Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Pesticides in Streams, Streambed Sediment, and Ground Water, 1974-94

By James D. Fallon, Alison L. Fong, and William J. Andrews

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URL:http/ /wwwrvares.er.usgs.gov/nawqa/nawqa_home.html

FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for, and likely consequences, of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Chief Hydrologist

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Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
square mile (mi^2)	2.590	square kilometer
degrees Fahrenheit (F)	(temperature°F – 32)/1.8	degrees Celsius

Pesticide concentrations in water are given in metric units of micrograms per liter (µg/L). Micrograms per liter is a unit expressing the concentration of pesticide in a solution as mass (micrograms) of pesticide per unit volume (liter) of water. One microgram per liter is equivalent to one unit of pesticide in a billion equal units of water. Pesticide concentrations in streambed sediment are given in metric units of micrograms per kilogram (µg/kg). Micrograms per kilogram is a unit expressing the concentration of pesticide sorbed to the sediment as mass (micrograms) of pesticide per unit mass (kilogram) of sediment. One microgram per kilogram is equivalent to one unit of pesticide in a billion equal units of sediment, or one part per billion.

Acronyms used in this report:

MCES—Metropolitan Council Environmental Services
MDA—Minnesota Department of Agriculture
MDH—Minnesota Department of Health
MPCA—Minnesota Pollution Control Agency
NASQAN—National Stream Quality Accounting Network
NAWQA—National Water-Quality Assessment
STORET—Storage and Retrieval water-quality data base maintained by the U.S. Environmental Protection Agency
TCMA—Twin Cities metropolitan area
USACE—U.S. Army Corps of Engineers
USEPA—U.S. Environmental Protection Agency
USGS—U.S. Geological Survey
WDNR—Wisconsin Department of Natural Resources

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ABSTRACT

Available data on pesticides in streams, streambed sediment, and ground water from Federal, state, and local agencies are reviewed for part of the Upper Mississippi River Basin study unit of the National Water-Quality Assessment Program. The analysis focuses on a smaller study area encompassing 19,500 square miles that includes the Upper Mississippi River Basin from Lake Pepin upstream to sampling stations on the Mississippi River near Royalton, Minnesota, and the Minnesota River near Jordan, Minnesota, and the entire drainage basins of the St. Croix, Vermillion, and Cannon Rivers. Assessment is generally restricted to two groups of pesticides—the most frequently detected herbicides and organochlorine insecticides—although pesticides rarely or never detected are noted.

Herbicides, including alachlor, atrazine, cyanazine, or metolachlor, were detected in every stream sampled except the Kettle River. Streams draining row-crop areas had the most herbicide detections. Atrazine was the most widely detected herbicide, with detections in all streams sampled except the Kettle River. Concentrations of atrazine, metolachlor, and cyanazine were greatest in July and detectable most of the year at very low (parts-per-trillion) concentrations. The herbicides EPTC and trifluralin were never detected, although they were used in amounts equal to or greater than those detected, reflecting the fact that some herbicides are less persistent than others. A small urban stream draining part of the Lake Harriet Watershed in Minneapolis, Minnesota, contained substantial concentrations of pesticides as well. Eighty-five percent of runoff events sampled in this entirely urbanized watershed had detections of herbicides commonly used for residential purposes, and 43 percent of the events had detections of alachlor, atrazine, cyanazine, or metolachlor—herbicides used predominantly for agriculture. Pesticide concentrations in urban runoff remained well above detection limits throughout the summer, indicating repeated applications of pesticides.

Selected organochlorine insecticides, banned since the 1970's, still were detected in recent streambed-sediment samples. Three insecticides, 4,4'-DDT, heptachlor, and lindane, and their metabolites account for almost two-thirds of the organochlorine insecticides detected. Organochlorine insecticides were detected more frequently in streambed sediment than in streamwater. Detections in both phases were most frequent within or downstream of the Twin Cities metropolitan area, indicating that most of these insecticides originated from the Twin Cities metropolitan area.

The most frequently detected herbicides in ground water were the same as those frequently detected in streams. Most detections were found in the sand and gravel aquifers underlying agricultural areas, including the Anoka Sand Plain and Bonanza Valley. Atrazine, deethylatrazine, and deisopropylatrazine were detected most frequently. Detection frequencies of atrazine were extremely variable among the various agencies, ranging from 0 to 66.7 percent, probably as a result of different sampling purposes, well locations, and detection levels. Atrazine and atrazine metabolites were the only pesticides detected in bedrock aquifers, with detections found mainly in the agriculture-dominated southeastern part of the study area where bedrock commonly outcrops near the surface. Thus, most detections of herbicides in ground water were found in environmental settings where ground water is vulnerable to contamination.

Atrazine was the only pesticide that equaled or exceeded a maximum contaminant level (of 3.0 micrograms per liter) for drinking water. Two stream samples from a small urban watershed in Minneapolis had atrazine concentrations of 3.6 and 3.8 micrograms per liter, and one ground-water sample had a concentration of 3.0 micrograms per liter. Trace concentrations (less than 0.06 micrograms per liter) of the organochlorine insecticides chlordane, dieldrin, endrin, and heptachlor exceeded chronic freshwater-quality criteria in stream samples from the Mississippi, Minnesota, St. Croix, and Vemillion Rivers in 1981 and 1990.

INTRODUCTION

In 1991, the USGS began full implementation of the NAWQA. Major activities of the NAWQA take place within a set of hydrologic systems called study units. Study units comprise diverse hydrologic systems of river basins, aquifer systems, or both. The Upper Mississippi River Basin NAWQA study unit, which encompasses an area of about 47,000 mi^2, includes the entire drainage area of the Mississippi River Basin upstream from the outlet of Lake Pepin (fig. 1). The study unit includes areas of rich agricultural lands, forests, wetlands, prairies, and a major urban area. Water quality of the Upper Mississippi River, which contains the headwaters of the largest river in the Nation, is of concern due to reliance on streamwater for water users, for a source of drinking water by major municipalities in the basin, and for good quality water to maintain the health of regional aquatic ecosystems. Ground water is the principal source of potable water to smaller municipalities and domestic water systems in the study unit. Ground water in unconfined sand and gravel aquifers of glacial and alluvial origins is particularly susceptible to degradation from human activities at the land surface. Ground water in these sand and gravel aquifers and in adjoining bedrock aquifers is typically hydraulically connected to rivers throughout the study unit. These features make the Upper Mississippi River Basin study unit an essential component of a comprehensive national assessment of water quality.

The first phase of investigation in the study unit, lasting from 1994–99, is focused principally on the effects of the seven-county TCMA on water quality and aquatic ecosystems. As a result, this retrospective analysis focuses on a smaller study area, encompassing 19,500 mi^2 of the eastern portion of the Upper Mississippi River Basin study unit (fig. 1). This study area includes the part of the Upper Mississippi River Basin from Lake Pepin upstream to sampling stations on the Mississippi River near Royalton, Minnesota, and the Minnesota River near Jordan, Minnesota, where long-term water-quality data are available, and the entire drainage basin of the St. Croix River. Most of the TCMA, with a population of about 2,290,000, is included in the south-central part of the study area.

Pesticides are used throughout the Upper Mississippi River Basin study unit—especially in agricultural and urban areas. Once applied, a small percentage of pesticides often enter streams in runoff (Thurman and others, 1992), in ground-water discharge (Squillace and others, 1993), in atmospheric deposition from aerosols and rainfall (Buser, 1990; Majewski and Capel, 1995), and in ground water through infiltration. Pesticides in streams and ground water are a concern because low concentrations of these compounds can have toxic, mutagenic, or carcinogenic effects in aquatic biota and humans (U.S. Environmental Protection Agency, 1994; Patlak, 1996). Very low concentrations of many pesticides in water are suspected of, or are known to, disrupt the endocrine systems of animals and humans, thereby interfering with their hormonal, sexual, and reproductive viabilities (Colborn and Clement, 1992).

Purpose and Scope

This report describes the presence and distribution of the most frequently detected pesticides in streams, streambed sediment, and ground water in the study area from 1974–94. Summaries are presented for selected pesticides in stream, streambed-sediment, and ground-water samples collected by the MCES, MDA, MDH, MPCA, USACE, USGS, and WDNR, applying to periods for which the most data were available. This report also summarizes estimated quantities of the most used herbicides and insecticides for agriculture in the Upper Mississippi River Basin study unit and describes possible relations between the pesticide use and the presence of these pesticides in streams and ground water. This report focuses on synthetic-organic herbicides and insecticides because these pesticides are of concern to environmental and human health (Nowell and Resek, 1994). Furthermore, synthetic-organic pesticides can be distinguished from other sources in the environment because they are used exclusively as pesticides, unlike inorganic pesticides such as copper or arsenic. Insecticides and nematicides collectively are referred to as insecticides in this report.

Many pesticides used in the study unit were either not analyzed or not detected in water or in sediment. This report focuses on the most frequently analyzed and detected herbicides, insecticides, and related metabolites and isomers in water and streambed sediment. For brevity, metabolites and isomers of pesticides also are referred to as pesticides. Assessment is restricted to two groups of pesticides—the most frequently detected herbicides and most frequently detected insecticides. The most frequently detected herbicides for streams and ground water include atrazine, deethylatrazine, deisopropylatrazine, alachlor, cyanazine, metolachlor, and simazine. The most frequently detected insecticides for streams and streambed sediment include aldrin, chlordane, 4,4'-DDT, 4,4'-DDD, 4,4'-DDE, dieldrin, endrin, γ-HCH (or lindane), α- and δ-HCH, heptachlor, heptachlor epoxide, and toxaphene. Fungicides are not included because fungicides were rarely analyzed and were not detected in analyses of samples compiled for this report.

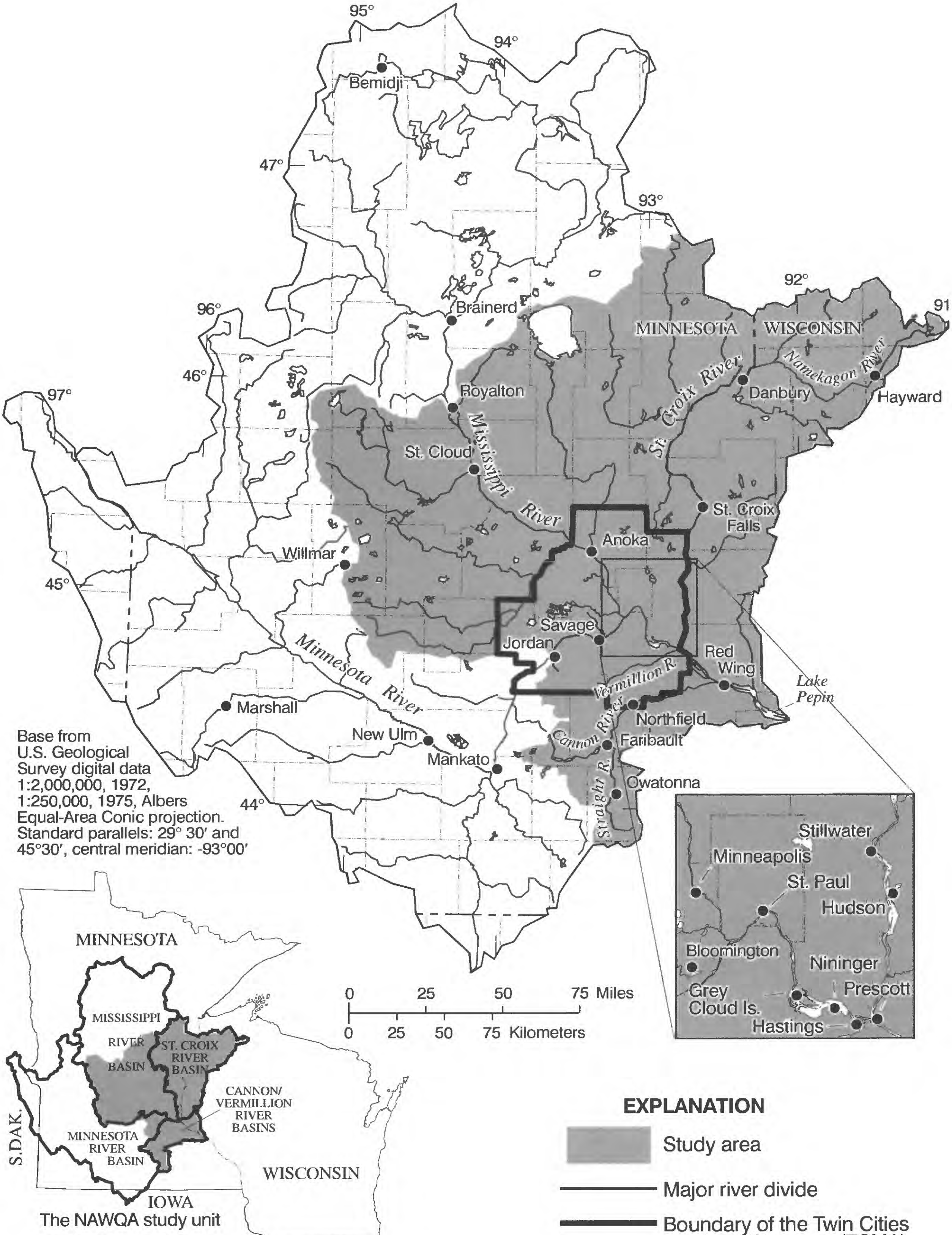

Figure 1.--Location of the study area, selected towns and major cities in the Upper Mississippi River Basin (NAWQA) study unit.

Environmental Setting of the Study Unit

The environmental setting of the Upper Mississippi River Basin study unit is described by Stark and others (1996). A summary here emphasizes the major components of the environmental setting in the study unit that may affect the distribution and transport of pesticides in the study area. Main components include climate, surficial hydrology and runoff, soils, surficial and bedrock hydrogeology, and land cover and land use.

Climate and land cover are probably the two most important factors of the environmental setting affecting the presence of pesticides in streams and ground water. The climate is subhumid continental (Stark and others, 1996). The average number of frost-free days ranges from about 160 days in the south to 100 days in the north (Borchert and Gustafson, 1980). Average annual precipitation ranges from about 22 in. in the western part of the study unit to 32 in. in the eastern part. About three-fourths of the annual precipitation falls during the growing season (Baker and others, 1979). Annual precipitation and potential evapotranspiration are most variable in the west. Runoff is variable but generally is least in the west and greatest in the northeast. Most of the annual runoff occurs in spring and early summer from snowmelt flowing over frozen soils and rains falling on saturated soils. The Upper Mississippi River derives most of its discharge from three major rivers—the Mississippi, Minnesota, and St. Croix—all of which converge in the TCMA (fig. 1).

Land cover generally consists of one or a mix of three types: agriculture, forest, or urban (fig. 2). Agriculture is the dominant land cover in the southwest and (with the categories of agriculture, and agriculture and forest in fig. 2) comprises about 63 percent of the study unit, according to the land-cover classification system of Anderson (1967) and USGS land-use and land-cover data (U.S. Geological Survey, 1990). Mixed deciduous and coniferous forests (forest and woodland, and forest and agriculture, fig. 2) cover about 22 percent, primarily in the northeastern part. Urban and suburban (urban and built-up area, fig. 2) land covers 2 percent of the study unit, primarily in the TCMA. The estimated population of the study unit in 1990 was about 3,640,000, of whom 2,290,000 live in the seven-county TCMA (U.S. Bureau of the Census, 1991). Open water and wetlands cover 13 percent, and other land uses occupy about 1 percent of the study unit.

Croplands comprise about 74 percent of the agricultural land in the study unit (based on 1987 data from Battaglin and Goolsby, 1994). Crops planted, in order of decreasing acreage, include: corn, soybeans, and all hay, wheat, and oats (based on 1993 data from the Iowa Agricultural Statistics, 1994; Minnesota Agricultural Statistics Service, 1994; South Dakota Agricultural Statistics Service, 1994; and Wisconsin Agriculture Statistics Service, 1994). Corn and soybean production dominate most of the west and south, especially the Minnesota River Basin, whereas dairy regions in the north and southeast have the greatest percentage of land in oats, hay, and pasture (Paulson, 1994). Distribution of crop types results partly from areal differences in climatic characteristics, including the number of frost-free days and average annual precipitation, which influence the type of crops that can be grown.

Surficial geology consists of a nearly continuous veneer of up to 100 ft of unconsolidated glacial and fluvial deposits on bedrock uplands, and up to 600 ft of deposits in bedrock valleys and in areas of terminal moraine (Schoenberg, 1990). These unconsolidated materials, which were deposited by continental glaciers during the Pleistocene Epoch, progressively thin toward the northeast and southeast (Trotta and Cotter, 1973; Woodward, 1986). Surficial sand and gravel aquifers, which cover about one-third of the study unit, consist primarily of glacial outwash and alluvium (fig. 3). The most extensive outwash-covered plains are located in east-central Minnesota (the Anoka Sand Plain) and in northwestern Wisconsin. Water in sand and gravel aquifers is generally of acceptable quality for domestic, industrial, and irrigation purposes.

Soils formed on the glacial deposits and alluvium (fig. 3) that cover most of the study unit range from heavy, poorly drained clayey soils on glacial till to light, well-drained sandy soils on glacial outwash and alluvium. Crop production is greater in poorly drained soils that are artificially drained than in unaltered, poorly drained soils; so much of the poorly drained soil has been artificially drained and ditched, especially in the southwestern part. Leach and Magner (1992) estimated that, in the Minnesota River Basin where artificial drainage is greatest, 80 percent of the wetlands have been drained.

Bedrock aquifers are the most commonly used sources of ground water, due to the larger yields generally obtainable from wells completed in these aquifers. The principal bedrock aquifers in the study unit consist of sandstones and dolomites in the Hollandale Embayment (Delin and Woodward, 1984), a hydrogeologic system containing up to 1,200 ft of sedimentary strata that underlie the TCMA (fig. 4). This bedrock hydrogeologic system can be divided into four major aquifers, in descending order: the St. Peter, Prairie

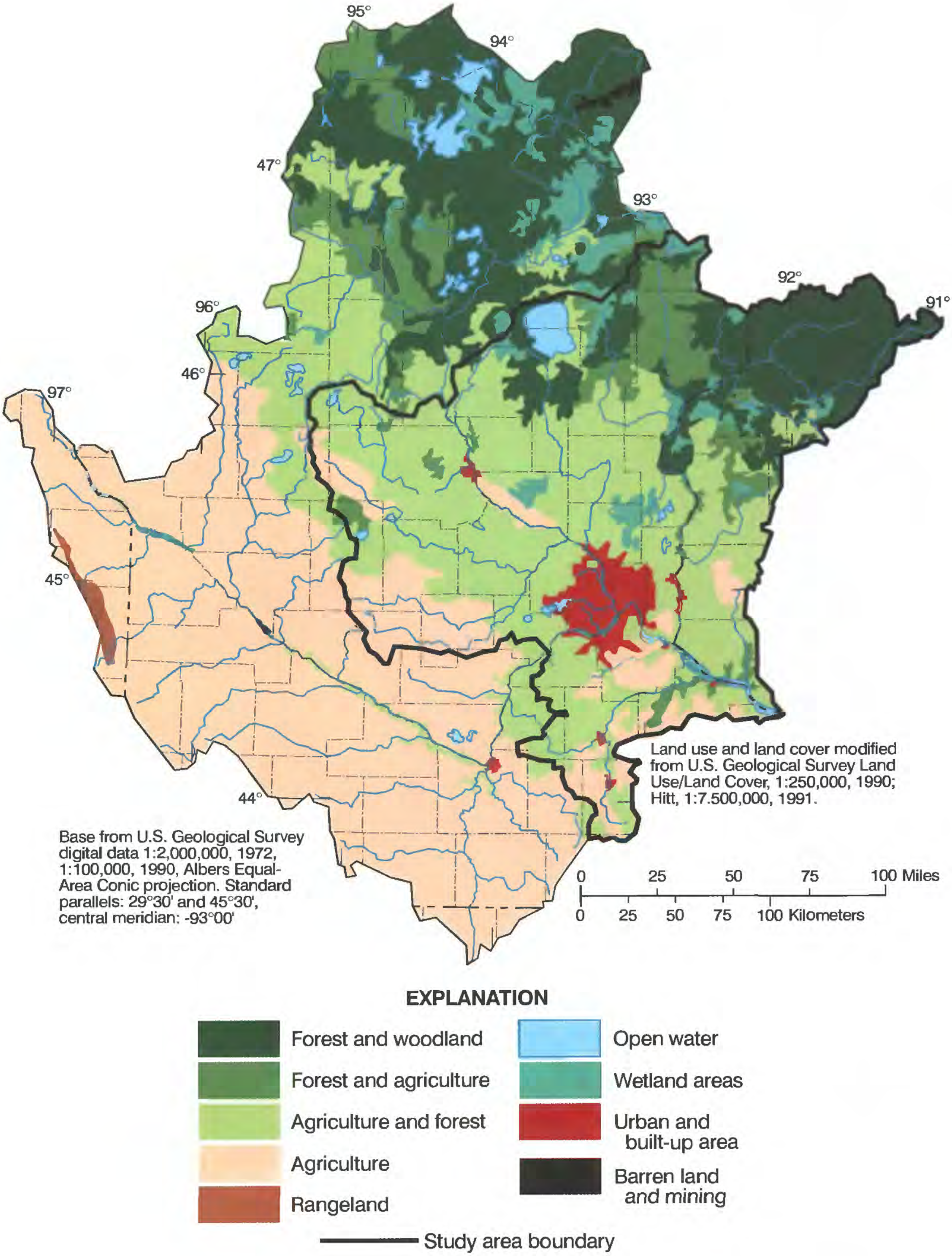

Figure 2.--Land use and land cover in the Upper Mississippi River Basin study unit.

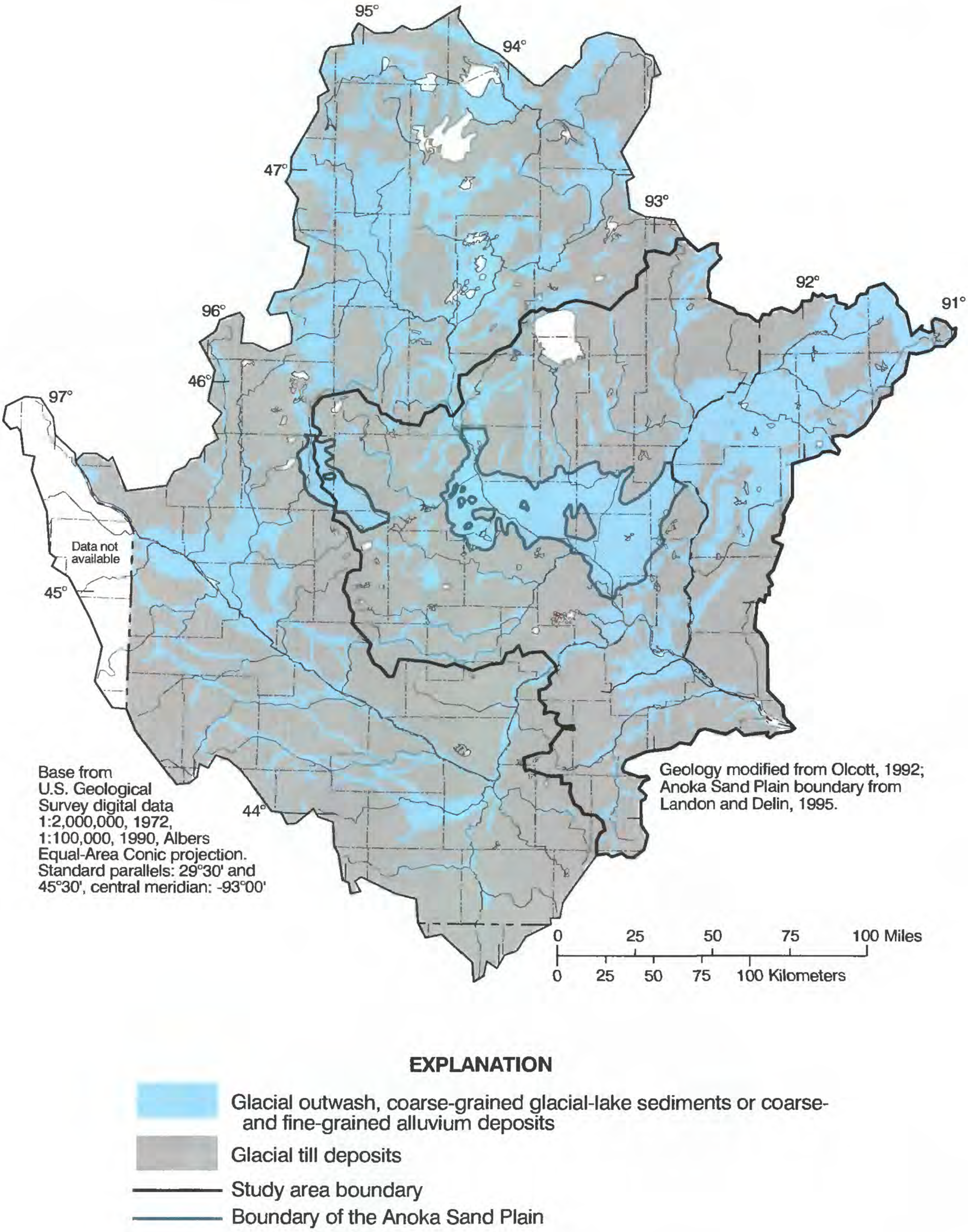

Figure 3.--Surficial geology in the Upper Mississippi River Basin study unit.

