Science for Solutions

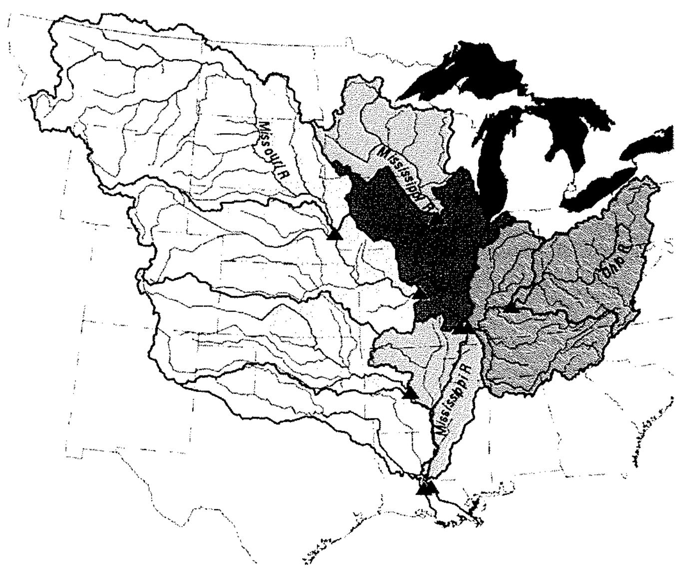
NOAA COASTAL OCEAN PROGRAM
Decision Analysis Series No. 17

Flux and Sources of Nutrients in the Mississippi–Atchafalaya River Basin

Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico

Donald A. Goolsby, William A. Battaglin, Gregory B. Lawrence, Richard S. Artz, Brent T. Aulenbach, Richard P. Hooper, Dennis R. Keeney, and Gary J. Stensland

May 1999



U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
National Ocean Service
Coastal Ocean Program

GULF OF MEXICO HYPOXIA ASSESSMENT

This report is the third in a series of six reports developed as the scientific basis for an integrated assessment of the causes and consequences of hypoxia in the Gulf of Mexico, as requested by the White House Office of Science and Technology Policy and as required by Section 604a of P.L. 105-383. For more information on the assessment and the assessment process, please contact the National Centers for Coastal Ocean Science at (301) 713-3060.

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Total nitrogen yields, in kg/km2/yr
90 to 320
630 to 680
890 to 1,000
1,690
▲ gaging station

Cover image: Spatial distribution of total nitrogen yields (/km^2/yr) in nine large basins during 1980–96.

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May 1999

U.S. DEPARTMENT OF COMMERCE
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Contents

List of Figures and Tables

FIGURES

TABLES

Conversion Factors and Abbreviations

MULTIPLY	BY	TO OBTAIN
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square kilometer (km^2)	0.3861	square mile
cubic kilometer (km^3)	0.2399	cubic mile
centimeter (cm	0.3937	inch
liter (L)	1.057	quart
milliliter (mL)	0.03381	fluid ounce
kilogram (kg)	2.205	pound, avoirdupois
metric ton (t)	2,205.0	pound, avoirdupois
cubic meter per second (m^3/s)	35.31	cubic feet per second
kilogram per square kilometer (kg/km^2)	0.008924	pounds per acre

CONCENTRATION UNIT	APPROXIMATELY EQUALS
milligram per liter (mg/L)	part per million

The following equations were used to compute flux of chemicals:

concentration (mg/L) x flow (m^3/s) x 8.64 x 10^{-2} = metric tons per day

concentration (mg/L) x flow (m^3/s) x 8.64 x 10^{-5} = kilogram per day

Acknowledgments

Because of this report's comprehensive nature and broad scope, its preparation required the collaboration and assistance of many people. Scientists who contributed significantly to this effort but are not listed as authors include: Robert Hoeft, University of Illinois; Michael Burkart, U.S. Department of Agriculture/Agricultural Research Service (USDA/ARS), Ames, Iowa; Gyles Randall, University of Minnesota, Southern Experiment Station; and Keith A. Kelling, University of Wisconsin.

We also wish to acknowledge the efforts of U.S. Environmental Protection Agency (USEPA) scientists and managers in EPA Regions III, IV, V, VI, VII, and VIII, and the National Health and Environmental Effects Research Laboratory in Gulf Breeze, Florida, who assisted in the compilation of point-source discharge data. This effort was coordinated by Larinda Norton at the Gulf of Mexico Program Office at Stennis Space Center, Mississippi, and Mary Belefski at EPA headquarters in Washington, D.C.

Other scientists who assisted with data compilation and management include: Yvonne H. Baevsky, Laurie L. Boyer, Gail Thelin, Larry Puckett, and Kathy Fitzgerald, U.S. Geological Survey (USGS); Gary Lear, USEPA; David James, USDA/ARS; and John Miller, U.S. Army Corps of Engineers. Manuscript preparation was completed with significant assistance from Laurie L. Boyer, USGS. We thank John Flager of the USGS for his review of the report and for his advice and many helpful suggestions for preparation of the manuscript; Richard Alexander and Greg Clark of the USGS for their technical review of the manuscript; and eight anonymous reviewers selected by the Committee on Environment and Natural Resources (CENR) Editorial Board and George Hallberg of the Cadmus Group for their technical review of the manuscript.

We wish to acknowledge Gary Stensland of the Illinois State Water Survey in Champaign, Illinois, for his assistance in preparing the section of this report on atmospheric deposition of nitrogen compounds. For his contribution he is included as a co-author of this report, but we wish to note that his involvement was limited to section 5.1, Atmospheric Inputs to the Mississippi–Atchafalaya River Basin.

Funding to support the preparation of this report was provided by the following USGS Programs: National Stream Quality Accounting Network, Toxic Substances Hydrology, and National Trends Network.

Foreword

Nutrient overenrichment from anthropogenic sources is one of the major stresses on coastal ecosystems. Generally, excess nutrients increase algal production and the availability of organic carbon within an ecosystem—a process known as eutrophication. Scientific investigations in the northern Gulf of Mexico have documented a large area of the Louisiana continental shelf with seasonally depleted oxygen levels (< 2 mg/l). Most aquatic species cannot survive at such low oxygen levels. The oxygen depletion, referred to as hypoxia, forms in the middle of the most important commercial and recreational fisheries in the conterminous United States and could threaten the economy of this region of the Gulf.

As part of a process of considering options for responding to hypoxia, the U.S. Environmental Protection Agency (EPA) formed the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force during the fall of 1997, and asked the White House Office of Science and Technology Policy to conduct a scientific assessment of the causes and consequences of Gulf hypoxia through its Committee on Environment and Natural Resources (CENR). A Hypoxia Working Group was assembled from federal agency representatives, and the group developed a plan to conduct the scientific assessment.

The National Oceanic and Atmospheric Administration (NOAA) has led the CENR assessment, although oversight is spread among several federal agencies. The objectives are to provide scientific information that can be used to evaluate management strategies, and to identify gaps in our understanding of this complex problem. While the assessment focuses on hypoxia in the Gulf of Mexico, it also addresses the effects of changes in nutrient concentrations and loads and nutrient ratios on water quality conditions within the Mississippi–Atchafalaya River system.

As a foundation for the assessment, six interrelated reports were developed by six teams with experts from within and outside of government. Each of the reports underwent extensive peer review by independent experts. To facilitate this comprehensive review, an editorial board was selected based on nominations from the task force and other organizations. Board members were Dr. Donald Boesch, University of Maryland; Dr. Jerry Hatfield, U.S. Department of Agriculture; Dr. George Hallberg, Cadmus Group; Dr. Fred Bryan, Louisiana State University; Dr. Sandra Batie, Michigan State University; and Dr. Rodney Foil, Mississippi State University. The six reports are entitled:

Topic 1: Characterization of Hypoxia. Describes the seasonal, interannual, and long-term variations of hypoxia in the northern Gulf of Mexico and its relationship to nutrient loadings. *Lead: Nancy N. Rabalais, Louisiana Universities Marine Consortium.*

Topic 2: Ecological and Economic Consequences of Hypoxia. Evaluates the ecological and economic consequences of nutrient loading, including impacts on the regional economy. *Co-leads: Robert J. Diaz, Virginia Institute of Marine Science, and Andrew Solow, Woods Hole Oceanographic Institution, Center for Marine Policy.*

Topic 3: Flux and Sources of Nutrients in the Mississippi–Atchafalaya River Basin. Identifies the sources of nutrients within the Mississippi–Atchafalaya system and Gulf of Mexico. *Lead: Donald A. Goolsby, U.S. Geological Survey.*

Topic 4: Effects of Reducing Nutrient Loads to Surface Waters Within the Mississippi River Basin and Gulf of Mexico. Estimates the effects of nutrient-source reductions on water quality. *Co-leads: Patrick L. Brezonik, University of Minnesota, and Victor J. Bierman, Jr., Limno-Tech, Inc.*

Topic 5: Reducing Nutrient Loads, Especially Nitrate–Nitrogen, to Surface Water, Ground Water, and the Gulf of Mexico. Identifies and evaluates methods for reducing nutrient loads. *Lead: William J. Mitsch, Ohio State University.*

Topic 6: Evaluation of the Economic Costs and Benefits of Methods for Reducing Nutrient Loads to the Gulf of Mexico. Evaluates the social and economic costs and benefits of the methods identified in Topic 5 for reducing nutrient loads. *Lead: Otto C. Doering, Purdue University.*

These six individual reports provide a foundation for the final integrated assessment, which the task force will use to evaluate alternative solutions and management strategies called for in Public Law 105-383.

As a contribution to the Decision Analysis Series, this report provides a critical synthesis of the best available scientific information regarding the ecological and economic consequences of hypoxia in the Gulf of Mexico. As with all of its products, the Coastal Ocean Program is very interested in ascertaining the utility of the Decision Analysis Series, particularly with regard to its application to the management decision process. Therefore, we encourage you to write, fax, call, or e-mail us with your comments. Our address and telephone and fax numbers are on the inside front cover of this report.

David Johnson, Director
Coastal Ocean Program

Donald Scavia, Chief Scientist
National Ocean Service

Executive Summary

QUESTIONS ADDRESSED

This report addresses the following two questions:

- What are the loads (flux) of nutrients transported from the Mississippi–Atchafalaya River Basin to the Gulf of Mexico, and where do they come from within the basin?
- What is the relative importance of specific human activities, such as agriculture, point-source discharges, and atmospheric deposition in contributing to these loads?

These questions were addressed by first estimating the flux of nutrients from the Mississippi–Atchafalaya River Basin and about 50 interior basins in the Mississippi River system using measured historical streamflow and water quality data. Annual nutrient inputs and outputs to each basin were estimated using data from the National Agricultural Statistics Service, National Atmospheric Deposition Program, and point-source data provided by the USEPA. Next, a nitrogen mass balance was developed using agricultural statistics, estimates of nutrient cycling in agricultural systems, and a geographic information system. Finally, multiple regression models were developed to estimate the relative contributions of the major input sources to the flux of nitrogen and phosphorus to the Gulf of Mexico.

MAJOR FINDINGS

The major findings from this assessment are summarized below.

Flux and Sources of Nutrients

- The current (1980–96) mean annual flux of total nitrogen from the Mississippi–Atchafalaya River Basin to the Gulf of Mexico is about 1.6 million metric tons, and the average total nitrogen yield for the entire basin is 489 kg/km^2/yr. The nitrogen is about 61% nitrate, 37% dissolved and particulate organic N, and 2% ammonium.
- Nitrate concentrations in the Mississippi River and some of its tributaries in the upper Midwest have increased two- to five-fold in the last century.
- Nitrate flux from the Mississippi Basin to the Gulf of Mexico has averaged nearly 1 million metric tons per year since 1980 and is about three times larger than it was 30 years ago. Most of the increase in nitrate flux to the Gulf occurred between 1970 and 1983.
- Streamflow in the Mississippi River also increased about 30% during 1970–83 as a result of increased precipitation. The increase in nitrate flux to the Gulf is attributed to both an increase in nitrate concentration and an increase in streamflow.

- Since about 1980, the annual nitrogen flux has become highly variable due, in part, to variable amounts of precipitation and increased annual nitrogen inputs to the basin. Episodic events, such as the 1993 flood, can nearly double the annual nitrate flux to the Gulf as a result of increased leaching of nitrate from the basin's soil/ground-water system. High annual nitrate fluxes associated with flood events can be expected to occur in the future.
- The 1980–96 average annual flux of phosphorus to the Gulf was about 136,000 metric tons. On average about 69% of the phosphorus is in particulate and/or organic material, and 31% is transported as dissolved orthophosphate. There has been no statistically significant increase or decrease in the annual flux of phosphorus since records began in the early 1970s.
- The average annual flux of dissolved silica to the Gulf for 1980–96 was 2.1 million metric tons (as Si). Dissolved silica concentrations in the Lower Mississippi River decreased from 4–5 mg/L in the 1950s to about 3 mg/L in the mid-1970s. However, there has been no statistically significant long-term decrease in the flux of dissolved silica to the Gulf. This apparent contradiction results, in part, from an increase in streamflow, which could dilute silica concentrations without altering the flux. Removal of dissolved silica by increased diatom production in the Mississippi River as a result of increased nitrogen concentrations is another possible reason for the decrease.
- The principal source areas for the nitrogen that discharges to the Gulf are watersheds draining intensively cultivated regions in southern Minnesota, Iowa, Illinois, Indiana, and Ohio. These regions contribute several times more nitrogen per unit area than other areas.
- Streams draining Iowa and Illinois contribute as much as 35% of the total nitrogen flux of the Mississippi River during years of average rainfall, and much more during years of high rainfall. However, these two states comprise only about 9% of the area of the Mississippi–Atchafalaya Basin. During the flood year of 1993, Iowa, with only 4.5% of the basin area, contributed about 35% of the nitrate discharged to the Gulf of Mexico. Because these amounts assume no in-stream losses of nitrogen in the Mississippi River, they represent maximum contributions. Some in-stream nitrogen losses probably occur, but they are believed to be relatively small in large rivers, such as the Mississippi.
- The soils, unsaturated zones, and ground-water systems underlying cropland in the basin serve as storage reservoirs that can accumulate and store nitrogen. Accumulation of nitrate can be significant during years with low crop yields and dry climatic periods when leaching by precipitation is minimal. During periods of high precipitation, large amounts of the accumulated nitrate can be leached from these reservoirs into agricultural drains and streams, and eventually discharged to the Gulf of Mexico.
- Drainage of agricultural land by tile drains and other means contributes to the high nitrate concentrations and flux in the Mississippi River. Tile drains short-circuit the flow of ground water by draining the top of the ground-water system into tile lines and ditches, and eventually to the Mississippi River. Tile drainage water can have very high nitrate concentrations.

Relative Importance of Human Activities in Contributing to Nutrient Flux

- Nonpoint sources contribute about 90% of the nitrogen and phosphorus discharging to the Gulf of Mexico. Agricultural activities are the largest contributors of both nitrogen and phosphorus. Multiple-regression models showed fertilizer plus mineralized soil organic nitrogen to be the largest nitrogen source, contributing about 50% of the annual total nitrogen flux to the Gulf.

However, nitrogen inputs from fertilizer and mineralized soil are so strongly correlated that the relative importance of each of these sources could not be determined. Nitrogen sources, such as atmospheric deposition, ground-water discharge, and soil erosion, which are associated with basin runoff, are estimated to contribute 24% of the total nitrogen flux to the Gulf. Animal manure is estimated to contribute about 15% of the nitrogen flux, and municipal and industrial point sources contribute about 11%. Legumes do not appear to be significant contributors of nitrogen to the Gulf.

- About 31% of the phosphorus flux to the Gulf is estimated to come from fertilizer, 18% is from manure, and 10% is from municipal and industrial point sources. About 41% of the annual phosphorus flux comes from sources that are not quantified but are associated with basin runoff. The most important of these is believed to be phosphorus in sediment associated with soil erosion.
- Of all of the major agricultural nitrogen inputs to cropland, only fertilizer and legume inputs have increased significantly since the 1950s. Fertilizer nitrogen input has increased seven-fold, and fixation of nitrogen by legumes has increased by about 50%. The nitrogen input to the basin from animal manure has actually decreased slightly over the last 40 years, although the spatial pattern of the manure input has changed from a highly dispersed to a highly concentrated distribution. The amount of nitrogen removed from the basin in harvested crops has more than doubled since the 1950s, paralleling the increase in fertilizer use.
- In contrast to results reported for Chesapeake Bay and elsewhere in the eastern United States, atmospheric deposition appears to be a significant but relatively small contributor to the total nitrogen flux to the Gulf of Mexico. Atmospheric inputs (wet and dry) of nitrate are very significant in watersheds in much of the upper Ohio River Basin, and atmospheric deposition of ammonia, presumably from manure, is high in Iowa and parts of Minnesota and Illinois. However, these inputs are small relative to other nitrogen inputs to most of the Mississippi–Atchafalaya River Basin.
- Atmospheric deposition of nitrogen on a 30,000-km^2 area (twice the size of the hypoxic zone) of the Gulf of Mexico is estimated to be less than 1% of the nitrogen input to the Gulf from the Mississippi–Atchafalaya River Basin.
- In the future, the flux of nitrate to the Gulf will most likely respond quickly and dramatically to variations in precipitation and runoff. Because of the readily available pool of nitrate in the soil/ground-water system and the extensive drainage network, nitrate fluxes will be high in wet years and low in dry years. However, the nitrogen balance of the soil/ground-water system will adjust relatively slowly to increases or decreases in nitrogen inputs and outputs. As a result, the flux of nitrate to the Gulf will most likely change slowly in response to changes in nitrogen inputs. The response time of the basin to changes in inputs and outputs is unknown, but may be several years, or longer. This implies that it could take several years, or longer, for the effects of significant reductions (20%) in nitrogen inputs to produce a noticeable reduction in nitrogen flux to the Gulf of Mexico. In the short term, precipitation and runoff will control nitrate flux.

CHAPTER 1

Introduction

1.1 PURPOSE AND SCOPE OF THIS REPORT

The CENR Topic 3 team was asked to determine the flux and sources of nutrients transported from the Mississippi River Basin to the Gulf of Mexico. Nutrients of concern for this assessment are nitrogen, phosphorus, and silica. The first part of this task was to identify where the nutrients come from in the basin and which parts of the basin contribute the most significant flux of nutrients to the surface-water system. The second part was to estimate the relative importance of specific human activities, such as agriculture, point-source discharges, and atmospheric emissions, in contributing nutrient flux to the Mississippi River and Gulf of Mexico. This report presents the results of the assessment. It is based entirely on an analysis of existing information.

1.2 THE MISSISSIPPI–ATCHAFALAYA RIVER BASIN

The Mississippi River Basin is the largest river basin in North America and the third largest river basin in the world (van der Leeden et al. 1990). Only the Amazon River Basin in South America and the Congo River Basin in Africa are larger. About 70 million people live within the Mississippi River Basin, whose drainage area includes all or parts of 30 states.

The basin is one of the most productive farming regions in the world, producing the majority of the corn, soybeans, wheat, cattle, and hogs grown in the United States. Because of this intensive agriculture, the majority of all fertilizers and pesticides used in the United States are applied to cropland within the basin. About 58% of the basin is cropland (Figure 1.1). Other significant land uses and their percentages of the basin include woodland (18%), range and barren land (21%) , wetlands and water (2.4%), and urban land (0.6%). Runoff from these diverse land uses discharges into streams and reservoirs, carrying with it suspended sediment, naturally occurring chemicals weathered from the soil, and such contaminants as nutrients and pesticides from urban and agricultural activities in the basin. The water, along with much of its dissolved and suspended contents, eventually flows into the Mississippi River and ultimately discharges into the Gulf of Mexico. Naturally occurring chemicals and man-made contaminants also leach to ground-water systems. This water eventually is discharged to streams and rivers that flow into the Mississippi River. The ground water and its associated chemical load can take from a few days to decades, or longer, to reach a point of discharge on a river (Winter et al. 1998).

The Gulf of Mexico has one of the most productive fisheries in the world. The combined economic value of the farm industry of the Mississippi River Basin and the fishing industry of the Gulf is estimated to be more than $100 billion (Malakoff 1998). The land-use and cultural changes that have occurred in the basin this century have had measurable and sometimes deleterious effects on the quality of water in the Mississippi River, its tributaries, and the Gulf of Mexico. In particular, increases in the flux (loads) of nutrients transported from the basin in recent decades are believed to contribute to eutrophication, algal blooms, and hypoxia in the Gulf of Mexico (Rabalais et al. 1996). Further, it is likely that changes in land use and increases in nutrient flux will continue as the population of the basin grows and as crop production increases to meet the growing national and global demands for food.

1.3 HYDROLOGY

The Mississippi–Atchafalaya River Basin (MARB) drains an area of nearly 3,208,700 square kilometers (km^2), or about 41% of the conterminous United States (Figure 1.1). It extends from the Appalachian Mountains in western Pennsylvania and New York to the Rocky Mountains in western Montana and from southern Canada to the Gulf of Mexico. The mainstem of the Mississippi River originates in northern Minnesota and flows southward more than 3,700 km to the Gulf. At St. Louis, Missouri, its flow nearly doubles from about 3,530 m^3/s to 6,790 m^3/s, due to inflow from the Missouri and Illinois Rivers. About 320 km downstream from St. Louis the Mississippi's flow more than doubles again to about 15,340 m^3/s due to inflow from the Ohio River. From its confluence with the Ohio River to Vicksburg, Mississippi—a distance of about 860 river km—the average flow of the river increases only about 14%, to 17,400 m^3/s, with most of this increase coming from the Arkansas and White Rivers. About 225 km downstream from Vicksburg nearly 25% of the Mississippi's flow, on average, is diverted to the west through the Old River outflow channel. The diverted flow combines with the Red and Ouachita Rivers to form the Atchafalaya River, which is comprised predominately of Mississippi River water. The Atchafalaya then flows southward about 200 km to the Gulf.

The combined long-term average annual discharge of the Mississippi and Atchafalaya Rivers to the Gulf of Mexico is about 19,920 m^3/s based on streamflow records (1950–96) for the Mississippi at Tarbert's Landing, Mississippi (near St. Francisville), and the Atchafalaya River at Simmsport, Louisiana (streamflow data provided by the U.S. Army Corps of Engineers). Streamflow varies considerably over long periods of time. For example, the mean annual flow of the Mississippi increased about 30% between 1955 and 1996 (see section 4.2.1).

Figure 1.2 is a hydrograph of daily streamflow for the Mississippi River at Vicksburg, Mississippi, for the period 1980–97. The seasonal pattern of streamflow shown in this figure is typical of other large unregulated rivers in the Mississippi River Basin (MRB). Streamflow is lowest in the fall, with the lowest flows occurring in September and October. Streamflow typically begins to increase in mid-winter and usually reaches a peak in April or May (Baldwin and Lall 1999). The majority of the annual transport of water, sediment, nutrients, and other chemicals from the Mississippi and its tributaries occurs between December and June of each year.

The hydrology of the Mississippi River system has been greatly altered by locks, dams, and reservoirs since the early 1900s (Meade 1995). The Mississippi has a series of 29 lock-and-dam structures between St. Louis, Missouri, and St. Paul, Minnesota, which have been constructed to maintain water sufficiently deep for navigation by boats and barges. Similarly, the Ohio River currently (1999) has 20 lock-and-dam structures for navigation between its mouth at Cairo, Illinois, and Pittsburgh, Pennsylvania. Also, two large tributaries to the Ohio River—the Tennessee and Cumberland River—have large reservoirs just above their confluence with the Ohio. The Missouri River has a series of large reservoirs in Montana and North and South Dakota, most of which were constructed and filled in the 1950s and early 1960s. The storage capacity of these reservoirs is equal to several years of discharge of the Missouri River and has a significant effect

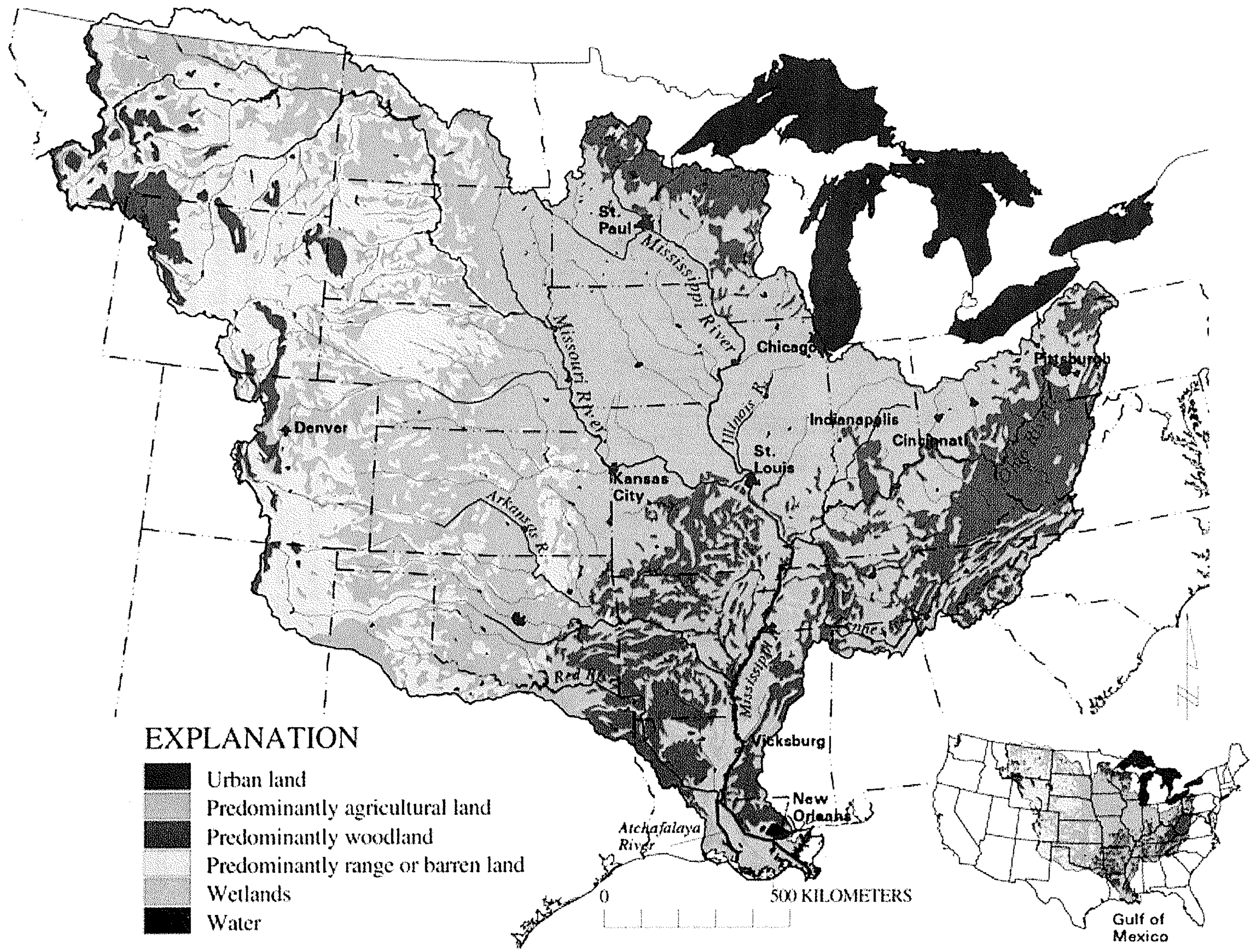


FIGURE 1.1. Drainage and land use in the Mississippi–Atchafalaya River Basin.

on the transport of water, sediment, and nutrients. In addition to storing water, the reservoirs on the Missouri River and the pools formed behind the lock-and-dam structures on the Mississippi and Ohio Rivers also trap organic and inorganic material, including sediment (Meade 1995), nutrients, and organic carbon, altering the flow of these materials to the Gulf of Mexico. For example, since construction of the Missouri River reservoirs, sediment discharge from the MRB to the Gulf has decreased by more than 50% (Meade and Parker 1985).

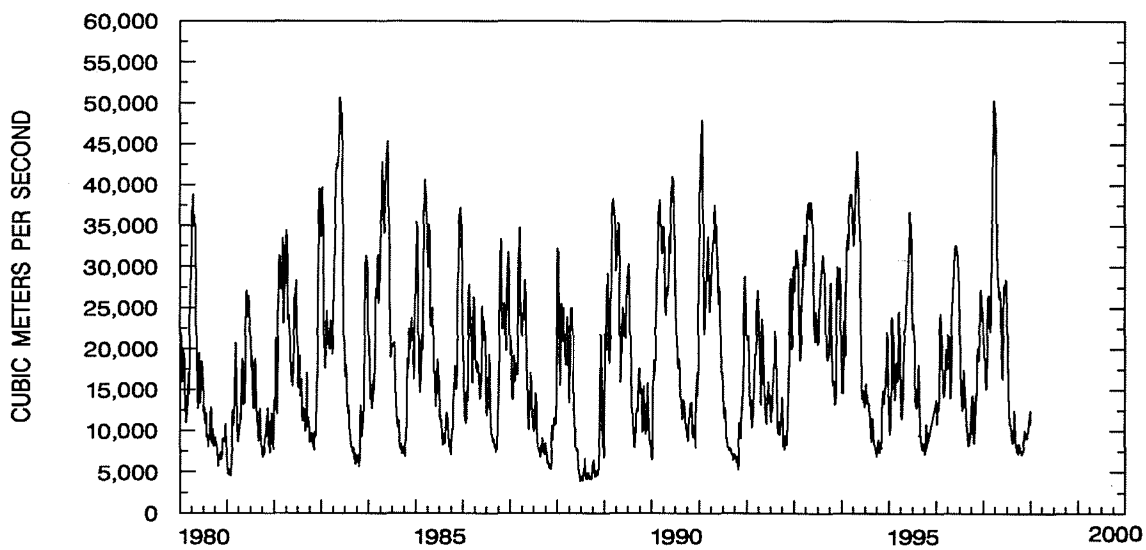


FIGURE 1.2. Daily mean streamflow for the Mississippi River at Vicksburg, Mississippi. *(Data from U.S. Army Corps of Engineers, Vicksburg, MS).*

1.4 PHYSICAL, LAND USE, AND CULTURAL FEATURES

The climate, land use, soils, and population vary widely across the MRB. The annual runoff ranges from less than 5 centimeters (cm) per year in the arid western part of the basin to more than 60 cm per year in the humid eastern part. The central part of the basin is used primarily for cropland (Figure 1.3) and produces most of the corn, soybeans, wheat, and sorghum grown in the United States. In some parts of the MRB—particularly in Iowa, Illinois, and Indiana—more than 50% of all land in some hydrologic accounting units is used for growing crops (indicated by the red areas in Figure 1.3). Most of the fertilizers and pesticides used in the United States are applied to cropland in this part of the basin. Large numbers of livestock (cattle and hogs) and poultry also are produced in the central part of the basin.

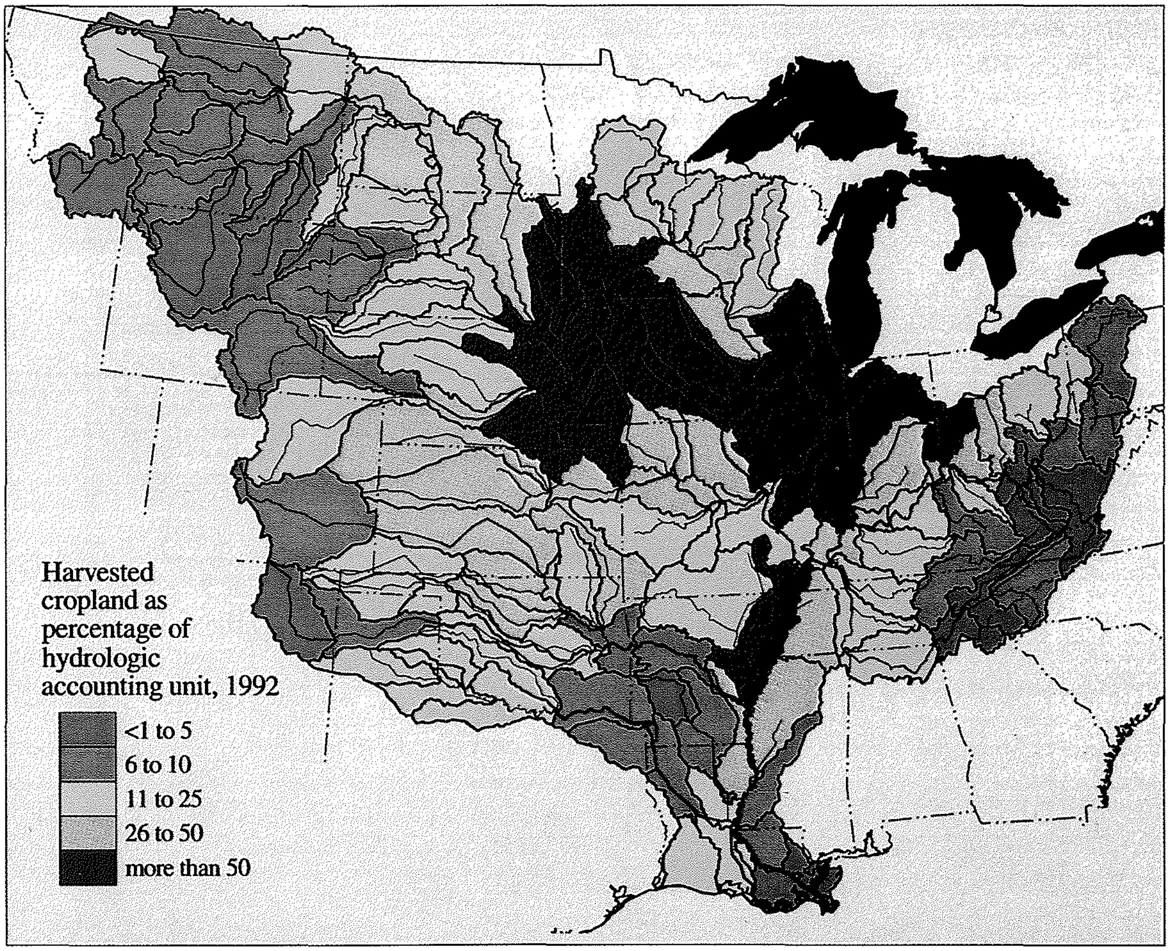


FIGURE 1.3. Harvested cropland in the Mississippi River Basin as a percentage of area of hydrologic accounting units.

During 1870–1920 and 1945–60, the central part of the MRB was subjected to extensive agricultural drainage to lower the water table to make farming more economical and efficient (Zucker and Brown 1998; Pavelis et al. 1987). This practice essentially drains the top of the ground water system into tile lines and ditches that flow into streams, rivers, and eventually the Mississippi River. More than 50 million acres of mostly cropland in the MRB have been drained by tile lines, ditches, and other means. Figure 1.4 shows the percentage of land in each hydrologic accounting unit in the MARB that has been drained.

Woodland is more common in the eastern, north central, and south central parts of the MRB (Figure 1.1). Rangeland and barren land are common in the western part of the basin, while wetlands are most common in the extreme northern and extreme southern parts. Most of the MRB's 70 million people live in the eastern half, particularly in the Ohio Basin, as illustrated by the red areas in Figure 1.1 and the red and pink areas in Figure 1.5.

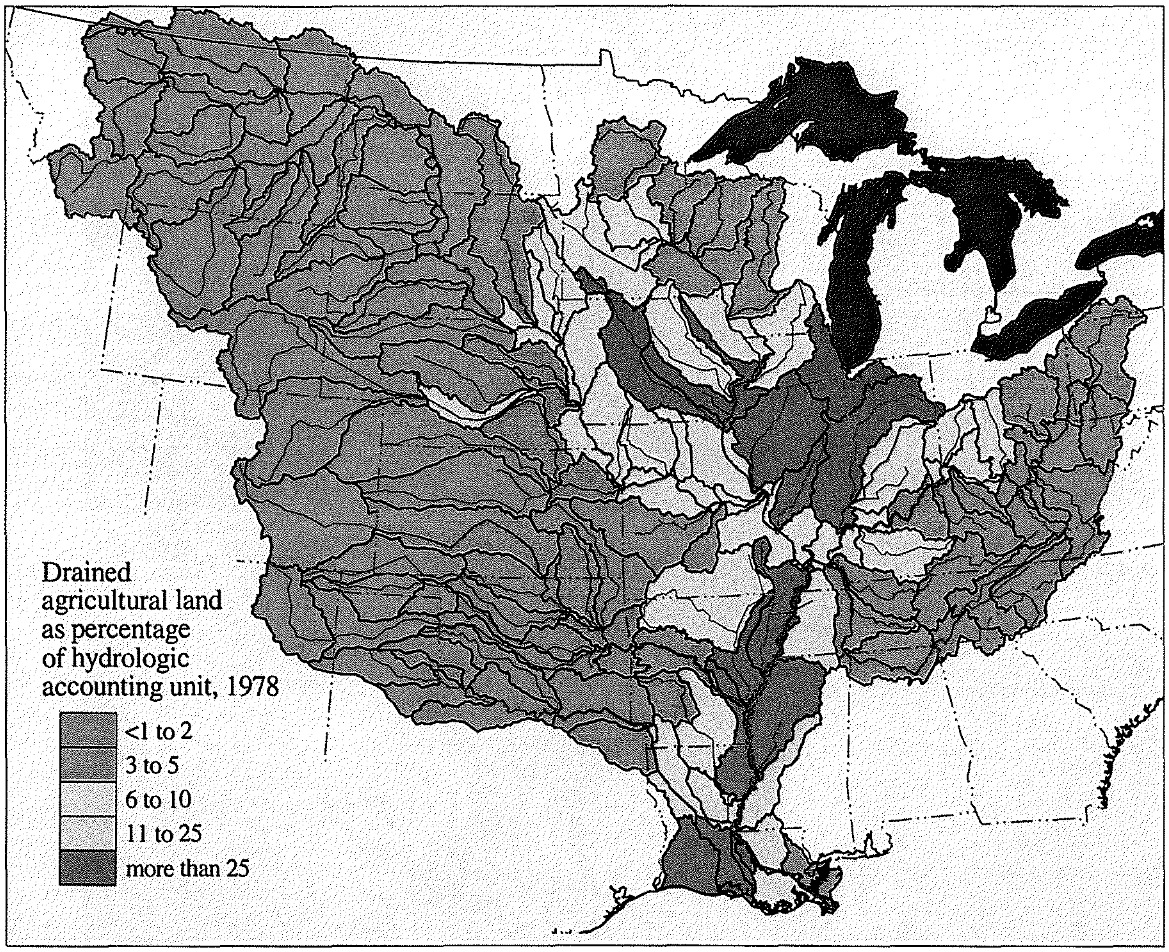


FIGURE 1.4. Drained agricultural land in the Mississippi River Basin as a percentage of the area of hydrologic accounting units.

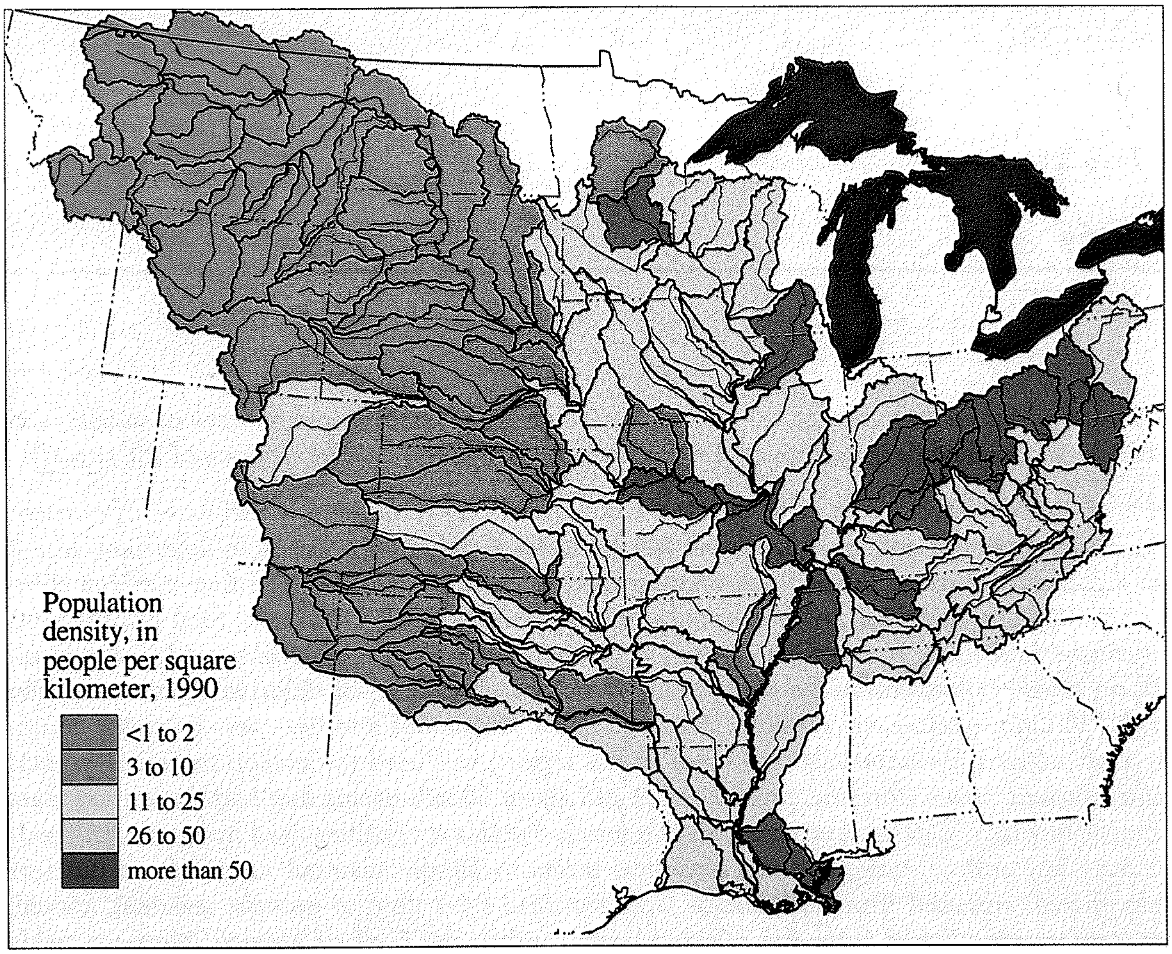


FIGURE 1.5. Density of population within hydrologic accounting units in the Mississippi River Basin.

CHAPTER 2

Methods

This section provides an overview of the methods used to assess the flux and sources of nutrients in the MARB. More detailed descriptions of the methods are presented in later sections of the report.

The first step in the assessment was to develop annual and long-term average estimates of nutrient fluxes (mass transport per unit time) from the MARB to the Gulf of Mexico and to determine where the most significant nutrient fluxes were coming from within the MARB. The five nutrient compounds considered most critical to the hypoxia issue were nitrate, total nitrogen, total phosphorus, orthophosphate, and silica. Flux estimates were developed for each of these compounds using available data on nutrient concentrations and stream discharge. Estimates of chloride fluxes were also developed. Chloride, a nonreactive solute, was used to develop ratios and test mass balances. Multiple-regression analysis (described in detail later in this report) was used to develop statistical models to estimate nutrient fluxes from the entire MARB and about 50 sub-basins that had streamflow data and sufficient historical data on nutrient concentrations. Predictor variables used in regression models were daily streamflow, time, and mathematical terms to handle seasonal variations in nutrient flux. Daily fluxes estimated from the models were summed over time to provide seasonal, annual, and long-term average fluxes from the selected basins and to the Gulf of Mexico. Nutrient yields (mass per unit area per unit time) were calculated by dividing the estimated annual fluxes by basin areas. This normalized the nutrient fluxes and provided a means to compare nutrient contributions among basins of all sizes.

The second step in this assessment was to estimate the annual inputs of nitrogen and phosphorus to the MRB from all major known sources. The inputs considered included agriculture (fertilizer, manure, legumes, and soil mineralization), atmospheric deposition of nitrate (wet and dry) and ammonium, and municipal and industrial point sources. Inputs of newly formed nitrogen from fertilizer, legumes, and atmospheric deposition of nitrate (Jordan and Weller 1996; Howarth et al. 1996) were differentiated from nitrogen that was already in the system (recycled nitrogen). These recycled nitrogen inputs, which include manure, mineralization of soil organic matter and plant residue, and atmospheric deposition of ammonium, can be the immediate source of some of the nitrate that leaches into streams and ground water, just as can the newly formed nitrogen. A geographic information system (ARC/INFO) was used to develop estimates of annual nutrient inputs and outputs for selected basins and to display the spatial distribution of these inputs and outputs. Finally, a nitrogen mass balance was developed for the basin to estimate the total inputs of nitrogen (new and recycled) and total outputs of nitrogen from the MARB on an annual basis. The mass balance also provided a means to estimate the amount of nitrogen that might be available for leaching to streams and ground water.

2.1 SOURCES AND DESCRIPTION OF DATA

The nutrient concentration data used in this analysis to develop flux estimates were obtained from the U.S. Geological Survey (USGS) National Water Information System (NWIS) database. These data were collected as part of various USGS programs in the basin during 1974–97. The principal source of data on nutrient concentrations used in this assessment is the USGS National Stream Quality Accounting Network (NASQAN) (Ficke and Hawkinson 1975; Alexander et al. 1996). This program conducted extensive sampling for nutrients in the 1970s and early 1980s. The sampling was continued at a reduced scale and frequency through the early 1990s, at which time the program was redesigned to focus on large rivers, such at the Mississippi (Hooper et al. 1997). Data on nitrate, ammonia, total organic nitrogen, ortho and total phosphorus, and silica were collected routinely since the start of the NASQAN program. Additional nutrient data were obtained from the USGS National Water Information System (NWIS). These data were collected as part of various USGS programs beginning in the early 1900s. Data from reports published in the early 1900s were also used. Table 2.1 describes the analytical methods used to obtain these data. Nitrate was analyzed by the phenoldisulfonic acid method (Rainwater and Thatcher 1960) before the early 1970s, and by cadmium reduction afterward. The two methods are reported to have comparable accuracy (Friedman and Fishman 1989). The possible implications of this change in methods for analyzing long-term trends are discussed in section 3.2.

TABLE 2.1. Analytical methods used to determine nutrient concentrations in water samples used in this assessment.

Nutrient	Period	Analytical Method	References
Nitrate	Pre-1970	Colorimetric phenoldisulfonic acid	Rainwater and Thatcher 1960
	1970–96	Colorimetric cadmium reduction	Fishman and Friedman 1989
Organic nitrogen	1975–96	Colorimetric kjeldahl	Fishman and Friedman 1989
Orthophosphate	1975–96	Colorimetric phosphomolybdate	Fishman and Friedman 1989
Total phosphorus	1975–96	Digestion, colorimetric phosphomolybdate	Fishman and Friedman 1989
Silica	Pre–1980	Colorimetric molybdate	Fishman and Friedman 1989
	1980–96	Colorimetric molybdate and inductively coupled plasma	Fishman and Friedman 1989

A large body of additional data on nutrient concentrations is available from numerous state, local, and federal agencies in the MRB. However, these data were not used because of the short time frame for this analysis and the effort that would have been required to obtain the data and ensure that sample collection and analytical methods were comparable with USGS methods.

Daily streamflow data used in this report were obtained from several sources. Streamflow data for the Lower Mississippi, Atchafalaya, and Red Rivers were obtained from the U.S. Army Corps of Engineers. The Tennessee Valley Authority provided streamflow data for the Tennessee River. The remaining streamflow data were obtained from the USGS/NWIS.

Data on nitrogen and phosphorus inputs and outputs in agriculture were obtained from numerous sources. Data on crop production, livestock, and poultry were obtained from the U.S. Department of Commerce's (USDC's) Census of Agriculture and the U.S. Department of Agriculture's (USDA's) National Agricultural Statistics Service (NASS). These data were used to develop estimates of nitrogen and phosphorus inputs from legume crops and animal manure, and nitrogen and phosphorus outputs in harvested crops. Data on nitrogen and phosphorus inputs from fertilizer were obtained from NASS, the Tennessee Valley Authority, the Fertilizer Institute, and published reports. Nitrogen inputs and outputs from soil mineralization and immobilization, denitrification, and volatilization were obtained through the assistance of soil scientists in the USDA and the academic sector, and from the literature. Methods used to obtain agricultural inputs and outputs are described in detail later in this report.

Recent (1996) data on nitrogen and phosphorus from municipal and industrial point sources for more than 11,000 facilities in the MARB were developed by the U.S. Environmental Protection Agency (USEPA). The methods used to develop these estimates are described in detail later in this report. Historical data on point-source discharges were obtained from published reports.

Nitrogen inputs to the MARB from atmospheric wet deposition were estimated from data on nitrate and ammonium in rainfall obtained from the National Atmospheric Deposition Program (NADP). Nitrogen in dry deposition was estimated with statistical models using data from the CASTNet (Clean Air Status and Trends Network), AIRMoN (Atmospheric Integrated Research Monitoring Network), and NADP programs. Atmospheric deposition of nitrogen on the Gulf of Mexico was estimated based on a literature review and very limited deposition data.

2.2 SELECTION OF BASINS FOR FLUX ESTIMATION

Estimates of nutrient flux in the MARB were made at three scales: the entire Mississippi–Atchafalaya River Basin, 9 large basins that in aggregate comprise the MARB, and 42 smaller basins, referred to as interior basins. The largest scale, the entire MARB, shown in Figures 1.1 and 2.1, provided long-term (42 years) estimates of nutrient flux to the Gulf of Mexico from the entire basin. Historical data available at two sampling stations listed in Table 2.2—the Mississippi River at St. Francisville, Louisiana, and the Atchafalaya River at Simmsport, Louisiana—provided estimates of nutrient flux at this scale. The St. Francisville site, located about 150 miles upstream from New Orleans, Louisiana, provided estimates of nutrient flux to the Gulf via the Mississippi River channel and the nutrient flux diverted into the Atchafalaya River. Data on nitrate and silica concentrations have been collected at this site numerous times each year since 1955. The Atchafalaya site provided estimates of nutrient flux to the Gulf from the Red and Ouachita Rivers and the Mississippi River diversion via the Old River Outflow Channel.

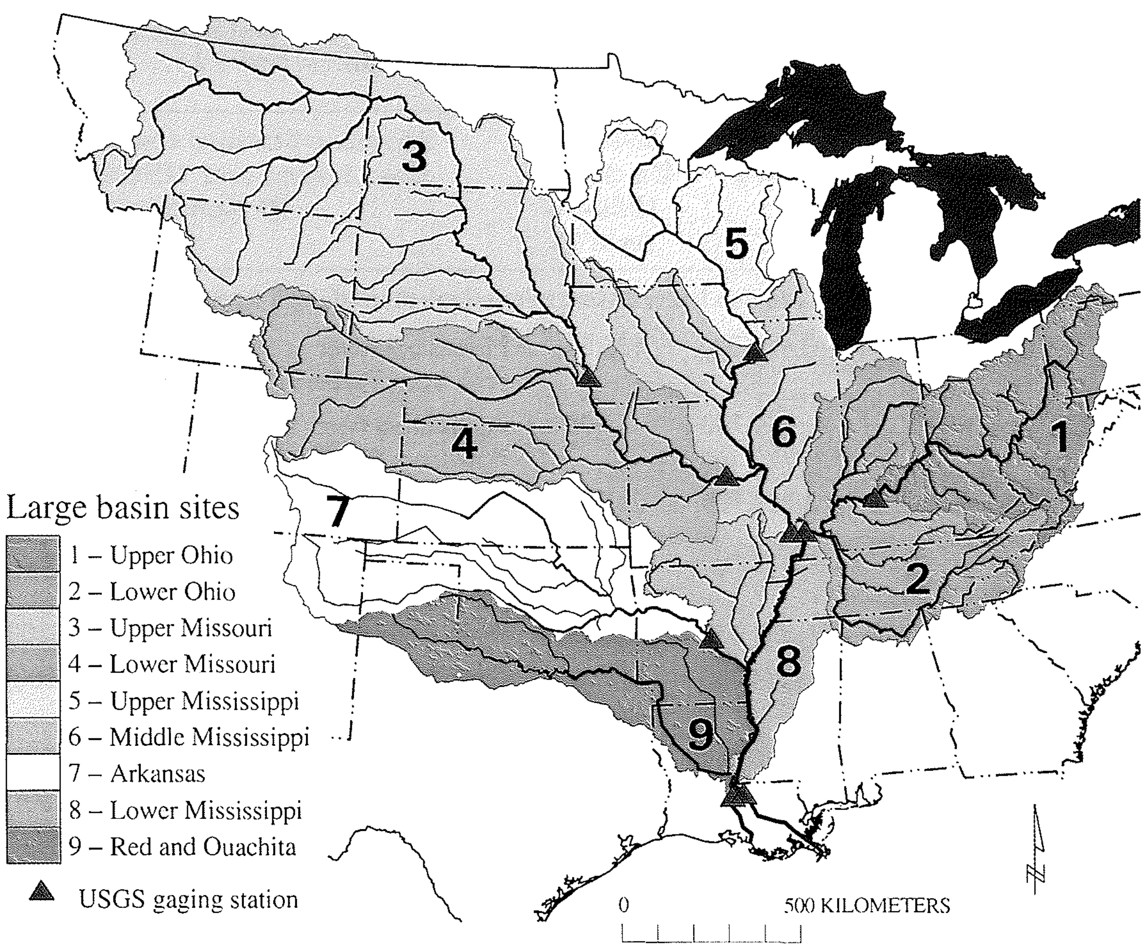


FIGURE 2.1. Location of nine large basins used for nutrient flux and yield estimates. NOTE: See Table 2.2 for descriptions.

