Left running head: R. E. Turner, N. N. Rabalais, R. B. Alexander, and R. W. Howarth

Right running head: Mississippi River Nutrient and Organic Matter Loads

Causes of Gulf of Mexico Hypoxia I: Characterization of Nutrient and Organic Matter Loads

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KEY WORDS: Mississippi River, dead zone, hypoxia, nutrient loading, nutrient ratios, eutrophication

16 August 2006

ABSTRACT

This is an update of the science supporting the science supporting the Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001). We provide an update of the analysis of the spatial and temporal patterns of nutrient and organic matter delivery to the northern Gulf of Mexico, including seasonality and interannual variability of freshwater flow and associated constituent loads. The discharge of the Mississippi River watershed varies within the 200 year data history, whose variations are responsive to climate change, but are not demonstrably increasing or increasing. However, about thirty percent of the Mississippi River is now shunted westward to form the Atchafalaya River, and undoubtedly changed stratification on the shelf and re-distributed the nutrient loads in the process. Data on nitrogen concentrations from the early 1900s confirm observations that the seasonal and annual concentrations in the lower river have changed considerably since then, including a higher spring loading following the increase in fertilizer applications after World War II. Within the last 15 years, the loading of total nitrogen (TN) has fallen, but the loading of total phosphorus (TP) has risen slightly, resulting in a decline in the TN : TP ratios. The present TN : TP ratios hover around an annual value indicative of potential N limits on phytoplankton growth, or balanced growth limitation, but not P limitation. Nitrogen : Silicate ratios are near the Redfield ratios indicative of growth limitations on diatoms.

Although nutrient concentrations are relatively high compared to that in many other large rivers, the water quality in the Mississippi River is not unique in terms of system behavior, whose output is described by a variety of land-use models. There is no net removal of nitrogen from water flowing through the Atchafalaya basin, but the concentrations of TP and suspended sediments are lower at the exit point (Morgan City) than in the Mississippi River water entering the Atchafalaya basin. The removal of nutrients entering offshore waters through river diversions is presently less than 1% of the total loadings going directly offshore, and would be less than 8% if the entire coast were engineered for only that purpose. Chemical transitions at the river mouth occur, and storages change seasonally, but measurements are not available nor are trends even estimated. The science-based conclusions about nutrient loads and sources to the hypoxic zone off Louisiana in the Action Plan are sustained by research and monitoring occurring in the subsequent ten years. Water-quality monitoring of the main stem of the lower Mississippi and Atchafalaya Rivers has recently improved with the re-establishment of several previously monitored sites, but the monitoring is far from complete; main stem monitoring sites above New Orleans have been discontinued and monitoring of the tributaries of the Mississippi River, critical for identifying pollutant sources, has declined precipitously over the last decade.

INTRODUCTION

The Mississippi River, the largest in the North American continent, discharges an average 580 km^3 of fresh water per year to the northern Gulf of Mexico through two main distributaries: the birdfoot delta southeast of the city of New Orleans, LA, and the Atchafalaya River 200 km to the west which is formed by the Red River and diverted Mississippi River (Meade 1995; Fig.1). The Mississippi and Atchafalaya rivers are the primary sources of fresh water, nitrogen and phosphorus to the northern Gulf of Mexico, delivering 80 percent of the freshwater inflow, 91 percent of the estimated annual nitrogen load, and 88 percent of the phosphorus load for the water years 1972-1993 (Dunn 1996). This river is the third, eighth and sixth largest river in the world in terms of its length, discharge and sediment yield, respectively (Milliman and Meade 1983).

Fig. 1. The Mississippi River drainage basin and major tributaries. 1 = upper Mississippi; 2 = Ohio; 3 = Missouri; 4 = Arkansas; 5 = lower Mississippi; 6 = Red.

The Mississippi River nutrient load is delivered to a continental shelf with the largest zone of oxygen-depleted coastal waters in the United States, and the entire western Atlantic Ocean (Rabalais et al. 2002a, b). The size of the Gulf of Mexico hypoxic zone has reached 20,000 km^2 in mid-summer (Rabalais et al. 2002a), and ranks second in area behind a similar coastal hypoxic zones in the Baltic. The hypoxic zone in the northern Gulf of Mexico (average for 1993-2005) 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 2002b).

Causal linkages between the nutrient load from the Mississippi River watershed and the formation, maintenance and dimensions of this hypoxic zone formed the basis for the Federal-State-Tribal Action Plan delivered to the White House in 2001 (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001). This agreement included a quantitative environmental goal to reduce the 5-year running average of the areal extent of Gulf hypoxia to less than 5,000 square kilometers by 2015, consistent with historical data and model predictions**.** The Action Plan endorsed a 30 % nitrogen load reduction to reach that goal whose implementation was to be based primarily on voluntary, incentive-based sub-basin strategies (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001; Rabalais et al. 2002a).

A programmatic review of the scientific basis supporting the interagency agreement and management options is to be conducted every five years. The foundation documents for the Action Plan included an extensively-reviewed analysis of the nutrient loads to the Gulf of Mexico (Goolsby et al. 1999). Most of the water quality data included in this document were necessarily collected several years before the report was concluded. Because of improvements in data collection and management, the mandated five year review can include 10 years of data not previously available. Further, funding for research and interest in both nutrient loading and hypoxia increased in the last decade, and so there are many new science initiatives and analyses pertinent to policy development. The purpose of this analysis is to review this new information developed since the Goolsby et al. (1999) report. We ask what key information in the Goolsby et al. (1999) report has been confirmed, revised or needs to be re-examined in light of post-Action Plan developments. Our specific questions are geographically constrained to landward of coast. We do not explore the causal linkages between nutrient loading and the size of the hypoxic zone. These linkages are addressed in companion analyses by Rabalais et al. (2006) and Justic' et al. (2006). The distribution of the loads once delivered to the shelf are addressed in these two analyses, and in a review of the physical oceanography (DiMarco et al. 2006). We address the following general questions:

1. What are the relevant magnitudes and long-term trends of different chemical forms of nutrients and organic matter delivered to the Gulf from riverine sources?
2. What changes have occurred since 1996 in the temporal (annual and seasonal) characteristics of Mississippi/Atchafalaya River nutrient (N, P, and Si) and organic matter loads, and freshwater discharge, to the Gulf of Mexico that are pertinent to the development and maintenance of hypoxia during summer?
3. Aside from the Mississippi and Atchafalaya Rivers, are there other important sources of nutrients, organic matter and freshwater discharge that influence hypoxia?
4. Is the current monitoring of freshwater discharge, sediment loading and nutrient loading adequate to characterize the riverine inputs that contribute to hypoxia on the shelf?

We address these questions by integrating key published research results of the last ten years with results from water quality monitoring programs conducted by the United State

Geological Survey (USGS) and university-based monitoring at Baton Rouge, LA. Source materials and methods will be provided separately in each section that follows on: a) river discharge, b) nutrient concentrations, ratios, and loadings, c) land-use and water quality relationships, and, d) possible transformation and sinks before water mixes with offshore waters. The principal constituents discussed are N, P, Si, C, and suspended sediments.

a) River discharge

The Goolsby et al. (1999) report determined that the primary source of nutrients to the northern Gulf of Mexico is the Mississippi River. Variations in its discharge have consequences to loading rates. It is important to be aware of these variations because of their effects on the nutrient variations have on vegetative cover and farming practices. There is significant inter-annual variability in the discharge of the Mississippi River (Fig. 2) and a seasonal peak in March-May and low discharge in late summer-fall. Trends, if any exist, are subject to the period of record examined. The 1817-2002 average discharge rate for the lower Mississippi River is remarkably stable at about 16,000 $m^3 s^{-1}$. 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 % y^{-1}, or 20 %. The discharge records for the Mississippi River reflect the known decadal-scale drought and flood features documented through surrogate and actual measures, and are evident among basins. The variations in discharge at Vicksburg and long-term records from the Illinois and Ohio Rivers, for example, demonstrate a close correspondence indicating that "the numerous dams and locks built along the Ohio river between 1929 and 1980 have not altered the overall variation in annual mean daily flow" (Poore et al. 2006; p. 3). Sparks et al. (1998), however, looked at a finer scale record and demonstrated that, from 1878 to 1996, the variance has changed at mile 137 on the Illinois River, where the flood peaks were higher and more frequent, and there were fewer years of low, stable water flow. Zhang and Schilling (2006) showed that the baseflow increased since the1940s because of cropping changes.

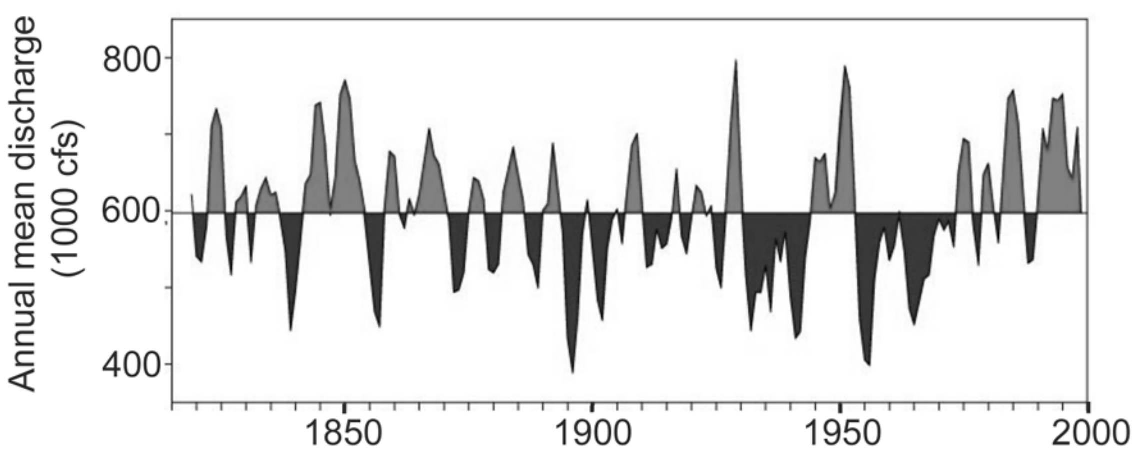

Fig. 2. A smoothed (3-year moving average) mean annual discharge of the Mississippi River at Vicksburg, MS from 1817 to 2000 (adapted from Poore et al. 2006). The horizontal line is the mean for all years. 1000 cfs ($ft^3 sec^{-1}$) = 28.32 cms ($m^3 sec^{-1}$).