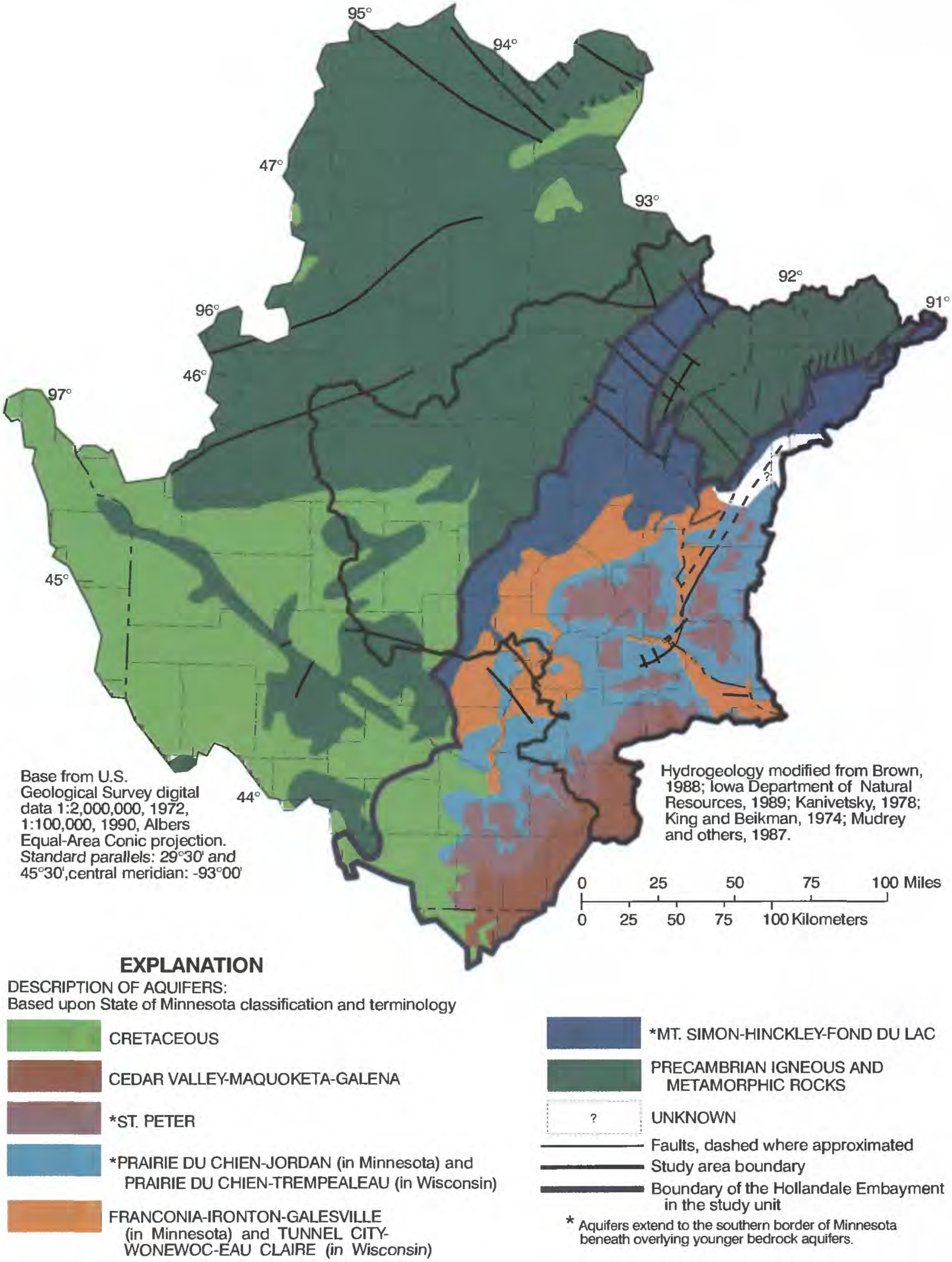

Figure 4.--Bedrock hydrogeology of the Upper Mississippi River Basin study unit.

du Chien-Jordan (Prairie du Chien-Trempeleau in Wisconsin), Franconia-Ironton-Galesville (Tunnel City-Wonewoc-Eau Claire in Wisconsin), and the Mt. Simon-Hinckley-Fond du Lac (Adolphson and others, 1981). Aquifers are separated by confining units described in the stratigraphic column by Stark and others (1996). In some western and northern parts of the study unit, where productive sand and gravel aquifers are not present, sandstones and fractured igneous and metamorphic rocks supply limited quantities of water (Anderson, 1986; Woodward and Anderson, 1986). Bedrock aquifers in the southeast are more susceptible to contamination by pesticides because these aquifers are unconfined, subcrop beneath thin, permeable unconsolidated deposits, and receive the greatest amount of recharge.

Pesticide Use in the Study Unit

Agriculture accounts for three-fourths of pesticide use nationally (Aspelin, 1994), so most estimates of pesticide use focus on agriculture. Pesticide-use data for agriculture in the study unit were computed from 1987 estimates of pesticide application rates used on crops (Gianessi and Puffer, 1991and 1992) and acres of crops planted by county. The herbicides and insecticides used in greatest quantities include, in order of decreasing use, the herbicides EPTC, alachlor, cyanazine, metolachlor, trifluralin, acetochlor, atrazine, and 2,4-D and the insecticides carbofuran, chlorpyrifos, aldicarb, fonofos, and methyl parathion. Herbicide use is about 28 times greater than insecticide use in agriculture because herbicides generally are applied at greater quantities, more frequently, and to broader areas than insecticides. Classes of pesticides, estimated quantities applied, and the crops they are applied to are presented in table 1 (tables 1–18 are in the Supplemental Information section at the back of the report).

The types of herbicides used in agriculture vary across the study unit. Most herbicides are used in row-crop agriculture, especially for corn and soybeans. The spatial distribution of atrazine use, a herbicide used for corn, is shown in figure 5a. Atrazine use is shown because it is frequently detected in water and because the distribution of atrazine use is similar to other herbicides used for row crops, such as EPTC, alachlor, cyanazine, metolachlor, acetochlor, and 2,4-D. Atrazine use is restricted primarily to agriculture, so little or no atrazine is used in counties with dominant urban or forest land use. The greatest quantities of these herbicides are applied in the southwestern, southern, and eastern parts of the study unit where corn and soybean crop production dominate. Application rates of MCPA, a herbicide used for small grains, but not for corn or soybeans, are shown in Figure 5b. Application rates of MCPA are greatest in the western parts of the study unit because a larger percentage of agricultural land is planted with small grains in these areas.

Herbicide-use data for urban and forested areas of the study unit are limited to local surveys, product registrations, and inferences from national studies. Some herbicides used in urban and forested areas also are used in agriculture. A survey by Creason and Runge (1992) reported that 2,4-D was the most used herbicide in TCMA lawns and gardens and that application rates were similar to those of agricultural areas of Minnesota. These results are consistent with a national study by Whitmore and others (1992) who estimated the number of applications of herbicides made in lawns and gardens. Five of the 15 most used herbicides for agriculture in the study unit also are used in urban environments, according to Whitmore and others (1992) (in order of decreasing number of applications: 2,4-D, glyphosate, dicamba, trifluralin, and pendimethalin; table 1). Herbicide quantities used in forestry are not available, but about 2 percent of forested land in the United States is treated with pesticides annually (Larson and others, 1997). Herbicides registered for use in forest and seed-orchard production in the study unit include 6 of the 15 most frequently used in agriculture: atrazine, 2,4-D, glyphosate, metolachlor, pendimethalin, and trifluralin (Kachadoorian and others, 1995a). Thus, at least four nationally significant herbicides (2,4-D, glyphosate, pendimethalin, and trifluralin) may be used in substantial quantities in agricultural, urban, and forested areas of the study unit.

Insecticide use also varies by land use and location. Application rates for two of the three most used insecticides in agriculture, carbofuran and aldicarb, are shown in figure 6. Geographical differences in the application rate of these two insecticides reflect the different cropping patterns. Carbofuran is used on corn and many produce crops, including potatoes, sweet corn, cucumbers, and strawberries. Use is greatest in the Lower Minnesota River Basin where primarily corn is grown and within and near the TCMA where considerable produce is grown. Aldicarb is used on soybeans, sugar beets, and sweet potatoes and has the greatest application rates in the Minnesota River Basin, where soybeans are grown, and in the extreme northwest, where sugar beets are grown. No urban insecticide-use data are available for the study unit, but 5 of the 10 most frequently used insecticides for agriculture in the study unit also are used in homes and

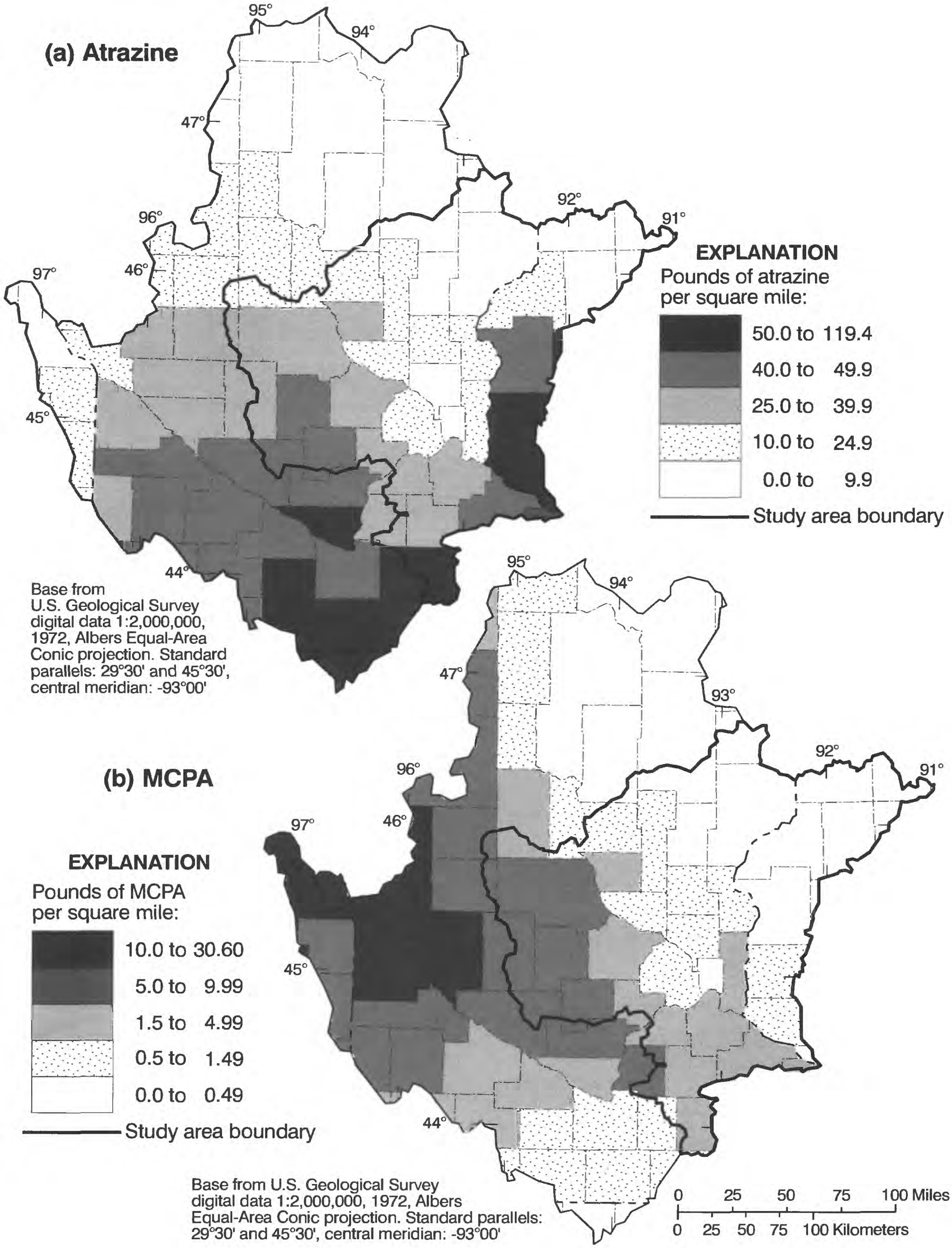

Figure 5.--(a) Atrazine and (b) MCPA use, by county, in the Upper Mississippi River Basin study unit, 1989 (data from Gianessi and Puffer, 1991).

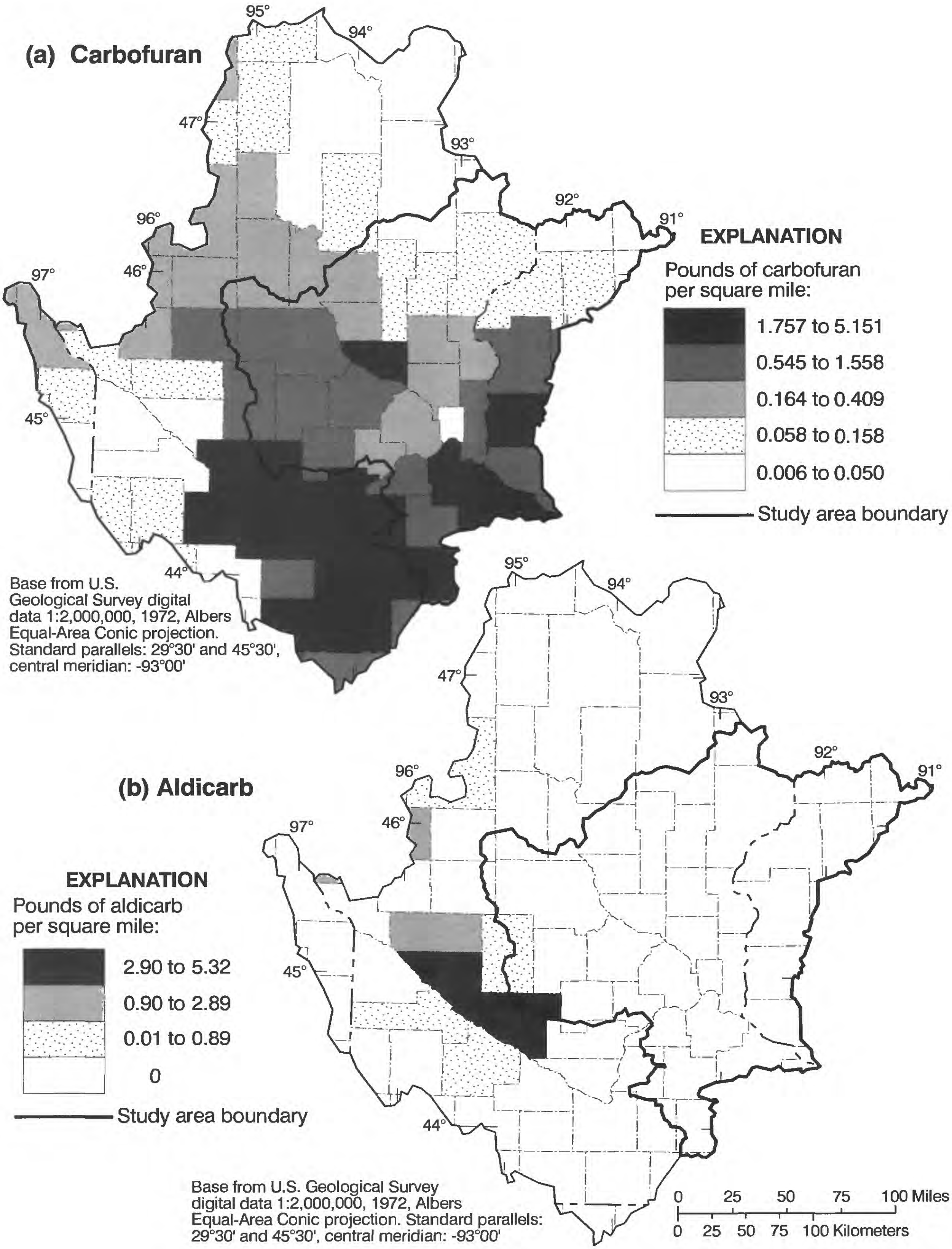

Figure 6.--(a) Carbofuran and (b) aldicarb use, by county, in the Upper Mississippi River Basin study unit, 1989 (data from Gianessi and Puffer, 1992).

gardens nationally, based on data from Whitmore and others (1992). These are, in order of decreasing number of home applications: diazinon, chlorpyrifos, carbaryl, permethrin, and malathion. Insecticides registered for use in forested areas of the study unit include five of the most frequently used insecticides in agriculture (table 1), as well as esfenvalerate, azinphos methyl, dimethoate, naled, and methoxychlor (Kachadoorian and others, 1995b).

In addition to insecticides currently used, a number of organochlorine insecticides were commonly used in the 1950's to 1970's. These pesticides were used primarily in agricultural areas, although some (DDT, chlordane, heptachlor, and lindane) also were used in urban areas to control mosquitoes and termites and to treat lumber (Sine, 1993; Majewski and Capel, 1995). Uses of these pesticides have been restricted or banned because of reduced effectiveness and concern about their environmental toxicity, bioaccumulation, and persistence. In 1966, more than 60 percent of all pesticides used were organochlorines, but use recently has dropped to less than 5 percent (Michael Majewski, U.S. Geological Survey, written commun., 1994).

Data Sources, Review, and Analysis

Sources of data pertaining to pesticides in streams, streambed sediment, and ground water, for this report, include the River Toxics Monitoring Program of the MCES; the MDA; the Safe Drinking Water Program for public water supplies of the MDH; the USEPA's Storage and Retrieval data base, which includes data from the MPCA; the USACE-St. Paul District; the USGS, including the Water Data Storage and Retrieval System data base; and the WDNR.

The data summarized in this report were compiled from paper and electronic data bases. Only the most frequently detected pesticides in the study area are summarized in the text and figures, although lists of all pesticides analyzed, as well as sampling purposes, locations, and methods of collection and analysis, are included in table 2. Except where noted, pesticide analyses from different agencies are summarized separately because sampling purposes, collection methods, sampling periods, analytical methods, detection levels, and pesticides analyzed varied among agencies. No time-trend analyses of pesticide concentrations were included because method detection levels often decreased with time and because of insufficient data.

Agencies collecting stream samples for pesticides include the MCES, MDA, MPCA, and USGS. The MCES was the only agency to regularly sample for organochlorine insecticides in water. Samples were collected from 14 sites on the Mississippi, Minnesota, St. Croix, and Vermillion Rivers during 1981–93. The MPCA and the MDA jointly collected the greatest number of samples for herbicides from 14 sites draining predominantly agricultural areas during May, June, or July 1988–93. Hereinafter, the streamwater samples collected jointly by the MPCA and MDA are referred to as MPCA samples. In a separate study of pesticides in urban storm runoff, the MDA collected runoff samples for herbicides and insecticides from 41 storms during 1992–93 from a storm sewer draining part of the Lake Harriet Watershed in Minneapolis, Minnesota (Wotzka and others, 1994). The USGS sampled 15 sites for herbicides and insecticides between 1975–92. The USGS also used analytical methods that could detect dissolved pesticides at very low concentrations (parts per trillion) at sites on the mainstems of the Mississippi, Minnesota, and St. Croix Rivers.

Streambed-sediment samples were collected by the MCES, MPCA, USACE, USGS, and WDNR and analyzed mostly for organochlorine insecticides. The MCES sampled 12 sites on the Mississippi, Minnesota, St. Croix, and Vermillion Rivers each fall during 1982–85, 1987, and 1988. The MPCA sampled 11 sites on the Straight and Cannon Rivers in 1978. The USACE sampled the longest period (1974–92) and the most extensive reaches of the Mississippi, St. Croix, and Minnesota Rivers within and downstream of the TCMA. Only USACE samples collected from the upper 4 in. of the streambed are included so that the sample methods used were similar to those of other agencies. The USGS sampled five sites from 1975–82 on the Mississippi, Minnesota, and Namekagon Rivers. The USGS also sampled in cooperation with the WDNR from 1991–94 to compare organochlorine-insecticide concentrations in the Mississippi and St. Croix Rivers before and after the flood of 1993 (Sullivan and Moody, 1996). Illustrations of detection frequencies in streambed sediment were made with data combined from agencies to simplify results.

Agencies that sampled ground water for herbicides included the MDA, MDH, MPCA, USGS, and WDNR. The MDA sampled 107 monitoring wells in agricultural areas from 1987–93. The MDH sampled 87 public-supply wells from 1988–94. The MPCA sampled 11 domestic wells during 1988–89. The USGS sampled 227 domestic and monitoring wells throughout the Minnesota part of the study area from 1983–94. The WDNR sampled 156 domestic and public-supply wells in the Wisconsin part of the study area from 1988–94. The USGS and WDNR also analyzed for triazine herbicides using enzyme-linked immunosorbent assay, or immunoassay, techniques. Pesticide concentrations determined by immunoassay are semi-quantitative because these methods often cannot distinguish pesticides with similar molecular structures. For this reason, results of triazine concentrations determined by immunoassay are summarized separately.

The frequency that individual wells were sampled varied widely, so only data from the last sample collected from each well were included to avoid overweighting data from more frequently sampled wells. This method also is more representative of recent ground-water quality. Analyses from wells with insufficient or erroneous aquifer documentation were excluded from the data. Data were grouped by agency and by type of aquifer sampled—bedrock or sand and gravel. Herbicide data were not grouped together for all agencies because of different sampling methods, different detection limits, and statistical tests of detection frequencies that indicated the data sets were not similar. Data from all bedrock aquifers were summarized together for each agency because of the limited number of samples from individual aquifers sampled by each agency. Sand and gravel aquifers were not subdivided into surficial or buried (confined by clay) aquifers because buried aquifers may not be truly confined, but rather may be overlain by discontinuous clay or till lenses, and because only two agencies (MDA and MPCA) used this subdivision. Aquifer designations for wells sampled by the USGS in Minnesota and the MDH were made by matching unique well numbers in the Minnesota Geological Survey's County Well Index data base, which contained aquifer information. Samples collected by the MDH are sometimes blended samples from wells in well fields, so information on exact well depth was not always available. Well logs were examined to determine aquifer designations for wells sampled by the WDNR.

Acknowledgments

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PESTICIDES IN STREAMS, STREAMBED SEDIMENT, AND GROUND WATER

Several of the most frequently used pesticides in the Upper Mississippi River Basin study unit have been detected in streams, streambed sediment, and ground water in the study area. Herbicides were detected most in streams and ground water, whereas organochlorine insecticides were frequently detected in streambed sediments.

