

# Hypoxia in the Northern Gulf of Mexico: Description, Causes and Change<sup>1</sup>

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## Abstract

Nutrient over-enrichment in many areas around the world is having pervasive ecological effects on coastal ecosystems. These effects include reduced dissolved oxygen in aquatic systems and subsequent impacts on living resources. The largest zone of oxygen-depleted coastal waters in the United States, and the entire western Atlantic Ocean, is found in the northern Gulf of Mexico on the Louisiana/Texas continental shelf influenced by the freshwater discharge and nutrient load of the Mississippi River system. The mid-summer bottom areal extent of hypoxic waters ( $\leq 2 \text{ mg l}^{-1} \text{ O}_2$ ) in 1985-1992 averaged 8,000 to 9,000 km<sup>2</sup> but increased to up to 16,000 to 20,000 km<sup>2</sup> in 1993-2000. Hypoxic waters are most prevalent from late spring through late summer, and hypoxia is more widespread and persistent in some years than in others. Hypoxic waters are distributed from shallow depths near shore (4 to 5 m) to as deep as 60 m water depth but more typically between 5 and 30 m. Hypoxia occurs mostly in the lower water column but encompasses as much as the lower half to two-thirds of the water column. The Mississippi River system is the dominant source of fresh water and nutrients to the northern Gulf of Mexico. Mississippi River nutrient concentrations and loading to the adjacent continental shelf have changed in the last half of the 20<sup>th</sup> century. The average annual nitrate concentration doubled, and the mean silicate concentration was reduced by 50%. There is no doubt that the average concentration and flux of nitrogen (per unit volume discharge) increased from the 1950s to 1980s, especially in the spring. There is considerable evidence that nutrient enhanced primary production in the northern Gulf of Mexico is causally related to the oxygen depletion in the lower water column. Evidence from long-term data sets and the sedimentary record demonstrate that historic increases in riverine dissolved inorganic nitrogen concentration and loads over the last 50 years are highly correlated with indicators of increased productivity in the overlying water column, i.e., eutrophication of the continental shelf waters, and subsequent worsening of oxygen stress in the bottom waters. Evidence associates increased coastal ocean productivity and worsening oxygen depletion with changes in landscape use and nutrient management that resulted in nutrient enrichment of receiving waters. Thus, nutrient flux to coastal systems has increased over time due to anthropogenic activities and has led to broad-scale degradation of the marine environment.

## Introduction

There is increasing concern in many areas around the world that an oversupply of nutrients from multiple sources is having pervasive ecological effects on shallow coastal and estuarine areas. Marine plants provide essential habitat, and there are well-established positive relationships between dissolved inorganic nitrogen flux and phytoplankton primary production (e.g., Nixon et al. [1996], Lohrenz et al. [1997]). In addition, data from 36 marine systems show a relationship between fisheries yield and primary production [Nixon, 1988]. There are thresholds, however, where the load of

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<sup>1</sup> Pages 1-36 in Rabalais, N. N. and R. E. Turner, eds., *Coastal Hypoxia: Consequences for Living Resources and Ecosystems*, Coastal and Estuarine Studies No. 58, American Geophysical Union, Washington, D.C.

nutrients to a marine system causes water quality degradation and detrimental changes to fisheries [Caddy, 1993].

While a variety of changes may result in the increased accumulation of organic matter in a marine system (= eutrophication, as defined by Nixon [1995]), the most common single factor is an increase in the amount of nitrogen and phosphorus marine waters receive. With an increase in the world population, a focusing of that populous in coastal regions and agricultural expansion in major river basins, eutrophication is becoming a major environmental problem in coastal waters throughout the world. Humans have altered the global cycles of nitrogen and phosphorus over large regions and increased the mobility and availability of these nutrients to marine ecosystems [Peierls et al., 1991; Howarth et al., 1995, 1996; Vitousek et al., 1997; Howarth, 1998; Caraco and Cole, 1999]. These human-controlled inputs are the result of human populations and their activities, particularly the application of nitrogen and phosphorus fertilizers, nitrogen fixation by leguminous crops, and atmospheric deposition of oxidized nitrogen from fossil-fuel combustion. Changes in the relative proportions of these nutrients may exacerbate eutrophication, favor noxious algal blooms and aggravate conditions of oxygen depletion [Officer and Ryther, 1980; Smayda, 1990; Conley et al., 1993; Justic' et al. 1995a,b; Turner et al., 1998].

The impairment of waters from nutrient over-enrichment goes well beyond scummy-looking water to threatening the suitability of water for human consumption and impairing the sustained production of useful forms of aquatic life. Excess nutrients lead to degraded water quality through increased phytoplankton or filamentous algal growth. Increasing nutrient loads are the cause of some noxious or harmful algal blooms (HABs), including some toxic forms. Secondary effects include increased turbidity or oxygen-depleted waters (= hypoxia) and eventually loss of habitat with consequences to marine biodiversity and changes in ecosystem structure and function. Over the last two decades it has become increasingly apparent that the effects of eutrophication, including oxygen depletion, are not minor and localized, but have large-scale implications and are spreading rapidly [Rosenberg, 1985; Diaz and Rosenberg, 1995; Anderson, 1995; Nixon, 1995; Paerl, 1995, 1997].

Water with less than 2 mg l<sup>-1</sup> dissolved oxygen is said to be hypoxic. Hypoxia occurs naturally in many parts of the world's marine environments, such as fjords, deep basins, open ocean oxygen minimum zones, and oxygen minimum zones associated with western boundary upwelling systems [Kamykowski and Zentara, 1990]. Hypoxic and anoxic (no oxygen) waters have existed throughout geologic time, but their occurrence in shallow coastal and estuarine areas appears to be increasing [Diaz and Rosenberg, 1995]. The largest zone of oxygen-depleted coastal waters in the United States, and the entire western Atlantic Ocean, is in the northern Gulf of Mexico on the Louisiana/Texas continental shelf at the terminus of the Mississippi River system (Plate 1). The size of the Gulf of Mexico hypoxic zone reaches 20,000 km<sup>2</sup> in mid-summer [Rabalais, 1999], and ranks third in area behind similar coastal hypoxic zones on the northwestern shelf of the Black Sea and in the Baltic basins. The hypoxic zone in the northern Gulf of Mexico (average for 1993-1999) is about the size of the state of New Jersey or the states of Rhode Island and Connecticut combined. Its extent on the bottom is twice the total surface area of the whole Chesapeake Bay, and its volume is several orders of magnitude greater than the hypoxic water mass of Chesapeake Bay [Rabalais, 1998].

The watershed that drains through the Mississippi and Atchafalaya Rivers to the Gulf of Mexico is also immense (Plate 1). The Mississippi River system ranks among the world's top ten rivers in length, freshwater discharge and sediment delivery and drains 41% of the lower forty-eight United States [Milliman and Meade, 1983]. Thus, the dimensions of the problem and the drainage system that affect it are of much greater magnitude than most nutrient-driven eutrophication problems elsewhere.

The linked Mississippi River system and the northern Gulf of Mexico is an example of the worldwide trend of increasing riverborne nutrients and worsening coastal water quality. Model simulations, research studies, empirical relationships and retrospective analyses of the sedimentary record have produced considerable evidence that nutrient loading from the Mississippi River system is the dominant factor in controlling the extent and degree of hypoxia and its worsening in the last century [Rabalais et al., 1996, 1999].

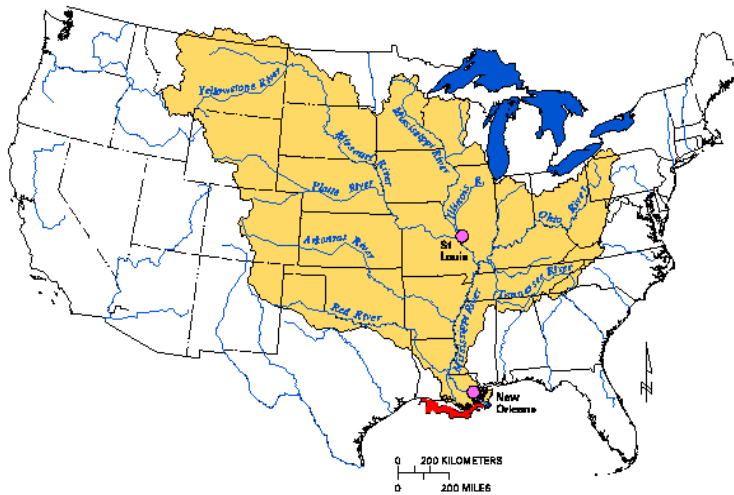


Plate 1. Mississippi River drainage basin and major tributaries, and general location of the 1999 midsummer hypoxic zone [Rabalais, 1999]. (From Goolsby [2000], used with permission of the author).

Despite recent advances in identifying links between Mississippi River system discharge and nutrient loads and coastal hypoxia in the Gulf of Mexico, defining the ecological and economic consequences of hypoxia on the living resources of the northern Gulf of Mexico has proven difficult. Long-term fisheries data are lacking, as are data specific to present-day distribution and abundance of living resources. Ecosystem level changes have occurred, however, consistent with changes in Mississippi River system discharge and nutrient loads. In this chapter, we describe the phenomenon of hypoxia in the Gulf of Mexico, its physical and biological causes, the close coupling of hypoxia with Mississippi River effluents, and the historical changes in river constituents and hypoxia that parallel each other. Against this background of watershed landscape changes, human activities, and worsening hypoxic conditions in the Gulf of Mexico, the subsequent chapters detail the state of knowledge of hypoxia on living resources of the northern Gulf within the broader context of patterns already demonstrated elsewhere in the world's coastal waters.

## Definition

Oxygen is necessary to sustain the life of most higher organisms, including the fish and invertebrates living in aquatic habitats. The normal condition is for surface water dissolved oxygen to be mixed or diffused into the lower water column where oxygen has been consumed by organisms, particularly by the micro-organisms. When the supply of oxygen to the bottom is cut off due to stratification or the consumption rate of oxygen during the decomposition of organic matter exceeds supply, oxygen concentrations become depleted.

The point at which various animals are affected by low oxygen concentration varies, but generally effects start to appear when oxygen drops below 2 or 3 mg l<sup>-1</sup> (ppm) [Tyson and Pearson, 1991; Diaz and Rosenberg, 1995]. For seawater, this concentration is only about 20 to 30% of full saturation and is insufficient to support most larger aerobic organisms. The operational definition for hypoxia in the northern Gulf of Mexico is < 2 mg l<sup>-1</sup> (2.8 ml l<sup>-1</sup>), because trawlers seldom capture any shrimp or demersal fish in their nets below that value [Pavela et al., 1983; Leming and Stuntz, 1984; Renaud, 1986]. The oxygen concentration of surface waters is typically > 8 mg l<sup>-1</sup> if they are 100% saturated with oxygen at summertime temperature and salinity conditions.

For consistency, most dissolved oxygen concentrations in this book are expressed in units of  $\text{mg l}^{-1}$ , but some are also converted to  $\text{ml l}^{-1}$ . An oxygen concentration expressed as % saturation is the % of air saturation at the ambient temperature and salinity. Physiologically relevant units are often given in oxygen tension with the unit of torr (mm mercury).

