

Prepared in cooperation with the City of Oklahoma City

Evaluation and Trends of Land Cover, Streamflow, and Water Quality in the North Canadian River Basin near Oklahoma City, Oklahoma, 1968–2009



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By Rachel A. Esralew, William J. Andrews, and S. Jerrod Smith

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m ²)
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km ²)
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m ³)
million gallons (Mgal)	3,785	cubic meter (m ³)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
acre-foot (acre-ft)	1,233	cubic meter (m ³)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
Mass		
ton per day (ton/d)	0.9072	metric ton per day
Pressure		
atmosphere, standard (atm)	101.3	kilopascal (kPa)

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

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

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).

Water year is the 12-month period October 1 through September 30 and is named for the year in which it ends.

Evaluation and Trends of Land Cover, Streamflow, and Water Quality in the North Canadian River Basin near Oklahoma City, Oklahoma, 1968–2009

By Rachel A. Esralew, William J. Andrews, and S. Jerrod Smith

Abstract

The U.S. Geological Survey, in cooperation with the city of Oklahoma City, collected water-quality samples from the North Canadian River at the streamflow-gaging station near Harrah, Oklahoma (Harrah station), since 1968, and at an upstream streamflow-gaging station at Britton Road at Oklahoma City, Oklahoma (Britton Road station), since 1988. Statistical summaries and frequencies of detection of water-quality constituent data from water samples, and summaries of water-quality constituent data from continuous water-quality monitors are described from the start of monitoring at those stations through 2009. Differences in concentrations between stations and time trends for selected constituents were evaluated to determine the effects of: (1) wastewater effluent discharges, (2) changes in land-cover, (3) changes in streamflow, (4) increases in urban development, and (5) other anthropogenic sources of contamination on water quality in the North Canadian River downstream from Oklahoma City.

Land-cover changes between 1992 and 2001 in the basin between the Harrah station and Lake Overholser upstream included an increase in developed/barren land-cover and a decrease in pasture/hay land cover. There were no significant trends in median and greater streamflows at either streamflow-gaging station, but there were significant downward trends in lesser streamflows, especially after 1999, which may have been associated with decreases in precipitation between 1999 and 2009 or construction of low-water dams on the river upstream from Oklahoma City in 1999.

Concentrations of dissolved chloride, lead, cadmium, and chlordane most frequently exceeded the Criterion Continuous Concentration (a water-quality standard for protection of aquatic life) in water-quality samples collected at both streamflow-gaging stations. Visual trends in annual frequencies of detection were investigated for selected pesticides with frequencies of detection greater than 10 percent in all water samples collected at both streamflow-gaging stations. Annual frequencies of detection of 2,4-dichlorophenoxyacetic acid and bromacil increased with time. Annual frequencies of detection of atrazine, chlorpyrifos, diazinon, dichlorprop, and lindane decreased with time.

Dissolved nitrogen and phosphorus concentrations were significantly greater in water samples collected at the Harrah station than at the Britton Road station, whereas specific conductance was greater at the Britton Road station. Concentrations of dissolved oxygen, biochemical oxygen demand, and fecal coliform bacteria were not significantly different between stations.

Daily minimum, mean, and maximum specific conductance collected from continuous water-quality monitors were significantly greater at the Britton Road station than in water samples collected at the Harrah station. Daily minimum, maximum, and diurnal fluctuations of water temperature collected from continuous water-quality monitors were significantly greater at the Harrah station than at the Britton Road station. The daily maximums and diurnal range of dissolved oxygen concentrations were significantly greater in water samples collected at the Britton Road station than at the Harrah station, but daily mean dissolved oxygen concentrations in water at those streamflow-gaging stations were not significantly different.

Daily mean and diurnal water temperature ranges increased with time at the Britton Road and Harrah streamflow-gaging stations, whereas daily mean and diurnal specific conductance ranges decreased with time at both streamflow-gaging stations from 1988–2009. Daily minimum dissolved oxygen concentrations collected from continuous water-quality monitors more frequently indicated hypoxic conditions at the Harrah station than at the Britton Road station after 1999. Fecal coliform bacteria counts in water decreased slightly from 1988–2009 at the Britton Road station.

The Seasonal Kendall's tau test indicated significant downward trends in flow-adjusted dissolved phosphorus concentrations from 1988–2009 in water samples collected at the Britton Road station. Trends in water quality were analyzed before and after 1999 because of trends in streamflow after 1999. For the period 1988–98, there were significant downward trends in nitrogen and phosphorus. For the period 1999–2009, there were also significant downward trends in flow- and temperature-adjusted dissolved oxygen concentrations in water samples collected at the Harrah station, significant upward trends in flow-adjusted dissolved nitrogen concentrations in water samples collected at both stations, and

significant upward trends in flow-adjusted dissolved phosphorus concentrations only at the Harrah station.

Statistically significant differences in concentrations of water-quality constituents and trends in water-quality constituents may have been caused, in part, by changes in streamflow and discharges from wastewater-treatment plants. Urban development, population growth, and agricultural activities, including application of treated biosolids along the riparian corridor of the North Canadian River upstream from these stations, also may have affected trends in water quality in the river.

Introduction

The U.S. Geological Survey (USGS), in cooperation with the city of Oklahoma City, collected water samples at two streamflow-gaging stations (referred to as “stations” in the remainder of this report) downstream from much of the Oklahoma City metropolitan area on the North Canadian River (fig. 1). Some samples have been collected since 1968 for analysis of physical properties and concentrations of major ions, nutrients, selected pesticides, and fecal-indicator bacteria to determine the effects of effluent from wastewater-treatment plants (WWTPs) and urban areas on water quality in the basin. The North Canadian River near the Harrah, Oklahoma, station (referred to in the remainder of this report as “the Harrah station”) may be moved in response to recent (2010) channel changes (fig. 2). A summary of water-quality data and documentation of water-quality trends at the current station location would be beneficial for city officials for future comparisons to water-quality data collected at a new station location.

The Oklahoma City-North Canadian WWTP, managed by the city of Oklahoma City, is the largest WWTP in the basin, discharging 15–50 million gallons per day of treated municipal wastewater effluent (referred to in the remainder of this report as effluent) to the river about 7 miles upstream from the Harrah station (fig. 1). At this WWTP, as well as other WWTPs managed by the city, aerobic, activated-sludge, and liming treatments generally are used to precipitate out solids, remove organic compounds, and disinfect wastewater (Perry Soltani, city of Oklahoma City, oral and written commun., June 2008). Description of the effects of effluent discharges to the North Canadian River on water quality at the Harrah station is needed by city officials for assessment of the effects of past wastewater-management practices, changes in land cover, and for compliance with waste-load-allocation requirements.

Comparison of historical water quality at the Harrah station and at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station (upstream from the outfall of the Oklahoma City-North Canadian municipal WWTP and the Harrah station and referred to in the remainder of this report as the “Britton Road station,” fig. 1) was needed to evaluate the effects of municipal wastewater effluent and land-cover changes on water

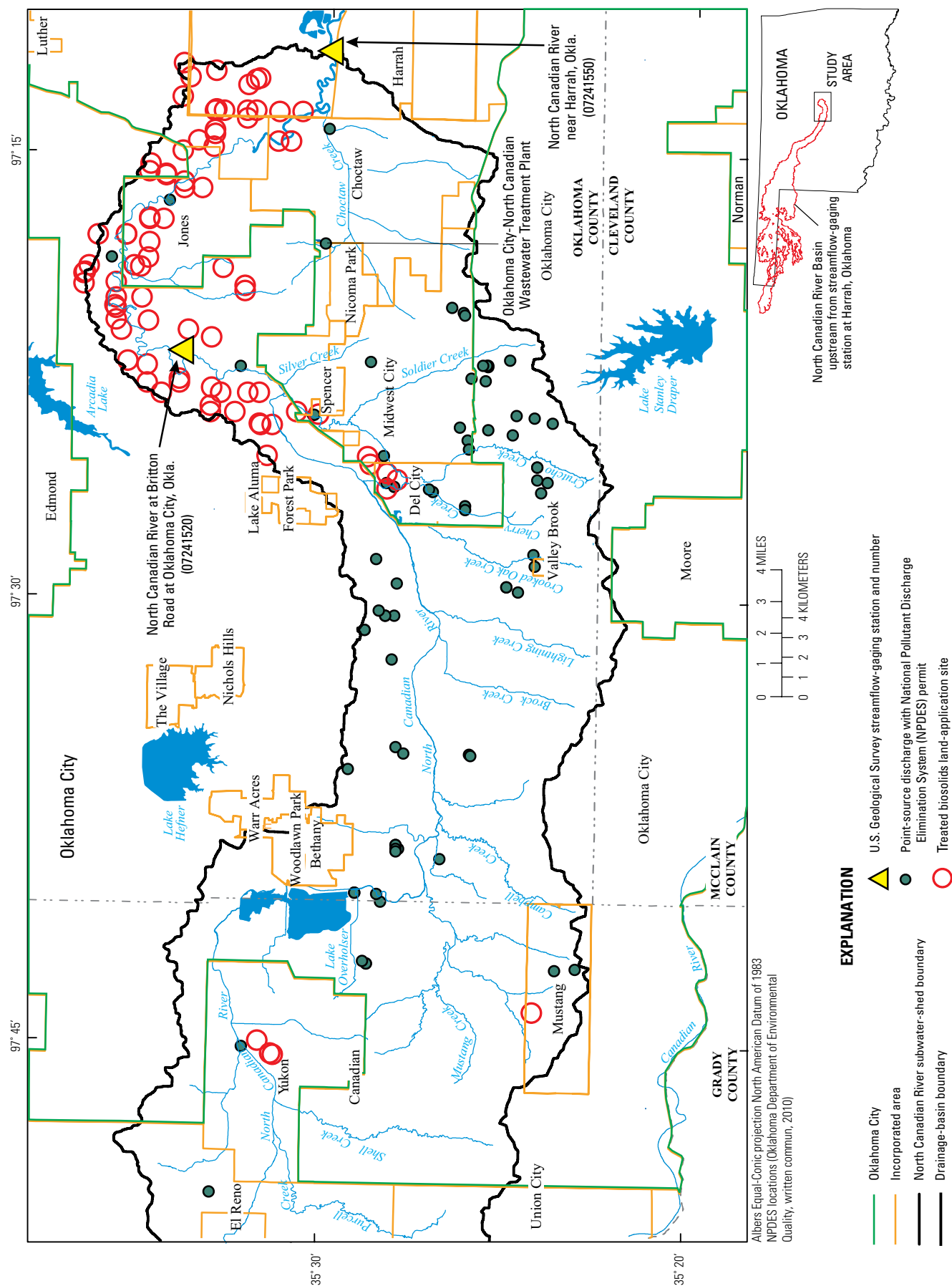
quality in the North Canadian River. Water-quality samples have been collected at the Harrah station since 1968 and the Britton Road station since 1988.

Physical properties of water (referred to in this report as physical properties), such as specific conductance, pH, water temperature, and dissolved oxygen concentration, can have substantial effects on water quality and aquatic habitat and changes in these constituents may cause changes in other water-quality characteristics. For example, decreases in dissolved oxygen concentration in a river may indicate enrichment of organic compounds by effluent discharges and other sources. These organic compounds can result in oxygen consumption through aerobic metabolism and can cause hypoxia in a water body. Increases in specific conductance and changes in pH may indicate increases in dissolved solids from urban runoff, and specific conductance and pH may also affect toxicity and solubility of metals (Linnik and Nabivanets, 1977; Granato and others, 1995). Comparison of continuously measured physical properties between the Britton Road and Harrah stations may identify differences between stations in water quality that may not be observed from analysis of periodic or discrete samples, including diurnal or storm-hydrograph fluctuations. For example, discrete water-quality samples in the North Canadian River typically were collected during daylight hours, which would not be representative of nocturnal water quality (Brigham and others, 2002).

Substantially elevated concentrations of nutrients, including nitrogen and phosphorus, and biological constituents, including fecal-indicator bacteria and chlorophyll *a*, can be indicators of point and nonpoint source contamination, such as effluent from a WWTP or runoff from agricultural or urban areas (Dierberg, 1991). Changes in flow-adjusted concentrations of physical properties, nutrients, and biological indicators in water samples collected from the Britton Road and Harrah stations may indicate if substantial effluent discharges or changes in land cover between those stations resulted in differences in water-quality characteristics. Trend analysis of nutrient, biological, and physical-property concentrations may indicate if changes in wastewater-treatment practices or in land cover are affecting water quality in the North Canadian River.

Pesticides applied to control insects, weeds, and crop diseases in agricultural and suburban areas can adversely affect water quality (Gilliom and others, 2006). As reported in Brigham and others (2002), some pesticides have been commonly detected in small concentrations in the North Canadian River. Analysis of the frequencies of detection of pesticides, and changes in detection frequencies of pesticides with time, can be useful for identification of pesticides that are most prevalent in this reach of the North Canadian River and for determination of increases or decreases of pesticide concentrations in this reach.

Water-quality data from discrete samples represent water quality only at the time and place the samples were collected. If samples used in analysis are not representative of typical streamflow, water-quality data may be biased. Comparison of



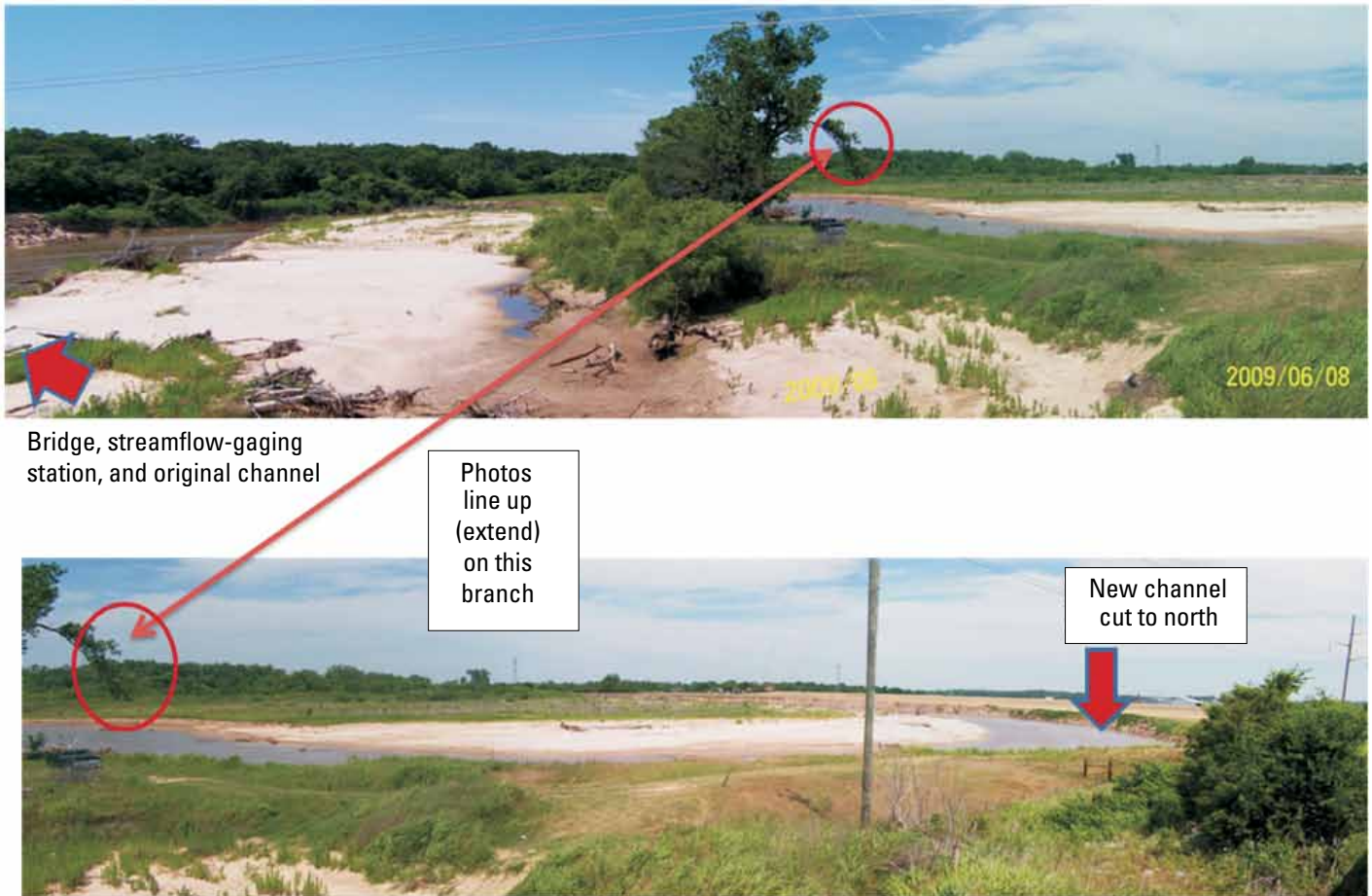


Figure 2. Panoramic view of channel shift after high streamflow at the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 2009.

streamflows at the time of sample collection to typical streamflow can be used to determine if historical biases are present in sampling protocols that may affect interpretation of statistical summaries and trends of water-quality data. Concentrations of many water-quality constituents correlate to streamflow. For example, high streamflow may increase contributions of constituents such as nutrients and sediment from nonpoint sources but cause dilution of those same constituents in point sources, such as WWTP effluent. Identification of trends in streamflow is useful for evaluation of potential causes of trends in water quality, because long-term trends in streamflow may cause trends in other constituent concentrations. Anthropogenic activities such as diversions, withdrawals, regulation, and changes in land cover that affect long-term streamflow trends also may change relations between streamflow and constituent concentrations. The North Canadian River Basin immediately upstream from the Britton Road and Harrah stations is predominantly urban with mixed agricultural land cover (Brigham and others, 2002). Increases in urban development and population growth accompanied by decreases in forested area and changes in agricultural land cover may cause changes in nutrient, sediment, and biological constituent concentrations

in rivers. For the remainder of this report, the term “developed” and “development” refer only to urbanization and other types of anthropogenic alterations of land surface.

Purpose and Scope

The purpose of this report is to evaluate and summarize water-quality data and identify trends in selected water-quality constituents (fecal-indicator bacteria, chlorophyll *a*, and dissolved concentrations of oxygen, nitrogen, and phosphorus) in water samples collected at the Britton Road (1988–2009) and Harrah (1968–2009) stations. This report also describes land cover and streamflow characteristics that can affect water quality at these stations.

This report describes (1) the study area, (2) data analyzed and data-analysis methods, (3) changes in land cover in basins upstream from the two stations, (4) trends in streamflow and comparison of streamflow at times of water-sample collection to the historical range of streamflow, (5) summary and analysis of water-quality data including (a) summary statistics

of historical water-quality data and analysis of frequencies of exceedance of water-quality criteria, (b) analysis of frequencies of detection of pesticides, (c) differences in concentrations of selected nutrients, biological, and physical properties between the stations, (d) trends in selected nutrient, biological, and physical properties with time, and (e) potential causes of differences and trends with time in selected water-quality constituents.

This report updates part of the work of Brigham and others (2002) that evaluated trends in selected constituent concentrations at five water-quality monitoring stations on the North Canadian River through 1999 and evaluated the sampling network with respect to areal coverage, sampling frequency, and analytical schedules. Unlike Brigham and others (2002), trends in major and minor inorganics generally were not analyzed and were beyond the scope of this report. This report provides information needed to advance knowledge of the regional hydrologic system, provide information concerning the sources of contaminants entering streams, and determine the effects of land cover on surface-water quality (Larson, 2009).

Description of Study Area

The basin areas contributing streamflow to the Britton Road and Harrah stations are 8,514 and 8,602 square miles, respectively (U.S. Geological Survey, 2010). This basin has a large range of streamflow, water-use, landscape, and climate characteristics. This section describes basin characteristics that may affect streamflow and water quality at the Britton Road and Harrah stations.

Streamflow and Water-Use Characteristics

The source of the North Canadian River is in the high plateau region in Union County, New Mexico (fig. 3). The North Canadian River enters Oklahoma in southwestern Cimarron County, Oklahoma. Part of the basin lies in the Texas Panhandle upstream from where the river is impounded by the Optima Lake Dam in Texas County, Oklahoma (Oklahoma Water Resources Board, 1997).

Because of large groundwater withdrawals and relatively small recharge of the High Plains aquifer in the western part of the basin since 1972 (fig. 4), most areas upstream from the Optima Lake Dam only contribute streamflow during substantial runoff events (Wahl and Tortorelli, 1997) and some areas do not contribute any notable streamflow (Smith and Esralew, 2010). Non-contributing areas in the North Canadian River Basin (fig. 3) also coincide with areas having numerous playa lakes (Smith and Esralew, 2010). Streamflow in that part of the basin continued to decline through 2008 (Esralew and Lewis, 2010).

Downstream from the Optima Lake Dam and in downstream order, the North Canadian River has been regulated

by Fort Supply Lake since 1942, Canton Lake since 1948, and Lake Overholser since 1919 (Oklahoma Water Resources Board, 1997) (fig. 3). The city of Oklahoma City owns water storage in Canton Lake and relies on water in the lake to help replenish the downstream Lakes Overholser and Hefner (fig. 1). Large volumes of water are released periodically from Canton Lake that substantially increase streamflow in downstream reaches of the North Canadian River, such as a 15,000 acre-foot of water released in January 2007 to help supplement downstream lake levels after a local drought (Oklahoma Water Resources Board, 2007; Tortorelli, 2008). Lake Overholser is in the Oklahoma City metropolitan area and is connected to Lake Hefner by a canal. Lake Hefner was constructed in 1947 primarily to supply water needs of the city of Oklahoma City (Oklahoma Water Resources Board, 1997) (figs. 1 and 3). The Overholser Canal is used to transfer water between those lakes to meet water-supply needs (The City of Oklahoma City, 2010).

Annual mean streamflow at the Harrah station was 496 cubic feet per second (ft³/s) from 1968–2009 (U.S. Geological Survey, 2010, table 1). For the period of common operation of both stations (1988–2009), the annual mean streamflow at the Britton Road station was 473 ft³/s and was 601 ft³/s at the Harrah station. The difference in mean annual streamflow at the Harrah station between water years 1968–2009 and 1988–2009 probably was caused by differences in precipitation, with the early 1980s to 2000 being an unprecedented wet period in Oklahoma (Garbrecht and Schneider, 2007).

Use of surface water and groundwater in the basin can affect streamflows and water quality in rivers. Surface-water use in the North Canadian River Basin from 1950–2005 was predominantly for public supply, especially in the Oklahoma City metropolitan area (Tortorelli, 2009). Groundwater use in the aquifers underlying the North Canadian River Basin during that period was predominantly from the Central Oklahoma aquifer for public-water supply, and the High Plains and North Canadian River Alluvial and Terrace aquifers for irrigation (Tortorelli, 2009). Groundwater in and near the Britton Road and Harrah stations is stored primarily in two aquifers: the North Canadian River Alluvial and Terrace aquifer and the Central Oklahoma aquifer. The North Canadian River Alluvial and Terrace aquifer consists of unconsolidated deposits that typically have shallow depths to water and large permeability, with well yields ranging from 10 to 1,200 gallons per minute (Oklahoma Water Resources Board, 1997). The Central Oklahoma aquifer is a bedrock aquifer that consists of the Permian-age Garber Sandstone, Wellington Formation, and the Chase, Council Grove, and Admire Groups (Oklahoma Water Resources Board, 1997; Osborn and others, 1998). Groundwater in the Central Oklahoma aquifer generally is not well-connected with surface-water in the North Canadian River, whereas groundwater from the North Canadian River Alluvial and Terrace aquifer is well-connected with surface water. Increasing water use in the North Canadian River Basin may affect streamflow and water-quality characteristics.

6 Evaluation and Trends of Land Cover, Streamflow, and Water Quality in the North Canadian River Basin

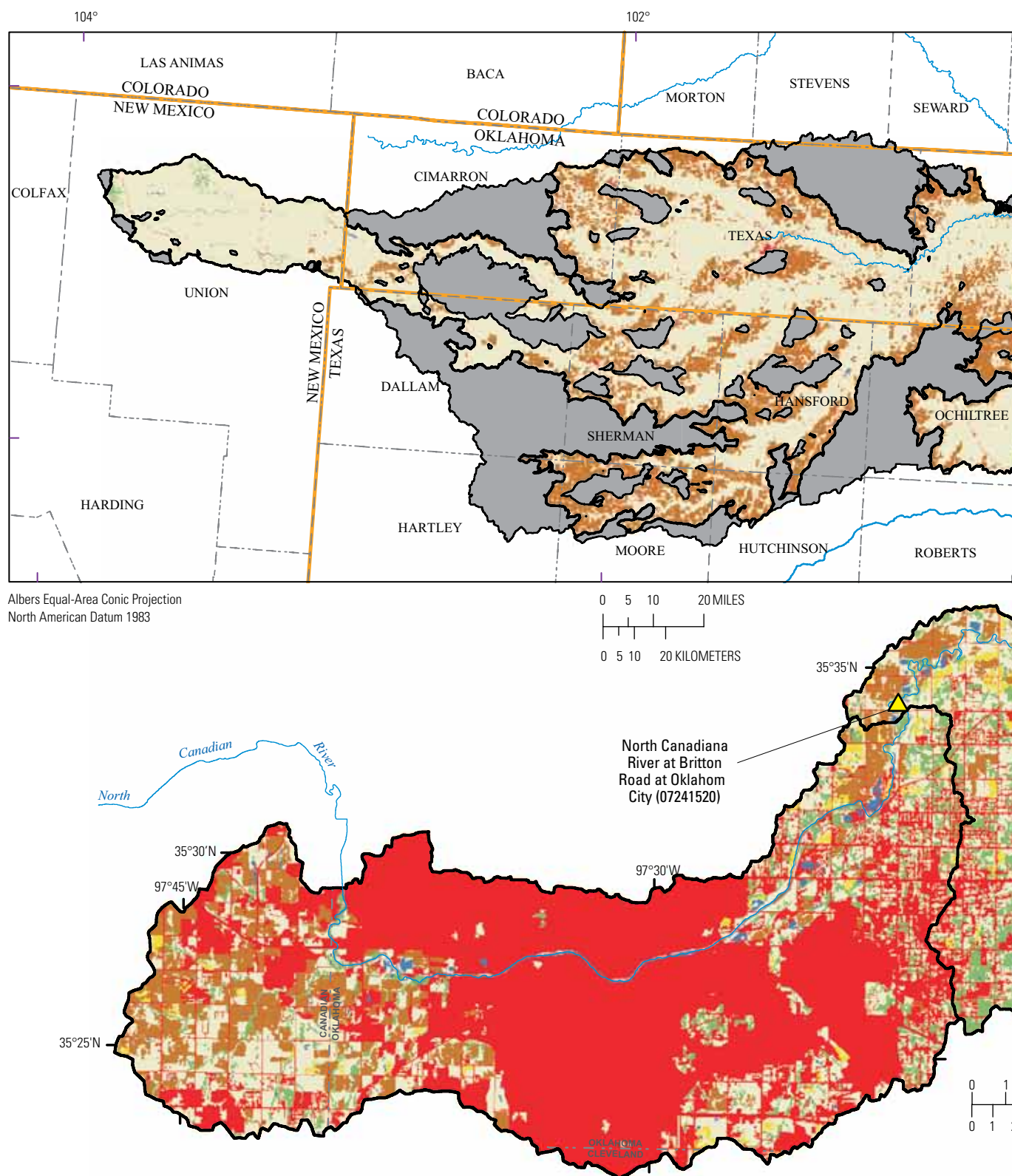


Figure 3. Land cover in the basin upstream from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 2001.

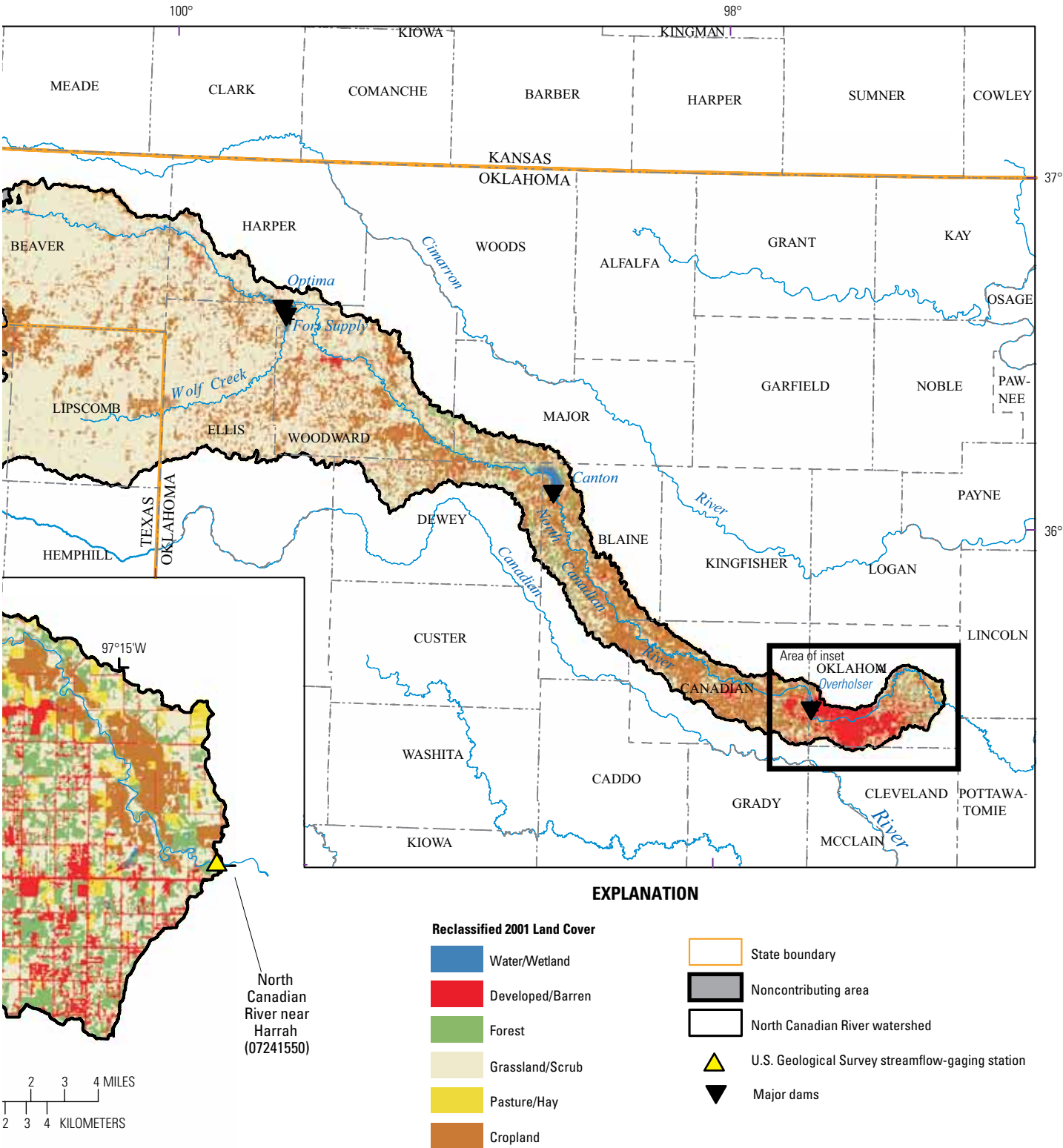


Figure 3.—Continued.

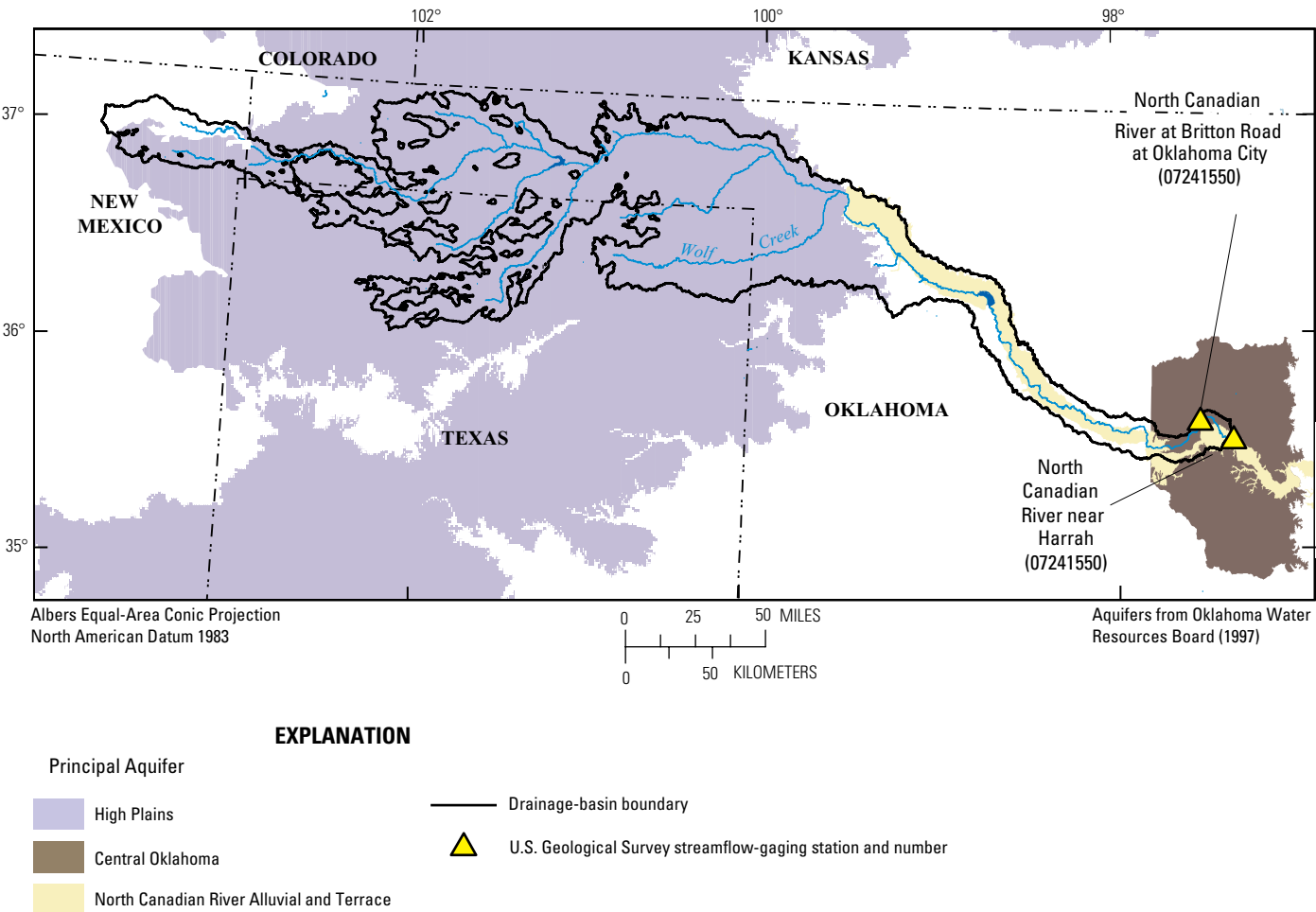


Figure 4. Major aquifers in the basin upstream from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station.

Table 1. Streamflow statistics for the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

[mi², square mile; ft³/s, cubic foot per second]

Station name (number, fig. 1)	Period of record for station	Contrib- uting drainage area (mi ²)	Annual mean stream- flow (ft ³ /s)	Range of daily mean streamflow		Range of instantaneous streamflow at time of sample collection	
				Minimum streamflow (ft ³ /s and date)	Maximum streamflow (ft ³ /s and date)	Minimum streamflow (ft ³ /s and date)	Maximum streamflow (ft ³ /s and date)
North Canadian River at Britton Road at Oklahoma City, Okla. (07241520)	1988–2009	8,514	473	7.0 (08/10/2009)	38,000 (08/09/1993)	12.0 (02/27/2006)	12,200 (08/21/2007)
North Canadian River near Harrah, Okla. (07241550)	1968–2009	8,602	496	28 (08/08/1972)	27,200 (05/29/1987)	42 (10/5/1972)	23,800 (05/29/1987)

Public-supply water use in the North Canadian River Basin and the Central Oklahoma aquifer increased after 2000 (Tortorelli, 2009). There also have been increases in public water-supply permits for wells completed in the North Canadian River Alluvial and Terrace aquifer during that period (C.R. Neel, Oklahoma Water Resources Board, oral and written commun., October 2010).

Landscape and Climate Characteristics

Land cover in the North Canadian River Basin changes substantially from the west to the east, but is predominantly grassland/shrub (fig. 3). Grassland/shrub areas in the part of the basin west of Major and Dewey Counties transition into increasing amounts of cropland to the east from Blaine County to Canadian County. In eastern Canadian County and Oklahoma County, land-cover transitions from mixed agricultural (cropland, pasture/hay), grassland/shrub, and developed to predominantly developed in the Oklahoma City

metropolitan area. East of the metropolitan area, land cover transitions to a mix of forest, cropland, and pasture/hay as the river flows toward the Harrah station.

Landscape characteristics of the North Canadian River Basin upstream from the Harrah station are variable. The North Canadian River Basin includes parts of four U.S. Environmental Protection Agency (USEPA) Level III ecoregions (fig. 5, Woods and others, 2005). Ecoregions summarize areas with similar climatic and geologic characteristics (Omernik, 2004). From the headwaters to the Harrah station, ecoregions in the basin include: the High Plains, Southwestern Tablelands, Central Great Plains, and Cross Timbers (fig. 5). Geologic, topographic, and land-cover features downstream from Optima Lake Dam probably affect streamflow and water quality at the Britton Road and Harrah stations more than areas upstream from the dam (as described in the previous section “Streamflow and Water-Use Characteristics”). This lower part of the basin is in the Central Great Plains and Cross Timbers Ecoregions that are described in greater detail in this section.

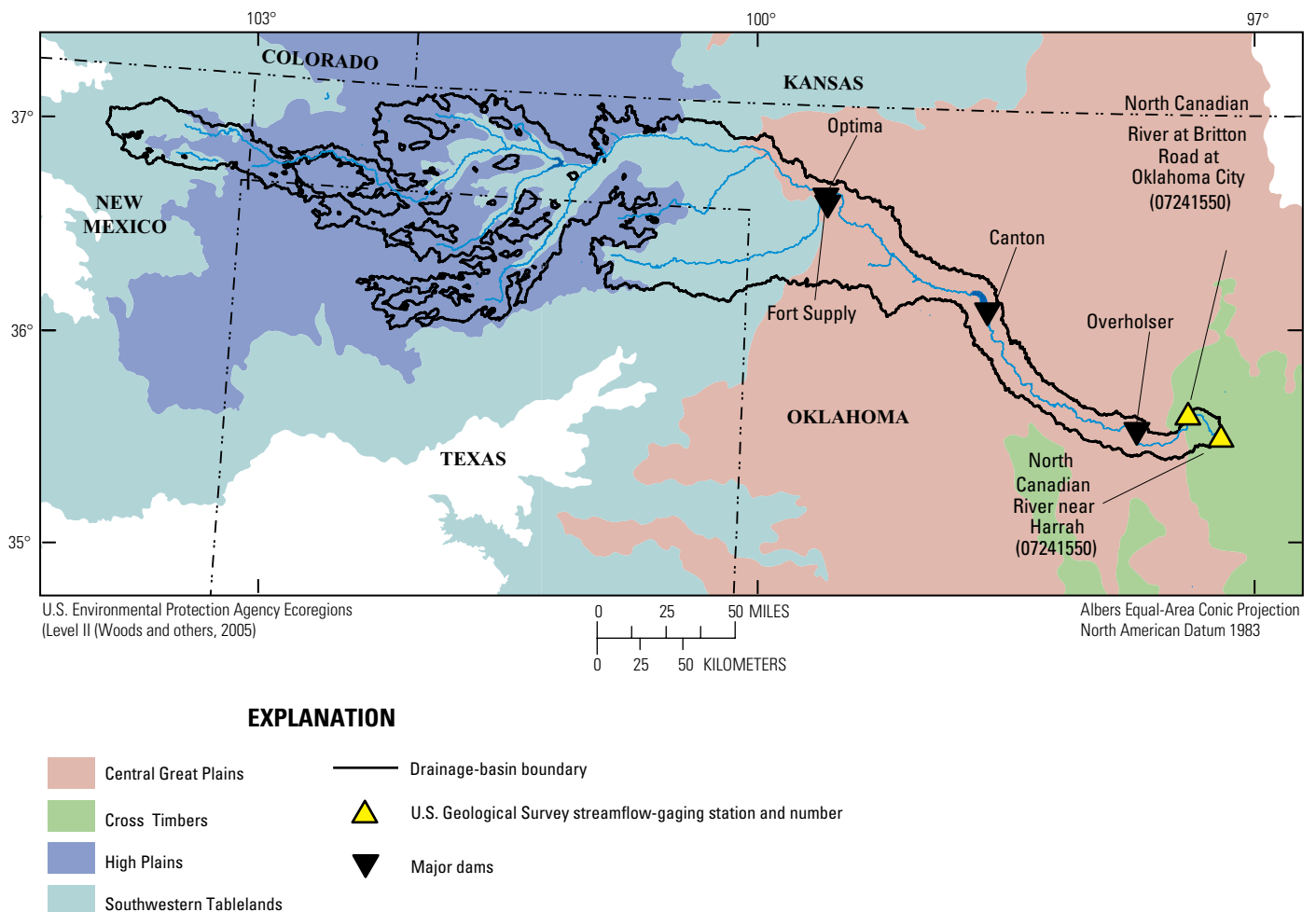


Figure 5. Level III ecoregions in the basin upstream from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station.

The part of the basin between the Lake Optima Dam and the Britton Road station is in the Central Great Plains Ecoregion (fig. 5). This ecoregion is characterized by red, Permian-age sedimentary rocks and includes salt plains, gypsum karst, and Pleistocene-age sand dunes. Suspended sediment loads in the North Canadian River are large after periods of runoff, with cropland areas contributing greater amounts of sediments and sediment-sorbed nutrients to streams than rangelands in the basin (Woods and others, 2005). Water quality in this part of the basin may contain high mineral content from dissolution of salt or gypsum deposits. Grazing and irrigated crops are the most common land-cover types in this part of the Central Great Plains Ecoregion. The eastern boundary of this ecoregion is the eastern limit of America's winter wheat belt, with primary crops in this ecoregion being wheat, alfalfa, and grain sorghum, with soybeans planted in areas with greater rainfall (Woods and others, 2005). Some riparian corridors in this ecoregion are wooded and may have invasive woody vegetation such as eastern red cedar that can alter streamflow dynamics through evapotranspiration and streambank stabilization (Duesterhaus, 2008; Zou and others, 2010).

Most of the basin between the Britton Road and Harrah stations is in the Cross Timbers Ecoregion (fig. 5) that is characterized by woodland (notably blackjack oak), savanna, and prairie. Soils, mostly developed on sandstone in this ecoregion, are porous, coarse-textured, and highly erodible when disturbed (Woods and others, 2005). In the drier months of summer, streamflow can seep from the North Canadian River into surrounding aquifers (streamflow decreases with distance). In some reaches, streamflow periodically decreases to negligible amounts on the wide, sandy, river channel (Woods and others, 2005). Large oilfields were developed in the western part of this ecoregion in the early 20th century. Oil-production activities may have caused increased salinity in the river from discarded brines, drilling muds, and petroleum

waste products (Woods and others, 2005); however, the area and density of oil production in the North Canadian River Basin has been decreasing with time (Brigham and others, 2002). Raising livestock and crops are major components of land cover in this part of the basin, with cropland being primarily limited to valleys near channelized streams. Cultivation of crops can cause degradation of aquatic habitat and greater vulnerability of the floodplains in this part of the basin due to erosion, which can increase sediment and nutrient loads in the river (Woods and others, 2005).

