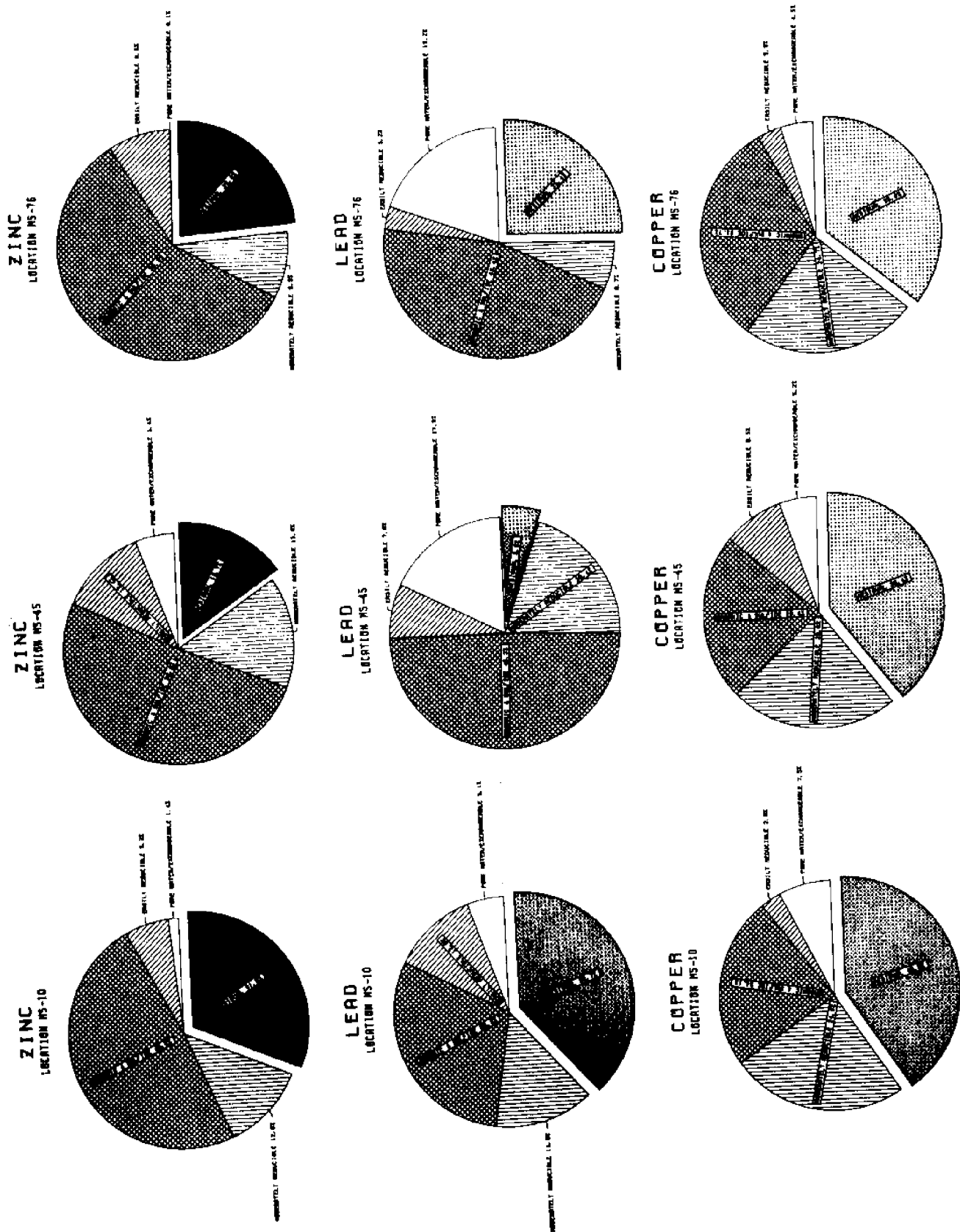


Fig. 7.-- Site partitioning behavior for selected samples from Mississippi Sound.