## Causes

Two principal factors lead to the development and maintenance of hypoxia. First, the water column must be stratified so that the bottom layer is isolated from the surface layer and the normal resupply of oxygen. The physical structure is dictated by water masses that differ in temperature or salinity or both. Fresher waters derived from rivers and seasonally-warmed surface waters are less dense and reside above the saltier, cooler and more dense water masses near the bottom. Second, there is decomposition of organic matter that reduces the oxygen levels in the bottom waters. The source of this organic matter is mostly the result of phytoplankton growth stimulated by nutrients delivered to the coastal ocean with the riverine freshwater supply. The concentrations and total loads of nitrogen, phosphorus and silica to the coastal ocean influence the productivity of the phytoplankton community as well as the types of phytoplankton that are most likely to grow. The carbon that is produced by phytoplankton is the base of the marine food web that supports further production by multi-celled organisms including zooplankton and fish. Not all of the carbon produced in the surface waters becomes incorporated into the food web. Some of the algal cells die and sink to the bottom; others are grazed by zooplankton and are incorporated into fecal pellets that also sink to the bottom. Many algal cells and fecal pellets sink to the bottom as aggregates, or marine snow. Thus, a high percentage of the organic matter produced in coastal waters reaches the bottom and becomes the source for aerobic decomposition and causes hypoxia.

The relative importance of both physical structure and biological productivity in the development of hypoxia varies among environments and over an annual cycle. In the northern Gulf of Mexico the two factors are complexly inter-related and directly linked with the dynamics of the Mississippi and Atchafalaya river discharges. The Mississippi and Atchafalaya rivers are the primary riverine sources of fresh water to the Louisiana continental shelf [Dinnel and Wiseman, 1986] and to the Gulf of Mexico (80% of freshwater inflow from U.S. rivers to the Gulf [Dunn, 1996]). The discharge of the Mississippi River system is controlled so that 30% flows seaward through the Atchafalaya River delta and 70% flows through the Mississippi River birdfoot delta. The former enters through two outlets into Atchafalaya Bay, a broad shallow embayment; the latter enters the Gulf through multiple outlets, some in deep water and some in shallow water. Approximately 53% of the Mississippi River Delta discharge flows westward onto the Louisiana shelf [U.S. Army Corps of Engineers, 1974; Dinnel and Wiseman, 1986], and the general flow of the Atchafalaya River effluent is to the west.

The variability in freshwater discharge on seasonal, annual, decadal and longer scales underlies many important physical and biological processes affecting coastal productivity and food webs. There is significant interannual variability in the annual discharge with the peak in March-May and low discharge in late summer-fall (Figs. 1 and 2). The 1900-1992 average discharge rate (decadal time scale) for the lower Mississippi River is remarkably stable at about  $14,000 \text{ m}^3 \text{ s}^{-1}$ . There was a decrease in flow during the 1950s and 1960s, and the 1990s have been a period of higher discharge. The discharge of the Mississippi River increased from 1935 to 1995 at  $0.3\% \text{ y}^{-1}$ , or by 20%. The stage height, however, did not increase over the same period. There is some question as to the existence of a trend in discharge from the system, with the reported differences likely attributable to the period of record examined.

The discharge of the Atchafalaya increased during the course of the most complete record (1930-1997) [Bratkovich et al., 1994], as the U.S. Army Corps of Engineers allowed more Mississippi River water to enter the Atchafalaya basin at a diversion above St. Francisville, Louisiana. Less obvious is an increasing trend in the Mississippi River discharge as measured at Tarbert Landing. This trend is also statistically significant and

increasing. It appears to be due to a tendency for increasing discharge in September through December. This period, however, is least important in the timing of important biological processes that lead to the development of hypoxia or the physical processes important in its maintenance. If a longer period of annual discharge were considered (e.g., from Turner and Rabalais [1991] for the early 1800s to present), the trends since the 1950s are obvious but are concealed within high interannual variability and no long-term change over a century and a half (Fig. 1).

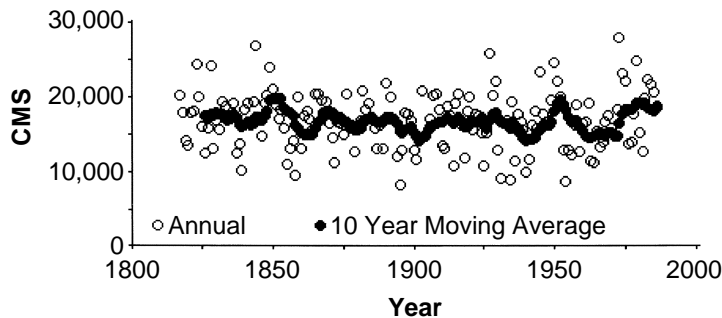


Figure 1. The annual discharge of the Mississippi River at Vicksburg, Mississippi ( $\text{m}^3 \text{s}^{-1}$ ) with a 10-y moving average superimposed (data from U.S. Army Corps of Engineers). (From Rabalais et al. [1999].)

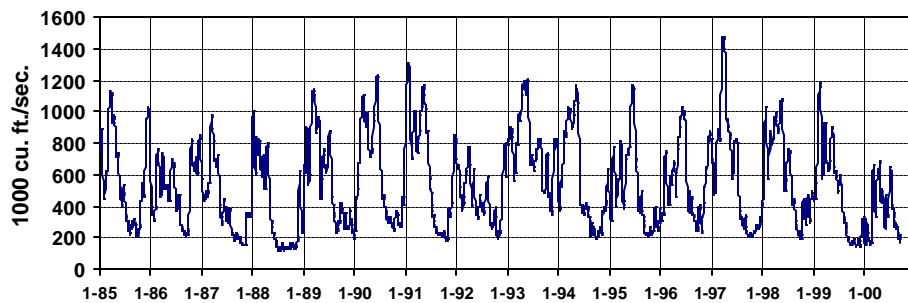


Figure 2. Daily discharge of the Mississippi River at Tarbert Landing. (Data from the U.S. Army Corps of Engineers.) (Modified from Rabalais et al. [1999].)

Freshwater discharge and seasonal atmospheric warming control the strength of stratification necessary for the development and maintenance of hypoxia. The depth of the main pycnocline (depth of greatest change in density) does not always track the depth of the oxycline (Fig. 3). The existence of a strong near-surface pycnocline, usually controlled by salinity differences, is a necessary condition for the occurrence of hypoxia, while a weaker, seasonal pycnocline, influenced by temperature differences, guides the morphology of the hypoxic domain [Wiseman et al., 1997]. Stratification goes through a well-defined seasonal cycle that generally exhibits maximum stratification during summer and weakest stratification during winter months (Fig. 4). This is due to the strength and phasing of river discharge, wind mixing, regional circulation and air-sea heat exchange processes.

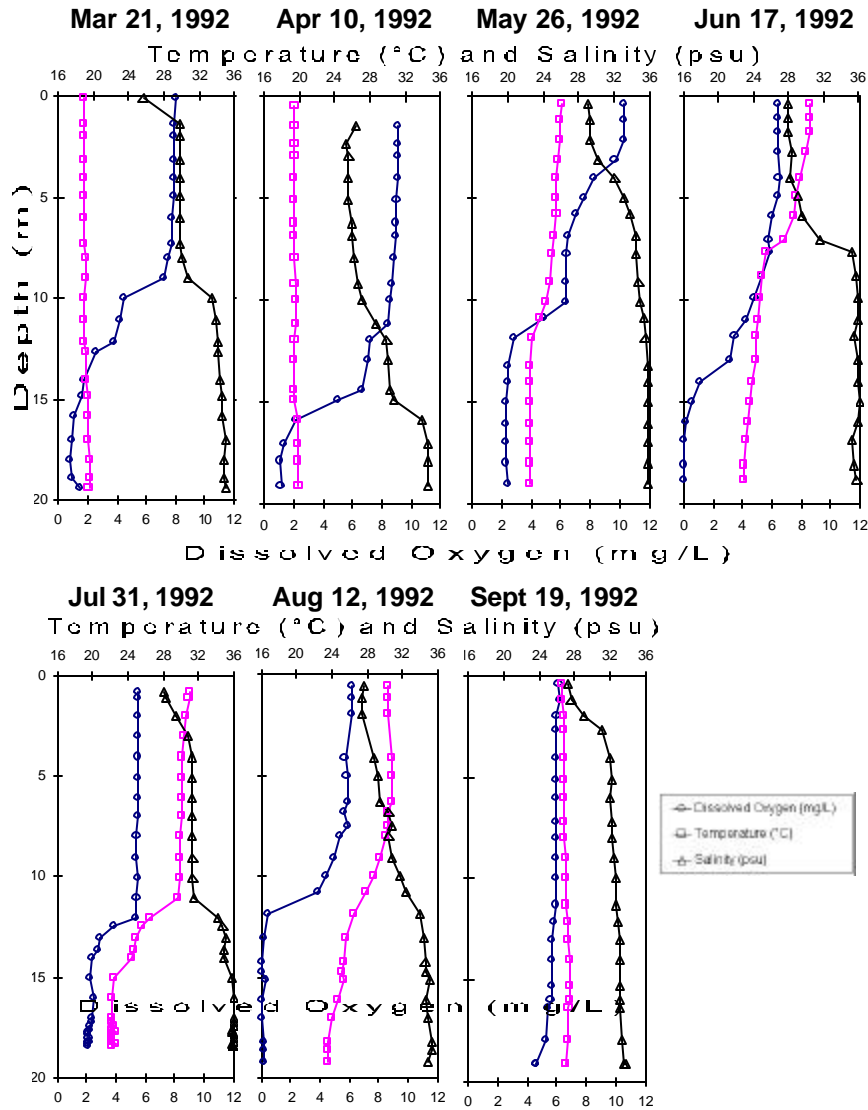


Figure 3. Water column profiles for temperature, salinity and dissolved oxygen for dates of monthly sampling at station C6B off Terrebonne Bay on the southeastern Louisiana shelf in 1992 [derived from Rabalais, Turner and Wiseman, unpublished data]. Station location is identified in Figure 6.

## Dimensions and Variability of Hypoxia

### *Historical Occurrence and Geographic Extent*

Accounts of low oxygen from the Gulf of Mexico for the mid-1930s [Conseil Permanent International pour l'Exploration de la Mer, 1936] were not about continental shelf hypoxia, but described the oxygen minimum layer, an oceanic feature at 400-700 m depth. Coastal hypoxia was first reported in the northern Gulf of Mexico in the early 1970s off Barataria and Terrebonne/Timbalier Bays as part of environmental assessments of oil production [Ward et al., 1979] and transportation studies [Hanifen et al., 1997].

Following the initial discovery of hypoxia in 1972-1974, Ragan et al. [1978] and Turner and Allen [1982a] surveyed the shelf in 1975 and 1976 and found low oxygen in the warmer months west of the Mississippi and Atchafalaya River discharges. Environmental assessments and studies of oil and gas production revealed low oxygen conditions in most inner shelf areas of Louisiana and Texas studied in mid-summer for the period 1978-1984 (summarized in Rabalais [1992], Rabalais et al. [1999]).

