## NATURAL AND ANTHROPOGENIC CONTROLS ON THE GEOCHEMISTRY OF NORTHERN GULF OF MEXICO ESTUARINE SEDIMENTS

Wayne C. Isphording<sup>1</sup>, Harriet M. Perry<sup>2</sup>, and Christine B. Trigg<sup>2</sup> <sup>1</sup> Department of Geology-Geography, University of South Alabama, Mobile, Alabama <sup>2</sup> Gulf Coast Research Laboratory, University of Southern Mississippi, Ocean Springs, Mississippi

### INTRODUCTION

## **ESTUARINE SEDIMENTS**

Pritchard (1967) defined an estuary as "a semi-enclosed coastal body of water which has free connection with the open sea and within which seawater is measurably diluted with fresh water from land drainage." Estuaries are transition zones between marine and non-marine depositional systems. Sixteen major estuaries are present in the Gulf of Mexico between the Florida Keys and the Texas-Louisiana border (Figure 1). Annually, they receive nearly 50 percent of the total drainage from the continental United States. Each second, approximately one million cubic feet of water enters the Gulf of Mexico through the numerous bays and estuaries that fringe the southern margin of the United States (Wilson and Iseri 1969). The quantity of water entering the Gulf of Mexico, however, is not evenly distributed. The area west of the Mississippi River represents about 20 percent of the Gulf drainage, but because of its drier climate supplies only six percent of the total discharge to the Gulf. The area east of the Mississippi River watershed and extending to the eastern margin of the Apalachicola River basin encompasses seven percent of the total Gulf drainage area, but contributes 18 percent of the total discharge because of its wetter climate. The Mississippi River watershed system receives runoff from nearly 1.2 million square miles and provides over 70 percent of the total discharge from the United States to the Gulf of Mexico. Unlike the Mississippi River which discharges directly into the Gulf of Mexico, most of the remaining rivers discharge into the estuaries and these, in turn, trap significant portions of the transported sediment load (Table 1). The numerous watershed areas emptying into these systems drain regions of marked diversity in bedrock and population; hence natural and anthropogenic contaminants carried by the rivers differ widely (Isphording et al. 1989). Further, because of differences in the flow regimes of the contributing rivers and the physical parameters operating in each basin, each of the bays is characterized by distinct differences in sediment composition and texture. These differences control the quantity and manner by which contaminants that are transported into the bays as natural, municipal, and industrial effluent become incorporated into the sediments (Isphording et al. 1985, Isphording et al. 1989).

Depositional rates in northern Gulf estuaries are slow and average about 2.0 mm per year (Table 2). Consequently, bioturbation by infaunal burrowing organisms causes reworking of the sediment at a rate far exceeding the rate of introduction of new sediment. Emery and Uchupi (1972) estimated that if all suspended sediment carried by rivers (other than the Mississippi) were deposited in the fringing estuaries and lagoons along the U.S. Atlantic and Gulf Coasts, then these features would be completely filled in less than 10,000 years, assuming no sea level changes. Dardeau et al. (1992) noted that "...estuaries are ephemeral features having life spans over only thousands to a few tens of thousands of years." Similarly, Schubel and Hirschberg (1978) concluded that, once formed, estuaries are rapidly destroyed by sediment filling. Nichols (1989), however, observed that the majority of 22 estuaries that he studied in the eastern United States have a "near balance of accretion" and therefore may persist far longer than the few millennia predicted from annual accumulation rates. Using simple depositional models to predict the life of an estuary is hazardous at best. These models do not consider the effects of natural phenomena that can markedly alter the volumes of sediments that are deposited in estuaries, bays, and lagoons. Isphording (1994) described the removal of nearly 300 million tons of sediment from the Mobile Bay estuary during a 24 hour period associated with the passage of Hurricane Frederick in 1979. Nearly 90 million tons of sediment were removed from Apalachicola Bay during the passage of Hurricane Elena near Apalachicola Bay in 1985. Fine silts and clays, as well as organic matter, are the materials most readily re-suspended in the water column by the turbulent and scouring action of strong currents. These materials, in turn, are also those with the greatest ability to absorb contaminants. Hence, any activity that acts to remove such sediments from an estuary can be expected to also bring about a reduction in levels of heavy metal contamination. This is demonstrated in Table 3 which shows pre- and post-hurricane levels of several heavy metals, as well as organic carbon, for both Mobile Bay, Alabama, and Apalachicola Bay, Florida.

-27-

#### ESTUARINE CHEMISTRY

Of all aquatic systems, estuaries provide the greatest diversity in water composition and hydrology. The mixing of fresh and salt water results in the development of a number of different physical and chemical sub-environments and these, in turn, support a variety of biotic communities (Vernberg and Vernberg 1981). The distribution and stability of these sub-environments depend largely on features such as basin morphology, temperature, salinity, and circulation patterns, and these parameters continually interact in any given basin to exert controls on the physical and chemical nature of estuarine waters (Dardeau et al. 1992).

Estuaries receive sediments from a combination of fluvial, marine, eolian, and biological sources (Rusnak 1967). The salinity contrast between seawater and river water plays an important role in reducing mixing of estuarine waters, causing the freshwater to spread out over the denser seawater. This chemical contrast causes flocculation of clay particles that are carried into the estuaries, reducing the amount of sediment that is carried through the estuary out into the Gulf of Mexico. The result is that most estuaries possess significant quantities of clay-sized material in their bottom sediments (Isphording et al. 1989). This has important consequences from a contaminant standpoint, because clay-sized particles, with their high surface area per unit volume, are favorite sites for sorption of organic and inorganic contaminants.

