

**Prepared in cooperation with Missouri Department of Natural Resources**

# **Surface-Water Quality Conditions and Long-Term Trends at Selected Sites within the Ambient Water-Quality Monitoring Network in Missouri, Water Years 1993–2008**



**U.S. Department of the Interior U.S. Geological Survey**



**Cover photos.** *A*, Upstream view of the Grand River near Sumner site (Jacob Morris, U.S. Geological Survey). *B*, Upstream view of the South Fabius River near Taylor site (Dean Fryer, U.S. Geological Survey). *C*, Downstream view of the Gasconade River above Jerome site (Bruce Ponzer, U.S. Geological Survey). *D*, Upstream view of the Current River near Doniphan site (Dean Fryer, U.S. Geological Survey). *E*, Downstream view of the Elk River near Tiff City site (Bruce Ponzer, U.S. Geological Survey). *F*, Upstream view of the Wilson Creek near Brookline site (Matthew Williams, U.S. Geological Survey).

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# **Conversion Factors and Datums**

Inch/Pound to SI



Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

#### $\textdegree$ F=(1.8× $\textdegree$ C)+32

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

 $^{\circ}$ C=( $^{\circ}$ F-32)/1.8

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at  $25 °C$ ).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Water year in U.S. Geological Survey reports is the 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 2008, is called the "2008 water year".

# <span id="page-8-0"></span>**Surface-Water Quality Conditions and Long-Term Trends at Selected Sites within the Ambient Water-Quality Monitoring Network in Missouri, Water Years 1993–2008**

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# **Abstract**

The U.S. Geological Survey, in cooperation with the Missouri Department of Natural Resources, collects data pertaining to the surface-water resources of Missouri. These data are collected as part of the Missouri Ambient Water-Quality Monitoring Network and constitute a valuable source of reliable, impartial, and timely information for developing an improved understanding of water resources in the State.

Six sites from the Ambient Water-Quality Monitoring Network, with data available from the 1993 through 2008 water years, were chosen to compare water-quality conditions and long-term trends of dissolved oxygen, selected physical properties, total suspended solids, dissolved nitrate plus nitrite as nitrogen, total phosphorous, fecal indicator bacteria, and selected trace elements. The six sites used in the study were classified in groups corresponding to the physiography, main land use, and drainage basin size, and represent most stream types in Missouri.

Long-term trends in this study were analyzed using flowadjusted and non-flow adjusted models. Highly censored datasets (greater than 5 percent but less than 50 percent censored values) were not flow-adjusted. Trends that were detected can possibly be related to changes in agriculture or urban development within the drainage basins. Trends in nutrients were the most prevalent. Upward flow-adjusted trends in dissolved nitrate plus nitrite (as nitrogen) concentrations were identified at the Elk River site, and in total phosphorus concentrations at the South Fabius and Grand River sites. A downward flowadjusted trend was identified in total phosphorus concentrations from Wilson Creek, the only urban site in the study. The downward trend in phosphorus possibly was related to a phosphorus reduction system that began operation in 2001 at a wastewater treatment plant upstream from the sampling site. Total suspended solids concentrations indicated an upward non-flow adjusted trend at the two northern sites (South Fabius and Grand Rivers). The increase in total suspended solids concentrations could be because of soil erosion from land cultivated for row crops. Most trace element data examined

in the study were highly censored and could not be used for flow-adjusted trend analyses.

Water-quality conditions were assessed to explore relations between data from sites and to the State water-quality standards where applicable for selected constituents. Streamflow varied at each site because of drainage area, land use, and groundwater inputs. Dissolved oxygen and water temperature were similar at all sites except the urban site located on Wilson Creek. Specific conductance was similar between the most northern (South Fabius and Grand River sites) and the most southern sites (Current and Elk River sites). Total suspended solids concentrations were near the method reporting level at all sites, except the northern sites. Streams in northern Missouri are more turbid than streams in southern Missouri and are affected by large volumes of sediment deposition because of soil erosion from land cultivated for row crops.

Geometric means of *Escherichia coli* were calculated from the recreational seasons within the study period. Only the Grand River site exceeded the whole-body-contact standard for frequently used waters. The South Fabius and Grand River sites and the Wilson Creek site had statistically larger densities of both fecal indicator bacteria types than the remaining sites.

# **Introduction**

The U.S. Geological Survey (USGS), in cooperation with the Missouri Department of Natural Resources (MDNR), collects data pertaining to the surface-water resources of Missouri. These data are collected as part of the Missouri Ambient Water-Quality Monitoring Network (AWQMN) and are stored and maintained by the USGS National Water Information System (NWIS) database. These data constitute a valuable source of reliable, impartial, and timely information for developing an improved understanding of the water resources of the State. To make this information readily available, these data have been published annually by water year (October 1 through September 30) since the inception of the AWQMN in 1964 (U.S. Geological Survey, 1964–2005; U.S. Geological Survey 2006–2008). Historical as well as current data also can <span id="page-9-0"></span>be accessed from the Internet-based version of NWIS at *http:// waterdata.usgs.gov/nwis* (U.S. Geological Survey, 2010).

The MDNR is responsible for the implementation of the Federal Clean Water Act (CWA) in Missouri. Section 305(b) of the CWA requires that each State develop a water-quality monitoring program and periodically report the status of its water quality (U.S. Environmental Protection Agency, 1997). Water-quality status is described in terms of the suitability of the water for various uses, such as drinking water, fishing, swimming, and aquatic life; these uses are formally defined as "designated uses" in State and Federal Regulations. Section 303(d) of the CWA requires that certain waters that do not meet applicable water-quality standards be identified and Total Maximum Daily Loads (TMDLs) be determined for these waters (U.S. Environmental Protection Agency, 1997). TMDLs establish the maximum amount of a contaminant that a water body can assimilate and still meet the water-quality standards. Separate TMDLs address each contaminant for each water body.

Missouri has an area of approximately 69,000 square miles (mi<sup>2</sup>) with 22,216 miles (mi) of classified streams that support recreation, agriculture, industry, transportation, and public utilities. An estimated 8,541 mi of streams are adversely affected or impaired by various physical changes or chemical contaminants. These impairments can result in the loss of at least one of the water body uses designated for these streams (Missouri Department of Natural Resources, 2009).

Public agencies that protect and manage water resources have a critical need for information gained through waterquality monitoring. Information from water-quality monitoring is needed to assess the existing conditions of water resources; to design preservation, management, and remediation programs; and to evaluate the effectiveness of such programs (Intergovernmental Task Force on Monitoring Water Quality, 1995). Monitoring also is needed to document compliance with local, State, and Federal regulations and permits. In addition, the results of water-quality monitoring are needed to detect and define trends in water quality and to identify emerging water-quality concerns.

## **The Ambient Water-Quality Monitoring Network**

The AWQMN was established in 1964 with 18 surfacewater quality sites and increased to 41 sites by 1986. During the early 1990's, the network decreased to only 5 sites because of State funding limitations, but by 1994, the AWQMN increased to 39 sites. By the 2008 water year, the program consisted of 67 sites (Otero-Benítez and Davis, 2009b).

The objectives of the AWQMN are to (1) obtain information on the quality and quantity of surface water within the State; (2) provide a historical water-quality database that can be used by State planning and management agencies to make informed decisions about cultural effects on the surface waters of the State; and (3) provide consistent data-collection methods, laboratory analysis, and data reporting (Otero-Benítez and Davis, 2009a, 2009b).

The purpose of this report is to describe the water-quality assessment, including water-quality conditions and long-term trends, at six AWQMN sites from water years 1993 through 2008. Constituents used in this report are dissolved oxygen (DO), physical properties (specific conductance and water temperature), total suspended solids (TSS), nutrients (dissolved nitrate plus nitrite as nitrogen and total phosphorous), fecal indicator bacteria [*Escherichia coli* (*E. coli*) and fecal coliform], and trace elements (dissolved and total recoverable lead and zinc). Other constituents also analyzed during the study period but not used for analysis include major ions, other trace elements, and pesticides at selected sites. The six sites were chosen for this study based on their geographical distribution within the physiographic regions, main land use, and drainage basin size to represent the stream diversity within Missouri, as well as their long period of record.

## **Description of Study Area**

The sites used in the study (fig. 1) are classified in groups corresponding to the physiography, main land use, or unique station type (Otero-Benítez and Davis, 2009a, 2009b; table 1). Sites also were used based on their long period of record.

## Physiography

Missouri has three major physiographic provinces within its State boundaries—Central Lowland, Ozark Plateaus, and Coastal Plain (Fenneman, 1938; fig. 2). The Central Lowland Province occupies a large amount of area in the central United States. Within Missouri, the province is divided into two different sections: the Dissected Till Plains section north of the Missouri River and the Osage Plains section in western Missouri (fig. 2). The Osage Plains section was not affected by glaciation (Fenneman, 1938) and is underlain mostly by soft shales with interbedded sandstones and limestones (Adamski and others, 1995). The Dissected Till Plains section is a mostly flat till plain, covered by loess (Fenneman, 1938). The topography typically is gently rolling hills with some steeper slopes near streams. Streams in this section are less steep than those in the Ozark Plateaus Province. Springs in the Plains sections are smaller and do not contribute to overall streamflow (Vineyard and Feder, 1974).