The nine large basins were selected to provide estimates of nutrient flux at a large-basin scale and to develop solute balances for nutrient flux in the MARB. These basins are shown in Figure 2.1 and are described in Table 2.2. They cover nearly the entire MARB, except for a small area in southern Louisiana, and provide data on the relative contributions of nutrient flux to the Gulf of Mexico from nine large areas of the MARB. Because of the cumulative nature of streamflow in these basins, it was necessary to calculate the flux from some of the basins as the difference in flux measured at upstream and downstream sampling stations. The sum of the nutrient fluxes measured for these 9 basins is nearly equal to the total flux from the MARB to the Gulf of Mexico. Only a small area (< 2% of the MARB) in southern Louisiana below St. Francisville on the Mississippi River and below Melville on the Atchafalaya River is not included.

The 42 interior basins were selected to provide detailed information on nutrient fluxes and nutrient yields in various parts of the MARB and to help identify areas having abnormally high inputs. These 42 basins are shown in Figure 2.2. Table 2.3 presents a listing of the basins and their drainage areas, number of years of nutrient data, average discharges, average runoff, population density, and percent cropland.

TABLE 2.2. Sites used to estimate nutrient flux from nine large basins and from the entire Mississippi–Atchafalaya River Basin. NOTE: Locations are shown in Figure 2.1.

Large Basin Map ID	Basin Name	Area (km^2)	Average Discharge 1980–96 (in m^3/s)	Sampling Stations Used for Flux Calculations and USGS Station ID Number
	Outflow to Gulf of Mexico from Entire Mississippi–Atchafalaya River Basin			
1–8	Mississippi River	~2,967,000	15,390	Mississippi River at St. Francisville, LA, streamflow from Tarbert's Landing, MS
	Atchafalaya River	241,700	6,600	Atchafalaya River at Melville, LA, and streamflow from Simmsport, LA
1–9	Entire Mississippi–Atchafalaya Basin	3,208,700	21,990	Mississippi River at St. Francisville, LA, plus Atchafalaya River at Melville, LA
	Large Basins			
1	Upper Ohio	251,230	3,620	Ohio River at Cannelton Dam, KY (03303280)
2	Lower Ohio	274,800	4,760	Ohio River at Grand Chain, IL (03612500) and Ohio River at Cannelton Dam, KY
1 + 2	Entire Ohio Basin	526,030	8,380	Ohio River at Grand Chain, IL (03612500)
3	Upper Missouri	836,050	1,015	Missouri River at Omaha, NE (06610000)
4	Lower Missouri	521,630	1,763	Missouri River at Hermann, MO (06934500) and Missouri River at Omaha, NE
3 + 4	Entire Missouri Basin	1,357,680	2,778	Missouri River at Hermann, MO (06934500)
5	Upper Mississippi	221,700	1,596	Mississippi River at Clinton, IA (05420500)
None	Mississippi River above Missouri River Basin	444,200	3,687	Mississippi River below Grafton. IL (05587455)
6	Middle Mississippi	267,800	2,519	Mississippi River at Thebes, IL (07022000) Mississippi River at Clinton, IA; Missouri River at Hermann, MO
7	Arkansas	409,960	1,448	Arkansas River at Little Rock, AR (07263620)
8	Lower Mississippi	184,000	2,925	Mississippi River at St. Francisville, LA (07373420), and streamflow from Tarbert's Landing, LA; Old River outflow at Knox Landing (Mississippi diversion); Arkansas R. at Little Rock, AR; Ohio River at Grand Chain, IL; Mississippi River at Thebes, IL
9	Red and Ouachita	242,700	2,349	Atchafalaya River at Melville. LA (07381495), and streamflow from Atchafalaya at Simmsport, LA; Old River outflow at Knox Landing, LA

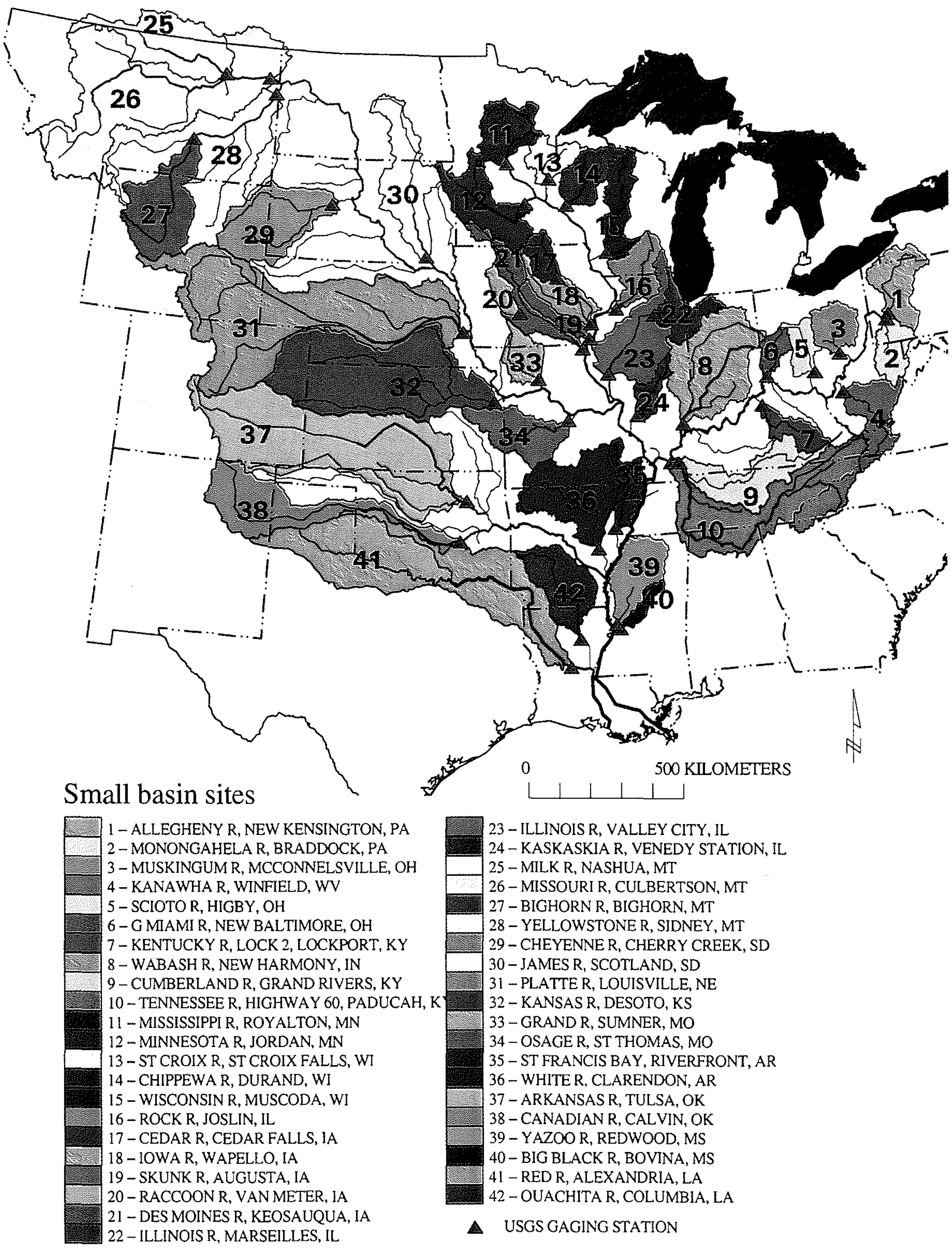


FIGURE 2.2. Location of 42 interior basins used for nutrient flux and yield estimates. NOTE: See Table 2.3 for descriptions.

TABLE 2.3. Sites used to estimate nutrient flux from 42 interior basins during 1980–96.
NOTE: Basin locations are shown in Figure 2.2.

Basin ID No.	Name and Location of Sampling Station Used for Flux Estimation	Area (km^2)	Years of Nutrient Data	Average Discharge (m^3/s)	Annual Runoff (cm/yr)	People per km^2	Percent Crop-land
1	Allegheny River at New Kensington, PA	29,800	16	574.9	60.83	39.1	2.5
2	Monongahela River at Braddock, PA	19,000	16	354.0	58.77	65.4	1.3
3	Muskingham River at McConnelsville, OH	19,200	13	234.8	38.55	70.8	14.3
4	Kanawha River at Winfield, WV	30,600	16	498.4e*	51.37	28.1	0.5
5	Scioto River at Higby, OH	13,300	16	139.6	33.12	107.8	45.6
6	Great Miami at New Baltimore, OH	9,900	14	103.9	33.14	133.7	46.6
7	Kentucky River at Lockport, KY	16,000	14	216.4	42.65	40.0	1.5
8	Wabash River at New Harmony, IN	75,700	8	886.7	36.93	47.1	53.6
9	Cumberland River near Grand Rivers, KY	45,600	7	906.2	62.67	38.3	4.1
10	Tennessee River near Paducah, KY	104,500	10	1.711.7	51.66	37.7	3.1
11	Mississippi River near Royalton, MN	30,000	15	148.9	15.65	8.0	4.0
12	Minnesota River at Jordan, MN	42,000	16	184.4	13.84	9.8	56.6
13	St. Croix River at St. Croix Falls, WI	16,200	15	142.4	27.73	8.8	4.5
14	Chippewa River at Durand, WI	23,300	15	231.4	31.33	11.9	6.3
15	Wisconsin River at Muscoda, WI	26,900	15	265.9	31.17	18.3	8.9
16	Rock River near Joslin, IL	24,700	17	216.6	27.65	56.5	43.8
17	Cedar River at Cedar Falls, IA	12,260	16	122.3	29.03	19.2	70.0
	(daily streamflow measured at Waterloo, IA)	(13,330)					
18	Iowa River at Wapello, IA	32,400	17	288.9	28.13	24.2	65.3
19	Skunk River at Augusta, IA	11,100	17	92.6	26.33	18.7	57.2
20	Raccoon River at Van Meter/Des Moines, IA	8,900	14	67.7	24.02	10.6	73.9
21	Des Moines at St. Francisville, MO	37,040	14	274.7	23.80	20.8	62.4
	(daily streamflow measured at Keosaqua, IA)	(36,400)					
22	Illinois River at Marseilles, IL	21,400	14	328.2	48.37	305.4	54.2
23	Lower Illinois River Basin	47,400	15	430.7	28.66	49.2	63.6
--	Illinois River at Valley City, IL (basins 22 & 23)	68,800	15	758.6	34.79	128.9	60.7
24	Kaskaskia River near Venedy Station, IL	11,400	13	101.4	28.03	22.7	56.8
25	Milk River near Nashua, MT	57,800	15	13.0	0.71	0.6	< 0.1
26	Missouri River near Culbertson, MT	237,100	14	267.9	3.56	1.4	< 0.1
27	Bighorn River near Bighorn, MT	59,300	13	93.4e*	4.97	1.5	0.1
28	Yellowstone River near Sydney, MT	179,000	16	314.1	5.53	1.8	0.2
29	Cheyenne River at Cherry Creek, SD	61,900	15	20.7	1.06	3.0	0.2
30	James River near Scotland, SD	55,800	14	18.7	1.06	3.0	14.6
31	Platte River near Louisville, NE	222,200	17	250.1	3.55	14.2	10.9
32	Kansas River at Desoto, KS	154,800	13	220.6	4.50	5.9	17.5
33	Grand River near Sumner, MO	17,800	14	148.4	26.30	5.9	23.3
34	Osage River below St. Thomas, MO	37,600	15	390.2	32.74	12.0	11.8
35	St. Francis Bay at Riverfront, AR	16,800	15	178.4e*	33.49	19.5	34.6
36	White River at Clarendon, AR	66,200	7	761.8e*	36.29	13.0	7.2
37	Arkansas River at Tulsa, OK	193,300	16	268.5	4.38	10.4	5.5
38	Canadian River at Calvin, OK	72,400	15	66.8	2.91	5.8	1.6
39	Yazoo River at Redwood, MS	32,600	14	475.8e*	46.02	14.6	15.1
40	Big Black River near Bovina, MS	7,300	15	120.9	52.19	12.9	3.7
41	Red River at Alexandria, LA	174,800	13	988.9	17.84	11.5	2.2
42	Ouachita River near Columbia, LA	40,500	14	543.7e*	42.33	15.1	1.7

**Streamflow was measured only when water samples were collected.*

There were insufficient historical data on nutrient concentrations to estimate nutrient flux at this scale for the entire MARB. However, these 42 basins cover the full range of land uses and population density in the MARB and provide a good spatial representation of the entire basin. Also, the aggregate drainage areas of these 42 basins account for about 70% of the drainage area of the MARB. Data were available at many of these sites to estimate nutrient flux for the 17-year period from 1980 to 1996. The actual number of years for which nutrient data were available and flux estimates were made for each of these basins is shown in Table 2.3. Nutrient yields from these 42 basins were used in conjunction with data on nutrient inputs to the basins from point and nonpoint sources to examine the relative importance of specific human activities in contributing nutrients to streams in the MARB.

CHAPTER 3

Nutrient Concentrations

Data on the concentrations of nutrients are needed to estimate nutrient flux to the Gulf of Mexico. However, nutrient concentrations also are of importance in addressing the overall water quality and health of streams in the MARB. High concentrations of nitrogen and phosphorus in streams can cause eutrophication and can present problems for public drinking-water supplies. These nutrients are derived from both natural sources and sources associated with human activities, such as waste disposal and agriculture. Human activities can lead to significant increases in nitrogen and phosphorus concentrations in streams, which, in turn, can lead to increased nutrient flux in streams and to the Gulf. This section briefly summarizes data on current and historical nutrient concentrations in the basin and discusses their temporal and spatial patterns. A more detailed discussion of the water quality in the MARB is presented in a companion CENR hypoxia assessment report (Brezonik et al. 1999).

3.1 CURRENT NITROGEN CONCENTRATIONS

The mean concentrations of nitrogen, phosphorus, silica, and chloride in water discharging from the large basins selected for this study (Figure 2.1) appear in Table 3.1. Mean concentrations for the 42 interior basins (Figure 2.2) are summarized in Table 3.2. Nitrogen is the nutrient believed to be most responsible for producing the increased growths of algae in the Gulf that lead to seasonal oxygen depletion and hypoxia (Rabalais et al. 1996).

The two principal forms in which nitrogen occurs in streams of the MARB are nitrate (NO_3^-) and organic nitrogen (dissolved and particulate). Significant amounts of ammonia (mostly NH_4^+) also may occur in some stream reaches, particularly downstream from sources of municipal and animal wastes. However, ammonia is quickly transformed to nitrate, and concentrations are generally much less than 0.1 mg/L in the lower reaches of the Mississippi River (Antweiler et al. 1995). Trace amounts of nitrite (NO_2^-) nitrogen also occur briefly during the oxidation of ammonia to nitrate, which is the end product of the aerobic biochemical oxidation of organic and ammonia nitrogen in soil and water. Nitrate is the most soluble and mobile form of nitrogen and is easily leached from soils by precipitation into ground water, tile drains, and streams.

The distribution of nitrate plus nitrite–nitrogen, hereafter referred to as nitrate, at the sites representing the 42 interior basins is shown in boxplot A of Figure 3.1. As the figure shows, there are two distinct groups of basins: 12 have median nitrate concentrations ranging from about 2.5 mg/L to more than 6 mg/L, while the remaining 30 have medians of less than 1.5 mg/L. Boxplot A of Figure 3.1 also shows that the maximum nitrate concentration at several of these sites occasionally exceeds the drinking-water standard of 10 mg/L.

TABLE 3.1. Mean concentrations (mg/L) of nitrogen, phosphorus, silica (Si), and chloride at large river sites in the Mississippi–Atchafalaya River Basin during 1980–96.

Station Name & Location	Number of Samples	Nitrate Plus Nitrite–Nitrogen	Ammonia Nitrogen	Total Organic & Ammonia Nitrogen	Organic Nitrogen	Total Nitrogen	Ortho-phosphorus	Total Phosphorus	Silica	Chloride
Ohio R. at Cannelton Dam, KY	65	1.240	0.089	0.750	0.66	1.98	0.037	0.176	2.13	20.1
Ohio R. at Grand Chain, IL	181	1.020	0.053	0.580	0.52	1.59	0.035	0.117	2.17	14.6
Mississippi R. at Clinton, IA	157	1.720	0.079	1.080	1.00	2.67	0.063	0.158	3.53	12.4
Mississippi R. at Grafton, IL	111	2.780	0.123	1.420	1.29	4.2	0.093	0.243	3.33	23.5
Missouri R. at Omaha, NE	76	1.020	0.101	1.370	1.27	2.42	0.043	0.328	4.00	12.8
Missouri R. at Hermann, MO	227	1.230	0.052	1.050	1.00	2.24	0.082	0.275	4.66	17.7
Mississippi R. at Thebes, IL	225	2.410	0.096	1.250	1.15	3.56	0.090	0.285	4.10	21.5
Arkansas R. at Little Rock, AR	129	0.280	0.077	0.730	0.65	1.01	0.035	0.096	1.86	89.7
Mississippi R. at St. Francisville, LA	196	1.410	0.050	0.880	0.82	2.26	0.064	0.200	2.89	20.0
Atchafalaya R. at Melville, LA	192	1.040	0.052	0.810	0.76	1.85	0.052	0.197	2.95	27.9

TABLE 3.2. Mean concentrations (mg/L) of nitrogen and phosphorus compounds, silica (Si), and chloride in the 42 interior basins: 1980-96.

Basin ID	Basin Name and Location of Sampling Site	Number of Samples	Nitrate Plus Nitrite as N	Ammonia as N	Total Organic & Ammonia Nitrogen	Total Organic Nitrogen	Total Nitrogen	Orthophosphate	Total Phosphorus	Silica	Chloride
1	Allegheny R. at New Kensington, PA	76	0.647	0.081	0.40	0.32	1.05	< 0.004	0.042	2.04	15.4
2	Monongahela R. at Braddock, PA.	71	1.062	0.154	0.54	0.39	1.60	0.002	0.062	2.26	13.8
3	Muskingham R. at McConnelsville, OH	84	1.432	0.123	0.88	0.75	2.31	0.017	0.122	2.45	51.4
4	Kanawha R. at Winfield, WV	78	0.579	0.132	0.52	0.39	1.11	0.013	0.054	2.34	11.8
5	Scioto R. at Higby, OH	76	3.561	0.108	1.17	1.06	4.60	0.242	0.380	2.55	43.7
6	Great Miami R. at New Baltimore, OH	91	3.938	0.192	1.31	1.12	5.25	0.261	0.433	2.39	58.8
7	Kentucky R. at Lockport, KY.	124	0.927	0.047	0.61	0.57	1.54	0.073	0.188	2.26	14.0
8	Wabash R. at New Harmony, IN	44	2.549	0.069	1.16	1.09	3.68	0.049	0.260	2.56	26.1
9	Cumberland R. near Grand Rivers, KY	49	0.357	0.058	0.65	0.59	1.00	0.021	0.085	1.48	5.4
10	Tennessee R. near Paducah, KY	56	0.245	0.061	0.53	0.47	0.78	0.019	0.063	1.73	8.5
11	Mississippi R. near Royalton, MN	85	0.148	0.061	0.75	0.69	0.90	0.004	0.043	4.26	4.8
12	Minnesota R. at Jordan, MN	122	4.186	0.154	1.50	1.34	5.75	0.072	0.218	7.95	32.0
13	St. Croix R. at St. Croix Falls, WI	47	0.180	0.060	0.72	0.65	0.90	0.001	0.051	5.23	3.2
14	Chippewa R. at Durand, WI	95	0.520	0.082	0.78	0.70	1.30	0.035	0.102	4.33	5.4
15	Wisconsin R. at Muscoda, WI	96	0.514	0.079	0.87	0.79	1.38	0.021	0.084	2.55	11.5
16	Rock R. near Joslin, IL	152	3.486	0.125	1.67	1.55	5.16	0.091	0.299	2.63	33.3
17	Cedar R. at Cedar Falls, IA	83	4.670	0.099	1.34	1.24	6.40	0.097	0.230		23.1
18	Iowa R. at Wapello, IA (includes Cedar R. Basin)	105	4.989	0.139	1.83	1.69	6.83	0.106	0.308	5.16	28.2
19	Skunk R. at Augusta, IA	108	4.225	0.147	1.58	1.43	5.71	0.092	0.297	5.33	19.9
20	Raccoon R. at Van Meter-Des Moines, IA	48	6.665	0.087	1.03	0.94	7.57	0.091	0.177		24.3
21	Des Moines R. at Keosauqua–St., Francisville, MO (includes Raccoon R. Basin)	88	4.243	0.121	1.67	1.55	5.92	0.091	0.233	4.75	25.2
22	Illinois R. at Marseilles, IL	175	4.257	0.655	1.71	1.05	5.95	0.250	0.414	2.73	74.0
23	Illinois R. at Valley City, IL	187	4.123	0.150	1.38	1.22	5.46	0.131	0.322	2.71	52.0
24	Kaskaskia R. near Venedy Station, IL	121	0.830	0.109	1.27	1.17	2.09	0.088	0.295	2.01	29.6
25	Milk R. at Nashua, MT	93	0.047	0.102	1.16	1.06	1.21	0.012	0.170	3.02	32.7
26	Missouri R. near Culbertson, MT	58	<0.072	0.083	0.79	0.70	0.72	0.013	0.088	3.27	9.5
27	Bighorn R. at Bighorn, MT	86	0.290	0.092	0.71	0.61	1.00	0.001	0.053	3.56	12.0
28	Yellowstone R. near Sydney, MT	98	0.214	0.084	0.87	0.80	1.09	0.004	0.167	4.52	12.6
29	Cheyenne R. near Cherry Creek, SD	104	0.815	0.112	1.95	1.76	2.75	0.028	0.990	3.57	64.4
30	James R. near Scotland, SD	107	0.227	0.157	1.92	1.76	2.07	0.106	0.283	6.32	49.6
31	Platte R. near Louisville, NE	267	1.057	0.103	1.88	1.77	2.99	0.175	0.544	12.45	50.3
32	Kansas R. at Desoto, KS	100	0.702	0.120	1.45	1.33	2.14	0.130	0.384	3.25	81.8
33	Grand R. near Sumner, MO	132	0.775	0.103	1.70	1.60	2.48	0.04	0.292	4.56	10.0
34	Osage R. below St. Thomas, MO	97	0.324	0.046	0.59	0.54	0.91	0.018	0.053	2.03	6.0
35	St. Francis Bay at Riverfront, AR	97	0.203	0.057	0.80	0.74	1.00	0.074	0.205	5.65	6.6
36	White R. at Clarendon, AR	41	0.254	0.068	0.73	0.66	0.99	0.01	0.134	2.77	5.0
37	Arkansas R. at Tulsa, OK	95	0.517	0.129	1.05	0.92	1.57	0.086	0.139	2.46	444.3
38	Canadian R. at Calvin, OK	93	0.443	0.105	1.45	1.35	1.91	0.072	0.285	3.96	185.2
39	Yazoo R. at Redwood City, MS	89	0.399	0.083	0.92	0.84	1.32	0.033	0.244	3.28	5.1
40	Big Black R. near Bovina, MS	94	0.139	0.074	0.85	0.77	0.99	0.037	0.227	4.26	9.9
41	Red R. at Alexandria, LA	126	0.128	0.066	0.88	0.84	1.01	0.019	0.168	2.64	72.9
42	Ouachita R. near Columbia, LA	92	0.168	0.092	0.76	0.67	0.93	0.021	0.077	3.27	30.2

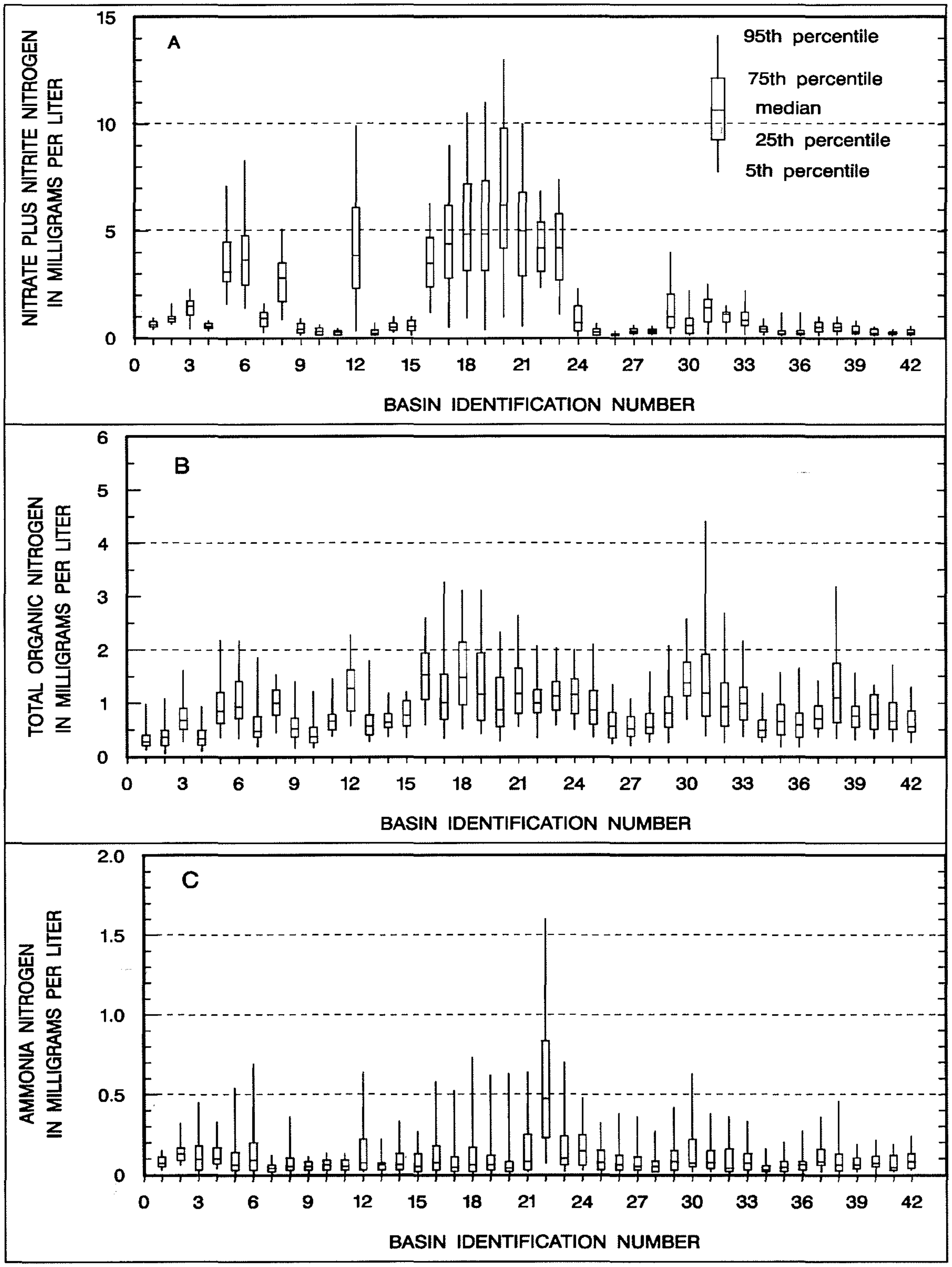


FIGURE 3.1. Boxplots showing the distribution of (A) nitrate plus nitrite, (B) total organic nitrogen, and (C) ammonia nitrogen concentrations in the 42 interior basins.

Comparison of the nitrate concentrations with land use and population data in Table 2.3 shows that the high nitrate concentrations are associated with basins having either a high percentage of land in row crops (corn, soybeans, or sorghum) or a high population density (people per km^2), or both. The generalized relation between mean nitrate concentrations and percent cropland is shown in Figure 3.2. Basin 20 (Raccoon River, IA) had the highest mean nitrate concentration (6.7 mg/L) (median: 6.4 mg/L) and the highest percent cropland (74%). Basins 5 and 6 in Ohio and basin 22 in Illinois have population densities ranging from 100 to more than 300 people per km^2 and more than 45% of the basins in row crops (Table 2.3). The range of row cropland expressed as a percentage of the basin area for the 12 basins with highest median nitrate concentrations was 44–74%. The percentage of row crop land in the remaining 30 basins, except basin 24, was < 0.1–35%. The mean nitrate concentration in basin 24 (Kaskaskia River, IL) was much lower (0.83 mg/L) (median: 0.59 mg/L) than would be expected based on the relation to percent cropland given in Figure 3.2. This can probably be attributed, at least in part, to two large reservoirs on the Kaskaskia River in which nitrate could be assimilated by algae and subsequently be stored in lake sediments as particulate organic N. Another possible nitrate removal mechanism is denitrification in anoxic bed sediments of the reservoir, which would be promoted by the longer residence time of water in the reservoir (Howarth 1996). Basin 35 (St. Francis Bay, AR) also does not fit the relation in the figure, possibly because most of the row cropland in this basin is soybeans, which require very little nitrogen from external sources.

Boxplots B and C of Figure 3.1 show the distribution of total organic nitrogen (dissolved and particulate) and ammonia nitrogen. Median values for total organic nitrogen (TON) range from < 0.5 mg/L to about 1.5 mg/L. The highest concentrations of TON are associated with high population density, intense cropland activity, and/or high suspended-sediment concentrations. Median concentrations of ammonia were < 0.2 mg/L in all 42 basins, except the upper Illinois River (basin 22). This basin is dominated by municipal wastes from the Chicago metropolitan area and had a median ammonia concentration of about 0.5 mg/L. Ammonia concentrations in basin 23 (lower Illinois River Basin), which receives the inflow from basin 22, are similar to those in other basins and provide evidence for the rapid conversion of ammonia to nitrate.

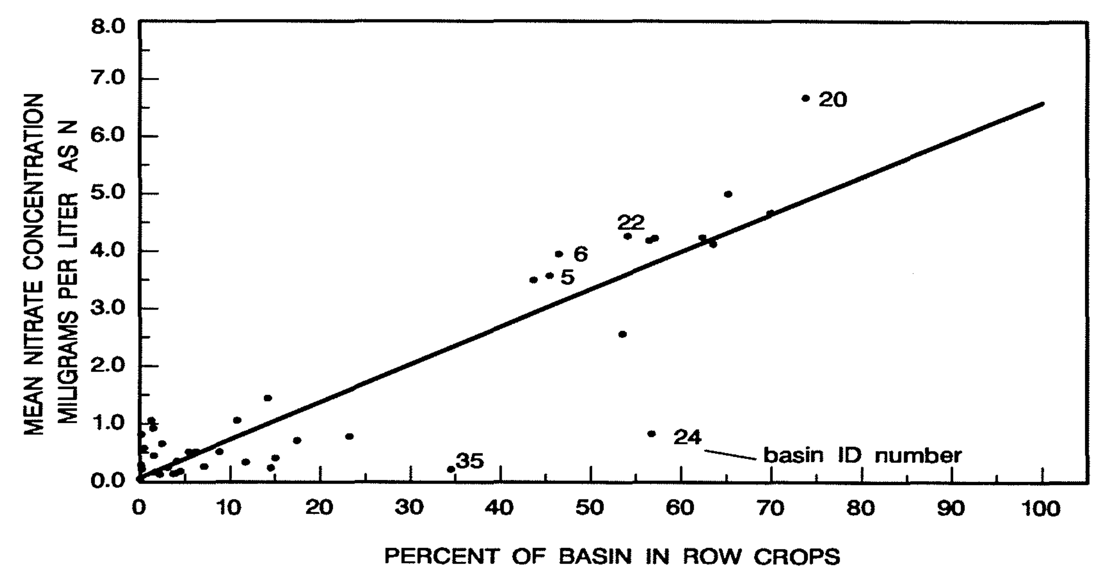


FIGURE 3.2. Relationship between mean nitrate concentrations and percent of the Mississippi River Basin in row crops. NOTE: Data are presented in tables 2.3 and 3.3.

Nitrate concentrations in basins where the supply of nitrate in soils is abundant can vary seasonally over a large range in response to climatic and hydrologic conditions. Concentrations tend to be highest in the late winter and spring when streamflow is highest, and lowest in the late summer and fall when streamflow is low. This is illustrated in Figure 3.3, which is a plot of daily nitrate concentrations and streamflow in the Raccoon River at Des Moines, Iowa, for the period 1983–89, based on nitrate data collected by the Des Moines Water Treatment Plant..

The direct relationship between nitrate concentrations and streamflow in the Midwest has been reported by other investigators (Keeney and DeLuca 1993; Lucey and Goolsby 1993; Fenelon 1998). It indicates that most of the nitrate in these streams is from nonpoint sources. If the nitrate were predominantly from point sources, concentrations would decrease as streamflow increases due to dilution. Instead, nitrate concentrations in streams increase in response to rainfall or snowmelt that leaches nitrate that has accumulated in the soil. There is scientific evidence that nitrate levels can build up in soils during dry years from mineralization processes and reduced uptake by crops, and can be flushed out in larger than normal amounts in succeeding wet years (Randall et al. 1995). Nitrate can enter the streams though agricultural drains, ground-water discharge, and direct runoff. Nitrate concentrations generally decrease in the summer and fall as streamflow and agricultural drainage decrease (Figure 3.3). Assimilation of nitrate by agricultural crops on the land and aquatic plants in streams also helps decrease the nitrate concentrations in streams during the summer. In-stream denitrification rates would also increase during the summer due to increased temperatures and longer residence times of water in the streams.

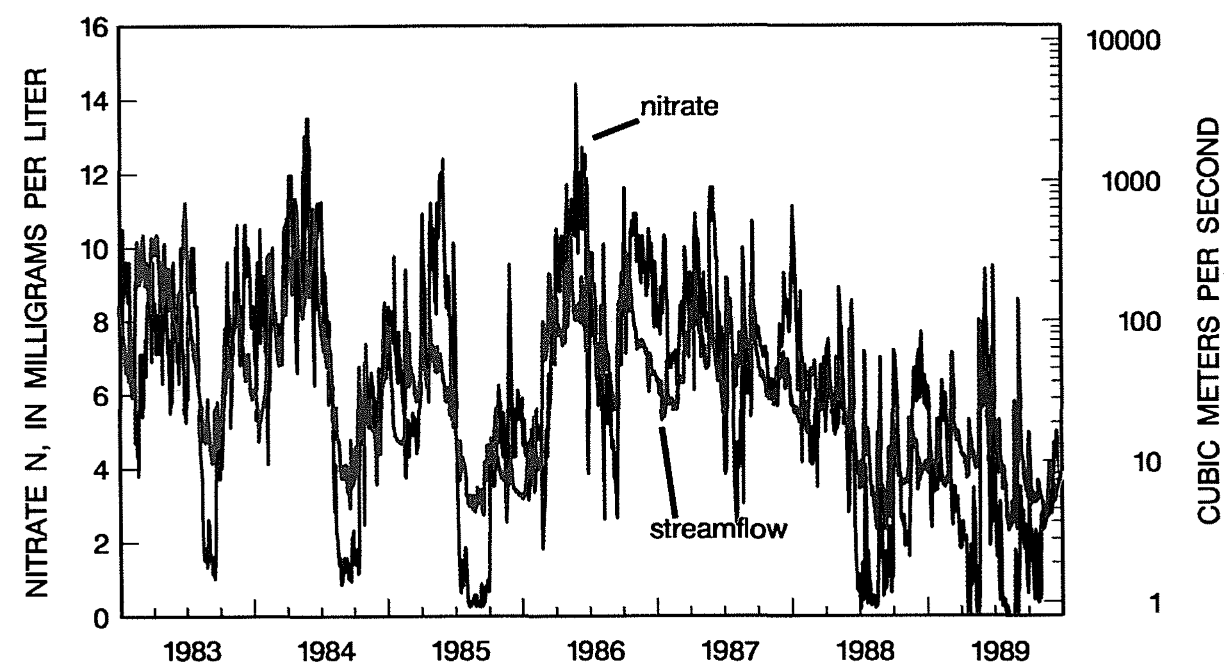


FIGURE 3.3. Daily streamflow and daily nitrate concentrations in the Raccoon River at Des Moines, Iowa, during 1983–89. (*Nitrate data from Des Moines Water Treatment Plant.*)

Agricultural drainage plays a major role in transporting nitrate from cropland to streams in the MARB. More than 50 million acres, mostly cropland, have been drained in Illinois, Indiana, Iowa, Ohio, Minnesota, Missouri, and Wisconsin (Pavelis et al. 1987). This practice Òshort circuitsÓ the flow of water by draining the top of the saturated zone into tile drains, ditches, and streams, and eventually the Mississippi River. Drainage practices can result in the leaching of large amounts of nitrate from the soil and unsaturated zones into the drains and ditches. Nitrate concentrations in agricultural drains can be very high—20–40 mg/L nitrogen or more (Fenelon 1998; Gentry et al. 1998; Zucker and Brown 1998; David et al. 1997; Randall et al. 1997).

3.2 HISTORICAL NITROGEN CONCENTRATIONS

Historical data on nitrogen concentrations in the MARB are available from numerous publications. Some of the earliest data on nitrogen concentrations were published in a report by the University of Illinois (Palmer, no date). Nitrogen data were also published by USGS in a report containing testimony from a lawsuit heard by the U.S. Supreme Court in 1905 on pollution of the Illinois and Mississippi Rivers by Chicago sewage (Leighton 1907). These reports also contain data on hundreds of analyses for nitrate, nitrite, ammonia, and organic nitrogen on samples from the Illinois River Basin and Mississippi River in the vicinity of St. Louis, Missouri, during 1897–1902.

Historical nutrient data are also available from a USGS study in which water samples were collected daily during 1906–07 from 62 major rivers in the eastern half of the United States. Sampling sites included several sites on the Mississippi River from Minneapolis, Minnesota, to New Orleans, Louisiana, and sites on rivers in Arkansas, Illinois, Indiana, Iowa, Minnesota, Ohio, and Pennsylvania. The daily samples were composited at about 10-day intervals and analyzed for numerous solutes, including nitrate. Results of these analyses have been published in at least two USGS reports (Dole 1909 and Clarke 1924). A search of the USGS NWIS database provided additional data on nitrate concentrations for several rivers in Iowa, including the Cedar, Raccoon, and Des Moines Rivers for 1944–51, and for sites on the Ohio and Mississippi Rivers for 1954 to the present.

While the historical nitrate concentrations probably do not represent natural background conditions, they do provide a baseline from which changes that have occurred in the past 90–100 years can be determined. Table 3.3 summarizes historical nitrate concentrations in a few interior basins in the MARB from the late 1890s to about 1965. Mean concentrations for samples collected from these same streams during 1980–96 near where the historical samples were obtained are shown for comparison.

Table 3.4 contains similar data for sites on the Arkansas, Mississippi, and Missouri Rivers. These data clearly show that the concentration of nitrate in the Mississippi River and its tributaries has increased significantly in the last 100 years. No attempt was made to determine streamflow conditions for the historical data. Nevertheless, the results shown in Tables 3.3 and 3.4 suggest that average nitrate concentrations in the small rivers and the Mississippi and Missouri Rivers have increase by factors of two to more than five. The only exception is the Arkansas River, in which nitrate concentrations appear to have decreased; this exception may be the result of recently constructed impoundments on the river that would create an environment more favorable to the growth of algae and conversion of nitrate to organic matter. Impoundments can also increase the rate of denitrification due to increased retention time and increased contact between water and benthic deposits (Howarth et al. 1996).

TABLE 3.3. Historical and current (1980–96) nitrate concentrations in the small streams in the Mississippi River Basin. *(From Leighton 1907, Dole 1909, and Clarke 1924.)*

Basin	River Basin Name	Mean Concentrations Year(s)	N	mg/L
ß	Allegheny River	1906–07	35	0.16
		1980–96	76	0.65
3	Muskingum River	1906–07	27	0.36
		1980–96	84	1.43
8	Wabash River	1906–07	31	1.44
		1980–96	44	2.55
12	Minnesota River	1906–07	30	0.32
		1980-96	122	4.19
16	Rock River	1906–07	36	0.86
		1980–96	152	3.49
17	Cedar River	1906–07	37	0.70
		1944–50	175	1.53
		1980–96	83	4.67
20	Raccoon River	1945–47	55	2.93
		1980–96	48	6.67
21	Des Moines River	1906–07	37	0.75
		1955–65	28	3.02
		1980–96	88	4.24
22	Upper Illinois River	1896–99	Weekly	1.89
		1906–07	36	1.49
		1980–96	175	4.25
23	Lower Illinois River	1897–99	Weekly	1.01
		1906–07	36	0.97
		1980–96	187	4.12

TABLE 3.4. Historical nitrate concentrations for sites on the Arkansas, Mississippi, and Missouri Rivers.

Location	Mean Concentrations Year(s)	N	mg/L
Arkansas River at Little Rock, AR	1906–07	22	0.45
	1980–96	129	0.28
Mississippi River at Minneapolis/ Ninninger, MN	1906–07	35	0.32
	1980–96	67	2.40
Wabash River at Vincennes/New Harmony, IN	1906–07	31	1.44
	1980–96	44	2.55
Mississippi River at Moline, IL/Clinton, IA	1906–07	17	0.41
	1980–96	157	1.72
Mississippi River at Grafton, IL	1899–1900	123	0.40
	1980–96	131	2.63
Mississippi River at New Orleans, LA/St. Francisville, LA	1900–01	9	0.14
	1905–06	52	0.56
	1955–65	308	0.65
	1980–96	182	1.45
Missouri River at Fort Bellefontaine, MO/Hermann, MO	1899–1900	63	0.54
	1980–96	227	1.23

The longest uninterrupted data set on nitrate concentrations in the MARB is from the Mississippi River at St. Francisville, Louisiana. Samples have been collected at this site each year since late 1954. From 1954 to 1967 samples were collected daily and composited at 10- to 30-day intervals for analysis. Compositing was discontinued in late 1967, and all subsequent analyses were on discrete samples. A similar data set is available for the Ohio River at Grand Chain, Illinois, for 1954–97, but no samples were collected in several years during this period. The St. Francisville data set has been used extensively by scientists to estimate nitrate flux to the Gulf of Mexico and determine long-term changes in Mississippi River water quality (Turner and Rabalais 1991; Bratkovich et al. 1994; Rabalais et al. 1996; Goolsby et al. 1997). Figure 3.4 shows the long-term patterns in nitrate concentrations at these two sites. The average annual nitrate concentration at St. Francisville has more than doubled since 1954–60. The minimum and maximum annual concentrations have also more than doubled. In contrast, nitrate concentrations appear to have changed very little in the lower Ohio River over the last four decades. These long-term data indicate that the increase in nitrate concentrations at St. Francisville must be caused primarily by increased nitrate concentrations in water entering the Mississippi River from sources other than the Ohio River Basin.

As noted in section 2.1 and Table 2.1, a significant change in the analytical method for nitrate occurred in the early 1970s. Two lines of evidence indicate this method change did not contribute to the upward trend in nitrate concentrations observed at St. Francisville (Figure 3.4A). First, the upward trend in nitrate concentrations occurred gradually from about 1970 to 1980. Most of the concentration change occurred after the switch to the cadmium reduction method. The concentration change would have occurred abruptly if it were caused by the change in analytical methods. Second, samples collected from the Ohio River at Grand Chain (Figure 3.4B), were analyzed for nitrate by the same methods used on the samples from St. Francisville. These samples do not show the trend in nitrate concentration shown in the St. Francisville data.

3.3 CURRENT PHOSPHORUS CONCENTRATIONS

No data on phosphorus (P) concentrations in the MARB were found prior to 1972. Data on ortho P and total P concentrations at large basin sites for 1980–96 are summarized in Table 3.1. Phosphorus concentrations in the 42 interior basins are summarized in Table 3.2 and Figure 3.5. Orthophosphate is the principal form of dissolved P and the only form of P that that can be utilized by algae, bacteria, and plants (Correll 1998). It typically constitutes one-third to one-tenth of the total P in small and large streams of the MARB. The remaining P is mostly in particulate form, which must be converted to orthophosphate by biogeochemical processes to become available to aquatic plants. The median concentration of ortho P in most of the 42 interior basins (Figure 3.5A) is less than 0.1 mg/L. However, the median concentrations in those basins having a high density of people and/or cropland were 0.1–0.25 mg/L. These, in general, are the same basins that had high nitrate concentrations. The spatial distribution of total P concentrations (Figure 3.5B) is similar to that of ortho P, except basins with high concentrations of suspended sediment also tend to have high total P concentrations. There is no apparent long-term trend in either ortho P or total P concentrations or in the ratio of ortho to total P in the Mississippi River at St. Francisville since the period of record began in the early 1970s.

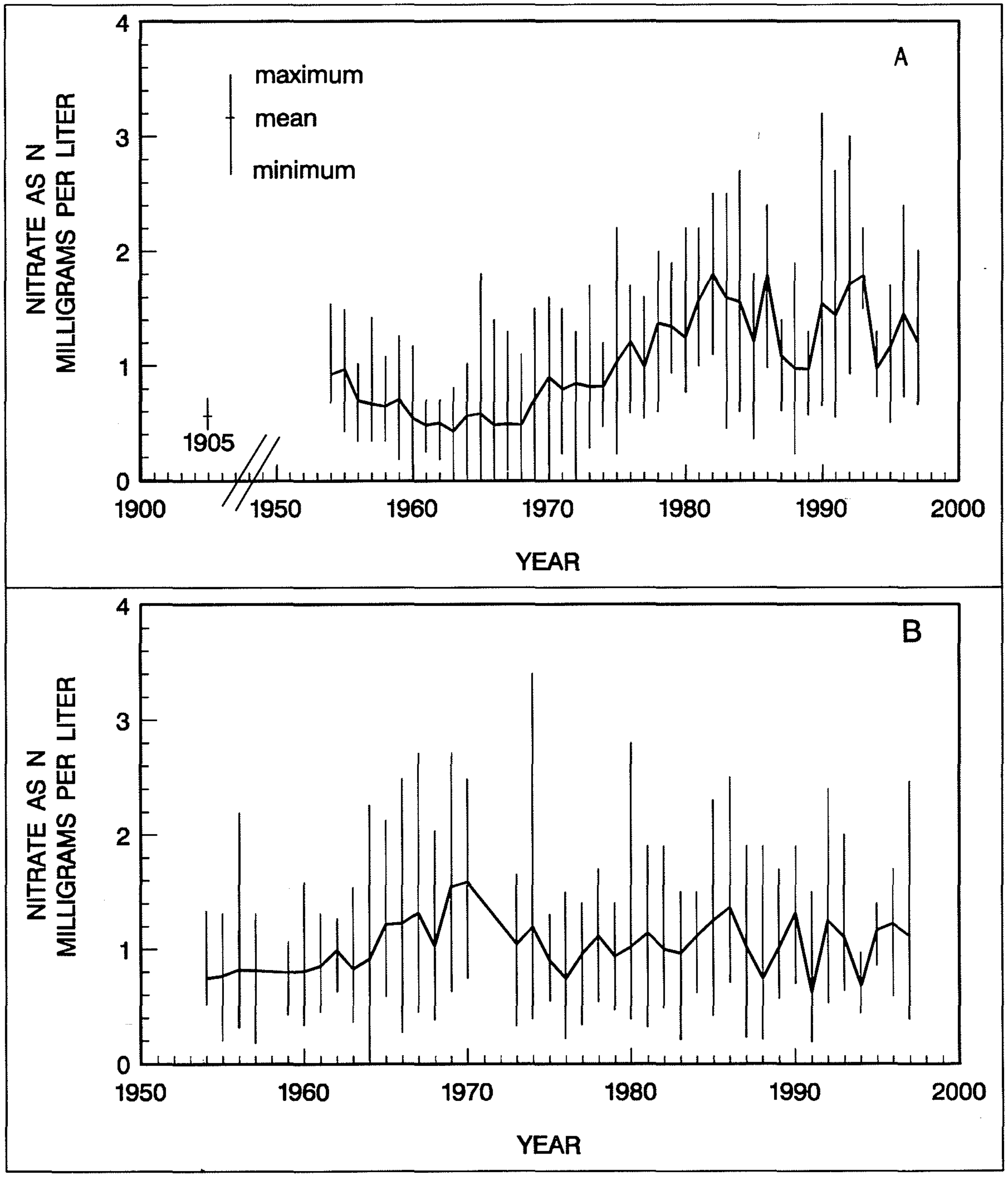


FIGURE 3.4. Long-term patterns in nitrate concentrations in (A) the Mississippi River at St. Francisville, Louisiana, and (B) the Ohio River at Grand Chain, Illinois.

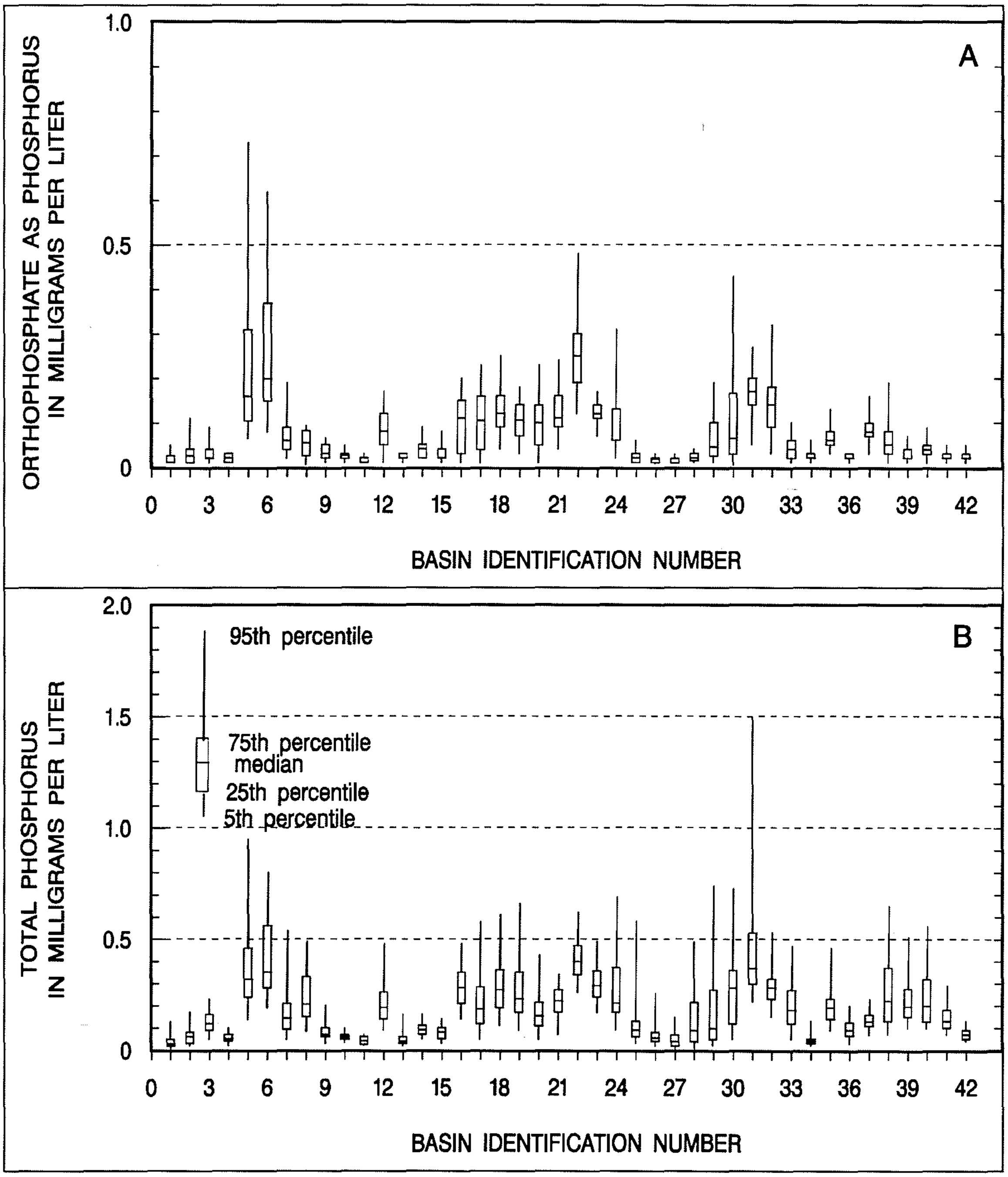


FIGURE 3.5. Boxplots showing the distribution of (A) orthophosphate and (B) total phosphorus concentrations in 42 interior basins.