Mineralogical speciation of the bottom sediment clays also exerts controls on contaminants. Estuaries in the eastern Gulf are largely dominated by kaolinitic clays (e.g., Apalachicola Bay, St. Andrew Bay, Pensacola Bay). This arises from the fact that the sediments in these bays are derived from reworking of older Coastal Plain deposits and from the weathering of rocks of the Piedmont and Blue Ridge Provinces. Those estuaries in the central Gulf (Mobile Bay, Mississippi Sound, Lake Pontchartrain, Barataria Bay, Timbalier Bay) show a clay mineralogy dominated by Smectite Group clays. These clays represent materials derived from weathering of Tertiary-age rocks in the Western Interior, Rocky Mountains, Cumberland Plateau, and Valley and Ridge Provinces. The importance in the speciation lies in the fact that Smectite Group clays are not only characteristically smaller in size than kaolinitic clays (and hence have a greater surface area for sorption of contaminants), but also possess higher cation exchange capacities, which enhance their ability to absorb metals. Consequently, eastern Gulf estuaries are characterized by somewhat lower levels of heavy metal contaminants than are their central and western Gulf counterparts (Table 4).

# ENVIRONMENTAL PROBLEMS IN ESTUARINE SYSTEMS

Environmental problems in northern Gulf estuaries arise as a consequence of both natural and anthropogenic causes. Storms may bring about major changes in estuarine morphology and sediment distribution and may markedly alter, or damage, the protective barrier islands. Sediment loads carried by rivers continually bring detrital materials into the estuaries and, in rare instances, have actually filled the estuaries to the point of near destruction. Increasing amounts of heavy metals, pesticides, herbicides, and other organic compounds are continually being transported into the estuaries, some of which have acted as "sinks" for these compounds. The U.S. Environmental Protection Agency (1986) identified major areas of concern for coastal waters as follows: toxic contamination, eutrophication and hypoxia, pathogen contamination, habitat loss and alteration, and changes in living resources. Dardeau et al. (1992), in their review of the biotic and abiotic parameters and processes associated with estuarine waters, included an excellent overview of the environmental problems and concerns as identified by the EPA (1986).

#### **Causes of Estuarine Degradation**

Siltation/Turbidity. Both point and non-point sources of siltation and turbidity can substantially impact aquatic habitats. The effects of construction and development on habitat and biological resources can be locally significant and conspicuous. Waterfront development (bulkheading, excavating for construction of boat slips, and dredging and filling of shoreline areas) not only destroys wetlands, but increased siltation and turbidity caused by these activities can alter biotic communities in the estuary. Light attenuation resulting from turbidity limits the occurrence and density of seagrass beds (U.S. EPA 1994a), and siltation may render otherwise favorable areas unsuitable for shellfish production (Perry and Cirino 1998).

Although siltation and turbidity associated with dredging operations are usually temporary, incursion of fine silt and clay into shellfish areas may have harmful (or even disastrous) effects on commercial oyster reefs and their allied fauna. Brett (1975) reported that the large concentrations of sediments suspended during dredging of the main ship channel in Mobile Bay were observed to move a distance of 5,000 feet (1,524 m) along the bottom as a turbidity current when driven by the tide. Fortunately, tidal movement of dredged material is probably limited to a few months following initial deposition. Dredged material tends to de-water and consolidate, and it becomes very difficult to erode after it has settled over a period of time. An investigation describing the effects of open-water disposal of maintenance dredging material in the Mobile Bay estuary by Clarke and Miller-Way (1992) indicated that major effects to the biota were largely limited to within 1,500 m of the discharge point and that recovery to pre-disposal conditions was essentially complete within 12 weeks.

**Toxic Contaminants.** A myriad of activities can lead to significant quantities of toxic materials being delivered to an estuary. Agricultural use has been shown to contribute sizeable quantities of pesticides and herbicides by virtue of leaching of cultivated soils and subsequent runoff. Prior to passage of the National Pollution Discharge Elimination System (NPDES) and Clean Water Act in the 1970s, municipal and industrial discharges contributed significant amounts of contaminants to the environment (Taylor 1979, Cousma et al. 1979), and anthropogenic point sources continue to rank as the principal source of most pollutants. The U.S. EPA (1994b) estimated that 13 million pounds of toxic substances were released from industrial and municipal sites into drainage areas of the Gulf of Mexico in 1989.

Discharge by municipal and industrial sources, release by natural sources, and agricultural run-off control what metals or organic compounds will be released into the river systems that empty into the estuaries, whereas sedimentological, circulatory, and physico-chemical conditions in the estuary itself determine the quantity of the contaminant that is sorbed by the bottom sediments and the degree to which contaminants pass through the estuary and out into the Gulf of Mexico. The degree to which such flushing actually takes place is surprisingly less than might be imagined. In a recent investigation of the Mobile Delta-Mobile Bay system, Isphording et al. (1996) reported that the annual quantity of sediment carried into the Mobile Delta from the Mobile River system amounted to 4.42 billion kg (4.87 million tons). Of this, approximately 30% was deposited in the delta and 45%, or 3.23 billion kg (3.58 million tons), was deposited in Mobile Bay. Only 1.02 kg (1.12 million tons), or 23% of the original quantity carried into the head of the delta, actually exited the bay. Because only a limited portion of the incoming sediment is actually carried through the bay, and given the fact that approximately 189 million gallons of industrial and municipal effluent are discharged into Mobile Bay each day just from sources in the Mobile area, it is not surprising that Mobile Bay has been described as the most impacted estuary in the entire northern Gulf of Mexico (Isphording and Flowers 1987).