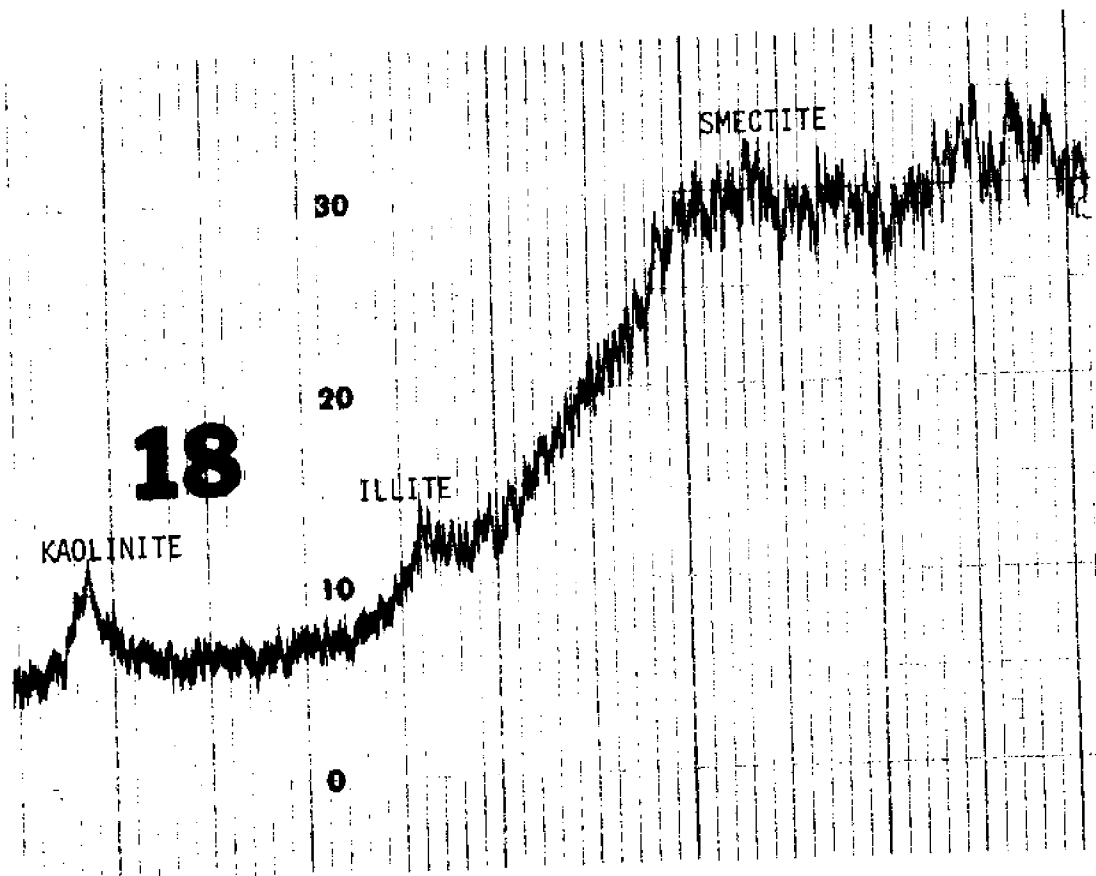
information shown for lead, nickel and vanadium on Figure 7 is of particular significance because it represents the first such data on this aspect of these metals that has appeared in the scientific literature. As with the other metals, however, the variability seen in the partitioning behavior for lead, nickel and vanadium confirms that a number of complex factors interact to control the percentages present in any given phase. These include: size distribution, clay mineralogy, redox potential at time of deposition, speciation and abundance of organic and sulfide compounds present in the bottom sediments, and the availability of iron and manganese compounds at the depositional site. Hence, no single variable exists that can be used as a "predictor" for partitioning behavior. Further, neither can the elements position in the Periodic Table be used as a guide to its partitioning. Nickel and copper, elements 28 and 29, are similar in electronic chemistry but are seen to display obviously different partitioning behavior in the three samples. This would strongly suggest that their manner of partitioning is probably a function of variables existing at the sediment-water interface at the time of deposition.

