Historical Nitrogen and Phosphorus Loadings to the Northern Gulf of Mexico

NOAA Technical Memorandum NOS NCCOS 85

Cover Photo: A bird's eye view of a bird's foot delta - the Passes of the Mississippi River. Credit: NOAA Photo Library

Citation for this Report:
Whitall, D.R. 2008. Historical Nitrogen and Phosphorus Loadings to the Northern Gulf of Mexico NOS NCCOS 85. Silver Spring, MD. NOAA/NOS/Center for Coastal Monitoring and Assessment. 25 pp. For copies of this report, please contact David Whitall (dave.whitall@noaa.gov)

Historical Nitrogen and Phosphorus Loadings to the Northern Gulf of Mexico

David Whitall
Center for Coastal Monitoring and Assessment
NOAA/NOS/NCCOS, 1305 East/West Highway, Silver Spring, MD 20910

NOAA Technical Memorandum NOS NCCOS 85

November 2008

United States Department of Commerce

Carlos M. Gutierrez
Secretary

National Oceanic and Atmospheric Administration

Conrad C. Lautenbacher, Jr.
Vice Admiral (Ret.), Administrator

National Ocean Service

John H. Dunnigan
Secretary Assistant Administrator

Table of Contents

List of Figures ……………………………………………………………v

I. Introduction ……………………………………………………………1
Eutrophication……………………………………………………………1
Hypoxia ……………………………………………………………1
Sources of Nitrogen and Phosphorus……………………….…………………..2

II. Objective ………………………………………………………………..2

III. Data Sources and Methods ……………………………………………………2

IV. Results ………………………………………………………………………3
Long Term Trends in Riverine Loading………………………………………3
Seasonal Patterns in Riverine Loading…………………..…………………3
Covariation in Nutrient Loads……………………...………………………3
Trends in Fertilizer Use……………………………………..……………3
Trends in Atmospheric Deposition……………………………………………4
Trends in Human Population…………………….…………………………4

V. Discussion ……………………………………………………………………...4
Link to Hydrology………………………………………………………4
Stoichiometry……………………………………………………………4
Modeling Implications……………………..……………………………5
Management Implications………………………………………………5

VI. Acknowledgments……………………………………………………………..6

VII. References……………………………………………………………………..7

VIII. Figures………………………………………………………………………..11

List of Figures

Figure 1: Annual hypoxia in the northern Gulf of Mexico …………………………...11

Figure 2: Location of USGS riverine monitoring stations ……………………………11

Figure 3: Time series of monthly total nitrogen (TN) loadings for the Mississippi River from 1974-2008……………………………………………11

Figure 4: Time series of monthly nitrate + nitrite (NO_3^- + NO_2^-) loadings for the Mississippi River from 1974-2008……………………………………………11

Figure 5: Time series of monthly total Kjeldahl nitrogen (TKN) loadings for the Mississippi River from 1974-2008…………………………………...……..11

Figure 6: Time series of monthly ammonia (NH_3) loadings for the Mississippi River from 1974-2008……………………………………………………………..11

Figure 7: Time series of monthly total phosphorus (TP) loadings for the Mississippi River from 1974-2008……………………………………………………………12

Figure 8: Time series of monthly total nitrogen (TN) loadings for the Atchafalaya River from 1979-2008……………………………………………………………12

Figure 9: Time series of monthly total Kjeldahl nitrogen (TKN) loadings for the Atchafalaya River from 1979-2008…………………………………………….12

Figure 10: Time series of monthly ammonia (NH_3) loadings for the Atchafalaya River from 1979-2008…………………………………………………………….12

Figure 11: Time series of monthly nitrate + nitrate (NO_3^- + NO_2^-) loadings for the Atchafalaya River from 1979-2008……………………………………………..12

Figure 12: Time series of monthly total phosphorus (TP) loadings for the Atchafalaya River from 1979-2008…………………………………………………………….12

Figure 13a: Time series of monthly molar ratio of dissolved inorganic nitrogen (DIN) to dissolved inorganic phosphorus (DIP) in combined loadings for the Mississippi and Atchafalaya Rivers from 1979-2008…………………………..13

Figure 13b: Time series of monthly molar ratio of total nitrogen (TN) to total phosphorus (TP) in combined loadings for the Mississippi and Atchafalaya Rivers from 1979-2008……………………………………………………………13

Figure 14: Time series of monthly total nitrogen (TN) loadings for the Mississippi River from 1993-1994……………………………………………………………..13

Figure 15: Seasonal mean loading of nitrate + nitrite, total Kjeldahl nitrogen (TKN), ammonia, total phosphorus and total nitrogen for the Mississippi River from 1974-2008…………………………………………………………………………13

Figure 16: Seasonal mean loading of nitrate + nitrite, total Kjeldahl nitrogen (TKN), ammonia, total phosphorus and total nitrogen for the Atchafalaya River from 1979-2008…………………………………………………………………………13

Figure 17: Seasonal mean ratio of total nitrogen (TN) to total phosphorus (TP) for the combined loadings of the Mississippi and Atchafalaya Rivers from 1974-2008………………………………………………………………………..13

Figure 18: Spearman correlations of Nitrate plus Nitrite, TKN, TP and TN loadings for the Mississippi River for the period 1974 to 2008…………………………14

Figure 19: Spearman correlations of Nitrate plus Nitrite, TKN, TP and TN loadings for the Atchafalaya River for the period 1979 to 2008………………………...14

Figure 20: Sale of nitrogen and phosphorus fertilizers in the Mississippi River watershed for the period 1974 to 1991. From the NOAA CADS database (2007)………………………………………………………………………14

Figure 21: Sale of nitrogen and phosphorus fertilizers in the “large source states” of Mississippi River watershed for the period 1974 to 1991……………………..14

Figure 22: Location of National Atmospheric Deposition Program wet deposition monitoring sites in the study area……………………………………………...14

Figure 23: Wet inorganic nitrogen deposition from National Atmospheric Deposition site LA12 (Iberia Parish, Louisiana). …………………………………………14

Figure 24: Wet inorganic nitrogen deposition from National Atmospheric Deposition site LA30 (Washington Parish Parish, Louisiana)………………...15

Figure 25: Wet inorganic nitrogen deposition from National Atmospheric Deposition site MS10 (Hinds County, Mississippi)…………………………...15

Figure 26: Wet inorganic nitrogen deposition from National Atmospheric Deposition site TX21 (Gregg County, Texas)…………………………………15

Figure 27: Human population for the Mississippi River Basin (including Atchafalaya watershed)………………………………………………………..15

Figure 28: Relationship between annual TN load and average flow for the Mississippi River……………………………………………………………...15

Figure 29: Relationship between annual TP load and average flow for the
Mississippi River……………………………………………………………15

Figure 30: Schematic of hypoxia model………………………………………………16

Figure 31: Relationship between hypoxic zone length and hypoxic zone area………..16

INTRODUCTION

Eutrophication

Primary productivity in many coastal systems is nitrogen (N) limited; although, phytoplankton productivity may be limited by phosphorus (P) seasonally or in portions of an estuary. Increases in loading of limiting nutrients to coastal ecosystems may lead to eutrophication (Nixon 1996). Anthropogenically enhanced eutrophication includes symptoms such as loss of seagrass beds, changes in algal community composition, increased algal (phytoplankton) blooms (Richardson et al. 2001), hypoxic or anoxic events, and fish kills (Bricker et al. 2003).

Hypoxia

Coastal hypoxia is a widespread environmental problem in the United States. Forty out of one hundred thirty eight estuaries in the U.S. exhibit moderate to severe hypoxia (Bricker et al. 1999). Sustained or recurring low oxygen conditions can lead to faunal mortalities, food web alterations, loss of habitat, and impacts to fisheries.

Much publicity, research and policy attention has been given to the extensive hypoxic zone in the northern Gulf of Mexico commonly referred to as the "Dead Zone." Bottom water oxygen concentrations of less than 2 mg/L form in large areas off the Louisiana and Texas coasts annually during the spring and summer. The size of this hypoxic area averaged 8,300 km^2 from 1985 to 1992 and increased to an average of 16,000 km^2 from 1993-2001 (Rabalais et al. 2002), with a maximum size of over 20,000 km^2 in 2003 (Rabalais 2008). The overall trend in hypoxia is increasing from 1985 to 2008 (Figure 1, Rabalais 2008).

