Geochemistry and Diagenesis of Tidal-Marsh Sediment, Northeastern Gulf of Mexico

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By VERNON E. SWANSON, ALONZA H. LOVE, *and* IRVING C. FROST

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Componential analysis and depositional
patterns of the dominantly humic types
of the 10–40 percent organic matter in
the sandy sediment of an extensive
Juncus *tidal marsh*

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GEOCHEMISTRY AND DIAGENESIS OF TIDAL-MARSH SEDIMENT, NORTH-EASTERN GULF OF MEXICO

By Vernon E. Swanson, Alonza H. Love, and Irving C. Frost

ABSTRACT

The area of investigation is a coastal belt 5 miles wide and 80 miles long in southwestern Taylor and Dixie Counties, Fla., between the Aucilla River on the north and Suwannee River on the south. The coastal region along this part of the Gulf of Mexico consists of a broad, very shallow marine shelf, a *Juncus* tidal marsh 1-4 miles wide, and a low-lying, generally swampy pine-palmetto forest area extending some 20–50 miles inland. A thin veneer of peaty mud in the tidal marsh, of carbonaceous sand in the tidal streams, and of calcareous sand near shore has been deposited in the last few thousand years on bedrock limestone of Eocene and Oligocene age.

Samples were collected from the top 1 meter of sediment at 70 localities to provide 148 samples, including those from 24 cores. These samples were described from observations made under the microscope and were analyzed for contents of organic carbon, total alkaline-soluble humic substances (humic and fulvic fractions), benzene-soluble substances (bitumen), total and free sulfur, mineral carbon, and major and minor elements. The moisture content, sediment mineralogy, organic-element composition, percent ash, and percents saturated and aromatic hydrocarbons were determined for representative samples. Salinity, temperature, pH, and Eh were determined for both water and sediment at each sample locality.

The salinity of offshore Gulf of Mexico water was 25–31 parts per thousand and of the water flooding the tidal marsh 20–25 parts per thousand, but the salinity of stream water was highly variable, depending on water depth, distance from mouth, and tide stage. The pH of bottom water generally ranged from 7.6 to 8.4, and the Eh, from −80 to +300 millivolts. The pH and Eh of the upper 5 centimeters of bottom sediment were consistently lower, the pH generally ranging from 6.0 to 7.7, and the Eh, from −35 to −300 millivolts; the greater the amount of organic matter in the sediment, the correspondingly lower were the pH and Eh values.

On the basis of grain size and amount of organic matter, the sediment in the tidal marsh was readily classified as peaty sandy mud, carbonaceous muddy sand, and relatively clean sand, corresponding to organic-matter contents of 15–40, 4–15, and 0.1–4 percent, respectively. More than 90 percent of the inorganic component of the sediment in most samples is poorly sorted silt- to medium-sized quartz and amorphous silica; iron sulfide minerals are second most abundant;

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and clay minerals and calcareous shell material are minor constituents, rarely constituting more than a few percent. Peaty sandy mud, which contains an average of 27 percent organic matter, is the most abundant tidal-marsh sediment, and below a depth of 40 centimeters commonly contains at least 10 percent pyrite.

The river sediment and some offshore sediment are lithologically very variable. Content of organic matter generally ranges from 0.5 to 5 percent, and of calcareous shell material, from 0.2 to 8 percent; quartz grains compose most of the remainder. The characteristic light-colored calcareous sand more than 1 mile offshore contains less than 1 percent organic matter and from 3 to 20 percent shell material; its main constituent is quartz.

The abundant organic matter in the tidal-marsh sediment originates from two sources. The major source, which contributes 80 percent of the organic matter, is humic material derived from the inland swamp-forest areas and delivered to the Gulf of Mexico by streams. This humic material is 75 percent decomposed plant particles and 25 percent flocculated organic acids that are kept near shore by wave action and that are flushed onto the marsh by tides, to be deposited from suspension in the still water at, and shortly after, high tide. The remaining 20 percent of the organic material is derived locally. It is semi-indigenous humic material mainly derived from the *Juncus* (speargrass) marsh plant and, to a minor extent, from nearshore seagrasses such as *Thalassia*.

About 25 percent of the organic matter in the tidal-marsh sediment is composed of alkaline-soluble humic substances. A decrease in the percentage of these substances with greater depth and a decrease in the percentage of its fulvic fraction with greater depth in the characteristic peaty mud are interpreted as indications of relatively rapid geochemical diagenesis of the organic matter with a very shallow depth of burial. The change from readily oxidized hydrous iron sulfide in the upper 25 centimeters of mud to relatively stable less hydrous iron sulfide from 25- to 40-centimeter depths, to stable pyrite below 40 centimeters, coupled with the increase of calculated iron sulfide from about 2 percent in the upper 10 centimeters to as much as 21 percent below 40 centimeters, also indicates rapid diagenesis at shallow depth of burial.

The average bitumen content of the tidal-marsh sediment ranges from 0.12 percent of the peaty sandy mud to 0.012 percent of the relatively clean sand, and represents, respectively, 0.44 and 0.51 percent of the total organic matter. The bitumen content of the offshore calcareous sand is low, 0.006 percent, but it represents 0.92 percent of the organic matter, or about twice the bitumen per unit organic matter than that of the tidal-marsh sediment. Furthermore, hydrocarbons, presumably derived from marine organisms, make up about 40 percent of the bitumen in the offshore sand, as compared to 24 percent of the bitumen in the marsh sediments derived from land plants. Considering these differences, and (1) the strong retentivity of the abundant solid organic particles in the marsh sediment for the liquid and otherwise potentially mobile petroleum-forming compounds, and (2) the dominant derivation of the bitumen from the marsh sediment from plant spores, pollen, resin, and waxes that are resistant to bacterial or long-term diagenetic change, the authors believe that the offshore sand is the more likely source for migratable petroleum.

In addition to iron (as FeS_2), manganese, cobalt, chromium, copper, molybdenum, nickel, and vanadium are slightly concentrated in the organic-matter-rich tidal-marsh sediment; and, like iron, some of these metals increase as depth of sediment increases. The marked decrease of calcium, magnesium, strontium, and mineral carbon within the upper 25 centimeters of the tidal-marsh sediment is largely explained by the dissolution and removal of calcareous shell material by acidic water.

INTRODUCTION

The primary purpose of this study is the presentation of the depositional framework of a modern tidal-marsh environment in Florida that, we hope, will prove useful for future detailed organic geochemical and field stratigraphic investigations. The general interrelations and distributions of major sediment types and organic components in an extensive tidal-marsh area were determined to better identify and interpret the tidal-marsh environment of deposition for sedimentary rock facies and to identify the more diagnostic organic components and their biologic precursors in this environment.

Regional stratigraphic relations have suggested many interpretations of a tidal-marsh origin for carbonaceous sedimentary rocks, but factual supporting data, particularly on the complex types and distribution of the abundant carbonaceous material in the rocks, have been lacking. For example, the explanation by Grabau (1906, p. 593–613) that the widespread Chattanooga Shale, and the lithologically equivalent rocks of Devonian age in the Southeastern United States, represented a broad time-transgressive tidal-marsh deposit is still held as a possible explanation of the genesis of this rock unit. Rocks of Pennsylvanian age in the Midcontinent (Zangerl and Richardson, 1963, p. 231) and of Cretaceous age in the Western Interior (Sears and others, 1941, p. 116–119; Fisher and others, 1960, p. 38–40) of the United States have been interpreted, and probably rightfully so, as tidal or coastal marsh deposits of a transgressive or regressive sea. Certainly, each geologist can call to mind numerous other sedimentary rock units which he has studied that suggest deposition in a tidal-marsh area. A note of interest is that Klein (1970) has apparently identified 428 rock units that were deposited in the tidal zone and has suggested that these units be termed "tidalites."

Detailed organic geochemical studies that involve complex chemical methods and expensive, sophisticated analytical instruments are becoming common and have produced a wealth of new knowledge. Many of these studies have provided the bases for determining the environmental source, the biologic precursors, and the diagenetic changes of organic material in sediment. The laboratory techniques permit isolation and exact measurements of precisely defined compounds (such as an individual amino acid and a single normal alkane) or of organic carbon, oxygen, and sulfur isotopes

For example, the origin and the persistence of pristane through the food chain of pelagic organisms, and the identification of this compound in sediments and petroleum (Blumer and others, 1964), should be judged an important key in the geochemical history of petroleum.

Similarly, Hodgson, Baker, and Peake (1967) have unraveled chlorophyll-porphyrin relations that are basic in the understanding of petroleum genesis. Parker and his colleagues (for example, Parker and Leo, 1965; Winters and others, 1969), by identification of distinctive fatty acids and hydrocarbons in blue-green algae, have indicated that this abundant primitive plant type is a major contributor to the altered organic matter in recent and ancient sediments. Sackett and Thompson (1963) have shown the usefulness of C^{13}/C^{12} determinations in the definition of areal distribution patterns of organic matter derived from terrestrial, brackish-water, and marine organisms.

Eglinton and Calvin (1967) have reviewed the applicability to geology of "chemical fossils"—specific organic compounds that can be used as geobiologic markers of animals or plants that lived in the past but whose morphologic features have been destroyed. A more comprehensive review of organic geochemistry as a field that has direct bearing through the disciplines of biology, biochemistry, and organic chemistry into the geology of coal, petroleum, oil shale, and carbonaceous sediment is a book edited by Eglinton and Murphy (1969). A detailed application and evaluation of organic geochemistry toward the broader understanding of the well-known Green River Formation has been reviewed by Bradley (1970), and of the highly complex and varied genesis of petroleum, by Erdman (1965).

In addition to the types of investigation commonly considered in organic geochemistry, extensive investigations in soil chemistry (for example, Kononova, 1966; Stevenson, 1960; also see Burges, 1960; Breger, 1964) and in the chemistry of coal (Francis, 1954) should also be included. These investigations are especially pertinent to any organic geochemical study dealing with the humic, or kerogen, type of organic matter, which, after all, generally makes up more than 90 percent of the organic matter in both recent and most ancient sediments.

In this investigation, the sediment and its organic material and the geochemical processes attendant with deposition and shallow burial are described for only one—but an areally extensive one—tidal-marsh area. Other studies of recent sediment in other tidal-marsh areas are those for the Wadden Sea area of the Netherlands; for example, Van Straaten (1951, 1954); for the North Sea coast of Germany (Häntzschell, 1939; and many reports published by investigators at the Senckenberg-am-Mer research institution); for California, by Stevenson and Emery (1958), Phleger and Bradshaw (1966), and Warme (1971); for the New England area, by Bradley (1957), Redfield and Rubin (1962), Bloom (1964), and Rhoads (1967); for Georgia, by Hoyt, Weimer, and Henry (1964) and Marland and Henry (1969);

and for the Everglades of southern Florida, by Spackman, Scholl, and Taft (1964), and Spackman, Riegal, and Dolsen (1969). Kurz and Wagner (1957) presented an informative and interesting study of the types and distribution of tidal-marsh and adjacent forest plants and their relation to chemical parameters of the soil and rising sea level in the coastal areas of northern Florida. Review papers on tidal-marsh sediments and processes have been published by Van Straaten (1961), Klein (1967), and Zenkovich (1967, p. 618–670). Broader coverage of tidal-marsh ecology is presented by several authors in a treatise edited by Hedgpeth (1957a) and in a book edited by Lauff (1967).

ACKNOWLEDGMENTS

AREA OF STUDY

The coastal region of the northeastern part of the Gulf of Mexico consists of a broad shallow marine shelf, a tidal marsh, and a low-lying, commonly swampy, pine-forested area extending some 50 miles inland.

An 80-mile stretch of tidal marsh described in this report (fig. 1), still largely in its natural state, forms a continuous, monotonous fringe of marshgrass from the Aucilla River on the north to the Suwannee River on the south (fig. 2). Most of the marsh is 1–4 miles across and is regularly inundated twice each day by saline water to a depth of a few inches to about 2 feet. The general tide range, from low-tide level to high-tide level, is 2.5–3.5 feet (U.S. Coast and Geodetic Survey Charts 1259, Crystal River to Horseshoe Point, Fla.; 1260, Horseshoe Point to Rock Islands, Fla.; and 1261, Apalachee Bay, Fla.).

This area was selected for study because it is probably both the least affected by man and the least poluted area in the subtropical coastal areas of the United States. Furthermore, the absence of major delta-building rivers and the presence of a very broad shallow offshore shelf provide a large and uniform sediment depositional pattern that is comparable to environments of deposition postulated for shorelines of many ancient epicontinental seas.

The actual areal extent of the study area was arbitrarily limited, inasmuch as the tidal-marsh fringe extends many tens of miles to the south and southeast of the study area and many tens of miles to the northwest and west, where an even broader marsh area extends inland from the coast of Apalachee Bay. The factors determining the area of study were (1) the increase to the south of coastal communities, with consequent disruption of natural sedimentation and geochemical processes; (2) the presence of metropolitan Tallahassee, Fla., in the headwaters area of the St. Marks River, which is northwest of the Aucilla River, the north boundary of the study area. Tallahassee has had or has man-maintained dams, barge channels, and some industrial plants on the banks of the St. Marks River, all of which have undoubtedly affected the normal processes of sediment accumulation.

Within the study area, all the streams, except for the Suwannee River, have relatively small and unpopulated drainage basins. Study was not made, nor were samples collected, within 5 miles of the mouth of the Fenholloway River, which is southwest of Perry, Fla., mainly because of obvious and serious pollution caused by a large woodpulp paper plant some 21 miles upstream. The results of an extensive investigation of this industrial-waste pollution in the river and in the Gulf of Mexico water near the river mouth that involved hydrographers, hydrologists, microbiologists, bacteriologists, water chem-
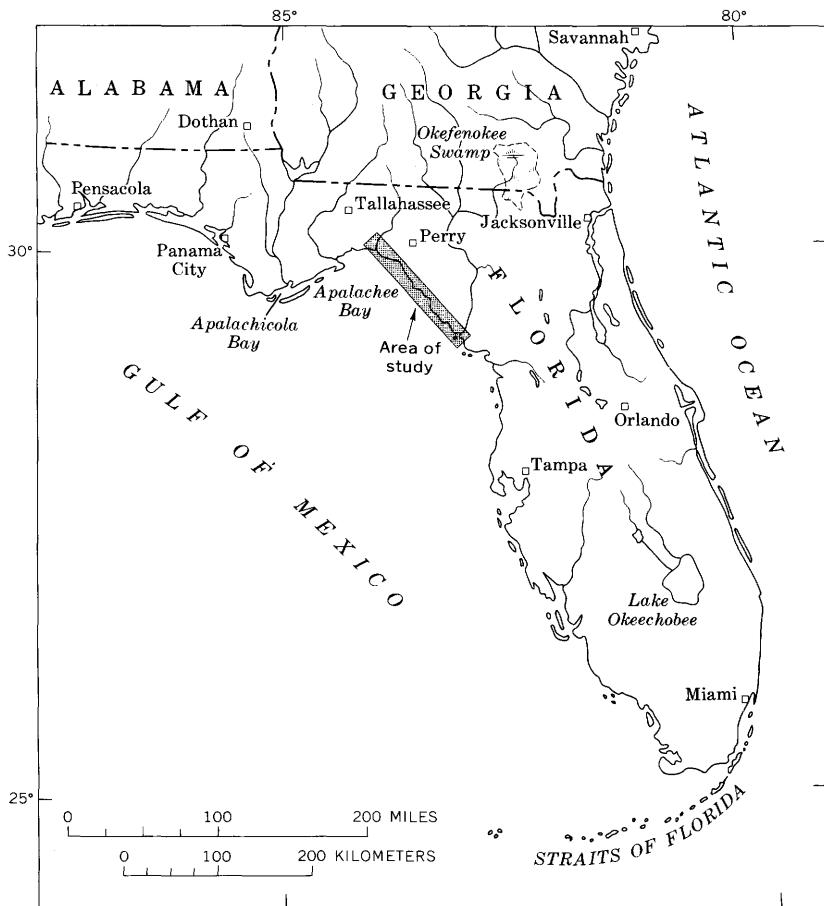
FIGURE 1.—Location of tidal-marsh area studied, northeastern coast of Gulf of Mexico.

ists, and sanitary engineers have been summarized by Saville (1966, p. 103–202). The abnormally high concentration of orthophosphate in the Fennholloway River has also been depicted on a map by Kaufman (1969).

Typical views (fig. 3) and a generalized transect (fig. 4) indicate the setting where the tidal-marsh sediment, which contains abundant plant remains, is accumulating. The plant that almost exclusively covers the marsh is *Juncus roemerianus* Scheele (identified by James A. Erdman), informally dubbed speargrass but also known as needle-grass or brown or black rush. This plant has a single tubular grayish-green stalk which is about 1 cm (centimeter) in diameter at its base and tapers to a sharp point at the top. The *Juncus* is generally 3–7 feet
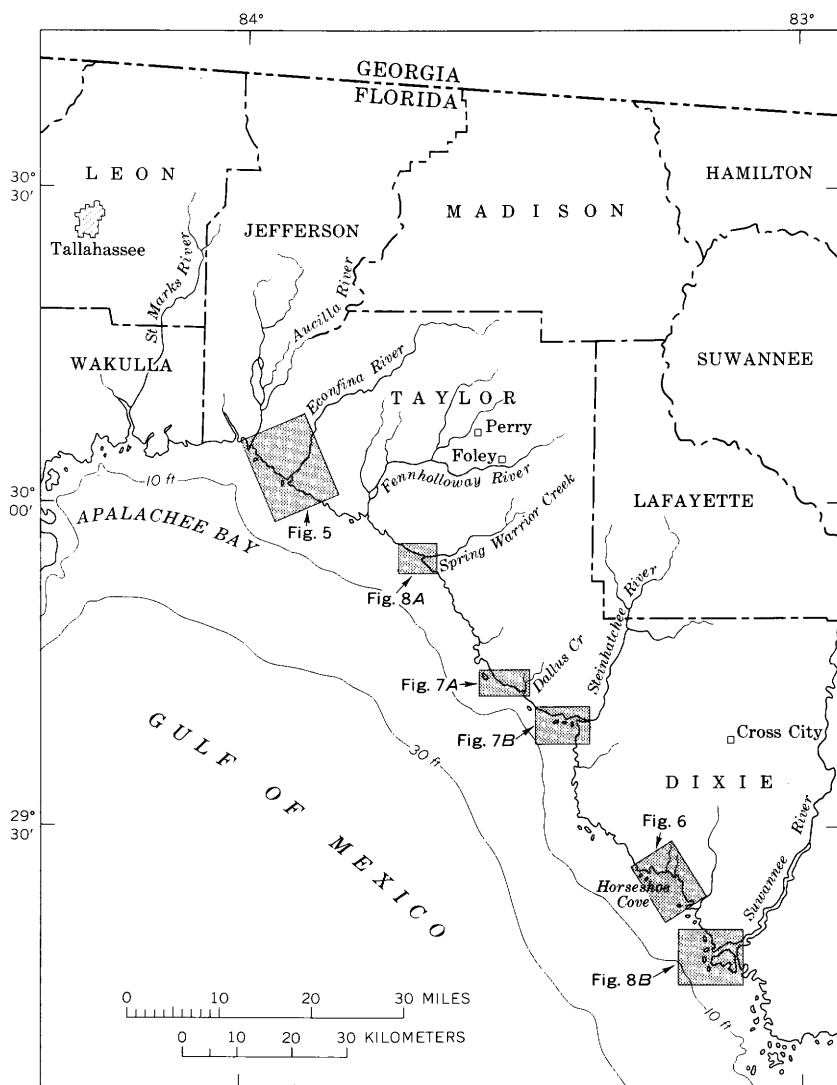
FIGURE 2.—Index map of northwest-central Florida showing major geographic features and location of the areas of figures 5–8.

(about 1–2 m) tall. It grows densely, and it appears to be impassable but is relatively easy to walk through and work in. After one's foot sinks into ankle-deep black mud, sufficiently solid footing is generally provided by the combination of dead speargrass and the rootmat.

The only other major plant distinguished in the tidal marsh was *Spartina alterniflora* Loisel (identified by James A. Erdman), commonly called smooth cordgrass or simply pioneer marshgrass. Its
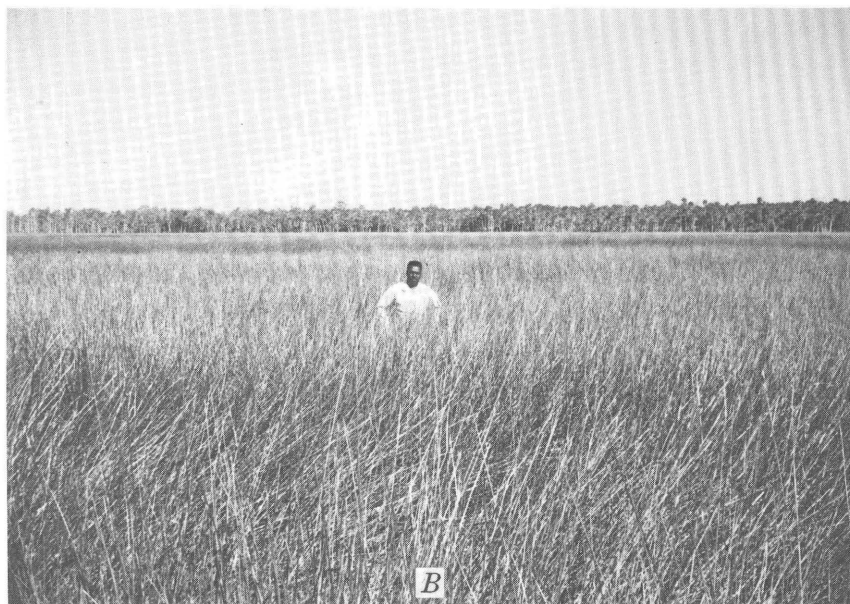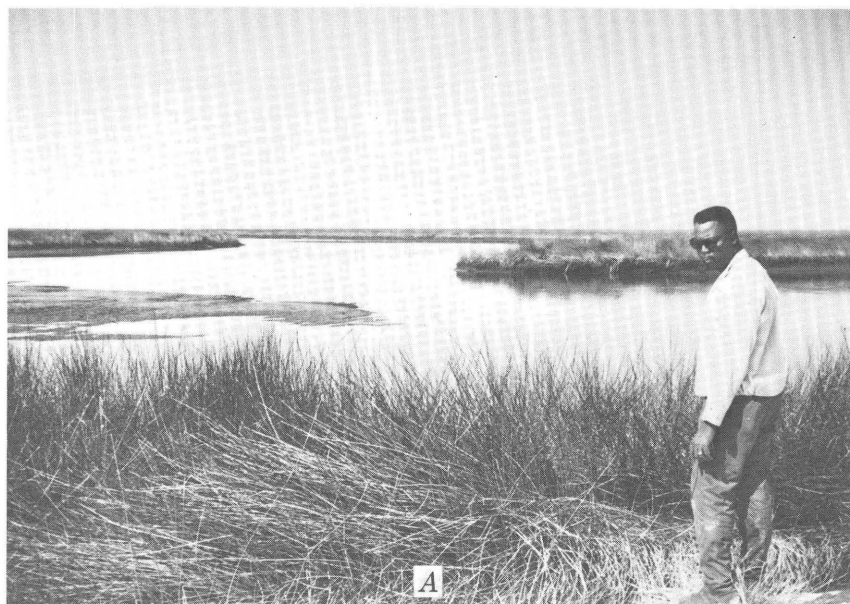
FIGURE 3.—Typical views of tidal-marsh area, near Spring Warrior Creek; A, view along stream channel toward Gulf of Mexico (about 1 mile away), at low tide; B, view inland across tidal marsh, showing A. H. Love in 4-foot-tall *Juncus* marshgrass; cabbage palms fringe forested area on skyline.
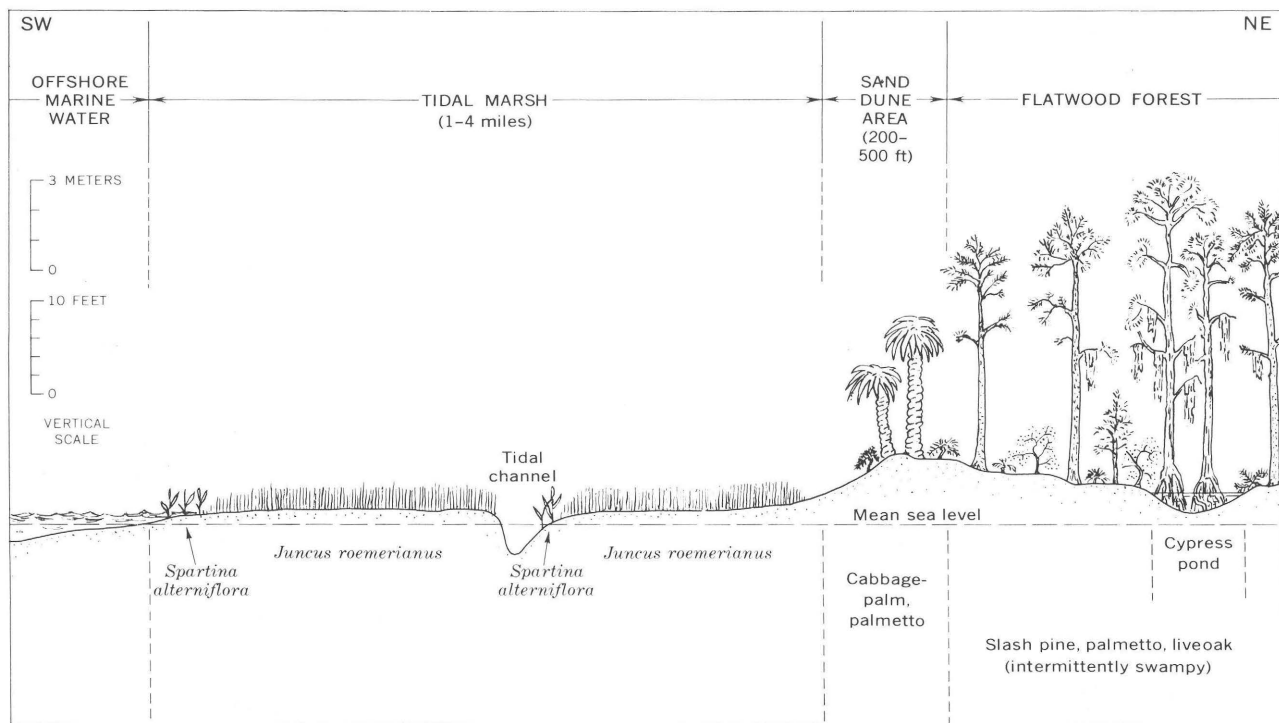
FIGURE 4.—Transect showing vegetation zones and principal plant types from Gulf of Mexico, across tidal marsh, to inland forest.

distribution is very limited; it is generally confined to very narrow strips of new mud deposited at the margins of small tidal ponds or to the banks of newly deposited mud along the meandering channels of tidal creeks. *Spartina* is readily differentiated from *Juncus* by its brighter and lighter green color and its semiflat bladed fronds. Reviews of the distribution of these and other marsh plants are presented by Kurz and Wagner (1957, p. 25–31, 101–104) and by Hedgpeth (1957v, p. 724–729).