Hypoxia on the upper Texas coast is usually an extension of the larger hypoxic zone off Louisiana, although isolated areas may be found farther to the south (e.g., off Galveston and Freeport, Texas) [Harper et al., 1991; Pokryfki and Randall, 1987]. Isolated areas may be an artifact of the sampling, and very few systematic surveys have been conducted in this area with the exception of the summer SEAMAP cruises [Gulf States Fisheries Commission, 1982, et seq.]. Mid-summer SEAMAP cruises documented hypoxia on the Texas coast in small, isolated areas in 1983, none in 1984-1985, and again in localized areas in most years between 1991-1997 [J. K. Craig, unpublished data]. Most instances of hypoxia along the Texas coast are infrequent, short-lived, and limited in extent [Rabalais, 1992].

Hypoxia has been documented off Mississippi Sound during high stages of the Mississippi River and off Mobile Bay in bathymetric low areas [Rabalais, 1992]. There are usually more reports in flood years or when more Mississippi River water moves to the east of the birdfoot delta. Hypoxia east of the Mississippi River is infrequent, short-lived, and limited in extent [Rabalais, 1992]. From limited data where both sides of the delta were surveyed for hydrographic conditions including dissolved oxygen [Turner and Allen, 1982a], there was no evidence that the area of low oxygen formed a continuous band around the delta.

### *Mid-Summer Extent and Variability*

The distribution of hypoxia on the Louisiana shelf has been mapped in mid-summer (usually late July to early August) over a standard 60- to 80-station grid since 1985 (representative maps in Fig. 4). Hypoxic waters are distributed from shallow depths near shore (4 to 5 m) to as deep as 60 m water depth [Rabalais et al., 1991, 1998, 1999], but more typically between 5 and 30 m.

For the period from 1985 to 1992, the zone of hypoxia was usually in a configuration of disjunct areas to the west of the deltas of the Mississippi and Atchafalaya Rivers, and the bottom area averaged 7,000 to 9,000 km<sup>2</sup> (1986 and 1990 are illustrated in Fig. 4, areas for all years are in Fig. 5). Hypoxia in mid-summer 1988 was confined to a single inshore station off Terrebonne Bay on Transect C. A reduced grid was mapped in 1989, and was, therefore, not comparable to data from other years. Bottom water hypoxia was continuous across the Louisiana shelf in mid-summer of 1993-1997, and the area (16,000 to 18,000 km<sup>2</sup>) was twice as large as the 1985-1992 average (1996 is illustrated in Fig. 4). The somewhat smaller size of the hypoxic area in July 1997 was likely due to the passage of Hurricane Danny that either caused wind mixing and reaeration or forced the hypoxic water mass closer to shore. The 1998 hypoxia was concentrated on the eastern and central Louisiana shelf from the Mississippi River delta to Marsh Island near Atchafalaya Bay and in deeper water than usual. The largest area of bottom-water hypoxia to date (20,000 km<sup>2</sup>) was mapped in July of 1999 [Rabalais, 1999]. Time or other logistical constraints often prevent the complete mapping of the extent of hypoxia, either in the offshore direction or to the west. Thus, the areal extent of bottom-water hypoxia generated from these surveys is a minimal estimate. The area estimations vary within a summer, and they should not be over-interpreted in making year-to-year comparisons or identifying trends.

There were extensive areas of hypoxia during multiple July cruises in 1993 and 1994, three and two, respectively. The multiple cruises demonstrate that the large area of hypoxia is persistent over two to three weeks, at least, although changing in configuration.

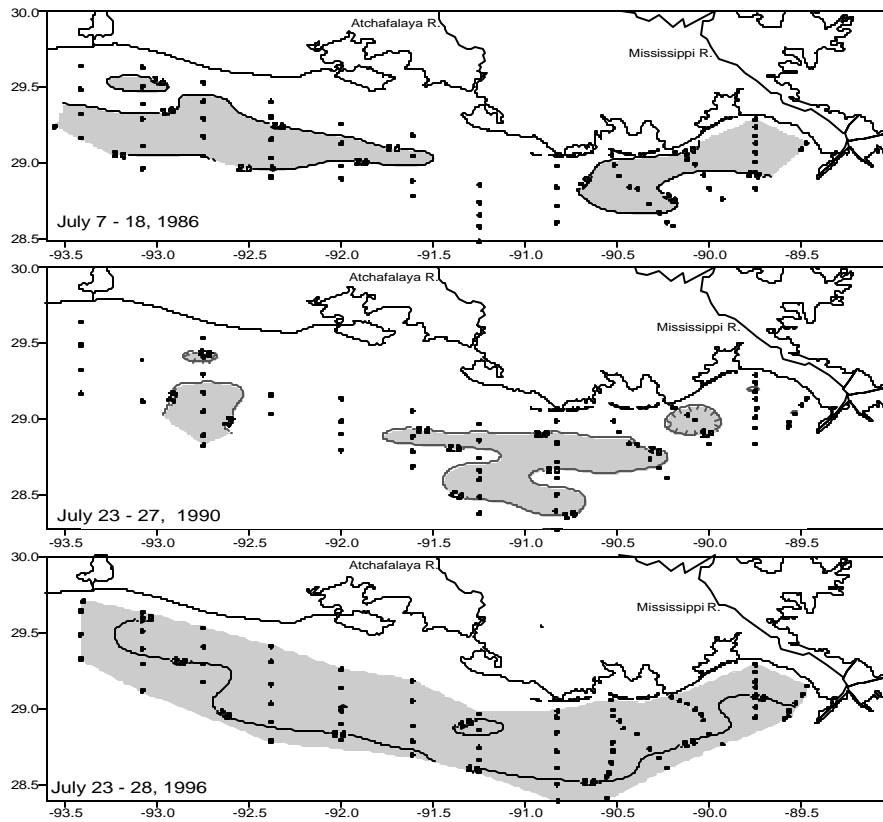


Figure 4. Distribution of bottom water less than  $2 \text{ mg l}^{-1}$  dissolved oxygen in mid-summer of the years indicated (from Rabalais et al. [1991, 1999]).

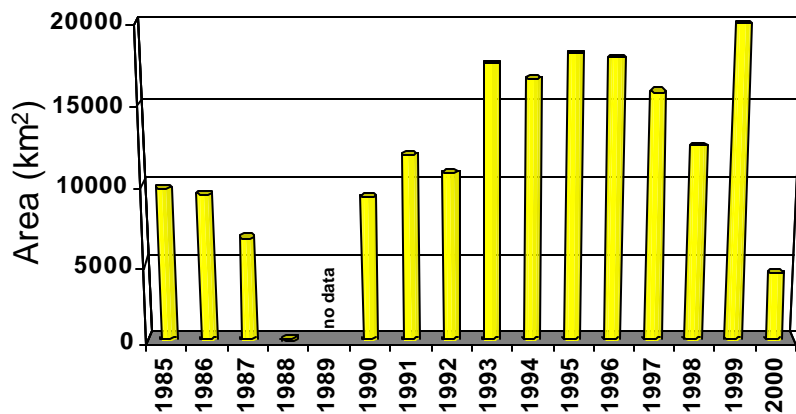


Figure 5. Estimated areal extent of bottom water hypoxia ( $\leq 2 \text{ mg l}^{-1}$ ) for mid-summer cruises in 1985-2000 (modified from Rabalais et al. [1998, 1999]).

A compilation of fifteen mid-summer shelfwide surveys (1985-1999) (Fig. 6) illustrates that the frequency of occurrence of hypoxia is higher to the west of the Mississippi and Atchafalaya Rivers in a down-current direction from the freshwater discharge and nutrient load. Other gradients in biological parameters and processes are also evident in a decreasing gradient away from the river discharges [Rabalais et al., 1996; Rabalais and Turner, 1998].



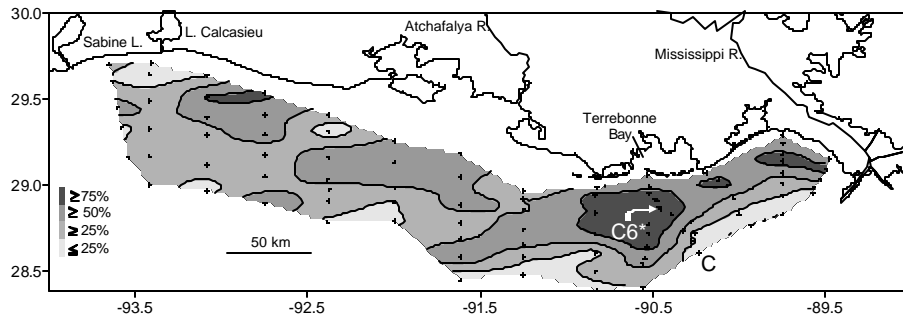


Figure 6. Distribution of frequency of occurrence of mid-summer bottom-water hypoxia over the 60- to 80-station grid from 1985-1999 [derived from Rabalais, Turner and Wiseman, various published and unpublished data]. Station C6\*, which incorporates data from C6, C6A and C6B, is identified.

### *Hypoxia in Flood and Drought Conditions*

Conditions during extreme events such as the 1993 flood or the 1988 or 2000 droughts emphasize the importance of river discharge and nutrient load in defining the mid-summer extent of hypoxia [Rabalais et al., 1991, 1998]. The influence of the Mississippi River system was magnified during the 1993 flood. Above-normal freshwater inflow and nutrient flux from the Mississippi and Atchafalaya Rivers from late spring into mid-summer and early fall [Dowgiallo, 1994] were clearly related in time and space to the seasonal progression of hypoxic water formation and maintenance and its increased severity and areal extent on the Louisiana-Texas shelf in 1993 [Rabalais et al., 1998]. Flood conditions resulted in a higher flux of nutrients to the Gulf, higher concentrations of dissolved nutrients in Gulf surface waters, lower surface water salinity, higher surface water chlorophyll *a* biomass, increased phytoplankton abundance, modeled greater carbon export from the surface waters, increased bottom water phaeopigment concentrations (an indicator of fluxed degraded surface water chlorophyll *a* biomass), lower bottom water oxygen concentrations compared to the long-term averages for 1985-1992 and a doubled size of the zone [Dortch, 1994; Goolsby, 1994; Justic' et al., 1997; Rabalais et al., 1998].

A 52-yr low-river flow of the Mississippi River occurred in 1988. Discharge began at normal levels in 1988 and dropped to some of the lowest levels on record during the summer months (Fig. 2). In early June 1988, hydrographic conditions on the southeastern Louisiana shelf were similar to those observed in previous years, i.e., a stratified water column and some areas of oxygen-deficient bottom waters [Rabalais et al., 1991]. By mid-July, few areas of lower surface salinity were apparent, there was little density stratification, and low oxygen conditions were virtually absent. Reduced summer flows in 1988 also resulted in reduced suspended sediment loads and nutrient flux and subsequent increased water clarity across the continental shelf. The critical depth for photosynthesis was greater than the depth of the seabed, and there likely was photosynthetic production of oxygen in bottom waters [Rabalais et al., 1991]. A typical seasonal sequence of nutrient-enhanced primary production and flux of organic matter progressed in the spring and led to the formation of hypoxia, but hypoxia was not maintained because of weak stratification and improved light conditions in bottom waters that allowed for some photosynthesis.

Drought conditions in spring 2000 throughout the watershed resulted in decreased discharge (Fig. 2) and nutrient flux so that the typical spring sequence of increased productivity, phytoplankton biomass and carbon flux was diminished in importance. Less productivity, coupled with windy spring weather that prevented the usual development of stratified waters, resulted in little development of hypoxia in the spring. Discharge reached mean levels in the summer and hypoxia eventually developed although over a smaller area (4,400 km<sup>2</sup>). While the total discharge in 1988 and 2000

between the months of January-May was similar, the resulting response of the system and distribution of hypoxia were quite different in the two spring-summer sequences.