3.4 CURRENT AND HISTORICAL DISSOLVED SILICA CONCENTRATIONS

Dissolved silica is present in natural waters primarily as silicic acid H_4SiO_4 or $Si(OH)_4$ (Stumm and Morgan 1981). This report presents concentrations of dissolved silica as Si. Silica concentrations are summarized in Table 3.1 for the large basins and in Table 3.2 and Figure 3.6A for the 42 interior basins.

The highest silica concentrations are in basins 31 (Platte River, Nebraska), 30 (James River, South Dakota), and 12 (Minnesota River, Minnesota). Basins 19 and 21 in Iowa and basin 35 in Arkansas also have above-average silica concentrations. The Minnesota River (12) and the two basins in Iowa have a high percentage of cropland, but the other basins that have high silica concentrations are not associated with cropland. It is more likely that the soils and hydrology of the basins, especially ground-water contributions, are more closely related to silica concentrations than are human activities.

The long-term trend in silica concentrations in the Mississippi River at St. Francisville, Louisiana, is shown in figure 3.6B. Average silica concentrations in the mid- to late 1950s were 4 to 5 mg/L and were similar to those reported by Dole (1909) in 1905–06. Silica concentrations appear to have gradually declined from 4–5 mg/L in the 1950s to about 3 mg/L in the mid-1970s and have remained near that level through 1997. The reasons for this downward trend prior to the mid-1970s are not known for certain. Turner and Rabalais (1991) and Rabalais and others (1996) first reported this trend and hypothesized that it may have been caused by increased diatom production in the basin as a result of increased phosphorus inputs to streams due to increasing fertilizer use. The diatoms could remove dissolved silica from the riverine system and convert it to biogenic silica that could be deposited in river sediments or transported to the Gulf in particulate form. The decrease could also be due, in part, to dilution caused by increased streamflow (see section 4.2).

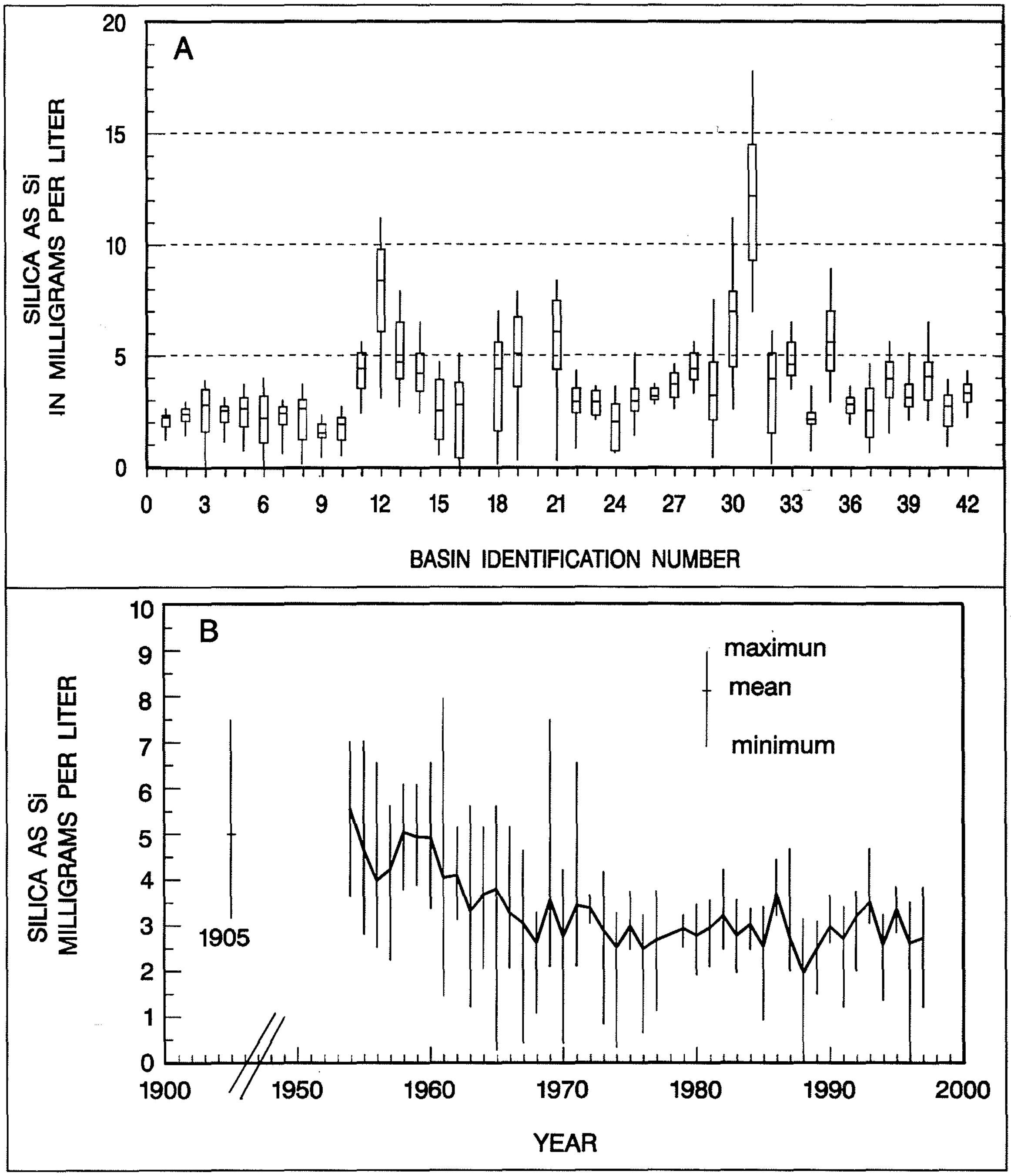


FIGURE 3.6. (A) Boxplots showing the distribution of silica concentrations in the 42 interior basins, and (B) long-term pattern in silica concentrations in the Mississippi River at St. Francisville, Louisiana, 1955–96.

CHAPTER 4

Nutrient Flux and Sources

Previous investigators (Turner and Rabalais 1991; Smith et al. 1993; Alexander et al. 1996; Dunn 1996; Howarth et al. 1996; Goolsby et al. 1997) have reported on the annual flux of nitrogen and/or phosphorus to the Gulf. Antweiler et al. (1995) estimated the flux of nitrate and determined its predominant source areas in the Mississippi Basin during 1991–92. Lurry and Dunn (1997) estimated the long-term (1974–94) average annual flux of total N and total P at about 40 gauging stations within the MARB. Smith et al. (1997) estimated the total N and total P flux at 414 NASQAN stations in the United States and used a spatial referencing model (SPARROW) to estimate the N and P yields at more than 2,000 U.S. stream locations. These studies provided much information on nutrient flux in the MARB and were invaluable in developing the nutrient flux estimates presented in this report.

Flux estimates are presented in this report for the entire MARB, 9 large basins, and 42 interior basins. The locations of these basins and the stations used to develop the flux estimates were previously described in section 2.2 and in Tables 2.2 and 2.3 and are shown in Figures 2.1 and 2.2. Flux estimates were made for nitrate, total nitrogen, orthophosphate, total phosphorus, silica, and chloride. The chloride flux estimates were used in validating nutrient balances and are not discussed in this report.

4.1 FLUX ESTIMATION METHODS

The mass flux of a solute past a measurement station is defined as the product of the solute concentration (expressed in mass per volume) and the water discharge (volume per time), yielding the solute mass per unit time. Water discharge is measured frequently enough (every 15 minutes to one hour) that it is essentially a continuous measurement. The accuracy of discharge data varies from station to station but is usually within 10% of the reported value. The accuracy of discharge for each USGS gauging station is published in USGS annual water data reports for each state. Accuracy information is not available for discharge data obtained from other sources, but the accuracy is assumed to be similar to that of USGS data. Solute concentrations, however, are measured much less frequently because of the high costs of sample collection and chemical analysis. The accuracy of solute concentrations are also quite high, usually within a few percent, based on quality control data.

Three basic approaches can be used to interpolate concentration between measurements:

- *Averaging.* The concentration of all samples collected during the period of interest can be averaged (generally a flow-weighted average is calculated). The average concentration is multiplied by the total water discharge during the period to estimate flux. The standard error of the average concentration can be used to estimate the precision of the flux estimate. This approach assumes that the samples were collected in a "representative" fashion. The reliability of the flux estimates using this approach depends on the number of observations during the period.
- *Interpolation.* Concentrations can be estimated by linearly interpolating between observations (or by using some other interpolation method, such as a cubic spline). No estimate of the standard error is possible using this approach, as concentrations are assumed to be smoothly varying between observations. Because the reliability of this estimate is also strongly dependent upon the frequency of the observations, this method is best used when sampling frequencies are high relative to the frequency of forcing functions that determine solute concentration.
- *Multiple regression.* A multiple-regression model is developed to relate concentration (or flux) to more frequently measured variables, such as stream discharge. This approach has the advantage of not being so dependent on the sampling frequency because the model's parameters are estimated using all available data. Furthermore, if certain statistical assumptions are met, the standard error of the flux estimate can be readily calculated. This approach, however, requires substantially more effort and is subject to a variety of statistical considerations. Because the CENR hypoxia analysis required short-term (annual or seasonal) estimates of flux and the sampling frequency in our data set was generally monthly or less frequent, we decided that this was the best approach to flux estimation.

4.1.1 Model Structure

Consistent with many past studies (e.g., Cohn et al. 1992), a seven-parameter model was fit of the form

$$\ln[\Phi] = \beta_0 + \beta_1 \ln[Q/\bar{Q}] + \beta_2 (\ln[Q/\bar{Q}])^2 + \beta_3 [T - \bar{T}]$$
$$+ \beta_4 [T - \bar{T}]^2 + \beta_5 \sin[2\pi T] + \beta_6 \cos[2\pi T] + \varepsilon \qquad (1)$$

where:

ln[ ]	is the natural logarithm of the argument in brackets
Φ	is the flux of the solute ($C \cdot Q$)
C	is the solute concentration
Q	is the daily average discharge
$\bar{Q}$	is a centering term (a constant) to ensure that the linear and quadratic flow terms are independent
T	is time, expressed in decimal years and
$\bar{T}$	is a centering term (a constant) to ensure that the linear and quadratic time terms are independent
ε	is the error term
$\beta_0 \ldots \beta_6$	are the fitted parameters in the multiple regression model

This model captures the dependence of concentration on discharge, season (the sine and cosine terms), and any long-term trend. Quadratic terms were included to account for curvature that remained after transformation. Model parameters were estimated using the SAS system (SAS Institute Inc., 1990a, 1990b). Standard diagnostics (e.g., plots of observed vs. predicted values, and various residual plots) were calculated and examined for all models. All terms were retained in the models even if the model parameters were not significant to simplify calculation of models across all sites and solutes. Inclusion of the insignificant terms does not change the flux estimates appreciably, and the estimation of the additional parameter caused a small proportional decrease in the degrees of freedom in the regression because of the large number of observations available.

Slight modifications were made to the model at some of the large river sites. Discharges of upstream tributaries were substituted for at-site discharge because these values better captured the variations in concentration. For example, the solute flux models for the Mississippi at St. Francisville, Louisiana, used discharges from the mouths of the Missouri and Ohio and the discharge of the Mississippi above its confluence with the Missouri because each of the rivers has different solute concentrations. When upstream discharges are used, they are lagged to account for the time required for the water to flow between the sites. Two stations (Cedar River at Cedar Falls, Iowa—basin 17, and Raccoon River at Van Meter-Des Moines, Iowa—basin 20) had gaps in concentration data in the middle of the study period. For these stations, the quadratic time term was removed to prevent a spurious model form to be fit. The coefficients of determination (R^2) for these models are quite high because flux, which includes the independent variable Q, is being estimated. Although this poses no problem for parameter estimation, model diagnostics are misleading because the same variable is both an independent and a dependent variable. However, the R^2 does correctly reflect that most of the variability in the calculation of flux comes from discharge (which is measured) and not from concentration (which is estimated).

Daily streamflow was not measured at sites 17 and 21 (Table 2.3) and streamflow from a nearby gauging station was used in the regression model to estimate nutrient flux. For six sites (basins 4, 27, 35,36, 39, and 42—see Table 2.3), continuous measurement of streamflow was not available. For these sites, flux was estimated using the discharges made when samples were collected and flow-weighted average nutrient concentrations. Annual runoff was estimated from the average of the measured discharges.

As part of the model evaluation, outliers and points of high leverage were identified from scatter plots. These unusual points, which accounted for less than 6% of the points at any site, were eliminated from the analysis. In addition to eliminating outliers, in many cases it was necessary to remove values less than the detection limit when these affected model fit. When the percentage of samples that had concentrations below the detection limit was greater than 20%, a flow-weighted average instead of the regression method was used to estimate flux. Errors in the flux estimates are determined by calculating the mean square error of the flux estimates on an annual basis for every site/solute combination, using the approach by Gilroy et al. (1990). Error estimates for long-term average fluxes (multiple years) were determined by averaging the annual mean square errors.

4.2 FLUX OF NUTRIENTS TO THE GULF OF MEXICO

The average annual flux of nutrients from the MARB to the Gulf of Mexico for 1980–96 is summarized in Table 4.1. The table also shows the standard errors of the flux estimates. This 17-year period included the drought of 1988-89 when fluxes were very low and the flood of 1993 when fluxes were very high. Thus, the fluxes in the table are believed to be representative of current average conditions. The average flux of all forms of nitrogen was 1,567,900 +/- 58,470 metric tons/yr (metric tons per year). This is almost identical to the flux estimate of 1,597,000 metric tons/yr by Dunn (1996) for 1972–93 and only slightly less than the 1982–87 estimate of 1,824,000 metric tons/yr made by Turner and Rabalais (1991). The total N flux is about 61% nitrate and 2% ammonia, and the remaining 37% is dissolved and particulate organic nitrogen. Normalized to drainage area the yield of total N is 489 kg/km^2/yr for the entire MARB, and the yield of nitrate is 297 kg/km^2/yr (Table 4.2) for 1980–96. About three-quarters of the N flux from the MARB enters the Gulf via the Mississippi River channel, and the remainder discharges through the Atchafalaya River. However, nearly all of the nitrogen discharging from the Atchafalaya comes from the Mississippi by way of the Old River diversion. Only about 4% of the nitrogen flux to the Gulf is from the Red and Ouachita River Basins.

TABLE 4.1. Mean annual flux of nutrients from the Mississippi–Atchafalaya River Basin to the Gulf of Mexico, 1980–96.

Nutrient	Mean Flux	Percent of Total	Standard Error of Estimate	
	Metric Tons		*Metric Tons*	*% of Mean*
Nitrogen (N), Total	**1,567,900**	**100**	**58,470**	**3.7**
Nitrate	952,700	61	37,030	3.9
Ammonium	31,000	2	--	--
Dissolved organic N	376,000	24	--	--
Particulate organic N	204,000	13	--	--
Phosphorus (P), Total	**136,500**	**100**	**9,130**	**6.7**
Orthophosphate	41,770	31	2,658	6.4
Particulate phosphorus	94,730	69	--	--
Silica (Si), Dissolved	**2,316,800**	--	**289,700**	**12.5**

The average annual flux of total phosphorus was 136,500 +/- 9,130 t, of which 31% was dissolved orthophosphate and the remaining 69% was in particulate form. This can be compared with Dunn's (1996) estimate of 143,100 metric tons/yr and Turner's and Rabalais's (1991) estimate of 106,500 metric tons/yr. The flux of dissolved silica as Si averaged 2,316,800 +/- 289,700 metric tons/yr. When normalized for the basin area, the yields are 42, 13, and 722 kg/km^2/yr for total P, ortho P, and silica (Si), respectively (Tables 4.4 and 4.6). A very large, but unknown, amount of silica was also present in the suspended and colloidal sediment transported to the Gulf. Most of the suspended silica is in the form of quartz and other relatively insoluble aluminosilicate minerals, but some is no doubt present as diatom remains. Some unknown portion of this suspended silica could decompose and become available in the Gulf. About 90% of the phosphorus and 87% of the silica entering the Gulf from the MARB comes from the Mississippi River Basin; the remainder is from the Red and Ouachita Basins.

Nutrient fluxes varied over a wide range during each year and from year to year due to seasonal and annual variations in rainfall and runoff. Figure 4.1 is a plot of the regression model estimates of the daily flux of nitrate from the Mississippi River Basin to the Gulf during 1980 to mid-1998. This plot illustrates the dramatic seasonal pattern in nitrate flux to the Gulf that occurs each year. The daily flux of nitrate varies from a low of several hundred metric tons per day during low streamflow in the fall to several thousand metric tons per day during high streamflow in the spring and summer. The seasonal flux of phosphorus and silica follows similar patterns.

The annual flux of nitrate to the Gulf increased significantly over the period 1955-96 as shown in Figure 4.2. This increase in flux parallels the increase in concentration shown in Figure 3.4A. A Kendall's tau test for trend (Helsel and Hirsch 1992) shows the increase in nitrate flux to be highly significant ($p < 0.001$), with a trend slope of about 19,000 metric tons/yr. For the first 15 years of this period (1955–70) nitrate flux averaged 328,000 metric tons/yr. However, for the last 17 years (1980–96) the nitrate flux averaged 952,700 metric tons/yr, almost a three-fold increase. Essentially all of this increase occurred between about 1970 and 1983. There is no statistically significant trend, upward or downward in nitrate flux since 1980, even if the flood year of 1993 is removed. Essentially all of the increase in total nitrogen (nitrate plus organic N) that has occurred since 1970 (Figure 4.2) can be attributed to nitrate. The trend in the annual flux of organic nitrogen is not statistically significant ($p = 0.23$) for this period. The large year-to-year differences in flux are caused by variations in streamflow (Figure 4.2). The flux of nitrate was relatively low during the drought years of 1987–89 (500,000-700,000 t), but was high (> 1,500,000 t) during the flood year of 1993. Nitrate flux was also high during 1979 and during the early 1980s, when streamflow was abnormally high. However, nitrate flux was noticeably lower during a high streamflow period in the early 1970s than in later years. Both streamflow and nitrate flux have become much more variable in the last 25 years.

The average 1980–96 total N yield for the entire MARB was estimated to be 489 kg/km^2/yr. Howarth (1998) and Howarth et al. (1996) estimated the total N yield for the Mississippi Basin to be 2.5–7.4 times more than the estimated "pristine" yield of 76–230 kg/km^2/yr for the North Atlantic Basin. The average total N yields for the MARB determined from this assessment are 2.2–6.5 times more than the yields for "pristine" conditions and are almost identical to the yield increase for the Mississippi Basin suggested by Howarth et al. (1996).

Figure 4.3 shows the annual flux of total phosphorus for 1972–96. Although there are significant year-to-year variations in the flux of phosphorus due to differences in streamflow, the Kendall's tau test (Helsel and Hirsch 1992) showed no statistically significant ($p = 0.24$) long-term trend. One can hypothesize that the flux of P to the Gulf was considerably higher prior to completion of the Missouri River reservoirs in the 1950s than it is today. Nearly 70% of the phosphorus flux to the Gulf is associated with suspended sediment (Table 4.1), and the construction of these reservoirs cut the sediment flux to the Gulf nearly in half (Meade and Parker 1985). However, the P associated with the suspended sediment would have to be converted to dissolved ortho P in order for it to be available to algae and other aquatic plants (Correll 1998).

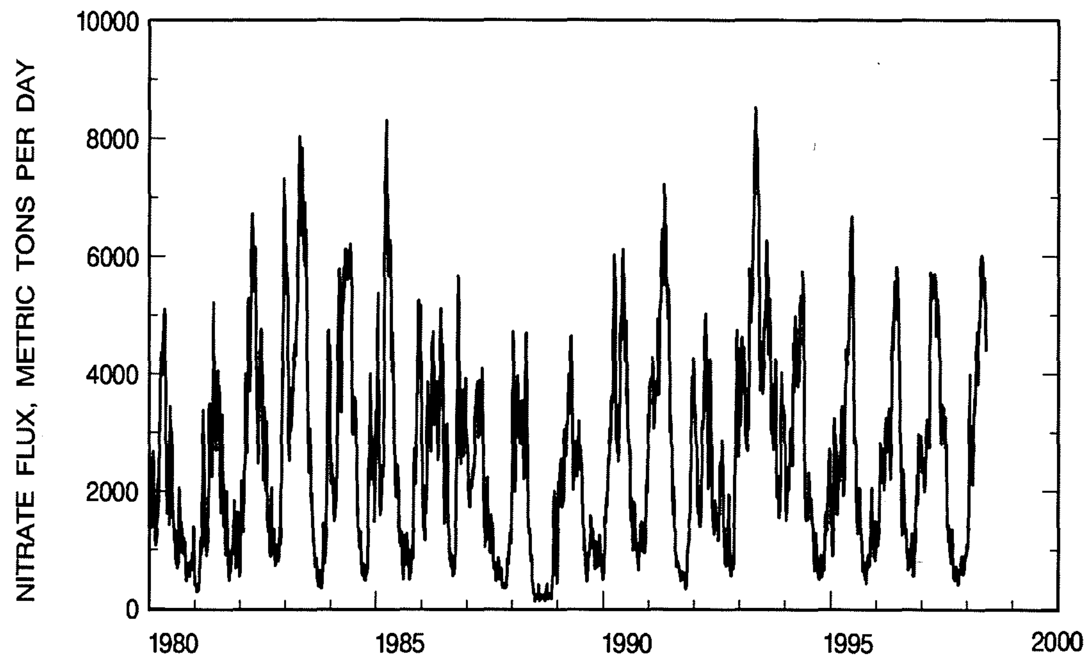


FIGURE 4.1. Hydrograph of the daily flux of nitrate in the Mississippi River at St. Francisville, Louisiana, 1980–98.

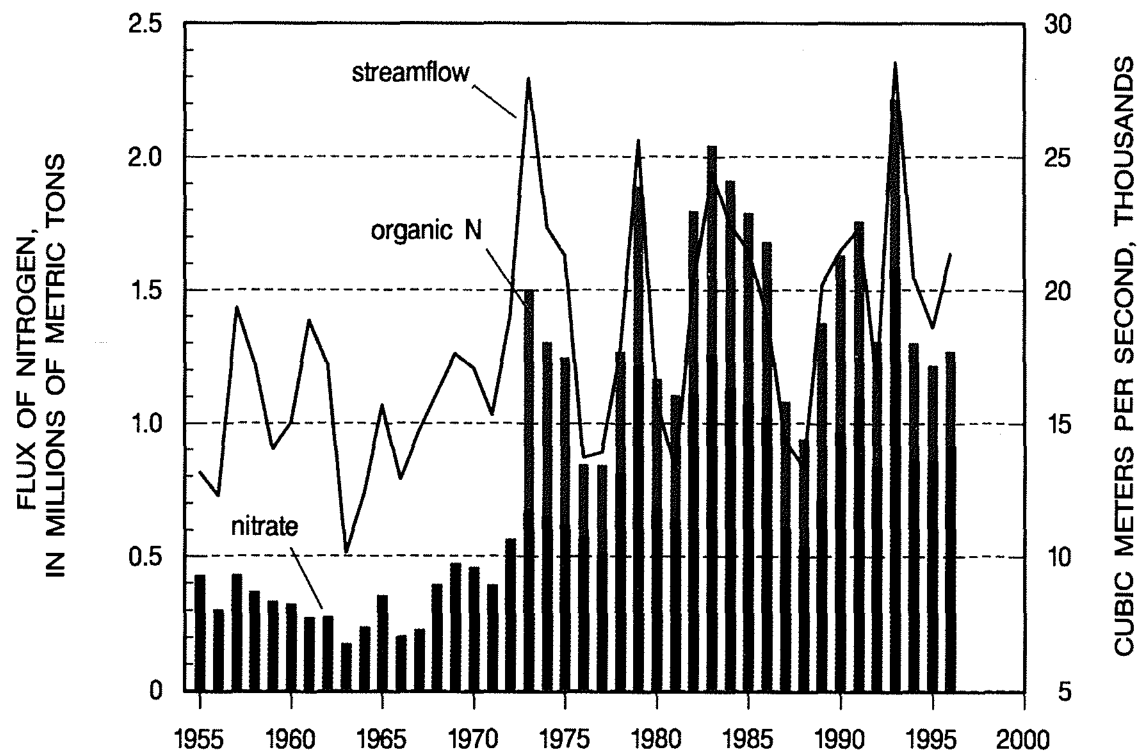


FIGURE 4.2. Annual flux of nitrate and organic nitrogen and mean annual stream flow from the Mississippi River Basin to the Gulf of Mexico.

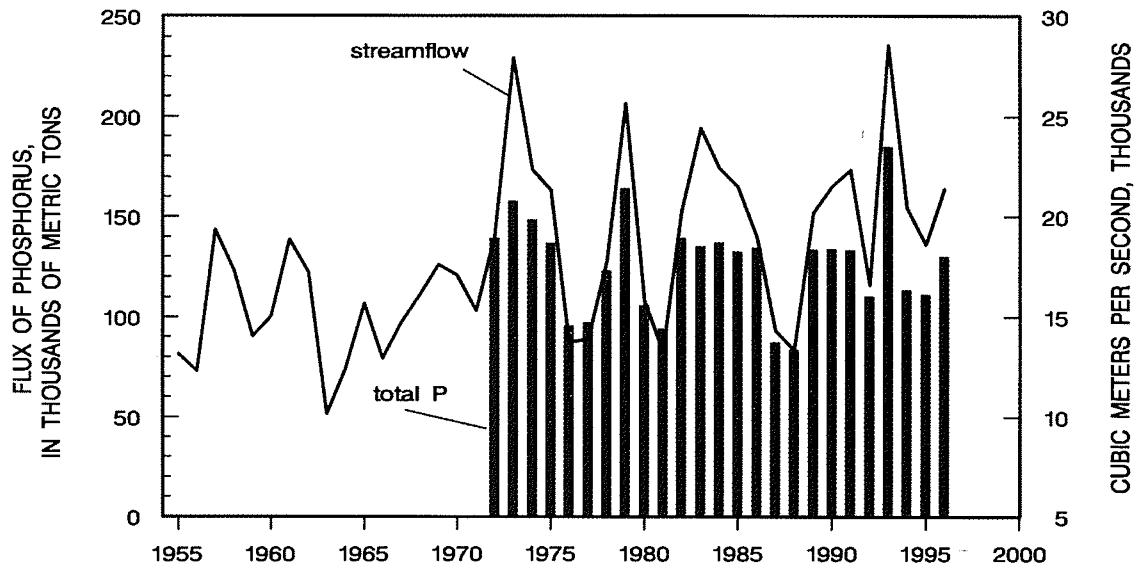


FIGURE 4.3. Annual flux of total phosphorus and mean annual streamflow from the Mississippi River Basin to the Gulf of Mexico.

The annual flux of dissolved silica for 1955–96 is shown in Figure 4.4. As with phosphorus, the silica flux also varies considerably from year to year due to variations in streamflow. However, there is no statistically significant ($p > 0.9$) long-term trend in silica flux. Figure 3.6B showed that the concentrations of silica decreased 30% or more from the 1950s to the 1970s. However, there is no corresponding decrease in the annual flux of silica (Figure 4.4). The reasons for this apparent contradiction are not known. Part of the reason may be related to changes in streamflow since the early 1960s and the availability of dissolved silica that can be transported into streams in the MARB. There have been no known significant anthropogenic additions of silica to the basin over the past 40 years. Thus, the supply of soluble silica available for transport into streams is controlled by the natural weathering of soils and minerals. Unless higher precipitation results in an increase in the weathering rate, silica could be leached from the soil faster than it is produced by weathering processes. This would cause dilution of silica concentrations in the receiving streams. Thus, an increase in precipitation and streamflow could decrease silica concentrations with no net change in the annual silica flux. Removal of silica from streams by increased diatom production, as hypothesized by Turner and Rabalais (1991) and Rabalais et al. (1996), would also reduce dissolved silica concentrations, but would also reduce the flux of dissolved silica.

In addition to the MARB, several other rivers along the Gulf coast discharge small amounts of nutrients to the Gulf of Mexico. Dunn (1996) estimated the total nitrogen and phosphorus inflows to the Gulf from 37 streams discharging to the Gulf between southwest Texas and southern Florida. Dunn's estimates included nine large rivers, in addition to the MARB, in the region from the Sabine River on the Louisiana–Texas border to Perdido River on the Alabama–Florida border. The combined average total nitrogen flux from these streams for 1972–93 was estimated to be 81,000 metric tons/yr. This is equal to about 5% of the total nitrogen discharge of the MARB. The estimated total phosphorus flux from these nine rivers was 8,890 metric tons/yr, which is about 6.5% of the Mississippi River's total phosphorus discharge. These results clearly show that the MARB is the principal source of nitrogen, phosphorus, and probably dissolved silica entering the Gulf of Mexico via streams.

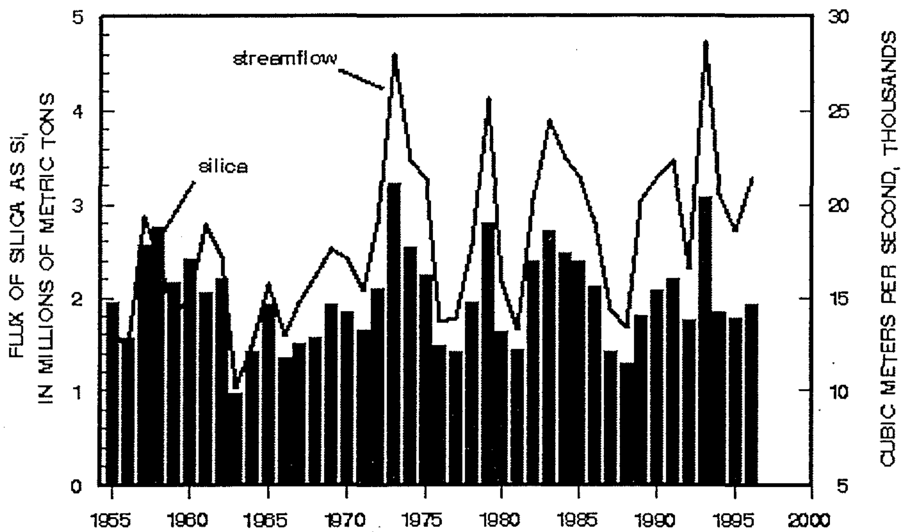


FIGURE 4.4. Annual flux of silica and mean annual streamflow from the Mississippi River Basin to the Gulf of Mexico.

4.2.1 Climate Effects on Nutrient Flux

The average annual streamflow increased significantly during 1955–97—the period that is the focus of this report. Streamflow was approximately 30% higher during 1980–96 than during 1955–70. A Kendall's tau test on the mean annual streamflow showed a statistically significant trend ($p = 0.001$) with a slope of 158 m^3/s/yr. Some of this increase is the result of long-term climatic variation, and some is driven by shorter-term climatic cycles. Baldwin and Lall (1999) analyzed streamflow from the Mississippi River at Clinton, Iowa, for 1874–96 and reported a long-term, U-shaped trend in average annual discharge, with the beginning and end experiencing high flows. The period 1955–96 showed a particularly large increase in flows. A 10-year Loess regression through the average annual discharge data showed decadal-scale trends. This value has a minimum of less than 1,132 cm in the late 1950s, and increases to over 1,700 cm by the late 1990s. The higher flows in the latter half of the century are attributed to increased precipitation throughout the year, particularly to warmer, wetter springs (Baldwin and Lall 1999). Angel and Huff (1995) analyzed frequency characteristics of rainfall in the MARB from records dating back to 1901, and found a 20% increase in the number of extreme one-day rainfall events.

The higher precipitation and streamflow in the later time period could influence nitrate flux in several ways. First, the volume of flow would be larger and more nitrate would be transported, unless concentrations decreased. Second, the higher precipitation could leach more accumulated nitrate from soils in the basin into tile drains and ditches, and would actually cause nitrate concentrations in streams to increase, as previously noted in section 3.1.1. Third, higher streamflow would decrease both the contact time of water in the river with bottom deposits and the rates of denitrification (Howarth et al. 1996). The combination of higher nitrate concentrations and higher streamflow, and possibly decreased denitrification during 1980–96, would produce significant increases in nitrate flux.

4.3 SOURCES OF NITROGEN

Sources of nutrients in the MARB were evaluated at two scales—the large-basin scale shown in Figure 2.1 and the smaller, interior-basin scale shown in Figure 2.2. At the large-basin scale it was possible to develop estimates of the nutrient load contributions from each basin to the total nutrient load discharged from the MARB to the Gulf of Mexico. The interior basins provided a more precise indication of the watersheds and the land uses and human activities that were most significant in contributing nutrients to the Mississippi River and the Gulf. A summary of the nutrient flux data for nitrogen is presented in Table 4.2 for each of the large basins and in Table 4.3 for each of the 42 interior basins. Each table shows the average annual runoff and nitrogen flux for 1980–96, along with the standard error of estimates, expressed as a percentage of the nitrogen flux and yields. Also shown is the average nitrogen yield, which is the nitrogen flux divided by the drainage area. This normalizes the flux and makes it possible to determine which basins are abnormally large contributors of nutrients per unit area. In addition, Table 4.2 estimates the percentage each of the nine large basins contributes to the nitrate and total nitrogen flux to the Gulf of Mexico.

The estimated percentage nitrogen contributions presented in Table 4.2 assume no in-stream losses of nitrogen between the outflow point of each large basin and the Gulf. Three lines of evidence suggest in-stream nitrogen losses in large rivers are small. Nitrogen yield estimates for the large rivers and the smaller interior basins are within 7% when compared for the Upper and Lower Ohio; Upper, Middle, and Lower Mississippi; and Lower Missouri Basins. The Upper Missouri and Arkansas basins—which contain large reservoirs, have low precipitation rates, and have very low yields—were excluded from this calculation. The total nitrogen yield for this area (1,668,400 km^2) determined from the large-basin fluxes in Table 4.2 is 826 kg/km^2/yr. The total nitrogen yield for 30 interior basins, which comprise 62% of the area of the large basins, is 880 kg/km^2/yr. This small difference, which is about 6% and well within the standard errors, indicates that no significant denitrification losses occur between the outlets of the interior basins and the Gulf of Mexico. In other words, most of the nitrogen that is discharged into the Ohio, Missouri, and Mississippi Rivers from smaller streams is ultimately transported to the Gulf.

The second line of evidence is based on the results of a model that Howarth et al. (1996) applied to rivers draining to the North Atlantic Ocean. The model relates nitrogen retention, which is largely denitrification, to the ratio of mean depth to residence time of rivers. The deeper the rivers are, the less time nitrogen in the water column is in contact with benthic zones where denitrification could occur. They suggest that 5–20% of the nitrogen inputs to streams may be lost through denitrification in larger rivers. The Ohio, Missouri, and Mississippi Rivers used in the CENR assessment should be near the low end of their denitrification estimate. Short-term removal of nutrients in algal and plant biomass should be accounted for in the long-term flux estimates if these nutrients are later released in dissolved or particulate forms. The above discussion suggests that most of the nitrogen that enters the Ohio, Lower Missouri, and Mississippi Rivers is eventually discharged to the Gulf of Mexico. However, denitrification probably results in significant losses of nitrogen in streams smaller and shallower than the large rivers used in this assessment. Howarth et al.'s (1996) model would suggest that very large nitrogen losses via denitrification would occur within the interior basins used in this assessment.

TABLE 4.2. Average annual flux and yields of nitrogen from large watersheds in the Mississippi–Atchafalaya River Basin during 1980–96, estimated from regression models.

Basin Name/ID and Location of Flux Estimation Sites	Area	Runoff	Nitrate Flux	Nitrate Yield	Nitrate Std. Error	Total N Flux	Total N Yield	Total N Std. Error	Percent of Flux to Gulf of Mexico	
	km²	*cm/yr*	*metric tons*	*kg/km²/yr*	*percent*	*metric tons*	*kg/km²/yr*	*percent*	*Nitrate*	*Total N*
Entire Ohio River Basin	**526,000**	**50.2**	**323,500**	**620**	**5.1**	**495,900**	**940**	**3.9**	**34.0**	**31.6**
Upper Ohio River Basin (1)	251,200	45.4	150,700	600	4.4	251,800	1,000	4.7	15.8	16.1
Lower Ohio River Basin (C)(2)	274,800	54.6	172,700	630		244,100	890		18.1	15.5
Entire Missouri River Basin	**1,357,700**	**6.5**	**125,900**	**90**	**7.1**	**239,100**	**180**	**4.8**	**13.2**	**15.2**
Upper Missouri River Basin (3)	836,100	3.8	30,600	40	14.2	72,900	90	10.0	3.2	4.6
Lower Missouri River Basin (C)(4)	521,600	10.7	95,200	180		166,300	320		10.0	10.6
Entire Mississippi and Missouri River Basins above Ohio River	**1,847,200**	**11.8**	**537,000**	**290**	**4.3**	**840,600**	**460**	**4.0**	**56.4**	**53.6**
Upper Mississippi River Basin (5)	221,700	22.7	104,000	470	10.2	149,800	680	4.5	10.9	9.6
Entire MRB above Missouri River	444,200	26.2	368,400	830	7.4	516,600	1,160	5.2	38.7	32.9
Middle MRB (C)(6)	267,800	29.7	307,100	1,150		451,700	1,690		32.2	28.8
Entire Mississippi R., Including Flux Diverted into Atchafalaya R.	**2,967,000**	**21.3**	**933,500**	**320**	**3.4**	**1,507,300**	**520**	**3.4**	**98.0**	**96.1**
Arkansas River at Little Rock (7)	410,000	11.1	18,800	50		54,900	130	6.2	2.0	3.5
Lower MRB (C)(8)	184,000	50.1	54,200	290		115,800	630		5.7	7.4
Atchafalaya River										
Mississippi River diversion into Atchafalaya River	Ind.		201,900			325,700			21.2	20.8
Red & Ouachita River Basins (C)(9)	241,700	30.7	19,200	80		60,500	250		2.0	3.9
Entire MARB Flux to Gulf	**3,208,700**	**20.0**	**952,700**	**297**	**Est. < 5**	**1,567,900**	**489**	**Est. < 5**	**100.0**	**100.0**
Mississippi River flux to Gulf at Tarbert's Landing, LA (C)	Ind.		731,600			1,181,600			76.8	75.4
Atchafalaya River flux to Gulf at Melville, LA	Ind.		221,100		5.8	386,300		5.4	23.2	24.6

NOTES: See Figure 2.1 for locations of flux estimation sites; (C) is calculated as the difference between sites; Ind. = Indeterminate.

TABLE 4.3. Average annual flux and yields of nitrate and total nitrogen from the 42 interior basins during 1980–96, estimated with regression models.

Basin ID	Basin Name and Location of Sampling Site	Data Used	Runoff	Nitrate Flux as N	Nitrate Yield	Nitrate Flux Std. Error	Total N Flux	Total N Yield	Total N Std. Error
		yrs	*cm/yr*	*metric tons*	*kg/km²/yr*	*%*	*metric tons*	*kg/km²/yr*	*%*
1	Allegheny R. at New Kensington, PA	16	60.8	13,610	460	6.1	20,120	680	5.1
2	Monongahela R. at Braddock, PA	16	58.8	11,100	580	6.7	16,010	840	6.3
3	Muskingham R. at McConnelsville, OH	12	40.0	14,590	760	10	20,320	1,060	6.7
4	Kanawha R. at Winfield, WV**	78s	50.0	9,490	310	13.6	17,100	560	14.2
5	Scioto R. at Higby, OH	15	33.1	18,230	1,370	6.7	23,330	1,750	6.8
6	Great Miami at New Baltimore, OH	14	33.1	14,690	1,480	10.1	19,560	1,980	8.2
7	Kentucky R. at Lockport, KY	14	42.6	7,210	450	7.6	11,560	720	5.8
8	Wabash R. at New Harmony, IN	17	36.9	97,100	1,280	13.6	119,710	1,580	6.8
9	Cumberland R. near Grand Rivers, KY	7	62.7	16,330	360	na	32,860	720	na
10	Tennessee R. near Paducah, KY	17	51.7	24,010	230	10.9	49,050	470	0.9
11	Mississippi R. near Royalton, MN	15	15.7	880	29	9.0	5,030	170	11.2
12	Minnesota R. at Jordan, MN	16	14.0	50,270	1,200	13.1	53,800	1,280	8.4
13	St. Croix R. at St. Croix Falls, WI	15	27.7	920	57	15.3	3,690	230	47.3
14	Chippewa R. at Durand, WI	15	31.3	3,920	170	6.9	9,380	400	4.7
15	Wisconsin R. at Muscoda, WI	15	31.2	5,660	210	9.3	12,160	450	3.7
16	Rock R. near Joslin, IL	16	27.6	30,800	1,250	7.1	37,340	1,510	2.6
17	Cedar R. at Cedar Falls, IA	16	29.0	33,280	2,500	11.4	36,570	2,750	9.6
18	Iowa R. at Wapello, IA (includes Cedar R. Basin #17)	16	28.8	57,450	1,770	7.7	74,200	2,290	6.4
19	Skunk R. at Augusta, IA	16	26.6	17,280	1,560	14	22,450	2,020	1.7
20	Raccoon R. at Van Meter/Des Moines, IA	14	24.0	23,240	2,610	15.1	27,520	3,090	3.5
21	Des Moines at St. Francisville, MO (includes Raccoon R. Basin #20)	14	23.8	61,560	1,690	14.9	67,440	1,850	9.6
22	Illinois R. at Marseilles, IL	14	48.4	48,660	2,270	4.7	66,710	3,120	2.7
23	Lower Illinois R. Basin	14	28.7c	64,800c	1,368c	na	78,300c	1,650	na
--	Illinois R. at Valley City, IL (#22 & 23)	15	34.5	113,660	1,650	5.3	144,320	2,100	3.6
24	Kaskaskia R. nr. Venedy Station, IL	13	28.0	4,430	390	12.2	8,360	730	6.9
25	Milk R. near Nashua, MT	15	0.7	90	2	13.0	820	14	12.6
26	Missouri R. near Culbertson, MT	14	3.6	560	2	9.7	5,680	24	16.9
27	Bighorn R. near Bighorn, MT**	86s	5.7	880	15	6.9	2,950	50	7.0
28	Yellowstone R. near Sydney, MT	16	5.5	2,780	16	9.5	11,450	64	9.4
29	Cheyenne R. at Cherry Creek, SD	14	1.1	840	14	27.1	3,440	56	22.7
30	James R. near Scotland, SD	14	1.1	230	4	19.9	1,170	21	8.9
31	Platte R. near Louisville, NE	16	3.6	12,380	56	7.1	31,650	140	6.6
32	Kansas R. at Desoto, KS	13	4.5	7,240m	47m	9.0	22,670	150	9.3
33	Grand R. near Sumner, MO	14	26.3	9,480	530	19.4	22,710	1,280	12.0
34	Osage R. below St. Thomas, MO	15	32.7	5,890	160	13.1	15,410	410	12.0
35	St. Francis Bay at Riverfront, AR**	97s	33.5	2,020	120	28.0	6,690	400	16.3
36	White R. at Clarendon, AR**	41s	33.9	9,430	142	41.3	27,300	412	23.4
37	Arkansas R. at Tulsa, OK	16	4.4	9,540	49	17.1	13,920	72	9.6
38	Canadian R. at Calvin, OK	15	2.9	1,010	14	25.5	5,070	70	17.3
39	Yazoo R. at Redwood, MS**	89s	54.8	5,430	166	9.8	18,760	605	9.2
40	Big Black R. near Bovina, MS	15	52.2	830	110	14.1	4,420	600	9.9
41	Red R. at Alexandria, LA	13	17.8	7,760	44	11.5	35,610	200	8.2
42	Ouachita R. near Columbia, LA**	92s	42.8	2,060	50	13.5	14,550	360	12.7

***Estimated from flow-weighted mean concentrations and discharge at time of sampling.*

NOTE: s = number of samples; na = not available; m = calculated from flow-weighted mean concentration

The third line of evidence is from stable isotope data on the $\delta^{15}N$ and $\delta^{18}O$ of nitrate in water samples collected in April 1998 from the Ohio River at Grand Chain, Illinois, and from the Mississippi River at Thebes, Illinois, and St. Francisville, Louisiana (see Table 2.2 and Figure 2.1 for locations). The isotopic ratios $\delta^{15}N$ and $\delta^{18}O$ of nitrate measured at St. Francisville (+6.5 and +8.3 per mil) are essentially the same as would be predicted by simple mixing of water from the two sources (+6.5 and +8.8 per mil) (Kendall et al. 1999). The estimated travel time from the Ohio River confluence with the Mississippi River to St. Francisville was about seven days. These preliminary results suggest there was no appreciable loss of nitrate from denitrification in this reach of the Mississippi River during the seven-day period. Denitrification would result in an increase (enrichment) in the $\delta^{15}N$ and $\delta^{18}O$ of the remaining nitrate.

Given the assumption that nitrogen is conservative in large rivers, the data in Table 4.2 show that the Ohio River basin, on average, contributes about 34% of the nitrate and 32% of the total nitrogen discharged by the MARB to the Gulf. About 56% of the nitrate and 54% of the total nitrogen comes from the Mississippi River Basin above the Ohio River Basin. The Missouri Basin contributes about 15% of the total N, and the combined Upper and Middle Mississippi Basins contribute about 39%. The Lower Mississippi Basin contributes less than 8% of the N and the combined Arkansas, Red, and Ouachita Basins contribute less than 8%. The Middle Mississippi Basin, with only 8.5% of the MARB drainage area, contributes about 33% of the nitrate discharging to the Gulf and the largest amount of nitrate and total nitrogen per unit area (Figure 4.5). The respective nitrate and total nitrogen yields from this basin are 1,150 and 1,690 kg/km^2/yr, which are nearly 90% higher than the Ohio Basin and more than 100% higher than the Upper Mississippi Basin (Table 4.2). These yield estimates are similar to those presented by Smith et al. (1997). As will be shown later in this report, the high nitrogen yields in this basin are primarily associated with intensive agriculture. Nitrogen yields in the western half of the MARB are relatively low—320 kg/km^2/yr or less, and less than the entire MARB average of 489 kg/km^2/yr (Table 4.2). This can be attributed largely to the drier climate, lower runoff, and different land uses in this part of the MARB.

Figure 4.6 shows the temporal pattern in annual nitrogen yields for three large basins and the entire Mississippi Basin for 1970–96. The annual yields vary considerably, depending on precipitation. The Middle Mississippi Basin has the greatest variability. The nitrate yield from this basin ranged from about 250 kg/km^2 in 1989 to more than 2,500 kg/km^2 in the flood year of 1993. The large variability in nitrate yields, which comprises most of the nitrogen, discharging from this basin is an indication that large amounts of nitrate are available for leaching from the soils, unsaturated zone, and ground water of the basin. It also indicates that the amount of nitrate delivered to streams is largely determined by precipitation. This basin tends to dominate the amount of nitrogen discharged by the MARB to the Gulf, even though is comprises only about 8.5% of the area of the MARB.

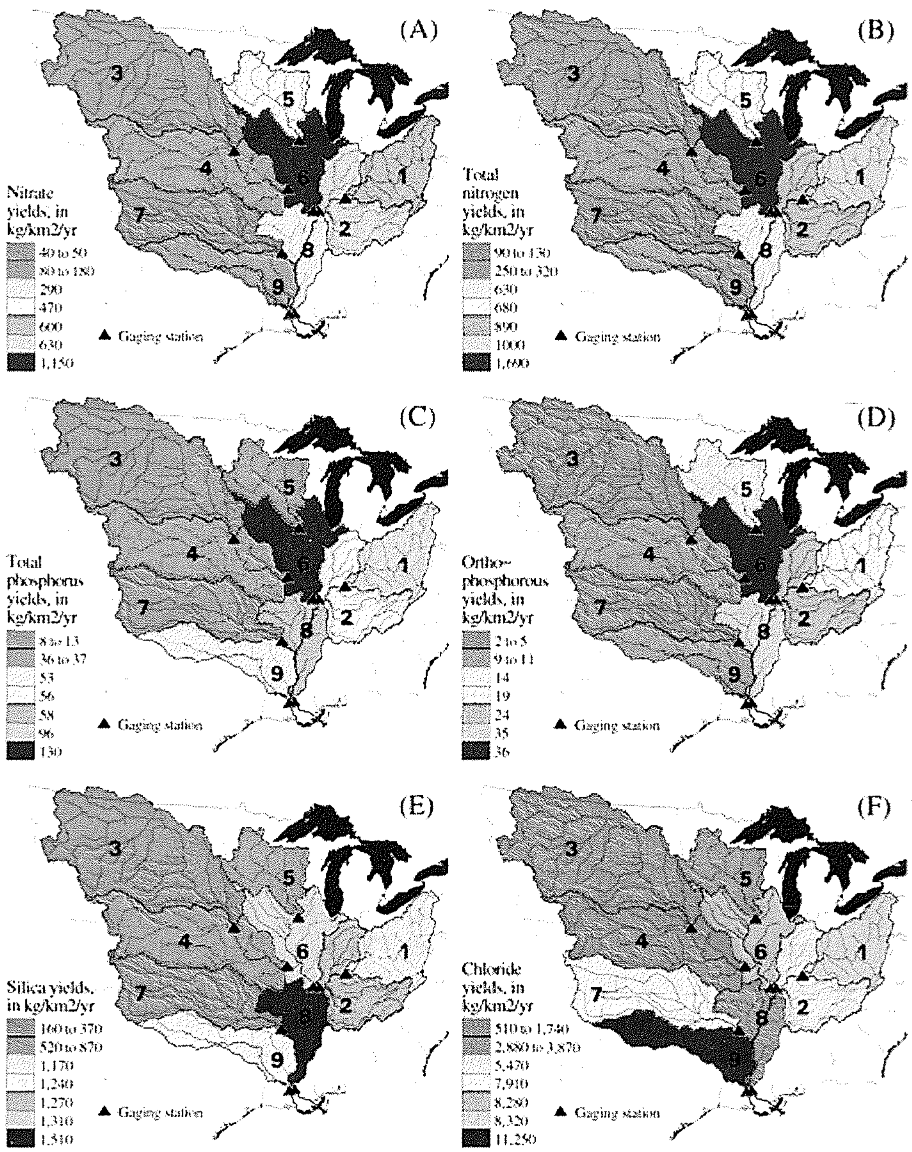


FIGURE 4.5. Spatial distribution of the average nutrient and chloride yields in nine large basins during 1980–96: (A) nitrate–nitrogen, (B) total nitrogen, (C) total phosphorus, (D) orthophosphate phosphorus, (E) silica as Si, and (F) chloride.