Previous studies have demonstrated that the size of the hypoxic zone during late summer is well correlated to riverine nitrogen loadings (Scavia et al. 2003). Nutrient loadings stimulate phytoplankton production, which increases the biochemical oxygen demand of the system, leading to bottom water hypoxia. While ecosystem level impacts of hypoxia are often difficult to quantify, previous studies have demonstrated habitat implications of low oxygen on shrimp and Atlantic croaker (Craig and Crowder, 2005) and that brown shrimp landings are negatively correlated with hypoxia in the region (Zimmerman and Nance 2001, O'Connor and Whitall 2007).

In 1997, in response to this recurring ecological phenomenon, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (2001) was established as a joint federal/state/tribal and stakeholder group to consider options for responding to Gulf of Mexico hypoxia. The Task Force agreed on a goal to reduce the 5-yr running average of hypoxic area to below 5,000 km^2 by 2015 (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force 2001). The action plan also suggests that a 30% reduction from the 1980–1996 average nitrogen load would be needed to reach that goal. However, the model scenarios enumerated in Scavia et al. (2003) suggest that a 30% reduction might not be sufficient to reach this goal due to interannual variability in the system.

Sources of Nitrogen and Phosphorus

Increases in human population, combined with growth in the industrial and agricultural sectors, has significantly altered the quantities and composition of nitrogen (N)-containing pollutants released to the environment (Galloway et al. 1995; Vitousek et al. 1997). Of particular concern is urban and suburban development in the near coastal zone. Point discharges (i.e., wastewater, industrial discharges, stormwater overflow discharges) as well as non-point sources (agricultural, urban runoff) associated with this development has led to an increase in N released into the coastal zone (Driscoll et al. 2003). Previous studies have shown a strong correlation between human population and elevated riverine fluxes of N to estuaries (Peierls et al. 1991, Howarth et al. 1996, Castro et al. 2000). Atmospheric deposition of N (AD-N) has also been identified as a potentially important source of N for many coastal ecosystems (Valiela et al. 1992, Nixon 1996, Paerl et al. 2002, Whitall et al. 2004).

Anthropogenic sources of phosphorus include fertilizer (agricultural, golf course and lawn), animal wastes, yard clippings, soil erosion, and detergents/cleaning agents. The agricultural sources of phosphorus include: agricultural fertilizer, animal waste, soil loss, manure spreading, and lagoon leakage (Barr Engineering 2004).

In addition to being multiple source pollutants, nutrient pollution is often a multi-state and even international management issue because airshed and watershed boundaries also span political boundaries. Large watersheds with coastal drainages, such as Chesapeake Bay, Long Island Sound and the Mississippi River Basin, are influenced by the effects of urban and agricultural development many hundreds of miles inland. Furthermore, some estuaries, such as Tijuana Estuary watershed, which is co-located in the U.S. and Mexico, transcend international boundaries, making which makes management even more challenging.

OBJECTIVE

The purpose of this analysis is to examine the historical fluxes of N and P to the northern Gulf of Mexico and discuss the implications that this may have for primary productivity, hypoxia and management strategies.

DATA SOURCES AND METHODS

Monthly riverine loading data are from US Geological Survey (USGS) gauging stations on the Mississippi (St. Francisville, LA) and Atchafalaya (Melville, LA) Rivers (Figure 2). The period of record spans from July 1974 to June 2008 for the Mississippi and from July 1979 to June 2008 for the Atchafalaya (USGS 2008). Atmospheric deposition values, for 4 representative sites in the near coastal area, are from the National Atmospheric Deposition Program (NADP). Fertilizer sales data are from the NOAA CADS database (NOAA 2007). United States population data are from the U.S. Census Bureau (Envirocast 2007). Because these data were not normally distributed (Shapiro-Wilks test), non-parametric statistics were used to evaluate correlations (Spearmann's Rho) and seasonal differences (Wilcoxon test) using JMP Statistical Software (SAS Institute).

RESULTS

Long Term Trends in Riverine Loading

In the Mississippi River, nitrogen species (TN, nitrate plus nitrite, TKN, ammonia) are generally decreasing (Figures 3-6). Conversely, total phosphorus (TP) is increasing (Figure 7). In the Atchafalaya River, TN, TKN and ammonia are decreasing (Figures 8-10), while there is no trend in nitrate or TP. Trends in the N:P ratios for the total loadings to the northern Gulf of Mexico (Mississippi and Atchafalaya Rivers combined) were analyzed as well. Ratios of TN:TP and DIN:DIP are both decreasing (Figure 13). It should be noted that one can find short term (e.g. 1-3 year) trends in some constituents, but these should be viewed as acute patterns which may be driven by temporary shifts in climatology or nutrient inputs (e.g. Figure 14) which are not reflective of the long term trend (Figure 3).

Seasonal Patterns in Riverine Loading

There is significant seasonal variability in the monthly riverine loadings. In the Mississippi River, all seasons for all constituents are significantly different (α=0.05) from each other with the exception of summer and winter loads, which are not significantly different for the nitrogen species. Loads are generally significantly highest in the spring and lowest in the fall (Figure 15). In the Atchafalaya River (Figure 16), loadings for each constituent are generally highest in the spring and generally lowest in the fall and differ significantly by season. Exceptions to this are ammonia, where spring and winter are not significantly different but are greater than summer and fall loads, and TN and TP, where summer and winter loads are not significantly different from each other. Ratios of TN:TP and DIN:DIP (Mississippi and Atchafalaya Rivers combined) were generally highest in the spring and lowest in the fall (Figure 17). All seasons were significantly different (α=0.05) for DIN:DIP and all seasons were significantly different for TN:TP, except for winter and fall, and, summer and spring.

Covariation of Nutrient Loads

The extent to which nutrient constituent loads co-vary may lend insight into the likelihood that they originate from the same sources. If two constituents strongly co-vary they may be originating from the same source. Alternatively, their source signals may be getting integrated over the large watershed area. If two constituents are independent of each other, this would suggest that different sources, or that in stream processing, are driving the loading patterns. The monthly loading data reflect a variety of covariances between nutrient constituents (Figures 18 and 19). For example, TN and TP are relatively well correlated, whereas ammonia and nitrate are not well correlated. The degree of covariance for each constituent also varies between the Mississippi and Atchafalaya Rivers. Obviously, autocorrelation exists between some analytes, such as TN and nitrate because nitrate is a component of TN.

Trends in Fertilizer Use

Both N and P fertilizer use in the Mississippi River Basin increased from 1974 to 1991 as shown in Figures 20 and 21 (note: compiled fertilizer sales data from NOAA's CADS ends at 1991). These patterns hold both for the basin as a whole as well as for the states in the basin which have been identified as contributing the majority of the nutrient load to the Gulf (EWG, 2006). It is important to note that the temporal patterns in fertilizer use do not directly correspond to the observed riverine loads. The unusual increase in N loading 1982-1984 (Figure 3) actually corresponds to a decrease in fertilizer use in the same time period (Figures 20 and 21). This reinforces the concept that nitrogen is a multiple source pollutant. Furthermore, this decoupling may indicate the importance of watershed processing, including potential groundwater impacts.

Trends in Atmospheric Nitrogen Deposition

Wet nitrogen deposition (National Atmospheric Deposition Program data) from four sites in the lower watersheds (Figure 22) show decreasing or relatively steady nitrogen deposition fluxes since the early 1980s (Figures 23-26). These modest improvements may be related to the Clean Air Act Amendments of 1990. It should be noted that NADP data are wet inorganic deposition (i.e. DIN in precipitation) only. Patterns in organic N deposition and dry deposition (particles and gases) may be different, but substantial data for these fluxes are not available except in a few localized studies.

Trends in Human Population

Population can be used as a surrogate for wastewater treatment plant and septic system nutrient inputs (Castro and Driscoll 2002). The population of the Mississippi River Basin (including the Atchafalaya) increased by 18% from 1970 to 2000 (Figure 27).