Timing and amounts of annual precipitation also can affect streamflow and water quality in the North Canadian River. Mean annual precipitation in the basin upstream from the Harrah station ranges from less than 15 inches per year in the western headwaters to about 38 inches per year near the Harrah station (Esralew and Smith, 2010, pg. 24). Precipitation falls on the basin mostly in the form of widespread rains and locally intense thunderstorms and generally is greatest in late spring and early autumn (Eddy, 1982).

Urban Development

Water quality and streamflow at the Britton Road and Harrah stations probably are affected by increases in development in the Oklahoma City metropolitan area upstream from the stations (see section titled "Evaluation of Changes in Land Cover"). Population in Canadian and Oklahoma Counties, the two counties closest to the Britton Road and Harrah stations, has been steadily increasing in the past several decades (fig. 6, U.S. Census Bureau, 2001). The rate of population growth is substantially greater in Oklahoma County, because substantial population growth in the Oklahoma City metropolitan area is mostly in Oklahoma County.

Water quality at both stations can be affected by effluent discharge from WWTPs and other point-source discharges, in

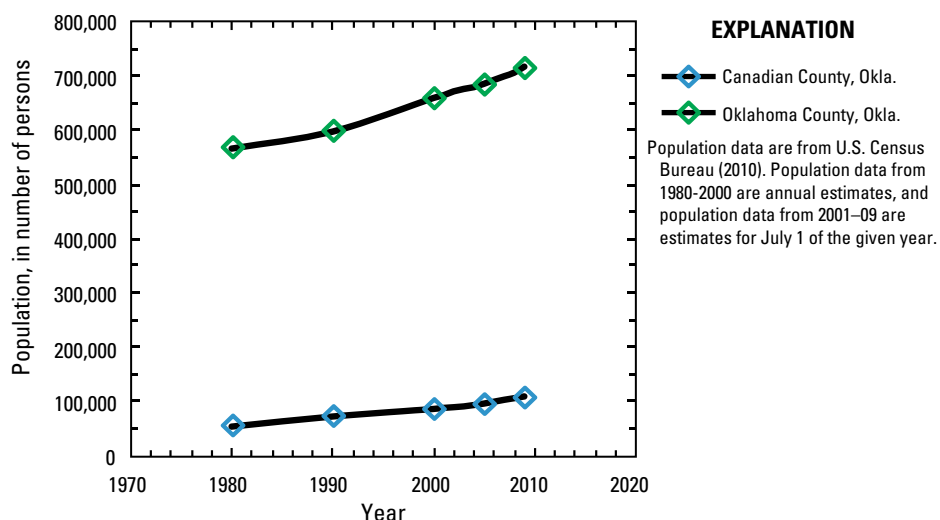


Figure 6. Populations of Canadian and Oklahoma Counties, Oklahoma, 1980–2009.

addition to effluent discharged at the Oklahoma City-North Canadian WWTP between the Britton Road and Harrah stations (fig. 1). Municipal WWTPs managed by Oklahoma City and several smaller cities (serving a combined population of about 700,000 people in 2009, U.S. Census Bureau, 2001) discharge to the river or its tributaries. Numerous other facilities also have permits to discharge commercial or industrial waste under the USEPA National Pollutant Discharge Elimination System (NPDES) in the basin near the Britton Road and Harrah stations, mostly on the eastern side of Oklahoma City metropolitan area (fig. 1).

Upstream modifications to the North Canadian River in Oklahoma City may have affected streamflow and water quality at the Britton Road and Harrah stations. The U.S. Army Corps of Engineers finished construction of the North Canadian River Floodway in 1958. The purpose of the floodway, which was built from about 4 miles downstream from Lake Overholser to Spencer, Oklahoma, was to contain the 1-percent chance exceedance peak streamflows (100-year flood frequency). Construction of the 13.6-mile floodway principally consisted of straightening, widening, and realigning the North Canadian River near Oklahoma City (U.S. Army Corps of Engineers, 2000). Floodway modifications, land development, and oil-exploration activities along the floodway caused extensive losses of aquatic ecological resources in that area (U.S. Army Corps of Engineers, 2000). To restore aquatic habitat and enhance aesthetic resources along the river, Oklahoma City approved an ordinance in December 1993 providing funds for nine Metropolitan Area Projects that included development of the North Canadian Riverfront (Triad Design Group, 2010). The North Canadian Riverfront development plans included construction of three low-water dams to create impoundments of the river near the downtown area of Oklahoma City. Construction began on the first low-water dam in Oklahoma City in June 1999 (U.S. Army Corps of Engineers, 2000).

Methods of Analysis

This section of the report describes methods used to select and screen data used in analysis. This section also describes methods used to analyze changes in land cover, to characterize and identify trends in streamflow, and to summarize water-quality data and identify trends in selected constituents.

Selection of Water-Quality Sample Data and Streamflow Data for Analysis

The USGS began sample collection for water-quality analysis at the Harrah station on March 19, 1903, with the majority of the samples being collected since 1968. Continuous streamflow data also have been available for the Harrah station since 1968 and are summarized as daily mean

streamflows (referred to in this report as “daily streamflow”). Water-quality and daily streamflow data have been collected at the Britton Road station, 7 miles upstream from the Harrah station, since October 1988. For this report, water-quality and daily streamflow data collected from October 1968 through August 2009 at the Harrah station and from October 1988 through August 2009 at the Britton Road station were summarized. Water-quality and streamflow data were stored and retrieved from the USGS National Water Information System (NWIS) database (<http://nwis.waterdata.usgs.gov/usa/nwis>).

Historically, water-quality samples were analyzed at several laboratories, and some of the samples were split between multiple laboratories. More than 90 percent of the samples and constituents were analyzed at USGS laboratories, including the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, the Atlanta Central Laboratory in Atlanta, Georgia, the Wisconsin District Mercury Laboratory in Madison, Wisconsin, and the Oklahoma Water Science Center Laboratory (OKWSCL) in Oklahoma City, Oklahoma. Some of the water samples were sent to non-USGS laboratories, including the Oklahoma State Health Department Laboratory and the University of Iowa State Hygienic Laboratory.

Selected water-quality and streamflow data from both stations are summarized in this report. Because of the complex history of the data-collection practices and procedures, data were evaluated to ensure that the quality of the data was consistent prior to data analysis. Periodically, samples were split between laboratories and analyzed for similar constituents. For example, several samples collected at the stations in the late 1970s were sent to the Oklahoma State Health Department Laboratory and the NWQL to evaluate the comparability of data produced by both laboratories. Data were screened so that only one constituent per sample was selected for analysis in this report to avoid biases in summary statistics, data comparisons, and trend analyses. In cases where a single sample was analyzed by more than one laboratory, preference was given to water-quality samples analyzed by the NWQL because a majority of the water-quality data were produced by that laboratory and quality-control practices of that laboratory are well-documented (Pritt and Raese, 1995).

Most of the samples collected at the Harrah station from 1968 to 1975 were composite samples, which were collected separately over a period of time and composited prior to analysis. Composite samples generally were representative of ranges of days with similar hydrologic conditions (Jonathan Scott, U.S. Geological Survey, oral and written commun., 2010). Concentrations from composite samples could not be compared to instantaneous sample concentrations using summary statistics, data comparisons, or trend analyses because composite sample concentrations reflect average rather than instantaneous concentrations at a known date and time. Composited samples were excluded from the analysis.

Continuous water-quality monitors measuring physical properties at 30-minute to 1-hour intervals have been operated

at both stations since October 1988 and these data were stored in the NWIS database. Measured physical properties include specific conductance, pH, water temperature, and dissolved oxygen concentration. Continuous pH was measured at the Harrah station but not at the Britton Road station. Daily minimum, maximum, and mean specific conductance, water temperature, and dissolved oxygen, and daily median pH were computed from instantaneous data collected by continuous water-quality monitors. These daily summaries of instantaneous concentrations are collectively referred to as “daily values” in this report. However, some of the instantaneous concentrations were discarded because of equipment malfunction, excessive biological fouling, or inundation of the monitor chamber with sediment blocking water flow (Wagner and others, 2006). Daily values were not computed when substantial numbers (greater than 20 percent) of instantaneous concentrations were discarded.

Instantaneous streamflow data at the time of sample collection, daily mean streamflow data, and annual mean streamflow are available from NWIS. Instantaneous streamflow data from streamflow-gaging stations are collected as stage data, from which instantaneous streamflows are estimated from rating curves (Rantz and others, 1982). Daily mean streamflow is the mean of instantaneous discharges for a day (Buchanan and Somers, 1976). Daily mean streamflow data are available since 1968 for the Harrah station and since 1988 for the Britton Road station.

Quality Assurance and Quality Control

Physical properties, alkalinity, nutrients, fecal-indicator bacteria, and some pesticides were analyzed in 1 to 15 replicate samples collected in the field at both of the water-quality monitoring stations on the North Canadian River from 1977–2005 (table 2). Most constituent concentrations from replicate samples had small relative percent differences between environmental and replicate samples (table 2).

Only small concentrations of sodium and silica were detected in blank samples, which consisted of deionized and purified water processed through cleaned field-sampling equipment (table 3). Median recoveries of organic-compound surrogate samples ranged from greater than 50 percent to greater than 100 percent in those samples, and concentrations of most of the other water-quality constituents were at or only slightly greater than laboratory reporting levels (table 3).

Analysis of Changes in Land Cover

Changes in land cover from 1992 to 2001 were summarized and evaluated in the North Canadian River Basin upstream from the Britton Road and Harrah stations. Using the Environmental Systems Research Institute (ESRI) geographic information system (GIS) software ArcGIS (Environmental Systems Research Institute, 2009),

percentages of land-cover categories in the basins upstream from each of the stations were computed from coverages from the National Land Cover Dataset (NLCD, U.S. Geological Survey, 2002) made in 1992 and 2001. Land-cover categories were summarized over the entire North Canadian River Basin upstream from Harrah and over four subbasin segments defined by the two stations and dams (Lake Overholser and Canton Lake). All basin and subbasin boundaries were delineated using Oklahoma StreamStats (Smith and Esralew, 2010). For the remainder of this report, the basin area between the Harrah and Britton Road stations is referred to as HBR, the basin area between the Britton Road station and the Lake Overholser Dam is referred to as BRO, the basin area between the Lake Overholser Dam and the Canton Lake Dam is referred to as LOC, and the basin area upstream from the Canton Lake Dam to the headwaters of the North Canadian River Basin is referred to as CLH.

Percentages of land-cover-categories in the subbasin segments upstream were computed from raster datasets representing conditions in 1992 (U.S. Geological Survey, 2002) and 2001 (Homer and others, 2004). The land-cover datasets were obtained from the USGS seamless data server for use in the GIS. Both land-cover datasets had resolutions of 30 meters and were reclassified into six categories to enable visual and quantitative analysis of land-cover changes from 1992 to 2001 (table 4).

Remote-sensing methods used to create the 1992 and 2001 land-cover datasets were slightly different (Fry and others, 2009). Such differences may result in misinterpretation of changes in land-cover classification because a change in analysis method may lead to a change in land cover that is not accurate. For example, differences in methods for determination of whether land cover is grassland/shrub or an agricultural land-cover such as cropland or pasture/hay may result in different classifications between these coverages because of classification of fallow rotations of wheat, sorghum, or other crops as grassland/shrub at the time of coverage creation (Fry and others, 2009). Although inconsistencies in classification method may result in some inaccurate classifications, the NLCD coverages provided an accessible and relatively consistent framework for general comparison of land-cover changes in the North Canadian River Basin.

Land-cover categories that changed between 1992 and 2001 were computed and mapped to identify spatial trends. Because all scenarios of classification changes could not be easily mapped, specific change classes for the land-cover categories were selected for analysis that had noticeable changes over time and were assumed to have the most substantial effect on water quality. These change classes included: (1) areas that were water/wetland in either coverage, (2) areas that remained developed, (3) areas that changed to developed from another class, (4) areas that changed to cropland from another class and that changed from cropland to another class, (5) areas that changed from forest to another class, (6) areas of forest, grassland/scrub, pasture/hay, and cropland that did not change; and (7) other areas that did not fall into any of those

Table 2. Relative percent differences of constituents analyzed in duplicate samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1977–2005.

[°C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter]

Water-quality constituent	Number of duplicate samples	Median relative percent difference ¹	Range of relative percent differences
North Canadian River at Britton Road at Oklahoma City, Oklahoma, 1988–2005			
Water temperature, in degrees Celsius	7	0	0–0.6
Specific conductance, in $\mu\text{S}/\text{cm}$ at 25 degrees Celsius	6	0	0
pH	7	0	0–.37
Carbon dioxide, in mg/L	1	7	7
Biochemical oxygen demand, 5 days at 20°C, in mg/L	1	0	0
Dissolved alkalinity, in mg/L as CaCO_3	1	0	0
Dissolved bicarbonate, in mg/L	1	0	0
Dissolved carbonate, in mg/L	1	0	0
Total acid-neutralizing capacity, in mg/L as CaCO_3	1	0	0
Dissolved ammonia plus organic nitrogen, in mg/L	2	0	0
Total ammonia plus organic nitrogen, in mg/L	1	19	19
Dissolved ammonia, as nitrogen, in mg/L	5	20	0–110
Dissolved nitrite, as nitrogen, in mg/L	5	0	0–29
Dissolved nitrate, as nitrogen, in mg/L	1	36	36
Dissolved nitrite plus nitrate, as nitrogen, in mg/L	5	1.3	.70–36
Dissolved orthophosphate, as phosphorus, in mg/L	4	2	.60–47
Dissolved phosphorus, in mg/L	3	1.2	0–1.5
Total phosphorus, in mg/L	1	0	0
Fecal coliform bacteria, in colony forming units per 100 milliliters	1	0	0
Fecal streptococcal bacteria, in colony forming units per 100 milliliters	1	0	0
Total residue, in mg/L	1	23.5	23.5
Isophenphos surrogate, in percent recovery	1	58	58
Total carbophenothion, in $\mu\text{g}/\text{L}$	2	0	0
Total diazinon, in $\mu\text{g}/\text{L}$	2	0	0
Total disulfoton, in $\mu\text{g}/\text{L}$	2	0	0
Total ethion, in $\mu\text{g}/\text{L}$	2	0	0
Total fonofos, in $\mu\text{g}/\text{L}$	2	0	0
Total malathion, in $\mu\text{g}/\text{L}$	2	0	0
Total methyl parathion, in $\mu\text{g}/\text{L}$	2	0	0
Total parathion, in $\mu\text{g}/\text{L}$	2	0	0
Total phorate, in $\mu\text{g}/\text{L}$	2	0	0
Total tribuphos, in $\mu\text{g}/\text{L}$	2	0	0
North Canadian River near Harrah, Oklahoma, 1977–2003			
Water temperature, in degrees Celsius	15	0	0–48
Specific conductance in $\mu\text{S}/\text{cm}$ at 25 degrees Celsius	14	.25	0–8.8
Dissolved oxygen, in mg/L	8	0	0–16
pH	15	0	0–7.9
Carbon dioxide, in mg/L	1	4.4	4.4
Chemical oxygen demand, in mg/L	1	38	38

Table 2. Relative percent differences of constituents analyzed in duplicate samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1977–2005.—Continued[°C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; $\mu\text{g}/\text{L}$, micrograms per liter]

Water-quality constituent	Number of duplicate samples	Median relative percent difference ¹	Range of relative percent differences
North Canadian River near Harrah, Oklahoma, 1977–2003—Continued			
Dissolved alkalinity, in mg/L as CaCO_3	2	0	0
Dissolved bicarbonate, in mg/L	1	0	0
Dissolved carbonate, in mg/L	1	0	0
Dissolved ammonia plus organic nitrogen, in mg/L	1	0	0
Dissolved ammonia as nitrogen, in mg/L	5	0	0–111
Dissolved nitrite as nitrogen, in mg/L	4	34	0–67
Dissolved nitrate as nitrogen, in mg/L	1	11	11
Dissolved nitrite plus nitrate as nitrogen, in mg/L	3	.52	.20–12
Dissolved orthophosphate as phosphorus, in mg/L	4	3.5	1.4–12
Dissolved phosphorus, in mg/L	2	.64	.60–.67
Fecal coliform bacteria, in colony forming units per 100 milliliters	1	0	0
Fecal streptococcal bacteria, in colony forming units per 100 milliliters	1	0	0
Residue on evaporation at 180°C, in mg/L	3	3.4	.10–8.6
Dissolved residue, in tons per day	5	4.2	0–8.9
Dissolved residue, in tons per acre-foot	4	4.8	0–8.4

¹ Relative percent difference (RPD) calculated as $\text{RPD} = ((E-R)/((E+R)/2)) * 100$, where E is the concentration in the environmental sample and R is the concentration in the replicate sample.

categories. These categories of classifications that changed were mapped by coding grid cells with a different color on the map in one of the listed categories.

Conversion of less-developed (forest, grassland) land cover to urban areas is likely to affect water quality. Urban areas contribute nutrients, pathogens, and pesticides from effluent contributions of WWTPs and nonagricultural coverages such as from urban and suburban landscaping, sediment from areas of land disturbance, organic compounds such as polyaromatic hydrocarbons, and metals. Increases in impervious surface can also increase runoff of these contaminants (Hill, 1981; Osborne and Wiley, 1988; Sliva and Williams, 2001; Brigham and others, 2002; Gilliom and others, 2006; Dubrovsky and others, 2010; Yang and others, 2010). An assumption was made that most areas developed in 1992 remained developed in 2001; therefore, changes in areas from developed to another classification were not analyzed unless changes occurred as a result of differences in classification methodology between the two coverages.

Areas that changed to and from cropland were likely to affect water quality because agricultural land cover tends to increase in-stream concentrations of nitrogen, phosphorus, and sediment (Hill, 1981; Osborne and Wiley, 1988; Johnson and others, 1997; Arheimer and Liden, 2000). In addition, the presence and concentration of pesticides in streams have been reported to be positively correlated to percent of the basin

classified as agricultural lands, especially cropland (Willis and McDowell, 1982).

Areas that changed from forest to a classification other than developed and cropland were identified. Removal of forested land-cover can also substantially affect water quality by increasing erosion of sediment and sediment-sorbed nutrients. An assumption was made that most areas not forested in 1992 did not change to forested in 2001 unless as a result of differences in classification methodology between the two coverages.

Pasture/hay land-cover also can affect water quality. Overgrazed rangeland can produce increased runoff and sediment to streams. Cattle grazing may increase erodibility of soils that contribute sediment, sediment-sorbed nutrients, and increase runoff of bacteria from animal feces (Doran and Linn, 1979). Confined animal-feeding operations (CAFO) also can contribute substantial quantities of nutrients and bacteria to streams and can be associated with pasture/hay land cover (Mallin and Cahoon, 2003).

Analysis of Streamflow Data

This section describes methods used to identify significant streamflow trends. Water quality typically is affected by streamflows, with trends of streamflows being a potential causative factor in changes in water quality with time.

Table 3. Constituent concentrations analyzed in blank samples accompanying water-quality samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

[°C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; CaCO_3 , calcium carbonate; <, less than; NTRU, nephelometric turbidity ratio units]

Water-quality constituent	Number of blank samples	Median detected concentration	Range of detected concentrations
pH, measured in laboratory	2	8.6	8.6–8.7
Specific conductance, in $\mu\text{S}/\text{cm}$ at 25°C	2	6.0	<5.0–7.0
Turbidity, in NTRU	1	<2.0	<2.0
Total bisphenol-A-d3 surrogate, in percent recovery	1	120	120
Total caffeine-13C, surrogate, in percent recovery	1	69	69
Total decafluorobiphenyl, surrogate, in percent recovery	1	57	57
Total isenphos, surrogate, in percent recovery	6	65	28–66
Dissolved solids residue on evaporation, in mg/L	3	<10	<10
Total suspended solids, in mg/L	1	<15	<15
Dissolved calcium, in mg/L	5	.04	<.02–.17
Dissolved magnesium, in mg/L	5	<.020	<.008–.016
Dissolved potassium, in mg/L	5	<0	<0–<.16
Dissolved sodium, in mg/L	5	.06	.06–.59
Total acid neutralizing capacity, in mg/L as CaCO_3	3	<5.0	<5.0–<8.0
Dissolved bromide, in mg/L	3	<.020	<.020
Dissolved chloride, in mg/L	5	<.12	<.12–.20
Dissolved fluoride, in mg/L	5	<.09	<.08–.07
Dissolved silica, in mg/L	5	.05	.02–2.3
Dissolved sulfate, in mg/L	5	<.18	<.18
Dissolved ammonia plus organic nitrogen, in mg/L	1	<.10	<.10
Total ammonia plus organic nitrogen, in mg/L	1	<.10	<.10
Dissolved ammonia, in mg/L	1	<.026	<.026
Dissolved ammonia as nitrogen, in mg/L	2	<.020	<.020
Dissolved nitrite plus nitrate as nitrogen, in mg/L	2	<.016	<.016
Dissolved nitrite as nitrogen, in mg/L	1	<.002	<.002
Dissolved organic nitrogen, in mg/L	1	<.10	<.10
Total organic nitrogen, in mg/L	1	<.10	<.10
Dissolved orthophosphate as phosphorus, in mg/L	1	<.008	<.008
Dissolved phosphorus, in mg/L	1	<.006	<.006
Total phosphorus, in mg/L	1	<.008	<.008
Dissolved nitrogen, in mg/L	1	<.12	<.12
Total nitrogen, in mg/L	1	<.12	<.12

Time-Series Trends in Streamflow Characteristics

Streamflow characteristics computed from daily mean streamflow at the two stations were analyzed to investigate trends during the study period. Qualitative and quantitative

analyses of trends in streamflow with time were performed for this report.

Hydrographs with Locally Estimated Scatterplot Smoothing (LOESS) curves in daily mean streamflow were created to qualitatively examine changes in streamflow with time. LOESS is a nonparametric regression procedure that

Table 4. Reclassification scheme used to analyze changes in land-cover categories in the National Land Cover Dataset between 1992 and 2001.

[XX - classification code from National Land Cover Dataset (U.S. Geological Survey, 2002; Homer and others, 2004)]

1992 classification scheme	2001 classification scheme	Simplified classification scheme used in this report to analyze changes in land-cover categories
11 - Open water 12 - Perennial ice/snow	11 - Open water 12 - Perennial ice/snow	Water/wetland
91 - Woody wetlands 92 - Emergent herbaceous wetlands	90 - Woody wetlands 95 - Emergent herbaceous wetland	
21 - Low intensity residential 22 - High intensity residential 23 - Commercial/industrial/transportation	21 - Developed, open space 22 - Developed, low intensity 23 - Developed, medium intensity 24 - Developed, high intensity	
31 - Bare rock/sand/clay 32 - Quarries/strip mines/gravel pits 33 - Transitional	31 - Barren land 32 - Unconsolidated shore	
41 - Deciduous forest 42 - Evergreen forest 43 - Mixed forest	41 - Deciduous forest 42 - Evergreen forest 43 - Mixed forest	Forest
51 - Shrubland	52 - Scrub/shrub	Grassland/scrub
71 - Grasslands/herbaceous	72 - Grassland/herbaceous	
81 - Pasture/hay	81 - Pasture/hay	Pasture/hay
82 - Row crops 83 - Small grains 84 - Fallow 85 - Urban/recreational grasses	82 - Cultivated crops	Cropland

reduces the influence of outliers and can be used to identify a smooth or trend line for the entire range of data (Cleveland and Devlin, 1988; Helsel and Hirsch, 2002). All bar charts and LOESS curves of streamflow were produced with statistical routines in the computer software Spotfire S+ 8.1.1 (TIBCO Software Incorporation, 2008). LOESS curves were used to illustrate changes with time and were not used to determine statistical significance of trends.

Hydrographs with LOESS curves also were created for selected annual streamflow statistics, including mean annual streamflow, annual 10th, 50th, and 90th percentile streamflow exceedance (the streamflow exceeded 10, 50 and 90 percent of the time for each year), and annual 7-day minimum (the minimum of 7-day moving average streamflow for each year). For the remainder of this report, mean annual streamflow is referred to as Q_{mean} , the 10th, 50th, and 90th percentile streamflow exceedances are referred to as the Q_{10} , Q_{50} , and Q_{90} , respectively, and the annual 7-day minimum is referred to as the $7Q_{\text{min}}$. The Kendall's tau test was used to determine if trends in streamflow characteristics with time were statistically significant (Hirsch and others, 1982). Kendall's tau trend analysis was applied to Q_{mean} , Q_{10} , Q_{50} , Q_{90} , and the $7Q_{\text{min}}$

using the Spotfire S+ 8.1.1 S+ program (TIBCO Software Incorporation, 2008).

The Kendall's tau test (Kendall and Gibbons, 1990) is a nonparametric statistical test that can be used to indicate the likelihood of upward or downward trends in data with time. Tau coefficients range from -1.0 to 1.0; a tau of -1.0 indicates that every data observation decreased with time, and a tau of 1.0 indicates that every data observation increased with time. Kendall's tau test is effective for identifying trends in streamflow because extremely high or low data outliers and skewness in the dataset do not affect the outcome of the test (Helsel and Hirsch, 2002).

A trend slope is a measure of the magnitude of a trend that was computed using the Sen Slope Estimator (Sen, 1968; Helsel and Hirsch, 2002). The Sen slope is estimated by computing the median of all possible slopes between each possible two-point data pair in the time series, and like Kendall's tau, is insensitive to extreme outliers (Dietz, 1989; Helsel and Hirsch, 2002, p. 267).

Time was the only variable compared to streamflow in the application of Kendall's tau test in this report. However, variables other than time can substantially affect streamflow.

Significant or substantial correlation between annual precipitation and annual streamflow may obscure underlying trends in streamflow, such as downward trends caused by factors of development, streamflow regulation, and withdrawals from a basin. By removing the annual variation in streamflow caused by precipitation, background underlying trends in streamflow can be observed (Helsel and Hirsch, 2002, p. 329). For this report, removing the effects of annual precipitation from streamflow trends is referred to as “precipitation-adjusted” streamflow.

Precipitation-adjusted trends were calculated for all annual streamflow statistics described in this report. Precipitation-adjusted streamflow was computed from the error residuals from a regression between annual streamflow and annual precipitation (Helsel and Hirsch, 2002, p. 331–335; Esralew and Lewis, 2010). Significant trends in precipitation-adjusted streamflow with time, as indicated by Kendall’s tau, indicate that factors other than the variation of precipitation may have caused changes in annual streamflows. Precipitation-adjusted streamflow was calculated for each streamflow characteristic using annual precipitation from National Weather Service Climate Divisions (National Oceanic and Atmospheric Administration, 2010) as independent variables. An assumption was made that annual precipitation from climate divisions OK-4 and OK-5 in central Oklahoma, which are the closest to the two stations, would have greater correlation to streamflow at the two stations than precipitation from climate divisions further upstream.

In regression analysis, variance may be biased because of dependence of the error residuals as a result of serial auto-correlation (Helsel and Hirsch, 2002, p. 252). Serial auto-correlation is correlation between a data point and its adjacent points in a time series (Helsel and Hirsch, 2002, p. 251–252). Previously described procedures used to compute trends in precipitation-adjusted streamflow volume incorporate same-year data-pairs of precipitation and streamflow in the regression relation but such pairing may cause error residuals to be affected by serial auto-correlation if annual streamflow is correlated to precipitation from previous years (Esralew and Lewis, 2010).

Annual streamflow statistics also can be biased by serial auto-correlation caused by correlation of annual streamflow to precipitation from previous years. For example, groundwater from the North Canadian River Alluvial and Terrace aquifer may be a substantial source of water for streamflow and can be influenced by long-term recharge that can be affected for a number of years by above- or below-average annual precipitation. To reduce serial auto-correlation in error residuals from a regression between same-year data pairs of annual precipitation and the annual streamflow characteristic, lagged annual precipitation from up to $n-2$ years, where n is the year of precipitation-adjusted streamflow, was tested as an independent variable in regression analysis.

Forward and backward stepwise linear regression procedures were used to select the annual precipitation parameters for precipitation-adjustment by calculation of all possible

linear regressions for estimation of annual streamflow using annual precipitation and lagged annual precipitation from climate divisions OK-4 and OK-5. Natural logarithms of annual streamflow and annual precipitation were computed to improve the fit of each model (Helsel and Hirsch, 2002, p. 332). The most optimal regression model was selected by minimizing the Predicted REsidual Sum of Squares (PRESS) statistic (Myers, 1990). In addition to minimization of the PRESS statistic, only models in which all precipitation parameters were significantly correlated to streamflow were selected for precipitation-adjustment. A partial t-test from a linear regression, which is a test to determine if the correlation between independent variables is statistically significant in the presence of other independent variables (Fisher, 1924; Helsel and Hirsch, 2002, p. 311–312), was used to evaluate the correlation between annual precipitation and annual streamflow. The null hypothesis of no correlation between each independent variable and the dependent variable was rejected and variables were described as being significantly correlated if the p-value from the partial t-test was less than or equal to 0.05. The p-value was used to determine statistical significance for all remaining statistical tests in this report. If there was no significant correlation between any of the precipitation parameters and streamflow, the precipitation parameter was not used in the final precipitation-adjustment regression.

Independent variables identified in the most optimal regression with a minimized PRESS were used in a LOESS regression to compute error residuals. A LOESS regression (Cleveland and Devlin, 1988) was used to describe the relation between each annual streamflow characteristic and annual precipitation and lagged annual precipitation from climate divisions OK-4 or OK-5 for both stations for use in calculation of precipitation-adjusted trends. This method is robust because use of distance and residual-weighting functions with weighted least squares avoids complex data transformations and minimizes the influence of outliers in fitting a smooth line to the data (Schertz and others, 1991, p. 24). The LOESS regression was calculated on the natural logarithms of each annual streamflow characteristic and annual precipitation to improve the fit of the LOESS regression, (referred to as a “log-log LOESS” regression in the remainder of the report).

The Kendall’s tau test was applied to error residuals from the log-log LOESS regression and time. Precipitation-adjusted streamflow from error residuals (R) was computed as:

$$R = Y - \hat{Y} \quad (1)$$

where,

Y is observed natural logarithm of each annual mean streamflow characteristic, and

\hat{Y} is the fitted streamflow from the LOESS regression using the natural logarithm of annual precipitation and lagged annual precipitation from climate divisions OK-4 or OK-5 to estimate each annual streamflow characteristic.

Analysis of Streamflow at the Time of Sample Collection

Boxplots were made for daily mean streamflow on all recorded days and on days of collection of water-quality samples to illustrate the ranges of streamflow represented by historic water-quality samples collected at the two stations and to identify potential biases in sample collection. Differences between these distributions may indicate that water-quality samples were not collected at streamflows representative of all streamflows in the sampling periods. The Wilcoxon rank-sum test (also referred to as the Mann-Whitney test, Helsel and Hirsch, 2002, p. 118, and referred to as the “rank-sum test” in the remainder of this report) was used to determine whether locations of distribution of streamflows at times of sample collection were significantly different than the locations of distribution of daily mean streamflows at each station. For data from the Harrah station, these comparisons were made for the periods 1968–2009 and 1988–2009. For data from the Britton Road station, these comparisons were made for the period 1988–2009.

Graphical comparisons of streamflows at the times of sampling at the two stations were done by computing flow-duration and sample-duration curves. Flow-duration curves are graphical representations of the percentage of the time that streamflow for a given time step (for example, a daily time step) is equaled or exceeded during a specified period. Sample-duration curves represent the percentage of time that streamflow at the time of sample collection was equaled or exceeded. Flow-duration curves were compared to sample-duration curves to qualitatively evaluate whether streamflow during sample collection was representative of the probability of streamflow exceedance during the sampling periods. Flow-duration and sample-duration curves were computed based on methods described in Searcy (1959) and Vogel and Fennessey (1994). Flow-duration and sample-duration curves were calculated only for 1988–2009 because most of the water samples were collected during that period.

Analysis of Water-Quality Data

This section describes methods used to summarize water-quality data in this report, including: statistical summaries of water-quality data; determination of frequencies of detection of pesticides; comparisons of selected nutrient, biological, and physical-property concentrations between stations; and qualitative and quantitative analysis of trends of selected constituent concentrations with time.

Statistical Summaries of Water-Quality Data

To summarize water-quality data for selected constituents collected at the Britton Road and Harrah stations, the following computations were made: number of samples, number of detected concentrations, percent of samples with detected

concentrations, minimum concentration, 10th percentile concentration, 25th percentile concentration, median, 75th percentile concentration, 90th percentile concentration, maximum concentration, percent of samples exceeding selected water-quality criteria, date of first sample, and date of last sample. Selected water-quality data from samples collected at the Harrah station were summarized from 1968–2009 and at the Britton Road station from 1988–2009. Date of first sample, date of last sample, and number of samples apply only to samples included in calculation of the summary statistics and do not include samples that were not considered in this report (such as composite samples). Continuously measured physical properties and cross-sectional measurements of physical properties made near the time of water-sample collection (for example: temperature, dissolved oxygen, specific conductance, turbidity, and pH) also were not included for computation of summary statistics.

Estimates of data distributions for small datasets are likely to be invalid or erroneous and are subject to substantial influence from outliers (Helsel and Hirsch, 2002). For this report, constituent datasets with less than 10 available samples were considered to be small, so the 10th, 25th, 75th, and 90th percentile concentrations were not reported for those constituents.

Many constituent concentrations were censored with some values reported to be less than a specified laboratory reporting level (LRL). Some of the LRLs changed during the sampling period in response to changes in constituent detection capabilities. Modification of the Kaplan-Meier method of nonparametric description of the cumulative distribution of censored data was used to estimate distributions of left-censored datasets in this report (Helsel, 2005; Antweiler and Taylor, 2008). Antweiler and Taylor (2008) reported that for high degrees of censoring (above 70 percent), both nonparametric and parametric techniques are unreliable for estimating distribution quantiles of datasets. For purposes of statistical summary in this report, if the percent of censored concentrations for a constituent at a station was greater than 70 percent, all censored values and detected values below the censored values were re-coded to the largest censored value in the dataset, with minimums, maximums, and quantiles computed using ranking methods (Helsel and Hirsch, 2002; Helsel, 2005).

Some samples had values of zero for some constituent concentrations (mostly in samples collected prior to 1985) before detection limit standards were applied to analytical results (J. Scott, U.S. Geological Survey, oral and written commun., 2010). Because no reporting-limit information was available for those data, those constituent concentrations were not censored and were treated as zero for calculation of minimums, maximums, and quantiles of datasets. However, censored concentrations were not re-coded for computation of the number of samples with detected concentrations. In this report, constituent concentrations of zero were treated as non-detected concentrations for computing the total number of samples with detected concentrations because an assumption was made that

the constituents were not detected during analysis. The number of samples with detected concentrations was computed for all constituents except percent saturation of dissolved oxygen, water temperature, and pH.

Although drinking-water-quality standards can be applied as a measure of surface-water contamination, Criterion Continuous Concentrations (CCCs) (U.S. Environmental Protection Agency, 2010a) were used in this report as standards of surface-water contamination by natural or man-made compounds. CCCs are estimates of the greatest concentration of a substance in surface water to which aquatic communities can be exposed for an indefinite time period without causing deleterious effects (U.S. Environmental Protection Agency, 2010a). Percentages of samples with concentrations exceeding CCCs were not determined if data were not available to determine if the sample concentration exceeded the CCC or if the CCC was less than a censored concentration for a given sample. In such cases, sample concentrations were assumed not to exceed the CCC for a constituent in a sample group.

Hardness (expressed as milligrams per liter (mg/L) of calcium carbonate) can substantially affect the toxicity of some metals such as cadmium, lead, nickel, and zinc. The CCCs for these metals are computed using a function that includes hardness as a variable (U.S. Environmental Protection Agency, 2010a). Hardness was not analyzed for all of the water samples at the Harrah station, particularly prior to 1988. The CCC could not be determined for metals when hardness concentrations were not available. Most CCCs for metals are applied only to dissolved concentrations, unless otherwise noted. Additionally, a conversion factor was applied to the hardness-dependent metal criteria function to convert the criteria from total recoverable concentrations to dissolved concentrations.

Frequency of Detection of Pesticides

Frequency of detection of a pesticide is the percent of data with a detected (non-censored) concentration of a pesticide. Frequencies of detection of pesticides from samples collected from 1988–2009 were graphed for both stations, and frequencies of detection of pesticides from samples collected from 1968–2009 were graphed separately for water samples collected at the Harrah station. Scatterplots of the annual frequency of detection by water year were created for pesticides with frequencies of detection greater than 10 percent for both stations.

Although frequencies of detection were determined as percents of collected samples for analyzed pesticides, differences in the sampling frequency of some pesticides may limit comparison of detection frequencies between pesticides or between years. Prior to 1988, sampling frequencies of some pesticides at the Harrah station varied substantially. From 1988–2009, similar selected pesticides were analyzed at least quarterly in water samples collected at both stations. From 1994–2009, selected pesticides (carbophenothion, chlorpyrifos, diazinon, disulfoton, ethion, fonofos, malathion, methyl parathion, parathion, phorate, and tribufos) were analyzed

in samples collected during summer months in addition to the quarterly sampling schedule. Additional sampling during summer months may have increased the probability that some pesticides were detected because of increased application of some of those chemicals during the growing season, which includes the summer months.

Comparison of Selected Water-Quality Constituents Between Stations

Selected nutrient, biological, and physical-property concentrations from water samples collected at the Britton Road station were compared to those from water samples collected at the Harrah station for the common sampling period of 1988–2009. Physical properties measured by continuous water-quality monitors also were compared between the stations from 1988–2009. These data were compared to evaluate the effect of the Oklahoma City-North Canadian WWTP (fig. 1) and other nonpoint or point discharges on water quality between the stations.

Comparison of Selected Nutrient, Biological, and Physical-Property Data from Water Samples Between Stations

Comparison of the locations of distribution (how groups of data are relatively distributed) of selected water-quality constituents measured in water samples at the Britton Road and Harrah stations from 1988–2009 were made using the nonparametric Wilcoxon rank-sum and signed-rank tests (Wilcoxon, 1945; Helsel and Hirsch, 2002). The following constituents were analyzed with these tests: dissolved oxygen, specific conductance, 5-day biological oxygen demand (BOD), fecal coliform bacteria, and dissolved nitrogen and phosphorus. These constituents were considered to be indicators of contamination from effluent or other point or nonpoint source contamination in the river.

Increased nitrogen and phosphorus concentrations, which can cause eutrophication (excessive plant growth), can enter streams in wastewater effluent and in agricultural and urban runoff (Sharpley, 1995; U.S. Geological Survey, 1999). Eutrophication can cause depletion of dissolved oxygen in water from microbial breakdown of algae, an increase in biological oxygen demand, and a decrease in dissolved oxygen. Total (sum of types of) nitrogen and phosphorus (referred to in this report as “dissolved nitrogen” and “dissolved phosphorus”) were consistently analyzed from filtered samples at these Britton Road and Harrah stations, therefore only dissolved nitrogen and phosphorus were evaluated for trends with time. Hypoxia (dissolved oxygen concentrations less than 2 mg/L) is fatal to some fish species (Texas Agrilife Extension Service, 2009).

Specific conductance is the ability of water to conduct an electric current. Specific conductance increases with increasing concentrations of total dissolved solids (TDS). TDS and individual cations and anions can come from a variety of

natural and anthropogenic sources including, but not limited to, dissolution of natural salts and rocks, urban and agricultural runoff, leaching of soil contamination, and point source contamination from effluent (Wiebel, 1964), and gas and oil production (Fillo and others, 1992).

Biological oxygen demand (BOD) is a measure of the amount of dissolved oxygen consumed by microorganisms to decompose organic matter in water. Large BOD concentrations indicate large organic-matter content and bacteria counts in streams that may be associated with wastewater treatment or other sources of organic waste. Most pristine rivers have a BOD less than 1 mg/L and rivers moderately polluted with organic matter have BODs between 2 and 8 mg/L (Clescerl and others, 1999).

Fecal coliform bacteria are facultative anaerobes (can survive in the absence of oxygen) that normally reside in the intestinal tract of warm-blooded animals. However, fecal coliform bacteria can be found in a wide variety of environmental matrices (terrestrial soils, aquatic sediment, submerged vegetation, and water) outside of warm-blooded animals (Badgley and others, 2001). Although not necessarily harmful, these bacteria can indicate the presence of other pathogenic (disease-causing) strains of bacteria, viruses, and protozoa that live in digestive systems of mammals (Clescerl and others, 1999).

The rank-sum test was used to investigate whether the locations of distributions of concentrations of these waste-indicator constituents were significantly different upstream (at the Britton Road station) and downstream (at the Harrah station) from the outfall of the Oklahoma-City North Canadian WWTP. An assumption of the rank-sum test is that data come from independent distributions (Helsel and Hirsch, 2002, p. 118). Samples were collected at the Britton Road and Harrah stations on or close to the same date every month. Extraneous variables that affect water quality, such as streamflow and temperature, were likely to have been similar for both stations during sampling trips. These similarities may result in non-independence of constituent concentrations between samples collected during the same sample trip that may affect results of the rank-sum test. Non-independence of concentrations between stations may have obscured the differences in concentrations between the two groups.

The signed-rank test (Wilcoxon, 1945) is a non-parametric test in which the null hypothesis is that the median difference between paired observations (such as concentrations of constituents from samples collected from both stations during the same sample trip) is equal to zero. Both tests were used to ensure that significance of differences in the distribution of selected constituent concentrations at both stations were determined without violating assumptions of non-independence.

Hypothesis testing using the rank-sum and signed-rank tests may be complicated by the presence of multiple reporting levels (Helsel and Hirsch, 2002, p. 369). Helsel and Hirsch (2002) indicated censoring all data at the largest reporting level is a robust method that can be used for non-parametric tests; because a non-parametric test uses data ranks instead of

data magnitude, this method was assumed to be acceptable and should not have significantly affected p-values for data sets because in each case only a small number of samples (10 percent or less) were censored (Helsel and Hirsch, 2002, p. 369).

Comparison of Daily Values and Range of Concentrations of Physical Properties from Continuous Water-Quality Monitors

The locations of distribution of daily values of dissolved oxygen, specific conductance, and temperature from continuously measured physical properties were compared between stations using the rank-sum and signed-rank tests. Signed-rank pairs were daily values computed for the same day if data were available for that day. Boxplots were made to qualitatively show differences in the locations of distributions of daily values between stations and between ranges of daily minimum, daily mean (or median for pH), and daily maximum concentrations. The signed-rank test (Helsel and Hirsch, 2002), used to compare medians of multiple datasets, was used to determine the statistical significance of differences among daily minimums, mean (or median), and maximums of constituents between the two stations.

Daily minimum and maximum concentrations for each constituent were used to compute diurnal ranges in continuously monitored constituents. Diurnal ranges in dissolved oxygen, specific conductance, and temperature were compared between stations using the rank-sum test and signed-rank test. Similar to the test for daily values, signed-rank pairs were diurnal ranges computed for the same day only if daily values were available for both stations on that day.

Qualitative Trend Analysis of Selected Biological and Physical Properties

Graphs of fecal coliform bacteria and chlorophyll *a* concentrations in water samples and summaries of daily values of physical properties were graphed to visually evaluate temporal trends in those constituent concentrations. Daily values of physical properties were computed from data measured by real-time water-quality monitors.

Fecal Bacteria and Chlorophyll *a*

Like fecal coliform, fecal streptococci bacteria are indicators of bacteria from feces. Fecal streptococci bacteria generally are more resistant to environmental stress and chlorination than fecal coliform bacteria, and generally persist longer in the environment than fecal coliform bacteria (Gleeson and Gray, 1997). Fecal-indicator bacteria data were analyzed from samples collected from the Harrah station since 1976. However, fecal coliform and fecal streptococci were plotted only for samples collected from 1988–2009 for comparison of qualitative trends in counts of these bacteria between the two stations.