The Ozark Plateaus Province is divided into two sections known as the Salem Plateau and the Springfield Plateau (Fenneman, 1938; fig. 2). The Salem Plateau predominantly is dolomite whereas the Springfield Plateau is abundant in limestone and chert. Precambrian igneous rocks crop out in an area known as the St. Francois Mountains in southeastern Missouri. The Salem Plateau is intensely wooded, has steep, rugged topography with narrow valleys, dendritic drainages, and steep main channel gradients. The Springfield Plateau has less relief than the Salem Plateau with gently rolling hills that

<span id="page-10-0"></span>

**Figure 1.** Location of study sites.

**Current River—**Salem Plateau, forested and agriculture **Elk River—**Springfield Plateau, agriculture and forested

<span id="page-11-0"></span>**(percent) Stream classificationa Period of recordb Mean annual streamflowc (ft3/s) Agriculture Forest Urban** Mean annual streamflow<sup>c</sup> 4,782 2,539 2,912  $(H^3/S)$ 527 866 "Date range shown as period of record is not the entire period of record available for some sites. The period shown is the largest period with no interruption in collection between water Date range shown as period of record is not the entire period of record available for some sites. The period shown is the largest period with no interruption in collection between water e68 to current year 07052152 37°08′49.7″ 93°22′31.7″ 51 14 10 76 Springfield Plateau, urban October 1993 to to current year to current year to current year 05500000 39°53′47.9″ 91°34′48.6″ 620 74 21 4 Dissected Till Plains, agriculture November 1992 to current year January 1978 to October 1993 to November 1992 to current year November 1992 November 1992 January 1978 to November 1992 August 1967 to 06902000 39°38′24.1″ 93°16′25.3″ 6,880 76 18 5 Dissected Till Plains, agriculture August 1967 to November 1992 current year current year current year current year current year current year of record<sup>®</sup> Period Dissected Till Plains, agriculture Dissected Till Plains, agriculture Springfield Plateau, agriculture 07189000 36°37′53″ 94°35′12″ 872 42 51 7 Springfield Plateau, agriculture 06930800 37°55′12″ 91°58′33″ 2,570 35 60 5 Salem Plateau, forested and 07068000 36°37′19″ 90°50′51″ 2,038 13 83 3 Salem Plateau, forested and Salem Plateau, forested and Salem Plateau, forested and Springfield Plateau, urban classification<sup>ª</sup> **Stream** and forested and forested agriculture agriculture Gasconade River above Jerome South Fabius River near Taylor<sup>d</sup> Gasconade River above Jerome South Fabius River near Taylord Wilson Creek near Brookline Table 1. Information for selected Missouri Ambient Water-Quality Monitoring Network sites.<br>[USGS, U.S. Geological Survey, m<sup>2</sup>; square miles; ft<sup>3</sup>/s, cubic feet per second; <sup>o</sup>, degress; <sup>/</sup>; minutes; <sup>\*</sup>, seconds]<br>Site U Wilson Creek near Brookline Grand River near Sumner<sup>d</sup> Current River at Doniphan<sup>d</sup> Grand River near Sumnerd Current River at Doniphan<sup>®</sup> Elk River near Tiff City Elk River near Tiff City  $\sim$  $\overline{4}$  $\overline{6}$ 76  $\epsilon$  $\overline{a}$ **Basin land use**  $\overline{a}$  $\frac{8}{18}$  $\boldsymbol{\mathcal{S}}$  $\overline{21}$ 83 51  $\overline{7}$ 76 35  $\overline{4}$  $\overline{13}$  $\overline{c}$ 620 6,880 2,570 2,038 872 51 **)** <sup>a</sup>Modified from Otero-Benitez and Davis, 2009a, 2009b. aModified from Otero-Benítez and Davis, 2009a, 2009b. 91°34'48.6" 93°16'25.3"  $93^{\circ}22'31.7''$ 91°58'33" 90°50'51" 94°35'12" 39°53'47.9" 39°38'24.1" 37°08'49.7"  $37^{\circ}55'12''$  $36°37'53"$  $36°37'19"$ 05500000 06902000 06930800 07052152 07068000 07189000  $\overline{5}$  $\circ$  $\tilde{3}$ 4 $\overline{\mathcal{L}}$ years.  $\overline{\phantom{0}}$ 

"Mean annual streamflow shown is calculated from the date range listed in period of record. Steamflow gaging stations may have longer period of record than the water-quality collection<br>period used in this table (U.S. Geolo Mean annual streamflow shown is calculated from the date range listed in period of record. Steamflow gaging stations may have longer period of record than the water-quality collection period used in this table (U.S. Geological Survey, 1964–2005, 2006–2008, 2010).

<sup>4</sup>About 1 percent of the land use in this basin is water. dAbout 1 percent of the land use in this basin is water. "Streamflow data from water year 2001 to current year (2010). eStreamflow data from water year 2001 to current year (2010).

<span id="page-12-0"></span>

**Figure 2.** Physiographic regions of Missouri.

<span id="page-13-0"></span>generally are equally divided between wooded and pasturelands. Sinkholes and springs are common in both the Salem and Springfield Plateaus, but are more prevalent and larger in the Salem Plateau (Vineyard and Feder, 1974).

The Coastal Plain Province is located in the area commonly referred to as the "boot heel" of Missouri and is known as the Mississippi Alluvial Plain (fig. 2). This province has a very gentle slope in the delta and bottomlands of the Mississippi River and its tributaries (Fenneman, 1938).

The six sites chosen for this study represent all physiographic regions except the Mississippi Alluvial Plain section (fig. 2) and are classified within the Salem and Springfield Plateaus and the Dissected Till Plains section. Each category is subdivided into more distinct classes based on land use (table 1).

### Land Use

Land use in Missouri primarily is agricultural and forested (fig. 3). In the Dissected Till Plains, land use is agricultural and includes row crops such as corn, soybeans, and wheat, and livestock such as cattle, hogs, and poultry. Land use in the Ozark Plateaus Province predominantly is agricultural (cattle and poultry production) in the Springfield Plateau and mainly is forested with some agriculture in the Salem Plateau. Agricultural land use in the Mississippi Alluvial Plain mostly is row crops, such as cotton, rice, and sorghum. Three major urban areas are located in Missouri—Kansas City, St. Louis, and Springfield (figs. 1, 3). The estimated population of Missouri is 5.88 million people (U.S. Census Bureau, 2008). Land-use percentages of the drainage basins for the six sites used in this study are listed in table 1.

### Climate

Missouri has a temperate climate with a mean annual temperature of 55 degrees Fahrenheit (°F) from 1993 through 2008, and a mean annual precipitation of 43.5 inches per year (in/yr) across the State (National Oceanic and Atmospheric Administration, 2009). The climate of Missouri follows a gradient diagonally across the State from northwest to southeast, with lower temperatures in the northwest and larger annual precipitation in the southeast (University of Missouri, 2009). Typically, most rainfall in Missouri occurs from April through July. Thundershowers are common in September and October, but can occur at any time. Measurable precipitation occurs approximately 100 days a year, with nearly one-half of the days as thunderstorms. Snowfall varies from 18 to 24 inches (in.) north of the Missouri River to an average of 8 to 12 in. in the southern one-half of the State (University of Missouri, 2009).

Rainfall departures from normal total annual precipitation (1993 to 2008) were analyzed at National Weather Service precipitation gages located near the six sites used in the study (fig. 1). Annual departures were available for calendar years

1993 through 2008 for all precipitation gages except the Sumner gage (site 2; fig. 1), which did not have data for 1993 (fig. 4; National Oceanic and Atmospheric Administration, 1993–2008). A precipitation gage was available in the town of Jerome (site 3; fig. 1); however, the data available were limited and the gage was discontinued in 1999. The nearest weather station located in the nearby town of Rolla was used to assess the precipitation departures for the study period. All gages recorded above-average precipitation in 1993 and 2008. All gages recorded above-average precipitation in 1998 except the Doniphan gage (site 5; fig. 1), which recorded a slight negative departure from average precipitation (fig. 4). Belowaverage precipitation was recorded at all gages in 2000 and 2005 (fig. 4).

## Summary of Hydrologic Conditions

Surface-water streamflow conditions in Missouri vary seasonally and tend to reflect precipitation patterns. A 100 year flood occurred along the Missouri and Mississippi Rivers during the 1993 water year as a result of an abnormally large and persistent increase of precipitation in the region (Johnson and others, 2004). Many smaller streams in the State also were affected by the flooding. During the 2007 water year, Missouri once again experienced storm systems that produced flooding during the spring and summer. In the 2008 water year, Missouri had its wettest year to date, with 57.28 in.; 16.52 in. above the State's long-term mean based on precipitation data collected since 1895 (National Oceanic and Atmospheric Administration, 2009).

Annual mean streamflows at the six sites were plotted for the study period (fig. 5). Annual data were available at all sites for the entire study period except site 4, which only had streamflow data from the 2001 through 2008 water years. The five remaining sites followed similar trends in annual mean streamflow during the study period. The highest annual mean for the entire period of record for sites 1, 2, and 6 was the 1993 water year. Sites 3 and 5 recorded the highest annual mean in the 1985 water year, which was another flood year. The streamflow at site 4 is affected by effluent discharges from the Springfield Southwest Wastewater Treatment Plant (SWWTP), particularly at low flows, and may not exhibit streamflow patterns typical of streams where the flow is determined primarily by precipitation and groundwater inputs. Annual mean streamflow data for each site are shown in table 1.

# **Methods of Study**

The six sites within the AWQMN were chosen to evaluate water-quality conditions and long-term trends of selected physical properties and constituents from the 1993 through 2008 water years. Hereinafter, each site will be referred to as a site number (1 through 6). The numerical reference will

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<span id="page-15-0"></span>

**Figure 4.** Departure from normal total annual precipitation during the study period collected at precipitation gages near sites, calendar years 1993 through 2008.

follow the same downstream order as the USGS station identifiers (table 1; fig. 1). Sites will be referred to as the following: site 1, South Fabius River near Taylor (USGS identifier 05500000); site 2, Grand River near Sumner (USGS identifier 06902000); site 3, Gasconade River above Jerome (USGS identifier 06930800); site 4, Wilson Creek near Brookline (USGS identifier 07052152); site 5, Current River at Doniphan (USGS identifier 07068000); and site 6, Elk River near Tiff City (USGS identifier 07189000).

## **Description of Sampling Network**

The six sites from the AWQMN were chosen based on their location, stream classification, main land use, and drainage basin size (table 1). Each site has a different classification, land use, or size that represents most stream types in Missouri. The sites also were chosen because of the long-term period of record available and the sampling frequency during the period of record. Each site had at least 15 years of water-quality data available. The sampling frequency at the six sites varied over the period of record, but was consistent enough to include data for all months. Sampling frequency within the AWQMN is determined by several factors, including the size of the drainage basin, effects from land use and human-influenced activity, history of the water chemistry, the need for data, and cost (Otero-Benítez and Davis, 2009a, 2009b).