Correlation Analysis.-- Correlation analysis of all metals with each other and total carbon, redox potential, conductivity, sorting, percent clay and percent sand was carried out to see if any apparent relationships existed among these variables. Zinc, manganese, vanadium, chromium, aluminum and iron all showed strong correlations with percentage of clay in the sample but, unexpectedly, nickel, barium and copper did not. The latter three elements, in fact, showed no correlation coefficients with any variable greater than 0.4. The cause of this is unclear but, in the case of barium (at least in Lake Borgne) may result from the fact that the metal is not partitioned in clays, iron and manganese oxides or organic compounds but rather is present as a non-indigenous material (drilling mud) from the numerous oil wells that are present. This behavior is opposite to that previously found for the element in Mobile Bay (see Isphording, 1982). Zinc and iron also

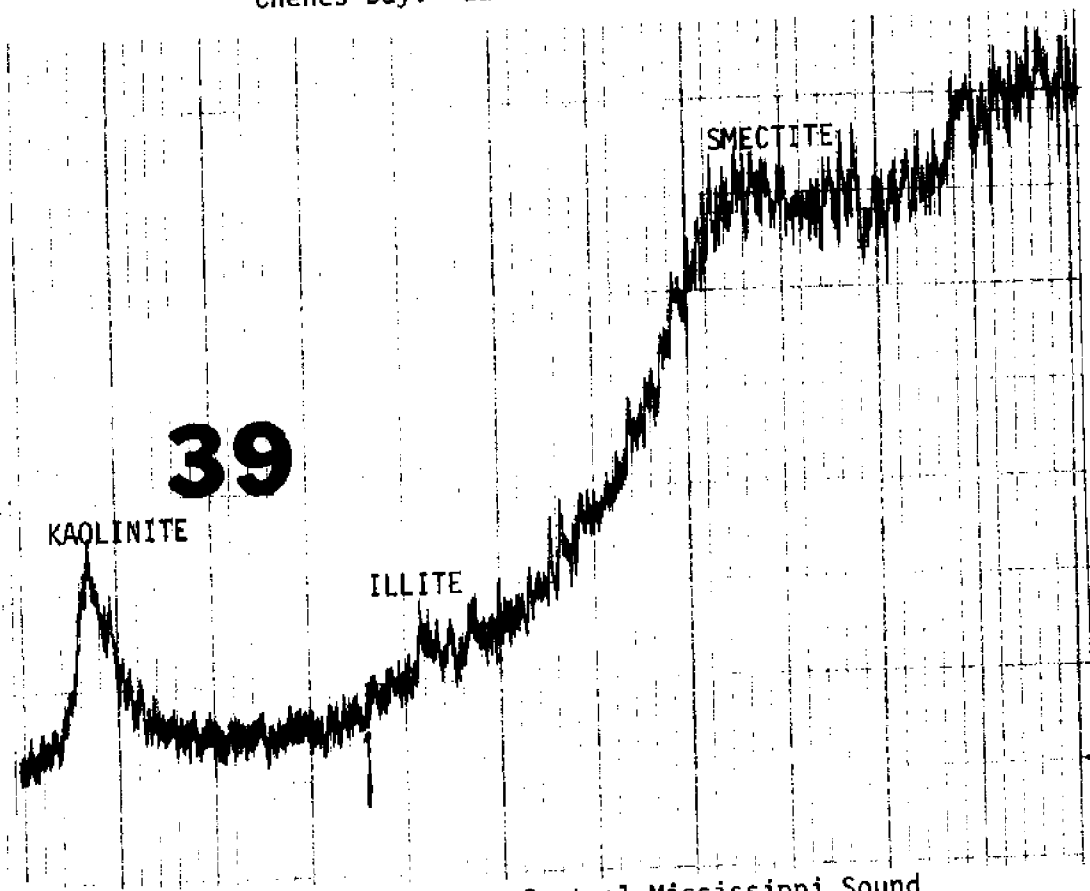
were observed to correlate strongly (greater than 0.6) with the percent of carbon in the sample. This correlation may simply reflect the large quantity of these metals that customarily partition with the organic phase.