Chlorophyll *a* concentrations not corrected for pheophytin (referred to as “uncorrected” chlorophyll *a* in this report) were analyzed for samples collected at the Harrah station from 1975–77. Uncorrected chlorophyll *a* and chlorophyll *a* corrected for pheophytin (referred to as “corrected” chlorophyll *a* in this report) were determined for samples collected from 1984–96. Pheophytin is a natural degradation product of chlorophyll and has a peak light absorption in the same spectral range as chlorophyll *a*. Corrected chlorophyll *a* concentration was measured by absorbance of light after treatment with hydrochloric acid when the pheophytin concentration was relatively large (Clescerl and others, 1999). Uncorrected and corrected chlorophyll *a* were plotted with LOESS curves from 1984–96, but uncorrected chlorophyll *a* concentrations were not plotted from 1975–77 because of the substantial gap in available data between 1977 and 1984 and because only 11 samples were analyzed for that constituent during those 3 years. The concentration of chlorophyll *a* from periphyton, a mixture of algae, cyanobacteria, heterotrophic microbes, and detritus attached to submerged surfaces, was determined for samples collected from 1977–83 but was not graphed because only 24 samples were analyzed for this constituent and trends in those data were not apparent. Chlorophyll *a* concentrations were not analyzed in water samples collected at the Britton Road station. For graphical plots of concentrations of those constituents with time by LOESS curves, censored concentrations were omitted when generating the LOESS curve but were depicted in the graph using a gray bar to denote a range of possible data values using a technique described in Helsel (2005).

Continuously Measured Physical Properties

Daily mean dissolved oxygen concentration, specific conductance, temperature, and daily median pH with time are shown in this report in graphs with LOESS curves to illustrate changes in those constituents from 1988–2009. Monthly average diurnal ranges of these four physical properties also were computed and graphed with time with LOESS curves for 1988–2009 in this report. Physical-property concentrations collected during selected shorter periods also were graphed to demonstrate diurnal ranges in physical-property concentrations.

Analysis of Dissolved Oxygen and Nutrient Concentrations with Time

Trends in concentrations of dissolved oxygen, dissolved nitrogen, and dissolved phosphorus with time were evaluated at the Britton Road and Harrah stations from 1988–2009 to determine whether changes in wastewater treatment and land cover affected dissolved oxygen and nutrient concentrations in the North Canadian River. Trend analyses were done using the S-Plus statistical program S-Estimate Trend (S-ESTREND) (Schertz and others, 1991) that computes trends with time in water-quality data. The S-ESTREND program is designed

to detect monotonic trends (increase, decrease, or no trend, but not, for example, change from an increase to a decrease) in constituent concentration. The trend-detection techniques supplied by this program include Seasonal Kendall’s tau test, which is a nonparametric method for use with uncensored or minimally censored data with only one reporting level (Hirsch and others, 1982).

Seasonality can affect some water-quality constituents, especially concentrations of nutrients and bacteria, because of variability in streamflow, temperature, and land cover. Seasonality may prevent the detection of monotonic trends because of strong periodicity and serial auto-correlation of data (Schertz and others, 1991). The Seasonal Kendall’s tau test reduces the effect of seasonal variation by restricting the possible comparisons to water-quality samples that are collected during the same season and is calculated as a summation of the Mann-Kendall test statistics from each seasonal period (Hirsch and others, 1982). In this report, seasons were defined as 12 seasons per year (or monthly) because monthly water-quality data were available for the period of comparison (1988–2009) and use of 12 seasons ensures that most or all of the data are considered in the trend test (Schertz and others, 1991, p. 14).

In this report, the Seasonal Kendall’s tau test was used only to test the significance of trends in water quality with time. Similar to the effect of precipitation on streamflow, exogenous variables other than time can have considerable influence on water quality. For example, many dissolved water-quality constituents contributed by point sources, such as effluent from WWTPs, tend to decrease in concentration as streamflow increases because of dilution of discharged effluent. A statistically significant correlation between constituent concentration and streamflow may obscure underlying trends with time or other variables.

Use of a flow-adjustment technique removes the effects of streamflow variability on concentrations of water-quality constituents by computing a time series of flow-adjusted concentrations and evaluating those data for a trend with time (Helsel and Hirsch, 2002). Similar to precipitation-adjusted streamflow, flow-adjusted concentrations are the error residuals from a regression between concentration and streamflow at the time of sample collection (Helsel and Hirsch, 2002, p. 331–335). Flow-adjusted concentrations were calculated for each constituent using a best-fit least squares regression. The Seasonal Kendall’s tau test was applied to error residuals and time similar to the approach used for calculation of precipitation-adjusted streamflow trends. Significant trends in flow-adjusted concentrations determined by p-values of the Seasonal Kendall’s tau test would indicate that factors other than variation of streamflow may have caused changes in concentration, such as changes in water treatment or land cover.

A best-fit flow-adjustment regression model was investigated using an automated procedure in S-ESTREND software. The automated procedure computes the PRESS statistic for each of 11 regression models and selects the regression model with the minimum PRESS for all models. Such regression

models can be linear, log-linear, or hyperbolic (Schertz and others, 1991, p. 22).

Although S-ESTREND selects the model with the lowest PRESS, other quality metrics, such as metrics that characterize the suitability of use of independent variables and variance of error residuals, were investigated to determine if the selected regression was optimal for calculation of flow-adjusted concentrations. Details about these quality metrics are documented in Helsel and Hirsch (2002) and Schertz and others (1991). Some regression models are difficult to calculate because a good fit cannot be obtained. As an alternative, similar to the precipitation-adjustment procedure, a log-log LOESS regression may be fit to concentration and streamflow data or to log-transformed concentration and natural log-transformed streamflow data.

Three types of regression models were evaluated to determine the best model: best-fit models from minimized PRESS, LOESS regressions between concentration and streamflow, and LOESS regressions between log-transformed concentration and log-transformed streamflow. Streamflow associated with each sample was used in the regression analysis. Similar to precipitation-adjustment procedures, a partial t-test was used to evaluate the correlation between streamflow at the time of sample collection and constituent concentration. If there was no statistically significant correlation between streamflow and constituent at a p-value greater than 0.05, streamflow adjustment was not justified and was not calculated.

Water temperature also can affect dissolved oxygen concentration and, similar to streamflow variability, may obscure underlying trends in dissolved oxygen concentration related to anthropogenic (non-climatic) factors. As water temperature increases, the solubility (and equilibrium concentration) of oxygen decreases (Hem, 1985, p. 155). The Seasonal Kendall's tau test was used to test trends in water temperature-adjusted dissolved oxygen concentrations using the same methods previously described for flow adjustment in the Analysis of Streamflow Data section of this report.

Evaluation of Changes in Land Cover

Land-cover characteristics in the two subbasins closest to the Britton Road and Harrah stations, HBR (Harrah to Britton Road) and BRO (Britton Road to Lake Oversholer), were substantially different, indicating that water-quality characteristics may be different between stations. Land cover in the HBR subbasin was predominantly grassland/shrub and forest, whereas land cover in the BRO subbasin was predominantly developed/barren and grassland/shrub (figs. 7 and 8, table 5). Land cover in those two subbasins was notably different than those in the LOC (Lake Overholser to Canton Lake) subbasin, which was predominantly cropland, and the CLH (Canton Lake to Headwaters) subbasin, which was predominantly grassland/shrub.

Predominant land-cover changes between 1992 and 2001 in the HBR and BRO subbasins were increases in developed/barren land cover and decreases in pasture/hay land cover. In upstream parts of the basin, the predominant land-cover changes between 1992 and 2001 in the LOC subbasin were an increase in grassland/shrub land cover and a decrease in pasture/hay land cover; changes in the CLH subbasin were an increase in grassland/shrub land cover and a decrease in cropland land cover (table 5).

Although land-cover characteristics and spatial distribution of classes that changed between 1992 and 2001 in the HBR and BRO subbasins were different, the predominant change in class in these subbasins was a change from other classes to a developed class. However, larger areas changed to developed classes in the BRO subbasin than in the HBR subbasin and a large area in the BRO subbasin remained developed. Changes to and from cropland areas were observed in the upper parts of the BRO subbasin and parts of the HBR subbasin near the North Canadian River floodplain, although net cropland losses were observed in both subbasins (fig. 7). Limited patches of forested areas changed to non-forest classes in the HBR subbasin.

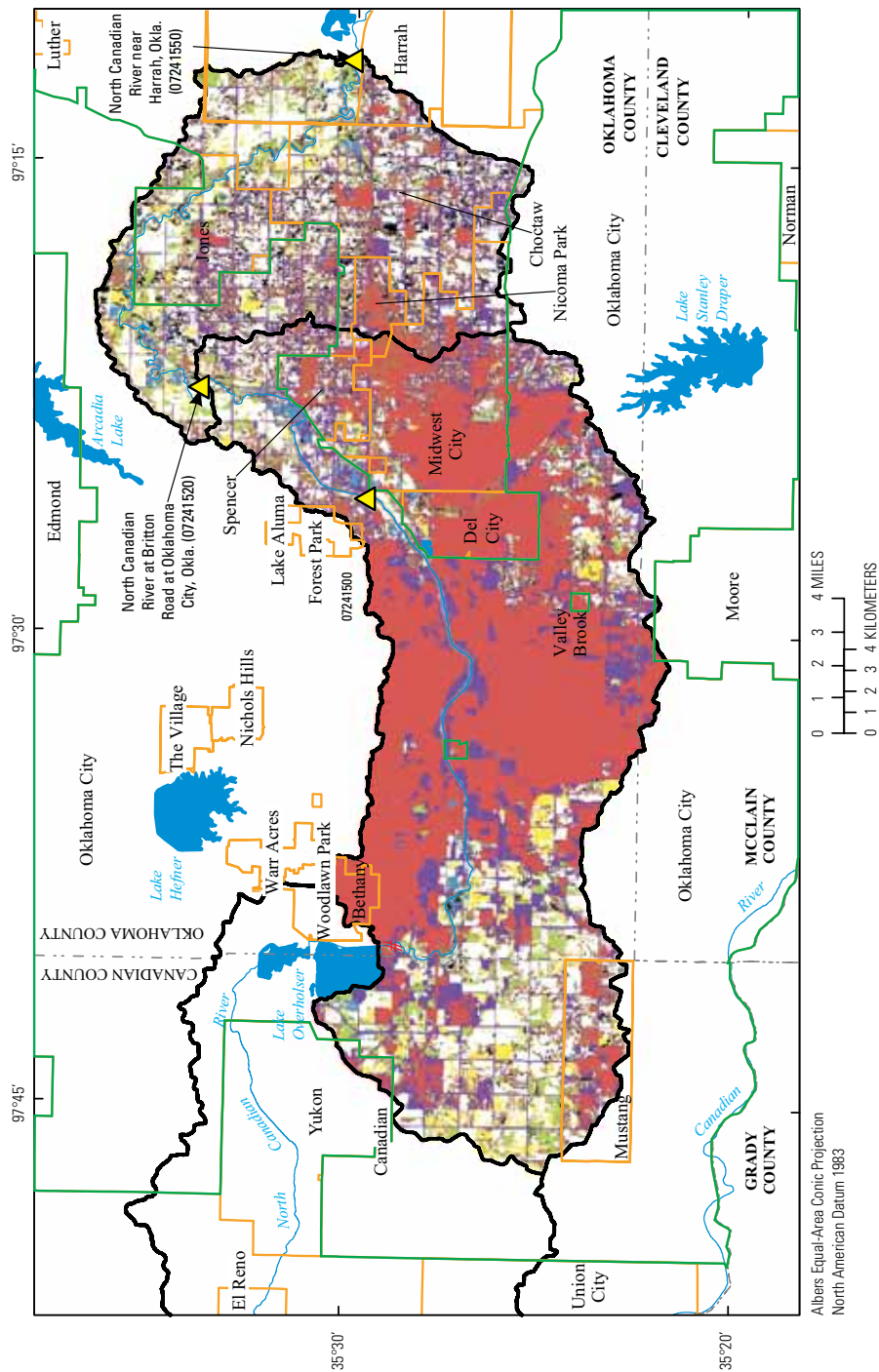
Interpretation of these results as true changes in land-cover categories may have been affected by use of the NLCD (see section titled "Evaluation of Changes in Land Cover"). Net gains in grassland/shrub areas and net losses in pasture/hay and cropland areas may have been caused by fallow rotations of wheat, sorghum, or other crops during classifications of the 1992 and 2001 land-cover categories or by slight changes in classification procedures between grasslands and pastures for those coverages.

Evaluation of Streamflow

This section describes trend analysis of annual streamflow statistics at the Britton Road and Harrah stations. This section also describes results of statistical comparison of daily mean streamflow data at the time of sample collection at both sampled stations to all daily mean streamflow data at those stations from 1988–2009.

Trends in Streamflow

Hydrographs with LOESS curves for daily mean streamflow indicated increases in streamflow at both stations until about 1999, followed by decreases in streamflow until 2004 (fig. 9). Slopes of the LOESS curves indicated that daily mean streamflow generally increased from 2004–09 at both stations. This increase was observed even though daily mean streamflow was lowest during water year 2006 (fig. 9) and streamflow was generally less during the period 2002–06, which was considered to be a hydrologic drought, especially for Climate Division OK-5 (Tortorelli, 2008). Increases may have been



Land-cover categories reclassified from the 1992 National Land Cover dataset		Water/ Wetland	Developed/ Barren	Forest	Grassland/ Scrub	Pasture/ Hay	Cropland
Water/ Wetland	99	99	99	99	99	99	99
Developed/ Barren	99	98	10	10	10	2	2
Forest	99	1	0	3	3	2	2
Grassland/ Scrub	99	1	10	0	10	2	2
Pasture/ Hay	99	1	10	10	0	2	2
Cropland	99	1	4	4	4	4	0

Land-cover categories reclassified from the 2001 National Land Cover dataset

Water/ Wetland	Developed/ Barren	Forest	Grassland/ Scrub	Pasture/ Hay	Cropland
99	99	99	99	99	99
99	98	10	10	10	2
99	1	0	3	3	2
99	1	10	0	10	2
99	1	10	10	0	2
99	1	4	4	4	0

Land-cover categories reclassified from the 1992 National Land Cover dataset

EXPLANATION

Prioritized list of change classes

- 99 Water/wetland in either coverage
- 98 Remained developed
- 0 No change
- 1 Changed to developed
- 2 Changed to cropland
- 3 Changed from forest
- 4 Changed from cropland
- 10 Other change

Figure 7. Change in land cover using six reclassified land-cover categories from the 1992 and 2001 National Land Cover Dataset upstream from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations.

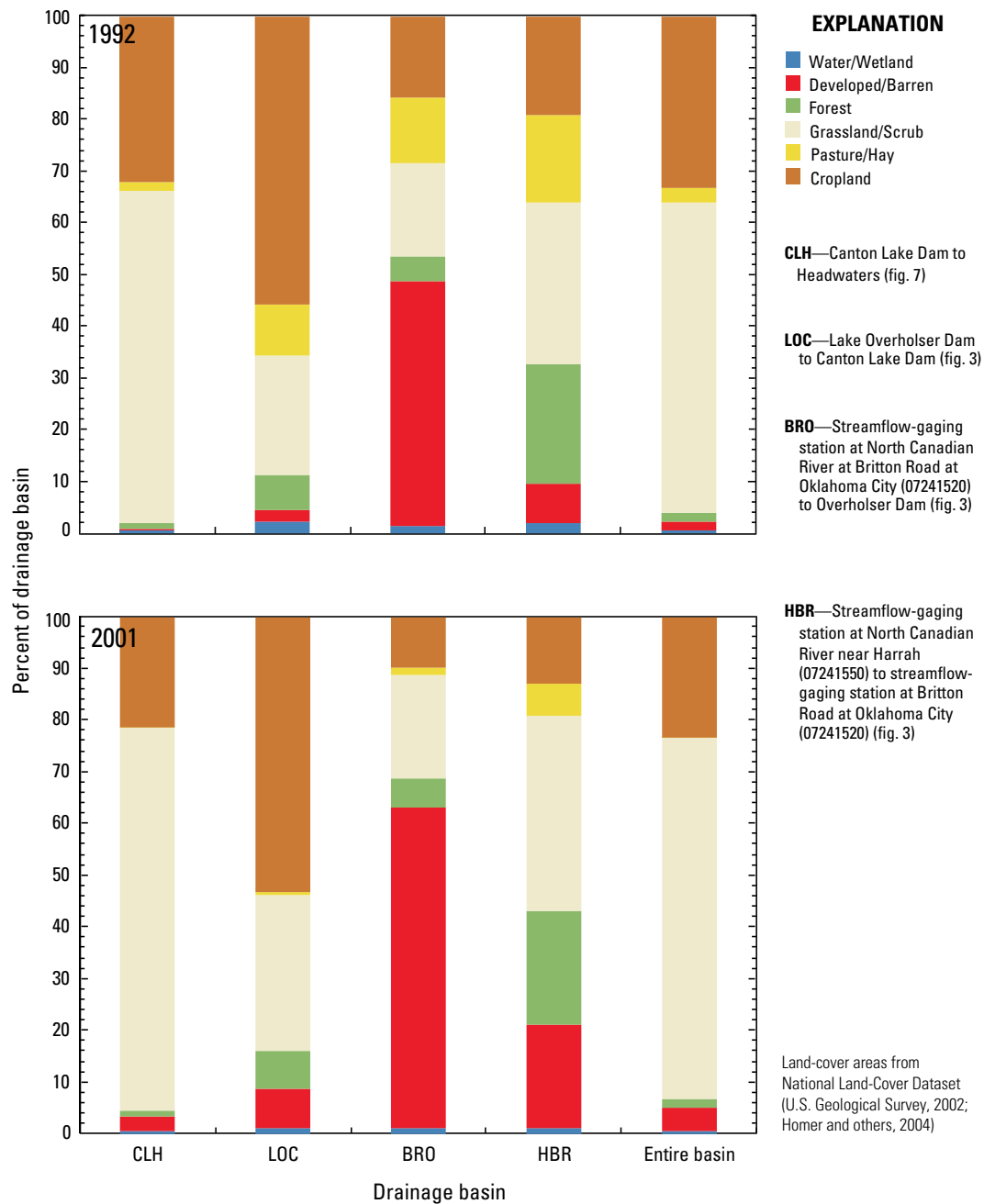


Figure 8. Percentages of land cover for six reclassified land-cover categories from the 1992 and 2001 National Land Cover Datasets in four subbasins of the North Canadian River Basin upstream from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station.

Table 5. Changes in six reclassified land-cover categories between 1992 and 2001 in four subbasins of the North Canadian River Basin upstream from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station.

[HBR, drainage basin between North Canadian River near Harrah, Oklahoma, and North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging stations (fig. 3); BRO, the drainage basin between the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the Overholser Dam (fig. 3); LOC, the drainage basin between Lake Overholser Dam and Canton Lake Dam (fig. 7); CLH, the drainage basin between Canton Lake Dam to the headwaters of the North Canadian River Basin (fig. 7); <, less than; %, percent; green font represents an increase in a land-cover category, and red font indicates a decrease in a land-cover category]

Land-cover category ¹		HBR		BRO		LOC		CLH		Entire basin	
		Area (square miles)	Percent of drain-age basin	Area (square miles)	Percent of drain-age basin	Area (square miles)	Percent of drain-age basin	Area (square miles)	Percent of drainage basin ²	Area (square miles)	Percent of drain-age basin
1992	Water/wetland	1.6	<0.1	2.9	<0.1	15.1	<0.1	31.7	<0.1	51.3	0.5
	Developed/ barren	6.6	10.0	94.9	50.0	16.8	<.1	49.8	1.0	168	1.60
	Forest	20.1	20.0	9.7	<.1	47.5	1.0	87.2	1.0	164	1.6
	Grassland/ scrub	27.2	30.0	36.1	20.0	162	20.0	5,960	64.0	6,190	60.2
	Pasture/hay	14.7	20.0	25.2	10.0	69.9	10.0	167	2.00	277	2.70
	Cropland	16.7	20.0	31.9	20.0	394	60.0	2,990	32.0	3,430	33.4
2001	Water/wetland	.9	1.1	2.1	1.0	7.9	1.1	41.2	.4	52.1	.50
	Developed/ barren	17.2	19.9	124	62.0	53.4	7.6	266	2.9	461	4.5
	Forest	19.1	22.0	11.4	6.0	51.3	7.3	98.1	1.1	180	1.8
	Grassland/ scrub	32.9	38.0	40.2	20.0	214	30.3	6,880	74.1	7,170	69.8
	Pasture/hay	5.3	6.1	2.8	1.0	2.6	.4	2.5	<.1	13.1	.10
	Cropland	11.3	13.0	20.0	10.0	376	53.4	1,990	21.5	2,400	23.4
Change (1992– 2001)	Water/wetland	-.63	-7%	-.7	-4%	-7.3	-1.0%	9.5	.1%	.8	0%
	Developed/ barren	10.6	12.2%	29.3	14.6%	36.6	5.2%	217	2.3%	293	2.9%
	Forest	-.99	-1.1%	1.7	.9%	3.8	.5%	11.0	.1%	15.6	.2%
	Grassland/ scrub	5.75	6.6%	4.1	2.0%	51.9	7.4%	921	9.9%	982	9.6%
	Pasture/hay	-9.39	-10.8%	-22.5	-11.2%	-67.3	-9.5%	-165	-1.8%	-264	-2.6%
	Cropland	-5.35	-6.2%	-11.9	-5.9%	-17.8	-2.5%	-994	-10.7%	-1,030	-10.0%

¹ Land-cover categories were reclassified from the National Land-Cover Dataset (U.S. Geological Survey, 2002; Homer and others, 2004) to create consistent categories for comparison of changes (table 4).

² Percents may not add to 100 because of rounding.

observed over the period 2004–09 because daily mean streamflow substantially increased during water year 2007 compared to water year 2006 (fig. 9). Water year 2007 was one of the wettest years on record for most basins in Oklahoma (Blazs and others, 2007). Annual streamflow trends with time generally were consistent between stations but varied from greater to lesser streamflow (fig. 10). Significant trends were not detected for streamflow statistics that represented median and greater annual streamflow (Q_{mean} , Q_{10} , and Q_{50}) at either

station (table 6). Significant downward trends with time were detected for annual streamflow characteristics that represented lesser streamflow (Q_{90} and $7Q_{\text{min}}$) at both stations.

Most annual streamflow statistics for both stations were significantly correlated to annual precipitation or lagged annual precipitation, with the exception of the Q_{90} for the Britton Road station that was not correlated to any annual precipitation statistic. Trends in precipitation-adjusted Q_{90} for the Britton Road station were not determined because of that lack

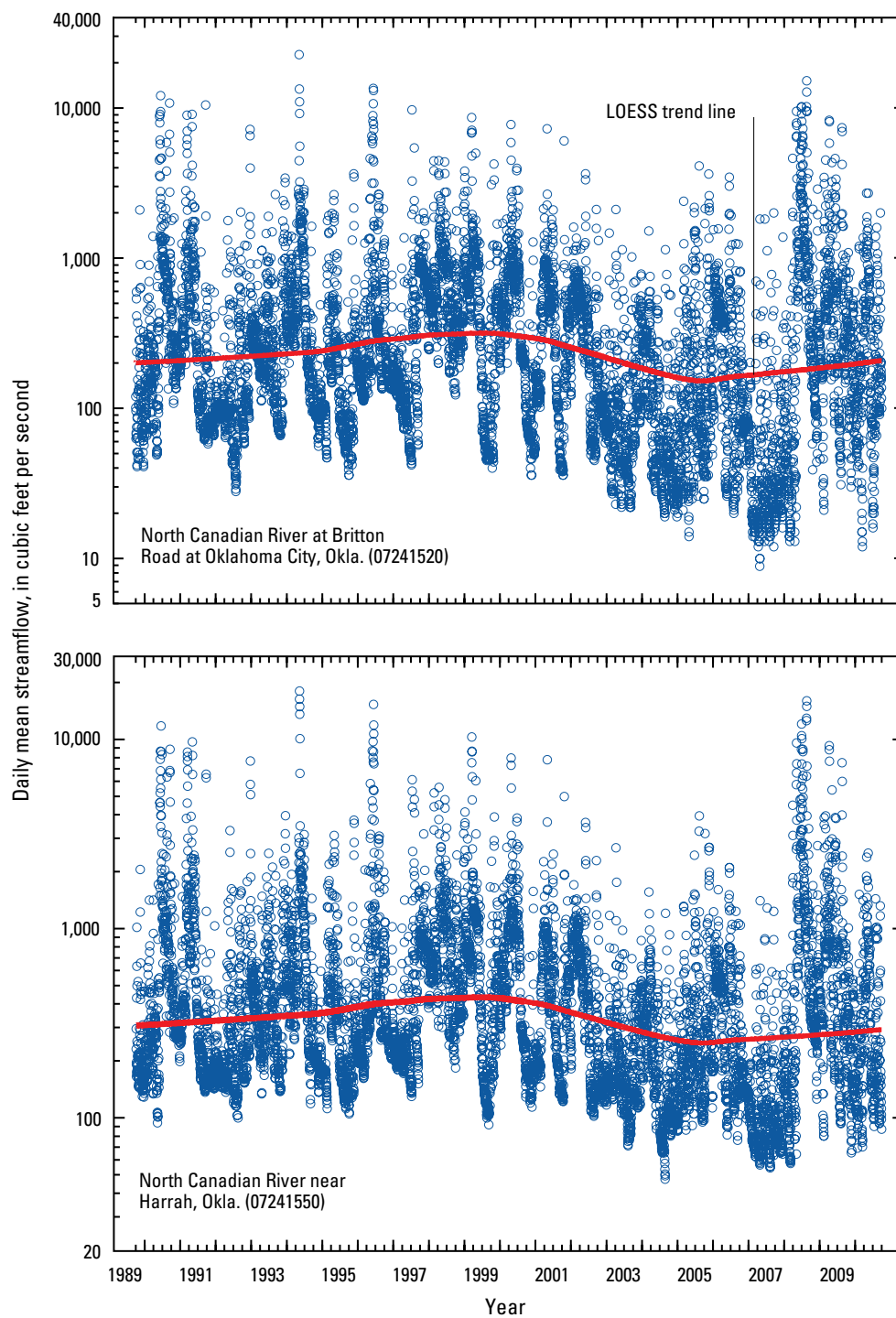


Figure 9. Daily mean streamflow at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

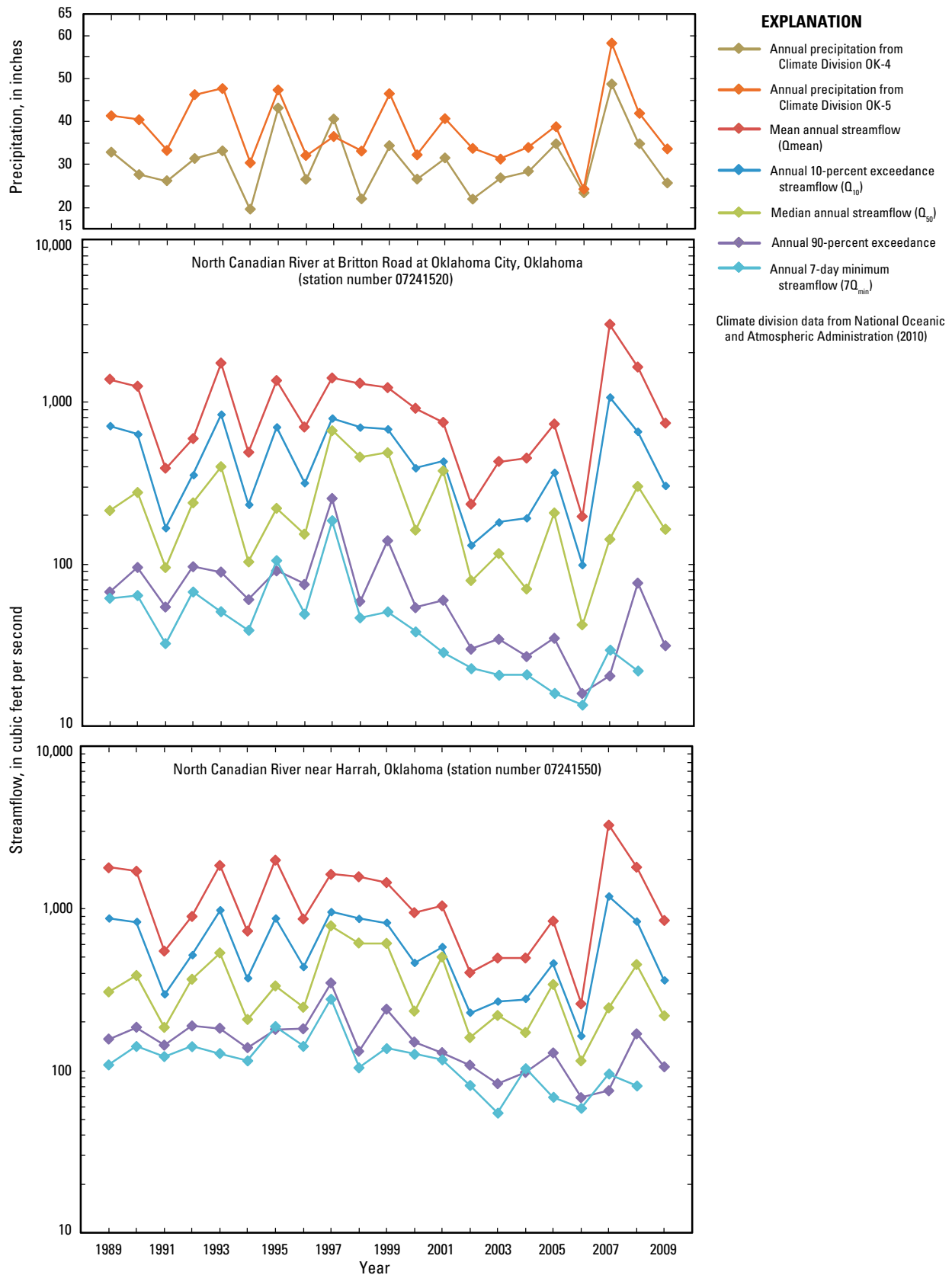


Figure 10. Annual precipitation in two National Weather Service Climate Divisions and annual streamflow statistics for the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

Table 6. Results of trend analysis for annual streamflow statistics, and annual streamflow statistics adjusted for changes in annual precipitation, for two streamflow-gaging stations on the North Canadian River, Oklahoma.

[Q_{mean} , mean annual streamflow; Q_{10} , annual ten-percent exceedance streamflow; Q_{50} , median annual streamflow; Q_{90} , annual ninety-percent exceedance streamflow; $7Q_{\text{min}}$, annual seven-day minimum streamflow; Tau, Kendall's tau; p-value, probability value; OK-4, annual precipitation from National Weather Service Climate Division Oklahoma-Four; OK-5, annual precipitation from National Weather Service Climate Division Oklahoma-Five; NA, not applicable; --, not calculated; results shaded in red are statistically significant at a p-value of 0.05]

Station	Stream-flow statistic	Trends			Precipitation-adjusted trends			Precipitation-adjustment model variables					Model residual standard error
		Slope (percent/year)	Tau	p-value	Slope (percent/year)	Tau	p-value	OK-4 1-year lag	OK-4 2-year lag	OK-1 1-year lag	OK-5 2-year lag	OK-5 1-year lag	
North Canadian River at Britton Road at Oklahoma City, Oklahoma (07241520), 1968–2009	Q_{mean}	--	-0.181	0.2639	--	-0.1619	0.319	Not used	Used	Not used	Not used	Not used	0.105
	Q_{10}	--	-.1143	.4874	--	-.0857	.6077	Not used	Used	Not used	Not used	Not used	.081
	Q_{50}	--	-.1619	.319	--	-.2286	.1558	Not used	Used	Not used	Not used	Not used	.242
	Q_{90}	-6.6	-.4571	.0041	NA ¹	NA	NA	Not used	Not used	Not used	Not used	Not used	NA
	$7Q_{\text{min}}$	-7.6	-.5789	.0004	--	-.2842	.0855	Not used	Used	Not used	Not used	Not used	.484
	Q_{mean}	--	-.2286	.1558	--	-.2857	.0748	Used	Not used	Not used	Used	Not used	.182
	Q_{10}	--	-.200	.2157	--	-.1905	.2389	Used	Not used	Not used	Used	Not used	.200
North Canadian River near Harrah, Oklahoma (07241550), 1988–2009	Q_{50}	--	-.181	.2639	--	.1524	.3492	Not used	Not used	Not used	Used	Not used	.229
	Q_{90}	-3.4	-.4857	.0023	--	-.2476	.1235	Used	Not used	Not used	Not used	Used	.259
	$7Q_{\text{min}}$	-3.7	-.4737	.0039	--	-.2947	.0744	Not used	Not used	Not used	Not used	Not used	.410
								Used	Used	Used	Used	Used	

¹ Streamflow statistic was not significantly correlated (95-percentile confidence interval) to any precipitation variable used in the precipitation-adjustment model, therefore precipitation-adjusted trends were not calculated.

of significant correlation. Annual streamflow statistics that represented median and greater streamflow (Q_{mean} , Q_{10} , and Q_{50}) were not as strongly correlated to precipitation as annual streamflow characteristics that represented less streamflow (Q_{90} and $7Q_{\text{min}}$). Correlation between streamflow and precipitation can be compared among streamflow statistics by observing differences in the residual standard error of a correlation (table 6), with lower values representing stronger correlation. Variability of the Q_{10} , Q_{50} , and Q_{mean} streamflow statistics were observed to more closely match variability in annual precipitation in climate divisions OK-4 and OK-5 than variability in the Q_{90} and $7Q_{\text{min}}$ (fig. 10).

Significant trends in precipitation-adjusted annual streamflow were not detected for any of the streamflow statistics for either station (table 6). However, the p-value of Kendall's tau for the $7Q_{\text{min}}$ was less than 0.1, close to the significance level of 0.05 (table 6). In addition, a decline in the Q_{90} and $7Q_{\text{min}}$ can be visually identified after 1998 (fig. 10). Although not statistically significant at the 95-percent confidence level, these results indicate that low flow may be decreasing in the basin, especially after 1998. If present, slight decreases in the Q_{90} and $7Q_{\text{min}}$, even after precipitation-adjustment, may be caused by changes in water demand that affect streamflow regulation and groundwater withdrawals in the basin, or by changes in the streamflow regime as a result of construction of low-water dams in Oklahoma City from 1998–99.

Streamflow at the Time of Sample Collection

Results of the Wilcoxon rank-sum tests (table 7) indicated that daily mean streamflows on days of sample collection were not significantly different from daily mean streamflows

for the period of 1988–2009 at both stations. However, daily mean streamflow on days of sample collection was significantly less than daily mean streamflow for 1968–2009 at the Harrah Station (fig. 11), although the differences were small. Statistical similarities in the locations of distribution of daily mean streamflow on days of sample collection and daily mean streamflow for 1988–2009 (table 7) indicated that water-quality samples collected during this period were representative of streamflow during that period. Because daily mean streamflow on days of sample collection for 1968–2009 were less than all daily mean streamflow, samples collected prior to 1988 may have been biased to lesser streamflow.

Flow-duration and sample-duration curves (fig. 12) generally support results from the rank-sum tests, but there were differences along the probability exceedance curves. Most differences between daily mean streamflow on days of sample collection and daily mean streamflow on all days of sample collection at the lesser percentile probabilities (less than 5 percent) and greater percentile probabilities (greater than 95 percent) were observed for the Britton Road station and the Harrah station from 1988–2009. Streamflow exceedance for sample daily mean streamflow was greater than streamflow exceedance for all daily mean streamflow at the same probability percentile in these ranges, indicating that whereas samples may have been collected during some substantial storm events and low-flow conditions, not enough samples may have been collected at the greatest and smallest ends of the streamflow regime to be representative of typical streamflow at these stations. Differences in daily mean streamflow on days of sample collection and all days for the Harrah station from 1968–2009 were not observed near percentile end-points (percentiles less than 5 percent and greater than 95 percent), but daily mean streamflow on days of sample collection generally was less than daily mean streamflow on all days along most of the duration curve, supporting results of the rank-sum test.

Table 7. Results of Wilcoxon rank-sum test for comparison of the distribution of daily mean streamflow on the day of sample collection and all days at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations.

[Z-score, normal test statistic with correction for ties; p-value, probability value; values in red indicate statistically significant differences between groups of data at 95-percent confidence level (probability value less than or equal to 0.05)]

Station	Period of record tested	Number of samples tested	Wilcoxon rank sum	
			Z-score	p-value
North Canadian River at Britton Road at Oklahoma City, Okla. (07241520)	1988–2009	258	0.3125	0.7547
North Canadian River near Harrah, Okla. (07241550)	1968–2009	1,147	2.6597	.0078
	1988–2009	253	-.3280	.7429

Evaluation of Water Quality

This section describes statistical summaries of water-quality data, frequencies of detection of pesticide data; comparison of differences between the stations in nutrient, biological, and physical-property concentrations from discrete water samples and continuous water-quality monitors; and qualitative and quantitative analysis of trends with time in concentrations of selected physical properties, nutrients, and biological constituents. An evaluation of constituents that most frequently exceeded the CCC and a description of frequently detected pesticides are presented. Results from statistical comparisons and qualitative trends in summaries of daily values of physical properties measured from continuous water-quality monitors, and selected plots of shorter periods of instantaneous physical-property concentrations are presented in the section titled “Characteristics and Qualitative Trends of Physical Properties Measured from Continuous Water-Quality Monitors” in this report.

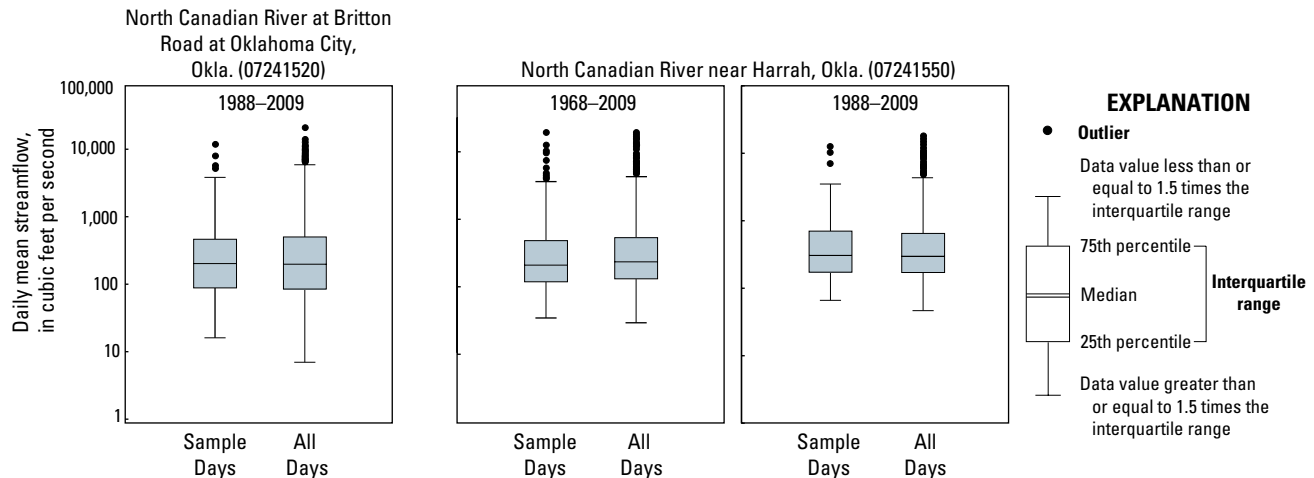


Figure 11. Distribution of daily mean streamflow on days of sample collection and on all days during selected periods at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

Statistical Summary of Water-Quality Data

Statistical summaries were calculated for 157 constituents analyzed in water samples collected at the Britton Road and Harrah stations (appendixes 1 and 2). Those constituents included physical properties and chemical constituents, major inorganics (metals and nonmetals), nutrients, microbiological and biological constituents, minor inorganics (metals and nonmetals), organic compounds (pesticides and other organic compounds), one radiochemical constituent, and sediment.

Frequency of Exceedance of Criteria Continuous Concentrations

Percentages of samples used in computation of summary statistics that exceeded the Criteria Continuous Concentration (CCC) were calculated for 24 constituents. Most samples did not contain constituents in concentrations that exceeded the CCC (appendixes 1 and 2). Constituent concentrations exceeded the CCC for at least 1 sample for 10 constituents analyzed from samples collected at the Britton Road station and for 16 constituents analyzed from samples collected at the Harrah station. Concentrations of dissolved chloride, cadmium, and dissolved lead most frequently exceeded the CCC for samples collected from the Britton Road station (10, 7.1, and 4.8 percent respectively) (appendix 1). Concentrations of dissolved chloride, dissolved lead, and chlordane most frequently exceeded the CCC for samples collected from the Harrah station (39.2, 12.4, and 10.2 percent, respectively) (appendix 2).

Dissolved chloride concentration was the constituent that exceeded the CCC most frequently at both stations. Dissolved chloride concentrations may be increased in the North Canadian River from natural and anthropogenic sources. Natural sources of chloride in the river may include

seepage of brines from buried geologic units, chloride in atmospheric precipitation, and dissolution of salts in shallow geologic units, particularly in the western half of the basin. Major anthropogenic sources of chloride in surface waters are agricultural runoff, urban runoff (including chloride from the application of halite for road de-icing), discharges from municipal WWTPs and other industrial plants, and oil and gas production (Birge and others, 1985). Prior to the 1970s, brines and petroleum wastes typically were disposed in open, unlined pits. Thousands of these abandoned pits may be an additional source of chloride in the North Canadian River (Brigham and others, 2002). Excessive chloride concentrations can be toxic to freshwater fish and other aquatic animals, especially chlorides in association with potassium, calcium, and magnesium (Ellis, 1937; Biesinger and Christensen, 1972). A graph of chloride concentrations with time and a LOESS curve (fig. 13) indicates that chloride concentrations declined after 1979 at the Harrah station and after water sample collection began at the Britton Road station in 1988. Exceedances of the chloride CCC at the Britton Road station were rare after 1989. Investigation of trends in other cations, which may indicate brines and other petroleum wastes, was beyond the scope of this report, but is discussed in a previous investigation (Brigham and others, 2002).

Cadmium and lead are metals associated with batteries, combustion of fossil fuels, and transportation (Agency for Toxic Substances and Disease Registry, 2007a, 2008a). Ingestion of cadmium can irritate the stomach, damage kidneys, lungs, and bone tissues. Some compounds of cadmium and lead have been determined to be carcinogens (Agency for Toxic Substances and disease Registry, 2007a, 2008a).

