

Geochemistry of Bottom Sediments Matagorda Bay System, Texas

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BUREAU OF ECONOMIC GEOLOGY

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GEOCHEMISTRY OF BOTTOM SEDIMENTS-MATAGORDA BAY SYSTEM, TEXAS

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ABSTRACT

Approximately 800 sediment samples from stream beds and bay bottoms of water bodies that compose the Matagorda Bay system were collected and analyzed. Shell-sand-mud ratios and total organic carbon content were determined, and 20 trace elements were detected.

In general, highest concentrations of trace elements coincide with deep areas of water bodies, areas of mud accumulation, and areas with high total organic carbon content. Zirconium, calcium, strontium, and mercury do not follow the distribution patterns of most other elements. Zirconium (Zr) is concentrated in sand located chiefly along bay margins and in tidal deltas; high Zr values result from the physical concentration of zircons as heavy mineral placers associated with sand bodies. Calcium and strontium distributions coincide with distribution of shell material. Mercury distribution is restricted to Lavaca Bay and northwestern Matagorda Bay.

When concentrations of 20 trace metals in the Matagorda Bay system are compared with concentrations of elements in the crust, shale or clay, and seawater, it is found that (1) Matagorda Bay sediment contains trace elements in about the same concentrations as crustal rocks and shale but exhibits concentrations higher than seawater, and (2) only two elements, boron and mercury, identified within bay-system sediment exhibited anomalously high concentrations. These high concentrations are believed to result from man's activities within the Texas Coastal Zone.

INTRODUCTION

The Texas Gulf shoreline comprises approximately 370 miles (595 km) of erosional deltaic headlands, barrier islands, peninsulas, and one small, active oceanic delta. Between the barrier islands and peninsulas and the uplands are numerous estuaries, bays, and lagoons. Larger water bodies—such as Trinity-Galveston, Matagorda, and Corpus Christi Bay systems—occupy river valleys that were eroded during Pleistocene glacial episodes. Some of the smaller water bodies that are elongate parallel to the Gulf shoreline—such as West Bay, East Matagorda Bay, Espiritu Santo

Bay, and south Laguna Madre--overlie Pleistocene drainage divides or abandoned Holocene deltas. These elongate water bodies originated when a part of the Gulf of Mexico was restricted landward of peninsulas and barrier islands.

Estuaries, bays, and lagoons are important to the people of Texas for recreation and revenue. Many uses are made of Texas coastal waters and the underlying substrate, including boating, sport and commercial fishing, shrimping, siting petroleum exploration and production platforms, filling wetlands with dredge material, and disposing chemical and solid waste.

Man's activities within the Coastal Zone, and within the drainage basin which supplies water and sediment to the coastal water bodies, have a direct and immediate effect upon the physical, chemical, and biological character of estuaries, bays, and lagoons. Some of man's activities are reflected in the bay sediment and associated trace metals.

Objectives of this study are: (1) to map sediment distribution within the Matagorda Bay system; (2) to relate sediment type to bathymetry, areas of sediment input, and processes operating within the bay; (3) to determine the distribution and concentration of organic carbon and trace metals; (4) to establish the relationships among organic carbon, trace metals, and sediment type; and (5) to delineate areas of anomalously high trace-metal concentration. High trace-metal concentration should indicate wastes introduced into the bay system by man. Because of toxicity it is important to know the extent and concentration of critical heavy metals, such as mercury.

Matagorda Bay was selected for this study because it is a bay system that has been less influenced by man's activities. Consequently, sediment and trace-metal distribution determined from this study provides a base line for subsequent comparative studies. This is the second part of a two-part study made by the Bureau of Economic Geology in cooperation with the General Land Office. The first study (McGowen and Brewton, 1975) documented direction and rate of change of Gulf and mainland shore-lines and presented some ideas on probable causes of shoreline erosion. Sampling of bay bottom sediment was conducted between June 1972 and June 1973. Chemical analyses were made from 1972 to 1973, and determination of mud-and-shell ratio of sediment samples was made from 1973 to 1974.

TEXAS COASTAL WATERS: GENERAL STATEMENT

Texas bays, estuaries, and lagoons are separated from the Gulf of Mexico by a system of barrier islands and peninsulas. Larger bays and estuaries occur along the central and upper parts of the Texas Coastal Zone; size of bays generally decreases along the lower coast. The present size of bays was predetermined to a large degree by the size of Pleistocene rivers which eroded valleys now occupied by bays and estuaries. Shoreline erosion, which has occurred since the sea reached its present level, has enlarged the bays.

Sediment is deposited in bays, estuaries, and lagoons by rivers that discharge at the heads of bays, by eroding mainland shorelines, and by the Gulf of Mexico through tidal inlets (mostly under normal sea conditions) and across barrier islands and peninsulas during storms. Type of sediment delivered to the Coastal Zone by Texas streams is determined by climate and source area. Identifiable sediment deposited in bays, estuaries, and lagoons from the Gulf of Mexico is mostly sand, shell, and rock fragments eroded from the inner shelf, shoreface, and beaches by tropical storms and hurricanes.

Rainfall decreases from east to west across the state, and temperature and evaporation increase from east to west. These climatic conditions are reflected in (1) vegetation cover (dense in the east and sparse in the west); (2) the type of fluvial systems that traverse the Coastal Plain (continuously flowing sinuous streams in the east, and straight-to-sinuous flashy streams to the west); and (3) sediment delivered to the bays, estuaries, and lagoons (streams in the east are characterized by a high suspension-load/bed-load ratio, whereas streams in the west have a high bed-load/suspension-load ratio).

Texture of bay, estuary, and lagoon sediment is generally (1) coarsest at river mouths, along bay margins where erosion of Pleistocene deposits is prevalent, near tidal inlets, and adjacent to barrier islands and peninsulas; and (2) finest in the deep bay-center areas. The relative proportion of mud (fine-grained sediment) to sand (coarse-grained sediment) is greatest in the bays of the upper Texas coast and least in the bays and lagoons of the lower coast; this is chiefly a reflection of decreasing rainfall from east to west across the state.

When all Texas bays, estuaries, and lagoons are considered, non-terrigenous sediment composes an insignificant part of the fill. Non-terrigenous deposits occur in shell beaches, spits, and berms situated along bay margins and in oyster reefs. Oyster reefs were numerous in the area just west of the Colorado River delta system on the

east and Copano Bay on the west. Bays in this area are typified by salinity that ranges from almost fresh to marine. Salinity varies directly with the volume of fresh-water inflow.

Some bay-margin deposits are characterized by high shell content. These deposits were reworked by wave and current activity and are representative of slow sediment accumulation rates and/or high rates of biological productivity. Oyster reefs are commonly flanked by shell debris, and oyster shell spits develop downcurrent from some reefs and headlands.

Depths of bays range from about 2 to 16 feet (0.6 to 5 m). The larger bays are the deepest. Depths of bays are maintained by wave activity, which resuspends much of the fine sediment, and by removal of fine sediment from the bays through tidal inlets. Other processes that aid in depth maintenance are compaction of recent bay muds and subsidence related to tectonics, compaction of older sediments, and man's activities.

MATAGORDA BAY AREA: GENERAL SETTING

The Matagorda Bay study area includes deltaic headlands, peninsulas, barrier islands, large bays and estuaries, and gently seaward-sloping uplands that terminate at the mainland shoreline. Matagorda Bay system and its environs include parts of Matagorda, Calhoun, Victoria, and Jackson Counties (fig. 1). Size of the area is approximately 2,000 square miles (5,200 km²)--1,470 square miles (3,822 km²) of uplands, 455 square miles (1,183 km²) of bays and estuaries, and 75 square miles (195 km²) of peninsulas, barrier islands, and tidal deltas (McGowen and Brewton, 1975).

Physiographic elements that constitute the area are Matagorda Peninsula and Matagorda Island; Pleistocene uplands; rivers and small streams that dissect the uplands and deltas at the mouths of these streams; and bays whose average and maximum depths are approximately 6 and 14 feet (2.7 and 4.3 m), respectively. Most of the bay system that lies west of the Colorado River delta is characterized by water bodies that are elongate approximately perpendicular to the Gulf shoreline. These water bodies (estuaries) occupy drowned river valleys; small to moderate streams discharge at the heads of most of them. The northeast-southwest elongate segment of the system developed within a Pleistocene drainage-divide area, chiefly through the westward accretion of Matagorda Peninsula. The elongate northeast-southwest bay segment, which includes all of East Matagorda Bay and part of west Matagorda Bay, is in effect a shallow lagoon.

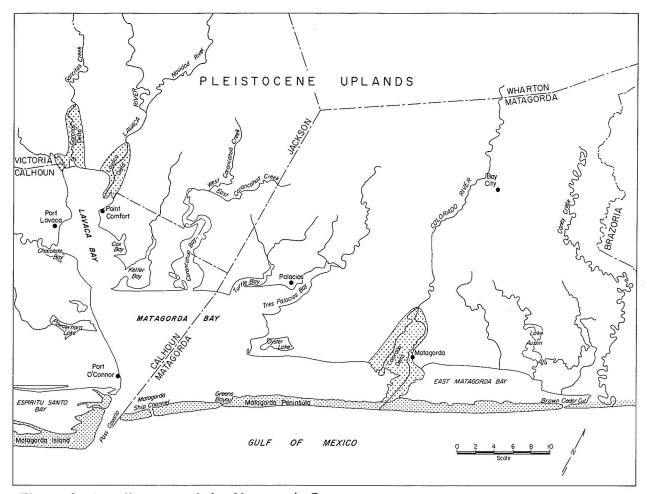


Figure 1. Locality map of the Matagorda Bay area.

Several rivers and creeks discharge water and sediment into the Matagorda Bay system. Larger streams, such as the Colorado and Lavaca Rivers and Garcitas Creek, have constructed deltas along bay margins. The Colorado River delta, the largest of the deltas, has prograded across Matagorda Bay.

Climate of the Matagorda Bay area is humid subtropical (U. S. Department of Commerce, 1958 to 1969). Rainfall and temperature (fig. 2) are almost identical at four weather stations in the vicinity of Matagorda Bay. Rainfall distribution graphs show two peaks, one in June and one in September, that coincide with thunderstorm and hurricane occurrences, respectively.

Wind data collected at the Victoria weather station show surface winds to be chiefly onshore (fig. 3). Prevailing winds for the period 1951 to 1960 were from the south-southeast, whereas strongest winds during the same period were from the northwest.

Hurricanes and tropical storms are naturally occurring phenomena of the Atlantic, Caribbean, and Gulf Coast areas. Hurricanes are storms of tropical origin

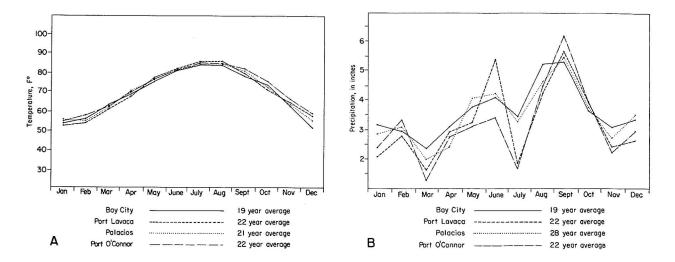
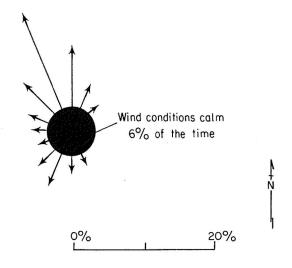


Figure 2. Temperature and rainfall distribution for Bay City, Port Lavaca, Palacios, and Port O'Connor. (A) Mean monthly temperature, (B) Mean monthly precipitation. (See U.S. Department of Commerce, Climatological Summary, Bay City, 1943-1961, and from Environmental Science Services Administration, U.S. Department of Commerce, Palacios, 1941-1968; Port Lavaca, 1947-1968; and Port O'Connor, 1948-1969.)

Figure 3. Percentage frequency of surface wind direction (annual). Data from Victoria Weather Station (U.S. Department of Commerce, Local Climatological Data, Victoria, Texas, 1958-1969).



with cyclonic circulation of 74 mph (119 km/h) or higher (Dunn and Miller, 1964). Hurricanes strike the Texas coast on the average of once every two years (Hayes, 1965, 1967). These storms strike most frequently during August and September. Effects of hurricanes on coastal environments have been discussed by Price (1956), Hayes (1965, 1967), Behrens (1969), Scott and others (1969), Andrews (1970), McGowen and others (1970), Brown and others (1974), and McGowen and Scott (1975). The role played by tropical storms and hurricanes is significant in sediment transport and deposition with respect to the Matagorda Bay system. Depending upon the location of

a storm center, sediment may be transported from the Gulf shoreface, beach, and barrier islands into the estuaries, bays, and lagoons; or sediment may be transported from these water bodies seaward through tidal inlets and storm channels during hurricane approach, landfall, and passage inland. Some hurricanes are accompanied by heavy rain that floods large areas of coastal lowlands. Under these flood conditions rivers transport large volumes of water and sediment to estuaries and bays.

In the northern Gulf of Mexico tides are chiefly diurnal (one high and one low water level each tidal day). Tidal range is low. The mean diurnal range is 1.7 feet (0.5 m) at Freeport Harbor and 1.4 feet (0.4 m) at Pass Cavallo (U.S. Department of Commerce, 1973). Tidal currents are an important sand-transporting mechanism in tidal pass areas. Within the bay system astronomical tides play a minor role in sediment transport. The wind generates waves (commonly 2 to 3 foot [0.6 to 0.9 m]) that suspend bottom sediment that may then be transported by wind-generated currents.

MATAGORDA BAY SYSTEM

Matagorda Bay system comprises numerous large and small water bodies. These are, from east to west, (1) East Matagorda Bay, (2) Lake Austin, (3) Matagorda Bay, (4) Oyster Lake, (5) Tres Palacios Bay, (6) Turtle Bay, (7) Carancahua Bay, (8) Keller Bay, (9) Cox Bay, (10) Lavaca Bay, (11) Powderhorn Lake, and (12) Espiritu Santo Bay (fig. 4). Water and sediment are supplied to the Matagorda Bay system through small to large streams. These are from east to west, (1) Boggy Bayou, (2) Live Oak Bayou, (3) Peyton Creek, (4) Big Boggy Creek, (5) Colorado River, (6) West Branch of the Colorado River, (7) Tres Palacios Creek, (8) Cashs Creek, (9) Turtle Creek, (10) Reed Creek, (11) Carancahua Creek, (12) Keller Creek, (13) Lavaca River, (14) Garcitas Creek, (15) Placedo Creek, (16) Chocolate Bay, and (17) Coloma Creek (fig. 4).

Bathymetry

Bathymetry of the Matagorda Bay system was determined from the following National Oceanic and Atmospheric Administration (NOAA) Nautical Charts: No. 889-SC (scale 1:40,000); No. 889 (scale 1:40,000); No. 11315 (scale 1:40,000); and No. 1284 (scale 1:80,000). Soundings depicted on these nautical charts represent depths at mean low water.

