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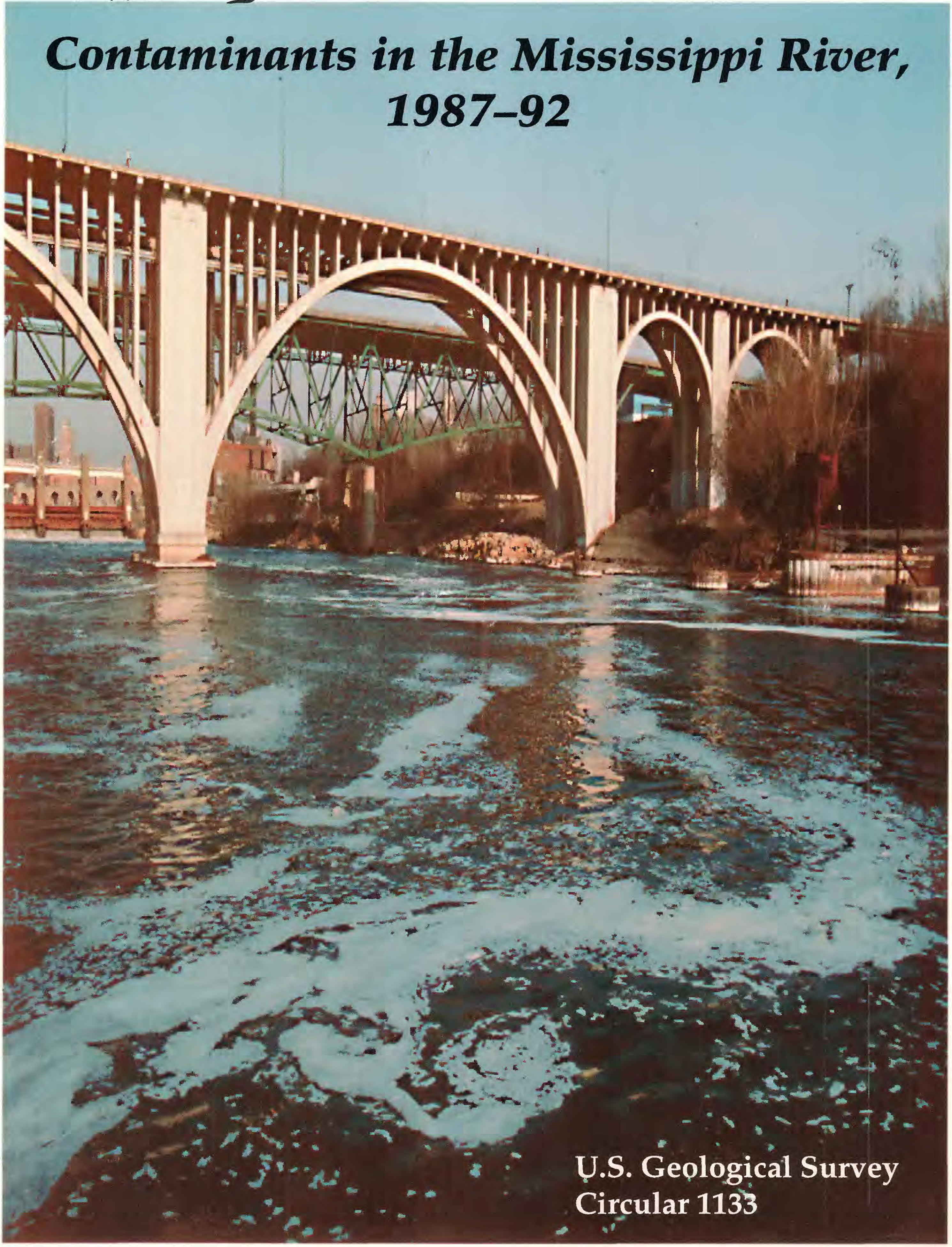
Contaminants in the Mississippi River, 1987–92



U.S. Geological Survey
Circular 1133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Quad Cities
Illinois River
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ILLINOIS
40°
40°
Valley City
Missouri
River
Winfield
Hardin
95°
St. Charles
Hermann
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85°
Ohio
River
Uniontown
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Smithland
KENTUCKY
Grand Chain / Olmsted
Hickman
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TENNESSEE
Fulton
Arkansas
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Memphis
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85°
Helena
ARKANSAS
Arkansas City
Yazoo River
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MISSISSIPPI
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Atchafalaya R.
St. Francisville
Baton
Rouge
30°
30°
Belle
Chasse
New Orleans
Head of Passes
90°
GULF OF MEXICO

Contaminants in the Mississippi River, 1987–92

Edited by Robert H. Meade

U.S. GEOLOGICAL SURVEY CIRCULAR 1133

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
GORDON P. EATON, Director

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

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
millimeter (mm)	0.03937	inch
micrometer (µm)	0.00003937	inch
liter (L)	1.057	quart
milliliter (mL)	0.03381	fluid ounce
kilogram (kg)	2.205	pound, avoirdupois
metric ton	2205	pound, avoirdupois
cubic meter per second (m^3/s)	35.31	cubic foot per second
kilogram per square kilometer (kg/km^2)	0.008924	pounds per acre

Concentration unit	Equals
milligram per gram (mg/g)	part per thousand
milligram per kilogram (mg/kg)	part per million
microgram per gram (µg/g)	part per million
nanogram per gram (ng/g)	part per billion (10^9)

Concentration unit	Approximately* equals
gram per cubic meter (g/m^3)	part per million
milligram per liter (mg/L)	part per million
microgram per liter (µg/L)	part per billion (10^9)
nanogram per liter (ng/L)	part per trillion (10^{12})

* At the concentrations encountered in this study, and considering the detection limits of the analytical methods employed, these units can be considered equal in the context of this report.

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

ACKNOWLEDGMENTS

Because it covered so many aspects of water quality, along 3,000 kilometers of the continent's largest river system, this study required the collaboration of a large number of people—only a few of whom are listed among the chapter authors. Others who made substantial contributions to the investigation, execution, and completion of the study are listed below, with our thanks. Those listed without affiliation are (or were) members of the U.S. Geological Survey (USGS).

Among those influential in getting the study started, the late Robert C. Averett played a central role, and the completion of this report is part of Averett's lasting legacy as our colleague and mentor. Other important instigators were E.M. Thurman, R.G. Wolff, and E.D. Andrews.

Once the program was under way, we received help and encouragement at critical junctures from: U.S. Senator Rudy Boschwitz; Holly Stoerker, Upper Mississippi River Basin Association; Gail Carmody, U.S. Fish and Wildlife Service; Dan Helwig, Minnesota Pollution Control Agency; John Sullivan, Wisconsin Department of Natural Resources; Donald F. Boesch and Paul W. Sammarco, Louisiana Universities Marine Consortium.

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Scientists who participated as colleagues in the field but did not, for one reason or another, end up among the chapter authors included: Brent McKee, LUMCON; Alan Shiller and Jim Krest, University of Southern Mississippi; Patricia Brown, Wesley Campbell, C.C. Cranston, T.F. Kraemer, D.A. Martin, James Ranville, T.F. Rees, and R.F. Stallard.

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Daniel Gipe and people at Hermann Sand and Gravel Company in Hermann, Missouri; Captain William Carroll and the people at Gateway River Cruises in St. Louis, Missouri; Kent Hoffmeister and the workers at Missouri Dry Dock and Repair Company in Cape Girardeau, Missouri; the U.S. Coast Guard Station in Keokuk, Iowa, and Hickman, Kentucky; John Janoush and the people at Janoush Marine, Inc., in Rosedale, Mississippi; Mary Hosemann and the people working on the *Spirit of Vicksburg* in Vicksburg, Mississippi; and the people running the New Roads Ferry at St. Francisville, Louisiana, and the Belle Chasse Ferry at Belle Chasse, Louisiana.

Laboratory analyses of our samples were provided by C.J. Anderson, P.J. Cinotto, B.F. Connor, J.A. Kammer, C. Klimper, W.J. Matthes, E.K. Naughton, M.C. Noriega, M.P. Pavelich, M.P. Schroeder, M.J. Werito, and M.T. Woodworth. Assisting in our laboratories were Jonathan Fischer, P.W. Mahan, Mike Meyer, Mike Pomes, and Diana Aga.

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All photographs were taken by the editor.


MONTANA
NORTH DAKOTA
MINNESOTA
Yellowstone River
Missouri
SOUTH DAKOTA
River
WYOMING
WISCONSIN
MISSISSIPPI RIVER
MICHIGAN
IOWA
NEBRASKA
Platte River
Illinois River
PENNSYLVANIA
INDIANA
OHIO
River
COLORADO
ILLINOIS
Ohio
WEST VIRGINIA
St Louis
KANSAS
Missouri R
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KENTUCKY
OKLAHOMA
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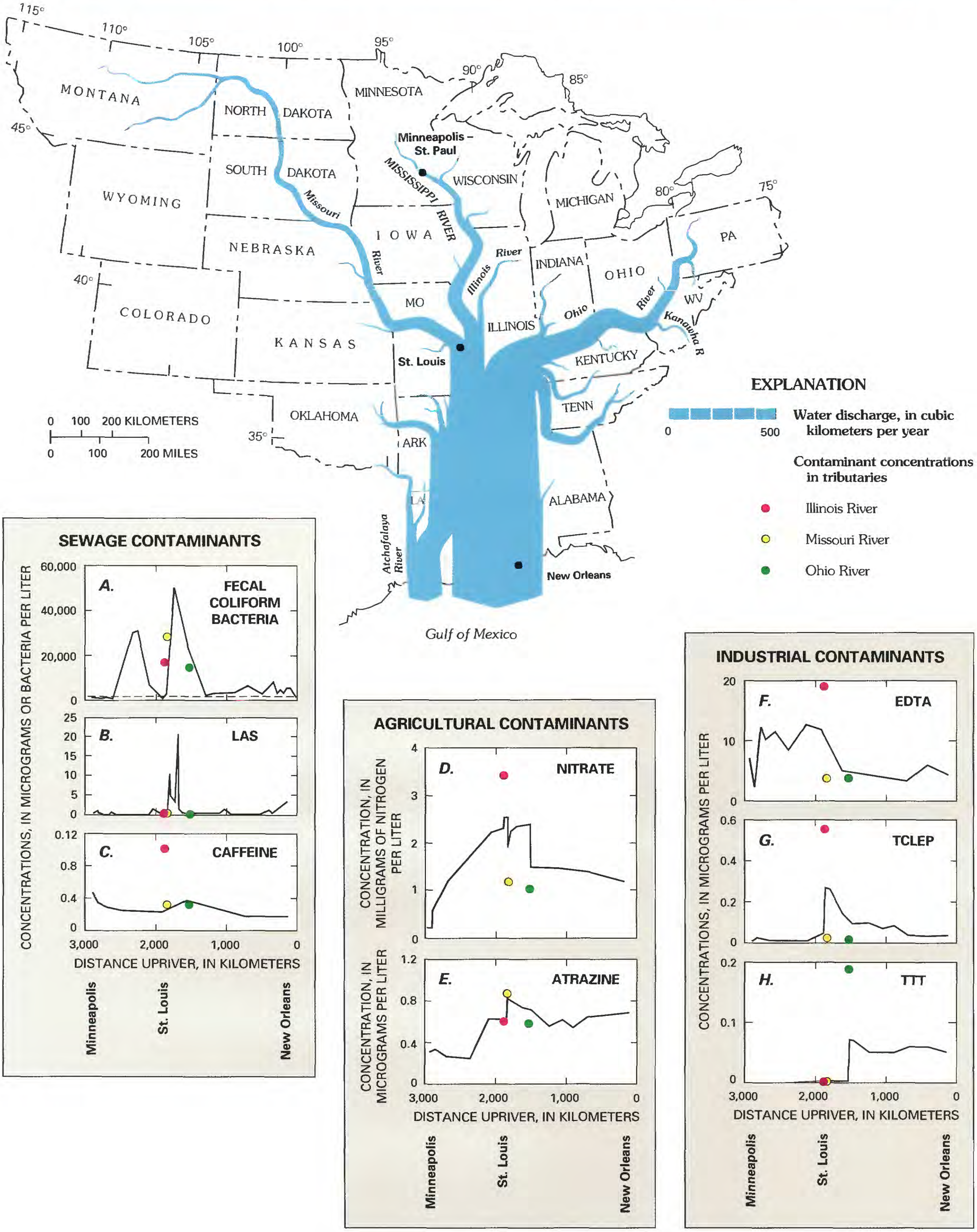
Figure 1 *Dissolved Contaminants*



Executive Summary

Robert H. Meade and Jerry A. Leenheer

Dissolved Contaminants

Figure 1 The waters of the Mississippi River carry dissolved contaminants and bacteria that originate from a variety of municipal, agricultural, and industrial sources. The map shows the amounts of water discharged by the Mississippi River and its main tributaries during an average year. About 2 percent of the average discharge of the Mississippi River comes from municipal and industrial point sources. The distribution of contaminants along the Mississippi River depends on the nature and location of their sources, the degree of wastewater treatment, the stability of the contaminants, and their dilution by receiving waters. The graphs below the map show the concentrations of contaminants dissolved in the Mississippi River between Minneapolis-St. Paul and the Gulf of Mexico. The data in the graphs are generalized from the results of chemical analyses of representative samples of water collected at 10–15 sites along the Mississippi River: on as many as 10 separate occasions during 1987–92 downriver of St. Louis, and on 3 separate occasions during 1991–92 upriver of St. Louis.

As the Mississippi River flows southward from its headwaters in the northern Midwest, its discharge is more than doubled by the waters it receives from the Illinois and Missouri Rivers. This combined discharge is more than doubled again as it is joined by the waters of the Ohio River. About 500 kilometers upriver of its principal mouth, the Mississippi River bifurcates, and one-fourth of its discharge is diverted down the Atchafalaya River to the Gulf of Mexico.

A Fecal coliform bacteria derived from human and animal wastes survive only briefly in river water, but their average concentrations exceed the maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency of 2,000 per liter for recreational use in much of the Mississippi River because of incomplete wastewater treatment.

B Linear alkylbenzenesulfonate (LAS) is a biodegradable detergent, primarily derived from domestic sewage. Its presence in high concentrations in the Mississippi River in the St. Louis metropolitan area corresponds with the elevated counts of coliform bacteria, and probably reflects the incomplete treatment of wastewaters discharged into the river.

C Caffeine is a stimulant chemical in coffee and soft drinks. Because it is consumed only by humans, it is an indicator of domestic sewage and illustrates the extent to which sewage is diluted by the river. Concentrations of caffeine in municipal wastewaters usually range between 20 and 300 micrograms per liter (μg/L). The much lower concentrations of 0.02–0.04 μg/L of caffeine shown in the graph indicate that municipal wastewaters may be diluted as much as a thousandfold after they are well mixed into the Mississippi River.

Dissolved Contaminants — Continued

D and E Agricultural contaminants enter the rivers from mostly nonpoint sources, usually as runoff from croplands during spring and summer.

D Nitrate in the Mississippi River comes mostly from fertilizers. Its concentration in the river fluctuates seasonally, depending on when fertilizers are applied to farmlands and the timing of rainfall and runoff. Nitrate concentrations are generally smaller in the Mississippi River below the confluence of the Ohio River; the major portion of nitrate in the Mississippi River is derived from the tributaries that drain intensively farmed regions in Illinois, Iowa, and Minnesota.

E Atrazine is a pre-emergent herbicide used mainly on cornfields. It is nearly ubiquitous in the Mississippi River. Atrazine concentrations usually are greatest near St. Louis, Missouri, because of inputs from the Missouri, Illinois, and other rivers that drain the farming regions of the Corn Belt. Concentrations usually are smaller in the Lower Mississippi because of dilution by water from the Ohio River. Atrazine concentrations vary seasonally, and occasionally exceed the maximum contaminant level for treated drinking water of 3 micrograms per liter for a few days during the spring runoff in the Mississippi River between St. Louis and the Ohio River confluence.

F Ethylenediaminetetraacetic acid (EDTA) is the dissolved organic chemical contaminant present at the greatest concentration in the Mississippi River. Generally considered nontoxic, this chemical is a general indicator of industrial contamination, and it is found in the Mississippi River at about one-fourth of the concentration found in some European rivers.

G and H Two examples of contaminants from industrial point sources are tris-2-chloroethylphosphate (TCLEP) and 1,3,5,-trimethyl-2,4,6-triazinetrione (TTT).

G TCLEP is a flame retardant that is added to polyurethane foams and textiles, and, in the Mississippi River system, it is derived almost exclusively from the Illinois River Basin. Its exclusive source and its persistence in solution make TCLEP a useful tracer and indicator of waters from the Illinois River as they mix with waters from other tributaries down the Mississippi River.

H TTT is a by-product of the manufacture of methylisocyanate. Its overwhelmingly singular source in the Mississippi River system is in the basin of the Kanawha River of West Virginia, a tributary of the Ohio River. Proportions of TTT dissolved in the water can be used to follow the mixing of the Kanawha River with the Ohio, and the Ohio River with the Mississippi River.

This volume contains a selection of some of the more interesting results of a 5-year study conducted by the U.S. Geological Survey of contaminants in the Mississippi River and some of its major tributaries. During the first 3 years of the study, 1987–90, the rivers were sampled on seven different occasions between St. Louis, Missouri, and New Orleans, Louisiana. During the last 2 years of the study, 1991–92, the scope of the program was increased to include three further samplings of the full length of the river between Minneapolis-St. Paul, Minnesota, and New Orleans. The sampling and analytical efforts were focused on three phases of contaminants in the rivers: (1) contaminants transported in the dissolved phase, (2) contaminants transported in the adsorbed phase—that is, in association with the suspended silts and colloids—and (3) contaminants stored in the bottom sediments in the navigation pools of the Upper Mississippi River.

Contaminants were assessed for the period of sampling, 1987–92. Given that samples were collected no more frequently than twice a year, the 5-year period was not sufficiently long to establish any time trends—whether, that is, the contaminant levels were increasing or decreasing. Included in the analysis were only a few data that had been collected before our study. Yet to be assessed are the subsequent effects on river quality of the great flood of 1993. Contaminants are assessed mostly in a spatial rather than a temporal context. This report, in other words, is a snapshot rather than a chronicle.

Some of the findings represent new information, whereas many of the results confirm previously known aspects of the distribution of contaminants in the river, as described, for example, in the volumes by Costner and Thornton (1989), Scarpino (1985, especially pages 151–186), and Wiener and others (1984). This summary includes three figures that demonstrate the three phases of contaminant occurrence listed in the first paragraph. Further details of each of the contaminants portrayed here, as well as of other contaminants, are given in the chapters that follow.

SUGGESTIONS FOR READING THIS REPORT

The chapters on the individual contaminant groups (heavy metals, pesticides, nutrients, polychlorinated biphenyls, and other organic contaminants) are organized to be read easily at different levels. For readers who want an overview in the shortest amount of time, the figures and their captions contain much of the relevant information. For readers having more time or interest, the main text of each chapter (which is set in three column format, like this page) provides further information and analysis. For readers who want to inspect entire data sets and evaluate analytical methods, each chapter contains bibliographic references to the U.S. Geological Survey Open-File Reports and Water-Resources Investigations Reports that contain the basic data and complete descriptions of the procedures that were used to obtain them.

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Scarpino, P.V., 1985, Great river—An environmental history of the Upper Mississippi, 1890–1950: Columbia, Missouri University Press, 219 p.

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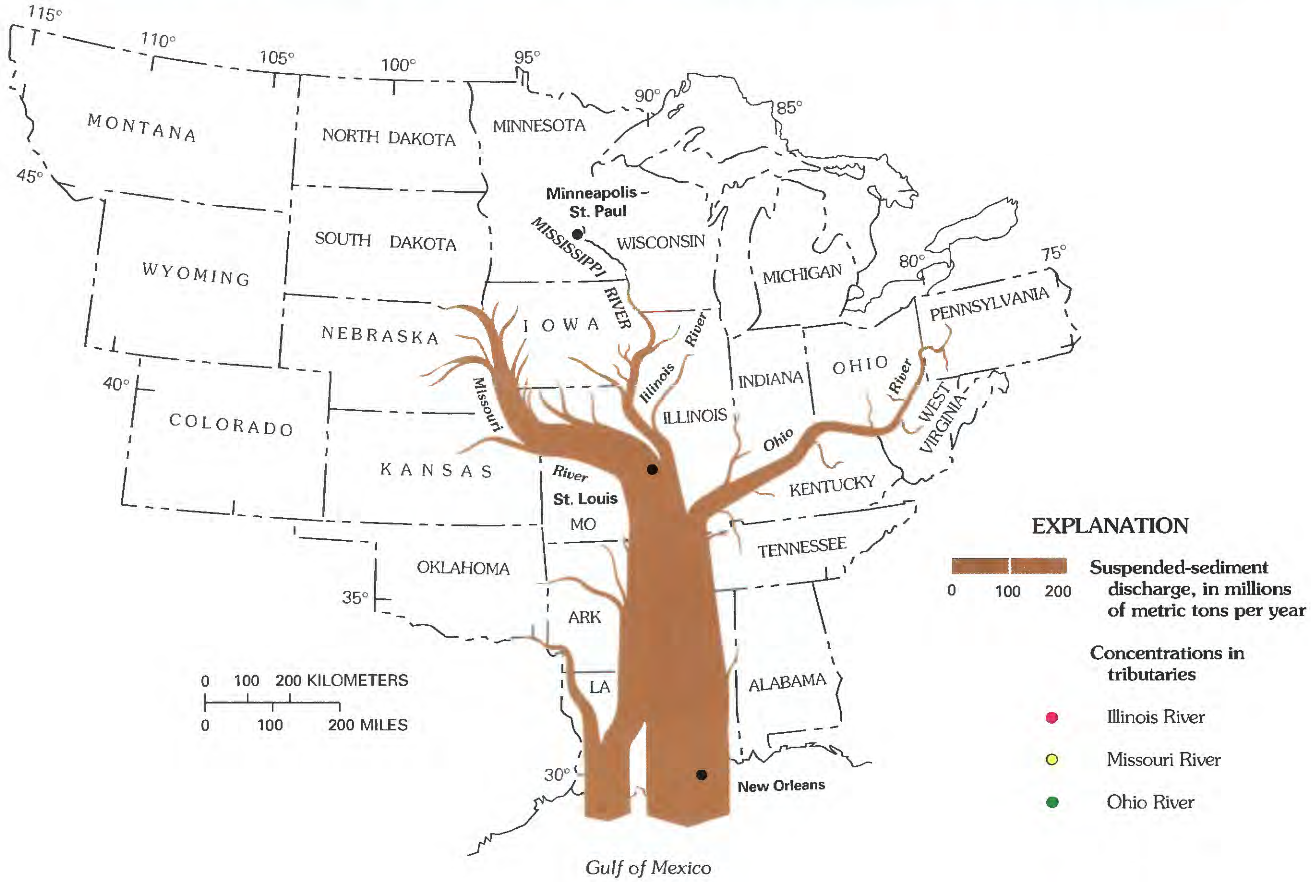
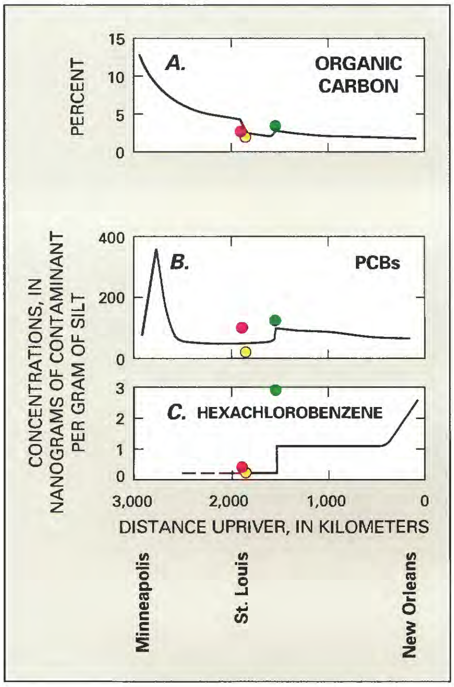
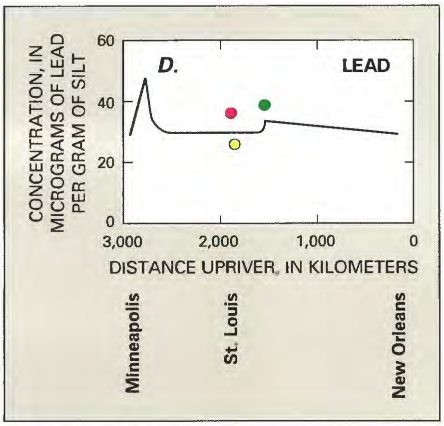
Figure 2 *Contaminants in Suspended Sediment*







Contaminants in Suspended Sediment

Figure 2 The suspended sediments that are transported by the Mississippi River and its tributaries adsorb and carry contaminants. Organic contaminants such as polychlorinated biphenyls (PCBs) and inorganic contaminants such as lead are many times more likely to adhere to sediment particles than to remain in the dissolved phase. The map shows the amounts of suspended sediment discharged by the Mississippi River and its main tributaries during an average year near 1990. The graphs arranged below the map show the concentrations of constituents adsorbed on the sediments in suspension in the main-stem Mississippi River between Minneapolis-St. Paul and the Gulf of Mexico. The data in the graphs are generalized from the results of chemical analyses of representative samples of suspended sediment collected at 10–15 sites along the Mississippi River: on as many as 10 separate occasions during 1987–92 downriver of St. Louis, and on 3 separate occasions during 1991–92 upriver of St. Louis.

Suspended-sediment discharges in the Upper Mississippi River are fairly small when compared to those of the major tributaries. The sediment discharge of the Upper Mississippi River is increased five- to tenfold by the sediment discharge of the Missouri River. The average sediment load in the main stem is increased by another significant increment by the contribution from the Ohio River.

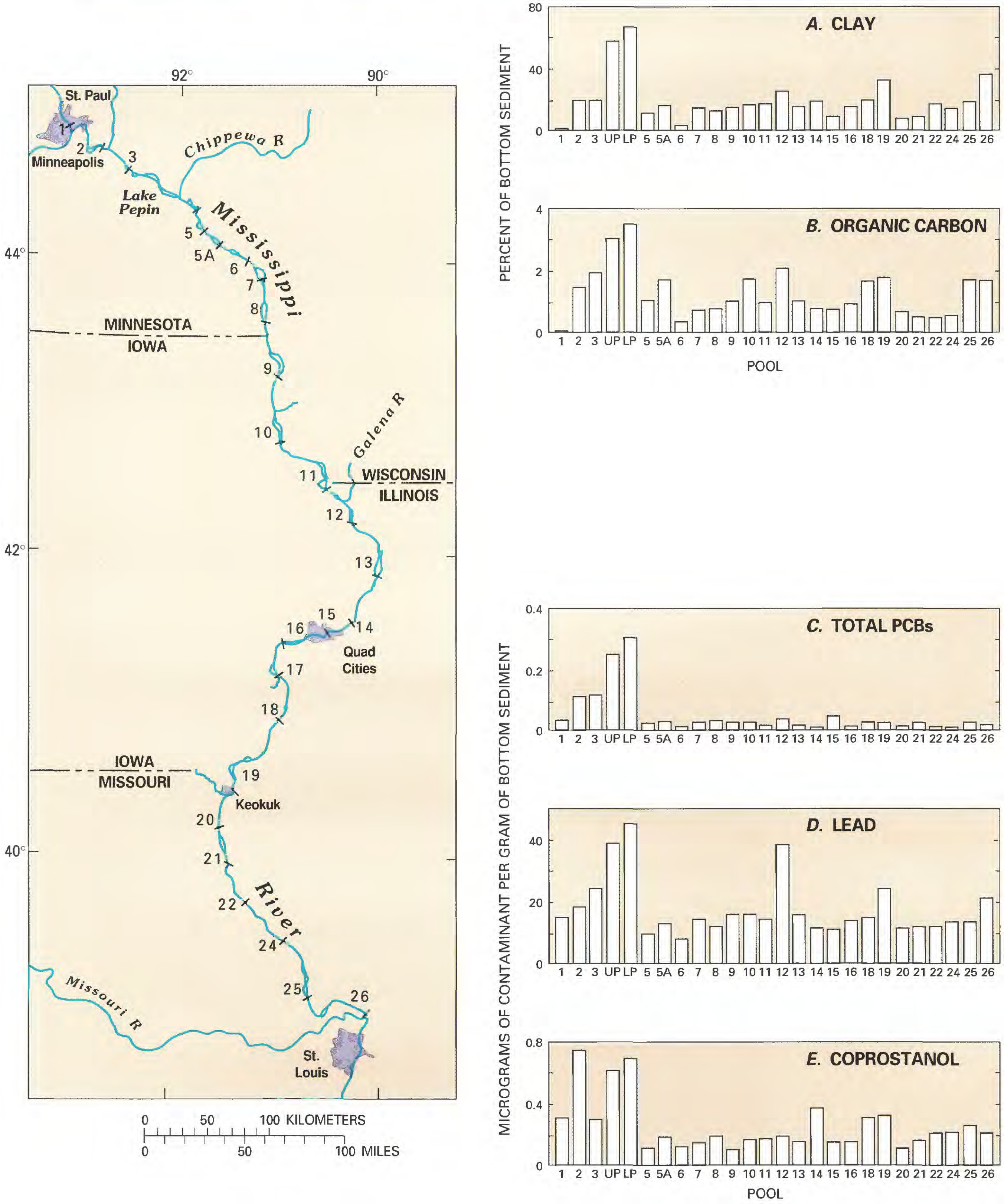
A Organic carbon (expressed here as weight percent of dried suspended silt) is proportionately greater in the uppermost Mississippi River, and its proportion decreases downriver. Particulate organic carbon in the Mississippi River is mostly natural, but it affects the ways in which contaminants, especially organic contaminants, are adsorbed by suspended sediment. The Missouri and Illinois Rivers transport suspended sediment in which organic carbon is somewhat less concentrated; where these two tributaries enter the Mississippi (near river kilometer 1850), the organic carbon percentages are decreased by dilution. Organic carbon percentages in the suspended sediment of the Ohio River, on the other hand, are typically greater than those in the Missouri and Illinois Rivers, and the organic carbon in suspended sediment is increased slightly where the Ohio River joins the Mississippi (river kilometer 1535).

B Polychlorinated biphenyls (PCBs), which are organic contaminants that were formerly used widely in industrial applications, are typically most concentrated on the suspended sediments in the Upper Mississippi River near Minneapolis-St. Paul. The difference between PCB concentrations on the suspended sediments near Minneapolis and those near St. Louis is due mostly to the greater amounts of suspended sediment in the river at the latter city, rather than an indication that Minneapolis-St. Paul contributed 5–10 times more PCBs to the river than did St. Louis. The high concentrations in the upper river decrease rapidly downriver, and they are increased significantly only as the suspended sediment from the Ohio River, which usually contains more PCBs than that in the middle reaches of the Mississippi River, enters and mixes.

C Hexachlorobenzene, another organic contaminant of industrial origin, is predominantly derived from two main sources in the Mississippi River Basin: (1) the Ohio River, which enters the Mississippi at river kilometer 1535, and (2) the industrial corridor along the lowermost 400 kilometers of the Mississippi River.

D Lead and other heavy metals are associated with the suspended sediments along the length of the Mississippi River. Spatial variations in their concentrations are less pronounced than those of PCBs and hexachlorobenzene. However, they do tend to be most concentrated on the suspended sediments in the river just downstream from Minneapolis-St. Paul (as in the case of PCBs, because of the relative scarcity there of suspended sediment), and they show slight increases related to more concentrated inputs from the Ohio River.

Figure 3 *Contaminants in Bed Sediments*



Contaminants in Bed Sediments

Figure 3 The Upper Mississippi River is partly impounded by control structures which form pools that trap sediments and their adsorbed contaminants. Twenty-nine locks and dams, built mostly for navigation, control the depth and, to a lesser extent, the flow of the river between Minneapolis and St. Louis. Twenty-six of these control structures form major pools that trap and retain sediment and contaminants in varying degrees. The two largest pools are Lake Pepin, a natural pool formed by the partial damming of the Mississippi River by the sand delta of the tributary Chippewa River, and Pool 19, the impoundment behind the hydroelectric dam at Keokuk, Iowa, the highest major dam on the upper river.

The bottom sediments of 25 of these pools (1–26, except for Pool 17) were sampled during 1991–92. In each pool, 15–20 samples of the surficial sediment stored in the backwater areas of the lower reaches of the pool were collected and combined into a composite sample, which was analyzed for a number of characteristics and contaminants, some of which are portrayed in the figure. On the horizontal axes of the graphs: UP = upper Lake Pepin; LP = lower Lake Pepin.

A Percent clay, a measure of the fineness of the sediment particles stored on the bottoms of the pools, is shown in the graph as percent finer than 0.004 millimeter. Fineness is an important attribute in the retention of contaminants because the finer sediments have greater total surface areas (compared to coarser sediments) with which contaminants may react or onto which contaminants may be adsorbed. The most concentrated accumulation of the finest sediments in the pools of the Upper Mississippi River is in Lake Pepin. Other large impoundments, Pools 19 and 26, have trapped sediments that are finer than those in smaller pools. Clay and other fine sediment particles have more time and opportunities to settle and be deposited in the larger deeper pools than in the smaller shallower ones.

B Particulate organic carbon usually is found most abundantly in association with the finest sediments. In the pools of the Upper Mississippi River, organic carbon shows a strong correlation (although not an identical distribution) with percent clay. Independent of its associations with fine sediment, organic carbon is a strong determinant in the adsorption of contaminants—especially organic contaminants—by sediments.

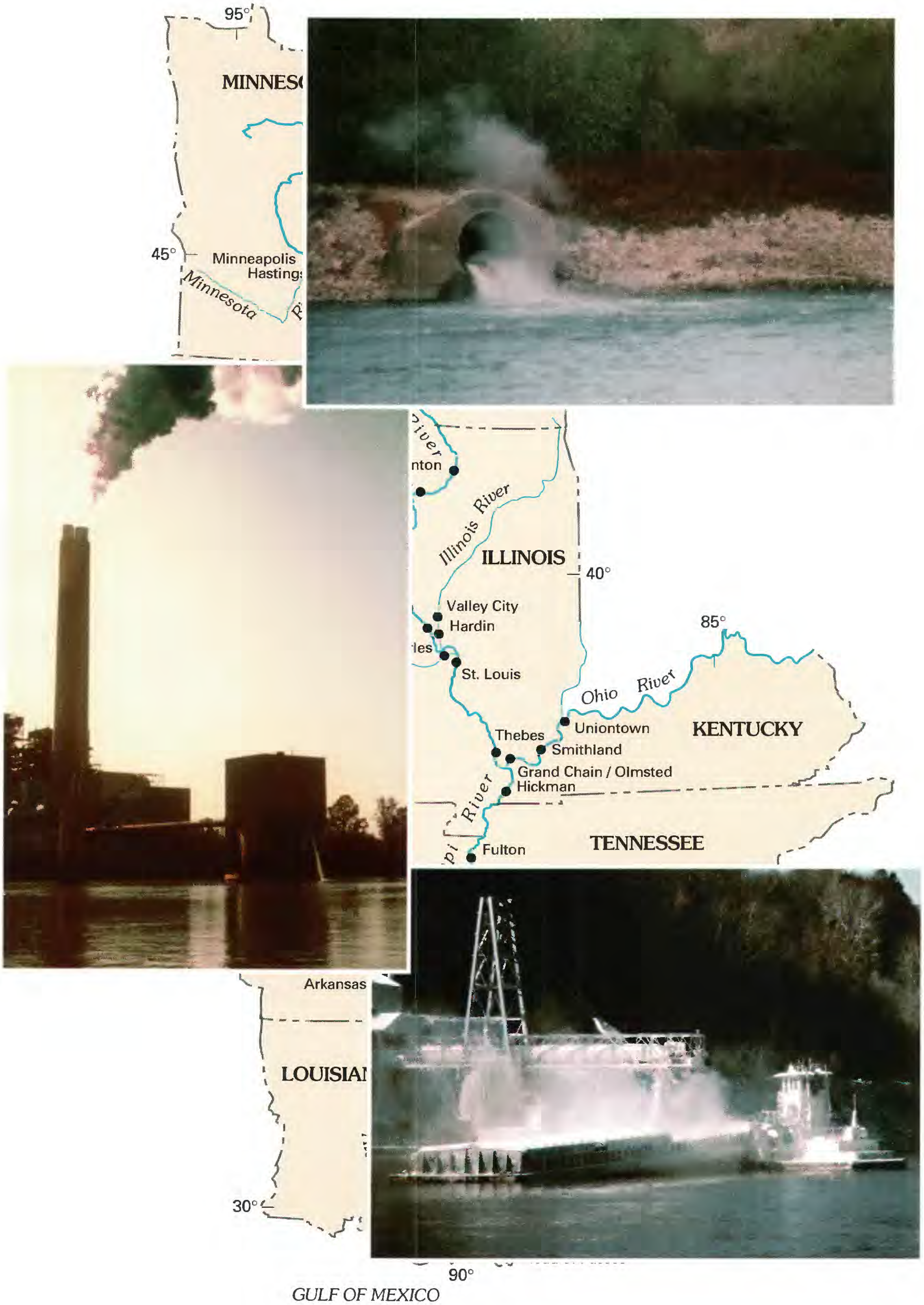
The distributions of the contaminants adsorbed by the bottom sediments in the pools of the Upper Mississippi River reflect two main factors: (1) the affinities of the contaminants for fine particles and organic carbon, and (2) local sources of contaminants.

C Polychlorinated biphenyls (PCBs) are manmade organic compounds, formerly used extensively in industrial applications. Although banned for many years, PCBs still persist in the bottom sediments in the pools of the Upper Mississippi River. They are found in the greatest concentrations in the pools farthest upriver, and especially in the fine-grained carbon-rich sediments on the bottom of Lake Pepin. Lower concentrations in the pools farther downriver suggest that the principal sources of PCBs in the Upper Mississippi River were centered in and near the Minneapolis-St. Paul metropolitan area, and that Lake Pepin has trapped and retained most of the PCBs, retarding their further transport downriver.

Contaminants in Bed Sediments — Continued

D Lead comes from natural and manmade sources, but its sources in the Upper Mississippi River are mostly industrial and municipal. Sediments having concentrations greater than 40 micrograms of lead per gram of sediment are considered "moderately polluted." The highs and lows of lead concentration in the pools of the Upper Mississippi River mimic almost exactly the highs and lows of the percent clay with one notable exception. Pool 12 includes the mouth of the Galena River, which drains an area that was mined extensively for lead some years ago; the higher concentrations in Pool 12 may reflect the input of lead-bearing sediment. The high concentrations of lead in the sediments of Lake Pepin and Pool 19, however, probably reflect mostly the general affinity of lead for fine sediment.

E Coprostanol is a fecal sterol found in the excrement of humans and animals. It is not destroyed completely by normal sewage treatment, and so its presence in the sediments of the Upper Mississippi River is an indicator of human or animal wastes. The high concentrations of coprostanol in Lake Pepin and Pool 19 at least partly reflect the affinity of coprostanol for fine sediment. The high concentrations of coprostanol in the sediments of Pool 2 reflect the large discharges of treated human wastes in the Minneapolis-St. Paul area. Less easy to explain is the high concentration of coprostanol in Pool 14, which is upriver of the Quad Cities (Moline-Rock Island, Illinois, and Davenport-Bettendorf, Iowa), and therefore cannot be due to a large municipal source.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GULF OF MEXICO

Introduction

Robert M. Hirsch

The U.S. Geological Survey (USGS) is the Nation's principal earth-science agency. Its mission is to assess the land, water, and mineral resources of the Nation and to conduct basic and applied research designed to improve the understanding of the Earth and to improve approaches to the study of the Earth. In 1987, a group of USGS chemists and hydrologists undertook a research project to examine the Mississippi River and its tributaries in a way that had not been done before. The project examined a variety of intriguing research questions concerning the transport and storage of a variety of contaminants in large rivers. At the same time, it created, for the first time, a highly comprehensive set of data describing the movement of a wide range of contaminants from the major tributaries and down the main stem of this all-important river. With its laboratories and with its broad mix of practitioners of the different phases of river science—hydrologists, chemists, physicists, sedimentologists, geologists—the USGS was well equipped to undertake such a study.

The Mississippi River is important in several contexts. (1) It serves as drinking-water supply for 70 cities and towns. Thus, the contaminants in the waters of the Mississippi River have the potential for detrimental health effects on these consumers of river water. Some of these contaminants, of course, are removed in water-treatment plants, but some persist regardless of the treatment process. The analysis of river waters provides an indication of the potential for drinking-water contamination. (2) The birds, fish, and other organisms that live in or adjacent to the Mississippi River are affected by contaminants. Thus, there is a basis for interest from an ecological perspective as well as from the perspective of the health of humans who consume the birds and fish. (3) The Mississippi River is a significant source of water, sediment, and nutrients to the Gulf of Mexico. The chemical characteristics of these flows are important to the health and productivity of coastal and marine ecosystems. (4) The Mississippi River drains 41 percent of the conterminous United States, in which area reside 27 percent of the Nation's population. The contaminants moving through the river system are an excellent measure of what is being introduced into the Nation's waterways by human activities. In a sense, they are "report cards" on the Nation's efforts at water-pollution control. Or, to use the analogy of the great tropical ecologist Harald Sioli, "River water is the urine of the landscape," and the quality of the waters of the Mississippi is a monitor of the health of a substantial portion of the "body" of the Nation.

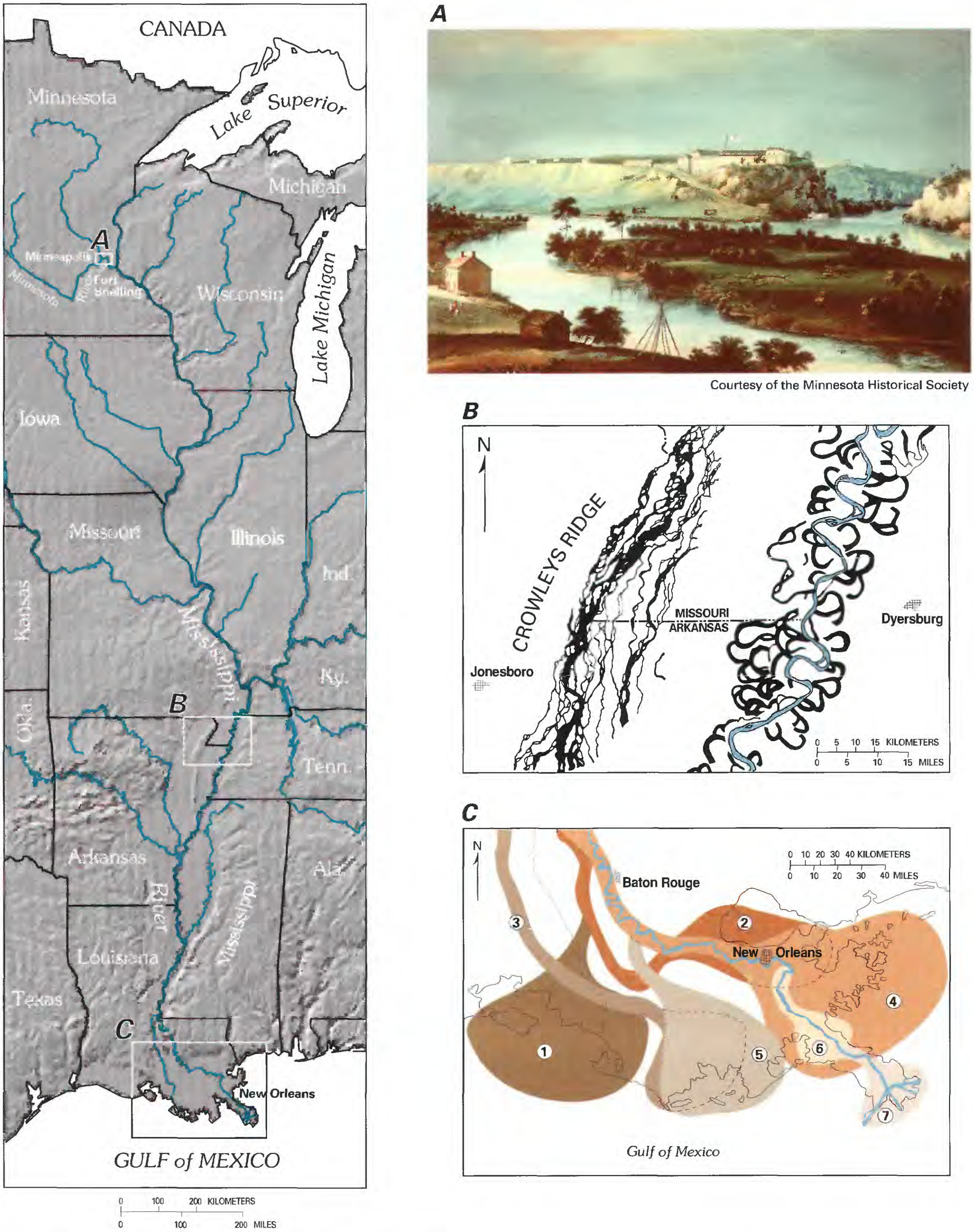
The study, the results of which are reported in this volume, included nearly the full length of the Mississippi River and sampled the waters within and along the boundaries of 11 different States. Ten research and sampling cruises were completed during 1987 through 1992. The study ended before the unprecedented flooding in the summer of 1993. However, the study has provided a baseline for comparison that has been used in the analysis of the movement of contaminants during the flood.

Introduction — Continued

By sampling the river repeatedly, in high flows, in low flows, in the different seasons, one may learn something of the dynamics of contaminant movement through the river system. For example, one learns: what tributary contributes the largest amounts of certain contaminants; what times of year the contaminants enter the river; whether a contaminant, once it enters the river, continues to move downstream with the water, or is lost from the system as a result of chemical reaction, uptake by organisms, volatilization to the atmosphere, or storage on the riverbed or flood plain? Development of effective national and regional strategies for water-quality management demands knowledge of the sources, movement, and storage of contaminants and their reactions throughout the river system.

The purposes of this report are to provide an overview of the new knowledge developed in this study and to provide access to a body of comprehensive and consistent data that can be compared with data collected years and decades hence to help understand and evaluate the changes in the river and future progress (or lack of it) in water-quality management.

Figure 4 *Geologic Settings*



Courtesy of the Minnesota Historical Society

Setting: Geology, Hydrology, Sediments, and Engineering of the Mississippi River

Robert H. Meade

Geologic Settings

Figure 4 The Mississippi River follows the trend of an ancient continental rift system down the center of North America, flowing through different landscapes that record different geologic histories (Redfern, 1983). Three vignettes (A, B, and C) in this figure exemplify some of the different processes that shaped the landscapes during the latest ice ages and during the 10,000 years since the ice melted away.

A The Upper Mississippi River ("Upper" is conventionally assigned to the Mississippi above its confluence with the Ohio) flows for much of its length through a valley 1–10 km wide between bluffs that stand 50–100 m above the river and its fringing flood plain. The painting, done in 1844 by John Casper Wild, shows the bluffs above the confluence of the Minnesota (left) and Mississippi (right) Rivers, at the site of Fort Snelling, which is now included in the city of Minneapolis. The bluff-bordered river valleys here and farther down the Upper Mississippi were formed by a combination of glacial and riverine processes. The great ice ages of the Pleistocene epoch gave the basin of the Upper Mississippi much of the shape that we consider characteristic today. Pre-existing river valleys were widened and deepened by the ice as it pushed its way south. Between and after the ice ages, the rivers transported and rearranged the sediments in the valleys by meandering across them and constructing islands and flood plains. The main valley in the painting (upper left to lower right) formed mostly when the ice-age predecessor to the Minnesota River (called Glacial River Warren) was the main outlet of a large lake, Lake Agassiz, that was dammed along its northern margin in southern Canada by the retreating ice sheet. The small notch out of which the Mississippi River is flowing (upper right in painting) was cut, mostly after the demise of Glacial River Warren, by a retreating headcut that can be seen today at St. Anthony Falls, 13 km upriver of the confluence with the Minnesota River.

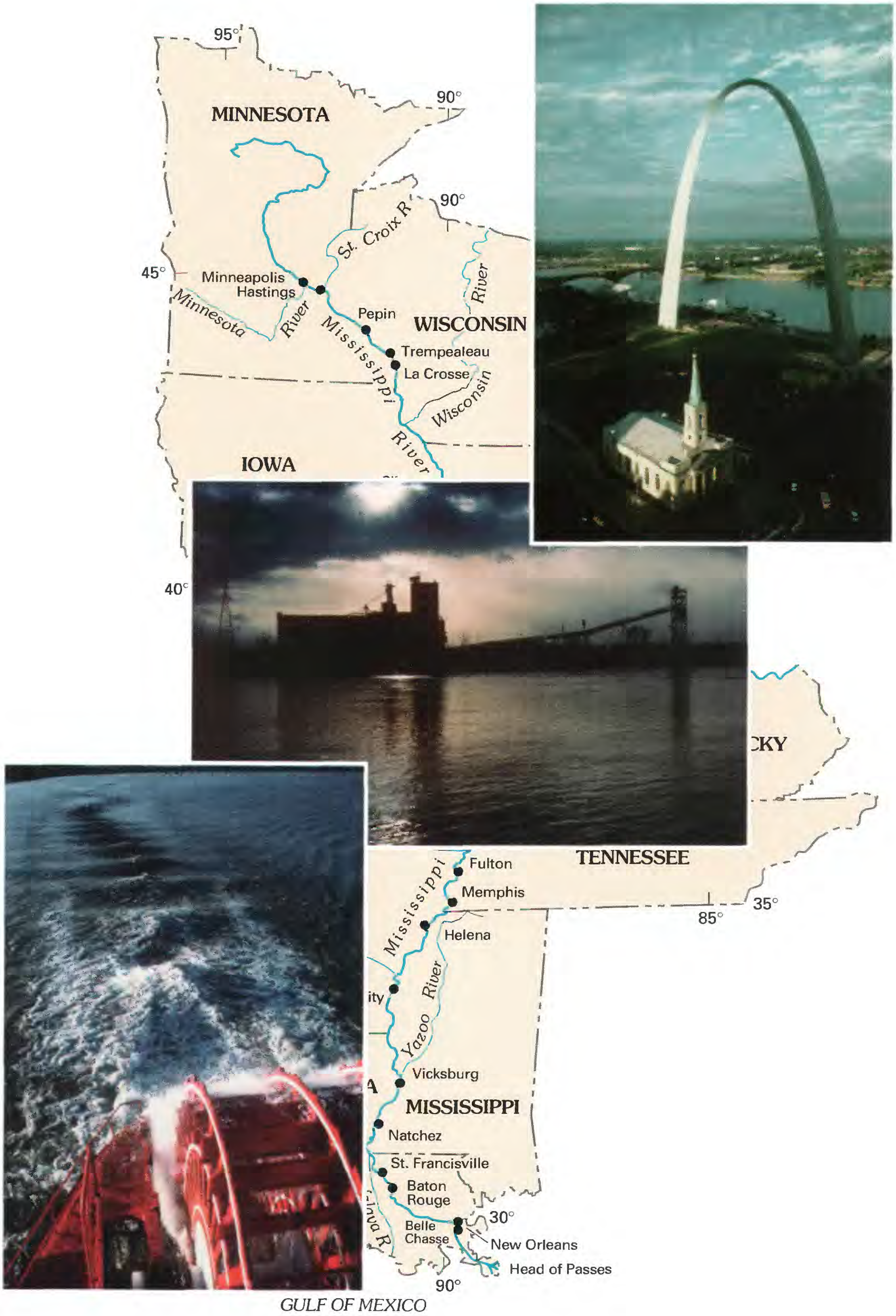
B The Lower Mississippi River flows along and through a wide alluvial plain formed by the river and its predecessors. Vignette B (taken from R.T. Saucier, 1991) shows the contrast in stream patterns between those formed during the latest ice age (left) and those formed since the ice ages. Typical of glacial meltwater rivers heavily laden with coarser sediments are the so-called "valley trains" like those shown in the western half of the vignette. Even though no great river has flowed there for thousands of years, the braided and anastomosing pattern still shows on the landscape and is clearly visible from the air. The present pattern, in which the Mississippi River meanders through a belt 20–30 km wide defined by the traces and remnants of older meanders through which the river once flowed, is typical of most of the length of the lower river.