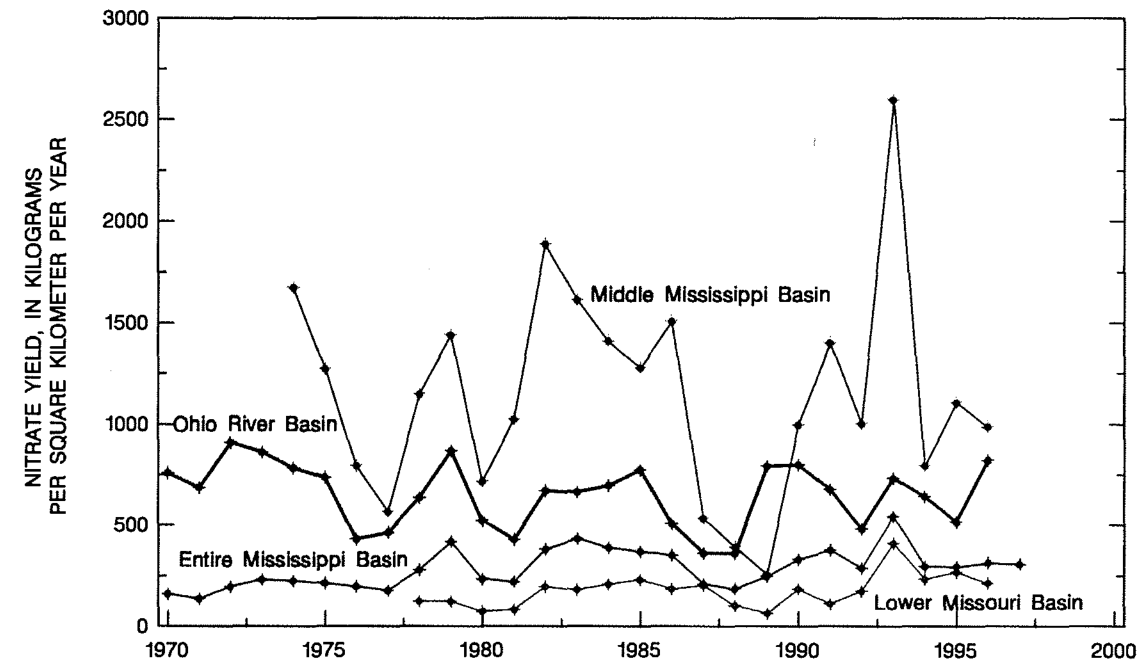
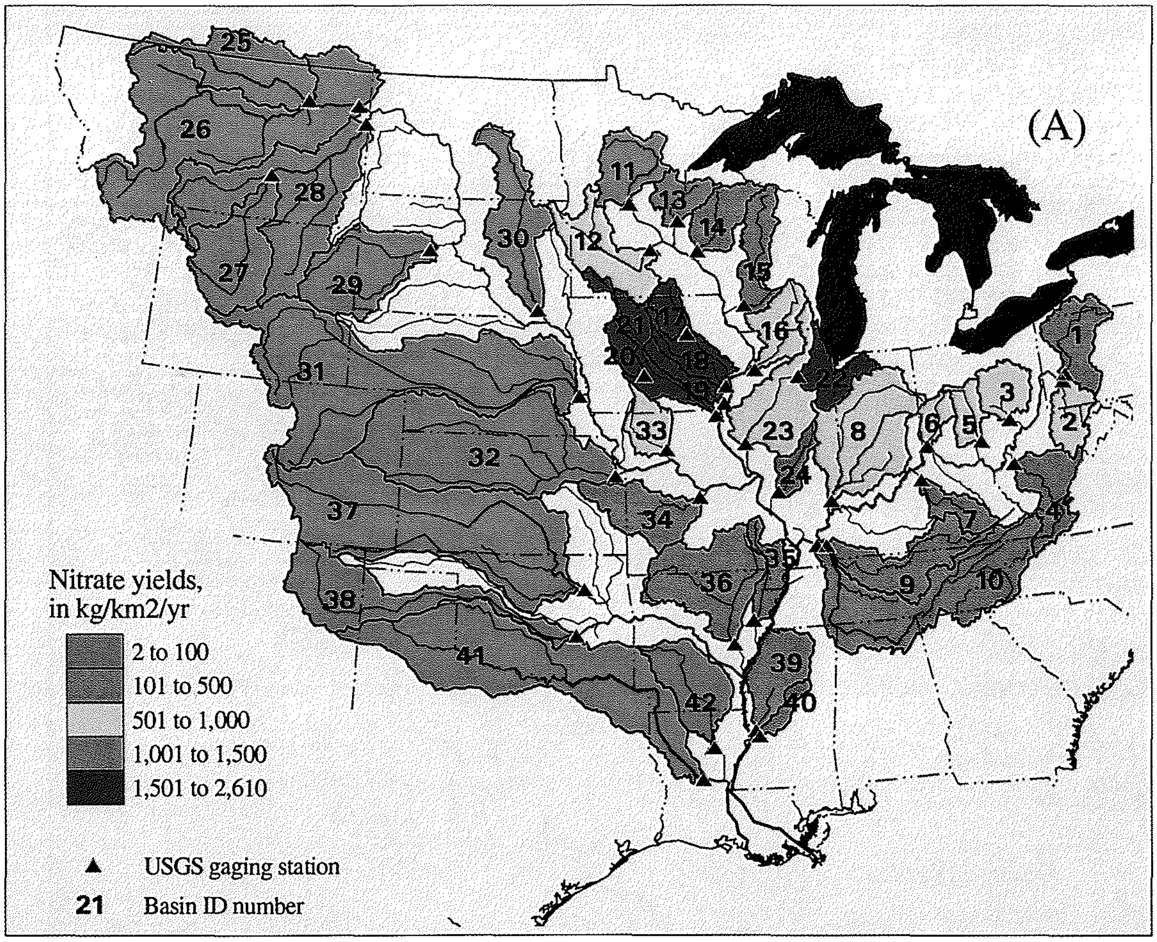


FIGURE 4.6. Temporal patterns in nitrate yields in the Middle Mississippi, Ohio, Lower Missouri, and entire Mississippi River Basin, 1970–96. NOTE: See Figure 2.1 for site locations.

The sources of nitrogen in the MARB are shown in greater detail with data on the average annual fluxes and yields presented in Table 4.3 for the 42 interior basins. The spatial patterns in average annual nitrate and total nitrogen yields, which are very similar, are shown graphically in Figures 4.7A and 4.8A. The distribution of the annual yields of nitrate and total nitrogen for each basin are shown in the form of boxplots in Figures 4.7B and 4.8B for 1980–96. The highest average annual total nitrogen yields range from 1,000 to more than 3,000 kg/km^2/yr and occur in a band extending from southwestern Minnesota across Iowa, Illinois, Indiana, and Ohio. Annual average yields of 1,800 to more than 3,100 kg/km^2/yr occur in the Des Moines (20 plus 21), Iowa (17 plus 18), and Skunk River Basins in Iowa (Table 4.3 and Figure 4.8A); the upper Illinois River Basin (22), and the Great Miami Basin in Ohio (6). During years with high precipitation the total nitrogen yield from these five river basins (Iowa, Skunk, Des Moines, Illinois, and Great Miami) can be 3,000 to more than 7,000 kg/km^2/yr (Figure 4.8B. Discharge from these five basins alone can account for as much as 21% of the total nitrogen discharge from the MARB during average years and more than 30% during flood years, such as 1993. The nitrate discharged from these basins during 1993 was equivalent to more than 37% of the nitrate discharged to the Gulf. The Minnesota River Basin (12), Rock River (16) and Lower Illinois River (23) in Illinois, Grand River (33) in Missouri, Wabash River (8) in Indiana, and Muskingham (3) and Scioto (5) Rivers in Ohio have nitrogen yields of 1,000–1,800 kg/km^2/yr. Other basins adjacent to these, but not shown in the figures because of insufficient data, may have similar nitrogen yields. Nitrogen yields were generally 500–1,000 kg/km^2/yr in basins south of the Ohio River and generally less than 500 kg/km^2/yr in the Missouri, Arkansas, and Lower Mississippi Basin. Many of the drier basins in the western part of the MARB had nitrogen yields of less than 100 kg/km^2/yr.



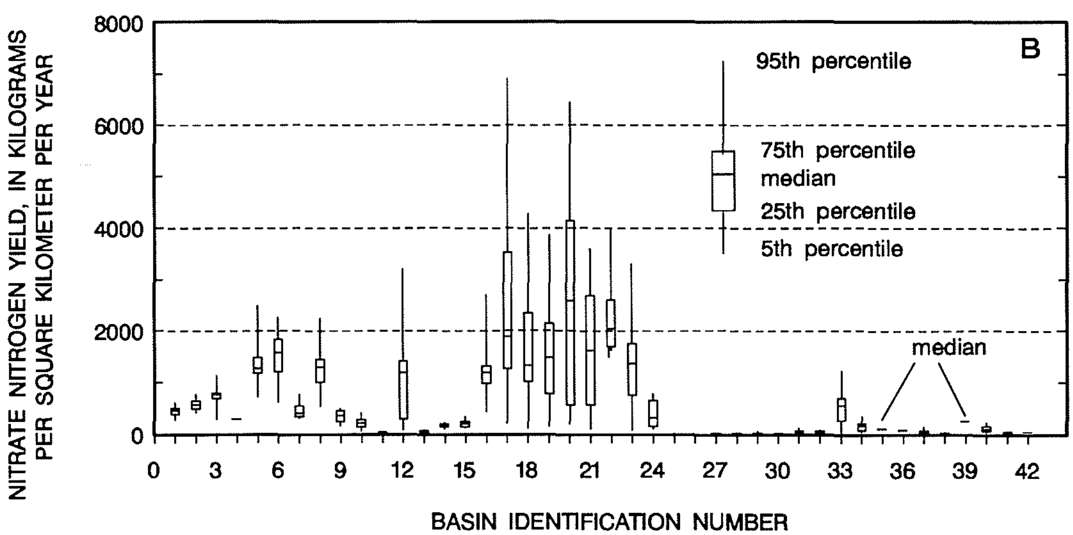
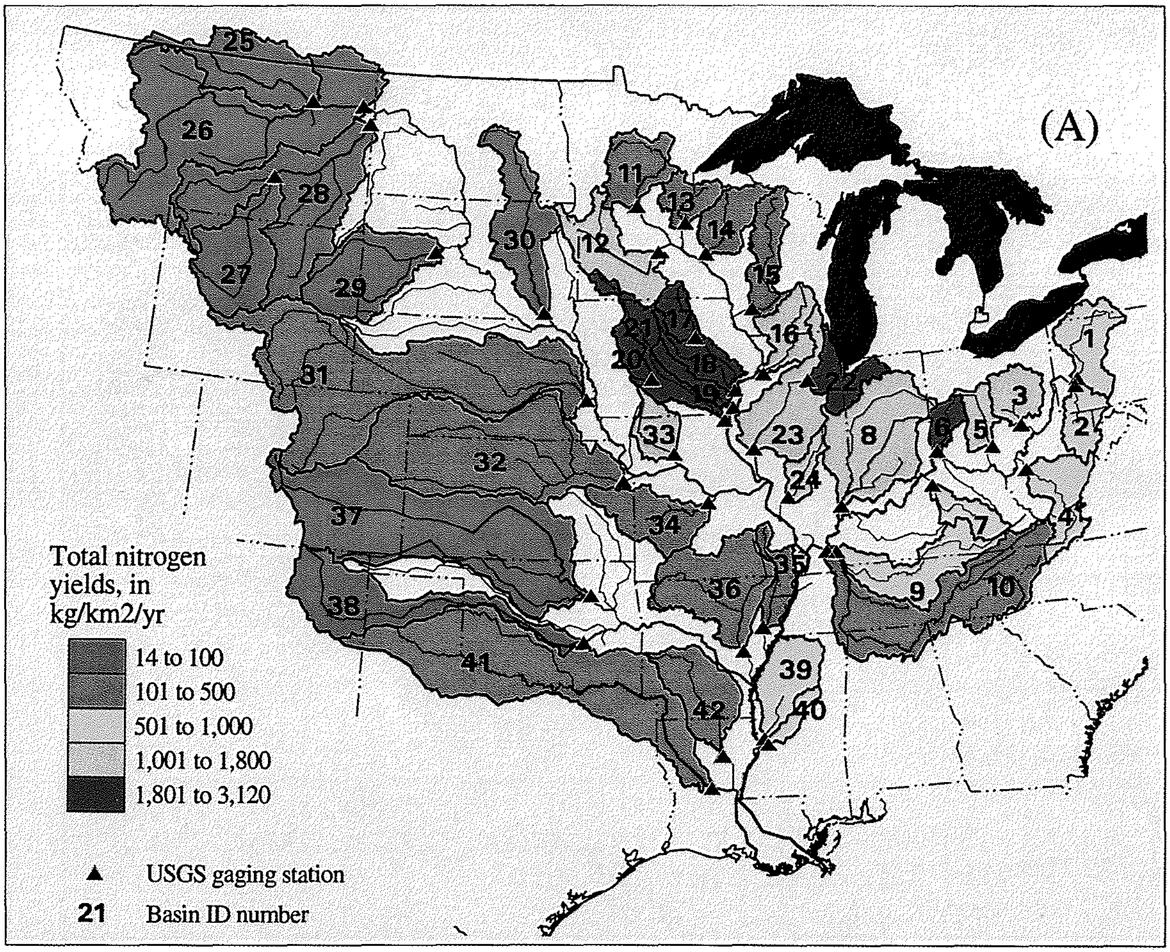


FIGURE 4.7. (A) Spatial distribution of nitrate yields in the 42 interior basins, and (B) box-plots showing distribution of nitrate yields in the 42 interior basins. NOTE: Dashes (–) show median yields for several sites where other statistics could not be calculated.



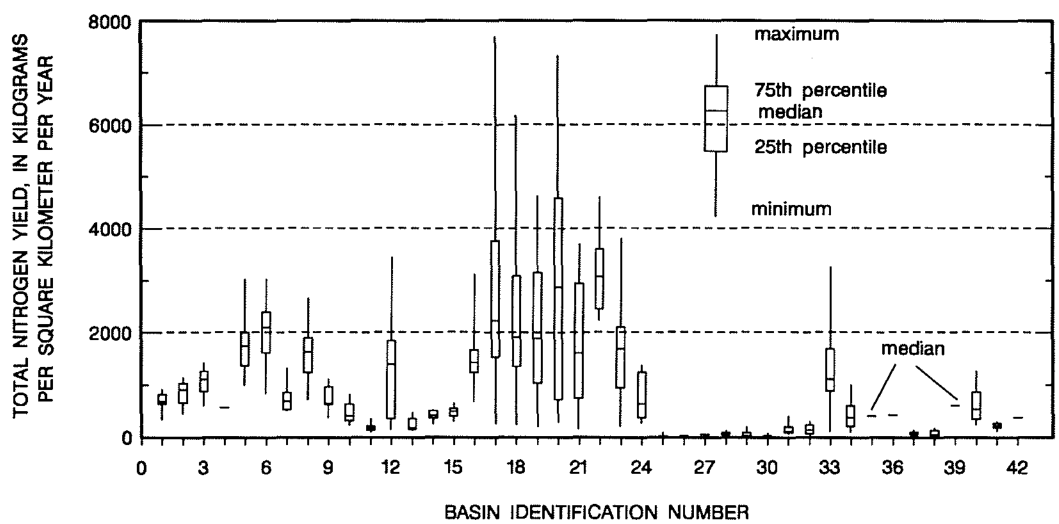


FIGURE 4.8. (A) Spatial distribution of total nitrogen yields in the 42 interior basins, and (B) boxplots showing distribution of total nitrogen yields in the 42 interior basins. NOTE: Dashes (–) show median yields for several sites where other statistics could not be calculated.

The large range in annual yields of nitrogen shown in Figures 4.7B and 4.8B can be attributed largely to year-to-year variations in precipitation and leaching of nitrogen from nonpoint sources. During dry years there is little rainfall to transport nitrogen (mainly nitrate) from the soil and unsaturated zone to streams. Under these conditions nitrogen yields are low, and nitrogen inputs from point sources may dominate in some streams. During periods of high precipitation nitrate that has accumulated in the soil can be flushed into streams via agricultural drains, ground-water discharge, and overland flow. Basins with large point-source inputs, such as the Upper Illinois River (basin 22) with more than 300 people per km^2, exhibit a different pattern in annual yields. The minimum annual yield is very high because of sustained year-round direct inputs to the stream. The range in nitrogen flux is small because this input is not greatly affected by precipitation. Much of the year-to-year variability that does occur in basin 22 may be due largely to varying amounts of precipitation leaching varying amounts of nitrogen from soils in the basin. Several other basins (5–Scioto, 6–Great Miami, 8–Wabash, and 16–Rock) that also have above-average population densities show this same pattern but to a lesser extent.

The nitrogen flux and yield estimates presented in the foregoing discussion represent the amounts of nitrogen delivered near the mouths of the streams to larger rivers, usually the Ohio, Missouri, or Mississippi, and to the Gulf of Mexico. As previously discussed, they do not account for any in-stream losses such as denitrification or burial in reservoirs or on flood plains before water reached the sampling point. These processes would not significantly affect our estimates of nitrogen flux from the MARB to the Gulf of Mexico. However, if denitrification is significant in large rivers, this could affect our estimates of the percentage contributions from basins within the MARB (Table 4.2). The percentage of nitrogen contributed to the Gulf by the farthest upstream basins could be overestimated, and the percentage contributed by the farthest downstream basins could be underestimated.

4.4 Sources of Phosphorus

The average annual flux and yields of orthophosphate and total phosphorus are summarized in Table 4.4 for the large basins. The Middle Mississippi and Ohio Basins are the largest contributors of both ortho- and total phosphorus to the Gulf of Mexico. The Middle Mississippi contributes about 25% of the total phosphorus discharged by the MARB, and the Ohio contributes about 29%. About 19% of the total phosphorus comes from the Missouri Basin, 6% comes from the Upper Mississippi Basin, and another 12% comes from the Lower Mississippi and Arkansas Basins. Phosphorus yields for the large basins are shown in Figures 4.5C and 4.5D. The Middle Mississippi Basin has the highest total phosphorus yield of 130 kg/km^2/yr (Figure 4.5C). Phosphorus yields in the Upper and Lower Ohio Basin and Lower Mississippi Basin range from 56 to 96 kg/km^2/yr, and yields are 8–53 kg/km^2/yr elsewhere in the MARB. The highest yields of orthophosphate, 35 and 36 kg/km^2/yr, are in the Lower and Middle Mississippi Basin (Figure 4.5D). The phosphorus discharged from all of the large basins is predominantly in particulate form, with dissolved orthophosphate comprising only about 20–30% of the total phosphorus.

The phosphorus flux and yields for the 42 interior basins are presented in Table 4.5. These estimates are considerably less precise than the phosphorus and the nitrogen flux estimates for the large basins (Table 4.4), as indicated by the large standard errors, which show that variables in addition to those used in the regression models are important in controlling the flux of phosphorus. The interior basins with the highest ortho- and total phosphorus yields (Figures 4.9A and 4.10A) are generally the same ones that had the highest nitrogen yields (Figures. 4.7A and 4.8A). They are also the ones that have the largest amount of variability in annual phosphorus

TABLE 4.4. Average annual flux and yields of phosphorus from large watersheds in the Mississippi–Atchafalaya River Basin, during 1980–96, estimated from regression models.

Basin Name/ID and Location of Flux Estimation Sites	Area	Runoff	Ortho P Flux	Ortho P Yield	Ortho P Standard Error	Total P Flux	Total P Yield	Total P Standard Error	Percent of Flux to Gulf of Mexico	
	km²	*cm/yr*	*metric tons*	*kg/km²/yr*	*percent*	*metric tons*	*kg/km²/yr*	*percent*	*Ortho P*	*Total P*
Entire Ohio River Basin	**526,000**	**50.2**	**11,230**	**21**	**10.1**	**39,400**	**75**	**7.9**	**26.9**	**28.9**
Upper Ohio River Basin (1)	251,200	45.4	4,750	19	27.2	24,100	96	10.1	11.4	17.7
Lower Ohio River Basin (C)(2)	274,800	54.6	6,510	24		15,300	56		15.6	11.2
Entire Missouri River Basin	**1,357,700**	**6.5**	**7,060**	**5**	**4.4**	**26,000**	**19**	**6.4**	**16.9**	**19.0**
Upper Missouri River Basin (3)	836,100	3.8	1,320	2	18.3	6,400	8	14.1	3.2	4.7
Lower Missouri River Basin (C)(4)	521,600	10.7	5,720	11		19,500	37		13.7	14.3
Entire Mississippi and Missouri River Basins above Ohio River	**1,847,200**	**11.8**	**19,060**	**10**	**5.0**	**68,700**	**37**	**5.2**	**45.6**	**50.3**
Upper Mississippi River Basin (5)	221,700	22.7	3,120	14	10.5	8,000	36	5.4	7.5	5.9
Entire MRB above Missouri River	444,200	26.2	11,920	27	9.1	25,900	58	5.8	28.5	19.0
Middle MRB (C)(6)	267,800	29.7	9,550	36		34,700	130		22.9	25.4
Entire Mississippi R., Including Flux Diverted into Atchafalaya R.	**2,967,000**	**21.3**	**39,490**	**14**	**4.9**	**123,800**	**42**	**6.5**	**94.5**	**90.7**
Arkansas River at Little Rock (7)	410,000	11.1	1,900	5	16.9	5,100	13	7.4	4.5	3.7
Lower MRB (C)(8)	184,000	50.1	6,400	35		10,600	58		15.3	7.8
Atchafalaya River										
Mississippi River diversion into Atchafalaya River	Ind.		8,690			26,800			20.8	19.6
Red & Ouachita River Basins (C)(9)	241,700	30.7	2,280	9		12,700	53		5.5	9.3
Entire MARB Flux to Gulf	**3,208,700**	**20.0**	**41,770**	**13**	**Est. <6**	**136,500**	**42**	**Est. <7**	**100.0**	**100.0**
Mississippi River flux to Gulf at Tarbert's Landing, LA (C)	Ind.		30,800			97,000			73.7	71.1
Atchafalaya River flux to Gulf at Melville, LA	Ind.		10,970		7.7	39,500		7.5	26.3	28.9

NOTES: See Figure 2.1 for locations of flux estimation sites; (C) is calculated as the difference between sites; Ind. = Indeterminate.

TABLE 4.5. Average annual flux and yields of orthophosphate and total phosphorus from the 42 interior basins during 1980–96, estimated with regression models.

Basin ID	Basin Name and Location of Sampling Site	Data Used	Runoff	Ortho P Flux	Ortho P Yield	Ortho P Std. Error	Total P Flux	Total P Yield	Total P Std. Error
		yrs	*cm/yr*	*metric tons*	*kg/km²/yr*	*%*	*metric tons*	*kg/km²/yr*	*%*
1	Allegheny R. at New Kensington, PA	16	60.8	142	4.8	13.7	982	33.0	15.8
2	Monongahela R. at Braddock, PA	16	58.8	97	5.1	22.2	798	42.0	16.7
3	Muskingham R. at McConnelsville, OH	12	40.0	191	9.9	27.4	1,167	60.8	9.1
4	Kanawha R. at Winfield, WV**	78s	50.0	180	6.0	11.0	850	28.0	15.2
5	Scioto R. at Higby, OH	15	33.1	600	45.1	14.1	1,166	87.7	9.3
6	Great Miami at New Baltimore, OH	14	33.1	570	57.6	16.2	1,221	123.3	6.0
7	Kentucky R. at Lockport, KY	14	42.6	541	33.8	15.1	1,477	92.3	8.3
8	Wabash R. at New Harmony, IN	17	36.9	1,901	25.1	57.3	6,938	91.7	12.2
9	Cumberland R. near Grand Rivers, KY	7	62.7	857	18.8	na	2,542	55.7	na
10	Tennessee R. near Paducah, KY	17	51.7	2,106	20.2	40.7	3,985	38.1	9.0
11	Mississippi R. near Royalton, MN	15	15.7	65	2.2	16.3	219	7.3	10.7
12	Minnesota R. at Jordan, MN	16	14.0	722	17.2	36.3	1,353	32.2	7.3
13	St. Croix R. at St. Croix Falls, WI	15	27.7	38	2.3	34.4	156	9.6	55.9
14	Chippewa R. at Durand, WI	15	31.3	280	12.0	18.7	737	31.6	7.6
15	Wisconsin R. at Muscoda, WI	15	31.2	226	8.4	18.1	661	24.6	6.9
16	Rock R. near Joslin, IL	16	27.6	889	36.0	37.0	2,083	84.3	5.0
17	Cedar R. at Cedar Falls, IA	16	29.0	1,158	87.0	34.6	1,135	85.3	13.1
18	Iowa R. at Wapello, IA (includes Cedar R. Basin #17)	16	28.8	2,019	62.3	27.0	3,076	94.9	9.1
19	Skunk R. at Augusta, IA	16	26.6	463	41.7	20.9	1,338	120.5	12.5
20	Raccoon R. at Van Meter/Des Moines, IA	14	24.0	396	44.5	43.7	755	84.8	18.0
21	Des Moines at St. Francisville, MO (includes Raccoon R. Basin #20)	14	23.8	1,350	37.1	26.2	2,334	64.1	9.6
22	Illinois R. at Marseilles, IL	14	48.4	2,222	103.8	5.9	4,078	190.5	3.2
23	Lower Illinois R. Basin	14	28.7c	1,168c	24.6c	na	3268c	69.0c	na
--	Illinois R. at Valley City, IL (entire (Illinois R. basins #22 & 23)	15	34.5	3,390	49.3	11.3	7,346	106.8	4.4
24	Kaskaskia R. nr. Venedy Station, IL	13	28.0	575	49.3	30.7	919	80.7	9.8
25	Milk R. near Nashua, MT	15	0.7	10	49.3	24.3	185	3.2	15.4
26	Missouri R. near Culbertson, MT	14	3.6	132	49.3	21.5	796	3.4	17.5
27	Bighorn R. near Bighorn, MT**	86s	5.7	33	0.6	12.5	164	2.8	13.0
28	Yellowstone R. near Sydney, MT	16	5.5	133	0.7	14.5	2,302	12.9	17.6
29	Cheyenne R. at Cherry Creek, SD	14	1.1	32	0.5	57.1	1,639	26.5	52.9
30	James R. near Scotland, SD	14	1.1	225	4.0	45.6	254	4.5	17.7
31	Platte R. near Louisville, NE	16	3.6	1,666	7.5	10.3	5,447	24.5	6.9
32	Kansas R. at Desoto, KS	13	4.5	1,024	6.6	24.6	3,134	20.2	10.1
33	Grand R. near Sumner, MO	14	26.3	303	17.0	15.9	3,271	183.8	13.7
34	Osage R. below St. Thomas, MO	15	32.7	345	9.2	19.9	729	19.4	10.3
35	St. Francis Bay at Riverfront, AR**	97s	33.5	445	26.6	20.2	1,320	78.7	15.1
36	White R. at Clarendon, AR**	41s	33.9	560	8.4	21.4	2,940	44.4	29.2
37	Arkansas R. at Tulsa, OK	16	4.4	931	4.8	24.4	1,217	6.3	9.4
38	Canadian R. at Calvin, OK	15	2.9	206	2.8	40.3	881	12.2	16.6
39	Yazoo R. at Redwood, MS**	89s	54.8	510	15.6	13.6	4,000	122.0	12.1
40	Big Black R. near Bovina, MS	15	52.2	156	21.4	20.4	1,061	145.3	8.5
41	Red R. at Alexandria, LA	13	17.8	921	5.3	28.1	5,935	34.0	8.6
42	Ouachita R. near Columbia, LA**	92s	42.8	446	11.0	21.2	1,275	31.5	12.7

***Estimated from mean concentrations and discharge at time of sampling.*

NOTE: s = number of samples; na = not available; c = calculated as a difference between two sites.

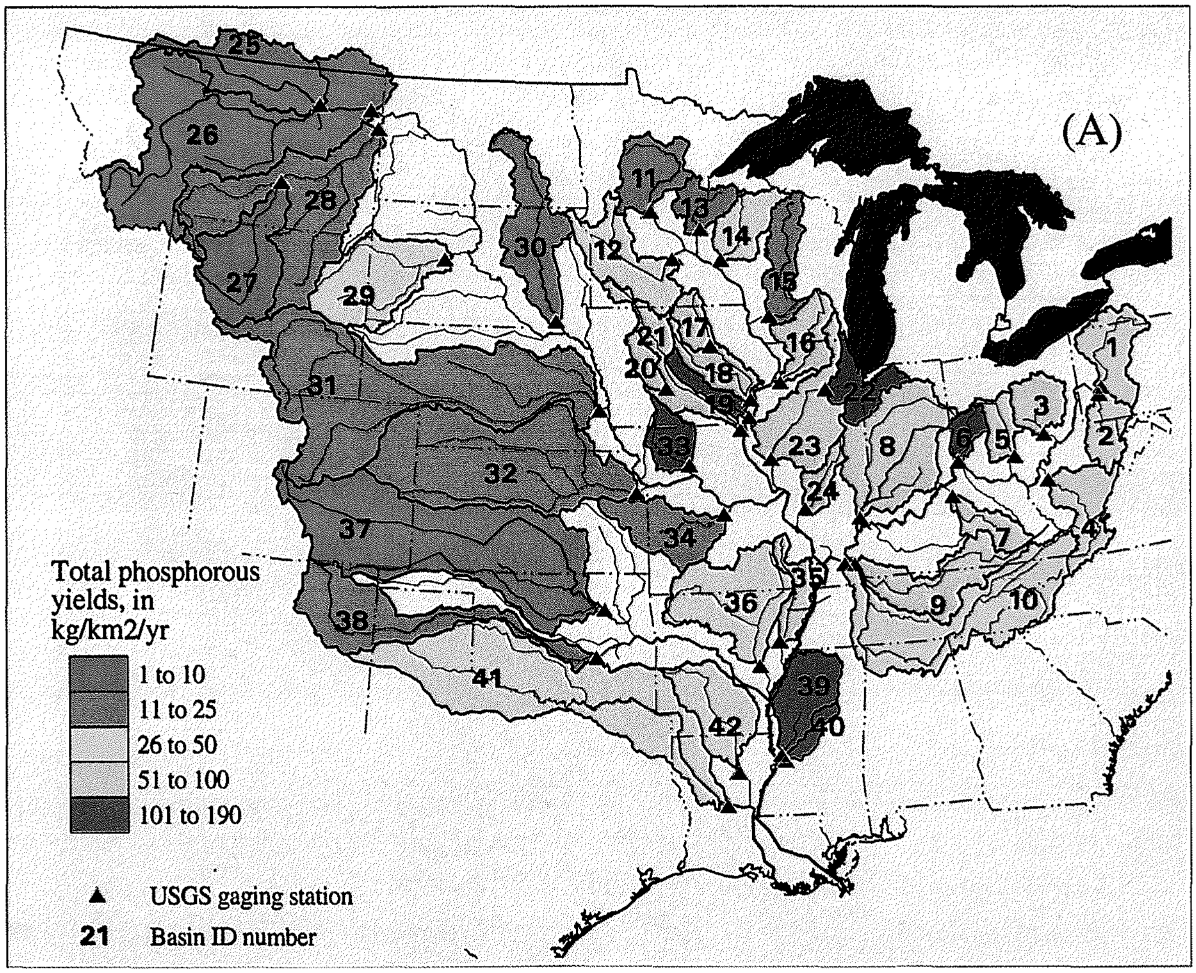
yields as shown by the boxplots in Figures 4.9B and 4.10B. These basins extend from north central Iowa eastward across Ohio. The total P yields from these basins range from about 50 to 190 $kg/km^2/yr$. The highest phosphorus yield is from the Upper Illinois Basin (#22), which has the highest population density and large point-source inputs from the Chicago area. These point-source inputs are also shown by the high median and minimum annual yield values in the boxplots (Figures 4.9B and 4.10B) for basin 22. Orthophosphate comprises from 25% to more than 50% of the total phosphorus in most of these basins. The highest percentages of orthophosphate are generally in basins that have high population densities or a large percentage of the basin in cropland, or both. The total phosphorus yields were also high in basins 39 and 40 in Mississippi and basin 33 in northwestern Missouri (Figure 4.9). However, in these basins 85–90% of the phosphorus is in particulate form (Table 4.5), indicating that sediment is the principal source of phosphorus in these basins. The dissolved orthophosphate present in these streams and transported into the Gulf of Mexico is readily available for use by aquatic plants. However, the particulate forms of phosphorus must be converted to orthophosphate by chemical or microbiological processes before plants can use it.

A comparison of phosphorus yields from the interior basins with yields from the large basins indicates that there is no significant net loss of phosphorus in the large rivers. The average yields from the Upper and Lower Ohio, Lower Missouri, and Upper, Middle, and Lower Mississippi Basins are 61 and 19 $kg/km^2/yr$ for total phosphorus and orthophosphorus. The average yields measured for 30 interior basins that comprise about 60% of the large-basin area are 67 and 22 $kg/km^2/yr$ for total phosphorus and orthophosphorus, respectively. The similarity of these values suggests that there is little net in-stream loss or gain in phosphorus over the long term in the large river basins. The main process for phosphorus removal would be deposition of sediment. This probably does not occur to any significant degree, except in basins with large mainstem reservoirs.

4.5 SOURCES OF SILICA

The average annual flux and yields of silica in the nine large basins are shown in Table 4.6 and Figure 4.5E. There is no clearly dominant source of silica at this scale. The fluxes are generally proportional to the amount of streamflow contributed by each basin. The silica yields fall within a fairly narrow range (1,170–1,510 $kg/km^2/yr$), except for the Upper Mississippi Basin and the more arid western half of the MARB, where yields were lower because of less runoff.

The flux and yields of silica from the 42 interior basins are shown in Table 4.7 and Figure 4.11A. Even at this scale, there are no clearly dominant source areas. Silica yields in most basins in the eastern part of the MARB are about 1,000–2,320 $kg/km^2/yr$. Basins with the highest yields (> 1,500 $kg/km^2/yr$) are scattered throughout this area and do not appear to be associated with any particular land use or human activity. Basins with the highest average annual silica yields (e.g., basins 13, 18, 19, and 21) also generally have the largest variability in annual yields (Figure 4.11B). This suggests that leaching of silica from these basins is more affected by precipitation than in the other basins. The reasons for this have not been determined, but may include geochemical and hydrologic processes. Silica is derived from the dissolution of silicate minerals in soils and rocks. Therefore, the rate at which silica is transported into streams is more likely to be regulated by geochemical process, such as pH and the mineralogy of soil and rocks, and by hydrologic processes, such as ground-water contributions to streams, than by human activities.



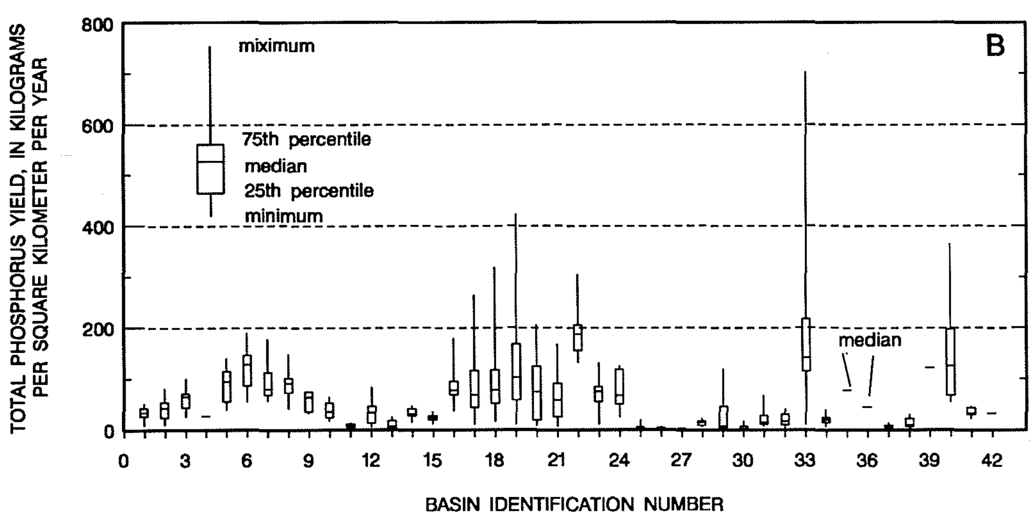
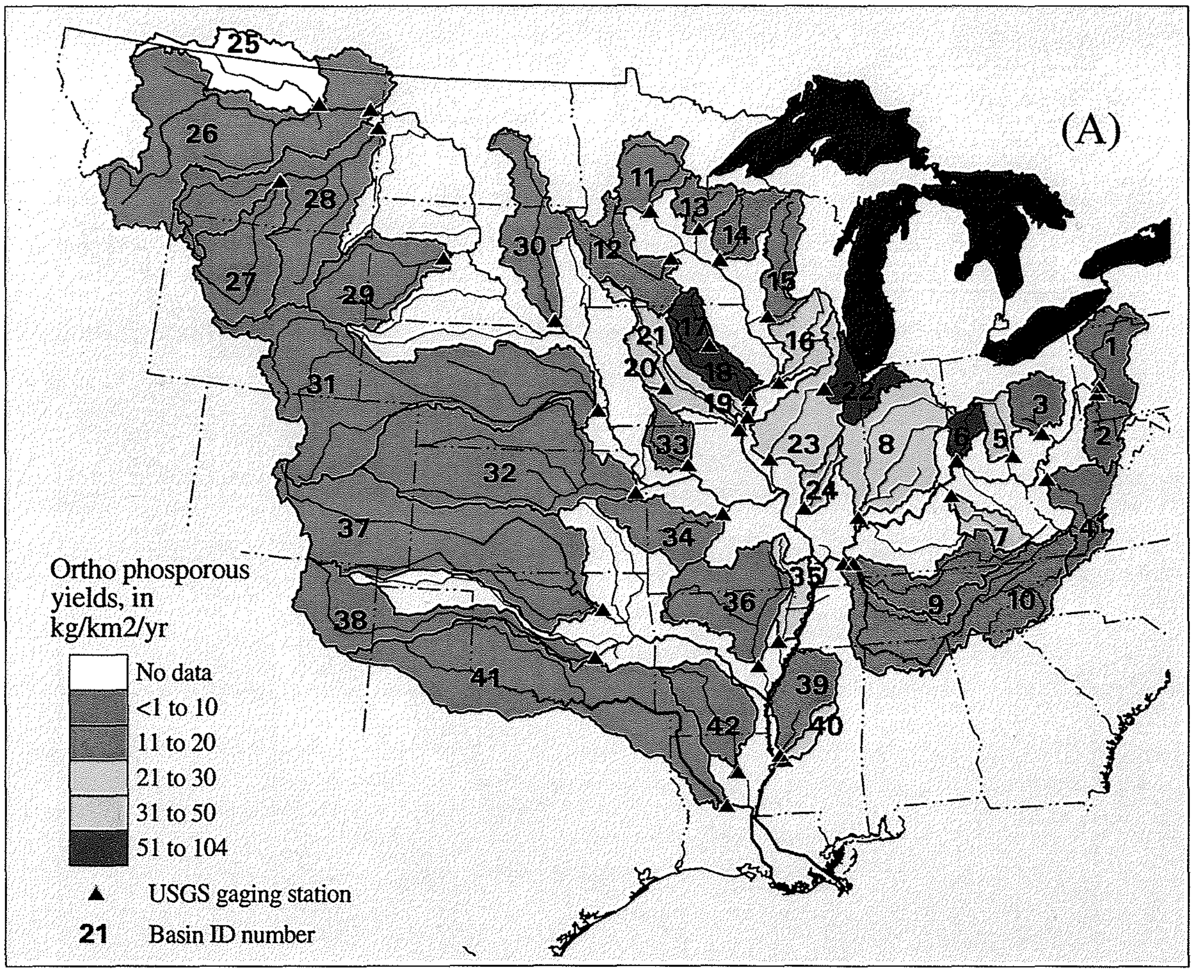


FIGURE 4.9. (A) Spatial distribution of total phosphorus yields in the 42 interior basins, and (B) boxplots showing distribution of total phosphorus yields in the 42 interior basins. NOTE: Dashes (–) show median yields for several sites where other statistics could not be calculated.



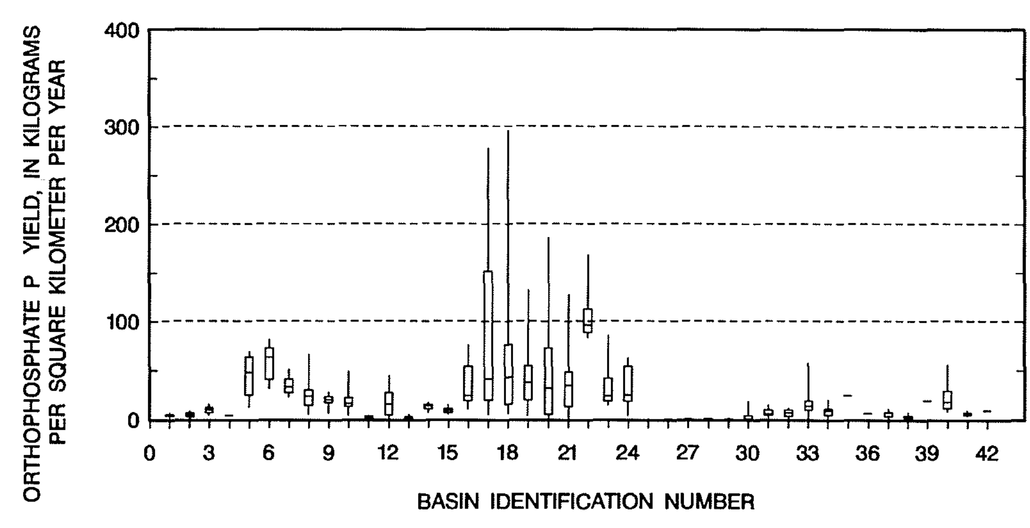


FIGURE 4.10. (A) Spatial distribution of orthophosphate yields in the 42 interior basins, and (B) boxplots showing distribution of orthophosphate yields in the 42 interior basins. NOTE: Dashes (–) show median yields for several sites where other statistics could not be calculated.

TABLE 4.6. Mean annual flux and yields of silica (Si) and chloride from large watersheds in the Mississippi–Atchafalaya River Basin during 1980–96, estimated from regression models. NOTES: See Figure 2.1 for locations of flux estimation sites; (C) is calculated as the difference between sites; Ind. = Indeterminate.

Basin Name/ID and Location of Flux Estimation Sites	Area	Runoff	Silica Flux	Silica Yield	Silica Std. Error	Chloride Flux	Chloride Yield	Chloride Std. Error	Percent of Flux to Gulf of Mexico	
	km²	*cm/yr*	*mt*	*kg/km²/yr*	*percent*	*mt*	*kg/km²/yr*	*percent*	*Silica*	*Chloride*
Entire Ohio River Basin	**526,000**	**50.2**	**642,500**	**1,220**	**7.5**	**3,595,000**	**6,830**	**4.4**	**27.7**	**24.9**
Upper Ohio River Basin (1)	251,200	45.4	292,800	1,170	13.0	2,091,500	8,320	4.9	12.6	14.5
Lower Ohio River Basin (C)(2)	274,800	54.6	349,700	1,270	na	1,503,500	5,470	na	15.1	10.4
Entire Missouri River Basin	**1,357,700**	**6.5**	**404,400**	**300**	**3.8**	**1,331,400**	**980**	**2.3**	**17.5**	**9.2**
Upper Missouri River Basin (3)	836,100	3.8	131,900	160	5.6	422,600	510	3.5	5.7	2.9
Lower Missouri River Basin (C)(4)	521,600	10.7	272,400	520	na	908,800	1,740	na	11.8	6.3
Entire Mississippi and Missouri River Basin above Ohio River	**1,847,200**	**11.8**	**947,900**	**510**	**6.5**	**4,188,600**	**2,270**	**2.0**	**40.9**	**29.0**
Upper Mississippi River Basin (5)	221,700	22.7	192,400	870	64.5	638,700	2,880	3.5	8.3	4.4
Lower MRB above Missouri River	444,200	26.2	477,700	1,080	18.2	2,550,400	5,740	3.1	20.6	17.6
Middle MRB (C)(6)	267,800	29.7	351,100	1,310		2,218,500	8,280		15.1	15.3
Entire Mississippi River, Including Flux Diverted into Atchafalaya River	**2,967,000**	**21.3**	**2,017,600**	**690**	**11.0**	**11,738,900**	**4,030**	**2.1**	**87.0**	**81.2**
Arkansas River at Little Rock (7)	410,000	11.1	149,700	370	18.9	3,243,100	7,910	7.5	6.5	22.4
Lower MRB (C)(8)	184,000	50.1	277,400	1,510	na	712,200	3,870	na	30.7	4.9
Atchafalaya River										
Mississippi River diversion into Atchafalaya River	Ind.		434,800	na	na	2,522,800			18.8	17.4
Red & Ouachita River Basins (C)(9)	241,700	30.7	299,200	1,240	na	2,718,800	11,250		12.9	18.8
Entire MARB Flux to Gulf	**3,208,700**	**20.0**	**2,316,800**	**722**	**Est. ~12**	**14,457,700**	**4,506**	**Est. <4**	**100.0**	**100.0**
Mississippi River flux to Gulf at Tarbert's Landing, LA (C)	Ind.		1,582,800	na	na	9,216,100	na	na	68.3	63.7
Atchafalaya River flux to Gulf at Melville, LA	Ind.		734,000	na	23.1	5,241,600	na	4.7	31.7	36.3

TABLE 4.7. Average flux and yields of silica and chloride from the 42 interior basins during 1980–96, estimated with regression models.

Basin ID	Basin Name and Location of Sampling Site	Data Used	Runoff	Silica Flux as N	Silica Yield	Silica Std. Error	Chloride Flux	Chloride Yield	Chloride Std. Error
		yrs	*cm/yr*	*metric tons*	*kg/km²/yr*	*%*	*metric tons*	*kg/km²/yr*	*%*
1	Allegheny R. at New Kensington, PA	16	60.8	39,190	1,320	6.2	246,840	8,280	3.9
2	Monongahela R. at Braddock, PA	16	58.8	25,760	1,360	4.7	135,000	7,110	6.1
3	Muskingham R. at McConnelsville, OH	12	40.0	30,960	1,610	23.0	271,950	14,160	3.5
4	Kanawha R. at Winfield, WV**	78s	50.0	40,900	1,340	15.2	123,000	4,020	8.0
5	Scioto R. at Higby, OH	15	33.1	13,100	980	11.3	145,620	10,950	3.9
6	Great Miami at New Baltimore, OH	14	33.1	15,210	1,540	46.5	122,270	12,350	3.1
7	Kentucky R. at Lockport, KY	14	42.6	17,670	1,100	7.7	64,930	4,060	6.0
8	Wabash R. at New Harmony, IN	17	36.9	98,860	1,310	26.9	619,110	8,180	3.3
9	Cumberland R. near Grand Rivers, KY	7	62.7	50,590	1,110	na	148,600	3,260	na
10	Tennessee R. near Paducah, KY	17	51.7	114,400	1,090	21.2	399,570	3,820	4.8
11	Mississippi R. near Royalton, MN	15	15.7	19,650	650	7.5	20,260	680	4.2
12	Minnesota R. at Jordan, MN	16	14.0	52,280	1,240	12.4	132,270	3,150	3.0
13	St. Croix R. at St. Croix Falls, WI	15	27.7	31,720	1,960	28.3	12,670	780	15.6
14	Chippewa R. at Durand, WI	15	31.3	31,230	1,340	5.4	37,080	1,590	2.7
15	Wisconsin R. at Muscoda, WI	15	31.2	21,600	800	18.7	104,510	3,890	3.4
16	Rock R. near Joslin, IL	16	27.6	43,040	1,740	46.4	207,630	8,410	1.4
17	Cedar R. at Cedar Falls, IA	16	29.0	no data	--	--	76,240	5,730	6.4
18	Iowa R. at Wapello, IA (includes Cedar R. Basin #17)	16	28.8	75,090	2,320	35.9	209,690	6,470	4.4
19	Skunk R. at Augusta, IA	16	26.6	19,820	1,790	21.3	43,680	3,930	3.9
20	Raccoon R. at Van Meter/Des Moines, IA	14	24.0	no data	--	--	41,360	4,650	6.1
21	Des Moines at St. Francisville, MO (includes Raccoon R. Basin #20)	14	23.8	75,800	2,080	26.8	158,430	4,350	5.1
22	Illinois R. at Marseilles, IL	14	48.4	29,720	1,390	9.5	682,720	31,900	2.8
23	Lower Illinois R. Basin	14	28.7c	40,430c	850	na	368,220c	7,770	na
--	Illinois R. at Valley City, IL (#22 & 23)	15	34.5	70,150	1,020	28.6	1,050,940	15,280	2.6
24	Kaskaskia R. nr. Venedy Station, IL	13	28.0	11,190	970	20.1	62,750	5,500	4.5
25	Milk R. near Nashua, MT	15	0.7	1,490	26	16.6	5,700	99	6.2
26	Missouri R. near Culbertson, MT	14	3.6	26,370	110	4.8	80,650	340	2.5
27	Bighorn R. near Bighorn, MT**	86s	5.7	10,670	180	5.0	34,900	590	4.2
28	Yellowstone R. near Sydney, MT	16	5.5	44,560	250	4.9	107,800	600	4.1
29	Cheyenne R. at Cherry Creek, SD	14	1.1	3,500	57	28.4	18,370	300	5.9
30	James R. near Scotland, SD	14	1.1	3,480	62	17.5	14,780	260	6.2
31	Platte R. near Louisville, NE	16	3.6	95,390	430	3.4	301,540	1,360	5.9
32	Kansas R. at Desoto, KS	13	4.5	43,450	280	23.7	248,430	1,600	5.1
33	Grand R. near Sumner, MO	14	26.3	18,790	1,060	8.1	28,180	1,580	3.7
34	Osage R. below St. Thomas, MO	15	32.7	28,670	760	13.1	68,360	1,820	4.5
35	St. Francis Bay at Riverfront, AR**	97s	33.5	24,500	1,460	11.1	28,770	1,720	9.4
36	White R. at Clarendon, AR**	41s	33.9	62,900	950	12.5	103,400	1,560	11.6
37	Arkansas R. at Tulsa, OK	16	4.4	42,770	220	31.9	2,614,170	13,520	9.1
38	Canadian R. at Calvin, OK	15	2.9	9,740	130	14.7	169,840	2,350	6.2
39	Yazoo R. at Redwood, MS**	89s	54.8	45,500	1,390	8.1	58,200	1,780	6.0
40	Big Black R. near Bovina, MS	15	52.2	11,720	1,610	7.5	19,870	2,720	6.8
41	Red R. at Alexandria, LA	13	17.8	91,220	520	19.9	1,657,290	9,480	8.6
42	Ouachita R. near Columbia, LA**	92s	42.8	51,460	1,270	11.2	368,600	9,110	9.9

***Estimated from mean concentrations and discharge at time of sampling.*

NOTE: s = number of samples; na = not available; c = calculated as a difference between two sites.

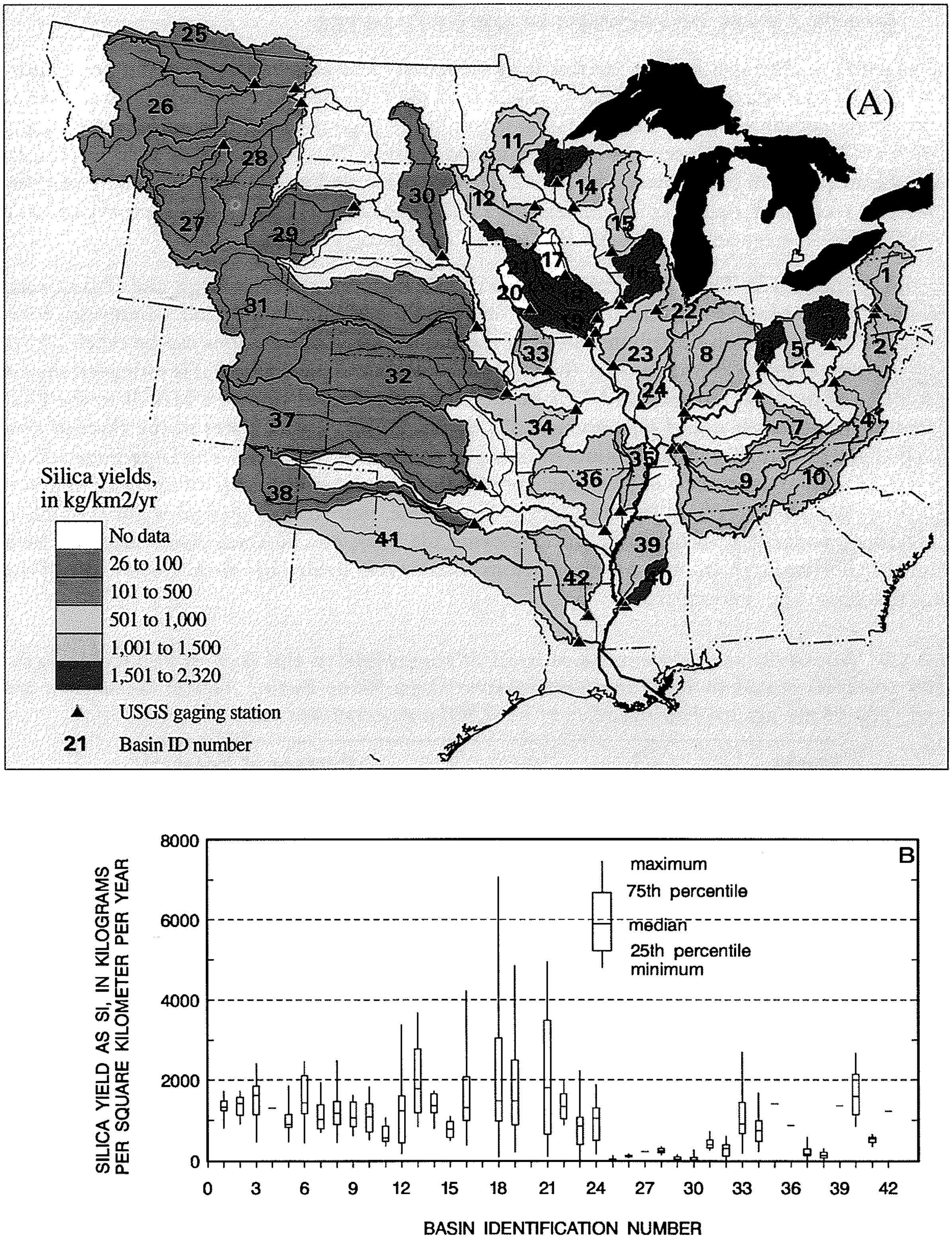


FIGURE 4.11. (A) Spatial distribution of silica (Si) yields in the 42 interior basins, and (B) boxplots showing distribution of Si yields in the 42 interior basins. NOTE: Dashes (–) show median yields for several sites where other statistics could not be calculated.