East Matagorda Bay ranges from a few inches to more than 4 feet (1.2 m) deep. Shoal areas are located adjacent to Brown Cedar Cut, an active tidal inlet (Piety,

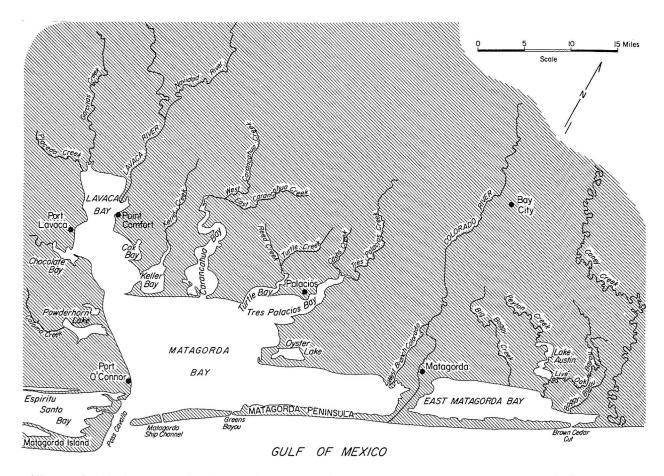


Figure 4. Major water bodies and associated contributory streams, Matagorda Bay area.

1972), and near the Colorado River where bay sediment represents the subaqueous extension of the Colorado River delta. The deepest part of the bay assumes an elongate trend that parallels the long axis of the water body.

The west part of Matagorda Bay includes a large water body that extends from the Colorado River delta westward to the Port O'Connor - Powderhorn Lake area. It is bound on the south by the Matagorda Peninsula, and to the west, north, and east, dominantly, by Pleistocene uplands. Water depths range from a few inches to approximately 14 feet (4 m). Most of the bay is approximately 10 feet (3 m) deep. Extensive shoal-water areas are located west of the Colorado River delta; a smaller shallow-water area is situated at Palacios Point.

Small tributary bays are shallow at bay heads and deepen generally toward bay mouths. Carancahua Bay is shallow at its mouth (2 to 4 feet, or 0.6 to 1.2 m) because of sediment accumulation through longshore drift processes. Maximum depths of Turtle and Carancahua Bays are about 4 feet (1.2 m), whereas the maximum depth of Tres Palacios Bay is more than 6 feet (1.8 m).

Maximum depth of Lavaca Bay is approximately 8 feet (2.4 m). Water is somewhat more shallow between Matagorda and Lavaca Bays because of spit elongation. Chocolate and Keller Bays are tributary to Lavaca Bay and have maximum depths of approximately 2 and 4 feet (0.6 to 1.2 m), respectively.

The eastern part of Espiritu Santo Bay is included in the study of the Matagorda Bay system. Extensive shoal areas to the west of Pass Cavallo are representative of the subaqueous extension of the flood tidal delta. To the west of the tidal delta, water depth increases to about 8 feet (2.4 m).

Water and Sediment Sources

Water and sediment are supplied to the Matagorda Bay system through natural and man-made tidal inlets, storm channels, major and minor streams that traverse the uplands, and runoff from the uplands. Sediment is also supplied by erosion of mainland shorelines. Water is exchanged between the bay system and the Gulf of Mexico through Brown Cedar Cut, the lower 1.5 miles (0.93 km) of the Colorado River; infrequently through Greens Bayou; Matagorda Ship Channel; and Pass Cavallo (fig. 4). Brown Cedar Cut, the only tidal inlet for East Matagorda Bay, has a maximum depth of about 8 feet (2.4 m); it rapidly decreases in depth seaward and bayward (Mason and Sorensen, 1971; Piety, 1972). Greens Bayou is a storm channel that is only open when hurricanes make landfall in the immediate area; it functions as an inlet for a few months following passage of a storm. Matagorda Ship Channel has a maintained depth of 36 feet (11 m). Because it is jettied, virtually no sand is transported from the Gulf of Mexico into the bay through it. The volume of water exchanged between the Gulf of Mexico and the Matagorda Bay system through Pass Cavallo has greatly decreased since the dredging of Matagorda Ship Channel (Harwood, 1973). The net result of the decrease is the shoaling of Pass Cavallo, which is now approximately 9 to 30 feet (2.7 to 9 m) deep.

FIELD PROCEDURES

More than 800 bottom-sediment samples were collected from the Matagorda Bay system using a 1-cubic-foot $(0.03~\text{m}^3)$ clam-shell sampler. Samples were taken on approximately 1-mile (1.6~km) centers both in the bays and for up to 20 miles (32.2~km) inland along navigable streams that discharge into the bays. Bottom-sediment samples were collected for textural analyses, determination of total organic carbon, and semiquantitative analyses for trace elements.

Proposed sample locations were plotted on navigation charts and topographic maps. Actual location of each sample station was determined by resection, using either a brunton compass or a sextant. Within large water bodies, such as west Matagorda Bay, where the shoreline could not be seen from the bay center, sample locations were estimated by steering a given compass heading, at constant speed, for a specific number of minutes.

Approximately 140 cubic inches (2,293 cm³) of sediment were placed in a plastic bag to be analyzed for determining (1) shell-sand-mud ratio, (2) trace element content, and (3) percentage of total organic carbon. The remainder of the sample was passed through a 2-mm screen to retain molluscs; samples were not treated with formalin to preserve the soft parts of the live molluscs.

LABORATORY PROCEDURES

At the Bureau's sedimentation laboratory, samples were split for determination of (1) total organic carbon, (2) trace metal content, and (3) shell-sand-mud ratio. Total organic carbon percentage for each sample was determined by the Bureau's mineral studies laboratory; trace metal geochemistry was performed by the U.S. Geological Survey at Denver, Colorado.

Sediment Analysis

The procedure for determining the shell-sand-mud ratio for Modern sediment from the Matagorda Bay system was adapted from Folk (1974). Each bulk sample was weighed dry, then immersed in a calgon solution and disaggregated with a mechanical mixer. Next the sample was wet-sieved through U.S. Standard Sieve Mesh Nos. 20 $(0.25\ \phi)$ and 230 $(4.0\ \phi)$. Materials retained on the 20- and 230-mesh sieves were then designated shell and sand fractions, respectively. Sediment that passed through the 230-mesh sieve was collected in the pan and represented the mud fraction (less than $4.0\ \phi$). The respective fractions (>0.25\ \phi, >4.0\ \phi, and <4.0\ \phi) were then dried and weighed, and the shell-sand-mud ratio was calculated. Sand that was retained on the 230-mesh sieve was treated with concentrated hydrochloric acid (HCL) to remove calcareous shell material. The remaining sediment represented total percentage terrigenous sand. Weight of shell retained on the 20-mesh sieve was added to weight of shell material retained on the 230-mesh sieve to derive the total percentage of shell.

Several samples, exhibiting the full spectrum of shell-sand-mud ratios of Matagorda Bay system deposits, were subjected to complete grain-size analysis. The bulk sample was dried, weighed, immersed in calgon solution, then disaggregated as described above. The sample was then wet-sieved through a nest of 35-, 50-, and 230-mesh sieves ($1.0 \, \phi$, $1.75 \, \phi$, and $4.0 \, \phi$, respectively). Sediment retained on each of these screens was then dried and weighed. Sediment that passed through the 230-mesh sieve was transferred to a 1,000-ml cylinder and dispersed. Hydrometer analyses were performed as outlined in test method TEX-110-E (Texas Highway Department, 1962). Grain size diameters and percentages were then plotted on semilogarithmic paper and an accumulative curve was plotted from the data.

Trace Metal Determination

Bottom samples from the Matagorda Bay system were analyzed for 30 elements using a Direct-Current Arc Spark Emission Spectrograph (Grimes and Marranzino, 1968). This semiquantitative method is designed for geochemical reconnaissance work. Mercury content was determined by the mercury vapor detector method (Vaughn, 1967).

Sediment samples were sent to Dr. C. W. Holmes, U.S. Geological Survey at Corpus Christi, for determination of trace metal content. These samples were subsequently sent to Denver, Colorado, where they were processed using the six-step semiquantitative spectrographic method. The whole sediment sample was air dried, sieved through an 80-mesh $(2.5 \, \phi)$ screen, split, and pulverized. Ten mg of the prepared sample were mixed with 20 mg of graphite, then burned to completion using 12 amperes. Wavelengths of the contained elements were recorded on film, which was then compared with standard films for trace element determination.

Through semiquantitative spectrographic analyses, 20 out of a possible 30 elements that could be delimited by this process were found in quantities sufficient for their detection. Limits of detection are given in table 1 (table modified from Grimes and Marranzino, 1968).

Determination of Organic Carbon by Wet Combustion

Most of the sediment in the Matagorda Bay system contains remains of organisms (plant or animal) that accumulated with the sediment. Much of this organic material is no longer recognizable and occurs in the sediment as disseminated products of decomposition of tissue or skeletal material. Because of the nature and size of the

Table 1. Limits of analytical determination: 20 elements in Matagorda Bay system sediment (lower and upper limits ppm)

					
Element	Lower limit	Upper limit			
Boron	10	2,000			
Barium	5	5,000			
Beryllium	1*	1,000			
Calcium	500	200,000			
Cobalt	5	2,000			
Chromium	5	5,000			
Copper	2	20,000			
Iron	500	200,000			
Lanthanum	20	1,000			
Magnesium	200	100,000			
Manganese	10	5,000			
Niobium	10*	2,000			
Nickel	2	5,000			
Lead	10	20,000			
Strontium	50	5,000			
Titanium	10	10,000			
Vanadium	10	10,000			
Yttrium	10*	200			
Zirconium	20	1,000			

^{*}Limit of lower range of detection is reached by beryllium, niobium, and yttrium.

Table 2. Relative composition of animal and plant tissue (after Gross, 1971).

	Carbon	Soft t	issues Phosphoru	Hard tissues
Phytoplankton	100	16	1.7	Opal (diatoms) CaCO ₃ (coccolithophores)
Zooplankton	100	16	2.4	Chitin Phosphate (apatite)
Bacteria	100	18	5.5	
Molluscs	100	21	1.5	CaCO ₃
Fish	100	23	3.8	Phosphate (apatite)
Mammals	100	18	8.9	
Angiosperms	100	6	0.5	

carbonaceous material, it is physically impossible to separate it from the sediment. As a consequence, most knowledge about abundance and composition of disseminated organic matter is derived from chemical analyses (Gross, 1971).

Organic matter contained in Matagorda Bay system deposits is assumed to be representative of tissue or skeletal debris. Tissue and decomposition products are chiefly carbonaceous compounds. Skeletal remains include carbonates, silica, or phosphate compounds (Gross, 1971). Elemental composition of some organisms is shown in table 2.

Carbon, the most abundant element, constitutes about half of plant and animal tissue on an ash-free basis. Organic carbon analyses provide the most sensitive and reliable test for abundance of biogenic material in sediment. Sulfur is a constituent of certain organic compounds, but its abundance in sediments is not a useful indicator of organic matter (Gross, 1971).

In addition to carbon, nitrogen, and phosphorus, organic matter comprises a complex of compounds with high molecular weights such as lipids, carbohydrates, proteins, pigments, and lignins. Matagorda Bay system sediment was not analyzed for these compounds because of the highly specialized techniques and equipment such analysis requires.

Each sediment sample was split and air-dried at room temperature, then ground until it was fine enough to pass through a 140-mesh $(3.25 \, \phi)$ sieve. Analyses for total organic carbon were determined from whole sediment samples; size fractionation was not performed in the laboratory. The wet-combustion method (Jackson, 1958; Gross, 1971) was used to determine organic carbon content of Matagorda Bay system sediment. The method shown in table 3 is used by Larry McGonagle, chemist, Mineral Studies Laboratory, Bureau of Economic Geology.

SEDIMENT DISTRIBUTION

Bottom sediment of the Matagorda Bay system comprises six sediment classes: (1) shell, (2) sand, (3) mud, (4) muddy sand, (5) sandy mud, and (6) muddy shelly sand (fig. 5). This sediment is derived from several sources such as major streams, shoreline erosion, the Gulf of Mexico notably during tropical storms, and biological activity within the bay complex (Byrne, 1975; McGowen and Brewton, 1975; McGowen and others, 1976a, 1976b; Wilkinson and Byrne, 1977; Wilkinson and McGowen, 1977).

Shell deposits accompany oyster reefs (reef flanks deposits), occur in some tidal inlets (such as between Matagorda and Carancahua Bays), and occupy some bay-margin areas where oyster clumps have been transported onshore (fig. 6). Shell deposits as

Table 3. Procedure to determine organic carbon by wet combustion.

- Place 2.0 grams air-dried sample (140 mesh) into a 300-ml Erlenmeyer Flask.
- Add 10 ml of 1 normal K₂Cr₂O₇ solution to each flask. Add 10 ml of 1 normal K₂Cr₂O₇ to an empty flask for use as a control. Add 20 ml of Ag₂SO₄ solution in concentrated H₂SO₄ (use fume hood) to each flask, including the control.
- 3. Heat each flask to 150°C within 1 minute.
- 4. Dilute each flask to 150 ml with distilled water.
- Transfer to a 250-ml centrifuge tube and centrifuge for 10 minutes at 2.200 rpm and return supernatant liquid to original 300-ml Erlenmeyer Flask.
- 6. Add to each flask
- (a) 10 ml of 85 percent H₃ PO₄
- (b) 0.2 gram NaF
- (c) 5 drops of diphenylamine indicator
- Back titrate with 1 normal FeSO₄ in dilute H₂SO₄; beyond the blue to green end point.
- 8. Calculate with the formula

% organic carbon = $\frac{\text{mI FeSO}_4 \text{ (control)} - \text{mI FeSO}_4 \text{ (sample) } 0.3}{\text{weight of sample}}$

Reagents*

- 1. Potassium dichromate (1 normal): Dissolve 49.04 grams reagent grade $K_2Cr_2O_7$ in distilled water and dilute to 1 liter.
- 2. Sulfuric acid silver sulfate solution: Add 25 grams reagent-grade $\rm Ag_2SO_4$ per liter of concentrated $\rm H_2SO_4$.
- 3. Ferrous sulfate sulfuric acid solution: Dissolve 278.0 grams of reagent-grade $FeSO_4 \cdot 7H_2O$ in water and add 15 ml of concentrated H_2SO_4 and dilute to 1 liter.
- Diphenylamine indicator: Dissolve 0.5 gram of diphenylamine indicator in 100 ml of concentrated H₂SO₄ and pour carefully into 20 ml of cold distilled water.

^{*}See Gross, 1971, p. 589.