Geologic Settings — Continued

C

Where the Mississippi River meets the Gulf of Mexico, its delta has a complex history that has been described in classic papers by C.R. Kolb and J.R. Van Lopik (1958, 1966). The succession of different river channels and delta lobes during the last 5,000 years are numbered from oldest (1) to youngest (7) in Vignette C. Let John McPhee (1989, p. 5–6) recount the story:

> "Southern Louisiana exists in its present form because the Mississippi River has jumped here and there within an arc about two hundred miles wide, like a pianist playing with one hand—frequently and radically changing course, surging over the left or the right bank to go off in utterly new directions. Always it is the river's purpose to get to the Gulf by the shortest and steepest gradient. As the mouth advances southward and the river lengthens, the gradient declines, the current slows, and sediment builds up the bed. Eventually, it builds up so much that the river spills to one side. Major shifts of that nature have tended to occur roughly once a millennium. The Mississippi's main channel of three thousand years ago is now the quiet water of Bayou Teche [3], which mimics the shape of the Mississippi......Eight hundred years before the birth of Christ, the channel was captured from the east [4]. It shifted abruptly and flowed in that direction for about a thousand years. In the second century A.D., it was captured again, and taken south, by the now unprepossessing Bayou Lafourche [5], which, by the year 1000, was losing its hegemony to the river's present course, through the region that would be known as Plaquemines [6, 7]."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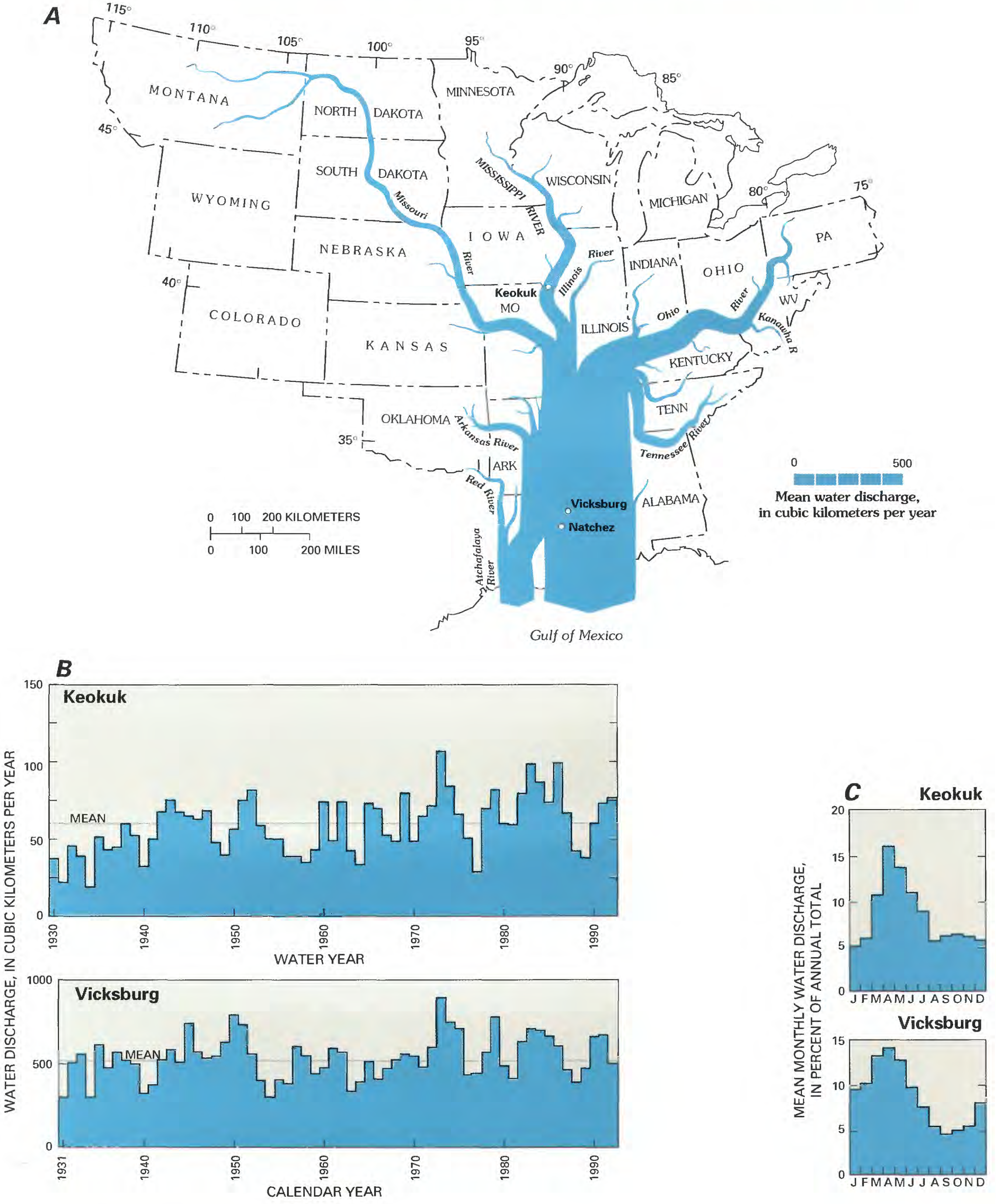
GULF OF MEXICO

Figure 5 *Water Discharge*



Water Discharge

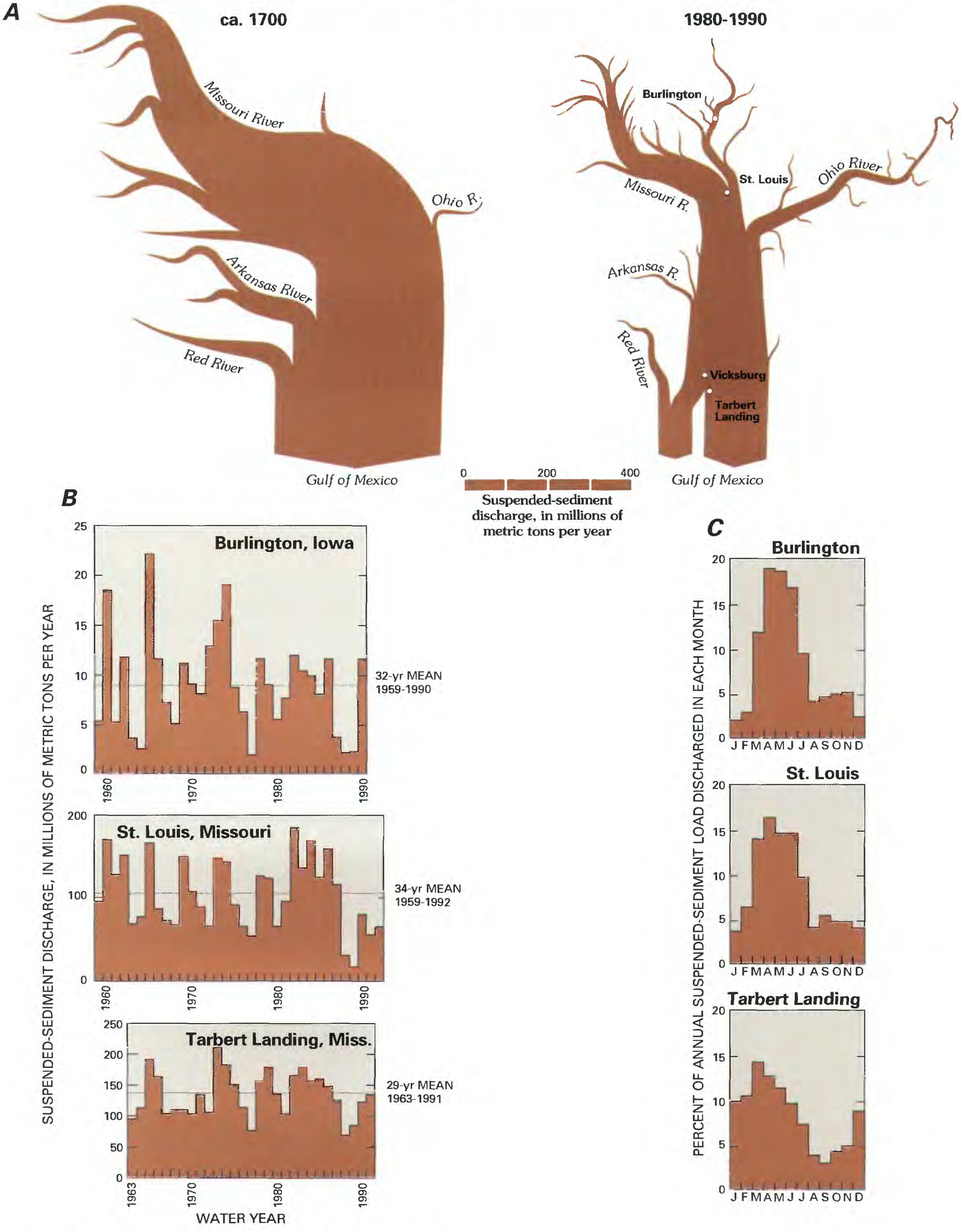
Figure 5 The Mississippi River discharges an average of 520 cubic kilometers of water each year past the cities of Vicksburg and Natchez, Mississippi. This represents the greatest amount of water discharged by the river while it still is confined to a single channel, but it does not represent all water that the Mississippi River system discharges to the Gulf of Mexico. The river bifurcates 77 km below Natchez, and the lesser of its two main distributaries is joined by another significant tributary, the Red River. The two outlets of the Mississippi River eventually discharge a combined average of 580 cubic kilometers per year (or about 420 billion gallons per day) of freshwater to the Gulf of Mexico. This discharge ranks seventh in the world, being exceeded only by those of the Amazon, Congo (or Zaire), Orinoco, Yangtze, the combined Ganges-Brahmaputra, and Yenisey Rivers.

A Not all parts of the Mississippi River drainage basin contribute water in equal measure. Nearly one-half the water discharged to the Gulf is contributed by the Ohio River and its tributaries (including the Tennessee) whose combined drainage areas constitute only one-sixth of the total area drained by the Mississippi. By contrast, the Missouri River drains 43 percent of the total area but contributes only 12 percent of the total water. As the Mississippi flows southward from its headwaters in the northern Midwest, its discharge is more than doubled by the waters it receives from the Illinois and Missouri Rivers. This combined discharge, in turn, is more than doubled again as it joins the waters of the Ohio River.

B Just as the spatial distribution of sources of water in the Mississippi River is uneven, so is the temporal distribution of river flow. Shown here are the yearly flows of the Mississippi since 1930 at Keokuk, Iowa, and since 1931 at Vicksburg, Mississippi. Keokuk is at the Iowa-Missouri State line, 235 and 270 km, respectively, up the Mississippi from its confluences with the Illinois and Missouri Rivers. Vicksburg is downriver of the mouth of the Arkansas River and upriver of the Atchafalaya diversion (see fig. 10B), and the discharges recorded at Vicksburg represent the largest and most integrated flows measured in the Mississippi River system. The two graphs are drawn so that the long-term mean discharges at the two stations are represented equally; although the mean discharges at the two stations differ by a factor of nine, the scales and ranges of variability can be compared directly by simple visual inspection. Wet years and dry years at the two cities generally coincide. The range of flow variation is somewhat less extreme at Vicksburg than at Keokuk, which is a reflection of the damping influence of flows from the intervening large tributaries, especially the Illinois, Missouri, Ohio, and Arkansas Rivers. The ratio between the extreme maximum and minimum yearly discharges shown here (1973 compared to 1934) is 5.5 at Keokuk but only 3.1 at Vicksburg.

C Average seasonal differences in river discharge are on the same order as the extreme annual differences between wet and dry years. Shown here are mean monthly discharges at Keokuk and Vicksburg for the same periods of record as shown in B. In nearly all years along the length of the Mississippi River, mean discharges during the high-water months can be expected to be about three times the discharges during the low-water months. At Keokuk, spring runoff usually begins quickly, in response to the melting of ice on the river. At Vicksburg, the usually high flows from the Ohio River during the months of December through March give a more gradual beginning to the annual peak of spring runoff.

Figure 6 *Suspended-Sediment Discharge*



Suspended-Sediment Discharge

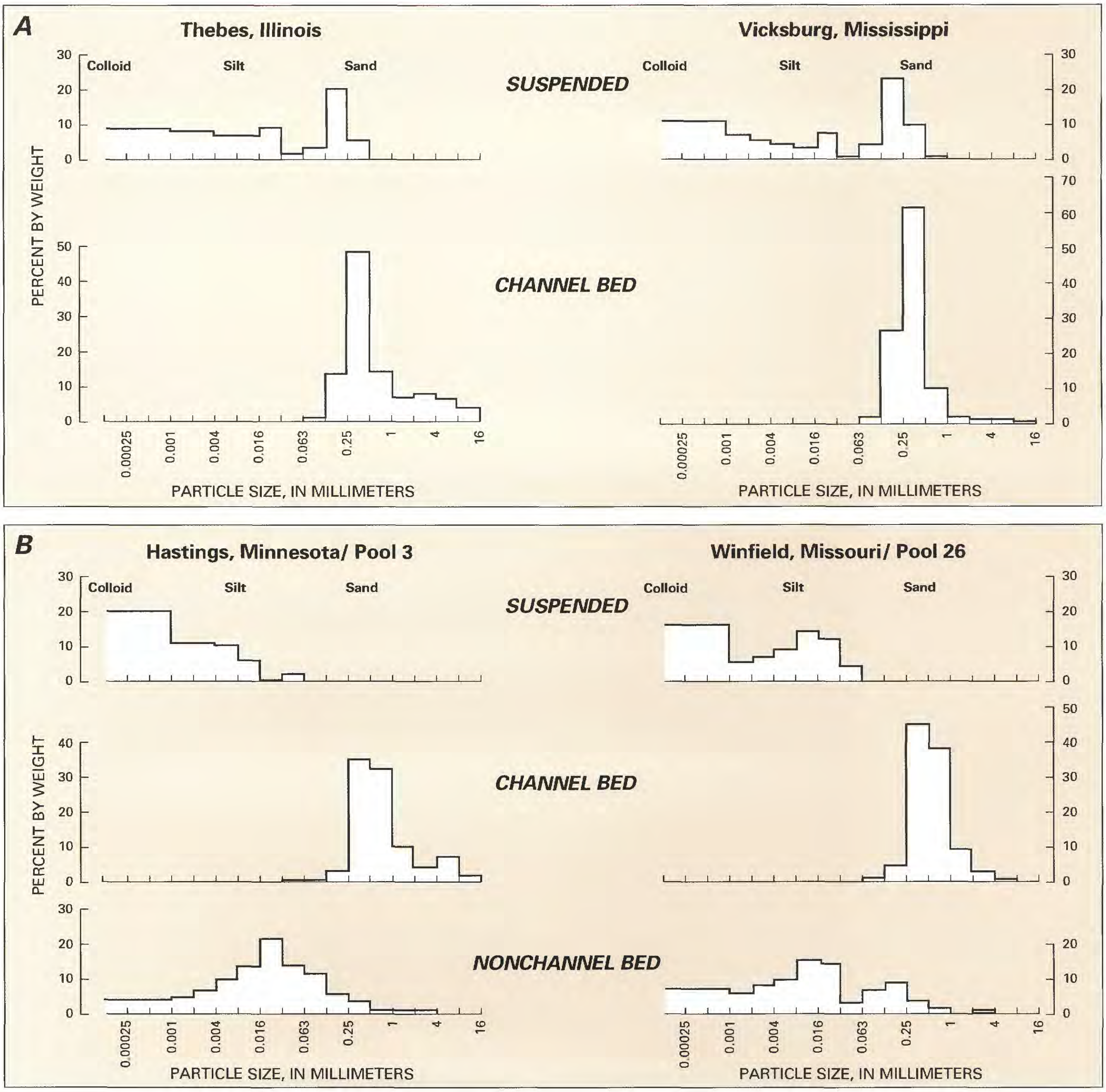
Figure 6 The Mississippi River now discharges an average of about 200 million metric tons of suspended sediment per year past Vicksburg and eventually to the Gulf of Mexico. This sediment discharge to the ocean ranks about sixth in the world today, being equaled or exceeded by those of four rivers of Asia (the Yellow and Yangtze Rivers of China, the Ganges-Brahmaputra of India and Bangladesh, and probably the Irrawaddy River of Burma) and two rivers of South America (the Amazon River of Brazil and possibly the Magdalena River of Colombia).

A The suspended-sediment loads carried by the Mississippi River to the Gulf of Mexico have decreased by one-half since the Mississippi Valley was first settled by European colonists. This decrease has happened mostly since 1950, as the largest natural sources of sediment in the drainage basin were cut off from the Mississippi River main stem by the construction of large reservoirs on the Missouri and Arkansas Rivers (see fig. 8). This large decrease in sediments from the western tributaries was counterbalanced somewhat by a five- to tenfold increase in sediment loads in the Ohio River—an increase that has resulted from deforestation and rowcrop farming. Further complicating the picture today is the controlled diversion of part of the water and sediment from the Mississippi River below Vicksburg into the Old River Outflow Channel and the Atchafalaya River (see fig. 10B). The average suspended-sediment discharges portrayed for 1980–90 are taken mainly from the extensive compilations of M.P. Keown and his colleagues (1981, 1986) and of R.S. Parker (1988).

B Temporal variation of suspended-sediment discharge in the Mississippi River is more pronounced than that of water discharge (compare with fig. 5B). Shown here are the yearly totals of suspended sediment discharged past three long-term monitoring stations: Burlington, Iowa, 335 km upriver of the confluence with the Missouri River; St. Louis, Missouri, 25 km downriver of the confluence with the Missouri River; Tarbert Landing, Mississippi, 13 km downriver of the Atchafalaya diversion at Old River. Sediment discharges shown for Burlington and Tarbert Landing are based on data of the U.S. Army Corps of Engineers (Rock Island and New Orleans Districts). Although records of sediment at all three stations began some years prior to 1959, only partial records are shown here to eliminate the confusion that might have been introduced by including pre-reservoir sediment discharges at St. Louis (see fig. 8) and pre-diversion sediment discharges at Tarbert Landing (see fig. 10B). The three graphs are drawn so that the long-term mean sediment discharges at all three stations are represented equally and the scales and ranges of variability may be compared by simple visual inspection. Years of high and low sediment discharges generally coincide at all three stations, but the range of year-to-year variation is more extreme in the upper river than in the lower river. The ratios between extreme maximum and minimum yearly suspended-sediment discharges for the periods of record shown here are 11.7 at Burlington, 9.2 at St. Louis, and only 2.8 at Tarbert Landing. Even during 1988 and 1989, when sediment discharges in the upper river were especially small, the Ohio River contributed enough sediment to damp the extremes of year-to-year variation at Tarbert Landing.

C Average seasonal differences in river-sediment discharges are of the same order as extreme annual differences between wet and dry years in the Upper Mississippi, and they exceed the range of year-to-year differences in the Lower Mississippi. Shown here are the monthly average suspended-sediment discharges at Burlington, St. Louis, and Tarbert Landing for the same periods of record as shown in B. In the Upper Mississippi River (Burlington), average suspended-sediment discharges during the high-water months following ice breakup are nearly ten times greater than discharges during midwinter months when the river usually is covered with ice. In the Lower Mississippi (Tarbert Landing), the late winter-early spring runoff from the Ohio River contributes sediment during the months of December through March. Even with this temporal offset in tributary contributions, the maximum monthly sediment discharge (March) in the lower river averages five times greater than the minimum monthly discharge (September).

Figure 7 ***Particle Sizes of Sediments***



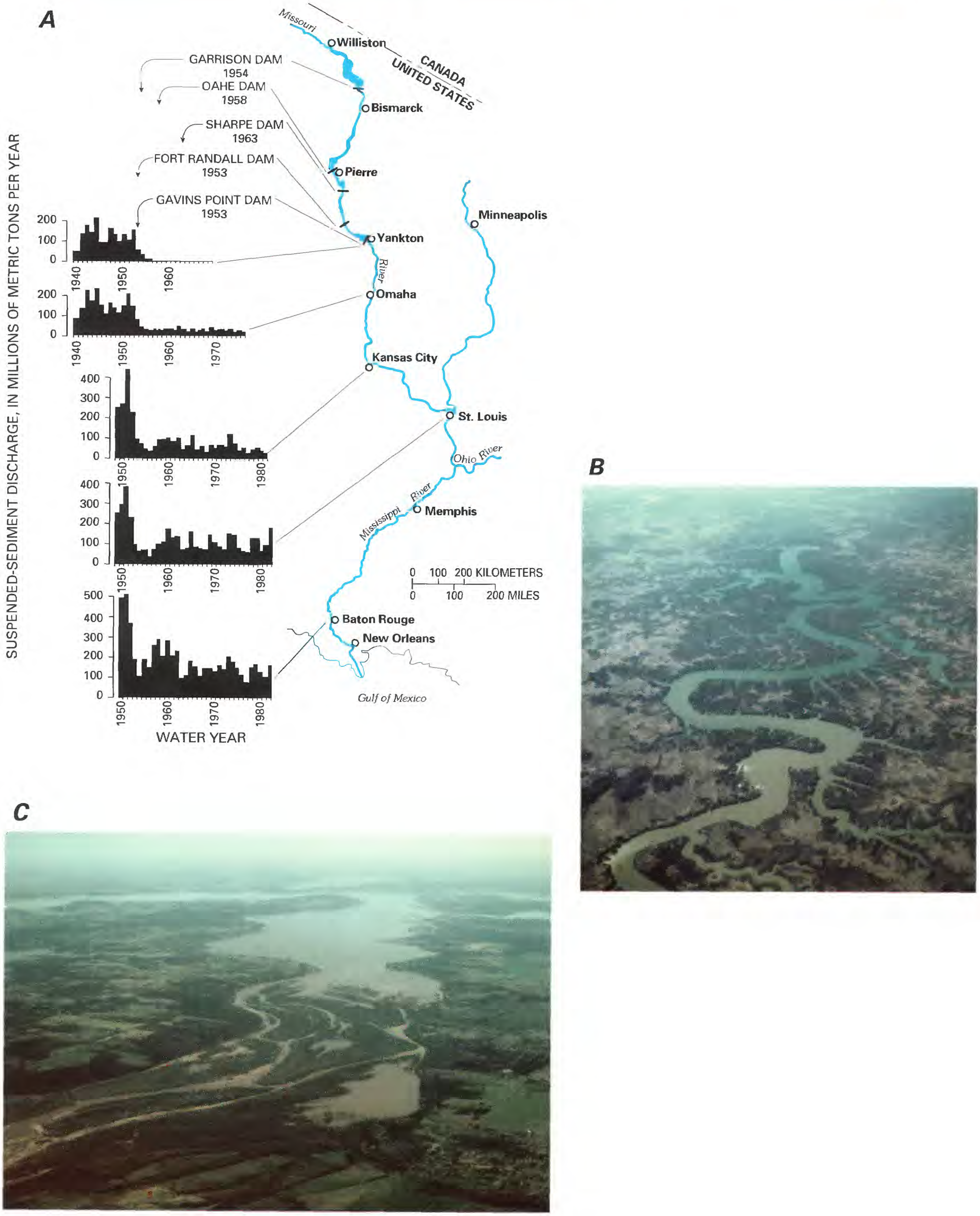
Particle Sizes of Sediments

Figure 7 Sediment particles in the Mississippi River range in size from the very finest clays or colloids to coarse sand and gravel. Different sizes of particles are found in suspension and on the river bed, and the interrelations between the sediments being transported in suspension and those stored or being transported along the riverbed are complex and variable. The finest particles play the largest role in the transport and storage of toxic contaminants.

A In the freely flowing reaches of the Mississippi River downstream from St. Louis, part of the suspended-sediment load interacts with the channel bed and part of it is independent of any such interaction. The examples shown here are data collected from the Mississippi River at Thebes, Illinois, on June 10, 1989, and at Vicksburg, Mississippi, on March 27, 1989. The channel bed at these two sites (and through most of the 1850-km length of the Mississippi between St. Louis and the Gulf of Mexico) consists almost entirely of sand and fine gravel, with few particles, if any, finer than 0.063 mm (millimeter) in diameter. Some of the finest sand (mostly 0.125–0.25 mm) is mobilized from the channel bed to become part of the suspended sediment; hydraulic engineers refer to such sand in suspension as "bed-material load" because it usually represents an exchange of sand particles between the river waters and the beds over which they flow. Most of the sediment in suspension, however, is finer than sand. To aid in understanding the chemistry of the suspended matter, we have divided the fine suspended sediment into two fractions called "silt" and "colloid." The division between the two fractions is here defined arbitrarily at about 0.001 mm. The relative volumes of silt and colloid shown in the figure represent the sizes of the individual particles after they have been disaggregated in the laboratory with a dispersing agent. In the river itself, most of the colloid-size particles are found in aggregates that are large enough to be transported and deposited as silt particles.

B In the Upper Mississippi River, which has been dammed in order to form a series of lakes to provide depth sufficient for barge navigation (see fig. 10A), the sizes of the particles in both the bed sediments and suspended sediments are distributed differently from those in the unimpounded reaches of the lower river. The examples shown here are data collected from the Mississippi River at Hastings, Minnesota, in the upper end of navigation Pool 3 on October 10, 1991, and from the nonchannel areas of lower Pool 3 on October 11, 1991; and from the Mississippi River near Winfield, Missouri, at the upper end of Pool 26 on July 24, 1991, and from the nonchannel areas of lower-middle Pool 26 on November 1, 1991. In the navigation channels, the bed sediments consist largely of sand, as they do in the channels of the freely flowing lower river. Suspended sediments, however, consist almost entirely of silt and colloidal particles and contain very little sand except during floods. In the shallow nonchannel areas of the navigation pools, which cover the former flood plains of the upper river, the bed sediment is typically intermediate in size—finer than the bed material in the main channels but generally coarser than the bulk of the sediment in suspension.

Figure 8 *Effects of Reservoirs*



Effects of Reservoirs

Figure 8 Reservoirs reduce the sediment discharges of the Mississippi River and its tributaries by trapping sediment that otherwise would have been transported downriver.

A The Missouri River has been the principal supplier of sediment to the Mississippi River since the end of the last ice age. The graphs show the annual discharges of suspended sediment measured by the U.S. Army Corps of Engineers and the USGS at three gaging stations on the Missouri River and two gaging stations on the Mississippi River over a period of about four decades. After five large dams were completed for hydroelectric power and irrigation above Yankton, South Dakota, between 1953 and 1963, the discharge of sediment from the Upper Missouri River Basin virtually was stopped. Following the closure of Fort Randall Dam and Gavins Point Dam in 1953, downriver sediment discharges were diminished immediately, and the effect could be observed all the way down to the mouth of the Mississippi River. Sediment discharges to the Gulf of Mexico in 1992 were less than one-half of what they were before 1953.

B In this downriver view (looking west-southwest) of Lake Cumberland, a reservoir on the Cumberland River in Kentucky, sediment-laden brown water can be seen flowing into the upper end of the lake during late winter (February 28, 1988); the sediment gradually settles out to leave blue water farther down the lake.

C Deltas form where rivers flow into reservoirs, especially if the inflowing rivers transport substantial amounts of sand. This large sand delta has formed where the Canadian River flows into Lake Eufala, a large reservoir in eastern Oklahoma near where the Canadian River joins the Arkansas River. The view is down Lake Eufala (looking east-northeast) in early spring (March 25, 1988).

Figure 9 *Engineering Activities*

Engineering Activities

Figure 9 For more than 270 years, the banks and the channel of the Mississippi River have been engineered for various purposes: originally, starting about 1720, for flood control; eventually, starting about a century later, for navigation.

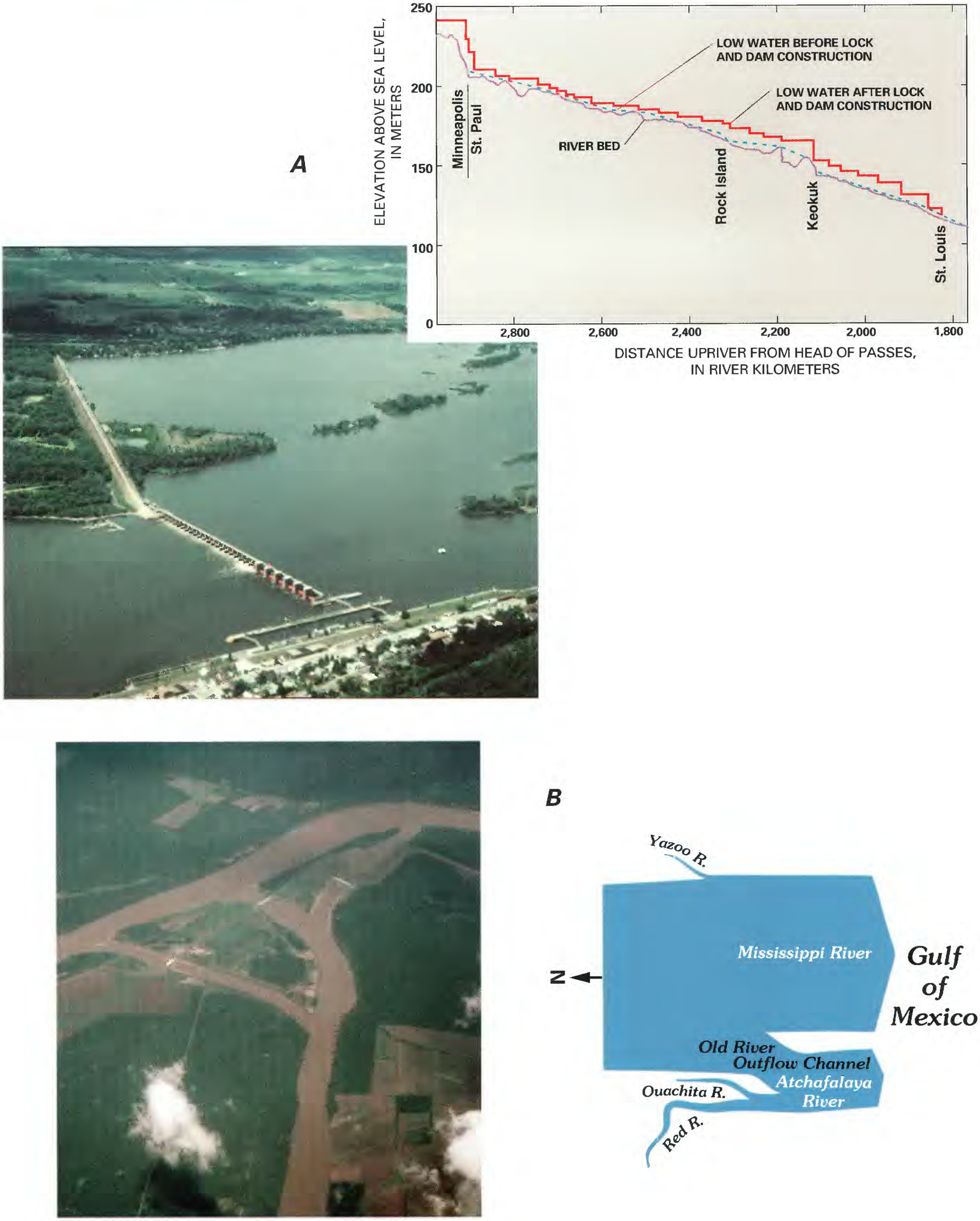
A The Lower Mississippi River from Cairo, Illinois, to the Gulf of Mexico is constrained by a system of flood-control levees that is longer than the Great Wall of China. The Z-shaped levee in this photograph (view north) separates the active flood plain of the Mississippi River (left of levee) from intensively cultivated cropland in the fertile "Delta" region of Mississippi about 30 km upriver of Vicksburg.

B Dikes and wing dams are constructed to focus the main flow of the river into the navigation channels, and they encourage sediment to deposit in areas of the river that lie outside the navigation channels. These dikes have allowed sandbars to grow and stabilize into permanent islands along the right (western) bank of the Mississippi River about 10 km upriver of Cape Girardeau, Missouri. The sediment stored behind and between dikes such as these is virtually immobilized and is unlikely to be resuspended for transport downriver during the foreseeable future.

C Bank-protection measures are applied along most of the Mississippi to impede erosion and to maintain the shape of the navigation channel. Shown here is an articulated concrete mat that is laid like carpet on the riverbank by a special machine. Other banks along the Mississippi are stabilized by boulder-size rock fragments that are quarried from bluffs near the banks of the Upper Mississippi and brought downriver by barge. One effect of the bank stabilization is to prevent the remobilization of sediment previously deposited on the flood plains of the river.

D Despite the controls on water flow and sedimentation that are provided by dikes and other engineering works, some reaches of the river require periodic dredging to maintain the depth of water necessary for navigation. In the Lower Mississippi, as shown in the photograph, the dredged material is frequently piped out to the fast flowing part of the river to be discharged. In the Upper Mississippi, where sand is frequently the material dredged, large spoil banks and artificial islands have been built alongside the main navigation channel.

Figure 10 *Major Engineering Works*



Major Engineering Works

Figure 10 The two most prominent examples of river engineering on the Mississippi are the lock-and-dam system on the upper river and the Atchafalaya diversion on the lower river.

A The entire 1080-km reach of the Upper Mississippi River between Minneapolis, Minnesota, and St. Louis, Missouri, is controlled for barge navigation by a series of 29 lock-and-dam structures (O'Brien and others, 1992). One of these structures—the first to be completed, in 1913, at Keokuk, Iowa—was built to impound water to generate hydroelectric power. The other 28 structures were built, mostly during the 1930s, to maintain a minimum river depth of 9 feet (2.7 meters) for barge navigation.

Before the dams were built, navigation during low-water periods was extremely hazardous, if not impossible, across rapids such as those at Keokuk and Rock Island, and it was difficult in many other reaches of the upper river. The lower reaches of the navigation pools, such as the one shown in the photograph, are shallow lakes in which former flood plains, previously inundated for infrequent short periods, are now permanently under water. These shallow lakes are storage areas for fine-grained sediments and the contaminants adsorbed to them.

B About 500 km upstream from its main outlet to the Gulf of Mexico, the Lower Mississippi River is partly diverted into the Atchafalaya River. About one-fourth, on average, of the water that flows down the Mississippi River past Vicksburg is diverted at a place called "Old River" to join the waters of the Red and Ouachita Rivers in forming the Atchafalaya River (McPhee, 1989). The diagram on the lower right is an excerpt of figure 5A that has been enlarged and rotated 90 degrees so that the direction of flow is to the right. The accompanying photograph (view east, June 1991) shows the Mississippi River flowing from center left to upper right. In the foreground is the Old River Outflow Channel (flow west toward the viewer), an artificial channel that joins the Red River just off the lower edge of the photograph to form the Atchafalaya. Three artificial channels, each containing a control structure, divert water from the Mississippi River into the Old River Outflow Channel: (1) the original channel, in the center, contains the Old River Control Structure, completed in 1963; (2) the southernmost channel (upper right in photograph) contains the Old River Auxiliary Control Structure, completed in 1987; and (3) the northernmost channel (left center) contains a low-head hydroelectric power dam, completed in 1990 and having a rated capacity of 194 megawatts, which supplies electricity to communities in Louisiana.

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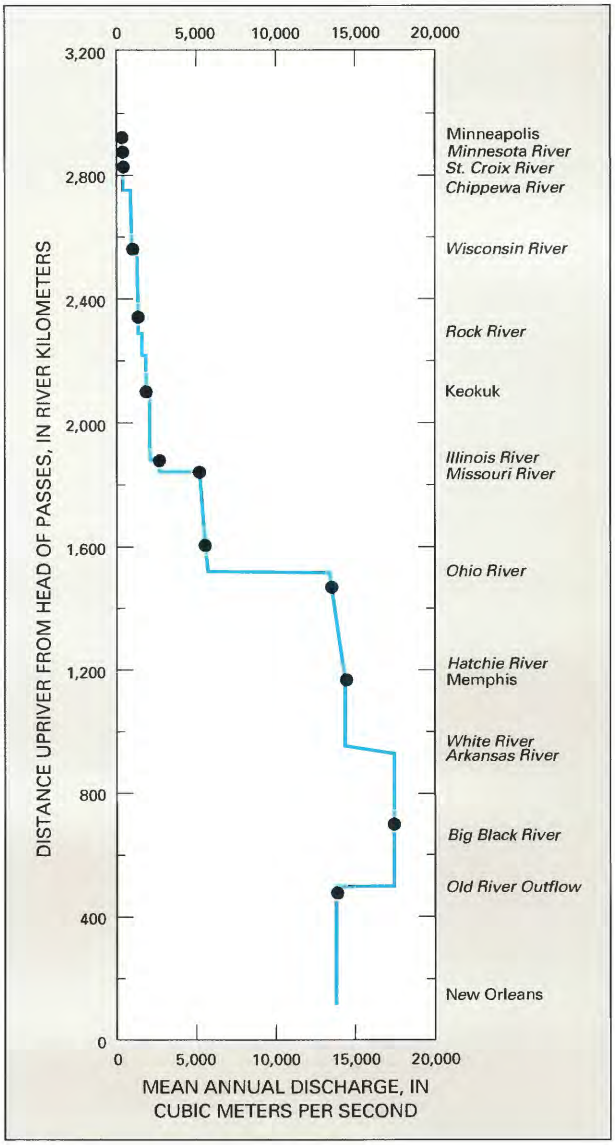
Figure 11 *Discharge of River Water*



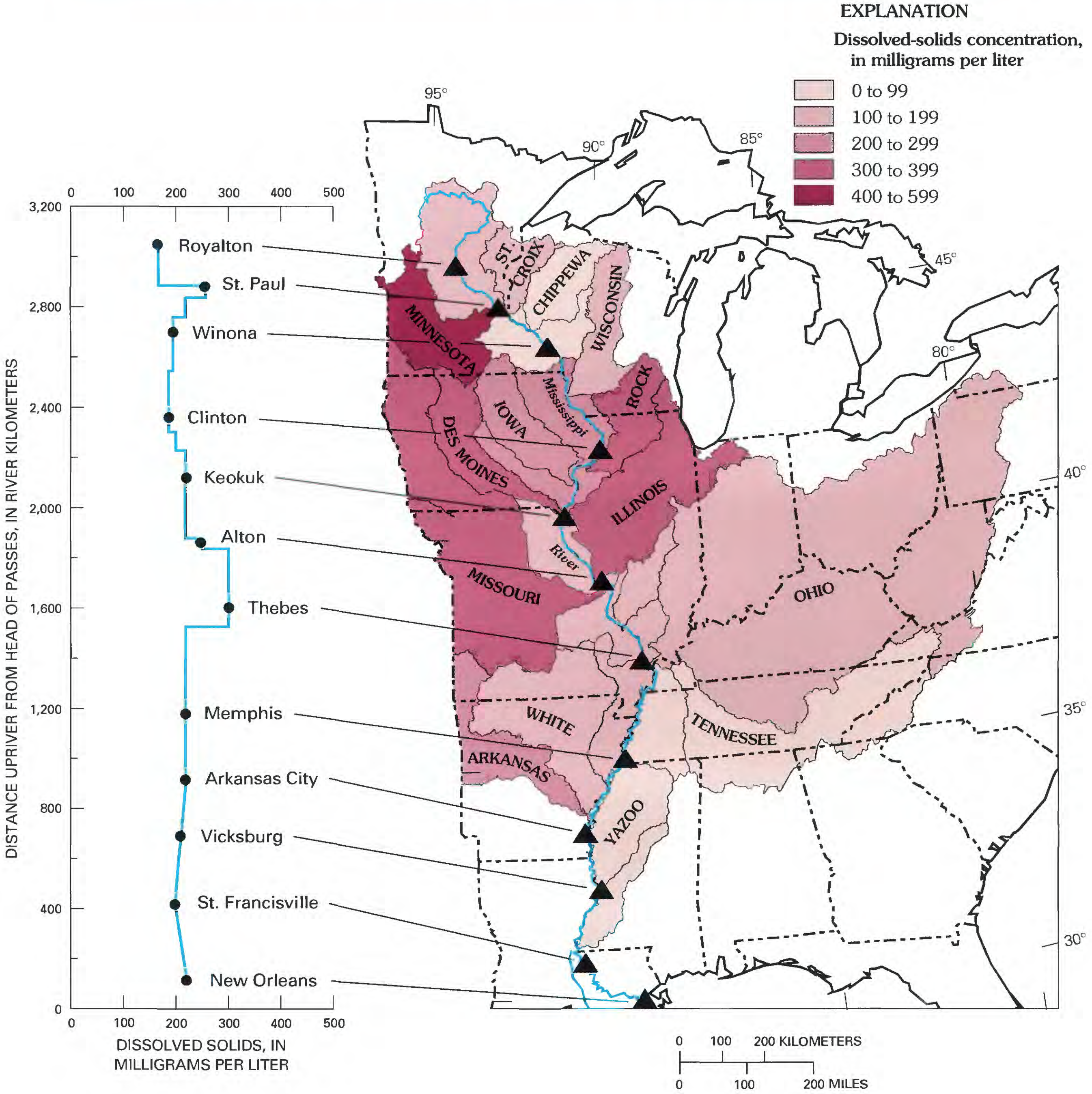
Setting: Chemical Character of the Mississippi River

John A. Moody and William A. Battaglin

Discharge of River Water

Figure 11 To understand the chemical character of the Mississippi River, we first have to understand how the river is nourished by its tributaries. The effects of tributaries on river chemistry depend less on their absolute water discharges than on their relative contributions to the local water discharge of the Mississippi River. Tributaries whose discharges would hardly qualify them as significant contributors to the Lower Mississippi River are highly significant contributors of water, sediment, and contaminants to the Upper Mississippi River. In this graph are plotted the mean discharges of the Mississippi River for the period of record prior to 1989 (data from U.S. Army Corps of Engineers and USGS; for a somewhat different portrayal of the same data, see figure 5A). The mean water discharge in the Mississippi River at a site 8 km upstream from the Minneapolis city limits is 225 cubic meters per second (m^3/s). Thirty-two kilometers farther downstream, the average discharge is increased by about 50 percent as the Minnesota River joins the Mississippi in downtown Minneapolis. For the next 772 kilometers, the average water discharge of the Mississippi River increases slowly to about 1,810 m^3/s at Keokuk, Iowa. Just upstream from St. Louis, Missouri, the contributions from the Illinois and Missouri Rivers more than double the mean water discharge to 5,140 m^3/s. In a relatively short distance of 290 km downstream from St. Louis, the Ohio River again more than doubles the water discharge so that just downstream from the Mississippi-Ohio confluence the Lower Mississippi River discharge averages 13,500 m^3/s. The Lower Mississippi River is now transporting so much water that, in a relative sense, the White and Arkansas Rivers are the only major tributaries between the Ohio River and the Gulf of Mexico. Their combined contribution is only about 10 percent of the Lower Mississippi River's discharge but this equals the discharge of the Upper Mississippi River at Keokuk, Iowa. Tributaries like the Hatchie River in Tennessee and the Big Black River in Mississippi have mean discharges similar to that of the Minnesota River but only contribute about 1 percent of the mean discharge of the Lower Mississippi River. Even though the Hatchie and Big Black Rivers contribute as much water as the Minnesota River, their local effects on the discharge of the Mississippi River are only about one-fiftieth of the local effect of the Minnesota River.

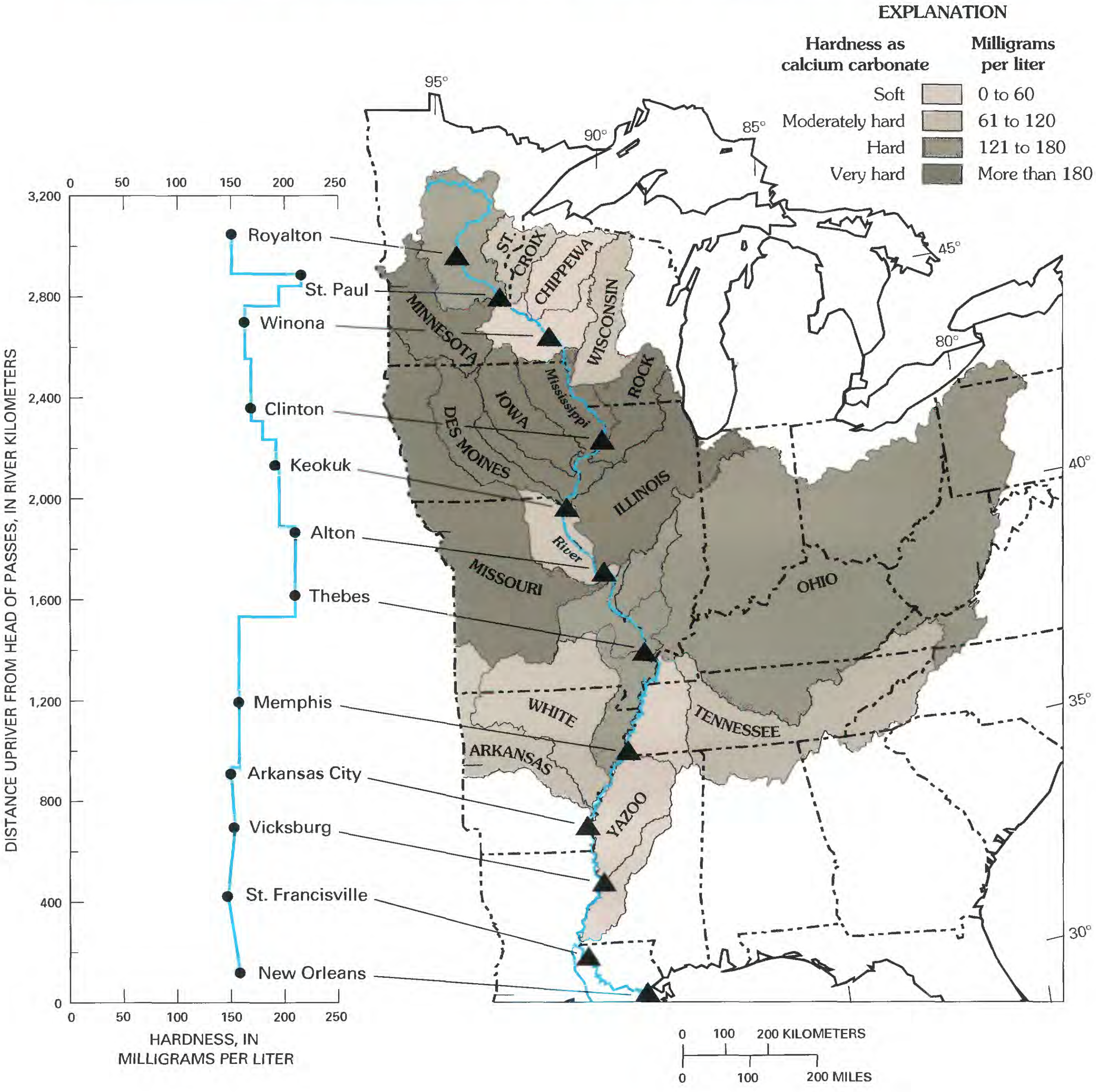
Figure 12 *Dissolved Solids in River Waters*



Dissolved Solids in River Waters

Figure 12 The amount of dissolved chemicals or dissolved solids in river water depends on the solubility of the rocks and soil and the rainfall within a drainage basin. The map shows the dissolved solids (DS, in milligrams per liter, or mg/L) added to the Mississippi River by some of its tributaries; the median concentration of dissolved solids shown for each basin is the median value in water samples collected at the gaging station closest to the mouth of the tributary. The graph on the left side of the figure shows the variation of the median concentration of dissolved solids along the length of the Mississippi River for the period from 1970 through 1991. Triangles on the map show the locations of the gaging stations that are represented as dots on the graph. The median concentration of DS in the Mississippi River upstream from St. Paul, Minnesota, is about 170 mg/L. This increases sharply with the addition of water from the Minnesota River (median concentration is 550 mg/L)—a western tributary draining plains developed on fairly soluble sedimentary rocks in a region of relatively low mean annual precipitation (50–70 cm/yr; all precipitation figures are taken from U.S. Geological Survey, 1970, p. 97–99). Downstream from the Minnesota River, the eastern tributaries (St. Croix, Chippewa, and Wisconsin Rivers) drain terranes varying from glacial gravel and sand deposits in the northeast to sandstone and limestone hills along the Mississippi River and receiving slightly greater precipitation (70–80 cm/yr). These tributaries contribute water with low DS concentrations (74 to 129 mg/L) which dilute the DS concentration in the Mississippi River below St. Paul, Minnesota. However, downstream from Clinton, Iowa, the Rock, Iowa, Des Moines, Illinois, and Missouri Rivers have median DS concentrations between 280 and 380 mg/L and thus increase the DS concentration of the Mississippi River in a series of steps, up to a maximum of 300 mg/L at Thebes, Illinois. These tributaries drain a predominantly agricultural region (with the exception of the Illinois River, which also drains the urban areas of Chicago, Peoria, and Springfield, Illinois) consisting of plains underlain by relatively soluble sedimentary rocks and receiving a wider range of precipitation (40–100 cm/yr). The Ohio River drains mostly hilly and mountainous terranes composed of predominantly insoluble rocks that receive relatively high precipitation (100–130 cm/yr) resulting in a high discharge (7,750 m^3/s) with a relatively low DS concentration (170 mg/L). When this large amount of Ohio River water mixes with the Upper Mississippi River water, the DS concentration in the Mississippi is reduced to about 220 mg/L. The concentration in the Mississippi River remains nearly constant at sites farther downstream to New Orleans because the eastern tributaries (like the Yazoo River) to the Lower Mississippi River drain the alluvial plain and adjacent uplands that receive the highest precipitation (130–150 cm/yr), contain low DS concentrations (53–75 mg/L), and discharge relatively small volumes of water into the Lower Mississippi River.

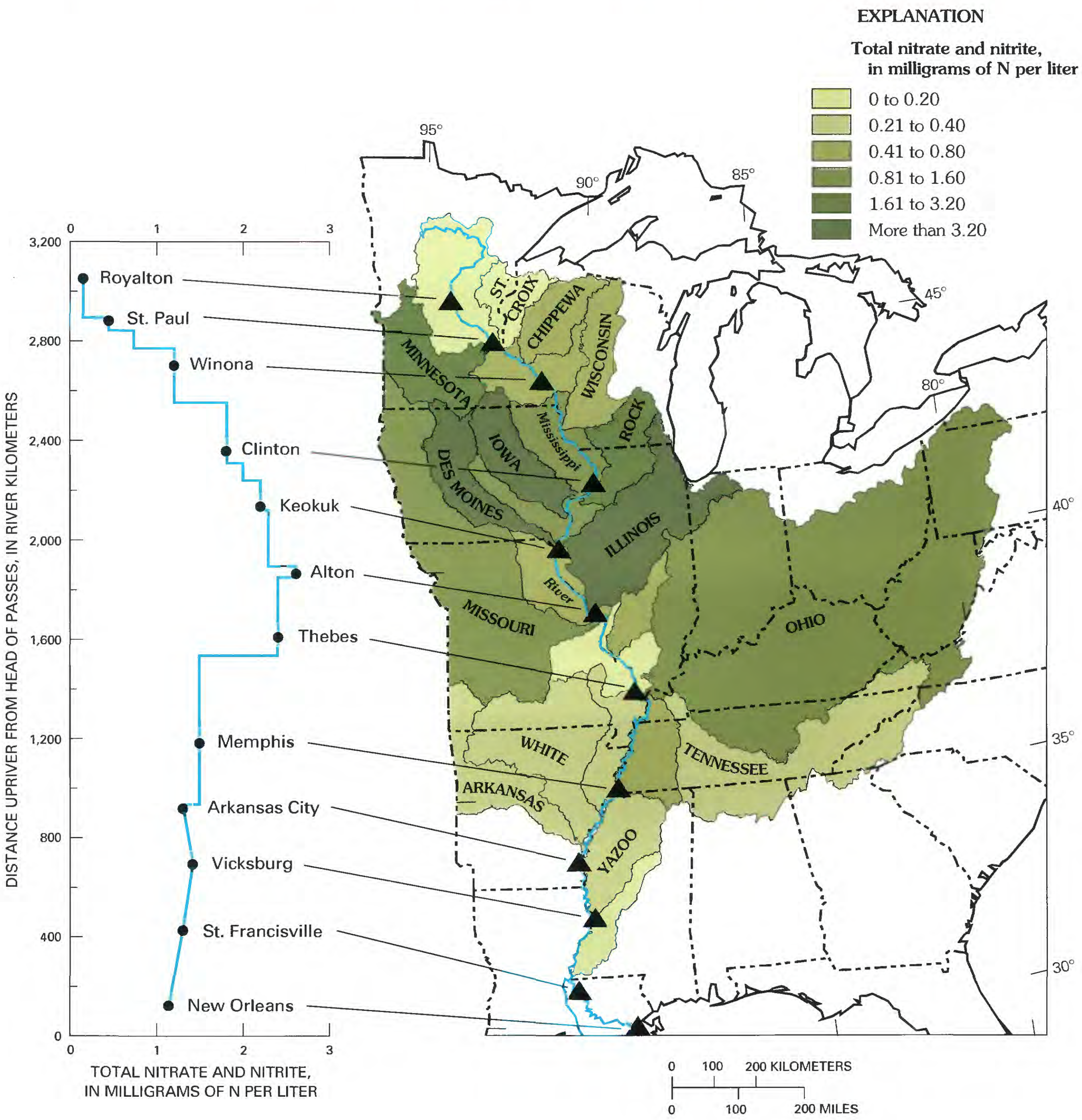
Figure 13 *Hardness of River Waters*



Hardness of River Waters

Figure 13 Both natural and human-influenced sources contribute chemicals to the dissolved solids of the Mississippi River. The chemicals can be separated into two groups based upon their electrical charge. The major positively charged chemical ions (cations) are calcium, magnesium, sodium, and potassium, and the major negatively charged chemical ions (anions) are bicarbonate, chloride, sulfate, and nitrate. The hardness of water increases as more calcium and magnesium ions are dissolved by tributary water flowing over naturally occurring rock sources in each river basin. Hardness is reported as the equivalent concentration of calcium carbonate in milligrams per liter. The value of hardness shown in the map for each basin is the median value in water samples collected at the gaging station closest to the mouth of the tributary. The graph on the left side of the figure shows the variation of the median hardness along the length of the Mississippi River for the period from 1970 through 1991. The water in the Mississippi River upstream from St. Paul, Minnesota, is hard (median value is 151 mg/L), but the water becomes very hard when it mixes with the very hard water of the Minnesota River (median value is 419 mg/L). The waters of the St. Croix, Chippewa, and Wisconsin Rivers are soft to moderately hard (median values range from 59 to 98 mg/L), and these tributaries again effectively dilute, downstream from St. Paul, Minnesota, the concentration of calcium and magnesium ions that determine the water hardness. In a pattern similar to that for dissolved solids, tributary inflows from the Rock, Iowa, Des Moines, Illinois, and Missouri Rivers increase the hardness of the Mississippi River downstream from Clinton, Iowa, in a series of steps to a maximum hardness of 208 mg/L (very hard) at Thebes, Illinois, just upstream from the confluence of the Mississippi and Ohio Rivers. The Ohio River, which is moderately hard (117 mg/L), decreases the hardness of the Mississippi River from very hard to hard. The water remains hard (140–154 mg/L) at gaging stations between the Mississippi-Ohio River confluence and New Orleans, Louisiana.