The inner or landward boundary of the tidal marsh is marked by a commonly conspicuous band several hundred feet wide of cabbage palm trees that stand 20–40 feet (6–12 m) high and of palmetto which forms the underbrush (fig. 4). Beyond this band is the complex fresh-water flora of intermittent swampland dominated by the flatwood forest of pine trees, liveoak, and palmetto. Interspersed in this area are permanent fresh-water ponds, generally circular to oval and several hundreds of feet across, that are characterized by huge cypress trees. Most of the cypress and the pine are draped with Spanish moss. The present investigation was limited to the tidal marsh and the marine shelf, but certainly the palm-pine-cypress flora contributed significant amounts of comminuted plant material that ultimately was included in the organic mass deposited in the tidal marsh.

The seaward boundary between the tidal marsh and marine Gulf of Mexico water at any one spot is generally line-sharp, and even a vertical embankment 1–3 feet high can be seen at many places during low tide. In a few areas, however, for example, south-southeast of the mouth of the Econfina River and off the mouth of Spring Warrior Creek (fig. 2), the bottom sediment in the 2–5 feet of water extending as far as 3 miles offshore is a muddy sand supporting a scattered to extensive growth of common seaweed, tentatively identified as *Thalassia* (Phillips, 1960, p. 44–46). This seaweed traps sediment, and the *Thalassia* areas probably will slowly become tidal marsh—and certainly would rapidly become tidal marsh with slight lowering of sea level.

Except for fish, abundant pelecypods and gastropods in sandy offshore areas, and oysters on the irregularly distributed oyster banks generally near the mouths of tidal channels, animals were rarely and only locally observed in the tidal marsh area. A few emergent intertidal sandbanks at times were seemingly a moving mass of small fiddler crabs, and snails commonly were attached to the lower parts of *Juncus* stalks. Only a few turtles and deer and one unidentified snake were seen in the tidal marsh during the many weeks of fieldwork. Several varieties of gnats and flies were always bothersome; but, fortunately, mosquitoes were not a problem, except in the fresh-water marsh areas farther inland.

No effort was made to evaluate the undoubtedly complex community of burrowing organisms in this marsh environment, such as has been done for other areas (Hedgpeth, 1957b; Rhoads, 1967). Nor was the bacteria population studied, particularly the anaerobic sulfate-reducing bacteria active a few centimeters below the surface of the tidal-marsh muds. The reader is referred to ZoBell and Feltham (1942), ZoBell (1946), and especially to Oppenheimer (1960) for discussions of the relatively very slow rate of bacterial decomposition of organic matter under the pH–Eh conditions determined in the tidal marsh.

Five river-mouth areas and four tidal-marsh strips were selected to represent the 80-mile stretch of tidal marsh that includes the entire coastline of Taylor and Dixie Counties, Fla. (fig. 2). These spaced areas, excluding the Fenholloway River, cover about half the total area, and localities of sample stations for each of the major sampled areas are shown on the maps of figures 5–8.

The several major streams within the area that discharge into the Gulf of Mexico slowly contribute sediment, both organic and mineral, to the tidal marsh, and, undoubtedly, to areas far out in the gulf. These streams are not now a separate environment of deposition, but are simply channels, with itinerant sediment, cutting across the present tidal marsh. If sea level were to rise sufficiently, however, these channels would be filled with sand and would form the channel sandstone features familiar to stratigraphers.

What are here termed "river-mouth sediments" are those sediments temporarily accumulating in the river channel a few miles inland from the Gulf of Mexico and those sediments deposited as far as 4 miles out into the gulf. Although the samples that were collected in the river channels a few miles inland are spatially related to the tidal-marsh environment, they are from transient sediment that eventually will be swept seaward to be deposited in the shallow offshore marine environment.

A description of a traverse of one of the rivers in the area, the Econfina River (fig. 5), will illustrate the general role of these streams and of their sediment load. Ten miles inland, the slowly moving river water is very clear—but medium to dark tea colored—and is rarely more than 5 feet deep. Bedrock and blocks of the Suwannee Limestone of Oligocene age (Cooke, 1945, pl. 1) form the riverbed to within about 1 mile from the mouth of the river; carbonaceous sand and silt form the riverbed to the gulf. The river gradient is very low, and the river with its many smaller tributary streams drains low flat land which is rarely more than 30 feet above sea level and which has large areas of intermittent swamps with dense vegetation. Much of the tributary and river water is from springs, but during, and for several
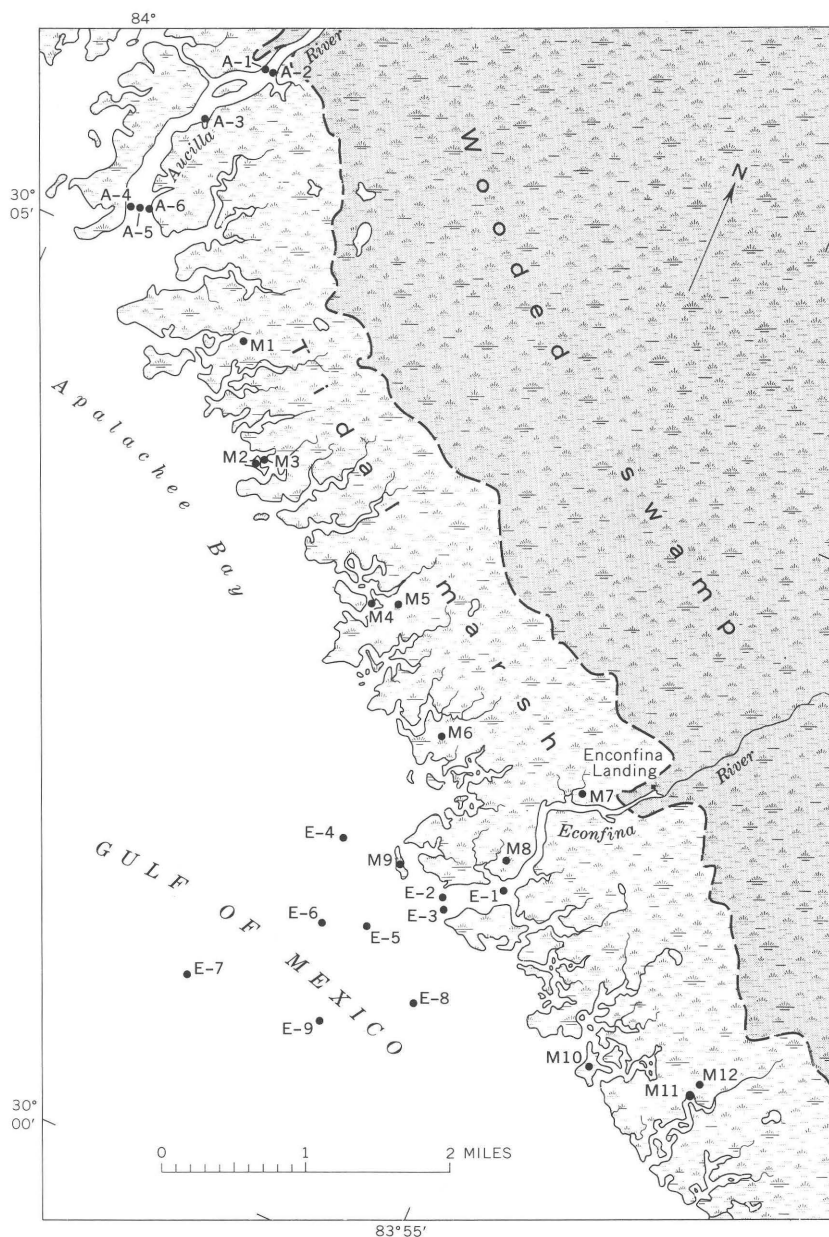
FIGURE 5.—Tidal-marsh (M2) and river-mouth (E–2) sample localities, Aucilla River and Econfina River area.

weeks after, the frequently heavy rains, the water in swamp areas rises and slowly flushes abundant soluble and particulate organic matter into the river.

The streams studied were, from northwest to southeast, the Aucilla and Econfina Rivers (fig. 5), Spring Warrior Creek (fig. 8A), Dallus Creek (fig. 7A), Steinhatchee River (fig. 7B), and the Suwannee River (fig. 8B). The Suwannee River is, by far, the longest, with its headwaters some 125 miles to the north in the Okefenokee Swamp, Ga. Dallus Creek is the shortest (though its mouth is 0.3 mile wide), with its headwaters in the tidal marsh about 2 miles inland. The approximate lengths of the other streams are Aucilla River, 65 miles; Econfina River, 35 miles; Steinhatchee River, 25 miles; and Spring Warrior Creek, 15 miles.

Several other major creeks within the area which have lengths comparable to those of Spring Warrior and Dallus Creeks were not studied, but the only major river not sampled was the Fennholloway River.

Areas of tidal marsh were studied, and samples collected, between the streams cited above, including the Horseshoe Cove area (fig. 6), which is about 10 miles northwest of the mouth of Suwannee River. The tidal-marsh localities are numbered from M1 to M25, generally from the northwest to southeast; river-mouth localities are generally in order from those upstream to those farthest offshore, and are designated by an identifying prefix; for example, "E" for Econfina River samples.

GEOLOGIC SETTING

The Quaternary sediments described in this report are a thin veneer of mud and sand no more than a few meters thick that accumulated, and are accumulating, on a shallow tectonically stable limestone platform of Suwannee Limestone of Oligocene age between the Aucilla and Steinhatchee Rivers (Taylor County), and of the Ocala Limestone of Eocene age between the Steinhatchee and Suwannee Rivers (Dixie County). The distribution and the character of the Suwannee Limestone in this area have been described by Cooke (1945, p. 86–101), and of the Ocala Limestone, by Puri (1957, p. 17–57, 78, 85), and by Puri, Yon, and Oglesby (1967, p. 63–97).

An extensive review of the Quaternary eustatic transgressions and regressions of marine water in the Apalachicola Bay area, about 75' miles to the west, has been written by Schnable and Goodell (1968), and in large part the findings are applicable to the area described here.

We have studied the upper 1 m (meter) of sediment deposited in about the last 3,500 years, while sea level has been slowly rising
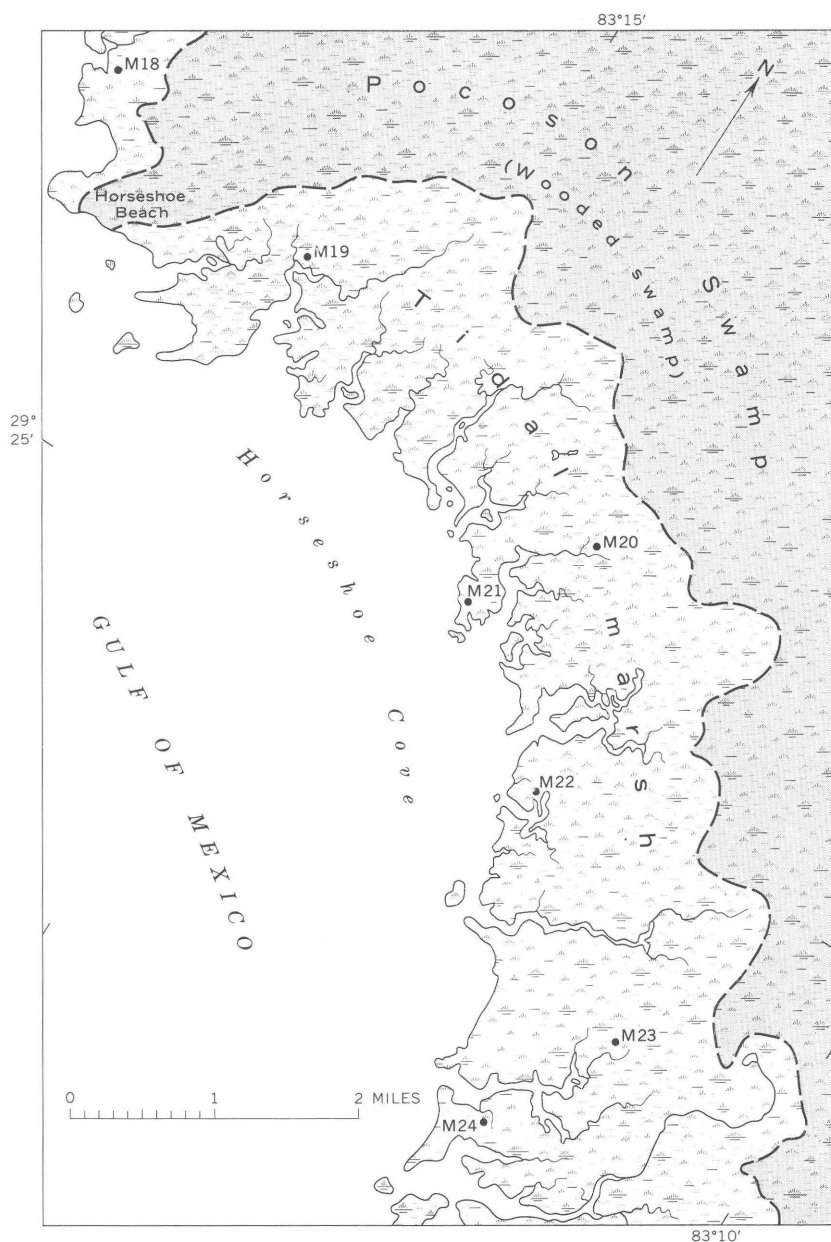
FIGURE 6.—Localities of tidal-marsh cores (M20), Horseshoe Cove area.
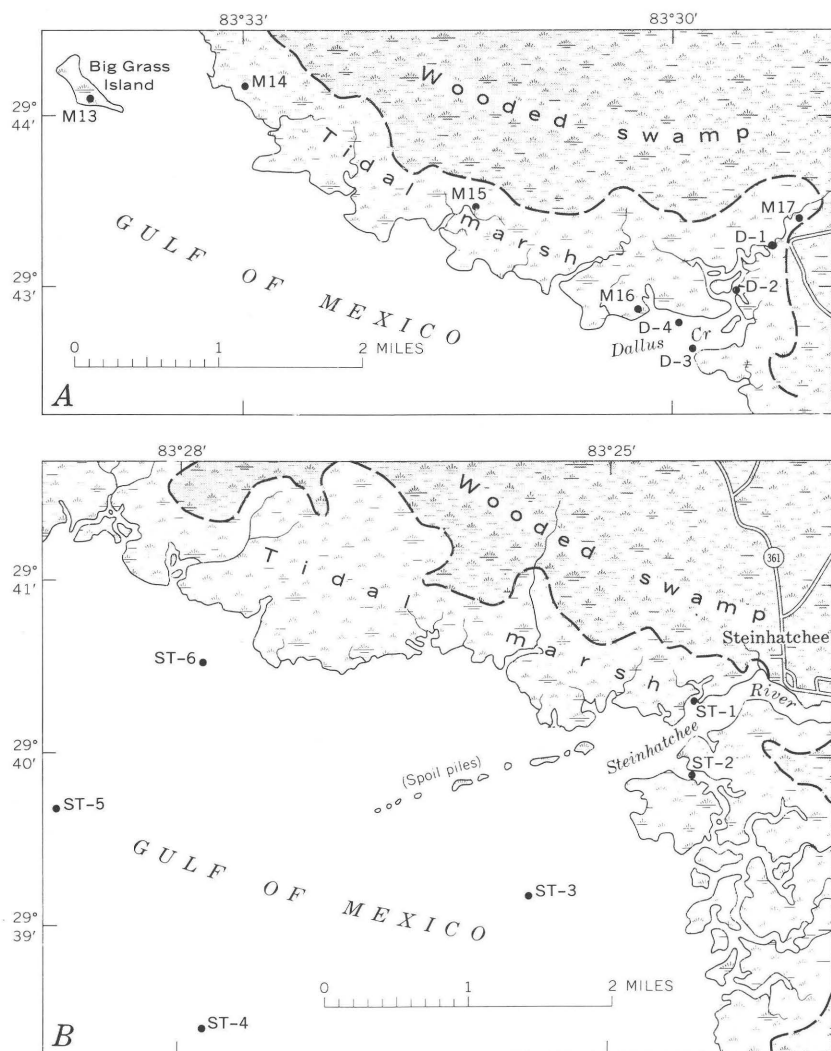
FIGURE 7.—Tidal-marsh (M14) and stream-mouth (ST–3) sample localities.
A, Dallus Creek area; B, Steinhatchee area.

(Scholl and Stuiver, 1967, p. 451; Schnable and Goodell, 1968, p. 56).
This estimate of age is supported by data obtained by Coultas (1969,
p. 122); from a tidal-marsh sediment about 3 miles from the mouth of
the St. Marks River, about 10 miles west of the northwest boundary
of the area of this report, the radiocarbon age of a pine trunk found
at a depth of 145–175 cm was 5,280 ±320 years B.P. (before present),
and that of disseminated organic material at a depth of 119–145 cm
was 3,075 ±150 years B.P.
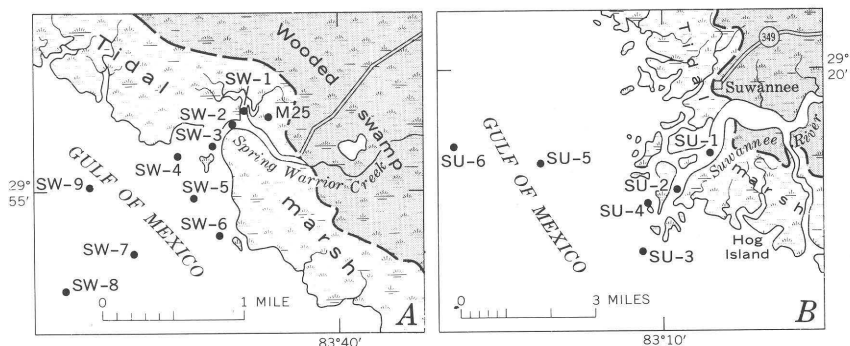
FIGURE 8.—Tidal-marsh (M25) and stream-mouth (SU–4) sample localities.
A, Spring Warrior Creek area; *B*, Suwannee area.

FIELD AND LABORATORY INVESTIGATIONS

FIELDWORK

The major objective of the fieldwork for this study was to collect a suite of representative samples and in-place correlative chemical measurements that would provide both general descriptive information and specific chemical data on recent sedimentation and geochemical processes in a subtropical tidal marsh environment. The fieldwork was divided into two periods of study—one during the spring of 1967 which was used to obtain samples and data on sediments at, and just seaward from, the mouths of streams flowing through the tidal marsh and the second period in the fall of 1967 which was devoted to the tidal marsh itself.

An 18-foot fiberglass boat with outboard engines, equipped with necessary coring gear for sample collection and instruments for chemical measurements, was used for all fieldwork. The boat was transported by trailer to the most convenient landing-slips that were located within a few miles of the mouths of the rivers flowing into the Gulf of Mexico. The shallow-draft boat permitted ready access far into the tidal marsh through the many channels, yet was adequate for work as far as 4 miles from shore into the Gulf of Mexico.

The routine of fieldwork was to occupy a station; locate the station on a topographic map (scale 1:24,000) by compass-line intersections; obtain salinity, temperature, pH, and Eh measurements of surface and bottom water; collect sample using appropriate corer (piston-type Phleger, or, for tidal muds, simply a cork-capped clear plastic tube) or a clamshell grab sampler; determine pH and Eh of sediment; and freeze samples as soon as possible on return to field headquarters. Samples were kept frozen until time of preparation for analysis. A total of 69 stations were occupied and, after segmentation of cores into

sample units, a total of 148 samples were individually analyzed and studied.

A field laboratory was established in a small rented house during the first period of field study to test the practicability of providing analyses on the spot that would support a reconnaissance-type organic geochemical field investigation. Except for the necessary, but limited, laboratory glassware and a portable balance shipped from Denver, Colo., all chemicals and distilled water were purchased at a local drug-store in Perry.

In this field laboratory, 38 sediment samples were dried in a kitchen oven at 45° C, were ground and sieved, and sediment and grain-size descriptions were prepared. Organic carbon contents of both sediment and water samples were determined by the standard Walkley-Black method. Analysis for alkaline-soluble humic substances and the subsequent determinations of humic and fulvic fractions were also accomplished by a slight modification of the standard method which will be described.

The same chemical determinations were subsequently run on splits of the same 38 samples in our Denver, Colo., laboratories (as reported in tables 2 and 3), and the results compared with the field analyses. Except for samples that contained less than 0.5 percent organic carbon, the field determinations were within ±15 percent of those produced in the Denver laboratories. Thus, organic analyses can be simply, rapidly, and inexpensively obtained in the field, and we found the results to be of definite value in the reconnaissance phase of this investigation.

Water salinities were measured at most localities, but ranges and averages are not included in the tables because salinities varied greatly with the times of measurement during the tide cycle. Except where the water was very shallow, less than 3 feet (0.9 m), the surface water had a lower salinity than the bottom water. In water 0.5–4 miles offshore, the maximum salinity measurements ranged from 25.5‰ (parts per thousand) off the mouth of the Econfina to 30.5‰ off the mouths of the Steinhatchee and Suwannee Rivers. In these shallow (5–13.5 ft) offshore waters, the salinity of the surface water was only 0.1–0.2‰ greater than that of the bottom water. Predictably, the lowest salinity measurements recorded were those made during ebb tide at stations farthest upstream in the rivers; for example, 0.7‰ at station A–1 on the Aucilla River and 0.3‰ at station SU–1 on the Suwannee River. No routine attempt was made to determine the distance of penetration of saline water upstream, but a spot check at high tide about 5 miles upstream from the mouth of the Aucilla River showed a salinity of 6‰.