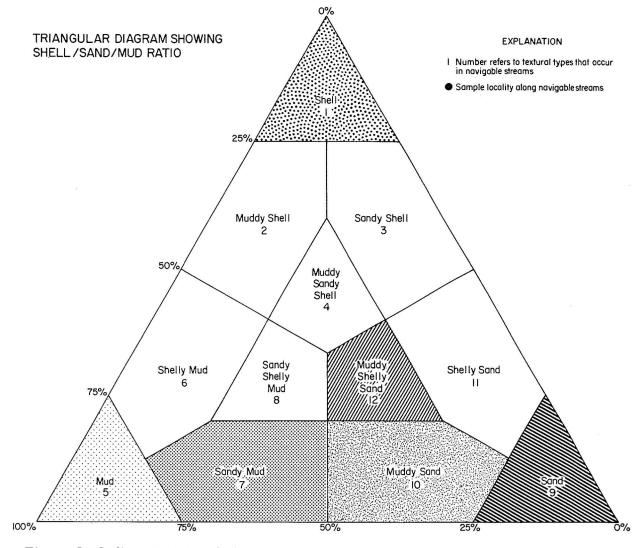


Figure 5. Sediment textural classes.

shown on this map consist mostly of valves of <u>Crassostrea virginica</u>; size range of shell is approximately 2.0 mm to 20 cm.

Sand as depicted in figure 6 consists of both terrigenous clastic material (predominantly quartz) and shell debris. Terrigenous clastic and shell sand range in diameter from 0.06 mm to 2.0 mm. The terrigenous clastic fraction falls almost entirely within the very fine and fine sand sizes. Sand is found chiefly in bay margins and tidal inlets; it accumulates in the shallow bay areas and in the high physical energy environments. Sand along the bay side of Matagorda Peninsula was eroded from the inner shelf and shoreface during hurricanes and was transported from the Gulf of Mexico through storm channels into bay margin areas. Sand is also transported from

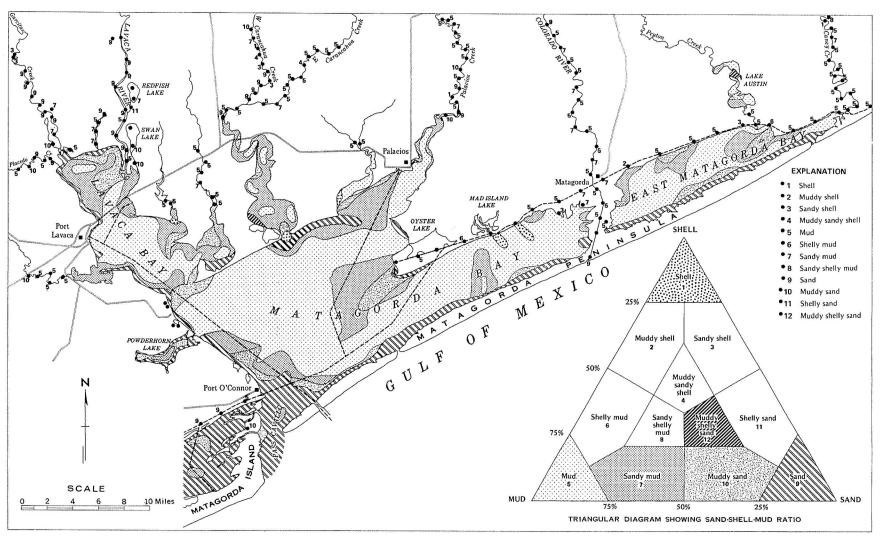


Figure 6. Sediment distribution map.

the Gulf of Mexico into Matagorda Bay through tidal inlets such as Brown Cedar Cut and Pass Cavallo. Elsewhere, sand along bay margins results from erosion of Pleistocene fluvial-deltaic and strandplain deposits that constitute the mainland bay margins, and from rivers that discharge directly into the bay system.

Mud is the dominant sediment type in the Matagorda Bay system. described in this report, is predominantly clay with admixtures of silt, sand, and shell (fig. 6). Deep parts of bays and areas farther from sites of sediment input are characterized by mud. Most of the mud is olive gray to greenish gray. In some baymargin areas where Pleistocene deposits are exposed, mud is reddish brown. Surface sediment in small streams, abandoned segments of large streams, and the Gulf Intracoastal Waterway is chiefly mud; sediment types for these areas are shown by a number that indicates a specific sediment type (fig. 5). Abandoned or dammed segments of large streams that are now sites of mud accumulation are Caney Creek (a former course of the Colorado River) and the lower reach of the Colorado River below the dam at Bay City. Smaller streams that intermittently discharge fresh water and sediment into the bays also have muddy bottom sediment. Most of the mud that covers the floors of the Matagorda Bay complex was transported to the area by the Colorado River, Palacios Creek, Carancahua Creek, Lavaca River, Garcitas Creek, and Placedo Creek (fig. 6).

Muddy sand, like sand, generally occupies the shallow parts of bays. Along the bay margin adjacent to Matagorda Peninsula, muddy sand is transitional between shoal-water sand and the deeper-water mud. In the Pass Cavallo area, muddy sand is associated with the flood-tidal delta and grades bayward into sandy mud. Elsewhere muddy sand has accumulated downcurrent from erosional shoreline segments (for example, the east end of East Matagorda Bay, southwest of Oyster Lake, southwest of Palacios, and between Lavaca and Matagorda Bays). At the head of Lavaca Bay sandy mud is associated with the Lavaca River and its delta.

Sandy mud normally accumulates in the shallow bay areas. Toward bay centers sandy mud grades into mud, and toward the bay margin it may grade into muddy sand and sand or it may abut the mainland shoreline (see Carancahua and Lavaca Bays). Sandy mud is rare in bay-margin areas adjacent to Matagorda Peninsula because of the dominant sand source from the Gulf of Mexico via hurricane storm-surge channels. Where physical processes have been less intense but more consistent, there generally has been a downcurrent transition from sand or muddy sand into sandy mud (for example, southwest of Oyster Lake, the vicinity of Pass Cavallo, and in the Palacios

area). Sandy mud is also associated with some rivers and deltas (for example, the Colorado delta which separates East Matagorda Bay and Matagorda Bay, and at the head of Lavaca Bay). Much of the sediment in Carancahua Bay was derived from erosion of Pleistocene fluvial-deltaic deposits exposed in the cliffed bay shoreline.

Muddy shelly sand is a minor bottom surface sediment type in the Matagorda Bay system. This sediment type was observed in only three areas: Lake Austin, alongshore east of Palacios, and near the west shore of the southwest part of Carancahua Bay. Rangia sp. is the dominant shell in Lake Austin, whereas Crassostrea virginica is dominant in the two other areas.

Distribution of various sediment types is controlled by (1) location of areas of sediment input (for example, river mouths and hurricane washover channels); (2) water depth (fine-grained material normally accumulates in deeper water); (3) interaction of fetch and prevailing winds (wind blowing across large, open, water bodies generates large waves that begin to feel bottom upon reaching shallow water and break, thereby redistributing sediment to generate sandy and shelly deposits); and (4) biological activity (sea grasses form obstructions to currents and tend to trap fine- and coarse-grained sediment, and molluscs build reefs). Sediment distribution can be used to predict the location of high concentrations of such elements as organic carbon, which has an affinity for mud; strontium, calcium, and manganese, which tend to be enriched in carbonate sediment (Krauskopf, 1967); and zirconium and rare earths, which are concentrated by physical processes in the sandy deposits. Furthermore, certain elements are concentrated in muds or clays by adsorption or substitution.

TOTAL ORGANIC CARBON

Sources of carbon in the surface sediment of the Matagorda Bay system are (1) upland plant material transported to the bays by streams, (2) marshes that flank much of the bay system, (3) marine grasses, and (4) soft and hard parts of animals that inhabit the bays. Streams discharge into Lake Austin, Powderhorn Lake, and Matagorda, Tres Palacios, Carancahua, Keller, and Lavaca Bays. Marshes and marine grass flats produce great amounts of organic material; some of this material is incorporated into surface sediment. The larger marsh areas occur along the shore of East Matagorda and Matagorda Bays in the area between Caney Creek and Oyster Lake, along the bay margin of Matagorda Peninsula, on Matagorda Island (west of Pass Cavallo), on the Colorado delta, and at the head of Lavaca Bay. Marine grasses are sparsely distributed throughout the bay system, but have developed best along sandy bay margins, particularly adjacent to Matagorda Peninsula and Matagorda Island.

Percentage of organic carbon was determined for each sample and these values were contoured at 0.5-percent intervals (fig. 7). Total organic carbon distribution exhibits the same general trend as sediment distribution. Values less than 0.5 percent occur along bay margins and adjacent to tidal inlets; these are, for the most part, areas of high sand percentages. Organic carbon in the range 0.5 to 1.0 percent occupies most of the bay area; associated sediment type is predominantly mud. Sediment with greater than 1.0 percent organic carbon occurs in patches in the deeper parts of bays and in the vicinity of river mouths, although not directly at the mouth.

It appears that high organic carbon in bay sediment is related to grain size rather than to proximity of rooted vegetation (marshes and grass flats). Particulate organic carbon may be adsorbed to fine-grained sediment, especially to clay minerals.

Sediment in streams that discharge into the Matagorda Bay system contains organic carbon in the same range as bay sediment. Streams characterized by sediment with a high mud content contain the highest percentage organic carbon. Caney Creek, Colorado River, Palacios Creek, East Carancahua Creek, and Keller Creek all have carbon contents greater than 1.0 percent. Surface sediment in West Carancahua Creek, Lavaca River, Garcitas Creek, and Placedo Creek is sand and contains from less than 0.5 to 1.0 percent organic carbon; most sediment contains less than 0.5 percent carbon.

Preservation of organic matter in sediment is a product of a reducing environment, and organic material serves as an important reducing agent. Partly decomposed organic material is a component of most sediment and makes up about 2 percent (by weight) of all sedimentary rocks (Krauskopf, 1967).

TRACE METAL DISTRIBUTION

Trace metals do not remain in solution for long periods of time since they are readily complexed with organic material or adsorbed by clay minerals. Trace metals may, at the time of their introduction into river and bay waters, already be fixed in mineral lattices and/or to particulate organic matter prior to deposition. Bottom sediment--rather than water samples, suspended sediment, or aquatic organisms--was sampled for this study because it is the most desirable medium for a synoptic trace-metal reconnaissance (Rickert and others, 1977). Water samples are perhaps the least desirable for trace-metal analyses because a water sample collected from a flowing river represents the conditions that exist at a single instant in time. If discharge of metal wastes is intermittent, periodic water samples collected downstream may show

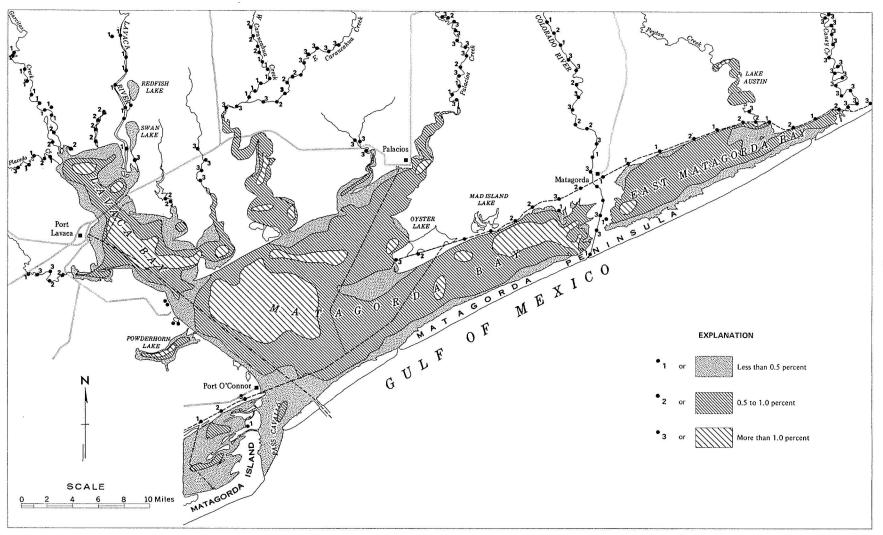


Figure 7. Organic carbon distribution map.

no pollution. If metal discharge were constant, water samples collected at some distance from the source may show no pollution because the metals could be adsorbed onto sediment particles during downstream passage.

Suspended sediment can be an excellent medium for determining trace metal occurrence during specific runoff events. Suspended sediment is too transitory, however, to provide a sound sampling basis for basinwide surveys.

Aquatic organisms are a poor medium for determining the basinwide occurrence of trace metals. A major deterrent in using organisms is the improbability of finding enough of a specific life stage of a selected organism at all predetermined sampling sites. Therefore, as in the work of Rickert and others (1977) bottom sediment of the Matagorda Bay system was chosen as the preferred sampling medium for trace-metal determination. Because this study was designed to establish baseline data, and because time and funding precluded monitoring or reoccupation of sample stations, the only samples that would provide adequate data were bottom sediment samples.

Distribution of trace elements in sediment is complex and follows no simple rule. Trace metal distribution is controlled in part by sediment size, sedimentation rate, location of trace-metal source, and the quantity and nature of associated organic material. Several studies suggest that one or more of the previously mentioned factors controls trace-metal accumulation (Hirst, 1962; Lineback and Gross, 1972; Collinson and Shimp, 1972; Frye and Shimp, 1973; and Volkov and Fomina, 1974).

More than 800 bottom sediment samples from the Matagorda Bay system were analyzed for 30 elements. Of the 30 elements, 20 were identified in sediment samples taken from the Matagorda Bay system. The following is a discussion of the distribution of these 20 trace metals.

Boron

Boron (B) content of sediment is supposedly related to salinity of the environment in which it accumulated (see Degens, 1965, p. 40). Boron content of ancient sediments has been used to distinguish between marine and fresh-water clays. Marine clays high in illite contain 100 to 200 ppm boron, whereas fresh-water clays contain 10 to 50 ppm. Clays in the Matagorda Bay system are dominantly montmorillonite. In the bottom sediment of the Matagorda Bay system, boron ranges from about 50 to about 200 ppm. These values are in the range of both fresh-water and marine clays as reported by Degens (1965). Low boron values, about 50 ppm, occur in bottom sediment throughout the bay system and in most of the sediment from fluvial systems (fig. 8).

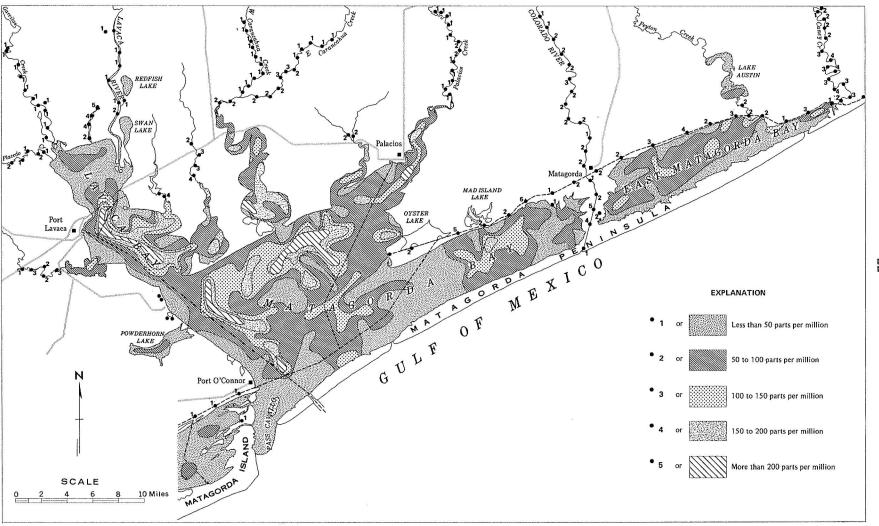


Figure 8. Boron distribution map.