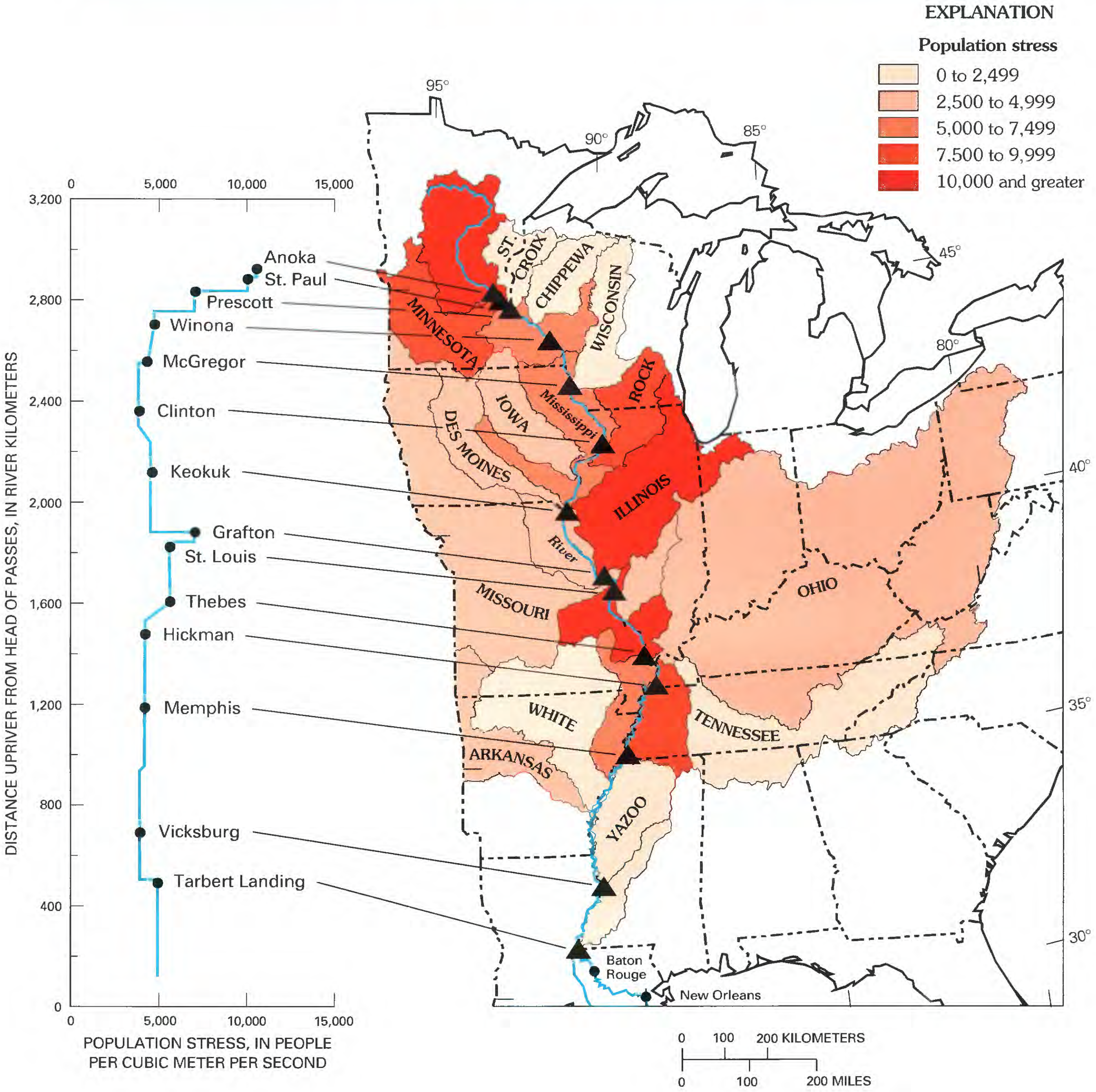
Figure 14 *Nitrate in River Waters*



Nitrate in River Waters

Figure 14 A wide range of human activities adds chemicals to rivers. The use of common salt, sodium chloride, to deice highways has contributed to the chloride concentration in rivers. Burning fossil fuels creates sulfur compounds that are major sources of sulfate for river water (Hem and others, 1990). In fact, the contribution of sulfur to rivers from anthropogenic sources may now be about one-half as much as from natural sources (Berner, 1971). Spreading fertilizers consisting of phosphate, nitrite, and nitrate compounds on cropland eventually adds to the total concentration of these chemicals in rivers as do other human activities such as the disposal of sewage effluents from metropolitan areas. Wastes from livestock production also add nitrogen compounds. The pattern of nitrate and nitrite concentration in the Mississippi River differs from the pattern for dissolved solids and hardness. The figure shows the combined nitrate and nitrite concentration (predominantly nitrate) in milligrams of nitrogen per liter. The value of nitrate and nitrite shown on the map for each basin is the median value in samples collected at the gaging station closest to the mouth of the tributary. The graph on the left side of the figure shows the variation of the median nitrate and nitrite concentrations along the length of the Mississippi River for the period from 1970 through 1991. Upstream from St. Paul, Minnesota, the median concentration of nitrate plus nitrite is 0.16 mg/L but then steadily increases step by step with each downstream addition of water from the Minnesota (2.8 mg/L), Rock (2.9 mg/L), Iowa (5.5 mg/L), Des Moines (3.7 mg/L), and Illinois (3.5 mg/L) Rivers. At Alton, Illinois, just upstream from the Mississippi-Missouri confluence near St. Louis, Missouri, the median concentration of nitrate and nitrite in the Mississippi River reaches a maximum of 2.6 mg/L. Downstream from Alton, the Missouri (1.1 mg/L) and Ohio Rivers (1.0 mg/L) successively dilute the nitrate and nitrite concentration so that it remains nearly constant at about 1.4 mg/L at gaging stations in the Lower Mississippi River. Although maximum concentrations for the Mississippi River have never exceeded the maximum contaminant level for drinking water of 10 mg/L, concentrations in several of the tributaries (Minnesota, Iowa, and Des Moines Rivers) in heavily farmed regions have exceeded the maximum contaminant level on occasion. Further details of nitrate and nitrite are discussed in the chapter, "Nutrients in the Mississippi River."

Figure 15 *Population Stress*



Population Stress

Figure 15 The concentrations of contaminants in the water represent stresses on the river system that depend upon the human population within a tributary basin and the capacity (as measured by the mean discharge) of the Mississippi River and its tributaries to reduce the concentration of contaminants by dilution. The population stress has been computed for 23 gaging stations in tributary basins and for 14 gaging stations on the Mississippi River as the ratio of the human population upstream from the gaging station to the mean discharge (in cubic meters per second) at each gaging station. The populations upstream from the gaging stations on the Mississippi River were taken from the 1990 census (U.S. Bureau of the Census, 1990). The mean water discharge is based on the period of record prior to 1989. The graph on the left side of the figure shows the variation of the population stress along the length of the Mississippi River. The dense population of St. Paul and Minneapolis, Minnesota, (about 3.2 million people) and the small water discharge (310 m^3/s) combine to create a high population stress of about 10,000 people per cubic meter per second. This initial high population stress decreases as each downstream tributary adds more water to the Mississippi River, until at Keokuk, Iowa, it reaches a minimum of 4,600 people per cubic meter per second. It increases near St. Louis, Missouri, along the reach of the river downstream from the mouth of the Illinois River, which has the highest population stress of the tributary basins (14,600 people per cubic meter per second), caused by the population of the Chicago metropolitan area. Another increase on the main stem occurs along the reach of the river between Baton Rouge and New Orleans, Louisiana. The population stress suggests that within and downstream from these three reaches of the Mississippi River (Minneapolis-St. Paul, St. Louis, and Baton Rouge-New Orleans), one should expect increases in anthropogenic contaminants. The chapters that follow contain numerous examples of such increases.

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Figure 16 *Research Vessel*

Figure 16 A program to sample a river as large as the Mississippi (specifically, a total length of 2,800 river kilometers between the uppermost station near Minneapolis/St. Paul and the lowermost station below New Orleans) is best carried out aboard a ship that can serve simultaneously as sampling platform, laboratory, and dormitory. The ship that filled all these functions was Research Vessel (R/V) *Acadiana*, owned and operated by the Louisiana Universities Marine Consortium. *Acadiana* is 17 meters long, 5.5 meters wide, and has a shallow enough draft (1.2 meters) to operate in most parts of the Mississippi River and in many of its major tributaries. In the configuration shown here, *Acadiana* has two onboard laboratories and bunk space for seven scientists plus a crew of two.

Sampling the Big Rivers

Robert H. Meade, John A. Moody, and Herbert H. Stevens, Jr.

History of the Study: 1987–92

This study of the Mississippi River and its tributaries began in 1987 when a group of scientists in the U.S. Geological Survey (USGS) joined forces to pursue some of the intriguing research questions concerning the transport and storage of contaminants in large rivers. The assemblage of researchers included hydrologists, chemists, physicists, sedimentologists, and geologists who collectively had enough aggregate expertise to begin a study of the continent's largest river. At least three research questions piqued the collective interests of the group and were amenable to a multidisciplinary approach: (1) How are contaminants partitioned between the dissolved and adsorbed phases—that is, does the contaminant travel in the river in true solution (as salt is dissolved in sea water) or does it travel piggyback, adsorbed onto the particles of sediment that are suspended in the river? (2) How do contaminants, dissolved or adsorbed, mix at large river confluences? (3) How are sediments and their adsorbed contaminants stored and remobilized in big rivers? In addition to the research results of these questions, a principal outcome of the study was an assessment of the status of selected contaminants in the Mississippi River. In the course of pursuing research goals in a riverwide context, making repeated sampling trips at different seasons of the year, a body of information inevitably accumulated that could shed new light on the levels of many contaminants in the river. This assessment, rather than the original research goals, is the subject of the present report.

During the first 3 years of the study, July 1987 to June 1990, seven research and sampling cruises were made aboard the research vessel, *Acadiana*. Sampling usually began at Winfield, Missouri, 100 kilometers upstream from St. Louis and 30 and 70 kilometers, respectively, upstream from the confluences of the Mississippi with the Illinois and Missouri Rivers. Downriver from Winfield, the primary strategy was to sample the Mississippi main stem and several of the major tributaries (Illinois, Missouri, Ohio, White, Arkansas, and Yazoo Rivers) in a downstream sequence, trying to follow approximately the same mass of water downriver. Although we did not always succeed in following the same mass of water, we usually were able to observe the changes that occurred in the water after the Mississippi had received inflows from the major tributaries or after the water and its load of sediment and contaminants had traveled several hundred kilometers downstream. The initial phases of the study were focused on the Lower Mississippi River, downriver of the navigational locks and dams, because of the availability of new techniques for sampling the freely flowing waters of large rivers and because of our initial reluctance to deal with the extra complexity of the transport and deposition of contaminants in a river that was impounded by a series of large dams.

All this was to change during 1990. During the second half of 1988, after the first three of our sampling cruises had been completed, the Greenpeace ship *Beluga* conducted a well-publicized trip along the Illinois and Mississippi Rivers and, in December 1989, Greenpeace released its report, "We All Live Downstream: The Mississippi River and the National Toxics Crisis". In January 1990, the USGS was contacted by the office of then Senator Rudy Boschwitz of Minnesota, who asked the USGS to extend its existing study into the Upper Mississippi River, especially into the reach of the river between St. Louis and The Twin Cities of Minneapolis and St. Paul, and produce a report summarizing our results. Soon thereafter, members of Congress from other States along the Mississippi—Arkansas, Illinois, Iowa, Louisiana, Missouri, Tennessee, Wisconsin—joined Senator Boschwitz in his request.

The response to this request was a change in the goals of our program from mainly research to mainly assessment, and an expansion of the scope of the program to include the much different hydrologic setting of the upper river. This expansion required an augmentation of the primary strategy for sampling the contaminants car-

Figure 17 *Sampled Sites*

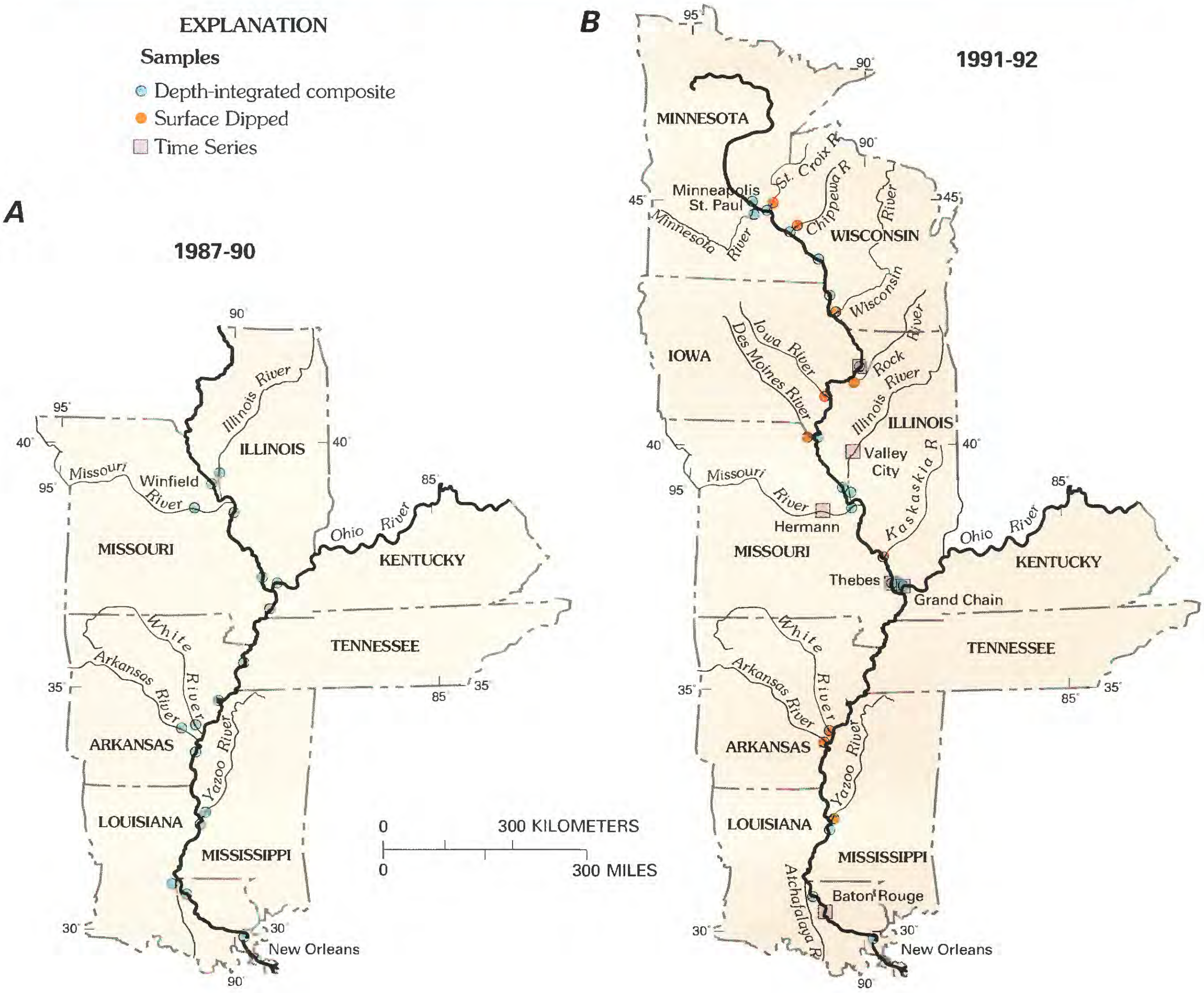


Figure 17 The flowing waters of the Mississippi River and its principal tributaries were sampled repeatedly at critical sites during our studies.

A During 1987–90, our studies focused on the lower and middle reaches of the Mississippi River—from the vicinity of its confluences with the Illinois and Missouri Rivers to a point a few kilometers below New Orleans.

B During 1991–92, the emphasis shifted to the Upper Mississippi River, while the sampling of the Lower Mississippi was continued at a reduced number of sites. Furthermore, time-series samples were collected at three sites on the Mississippi River and at three sites on major tributaries.

ried by the flowing waters to include a second strategy for sampling the contaminants that were stored with the sediment deposited on the bottoms of the navigation pools of the Upper Mississippi.

Sampling the Flowing Waters

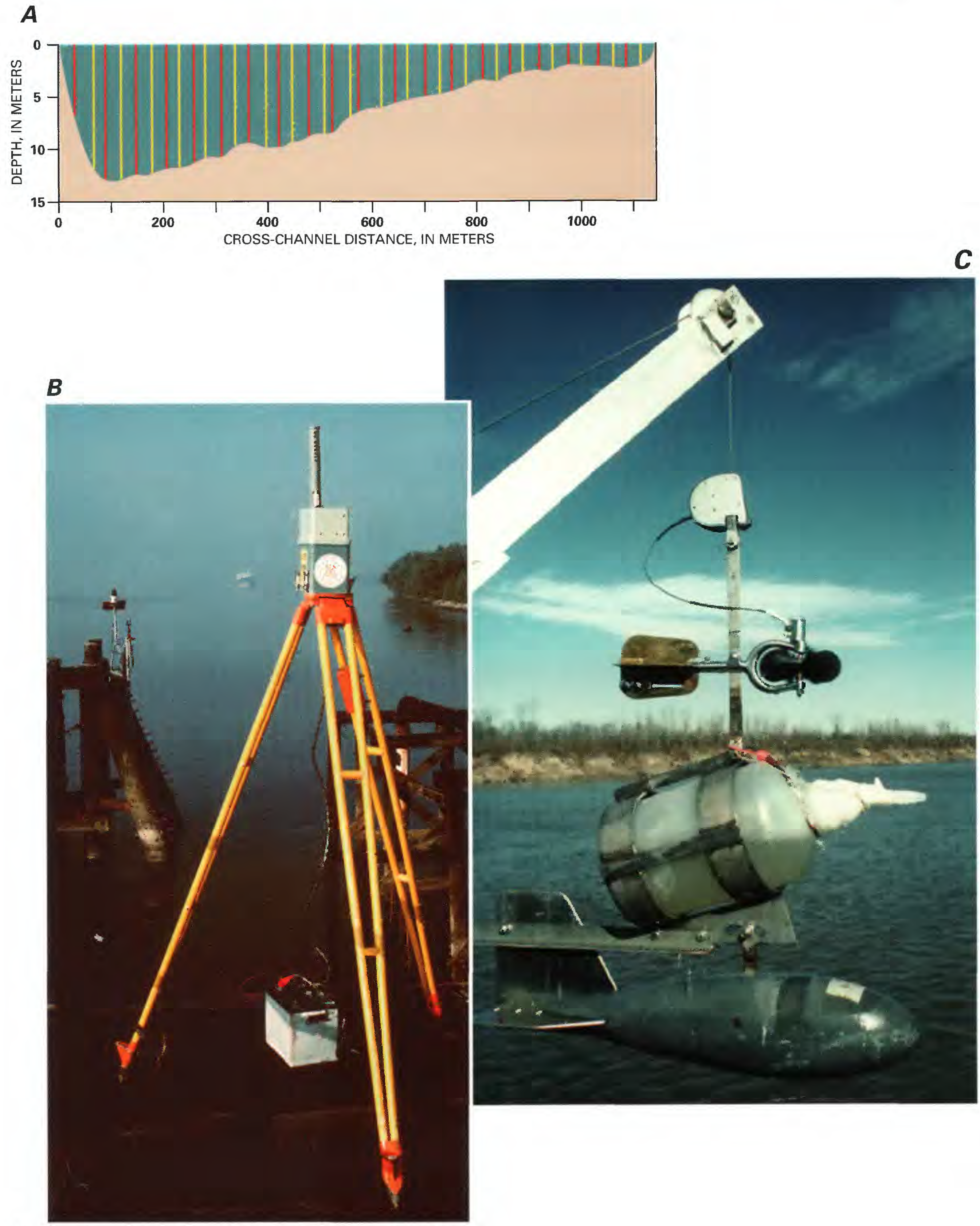
The flowing waters of the big rivers are sampled to measure the contaminants transported in solution as well as the contaminants adsorbed onto the sediment particles suspended in the water. To measure a dissolved contaminant being transported by the river, one needs to know: (1) the water discharge (expressed as the number of cubic meters of water that flows by a point along the river each second); and (2) the concentration of the contaminant (expressed as the number of grams per cubic meter of water). By multiplying discharge times concentration, one obtains what is called "load," or the number of grams of dissolved contaminant flowing downriver each second. To measure a contaminant adsorbed on suspended sediment, one needs to know: (1) the water discharge; (2) the concentration of suspended sediment (expressed as the number of kilograms per cubic meter of water); and (3) the concentration of the adsorbed contaminant (expressed as grams of contaminant per kilogram of suspended sediment). The load of adsorbed contaminant (grams per second or tons per day) is the product of water discharge times suspended-sediment concentration times contaminant concentration.

Two principal methods were used to collect water samples for determining concentrations and loads. Both methods take into consideration that the velocity of flow and the concentrations of suspended sediment and even dissolved matter are not distributed uniformly across the widths of large rivers. Flow velocities usually are greatest at the river surface in midstream and they decrease toward the bottom and banks of the river. Sediment concentrations usually are greatest near the river bottom and smallest at the river surface. After large tributaries enter the Mississippi, their waters may not mix thoroughly for 100–200 km downstream. Were it not for these inhomogeneities, one simply could dip a bottle or bucket into the middle of the flowing river, analyze the water collected, and multiply the concentrations times the discharge to calculate the loads. Indeed, this simple method has been used around the world for many years to sample the chemical compositions of rivers large and small. But the results of this sampling approach cannot be evaluated for their accuracy because the point at the centroid of water flow and the point where the contaminant concentration is the representative average of a river cross section are seldom obvious, unless extensive sets of detailed measurements have been collected beforehand.

Our standard method of collecting representative amounts of river water for the analysis of contaminant loads samples the full depth and width of the river. By this method, a sampler is lowered to the bottom of the river and raised back to the surface, collecting water through the full depth of the river, at a number of locations spaced equidistantly across the river from bank to bank. The resulting sample is called a depth-integrated composite. The sampler is designed to admit water at the velocity at which it is flowing in the river, and the sampler travels to the bottom and back at the same vertical speed each time. It collects the most water where the river flows fastest and deepest, and the least water where the river flows slowest and shallowest; the resulting sample is thereby weighted for water discharge. This method has been the standard for many years for sampling smaller rivers. Scaling it up for larger rivers such as the Mississippi is simple in principle but has proven more complicated in actual practice. Working from a moving ship in flowing water requires microwave positioning equipment or some other means of finding and maintaining the appropriate locations for collecting samples in a cross section of the river. A specially designed hydraulic winch and a sampler consisting of an initially collapsed Teflon bag inside a plastic bottle are required to collect the fast and deep waters of the Mississippi. Deploying the navigation equipment, positioning the ship, and collecting a representative sample in sufficient volume for all the required analyses usually kept the ship's crew and half a dozen scientists busy for the better part of a day at most of our sampling cross sections.

Representative small amounts of the depth-integrated composite were taken for the analysis of such things as herbicides, surfactants, dissolved heavy metals, and suspended sediment. The bulk of the depth-integrated sample was passed first through a centrifuge and then through an ultrafiltration apparatus to separate most of the water from the suspended sediment in preparation for chemical analysis for adsorbed heavy metals and other inorganic constituents. Every gram of suspended sediment that was recovered this way required processing from 5 to 100 liters of river water: 5 to 10 liters in most places in the Lower Mississippi where sediment

Figure 18 *Sampling Flowing Waters*



Sampling Flowing Waters

Figure 18 Obtaining representative samples of the flowing waters of the Mississippi River and its larger tributaries required special procedures and equipment, some of which are illustrated here.

A In a typical cross section of the Mississippi River, representative amounts of water were collected, through the full river depth from the surface to the bottom, at locations spaced at approximately equal intervals across the river. All the water collected at the locations across the river was combined into a single composite sample. At many cross sections, two separate composites (shown here as red and yellow) were collected so comparisons could be made to assess the precision of the sampling procedure.

B Sampling from a freely moving vessel in a large river requires a precise means of determining the location and motion of the vessel. Microwave positioning equipment served that purpose. Shown in the photograph is one of several remote units that were placed at known positions on the riverbanks at or near the sampling sites. Aboard the vessel (not shown in the photograph) was a master microwave unit that measured the distances from the remote units and thereby determined the relative position of the vessel.

C The array of equipment for measuring water velocity and for sampling the flowing waters and suspended sediment consisted of, from top to bottom,

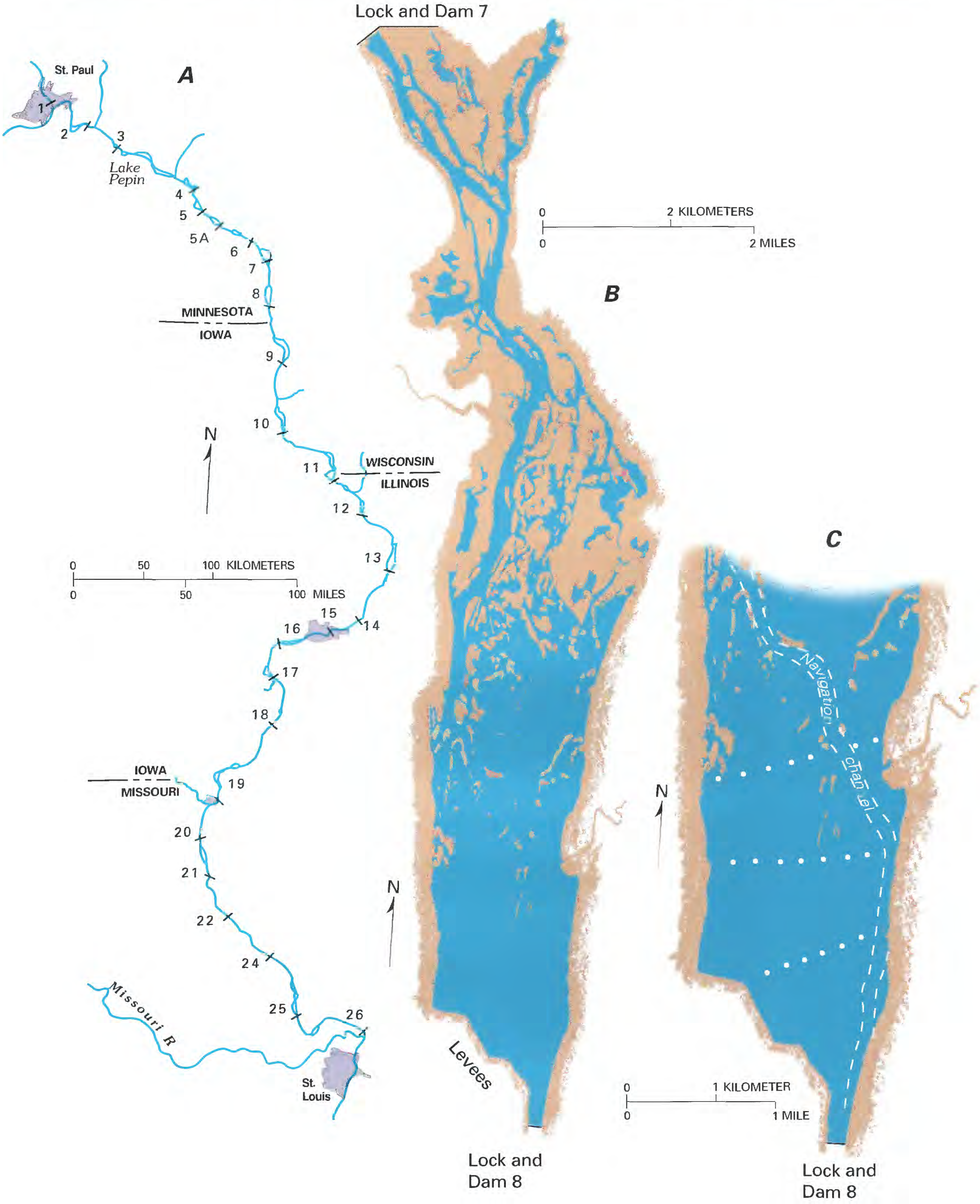
(1) a current meter, similar in design to the familiar anemometer that is commonly used to measure windspeed,

(2) a sampling bottle, containing a collapsed Teflon bag (shown here partly filled) that expanded as it received the incoming sample, and fitted in front with an isokinetic nozzle that was designed to admit water and suspended sediment in proportion to the velocity at which they were moving in the river, and

(3) a sounding weight of either 150, 200, or 300 pounds—depending on how fast and deep were the waters being sampled.

The hydraulic winch that was used to lower and raise the sampling array is not shown in the photograph.

Figure 19 ***Sampling Navigation Pools***



Sampling Navigation Pools

Figure 19 The contaminants adsorbed to the sediments deposited in the backwater areas of the navigation pools of the Upper Mississippi River were sampled to obtain representative average concentrations for each pool.

A The Upper Mississippi River between Minneapolis/St. Paul and St. Louis is segmented by 26 principal navigation pools.

B A "typical" pool (Pool 8, in this example) consists of three parts: an upper section, characterized by riverine channels and emergent flood plains; a middle section, characterized by numerous islands, parts of which are deltaic in origin but most of which are the elevated areas of the flood plains that flanked the river channels before the pool was inundated; a lower section, characterized by a shallow expanse of open water.

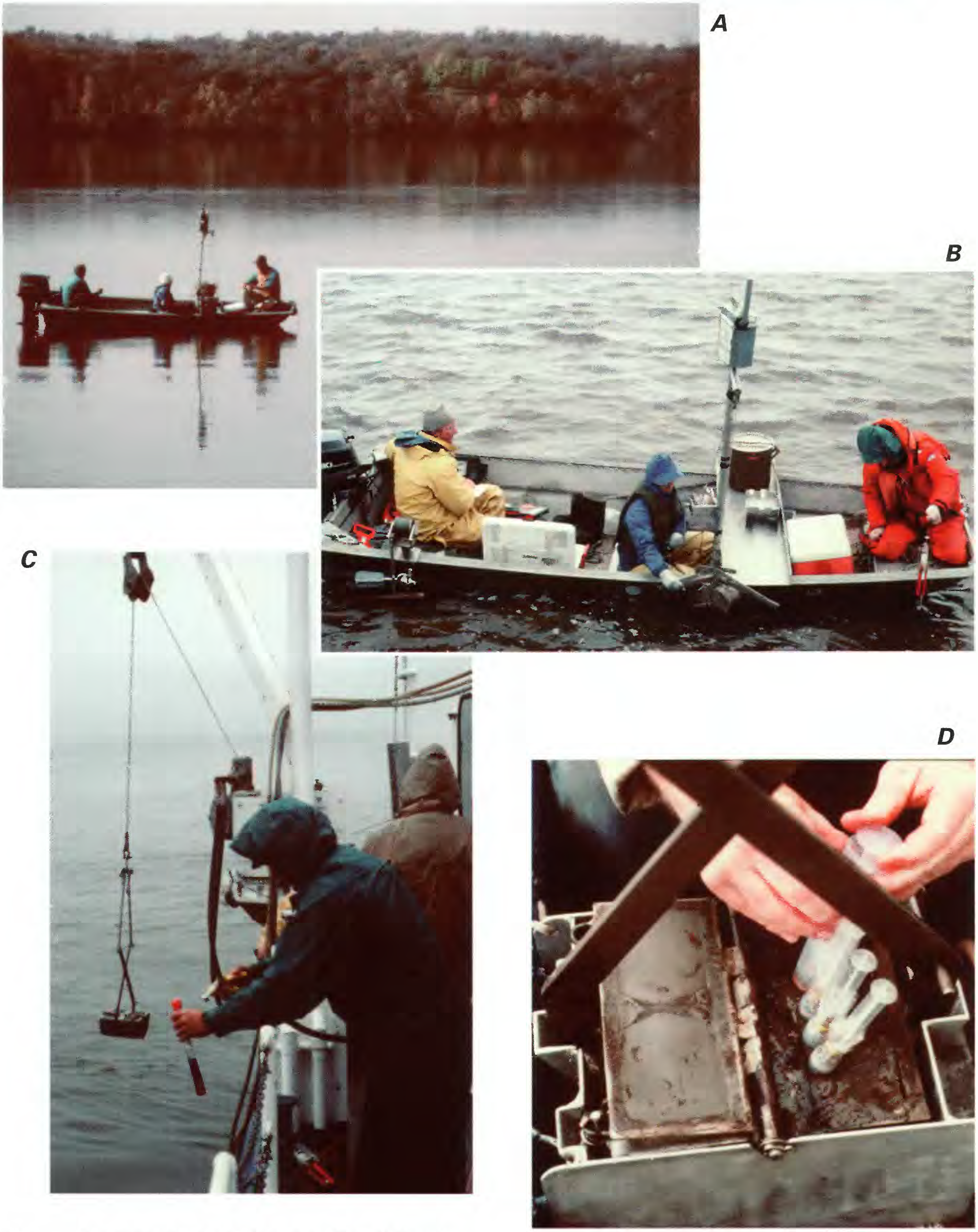
C Sampling was concentrated in the lower sections of the pools (Pool 8 is again the example)—outside the main navigation channel—because this is where fine-grained sediments and their adsorbed contaminants are most likely to be stored. Samples were collected at 15–20 locations per pool (shown here as three linear rows of white dots), which was sufficient to obtain a representative average, without seeking either "hotspots" or pristine areas.

concentrations are moderate to large; 50 to 100 liters of water in some places in the Upper Mississippi (downriver of Lake Pepin, especially) where concentrations are very small.

Our second principal method for collecting the flowing waters was by pumping them directly out of the river. Because the analyses for some of the adsorbed contaminants required larger quantities of suspended sediment than we were able to recover by depth-integrated sampling, we adopted the more expedient method of pumping water from the river, usually from a depth halfway between the surface and bottom. The pumping method collected 5 to 10 times the amount of water that could be collected in the same time by the depth-integrated sampling. Consequently, 5 to 10 times the amount of suspended sediment could be recovered, making it increasingly possible to measure many of the industrial and other contaminants that are difficult to detect on small quantities of sediment. The quantities of water pumped in the different parts of the channel were proportional to the water discharges there. The disadvantage of the pumping method is that it does not sample the full depth of the river. However, because depth-integrated samples were being collected at the same time at the same locations, comparative studies were made to show that, for the suspended particles with which contaminants are preferentially associated, the pumped sample was accurately representative of what was being transported in the full depth of the river. A typical pumped sample was somewhere between 500 and 1,000 liters (one-half ton to a ton, that is) of river water, which required 6 to 10 hours to collect and many more hours of shipboard processing to separate all the water from the suspended sediment.

Despite its disadvantages, a secondary method of dipping bottles into the surfaces of the rivers was used to obtain some samples. This sampling method was used most consistently in the tributaries of the Upper Mississippi River that were too shallow to be navigated by R/V *Acadiana* and had to be sampled from a small boat. The procedure consisted simply of dipping bottles into the tributaries near their estimated centroids of water discharge. The concentrations of contaminants in these surface-dipped samples are useful for computing *approximate* downriver loads, so long as the contaminant is transported in solution and the river waters being sampled are well mixed from top to bottom and from bank to bank. In other circumstances, the concentrations of surface-dipped samples may be more indicative than definitive.

Figure 20 *Sampling Bed Sediments*



Sampling Bed Sediments

Figure 20 The sediments and their adsorbed contaminants on the bottoms of the navigational pools of the Upper Mississippi River were sampled by fairly traditional means.

A and B The shallow backwater areas of most of the navigation pools were sampled from a small boat. Sampling equipment consisted of a clamshell grab (midboat) and gravity corer (forward). Also measured were current velocity (aft) and the position of the boat (microwave unit atop the pole).

C In the deeper pools such as Pool 19 (shown here) or Lake Pepin, bottom-sediment samples were collected directly from Research Vessel *Acadiana.*

D From the sediment recovered in the clamshell grab, separate subsamples were taken for the analysis of organic constituents such as PCBs and coprostanol. Samples for heavy-metal analysis were taken separately with a plastic gravity corer so as to avoid any error caused by the introduction of extraneous metal from the sampling equipment itself.

Sampling the Stored Sediments in the Pools of the Upper River

The Upper Mississippi River between St. Louis and Minneapolis/St. Paul is controlled, mostly for navigation, by a series of 29 locks and dams, and its hydrologic characteristics are markedly different from those of the freely flowing middle and lower river between St. Louis and the Gulf of Mexico. Each dam between Minneapolis and St. Louis artificially deepens, widens, and slows the river above it, allowing sediment to settle in the pool that forms behind the dam. These pools form a series of small lakes that trap and store some of the sediment and adsorbed contaminants that are being transported downriver. How much of the incoming contaminant load is stored in one of these pools, or for how long, depends on a number of things: the size and shape of the pool, how often the pool is flushed by large floods, and whether the contaminant in question is transported in solution or is adsorbed onto sediment particles. In general, the contaminants most likely to remain in storage are those adsorbed onto sediment particles that have been deposited in the backwater areas of large pools.

The contaminants adsorbed onto the sediments stored in the pools of the Upper Mississippi River were sampled by conventional means. A clamshell grab and a small plastic corer were used to collect samples of the uppermost 10 cm of the silt or mud that lay on the bottom at 15 to 20 places in the shallow or backwater areas of the navigation pools. In only the two largest pools, Lake Pepin and Pool 19, were the waters sufficiently deep to allow the bed samples to be collected directly from *Acadiana*. In the remainder of the pools, samples were collected over the side of a 14-foot-long boat. The locations in the pools where the samples were collected were fixed by their distances (determined by microwave-distancing equipment) and bearings from objects or landmarks whose positions were known.

Sampling the stored bed sediments of a pool took four people most of a day. Equal quantities of each of the 15 to 20 grab samples collected in each pool were combined into a single batch sample for analysis of organic compounds such as PCBs and sewage contaminants such as coprostanol. Core samples were kept separate for individual analyses for heavy metals.

Sampling the Length of the River

A third major strategy employed in this study was longitudinal sampling along the center line of the river. This was an opportunistic strategy that exploited the long traverse that *Acadiana* had to make at the beginning of each sampling cruise from her home port near New Orleans, Louisiana, to the farthest upriver point where the regular downriver sampling was begun (Winfield, Missouri, or Minneapolis, Minnesota). On the upriver traverse, the vessel took 10–11 days to reach Minneapolis, depending on the strength of the river currents. So as not to waste this opportunity to sample the river continually along its full length, a strategy was devised whereby the vessel was slowed down sufficiently every 10 miles or so to collect samples of water from about a meter below the river surface. Samples usually were taken in the middle of the river, but, where the waters were not well mixed (below major tributary confluences, for example), samples were collected at several points across the river. This procedure would not have been valid for sampling constituents associated with sediment particles, but it provided unique information on the spatial and temporal distributions of such compounds as herbicides and dissolved sewage contaminants.

Time-Series Sampling at Fixed Locations

A limited number of contaminants were sampled at fairly frequent intervals, usually once or twice a week, for limited periods at fixed stations on the Mississippi River and some of its tributaries. The specific contaminants that were sampled in this manner were herbicides and nutrients, for which the Mississippi River main stem was sampled at Clinton, Iowa, Thebes, Illinois, and Baton Rouge, Louisiana. Tributaries sampled in this manner were the Illinois, Missouri, and Ohio Rivers.

Further Information

More detailed accounts of the procedures used to sample the Mississippi River are given in the following reports.

Leenheer, J.A., Meade, R.H., Taylor, H.E., and Pereira, W.E., 1989, Sampling, fractionation, and dewatering of suspended sediment from the Mississippi River for geochemical and trace-contaminant analysis, *in* Mallard, G.E., and Ragone, S.E., eds., U.S. Geological Survey Toxic Substances Technical Meeting, Phoenix, Arizona: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 501–511.

Meade, R.H., and Stevens, H.H., Jr., 1990, Strategies and equipment for sampling suspended sediment and associated toxic chemicals in large rivers—with emphasis on the Mississippi River: The Science of the Total Environment, v. 97/98, p. 125–135.

Moody, J.A., 1993, Evaluation of the Lagrangian scheme for sampling the Mississippi River during 1987–90: U.S. Geological Survey Water-Resources Investigations Report 93-4042, 31 p.

___ ed., 1995, Chemical data for water samples collected during four upriver cruises on the Mississippi River between New Orleans, Louisiana, and Minneapolis, Minnesota, May 1990-April 1992: U.S. Geological Survey Open-File Report 94-523, 297 p.

___ ed., 1995, Hydrologic, sedimentologic, and chemical data describing surficial bed sediments in the navigation pools of the Upper Mississippi River, July 1991-April 1992: U.S. Geological Survey Open-File Report 95-708.

Moody, J.A., and Meade, R.H., 1992, Hydrologic and sedimentologic data collected during three cruises at low water on the Mississippi River and some of its tributaries, July 1987 through June 1988: U.S. Geological Survey Open-File Report 91-485, 143 p.

___ 1993, Hydrologic and sedimentologic data collected during four cruises at high water on the Mississippi River and some of its tributaries, March 1989 through June 1990: U.S. Geological Survey Open-File Report 92-651, 227 p.

___ 1994, Evaluation of the method of collecting suspended sediment from large rivers by discharge-weighted pumping and separating it by continuous-flow centrifugation: Hydrological Processes, v. 8, p. 513–530.

___ 1995, Hydrologic and sedimentologic data collected during three cruises on the Mississippi River and some of its tributaries from Minneapolis, Minnesota, to New Orleans, Louisiana, July 1991-May 1992: U.S. Geological Survey Open-File Report 94-474, 159 p.

Moody, J.A., and Troutman, B.M., 1992, Evaluation of the depth-integration method of measuring water discharge in large rivers: Journal of Hydrology (Amsterdam), v. 135, p. 201–236.

Rees, T.F., Leenheer, J.A., and Ranville, J.F., 1991, Use of a single-bowl continuous-flow centrifuge for dewatering suspended sediments—Effect on sediment physical and chemical characteristics: Hydrological Processes, v. 5, p. 201–214.

Figure 21 *Sources and Sinks of Heavy Metals*

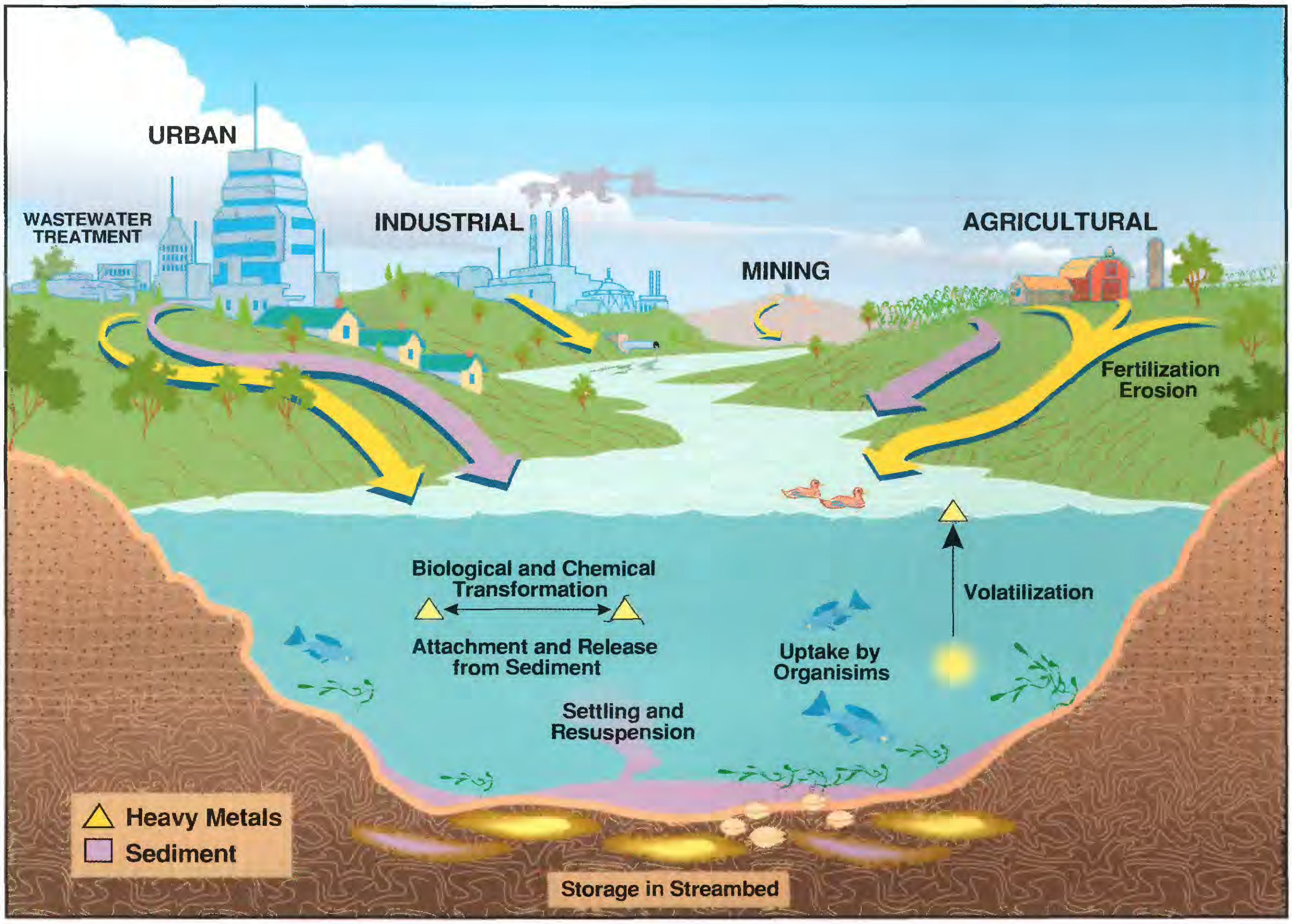


Figure 21 Heavy metals are released to the Mississippi River from numerous sources. Typical sources are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural cultivation and fertilization. Heavy metals are transported as either dissolved species in water or as an integral part of suspended sediments. Heavy metals may be volatilized to the atmosphere or stored in riverbed sediments. Toxic heavy metals are taken up by organisms; the metals dissolved in water have the greatest potential of causing the most deleterious effects.

Heavy Metals in the Mississippi River

John R. Garbarino, Heidi C. Hayes, David A. Roth,
Ronald C. Antweiler, Terry I. Brinton, and Howard E. Taylor

Introduction

Metals in the Mississippi River come from natural as well as artificial sources. Metals that are naturally introduced into the river come primarily from such sources as rock weathering, soil erosion, or the dissolution of water-soluble salts. Naturally occurring metals move through aquatic environments independently of human activities, usually without any detrimental effects. However, as the valleys of the Mississippi River and its tributaries were settled and industrialized, the metals added by human activities have affected the water quality of the Mississippi River and ultimately the Gulf of Mexico. Some of these metals are essential for proper metabolism in all living organisms yet toxic at high concentrations; other metals currently thought of as nonessential are toxic even at relatively low concentrations.

Health Significance of Metals in the Environment

The metallic elements can be categorized into two groups. The heavy metals are those having densities five times greater than water, and the light metals, those having lesser densities. Well-known examples of heavy metallic elements are iron, lead, and copper. Examples of light metals are sodium, magnesium, and potassium. Humans consume metallic elements through both water and food. Some metals such as sodium, potassium, magnesium, calcium, and iron are found in living tissue and are essential to human life—biological anomalies arise when they are depleted or removed. Probably less well known is that currently no less than six other heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg and others, 1979). Even these metals, however, can become toxic or aesthetically undesirable when their concentrations are too great. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 1 lists metals according to their toxicities.

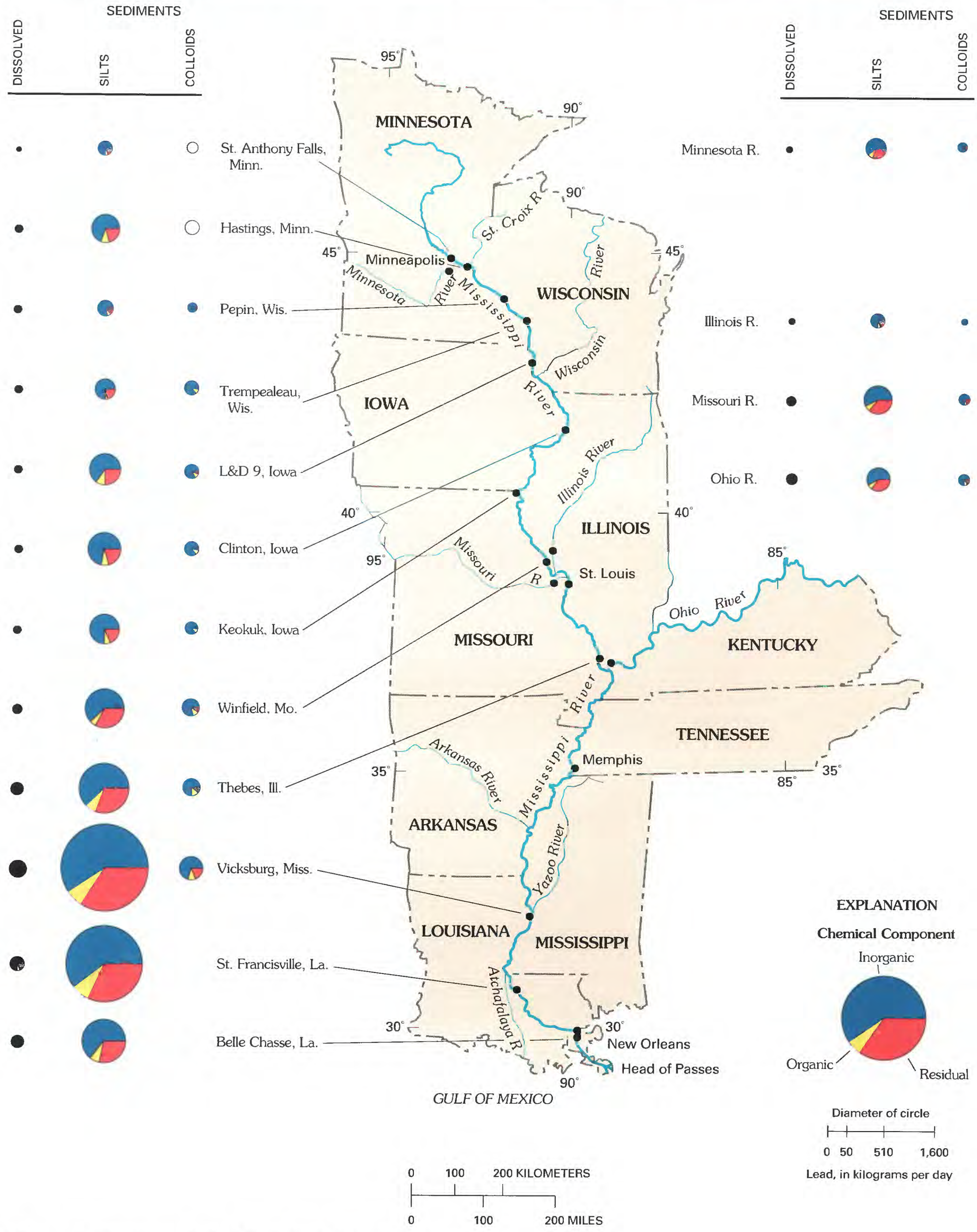
No specific health guidelines for heavy metals associated with suspended or bed sediments have been established by the U.S. Environmental Protection Agency. This lack of national guidelines based on concise scientific criteria causes difficulty when evaluating the environmental effects of heavy metals in sediments. Several different criteria have been defined, primarily on the basis of observed effects on aquatic life (Lyman and others, 1987). Table 2 (page 57) lists criteria for open-water disposal of polluted sediments that can be used for comparison purposes.

Sources of Metals in the Mississippi River

Heavy metals in the Mississippi River originate from either natural processes or human activities. Natural erosion and weathering of crustal materials take place over long periods of time and the amount of heavy metals released is small. However, the potential for contamination is increased when mining exposes metal-bearing ores. When compared to the natural exposure of ore bodies through erosion, the exposure rate through mining is over ten times faster for lead and zinc (Massachusetts Institute of Technology, 1970). Leaching of mine tailings and drainage from mined areas can introduce substantial amounts of metals into the river.

Two of the largest lead-zinc mining areas in the world are located along the Mississippi River. The reach of the Mississippi River between Prairie du Chien, Wisconsin, and Galena, Illinois, passes through the Upper Mississippi Valley lead-zinc district of southwest Wisconsin, northwest Illinois, and northeast Iowa. The New Lead Belt lies in southeast Missouri adjacent to the Mississippi River downriver of St. Louis, Missouri.