Streams

Stream samples for pesticide analyses were collected by four agencies: the MCES, MDA, MPCA, and USGS (fig. 7, tables 3–6; site numbers on fig. 7 correspond with site numbers in tables 3–6). Stream samples were collected by the MPCA during the spring and summer and analyzed for herbicides, insecticides, and fungicides (table 3). The group of pesticides analyzed included 8 of the 15 most used herbicides, 6 of the 10 most used insecticides and the second most used fungicide for agriculture in the study unit. The most frequently detected pesticides were the herbicides alachlor, atrazine, cyanazine, and metolachlor, which are applied predominantly to corn and soybeans (table 1); and deethylatrazine, a metabolite of atrazine. No insecticides or fungicides were detected. Herbicide concentrations were below maximum contaminant levels established by the USEPA (1994). Although many of the most used herbicides were detected, others were absent. EPTC, for example, was the most used herbicide in the study unit, but was not detected. Detections are probably related to pesticide class, because the five pesticides detected were acetanilide or triazine herbicides, while none of the other classes were detected. Acetanilides and triazines generally persist longer and are easier to analyze for than many of the other pesticides currently used (Lartiges and Garrigues, 1995). Also, EPTC may be incorporated into the soil.

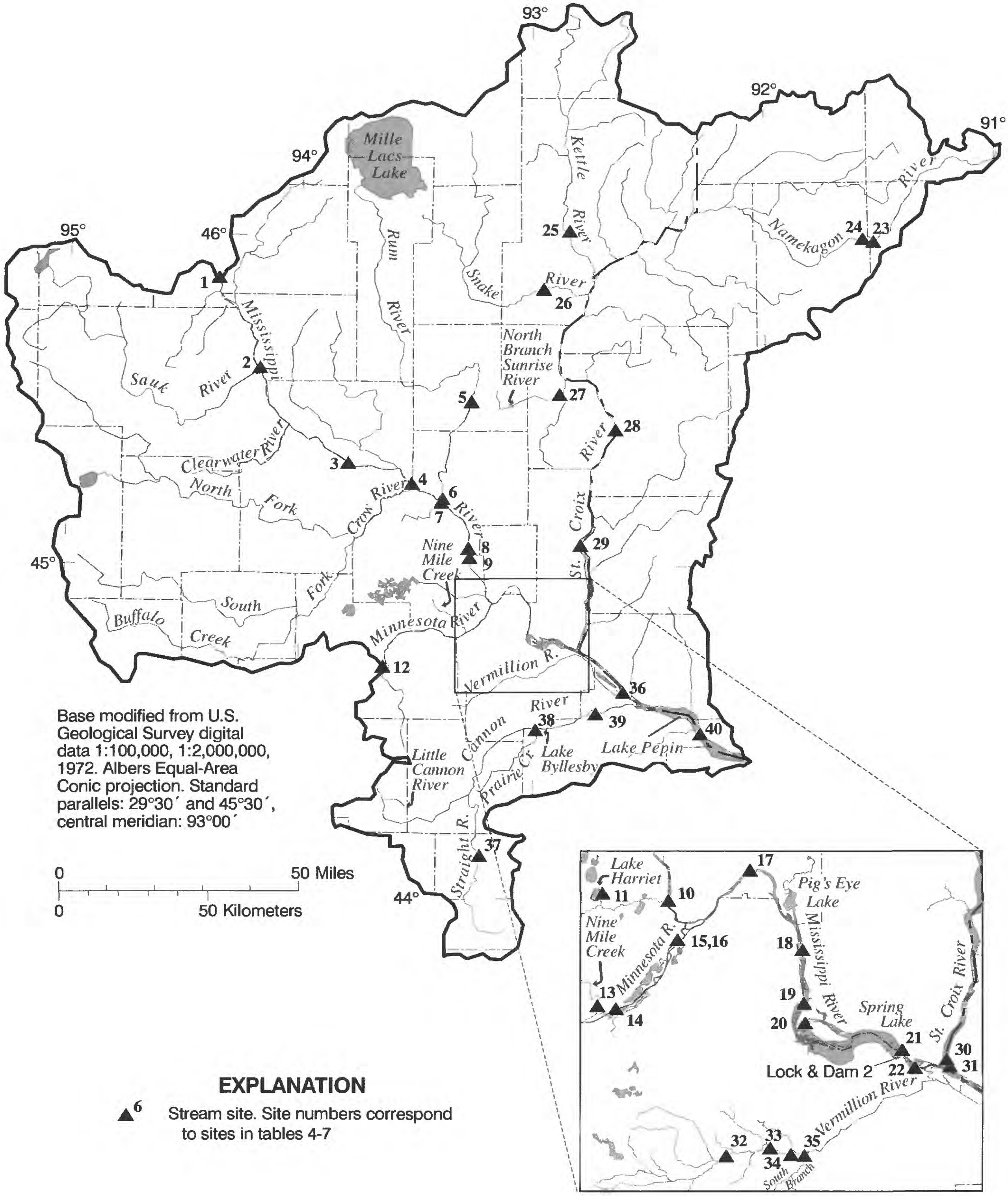


Figure 7.--Locations of stream sites sampled for pesticides by the Metropolitan Council Environmental Services, the Minnesota Department of Agriculture, the Minnesota Pollution Control Agency, and the U.S. Geological Survey, in the study area.

Atrazine was the most widely detected pesticide in samples analyzed by the MPCA, with detections in all streams sampled except the Kettle River (fig. 8). Atrazine was detected in 44 percent of all samples, compared to 23 percent for cyanazine and metolachlor, 17 percent for alachlor, and 6 percent for deethylatrazine (the detection limit for deethylatrazine was 0.40–0.48 μg/L higher than other herbicides). Similarly, atrazine was detected at the most sites (13), followed by cyanazine and metolachlor (9 sites each), alachlor (8 sites), and deethylatrazine (5 sites). The Minnesota and Cannon Rivers had the greatest number of detections of all herbicides, followed by the Sauk, Straight, and Crow Rivers. Detections of these herbicides are related to land use, as the areas where these pesticides were detected most frequently correspond to areas of greatest agricultural intensity.

Pesticide concentrations in streams are often greatest in summer during the application season. The herbicides detected generally are applied immediately before or after crops emerge. The MPCA data indicate when these herbicides are most vulnerable to being transported by runoff into streams. Figure 9 shows the monthly distribution of atrazine concentrations at all sites for May, June, and July. Atrazine, metolachlor, and cyanazine concentrations (median and peak) were lowest and varied least in May and were greatest in July. Alachlor concentrations were greatest in June, and alachlor was detected only once in July. Although no samples were collected during other months, these 3 months of the growing season generally have been shown to produce the greatest herbicide concentrations in streams (Schottler and others, 1994). July also represents the period of greatest annual streamflow variability (Stark and others, 1996), so the amount of herbicides transported by streams in July can vary greatly.

The MPCA data may not represent the maximum annual herbicide concentrations. Streams were sampled by the MPCA under base-flow conditions or more than 1 day after streamflow peaks, as figure 10 shows for atrazine concentrations in the Crow River during 1991–93. Studies of herbicide transport have found that annual maximum herbicide concentrations generally coincide with the first significant runoff event following application (Baker and Richards, 1990; Goolsby and Battaglin, 1993), then decrease through successive streamflow peaks. Herbicide concentrations in the MPCA samples probably do not represent maximum concentrations for these months because samples were not collected near streamflow peaks.

A study by the MDA (Wotzka and others, 1994) investigated the types and quantities of pesticides, including herbicides and insecticides, detected in urban storm runoff (table 4). Runoff samples were collected by automatic sampler from a storm sewer draining part of the Lake Harriet Watershed in Minneapolis, Minnesota. Eighty-five percent of the runoff events sampled had detections of 2,4-D, dicamba, MCPA, or MCPP—herbicides commonly used for lawn and turf care in residential areas. Forty-three percent of the runoff events sampled had detections of herbicides primarily restricted to agricultural uses, albeit at lower concentrations, including alachlor, atrazine, cyanazine, and metolachlor. Concurrent analyses of pesticides in rain samples collected by Wotzka and others (1994) suggested that concentrations of these agricultural herbicides (alachlor, atrazine, cyanazine, and metolachlor) were imported to the watershed by atmospheric deposition.

Total mean concentrations (the sum of the mean concentration of each pesticide in a runoff event) in the urban runoff samples ranged from 1.0 to 70 μg/L and were greatest during summer months. Concentrations remained one to two orders of magnitude greater than the 0.2-μg/L detection limit throughout the summer. Wotzka and others (1994) reasoned that concentrations remained high for a long period in urban runoff because pesticides are applied more frequently and for a longer period in urban areas than in agricultural areas.

Pesticide concentrations previously described were determined from samples collected from May through September, which coincides with the growing season when most pesticides are applied. Analyses of samples from the USGS indicate that many herbicides are detectable at low-level (parts-per-trillion) concentrations after the growing season (table 5). Thirteen of the 25 pesticides analyzed from samples collected in August and October 1991 and April 1992 were detected in the Minnesota, Mississippi, and St. Croix Rivers. Atrazine and deethylatrazine were detected in every sample. Ratios of deethylatrazine-to-atrazine concentrations in samples collected ranged from 0.8–1.0 in April 1992, which Thurman and others (1992) suggest is indicative of atrazine applied the year before. This indicates that some herbicides may persist at low concentrations for extended periods. Besides atrazine, other herbicides also were detected after the growing season, although concentrations were generally lower and persistence was shorter. All concentrations were below applicable drinking-water standards and freshwater-quality criteria.

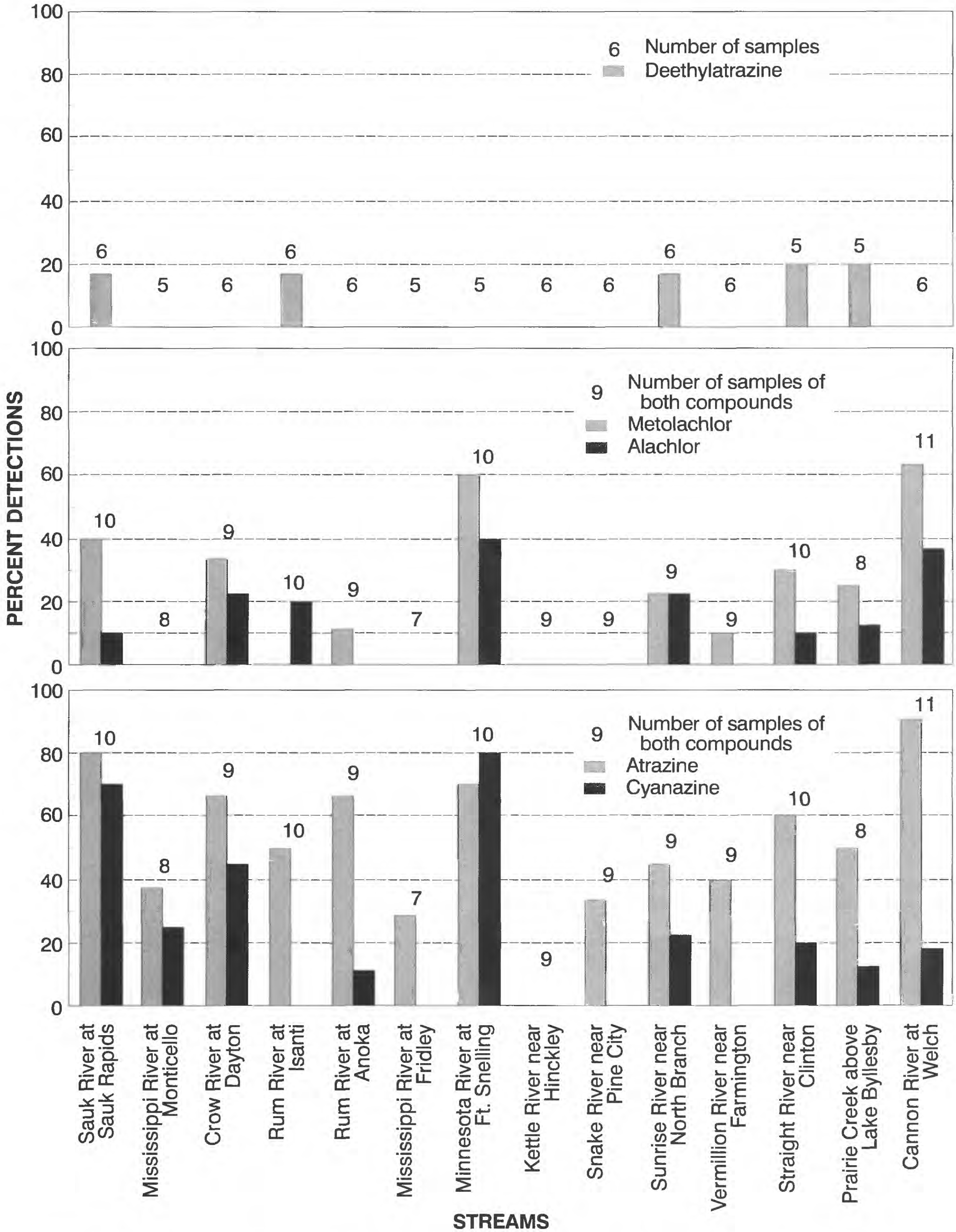


Figure 8.--Detection frequencies for herbicides in Minnesota streams sampled by the Minnesota Pollution Control Agency and analyzed by the Minnesota Department of Agriculture, in the study area, May-July 1988-93.

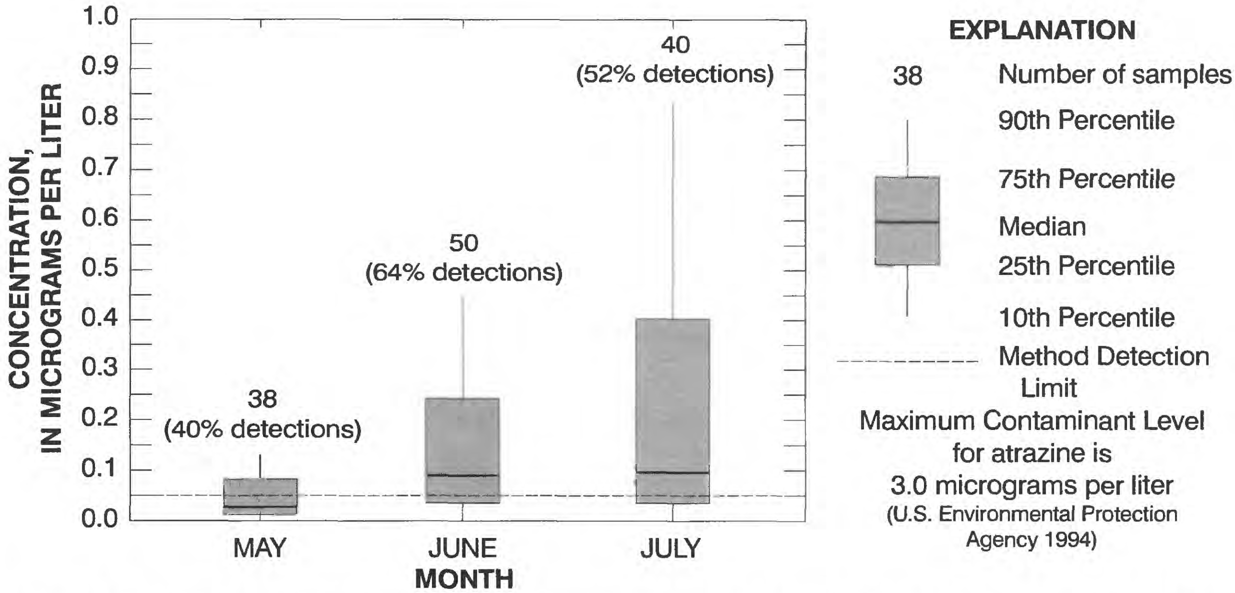


Figure 9.--Atrazine concentrations in streams sampled by the Minnesota Pollution Control Agency and analyzed by the Minnesota Department of Agriculture, in the study area, May-July 1988-93.

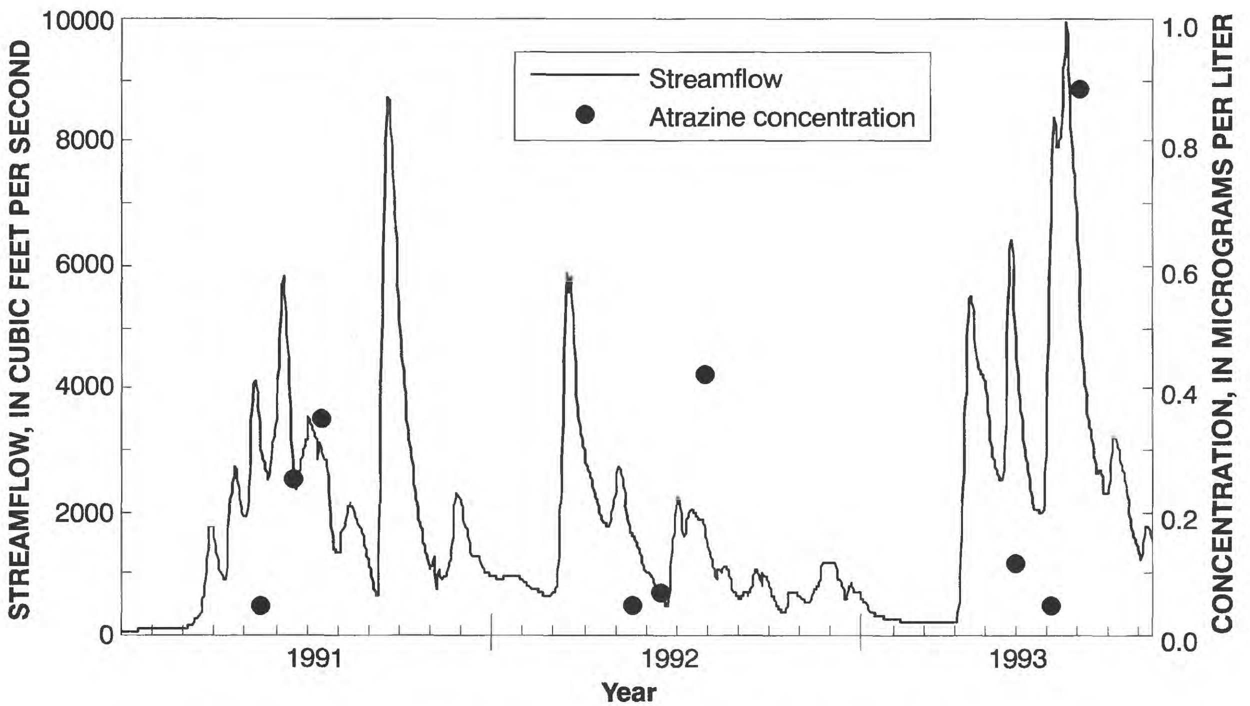


Figure 10.--Atrazine concentrations and streamflow in the Crow River, 1991-93.

Only the MCES routinely analyzed stream samples for organochlorine insecticides (table 6, fig. 11). Organochlorine insecticides are hydrophobic, so only a small fraction of these insecticides would be expected in the dissolved phase in water. The MCES analyses were of unfiltered water samples, so some of the insecticides detected may have been sorbed to suspended sediment in the samples. Six insecticides were detected one or more times, each at concentrations less than 0.06 µg/L (chlordane, endrin, dieldrin, γ-HCH or lindane, α-HCH, and heptachlor). Seventy percent of the insecticides were detected in 1981, the first year of analysis. The USEPA's chronic ambient water-quality criteria for protection of aquatic life (Nowell and Resek, 1994) were exceeded 15 times for concentrations of chlordane, dieldrin, endrin, and heptachlor (table 6). Criteria were exceeded on the Mississippi River from Anoka to Lock and Dam 3, the Minnesota River, the St. Croix River, and the Vermillion River. Criteria were exceeded 10 times in 1981 and most recently in 1990 on the Vermillion River. The most organochlorine insecticides were detected at the three sites in the TCMA on the Mississippi River upstream of the Minnesota River. The greater detection frequency in the Mississippi River upstream of the Minnesota River suggests that most of the insecticides detected originated from the TCMA.

Streambed Sediment

Streambed-sediment samples for organochlorine insecticide analyses were collected by five agencies: the MCES, MPCA, USACE, USGS, and WDNR (fig. 12, tables 7–11; site numbers on fig. 12 correspond with site numbers in tables 7–11). Most samples were collected in the late 1970's and early 1980's when many organochlorine insecticides were banned or restricted from use in the United States.

Figure 13 shows detection frequencies of the 13 most frequently detected insecticides in samples collected by all agencies. Three insecticides (4,4'-DDT, heptachlor, and γ-HCH) and their metabolites or isomers (4,4'-DDD, 4,4'-DDE, heptachlor epoxide, α-HCH, and δ-HCH) account for almost two-thirds of the number of detections. The insecticide 4,4'-DDT and metabolites 4,4'-DDD and 4,4'-DDE together were the most frequently detected, followed by γ-HCH and two

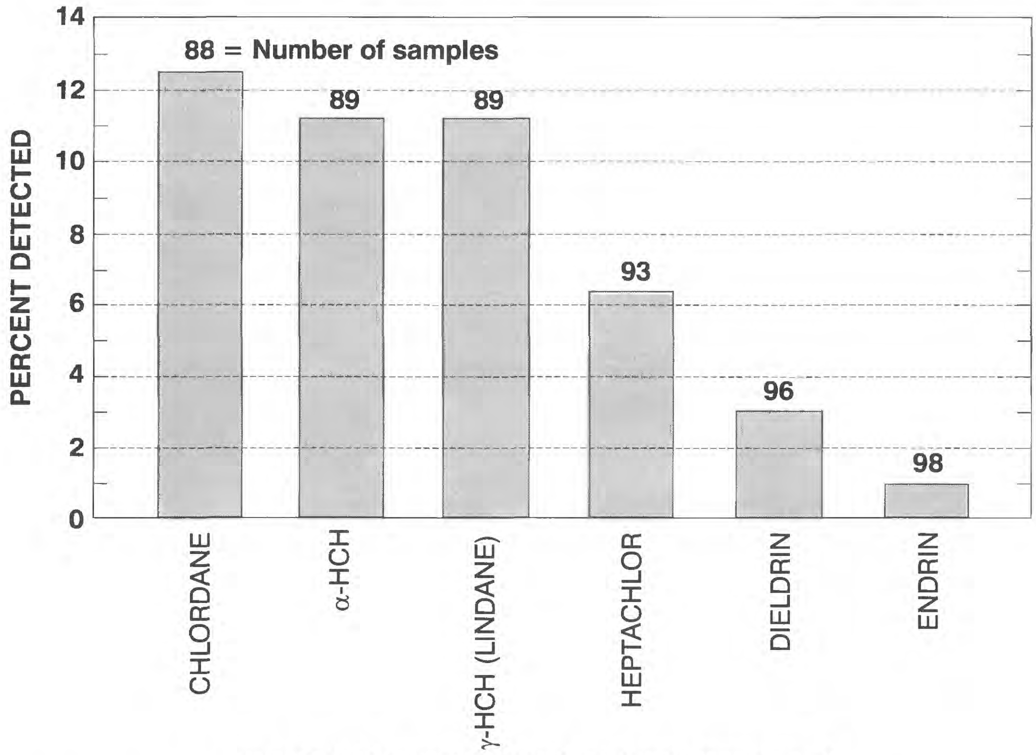


Figure 11.--Detection frequencies of organochlorine insecticides in streams sampled by the Metropolitan Council Environmental Services in the study area, 1981-93.