**Eutrophication and Hypoxia.** Nutrient enrichment is a common phenomenon in estuaries and may result from natural or man-related causes. Discharges of municipal effluent and from septic tank systems, as well as agricultural runoff, can create overloading of nitrate-nitrogen in streams draining into estuaries (Basnyat et al. 1996). Marine coastal waters are considered to be nitrogen-limited, and freshwater

systems are phosphorus-limited (Dudley 1992). Both nutrients are important to estuarine ecosystems. When excessive loads of nitrogen and phosphorus occur, accelerated eutrophication takes place, and this can lead to massive algal blooms, decreased light availability, changes in the biotic community, altered trophic structure, and decreased biological diversity (Dudley 1992). Changes in the ratios of selected nutrients, particularly nitrogen, phosphorus, and silicon, can alter phytoplankton community dynamics. Turner and Rabalais (1991) noted that the decrease in the Si:N ratio in riverine input from the Mississippi River may have a profound impact on phytoplankton species availability, carbon flux, and hypoxia. Changes in the Si:P and Si:N ratios have been implicated in the increase in noxious and toxic algal blooms and in phylogenetic shifts in phytoplankton biomass (U.S. EPA 1994c). Changes in phytoplankton community structure may have deleterious effects on marine food webs.

Nutrient enrichment may also cause oxygen depletion through an increase in organic loading. Sinking of excessive organic material and subsequent decomposition can reduce oxygen concentrations in bottom waters, and in stratified water columns, this can lead to anoxic conditions. Physicochemical characteristics of estuaries help to determine the impact of loading. High point source loading to Delaware Bay creates nutrient levels 10 times those found in Mobile Bay, in spite of the fact that the loading per unit volume is 4 times greater for Mobile Bay. Additionally, the high concentrations in Delaware Bay support 3 times the phytoplankton biomass present in Mobile Bay (Pennock et al. 1995). High suspended sediment concentrations and strong vertical tidal mixing act to limit hypoxic/anoxic conditions in Delaware Bay and provide the bay with a high capacity to assimilate nutrients. Mobile Bay, in contrast, experiences significant periods of bottom water hypoxia and anoxia (especially during the summer) because of strong salinity-dominated stratification and attenuated tidal mixing.

Of serious concern in the Gulf of Mexico is the seasonal occurrence of a large hypoxic area at the terminus of the Mississippi River. The hypoxic zone extends from the mouth of the river westward toward the Louisiana/Texas border. It has continued to increase in size and covered an estimated 17,000 km<sup>2</sup> in 1997. This area has been characterized as the largest, most severe and most persistent zone of hypoxia in the United States and it occurs in an area of high fishery production (U.S. EPA 1994c).

Pathogenic Contamination. Many pollutants in coastal waters have the potential to produce acute and chronic human health problems. Pathogenic micro-organisms are associated with both point and non-point source pollution. Municipal wastewater sewage poses the greatest risk of

-29-

infectious disease (U.S. EPA 1993). Humans can be exposed to potentially harmful contaminants through consumption of fish and shellfish and by direct contact with water and aerosols. Hepatitis, cholera, and gastroenteritis are caused by water- and seafood-borne pathogens (U.S. EPA 1993). A wide variety of viral and bacterial species cause illness, and most are associated with molluscan shellfish: oysters, clams, or snails. Shellfish, in particular, harbor pathogenic bacteria and viruses that arise from human and animal waste. These pathogens enter coastal waters through discharge of raw sewage, discharge from septic systems, sewage treatment plants, boats and ships, dumping of sewage sludge, and surface water and agricultural runoff. Presence of pathogens associated with human and animal waste is the primary criterion used to limit harvest of shellfish. Closure of molluscan shellfish beds has increased in the Gulf. Livingston (1984) reported a 3200% increase in closure of shellfish beds in Louisiana between the years 1965 and 1971 (2,388 hectares vs 80,459 hectares).

Destruction of Habitat. Dardeau et al. (1992) noted that since the 1700s, approximately 50% of the coastal wetlands have been destroyed with highest rates occurring over the past three decades. Anthropogenic alterations to wetlands include construction of canals and channels; dredging and disposal of dredge spoil; draining and filling; industrial, municipal, and agricultural point and non-point source discharges and runoff; and loss of freshwater inflow and sediment deposition through construction of dams (U.S. EPA 1994a). Physical and biological processes that can impact estuaries include erosion, rising sea level, subsidence, storms and drought, floods, phytoplankton blooms, "eat-outs" (e.g. nutria), and plant diseases (U.S. EPA 1994a). Continuing development and population increases in coastal areas pose serious threats to estuaries through habitat loss and alteration and water quality degradation. Aside from the physical alteration of shorelines associated with these activities, dumping of spoil creates shallow bathymetric conditions that affect the indigenous biota. Oxygen depletion may take place in the summer months because of salinity stratification in sinks created by shallow water conditions. When water masses low in dissolved oxygen are forced against beach areas, demersal fishes and crustaceans move shoreward in a moribund state creating "jubilees." While this phenomenon is eagerly awaited by the populace who rush to harvest the fish and crabs, it is symptomatic of the problems that many estuaries face. Man-caused bathymetric changes have caused restrictions in circulation which have resulted in some estuaries no longer being able to assimilate oxygen demand in the summer, thereby impacting the biota (May 1973).