Chlordane is an organochlorine compound used as a pesticide (including for termite control) and is a toxic chemical that affects the nervous system, digestive system, and liver of people and animals. The USEPA banned all uses of chlordane

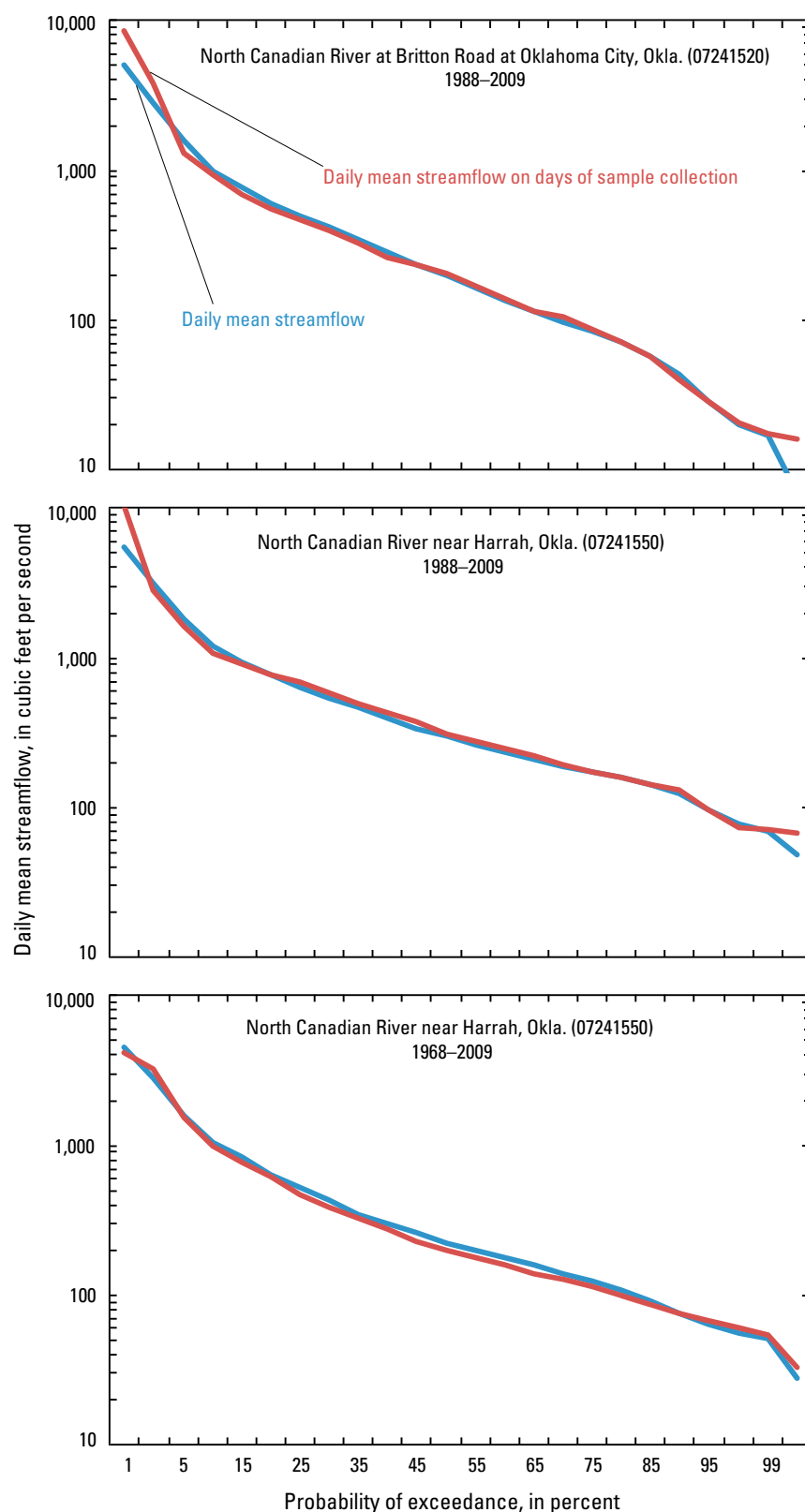


Figure 12. Probability of exceedance of daily mean streamflow on days of sample collection and on all days at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

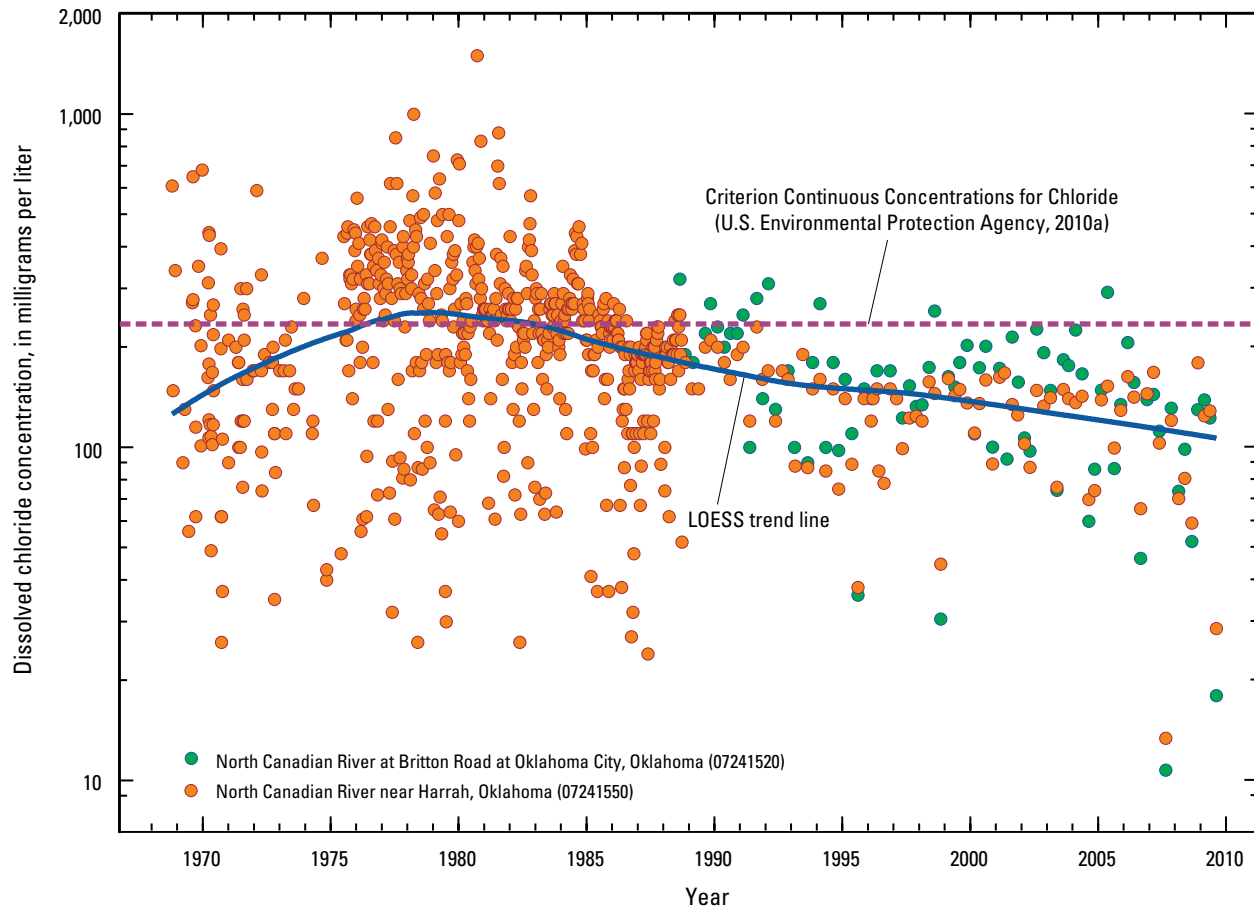


Figure 13. Dissolved chloride concentrations in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

in 1988 (Agency for Toxic Substances and Disease Registry, 1995). About 10 percent of water samples collected at the Harrah station had chlordane concentrations exceeding the CCC (0.0043 micrograms per liter (mg/L), appendix 2, U.S. Environmental Protection Agency, 2010a); about 2 percent of water samples collected at the Britton Road station had chlordane concentrations exceeding the CCC (appendix 1). Quantitative evaluation of CCC exceedance for chlordane was limited because the laboratory reporting level was two orders of magnitude greater than the CCC of 0.0043 mg/L. Most exceedances of the CCC for chlordane were observed prior to the date that chlordane use was banned, indicating that the ban of chlordane use may have reduced chlordane concentrations at these stations.

Analysis of Frequency of Detection of Pesticides

Frequencies of detection of pesticides, expressed as a percent of samples in which pesticides were detected, were graphed as a bar graph (fig. 14). Frequencies of detection of pesticides from samples collected from 1988–2009 were

graphed for both stations, and detection of pesticides from samples collected from 1968–2009 were graphed separately for the Harrah station. Although frequencies of detection were determined for all pesticides for the sampling period and annual frequencies of pesticide detection were computed, differences in the sampling frequency of some pesticides may preclude comparing detection frequencies between pesticides. Prior to 1988, sampling frequencies of certain pesticides at the Harrah station varied substantially. Starting in 1988, all pesticides were sampled at least quarterly at both stations. Starting in 1994, some pesticides (carbophenothion, chlorpyrifos, diazinon, disulfoton, ethion, fonofos, malathion, methyl parathion, parathion, phorate, and tribufos) were analyzed in samples collected during summer months in addition to the quarterly sampling schedule.

Bar graphs indicated that frequencies of detection of pesticides greater than 10 percent were more common for water samples collected at the Harrah station than at the Britton Road station from 1988–2009, with the exception of dichlorprop, which had greater frequencies of detection at the Britton Road station (fig. 14). Frequencies of detection for pesticides

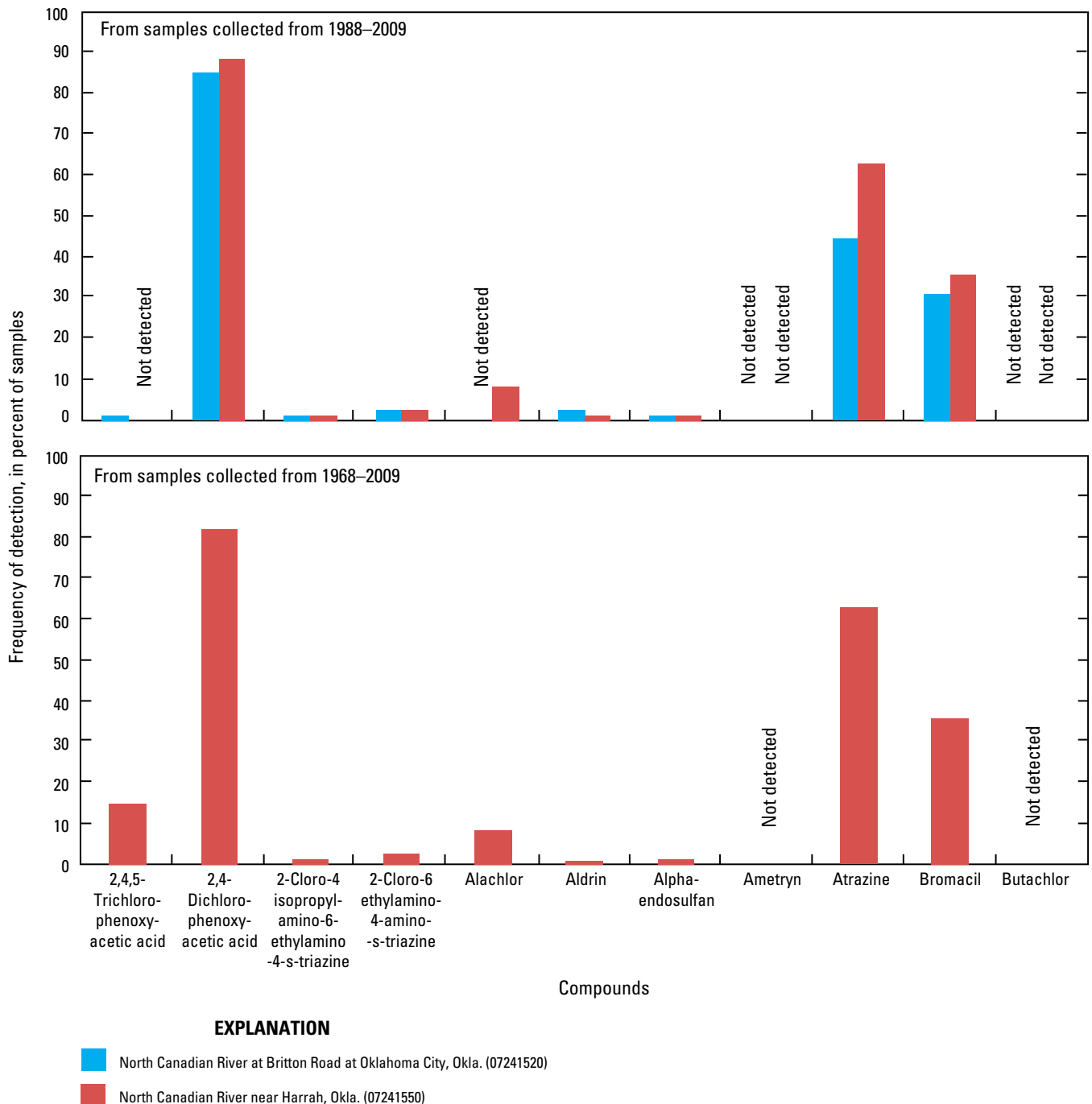


Figure 14. Frequencies of detection of pesticides analyzed in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

at the Harrah station were similar for the years 1968–2009, probably because most pesticide samples were collected during the later period 1988–2009 (fig. 14).

In water samples collected at the Harrah station, frequencies of pesticide detection were greatest for diazinon, 2,4-dichlorophenoxyacetic acid (2,4-D), and dieldrin (83, 82, and 75 percent, respectively). In water samples collected at

the Britton Road station, frequencies of pesticide detection were greatest for 2,4-D, lindane, and diazinon (85, 65, and 63 percent, respectively).

Diazinon is an organophosphate insecticide that is mobile and moderately persistent. Diazinon is most commonly contributed to surface water by urban and agricultural runoff, and effluent from WWTPs (Agency for Toxic Substances

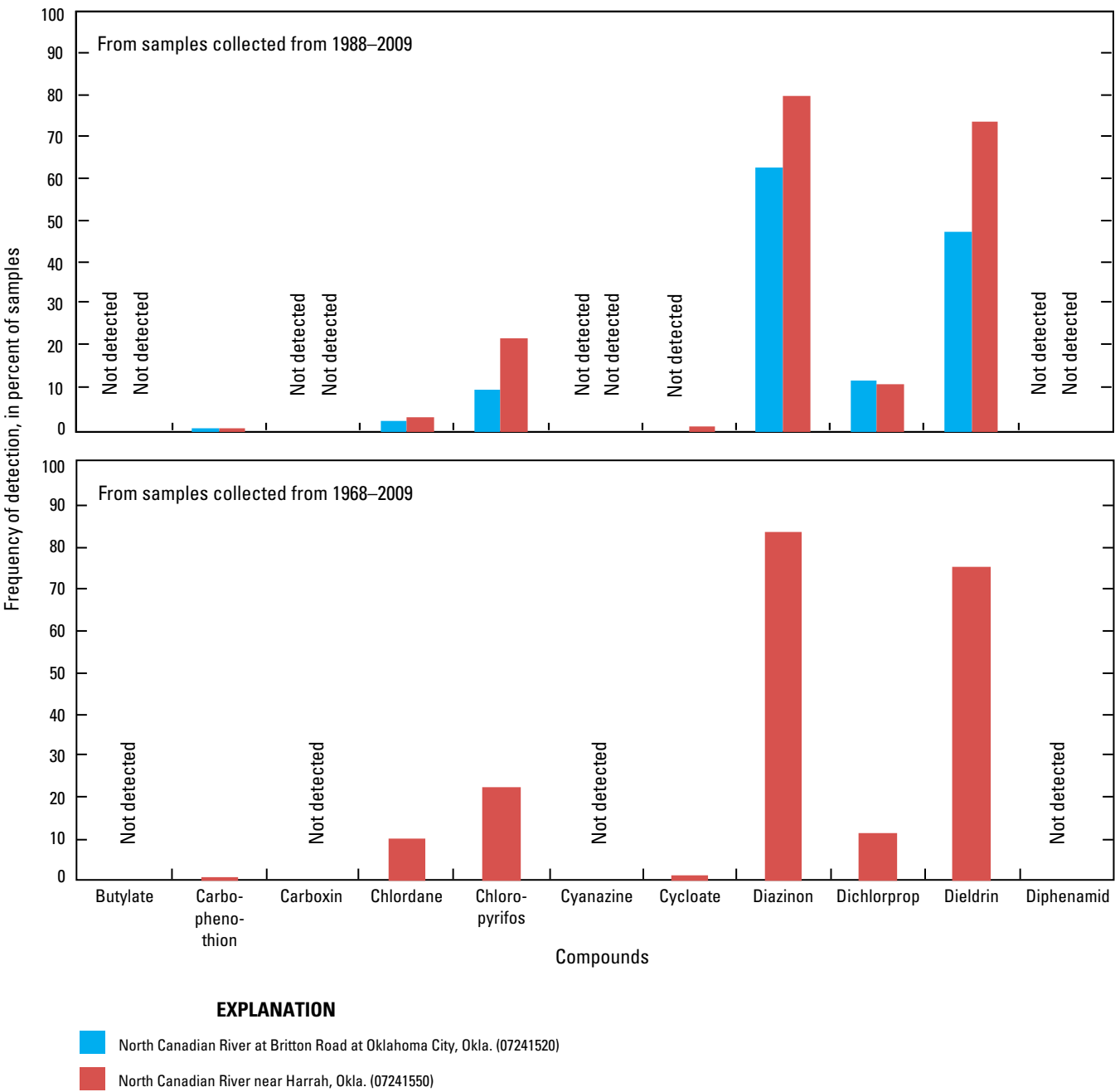


Figure 14.—Continued.

and Disease Registry, 2008b). Diazinon was one of the most widely used insecticides in the United States during the 1970s and 1980s. This insecticide was used mainly for household and garden pest control in urban settings and to control insects in fruit, nut, and vegetable crops in agricultural settings (Gilliom and others, 2006). Diazinon has been banned from sale for outdoor and non-agricultural uses since 2004 because of its toxicity to aquatic life, particularly invertebrates (U.S. Environmental Protection Agency, 2000). Diazinon concentrations exceeded the CCC in 3.6 percent of water samples

collected at the Harrah station (appendix 2) and 4.7 percent of water samples collected at the Britton Road station (appendix 1). Starting in 1994, diazinon was analyzed in quarterly samples and during summer months, which may have caused greater frequencies of detection of this insecticide compared to other pesticides not analyzed during summer months.

2,4-D is an chlorophenol herbicide used since the mid-1940s and is an ingredient in more than 650 agricultural and home-use products (Agency for Toxic Substances and Disease Registry, 1999). Application rates for 2,4-D were the

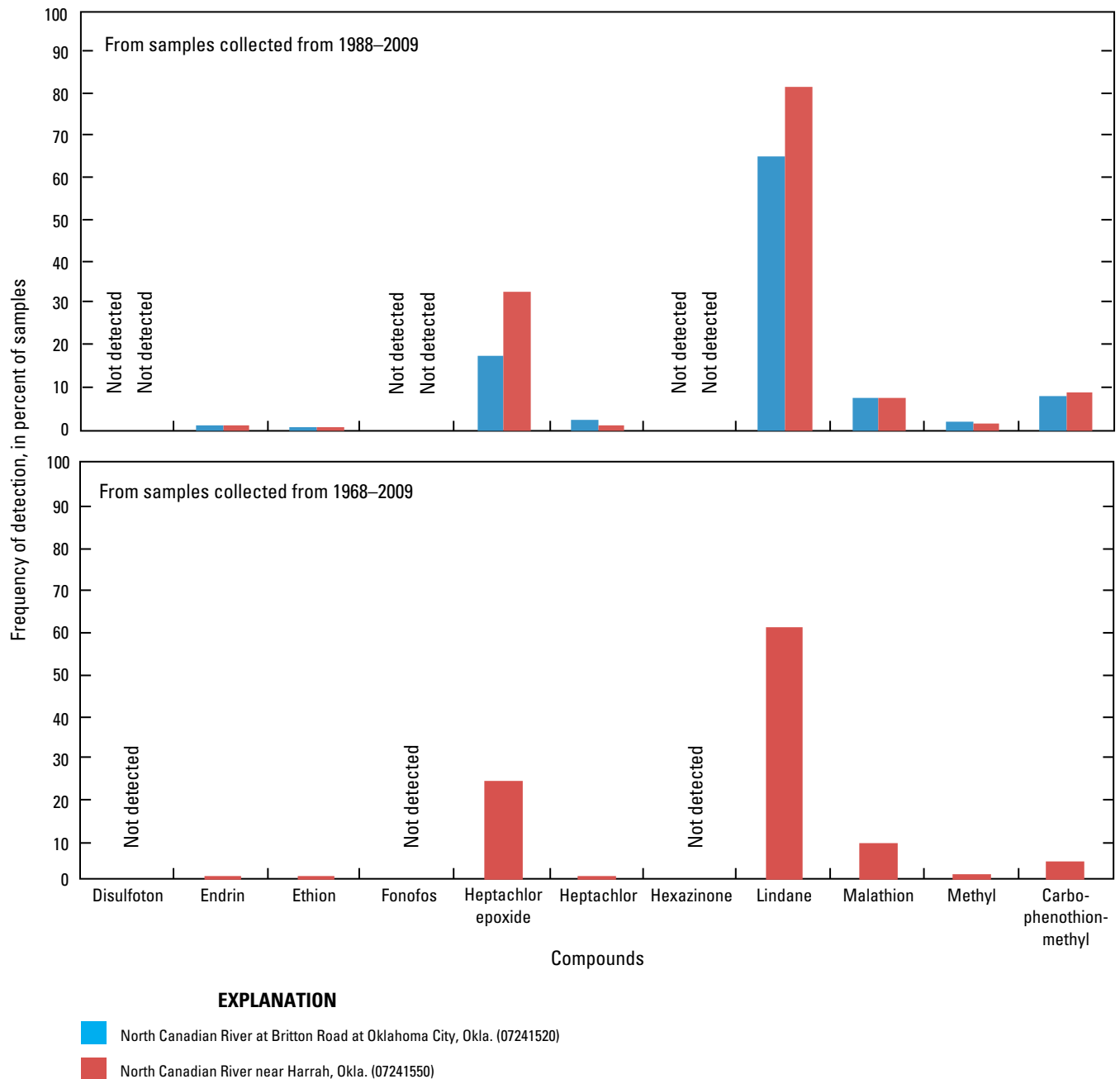


Figure 14.—Continued.

highest of any pesticide in Oklahoma and Canadian Counties (Battaglin and Goolsby, 1994). A CCC for 2,4-D has not been established.

Dieldrin is an insecticide and a by-product of the pesticide aldrin. From 1950–74, dieldrin was used to control insects on cotton, corn, and citrus crops as well as to control locusts and mosquitoes, as a wood preservative, and for termite control (Agency for Toxic Substances and Disease Registry, 2002). Most uses of dieldrin were banned in 1987 and it is no longer produced in the United States because of

harmful effects on humans, fish, and wildlife (Agency for Toxic Substances and Disease Registry, 2002). Dieldrin concentrations exceeded the CCC for 0.8 percent of water samples collected at the Harrah station (appendix 2) and did not exceed the CCC for any water samples collected at the Britton Road station.

Pesticides with frequencies of detection greater than 10 percent in water samples collected at both stations include 2,4-D, atrazine, bromacil, chlorpyrifos, diazinon, dichlorprop, dieldrin, heptachlor epoxide, lindane, and simazine.

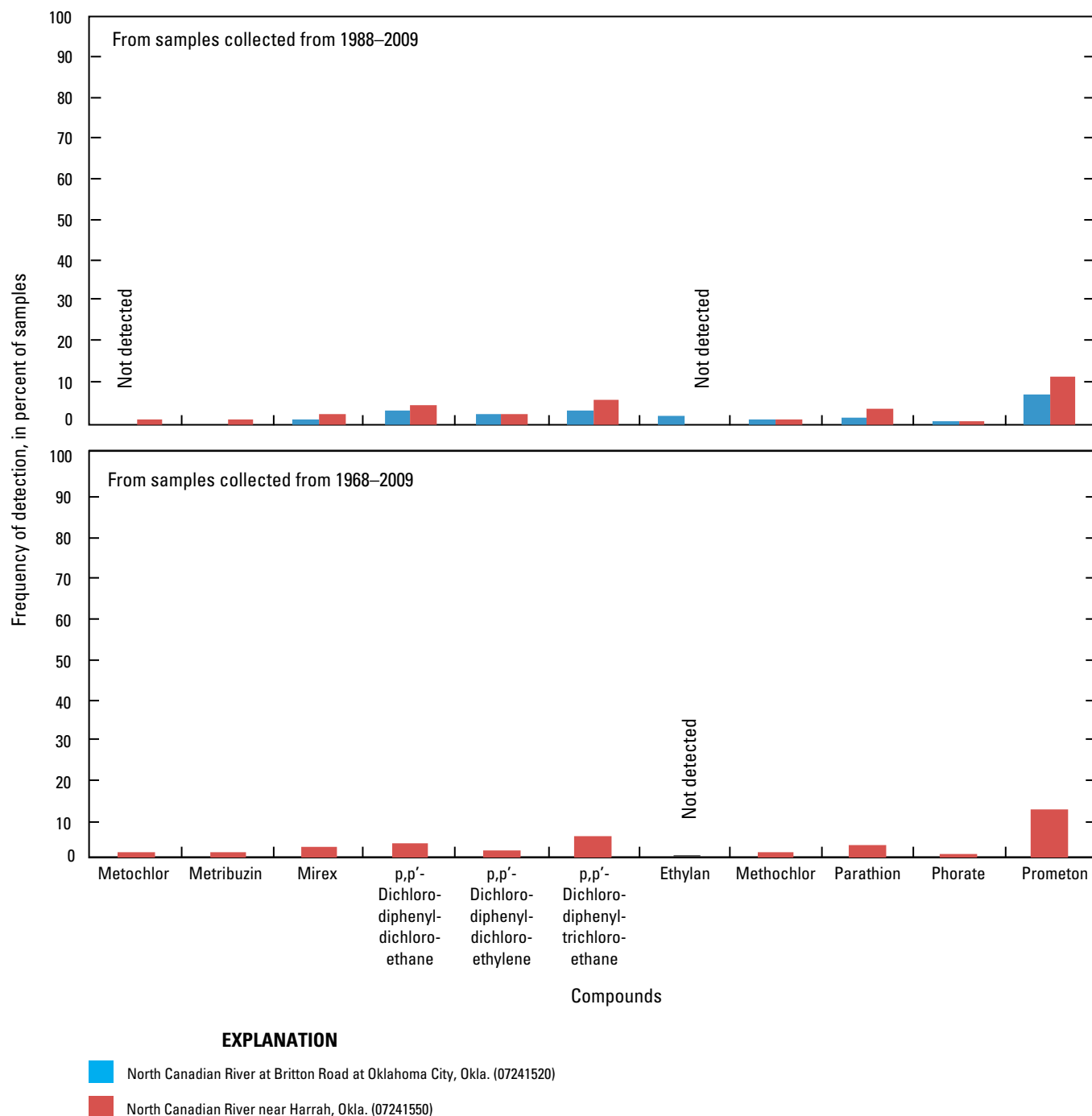


Figure 14.—Continued.

Evaluation of qualitative trends in frequencies of detection of pesticides by water year for all pesticides with frequencies of detection greater than 10 percent indicated that frequencies of detection of many of these pesticides decreased with time (fig. 15).

Annual frequencies of detection of atrazine, chlorpyrifos, diazinon, dichlorprop, and lindane decreased with time at one or both stations. Annual frequencies of detection of atrazine decreased from 1988–2009 (fig. 15). This widely used

herbicide was detected in all samples collected prior to 1992 but was detected in less than 50 percent of the water samples collected from 2004–09 (fig. 15). Annual frequencies of detection of chlorpyrifos, an organophosphate insecticide restricted for home and agricultural use by USEPA in 2001 (Agency for Toxic Substances and Disease Registry, 1997), decreased from 1990–2009 and was not detected in water samples collected from 2001–06. Starting in 1994, chlorpyrifos was analyzed quarterly and during summer months, which may have caused

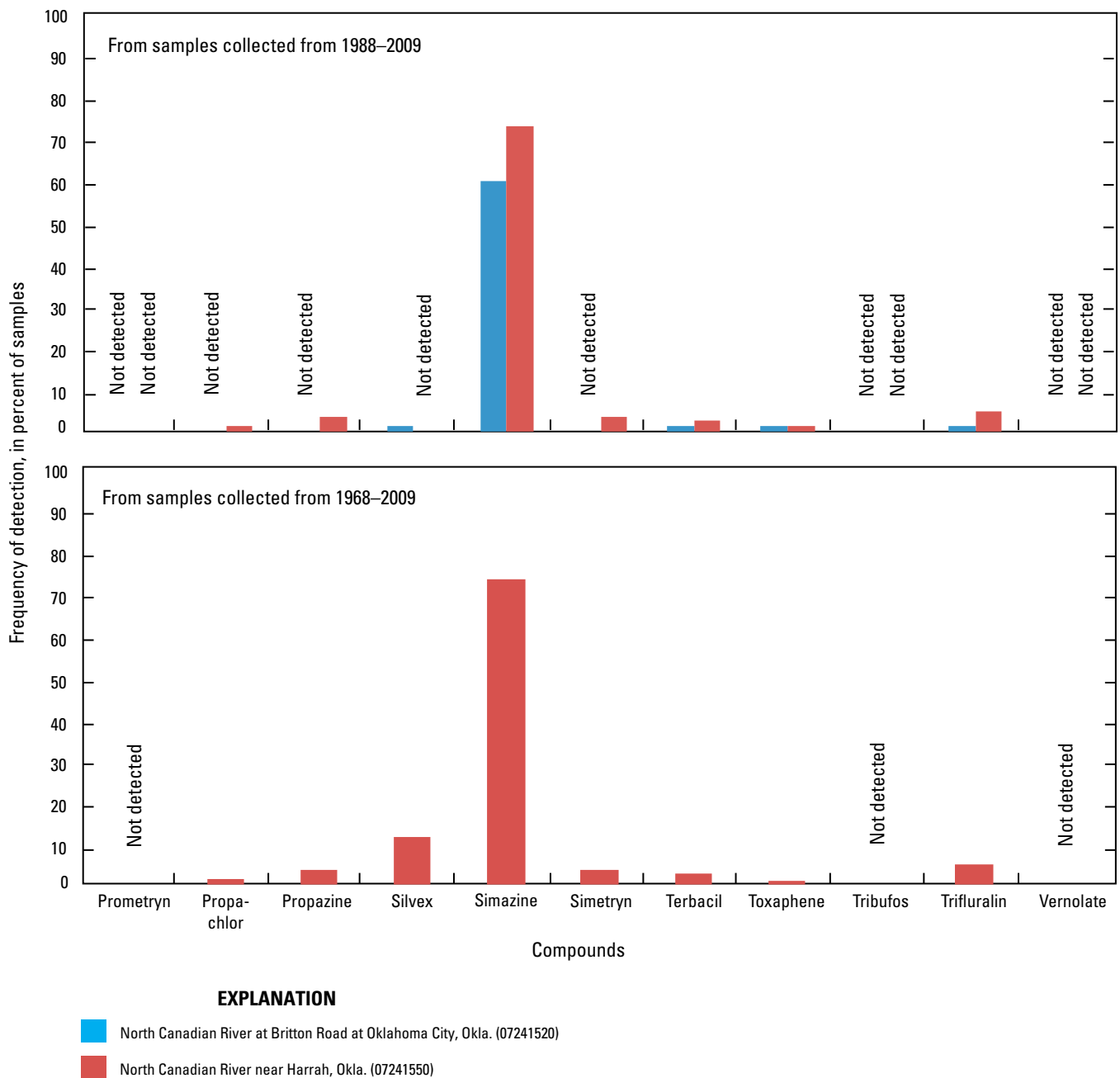


Figure 14.—Continued.

greater frequencies of detection of this insecticide compared to pesticides not analyzed during summer months. Annual frequencies of detection of diazinon decreased from 1972–2009. In most years prior to 1998, diazinon was detected in all of the water samples whereas frequencies of detection decreased thereafter. Annual frequencies of detection of dichlorprop, a chlorophenoxy herbicide mostly used on residential lawns but banned for agricultural use on crops (U.S. Environmental Protection Agency, 2007), decreased most notably after 2001

and was not detected in water samples collected after 2005. Lindane is an organochlorine insecticide and a pharmaceutical used for treatment of lice and scabies that has been banned for agricultural uses since 2009 (Agency for Toxic Substances and Disease Registry, 2005). Annual frequencies of detection of lindane decreased slightly from 1988–2009. Frequencies of lindane detection in the water samples ranged from 75 to 100 percent per year from 1988–95, and 0 to 100 percent from 1996–2009.

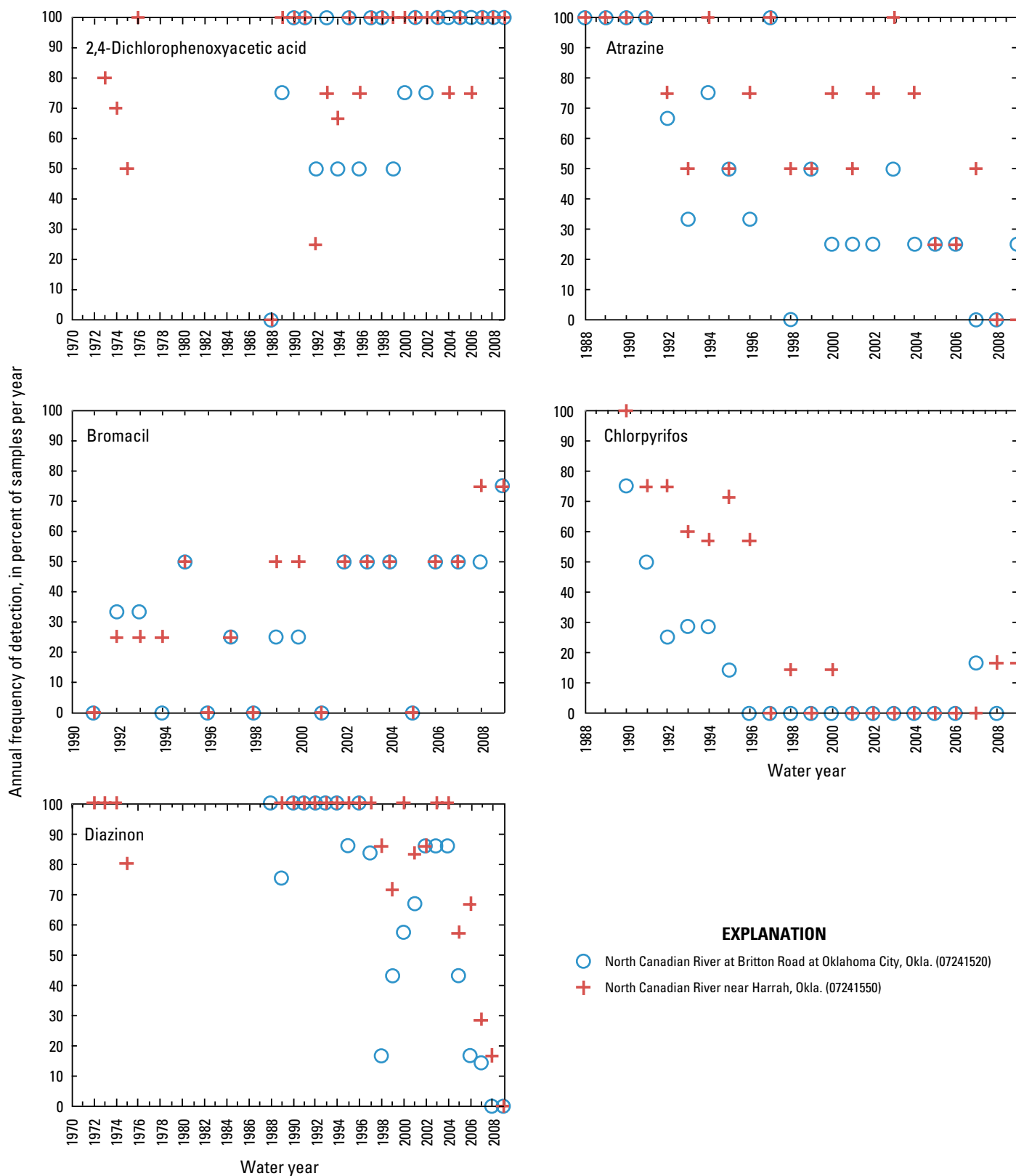


Figure 15. Annual frequencies of detection of pesticides in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1968–2009.

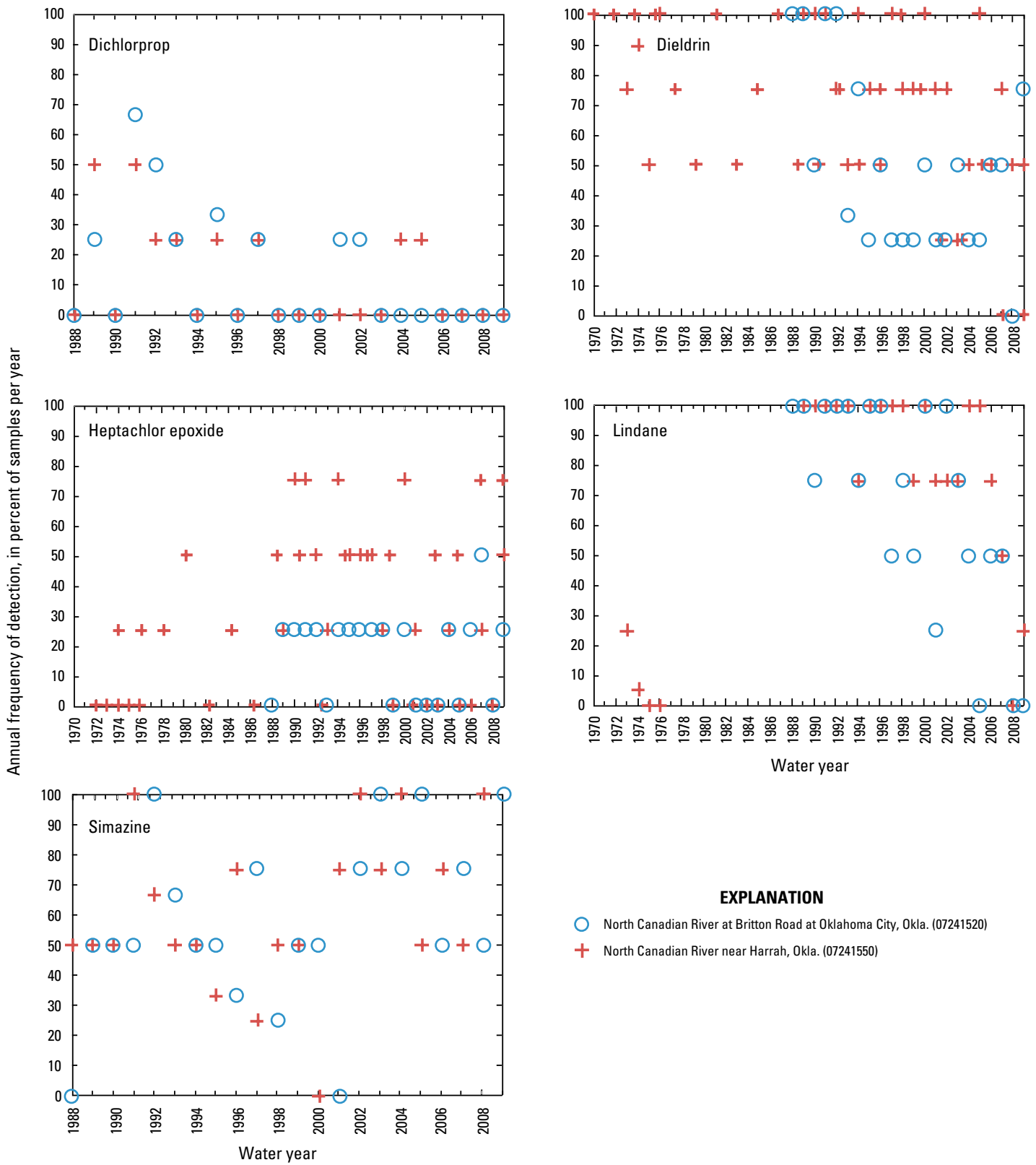


Figure 15.—Continued.

Annual frequencies of detection of 2,4-D and bromacil increased with time (fig. 15). Annual frequencies of detection of 2,4-D were highly variable but increased slightly from 1988–2009. 2,4-D was detected in all water samples collected at the Britton Road station since 2003 and in all water samples collected at the Harrah station since 2007. Annual frequencies of detection of bromacil, a general use herbicide used for brush control on non-cropland areas (U.S. Environmental Protection Agency, 1997), increased from 1990 to 2009. Prior to 2001, bromacil was detected in less than 50 percent of the water samples, whereas after 2001 (with the exception of 2005), it was detected in 50 percent or more of the samples.

There were no observed upward or downward trends in annual frequencies of detection of dieldrin, heptachlor epoxide, or simazine (fig. 15). Heptachlor epoxide is a chlorinated cyclodiene insecticide and probable human carcinogen (Agency for Toxic Substances and Disease Registry, 2007b). Simazine is a triazine herbicide used to control broad-leaf weeds and annual grasses (U.S. Environmental Protection Agency, 2010b). There were greater frequencies of detection of dieldrin and heptachlor epoxide in water samples collected at the Harrah station than at the Britton Road station.

Differences in Physical Properties, Nutrients, and Fecal Coliform Bacteria from Water Samples Between Stations

The locations of distribution of dissolved phosphorus concentration, dissolved nitrogen concentration, and specific conductance were significantly different between stations based on the Wilcoxon rank-sum and signed-rank tests (fig. 16, table 8). Dissolved nitrogen and phosphorus concentrations were significantly greater at the Harrah station than at the Britton Road station, whereas specific conductance was greater at the Britton Road station (fig. 16). The locations of distribution of dissolved oxygen, BOD, and fecal coliform concentrations were not significantly different between the stations (table 8). The median fecal coliform concentration for both stations exceeded the “primary body contact” limit for streams, set by the State of Oklahoma, of 400 colonies per 100 milliliters (State of Oklahoma, 2006).

Characteristics and Qualitative Trends of Physical Properties Measured from Continuous Water-Quality Monitors

This section describes characteristics and qualitative trends of daily values of specific conductance, pH, temperature, and dissolved oxygen concentration measured by continuous water-quality monitors. Selected graphs of shorter measurement periods of physical property concentrations are included to show diurnal variation in concentrations of those properties.

Specific Conductance

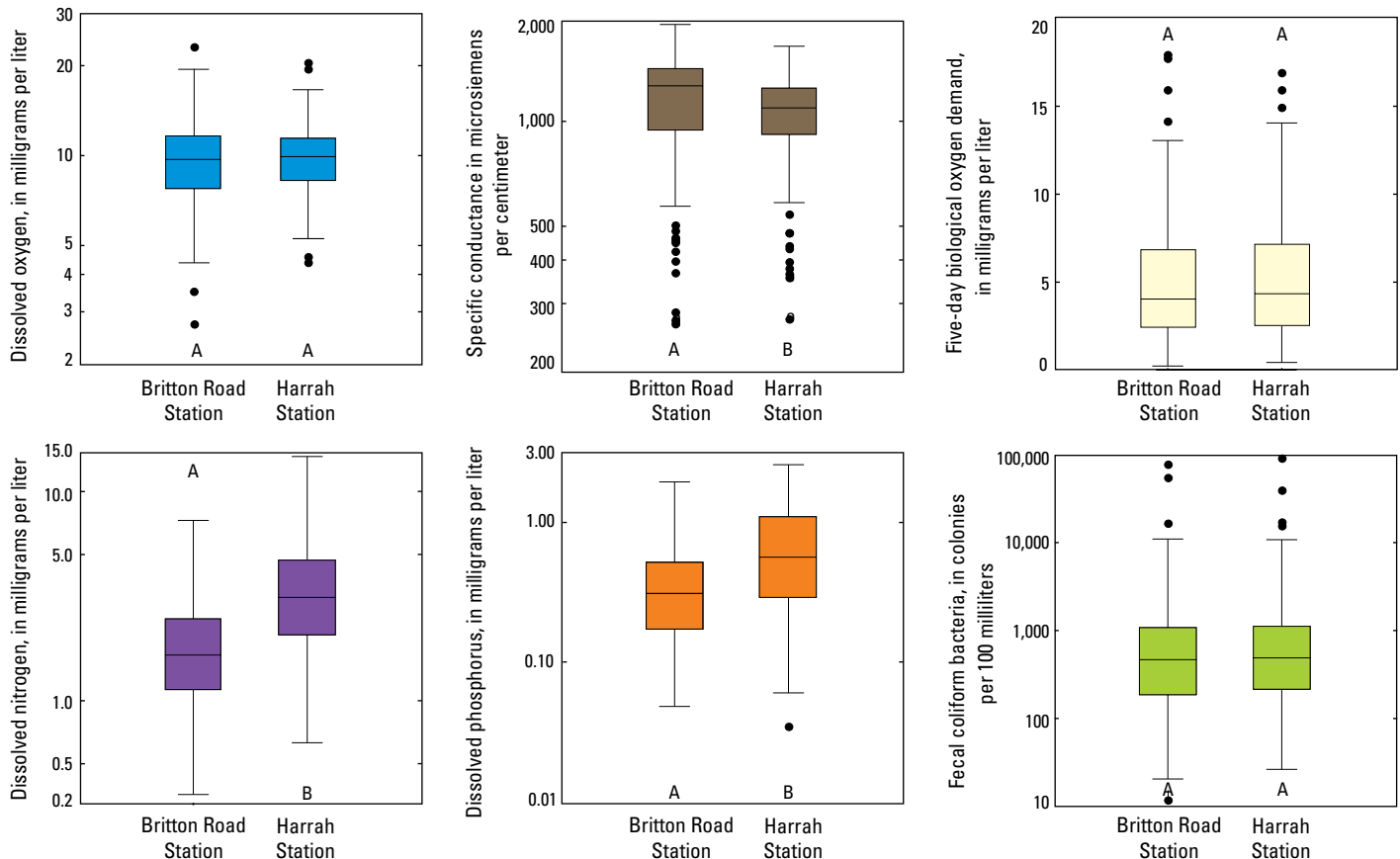
Variations in daily maximum and minimum specific conductance were substantial during some periods, as shown on figure 17 for August 2007. No diurnal patterns in specific conductance were observed. Specific conductance tended to be inversely correlated to streamflow as increases in streamflow tend to dilute concentrations of ionic substances from groundwater seepage, which dominates streamflow at base flow. The substantial decrease in specific conductance on August 20, 2007 (fig. 17), followed by a gap in available data because of equipment malfunction resulting from an extreme high-flow event (J.R. Hanlon, U.S. Geological Survey, oral and written commun., June 2010) at both stations, coincided with increases in daily mean streamflow from more than 100 ft³/s to more than 10,000 ft³/s from August 20–23, 2007.