4.6 STATE-LEVEL NITROGEN FLUX ESTIMATES

The nitrogen flux estimates for the interior basins were used to develop rough estimates of how much nitrogen most states in the MARB contribute to the Gulf of Mexico. The estimates assume there are no significant in-stream denitrification losses in the large rivers and are un-affected by any denitrification losses that may occur within the interior basins. The total nitrogen yield was calculated for the area of each state covered by the 42 interior basins, and was then multiplied by the portion of each state that drains to the Mississippi. The resulting estimates were expressed as a percentage of the average annual nitrogen flux to the Gulf during 1980-96.

The results, presented in Table 4.8, show that, on the average, the states of Iowa and Illinois each contributes 16-19% of the total annual nitrogen flux from the MARB to the Gulf. Minnesota, Indiana, Ohio and Missouri each contributes 6-9% of the annual flux. Contributions can be much higher during years with extreme events, such as the 1993 flood. For example, in 1993 it is estimated that as much as 30% of the total nitrogen and 35% of the nitrate discharged from the MARB to the Gulf originated in Iowa, which drains only about 4.5% of the MARB. Other states in the flooded area also contributed abnormally large amounts of nitrogen to the Gulf that year. The large fluxes of nitrogen during flood events, such as 1993, are an indication that large quantities of nitrogen in a mobile form (nitrate) are present in the soils, unsaturated zone, and shallow ground-water systems in these states. Agricultural drainage practices employing tile lines, etc., in these states may also be a factor in transporting large amounts of nitrate from source areas to streams more quickly than if the drainage practices were not in place.

TABLE 4.8. Approximate percentage of total nitrogen flux to the Gulf of Mexico contributed by selected states in the Mississippi–Atchafalaya River Basin. NOTE: Percentages are based on 1980–96 average total nitrogen flux of 1,567,900 metric tons per year.

States	Percent of Total Nitrogen Flux
Pennsylvania, Oklahoma, West Virginia, Nebraska, South Dakota	< 2
Kentucky, Louisiana, Mississippi, Tennessee, Wisconsin, Arkansas, Kansas	2–5
Minnesota, Indiana, Ohio, Missouri	6–9
Iowa, Illinois	16–19

CHAPTER 5

Nutrient Inputs and Outputs

Nutrients are chemical elements that are essential for plant and animal growth and development. The nutrient requirements for plants and animals vary by species and environment. Nutrients occur naturally in soils, but also are added to soils in commercial fertilizers and manure. This chapter focuses on the inputs and outputs of two nutrients: nitrogen (N) and phosphorus (P), in the MARB. Silica (Si) is also an important nutrient in the basin. However, anthropogenic inputs of silica, including Si-based ingredients in certain pesticides and fertilizers (Meister 1997), are likely to be insignificant relative to the natural inputs that include dissolution of certain rock types and clay minerals. This chapter is divided into four sections: inputs to the MARB from the atmosphere, inputs and outputs from agriculture, inputs from municipal and industrial point sources, and atmospheric inputs directly to the Gulf of Mexico. In general, nutrient sources were quantified using the best available data or the most current estimation technique. A geographic information system (GIS) was used to manage and manipulate nutrient input and output data.

5.1 ATMOSPHERIC INPUTS TO THE MISSISSIPPI–ATCHAFALAYA RIVER BASIN

Through human activities, the deposition of biologically available N from the atmosphere has increased to rates that are significant in relation to rates of natural fixation of N_2 (Vitousek et al. 1997). In the northeastern United States, atmospheric deposition of N has been recognized as a major factor in the overfertilization of forest ecosystems (often termed N saturation) and the acidification of freshwater lakes and streams (Aber et al. 1995; Stoddard 1994). Atmospheric deposition of N has also been identified as a significant contributor to the eutrophication and hypoxia of Chesapeake Bay (Magnien et al. 1995). Assessment of nitrogen cycling in the Mississippi River Basin, therefore, requires the spatial and temporal quantification of N deposition rates from the atmosphere.

5.1.1 Methods

The general approach for quantifying atmospheric deposition of N was to (1) apply existing data sets where possible, and (2) estimate deposition for regions where data were not available on the basis of empirical relations developed from the existing data and information from peer-reviewed publications. Atmospheric deposition models for refining N deposition estimates were not developed or applied in this study due to insufficient data for the watershed scales used in this assessment.

5.1.2 Available Data

In general, measurements of atmospheric deposition of N can be categorized as wet deposition (which falls as rain or snow), or dry deposition (particles or vapor deposited from the atmosphere primarily during periods of no precipitation).

Wet deposition is monitored year-round at approximately 200 sites through the National Acid Deposition Program/National Trends Network (NADP/NTN). The distribution of these sites is approximately uniform nationwide. At each site, precipitation is collected for chemical analysis in a polyethylene bucket that remains covered, except when precipitation is falling. Through this method, deposition of NO_3 and NH_4 is determined weekly. Wet deposition data analyzed for this report were collected from 1984 through 1996. These data and further information on the NADP/NTN are available on the World Wide Web (http://nadp.sws.uiuc.edu; accessed 1998).

Dry deposition is monitored at approximately 60 sites nationwide through several programs that operate under EPA's Clean Air Status and Trends Network (CASTNet; Clarke et al. 1997). Two-thirds of these sites are located east of the Mississippi River; all but three of the remainder are located from the Rocky Mountains to the West Coast. Dry deposition is determined at these sites by measurements of air concentrations 10 m above the ground and an inferential model of deposition velocities, described in Hicks et al. (1985). Air concentrations are determined by a three-stage filter pack that contains a Teflon™ filter, a nylon filter, and a cellulose filter, in sequence. Air is continuously pulled through these filters at 1.50 L min^{-1} at eastern sites and 3.00 L min^{-1} at western sites. Particulate NO_3 and NH_4 are collected by the Teflon™ filter; HNO_3 vapor, by the nylon filter; and SO_2, by the cellulose filter, although this filter also collects indeterminate forms of N. Gaseous NH_3 is not collected by filter pack. Meteorological and vegetation conditions are also monitored at each site to provide data necessary for modeling deposition velocities. Wet deposition was monitored at approximately one-third of the sites by the same method as used by the NADP/NTN. Dry deposition data analyzed for this report were collected from 1988 (the first complete year of operation for most sites) through 1994. Data from 1995 and 1996 were incomplete at most sites; therefore, these two years were excluded.

5.1.3 Estimation Methods

Wet deposition data from the NADP/NTN database were converted to GIS point coverages of annual wet deposition of NO_3 and NH_4. Inverse distance weighted (IDW) interpolation was performed on the points to create a grid of 6.25 km^2 cells over the coterminous United States. Deposition values were determined for each cell by IDW interpolation from a combination of sample points. Zonal statistics were performed to sum the cell values by watershed for each year (1984–96). For the purposes of presentation and budget estimates, the cells were aggregated into polygons to determine a single value for each area that represents an accounting unit (area based on drainage divides) or watershed used in this analysis (Figures 2.1 and 2.2).

The locations of CASTNet monitoring sites were not suitable for interpolating a surface of dry deposition in the Mississippi Basin. Therefore, sites were selected within the basin at which both dry and wet deposition were monitored to determine if the spatial distribution of dry deposition could be estimated from the data collected at NADP/NTN sites (Figure 5.1). The single exception is the data from Wyoming, which include NADP data collected at Snowy Ridge, Wyoming (site code WY00), and CASTNet data collected at Centennial, Wyoming (site code CNT169). These monitoring stations were paired because they are less than 100 km apart, and they represent the only location in the western part of the basin where dry and wet deposition measurements could be related. Comparisons between wet and dry deposition were possible at 12 sites east and 2 sites west of the Mississippi River. Seasonal values were compiled from the weekly data of these 14 sites for December–February, March–May, June August, and September-November. Seasons with missing weekly values were omitted. This approach enabled 147 values of dry deposition to be directly compared with wet deposition.

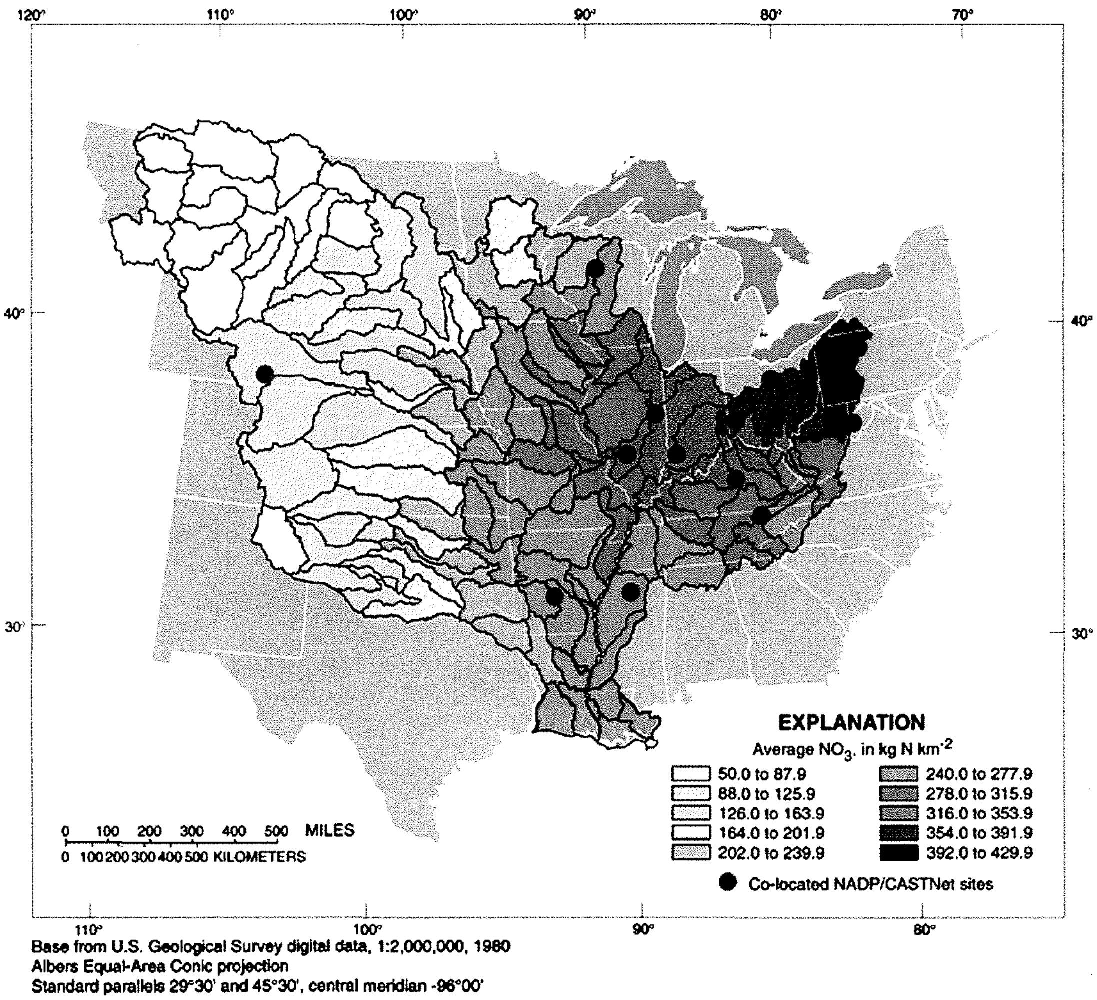
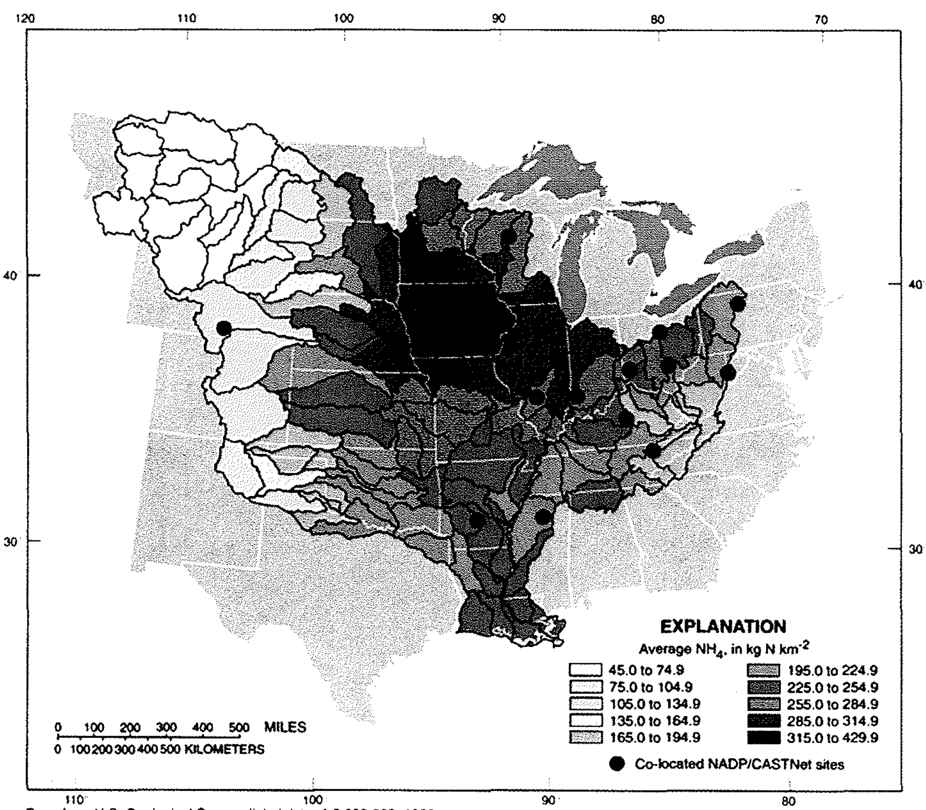


FIGURE 5.1. Wet deposition of NO_3^-, averaged for 1990–96 data from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/) **in each the 133 accounting units that make up the Mississippi River Basin.** NOTE: Blue circles indicate where NADP and CASTNet (Clean Air Status and Trends Network) sites are co-located.

5.1.4 Results—Wet Deposition

No trend in the rates of wet deposition of either NO_3^- or NH_4^+ was observed between 1984 and 1996 for values representing the overall basin. The lowest deposition rates were recorded in the drought years of 1988 and 1989. The highest rates of wet deposition of NO_3^- within the basin were consistently in an area that extends from central Ohio eastward to the basin boundary (Figure 5.1). Wet deposition rates of NO_3^- generally decrease southward and westward from Ohio. The highest rates of wet deposition of NH_4^+ are centered in Iowa and generally decrease in all directions (Figure 5.2); the lowest rates of wet NH_4^+ deposition are in Montana.



Base from U.S. Geological Survey digital data, 1:2,000,000, 1980
Albers Equal-Area Conic projection
Standard parallels 29°30' and 45°30', central meridian -96°00'

FIGURE 5.2. Wet deposition of NH_4^+, averaged for 1990–96 data from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/) in the 133 accounting units that make up the Mississippi River Basin. NOTE: Blue circles indicate where NADP and CASTNet (Clean Air Status and Trends Network) sites are co-located.

The average wet deposition for the interior basins also reflect this pattern. The highest wet NO_3^- deposition was observed in interior basin 2, the Monongahela River at Braddock, Pennsylvania (427 kg N km^{-2}), whereas NH_4^+ deposition was highest in interior basin 20, the Raccoon River at Van Meter, Iowa (344 kg N km^{-2}; Figure 5.3 and Table 5.1). The highest total wet deposition was estimated at 665 kg N km^{-2}, in interior basin 22, the Illinois River at Marseilles, Illinois—more than six times that estimated for basin 27, the Bighorn River at Bighorn, Montana (105 kg N km^{-2}). Wet deposition of NH_4^+ was about 80% of wet NO_3^- deposition when averaged over the entire basin.

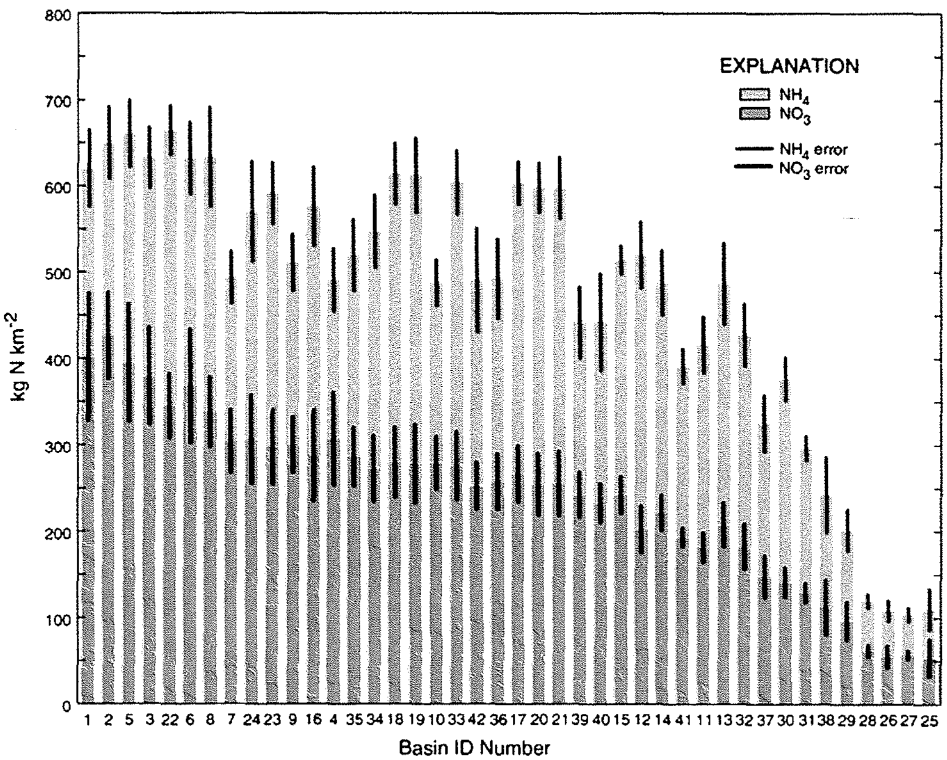


FIGURE 5.3. Wet deposition of NO_3^- and NH_4^+ in 42 sub-basins of the Mississippi River Basin, averaged for 1990–96 data from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/). NOTE: Vertical lines represent 1 standard deviation.

TABLE 5.1. Wet, dry, and total nitrogen deposition values (kg N/km^2) for the overall Mississippi–Atchafalaya River Basin (MARB) and 42 interior basins averaged for 1990–96.

Watershed Number	Wet Deposition NO_3^-	Wet Deposition NH_4^+	Dry NO_3^- Deposition	Total NO_3^- and Organic N Deposition
MRB	200	203	140	440
1	402	219	281	838
2	427	224	299	889
3	380	254	266	805
4	308	184	216	647
5	396	266	277	838
6	369	264	258	785
7	305	190	213	642
8	339	296	237	735
9	300	212	210	639
10	280	208	196	598
11	182	235	128	414
12	203	317	142	476
13	209	279	146	477
14	222	266	155	500
15	243	273	170	542
16	288	290	201	634
17	268	337	187	606
18	281	334	196	631
19	279	334	195	628
20	255	344	179	584
21	256	342	179	585
22	346	319	242	755
23	298	295	209	655
24	308	263	215	666
25	60.8	57.1	37.6	119
26	55.4	54.5	38.8	122
27	57.6	47.7	40.3	124
28	61.5	60.3	43.1	135
29	97.5	105	68.3	217
30	142	236	99.3	336
31	130	168	90.8	295
32	183	245	128	418
33	277	328	194	622
34	273	274	191	602
35	288	233	201	619
36	259	234	181	564
37	149	179	104	335
38	124	131	78.9	253
39	244	200	171	525
40	234	210	164	508
41	194	198	136	428
42	254	238	178	554

5.1.5 Relations Between Wet and Dry Deposition

A statistically significant positive correlation was observed between total dry and total wet deposition for the seasonal data at the 14 sites (Figure 5.4). However, significant variability in dry deposition measurements was not explained by wet deposition measurements (R^2 = 0.18). The relation between wet and dry deposition varied at the individual sites from the moderately strong correlation observed at Parsons, West Virginia (R^2 = 0.50), to statistically insignificant correlation at several sites. The average ratio of total dry deposition (particulate NO_3^- and NH_4^+ plus HNO_3 vapor) to total wet deposition (NO_3^- plus NH_4^+) for the 14 sites was 0.47. Individual values of the ratio of total dry deposition to total wet deposition ranged from 0.13 to 1.9, but 76% of these values were from 0.13 to 0.69 (Figure 5.5). The value of average dry NO_3^- deposition (particulate NO_3^- plus HNO_3 vapor) divided by the average wet NO_3^- deposition was 0.70. Wet NO_3^- deposition did not explain a large amount of the variability in dry NO_3^- deposition (R^2 = 0.21). There was considerable variability in total dry deposition measurements among sites, and no geographical pattern was evident. If averaged for all sites and seasons, total dry N deposition was comprised of 81% HNO_3 vapor, 16% particulate NH_4^+, and 3% particulate NO_3.

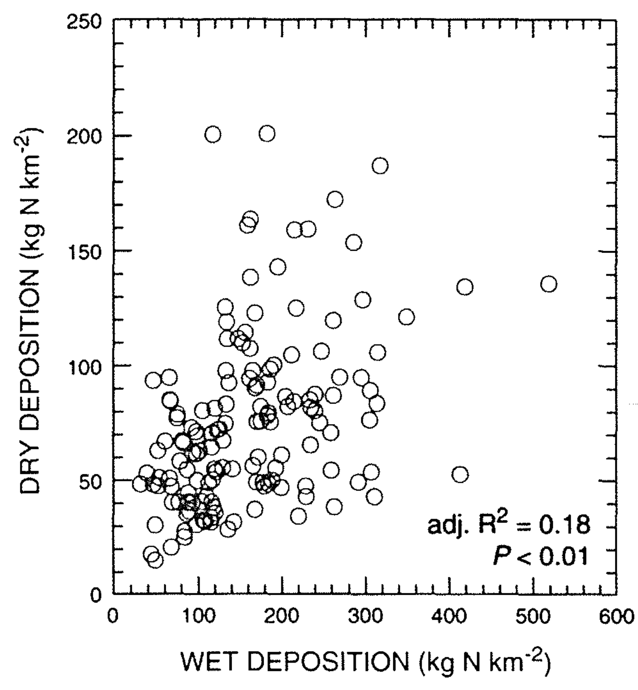


FIGURE 5.4. Dry deposition data from CASTNet (Clean Air Status and Trends Network) as a function of wet deposition data from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/) at 14 sites in the Mississippi River Basin where dry and wet deposition measurement stations are co-located. NOTE: Values represent seasonal totals (winter, December–February; spring, March–May; summer, June–August; fall, September–November) from January 1989 through November 1994. (*CASTNet data from Clarke et al. 1997.*)

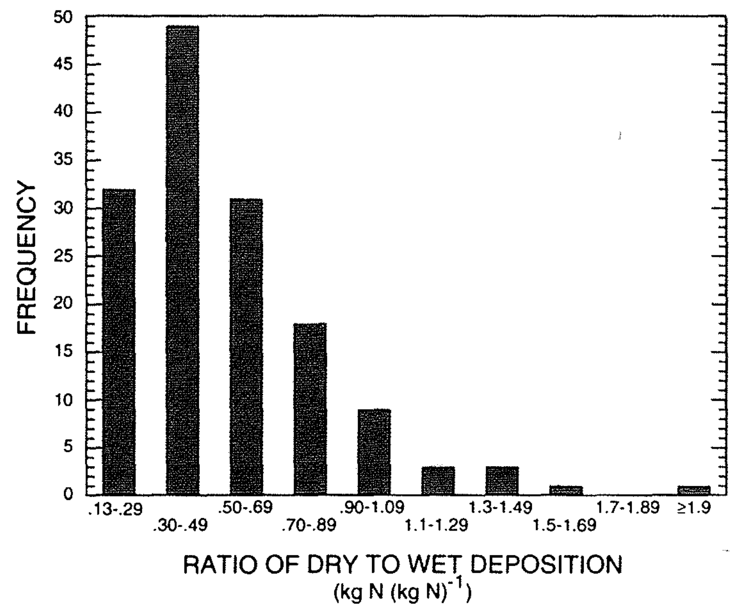


FIGURE 5.5. Distribution of the ratio of dry deposition data from CASTNet (Clean Air Status and Trends Network) to wet deposition data from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/) at 14 sites in the Mississippi River Basin where dry and wet deposition measurement stations are co-located. NOTE: Values represent seasonal totals (winter, December–February; spring, March–May; summer, June–August; fall, September–November) from January 1989 through November 1994. (*CASTNet data from Clarke et al. 1997.*)

Average deposition for 1990–96, of wet NO_3^- and NH_4^+, dry NO_3^-, and total NO_3^- are summarized in Table 5.1 for the entire MARB and for the 42 interior basins. Examples of N-deposition fractions are shown in Figure 5.6 for 4 sites along a west to east transect in the basin for the period December 1, 1992, through November 30, 1993. Depositions of all five fractions were lowest at the Wyoming site, and total N deposition at this site was less than half the deposition at the Ohio site. Highest wet deposition of NO_3^- was measured at the West Virginia site, whereas highest wet NH_4^+ deposition was measured at the Illinois site, and highest HNO_3 deposition was observed at the Ohio site. Total N deposition at the Illinois site was more similar to values at the West Virginia site than at the nearby Ohio site.

The dry fractions shown in Figure 5.6 represent N forms that are collected by the first two filters in the three-stage filter pack. The third filter, however, also collects a significant amount of N in compounds that are unidentified. Without knowledge of the chemical form of N collected by the third filter, a deposition velocity cannot be developed; therefore, deposition rates cannot be estimated. To evaluate the potential magnitude of N deposition that could be contributed by these unidentified forms, the deposition velocity developed for HNO_3 vapor was applied to the air concentrations of N measured by the third filter. Averaged for all sites and seasons, N collected by the third filter was 46% of N collected as HNO_3 vapor by the second filter. If the deposition velocities for N particles had been applied, the deposition rate would have been considerably lower because the deposition velocities of HNO_3 vapor are at least an order of magnitude higher than the deposition velocities of N particles.

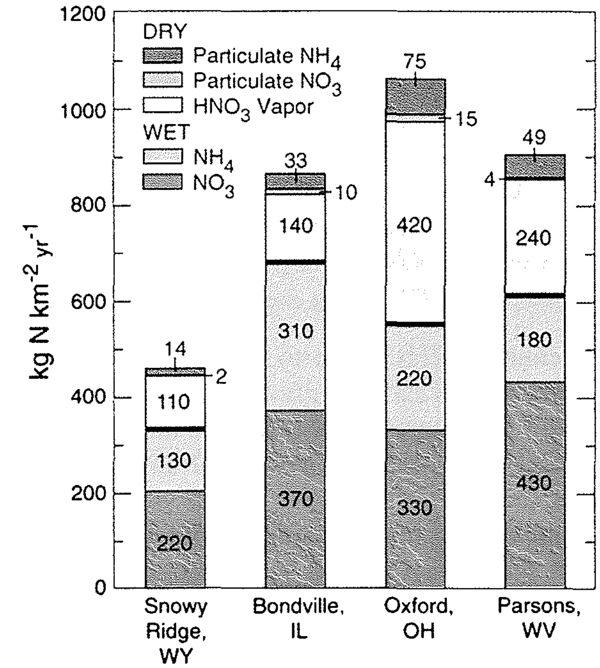


FIGURE 5.6. Chemical species of wet deposition data from the National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/) **and dry deposition data from CASTNet** (Clean Air Status and Trends Network) **measured at 4 sites on a west-to-east transect across the Mississippi River Basin for December 1992 through November 1993.** (*CASTNet data from Clarke et al. 1997.*)

5.1.6 Discussion

The regional patterns of wet deposition of NO_3^- and NH_4^+ reflect the regional patterns of emissions and atmospheric transport processes. The highest rates of NO_3^- deposition occur in Ohio and Pennsylvania (Figure 5.1), northeast of the concentration of high-emitting electric utility plants located in southern Indiana and western Kentucky (NAPAP 1993). Fossil fuel combustion is a known source of NO and NO_2, which are oxidized in the atmosphere to form HNO_3 vapor and particulate NO_3^-. Particulate NO_3^- can have a long residence time in the atmosphere, which facilitates long-range transport. Once formed, HNO_3 vapor has a high deposition velocity and a relatively short residence time, although it can react with other pollutants such as NH_3 to form particles with low deposition velocities. Significant atmospheric transport of N from midwestern power plants to the northeastern states has been well established (NAPAP 1993).

Wet and dry deposition of NH_4^+ is generally attributed to NH_3 emissions from high concentrations of livestock and N fertilization of croplands (Vitousek et al. 1997). Dry deposition estimates do not include dry deposition of NH_3, which could be significant relative to wet and dry deposition of NH_4^+ (Ferm 1998). Emissions from automobiles can also contribute atmospheric NH_3, but in the South Coast Air Basin of California, which includes Los Angeles and surrounding developed areas, estimates of NH_3 emissions from automobiles did not exceed agricultural sources (Fraser and Cass 1998). The highest levels of wet NH_4^+ deposition in the Mississippi Basin are centered in Iowa, an intensively agricultural state (Figure 5.2).

In contrast to NO and NO_2 released from fossil fuel combustion, NH_3 released to the atmosphere is already in a highly water-soluble form that is effectively scavenged by precipitation and vegetation. This characteristic results in deposition of NH_3 closer to sources than deposition of other forms of N emitted to the atmosphere. Transport distance, however, depends on wind speed and reactions with other pollutants. Modeled estimates of NH_3 transport by Asman and van Jaarsveld (1992) indicated that 46% of emitted NH_3 was deposited within 50 km of the source; 40% as dry deposition and 6% as wet deposition. Results from a separate modeling effort described in Ferm (1998) indicated that 49% of NH_3 emitted in a 22,000-km^2 region in Sweden was deposited within this same region, with 21% as dry deposition and 28% as wet deposition.

Although a large fraction of emitted NH_3 tends to be deposited near its source, reactions with H_2SO_4 and HNO_3 to form particulate NH_4^+ can greatly increase transport. Therefore, high atmospheric concentrations of SO_2 and NO_x significantly enhance transport of NH_3. Deposition research in the Netherlands found that NH_x deposition beyond 300 km of the source was halved approximately every 450 km, a pattern similar to that of SO_x compounds (Ferm 1998). High emissions of SO_2 and NO_x in Illinois, Kentucky, Indiana, and Ohio most likely enhance the transport of NH_4 from the agricultural regions in the central part of the Mississippi Basin to eastern sections of the basin, as well as across the basin boundary.

Based on NADP and CASTNet data, NH_4^+ deposition represents approximately 35% of total N deposition in the MARB, but the collection methods of both programs probably result in an underestimation of this fraction. Some of the NH_4^+ collected by NADP buckets may be converted to organic nitrogen through microbial assimilation between the time of deposition and the weekly collection (Vet et al. 1989). And the three-stage filter pack used in the CASTNet program is designed to collect NH_4^+ particles, but not NH_3, which has a deposition velocity approximately five times higher than that of the NH_4^+ particles (Ferm 1998). Deposition of gaseous NH_3, therefore, is likely to represent a significant fraction of dry deposition, but primarily in the vicinity of sources because of the short residence time of NH_3 in the atmosphere.

Other fractions of N deposited from the atmosphere include organic forms, such as peroxyacetyl NO_3^-(PAN). Most of the studies of organic N in the atmosphere, however, have been investigations of urban air quality. One exception is the recent study of Scudlark et al. (1998), in which deposition of organic N in precipitation was measured in the Chesapeake Bay watershed. This study showed that organic N comprised approximately 20% of total N in wet deposition, and that to obtain reliable estimates, samples needed to be collected daily. The N collected by the third filter of the CASTNet filter packs may include some of the same organic-N compounds measured in precipitation in the Scudlark et al. (1998) study.

The wet deposition of NO_3^- and NH_4^+ are the least uncertain of the N deposition estimates discussed above. The wet-only bucket approach is a direct measurement of deposition that does not require additional meteorological measurements or modeling. The large number of sites distributed nationwide also enables realistic interpolation for regional or watershed assessments. However, monitoring of organic N in precipitation is needed to evaluate the temporal and spatial variability of this fraction.

Dry deposition estimates have a higher degree of uncertainty than the wet deposition estimates, but the level of uncertainty is difficult to quantify. Eddy correlation techniques provide a direct measurement that can be compared with the filter pack/deposition velocity modeling approach, but this method can only be used for short measurement periods (30–120 minutes) and cannot be used to measure HNO_3 deposition. The uncertainty in the accuracy of dry deposition of HNO_3 vapor and NO_3^- particles has been subjectively estimated by Clarke et al. (1997) to be 40%. The precision of CASTNet measurements of deposition is approximately 12% for HNO_3 vapor and 17% for NO_3^- particles (Clarke et al. 1997). The current location of CASTNet monitoring sites is a severe limitation on efforts to accurately estimate dry deposition in the region between the Mississippi River and the Rocky Mountains.

A limited number of investigations have shown that dry deposition can vary greatly over distances less than a kilometer, particularly in varied terrain (Clarke et al. 1997). The importance of these small-scale variations, however, may significantly decrease at some larger scale. Examples of this scale effect have been identified for measurements of streamflow (Wood et al. 1989) and stream chemistry (Wolock et al. 1997). Defining how spatial variation of CASTNet measurements vary with scale would significantly increase the utility of these data.

5.1.7 Budget Implications

Despite the uncertainties of dry deposition estimates, the CASTNet measurement approach is sufficiently reliable to indicate that, in general, dry deposition is (1) positively correlated with wet deposition and (2) of similar magnitude to wet deposition. This information can be used in conjunction with NADP data to estimate total deposition of N (wet plus dry) to subregions of the basin for the purpose of N budget estimates. Wet and dry deposition of NO_3^- compounds should be considered a budget input because these compounds originate largely from combustion of fossil fuels, which otherwise would be unavailable for biological utilization. Dry deposition of HNO_3 and NO_3^- can be approximated throughout the basin by multiplying wet deposition of NO_3^- by the fraction dry deposition/wet deposition (0.70), determined at the 14 sites where wet and dry deposition measurement stations were co-located. Dinnel (1998) determined a value of 0.75 for this fraction with 1990–92 CASTNet and NADP data.

Organic N deposition is likely to contribute to atmospheric N inputs, although the magnitude of the deposition rate is highly uncertain. If the fraction of organic N/total N in wet deposition measured by Scudlark et al. (1998) is assumed to be similar to the fraction that occurs in the Mississippi Basin, wet deposition of organic N in the basin can be estimated as 0.25 multiplied by total wet deposition. To determine an estimate of dry deposition that includes organic N, wet deposition can be multiplied by the fraction of dry deposition that includes N collected by the third filter/wet deposition (1.0), although the third filter of the filterpack air sampler may also collect inorganic forms of N.

Wet and particulate NH_4^+ comprise a significant fraction of atmospheric N deposition throughout the basin. Results show (1) the region of highest NH_3 deposition is in the center of the basin, (2) half or more of emitted NH_3 is deposited within 300 km of the source, and (3) the lowest deposition is on the western (windward) side of the basin. Most of the NH_4^+ deposition within the basin, therefore, is likely to be the result of internal sources, which indicates that the overall basin can be considered a net source of NH_3 emissions. The substantial variability of NH_4^+ deposition within the basin, however, means that some basins are net sources, whereas others are net sinks. Because most of the NH_4^+ emissions are either directly or indirectly the result of the use of fertilizers and manure, budget estimates that include fertilizer or manure inputs of N would overestimate total inputs, if atmospheric deposition of NH_4 is also included (Howarth et al. 1996). The atmospheric deposition of NH_4^+, therefore, should be considered an internal transport process, rather than a basin input.

5.2 AGRICULTURAL INPUTS AND OUTPUTS

Agricultural activities, such as row crop cultivation and livestock production, can be significant non-point-source inputs of N and P. The application of commercial fertilizer to cropland is the primary input of "new" N and P in most areas of the MARB. In many parts of the basin, fixation of atmospheric N by legumes is a significant input of "new" N, and animal manure is a significant input of "recycled" N and P. Mineralization of organic matter in agricultural soils can also be considered an agricultural input of recycled N and P, which is largely a combination of mineral N and P inherent to the soil, microbially immobilized fertilizer or manure, and organic crop remains (Gentry et al. 1998; Cambardella et al. 1999).

Rates of mineralization are largely controlled by cover type and soil tillage. Nutrients can be removed in harvested crops. Nutrients in harvested crops can be exported from the basin in food or animal products, or can be consumed and cycled again within the basin. N can also be lost by volatilization from soils, manure, or plants during senescence, or by denitrification in the soils, wetlands, and river bottoms. Both N and P can be immobilized in the soil zone and lost from cropped areas with soil erosion. Management practices on cropped land, such as conservation tillage and crop rotation, can reduce nutrient losses, while tile drainage will most likely increase nutrient losses from cropped land (NRC 1993; Gentry et al. 1998). Nutrients are consumed by forested land and wetlands, so these landscapes will ultimately affect the nutrient budget by reducing nutrient losses from watersheds (Mitsch and Gosselink 1993; Aber et al. 1995; Gersburg et al. 1983; Nolan et al. 1997; Battaglin and Goolsby 1998). Use of riparian buffer strips has been suggested by many researchers as a means to intercept agricultural pollutants in sediment, runoff, and shallow ground-water flow before they can reach streams (NRC 1993).

Estimates of annual N and P inputs from agricultural sources were compiled for the 20 states listed below, which comprised most of the agricultural land in the MARB during 1951–96. These estimates are used to show temporal trends in N and P inputs and outputs, and in developing state- and MARB-level N and P budgets, discussed later in this report.

Arkansas	Kansas	Missouri	South Dakota
Colorado	Kentucky	Montana	Tennessee
Illinois	Louisiana	Nebraska	West Virginia
Indiana	Minnesota	Ohio	Wisconsin
Iowa	Mississippi	Oklahoma	Wyoming

Estimates of N and P inputs and outputs associated with agriculture were also compiled by county for 1992. These estimates are used here to show a more detailed picture of the spatial distribution of inputs and outputs and, later in the report, to make comparisons with nutrient yield estimates at the three basin scales—the MARB, the nine large basins, and the 42 interior basins.

5.2.1 Fertilizer

Until the 19th century, increased food production in the United States was largely the result of an expanding cropland base, the addition of nutrients in animal manure, and the mining of soil nutrients. By the 20th century, soil fertility and crop yields were maintained by the addition of N and P containing natural waste materials, such as animal manure, seaweed, bonemeal, and guano. Beginning in the 1940s manufactured fertilizers, such as superphosphates, urea, and anhydrous ammonia, replaced most "natural" fertilizers (USDA 1997). Since the 1960s, the yields per acre for major crops have doubled. Some of this increase can be attributed to better plant hybrids, and some can be attributed to increased application of crop nutrients. Figure 5.7 shows the estimated N content of commercial fertilizers sold in the 20 basin states during 1951–96. The state-level fertilizer N inputs were compiled from Alexander and Smith (1990), Battaglin and Goolsby (1995), and USDA (1998). These estimates include both agricultural and nonagricultural fertilizer sales. Estimates of nonagricultural fertilizer use represent 5–20% of the total use (H. Taylor, USDA, written communication, 1998). During 1951–96, annual fertilizer inputs increased form < 1 to > 6 million metric tons.

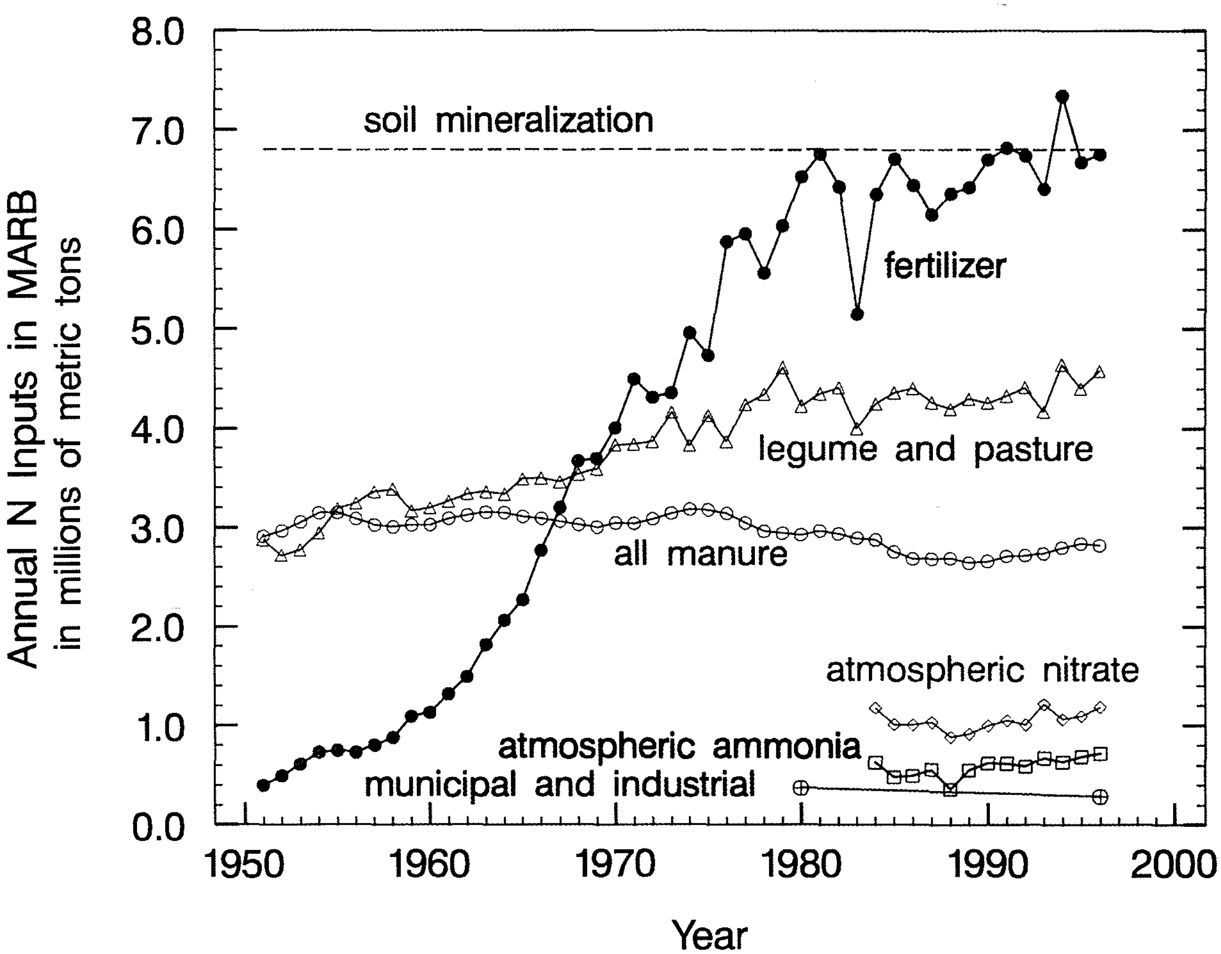


FIGURE 5.7. Annual nitrogen inputs to the Mississippi–Atchafalaya River Basin, 1951–96
NOTE: See text for sources of data and methods used to estimate inputs.

Fertilizer applications have a spatial pattern closely related to the pattern of crop production. Figure 5.8A shows the spatial distribution of N inputs in kilograms N per square kilometer per year (kg N/km^2/yr) from commercial fertilizer. These use estimates by hydrologic accounting unit (Seaber et al. 1987) were generalized from 1992 county-level data developed from reported state sales totals and estimates of county-level expenditures for fertilizer from the 1992 Census of Agriculture (USDC 1995). In much of the upper Midwest, including most of Iowa, Illinois, and Indiana, inputs of N from commercial fertilizer exceed 5,000 kg N/km^2/yr (Figure 5.8A). In this same area, inputs of P from commercial fertilizer exceed 1,000 kg P/km^2/yr. Tables 5.2 and 5.3 contain estimates of the N and P inputs in fertilizer for the three basin scales.

Plants only use a portion of the N and P in applied fertilizers. The unused N and P, which can be 50% or more of the applied amount, is retained in the soil or lost from the soil through volatilization, leaching, or erosion (Oberle and Keeney 1990; Barry et al. 1993; David et al. 1997; Cambardella et al. 1999). Fertilizer stabilizers, nitrification inhibitors, and slow-release formulations can help reduce nutrient loss by delaying nutrient mobilization or timing nutrient release to better coincide with crop demands (USDA 1997; Diez et al. 1996; Serna et al. 1996).

5.2.2 Legume Fixation

Certain crops and native plants belonging to the legume family, such as clovers, alfalfa, and beans, establish a symbiotic relationship with microbes from the rhizobium family. These microbes reside in nodules on the roots of host plants and can fix atmospheric N, which is either used by the legume plant or remains in the soil where it can undergo mineralization and nitrification. The amount of N fixed by crops varies as a function of the crop yield (Barry et al. 1993); soil conditions, such as the availability of inorganic N, drainage, pH, and moisture content; and climatic conditions. Rates of fixation range from < 500 kg N/km^2/yr for some types of beans and clover to > 60,000 kg N/km^2/yr for alfalfa. Estimates of N fixation in pastureland range from 100 to 1,500 kg N/km^2/yr (Jordan and Weller 1996). Legume crops use more N than they fix. Soybean crops will use symbiotically fixed N, mineralized soil N, and maybe even some organic N to meet their N requirements (Barry et al. 1993; David et al. 1997; Gentry et al. 1998). Even when other conditions are favorable, the presence of available N in the soil will discourage N fixation by legumes (Buckman and Brady 1969; Gentry et al. 1998). Some nonlegume species of plants can also fix nitrogen, but are not considered in this report, nor is the fixation of N by nonsymbiotic bacteria, which is estimated to be less than 700 kg N/km^2/y (Barry et al. 1993).

For this study, N inputs from fixation by legumes were estimated using crop and pastureland data by state from USDA (1998) and by county from the 1992 Census of Agriculture (USDC 1995). Table 5.4 lists the N-fixation rates used in this study and the range of estimates reported in the literature (Meisinger and Randall 1991; NRC 1993; Troeh and Thompson 1993). Many of the N-fixation rates used in this study are the same as those used by Jordan and Weller (1996). Pasture and rangeland in Minnesota, Iowa, Missouri, Louisiana, and states to the east were assigned a pasture N-fixation rate, while the rangeland N-fixation rate was used for pasture and rangeland in western states. Figure 5.7, which shows the amounts of N estimated to have been fixed annually by legumes and pasture in the 20 basin states for 1951–96, indicates that during 1950–90, legume-N inputs increased by 2.5–4.0+ million metric tons/yr. Figure 5.8 shows an estimate of the N fixed by all legumes in 1992 by hydrologic accounting unit. In much of the upper Midwest, including large parts of Iowa, Illinois, Missouri, Minnesota, and Indiana, inputs of N from legume fixation exceed 2,800 kg N/km^2/yr (Figure 5.8B). Estimates of the total N fixed by all legumes, alfalfa, nonalfalfa hay, pasture, and rangeland for the three basin scales are presented in Table 5.2.

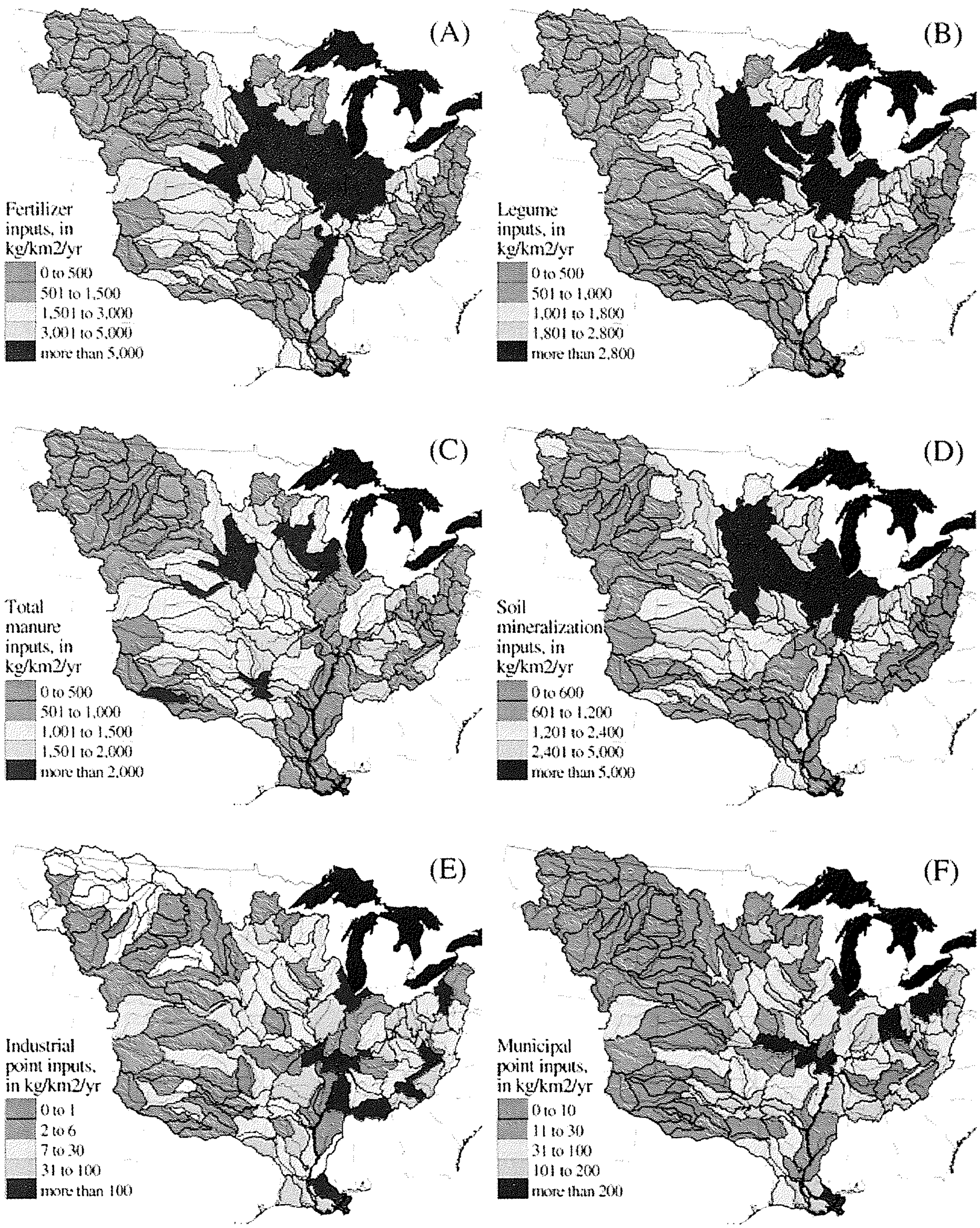


FIGURE 5.8. Nitrogen inputs in hydrologic accounting units in 1992 from (A) fertilizer, (B) legumes, (C) livestock manure, (D) soil mineralization, (E) industrial point sources, and (F) municipal point sources.

TABLE 5.2. Estimated annual inputs of nitrogen as N in the Mississippi–Atchafalaya River Basin, 9 large sub-basins, and 42 interior basins (in metric tons).