The drainage basins of the six sites vary in size and land use (table 1; figs. 1–3). Site 1 is located within the South Fabius River Basin, which drains mostly agricultural land and drains directly into the Mississippi River. Site 2 is located in the Grand River Basin, the largest basin in the

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**Figure 5.** Annual mean streamflow for each site, water years 1993 through 2008.

<span id="page-17-0"></span>study, and drains mostly agricultural land directly into the Missouri River. This basin is not confined to Missouri but also has approximately one-third of its drainage area in Iowa (U.S. Geological Survey, 2001). The basins containing site 3 (Gasconade River Basin) and site 5 (Current River Basin) are located next to each other, but drain in different directions. The Gasconade River Basin drains north into the Missouri River, whereas the Current River Basin drains south into the Black River in Arkansas, which, in turn, flows into the Mississippi River. The Gasconade River drains forested and some agricultural land, most of which is dedicated to cattle grazing. The Current River drains mostly forested and some agricultural lands. The smallest basin in the study is Wilson Creek, which contains site 4 and drains into the James River. This site is mostly urban (76 percent; U.S. Geological Survey, 2001) and is located downstream from the SWWTP. Site 6 drains forested and agricultural land, most of which is dedicated to poultry production and cattle grazing. Site 6 also has a small portion of its drainage area outside of Missouri, with approximately one-fourth of the Elk River Basin in Arkansas (U.S. Geological Survey, 2001).

## **Sample Collection and Analysis Methods**

The methods used by the USGS for collecting and processing representative surface-water quality samples are presented in detail in U.S. Geological Survey (variously dated). Onsite measurements including DO, pH, specific conductance, and water temperature were performed at each site in accordance to methods described in Wilde (chapter sections variously dated). Samples collected and analyzed for fecal indicator bacteria (*E. coli* and fecal coliform) used the membrane filtration procedure described in Myers and others (2007). Methods used by the USGS for collecting and processing representative samples for suspended solids and nutrients are presented in U.S. Geological Survey (2006) and Wilde and others (2004).

All chemical analyses were performed by the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, using procedures described in Fishman and Friedman (1989) and Fishman (1993). The NWQL uses method reporting conventions (Childress and others, 1999) for establishing the minimum concentration above which a quantitative measurement can be made. These reporting conventions are the method reporting level (MRL) and the laboratory reporting level (LRL). The MRL is defined by the NWQL as the smallest measured concentration of a substance that can be reliably measured using a given analytical method. The method detection level (MDL) is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the concentration is greater than zero (Childress and others, 1999). A long-term method detection limit (LT-MDL) is a detection level obtained by determining the standard deviation of 20 or more MDL spiked-sample measurements conducted

over an extended period of time. The LRL is computed as twice the LT-MDL.

About 10 to 15 percent of all water-quality samples collected annually for the AWQMN were quality-control (QC) samples, which were collected to assure data were of sufficient quality to meet the needs of the State of Missouri. Field equipment blanks were collected to detect contamination and carry-over between environmental samples. Replicate environmental samples also were collected to monitor consistency in sample collection and processing techniques and analytical precision. Thirty-two field equipment blanks and 47 replicate environmental samples were collected among the 6 sampling sites during the study period (U.S. Geological Survey, 1993– 2005; U.S. Geological Survey 2006–2008). Most constituent concentrations were equal to or less than the MRL or LRL in the field equipment blanks with the following exceptions: one dissolved zinc detection [LRL 4 μg/L (micrograms per liter), detected concentration of 5 μg/L] and one total recoverable zinc detection (LRL 2  $\mu$ g/L, detected concentration of 6  $\mu$ g/L). These results indicate that samples are not being contaminated, and carry-over between environmental samples is not occurring during sample collection and processing. Most constituent concentrations in the replicate environmental samples were comparable and within laboratory analytical error. These results indicate that there is consistency in sample collection and processing techniques and analytical precision.

## **Data Analysis Methods**

Boxplots are used to graphically display the distribution of data at multiple sites (Helsel and Hirsch, 2002). Boxplots provide a visual summary of the  $25<sup>th</sup>$ ,  $50<sup>th</sup>$ , and  $75<sup>th</sup>$  percentiles and any extreme values in the distribution. The boxplot consists of the median value  $(50<sup>th</sup>$  percentile) plotted as a horizontal line, and a box is drawn from the  $25<sup>th</sup>$  percentile to the 75th percentile. The box length, also known as the interquartile range (IQR), represents one-half of the values. The IQR is insensitive to the presence of extreme values in the distribution. If a median value does not divide the box into two equal parts, it indicates asymmetry in the data distribution. Adjacent values are outside the box and, if within 1.5 times the IQR, are shown as whisker lines. The length of the whisker connected to the 75<sup>th</sup> percentile represents the value of the largest adjacent value; the length of the whisker connected to the  $25<sup>th</sup>$ percentile represents the smallest adjacent value. Values that are more extreme in either direction than the adjacent values are plotted individually. The values equal to 1.5 to 3.0 times the IQR are called "far-out values" and are represented by an 'x' (D.R. Helsel, U.S. Geological Survey, written comm., 1989). Values greater than the "far-out values" are represented by a circle. If the median of the data equals the  $25<sup>th</sup>$  percentile, no center line is shown. If the median of the data equals both the  $25<sup>th</sup>$  and  $75<sup>th</sup>$  percentiles, the box will be plotted as a single line. Concentration values reported less than the MRL, less than the LRL, or as "E" (estimated to be below the MRL or

<span id="page-18-0"></span>LRL) were included in each distribution as a concentration value equal to the MRL or LRL, depending on the constituent reporting convention. Although the reporting levels of the constituents analyzed varied throughout the study period as laboratory technologies and the data requirements of the State changed, censored data (data reported as less than a given value) for each constituent were set to one reporting level in order to use nonparametric statistical analyses. The censoring level selected for statistical analyses of each constituent was the highest reporting level reported during the study period. Any boxplots made with these censored data were modified by making the lower limit of the box equal to the reported value. Constituents that were highly censored, such as dissolved lead, were not plotted because so few measurements were greater than the censoring level.

The nonparametric Kruskal-Wallis rank-sum test (Helsel and Hirsch, 2002) was used to test for significant differences in the medians of the data among the six sites. Median values of the constituents were determined to be significantly different when the "attained significance level" (p-value) was less than 0.05. If significant differences were noted, a Tukey's multiple comparison test was performed on the rank-transformed data to identify similarities between all sites (Helsel and Hirsch, 2002). Nonparametric ranking tests were used because data for constituents such as TSS, nutrients, and trace elements were highly censored. In order to correctly represent the censored values, the ranks were tied at a value lower than the censoring level selected for each constituent (Helsel and Hirsch, 2002). For instance, if there were 19 censored values in the dataset, all censored values would be assigned a rank of 10, which is the mean of ranks 1 through 19. The next highest value above the censoring level obtained the rank of 20, so that all data above the censoring level had ranks identical to what would have been obtained had no censored data been present (Helsel and Hirsch, 2002). If censoring was greater than 50 percent of the total dataset, the Tukey test was not performed.

All long-term trend analyses were performed in the TIBCO Spotfire S+® program using the USGS library package ESTREND. The ESTREND library uses a system known as S-ESTREND to manage data for multiple stations and constituents for long periods of time. All constituents were analyzed using a Seasonal Kendall test (Helsel and Hirsch, 2002) to define the maximum number of seasons with available data in the study period. Some constituents were analyzed using a flow-adjusted trend test on concentrations, whereas datasets with large amounts of censored values were analyzed by non-flow adjusted trend tests. The determination of which adjustment was best for a constituent was based on the amount of censored values in the dataset. If censored values were 5 percent or less of the total dataset, a flow-adjusted trend test was performed. If the values were highly censored (between 6 and 50 percent of the entire dataset), no flow-adjustment could be used, and only a linear regression could be performed. No trend tests were performed if censored values exceeded 50 percent of the dataset.

The flow-adjustment models initially were chosen by the prediction error sum of squares (PRESS) statistic. The PRESS statistic can be used to assess the quality of a multiple regression equation when conducting analyses utilizing standardized residuals (Helsel and Hirsch, 2002). The standardized residuals also are known as a measure of outliers in the direction of y. Streamflow was used as the standard (x) to which all constituents (y) were adjusted to, unless the censored values were greater than 5 percent, in which case no flow adjustment was used. The S-ESTREND system fits 11 different models, evaluated by means of the PRESS statistic, to find the most appropriate model for the constituent while adjusting the constituent to streamflow. Other models such as log-based and LOWESS (LOcally WEighted Scatterplot Smoothing) models also were analyzed to find the absolute best model for the constituent. Model selection was based on the p-value associated with each regression model and the quantile plots of the concentration of each constituent in relation to the streamflow. If a trend was detected for a constituent, the significance (upward, downward, or no significance) was determined by the p-value and the estimated trend in percent per year from the model calculations.

Step-trend analysis was used to study changes in concentrations from before and after a known event. The Wilcoxon rank-sum test was used to test whether or not data collected before and after an event differed (Helsel and Hirsch, 2002). A significant difference was noted if the associated p-value was less than 0.05.

# **Assessment of Water Quality**

Water-quality conditions were assessed to explore the relations between data from sites as well as the State waterquality standards where applicable. Long-term trends were used to determine if water-quality conditions at the six sites have improved, declined, or remained the same from water year 1993 through 2008. Water-quality data are available in the USGS National Water Information System (*http:// waterdata.usgs.gov/nwis*).