Daily mean specific conductance at the Britton Road station ranged from 147 to 2,390 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) with a smallest daily minimum of 22 $\mu\text{S}/\text{cm}$ and a largest daily maximum of 2,730 $\mu\text{S}/\text{cm}$ (data available at <http://waterdata.usgs.gov/ok/nwis/current/?type=quality&group%20Key=basin%20cd>). Daily mean specific conductance at the Harrah station ranged from 147 to 2,390 $\mu\text{S}/\text{cm}$ with a smallest daily minimum of 129 $\mu\text{S}/\text{cm}$ and a largest daily maximum of 2,040 $\mu\text{S}/\text{cm}$. The greatest diurnal ranges at the Britton Road and Harrah stations were 2,258 $\mu\text{S}/\text{cm}$ and 1,217 $\mu\text{S}/\text{cm}$ respectively.

Daily maximum, mean, and minimum specific conductance concentrations were significantly greater at the Britton Road station than at the Harrah station (fig. 18, table 9), consistent with differences in specific conductance in water samples collected at the two stations. The diurnal range of specific conductance, measured in August 2007, also was significantly greater at the Britton Road station than at the Harrah station (fig. 19). In general, daily mean specific conductance decreased from 1988–2009 at the two stations, based on slopes of the LOESS curves (fig. 20). That pattern is similar to the temporal pattern of dissolved chloride concentration (fig. 13). The greatest rate of decrease in specific conductance started in 1999. After 2004, daily mean specific conductance continued to decrease at the Britton Road station but remained nearly constant at the Harrah station (fig. 20). Similar to daily mean specific conductance, LOESS curves indicated that diurnal ranges of specific conductance also decreased at both stations from 1988–2009 (fig. 21). However, LOESS curves indicated that diurnal ranges in specific conductance stabilized at the Britton Road station after 1999 and after 2004 at the Harrah station (fig. 21).

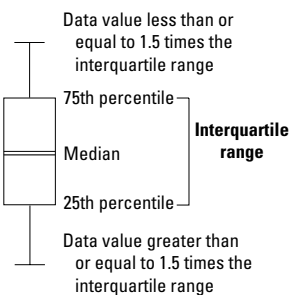
pH

Diurnal variations in continuously measured pH were not notable at the Harrah station in July 2007 (fig. 22). Peaks in pH generally corresponded to periods of lesser streamflow



EXPLANATION

• Outlier



A Daily constituent distributions with the same letter are not significantly different (p less than or equal 0.05 of the Wilcoxon signed-rank test)

Britton Road Station, North Canadian River at Britton Road at Oklahoma City, Okla. (07241520)

Harrah Station, North Canadian River near Harrah, Okla. (07241550)

Figure 16. Distribution of concentrations of selected constituents in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

when base-flow contributions from groundwater seepage represented a greater part of streamflow. Daily median pH values generally were slightly alkaline (greater than 7.0). At the Harrah station from 1988–2009, most daily median pH values were greater than 8.0, with some daily median pH values exceeding 9.0 (fig. 23). Daily median pH ranged from 6.5 to 9.3. The greatest diurnal range at the Harrah station was 2.0 pH units. Daily median pH at the Harrah station did not change notably for 1988–2009 based on the slopes of the LOESS curves, but daily median pH did increase

slightly until 1998, decreased slightly from 1999–2004, and increased slightly thereafter. LOESS curves indicated that the diurnal range of pH was variable from 1988–2009 (fig. 24).

Water Temperature

There were substantial diurnal fluctuations in water temperature at the two stations, with the highest water temperatures being associated with mid-day. For example, during

Table 8. Results of Wilcoxon rank-sum and signed-rank tests for comparison of concentrations of selected constituents in water samples collected from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

[$\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; Z-score, normal test statistic with correction for ties; p-value, probability value; values in red indicate statistically significant differences between groups of data at 95-percent confidence level (probability value less than or equal to 0.05); <, less than]

Constituent	Wilcoxon rank-sum		Wilcoxon signed-rank	
	Z-score	p-value	Z-score	p-value
Dissolved oxygen, in mg/L	-0.8394	0.4012	1.017	0.3091
Specific conductance, in $\mu\text{S}/\text{cm}$ at 25 degrees celcius	5.5533	<.0001	9.739	<.0001
Five-day biochemical oxygen demand, in mg/L at 20 degrees Celsius	-.8840	.3767	-2.417	.0157
Dissolved phosphorus, in mg/L	-7.4950	<.0001	11.916	<.0001
Dissolved nitrogen, in mg/L	-9.3588	<.0001	-12.354	<.0001
Fecal coliform count, in colonies per 100 milliliters	-1.4439	.1488	-.971	.3317

July 2007, daily fluctuations in water temperature ranged from about 0.5 to 5.0 °C (fig. 25). There was a drop in temperature proceeded by decreases in diurnal fluctuations from July 7 to 17, 2007, which represented a period of increased streamflow from a precipitation event. Daily minimum and maximum water temperature at the Britton Road station ranged from -1.7 to 32.5 °C, respectively. Daily mean water temperature at the Harrah station ranged from -0.3 to 32.7 °C with the smallest daily minimum being -1.5 °C and a largest daily maximum being 37 °C. Maximum diurnal temperature ranges were 20.4 °C for the Britton Road station and 14 °C at the Harrah station. Daily mean water temperatures at both stations typically were near 0 °C in January, and near 30 °C during mid-summers from 1988–2009 (fig. 26). Wilcoxon signed-rank test results indicated that daily minimum and daily maximum water temperatures were significantly different between stations (table 9), with greater minimum and maximum temperatures in water at the Harrah station than at the Britton Road station (figs. 18 and 25). Rank-sum test results indicated that daily mean temperatures were not statistically different between the stations, and were not statistically different from daily maximum temperature at the Britton Road station (fig. 18). However, the signed-rank test indicated that daily mean temperature was significantly greater at the Harrah station than at the Britton Road station on paired days (table 9). Although the maximum diurnal temperature range was greater at the Britton Road station than at the Harrah station, the rank-sum and signed-rank tests indicated that diurnal temperature fluctuations were significantly greater at the Harrah station (fig. 19, table 9). There were general increases of about 1 to 2 °C in daily and diurnal water temperature values from 1988–2009 at both stations, based on slopes of the LOESS curves (fig. 26). Those increases were gradual over the time period, with no notable inflections in the trend line. Similar to daily mean temperature, monthly mean diurnal temperature ranges demonstrated general increases in diurnal temperature fluctuations (fig. 27).

Dissolved Oxygen

Similar to water temperature, there was substantial diurnal variability in dissolved oxygen concentration at both stations. For example, dissolved oxygen concentrations ranged between about 7 and 12 mg/L on some days. Diurnal variability in dissolved oxygen typically was less on days with elevated streamflow from precipitation events, such as from July 1 to July 7 and July 9 to July 17, 2007 (fig. 28). Daily mean dissolved oxygen concentration at the Britton Road station ranged from 1.9 mg/L to 24 mg/L with a smallest daily minimum of 0.2 mg/L and a largest daily maximum of 25 mg/L . Daily mean dissolved oxygen concentration at the Harrah station ranged from 1 mg/L to 18.7 mg/L with a smallest daily minimum of 0.1 mg/L and a largest daily maximum of 23.7 mg/L . The greatest diurnal ranges in dissolved oxygen concentration at the Britton Road and Harrah stations were 20.8 mg/L and 23.7 mg/L , respectively. Minimum dissolved oxygen concentrations typically were measured at night (fig. 28), likely caused by cessation of the light cycle of photosynthesis by aquatic plants, respiration by plants, and respiration of aerobic bacteria breaking down organic matter in the water column and bed sediments during those hours (Hem, 1985). Hypoxia was observed periodically at both stations, mostly from spring through the late summer months (April through September).

During some summer days, when algae and other aquatic plants produce relatively large amounts of oxygen by photosynthesis, daily maximum dissolved oxygen concentrations between 20 and 25 mg/L were recorded (fig. 18). Such concentrations are super-saturated compared to the equilibrium concentration of 7.54 mg/L dissolved oxygen at 30 °C (Hem, 1985). Super-saturated daily maximum dissolved oxygen concentrations also were observed during non growing-season days and may be attributable to low water temperature and ice formation (Mathias and Barica, 1985), extreme changes in barometric pressure (Craig and Weiss, 1971), or entrainment of air in water by turbulent streamflow (Clark, 1977).

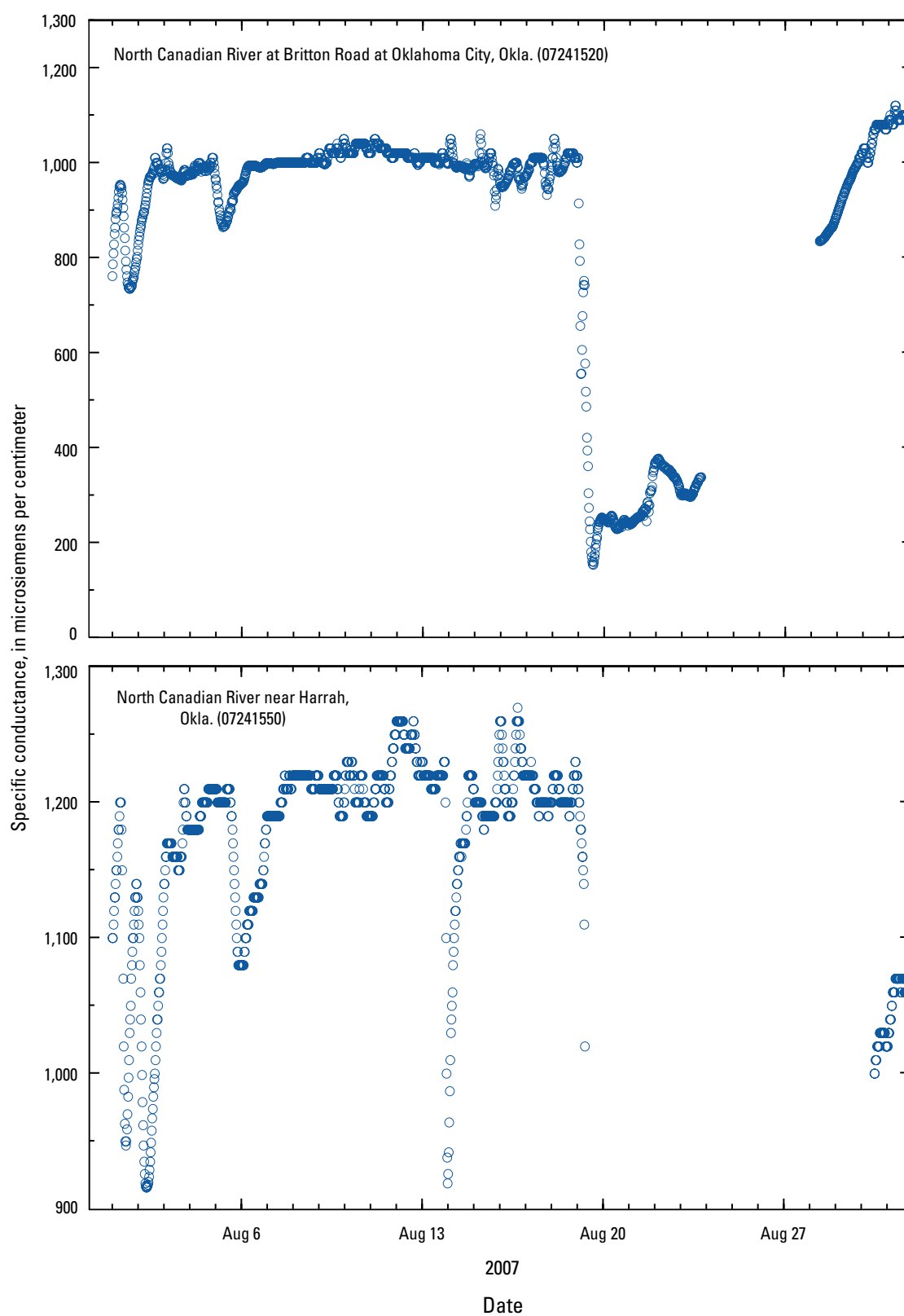


Figure 17. Instantaneous specific conductance measured at 30-minute intervals in August 2007 at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations.

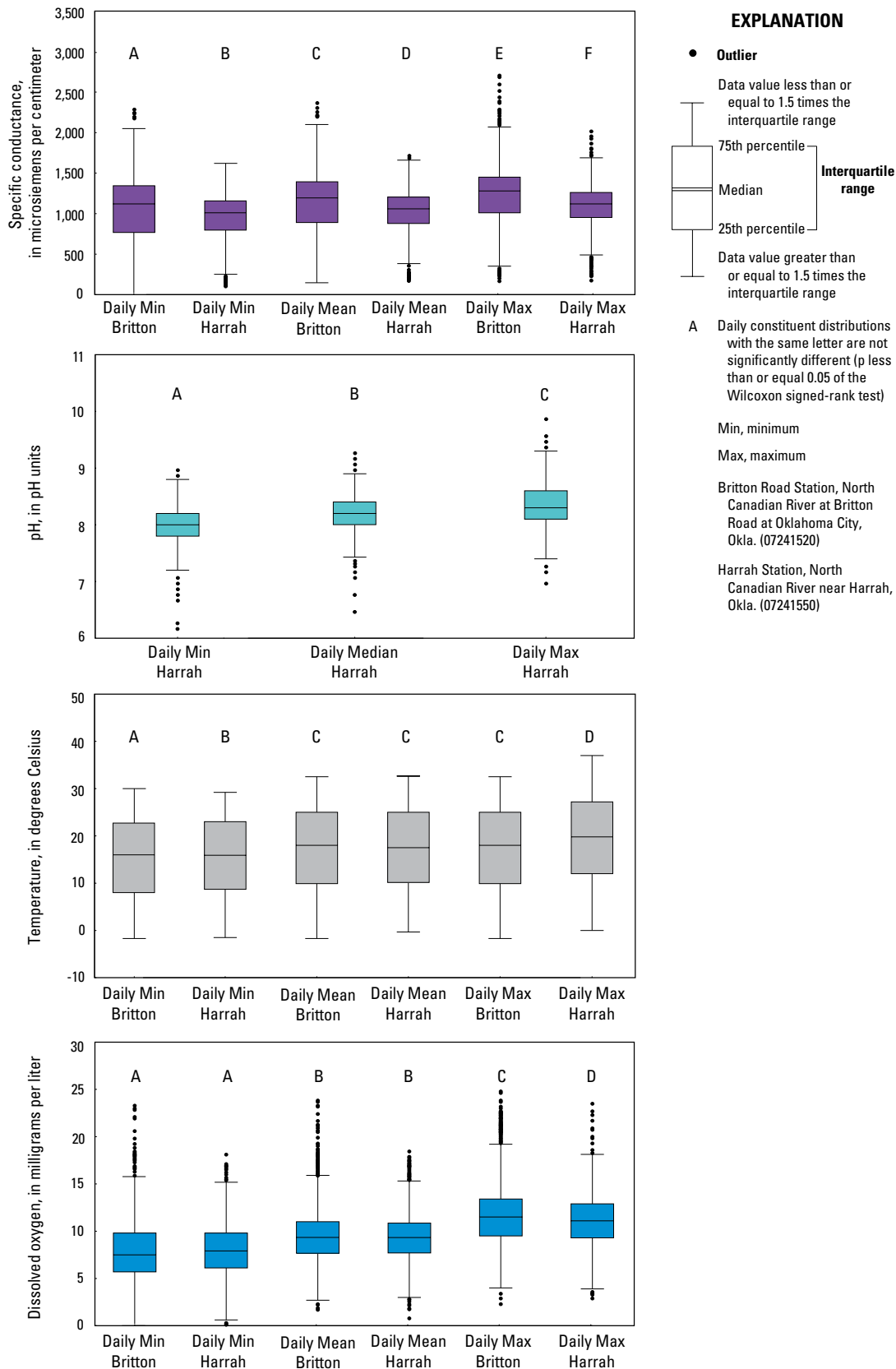
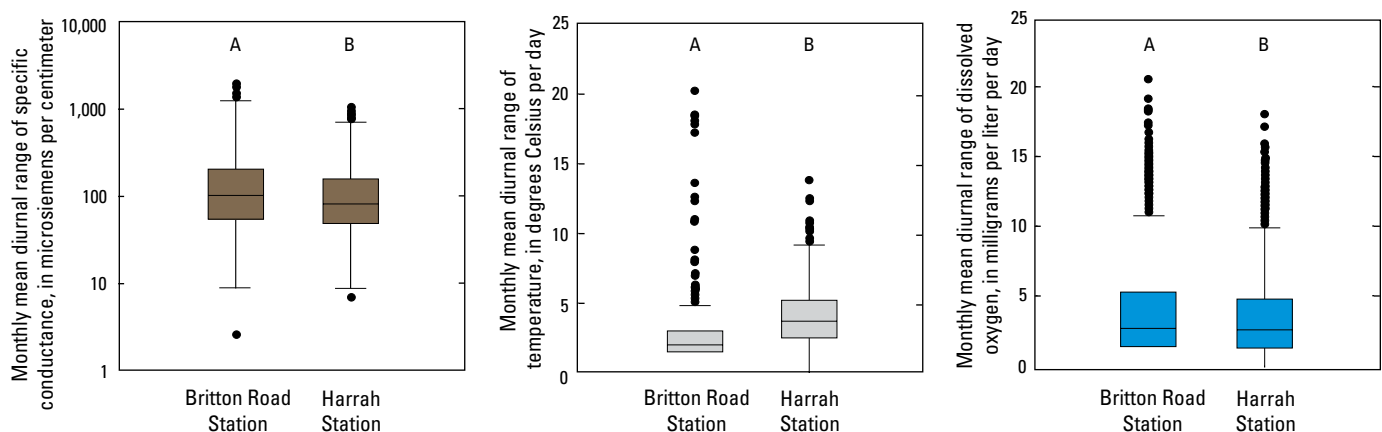


Figure 18. Daily mean specific conductance, pH, temperature, and dissolved oxygen concentration from continuous-monitor measurements at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

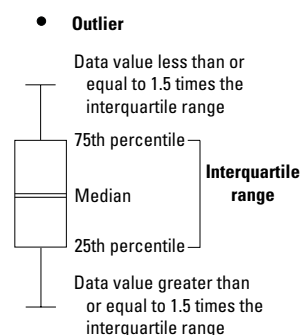
Table 9. Results of Wilcoxon rank-sum and signed-rank tests for comparison of daily values of physical water-quality properties, computed from continuous water-quality monitor measurements, between the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

[Minimum daily value, minimum of instantaneous values for a day; Mean daily values, mean of instantaneous values for a day; Maximum daily values, maximum of instantaneous values for a day; Diurnal range, maximum daily value minus minimum daily value; Rank-sum, Wilcoxon rank-sum test; Signed-rank, Wilcoxon signed-rank test; z-score, normal test statistic with correction for ties; p-value, probability value; values in red shade indicate statistically significant differences between groups of data collected at the two streamflow-gaging stations at 95-percent confidence level (probability value less than or equal to 0.05); <, less than]

Daily value type	Time period	Dissolved oxygen (milligrams per liter)		Specific conductance (microsiemens per centimeter)		Water temperature (degrees Celsius)	
		Median	p-value	Z-score	p-value	Z-score	p-value
Minimum daily values	Rank-sum	-0.56	0.571	18.0	<0.0001	3.4	<0.0001
	Signed-rank	4.13	<.0001	-17.9	<.0001	18.3	<.0001
Mean daily values	Rank-sum	1.72	.085	22.6	<.0001	-.5	.616
	Signed-rank	9.10	<.0001	23.4	<.0001	-10.7	<.0001
Maximum daily values	Rank-sum	6.14	<.0001	27.8	<.0001	14.3	<.0001
	Signed-rank	11.50	<.0001	29.0	<.0001	46.6	<.0001
Diurnal range	Rank-sum	5.22	<.0001	11.5	<.0001	57.0	<.0001
	Signed-rank	8.64	<.0001	11.5	<.0001	58.1	<.0001



EXPLANATION



A Daily constituent distributions with the same letter are not significantly different (p less than or equal 0.05 of the Wilcoxon signed-rank test)

Britton Road Station, North Canadian River at Britton Road at Oklahoma City, Okla. (07241520)

Harrah Station, North Canadian River near Harrah, Okla. (07241550)

Figure 19. Monthly mean diurnal ranges of specific conductance measured by continuous monitors at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

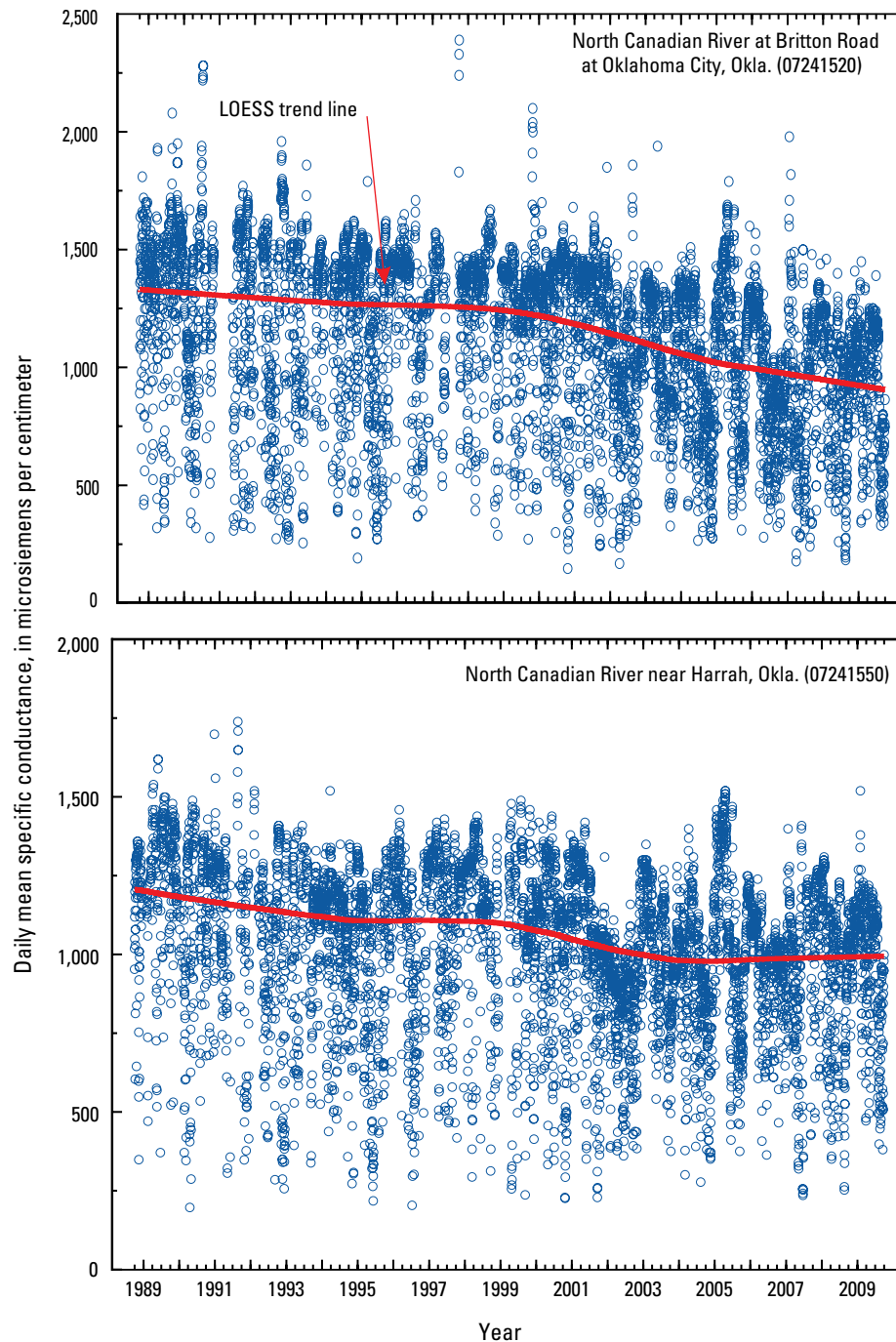


Figure 20. Daily mean specific conductance computed from continuous-monitor measurements at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

There were significant differences in maximum dissolved oxygen concentrations and the diurnal range of concentrations between the two stations. Rank-sum tests indicated that the locations of distribution of daily maximum dissolved oxygen concentrations and diurnal ranges of dissolved oxygen concentrations were significantly greater at the Britton Road station than at the Harrah station (fig. 19, table 9). Although

there were significant differences in maximum and diurnal dissolved oxygen concentrations, the locations of distribution of daily mean and daily minimum dissolved oxygen concentrations were not significantly different between stations (fig. 18, table 9), which is consistent with significant differences in dissolved oxygen concentrations in water samples collected at the two stations (fig. 16, table 8). Signed-rank tests, however,

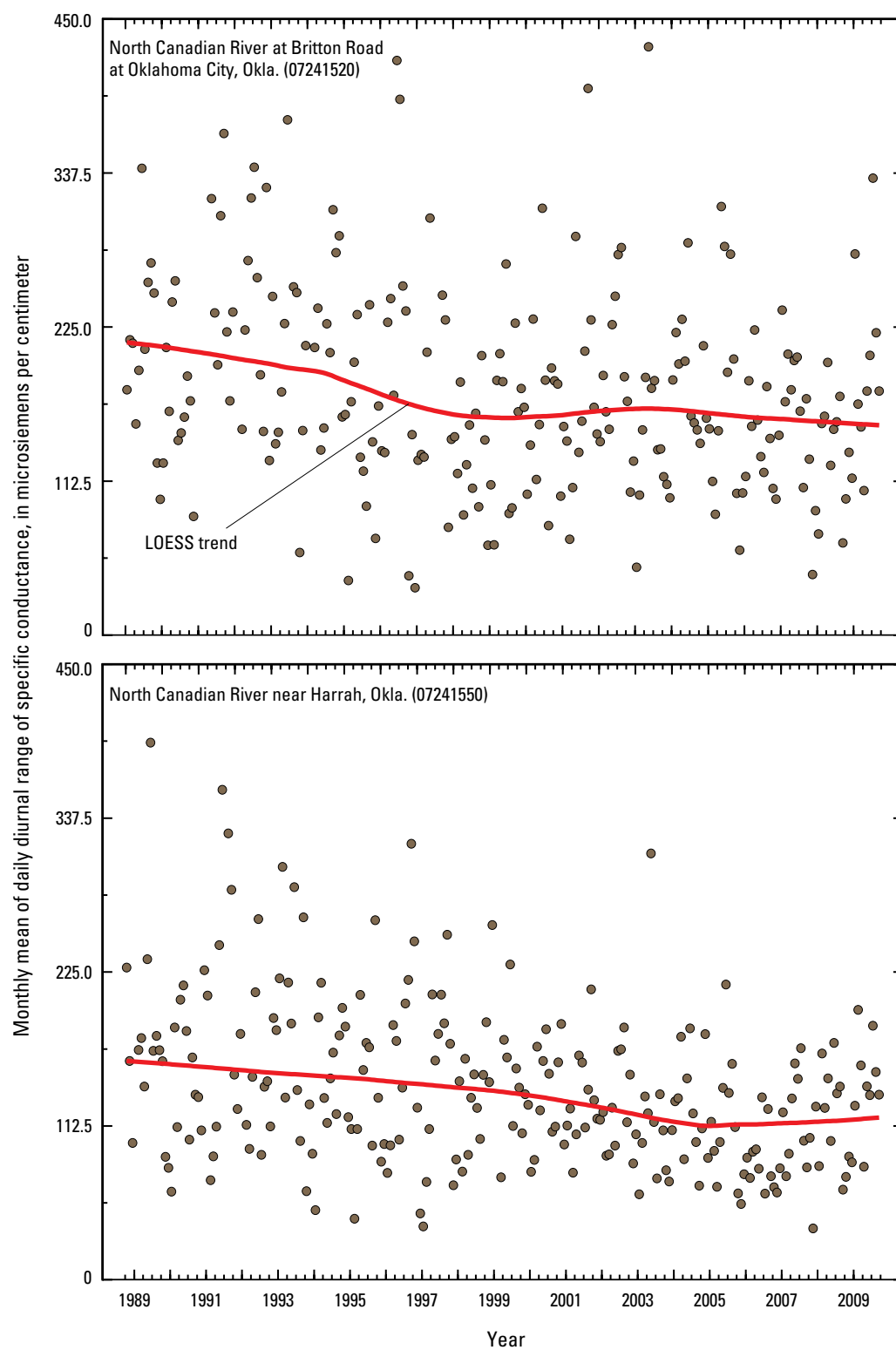


Figure 21. Monthly means of diurnal ranges of specific conductance measured by continuous monitors at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

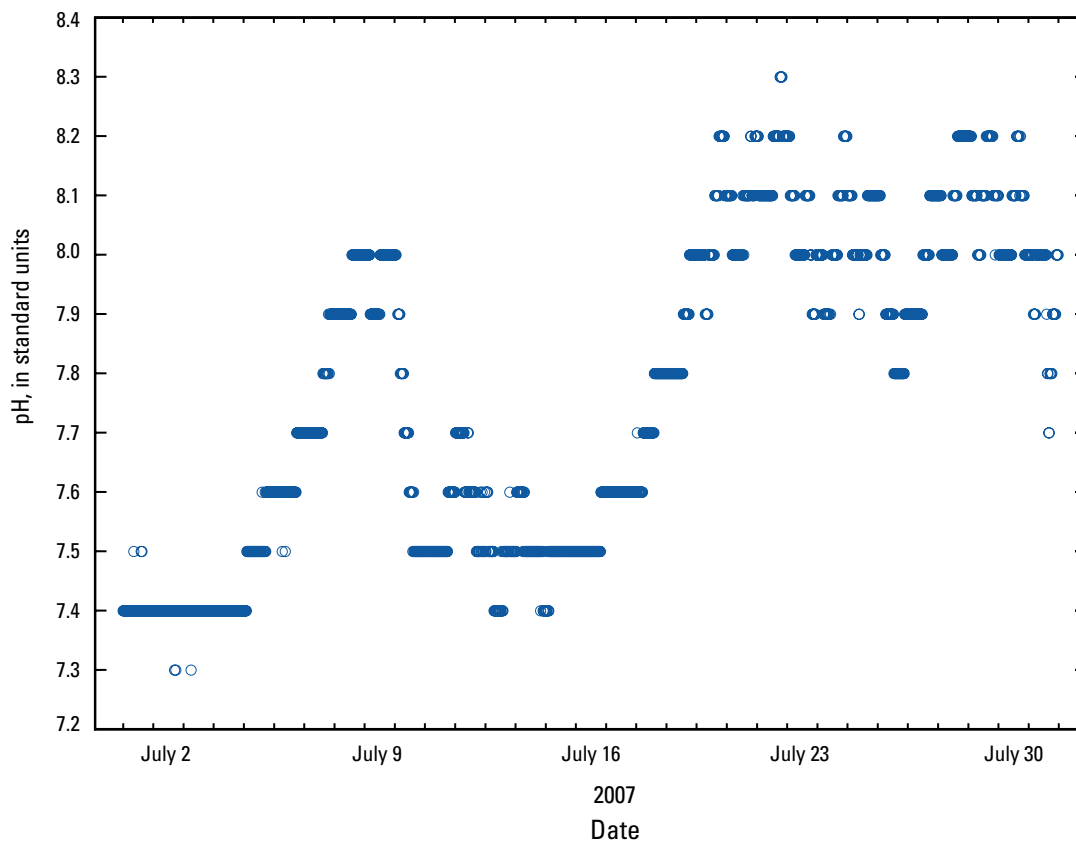


Figure 22. pH values measured at 30-minute intervals in July 2007 at the North Canadian River near Harrah, Oklahoma, streamflow-gaging station.

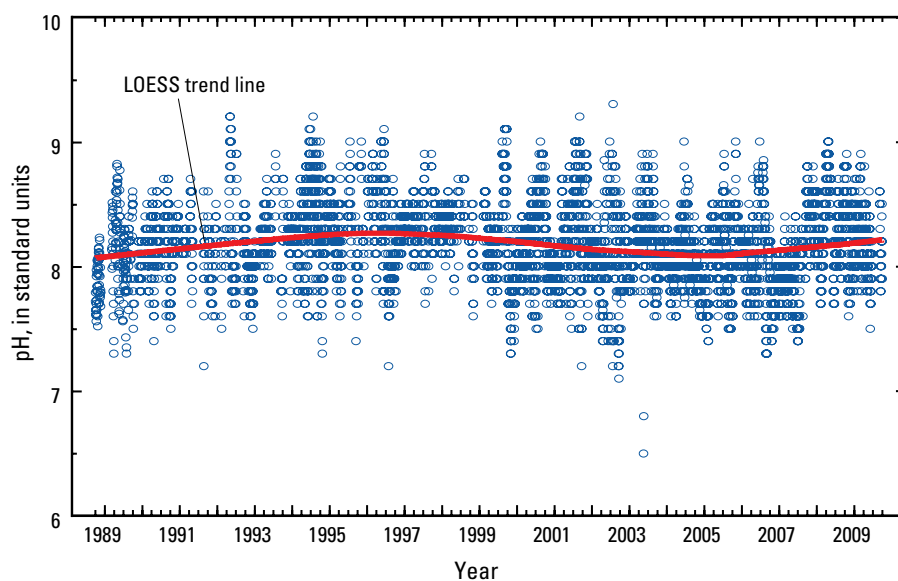


Figure 23. Daily median pH computed from continuous-monitor measurements at the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1988–2009.

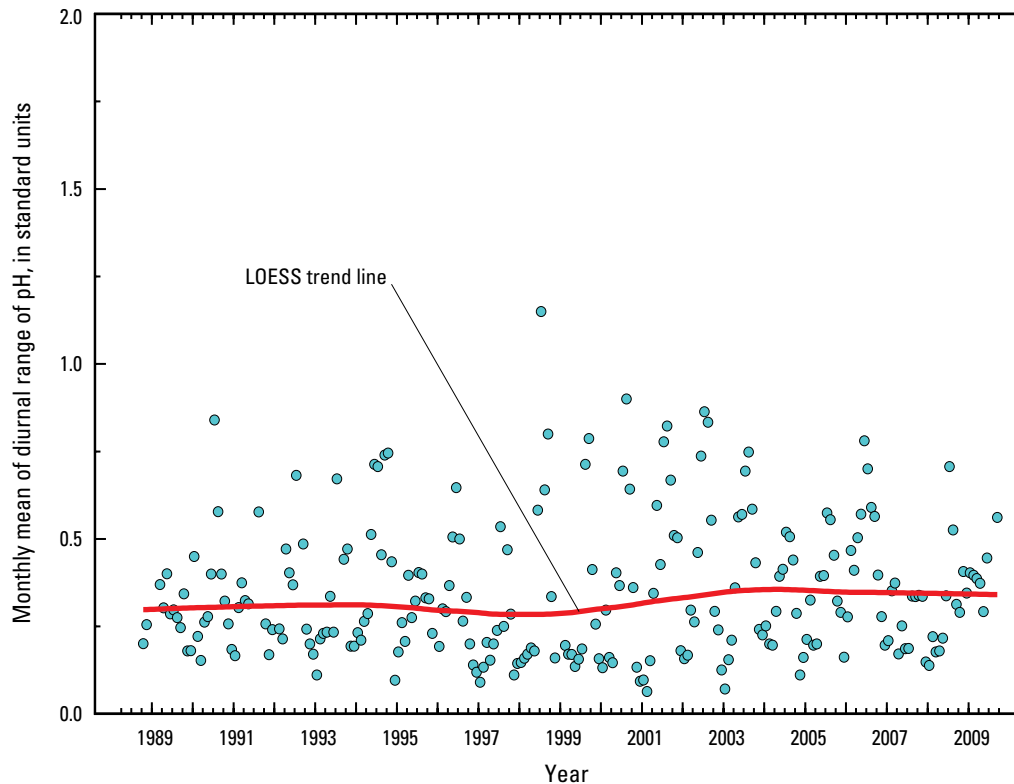


Figure 24. Monthly means of diurnal ranges of pH measured from continuous monitors at the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1988–2009.

indicated that the median and distribution of daily minimum, daily mean, and daily maximum and diurnal concentrations on paired days were all significantly greater at the Britton Road station than the Harrah station (figs. 18 and 19, table 9).

Based on LOESS curves, daily mean dissolved oxygen concentrations increased slightly and gradually from 1988 to 2004 at the Britton Road station and from 1988 to 2002 at the Harrah station, and decreased slightly thereafter (fig. 29). No obvious trends were detected in the monthly mean diurnal range of dissolved oxygen concentrations from 1988–2009, although there was substantial variability in those mean concentrations (fig. 30). Extremely low (less than 2 mg/L) daily mean dissolved oxygen concentrations were more frequent after 1999. To investigate this trend, an additional graph was created to show a LOESS curve fit to daily minimum dissolved oxygen with time (fig. 31). Daily minimum dissolved oxygen decreased notably at the Harrah station after 1999. In addition, minimum dissolved oxygen concentrations indicated more hypoxic conditions at the Harrah station compared to the Britton Road station after 1999.

Qualitative Trends in Biochemical Oxygen Demand, Fecal Bacteria, and Chlorophyll *a*

Biochemical oxygen demand (BOD) concentrations generally increased with time, starting about 1994, in water samples collected at the Britton Road and Harrah stations.

After about 1999, BOD concentrations remained stable at the Britton Road station, but gradually decreased at the Harrah station (fig. 32).

Counts of fecal coliform were highly variable at both stations. There were slight decreases in fecal coliform bacteria counts from 1988–2009 at the Britton Road station, indicated by the LOESS curve fit to those data (fig. 33). There were no clear directional changes in the LOESS curve fit to fecal coliform bacteria counts with time in water samples collected at the Harrah station. Like fecal coliform bacteria, counts of fecal streptococcal bacteria were highly variable with time at both stations (fig. 34). There were slight upward trends in counts of fecal streptococcal bacteria for most of the period from 1988–2009 at both stations (fig. 34).

Chlorophyll *a* concentrations corrected and not corrected for pheophytin concentration increased slightly with time in water samples collected at the Harrah station (fig. 35). Although the slope of the LOESS curve for uncorrected chlorophyll *a* appeared to increase substantially after 1984, substantially fewer samples were collected prior to 1987, which may have biased the slope of the line if those samples were not representative of typical chlorophyll *a* concentrations. For samples collected after 1987, similar slopes of the LOESS curve for uncorrected and corrected chlorophyll *a* concentrations indicate that the effect of pheophytin on chlorophyll *a* concentrations probably did not change with time.

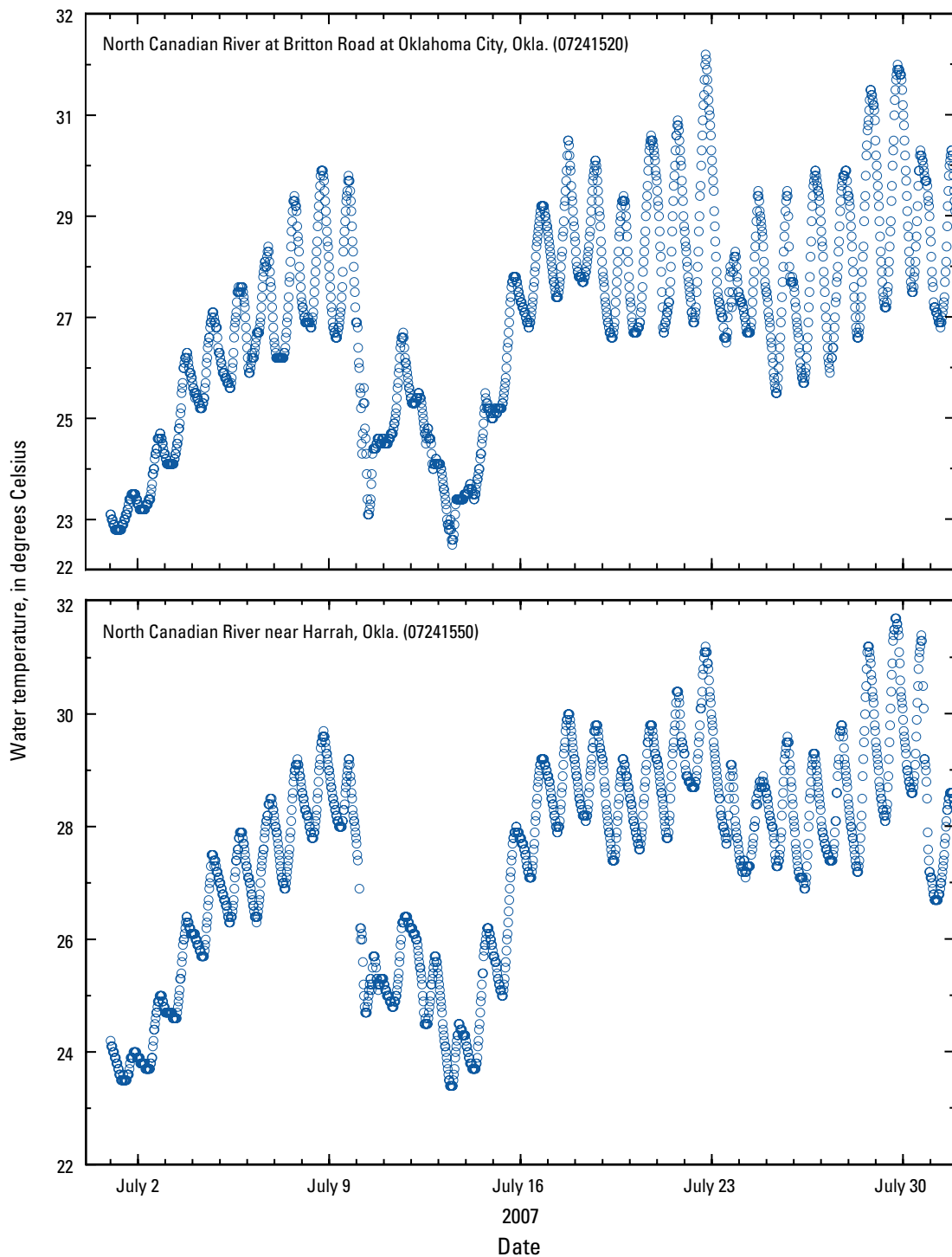


Figure 25. Instantaneous water temperature measured at 30-minute intervals in July 2007 at the North Canadian River, Oklahoma, at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations.