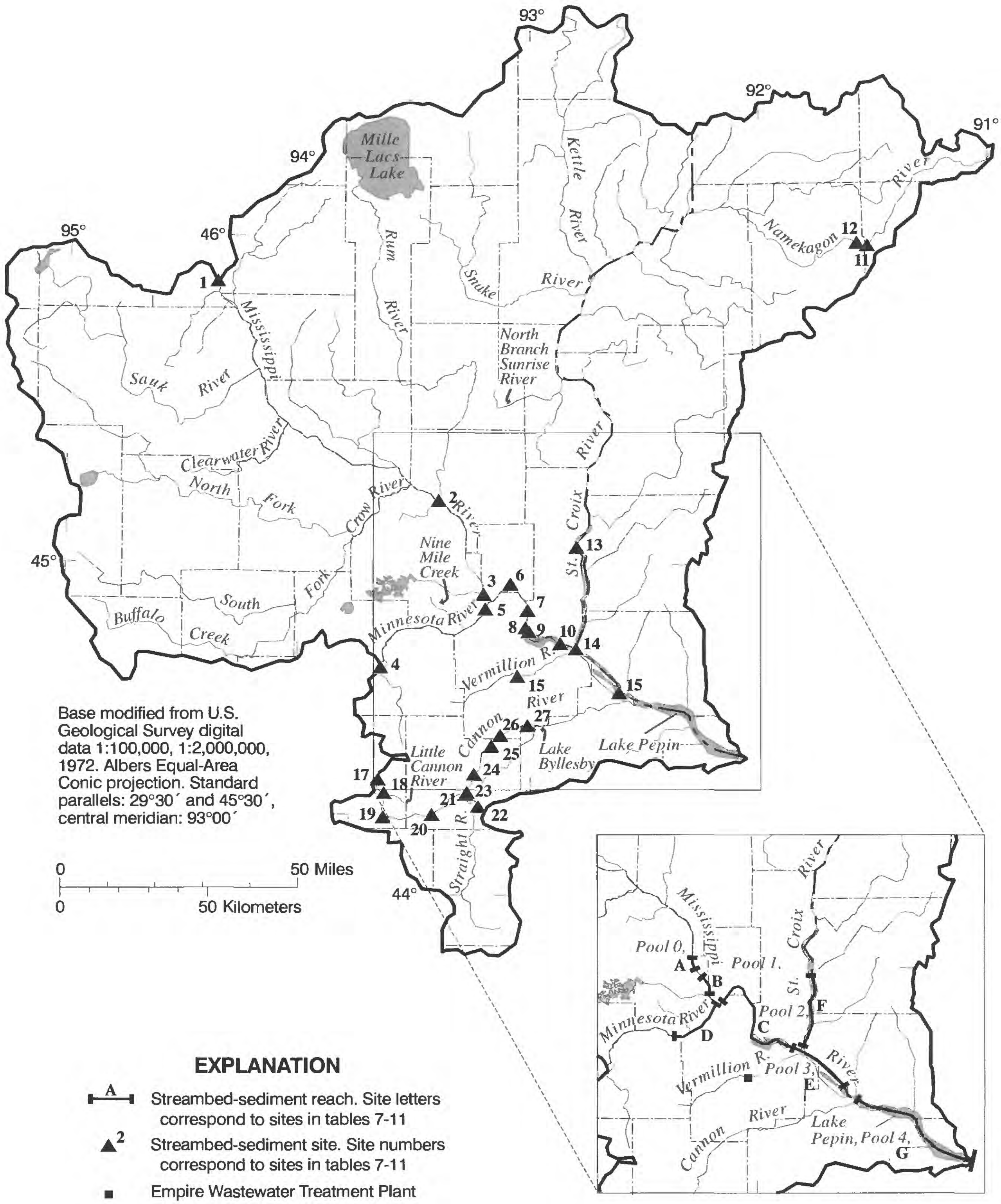


Figure 12.--Locations of streambed-sediment sites and reaches sampled for pesticides by the Metropolitan Council Environmental Services, the Minnesota Pollution Control Agency, U.S. Army Corps of Engineers, the U.S. Geological Survey, and the Wisconsin Department of Natural Resources, in the study area.

isomers, α-HCH and δ-HCH. Chlordane was the most frequently detected parent insecticide. Concentrations in all samples were generally less than 10 μg/kg, but six samples each had an isolated organochlorine concentration greater than 20 μg/kg: 4,4'-DDT (700 μg/kg), chlordane (267 μg/kg), 4,4'-DDE (49 and 50 μg/kg), α-HCH (24 μg/kg), and 4,4'-DDD (21 μg/kg) (tables 7–11). Pool 2 of the Mississippi River had the greatest number of maximum concentrations of each insecticide with eight, followed by the Minnesota River with three (tables 7–11).

To investigate the geographical distribution of detections of organochlorine insecticides, detection frequencies for eight insecticides that were analyzed in common by the MCES, MPCA, USACE, USGS, and WDNR were plotted by stream reach (fig. 14). The percentage of detections shown in figure 14 refers to the total number of detections for all eight compounds divided by the total number of analyses of all eight compounds.

The effects of urban land use on stream quality may be observed by comparing detection frequencies upstream and downstream of the TCMA on the Mississippi, Minnesota, and St. Croix Rivers because the TCMA is located near the confluence of these three rivers. Figure 14 shows that organochlorine insecticides generally were detected less frequently in stream reaches located upstream of the TCMA (the Mississippi River near Royalton and Pool 0; the Minnesota River, river miles 30–15; and the St. Croix and Namekagon Rivers above river mile 16; Pool 0 lies within the TCMA, but most samples were collected upstream of the effects of the TCMA) than downstream (the Mississippi River, Pools 1–4; the Minnesota River, river miles 15–0.3; the St. Croix River, river miles 16–0; and the Vermillion River). The three greatest detection frequencies were observed within or immediately downstream of the TCMA (the Mississippi River, Pool 1; the Minnesota River, river miles 15–0.3; and the Vermillion River). The increase in detection frequencies from upstream to downstream of the TCMA was observed in the data of every agency. The increase is

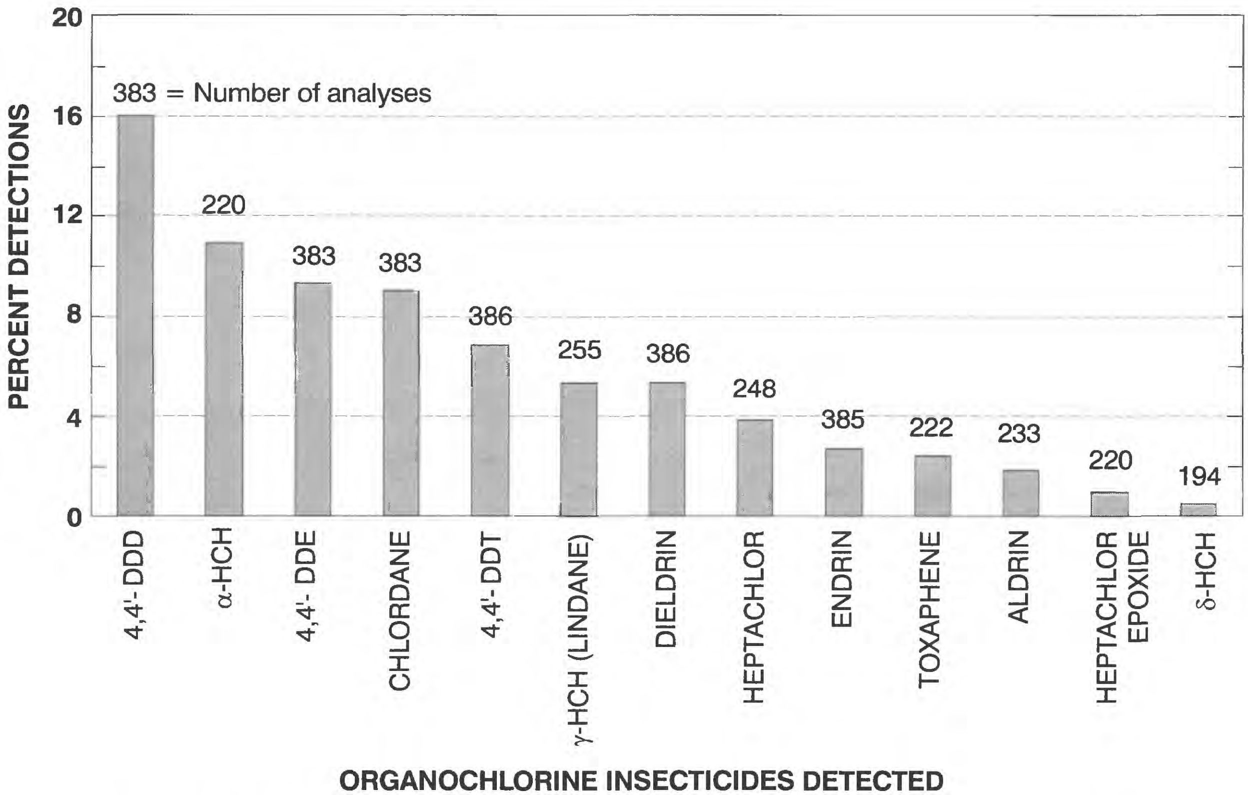


Figure 13.--Detection frequencies of organochlorine insecticides in streambed sediment in the study area, 1974-94 (Metropolitan Council Environmental Services, Minnesota Pollution Control Agency, U.S. Army Corps of Engineers, and U.S. Geological Survey).

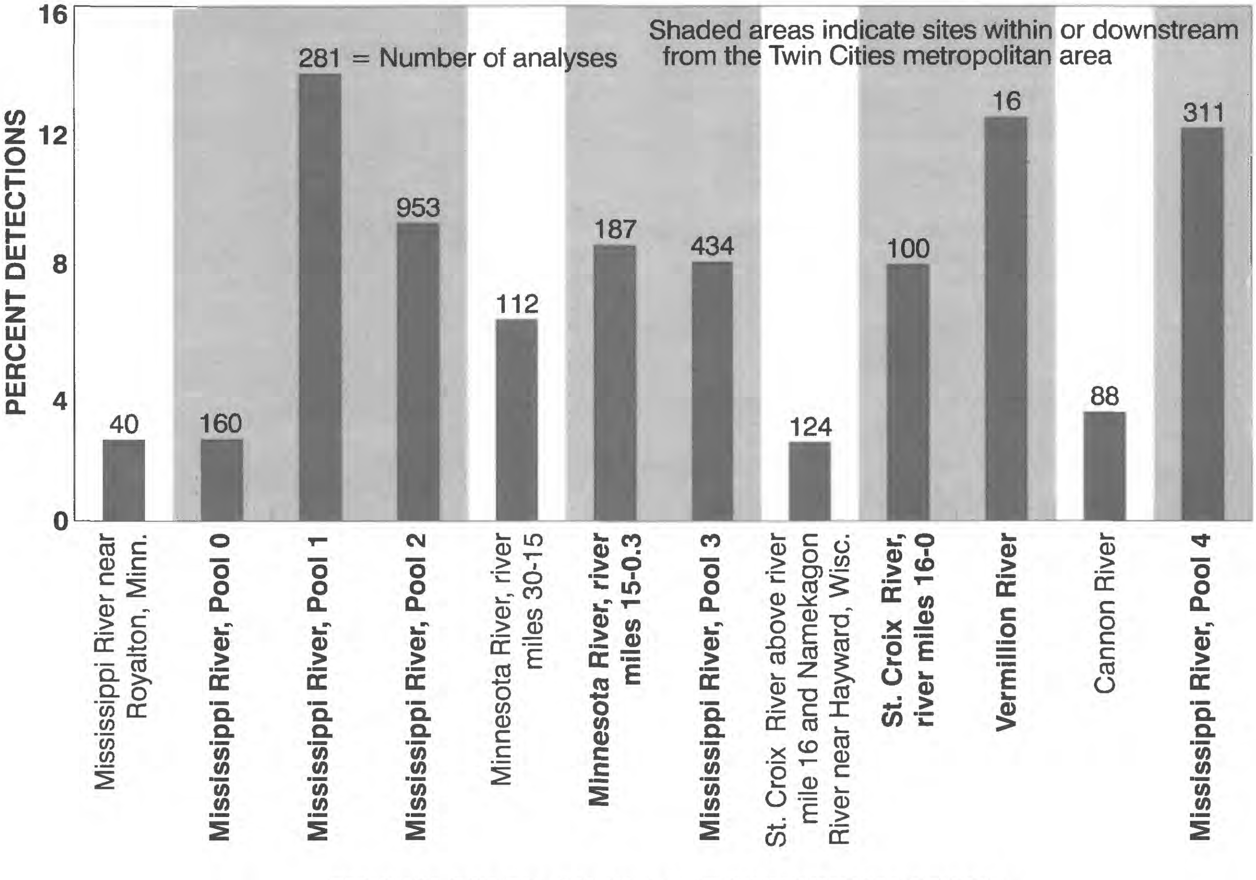


Figure 14.--Combined detection frequencies for eight organochlorine insecticides in streambed sediment, by stream reach in the study area, 1974-94 (Metropolitan Council Environmental Services, Minnesota Pollution Control Agency, U.S. Army Corps of Engineers, U.S. Geological Survey, and Wisconsin Department of Natural Resources).

even apparent on the Minnesota River, which drains land used predominately for agriculture. Although insecticides often are associated with agricultural land use, urban areas also may contribute to insecticide contamination. Detection frequencies on the Mississippi River decreased successively in navigation Pools 1–3 within and below the TCMA, but increased in Pool 4. Pool 4 includes Lake Pepin, a natural lake on the Mississippi River that may act as a more efficient sediment and hydrophobic pesticide trap than other navigation pools because of its larger volume and longer residence time.

The Vermillion River, which is a small stream that was sampled downstream of a TCMA wastewater-treatment plant, had one of the greatest detection frequencies. These high detection frequencies may be associated with urban land use, but they may be a consequence of the lower number of analyses than at other sites.

The geographic distribution of various organochlorine insecticides detected (fig. 15) is similar to the distribution of detection frequencies. Of those insecticides commonly analyzed, the number of different insecticides detected in the Mississippi River successively increased from upstream of the TCMA (near Royalton, Minnesota) through the TCMA (Pools 0, 1, and 2). Most of the insecticides were detected in Pool 2, which had detections of all eight commonly analyzed insecticides. Samples from Pool 2 were collected downstream of small tributaries draining the TCMA and upstream and downstream of the Minnesota River confluence, so the large number of insecticides detected there reflect the different urban and agricultural sources. The number of insecticides detected decreased in each successive pool downstream in the Mississippi River (Pools 3 and 4). Similarly, for the Minnesota and St. Croix Rivers, more insecticides were detected downstream of the TCMA (river miles 15–0.3 and 16–0, respectively) than upstream (near Jordan and above river mile 16, respectively), although fewer analyses were available for these rivers.

Time trends in organochlorine insecticide concentrations were not determined because these data contain many factors that confound trend analyses: inconsistent sampling sites, analytical methods, and sampling frequencies; decreasing detection limits from 1974–94 that vary by orders of magnitude for consecutive samples; and small percentages of samples with detections. Figure 16, for example, shows detection limits and detections of 4,4'-DDD in Pool 2 of the Mississippi River for the period of record. These data best show detected concentrations and an apparent decrease in detection limits, but even these data would show no trends or even detections if data were censored using the greatest detection limit of 14.0 μg/kg—a technique used to remove bias from data sets. One general observation about organochlorine insecticide concentrations through time may be made—maximum concentrations were detected before 1988.

Ground Water

Herbicides were detected in both sand and gravel and bedrock aquifers. More than twice as many samples were collected from wells completed in sand and gravel aquifers than bedrock aquifers. Most wells sampled in sand and gravel aquifers were located in the northern one-half of the study area, whereas most wells in bedrock aquifers were sampled in the southern part.

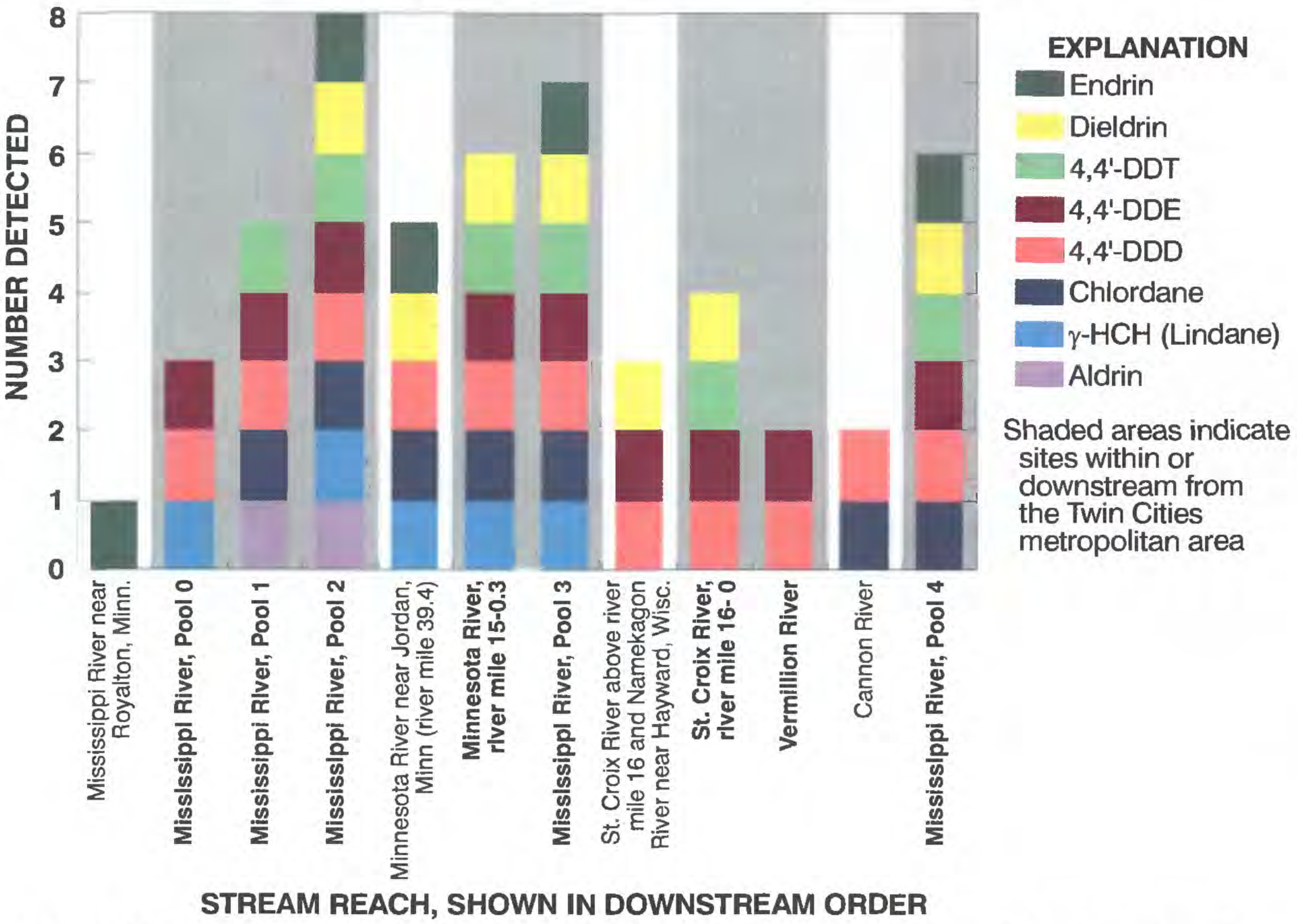


Figure 15.--Organochlorine insecticides detected in streambed sediment by stream reach in the study area, 1974-94 (Metropolitan Council Environmental Services, Minnesota Pollution Control Agency, U.S. Army Corps of Engineers, U.S. Geological Survey, and Wisconsin Department of Natural Resources).

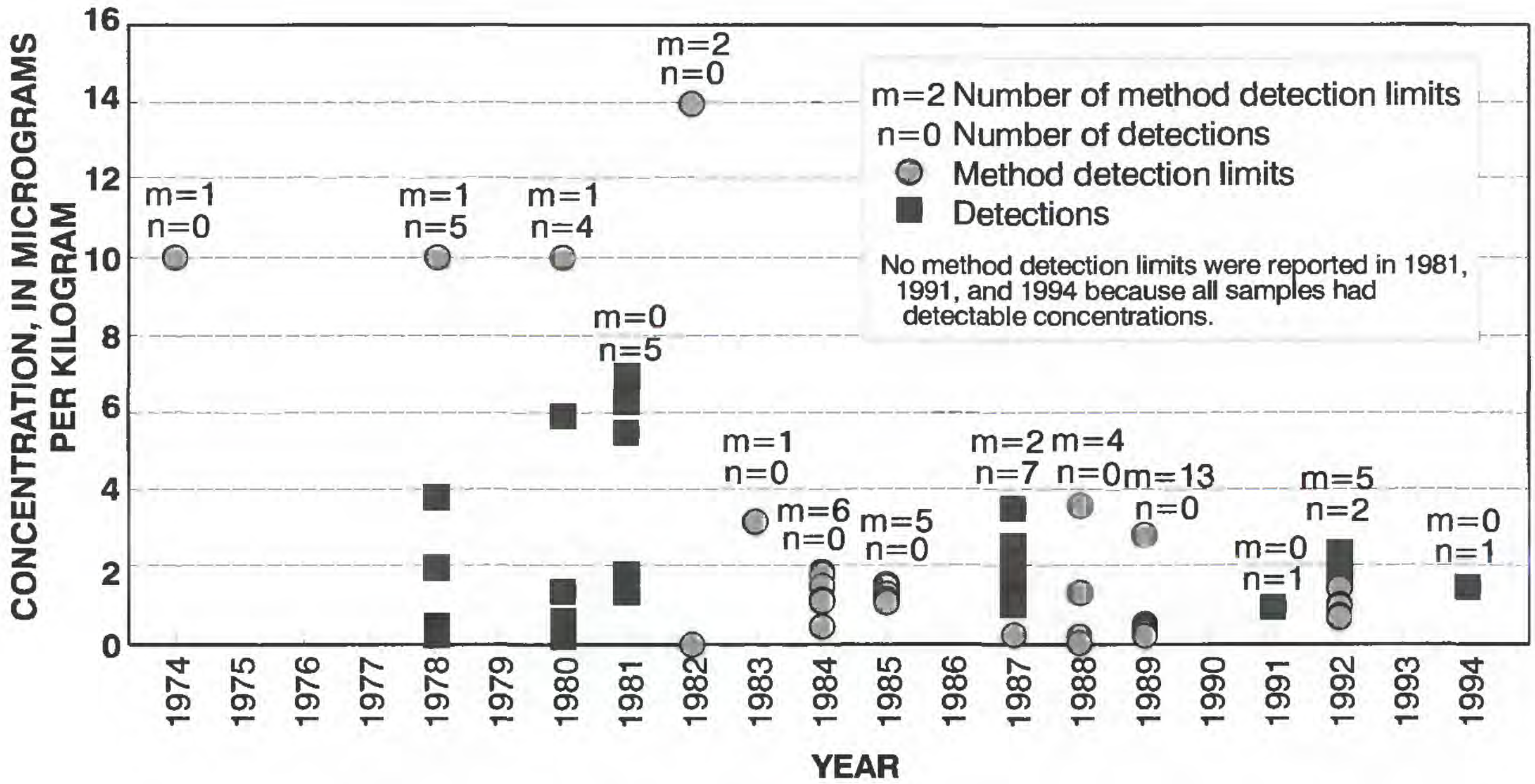


Figure 16.--Method detection limits and detections of 4,4'-DDD in Pool 2 of the Mississippi River, 1974-94 (U.S. Army Corps of Engineers).

Sand and Gravel Aquifers

The seven most frequently detected herbicides in water were detected in sand and gravel aquifers in the study area (fig. 17, tables 12–17). Wells with detections generally were in agricultural areas underlain by outwash and alluvium, particularly in the Anoka Sand Plain and in the area known as the Bonanza Valley (Delin, 1990) (fig. 3). None of the herbicide concentrations from wells in sand and gravel aquifers exceeded the maximum contaminant levels set by the USEPA (table 18). Atrazine and its metabolites were the most frequently detected herbicides, although detection rates ranged from 0 to 66.7 percent for the various agencies. Only the USGS and WDNR analyzed for and detected deethylatrazine and deisopropylatrazine. Alachlor, cyanazine, metolachlor, and simazine were detected in less than 5 percent of samples. All of the agencies that sampled sand and gravel aquifers analyzed unfiltered ground-water samples for total concentrations, but the USGS also analyzed some filtered ground-water samples for dissolved concentrations.