DISCUSSION

Link to Hydrology

Because nutrient loadings are predominantly from non-point sources, one would expect loadings to be tightly couple to riverine flow (Figures 28, 29). However, only nitrogen loadings are significantly correlated to flow. This may reflect significant differences in sources or in watershed transport processes between N and P.

Stoichiometry

The Redfield ratio (16 units of nitrogen to 1 unit of phosphorus) is an approximation of algal nutrient requirements and can vary depending on a variety of factors including: the stage of algal cell division, changes in light intensity or quality, or temperature (Correll 1987). Even considering these limitations, measurement of nitrogen and phosphorus ratios in coastal waters provides a useful metric for evaluating the possible effects of increased loadings of these nutrients (Bowman et al. 2000).

There has been some debate as to how to best calculate N:P ratios in riverine loadings to the northern Gulf of Mexico. Because N:P ratios are important from a phytoplankton response perspective, the ratio should only consider bioavailable N and P. For this purpose, some experts (e.g. USEPA 2004) have argued that ambient DIN:DIP is the appropriate ratio, as inorganic N and P are most bioavailable to phytoplankton. However, it has been well documented that urea and other fractions of organic N can be bioavailable to phytoplankton (Peierls and Paerl 1997, Pinckney et al. 1999). Therefore, using DIN will significantly underestimate the total amount of bioavailable N. Further complicating this matter is the fact that the measurements presented in this paper are riverine loads, not ambient offshore concentrations. Because biogeochemical transformations occur as the nutrients move downstream from the USGS gauging stations, considering only DIN and DIP will likely underestimate the total bioavailable N and P, as more nutrients are converted from recalcitrant forms to more bioavailable forms. Conversely, examining only TN and TP will likely overestimate the total bioavailable N and P.

Because of this uncertainty, this paper examines both DIN:DIP and TN:TP. Not surprisingly, comparing the TN:TP and DIN:DIP ratios to the Redfield ratio yields different results. For DIN:DIP, loadings data suggest P limitation except in the fall when N is generally limiting. However, TN:TP loadings data suggest N limitation. Furthermore, there are seasonal differences, especially for DIN:DIP which suggests P limitation, except in the fall.

These differences, combined with the debate over how best to calculate N:P ratios in coastal waters, speaks to the need for better quantification of nutrient processing and biological utilization of nutrients, as well as more robust temporal and spatial ambient nutrient data from the Mississippi River Plume and shelf environments.

Modeling Implications

Quantitative models exist which can annually predict the size of this area of hypoxia. One of these model is based on Scavia et al. (2003) and was constructed using 18 years of field data. The model uses a suite of input parameters including: organic matter load (which is derived from USGS riverine nitrogen loading values from the Mississippi and Atchafalaya Rivers), a first order oxygen reaeration constant, a first order organic matter decomposition and downstream advection of sub pycnoclinal waters (Figure 30). Loading data from the USGS stations at St. Francisville and Melville are used for the loadings for the Mississippi and Atchafalaya Rivers, respectively. May and June riverine loading data (total nitrogen) is used to determine the biochemical oxygen demand load because nitrogen is often considered to be the limiting nutrient for algal production (Justic et al. 1997). Because TN and TP are strongly correlated (Figures 18 and 19), the model could be modified to be run using TP loads. There is considerable uncertainty in the advection term and this uncertainty is quantified via Monte Carlo analysis. The model predicts the length of the hypoxic zone, which is well correlated to the total hypoxic area (Figure 31). This model could be used as a management tool to evaluate the relative effectiveness of proposed management strategies for reducing nutrient pollution to the northern Gulf.

Management Implications

Reducing one nutrient alone (either N or P) will not solve the problem because the system is overloaded with nutrients. For example, focusing on only nitrogen will only lead to switching the system from P limitation to N limitation. Coastal nutrient pollution is a multi-source problem, and in the case of N a multi-media (air and water) problem, which is manifested in a cascade of environmental effects (Galloway et al. 2003). The complex nature (multi-media, multi-source, multi-state, multi-effect) of coastal nutrient pollution necessitates the development of integrated management plans. Unfortunately, in the U.S., air management legislation (e.g. Clean Air Act) and management of coastal waters (e.g. Clean Water Act, Coastal Zone Management Act) are not coordinated. The Total Maximum Daily Load (TMDL) requirements under the Clean Water Act and other state level management plans, which have been designed to address coastal N pollution, often do not adequately consider the role of AD-N in estuarine N loading (NCDENR 1999, NYDEC and CTDEP 2000). Similarly, air quality standards have failed to consider the impact of atmospheric N emissions on coastal water quality (e.g. secondary standards). It is strongly recommended that management of this system be approached in an integrated manner that recognizes contributions from various sources (i.e. point sources, atmospheric deposition and other non-point) and across state and international borders (the Mississippi River watershed contains 31 states and extends into Canada). The Mississippi River/Gulf of Mexico Watershed Nutrient Task Force should continue to work to integrate multi-state programs among agencies responsible for air and coastal waters management.

ACKNOWLEDGMENTS
Support for this work was provided by NOAA's National Centers for Coastal Ocean Science. The author would like to thank B. Aulenbach (USGS) for his cooperation in supplying USGS riverine loading data and two reviewers, S. Bricker and K. Kimbrough, for their valuable comments which greatly improved the manuscript.

REFERENCES

Barr Engineering Company for Minnesota Pollution Control Agency. Detailed Assessment of Phosphorus Sources in Minnesota Watersheds. February 2004. 26 January 2005. Available online at: http://www.pca.state.mn.us/hot/legislature/reports/phosphorus-report.html.

Bowman, M.L., J. Gerritsen, G, Gibson, B. Synder. 2000. Estuarine and Coastal Marine Waters: Bioassessment and Biocriteria Technical Guidance. Available online at: http://www.epa.gov/waterscience/biocriteria/States/estuaries/bio_ch3.pdf

Bricker, S.B., J.G. Ferreira, and T. Simas. 2003. An Integrated Methodology for Assessment of Estuarine Trophic Status. Ecol. Modeling 169: 39-60.

Bricker S., C. Clement, D. Pirhalla, S. Orlando, S. Farrow. 1999. National Estuarine Eutrophication Assessment: Effects of Nutrient Enrichment in the Nation's Estuaries. NOAA, National Ocean Service, Special Projects Office and the National Centers for Coastal Ocean Science. Silver Spring, MD.

Castro, M., C. Driscoll, T. Jordan, W. Reay, W. Boynton, S. Seitzinger, R. Styles, W. Boynton, and J. Cable. 2000. Contribution of atmospheric deposition to the total nitrogen loads of thirty-four estuaries on the Atlantic and Gulf Coast of the United States. In: Valigura, R., Editor, 2000. Atmospheric nitrogen deposition in coastal waters. Coastal Estuarine Science Series vol. 57**,** AGU Press, Washington (DC), pp. 77–106.

Castro M.S., C.T. Driscoll. 2002. Atmospheric nitrogen deposition to estuaries in the mid-Atlantic and northeastern United States. Environmental Science and Technology 36: 3242–3249.

Craig, K. and L. Crowder. 2005. Hypoxia-induced habitat shifts and energetic consequences in Atlantic croaker and brown shrimp on the Gulf of Mexico shelf. Mar. Ecol. Prog. Series 294: 79-94.

Driscoll, C., D. Whitall, J. Aber, E. Boyer, M. Castro, C. Cronan, C. Goodale, P. Groffman, C. Hopkinson, K. Lambert, G. Lawrence and S. Ollinger. 2003. Nitrogen pollution in the northeastern United States: Sources, effects and management options. BioScience 53: 357-374.

Correll, D.L. 1987. Nutrients in Chesapeake Bay. Pages 298-320 *in* S.K. Majumdar, L.W. Hall, Jr. and H.M. Austin (editors). Contaminant Problems and Management of Living Chesapeake Bay Resources. Pennsylvania Academy of Science.