Clay Mineralogy

The clay mineral suite of Mississippi Sound consists, dominantly, of the minerals smectite, illite (clay mica), and kaolinite. Other minerals detected included chlorite, mixed layer clays and, in eastern Mississippi Sound, trace amounts of zeolites. The latter are also present in small amounts in the clay mineral suite of Mobile Bay and their presence in the eastern portion of the sound undoubtedly evidences the transport of material from Mobile Bay, via Pass aux Herons. Information on the clay mineralogy of the sound may be found in studies by Reynolds and Thompson (1976), Milne and Schott (1956) and Isphording and Lamb (1980). Overall trends within the sound tend to show higher percentages of smectite toward the east and higher kaolinite contents to the west. Elevated smectite amounts in the Eastern Sound again reflects, at least in part, a Mobile Bay source. Rivers draining into Mobile Bay drain the sixth largest watershed area in the United States (120,000 square kilometers), much of which consists of rocks of Paleozoic and Precambrian age. The clay mineral suite is dominated by smectite clay hence, not surprisingly, that of Mobile Bay (and Eastern Mississippi Sound) is similarly rich in smectite. Approximate percentages for the various clays in the Eastern Sound are as follows: Smectite, 70 percent; Kaolinite, 20 percent and Illite, 10 percent. Further to the west, kaolinite becomes more abundant and was the dominant mineral in samples collected north of Horn Island (Kaolinite, 55 percent; Smectite, 40 percent and Illite, 5 percent). This mineralogy reflects reworking of older Pleistocene deposits in the Gulf and also material brought in by the Pascagoula, Escatawpa and Tchoutacabouffa Rivers. Samples from Western Mississippi Sound and from Lake Borgne show a return to the dominance of 14 angstrom

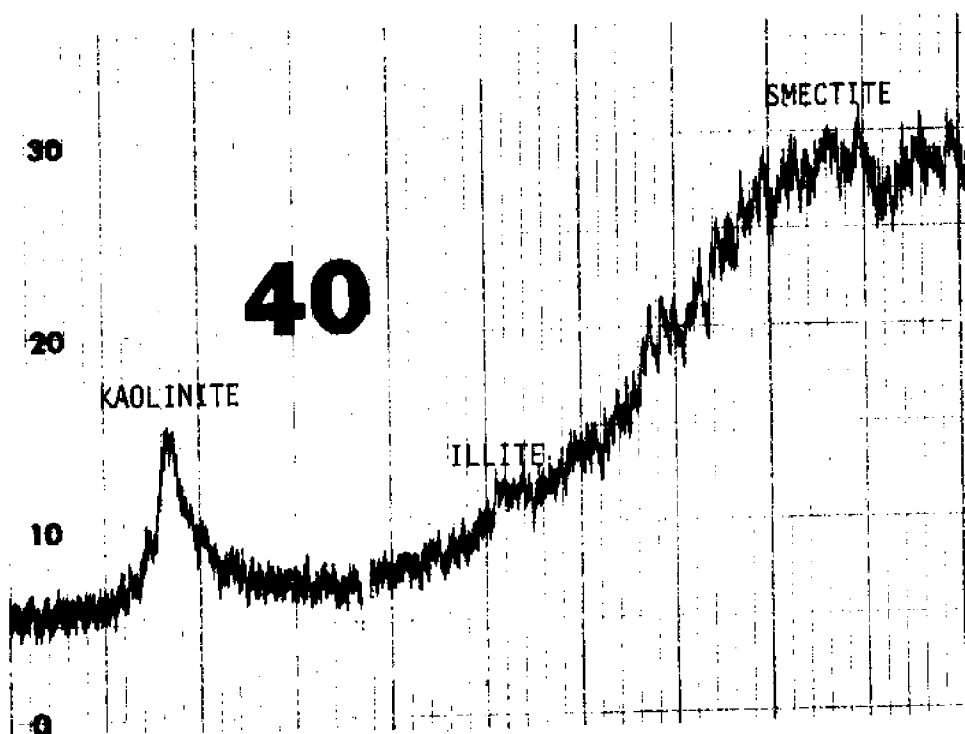


Sample 18 - just offshore of Grand Batteur Island (Point aux Chenes Bay. Eastern Mississippi Sound.