Not all of the Mississippi River flows to the ocean through the birdfoot delta, located south of New Orleans. One effect of the disastrous 1927 flood was the construction of controlled diversion of a portion of the Mississippi River at St. Francisville, LA. A portion of the Mississippi River joins with the Red River to form the Atchafalaya River, whose flow is regulated to equal 30% of the Mississippi River near Simmesport, Louisiana (Fig. 3). The Atchafalaya River enters the Gulf of Mexico south of Morgan City, Louisiana.

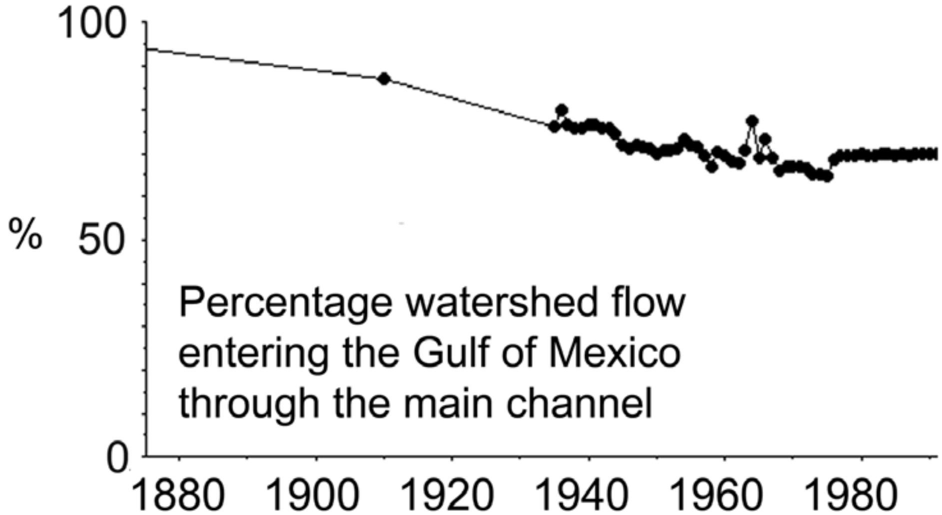

Fig. 3. The percent of the Mississippi River channel flow that continues to New Orleans, LA (from Turner et al., ms).

b) Nutrient concentrations

The concentration of silicate and various forms of nitrogen and phosphorus has been measured frequently over the last 40 years at St. Francisville and New Orleans, LA, and were discussed in Goolsby et al. (1999). These data show that the average annual nitrate concentration since the 1960s has risen while that of silicate has fallen, resulting in a decline in the silicate : nitrate+nitrite (SiO_2 : NO_{3+2}) molar ratio from 4 : 1 to 1 : 1. Two recent analyses of trends in nutrient concentrations at 11 stations on the Mississippi River tributaries suggest that the concentrations of some nutrients have been somewhat stable over the last 20 years, and especially in smaller watershed units (Turner and Rabalais 2004; Alexander and Smith 2006). A notable pattern is that total phosphorus (TP) and suspended sediment concentrations declined at some mainstem and tributary sites from the mid 1970s to 1994 (this is supported by both studies), whereas nitrate increased at many of these same sites (Alexander and Smith 2006). Both studies find that there were a similar number of stations with a rising and falling concentrations of total nitrogen (TN). The decline in total phosphorus (TP) and suspended sediment is part of a broader spatial pattern at many other sites in the basin (noted by Alexander and Smith 2006), and is especially apparent at sites in the western portions of the basin (i.e., Missouri, Arkansas-Red). The decline in TP is perhaps partially related to State detergent bans (i.e., P in municipal wastewater effluent fell by about 50 % from the 1970s to mid-1990s.). The nutrient load is partially determined by discharge and concentration, and so a large change at a small tributary could be compensated for by a small change at a large tributary. The sum effect of the individual station changes on nutrient concentrations at St. Francisville, LA, from 1975 to 1996, compared to the 1997-2005 was not a decline in TP concentration, but a rise of 12 %, and a TN concentration that declined 17%, creating a 26% decline in the TN : TP ratio.

Some supplementary data were collected at Baton Rouge, LA, from 1995 to 2005, and analyzed at one of the author's laboratory (RET) (Fig. 4). The concentration of TN, dissolved inorganic nitrogen (nitrate+nitrite+ammonium; DIN), ortho-phosphate, TP, silicate and suspended sediments show considerable seasonal variations. The minimum seasonal value for TN, for example, is one third of the peak of seasonal values. But there are no obvious increases or decreases in concentration, because of the wide range of values.

The seasonal patterns in nitrate and silicate concentration in the Mississippi River main channel changed during the last century. There was no pronounced peak in nitrate concentration in 1905/6 or in 1933/4, 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). Compared to before the 1950s, the seasonal summer-fall maximum in silicate concentration, in contrast, was no longer evident. The seasonal peaks in nitrate, silicate and phosphorus have not changed in the last 10 years at Baton Rouge (data not shown).

Part of the Mississippi River is diverted westward to join the Red River to form the Atchafalaya River. This river flows through the largest contiguous swamp in the US. The swamp is a depressional basin with extensive natural vegetation and parallel flood protection levees constraining flow to a north to south direction. There are water quality monitoring stations at the northern and southern limits of the Atchafalaya River that were used to quantify how much the nutrient concentrations change as water moves through the basin. A comparison of the concentration of nutrients (nitrate, total nitrogen (Kjeldahl nitrogen + nitrate), total carbon and total phosphorus) at the upstream (Simmesport, LA) and downstream (Morgan City, LA) monitoring stations is in Table 1 for the average concentrations for all years and the nutrient ratios at the upstream and downstream station for upstream and downstream samples collected within 7 days of each other. The nitrate concentration did not change noticeably from upstream to downstream locations, and the paired samples show a 4 % increase which is not statistically-significant from no change. The total nitrogen concentration decreased 6 % (not a statistically-significant difference from no change), primarily because the Kjeldahl nitrogen concentration is reduced by 14 % as it flows through the basin. The contribution of sewerage from the population in the basin (4.4 kg N y^{-1} per person) is but 0.07 % of the total nitrogen flux through the basin, and thus cannot be the source of the excess nitrate downstream. The total carbon and total phosphorus concentration in upstream and downstream stations are much more variable than for nitrogen, and decrease by 10 and 28 %, respectively. The highest retention rate (of the constituents examined) was for total suspended solids (51 %). Calculations of the loadings into and out of the basin are not possible, yet, because the discharge estimates are unbalanced. This may be because the stage: discharge relationships for the Atchafalaya River at Simmesport from the 1930s to 2000 show that the stage height for the same discharge size declined when dredging for navigation was initiated in the 1960s, whereas the stage : discharge relationship became higher at Morgan City. A practical consequence of this changing stage : discharge relationship is that the US Army Corps of Engineers estimates of discharge will tend to overestimate the discharge at Simmesport, and underestimate the discharge at Morgan City. Estimates of nutrient loadings for the Atchafalaya Basin are not warranted, therefore, until a complete water balance is finalized. If the presently-available estimates of discharge are used, then they will show a net loss of water as it moves through the Basin, when no loss occurs.

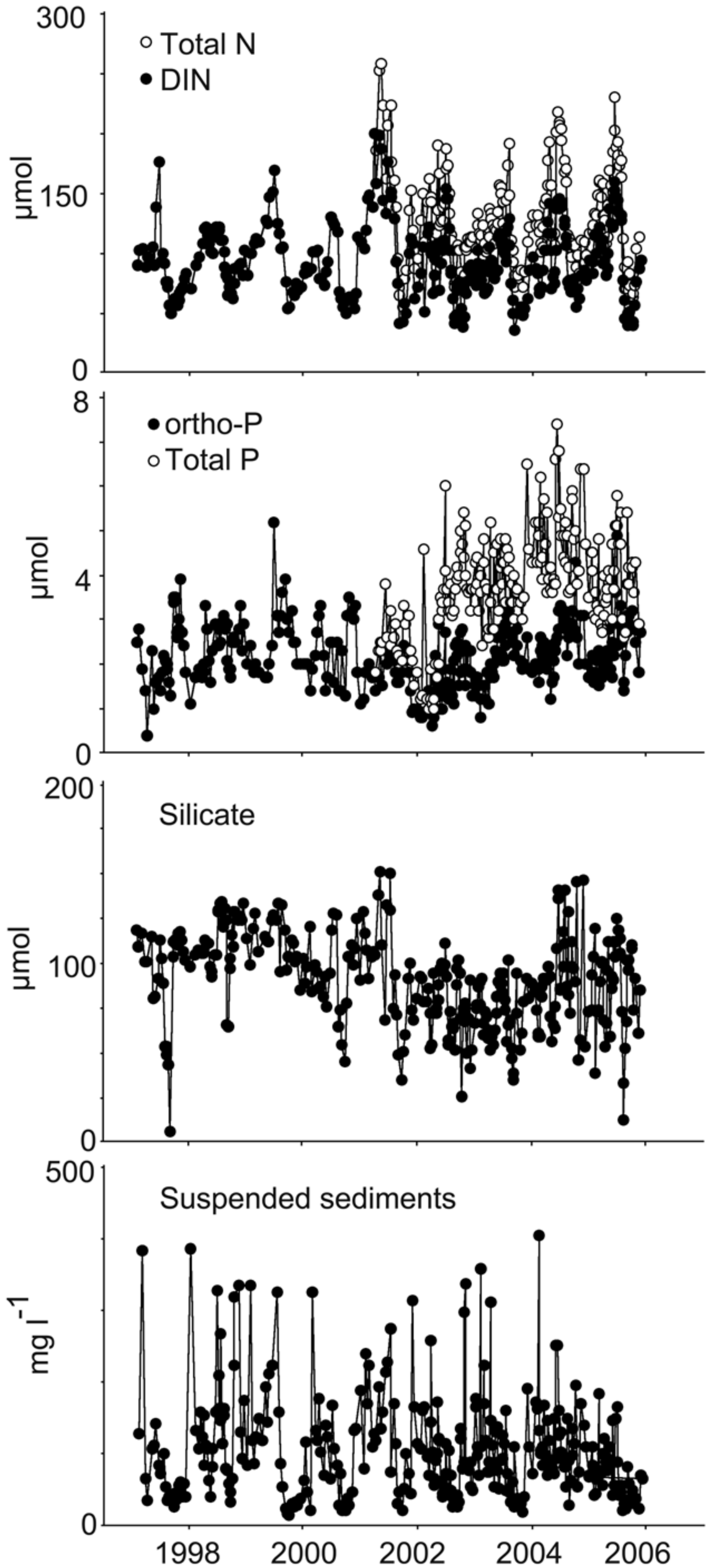

Fig. 4. The concentration of Total N, dissolved inorganic nitrogen (nitrate+nitrite+ ammonium), ortho-phosphate, Total P, silicate and suspended sediments measured biweekly, or more frequently, at Baton Rouge, LA.