Envirocast 2007. National Watersheds: Mississippi River Basin. Available online at: http://wrc.iewatershed.com/index.php?pagename=ow_regionalWatersheds_07

(EWG) Environmental Working Group. 2006. Dead in the Water. Available online at: http://www.ewg.org/reports/deadzone/top10.php

Galloway, J. N., W. H. Schlesinger, H. Levy II, A. Michaels, and J. L. Schnoor. 1995. Nitrogen Fixation: Anthropogenic Enhancement-Environmental Response, Global Biogeochem. Cycles 9:235–252.

Galloway, J. N., J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W. Howarth, E. B. Cowling, and B. J. Cosby. 2003. The nitrogen cascade. Bioscience 53:341-356.

R. W. Howarth, G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J. A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch and Zhu Zhao-Liang. 1996. Regional Nitrogen Budgets and Riverine N & P Fluxes for the Drainages to the North Atlantic Ocean: Natural and Human Influences Biogeochemistry 35:75-139.

Justic, D., N. Rabalais, E. Turner. 1997. Impacts of climate change on net productivity of coastal waters: implications for carbon budgets and hypoxia. Climate Research 8: 225-237.

Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. 2001. Action Plan for Reducing, Mitigating and Controlling Hypoxia in the Northern Gulf of Mexico. Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. Washington, D.C. Available online at: http://www.epa.gov/msbasin/taskforce/pdf/actionplan.pdf

(NADP) National Atmospheric Deposition Program (NRSP-3). 2008. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820. Available online at: http://nadp.sws.uiuc.edu/

(NCDENR) North Carolina Department of Environment and Natural Resources. 1999. Total Maximum Daily Load for Total Nitrogen to the Neuse River Estuary, NC. Available online at: http://h2o.enr.state.nc.us/mtu/aboutTMDL.html

(NYDEC and CTDEP). New York Department of Environmental Conservation and CT Department of Environmental Protection. 2000. A total maximum daily load analysis to achieve water quality standards for dissolved oxygen in Long Island Sound; 2000. Available online at: http://dep.state.ct.us/wtr/index.htm

(NOAA) National Oceanic and Atmospheric Administration, 2007. NOAA's National Coastal Assessment and Data Synthesis. Available online at: http://coastalgeospatial.noaa.gov/

Nixon S, J. Ammerman, L. Atkinson, V. Berounsky, G. Billen, W. Boicourt,

W. Boynton, T. Church, D. Ditoro, R. Elmgren, J. Garber, A. Giblin, R. Jahnke, N. Owens, M. Pilson, S. Seitzinger. 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35: 141-180.

O'Connor, T. and D. Whitall. 2007. Linking Hypoxia to Shrimp Catch in the Northern Gulf of Mexico. Marine Pollution Bulletin 54: 460–463.

Peierls, B. and H. Paerl. 1997. Bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton. Limnol. Ocean. 42: 1819-l 823

Peierls, B. L., N. F. Caraco, M. L. Pace, and J. J. Cole. 1991. Human influence on river nitrogen. Nature 350:386-387.

Paerl , H. W., R.L. Dennis and D. Whitall. 2002. Atmospheric deposition of Nitrogen: implications for nutrient over-enrichment of coastal waters. Estuaries 25:677–693.

Pinckney, J. L., H. W. Paerl and M. B. Harrington. 1999. Responses of the phytoplankton community growth rate to nutrient pulses in variable estuarine environments. Journal of Phycology 35:1455-1463.

Rabalais, N, E. Turner, D. Scavia. 2002. Beyond science into policy: Gulf of Mexico Hypoxia and the Mississippi River. BioScience 52:129-142.

Rabalais, N. 2008. Hypoxia in the northern Gulf of Mexico. Available online at: http://www.gulfhypoxia.net/results/

Richardson T, J. Pinckney, H. Paerl. 2001. Responses of estuarine phytoplankton communities to nitrogen form and mixing using microcosm bioassays. Estuaries 24: 828-839.

Scavia, D., N. Rabalais, E. Turner, D. Justic, W. Wiseman, Jr. 2003. Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. Limnology and Oceanography 48: 951-956.

(USEPA) U.S. Environmental Protection Agency. 2004. Review of Issues Related to Gulf of Mexico Hypoxia. US EPA Region 4. Atlanta, Georgia. Available online at: http://www.epa.gov/msbasin/taskforce/2006symposia/Reg4whitepaper0404draft.pdf

(USGS) U.S. Geological Survey. 2008. New Nutrient Flux Estimates for 2008. Available online at: http://co.water.usgs.gov/hypoxia/html/nutrients_new.html

Valiela, K. Foreman, M. LaMontagne, D. Hersh, J. Costa, P. Peckol, B. DeMeo-Andreson, C. D'Avanzo, M. Babione, C. Sham, J. Brawley and K. Lajtha. 1992. Couplings of watersheds and coastal waters: sources and consequences of nutrient enrichment in Waquoit Bay, Massachusetts. Estuaries **15**: 443–457

Whitall, D., M. Castro and C. Driscoll. 2004. Evaluation of management strategies for reducing nitrogen loadings to four U.S. estuaries. Science of the Total Environment 333: 25-36.

Zimmerman, R.J., and L. M Nance. 2001. Effects of hypoxia on the shrimp fishery of Louisiana and Texas. In: N.N., Rabalais, R. E. Turner Coastal Hypoxia: Consequences for Living Resources and Ecosystems. pp 293-310 American Geophysical Union: Washington, DC.

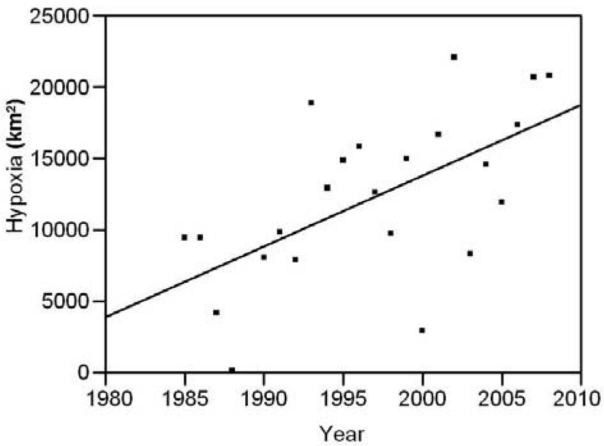

Figure 1: Annual hypoxia in the northern Gulf of Mexico (Rabalais 2008).

Figure 2: Location of USGS riverine monitoring stations for the Mississippi (St. Francisville) and Atchafalaya (Melville) Rivers.

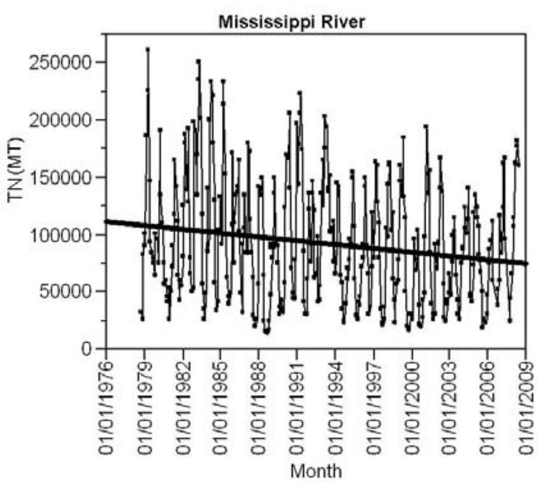

Figure 3: Time series of monthly total nitrogen (TN) loadings for the Mississippi River from 1974-2008. Line represents the linear trend, but does not imply statistical significance.

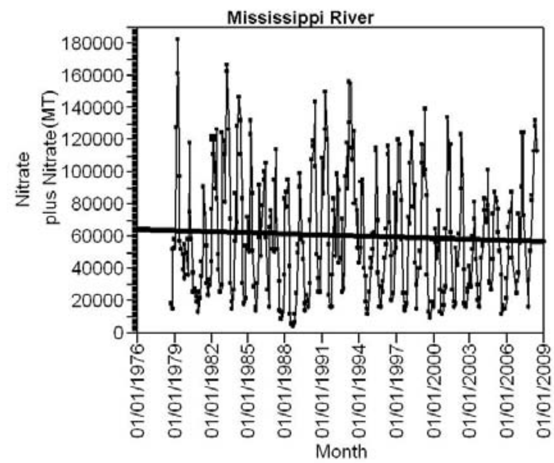

Figure 4: Time series of monthly nitrate + nitrite loadings for the Mississippi River from 1974-2008. Line represents the linear trend, but does not imply statistical significance.