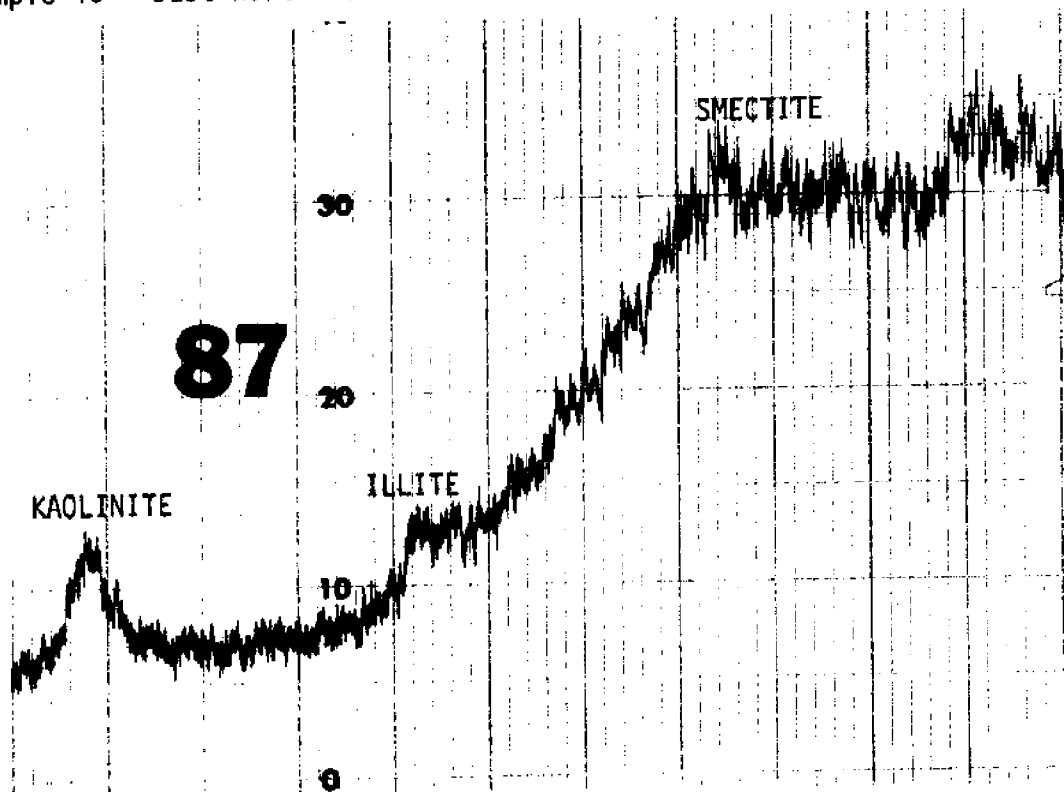


Sample 39 - Pascagoula Bay, Central Mississippi Sound

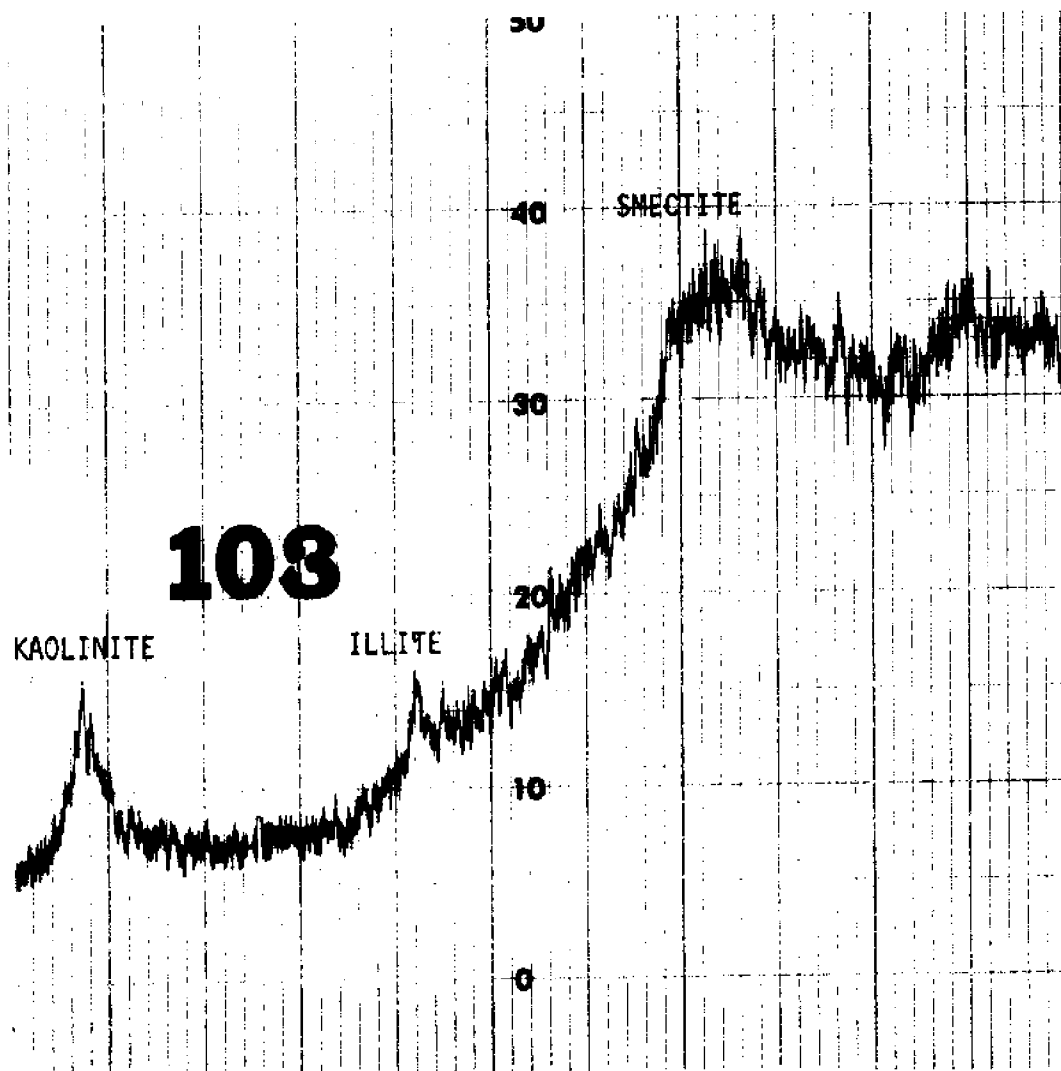
Fig. 8.-- X-ray diffractograms of Mississippi Sound sediments.