Basin ID and Name, and Location	Commercial Fertilizer	Legume Fixation	Nitrate in Atmospheric Wet & Dry Deposition	Industrial Point Sources	Mineralized Soil N	All Manure	Municipal Point Sources	NH_4^+ in Atmospheric Deposition
Entire MARB	6,803,171	4,033,716	1,326,367	85,635	6,803,452	3,251,280	200,786	602,084
9 Large Sub-basins								
1 Upper Ohio	326,975	297,028	172,801	13,535	297,304	205,873	49,934	48,033
2 Lower Ohio	839,586	409,330	162,125	16,526	565,248	314,704	18,690	52,868
3 Upper Missouri	622,232	75,2421	164,772	562	1,199,382	529,830	7,245	98,743
4 Lower Missouri	1,390,086	677,779	198,555	4,689	1,139,885	636,268	25,281	109,487
5 Upper Mississippi	599,159	472,270	109,621	2,600	1,084,434	332,153	6,856	64,295
6 Middle Mississippi	1,476,620	715,610	159,040	14,366	1,540,442	367,049	49,521	74,449
7 Arkansas	636,666	269,546	149,520	2,025	508,988	470,361	14,910	73,843
8 Lower Mississippi	526,827	287,498	234,304	33,204	229,305	130,384	13,373	28,208
9 Red and Ouachita	328,230	135,410	102,594	4,626	200,835	247,519	5,714	41,934
42 Interior Basins								
1 Allegheny River at New Kensington, PA	10,169	26,063	26,209	128	15,764	15,312	3,303	6,789
2 Monongahela River at Braddock, PA	7,272	16,388	15,742	388	9,631	9,577	2,587	3,606
3 Muskingham River at McConnelsville, OH	34,927	37,074	14,088	301	30,402	27,854	4,884	4,760
4 Kanawha River at Winfield, WV	13,614	15,602	18,207	503	10,075	17,292	1,385	4,610
5 Scioto River at Higby, OH	57,870	34,331	9,101	368	55,496	9,285	2,148	2,955
6 Great Miami at New Baltimore, OH	45,306	26,343	6,442	563	39,098	17,073	6,300	2,150
7 Kentucky River at Lockport, KY	15,691	14,722	9,354	244	20,390	16,904	911	2,443
8 Wabash River at New Harmony, IN	485,552	194,095	51,076	604	367,628	87,888	7,884	18,171
9 Cumberland River near Grand Rivers, KY	56,408	42,514	25,111	703	41,251	48,571	195	7,303
10 Tennessee River near Paducah, KY	108,919	76,762	58,679	9,560	63,786	118,624	8,815	18,319
11 Mississippi River near Royalton, MN	18,220	27,070	12,635	51	71,524	15,881	436	7,992
12 Minnesota River at Jordan, MN	218,883	125,093	19,854	255	402,737	58,156	387	14,304
13 St. Croix River at St. Croix Falls, WI	10,013	16,887	7,148	3	48,820	8,473	59	3,985
14 Chippewa River at Durand, WI	20,473	37,678	10,945	310	53,057	23,937	398	5,455
15 Wisconsin River at Muscoda, WI	38,581	46,565	14,149	590	79,272	32,523	511	6,928
16 Rock River near Joslin, IL	118,495	73,043	15,343	177	179,127	57,409	2,501	6,672
17 Cedar River at Cedar Falls, IA	88,198	34,829	7,443	139	122,699	21,211	647	4,282
18 Iowa River at Wapello, IA (includes Cedar River basin—17)	222,122	92,288	19,736	925	267,638	63,289	2,340	10,936
19 Skunk River at Augusta, IA	65,312	32,497	6,678	14	72,224	23,411	549	3,636
20 Raccoon R. at Van Meter/Des Moines, IA	63,020	30,872	4,964	186	91,949	17,297	321	3,033
21 Des Moines at St. Francisville, MO (includes Raccoon River basin—20)	215,034	119,334	20,759	557	327,882	60,777	2,737	12,745
22 Illinois River at Marseilles, IL	119,427	48,888	15,128	4,191	132,834	10,831	20,396	6,098
23 Lower Illinois River Basin (IRB)	320,096	136,973	29,906	1,897	393,718	38,218	3,775	12,912
-- Entire IRB (basins 22 and 23)	439,523	185,861	45,034	6,088	406,552	49,049	24,171	19,010
24 Kaskaskia River near Venedy Station, IL	75,063	33,232	6,210	36	48,042	10,877	181	2,275
25 Milk River near Nashua, MT	11,453	10,086	7,588	0	37,902	10,333	77	3,856
26 Missouri River near Culbertson, MT	78,451	89,212	30,173	13	158,123	71,180	705	14,603
27 Bighorn River near Bighorn, MT	28,993	18,460	7,230	38	4,771	18,185	213	2,998
28 Yellowstone River near Sydney, MT	56,032	71,100	22,573	74	28,571	67,471	913	10,063
29 Cheyenne River at Cherry Creek, SD	3,788	41,592	12,318	14	18,926	30,406	407	6,265
30 James River near Scotland, SD	91,865	95,074	18,046	5	272,735	62,531	825	13,493
31 Platte River near Louisville, NE	456,534	206,724	60,436	2,112	251,693	250,502	8,289	36,146
32 Kansas River at Desoto, KS	522,458	127,130	61,369	980	445,523	174,406	3,138	36,185
33 Grand River near Sumner, MO	40,250	52,764	10,437	0	69,401	25,511	362	5,697
34 Osage River below St. Thomas, MO	84,085	82,606	22,279	30	77,378	61,452	928	9,390
35 St. Francis Bay at Riverfront, AR	88,810	39,557	7,992	18	36,129	3,938	629	2,633
36 White River at Clarendon, AR	111,045	81,337	30,740	1,925	61,806	87,516	2,064	10,734
37 Arkansas River at Tulsa, OK	384,160	106,491	61,830	916	321,766	191,120	4,878	33,485
38 Canadian River at Calvin, OK	46,019	18,082	18,953	276	21,963	49,455	777	10,338
39 Yazoo River at Redwood, MS	95,159	44,550	13,274	0	35,109	11,204	829	4,180
40 Big Black River near Bovina, MS	12,629	3,559	3,014	0	3,455	3,130	80	973
41 Red River at Alexandria, LA	236,685	96,112	71,890	3,008	152,757	215,486	3,779	31,937
42 Ouachita River near Columbia, LA	23,754	14,650	19,032	1,256	14,561	26,782	1,174	6,029

TABLE 5.3. Estimated annual inputs of phosphorus as P in the Mississippi–Atchafalaya River basin, 9 large sub-basins, and 42 interior basins (in metric tons).

Basin ID	Basin Name and Location	Commercial Fertilizer	Industrial Point Sources	All Manure	Municipal Point Sources
Entire MARB		1,026,007	28,864	996,685	30,105
9 Large Sub-basins					
1	Upper Ohio	67,628	5,054	58,215	7,164
2	Lower Ohio	163,580	5,434	100,187	2,364
3	Upper Missouri	106554	581	166,797	977
4	Lower Missouri	163,765	4,071	198,386	4,816
5	Upper Mississippi	101,218	1,901	89,068	1,598
6	Middle Mississippi	237,769	6,260	124,282	7,018
7	Arkansas	68,079	1,483	140,671	2,211
8	Lower Mississippi	76,226	1,020	40,333	1,890
9	Red and Ouachita	34,697	1,022	74,015	802
42 Interior Basins					
1	Allegheny River at New Kensington, PA	3,297	21	3,177	385
2	Monongahela River at Braddock, PA	2,522	108	2,542	348
3	Muskingham River at McConnelsville, OH	6,181	534	7,133	726
4	Kanawha River at Winfield, WV	4,417	84	4,977	184
5	Scioto River at Higby, OH	10,242	277	2,891	444
6	Great Miami at New Baltimore, OH	8,028	907	5,560	934
7	Kentucky River at Lockport, KY	3,484	108	4,943	98
8	Wabash River at New Harmony, IN	87,640	543	31,595	767
9	Cumberland River near Grand Rivers, KY	13,533	383	14,573	25
10	Tennessee River near Paducah, KY	25,080	3815	35,350	1,371
11	Mississippi River near Royalton, MN	3,033	195	4,091	60
12	Minnesota River at Jordan, MN	36,603	154	19,326	55
13	St. Croix River at St. Croix Falls, WI	1,760	2	1,949	8
14	Chippewa River at Durand, WI	4,188	47	4,580	57
15	Wisconsin River at Muscoda, WI	7,893	365	6,834	60
16	Rock River near Joslin, IL	22,016	127	14,369	246
17	Cedar River at Cedar Falls, IA	12,621	73	7,828	98
18	Iowa River at Wapello, IA (includes Cedar River Basin—17)	30,978	257	23,310	313
19	Skunk River at Augusta, IA	8,952	3	8,778	80
20	Raccoon River at Van Meter/Des Moines, IA	8,638	87	6,394	47
21	Des Moines at St. Francisville, MO (includes Raccoon River Basin—20)	30,133	143	21,957	402
22	Illinois River at Marseilles, IL	21,187	2,256	3,583	3,366
23	Lower Illinois River Basin	55,678	1,211	13,615	342
--	Entire Illinois River Basin (basins 22 and 23)	76,865	3,467	17,198	3,708
24	Kaskaskia River near Venedy Station, IL	13,010	30	3,497	15
25	Milk River near Nashua, MT	2,638	0	3,275	11
26	Missouri River near Culbertson, MT	17,960	16	22,097	112
27	Bighorn River near Bighorn, MT	2,928	55	5,422	31
28	Yellowstone River near Sydney, MT	8,199	99	20,341	120
29	Cheyenne River at Cherry Creek, SD	639	22	9,061	48
30	James River near Scotland, SD	18,404	2	19,427	121
31	Platte River near Louisville, NE	47,961	1,795	75,782	2,245
32	Kansas River at Desoto, KS	56,202	1,275	54,288	501
33	Grand River near Sumner, MO	6,335	9	8,381	53
34	Osage River below St. Thomas, MO	12,105	35	18,971	116
35	St. Francis Bay at Riverfront, AR	12,325	19	1,242	89
36	White River at Clarendon, AR	13,670	37	26,957	240
37	Arkansas River at Tulsa, OK	40,961	796	55,581	753
38	Canadian River at Calvin, OK	4,861	8	14,647	111
39	Yazoo River at Redwood, MS	12,222	0	3,446	118
40	Big Black River near Bovina, MS	1,622	0	974	11
41	Red River at Alexandria, LA	24,561	516	63,981	541
42	Ouachita River near Columbia, LA	2,533	354	8,432	147

TABLE 5.4. Estimated rates of nitrogen fixation by legumes (in kg N/km²/yr).

Legume	Estimate Used	Low Estimate	High Estimate
Alfalfa	21,800	7,000	60,000
Soybeans	7,800	1,500	31,000
Other Hay	11,600	400	20,000
Cowpeas	4,000	4,000	10,000
Peanuts	8,600	4,000	8,600
Lentils	18,000	16,500	19,000
Dry Beans	4,000	200	21,500
Pasture (Midwest)	1,500	*	*
Rangeland (west)	100	*	*

NOTE: Table is modified from Meisinger and Randall 1991; NRC 1993; and Troeh and Thompson 1993.

5.2.3 Animal Manure

Animal manure can be a significant source of N, P, and other nutrients needed for crop growth. If applied to fields, manure can also add organic matter, improve soil quality, increase water- and nutrient-holding capacities, and increase resistance to soil compaction. Improper use or disposal of manure can lead to the buildup of N and P in soils and the loss of N and P to surface or ground water (NRC 1993). The nutrients in most animal manure are "recycled," since they originate from feed produced in the basin and given to the animals. The nutrient content of manure is highly variable and depends on such factors as type of feed, type and age of livestock, type of bedding material, and storage and handling practices. A common average composition estimate for manure is 0.5% N, 0.125% P, and 0.4% K (Troeh and Thompson 1993). These nutrient content percentages are about 20 times smaller than those commonly found in commercial fertilizers.

In a prior investigation, livestock inventory estimates from the 1987 Census of Agriculture (USDC 1989) and manure nutrient content estimates from the Soil Conservation Service's *Agricultural Waste Management Field Handbook* (1992) were used to estimate annual manure inputs in all U.S. counties (Puckett 1994). This manure was estimated to contain 5.9 million metric tons of N. Using the same data, Battaglin et al. (1997) estimated that about 3.5 million t of N and 1.2 million metric tons of P were generated annually in the MARB. These estimates did not account for losses of N (or P) from manure handling or storage, for animals with more than one marketing or life cycle per year, or for animals of differing size. More recently, Lander et al. (1998) calculated the amounts of nutrients available from livestock manure relative to crop requirements for U.S. counties. Although their estimates account only for animals in confined feeding operations, they do include multiple marketings per year and nutrient losses in storage and handling. These estimates are much smaller than those given by Puckett (1994). Using Lander et al.'s data, an estimated 0.5 million metric tons of N and 0.3 million metric tons of P are made available from manure for crops (or leaching) annually in the MARB.

In this study, the N and P inputs from manure were estimated by state for 1951–96 using livestock inventory data from the National Agricultural Statistics Service (NASS) (USDA (1998), and a strategy for estimating N and P in manure waste that is similar to the method used by Lander et al. (1998), Puckett (1994), and Hoeft (1998). This method was also applied to county-level data from the 1992 Census of Agriculture (USDC 1995). Coefficients used to estimate animal N and P production and losses during storage and handling are from the Midwest Planning Service–Livestock Waste Subcommittee (1985) or the Soil Conservation Service's (now National Resource Conservation Service) *Agricultural Waste Management Field Handbook* (1992). The method accounts for both multiple marketings per year and nutrient losses in storage, handling, and application. Estimates of manure nutrient inputs and losses were made separately for hogs, cattle, poultry, sheep, and horses, and were summed by county.

The N and P content in hog and pig manure was estimated using year-end inventory numbers from NASS or the Census of Agriculture. Hogs and pigs have less than a one-year life cycle, but the inventory numbers were assumed to be similar to inventories during the rest of the year. Data on numbers of animals by weight class were available from NASS but not from the Census of Agriculture, so when Census inventory numbers are used, all hogs and pigs were assumed to produce N and P at the rates estimated for 60–119-pound animals (Table 5.5).

TABLE 5.5. Estimates of the nitrogen and phosphorus voided in animal manure (in kilograms per day).

Animal	Nitrogen (*kg/day*)	Phosphorus (*kg/day*)
Hogs and Pigs	0.027	0.012
<60 lbs. hogs	0.009	0.004
60-119 lbs.	0.027	0.012
120-179 lbs.	0.031	0.013
>180 lbs. hogs	0.041	0.018
Milk Cows	0.204	0.032
Beef Cows	0.150	0.053
Dairy Heifers	0.141	0.018
Steers and Bulls	0.150	0.048
Slaughter Cattle	0.104	0.034
Chickens and Hens	0.0015	0.0006
Pullets and Broilers	0.0010	0.0003
Tom turkeys	0.0054	0.0020
Hen Turkeys	0.0034	0.0013
Sheep and Lambs	0.023	0.004
Horses and Ponies	0.127	0.022
People	0.0265	0.0075

NOTE: Table is modified from Midwest Planning Service–Livestock Waste Subcommittee 1985 and U.S. Soil Conservation Service 1992. NRC 1993; and Troeh and Thompson 1993.

The N and P content in cattle manure was estimated using year-end inventory numbers from USDA or the Census of Agriculture for milk cows, beef cows, steers and bulls, and heifers. Most milk and beef cows have a one-year or longer life cycle, so year-end inventory numbers are likely to be representative of inventories during the rest of the year. However, some heifers and steers are slaughtered during the year and may or may not be accounted for in these inventories. When Census of Agriculture data were used, it was assumed that one-half the number of steers and heifers inventoried were slaughtered during the year. When NASS data were used, it was assumed that as all steers, two-thirds of the beef heifers and all other heifers were slaughtered during the year. Slaughter animals were assumed to generate N and P for 170 days. Cattle were assumed to produce N and P in manure at the rates given in Table 5.5.

The N and P content in poultry manure was estimated using year-end inventory numbers from NASS or the Census of Agriculture on hens, pullets, broilers, and turkeys. Hens, pullets, and broilers all have a shorter than one-year life cycle, but year-end inventory numbers were assumed to be representative of inventories during the rest of the year. However, turkeys were assumed to be in residence for only part of the year (112–133 days). Poultry were assumed to produce N and P in manure at the rates given in Table 5.5. Again, the NASS and Census of Agriculture data categories did not match exactly, so some data-specific modifications to the calculations were made. For example, in NASS data, broiler chickens were reported as production over the year, while in the Census of Agriculture, they were reported as a year-end inventory.

The N and P content in sheep and horse manure was estimated using year-end inventory numbers from NASS or the Census of Agriculture on sheep, lambs, and horses, ponies. Sheep and lambs are likely to have a shorter than one-year life cycle, but year-end inventory numbers were assumed to be representative of inventories during the rest of the year. Sheep and horses were assumed to produce N and P in manure at the rates given in Table 5.5.

Figure 5.7 shows the amounts of N estimated to have been produced by livestock manure in the 20 basin states for 1951–96. It indicates that manure N inputs did not change significantly during this period. Figure 5.8C shows an estimate of the N produced in livestock manure in 1992 by hydrologic accounting unit, indicating that in parts of Iowa, Illinois, Wisconsin, Oklahoma, and Texas, inputs of N from manure exceed 2,000 kg N/km^2/yr. Estimates of the N and P inputs, in manure, for the three basin scales are given in Tables 5.2 and 5.3, respectively.

5.2.4 Soil Mineralization

The majority of the N and P in soils is in organic forms that are not readily available to higher plants. This organic N and P can be in the form of microbial biomass; crop remains, such as straw, stalks, and roots; or otherwise immobilized fertilizer and manure N and P. Mineralization is the process by which the organic N and P are converted to inorganic forms. These forms, such as ammonium, nitrate, and orthophosphate, can be used by plants and can leach to ground and surface water. Rates of N and P mineralization in soils are a function of many conditions, including soil moisture content, temperature, cover type, management practices, and soil organic content (Troeh and Thompson 1993; Powers et al. 1998; Gentry et al. 1998).

Mineralized N from soil organic matter is a significant source of nitrate, particularly in areas where the organic matter content is high or the climate is warm. The total nitrogen content of agricultural soils averages about 333,000 kg/km^2 in the upper 30 cm of soil (Troeh and Thompson 1993), of which all but about 1% is organic. Reported annual rates of N mineralization range from 0% to 50% of the organic N. Nitrogen mineralization rates in soils that are cultivated are generally much larger than rates in uncultivated soils but smaller than those on soils that are cultivated for the first time (Troeh and Thompson 1993). New crop residues decompose and mineralize more rapidly than old residues (Schepers and Mosier 1991). Some researchers have suggested that the addition of N fertilizer to soils increases the rate of organic N mineralization (Azam et al. 1993; Rao et al. 1991). Rates of N mineralization in soils can range from near zero in very dry sandy soils to more than 40,000 kg N/km^2/yr in soils cultivated for the first time (Troeh and Thompson 1993). N mineralization rates of 1–3% of the organic N are commonly used for agricultural regions of the U.S. Midwest (Oberle and Keeney 1990; Schepers and Mosier 1991; NRC 1993; Gentry et al. 1998). Schepers and Mosier (1991) suggest that rates of mineralization should be viewed with an uncertainty of 25–50%.

In this study, the potentially mineralizable N in soils was calculated (Burkart and James 1999) using information in the STATSGO soils database (USDA 1994). First, the mass of organic matter (in kg/km^2) in the upper 30 centimeters (cm) of soil was calculated as the product of the soil bulk density, percent organic matter content, and volume. The soil N content was estimated as 3% of the organic matter (Stevenson 1994). The soil organic N was estimated to mineralize at a rate of 2% per year in cultivated soils (Buckman and Brady 1969; Schepers and Mosier 1991; Gentry et al. 1998). Total potentially mineralizable N estimates were computed for STATSGO map units and then generalized to counties using area-weighted averages.

The mineralization model was applied only to cropped land. Research by Tate (1990) and Dodds et al. (1996) suggests that while mineralization occurs, little N is lost to ground water or streams from native tall-grass prairie land. Similarly, research by Friedland et al. (1991), Swank and Vose (1997), Kortelainen et al. (1997), and Miller and Friedland (1999) shows that although N mineralization occurs in forested soils, little of this N leaves the forest ecosystem. Therefore, data from the 1992 Census of Agriculture (USDC 1995) were used to estimate the percentage of each county that was cropped land. Then, total potential mineralizable N estimates, by county, were multiplied by the percent of cropped land in the county, to determine potentially mineralizable N (Burkart and James 1999). Estimates of potentially mineralizable N from soil organic matter for the three basin scales are given in Table 5.2. Figure 5.8 shows the spatial distribution of potentially mineralizable N in hydrologic accounting units in the MARB. In much of the upper Midwest, including large parts of Iowa, Illinois, Minnesota, and Indiana, potential inputs of mineralized soil N exceed 5,000 kg N/km^2/yr. The rates of mineralization reported here are similar to mineralization rates measured beneath Illinois soybean and corn crops of 8,800 and 13,300 kg N/km^2/yr, respectively (David et al. 1997).

The organic matter in soils also contains P in organic combinations, which can be mineralized by microbes or dissolved by water. The total phosphorous content of soils averages about 0.05%, or about 100,000 kg/km^2 in the upper 30 cm of soil (Troeh and Thompson 1993). Most of this P is bound in forms that cannot be readily used by higher plants. The availability of inorganic P in soils is a function of its solubility, which varies with soil pH, the presence of iron, aluminum- and manganese-containing minerals, organic matter content, and microbial activity, which varies with soil moisture content, and temperature. Unlike nitrate, phosphorus is not very water soluble, and when in contact with sediments or soils, dissolved phosphorus will tend to become bound by anion adsorption (NRC 1993). In nonagricultural soils the amount of P mineralized and available to plants at any one time is small and readily removed by the plants. In agricultural soils, P is frequently added in fertilizer or manure to meet the need of high-yield crops. Only a portion of the added P is available to and used by the crop; the remaining P is immobilized in the soil and available for mineralization. The loss of P from watersheds, both in solution and on sediment, is a function of P levels in watershed soils (NRC 1993). Most of the P lost from cropland is not in solution, but is bound to eroded soil particles (NRC 1993).

Few data are available on the rate of P mineralization in soils, and inputs of P from mineralization were not estimated in this report.

5.2.5 Nutrient Removal in Crops

Estimates of the amount of N and P removed from basins in harvested crops were calculated using crop acreage from NASS or the 1992 Census of Agriculture, and crop yields by state from NASS. Estimates of the N and P content of harvested crops are from Meisinger and Randall (1991), Troeh and Thompson (1993), and Lander et al. (1998). The crops included in the calculation are alfalfa, corn, sorghum, soybeans, wheat, other hay, pasture, and rangeland.

The coefficients for N and P removal in harvested crops used in this study appear in Table 5.6. N and P removal in grazed pasture was calculated using grazed cropland and pasture acreage data from NASS or pasture and rangeland data from the 1992 Census of Agriculture. The coefficients for N and P removal per unit for pasture and rangeland were the same as for other hay, but yields were reduced to account for the lower productivities of these landscapes (Jordan and Weller 1996). In this study, one-half of the other hay yield was applied to grazed cropland, one-fourth to pasture, and one-tenth to rangeland.

TABLE 5.6. Estimated rates of nitrogen and phosphorus removal in harvested crops (in kg N or P per common yield unit).

Crop	Unit	Nitrogen	Phosphorus
Alfalfa	Ton	23.6	2.10
Corn for Grain	Bushel	0.331	0.068
Corn for Silage	Ton	3.27	0.427
Sorghum for Grain	Bushel	0.363	0.082
Sorghum for Silage	Ton	6.70	1.11
Soybeans	Bushel	1.72	0.163
Wheat	Bushel	0.499	0.091
Other Hay	Ton	20.0	6.94
Pasture	Ton	20.0	6.94

Note: Table is modified from Meisinger and Randall 1991; Troeh and Thompson 1993; and Lander et al. 1998.

Figure 5.9 shows the estimated amounts of N removed with harvested crops and grazed pasture and rangeland in the 20 basin states for 1951–96. It indicates that removals increased from about 4 to nearly 10 million metric tons/yr during this period. Figure 5.10A shows an estimate of the N removed in harvested crops and pasture in 1992 by hydrologic accounting unit. In much of the upper Midwest, including most of Iowa, Illinois, and Indiana, these outputs of N exceed 7,000 kg $N/km^2/yr$ (Figure 5.10). Estimates of the N and P outputs in harvested crops and grazed pasture for the three basin scales are given in Tables 5.7 and 5.8, respectively.

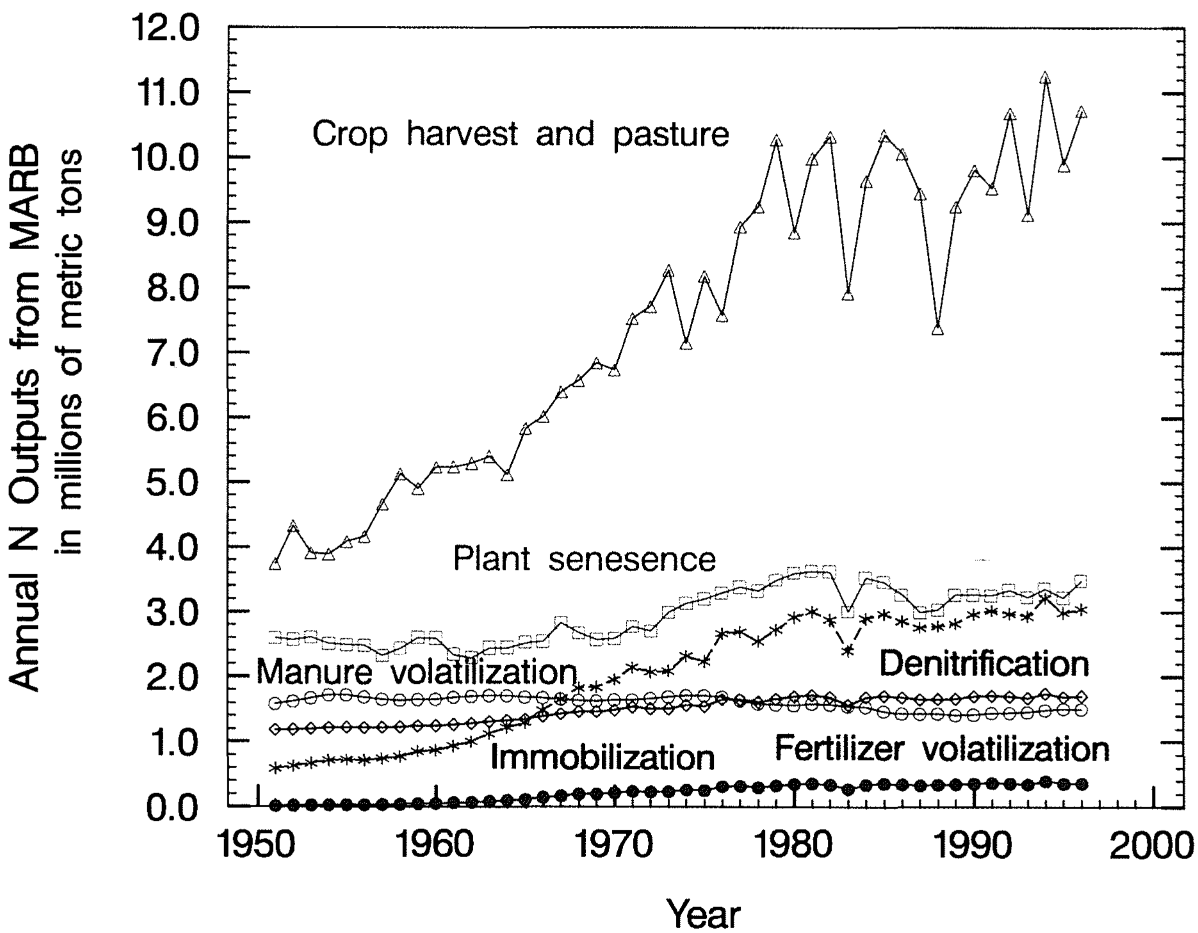


FIGURE 5.9. Annual nitrogen outputs from the Mississippi–Atchafalaya River Basin, 1951–96. NOTE: See text for sources of data and methods used to estimate outputs.

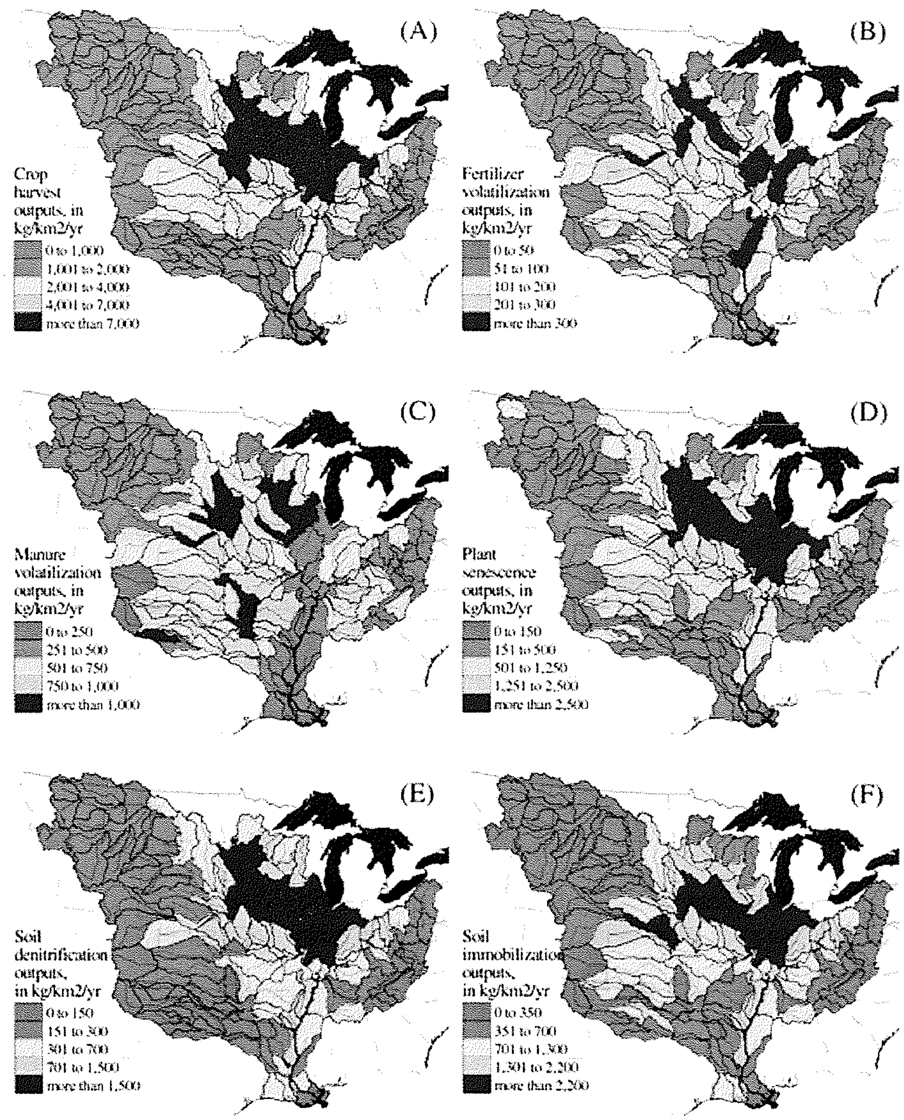


FIGURE 5.10. Nitrogen outputs in hydrologic units in 1992 from (A) harvested crops, (B) fertilizer volatilization, (C) manure volatilization, (D) plant senescence, (E) soil denitrification, and (F) soil immobilization.

TABLE 5.7. Estimated annual outputs of nitrogen as N in the Mississippi–Atchafalaya River Basin, 9 large sub-basins, and 42 interior basins (in metric tons).

Basin ID and Name, and Location	Crop Harvest	Pasture Grazing	Crop Senescence	Soil Denitrification	All Manure Losses	Soil Immobilization	Fertilizer Volatilization	River Flux
Entire MARB	8,553,901	1,168,807	3,011,547	1,787,109	1,733,922	2,949,661	398,164	1,507,312
9 Large Sub-basins								
1 Upper Ohio	524,623	70,260	133,975	89,991	110,610	175,273	19,176	251,800
2 Lower Ohio	1,032,228	85,205	324,886	212,329	166,401	367,048	41,757	244,100
3 Upper Missouri	1,065,000	299,967	485,762	191,241	284,797	277,508	49,140	72,900
4 Lower Missouri	1,572,139	205,943	532,304	223,868	341,196	577,008	79,283	166,300
5 Upper Mississippi	844,196	36,580	313,855	323,646	176,112	256,579	36,940	149,800
6 Middle Mississippi	2,190,674	50,005	759,476	521,626	191,166	606,099	71,349	451,700
7 Arkansas	578,820	233,525	224,837	64,958	252,767	281,083	43,922	54,900
8 Lower Mississippi	507,213	55,735	156,426	91,563	69,237	227,328	31,559	115,800
9 Red and Ouachita	214,877	124,590	72,932	50,302	132,337	152,405	22,665	60,500
42 Interior Basins								
1 Allegheny River at New Kensington, PA	29,434	2,765	5,366	5,819	8,304	10,945	804	20,121
2 Monongahela River at Braddock, PA	15,793	4,315	1,702	3,038	5,204	7,621	536	16,011
3 Muskingham River at McConnelsville, OH	70,128	5,469	17,321	10,443	14,901	17,322	1880	20,322
4 Kanawha River at Winfield, WV	14,052	8,189	1,033	3,359	9,400	10,879	748	20,634
5 Scioto River at Higby, OH	99,392	1,644	34,193	14,476	4,910	24,267	3,115	23,335
6 Great Miami at New Baltimore, OH	77,116	1,137	26,426	11,742	8,809	18,867	2,427	19,556
7 Kentucky River at Lockport, KY	14,726	8,213	1,391	4,058	9,207	8,882	1,138	11,563
8 Wabash River at New Harmony, IN	645,898	10,188	221,188	142,744	45,048	198,126	22,728	118,244
9 Cumberland River near Grand Rivers, KY	56,997	18,990	11,525	10,637	26,218	29,409	3,371	32,859
10 Tennessee River near Paducah, KY	95,008	37,598	18,896	23,775	63,314	59,745	4,696	49,496
11 Mississippi River near Royalton, MN	35,208	4,262	9,089	18,798	8,492	9,908	1,166	5,031
12 Minnesota River at Jordan, MN	303,687	3,269	135,685	110,289	30,145	88,100	14,290	53,802
13 St. Croix River at St. Croix Falls, WI	19,311	2,207	4,570	12,203	4,585	5,669	646	3,688
14 Chippewa River at Durand, WI	36,814	2,805	9,837	15,931	12,973	10,802	1,354	9,384
15 Wisconsin River at Muscoda, WI	50,199	3,428	15,429	24,254	17,559	18,354	2,552	12,163
16 Rock River near Joslin, IL	166,462	3,083	63,524	56,023	30,634	49,134	6,351	37,338
17 Cedar River at Cedar Falls, IA	125,770	1,034	47,543	37,715	10,821	35,639	4,380	36,570
18 Iowa River at Wapello, IA (includes Cedar River basin–17)	323,354	4,879	116,305	87,790	32,460	90,032	10,534	74,200
19 Skunk River at Augusta, IA	103,773	2,688	34,948	25,148	12,008	26,763	3,001	22,446
20 Raccoon R. at Van Meter/Des Moines, IA	103,508	1,431	35,132	27,960	8,875	25,332	2,896	27,520
21 Des Moines at St. Francisville, MO (includes Raccoon River basin–20)	363,372	8,615	124080	98,437	31,457	87,543	10,288	67,436
22 Illinois River at Marseilles, IL	176,141	990	62,449	42,511	5,635	49,304	5,520	66,713
23 Lower Illinois River Basin (IRB)	467,607	5,611	163,400	97,989	19,763	130,249	14,621	78,330
-- Entire IRB (basins 22 and 23)	643,748	6,601	225,849	140,500	25,398	179,553	20,141	145,043
24 Kaskaskia River near Venedy Station, IL	107,578	1,157	35,521	19,899	5,665	30,391	3,397	8,364
25 Milk River near Nashua, MT	20,248	13,487	15,903	1,014	5,602	5,657	1,232	816
26 Missouri River near Culbertson, MT	112,704	81,813	72,262	5,151	38,675	36,356	8,393	5,678
27 Bighorn River near Bighorn, MT	12,046	17,237	3,175	642	9,930	13,189	1,838	3,091
28 Yellowstone River near Sydney, MT	52,685	75,595	16,033	1,998	36,797	27,882	4,417	11,445
29 Cheyenne River at Cherry Creek, SD	25,330	29,428	4,330	3,090	16,583	5,212	356	3,442
30 James River near Scotland, SD	146,272	12,564	88,031	35,832	33,619	38,425	9,060	1,168
31 Platte River near Louisville, NE	443,371	79,694	158,117	51,915	134,762	187,499	24,712	31,651
32 Kansas River at Desoto, KS	480,333	60,953	190,014	53,497	93,686	212,539	29,998	22,673
33 Grand River near Sumner, MO	85,477	9,382	22,294	17,731	13,661	18,119	2,467	22,715
34 Osage River below St. Thomas, MO	109,209	21,913	23,041	18,603	33,029	38,904	5,498	15,406
35 St. Francis Bay at Riverfront, AR	87,477	1,616	28,713	13,759	2,116	35,909	6,189	6,814
36 White River at Clarendon, AR	101,860	33,012	22,693	27,782	46,244	51,966	7,851	21,089
37 Arkansas River at Tulsa, OK	328,631	90,258	149,729	30,259	103,591	161,393	25,464	13,920
38 Canadian River at Calvin, OK	33,413	57,763	14,759	3,429	26,852	22,210	3,573	5,071
39 Yazoo River at Redwood, MS	74,704	7,580	23,101	15,131	6,074	40,752	3,928	27,709
40 Big Black River near Bovina, MS	4,958	2,336	1,212	1,993	1,692	5,678	521	4,415
41 Red River at Alexandria, LA	153,823	116,598	54,328	26,093	115,716	107,416	17,975	35,607
42 Ouachita River near Columbia, LA	17,658	5,654	3,323	8,636	13,804	15,180	1,532	13,873

TABLE 5.8. Estimated annual outputs of phosphorus as P in the Mississippi–Atchafalaya River Basin, 9 large sub-basins, and 42 interior basins (in metric tons).

Basin ID	Basin Name and Location	Crop Harvest	Pasture Grazing	River Flux
Entire Mississippi–Atchafalaya River Basin		1,381,471	415,581	123,807
Large Sub-basins				
1	Upper Ohio	89,662	24,404	24,100
2	Lower Ohio	168,072	29,626	15,300
3	Upper Missouri	170,016	104,182	6,400
4	Lower Missouri	266,326	72,321	19,500
5	Upper Mississippi	130,654	12,710	8,000
6	Middle Mississippi	323,613	17,397	34,700
7	Arkansas	112,600	86,613	5,100
8	Lower Mississippi	70,867	19,575	10,600
9	Red and Ouachita	44,947	45,763	12,700
42 Interior Basins				
1	Allegheny River at New Kensington, PA	5,815	959	982
2	Monongahela River at Braddock, PA	3,434	1,497	798
3	Muskingham River at McConnelsville, OH	11,156	1,897	1,167
4	Kanawha River at Winfield, WV	3,430	2,843	107
5	Scioto River at Higby, OH	13,911	570	1,166
6	Great Miami at New Baltimore, OH	10,938	394	1,221
7	Kentucky River at Lockport, KY	3,779	2,856	1,477
8	Wabash River at New Harmony, IN	93,420	3,535	6,932
9	Cumberland River near Grand Rivers, KY	13,174	6,614	2,542
10	Tennessee River near Paducah, KY	22,993	13,081	3,998
11	Mississippi River near Royalton, MN	5,956	1,479	219
12	Minnesota River at Jordan, MN	43,173	1,134	1,353
13	St. Croix River at St. Croix Falls, WI	3,505	766	156
14	Chippewa River at Durand, WI	6,650	978	737
15	Wisconsin River at Muscoda, WI	8,878	1,196	661
16	Rock River near Joslin, IL	27,092	1,070	2,083
17	Cedar River at Cedar Falls, IA	18,809	359	1,135
18	Iowa River at Wapello, IA (includes Cedar River basin–17)	48,158	1,693	3,076
19	Skunk River at Augusta, IA	15,116	932	1,338
20	Raccoon River at Van Meter/Des Moines, IA	14,600	496	755
21	Des Moines at St. Francisville, MO (includes Raccoon River basin–20)	51,525	3,033	2,334
22	Illinois River at Marseilles, IL	25,756	343	4,078
23	Lower Illinois River basin	67,299	1,947	733
--	Entire Illinois River basin	93,055	2,290	3,345
24	Kaskaskia River near Venedy Station, IL	15,365	401	919
25	Milk River near Nashua, MT	3,659	4,680	185
26	Missouri River near Culbertson, MT	19,475	28,389	796
27	Bighorn River near Bighorn, MT	1,566	5,981	31
28	Yellowstone River near Sydney, MT	7,800	26,231	2,302
29	Cheyenne River at Cherry Creek, SD	3,617	10,211	1,639
30	James River near Scotland, SD	24,348	4,360	254
31	Platte River near Louisville, NE	75,220	28,075	5,447
32	Kansas River at Desoto, KS	88,160	21,587	3,134
33	Grand River near Sumner, MO	12,658	3,255	3,271
34	Osage River below St. Thomas, MO	20,881	7,604	729
35	St. Francis Bay at Riverfront, AR	11,240	572	400
36	White River at Clarendon, AR	18,036	11,455	381
37	Arkansas River at Tulsa, OK	59,461	34,049	1,217
38	Canadian River at Calvin, OK	6,754	20,052	881
39	Yazoo River at Redwood, MS	9,628	2,630	608
40	Big Black River near Bovina, MS	1,005	810	1,061
41	Red River at Alexandria, LA	35,608	42,969	5,935
42	Ouachita River near Columbia, LA	3,676	1,961	364

5.2.6 Volatilization Losses

Several forms of N are volatile, including molecular nitrogen (N_2), ammonia (NH_3), and N oxides (NO, N_2O). Bouwman et al. (1997) lists rates of NH_3 loss from synthetic fertilizers in temperate climates that range from 2% to 20% depending upon the fertilizer type, and rates listed by Meisinger and Randall (1991) range from 0% to 60%. Buckman and Brady (1969) suggest that volatilization losses of 20–40% of the N in fertilizer applications to poorly drained soil would not be uncommon. Bouwman et al. (1997) list rates of NH_3 loss from animal manure that range from 4% to 36%. N can also be lost by volatilization from soils or plants during senescence.

A portion of the N in some fertilizers, primarily urea, is lost during application due to volatilization of ammonia. The rate of volatilization varies by fertilizer type, application method, climate, and soil pH (Meisinger and Randall 1991; Bouwman et al. 1997). The loss of N via direct volatilization of ammonium fertilizers is probably minimal because these fertilizers are almost always injected or incorporated into soils (Troeh and Thompson 1993). For this study, states are designated as dry (Colorado, Kansas, Oklahoma, Montana, Nebraska, New Mexico, North Dakota, South Dakota, and Wyoming), humid (Alabama, Arkansas, Georgia, Louisiana, Mississippi, North Carolina, Tennessee, and Virginia), or subhumid (all other states).

Table 5.9 gives the rates of fertilizer loss used in this report. These values are estimates based on the rates reported in Meisinger and Randall (1991) and Bouwman et al. (1997). Estimates of the N output in fertilizer volatilization for the three basin scales are given in Table 5.7. Figure 5.9 shows estimates of N volatilized from fertilizer in the 20 basin states for 1951–96 and indicates that these amounts increased slightly during this period. Figure 5.10B shows the spatial distribution of N output in fertilizer volatilization in hydrologic accounting units in the MARB. In much of the upper Midwest, including parts of Iowa, Illinois, and Indiana, rates of N volatilization from fertilizer exceed 300 kg N/km^2/yr.

TABLE 5.9. Estimated rates of nitrogen (ammonia) volatilization from fertilizer, as a percent.

Fertilizer Type	Percent Loss in Humid States	Percent Loss in Subhumid States	Percent Loss in Dry States	Range of Reported Loss Estimates
Urea	10	15	20	0–40
Ammonium Nitrate	2	5	8	0–30
Anhydrous Ammonia	2	3	4	0–5
Nitrogen Solutions	3	4	5	0–20
Other Forms	4	6	8	0–60

NOTE: Table is modified from Meisinger and Randall 1991 and Bouwman et al. 1997.

A significant portion of the N in animal manure is lost during storage, handling, and application. P is assumed not be lost from volatilization during manure storage, handling or application, but some P is likely to be lost from runoff and erosion. Less than half of the P voided in manure is economically recoverable by crops (NRC 1993). Most of the N loss is likely to be from the volatilization of ammonia. The losses of N were calculated separately for manure from hogs, cattle, poultry, sheep, and horses (only included in 1992 Census of Agriculture estimates) using loss coefficients from Meisinger and Randall (1991) or from the Midwest Planning Service–Livestock Waste Subcommittee

(1985). The estimates of N loss by animal class were summed by county to get the "all manure loss" values in Table 5.7.

Losses of N from manure are a function of the manure type; climate; and storage, handling, and application practices. This study includes the following assumptions and estimates:

- 20% of the hog manure is stored and handled as a solid, 52% using pits, and 28% using lagoons; 42% of the N in hog manure is lost in storage and handling, and 12% of the remaining N is lost during application.
- 88% of cattle manure is handled in open lots, and 12% is handled as a liquid; 42% of the N in cattle manure is lost in storage and handling, and 21% of the remaining N is lost during application.
- 40% of the N in poultry manure is lost in storage and handling, and 16% of the remaining N is lost during application.
- 45 % of the N in sheep and horse manure is lost in storage and handling, and 23% of the remaining N is lost during application.

The storage and handling losses used for several states were modified slightly from the percentages given above to reflect local conditions. These modifications were based on the recommendations of state soil scientists and agronomists and are applied only to the nutrient budget calculations that used the NASS data (Figure 5.9). Estimates of the N output in manure volatilization for the three basin scales appear in Table 5.7. Figure 5.9 shows the amounts of N estimated to have been volatilized annually from livestock manure for the 20 states in the MARB for 1951–96. Figure 5.10C shows the spatial distribution of N output in manure volatilization in hydrologic accounting units in the MARB in 1992 based on the Census of Agriculture data.

Nitrogen can also be lost directly from plants. This loss occurs primarily as ammonia volatilization from the senescing leaves of plants. This loss generally occurs toward the end of the growing season, and has been estimated for crops to be 0–8,000 kg N/km^2 (Francis et al. 1993; Meisinger and Randall 1991; Schepers and Mosier 1991; Bouwman et al. 1997). Rates of N loss from plant volatilization are likely to vary with crop type, crop health, climate, fertilization rate, and soil conditions; however, insufficient data are available to refine estimates by region or other factors (Bouwman et al. 1997).

In this study, N lost via volatilization from crops is estimated using crop acreage data from NASS or the 1992 Census of Agriculture and the volatilization rates in Table 5.10 (Francis et al. 1993; Burkart and James 1999). These rates are generally higher than the 400–1,600 kg/N/km^2 used by Meisinger and Randall (1991) and the 250 kg/N/km^2 used by Bouwman et al. (1997). Estimates of the N output during plant senescence for the three basin scales appear in Table 5.7. Figure 5.9 shows the amounts of N estimated to be lost from plant senescence in the 20 basin states for 1951–96 and indicates that losses increased slightly during this period. Figure 5.10C shows the spatial distribution of N output during plant senescence in hydrologic accounting units in the MARB in 1992.

N is also volatilized from manure of wild animals, soils under natural vegetation, noncrop vegetation, burning of crop or forest biomass, fossil fuel combustion, and some industrial processes (Bouwman et al. 1997). However, the N volatilization from these processes is not estimated in this report.

TABLE 5.10. Estimated rates of nitrogen (ammonia) volatilization from senescing plant leaves (in kg N per square kilometer).

Crop	Senescence Rate
Corn–All Types	6,000
Soybeans and Other Beans	4,500
Wheat and Other Grains	3,500
Sorghum–All Types	900

NOTE: Table is modified from Francis et al. 1993 and Burkart and James 1999.

5.2.7 Denitrification Losses

Significant amounts of N are lost by denitrification, a microbial process that occurs in soils. Microbial respiration of nitrate produces N_2O and N_2 gases that eventually escape to the atmosphere. Rates of denitrification vary by soil drainage class, because drainage affects the potential for saturation or water retention. Denitrification occurs most rapidly under low-oxygen conditions associated with water-saturated or poorly drained soils, such as those found in wetlands and river bottoms. Denitrification losses can occur episodically when rainfall or irrigation saturates soils (Gentry et al. 1998; Kellman and Hillaire–Marcel 1998).

In this study, rates of denitrification in agricultural soils are estimated by state using estimates of average soil organic matter and extent of hydric soils (Burkart and James 1999), and tables of denitrification rates from Meisinger and Randall (1991). Table 5.11 shows the average percent organic matter and denitrification rates as a percentage of N inputs used in this study for the states entirely or partly within the MARB. The denitrification rates in Table 5.11 were applied to 60% of the residual fertilizer N (adjusted for volatilization), 100% of the mineralized soil N, and 60% of the atmospheric nitrate (wet and dry NO_3). The rates were doubled and applied to 90% of the residual (adjusted for storage, handling, and application loss) swine manure N, 75% of the residual poultry manure N, and 45% of the residual cattle and other manure N (Meisinger and Randall 1991). Estimates of the N output from denitrification in agricultural soils for the three basin scales appear in Table 5.7. Figure 5.9 shows the amounts of N estimated to have been lost from soil denitrification in the 20 basin states for 1951–96, and indicates that losses increased slightly during this period. Figure 5.10E shows the spatial distribution of N output from denitrification in hydrologic accounting units in the MARB in 1992.

5.2.8 Immobilization

Immobilization is the process by which plants or microbes convert inorganic ions, such as nitrate to organic N-containing compounds. This process is often considered to be the reverse of mineralization, and over the long term these two processes should balance, unless nitrogen is removed from the system (Troeh and Thompson 1993; Gentry et al. 1998). Immobilization is generally slower than mineralization, except immediately after the addition of N in crop residues, manure, or fertilizer. The rates of mineralization and immobilization of N are generally small relative to the size of the soil organic N pool (Power and Broadbent 1989). Estimates of the rate of fertilizer N immobilized in soil from various cropping systems ranged from 20% to 40% of the input (Power and Broadbent 1989; Peterson and Frye 1989).

TABLE 5.11. Estimated average soil organic content and denitrification rate for states in the Mississippi–Atchafalaya River Basin.

Basin States	Average Organic Content Percentage of Soil	Estimated Denitrification Rate as a Percentage of Available N Inputs
Alabama	1.1	15
Arkansas	1.3	15
Colorado	1.1	2
Georgia	1.6	15
Illinois	2.6	20
Indiana	2.9	20
Iowa	3.5	20
Kansas	2.0	5
Kentucky	1.6	10
Louisiana	2.8	20
Maryland	1.5	10
Minnesota	5.0	20
Mississippi	1.1	15
Missouri	1.7	15
Montana	1.2	2
Nebraska	2.3	10
New Mexico	0.7	2
New York	2.7	15
North Carolina	2.5	10
North Dakota	2.4	10
Ohio	2.1	15
Oklahoma	1.3	5
Pennsylvania	1.7	15
South Dakota	2.0	10
Tennessee	1.3	10
Texas	1.2	5
Virginia	1.3	10
West Virginia	1.5	10
Wisconsin	5.0	20
Wyoming	0.8	2

NOTE: Table is modified from Meisinger and Randall 1991 and Burkart and James 1999.

In this study we assumed that 40% of residual fertilizer N after volatilization losses and 40% of the nitrate from atmospheric deposition (wet plus dry) are immobilized by organisms in the soil and are not readily available for denitrification or utilization by crops. Manure N is already largely in an immobilized form and is not added to the immobilization output. A portion of the N that is mineralized from soils can be immobilized, and the N taken up by the crop but not removed in harvest is also immobilized. These two potential immobilization outputs are not quantified in this report. Estimates of the N output from immobilization in agricultural soils for the three basin scales appear in

Table 5.7. Figure 5.9 shows the amounts of N estimated to have been immobilized in the soil in the 20 states for 1951–96, indicating an increase of about 0.5–3.0 million metric tons/yr during this period. Figure 5.10F shows the spatial distribution of N output by immobilization in hydrologic accounting units in the MARB in 1992. Like estimates of N from mineralization of soil, estimates of N immobilization rates should be viewed with an uncertainty of 25–50%.

P is also immobilized in the soil, but estimates of the rate at which this process occurs could not be found. Several researchers suggest that nearly all of the added organic or inorganic P is adsorbed on soil minerals and unavailable for plant use (NRC 1993; Troeh and Thompson 1993).

5.2.9 Erosion

Some of the N and P in soil organic matter is also lost from soils by erosion. Soil erosion from forest land and grasslands is generally less than 100,000 kg soil/km^2/yr. Erosion losses from cropped soils are larger: losses of several million kilograms of soil per km^2/yr are common, and some annual losses are exceed 20 million kg soil/km^2/yr (Troeh and Thompson 1993). Only a small fraction of the eroded material from soils is N or P, but the eroded material is likely to contain more fine sediments and higher percentages of organic matter and N and P than the parent soil (Buckman and Brady 1969). Sediment-bound N losses from agricultural land typically are less then 400 kg/km2/yr (Schepers and Fox 1989). The N and P losses from soil erosion were not estimated here; some of these losses can be can be accounted for in the suspended N and P flux in rivers discussed in chapter 4 of this report.

5.3 MUNICIPAL AND INDUSTRIAL INPUTS

Municipal sewage treatment plants and many industries—including plastics and nitrogen fertilizer manufacturers, refuse systems, beef cattle feedlots, wet corn milling, steel mills, and petroleum refineries—discharge significant quantities of N and P into rivers. These discharges are often referred to as "point sources" of contaminants. Specific industry discharges vary considerably in different regions of the MARB.