### *Temporal Variability*

Critically depressed dissolved oxygen concentrations occur below the pycnocline from as early as late February through early October and nearly continuously from mid-May through mid-September. In March, April and May, hypoxia tends to be patchy and ephemeral; it is most widespread, persistent, and severe in June, July and August [Rabalais et al., 1991, 1999]. The low oxygen water mass on the bottom during peak development in the summer changes configuration in response to winds, currents and tidal advection. The persistence of extensive and severe hypoxia into September and October depends primarily on the breakdown of stratification by winds from either tropical storm activity or passage of cold fronts. Hypoxia is rare in the late fall and winter.

Hypoxia occurs not only at the bottom near the sediments, but well up into the water column (Fig. 3). Depending on the depth of the water and the location of the pycnocline(s), hypoxia may encompass from 10% to over 80% of the total water column, but normally only 20 to 50%. Hypoxia may sometimes reach to within 2 m of the surface in a 10-m water column, or to within 6 m of the surface in a 20-m water column. Anoxic bottom waters can occur, along with the release of toxic hydrogen sulfide from the sediments.

Continuously recording oxygen meters were deployed near the bottom at a 20-m station off Terrebonne Bay (example for 1993 in Fig. 7). There was variability within the year and between years, but the pattern generally depicted is for (1) a gradual decline of bottom oxygen concentrations through the spring with reoxygenation from wind-mixing events, (2) persistent hypoxia and often anoxia for extended parts of the record in May-September, (3) isolated wind-mixing events in mid-summer that reaerate the water column followed by a decline in oxygen similar to that seen in the spring, (4) isolated intrusion of higher oxygen content waters from deeper water during upwelling favorable wind conditions, then a relaxation of the winds and a movement of the low oxygen water mass back across the bottom at the site of the oxygen meter, and (5) wind mixing events, either tropical storms or hurricanes or cold fronts in the late summer and fall that mix the water column sufficiently to prevent prolonged instances of dissolved oxygen concentrations less than 2 mg l<sup>-1</sup>.

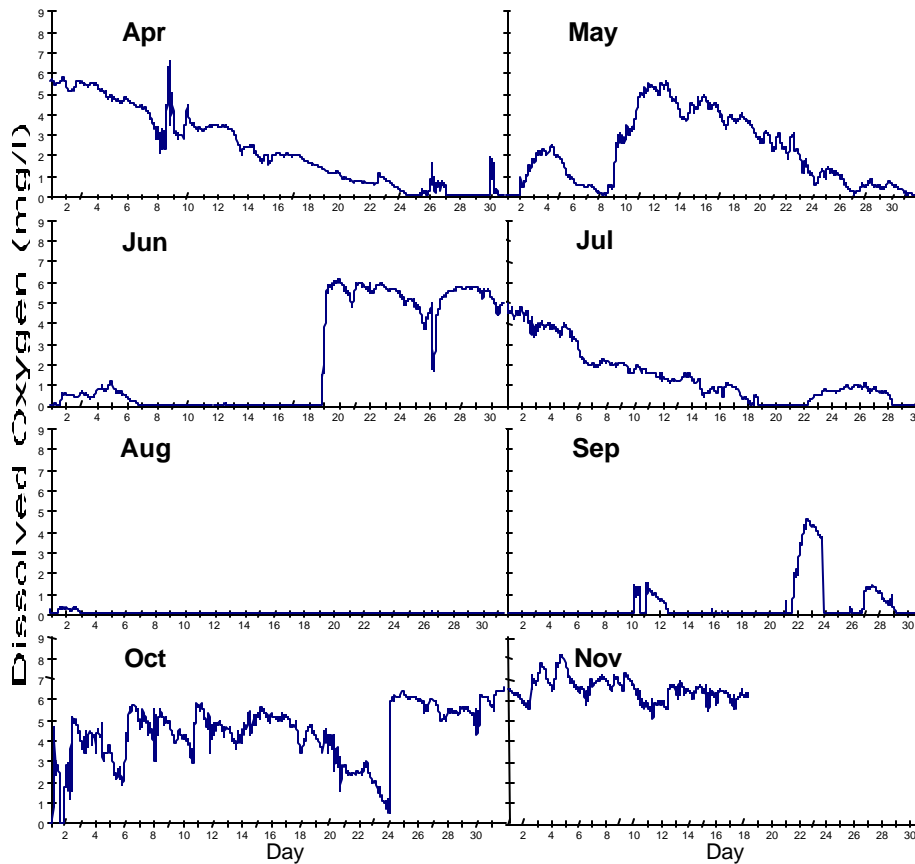


Figure 7. Time-series of near-bottom (19 m in a 20-m water column) dissolved oxygen concentration ( $\text{mg l}^{-1}$  in 1-h intervals) at station C6B (see Fig. 6) for 1993 (modified from Rabalais et al. [1999]).

## Mississippi River Discharge, Nutrient Load and Hypoxia

Although the Mississippi River discharges organic matter, whose decomposition could consume oxygen, the principal source of organic matter reaching the hypoxic bottom waters is from *in situ* phytoplankton production [Turner and Allen, 1982b; Rabalais et al., 1992; Turner and Rabalais, 1994a; Eadie et al., 1994; Justic' et al., 1996, 1997]. The variability in primary production in the northern Gulf impacted by the Mississippi River is quite high, due to the dynamic and heterogeneous conditions found in the river/ocean mixing zone. The highest values of primary production and chlorophyll *a* biomass (Fig. 8) are typically observed at intermediate salinities within the Mississippi River plume and across the broad region of the Louisiana shelf influenced by the river and coincide with non-conservative decreases in nutrients along the salinity gradient (Fig. 8) [Rabalais and Turner, 1998; Lohrenz et al., 1999]. Salinities of 20 to 30 psu are typical across broad regions of the Louisiana inner shelf for much of the year, and high production and chlorophyll biomass occur over broad areas (Plate 2). The rates of primary production along a salinity gradient of the Mississippi River plume are constrained by low irradiance, mixing in the more turbid, low salinity regions of the plume, and by nutrient limitation outside the plume—a pattern typical of other major rivers including the Amazon [DeMaster et al., 1986; Smith and DeMaster, 1996], Huanghe [Turner et al., 1990] and Changjiang [Xiuren et al., 1988].

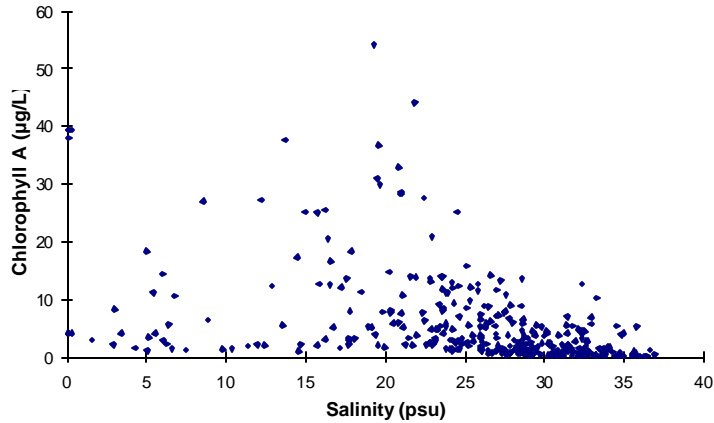


Figure 8. Relationship of surface chlorophyll *a* and salinity for six cruises (April 1992, October 1992, April 1993, July 1993, April 1994, July 1994) from 89.5°W to 97°W, 5 m to 50 m depth. One value (209  $\mu\text{g l}^{-1}$  at 13.7 psu) was deleted from the plot. (From Rabalais and Turner [1998].)

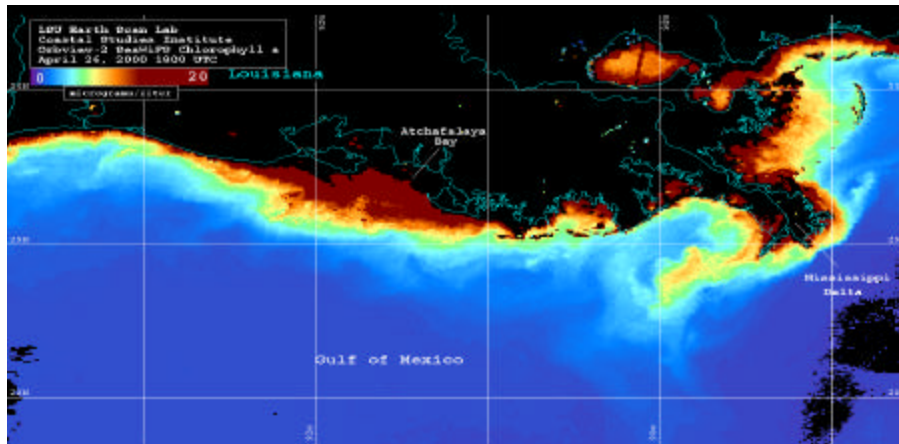


Plate 2. Orbview-2 SeaWiFS satellite image from April 26, 2000, during below average discharge of the Mississippi River, showing estimated chlorophyll along the Louisiana coast. Image supplied by Nan D. Walker, used with permission of the Earth Scan Laboratory, Louisiana State University.

The high rates of primary production in the inner shelf of the northern Gulf of Mexico can be attributed to nutrient loading from the Mississippi and Atchafalaya rivers and buoyancy flux that keeps recycled nutrients in the photic zone [Riley, 1937; Thomas and Simmons, 1960; Sklar and Turner, 1981; Lohrenz et al., 1990]. In the continental shelf waters of the northern Gulf of Mexico, there is a strong relationship between river-borne nutrient flux, nutrient concentration, primary production and net production. Primary production near the river delta and on the southeastern Louisiana shelf is significantly correlated with nitrate + nitrite concentrations and fluxes [Lohrenz et al., 1997]. Even stronger correlations were observed between the concentration of orthophosphate and primary production, but these were not significant (smaller sample size). Peak nutrient inputs generally occur in the spring with peak river discharge in March-May, although there is a temporal lag (1 mo) in nitrate load behind peak discharge [Justic' et al., 1997]. Net production at station C6\* off Terrebonne Bay lags 1 mo from the peak nitrate load (Fig. 9).

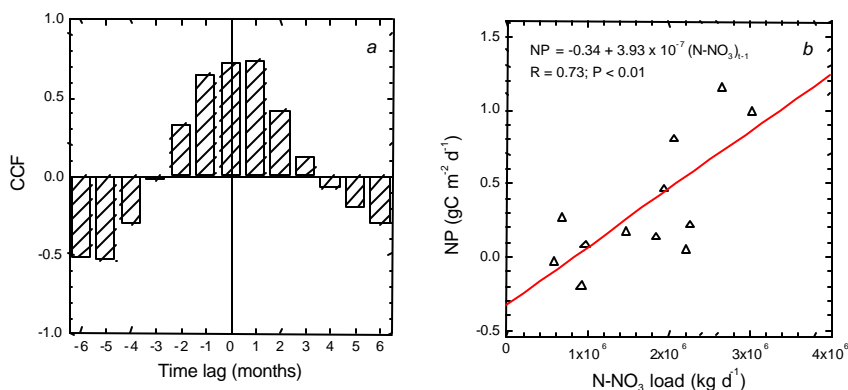


Figure 9. Left panel: Cross correlation function (CCF) for Mississippi River nitrate flux at Tarbert Landing and net production of the upper water column (1-10 m at station C6\* in 20-m depth off Terrebonne Bay, see Fig. 6). Right panel: best-fit time-delayed linear model for the regression of net production (NP) on nitrate load. The model is  $NP_t = -0.34 + 3.93 \times 10^{-7} (N-NO_3)_{t-1}$  where  $t$  and  $t-1$  denote values for the current and preceding months, respectively. Symbols denote monthly averages for the period 1985-1992. (From Justic' et al. [1997], used with permission of the author.)