Sample 40 - Just north of Horn Island, Central Mississippi Sound



Sample 87 - One mile south of mouth of St. Louis Bay, Western Mississippi Sound.



Sample 103 - One mile south of mouth of Pearl River,
Lake Borgne.

clays with Smectite comprising approximately 55 percent, Kaolinite, 35 percent and Illite approximately 10 percent in these samples. Elevated Smectite levels in these samples can be traced to material derived from both the Pearl River system and that brought in from Lake Pontchartrain through the Rigolets Channel. Typical X-ray diffractograms are presented in Figure 8 for each region of the sound.

Carbon Analyses

Organic Carbon.-- The results of carbon analyses, both for total organic carbon (TOC) and for carbonate carbon were in essential agreement with those observed by O'Brien (1980). Organic carbon ranged from 0.0 percent in high energy areas (beaches and tidal passes between barrier islands) to 6.03 percent for one sample collected in Rigolets Channel, near its entrance to Lake Borgne. Other samples having in excess of 2.0 percent included those from St. Louis Bay (one analysis indicating 3.54 percent), those in, and near the mouth of, Biloxi Bay and a number of samples collected near the mouth of the Pascagoula River. From an overall standpoint, organic carbon was found to increase in a westerly direction, with lowest values present in the Eastern Sound and highest levels in Lake Borgne (see Table 2 and Figure 9).

<u>Area</u>	<u>Mean Total Organic Carbon</u>	<u>Mean Carbonate Carbon</u>	<u>Mean Total Carbon</u>
Eastern Sound	0.73	0.93	1.68
Central Sound	0.79	0.91	1.74
Western Sound	0.81	0.52	1.45
Lake Borgne	0.90	0.36	1.24

Table 2.-- Organic carbon, carbonate carbon and total carbon levels for Mississippi Sound (in percent).