Table 1. The concentration of nutrients (mg l^{-1}) in the Atchafalaya River at Simmesport, LA. (upstream) and Morgan City, LA (downstream) from 1980 to 1993. Data are from State and Federal water quality monitoring records (the numbers in the parentheses are the sample size (n) and $\pm$1 standard error; n / S.E.). The column for 'Change' is the difference in the average values for paired samples (the number of paired samples is in parentheses). From Turner (1999).

	Simmesport (upstream)	Morgan City (downstream)	Change (percent)
Total Organic Carbon (TC)	6.07	5.70	-10 %
(mg C l^{-1})	(114/0.16)	(122/0.14)	(111)
Total Phosphorus (TP)	0.287	0.206	-28 %
(mg P l^{-1})	(89/0.15)	(110/0.0099)	(89)
Total Kjeldahl Nitrogen (TKN)	0.90	0.77	-14 %
(mg N l^{-1})	(97/0.030)	(121/0.019)	(89)
Nitrate (NO_3)	0.86	0.90	+4 %
(mg N l^{-1})	(99/0.040)	(118/0.036)	(89)
Total Nitrogen (TN = TKN+NO3)	1.78	1.78	-6 %
(mg N l^{-1})	(92/0.053)	(115/0.047)	(89/0.048)
Total Suspended Solids (TSS)	181.0	91.6	-51 %
(mg l^{-1})	(107/14.8)	(127/5.4)	(89)

c) Nutrient ratios

Seasonal variations in nutrient concentrations affect nutrient availability. In particular, there is nearly a two-fold difference in nitrate load over the course of the year, but only small annual variations in the silicate and total phosphorus load. 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 molar ratios) during the rest of the year. With nutrient concentrations so closely balanced, Justic' et al. (1995) 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 co-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 molar ratio within the major riverine effluents and differences in Si : N molar 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 molar 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. A relative loss of diatoms may result in an altered marine food web and altered carbon flux from surface to bottom waters as prey items change and grazing influences shift. The changes in carbon flux will influence the size, duration and severity of the hypoxic zone.

The annual average silicate : nitrate molar ratio at St. Francisville, LA, 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 (Turner and Rabalais 1991). The molar ratio appeared stable at about 1 : 1 through 1997. The average molar ratios of N : Si, N : P and Si : P are currently 1.1, 15 and 14, respectively, and closely approximate the Redfield ratios (Redfield 1958) of 16 : 16 : 1 :: N : Si : P. The general pattern in the large rivers of the world are that the ratios are moving, or have moved, from ratios that were most likely to be P-, but not Si-limiting to phytoplankton growth, towards a P and Si-limiting situation (Turner et al. 2003b).

The monthly molar ratios of TN : TP, DIN : ortho-P, DIN : TP, SiO_2 : DIN, and SiO_2 : TN from 1974 to 2004 at St. Francisville, LA, are shown in Fig. 5 (data are from the USGS website for 2004. Nutrient load estimates for 2004, http://co.water.usgs.gov/hypoxia/html/nutrients_new.html). These five ratios demonstrate a distinct seasonal pattern moving about an annual mean. The molar ratio of TN : TP rises from the mid-1970s to the mid-1980s with a peak around 40 : 1, and then declined to about 20 : 1 up to 2004. There is a slight decline in the seasonal minimum and maximum of the DIN : ortho-P molar ratio since 1980, when the ortho-P data became available. The DIN : TP molar ratio, in contrast, remained between 10 : 1 and 20 : 1 from 1980 to 2004, and mirrors that of TN : TP, but with less variation. The molar ratio of SiO_2 : DIN parallels that of SiO_2 : TN. The latter molar ratio fluctuates around 0.8 : 1.

The TN : TP and SiO_2 : DIN molar ratios became closer to the Redfield ratios in the last 5 years (Fig. 5). A frequency distribution of nutrient ratios (dissolved silicate : dissolved inorganic nitrogen, DSi : DIN; and TN : TP) in the nutrient loads at St. Francisville, LA are in Fig. 6. Monthly data are from the USGS and divided into all data, data for spring for all years, for all years > 2000, and for spring in all years > 2000. The DSi : DIN molar ratios have been > 1 : 1 for all years, but are skewed closer to 1 : 1 since 2000, and less than 1 : 1 in the spring. The monthly values for TN : TP molar ratios have been distributed mostly between 20 and 30 : 1, but with values < 20 : 1 since 2000, the spring values were all < 30: 1. These results from sampling at Baton Rouge, LA (Fig. 5) are comparable with the changes in molar ratio observed at St. Francisville (Fig. 5).

The molar ratio of DIN : ortho-P in the river (Fig. 5) is considerably above the 'Redfield ratio' of 16 : 1, but the molar ratio of TN : TP, decreased in the last 20 years and is now close to 20 : 1 (Fig. 5). Several broadly based analyses suggest that the inorganic molar ratios should not be used to define phytoplankton growth limitation in marine waters, especially when the TN : TP values are available. Dodds (2003), for example, criticized the use of inorganic nitrogen and phosphorus as an inadequate substitute for measurements of TN and TP when applying Redfield ratios to determine trophic conditions and nutrient deficiencies. Guilford and Hecky (2000) reviewed the basis for using the inorganic or total N : P molar ratios to measure nutrient limitation in freshwater and marine ecosystems, and concluded that the TN : TP molar ratio was the most efficacious ratio to discern whether nitrogen or phosphorus limited phytoplankton growth. They demonstrated that a TN : TP molar ratio of < 20 : 1 was indicative of a nitrogen, not phosphorus limited system. A TN : TP molar ratio of > 50: 1 indicates P limitation. The average TN : TP molar ratio in the Mississippi River is far below what would be likely to be a P-limited system, but it is, according to Guilford and Hecky's analysis (2000), indicative of an N-limited system (Fig. 5).

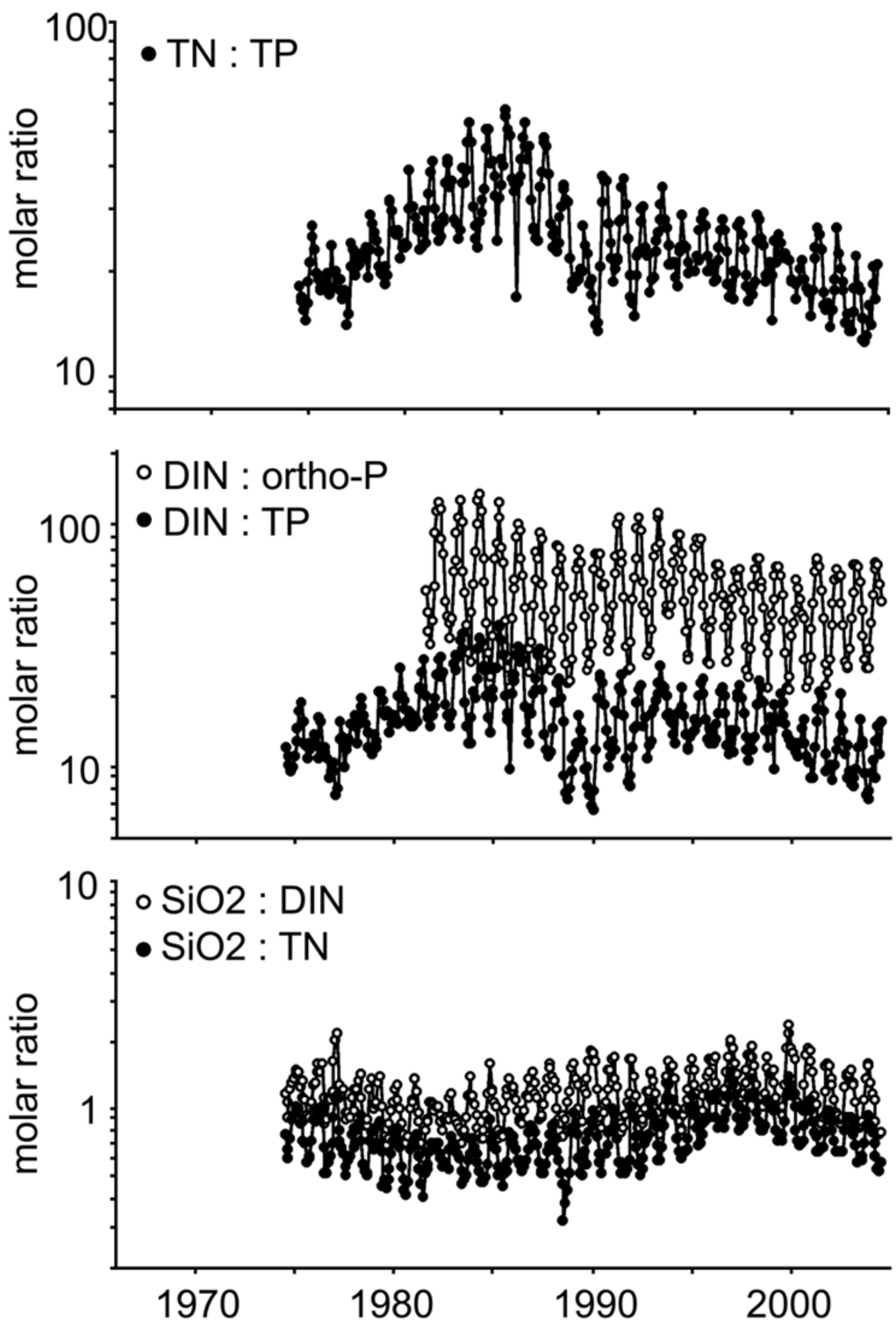

Fig. 5. The monthly nutrient ratios (molar) in water flowing down the main channel of the Mississippi River and into the Gulf of Mexico.