Figure 22 *Lead in River Waters and Sediments*



Lead in River Waters and Sediments

Figure 22 Like most of the heavy metals in the Mississippi River, lead is transported largely in association with the suspended sediments. The areas of the dots and pie diagrams on the left side of the figure are proportional to the quantities of lead that were being transported down the Mississippi River at 12 sites sampled during July-August 1991; the dots and pie diagrams on the right side of the figure show the inputs from four main tributaries (complete tabulations of the data are given by Hayes, 1993). The lead loads transported by suspended sediment, both silt and colloid, were larger than the dissolved loads because lead is a strongly "hydrophobic" element—that is, it adsorbs onto sediment particles more readily than remaining in solution by a factor of thousands to one. The suspended silt loads are greater than the colloidal loads because the river transports much more silt than colloid. The quantities of colloid in suspension, for example, were so low at the two most downstream sites sampled during this trip that not enough could be collected for chemical analysis.

Both the silt and colloid fractions were analyzed further to determine in detail how the lead is associated with the sediments. More than one-half the lead in the sediment phases is designated "inorganic," which means that it is an inorganic salt or a component of the iron and manganese hydroxides that coat the surfaces of the sediment particles. The second largest percentage of the lead is called "residual," meaning lead sulfide (galena) or other minerals that contain lead. Usually less than 10 percent of the lead is associated with organic material in the suspended sediment. The blank pie diagrams for St. Anthony Falls and Hastings indicate that there was not enough material to obtain the distribution of lead in the suspended colloid. However, enough colloid was available to determine the total amount of lead present and therefore calculate the corresponding load.

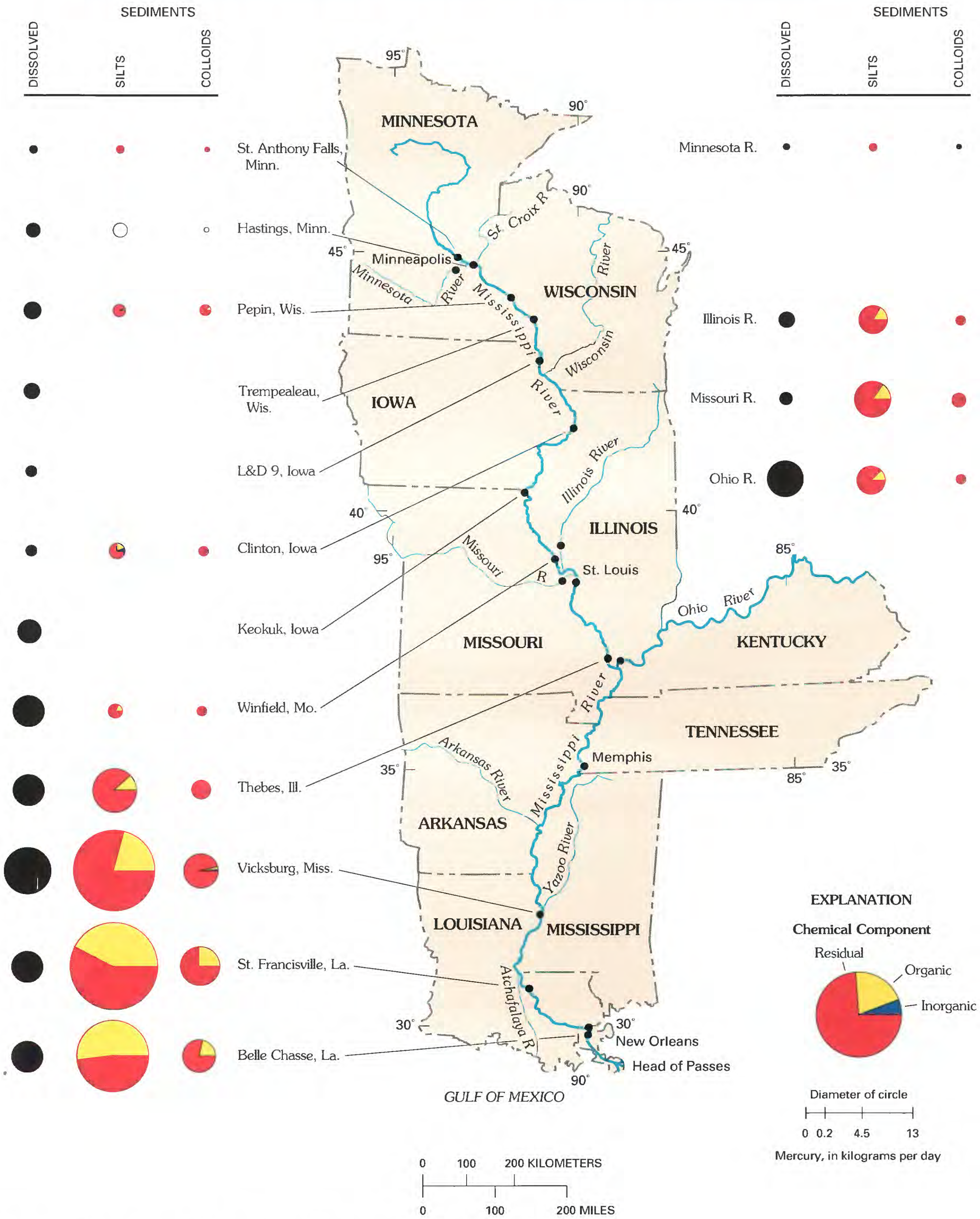
Cadmium is distributed in suspended sediment in much the same way as lead, with the largest proportion being inorganic. Chromium and copper, on the other hand, have much greater residual than inorganic components.

Table 1. Classification of naturally occurring metals according to their toxicity and availability in the hydrologic environment (from Wood, 1974)

[Metals that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks are in italics]

Nontoxic		Low toxicity		Moderate to high toxicity			
Aluminum	Magnesium	Barium	*Praseodymium*	*Actinium*	Indium	Polonium	Uranium
Bismuth	Manganese	*Cerium*	*Promethium*	Antimony	*Iridium*	*Radium*	Vanadium
Calcium	Molybdenum	*Dysprosium*	*Rhenium*	Beryllium	Lead	*Ruthenium*	Zinc
Cesium	Potassium	*Erbium*	*Rhodium*	Boron	Mercury	Silver	*Zirconium*
Iron	Strontium	*Europium*	*Samarium*	Cadmium	Nickel	*Tantalum*	
Lithium	Rubidium	*Gadolinium*	Scandium	Chromium	*Niobium*	Thallium	
	Sodium	*Gallium*	*Terbium*	Cobalt	*Osmium*	Thorium	
		Germanium	Thulium	Copper	Palladium	*Titanium*	
		Gold	*Tin*	*Hafnium*	Platinum	*Tungsten*	
		Holmium	*Ytterbium*				
		Neodymium	Yttrium				

Figure 23 *Mercury in River Waters and Sediments*



Mercury in River Waters and Sediments

Figure 23 The transport of mercury in the Mississippi River differs from that of lead in three important respects. First, there is considerably less mercury than lead in the river; notice the difference in the scales between this and the preceding figure. Second, a greater proportion of mercury is transported in the dissolved phase. Third, most of the mercury in the sediment phases is residual, most likely as mercury sulfides, and the remainder is associated with the organic matter in suspension. The dots and pie diagrams in the figure represent samples collected during the downriver cruise of October-November 1991 at 12 sites on the Mississippi River (left) and in 4 major tributaries (right). Complete tabulations of the data are given by Roth (1994). The percentage of mercury in the organic phase of the silt increased downriver of Thebes. Toxicological implications of this increase are strong because the human body absorbs organic forms of mercury 14 times more readily than inorganic forms (Task Group on Metal Accumulation, 1973). Mercury concentrations in both silts and colloids at Trempealeau, Lock & Dam 9, and Keokuk were not determined; therefore, loads could not be calculated.

Major sources of toxic metals arising from human activities are domestic and industrial wastewaters and their associated solid wastes. On the average, the USEPA estimates that 81 percent of the metals introduced into wastewater treatment plants comes from various regulated industries that dispose of their wastes into municipal sewer systems and that about 19 percent comes from consumer households in the form of common household products (U.S. Environmental Protection Agency, 1986). Cadmium, chromium, copper, lead, and mercury are used extensively in industries along the Mississippi River (table 3, page 59). The two main by-products of municipal treatment plants are solid wastes and treated wastewater. In the most common form of treatment, 70 to 90 percent of cadmium, chromium, copper, lead, and zinc are removed as solid wastes (Lester, 1983). The other 10 to 30 percent of these heavy metals remain dissolved in the water that is released back into the river. The concentration and transport of several heavy metals in treated effluent from a wastewater-treatment plant are shown in table 4 on page 61. Note that, in undiluted wastewater, the concentrations of cadmium, chromium, copper, and mercury exceed USEPA aquatic life standards, and concentrations of cadmium, chromium, lead, and mercury exceed the USEPA drinking water standards listed in table 2. The solid waste or sewage sludge is commonly disposed in landfills or sold as fertilizer. Heavy metals can be released through leaching of sewage sludge in landfills. Sewage sludge also contains plant nutrients and compares favorably to other fertilizers in crop production. The amount of sewage sludge that can be applied to

Table 2. U.S. Environmental Protection Agency maximum contaminant levels for heavy-metal concentrations in drinking water and water supporting aquatic life, and criteria for open-water disposal of polluted sediments

[µg/L, microgram per liter; µg/g, microgram per gram; >, greater than; <, less than; --, no guideline available]

	Cadmium	Chromium	Copper	Lead	Mercury	Uranium
Drinking water, in µg/L[1]	5	100	[2]1,000	15	2	[3]20
Water supporting aquatic life, in µg/L[4]	12	100	20	100	0.05	--
Natural sediments, nonpolluted, in µg/g[5]	--	<25	<25	<40	<1	--
Natural sediments, moderately polluted, in µg/g[5]	--	25 to 75	25 to 50	40 to 60	--	--
Natural sediments, heavily polluted, in µg/g[5]	>6	>75	>50	>60	>1	--

[1] U.S. Environmental Protection Agency, 1992.

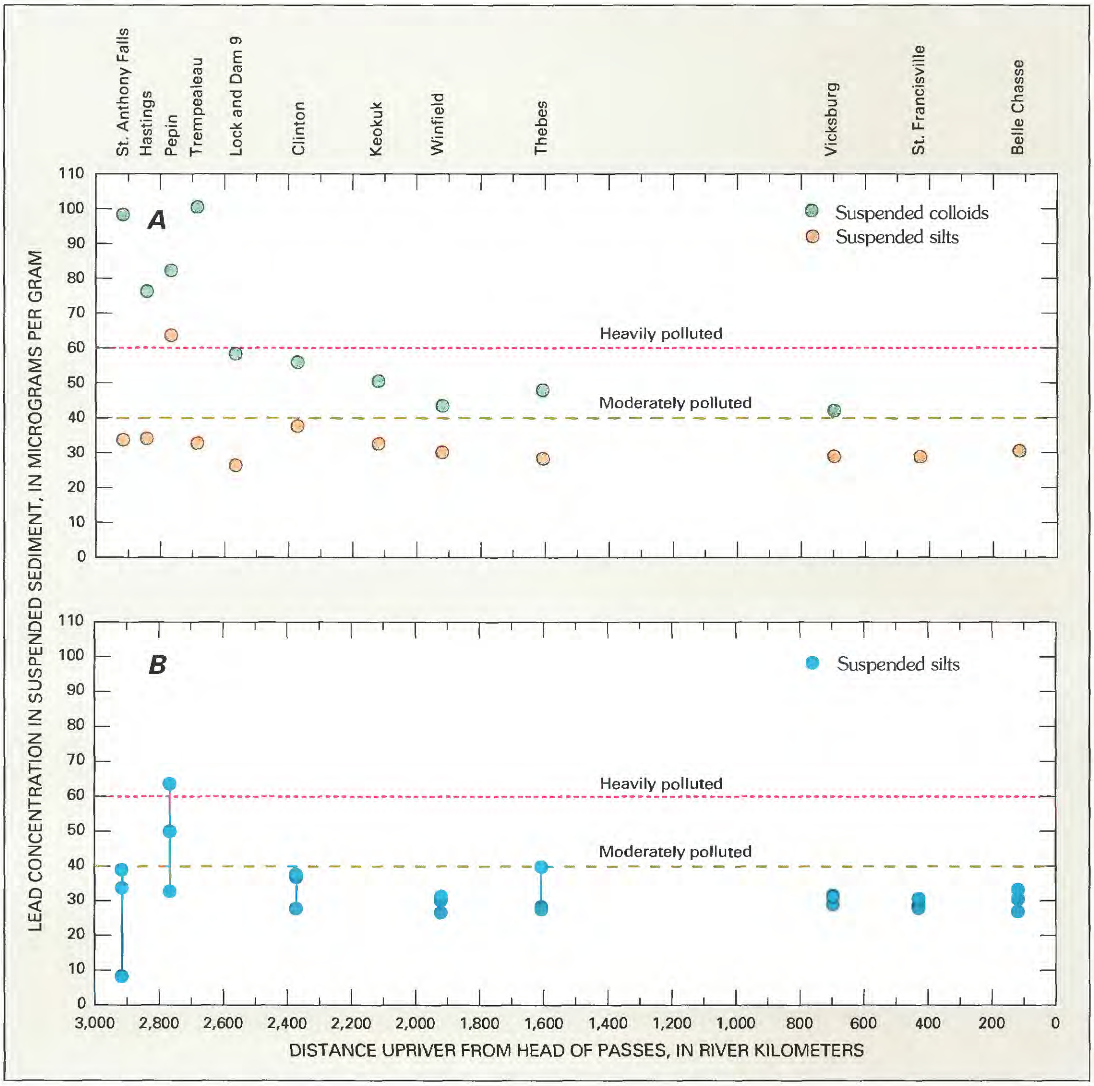
[2] Secondary maximum contaminant level based on esthetic water quality.

[3] Proposed maximum contaminant level.

[4] U.S. Environmental Protection Agency, 1982.

[5] Great Lakes Water Quality Board, Dredging Subcommittee, 1982.

Figure 24 *Lead in Silts and Colloids*



cropland is regulated by the USEPA and depends on the concentration of heavy metals in the sludge and the soil chemistry of the cropland. Some toxic heavy metals, especially cadmium, have been found at elevated concentrations in corn kernels harvested from soils fertilized with sewage sludge (Kiemnec and others, 1990).

Rural cropland and pasture land abound along the Mississippi River and its tributaries. Soil cultivation accounts for at least 90 percent of the soil erosion in the more humid areas of the United States, and it increases the amount of sediment introduced into the streams and rivers (McElroy and others, 1975). Millions of tons of fertilizers and pesticides are applied to croplands every year. Cultivated soils can become enriched with toxic metals associated with these applications. Although the concentrations may vary between specific formulations, many of these fertilizers contain chromium, copper, iron, manganese, nickel, and zinc. Selected pesticides use heavy metals such as mercury as an integral component. During the late spring and early summer, after fertilizers and pesticides have been applied, the runoff from rain flushes these contaminants into the Mississippi River. For example, the uranium concentration in the Mississippi River is 20 times that found in the Amazon River, a result linked to the specific use of phosphate fertilizers (Spalding and Sackett, 1972).

The atmosphere is also a source of metal contamination to aquatic environments. Metal-containing particulates that are washed from the atmosphere by rain and snow

Lead in Silts and Colloids

Figure 24 Concentrations of lead in suspended sediments are greater and more variable in the Upper Mississippi than in the Lower Mississippi River. Lead concentrations shown in these graphs are the totals of inorganic, organic, and residual (see fig. 22). Complete data are tabulated by Hayes (1993).

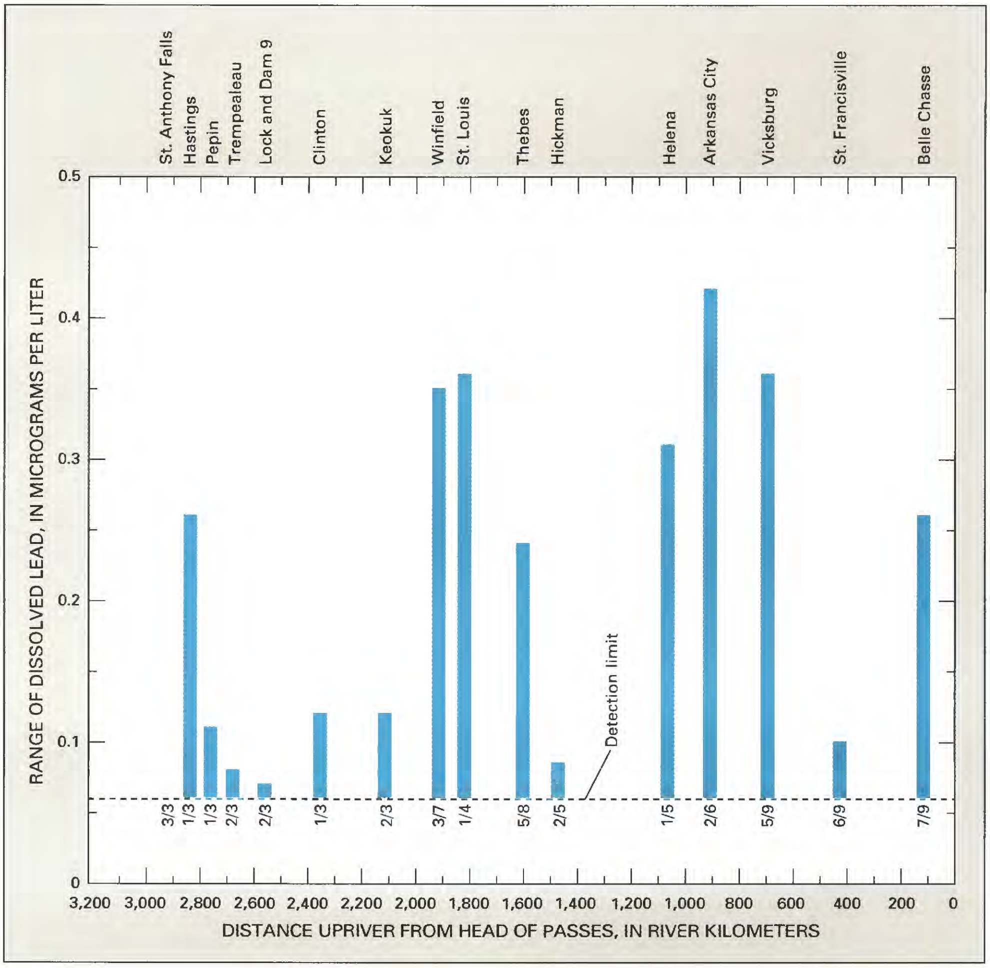
A Lead concentration in colloidal sediments is generally greater than or equal to the concentration in silts. Data shown in this graph are from suspended sediments collected during the downriver cruise of July-August 1991. Lead concentrations in colloids decrease markedly downriver; concentrations in silts also decrease downriver, but less markedly. Concentrations of lead at some sites in the uppermost river exceed the guideline of 60 micrograms per gram (µg/g) for heavily polluted sediments. Cadmium, chromium, and copper concentrations were similar to those of lead in that they were greater in the colloidal fraction, decreased downriver, and reached a fairly constant level downriver of Winfield, Missouri. Suspended sediment was heavily polluted with chromium and copper at 75 percent of all the locations sampled on the Mississippi River main stem.

B The variability of concentrations of lead in suspended silts in the Mississippi River main stem decreases markedly downriver. Shown in this graph are the concentrations of lead in suspended silts collected during the three downriver cruises of July-August 1991, October-November 1991, and April-May 1992. Concentrations in the upper river differed seasonally by factors of two or more; those in the lower river registered seasonal differences of only 10 to 15 percent. The greater variability in the upper river probably reflects a diversity of sediment sources and the impoundment of sediment behind the navigation dams. The downriver increase in the uniformity of the concentration probably reflects the progressive homogenization of the suspended sediment by repeated episodes of deposition and resuspension. The concentrations of 27 to 34 µg/g that were measured during 1991–92 in the lowest reaches of the Mississippi River are similar to the 32±3 µg/g measured by Trefry and others (1985) in samples collected there during 1982–83.

Table 3. Selected heavy metals presently or formerly used in major industries along the Mississippi River (from Boyer, 1984, and Dean and others, 1972)

Industry	Cadmium	Chromium	Copper	Lead	Mercury
Machinery products	X	X	X	X	X
Paint pigment and ink	X	X	X	X	X
Electroplating	X	X	X	X	
Textile mill		X	X		
Wood, pulp and paper		X	X	X	X
Organic chemicals	X	X		X	X
Inorganic chemicals	X	X	X	X	X
Rubber manufacturing		X		X	
Iron and steel foundries		X		X	
Nonferrous metal foundries	X		X	X	
Leather processing		X			
Petroleum refining		X	X		
Steam-generation powerplants		X	X		

Figure 25 *Range of Lead Dissolved in River Waters*



are deposited in drainage basins and find their way into lakes and rivers. As of 1973, the total nationwide airborne particulate emissions were distributed basically among three sources: 51 percent from industrial processes, 29 percent from fossil-fuel combustion, and 20 percent from miscellaneous burning practices (Magee and others, 1973). Since 1973, vehicle emissions (and perhaps other emissions as well) have decreased. Stone and rock crushing, iron and steel foundries, grain-handling operations, and cement production emit the greatest percentage of the particulates. Coal, used extensively for power generation, often contains significant concentrations of metals such as vanadium, copper, nickel, chromium, zinc, lanthanum, cobalt, molybdenum, gallium, germanium, tin, and mercury (Magee and others, 1973). Automobile fuels have historically contained lead additives for valve lubrication, but their usage is slowly being phased out.

The Fate of Metals in the Mississippi River

The numerous studies of the heavy-metal water quality of the Mississippi River that have been conducted over the last several decades have emphasized mostly the water quality in specific regions of either the lower reaches of the river (Everett 1971; Hartung, 1974; Presley and Trefry, 1980; Shiller and Boyle, 1983; Newchurch and Kahwa, 1984; Trefry and others, 1986) or the upper reaches of the river (Eisenreich and others, 1980; Water Quality Work Group of the Great River Environmental Action Team, 1980a, 1980b; Bailey and Rada, 1984; Buhl and McConville, 1984; Wiener and others, 1984). The water quality of the Mississippi River at selected locations has also been reported (Briggs and Ficke, 1978; DeLeon and others, 1986; Smith and others, 1987; Costner and Thornton,

Range of Lead Dissolved in River Waters

Figure 25 None of the concentrations of *dissolved* heavy metals that were measured in the Mississippi River during 1987–92 exceeded the USEPA standards for drinking water or the standards for aquatic life. Shown in the graph are the concentrations of dissolved lead measured in depth-integrated composite samples collected during 1987–92 between Minneapolis and New Orleans (complete tabulations of the data are given by Brinton and others, 1995, and Garbarino and others, 1995). All the concentrations shown here were less than the drinking-water standard by a factor of at least 100. More than one-half of the samples collected had dissolved lead concentrations too small to be measured; in the fraction given at the lower end of each bar, the denominator is the total number of samples analyzed from that site, and the numerator is the number of analyses in which the concentration of lead was less than the detection limit of 0.06 µg/L. The principal tributaries sampled generally contained metal concentrations greater than the main stem Mississippi River. However, these concentrations decreased downstream from the confluences through simple dilution, precipitation, or adsorption onto sediments. The concentrations of heavy metals are controlled by the volume of the flow of the Mississippi River and are greater during the late fall and winter when freezing temperatures decrease river flow and sediment concentrations than in the spring and early summer when runoff is high. Some fluctuations in concentrations can be attributed to seasonal releases of metals from specific sources.

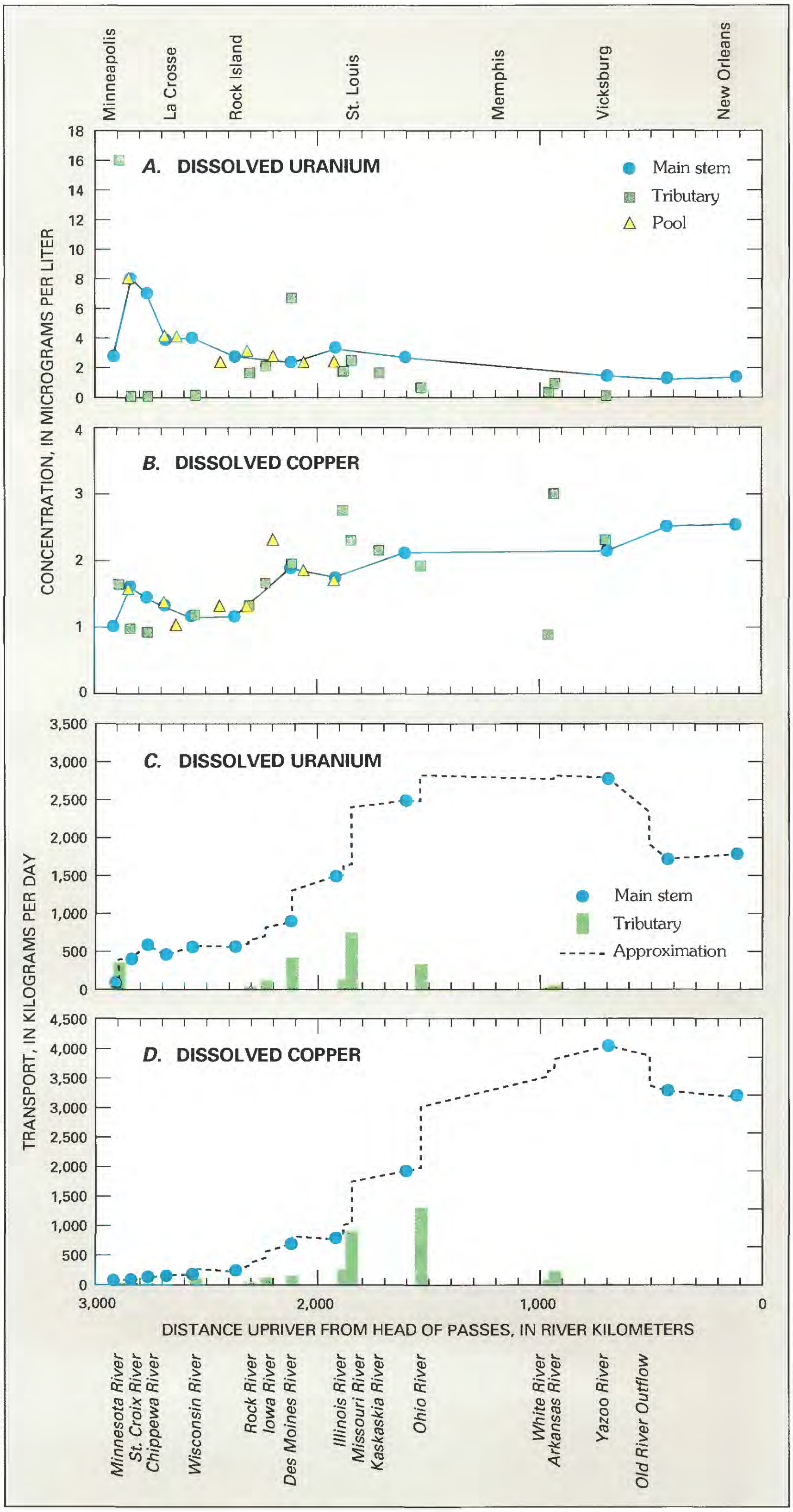
Table 4. Average releases of heavy metals into the Mississippi River from a large metropolitan wastewater-treatment plant in St. Paul, Minnesota (from Costner and Thornton, 1989)

[µg/L, microgram per liter]

	Cadmium	Chromium	Copper	Lead	Mercury
Concentration in µg/L	36	470	280	69	2.8
Daily transport in kilograms per day	2.2	29	17	4.3	0.17
Annual transport in metric tons per year	0.8	11	6.2	1.6	0.06

1989; Taylor and others, 1990). However, our study assesses the heavy-metal contamination through the full length of the Mississippi River from Minneapolis, Minnesota, to the Gulf of Mexico. Over the 5-year assessment period, the effects of seasonal variation and changes in the river flow rate could be evaluated. The water and sediment samples were collected by the same group of scientists during the entire study using proven sampling protocols. In addition, all samples were analyzed by one group of scientists in a single laboratory using state-of-the-art instrumentation and methodology. Heavy metals released into the Mississippi River, by both natural processes and human activities, can be distributed among several different forms within the water environment as shown in figures 22 and 23. Metals can be either transported with the water and suspended sediment or stored within the riverbed bottom sediments. Heavy metals are transported as (1) dissolved species in the water, (2) suspended insoluble chemical solids, or (3) components of the suspended natural sediments. Metals dissolved in the water can exist as hydrated metal ions or as aqueous metal complexes with other organic or inorganic constituents. Water-insoluble inorganic (non-carbon-containing, except for carbonates) chemical solids such as metal hydroxides may be formed, as may organic (carbon-containing) chemical solids, such as those associated with compounds derived from the decay of living organisms. Both inorganic and organic solids can be transported with the water as individual entities or as chemical coatings on suspended sediments. In addition, mineral components of suspended sediments themselves can contain heavy metals. Heavy-metal solids can also be stored in river-bottom sediments. Suspended sediments and metallic

Figure 26 *Uranium and Copper Dissolved in River Waters*



Uranium and Copper Dissolved in River Waters

Figure 26 Although they are well within drinking-water standards, concentrations and loads of dissolved heavy metals in the Mississippi River give clues to their sources. The data for dissolved uranium and dissolved copper shown here were collected during the downriver sampling cruise of April-May 1992. Represented in the figure are depth-integrated composite samples of the flowing main stem (circles) and four tributaries (the Minnesota, Illinois, Missouri, and Ohio Rivers: squares and bars), areally composited samples of backwaters in the navigation pools (triangles), and samples of water dipped from surfaces of tributaries other than the four listed above (squares and bars). The complete data are tabulated by Garbarino and others (1995).

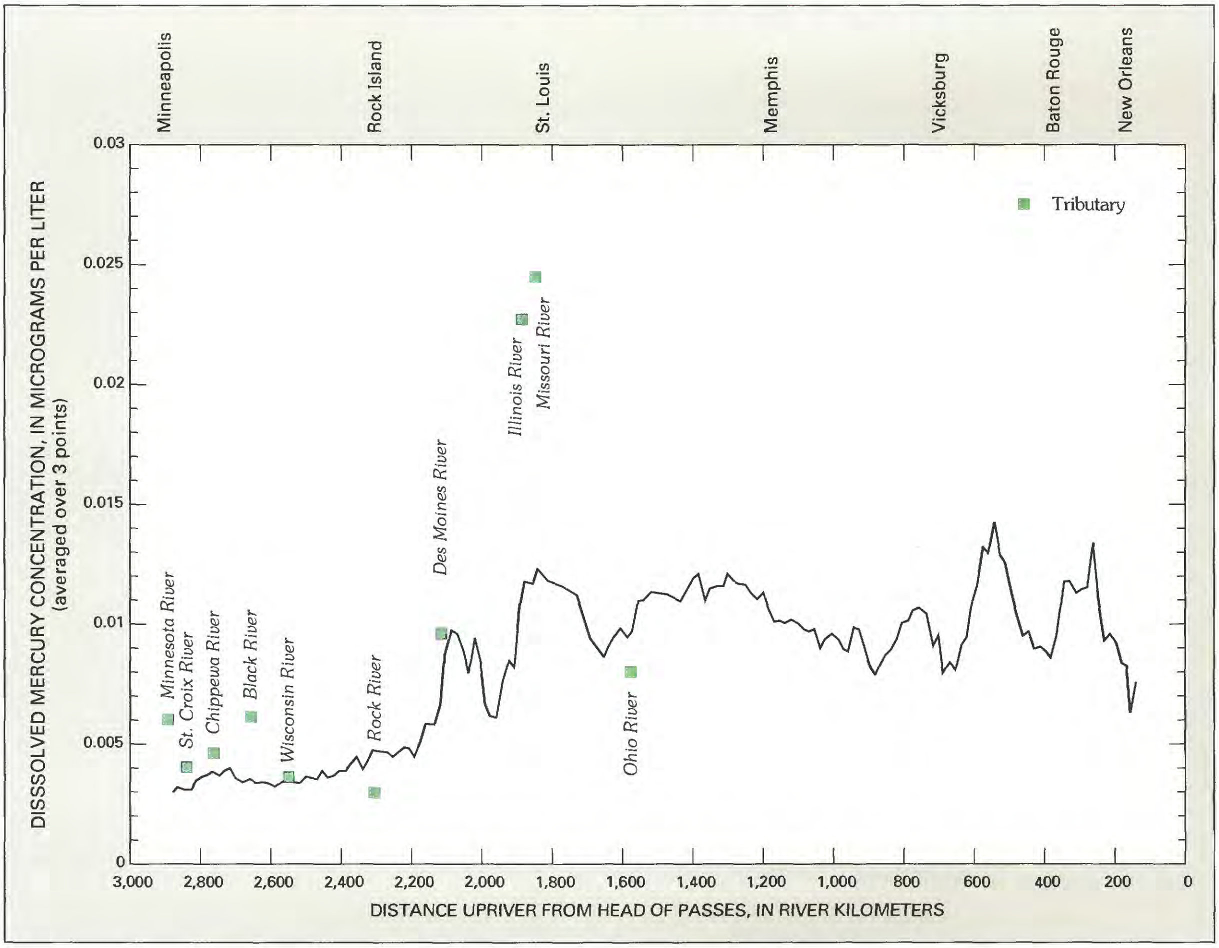
A Uranium dissolved in the Mississippi River comes, in large part, from phosphate fertilizers applied to croplands. Uranium occurs naturally in phosphate rock that is mined for fertilizer. Rain falling on fertilized croplands washes some uranium-containing fertilizer from the fields into streams and rivers. Concentrations of dissolved uranium are greatest in the Upper Mississippi River. Tributaries like the Minnesota and Des Moines Rivers, which drain areas that are farmed intensively for corn and other grains, have high concentrations of dissolved uranium that increase the concentrations in the Mississippi River downstream from their confluences.

B Copper dissolved in the Mississippi River comes mostly from industrial and municipal wastewaters. Concentrations of dissolved copper generally increase in the downriver direction, especially near urban centers. Some tributaries carry greater concentrations of copper than the main stem Mississippi, but their influences on main stem concentrations seem to be minimal

C The transport of dissolved uranium downriver depends on water discharge as well as on the concentration of the element in solution. Transports usually are greater during high-flow periods such as spring runoff (shown here) than during periods of lower flow. For example, the transport of dissolved uranium measured at Vicksburg during the spring sampling trip shown here was twice the transport measured at the same site the previous November—even though the dissolved concentrations were virtually the same. During the sampling trip shown here, the Mississippi River was receiving high loads of dissolved uranium from the Minnesota and Des Moines Rivers (because of their high concentrations) and from the Missouri and Ohio Rivers (because of their high water discharges). The abrupt decrease in uranium transport near river kilometer 500 represents the Old River Outflow where about one-fourth of the flow of the Mississippi River is diverted into the Atchafalaya River.

D The transport of dissolved copper in the Mississippi River, like that of dissolved uranium, varies directly with the water discharge. The most significant increases in the transport of dissolved copper occur at the confluences of the Mississippi with the Missouri and Ohio Rivers.

Figure 27 *Mercury Dissolved in River Waters*



chemical solids are stored in riverbed sediment after they aggregate to form large, denser-than-water particles that settle from the water when the river's flow is not sufficient to keep them in suspension.

The different chemical forms of heavy metals in the river influence their availability and toxicity to organisms. Heavy metals are readily available to aquatic organisms and pose a significant health hazard when they are present as dissolved inorganic or organic species in the water or loosely adsorbed to particulate surfaces. When heavy metals are present as components of particulates, such as inorganic metal-hydroxide coatings or metal-organic compounds, some chemical alterations are required before they can be released and become biologically available. Even stronger chemical reactions are required to release heavy metals that are integral parts of the minerals composing river sediments.

The water chemistry of the Mississippi River, the aqueous chemistry of individual heavy metals, the type and surface area of the particulates present in the Mississippi River, and other hydrologic factors control where the metals will be found. The water chemistry is controlled by many complex factors such as water acidity and the type and concentration of the major inorganic compounds, organic compounds, and suspended sediment. Many of these factors are also influenced by seasonal variation in river flow and temperature, and the decomposition of vegetation. The Mississippi River, like the majority of natural waters in the United States, can be described as having bicarbonate-type water because bicarbonates, especially calcium bicarbonate, predominate as the dissolved salt (Water Quality Work Group of the Great River Environmental Action Team, 1980b). Bicarbonate water is slightly alkaline rather than acidic. An aqueous solution of baking soda is a good example of an alka-

Mercury Dissolved in River Waters

Figure 27 Mercury dissolved in the Mississippi River is derived (like copper) from municipal and industrial sources. The distribution of dissolved mercury in the Mississippi can be shown in more detail than that of other heavy metals (such as uranium and copper, shown in the previous figure) because samples were collected specifically for mercury analyses during upriver transects. Shown in the graph are the concentrations of dissolved inorganic mercury in samples collected from the river surface at 15- to 20-kilometer intervals between New Orleans and Minneapolis during the upriver cruise of September 25-October 4, 1991 (a complete tabulation of the data is given by Roth, 1994). The line in the graph represents the average of the concentrations of each three adjacent samples (that is, a 3-point moving average) over 45- to 60-kilometer reaches of the river. Mercury concentrations were lowest in the upper reaches and gradually increased downriver. Large concentrations were measured downstream from tributaries such as the Des Moines, Illinois, and Missouri Rivers and near large metropolitan and industrial centers, specifically St. Louis, Missouri, Vicksburg, Mississippi, and below Baton Rouge, Louisiana. Farther downstream from each of these inputs, the concentration of dissolved mercury appears to have decreased; these decreases may be due to transformations of inorganic mercury to organic forms or to its adsorption onto sediment rather than to a decrease in the overall concentration of mercury in the river.

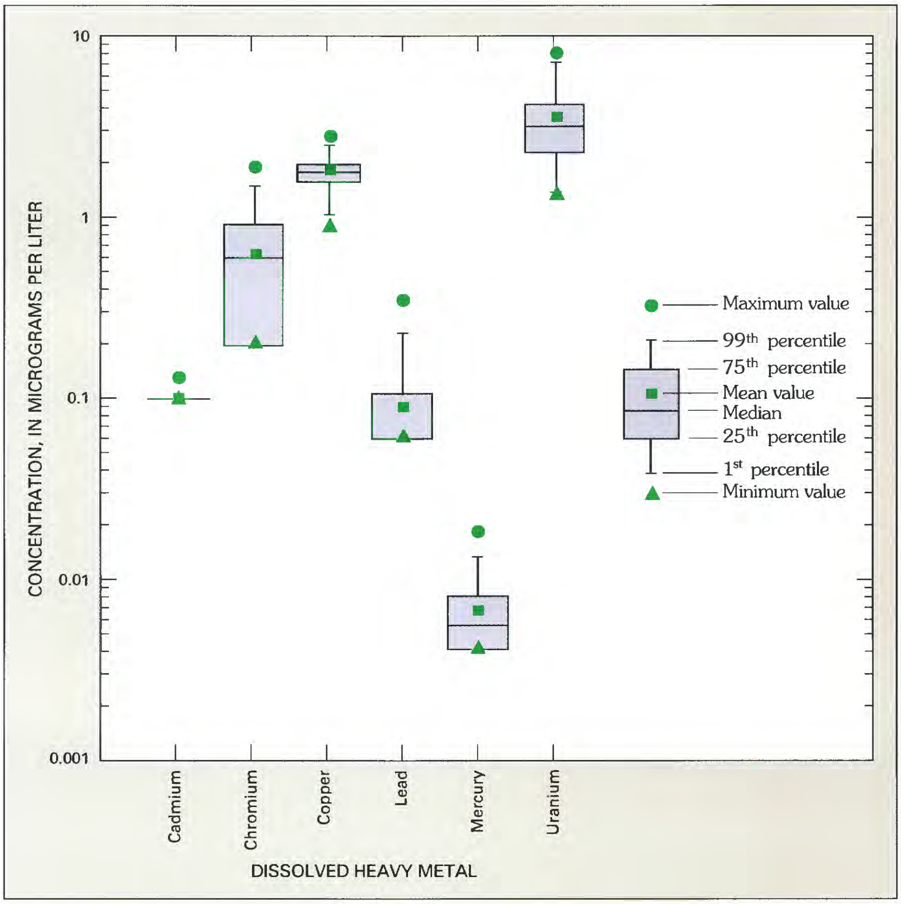
line solution, whereas orange juice is an acidic solution. The major fraction of heavy metals released into alkaline natural waters becomes associated with either the suspended particulates or the bed sediments. This association reduces or eliminates dissolved heavy metals, which are usually the most toxic form. For example, dissolved lead and zinc compounds from mine wastes tend to be adsorbed onto natural silt and clay sediments or organic matter, rather than staying dissolved in the water of the Mississippi River (Jennett and others, 1973). In contrast, most of the light metals tend to remain as dissolved species in the water.

Heavy-Metal Water Quality of the Mississippi River

The brief glimpse at the heavy metals in the Mississippi River described in this chapter generally was based on data collected during the summer and autumn of 1991 and the spring of 1992. Data that were collected in the Lower Mississippi River during 1987–90 (Brinton and others, 1995) reinforce the findings presented here. Concentrations of toxic heavy metals dissolved in the water in the 2,900 km reach of the Mississippi River from Minneapolis, Minnesota, to Belle Chasse, Louisiana, are well below USEPA guidelines for drinking water and water that supports aquatic life. However, heavy metals associated with suspended sediments exceeded the pollution guidelines at many of the main-stem sampling locations. Heavy-metal concentrations in the suspended sediments were generally greater in the small colloidal-sized particles than the larger silt-sized particles. Even though the colloids compose a significantly lower percentage of the total suspended sediment, their heavy-metal concentrations are greater, and they are small enough to pass through some of the filtering systems used in water-treatment facilities. Sediments stored in pools upstream from every lock and dam of the Upper Mississippi River also have elevated heavy-metal concentrations. The biological accessibility to heavy metals associated with suspended and stored sediment also depends on the chemical form in which the metal exists. A high percentage of the heavy metals in all the sediment sizes exist in chemical forms that can be dissolved if appropriate conditions driven by chemical or biological processes are present.

Concentrations of dissolved heavy metals and those associated with suspended sediment vary seasonally. Dissolved heavy-metal concentrations are generally greater during periods when the river flow is low, during droughts and winter months, because the decrease in water volume decreases dilution effects and the decrease in suspended sediment concentrations decreases metal-scavenging processes. Conversely, the increases in river flow during the warmer months either dilute heavy metal concentrations with greater

Figure 28 *Metals Dissolved in River Waters*



volumes of water or decrease dissolved metal concentrations through increased scavenging processes resulting from higher suspended-sediment concentrations. As a result, heavy-metal transport on suspended sediment increases during high-flow periods. Wastewater treatment, agricultural practices, and mining activities all influence the water quality. Crop fertilization periodically introduces specific heavy metals into the hydrologic system after spring applications and spring runoff. Discharges from wastewater-treatment facilities and industrial manufacturing activities cause increases in heavy-metal concentrations near major urban areas.

Whether the loads and concentrations of heavy metals in the Mississippi River have increased or decreased in recent years is difficult to determine. Although most of the heavy metals in the river are associated with sediment, most of the previous studies have focused on the dissolved metals. Even for the dissolved metals, comparisons are difficult to draw between earlier and more recent data because analytical laboratory techniques have become markedly more sensitive in the last decade and field sampling techniques have not been adequately standardized. Specific conclusions about increases or decreases in heavy metals with time in the Mississippi River are tenuous at best.

Metals Dissolved in River Waters

Figure 28 Statistical analysis of dissolved heavy-metal concentrations measured at all main-stem locations of the Mississippi River during the July-August 1991, October-November 1991, and April-May 1992 cruises indicate that cadmium, chromium, copper, lead, and uranium varied little with season. Of 36 samples collected during this period only one cadmium concentration was greater than the detection limit of 0.1 µg/L. In 11 of the 36 samples, concentrations of chromium were less than the detection limit of 0.2 µg/L. In 20 of the 36 samples, lead concentrations were less than the detection limit of 0.06 µg/L. Dissolved mercury was less than the detection limit of 0.004 µg/L in 15 of the 36 samples. All the samples contained measurable concentrations of copper and uranium.

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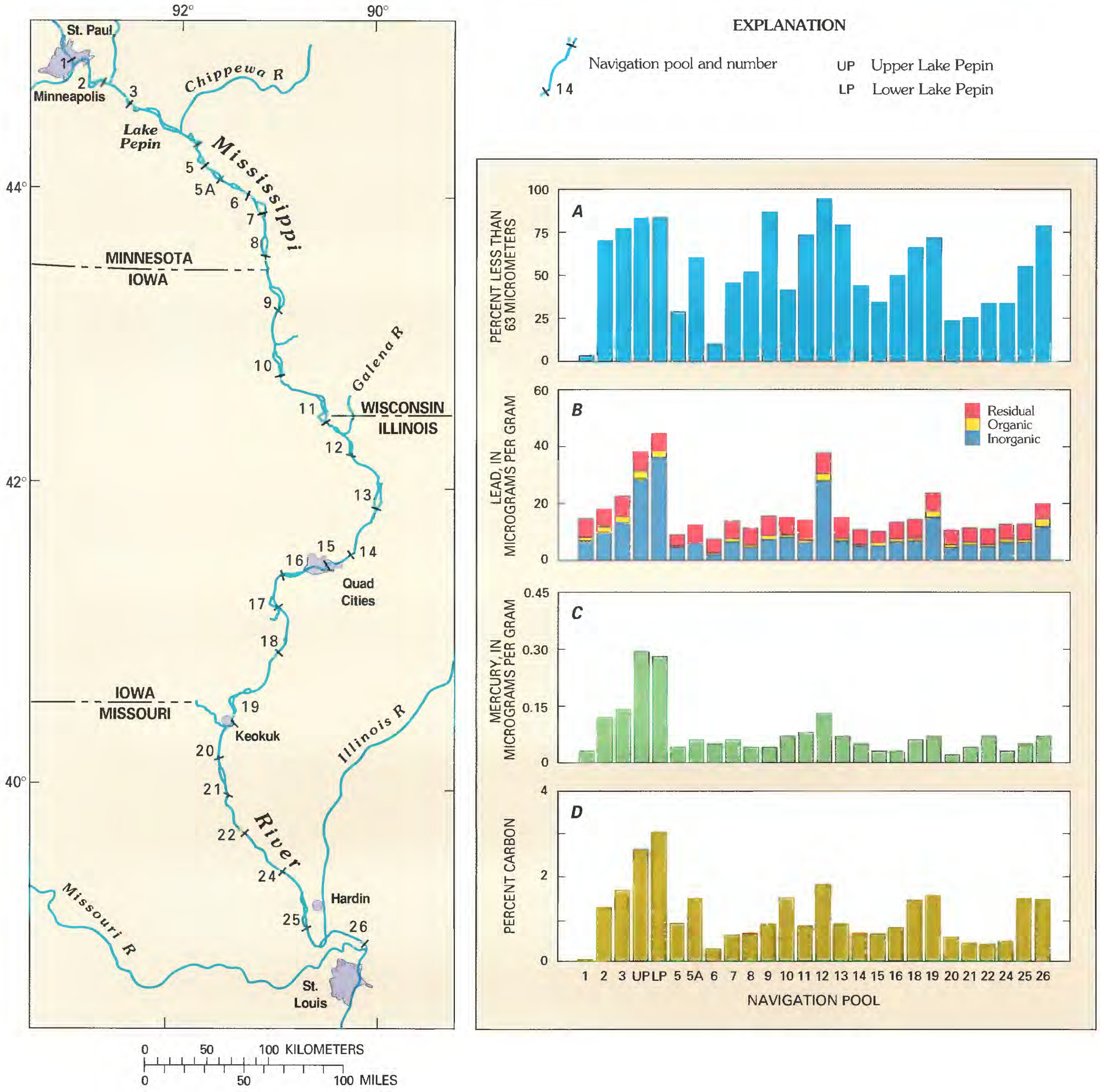
Figure 29 *Lead and Mercury in Bed Sediments*



Lead and Mercury in Bed Sediments

Figure 29 The bed sediments stored in the nonchannel (backwater) areas of the navigation pools of the Upper Mississippi River contain substantial quantities of heavy metals. However, the concentrations of lead and mercury in these bed sediments are generally less than those measured in the suspended sediments in transport; and, in the case of lead, the concentrations usually are less than the criterion value of 40 μg/g for moderately polluted sediment. Data used in this figure are the concentrations measured in a composite sample derived from 15–20 bed samples collected from the lower reaches of each navigation pool. The difference between lead and mercury concentrations measured in the bed sediments and in suspended sediments is mostly due to the differences in sediment particle size. Bed sediment samples were composed of a wide variety of particle sizes that ranged from coarse sand to colloid (see fig. 7B), markedly different than the suspended sediment. In addition, bed sediment samples were not separated into individual particle-size fractions prior to analysis, as was the case for suspended sediment, but rather were analyzed as a whole. As a result, the heavy-metal concentrations measured in the bed sediments would be expected to be lower because of the presence of less metal-laden sand particles. Complete data are tabulated in the reports by Hayes (1993) and Roth and others (1995).

A The distribution of bed-sediment particle sizes in navigation pools of the Upper Mississippi River depends on factors such as pool size and configuration. More than 80 percent of the bed sediment collected from Lake Pepin, Pool 9, Pool 12, Pool 13, and Pool 26 was composed of silt and colloid particles (shown here as percent finer than 63 micrometers); more than 70 percent of the sediment collected in Pools 2, 3, 11, and 19 was silt and colloid. The bed sediments collected from the rest of the pools contained significantly lower percentages of silt and colloid.

B In bed sediments collected from 25 navigation pools of the Upper Mississippi River between July 1991 and April 1992, the greatest concentrations of lead were in Lake Pepin, Pool 12, Pool 19, and Pool 26. Lake Pepin, a large and narrow natural lake, is known to trap large proportions of the suspended sediment that the Mississippi River delivers to it from the north. Pool 12 receives inflow from the Galena River, which drains a lead and zinc mining district. Lead leaching from the lead mines has an affinity for sediment. However, the relation of the high lead concentration in Pool 12 to the nearby mining district has not been confirmed. The high lead concentrations could simply be a result of the large proportion of fine bed-sediment material present in the pool. Pool 19 is the largest of the artificial pools, not as large as Lake Pepin, but more likely than the other smaller pools to trap and retain sediments and their associated contaminants. Elevated lead concentrations in the bed sediment of Pool 26 suggest a link to the input of lead-laden sediment from the Illinois River. Grab samples of the bed sediment collected from the Illinois River near Hardin, Illinois, contained 25 μg/g of lead, or about twice the concentration found in the bed sediments from Pool 25. Cadmium, chromium, copper, nickel, and zinc followed nearly the same trend as lead, with bed-sediment concentration maximums at Lake Pepin, Pool 12, Pool 19, and Pool 26. Only bed sediments from Lake Pepin, and possibly from Pool 12, can be described as moderately polluted in lead. In most pools, approximately 50 percent of the lead in the bed sediment was associated with the inorganic component, 40 percent with the residual component, and 10 percent with the organic component. The greatest proportions of the inorganic component were found where the lead concentrations were highest. Therefore, most of the lead in the pool bed-sediment environment may be readily accessible and could be released if the proper conditions existed. Other heavy metals—cadmium, chromium, and copper—had their greatest percentages in the residual component. Except for cadmium, the proportions of heavy metals designated as inorganic, organic, and residual were similar to those in the main-stem suspended sediments. The concentrations shown in the figure are similar to earlier data collected by Bailey and Rada (1984), who reported the following average concentrations of lead in bed sediments: 40 µg/g in Lake Pepin, 13 µg/g in Pool 5, and 14 µg/g in Pool 9.

C and D Mercury concentrations in pool bed sediments of the Upper Mississippi River can be correlated to the organic carbon content of the sediments. Mercury concentrations in the bed sediments of most pools, except for Lake Pepin, were not large enough to cause adverse toxicological effects. Bed-sediment mercury concentrations in Lake Pepin exceeded 0.18 µg/g, a level that has been shown to increase the mortality rates in fish embryos, eggs, and larvae (Birge and others, 1977). Mercury can bioaccumulate in many aquatic organisms, especially fish, by direct ingestion of suspended or bed-sediment particles. High organic-carbon concentrations in the presence of mercury in the bed sediments increase the methylation rate of mercury and subsequently increase the absorption and retention of mercury in fish and human tissues. Lake Pepin, Pools 2, 3, 12, 19, and 26 are the most likely areas in which this might occur because of the high percent organic carbon in their bed sediments.