In a prior investigation using data from the late 1970s, Gianessi and Peskin (1984) and Battaglin et al. (1997) estimated that municipal sewage treatment plants and industrial facilities respectively discharged about 264,000 and 106,000 metric tons of N annually in the MARB. In 1998, EPA initiated a study to determine the best estimate of the total N and P discharged annually by each of the National Pollutant Discharge Elimination System (NPDES)-regulated point sources in the MARB. The final version of the database contains estimates of 1996 total N and total P discharges for about 11,500 facilities ranging in size and significance from a campground (~0.01 metric tons of N/yr) to a Chicago municipal sewage treatment plant (~10,000 metric tons of N/yr).

The estimates of N and P in municipal and industrial discharge presented in this report only account for permitted discharges from facilities contained in the NPDES database. They do not account for dumping or other illegal discharges of N or P from any facility. Municipal and industrial facilities (and motor vehicles) also emit N-containing compounds to the atmosphere, a portion of which is returned to the basin in wet and dry atmospheric deposition (Jaworski et al. 1997). Emissions of N to the atmosphere from municipal and industrial facilities and motor vehicles are not estimated in this report. Some of the atmospherically emitted N that is returned to the basin is measured as atmospheric deposition (see section 5.1 of this chapter).

5.3.1 Methods

The U.S. Environmental Protection Agency (EPA) provided annual N and P discharge estimates for each of the NPDES-regulated point sources in the MARB, using the methods and procedures presented in USEPA 1998a. The final version of the methods used and resulting database is presented in Tetra Tech, Inc. 1998. The EPA database contains estimates of total N and total P discharges in 1996 for about 11,500 facilities. The new discharge estimates were based largely on NPDES data found in EPA's Permit Compliance System. Where no other data existed, the information was estimated by applying typical pollutant concentrations and typical facility flows, as described by NOAA (1998). To the extent possible, data for N from all seasons were obtained for each facility to get a reasonable assessment of the annual load, since the nitrogen cycle is temperature-dependent.

For this study, estimates of N and P discharges by facility are summed within 8-digit hydrologic units (Seaber et al. 1987). Municipal and industrial discharges are kept separate. In some cases, location information was not available, and the facility could not be assigned to an 8-digit hydrologic unit. Nutrient discharges from these facilities are added only to the estimates of total input to the MARB, and are not assigned to any of the 9 large or 42 interior basins. The estimated N discharge from unassigned facilities is only 5.5% of the total N discharge in the basin, but more than 20% of the industrial N discharge is unassigned. An area-weighted summing algorithm was used to compute estimates of nutrient discharges from point sources for the three basin scales.

5.3.2 Results

Tables 5.2 and 5.3 provide estimates of the annual input of N and P for the three basin scales from municipal and industrial facilities. Estimates of the total N input from both municipal and industrial facilities and in hydrologic accounting units in the MARB appear in Figure 5.8. The current estimates are similar but are generally lower than the historical estimates made using data from the 1970s (Figure 5.7) (Gianessi and Peskin 1984; Battaglin et al. 1997). An estimated 200,786 metric tons of N and 30,105 metric tons of P are discharged annually from municipal sewage treatment plants in the MARB, while an estimated 85,635 metric tons of N and 28,864 metric tons of P are discharged annually from industrial facilities (Table 5.12). It is unknown if the differences between current and historical estimates of nutrients point discharges are real or a function of improved data gathering and analysis.

TABLE 5.12. Estimated point-source nitrogen and phosphorus discharges for the Mississippi–Atchafalaya River Basin (in metric tons/year).

Source Category	Estimated Discharge (1996)		Estimated Error		Historic Estimates (late 1970s)	
	N	*P*	*N*	*P*	*N*	*P*
Municipal Point Sources	200,786	30,105	40,800	6,100	264,000	55,000
Industrial Point Sources	85,635	28,864	22,000	32,200	106,000	15,000
Total	286,400	59,000	62,800	38,300	370,000	70,000

5.4 ATMOSPHERIC INPUTS DIRECTLY TO THE GULF OF MEXICO

Measurements of atmospheric deposition directly to the waters of the Gulf of Mexico are nearly nonexistent. A few precipitation events and filterpack estimates from one cruise (Parungo and Miller 1988; Parungo et al. 1990) provide a little wet and dry deposition data for the western half of the Gulf. Otherwise, all available data used in this summary were from land-based stations, primarily from the U.S. located along the Gulf coast. Available data are discussed in this section.

5.4.1 Dry Deposition

Dry deposition to Gulf waters can be estimated from available data with two approaches: (1) by using chemical concentration data collected aboard ship, coupled with appropriate deposition velocities, and (2) by extrapolating filterpack information from land-based sites, such as those managed through the EPA's Clean Air Status and Trends Program (CASTNet). Land-based deposition information represents a point measurement, typically valid for a small region of homogeneous fetch and land cover (Meyers and Sisterson 1990). In addition, the factors that control dry deposition in the coastal zone are believed to be vastly different from those for inland areas, and are largely controlled by poorly quantified processes involving sea salt aerosols (Keene et al. 1990). However, shoreline air concentration data can be quite indicative of nearby coastal regimes, since concentrations respond slowly to surface changes.

5.4.1.1 SUMATRA, FLORIDA, CASTNET SITE

Estimates of nitrogen deposition along the Gulf coast are extremely rare. Only three dry deposition monitoring sites are known to be operational within several hundred kilometers of the Gulf of Mexico, and data exist for only two of them. Even for these two, the data cannot yet be accepted without considerable caution because of the complicating effects of sea salt and local surface complexity, as mentioned above. The Sumatra, Florida, site (approximately 20 km north of Apalachicola, Florida) has been operated by CASTNet since December 1988. Data are available via an EPA web site (USEPA 1998b). Unpublished estimates of the ratio of dry deposition to total deposition of nitrogen generated using CASTNet data indicate that dry deposition of nitrogen constitutes about half of total deposition near the Sumatra site. Unpublished kriged estimates of all CASTNet data indicate that dry deposition of nitrogen ranges from about one-third to one-half of total deposition for the coastal Gulf region east of Texas. These estimates should probably be ignored, given the paucity of data in this region. Extrapolation over the open waters of the Gulf cannot be done with any certainty.

5.4.1.2 TAMPA BAY NATIONAL ESTUARY PROGRAM DATA

The Tampa Bay National Estuary Program has established precipitation chemistry and inferential method dry deposition filterpack (wet and dry) stations. Precipitation measurements are discussed below. In this particular case, deposition monitoring is performed according to a set of protocols designed to account for complications arising from sea salt aerosols—an approach different from that mentioned above for the CASTNet site. Dry deposition estimates to the water of Tampa Bay indicate that nitric acid deposition is approximately twice as great as nitrate deposition from precipitation—on the order of 7 kg/ha/yr (Greening 1998). Although this is a very large number, it is probably not a particularly relevant value because the site exposure is near the Gandy Bridge, which is close to a number of very large utility emission sources. The site is likely to be quite representative of Tampa Bay, but not the open waters of the Gulf.

5.4.1.3 Long Key Program

NOAA's Air Resources Laboratory is in the process of establishing a deposition program near the Long Key Marine Laboratory on a jetty facing Florida Bay. Meteorological measurements, as well as aerosol and gas measurements of ammonia, oxides of nitrogen, nitric acid, aerosol nitrate, ortho- and total phosphorus, and base cations will be made on a seven-meter tower. Major ions in precipitation, including nitrate and ammonium will also be measured nearby. The infrastructure is in place, and meteorological data are being collected. Chemical data should become available within the next year.

5.4.1.4 IMPROVE Data

The IMPROVE (Interagency Monitoring of Protected Visual Environments) program operates a sampling site southeast of the Sumatra CASTNet site, near Chassahowitzka Bay, Florida. The Chassahowitzka data include estimates of ammonium nitrate concentration; no dry deposition estimates are available (Porter 1998).

5.4.1.5 Parungo Air Chemistry Studies over the Gulf of Mexico

Dry deposition rates were estimated from concentration measurements made during a research cruise conducted in the summer of 1986 by a group of scientists from the United States and Mexico. The project was designed to investigate chemistry over the Gulf of Mexico (Parungo et al. 1990; Parungo and Miller 1988). This cruise generated the only known published estimates of deposition from samples in the region of interest collected in Gulf waters.

Approximately 22 aerosol samples were collected in an area that stretches from coastal waters near New Orleans, Louisiana, along the coasts of Texas and Mexico to Progreso Merida (Yucatan) and back to New Orleans across the open Gulf waters. Mass concentrations of nitrate were less than 1 $\mu g/m^3$ throughout the Gulf, except near the port cities of Galveston, New Orleans, Veracruz, and Merida, where maximum values were all less than 4 $\mu g/m^3$. It was determined that the large particles contained a large fraction of the nitrate. Because large particles have high rates of dry deposition and low residence time, nitrate concentrations decreased rapidly with distance from the shore. Based on the methodology of Slinn and Slinn (1980) and a number of assumptions regarding particle size distributions, it was estimated that the average dry deposition was approximately 3.3 kg/ha/yr for NO_3, and about 0.1 kg/ha for NH_4^+ to the entire Gulf. An area of 1.5 x 10^7 km^2 was assumed.

5.4.2 Wet Deposition

5.4.2.1 National Atmospheric Deposition Program

By far the greatest single source of potentially relevant data for this study is available through the National Atmospheric Deposition Program (NADP/NTN 1997). Ten stations are within approximately 100 km of the Gulf coast, nine operating according to the usual weekly wet-only sampling protocol (Bigelow and Dossett 1993) and one operating according to NOAA Atmospheric Integrated Research Monitoring Network (AIRMoN) protocol. The nine weekly sites are: Beeville and Attwater Prairie Chicken National Wildlife Refuge, Texas; Iberia Research Station and Southeast Research Station, Louisiana; Quincy, Bradford Forest, Chassahowitzka, Verna Well Field, and Everglades National Park, Florida. The AIRMoN station is located in Tampa Bay, Florida. Information regarding these and all other NADP stations is available via the NADP web site: http:/nadp.sws.uiuc.edu.

Using a least-squares method of interpolating between stations, NADP has developed a set of annual and seasonal concentration and wet deposition maps for the United States. For 1994, 1995, and 1996, these maps are posted on the NADP web site for major ions, including nitrate and ammonium. For each of these years, deposition values are typically higher in the regions surrounding New Orleans and perhaps Tampa/St. Petersburg. Deposition values tend to be lowest along the southern Texas coast and range from about 1 to 3 kg/ha of NO_3 (as N), and about 1.0 to 3.2 kg/ha of NH_4^+ (as N). Although a fairly broad range of estimated deposition is found, average deposition of total inorganic nitrogen via precipitation along the U.S. Gulf coast is typically on the order of 3–4 kg/ha N/yr, with NO_3^- accounting for about 60% of total N deposited.

If the NADP data are used to estimate deposition off the Louisiana coast, total N deposition would be adjusted upward, primarily because of increased deposition of NH_4^+. NH_4^+ deposition would be expected to be over 2.0 kg/ha/yr (as N), bringing total inorganic N deposition to nearly 5.0 kg/ha/yr. NO_3^- deposition during the spring and summer typically accounts for well over half of the annual deposition, a time of year when prevailing winds are generally from the south. As with most coastal areas, NH_4^+ deposition during the spring and summer would be expected to account for up to about 75% of total annual ammonium deposition. Deposition of NH_4^+ is typically much lower during the fall and winter months.

The AIRMoN-wet station located near the center of Tampa Bay has been operational since about August 1996. The NADP web page currently contains data through June 1997. Using the 11 months of available data and converting to elemental N, the Tampa Bay station indicates total N deposition for the period of about 3.4 kg/ha when weighted to cover an entire year. Given that this estimate was made independently of the NADP estimate, it is probably safe to conclude that coastal deposition of inorganic N via precipitation is less than 4 kg/ha N/yr for much of the Gulf coast.

It should be mentioned that estimates of ammonium deposition calculated from NADP weekly data are biased approximately 15% low, on an annual volume-weighted mean basis, relative to samples collected on a daily basis and are then preserved through chilling or analyzed quickly. Studies by Vet et al. (1989) and others have repeatedly shown that unpreserved weekly samples under-report NH_4^+. Unpublished data by R.S. Artz, NOAA, indicate that this is also the case when NADP weekly data are compared to daily AIRMoN-wet values. Corroboration of this phenomenon is possible through comparison of collocated NADP weekly and AIRMoN-wet data for such stations as State College, Pennsylvania, or Bondville, Illinois, using data posted on the NADP web site.

5.4.2.2 FLORIDA ATMOSPHERIC DEPOSITION STUDY

Results of data collection from the Florida Atmospheric Deposition Study (FADS) were reported by Hendry et al. (1981). Total nitrogen (including organic nitrogen) was measured at 24 locations throughout the state, primarily using bulk (wet plus dry) collectors. Four of the stations used wet/dry collectors; precipitation samples from the wet-side buckets were collected every two weeks. (The dry deposition methodology used in this program is generally unreliable because the polyethylene buckets used are a poor surrogate for most natural surfaces, whether they be water, soil, or biological; thus, the dry deposition estimates are ignored here.) The wet deposition estimates appear to be quite good. Inorganic nitrogen fluxes via wet-only precipitation measured in the FADS study range from 3.2 kg/ha/yr to 4.4 kg/ha/yr, with a mean of 3.9 kg/ha/yr for the entire state, in good agreement with the NADP estimates.

Hendry et al. (1981) also noted that the deposition of inorganic nitrogen in Florida precipitation had apparently increased by approximately a factor of three between the time of an earlier study by Junge (1958, 1963) and the FADS program of 1978–79. No similar increase has been observed in the past 20 years. It is believed that Junge's measurements were reasonably good, but this is probably impossible to prove. Based on values presented for the Gulf coast in Junge (1963), similar differences would be expected along other parts of the Gulf coast.

5.4.2.3 Gulf of Mexico Cruise Data

The Parungo cruise (Parungo and Miller 1988; Parungo et al. 1990) also produced estimates of wet deposition based on 27 precipitation samples, many collected sequentially during about seven individual events. Samples were collected using simple Teflon funnel and polyethylene bottle systems, deployed in a manner to exclude dry deposition. Wet deposition calculated from the concentration and rainfall depth data indicated exceptionally high mean values of 19 kg/ha for NO_3^- and 3.0 kg/ha for NH_4^+ if an annual rainfall of 110 cm is assumed. This translates to an annual loading of total precipitation N of approximately 6.5 kg/ha, well over 50% greater than estimated for along the Gulf coast using NADP data. These values may be fairly accurate. However, given a nearly complete lack of information regarding quality assurance practices, the lack of a good statistical sample, and the fact that samples were captured during the summer, it is difficult to recommend that these values be extrapolated to provide annual estimates.

5.4.2.4 Xalapa, Veracruz, Mexico, Precipitation Chemistry Estimates

Baez et al. (1997) published the results of precipitation chemistry measurements collected between 1993 and 1995. Sampling was performed in Xalapa, Veracruz, on the eastern flanks of the Sierra Madre Oriental facing the coastal prairies of the Gulf of Mexico. Unlike all of the other stations cited in this section, the Xalapa site was well above sea level, located at 1,370 MSL. Still, this station is the only site collecting data for any significant duration located near the Mexican coast. Based on data collected in 1994 and 1995 (1993 data were reported to be about a factor of five lower in deposition and were ignored in this analysis), the total annual loading of nitrogen is estimated to be approximately 3.7 kg/ha, but with a few interesting differences compared to U.S. precipitation. NH_4^+ in the Xalapa samples constitutes about 75% of total N; NO_3^- is relatively much less significant. Also, deposition during the dry season (approximately 26% of total measured precipitation, November through April) is much cleaner than during the summer wet season. When compared to NADP data collected for a similar period near Beeville, Texas, NH_4^+ levels in Xalapa are roughly double those in Beeville, but NO_3^- levels are on the order of 80%. The net effect is that total N deposition appears to be fairly similar between near-coastal areas of central Mexico and southern Texas on an annual basis.

5.4.3 Wet Plus Dry Deposition

As seen from the discussion above, there are few data with which one can confidently estimate total deposition to coastal regions around the Gulf, let alone the open waters. Still, a few estimates are possible. First, wet and dry samples from the Parungo cruise provided an opportunity to estimate ratios of wet and dry deposition of nitrogen compounds over the open Gulf. By scaling the few events collected aboard ship, Parungo et al. (1990) estimated that the wet/dry ratio is approximately 5.8 for NO_3^- and 20 for NH_4^+. Assuming that these numbers are reasonable, and both appear compatible with historical estimates derived from studies of radioactive fallout that typically yield a wet/dry ratio of about 10, the dry deposition of nitrogen compounds can be safely ignored over the open ocean of the Gulf. Unfortunately, it is probably not safe to assume that these estimates are robust, given that the wet deposition values for total N are substantially larger than all of the other land-based estimates, and there is little reason to expect that wet deposition would be greater far downwind from major emission sources.

5.4.4 Model Estimates

In what is perhaps the first real summary regarding the body of nitrogen cycling in the North Atlantic Ocean (Howarth 1996), output from four computer models was compared with values presented from various measurement programs for the North Atlantic Ocean (Prospero et al. 1996). These models produced a value of 1.75 kg/ha of NO_3^- (as N) for the Everglades, Florida, compared with an estimated measured value for the period of 1.70 kg/ha N. For NH_4^+, agreement was almost as good with the models, indicating a loading of 1.3 kg/ha N and the measurements showing 1.36 kg/ha. The range in the model estimates for NO_3^- was about a factor of two, but was only about 10% for NH_4^+.

Prospero et al. (1996) also provided model estimates for the eastern Gulf of Mexico, the coastal region of the Mississippi River, and the western Gulf of Mexico. The estimate for NO_3^- for the Mississippi River region is about 4.2 kg/ha/yr, compared with 2.5 and 2.8 kg/ha/yr, respectively, for the eastern and western Gulf. Reduced nitrogen species (NH_4/NH_3) in coastal areas of the Mississippi River were estimated to be approximately 2.5 kg/ha/yr, compared to 2.0 kg/ha/yr for the western Gulf. No estimate was provided for the eastern Gulf.

5.4.5 Comparisons with Chesapeake Bay and the Open Atlantic Ocean

If we discount the values measured from the Parungo cruise and ignore the local dry deposition contribution to Tampa Bay, the likely range of deposition the Gulf of Mexico is on the order of 3.5–5.5 kg/ha/year, largely depending on the magnitude of the dry fraction. If, as Parungo et al. (1990) assert, dry deposition is nearly negligible over open waters of the Gulf, 3.5 kg/ha/yr would be a reasonable estimate for areas within a few hundred kilometers of the shore. Nearer to shore, however, 5.5 kg/ha/yr is probably a better estimate. For Gulf waters near southern Louisiana, a value approaching 7 kg/ha/yr appears likely.

For purposes of comparison, estimates are also given for direct deposition to Chesapeake Bay. Valigura et al. (1996 and references therein) estimated that wet plus dry deposition of inorganic nitrogen (excluding dry deposition of NH_4^+) is approximately 5.8 kg/ha/yr, just a bit larger than estimated for the Gulf. This assumes that the mean annual wet deposition of NO_3^- is approximately 3 kg/ha/yr, and NH_4^+ is approximately 1 kg/ha/yr. The balance is dry deposition, primarily of nitric acid.

5.4.6 Meteorological Considerations

Because few of these data were generated from samples collected over water (and none over an appropriate length of time following a rigorous quality assurance program), it is assumed that deposition over water, particularly near coastal waters, is similar to that from the continent. Obviously, this assumption typically will break down as a function of distance from land, and as a function of prevailing wind. If the wind does not blow from a land mass, the local land-based measurements become fairly worthless.

To get a good fix on this issue, wind speed and direction were compiled using the 1995 U.S. Navy *Climatic Atlas of the World* for the area south of central Louisiana and are presented in Table 5.13. For the hypoxic area of the Gulf, it is clear that wind with a northerly component is common in the winter and less common in the summer. However, transport from either the east or the west is common any time of year, making it difficult to rule out the influence of atmospheric sources to the hypoxic zone from any of the northern Gulf states or from northern Mexico. These data give no understanding regarding additional complications from sea breezes. The values shown above provide a good first estimate of deposition; however, additional measurements made directly in the hypoxic zone may be considerably different.

TABLE 5.13. U.S. Navy Climatic Atlas of the World (1995) grid point data for latitude 28.0 N, longitude 92.0 W, near Morgan City, Louisiana.

	Wind Direction							
	N	*NE*	*E*	*SE*	*S*	*SW*	*W*	*NW*
July								
Wind Speed (meters/second)	4.32	4.14	4.85	4.84	4.45	4.33	4.30	4.58
Percent of Time	2.76	2.84	12.88	22.16	22.94	13.00	10.70	5.70
January								
Wind Speed (meters/second)	7.86	7.28	6.65	6.01	5.97	5.70	7.82	8.80
Percent of Time	15.74	15.25	18.21	15.27	14.81	5.90	4.45	9.39

CHAPTER 6

Linking Nutrient Flux to Nutrient Inputs and Human Activities

Preceding chapters of this report have discussed the flux of nutrients from the MARB to the Gulf of Mexico and have shown which regions within the MARB contribute abnormally large amounts of nutrients to the Mississippi River system. Nutrient inputs and outputs of significance from all known major human activities and natural sources in the MARB have been estimated and discussed. The goals of this chapter are to examine the relations between nutrient flux and nutrient inputs associated with human activities in the 42 interior basins and to determine which human activities are most significant in contributing nutrients to rivers in the MARB and the Gulf. These goals were approached in several ways. First, a graphic approach was used to compare nutrient inputs and outputs based on observations and data. Second, a mass balance for the entire MARB was constructed to graphically compare the relative importance of nitrogen inputs and outputs. The residuals from the N mass balance (N inputs minus N outputs) were examined through time from 1951 through 1996. Third, a statistical approach was used to relate nutrient outputs from the 42 interior basins (yields) to nutrient inputs and human activities using multiple regression analysis. Results from the regression models are used to estimate the N and P contributions to the Gulf from the major N and P sources.

6.1 GRAPHIC APPROACH

Graphics were developed to visually examine the relations between the amounts of N and P discharged from the 42 interior basins in streamflow (outputs) and the amounts of N and P added to the basins (inputs) from various human activities. Figures 6.1A–F are scatter plots showing the relation between the 1980–96 mean annual N yields from the basins and N inputs from fertilizer, mineralized soil, legumes, animal manure, atmospheric deposition of nitrate (wet and dry), and point-source discharges. The basins have been coded to show whether they are in the Ohio Basin (black), Upper or Middle Mississippi Basin (red), Missouri Basin (blue), or Lower Mississippi Basin (green). The N inputs used in this figure were discussed in chapter 5 of this report and are summarized in Table 5.2. The N yields shown in this figure are from Table 4.3.

These scatter plots show how the N yields vary with each of the six N inputs. The yield–input relation is best for fertilizer N, mineralized soil N, and legume N (Figures 6.1A, B, and C). These are the three largest inputs, covering a range from < 100 to > 7,000 kg/km^2/yr. These three figures show that the largest inputs of N are from fertilizer, mineralized soil, and legumes, and the highest N yields are in the Upper and Middle Mississippi River Basin (red). The relation is somewhat poorer for N inputs from animal manure (Figure 6.1D). The highest manure N inputs are in the Upper and Middle Mississippi Basins. The relation is poorest for N inputs from

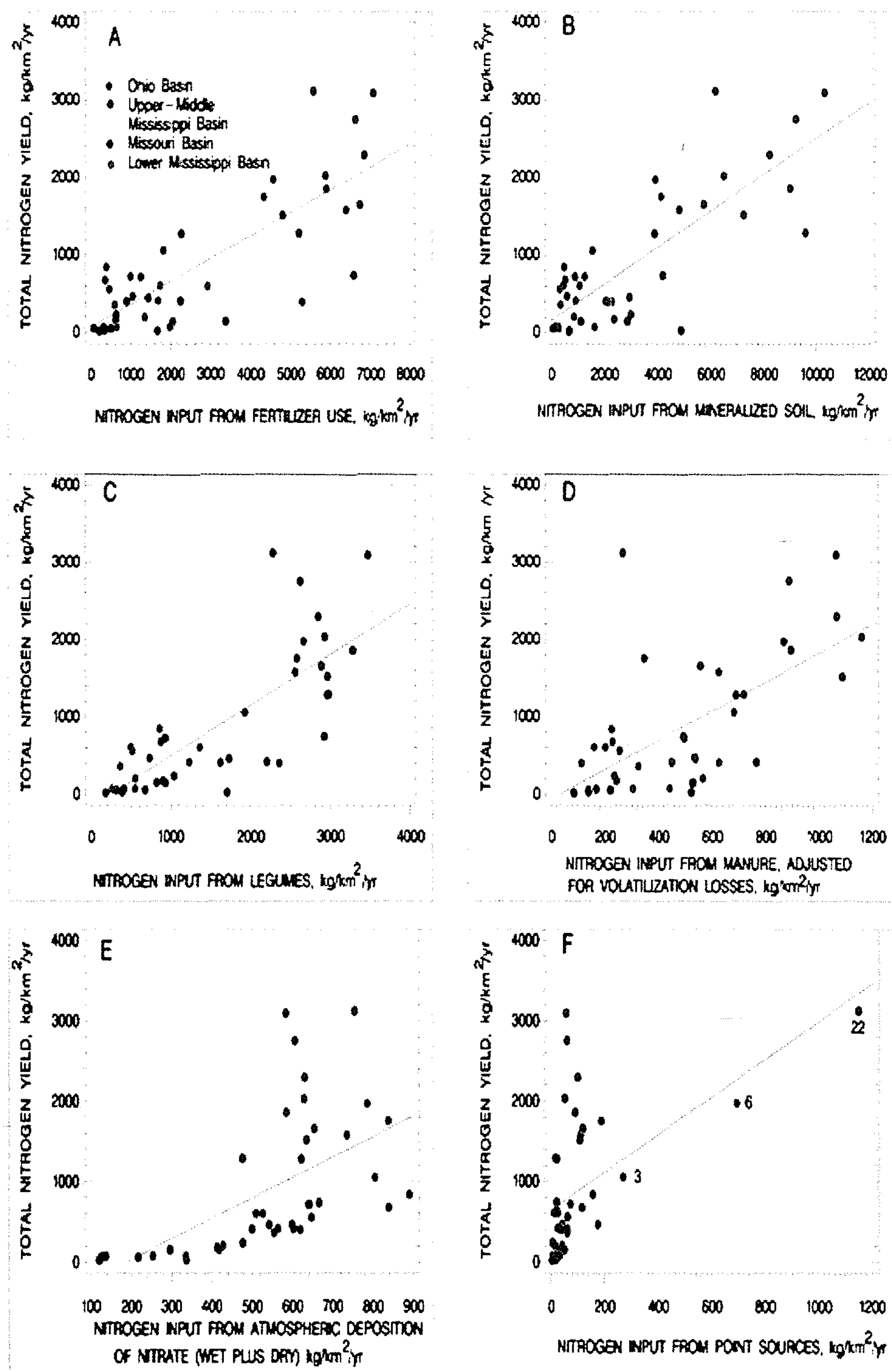


FIGURE 6.1. Scatter plots showing relationships between total nitrogen yield and nitrogen inputs from (A) fertilizer, (B) mineralized soil, (C) legumes, (D) manure, (E) atmospheric deposition of nitrate (wet plus dry), and (F) municipal and industrial point sources.

atmospheric deposition and point sources (Figures 6.1E and 6.1F). The largest N inputs from atmospheric deposition are in the Ohio Basin (black). However, the highest N yields are in the Upper and Middle Mississippi Basins, which have lower atmospheric N inputs. There appears to be a linear trend in the relation between N yield and atmospheric inputs, but the N yields for a number of basins plot far above the trend line (Figure 6.1E). These are basins in Iowa and Illinois (Upper and Middle Mississippi Basin) that have large agricultural inputs of N. This figure indicates atmospheric deposition of N is an important source of N in parts of the Ohio River Basin but is less important in the Upper and Middle Mississippi Basins. As shown in Figure 6.1F, there is very little relation between N yields and point-source inputs, except for three basins with point-source inputs greater than 200 kg/km^2/yr. These basins are the Muskingham (3), Great Miami (6), and Upper Illinois River (22). For the remaining basins, the N yield varies from near 0 to more than 3,000 kg/km^2/yr, with little variation in point-source inputs.

Figure 6.2A shows the relation between the yields of nitrate and organic N from each of the basins and N inputs from point sources. The N yields and point-source inputs for the entire MARB are shown on the right side of the graph for comparison with the individual basins. The height of each bar represents the mean annual total N yield (organic N plus nitrate-N) of the 42 basins for 1980–96, as estimated from the regression models (Table 4.3). The green part of each bar represents the amount of the annual total N yield that occurred as dissolved and suspended organic N. The remainder of the bar (red plus blue portions) represents the amount of the total N yield that occurred as nitrate. The blue part of each bar, which has been overlaid on the nitrate portion of the bar, represents the maximum total N yield that could have been derived from point-source discharges within the basin. The remainder of the N is from nonpoint sources.

For example, the total N yield of basin 3 is about 1,060 kg/km^2/yr. Of this amount, about 760 kg/km^2/yr is nitrate, and the remainder, 300 kg/km^2/yr, is organic N. Point-source N inputs to this basin could account for as much as 270 kg/km^2/yr. The remainder, 790 kg/km^2/yr, is from nonpoint sources. The point-source yields (blue bars) shown in this figure assume no loss of N between the points where the discharges occur and the terminus of the basin. The actual amount of point-source N discharging from each basin may be significantly less than that indicated by Figure 6.2A due to in-stream losses, such as denitrification. If point-source losses are significant, then the yields of N derived from nonpoint sources would be larger than shown in Figure 6.2A.

Figure 6.2A shows that except in a few basins, the point-source inputs comprise only a small part of the annual N yields of these streams. Exceptions include basins 3, 6, 10, and 22. Point-source inputs to basin 6, Great Miami River in Ohio, could account for as much as one-third of the N yield of this basin. Point-source inputs to basin 22, Upper Illinois River in Illinois, which receives discharges from the Chicago area, could account for as much as one-third of the N yield of this river. Point-sources inputs to basin 3, Muskingham River Basin in Ohio, could account for about 25% of the average N yield. The Tennessee River Basin in Kentucky and Tennessee (10) has large N inputs from industrial sources, and the combined municipal and industrial point sources in this basin could account for as much as 40% of the average N yield, assuming in-stream N losses are not significant.

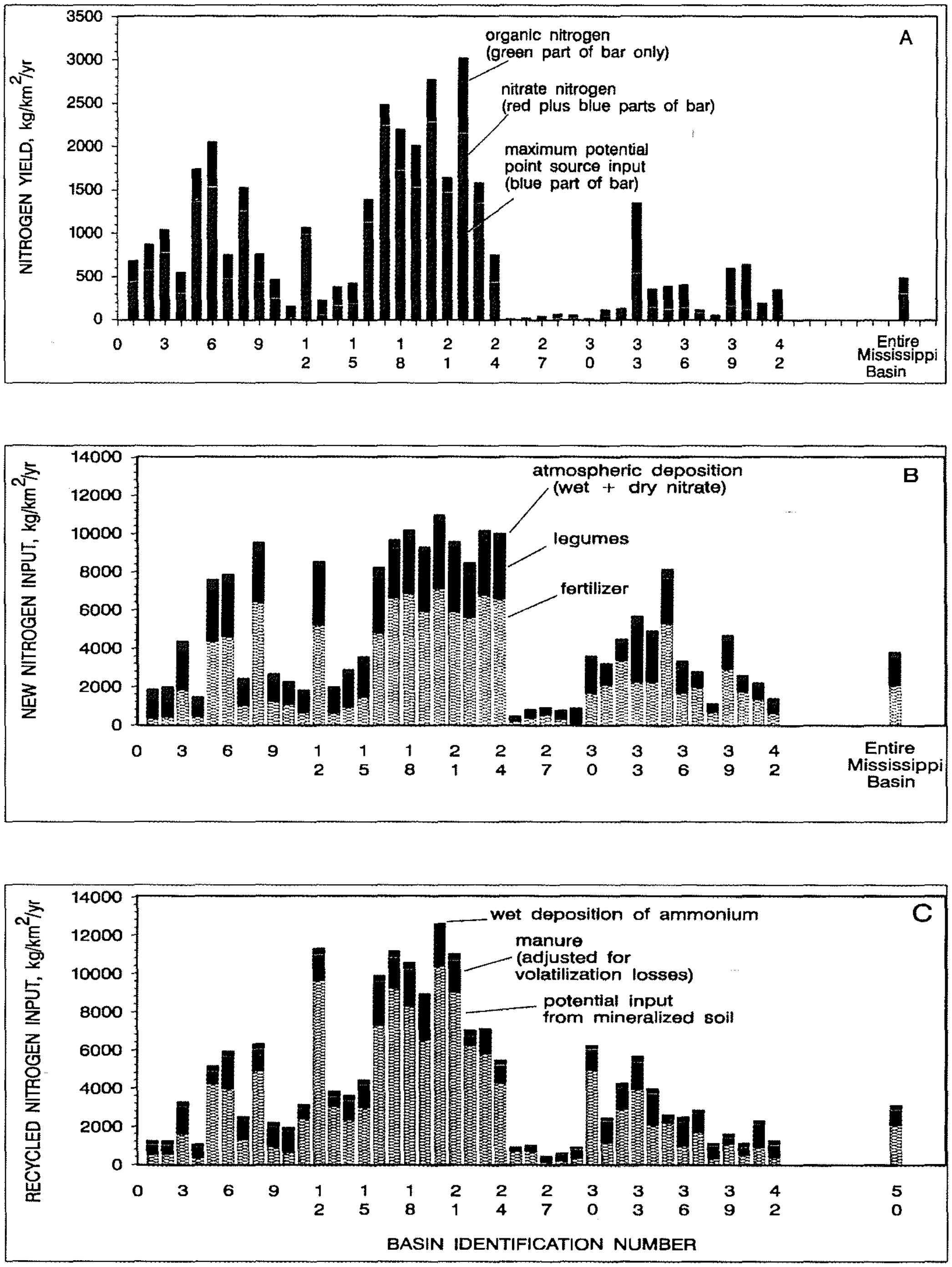


FIGURE 6.2. (A) Nitrogen yields (river outputs from basins) and point-source nitrogen inputs in the 42 interior basins and the entire Mississippi–Atchafalaya River Basin (MARB). NOTE: Heights of the bars show the total nitrogen yields (organic N plus nitrate). Organic N yield is the green part of the bar. The remainder of the bar (red plus blue portions) is nitrate yield. The blue part of the bar shows the maximum amount of the N yield that could be derived from point sources. **(B) Inputs of newly fixed nitrogen to the 42 interior basins and the MARB from fertilizer, N fixation by legumes, and atmospheric deposition (wet and dry) of nitrate. (C) Inputs of recycled nitrogen derived from manure, potential mineralization of soil organic nitrogen and plant residue, and atmospheric wet deposition of ammonium.**

For the entire MARB, municipal and industrial point sources, at a maximum, could only account for about 18% of the mean annual total N yield of the basin (Figure 6.2A). This assumes no in-stream removal of the point-source N, which is unlikely since some of these discharges are to small streams. Expressed in terms of the average annual N flux, point sources could, at the most, comprise about 287,000 of the 1,567,900 metric tons of N discharged annually from the MARB to the Gulf.

The 42 interior basins examined in this assessment comprise about two-thirds of the area of the MARB and are believed to be representative of all point- and nonpoint-source N inputs in the entire basin. They include the inputs from most, but not all, large cities in the basin. Specifically, several large cities discharging N from point sources directly to the Mississippi River are not included at the 42-basin scale. However, these cities are included at the Mississippi Basin scale and are included in the 287,000 metric tons of point-source N discussed above. The point-source N contributions to the Mississippi River are expected to remain relatively constant throughout the year. Consequently, during low-flow conditions point sources would contribute a larger percentage of the N yield of the Mississippi River, and during high flows they would contribute a smaller percentage. If point-source inputs are relatively constant, then the large increases in N flux that occur in the Mississippi River most years during the spring and summer (see Figure 4.1) when streamflows are high must be from nonpoint sources.

Figure 6.2B shows the annual inputs of new N to the 42 interior basins and to the entire MARB from fertilizer, N fixation by legumes, and atmospheric deposition of nitrate (wet plus dry). These inputs are referred to as new N because they represent new amounts of N added to the MARB each year (Jordan and Weller 1996; Howarth et al. 1996). The inputs of N from fertilizer and legumes were calculated from data in the 1992 Census of Agriculture and were presented in Table 5.2 of this report. These inputs have been normalized to drainage area to make it easier to compare N inputs among basins and with N outputs (yields) in Figure 6.2A. Figure 6.2B shows that N from fertilizer is the largest input of new N to most of the 42 basins and to the entire MARB. Fertilizer N accounts for more than half of the new N added annually to these basins and to the MARB. On average, legumes account for about one-third of the new N inputs, and atmospheric deposition of wet and dry forms of nitrate accounts for slightly more than 10%. New N inputs to the 42 basins (Figure 6.2B) are typically three to six times larger than the N outputs (Figure 6.2A), but in general the basins with the largest new N inputs are also the ones with the largest N outputs in streamflow. Also, the basins with the highest fertilizer N inputs are generally the ones with the largest N outputs. These three inputs form part of the pool of inorganic N in MARB soils. This inorganic N pool is subject both to removal by crops and such biochemical processes as denitrification and immobilization in soil organic matter, and to leaching to ground water and streams.

Figure 6.2C shows the annual recycled N inputs to the 42 basins from mineralized soil organic matter and manure (adjusted for volatilization losses of NH_3), and atmospheric deposition of ammonium N. These inputs are referred to as recycled N because they either were already in the basin in the form of soil organic matter or were added to the basin during the year in manure or atmospheric deposition of ammonium N. The manure N is largely derived from the N in fertilizer and mineralized soil N. Likewise, the ammonium N in atmospheric deposition is derived largely from animal manure, which may also have originated from fertilizer or mineralized soil N.

Although mineralization of organic matter in the soil constantly removes N from the soil organic N pool, N is also being returned to the soil organic N pool in the form of plant litter, debris, and manure, and immobilization of inorganic N by soil microorganisms. Recent research (Drinkwater et al. 1998) suggests that cropping systems that use legumes and manure do not deplete soil N, but can actually increase both soil N and carbon. While the recycled N normally is not a new source of N to the basin, it does represent a source of N that can readily be mineralized to inorganic N and leach to streams and ground water as nitrate if not used by crops or denitrified. Thus, from the standpoint of potential sources of N to streams and the Gulf of Mexico, recycled N is just as important a source as the new N.

The mineralized soil N in Figure 6.2C represents the amount of N that could be mineralized to ammonium and nitrate from the pool of organic matter, and microbial biomass in the upper 30 cm of soil during one year, and that could become available for uptake by crops. The mineralized soil N represents the majority of the recycled N. The manure N shown in Figure 6.2C is the amount available after volatilization losses. Typically, more than half the N in manure is lost through volatilization during storage and application. The manure N that is applied to cropland is largely in organic form and must be decomposed to inorganic N before it is available to crops or for leaching to water resources. The ammonium N shown in Figure 6.2C represents the amount of ammonia measured in atmospheric wet deposition (see Table 5.1). Its principal source is manure. Dry deposition of ammonium was not estimated for this assessment. However, the literature suggests dry deposition is a significant source of ammonium (see section 5.1).

As figures 6.2B and C show, the amount of inorganic N potentially available each year from mineralized soil organic matter is comparable to the new N added in fertilizer and is potentially a large source of N to streams. These figures also show that, in general, the basins with the large potential mineralized soil N inputs are also the basins with large fertilizer N input, and the ones with large N outputs (yields) (Figure 6.2A). The data on N inputs and outputs presented in Figures 6.2A–C provide compelling evidence that fertilizer N and mineralized soil N are major sources of N to streams. The N input from legumes is also significant (Figure 6.2B). However, it has been shown that the amount of N removed in harvested legumes, such as soybeans, generally exceeds the amount of N they symbiotically fix from the atmosphere. Additional inorganic N to meet crop needs may be derived from mineralized soil, since soybeans are fertilized less frequently and at lower rates than corn (see section 5.2.3; David et al. 1997). Thus, legumes that are harvested (e.g., soybeans) generally are not net contributors of N to the soil system.

Figure 6.3A shows the yields of P from the 42 interior basins. The height of the bars represents the total P yield. The suspended P yield is represented by the green portion of the bar, and the dissolved ortho P yield is represented by the red. Figure 6.3B shows the amounts of the total P that could be derived from municipal and industrial point sources. The inputs shown here assume no in-stream losses between the source and terminus of the basin; hence, they represent maximums.

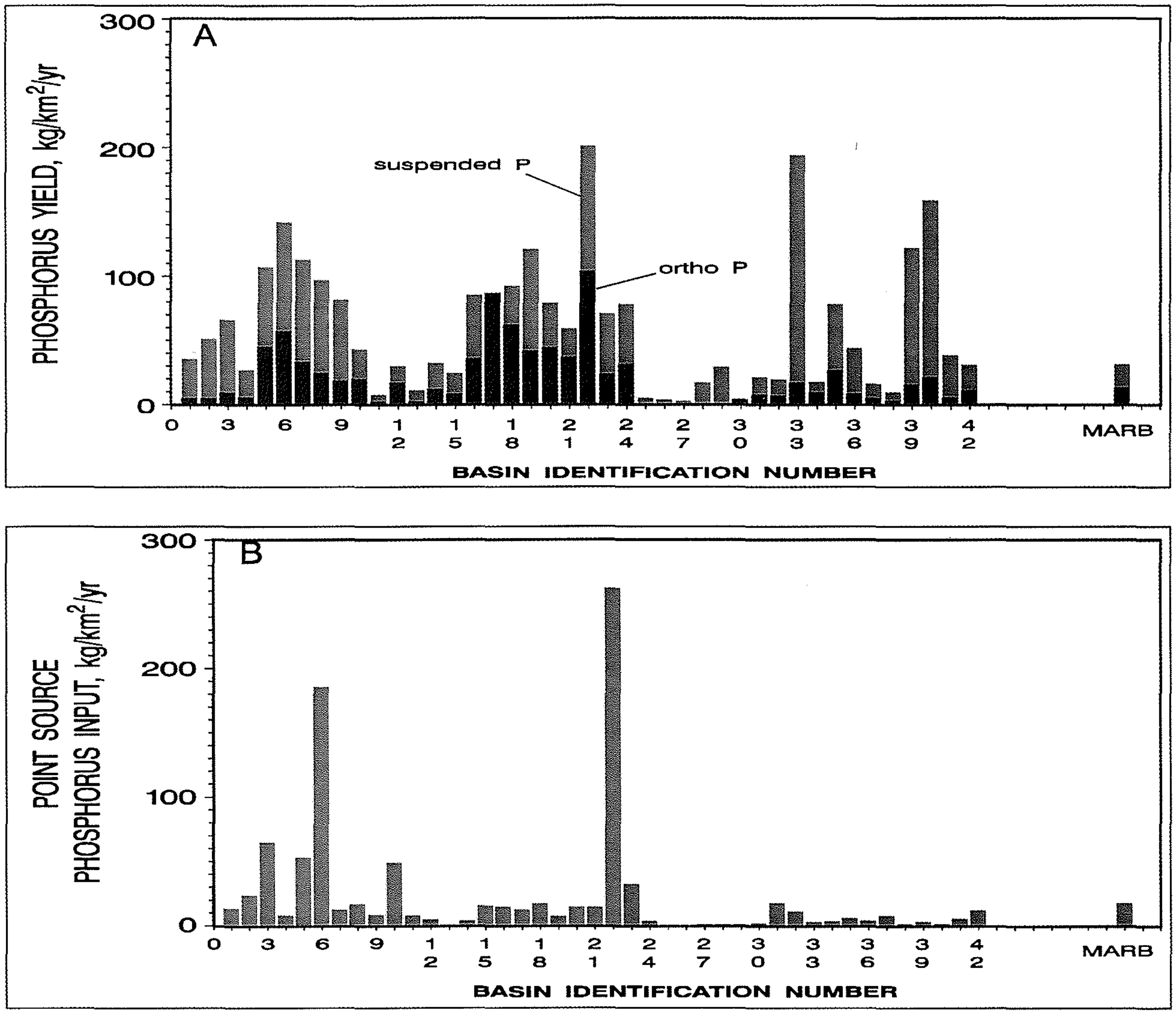


FIGURE 6.3. Bar graphs showing (A) yields of orthophosphate, suspended and total phosphorus and (B) phosphorus inputs from point sources in 42 interior basins and the entire Mississippi–Atchafalaya River Basin.

Several basins, notably the Muskingham (3), Scioto (5), Great Miami (6), Tennessee (10), and Upper Illinois (22), have relatively large point-source inputs of P. These same basins have relatively large point-source inputs of N (Figure 6.2A). In four basins—3, 6, 10, and 22—the reported point-source inputs equaled or exceeded the estimated annual yields of total P for the basins. The reasons for this discrepancy are not known but could include in-stream loss of P, errors in the phosphorus flux estimates, errors in the point-source flux estimates, or all three. Table 4.5 shows that the standard errors in the total phosphorus flux estimates for these basins are about +/- 10%, and Table 5.13 shows the error in point-source estimates of phosphorus inputs could be more than +/- 50%. Thus, estimation errors can easily explain the discrepancy for these four basins. Some of the point-source phosphorus may be temporarily or permanently removed from the streams through biological processes or physiochemical processes, such as adsorption on sediment particles and subsequent deposition of the sediment. In most of the remaining interior basins, point sources represent a relatively small percentage of the total phosphorus yield of the streams. For the entire MARB the maximum point-source inputs of phosphorus (about 59,000 metric tons) are equivalent to about 43% of the 136,500 metric tons of phosphorus discharged annually from the basin to the Gulf of Mexico. This is a maximum value and assumes no losses between the sources and the Gulf, which is highly unlikely.

6.2 Nitrogen Mass Balance

Analysis presented in previous sections of this report indicates a strong linkage between nitrogen flux in the Mississippi River and agricultural activities. In an attempt to examine this linkage more closely, an N mass balance was developed for the MARB. The goals of the mass balance were to (1) examine the relative importance of all significant N inputs and outputs in the MARB, (2) determine how the N balance has changed over the period 1951–96, and (3) determine if there is a relation between changes in the N mass balance and the increased flux of nitrate to the Gulf of Mexico. Unlike N mass balances developed by Howarth and others, (1996), and Jordan and Weller (1996), we have attempted to account for internal recycling of N within the MARB. This was done because our mass balance was developed annually for 45 years, and we wanted to analyze the long-term patterns in the balance. The mass balance was developed for 20 states that comprise the majority of the MARB, largely from data reported annually by the U.S. Department of Agriculture, National Agricultural Statistics Service, and data on fertilizer sales, atmospheric deposition of N, and point sources of N. The mass-balance approach was developed with the assistance of soil scientists and agronomists in the Midwest (Hoeft 1998). Specific details about the sources of the data and the methods used to estimate N inputs and outputs in the MARB were described in chapter 5 of this report.

All known major inputs and outputs of N during 1951–96 in the 20 major states in the MARB are summarized graphically in Figures 5.7 and 5.9. These data were used to develop an N mass balance for the MARB each year during that period. All N inputs and outputs were summed for each year. Inputs included N additions from fertilizer, legumes, atmospheric deposition, manure, potentially mineralizable soil organic N, and point sources. Estimates of atmospheric deposition were not available prior to 1984. Therefore, atmospheric deposition for 1951–83 was estimated as the average of the 1984–90 atmospheric deposition (see Figure 5.7). This may have over-estimated atmospheric deposition inputs in the early part of this period. Point sources, which are minor, are assumed to be constant throughout the period. Outputs included N removal in harvested crops, manure and fertilizer volatilization, plant senescence, denitrification, and immobilization in soil. The residual N was calculated as the N inputs minus the N outputs for each year. The residual includes the N leached to ground water and discharged from the MARB to the Gulf of Mexico. It also includes all errors in N inputs and outputs. Unfortunately we were not able to develop an estimate of the magnitude of these errors. The largest errors are likely to come from mineralization of soil organic N and immobilization. The implications of potential errors in these variables in the N mass balance are provided in the following discussion.

Mineralization of soil organic N was estimated from the organic matter content of the upper 30 cm. (12 in.) of soil as given in the STATSGO data base (USDA 1994; Burkart and James 1999; also see section 5.2.4). The soil organic material was assumed to contain 3% N and to mineralize at a constant rate of 2% per year, producing a constant annual inorganic N input from the soil. However, the assumed constant mineralization rate is almost certainly not true over the 45-year period of our mass balance. Changes in tillage practices in recent decades and variations in soil moisture and temperature would affect mineralization rates. Also, the increased use of fertilizer is reported to increase soil mineralization rates (David et al. 1997; Jenkinson et al. 1985) and could also increase the N content of the soil organic matter through increased immobilization of N in microbial biomass.

Research using ^{15}N-labeled fertilizer indicates that application of fertilizer at high rates can lead to a buildup of an easily mineralizable pool of soil organic N (Stevens et al. 1993). Recent research in Illinois (Hoeft 1999) suggests that the N immobilized from fertilizer by soil microbes mineralizes the following year as much as seven times faster than the 2% per year use in our soil mineralization calculations. Figure 5.9 shows that the estimated immobilization of N increased from about 0.5 million metric tons/yr in 1951 to 3 million metric tons/yr in 1996. These estimates account for the increased use of fertilizer during this period, but not any increase in mineralization rates. In addition, the amount of plant residue that remains after crop harvest has most likely increased with increased crop yields and changes in tillage practices. This recycled plant residue and immobilized N becomes part of the soil organic N pool and is available for mineralization to nitrate in subsequent years. We have accounted for immobilization in the output side of our mass balance, but have not accounted for any mineralization of the immobilized N in our budget. If this input is significant, then our mass balance underestimates N inputs by not including the immobilized N as an additional source. Mineralization of additional N from this source would increase the input side of the N balance and could significantly increase the N residuals.

N inputs, outputs, and residuals from the mass balance calculations are plotted against time (years) in Figure 6.4A for the early 1950s through 1996. The figure shows that both the inputs and outputs have increased dramatically since about 1951. Total N inputs have increased from about 13 million to nearly 22 million metric tons/yr, and total N outputs have increased from about 10 million to about 21 million metric tons/yr. Outputs have increased at a faster rate than inputs. From 1951 to 1971 N inputs generally were 3–4 million metric tons/yr greater than outputs, but since 1978 inputs generally are 1–2 million metric tons/yr greater than outputs. The change in the relation between N inputs and outputs is shown more clearly in the residuals (Figure 6.4A), which declined slightly from about 3.5 to 3.0 million metric tons/yr between 1955 and 1970, but then declined rapidly from about 3 to about 1 million metric tons/yr between 1969 and 1978. Essentially no change in residuals has occurred since 1980, although they have become highly variable from year to year. The residuals decreased most rapidly when fertilizer use and N outputs in harvested crops increased most rapidly. Fertilizer use and N output in harvested crops leveled off around 1980, at about the same time the residuals leveled off. A decrease in the N residuals with time may be an indication of increased efficiency in use of N in crop production, or it may just be the result of underestimating inputs, such as mineralization, or overestimating N outputs.