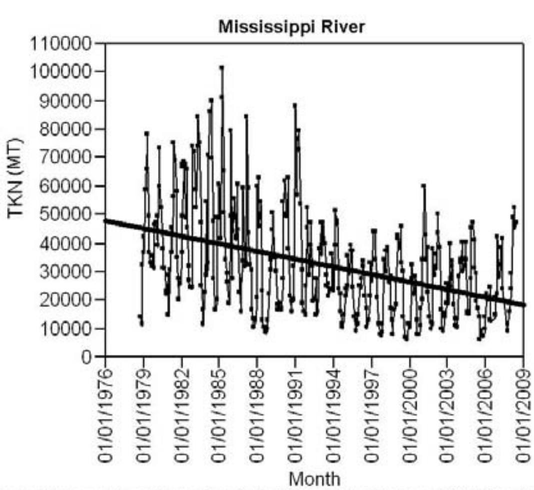

Figure 5: Time series of monthly total Kjeldahl nitrogen (TKN) loadings for theMississippi River from 1974-2008. Line represents the linear trend, but does not imply statistical significance.

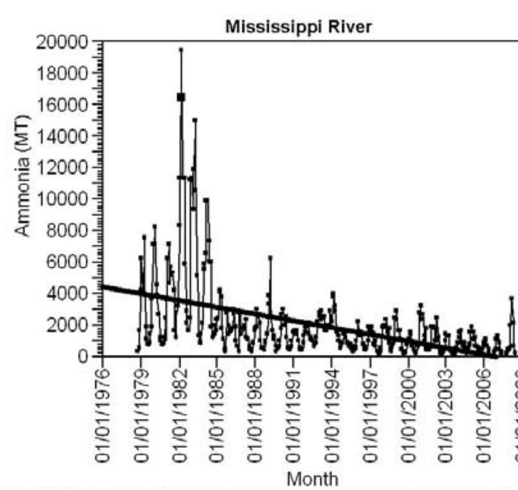

Figure 6: Time series of monthly ammonia loadings for the Mississippi River from 1974-2008. Line represents the linear trend, but does not imply statistical significance.

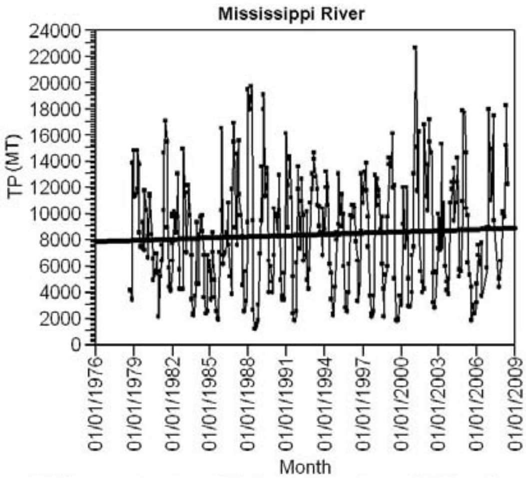

Figure 7: Time series of monthly total phosphorus (TP) loadings for the Mississippi River from 1974-2008. Line represents the linear trend, but does not imply statistical significance.

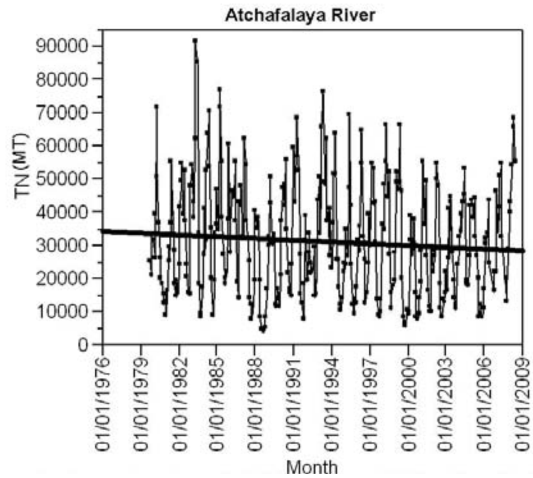

Figure 8: Time series of monthly total nitrogen (TN) loadings for the Atchafalaya River from 1979-2008. Line represents the linear trend, but does not imply statistical significance.

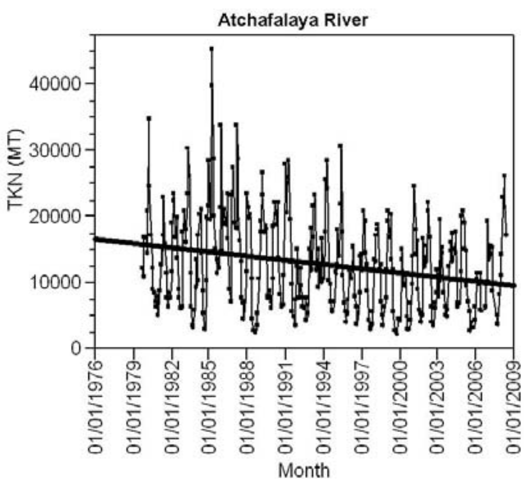

Figure 9: Time series of monthly total Kjeldahl nitrogen (TKN) loadings for the Atchafalaya River from 1979-2008. Line represents the linear trend, but does not imply statistical significance.

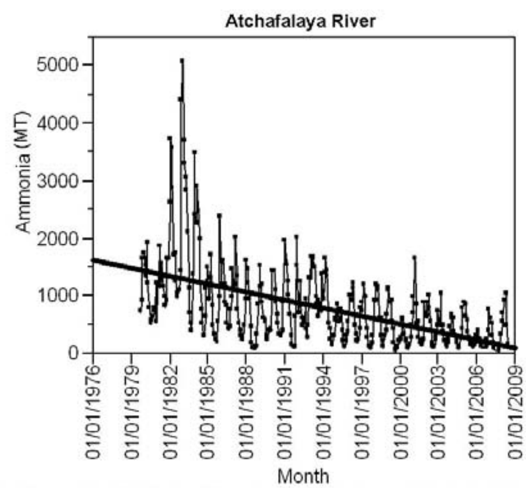

Figure 10: Time series of monthly ammonia loadings for the Atchafalaya River from 1979-2008. Line represents the linear trend, but does not imply statistical significance.

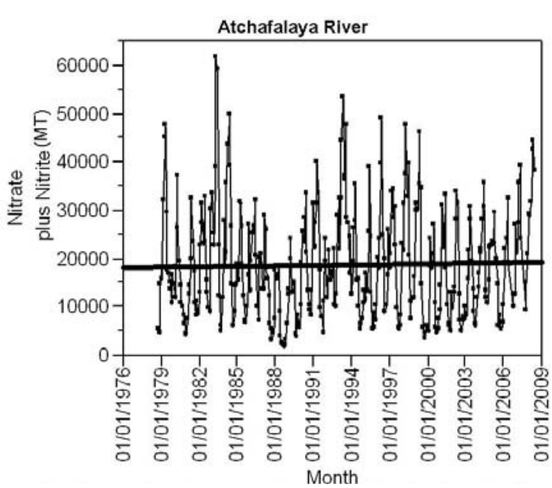

Figure 11: Time series of monthly nitrate + nitrate loadings for the Atchafalaya River from 1979-2008. Line represents the linear trend, but does not imply statistical significance.

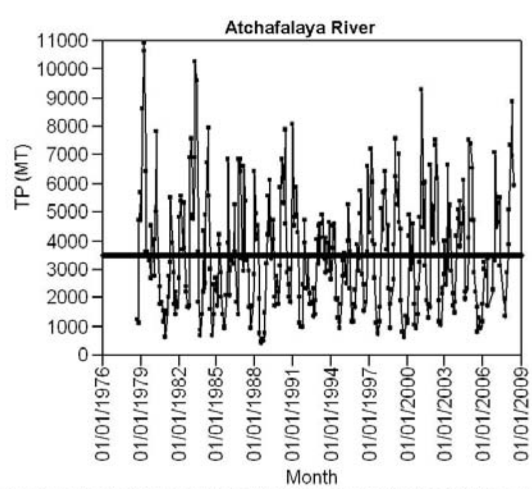

Figure 12: Time series of monthly total phosphorus (TP) loadings for the Atchafalaya River from 1979-2008. Line represents the linear trend, but does not imply statistical significance.