Low values occur in both coarse- and fine-grained sediment, and in tidal passes where salinity is that of normal marine water, as well as at heads of bays where there is fresh-water influx. There is no orderly increase in boron content from bayhead to tidal inlet.

The higher B values, 150 to more than 200 ppm, fall mostly in the deep parts of the bays and are associated for the most part with mud or sandy mud. Sediment with high boron content corresponds closely with the highest values of organic carbon.

Most of the streams that discharge into the bay system have surface sediment with boron percentages less than 100 ppm. Caney Creek, an inactive stream, contains as much as 200 ppm B. Colorado River sediment is low in B except for two areas (both are mud and occur between the town of Matagorda and the Gulf of Mexico) where concentration is 150 to more than 200 ppm. Another area of high B concentration associated with fluvial sediment is an abandoned segment of the Lavaca River just north of the head of Lavaca Bay and west of Lavaca River. Highest B concentration here is greater than 200 ppm; the sediment type is sand.

Barium

Barium (Ba) concentration ranges from about 300 to about 500 ppm (lower limit of determination is 5 ppm) in both the bay system and in the streams that discharge into the bays (fig. 9). Low values (less than 300 ppm) are distributed throughout the bay system, along the bay margin as well as bay centers, and in all sediment types. High values (more than 500 ppm) fall in the same general areas as those for B, except in East Matagorda Bay where B values are low. High Ba concentrations are in the deep parts of Pass Cavallo; this trend transects sediment boundaries and the Gulf Intracoastal Waterway and Matagorda Ship Channel.

High Ba values within the bays are mostly associated with muds that lie in relatively protected areas (center of Carancahua Bay and Powderhorn Lake), or in areas that have been compartmentalized by a system of ship and barge channels (the large area in north Matagorda Bay).

Sediment in the fluvial systems exhibits the same range of Ba values as bay sediment. Abandoned channels (Caney Creek and part of Lavaca River) and rivers that have been dammed (the Colorado is dammed at Bay City) are characterized by Ba values in excess of 500 ppm. Sediments of unaltered streams have significantly lower Ba values.

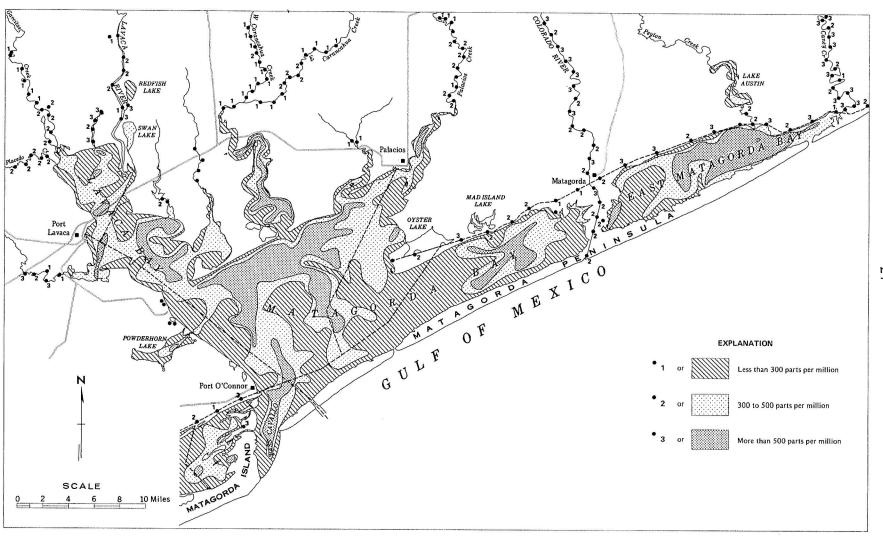


Figure 9. Barium distribution map.

Beryllium

Concentration of beryllium (Be) in the Matagorda Bay system and associated fluvial feeder systems is low, ranging from about 1 to about 3 ppm (fig. 10; lower limit of detection for Be is 1 ppm). The distribution pattern of Be is similar to that of B and Ba; lowest values tend to lie along bay margins, and highest values lie in the deeper mud-rich areas. The highest values (more than 3 ppm) coincide with high C, B, and Ba values.

Beryllium concentration is highest (around 3 ppm) in Caney Creek, and lowest (mostly less than 1 ppm) in West Carancahua Creek, Lavaca River, and Garcitas Creek. All the other streams are characterized by intermediate values (1 to 3 ppm).

Calcium

Values of calcium (Ca) are expressed as percentages of the total sample; percentages range from about 1 to about 5 (fig. 11; lower limit of detection for Ca is 500 ppm). If expressed as ppm, values would range from about 10,000 to about 50,000. Lowest Ca values are found in sediment along bay margins and bayheads. Bay-margin deposits are mostly sands, and those at bayheads (where streams debouch into the bays) are mostly sandy muds.

Calcium values in the range of 1 to 3 percent are dispersed over a large area of the bay system. Calcium in this range occurs in sediment of all textural types.

Distribution of calcium in the 3-to 5-percent range coincides with trends of ship and barge channels, oyster reefs, shell spits and beaches, and some tidal inlets and bay bottoms that have been dredged for shell. Highest Ca values (more than 5 percent) fall in the same areas as Ca in 3- to 5-percent range. High Ca values occur in sediment containing a relatively high shell content.

Fluvial deposits are characteristically low in Ca. Most sediment contains less than 1 to 3 percent Ca. Values of 3 to greater than 5 percent are dominant in the Colorado River; these high values result from a saltwater wedge that moves upriver toward Bay City and from the local proliferation of molluscs such as <u>Mulinia lateralis</u>. Samples from other streams (for example, Caney, Palacios, West Carancahua, Garcitas, and Placedo Creeks) have Ca values greater than 5 percent; these values reflect local presence of <u>Rangia sp.</u> and fresh-water clams.

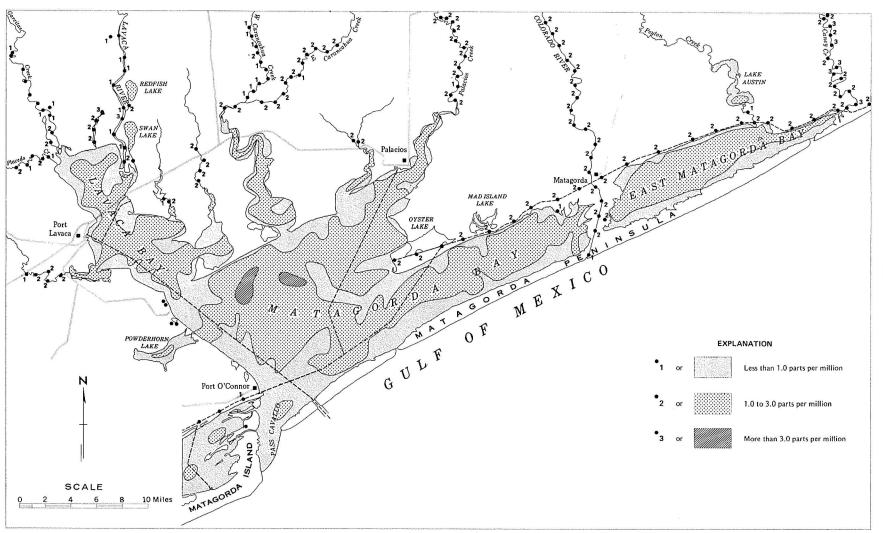


Figure 10. Beryllium distribution map.

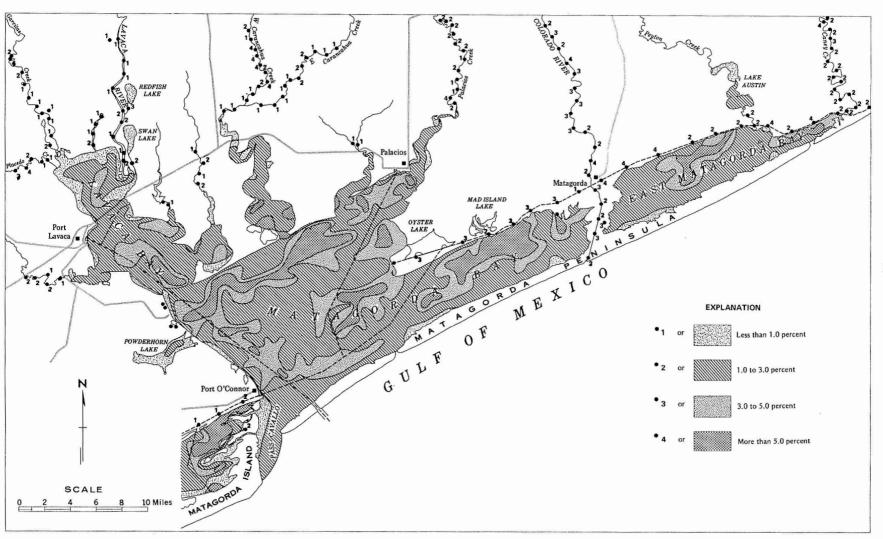


Figure 11. Calcium distribution map.

Cobalt

Sediment within the Matagorda Bay system contains cobalt (Co) in the range of about 10 ppm to approximately 20 ppm (fig. 12; lower limit of detection for Co is 5 ppm). Streams that discharge into the bay system have sediment with Co values that range from about 10 to more than 15 ppm. There are, however, concentrations of Co in the 15 to more than 20 ppm range in a few stream sediment samples.

Most of the bottom sediment in the bay system is characterized by less than 10 ppm Co. These values occur in all water depths (from shallow bayhead to the deeper bay centers, tidal inlets, and ship channels) and in all sediment textural types.

Cobalt in the 10 to 15 ppm range has a smaller area of distribution than the less than 10 ppm range and resides for the most part along bay axes. Sediment associated with 10 to 15 ppm Co is mostly mud; other textural types are sandy mud and muddy sand.

Most of the highest percentages of Co (15 to more 20 ppm), like most of the previously mentioned heavy metals, occur in deeper parts of bays in mud and are closely associated with areas of high organic carbon content. Some areas of high Co content occur with muddy sand and where organic carbon content is less than 1 percent.

Values of 15 to greater than 20 ppm Co are rare in fluvial sediment. Some sediment in Keller and East Carancahua Creeks contains 15 to 20 ppm Co. Sediment type is mud and muddy sandy shell, respectively, and C content is more than 1 percent. Highest concentration of Co in fluvial deposits is in West Carancahua Creek where sediment types are shell and muddy shelly sand and C concentration is 0.5 to 1 percent.

Chromium

Bay and fluvial sediment contains about 50 to about 70 ppm Cr (fig. 13; lower limit of determination for Cr is 5 ppm). Distribution of Cr follows the same general trend as most of the previously mentioned heavy metals. Lower concentrations occur in bayheads, bay margins, and tidal inlets. Higher Cr concentrations (50 to more than 70 ppm) parallel bay axes, and, for the most part, are associated with mud that resides in the deeper bay segments. All sediment types contain Cr in concentrations less than 50 ppm.

Chromium content of most of the fluvial sediment is less than 50 ppm. Most streams that debouch into the Matagorda Bay system contain sediment with Cr concentrations more than 70 ppm. Only one of these streams' sediment types was sand; each of the others was mud. In addition to being associated with predominantly fine-grained sediment, the high Cr values corresponded with C values of 1 percent or more.

Copper

Copper (Cu) has a distribution pattern similar to that of Cr. Concentrations of copper in sediment of the bay and fluvial systems range from about 10 to approximately 20 ppm (fig. 14; lower limit of Cu determination is 2 ppm). Like Cr, Cu occurs in low concentrations (less than 10 ppm) in all bay segments, in almost all sediment types, and in the shallow as well as the deep parts of bays. The higher Cu values (10 to more than 20 ppm) are distributed in a pattern almost identical to that of Cr.

Highest Cu values (more than 20 ppm) are detected in Caney Creek, Colorado River, East and West Carancahua Creeks, Keller Creek, active Lavaca River and its abandoned segment to the west, and Placedo Creek. The sediment that contains high Cu concentrations is mud, sandy mud, sand, and sandy shell. Total organic carbon values range from less than 0.5 to more than 1 percent; the relationships among Cu content, sediment texture, and percentage organic carbon are not one to one.

Iron

Iron (Fe) concentrations range from about 3 to about 5 percent (fig. 15; lower limit of Fe determination is 500 ppm). Low values (less than 3 percent) in the bay system are detected in all sediment types, and in the shallow as well as deep parts of the bays. Higher concentrations of Fe (3 to more than 5 percent) tend to be in the deep parts of bays, and iron concentration of more than 5 percent is restricted almost exclusively to the mud facies. There are similarities in the distribution of the highest concentrations of Cr, Cu, and Fe.

Fluvial sediment containing more than 5 percent Fe occurs in Caney Creek, Colorado River, Keller Creek, Lavaca River and its abandoned river segment west of it, Placedo Creek, and Chocolate Bay (see fig. 4 for location). Approximately 90 percent of the fluvial deposits containing more than 5 percent Fe is mud; the rest is sand. High iron concentrations are not restricted either to sediment with high organic carbon content or to mud.

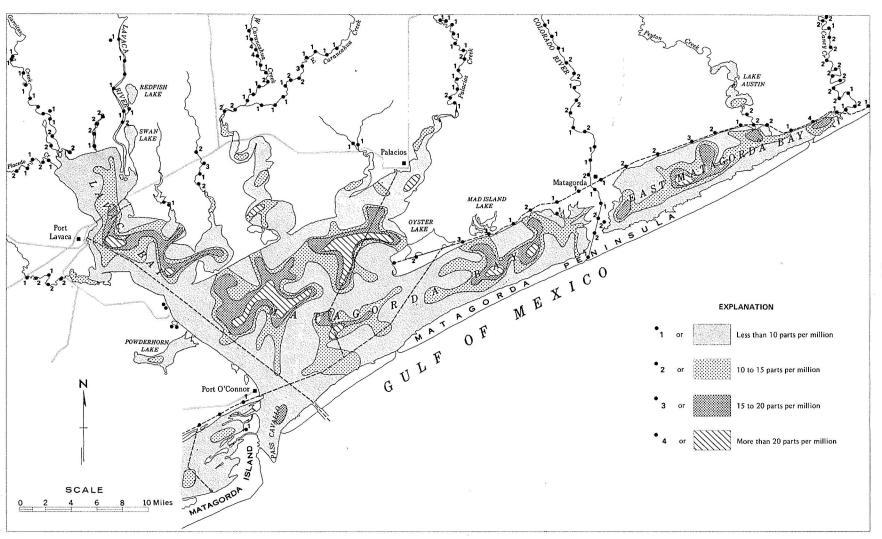


Figure 12. Cobalt distribution map.