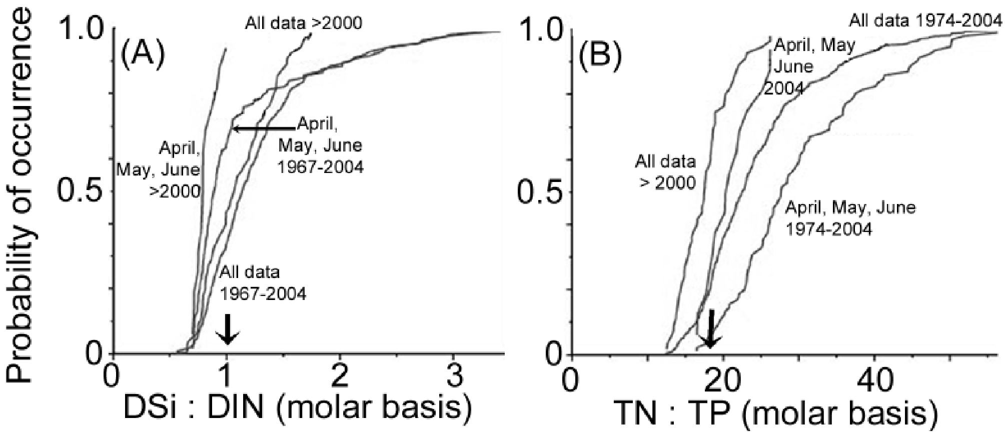

Fig. 6. Frequency distributions of nutrient molar ratios for nutrient loads in the Mississippi River at St. Francisville, LA for (a) dissolved silicate : dissolved inorganic nitrogen (DSi : DIN) and (b) total nitrogen : total phosphorus (TN : TP). Data are from the USGS and are shown separately for all data collected during the period of record, data for the spring for all years, for all years > 2000, and for spring in all years 2000-2004. Arrows indicate the Redfield ratios.

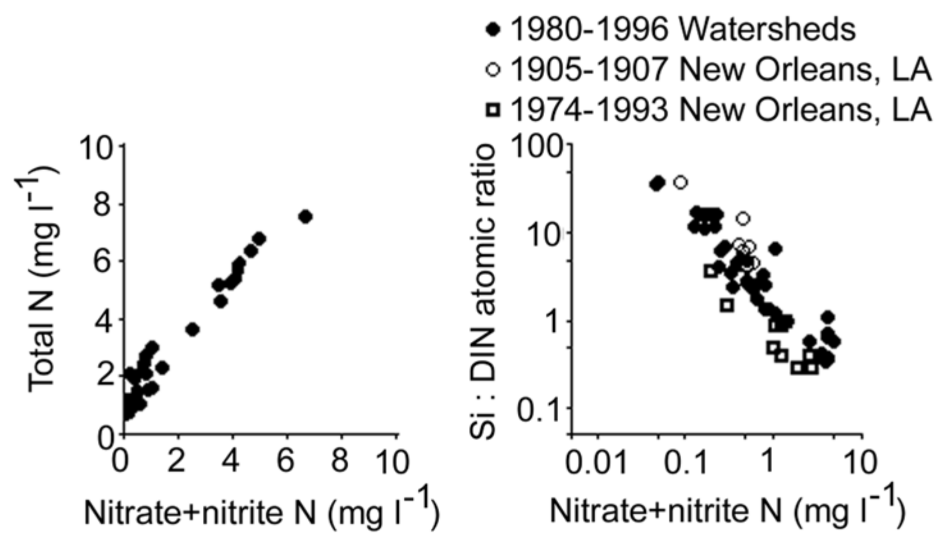

Fig. 7. Left: The relationship between total nitrogen (Y axis) and nitrate+nitrite concentration (X axis) for 42 sub-watersheds of the Mississippi River Basin (from data in Goolsby et al. 1999). Right: The molar ratio of the dissolved Si-silicate : nitrate+nitrite molar ratio versus dissolved nitrate+nitrite concentration for 42 sub-watersheds of the Mississippi River Basin (from data in Goolsby et al. 1999; 1980-1996 data) and for 529 individual sampling events at New Orleans (from Turner and Rabalais 2004).

The statistical relationships between nitrate concentration and TN and the SiO_2 : DIN molar ratio suggest that the main determinant of the variations is nitrate concentration.   There is a direct relationship between the concentration of NO_{3+2} and both the molar ratios of DIN : ortho-P and of DIN : TP (Turner et al. 2006b). The DIN : ortho-P and DIN : TP molar ratios range between a minimum molar ratio of about 20 : 1 and 10 : 1, respectively, and a maximum of 100 and 30, respectively, over the range of NO_{3+2} concentration. There was a lower SiO_2 : DIN and a lower SiO_2 : TN molar ratio as the NO_{3+2} load increased; both molar ratios were < 1 : 1 at the highest nitrate concentration.

The variability in the SIO_2 : DIN and the TN : TP molar ratio observed in the monthly loading at St. Francisville is inversely related (Fig. 8). The TN : TP molar ratio increases as the SIO_2 : DIN declines. This pattern is also observed in the world's largest rivers (Turner et al. 2003a). One consequence of this pattern is that management of one nutrient intended to achieve one nutrient ratio cannot be done in isolation of others. Management of nutrient ratios cannot be done in isolation of each other. In other words, managing nitrogen is important to achieving a particular N : Si : P goal, because the concentration of nitrogen has greater influence on nutrient ratios than the others. Also, attention on nitrogen is necessary to affect both the species composition and the rates of primary production.

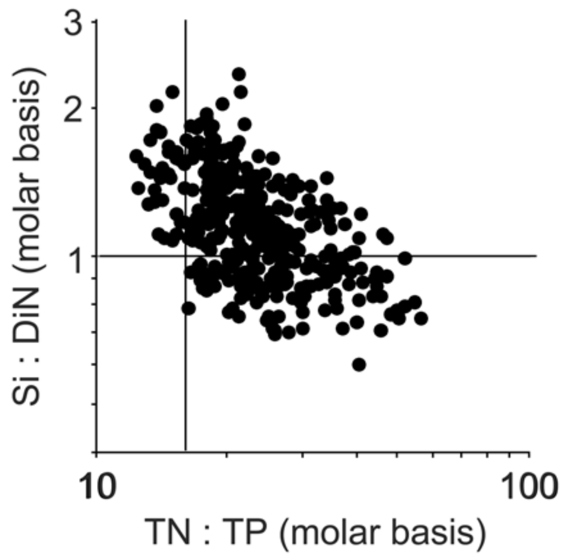

Fig. 8. The relationship between the molar ratio of TN : TP and Si : DIN for monthly samples at St. Francisville from 1967 to 2004. The horizontal and vertical lines are the Redfield ratios for TN : TP and Si : DIN, respectively.

d) **Nutrient loading of the Mississippi and Atchafalaya Rivers**

A river's nutrient load is the product of nutrient concentration X discharge and is often normalized per unit watershed area, or yields (kg km^{-2} yr^{-1}). The average yields of nutrients for the entire Mississippi River watershed are in Table 2. Different time intervals and methods for computing yields were used by the authors in this table. All of these authors except for Goolsby et al. (1999) used some combination of monthly or annual averages of solute concentration times discharge to calculate the average yield. Goolsby et al. (1999) used multiple regression models (Cohn et al. 1992) relating various quadratic, sine, and cosine functions, with discharge, solute concentration, and empirically-defined constants to estimate average daily fluxes which were then summed to produce an annual long-term average.

The yields of TP in Table 2 are within the same order of magnitude, as they should be, because they were based on a similar water quality data record collected by one agency (data records for the last 4 decades, but not necessarily for the same time period). The range of yields for TP varies from 32 to 45 kg km^{-2} yr^{-1}, 244 to 200 kg km^{-2} yr^{-1} for nitrate, 398 to 483 kg km^{-2} yr^{-1} for total nitrogen, 610 to 733 kg km^{-2} yr^{-1} for silicate, and 1052 to 1795 kg km^{-2} yr^{-1} for total organic carbon. The highest nitrate yield among the 7 sub-basins examined by Turner and Rabalais (2004) is from the Upper Mississippi watershed, and the highest silicate and total organic loading is from the Ohio-Tennessee watershed. The highest TP and TN yields are from the lower Mississippi River (Fig. 1), which also has the highest suspended sediment yields.

The Mississippi River contributes substantially to the nutrient loadings going into the lower Atchafalaya River. But the dominant flows go through the main channel past New Orleans, and into the Gulf of Mexico. The 1996-2004 loadings from the main channel of the Mississippi River to the northern Gulf of Mexico represent 75, 78, 71 and 68% of the total nitrogen, nitrate-nitrite, total phosphorus, and silica loadings, respectively, of the combined flows of the Mississippi and Atchafalaya Rivers (Turner and Rabalais 2004), which is identical to the results described by Goolsby et al. (1999; Table 3).

Table 2. Estimated yields (kg km^{-2} yr^{-1}) of suspended sediment, total phosphorus, nitrate-N, total nitrogen, silicate and organic carbon from the Mississippi River watershed at St. Francisville, LA. ND = not estimated.

	kg km^{-2} yr^{-1}					
Source	Suspended Sediments	Total Phosphorus	Nitrate-N	Total Nitrogen	Si	TOC
Keown et al. (1986)	65,380	ND	ND	ND	ND	ND
Malcomb and Durum (1976)	ND	ND	ND	ND	ND	1,052
Smith et al. (1996)	33,975	37.7	244	ND	ND	ND
Lurry and Dunn (1997)	ND	34	ND	398	ND	ND
Goolsby et al. (1999)	ND	32	302	497	733	ND
Turner and Rabalais (2004)	52,347	45	300	483	610	1,403
Trefry (1994)	ND	ND	ND	ND	ND	1,795

Table 3. The mean-annual loadings of total nitrogen, nitrate+nitrite, total phosphorus, and silica discharged from the Mississippi-Atchafalaya River Basin (MARB) as measured on the Mississippi River at St. Francisville, LA and the Atchafalaya River at Melville, LA.