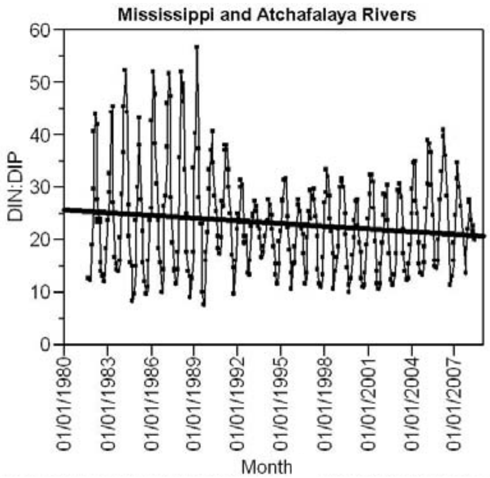

Figure 13a:Time series of monthly molar ratio of dissolved inorganic nitrogen (DIN) to dissolved inorganic phosphorus (DIP) in combined loadings for the Mississippi and Atchafalaya Rivers from 1979-2008

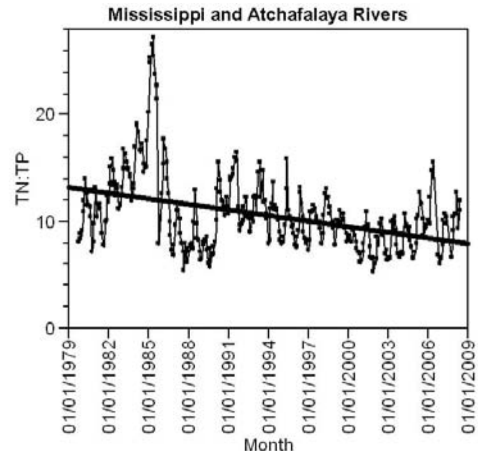

Figure 13b: Time series of monthly molar ratio of total nitrogen (TN) to total phosphorus (TP) in combined loadings for the Mississippi and Atchafalaya Rivers from 1979-2008. Line represents the linear trend, but does not imply statistical significance.

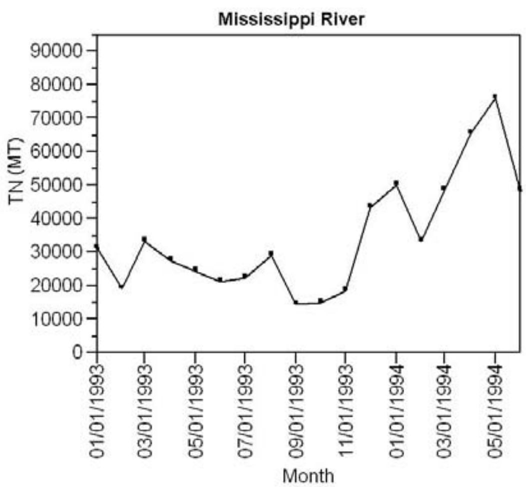

Figure 14: Time series of monthly total nitrogen (TN) loadings for the Mississippi River from 1993-1994.

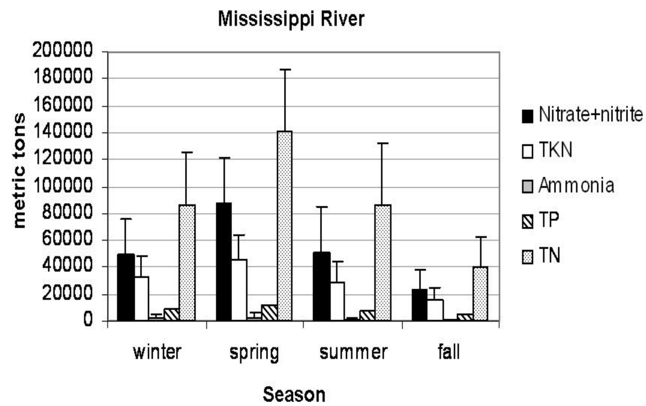

Figure 15: Seasonal mean loading of nitrate + nitrite, total Kjeldahl nitrogen (TKN), ammonia, total phosphorus and total nitrogen for the Mississippi River from 1974-2008. All seasons for all constituents are significantly different (Wilcoxon, α=0.05) from each other with the exception of summer and winter loads, which are not significantly different for the nitrogen species.

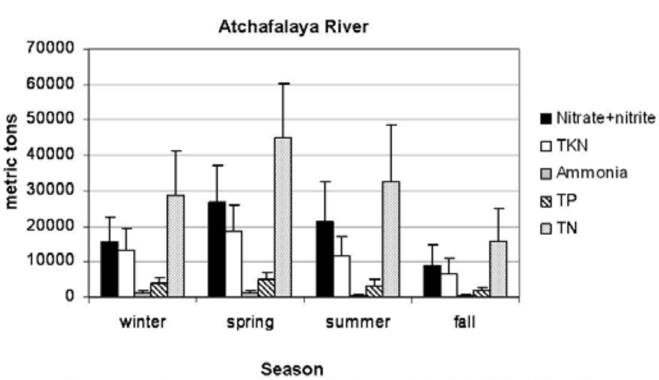

Figure 16: Seasonal mean loading of nitrate + nitrite, total Kjeldahl nitrogen (TKN), ammonia, total phosphorus and total nitrogen for the Atchafalaya River from 1979-2008. Loadings for each constituent are generally highest in the spring and generally lowest in the fall and differ significantly by season (Wilcoxon, α=0.05). Exceptions to this are ammonia, where spring and winter are not significantly different but are greater than summer and fall loads, and TN and TP, where summer and winter loads are not significantly different from each other.

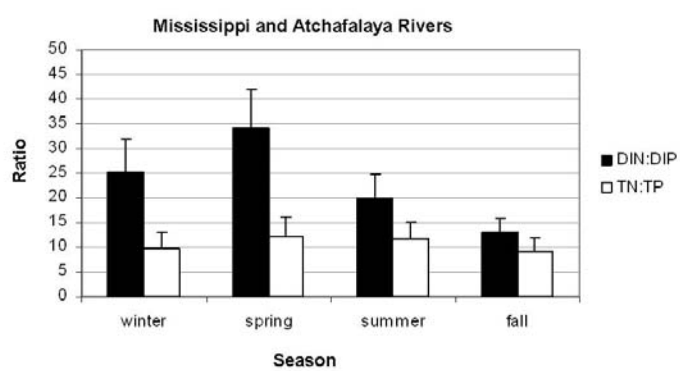

Figure 17: Seasonal mean ratio of total nitrogen (TN) to total phosphorus (TP) for the combined loadings of the Mississippi and Atchafalaya Rivers from 1974-2008. All seasons were significantly different (Wilcoxon, α=0.05) for DIN:DIP and all seasons were significantly different for TN:TP, except for winter and fall, and, summer and spring.

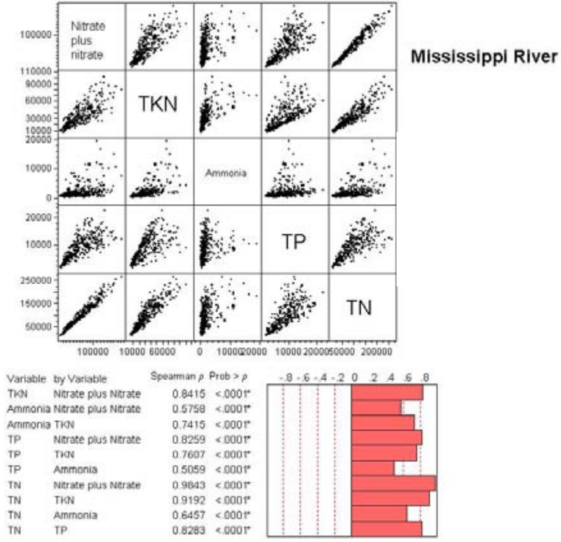

Figure 18: Spearman correlations of Nitrate plus Nitrite, TKN, ammonia, TP and TN loadings for the Mississippi River for the period 1974 to 2008.