Detection frequencies and the types of herbicides detected varied between agencies (fig. 18). The USGS detected deethylatrazine, atrazine, and deisopropylatrazine in 58.7, 31.8, and 13.0 percent of the wells, respectively, in unfiltered water samples. Detection frequencies were higher in samples collected by the USGS than those from other agencies because some samples were screened by immunoassay so that only samples with positive detections of triazine compounds were analyzed by gas chromatography/mass spectrometry. Concentrations ranged from 0.04 to 2.3 μg/L (table 12). Cyanazine, metolachlor, and simazine were detected in less than 5 percent of unfiltered water samples. In filtered water samples, deethylatrazine, atrazine, deisopropylatrazine, and metolachlor were detected in 66.7, 54.2, 4.3, and 4.2 percent of the wells sampled by the USGS, respectively (table 13). The MDA detected atrazine in samples from 26 percent of the wells in sand and gravel aquifers. Concentrations ranged from 0.05 to 1.38 μg/L (table 14). Alachlor and metolachlor were detected in less than 5 percent of the wells sampled. The WDNR detected deethylatrazine and atrazine in 8.1 and 2.2 percent of the wells sampled in Wisconsin, respectively. Concentrations ranged from 1.0 to 1.4 μg/L (table 15). The MDH and the MPCA found no detectable herbicide concentrations in the wells they sampled in sand and gravel aquifers (tables 16 and 17).

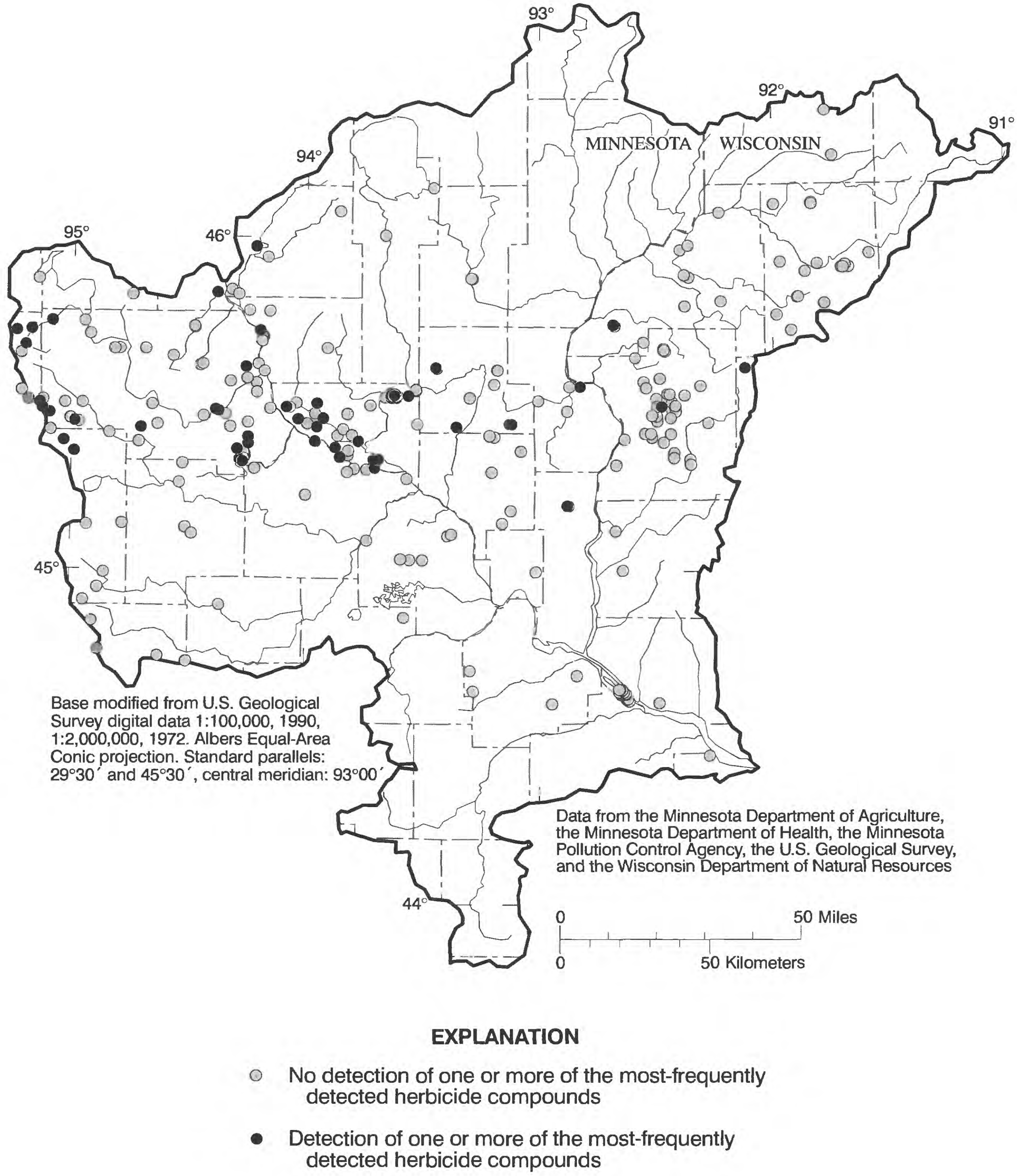
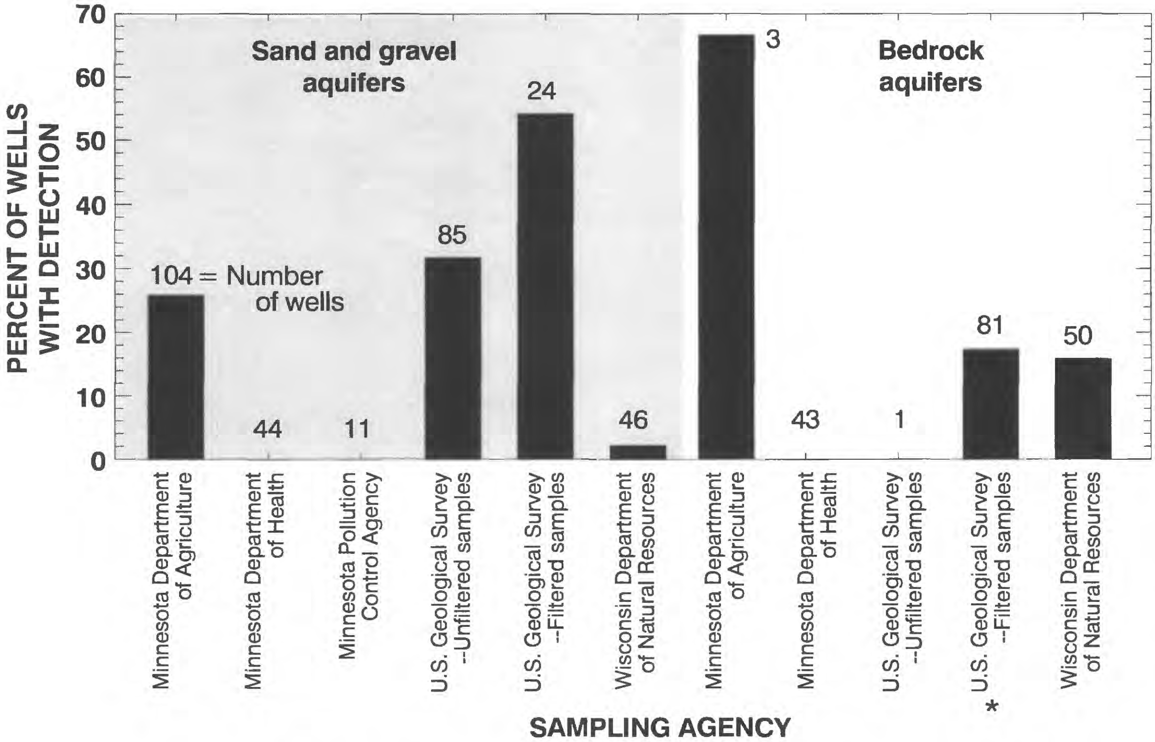


Figure 17.--Locations of wells completed in sand and gravel aquifers in the study area sampled for the most frequently detected herbicides.



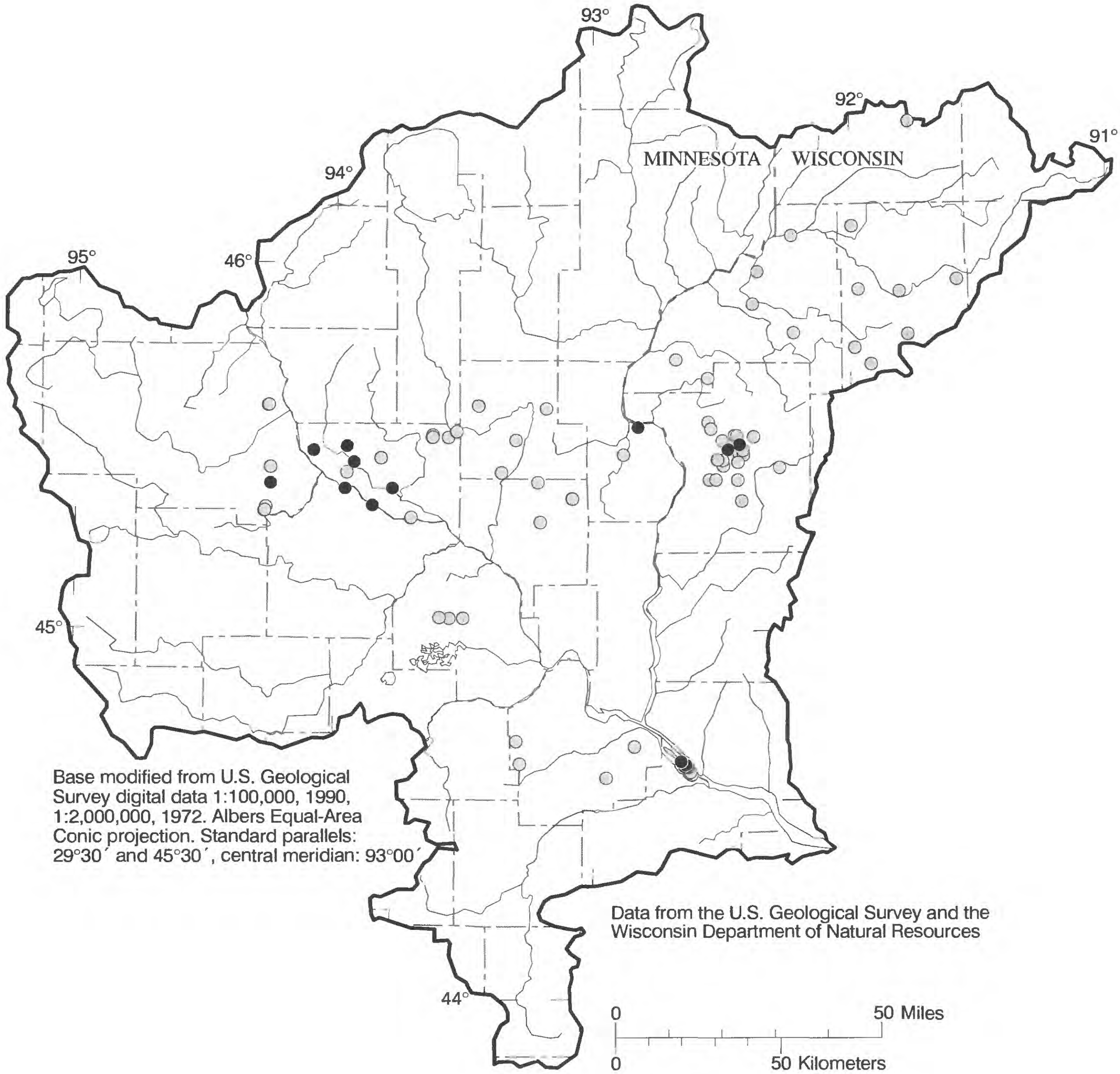
* This bar refers to percent detection for triazine compounds determined by immunoassay.

Figure 18.--Detection frequencies for atrazine from wells sampled in the study area, 1983-94.

Differences in the percentages of herbicide detections between wells sampled by different agencies are probably due to several factors. Each agency sampled different numbers of wells and had its own sampling procedures, analytical methods, detection limits, sampling designs, and sampling locations. In addition to screening some samples, the USGS sampled monitoring wells and domestic wells for local and regional studies. The MDA mainly sampled shallow monitoring wells in agricultural areas where herbicides were known to be used. The MDH and MPCA wells were located in agricultural and nonagricultural areas. The MDH sampled public-supply wells, which are frequently deeper wells and are pumped at greater rates than those sampled by other agencies. Wells sampled by the MPCA were part of a statewide base-line monitoring network that included domestic and public-supply wells. The WDNR sampled domestic and public-supply wells as part of a statewide monitoring network. Low detection rates for wells sampled by the WDNR could be due to the fact that, in the southern parts of the study area in Wisconsin, wells completed in sand and gravel aquifers can be up to several hundred feet deep. Thus, these aquifers are less susceptible to contamination than shallower wells sampled by other agencies.

Statistical analysis of herbicide detections in wells with reliable depth data reveal the significance of well depth. The median depth of wells with herbicide detections was 19.0 ft, based on 318 wells with reliable well-depth information. The median depth of wells without herbicide detections was 29.0 ft. Based on the nonparametric Mann-Whitney test, there is a significant difference in well depths for the two groups at a confidence level of 95 percent.

Immunoassay analyses of triazine herbicides in wells were performed by the USGS and the WDNR (fig. 19). Detections occurred mainly in agricultural areas underlain by outwash (figs. 2 and 3). Triazines were detected in 18.3 and 5.9 percent of the unfiltered samples by the USGS and WDNR, respectively (fig. 20, tables 12 and 15). Triazine concentrations determined by immunoassay are not summarized in this report because immunoassay results are considered semi-quantitative.



EXPLANATION

○ No detection of triazines

● Detection of triazines

Figure 19.--Locations of wells completed in sand and gravel aquifers in the study area sampled for triazine compounds (analyzed by immunoassay).

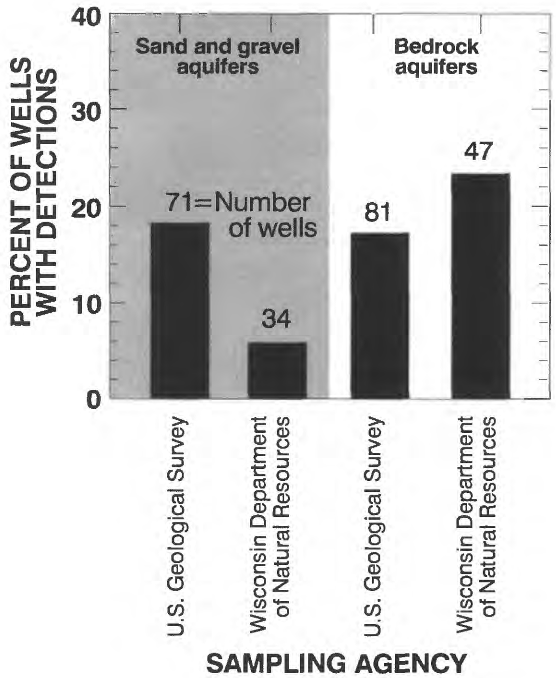


Figure 20.--Detection frequencies for triazine compounds from wells sampled in the study area.

Bedrock Aquifers

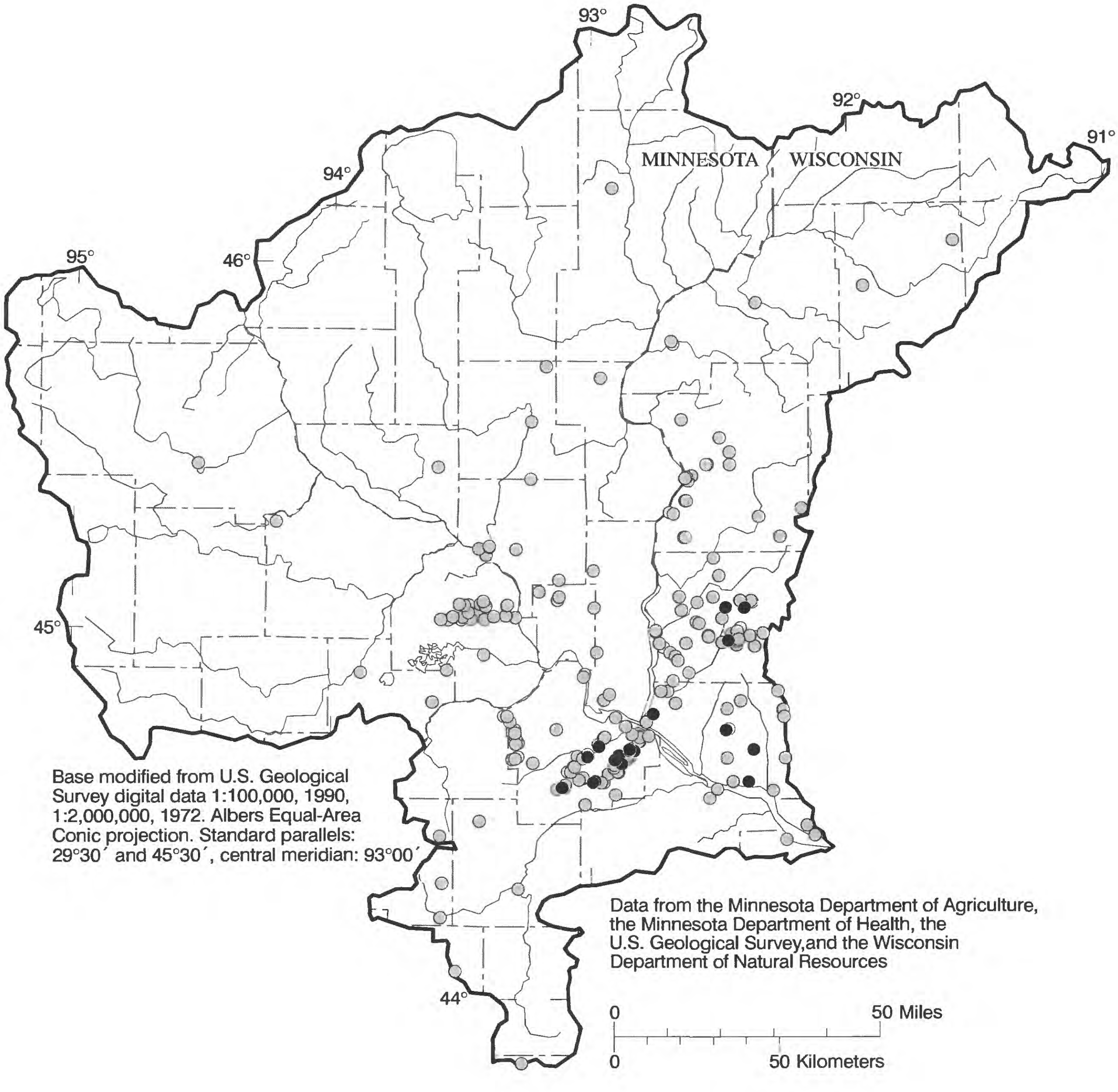
About 69 percent of the wells in bedrock aquifers were located in the Prairie Du Chien-Jordan (Prairie Du Chien-Trempealeau in Wisconsin) aquifer, which is the most widely used bedrock aquifer in the study area. There were not enough data pertaining to individual bedrock aquifers to analyze the data by discrete aquifers. Atrazine, deethylatrazine, and deisopropylatrazine were detected in water samples from bedrock aquifers. The wells with detections are located mainly in the southeastern part of the study area (fig. 21) where the bedrock commonly outcrops near the surface or is in hydraulic connection with surficial aquifers in buried bedrock valleys. Atrazine was the only herbicide detected by all agencies in water from bedrock aquifers. Only the USGS and WDNR analyzed and detected deethylatrazine and deisopropylatrazine. One water sample from the WDNR had an atrazine concentration of 3.0 µg/L (table 15), which is equal to the annual maximum contaminant level set by the USEPA (table 18). No other samples had concentrations equaling or exceeding the maximum contaminant levels. All of the agencies sampling bedrock aquifers used unfiltered ground-water samples for their analyses, and the USGS also analyzed some filtered ground-water samples.

Detection frequencies for the USGS filtered samples are positively biased because samples were first screened using triazine immunoassay (fig. 18, tables 12 and 13); only samples with detections of triazines by immunoassay were analyzed by gas chromatography/mass spectrometry (Smith and Nemetz, 1996). All of the 12 filtered samples analyzed by gas chromatography/mass spectrometry had detectable concentrations of atrazine. The concentrations ranged from 0.1 to 0.66 µg/L (table 13). Only one unfiltered sample was analyzed for atrazine, and the concentration was below the detection limit. Deethylatrazine was detected in one of two filtered samples, with a concentration of 0.32 µg/L. Unfiltered samples had deethylatrazine concentrations of 0.14 to 2.28 µg/L. Deisopropylatrazine had a 90.9 percent detection rate for unfiltered samples, with concentrations from 0.14 to 2.23 µg/L, and no detections in two filtered samples.

The WDNR detected atrazine in 16 percent of the bedrock wells sampled in Wisconsin, with concentrations ranging from 0.64 to 3.0 µg/L (fig. 18, table 15). Deethylatrazine was detected in 14.3 percent of the wells sampled by the WDNR, with concentrations ranging from 1.1 to 3.9 µg/L (table 15). The MDA detected atrazine in two of the three bedrock wells sampled, with concentrations of 0.2 µg/L (fig. 18, table 14). The MDH found no detectable herbicide concentrations in bedrock wells sampled (fig. 18, tables 16 and 17).

The differences in the herbicide detection rates between the different agencies in bedrock aquifers is probably due to the same factors listed for the sand and gravel aquifers—different numbers of analyses, sampling procedures, laboratories, detection limits, sampling designs, sample locations, and well depths. The median depth of wells completed in bedrock aquifers was 185 ft for wells with herbicide detections and 250 ft for wells without detections. There was not a significant difference at a confidence level of 95 percent in well depths between the two groups, according to the nonparametric Mann-Whitney test. Not all of the wells sampled had well-depth data available, so pesticide detections were compared to well depth for 171 wells completed in bedrock with reliable well-depth data.

Triazine herbicide immunoassay screening of ground-water samples was performed by the USGS and the WDNR. A map of triazine detections in bedrock aquifers (fig. 22) shows patterns similar to those for the most frequently detected herbicides analyzed by gas chromatography/mass spectrometry, with detections occurring mainly in the southeastern part of the study area where bedrock commonly outcrops near the



EXPLANATION

- ◎ No detection of one or more of the most-frequently detected herbicide compounds.
- ● Detection of one or more of the most-frequently detected herbicide compounds

Figure 21.--Locations of wells completed in bedrock aquifers in the study area sampled for most frequently detected herbicides.

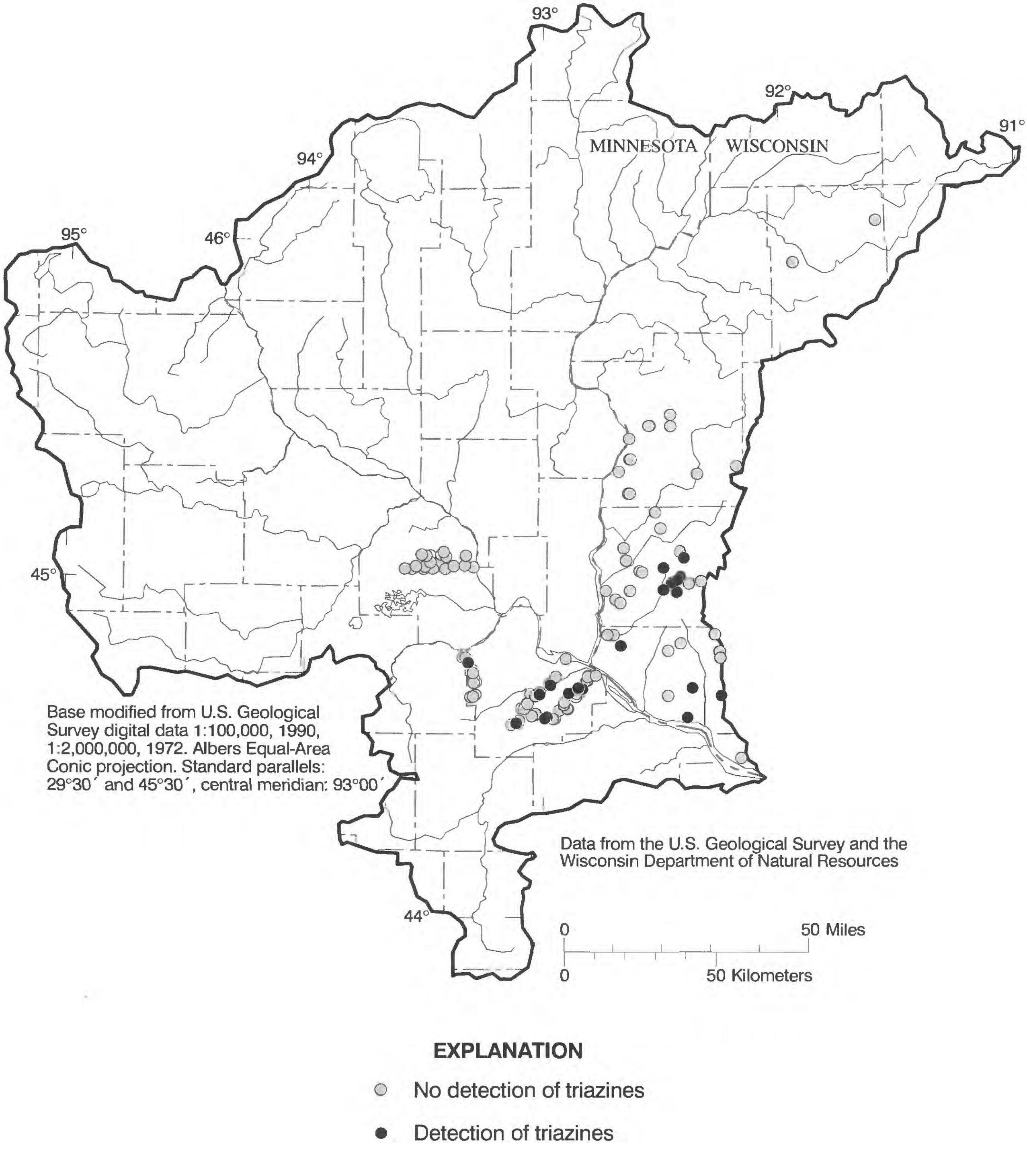


Figure 22.--Locations of wells completed in bedrock aquifers in the study area sampled for triazine compounds (analyzed by immunoassay).

surface. In unfiltered samples, 17.3 and 23.4 percent had detections of triazines, by the USGS and WDNR, respectively (fig. 20, tables 12 and 15).