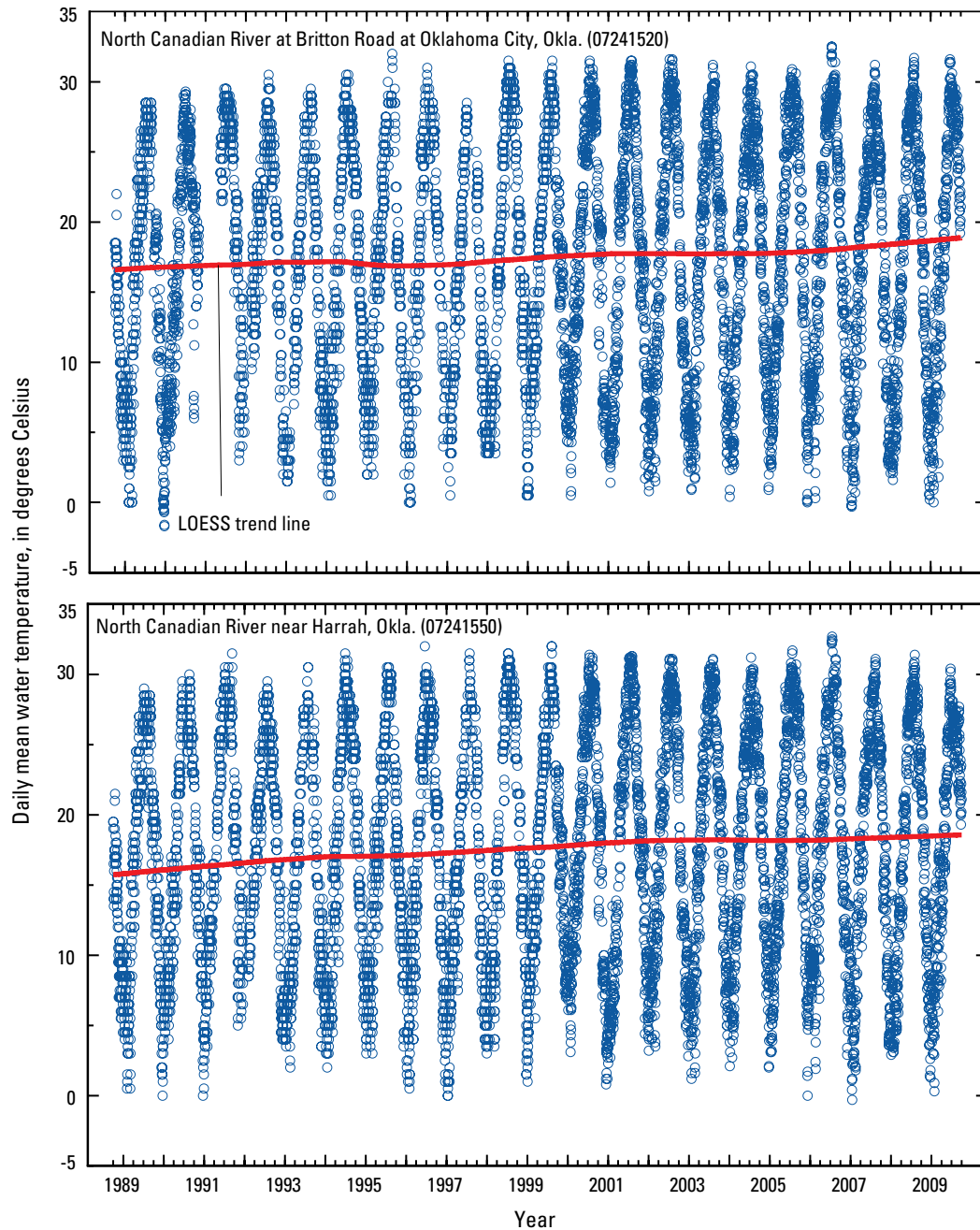


Figure 26. Daily mean water temperature computed from instantaneous continuous-monitor measurements at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

Quantitative Trends in Dissolved Oxygen and Nutrients

No significant trends with time were observed in dissolved oxygen, nitrogen, and phosphorus concentrations (table 10) from 1988–2009. Although no significant trends were detected, Kendall's tau was positive for dissolved oxygen and nitrogen concentrations with time, and was negative for dissolved phosphorus.

Flow adjustment was applied to dissolved nitrogen and phosphorus concentrations. Water-temperature adjustment and flow adjustment were applied to dissolved oxygen concentrations because those parameters were significantly correlated to dissolved oxygen concentration at a p-value of 0.05. PRESS statistics and partial t-test results indicated that relations between streamflow and water temperature accounted for more of the variability in dissolved oxygen concentration than each individual variable. The log-log LOESS model was the

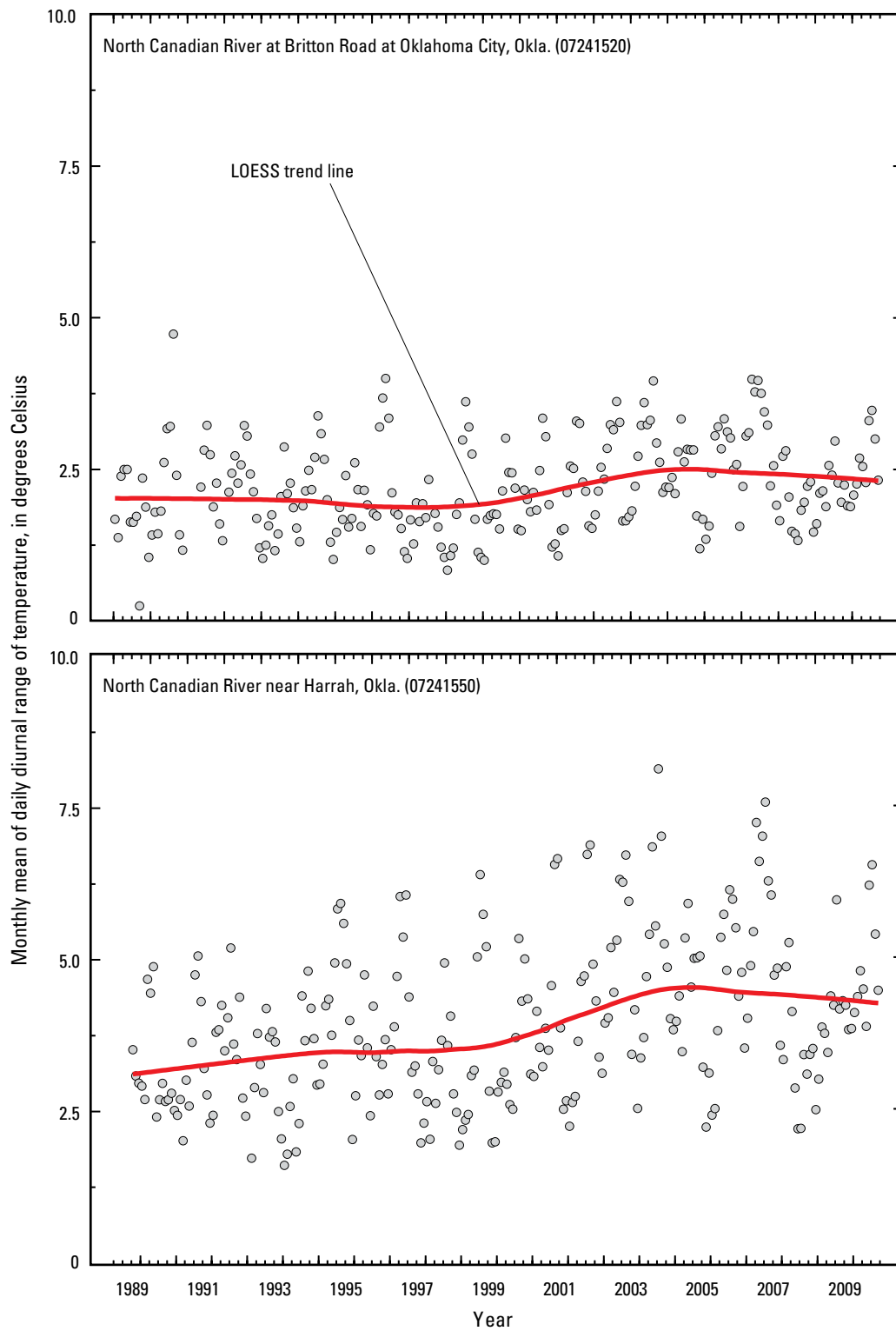


Figure 27. Monthly mean of diurnal ranges of temperature measured by continuous monitors at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

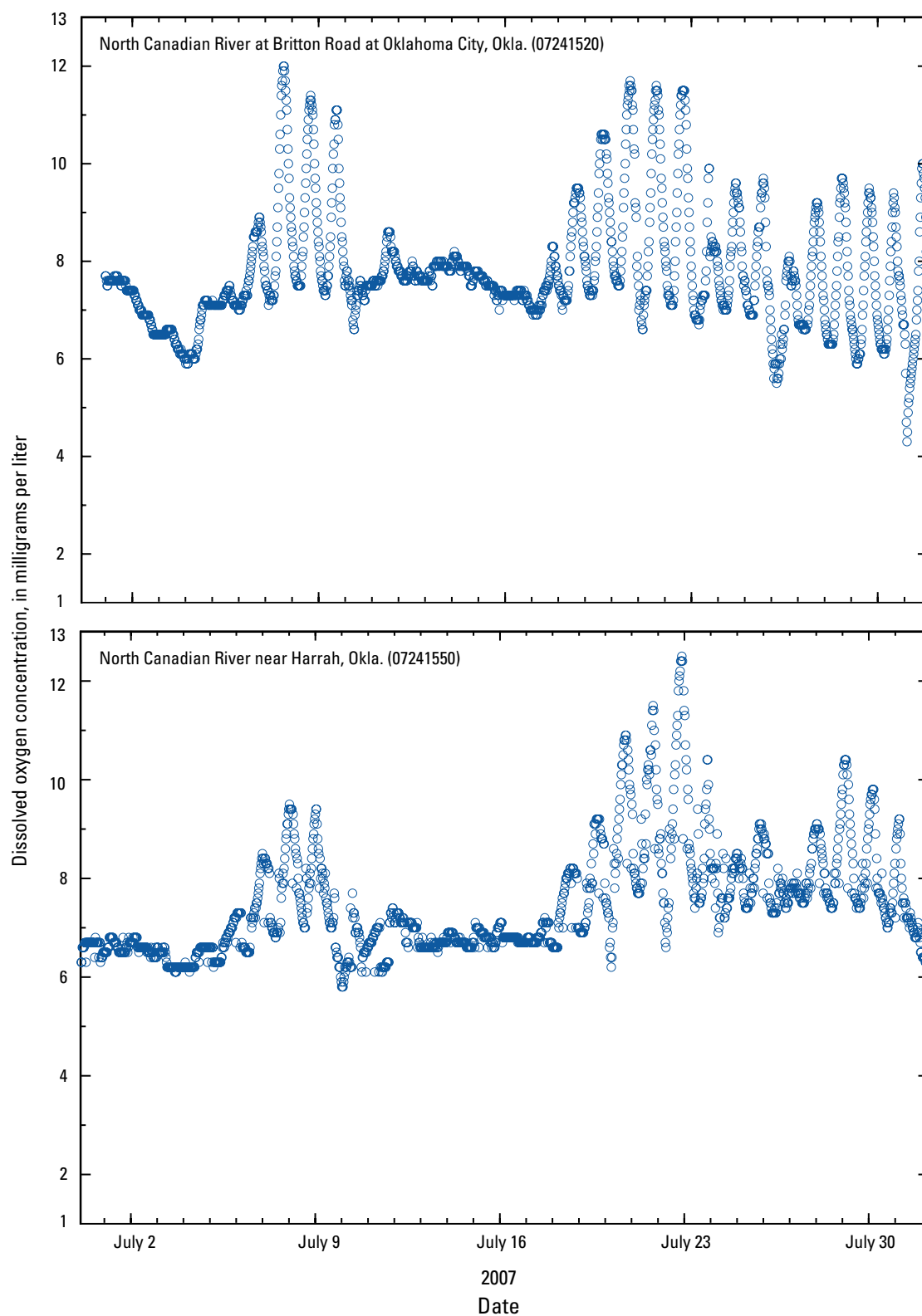


Figure 28. Dissolved oxygen concentration measured at 30-minute intervals in July 2007 at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations.

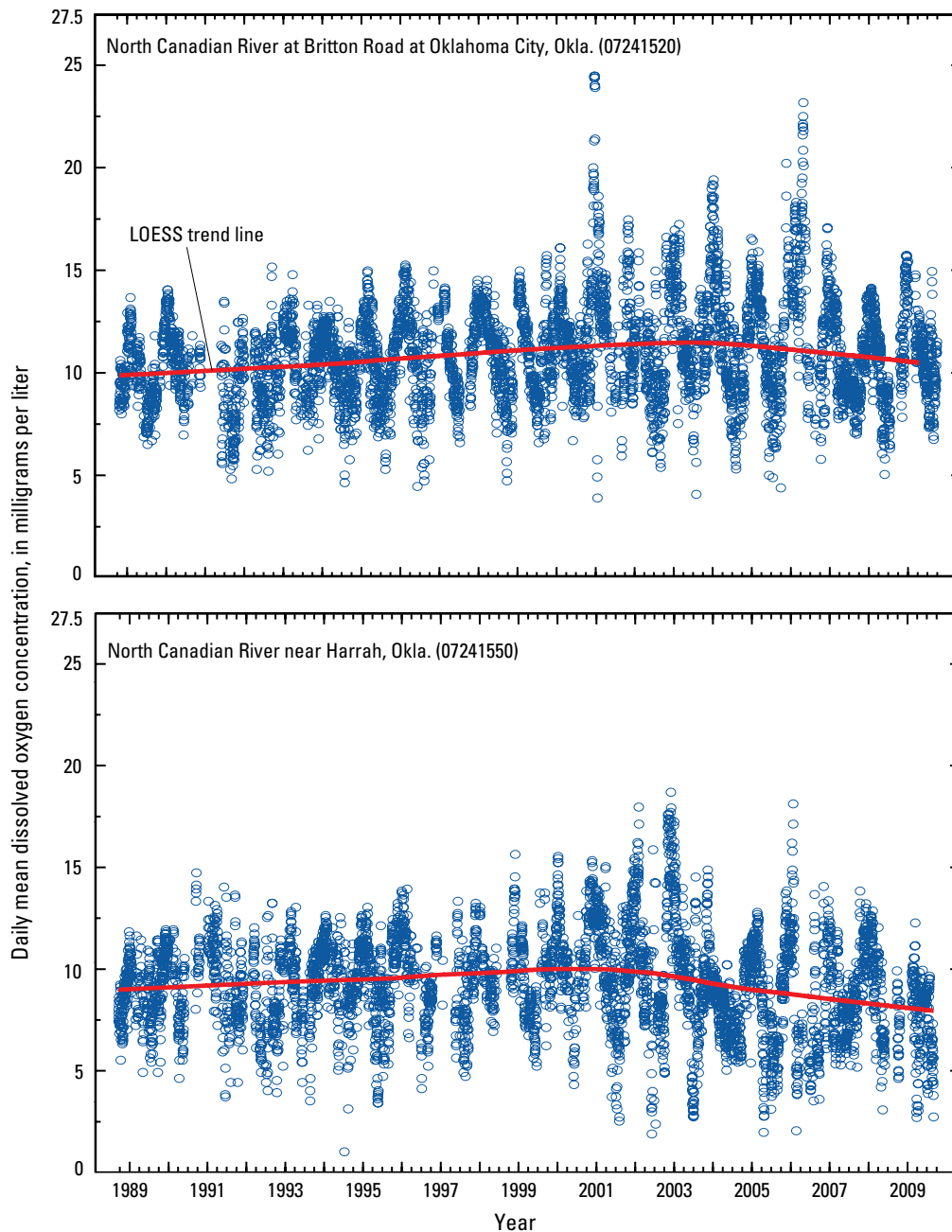


Figure 29. Daily mean dissolved oxygen concentrations computed from continuous-monitor measurements at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

best model for flow-adjustment for dissolved nitrogen and phosphorus concentrations because the best linear regression and the LOESS regression for untransformed concentrations and streamflow did not result in normally distributed error residuals for either constituent. The log-log LOESS model also was the best model for adjustment of dissolved oxygen concentrations using streamflow and water temperature because the PRESS was less for the log-log LOESS regression than for the best linear regression for this constituent.

Relations between streamflow and dissolved nitrogen and phosphorus concentrations were negative, indicating that as streamflow increases, dissolved nutrient concentrations were diluted (figs. 36 and 37). Although trends in unfiltered (total) nitrogen and phosphorus concentrations were not analyzed because of a short record, relations between streamflow and total concentrations of nitrogen and phosphorus also were negative (fig. 38). These relations indicate that most of the nitrogen and phosphorus concentrations in water

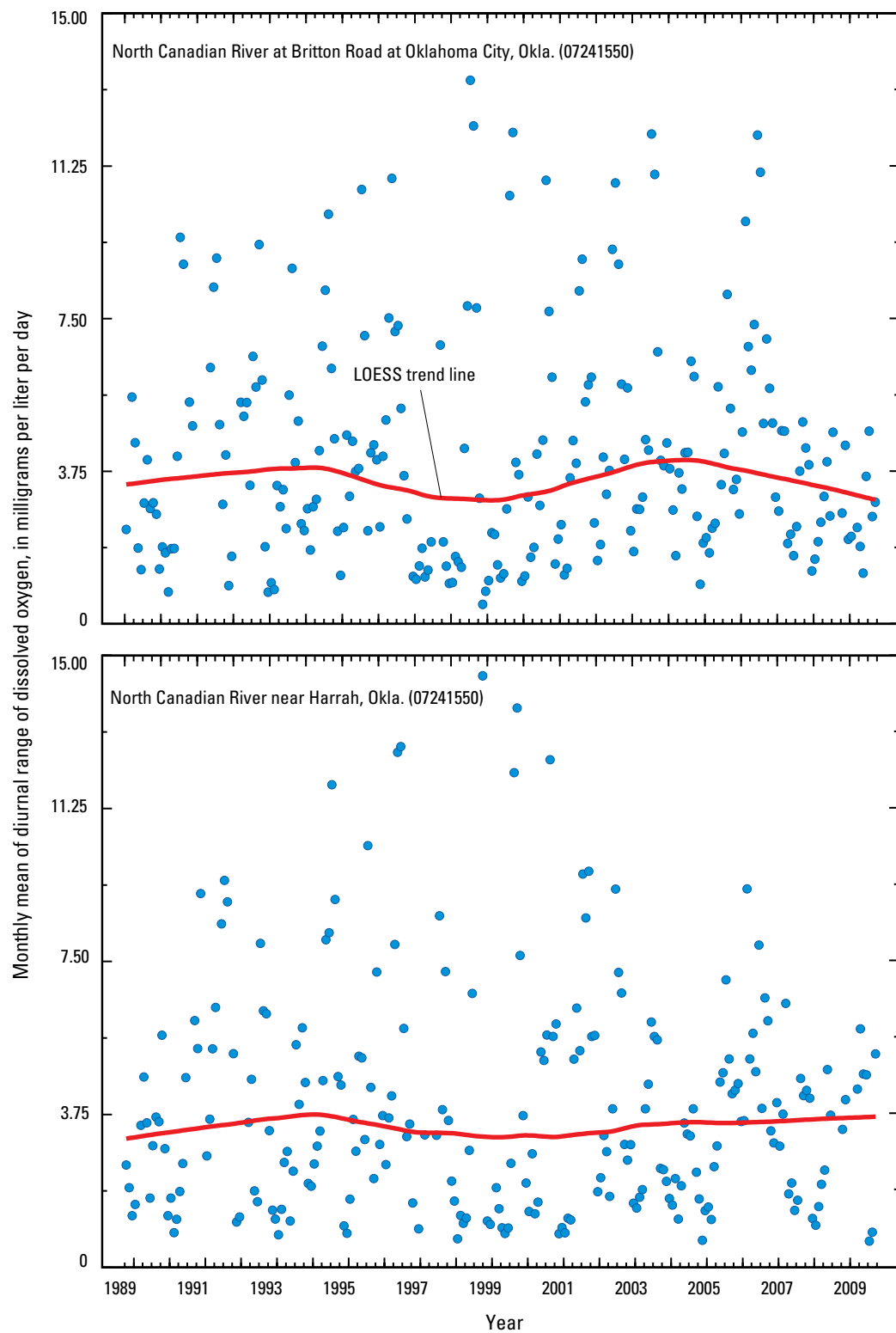


Figure 30. Monthly means of diurnal ranges of dissolved oxygen measured by continuous monitors at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

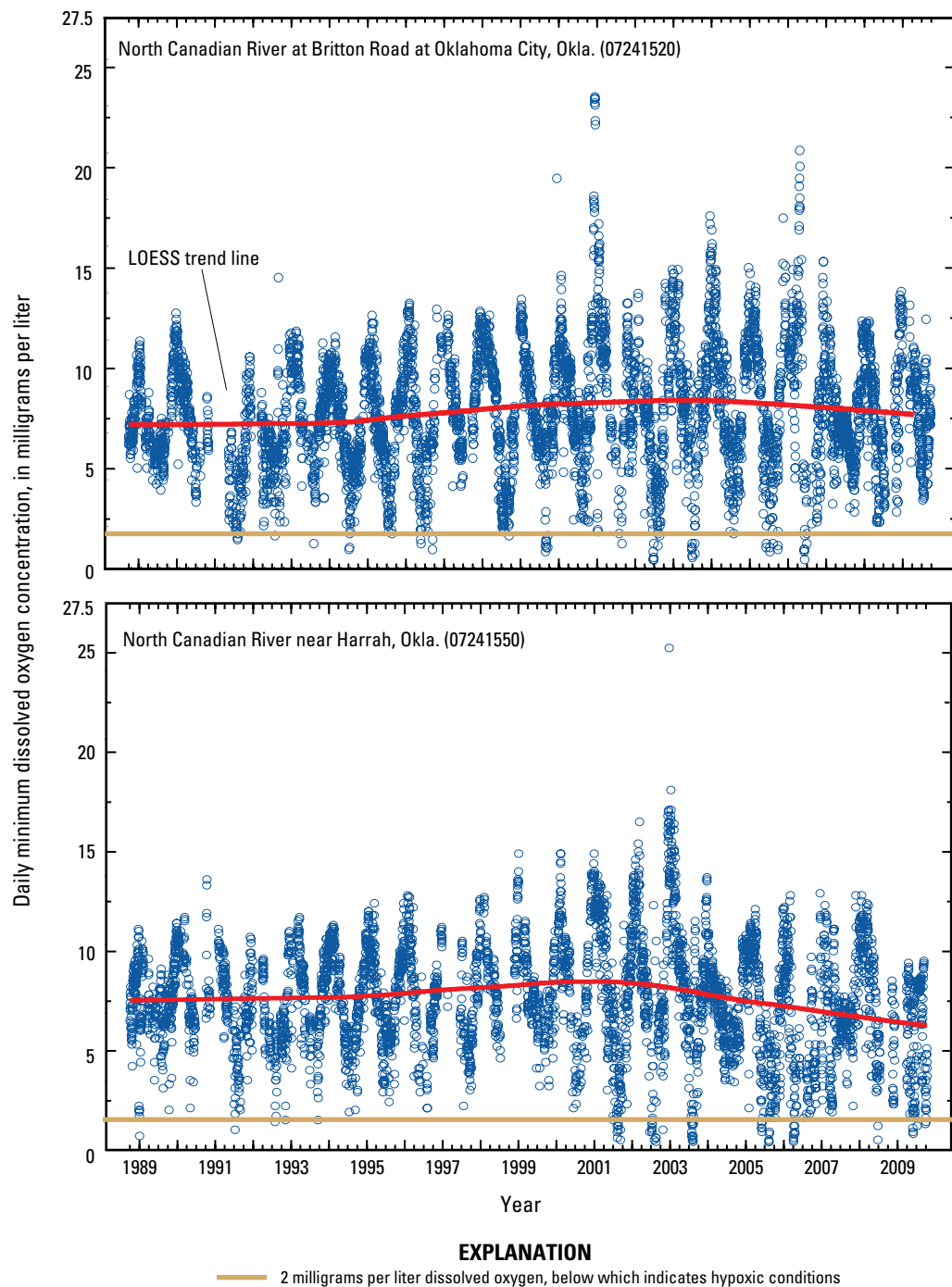


Figure 31. Daily minimum dissolved oxygen concentrations computed from continuous-monitor measurements at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

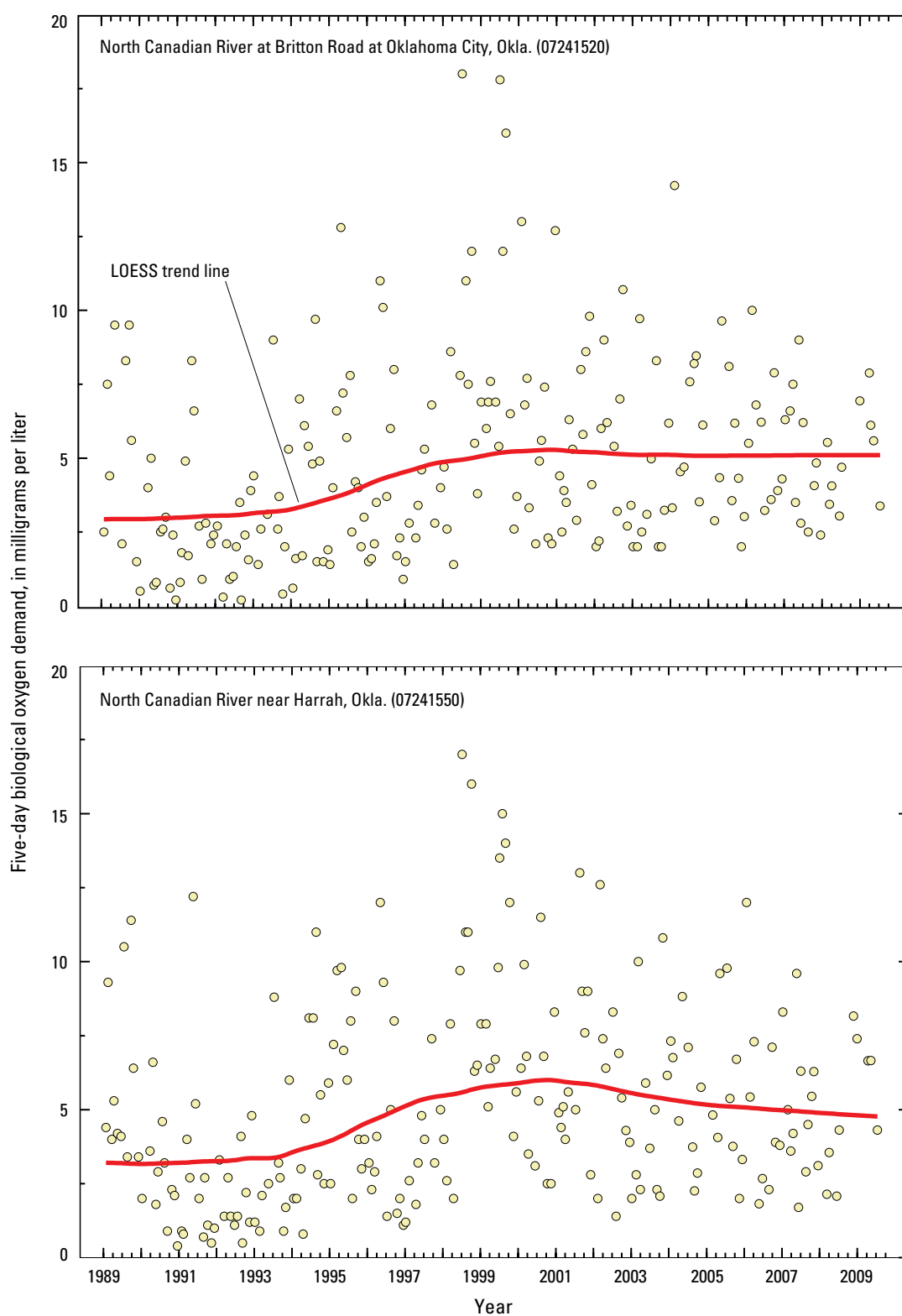


Figure 32. Biological oxygen demand (BOD) of water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

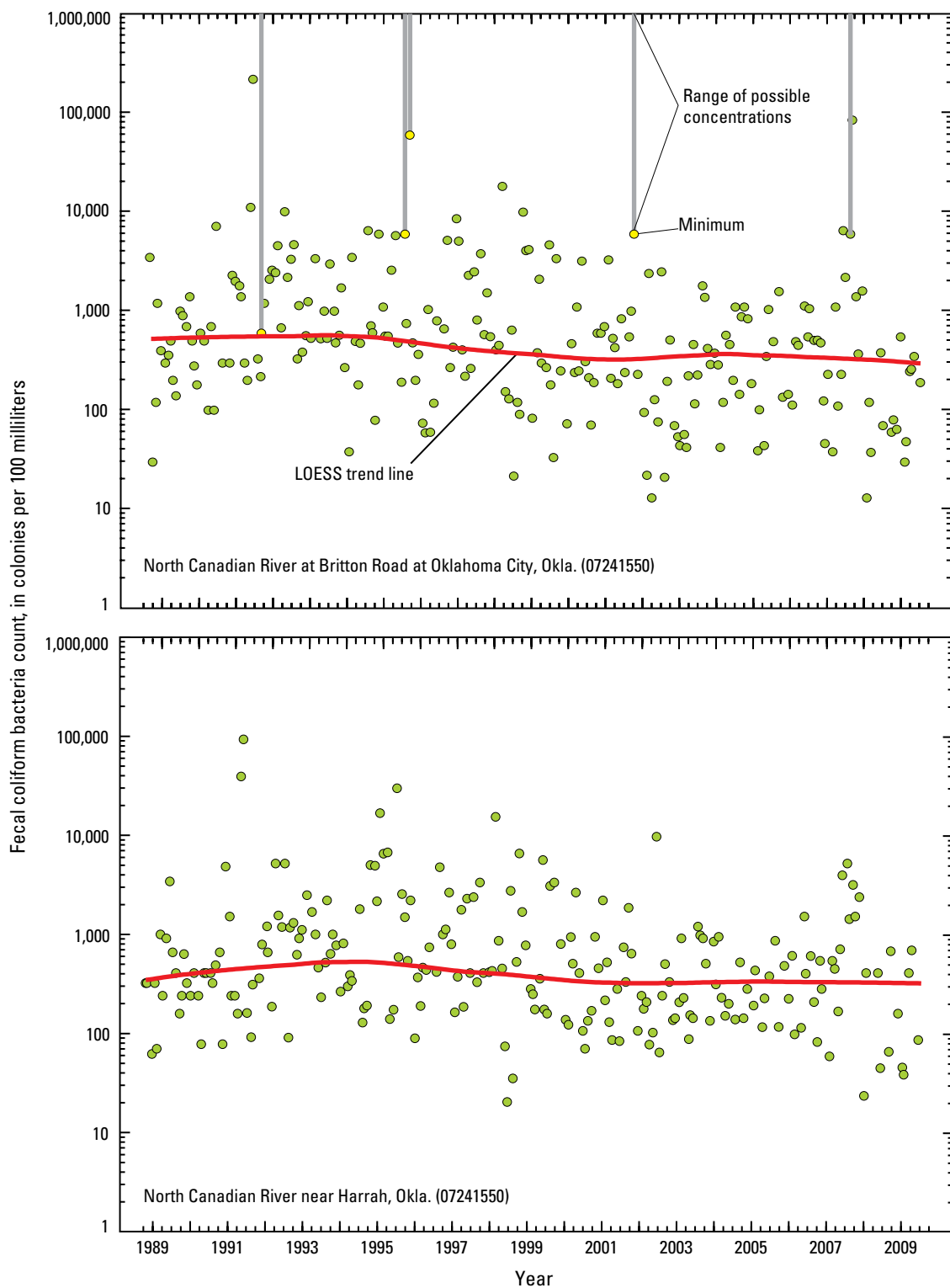


Figure 33. Fecal coliform bacteria counts of water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

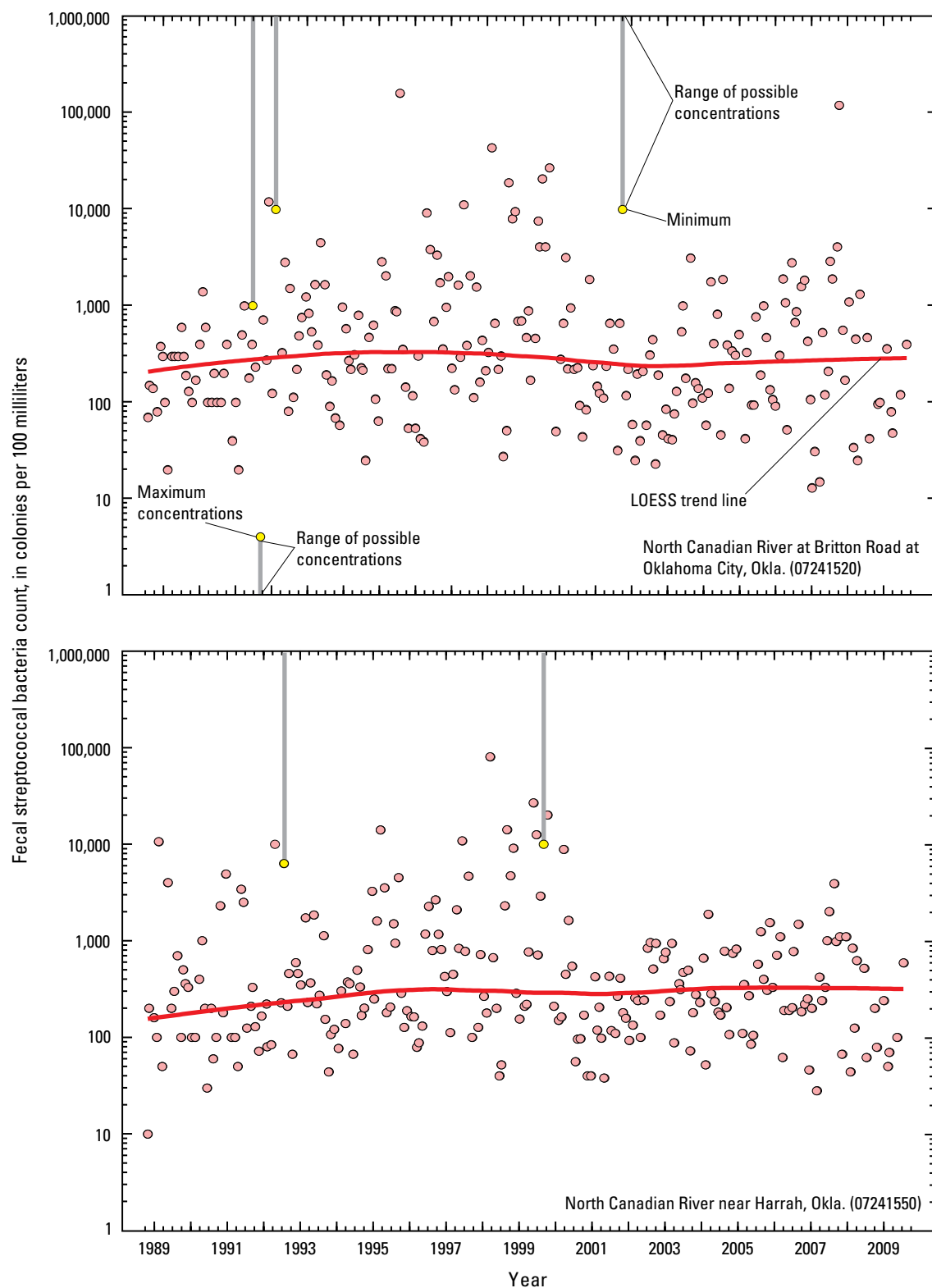


Figure 34. Fecal streptococcal bacteria counts of water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

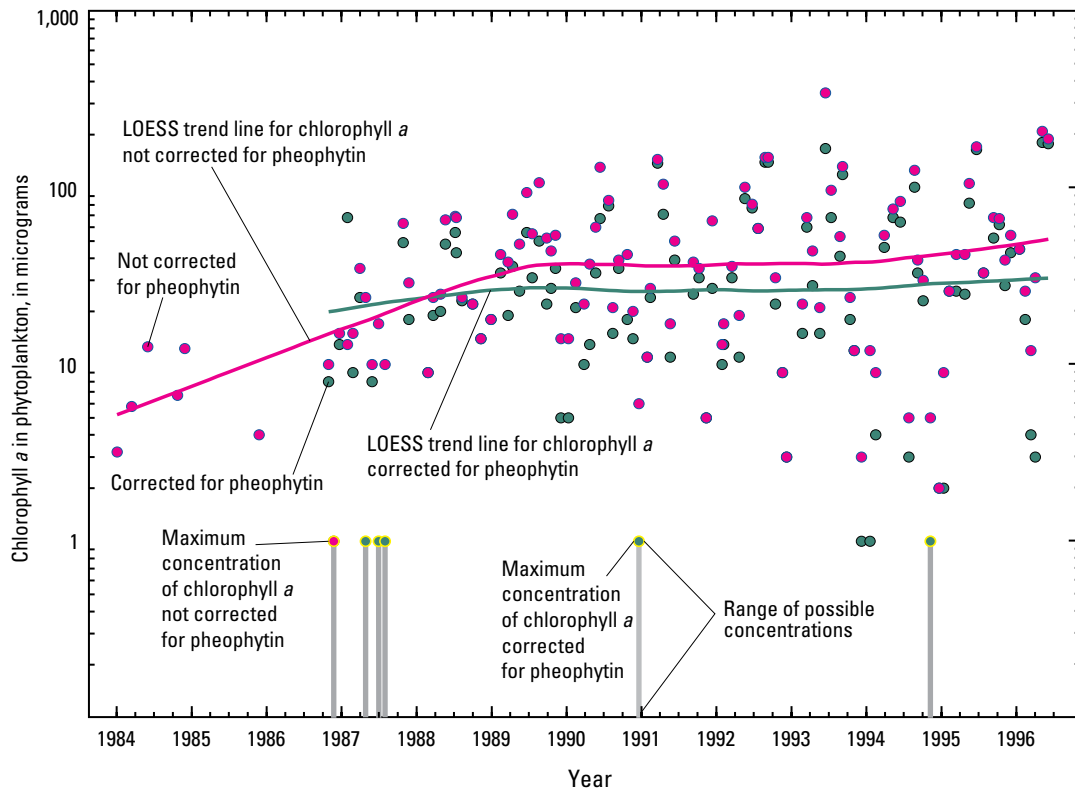


Figure 35. Chlorophyll *a* concentrations of water samples collected at the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1984–1996.

at the Britton Road and Harrah stations probably were from point sources, such as effluent from municipal WWTPs upstream from these stations, which are diluted by storm events.

There were no significant trends in flow-adjusted dissolved nitrogen and flow-adjusted and water-temperature-adjusted dissolved oxygen concentrations from 1988–2009 at either station (figs. 36 and 39, table 10). Significant downward trends in flow-adjusted dissolved phosphorus concentrations were detected in water samples collected at the Britton Road station, but not in water samples collected at the Harrah station (fig. 37, table 10).

Graphs of dissolved nitrogen and phosphorus concentrations with time indicate a potential change in trends caused by changes in streamflow or changes in water quality. Inflections in the LOESS curves fit to dissolved nitrogen and phosphorus concentrations and flow-adjusted dissolved nitrogen and phosphorus concentrations around the years 1998–99 (figs. 36–37, and 39) indicate that a change in streamflow, water quality, or both, may have taken place during that time. There were statistically significant downward trends in the Q_{90} and $7Q_{min}$ at both stations after 1998. Although not statistically significant after precipitation-adjustment, decreases in the annual Q_{90} and $7Q_{min}$ have been visually detected since

1999 (fig. 10), indicating decreases in low flow in response to changes in streamflow regulation or water demand (see section titled “Evaluation of Streamflow”). Changes in streamflow may change relations between nutrient concentrations and streamflow, causing changes in flow-adjusted concentrations. LOESS curves indicate that dissolved nitrogen and phosphorus concentrations decreased from 1988–98, and increased from 1999–2009.

Significance of monotonic trends with time in dissolved oxygen, nitrogen, and phosphorus concentrations also were evaluated separately for water samples collected at the Britton Road and Harrah stations from 1988–98 and 1999–2009 with the Seasonal Kendall’s tau test. Although an inflection in the plot of dissolved oxygen with time was not as clearly observed as inflections in the plots for nutrients, trends were also re-assessed for dissolved oxygen for the two separate periods to be consistent. Trend-analysis procedures for dissolved oxygen and nutrient concentrations during both periods were the same as those used to analyze the period 1988–2009.

There were no significant trends in dissolved oxygen concentration from 1988–99 in water samples collected at either station before or after adjustment for precipitation and temperature (table 10). From 1999–2009 there were significant downward trends in dissolved oxygen concentration in

Table 10. Results of Seasonal Kendall's tau tests of time trends of dissolved oxygen, nitrogen, and phosphorus in water samples collected at two streamflow-gaging stations on the North Canadian River, Oklahoma, 1988–2009.

[Tau, Kendall's tau; p-value, probability level; Raw, monotonic trend in constituent concentration without flow adjustment; Flow adjusted, trend adjusted for streamflow; mg/L, milligrams per liter; Britton Road, North Canadian River at Britton Road at Oklahoma City, Oklahoma (U.S. Geological Survey station identification number 07241520); Harrah, North Canadian River near Harrah, Oklahoma (U.S. Geological Survey station identification number 07241550); results shaded in red are statistically significant at a p-value of 0.05]

Constituent	Station	Raw			Flow adjusted		
		Tau	p-value	Slope (mg/L)	Tau	p-value	Slope (mg/L)
1988–2009							
Dissolved oxygen, in mg/L	Britton Road	+0.15	0.076	0.064	+0.140	0.091	0.006
	Harrah	+0.11	.181	.047	+0.090	.242	.003
Dissolved nitrogen, in mg/L	Britton Road	+0.09	.273	.020	-.001	.995	.000
	Harrah	+0.15	.109	.053	+0.125	.112	.011
Dissolved phosphorus, in mg/L	Britton Road	-.02	.811	-.001	-.200	.028	-.019
	Harrah	-.04	.693	-.005	-.120	.282	-.011
1988–1998							
Dissolved oxygen, in mg/L	Britton Road	.017	.912	.016	-.09	.577	-.007
	Harrah	+0.12	.271	.100	+0.14	.211	.009
Dissolved nitrogen, in mg/L	Britton Road	-.310	.015	-.126	-.28	.041	-.070
	Harrah	-.320	.030	-.175	-.27	.035	-.043
Dissolved phosphorus, in mg/L	Britton Road	-.410	.012	-.036	-.42	.012	-.087
	Harrah	-.520	.006	-.106	-.53	.008	-.154
1999–2009							
Dissolved oxygen, in mg/L	Britton Road	-.20	.030	-.149	-.13	.194	-.009
	Harrah	-.30	.032	-.250	-.28	.023	-.018
Dissolved nitrogen, in mg/L	Britton Road	+0.14	.182	.057	+0.24	.011	.031
	Harrah	+0.14	.266	.110	+0.32	.010	.051
Dissolved phosphorus, in mg/L	Britton Road	+0.06	.629	.007	+0.09	.284	.016
	Harrah	+0.09	.375	.023	+0.31	.015	.060

water samples collected at both stations before adjustment for precipitation and temperature, and a significant downward trend in dissolved oxygen concentration in water samples collected at the Harrah station after adjustment for precipitation and temperature.