The spring delivery of nutrients initiates a seasonal progression of biological processes that ultimately lead to the depletion of oxygen in the bottom waters. The rates of primary production in the surface waters of the Mississippi River-influenced continental shelf are high (290 to  $> 300 \text{ g C m}^{-2} \text{ y}^{-1}$ ) [Sklar and Turner, 1981; Lohrenz et al., 1990]. One might expect that the vertical export of particulate organic carbon (POC) would also be high and be roughly proportional to the quantity of carbon fixed in the surface waters. Although the overall flux of POC on the continental shelf influenced by the Mississippi River is high, the relationship between POC export and primary production is quite variable in time and space. Redalje et al. [1994] examined the relationship between primary production and the export of POC from the euphotic zone determined with free-floating sediment traps. Productivity and POC exports exhibited similar trends in spring and fall, but were uncoupled in summer. The lowest ratio of export to production coincided with the time when production was greatest, and the highest ratios occurred when production was the lowest. Export ranged from low values of 39% during July-August 1990 to high values during March 1991, when export exceeded measured water column-integrated primary production by a factor of two.

In another study of the vertical flux of particulate material, particle traps were deployed on an instrument mooring within the zone of recurring hypoxia at depths of 5 m and 15 m in a 20-m water column in spring, summer and fall of 1991 and 1992 (station C6B off Terrebonne Bay, Fig. 6) [Qureshi, 1995]. Carbon flux was approximately 500 to 600  $\text{mg C m}^{-2} \text{ d}^{-1}$  in 15-m water depth [Qureshi, 1995]. A rough estimate of the fraction of production exported from the surface waters (compared to seasonal primary production data of Sklar and Turner [1981]) was highly variable and ranged from 10 to 200% with higher percentages in spring [Qureshi, 1995]. A large proportion of the POC that reached the bottom was incorporated in zooplankton fecal pellets (55%), but also as individual cells or in aggregates. Both phytoplankton and zooplankton fecal carbon flux were greater in the spring and the fall than in the summer.

The oxygen consumption rates in near-bottom waters of the seasonally oxygen-deficient continental shelf were measured during spring and summer cruises in several years [Turner et al., 1998; Turner and Rabalais, 1998]. Respiration rates varied between 0.0008 to 0.29  $\text{mg O}_2 \text{ l}^{-1} \text{ h}^{-1}$ , and were sufficient to reduce the *in situ* oxygen concentration to zero in less than four weeks. The rates were inversely related to depth and decreased westward of the Mississippi River delta, consistent with the decrease in nutrients, chlorophyll *a* and total pigment concentrations, and the relative proportion of surface-to-bottom pigments. The amount of phytoplankton biomass in the bottom waters across the Louisiana inner and middle continental shelf is high, often exceeding  $30 \mu\text{g l}^{-1}$ , and a high percentage is composed of phaeopigments [Rabalais and Turner, 1998]. The respiration rate is proportional to phytoplankton pigment concentration [Turner and

Allen, 1982b], and, thus, higher rates of oxygen consumption would be expected where higher flux of material reaches the lower water column and sediments. Respiration rates per unit phytoplankton pigment were highest in the spring, in shallower waters, and also closest to the Mississippi River delta.

The high particulate organic carbon flux to the 15-m moored trap was sufficient to fuel hypoxia in the bottom waters below the seasonal pycnocline [Qureshi, 1995; Justic' et al., 1996]. The flux of organic material in summer, while it sustained hypoxia, was incremental to the majority flux of particulates in the spring [Qureshi, 1995]. Because the moored sediment traps were serviced by divers, they were not deployed from late fall through early spring when high fluxes might have occurred that also fueled the consumption of oxygen.

There is a time lag between nutrient delivery and production in the surface waters, and a subsequent lag in flux of carbon to the lower water column and oxygen uptake in the lower water column and sediments. The spatial and temporal variability in the distribution of hypoxia is, at least partially, related to the amplitude and phasing of the Mississippi River discharge and nutrient fluxes [Pokryfki and Randall, 1987; Justic' et al., 1993]. An annual sequence of salinity, surface chlorophyll *a*, bottom oxygen and bottom total pigments are illustrated in Figure 10. Net productivity (a surrogate for excess carbon available for export) of the upper water column appears to be an important factor controlling the accumulation of organic matter in coastal sediments and development of hypoxia in the lower water column. The seasonal dynamics of net productivity in the northern Gulf of Mexico are coherent with the dynamics of freshwater discharge [Justic' et al., 1993]. The surface layer (0 to 0.5 m at station C6\*) shows an oxygen surplus relative to the saturation values during February-July; the maximum occurs during April and May and coincides with the maximum flow of the Mississippi River. Peak chlorophyll *a* biomass in the surface waters, a surrogate for net productivity, occurs in spring at station C6\* in the core of the hypoxic zone (Fig. 10). The bottom layer (approximately 20 m), in contrast, exhibits an oxygen deficit throughout the year, but reaches its highest value in July (Fig. 10). Bottom hypoxia in the northern Gulf is most pronounced during periods of high water column stability when surface-to-bottom density differences are greatest (demonstrated by reduced surface salinity in spring and summer in Fig. 10) [Rabalais et al., 1991]. The correlation between Mississippi River flow and surface oxygen surplus peaks at a time-lag of one month, and the highest correlation between discharge and bottom oxygen deficit is for a time-lag of two months [Justic' et al., 1993]. A similar cross-correlation analysis verified that the seasonal maximum in net production lags riverine nitrate flux by one month (Fig. 9) [Justic' et al., 1997]. These findings suggest that the oxygen surplus in the surface layer following high flow depends on nutrients ultimately coming from the river that are regenerated many times. An oxygen surplus also means that there is an excess of organic matter derived from primary production that can be redistributed within the system; much of this will eventually reach the sediments.

Similar relationships with freshwater discharge and oxygen depletion in bottom waters at stations west of the Atchafalaya River delta and expected direction of materials and freshwater flux were identified by Pokryfki and Randall [1987]. Time lags were apparent between values of river discharge, bottom dissolved oxygen and salinity. The highest cross-correlation coefficient between bottom water dissolved oxygen (in the area off the Calcasieu estuary) and river discharge (from the Atchafalaya) was  $-0.51$  at a lag of two months. Their linear regression model did not include any factors for biological processes, and the accuracy would have been improved by "incorporating a biological component into the time series" [Pokryfki and Randall, 1987].

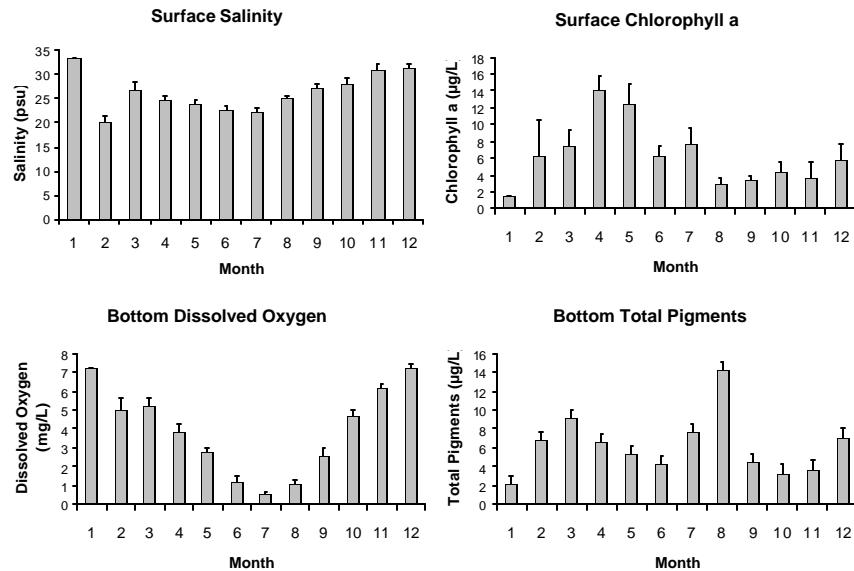


Figure 10. Surface and bottom water quality for station C6\* (composite data for stations C6A, C6B and C6, Fig. 6) for 1985-1997 average conditions ( $\pm$  s.e.).  $n$  ranges between 1-10 for winter, 10-20 for spring and fall and 20-40 for summer. (Modified from Rabalais et al. [1998].)

## Nutrient Sources and Changes

The Mississippi River is the largest source of freshwater and nutrients to the northern Gulf of Mexico. This watershed, like others, has undergone major changes affecting water quality since the Native American culture was displaced by mostly European immigrants in the early 1800s. Major alterations in the morphology of the main river channel and widespread landuse patterns in the watershed, along with anthropogenic additions of nitrogen and phosphorus, have resulted in dramatic water quality changes this century [Turner and Rabalais, 1991]. The river has been shortened by 229 km in an effort to improve navigation, and has a flood-control system of earthwork levees, revetments, weirs, and dredged channels for much of its length. These modifications have left adjacent lands drier and more susceptible to massive conversion to farmland [Abernethy and Turner, 1987]. More than half of the original wetlands in the United States have been lost to drainage practices [Zucker and Brown, 1998]. Much of this wetland loss is related to agricultural expansion.

Water quality in streams, rivers, lakes and coastal waters may change when watersheds are modified by alterations in vegetation, sediment balance, conversion of forests and grasslands to farms and cities, and increased anthropogenic activities that accompany increased population density, e.g., fertilizer application, sewage disposal or atmospheric deposition [Peierls et al., 1991; Turner and Rabalais, 1991; Howarth et al., 1996; Caraco and Cole, 1999]. The estimate of current river nitrogen export from the Mississippi River is 2.5- to 7.4-fold higher than from the watershed during pre-agricultural and pre-industrial or "pristine" conditions [Howarth et al., 1996].

In an average year the Mississippi River discharges nearly 1.6 million mt of nitrogen to the Gulf of Mexico, of which 0.95 million mt is nitrate and 0.58 million mt is organic nitrogen [Goolsby et al., 1999]. The principle sources of inputs of nitrogen to the Mississippi River system are soil mineralization, fertilizer application, legume crops, animal manure, atmospheric deposition, and municipal and industrial point discharges (Fig. 11). The highest inputs within the watershed are above the confluence of the Mississippi and Ohio Rivers (Plate 3, upper panel), and not surprisingly the yields are from sub-basins where inputs are the greatest (Plate 3, lower panel). High inputs and yields are characteristic of sub-basins where precipitation is high and agricultural drainage

is extensive, resulting in the high rates of transport of soluble nitrate into streams, the Mississippi River and the Gulf of Mexico.