	Mean annual loadings (mt) (% of the total MARB load contributed by each river)			
	Atchafalaya R. at Melville, LA		Mississippi R. at St. Franscisville, LA	
Constituent	1980-96	1996-2004	1980-96*	1996-2004
Total nitrogen	386,300 (25)	339,773 (27)	1,181,600 (75)	910,426 (73)
Nitrate-nitrite	221,100 (23)	221,086 (86)	731,600 (77)	638,351 (74)
Total phosphorus	39,500 (29)	39,763 (28)	97,000 (71)	101,004 (72)
Silicate	734,000 (32)	1,191,046 (29)	1,582,800 (68)	2,959,191 (71)

* Mean annual loadings reported in Goolsby et al. (1999)

Suspended sediments, organic carbon, and inorganic nutrients are co-related in river water. The suspended sediment yields changed over the last 150 years (Table 4). Land clearing in the watershed beginning after 1800 was accompanied by a major increase in soil erosion, and hence sediment yield, but remains without a precise quantification. The estimates of higher suspended sediment yields after European colonization would have been accompanied by a release in soil carbon and nutrients, followed by another release during the period of extensive land drainage about 90 years ago. These commonly observed soil losses eventually led to the formation of the Soil Conservation Service in the 1930s (Fig. 9). These known periods of land clearing and farm expansion were accompanied by water quality changes offshore (Turner and Rabalais 2004).

Table 4. Different estimates of suspended sediment loading to the Gulf of Mexico from the Mississippi River Basin.

Period of Record	kg km^{-1} yr^{-1}	Source
<1850	lower	(Turner and Rabalais 2004)
1879 to 1880	107,297	Fisk 1952; estimate 1
1879 to 1880	102,691	Fisk 1952; estimate 2
1851 to 1930s	117,933	postulated in Curtis et al. (1973)
circa 1890s	94,220	Dole and Stabler (1909)
1949 - 1961	85,463	Judson and Ritter (1964)
1956-1967	90,600	Curtis et al. (1973)
1963-1979	64,201	Milliman and Meade (1983)
1970 to 1988	65,380	Keown et al. (1986)
1980 to 1988	33,975	Smith et al. (1996)
1974 to 1993	52,347	Turner and Rabalais 2004

Not all of the eroded sediments find their way to the Gulf of Mexico. Many dams were constructed after WWII, particularly on the Missouri River, which dominates the suspended sediment loading among the 6 sub-basin shown in Fig 1. The suspended sediment load to the Gulf of Mexico now is about one-half of the load in the mid-1800s (Table 1). Changes in the suspended sediment loading rates also affects the loading of other carbon and nitrogen loads. A recent estimate of the dissolved organic carbon (DOC) loading to the Gulf of Mexico is 3.1×10^{-3} Pg yr^{-1} (Bianchi et al. 2004). The fluxes of particulate organic carbon (POC) and particulate nitrogen (PN) in the Mississippi River were estimated at 0.80×10^9 and 0.078×10^9 kg yr^{-1}, respectively (Duan and Bianchi 2006). From these estimates we see that the POC and PN fluxes were close to, or approximately one third, of the previous estimates (8.0×10^9 kg C yr^{-1}, Milliman and Meade 1983; 2.5×10^9 kg C yr^{-1}, Trefry 1994; 0.21×10^9 kg TN yr^{-1}, Goolsby et al. 2000).

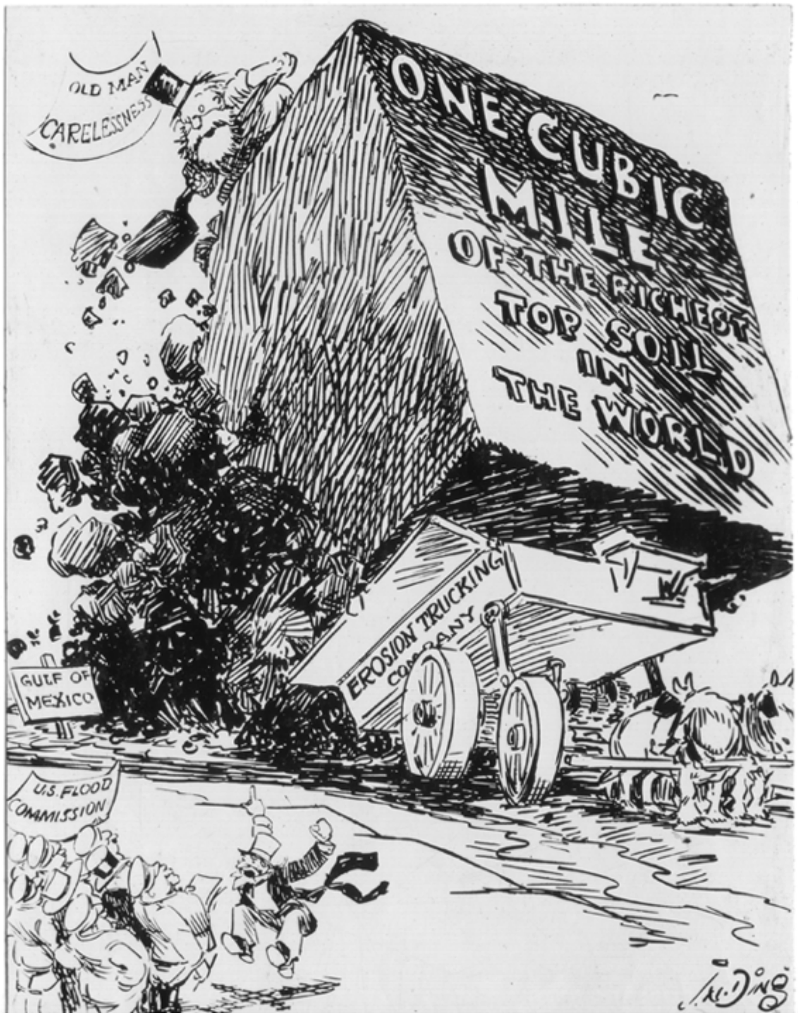

Fig. 9. "One cubic mile of the richest top soil in the world" is shown being delivered to the Gulf of Mexico, as an excited caricature of Uncle Sam is agitating to get the attention of the U.S. Flood Commission to do something about it. Photo (circa 1935) 114SC 28, MO2, from Audiovisual Records RG 114, Soil Conservation Service, Missouri State Conservationist, Box 1, Coordinated Plan of Soil Erosion Control, U.S. Department of Agriculture, Soil Conservation Service, Bethany Missouri. National Archives and Records Administration, Kansas City, MO.

The organic carbon in the lower Mississippi River consists of POC and DOC derived from both terrestrial and phytoplankton sources (Benner and Opsahl 2001; Bianchi et al. 2002, 2004; Dagg et al. 2005**)**. The relative importance of these different sources is influenced by discharge and suspended particulate matter (SPM). There are more phytoplankton during low flow stages when there is more light available, and there is a greater contribution of phytoplankton-derived DOC during these low flow periods (Bianchi et al. 2004). However, there is also likely to be more settlement of phytoplankton during the lower, compared to the higher, flow stages, as limited data in Dagg et al. (2005) demonstrates. Recent work (Goni et al. 1997, 1998; Onstad et al. 2000; Gordon and Goni 2003) has suggested that much of the terrestrially-derived organic carbon delivered from the lower MR to the shelf is composed of C_3 and C_4 plants and materials from eroded soils in the northwestern grasslands of the Mississippi River drainage basin. These investigators also concluded that C_4 plant material was transported greater distances offshore because of its characteristically smaller grain size. Woody angiosperm material preferentially settles within the lower Mississippi River and in the proximal portion of the dispersal system on the shelf (Bianchi et al. 2002).

Trends in the monthly nutrient flux at St. Francisville, LA, can be computed annually using the USGS's NASQAN (National Stream Quality Accounting Network) approved method for calculating nutrient loads using the generalized SAS ESTIMATOR model without the time-squared term. This model is described in Goolsby et al. (1999), and is based on the work of Gilroy et al. (1990) and Cohn et al. (1992). The annual and monthly estimates are available on the USGS website (http://co.water.usgs.gov/hypoxia/html/nutrients_new.html). Loads calculated at St. Francisville use flow from the Mississippi River at Tarbert Landing, Mississippi, and at the Old River Control Structure near Knox Landing, Louisiana. The loads were calculated as mt of nitrate + nitrite nitrogen (NO_{3+2}), ammonium nitrogen (NH4), dissolved inorganic nitrogen (DIN; NO_{3+2} + NH_4), total nitrogen (TN = Kjeldahl nitrogen + NO3+2), ortho-phosphate phosphorus (ortho-P), total phosphorus (TP) and dissolved silicate (SiO2).

The minimum and maximum river discharge, the monthly average discharge, and the May discharge in the Mississippi River is not demonstrably increasing or decreasing for the period 1968 to 2004 ($p > 0.4$; Fig. 10). The monthly maximum load of NO3+2 is > 67 % (+/- 1 %; +/- 1 SE) of the load of TN ($R^2 = 0.98$). In contrast to the trends of discharge and TP, the load of NO3+2 increased from less than 50,000 mt in 1968 to above 120,000 mt in 1985, while the baseline flow remained low, and then declined to an intermediate level of around 70,000 mt. The monthly load of ortho-P averages 21 % (+/- 1 %; +/- 1 SE) of the load of TP ($R^2 = 0.54$); both have been fairly stable after the rise in nitrate loading. The dissolved silicate load is quite variable on a monthly basis, but stable around an average annual value of 100,000 mt (Fig.10).

The monthly loads of TN, TP, nitrate and silicate at St. Francisville, LA, from 1997 to 2004 are linearly related to the nutrient loads in the Atchafalaya River at Melville, LA, in the middle of the Atchafalaya swamp (Fig. 11). The slopes of the lines are nearly statistically equal, except for the comparison of TP loadings at the two locations. For that one exception, the slope becomes 0.34 when the values above 5000 mt @ Melville are removed. There is, therefore, a strong dependence of nutrient loading in the Atchafalaya River on the nutrient content of the Mississippi River. In other words, the content of the Red River is a minor influence on the concentration of nutrients reaching the Atchafalaya delta. When combined with the information in Table 1, we conclude that the loading of these constituents at Morgan City are driven by the loading in the main stem of the Mississippi River, and not modified significantly during its transit downstream, or diluted by the constituents in the Red River. The loading at the mouth of the Mississippi River is, therefore, expected to be a fairly stable and proportional load of the sum of the loads from the Mississippi and Atchafalaya Rivers.