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Figure 30 *Nutrients Dissolved in River Waters*

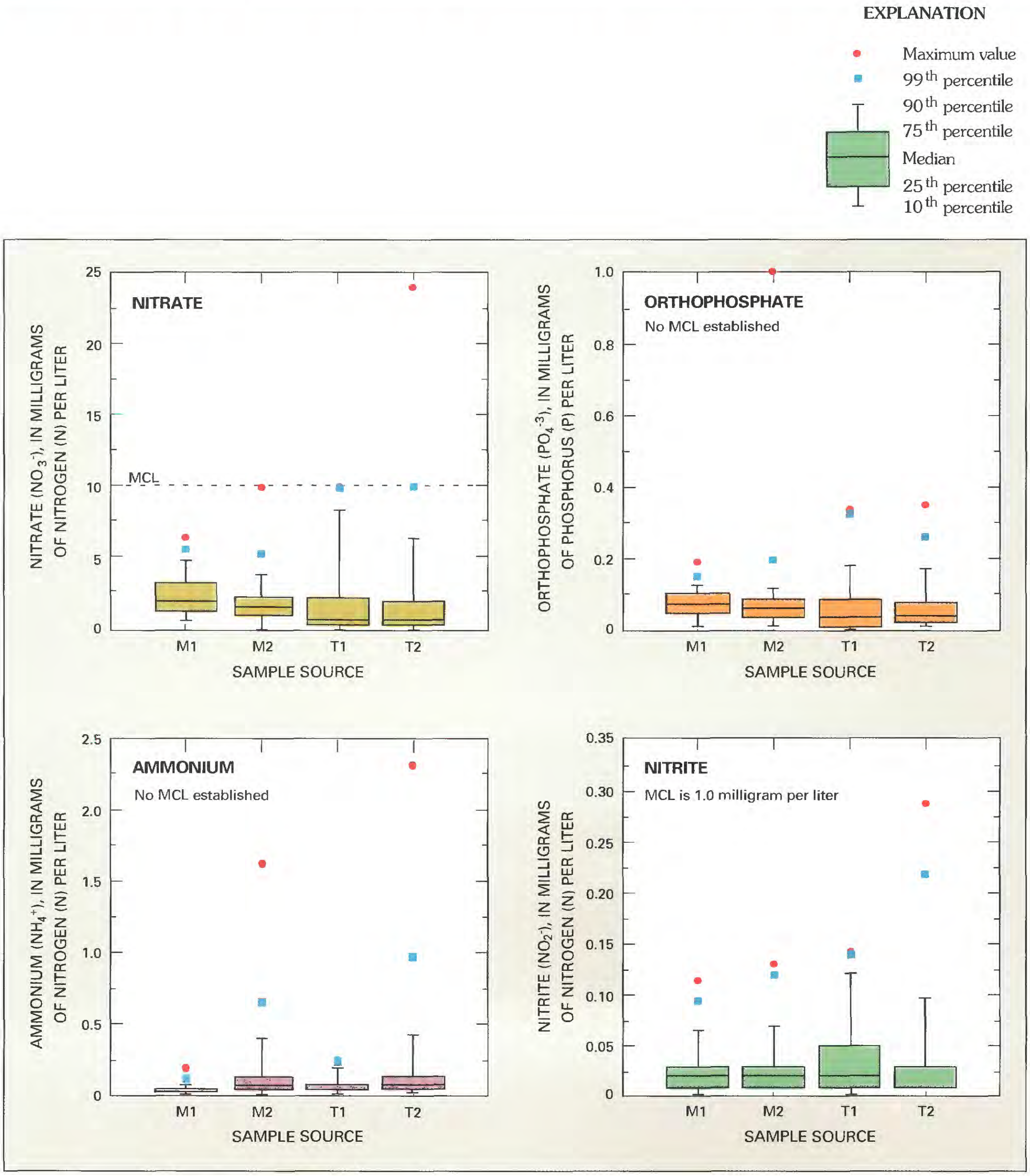


Figure 30 Of four major nutrient compounds in the Mississippi River and its tributaries, only nitrate is found in concentrations approaching the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL). Orthophosphate usually is present in low concentrations, and concentrations of ammonium and nitrite usually are insignificant. The box plots show the medians and ranges of values determined in the Mississippi River main stem (M1, M2) and in tributaries (T1, T2). Values determined during 1991–92 are labeled M1 and T1 (see table 7 for a statistical summary of the data; see Antweiler and others, 1995, and Garbarino and others, 1995, for a detailed listing of the data), and those at monitoring stations of the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) during 1979–91 are labeled M2 and T2.

Nutrients in the Mississippi River

Ronald C. Antweiler, Donald A. Goolsby, and Howard E. Taylor

Nutrients are chemical elements and compounds in the environment from which living things synthesize living matter: their body cells and tissues, their genetic material, their energy-bearing molecules, and their reproductive cells. In this discussion of water quality in the Mississippi River, four nutrient compounds are described: nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and orthophosphate (PO_4^{-3}). These are the most significant inorganic forms of two elements, nitrogen and phosphorus, that commonly limit the productivity of plants.

Nitrate and nitrite at high concentrations are known to have toxic effects on humans. The U.S. Environmental Protection Agency (USEPA), mandated by Public Laws 89-753 (the Clean Water Restoration Act of 1966) and 92-500 (the Federal Water Pollution Control Act Amendments of 1972), has established drinking-water standards for both of these to protect public health (Sceery, 1992; U.S. Environmental Protection Agency, 1991a, 1991b; table 5). If the concentration of nitrate or nitrite is high in the raw water supply (for example, the Mississippi River), the cost of treatment increases. Ammonia also is known to be toxic to aquatic organisms, and the USEPA also has established criteria for this compound in surface waters (U.S. Environmental Protection Agency, 1985, 1992). Maximum contaminant levels have not been established for orthophosphate.

Plant productivity caused by nutrients is another factor of concern.

Table 5. U.S. Environmental Protection Agency maximum contaminant levels (MCLs) for nitrogenous nutrients in drinking water (from Sceery, 1992, and U.S. Environmental Protection Agency, 1985, 1991a, b, 1992)

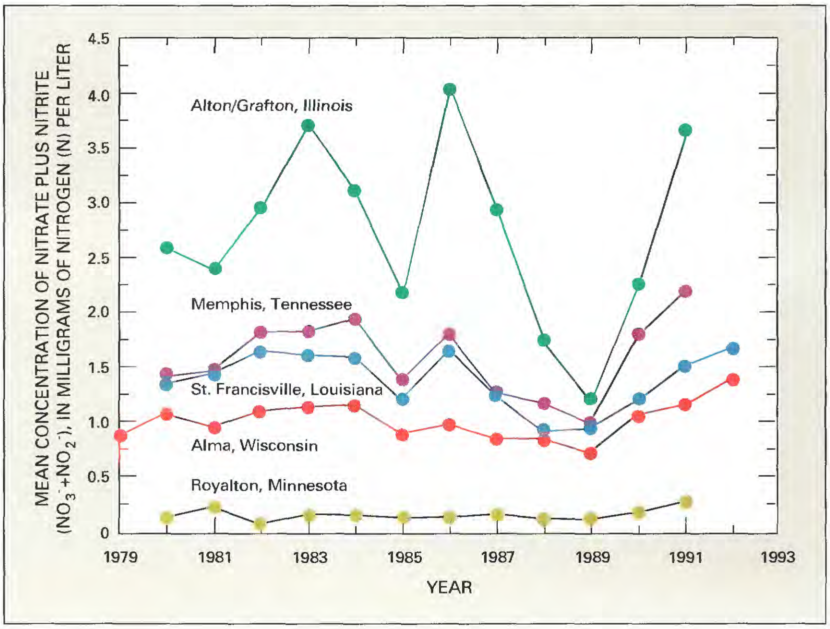
Nutrient	Maximum contaminant level, in milligrams of nitrogen per liter
Nitrate plus nitrite	10
Nitrate	10
Nitrite	1
Ammonia	[1]None

[1] Although there is no MCL for ammonia, there is an aquatic life toxicity criterion for it; this criterion is a function of pH, temperature, and organisms present (U.S. Environmental Protection Agency, 1985). For the conditions in the Mississippi River, this level is always greater than 0.6 milligram of nitrogen per liter.

In lakes, nutrient enrichment almost always increases algal production, a condition known as *cultural eutrophication*. One effect of eutrophication is that an abundance of algae may cause taste and odor problems in drinking-water supplies. A second effect of eutrophication is the increased uptake of dissolved oxygen by bacteria in response to higher concentrations of organic matter. If oxygen is taken up by decaying organic matter faster than it is imported from the atmosphere or produced by photosynthesis, it becomes depleted, and the aquatic species that require it are adversely affected. Furthermore, oxygen depletion causes basic changes in the chemical environment that allow materials (including many metals) that were formerly precipitated or tied to the sediments to become soluble and, therefore, mobile.

In large turbid rivers such as the Mississippi, rapid stream velocities and reduced light penetration into the water may inhibit primary productivity. In the Mississippi River, eutrophication may be limited to slow-flowing reaches behind locks

Figure 31 *Nitrate in River Waters*



and dams and to backwaters and eddies. The major response of plants to the nutrients in the Mississippi River is delayed until the water reaches the estuarine regions along the coast of the Gulf of Mexico, where velocities decrease and sediment settles out of the water, allowing light to penetrate and algae to bloom. For example, the fish production of the Barataria Basin, one of these estuarine regions, has become endangered by eutrophication (Hanor, 1988; Madden and others, 1988; Craig and Day, 1976); thus, the nutrients supplied by the Mississippi River are of concern to the coastal areas of the Gulf of Mexico.

The sources of nutrients in surface waters can be broadly divided as *natural* and *anthropogenic* (see table 6). Natural sources are generally ubiquitous; however, their contribution is usually low because, over the course of time, natural systems have established balances between the production and consumption of nutrients. Anthropogenic sources arise from many activities. In the agricultural setting of the Mississippi River drainage, farmers increase the productivity and yield of their crops by use of chemical fertilizers. If more fertilizers are applied than are used by the crops, they can move into ground and surface waters and become a major source of nutrients in rivers. Other major sources of nutrients in surface waters are domestic and animal wastes. Although municipal wastewater is treated, only a fraction of the nutrients is removed. In addition to the nutrients derived from human sewage, municipal wastewater also contains nutrients from such things as lawn fertilizers and household cleaners and detergents. Other anthropogenic sources of nutrients are industrial, either from the manufacture of fertilizers or as by-products of other manufacturing processes.

During the last 80 years, there has been a marked increase in the concentration of nitrate in the Lower Mississippi River that has been attributed to the increasing use of fertilizers (Turner and Rabalais, 1991). Before 1940, nitrate concentrations ranged from 0.2–0.4 milligram of nitrogen per liter (mg N/L); since 1940, they have ranged from 1.0–1.2 mg N/L. In the last 10 to 15 years, however, nitrate concentrations do not appear to have changed.

Time-series data collected at Baton Rouge and elsewhere were combined and integrated to estimate that the Mississippi River delivered about 900,000 metric tons of nitrate and 35,000 metric tons of orthophosphate to the Gulf of Mexico during the year, April 1991-April 1992. If we

Nitrate in River Waters

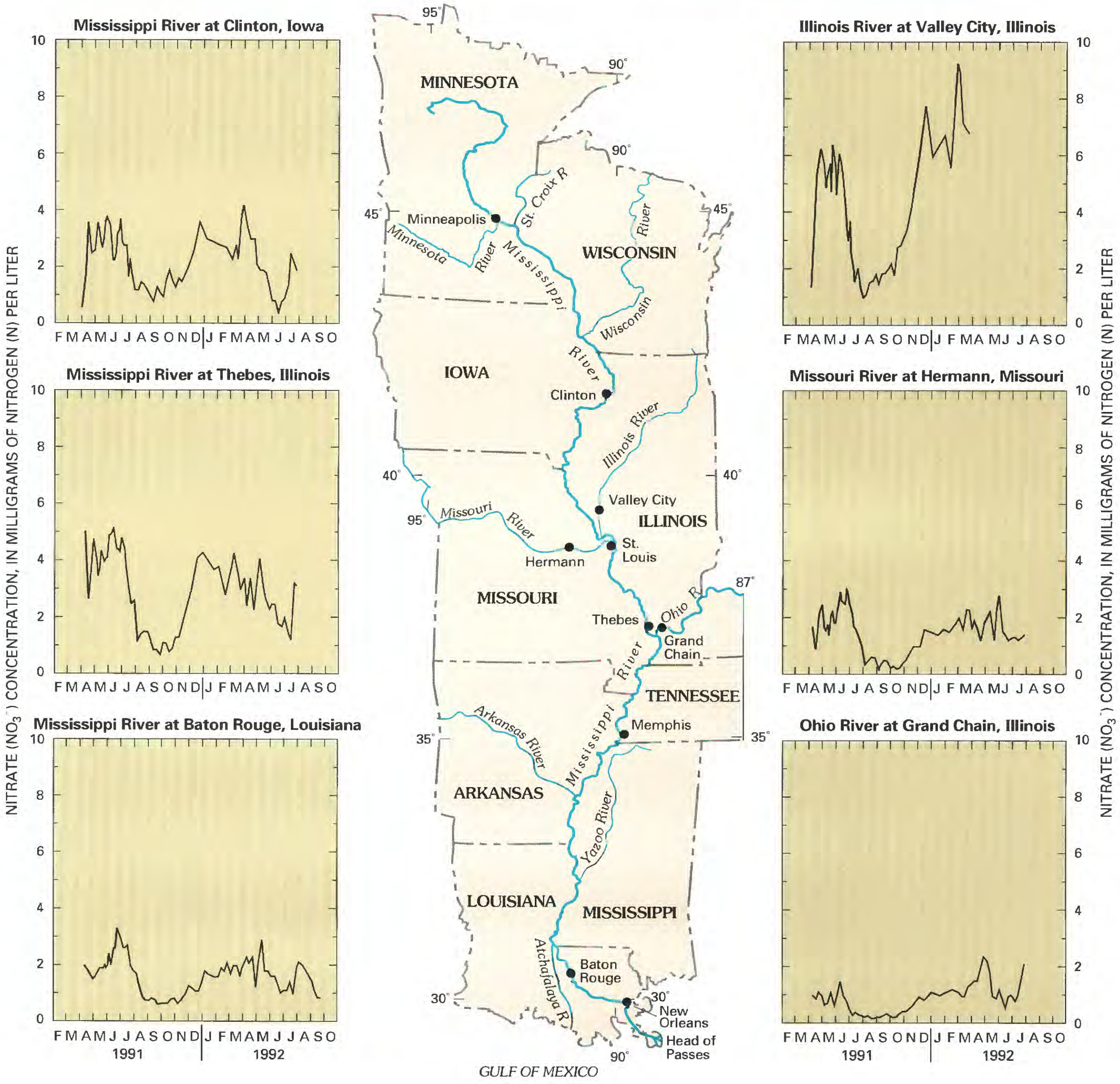
Figure 31 During the last decade and a half, there has been no significant change in the concentrations of nitrate and nitrite in the Mississippi River. Shown here are the yearly mean concentrations of nitrate plus nitrite at monitoring stations of the U.S. Geological Survey's National Stream Quality Accounting Network (NASQAN) on the Mississippi River. The lower four lines represent the upper river at Royalton, Minnesota (upriver of the Twin Cities), and Alma, Wisconsin (Lock and Dam 4), and the lower river at Memphis, Tennessee, and St. Francisville, Louisiana. The uppermost line shows considerably more scatter than the other four, which probably is related to variable inputs of nitrate from the Illinois River; the Illinois enters the Mississippi at Grafton (a few kilometers upriver of Alton), and it usually contains higher concentrations of nitrate than the other major tributaries of the Mississippi (see fig. 32).

Table 6. Sources of nutrients in surface waters

- **Natural**
  (Noncontaminant)
- **Anthropogenic**
  (Contaminant)
  - **Agriculture**
    - Chiefly fertilizers
  - **Feedlots and slaughterhouses**
    - Animal wastes
  - **Domestic wastes**
    - Human sewage
    - Lawn fertilizers
    - Household products
  - **Industrial wastes**
    - Fertilizer manufacturing
    - Petrochemical by-products
    - Agrochemical by-products

assume that all nitrate in the Mississippi River before 1940 originated from natural sources, the increase since 1940 provides a rough estimate that at least 75 percent of the nitrate in the Mississippi River today is anthropogenic in origin. Most of that 75 percent apparently comes from nonpoint agricultural sources. It is estimated that more than 5.5 million metric tons of nitrogen fertilizer were applied to cropland in the Mississippi River Basin in 1991 (U.S. Department of Agriculture, 1992; J.J. Fletcher, West Virginia University, unpubl. data,1992). The 900,000 metric tons of nitrate discharged by the Mississippi River into the Gulf of Mexico was therefore equivalent to about 16 percent of the nitrogen fertilizer applied to cropland in one year. In contrast, most of the ammonium that enters the Mississippi River probably originates from either industrial or municipal waste.

Figure 32 *Nitrate Variations Through Time*



Mississippi River at Clinton, Iowa

Mississippi River at Thebes, Illinois

Mississippi River at Baton Rouge, Louisiana

Illinois River at Valley City, Illinois

Missouri River at Hermann, Missouri

Ohio River at Grand Chain, Illinois

Nitrate Variations Through Time

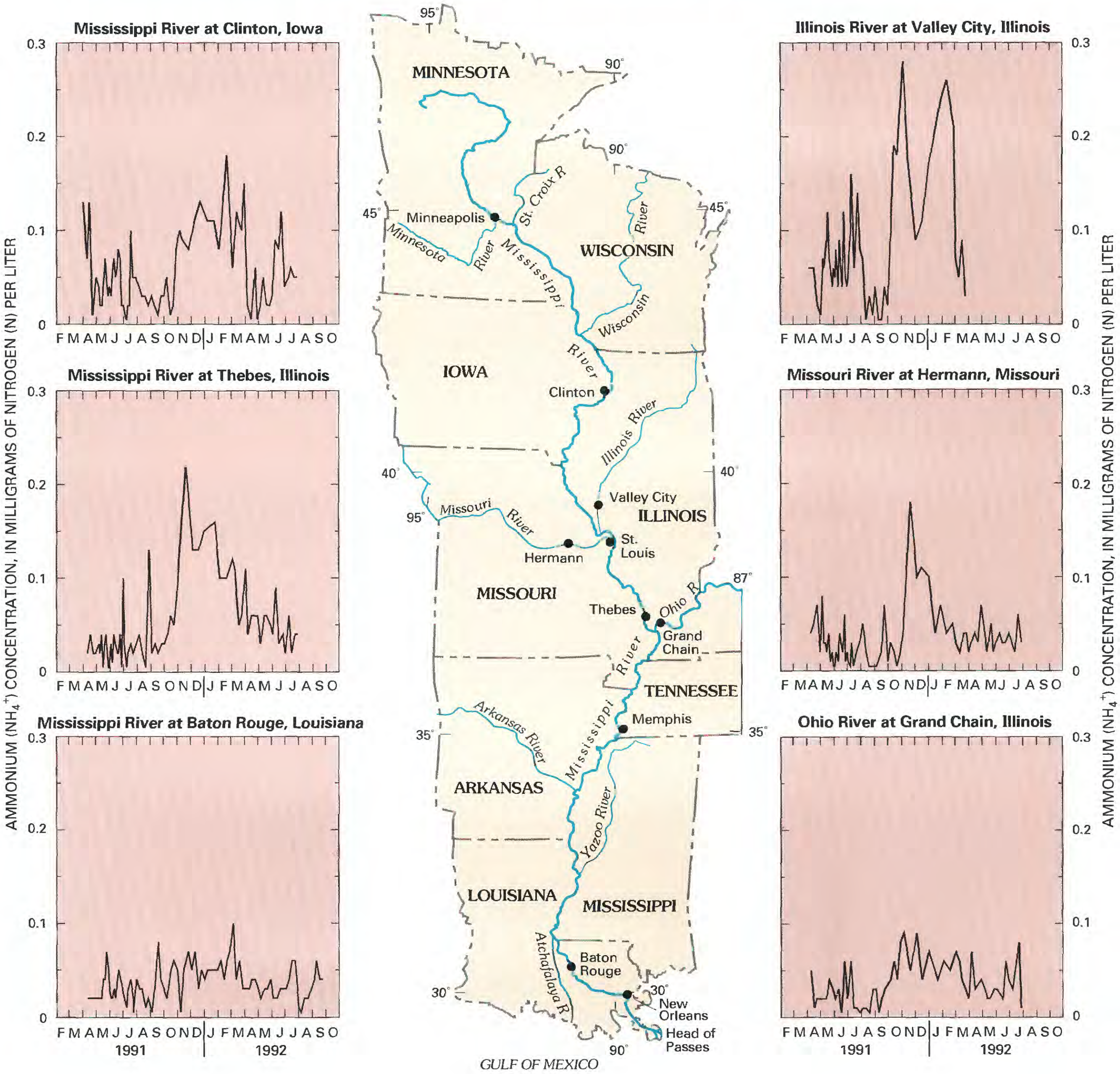
Figure 32 Nitrate concentrations in the Mississippi River and its tributaries vary seasonally, usually being higher in winter, spring, and early summer and lower in late summer and early autumn. The data shown in the graphs are from samples collected at weekly or biweekly intervals between March 1991 and September 1992 at six sites: three on the Mississippi River main stem and three in the lower reaches of principal tributaries. For a complete listing of the data, see Coupe and others (1995). The maximum contaminant level for nitrate in drinking water (10 milligrams of nitrogen per liter, a level that corresponds to the top of the graphs) was not exceeded in any of the samples collected at the six sites during the period shown here. The highest concentrations of nitrate were recorded in the Illinois River, which drains extensive agricultural areas and receives municipal wastes from Chicago and other cities.

Virtually all of the sharp increases of ammonium concentration in samples, such as those illustrated in figures 34 and 35, corresponded to metropolitan centers on the river. This association, coupled with data on fecal coliforms and surfactants (see the chapter, "Organic contamination of the Mississippi River from municipal and industrial wastewater"), suggests that most ammonium ions in the river originate from municipal waste.

The source of nitrite is more difficult to assess. Although there was probably a significant contribution from non-point sources, nitrite, like ammonium, was being removed by biotic utilization or conversion to nitrate, and hence this contribution was minimized.

To summarize: In terms of human health, nitrate is the only nutrient compound that represents a problem in the Mississippi River system; nitrate concentrations in many of the Mississippi River's tributaries in Iowa, Minnesota, and northern Illinois approach and occasionally exceed the USEPA drinking-water standard (table 5; see also Lucey and Goolsby, 1993). In addition to the public health question, nitrate represents an ecological problem as well. Because it is not removed quickly, nitrate is accumulating in the Gulf of Mexico; each year, the Mississippi delivers a large quantity (900,000 metric tons between April 1991 and April 1992) to the Gulf and therefore merits concern in terms of potential eutrophication. The largest sources of this nitrate are most likely fertilizers used in agriculture. Although the concentrations of nitrate in the Mississippi River have increased since the turn of the century, these levels have been virtually unchanged over the last 10 to 15 years. Hence, although nitrate concentrations may be high, they appear to have stabilized.

Figure 33 *Ammonium Variations Through Time*



Ammonium Variations Through Time

Figure 33 Ammonium concentrations generally are highest in winter (December through March) when river water temperatures are lowest. This pattern is not so much related to seasonal supplies of ammonium as it is to water temperatures. During the warmer months, ammonium is less persistent in oxygenated river water because it is more rapidly utilized by bacteria and algae or more rapidly oxidized to nitrate or nitrite. Data shown in the graphs are based on the same samples as the nitrate data shown in figure 32 (see Coupe and others, 1995, for a complete listing).

Table 7. Summary statistics of nutrient concentrations during 1991–92 in the Mississippi River and all measured tributaries (M1 and T1 in fig. 30)

[Concentrations are in milligrams per liter as nitrogen or phosphorus.]

Statistic	Nitrate	Nitrite	Ammonium	Orthophosphate
Mississippi River				
Number of samples	576	577	570	582
Minimum concentration	.30	<.001	<.006	<.001
Maximum concentration	6.27	.115	.155	.178
Mean concentration	2.38	.023	.015	.075
Standard deviation	1.35	.020	.018	.039
Median concentration	2.13	.020	.010	.080
Tributaries (collectively)				
Number of samples	196	194	176	190
Minimum concentration	.01	<.001	<.006	<.001
Maximum concentration	9.91	.141	.177	.330
Mean concentration	2.22	.034	.035	.060
Standard deviation	2.79	.034	.039	.064
Median concentration	.75	.020	.020	.034

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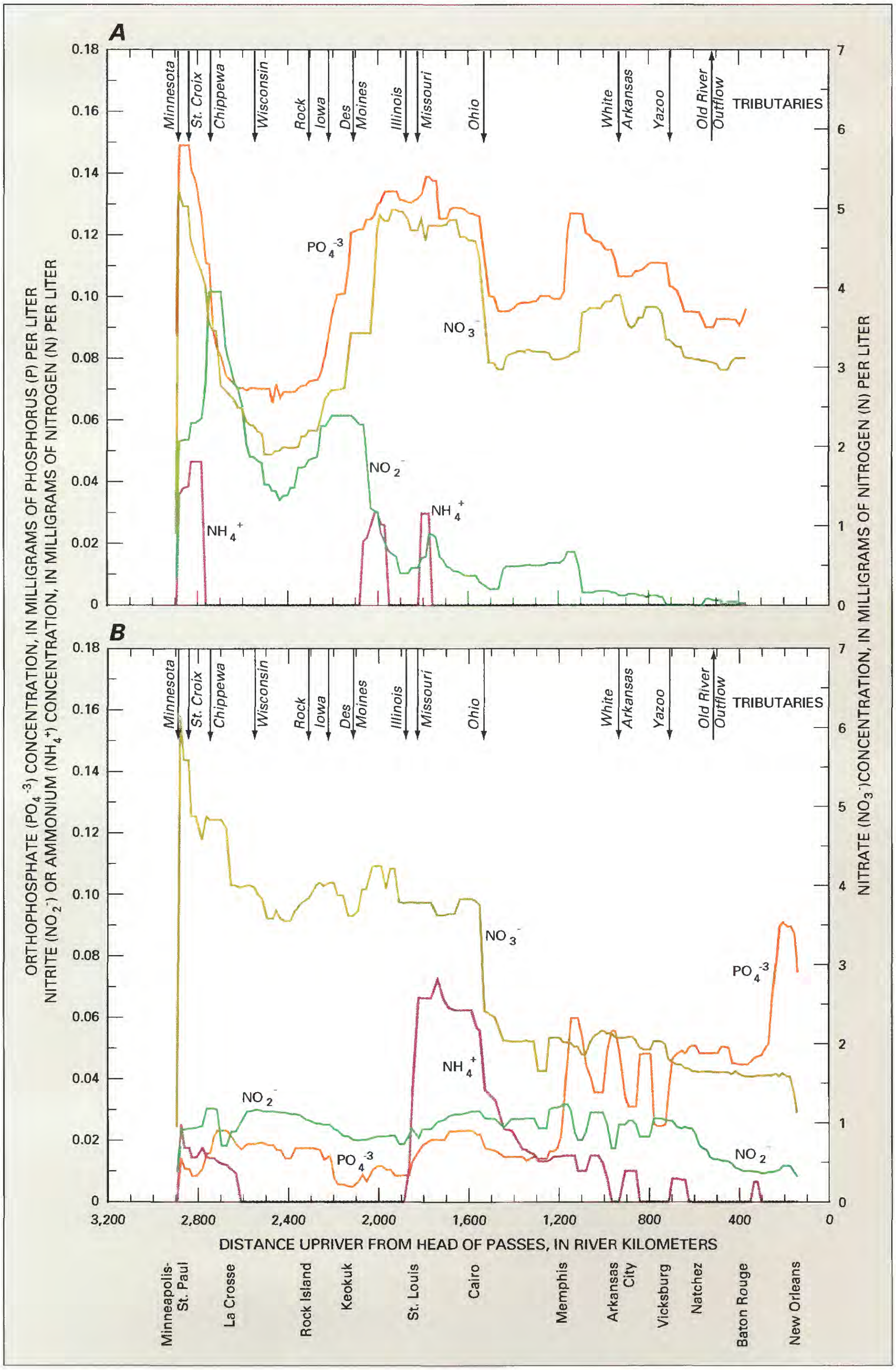
Figure 34 *Nutrient Concentrations*



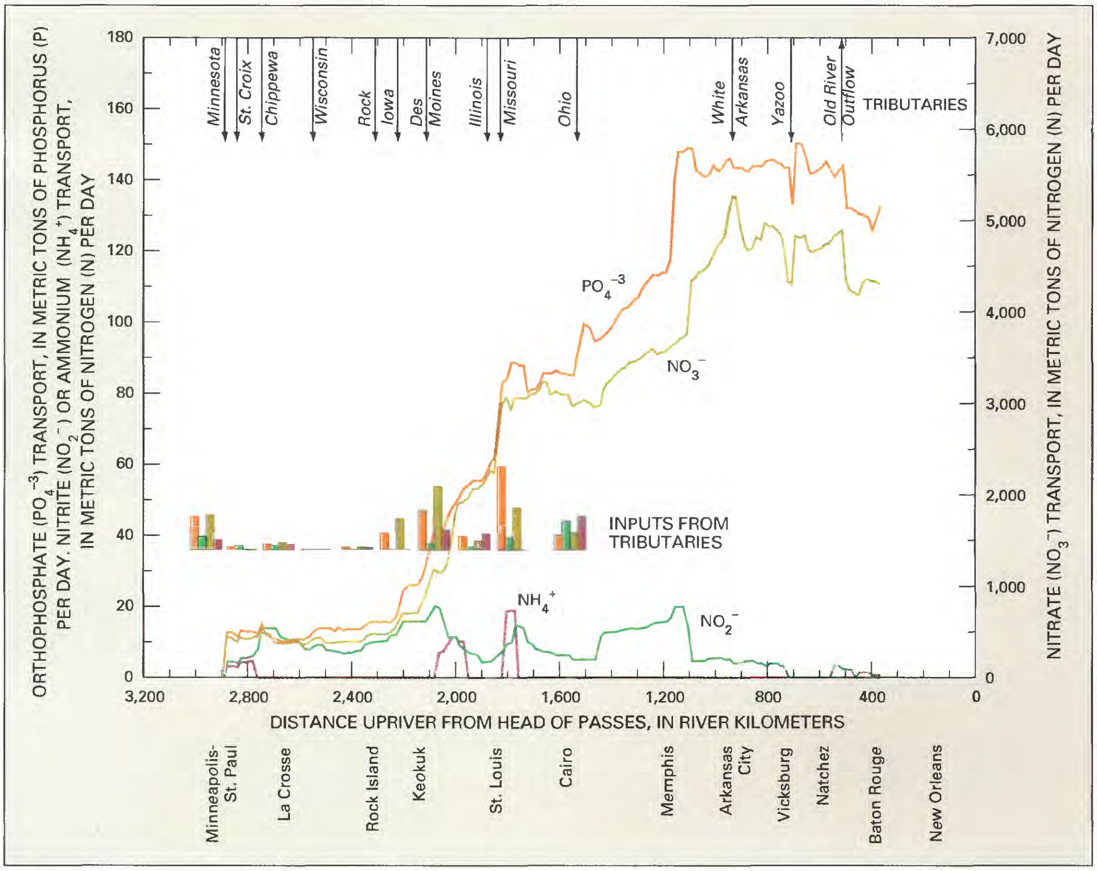
Nutrient Concentrations

Figure 34 Spatial variations of nutrients along the length of the Mississippi River demonstrate the interplay between the input sources that increase their concentrations and the processes of dilution and decomposition that decrease their concentrations. Data shown here in A and B were collected during two upriver cruises (see "Sampling the Length of the River" on page 49) wherein samples were taken approximately every 10 miles near the center of the river. Complete tabulations of the data are given by Antweiler and others (1995).

A Data collected during the upriver cruise of June 23-July 2, 1991, showed (1) increases and decreases in nitrate and orthophosphate that were related mainly to inputs and dilutions by tributaries, and (2) downstream decreases of nitrite and ammonium that were related mostly to uptake by organisms or oxidation to nitrate. Concentrations of nitrate (NO_3^-) and orthophosphate (PO_4^{-3}) fluctuated in near parallel fashion, showing the following features, in downriver sequence: highest concentrations just below the mouth of the Minnesota River; rapid decreases in concentration between the mouth of the Minnesota River and kilometer 2500 (northern border of Iowa) owing mostly to dilution by tributary inflows that have lower concentrations; rapid increases in concentration as the river flowed past Iowa and northern Illinois, probably owing to more concentrated inputs from rivers like the Iowa and Des Moines; no appreciable changes in concentration at or below the mouth of the Missouri River; marked dilutions from the less concentrated waters of the Ohio River; few large changes in concentration in the lower Mississippi River, except for peaks between river kilometers 650 and 1100 that probably reflected pulses of runoff of stormwaters that fell a few weeks earlier in agricultural areas of Iowa and Illinois. Ammonium (NH_4^+) concentrations showed as three distinct spikes that appeared and disappeared rapidly: one below the Minnesota River and the Twin Cities, one below the Des Moines River and Keokuk, and one below St. Louis. Once ammonium has been introduced into the river, it decreases quickly as it is assimilated by bacteria and algae, converted to nitrate or nitrite, or removed by adsorption onto sediments. After reaching a peak concentration downriver of Lake Pepin (near river kilometer 2700), nitrite (NO_2^-) showed a general decrease downriver, punctuated most notably by an increase between kilometers 2400 and 2100 and another small increase near St. Louis. Nitrite, like ammonium, is removed by natural processes—its utilization by bacteria and algae and its oxidation to nitrate are the most likely possibilities—but not as rapidly as ammonium. Like ammonium, most of the nitrite probably originates from point sources.

B Data collected during the upriver cruise of March 25-April 4, 1992, show substantial differences when compared with the data collected the previous summer (shown in A). These differences in concentrations reflected seasonal differences in the sources of nutrients and in the rates at which nutrients are utilized or transformed in the river. Nitrate (NO_3^-) concentrations again were highest in the Minneapolis-St. Paul area and decreased downriver to about kilometer 2400, below which point they remained fairly constant until they were diluted by the waters of the Ohio River. Orthophosphate (PO_4^{-3}) concentrations were lower than during the previous summer, especially in the upper river; the spikes or peaks of concentration between river kilometers 1100 and 650 may have resulted from storm events upriver that flushed in waters that were rich in orthophosphate. Ammonium (NH_4^+) concentrations again appeared as spikes, but these spikes were broader, reflecting the slower rates of removal or utilization during the early spring that are related to lower temperatures, slower growth cycles, or less incident radiation (sunlight). Persistent concentrations of nitrite (NO_2^-) along most of the length of the river suggest that mechanisms for its disappearance, such as uptake or oxidation, also were retarded during the early spring period of March-April 1992.

Figure 35 *Nutrient Transports*



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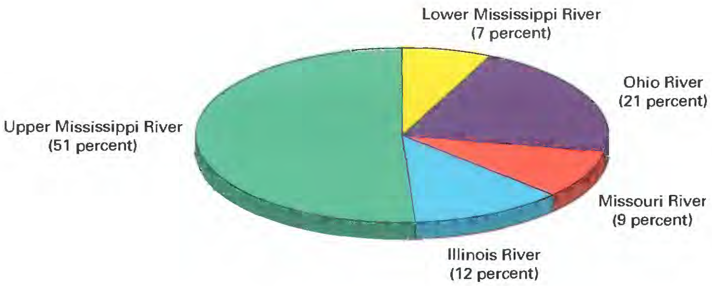
Nutrient Transports

Figure 35 When nutrient data are graphed in terms of their fluxes or transports rather than their concentrations, they show that the transports of nitrate (NO_3^-) and orthophosphate (PO_4^{-3}) mostly increase downriver. This means that the processes that add nitrate and orthophosphate to the river are more prevalent than the processes that remove them. Transports of nitrite (NO_2^-) and ammonium (NH_4^+), on the other hand, generally decrease downriver because, in their cases, the removal mechanisms prevail. Shown here are the data from the upriver cruise of June 23-July 2, 1991: concentrations shown in figure 34A have been multiplied by water discharges to compute the downriver transports of dissolved nutrients in tons per day (1 metric ton = 1000 kg = 2205 pounds). Significant inputs from tributaries are shown by bars near the center of the graph; the individual nutrients are identified by bar colors which correspond to those of the curves. Concentrations of nitrate and orthophosphate showed parallel fluctuations during the sampling period. The initial loading to the Mississippi River from the Minnesota River represented the total transport of these two compounds for the next 600 km (to river kilometer 2250); this implies that over this distance, additions of nitrate and orthophosphate from tributaries and point sources were negligible, or that gains of these ions were balanced by their losses. From kilometer 2250 (near the confluence with the Iowa River) downriver to St. Louis (kilometer 1800), loads increased steadily from contributions from tributaries. The Iowa River at kilometer 2240, the Des Moines River at kilometer 2100, and the Missouri River at kilometer 1850 each added a large increment of nitrate and orthophosphate (see the bars in the middle of the graph). Because the Ohio River added relatively small amounts of nutrients, its effect can barely be distinguished on the graph. The large increases in the curves at about kilometer 1100 (south of Memphis, Tennessee) probably were caused by a storm event several weeks earlier in Iowa or Illinois, which flushed large quantities of these compounds into the river. The decreases in the curves at about kilometer 500 are caused by the Old River outflow, which removes substantial amounts of the water and dissolved nutrients from the Mississippi River. Ammonium (NH_4^+) loads were introduced into the river from point sources, most likely municipal wastes, and they decreased within relatively short distances downriver. Nitrite (NO_2^-) load behaved in a fashion somewhere between nitrate load and ammonium load: its points of introduction were generally not spikes, yet it clearly was being utilized or converted to other forms of nitrogen faster than it was being introduced—as reflected in the downriver decrease in nitrite load. Places where nitrite was introduced were not always related to entering tributaries; the sharp increase in nitrite load near river kilometer 2700 (Lake Pepin), for example, cannot be related to tributary inputs.

Figure 36 *Nitrate Sources*

Sources of Nitrate in the Mississippi River



Water discharge in the Mississippi River Basin

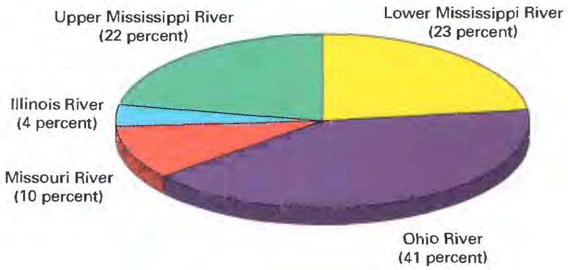


Figure 36 Disproportionately large quantities of the nitrate in the Mississippi River, on average, are derived from the upper-basin States of Minnesota, Iowa, and Illinois. Slightly more than one-half the total nitrate load in the system is derived from the Upper Mississippi River Basin, which supplies less than one-fourth of the total water. Conversely, the Ohio River supplies 41 percent of the total water, but only 21 percent of the total nitrate load. The Missouri River is the only major tributary whose nitrate load corresponds closely to its proportion of the water discharge.

Figure 37 *Nitrogen Applied to Croplands*

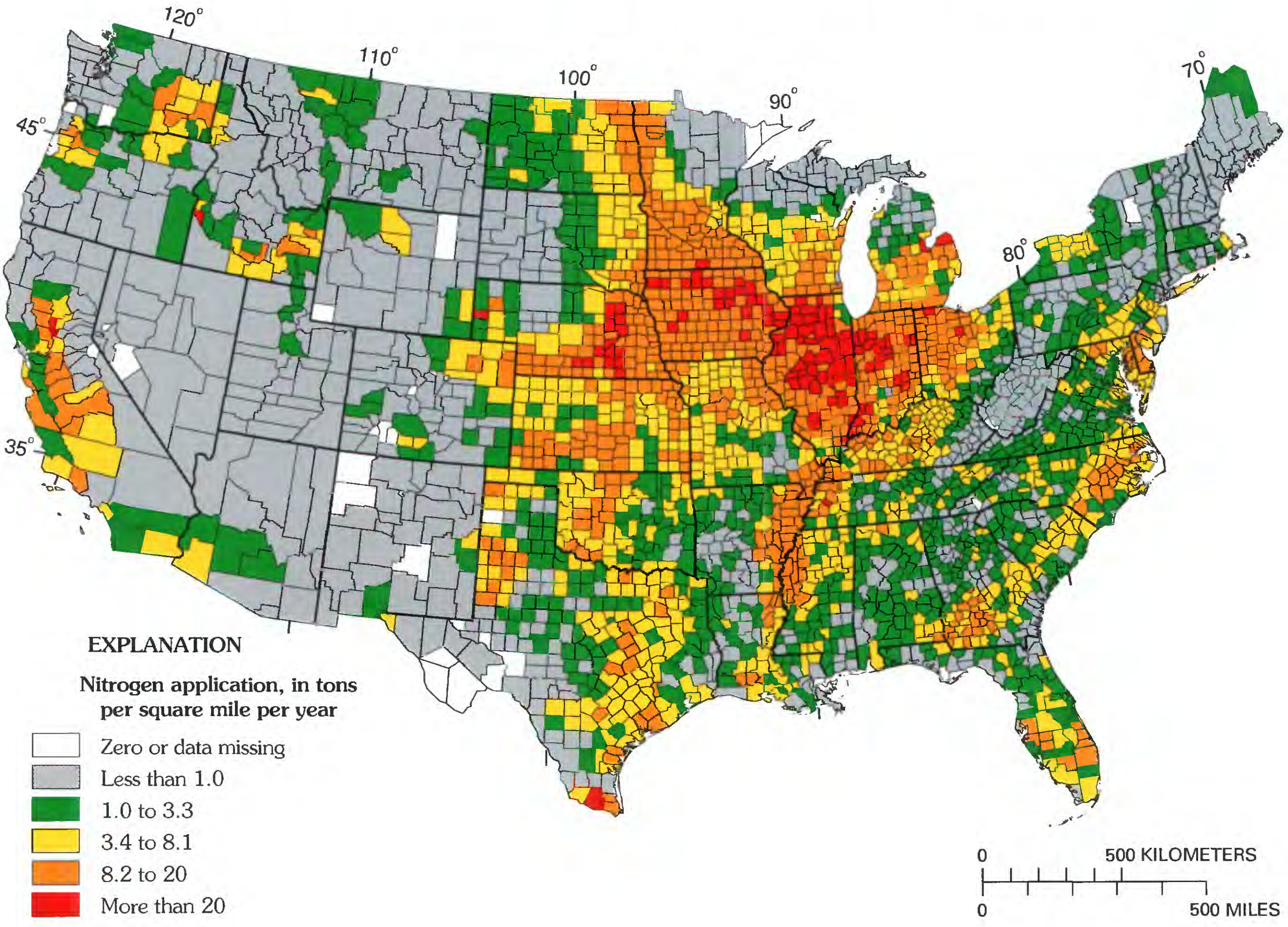


Figure 37 An estimated 5.5 million metric tons of nitrogen fertilizer were applied to croplands in the Mississippi River Basin during 1991. This map was prepared by W.A. Battaglin of the U.S. Geological Survey to show the geographical distribution of the estimated use of nitrogen fertilizer in the Nation during 1991. County estimates were made by J.J. Fletcher of West Virginia University, using fertilizer expense estimates from the 1987 Census of Agriculture. State totals were compiled by the National Fertilizer and Environmental Research Center of the Tennessee Valley Authority. Agricultural lands of the Corn-Belt States of Iowa, Illinois, Indiana, and Minnesota clearly are potential sources of nutrients in the Mississippi River.

Figure 38 *Harvested Croplands*

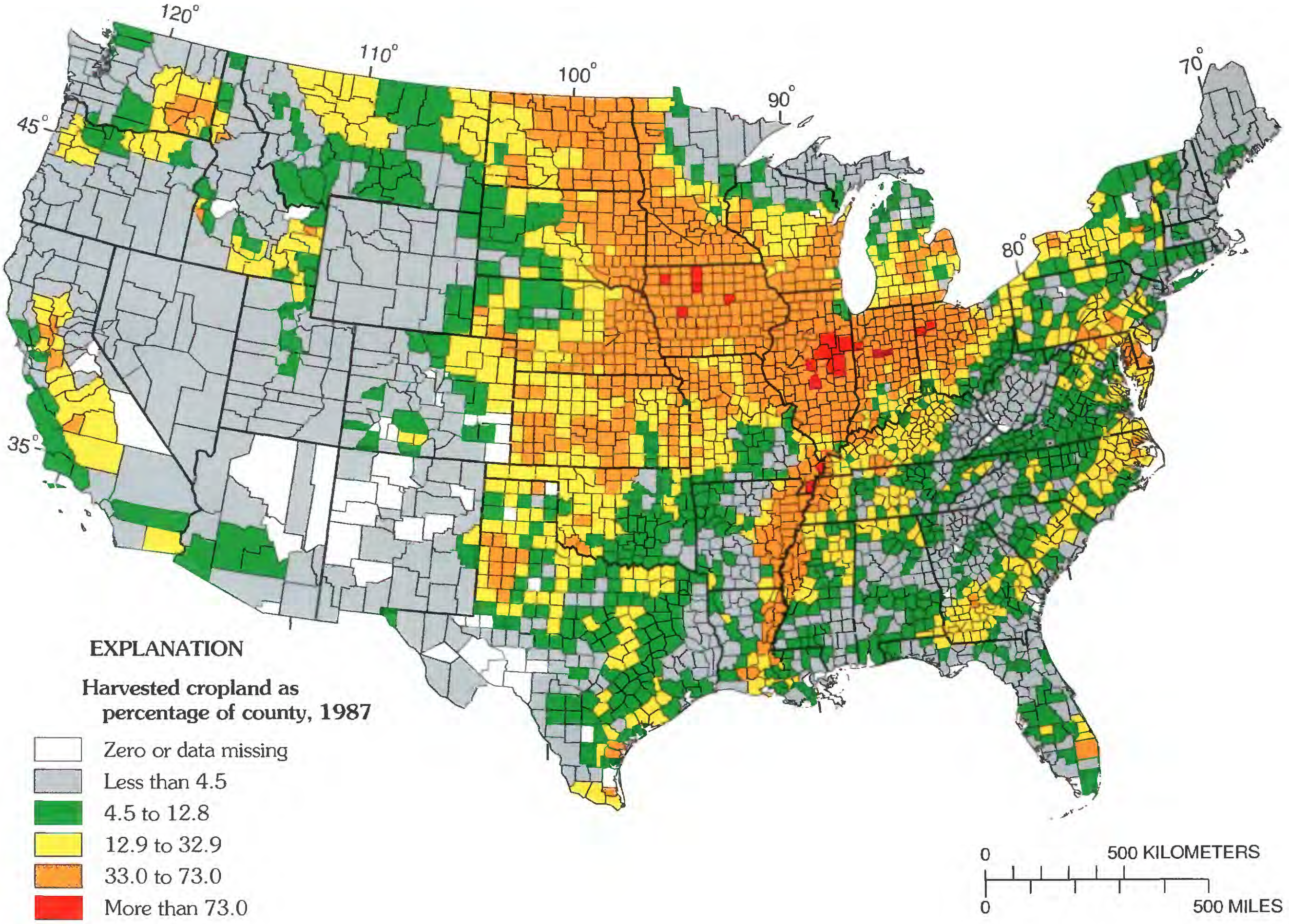


Figure 38 Cropland in the United States is concentrated most heavily in the areas drained by the Mississippi River. In this map, prepared by W.A. Battaglin of the U.S. Geological Survey from data supplied by the U.S. Department of Commerce, Bureau of the Census, Census of Agriculture, harvested cropland is expressed as a percentage of the total area of each county. The Mississippi River Basin contains about 65 percent of the total harvested cropland in the Nation, producing about 80 percent of the corn and soybeans, and much of the cotton, rice, sorghum, and wheat (U.S. Department of Agriculture, 1985; U.S. Department of Commerce, 1989).

Pesticides in the Mississippi River

Donald A. Goolsby and Wilfred E. Pereira

Introduction

The Mississippi River basin contains the largest and most intensively farmed region in the Nation. In order to increase yields from crops, large amounts of pesticides are used to protect against weeds, insects, and other pests. The major categories of pesticides are herbicides, insecticides, and fungicides. It is estimated that about two-thirds of all pesticides used for agriculture in the United States are applied to cropland and pasture land in the Mississippi River Basin (Gianessi and Puffer, 1990). The intense use of pesticides is of concern because of potential adverse effects on the quality and use of water resources. The most immediate concerns are for aquatic life and for the 18 million people in the basin who rely on surface-water sources for drinking water.

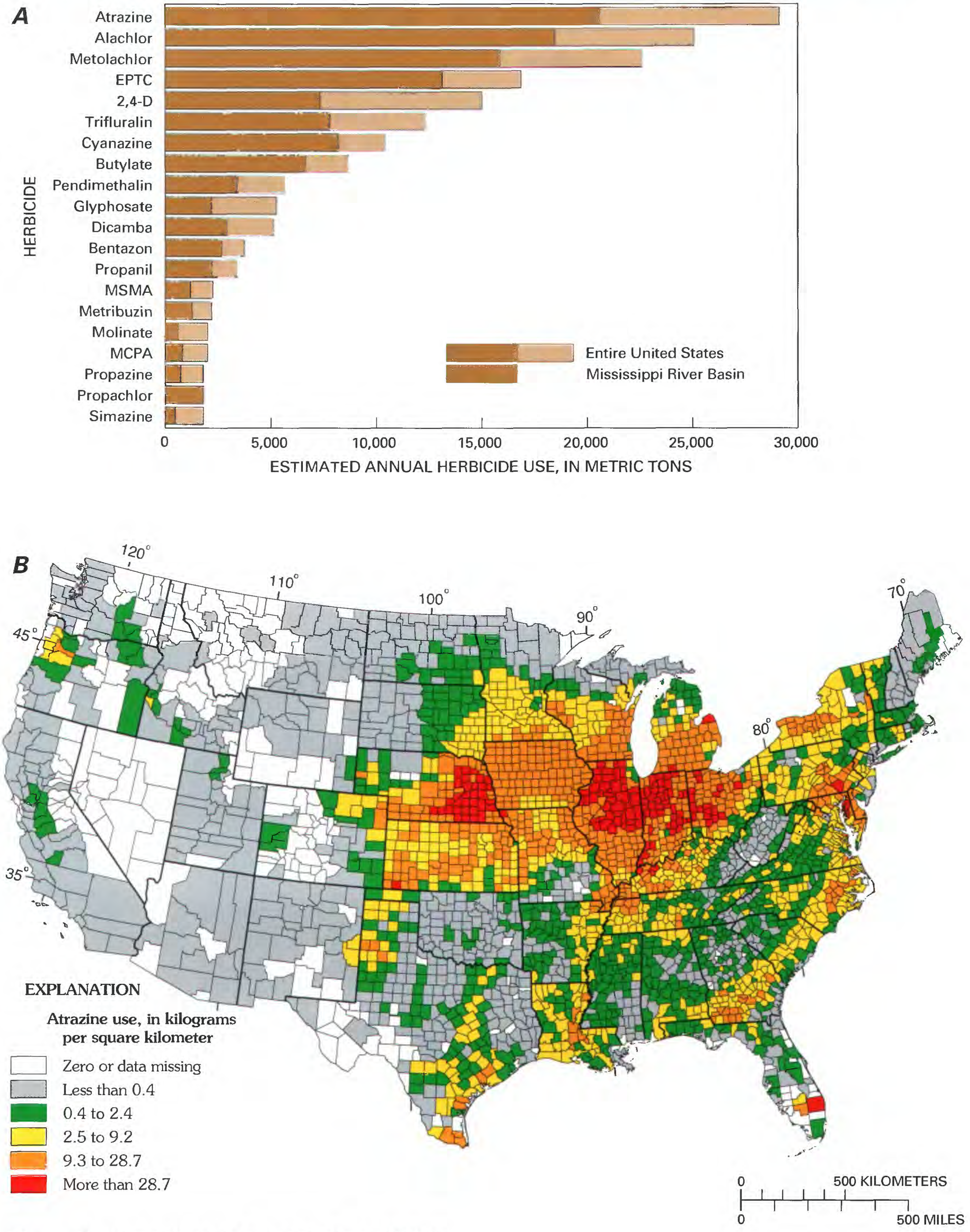
Many of the pesticides used in the basin are present in the Mississippi River and its tributaries. A regional-scale study of a 10-State area in the upper Midwest showed that large amounts of herbicides are flushed into streams during storm runoff in late spring and summer each year, following application of herbicides to cropland (Thurman and others, 1992). Storm runoff produces high concentrations of many herbicides in streams across the upper Midwest from Nebraska to Ohio for periods of several weeks to several months. Concentration of herbicides in some small streams may exceed 100 micrograms per liter (μg/L) for short periods of time. Flow from these streams, in turn, transports significant amounts of herbicides into large rivers such as the Missouri, Ohio, and Mississippi, and eventually to the Gulf of Mexico (Pereira and Rostad, 1990; Goolsby and others, 1991; Pereira and Hostettler, 1993).

Sources and Properties of Pesticides

Pesticides include a wide variety of synthetic organic and inorganic compounds used to control weeds, insects, nematodes and other pests. The U.S. Environmental Protection Agency (Aspelin and others, 1992) estimated that in 1991 about 490 million kilograms (kg) of pesticides were used annually in the United States. These include herbicides (285 million kg), insecticides (113 million kg), and fungicides (54 million kg). About three-fourths of the total annual pesticide use is for agriculture (Aspelin and others, 1992). In 1991, about 218 million kg of pesticides were used on major field crops alone, of which about 84 percent were herbicides (U.S. Department of Agriculture, 1992).

Pesticides derived from point and nonpoint sources in the Mississippi River basin are transported into the Mississippi River in runoff from agricultural and urban areas, discharge from reservoirs and aquifers, and atmospheric deposition (Nations and Hallberg, 1992). The physiochemical properties of the pesticides themselves, as well as other factors such as usage, rainfall, and farming practices, are important in governing the amounts and concentrations that actually occur in streams. Several important physiochemical properties of the most widely used pesticides in the Mississippi River basin are given in table 8. These include water solubility, soil half-life, and soil sorption coefficient (K_{oc}). Water solubility determines how easily pesticides wash off soil and crop residues and how easily they leach through the soil. Pesticides with solubilities greater than about 30 milligrams per liter (mg/L) are considered to be soluble and more likely to wash off the soil during storms. Soil half-life is the length of time required for pesticides to degrade in the soil to one-half their previous concentration. The longer the soil half-life the more persistent the pesticide, and the longer it will be available to wash off in storm runoff. The half-life of pesticides, once they are in surface water, is generally much longer than in soil because water contains much less organic matter and fewer micro-organisms to degrade the pesticides. Many pesticides are highly persistent in streamwater

Figure 39 Herbicides Applied to Croplands



Herbicides Applied to Croplands

Figure 39 Most of the pesticides used in the Mississippi River Basin are herbicides used for weed control. Data portrayed in this figure, representing the years 1987–89, were obtained from Resources for the Future (Gianessi and Puffer, 1990).