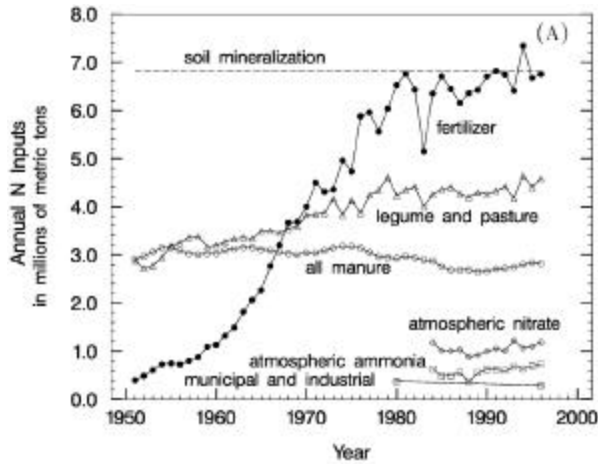


Figure 11. Annual nitrogen inputs from major sources in the Mississippi River Basin, 1951-96, (from Goolsby [2000], modified from Goolsby et al. [1999], used with permission of the author).

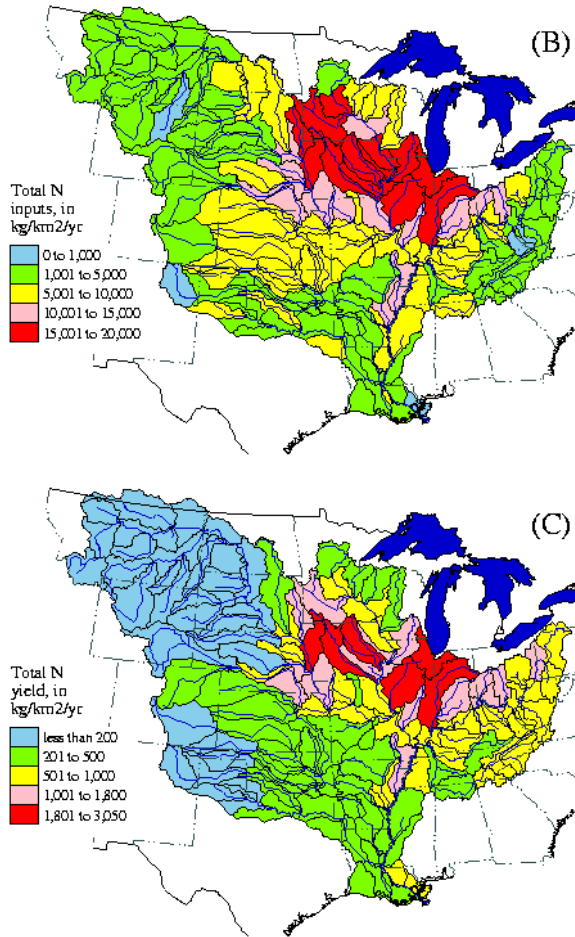


Plate 3. Upper panel: Nitrogen inputs in hydrologic accounting units of the basin during 1992, based on data from the 1992 Census of Agriculture. Lower panel: Average annual nitrogen yields of streams in the basin for 1980-96. (From Goolsby [2000], modified from Goolsby et al. [1999], used with permission of the author).



Large-scale industrial production and use of nitrogen and phosphorus fertilizer in the United States began in the mid-1930s and climbed to a peak in the 1980s [Turner and Rabalais, 1991]. Phosphorus fertilizer use in the United States reached a plateau around 1980, whereas nitrogen fertilizer use is still increasing (Fig. 12). Forty-two percent of the nitrogen fertilizer and 37% of the phosphorus fertilizer used annually in the United States from 1981 to 1985 was applied in states that are partially or completely in the Mississippi River watershed, where it equaled 4.2 million mt of nitrogen (as N) and 0.53 million mt of phosphorus (as P). Turner and Rabalais [1991] estimated that a maximum of 44% of the applied nitrogen and 28% of the applied phosphorus may have made its way to the Gulf of Mexico. Subtracting a natural loading estimate (riverine fluxes prior to World War II), they estimated that the maximal loading from fertilizer sources probably represents no more than 22% of the applied fertilizer.

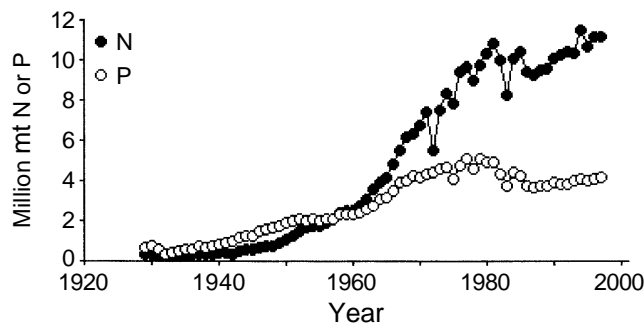


Figure 12. Nitrogen (as N) and phosphorus (as phosphate) fertilizer use this century in the United States up to 1997 (from USDA annual agriculture statistical summaries). (From Rabalais et al. [1999].)

Mississippi River nutrient concentrations and loading to the adjacent continental shelf have changed dramatically this century, with an acceleration of these changes since the 1950s [Turner and Rabalais, 1991, 1994a; Rabalais et al., 1996]. Turner and Rabalais [1991] examined water quality data for four lower Mississippi River stations for dissolved inorganic nitrogen (as nitrate), phosphorus (as total phosphorus) and silicon (as silicate). The mean annual concentration of nitrate was approximately the same in 1905-1906 and 1933-1934 as in the 1950s, but it has doubled in the last 40 years (Fig. 13). The increase in total nitrogen is almost entirely due to changes in nitrate concentration. The mean annual concentration of silicate was approximately the same in 1905-1906 as in the early 1950s, then it declined by 50%. Concentrations of nitrate and silicate appear to have stabilized, but trends are masked by increased variability in the 1980s and early 1990s data. Although the concentration of total phosphorus appears to have increased since 1972, variations among years are large.

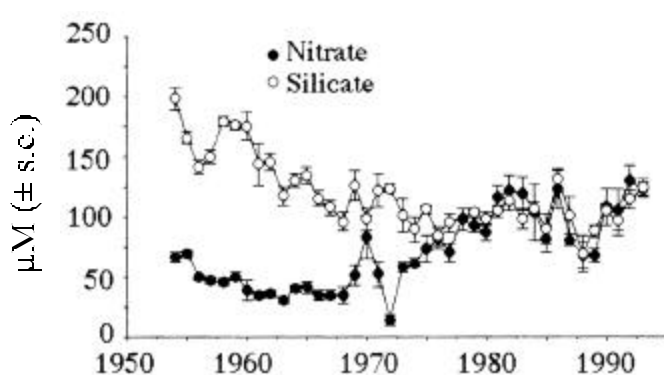


Figure 13. The average annual concentration ( $\mu\text{M} \pm 1 \text{ S.E.}$ ) of nitrate and silicate in the Mississippi River at New Orleans (modified from Turner et al. [1998]).

The silicate:nitrate ratios have changed as the concentrations varied. The Si:N atomic ratio was approximately 4:1 at the beginning of this century, dropped to 3:1 in 1950 and then rose to approximately 4.5:1 during the next ten years, before plummeting to 1:1 in the 1980s. The ratio appears stable at 1:1 through 1997 with little variation. The average atomic ratios of N:Si, N:P and Si:P are currently 1.1, 15 and 14, respectively, and closely approximate those of Redfield [1958] of 16:16:1, N:Si:P [Justic' et al., 1995a, b].

The seasonal patterns in nitrate and silicate concentration have also changed during this century. There was no pronounced peak in nitrate concentration earlier this century, whereas there was a spring peak from 1975 to 1985, presumably related to seasonal agricultural activities, timed with long-term peak river flow [Turner and Rabalais, 1991]. A seasonal summer-fall maximum in silicate concentration, in contrast, is no longer evident. Consequently the seasonal signal of Si:N atomic ratio has also changed. The seasonal shifts in nutrient concentrations and ratios become increasingly relevant in light of the close temporal coupling of river flow to surface water net productivity (1-mo lag) and subsequent bottom water oxygen deficiency (2-mo lag) [Justic' et al., 1993].

Justic' et al. [1995a] compared data for two periods: 1960-1962 and 1981-1987 (Table 1). Substantial increases in N (300%) and P (200%) concentrations occurred over several decades, and Si decreased (50%). [No data on total P concentration in the Mississippi River were reported prior to 1973; however, total P in the river showed a moderate increase between 1973 and 1987. By applying a linear least-squares regression on the 1973-1987 data, they estimated ( $p < 0.01$ ) that the total P concentration increased two fold between 1960-1962 and 1981-1987.] Accordingly, the Si:N ratio decreased from 4.3 to 0.9, the Si:P ratio decreased from 40 to 14, and the N:P ratio increased from 9 to 15. By applying the Redfield ratio as a criterion for stoichiometric nutrient balance, one can distinguish between P-deficient, N-deficient, and Si-deficient rivers, and those having a well balanced nutrient composition. The nutrient ratios for the Mississippi River (1981-1987 data base) show an almost perfect coincidence with the Redfield ratio. The proportions of Si, N and P have changed over time in such a way that they now suggest a balanced nutrient composition.

TABLE 1. Changes in concentrations and atomic ratios of nitrogen (N), phosphorus (P) and silica (Si) in the lower Mississippi River and the northern Gulf of Mexico; x - mean value, n - number of data, S - standard error,  $p < 0.001$  - highly significant difference in nutrient concentrations between the two periods, based on a two-sample t-test. (Modified from Justic' et al. [1995a].)

		Mississippi River		Northern Gulf of Mexico	
		1960-62 <sup>d</sup>	1981-87	1960 <sup>e</sup>	1981-87
Nutrient concentration ( $\mu\text{M}$ ):					
	X	36.5	114	2.23	8.13
N <sup>a</sup>	n	72	200	219	219
	S	2.9	6.0	0.16	0.60
			( $p < 0.001$ )		
	x	3.9	7.7	0.14	0.34
P <sup>b</sup>	n	-	234	231	231
	S	-	0.4	0.01	0.02
			( $p < 0.001$ )		
	x	155.1	108	8.97	5.34
Si <sup>c</sup>	n	72	71	235	235
	S	7.5	4.3	0.55	0.33
			( $p < 0.001$ )		
Average atomic ratios:					
	Si:N	4.2	0.9	4.0	0.7
	N:P	9	15	16	24
	Si:P	39.8	14	64	16

<sup>a</sup>N-NO<sub>3</sub> for the Mississippi, dissolved inorganic nitrogen (DIN=NO<sub>3</sub>+NH<sub>4</sub>+NO<sub>2</sub>) for the Gulf of Mexico

<sup>b</sup>total P for the Mississippi, reactive P for the Gulf of Mexico

<sup>c</sup>reactive Si

<sup>d</sup>Turner and Rabalais [1991], for N and Si, reconstructed for P

<sup>e</sup>reconstructed data

Despite being balanced on an annual basis, seasonal variations in nutrient inputs can affect nutrient availability. In particular, there is nearly a two-fold difference in nitrate supply over the course of the year [Turner and Rabalais, 1991], but only small annual variations in the silicate and total phosphorus supply. Consequently, the nutrient supply ratios vary around the Redfield ratios on a seasonal basis, with silicate and phosphorus in the shortest supply during the spring and nitrogen more likely to be limiting (based on ratios) during the rest of the year. With nutrient concentrations so closely balanced, Justic' et al. [1995b] proposed that any nutrient can become limiting, perhaps in response to small differences in nutrient supply ratios such as these, or conversely that no single nutrient is more limiting than others. These seasonal differences in nutrient ratios occur with seasonal variation in river flow, so that the riverine supply of all nutrients is least in low flow periods. Fluctuations in the Si:N ratio within the major riverine effluents and differences in Si:N ratios between the effluents of the two rivers are believed to be major determinants in estuarine and coastal food web structure on a seasonal and annual basis, with major implications to the cycling of oxygen and carbon [Turner et al., 1998]. As the Si:N ratio falls from above 1:1 to below 1:1, there may be shifts in the phytoplankton community from diatoms to an increasing flagellated algal community, including those that are potentially harmful, an altered marine food web by reducing the diatom-to-zooplankton-to higher trophic level connection, altered carbon flux to the lower water column and sediments as prey items change and grazing influences shift, and subsequent changes in the severity and expanse of hypoxia.