A spread of a layer of fresh water over the more dense saline water was clearly and consistently observed near the mouths of the streams,

but salinity varied according to time and place that measurements were made. The maximum differences in salinity noted were near the mouth of the Aucilla River (fig. 5), where salinities of the top and bottom water, respectively, were 0.5 and 15.3‰ (sta. A–3), 5.5 and 22.5‰ (sta. A–4), and 8.6 and 23.3‰ (sta. A–5). Other examples of this salinity difference between top and bottom water were 18.5 and 23.3‰ (sta. E–3), and 20.3 and 24.4‰ (sta. E–6) near the mouth of the Econfina River (fig. 5) ; and 7.8 and 13.1‰ (sta. SU–3) at the mouth of the Su-wannee River (fig. 8B). Generally, however, mixing of fresh and sa-line water by wind and tidal action in this shallow-water coastal area is fairly rapid, and at most of the sample stations the differences between salinities of surface and bottom water were from 0.1 to 1.0‰.

The salinity of the high-tide water that submerged the tidal marsh was not routinely measured, but the measurements that were made ranged from 20 to 25‰.

Just as salinity varies according to the amount of mixing of fresh water and saline Gulf of Mexico water at different times in the tide cycle, so do pH and Eh values of the bottom water vary. Phleger and Bradshaw (1966, fig. 2, p. 1552) have documented the pattern of changes in salinity, pH, and Eh (measured as percent oxygen) of water 1 cm above sediment during a 24-hour period in a tidal marsh in California. The shallow offshore Gulf of Mexico water, 5–15 feet deep, is thoroughly agitated and mixed, so that the bottom water generally has a salinity of about 30‰, a pH of 8.0, and an Eh of +100 mv (millivolts). Similarly, the tide water that flushes over the marsh generally has a salinity of about 25‰, a pH of 7.9, and an Eh of +175 mv.

Table 1 presents the pH and the Eh values both of the bottom 5 cm of bottom water and of the upper 5 cm of bottom sediment at the time of sample collection. Before and after each measurement, the instru-ments were standardized by use of appropriate pH buffer and ZoBell solutions. As depth in the sediment became greater, the values for pH and Eh became lower than those for the uppermost 5 cm, as indicated by several measurements. These measurements showed that the river and the tidal marsh sediment 10–70 cm below the surface generally had a pH in the 4.5–6.0 range, and an Eh range of −250 to −400 mv. Kurz and Wagner (1957, p. 53) reported pH readings in *Juncus* marsh sediment in northern Florida as low as 3.6 at a depth of 30 inches (76 cm), but a 4.3–5.6 range was common. Determinations based on all available information indicate that acid and reducing conditions continuously prevail from a few centimeters from the sediment sur-face downward, even in sand covered by water that is almost always in a state of motion.

TABLE 1.—*Summary of pH and Eh measurements at sediment-water interface*

Position of measurement	Offshore			River			Tidal-marsh channel			Tidal-marsh flat		
	Range	Average	Number of localities	Range	Average	Number of localities	Range	Average	Number of localities	Range	Average	Number of localities
pH												
Lowest 5 cm of water_____	7.6–8.4	8.2	14	7.6–8.4	7.8	10	7.5–7.7	7.6	4	7.2–8.5	8.0	12
Uppermost 5 cm of sediment_____	6.9–7.8	7.3	14	5.3–7.6	7.1	10	6.3–7.1	6.8	4	4.8–7.5	6.8	16
Eh												
[In millivolts]												
Lowest 5 cm of water_____	+40–+200	+110	15	−80–+300	+140	12	+50–+150	+85	4	+70–+225	+165	12
Uppermost 5 cm of sediment_____	−350–−185	−265	15	−400–+60	−210	12	−315–−240	−280	4	−270–+120	−130	16

LABORATORY METHODS

After the frozen samples were air dried at 45° C, a representative fraction of each was described and classified by lithology, which was determined by study under a binocular microscope. Cores were initially segmented on the basis of megascopically observed lithologic units; subsequently, the uppermost 10 cm of sediment was separated as a special sample, and most of the underlying lithologic units were divided into 15-cm segments. A total of 148 samples were thus produced for microscopic description and chemical analysis.

In addition to the measurements of Eh and pH in the field, nine different chemical determinations were routinely run on each of the samples in the laboratory. These were total carbon, mineral carbon, organic carbon (by difference), total alkaline-soluble humic substances (by determination of soluble humic and fulvic fractions), bitumen, free sulfur, total sulfur (only on 102 tidal-marsh samples), and semi-quantitative emission spectrographic analysis. In addition, moisture content was determined on 19 samples, percent ash was determined on about half of the humic and fulvic fractions and organic-element composition on 20 of these fractions, the hydrocarbon-asphalt fractions were determined on 26 bitumen samples, and mineralogy by X-ray diffraction analysis was determined on six representatives samples. The laboratory chemical procedures that were used were those described by Palacas, Swanson, and Love (1968, p. C99–C100), and procedures for the bitumen fractionation were those presented by Ferguson (1962, p. 1614). The terms used to describe the organic matter and its fractions are given in figure 9.

The subdivision of organic matter into particulate fragments, humate, and bitumen is intended to convey the nature of the deposited organic components; these terms are of value in classifying the organic matter by parameters such as morphology, precursors, and sedimentation processes. The particulate fragments were deposited as solid predominantly woody particles; the humate as flocculated organic acids (naturally water-soluble humic substances) from tea-colored stream water; and the bitumen either as particles such as spore or pollen exines or as sorbed or colloidally dispersed waxy oily substances.

The next level of subdivision in figure 9 is based on chemical procedures in the laboratory by which the three groups of deposited organic materials are most clearly identified. In very recently deposited sediment, all the humate is dissolved by alkaline solutions (for example, NaOH), but it is recognized that a very small part of the decomposed woody fragments may also be dissolved. Benzene extraction may or may not dissolve all of the bitumen in the sediment, but this procedure provides the most useful reproducible results for com-
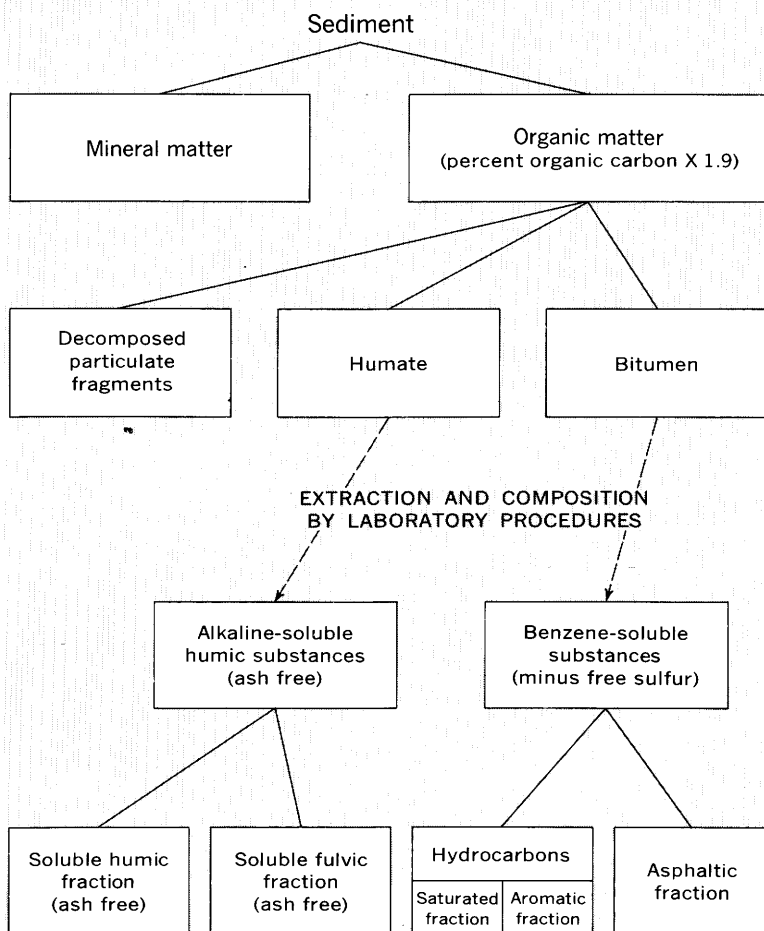
FIGURE 9.—Diagram indicating terms used in describing organic matter in sediment, and the fractions separated in the laboratory by chemical procedures.

parison of amounts and composition of bitumen from sample to sample. The chemical fractionation of the alkaline- and benzene-soluble substances is the final subdivision as indicated in figure 9. The terms "soluble humic fraction" and "soluble fulvic fraction" are, in general, similar to the terms "humic acids" and "fulvic acids" used by soil scientists, but the known variability and complexity of the chemical composition of these fractions in sediment and the confusion as to the types and amounts of laboratory-derived products yielded by widely differing chemical methods led the authors to the adoption of the indicated terminology. The term "hydrocarbons" is widely and

clearly understood, but the "asphaltic fraction" is a general group of widely differing and complex compounds that can only be defined as petroleumlike material associated with hydrocarbons.

The most useful analysis in a study of organic matter in sediments other than the ultimate (organic element) analyses is, of course, the analyses for percent organic carbon. Organic carbon values were obtained by the standard procedure of calculating the difference between total carbon determined by combustion and carbonate carbon determined by the gasometric method. For this report, the percentages of organic carbon are multiplied by a factor of 1.9 to provide data on total organic matter in sediment.

Carbon, however, is just one of the five major organic elements—carbon, hydrogen, oxygen, nitrogen, and sulfur—so the amount of total organic matter is here considered to be a necessary and meaningful quantitative determination against which other organic analyses should be related for three important reasons: (1) In an organic geochemical study of sediments, organic matter and the mineral matter are the major components of initial interest, and all subsequent fractionations of the organic matter should be quantitatively designated as percent or parts per million of the total organic matter. (2) Without identifiable morphologic structures, the amount and elemental composition of the organic matter provide the simplest clues toward identification of the dominant group(s) of biologic precursors (plant or animal, marine or land organisms), and toward systematic identification of the biochemical and geochemical alterations. (3) Because the chemically separated fractions of organic matter are also composed of the five major organic elements in distinctive, but highly variable, amounts, meaningful quantitative correlations of the fractions should be based on the total organic mass from which the fractions were derived.

Ideally, the organic matter should be physically separated from the minerals in the sediment, should be determined as an exact percentage of the total sediment, should be submitted separately for the many types of organic chemical analysis, and should be amenable to detailed microscopic study. Currently known methods of separation, however, have two defeating disadvantages for a study of hundreds of sediment samples: (1) No method for rapid, efficient, or complete separation of organic material from mineral matter is known, and the methods generally employed consume an inordinate amount of time. (2) The chemical methods commonly used, for example dissolution of most of the mineral matter in concentrated acids such as HCl and HF, cause an unknown and definitely variable change in the physical makeup and chemical composition of the organic matter.

Ashing of a sediment sample, though a simple and rapid procedure, provides a crude measure of percent total organic matter. However, unknown and variable amounts of inorganic minerals, particularly sulfides, are volatilized, which distorts the true value of percent organic matter. In addition, the organic matter itself is destroyed, precluding further study; this method, therefore, is of very limited value.

The percentages of organic carbon multiplied by a factor of 1.9 provide the most useful and easily determined data on the amounts of total organic matter in the sediment. This factor was determined as applicable for organic matter in recent sediment in Choctawhatchee Bay, Fla. (Palacas and others, 1968, p. C99–C100), and for sediment from two small estuaries in the Pamlico Sound area, North Carolina (Berryhill and others, 1972). On the basis of ultimate analyses and percent ash determinations, the factor of 1.9 was also determined to be applicable to the tidal-marsh sediments described here. Other similarly established conversion factors used are: 2.2 times the percent carbon for determining the ash-free soluble fulvic fraction; and an average 10.11 percent ash, based on 64 determinations, to provide the values for the ash-free alkaline-soluble humic fraction. Bitumen values that are reported are the benzene-extractable fractions from which the free sulfur has been removed; the free sulfur so removed is reported separately.

Midway during the laboratory work a change was made in the analytical procedure for determining the amount of the fulvic fraction in the alkaline-soluble organic matter. The change was made from the process of flocculating and weighing the dried fulvic fraction to one of evaporating to dryness the entire solution remaining after flocculation of the humic fraction, followed by determining organic carbon in the fulvate salt residue. During this changeover in procedure, some questionable fulvic-fraction values resulted, which are indicated in tables 2 and 3 by enclosure in parentheses.

SEDIMENT TYPES

For systematic discussion, the variety of sediments in the tidal-marsh area are divided (1) by geomorphic position and (2) by grain size and amount of organic matter. The area consists of two major generally sharply divided environments of sediment deposition—the tidal marsh that is made up of a muddy sediment containing abundant organic matter and the adjacent offshore marine environment that consists of relatively clean sand but that includes calcareous shell material. Most of the samples were collected from the tidal marsh, including 24 cores and a set of seven specially selected samples. The remainder of the samples collected were those from the bottom sediment in and near the mouths of streams (20 samples) and as far as 4 miles offshore in the Gulf of Mexico (20 samples).

CLASSIFICATION

Distinction of three types of marsh sediment was based primarily on relative amounts of organic material: (1) peaty sandy mud, containing more than 15 percent organic matter (52 samples); (2) carbonaceous muddy sand, containing less than 15 percent but more than 4 percent organic matter (21 samples); (3) relatively clean sand, containing less than 4 percent organic matter (24 samples). The typical vertical distribution and interrelations of these three sediment types are diagrammatically shown in figure 10.

The threefold classification utilizes grain size as a secondary parameter. The most fine-grained sediment, the peaty sandy mud, contained 10–25 percent of fine to very fine sand. Most of the relatively clean sand, though poorly sorted, was medium in grain size and generally consisted of more than 90 percent of fine, medium, and coarse particles. The carbonaceous muddy sand is an intermediate category, with the percentage of sand and the range in grain size generally very clearly distinguishable from those characteristic of either the peaty sandy mud or the relatively clean sand. Sediment descriptions and organic carbon analyses clearly indicate that the amount of organic matter decreases as the percentage of sand and the grain size increases; this change provided a very convenient and useful basis on which to classify and characterize the tidal-marsh sediment.

Of the total of 24 cores of tidal-marsh sediment, six (one-fourth) of the cores (M1, M2, M12, M15, M17, M21), consisted entirely of peaty sandy mud (table 2). All except the lowest sample in eight of the other cores (M5, M6, M8, M10, M14, M19, M22, M24) were also peaty sand mud; these cores generally "bottomed out" in relatively clean sand, commonly with a sharp contact between the mud and sand. Thus, 14 of the 24 cores can be considered to be typical tidal-marsh cores, with the upper 30–75 cm consisting of typical tidal-marsh mud (fig. 10).

Seven of the remaining 10 cores (M7, M9, M13, M16, M18, M20, M23) have either the mud or the carbonaceous muddy sand in the upper 10–25 cm, grading downward into relatively clean sand. Three other cores (M3, M4, M11) were taken in small narrow tidal-marsh creek channels, which typically have relatively clean sand as the bottom sediment.

The characteristic admixture of silt- and sand-sized quartz and the poor sorting in the tidal-marsh sediment can be rationally explained. Two obvious sources of poorly sorted quartz sand parallel the tidal marsh; namely, the low, rounded sand dunes on the landward side of the tidal marsh, which are now partly covered with vegetation, and the sand that forms the offshore sediment. Fairly strong intermittent

THICKNESS

VERTICAL
SCALE

Juncus roemerianus (spear grass or
brown rush) 3–7 feet tall

0 cm

(Tidewater)

10 cm

Black peaty sandy mud (25 percent organic matter),
penetrated by speargrass stems (excluded from
sample); organic matter mainly minute plant frag-
ments

10

20 cm

Brownish-black peaty sandy mud (20 percent organic
matter); rootmat dominant in upper 15 cm, rootlets
decreasing downward

20

30

40

30 cm

Brownish-black peaty sandy mud (25 percent organic
matter), mainly decomposed black shreds of plant
material; microscopic aggregates of pyrite increas-
ingly abundant below 40 cm

50

60

10 cm

Brown carbonaceous muddy sand (5 percent organic
matter), unidentifiable microscopic-size decayed
plant fragments, and humate coating sand grains

70

10 cm

Medium-gray relatively clean quartz
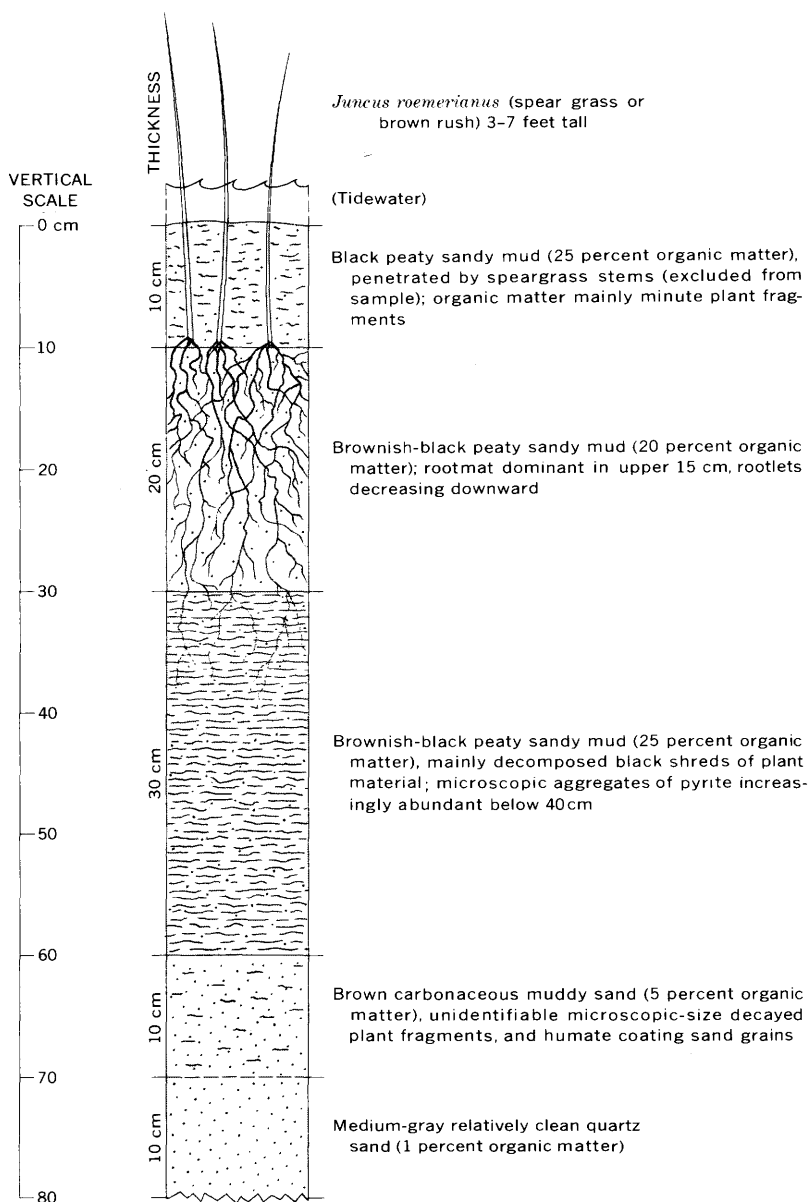sand (1 percent organic matter)

80

FIGURE 10.—Diagram of a typical tidal-marsh core and sediment description.
Except where distinct lithologic contacts existed, cores were routinely
sampled as follows: Top sample, 10 cm; top of rootmat to sand, 15-cm
intervals; bottom sand sample, generally 5–15 cm thick.

TABLE 2.—*Chemical analyses and sediment types of 97 samples from 24 tidal-marsh cores and of seven related samples*

[All data in percent except as otherwise indicated; all organic determinations reported on a moisture- and ash-free basis; values in parentheses are approximate only; N.d., not determined]

Station and sample No.	Sediment type	Depth in core (cm)	Organic carbon	Organic matter	Alkaline-soluble humic substances		Soluble humic fraction			Soluble fulvic fraction			Bitumen		Sulfur				Mineral Carbon
					Total	As percentage of organic matter	Total	As percentage of total humic substances	As percentage of total organic matter	Total	As percentage of total humic substances	As percentage of total organic matter	Total	As percentage of total organic matter	Total	Total S ÷ organic matter	Free sulfur	Free S as percentage of total S	
							Cores of tidal-marsh sediment												
M1-A ___ Peaty sandy mud ___		0–10	11.9	22.6	6.97	30.8	5.43	77.9	24.0	1.54	22.1	6.8	0.075	0.33	0.84	3.7	0.090	10.67	0.04
B ___ do ___		10–25	10.6	20.1	(5.96)	(29.6)	4.91	(82.4)	24.4	(1.05)	(17.6)	(5.2)	.087	.43	1.30	6.4	.075	5.77	.02
C ___ do ___		25–40	13.5	25.7	7.30	28.5	6.35	87.1	24.8	.94	12.9	3.7	.087	.34	6.37	24.8	.009	.14	<.01
D ___ do ___		40–61	14.3	27.2	(6.58)	(24.2)	5.98	(90.1)	22.0	(.60)	(9.1)	(2.2)	.100	.37	6.45	23.7	.006	.09	.03
M2-A ___ do ___		0–10	14.4	27.4	3.69	13.5	2.60	70.5	9.5	1.09	29.5	4.0	.169	.62	3.86	14.1	.085	2.19	.01
B ___ do ___		10–20	17.4	33.1	4.67	14.1	3.80	81.4	11.5	.87	18.6	2.6	.165	.50	3.70	11.2	.057	1.54	.03
C ___ do ___		20–31	12.5	23.8	3.78	15.9	3.32	87.9	14.0	.46	12.1	1.9	.078	.33	6.92	29.1	.005	.08	.02
M3-A ___ do ___		0–10	10.8	20.5	4.92	24.0	3.24	65.7	15.8	1.69	34.3	8.2	.056	.27	1.70	8.3	.023	1.35	.21
B ___ Carbonaceous muddy sand.		10–25	7.6	14.4	3.24	22.4	2.24	69.1	15.5	1.00	30.9	6.9	.044	.31	1.63	11.3	.002	.13	.06
C ___ do ___		25–33	2.8	5.3	.97	18.2	.68	69.9	12.7	.29	30.1	5.5	.016	.30	.60	11.3	.002	.30	.07
D ___ Relatively clean sand ___		33–48	.7	1.3	.24	17.9	.13	56.7	10.1	.10	43.3	7.7	.005	.38	.24	18.1	.001	.29	.06
E ___ do ___		48–63	.6	1.1	.19	16.3	.11	60.5	9.9	.07	39.5	6.5	.005	.47	.28	24.6	.001	.50	.14
F ___ do ___		63–68	.7	1.3	.32	24.2	.13	40.6	9.8	.19	59.4	14.4	.004	.29	.85	63.9	.002	.22	.03
M4-A ___ do ___		0–10	.2	.4	.24	62.0	.14	60.8	37.6	.09	39.2	24.3	.005	1.24	.20	52.6	.001	.25	.83
B ___ do ___		10–23	1.2	2.3	.40	17.7	.28	68.8	12.2	.13	31.2	5.5	.003	.11	.33	14.5	<.001	.06	<.01

TABLE 2.—*Chemical analyses and sediment types of 97 samples from 24 tidal-marsh cores and of seven related samples*—Continued

[All data in percent except as otherwise indicated; all organic determinations reported on a moisture- and ash-free basis; values in parentheses are approximate only; N.d., not determined]