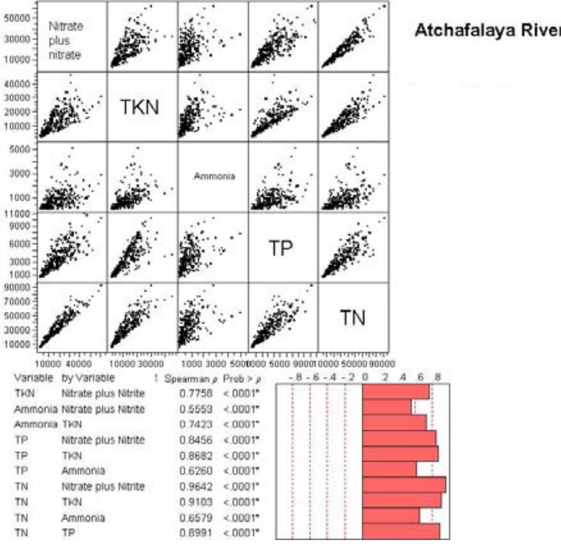

Figure 19: Spearman correlations of Nitrate plus Nitrite, ammonia, TKN, TP and TN loadings for the Atchafalaya River for the period 1979 to 2008.

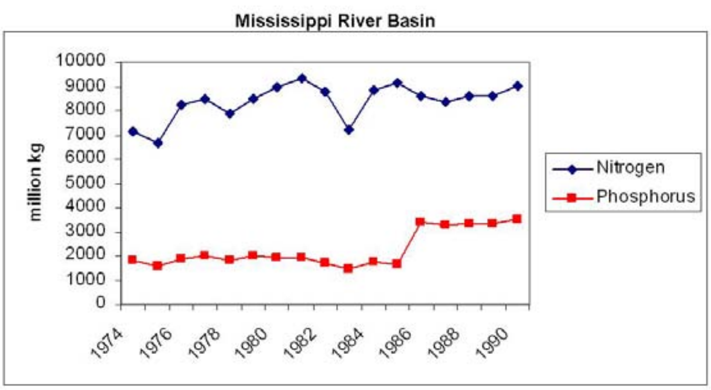

Figure 20: Sale of nitrogen and phosphorus fertilizers in the Mississippi River watershed for the period 1974 to 1991. From the NOAA CADS database (2007).

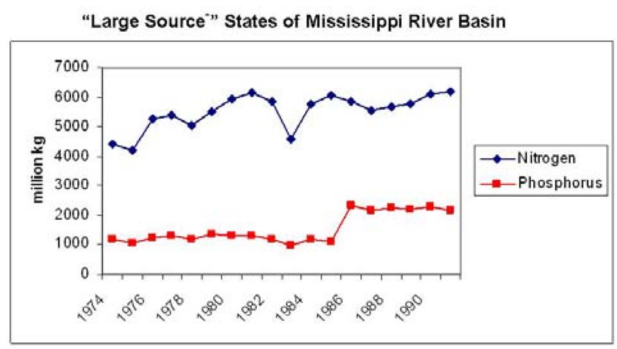

Figure 21: Sale of nitrogen and phosphorus fertilizers in the "large source states" of Mississippi River watershed for the period 1974 to 1991. From the NOAA CADS database (2007). These states contain high polluting counties which account for 15% of the watershed area and 80% of the N loading (EWG, 2006). States include: Arkansas, Illinois, Indiana, Iowa, Kentucky, Louisiana, Michigan, Minnesota, Mississippi, Missouri, Nebraska, Ohio, Oklahoma, South Dakota, Tennessee and Wisconsin.

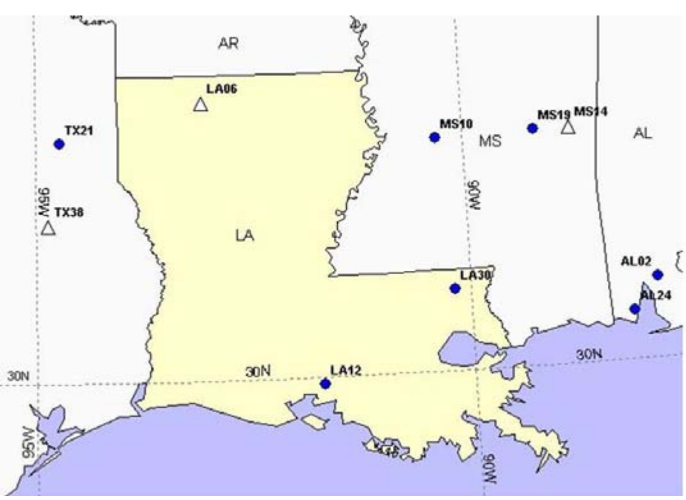

Figure 22: Location of National Atmospheric Deposition Program wet deposition monitoring sites in the study area.

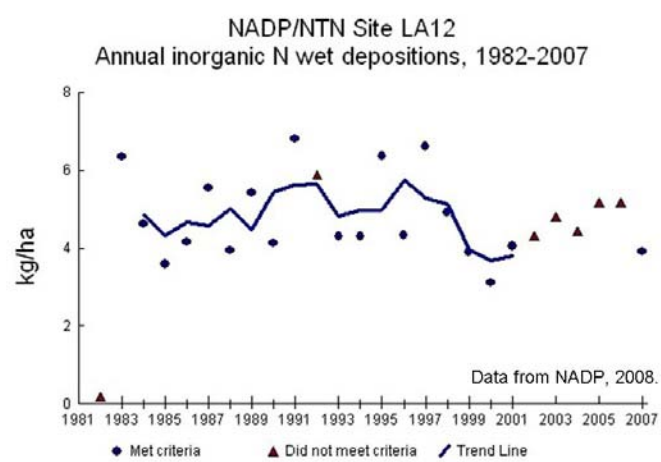

Figure 23: Wet inorganic nitrogen deposition from National Atmospheric Deposition site LA12 (Iberia Parish, Louisiana). The trend line is composed of a three-year, centered, weighted-moving average value. Points depicted with triangles did not meet the NADP criteria for completeness (NADP, 2008) and are not included in the trend line.

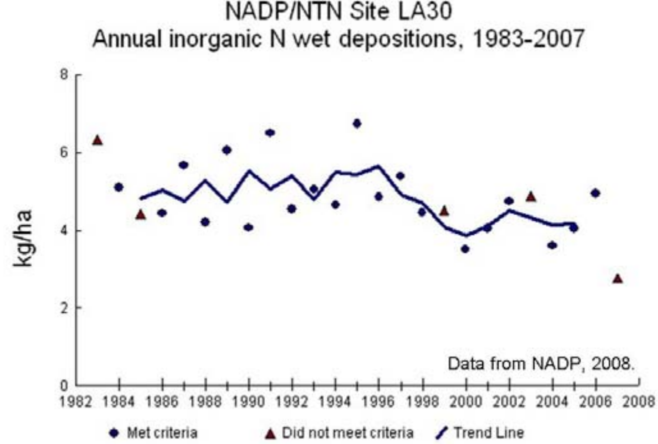

Figure 24: Wet inorganic nitrogen deposition from National Atmospheric Deposition site LA30 (Washington Parish Parish, Louisiana). The trend line is composed of a three-year, centered, weighted-moving average value. Points depicted with triangles did not meet the NADP criteria for completeness (NADP, 2008) and are not included in the trend line.