From 1988–98, there were significant downward trends in dissolved nitrogen concentration in water samples collected at both stations before and after adjustment for flow (table 10). From 1999–2009, significant upward trends in flow-adjusted dissolved nitrogen were detected for water samples collected at both stations (table 10).

Similar to nitrogen, there were significant downward trends in dissolved phosphorus from 1988–99 at both stations before and after flow adjustment. From 1999–2009, there were no significant trends in dissolved phosphorus concentration in water samples collected at either station before adjustment for flow from 1999–2009, and there only were significant upward

trends in this parameter for water samples collected at the Harrah station after flow adjustment (table 10).

Potential Sources of Differences and Trends in Constituent Concentrations

Significant differences and trends in water quality may be caused, in part, by changes in water quality and effluent discharge from WWTPs, substantial development and population growth in the basin upstream from the stations, and agricultural practices in the basin, including application of treated biosolids along the riparian corridor of the North Canadian River. Specifically, significant differences in nutrients and specific conductance between the two stations, and upward trends in nutrients and downward trends in dissolved

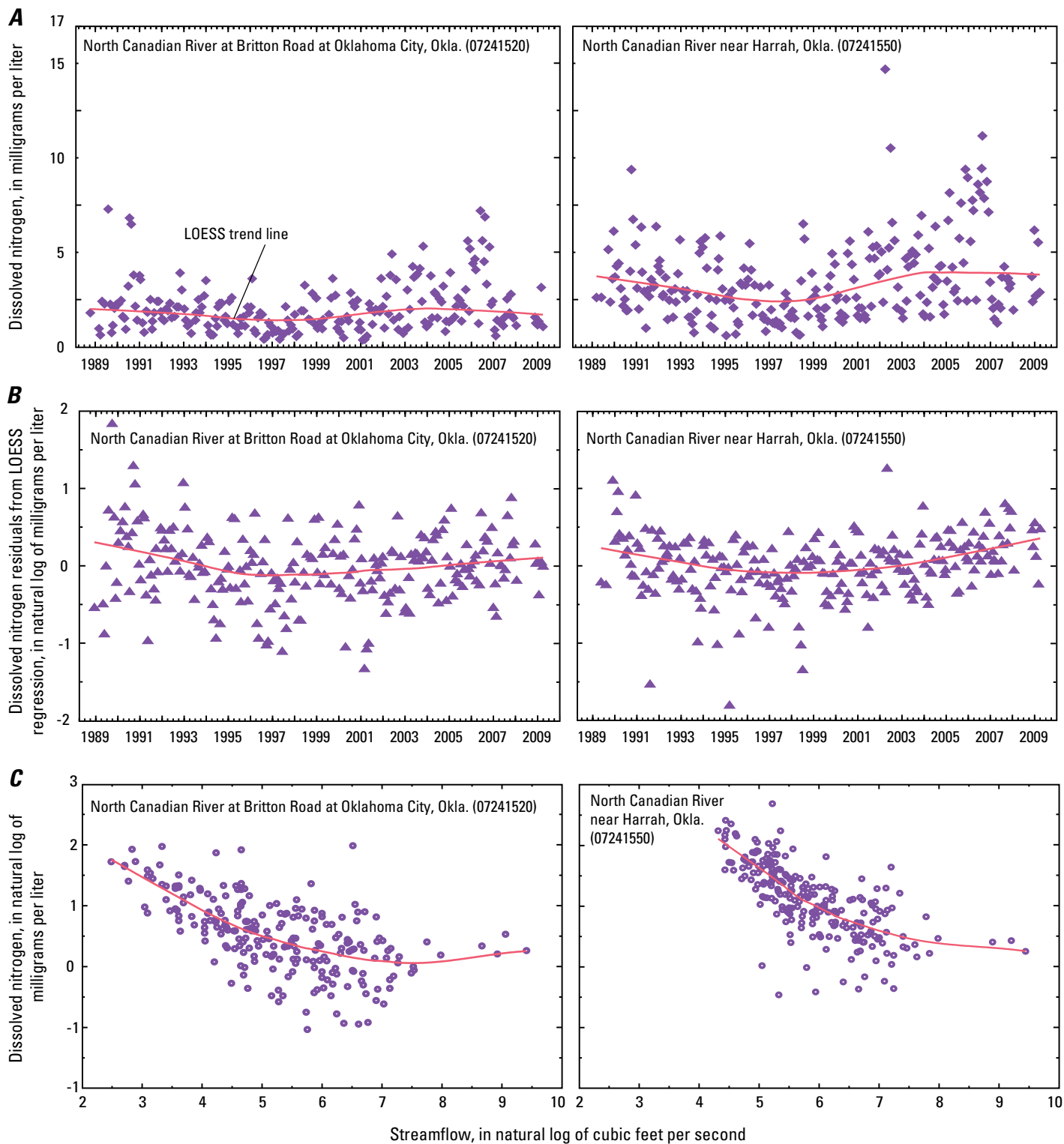


Figure 36. Trends in dissolved nitrogen concentration in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations of (A) dissolved nitrogen with time, (B) flow-adjusted dissolved nitrogen (error residuals) from a LOESS regression, and (C) relation between dissolved nitrogen and streamflow, 1988–2009.

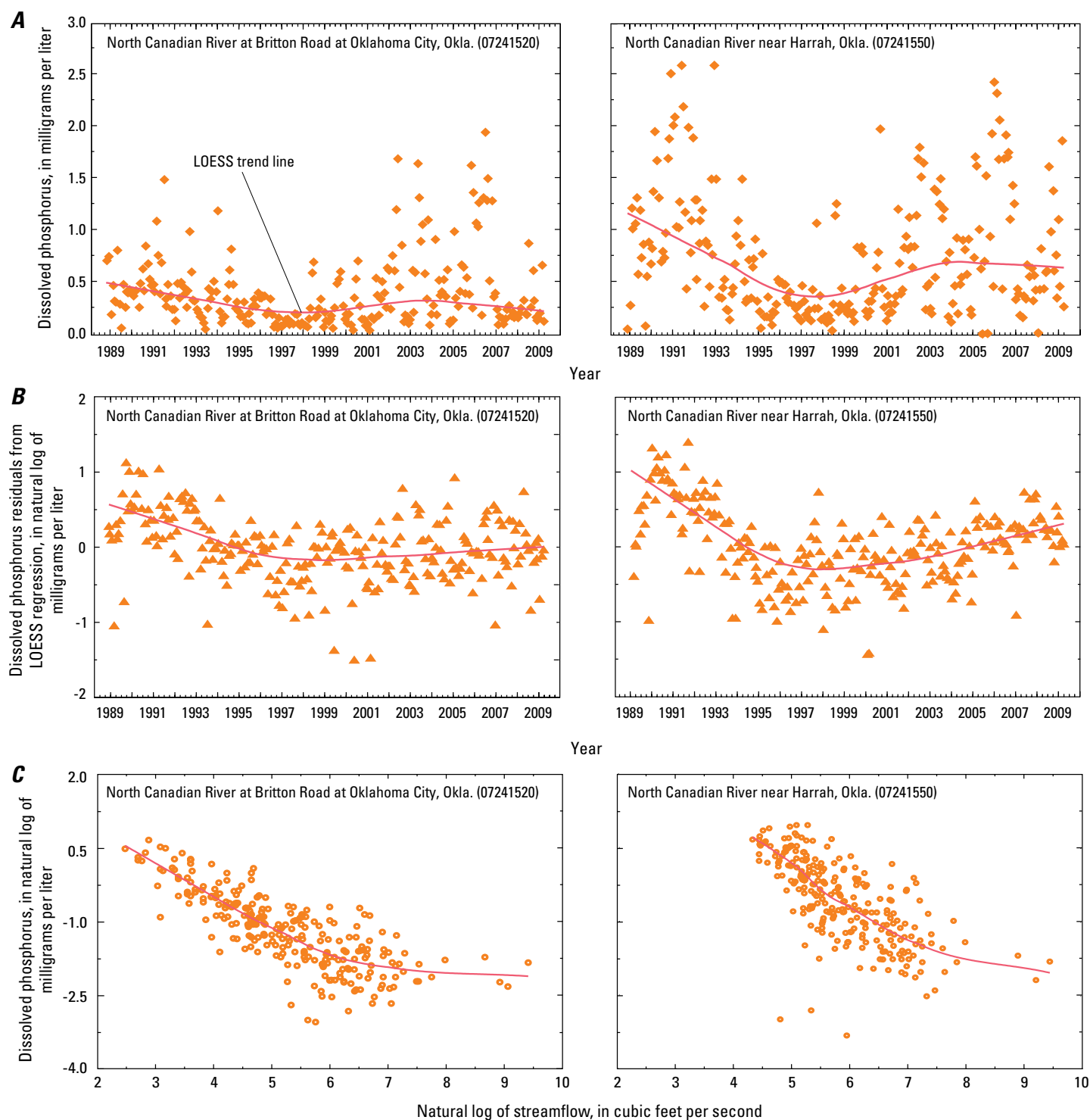


Figure 37. Trends in dissolved phosphorus in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations of (A) dissolved phosphorus with time, (B) flow-adjusted dissolved phosphorus (error residuals) from a LOESS regression, and (C) relation between dissolved phosphorus and streamflow, 1988–2009.

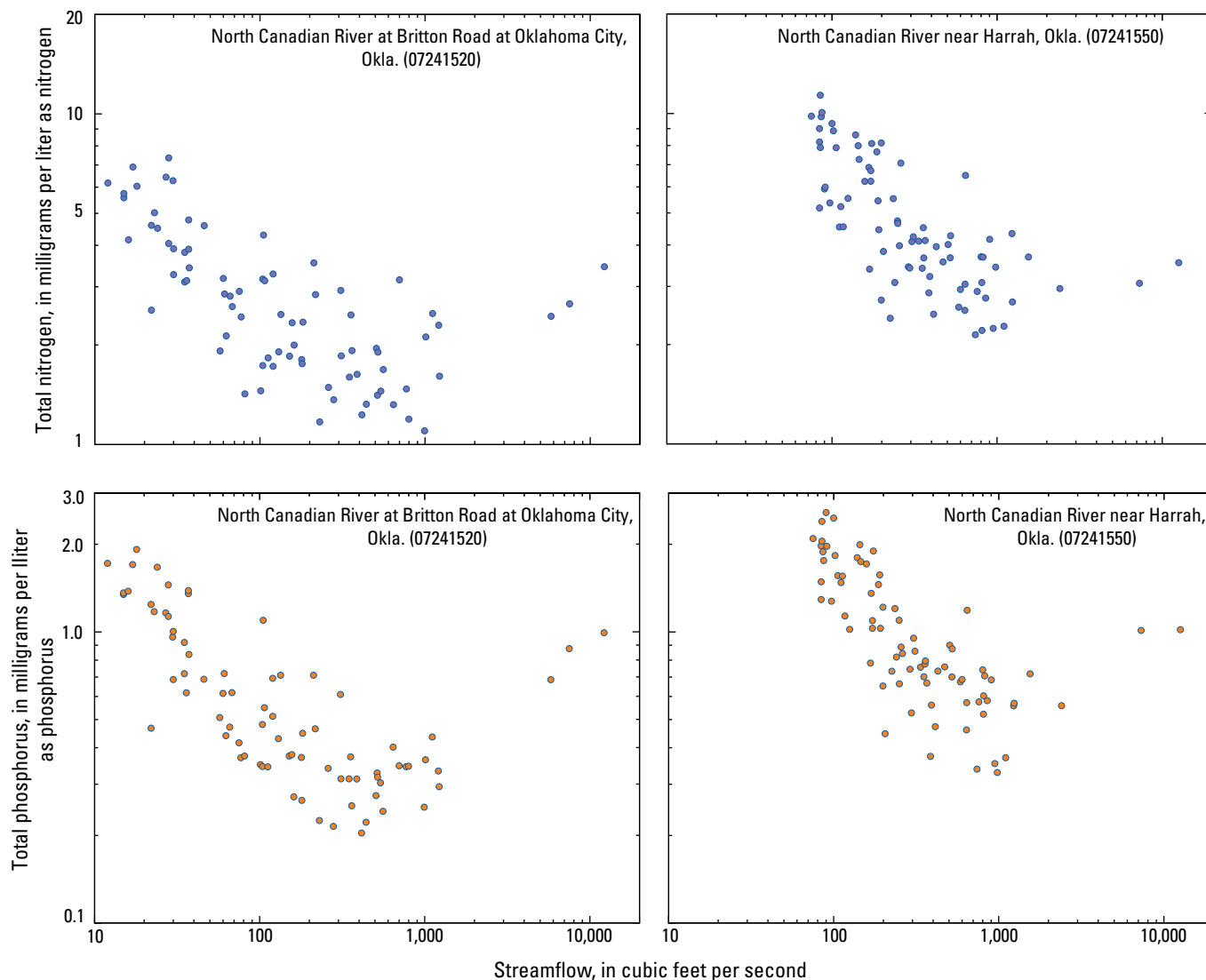


Figure 38. Relations of total nitrogen and total phosphorus at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 2003–09.

oxygen from 1999–2009 may be caused by these factors or changes in these factors in the part of the basin between the two stations.

Contribution of Wastewater Effluent

To investigate the influence of recent wastewater discharges, total suspended solid (TSS) load data were obtained from the National Pollutant Discharge Elimination System (NPDES) permit program database (U.S. Environmental Protection Agency, 2010c). TSS load data were obtained for samples collected from March 2005–09 at seven WWTPs that discharge to tributaries or the main stem of the North Canadian River near the Britton Road and Harrah stations (table 11).

Substantially greater volumes of effluent discharged to the river upstream from the Harrah station compared to upstream from the Britton Road station (table 11) may be part of the cause of significantly greater dissolved nitrogen and phosphorus concentrations, and BOD (on paired sample trips only) and significantly lesser dissolved oxygen concentrations (daily maximum, and daily maximum, mean, and minimum on paired days) at the Harrah station.

However, locations of distribution of BOD and fecal coliform concentrations, as tested by the rank-sum test, were not significantly different between the stations, indicating that quantities of these constituents are not substantially elevated by treated municipal wastewater discharge from WWTPs upstream from the Harrah station. Similar BOD concentrations between the stations may be the result of the distance

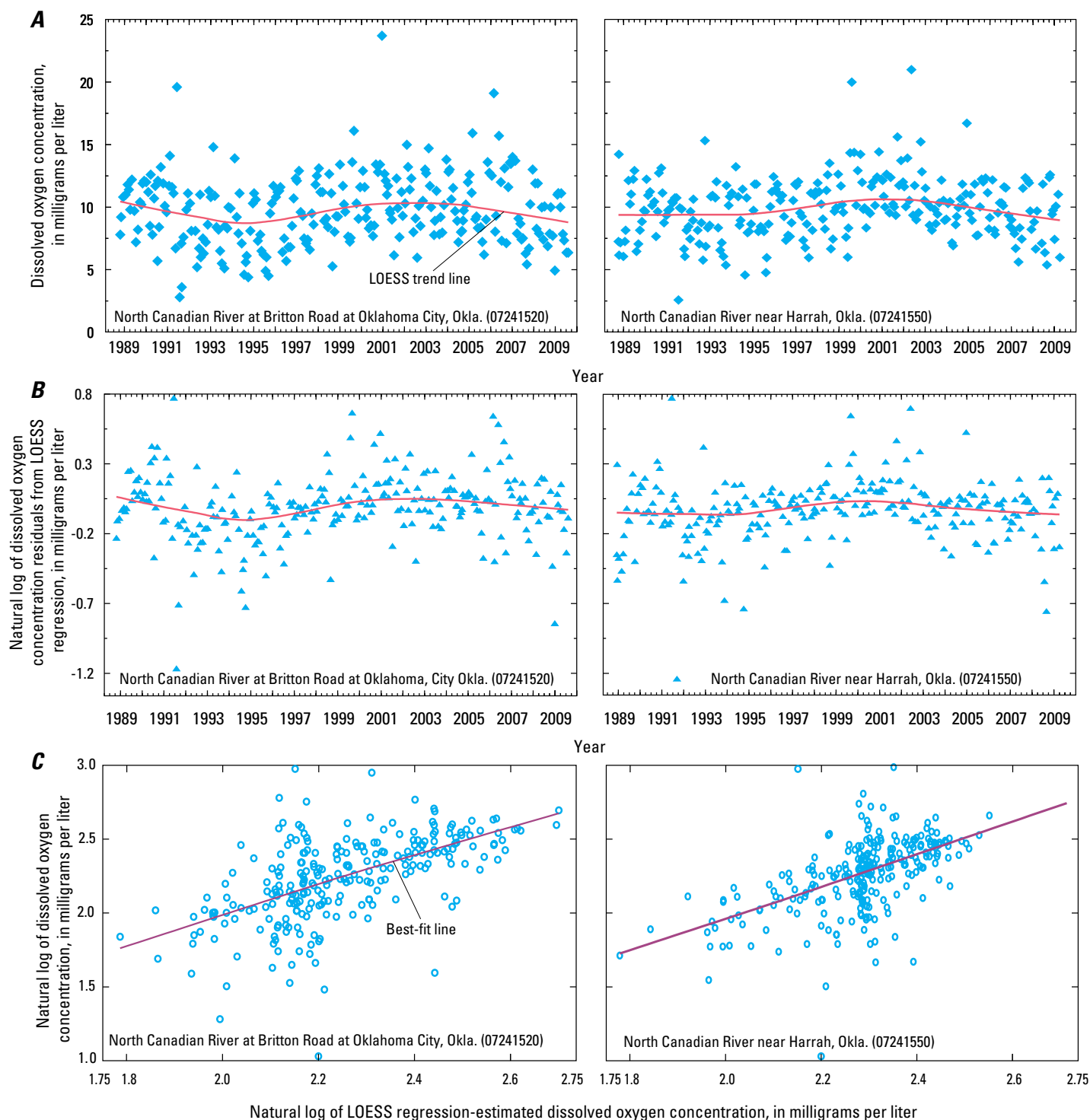


Figure 39. Trends in dissolved oxygen concentration in water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations of (A) dissolved oxygen with time, (B) flow-adjusted dissolved oxygen (error residuals) from a LOESS regression, and (C) the relation between dissolved oxygen and streamflow, 1988–2009.

Table 11. Locations of selected wastewater-treatment plants that discharge effluent in the North Canadian River Basin in central Oklahoma.

[NPDES, National Pollutant Discharge Elimination System; TSS, total suspended solids; effluent, wastewater effluent; Britton Road, North Canadian River at Britton Road at Oklahoma City, Oklahoma; Harrah, North Canadian River near Harrah, Oklahoma]

Facility name ¹	NPDES permit number	Latitude (decimal degrees)	Longitude (decimal degrees)	Closest downstream streamflow-gaging station ²	Median TSS load (pounds/day) from samples collected from effluent, 2005–09 ¹
Yukon	OK0028584	35.532817	-97.755602	Britton Road	124
Del City	OK0026085	35.467723	-97.439854	Britton Road	61.2
Midwest City	OK0026841	35.505017	-97.400301	Britton Road	240
Spencer	OK0022535	35.538039	-97.373539	Britton Road	7.20
Oklahoma City - North Canadian	OK0036978	35.596906	-97.312868	Harrah	1,970
Jones	OK0030996	35.57080	-97.280214	Harrah	5.50
Oklahoma City - Dunjee Park	OK0030520	35.50050	-97.304216	Harrah	3.40

¹ Facility name, permit number, location, and TSS data obtained from U.S. Environmental Protection Agency Enforcement and Compliance History Outline (ECHO), available online at http://www.epa-echo.gov/echo/compliance_report_water_icp.html.

² The only streamflow-gaging stations considered were North Canadian River at Britton Road at Oklahoma City, Okla., (U.S. Geological Survey station number 07241520) or North Canadian River near Harrah, Okla., (U.S. Geological Survey number 07241550).

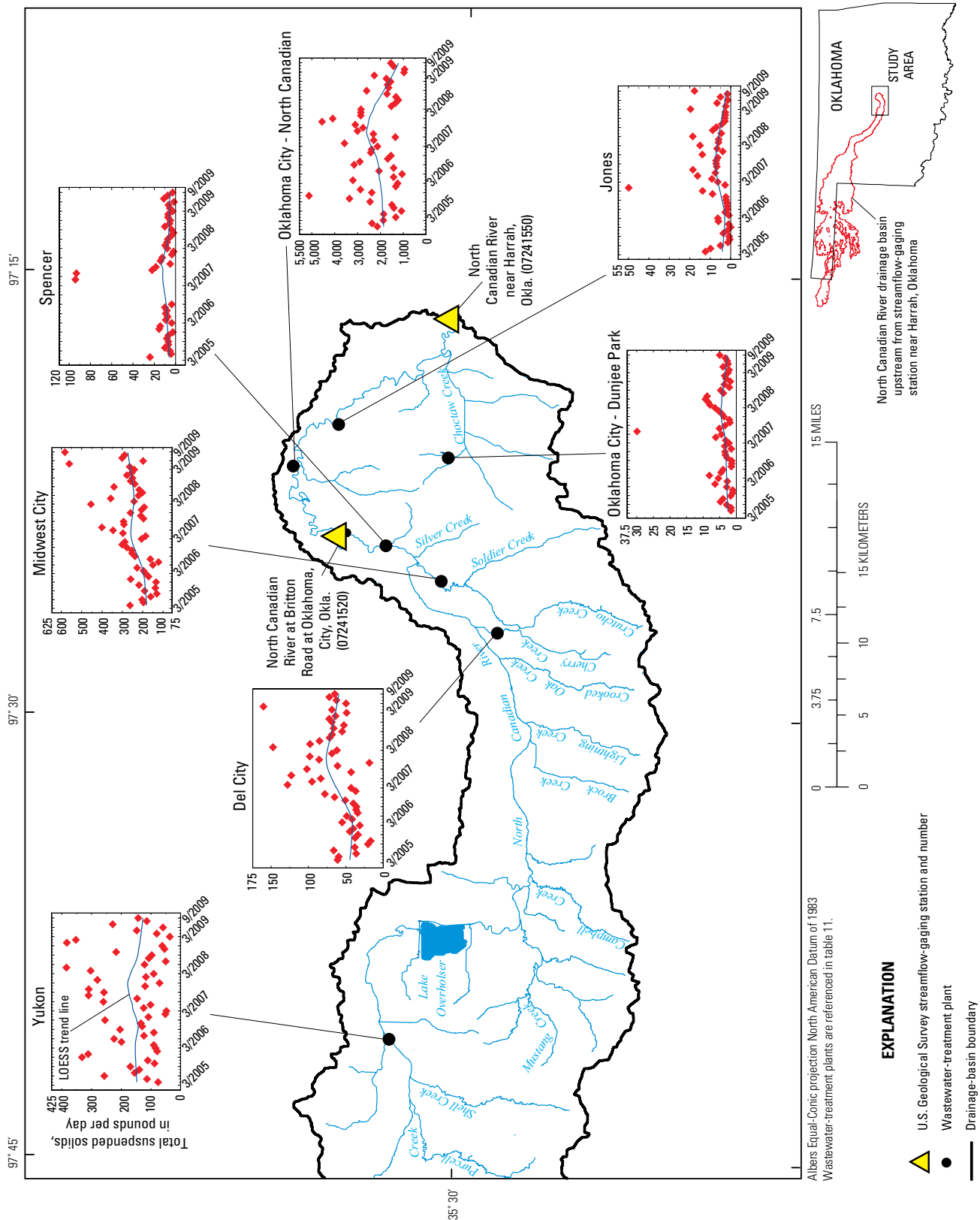
of the stations downstream from WWTPs, which may allow for BOD to decrease because of settling and decomposition of oxidizable organic matter (Chapra, 1997, p. 353–355). Because fecal coliform bacteria cannot be used to distinguish between animal and human sources of fecal contamination (Gleeson and Gray, 1997), effluent may not be the only source of fecal coliform bacteria. Effective treatment and disinfection of municipal wastewater should produce effluent with negligible counts of such bacteria. Other sources of fecal coliform bacteria can include leachate or runoff of animal wastes, septic systems, applied biosolids, or long-lived bacteria in streambed sediments and on aquatic plants. These sources seem to be substantial, as indicated by large fecal coliform counts in water samples collected at both stations. Variability in BOD concentration and fecal coliform counts also may be affected by differences in the effectiveness of treatment practices at WWTPs. Such variability in the quality of wastewater effluent may outweigh consistent differences in concentrations between stations, resulting in no significant difference in the concentrations of selected constituents in water samples collected at these stations.

Changes in TSS loads discharged by WWTPs to the North Canadian River near the Britton Road and Harrah stations may indicate changes in nutrient loading from point sources to the North Canadian River. Negative correlations of dissolved nitrogen and phosphorus concentrations to streamflow (figs. 36 and 37) are more indicative of effluent sources of those nutrients than nonpoint sources for the basins upstream from the Britton Road and Harrah stations, because nutrients from point sources typically are diluted by greater streamflows.

Significant downward trends in dissolved nitrogen and phosphorus concentrations in the North Canadian River from 1988–98 were described in Brigham and others (2002). Brigham and others (2002) reported that most of these changes probably were attributable to improvements in municipal wastewater-treatment practices, including filtering for ammonia and solids as well as restricting discharges of industrial wastewater into the municipal wastewater-treatment system.

Increases in wastewater discharge may have caused significant downward trends in adjusted dissolved oxygen concentration at the Harrah station, caused by significant upward trends in adjusted nutrients at one or both stations from 1999–2009. Increases in quantities of wastewater discharge probably occurred because of increases in population in the area from 1988–2009.

Graphs of TSS load in effluent with time were made to determine if there have been notable changes in TSS load since March 2005. LOESS curves were fit to those data to indicate possible trends in TSS load with time at the stations (fig. 40). TSS load from effluent samples were highly variable but slopes of the LOESS curves indicate upward trends in TSS loading by the Del City and Midwest City WWTPs that discharge upstream from the Britton Road station. There was a slight upward trend for TSS loading at the Oklahoma City–Dunjee Park WWTP that discharges upstream from the Harrah station. There was no consistent trend in TSS loads at the largest contributor of effluent to the North Canadian River near the two stations, the Oklahoma City–North Canadian WWTP (fig. 40, table 11). Turbidity, which is related to total suspended solids, increased slightly at both the Britton Road and Harrah stations from 1988–2009 (fig. 41).



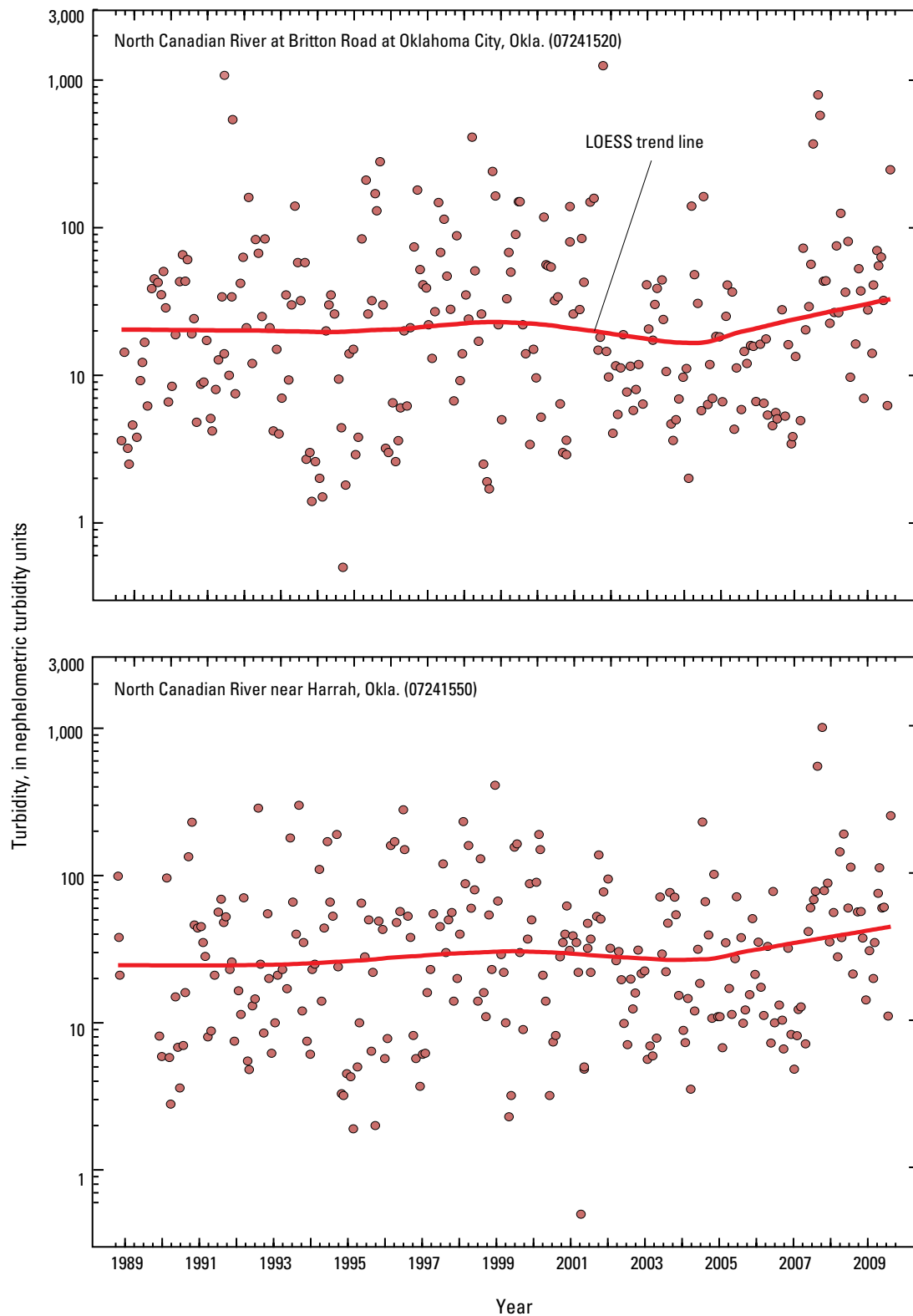


Figure 41. Turbidity with time of water samples collected at the North Canadian River at Britton Road at Oklahoma City, Oklahoma, and the North Canadian River near Harrah, Oklahoma, streamflow-gaging stations, 1988–2009.

Population growth and slight upward trends in TSS loads from some wastewater-treatment plants may be part of the cause of upward trends in dissolved nitrogen concentration in the North Canadian River from 1999–2009, but do not account for the different trends for dissolved oxygen and phosphorus concentrations in water samples collected at the two stations. Differences in trends with time in dissolved phosphorus concentrations in samples collected at the two stations may be associated with significantly greater nutrient concentrations at the Harrah station (fig. 16, table 8). The slope of the LOESS curve fit to dissolved nitrogen concentration with time was greater for water samples collected at the Harrah station than at the Britton Road station (fig. 36, table 10), and upward trends in flow-adjusted dissolved phosphorus concentration were detected at the Harrah station (fig. 37, table 10), supporting the theory that nutrient concentrations are greater at the Harrah station as a result of a greater inflows of effluent upstream from that station.

Significant downward trends in adjusted dissolved oxygen concentrations, and significant upward trends in nutrient concentrations in water samples collected at the Harrah station from 1999–2009 indicate increased discharges of nutrients and other compounds that increase eutrophication. Presence of oxidizable organic compounds in effluent also can affect the biological oxygen demand and dissolved oxygen concentrations. Organic nitrogen and ammonia from effluent also may contribute to consumption of dissolved oxygen during the microbiological process of nitrification to form nitrate and nitrite (Chapra, 1997). However, there were no changes in BOD at the Britton Road station and small decreases in BOD at the Harrah station (fig. 32), which do not support the theory that increases in effluent discharge are the primary cause of decreases in dissolved oxygen at these stations.

Changes in the ratio of effluent to receiving streamflow caused by decreases in low streamflow after 1999 (fig. 10) may also have caused upward trends in nutrient concentrations and downward trends in dissolved oxygen concentrations. If effluent discharges were constant or increased with time but low-flow has decreased, dilution of effluent may be decreasing with time resulting in increases in nutrient concentrations and accompanying decreases in dissolved oxygen concentration. Decreases in low streamflow after 1999 may be a result of changes in precipitation, temperature, or anthropogenic activities (see section titled “Evaluation of Streamflow”).

Decreases in dissolved oxygen concentration caused by discharges of effluent or runoff from other sources, which may have increased sediment oxygen demand (SOD) or increased water temperature, also may have affected phosphorus concentrations. Phosphorus in the aerobic surface layer of waterbodies tends to be sorbed to precipitated iron hydroxides, minimizing phosphorus dissolution. Where dissolved oxygen concentrations decline to near 0 mg/L, iron hydroxides are reduced and dissolved and may release dissolved phosphorus (Chapra, 1997). Decreases in dissolved oxygen concentration and increases in the frequency of hypoxic conditions

after 1999 at the Harrah station (fig. 31, table 10) may have increased dissolution of phosphorus from river channel bed sediments, which may have been a cause of increased dissolved phosphorus concentrations in water samples collected at this station after 1999.

Agricultural Practices

Negative correlations of dissolved nitrogen and phosphorus concentrations with streamflow indicated that effluent sources of nutrients were greater than nonpoint sources (figs. 36 and 37) in the subbasins upstream from these stations. However, upward trends in flow-adjusted nutrient concentrations indicate that nonpoint sources may be substantial sources of nutrients in the river.

Land application of treated biosolids may be another source of upward trends in dissolved nitrogen and phosphorus concentrations, downward trends in dissolved oxygen concentrations, and in significantly greater dissolved nitrogen and phosphorus concentrations at the Harrah station than at the Britton Road station. Treated biosolids are nutrient-rich organic materials from municipal wastewater treatment that consist of filtered, settled, and metabolized organic compounds collected as slurry and dewatered (U.S. Environmental Protection Agency, 2009). Treatment of biosolids typically includes liming for disinfection and addition of coarse organic material such as wood chips and compost to create heat for disinfection purposes and breakdown complex organic compounds. Treated biosolids are typically used as alternatives to inorganic fertilizers (U.S. Environmental Protection Agency, 2010d). There are numerous land-application areas for treated biosolids on and near the floodplain of the North Canadian River, with a greater number of these areas being in the subbasin between the Britton Road and Harrah stations than in the subbasin upstream from the Britton Road station (fig. 1).

Nutrient and organic compounds in fertilizers, soils, and treated biosolids may reach the river through groundwater leaching or by erosion of soil particles containing varying concentrations of such compounds. As population and development increase in the basin, wastewater-treatment facilities may need to process increased amounts of municipal and industrial waste to meet NPDES effluent discharge regulations. Exportation and application of treated biosolids as fertilizer may increase in the future to reduce amounts of nutrients and organic compounds discharged directly to the river at outfalls of wastewater-treatment plants. Such a shift in waste application may be the cause of some of the greater nutrient concentrations and more significant trends in nutrient concentrations in water samples collected at the Harrah station than at the Britton Road station.

Other nonpoint sources of nutrients also may contribute nitrogen and phosphorus to the North Canadian River. Such sources can include leaching or runoff of fertilizer applied to cropland, and waste from livestock raised on rangeland and in confined animal feeding operations. Nitrogen contributed

from fertilizer and animal manure in central Oklahoma is substantial compared to other areas of the U.S. (Puckett, 1994). As of 1985 in the North Canadian River Basin, nitrogen loading by fertilizers was estimated to have exceeded 7 tons per square mile and nitrogen loading from animal sources was estimated to have exceeded 4 tons per square mile in Canadian, Blaine and Kingfisher Counties in Oklahoma (Alexander and Smith, 1990). However, land-coverage changes from 1992 to 2001 indicate decreases in agricultural land cover and increases in urban land cover in the subbasin upstream from both stations (fig. 8, table 5). Such changes are likely to decrease nutrient concentrations in the river, with loading rates of fertilizers and animal wastes in suburban developments being about one-half as much as in agricultural areas (Dubrovsky and others, 2010). Although agricultural land area decreased between 1991 and 2002, increases in application of commercial fertilizers upstream from the two stations could cause increases in dissolved nutrients in the river, but evaluation of changes in the quantity of fertilizer applied and its relation to sources of nutrients in the basin was beyond the scope of this report.

Decreases in agricultural land cover also may have caused decreases in the frequencies of detection of the pesticide compounds atrazine, chlorpyrifos, and diazinon in the river, some of which continue to be used for pest or weed control. Decreases in lindane are more likely to be associated with restrictions on use of this insecticide in the United States rather than decreases in agricultural land cover in the basin.

Other Urban Sources

Increases in urban land cover between 1992 and 2001 were greater than changes in other individual land-cover categories in the basin (fig. 8, table 5). Other causes of trends in nutrients and dissolved oxygen may have been factors associated with increases in development in the North Canadian River Basin. Leachate from septic systems; leaking underground waste storage systems; increases in fertilizer application on suburban lawns, highway and urban runoff; and increases in combined sewer overflows may be causes of increases in dissolved nutrient concentrations and decreases in dissolved oxygen concentrations at both stations.

Increases in development also may be associated with erosion as a result of land disturbance, and stormwater runoff that may have caused increases in sediment concentrations in the North Canadian River. Increases in sediment concentrations can cause decreases in dissolved oxygen concentrations because of Sediment Oxygen Demand (SOD) and increases in phosphorus sorbed to sediments. Decreases in dissolved oxygen concentrations also may have contributed to upward trends in dissolved phosphorus at the Harrah station (see section titled "Contribution of Wastewater Effluent"). Sediment concentration data were only available from 1982–86 so long-term trends could not be analyzed. Turbidity, however, can be used to indicate increases in suspended sediment because this

constituent is strongly correlated to sediment concentrations (Rasmussen and others, 2003). A graph of turbidity with time with a LOESS curve fit to those data (fig. 41) indicated that there were increases in turbidity in water samples collected at both stations since 2003. Increasing sediment concentrations may have contributed to downward trends in dissolved oxygen concentration and upward trends in dissolved phosphorus concentration at the Harrah station.

There were no significant trends in dissolved oxygen and phosphorus concentrations at the Britton Road station although there were upward trends with time in the LOESS curve fit to turbidity with time and greater increases in urban land cover in the subbasin between the Britton Road station and Lake Overholser from 1992–2001 (table 5) than in the subbasin between the Britton Road and Harrah stations. These inconsistent observations indicated that other factors may have affected dissolved oxygen and nutrient concentrations at the Britton Road station and other factors or a combination of factors may have caused downward trends in dissolved oxygen concentration at the Harrah station.

Atmospheric deposition also may be a source of nitrogen in the basin. Nitrogen in atmospheric deposition originates primarily from combustion of fossil fuels, and is mostly associated with industrial fuel combustion, electric utilities, and transportation (Puckett, 1994). For example, concentrated areas of deposition have been observed near highways with urban and highway drainage systems channeling the flux of nitrogen downstream (Fisher and Oppenheimer, 1991; Hinga and others, 1991). Upward trends in nitrogen at both stations, especially the Britton Road station, may be associated with development and population growth near the stations.

Decreases in specific conductance and dissolved chloride may have been caused by a reduction in storage of brines and petroleum wastes in open or unlined pits prior to about 1970. However, abandoned pits may have continued to be a source of chloride in the North Canadian River since that time (Brigham and others, 2002).

Increases in the frequency of detection of 2,4-D and bromacil may be related to increases in urban and suburban pesticide application in areas of increasing development. Both of those pesticides are herbicides used to control broad-leaf weeds and may be used extensively on residential, commercial, or industrial land for landscape maintenance.

Summary

The U.S. Geological Survey, in cooperation with the city of Oklahoma City, collected water-quality samples at the North Canadian River near Harrah, Oklahoma (the Harrah station), since 1968, and the North Canadian River at Britton Road at Oklahoma City, Oklahoma (the Britton Road station), since 1988. The North Canadian municipal wastewater-treatment plant, managed by the city of Oklahoma City, is the largest wastewater-treatment plant in the basin and discharges effluent between the Britton Road and Harrah stations.

Water-quality constituent concentrations were summarized over the period of record, and trends in concentrations and frequencies of detection of selected constituents with time were evaluated to determine if changes in land cover, streamflow, and other potential sources of water contamination in the basin had significant effects on water quality in the North Canadian River downstream from Oklahoma City.

The predominant land-cover changes between 1992 and 2001 in the basin between the Harrah station and Lake Overholser were an increase in developed/barren land cover and a decrease in pasture/hay land cover. There were no significant trends with time in median and higher streamflow at either station. There were significant downward trends in streamflow characteristics that represented lower streamflow at both stations. There were no significant trends in precipitation-adjusted annual streamflow at either station. Daily mean streamflows on days of sample collection were not significantly different from all daily mean streamflow for 1988–2009 at both stations.

Statistical summaries, frequencies of detection, and percentages of samples with concentrations exceeding Criterion Continuous Concentrations were calculated for 157 water-quality constituents for both streamflow-gaging stations. Concentrations of dissolved chloride, dissolved cadmium, and dissolved lead most frequently exceeded the Criterion Continuous Concentrations in water samples collected at the Britton Road station. Concentrations of dissolved chloride, lead, and chlordane most frequently exceeded the Criterion Continuous Concentrations in water samples collected at the Harrah station. Visual trends in annual frequencies of detection were investigated for selected pesticides with frequencies of detection greater than 10 percent in all water samples collected at both streamflow-gaging stations. There were more pesticides with frequencies of detection greater than 10 percent in water samples collected at the Harrah station than at the Britton Road station from 1988–2009. Annual frequencies of 2,4-dichlorophenoxyacetic acid and bromacil increased with time. Annual frequencies of atrazine, chlorpyrifos, diazinon, dichlorprop, and lindane decreased with time. Annual frequencies of detection of dieldrin, heptachlor epoxide, and simazine did not change with time.

Dissolved nitrogen and phosphorus concentrations were significantly greater in water samples collected at the Harrah station than at the Britton Road station, whereas specific conductance was greater at the Britton Road station. Concentrations of dissolved oxygen, biochemical oxygen demand, and counts of fecal coliform bacteria were not significantly different between stations. Daily maximum, mean, and minimum specific conductance were significantly greater at the Britton Road station than at the Harrah station. Daily minimums and maximums and diurnal fluctuations of water temperature were significantly greater at the Harrah station than at the Britton Road station. Daily maximum and diurnal range of dissolved oxygen concentrations were significantly greater at the Britton Road station than at the Harrah station.

Daily mean and monthly mean diurnal water temperature ranges increased with time. Daily mean and monthly mean diurnal specific conductance at the two stations decreased with time. There were small downward trends in daily mean dissolved oxygen in water samples collected at both stations and low daily mean dissolved oxygen concentrations were measured more frequently after 1999.

Slight decreases in fecal coliform bacteria counts occurred from 1988–2009 in water samples collected at the Britton Road station. There were no trends with time, however, in fecal streptococcal bacteria counts in water samples collected at either station. Chlorophyll *a* concentrations did not change with time at the Harrah station in water samples collected after 1987.

For the period 1988–2009, the Seasonal Kendall's tau test indicated only significant downward trends in flow-adjusted dissolved phosphorus at the Britton Road station. For the period 1988–98, there were no significant trends in dissolved oxygen concentrations at either station before or after flow adjustment, and significant downward trends in nitrogen and phosphorus were indicated before and after flow adjustment. For the period 1999–2009, there were significant downward trends in dissolved oxygen at both stations. For the period 1999–2009, there were also significant downward trends in flow- and temperature-adjusted dissolved oxygen concentrations in water samples collected at the Harrah station, significant upward trends in flow-adjusted dissolved nitrogen concentrations in water samples collected at both stations, and significant upward trends in flow-adjusted dissolved phosphorus concentrations only at the Harrah station.