**Califaction**. Activities leading to the discharge of heated water may also impact biota in an estuary. This arises from the fact that as water temperature rises, dissolved oxygen

(DO) levels decrease. Under extreme conditions (such as in proximity to the discharge of cooling water by power plants), the amount of DO may drop from a normal ambient level of 6-7 mg/l to 3 mg/l, or less. Levels of 3 mg/l or less create intolerable conditions for most forms of aquatic life. A severe decrease in DO also has a demonstrable effect on levels of nutrient fluxes in an estuary. Attenuation of phosphorus and nitrogen levels is presumably brought about by a dependency of microbial and physico-chemical processes on both temperature and DO. It has been shown that the presence of labile organic matter (e.g., chlorophyll a) exerts a regulatory effect on the maximum rate of nutrient release by sediments in an estuary (Cowan et al. 1996). While this has not yet been a major problem in northern Gulf of Mexico estuaries, it has created significant problems in other locations around the world and has been implicated as a cause in the destruction of seagrass beds in Pensacola and Biscayne Bays in Florida (Burton 1976, Zieman 1970).

# MEASUREMENT OF CONTAMINANTS AND CHEMICAL SPECIATION

#### Speciation/Bioavailability

The term "contaminant" (or "pollutant") tacitly implies that a particular organic or inorganic material is present in a bioavailable form that has potential of causing harm to the biota. Bioavailability, however, is a highly complex phenomenon that depends on the speciation of the contaminants, the kinds of organisms affected, the genetic adaptation of organisms to the site, climate, season, diseases, and synergistic and antagonistic effects of other heavy metals and organic compounds that are present (Sager 1989). Maturity of the organism is also important because adult species often are able to tolerate levels of contaminants that would be toxic to immature or larval forms. Further, a variety of resistance mechanisms have evolved to protect the biota from toxic effects. These include, but are not limited to, metal precipitation, complexation to organic ligands, volatilization, alkylation, hydrolysis, oxidation, and reduction (Wood 1989). Regardless of the operable defensive mechanisms, measurement of the total quantity of a metal present in bottom sediments offers little true information on its contamination potential. To obtain that, one must determine the actual speciation of the metal in the sediment. The importance of determining the actual speciation (partitioning) of a metal lies in the fact that, depending upon how the metal is partitioned, it may or may not be in a form that allows its subsequent release back into the water column or its remobilization and absorption into the tissues of indigenous biota (Luoma and Bryan 1978). This distinction is especially important for assessing ecological damage of contaminated sediments and the possibility of bioaccumulation and biomagnification of heavy metals by biota.

-30-

Several factors are important in controlling the manner by which ions become absorbed by bottom sediments in a depositional basin. Among the more important are sediment texture and mineralogy and the physico-chemical conditions existing at the sediment-water interface at the time of deposition. Gambrell et al. (1980) have discussed the importance of redox conditions and pH as controls in partitioning behavior. Sweeney (1984) has shown that particle size is correlative with metal levels in sediments, and Isphording and Shaw (1980) stressed the importance of organic content and clay mineralogy as further controlling factors. Hence, a number of variables influence not only how much of a metal becomes adsorbed by bottom sediments but also the manner by which the metal becomes incorporated. To identify the latter, the methodology of choice remains ion site partitioning analysis.

#### Ion Site Partitioning

Engler et al. (1977) described one of the first efficient metal "stripping" procedures that allowed the percentage of a metal in a sediment to be partitioned into: (1) a pore water fraction, (2) an exchangeable ion phase, (3) an easily reducible phase (ions associated with disseminated manganese oxy-hydroxides), (4) ions associated with sulfides, organic compounds, and organo-metallically chelated forms, (5) a moderately reducible phase (metals associated with iron oxy-hydroxides), and (6) a residual phase (metals occupying defect positions in the crystal lattice or occurring in octahedral or tetrahedral sites in the lattices of clays. This procedure has been since modified by a number of researchers (Tessier and Campbell 1987; Khalid et al. 1981). While no sequential extraction procedure exists by which one reagent can completely extract a metal from one phase without having some effect on other phases, sequential extraction does provide the best estimate presently available as to the true toxic potential of a sediment. An example which clearly demonstrates the merit of using this methodology in environmental analysis is provided in the following paragraphs.

Mobile Bay, Alabama. Ion site partitioning analyses were carried out on bottom sediment samples from Mobile Bay, Alabama, for zinc, copper, lead, and vanadium. The results of these analyses are shown in Table 5. Zinc is seen to be largely partitioned into four phases, the easily reducible phase (9.1%), the moderately reducible phase (13.8%), the organic-sulfide phase (61.6%), and the residual phase (15.3%). The average level of this metal in the bay is 120 mg/kg (ppm). Hence, 15.3% (18 ppm) of this metal would be totally unavailable to the biota because it is locked in the residual phase where it is tightly bound in the lattice of clay minerals. The 61.6% held in the organic-sulfide phase (74 ppm) is stable as long as the sediments are in a reducing (-Eh) environment. The easily and moderately reducible

phases are stable under opposite conditions; an oxidizing (+Eh) environment. Because most bottom feeding organisms (oysters, crabs, clams, etc.) live in oxidizing to weakly reducing conditions, it is the organic-sulfide phase that is unstable, and the portion of the zinc (74 ppm) held in that phase is potentially available.

Copper behaves in somewhat a similar manner, except that a greater quantity (31.7%) is locked in the residual phase and considerably less is present in the organic-sulfide phase (Table 5). Nearly half of the copper that is partitioned in the reducible phases (46.9%) is present in a form that is stable throughout most of Mobile Bay. A further 31.7% is similarly unavailable because it is locked in the residual phase. Hence, although the average abundance of this element in bay sediments is 32 ppm, over 78% of that (25 ppm) is essentially unavailable to the biota. Thus, of the total amount (32 ppm) only 7 ppm is potentially sorbable by filter-feeding organisms.