## Historical Trends in Productivity and Hypoxia

One might expect a propensity for high productivity and development of hypoxia, given the high volume of fresh water and associated nutrients delivered by the Mississippi River into a stratified coastal system. Unfortunately, the long-term data sets that demonstrate changes in surface water production and bottom water dissolved oxygen, such as available for the northern Adriatic Sea and areas of the Baltic and northwestern European coast, are few for the northern Gulf of Mexico. Therefore, biological, mineral or chemical indicators of surface water production and hypoxia preserved in sediments that accumulate under the plume of the Mississippi River (Fig. 14) provide clues to prior hydrographic and biological conditions. Sediment cores analyzed for different constituents [Turner and Rabalais, 1994a; Eadie et al., 1994] document eutrophication and increased organic sedimentation in bottom waters, with the changes being more apparent in areas of chronic hypoxia and coincident with the increasing nitrogen loads from the Mississippi River system

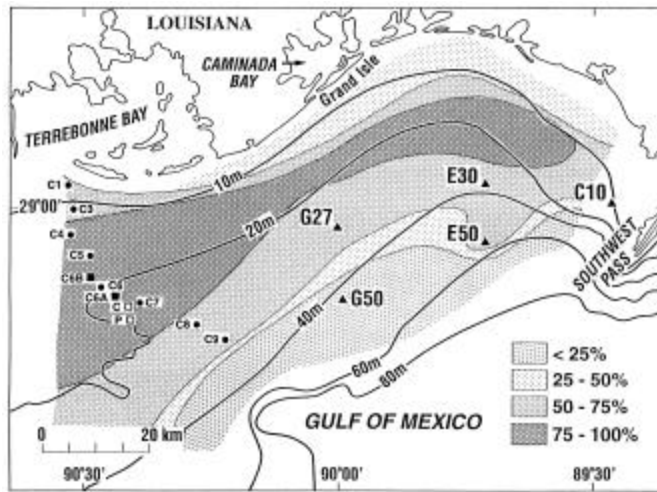


Figure 14. Station locations within the Mississippi River bight for hypoxia monitoring on transect C (closed circles), mooring locations (C6A and C6B) (closed squares), coring stations (closed triangles, those referred to in text are labeled). Stippling corresponds to frequency of occurrence of mid-summer hypoxia at monitoring stations (1985-1987, 1990-1993 [Rabalais, Turner and Wiseman, unpublished data]). (Modified from Rabalais et al. [1996].)

### *Indicators of Productivity*

Although the marine ecosystem influenced by the Mississippi River discharge exhibits signs of incipient Si limitation, the overall silicate-based productivity of the ecosystem on the southeastern Louisiana shelf influenced by Mississippi River discharge appears to have increased in response to the increased nitrogen load. This is evidenced by (1) equal or greater diatom community uptake of silica in the mixing zone, compared to the 1950s [Turner and Rabalais, 1994b], and (2) greater accumulation rates of biogenic silica (BSi) in sediments beneath the plume (Fig. 15) [Turner and Rabalais, 1994a].

Turner and Rabalais [1994a] quantified the silica in the remains of diatoms sequestered as biologically bound silica (BSi) in dated sediment cores from the Mississippi River bight. Relative changes in the % BSi reflect changes in *in situ* production [Conley et al., 1993]. The pattern in % BSi in dated sediment cores parallels the documented increases in nitrogen loading in the lower Mississippi River, over the same period that silicate concentrations have been decreasing [Turner and Rabalais, 1994a] (Fig. 15). The increased % BSi in Mississippi River bight sediments is direct evidence for the increase in flux of diatoms from surface to bottom waters beneath the Mississippi River plume. The highest concentrations of BSi were in sediments deposited in 25 to 50 m water depth in the middle of the sampling area. The % BSi in sediments from deeper waters (110 and 200 m) was generally stable through time, but rose in the shallower stations (10 and 20 m) around 1900 (not illustrated in Fig. 15). At the intermediate depths (27 to 50 m), where both the % BSi concentration and accumulation rates were highest, coincidental changes in the % BSi with time were evident, especially in the 1955 to 1965 period (a rise and fall) and a post 1975 (1980?) rise that was sustained to the sampling date (1989) (Fig. 15).

The increase in % BSi in sediments from the mid 1850s to the early 1900s support the hypothesis of Mayer et al. [1998] that organic nitrogen associated with the suspended sediment load may be a relatively large proportion of the total nitrogen load in river-dominated coastal regions. The % BSi peaks and declines around the mid-1800s and later around 1925 are causally related to the expansion of land clearing and land drainage efforts within the Mississippi River basin [Turner and Rabalais, unpublished data]. The trough in the 1930s to 1945 era is coincidental with the Great Depression and World War II, and the accelerated accumulation since the 1950s is associated with the tripling in the

dissolved inorganic nitrogen flux. Mayer et al. [1998] predicted that the relative importance of the organic nitrogen associated with the suspended load would become less important in the Mississippi River as the suspended load decreased and as the anthropogenic dissolved inorganic nitrogen load increased.

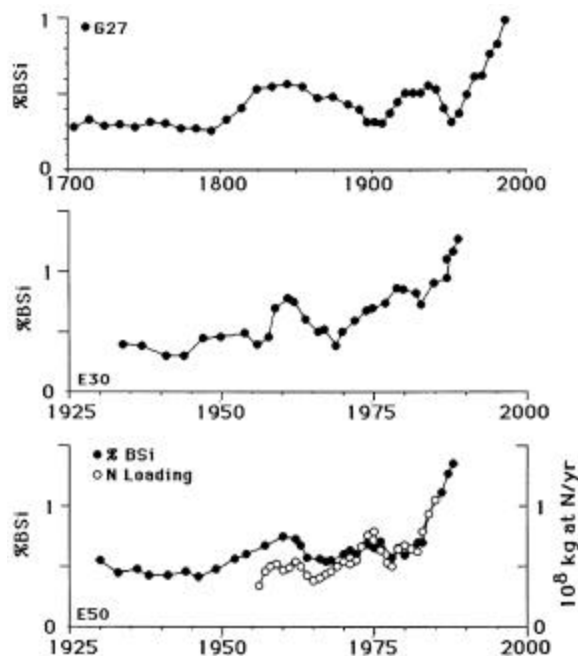


Figure 15. The average concentration of biologically bound silica (BSi) in sediments in each section of three dated sediment cores from stations in the Mississippi River Bight in depths of 27 to 50 m (stations in Fig. 14). A 3-y running average is plotted by time determined from Pb-210 dating. The figure for station E50 is superimposed with a 3-y average nitrogen loading from the Mississippi River. (Modified from Turner and Rabalais [1994a].)

The organic accumulation in the middle of the Mississippi River bight during the 1980s was  $90 \text{ g C m}^{-2} \text{ y}^{-1}$ , based on sedimentation rates and % carbon of the sediments [Turner and Rabalais, 1994a]. This is approximately 30% of the estimated annual phytoplankton production [Sklar and Turner, 1981; Lohrenz et al., 1990]. If the assumption is made that the BSi:C ratio at the time of deposition remained constant this century, then the increased BSi deposition represents a significant change in carbon deposition rates (up to 43% higher in cores dated after 1980 than those dated between 1900 to 1960). These results are corroborated by the same rate of increase in marine-origin carbon in sediment cores also collected within the Mississippi River bight (near station E30 of Turner and Rabalais [1994a]) [Eadie et al., 1994]. They estimated accumulation rates of about  $30 \text{ g C m}^{-2} \text{ y}^{-1}$  in the 1950s to  $50\text{-}70 \text{ g C m}^{-2} \text{ y}^{-1}$  at present. The rate of burial was significantly higher at a station within the area of chronic hypoxia (approximately  $70 \text{ g C m}^{-2} \text{ y}^{-1}$ ), in comparison with another site at which hypoxia had not been documented (approximately  $50 \text{ g C m}^{-2} \text{ y}^{-1}$ ). The  $\delta^{13}\text{C}$  partitioning of organic carbon into terrestrial and marine fractions further indicated that the increase in accumulation of carbon in both cores was exclusively in the marine fraction. The accumulation of carbon in the sediments analyzed by Eadie et al. [1994] was strongly correlated with Mississippi River nitrate flux.

### *Indicators of Hypoxia*

The surrogates in the dated sediment cores for oxygen conditions indicate an overall increase in oxygen stress (in intensity or duration) in the last 100 years, which seems especially severe since the 1950s and coincident with the onset of increases in riverine

nitrogen loading. The average glauconite abundance, a sediment mineral indicative of reducing environments and geologic anoxic settings, is ~5.8% of the coarse fraction of sediments from 1900 (oldest date in core collected near station E30, Fig. 14), rises to a transition point in the early 1940s and is ~13.4% afterwards [Nelsen et al., 1994]. These data suggest that hypoxia may have existed before the 1940 time horizon (at least to 1900) and that subsequent anthropogenic influences have exacerbated the problem.

Benthic foraminiferans, protozoans with calcium carbonate embedded cell walls, are useful indicators of reduced oxygen levels or carbon-enriched sediments or both [Sen Gupta et al., 1981; Sen Gupta and Machain-Castillo, 1993]. Benthic foraminiferal density and diversity were generally low in the Mississippi River bight, but a comparison of assemblages in surficial sediments from areas differentially affected by oxygen depletion indicated that the dominance of *Ammonia parkinsoniana* over *Elphidium* spp. (A-E index) was much more pronounced under hypoxia than in well-oxygenated waters (Fig. 16). The relative abundance of *A. parkinsoniana* was correlated with % BSi (i.e., a food source indicator) in sediments [Sen Gupta et al., 1996]. The A-E index also correlated strongly with the percentage of total organic carbon in surficial sediments. Thus, the index is affected by seasonal hypoxia produced by phytoplankton blooms that are recorded in the sediments in % BSi and carbon content. In the context of modern hypoxia, species distribution in dated sediment cores revealed stratigraphic trends in the *Ammonia/Elphidium* ratio that indicate an overall increase in oxygen stress (in intensity or duration) in the last 100 years (Fig. 16). In particular, the stress seems especially severe since the 1950s. It is notable that there is no trend in the A-E index for station G50 outside the zone of persistent hypoxia and that the index in 1988 for station C10 fell off the trend line (i.e., no low oxygen during the mid-summer 1988 cruise). In the last 100 years, both *Ammonia* and *Elphidium* become less important components of the assemblage, while *Buliminella morgani* shows an unusual dominance (also see Blackwelder et al. [1996]). *B. morgani*, a hypoxia-tolerant species, is known only from the Gulf of Mexico and dominates the population (> 50%) within the area of chronic seasonal hypoxia [Blackwelder et al., 1996]. It increased markedly upcore in the sediments analyzed by Blackwelder et al. [1996] and for station G27 of the Sen Gupta et al. [1996] study. *Quinqueloculina* (a significant component of the modern assemblage only in well-oxygenated waters) has been absent from the record of the G27 core since the early 1900s, but was a conspicuous element of the fauna in the previous 200 years. The historical absence of *Quinqueloculina* since 1900 at station G27 matches the presence of glauconite at station 10 since 1900. The occurrence of *Quinqueloculina* prior to 1870, however, indicates that oxygen stress was not a problem before then.