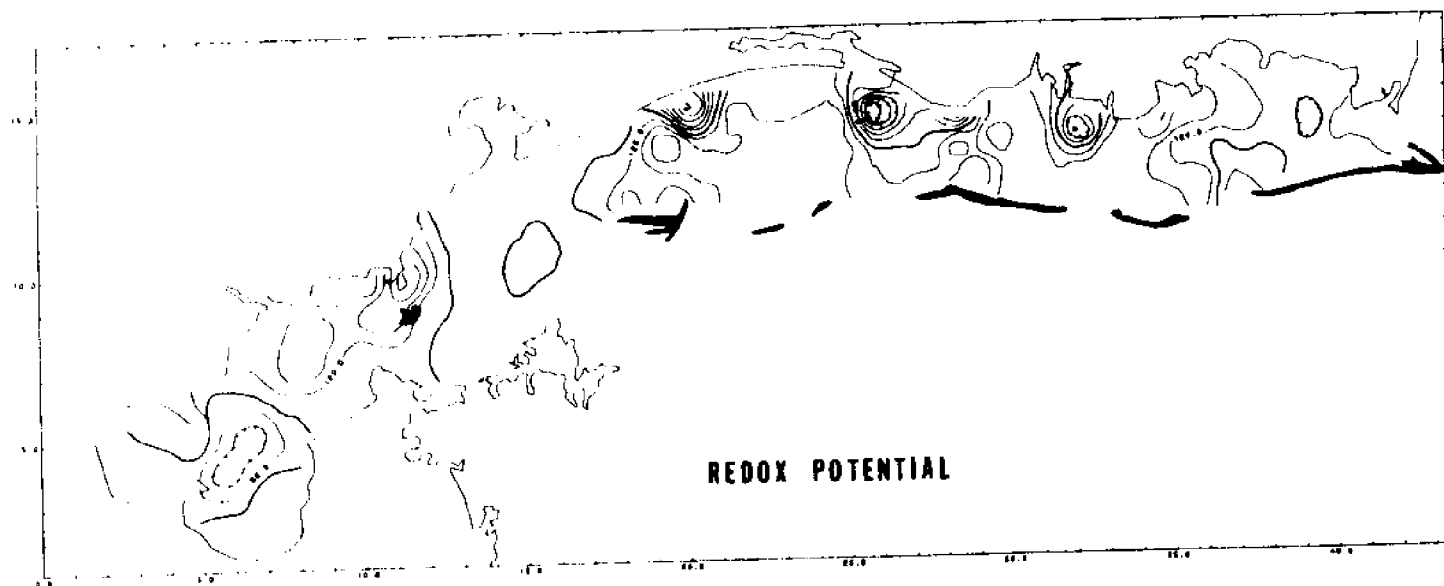
Carbonate Carbon.-- Carbonate carbon was found to behave in a manner opposite to that of organic carbon in that there was a distinct decrease in a westerly direction (see Table 2). Highest values (those greater than 1.0 percent) were observed in

Eastern Mississippi Sound, associated with oyster reefs. Similar elevated values were also obtained for samples collected near reefs near Pass Christian. Lowest amounts (less than 0.1 percent) were found immediately behind Dauphin Island and in the area south (and west) of Deer Island.