A The 20 most heavily used herbicides are shown in this graph. The most heavily applied herbicides are atrazine, alachlor, and metolachlor, which are used in the production of corn and soybeans.

B Atrazine is used most heavily in the upper Midwest, generally to control broad-leaved weeds in cornfields. Other herbicides used extensively on corn and soybean fields have geographical patterns of use similar to that of atrazine, but the amounts are somewhat less.

Table 8. Physiochemical properties, health-based limits for drinking water, and aquatic-life guidelines for selected major pesticides used in the Mississippi River Basin

[mg/L, milligram per liter; g/mL, gram per milliliter; µg/L, microgram per liter; --, no data or none available]

Pesticide	Solubility[1] (mg/L)	Sorption coefficient (K_{oc})[1] (g/mL)	Soil half-life[1] (days)	Maximum contaminant level[2] (µg/L)	Health advisory[2] (µg/L)	Canadian aquatic life guidelines (µg/L)
			Herbicides			
Alachlor	240	170	15	2	--	--
Atrazine	33	100	60	3	3	[3]2
Bentazon	2,300,000	35	20	--	20	--
Butylate	46	126	12	--	350	--
Cyanazine	170	190	14	--	1	[4]2
2, 4-D	([11])	([12])	10	--	70	[5]4
EPTC	375	280	30	--	--	--
Metolachlor	530	200	20	--	70	[6]8
Metribuzin	1,220	41	30	--	200	[7]1
Molinate		190	21	--	--	--
Propachlor	613	80	6	--	90	--
Propanil		188	1	--	--	--
Propazine	--	--	--	--	10	--
Simazine	6.2	138	75	4	4	[8]10
Trifluralin	0.3	7,000	60		5	[9]0.2
			Insecticides			
Carbaryl	114	200	10	--	700	--
Carbofuran	351	22	50	40	40	[10]1.75
Chlorpyrifos	2	6,070	30	--	20	--
Diazinon	40	500	40	--	0.6	--

[1] Becker and others, 1989.

[2] U.S. Environmental Protection Agency, 1995.

[3] Trotter and others, 1990.

[4] Pauli and others, 1991a.

[5] Task Force on Water Quality Guidelines.

[6] Kent and others, 1991.

[7] Pauli and others, 1990.

[8] Pauli and others, 1991b.

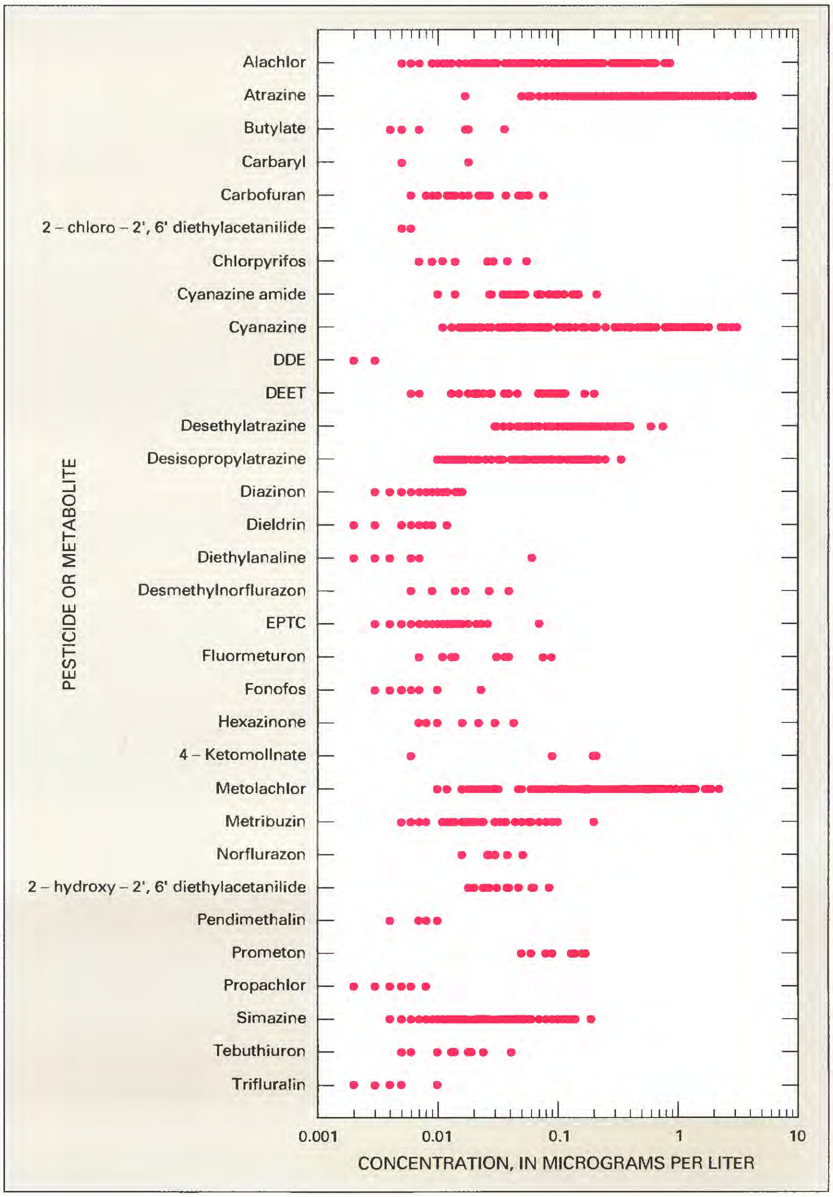
[9] Kent and others, 1992.

[10] Trotter and others, 1989.

[11] Varies; 1 mg/L for 2,4-D ester; greater than 700,000 mg/L for 2,4-D amine.

[12] pH dependent.

Figure 40 *Pesticides in the River*



and in reservoirs, but very little specific information is available on pesticide half-lives in natural water bodies. The soil sorption coefficient is a measure of the tendency of a pesticide to attach to soil particles. The larger the K_{OC} value the more strongly the pesticide will be adsorbed to soil. Those with K_{OC} values less than about 500 tend to be transported primarily in the dissolved phase. Those with K_{OC} values of more than 1000 are transported primarily on suspended-sediment particles.

The physiochemical properties listed in table 8 indicate that relatively soluble and mobile compounds such as atrazine, alachlor, metolachlor, and many other herbicides are transported primarily in the dissolved phase. This group of compounds includes the majority of pesticides in use today. However, soil half-life and other factors such as intensity of use, application methods, and climatic conditions are also important in determining transport in surface water. Most of the older "first generation" chlorinated insecticides, such as DDT, chlordane, and dieldrin (not shown in table 8), are insoluble in

Pesticides in the River

Figure 40 The concentrations of 32 pesticides and pesticide-degradation products dissolved in waters collected from the main-stem Mississippi River during 1987–92 are shown here in dot plots. These plots show the distribution and range in concentration for each pesticide. Each dot represents one sample. The dot plots summarize a diverse body of data that represents concentrations during different seasons of the year at numerous locations. The samples on which the plots are based were collected (1) during 10 downriver sampling trips between July 1987 and May 1992 and (2) approximately weekly at 3 fixed stations on the Mississippi River (Clinton, Iowa; Thebes, Illinois; Baton Rouge, Louisiana) from April 1991 through September 1992. The concentrations of pesticides measured near the mouths of tributaries that flow into the Mississippi River generally are slightly higher than those shown in this figure. Specific sampling locations and analytical data are given by Coupe and others (1995) and Pereira and others (1995).

water, have long soil half-lives, and large K_{oc} values. Consequently, they are transported primarily on sediment particles. Most of these first-generation chlorinated insecticides are banned and are no longer used in the United States, but continue to persist in the Mississippi River Basin from previous use because of long soil half-lives. Also, because these chlorinated insecticides are relatively insoluble in water and have large K_{oc} values, they partition into the organic coatings of sediments or accumulate in the fatty tissues of fish and other stream biota (Moore and Ramamoorthy, 1984), which is not true for most pesticides currently in use.

Drinking-Water Standards and Aquatic-Life Guidelines

The maximum contaminant levels (MCLs), or drinking-water standards, that have been established by the U.S. Environmental Protection Agency (1995) for several pesticides also are shown in table 8. MCLs are based on annual average concentrations and are legally enforceable under the Safe Drinking Water Act. MCLs are based on analyses of a minimum of four samples per year, and a violation occurs only if the average concentration in these samples exceeds the MCL. Further, MCLs apply to water delivered at the tap and not the raw water source. However, conventional water treatment removes very little of the water-soluble pesticides currently used in the Mississippi River Basin. At present (1995) MCLs are established only for individual compounds and do not consider the possible effects of complex mixtures of pesticides and their degradation products.

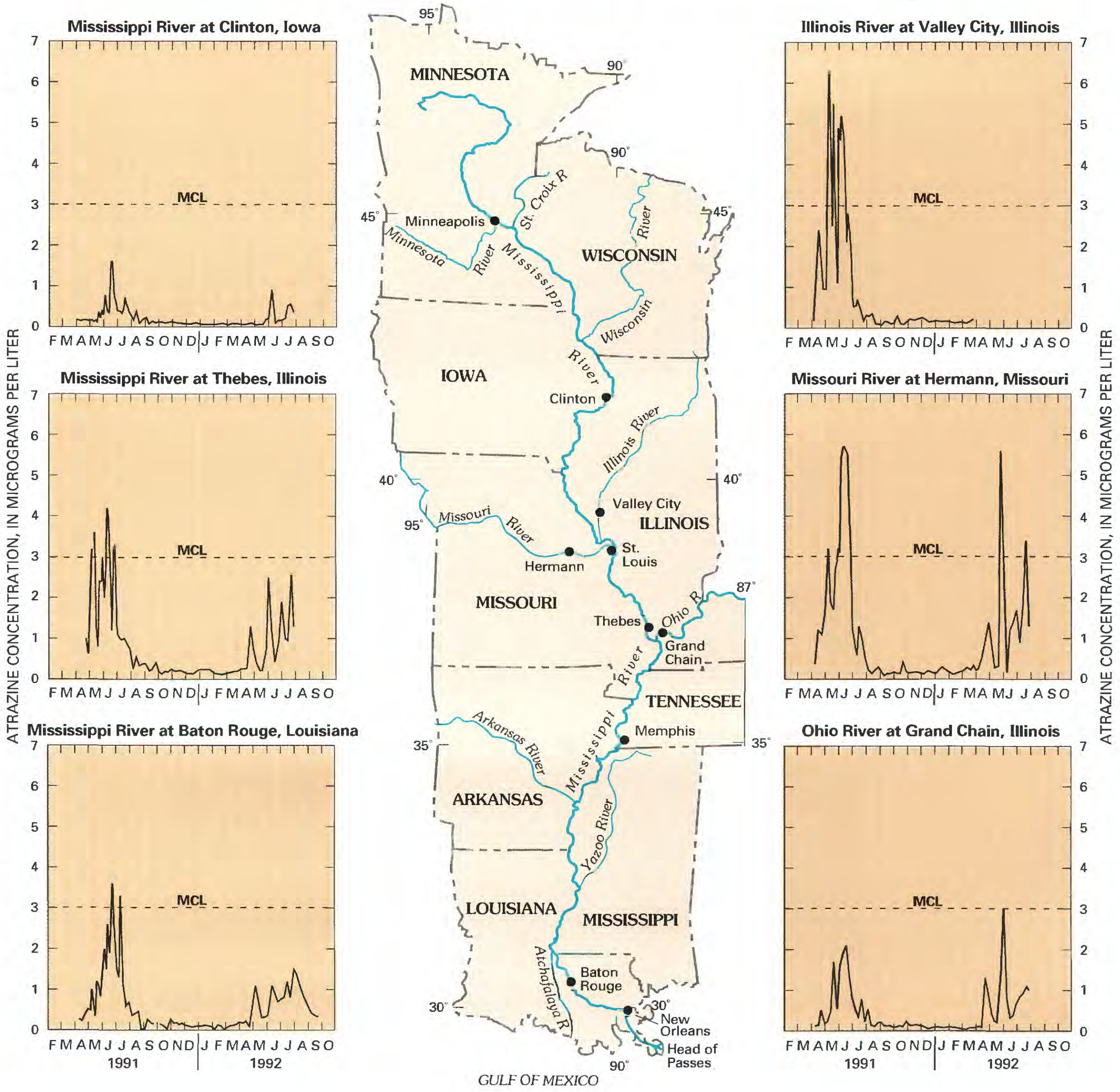
Health advisories (HAs) have been established for many other pesticides (table 8). HAs are the recommended maximum concentrations in drinking water for lifetime exposure and are not legally enforceable. However, in time, the lifetime HAs for many pesticides may become enforceable MCLs.

Many pesticides may have adverse effects on aquatic life, but at present (1995), the U.S. Environmental Protection Agency has established standards or criteria for aquatic life for very few current-generation pesticides. However, Environment Canada has established water-quality guidelines for specific water uses in Canada that include drinking water, aquatic life, and agricultural uses of water (Wong and Kent, 1988). The guidelines are numerical concentrations recommended to support and maintain a designated water use. Because U.S. guidelines or criteria for aquatic life do not presently exist for most pesticides in current use, the Canadian pesticide water-quality guidelines, where available, have been included in table 8 as points of reference for pesticide concentrations measured in the Mississippi River Basin.

Occurrence and Temporal Distribution of Pesticides in Water

More than 40 pesticides and pesticide degradation products were detected during 1987–92 in water samples collected from the Mississippi River or from the mouths of large rivers that flow directly into the Mississippi (Goolsby and Battaglin, 1993). Thirty-two pesticides and pesticide degradation products that were detected in 5 percent or more of the nearly 600

Figure 41 *Atrazine Variations Through Time*



Atrazine Variations Through Time

Figure 41 Pronounced seasonal variations are typical of pesticide concentrations in the Mississippi River and its tributaries. Atrazine, the example portrayed in this figure, is more concentrated during late spring and early summer than during other parts of the year. Concentrations shown here are based on samples collected approximately weekly (more frequently during late spring and early summer, less frequently at other times). Runoff caused by rainstorms following the application of atrazine to cornfields early in the growing season flushes a portion of the atrazine into streams that eventually flow into the Mississippi River. Most other major herbicides show a seasonal pattern of runoff similar to that of atrazine. Data from two growing seasons, 1991 and 1992, are shown here. The differences in concentrations between 1991 and 1992 probably are caused by differences in the intensity and timing of rainfall. Pesticides will be transported in storm runoff as long as their residues remain on the soil or on plant surfaces. As the growing season progresses and wanes, concentrations of pesticides in storm runoff decrease to low levels. For a few weeks of 1991 and 1992, concentrations of atrazine, cyanazine, and (to a lesser extent) alachlor reached or exceeded maximum contaminant levels (MCLs) or health advisories (HAs). However, the average annual concentrations of these compounds were well below these health-based limits. Therefore, these pesticide concentrations did not violate the Safe Drinking Water Act or make the water unsuitable for public supply.

water samples collected during the study period are shown in figure 40. The pesticides detected most frequently and in highest concentrations were the most extensively used compounds with low K_{oc} values such as atrazine, alachlor, metolachlor, and cyanazine. In contrast, several other extensively used compounds such as butylate, EPTC, and trifluralin (fig. 39A) were detected infrequently and in low concentrations. The most persistent compounds were alachlor, atrazine, cyanazine, desethylatrazine (an atrazine degradation product), metolachlor, and simazine, all of which are herbicides. These herbicides were detected in low concentrations in more than 75 percent of the samples analyzed. Two herbicides, atrazine and metolachlor, were detected in more than 95 percent of the samples. Although numerous pesticides were detected in many samples, only three compounds, atrazine, alachlor, and cyanazine, exceeded MCLs or HAs in only a small percentage of samples. The average annual concentrations were far below MCLs or HAs. Atrazine and cyanazine concentrations in a few samples also exceeded the Canadian aquatic-life guidelines (compare concentrations shown in figure 40 with the guidelines listed in table 8).

For a period of several weeks during May through July, atrazine, cyanazine, and to a lesser extent alachlor concentrations in the Mississippi River main stem and in tributaries may exceed MCLs or HAs. However, because the annual average concentrations of these compounds are well below health-based limits, there is no violation of the Safe Drinking Water Act and the water would be considered suitable for public supply from the standpoint of pesticides.

Spatial Distribution of Pesticides in Water

The majority of all pesticides used in the Mississippi River Basin are applied in the upper part of the basin. Consequently, streams draining Illinois, Iowa, Indiana, eastern Nebraska, and southern Minnesota contribute the largest quantities of pesticides to the Mississippi River. As water flows downriver from the Minneapolis area, inflow from tributary streams results in large and often dramatic increases in pesticide concentrations during May through July, as illustrated in figure 44.

Mass Transport of Pesticides

Two major objectives of our Mississippi River study were to determine the predominant source areas for pesticides and to estimate the mass transport of these

Figure 42 *Herbicide Variations Through Time*

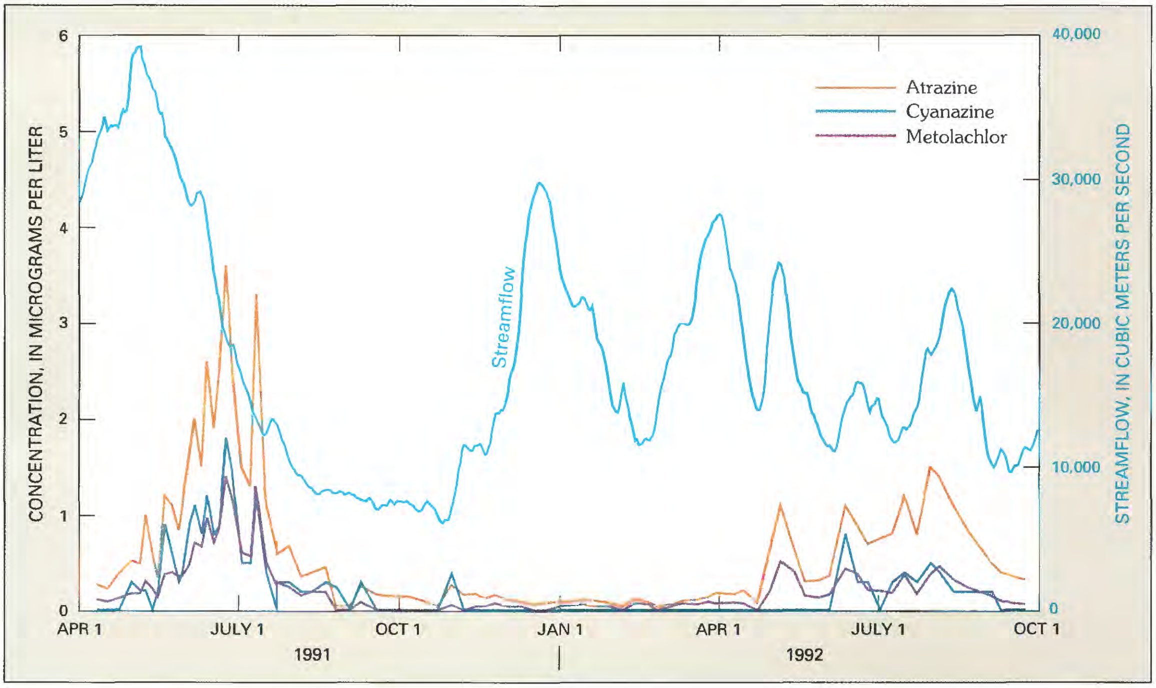


Figure 42 Temporal variations in the concentrations of herbicides in the Mississippi River reflect two factors: (1) the application of the herbicides on croplands, and (2) the rainfall and runoff events that follow the applications. This figure shows the concentrations of three herbicides measured in the Mississippi River at Baton Rouge, Louisiana, at weekly to biweekly intervals between April 1991 and September 1992. Plotted in the figure is the streamflow at Baton Rouge plus the flow diverted into the Atchafalaya River above Baton Rouge. The heavier rainfalls during the planting and post-planting periods in 1991 resulted in greater streamflows, more flushing of herbicides from the fields, and higher herbicide concentrations than in 1992.

chemicals from major tributaries into the Mississippi River and to the Gulf of Mexico for a 1-year period. The transport for each pesticide of interest was calculated for each day of the year using either measured or estimated daily pesticide concentrations and mean daily streamflow. Pesticide concentrations were estimated by linear interpolations for days on which no samples were collected. The estimated daily transports were then summed to obtain an estimate of annual transport. Mass-transport estimates were made in this manner for the six sites where approximately weekly samples were collected. The annual mass transport of pesticides to the Gulf of Mexico was estimated from concentrations measured at Baton Rouge, Louisiana, and streamflow at Baton Rouge plus the streamflow diverted from the Mississippi into the Atchafalaya River upstream from Baton Rouge (fig. 45). Loads of 21 major pesticides and degradation products transported by the Mississippi River at four locations and by three major tributaries during a 1-year period (April 1, 1991, through March 31, 1992) are given in table 9.

Iowa and Illinois are the predominant sources for most pesticides transported by the Mississippi River. The Upper Mississippi River Basin, excluding the Missouri River Basin, constitutes about 22 percent of the total Mississippi River drainage basin, but contributes about 40 percent of the atrazine, and 50 percent or more of many other pesticides transported by the Mississippi River (table 9). The area receives essentially all of the streamflow discharged from Iowa and Illinois, which contain the most intensive crop-production areas in the basin (fig. 38). These two States apparently also are the sources for much of the agricultural chemicals transported by the Mississippi River. The Ohio River Basin is the source of about one-half the butylate and most of the simazine transported by the Mississippi River (table 9), and the Missouri River Basin is the predominant source for trifluralin.

Although the annual mass transport appears to be large for several pesticides (table 9), it represents only a small fraction, generally less than 3 percent, of the pesticide mass applied annually to cropland in the basin. The mass of pesticides discharged from the Mississippi River Basin to the Gulf of Mexico during April 1991 through March 1992 expressed as a percentage of the annual mass applied to cropland was 0.2 percent for alachlor, 0.8 percent for metolachlor, 1.6 percent for atrazine and cyanazine, and 2.7 percent for simazine. A similar fraction of the mass of these pesticides applied in the Illinois, Ohio, and Missouri River Basins was discharged from these rivers. These percentages may be higher or lower in other years, depending on rainfall patterns.

Summary

Most streams throughout the Midwestern United States contain water with high concentrations of pesticides for several weeks to several months following the application of pesticides to farmlands. Concentrations generally are largest and may briefly exceed health-based limits for drinking water during runoff from the first storms after application. Concentrations decrease during later runoff events. More than 40 pesticides and pesticide degradation products were detected in the Mississippi River. Most of these were at concentrations less than 0.5 μg/L. Maximum concentrations during 1991–92 of the most extensively used herbicides such as alachlor, atrazine, cyanazine, and metolachlor ranged from 3 μg/L to about 6 μg/L in large rivers such as the Mississippi, Missouri, and Ohio, compared to 50 to more than 100 μg/L reported in previous studies of smaller tributaries. These high concentrations generally represent extreme conditions that do not persist past midsummer. The average annual concentrations of all pesticides measured in the Mississippi River are well below health-based limits and do not violate the Safe Drinking Water Act. Low concentrations (0.05 to 0.2 μg/L) of a few pesticides are detectable year-round in the Mississippi River Basin owing to storage and subsequent discharge from surface- and ground-water reservoirs. The total mass of pesticides discharged from the Mississippi River and its major tributaries from April 1991 through March 1992 represents a small fraction (from less than 0.1 to about 3 percent) of the amounts applied. About 40 percent of the atrazine mass and more than 50 percent of the mass of many other heavily used pesticides discharged to the Gulf of Mexico originate in the Upper Mississippi River Basin, above the confluence with the Missouri River. This area constitutes only about 22 percent of the drainage area of the Mississippi River Basin. Varying climatic conditions cause considerable variation in the maximum annual pesticide concentrations and in the annual loads. Wet years with intense rainfall shortly after application of pesticides tend to have the highest pesticide concentrations in streams and the highest loads.

Figure 43 *Atrazine at Vicksburg*

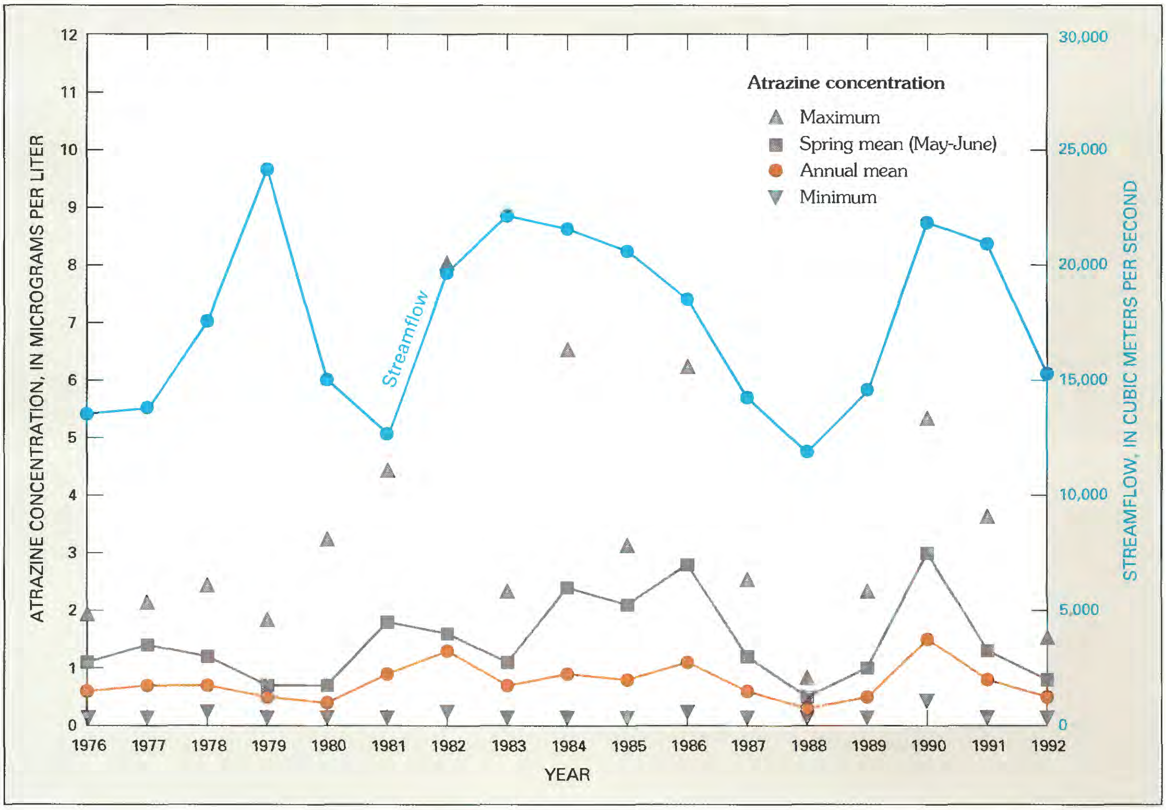


Figure 43 Long-term records on atrazine concentrations in the Lower Mississippi River at Vicksburg, Mississippi, are shown in this figure. Concentration data for 1976–90 were collected by Ciba Geigy (the manufacturer of atrazine), its contractors, and other chemical companies, and are based on 11–51 samples per year (Tierney, 1992). Concentration data for 1991–92 are those shown in figures 41 and 42 for the station at Baton Rouge (Coupe and others, 1995). Mean annual streamflows are those measured in the Mississippi River at Vicksburg, Mississippi. The minimum, mean, and maximum values of atrazine concentration show no apparent upward or downward trends during the 17 years portrayed here, but after the mid-1980s the mean and maximum concentrations do tend to parallel the year-to-year increases and decreases of streamflow.

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Table 9. Estimated loads of pesticides, in kilograms, transported by the Mississippi River and major tributaries, April 1991 through March 1992

[--, no load estimate]

Pesticide	Illinois River	Missouri River	Ohio River	Mississippi River above Missouri River[1]	Mississippi River at Thebes, Ill.[2]	Mississippi River below Ohio River[3]	Mississippi River at Baton Rouge, La.[6]
Alachlor	8,790	7,870	4,970	35,000	42,900	47,900	33,700
Atrazine	35,800	68,400	57,000	121,000	189,000	246,000	321,000
Desethylatrazine[4]	4,170	6,380	12,500	23,000	29,400	41,900	41,500
Desisopropylatrazine[4]	40	2,030	879	170	2,200	3,080	3,200
Atrazine sum[5]	40,000	76,800	70,400	144,000	221,000	291,000	365,700
Butylate	207	308	1,170	962	1,270	2,440	--
Carbaryl	7	9	481	89	98	579	--
Carbofuran	357	1,190	301	1,810	3,000	3,300	--
Chlorpyrifos	186	7	14	44	51	65	--
Cyanazine	19,800	31,300	13,400	81,700	113,000	126,000	127,000
Diazinon	289	80	103	213	293	396	--
Dieldrin	33	350	0	0	125	125	--
EPTC	516	105	130	826	931	1,060	--
Fonofos	112	49	12	387	436	448	--
Metolachlor	18,900	24,700	20,200	62,500	87,200	107,000	123,000
Metribuzin	600	1,420	545	3,090	4,510	5,060	6,810
Prometon	514	433	822	767	1,200	2,020	--
Propazine	6	78	0	44	122	122	--
Propachlor	30	171	0	0	64	64	--
Pendimethalin	8	51	14	257	308	322	--
Simazine	864	1,090	9,370	3,250	4,340	13,700	12,500
Trifluralin	48	248	101	158	406	507	--

[1] Calculated from load in Mississippi River at Thebes, Ill., minus load from Missouri River.

[2] Above confluence with Ohio River.

[3] Below confluence with Ohio River; calculated from loads in Mississippi River at Thebes, Ill., plus load from Ohio River.

[4] Atrazine metabolite.

[5] Atrazine plus metabolites.

[6] Approximate transport from Mississippi River Basin to Gulf of Mexico, includes diversion into Atchafalaya River but not the contributions from the Red River.

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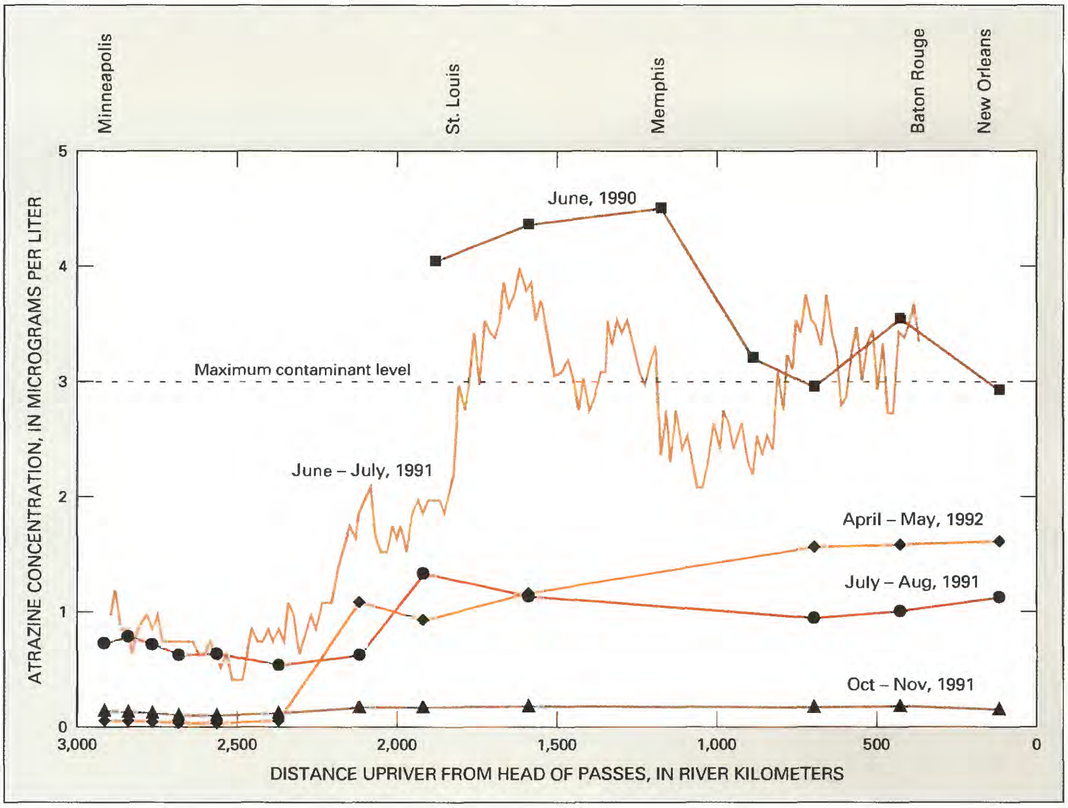
Figure 44 *Atrazine Along the River*



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Atrazine Along the River

Figure 44 Atrazine concentrations in the Mississippi River are consistently low for the first 600 kilometers below Minneapolis, and they increase rapidly downriver as the river collects water from tributaries that drain the Corn Belt. Shown here are measurements of atrazine in waters collected from the Mississippi River during five different sampling trips: the discrete points connected by straight-line segments represent samples collected in downstream sequences; the continuous line labeled June-July 1991 represents samples collected from the river, at 10-mile intervals, in upriver sequence. Highest concentrations were measured during the months immediately following the application of atrazine (June 1990, June-July 1991). Details are best shown in the data of June-July 1991, which represent the most intensive sampling: a doubling of atrazine concentrations between river kilometers 2250 and 2000, where the Rock, Cedar, and Des Moines Rivers deliver pesticides, including atrazine, from northern Iowa and Illinois; another significant increase below river kilometer 1900 as a result of inflows from the Illinois and Missouri Rivers; a decrease near kilometer 1530 where the Mississippi is diluted by inflow from the Ohio River. The variability in atrazine concentration between river kilometer 1530 and Baton Rouge probably results from short-term storm runoff pulses entering the Mississippi from the Missouri River and other major tributaries (Moody and Goolsby, 1993). These runoff pulses have high concentrations of pesticides and can produce water masses in the Mississippi River that are interspersed with water containing lower concentrations. This is analogous to turning on a point source of pesticide for a few days and then turning it off. This kind of spatial variability was also observed during another upriver transect (not shown in the figure) made in late May 1990, and to a lesser extent in upriver transects conducted in late September 1991 and late March 1992. Details of procedures for collecting and analyzing the samples and complete listings of the data represented in the figure are given by Goolsby (1995) and Pereira and others (1995).

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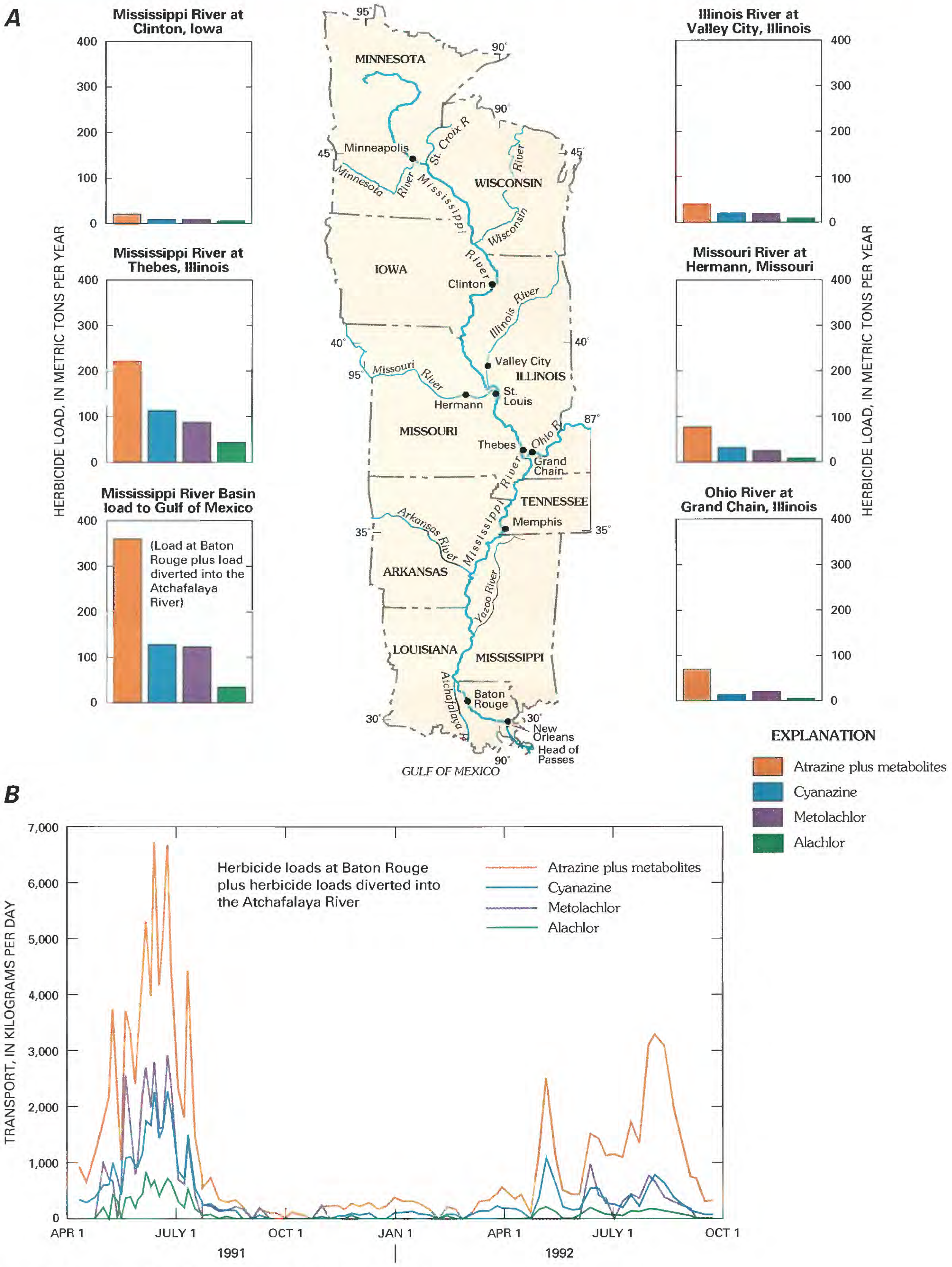
Figure 45 *Herbicide Transports*



Herbicide Transports

Figure 45 The four pesticides (all herbicides) transported in the largest quantities by the Mississippi River are atrazine (plus two of its metabolites, desethylatrazine and desisopropylatrazine), cyanazine, metolachlor, and alachlor.

A The loads of these four herbicides discharged to the Gulf of Mexico during the 1-year period from April 1, 1991, through March 31, 1992, ranged from 365,700 kg for atrazine and its metabolites to 33,700 kg for alachlor. This was a period of slightly greater than average streamflow, so these figures might represent herbicide transports somewhat greater than average. Most of the herbicides discharged into the Mississippi River originate in the Upper Mississippi, Missouri, and Ohio River Basins. Except for atrazine, there appear to be no significant inputs of most herbicides between the Ohio River confluence and Baton Rouge, a distance of about 1,160 river kilometers. This distance represents a traveltime in the river of about 10 days. The annual alachlor load in this reach decreased from 47,900 kg below the Ohio River confluence to 33,700 kg at Baton Rouge, a decrease of about 30 percent. This decrease is believed to be due primarily to degradation (and, possibly, volatilization) of alachlor in the Mississippi River.

B Temporal distributions of the rates at which the four major herbicides were transported by the Mississippi River to the Gulf of Mexico have been calculated here from the data on streamflow and concentrations, much of which was shown earlier in figure 42. For complete data, see Coupe and others (1995). Most of the herbicide transport during this period of study occurred during May and June, shortly after herbicide application. Maximum transport rates were about 6,500 kg per day for atrazine and two of its metabolites, about 3,000 kg per day for metolachlor, about 2,000 kg per day for cyanazine, and about 700 kg per day for alachlor. Other herbicides were transported at much lower rates. The rates of transport and total masses of these four herbicides transported were considerably lower in 1992 than in 1991, probably as the result of less intense rainfall and less flushing of herbicides from cropland in 1992.

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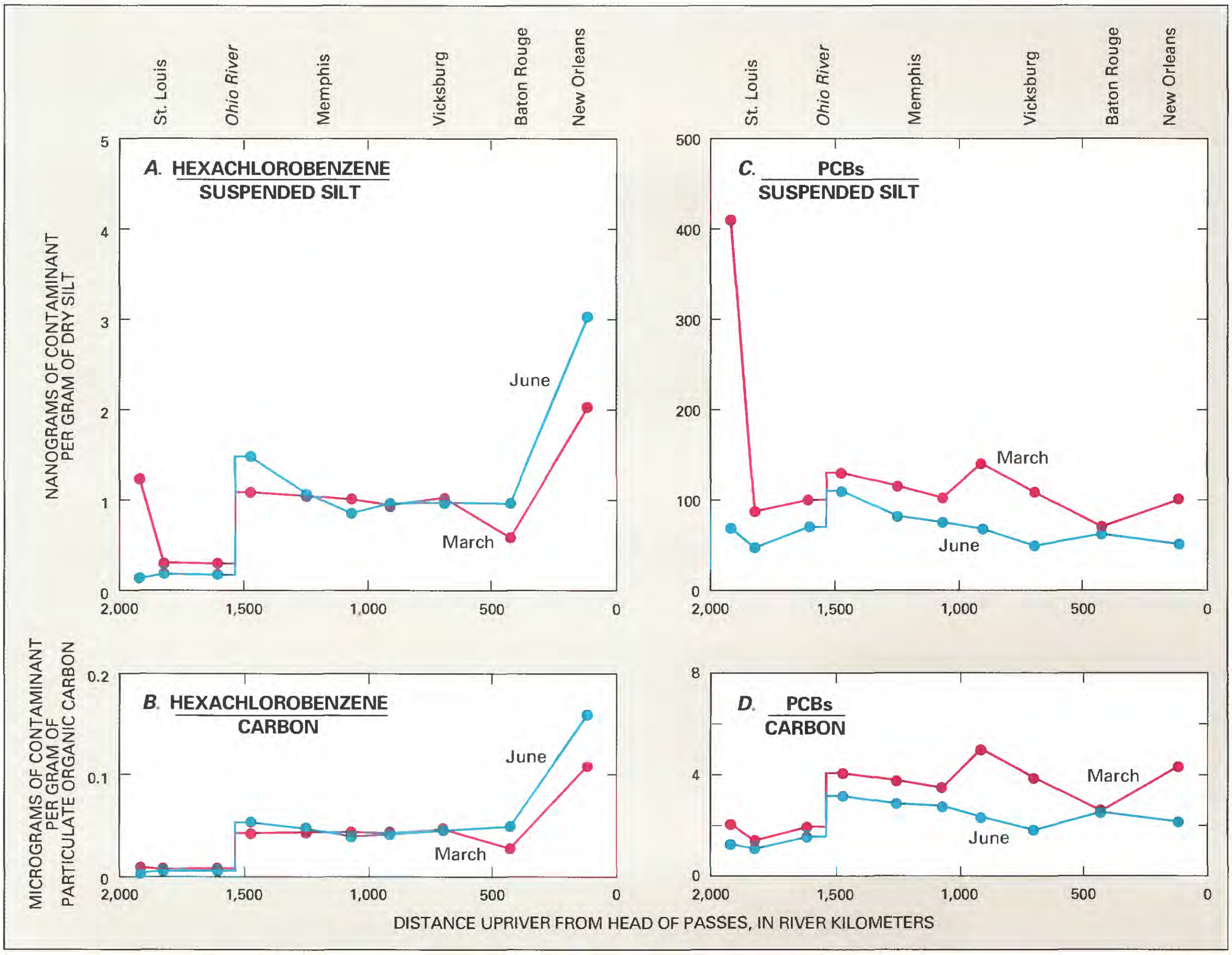
Figure 46 *Hexachlorobenzene and PCBs in Silts*



Polychlorinated Biphenyls and other Synthetic Organic Contaminants Associated with Sediments and Fish in the Mississippi River

Colleen E. Rostad, LaDonna M. Bishop, Geoffrey S. Ellis,
Thomas J. Leiker, Stephanie G. Monsterleet, and
Wilfred E. Pereira

Hexachlorobenzene and PCBs in Silts

Figure 46 Many of the sparingly soluble organic contaminants found in the Mississippi River, such as hexachlorobenzene and PCBs (polychlorinated biphenyls), are associated with the suspended sediments. Their distributions on the sediments in the river reflect the sources of the contaminants. Once they are in the river, many of these contaminants are most concentrated in the fractions of the sediment that contain the most organic carbon. Data shown here are for suspended silts collected from the river during downriver sampling cruises in March 1989 and June 1989. Total PCBs are defined here as the sum of the penta-, hexa-, hepta-, and octachlorinated biphenyl homologs. Complete data are tabulated in the report by Rostad, Bishop, and others (1995).

A Concentrations of hexachlorobenzene in the suspended silt of the Mississippi River main stem clearly show the two principal sources of this contaminant. The marked increases near river kilometer 1530 are due to the input from the Ohio River, which supplies many times more hexachlorobenzene than does the Upper Mississippi River. A further increase in hexachlorobenzene occurs as the Lower Mississippi River flows through Louisiana between St. Francisville (river kilometer 428) and Belle Chasse (river kilometer 117); this increase is probably related to the large number of halogenated hydrocarbon manufacturing industries along this part of the river between Baton Rouge and New Orleans.

B Organic carbon in the suspended sediment is a strong determinant in the adsorption of sparingly soluble organic contaminants like hexachlorobenzene. When the contaminant concentrations are normalized to organic carbon, as they are in this graph, some of the irregularities in the contaminant-silt relation are smoothed out. The suspended silt collected at river kilometer 1920 (Winfield, Missouri) during March 1989 contained a very high proportion of organic carbon and a high concentration of hexachlorobenzene for the silt of the Upper Mississippi River (fig. 46A). However, when the hexachlorobenzene concentration is expressed in relation to organic carbon, as it is here in figure 46B, the concentration is consistent with concentrations measured at other times and locations in the upper river.

C The concentrations of total PCBs in the suspended silt in the middle and lower reaches of the Mississippi River are less visibly related to specific sources than those of a contaminant like hexachlorobenzene. One reason for this is that the sources of PCBs have been more diverse and disseminated than those of hexachlorobenzene. Perhaps even more important is that in the nearly two decades since the disposal of PCBs into the river has been curtailed, the repeated deposition and resuspension of contaminated silts has resulted in a partial homogenization of PCB concentrations along the length of the river and a blurring of some of the more abrupt changes in distribution that indicated specific sources.

D PCBs also are strongly associated with the organic carbon in the suspended sediments of the Mississippi River. By expressing the PCB concentrations in relation to organic carbon, this graph eliminates the seemingly anomalous concentration of PCBs measured at kilometer 1920 during March 1989 (fig. 46C) and emphasizes the marked increase in PCB concentration associated with the influx of suspended sediment from the Ohio River.

Introduction

Suspended material in the Mississippi River transports the following sparingly soluble synthetic chlorinated pesticides and industrial chemicals: aldrin, chlorthalonil, chlordane, DCPA, DDT, DDE, DDD, dieldrin, endrin, heptachlor, heptachlor epoxide, hexachlorobenzene, lindane, methoxychlor, mirex, pentachloroanisole, pentachlorobenzene, polychlorinated biphenyls (PCBs), and trifluralin. Although our analyses detected all of these compounds, the discussion here is focused on four, whose sources are industrial, agricultural, or residential. The PCBs are a very stable family of industrial chemicals previously used primarily in urban and industrial areas in electrical transformers and capacitors, heat-transfer and hydraulic fluids, lubricants, plasticizers, and many other products. Chlordane or chlordan, sold under many names such as Toxichlor, Chlortox, Dowchlor, and Octachlor, is a broad-spectrum insecticide formerly used on agricultural land for control of corn rootworm and on residential land for control of household and lawn pests. DCPA, also called chlorthal, is sold as Dacthal or Dacthalor for nonsystemic pre-emergence control of grasses for both agricultural (radishes, onions, broccoli and cauliflower) and residential uses. Of these, only DCPA is currently in use. Hexachlorobenzene, sometimes called HCB or perchlorobenzene, is marketed as Anticarie, Bent-cure, Bent-no-more, and No Bunt (Royal Society of Chemistry, 1991). It is a selective fungicide formerly used on wheat seed but is also a common starting material or by-product used in the chemical industry. Some of these compounds were first introduced into the environment as long as 40 years ago, and, although the use of PCBs and chlordane has been banned in the United States, they still persist in the environment today because they are not easily degraded. These compounds were found in sediments from most of the sites we sampled.

Many toxic chemicals, including most heavy metals and the majority of the U.S. Environmental Protection Agency (USEPA) Priority Pollutants, are primarily associated with sediments (Ongley and others, 1992). These sparingly soluble compounds may be transported in the environment by direct surface runoff or by resuspension of contaminated bed sediments in rivers. Because they are not water soluble, they associate with sediment or move into organisms and thus enter into food chains. They can bioaccumulate; for example, after a fish eats a contaminated insect, the contaminants are not degraded or metabolized but instead are retained by the fat in the fish tissue. The fish eats many insects and continues to accumulate the contaminants. As additional contaminated insects are consumed, higher concentrations build up in the fish tissue. Biomagnification takes place, when each level of the food chain contains higher concentrations than the level below it. If a bird eats this highly contaminated fish, the bird may also retain the contaminant in its tissue. If a human eats the fish, the contaminant can also accumulate in human tissue.

PCBs, chlordane, DCPA, and

hexachlorobenzene usually are detected in association with the suspended material in the river but not in the water itself. This behavior is expressed numerically as "partition coefficients," which for these compounds are large. The partition coefficient is a laboratory-determined ratio of the amount of a compound associated with the sediment to the amount associated with the aqueous phase. It is characteristic of each chemical and ranges from 1 to 10,000,000. This ratio allows prediction of how the compound behaves in the environment, because it indicates whether a compound will be found in the aqueous phase or the sediment phase. A small partition-coefficient value means the compound will have an affinity for the aqueous phase, not the sediment phase, and will most likely remain dissolved under most conditions. A large value means the compound will instead associate with an organic phase, like the organic carbon of sediments, or in the fat of fish tissue. Compounds with large partition coefficients are more likely to be found associated with available organic matter, whether it is bed sediment, suspended sediment, fish tissue, or aquatic insects.

Synthetic compounds enter the river from point and nonpoint sources. Point sources are discrete, such as manufacturing plants or accidental spills. Although there can be many point sources, each has an individual effect on the environment at that point as well as downstream. Nonpoint sources are more general, reflecting overall widespread usage of chemicals in the environment, such as atrazine from farmlands. PCBs, which probably came from industrial point sources in the past, are now widely distributed in the environment, and as a result, are now considered to be from nonpoint sources. Chlordane was used extensively on corn and, more recently, on lawns and in residences for termite control before it was banned by USEPA. DCPA use is currently residential and agricultural. Both chlordane and DCPA have been so widely used that their sources are now considered nonpoint. Hexachlorobenzene, however, has specific industrial uses as well as agricultural uses, and therefore can come from point sources as well as nonpoint sources.

The toxicity of these compounds is quite high to some organisms. Most of the time, however, only trace concentrations of these compounds are present in environmental waters. The precise health effects of such trace concentrations are often subtle and, therefore, difficult to pinpoint in the environment or the general human population. For example, chlordane is classified by USEPA as a probable human carcinogen (U.S. Environmental Protection Agency, 1986). Because chlordane is present in trace amounts in food and water (Cochrane and others, 1975), and because humans can barely metabolize it, the amount present in human fatty tissue has been found to increase with age. The main target organ for carcinogenic effect from chlordane is the liver, but other organs of the body are also susceptible to its effects. In a 1973–74 study conducted in Mississippi and Arkansas, 54 percent of human breast milk samples contained chlordane residues at trace levels or higher (Strassman and Kutz, 1977). At large concentrations, chlordane is known to cause blood anemia, leukemia, and problems of the central nervous system.