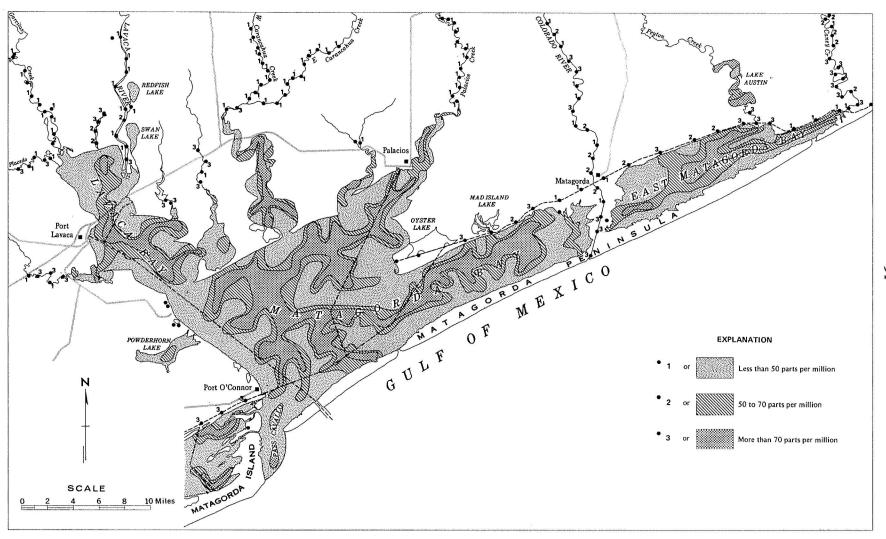


Figure 13. Chromium distribution map.

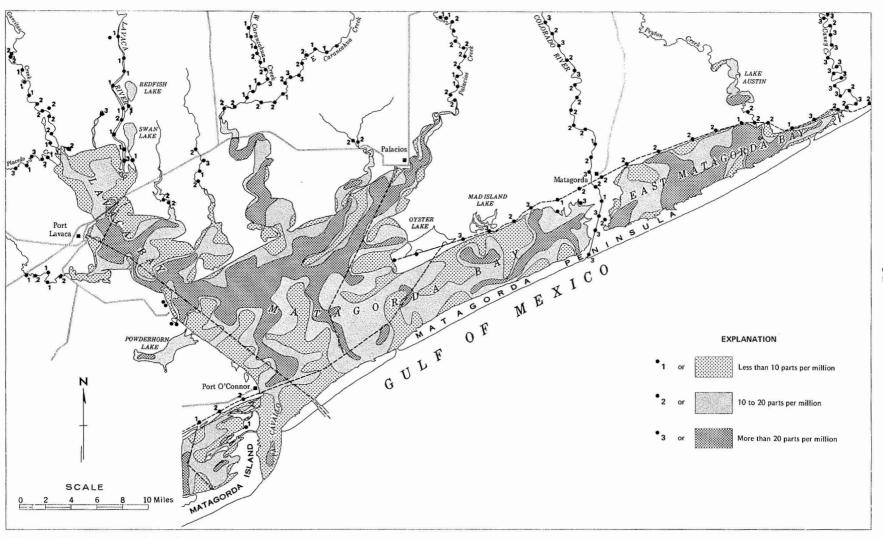


Figure 14. Copper distribution map.

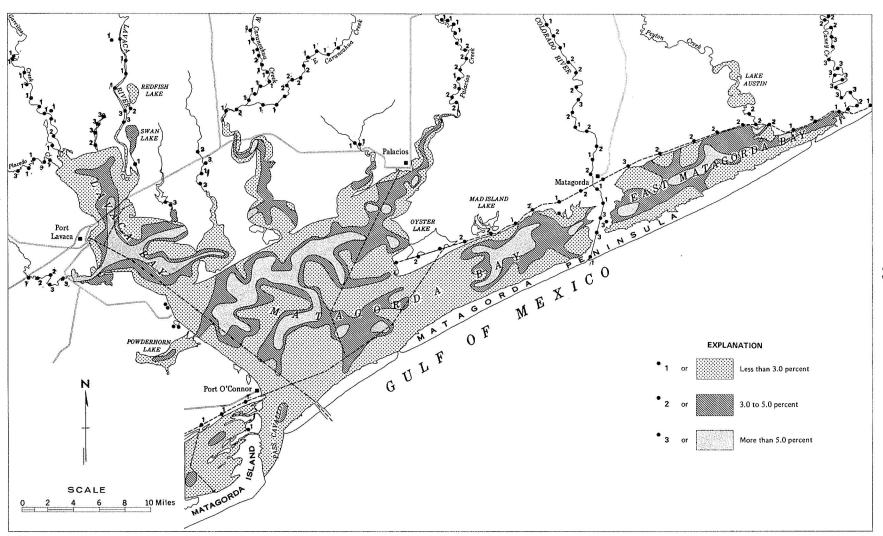


Figure 15. Iron distribution map.

Mercury

Compared to the previously discussed heavy metals, mercury (Hg) exhibits an anomalous distribution pattern. Concentration of Hg in bay sediment ranges from about 25 to 175 ppm. Fluvial sediment has uniformly low (less than 25 ppm) Hg concentration (fig. 16). Most of the sediment of the Matagorda Bay system contains less than 25 ppm Hg. This pattern extends into all water depths and includes all sediment textural types. High Hg concentration is restricted to Lavaca Bay and the northwestern part of western Matagorda Bay. Hg values in these areas vary from 25 to 175 ppm. Charted on a map the values form a concentric pattern much like an elongate bull's eye. Holmes (1977) shows that mercury is highly concentrated in the upper 5 to 7 cm of sediment and decreases to background levels deeper than 7 cm below the sediment-water interface. The clamshell sampler used in this study recovered sediment from the surface to about 15 cm deep.

Since the values in fluvial sediment are in the 0.0 to 25 ppm range throughout the bay system (even those areas that drain rice fields in which fungicides with Hg have been used), it appears that Hg was not transported to the bays through fluvial systems.

Most of the area of high Hg concentration lies east of the Matagorda Ship Channel. The highest concentration of Hg is in Lavaca Bay. This pattern is confined to the deep part of the bay (a sedimentary sill separates Lavaca Bay from Matagorda Bay), where sediment type is mud and the organic carbon content is more than I percent. Mercury content decreases to 0.0 to 25 ppm across the sedimentary sill separating Lavaca and Matagorda Bays and then increases to 50 to 75 ppm in Matagorda Bay. This high concentration coincides with an increase in water depth, muddy sediment, and greater than I percent organic carbon occurrence.

Lanthanum

Lanthanum (La) values for the Matagorda Bay system and its associated fluvial feeder system range from about 30 ppm to approximately 50 ppm (fig. 17; lower limit of La determination is 20 ppm). Distribution of La closely parallels that of Cr, Cu, and Fe. Lower values (less than 30 ppm) are found in all water depths and sediment types. The highest values, for the most part, occur in the deep bay segments and are associated with mud. Some high La values coincide with sediment containing more than I percent organic carbon.

Caney Creek, Colorado River, Carancahua Creek, Keller Creek, Placedo Creek, Chocolate Bay, and abandoned segments of Lavaca River and Garcitas Creek, all have sediment with La values in excess of 50 ppm. Approximately 95 percent of the fluvial sediment with high La concentration is mud, and approximately 80 percent of the samples contained more than 1 percent organic carbon.

Magnesium

Bay and fluvial sediment in the study area contains magnesium (Mg) in the range of about 1 to approximately 1.5 percent (fig. 18; lower limit of determination of Mg is 200 ppm). Like most of the heavy metals in the Matagorda Bay system, Mg occurs in low concentrations with all sediment textural types and in both the shallow and deep bay segments. In general, high Mg values (greater than 1.5 percent) coincide with muds that reside in the deeper parts of bays. Areas of high Mg content coincide with high concentrations of Cr, Cu, and Fe; distribution patterns of these metals are different in detail. Some overlap in the areas of high magnesium and organic carbon content.

Sediment in Caney Creek, Colorado River, Keller Creek, Lavaca River and its abandoned channel, Placedo Creek, and Chocolate Bay contains Mg in excess of 1.5 percent. Approximately 96 percent of the fluvial sediment with high Mg values is mud. Approximately 84 percent of the sediment with high Mg content also contained more than 1 percent organic carbon.

Manganese

Concentrations of manganese (Mn) in bay and fluvial sediment of the Matagorda Bay area range from about 300 ppm to about 700 ppm (fig. 19; lower limit of determination of Mn is 10 ppm). Manganese has a general distribution pattern similar to Cr, Cu, Fe, and Mg; their distributions differ in detail. Low Mn values in bay sediment are not controlled by water depth or depositional facies. The higher Mn concentrations in bay sediment follow approximately the same trend as the other heavy metals; Mn in the greater than 700 ppm range corresponds generally with deep bay segments and fine-grained sediment, and it overlaps somewhat with organic carbon content of more than 1 percent.

Fluvial sediment containing more than 700 ppm Mn occurs in Caney Creek, West Carancahua Creek, Placedo Creek, and Chocolate Bay. Of these samples approxi-

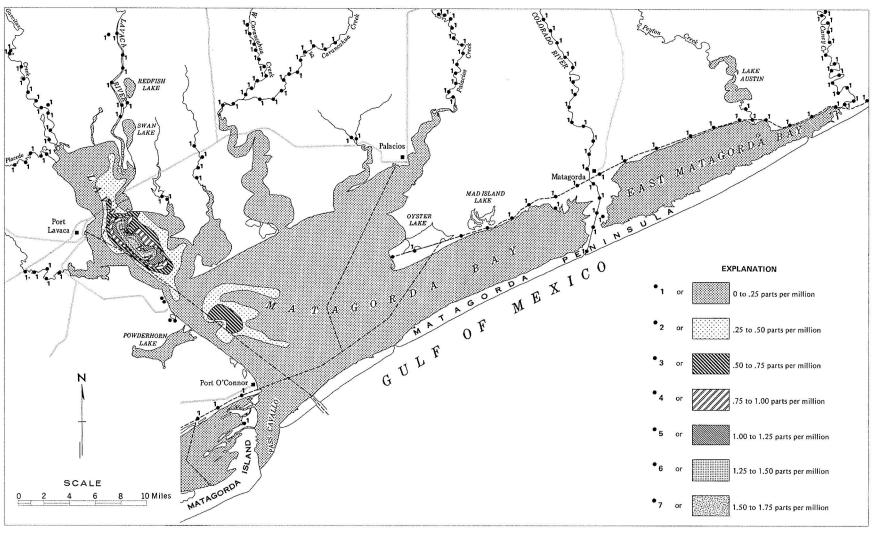


Figure 16. Mercury distribution map.

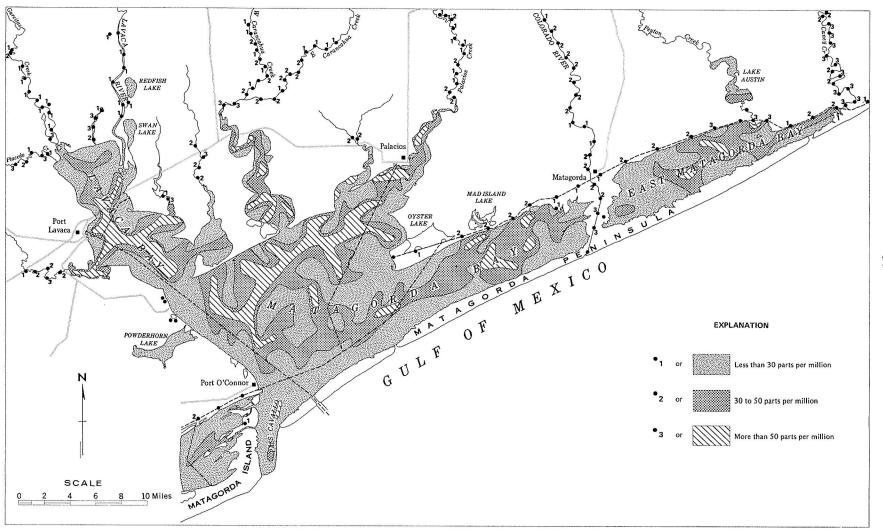


Figure 17. Lanthanum distribution map.

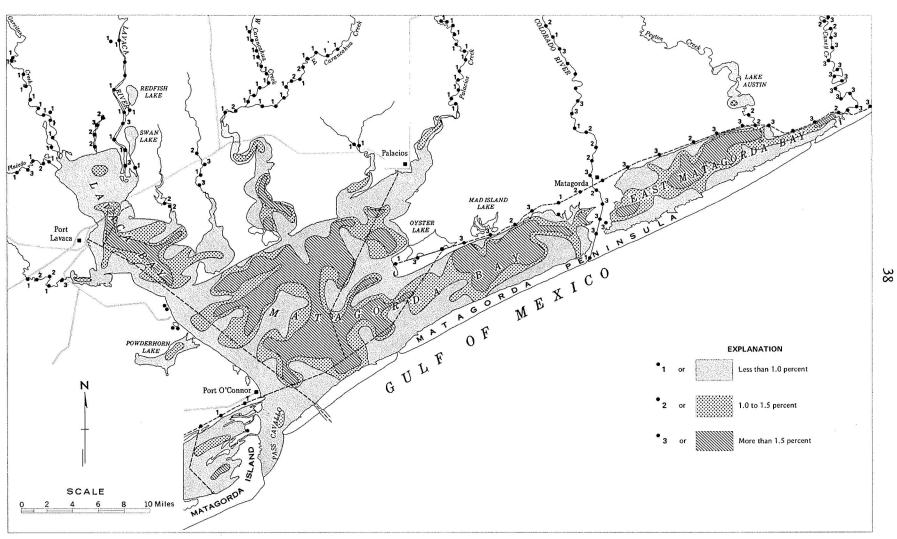


Figure 18. Magnesium distribution map.