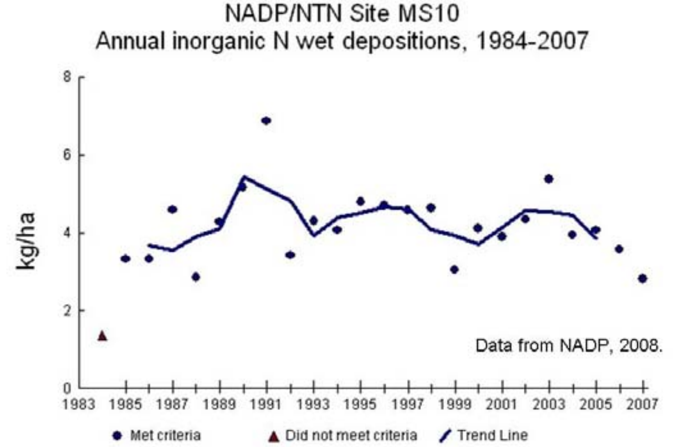

Figure 25: Wet inorganic nitrogen deposition from National Atmospheric Deposition site MS10 (Hinds County, Mississippi). The trend line is composed of a three-year, centered, weighted-moving average value. Points depicted with triangles did not meet the NADP criteria for completeness (NADP, 2008) and are not included in the trend line.

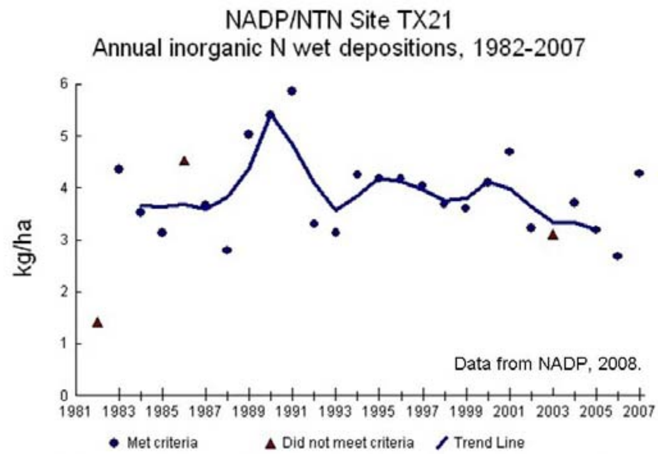

Figure 26: Wet inorganic nitrogen deposition from National Atmospheric Deposition site TX21 (Gregg County, Texas). The trend line is composed of a three-year, centered, weighted-moving average value. Points depicted with triangles did not meet the NADP criteria for completeness (NADP, 2008) and are not included in the trend line.

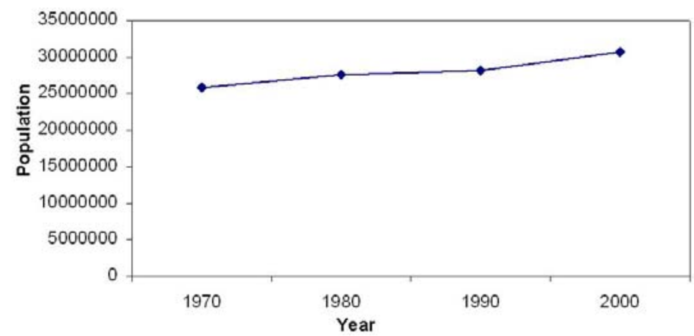

Figure 27: Human population for the Mississippi River Basin (including Atchafalaya watershed). From U.S. Census data 1970-2000.

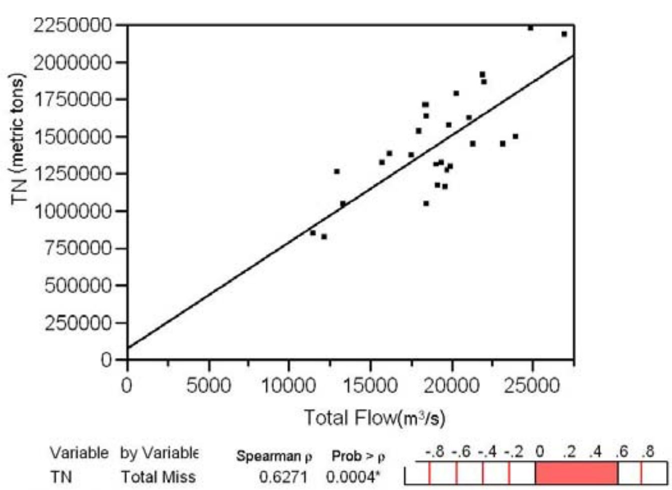

Figure 28: Relationship between annual TN load and average flow for the Mississippi River. Line represents the linear trend, but does not imply statistical significance. Spearman rank correlation coefficient is significant at α=0.05.

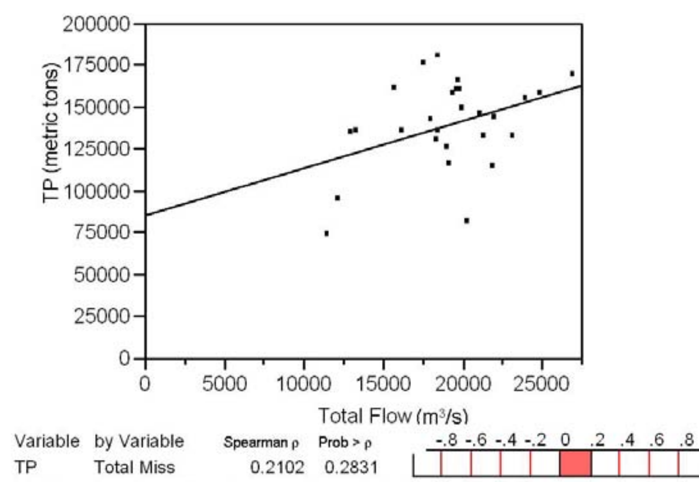

Figure 29: Relationship between annual TP load and average flow for the Mississippi River. Line represents the linear trend, but does not imply statistical significance. Spearman rank correlation coefficient is not significant at α=0.05.

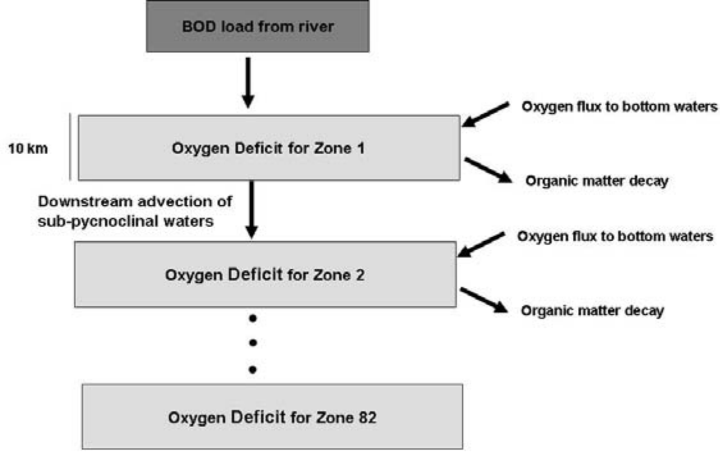

Figure 30: Schematic of hypoxia model.

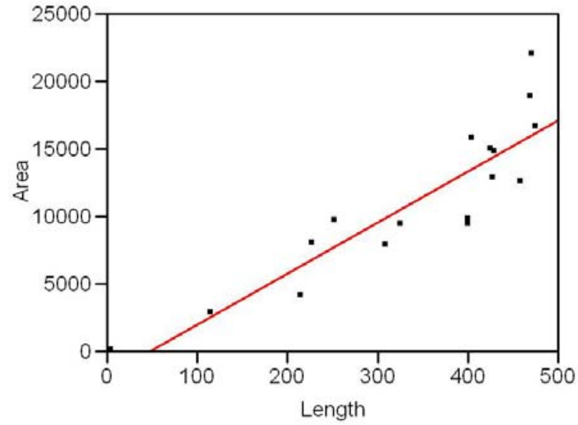

Figure 31: Relationship between hypoxic zone length and hypoxic zone area. e area.

United States Department of Commerce

Carlos M. Gutierrez
Secretary

National Oceanic and Atmospheric Administration

Vice Admiral Conrad C. Lautenbacher, Jr. USN (Ret.)
Under Secretary of Commerce for Oceans and Atmospheres

National Ocean Service

John H. Dunnigan
Assistant Administrator for Ocean Service and Coastal Zone Management