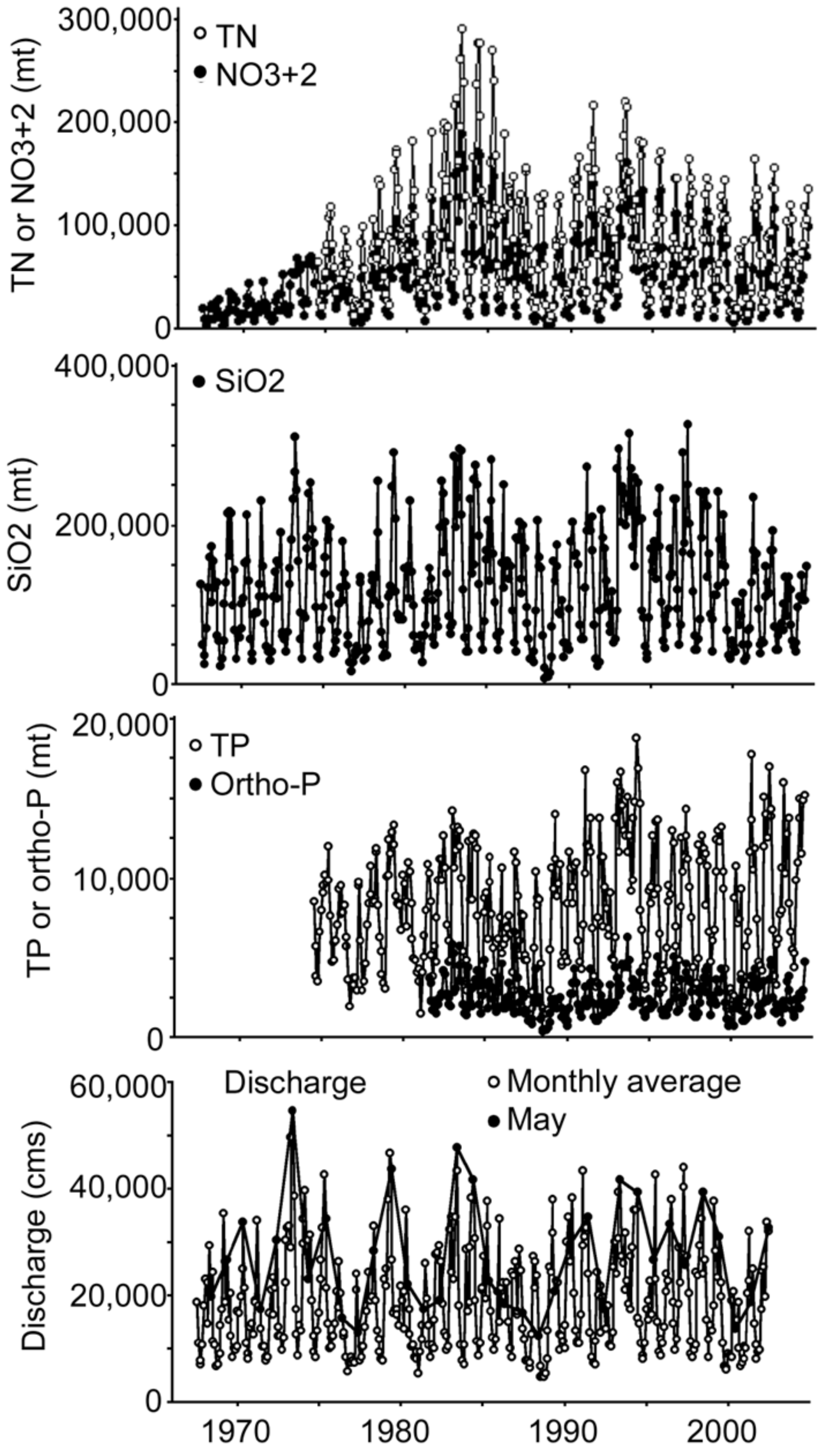

Fig. 10. The monthly discharge (cms = $m^3\ s^{-1}$) and nutrient load of TP, TN, NO_{3+2}, and SiO_2 (mt) flowing down the main channel of the Mississippi River and into the Gulf of Mexico from 1968 to 2004. The May values are the filled circles. Station locations are at St. Francisville, LA, for concentrations, and at Tarbert Landing for discharge (downstream of St. Francisville).

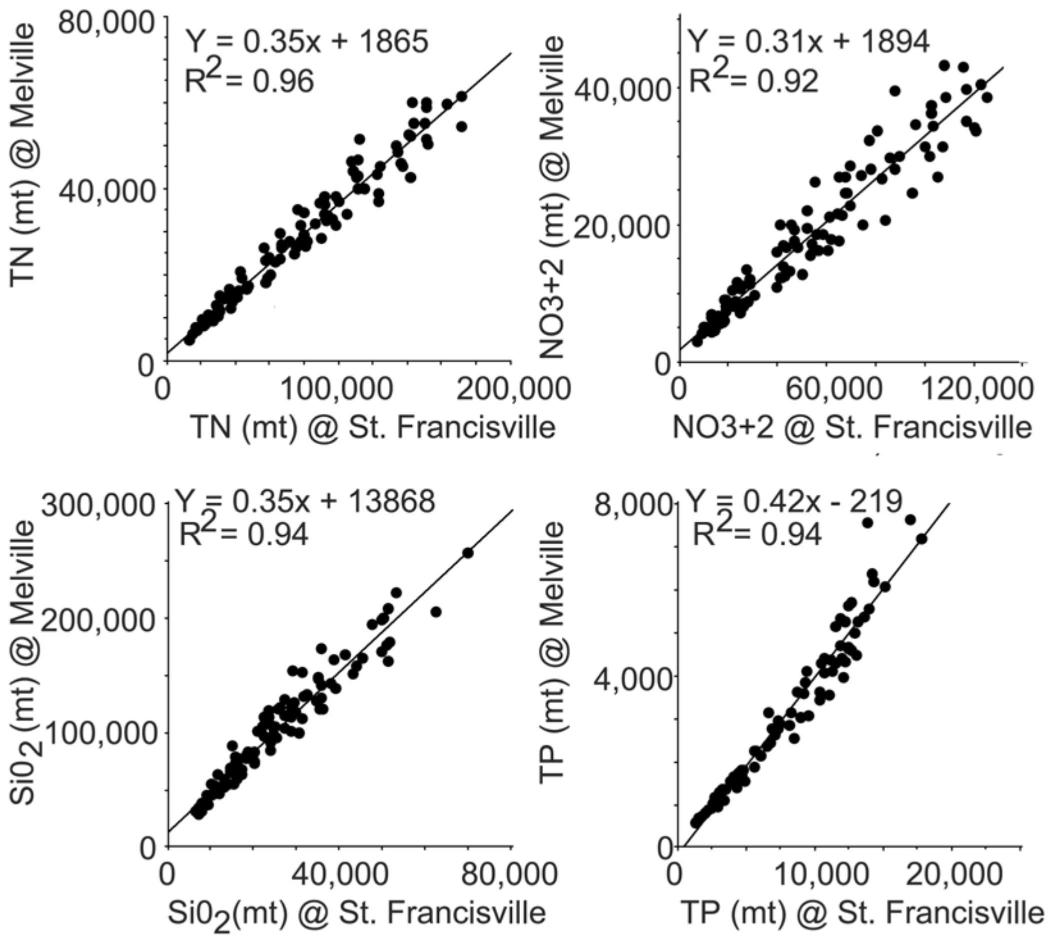

Fig. 11. The monthly loading of total nitrogen (TN), nitrate + nitrite (NO_{3+2}), silicate ($Si0_2$) and total phosphorus (TP) in the Atchafalaya River at Melville, LA, and in the Mississippi River at St. Francisville, LA, from 1967 to 2004.

e) **Additional carbon sources**

One additional source of carbon (and the associated nitrogen and phosphorus) deserves quantification because of comments provided over the years since the Action Plan was completed. This source is the carbon released from eroding wetlands on a coastline whose wetland loss rates were 11,117 ha yr^{-1} from 1955 to 1978 (Baumann and Turner 1990), and dropped to 2470 ha yr^{-1} from 1990 to 2000 (Morton et al. 2005).   There are at least two issues regarding the importance of marsh-derived carbon to the loading of organic loading offshore. The first issue is whether this marsh-derived C is significant and released in a timely manner. The second is whether the wetland-derived carbon is respired before it arrives offshore. The amounts of the wetland-derived carbon can be estimated, but determining the susceptibility to decomposition is problematic, so we chose to overestimate the loading to offshore with this preliminary estimate.

Some assumptions were made to make a first estimate of potential organic loading from eroded wetlands: (a) All carbon from a 1 m deep layer was presumed to be 100 % labile, but not respired until it exited the estuary, and was evenly distributed offshore over a hypoxic zone of 15,000 km^2, but not anywhere else on the shelf. (b) The carbon content of the wetland soil profile was assumed to be 3.8 % organic matter by volume (Turner et al. 2001), 1.14 g organic per cm^{-3}, and 50 % carbon. The potential amount estimated to be released is 37 g C m^{-2} y^{-1} and compares to a surface primary production rate of 10 X that value. Thus the carbon from decaying wetlands appears to be relatively small compared to the river nutrient-enhanced primary production spread out over the same continental shelf (300 g C m^{-2} y^{-1}; Sklar and Turner 1981). The assumptions involved in this estimate of how much might be released from a decaying wetland system clearly result in an overestimate of the actual flux of marsh-derived carbon going to the offshore zone, and the carbon exported will not be distributed evenly on the shelf. We conclude that it is highly unlikely that Louisiana's fragmenting wetlands are a significant carbon source for bottom water respiration in the hypoxic zone.

f) **Wetland interactions**

Nutrients in the river may not reach offshore waters if they are denitrified or buried as water passes through coastal wetlands. Suggestions regarding the importance of this wetland-water interaction were embedded in the foundation documents, and eventually published (Mitsch et al. 2001). Their idea was to explore how much nitrogen was removed under present conditions and how much might be removed with the construction of additional river diversions. We conducted a similar analysis using the following assumptions which err on the side of excessively high estimates: (a) the area of wetland is 10,093 km^2 (Baumann and Turner 1990), (b) the low and high discharge (13 and 26 % of the river) is spread over 5,000 and 10,000 km^2, and (c) the removal/retention is less than 30 % and proportional to flow (Table 5). Kesel (1988) estimated that less than 3 % of the river discharge went over the natural levees or through crevasses as unconstrained overbank flow (before navigation and flood protection levees). The present-day Davis Pond and Caenarvon diversions upstream and downstream from New Orleans, respectively, have an average flow of about 0.65 % of the Mississippi River near New Orleans, and are projected to affect about 8 % of the coastal wetlands. The pre-colonization nitrogen retention/denitrification resulting from overbank flow is less than 1 %, and the two present-day diversion might collectively reduce nutrient loading by the river by less than 1 %. The proposed removal of nitrogen from water flowing over 99 % of the coastal wetlands was projected to result in the loss of 8 % of the nitrogen. Based on proportional amounts, then the present 0.65 % river diversion would result in the removal of 0.2 % of the river's nitrogen. The engineering miracles necessary to spread the diverted water evenly over the wetlands are daunting tasks, even if the necessary levees are an acceptable environmental cost. Increasing the capacity for diversion by a factor of ten times more than presently in operation is not likely to exist within the next few decades. Using the logic and numbers of Mitsch et al.'s (2001) analysis leads one to conclude that there will be an insignificant reduction in the nitrogen loading from river to sea, as a result of river diversions, as presently constructed and used.