## **Water-Quality Conditions**

The comparison of data among sites (also known as status) was used to determine the water-quality conditions at all six sites from water years 1993 through 2008. All sites were compared by streamflow, DO, physical properties (specific conductance and water temperature), TSS, nutrients [dissolved nitrate plus nitrite as nitrogen (hereinafter referred to as dissolved nitrate plus nitrite) and total phosphorus], fecal indicator bacteria (*E. coli* and fecal coliform), and trace elements (dissolved and total recoverable lead and zinc). Summary statistics were calculated for selected water-quality constituents during the study period (table 2).

<span id="page-19-0"></span>



[ft<sup>2</sup>/s, cubic feet per second; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; N, nitrogen; P, phosphorous; E. coli, Escherichia coli; col/100 mL, [ft3/s, cubic feet per second; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; N, nitrogen; P, phosphorous; E. coli, *Escherichia coli*; col/100 mL, Table 2. Summary statistics for selected constituents, water years 1993 through 2008.-Continued **Table 2.** Summary statistics for selected constituents, water years 1993 through 2008.—Continued

<span id="page-21-0"></span>Water-quality standards for DO, water temperature, fecal indicator bacteria, and trace elements are listed in Missouri Department of Natural Resources (2008). These criteria are modified every 3 years to assess the current water-quality conditions. The criteria are based on several different stream classifications as defined by the MDNR. Some of the streams, or sections of the streams in which the sites are located, are classified in three or more of the following categories: irrigation; livestock and wildlife watering; protection of aquatic life; drinking-water supply; whole-body contact recreation, such as swimming (class A) and less frequently used waters (class B); secondary-contact recreation, such as boating or streambank activities such as fishing, where body contact with the water can be possible; and cool- and cold-water fisheries. The six sites and the Missouri stream classifications and use designations are listed in table 3. Not all of the classifications and use designations listed apply to the location of the sites used in this study; however, the State criteria are shown on the boxplots in figure 6 as a reference.

## Streamflow, Dissolved Oxygen, Physical Properties, and Total Suspended Solids

Streamflow varied at each site because of drainage area, land use, and groundwater inputs. Instantaneous streamflow measured at the time the surface water-quality samples were collected has been used to evaluate the status of conditions over the study period. Median instantaneous streamflows ranged from 48 cubic feet per second  $(\text{ft}^3/\text{s})$  at site 4 to 2,000 ft<sup>3</sup>/s at site 5. All six sites had statistically different median streamflows for the study period except sites 2 and 3 (fig. 6). Site 2 has a drainage area almost three times larger than site 3; and the drainage areas of sites 3 and 5 are similar (table 1). Springs, which contribute substantially to streamflow in the Ozark Plateaus, are prevalent in the Salem Plateau. Big Spring, which is the largest spring in the Ozark region of Missouri and Arkansas (Vineyard and Feder, 1974) with a

mean discharge of 446 ft<sup>3</sup>/s (U.S. Geological Survey, 2010), is located upstream from site 5.

The DO was determined by two different measurements—concentration in milligrams per liter and percent saturation. The State criteria for DO refer to the milligrams per liter measurement and require a value no less than 5 milligrams per liter (mg/L) for warm-water and cool-water fisheries and 6 mg/L for cold-water fisheries (Missouri Department of Natural Resources, 2008; fig. 6). Most of the statistical analyses in this study used percent saturation of DO. Median DO concentration and percent saturation ranged from 9.1 mg/L at site 3 to 14.6 mg/L at site 4 and 90 percent at site 2 to 166 percent at site 4 (table 2). The graphical representation of DO in milligrams per liter and percent saturation indicates site 4 as the most significantly different (fig. 6). Site 4 is located downstream from the Springfield SWWTP and is the only urban site in the study (fig. 1). Wastewater-treatment (WWT) facilities generally use ozone during the disinfection treatment. Ozone is unstable and once released from the SWWTP, decays to ordinary diatomic oxygen when mixed with the native stream waters, resulting in super saturation conditions likely causing the elevated DO measurements at site 4.

Specific conductance measurements provide an indication of dissolved ion concentrations. Median specific conductance values ranged from 294 microsiemens per centimeter at 25 degrees Celsius ( $\mu$ S/cm at 25 °C) at site 6 to 957  $\mu$ S/cm at  $25 \text{ °C}$  at site 4 (table 2). Specific conductance was similar between the most northern sites (sites 1 and 2) and between the most southern sites (sites 5 and 6; fig. 6). The IQR at sites 3, 5, and 6 is smaller than at the other sites (fig. 6). Springs contribute to streamflow at these three sites throughout the year. Spring discharge is dependent on the amount of rainfall that infiltrates to the subsurface. The specific conductance of the spring water is determined by subsurface residence time and is fairly constant throughout the year, thus attenuating changes in specific conductance in the stream. Springs do not contribute substantially to the streamflow at sites 1 and 2, and thus specific conductance tended to increase as precipitation

**Table 3.** State stream classifications and use designations of site streams.

[USGS, U.S. Geological Survey; IRR, irrigation; LWW, livestock and wildlife watering; AQL, protection of aquatic life; DWS, drinking-water supply; WBC, whole-body contact recreation; SCR, secondary contact recreation; CLF, cool-water fishery; CDF, cold-water fishery; X, designation applies; --, not applicable]

<b>Site</b> number (fig. 1)	<b>USGS</b> station number	<b>Stream</b>	<b>Classification/use designation<sup>a</sup></b>							
			<b>IRR</b>	<b>LWW</b>	AOL	<b>DWS</b>	<b>WBC</b>	<b>SCR</b>	<b>CLF</b>	<b>CDF</b>
	05500000	South Fabius River	X	X	X	$\overline{\phantom{a}}$	X	$- -$		
$\overline{2}$	06902000	<b>Grand River</b>	X	X	X	X	Х	X	$- -$	
3	06930800	Gasconade River	$-$	X	X	$\overline{\phantom{a}}$	Х	X	X	$- -$
4	07052152	Wilson Creek	$-$	X	X	$\qquad \qquad -$	X	$-$	$- -$	--
5	07068000	Current River	$-$	X	X	$-$	X	X	$-$	X
6	07189000	Elk River	X	X	X	$-$	X	X	X	--

a Recreation classifications and use designations as listed in Missouri Department of Natural Resources (2008). Stream reaches in which the listed classification and uses are shown may vary and may not include the site location.

<span id="page-22-0"></span>





<span id="page-24-0"></span>decreases, and dilution of ions is less likely to occur (Vineyard and Feder, 1974). The overall effect is a wider range of specific conductance values at sites 1 and 2 than at sites 3, 5, and 6 as illustrated by the IQR (table 2).

Water temperature was similar for all sites in the study except site 4; however, sites 4 and 6 were similar. Site 4 has a substantially smaller drainage area and streamflow than the other sites (table 1; fig. 6), and much of the flow is contributed by discharges from the Springfield SWWTP, particularly at low flow. Water temperatures would be expected to be greater at site 4 than the other sites and less affected by ambient air temperatures. Large variations were shown in sites 1 and 2 (fig. 6). Both sites are located in the northern one-half of the State and are more susceptible to freezing conditions in the winter, yet still had a large increase in temperatures during the summer.

The TSS concentrations generally were reported at the MRL of 10 mg/L, except for sites 1 and 2 and some samples collected during higher streamflows at all sites (fig. 6). Median and maximum TSS concentrations were 17 and 2,000 mg/L at site 1 and 81 and 2,400 mg/L at site 2 (table 2). The median at the remaining sites was less than  $($   $>$  10 mg/L, and the largest maximum concentration at sites other than sites 1 and 2 was 470 mg/L at site 5. Streams in northern Missouri are more turbid than southern streams and are affected by large volumes of sediment deposition because of soil erosion from land cultivated for row crops (Missouri Department of Natural Resources, 2009).

### **Nutrients**

Nutrients, such as nitrogen and phosphorus, are important to all life and can be introduced to surface waters from natural or human influences. Some natural sources of nutrients are runoff from forests or other natural habitats, erosion of soils, and decay of plants and animals. Human influenced sources of nutrients can be from sewage effluent, leaking septic tanks, waste runoff from urban areas, improper management of concentrated animal feeding operations (CAFO), runoff from fertilized fields, pasturelands where cattle are grazed and where manure has been applied as fertilizer, and industrial or domestic waste discharges. Dissolved nitrate plus nitrite and total phosphorus concentrations were chosen to determine the nutrient status at the sites because nutrients in these forms most commonly are found in natural waters, and the laboratory methods have not varied during the study period.

Dissolved nitrate plus nitrite concentrations were significantly different at sites 4 and 6 than other sites (fig. 6). Median dissolved nitrate plus nitrite concentrations ranged from 0.24 mg/L at sites 3 and 5 to 10 mg/L at site 4 (table 2; fig. 6). Dissolved nitrate plus nitrite concentrations ranged from 1 mg/L to 28 mg/L at site 4 throughout the study period. Nitrogen concentrations, including nitrate plus nitrite, can be large in WWT plant effluent, and when concentrations are large, algal blooms in receiving streams can result. The lowest median

dissolved nitrate plus nitrite concentrations were detected at sites 3 and 5, which are located in predominantly forested areas where there are fewer nutrient sources. The large amount of row crop agriculture in the basins containing sites 1 and 2 could produce larger concentrations of dissolved nitrate plus nitrite as the result of fertilizer use and soil erosion. Livestock, such as hogs and cattle, also are prevalent near sites 1 and 2. Site 6 is located in an agricultural area as well but mostly consists of poultry and cattle production rather than row crops. The water-quality standard for nitrate as nitrogen is 10 mg/L for a drinking-water supply (Missouri Department of Natural Resources, 2008).

Median total phosphorus concentrations ranged from  $\leq 0.06$  mg/L at site 5 to 0.43 mg/L at site 4 (table 2; fig. 6). In 1993, the Springfield SWWTP completed facility improvements that decreased the phosphorus concentration in effluent discharged into Wilson Creek by an average of 40 percent. In March 2001, the SWWTP introduced an advanced phosphorus reduction system, which decreased the typical phosphorus discharge levels to less than 0.5 mg/L (City of Springfield, 2009); the median total phosphorus concentration at site 4 was 0.43 mg/L. Of the three sites in basins containing large percentages of agricultural land (sites 1, 2, and 6; table 1; fig. 3), the median total phosphorus concentration at site 2 was significantly different. Total phosphorus concentrations never exceeded 0.5 mg/L at sites 3 and 5 during the study period.