Station and sample No.	Sediment type	Depth in core (cm)	Organic carbon	Organic matter	Alkaline-soluble humic substances		Soluble humic fraction			Soluble fulvic fraction			Bitumen		Sulfur				Mineral Carbon
					Total	As percentage of organic matter	Total	As percentage of total humic substances	As percentage of total organic matter	Total	As percentage of total humic substances	As percentage of total organic matter	Total	As percentage of total organic matter	Total S	Total S ÷ organic matter	Free sulfur	Free S as percentage of total S	
Cores of tidal-marsh sediment—Continued																			
M5-A	Peaty sandy mud	0–10	16.6	31.5	4.79	15.2	3.35	69.9	10.6	1.44	30.1	4.6	.063	.20	2.66	8.4	.003	.12	.04
B	do	10–25	13.7	26.0	4.50	17.3	3.53	78.3	13.6	.98	21.7	3.8	.083	.32	2.74	10.5	.002	.09	<.01
C	do	25–40	14.7	27.9	4.22	15.1	3.25	77.2	11.6	.96	22.8	3.4	.083	.30	3.84	13.7	.001	.03	.02
D	do	40–54	12.3	23.4	2.12	9.1	1.42	67.0	6.1	.70	33.0	3.0	.061	.26	3.13	13.4	.001	.04	.01
E	Relatively clean sand	54–60	2.0	3.8	1.09	28.6	.81	74.4	21.3	.28	25.6	7.3	.023	.60	.73	19.2	.001	.11	.04
M6-A	Peaty sandy mud	0–10	11.0	20.9	5.68	27.2	4.00	70.3	19.1	1.69	29.7	8.1	.063	.30	1.03	4.9	.019	1.81	.21
B	do	10–25	9.9	18.8	4.28	22.8	3.36	78.5	17.9	.92	21.5	4.9	.056	.30	.26	1.4	.032	12.42	.02
C	Relatively clean sand	25–40	2.0	3.8	.82	21.5	.68	83.3	17.9	.14	16.7	3.6	.019	.50	.86	22.6	.001	.08	.02
M7-A	Carbonaceous muddy sand.	0–10	6.0	11.4	3.99	35.0	2.76	69.3	24.3	1.23	30.7	10.8	.060	.53	.39	3.4	.084	21.49	.06
B	do	10–25	2.3	4.4	1.72	39.4	1.05	60.6	23.9	.68	39.4	15.5	.018	.41	.17	3.9	.119	70.05	<.01
C	do	25–40	2.2	4.2	1.42	33.9	.89	63.0	21.4	.52	37.0	12.5	.015	.35	.31	7.4	.016	5.23	.04
D	Relatively clean sand	40–55	1.8	3.4	1.09	31.9	.81	74.2	23.7	.28	25.8	8.2	.014	.42	.50	14.6	.001	.18	.03
E	do	55–61	.8	1.5	.53	34.8	.35	66.3	23.1	.18	33.7	11.7	.009	.59	.63	41.4	.001	.11	<.01
M8-A	Peaty sandy mud	0–18	11.9	22.6	5.81	25.7	4.41	75.8	19.5	1.40	24.2	6.2	.134	.59	1.24	5.5	.075	6.01	.01
B	Relatively clean sand	18–22	1.8	3.4	1.32	38.7	1.00	75.8	29.5	.32	24.2	9.4	.028	.81	1.03	30.1	<.001	.04	<.01

M9-A	Peaty sandy mud	0-10	18.6	35.3	5.28	14.9	3.79	71.7	10.7	1.49	28.3	4.2	.106	.30	4.08	11.5	.004	.09	.03
B	Carbonaceous muddy sand.	10-26	4.0	7.6	1.43	18.9	1.09	75.7	14.3	.35	24.3	4.6	.014	.18	1.52	20.0	.002	.16	.42
C	Relatively clean sand	26-31	1.6	3.0	.30	10.0	.18	60.1	6.0	.12	39.9	4.0	.003	.11	.89	29.3	.001	.13	1.04
M10-A	Peaty sandy mud	0-10	14.5	27.6	9.46	34.4	7.03	74.2	25.5	2.44	25.8	8.9	.077	.28	1.91	6.9	.141	7.36	.04
B	do	10-20	8.3	15.8	7.69	48.8	6.37	82.8	40.4	1.32	17.2	8.4	.115	.73	3.08	19.5	.080	2.56	<.01
C	do	20-30	12.2	23.2	8.47	36.5	7.65	90.3	33.0	.82	9.7	3.5	.185	.80	5.87	24.7	<.001	<.01	.03
D	Carbonaceous muddy sand.	30-40	2.6	4.9	1.95	39.4	1.53	78.4	30.9	.42	21.6	8.5	.037	.75	1.50	30.4	<.001	<.01	.03
M11-A	Relatively clean sand	0-12	1.4	2.7	.71	26.7	.43	61.0	16.3	.28	39.0	10.4	.006	.23	.42	15.8	.005	1.24	.04
M12-A	Peaty sandy mud	0-10	13.1	24.9	(6.89)	(27.7)	5.23	(75.8)	21.0	(1.67)	(24.2)	(6.7)	.089	.36	2.03	8.2	.022	1.08	.03
B	do	10-25	10.3	19.6	(5.00)	(25.6)	4.04	(80.8)	20.7	(.96)	(19.2)	(4.9)	.056	.29	2.49	12.7	.010	.39	<.01
C	do	25-40	14.6	27.7	(6.22)	(22.4)	5.34	(85.7)	19.2	(.89)	(14.3)	(3.2)	.117	.42	8.01	28.9	.002	.03	<.01
D	do	40-55	10.7	20.3	(5.74)	(28.2)	5.17	(90.1)	25.4	(.57)	(9.9)	(2.8)	.098	.48	3.53	17.4	<.001	<.01	<.01
M13-A	Carbonaceous muddy sand.	0-10	4.5	8.6	(1.43)	(16.7)	.91	(63.6)	10.6	(.52)	(36.4)	(6.1)	.026	.31	.42	4.9	(.032)	(7.74)	<.01
B	do	10-25	2.5	4.8	(1.05)	(22.2)	.65	(62.2)	13.8	(.40)	(37.8)	(8.4)	.008	.18	.22	4.6	(.007)	(3.41)	.02
C	Relatively clean sand	25-43	.8	1.5	(.20)	(13.5)	.14	(70.7)	9.5	(.06)	(29.3)	(3.9)	.004	.24	.19	12.5	(.001)	(.53)	.01
M14-A	Peaty sandy mud	0-10	11.2	21.3	(4.03)	(18.9)	2.82	(70.1)	13.3	(1.20)	(29.9)	(8.5)	.060	.28	2.2	10.3	.049	2.23	.14
B	do	10-25	9.2	17.5	3.44	19.6	2.65	76.9	15.1	.79	23.1	4.5	.180	1.03	7.0	40.1	.005	.07	<.01
C	do	25-47	15.4	29.3	(3.06)	(10.9)	2.40	(78.4)	8.2	(.66)	(21.6)	(5.3)	.118	.40	8.5	29.1	.003	.03	.01
D	Relatively clean sand	47-62	1.9	3.6	.61	16.9	.52	84.5	14.3	.09	15.5	2.6	.019	.54	.92	25.5	.001	.10	<.01
E	do	62-77	.9	1.7	.40	23.5	.30	75.2	17.7	.10	24.8	5.8	.012	.68	.50	29.2	.001	.22	<.01
M15-A	Peaty sandy mud	0-10	21.8	41.4	10.34	25.0	7.45	72.0	18.0	2.89	28.0	7.0	.230	.55	2.30	5.5	.080	3.49	.06
B	do	10-25	20.3	38.6	9.10	23.6	7.29	80.1	18.9	1.81	19.9	4.7	.286	.74	3.01	7.8	<.001	<.01	.15
C	do	25-35	15.1	28.7	5.90	20.6	4.80	81.4	16.7	1.10	18.6	3.8	.990	3.45	5.88	20.5	.002	.04	<.01
M16-A	Peaty sandy mud	0-10	12.4	23.6	5.65	24.0	3.61	63.9	15.3	2.04	36.1	8.6	.144	.61	.71	3.0	.153	21.51	.02
B	Carbonaceous muddy sand.	10-25	5.9	11.2	2.52	22.5	1.46	57.9	13.0	1.06	42.1	9.5	.048	.42	.50	4.5	.074	14.80	<.01
C	Relatively clean sand	25-40	1.8	3.4	.80	23.4	.51	63.7	14.9	.29	36.3	8.5	.025	.73	.26	7.6	.002	.81	.01
D	Carbonaceous muddy sand.	40-43	2.2	4.2	.84	20.0	.47	55.8	11.2	.37	44.2	8.8	.029	.69	.41	9.8	.001	.15	.01
M17-A	Peaty sandy mud	0-10	18.2	34.6	11.69	33.8	8.71	74.4	25.2	2.99	25.6	8.6	.152	.44	1.23	3.6	.062	5.00	.09
B	do	10-25	10.2	19.4	(6.66)	(34.4)	5.00	(74.9)	25.7	(1.67)	(25.1)	(8.6)	.085	.44	1.27	6.5	.023	1.82	.07
C	do	25-40	14.7	27.9	9.72	34.8	7.33	75.4	26.2	2.40	24.6	8.6	.125	.45	2.68	9.6	.018	.69	.05
D	do	40-55	16.7	31.7	(9.34)	(29.4)	7.28	(78.0)	22.9	(2.05)	(22.0)	(6.5)	.140	.44	4.64	14.6	.007	.16	.04
E	do	55-70	16.4	31.2	7.19	23.1	5.79	80.6	18.6	1.40	19.4	4.5	.135	.43	12.50	40.1	.004	.03	.03
F	do	70-76	17.7	33.6	(7.72)	(22.9)	6.17	(80.0)	18.4	(1.54)	(20.0)	(5.0)	.101	.30	11.42	33.9	.004	.03	.06

TABLE 2.—*Chemical analyses and sediment types of 97 samples from 24 tidal-marsh cores and of seven related samples*—Continued

[All data in percent except as otherwise indicated; all organic determinations reported on a moisture- and ash-free basis; values in parentheses are approximate only; N.d., not determined]

Station and sample No.	Sediment type	Depth in core (cm)	Organic carbon	Organic matter	Alkaline-soluble humic substances		Soluble humic fraction			Soluble fulvic fraction			Bitumen		Sulfur				Mineral Carbon
					Total	As percentage of organic matter	Total	As percentage of total humic substances	As percentage of total organic matter	Total	As percentage of total humic substances	As percentage of total organic matter	Total	As percentage of total organic matter	Total S	Total S ÷ organic matter	Free sulfur	Free S as percentage of total S	
Cores of tidal-marsh sediment—Continued																			
M18–A	Carbonaceous muddy sand.	0–10	5.4	10.3	2.17	21.2	1.27	58.3	12.3	.91	41.7	8.8	.034	.33	.53	5.2	.060	11.45	.15
B	do	10–25	2.8	5.3	1.03	19.3	.71	68.7	13.3	.32	31.3	6.1	.032	.59	.42	7.9	.014	3.43	<.01
C	Relatively clean sand	25–34	2.0	3.8	.63	16.6	.39	61.0	10.1	.25	39.0	6.5	.019	.50	.31	8.2	.005	1.45	<.01
M19–A	Peaty sandy mud	0–10	14.2	27.0	N.d.	N.d.	4.87	N.d.	18.1	N.d.	N.d.	N.d.	.091	.34	1.83	6.8	.128	6.99	1.30
B	do	10–25	16.9	32.1	N.d.	N.d.	6.78	N.d.	21.1	N.d.	N.d.	N.d.	.069	.21	2.93	9.1	.078	2.66	.11
C	do	25–40	11.7	22.2	N.d.	N.d.	3.65	N.d.	16.4	N.d.	N.d.	N.d.	.057	.26	3.01	13.5	.006	.21	.05
D	Carbonaceous muddy sand.	40–55	7.9	15.0	N.d.	N.d.	2.64	N.d.	17.6	N.d.	N.d.	N.d.	.060	.40	2.29	15.3	.007	.32	<.01
E	do	55–69	3.7	7.0	1.42	20.2	1.14	79.9	16.2	.28	20.0	4.0	.028	.39	1.25	17.8	.007	.57	.03
M20–A	do	0–10	5.7	10.8	(2.72)	(25.1)	1.72	(63.2)	15.9	(1.00)	(36.8)	(9.2)	.024	.22	.57	5.3	.024	4.23	.14
B	do	10–25	2.4	4.6	1.43	31.5	1.25	86.9	27.3	.19	13.1	4.1	.036	.80	.23	5.1	.039	17.09	.03
C	Relatively clean sand	25–40	1.1	2.1	.87	41.6	.67	76.5	31.8	.20	23.5	9.8	.013	.60	.34	16.3	.004	1.15	<.01
D	do	40–58	1.8	3.4	1.54	45.0	1.23	79.6	35.8	.31	20.4	9.2	.021	.62	.55	16.1	.001	.22	.02
E	do	58–78	.8	1.5	.87	56.6	.71	82.4	46.7	.15	17.6	9.9	.010	.66	.35	23.0	<.001	<.01	<.01

Sample	Description	Depth																	
M21-A	Peaty sandy mud	0-10	20.5	40.0	9.90	25.4	7.13	72.0	18.3	2.78	28.0	7.1	.140	.36	2.20	5.6	.219	9.94	.02
B	do	10-25	20.1	38.2	10.64	27.9	8.92	83.9	23.4	1.71	16.1	4.5	.298	.78	3.26	8.5	.019	.60	.03
C	do	25-40	20.0	38.0	10.59	27.9	9.33	88.1	24.5	1.26	11.9	3.3	.191	.50	3.93	10.3	.002	.06	.01
D	do	40-55	14.2	27.0	7.07	26.2	6.63	93.8	24.6	.44	6.2	1.6	.098	.36	3.82	14.2	.001	.04	.01
E	do	55-63	14.2	27.0	6.35	23.5	5.46	86.0	20.2	.89	14.0	3.3	.073	.27	3.98	14.8	.002	.06	.02
M22-A	do	0-10	16.9	32.1	N.d.	N.d.	6.95	N.d.	21.7	N.d.	N.d.	N.d.	.114	.36	1.21	3.8	.084	6.93	.02
B	do	10-25	17.2	32.7	N.d.	N.d.	7.75	N.d.	23.7	N.d.	N.d.	N.d.	.172	.53	1.59	4.9	.120	7.49	.02
C	do	25-40	11.6	22.0	N.d.	N.d.	6.22	N.d.	28.2	N.d.	N.d.	N.d.	.295	1.34	2.48	11.3	.016	.65	<.01
D	Carbonaceous muddy sand.	40-55	6.4	12.2	N.d.	N.d.	2.99	N.d.	24.6	N.d.	N.d.	N.d.	.104	.85	1.89	15.5	.001	.05	.07
E	do	55-65	4.2	8.0	N.d.	N.d.	1.92	N.d.	24.1	N.d.	N.d.	N.d.	.041	.52	2.00	25.1	.001	.03	<.01
M23-A	do	0-10	2.7	5.1	(1.29)	(25.1)	.94	(72.8)	18.3	(.36)	(27.2)	(6.9)	.013	.26	.22	4.3	.009	3.86	.06
B	Relatively clean sand	10-25	1.0	1.9	.82	43.1	.51	62.2	26.8	.31	37.8	16.3	.010	.53	.05	2.6	.002	3.80	<.01
C	do	25-40	.5	1.0	.41	43.1	.18	44.2	19.1	.23	55.8	24.1	.004	.37	.07	7.4	.003	4.14	<.01
D	do	40-49	.6	1.1	.43	37.7	.31	71.5	27.0	.12	28.5	10.8	.005	.40	.24	21.1	.003	1.21	<.01
M24-A	Peaty sandy mud	0-10	15.1	28.7	7.36	25.7	5.24	71.2	18.3	2.12	28.8	7.4	.115	.40	1.82	6.3	.110	6.02	.04
B	do	10-25	13.5	25.6	5.39	21.0	4.20	77.9	16.4	1.19	22.1	4.6	.129	.50	2.77	10.8	.071	2.55	.02
C	do	25-40	12.9	24.5	6.02	24.6	4.91	81.6	20.1	1.11	18.4	4.5	.091	.37	3.44	14.0	<.001	<.01	.02
D	do	40-55	12.1	23.0	6.67	29.0	5.71	85.6	24.8	.96	14.4	4.2	.088	.38	3.46	15.1	<.001	<.01	.02
E	do	55-70	8.3	15.8	3.90	24.7	3.24	83.1	20.5	.66	16.9	4.2	.058	.37	2.31	14.7	<.001	<.01	.01
F	Carbonaceous muddy sand.	70-79	3.0	5.7	1.39	24.3	1.12	80.8	19.6	.27	19.2	4.7	.018	.31	.73	12.8	.006	.85	<.01
G	Relatively clean sand	79-94	1.2	2.3	.76	33.2	.59	78.6	26.1	.16	21.4	7.1	.009	.40	.28	12.3	.004	1.55	.02

Selected samples, uppermost 4–5 centimeters homogeneous mud-sand layer

Sample	Description	Depth																	
M19-U	Peaty sandy mud	0-4.5	13.4	25.5	5.22	20.5	2.80	53.7	11.0	2.42	46.3	9.5	.084	.33	1.83	7.2	.181	9.90	1.90
M20-U	Carbonaceous muddy sand.	0-5	6.3	12.0	2.25	18.8	1.22	54.0	10.2	1.04	46.0	8.7	.034	.28	.71	5.9	.039	5.52	.41
M23-U	do	0-4.5	7.2	13.7	2.69	19.7	1.48	55.1	10.8	1.21	44.9	8.8	.035	.26	.34	2.5	.003	.76	.14
M24-U	Peaty sandy mud	0-4	15.8	30.0	6.65	22.2	4.21	63.2	14.0	2.45	36.8	8.2	.072	.24	1.50	5.0	.070	4.65	.14
MX-U	do	0-4	16.5	31.3	5.93	18.9	3.10	52.3	9.9	2.82	47.7	9.0	.062	.20	1.65	5.3	.030	1.81	1.29

Live stems and dead surface litter of dominant marsh grass

Sample	Description																		
MX-JL	*Juncus*, live stems		48.4	94.7	12.82	13.5	7.33	57.2	7.7	5.48	42.8	5.8	1.056	1.11	.11	.12	.013	11.2	N.d.
JD	*Juncus*, dead stems		50.5	96.7	14.71	15.2	8.21	55.8	8.5	6.51	44.2	6.7	1.055	1.09	.17	.17	.013	7.6	N.d.

winds churn up and distribute some sand throughout the tidal marsh from both sources, directly by wind from the dunes and by surging waves of water from the offshore sand.

Hurricanes, which cause drastic changes in shorelines and sediment distribution, occur on the average of every 6–10 years for any one coastal area of the Gulf of Mexico. Over a period of several thousand years, many hurricanes have undoubtedly passed through the tidal-marsh area of this investigation. With each hurricane, certainly the upper 5–10 cm of sediment was suddenly and violently churned up; however, because of the very shallow water over a reach of 100 miles offshore (gradient, about 1½ ft per mi, or 30 cm/km), only the sand nearest the shore is caught in the onshore surge of water. This sand is rapidly intermixed and redeposited with the marsh mud, and is now represented in the predominant poorly sorted peaty sandy mud cored during this investigation.

An overall description, then, is that the 80-mile stretch of tidal marsh along the northeastern Gulf of Mexico coastline is blanketed with a black organic-rich mud that is 30 cm to at least 75 cm thick. Organic matter in this sandy mud averages about one-fourth (27.0 percent) of the total sediment by dry weight and generally ranges from 20 to 30 percent.

PEATY SANDY MUD

Peaty sandy mud is the most characteristic and abundant of the recently deposited and now-accumulating tidal-marsh sediments. When this mud is collected, it is always wet and is black to very dark brownish black, and one's boots readily sink into it to a depth of 5–30 cm. The slurp and suction on walking through this relatively homogeneous, cohesive, and generally odoriferous mud, and the many hours spent cleaning the mud from boots are vivid memories of fieldwork in the marshes. When dried, the mud is medium brownish black to dark yellowish brown. Dried sediment from the rootmat and below (fig. 10) generally crumbles readily, but the samples of the upper 4–10 cm cakes into hard chunks.

The mineral fraction of the mud is generally more than 90 percent quartz and amorphous silica fragments of spicules and diatoms. Most of the quartz grains are subangular, very poorly sorted, and are mainly of silt size but range from clay size to medium sand size; the smaller grains of quartz are clear and subangular, and thus are difficult to distinguish from the spicule and diatom fragments. The remainder of the mineral fraction consists of a few percent of heavy minerals, mainly magnetite and ilmenite, variable amounts of iron sulfide minerals, fossil calcareous shell fragments, and a very small amount of clay.

The mineralogy of four representative samples of peaty sandy mud from the tidal marsh (table 2, M5–A and C, M17–E, MX–U) was determined by X-ray diffraction analysis by Paul D. Blackmon (written commun., 1971). The estimated amounts of identified components confirmed the observations made of the sediment under the microscope and the semiquantitative spectrographic analyses of individual elements. Quartz grains and fragments of amorphous silica (for example, diatoms and spicules) were the dominant inorganic material in all four samples; pyrite was present in all four samples and was estimated to be 5–10 percent of sample M5–C and about 20 percent of sample M17–E; calcite was present only in trace amounts, except in sample MX–U (upper 4 cm of mud) which had 5–10 percent calcite; and montmorillonite, kaolinite, and a clay identified as "aluminum interlayered-vermiculate and montmorillonite" were present in trace amounts in each of the four samples.

Fragments of amorphous silica spicules and diatoms were seen in every sample. The sediment is virtually noncalcareous, except for a few mollusk shells, shell fragments, or partly dissolved shell material observed in the upper 10–20 cm of just a few of the 52 sandy mud samples. The absence of shell material from samples below 20 cm indicates that the sediment is sufficiently acid to have caused complete dissolving of the shells. Only a very few foraminiferal, radiolarian, and ostracode tests were observed in study of the samples. Fecal pellets were scarce.

Organic matter is abundant, generally more than 20 percent, in all samples and varies greatly in appearance, from discrete only slightly compressed stalk and root segments of marsh grass to a humate stain on mineral grains. The organic matter in the upper 5 cm and below a depth of 25 cm in the sediment is dominantly dark-brown to black minute particles which are nonidentifiable, except as decomposed plant material. The odor of H_2S in the wet sediment is generally very strong, noticeable even when one is walking through the marshgrass, and is exceptionally strong in the mud from a few centimeters below the surface to the bottom of most cores.

CARBONACEOUS MUDDY SAND

Carbonaceous muddy sand falls between peaty sandy mud and relatively clean sand in texture and organic content. About half the 21 samples of carbonaceous muddy sand in the cores (table 2) are actually gradational sediment between the overlying peaty mud and the underlying clean sand; the other half of the samples are solely associated with the cleaner sand samples and differ only in that they are finer grained and contain more than 4 percent organic matter. Most

chemical analytical values, as a group, however, clearly support the classifying of the carbonaceous muddy sand distinctly different from the other two sediment types.

As in the other two lithologic groups, the most dominant mineral matter in carbonaceous muddy sand is clear quartz. The quartz is very poorly sorted and is mainly very fine to fine grained; but silt-sized grains, which include amorphous silica fragments, are common. Clay, heavy dark minerals such as magnetite, and other minerals such as zircon constitute but a few percent of the sand.

The organic matter is mainly of two types: (1) fragmented brownish-black plant material such as decomposed woody shreds and (2) brown to brownish-black humate that stains or coats the quartz grains. Calcareous shells or shell fragments are generally absent. When the sediment is wet, an H_2S odor is invariably present, but it is moderate in comparison to that emanating from the peaty mud at depths of 10 cm or more.

RELATIVELY CLEAN SAND

The term "relatively clean sand" is ascribed for two reasons: (1) to contrast a distinct sediment type from the carbonaceous muddy sand just described; and (2) to differentiate the medium-gray to light-olive-gray sand in the tidal-marsh cores from the nearly white beach and dune sand, which is marginal to the tidal marsh in some areas and which is very common in broad areas of other parts of the Florida gulf coast.

The relatively clean sand, whether in samples at the bottom of the 15 peaty sediment cores or from the bottom of the tidal-marsh creeks (3 cores), is invariably poorly sorted and is composed mainly of medium- to fine-sized clear quartz grains. Frosted subrounded coarse grains are scattered throughout most samples, and angular very fine-sized and silt-sized grains also are common. Fragments of clear siliceous radiolarian or sponge spicules and diatom fragments were observed in most samples, but rarely composed more than a few percent of the sand. Similarly, dark heavy minerals were commonly observed, but they composed less than 1 percent of most sand samples.