Table 5. A summary of projected nitrogen removal/retention rates for different amounts of water leaving the main channel of the Mississippi River and over coastal wetlands.

Path into estuaries via	% annual discharge	% all coastal wetland area	% N retained/denitrified
Unconstrained overbank flow and crevasses (Kesel 1988)	<3	?	<1
Caenarvon + Davis pond	0.65	8	<1
Mitsch et al. (2001) – proposed low	13	50	4
Mitsch et al. (2001) – proposed high	26	99	8

g) Landuse and water quality models

A key conclusions of the Goolsby et al. (1999) report concerned the source of nitrogen loading delivered by the Mississippi River. They concluded that about 90 % of this N loading was from non-point sources. This conclusion was reasonable when it was made, and has been confirmed in several ways since, particularly by using models driven by landuse and water quality. We hasten to add that models often have difficulty accounting for the influences of factors such as changes in wetland drainage, subsurface drainage of cropland, stream channelization, as well as the spatial applications of fertilizer and manure. This is because data are lacking, and because many factors influencing nutrient flux have changed simultaneously over time making it difficult to identify precise cause and effect relationships between factors and changes in N fluxes. Changes in subsurface drainage of cropland, for example, could potentially have a large influence (McIsaac and Hu 2004), but the data on this practice are woefully incomplete.

Variations in estimates of nitrogen yields from the MRB and its coastal watersheds are statistically described by the percent of land in cropland and population density (Turner and Rabalais 2004; Donner 2002, 2003; Donner and Kucharik 2003a, b). There is some difference in the statistical significance of variables in each data set, in part because of differences in climate, soils, land use, and subsurface drainage, as well as a mismatch of census data, stream discharge records, and land use for both data sets. Population density is another representative indicator of nitrogen transformation and sources in the landscape. Peierls et al. (1991) and Howarth et al. (1996), for example, described a strong relationship between population density and nitrogen yields for several large river watersheds. A multiple regression equation, predicting nitrogen yield on the basis of the land in crops and population density, explains 78 to 83 % of the variation for the three individual data sets, and 60 % for all data sets combined (Turner and Rabalais 2004). Both population density and land use affect water quality. The annual per capita yield in these regression equations ranges from 2.3 to 9.7 kg TN per capita, with the coastal data sets having a lower per capita yield (Turner and Rabalais 2004; 2.6 kg TN per capita compared to 5.3 to 9.7 kg TN per capita for the MRB). The loading of P among watersheds is also heavily influenced by population density and landuse intensity (Caraco 1995).

The variability in TP yield (TP; kg km^{-2} yr^{-1}) and per capita density (persons km^{-2}) and for watersheds within the Mississippi River Basin is in Table 6 (using data in Goolsby et al. 1999, and Lurry and Dunn 1997). The adjusted coefficient of determination (R^2) was 0.86 and 0.46, for the Lurry and Dunn (1997) and Goolsby et al. (1999) data sets, respectively (Table 6). The difference in R^2 values may be because the average watershed size was 8.6 times larger in the data set developed by Lurry and Dunn (1997) compared to the data developed by Goolsby et al. (1999). The use of data from larger watersheds would tend to dampen out the variability arising from the effects of channel morphology (e.g., Alexander et al. 2000). The area of the watershed in cropland had a statistically significant effect on TP yield at the $p = 0.001$ in the Goolsby et al. (1999) data set, but $p > 0.09$ for the Lurry and Dunn (1997) data set.

Table 6. Multiple linear regression equations describing the variation in total phosphorus yield (TP, kg km^{-2} yr^{-1}) for various watersheds of the Mississippi River Basin, and the independent variables: % cropland and per capita density. All results are significant at a $p = 0.001$ level of confidence. NS = not significant.

A. Data set	Number	Average Size (1000 km^2)	Intercept kg TP km^{-2} yr^{-1}	Adjusted R^2	TP (± 1 Std. Error) Per Capita	% Cropland
Mississippi River Basin						
1. Goolsby et al. (1999)	41	57	26.8	0.46	0.39 (± 0.12)	0.80 (± 0.24)
2. Lurry and Dunn (1997)	38	493	23.9	0.86	0.55 (± 0.82)	N.S.

McIsaac et al. (2002) provided a comparison of several empirical models of riverine nitrate flux in the Mississippi River watershed using land use, atmospheric loading and soil organic N. Their results and those presented here substantiate the observations and calculations of many that human intervention within the natural landscape has re-formed stream and river water quality on the scale of the world's largest river basins (e.g., Turner and Rabalais 1991; Howarth et al. 1996; Jordan et al. 1997; Caraco and Cole 1999).

Analyses of smaller watershed monitoring data also document the effect of present land use on stream water quality. Jordan et al. (1997) showed that nitrate yields went up, and the Si : N yield down as the cropland area increased for 27 watersheds of Chesapeake Bay. Smart et al. (1985) studied watersheds in the Missouri Ozarks in the summer of 1979 and found that the nitrogen content went up as the land in pasture increased. They concluded that the stream nutrient concentrations were more strongly related to land use, than to bedrock geology. Their simple multiple regression equation explained 43 % of the variation in TP, using watershed size and the percentage land as urban area. Eighty-percent of the variation in TN was explained (in a statistical sense), using the percentage land in pasture and urban area. Perkins et al. (1998) showed similar results for all four major types of Missouri watersheds, as did Jones et al. (1976)

for 34 watersheds in northwestern Iowa (3 year data set). The molar ratios in the water are subject to the type of land use, as well. For example, Arbuckle and Downing (2001) showed that water flowing from 113 Iowa landscapes dominated by row crops had high N : P molar ratios (molar ratios > 100), whereas landscapes dominated by pasture lands had low molar ratios (molar ratios about 16 : 1).

Regional mass balances of reactive nitrogen inputs and outputs provide a quantitative assessment of the sources of reactive nitrogen and can suggest the approximate scale and scope of remediation alternatives. Such mass balances have shown that average annual riverine N flux is highly correlated with average annual net anthropogenic N input (NANI) to the drainage basin (Howarth et al. 1996, Boyer et al. 2002). NANI is the sum of fertilizer, biological fixation associated with crops and atmospheric deposition of oxides of nitrogen minus the N exported in food and feed. The values of inputs and outputs can be estimated from annual agricultural and census statistics and data from the National Atmospheric Deposition Program.

Working within an N budgeting framework, McIsaac et al. (2002) compared different approaches to estimating N fluxes within the basin and concluded that several of the fluxes used by Goolsby et al. (1999) were problematic. Including these terms in the N budget led to a negative correlation between residual N inputs to the landscape and riverine N fluxes. When7 these problematic fluxes were removed from the overall N budget, the resulting estimate of residual N was positively correlated with riverine N fluxes. These problematic N fluxes included ammonia volatilization from soils and crop canopy, mineralization and immobilization. The resulting model replicated the actual data quite well (Fig. 12).

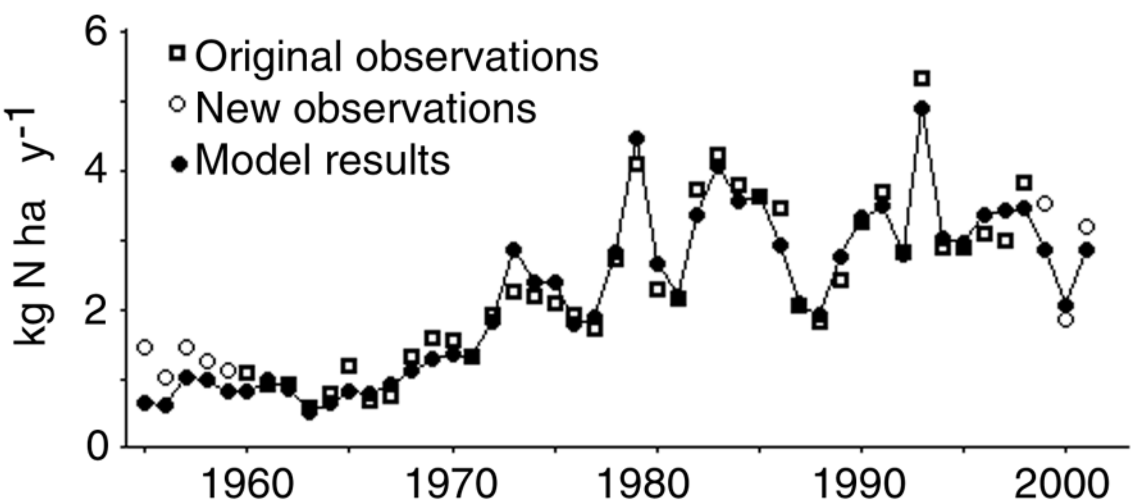

Fig. 12. Mississippi River nitrate N flux: the observed and modeled estimates using annual water yield and net N Input for the Mississippi River Basin (estimated by McIsaac, in Turner et al. 2006b). The original N input data are available in Goolsby et al. (1999), which began in 1951, and the first year that could be modeled using a 9 year lag was 1960.