## Fecal Indicator Bacteria

Of the constituents analyzed in this study, fecal indicator bacteria are among the most stringently monitored by the MDNR. The fecal indicator bacteria standards apply only to the recreational period of April 1 through October 31. The *E coli* standard began in 2005 and was the only whole-bodycontact standard used after December 31, 2008; fecal coliform was used for the State standard before that date. Missouri has three recreational classes of waters: (1) whole-body contact class A (WBC-A) used for high-use waters; (2) whole-body contact class B (WBC-B) for less frequently used waters; and (3) secondary-contact recreation (SCR) such as fishing, wading, boating, or any other activity that does not involve swimming or floating in the water (Missouri Department of Natural Resources, 2008).

The MDNR uses a geometric mean of all samples collected at a particular site during the recreation period to determine if the *E. coli* standard has been exceeded. A geometric mean is the average of the natural logarithms converted back to their original units and should be close to the median (Helsel and Hirsch, 2002). The current standard for *E. coli* is 126 colonies per 100 milliliters (col/100 mL) for WBC-A, 206 col/100 mL for WBC-B, and 1,134 col/100 mL for SCR waters (Missouri Department of Natural Resources, 2008; table 4). The whole-body-contact standards apply to most stream reaches where the sites are located. The sites and their State classification are listed in table 4, as well as

<span id="page-25-0"></span>**Table 4.** Recreational classes, State standards, geometric means pertaining to the State *Escherichia coli*  standards during the recreational season (April to October), and median values, water years 1993 through 2008.

[USGS, U.S. Geological Survey; col/100 mL, colonies per 100 milliliters; WBC, whole-body-contact recreation; B, less frequently used waters; --, not applicable; A, high-use waters; SCR, secondary-contact recreation]

<b>Site</b>	<b>USGS</b>		Recreation class <sup>a</sup>			<b>State standard for class</b>	<b>Geometric</b>	<b>Median</b> <sup>b</sup> $\left( \text{col}/100 \text{ mL} \right)$	
number (fiq. 1)	station number	<b>Stream</b>	<b>Primary</b>	<b>Secondary</b>	<b>Primary</b> <b>Secondary</b>		mean (col/100 mL)		
	05500000	South Fabius River	WBC-B		206		121	65	
$\mathfrak{D}$	06902000	<b>Grand River</b>	WBC-A	<b>SCR</b>	126	1,134	181	66	
3	06930800	Gasconade River	WBC-A	<b>SCR</b>	126	1.134	13	10	
4	07052152	Wilson Creek	WBC-B	$-$	206	$- -$	74	73	
5	07068000	Current River	WBC-A	<b>SCR</b>	126	1.134		6	
6	07189000	Elk River	WBC-A	<b>SCR</b>	126	1.134	30	21	

a Recreation classifications as listed in Missouri Department of Natural Resources (2008). Stream reaches in which the listed classification are shown may vary and may not include the site location.

b Median values also shown in table 2 and are calculated from all available data from water years 1993 through 2008.

the geometric mean computed for the recreational seasons during the study period. The geometric mean for each site also is included on figure 6 for comparison with the median densities.

The geometric means of *E. coli* were calculated from the recreational seasons within the study period, and they indicate that only site 2 exceeded the WBC-A standard of 126 col/100 mL by 55 colonies (table 4; fig. 6). The WBC-B and SCR standards (206 col/mL and 1,134 col/mL) were not exceeded at any sites within the recreational seasons during the study period. The geometric means of the *E. coli* densities ranged from 7 col/100 mL at site 5 to 181 col/100 mL at site 2 (table 4; fig. 6). The geometric means and median densities of *E. coli* were relatively similar at all sites except sites 1 and 2; the geometric means were nearly twice the median densities at both sites relative to the other four sites (table 4). The difference in the geometric mean of the seasonal data and the median density of all data collected at sites 1 and 2 possibly was the result of larger streamflows during sample collection or because higher colony densities were measured during the recreational season than during the winter at these two sites. Fecal indicator bacteria generally are associated with suspended sediment. Sites 1 and 2 are located on streams in northern Missouri that are more turbid because of soil erosion. Although bacteria density increases generally are related to suspended sediment increases in surface water (Wilkinson and others, 1995), regression analyses at the predominantly agricultural sites were not possible. No suspended-sediment concentrations were collected at the sites, and the TSS concentration data were only collected two to four times per water year until the 2001 water year, which created a small dataset for linear regressions.

The fecal indicator bacteria show median densities for all sites were at or less than the State standards for the study period (table 2; fig. 6). Median densities ranged from 6 col/100 mL at site 5 to 73 col/100 mL at site 4 for *E. coli*, and 11 col/100 mL at site 5 to 160 col/100 mL at site 2 for fecal coliform (table 2). The largest maximum densities were at site 1 (62,000 col/100 mL for *E. coli* and 160,000 col/100 mL for fecal coliform) and site 2 (25,000 col/100 mL for *E. coli* and 120,000 col/100 mL for fecal coliform). These sites are located in agricultural areas, where large CAFOs are in operation and manure is used as fertilizer on crop and pastureland. Median densities at site 4 for both fecal indicator bacteria types (73 col/100 mL for *E. coli* and 100 col/100 mL for fecal coliform) were similar to sites 1 and 2. However, the maximums for each (4,800 col/100 mL for *E. coli* and 7,500 col/100 mL for fecal coliform) were more similar to the maximum for site 3 (5,200 col/100 mL for *E. coli* and 8,200 col/100 mL for fecal coliform), which is mostly forested (table 1). Similarities between sites were consistent between the two fecal indicator bacteria types. Sites 1, 2, and 4 were statistically similar for both *E. coli* and fecal coliform. Sites 3 and 5 had similar *E. coli* densities, but different fecal coliform densities. Site 6 was significantly different from all sites for both fecal indicator bacteria types (fig. 6).

Most of the fecal indicator bacteria samples were collected during base-flow conditions through the study period, but some samples were collected during high-flow conditions (fig. 7). In addition, samples collected at the six sites were distributed rather equally among the recreational period (April through October) and the non-recreational months (November through March; fig. 8). Samples were collected during a larger range of streamflow conditions for sites 1, 2, and 6, resulting in a larger range in bacteria densities (fig. 7). Sites 1, 2, and 6

<span id="page-26-0"></span>

**Figure 7.** Relation of *Escherichia coli* and fecal coliform bacteria density to streamflow, water years 1993 through 2008.

<span id="page-27-0"></span>**Site 1 Site 2** 100,000 b  $\circ$  $\circ$  $\infty$  $\infty$ 10,000  $00000$  $\infty$   $\infty$  $\infty$   $\infty$   $\infty$  $\circ$  $\frac{1}{2}$  $\circ$  $\frac{1}{2}$  $\circ$ Θ  $\circ$  $\circ$  $00000$  $\circ$  $\circledcirc$  $\circ \circ \circ \circ$  $\infty$   $\infty$ 1,000  $\circ$  comences  $\frac{1}{2}$  $\circ$   $\circ$   $\circ$   $\circ$  $\circ \circ \circ \circ \circ$  $\circ$  000000  $\circ$  $\frac{1}{2}$ 8  $\circ$  appro  $\circ \circ \circ \circ$  $\circ$   $\circ$   $\circ$   $\circ$  $\frac{8}{3}$  $\circ$ 100 0  $\frac{8}{8}$ ESCHERICHIA COLI, IN COLONIES PER 100 MILLILITERS *ESCHERICHIA COLI*, IN COLONIES PER 100 MILLILITERS 10  $\frac{1}{2}$  $\circ$  $\circ$ 1  $\circ$ 0.1 **Site 3 Site 4** 100,000 10,000  $\circ$  $\circ$  $\circ$ 8  $\circ$  $\circ$  $\circ$  $\circ$ 1,000  $\circ$  apo  $\circ$  $\circ$  $\circ$  $\circ$  $\circ$  compared  $\circ$  $\cos \infty$  $\circ$  $\infty$  oo  $0 \oplus \infty$  $\circ$  compo  $\infty$  $\circ$   $\circ$  $\circ$   $\circ$  $\circledS$  $00000$  $0.00000$ 100  $\circ$  coro  $\circ$  $\begin{smallmatrix} 0 & 0 \\ 0 & 0 \end{smallmatrix}$  $\circ$  $\infty$  $\frac{1}{2}$  $\frac{1}{2}$  $\circ$  comp  $\circ$  $\circledcirc$  $0 0000$  $\frac{1}{8}$  $\alpha$  and  $\alpha$  $\text{conv}$ 10  $\circ$  $\circ$ 1 0.1 **Site 5 Site 6** 100,000 10,000  $\circ$  $\circ$  $\circ$  $\frac{1}{2}$  $\circ$  $\circ$  $\theta$ 1,000  $\infty$  o  $\infty$  o  $\circ$   $\circ$   $\circ$   $\circ$  $\circ$   $\circ$  $\circ$  $\circ \circ \circ \circ$ and road and  $\circ$  $\cos \alpha$  $\circ$  $\infty$  or  $\infty$  $\infty$ O  $\Theta$  $0000000$  $\circ$  as  $\circ$ 100  $\circ$  axo  $\infty$  $\infty$  onders  $\text{conv}$  $\infty$  $^{\circ}$  $\infty$  and  $\infty$ 000 000  $\circledcirc$  $00000$  $\infty$ 10  $\frac{1}{2}$  $O(0000)$ 1 0.1 **Site 1 Site 2** 100,000 ठ  $\sqrt{2}$  $\frac{1}{\circ}$  $\frac{1}{2}$ 10,000  $\frac{0}{0}$  $\infty$   $\infty$   $\infty$  $\circ$  compared  $\circ$  $\infty$   $\infty$  $\circ$   $\circ$   $\circ$  $0$  and  $00$  $\circ$  compared  $\circ$  $\Theta$  $\circ$  and  $\circ$  $\begin{minipage}{.4\linewidth} \hspace*{-0.25mm} \textbf{0} & \hspace*{-0.25mm$  $\bullet$   $\bullet$  $000000$  $\circ$  o o o  $\infty$  and  $\infty$  $\mathfrak{O}(\mathfr$  $\circ$  approx  $\circ$  $\begin{smallmatrix}\textcolor{red}{\bullet} & \textcolor{red}{\bullet} & \textcolor{red}{\bullet} & \textcolor{red}{\bullet} \ \textcolor{red}{\bullet} & \textcolor{red}{\bullet} & \textcolor{red}{\bullet} & \textcolor{red}{\bullet} \end{smallmatrix}$ **ි ගහ**ංගා **OBD ODDD** 1,000  $\circ \circ \bullet \circ \circ \circ \circ$  $\circ$  and an  $\circ$ **DOO ODD CDD**  $\overline{\text{conv}}$  $\circ$   $\circ$   $\circ$ 100 FECAL COLIFORM, IN COLONIES PER 100 MILLILITERS FECAL COLIFORM, IN COLONIES PER 100 MILLILITERS 10  $\circ$ 1  $\circ$ 0.1 **Site 3 Site 4** 100,000 10,000  $\circ$  $\Theta$  $\circ$  $\circ$  composed  $\circ$  $\infty$  $\circ$   $\circ$   $\circ$  $\circ$  $\circ$  onco  $\circ$ 1,000  $\circ$ CONDICATO **CONDED** 000000  $\infty$  $\circ$   $\circ$   $\circ$  $\circ$  and  $\circ$  $\frac{8}{2}$  $\circ$   $\circ$ 6  $\infty$ 00 00  $\circ \circ \circ \circ \circ$  $\circ$  occording  $\circ$  $\sim$  and  $\sim$  $\circ$ **CONDOCOD**  $\circ$  compare  $\circ$   $\circ$  $\circ$  and  $\circ$ 100 COOKING 800 10  $\Theta$  $\circ$  $\circ$ 1 0.1 **Site 5 Site 6** 100,000 10,000  $\circ$  $\circ$  $\infty$  o  $\infty$ ocomonio 1,000  $\overline{\phantom{0}}$  $\circ$  $\infty$   $\infty$  $\circ$  $\circ$  $\infty$  components of  $\infty$  $\infty$ **COMMON**  $\frac{1}{2}$  $\circ$  approx  $\frac{8}{9}$  $\frac{1}{2}$  $\infty$  and o  $\infty$  and  $\infty$ 100  $00$ **OCOCO**  $\infty$  and  $\infty$  $000000$ COLORO Î 10 ŏ 1  $0.1$ J F M A M J J A S O N D J F M A M J J A S O N D MONTH **EXPLANATION**