An even more striking example is seen for vanadium. This metal averages 163 ppm in Mobile Bay sediments, nearly twice that of any other bay in the northern Gulf. While this at first glance might seem alarming, the partitioning analyses indicated that 90.0% of this metal is tightly bound in structural sites and totally unavailable to the biota. An additional 7.8% is present in reducible forms that are stable under most oxidizing conditions. Of the 163 ppm average, 97.8%, or 159 ppm, is largely unavailable to the biota. Analyses run on oysters from Mobile Bay support this conclusion. Isphording (1991) reported levels of 1.1 ppm or less in 6 oyster samples collected from various locations around the bay.

The above example demonstrates the value of determining metal speciation in environmental investigations. Clearly, this is the type of information that should be used in assessing the toxic nature of sediment and not total abundance of an element.

#### SUMMARY

The estuarine systems that fringe the greater part of the Gulf of Mexico are a major asset to the Nation. The protected harbors that lie within these estuaries have attracted commercial enterprises, industries, international shipping, residents, fishermen, sportsmen, and naturalists for many years. The Gulf supports more than one-third of the nation's marine recreational fishing, and tourism-related dollars are estimated to be \$20 billion (U.S. EPA 1991). Approximately 45% of the U.S. shipping tonnage passes through Gulf ports, and the second largest marine transport industry is located in the Gulf of Mexico (U.S. EPA 1994a).

#### -31-

Coastal wetlands in the Gulf of Mexico encompass over 2 million hectares (five million acres), approximately half the national total. The quality and quantity of wetlands are important determinants of fisheries production (Turner and Boesch 1987). An estimated 95% of the commercial fish species landed and 85% of the sport fish species (by weight) spend at least a portion of their lives in coastal wetland and estuarine habitats (Thayer and Ustach 1981, Lindall and Thayer 1982). The Gulf has the largest and most valuable shrimp fishery in the U.S. and produced 41% of the U.S. total oyster production in 1991 (U.S. DOC 1992). Approximately 771 million kg (1.7 billion pounds) of fish and shellfish worth more than \$641 million ex-vessel were taken from Gulf waters in 1991, and the area produces more finfish, shrimp and shellfish annually than the South and Mid-Atlantic, Chesapeake Bay, and Great Lakes regions combined (U.S. DOC 1992).

Nearly 75% of the U.S. population now lives within a three hour drive of the coastal zone, and the area from Florida westward to the Texas-Mexico border continues to be the most desirable zone for new industrial development. These developments generate a number of environmental problems. Because of the great value of our coastal wetlands and estuaries, it is incumbent upon us to understand the sources of these problems and to plan to implement programs that will provide adequate protection to one of the Nation's most valuable resources.

#### **REFERENCES CITED**

- Basynat, P. L., K. Flynn, and B. Lockaby. 1996. <u>Relationships between landscaped characteristics and</u> <u>non-point source pollution inputs to coastal estuaries</u>. Final Report. USDC - National Oceanic and Atmospheric Administration, OCRM Award No. NA47OR097 Auburn University, Auburn, AL.
- Brett, C. E. 1975. <u>A study of the effects of maintenance</u> <u>dredging in Mobile Bay, Alabama</u>. Final Report. U.S. Army Corps of Engineers, Mobile District. Contract No. DACW-73C-0152. 1-46.
- Burton, J. D., L. B. Richardson, S. L. Margrey, and P. R. Able. 1976. Effects of low powerplant temperatures on estuarine invertebrates. <u>Journal Water Pollution Control</u> <u>Federation</u>. 48: 2259-2272.
- Clarke, D. and T. Miller-Way. 1992. <u>An environmental assessment of the effects of open-water disposal of maintenance dredging material in Mobile Bay, Alabama</u>. Misc. Paper D-92-1. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. 1-40.

- Cousma, B., M. Drago, M. Piccazzo, G. Scarpoini, and S. Gucci. 1979. Heavy metals in Liguria Sea sediments: distribution of Cr, Cu, Ni, and Mn in surficial sediments. <u>Marine Chemistry</u>. 8: 125-142.
- Cowan, J. L., J. R. Pennock, and W. R. Boynton. 1996. Seasonal in interannual patterns of sediment-water nutrient and oxygen fluxes in Mobile Bay, Alabama (USA): regulating factors and ecological significance. <u>Marine Ecology Progress Series</u>. 141: 229-245.
- Dardeau, M. R., R. F. Modlin, W. W. Schroeder, and J. P. Stout. 1992. Estuaries. Chap. in <u>Biodiversity of</u> <u>southeastern United States aquatic communities</u>, edited by C. T. Hackney, S. M. Adams, and W. A. Martin, 615-744. New York: John Wiley & Sons, Inc.
- Dudley, J. L. 1992. Secondary succession and nitrogen availability in coastal heathlands. Ph.D. Dissertation. Boston University.
- Emery, K. O. and E. Uchupi. 1972. Western North Atlantic Ocean: topography, rocks, structure, water, life, and sediment. <u>Memoirs American Association Petroleum Geologists</u>. 17: 1-532.
- Engler, R., J. M. Brannon, J. Rose, and G. Bigam. 1977. A practical selective extraction procedure of sediment characterization. Chap. in <u>Chemistry of Marine</u> <u>Sediments</u>, edited by T. F. Yen, 163-180. Ann Arbor Science Publications.
- Gambrell, R., R. Khalid, and W. Patrick. 1980. Chemical availability of mercury, lead, and zinc in Mobile Bay sediment suspensions as affected by pH and oxidationreduction conditions. <u>Environmental Science and Technology</u>. 14: 431-436.
- Isphording, W. C. 1991. Organic and heavy metal chemistry of Mobile Bay sediments. Alabama Geological Survey. U.S.G.S. Proj. no. 14-08-0001-A0775. Tuscaloosa, Alabama. 1-42.
- Isphording, W. C. 1994. Erosion and deposition in northern Gulf of Mexico. <u>Transactions Gulf Coast Association</u> <u>Geological Societies</u>. 44: 305-314.
- Isphording, W. C. and G. C. Flowers. 1987. Mobile Bay, the right estuary in the wrong place! In <u>Symposium on the</u> <u>natural resources of the Mobile Bay estuary</u>, edited by T.A. Lowery, 165-173. Mississippi-Alabama Sea Grant Consortium, Ocean Springs, MS.