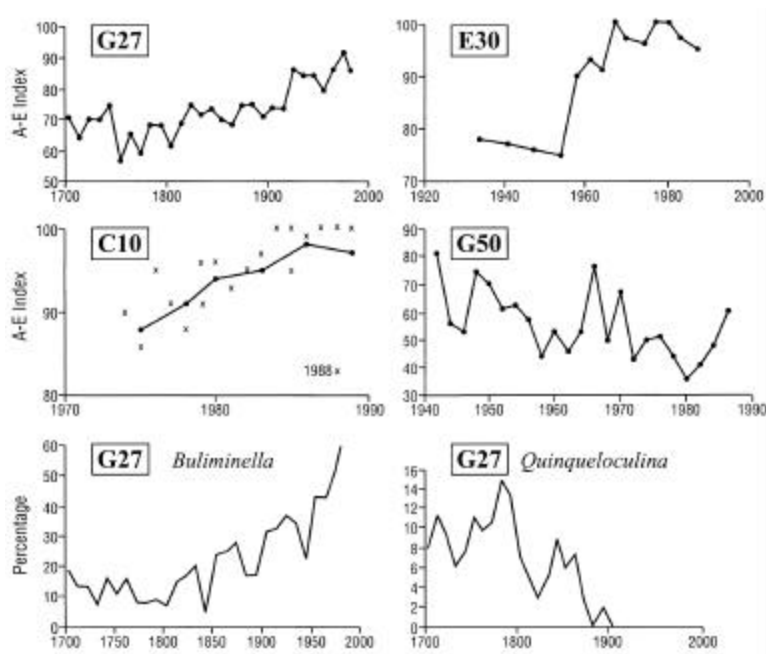


Figure 16. Changes in benthic foraminiferans with stratigraphic depth in  $^{210}\text{Pb}$ -dated sediment cores from the Mississippi River bight. A line connecting 3-y averages is superimposed on the data for C10; the 1988 outlier reflects the absence of summer hypoxia. Foraminiferans that indicate changes in oxygen stress (*Buliminella morgani* and *Quinqueloculina* sp.) are shown for G27. Note: the time scale is variable among plots. (Modified from Rabalais et al. [1996], Sen Gupta et al. [1996].)

### Global Patterns

There is a general consensus that the eutrophication of estuaries and enclosed coastal seas worldwide has increased over the last several decades [Nixon, 1995]. Evidence from many coastal seas suggests a long-term increase in frequency of phytoplankton blooms, including noxious forms [Smayda, 1990; Hallegraeff, 1993; Anderson, 1995]. Also, an increase in the areal extent and/or severity of hypoxia was observed, for example, in Chesapeake Bay [Officer et al., 1984], the northern Adriatic Sea [Justic' et al., 1987], some areas of the Baltic Sea (e.g., Andersson and Rydberg [1987]) and many other areas in the world's coastal ocean [Diaz and Rosenberg, 1995]. Diaz and Rosenberg [1995] documented that many systems are hypoxic now that were not historically, and others have expanded the geographic extent or increased in severity, either in lower dissolved oxygen concentrations or prolonged periods of exposure or both.

Long-term increases in nutrient concentrations in coastal waters along with increased primary production have been documented elsewhere in the world, e.g., the Baltic Sea [Larsson et al., 1985; Rosenberg, 1986; Wulff and Rahm, 1988], the Kattegat and Skagerrak [Rosenberg, 1986; Andersson and Rydberg, 1987], the sounds separating Sweden from Denmark [Rosenberg, 1986], the northwestern shelf of the Black Sea [Tolmazin, 1985], the northern Adriatic Sea [Faganeli et al., 1985; Justic' et al., 1987] and the Dutch coast of the North Sea [Fransz and Verhagen, 1985]. In the opinion of Diaz and Rosenberg [1995], no other environmental stressor has changed to the degree that oxygen depletion has in the last several decades.

Smaller and less frequent zones of hypoxia than that of the northern Gulf of Mexico occur in U.S. coastal and estuarine areas (e.g., New York Bight [Garside and Malone, 1978; Swanson and Sindermann, 1979; Falkowski et al., 1980; Swanson and Parker,

1988], Chesapeake Bay [Officer et al., 1984; Malone, 1991, 1992; Boynton et al., 1995], Long Island Sound [Welsh and Eller, 1991; Welsh et al., 1994; Parker and O'Reilly, 1991], Mobile Bay [Loesch, 1960; May, 1973; Turner et al., 1987], and the Neuse River estuary [Paerl et al., 1998]. Where sufficient long-term data exist, e.g., Chesapeake Bay, there is clear evidence for increases in nutrient flux, increased primary production, and worsening hypoxia. Thorough analyses of multiple indicators in sediment cores from the Chesapeake Bay indicate that sedimentation rates and eutrophication of the waters of the Bay have increased dramatically since the time of European settlement of the watershed [Cooper and Brush, 1991, 1993; Cooper, 1995; Karlson et al., 2000]. In addition, results indicate that hypoxia and anoxia may have been more severe and of longer duration in the last 50 years, particularly since the 1970s. The sediment core findings corroborate long-term changes in Chesapeake Bay water column chlorophyll biomass since the 1950s [Harding and Perry, 1997]. The parallels of the Chesapeake Bay eutrophication and hypoxia to those of the Mississippi River watershed and Gulf of Mexico hypoxia are striking, in particular those of the last half century.

## Consequences to Living Resources

Most marine systems respond to an increase in nutrient inputs with an increase in primary production. Shifts in the relative proportion of essential nutrients, as one or two increase and others remain the same or decrease, however, may result in altered phytoplankton communities and trophic links. There are examples of excessive nutrients and phytoplankton production leading to a shift in zooplankton communities from copepod-based to gelatinous zooplankton-based (i.e., jelly fish and ctenophores) [Zaitsev, 1993] with devastating effects on fisheries because of increased predation by the gelatinous zooplankton on fish larvae and other zooplankton. If surface productivity is enhanced in prey species that are preferred by the community of zooplankton grazers, then there will likely be increased productivity in pelagic and demersal populations that depend on either the living cells or the detrital material that sinks to the seabed, respectively. There are thresholds, however, where the load of nutrients to a marine system and the carbon produced exceeds the capacity for assimilation, and water quality degradation occurs with detrimental effects on components of the ecosystem and on ecosystem functioning.

When the depletion of oxygen worsens, the ability of organisms to reside either at the bottom or within the water column or even their survivability, is affected. When oxygen levels fall below critical values, those organisms capable of swimming (e.g., demersal fish, portunid crabs and shrimp) evacuate the area. The stress on less motile fauna varies, but they also experience stress or die as oxygen concentrations fall to zero. Important fishery resources are variably affected by direct mortality, forced migration, reduction in suitable habitat, increased susceptibility to predation, changes in food resources and disruption of life cycles. Prolonged oxygen depletion can cause mass mortalities in aquatic life, disrupt aquatic communities, cause declines in biological diversity, impact the capacity of aquatic systems to support biological populations, and disrupt the natural cycling of elements.

The effects of eutrophication, including hypoxia, are well known for some systems and include the loss of commercially important fisheries. The multi-level impacts of increased nutrient inputs and worsening hypoxia are not known for many components of productivity in the Gulf of Mexico, including pelagic and benthic, primary and secondary, food web linkages, and ultimately fisheries yield. Comparisons of ecosystems along a gradient of increasing nutrient enrichment and eutrophication or changes of a specific ecosystem over time through a gradient towards increasing eutrophication, provide information on how nutrient enrichment affects coastal communities. Work by Caddy [1993] in semi-enclosed seas demonstrates a continuum of fishery yield in response to increasing eutrophication. In waters with low nutrients, the fishery yield is low. As the quantity of nutrients increases, the fishery yield increases. As the ecosystem becomes increasingly eutrophied, there is a drop in fishery yield but the decreases are variable. The benthos are the first resources to be reduced by increasing frequency of



seasonal hypoxia and eventually anoxia; bottom-feeding fishes then decline. The loss of a planktivorous fishery follows as eutrophication increases, with eventually a change in the zooplankton community composition. Where the current Gulf of Mexico fisheries lie along the continuum of increasing eutrophication is part of the discussions found in this book.

As more and more of the United States' and world's coastal waters become hypoxic or as hypoxia increases in severity where it exists now—a trajectory proposed by many researchers and resource managers—what will happen to the habitats, the resource base, the food webs, and ultimately resources of importance for human consumption? The northern Gulf of Mexico is not unique among the world's coastal waters, nor immune to negative impacts, as hypoxia worsens. While there have been no catastrophic losses in fisheries resources in the northern Gulf of Mexico and, in fact, increases in the abundance of some components, the potential impacts of worsening hypoxic conditions are likely given the experience in other systems (e.g., Baltic and Black Seas) where there was a precipitous decline of ecologically and commercially important species.

Reducing excess nutrient delivery to estuarine and marine waters for the improvement of coastal water quality, including the alleviation of hypoxia, requires individual, societal and political will. Proposed solutions are often controversial and have societal and economic costs in a narrow and short-term sense. Yet, multiple, cost-effective methods of reducing nutrient use and delivery can be integrated into a management plan that results in improved habitat and water quality, both within the watershed and the receiving waters [National Research Council, 2000]. Successful plans with successful implementation and often with successful results span geopolitical boundaries, for example the Chesapeake Bay Agreement, the Comprehensive Conservation and Management Plans developed under the U.S. National Estuary Program for many of the nation's estuaries, a Long Island Sound agreement, the efforts of Denmark, Holland and Sweden, and international cooperation among the nations fringing the Baltic Sea as part of the Helsinki Commission [Boesch and Brinsfield, 2000]. These efforts are usually more successful in reducing point sources of nitrogen and phosphorus than with the multiple nonpoint sources of high solubility and growing atmospheric inputs of nitrogen. But success it is for examples such as coral recovery in Kaneohe Bay and for the improved water clarity and recovery of seagrass beds in Tampa and Sarasota Bays [Smith, 1981; Johansson and Lewis, 1992; Sarasota Bay National Estuary Program, 1995]. The growing decline of coastal water quality, and also the proven successes of reducing nutrients, are reasons enough for continued and expanded efforts to reduce nutrient overenrichment and the detrimental effects of hypoxia.

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