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**Sample**

**Figure 8.** Relation of *Escherichia coli* and fecal coliform bacteria density to month, water years 1993 through 2008.

<span id="page-28-0"></span>also drain a large percentage of agricultural land (table 1). Fecal indicator bacteria densities can increase in streams because of runoff from row crops as well as pasturelands where cattle are grazed and where manure has been applied as fertilizer, and as a result of improperly managed animal waste from hog and poultry production in CAFOs (Francy and others, 2000).

## Trace Elements

Water samples collected at the sites also were analyzed for selected trace elements, including dissolved and total recoverable lead and zinc. The State standards for lead and zinc vary with the hardness of the water and stream classifications (Missouri Department of Natural Resources, 2008). Dissolved lead concentrations analyzed during the study

period seldom exceeded the LRL of 1 μg/L (table 2) and are not shown in figure 6. Most total recoverable lead concentrations were equal to or less than the LRL at sites 3, 4, 5, and 6. Median total recoverable lead concentrations at site 2 were significantly different from those at the other sites. The largest total recoverable lead concentrations were detected in samples from sites 1 (64  $\mu$ g/L) and 2 (65  $\mu$ g/L). Trace elements, including lead, generally are associated with suspended sediment, and concentrations will tend to increase as suspended-sediment concentrations increase (Hem, 1985). No suspended-sediment concentration data were collected during the study period, but TSS data were available. To determine if total recoverable lead and zinc data from sites 1 and 2 are correlated with TSS, regression analyses were performed (fig. 9). The correlation used Kendall's tau and measured the strength of association between two constituents (Helsel



**Figure 9.** Correlation of total recoverable lead and zinc with total suspended solids at sites 1 and 2, water years 1993 through 2008.

<span id="page-29-0"></span>and Hirsch, 2002). A completely linear correlation will have a correlation coefficient  $(R^2)$  equal to 1. The  $R^2$  values were greater than 0.80 for both total recoverable lead and zinc with TSS at sites 1 and 2, indicating good correlations (fig. 9). One data point (sample collected on January 6, 1993) was removed from the total recoverable lead dataset for the correlation analysis at site 1, which made the  $R^2$  value more representative of the entire dataset. The total recoverable lead outlier did not fit historical data and could not be associated with higher streamflow or other possible effects. Before this data point was removed, the correlation was poor  $(R^2 = 0.26)$ .

Median dissolved zinc concentrations for all sites were equal to the LRL of 4 μg/L except at site 4. Median total recoverable zinc concentrations were at or less than the LRL of 2 μg/L at sites 3, 5, and 6, and similar to total recoverable lead. Sites 1 (3  $\mu$ g/L) and 2 (6  $\mu$ g/L) had median total recoverable zinc concentrations significantly larger than concentrations at sites 3, 5, and 6. The median concentrations of dissolved and total recoverable zinc were 39 and 40 μg/L at site 4, which were significantly larger than the other sites. The typical zinc concentration in effluent from the SWWTP is 40 μg/L (City of Springfield, 2009).

State water-quality standards for lead and zinc are in place for the protection of aquatic life, drinking water, and groundwater uses. The State criteria for aquatic life protection are based on dissolved trace element concentrations, except mercury, whereas drinking water and all other beneficial uses are based on total recoverable trace element concentrations (Missouri Department of Natural Resources, 2008). The State standard for lead is 15  $\mu$ g/L and 5,000  $\mu$ g/L for zinc in drinking water (Missouri Department of Natural Resources, 2008). The lower 56 river miles of the Grand River is the only stream reach designated as a drinking-water supply source. To calculate the State criteria for select trace elements for the protection of aquatic life, the water hardness is used. The State determines the hardness of the stream in question by calculating the  $25<sup>th</sup>$  percentile of a representative number of samples from the water body in question (Missouri Department of Natural Resources, 2008). Each site in the study has different water hardness (table 2), but for comparison purposes, the mean of the 25<sup>th</sup> percentiles of hardness concentrations for all sites was computed to get a mean hardness for the six sites studied, which was then used to find the chronic toxicity concentration to aquatic life for dissolved lead and zinc. The mean of the 25<sup>th</sup> percentile of hardness concentrations for all sites was about 145 mg/L. The corresponding chronic toxicity concentration for dissolved lead was about 3 μg/L, and the chronic toxicity concentration for dissolved zinc was about 129 μg/L (fig. 6). Samples with concentrations of dissolved lead and zinc that exceeded chronic toxicity concentrations were less than 25 percent of the total number of samples from all sites (fig. 6; table 2).

### **Long-Term Trends**

Long-term trends were analyzed for each site and constituent. The number of seasons used in the trend tests was analyzed, and 12 seasons (or monthly analyses) best represented all sites in the study, except site 4. Because site 4 has the smallest dataset, the best seasonal analysis for constituents collected during the study period was six (or bi-monthly). Some constituents were analyzed using a flow-adjusted trend test, whereas datasets with greater than 5 percent but less than or equal to 50 percent censored values, were analyzed by non-flow adjusted trend tests. Because datasets with more than 50 percent censored values can decrease the power of a trend test, no trend test was conducted on any constituent with censoring above this level. All TSS, dissolved lead, and total recoverable lead values were censored greater than 5 percent, but only sites 1 and 2 had less than 50 percent censored datasets. Data inputs for each model and the model outputs for flow and non-flow adjusted trends are in tables 5 and 6.

When flow-adjusted trend analyses were used, a large part of the variability in concentrations because of the natural fluxes in streamflow was removed, allowing for trends caused by other occurrences such as human-influenced effects to be assessed directly. When no flow adjustment could be used, all aspects of variability from natural and human influences were evaluated simultaneously.

## Flow-Adjusted Trends

#### Dissolved Oxygen and Physical Properties

DO, specific conductance, and water temperature were analyzed for long-term trends using flow-adjusted models. No data were censored for DO and any physical properties (table 5).

No significant long-term trends were detected for DO or water temperature. The p-values calculated by the trend tests indicated no significant differences during the study period  $(p$ -value  $< 0.05$ ). Trends in water temperature would be rare because it is seasonally dependent and follows a diurnal or sinusoidal trend both daily and seasonally. Significant trends in specific conductance were determined for three sites; a downward trend at site 1 and upward trends at sites 3 and 6 (table 5; fig. 10). Many natural and human-influenced occurrences can cause an increase or decrease in dissolved ion concentrations, thus causing a similar change in specific conductance. These occurrences could be because of increased contaminant loadings, such as wastewater discharges or land application of wastes.

#### **Nutrients**

Flow-adjusted models were used for dissolved nitrate plus nitrite datasets at all sites except sites 1 and 2, which contained more than 5 percent censored values. Of the four

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**Table 5.** Model output for flow-adjusted trends in concentrations, water years 1993 through 2008.

Table 5. Model output for flow-adjusted trends in concentrations, water years 1993 through 2008.