In samples underlying the peaty sandy mud many quartz grains are partly or wholly coated with a thin film of brown humate, which commonly accounts for 25–50 percent of the organic matter in these samples. The remainder of the organic material in the bottom samples of the peaty cores—and generally more than 75 percent of the organic matter in the sand in the creek beds—is dark brown to black microscopic shreds of decomposed plant matter.

An X-ray diffraction analysis of a relatively clean sand sample (table 2, M20–D) indicated more than 90 percent quartz, and only

traces of amorphous silica, montmorillonite, and kaolinite (Paul D. Blackmon, written commun., 1971).

UPPERMOST LAYER OF TIDAL-MARSH SEDIMENT

A thin surface layer of black mud is so characteristic over the entire tidal-marsh area that it deserves separate discussion. This top black sediment layer is consistently 4–10 cm thick and is generally peaty sandy mud or, less commonly, a very carbonaceous muddy sand.

Since the first reconnaissance of the marsh area a question has existed as to whether this distinctive upper layer is a wholly natural deposit. As previously mentioned, no samples were collected within 5 miles of the mouth of Fenholloway River because of the very obvious pollution caused by a large woodpulp plant 21 miles upstream from the river mouth and, to a minor extent, by some sewage from the city of Perry 18 miles upstream from the river mouth. Salville (1966, p. 177) stated, however, that little evidence of pollution exists in the tidal marsh and Gulf of Mexico beyond 3–5 miles from the mouth of the Fenholloway River. A second possible source of "pollution" is the many large pine tree farms and forested areas cut over in the past, that lie in fresh-water marshes (now cut with networks of drainage canals) behind the dune areas inland from the tidal marsh. These cut-over areas may unnaturally increase the amount of plant debris flushed downstream into the Gulf of Mexico. A third source of pollutants could be gasoline-combustion products from boat engines as the tidal-marsh area was, and is, highly productive in commercial and game fish. With regard to both commercial and game fishing, several residents discussed the possibility that pollution is the cause for the decline in catches and production of oysters, crabs, and fish within the last 25 years.

Evidence against the distinctive upper layer of organic-rich mud's being entirely a man-caused deposit includes the remarkably uniform distribution, thickness, and composition of the layer along more than 80 miles of coastline and the recorded rise in sea level in very recent time. Marmer (1952) made calculations based on changes in tide levels at Cedar Keys, Fla., which is about 15 miles south of the mouth of the Suwannee River, that sea level rose 0.4 foot (12 cm) between 1929 and 1950; this rise in sea level, alone, could account for the natural accumulation of the upper black mud layer in the tidal marsh. Furthermore, the microscopic characteristics of the sediment are indistinguishable from those of the mud at depths of at least 75 cm which is estimated to be a few thousand years old. As will be subsequently shown, no significant chemical differences were determined between this upper layer and the same sediment type at greater depths.

Certainly, the types and extent of pollution in this large tidal marsh should be determined precisely. However, this was not an objective of the studies reviewed here, and the sedimentological and geochemical processes involved in the deposition of the upper black layer will be considered herein to be natural processes that can be applied toward understanding similar ancient geologic environments of deposition.

RIVER-MOUTH SEDIMENTS

Forty samples of the upper 10 cm of sediment were collected (table 3) from about 2 miles upstream from the mouths of six streams to as far as 4 miles into the Gulf of Mexico off the mouths of the streams. Two to three samples were collected in traverses across the mouths of most of the streams.

The channels of these streams where they cross the tidal marsh are relatively shallow, most of them about 5 feet deep but one having a maximum measured depth of about 8 feet. Except for the Suwannee River, which has cut a series of braided channels across the tidal marsh, each of the other streams has a single wide mouth at the Gulf of Mexico. The gradient of the coastal shelf seaward is very low, and the bottom is nearly flat in this part of the Gulf of Mexico. The water depth rarely exceeds 15 feet within 5 miles of shore and generally is less than 50 feet within 25 miles of shore. The only noticeable irregularities on this gently sloping marine shelf are a few small islands or submerged sand bars 0.1–2 miles offshore.

The sediment at the bottom of the streams contains such diverse types as fragments of limestone, generally a few to several miles upstream from the Gulf of Mexico, to organic-rich sandy mud. Calcareous shells or fragments of them are common. No broadly consistent patterns in the distribution of sediment types were determined, except that organic-rich sandy mud generally occurs within a few tens of feet of the tidal-marsh shore along riverbanks and at the sea-tidal-marsh margin, and that relatively clean sand which contains abundant shell fragments extends seaward from this strip of mudbottom. Fine to medium sand containing variable, but generally small, amounts of organic matter characterizes the sediment in the main channels near the mouths of the streams.

Offshore from the mouths of the streams, in the Gulf of Mexico, two general types of sediment are distinguished. Dark- to medium-gray carbonaceous sandy mud, commonly containing calcareous shell material, extends seaward for less than 1 mile in irregularly shaped patches off the mouths of most streams. The second, and the more abundant, type is light-gray to yellowish-gray calcareous medium

sand, which is the typical sediment in the Gulf of Mexico near the mouths of the streams and offshore to a distance of at least 5 miles. An X-ray diffraction analysis indicated that this type of sand (table 3, ST–4), was more than 80 percent quartz; the remainder was calcite, aragonite, and a trace of montmorillonite (Paul D. Blackmon, written commun., 1971).

As shown in table 3, the above sediment types are simply considered as river sediment and offshore sediment, each sample being described separately. The river samples are listed sequentially from farthest upstream to river mouth, and the offshore samples are ordered generally from north to south. As in tidal-marsh sediment, increase in sand and grain size in both river and offshore sediments is accompanied by a decrease in organic matter; furthermore, the amount of organic matter in the sand generally decreases with distance from shore. See, for example, table 3, sample data ST–3–6 and SU–3–6).

ORGANIC MATTER

GENERAL RELATIONS

The extensive area of shallow water in the northeastern Gulf of Mexico and the broad adjacent lowland area of Florida do not form a single depositional environment characterized by sediment with abundant organic matter, but rather, several depositional environments. The two environments discussed here are separated by a sharp line that almost exactly coincides with the present coastline. One is the tidal-marsh environment, characterized by a very rich humic type of carbonaceous sediment, and the other is the contiguous shallow-water marine environment in which the sediment is mainly sand that contains a very small amount of organic matter which is predominantly derived from marine organisms.

On the basis of microscope study and chemical analyses presented, the composition of the organic matter that generally makes up 15–40 percent of the predominant tidal-marsh mud is determined to be about 75 percent of variably decomposed dark-brownish-black fragments from woody plants and grasses. The remaining 25 percent of the organic matter is estimated to be flocculated organic acids.

More than 99 percent of the organic matter in the tidal-marsh sediment is thus the humic type, derived primarily from woody plants and grasses that contain abundant cellulose and lignin. Most, if not all, of the cellulose has been decomposed to yield organic acids; plant fragments that remain are largely of degraded lignin (see Breger, 1964). The process of plant degradation and cellulose decomposition has been well described by Barghoorn (1949). Decomposition by bacteria and

TABLE 3.—*Chemical analyses and sediment*

[All data in percent except as otherwise indicated; all organic determinations reported on a

Station and sample No.	Sediment type	Distance upstream from mouth (miles)	Distance from bank (feet)	Depth of water (feet)	Organic carbon	Total organic matter (percent organic carbon X 1.9)	Alkaline-soluble humic substances Total	As percentage of organic matter
							River sediments,	
A–1____	Gray sandy mud____	1. 5	25	3. 3	1. 2	2. 3	0. 236	10. 3
2____	Brown muddy sand__	1. 5	15	4. 1	3. 7	7. 0	. 954	13. 6
3____	Brown sandy mud___	. 9	8	3. 4	2. 8	5. 3	1. 149	21. 7
4____	Gray sandy mud____	. 2	25	4. 7	1. 3	2. 5	. 371	14. 8
5____	Gray muddy sand___	. 2	450	7. 0	1. 7	3. 2	. 383	12. 0
6_____do_____		. 2	35	3. 9	1. 3	2. 5	. 350	14. 0
E–1____	Gray fine sand_____	. 5	350	4. 6	. 7	1. 3	. 186	14. 3
2____	Gray sandy mud____	. 05	300	5. 5	1. 2	2. 3	. 178	7. 7
3____	Gray fine sand_____	. 05	325	3. 6	. 4	. 8	(. 119)	(14. 9)
SW–1__	Gray medium sand__	. 55	20	3. 9	. 1	. 2	N.d.	N.d.
2__	Gray fine sand_____	. 45	25	4. 1	. 1	. 2	N.d.	N.d.
3__	Gray sandy mud____	. 25	300	3. 7	. 5	1. 0	N.d.	N.d.
4_____do_____		. 0	650	4. 6	1. 8	3. 4	N.d.	N.d.
D–1___	Brown fine sand_____	. 95	20	3. 2	. 4	. 8	. 093	11. 6
2____	Gray muddy sand___	. 55	30	5. 2	2. 4	4. 6	. 813	17. 7
3____	Gray fine sand_____	. 05	150	3. 4	1. 4	2. 7	(. 138)	(5. 1)
ST–1___	Gray medium sand__	. 8	75	3. 9	1. 1	2. 1	N.d.	N.d.
2_____do_____		. 6	50	7. 2	1. 0	1. 9	N.d.	N.d.
SU–1___	Brown medium sand_	2. 0	70	8. 5	. 2	. 4	. 255	63. 7
2___	Gray medium sand__	. 9	325	5. 6	. 2	. 4	. 141	35. 3
		Distance from shore (miles)					**Offshore sediment,**	
E–4____	Gray fine sand_____	0. 2		3. 9	0. 7	1. 3	N.d.	N.d.
5____	Gray sandy mud____	. 7		6. 6	5. 8	11. 0	0. 814	7. 4
6____	Gray fine sand_____	1. 1		4. 6	. 6	1. 1	N.d.	N.d.
7_____do_____		2. 5		5. 3	. 6	1. 1	N.d.	N.d.
8____	Shelly sandy mud___	1. 0		5. 0	. 6	1. 1	N.d.	N.d.
9____	Gray medium sand__	1. 4		5. 7	. 8	1. 5	N.d.	N.d.

types of 40 samples of river-mouth sediment

moisture- and ash-free basis; values in parentheses are approximate only; N.d., not determined]

Soluble humic fraction			Soluble fulvic fraction			Bitumen		Free sulfur	Mineral carbon
Total	As percentage of total—		Total	As percentage of total—		Total	As percentage of total organic matter		
	Soluble humic substance	Organic matter		Soluble humic substance	Organic matter				
upper 10 centimeters									
0. 058	24. 6	2. 5	0. 178	75. 4	7. 7	0. 006	0. 26	0. 007	0. 04
. 847	88. 8	12. 1	. 107	11. 2	1. 5	. 022	. 31	. 018	. 39
. 849	73. 9	16. 0	. 300	26. 1	5. 7	. 027	. 51	. 004	. 05
. 335	90. 3	13. 4	. 036	9. 7	1. 4	. 015	. 60	. 008	. 25
. 285	74. 4	8. 9	. 098	25. 6	3. 1	. 017	. 53	. 020	. 48
. 332	94. 8	13. 3	. 018	5. 2	. 7	. 012	. 48	. 010	. 19
. 184	98. 9	14. 2	. 002	1. 1	. 2	. 010	. 77	. 022	. 28
. 170	95. 5	7. 4	. 008	4. 5	. 3	. 008	. 35	. 015	1. 12
. 116	(97. 5)	14. 5	(. 003)	(2. 5)	(. 4)	. 003	. 37	. 006	. 09
N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	. 001	. 50	. 003	. 08
N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	. 001	. 50	. 001	. 08
. 012	N.d.	1. 2	N.d.	N.d.	N.d.	. 005	. 50	. 003	. 41
. 096	N.d.	2. 8	N.d.	N.d.	N.d.	. 014	. 41	. 031	. 51
. 085	91. 4	10. 6	. 008	8. 6	1. 0	. 007	. 87	. 003	<. 01
. 775	95. 3	16. 8	. 038	4. 7	. 8	. 019	. 41	. 007	. 01
. 129	(93. 4)	4. 8	(. 009)	(6. 6)	(. 3)	. 013	. 48	. 005	. 22
. 385	N.d.	18. 3	N.d.	N.d.	N.d.	. 013	. 62	. 017	. 45
. 157	N.d.	8. 3	N.d.	N.d.	N.d.	. 012	. 63	. 016	. 41
. 100	39. 2	25. 0	. 155	60. 8	38. 7	. 001	. 25	. 002	<. 01
. 084	59. 6	21. 0	. 057	40. 4	14. 3	. 001	. 25	. 003	. 01
upper 10 centimeters									
0. 077	N.d.	5. 9	N.d.	N.d.	N.d.	0. 009	0. 69	0. 001	0. 08
. 600	73. 7	5. 5	. 214	26. 3	1. 9	. 027	. 24	. 064	. 93
. 038	N.d.	3. 5	N.d.	N.d.	N.d.	. 004	. 36	. 005	. 44
. 042	N.d.	3. 8	N.d.	N.d.	N.d.	. 005	. 45	. 010	. 35
. 011	N.d.	1. 0	N.d.	N.d.	N.d.	. 003	. 27	. 020	3. 25
. 040	N.d.	2. 7	N.d.	N.d.	N.d.	. 007	. 47	. 004	. 44

TABLE 3.—*Chemical analyses and sediment types*

[All data in percent except as otherwise indicated; all organic determinations reported on a

Station and sample No.	Sediment type	Distance from shore (miles)	Depth of water (feet)	Organic carbon	Total organic matter (percent organic carbon X 1.9)	Alkaline-soluble humic substances	
						Total	As percentage o organic matter
						Offshore sediment,	
SW–5__	Gray sandy mud____	. 5	4. 9	2. 2	4. 2	. 106	2. 5
6_____	do_____	. 1	4. 2	2. 1	4. 0	N.d.	N.d.
7__	Shelly sandy mud___	1. 2	5. 8	2. 8	5. 3	. 111	2. 1
8_____	do_____	2. 0	5. 8	2. 1	4. 0	N.d.	N.d.
9_____	do_____	1. 5	5. 2	1. 8	3. 4	N.d.	N.d.
D–4____	Brown fine sand_____	. 1	3. 4	. 5	1. 0	. 031	3. 1
ST–3___	Shelly medium sand__	1. 0	5. 2	1. 5	2. 8	N.d.	N.d.
4_____	do_____	3. 0	11. 4	. 2	. 4	N.d.	N.d.
5_____	do_____	2. 1	13. 5	. 3	. 6	N.d.	N.d.
6___	Gray sandy mud____	. 2	4. 0	2. 3	4. 4	N.d.	N.d.
SU–3__	Gray medium sand___	. 5	4. 5	. 8	1. 5	. 235	15. 7
4___	Gray fine sand_____	. 05	3. 1	1. 4	2. 7	. 376	13. 9
5___	Brown medium sand_	2. 0	11. 2	. 1	. 2	. 006	3. 0
6___	Gray medium sand__	4. 0	11. 9	. 2	. 4	. 001	. 2

fungi was dominant when the plant material was a part of the forest humus, before transport by streams; and hydrolytic breakdown (Barghoorn, 1949, p. 9–10), rather than microbiologic attack, was dominant when the plant material was deposited as part of the tidal-marsh sediment. The high resistance to microbial attack of lignin and particularly the humic acids, which are the predominant alkaline-soluble organic substance discussed in this report, has been experimentally established by Lynch and Lynch (1959, p. 1479). The resulting solid organic material in the tidal-marsh sediment is, with little doubt, degraded lignin and flocculated organic acids and very minor amounts (less than 1 percent) of resin, terpene, and waxy substances, all resistant to further biologic attack or to geochemical alteration, except under conditions of extreme heat and pressure.

SOURCES

It is estimated both from direct observation and from the chemical composition of the organic constituents that 80 percent of the decomposed humic material in the sediment (fig. 11) has been derived from

of 40 samples of river-mouth sediment—Continued

moisture- and ash-free basis; values in parentheses are approximate only; N.d., not determined]

Soluble humic fraction			Soluble fulvic fraction			Bitumen		Free sulfur	Mineral carbon
Total	As percentage of total—		Total	As percentage of total—		Total	As percentage of total organic matter		
	Soluble humic substance	Organic matter		Soluble humic substance	Organic matter				
upper 10 centimeters									
.095	89.6	2.3	.011	10.4	.3	.011	.26	.025	.65
.097	N.d.	2.4	N.d.	N.d.	N.d.	.010	.25	.024	.68
.105	94.6	2.0	.006	5.4	.1	.017	.32	.031	3.19
.028	N.d.	.7	N.d.	N.d.	N.d.	.014	.35	.019	3.90
.042	N.d.	1.2	N.d.	N.d.	N.d.	.013	.38	.019	2.21
.024	77.4	2.4	.007	22.6	.7	.013	1.30	.004	.20
.020	N.d.	.7	N.d.	N.d.	N.d.	.009	.32	.007	3.54
.018	N.d.	4.5	N.d.	N.d.	N.d.	.003	.75	.010	1.15
.001	N.d.	.2	N.d.	N.d.	N.d.	.004	.67	.010	1.51
.055	N.d.	1.3	N.d.	N.d.	N.d.	.013	.29	.015	.69
.174	74.0	11.6	.061	26.0	4.1	.003	.20	.006	.07
.270	71.8	10.0	.106	28.2	3.9	.013	.48	.003	.08
.002	33.3	1.0	.004	66.7	2.0	.003	1.50	.002	.11
<.001	N.d.	N.d.	.001	N.d.	.2	.004	1.00	.001	.50

the thousands of square miles of swampy pine-palmetto forest and cypress ponds that lie inland from the coast. The two main types of this humic organic material, the solid partly decomposed plant fragments and the soluble organic acids, constitute about 60 and 20 percent, respectively, of the total organic matter. Both types are flushed from the inland area, carried by streams to the Gulf of Mexico, and almost immediately swept onto and deposited in the tidal marsh. Most of this material is thus deposited during the late-winter and midsummer periods of high rainfall, but even during times of low rainfall and low stream flow the stream water is dark tea colored from organic acids, which are flocculated by sea water and swept onto the tidal marsh.

The remaining 20 percent of the organic material (fig. 11) is believed to have been derived mainly from the dominant, ever-present marshgrass, *Juncus*, and, to a much lesser extent, from washed-in seagrasses such as *Thalassia*. These grasses, too, produce the two main types of humic material, solid decomposing plant fragments and their
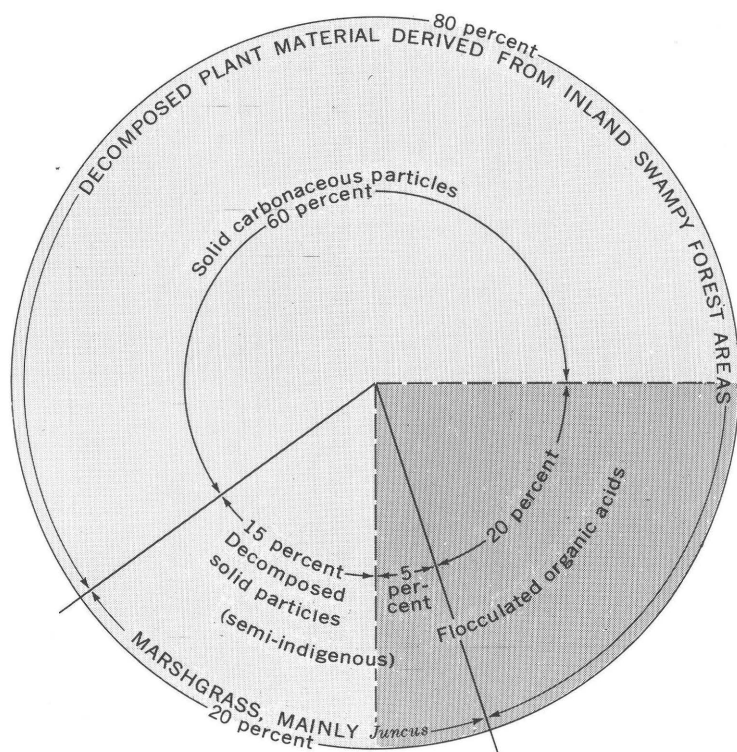
FIGURE 11.—Percentages of organic matter from different sources in tidal-marsh sediment.

water-soluble products, that constitute about 15 and 5 percent, respectively, of the total organic matter in the sediment.

This estimate that 20 percent of the organic matter is derived from the marshgrass and seagrass, which might seem questionably low and is contrary to the "*Spartina* and (or) *Juncus* peat" description used by Kurz and Wagner (1957, p. 113), is based on two types of evidence. (1) Dead decomposed *Juncus* stalk fragments and sparse *Thalassia* leaf blades are easily identified under the microscope in the upper 10–20 cm of sediment, as are viable and dead *Juncus* roots in samples 10–40 cm below the sediment surface; (2) the living and the dead *Juncus* materials are chemically distinct from the organic matter in the sediment as a whole, particularly in their hydrogen and nitrogen contents (table 4). The content and composition of the bitumen extracted from the marshgrass also differ markedly (table 7) from the organic matter as a whole; the bitumen content of the *Juncus* material is two to three times greater than that of the organic matter in

TABLE 4.—*Organic element composition of dominant marshgrass,* Juncus roemerianus [1]

[Analyses by Huffman Laboratories, Inc., Wheat Ridge, Colo. Values are on moisture- and ash-free basis; percent ash reported separately]

Sample No. Description	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
MX-JL Green stems of live plants_____	48.40	6.66	43.97	0.86	0.11	5.30
JD Gray stems of dead plants, surface litter_____	50.54	6.82	41.68	.79	.17	3.32
JLH Soluble humic fraction, 7.7 percent of MX-JL_____	61.31	6.07	28.09	4.36	.17	.78
JDH Soluble humic fraction, 8.5 percent of MX-JD_____	57.98	6.39	32.48	3.06	.09	4.34

[1] See table 2 for other analytical data.

the sediment, and the percentage of saturated hydrocarbons in the bitumen is 1/10–1/50 of that in the organic matter in the sediment. Moreover, when the spectrographic analyses of the ash of the living and the surface-litter *Juncus* are recalculated for comparison with analyses of the total organic matter in the sediment, *Juncus* could not possibly contribute more than 10 percent of the metals, such as chromium, copper, molybdenum, and vanadium, that are present in the sediment organic matter.

DEPOSITIONAL PROCESSES

The principles governing the deposition of clay in tidal-flat areas, described in detail by Van Straaten and Kuenen (1958), and the general dynamic and depositional conditions extant in tidal-flat areas described by Zenkovich (1967, p. 618–670) apply directly to the accumulation and concentration of organic matter in the Florida tidal-marsh area.

The organic matter that is delivered to the shallow water of the Gulf of Mexico by the slow-moving streams is immediately and dynamically involved in the almost constant onshore-wave action and tidal action. The light particles of woody material and the flocculated organic acids are kept in suspension by the wave action and are flushed into the marsh during high tide, which occurs twice each day. When the tidal flow gradually decreases in velocity near the time of high tide, the finest suspended organic particles are actually in the quietest and shallowest water and will be deposited. The ebb current, which is comparatively very slow and weak, is insufficient to remove the newly deposited organic material that adheres to other organic and mineral material. The thick *Juncus* and *Spartina* marshgrass also serves as a trapping mechanism, as well as providing an umbrella effect that protects the sediment from violent wind agitation.

As previously stated, 20 percent of the organic matter is derived from marshgrass and some seagrasses. This grass material is initially deposited as surface litter in the marsh and then is gently shifted around by tide waters. This litter, which is exposed to the air and repeatedly wetted and dried, is rapidly and simultaneously fragmented and decomposed, mostly into degraded lignin and flocculated organic acids, and is then incorporated into the mud. The dead root material of the marsh plants is much more slowly decomposed and is the only morphologically identifiable plant material at depths 20–40 cm in the sediment; retarded bacterial decomposition and some mixing by burrowing organisms, however, eventually obliterate most of this root material.