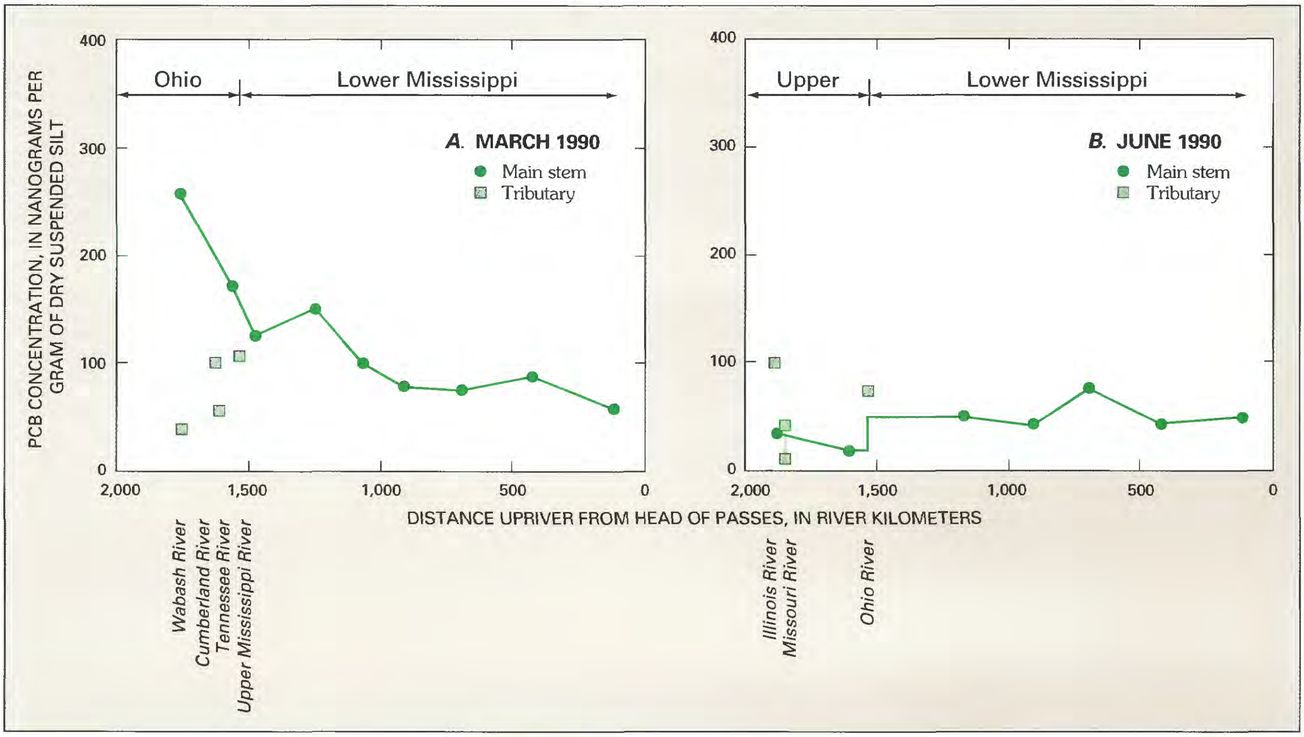
Contaminants Associated with Suspended Silt

PCBs were detected in almost every silt sample we analyzed. They were most prevalent in the Ohio River, which is the principal source of PCBs to the Lower Mississippi River (figs. 46C, 46D). The suspended sediments of other tributaries—the Missouri, White, Arkansas, and Yazoo Rivers—contain significantly smaller concentrations of PCBs than those of the Ohio. Within the Upper Mississippi River, PCB concentrations on suspended silts are greatest between Minneapolis-St. Paul and Lake Pepin, but they decrease markedly downriver because Lake Pepin acts as a trap for suspended sediment and its associated contaminants.

Chlordane also was detected in almost every silt sample we analyzed from the Mississippi River and its tributaries. In general, its distribution parallels that of PCBs throughout the river system: highest concentrations in the Upper Mississippi are found near Lake Pepin; largest inputs to the Lower Mississippi come from the Ohio River. Local exceptions do occur, such as the elevated concentrations of chlordane detected near Keokuk, Iowa, during July and October 1991. The higher concentrations of chlordane associated with the silt at this site also are reflected in the fish, for which the State of Missouri has issued a fish-consumption advisory, (Missouri Department of Health, 1990).

Total chlordane in this study is the sum of *cis*-chlordane, *trans*-chlordane, and *trans*-nonachlor. Of the three components, *trans*-nonachlor is the most resistant to environmental degradation. The ratio of *cis*- and *trans*-chlordane to *trans*-nonachlor is an indicator of

Figure 47 *PCBs from Ohio and Missouri Rivers*



the proportion of recently released chlordane to "weathered" chlordane. It does not, however, provide a specific time estimate of the weathering period involved. Weathered chlordane was associated with the silt during sample periods of spring runoff (March 1989 and 1990), which indicated the source of the chlordane to be resuspension of bed sediment or runoff of previously contaminated sediment rather than more recent environmental inputs of chlordane.

DCPA also is ubiquitous on the suspended silts of the Mississippi River and its principal tributaries. Concentrations of DCPA on silts usually do not vary widely from one part of the river to another, which indicates that DCPA comes from widely dispersed nonpoint sources rather than from specific regions or tributaries.

Hexachlorobenzene, in contrast, has more specific sources in the Mississippi River Basin. Suspended silts of the Ohio River carry concentrations of hexachlorobenzene that are consistently greater than those of the Upper Mississippi and its tributaries (Illinois and Missouri Rivers) by factors of 5 or more. The concentration of hexachlorobenzene increases significantly between St. Francisville (above Baton Rouge) and Belle Chasse (below New Orleans), Louisiana, as the river flows through an industrial corridor.

Contaminants Associated with Suspended Colloid

Colloids are very small organic or mineral particles that can barely be seen by the naked eye (Rees and Ranville, 1989). They make the water slightly turbid and do not settle out with time. Recent studies of contaminant solubility in natural

PCBs from Ohio and Missouri Rivers

Figure 47 Concentrations of organic contaminants on suspended sediment in the Mississippi River are variable, depending on which major tributary is contributing the most sediment at the time of sampling. Shown here are concentrations of total PCBs on suspended silts in the Lower Mississippi River during two periods of 1990—one when most of the silt in the main stem was being supplied by the Ohio River, and another when most was being supplied by the Missouri River. Complete data are tabulated in the report by Rostad, Bishop, and others (1995).

A During March 1990, most of the silt being transported in the Mississippi River system was in or from the Ohio River, and PCB concentrations were accordingly high. Data in this graph extend from Uniontown, Kentucky, on the Ohio River, down the Ohio to its confluence with the Mississippi River, and down the Mississippi to the Gulf of Mexico. That is, the uppermost 400 kilometers on the graph represent the lowermost 400 km of the Ohio River, and the Upper Mississippi is represented as a tributary to the Ohio and Lower Mississippi Rivers. Concentrations of total PCBs on the suspended silts were greatest in the Ohio River. All the major tributaries that joined the Ohio (Wabash, Cumberland, Tennessee, and Upper Mississippi Rivers) transported silts whose PCB concentrations were less than those in the Ohio River, which drains a more industrialized area.

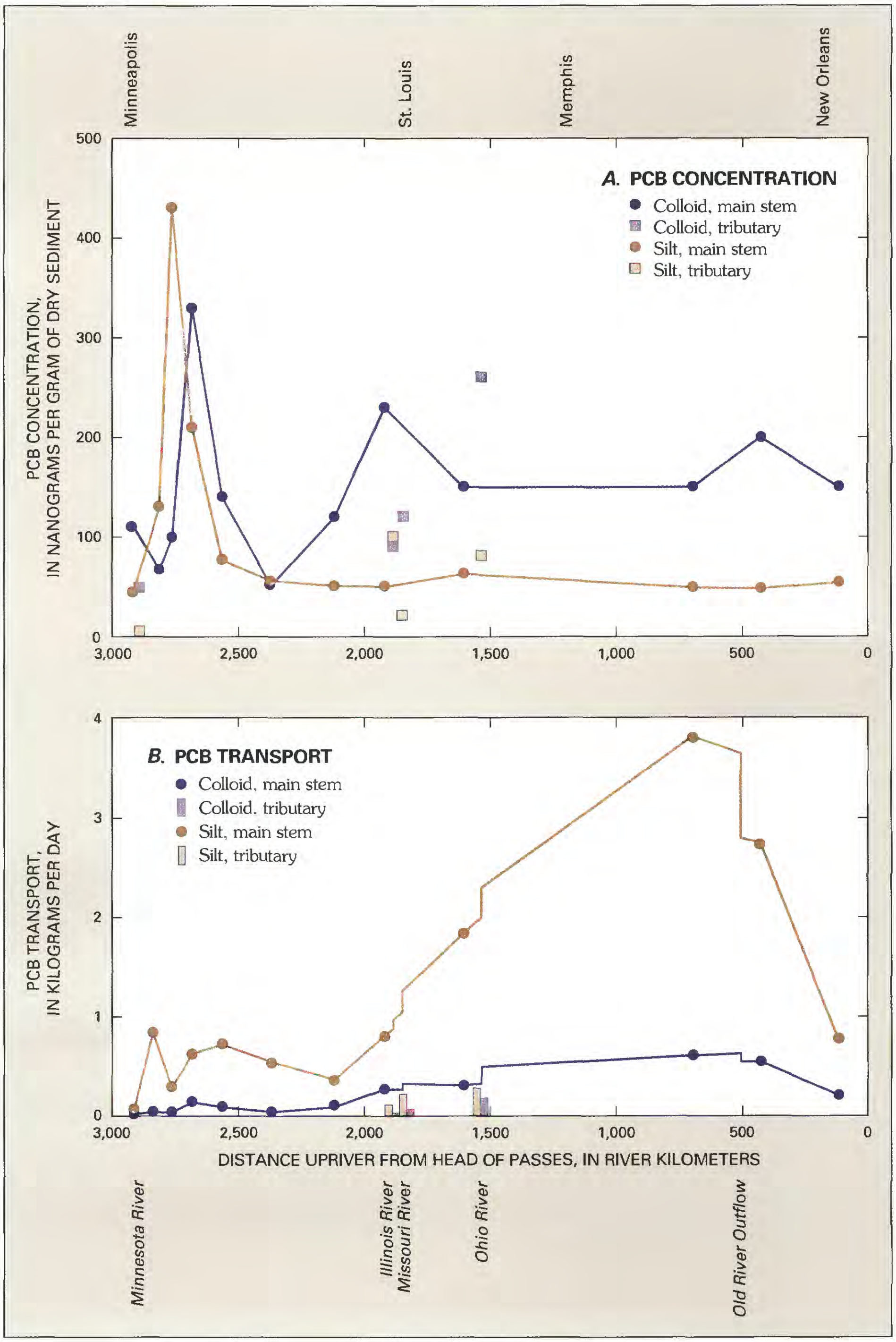
B During June 1990, most of the silt being transported in the Mississippi River was coming from the Missouri River, and PCB concentrations were accordingly lower than they had been during March. Data in the graph show PCB concentrations in the main-stem Mississippi River from Grafton, Illinois, to below New Orleans, Louisiana. PCB concentrations on silts were greater in the tributary Illinois and Ohio Rivers than in the main stem. Although most of the silt was coming from the Missouri River, no silt sample was taken at the time from the Missouri River itself. The probable concentration range of 10–40 nanograms per gram (ng/g) shown in the graph for PCBs in the Missouri River was inferred from the five other measurements that were made between 1988 and 1991 on suspended silts from the Missouri. Of the major tributaries to the Mississippi River that were sampled from 1988 through 1992, the Missouri River consistently supplied suspended silts having the smallest concentration of PCBs.

waters have found higher concentrations in the aqueous phase than thought possible. These findings were attributed to the possible presence of colloidal-sized particles (Baker and others, 1986). Separation of colloids from the aqueous phase is difficult and very little is known about their composition and behavior. Enough colloidal material was isolated during the July and October 1991 cruises for analysis of specific organic contaminants. Colloids in the Mississippi River average about 10 percent by weight of the total suspended material. Although the concentration of silt varies, the concentration of colloid seems to be fairly consistent.

Most toxic compounds travel in association with organic carbon, and the attribute of colloids that makes them especially important in the transport of pollutants is their high content of organic carbon. The colloid sampled in the Mississippi River averaged 15 percent organic carbon, which was substantially higher than that of the silt (3 percent). Colloidal material from the Upper Mississippi River was higher in organic carbon content than that from the Lower Mississippi River.

Colloid particles do not settle. Once a contaminant is adsorbed to a colloidal particle, its transport is probably consistent along the length of the river system. Silt transport, however, varies greatly in response to the variations in velocity, turbulence, and discharge of the river. The amount of contaminants transported by the colloids should be consistent, whereas the amount transported by the silt may vary widely.

Figure 48 *PCBs in Silts and Colloids*



PCBs in Silts and Colloids

Figure 48 Large proportions of the organic contaminants are associated with the colloidal fraction of the sediments suspended in the Mississippi River. "Colloid" was defined operationally in this study as the suspended matter that passed through the ultracentrifuge but was removed by the ultrafilter (see the chapter on "Sampling the Big Rivers"). In effect, the boundary between "colloid" and "silt" was about 0.1 micrometer, or one ten-thousandth of a millimeter. Data shown in the figure are from samples collected in the Mississippi River and four major tributaries during the downriver sampling cruise of July-August 1991. Complete data are tabulated in the report by Rostad, Monsterleet, and others (1995).

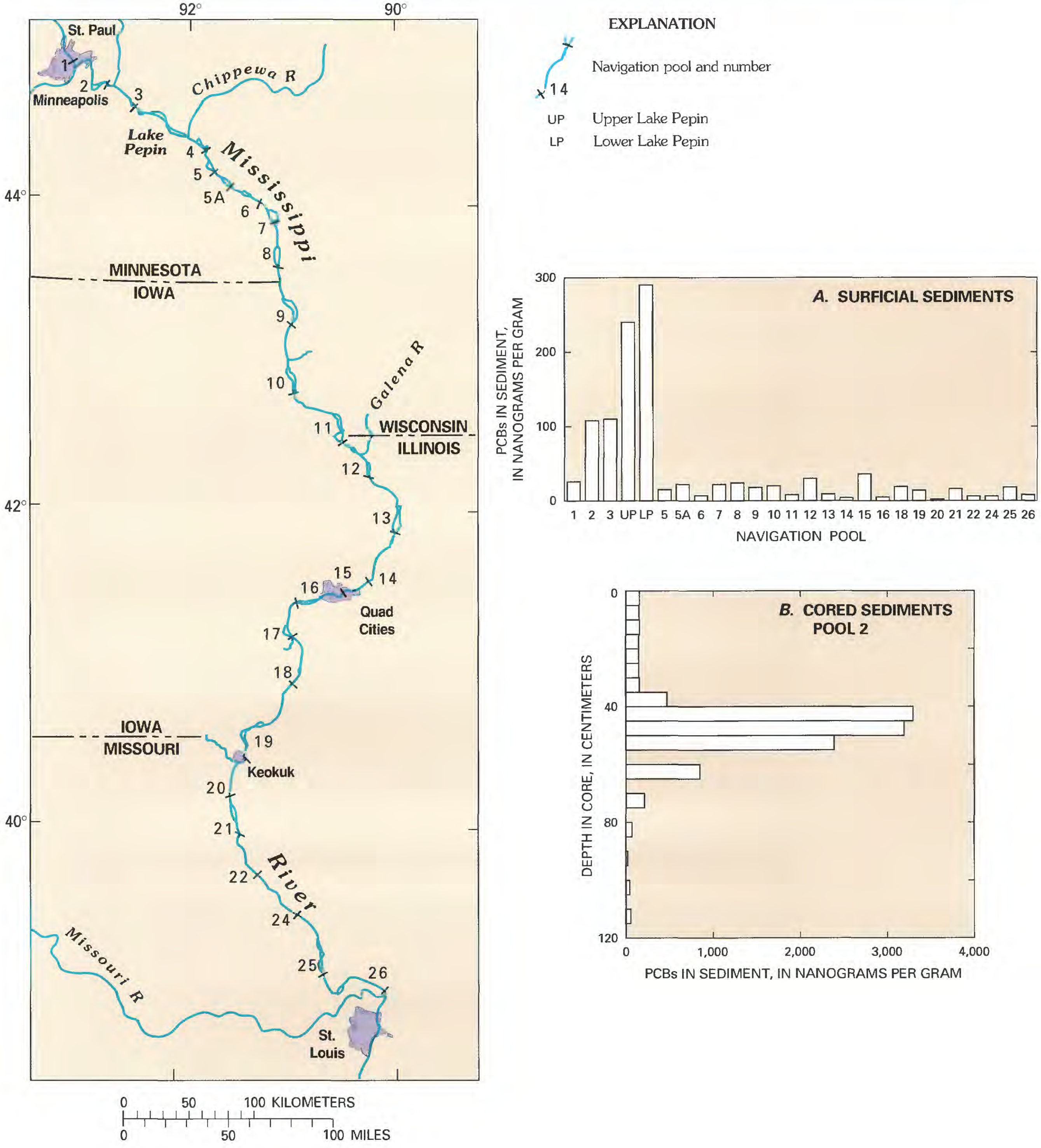
A In suspended sediments of the Mississippi River, concentrations of total PCBs usually are greater for colloids than for silts—not only because the colloidal material has more exposed surface area onto which PCBs can be adsorbed, but because colloids usually contain larger proportions of organic carbon. Data in the graph show that PCB concentrations are greatest in the uppermost Mississippi River for both the silt and colloid. Throughout most of the river system and the major tributaries, however, concentrations for the colloids are consistently greater than those for the silts.

B In terms of the total loads of PCBs transported by the Mississippi River, silt transport is more important than colloidal transport, simply because there is much more silt than colloid in suspension in the river. Transports shown in the graph are computed by multiplying the concentrations shown in figure 48A by the concentrations of silt and colloid in suspension and the discharge of the water. Even though concentrations of PCBs in colloids may exceed those in silts by factors of 2 or 3, the quantities of silt in suspension usually exceed those of colloids in suspension by factors near 10. Therefore, the total quantities of PCBs transported down the Mississippi River by silts are usually 3 to 5 times greater than those transported by colloids.

Contaminants Associated with Fish

Fish-consumption advisories have been issued at many sites along the Mississippi River, especially for carp and channel catfish. Most of these warnings are based on high concentrations in the fish of the ubiquitous compounds that are also found associated with the suspended material: PCBs, chlordane, DDT, and dieldrin. According to the U.S. Fish and Wildlife Service, concentrations of PCBs and chlordane in the fish in the Mississippi River remained relatively constant from 1976 to 1981 (Schmitt and others, 1983, 1985). The PCBs were most concentrated in fish in the Mississippi River near Pepin, Wisconsin, and in the Ohio River. Chlordane residues in fish were greatest in the Ohio River and in the Mississippi River at Cape Girardeau, Missouri. Highest hexachlorobenzene concentrations were in fish from the Mississippi River at Luling, Louisiana. DCPA concentrations in fish declined slightly from 1976 to 1981. A study by the Tennessee Department of Health and Environment that included more than 500 km of the Mississippi River upstream and downstream from Memphis showed how, in addition to the consistent background of these compounds, concentrations in fish can sharply increase near more heavily contaminated areas (Collins and others, 1989). Local studies have found that most severe cases of fish contamination occur near large urban areas (Iowa Department of Natural Resources, 1992).

Figure 49 *PCBs in Bed Sediments*



PCBs in Bed Sediments

Figure 49 Concentrations of PCBs stored in the bed sediments in the navigation pools of the Upper Mississippi River vary from place to place and according to the times at which the sediments were deposited.

A In the surficial bed sediments (that is, the sediments no more than 10 cm below the bottoms of the pools), the concentrations of total PCBs are large below Minneapolis-St. Paul, reach their greatest values in Lake Pepin, and are significantly smaller in the pools downriver of Lake Pepin. Data in the graph are from composite samples that were collected during 1991–92 at 15–20 locations in the lower reaches of each navigation pool and combined into a single sample (one per pool) for the analysis of total PCBs. Locations of the navigation pools are shown in the map on the left side of the figure. "UP" and "LP" in the graph denote Upper and Lower Lake Pepin. Data are tabulated in the report by Iverson and others (1995). Lake Pepin is the only large natural lake on the Mississippi River main stem below Minneapolis-St. Paul, and it apparently functions as the principal repository of many of the sediment-associated contaminants discharged from the metropolitan area. Furthermore, the high concentrations of organic carbon in this region of the river (see fig. 29D) probably increase the attraction between PCBs and the local sediments.

B The history of PCB contamination in the Upper Mississippi River is recorded in the sediments that have been deposited and stored in the navigation pools. Shown in the graph are the concentrations of total PCBs in a core taken in March 1989 from the bed sediments in a shallow backwater in the lower end of Pool 2, a few miles downriver from Minneapolis-St. Paul. Data were provided by Dan Helwig of the Minnesota Pollution Control Agency, Water Quality Division. Very high PCB concentrations of 2,000–3,000 nanograms per gram (ng/g) are found in the sediments deposited when large quantities of PCBs were allowed to enter the river, probably during the 1950s and 1960s. Following the cessation of the manufacture of PCBs, and the passage of State and Federal regulations restricting their use and disposal during the 1970s, concentrations of PCBs on sediments decreased markedly. The uppermost 35 cm of the core consisted of sediments in which concentrations consistently averaged about 150 ng/g. Because of the proximity to the Twin Cities, even these more recent PCB concentrations are greater than those in sediments stored farther downriver.

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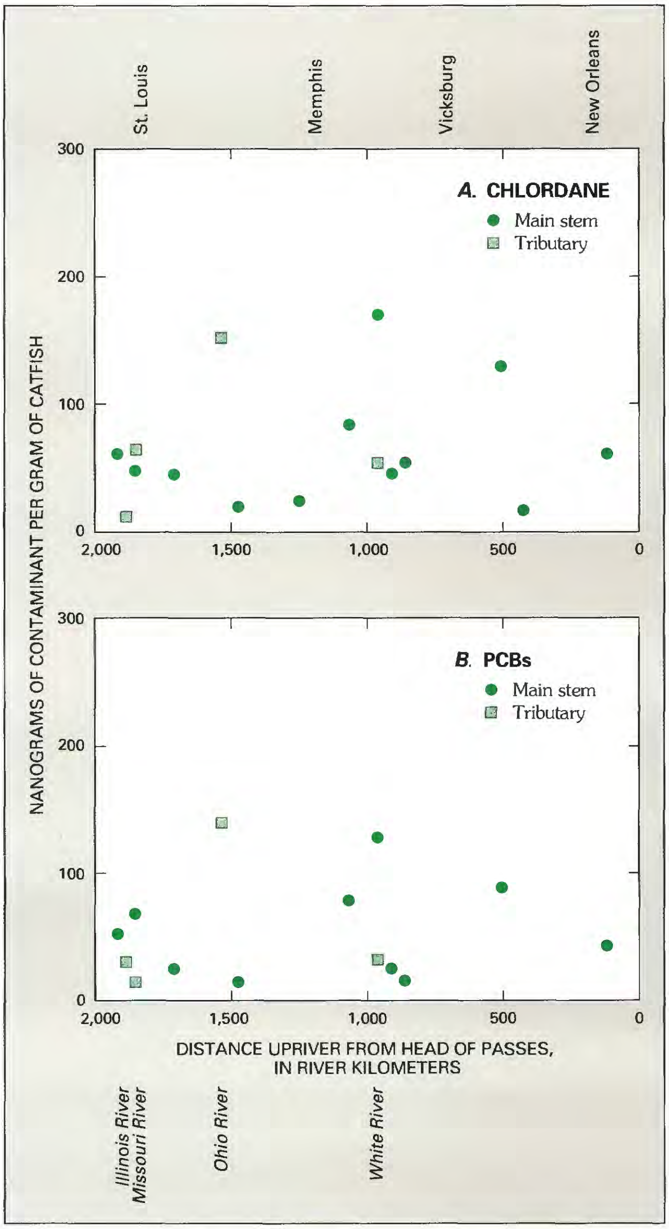
Figure 50 *Chlordane and PCBs in Catfish*



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Chlordane and PCBs in Catfish

Figure 50 Although banned for years, many halogenated organic contaminants persist in rivers and are ingested or absorbed by fish. Shown in the graphs are the concentrations of chlordane and PCBs in catfish taken from the Mississippi River and four of its tributaries during July-August 1987. One to four fish caught by hook and line at each location were homogenized in a blender and analyzed for PCBs and chlordane, as well as for other compounds such as hexachlorobenzene, DCPA, and DDT and its degradation products. Complete data are tabulated in the report by Leiker and others (1991).

A Chlordane is especially concentrated in catfish. Concentrations of chlordane shown here are substantially greater than those on the suspended sediment in the Mississippi River, which are almost always less than 10 (often less than 5) nanograms of chlordane per gram of suspended silt. Chlordane is especially lipophilic—that is, especially soluble in the fatty tissues of the fish—and difficult to metabolize. The action level for chlordane of 300 nanograms per gram, specified by the U.S. Food and Drug Administration (USFDA, 1986) corresponds to the top of the graph.

B PCB concentrations in catfish in the Mississippi River are comparable to those on suspended sediment. Although the "total" PCB shown here refers to the sum of the tetra-, penta-, hexa-, and heptachlorobiphenyls, this total is comparable to that of the penta-, hexa-, hepta-, and octachlorobiphenyls portrayed in the other figures of this chapter. The action level for PCBs of 2,000 nanograms per gram, specified by USFDA (1986), is well above the range of values shown here.

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Figure 51 *Fate of Contaminants in the River*

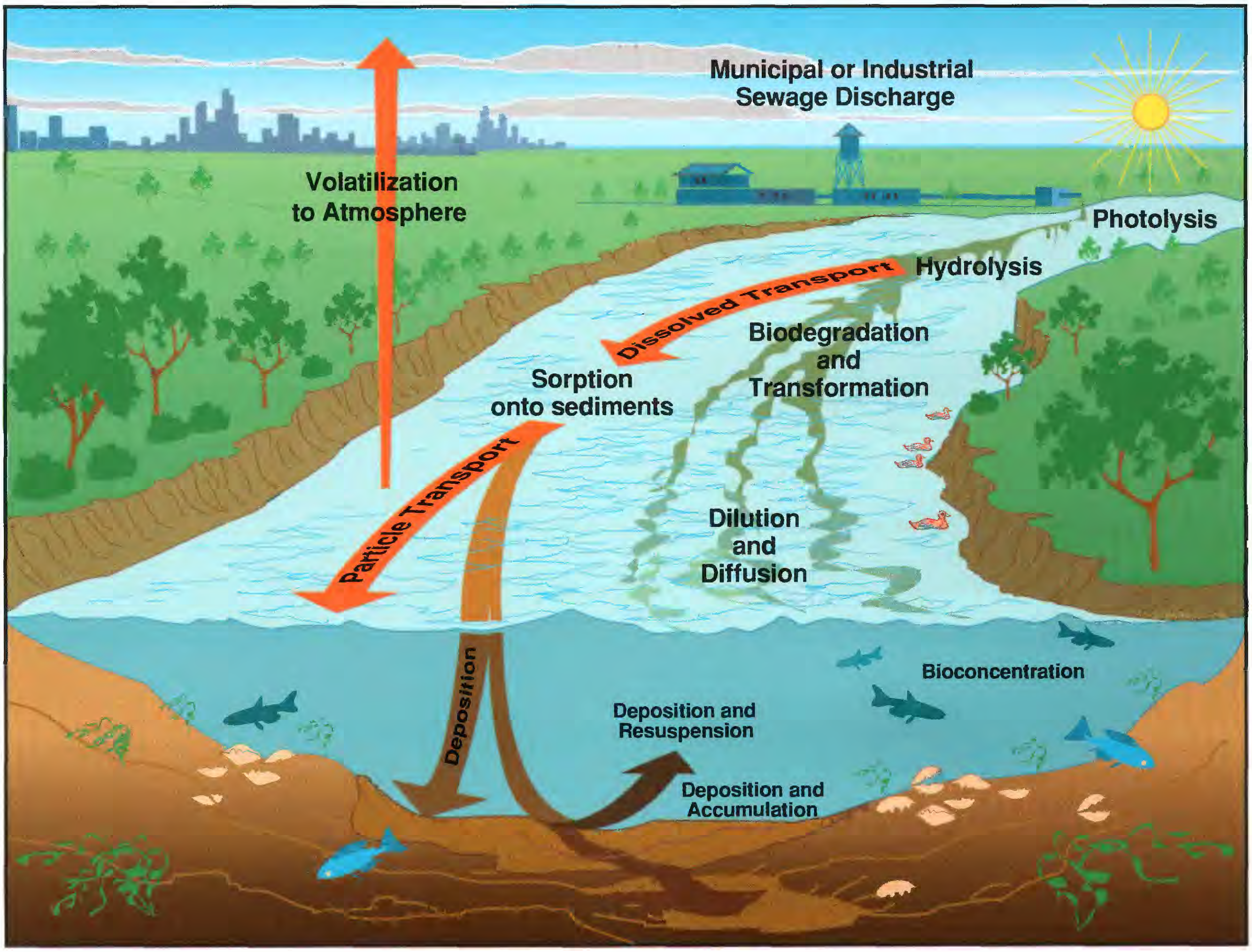


Figure 51 The most significant factors controlling the concentrations of organic contaminants in rivers are the physical processes of dispersion and dilution. Within this physical framework, the most significant chemical and biological processes controlling the fate of organic contaminants in the Mississippi River are (1) sorption to the sediment and removal by deposition, (2) desorption and diffusion of contaminants from bed sediments back into the water, (3) biological transformation to intermediate compounds, or biodegradation for complete removal, (4) volatilization to the atmosphere, (5) bioconcentration and magnification in the food chain, (6) photolysis, or the breakdown of contaminants under the influence of sunlight, and (7) hydrolysis, or the decomposition of contaminants by taking up the elements of water. Organic compounds of the type called "hydrophobic" (meaning that they prefer being sorbed onto sediment or organic particles to being dissolved in water) can be adsorbed onto sediments in concentrations that are a thousand to a million times greater than in the associated water. Once they are sorbed, the contaminants can be deposited and eventually become buried as sediments continue to accumulate. Buried contaminants can be remobilized, however, by resuspension of the sediments. Likewise, the sedimentary organic matter

may decompose, reintroducing its sorbed contaminants to the river by desorption and diffusion of organic colloids. If the contaminants are sorbed onto the sediments in high concentrations, they can adversely affect bottom-dwelling organisms. The tendency of a contaminant to sorb onto the sediment is frequently indicative of its capacity to bioconcentrate and become magnified in the food chain.

Many organic contaminants are biodegraded in rivers. Readily degradable compounds may have a biodegradation half-life (time for one-half of the mass of a compound to be removed) in a river environment of less than 1 day, depending on factors such as temperature, population of bacteria, availability of oxygen, and availability of nutrients. Other organic contaminants are resistant to biodegradation and have half-lives on the order of years. Compounds that are rapidly biodegraded under aerobic conditions, such as those found in a flowing stream, may persist under the anaerobic conditions that exist in buried sediments.

Some organic contaminants are volatile, and the major pathway for their removal from water is transfer to the atmosphere. The rate of volatilization is a function of the vapor pressure and water solubility of the compound, water temperature, and amount of turbulence in the water. A typical half-life for volatile organic compounds is on the order of a few hours; thus, even high concentrations can be rapidly attenuated in river systems.

All these processes—sorption, biodegradation, and volatilization, as well as photolysis and hydrolysis—interact in complex ways in the natural environment. For example, biotransformations can increase the solubility of a hydrophobic organic contaminant, which results in less sorption and greater mobility in the river. The Mississippi River is dynamic, and the distribution of contaminants between air, water, sediment, and organisms is continually changing with variations in the chemical, hydrological, and climatic regimes. The transportation of sediment-bound contaminants, for example, is episodic; most of the transport occurs during periods of high flow and bed scouring. Instream biodegradation rates usually decrease at lower temperatures. Ice cover during cold weather decreases the importance of volatilization as a removal pathway. High concentrations of dissolved organic matter can affect sorption, biodegradation, and volatilization of organic contaminants.

Introduction

The Mississippi River receives a variety of organic wastes, some of which are detrimental to human health and aquatic organisms. Urban areas, farms, factories, and individual households all contribute to contamination of the Mississippi River by organic compounds. This contamination is important because about 70 cities rely on the Mississippi River as a source of drinking water. Considerable gains have been made in the last two decades in controlling point-source contamination, but control of nonpoint-source contamination has been more difficult.

Among the topics that are discussed in this chapter and its figures are (1) a comparison of the present-day water quality of the river with historical trends, (2) the environmental processes controlling the occurrence and fate of organic contaminants, (3) the distributions and concentrations of organic contaminants in the water and sediments along the entire length of the river, and (4) the seasonal variability of some of the contamination patterns. Organic contaminants in the Mississippi River were assessed by collecting water and sediment samples between Minneapolis-St. Paul, Minnesota, and New Orleans, Louisiana, during 10 sampling cruises conducted in 1987–92, and analyzing the samples for the organic contaminants and indicator compounds listed in table 10.

Trends in Water Quality: A Historical Perspective

The relation between water pollution and public health has been recognized since the Colonial period, and increasing efforts have been made during the last century in the field of water pollution control. The earliest concerns with water pollution were about transmission of pathogenic diseases, such as typhoid, and obstruction of waterways by refuse from domestic and commercial sources. Anecdotal evidence from early reports indicates that development of metropolitan areas along the Mississippi River and its tributaries during the 1800s and early 1900s had a negative effect on water quality. The status of the Mississippi River at Minneapolis-St. Paul is illustrated by the following quotations:

"In 1888, the Engineers were called to remove a bar forming near the St. Paul waterfront. Dredging discovered that this bar was formed entirely of garbage dumped into the river by St. Paul. This area of the river had been shoaling for several years; the Corps was called in only when the smell became so objectionable that private citizens obtained an injunction against the governments of Minneapolis and St. Paul. Minneapolis dumped 500 tons of garbage a day just below the Falls of St. Anthony, and St. Paul added even more than that." (Tweet, 1984, p. 125–126.)

"During the months of low flows recorded for June, July, and August (1926), the pool above the High Dam was in a septic condition with the ebullition of large quantities of gas at the surface. On many occasions the surface of the pool was covered with sewage sleek, the oily floating substances contained in sewage, and was highly discolored for a considerable distance below the sewer outlets. Odors were noticeable at times, but usually in the vicinity of the larger sewer outlets. Below the High Dam septic conditions also prevailed in the back water pools during the summer." (Wisconsin State Board of Health, 1927, p. 310).

Gross contamination problems like these were gradually eliminated during the mid-1900s, but less obvious problems caused the quality of the Mississippi River to decline as population centers continued to grow. After World War II, the synthetic-organic chemical industry rapidly expanded and thousands of new chemicals eventually made their way into natural waters. Beginning about 1950, investigations into the occurrence of organic chemicals indicated that the Mississippi River had been significantly degraded by organic contaminants. Since the passing of pollution-control laws during the early 1970s, many of the obvious and readily correctable sources of contamination from industrial and municipal wastewater have been eliminated or diminished. Improvements in sewage-treatment plants have improved the water quality even though the population has continued to increase.

Municipal-and Industrial-Derived Wastewater: A Perspective on Today

Municipal wastewater is the aggregate of all water used and disposed of in a community. The mean per capita domestic wastewater flow rate for the United States is 200–500 liters per person per day. The synthetic-organic chemical composition of municipal wastewater is a function of the various products consumed by individual households and the

Table 10. Organic compounds measured to evaluate wastewater contamination of the Mississippi River, 1987–92

Contaminant	Abbreviation	Compounds and sources
Dissolved organic carbon	DOC	All natural and synthetic organic compounds; regional-scale natural sources.
Fecal coliform bacteria	None	Bacteria derived predominantly from human and livestock fecal wastes; from unchlorinated sewage effluents and feedlot and agricultural runoff.
Methylene-blue-active substances	MBAS	Composite measure of synthetic and natural anionic surfactants; predominantly from municipal sewage-wastewater discharges.
Linear alkylbenzenesulfonate	LAS	Complex mixture of specific anionic surfactant compounds used in soap and detergent products; primary source is domestic sewage effluent.
Nonionic surfactants	NP, PEG	Complex mixture of compounds derived from nonionic surfactants that includes nonylphenol (NP) and polyethylene glycol (PEG) residues; from sewage and industrial sources.
Adsorbable organic halogen	AOX	Adsorbable halogen-containing organic compounds, including by-products from chlorination of DOC and synthetic organic compounds, solvents and pesticides; from multiple natural and anthropogenic sources.
Fecal sterols	None	Natural biochemical compounds found predominantly in human and livestock wastes; primary source is domestic sewage and feedlot runoff.
Polynuclear aromatic hydrocarbons	PNA	Complex mixture of compounds, many of which are priority pollutants; from multiple sources associated with combustion of fuels.
Caffeine	None	Specific component of beverages, food products, and medications specifically for human consumption; most significant source is domestic sewage effluent.
Ethylenediaminetetraacetic acid	EDTA	Widely used synthetic chemical for complexing metals; from a variety of domestic, industrial, and agricultural sources.
Volatile organic compounds	VOC	A variety of chlorinated solvents and aromatic hydrocarbons; predominantly from industrial and fuel sources.
Semivolatile organic compounds	TTT, THAP	Wide variety of synthetic organic chemicals including priority pollutants and compounds such as trimethyltriazinetrione (TTT) and trihaloalkylphosphates (THAP); predominantly from industrial sources.

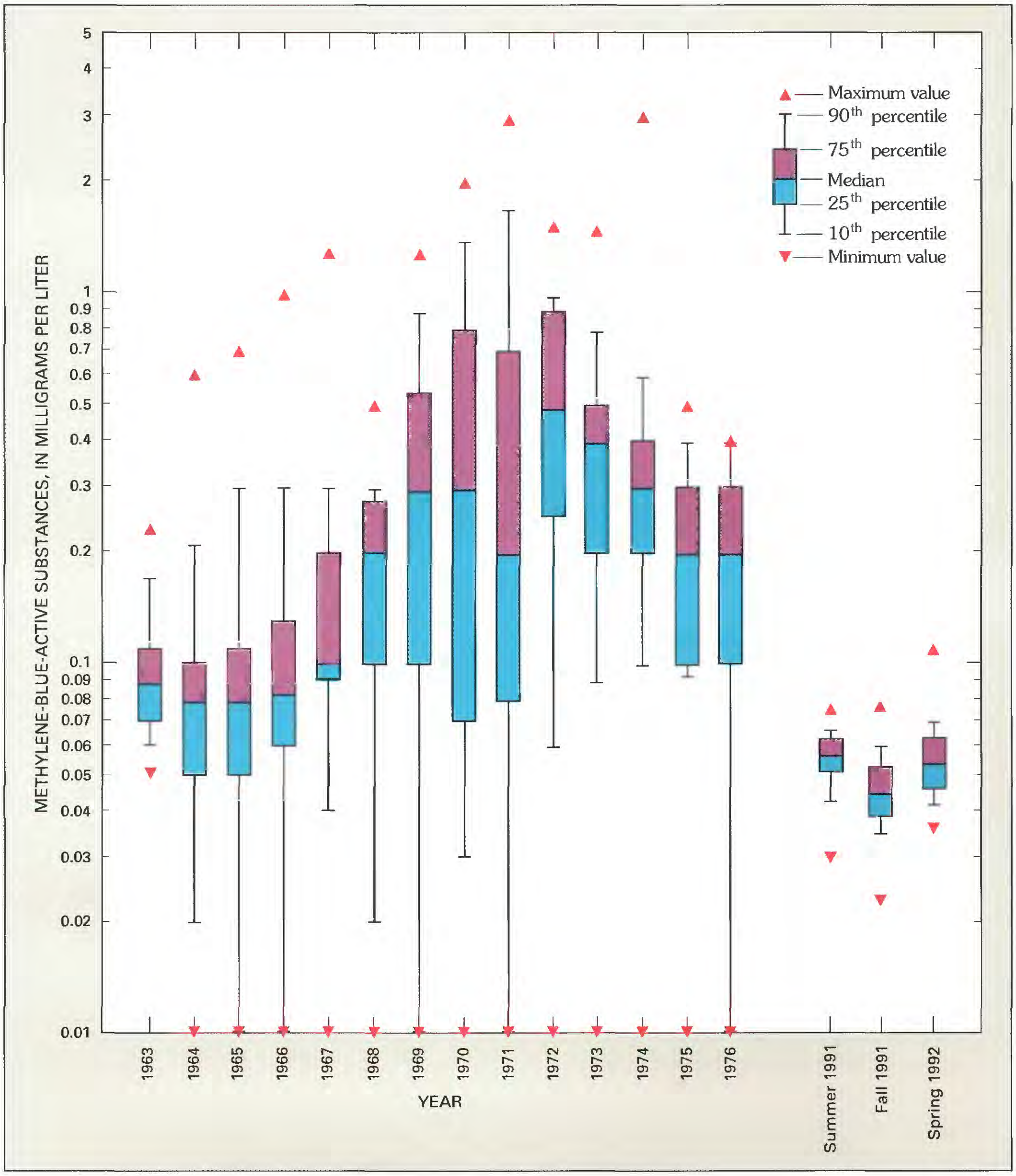
contribution of industrial effluents. Sewage effluents also contain a variety of natural organic chemicals from human waste and food products, a variety of microorganisms including bacteria and viruses, and a variety of inorganic chemicals.

In many metropolitan areas, domestic and industrial wastes and stormwater runoff are drained into a combined sewer. Combined-sewer overflows can contribute high waste loads for short time periods, and pollution loads vary as a function of discrete storm events. Combined-sewer overflows vary in composition with the density of population and the type of industry.

Municipal sewage and industrial wastewater are typically treated prior to their discharge into surface waters. Most municipal wastewater is treated by activated-sludge or trickling-filter methods that rely on sorption and biodegradation to remove organic contaminants. Removal efficiency for strongly sorbing, biologically labile, and volatile organic compounds ranges from 25 percent for primary treatment, 80 to 98 percent for secondary treatment, and greater than 98 percent for tertiary treatment. However, poorly sorbing and biologically recalcitrant compounds are not completely removed even during tertiary treatment. Depending on the type of treatment, removal of micro-organisms varies from negligible to more than 95 percent.

After effluent is discharged into a river, dilution becomes a major factor regulating the concentrations of dissolved chemicals. The stream-dilution factor is a function of streamflow and effluent discharge (stream-dilution factor = streamflow divided by cumulative effluent discharge). Stream-dilution factors determined for individual cities along the Mississippi River during this study varied: about 50 for Minneapolis-St. Paul, 500 for St. Louis, and 1500 for New Orleans. Stream-dilution factors for many small cities along the lower river were greater than 100,000. However, cumulative stream-dilution factors, determined using the combined effluent volumes for all upriver municipal discharges, including tributaries, were relatively constant along the entire river and ranged from 25 to 50, indicating that 2 to 4 percent of the river volume is contributed by municipal wastewater discharges.

Figure 52 *Surfactants in the River*



Stream-dilution factors vary as a function of season and long-term hydrological trends. For example, the Mississippi River discharges that were sampled during this study varied by a factor of two in the upper river and a factor of four in the lower river. Although stream-dilution factors can exceed 100,000, some contaminants such as fecal coliform bacteria can have concentrations up to millions of bacteria per liter in treated sewage effluents; thus, even small cities can contaminate the river with bacteria.

In addition to chemicals derived from domestic sources, municipal effluents also have an industrial component that varies depending on the type and number of industries present. For a given reach of the river, it may not be possible to distinguish contaminants introduced directly through onsite industrial discharges from contaminants introduced by industry through municipal wastewater. Likewise, urban runoff through storm sewers or from overland flow is a potential source of chemicals that may be difficult to distinguish from treated wastewater effluent. However, some synthetic-organic chemicals are

Surfactants in the River

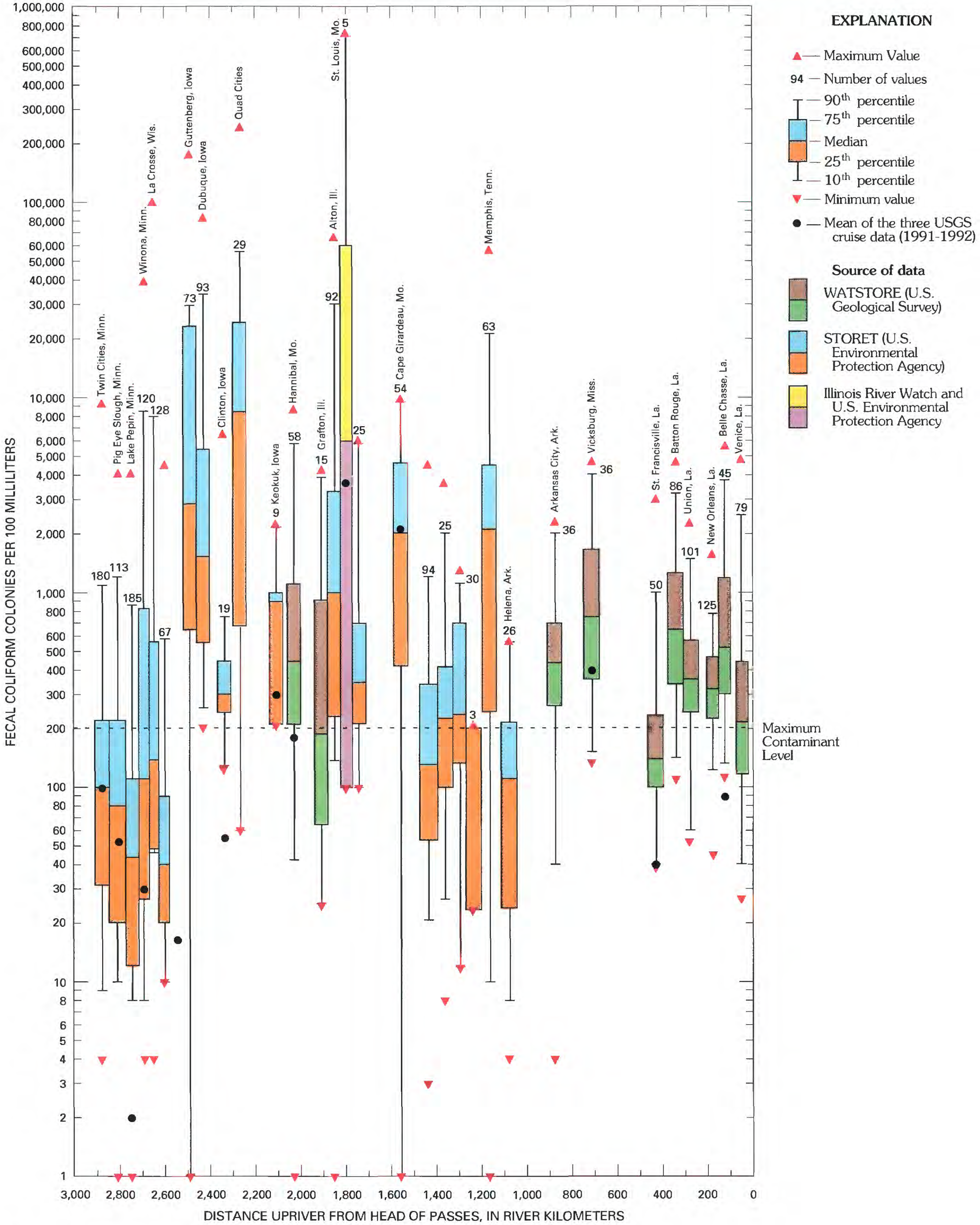
Figure 52 Anionic surfactants were studied in river waters during the 1950s to 1970s because they caused extensive foaming. Consequently, they have been measured for a long enough period (since 1958 in the Mississippi River) to provide an example of long-term trends in water quality. The foaming was the result of high concentrations of branched-chained alkylbenzenesulfonates (ABS) that were resistant to biological degradation during wastewater treatment and residence in rivers. Concentrations were frequently above the foaming threshold of about 0.5 milligram per liter (mg/L). Dilution was the primary attenuation mechanism for ABS. To remedy the foaming problem, the surfactant-manufacturing industry modified the chemical structure of the molecule to a more biodegradable linear side chain (LAS) which resulted in a significant decrease in concentrations during wastewater treatment and residence in rivers (Swisher, 1964). From 1959 to 1965, ABS concentrations in the Illinois River ranged from 0.4 to 9 mg/L; from 1965 to 1966, ABS+LAS concentrations ranged from about 0.2 to 0.3 mg/L (Sullivan and Evans, 1968; Sullivan and Swisher, 1969). After 1968, LAS concentrations decreased to less than 0.1 mg/L even though surfactant consumption increased by more than 30 percent. This example shows that it is possible to reverse certain pollution effects, in this case by the compulsory introduction of a more biodegradable material.

The box plots in the figure show the average annual concentrations of anionic surfactants (ABS plus LAS measured as methylene-blue-active substances) for all available sampling sites along the Mississippi River from 1963 to 1976 in the U.S. Environmental Protection Agency's STORET data base. Although the switchover from ABS to LAS occurred between 1964 and 1968, the concentrations of anionic surfactants in the Mississippi River continued to rise until 1971 or 1972, probably the result of increasing consumption rates and population density. Following 1972, concentrations decreased to the levels observed today, reflecting improvements in wastewater-treatment plants as the result of the Federal Water Pollution Control Act of 1972, which required secondary treatment of sewage effluents. The continued decrease of surfactant concentrations is shown in data collected during 1991–92, which are plotted on the right side of the graph.

unique and can be traced directly to specific industrial discharges.

Other significant sources of organic contamination along the Mississippi River are powerplants and pulp mills. A typical powerplant along the Upper Mississippi River uses about 6.6 cubic meters per second (m^3/s) of cooling water (Water Quality Work Group of the Great River Environmental Action Team, 1980a), which amounts to approximately 3 percent of the average Mississippi River discharge at Minneapolis. Powerplants use a variety of chemicals in their cooling water, including chlorine as a disinfectant to prevent biofouling, and metal-complexing agents to prevent scale buildup. Pulp mills also can discharge large quantities of wastewater. The mean discharge for six pulp mills located along the Mississippi River and its tributaries is about 1 m^3/s (Costner and Thornton, 1989), which is equal to about 10 percent of the municipal discharge for St. Louis. However, because of the high organic content of pulp-mill effluents, their organic loading to the river can be significant compared with municipal wastewaters. Pulp mills use a wide variety of organic chemicals, and the bleaching process produces significant amounts of chlorinated organic compounds. Another important source of organic contaminants is the application of agricultural chemicals such as fertilizers and pesticides. These chemical formulations are complex and consist of both active and inert ingredients. Many of the inert ingredients are solvents, surfactants, and builders that also are common in domestic and industrial products. Runoff from feedlots also contains high concentrations of organic matter and fecal coliform.

Figure 53 *Fecal Coliforms in the River*

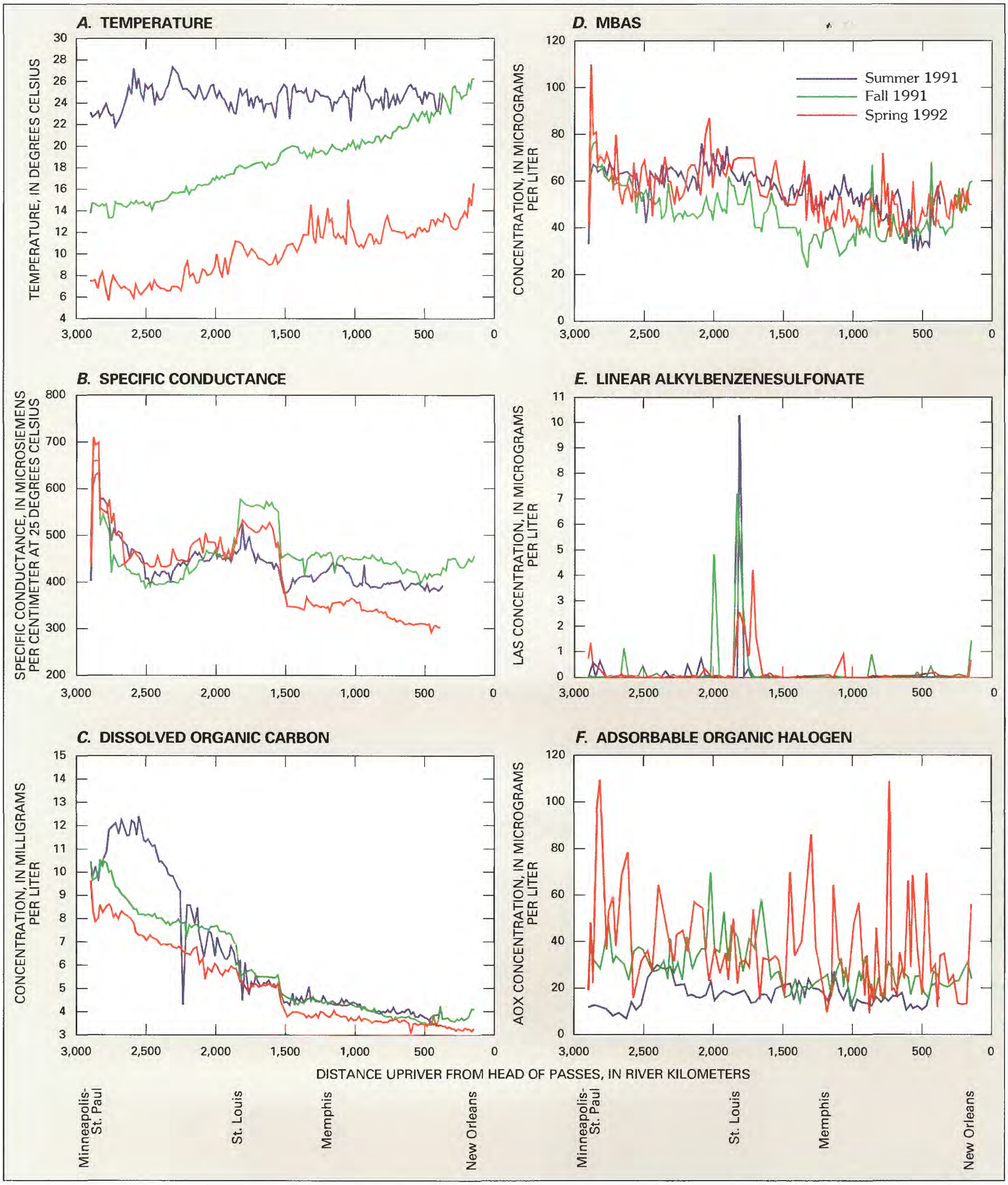


Fecal Coliforms in the River

Figure 53 Bacterial contamination of water is commonly assessed by measuring fecal coliform bacteria, which are present in untreated domestic sewage and animal wastes in extremely large concentrations (1,000 to 100,000 organisms per milliliter; American Public Health Association, 1992). The current maximum contaminant level for whole-body-contact recreation for fecal coliform bacteria is 200 organisms per 100 milliliter (mL). Coliform bacteria have been measured at many sites on the Mississippi River from the 1920s to the present. Fecal coliform concentrations as great as 100,000 organisms per 100 mL that were measured in the river in 1925–26 resulted from untreated sewage inputs near Minneapolis-St. Paul, Minnesota (Wisconsin State Board of Health, 1927). By the 1970s, improved wastewater treatment had greatly decreased fecal coliform concentrations in most of the river although high levels were still reported below Minneapolis-St. Paul and St. Louis, Missouri (Water Quality Work Group of the Great River Environmental Action Team, 1980a, 1980b). Fecal coliforms also are derived from animal waste and feedlot runoff.