[USGS, U.S. Geological Survey; R<sup>2</sup>, coefficient of determination between observed and predicted concentrations; significant trend if p-value is less than 0.05; --, poor model fit; Inf, not com-<br>metals comments are the ab [USGS, U.S. Geological Survey; R2, coefficient of determination between observed and predicted concentrations; significant trend if p-value is less than 0.05; --, poor model fit; Inf, not computed because sign of trend is different from sign of Kendall's tau]

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**Figure 10.** Flow-adjusted trends in physical properties, water years 1993 through 2008.



**Figure 10.** Flow-adjusted trends in physical properties, water years 1993 through 2008.—Continued



**Figure 10.** Flow-adjusted trends in physical properties, water years 1993 through 2008.—Continued

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**Figure 11.** Flow-adjusted trends in dissolved nitrate plus nitrite (as nitrogen) and total phosphorus concentrations, water years 1993 through 2008.

sites adjusted by streamflow, only site 6 showed a significant upward trend (table 5; fig. 11). Site 6 is located in the Elk River Basin, which is largely agricultural, including poultry (chickens and turkey) and cattle production (table 1; fig. 3). Poultry waste is used as a fertilizer for pastureland and row crops in the basin and could be introduced to the Elk River during storm runoff, increasing the dissolved nitrate plus nitrite concentrations. Agricultural statistics from the 1997, 2002, and 2007 census studies indicate that the number of cattle operations in the Elk River Basin, as well as the amount of commercial fertilizers applied, have stayed relatively stable during the study period, whereas poultry production has slightly increased (U.S. Department of Agriculture, 2007; table 7). In 1997, 506 operations housing about 25 million head of poultry were located in Barry, McDonald, and Newton Counties. Fertilizers were applied to about 177,000 acres of pasture and row crop fields. In 2007, there were 605 operations housing about 29 million head of poultry, and about 186,000 acres fertilized. No manure fertilizers were computed in the 1997 census to compare to the approximate 85,000 acres that were computed during the 2007 census.

The census data obtained from the U.S. Department of Agriculture were totaled for all counties containing parts of the river basins for sites with significant trends in nutrient concentrations. The animal head and crop counts may be greater than the information shown in table 7 because some data were not released by the U.S. Department of Agriculture to avoid disclosing information for individual farms. The census values referred to in this report have been rounded to the nearest whole number.



**Figure 11.** Flow-adjusted trends in dissolved nitrate plus nitrite (as nitrogen) and total phosphorus concentrations, water years 1993 through 2008.—Continued

A USGS study in the Upper Elk River Basin from 2004 to 2006 (Smith and others, 2007), included the analysis of the nutrients in surface water as well as streambed sediments. The study determined that nitrate as nitrogen varied in proportion to streamflow, indicating the larger concentrations possibly were caused by runoff from non-point sources. Seepage runs were performed in 2004 and again in 2006 to calculate nutrient loads over the course of the study. During the 2006 seepage run, nitrate as nitrogen concentrations increased in Little Sugar Creek, a tributary of the Elk River, particularly downstream from Bella Vista, Arkansas, whereas total phosphorus concentrations decreased (Smith and others, 2007). The population of the Bella Vista area as well as the number of large golf courses upstream from site 6 has increased during the past several years. Increased urban development, in addition to increased poultry populations during the study period, possibly caused the upward trend in dissolved nitrate plus nitrite concentrations at site 6 (fig. 11).

Total phosphorus data at all sites contained censored values. Sites 1, 2, 4, and 6 were analyzed by flow-adjusted models, and sites 1, 2, and 4 showed significant long-term trends in

the data (table 5; fig. 11). Total phosphorus concentrations at sites 1 and 2 show an upward trend with time, whereas site 4 shows a downward trend.

The increase in total phosphorus concentrations at sites 1 and 2 possibly was because of the agricultural land use in the basin. Cattle and crop production such as corn, soybeans, and wheat totaled for counties within the South Fabius River Basin (site 1) have stayed relatively stable from the 1997 agricultural census to the 2007 census (table 7). Poultry and hog production have changed substantially within the basin counties during the 10-year period. In 1997, the agricultural census estimated 153 operations housing about 3,800 head of poultry, and 307 hog operations housing about 153,000 hogs were located in the South Fabius River Basin counties (U.S. Department of Agriculture, 2007; table 7). During the 2002 census, hog operations had decreased to 181, and the hog population decreased to about 138,000 head, whereas the poultry operations and total head increased slightly (241 operations and about 4,900 head). Then during the 2007 census, poultry operations stayed about the same (228 operations), but the number of poultry increased to about 69,000 head; and



<span id="page-39-0"></span>[--, data not available. Data obtained from U.S. Department of Agriculture, National Agricultural Statistics Service, Census of Agriculture, 1997, 2007, accessed August 2009 at http://agcensus.usda. [--, data not available. Data obtained from U.S. Department of Agriculture, National Agricultural Statistics Service, Census of Agriculture, 1997, 2002, 2007; accessed August 2009 at *[http://agcensus.usda.](http://www.agcensus.usda.gov/)* Table 7. Agricultural census statistics in Missouri counties containing river basins where significant trends in nutrient data were detected. **Table 7.** Agricultural census statistics in Missouri counties containing river basins where significant trends in nutrient data were detected.

<sup>6</sup>Cattle head and operations used in table were totaled from beef, milk, and feedlot cattle. bCattle head and operations used in table were totaled from beef, milk, and feedlot cattle.

<sup>e</sup>Fertilizers in table were applied to both cropland and pastureland. cFertilizers in table were applied to both cropland and pastureland.

<sup>4</sup>Commercial fertilizers used in table include lime and soil conditioners. dCommercial fertilizers used in table include lime and soil conditioners.

<span id="page-40-0"></span>hog operations decreased to 146 operations, but the number of hogs being housed increased to about 199,000 head (U.S. Department of Agriculture, 2007; table 7). Between the 2002 and 2007 census, the number of family owned hog and poultry farms likely began to decrease as large commercial operations moved into the counties (John Ford, Missouri Department of Natural Resources, written commun., 2009).

In the Missouri counties within the Grand River Basin (site 2), the agricultural census in 1997 recorded 497 operations housing about 12,000 head of poultry (table 7). By the 2007 census, the operation totals increased about 50 percent to 750 housing about 23,000 head of poultry (U.S. Department of Agriculture, 2007; table 7). Cattle production was relatively stable between the 3 census years. Hog totals, similar to those in the South Fabius River Basin, changed between the 2002 and 2007 census years when private farms closed as large commercial operations moved into the basin. In 1997, 710 hog operations had about 360,000 hogs. By 2002 those numbers had decreased to 363 operations and about 114,000 hogs. As the commercial operations became established, the number of operations in the counties was near 300, but the number of hogs increased to about 550,000 head. Corn production in the basin counties increased, whereas soybean and wheat production decreased. In 1997, about 420,000 acres of corn, 814,000 acres of soybean, and 75,000 acres of wheat were cultivated. By 2007, corn production increased to about 525,000 acres, whereas soybean production decreased to about 780,000 acres and wheat decreased to about 60,000 acres. Fertilizer use steadily increased each census, as commercial fertilizers were applied to about 1 million acres in 1997, increasing to about 1.5 million acres in 2007. Of the 1.5 million acres fertilized, about 64,000 acres were fertilized with manure to both crop and pasturelands (U.S. Department of Agriculture, 2007; table 7).

The additional phosphorus reduction system at the SWWTP in 2001 has substantially decreased the phosphorus concentration in effluent discharged into Wilson Creek, contributing to a downward trend (table 6; fig. 11). A flowadjusted long-term trend is not the best trend test for site 4 because a known point in time exists where a distinct change in total phosphorus concentrations occurred; therefore, a step-trend analysis was performed on the total phosphorus data. The step-trend compared concentrations from before the phosphorus reduction system began operation in March 2001 to concentrations afterwards. The p-value from the step-trend test was less than 0.05, indicating a significant difference in the median from before and after the reduction system began. The median total phosphorus concentration for data collected before the reduction system began was 2.5 mg/L and for data collected after was 0.25 mg/L. The SWWTP phosphorus reduction is likely responsible for the significant downward trend in total phosphorus concentrations at site 4 (fig. 12).



**Figure 12.** Total phosphorous concentrations before and after introduction of advanced phosphorous reduction system at the City of Springfield Southwest Wastewater Treatment Facility, located downstream from site 4.

#### Fecal Indicator Bacteria

All sites were analyzed for flow-adjusted trends in *E. coli* and fecal coliform bacteria. No significant long-term trends in *E. coli* or fecal coliform bacteria densities were detected because p-values were all greater than 0.05 (table 5; fig. 13).

#### Trace Elements

Most trace element data used in the study were highly censored and could not be used for flow-adjusted trend analyses. Site 4 was the only site with uncensored dissolved and total recoverable zinc data. Larger concentrations of zinc at site 4 are to be expected because zinc is detected in the effluent of the Springfield SWWTP (City of Springfield, 2009). Downward trends were detected for both dissolved and total recoverable zinc concentrations (table 5; fig. 14). No processes

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**Figure 13.** Flow-adjusted trends in *Escherichia coli* and fecal coliform densities, water years 1993 through 2008.



**Figure 13.** Flow-adjusted trends in *Escherichia coli* and fecal coliform densities, water years 1993 through 2008.—Continued

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**Figure 14.** Flow-adjusted trends in zinc concentrations at site 4, water years 1993 through 2008.

have been used at the SWWTP to decrease zinc concentrations in the effluent. However, two circuit board manufacturers and several chrome plating operations that discharged effluent into the SWWTP along Wilson Creek have slowly decreased production during the past several years and have eventually gone out of business (James Burks, City of Springfield, Public Works Department, oral commun., 2009), which could have resulted in decreases in the zinc concentrations.