The surface of the accumulating organic matter and other sediment in the marsh is apparently in equilibrium with present mean sea level. Slow, but continuous, compaction of the sediment establishes room for more deposits, however, and given long-term, very slowly rising sea level, the thickness of mud rich in organic matter would increase accordingly.

A discussion of the analyses of the organic matter (tables 2, 3) follows. Data used for calculation of averages and ranges of organic matter in the tidal-marsh sediment are only those for the 97 samples from the 24 cores listed in table 2.

TIDAL-MARSH SEDIMENT
TOTAL ORGANIC MATTER

The most widespread and typical sediment in the tidal marsh is the brownish-black to black peaty sandy mud. The 52 samples of this type of sediment (table 2) contain an average of 27.0 percent organic matter by dry weight, and a maximum of 41.4 percent (M15–A). If the 14 cores of peaty sandy mud are considered representative of a sedimentary unit 30–75 cm thick that blankets the tidal marsh, this unit has an average of 26.4 percent organic matter (range, 19.9–36.3 percent in 14 cores). If this unit were consolidated rock, it would be about 15 cm (6 in.) thick and would be classified as a carbonaceous or coaly siltstone (Vine, 1962, fig. 29, p. 119), rather than a black shale (Swanson, 1961, p. 69). This rock classification would be based on the lack of lamination caused by the very poor sorting of the sediment and on the predominantly humic type of the organic matter.

The average content of organic matter in the 21 samples of carbonaceous muddy sand is 7.9 percent, and the range is 4.2–15.0 percent. As a rock type, this carbonaceous muddy sand would be simply a carbonaceous sandstone. Although the carbonaceous muddy sand commonly forms a gradational interval between the overlying peaty mud

and the clean sand below, it forms the upper 25–40 cm of sediment in four cores, M7, M13, M18, and M20 (table 2), and in these cores averages 6.7, 6.7, 7.8, and 7.7 percent total organic matter, respectively. Although the top sample in each of these cores contains the most organic matter, field observations show that stations M7 and M20 are at the landward edge of the tidal marsh and that stations M13 and M18 are at the seaward edge of the marsh; mixing with adjacent ancient dune sand and relatively smaller amounts of transported organic matter explains the absence of peaty sandy mud at M7 and M20, whereas relatively stronger tidal and wave action intermittently disperses the organic matter at M13 and M18.

The amount of total organic matter in the 24 samples of relatively clean sand averages 2.3 percent, and the range is 0.4–3.8 percent. Only one sample (M4–A), representing sand in the channel of a tidal creek, contained less than 1 percent organic matter. Too few samples of creek sand were collected for meaningful averages, but it is estimated that this sand generally contains about 2 percent organic matter, most of which is occluded particles of plant debris. The relatively clean sand samples that form the lowest part of the typical tidal-marsh cores of peaty mud contain an average of 3.1 percent organic matter. The organic matter in these sand samples consists of 25–50 percent humate, and the remainder consists of microscopic shreds of decomposed fragments of plant matter. As a rock type, the relatively clean sand would become a slightly carbonaceous or impure sandstone.

A fairly rapid and successful method for initial characterization of the organic matter in sediments is the determination of the relative amounts soluble in alkaline solutions and in organic solvents. These determinations are indicative, respectively, of the humic and sapropelic nature of the organic material, or, in some rocks, of the metal-adsorptive or oil-yielding character of the material.

ALKALINE-SOLUBLE HUMIC SUBSTANCES

As plants die and accumulate as surface debris, biochemical decay and physical disintegration act to form a complex organic mass generally referred to as humus (Waksman, 1936, p. ix–xi). Some of this humus is swept away by rainwater and streams as partly decomposed particles, which are ultimately deposited with other sediment. A variable fraction of the humus is oxidized and decomposed, mainly by fungi and bacteria, to become water soluble, giving rise to the dark-brown water typical of streams and lakes in subtropical and tropical areas. Most of this water-soluble organic matter is transported seaward and, generally by cation adsorption, is precipitated or flocculated; some may be similarly transported and deposited as clay-organic com-

plexes. Once flocculated and deposited, but before postdepositional processes of compaction and polymerization proceed too far, most of this organic matter can be redispersed or solubilized by alkaline solutions (Swanson and Palacas, 1965, B26–B27).

About 99 percent of the abundant organic matter in the tidal-marsh sediment is the particulate fragments and shreds of woody land and tidal-marsh plants and the alkaline-soluble organic matter derived from these decomposing plants. With time and increasing depth of burial, some of the particulate material will be further decomposed, but decomposition under anaerobic conditions is much retarded and minimal.

The amount of alkaline-soluble humic substances for each sample (table 2) represents the sum of the humic and fulvic fractions, each fraction calculated to an ash-free basis. The values for the fulvic fractions of 15 samples were estimated by extrapolation from data on adjacent samples, sediment type, and depth of burial; thus, the values for total alkaline-soluble humic substances for these samples are approximate only and are not included in the following discussions. These values are indicated in table 2 by enclosure in parentheses.

In general, a direct positive correlation exists between the percent total organic matter and the percent alkaline-soluble humic substances. This correlation is affected to some variable degree, however, by sediment type and depth of burial.

The amount of alkaline-soluble humic substances in the peaty sandy mud averages 6.6 percent and ranges from 2.12 to 11.69 percent. The alkaline-soluble humic substances average 24.4 percent of the organic matter and range from 9.1 to 48.8 percent (table 5).

There is a general pattern of change in the percentage of the organic matter that becomes alkaline soluble as sample depth increases. With reference to sample intervals shown in figure 9, the upper 10 cm of peaty sandy mud has less alkaline-soluble material than the underlying 10–20 cm, which includes the marshgrass rootmat; then, with greater depth, the percentage of the organic matter that is alkaline soluble slightly but steadily decreases. This general pattern in the tidal-marsh mud is best illustrated by cores M5, M17, and M21 (table 2).

Although distinct differences exist in the amounts of alkaline-soluble organic matter in the cores, no geographic pattern in these differences could be discerned. There is a consistency in amounts in each core of peaty sandy mud, however; for example, in core M2 the range of percentage of the organic matter that is alkaline soluble is 13.5–15.9, and in core M21 the range is 23.5–27.9 percent.

TABLE 5.—*Summary of alkaline-soluble humic substances and the soluble humic and fulvic fractions in the three types of tidal-marsh sediment*

[All values in percent and calculated to moisture- and ash-free basis. Samples having estimated values (tables 2, 3) excluded in this summary]

	Peaty sandy mud			Carbonaceous muddy sand			Relatively clean sand		
	Average	Range	Number of samples	Average	Range	Number of samples	Average	Range	Number of samples
Organic matter in sediment	27.0	15.8–41.4	52	7.9	4.2–15.0	21	2.3	0.4–3.8	24
Alkaline-soluble humic in sediment	6.6	2.12–11.69	35	1.8	.84–3.99	14	.7	.19–1.54	23
Percentage of organic matter	24.4	9.1–48.8	35	26.2	18.2–39.4	14	30.4	10.0–62.0	23
Soluble humic fraction in sediment	5.2	1.42–9.33	52	1.4	.47–2.99	21	.5	.11–1.23	24
Percentage of alkaline-soluble humic substances	78.1	63.9–93.8	35	69.6	54.0–86.9	14	67.9	40.6–84.5	23
Percentage of organic matter	19.7	6.1–40.4	52	18.1	10.6–30.9	21	20.7	6.0–46.7	24
Soluble fulvic fraction in sediment	1.4	.44–2.99	35	.6	.19–1.23	14	.2	.07– .32	23
Percentage of alkaline-soluble humic substances	21.9	6.2–36.1	35	30.4	13.1–44.2	14	32.1	15.5–59.4	23
Percentage of organic matter	5.2	1.6–8.9	35	7.9	4.0–15.5	14	9.7	2.6–24.3	23

In the carbonaceous muddy sand samples, which contain less organic matter, alkaline-soluble humic substances are on the average 1.8 percent of the sediment, and their range is 0.84–3.99 percent. An average of 26.2 percent of the organic matter in this sediment is alkaline soluble; the range is 18.2–39.4 percent. Three of the four samples whose organic matter is more than 30 percent soluble are consecutive samples in core M7.

The relatively clean sand, which contains the smallest amount of organic matter, contains the smallest amount of alkaline-soluble humic substances—an average of 0.7 percent and a range 0.19–1.54 percent. As percentage of the organic matter, however, the soluble substances range from 10.0–62.0 percent, and average 30.4 percent, or nearly one-third of the organic matter.

Thus: (1) The amount of alkaline-soluble organic substances is generally related to the amount of organic matter in the sediment, which is 6.6 percent of the peaty sandy mud, 1.8 percent of the carbonaceous muddy sand, and 0.7 percent of the relatively clean sand; (2) there is a general increase of alkaline-soluble humic substances with increasing grain size of the sediments—24.4, 26.2, and 30.4 per-

cent of the organic matter in the peaty sandy mud, carbonaceous muddy sand, and relatively clean sand, respectively; and (3) the percentage of the organic matter that is alkaline soluble in the peaty sandy mud regularly decreases as depth of burial increases, generally by about one-third within a 60-cm interval.

SOLUBLE HUMIC AND FULVIC FRACTIONS

When the filtered alkaline-soluble organic matter is subjected to a lowering of pH, or when excess cations such as Ca, Al, or Cu are added, a dark-brownish-black precipitate or flocculate is formed. When this precipitate is dried, it resembles fragmented black coal in that it has glistening surfaces and conchoidal fracture. As naturally precipitated in a sand, the humic material coats individual sand grains with a brown film, and, in some sand samples, the grains are actually cemented by this dark-brown coaly material.

After precipitation during analysis, the clear supernatent solution is commonly very light yellow to dusky yellow and includes organic material that is here termed the "soluble fulvic fraction." Although both the humic and fulvic fractions were in the solid state within the sediment, their solubilization, separation, and analysis provide further information on the chemistry and genesis of 10–60 percent of the total organic matter in the sediment. The pertinent chemical data on the humic and fulvic fractions of the individual tidal-marsh samples that are given in table 2 are summarized in table 5, and the organic element composition of some samples are presented in table 6.

The amount of soluble humic fraction in the peaty sandy mud is, without exception, greater than the fulvic fraction, averaging 78.1 percent of the alkaline-soluble organic matter; the fulvic fraction averages 21.9 percent (table 4). As percentage of the mud, the humic fraction makes up an average of 5.2 percent, and the fulvic fraction, 1.4 percent. These soluble fractions are, in fact, major components of the organic matter in the mud; the humic fraction averages 19.7 percent of the organic matter of the mud, and the fulvic fraction, 5.2 percent (table 5).

In the carbonaceous muddy sand, the humic and fulvic fractions constitute an average of 69.6 and 30.4 percent, respectively, of the alkaline-soluble organic matter. The humic fraction makes up an average of 18.1 percent of the organic matter in this sediment, and the fulvic fraction, 7.9 percent.

In the relatively clean sand, whose organic matter is almost one-third alkaline soluble, the humic fraction makes up an average of 67.9 percent of the total alkaline-soluble organic matter, and the fulvic fraction, 32.1 percent. Furthermore, the small amount of organic mat-

TABLE 6.—*Organic element composition of representative samples of soluble humic and fulvic fractions* [1]

[Analyses by Huffman Laboratories, Wheat Ridge, Colo. Values are on moisture- and ash-free basis; percent ash reported separately. Leaders (__) indicate no analysis]

Sample No.	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash
Humic fraction-tidal-marsh samples						
M1–C	57.95	4.95				12.49
5–E	51.42	5.41				3.76
6–B	55.18	5.28				13.13
10–A	58.72	5.56				11.40
17–B	56.54	5.09	32.93	4.13	1.31	19.01
18–A	54.23	5.99				6.03
19–U	54.17	5.94				3.26
20–E	56.10	5.36				16.01
Fulvic fraction-tidal-marsh samples						
M17–B	41.71	4.05	48.94	3.47	1.83	26.42
Humic fraction-river-mouth samples						
A–3	49.77	4.39				29.61
5	58.42	5.93	29.28	5.18	1.20	8.53
E–1	54.81	4.82				9.50
SW–7	50.45	5.57				9.81
D–2	57.44	4.65				11.18
ST–6	52.90	6.08				5.64
SU–1	52.70	4.74				21.08
4	57.35	5.28	31.93	5.03	.41	10.51
Fulvic fraction-river-mouth samples						
A–5	48.57	5.01				23.89
D–2	44.44	4.66				20.95
SU–1	41.44	4.26				37.26
4	46.48	4.82				25.71

[1] See tables 2 and 4 for other analytical data.

ter in this sand is composed of an average 20.7-percent soluble humic fraction and a 9.7-percent fulvic fraction.

As percentage of the organic matter the soluble humic fraction (M7, M9, M17), and, even more consistently, the fulvic fraction (M2, M5, M6, M15, M21) generally decrease slightly as depth increases (table 2). The minor exception, as mentioned previously, is that in some cores the sample 10–25 cm below the surface, which includes the marsh-grass rootmat, contains slightly more of these soluble materials than the upper 10 cm sample.

The soluble humic fraction, as percentage of the total alkaline-soluble organic matter, tends to increase as depth increases, with a corresponding decrease in the soluble fulvic fraction; this tendency is opposite to that observed in some estuary sediments in northwest Florida (Palacas and others, 1968, p. C104). The decrease in relative amount of the fulvic fraction suggests that the organic components of the fulvic fraction, characterized by greater solubility and lower average molecular weight, are transformed fairly rapidly into the less soluble humic-type components of greater molecular weight. Because the amount of the humic fraction, as percentage of the total organic matter, is greatest near the middle of the sediment richest in organic matter in the cores (for example, in cores M17, M21, M24), seemingly the biochemical conditions conducive to this transition are most pronounced at this position.

Too few analyses are available to present the exact organic composition of the soluble humic and fulvic fractions. The data obtained (table 6), however, show that the compositional differences between the two fractions are very similar to those obtained by the same procedures and recorded by Palacas, Swanson, and Love (1968, table 2) and by Berryhill, Swanson, and Love (1972, tables 6, 9). For example, the average carbon and hydrogen contents of the soluble humic fractions from the tidal marsh are 55.5 and 5.4 percent, respectively; those from the Choctawhatchee Bay estuary in northwest Florida (Palacas, Swanson, and Love, 1968, table 2) are 55.6 and 5.8, respectively.

The very minor differences in percentage content of different organic elements from sample to sample, for example, carbon (table 6), show no relation to sediment type or to depth of burial of the sample. It is suggested here that these minor differences are best explained by very slight differences in the overall composition of the organic matter in the samples or by small analytical errors. The relatively major differences in ash contents are inherent to the laboratory method used and have no geochemical significance; in this regard, 64 of the soluble humic extracts were ashed, and the average percent ash was 10.11, a factor used to calculate the ash-free amounts of 38 samples reported in table 2.

The organic composition of the humic and fulvic fractions, each of which represents a complex group of organic compounds, are greatly different. The distinctive and significant compositional differences are the carbon and oxygen contents. As shown in previously cited studies, and as indicated in table 6, the carbon content of the humic fraction is 10–15 percent greater than the carbon content of the fulvic fraction; by almost exactly the same amount, the oxygen content of the humic fraction is less than that of the fulvic fraction.

The above data concerning alkaline-soluble humic substances indicate the following relations:

1. As the amount of organic matter in the tidal-marsh sediment decreases, the amount of alkaline-soluble humic substances relative to total organic matter increases; thus, as much as 62 percent of the organic matter in the sand that has the least amount of organic matter is alkaline soluble.

2. The alkaline-soluble humic substances constitute an over all average of 27 percent of the organic matter of the tidal-marsh sediment, and these soluble substances consist of 71 percent humic and 29 percent fulvic fractions.

3. Comparison of the relative amounts of the humic and fulvic fractions show that the peaty sandy mud, which is the sediment that contains the largest amount of organic matter, contains on the average about 10 percent more of the soluble humic fraction than does the relatively clean sand, which is the sediment that contains the smallest amount of organic matter (78.1 compared to 67.9 percent).

4. The relative amounts of the two fractions, whether assessed in terms of percentage of total organic matter or percentage of alkaline-soluble organic matter, show distinctive differences among sediment types and with depth of burial; both fractions decrease as depth increases with the proportion of fulvic fraction becoming less as depth increases.

Thus, even in the topmost 1 m of sediment in the tidal marsh, geochemical diagenesis of the organic material rapidly takes place, one manifestation being that the relative amounts of soluble organic components, particularly the fulvic fraction, substantially decrease as depth of burial increases.

BITUMEN

Bitumen, which is that fraction soluble in the organic solvent benzene minus free sulfur (Palacas and others, 1968, p. C100, C103), is primarily derived from plant resins and waxes and from animal fats and oils. The concentration of bitumen can be considered as a measure of the potential crude oil in, or that which can readily be derived from, a sediment.

The organic matter in the tidal-marsh sediment is dominantly of plant origin, identified as woody material by microscope study and by its chemical composition, particularly its low hydrogen content. The bitumen content of this woody or humus-type organic matter in the tidal-marsh sediment is relatively low, averaging slightly less than 0.5 percent, most of which is probably dissolved resins and waxes. The

average bitumen content of the sediment in the 24 tidal-marsh cores is 0.08 percent. Bitumen analyses of the 102 tidal-marsh samples are reported in table 2.

To further indicate the type of potential crude oil in the sediment, the percentage of hydrocarbons in the bitumen was determined on 22 samples (table 7) by the method of silica-gel fractionation (Ferguson, 1962, p. 1614). Samples from six cores were selected to be representative, on a geographical and stratigraphic basis, of the tidal-marsh sediment. Hydrocarbons compose about 23 percent of the bitumen; nonhydrocarbons, or asphaltic substances, compose most of the remaining 77 percent.

The peaty sandy mud, which contains the most organic matter and is the most characteristic tidal-marsh sediment, on the basis of 51 samples is shown to contain an average of 0.12 percent bitumen and to range from 0.056 to 0.298 percent bitumen. (The anomalously high analysis of 0.990 percent for one sample, M15–C, is omitted from this summation because analytical error is suspected.) Excluding core M15, the 13 cores that consist solely of this mud or whose upper parts consist of this mud contain an average of 0.11 percent bitumen. Thus, the blanket of peaty sandy mud covering the tidal marsh can be said to contain 0.11 percent bitumen. The organic matter in this sediment averages 0.44 percent bitumen and ranges from 0.21 to 1.34 percent.

The carbonaceous muddy sand, containing 4–15 percent organic matter, has an average bitumen content of 0.035 percent and a range of 0.008–0.104 percent. A more meaningful range would be 0.013–0.060, however, inasmuch as only one of the 22 samples, M13–B, contained less than 0.013 percent and only one sample, M22–D, contained more than 0.060 percent. The average bitumen content of the organic matter in this sediment type is 0.41 percent , which is only very slightly less than the 0.44 percent average for the organic matter in the peaty sandy mud.

The average bitumen content of the 23 relatively clean sand samples was 0.012 percent, and the range was 0.003–0.023 percent. The average bitumen content of the organic matter in this sand is 0.51 percent, which is 20 percent greater than for the carbonaceous muddy sand, and 12 percent more than for the peaty sandy mud.

No consistent pattern can be discerned as to change of bitumen content with increase of depth in the cores. Out of a total of 24 cores, the amount of bitumen increases with increasing depth in three cores (M10, M15, and upper part of M22), and decreases with increasing depth in two cores (M2, and upper part of M19). Even when bitumen content is calculated as percentage of organic matter in the sediment, two cores (M15, M22) showed an increase of bitumen with increasing

TABLE 7.—*Hydrocarbon fractions of bitumen related to sediment type and total organic matter*

[All data in percent. Asphaltic fraction includes nonhydrocarbons remaining on silica-gel column, generally less than 10 percent, average 7.6 percent]

Station and sample No.	Sediment type	Depth in core (centimeters)	Organic matter (percent organic carbon ×1.9)	Bitumen	Bitumen as percent of organic matter	Saturated hydrocarbons	Aromatic hydrocarbons	Asphaltic fraction	Hydrocarbons as percent of bitumen	Hydrocarbons saturated ÷ Aromatic
							(percent of bitumen)			
Cores of tidal-marsh sediment										
M1–A	Peaty sandy mud	0–10	22.6	0.075	0.33	7.13	6.00	86.86	13.13	1.19
B	do	10–25	20.1	.087	.43	2.38	15.32	82.29	17.70	.16
C	do	25–40	25.7	.087	.34	3.53	20.00	76.46	23.53	.18
D	do	40–61	27.2	.100	.37	3.13	23.42	73.45	26.55	.13
M5–A	do	0–10	31.5	.063	.20	7.28	17.69	75.02	24.97	.41
B	do	10–25	26.0	.083	.32	4.50	20.23	75.26	24.73	.22
C	do	25–40	27.9	.083	.30	3.91	20.83	75.65	24.35	.19
D	do	40–54	23.4	.061	.26	2.16	24.57	73.27	26.73	.09
E	Relatively clean sand.	54–60	3.8	.023	.60	2.67	23.74	73.59	26.41	.11
M15–A	Peaty sandy mud	0–10	41.4	.230	.55	3.76	9.91	86.33	13.67	.38
B	do	10–25	38.6	.286	.74	4.85	11.10	84.05	15.95	.44
C	do	25–35	28.7	.990	3.45	6.85	10.31	83.85	17.16	.66
M17–A	do	0–10	34.6	.152	.44	4.93	9.47	85.59	14.40	.52
B	do	10–25	19.4	.085	.44	4.10	16.57	79.32	20.67	.25
C	do	25–40	27.9	.125	.45	4.68	16.25	79.06	20.93	.29
D	do	40–55	31.7	.140	.44	7.64	16.51	75.84	24.15	.46
E	do	55–70	31.2	.135	.43	4.04	14.22	81.74	18.26	.28
F	do	70–76	33.6	.101	.40	2.72	19.04	78.24	21.76	.14
M19–B	do	10–25	32.1	.069	.26	34.45	20.18	45.38	54.63	1.71
E	Carbonaceous muddy sand.	55–69	7.0	.028	.39	4.38	26.73	68.89	31.11	.16
M24–F	do	70–79	5.7	.081	.31	5.26	25.47	69.39	30.73	.21
G	Relatively clean sand.	79–94	2.3	.009	.40	4.32	25.10	70.58	29.42	.17
Live stems and dead surface litter of dominant marshgrass										
MX–JL	*Juncus*, live stems		94.7	1.056	1.12	0.29	14.96	84.74	15.25	.02
JD	*Juncus*, dead stems.		96.7	1.055	1.09	.15	15.21	84.63	15.36	.01
Sediment offshore from tidal marsh										
ST and SU [1]	Shelly sand	0–10	0.3	0.002	0.60	26.68	14.55	58.76	41.23	1.83
Sediment near mouth of stream										
D [1]	Sand	0–10	2.8	0.015	0.54	8.05	25.64	66.30	33.69	0.31

[1] Bitumen from several samples combined: ST and SU, samples ST–4, 5 and SU–5, 6; D, samples D–2–4.

depth, two other cores (M2, M10) showed a decrease with increasing depth, and one core (M17) showed a remarkable consistency throughout. Furthermore, there is no apparent correlation between bitumen content and geographic position, either within a small area or over the 80-mile-long area of study. It can only be concluded that bitumen distribution in the upper 1 m of recent tidal-marsh sediment is erratic, except that bitumen content increases as total organic matter in the sediment increases.

Table 7 presents results obtained from fractionating the bitumen into hydrocarbons and nonhydrocarbons in 22 samples from six tidal-marsh cores. The number of samples so treated are too few to assess precisely and verify patterns of distribution of hydrocarbons in the tidal marsh but are sufficient for general observations. The general range of hydrocarbons in the sediment is from 0.01 to 0.045 percent; the average hydrocarbon content in the peaty sandy mud is 0.023 percent, and in sand slightly less than 0.01 percent. The data do indicate that the hydrocarbons form an increasing percentage of the bitumen as depth increases in two cores, M1 and M15, but do not in cores M5 and M17. The conspicuously anomalous values for samples M15–C and M19–B are omitted from this summation because of suspected analytical error or contamination of the material.