-32-

- Isphording, W. C., F. D. Imsand, and G. C. Flowers. 1989. Physical characteristics and aging of Gulf Coast estuaries. <u>Transactions Gulf Coast Association</u> <u>Geological Societies</u>. 39: 387-402.
- Isphording, W. C., R. B. Jackson, and F. D. Imsand. 1996. Fluvial sediment characteristics of the Mobile River Delta. <u>Transactions Gulf Coast Association Geological</u> <u>Societies</u>. 46: 185-191.
- Isphording, W. C. and J. K. Shaw. 1980. Environmental monitoring program of MOEPSI well number 1-76 (Mobile State Lease 347, number 1) in Mobile Bay, Alabama. Volume 1, Environmental effects, sediments and trace metal chemistry. Final Report to Mobil Oil Exploration and Producing Southeast, Inc., New Orleans, Louisiana.
- Isphording, W. C., J. A. Stringfellow, and G. C. Flowers. 1985. Sedimentary and geochemical systems in transitional marine sediments in the northeastern Gulf of Mexico. <u>Transactions Gulf Coast Association Geological</u> <u>Societies</u>. 35: 397-408.
- Khalid, R., R. Gambrell, and W. Patrick. 1981. Chemical availability of cadmium in Mississippi River sediments. <u>Journal Environmental Quality</u>. 10:523-528.
- Lindall, W. N. and G. W. Thayer. 1982. Quantification of National Marine Fisheries Service habitat conservation efforts in the southeast region of the United States. <u>Marine Fisheries Review</u>. 44:18-22.
- Livingston, R. J. 1984. <u>The ecology of the Apalachicola Bay</u> <u>system: an estuarine profile</u>. Technical Report. U.S. Fish and Wildlife Serv., Off Biol. Serv. FWS/OBS/82-05.
- Luoma, S. N. and G. W. Gryan. 1978. Factors controlling the availability of sediment-bound lead to the estuarine bivalve Scrobicularia plana. Journal Marine Biology Association United Kingdom. 58:793-802.
- May, E. B. 1973. Extensive oxygen depletion in Mobile Bay, Alabama. <u>Limnology and Oceanography</u>. 18:353-366.
- Nichols, M. M. 1989. Sediment accumulation rates and relative sea-level rise in lagoons. <u>Marine Geology</u>. 88:201-219.
- Pennock, J. R. and J. H. Sharp and W. W. Schroeder. 1995. What controls the expression of estuarine eutrophication? Case studies of nutrient enrichment in the Delaware Bay and Mobile Bay estuaries, USA. In <u>Changes in the fluxes in estuaries</u>, edited by K. R. Dyer

- and R. J. Ortho, 139-146. International Symposium Series, ECSA22/ERF Symposium: Denmark.
- Perry, H. M. and J. Cirino. 1998. Biology of Commercial Oysters. National Fisheries Institute (In press).
- Pritchard, D. W. 1967. What is an estuary: a physical viewpoint. Chap. in <u>Estuaries</u>, edited by G. H. Lauff, 3-5. American Association Advancement Science Publication 83.
- Rusnak, G. A. 1967. Rates of sediment accumulation in modern estuaries. Chap. in <u>Estuaries</u>, edited by G. H. Lauff, 180-184. American Association Advancement Science Publication 83.
- Sager, M. 1989. The speciation of heavy metals in river sediments found by sequential leaching methods. In <u>Heavy metals in the environment</u>, edited by J. P. Vernet. 213-216.
- Schubel, J. R. and D. J. Hirschberg. 1978. Estuarine graveyards, climatic change, and the importance of the estuarine environment. In <u>Estuarine interactions</u>, edited by M. Wiley. 285-303. New York: Academic Press.
- Sweeney, M. D. 1984. Heavy metals in the sediments of an arctic lagoon, northern Alaska. M.S. Thesis. University of Alaska.
- Taylor, D. 1979. The effects of discharge from three industrialized estuaries on the distribution of heavy metals in the coastal sediments of the North Sea. <u>Estuarine and Coastal Marine Sciences</u>. 8:387-393.
- Tessier, A. and P. G. C. Campbell. 1987. Partitioning of trace metals in sediments: relationships with bioavailability. <u>Hydrobiologia</u>. 149:43-52.
- Thayer, G. W. and J. F. Ustach. 1981. Gulf of Mexico wetlands: value, state of knowledge and research needs. In Proceedings of a Symposium on Environmental <u>Research Needs in the Gulf of Mexico</u>. NOAA, Washington, D.C. 44-50.
- Turner, R. E. and D. F. Boesch. 1987. Aquatic animal production and wetland relationships: insights gleaned following wetland loss or gain. In <u>Ecology and</u> <u>Management of Wetlands</u>, edited by D. Hooks, 25-39. Croons Helms, Ltd. Beckenham, Kent, United Kingdom.
- Turner, R. E. and N. N. Rabalais. 1991. Changes in Mississippi River water quality this century: implications for coastal food webs. <u>Bioscience</u>. 41(3): 140-147.