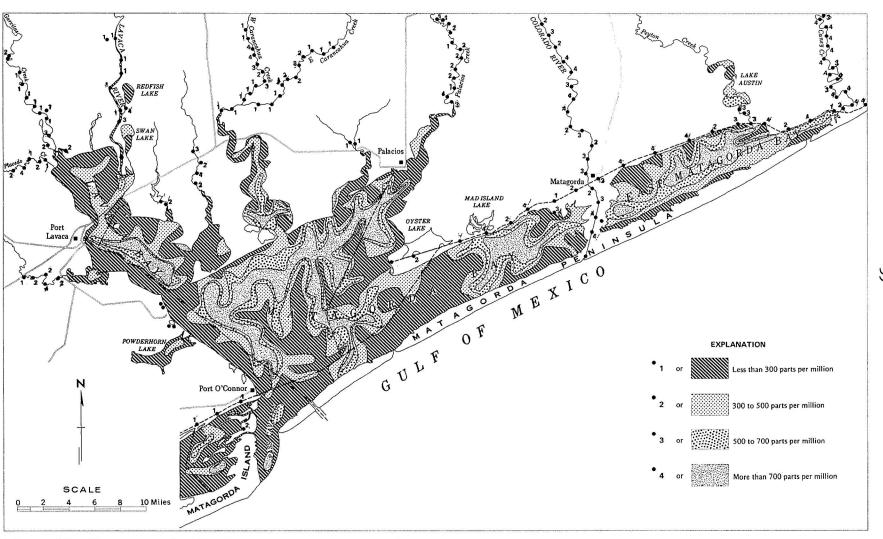


Figure 19. Manganese distribution map.

mately 70 percent are mud, 20 percent shell, and 10 percent sand. Manganese content in fluvial deposits seems to be related to sediment texture and organic carbon. Coarse-grained sand and shell sediment make up approximately 25 percent of the samples that contain high Mn values; these deposits are characterized by organic carbon content ranging from less than 0.5 to 1 percent. Seventy-five percent of the high-Mn-content samples are muds that have more than 1 percent organic carbon.

Niobium

The values of niobium (Nb) (about 10 ppm to about 20 ppm; lower limit of Nb determination is 10 ppm) are the same for bay and fluvial sediment in the Matagorda Bay area (fig. 20). Low values of Nb are distributed throughout the bay system in all sediment types and water depths. Intermediate values (10 to 20 ppm) also occur in the shallow and deep bay segments and are chiefly associated with the mud facies. Niobium in the 10 to 20 ppm range has a digitate pattern that extends from the larger segment of Matagorda Bay through some auxiliary bays into some of the fluvial feeder systems. High Nb values (>20 ppm) occur only in Espiritu Santo Bay adjacent to a dredged channel (see fig. 4 for location of Espiritu Santo Bay).

Fluvial sediment with high Nb concentrations occurs only in Caney Creek; sediment is mud with an organic carbon content of 1 percent. Other fluvial systems, except Tres Palacios Creek, West Carancahua Creek, and Lavaca River, have low and intermediate Nb values. Most of the fluvial deposits with intermediate Nb values contain 1 percent or more organic carbon. Approximately 85 percent of these samples were mud; 15 percent were sand and shell.

Nickel

Bay and fluvial sediment in the Matagorda Bay area contains less than 15 to more than 30 ppm nickel (Ni) (fig. 21; lower limit of determination of Ni is 2 ppm). Distribution of Ni within bay sediment is similar to that of Fe; details of distribution patterns are different. Low Ni values, as with some other heavy metals, are not restricted by water depth or sediment type. Intermediate Ni values (15 to 30 ppm) occur in somewhat deeper water and finer grained sediment than low Ni concentrations. Mud facies in the deep bay segments commonly contains the greatest amount of Ni. There is also some overlap between areas of high organic carbon percentage and areas of maximum nickel content.

Caney Creek, Colorado River, Carancahua Creek, Lavaca River and its abandoned channel, and Chocolate Bay all have sediment containing more than 30 ppm Ni. Of these samples 95 percent were mud and 5 percent were sand. Organic carbon content was 0.5 to 1 percent in 10 percent of the samples and more than 1 percent in 90 percent of the samples.

Lead

Lead (Pb) has a distribution pattern similar to that of most of the previously mentioned heavy metals. Concentrations of Pb in bay and fluvial sediment in the Matagorda Bay area range from about 20 to approximately 30 ppm (fig. 22; lower limit of Pb determination is 10 ppm). Low Pb concentrations (less than 20 ppm) are ubiquitous. High concentrations of Pb generally are in fine-grained sediment and in deep water. Lead in excess of 30 ppm is chiefly associated with the mud facies. There is considerable overlap between areas of high Pb and those of organic carbon content; however, some sediment with high Pb content contains less than 0.5 percent organic carbon.

Fluvial systems that have more than 30 ppm Pb are Caney Creek, Colorado River, West Carancahua Creek, and Chocolate Bay. Approximately 85 percent of the fluvial samples were mud; all but one of these samples contained more than 1 percent organic carbon. The other sediment type containing more than 30 ppm Pb was sandy shell; it contained less than 0.5 to more than 1 percent organic carbon.

Strontium

Strontium (Sr) concentrations in bay and fluvial sediment of the Matagorda Bay area range from about 100 to about 200 ppm (fig. 23; lower limit of determination of Sr is 50 ppm). Low values of Sr (less than 100 ppm) are confined mostly to shallow bay-margin areas and are associated with all sediment types. Intermediate values of Sr (100 to 200 ppm) cover the largest area of bay bottom and occur in all water depths and sediment types. Highest Sr values (greater than 200 ppm) have a patchy distribution similar to that of Ca. Sediment types with high Sr concentration are shell (gravel-sized shell debris), sand, muddy shelly sand, muddy sand, sandy mud, and mud; all occur in the shallow and deep parts of bays. Strontium, like calcite, is closely associated with shell material within bay sediment.

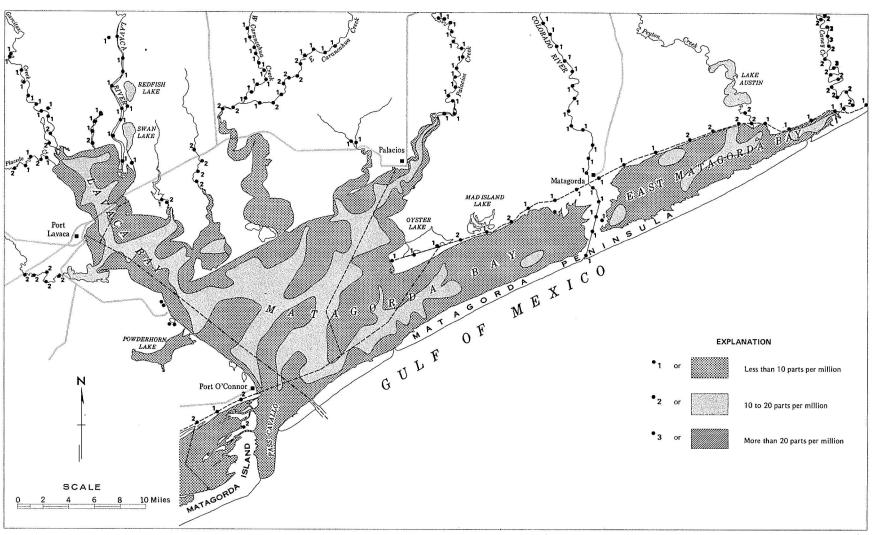


Figure 20. Niobium distribution map.



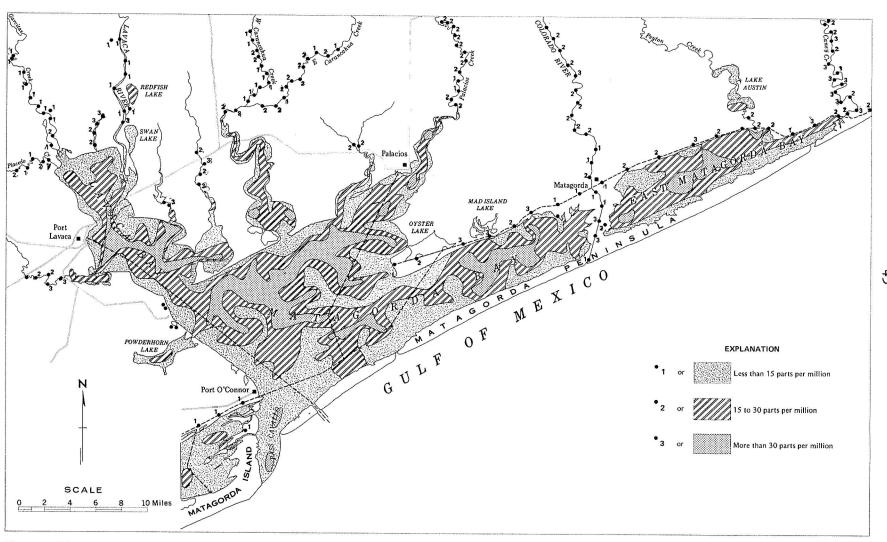


Figure 21. Nickel distribution map.

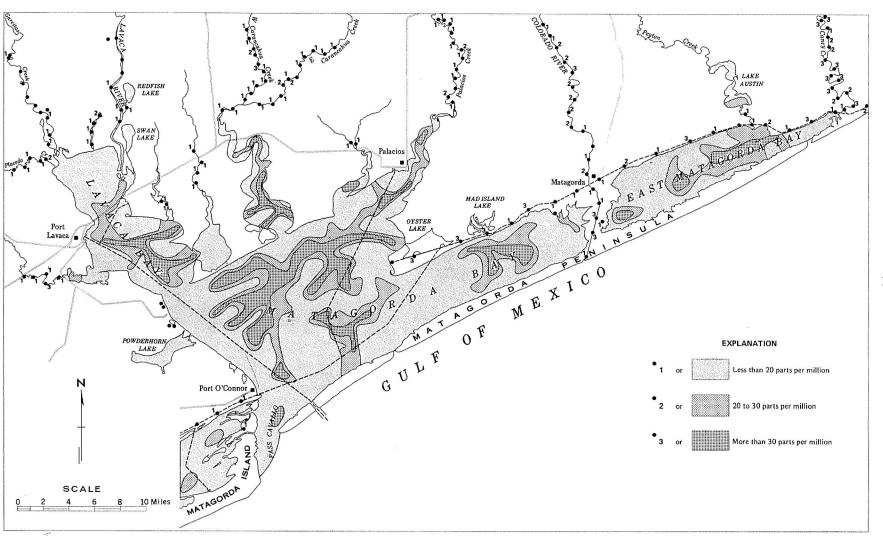


Figure 22. Lead distribution map.

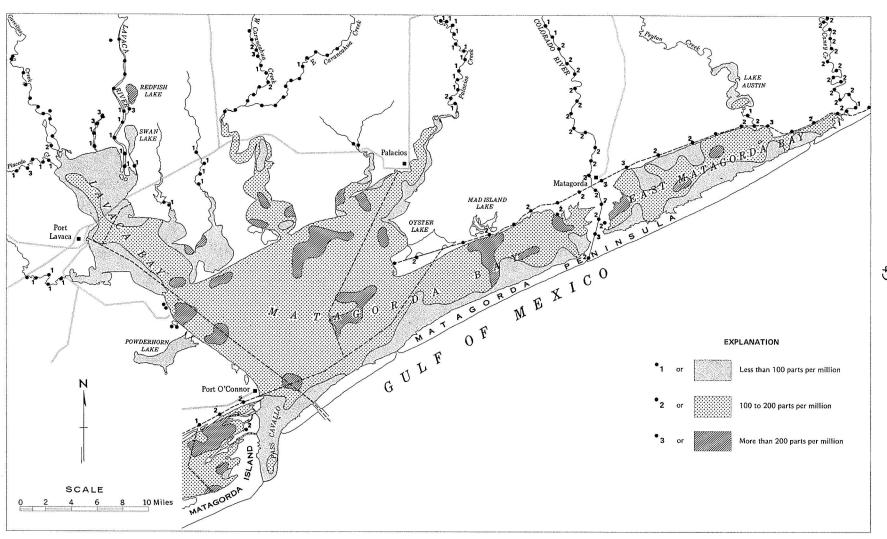


Figure 23. Strontium distribution map.

Very few fluvial sediment samples contained more than 200 ppm Sr. The Colorado River and Placedo Creek each had one sample with more than 200 ppm Sr. Two sediment samples taken from the abandoned segment of Lavaca River contained more than 200 ppm Sr. Texturally these samples were mud, muddy sand, and sand, and they contained less than 0.5 to more than 1 percent organic carbon.

Titanium

Titanium (Ti) in bay and fluvial sediment of the Matagorda Bay area has a range of approximately 0.3 to about 0.5 percent (fig. 24; lower limit of determination of Ti is 10 ppm). A large part of the bay is characterized by sediment with less than 0.3 percent Ti. Distribution of low concentration of Ti is independent of sediment type and water depth. Intermediate Ti values (0.3 to 0.5 percent) are associated mostly with deep parts of bay segments and muddy sediment. Highest values of Ti (more than 0.5 percent) exhibit a patchy distribution pattern, and the largest area lies one to two miles off the north shore of Matagorda Bay. Although Ti in the greater than 0.5-percent range is most commonly associated with mud facies, it also occurs in shell, sand, muddy sand, and sandy mud. The distribution of high Ti percentage is somewhat analogous to that of Fe and Mn; Ti overlaps some areas of high organic carbon content.

All of the fluvial feeder systems except West Carancahua Creek contain sediment with more than 0.5 percent Ti. Approximately 95 percent of the samples were mud; the other 5 percent were sand. More than 1 percent organic carbon occurred in 55 percent of the samples; the other samples contained 0.5 to 1 percent organic carbon.

Vanadium

Bay and fluvial sediment in the Matagorda Bay area contain less than 50 ppm to more than 100 ppm vanadium (V) (fig. 25; lower limit of V determination is 10 ppm). The distribution of V, particularly the higher values, is similar to that of Cr, Cu, Fe, and Mn. Lower V values (less than 50 ppm) mostly occur in the shallow bay segments and are associated with all textural types. Intermediate values of V commonly are found along bay axes, in deep parts of bay segments, and generally are associated with muddy sediment. A patchy distribution pattern characterizes the highest V values. Greater than 100 ppm V occurs most commonly in the mud facies; in parts of Matagorda, Carancahua, and Lavaca Bays high V values overlap with areas of more than 1 percent organic carbon.

All but four of the fluvial feeder systems (Tres Palacios Creek, East and West Carancahua Creeks, and Placedo Creek) have sediment with V values exceeding 100 ppm. Sediment type of all these samples was mud; 65 percent of these samples contained more than 1 percent organic carbon, and the remainder contained from 0.5 to 1 percent organic carbon.

Yttrium

Yttrium (Y) in bay and fluvial deposits of the Matagorda Bay area ranges from about 10 to about 30 ppm (fig. 26; lower limit of Y determination is 10 ppm). Distribution of low Y values (less than 10 ppm) corresponds closely to bay-margin sand. Yttrium values of 10 to 20 ppm occur in all water depths and sediment textural types. Distribution of Y in the 20 to 30 ppm and greater than 30 ppm ranges is near axes of the bays. The highest values of Y (greater than 30 ppm) are distributed similarly to the highest values of Fe and Mn; patterns of all these heavy metals vary one from the other in detail. In general, the higher concentration of Y occurs in the deep parts of the bays, in mud, and in places coincides with greater than 1 percent organic carbon.