Water-Quality Implications

Generalizations about the fate and distribution of pesticides reviewed in this report are affected by pesticide uses and properties, by the environmental settings in which pesticides are used, by the sampling designs and analytical methods of collecting agencies, and by how society regulates pesticide concentrations.

The spatial distribution of sampling sites for data presented in this report is not evenly distributed. Pesticide sample collections often are restricted to a subset of physical phases or environmental settings where pesticides are most expected because of costs associated with analyses. Physical properties of pesticides determine their susceptibility to be lost to runoff in the dissolved phase, or sorbed to sediment, or to be lost to ground water by leaching (table 1). Certain environmental settings may be more vulnerable to pesticide contamination than others, such as ground water underlying permeable soils in agricultural areas, and these settings are frequently sampled more than others. Nationally, 76 percent of pesticides are used for agriculture (Aspelin, 1994), so agricultural areas are most frequently sampled, especially for herbicides. The persistence and hydrophobicity of organochlorine insecticides increase their susceptibility to be transported in the sediments of rivers, so many large rivers are sampled for these insecticides. For these reasons, less information is available for pesticides in streams and ground water in forested and urban areas.

Concentrations of many pesticides in drinking water, streams, streambed sediment, and ground water are regulated by Federal and State agencies (table 18). Maximum contaminant levels of pesticides in drinking water are enforceable standards of annual average concentrations, based on toxicity studies and treatment feasibility, and established by the USEPA (Nowell and Resek, 1994; U.S. Environmental Protection Agency, 1994). Regulation of pesticide concentrations in drinking water has implications for pesticides in streams and ground water because these waters often are drinking-water sources and because removal of pesticides from drinking water often requires costly carbon filtration that most public water-treatment facilities lack (Miltner and others, 1989). Ambient water-quality criteria also have been established by the USEPA because of known or suspected adverse effects of pesticides on humans and aquatic organisms (Nowell and Resek, 1994). These criteria set nonenforceable guidelines for development of standards by states for pesticide concentrations in freshwater and sediment. Criteria to protect human health are based on the health risks of ingesting water or organisms (such as fish and shellfish) from freshwaters. Ambient water-quality criteria to protect aquatic organisms are based on toxicity calculations for both acute (instantaneous to 1-hour) and chronic (1- to 4-day) exposure to toxic compounds (Ware, 1994).

Streams

Pesticides were detected in streams draining agricultural, urban, and forested areas, even though most sampling designs focused on agricultural areas. The most frequently detected pesticides were triazine herbicides, atrazine and cyanazine, and the acetanilide herbicides, alachlor and metolachlor. These herbicides were most frequently sampled for and detected in southern and western streams draining agricultural parts of the study area. These herbicides are among the most used herbicides in the Upper Mississippi River Basin study unit (table 1) and among those that have a medium-to-large risk of loss to runoff in the dissolved phase (table 18) because of higher solubilities and longer persistence than many other herbicides and insecticides currently used.

Whereas pesticides often are associated with agriculture, this report shows that streams draining urban areas can contain significant concentrations of pesticides. Although the most frequently detected herbicides are used predominantly for agriculture, they also were detected in an entirely urbanized part of the Lake Harriet Watershed in Minneapolis. In fact, of all herbicide detections in streams, only the atrazine concentrations composited from urban runoff events in Minneapolis (3.6–3.8 μg/L, table 4) exceeded annual maximum contaminant levels for drinking water (table 18). The small drainage area (0.22 mi^2) of the watershed contributed to the high concentrations because smaller watersheds typically have sharper and higher peak flows and concentrations of these types of constituents than larger watersheds. Streams draining larger watersheds may transport a greater mass of pesticides, but at lower concentrations. Nevertheless, these concentrations are notable because atrazine is registered for agricultural use and because atrazine was detected in rainfall in the watershed, so the significant concentrations present in runoff were probably transported atmospherically into the watershed. Other herbicides detected in the urbanized Lake Harriet Watershed include two of the five most commonly used for residential purposes (2,4-D and dicamba), but not the other three (glyphosate, trifluralin, and pendimethalin). Herbicides were rarely detected in streams draining forested areas, but these streams were sampled much less frequently than other areas.

The herbicides, including alachlor, atrazine, cyanazine, metolachlor, and simazine, that were detected in streams under base-flow conditions in October and before pesticide application in April, also were detected in ground water. This indicates that one source of herbicides to streams is from ground-water discharge.

Other herbicides, such as EPTC, 2,4-D, and trifluralin, were used in agriculture as much or more than the frequently detected triazine and acetanilide herbicides (table 1) and were identified as having a medium risk of loss to runoff (Goss, 1992), but were rarely or never detected in agricultural areas. In general, these herbicides are less persistent than the triazines and acetanilides, and they are more difficult to identify and quantify at similar concentrations because of their physical properties (Lartiges and Garrigues, 1995).

Organochlorine insecticides were analyzed in samples from TCMA streams that received wastewater-treatment-plant discharge. Several organochlorine insecticides exceeded long-term consumption limits for children (chlordane) or freshwater-quality criteria for the protection of aquatic life (chlordane, dieldrin, endrin, and heptachlor). The presence of this class of persistent hydrophobic insecticides in streams has been less of a problem recently than in the past; 70 percent of the detections occurred in 1981, and the most recent year a criteria was exceeded was 1990.

Streambed Sediment

Organochlorine insecticides were the most frequently analyzed pesticides in streambed sediment because of their hydrophobic, toxic, and persistent characteristics. Although most organochlorine insecticide use was banned or restricted in the 1970's and 1980's, many insecticides were still detected in samples collected in the 1990's. Organochlorine insecticides were detected in every stream sampled except the Namekagon River (table 10), which implies ubiquity. However, 95 percent of the samples were collected from rivers just upstream of, within, or downstream of the TCMA, so little data are available to assess background concentrations. No organochlorine insecticide concentrations exceeded ambient water-quality criteria for sediment. It is difficult to determine temporal trends in organochlorine insecticide concentrations because of inconsistent detection levels. Several more years of data at current detection levels would be needed before trends can be calculated.

Assessment of other pesticides likely to be transported by sediment is incomplete. For example, four pesticides that are used in significant quantities in agricultural areas of the Upper Mississippi River Basin study unit are considered to have a large risk of loss sorbed to sediment (Goss, 1992): trifluralin, pendimethalin, glyphosate, and diazinon (table 1). Of these four pesticides, only diazinon was analyzed for but detected in less than 5 percent of all samples. Diazinon was detected in unfiltered water samples but no filtered samples. This indicates that diazinon is being transported with the sediment and may be detected in streambed sediment if it were analyzed for more frequently.

Ground Water

Pesticides were detected in about one-fifth of the wells sampled. The pesticides most frequently detected in ground water (alachlor, atrazine, cyanazine, metolachlor, and simazine) are similar to those frequently detected in streams. This is not unexpected because most of the physical properties that make pesticides, such as triazine and acetanilide herbicides, vulnerable to transport in the dissolved phase apply to both ground water and streams. Furthermore, the agencies, including the MDA, MPCA, and USGS, that sampled ground water also sampled streams and frequently used similar or identical analytical methods.

The environmental setting affects where pesticides are detected in ground water. In surficial aquifers, most wells with detections were located in agricultural areas underlain by outwash or alluvium, including the Anoka Sand Plain and the Bonanza Valley. More wells with detections in these areas may result partly from sample design because most wells sampled were located in agricultural areas. However, in areas of high permeability, pesticides applied at the surface may be readily transported to ground water. Similarly, in bedrock aquifers, most wells with detections were located in areas where bedrock commonly outcrops at the surface or is in hydraulic connection with surficial aquifers in buried bedrock valleys, making the bedrock aquifers vulnerable to contamination. Although no concentrations exceeded drinking-water standards, pesticides in ground water are a concern. Once present in ground water, pesticides persist longer than at the surface because of longer pesticide degradation rates and ground-water residence times. Furthermore, pesticides in ground water may be discharged to streams or to drinking-water supply wells.

Atrazine and alachlor, which were two of the six most used pesticides in the study area and are considered to have a high risk of loss to leaching to ground water (Goss, 1992), were detected in samples from wells. Others considered to have a high risk of leaching (bentazon, dicamba, and metribuzin) were not detected, either because they were not commonly analyzed for or because they were not used in as large quantities.

SUMMARY AND CONCLUSIONS

As part of a retrospective analysis of water-quality data, the Upper Mississippi River Basin study unit of the National Water-Quality Assessment Program, U.S. Geological Survey, summarized pesticide data for streams, streambed sediment, and ground water from water-quality data bases maintained by Federal, state, and local agencies. The analysis focuses on a study area encompassing 19,500 mi^2 that includes the Upper Mississippi River Basin from Lake Pepin upstream to sampling stations on the Mississippi River near Royalton, Minnesota, and the Minnesota River near Jordan, Minnesota, and the entire drainage basins of the St. Croix, Vermillion, and Cannon Rivers. Assessment is restricted to two groups of pesticides—the most frequently detected herbicides and most frequently detected insecticides. Herbicide data summarized for streams and ground water include atrazine, deethylatrazine, deisopropylatrazine, alachlor, cyanazine, metolachlor, and simazine. Insecticide data summarized for streams and streambed sediment include aldrin, chlordane, 4,4'-DDT, 4,4'-DDD, 4,4'-DDE, dieldrin, endrin, γ-HCH (or lindane), α- and δ-HCH, heptachlor, heptachlor epoxide, and toxaphene. Quantities of the most used herbicides and insecticides are estimated for agriculture in the Upper Mississippi River Basin study unit and possible relations between pesticide use and the presence of pesticides in streams and ground water are described.

Examination of pesticide-use and water-quality data contained in this report led to the following conclusions. In streams, trace concentrations of pesticides are ubiquitous—herbicides were detected at every site sampled except the Kettle River. Herbicides were detected most often in streams draining row-crop agricultural areas; the Minnesota and Cannon Rivers had the most detections, followed by the Sauk, Straight, and Crow Rivers. Atrazine was the most widely detected pesticide, with detections in all streams sampled except the Kettle River. Concentrations of atrazine, metolachlor, and cyanazine were greatest in July, although these herbicides and others are detectable most of the year at very low (parts-per-trillion) concentrations. The herbicides EPTC and trifluralin were never detected, although they were used in amounts equal to or greater than those detected, reflecting the fact that some herbicides are less persistent than others. A small urban stream draining part of the Lake Harriet Watershed in Minneapolis, Minnesota, contained substantial concentrations of pesticides as well. Eighty-five percent of runoff events sampled in this entirely urbanized watershed had detections of herbicides commonly used for residential purposes, and 43 percent of the events had detections of alachlor, atrazine, cyanazine, or metolachlor—herbicides used predominantly for agricultural purposes. Unlike pesticide concentrations in agricultural streams, pesticide concentrations in urban stormwater runoff remained well above detection limits throughout the summer, indicating repeated applications of pesticides.

Organochlorine insecticides were rarely detected in streamwater, but samples collected during 1981 and 1990 exceeded the U.S. Environmental Protection Agency's chronic freshwater-quality criteria for chlordane, dieldrin, endrin, and heptachlor on the Mississippi, Minnesota, St. Croix, and Vermillion Rivers, with concentrations less than 0.06 µg/L. Organochlorine insecticides in streams and streambed sediment were detected more frequently downstream of the Twin Cities metropolitan area than upstream, with the greatest detection frequencies located within or immediately downstream, suggesting that most of these insecticides originated from the Twin Cities metropolitan area.

Most detections of herbicides in ground water were in agricultural areas underlain by outwash and alluvium, including the Anoka Sand Plain and the Bonanza Valley. Atrazine, deethylatrazine, and deisopropylatrazine were the most frequently detected pesticides in ground water. Detection frequencies of atrazine were extremely variable, ranging from 0 to 66.7 percent among the various agencies, probably as a result of different sampling purposes, well locations, and detection levels. Atrazine and its metabolites were the only pesticides detected in bedrock aquifers, with detections found mainly in the southeastern part of the study area where bedrock commonly outcrops near the surface in agricultural areas. Thus, most detections of herbicides in ground water were observed in environmental settings where agriculture is practiced and ground water is vulnerable to contamination.

Detections are related to pesticide class and land use. The five herbicides most frequently detected in streams and ground water are triazine or acetanilide herbicides. Triazines and acetanilides are among the most used herbicides, persist longer, and are easier to analyze than many other pesticides currently used. Detection frequencies of insecticides, other than organochlorine insecticides, were lower than herbicides. These insecticides were rarely detected because application rates of insecticides applied for agriculture in the Upper Mississippi River Basin study unit are about 28 times less than herbicides, because most insecticides degrade more rapidly than herbicides, and because insecticides are analyzed for less frequently than herbicides. Organochlorine insecticides were detected more frequently in streambed sediment than in streamwater. Although most organochlorine insecticides have been banned since the 1970's, they still were detected in the most recent streambed-sediment samples. Three insecticides, 4,4'-DDT, heptachlor, and lindane, and their metabolites and isomers account for almost two-thirds of the organochlorine insecticides detected.

Atrazine was the only pesticide that equaled or exceeded a maximum contaminant level (of 3.0 μg/L) for drinking water. Two stream samples from the Lake Harriet Watershed in Minneapolis had atrazine concentrations of 3.6 and 3.8 μg/L, and one ground-water sample had a concentration of 3.0 μg/L. Trace concentrations (less than 0.06 μg/L) of organochlorine insecticides in streams exceeded the U.S. Environmental Protection Agency's chronic freshwater-quality criteria for the protection of aquatic organisms in several samples collected from the Mississippi, Minnesota, St. Croix, and Vemillion Rivers during 1981 and 1990. Concentrations of all other pesticides in streams, streambed sediment, and ground water were below applicable standards and sediment-quality criteria, so, whereas pesticides are present in waters of the study area, concentrations are generally below levels currently considered safe for drinking water and aquatic organisms.

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Supplemental Information

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Table 1.--Estimated quantities of herbicides and insecticides used for agriculture in 1989 in the Upper Mississippi River Basin study unit (Gianessi and Puffer, 1991and1992), frequently used herbicides and insecticides for lawns and gardens nationally (Whitmore and others, 1992), and risks of pesticide transport (Goss, 1992)

[SW, streams; SED, stream sediment; GW, ground water]

Pesticides, grouped by type and ranked by quantity, applied in study unit and study area; ***italicized text indicates pesticide has significant nonagricultural use nationally***	Pesticide class	Crops and land commonly applied to in Minnesota and Wisconsin	Risk of potential transport by runoff in dissolved phase (SW) or in solid phase (SED), and by leaching to ground water (GW); S, small; M, medium; L, large SW	SED	GW	Quantity applied for agricultural purposes in study unit (and study area), in thousands of pounds of active ingredient
		Herbicides				16,900 (6,850)
1. EPTC	Thiocarbamate	corn, beans, potatoes, alfalfa	M	S	S	4,490 (1,850)
2. Alachlor	Acetanilide	corn, beans, sweet corn	M	S	M	2,400 (991)
3. Cyanazine	Triazine	corn, sweet corn	M	S	M	1,650 (680)
4. Metolachlor	Acetanilide	corn, beans, potatoes, sweet corn	L	M	L	1,590 (657)
5. ***Trifluralin***	Dinitroaniline	beans, small grains, alfalfa, corn	M	L	S	1,260 (521)
[a]Acetochlor—1994 rates	Acetanilide	corn only				1,130 (356)
6. Atrazine	Triazine	corn, pasture, sweet corn, sod	L	M	L	1,080 (447)
7. ***2,4-D***	Chlorinated phenoxy	pasture, small grains, corn	M	S	M	612 (252)
8. Butylate	Thiocarbamate	corn, sweet corn				494 (204)
9. Bentazon	Organophosphate	beans, corn, small grains, alfalfa	M	S	L	483 (199)
10. ***Dicamba***	Benzoic acid derivative	pasture, corn, small grains	M	S	L	483 (199)
11. ***Pendimethalin***	Dinitroaniline	corn, beans, potatoes, grains	M	L	S	425 (175)
12. ***Glyphosate***	Organophosphate	corn, beans, grains, pasture, other uses	L	L	S	416 (171)
13. MCPA	Chlorinated phenoxy	small grains, peas	M	S	L	175 (72.1)
14. Propachlor	Acetanilide	corn, peas, pumpkins, squash	M	S	S	93.8 (38.7)
15. Metribuzin	Triazinone	beans, potatoes, alfalfa, grains	L	S	L	84.4 (34.8)
		Insecticides				605 (251)
1. Carbofuran	Carbamate	corn, potatoes, sweet corn, cucumbers, sunflowers, strawberries, forests	L	M	L	200 (82.5)
2. ***Chlorpyrifos***	Organophosphate	corn, sugar beets, alfalfa, sweet corn, cranberries	S	M	S	184 (75.9)
3. Aldicarb	Carbamate	soybeans, sugar beets, sweet potatoes	M	S	L	110 (45.2)
4. Fonofos	Organophosphate	corn, sweet corn, cabbage	L	S	S	53.1 (21.9)
5. Methyl parathion	Organophosphate	corn, sweet corn, sunflowers, alfalfa, forest	M	M	S	44.9 (18.5)
6. ***Malathion***	Dithioate	fruits, vegetables, forests				7.78 (3.21)
7. Terbufos	Organophosphate	corn, sugar beets, sweet corn	M	S	S	5.02 (2.07)
8. ***Permethrin***	Pyrethroid	corn, potatoes, alfalfa, soybeans, forests	S	M	S	4.02 (1.66)
9. ***Diazinon***	Organophosphate	corn, cranberries, cabbage	L	L	S	0.48 (0.2)
10. ***Carbaryl***	Carbamate	corn, carrots, cranberries, potatoes, green beans, forests	M	S	S	0.06 (0.02)

[a]Acetochlor is a herbicide that was reregistered in 1993 for weed control exclusively on corn and is included in table 1 for an approximate comparison to other herbicide usages. Estimates of acetochlor were made from State reports of corn acreage planted by county in 1993 (Iowa Agricultural Statistics, 1994; Minnesota Agricultural Statistics Service, 1994; South Dakota Agricultural Statistics Service, 1994; Wisconsin Agricultural Statistics Service, 1994) and average acetochlor application rates for Iowa, Minnesota, South Dakota, and Wisconsin, based on a survey by the U.S. Department of Agriculture (U.S. Department of Agriculture, 1995). Because acetochlor is applied exclusively to corn fields, acetochlor use has come at the expense of other corn herbicides (shown in table 1) and would rank approximately sixth in quantity applied.

Table 2.--Sources of regional pesticide data in the Upper Mississippi River Basin study area

[MCES, Metropolitan Council Environmental Services; USEPA, U.S. Environmental Protection Agency; MDA, Minnesota Department of Agriculture; MDH, Minnesota Department of Health; MPCA, Minnesota Pollution Control Agency; USACE, U.S. Army Corps of Engineers; USGS, U.S. Geological Survey; WDNR, Wisconsin Department of Natural Resources; SW, streams; BS, streambed sediment; GW, ground water]

Source	Sampling purpose	Media sampled	Sampling and processing methods	Pesticide types analyzed	Rivers or regions sampled	Number of sites or wells sampled	Sampling frequency	Sampling period
MCES—River Toxics Monitoring Program	Determine the effectiveness of wastewater-treatment programs and compliance with Federal and State regulations. Sampling sites were located primarily upstream or downstream of the MCES wastewater-treatment-plant outflows.	SW, BS	SW—Grab samples were collected with stainless-steel buckets 3 feet below the water surface near the center of the main channel. Unfiltered water samples were analyzed using USEPA method 608 (Metropolitan Waste Control Commission, 1994).	insecticides	Mississippi, Minnesota, St. Croix, and Vermillion Rivers	14 sites	annually, in autumn	1981–93
			BS—Samples were collected from the upper 4 inches of sediment with a Petite Ponar dredge and composited in an enamel container with a stainless-steel spatula (Metropolitan Waste Control Commission, 1990).	insecticides	Mississippi, Minnesota, St. Croix, and Vermillion Rivers	12 sites	annually, in autumn	1982–88
MDA—Water Quality Monitoring Network	Monitor the extent and trends in pesticide contamination in ground water.	GW	Unfiltered water samples from monitoring wells were analyzed.	herbicides	Minnesota part of study area	107 wells	variable	1987–93
MDA, with Minneapolis Parks and Recreation Board and University of Minnesota	Monitor pesticides in storm runoff in an urban watershed.	SW	Composited storm-runoff samples collected by automatic sampler were filtered and analyzed.	herbicides, insecticides	Lake Harriet Watershed, Minneapolis, Minnesota	1 site	variable	1992–93
MDH—Safe Drinking Water Program	Determine compliance of treated ground-water community water supplies with State and Federal drinking-water standards.	GW	Unfiltered water samples from public-supply wells were analyzed.	herbicides	Minnesota part of study area	87 wells	quarterly to every 3 years	1988–94
MPCA—Storage and Retrieval (STORET) data base	Determine extent of pesticide contamination in streambed sediment.	BS, GW	BS—Samples were collected from the Straight and Cannon Rivers and analyzed for 17 organochlorine insecticides. No record of the sample-collection methods or sample purpose was available.	herbicides insecticides	Cannon and Straight Rivers	11 sites,	once	1978
	Ambient Ground-Water Monitoring Program—establish baseline ground-water-quality conditions.		GW—Unfiltered water samples from domestic wells were analyzed.	herbicides	Minnesota part of study area	11 wells	once	1988–89
MPCA and MDA	Monitor pesticide contamination in surface water, predominantly in agricultural areas.	SW	Filtered samples collected by the MPCA and analyzed by the MDA.	herbicides, insecticides	Mississippi River and eight tributaries in Minnesota	14 sites	1–3 samples in spring and summer	1988–93

Table 2.--Sources of regional pesticide data in the Upper Mississippi River Basin study area--Continued

[MCES, Metropolitan Council Environmental Services; USEPA, U.S. Environmental Protection Agency; MDA, Minnesota Department of Agriculture; MDH, Minnesota Department of Health; MPCA, Minnesota Pollution Control Agency; USACE, U.S. Army Corps of Engineers; USGS, U.S. Geological Survey; WDNR, Wisconsin Department of Natural Resources; SW, streams; BS, streambed sediment; GW, ground water]