-33-

- U. S. Department of Commerce. 1992. <u>Current Fishery</u> <u>Statistics No. 9100: Fisheries of the United States. 1991</u>. Fishery Statistics Division, National Marine Fisheries Service, NOAA, Silver Spring, Maryland.
- U.S. Environmental Protection Agency. 1986. Near Coastal Waters Strategic Options Paper. Washington, D.C.
- U.S. Environmental Protection Agency. 1991. <u>Gulf Facts</u>. Gulf of Mexico Program. John C. Stennis Space Center, Mississippi.
- U.S. Environmental Protection Agency. 1993. <u>Public Health</u> <u>Action Agenda for the Gulf of Mexico</u>. Gulf of Mexico Program. John C. Stennis Space Center, Mississippi. EPA 800-K-93-001:1-98.
- U.S. Environmental Protection Agency. 1994a. <u>Habitat</u> <u>Degradation Action Agenda for the Gulf of Mexico</u>. Gulf of Mexico Program. John C. Stennis Space Center, Mississippi. EPA 800-B-94-002:1-140.
- U.S. Environmental Protection Agency. 1994b. <u>Toxic</u> Substances and Pesticides Action Agenda for the Gulf

of Mexico. Gulf of Mexico Program. John C. Stennis Space Center, Mississippi. EPA 800-B-94-005:1-160.

- U.S. Environmental Protection Agency. 1994c. <u>Nutrient</u> <u>Enrichment Action Agenda for the Gulf of Mexico</u>. Gulf of Mexico Program. John C. Stennis Space Center, Mississippi. EPA 800-B-94-004:1-161.
- Vernberg, F. J. and W. B. Vernberg (eds.). 1981. <u>Functional</u> <u>adaptations of marine organisms</u>. New York: Academic Press.
- Wilson, A. and K. Iseri. 1969. River discharge to the sea from the shores of the Coterminous United States. <u>Hydrologic Investigation Atlas HA-282 (Revised)</u>. U.S. Geological Survey. Washington, DC.
- Wood, J. M. 1974. Biological cycles for toxic elements in the environment. <u>Science</u>. 183:1049-1052.
- Zieman, J. C. 1970. The effects of thermal effluent stress on the seagrass and macroalgae in the vicinity of Turkey Point, Biscayne Bay, Florida. M.S. Thesis. University of Miami.

-34-



Fig. 1 Principal bays and estuaries in the northern Gulf of Mexico: 1, Sabine Lake; 2, Calcasieu Lake; 3, Vermillion and Atchafalaya bays; 4, Timbalier Bay; 5, Barataria Bay; 6, Lake Pontchartrain-Lake Marapaus; 7, Mississippi Sound; 8, Mobile Bay; 9, Perdido Bay; 10 Pensacola Bay; 11, Choctawhatchee Bay; 12, St. Andrew Bay; 13, St. Joseph Bay; 14, Apalachicola Bay; 15, Tampa Bay; 16, Charlotte Harbor.