The box plots in the figure show fecal coliform concentrations along the Mississippi River from 1982 to 1992 obtained from the U.S. Environmental Protection Agency's STORET data base and the U.S. Geological Survey's WATSTORE data base. Data for St. Louis from the Illinois River Watch program and data from the current study for 1991–92 also are plotted in the figure. Median fecal coliform concentrations exceeded the standard by a factor of 10 or more near Guttenberg, Iowa, Rock Island, Illinois (Quad Cities), St. Louis and Cape Girardeau, Missouri, and Memphis, Tennessee. The standard was exceeded to a lesser extent at several other locations. Standards also were exceeded in the Rock, Iowa, Des Moines, Missouri, and Kaskaskia Rivers (data not shown in the figure). Although earlier studies (Water Quality Work Group of the Great River Environmental Action team, 1980a) showed the standards being exceeded near Minneapolis-St. Paul, our measurements showed coliform counts in that area that were lower than the standard, indicating efficient removal during wastewater treatment. The fecal coliform contamination near St. Louis during 1991–92 was consistent with data reported by the Water Quality Work Group of the Great River Environmental Action Team (1980b), and probably results from lack of chlorination of treated sewage effluent in the metropolitan area.

Figure 54 *Wastewater Contaminants Along the River*



Wastewater Contaminants Along the River

Figure 54 Distributions and concentrations of dissolved organic contaminants along the length of the Mississippi River are best viewed in the context of other physical and chemical properties of the river water. During the three upriver cruises in summer 1991, fall 1991, and spring 1992 (see "Sampling the Length of the River," page 49), samples were taken and measurements were made near the center of the river approximately every 10 miles between New Orleans and Minneapolis. On the left side of the figure are shown the distributions of three "background" variables—temperature, specific conductance, and dissolved organic carbon—to provide a context for viewing the contaminant data. On the right side of the figure are shown the distributions of three groups of dissolved organic contaminants—surfactants (MBAS and LAS) and adsorbable organic halogen (AOX). Complete tabulations of the data are given by Barber, Leenheer, and others (1995).

A During the upriver cruise of summer 1991, water temperatures were fairly uniform along the length of the river and ranged from 22° to 27°C. By early fall 1991, the temperatures near Minneapolis had decreased about 10° while temperatures near New Orleans remained at summer levels; water temperature between Minneapolis and New Orleans showed a regular increase in the downstream direction. By early spring 1992, temperatures near Minneapolis were about 15°C lower than the previous summer and they increased downstream. During the winter (data not shown) water temperatures between Minneapolis and LaCrosse, Wisconsin (kilometer 2660), were near 0°C. A major influence of the various temperature regimes is their effect on rates of instream biodegradation, which decreases with decreasing temperature. The rate of volatilization also is affected by temperature, and the presence of ice cover during the winter can reduce the transfer of contaminants to the atmosphere.

B Specific conductance is a measure of total inorganic dissolved solids, and the profiles measured during the three upriver cruises of 1991–92 generally resemble the long-term average profile of total dissolved solids in the Mississippi River shown in figure 12. Maximum values in the upper river were measured immediately below the confluence of the Minnesota River, which had the highest specific conductance of any tributary. Specific conductance decreased downstream as the result of dilution by low-conductivity tributaries such as the St. Croix, Chippewa, Black, and Wisconsin Rivers. The reach between the Illinois and Ohio Rivers (kilometers 1890 and 1530) had elevated specific conductance, reflecting the input of high-conductivity water from the Missouri River. Specific conductance decreased sharply as the Mississippi River received the more dilute waters of the Ohio River, and the lower river had relatively uniform values. There was little seasonal variability in specific conductance of the upper river. Seasonal variability in the reach between the Illinois and Ohio Rivers was controlled by the relative discharge from the Missouri River. Seasonal variability in the lower river was related to discharge, with the highest values recorded during low flow during the fall. Several spikes in the profiles were probably the results of point-source inputs and hydrological events that occurred upstream.

C Dissolved organic carbon (DOC) is a measure of the total dissolved organic matter in the Mississippi River, most of which is natural. Wastewaters are only minor contributors of DOC. The most obvious features of the DOC profiles shown in the figure were the high concentrations in the upper river that decrease downstream, the sharp decreases in concentration below the Ohio River, and the relatively uniform concentrations (about 4 mg/L) in the lower river. There were distinct seasonal differences in DOC concentrations in the upper river; seasonal differences in the lower river were much less pronounced. DOC has important geochemical implications for the occurrence and fate of organic contaminants because it can (1) increase the solubility and facilitate the transport of organic contaminants, (2) alter rates of biodegradation, (3) form complexes with trace metals, and (4) react during water treatment to produce potentially toxic byproducts (see next chapter).

D Surfactants are major ingredients of soaps and detergents, and their presence is an indication of the effect of domestic wastewater on the water quality of the Mississippi River. Total anionic surfactants were determined as methylene-blue-active substances (MBAS), which is a composite measurement of linear alkylbenzenesulfonate (LAS), LAS biological metabolites and impurities, other synthetic-anionic surfactants, and naturally occurring compounds such as humic substances. The graph shows that during the upriver cruises of 1991–92, MBAS were present throughout the Mississippi River and its tributaries at concentrations ranging from about 20 µg/L to 100 µg/L, values that are below the drinking-water standard of 500 µg/L. The MBAS profiles showed some of the same general trends as specific conductance and DOC, including values in the upper river that were slightly larger than those in the lower river. The greater variability and scatter in the MBAS data indicate the effects of multiple point-source inputs from municipal wastewater discharges. MBAS concentrations had peaks in the vicinity of major cities and decreased rapidly downstream because of dilution, biodegradation, and sorption to the sediments.

E Specific measurements for linear alkylbenzenesulfonate (LAS) were not strongly correlated with MBAS, and many of the samples with elevated MBAS had low levels of LAS. The annual consumption of LAS in the United States is about 300,000 metric tons per year (Schirber, 1989). LAS is readily biodegraded under aerobic conditions to form intermediate compounds and ultimately carbon dioxide, water, and sulfate (Swisher, 1987). Although LAS and its byproducts are nontoxic to humans, aquatic organisms can be sensitive to concentrations ranging from 10 to 1000 µg/L (Kimerle and Swisher, 1977; Kimerle, 1989). Measurable LAS concentrations in the Mississippi River were found near Minneapolis, St. Louis, and New Orleans. However, LAS concentrations drop below detectable levels within 80 km downstream from the major sources as the result of dilution and instream biodegradation. The St. Louis area has a stream-dilution factor (river discharge divided by municipal effluent discharge) of about 500, but has the highest LAS concentrations along the river. In contrast, the stream-dilution factor for Minneapolis is about 50 and concentrations are very low. The stream-dilution factor for New Orleans is about 1500, and concentrations are similar to those below Minneapolis-St. Paul.

F Adsorbable organic halogen (AOX) is a measure of dissolved chlorinated organic matter, including both volatile and nonvolatile compounds, some of which may be toxic. These compounds are difficult to measure individually, so the AOX measurement serves as an overall index of their combined effect on water quality. AOX comes from a variety of sources, in particular, the chlorination of natural organic matter during disinfection of sewage effluents, biofouling control in powerplant cooling waters, pulp-wood bleaching, and other industrial discharges. There also are significant natural sources of AOX. The graph shows AOX profiles for the three upriver cruises of 1991–92. Although concentrations and distributions varied significantly along the river and among cruises, spatial trends relative to river reach were not as apparent as for other constituents. The greatest concentrations occurred during the spring and may have been the result of flushing natural and atmospherically transported AOX from the soils or increased anthropogenic sources during spring runoff events. The multiple spikes during the spring and fall probably represent sporadic inputs from point sources. The concentrations of AOX in the Mississippi River exceeded those that would be expected from discharge of treated municipal sewage effluent, indicating that other sources such as pulp mills and powerplants also contribute AOX. For example, a single pulp mill can contribute 840 kilograms (kg) per day of AOX (Costner and Thornton, 1989) which is 5–10 percent of the total Mississippi River AOX load near the confluence with the Ohio River. A typical powerplant can contribute a daily load of 600 kg per day (Water Quality Work Group of the Great River Environmental Action Team, 1980a). In contrast, the municipal-treated sewage discharge from St. Louis contributes an average of about 250 kg of AOX per day.

Summary

A summary of the major organic contaminants identified, their range of concentrations, their water-quality criteria, and their environmental fate is presented in table 11. Fecal coliform bacteria was the only contaminant that exceeded health limits. Although concentrations of most organic compounds measured in this study were below regulatory limits, their distributions indicate that the entire Mississippi River has been contaminated by point and nonpoint sources. Significant sources of organic contaminants include municipal-wastewater discharge, urban runoff, power-plant cooling-water discharges, pulp-mill effluents, feedlot runoff, commercial and recreational river traffic and refueling, discharges from industrial facilities, and agricultural runoff.

The Mississippi River carries higher concentrations of organic contaminants in the vicinity of major metropolitan areas. Concentrations are typically greatest in the upper river where the stream-dilution factors are lowest. Major tributaries such as the Minnesota, Illinois, Missouri, and Ohio Rivers have significant effects on the organic chemistry of the Mississippi River. Seasonal differences are related to hydrologic, climatic, biological, and geochemical factors. Concentrations are greatest during periods of low flow (fall) and least during periods of high flow (spring). Likewise, concentrations of biologically labile and volatile organic compounds are greatest during the winter when temperatures are lowest.

Although the data presented here provide only a brief glimpse of the water quality of the Mississippi River, comparisons with historical data show trends of improving water quality for several constituents. The improvements can be related to: (1) changes made by the chemical manufacturing industry to address the environmental fate of problematic chemicals, and (2) improved wastewater treatment by municipal and industrial dischargers. Converting primary treatment facilities to secondary treatment has resulted in improved water quality, although chemicals that are not completely removed present a challenge for treatment technology.

Much remains to be learned about the sources, fates, and effects of organic contaminants on human health and aquatic ecology. The data presented in the figures for this chapter and in the detailed reports of supporting data (Barber, Leenheer, and others, 1995; Barber, Writer, and others, 1995; Leenheer, Noyes, and Brown, 1995; Leenheer, Barber, and others, 1995; Pereira and others, 1995) represent a benchmark for future reference. They indicate critical areas where research is needed to more clearly define potential problems, and provide a baseline against which future changes in the water quality in the Mississippi River can be measured.

Table 11. Summary assessment of organic contaminants in the Mississippi River and its major tributaries. Compound abbreviations are listed in table 10

[mg/L, milligram per liter; CFU/100 mL, colony-forming units per 100 milliliters; µg/L, microgram per liter; mg/kg, milligram per kilogram; nd, not determined; Sorp, sorption; Bio, biodegradation; Vol, volatilization; >, greater than]

Compound	Concentration		Drinking water standard	Aquatic[1] toxicity	Environmental fate affected by		
	River water	Bed sediment			Sorp	Bio	Vol
DOC	3–12 mg/L	nd	4 mg/L[2]	Unknown	Yes	Yes	No
Fecal coliform	2–700,000 CFU/100 mL	nd	[3]0	200 CFU/100 mL[6]	Yes	Yes	No
MBAS	20–100 µg/L	nd	500 µg/L[3]	250 µg/L[7]	Yes	Yes	No
LAS	0.1–10 µg/L	0.1–1 mg/kg[14]	None	25 µg/L[8]	Yes	Yes	No
NP	0.1–10 µg/L	nd	None	130 µg/L[9]	Yes	No	Yes
PEG	5–150 µg/L	nd	None	1,000 mg/L[10]	Yes	Yes	No
AOX	10–120 µg/L	nd	60 µg/L[4]	Unknown	Yes	Yes	Yes
Coprostanol	nd	0.1–1 mg/kg[14]	None	Unknown	Yes	Yes	No
Total PNAs	nd	0.1–16 mg/kg	0.1–0.4 µg/L[5]	4 mg/kg[11]	Yes	Yes	Yes
Caffeine	0.01–0.1 µg/L	nd	None	Unknown	Yes	Yes	No
EDTA	1–30 µg/L	nd	None	>1,000 µg/L[12]	No	No	No
Total VOC	0.2–3.1 µg/L	nd	5–1,000 µg/L[5]	>1,000 µg/L[13]	Yes	Yes	Yes
TTT	0.01–0.5 µg/L	nd	None	Unknown	No	No	No
THAP	0.01–1.4 µg/L	nd	None	Unknown	No	No	No

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[1] Aquatic toxicity of organic compounds is a complex issue that involves many factors including the characteristics of the particular chemical, concentration of the chemical, overall water composition, and the aquatic species under consideration. The scientific literature is rich in specific studies of aquatic toxicity for a wide range of compounds, species, and conditions. The data presented in this table, although limited, are representative of the range of concentrations shown to exhibit toxic effects for sensitive aquatic species.

[2] Pontius, 1993. Drinking water sources with more than 4 mg/L DOC may require pretreatment to minimize formation of disinfection by-product (see the following chapter by R.E. Rathbun).

[3] U.S. Environmental Protection Agency, 1994.

[4] Pontius, 1993. Although no MCLs have been established for AOX, anticipated MCLs for the total of five trihaloacetic acids that are measured as a component of the AOX have been proposed.

[5] Range of MCL values for individual compounds detected in this study. U.S. Environmental Protection Agency, 1994.

[6] Fecal coliform bacteria are not toxic to aquatic species, but rather are indicators of bacterial water quality. This standard is for human primary contact recreation (Dufour, 1984).

[7] MBAS is a nonspecific measure of LAS and related compounds. This value was established based on the assumption that 10 percent of the MBAS response comes from LAS (Kimerle, 1989).

[8] Kimerle, 1989.

[9] McLeese and others, 1981.

[10] Patoczka and Pulliam, 1990. Based on toxicity of linear alcohol ethoxylates that are parent compounds for PEG. PEG will have significantly lower toxicity than the parent compound.

[11] Persaud and others, 1993. Value listed is for sediment toxicity: PNAs are primarily sorbed to bed sediments.

[12] Curtis and Ward, 1981. At concentrations less than 500 µg/L, however, EDTA can reduce the toxicity of heavy metals by forming complexes that lower the concentrations of free metal ions.

[13] Verhaar and others, 1992.

[14] Range of values reported in the table and in figure 55 refers only to bed-sediment samples collected in the main-stem navigation pools. Values of 20 mg/kg of LAS and 7.5 mg/kg of coprostanol were measured in bed sediment in Pigs Eye Slough, which receives effluent from a wastewater-treatment facility in St. Paul, Minn.

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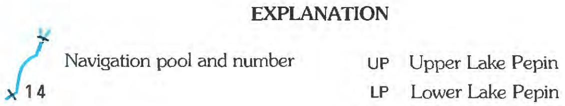
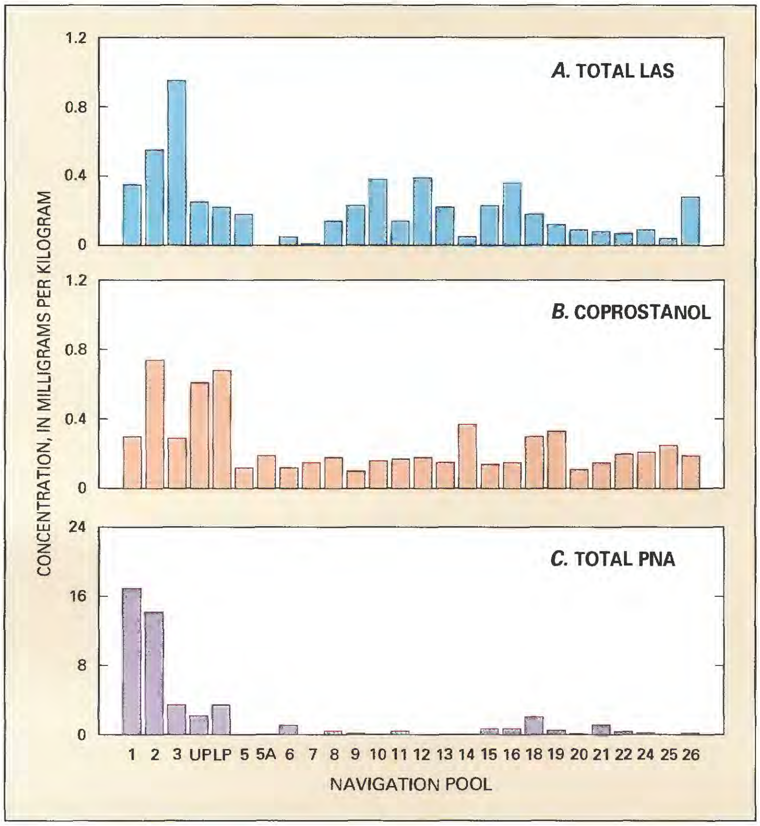
Figure 55 *Wastewater Contaminants in Bed Sediments*





Wastewater Contaminants in Bed Sediments

Figure 55 The sediments deposited and stored in the navigation pools of the Upper Mississippi River are contaminated with organic pollutants derived from municipal and other sources. Data in these three graphs are from samples of bed sediment collected during 1991–92 from the shallow areas of the navigation pools. Additional samples were collected from the shallow backwater areas of the unimpounded river at St. Louis and at Thebes, Illinois, 215 km downriver of St. Louis. Complete tabulations of the data are given in the reports by Writer (1992), Tabor (1993), Barber, Writer, and others (1995), and Writer and others (1995).

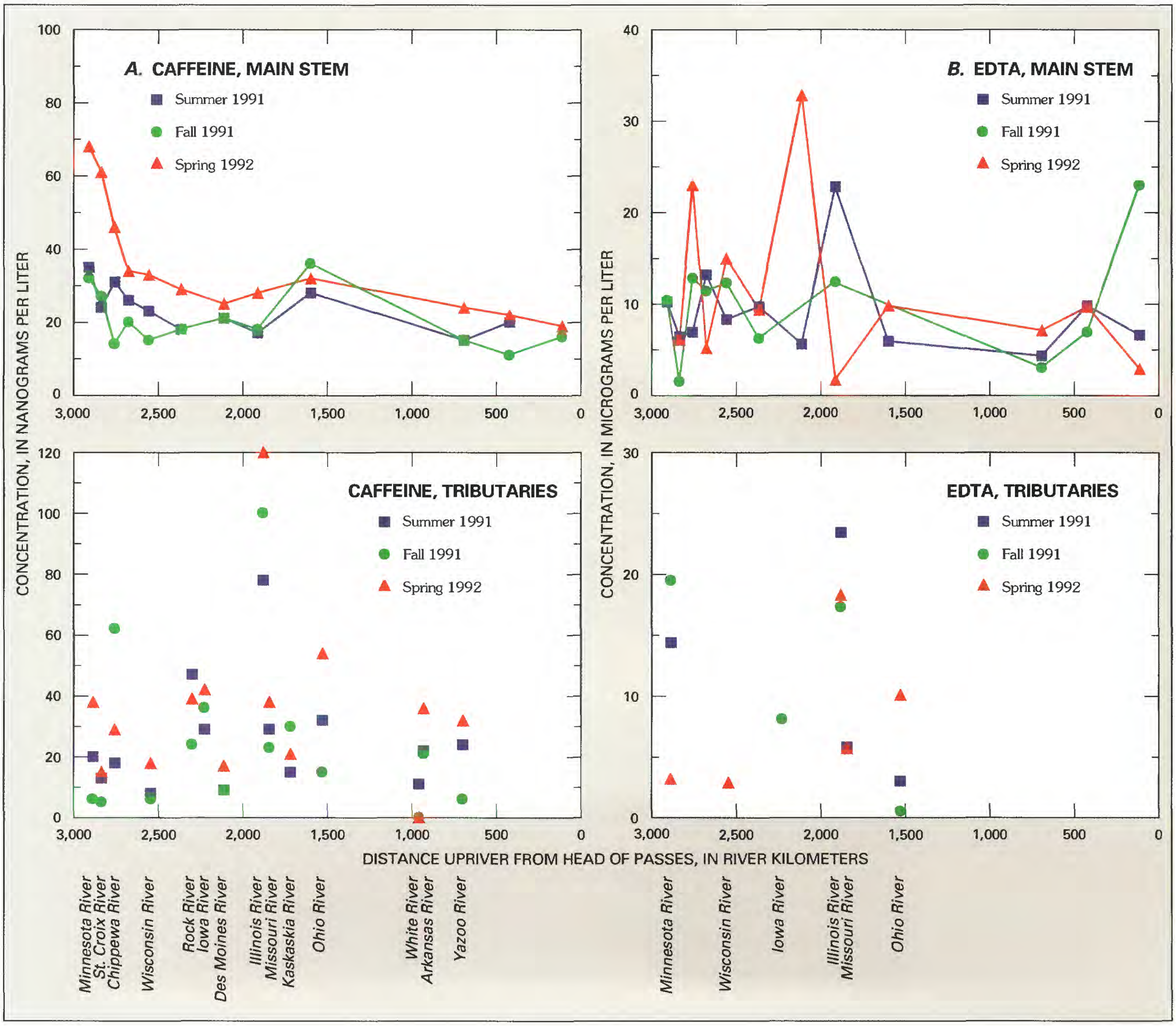
A Linear alkylbenzenesulfonate (LAS) is found in soaps and detergents, and its presence in river-bottom sediments indicates contamination by domestic and municipal wastes. The concentrations of LAS on bed sediments (about 0.1 to 1 milligram per kilogram (mg/kg) of sediment) are one to three orders of magnitude greater than those detected in the overlying water (0.00005 to 0.012 milligrams per liter (mg/L) of water). The data in the graph show a pattern that can be attributed to inputs from cities such as Minneapolis-St. Paul, LaCrosse, and Rock Island. Biodegradation removes LAS from the sediment—at rates that apparently are variable enough to complicate patterns of high and low concentrations attributed to local sources.

B Coprostanol is a fecal sterol that comes from human and livestock wastes. A properly operating wastewater-treatment plant will remove 95–99 percent of the coprostanol, resulting in concentrations ranging from 30 to 50 micrograms per liter (µg/L) in sewage effluents and from 1,400 to 7,900 mg/kg in sewage sludge (Walker and others, 1982). Between 85 and 95 percent of the coprostanol discharged in sewage effluents is associated with particulate matter that can be assimilated into bed sediments (Venkatesan and Kaplan, 1990). Data in the figure show that coprostanol concentrations ranged from 0.09 to about 0.8 mg/kg.

Concentrations in excess of 0.1 mg/kg indicate sewage contamination (Hatcher and McGillivary, 1979). Coprostanol is biodegraded more slowly than LAS, and its distribution in the upper river can be explained in terms of sources and sinks. Obvious sources of coprostanol are Minneapolis-St. Paul (Pool 2). Sites for the accumulation and storage of coprostanol-bearing sediments are the two largest pools in the upper river (Lake Pepin and Pool 19). During moderate to large flows, the sediments are likely to be swept out of the smaller shallower pools of the upper river and deposited in the larger deeper pools.

C Polynuclear aromatic hydrocarbons (PNAs) are organic compounds that are common contaminants in sediments, several of which are sufficiently toxic to be listed as priority pollutants by the U.S. Environmental Protection Agency. The sources of PNAs are complex, but they typically come from combustion processes. Urban runoff, municipal-wastewater discharges, wood-treatment facilities, petroleum development and processing, coal-storage facilities, and transportation networks (both land and river) all contribute PNAs to the Mississippi River. PNAs detected on the bed sediments include the priority pollutants naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, fluoranthene, anthracene, chrysene, pyrene, benzo[b]-fluoranthene, and benzo[k]fluoranthene. Concentrations of individual compounds ranged from less than 0.2 to about 10 mg/kg. Although only the elevated concentrations at Minneapolis-St. Paul (Pools 1 and 2) are clearly attributable to municipal sources, many of the PNAs detected in the other samples probably come from wastewater discharge and urban runoff.

Figure 56 *Caffeine and EDTA in River Waters*



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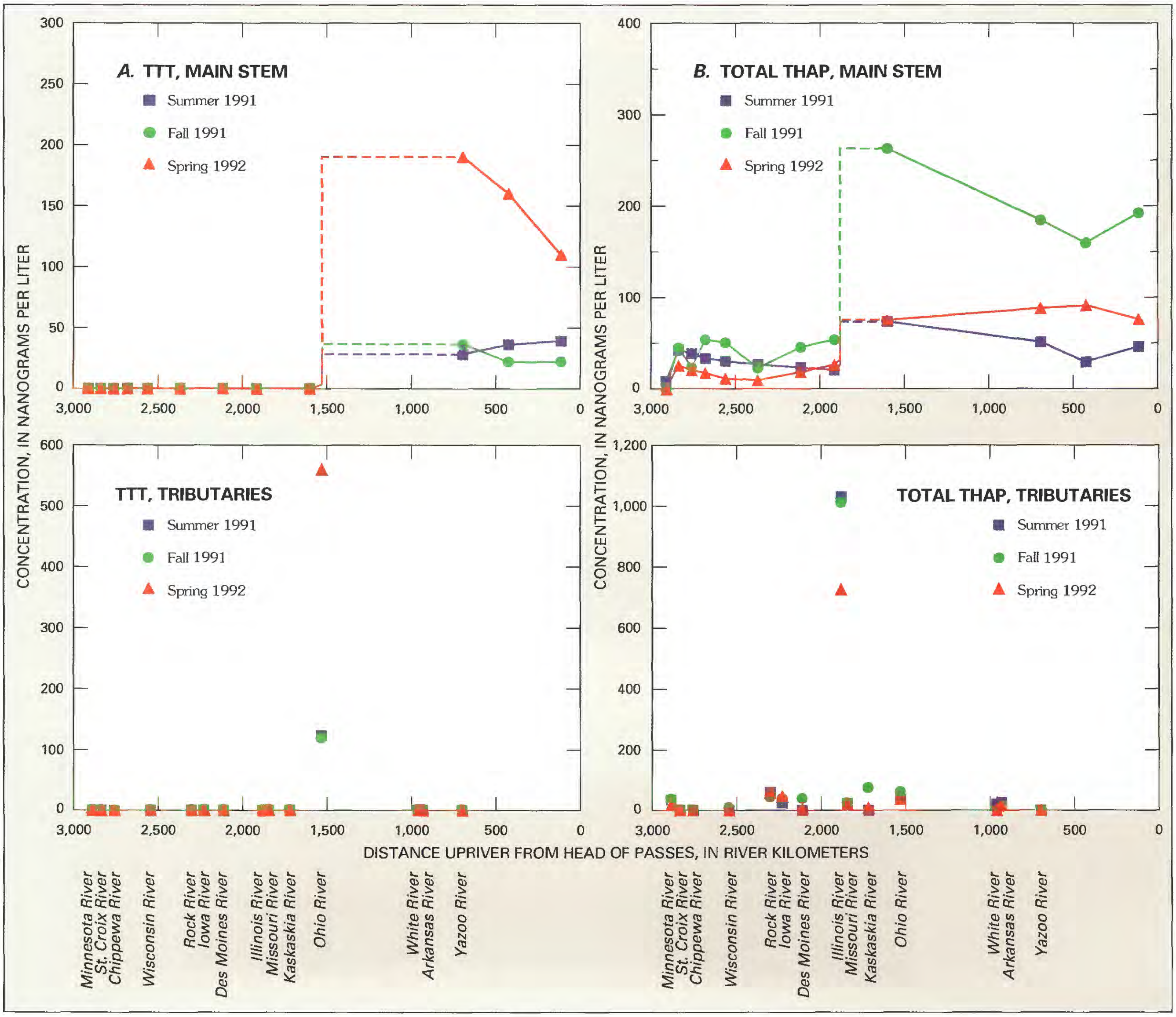
Caffeine and EDTA in River Waters

Figure 56 Caffeine and EDTA (ethylenediaminetetraacetic acid) are two of the more ubiquitous dissolved organic compounds in the Mississippi River. Neither compound is highly toxic to humans, but each is a specific indicator of contamination by wastewaters.

A Caffeine is a stimulant chemical in beverages such as coffee and soft drinks and in a variety of food products. Its concentrations in municipal wastewaters range from 20–300 µg/L (Rogers and others, 1986). The graphs show the concentrations of caffeine measured in the Mississippi River and its tributaries during the three downriver sampling cruises of 1991–92 (a complete tabulation of data is given by Pereira and others, 1995). Caffeine is a fairly specific tracer of domestic wastewaters, and its profile illustrates the effect of population density on water quality. The concentration gradient between river kilometers 2950 and 2600 shows inputs from Minneapolis-St. Paul into the relatively small upper river and the progressive dilution downstream by the Minnesota and St. Croix Rivers. The elevated concentrations of caffeine in the Illinois River are from the large population in the Chicago metropolitan area, and the abrupt increase in the Mississippi River near river kilometer 1850 is the result of input from the Illinois River. The gradual downstream decreases in caffeine concentrations in the river indicate instream degradation through biotic and abiotic processes in addition to dilution by tributaries. Caffeine occurs at similar concentrations to EDTA in sewage effluents, but it occurs at much lower concentrations in river water because of degradation and because it is not supplied by the industrial sources that also introduce EDTA.

B EDTA is used to form water-soluble complexes with insoluble metals in a wide variety of domestic and industrial applications, including stabilization of bleaching agents in laundry detergents, prevention of boiler scale formation in powerplants, addition as a preservative and clarifying agent in foods and beverages, use in fertilizers as a source of chelated metal micronutrients, and other applications in the metal-plating, photography, paper, and textile industries. The 1990 United States production of EDTA was 49,687 metric tons (U.S. International Trade Commission, 1990). EDTA is an indicator of total domestic and industrial wastewater inputs. EDTA has low toxicity to humans and aquatic organisms. The chief water-quality concerns are its ability to mobilize toxic metals from sediments and to stimulate algal growth by increasing the availability of nutrients such as iron and zinc. EDTA is not biologically degraded during wastewater treatment, but various EDTA salts and metal complexes have been observed to degrade in light (Alder and others, 1990). As a consequence of the lack of biodegradation, its high solubility in water, and large rates of production and usage, EDTA can be one of the most abundant organic contaminants in surface waters. The graphs show EDTA concentrations measured in the Mississippi River and four principal tributaries during the three downriver sampling cruises of 1991–92 (L.B. Barber, II, unpub. data, 1995). Concentrations were greater in the upper river than the lower river, and the peak concentrations occurred between kilometers 2250 and 1900 (between Dubuque and Keokuk, Iowa). The EDTA concentrations measured in the river were about five times greater than the concentrations that can be attributed to inputs of secondary treated municipal wastewaters. It is likely therefore that discharges from powerplants and other industrial sources contribute significantly to EDTA concentrations. The greatest tributary EDTA concentration was from the Illinois River, which probably reflects industrial and domestic wastewater inputs from the Chicago metropolitan area. In general, EDTA concentrations in the Mississippi River were lower than those reported for German rivers, which typically range from 10 to 60 µg/L (Frimmel and others, 1989).

Figure 57 *TTT and Flame Retardants in River Waters*



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TTT and Flame Retardants in River Waters

Figure 57 Some of the organic contaminants that are dissolved in the waters of the Mississippi River can be traced to unique sources. Two of these are TTT, an industrial by-product primarily contributed from the Kanawha River Valley of West Virginia, and flame retardant additives contributed almost exclusively from the Illinois River watershed. Because their sources are so restricted, these compounds can be used as tracers of the waters of their source tributaries as they mix with the other waters that make up the Mississippi River. Samples portrayed in the graphs were collected during the downriver cruises of 1987–92; complete tabulations of the data are given by Pereira and others (1995).

A TTT (1,3,5-trimethyl-2,4,6-triazinetrione) is a by-product of the manufacture of methylisocyanate. TTT has been reported in residual materials from a tank after the leak of methylisocyanate in Bhopal, India (D'Silva and others, 1986), in secondary effluent from a municipal and industrial wastewater-treatment plant in Illinois (Ellis and others, 1982), and in water from the Ohio River where it continues to be detected at 1–2 μg/L (Don Mackell, Louisville Water Company, Louisville, Kentucky, written commun., 1989). During the sampling cruises of 1987–92, the Ohio River was the major contributor of TTT to the Mississippi River, and the source was eventually traced to a location on the Kanawha River where methylisocyanate is manufactured and transported. TTT is a very stable compound and was detected in all water samples collected from the Mississippi River between the Ohio River and the Gulf of Mexico, indicating little or no degradation during 2300 kilometers of river transport.

B THAP (trihaloalkylphosphates) are used as flame-retardant additives in flexible and rigid polyurethane foams, and in textiles. THAP are relatively water-soluble compounds that have low bioconcentration factors and short half-lives in fish. THAP have been reported in municipal water supplies of cities adjoining the Great Lakes in Canada (Williams and others, 1982; Williams and Le Bel, 1981), in surface waters of Japan (Japan Environmental Agency, 1977–79), and in surface water, ground water, and drinking water in Italy (Galassi and Guzella, 1988).

The graphs show the concentrations of total THAP (sum of tris-2-chloroethylphosphate and two isomers of tris-2-chloropropylphosphate), that were detected in all water samples collected from the Mississippi River and its tributaries during the downriver sampling cruises of 1987–92. In addition to minor sources of THAP along the Mississippi River, there is a major source on the Illinois River. THAP are relatively stable and degrade only slightly during transport from St. Louis to the Gulf of Mexico, a distance of about 1850 kilometers.

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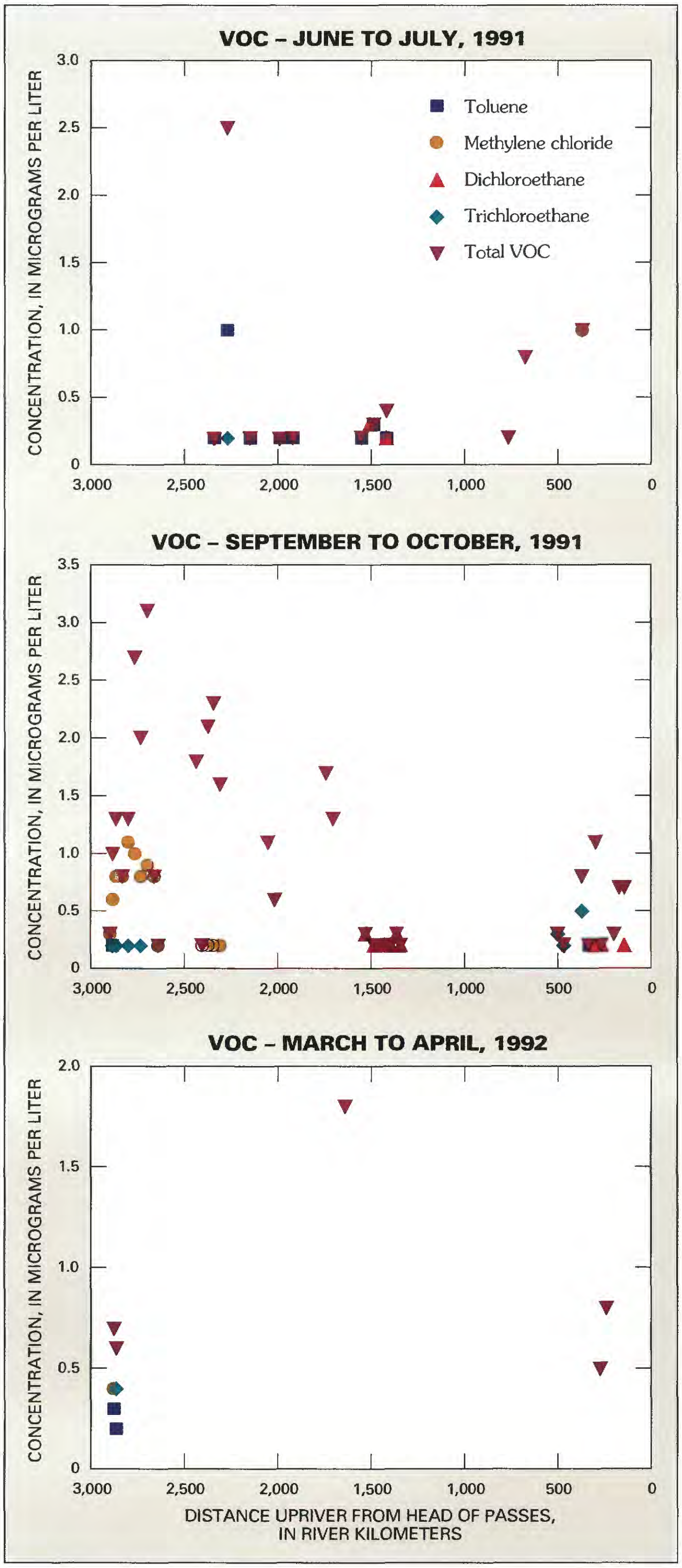
Figure 58 *Volatile Contaminants in the River*



Volatile Contaminants in the River

Figure 58 Volatile organic compounds (VOC) appear to be short lived in the Mississippi River, as would seem to be self-evident from the fact that the compounds are called "volatile." However, considerable effort was spent in testing the waters of the Mississippi River for their presence because (1) there are degrees of volatility and (2) some of the compounds are highly toxic. Sources of volatile organic compounds are industrial, municipal, and transportational (urban runoff and river traffic).

The graphs show several of the volatile organic compounds that were detected in significant concentrations in the midriver samples collected during the three upriver cruises of 1991–92. Of the 64 target compounds, for which 440 samples were analyzed, 32 were detected and only 19 occurred in more than 1 percent of the samples. Concentrations of total VOC ranged from 0.2 to 3.1 μg/L and were typically an order of magnitude below maximum contaminant levels. There was a seasonal trend in volatile compound concentrations; the greatest frequency of detections and highest concentrations occurred during the fall and winter. During the winter (data not shown in the graphs) concentrations increase significantly in the reaches of the river that become ice covered. The areas with the most significant contamination by volatile organic compounds were the reach downstream from Minneapolis-St. Paul, the reach downstream from the confluence of the Ohio and Mississippi Rivers, and the reach between Baton Rouge and New Orleans.

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Potentially Deleterious Effects of Chlorinating Mississippi River Water for Drinking Purposes

Ronald E. Rathbun

Introduction

An emerging issue in the treatment of drinking water is the role played by chlorine in the formation of toxic compounds. The idea that chlorine might be deleterious seems paradoxical because the addition of chlorine to public water supplies, which became a general practice during the early decades of this century, perhaps did more to increase human life spans than any other single event in history (Fairweather, 1990). Chlorine destroys the microbes that cause typhoid fever, cholera, and amoebic dysentery; as a result, these diseases have been virtually eradicated from the developed countries of the world. Within the last few decades, however, it has become evident that adding chlorine as a disinfectant to natural waters can result in the formation of chloroform and other carcinogenic or mutagenic compounds (Rook, 1974; Bellar and others, 1974). The importance of this issue may be summarized by the statement of R.J. Bull (1982) who concluded that "no other public health issue affects a larger proportion of the U.S. population than drinking water disinfection."

The Mississippi River is used by many of the cities and towns along its banks as a source of drinking water. As a standard practice, chlorine is added as a disinfectant to the waters that are extracted from the river before they are distributed to consumers through municipal water systems. As part of the assessment of the water quality of the Mississippi River, a set of laboratory experiments was done to assess the potential for forming toxic substances when river waters are chlorinated.

Background

The toxic by-product compounds formed during the chlorination of natural waters result from the reaction of free chlorine used for disinfection with the dissolved organic carbon (DOC) present in the water. The DOC is a complex mixture of organic compounds resulting from the decay of soil and plant organic matter (Thurman, 1985). Chemical and biological processes within aquatic systems also may contribute to the DOC. The DOC is present in varying concentrations and compositions in all natural waters. It is the DOC that serves as the precursor for the formation of the by-product compounds.

The by-products formed during the chlorination of natural waters can be divided into two classes of compounds. The first class consists of the trihalomethane (THM) compounds, which are chlorinated and brominated derivatives of methane. The four compounds commonly included in this class are chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$), and bromoform ($CHBr_3$). Chloroform is a known animal carcinogen (Pieterse, 1988). The other THM compounds formed during the disinfection process are carcinogenic and mutagenic (Simmon and Tardiff, 1978), and positive correlations have been observed between the concentrations of these compounds in drinking water and bladder cancer (Cantor and others, 1978). Positive correlations also were observed for brain cancer in both males and females and for lymphoma and kidney cancer in males. Concerns about possible health effects of these compounds (U.S. Environmental Protection Agency, 1975, 1979; National Academy of Sciences, 1977) resulted in the U.S. Environmental Protection Agency's establishing a maximum contaminant level (MCL) in drinking water of 100 micrograms per liter (μg/L) total of the four THM compounds. Other countries have more stringent requirements. Germany and Switzerland have an MCL of 25 μg/L (Pieterse, 1988). In addition, Amsterdam has stopped the chlorination of drinking water because of health concerns about the ingestion of these compounds (Pieterse, 1988).

The second class consists of a complex mixture of relatively nonvolatile compounds that have higher molecular weights than the THM compounds. Because of the large number of different compounds present in this mixture at small concentrations, identification and quantification of the individual compounds is difficult. Consequently, the concentration of these compounds is determined as a bulk parameter called the nonpurgeable total organic halide (NPTOX) concentration. As of 1994, no maximum contaminant level has been established for the NPTOX concentration in drinking water.

Experimental Procedure

The experiments evaluated the factors that influence the formation of toxic by-products during the chlorination process. These factors are the concentration of free chlorine used in the chlorination process, the pH at which the water is chlorinated, the water temperature, and the concentration and composition of the DOC of the source water. The distribution of the compounds among the chlorinated and brominated compounds depends on the bromide concentration of the source water. The free chlorine concentration is determined by the particular water-treatment process being used, and the pH is determined by a combination of the pH of the source water and the water-treatment process being used. The DOC and bromide concentrations, the composition of the DOC, and the temperature are determined by the characteristics of the source water.

Potentials for the formation of THM and NPTOX compounds upon chlorination of Mississippi River water were determined in samples that were collected from 12 sites along the river between Minneapolis, Minnesota, and New Orleans, Louisiana; the samples were shipped to the laboratory in Denver, Colorado, where the experiments were conducted. Formation potentials were determined as a function of pH and initial free chlorine concentration for 7 days at a temperature of 25°C. Formation potentials also were determined as a function of reaction time over 7 days for a pH of 8.14 and an initial free chlorine concentration of 30 milligrams per liter. Complete details of the experimental procedure and the data resulting from this study have been presented in other reports (Rathbun, 1995; Rathbun and Bishop, 1993, 1994).

Experimental Results

Potentials for the formation of the THM and the NPTOX compounds when water from the Mississippi River is chlorinated are presented in figure 59 as a function of distance above Head of Passes, Louisiana. Also presented in figure 59 are the DOC concentrations. The formation potentials decrease with distance downstream, in each case paralleling the decrease of the DOC concentration with distance downstream. This behavior clearly demonstrates the importance of the DOC as the precursor in the by-product formation process.

The effect of pH on the by-product formation process is demonstrated by the fact that NPTOX formation potential is considerably larger than the THM formation potential for a pH of 6.73, whereas the THM formation potential is slightly larger than the NPTOX formation potential for a pH of 9.70. For the intermediate pH of 8.14, the NPTOX formation potential is larger than the THM formation potential, although the difference is considerably less than the difference for pH 6.73. These results indicate that pH conditions in the water-treatment process that minimize the formation of the THM compounds tend to maximize the formation of the NPTOX compounds.

Potentials for the formation of the THM and the NPTOX compounds as a function of reaction time are presented in figure 60 for water samples from the river at Minneapolis, Memphis, and New Orleans. Concentrations of both types of compounds increased rapidly during the initial part of the experiment; more than one-half of the final concentrations was formed during the first day. Thereafter, the concentrations of both types of compounds increased gradually for the balance of the 7-day period.

Conclusion

Results of this study indicate that there is sufficient DOC in the Mississippi River that THM and NPTOX compounds will be formed when the water is disinfected with chlorine. The DOC concentration decreased with distance downstream between Minneapolis and New Orleans; the THM and NPTOX concentrations measured in the laboratory formation-potential experiments also decreased with distance downstream, paralleling the decrease of the DOC. The pH levels prevalent in the Mississippi River and pH values likely to be used in water disinfection are such that the NPTOX compounds are likely to form more abundantly than the THM compounds. However, if a more alkaline condition is used in the disinfection process, then the THM compounds are likely to form more abundantly than the NPTOX compounds. The formation potentials for the THM compounds, although less than the

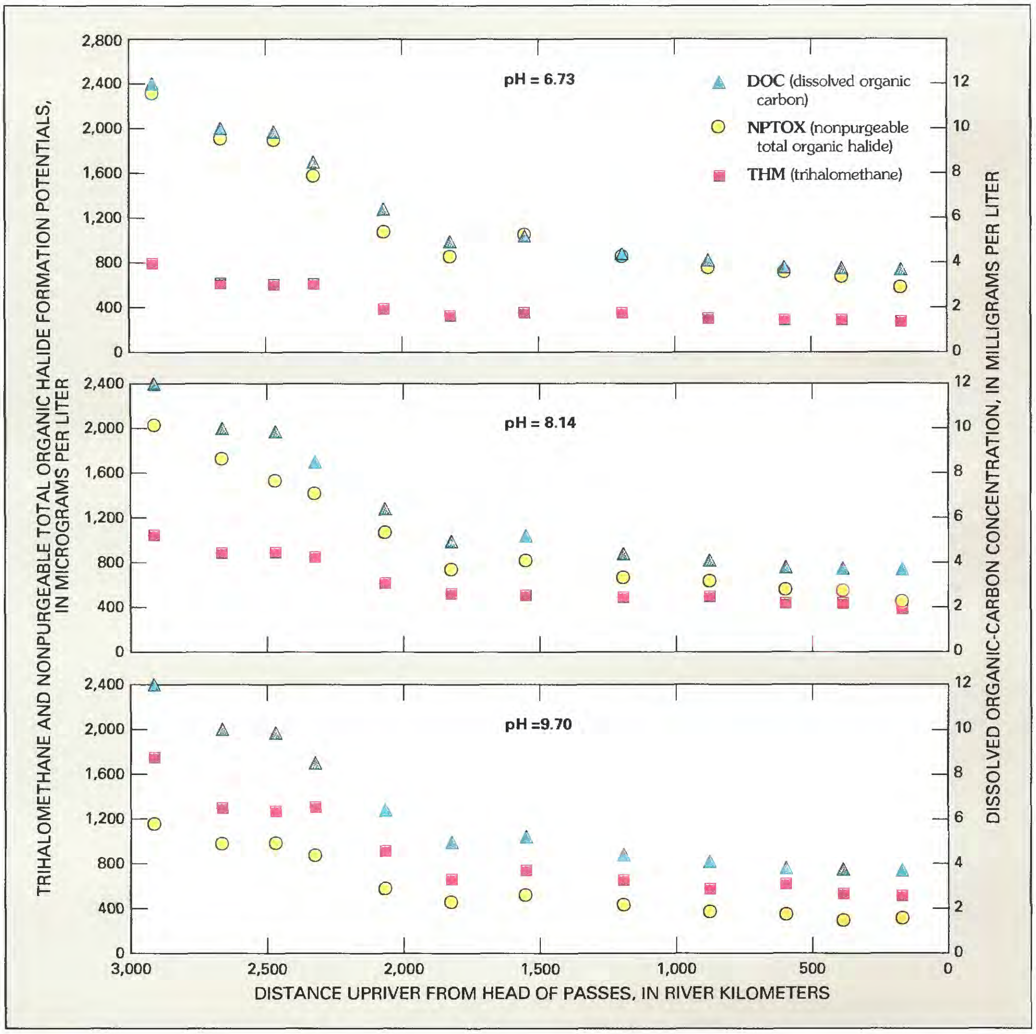

Figure 59 Results obtained in laboratory experiments show the potential for forming trihalomethane (THM) and nonpurgeable total organic halide (NPTOX) compounds during chlorination of waters collected at 12 sites along the Mississippi River during the summer of 1991. Potentials are graphed to show distance of the sampling sites upriver of Head of Passes, Louisiana, with Minneapolis to the left and New Orleans to the right. The graphs show the results of chlorination experiments conducted at three different values of pH: upper graph pH = 6.73 (slightly acid); middle graph pH = 8.14 (moderately alkaline); lower graph pH = 9.70 (strongly alkaline). The concentrations of dissolved organic carbon (DOC), measured at the beginnings of the experiments (shown by the triangles; same values in all three graphs), were greater in the upper-river waters than in the lower-river waters. Potentials of the formation of the toxic compounds generally parallel the DOC concentrations, but the relative importance of THM (squares) and NPTOX (circles) depends heavily on pH. At slightly acid and moderately alkaline pH (upper two graphs), NPTOX compounds form more readily than THM compounds. At strongly alkaline pH (lower graph), THM compounds form more readily than the NPTOX compounds.

potentials for the formation of the NPTOX compounds, were always in excess of the present MCL of 100 µg/L. This conclusion should be tempered by the fact that experimental conditions of initial free-chlorine concentration and reaction time used in these laboratory experiments were such as to maximize the formation of the THM and NPTOX compounds. The large formation potentials observed, however, indicate that care must be exercised in disinfecting river water with chlorine, particularly in water from the Upper Mississippi River.

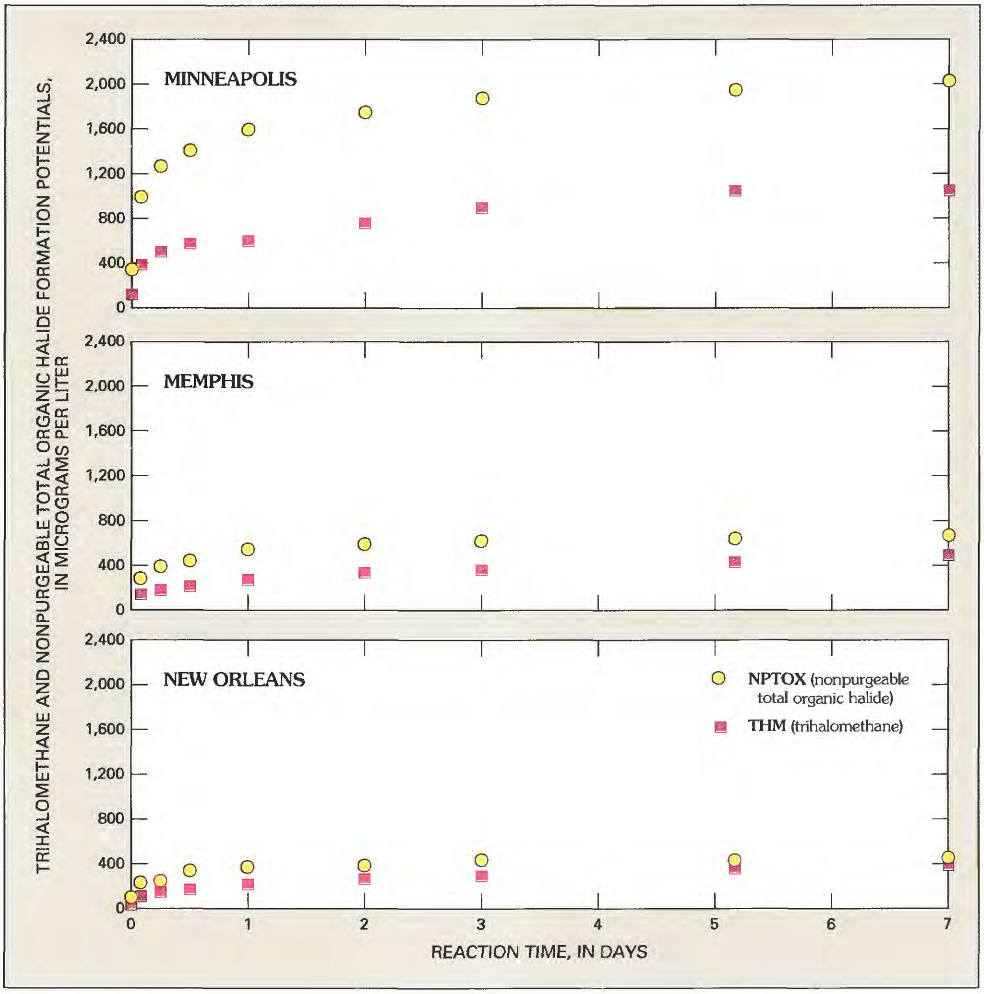

Figure 60 Results obtained in laboratory experiments show that the formation of trihalomethane (THM) and nonpurgeable total organic halide (NPTOX) compounds is initially very fast; the rate of formation decreases after about 1 day; several days are required to reach the maximum concentrations for both the THM and NPTOX compounds. The experiments portrayed in this figure were conducted on waters collected during the summer of 1991 from the Mississippi River at Minneapolis, Memphis, and New Orleans. All three experiments were conducted at a pH of 8.14, which is near the characteristic pH of most untreated waters of the Mississippi River.

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