The percentage of saturated hydrocarbons in the bitumen is relatively low, averaging 4.4 percent and ranging narrowly from 2.7 to 7.3 percent. The aromatic hydrocarbons average 18.1 percent of the bitumen, but range more widely from 6.0 to 26.7 percent. The amount of aromatic hydrocarbons thus exceeds the saturated hydrocarbons by about four times; however, ratios of saturated to aromatic hydrocarbons are highly variable, ranging from 0.09 to 1.19, though most are in the 0.1–0.5 range. This latter relation, coupled with the irregular distribution and small amounts of the total bitumen, indicate that the specific organic components within this humic type of organic matter vary considerably both qualitatively and quantitatively, and indicate that the identification of specific biologic precursors and the precise characterization of processes and rates of decomposition of organic matter in natural sediments will require more refined study.

The seemingly logical source for most of the organic matter in the sediment is the marshgrass *Juncus roemerianus*. Analyses of both the green live stems and the dead stems that commonly litter the surface are very similar (tables 2, 4, 7) ; furthermore, their bitumen yields are nearly identical, and the percentage of hydrocarbons in the bitumen are very similar. Comparison of analytical data for the marshgrass and for the organic matter in the sediment suggests that this dominant marshgrass might well be a major source of organic material. There is,

however, a major difference in the composition of the hydrocarbons of *Juncus* when compared to that of the organic matter in the sediment, particularly the topmost samples. The average percentage of saturated hydrocarbons in the bitumen of the four topmost analyzed samples (table 7, M1–A, M5–A, M15–A, M17–A) is 5.8 percent, which is more than 25 times greater than that in the *Juncus* samples. At least three explanations are possible for this striking difference:

1. The saturated hydrocarbons are so resistant to decay or chemical change that they are residually concentrated to an exceptional degree.
2. Almost immediately after burial in the anaerobic environment of the sediment, the asphaltic component of the bitumen, and possibly other fractions of the dominantly humic organic matter, are biochemically converted to saturated hydrocarbons.
3. Animal material, high in saturated hydrocarbons, contributes the major amount of these hydrocarbons to the sediment.

Only a specific detailed study, entailing collection of a large suite of biologic and sediment samples, followed by gas chromatographic-mass spectrometric and other analyses, will result in singling out the correct explanation or a combination of the explanations mentioned above. Maurer and Parker (1967) reported that the fatty acids (one of the nonhydrocarbon fractions of the bitumen not studied here) in marsh plants, including *Spartina alterniflora* but not *Juncus*, do not differ significantly in amounts or in carbon-number patterns from terrestrial plants, and so their results provide little information helpful in resolving the explanations posed above. Miller (1972) studied the distribution of normal fatty acids in two sediment cores, one from the tidal marsh near the mouth of the Aucilla River and the other from the mouth of the Econfina River. He related his data to the marsh flora, particularly to the rootmat of, presumably, *Juncus*; however, his results are inconclusive as they concern this paper because of the lack of related information on the amounts of total organic matter, knowledge of the different sources of the organic matter, and on extractable bitumen and its contained hydrocarbons.

RIVER-MOUTH SEDIMENT

The larger amounts of organic matter in sediment from the river channel or from the Gulf of Mexico (table 3) are generally near the riverbanks of the gulf shoreline and are secondarily related to grain size of the sediment accumulating in the dynamic river and near-shore environments. In contrast to the high percentage of organic matter in the tidal-marsh sediment, however, none of the 20 river

samples and only one of the 20 offshore samples exceeded 10 percent in organic matter.

The amount of organic matter in sediment in the lower reaches of the streams averages 1.8 percent and ranges from 0.2 to 7.0 percent; the offshore sediment averages 2.2 percent and ranges from 0.2 to 11.0 percent. The amount of organic matter in the main channel sand in the river sediment is only 0.9 percent; and, if nearshore sediment and the samples of previously described organic-rich mud and fine sand in the shallow-water patches of *Thalassia* off the mouths of the Econfina River and Spring Warrior Creek are excluded, the offshore-sand samples contain an average of about 0.6 percent.

The amount of organic matter that is alkaline soluble is considerably greater in the river-channel sediment than in the offshore sediment, generally about 15 percent in the former and less than 5 percent in the latter. This relation is most striking in the six channel- and offshore-sediment samples taken near the mouth of the Suwannee River, where the alkaline-soluble organic matter markedly decreases from 63.7 percent of the total organic matter 2 miles upstream from the river mouth to 0.2 percent 4 miles offshore.

From the 20 values reported, it is clear that the total and relative amounts of the soluble humic and fulvic fractions vary from one stream to another. For example, in bottom sediment of the Aucilla River, an average of 74.5 percent of the alkaline-soluble organic matter consists of the humic fraction, whereas comparable figures for the Econfina River, Dallus Creek, and the Suwannee River are 97.1, 93.4, and 49.4 percent, respectively. The few comparable values for the offshore sediment indicate that the dominant sediment type, the sand, has about 75 percent of its alkaline-soluble organic matter represented by the soluble humic fraction.

The element compositions of several of the soluble humic and fulvic fractions are given in table 6. The analyses are too few to define reliable and consistent differences as a function of type or geomorphic position of the sediment samples represented. In fact, internal differences in this group of data, for example the 9-percent difference in carbon content of the humic fractions from two Aucilla River samples (A3, A5), indicate the need for additional analyses.

The bitumen contents fairly closely parallel the amounts of organic matter in the sediment, as with most samples analyzed during this investigation. The only significant difference in the river and offshore sediment is that the bitumen contents of organic matter in the offshore sand are notably higher than those in the river sand. The organic matter in the offshore sand yields 0.84 percent bitumen; the river sediment, 0.49 percent. The value of 0.84 percent is also much higher

than the comparable average values of 0.44, 0.41, and 0.51 percent in the peaty sandy mud, carbonaceous muddy sand, and relatively clean sand, respectively, in the tidal marsh.

Determination of the hydrocarbon fractions of the bitumen from two composite samples are given in table 7. Except for the analytically suspect data on one of the tidal-marsh samples (M19–B), these two bitumen samples had the highest percentage of hydrocarbons of the 24 samples fractionated. The bitumen from shelly sand more than 2 miles offshore in the gulf had 41.23 percent hydrocarbons and the highest ratio of saturated to aromatic hydrocarbons, 1.83, of all 24 samples. High hydrocarbon values may well indicate the incorporation of abundant soft parts of marine organisms, or their residues, in the sediment. The bitumen from the sand near the mouth of Dallus Creek contained 33.69 percent hydrocarbons, which is about 11 percent more than the average for the tidal-marsh samples; but the saturated to aromatic hydrocarbon ratio of 0.31 is similar to that in most tidal-marsh samples.

RELATED INORGANIC CONSTITUENTS

MINERAL CARBON

The percentage of mineral (carbonate) carbon in the tidal-marsh sediment is very low, and the range of values is very small (table 2). All the samples from 14 of the 24 cores, including one 76 cm long, contained less than 0.1 percent mineral carbon; furthermore, except for the top 10–cm sample, six additional cores contained less than 0.1 percent.

In each of seven samples (out of the total of 102 samples) whose mineral carbon content exceeded 0.25 percent, calcareous mollusk shells or, more commonly, fragments of shells were observed, and it is this shell material ($CaCO_3$) that accounts for most, if not all, of the mineral carbon.

The highest mineral carbon content in the tidal-marsh sediment is, with few exceptions, in the top 10 cm. This uppermost layer in the 24 cores contains an average of 0.15 percent mineral carbon, and a range from 0.01–1.30 percent; only two of the samples contained more than 0.5 percent.

With minor exceptions, the amount of mineral carbon decreases as depth in the sediment increases, commonly to less than 0.01 percent just below the top 10 cm of sediment. Of 72 samples of sediment buried deeper than 10 cm, 27 samples contained less than 0.01 percent mineral carbon; if 0.005 percent is arbitrarily assigned to the 27 values reported as "<0.01" percent, the average mineral carbon content of tidal-marsh sediment below 10 cm is 0.03 percent.

The absence of shell material from most samples 10 cm or more below the surface is explained by a rapid decrease in pH with increase in depth—from about pH 7 at the surface to pH 4 at a depth of about 75 cm. Complete dissolution and disappearance of shell material apparently occurs just below the sediment surface. The control of pH, as a function of the amount of organic matter, and the consequent removal of carbonate shell material have been documented by Huang and Goodell (1970, p. 2096) for marine sediment in the Mississippi delta.

The mineral carbon content of the river and the offshore surface sediment samples (table 3) is somewhat erratic. Shell material was observed in all samples containing more than 0.25 percent mineral carbon and was abundant in samples containing more than 1 percent mineral carbon. The only sample of stream sediment (E–2) that contained more than 1 percent mineral carbon was collected from an area where oyster shells were common, and oyster shells were observed in the sample.

Most of the light-colored sand that is the typical sediment offshore in the Gulf of Mexico contains megascopic shells and shell fragments, mainly of pelecypods. The average mineral carbon content of this sediment can be predicted to be high; the average for 14 samples collected more than 0.5 mile from shore is 1.58 percent, indicating about 14.5 percent $CaCO_3$ shell material. The highest recorded value is 3.90 percent mineral carbon, indicating that the sample contained about 35 percent shell material.

The pH measurements made of the upper 5 cm of the river and offshore sediment at the time samples were collected indicated generally slightly alkaline conditions (table 1). Other field observations and the relatively low content of organic matter in the sediment indicate that acid waters probably do not exist above depths of about 25 cm; below this depth removal of shell material by dissolution would result in relatively clean quartz sand.

SULFUR

Carbonaceous rocks of every age the world over are characterized by high sulfur content, generally in the form of the iron sulfide minerals pyrite and marcasite. Coal commonly contains several percent sulfur (Francis, 1954, p. 493), and even marine black shales, particularly of the humic type (Swanson, 1961, p. 76), contain a few to several percent sulfur.

Genetically, the high sulfur contents of both recent sediment and sedimentary rocks are related to the organic matter. It has long been known that the sulfur in these sedimentary rocks is of two major

types, organically bound sulfur and inorganic sulfur. (See, for example, Francis, 1954, p. 486–487, 507–508). The proportions of the two types are highly variable, but in most rocks inorganic sulfur greatly predominates, generally by one to three orders of magnitude.

The organically bound sulfur generally is gradually released with the decomposition and diagenesis of the organic matter. Decomposition almost always creates an anaerobic environment within the sediment, and the anaerobic environment even extends above the sediment-water interface in stagnant water, as, for example, in the Black Sea and in some fjords. Within this anaerobic environment, the rate of decomposition of organic matter is greatly reduced, but the environment is conducive to the activity of sulfate-reducing bacteria—bacteria that exist, in part, by biochemically obtaining oxygen from the SO_4 ion common in sea water, and that generally leave either H_2S or the $HS-$ ion as their metabolic waste product. In the aqueous environment, the $HS-$ and the H_2S readily combine with available metal ions, most commonly iron, to form a hydrous metal sulfide that is eventually stabilized during diagenesis into, for example, iron sulfide, FeS_2.

With this summation of a general process that has been established by many investigators (see, for example, Hem, 1960; Oppenheimer, 1960, p. 253–257; Temple, 1964; Berner, 1967; Thorstenson, 1970), the distribution and interpreted early diagenetic changes involving sulfur in the tidal-marsh sediment can be reviewed. Furthermore, as will be shown, the fact that abundant stable iron sulfide (pyrite) is formed within a short time at very shallow sediment depth is believed to be of significance.

TOTAL SULFUR

The amount of total sulfur in the tidal-marsh sediment (table 2) has a wide range, 0.05–12.5 percent, and an overall average of 2.25 percent. The sulfur contents of entire cores also have a considerable range, 0.15–5.62 percent. All cores containing less than 1 percent sulfur are predominantly sand.

No geographic trend was noticed in the changes in sulfur content of tidal-marsh sediment within the 80-mile distance between the Aucilla River to the northwest and the Suwannee River to the southeast. Furthermore, the sulfur content of the cores showed no consistent increase or decrease with increasing depth of the sediment. Sulfur increases as depth increases in a few cores (table 2, cores M1, M15, and, except for increases of one sample in each, in M5 and M17) ; but sulfur content decreases as depth increases in other cores (M8, M9, M18, and, except for one sample in core M3).

A very significant and clear-cut increase of total sulfur with increasing depth of burial is indicated, however, if sulfur is related to the amount of organic matter in the sediment. Regardless of the percentage of organic matter, the amount of sulfur relative to amount of organic matter systematically and consistently increases with increasing depth, with but few minor exceptions. This relation is shown in table 2, in the column giving ratios of total sulfur and organic matter (for example, see cores M5, M12, M16, M22). This relation to organic matter is, of course, not intended to imply that the sulfur is chemically a part of the organic matter, but, rather that there is, without doubt, a clear diagenetic relation between the two components.

FREE SULFUR

The amount of free sulfur in the sediment, as recorded in tables 2 and 3, is the sulfur that is extracted by the nonpolar solvent benzene, and subsequently separated from the bitumen by a copper amalgam reduction. Regardless of whether the resulting "free sulfur" value represents the absolute total of elemental sulfur in the sample, the chemical procedure used was identical on all samples, and the values can be directly related to other constituents.

The amount of free sulfur determined in 102 tidal-marsh samples ranged from less than 0.001 to 0.219 percent (table 2). Without exception, however, only those samples from the upper 25 cm of sediment in the 24 cores contained more than 0.02 percent free sulfur. The decrease of free sulfur in the samples below 25 cm in the cores to the bottom samples in the cores by one to three orders of magnitude is strikingly apparent. In fact, free sulfur is all but absent from most of the deeper core samples.

In general, free sulfur forms from 5 to 20 percent of the total sulfur in the upper 10 cm of sediment; in some cores a high percentage of free sulfur is also characteristic of the sample from the 10 to 25 cm depth, but this, and other observed, irregularities in the decrease of free sulfur with increase in depth can readily be explained by change in type of sediment with depth. In every core consisting of peaty sandy mud, free sulfur is virtually absent below a depth of 40–55 cm.

Because of the almost invariable reducing condition in the uppermost few centimeters of tidal-marsh sediment (see table 1), the actual form of the so-called free sulfur in the undisturbed wet sediment certainly is not solid crystals or particles of yellow elemental sulfur. Probably some of the sulfur is in solution as the reduced HS^- ion, or as gaseous H_2S. When the sediment was dried in the laboratory, the HS^- was retained as free sulfur, and most of the H_2S was lost. Very

likely, a part of the free sulfur was bound to some metal ion in the undisturbed wet sediment as a very unstable hydrous metal sulfide, which, upon drying under oxidizing conditions in the laboratory, was readily converted to residual free sulfur and a metal hydroxide.

Without additional data, and without attempting a theoretical exposition on the chemistry of reduced inorganic sulfur in the tidal-marsh sediment, it is postulated here that the reduced sulfur goes through several transitional forms with increasing depth of burial. The reduced sulfur changes from largely dispersed HS^- ions and H_2S in the upper 10 cm, through unstable or easily oxidizable metal sulfide forms in the 10–25-cm interval, through a relatively stable amorphous metal sulfide in the 25–40-cm interval, and finally, to a stable crystalline metal sulfide, such as pyrite, below 40 cm. Such a transition series would account for the relative abundance of analyzed free sulfur in the upper 25 cm of most cores, and for its drastic decrease in amount, to nearly complete absence, with increasing depth below 25 cm.

All the river and Gulf of Mexico samples were of the upper 10 cm of sediment, and the important changes of amounts of sulfur with increasing depth and amount of organic matter are not determinable. The Eh measurements (table 1), however, indicate that the decrease of this free sulfur at depths greater than 10 cm would almost certainly follow a pattern similar to that described for the tidal-marsh cores.

MICROSCOPIC DISTRIBUTION AND FIELD OBSERVATIONS

Elemental sulfur was not observed during the study of sediment samples under the microscope. Yellow to yellowish-brown amorphous iron oxide was invariably seen, however, in the dried samples from the upper 25 cm of each core, but rarely below this depth. In samples from the 25- to 40-cm depth interval in several cores, notably M1 and M17 (table 2), a dark-bluish-black amorphous material with a very slight metallic luster was observed as a coating or an attachment to quartz grains; in sediment from the 40- to 70-cm interval, minute drusy bronze grains were observed, and heavy-mineral separation and X-ray diffraction analyses clearly showed that pyrite was abundant; marcasite was not identified (John W. Adams, written commun., 1970). In sample M17–E, aggregates of this FeS_2 mineral were as much as 3 mm across and were abundant. If, in fact, 90 percent of the total sulfur in this particular sample was in the form of pyrite, the sample would contain 21.0 percent FeS_2; this calculated amount is very similar to the estimate of about 20 percent pyrite made by Paul D. Blackmon (written commun., 1971), on the basis of an X-ray diffraction analysis of the sediment sample.

The conclusion reached, on the basis of these observations, is that on air drying of the frozen cores, ferric hydroxide (limonite?) and free sulfur formed in the upper 25 cm, but in the 25- to 40-cm depth interval the iron and sulfur are bound in an amorphous ferrous sulfide form that is sufficiently stable to be preserved on drying. Below 40-cm, this amorphous sulfide is crystallized into sizable and obvious metallic mineral aggregates of pyrite. The presence of pyrite at shallow depths in modern sediment, for example, in peat, lake mud, and Black Sea sediment, has been reported by many investigators (Van Straaten, 1951; Vallentyne, 1963; Hallberg, 1965–66).

This conclusion on the form of sulfur in the upper 25 cm of sediment is clearly substantiated by both field observations and observed color change of frozen samples during drying in air. Over a period of many years the senior author has walked several hundreds of miles of beach areas in most of the coastal States, including Alaska, with geologic hammer or a shovel. On digging into the wet shoreline sediment, a fairly sharp color-change boundary can be almost invariably intersected, below which the sediment is medium gray to black. For example, within the tidal zone along the Oregon coast, in light-colored medium sand subsequently determined to contain 0.5–1 percent organic matter, this boundary was commonly observed from 10 to 20 cm below the sediment surface; similarly, in a muddy sand containing only a few percent organic matter along the South Carolina coast, the boundary was only a few centimeters below the surface. In-place Eh measurements showed that this boundary approximately coincides with a 0.0 mv Eh; the sediment above the boundary has a positive Eh reading, and the underlying dark sediment, a negative Eh.

The color-change boundary is retained on freezing of the sediment; but when the core is split or extruded and the visible surface of the sediment is exposed to the air, one can observe the disappearance of the boundary and lightening of color of the sediment below the boundary. The medium-dark-gray color of a sand below the boundary, for example, will change to a dusky yellow within a few hours, dependent upon drying conditions; probably a fourth of the original darkness in color is caused by the sediments being wet, a fourth is caused by disseminated organic material, and about half by very unstable iron sulfide that rapidly oxidizes to ferric hydroxide and free sulfur.

The almost ever-present odor of H_2S in the tidal-marsh sediment should be mentioned again in connection with this discussion on sulfur. During sample collection and the drying of frozen samples, the strongest odor of H_2S comes from the samples having the largest amount of organic matter. The loss of sulfur in gaseous form, released during sample drying, is probably of appreciable amount in terms of the original in-place sulfur content of the sediment. The distinctive strong

odor of H_2S in samples, of whatever depth, suggests that excess reduced sulfur is available to bind all available metals in the sediment, either as common sulfide minerals, or, by simple reduction of metals, such as uranium from its soluble hexavalent form to its insoluble tetravalent form, uraninite.

The distribution and forms of sulfur in the organic-rich tidalmarsh sediment are summarized as follows: (1) Total sulfur content increases with increase in depth of burial; (2) free sulfur content is drastically reduced with increase in depth—most of the measured free sulfur was formed by oxidation of unstable sulfides when samples were air-dried; (3) in undisturbed sediment, sulfur is in the reduced forms HS^-, H_2S, and metal-sulfide minerals; (4) in the upper 25 cm of sediment, iron sulfide is in a very unstable hydrous form; from 25 to 40-cm depth a relatively stable black amorphous iron sulfide mineral exists; and below a 40-cm depth, pyrite is abundant.

The following examples show increase of iron sulfide content with increasing depth in cores of peaty sandy mud. The assumption is made in presenting these values that 90 percent of the total sulfur in the sediment is in the form of iron sulfide and that 10 percent is organically bound sulfur.

Core sample No.	Sample depth (centimeters)	Calculated iron sulfide (percent)
M1–A	0–10	1. 4
B	10–25	2. 2
C	25–40	10. 7
D	40–61	10. 9
M10–A	0–10	3. 2
B	10–20	5. 2
C	20–30	10. 0
M14–A	0–10	3. 7
B	10–25	11. 8
C	25–40	14. 3
M15–A	0–10	3. 9
B	10–25	5. 1
C	25–40	9. 9
M17–A	0–10	2. 1
B	10–25	2. 2
C	25–40	4. 5
D	40–55	7. 8
E	55–70	21. 0
F	70–76	19. 2

The distribution of sulfur is clearly related to the amount of organic matter and to the depth of sediment. In general, if the amount of organic matter in a typical peaty sandy tidal-marsh mud is constant, the amount of total sulfur increases from 3 to 10 times from the top to the bottom of the upper 1 m of sediment.

CHEMICAL COMPOSITION OF SEDIMENT

A semiquantitative DC–arc emission spectrographic analysis was made of each of the 148 sediment samples collected during the investigation. Laser-fired semiquantitative spectrographic analyses were also made of the ashed samples of 39 soluble humic fractions. The approximate percentages of some 25 elements were thus determined. The amounts of the common major elements, silicon, aluminum, magnesium, calcium, sodium, iron, titanium, and manganese, will be summarized first; then a summary of the amounts of minor elements, in alphabetical sequence, will be given.

TIDAL-MARSH SEDIMENT

Of the 102 samples, 91 contained more than 10 percent Si; nine of the other 11 samples contained about 10 percent Si, and two contained about 7 percent. Each of the 11 samples were peaty sandy mud that contained more than 30 percent organic matter. The silicon, as determined by study of the samples under the microscope, is primarily in the form of quartz and, in lesser amount, hydrous silica spines and skeletal fragments from sponges, diatoms, and Radiolaria. As indicated previously, this distribution of quartz and amorphous silica was confirmed by X-ray diffraction analyses. In the nine samples, the calculated sum of the amount of silica, organic matter, and iron sulfide account for 90 percent or more, by weight, of the sample; the two samples (table 2, M17–E, F) that contained about 7 percent Si were also the only two samples that contained about 10 percent Fe, and the sum of the silica, organic matter, and FeS_2 also was greater than 90 percent.

The general range of aluminum is 0.3–3.0 percent. All samples that contained 1 or more percent Al were peaty sandy mud, but the semiquantitive aluminum values did not show a distinct positive correlation with percentage of organic matter. In about half the 24 cores the percentage of aluminum decreased with depth increase, most noticeably in cores M6, M9, M13, and M14. Very likely, the aluminum is distributed unevenly between that adsorbed by organic matter and that contained by the small and variable amounts of clay minerals.

For magnesium, the general range is 0.05–0.7 percent for the 97 samples from cores; but three samples, each from the top 10 cm of

cores having shell material, contained 1.0–1.5 percent. The amount of magnesium decreased slightly with depth increase in most cores, core M22 (table 2) being an excellent example. In this core the magnesium content of five samples were from top to bottom, 0.7, 0.5, 0.3, 0.2, 0.15 percent.

The general range of calcium is 0.07–5 percent. In cores of peaty sandy mud, samples of the top 10 cm contained the most calcium, commonly 1–3 percent; samples of mud below 10 cm generally contained 0.3–0.7 percent calcium. This was to be expected because of the dissolution of shell material below 10 cm. Most of the carbonaceous and relatively clean sand samples contained the least amount of calcium, 0.5–0.2 percent.

Of the 24 cores, 17 showed a marked decrease of sodium content with increase in depth, from 1–5 percent in the top 10 cm to 0.1–0.5 percent at a depth of about 50 cm. Very likely, if all interstitial sea water were drained or squeezed out of the cores before drying, the sodium content of the samples would be decreased by about one order of magnitude.