Source	Sampling purpose	Media sampled	Sampling and processing methods	Pesticide types analyzed	Rivers or regions sampled	Number of sites or wells sampled	Sampling frequency	Sampling period
USACE	Determine bed-sediment quality during river channel dredging operations.	BS	Samples were collected from the Mississippi River at 0.1–5-mile increments from Minneapolis to the outlet of Lake Pepin, from the Minnesota River near Savage and near the mouth, and from the St. Croix River near Hudson and near the mouth. Samples were collected with a Ponar dredge, a Petite Ponar dredge, or a coring device (U.S. Army Corps of Engineers, water-quality data base, electronic commun., 1995). Only samples collected from the upper 4 inches of the streambed were included in this report, so USACE sample methods would be similar to those of other agencies.	insecticides	Mississippi, Minnesota, and St.Croix Rivers	67 river miles	variable	1974–92
USGS	Pesticide analyses made in the course of surface- and ground-water-quality investigations of a regional nature conducted in cooperation with State and local agencies.	SW, BS, G	SW—Depth- and width-integrated or grab samples, filtered or unfiltered samples. Depth-integrated or dip samples for very low-level (parts-per-trillion) pesticide analyses were collected with Teflon-lined equipment (Pereria and others, 1995).	herbicides, insecticides	study area	15 sites	variable	1975–92
			BS—Samples were collected from two sites located at the upstream boundaries of the study area for the NASQAN program—the Mississippi River near Royalton, Minnesota, and the Minnesota River near Jordan, Minnesota. Samples also were collected from eight sites in the Mississippi River in Pool 2 and from two sites on the Namekagon River near Hayward, Wisconsin.	herbicides, insecticides	Mississippi, Minnesota, and Namekagon Rivers	5 sites	variable	1975–82
			GW—Unfiltered or filtered water samples from domestic and monitoring wells were analyzed. Some samples were analyzed by enzyme-linked immunosorbent assay.	herbicides	Minnesota part of study area	227 wells	variable	1983–94
USGS and WDNR	Compare pesticide concentrations in streambed sediment of the Mississippi River before and after the 1993 flood.	BS	Streambed-sediment samples were collected from the downstream one-third of navigation pools. Samples were composited from 12–21 individual samples in 2–5 transects from each pool. The upper 2–4 inches of sediment were removed from stainless-steel van Veen dredges using Teflon-lined syringes, composited in clean bottles, chilled, and analyzed (Sullivan and Moody, 1996).	insecticides	Mississippi and St. Croix Rivers	18 river miles	once in 1991 or 1992 and once in 1994	1991–94
WDNR—Ground-Water Quality Monitoring Network	Monitor the quality of untreated ground water used for public water supplies and private wells.	GW	Unfiltered water samples from domestic and public-supply wells were collected and analyzed. Some samples were analyzed by enzyme-linked immunosorbent assay.	herbicides	Wisconsin part of study area	156 wells	quarterly to annually	1988–94

Table 3.--Pesticide concentrations detected in stream samples collected by the Minnesota Pollution Control Agency and analyzed by the Minnesota Department of Agriculture in the Upper Mississippi River Basin study area, May–July 1988–93[a]

[μg/L, micrograms per liter]

Site number, fig. 7	Sampling site	Years sampled	Number of samples (excluding replicates)	Alachlor: Number of detections	Alachlor: Concentration range (μg/L)	Atrazine: Number of detections	Atrazine: Concentration range (μg/L)	Cyanazine: Number of detections	Cyanazine: Concentration range (μg/L)	Metolachlor: Number of detections	Metolachlor: Concentration range (μg/L)	Deethylatrazine: Number of detections	Deethylatrazine: Concentration range (μg/L)
2	Sauk River at Sauk Rapids, Minn.	1989, 91–93	10	1	<0.02–0.01	8	<0.05–0.78	7	<0.10–1.65	4	<0.10–0.11	1	<0.5–0.25
3	Mississippi River at Monticello, Minn.	1991–93	8	0	<0.05	3	<0.05–0.16	2	<0.14–0.44	0	<0.10	0	<0.5
4	Crow River at Dayton, Minn.	1991–93	9	2	<0.05–0.27	6	<0.05–0.84	4	<0.10–1.13	3	<0.10–0.71	0	<0.5
5	Rum River at Isanti, Minn.	1989, 91–93	10	2	<0.02–0.16	5	<0.05–0.47	0	<0.10	0	<0.10	1	<0.5–0.25
6	Rum River at Anoka, Minn.	1991–93	9	0	<0.05	6	<0.05–0.26	1	<0.10–0.09	1	<0.10–0.05	0	<0.5
8	Mississippi River at Fridley, Minn.	1988, 89, 92, 93	7	0	<0.05	2	<0.05–0.11	0	<0.10	0	<0.10	0	<0.5
16	Minnesota River at Ft. Snelling, Minn.	1988, 89, 91–93	10	4	<0.02–0.55	8	<0.05–0.95	8	<0.10–1.12	6	<0.10–1.72	0	<0.5
25	Kettle River near Hinkley, Minn.	1991–93	9	0	<0.05	0	<0.05	0	<0.10	0	<0.10	0	<0.5
26	Snake River near Pine City, Minn.	1991–93	9	0	<0.05	3	<0.05–0.25	0	<0.10	0	<0.10	0	<0.5
27	Sunrise River near North Branch, Minn.	1991–93	9	2	<0.05–0.16	4	<0.05–0.49	2	<0.10–0.40	2	<0.10–0.84	1	<0.5–0.25
32	Vermillion River near Farmington, Minn.	1991–93	9	0	<0.05	4	<0.05–0.49	0	<0.10	1	<0.10–0.05	0	<0.5
37	Straight River near Clinton Falls, Minn.	1988, 89, 91–93	10	1	<0.02–1.11	6	<0.05–0.90	2	<0.10–0.70	3	<0.01–1.36	1	<0.5–0.25
38	Prairie Creek upstream of Lake Byllesby, Minn.	1991–93	9	1	<0.05	4	<0.05–0.12	1	<0.10–0.04	2	<0.10–0.05	1	<0.5–0.25
39	Cannon River at Welch, Minn.	1988, 89, 91–93	11	4	<0.05–0.24	10	<0.05–1.44	3	<0.10–2.25	7	<0.10–0.74	0	<0.5

[a]All samples were analyzed for the herbicides alachlor, atrazine, cyanazine, metolachlor, metribuzin, and trifluralin. During selected years, samples also were analyzed for deethylatrazine, deisopropylatrazine, diazinon, ethalfluralin, fonofos, phorate, prometon, simazine, terbofos, and treflan.

Table 4.--Most frequently detected pesticides in urban stormwater-runoff samples collected by the Minnesota Department of Agriculture from part of the Lake Harriet Watershed, Minneapolis, Minnesota, 1992–93[a]

[μg/L, micrograms per liter; site number 11, figure 7]

Pesticide	Percent detections[b]		Maximum concentration of composited runoff events (μg/L)[b]	
	1992	1993	1992	1993
Alachlor	8	22	1.0	1.5
Atrazine	21	44	***3.8***	***3.6***
Cyanazine	0	17	<0.2	1.1
2,4-D	67	90	6.4	7.4
Dicamba	33	50	2.6	2.6
MCPA	29	50	5.6	43
MCPP	62	90	12	16
Metolachlor	8	39	0.4	0.8

[a]Samples were analyzed for chlorpyrifos, deethylatrazine, deisopropylatrazine, diazinon, dichlorprop, EPTC, ethalfluralin, fonofos, methyl parathion, metribuzin, pendimethalin, phorate, prometon, propachlor, propazine, terbufos, trifluralin, and triclopyr. Analyses had detection limits of 0.2 μg/L.

[b]Based on composite samples of 21 storms in 1992 and 20 storms in 1993. Concentrations that exceeded the U.S. Environmental Protection Agency's (1994) annual maximum contaminant level of 3.0 μg/L for atrazine are italicized in bold print.

Table 5.--Pesticide concentrations detected in stream samples collected by the U.S. Geological Survey in the Upper Mississippi River Basin study area, 1975–92[a]

[μg/L, micrograms per liter; na, not available; unfiltered water samples are noted]

Site number (fig. 7)	Sampling site	Years sampled (frequency or purpose)	Number of analyses (excluding duplicates)	Pesticides detected	Number of detections	Detected concentrations (μg/L)	Detection limits (μg/L)
1	Mississippi River near Royalton, Minn.	1975–82 (biannually or quarterly)	10–22	unfiltered diazinon	2	0.01	0.01–1.0
9	Mississippi River above St. Anthony Falls, Minn.	1991, 92 (low-level analyses)	3	atrazine	3	0.056–0.73	0.005
				deethylatrazine	3	0.057–0.14	0.005
				deisopropylatrazine	2	0.025–0.055	0.010
				cyanazine	3	0.077–0.41	0.025
				cyanazine-amide	3	0.01–0.073	0.025
				metribuzin	1	0.008	0.005
				prometon	3	0.008–0.01	0.005
				simazine	3	0.012–0.025	0.005
				alachlor	3	0.005–0.011	0.005
				2-hydroxy-2',6'-diethylacetanilide	2	0.061–0.085	0.005
				metolachlor	3	0.018–0.12	0.005
				DEET	3	0.018–0.200	0.005
12	Minnesota River near Jordan, Minn.	1975–82, 90 (biannually or quarterly)	23	unfiltered diazinon	1	0.08	0.01
			1	unfiltered dicamba	1	0.01	0.01
13	Nine Mile Creek at Bloomington, Minn.	1990	1	unfiltered 2,4-D	1	0.03	0.01

Table 5.--Pesticide concentrations detected in stream samples collected by the U.S. Geological Survey in the Upper Mississippi River Basin study area, 1975–92[a]--Continued

[µg/L, micrograms per liter; na, not available; unfiltered water samples are noted]

Site number (fig. 7)	Sampling site	Years sampled (frequency or purpose)	Number of analyses (excluding duplicates)	Pesticides detected	Number of detections	Detected concentrations (µg/L)	Detection limits (µg/L)
15	Minnesota River at river mile 3.5, Minn.	1991, 92 (low-level analyses)	3	atrazine	3	0.042-0.900	0.005
				deethylatrazine	3	0.036-0.150	0.005
				deisopropylatrazine	1	0.150	0.010
				cyanazine	3	0.013-0.97	0.025
				cyanazine-amide	1	0.21	0.025
				metribuzin	1	0.037	0.005
				prometon	3	0.013-0.022	0.005
				simazine	3	0.008-0.027	0.005
				alachlor	3	0.018-0.44	0.005
				2-chloro-2',6'-diethylacetanilide	1	0.008	0.005
				2-hydroxy-2',6'-diethylacetanilide	2	0.029–0.053	0.005
				metolachlor	3	0.058–0.700	0.005
				DEET	3	0.005–0.081	0.005
16	Minnesota River at Ft. Snelling at St. Paul, Minn.	1978, 90	4	unfiltered DDE	1	0.01	0.01
19	Mississippi River near Grey Cloud Island, Minn. (14 sites)	1976	26	none	--	--	na
22	Mississippi River at Hastings, Minn.	1991, 92 (low-level analyses)	3	atrazine	3	0.056–0.79	0.005
				deethylatrazine	3	0.047–0.15	0.005
				deisopropylatrazine	1	0.100	0.010
				cyanazine	3	0.04–0.79	0.025
				cyanazine-amide	2	0.07–0.11	0.025
				metribuzin	1	0.019	0.005
				prometon	3	0.013–0.019	0.005
				simazine	3	0.012–0.029	0.005
				alachlor	3	0.013–0.250	0.005
				2-hydroxy-2',6'-diethylacetanilide	2	0.031–0.061	0.005
				metolachlor	3	0.045–0.42	0.005
				DEET	2	0.036–0.12	0.005
23	Namekagon River below Rainbow Creek near Hayward, Wis.	1981	2	unfiltered 2,4-D	1	0.01	0.01
24	Namekagon River at River Rat Landing near Hayward, Wis.	1981	2	none	--	--	0.01–0.1
28	St. Croix River at St. Croix Falls, Wis.	1976	1	none	--	--	0.01–0.1
30	St. Croix River at river mile 0.5, Wis.	1991, 92 (low-level analyses)	3	atrazine	3	0.017–0.280	0.005
				deethylatrazine	3	0.015–0.044	0.005
				cyanazine	1	0.043	0.025
				simazine	3	0.007–0.019	0.005
				alachlor	1	0.024	0.005
				2-hydroxy-2',6'-diethylacetanilide	1	0.069	0.005
				metolachlor	2	0.05–0.063	0.005

Table 5.--Pesticide concentrations detected in stream samples collected by the U.S. Geological Survey in the Upper Mississippi River Basin study area, 1975–92[a]--Continued

[μg/L, micrograms per liter; na, not available; unfiltered water samples are noted]

Site number (fig. 7)	Sampling site	Years sampled (frequency or purpose)	Number of analyses (excluding duplicates)	Pesticides detected	Number of detections	Detected concentrations (μg/L)	Detection limits (μg/L)
35	South Branch Vermillion River at Empire, Minn.	1980	5	unfiltered simazine	1	0.24	na
				unfiltered diazinon	1	0.01	na
				unfiltered dieldrin	1	0.01	na
				unfiltered 2,4-D	1	0.02	na
36	Mississippi River at Lock and Dam 3 near Red Wing. Minn.	1978	4	none	--	--	na
40	Mississippi River near Pepin, Wis.	1991, 92 (low-level analyses)	3	atrazine	3	0.045–0.72	0.005
				deethylatrazine	3	0.044–0.13	0.005
				deisopropylatrazine	1	0.11	0.010
				cyanazine	3	0.036–0.85	0.025
				cyanazine-amide	3	0.037–0.13	0.025
				metribuzin	1	0.023	0.005
				prometon	3	0.011–0.021	0.005
				simazine	2	0.018–0.045	0.005
				alachlor	3	0.01–0.31	0.005
				2-chloro-2',6'-diethylacetanilide	1	0.006	0.005
				2-hydroxy-2',6'-diethylacetanilide	1	0.027	0.005
				metolachlor	3	0.03–0.49	0.005
				DEET	2	0.02–0.17	0.005

[a]At selected sites, samples were analyzed for *alachlor*, *2-chloro-2',6'-diethylacetanilide*, *2-hydroxy-2',6'-diethylacetanilide*, aldrin, *ametryn*, *atrazine*, *deethylatrazine*, *deisopropylatrazine*, chlordane, chlorpyrifos, *cyanazine*, *cyanazine amide*, *DEET*, *diazinon*, dicamba, dieldrin, disyston, 2,4-D, 2,4-DP, 2,4,5-T, endosulfan I, endrin, ethion, ethyl trithion, *fluometuron*, fonofos, heptachlor, heptachlor epoxide, *hexazinone*, γ-HCH (lindane), malathion, methomyl, methoxychlor, methyl parathion, methyl trithion, *metolachlor*, *2,6-diethylaniline*, *metribuzin*, mirex, *molinate*, *4-ketomolinate*, *norflurazon*, *desmethylnorflurazon*, parathion, perthane, picloram, *prometon*, *prometryn*, propham, silvex, *simazine*, simetryn, *thiobencarb*, and toxaphene. Pesticides listed in italics were analyzed at parts-per-trillion concentrations.

Table 6.--Organochlorine insecticide concentrations detected in stream samples collected by the Metropolitan Council Environmental Services in the Upper Mississippi River Basin study area, 1981–93[a]

[μg/L, micrograms per liter]

Site number (fig. 7)	Sampling site (and river mile)	Years sampled	Number of samples	Insecticides detected	Number of detections	Detected concentrations (μg/L)	Detection limits (μg/L)
7	Mississippi River at Anoka, Minn. (871.6)	1981, 88–93	8	γ-HCH	1	0.001	0.001
				α-HCH	1	0.019	0.002
				chlordane	1	***0.02***	0.02–0.021
10	Mississippi River at Lock and Dam 1, Minn. (847.7)	1988–93	6	none	none	--	0.001–0.02
12	Minnesota River near Jordan, Minn. (39.4)	1981, 88–93	8	γ-HCH	2	0.002, 0.003	0.002
				α-HCH	1	0.009	0.001
				chlordane	1	***0.05***	0.02–0.021
				heptachlor	1	0.002	0.001
14	Minnesota River near Black Dog Power Plant, Minn. (8.5)	1988–93	6	none	none	--	0.001–0.02

Table 6.--Organochlorine insecticide concentrations detected in stream samples collected by the Metropolitan Council Environmental Services in the Upper Mississippi River Basin study area, 1981–93[a]--Continued

[μg/L, micrograms per liter]

Site number (fig. 7)	Sampling site (and river mile)	Years sampled	Number of samples	Insecticides detected	Number of detections	Detected concentrations (μg/L)	Detection limits (μg/L)
16	Minnesota River at Fort Snelling State Park, Minn. (3.5)	1981, 88–93	7	γ-HCH	1	0.006	0.002
17	Mississippi River at St. Paul, Minn. (839.1)	1981, 88–93	8	γ-HCH	1	0.001	0.002
				α-HCH	1	0.01	0.001
				chlordane	1	***0.06***	0.02–0.021
				heptachlor	1	***0.005***	0.001
18	Mississippi River at Newport, Minn. (831.0)	1981, 88–93	6	γ-HCH	1	0.002	0.001
20	Mississippi River at Grey Cloud Island, Minn. (826.7)	1981, 88–93	8	γ-HCH	2	0.003, 0.004	0.002
				α-HCH	1	0.005	0.001
				chlordane	2	***0.04, 0.06***	0.02–0.021
				dieldrin	1	***0.04***	0.003
				endosulfan I	1	0.014	0.002
				endrin aldehyde	1	0.016	0.012
				heptachlor	1	0.001	0.001
21	Mississippi River at Lock and Dam 2, Minn. (815.6)	1981, 88–93	8	γ-HCH	1	0.002	0.002
				α-HCH	1	0.002	0.001
				dieldrin	1	0.008	0.003
				endosulfan II	1	0.011	0.005
				endrin	1	***0.015***	0.004
29	St. Croix River at Stillwater, Minn. (23.3)	1981, 88–93	7	α-HCH	1	0.015	0.001
				chlordane	1	***0.05***	0.02–0.021
				dieldrin	1	***0.007***	0.003
				heptachlor	1	***0.006***	0.003
31	St. Croix River at Prescott, Wis. (0.3)	1988–93	8	α-HCH	1	0.009	0.001
				heptachlor	1	0.003	0.001
33	Vermillion River at Farmington, Minn. (20.6)	1988–93	6	α-HCH	1	0.02	0.001
				chlordane	1	***0.03***	0.007
34	Vermillion River below Empire Wastewater Treatment Plant, Minn. (15.6)	1988–93	6	α-HCH	1	0.007	0.001
				chlordane	1	***0.03***	0.02–0.021
36	Mississippi River at Lock and Dam 3, Minn. (796.7, 797.5)	1981, 88–93	7	γ-HCH	1	0.002	0.002
				α-HCH	1	0.01	0.001
				chlordane	2	***0.03, 0.06***	0.02–0.021
				heptachlor	1	0.003	0.001

[a]Selected samples were analyzed for the organochlorine insecticides chlordane, 4,4'-DDT, 4,4'-DDD, 4,4'-DDE, dieldrin, and endrin in all samples, and aldrin, γ-HCH (lindane), α-HCH, β-HCH, δ-HCH, endosulfan I, endosulfan II, endrin aldehyde, endosulfan-sulfate, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor, and toxaphene in selected samples. Insecticides exceeding the U.S. Environmental Protection Agency's ambient freshwater-quality criteria for the protection of aquatic organisms are italicized in bold print. Refer to table 18 for actual criteria. Quality-control data, including analyses of equipment and laboratory blanks, were used to evaluate sample contamination. When data indicated contamination of an analyte, results were noted in the text or censored below the greatest concentration of contamination. γ-HCH and α-HCH were detected in blank samples at concentrations similar to environmental samples.

Table 7.--Organochlorine insecticide concentrations detected in streambed-sediment samples collected by the Metropolitan Council Environmental Services in the Upper Mississippi River Basin study area, 1982–88[a]

[μg/kg, micrograms per kilogram]

Site number (fig. 12)	Sampling site (river mile)	Years sampled	Number of samples	Insecticides detected	Number of detections	Detected concentrations (μg/kg)	Detection limits (μg/kg)
2	Mississippi River at Anoka, Minn. (871.6)	1982–85, 87, 88	6	α-HCH	1	5	0.07–5.0
				γ-HCH	1	15	0.13–0.53
				heptachlor	1	5	0.07–0.6
3	Mississippi River at Lock and Dam 1 (847.7)	1983, 87, 88	3	4,4'-DDD	1	2.7	0.4–3.6
				4,4'-DDE	1	7.4	0.2–1.8
4	Minnesota River at Jordan, Minn. (39.4)	1983, 84, 87, 88	4	α-HCH	2	10, 13	0.04–0.53
				γ-HCH	1	9.8	0.08–1.2
5	Minnesota River at Ft. Snelling State Park (3.5)	1982–85, 87, 88	10[b]	α-HCH	1	15.0	0.05–13
				γ-HCH	1	0.4	0.11–1.2
				chlordane	1	32.6	1.1–12
				4,4'-DDD	3[b]	1.7–2.3	0.33–3.6
				4,4'-DDE	4[b]	0.01–1.7	0.01–0.8
				heptachlor	1	7.0	0.05–5.0
				toxaphene	1	8.0	3–100
6	Mississippi River at St. Paul, Minn. (839.1)	1982–85, 87, 88	12[b]	α-HCH	6[b]	0.98–7.9	0.04–5
				γ-HCH	2	0.44, 20	0.2–1.2
				chlordane	1	267	3.9–12
				4,4'-DDE	1	0.95	0.6–7.0
7	Mississippi River at Newport, Minn. (831.0)	1987, 88	2	4,4'-DDD	1	1.2	0.26–3.6
9	Mississippi River at Grey Cloud Island, Minn. (826.7)	1982–85, 87, 88	21[b]	α-HCH	2[b]	3.0, 4.9	0.5–5.0
				γ-HCH	2	1.2, 8.0	0.07–1.2
				δ-HCH	1	0.34	0.05–15
				4,4'-DDD	2[b]	1.1, 2.6	0.2–14
				4,4'-DDE	2[b]	0.9, 2.2	0.1–7.0
				heptachlor	2	0.33–9.0	0.05–5.0
10	Mississippi River at Lock and Dam 2 (815.6)	1982–85, 87, 88	21[b]	α-HCH	8[b]	1.2–13.0	0.05–5.0
				γ-HCH	2	4.1, 11.0	0.16–1.2
				endrin	2[b]	0.23, 0.28	0.26–10.0
				heptachlor	2	0.17, 5.0	0.05–5.0
13	St. Croix River at Stillwater, Minn. (23.3)	1984, 85, 87, 88	10[b]	4,4'-DDD	1	2.0	0.29–3.6
				4,4'-DDE	1	1.0	0.39–4.8
				dieldrin	1	0.32	0.15–1.6
14	St. Croix River at Prescott, Wis. (1.7, 0.3)	1983–85, 87, 88	5	4,4'-DDD	1	1.4	1.4–3.6
				dieldrin	1	0.59	0.16–1.6
15	Vermillion River below Empire WWTP (15.6)	1987, 88	2	4,4'-DDD	1	1.2	0.29–3.6
				4,4'-DDE	1	0.87	0.39–1.8
16	Mississippi River at Lock and Dam 3 (796.7, 797.5)	1982–85, 87, 88	15[b]	α-HCH	2	5.3, 6.1	0.06–5.0
				γ-HCH	2	2.1, 8.0	0.08–1.2
				heptachlor	2	0.07, 7.0	0.04–5.0
				toxaphene	1	3.0	3.0–120

[a]Samples were analyzed for the organochlorine insecticides aldrin, α-HCH, β-HCH, δ-HCH, γ-HCH (lindane), chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, endosulfan I, endosulfan II, sulfate, endrin, endrin aldehye, heptachlor, heptachlor epoxide, and toxaphene.

[b]Includes analyses of both discrete samples, collected from the left, right, or center sections of channel, and composites of discrete samples.