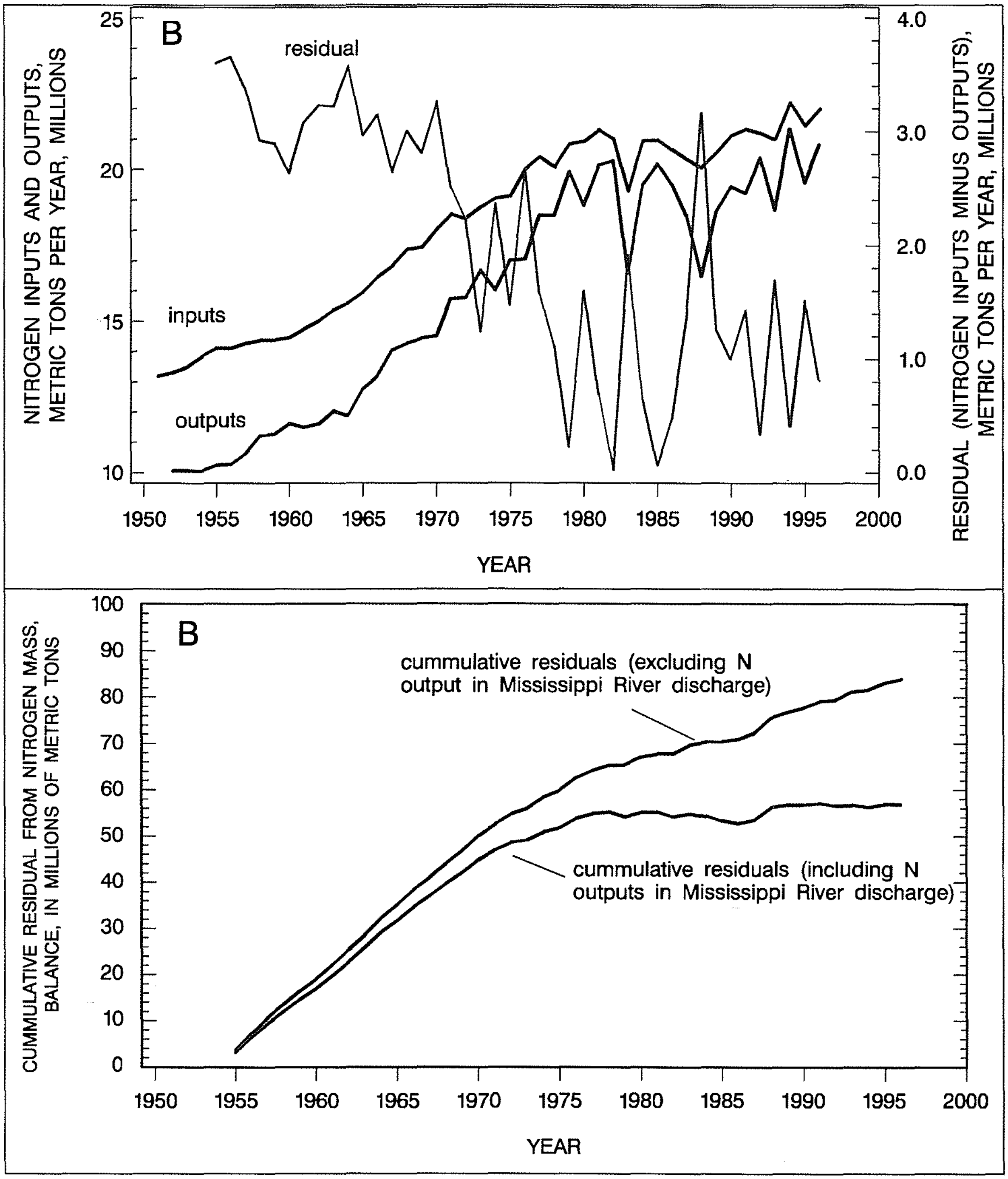


FIGURE 6.4. Graphs showing (A) the annual nitrogen inputs and outputs for the Mississippi–Atchafalaya River Basin from all major sources, and annual nitrogen residual (inputs minus outputs) from nitrogen mass balance for 1951–96. (B) Cumulative nitrogen residual for 1955–96.

Figure 6.4B shows the long-term trend in the cumulative residuals from the N balance for 1955–96. The upper line in the plot is the cumulative residual from the N mass balance, excluding the nitrate discharged from the MARB in streamflow. The bottom line is the cumulative residual with the nitrate discharged from the MARB included as an output. The difference between the two lines is the cumulative nitrate discharge to the Gulf of Mexico The pattern in these plots suggests that there was a constant relation between N inputs and outputs before about 1970. Between 1970 and 1978 this relation changed, and since 1978 a new relation has developed with N inputs and outputs being more equal.

One interpretation of the residuals pattern in Figures 6.4A and B is that during the 1950s and most of the 1960s the N inputs and outputs were at or near a steady state, but inputs exceeded outputs. From the late 1960s to about 1980, rapid changes occurred in the N balance as a result of a rapid increase in fertilizer use and increased crop production (see Figures 5.7 and 5.9). Fertilizer use more than tripled from about 2 million to nearly 7 million metric tons/yr, and N output in crops increased from about 6 million to more than 9 million metric tons/yr. Changes also occurred in agricultural policies and practices that increased crop production and efficiency. Acreage limits established by the federal government were removed from corn and grain production, use of herbicides on corn and soybean increased, producing increased crop yields, and new hybrids crop species also expanded. In some states, such as Illinois, there was a shift away from livestock production to more corn and soybean production (Hoeft 1998).

Crop yields increased as a result of these changes, and by about 1980 the relation between inputs and outputs was again constant (Figure 6.4B). The leveling off of fertilizer input, crop outputs, and the N residuals may indicate that a new steady-state condition was established about 1980. Figure 6.4B (bottom plot), which includes the output of nitrate in streamflow to the Gulf, indicates that the N inputs and outputs for the MARB have been approximately equal and at a steady state since about 1980. Also since about 1980, the trend in nitrate flux to the Gulf has leveled off (Figure 6.5) and has become highly variable. The large degree of variability in both the N residuals and the nitrate flux to the Gulf (Figure 6.5) is an indication of the high degree of sensitivity of these variables to climatic conditions, which affect both crop yields and nitrate leaching to streams and ground water. This variability may also be a consequence of the much larger annual inputs, outputs, and storage of N in the MARB during the last two decades. The residuals associated with the larger inputs and outputs are likely to be more sensitive to crop-growing conditions, especially weather, than when inputs and outputs were lower. In years with good growing conditions and good crop production, large amounts of N are removed in the crops and the residuals are low, indicating that the N outputs are about equal to the N inputs. The N outputs actually exceed N inputs during some years, if the N flux in streamflow to the Gulf is added to the output. This is possible if soil mineralization is higher than the estimated constant rate of 2% per year and if crops use the additional soil N. Crops may also use N added to the soil system in prior years, but not used due to excess inputs or poor growing conditions during those years. This, too, could result in the annual N outputs being larger than the N inputs.

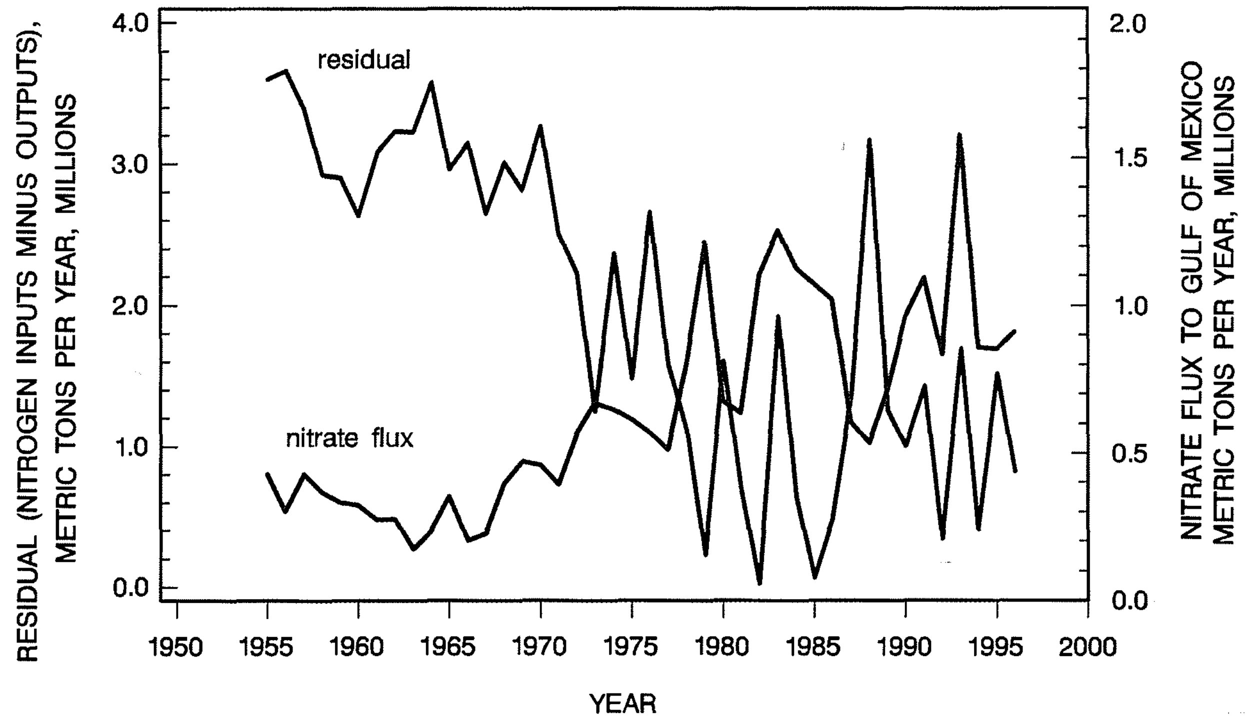


FIGURE 6.5. Graphs showing the relationship between the annual nitrogen residual from mass balance and annual flux of nitrate to the Gulf of Mexico for 1951–96.

Years with good crop yields and associated small N residuals generally are years with above-normal precipitation and high streamflow (Figure 6.6). However, the higher precipitation also results in increased infiltration and leaching of nitrate from the soil profile to surface and ground water and higher fluxes of nitrate to the Gulf. Examples of years meeting these conditions are 1972–74, 1979, 1982–86, and much of the 1990s (Figure 6.6). During drought years or years with poor growing conditions, crop production is down, residuals are larger (inputs >> outputs), but nitrate flux to the Gulf is also low due to reduced rainfall and less leaching of nitrate from the soil profile. Examples of years having these conditions are 1976–77, 1980–81 and 1987–88 (Figure 6.6). Much of the period from 1955 to 1970 also fits these criteria. The implications of this relation are that if precipitation is above normal in future years, crop yields will be good, but nitrate flux to the Gulf will also be high or higher than at present. Conversely, if the climate becomes drier, nitrate flux to the Gulf will decrease, and crop yields will likely be lower. The year-to-year variability in nitrate flux to the Gulf will remain high because of the large inputs and storage of N in the MARB.

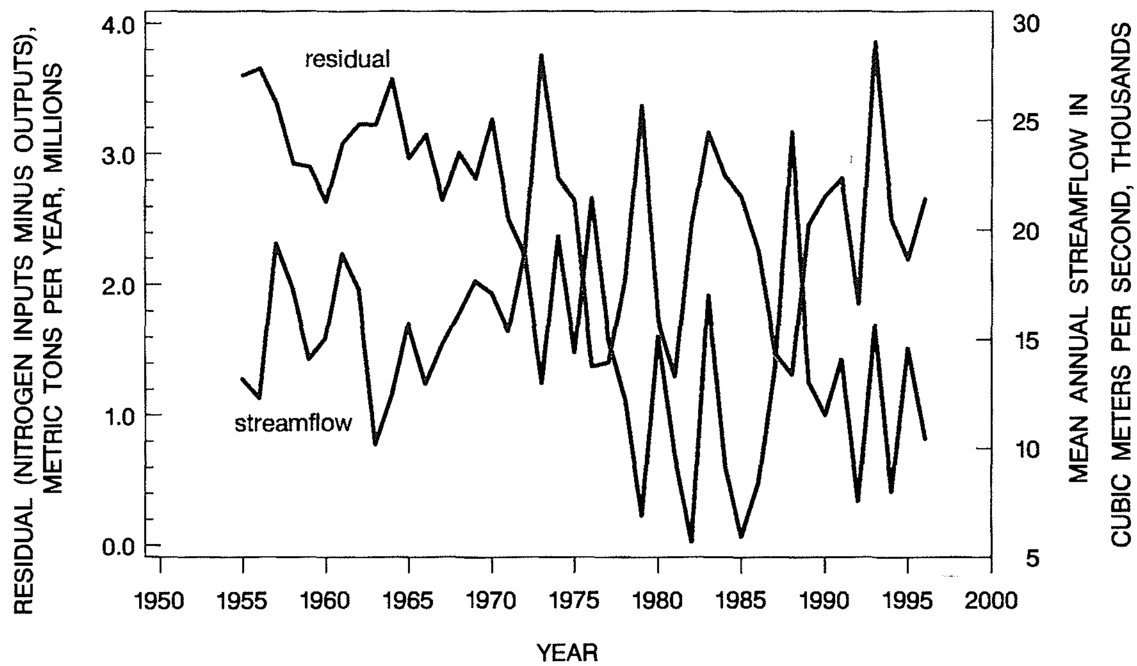


FIGURE 6.6. Graphs showing the relationship between the annual nitrogen residual from mass balance and the average annual streamflow from the Mississippi–Atchafalaya River Basin to the Gulf of Mexico.

A long-term average mass balance for the MARB for the period 1980–96 is presented in Table 6.1. The average mass balance results are also presented in Figure 6.7 in the form of a bar graph. The average annual N inputs to the MARB are about 21 million metric tons, of which about 60% is new N added to the basin each year, and the remainder represents recycled N. Fertilizer N accounts for slightly more than half of the new N inputs. N fixation by legumes contributes about 35% of the new N, and atmospheric deposition of nitrate (wet and dry forms) accounts for about 12%.

Mineralization of the soil organic N is the largest source (~75%) of recycled N, or N that was already in the system. Mineralized soil organic N is estimated to contribute about 6.5 million metric tons of inorganic N to the basin annually, an amount equivalent to the current annual input from fertilizer. However, as previously discussed, there is much greater uncertainty in the estimates of N from the soil than from fertilizer. Animal manure is another input of recycled N largely derived from crops produced in the basin. On average, more than half the N in animal manure is lost through volatilization, mostly as ammonia, during storage and application. The manure value in Table 6.1 represents the amount of N in applied manure after volatilization losses. N in manure represents about 15% of the total recycled N input. Atmospheric wet deposition of ammonia N, which is presumed to have originated within the basin, mostly from volatilization of ammonia from manure, represents about 7% on the total recycled inputs. Inputs of N from municipal and industrial point sources represent about 3% of the total recycled N inputs and are small in the overall budget. However, because they go directly into streams they may constitute a significant fraction of the N transported to the Gulf.

TABLE 6.1. Nitrogen mass-balance data for the Mississippi–Atchafalaya River Basin for 1980–96 (except as noted for atmospheric deposition and point sources). NOTE: Units are thousands of metric tons/yr.

Total Inputs	**20,931**
Total New Nitrogen	**12,233**
Fertilizer	6,495
Total Legumes	4,327
Soybeans	*1,616*
Alfalfa and other hay	*2,358*
Pasture and rangeland	*353*
Atmospheric Deposition (1990–96 average) (includes wet + dry nitrate and organic nitrogen)	1,411
Total Recycled Nitrogen	**8,698**
Manure (total adjusted for volatilization losses)	1,296
Potentially Mineralizable from Soil	6,464
Atmospheric Deposition—Wet Ammonia	651
Point-Source Inputs to Streams	287
Municipal (1996 data)	*201*
Industrial	*86*
Total Outputs	**20,869**
Atmospheric Deposition on Gulf (~500 kg/km^2/yr) **for an Arbitrary Area of 30,000 km^2** (twice the size of the hypoxic zone)	15
Volatilization Losses	**1,621**
Manure	1,488
Fertilizer	133
Crops and Pasture	**9,658**
Harvested Crops	8,309
Corn grain and silage	*2,360*
Soybeans	*3,071*
Alfalfa and hay	*1,892*
Wheat	*782*
Sorghum grain and silage	*204*
Pasture	1,349
Plant Senescence	**3,326**
Denitrification from Cropland Soil	**1,704**
Immobilization in Soil Organic Matter	**2,978**
Mississippi-Atchafalaya River Discharge (1980–96 average)	**1,567**
Residual (Inputs—Outputs) (0.3 % of inputs for N)	**62**

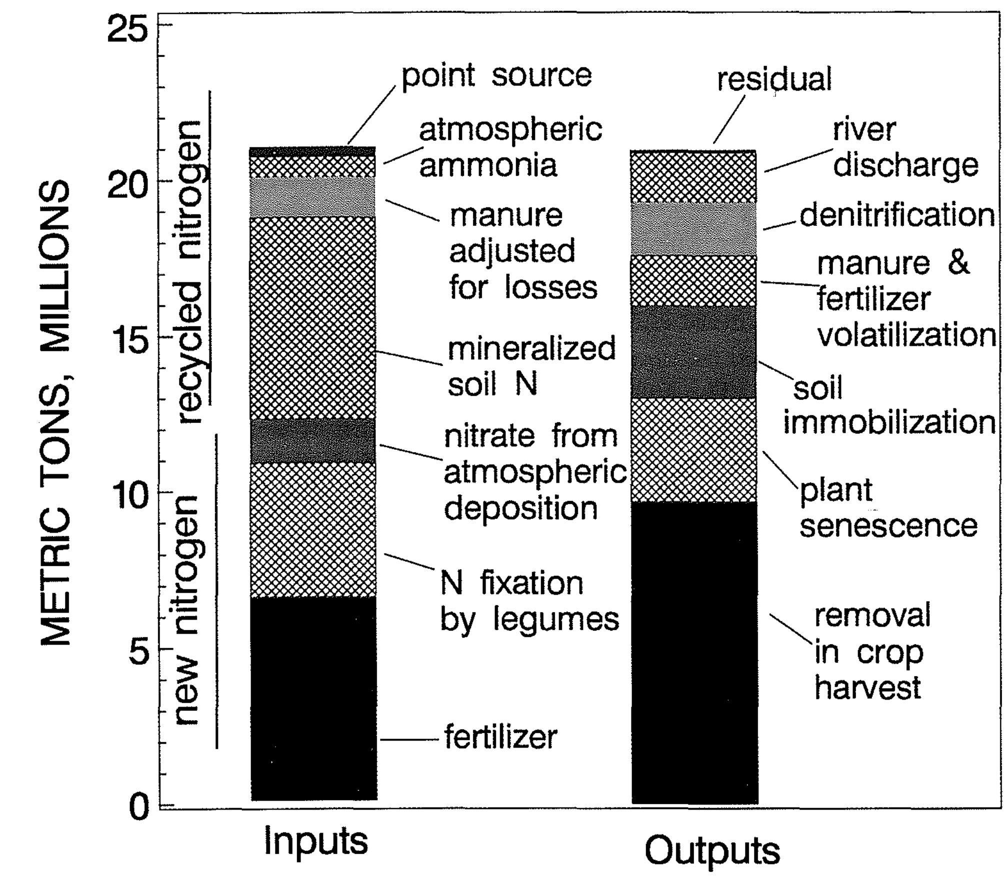


FIGURE 6.7. Bar graphs showing the average nitrogen mass balance for the Mississippi–Atchafalaya River Basin for 1980–96. NOTE: Mass balance includes estimates of all inputs and outputs known to be significant. Atmospheric deposition of nitrogen on the Gulf of Mexico is too small (15,000 metric tons) to be shown.

The estimated average annual N output from the MARB is nearly 21 million metric tons/yr and is about equal to the N input. The largest output is N removal in harvested crops and pasture. This amounts to about 9.6 million metric tons/yr, or 46% of the total outputs, and is nearly 50% larger than the fertilizer inputs. Other outputs, in order of importance are plant senescence (16%), immobilization of N in soil organic matter (14%), denitrification (8%), and manure and fertilizer volatilization (7.8%). Losses of N in stream discharge from the MARB to the Gulf are about 7.5% of the total N outputs and are a significant part of the N balance for the basin. Direct deposition of N on a 30,000-km^2 region of the Gulf is less than 0.1% of the N output (Table 6.1) and equal to about 1% of the MARB discharge of total N to the Gulf.

The N mass balance was useful in examining the relations between N flux in the Mississippi River and agricultural activity in the basin. There is a definite linkage. However, much more analysis, and refinement of the mass balance—especially the mineralization, immobilization, denitrification, and plant senescence components—are needed to better understand these linkages. This analysis, which will require a collaborative approach involving hydrologists, soil scientists, agronomists, and statisticians, could not be done within the time frame and constraints of this assessment.

6.3 Regression Models

Multiple-regression analysis was used in an attempt to determine which inputs and which human activities were the most important contributors of N and P to the MARB and the Gulf. Models were developed using the estimated nutrient inputs and nutrient yields for the 42 interior basins, and were applied to the entire MARB. The following explanatory variables were considered in the regression models for N: fertilizer N, legume N, atmospheric deposition of wet plus dry nitrate N, mineralized soil N, manure N, point sources of N, and basin runoff. For P, the variables considered were: fertilizer P, manure P, point sources of P, and basin runoff. The source of the N and P input data was the 1992 Census of Agriculture data in Tables 5.2 and 5.3, and the basin runoff and N and P yield data were the 1980–96 averages in Tables 4.3 and 4.5. The nutrient inputs and outputs for each basin were normalized by dividing them by the basin area. Multiple-regression models were developed using the SAS Reg procedure (SAS Institute 1990b). Regression diagnostics and residuals were examined to ensure the validity of the results.

6.3.1 Nitrogen Yield Models

Multiple-regression models were developed to relate the yields of total N and nitrate to the normalized inputs of N in the 42 interior basins. Model results were used to help determine which N inputs were the most significant contributors to the N yields of these basins and to the Gulf Multiple-regression analysis proved to be problematic because of the high degree of correlation between many of the explanatory variables, which presented problems in developing a regression model. For example, there was a strong relation between N input from fertilizer and N input from mineralized soil organic matter ($R^2 = 0.73$). Each was highly significant ($p < 0.001$) and about equally important as an independent variable in regression models if the other was not in the model. However, including both variables in a model caused problems with variance inflation, because both were apparently attempting to explain the same variation in total N yields. This problem was avoided by summing the N inputs from fertilizer and mineralization of soil organic N for each basin into a single variable, which will be referred to as the fertilizer–soil N pool. The model response to this new variable reflects the combined effects of both soil and fertilizer N inputs. Unfortunately, N inputs from fertilizer and soil are so closely interrelated that the individual effects of each source could not be separated with the multiple regression approach.

In addition, preliminary results showed that some of the variability in the total N yield could be explained by the variability in runoff from the basins. In general, as runoff increased, so did the total N yield. As a result, runoff was included in the regression model, even though it was not directly a source of N. There was also a strong relation between basin runoff and atmospheric deposition of nitrate ($R^2 = 0.65$). The highest atmospheric deposition of nitrate occurred in the Ohio River Basin (see Figure 6.1E), which also has the highest rainfall and runoff. Atmospheric deposition of nitrate was significant in the regression model if runoff was not included (p

< 0.01). However, the addition of runoff to the model made atmospheric deposition statistically insignificant ($p = 0.66$).

The variables used in the initial total N model were N inputs from the fertilizer–soil N pool (one variable), legumes, manure (adjusted for volatilization losses), atmospheric deposition of nitrate (wet and dry), point sources, and runoff. Since the primary goal of the regression analysis was to determine the relative contributions of the various N sources to the N flux to the Gulf, all input variables, except atmospheric deposition, were retained in the model. Atmospheric deposition of nitrate was not significant at the 0.5 probability level and was excluded. However, because of the strong correlation of atmospheric N with runoff, its effects inputs are represented in the model by runoff, as are other unmeasured N inputs, such as ground-water discharge and soil erosion. Parameter estimates for this model, units, and standard errors appear in Table 6.2. The final model with five explanatory variables is presented in equation 6.1, below. The model has an R^2 of 0.88, indicating that it explains 88% of the variability in total N yields.

(6.1) Total nitrogen yield = -384 + 0.134* (fertilizer-soil N pool) + 1.304* (point source) + 0.395* (manure) + 11.9* (runoff) - 0.115* (legume).

A regression model was also developed for nitrate N yield, using the same approach discussed above for total N yield. The model selected contained the same explanatory variables as the total N model. Results for the nitrate yield model appear in Table 6.2 and in equation 6.2, below:

(6.2) Nitrate yield = -358 + 0.14* (fertilizer-soil N pool) + 0.983* (point-source N) + 0.391* (manure N) + 7.21* (runoff) - 0.212* (legume N).

TABLE 6.2. Regression model results for total nitrogen[1] and nitrate[2] N yields from the 42 interior basins.

Independent Variable	Units	Mean Value for 42 Interior Basins	Parameter Estimate		Standard Error		p Value	
			Total N	*Nitrate N*	*Total N*	*Nitrate N*	*Total N*	*Nitrate N*
Intercept	kg/km²/yr		-384.0	-358.0	127.0	115.0	0.004	0.003
Fertilizer-Soil N Pool	kg/km²/yr	5,853	0.134	0.140	0.024	0.022	0.001	0.001
Point-Source N	kg/km²/yr	99	1.304	0.983	0.276	0.249	0.001	0.001
Runoff (represents atmospheric deposition, ground water, erosion, etc.)	cm/yr	28	11.900	7.220	3.110	2.810	0.001	0.014
Manure N (adjusted for volatilization losses)	kg/km²/yr	498	395.0	0.391	0.259	0.234	0.140	0.104
Legume N	kg/km²/yr	1,588	-0.115	-0.212	0.122	0.110	0.350	0.062
Atmospheric Deposition of Nitrate (wet plus dry)	kg/km²/yr	532	This variable was not used in the model. It is included in the runoff variable.				> 0.5	> 0.5

[1] *Model $R^2 = 0.88$; mean value of total N yield = 877 kg/km²/yr; root mean square error = 322 kg/km²/yr.*
[2] *Model $R^2 = 0.85$; mean value of nitrate N yield = 619 kg/km²/yr; root mean square error = 291 kg/km²/yr.*

Both models (equations 6.1 and 6.2 and Table 6.2) indicate that the fertilizer–soil N pool is the most important source of total N and nitrate N transported from the 42 interior basins. The combined inputs of fertilizer and soil N to the basins are large (see Figure 6.2 and mean value in Table 6.2), and the regression coefficients indicate that on the average 13–14% of this input may be transported in streamflow. For point sources, essentially 100% of the input is transported out of the basins in streamflow. This is indicated by the parameter coefficients in equations 6.1 and 6.2, which are near unity. Both models indicate that basin runoff is a significant predictor of N yields. However, runoff is not a source of N; rather, it represents undefined sources of N not in the model, including atmospheric deposition of N (see discussion at the beginning of this section), discharge of nitrogen from the ground water system, and perhaps N in soil erosion. The parameter coefficient in equation 6.1 suggests that on average, 1 cm of runoff transports about 11.9 $^{+}/_{-}$ 3.1 kg/km^2/yr of total N to streams from undefined inputs. The regression coefficients for legume N inputs are negative in both the total N and nitrate regression models, and the models have negative intercepts.

The negative coefficient for legume N inputs in the total N and nitrate regression models is puzzling at first. However, the following explanations suggest that legumes contribute little or no N to the Gulf of Mexico:

- First, in the total N regression model the legume N regression coefficient is not statistically significant ($p = 0.35$). But, it was retained in the model so that the total N and nitrate models would have the same variables.
- Second, the legume N inputs for the 42 basins are highly correlated ($p < 0.001$) with N inputs from fertilizer, soil, and manure, suggesting possible interactions in the regression models. For example, when the legume N input was entered into a nitrate regression model with either fertilizer or soil N input, the legume N regression coefficient was not statistically significant ($p > 0.35$). However, when legume N input was used in the nitrate yield model with the combined fertilizer–soil N input variable, it was significant ($p = 0.06$). The explanation for this must lie in the interaction among the legume–soil–fertilizer N inputs and nitrate yields in the regression model. In any case, the regression model results indicate that legumes make little or no contribution to the total N and nitrate yields in the MARB.
- Third, the data compiled for this assessment show that legume N outputs estimated for the MARB and the 42 interior basins significantly exceed the legume N inputs (see Table 6.1). For soybeans, the N output is about twice the N input from atmospheric N fixation. Thus, the net legume N inputs to these basins are negative, which means a large amount of N is taken from the soil N pool and removed in the harvested legume crops. If legumes were not harvested, but left on the cropland and the N returned to the soil, the net legume N inputs would be positive.
- Still another factor could be the corn–soybean rotation practice followed throughout the Corn Belt. In this practice, soybean is planted in a field one year, and corn is planted in the field the following year, because the residue from soybean crops provides a rotation benefit to corn crops. Typically, little or no fertilizer is applied to soybean crops. Thus, when soybean is grown, the N input from fertilizer is significantly reduced. This may indirectly contribute to a decrease in N inputs to streams and reduced N yields.

The negative intercept in equations 6.1 and 6.2 is believed to represent N losses and unmeasured N outputs. These include in-stream losses from denitrification within the interior watersheds and temporary or permanent storage of N in stream sediments and on floodplains. Denitrification is probably a major sink for nitrate in small watersheds and wetland areas within the interior basins, whereas it is less significant in large rivers. In small basins there is opportunity for much longer contact time between the overlying water column and stream sediments than in large streams. This provides more opportunity for denitrification to occur at the water–sediment interface, where anoxic or low-oxygen conditions can occur. The negative intercept may also be caused in part by unmeasured stream transport of N that has been assimilated into plant and animal biomass. Nitrogen transported in particles larger than about 2 millimeters escapes collection in water samples and, thus, is not measured or included in the yield estimates. Finally, the equation intercepts are not precisely known, as indicated by the large standard error of > 30%.

Since the 42 interior basins generally represent the entire MARB, the parameter coefficients in equations 6.1 and 6.2 can be applied to the area normalized N inputs to the entire MARB with a reasonable degree of confidence. These results can be used to estimate the relative contributions of each input source to the N yield of the MARB and the N flux to the Gulf of Mexico. Results of these estimates for total N are presented in Table 6.3.

TABLE 6.3. Estimated contributions of nitrogen input sources to the total nitrogen yield of the Mississippi–Atchafalaya River Basin and total nitrogen flux to the Gulf of Mexico.

Total Nitrogen Input Source	Normalized Input to Entire MARB	Coefficient from Regression Model 6.1	Contribution to MARB Yield *(kg/km²/yr)*	Contribution to Total N Flux to Gulf *(percent)*
Fertilizer–Soil N Pool	4,039 kg/km²/yr	0.134 +/- .024	541 +/- 97	50 +/ -9
Municipal and Industrial Point Sources	89 kg/km²/yr	1.304 +/- 0.276	116 +/- 25	11 +/- 2
Other Inputs Represented by Runoff (including atmospheric deposition, ground water, soil erosion)	22 cm/yr	11.9 +/- 3.11	262 +/ -68	24+ / -6
Manure (adjusted for volatilization losses)	404 kg/km²/yr	0.395 +/- 0.26	160 +/- 105	15 +/- 10
Legumes	1,348 kg/km²/yr	-0.115 +/- 0.122	-155 +/- 164	0
Predicted Total N Contributions from All N Sources				1,079+/-229 kg/km²/yr
N Losses and Unmeasured Outputs (model intercept)				-384 +/-127 kg/km²/yr
N Losses (removal by legumes)				-155+/-164 kg/km²/yr
Total N Yield of the MARB Predicted by Model 6.1				540+/-198 kg/km²/yr
Total N Yield of MARB Estimated in Table 4.2				489+/- ~25 kg/km²/yr

Application of regression equation 6.1 to the entire MARB indicates that about 1,079 kg/km²/yr of total N is derived from input sources in the MARB. About 384 kg/km²/yr (model intercept) of this input is lost to undetermined sinks in the MARB, such as denitrification, unmeasured outputs, and storage. In addition, it is estimated that legumes decrease total N yield by about 155 kg/km²/yr. However, this value is very uncertain because of the high standard error for the regression coefficient. Reasons for the decrease in yield attributed to legumes were previously discussed.

The model predicts the total N yield of the entire MARB to be about 540 kg/km^2/yr, which is close to the total N yield estimate of 489 kg/km^2/yr developed from flux data discussed in chapter 4 and summarized in Table 4.2. These results indicate that about 50% of the total N flux from the MARB to the Gulf is derived from the fertilizer–soil N pool. Point sources are estimated to contribute about 11% of the total N, which is about half the maximum potential contribution from point sources shown in Figure 6.1A and discussed in section 6.1. Animal manure may contribute about 15% of the total N flux to the Gulf, although there is considerable uncertainty about this number (see Table 6.3). About 24% of the total N is estimated to be derived from sources not in the model but represented in the model by runoff. These sources include atmospheric deposition, groundwater discharge to streams, and perhaps N contained in sediment transported into streams by soil erosion. It should be noted that N input from ground water and represented in the model by runoff is largely derived from agricultural activities. It can take months to years before the N that leaches to ground water is transported into streams, and ground water can continue to contribute N to streams long after all N sources are removed.

The contributions of N sources to the nitrate yield of the MARB and nitrate flux to the Gulf were estimated with equation 6.2 in the same manner as total N. The results, shown in Table 6.4, indicate that about 969 kg/km^2/yr of nitrate is derived from sources within the MARB.

TABLE 6.4. Estimated contributions of nitrogen input sources to the nitrate–nitrogen yield of the MARB and nitrate–nitrogen flux to the Gulf of Mexico.

Total Nitrogen Input Source	Normalized Input to Entire MARB	Coefficient from Regression Model 6.2	Contribution to MARB Yield *(kg/km^2/yr)*	Contribution to Total N Flux to Gulf *(percent)*
Fertilizer–Soil N Pool	4,039 kg/km^2/yr	0.14 +/- 0.022	565 +/- 89	58 +/- 9
Municipal and Industrial Point Sources	89 kg/km^2/yr	0.981 +/- 0.249	87 +/- 22	9 +/- 2
Other Inputs Represented by Runoff (including atmospheric deposition, ground water, soil erosion)	22 cm/yr	7.22 +/- 2.81	159 +/- 62	16 +/- 6
Manure (adjusted for volatilization losses)	404 kg/km^2/yr	0.391 +/- 0.234	158 +/- 94	16 +/- 9
Legumes	1,348 kg/km^2/yr	-0.212 +/- 0.11	-286 +/- 148	0
Predicted Total N Contributions from All N Sources			969 +/- 207 kg/km^2/yr	
N Losses and Unmeasured Outputs (model intercept)			-358 +/- 104 kg/km^2/yr	
N Losses (removal by legumes)			- 286 +/- 148 kg/km^2/yr	
Total N Yield of the MARB Predicted by Model 6.2			325 +/- 152 kg/km^2/yr	
Total N Yield of MARB Estimated in Table 4.2			297 +/- ~15 kg/km^2/yr	

About 358 kg/km^2/yr of the nitrate (model intercept) is lost to undetermined sinks, such as denitrification or storage in ground water. Legumes decrease nitrate yield by 286 kg/km^2/yr. (See earlier discussion for reasons for the decrease.) The model predicts a net basin nitrate yield of 325 kg/km^2/yr, which is close the estimate of 297 kg/km^2/yr determined from flux data discussed in chapter 4 and summarized in Table 4.2. The N input from the fertilizer–soil N pool is estimated to account for about 58% of the nitrate N flux to the Gulf (Table 6.4). Point sources contribute about 9% of the nitrate flux. Animal manure is estimated to contribute about 16% of the nitrate flux to the Gulf, and about 16% of the N flux to the Gulf is derived from undetermined inputs represented in the model by runoff.

The regression model results support the qualitative interpretations of Figures 6.1 and 6.2. The fertilizer–soil N pool appears to be the source of about 50–60% of the N transported to the Gulf of Mexico: about 10% is from point sources, 11–16% is from manure, and the remainder is from such sources as atmospheric deposition, ground-water discharge, and soil erosion. These results suggest that about 90% of the N flux to the Gulf is from nonpoint sources.

Although much of the nonpoint-source N is derived from agricultural activities, some is of natural origin and would be present in the MARB, regardless of human activity. Mineralization of soil organic N and decomposition of vegetation were probably the only significant sources of nitrate and dissolved organic N to the MARB and the Gulf before human development in the basin. No doubt, such activities as tillage, drainage, and addition of fertilizer have significantly increased N contributions from the soil. Additional nonpoint N contributions come from manure and atmospheric deposition. Urban runoff contributes N to streams in some parts of the MARB, but was not specifically addressed in this report because of insufficient data. However, because urban land comprises less than 1% of the MARB, the contribution of urban runoff to the N flux to the Gulf is believed to be very small. The spatial distribution of N inputs discussed in section 4.2 support this statement. With a few exceptions, the largest sources of N are basins dominated by agriculture, and not urban areas.

6.3.2 Total Phosphorus Yield Model

Multiple-regression analysis was used to examine the relation between total P yields and P inputs for the 42 interior basins. Explanatory variables used in the regression model were: P input from fertilizer, P input from point sources, P input from manure, and runoff. Runoff is not a P source, but it represents unmeasured inputs to streams, such as sediment, which contains the majority of the total P transported by streams. The results from this model are shown in Table 6.5 and in equation 6.3.

TABLE 6.5. Regression model[1] results for total phosphorus yields from 42 interior basins.

Independent Variable	Units	Mean Value for 42 Interior Basins	Parameter Estimate	Standard Error	p Value
Intercept	kg/km²/yr		-3.390	13.20	0.80
Fertilizer P	kg/km²/yr	436.0	0.047	0.02	0.02
Point Source P Inputs	kg/km²/yr	22.5	0.278	0.123	0.03
Runoff	cm/yr	28.0	0.905	0.313	0.006
Manure P	kg/km²/yr	315.0	0.027	0.036	0.448

[1]Model $R^2 = 0.43$; mean value of total P yield = 57 kg/km²/yr; root mean square error = 34 kg/km²/yr.

Point sources are also contributors of P, but are less important than fertilizer and sources represented by runoff. The model estimate of the coefficient for point-source input is 0.28, as opposed to near unity for point-source N inputs. This suggests that there could be considerable loss of P from the stream between the input sources and the terminus of the basin. P input from manure has a large uncertainty in the model, as indicated by the large standard error and high p value (Table 6.5). However, it is included so that the P contribution from this source can be estimated. The model intercept is not significantly different from zero ($p = 0.8$), suggesting there are no other significant inputs or losses of P that are not accounted for in the model.

(6.3) Total P yield = -3.39 + 0.047*(fertilizer P) + 0.278* (point-source P) + 0.027* (manure P) + 0.905*(runoff).

The total P model (equation 6.3 and Table 6.5) was applied to the area-normalized total P inputs for the entire MARB. The net total P yield estimated by the model for the entire MARB is 45 +/- 27 kg/km^2/yr (Table 6.6). Results of this analysis were used to estimate the relative contribution of the P sources to the total P flux to the Gulf of Mexico. The P fertilizer inputs are estimated to contribute about 31% of the total P discharged from the MARB to the Gulf (Table 6.6). Municipal and industrial point sources contribute about 10% of the P flux to the Gulf, which is about the same percentage that they contribute for total N. However, this is significantly less than the maximum potential contribution from point sources of more than 40%, discussed in section 6.1 and shown in Figure 6.3B, and suggests significant in-stream losses, errors in the point-source estimates, or errors in the flux estimates. About 17% of the phosphorus flux is from manure, although this value has much uncertainty, as indicated by the large standard error and high p value. Unmeasured P inputs represented in the model by runoff contribute about 40% of the total P flux to the Gulf. The most significant of these unmeasured inputs is hypothesized to be P in sediment from soil erosion. The estimated total P output from the MARB in suspended sediment is included in the total P yields of the streams; however, there is no estimate of the total P input to the streams in sediment.

TABLE 6.6. Estimated contributions of phosphorus input sources to the total phosphorus yield of the Mississippi–Atchafalaya River Basin and total phosphorus flux to the Gulf.

Phosphorus Input Source	Normalized Input to Entire MARB	Coefficient from Regression Model 6.3	Contribution to MARB Yield *(kg/km^2/yr)*	Contribution to Total P Flux to Gulf *(percent)*
Fertilizer–P	320 kg/km^2/yr	0.047 +/- .02	15 +/- 6	31 +/- 12
Municipal and Industrial Point Sources	18 kg/km^2/yr	0.278 +/- 0.123	5 +/- 2	10 +/- 4
Other Inputs Represented by Runoff	22 cm/yr	0.905 +/- 0.313	20 +/- 7	42 +/- 15
Manure	311 kg/km^2/yr	0.027 +/- 0.036	8 +/- 11	17 +/- 23
Predicted Total P Contributions from All P Sources				48 +/- 14 kg/km^2/yr
P Losses (model intercept)				- 3 +/- 13 kg/km^2/yr
Total P Yield of the MARB Predicted by Model 6.3				45 +/- 27 kg/km^2/yr
Total P Yield of MARB Estimated in Table 4.4				32 +/- ~7 kg/km^2/yr

CHAPTER 7

Research Needs

This assessment has identified several research needs and data gaps, which if addressed could provide a better scientific understanding of processes affecting the flux and sources of nutrients in the Mississippi–Atchafalaya River Basin. Improved understanding of these processes could lead to new practices, policies, and incentives targeted at reducing the loss of nutrients, such as nitrate, to surface- and ground-water systems within the basin. Reducing the loss of nutrients to streams in the basin could benefit the Gulf of Mexico by reducing the extent of hypoxia, and could also benefit the Upper Mississippi Basin by improving the quality of water in streams and aquifers. The identified research needs follow.

7.1 NITROGEN DYNAMICS IN SOILS

The sources of most N discharging to streams in the basin and to the Gulf are the soils and unsaturated zones underlying cropland. This near-surface zone can serve as a huge storage reservoir for N derived from mineralization of soil organic N, agricultural activities, and atmospheric deposition. The annual N inputs to and outputs from this reservoir have doubled in recent decades with the increased use of fertilizer, and have substantially increased the amount of N potentially available for leaching. Precipitation can leach N present in the form of nitrate from this reservoir to streams in runoff, agricultural drains, and ground water. Research is needed to find ways to "manage" the storage of N in this zone in a way that minimizes the accumulation of excess nitrate and minimizes the losses of nitrate from this zone to the hydrologic system. This research would include developing a better understanding of mineralization and immobilization processes, quick and easy ways to measure the amount and forms of N in the soil reservoir, and strategies to minimize leaching of nitrate from the soils to streams.

7.2 SMALL WATERSHEDS

Additional research is needed in small watersheds in both drained and undrained areas to better understand the dynamics and timing of nitrate transport from cropland to streams. Research is also needed to better define the extent and density of tile drainage and other agricultural drainage and to better understand the magnitude of the impact of these drainage practices on nutrient flux in large rivers. This could augment ongoing research in the MARB and should be designed to support the research needs outlined above in item (1).

7.3 In-stream Processes

There is currently much uncertainty about the role of in-stream processes, such as denitrification in removing N from streams in the basin. Although denitrification does not appear to be a highly significant process in removing N from large streams, it may be very important in small streams. Research is needed to examine the significance of denitrification in removing N leached from agricultural land, and to find ways to enhance this process in order to reduce leaching of nitrate to streams and ground water in the MARB.

7.4 SPARROW Model

The SPARROW model (spatially referenced regressions on watershed attributes; Smith et al. 1997) has been developed to estimate nutrient flux in unmeasured stream reaches. SPARROW uses a multiple-regression model based upon spatially referenced contaminant inputs, physical characteristics of the soil, and hydraulic properties of the stream reaches. In addition to predicting flux, the model allows the total flux to be apportioned among different input sources, such as fertilizer application, point sources, and atmospheric deposition, and to determine spatially where the flux comes from within a basin. Some work has been done to apply SPARROW to nutrient sources and transport in the Mississippi Basin (Smith et al. 1997; Alexander et al. 1999; also see SPARROW on the worldwide web at: *http://wwwrvares.er.usgs.gov/nawqa/sparrow/*). Further research and development on SPARROW are needed so that it can account for additional input and output terms, such as soil mineralization, crop export, immobilization, and annual variation in the location and quantity of precipitation.

7.5 Nitrogen Mass Balance

This assessment has made a first attempt at developing a nitrogen mass balance for the MARB. Some of the estimated inputs and outputs have large uncertainties. An effort should be made to improve upon this balance so that more precise estimates of the residual N that is available for leaching to surface and ground water can be developed. This can guide development of efforts to reduce N losses. Any effort to refine the N balance should be a multidisciplinary approach involving agronomists, soil scientists, hydrologists, and statisticians.

7.6 Stable Isotopes

Measurements of stable isotopes, such as ^{15}N and ^{18}O in the nitrate (NO_3) ion, may provide a means to identify specific sources of nitrate discharging to streams. Investigators have used isotopic techniques to determine mixing ratios of waters from different sources, to quantify such processes as denitrification, and to identify sources of N in water resources (Clark and Fritz 1997; Kendall 1998; Kellman and Hillaire–Marcel 1998). Most of the studies to date are from small study areas, and few have attempted to work with isotopes in large rivers (Kohl et al. 1971). A research effort to explore the utility stable isotopes for identifying N sources is currently underway in the basin (Battaglin et al. 1997), with support of EPA's Gulf of Mexico Program. This research should be continued and expanded if the technique proves to be useful.

7.7 Atmospheric Deposition in the MARB

Research is needed to improve estimates of wet and dry deposition of N compounds. This includes additional measurement stations to improve the spatial distribution of data needed to support spatial deposition models, such as described in Prospero et al. (1996). Improvements in air sampling techniques are needed to include NH_3 and organic N. Techniques are also needed to identify all of the forms of N now being collected by three-stage filter packs.

7.8 Atmospheric Deposition in the Gulf of Mexico

There is currently very little data on the direct atmospheric deposition of N on the waters of the Gulf of Mexico. The evidence that does exist suggests that atmospheric deposition of N is insignificant relative to other N inputs. Additional research on atmospheric deposition of N on the Gulf is needed to confirm or refute the current limited evidence. However, this research need should be given a lower priority than other needs listed in this chapter.

CHAPTER 8

Conclusions and Recommendations

8.1 CONCLUSIONS

This assessment has used available information to address two questions: (1) What are the loads (fluxes) of nutrients in the Mississippi–Atchafalaya River Basin and where do they come from, and (2) Which human activities are most significant in contributing the nutrients to the Mississippi River system? Nitrogen, phosphorus, and silica are addressed in this report. However most of the emphasis is on N, which is the nutrient of most concern to the hypoxia issue.

8.1.1 Flux and Sources

Analysis of historical records shows that the concentrations of nitrate in the Mississippi River and tributaries in the Upper Mississippi Basin have increased by factors of 2–5 since 1900. The current average annual N flux from the MARB to the Gulf of Mexico is about 1.6 million metric tons. The annual flux has approximately tripled during the last 30 years, with most of the increase coming between 1970 and 1983. Expressed as a yield, the average total N flux for 1980–96 is 489 $kg/km^2/yr$ and is estimated to be 2.2–6.5 times higher than baseline "pristine" conditions for the North Atlantic Basin (Howarth 1998). The average flux has changed very little since the early 1980s, but there are large year-to-year variations in N flux caused by variations in precipitation. During wet years the N flux can increase by 50% or more due to flushing of N that has accumulated in the soils and ground-water system in the basin. Episodic events, such as the 1993 flood, can and will continue to transport abnormally large quantities of nitrate to the Gulf. There has been no significant change in the flux of phosphorus since the early 1970s, when phosphorus records began, and no statistically significant change in the flux of silica since the 1950s, when silica records began.

The principal sources of N are watersheds in southern Minnesota, Iowa, Illinois, Indiana, and Ohio that drain agricultural land. This region contributes several times more N per unit area to the Mississippi River than do basins outside this region. Streams draining from two states, Iowa and Illinois, contribute on average, about 35% of the N discharged by the MARB, but comprise only about 9% of the total area of the MARB. In years with abnormally high precipitation they can contribute much more than this. For example, in 1993 Iowa alone with 4.5% of the area of the MARB, contributed about 35% of the nitrate discharged from the MARB to the Gulf.

8.1.2 Relative Importance of Human Activities in Contributing to Nutrient Flux

Several analytical approaches were used to examine the relative importance of human activities, such as agriculture and point-source discharges, and atmospheric deposition, in contributing nutrients to the MARB. These approaches included graphical comparisons, an N mass balance for the MARB, and multiple-regression models.

Results indicate that about 90% of the N flux to the Gulf of Mexico is derived from nonpoint sources. Agricultural activities are by far the largest contributors of N to streams in the MARB. The N sources and their estimated contribution to the flux of total N to the Gulf are: (1) input from the fertilizer–soil N pool (50%); (2) inputs associated with basin runoff, such as atmospheric deposition, ground-water discharge, and soil erosion (24%); (3) animal manure (15%); and (4) municipal and industrial point sources (11%). The major contributors and their relative contribution to the flux of total P to the Gulf are: (1) inputs associated with basin runoff, such as soil erosion (41%); (2) P from fertilizer (31%); (3) animal manure (18%); and (4) municipal and industrial point sources (10%). The point-source discharges are believed to be relatively constant, indicating that the large increases in nutrient flux during above-normal precipitation come from nonpoint sources. However, within a few highly urbanized basins in the Upper Mississippi Basin, municipal and industrial point sources are very important sources of N and P. Atmospheric deposition appears to be a relatively small contributor of overall flux of nitrogen to the Gulf. This is in sharp contrast to Chesapeake Bay and elsewhere in the eastern United States, where atmospheric deposition has been reported to be a major source of N.

Of the agricultural sources of N examined in this assessment (fertilizer, legumes, mineralization of soil, and manure) fertilizer and soil organic N are the most important sources of N. They appear to contribute about equally to the N flux in streams, although their individual contribution could not be quantified with regression models. Legumes do not appear to be significant contributors to the N flux of the Mississippi River. More N is removed in the harvested legumes, particularly soybeans, than they fix from the atmosphere. However, the residue remaining from legume crops provides a rotation benefit to crops that follow them. If not used, the mineralized N can leach to streams and ground water. Some legume N is also contributed to streams indirectly through animal manure. Fertilizer, and to a lesser degree legumes, are the only two sources of N that have increased significantly since the 1950s. Fertilizer use has increased nearly seven-fold since 1960, and the amount of N removed in harvested crops has more than doubled since 1960, paralleling the increase in fertilizer use.

8.1.3 Climatic Effects on Nutrient Flux

The average annual streamflow of the Mississippi River has increased by about 30% since the 1955–70 time period as a result of increased precipitation. This increase, in conjunction with increased N inputs, has resulted in increased leaching of nitrate, from agricultural land to ground water and streams, and has led to about a three-fold increase in N flux to the Gulf of Mexico.

In future years the flux of nitrate to the Gulf most likely will continue to respond quickly and dramatically to variations in precipitation and runoff. Because of the readily available pool of nitrate in the soil–ground-water system, N fluxes will be high in wet years and low in dry years. However, because of the huge soil–ground-water reservoir available for storage of nitrate in the MARB system, the flux of nitrate to the Gulf will most likely change very slowly in response to increases or decreases in N inputs. The N balance of the soil–ground-water system will have to adjust to changes in N inputs and outputs. The response time of the MARB to changes in N inputs and outputs is unknown, but may be several years or longer.

8.2 RECOMMENDATIONS

At present no programs or mechanisms are in place to determine if changes in nutrient flux in streams occur as a result of voluntary actions and new policies. Nutrient monitoring is being carried out at a few sites on large rivers, such as the Mississippi and Ohio, by the USGS National Stream Quality Accounting Network, but there are no coordinated data-gathering efforts at the small basin scale, which will be most sensitive to changes in nutrient inputs. The following recommendations address these concerns.

8.2.1 Nutrient Monitoring Program

Establish a nutrient monitoring program in the MARB designed to determine the effects of voluntary actions, changes in nutrient management practices, and new policies aimed at reducing the nutrient flux to the Gulf of Mexico. Such a program should consider the re-establishment of monitoring in some of the 42 interior basins (former NASQAN stations) used in this assessment. These sites have the benefit of a long period of historical data. Monitoring at this scale should be augmented by nutrient monitoring in selected small basins, where the effects of changes in nutrient inputs will be most noticeable. Any nutrient monitoring program that is established must include a plan for data compilation and for timely synthesis and dissemination of data to all interested parties.

8.2.2 Effluent Monitoring Program

Establish an effluent monitoring program designed to systematically improve current estimates of nutrients discharged to streams from municipal and industrial point sources.

8.2.3 Monitoring Atmospheric Deposition

Continue current programs to monitor nutrients from atmospheric wet deposition in the MARB, and expand the current limited monitoring of nutrients in atmospheric dry deposition. This information is needed to determine if nutrient-reduction strategies affect precipitation chemistry.

8.2.4 Interdisciplinary Forum

EPA and USDA should provide a forum for discussing nutrient budgets in large watersheds. Participants should include hydrologists, soil scientists, ecologists, and agricultural engineers. The forum would provide a means to establish a dialog between researchers from different fields of expertise. This kind of interdisciplinary exchange offers the best hope of addressing the complex issue of understanding the links between nutrient sources, cycling, flux in large watersheds, and hypoxia in the Gulf, and developing strategies to reduce excess nutrients.

8.2.5 Long-Term Research

Develop a long-term research effort that would collect the data and information needed to determine the relation between the three-dimensional extent of hypoxia in the Gulf (i.e., the volume of water in the Gulf affected by oxygen depletion) and the flux of nutrients from the MARB. This research would require collection of more extensive data on the extent of hypoxia in the Gulf than is currently being collected. That data would be quantified in terms of the volume of the Gulf affected and the amount of oxygen consumed. Existing and new nutrient monitoring data from the Mississippi River would be used to calculate the flux of nutrients entering the Gulf. Statistical or solute transport models, coupled with nutrient-dissolved oxygen models of the Gulf, would be developed and used to determine if there is a threshold nutrient flux for Mississippi River below which there is little or no problem from hypoxia. This research effort would logically be developed in conjunction with the proposed Global Ocean Ecosystems Dynamics (GLOBEC) program that NOAA has proposed for the Gulf of Mexico.

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