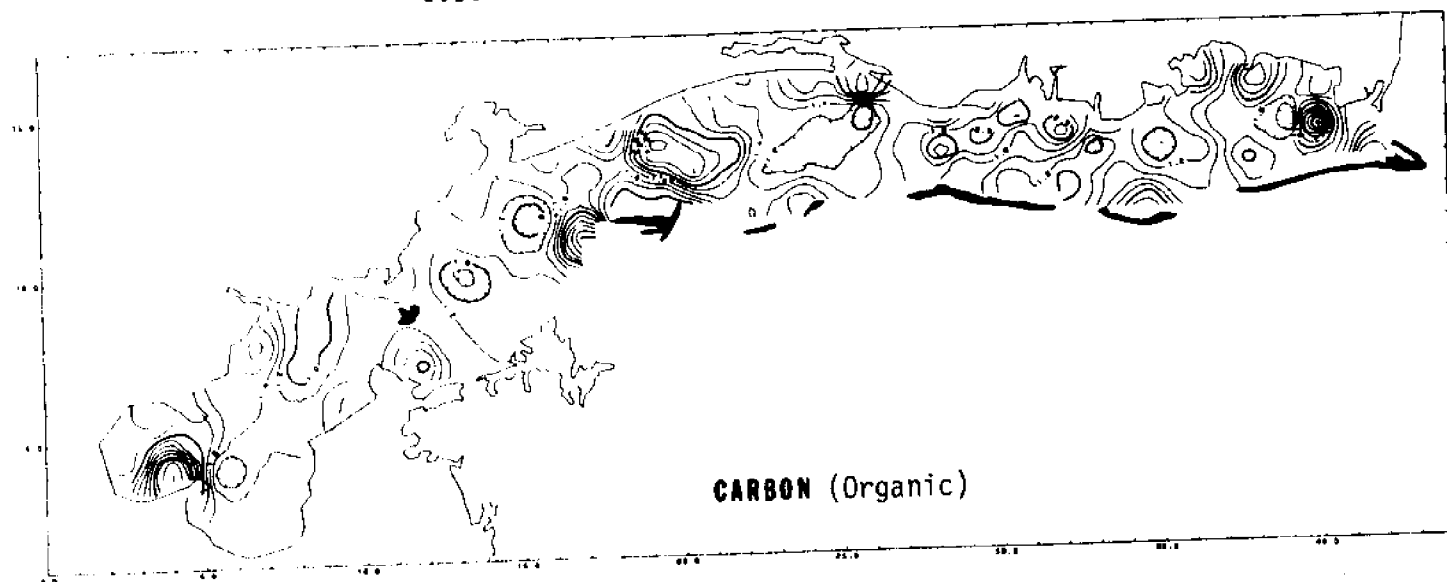
DATA STORAGE

The information (and maps) included in this report have been stored in the Department of Geology Save Library File at the University of South Alabama Computer Center. All maps, excepting the sediment map (Fig. 2), can be generated at any scale using a Nicolet-Zeta, 3653SX plotter, owned by the Geology Department. Additional information available includes data on the spatial distribution of redox potential and conductivity (Fig. 9), as well as temperature, dissolved oxygen and pH information that was not included in this report. Persons interested in obtaining these maps, or enlargements of those included in this report, should contact the writer at the following address:

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C.I. = 20



C.I. = 0.2 percent

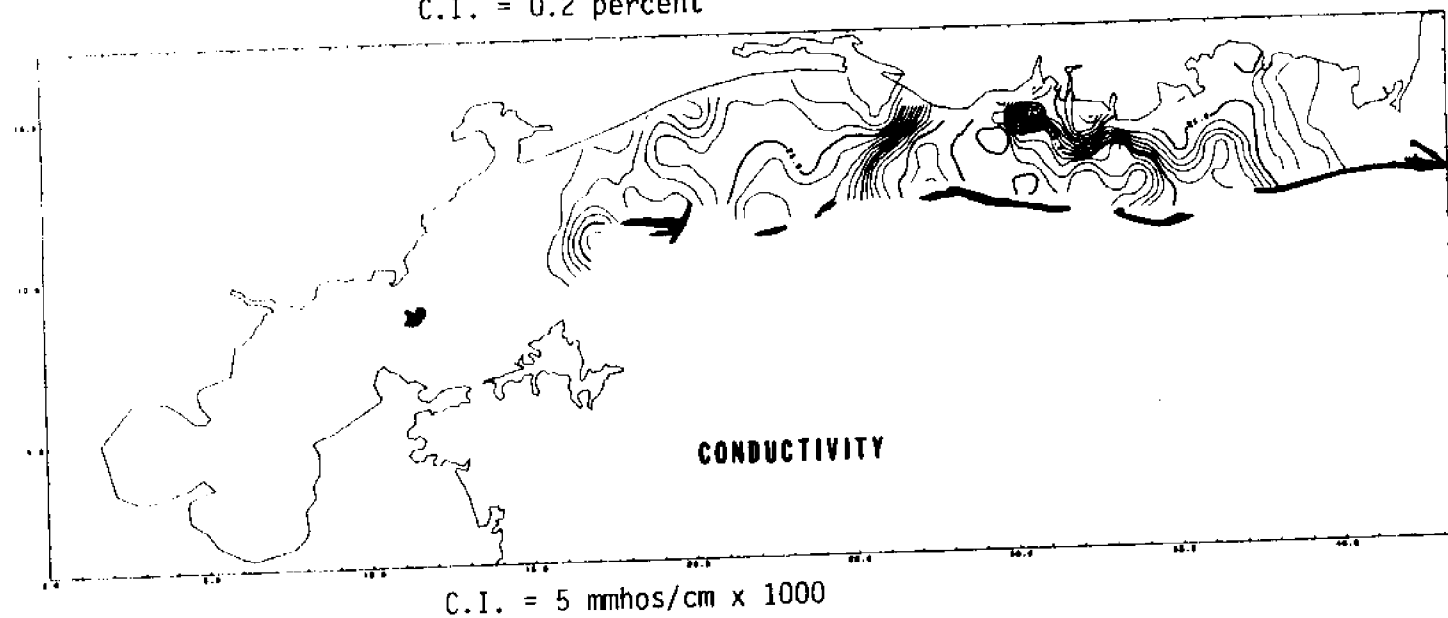

$$C.I. = 5 \text{ mmhos/cm} \times 1000$$

Fig. 9.-- Eh (redox potential), organic carbon and conductivity variation in Mississippi Sound.

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