-35-

# Table 1. Physical and hydrologic data for major Gulf of Mexico estuaries.

Major Tributaries	Drainage Area (square miles)	Average Annual Inflow (cfs)	Estuary Volume (billion cubic feet)	load to estuary (million tons/yr)	(tons/yr/sq.mi. of drainage area)
Nueces River	17,621	1,200	41.95	0.89	50.5
San Antonio River	10,857	4,100	24.57	1.25	115.1
Lavaca River	49,670	5,300	73.42	3.58	72.1
Trinity River	24,300	15,200	90.84	2.04	84.0
Sabine River	20,900	17,200	21.42	0.90	43.1
Vermillion River Atchafalaya River	98,500	223,800	136.7	37.50	380.7
Lake Salvador	2,884	5,600	97.20	0.37	128.3
Terrebonne River	2,361	4,500	54.16	not available	not available
Amite River	3,207	4,800	18.15	not available	not available
Lake Maurepas/ Tangipahoa River	5,697	7,600	203.8	0.76	133.4
Lake Pontchartrain Pearl River	14,457	21,400	2. 4. A. A.	2.37	163.9
Pearl River Pascagoula River	26,900	43,600	568.1	4.58	170.3
Mobile River	44,600	79,300	113.0	6.35	142.4
Perdido River	1,205	2,200	0.9677	0.47	390.0
Escambla/Yellow Rivers	6,990	11,600	50.95	1.08	154.5
Choctawhatchee River	5,369	8,500	50.94	1.03	191.8
Econfina River	1,130	4,500	31.28	0.34	300.9
Apalachicola River	20,500	29,100	53.65	0.70	34.1
Hillsborough/Manatee Rivers	2,598	2,400	12.30	0.21	80.8
Peace/Myakka Rivers	5,030	4,800	72.87	0.33	
	Malor TributariesNueces RiverSan Antonio RiverLavaca RiverTrinity RiverSabine RiverVermillion RiverAtchafalaya RiverLake SalvadorTerrebonne RiverAmite RiverLake Maurepas/ Tangipahoa RiverLake Pontchartrain Pearl RiverPearl RiverPeard RiverMobile RiverPerdido RiverEscambla/Yellow RiversChoctawhatchee RiverApalachicola RiverHillsborough/Manatee RiversPeace/Myakka Rivers	Major TributariesDrainage Area (square miles)Nueces River17,621San Antonio River10,857Lavaca River49,670Trinity River24,300Sabine River20,900Vermillion River98,500Lake Salvador2,884Terrebonne River2,361Arnite River3,207Lake Maurepas/ Tangipahoa River5,697Lake Pontchartrain Pearl River14,457Pearl River26,900Mobile River1,205Escambla/Yellow Rivers6,990Choctawhatchee River5,369Econfina River1,130Apalachicola River2,598Peace/Myakka Rivers5,030	Drainage Area (square miles)Average Annual Inflow (cfs)Nueces River17,6211,200San Antonio River10,8574,100Lavaca River49,6705,300Trinity River24,30015,200Sabine River20,90017,200Vermillion River98,500223,800Lake Salvador2,8845,600Terrebonne River2,3614,500Amite River3,2074,800Lake Maurepas/ Tangipahoa River5,6977,600Lake Pontchartrain Pearl River14,45721,400Pearl River2,36943,600Mobile River1,2052,200Escambla/Yellow Rivers6,99011,600Choctawhatchee River5,3898,500Econfina River1,1304,500Hillsborough/Manatee Rivers2,5982,400Peace/Myakka Rivers5,0304,800	Malor Tributaries Drainage Area (square miles) Average Annual (hillion cubic feet) Extuary Volume (hillion cubic feet)   Nueces River 17,621 1,200 41.95   San Antonio River 10,857 4,100 24.57   Lavaca River 49,670 5,300 73.42   Trinity River 24,300 15,200 90.84   Sabine River 20,900 17,200 21.42   Vermillion River 98,500 223,800 136.7   Lake Salvador 2,884 5,600 97.20   Terrebonne River 3,207 4,800 18.15   Lake Maurepas/ Tangipahoa River 5,697 7,600 203.8   Lake Maurepas/ Tangipahoa River 26,900 43,600 568.1   Mobile River 1,205 2,200 0.9677   Eace Anther River 5,369 11,600 50.95   Peard River 5,369 8,500 50.94   Peard River 1,30 4,500 31.28   Apalachicola River 1,130 4,500 31.28	Malor Tributaries Drainage Area (source million) Average Annual (million (solver) Extuary Volume (Million tonakyry) Index (cs) (Million (solver)   Nueces River 17,621 1,200 41,95 0,89   San Antonio River 10,857 4,100 24,57 1,25   Lavaca River 49,670 5,300 73,42 3,58   Trinity River 24,300 15,200 90,84 2,04   Sabine River 20,900 17,200 21,42 0,90   Vermillion River 28,84 5,600 97,20 0,37   Terrebonne River 2,361 4,500 54,16 not available   Amite River 3,207 4,800 18,15 not available   Lake Maurepas/ Tangjahoa River 26,900 43,600 568,1 4,58   Mobile River 1,205 2,200 0,9677 0,47   Escambia/Yellow Rivers 6,990 11,600 50.95 1,08   Pearl River 1,205 2,200 0,9677 0,47   Escambia/Yellow Rivers </td

-36-

## Table 2. Depositional rates for Atlantic and Gulf Coast estuaries.

Estuary	Deposition Rates (mm/yr)		
Narragansett Bay, MA	0.7		
Delaware Gay, NJ-DL	1.8		
Chesapeake Bay, MD-VA	3.7		
Apalachicola Bay, FL	1.6		
Choctawhatchee Bay, FL	2.2		
Mobile Bay, AL	1.0		
Atchafalaya Bay, LA	2.3		
Galveston Bay, TX	3.7		
San Antonio Bay, TX	2.2		
Copano/ Aransas Bays, TX	1.0		
Laguna Madre Bay, TX	1.2		

Table 3. Average heavy metal levels (mg/kg) in bottom sediments from Mobile Bay, Alabama, and Apalachicola Bay, Florida, before and after passage of major tropical cyclones.

	Mobil	e Bay	Apalachicola Bay		
Element	Before	After	Before	After	
Chromium	63	53	42	34	
Cobalt	29	17	64	51	
Copper	32	31	66	38	
Iron	35,648	30,650	31,041	29,234	
Vanadium	163	88	104	79	
Zinc	360	120	98	82	
Barium	**	102	155	88	

### -37-

Metal	Mississippi	Mobile	Perdido	Pensacola	Escambia	Blackwater	Apalachicola
Cadmium	1.0	1.1	1.0	1.1	0.9	1.0	1.2
Lead	15	51	nr	40	19	13	61
Iron	23,107	35,648	32,740	24,074	29,298	11,520	26,776
Nickel	24	57	36	16	9	3	28
Cobalt	13	15	27	10	12	5	18
Chrom.	57	63	15	56	40	13	34
Copper	20	32	31	19	9	3	37
Zinc	74	120	72	140	43	20	57

Table 4. Average bottom sediment heavy metal levels (mg/kg) for bays, estuaries, and coastal lagoons in the northern Gulf of Mexico.

Table 5. Ion Site Partitioning (ISP) analyses for Mobile Bay bottom sediments (percentages).

\_

Phases	Zinc	Copper	Lead	Vanadium	
Pore Water/Exchangeable	0.2	0.3	5.1	trace	
Easily Reducible	9.1	11.3	7.1	0.7	
Moderately Reducible	13.8	35.6	8.9	7.1	
Organic-Sulfide	61.6	21.1	37.4	2.2	
Structural	15.3	31.7	41.5	90.0	