### Non-Flow Adjusted Trends

#### Total Suspended Solids

The TSS data were highly censored at all sites. Many of Missouri's streams commonly have TSS concentrations that are less than the MRL, making long-term trend detection difficult (U.S. Geological Survey, 1964–2005, 2006–2008; Otero-Benítez and Davis, 2009a, 2009b). Non-flow adjusted trends were performed on TSS data from sites 1 and 2, which both had datasets with less than 50 percent censored values. The long-term trends could be determined only on data for the last 8 water years (2000 through 2008) because samples

for TSS data analyses were not regularly collected before the 2000 water year. Statistically significant upward trends were detected at both sites (table 6; fig. 15). The increase in TSS concentrations could be because of soil erosion from an increase in land cultivated for row crops. However, TSS is related to streamflow, and because this trend analysis was not flow adjusted, the upward trends may be related to flow as well as human-influenced effects.

#### **Nutrients**

Most nutrient data at the six sites were analyzed with flow-adjusted trend tests. Dissolved nitrate plus nitrite concentrations at sites 1 and 2 exceeded the 5 percent limit of censored values as did total phosphorus concentrations at site 3 and, therefore, were tested for non-flow adjusted trends. No significant trends were detected (table 6; fig. 15).

#### Trace Elements

Trace element data were highly censored at all sites. Trace element data were collected four times per water year during the study period, which made determining trends

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**Figure 15.** Non-flow adjusted trends in total suspended solids, dissolved nitrate plus nitrite (as nitrogen), and total phosphorus concentrations, water years 1993 through 2008.

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**Figure 16.** Non-flow adjusted trends in total recoverable lead and zinc concentrations, water years 2000 to 2008.

<span id="page-46-0"></span>more difficult. Long-term trends could be calculated for total recoverable lead concentrations at sites 1 and 2, and for total recoverable zinc concentrations at sites 1, 2, and 3. Only data from 2000 to 2008 were used because data collected before the 2000 water year were not collected consistently (table 6). No trends were indicated in the total recoverable lead and zinc concentrations at the three sites (table 6; fig. 16). Because the datasets were highly censored, the power of the trend tests was decreased, making the determination of a true trend difficult. No flow adjustment could be used because of the large amount of censored values; therefore, any long-term trend may be masked by year-to-year variability caused by streamflow differences.

# **Summary and Conclusions**

The U.S. Geological Survey (USGS), in cooperation with the Missouri Department of Natural Resources (MDNR), collects data pertaining to the water resources of Missouri. These data are collected as part of the Missouri Ambient Water-Quality Monitoring Network (AWQMN) and constitute a valuable source of reliable, impartial, and timely information for developing an improved understanding of water resources of the State. Information from water-quality monitoring performed by the USGS is needed to assess the existing conditions of water resources; to design preservation, management, and remediation programs; and to evaluate the effectiveness of such programs, as well as document compliance with local, State, and Federal regulations and permits. In addition, the results of water-quality monitoring are needed to detect and define trends in water quality and to identify emerging waterquality concerns.

Six sites from the AWQMN, with available data from the 1993 through 2008 water years, were chosen to study the water-quality conditions and long-term trends of dissolved oxygen, physical properties (specific conductance and water temperature), total suspended solids, nutrients (dissolved nitrate plus nitrite as nitrogen and total phosphorous), fecal indicator bacteria [*Escherichia coli (E. coli)* and fecal coliform], and trace elements (dissolved and total recoverable lead and zinc). The six sites used in the study are classified in groups corresponding to the physiography, main land use, and drainage basin size, and represent the stream diversity within Missouri. Sites used in the study were referred to as the following: site 1, South Fabius River near Taylor (USGS identifier 05500000); site 2, Grand River near Sumner (USGS identifier 06902000); site 3, Gasconade River above Jerome (USGS identifier 06930800); site 4, Wilson Creek near Brookline (USGS identifier 07052152); site 5, Current River at Doniphan (USGS identifier 07068000); site 6, Elk River near Tiff City (USGS identifier 07189000).

Water-quality conditions were assessed to explore relations between data from sites and to the State waterquality standards where applicable for selected constituents. Streamflow varied at each site because of drainage area, land use, and groundwater inputs. All six sites had statistically different streamflows for the study period, except sites 2 and 3. Dissolved oxygen concentrations were significantly different at site 4, which was the only urban site in the study. Specific conductance was similar between the most northern sites (sites 1 and 2) and between the most southern sites (sites 5 and 6) in the study. Water temperature was similar for all sites in the study except site 4. Total suspended solids concentrations generally were reported at the method reporting level at all sites, except sites 1 and 2. Streams in northern Missouri are more turbid than streams in southern Missouri and are affected by large volumes of sediment deposition because of soil erosion from land cultivated for row crops.

Site 4, located downstream from the Springfield Southwest Wastewater Treatment Plant (SWWTP), had the largest concentrations of dissolved nitrate plus nitrite during the study period; the median concentration was 10 milligrams per liter. In 1993, the SWWTP completed facility improvements that decreased the phosphorus concentration in effluent discharged into Wilson Creek by an average of 40 percent. In March 2001, the SWWTP introduced an advanced phosphorus reduction system, which decreased the average phosphorus discharge levels to 0.5 milligram per liter. Of the three sites with basins containing large percentages of agricultural land (sites 1, 2, and 6), median total phosphorus concentration at site 2 was significantly different. Total phosphorus concentrations never exceeded 0.5 milligram per liter at sites 3 and 5 during the study period.

The MDNR has set statewide standards for fecal indicator bacteria and are among the most stringently monitored constituents by the State. The State standards are used for *Escherichia coli* and apply only to the recreational period of April 1 through October 31. The standard is calculated from the geometric mean of all samples collected during the recreation period. The geometric means of *Escherichia coli* calculated from the recreational seasons within the study period show that only site 2 exceeded the whole-body-contact standard for frequently used waters. The whole-body-contact standard for less frequently used waters and the secondary contact recreation standard were not exceeded at any of the sites during the study period. The most northern sites (sites 1 and 2) and the only urban site (sites 4) in the study had statistically larger densities of both fecal indicator bacteria types than the remaining sites. Fecal indicator bacteria samples primarily were collected during base-flow conditions through the water year, but some samples were collected during high-flow conditions as well as the non-recreational months (November through March).

Dissolved lead concentrations analyzed during the study period seldom exceeded the laboratory reporting level of 1 microgram per liter. Median total recoverable lead data were equal to or less than the laboratory reporting level at all sites except the two northern sites. Median total recoverable lead concentrations at sites 1 and 2 were significantly larger than concentrations as sites 3, 5, and 6. The median concentrations

<span id="page-47-0"></span>of dissolved and total recoverable zinc were 39 and 40 micrograms per liter at site 4, which are significantly larger than the other sites, but are typical of concentrations in the SWWTP effluent. The State standards for lead and zinc varied with the hardness of the water and stream classifications.

 Long-term trends were analyzed at each site and for each constituent. All constituents were analyzed using the Seasonal Kendall test. Some constituents were analyzed using a flow-adjusted trend test, whereas datasets with greater than 5 percent but less than or equal to 50 percent censored values were analyzed by non-flow adjusted trend tests.

No significant long-term trends were detected for dissolved oxygen or water temperature. Significant trends in specific conductance were determined for three sites; a downward trend at site 1, and an upward trend at sites 3 and 6.

Dissolved nitrate plus nitrite concentrations for all sites, except sites 1 and 2 (which contained more than 5 percent censored values), could be analyzed by flow-adjusted models. Of the four sites adjusted by streamflow, only site 6 showed a significant trend (upward). The Elk River Basin is largely agricultural, most of which is poultry and cattle production. Agricultural statistics from the 1997, 2002, and 2007 census studies show that the number of cattle operations in the Elk River Basin, as well as the amount of commercial fertilizers that were applied, have stayed relatively stable over the study period, whereas poultry production increased. The increase in urban development upstream and the increase in poultry populations within the basin possibly have caused the upward trend in nutrient concentrations at the site.

Total phosphorus concentrations at four of the six sites were analyzed by flow-adjusted models. All of the sites showed significant long-term trends in the data except the site 6. The two northern sites showed an upward trend, whereas the urban site (site 4) had a downward trend in concentrations for the study period. The increase in total phosphorus concentrations at the northern sites could be from an increase in agricultural land use in the basins. The SWWTP upstream from site 4 on Wilson Creek began using a phosphorus reduction system in March 2001 that decreased the average phosphorus discharge levels to 0.5 milligram per liter, contributing to the downward trend in total phosphorus concentrations in Wilson Creek. A step-trend analysis was performed on the total phosphorus concentrations collected at site 4 to analyze the data before and after the phosphorus reduction system began operation at the treatment plant. A statistically significant difference was indicated between concentrations, indicating the reduction system was likely responsible.

Site 4 contained no censored values for dissolved and total recoverable zinc datasets and could be analyzed using flow-adjusted tests. Median concentrations of both dissolved and total recoverable zinc at the urban site are near the typical effluent zinc concentration of 40 micrograms per liter. Significant downward trends in dissolved and total recoverable zinc concentrations were indentified at the urban site. Two circuit board manufacturers and several chrome plating operations that discharged effluent into the wastewater treatment plant

have gone out of business during the past several years, which may have contributed to the significant downward trend in zinc concentrations.

Total suspended solids concentrations were highly censored at all sites. Only datasets from the two northern sites were censored less than 50 percent and could be analyzed by non-flow adjustment tests. Statistically significant upward trends were detected at both sites. The increase in total suspended solids concentrations could be because of soil erosion from land cultivated for row crops.

Trace element data at all sites were highly censored. Long-term trends could be calculated for total recoverable lead datasets at the two northern sites, and for total recoverable zinc datasets at sites 1, 2, and 3 using non-flow adjusted tests. No trends were indicated in the total recoverable lead and zinc data at the three sites.

The significant trends identified in the study were mainly among nutrient constituents. Most of the nutrient trends can be related to changes in agriculture and urban development. Other significant trends were identified in total suspended solids, particularly at the two northern sites where agriculture, soil erosion, and runoff are more pronounced. Analysis of additional long-term sites within the Ambient Water-Quality Monitoring Network would help determine if other trends in dissolved oxygen, physical properties, total suspended solids, nutrients, or trace elements can be detected within the State's surface waters.

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