The results from a variety of statistical and spreadsheet-based models are strikingly robust. They provide the explanation for the relative rise in nitrogen loading from the Upper Mississippi River basin during the last 100 years.

h) **Interactions/transformations in the mixing zone**

The quality and quantity of nutrients and sediments measured at upstream stations (e.g, above the fall line) may be different from those arriving at the coastal zone as a result of storage, transformation, or added inputs below the gauged locations. Seasonal sediment storage and remobilization has been documented for the lower Mississippi River below New Orleans (Meade and Parker 1985). The hydrologic control of sediment storage and remobilization has been characterized, and a Lagrangian transport model has been formulated, that reproduces the rate and timing of storage and remobilization in the lower Mississippi River (Demas and Curwick 1988; Mossa1996). During higher discharge stages increases in current velocities result in greater bottom shear stresses that can surpass threshold values for re-suspension (Mossa 1996). Conversely, during periods of low water discharge a salt-water wedge intrudes into the main stem Mississippi River channel from the Gulf of Mexico, forming a flow convergence zone whose position is predominantly controlled by the amount of water discharged, flow duration, wind velocity and direction, tides and water temperature (Soileau et al. 1989). Riverbed cores collected after the salt wedge had covered a site for ~3 months, exhibited elevated porewater concentrations of diagenetic products (e.g., dissolved organic carbon (DOC), inorganic nutrients), indicative of significant organic carbon re-mineralization (Sutula et al. 2004). Therefore, it is likely that the deposition, alteration and subsequent remobilization of materials on the riverbed during low discharge are quantitatively important to the flux, phase partitioning and reactivity of materials that reach the ocean during such periods. Processes within the river-ocean interface may, therefore, alter the partitioning (dissolved/particulate) or abundance/composition of dissolved/particulate materials delivered to the ocean.

i) **Monitoring station density and quality**

Water-quality monitoring of the main stem lower Mississippi and Atchafalaya Rivers has improved recently with the addition of sites below New Orleans and at Morgan City, LA; however, the monitoring is far from complete. Over the past three decades, the most comprehensive water-quality monitoring, based on depth and width integrated sampling, has been conducted by the USGS on the lower Mississippi at St. Francisville, LA, 265 miles upstream of the Gulf outlet, and on the lower Atchafalaya River at Melville, LA, 115 miles upstream from the Gulf. Beginning in 1996, USGS increased the frequency of sampling at these locations (Hooper et al. 1997) from bimonthly to monthly with additional sampling during high flows to support load estimation. Organic and inorganic carbon measurements were also added. However, monitoring was discontinued at two downstream sites, where samples had been collected historically, the Mississippi River at Belle Chase, LA (73 miles above the Gulf outlet) and at the Atchafalaya River at Morgan City, LA (31 miles above the Gulf). Several sites were also discontinued on the main stem of the lower Mississippi River between the Ohio River at Grand Chain, IL and St. Francisville, LA, where many major tributaries enter the river, including the Arkansas, White, and Yazoo rivers. State and local agencies monitor various sites along the lower Mississippi R., including Baton Rouge (e.g., see data in Fig 4) and many in the vicinity of New Orleans, but the sampling is often insufficient for estimating loads. Common problems include the lack of high-flow and depth and width integrated samples. Both sampling conditions are necessary for accurate load estimates with the latter especially important for obtaining concentration measurements that are representative of the entire flow volume. Accurate flow measurements and load estimates are difficult to obtain below Belle Chase and Morgan City because of the strong tidal influences on streamflow. In May 2006, the USGS re-established monitoring on the Mississippi River at Belle Chase and on the lower Atchafalaya River at Morgan City and at the Wax Lake outlet. USGS plans to continue monitoring at the two upstream sites, St. Francisville and Melville, to quantify any differences that may occur in concentrations between the upstream and downstream locations. Daily streamflow measurements are generally sufficient to support current water-quality monitoring in the lower reaches of the Mississippi and Atchafalaya rivers; flows have been historically measured on the Mississippi River at Tarbert Landing located above St. Francisville, LA and on Atchafalaya River at Simmesport, LA (25 miles above Melville, LA) and at the Atchafalaya River at Morgan City and the Wax Lake outlet.

Federal monitoring of the inland waters of the Mississippi River Basin, which is critical for identifying pollutant sources, has declined precipitously over the last decade (U.S. Commission on Ocean Policy 2004). For example, USGS NASQAN monitoring sites in the Mississippi River basin declined from more than 100 before 1995 (Alexander et al. 2000) to fewer than 20 sites in the last decade (Hooper et al. 1997). The current sites are located on the Mississippi main stem and selected major tributaries. Of the 42 sites that were used to estimate nutrient sources in the Mississippi River Basin as part of the first assessment (see Goolsby et al. 1999), only 12 are currently monitored.

The USGS annually updates their estimates of nutrient and silica loads for monthly and annual time periods for the monitored sites on the lower Mississippi (St. Francisville) and Atchafalaya (Melville) rivers, using rating-curve estimation procedures (USGS 2004; e.g., see data in Fig. 6). These procedures combine the most recent 12 to 18 annual water-quality measurements with those from the long-term record (consisting of more than 100-200 observations) and daily streamflow values for the sites to yield much more accurate load estimates than can be obtained by using only the individual measurements during a specific month or year of interest. The accuracy of the loads is lower for monthly than for annual estimates and is higher for nitrogen (total and nitrate-nitrite) than for phosphorus, carbon, and suspended sediment, which exhibit greater variability over time. For the Mississippi River at St. Francisville, the prediction accuracy of the monthly load estimates (for a one standard deviation uncertainty interval) ranges from +/-7 % for total nitrogen to +/-11 % for suspended sediment (95 % uncertainty intervals on the predictions would increase these percent errors by about a factor of two). The accuracy of the annual load estimates range from +/-3 % for total nitrogen to +/-6 % for suspended sediment. For the Atchafalaya River at Mellville, prediction accuracies are typically 25 % to 50 % lower than those for Mississippi River loads because of the higher variability in the concentrations and flows in the Atchafalaya. For example, accuracies in the monthly load estimates for the Atchafalaya River are +/-13 % and +/-16 % for total phosphorus and suspended sediment, respectively.

The accuracy of load estimates are considerably worse for shorter time periods (<monthly) and for monthly and annual estimates that are based on data from relatively few years of record (e.g., Horowitz 2003). Over periods of fewer than ten years, the current levels of accuracy are generally sufficient for detecting only very large annual changes in loads that may

occur in response to natural and managed changes in the watershed. Evaluations are needed to quantify the specific limits on detecting changes over time in the loads for the various water-quality constituents, based on current sampling frequencies and rating-curve models, and to determine whether the current levels of accuracy satisfy the requirements of existing statistical and mechanistic models of the nutrient dynamics and hypoxic conditions in the northern Gulf of Mexico.

j) **An update of the 1999 assessment**

(a) What are the major sources of nutrients delivered to the hypoxic zone?

The Mississippi River system contributes, by far, the major source of nutrients to the northern Gulf of Mexico where hypoxia is likely to develop. The relative contribution of direct atmospheric deposition of nitrogen to the total nitrogen load for an area twice the size of the hypoxic zone is 1 % (Goolsby et al. 1999). Groundwater sources to the area affected by hypoxia are unlikely to be important because of the lack of shallow aquifers along the Louisiana coast and the low potential for transfer in a cross-shelf direction to the area where hypoxia develops (Rabalais et al. 2002). The relative contribution of offshore sources of nutrients from upwelled waters is unknown, but expected to be minimal considering the alongshore current regime. The emphasis on nitrogen loading from non-point sources in the Mississippi River watershed appears warranted based on the nutrient ratios and temporal changes in nutrient loadings. The carbon from eroding wetlands at the coastline are not likely to be a significant source of carbon fueling the hypoxic zone offshore, because (a) the amount of carbon estimated to flow from disintegrating wetlands is not large enough to cause the formation of the hypoxic zone, including after re-aeration events, b) labile carbon is likely to be used before it leaves the estuary and be spread across the shelf, and, (c) landloss rates peaked before the beginning of the hypoxic zone started to be a regular occurrence on this shelf, and, (d) the hypoxic zone has a sustained size, whereas the land loss rates have descended to a historical low, post-1960s.

(b) What changes recently occurred in nutrient concentration and loads to the Gulf of Mexico?

Suspended sediment concentrations rose in the 1800s as the watershed was cleared of forests and the land plowed, fell after the 1930s, and particularly after the dams on the Missouri in the 1950s. A minor proportion of the Mississippi River nitrogen load is sequestered or denitrified as it passes through wetland ecosystems on the way to coastal waters (1 % or less). An analysis of water quality measurements made from 1996 to 2005, when compared to the data used by Goolsby et al. (1996), show that the average discharge of the Mississippi River is higher, but within the long-term variance for data collected since 1817. The variability in discharge can compensate for changes in nutrient concentration to result in situations where nutrient concentrations or ratios move in opposite direction to changes in individual nutrient loads over different intervals. The total load of TN and TP have been variable on a monthly basis from 1996 to 2005, but the annual load appears relatively stable. Compared to 1975 to 1996, the average 1997-2005 concentration of TN at St. Francisville, LA, declined 17% while the TP concentration rose 12%, creating a 26% decline in the TN : TP ratio to the point where N growth imitation of phytoplankton, rather than P limitation, appears likely.

(c) Are there significant modifications of the science used in the Action Plan?

We know of no significant changes in the conclusion that the Mississippi River watershed nutrient loadings are the dominant source in the northern Gulf of Mexico, including the hypoxic zone area.

ACKNOWLEDGMENTS
The NOAA Center for Sponsored Coastal Ocean Research, Coastal Ocean Program, Grants No. NA03NOS478003 to Louisiana Universities Marine Consortium and award NA06OP0529 to Louisiana State University supported the research and preparation of this manuscript. We thank T. Bianchi for contributions to the section on the transformation of materials in the mixing zone.

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Abbreviations

C	carbon
cms	cubic meters per second ($m^3 s^{-1}$)
DIN	dissolved inorganic nitrogen (nitrate+nitrite+ammonium)
DOC	dissolved carbon
Kjeldahl N	organic nitrogen + ammonium
N	nitrogen
N03+2 or NO_{3+2}	nitrate+nitrite
Ortho-P	ortho-phosphate
P	phosphorus
Pg	Peta
SiO2 or SiO_2	silicate
Si	Silica
TOC	total organic carbon
TN	total nitrogen = DIN + Kjeldahl nitrogen)
TP	total phosphorus