Only four of the fluvial feeder systems contain surface sediment having more than 30 ppm Y. All of these streams (Keller Creek, Lavaca River, Garcitas Creek, and Placedo Creek) discharge directly or indirectly into Lavaca Bay, which has a large area of Y in the more than 30-ppm range. About 25 percent of the fluvial samples containing more than 30 ppm Y were sand; the remaining samples were mud. The mud samples contained from 0.5 to more than 1 percent organic carbon, and the sand samples contained from less than 0.5 to 1 percent organic carbon.

Zirconium

Zirconium (Zr) content of bay and fluvial sediment of the Matagorda Bay area ranges from about 300 to about 700 ppm (fig. 27; lower limit of determination of Zr is 20 ppm). The lowest Zr values are distributed over a large area. They occur in the shallow and deep bay areas, and are associated with all sediment types. Zr in the 300-to 500-ppm range covers a much smaller area than the less than 300-ppm Zr group. Zr in this range is found in shallow and deep bay segments, and in all sediment types, but is most commonly associated with sand-bearing deposits. The total area of the bay system occupied by sediment with 500- to 700- ppm Zr is relatively small. Zirconium in this range is in sand, sandy mud, and muddy sand. Sediment containing the highest

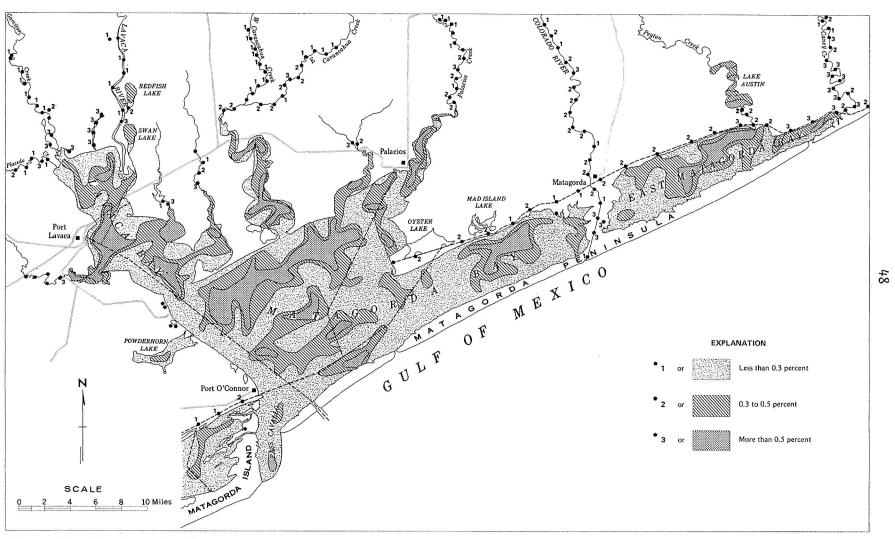


Figure 24. Titanium distribution map.

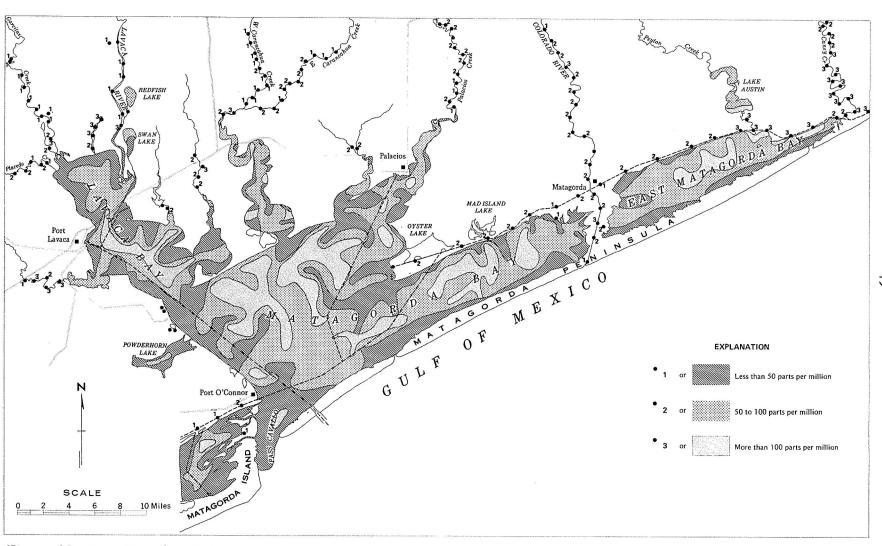


Figure 25. Vanadium distribution map.

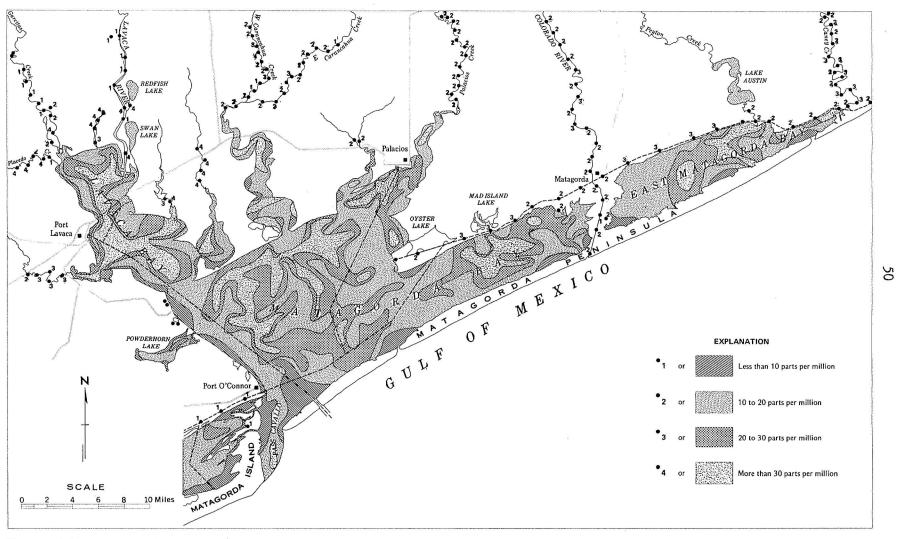


Figure 26. Yttrium distribution map.

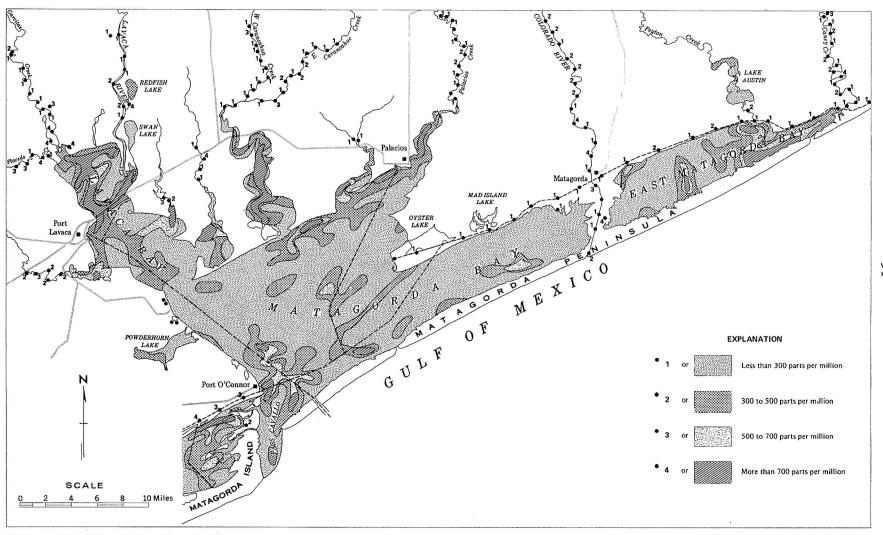


Figure 27. Zirconium distribution map.

Zr content (more than 700 ppm) covers a small part of the bay bottom and occurs near bay margins, in tidal channels, and in tidal deltas. Within Carancahua Bay and upper Lavaca Bay the highest Zr values are in bay margin areas and along bay axes. More than 700 ppm Zr is contained in sand, muddy sand, sandy mud, and some shell deposits. This distribution of the highest Zr values differs from that of most of the other heavy metals, which are in the deep bay segments and contained in mud having an organic carbon content of more than 1 percent.

Caney Creek, Colorado River, Keller Creek, Garcitas Creek, and Placedo Creek have sediment with Zr in the more than 700-ppm range. There are, however, only 7 samples from all these fluvial systems with more than 700 ppm Zr. Three mud, 3 sandy mud, and 1 muddy sand sample compose this group which has a total organic carbon content of less than 0.5 to more than 1 percent.

DISCUSSION

Average concentrations of the 20 trace elements (plus organic carbon) recognized in Matagorda Bay system bottom sediment were compared to concentrations of similar trace elements found in the Earth's crust, in shale, and in seawater (table 4). In general, element concentrations in the bottom sediment as in the Earth's crust and in shale are about the same. Trace element contents in shale (Krauskopf, 1967) and in clays and shales (Parker, 1967) are similar except for concentrations of Ba, C, Fe, Mg, and Mn. Parker's values for Ba and C exceed those of Krauskopf; C is ten times greater. Krauskopf reports higher values than does Parker for Fe, Mg, and Mn.

Comparing trace element data from crustal rocks, shale, seawater, and surface sediment from Matagorda Bay system (table 4) shows that trace element content of seawater is significantly lower than that of the crust, shale, and recent bay and fluvial sediment. Concentrations of Ba, Be, Co, Nb, and Y are about the same in crustal rocks, shale, and recent sediment of the Matagorda Bay system; these comparable concentrations suggest that the Matagorda Bay system is not polluted with Ba, Be, Co, Nb, or Y. Nevertheless, these concentrations may have increased since virgin conditions existed.

Trace elements found in higher concentrations in sediment of the Matagorda Bay system than in the Earth's crust and shale are B, Ca, C, La, Pb, Hg, and Zr. These higher concentrations in recent bay and fluvial deposits suggest that the elements are being concentrated through natural chemical and biological processes, and/or they are

Table 4. Comparison of average concentration of trace elements in the Earth's crust, shale, and seawater with trace element range in surface sediment of Matagorda Bay system (values in ppm).

Element	Crust	Shale	Seawater	Matagorda Bay
Barium (Ba)	425	580	0.03	<300->500
Beryllium (Be)	2.8	3	6 × 10 ⁻⁷	<1.0->3.0
Boron (B)	10	100	4.6	<50->200
Calcium (Ca)	4.1×10^{4}	2.5×10^{4}	400	<10,000->50,000
Carbon (C)	200	1,000	28	<5,000->10,000
Chromium (Cr)	100	100	0.00005	<50->70
Cobalt (Co)	25	20	0.0001	<10->20
Copper (Cu)	55	57	0.003	<10->20
Iron (Fe)	5.6 × 10 ⁴	4.7×10^{4}	0.01	<30,000->50,000
Lanthanum (La)	25	40	1.2×10^{-5}	<30->50
Lead (Pb)	12.5	20	0.00003	<20->30
Magnesium (Mg)	2.3×10^{4}	1.4×10^4	1,350	<10,000->15,000
Manganese (Mn)	950	850	0.002	<300->700
Mercury (Hg)	80.0	0.4	0.00003	0–175
Nickel (Ni)	75	95	0.002	<15->30
Niobium (Nb)	20	20	0.00001	<10->20
Strontium (Sr)	375	450	8.0	<100->200
Titanium (Ti)	5,700	4,500	0.001	<3,000->5,000
Vanadium (V)	135	130	0.002	<50->100
Yttrium (Y)	33	30	0.0003	<10->30
Zirconium (Zr)	165	200		<300->700

being introduced by man in concentrations that exceed natural background levels. The high values of B, C, Hg, and Zr are valid and indicate that the concentration is natural or induced by man. Since the sediment source for the Matagorda Bay system is dominated by older sedimentary rocks (predominantly shale and clay) it is assumed that neither La nor Pb are being concentrated in the Matagorda Bay system. Calcium values in bottom sediment of the Matagorda Bay system are higher than values in shales and about the same as those in the Earth's crust. High Ca values in the Matagorda Bay system coincide with areas of shell concentration.

Six trace elements in the bottom sediment of the Matagorda Bay system exhibit maximum values that are less than the averages for the Earth's crust and for shales.

These are Cr, Cu, Mn, Ni, Sr, and V. Since it has been shown that fine-grained sediment and organic carbon tend to adsorb trace elements and that water generally contains lesser concentrations of trace elements than does sediment (Rickert and others, 1977), it appears that Cr, Cu, Mn, Ni, Sr, and V have been depleted in the sediment and concentrated in the biosphere. Cr and Cu, as well as Cd, Hg, and Pb, are toxic, and knowledge of their levels of concentration in the biota of the Matagorda Bay system is important. Hill (in Berryhill, 1975) reported that certain species of polychaetes retain relatively high amounts of Cu.

Three elements, Fe, Mg, and Ti (table 4), contained in sediment of the Matagorda Bay system have values less than values in the Earth's crust and about the same as values in shale. Since the sedimentary rock source area is dominated by shale and clay, it is assumed that the values of Fe, Mg, and Ti in Matagorda Bay bottom sediment approximate the trace element content of source rocks.

Rare metals are concentrated in marine sedimentary rocks (and sediment), especially black shales and phosphorites (Krauskopf, 1956). Trace elements are removed from water and concentrated in sediment by several methods. They may be (1) adsorbed to clays, organic carbon, or hydroxides, (2) contained in the lattice of degraded clays, (3) precipitated as a sulfide, (4) removed by organisms and subsequently entombed in the sediment, (5) physically concentrated as heavy mineral placers (for example, zircons) within sand bodies, or (6) combined in the form of organo-metallic complexes.

Association of trace metals, water depth, sediment grain size, and organic carbon has been emphasized throughout this report. These associations are not unique to the Matagorda Bay system; they are common to recent fluvial, lacustrine, estuarine, and marine deposits throughout the world. A process of trace element concentration not documented by the Matagorda Bay study, but emphasized by others (for example, Krauskopf, 1956; Hirst, 1962; Cline and Chambers, 1977), is the scavenging action (adsorption) of other elements and compounds, particularly the hydroxides.

Three control mechanisms for concentration of elements (Krauskopf, 1956) are precipitation of sulfides within bottom sediment, adsorption, and biological processes. Adsorption, according to Krauskopf, involves materials for which trace elements have an affinity. These include clays, organic carbon, and hydroxides. A few elements are associated specifically with fine-grained sediment; these elements are Cr, Cu, and Pb (Krauskopf, 1956; Cline and Chambers, 1977). Co, Cr, Cu, Ni, and Pb have an affinity for organic carbon (Hirst, 1962; Cline and Chambers, 1977). Several trace metals are

adsorbed by Mn (OH)₄ and Fe (OH)₃; among these elements are Be, Co, Cr, Cu, Ni, Pb, and V (Krauskopf, 1956; Hirst, 1962; Cline and Chambers, 1977). Hirst (1962) reported the occurrence of B, Cr, and V in the lattice of degraded clays. Four elements (Ba, Hg, Li, and Ti) are adsorbed onto clays (Krauskopf, 1956; Hirst, 1962). Concentration of trace elements by physical and biological processes is important. Association of zircons with sand deposits was documented in the study of the Matagorda Bay system. Analyses of soft parts of vertebrate and invertebrate animals and study of the numerous plant species would be required to establish the associations among trace elements and biota of Matagorda Bay sediment; this was not included as a part of this investigation.