Of special interest are the amounts and distribution of iron because the iron easily combines with reduced sulfur, as described in the preceding section. Iron is the most abundant inorganic element in the tidal-marsh sediments, except for silicon and the oxygen in silica. The general range of iron content is 0.3–10.0 percent; only two of the 52 samples of peaty sandy mud, which contains the most organic matter, have less than 1 percent Fe. These two samples, M1–A and M16–A, were taken from the top 10 cm of sediment, where the iron would be the most soluble and subject to removal. Samples of the top 10 cm of peaty mud averaged about 2 percent Fe, whereas the average of the underlying peaty mud samples was about 5 percent. The general ranges of iron content of the carbonaceous sand and relatively clean sand are 0.5–0.7 and 0.2–0.5, respectively. Of all the inorganic elements, iron showed the most consistent increase with increase in depth in the tidal-marsh cores. This continuous increase is perfect, or nearly perfect, in the samples of cores M1, M5, M7, M14, M15, M22, and M24, all of which are predominantly sandy mud. This iron distribution parallels the increase of sulfur with increasing depth, which clearly substantiates the interpreted unstable iron sulfide in the upper 25 cm, the observed amorphous iron sulfide at a sediment depth 25–40 cm, the observed crystalline pyrite below 40 cm, and the overall consistent increase of iron sulfide with increasing depth in the cores.

Titanium has a relatively narrow range of concentration. It varies from 0.02 to 0.3 percent, and in 77 of the 97 samples from cores it occurs in the range of 0.07–0.15 percent. The amount seems unrelated

to sediment type or depth of sediment. The small amounts of observed ilmenite or rutile would account for the titanium in the tidal-marsh sediment.

Though generally present in minute amounts ranging from 0.0005 to 0.05 percent, manganese is slightly more abundant in the peaty sandy mud than in the other two sediment types. Most samples of mud contain 0.005–0.015 percent. The only two samples containing more than 0.015 percent Mn (M9–A which has 0.05 percent; and M17–A which has 0.03 percent) are peaty sandy mud samples that contain 35.3 and 34.6 percent organic matter, respectively. The manganese content of sediment types other than peaty sandy mud is in the 0.0005–0.005 percent range.

The boron content of the tidal-marsh sediment ranges from 0.002 to 0.015 percent. In 13 of the 24 cores, the boron content regularly decreases with increasing depth, commonly from 0.01 percent in the top 10 cm to 0.003 percent at the 50- to 60-cm depth interval. In the other 11 cores, the boron content tends to decrease or remains constant with depth. Most of the samples of the nonpeaty sediment types contain no more than 0.003 percent B.

The barium content of all samples has a range of 0.003–0.01 percent, and barium values show no correlation with depth or sediment type.

Beryllium was detected in only five samples in concentrations of 0.0001–0.0003 percent, which is about the limit of detection determined by the spectrographic method.

Cobalt was detected in 21 samples, in amounts between 0.0003 and 0.0007 percent, also very near the limit of detection. All the 21 samples were peaty sandy mud.

The chromium content of all samples is low, generally in the range of 0.0005–0.01 percent. The highest percentages of chromium are invariably in samples of peaty sandy mud, which contains from 0.003 to 0.01 percent Cr. Most of the relatively clean sand samples contain the small amounts, generally 0.0005 or 0.0007 percent Cr. Thus, there appears to be a crude correlation between chromium and organic matter.

Copper was detected in all but two samples of relatively clean sand (core M16). Generally, it ranges from 0.0002 to 0.007 percent. The highest values are in samples of peaty sandy mud. In some cores the amount of copper tends to remain constant or to decrease very slightly with increase in depth.

Molybdenum, nickel, and lead were detected in very small amounts in many samples; molybdenum generally ranges from 0.0003 to 0.005 percent; nickel, from 0.0003 to 0.003 percent; and lead, from 0.0005 to 0.002 percent. All three metals are more abundant in organic-rich

mud. Molybdenum showed a slight increase with increasing depth in a few cores and nickel and lead a slight decrease with increasing depth in some cores, but because all values reported are near the limit of detection, no significance is placed on these changes with depth.

Although lead was detected in only very small amounts in about half the samples, its relative abundance in surface samples suggests contamination by leaded gasoline used by many sport and commercial fishing-craft engines, and even may be lead from automobile and truck combustion engines that was sorbed by organic matter from inland areas and ultimately deposited in the tidal marsh. Of the 24 cores, lead content was highest in the top sample of 15 cores and was detected in only the top sample of seven cores. Each of the five specially collected samples of the uppermost 4–5 cm of the organic-rich layer (table 2) contained 0.001 or more percent lead. A concomitant concentration of bitumen in these same samples, with a distinctive combination of hydrocarbons, was not observed, mainly because the lighter hydrocarbons used in gasoline are rapidly volatilized or otherwise destroyed.

The general range for strontium, which was detected in all core samples, was 0.0007–0.03 percent, and like magnesium and calcium, the element decreases in abundance with increase in depth.

Vanadium was also present in measurable amounts in all samples, ranging from 0.0007 to 0.015 percent. As with several other metals, vanadium correlates positively with organic matter. Peaty sandy mud generally contained 0.003–0.007 percent, and six samples of this sediment type contained 0.01–0.015 percent.

All the sediment samples from the tidal marsh contained zirconium, generally in the range of 0.007–0.05 percent. Zirconium showed no consistent distribution among the sediment types.

The elements gallium, lanthanum, lithium, scandium, yttrium, and ytterbium were detected in relatively few of the 102 samples, but most of the values were at or near the limit of detection, generally in the 0.0001–0.001 percentage range.

RIVER-MOUTH SEDIMENT

All 40 sediment samples (table 3) collected near the mouths of the six streams contained more than 10 percent Si, supporting the lithologic descriptions that silt-sized quartz to medium quartz sand is the major component of the samples.

The aluminum content of the river-mouth sediment ranges from 0.2 to 1.5 percent; only two samples, A3 and E7, contain 1 percent or more. In general, the aluminum content of the river-mouth sediment is one-half to one-third that of the tidal-marsh sediment. It is assumed that

the relatively small amount of aluminum is adsorbed on the organic matter or is a component in clay minerals.

The river-mouth samples are all of the upper 10 cm of sediment and so the variation in the iron content with depth was not determined. The range of iron content in the river-mouth sediment is generally 0.1–1.5 percent; all eight samples that contained 1.0 and 1.5 percent Fe also contained more than 2.8 percent organic matter.

The range of magnesium content is generally 0.02–1.0 percent. Off-shore sediment (table 3) generally contained about 0.2 percent, and river sediment, about 0.1 percent. Only three samples contained more than 0.3 percent, one just off the mouth of the Econfina River, which contained about 1 percent, and two off the mouth of the Steinhatchee River which contained 0.7 and 0.5 percent.

The amount of calcareous shell material observed in the river-mouth samples was highly variable; as expected, the calcium content of the samples varied accordingly, from 0.03 to 10 percent.

Of the samples collected near the mouths of streams, those collected offshore contained about 1 percent sodium, whereas the river sediment generally contained about 0.3 percent. As in the tidal-marsh samples, sodium is largely accounted for by interstitial sea water collected and dried with the sediment.

As for the tidal-marsh samples, the content of titanium is fairly constant within a narrow range of 0.02–0.1 percent. The general range for manganese is 0.0005–0.01 percent, with the offshore samples having the greatest amounts.

The amount of boron in both the offshore and stream sediment is surprisingly low; 37 of 40 samples contained at most 0.003 percent B. A consistently higher boron content was found in the tidal-marsh mud, which was generally in the 0.003–0.015 range.

Although barium was detected in all the 40 river-mouth samples, the content is generally low, 0.002–0.007 percent; no correlation was noted between barium and lithologic type, amount of organic matter, or position in the streams or offshore.

Chromium was detected in all samples, but in very small amounts, generally between 0.0003 and 0.002 percent. The offshore- and stream-sediment values show no notable differences; but in any one area, for example sediments near the mouths of the Econfina River and Dallus Creek, chromium content increases with the amount of organic matter in the sediment.

Except for three samples collected across the mouth of the Aucilla River, A–4, 5, and 6, which contained 0.007, 0.002, and 0.0015 percent Cu, respectively, all other river-mouth sediment samples contained at most 0.001 percent Cu. Of the 40 samples collected, 30 contained 0.0001

or less percent. The greater copper content of the tidal-marsh samples, two-thirds of which contained at least 0.001 percent Cu, as compared to that of the river or offshore sediment, is readily apparent.

Molybdenum, nickel, and lead were detected in a few of the river-mouth sediments in very minor amounts. Molybdenum was detected in samples from the Econfina River and Dallus Creek areas in the 0.0003–0.0007 range, and only in samples that contained more than 2.5 percent organic matter. Nickel was detected in 29 samples, in the 0.0003–0.0007 range. No apparent relation to amount of organic matter or to geographic position was noted for these elements. Similarly, 10 values reported for lead, in the 0.001–0.003 range, showed no relation to content of organic matter or to geographic position.

Strontium and vanadium were detected in most samples. The strontium contents generally ranged from 0.001 to 0.05 percent and increased in direct proportion to the amount of calcium in the samples. The amount of vanadium was generally correlatable to the amount of organic matter in the sediment, but had a low range of 0.0007–0.005 percent. For most of the samples containing less than 1 percent organic matter, the vanadium content was below the limit of detection, or less than 0.0005 percent.

The distribution of zirconium in the 40 samples was very erratic, ranging from 0.003 to 0.1 percent.

SOLUBLE HUMIC FRACTION

The capacity of natural soluble humic substances to adsorb, transport, and concentrate metals has long been known (see, for example, references cited by Swanson and others, 1966, p. C177; Ong and others, 1970, p. C137). These substances, which make the stream waters in the tidal-marsh area brown or tea colored, are commonly precipitated on coming into contact with sea water (Swanson and Palacas, 1965, p. 26) and are deposited with detrital materials as humate. The consequence is an enrichment of metals in the humate-bearing sediment commonly 10 to several thousand times greater than in sediment without organic matter.

In an effort to determine the possible role of these formerly soluble humic substances in concentrating metals within the tidal-marsh sediment, the humic fraction, which averages 78.1 percent of the alkaline-soluble organic matter (table 4), was ashed and analyzed for 39 samples from 11 cores by the semiquantitative laser-fired spectrographic method (James M. Nishi, analyst). The analyses were calculated to an ash-free basis for comparison with semiquantitative spectrographic analyses of the whole samples.

Of the 30 elements looked for, the soluble humic fraction is enriched in only six: cobalt, chromium, copper, molybdenum, nickel, and vanadium. Of these six, only chromium is notably concentrated; the chromium content is generally 2–10 times greater than in the whole sample. Cobalt, copper, molybdenum, and nickel contents of the humic fraction are commonly 1½ to 3 times greater. The vanadium content is slightly higher in about one-third of the samples; for example, 0.007 percent in the humic fraction and 0.003 percent in the whole sample. Although tin was not detected in any of the whole-sediment samples, 0.002–0.03 percent Sn was detected in the ash of the humic samples.

On the assumption that the alkaline-soluble humic fraction represents a major part of the previously soluble humic substances, the above brief summary would indicate that metals are not greatly enriched in the humate in the tidal-marsh sediment. The distribution of several metals, particularly iron, chromium, copper, and vanadium, in the tidal-marsh sediment has been shown to be related to the total organic matter, but the naturally soluble humic substances are probably no more important in concentrating these elements than the decomposed and fragmented plant detritus in the sediment. The abundances of iron, manganese, cobalt, chromium, copper, molbydenum, nickel, and vanadium in the tidal-marsh sediment are about the same as those found in many ancient carbonaceous sedimentary rocks and in modern sediments from many environments of deposition (Tourtelot, 1970).

MOISTURE CONTENT

Moisture or water content was determined on 19 samples from 13 tidal-marsh localities. The method was simply a measurement of weight loss on air-drying a frozen chunk of sediment to constant weight at 60°C. Some compaction is known to take place during coring, but this apparently did not mask the changes in moisture content relative to type of sediment.

The peaty sandy mud had an average of 73 percent water (13 samples, range of 64–80 percent) ; the carbonaceous muddy sand, 41 percent (1 sample) ; and the relatively clean sand, 26 percent (3 samples, range of 23–28 percent). As might be expected, moisture content almost directly correlates with the percentage of organic matter in the samples—the greater the amount of organic matter, the greater the moisture content. No change in water content with shallow depth of burial was apparent.

The water content of the upper 1 m of tidal-marsh sediment is clearly and primarily a function of sediment type.

IMPLICATIONS FOR GENESIS OF OIL AND GAS

The probable source of many high-wax petroleums has been postulated as the predominantly terrigenous organic matter deposited in coastal marsh or nearshore marine environments (Hedberg, 1968; Biederman, 1969; Reed, 1969; Miller, 1972). The amounts, distribution, a few gas-chromatography analyses (Swanson and others, 1968, p. B36), and even the waxy appearance of the bitumen extracted from the tidal-marsh sediment do, indeed, seem to indicate that tidal-marsh mud might be a likely source of high-wax petroleum. Other considerations, however, indicate that the sparse bitumen in the nearby offshore sand, derived mainly from marine organisms, is a more likely source.

One reason for this conclusion has been well stated by Erdman (1961, p. 34–35):

In the freshly deposited sediments, the highly polar constituents of the organic fraction are preserved from loss during the early expulsion of water by adsorption on mineral constituents of the sediment. * * * At the same time, however, attraction [of the weakly polar constituents of petroleum] to the relatively hydrophobic surfaces of solid carbonaceous matter increases. The retentivity of the sediment during compaction for the constituents of petroleum thus becomes a function of the amount of solid carbonaceous material. Dynamically, the carbonaceous material will retard the migration of the constituents of petroleum. * * * If the proportion of the migrating organic material is too small in proportion to the stationary carbonaceous material, migration will be too slow to permit the [petroleum constituents] to escape from the sediment.

Erdman continued by noting that the above reasons explain why coals and presumably many black shales, that *now* have relatively high contents of extractable gaseous and liquid hydrocarbons and other petroleum constituents apparently failed to yield oil during their geologic history. This thesis was restated in a more detailed paper on the geochemical genesis of petroleum by Erdman in 1965 (p. 45–46).

The bitumen content in the typical tidal-marsh mud described in this report is relatively high, averaging 0.08 percent of the sediment in 24 cores; but it is less than 0.5 percent of the organic matter, which is predominantly solid decomposed woody plant fragments. The conclusion is that this bitumen, which includes the hydrocarbons and other petroleum constituents that would yield a high-wax oil, will firmly adhere to the solid organic material and thus be immobilized and retained through time, diagenesis, and compaction. Some very light hydrocarbon gases, for example, methane, might well be laterally or vertically expunged very slowly from the humic-rich sediment, however.

The offshore sand and some of the relatively clean sand in the tidal marsh, on the other hand, are porous and permeable. Although the amounts of bitumen per unit of sand are small, generally in the 0.005–0.015 percent range, the amounts volumetrically are vast, and these sands are good potential sources of hydrocarbons and associated petroleum-forming constituents. This thesis, pertaining to the tidal-marsh area described in this report, and to estuarine sediment in north-west Florida, was outlined in 1968 (Swanson and others, 1968), and has been presented in detail for esutarine sediment in Choctawatchee Bay, Fla. (Palacas and others, 1972).

SUMMARY

1. This investigation is limited to one tidal-marsh area, a belt 1–5 miles wide extending some 80 miles along the northeastern Gulf of Mexico, from the Aucilla River to the Suwannee River, Fla. Only the near offshore, tidal-stream, and tidal-marsh sediments, with their similarities and differences, are the subjects of this report. Sediment samples collected from the top 1 m of sediment were studied under the microscope and were routinely analyzed by a series of nine analytical methods; representative samples were subjected to five additional types of analysis. Interrelations of field observations and laboratory data are incorporated in this study.

2. The salinity of water in the streams is highly variable, depending on water depth, distance from mouth of steam, and tide stage. The pH of most of the bottom water is generally slightly alkaline, and the Eh is oxidizing or very slightly reducing.

    The pH and Eh of the sediment are generally related to the amount of organic matter in the sediment—the greater the amount of organic matter, the lower the pH and Eh. The pH of offshore sediment is generally neutral, but the tidal-marsh mud is slightly to very acidic. All Eh measurements indicated reducing conditions in the sediment; sandy offshore sediment was generally only slightly reducing, but the tidal-marsh mud was very reducing.

3. On the basis of grain size and amount of organic matter, the sediment in the tidal marsh is readily classified as peaty sandy mud, carbonaceous muddy sand, and relatively clean sand. The range in organic matter content is 15–40 percent, 4–15 percent, and 0.1–4 percent, respectively. More than 90 percent of the inorganic or mineral component of the sediment in most samples is silt- to medium-sized quartz and fragments of amorphous silica spines and skeletons. Pyrite is the second most abundant inorganic

mineral, and only a few percent of clay minerals are present. The small amount of $CaCO_3$ sharply decreased and disappeared with increasing depth of sediment. Calcareous shells are rapidly dissolved under the acid conditions existing at depths below 10–20 cm in the tidal-marsh sediments.

Offshore sand generally contained less than 1 percent organic matter, 3–20 percent calcareous shell fragments, with quartz making up the remainder.

4. Eighty percent of the abundant organic matter in the tidal-marsh sediment is humic material derived from the inland swamp-forest areas and delivered to the Gulf of Mexico by streams. The remaining 20 percent of the organic material, which is also of the humic type, is mainly derived from the stalks and root matter of the dominant *Juncus* marsh plant and, to a minor extent, from nearshore seagrasses such as *Thalassia*. The total mass of humic-type organic matter from both the inland forest and the nearshore plants is believed to have been deposited either as solid particles (75 percent) or as flocculated organic acids (25 percent).

The process of buildup of most of the organic matter in the tidal marsh is explained thus: The dominant high-energy onshore wave action restricts the distribution of the suspended low-density organic particles and flocculated organic acids, which are delivered to the Gulf of Mexico by the slowly moving stream water, to lateral movement along the coast. At flood tide the suspended organic matter is flushed onto the tidal marsh and deposited near the time of high tide, when the shallow water is the quietest. Once deposited, the particles adhere to adjacent sediment particles, resisting dislodgement during the relatively slower water movement during the ebb tide stage. The trapping effect of the abundant marshgrass also inhibits particle movement. At low tide, subsurface draining of interparticle water and partial drying of the uppermost mud on exposure to the air results in some compaction; in addition, the slight weight of the newly deposited material causes some compaction at greater sediment depth. Consequently, the deposited organic matter is made a part of the sediment column, and vertical space exists for deposition of more organic matter during the next high tide.

5. The overall average content of organic matter in the tidal-marsh sediment is 15.8 percent; the most characteristic sediment is peaty sandy mud, which contains an average of 27.0 percent organic matter. Slightly more than one-fourth of the organic matter is alkaline soluble, which is a measure of the flocculated organic acids or the humate content of the sediment. The soluble

humic fraction exceeds the fulvic fraction, average of 78 and 22 percent, respectively. The bitumen content averages 0.44 percent of the organic matter. The average percent of hydrocarbons in the bitumen is about 24 percent, with asphaltic compounds constituting the remainder.

In the tidal-marsh sediment, the percentage of organic matter that is alkaline soluble increases slightly as the grain size of the sediment increases, and the percentage of the fulvic fraction also increases. Although not as consistent, a similar relation exists for bitumen. It may be that the coarser sediment provides the porosity and the medium for greater mobility of these soluble fractions than the finer grained sediment, but more evidence is needed to support this possible conclusion.

6. The organic matter generally changes with increasing depth in the tidal-marsh sediment as exemplified by the decrease in the percentage of alkaline-soluble organic matter with increase in depth, and, particularly, by the decrease in the percentage of soluble fulvic fraction with increase in depth. Both changes are interpreted as indications of early and relatively rapid geochemical diagenesis of organic matter to less solubility and mobility of these humic-type organic components at shallow depth of burial. The lack of a pattern of change in amount or composition of bitumen with increasing depth suggests either that the hydrocarbons and the other petroleum constituents are firmly held and will not undergo movement or significant change, or that changes and mobilization must await greater depth of burial. Because of the strong retentivity of the abundant solid organic material for otherwise mobile petroleum compounds, the authors accept the first of these two possibilities as the more probable.

No geographically controlled changes in amounts or types of organic matter, or in the chemical components extracted from the organic matter, were determined in the tidal-marsh sediment.

7. Most of the river sediment is a slightly carbonaceous tan muddy quartz sand, and the offshore sediment is a light-colored quartz sand that contains abundant calcareous shell fragments.

The river, or stream, sediment contains an average of 2.2 percent organic matter. Alkaline-soluble organic matter constitutes about 18 percent of the organic matter; the soluble humic fraction is about 80 percent, and the fulvic fraction, about 20 percent. The bitumen averages 0.48 percent of the organic matter.

The dominant calcareous sand more than 1 mile from shore contains 0.9 percent organic matter. The average of the alkaline-soluble organic matter is only about 6 percent of the total organic matter; the humic and fulvic fractions represent about

74 and 26 percent, respectively. The average bitumen content of the typical offshore calcareous shelly sand is 0.84 percent of the organic matter, or about two times more bitumen per unit organic matter than the tidal-marsh sediment. In addition, hydrocarbons make up about 40 percent of the bitumen from this offshore sand, as compared to about 24 percent of the bitumen from the tidal-marsh sediment. The precursors of the bitumen in the offshore sands are largely derived from marine organisms, very different from the humic or woody organic matter in the tidal marsh, and the porous offshore sand is the much more likely "source bed" for petroleum.

8. The changes and early diagenetic concentration of sulfur as depth increases in the humic-rich tidal-marsh sediment is clearly demonstrated. The strongly negative Eh readings, the strong odor of H_2S, and the dark color of otherwise light-colored sediment indicate sulfur is in a reduced form even in the uppermost few centimeters of sediment. Most of this sulfur is very probably combined with iron as a very unstable iron sulfide within the upper 25 cm but rapidly oxidizes to ferric hydroxide and elemental sulfur when the sediment is dried; between 25 and 40 cm, and amorphous but more stable dark-bluish-black iron sulfide mineral coats the grains in the dried sediment, and bronze-colored aggregates of minute crystals of pyrite exist below 40 cm.

The amount of iron sulfide markedly increases as depth increases. In peaty sandy mud, an increase of 2–10 percent of iron sulfide is not uncommon; and, in one core, iron sulfide increased from about 2 percent in the upper 25 cm to 20 percent in the form of pyrite below 55 cm.

9. Some metals are slightly concentrated in the tidal-marsh sediment, and their concentration is directly related to the amount of organic matter. Metals that are enriched in the sediment because of the abundant organic matter are iron, manganese, cobalt, chromium, copper, molybdenum, nickel, and vanadium, though, except for iron, each is present as less than 0.1 percent of the sample. The soluble humic fractions contain only slightly greater amounts than the total organic matter. The anomalous concentration of lead in the upper 4–10 cm of tidal-marsh sediment throughout the area suggests contamination by leaded gasoline used by many fishing-craft engines.

10. This broad study of the tidal-marsh area has served to bring into focus specific types of investigations that are needed to understand more clearly the geochemical and geological factors common to this depositional environment. Examples, with suggested methods of study, are as follows:

Rate and results of early diagenesis.—As partly confirmed in this report, the most rapid rate of diagenesis in sediment with abundant humic material probably takes place during burial within the uppermost 1 m, and before significant compaction restricts interstitial fluid movement. Total removal of $CaCO_3$, the generation of H_2S and the formation of stable FeS_2, and the polymerization and the decrease in solubility of humic fractions are examples of surprisingly rapid diagenetic changes. Careful selection and preparation of several cores 2–4 m long of peaty sandy mud from the tidal marsh could be used to determine chronologically by carbon-14 dating the time required to stabilize specific organic and inorganic components to forms that would be retained through geologic time.

Movement of liquid organic compounds during compaction.— Theoretical considerations strongly suggest that liquid or potentially liquid hydrocarbons, for example, are firmly and permanently retained in fine-grained sediment that contains abundant solid carbonaceous material. A simply designed compaction apparatus could confirm or quantitatively modify this theory. Frozen cores of the three sediment types from tidal marsh that contain the indigenous high-wax bitumen could be artificially compacted within a sleeve of filtered connate water having a controlled pH of 4–5, Eh of -300 mv, a salinity of 30‰, and a known chemical composition. Periodic analysis of expelled fluid, programed on time, temperature, and compaction factors, would produce desired data.

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