Table 8.--Organochlorine insecticide concentrations detected in streambed-sediment samples collected by the Minnesota Pollution Control Agency in the Upper Mississippi River Basin study area, September 1978[a]

[μg/kg, micrograms per kilogram; --, not applicable]

Site number (fig. 12)	Sampling site	Number of samples	Insecticides detected	Detected concentrations (μg/kg)	Detection limits (μg/kg)
17	Cannon River at Gorman Lake near Cordova, Minn.	1	none	--	0.01–5.0
18	Little Cannon River at Sabre Lake near Cordova, Minn.	1	none	--	0.01–5.0
19	Cannon River at Lake Tetonka near Waterville, Minn.	1	chlordane	3.0	1.0
20	Cannon River at Highway 66 near Warsaw, Minn.	1	chlordane	4.0	1.0
21	Cannon River at Faribault, Minn.	1	4,4'-DDD	21.0	1.0
22	Straight River 1.5 miles east of Faribault, Minn.	1	α-HCH	24.0	1.0
23	Cannon River at Straight River confluence at Faribault, Minn.	1	none	--	0.01–5.0
24	Cannon River 3.5 miles northwest of Cannon City, Minn.	1	none	--	0.01–5.0
25	Cannon River above Northfield, Minn.	1	none	--	0.01–5.0
26	Cannon River northeast of Northfield, Minn.	1	none	--	0.01–5.0
27	Cannon River at Highway 56 near Randolph, Minn.	1	none	--	0.01–5.0

[a]Samples were analyzed for the organochlorine insecticides aldrin, γ-HCH (lindane), α-HCH, chlordane, 4,4'-DDT, 2,4'-DDT, 4,4'-DDD, 4,4'-DDE, 2,4'-DDE, dieldrin, endrin, and methoxychlor.

Table 9.--Organochlorine insecticide concentrations detected in streambed-sediment samples collected by the U.S. Army Corps of Engineers in the Upper Mississippi River Basin study area, 1974–92[a]

[μg/kg, micrograms per kilogram; --, not applicable]

Reach letter (fig. 12)	River reach sampled (river miles)	Years sampled	Number of samples	Insecticides detected	Number of detections	Detected concentrations (μg/kg)	Detection limits (μg/kg)
A	Mississippi River—Pool 0	1974, 75, 78,	16	4,4'-DDD	2	0.2, 1.3	0.1–10
	(857.6–854.9)	80, 89		4,4'-DDE	1	2.2	
B	Mississippi River—Pool 1	1974, 75, 78,	14	aldrin	1	0.12	0.09–0.1
	(853.0–847.9)	80, 82, 89	40	chlordane	7	1.0–6.0	1.0–15.36
			40	4,4'-DDD	12	0.3–3.6	0.1–10
			40	4,4'-DDE	5	1.0–49	0.1–10
			40	4,4'-DDT	9	0.2–2.2	0.1–10
C	Mississippi River—Pool 2	1974, 75, 78,	16	aldrin	3	0.4–1.1	0.09–1.02
	(843.36–814.4)	80–82, 84, 88,	32	γ-HCH	1	1.0	0.006–1.02
		89, 92	73	chlordane	11	0.83–11	0.04–10
			73	4,4'-DDD	16	0.20–7.0	0.01–10
			73	4,4'-DDE	9	0.5–7.3	0.01–10
			74	4,4'-DDT	6	0.4–9.7	0.01–10
			74	dieldrin	7	0.7–2.9	0.01–10
			74	endrin	2	0.2, 1.0	0.02–10
D	Minnesota River	1975, 78–80,	14	chlordane	2	1.0	1.0–15.36
	(14.6–0.1)	82, 89	14	4,4'-DDD	2	0.8	0.1–10
			14	4,4'-DDE	1	1.0	0.1–10
			15	4,4'-DDT	1	0.4	0.1–10
			15	dieldrin	2	0.5, 0.6	0.1–10

Table 9.--Organochlorine insecticide concentrations detected in streambed-sediment samples collected by the U.S. Army Corps of Engineers in the Upper Mississippi River Basin study area, 1974–92[a]

[μg/kg, micrograms per kilogram; --, not applicable]

Reach letter (fig. 12)	River reach sampled (river miles)	Years sampled	Number of samples	Insecticides detected	Number of detections	Detected concentrations (μg/kg)	Detection limits (μg/kg)
E	Mississippi River—Pool 3 (815.01–799.2)	1974, 78–82, 89	35	aldrin	1	0.15	0.09–0.1
				chlordane	3	0.4–8.0	1.0–15
				4,4'-DDD	2	1.4, 4.9	0.1–10
				4,4'-DDE	1	4.6	0.1–10
				4,4'-DDT	3	0.4–1.0	0.1–10
				dieldrin	1	1.0	0.1–10
				endrin	2	0.2	0.1–10
F	St. Croix River (17.5–0.6)	1980, 82, 89	8	none	none	--	0.07–1.48
G	Mississippi River—Pool 4 (763.5–794.5)	1974, 78–82, 88, 89	39	chlordane	2	7.1, 9.0	0.04–15.36
			39	4,4'-DDD	5	1.5–5.28	0.01–10
			39	4,4'-DDE	4	0.28–50	0.01–10
			40	4,4'-DDT	6	0.3–700	0.01–10
			40	dieldrin	3	0.2–1.2	0.01–10
			40	endrin	1	0.24	0.02–10

[a]Samples were analyzed for the organochlorine insecticides chlordane, 4,4'-DDT, 4,4'-DDD, 4,4'-DDE, dieldrin, and endrin in all samples, and aldrin, α-HCH, β-HCH, δ-HCH, γ-HCH (lindane), endosulfan I, endosulfan II, endosulfan-sulfate, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor, and toxaphene in selected samples.

Table 10.--Pesticide concentrations detected in streambed-sediment samples collected by the U.S. Geological Survey in the Upper Mississippi River Basin study area, 1975–82[a]

[μg/kg, micrograms per kilogram; na, not available; --, not applicable]

Site number (fig. 12)	Sampling site (and river mile)	Years	Number of samples	Insecticides detected	Number of detections	Detected concentrations (μg/kg)	Detection limits (μg/kg)
1	Mississippi River near Royalton, Minn. (956)	1975, 76, 78, 79, 82	5	endrin	1	0.1	0.1, na
				toxaphene	1	10	0.1, na
				chlordane	1	1.0	na
				mirex	1	0.1	na
4	Minnesota River near Jordan, Minn. (39.4)	1975–79, 81, 82	10	γ-HCH	1	0.1	0.1, na
				4,4'-DDD	1	4	0.1, na
				dieldrin	1	0.4	0.1, na
				endrin	2	0.1	0.1, na
				heptachlor	2	0.1, 0.11	0.1, na
				epoxide			0.1, na
				toxaphene	3	1, 10	na
				chlordane		0.1, 1.0	
8	Mississippi River near Grey Cloud Island at Inver Grove Heights, Minn. (8 locations, 823)	1976	8	chlordane	3	1–4.0	na
				4,4'-DDD	6	0.2–0.6	na
				dieldrin	2	0.1	na
				mirex	2	0.1	na
11, 12	Namekagon River below Rainbow Creek and below Rat Landing near Hayward, Wis. (66)	1981	2	none	--	--	na

[a]Samples were analyzed for aldrin, γ-HCH (lindane), chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, and toxaphene at all sites and atrazine, 2,4-D, diazinon, endosulfan I, ethion, ethyl trithion, methoxychlor, mirex, parathion, methyl parathion, simazine, silvex, and 2,4,5-T at selected sites.

Table 11.--Pesticide concentrations detected in streambed-sediment samples collected by the U.S. Geological Survey and the Wisconsin Department of Natural Resources in the Upper Mississippi River Basin study area, 1991–94[a]

[µg/kg, micrograms per kilogram]

Reach letter (fig. 12)	River reach sampled (and river mile)	Years	Number of samples	Insecticides detected	Number of detections	Detected concentrations (µg/kg)	Detection limits (µg/kg)
B	Mississippi River—Pool 1	1994	1	chlordane	1	1.0	1.0
	(853.0–847.9)			4,4'-DDD	1	0.5	0.1
				4,4'-DDE	1	0.4	0.1
C	Mississippi River—Pool 2	1991, 94	2	chlordane	2	1.0, 3.5	1.0
	(843.36–814.4)			dieldrin	2	0.1, 0.2	0.1
				4,4'-DDT	2	0.1, 0.4	0.1
				4,4'-DDD	2	1.0, 1.6	0.1
				4,4'-DDE	2	0.8, 1.2	0.1
E	Mississippi River—Pool 3	1992, 94	2	chlordane	1	3.0	1.0
	(815.01–799.2)			dieldrin	2	0.1, 0.3	0.1
				4,4'-DDT	2	0.2, 0.7	0.1
				4,4'-DDD	2	1.0, 3.8	0.1
				4,4'-DDE	2	1.1, 1.2	0.1
F	St. Croix River	1994	1	4,4'-DDT	1	0.1	0.1
	(17.5–0.6)			4,4'-DDD	1	0.4	0.1
				4,4'-DDE	1	0.7	0.1
G	Mississippi River—Pool 4	1992, 94	4	chlordane	4	2.0, 2.0, 4.0, 4.0	1.0
	(763.5–794.5)			dieldrin	3	0.3, 0.4, 0.6	0.1
				4,4'-DDT	2	0.3, 0.4	0.1
				4,4'-DDD	4	0.9, 1.0, 1.2, 1.6	0.1
				4,4'-DDE	4	0.9, 0.9, 1.0, 2.5	0.1

[a]Samples were analyzed for the organochlorine insecticides aldrin, γ-HCH (lindane), chlordane, 4,4'-DDT, 4,4'-DDD, 4,4'-DDE, dieldrin, endrin, heptachlor, heptachlor epoxide, 4,4'-methoxychlor, mirex, and toxaphene.

Table 12.--Frequencies of detection, numbers of wells sampled, detection limits, and concentration ranges of most frequently detected herbicides in unfiltered ground-water samples from wells completed in sand and gravel and bedrock aquifers analyzed by the U.S. Geological Survey in the Upper Mississippi River Basin study area, 1983–94[a]

[µg/L, micrograms per liter; --, not applicable; data for bedrock aquifers in parentheses]

Compound	Percent of wells with detections	Numbers of wells sampled	Detection limits (µg/L)	Range in detected concentrations (µg/L)
Alachlor	0 (0)	70 (1)	0.01, 0.05, 0.1	-- (--)
Atrazine	31.8 (0)	85 (1)	0.01, 0.05, 0.1	0.04–0.81 (--)
Cyanazine	3.6 (0)	55 (1)	0.1, 0.2	0.1 (--)
Deisopropylatrazine	13.0 (90.9)[b]	46 (11)	0.1, 0.06	0.06–0.98 (0.14–2.23)
Deethylatrazine	58.7 (100)[b]	46 (13)	0.03, 0.05	0.04–2.3 (0.14–2.28)
Metolachlor	2.8 (0)	70 (1)	0.01, 0.05, 0.1	0.1–0.45 (--)
Simazine	3.6 (0)	55 (1)	0.05, 0.1	0.05–0.1 (--)
Triazine compounds (immunoassay analysis)	18.3 (17.3)	71 (81)	0.01, 0.1	0.09–0.88 (0.13–1.3)

[a]Detection limits varied depending on sampling design and analytical method. Other compounds analyzed for in water samples from selected wells include: 2,4-DP, 2,4,5-T, 2,4-D, 2,6-diethylaniline, aldrin, α-HCH, ametryn, ametryne, atratone, azinphos methyl, benfluralin, butylate, carbaryl, carbofuran, chlordane, chlorpyrifos, cyprazine, DCPA, diazinon, dicamba, dieldrin, dimethoate, disulfoton, endosulfan I, endrin, EPTC, ethalfluralin, ethoprop, fonofox, heptachlor epoxide, heptachlor, lindane, linuron, malathion, methomyl, methoxychlor, methyl parathion, metribuzin, mirex, molinate, napropamide, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, parathion, pebulate, pendimethalin, permethrin, perthane, phorate, picloram, prometon, prometryne, pronamide, propachlor, propanil, propargite, propazine, propham, silvex, simetone, simetryne, tebuthiuron, terbacil, terbufos, thiobencarb, toxaphene, triallate, and trifluralin.

[b]Large percentages of these pesticides were detected because only samples testing positive for triazine compounds by immunoassay were analyzed by gas chromatography/mass spectrometry.

Table 13.--Frequencies of detection, numbers of wells sampled, detection limits, and concentration ranges of most frequently detected herbicides in filtered ground-water samples from wells completed in sand and gravel and bedrock aquifers analyzed by the U.S. Geological Survey in the Upper Mississippi River Basin study area, 1990–93[a]

[µg/L, micrograms per liter; --, not applicable; data for bedrock aquifers in parentheses]

Compound	Percent of wells with detections	Numbers of wells sampled	Detection limits (µg/L)	Range in detected concentrations (µg/L)
Alachlor	0 (0)	24 (2)	0.01, 0.05	-- (--)
Atrazine	54.2 (100[b])	24 (12)	0.05	0.03–0.81 (0.1–0.66)
Cyanazine	0 (0)	24 (2)	0.01, 0.2	-- (--)
Deisopropylatrazine	4.3 (0)	23 (2)	0.05	0.06 (--)
Deethylatrazine	66.7 (50[b])	24 (2)	0.02, 0.05	0.05–1.12 (0.32)
Metolachlor	4.2 (0)	24 (2)	0.01, 0.05	0.45 (--)
Simazine	0 (0)	24 (2)	0.01, 0.05	-- (--)

[a]Detection limits varied depending on sampling design and analytical method. Other compounds analyzed for in water samples from selected wells include: 2,4-DP, 2,4,5-T, 2,4-D, 2,6-diethylaniline, aldrin, α-HCH, ametryn, atratone, azinphos methyl, benfluralin, butylate, carbaryl, carbofuran, chlordane, chlorpyrifos, cyprazine, DCPA, diazinon, dicamba, dieldrin, dimethoate, disulfoton, endosulfan I, endrin, EPTC, ethalfluralin, ethoprop, fonofos, heptachlor epoxide, heptachlor, lindane, linuron, malathion, methomyl, methoxychlor, methyl parathion, metribuzin, mirex, molinate, napropamide, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, parathion, pebulate, pendimethalin, permethrin, perthane, phorate, picloram, prometon, prometryne, pronamide, propachlor, propanil, propargite, propazine, propham, silvex, simetone, simetryne, tebuthiuron, terbacil, terbufos, thiobencarb, toxaphene, triallate, and trifluralin.

[b]Large percentages of these pesticides were detected because only samples testing positive for triazine compounds by immunoassay were analyzed by gas chromatography/mass spectrometry.

Table 14.--Frequencies of detection, numbers of wells sampled, detection limits, and concentration ranges of most frequently detected herbicides in unfiltered ground-water samples from wells completed in sand and gravel and bedrock aquifers analyzed by the Minnesota Department of Agriculture in the Upper Mississippi River Basin study area, 1987–93[a]

[µg/L, micrograms per liter; --, not applicable; data for bedrock aquifers in parentheses]

Compound	Percent of wells with detections	Numbers of wells sampled	Detection limits (µg/L)	Range in detected concentrations (µg/L)
Alachlor	2.9 (0)	104 (3)	0.05	0.37–1.32 (--)
Atrazine	26.0 (66.7)	104 (3)	0.05	0.05–1.38 (0.2)
Cyanazine	0 (0)	104 (3)	0.10	-- (--)
Metolachlor	1.0 (0)	104 (3)	0.10	0.82 (--)

[a]Other compounds analyzed for in water samples from selected wells include: 2,4-D, EPTC, MCPA, aldicarb, butylate, carbaryl, carbofuran, chloramben, chlorpyrifos, deethylatrazine, deisopropylatrazine, dicamba, disulfoton, fonofos, linuron, methyl paration, metribuzin, pentachlorophenol, phorate, phosphamidon, picloram, propachlor, simazine, terbufos, and trifluralin.

Table 15.--Frequencies of detection, numbers of wells sampled, detection limits, and concentration ranges of most frequently detected herbicides in unfiltered ground-water samples from wells completed in sand and gravel and bedrock aquifers analyzed by the Wisconsin Department of Natural Resources in the Upper Mississippi River Basin study area, 1988–94[a]

[μg/L, micrograms per liter; --, not applicable; data for bedrock aquifers in parentheses]

Compound	Percent of wells with detections	Numbers of wells sampled	Detection limits (μg/L)	Range in detected concentrations (μg/L)
Alachlor	0 (0)	37 (50)	0.5, 1.0, 10	-- (--)
Atrazine	2.2 (16)	46 (50)	0.5, 1.0, 3.0, 10	1.4 (0.64–3.0)
Cyanazine	0 (0)	31 (19)	0.5, 1.0	-- (--)
Deisopropylatrazine	0 (0)	26 (14)	1.0	-- (--)
Deethylatrazine	8.1 (14.3)	37 (14)	0.5, 1.0, 3.0, 10	1.0-1.3 (1.1–3.9)
Metolachlor	0 (0)	35 (50)	0.5, 1.0, 10	-- (--)
Simazine	0 (0)	15 (32)	0.5, 1.0, 3.0, 10	-- (--)
Triazine compounds (immunoassay analysis)	5.9 (23.4)	34 (47)	0.5, 1.0	0.9–1.4 (0.5–8.4)

[a]Detection limits varied depending on sampling design and analytical method. Other compounds analyzed for in water samples from selected wells include: 2,4-D, aldicarb, aldicarb sulfone, aldicarb sulfoxide, aldrin, α-HCH, β-HCH, δ-HCH, γ-HCH (lindane), endosulfan I, endosulfan II, α-chlordane, butachlor, carbaryl, carbofuran, α-chlordane, γ-chlordane, cis-nonachlor, dalapon, 4,4'-DDT, diaminoatrazine, dicamba, dieldrin, dimethoate, dinoseb, diquat, endosulfan sulfate, endothall, endrin, endrin ketone, eptam, glyphosate, heptachlor, heptachlor epoxide, methomyl, methoxychlor, metribuzin, trans-nonachlor, oxamyl, phorate, picloram, silvex, terbufos, tetrahydrofuran, and toxaphene.

Table 16.--Frequencies of detection, numbers of wells sampled, detection limits, and concentration ranges of most frequently detected herbicides in unfiltered ground-water samples from wells completed in sand and gravel and bedrock aquifers analyzed by the Minnesota Department of Heath in the Upper Mississippi River Basin study area, 1988–94[a]

[μg/L, micrograms per liter; --, not applicable; data for bedrock aquifers in parentheses]

Compound	Percent of wells with detections	Numbers of wells sampled	Detection limits (μg/L)	Range in detected concentrations (μg/L)
Alachlor	0 (0)	44 (43)	0.5	-- (--)
Atrazine	0 (0)	44 (43)	0.5	-- (--)
Cyanazine	0 (0)	36 (19)	0.5	-- (--)
Metolachlor	0 (0)	44 (43)	0.5	-- (--)
Simazine	0 (0)	44 (43)	0.5	-- (--)

[a]Other compounds analyzed for in water samples from selected wells include: 2,4,5-T, 2,4,5-TP, 2,4-D, 2,4-DB, 3,5-dichlorobenzoic acid, 3-hydroxycarbofuran, 4-nitrophenol, 5-hydroxydicamba, DCPA-acid metabolites, acifluorofen, aldicarb, aldicarb sulfone, aldicarb sulfoxide, aldrin, alpha-chlordane, baygon, bentazon, butachlor, carbaryl, carbofuran, chloramben, dalapon, dicamba, dichlorprop, dieldrin, dinoseb, endrin, γ-chlordane, glyphosate, heptachlor, heptachlor epoxide, hexachlorobenzene, hexachlorocyclopentadiene, lindane, methiocarb, methomyl, methoxychlor, metribuzin, oxamyl, picloram, propachlor, toxaphene, and trans-nonachlor.

Table 17.--Frequencies of detection, numbers of wells sampled, detection limits, and concentration ranges of most frequently detected herbicides in unfiltered ground-water samples from wells completed in sand and gravel aquifers analyzed by the Minnesota Pollution Control Agency in the Upper Mississippi River Basin study area, 1988–89[a]

[µg/L, micrograms per liter; --, not applicable]

Compound	Percent of wells with detections	Numbers of wells sampled	Detection limits (µg/L)	Range in detected concentrations (µg/L)
Alachlor	0	11	0.16	--
Atrazine	0	11	0.05	--
Cyanazine	0	11	0.56	--
Metolachlor	0	11	0.12	--
Simazine	0	11	0.08	--

[a]Other compounds analyzed for in water samples from selected wells include: 2,4,5-T, 2,4-D, 3-hydroxy carbofuran, EPTC, aldicarb, aldicarb sulfone, aldicarb sulfoxide, butylate, carbaryl, carbofuran, chloramben, chloropyrifos, disulfoton, dyfonate, linuron, methyl parathion, metribuzin, phorate, phosphamidon, picloram, propachlor, silvex, terbufos, and trifluralin.

Table 18.--Drinking-water standards and water-quality criteria (Nowell and Resek, 1994) for the most frequently detected pesticides in the Upper Mississippi River Basin study area, 1974–94

[Pesticides with no U.S. Environmental Protection Agency standards or criteria are not listed; degradation products and isomers of pesticides are indented; concentrations are in micrograms per liter of water or in micrograms per kilogram of sediment; --, no applicable standard or criteria; MCL, Maximum Contaminant Level; MCLG, Maximum Contaminant Level Goal]

			Drinking water			Freshwater	Sediment
Pesticide (metabolites and isomers indented below parent compound)	Pesticide class	Media in which pesticides were detected (SW, streams; BS, streambed sediment; GW, ground water)	MCL[a]	MCLG	Long term consumption limits for adult (and child)	Maximum concentrations for protection of aquatic life, acute (and chronic)	Sediment-quality criteria
Herbicides							
Alachlor	Acetanilide	SW, GW	2.0	0	(100)	--	--
Atrazine	Triazine	SW, GW	3.0	3.0[a]	200 (50)	--	--
Deethylatrazine	Triazine	SW, GW	--	--	--	--	--
Deisopropylatrazine	Triazine	GW	--	--	--	--	--
Cyanazine	Triazine	SW, GW	--	1.0	70 (20)	--	--
Dicamba	Benzoic acid derivative	SW	--	--	1000 (300)	--	--
Metolachlor	Acetanilide	SW, GW	--	--	5000 (2000)	--	--
Simazine	Triazine	GW	4.0	--	200 (50)	100	--
2, 4-D	Chlorinated phenoxy	SW	70	--	--	--	--
Insecticides							
Aldrin	Organochlorine	BS	--	--	0.3 (0.3)	30	--
Chlordane	Organochlorine	BS	2.0	0	(0.05)	2.4 (0.0043)	309
4,4'-DDT	Organochlorine	BS	--	--	--	1.1 (0.001)	828
4,4'-DDD	Organochlorine	BS	--	--	--	0.6	--
4,4'-DDE	Organochlorine	BS	--	--	--	1,050	--
Diazinon	Organophosphate	SW	--	--	20 (5.0)	--	--
Dieldrin	Organochlorine	BS	--	--	2.0 (0.5)	2.5 (0.0019)	--
Endosulfan I	Organochlorine	SW	--	--	--	0.22 (0.056)	300
Endosulfan II	Organochlorine	SW	--	--	--	0.22 (0.056)	300
Endrin	Organochlorine	BS	2.0	--	16 (4.5)	0.18 (0.0023)	4,200
γ-HCH (or lindane)	Organochlorine	BS	0.2	--	120 (33)	2.0 (0.008)	157
α-HCH	Organochlorine	BS	--	--	20 (50)	100	--
β-HCH	Organochlorine	BS	--	--	--	100	--
δ-HCH	Organochlorine	BS	--	--	--	100	--
Heptachlor	Organochlorine	BS	0.4	0	17.5 (5)	0.52 (0.0038)	110
Heptachlor epoxide	Organochlorine	BS	0.2	0	0.1 (0.1)	0.52 (0.0038)	--
Toxaphene	Organochlorine	BS	3.0	0	--	0.73 (0.0002)	64.7

[a]Maximum contaminant level goal for atrazine in Wisconsin includes concentrations of atrazine, deethylatrazine, deisopropylatrazine, and diaminoatrazine (Wisconsin Department of Natural Resources, 1994).

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