Comparison of Trace Metal Concentration in Surface Sediment of Jarrett, Corpus Christi, Baffin, and Matagorda Bays

Association of trace metals, organic carbon, and sediment type have been discussed for Matagorda Bay system in this report. Berryhill and others (1972) reported similar associations for two estuarine bays in North Carolina (including Jarrett Bay). Holmes (1974) determined the abundance of trace elements in bottom sediments of Corpus Christi and Baffin Bays, Texas. Trace metal data for the four areas shown on table 5 were determined from whole sediment samples by the same semiquantitative method (Direct-Current Arc Spark Emission Spectrograph).

Organic carbon content of bottom sediment in North Carolina bays (Berryhill and others, 1972) is significantly higher (1,000 to 129,000 ppm) than in the Matagorda Bay system (5,000 to 10,000 ppm). The North Carolina bays and the Matagorda Bay system have comparable organic carbon distribution patterns. In general, organic carbon content increases directly with an increase in water depth and mud content.

In the Matagorda Bay system only B and Hg are present in amounts sufficiently high to indicate sources other than Quaternary and Tertiary sands and shales. Berryhill and others (1972) concluded that no anomalous concentrations of elements have environmental significance in bottom sediment of North Carolina bays. Co, Cu, Mo, Ni, Pb, and V were concentrated in ash of the humic and fulvic fractions of organic carbon within North Carolina bay sediment. With the exception of Ca, organic carbon (C), Hg (reported only for Matagorda Bay), and Nb, there is considerable overlap in the range of values for elements reported in bottom sediment of Texas and North Carolina bays. Calcium content is greater in Matagorda Bay than in the other bays (table 5). Organic carbon was not reported for Corpus Christi and Baffin Bays; it

Table 5. Comparison of range of trace elements in surface sediment of Jarrett, Corpus Christi, Baffin, and Matagorda Bays (values in ppm).

	Jarrett Bay	Corpus Christi Bay	Baffin Bay	Matagorda Bay
Ba	300-500	50-5,000	70-1,000	300-500
Be		1-2	1-2	1-3
В	100	10-300	10-200	50-200
Ca	5,000-7,000	700-20,000	1,000-20,000	10,000-50,000
С		NR	NR	5,000-10,000
Cr	50-70	15-300	5-100	50-70
Со	5	5-15	5-15	10-20
Cu	15-20	5-300	5-20	10-20
Fe	20,000-30,000	500-200,000	1,000-50,000	30,000-50,000
La	30-50	20-70	50-100	30-50
Pb	15-20	10-2,000	10-50	20-30
Mg	10,000-15,000	300-30,000	1,500-50,000	10,000-15,000
Mn	0-200	20-700	20-300	300-700
Hg	NR	NR	NR	0-175
Ni	15-20	5-70	5-30	15-30
Nb	0-10			10-20
Sr	100-150	100-1,500	100-3,000	100-200
Ti	3,000	50-5,000	200-10,000	3,000-5,000
V	10-70	100-150	10-150	50-100
Y	20-30	10-30	10-30	10-30
Zr	200-500	20-1,000	50-1,000	300-700

is considerably greater in the North Carolina bay sediment than in sediment of Matagorda Bay system. Mercury was reported only in the Matagorda Bay system where it is inferred to have been introduced by man. Niobium was not reported from Corpus Christi and Baffin Bays, and the Nb values reported for Matagorda Bay system and North Carolina bays are near the lower limit of determination, and therefore, are not significant.

Comparison of Trace Metal Concentration in Surface Sediment of Southern Lake Michigan and Matagorda Bay System

The abundance of ten trace elements from the upper few centimeters of bottom sediment in Lake Michigan is controlled by factors such as depth of water, organic carbon content, and distribution of iron oxide (Shimp and others, 1971). It was found that Cr, Cu, and Pb correlate well with organic carbon. A good correlation was found between iron oxide and Cr, Cu, Ni, and Mn. Organic carbon also showed a fair correlation with iron oxide. Two elements, Cu and Ni, exhibited a correlation with clay.

Comparison of concentration range of the ten trace elements and organic carbon from southern Lake Michigan (Shimp and others, 1971) with concentrations of the same

Table 6. Range of elemental concentration in surface samples, southern Lake Michigan and Matagorda Bay system.

Element	Southern Lake Michigan range ppm	Matagorda Bay range ppm	
В	2.0-92	<50->200	
Be	0.4-3.0	<1.0->3.0	
Co	5.0-24	<10->20	
Cr	10-136	<50->70	
Cu	7.0-78	<10->20	
La	8.0-34	<30->50	
Mn	160-5,700	<300->700	
Ni	8.0-58	<15->30	
Pb	20-172	<20->30	
V	7.0-98	<50->100	
Organic carbon (C)	0.19-4.73%	<0.5->1.0%	

elements in the Matagorda Bay system sediment indicates that Lake Michigan deposits generally exhibit higher concentrations (table 6).

Elements in Lake Michigan that are higher than those in Matagorda Bay system include Cr, Cu, Mn, Ni, and Pb. Organic carbon is also higher in Lake Michigan sediment than in Matagorda Bay system. Only B and La have higher concentrations in Matagorda Bay system sediment than in Lake Michigan deposits. Three elements in Lake Michigan sediments have about the same concentrations—Be, Co, and V.

CONCLUSIONS

Highest trace metal values are generally associated with high total organic carbon content, deep parts of bays, fine-grained sediment (predominantly mud), and/or abandoned fluvial channel segments. These associations indicate that trace metals are adsorbed to, or complexed with, organic debris and/or clay minerals. Certain elements or compounds (for example, Mn (OH)₄ and Fe (OH)₃) also adsorb other trace elements. Relationships among trace elements, total organic carbon, sediment types, and physical environments are complex. Fine-grained sediment accumulates in the lowest physical energy environments of the Matagorda Bay system; this includes feeder streams and associated abandoned stream segments. These environments occupy deep parts of bays and protected areas.

There are some apparent natural groupings or associations of trace metals, organic carbon, and fine-grained sediments (table 7). First, the highest concentrations of 15 of the 20 trace elements detected in Matagorda Bay system sediment are associated with muds and occur in the deep waters of the bay system (table 7; B, Ba, Be, Co, Cr, Cu, Hg, La, Mg, Mn, Ni, Pb, Ti, V, Y).

Table 7. Relationships among water depth, sediment type, organic carbon, and trace elements found in samples from Matagorda Bay systems, Texas.

Element	Range in values* Matagorda Bay sediment	Lower limit of determination (ppm)	Associations	
Organic carbon	< 0.5-> 1.0%	not applicable	Associated sediment type predominantly mud; highest percent in deeper parts of bays.	
Boron	<50->200	10	Highest values in mud in deeper parts of bays and associated with high C values; Caney Creek mud contains 200 ppm B.	
Barium	<300->500	05	Highest values in mud and deeper parts of bays; associated with high B and C values; high in abandoned channels.	
Beryllium	<1.0->3.0	01	High values in same areas where B, Ba, and C are high; high Be in Caney Creek.	
Calcium	<1.0->5.0%	500	High Ca values coincident with dredge channels, oyster reefs, shell spits, and beaches. Fluvial deposits low in Ca.	
Cobalt	<10÷>20	05	High Co values occur in areas where B, Ba, Be, and C are high and where mud is dominant sediment type. Fluvial sediment generally low in Co.	
Chromium	<50->70	05	Highest Cr values associated with mud, deeper parts of bays, and other trace metals; high Cr in streams in fine sediment and associated with $>$ 1% C.	
Copper	<10->20	02	Highest concentration of Cu parallels that of Cr in the bays; associated with all sediment types in fluvial systems but highest in abandoned channels.	
Iron	<3.0->5.0%	500	High values of Fe, Cu, and Cr have similar distribution. Most high Fe values in fluvial sediment are in mud; not restricted by sediment type or C %.	
Mercury	<25->175	not applicable	Anomalously high concentrations. Associated with fine sediment, high C content, and deeper bay water.	
Lanthanum	<30->50	20	Distribution parallels that of Cr, Cu, and Fe; highest values in mud in deeper parts of bays. La in fluvial sediment mostly mud with greater than 1.0% C.	
Magnesium	<1.0->1.5	200	High Mg values coincide with high values of Cr, Cu, and Fe; high Mg mostly in mud in deeper parts of bays. High Mg in fluvial systems is in mud with high C content.	
Manganese	<300->700	10	Distribution of Mn is similar to Cr, Cu, Fe, and Mg. High Mn values are in mud with high C content in deeper bay water. Fluvial systems have mud with high Mn and C values.	
Niobium	<10->20	10	Highest Nb values associated with dredge spoil; intermediate values occur in mud. Caney Creek contains some mud with high Nb and C values.	
Nickel	<15->30	02	Distribution of Ni similar to Fe; highest Ni values are in mud in deeper parts of bays; C values may or may not be high. Ni is high in fluvial mud with high C content; most common in Caney Creek.	
Lead	<20->30	10	Distribution similar to trace metals above; high concentration of Pb in deeper bay waters in mud; C may or may not be high. High Pb values in fluvial sediment are in mud with high C content.	
Strontium	<100->200	50	High Sr values have patchy distribution similar to Ca; Sr associated with shell. Few fluvial sediments had high Sr values.	
Titanium	<0.3->0.5%	10	Distribution of high Ti values is similar to Fe and Mn; high values of Ti are associated with shell, sand, and mud and do not appear dependent upon high C content. High Ti values ubiquitous in fluvial sediment; predominantly mud.	
Vanadium	<50->100	10	Distribution of high V values similar to Cr, Cu, Fe, and Mn; highest V values are found in mud in deeper parts of bays; some overlap with high C values. Fluvial sediment with V predominantly mud with high C content.	
Yttrium	<10->30	10	Highest Y values have similar distribution pattern to Fe and Mn; highest Y values are in mud in deeper parts of bays; may coincide with high C values. Only fluvial systems which discharge into Lavaca Bay have high Y values.	
Zirconium	<300->700	20	Highest Zr values are concentrated in sand, muddy sand, sandy mud, and some shell deposits; associated with bay margins, tidal channels, and tidal deltas. Few fluvial sediments are high in Zr; organic C not a factor in Zr concentration. Physical precesses tend to concentrate zircons with their hydraulic, quartz sand equivalents.	

^{*}ppm unless otherwise indicated

Second, organic carbon has an affinity for fine-grained sediment that accumulated in the deeper bay segments. Some organic carbon may also occur as the hydraulic equivalent of clay-size particles. Trace elements whose highest concentrations coincide with high carbon percentages are B, Ba, Be, Co, Hg, Mn, Ti, and Y.

Third, some other groups of elements may be controlled by adsorption capacity of other elements (possibly Fe or Mn). This group comprises nine elements: Cr, Cu, Fe, La, Mg, Ni, Ti, V, and Y.

A fourth group of elements (Ca, Nb, Sr, and Zr) exhibits little affinity for deep water and fine-grained sediment, organic carbon, or elements that serve to adsorb trace metals. Calcium and strontium display similar distribution patterns and are related to areas of shell production. Niobium is high in sediment adjacent to dredge spoil and possibly occurs in higher concentrations in deep water, although Byrne (1975) did not report Nb from cores from Lavaca Bay. High values of Nb are associated with abandoned channel sediment having high organic carbon content (for example, Caney Creek, see table 7). Zirconium is a constituent of the heavy mineral zircon, which is an accessory mineral in the more acidic igneous rocks. The Colorado River derives some sediment from the Llano Uplift where granitic rocks are exposed. Since zircon has a specific gravity between 4.6 and 4.7, small detrital zircons are hydraulic equivalents of sand-sized quartz whose specific gravity is 2.65. Zirconium has its highest concentration in sands of the Matagorda Bay system.

Sediment of the Matagorda Bay system was derived, for the most part, from older sedimentary rocks, which are characterized by a dominance of mudstone, claystone, and shale. Therefore, it seems reasonable to assume that trace metal and organic carbon content of shale (Krauskopf, 1967; table 4, this report) are representative of source rock content. When comparing trace metal and organic carbon content of shale with Matagorda Bay system sediment, it is revealed that (1) Ba, Be, Co, Fe, La, Mg, Pb, Ti, and Y concentrations are about equal in shale and surface sediment of the Matagorda Bay system, (2) Cr, Cu, Mn, Ni, Sr, and V concentrations are less in Matagorda Bay system than in shale, and (3) B, Hg, Ca, Zr, and organic carbon have greater concentrations in Matagorda Bay system sediment than in shale. These data, plus the sediment, water depth, and other previously discussed associations, suggest that only the high values of B and Hg result from man's activities.

According to Collins (1975) identification of B compounds can be used to identify sources of B that have leaked into oil wells, or into fresh-water lakes or streams. Like Cl, B is considered to be an element of marine origin. Boron compounds in brines and connate waters probably are derived from decay of the same organic materials that

were sources of petroleum. Shales, sandstones, and seawater contain about 100, 35, and 4.6 ppm B, respectively. Boron concentration in Matagorda Bay system sediment exceeds all of those values. Subsurface oil-field waters contain a trace to more than 100 ppm B (Collins, 1975). At the time sediment samples were being collected for this study, oil field brine with B was being discharged at several localities into the waters of the Matagorda Bay system.

Chemical waste containing Hg had been discharged into the bay system prior to the initiation of the study by an aluminum processing plant. Such activities had ceased before samples were collected for this study. High-Hg values were detected only in northwestern Matagorda Bay and in Lavaca Bay.

The method utilized to ascertain the level of concentration in bottom sediment of the Matagorda Bay system, as stated previously, provides semiquantitative results. When values of individual elements are mapped, distribution trends are clearly indicated. Concentration levels (stated as ppm for most elements, but as percent for those having high concentrations) resulting from this semiquantitative method are not absolute; a duplicate sample analyzed by the same method may not indicate exactly the same value. Lower and upper limits of determination are shown on table 1. Concentration values in bottom sediment samples from the Matagorda Bay system reach the lower limit of determination for Be, Nb, and Y. Lowest concentrations for these three elements may not be significant. Data for Nb indicate values ranging from 10 to 20 ppm; lower limit of determination is 10 ppm (table 1). Values for Nb obtained from the Matagorda Bay system are somewhat dubious. Upper limit of determination was not exceeded by any element detected in Matagorda Bay system sediment. Except for the lowest values for Be and Y, and the total range of values for Nb, concentration values for trace elements in the sediment of the Matagorda Bay system are adequate to detect distribution trends and to display associations among the various trace elements and water depth, organic carbon, sediment type, and trace elements.

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