Significant differences and trends in water quality may have been caused, in part, by changes in streamflow and in amounts and quality of effluent discharged from wastewater-treatment plants, substantial urban development and population growth in the basin upstream from the stations, and agricultural practices in the basin including application of treated biosolids along the riparian corridor of the North Canadian River between the Britton Road and Harrah stations. Negative correlations of dissolved nitrogen and phosphorus concentrations to streamflow indicated that point sources of phosphorus such as effluent from wastewater-treatment plants were more predominant than nonpoint sources, but increases in sediment loading associated with increases in land disturbance from urban development or other increases in nutrient contributions associated with urban development also may have contributed to increases in nutrient concentrations.

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Appendixes

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Physical properties							
Dissolved oxygen, in mg/L	2.8	6.36	7.8	9.7	11.6	13	23.7
Dissolved oxygen, in percent saturation	34.0	77.0	88.3	99.0	114	131	249
pH (field), in standard units	6.70	7.85	8.05	8.25	8.39	8.50	9.63
Specific conductance, in µS/cm at 25 degrees celsius	171	677	942	1,270	1,420	1,520	1,900
Water temperature, in degrees Celsius	.00	6.00	9.43	17.8	24.4	26.9	34.3
Turbidity, in nephelometric turbidity units	.50	3.71	6.64	19	43.4	122	1,250
Five-day biochemical oxygen demand, in mg/L at 20 degrees Celsius	.20	1.50	2.50	4.06	6.80	9.00	18.0
Dissolved solids dried at 180 degrees Celsius, in mg/L	158	422	616	787	903	941	1,060
Dissolved solids from water, in mg/L	139	388	575	746	858	899	1,030
Hardness, in mg/L as calcium carbonate	79.8	208	308	362	408	449	475
Dissolved noncarbonate hardness (field), in mg/L as calcium carbonate	20.5	48.4	78.8	114	162	202	245
Major inorganics, metals							
Dissolved calcium, in mg/L	21.4	52.8	67.4	87.6	100	110	115
Dissolved magnesium, in mg/L	6.04	18.0	28.4	34.8	40.1	43.9	47.0
Dissolved potassium, in mg/L	2.82	5.25	5.70	6.47	7.40	8.30	10.0
Dissolved sodium, in mg/L	11.2	63.2	93.5	121	147	170	200
Major inorganics							
Total acid neutralizing capacity, in mg/L as calcium carbonate	56.6	145	180	230	270	300	346
Alkalinity, filtered, in mg/L as calcium carbonate	40.0	130	165	208	244	285	340
Dissolved bicarbonate, in mg/L	49.0	157	195	245	294	339	415
Carbon dioxide, in mg/L	.099	1.32	1.85	2.50	3.64	5.28	60.2
Dissolved carbonate, in mg/L	<1	<1	<1	.60	3.75	9.00	28.0
Dissolved chloride, in mg/L	10.8	74.1	104	151	191	240	320
Dissolved fluoride, in mg/L	.10	.39	.49	.60	.67	.70	.90
Dissolved silica, in mg/L	3.22	5.90	8.43	10.8	13.6	15.3	19.6
Dissolved sulfate, in mg/L	29.5	53.2	90.9	160	213	240	310
Nutrients							
Dissolved ammonia plus organic nitrogen, in mg/L as nitrogen	.15	.40	.50	.70	1.00	1.46	7.00
Ammonia plus organic nitrogen, in mg/L as nitrogen	.599	.88	1.01	1.21	1.7	2.18	3.022
Dissolved nitrate plus nitrite, in mg/L as nitrogen	.024	.220	.440	.830	1.40	2.35	4.644

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Month of first sample	Month of last sample	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Physical properties							
Dissolved oxygen, in mg/L	--	--	10/1988	8/2009	255	255	100
Dissolved oxygen, in percent saturation	--	--	10/1988	8/2009	253	NA	100
pH (field), in standard units	--	--	10/1988	8/2009	256	NA	100
Specific conductance, in µS/cm at 25 degrees celsius	--	--	10/1988	8/2009	255	255	100
Water temperature, in degrees Celsius	--	--	10/1988	8/2009	257	NA	100
Turbidity, in nephelometric turbidity units	--	--	8/1988	8/2009	250	249	99.6
Five-day biochemical oxygen demand, in mg/L at 20 degrees Celsius	--	--	1/1989	7/2009	213	208	97.7
Dissolved solids dried at 180 degrees Celsius, in mg/L	--	--	8/1988	8/2009	83	83	100
Dissolved solids from water, in mg/L	--	--	8/1988	8/2009	79	79	100
Hardness, in mg/L as calcium carbonate	--	--	8/1988	8/2009	84	84	100
Dissolved noncarbonate hardness (field), in mg/L as calcium carbonate	--	--	8/1991	8/2009	69	69	100
Major inorganics, metals							
Dissolved calcium, in mg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved magnesium, in mg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved potassium, in mg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved sodium, in mg/L	--	--	8/1988	8/2009	84	84	100.0
Major inorganics							
Total acid neutralizing capacity, in mg/L as calcium carbonate	--	--	8/1988	8/2009	249	249	100.0
Alkalinity, filtered, in mg/L as calcium carbonate	--	--	7/1991	8/2009	213	213	100.0
Dissolved bicarbonate, in mg/L	--	--	7/1991	8/2009	213	213	100.0
Carbon dioxide, in mg/L	--	--	10/1988	8/2009	248	248	100.0
Dissolved carbonate, in mg/L	--	--	7/1991	8/2009	212	120	56.6
Dissolved chloride, in mg/L	230	10.0	8/1988	8/2009	80	80	100.0
Dissolved fluoride, in mg/L	--	--	8/1988	8/2009	82	82	100.0
Dissolved silica, in mg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved sulfate, in mg/L	--	--	8/1988	8/2009	81	81	100.0
Nutrients							
Dissolved ammonia plus organic nitrogen, in mg/L as nitrogen	--	--	10/1988	8/2009	240	240	100.0
Ammonia plus organic nitrogen, in mg/L as nitrogen	--	--	2/2003	7/2009	78	78	100.0
Dissolved nitrate plus nitrite, in mg/L as nitrogen	--	--	8/1988	8/2009	254	247	97.3

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Nutrients—Continued							
Dissolved nitrate, in mg/L as nitrogen	0.017	0.290	0.480	0.870	1.39	2.28	4.441
Dissolved nitrite, in mg/L as nitrogen	.004	.010	.020	.030	.060	.120	.470
Dissolved organic nitrogen, in mg/L	.06	.33	.44	.57	.83	1.12	6.88
Organic nitrogen, in mg/L	.49	.77	.91	1.08	1.32	1.83	2.697
Dissolved phosphate, in mg/L as phosphorus	.013	.100	.160	.250	.460	.940	2.48
Dissolved phosphorus, in mg/L	.048	.110	.170	.320	.510	.860	1.96
Phosphorus, in mg/L	.20	.26	.34	.46	.87	1.36	1.92
Dissolved nitrogen, in mg/L	.36	.75	1.13	1.70	2.46	3.76	7.28
Nitrogen, in mg/L	1.10	1.40	1.75	2.48	3.54	5.57	7.36
Microbiological							
Fecal coliform count, in colonies per 100 milliliters	<1	60	186	474	1,140	3,800	>60,000
Fecal streptococcal bacteria, in colonies per 100 milliliters	<1	46	107	297	813	2,874	>10,000
Minor inorganics, metals							
Dissolved barium, in µg/L	78.2	136	150	170	191	230	276
Dissolved beryllium, in µg/L	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6
Dissolved cadmium, in µg/L	<8	<8	<8	<8	<8	<8	<8
Dissolved chromium, in µg/L	<14	<14	<14	<14	<14	<14	<14
Dissolved cobalt, in µg/L	<13	<13	<13	<13	<13	<13	<13
Dissolved copper, in µg/L	1.42	1.68	1.68	3.28	5.00	7.08	28.0
Dissolved iron, in µg/L	2.83	2.83	4.65	8.14	13.0	21.5	36.1
Dissolved lead, in µg/L	.079	.090	.150	.240	.530	2.82	2.0
Dissolved lithium, in µg/L	5.33	15.0	24.3	32.8	38.0	44.0	51.0
Dissolved manganese, in µg/L	<1	2.31	4.94	14.6	32.1	79.3	220
Dissolved mercury, in µg/L	<.23	<.23	<.23	<.23	<.23	<.23	.4
Dissolved molybdenum, in µg/L	1.64	1.64	2.29	4.45	6.53	1.0	2.0
Dissolved nickel, in µg/L	<53	<53	<53	<53	<53	<53	<53
Dissolved silver, in µg/L	<9	<9	<9	<9	<9	<9	<9
Dissolved strontium, in µg/L	182	520	779	1,010	1,100	1,220	1,400
Dissolved vanadium, in µg/L	2.40	3.90	5.40	6.36	7.82	9.16	13.2
Dissolved zinc, in µg/L	1.24	1.30	2.90	7.00	13.0	19.8	69.8

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Month of first sample	Month of last sample	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Nutrients—Continued							
Dissolved nitrate, in mg/L as nitrogen	--	--	8/1988	8/2009	237	237	100.0
Dissolved nitrite, in mg/L as nitrogen	--	--	8/1988	8/2009	254	237	93.7
Dissolved organic nitrogen, in mg/L	--	--	10/1988	8/2009	207	207	100.0
Organic nitrogen, in mg/L	--	--	2/2003	7/2009	71	71	100.0
Dissolved phosphate, in mg/L as phosphorus	--	--	8/1988	8/2009	253	253	100.0
Dissolved phosphorus, in mg/L	--	--	9/1988	8/2009	251	250	99.6
Phosphorus, in mg/L	--	--	2/2003	7/2009	78	78	100.0
Dissolved nitrogen, in mg/L	--	--	10/1988	8/2009	228	228	100.0
Nitrogen, in mg/L	--	--	2/2003	7/2009	78	78	100.0
Microbiological							
Fecal coliform count, in colonies per 100 milliliters	--	--	8/1988	7/2009	237	231	97.5
Fecal streptococcal bacteria, in colonies per 100 milliliters	--	--	10/1988	7/2009	240	235	97.9
Minor inorganics, metals							
Dissolved barium, in µg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved beryllium, in µg/L	--	--	8/1988	8/2009	84	6	7.1
Dissolved cadmium, in µg/L	$e^{\{.7409[\ln(\text{hardness})]-4.719\}}$ (1.101672-[(ln hardness(0.041838))])	7.1	8/1988	8/2009	84	6	7.1
Dissolved chromium, in µg/L	11	.0	8/1988	8/2009	84	14	16.7
Dissolved cobalt, in µg/L	--	--	8/1988	8/2009	84	3	3.6
Dissolved copper, in µg/L	--	--	8/1988	8/2009	84	28	33.3
Dissolved iron, in µg/L	1,000	.0	8/1988	8/2009	84	58	69.0
Dissolved lead, in µg/L	$e^{\{1.273[\ln(\text{hardness})]-4.705\}}$ (1.46203-[(ln hardness(1.45712))])	4.8	8/1988	8/2009	84	42	50.0
Dissolved lithium, in µg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved manganese, in µg/L	--	--	8/1988	8/2009	84	79	94.0
Dissolved mercury, in µg/L	.77	.0	8/1988	5/2009	75	16	21.3
Dissolved molybdenum, in µg/L	--	--	8/1988	8/2009	84	28	33.3
Dissolved nickel, in µg/L	$e^{(0.8460*(\ln(\text{hardness}))-0.0584)}$ (0.997)	.0	8/1988	8/2009	84	23	27.4
Dissolved silver, in µg/L	--	--	8/1988	8/2009	84	7	8.3
Dissolved strontium, in µg/L	--	--	8/1988	8/2009	84	84	100.0
Dissolved vanadium, in µg/L	--	--	8/1988	8/2009	84	64	76.2
Dissolved zinc, in µg/L	$e^{(0.8473*(\ln(\text{hardness}))-0.884)}$ (0.986)	2.4	8/1988	8/2009	84	55	65.5

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Minor inorganics, non-metals							
Dissolved arsenic, in µg/L	1.71	2.18	3.00	3.99	4.88	5.43	7.00
Dissolved selenium, in µg/L	.24	.26	.29	.42	.65	.92	1.66
Organics, pesticides							
2,4,5-Trichlorophenoxyacetic acid, in µg/L	<.031	<.031	<.031	<.031	<.031	<.031	<.031
2,4-Dichlorophenoxyacetic acid, in µg/L	<.01	.01	.02	.07	.15	.27	2.5
2-Chloro-4-isopropylamino-6-amino-s-triazine, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	.20
2-Chloro-6-ethylamino-4-amino-s-triazine, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	.2
Alachlor, in µg/L	<.1	<.2	<.2	<.2	<.2	<.2	<.2
Aldrin, in µg/L	<.0019	<.0019	<.0019	<.0019	<.0019	<.0019	<.0019
.alpha.-Endosulfan, in µg/L	<.0021	<.0021	<.0021	<.0021	<.0021	<.0021	<.0021
Ametryn, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Atrazine, in µg/L	.049	.050	.060	.090	.100	.200	.520
Bromacil, in µg/L	<.02	<.02	.03	.13	.20	.35	1.2
Butachlor, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Butylate, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Carbophenothion, in µg/L	<.063	<.063	<.063	<.063	<.063	<.063	<.063
Carboxin, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Chlordane, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	.2
Chlorpyrifos, in µg/L	<.042	<.042	<.042	<.042	<.042	<.042	<.042
Cyanazine, in µg/L	<.1	<.2	<.2	<.2	<.2	<.2	<.2
Cycloate, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Diazinon, in µg/L	.0049	.009	.010	.010	.030	.060	.240
Dichlorprop, in µg/L	<.036	<.036	<.036	<.036	<.036	<.036	.300
Dieldrin, in µg/L	<.0006	<.0006	.0008	.001	.001	.002	.0035
Diphenamid, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Disulfoton, in µg/L	<.01	<.3	<.3	<.3	<.3	<.3	<.3
Endrin, in µg/L	<.025	<.025	<.025	<.025	<.025	<.025	<.025
Ethion, in µg/L	<.039	<.039	<.039	<.039	<.039	<.039	<.039
Fonofos, in µg/L	<.007	<.021	<.021	<.021	<.021	<.021	<.021
Heptachlor epoxide, in µg/L	<.009	<.009	<.009	<.009	<.009	<.009	<.009
Heptachlor, in µg/L	<.002	<.002	<.002	<.002	<.002	<.002	<.002
Hexazinone, in µg/L	<.2	<.3	<.3	<.3	<.3	<.3	<.3
Lindane, in µg/L	<.0006	<.0006	.0008	.0011	.0035	.008	1.00

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Month of first sample	Month of last sample	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Minor inorganics, non-metals							
Dissolved arsenic, in µg/L	150	0.0	8/1988	8/2009	84	84	100.0
Dissolved selenium, in µg/L	5	.0	8/1988	8/2009	84	35	41.7
Organics, pesticides							
2,4,5-Trichlorophenoxyacetic acid, in µg/L	--	--	8/1988	8/2009	82	1	1.2
2,4-Dichlorophenoxyacetic acid, in µg/L	--	--	8/1988	8/2009	82	70	85.4
2-Chloro-4-isopropylamino-6-amino-s-triazine, in µg/L	--	--	2/1991	8/2009	72	1	1.4
2-Chloro-6-ethylamino-4-amino-s-triazine, in µg/L	--	--	2/1991	8/2009	72	2	2.8
Alachlor, in µg/L	--	--	8/1988	8/2009	82	0	.0
Aldrin, in µg/L	--	--	8/1988	8/2009	84	2	2.4
.alpha.-Endosulfan, in µg/L	.046	.0	8/1988	8/2009	84	1	1.2
Ametryn, in µg/L	--	--	8/1988	8/2009	81	0	.0
Atrazine, in µg/L	--	--	8/1988	8/2009	81	36	44.4
Bromacil, in µg/L	--	--	2/1991	8/2009	71	22	31.0
Butachlor, in µg/L	--	--	2/1991	8/2009	72	0	.0
Butylate, in µg/L	--	--	2/1991	8/2009	71	0	.0
Carbophenothion, in µg/L	--	--	8/1988	8/2009	128	1	.8
Carboxin, in µg/L	--	--	2/1991	8/2009	70	0	.0
Chlordane, in µg/L	.0043	2.4	8/1988	8/2009	84	2	2.4
Chlorpyrifos, in µg/L	--	--	8/1990	8/2009	120	12	10.0
Cyanazine, in µg/L	--	--	8/1988	8/2009	82	0	.0
Cycloate, in µg/L	--	--	2/1991	8/2009	72	0	.0
Diazinon, in µg/L	.17	4.7	8/1988	8/2009	127	80	63.0
Dichlorprop, in µg/L	--	--	8/1988	8/2009	82	10	12.2
Dieldrin, in µg/L	.056	.0	8/1988	8/2009	84	40	47.6
Diphenamid, in µg/L	--	--	2/1991	8/2009	72	0	.0
Disulfoton, in µg/L	--	--	8/1989	8/2009	113	0	.0
Endrin, in µg/L	.036	.0	8/1988	8/2009	84	1	1.2
Ethion, in µg/L	--	--	8/1988	8/2009	128	1	.8
Fonofos, in µg/L	--	--	8/1990	8/2009	120	0	.0
Heptachlor epoxide, in µg/L	.0038	.0	8/1988	8/2009	84	15	17.9
Heptachlor, in µg/L	.0038	.0	8/1988	8/2009	84	2	2.4
Hexazinone, in µg/L	--	--	2/1991	8/2009	72	0	.0
Lindane, in µg/L	--	--	8/1988	8/2009	84	55	65.5

Appendix 1. Summary statistics of water-quality data from the North Canadian River at Britton Road at Oklahoma City, Oklahoma, streamflow-gaging station, 1988–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; >, greater than; NA, not applicable; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Month of first sample	Month of last sample	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Organics, pesticides—Continued							
Malathion, in µg/L	0.1	0.8	8/1988	8/2009	126	10	7.9
Methyl parathion, in µg/L	--	--	8/1988	8/2009	128	3	2.3
Carbophenothion-methyl, in µg/L	--	--	8/1988	5/1991	12	1	8.3
Metolachlor, in µg/L	--	--	8/1988	8/2009	82	0	.0
Metribuzin, in µg/L	--	--	8/1988	8/2009	82	0	.0
Mirex, in µg/L	.001	1.2	8/1988	8/2009	84	1	1.2
<i>p,p'</i> -Dichlorodiphenyldichloroethane (DDD), in µg/L	--	--	8/1988	8/2009	84	3	3.6
<i>p,p'</i> -Dichlorodiphenyldichloroethylene (DDE), in µg/L	--	--	8/1988	8/2009	84	2	2.4
<i>p,p'</i> -Dichlorodiphenyltrichloroethane (DDT), in µg/L	.001	2.4	8/1988	8/2009	84	3	3.6
Ethylan, in µg/L	--	--	8/1988	5/2000	47	1	2.1
Methoxychlor, in µg/L	.03	.0	8/1988	8/2009	84	1	1.2
Parathion, in µg/L	.013	.0	8/1988	8/2009	128	2	1.6
Phorate, in µg/L	--	--	8/1989	8/2009	121	1	.8
Prometon, in µg/L	--	--	8/1988	8/2009	82	6	7.3
Prometryn, in µg/L	--	--	8/1988	8/2009	82	0	.0
Propachlor, in µg/L	--	--	2/1991	8/2009	72	0	.0
Propazine, in µg/L	--	--	8/1988	8/2009	82	0	.0
Silvex, in µg/L	--	--	8/1988	8/2009	82	1	1.2
Simazine, in µg/L	--	--	8/1988	8/2009	82	49	59.8
Simetryn, in µg/L	--	--	8/1988	8/2009	82	0	.0
Terbacil, in µg/L	--	--	2/1991	8/2009	72	1	1.4
Toxaphene, in µg/L	.0002	1.2	8/1988	8/2009	84	1	1.2
Tribufos, in µg/L	--	--	8/1989	8/2009	124	0	.0
Trifluralin, in µg/L	--	--	8/1988	8/2009	82	1	1.2
Vernolate, in µg/L	--	--	2/1991	8/2009	72	0	.0
Organics, other							
Polychlorinated biphenyls, in µg/L	.014	.0	8/1988	8/2009	84	0	.0
Organic carbon, in mg/L	--	--	8/1988	8/2009	88	88	100.0
Polychlorinated naphthalenes, in µg/L	--	--	8/1988	5/2000	46	0	.0

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Physical properties							
Dissolved oxygen, in mg/L	1.60	5.92	7.39	9.00	10.8	12.3	>20.0
Dissolved oxygen, in percent saturation	12.5	67.4	79.5	92.9	108	133	>282
pH (field), in standard units	6.60	7.10	7.50	7.80	8.20	8.35	9.17
Specific conductance, in µS/cm at 25 degrees celsius	165	665	999	1,340	1,580	1,900	4,700
Water temperature, in degrees Celsius	.0	6.4	10	18	25.1	28.5	36
Turbidity, in Jackson turbidity units	.0	2.0	5.7	10	20	93	130
Turbidity, in nephelometric turbidity units	<.5	5.95	10.8	28.1	60.1	130	>1,000
Five-day biochemical oxygen demand, in mg/L at 20 degrees Celsius	<.9	2.08	4.00	7.40	14.0	23.0	84.0
Chemical oxygen demand, in mg/L	<10	30	40	50	65	81	450
Dissolved solids dried at 180 degrees Celsius, in mg/L	159	387	597	829	949	1,110	2,800
Dissolved solids from water, in mg/L	152	380	609	780	873	1,000	2,660
Hardness, in mg/L calcium carbonate	88.0	160	224	310	372	406	660
Dissolved noncarbonate hardness (field), in mg/L calcium carbonate	18.8	45.2	68.8	87.6	120	183	228
Total noncarbonate hardness (field), in mg/L calcium carbonate	11.0	42.5	70.0	130	180	225	500
Suspended solids, in mg/L	0	12	18	45	131	330	2,380
Major inorganics, metals							
Dissolved calcium, in mg/L	28.0	46.5	63.0	81.0	95.0	100	180
Dissolved magnesium, in mg/L	6.00	13.0	22.7	29.0	35.0	38.0	51.0
Dissolved potassium, in mg/L	1.00	5.80	7.20	8.90	11.0	13.0	18.0
Dissolved sodium plus potassium, in mg/L as sodium	27.0	48.0	110	190	270	340	440
Dissolved sodium, in mg/L	12.9	57.0	100	150	190	259	720
Major inorganics, non-metals							
Total acid neutralizing capacity (field), in mg/L as calcium carbonate	8.0	95.0	112	153	190	230	313

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Date of first sample (month/year)	Date of last sample (month/year)	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Physical properties							
Dissolved oxygen, in mg/L	--	--	5/1970	8/2009	582	581	99.8
Dissolved oxygen, in percent saturation	--	--	10/1970	8/2009	569	NA	99.8
pH (field), in standard units	--	--	10/1968	8/2009	1,143	NA	100
Specific conductance, in µS/cm at 25 degrees celsius	--	--	10/1968	8/2009	1,153	1,153	100
Water temperature, in degrees Celsius	--	--	5/1970	8/2009	1,004	NA	100
Turbidity, in Jackson turbidity units	--	--	12/1973	9/1978	34	33	97.1
Turbidity, in nephelometric turbidity units	--	--	10/1978	8/2009	264	263	99.3
Five-day biochemical oxygen demand, in mg/L at 20 degrees Celsius	--	--	6/1970	7/2009	419	413	98.6
Chemical oxygen demand, in mg/L	--	--	6/1970	9/1987	294	293	99.7
Dissolved solids dried at 180 degrees Celsius, in mg/L	--	--	10/1968	8/2009	923	923	100
Dissolved solids from water, in mg/L	--	--	3/1969	8/2009	401	401	100
Hardness, in mg/L calcium carbonate	--	--	10/1968	8/2009	626	626	100
Dissolved noncarbonate hardness (field), in mg/L calcium carbonate	--	--	8/1991	8/2009	84	84	100
Total noncarbonate hardness (field), in mg/L calcium carbonate	--	--	10/1968	10/1984	270	270	100
Suspended solids, in mg/L	--	--	8/1975	9/1979	75	73	97.3
Major inorganics, metals							
Dissolved calcium, in mg/L	--	--	10/1968	8/2009	570	570	100
Dissolved magnesium, in mg/L	--	--	10/1968	8/2009	571	571	100
Dissolved potassium, in mg/L	--	--	12/1973	8/2009	430	430	100
Dissolved sodium plus potassium, in mg/L as sodium	--	--	2/1979	1/1980	35	35	100
Dissolved sodium, in mg/L	--	--	10/1968	8/2009	637	637	100
Major inorganics, non-metals							
Total acid neutralizing capacity (field), in mg/L as calcium carbonate	--	--	10/1968	7/1988	276	276	100

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Major inorganics, non-metals—Continued							
Total acid neutralizing capacity (laboratory), in mg/L as calcium carbonate	85.0	130	160	192	223	249	306
Alkalinity, filtered, in mg/L as calcium carbonate	72.0	118	147	183	216	244	300
Dissolved bicarbonate, in mg/L	0	139	169	218	259	293	453
Bicarbonate, in mg/L	86.0	116	140	190	237	283	382
Carbon dioxide, in mg/L	.077	1.28	2.18	4.04	13.5	29.0	74.4
Dissolved carbonate, in mg/L	0	0	0	.2	3.0	8.0	37
Total carbonate, in mg/L	0	0	0	0	0	2	22
Dissolved chloride, in mg/L	13.4	80.0	136	200	278	390	1,500
Dissolved fluoride, in mg/L	.259	.4	.58	.71	.82	.93	1.21
Total fluoride, in mg/L	.40	.50	.60	.70	.85	1.00	1.10
Dissolved silica, in mg/L	1.10	6.00	7.80	9.92	12.0	13.9	16.0
Dissolved sulfate, in mg/L	15.0	50.0	94.0	134	170	220	5,100
Nutrients							
Dissolved ammonia plus organic nitrogen, in mg/L as nitrogen	0	.50	.70	1.21	3.90	9.00	23.0
Total ammonia plus organic nitrogen, in mg/L as nitrogen	.60	1.08	1.19	1.46	3.00	9.78	16.3
Dissolve nitrate plus nitrite, in mg/L as nitrogen	.02	.68	1.10	1.90	3.20	5.02	57.0
Total nitrate plus nitrite, in mg/L as nitrogen	<.1	.7	1.0	1.4	2.7	4.1	>10
Dissolved nitrate, in mg/L as nitrogen	0	.57	.99	1.76	2.95	4.92	56.0
Nitrate, in mg/L as nitrogen	.56	.64	.72	1.04	1.78	3.02	3.97
Dissolved nitrite, in mg/L as nitrogen	.006	.020	.030	.080	.210	.510	4.90
Nitrite, in mg/L as nitrogen	.02	.04	.05	.10	.26	.50	.71
Dissolved organic nitrogen, in mg/L	0	.40	.54	.80	1.26	2.50	11.0
Total organic nitrogen, in mg/L	.76	.94	1.06	1.23	1.41	1.86	8.60
Dissolved phosphate, in mg/L as phosphorus	0	.18	.35	.82	1.6	3.0	6.8
Phosphate, in mg/L as phosphorus	0	.45	.86	2.8	4.6	6.0	7.2
Dissolved phosphorus, in mg/L	.0034	.21	.39	.86	1.98	3.60	7.90
Phosphorus, in mg/L	<.01	.58	1.01	2.30	5.30	7.00	14.0

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Date of first sample (month/year)	Date of last sample (month/year)	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Major inorganics, non-metals—Continued							
Total acid neutralizing capacity (laboratory), in mg/L as calcium carbonate	--	--	6/1989	8/2009	539	539	100
Alkalinity, filtered, in mg/L as calcium carbonate	--	--	7/1991	8/2009	216	216	100
Dissolved bicarbonate, in mg/L	--	--	7/1991	8/2009	215	214	99.5
Bicarbonate, in mg/L	--	--	10/1968	7/1988	266	265	99.6
Carbon dioxide, in mg/L	--	--	10/1968	8/2009	792	792	100
Dissolved carbonate, in mg/L	--	--	7/1991	8/2009	214	115	53.7
Total carbonate, in mg/L	--	--	10/1968	7/1988	272	32	11.8
Dissolved chloride, in mg/L	230	39.2	10/1968	8/2009	673	673	100
Dissolved fluoride, in mg/L	--	--	12/1973	8/2009	91	91	100
Total fluoride, in mg/L	--	--	11/1975	9/1979	41	41	100
Dissolved silica, in mg/L	--	--	12/1973	8/2009	111	111	100
Dissolved sulfate, in mg/L	--	--	10/1968	8/2009	640	640	100
Nutrients							
Dissolved ammonia plus organic nitrogen, in mg/L as nitrogen	--	--	1/1990	8/2009	493	491	99.6
Total ammonia plus organic nitrogen, in mg/L as nitrogen	--	--	10/1976	8/2009	133	133	100
Dissolve nitrate plus nitrite, in mg/L as nitrogen	--	--	3/1973	8/2009	562	561	99.8
Total nitrate plus nitrite, in mg/L as nitrogen	--	--	7/1975	7/1988	46	44	95.7
Dissolved nitrate, in mg/L as nitrogen	--	--	10/1968	8/2009	591	589	99.7
Nitrate, in mg/L as nitrogen	--	--	4/1982	7/1988	18	18	100
Dissolved nitrite, in mg/L as nitrogen	--	--	3/1973	8/2009	520	513	98.7
Nitrite, in mg/L as nitrogen	--	--	4/1981	7/1988	19	19	100
Dissolved organic nitrogen, in mg/L	--	--	12/1973	8/2009	363	360	99.2
Total organic nitrogen, in mg/L	--	--	10/1982	8/2009	68	68	100
Dissolved phosphate, in mg/L as phosphorus	--	--	9/1977	8/2009	417	414	99.3
Phosphate, in mg/L as phosphorus	--	--	8/1976	7/1988	137	134	97.8
Dissolved phosphorus, in mg/L	--	--	12/1988	8/2009	417	415	99.5
Phosphorus, in mg/L	--	--	3/1973	8/2009	291	289	99.3

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Nutrients—Continued							
Dissolved nitrogen, in mg/L	0.55	1.60	2.40	3.77	6.15	10.0	17.0
Total nitrogen, in mg/L	1.70	2.40	3.40	4.64	7.26	9.82	113
Microbiological							
Fecal coliform count, in colonies per 100 milliliters	<80	145	280	840	4,000	28,000	>60,000
Fecal streptococcal bacteria, in colonies per 100 milliliters	<100	79	163	400	1,500	8,800	>10,000,000
Total coliform count, in colonies per 100 milliliters	<1,000	1,450	7,200	40,000	190,000	625,000	>6,000,000
Biological							
Total periphyton biomass, in grams per square meter	.04	.18	.51	1.80	4.70	7.30	10.7
Periphyton biomass, ash weight (inorganic content), in grams per square meter	.35	.82	2.92	10.4	33.2	47.6	52.6
Periphyton biomass, dry weight, in grams per square meter	.39	1.02	3.42	12.2	37.3	56.6	58.1
Periphyton biomass to chlorophyll ratio, unitless	22.6	28.2	126	420	612	1,280	17,500
Plankton biomass to chlorophyll ratio, unitless	59.2	70.3	146	262	1,340	3,100	4,770
Chlorophyll <i>a</i> in periphyton, in milligrams per square meter	0	.04	1.14	4.28	12.2	27.0	69.2
Chlorophyll <i>b</i> in periphyton, milligrams per square meter	0	0	.02	1.05	3.69	5.92	34.8
Chlorophyll <i>a</i> in phytoplankton corrected for pheophytin, in µg/L	0	2.0	11	24	49	82	181
Chlorophyll <i>a</i> in phytoplankton uncorrected for pheophytin, in µg/L	0	5.97	13.2	29.0	59.0	106	345
Chlorophyll <i>b</i> in phytoplankton, µg/L	0	0	0	5.14	32.1	50.6	57.3
Pheophytin <i>a</i> in phytoplankton, in mg/L	0	0	5.0	12	27	45	338
Minor inorganics, metals							
Dissolved barium, in µg/L	44.1	99.9	120	134	160	180	230
Dissolved beryllium, in µg/L	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6
Dissolved cadmium, in µg/L	0	0	0	0	1.0	3.0	21

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Date of first sample (month/year)	Date of last sample (month/year)	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Nutrients—Continued							
Dissolved nitrogen, in mg/L	--	--	12/1973	8/2009	402	402	100
Total nitrogen, in mg/L	--	--	11/1975	8/2009	129	129	100
Microbiological							
Fecal coliform count, in colonies per 100 milliliters	--	--	10/1976	7/2009	355	347	97.7
Fecal streptococcal bacteria, in colonies per 100 milliliters	--	--	10/1976	7/2009	367	359	97.8
Total coliform count, in colonies per 100 milliliters	--	--	11/1975	9/1987	133	119	89.5
Biological							
Total periphyton biomass, in grams per square meter	--	--	6/1978	1/1983	20	20	100
Periphyton biomass, ash weight (inorganic content), in grams per square meter	--	--	6/1978	1/1983	20	20	100
Periphyton biomass, dry weight, in grams per square meter	--	--	6/1978	1/1983	20	20	100
Periphyton biomass to chlorophyll ratio, unitless	--	--	6/1978	1/1983	19	19	100
Plankton biomass to chlorophyll ratio, unitless	--	--	5/1977	9/1978	10	10	100
Chlorophyll <i>a</i> in periphyton, in milligrams per square meter	--	--	12/1977	8/1983	24	22	91.7
Chlorophyll <i>b</i> in periphyton, milligrams per square meter	--	--	12/1977	8/1983	24	18	75.0
Chlorophyll <i>a</i> in phytoplankton corrected for pheophytin, in µg/L	--	--	10/1986	6/1996	107	100	93.5
Chlorophyll <i>a</i> in phytoplankton uncorrected for pheophytin, in µg/L	--	--	9/1975	6/1996	125	122	97.6
Chlorophyll <i>b</i> in phytoplankton, µg/L	--	--	5/1977	9/1978	11	7	63.6
Pheophytin <i>a</i> in phytoplankton, in mg/L	--	--	10/1986	6/1996	106	90	84.9
Minor inorganics, metals							
Dissolved barium, in µg/L	--	--	12/1987	8/2009	110	110	100
Dissolved beryllium, in µg/L	--	--	12/1987	8/2009	110	6	5.5
Dissolved cadmium, in µg/L	$e^{\{.7409[\ln(\text{hardness})]-4.719\}} (1.101672-[(\ln \text{hardness}(0.041838))])$	6.2	6/1970	8/2009	197	56	28.4

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Date of first sample (month/year)	Date of last sample (month/year)	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Minor inorganics, metals—Continued							
Total cadmium, in mg/L	--	--	12/1973	7/1979	37	16	43.2
Dissolved chromium, in µg/L	11	7.0	11/1969	8/2009	199	46	23.1
Chromium, in µg/L	--	--	12/1973	7/1979	31	24	77.4
Dissolved cobalt, in µg/L	--	--	12/1987	8/2009	110	2	1.8
Dissolved copper, in µg/L	--	--	5/1970	8/2009	207	103	49.8
Copper, in µg/L	--	--	12/1973	7/1979	37	30	81.1
Dissolved iron, in µg/L	1,000	.5	5/1970	8/2009	211	181	85.8
Iron, in µg/L	--	--	12/1973	9/1979	56	56	100
Dissolved lead, in µg/L	$e^{\{1.273[\ln(\text{hardness})]-4.705\}} (1.46203-[(\ln \text{hardness})(1.45712)])$	12.4	5/1970	8/2009	204	120	58.8
Lead, in µg/L	--	--	12/1973	7/1979	37	18	48.6
Dissolved lithium, in µg/L	--	--	12/1987	8/2009	110	110	100
Dissolved manganese, in µg/L	--	--	5/1970	8/2009	209	193	92.3
Manganese, in µg/L	--	--	12/1973	9/1979	56	56	100
Dissolved mercury, in µg/L	.77	1.5	12/1973	5/2009	137	33	24.1
Mercury, in µg/L	--	--	12/1973	7/1979	15	1	6.7
Dissolved molybdenum, in µg/L	--	--	3/1976	8/2009	111	27	24.3
Dissolved nickel, in µg/L	$e^{(0.8460*(\ln(\text{hardness}))-0.0584)} (0.997)$.0	5/1970	8/2009	133	45	33.8
Nickel, in µg/L	--	--	11/1975	7/1979	13	13	100
Dissolved silver, in µg/L	--	--	12/1987	8/2009	110	9	8.2
Silver, in µg/L	--	--	11/1975	7/1979	13	12	92.3
Dissolved strontium, in µg/L	--	--	12/1987	8/2009	110	110	100
Dissolved vanadium, in µg/L	--	--	12/1987	8/2009	110	74	67.3
Dissolved zinc, in µg/L	$e^{(0.8473*(\ln(\text{hardness}))-0.884)} (0.986)$	2.7	5/1970	8/2009	208	174	83.7
Zinc, in µg/L	--	--	12/1973	7/1979	37	36	97.3
Minor inorganics, non-metals							
Dissolved arsenic, in µg/L	150	.0	3/1976	8/2009	141	141	100
Arsenic, in µg/L	150	.0	11/1975	7/1979	14	11	78.6
Dissolved boron, in µg/L	--	--	10/1968	3/1976	15	15	100
Dissolved selenium, in µg/L	5	.0	5/1979	8/2009	140	51	36.4
Organics, pesticides							
2,4,5-Trichlorophenoxyacetic acid, in µg/L	--	--	5/1973	8/2009	116	17	14.7
2,4-Dichlorophenoxyacetic acid, in µg/L	--	--	5/1973	8/2009	117	96	82.1
2-Chloro-4-isopropylamino-6-amino-s-triazine, in µg/L	--	--	2/1991	8/2009	75	1	1.3

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Organics, pesticides—Continued							
2-Chloro-6-ethylamino-4-amino-s-triazine, in µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Alachlor, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	.60
Aldrin, in µg/L	<.0019	<.0019	<.0019	<.0019	<.0019	<.0019	<.0019
.alpha.-Endosulfan, in µg/L	<.001	<.0021	<.0021	<.0021	<.0021	<.0021	.0021
Ametryn, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Atrazine, in µg/L	.053	.080	.080	.10	.19	.30	2.0
Bromacil, in µg/L	0	0	.12	.18	.20	.45	4.60
Butachlor, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Butylate, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Carbophenothion, in µg/L	<.5	<.5	<.5	<.5	<.5	<.5	<.5
Carboxin, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	<.2
Chlordane, in µg/L	0	0	0	0	0	.1	.4
Chlorpyrifos, in µg/L	<.028	<.028	<.028	<.028	<.028	<.028	<.028
Cyanazine, in µg/L	<.1	<.2	<.2	<.2	<.2	<.2	<.2
Cycloate, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	.1
Diazinon, in µg/L	0	.01	.01	.04	.07	.11	.32
Dichlorprop, in µg/L	<.036	<.036	<.036	<.036	<.036	<.036	<.036
Dieldrin, in µg/L	0	0	.001	.002	.004	.02	.09
Diphenamid, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Disulfoton, in µg/L	<.01	<.3	<.3	<.3	<.3	<.3	<.3
Endrin, in µg/L	<.025	<.025	<.025	<.025	<.025	<.025	<.025
Ethion, in µg/L	<.026	<.026	<.026	<.026	<.026	<.026	<.026
Fonofos, in µg/L	<.007	<.02	<.02	<.02	<.02	<.02	<.02
Heptachlor epoxide, in µg/L	0	0	0	0	.001	.001	.004
Heptachlor, in µg/L	<.002	<.002	<.002	<.002	<.002	<.002	<.002
Hexazinone, in µg/L	<.2	<.3	<.3	<.3	<.3	<.3	<.3
Lindane, in µg/L	0	0	0	.0022	.010	.020	.051
Malathion, in µg/L	<.3	<.3	<.3	<.3	<.3	<.3	5.5
Methyl parathion, in µg/L	<.028	<.028	<.028	<.028	<.028	<.028	<.028
Carbophenothion-methyl, in µg/L	0	0	0	0	0	0	.01
Metolachlor, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	.2
Metribuzin, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Mirex, in µg/L	<.01	<.01	<.01	<.01	<.01	<.01	.01
<i>p,p'</i> -Dichlorodiphenyldichloroethane (DDD), in µg/L	0	0	0	0	0	0	.003

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Date of first sample (month/year)	Date of last sample (month/year)	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Organics, pesticides—Continued							
2-Chloro-6-ethylamino-4-amino-s-triazine, in µg/L	--	--	2/1991	8/2009	75	2	2.7
Alachlor, in µg/L	--	--	8/1988	8/2009	85	7	8.2
Aldrin, in µg/L	--	--	5/1973	8/2009	118	1	.8
.alpha.-Endosulfan, in µg/L	0.046	0.0	11/1988	8/2009	84	1	1.2
Ametryn, in µg/L	--	--	8/1988	8/2009	84	0	.0
Atrazine, in µg/L	--	--	8/1988	8/2009	84	53	63.1
Bromacil, in µg/L	--	--	2/1991	8/2009	73	26	35.6
Butachlor, in µg/L	--	--	2/1991	8/2009	75	0	.0
Butylate, in µg/L	--	--	2/1991	8/2009	75	0	.0
Carbophenothion, in µg/L	--	--	5/1974	8/2009	142	1	.7
Carboxin, in µg/L	--	--	2/1991	8/2009	73	0	.0
Chlordane, in µg/L	.0043	10.2	5/1973	8/2009	118	12	1.2
Chlorpyrifos, in µg/L	--	--	8/1990	8/2009	122	27	22.1
Cyanazine, in µg/L	--	--	8/1988	8/2009	84	0	.0
Cycloate, in µg/L	--	--	2/1991	8/2009	75	1	1.3
Diazinon, in µg/L	.17	3.6	6/1972	8/2009	165	137	83.0
Dichlorprop, in µg/L	--	--	8/1988	8/2009	81	9	11.1
Dieldrin, in µg/L	.056	.8	5/1973	8/2009	118	88	74.6
Diphenamid, in µg/L	--	--	2/1991	8/2009	75	0	.0
Disulfoton, in µg/L	--	--	8/1989	8/2009	115	0	.0
Endrin, in µg/L	.036	.0	5/1973	8/2009	118	1	.8
Ethion, in µg/L	--	--	5/1974	8/2009	142	1	.7
Fonofos, in µg/L	--	--	8/1990	8/2009	122	0	.0
Heptachlor epoxide, in µg/L	.0038	.8	5/1973	8/2009	118	28	23.7
Heptachlor, in µg/L	.0038	.0	5/1973	8/2009	118	1	.8
Hexazinone, in µg/L	--	--	2/1991	8/2009	74	0	.0
Lindane, in µg/L	--	--	5/1973	8/2009	118	71	60.2
Malathion, in µg/L	.1	.6	5/1973	8/2009	161	14	8.7
Methyl parathion, in µg/L	--	--	5/1973	8/2009	164	2	1.2
Carbophenothion-methyl, in µg/L	--	--	5/1974	5/1991	24	1	4.2
Metolachlor, in µg/L	--	--	8/1988	8/2009	85	1	1.2
Metribuzin, in µg/L	--	--	8/1988	8/2009	84	1	1.2
Mirex, in µg/L	.001	1.2	11/1988	8/2009	84	2	2.4
<i>p,p'</i> -Dichlorodiphenyldichloroethane (DDD), in µg/L	--	--	5/1973	8/2009	118	4	3.4

Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	Minimum value	10th percentile	25th percentile	50th percentile	75th percentile	90th percentile	Maximum value
Organics, pesticides—Continued							
<i>p,p'</i> -Dichlorodiphenyldichloroethylene (DDE), in µg/L	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
<i>p,p'</i> -Dichlorodiphenyltrichloroethane (DDT), in µg/L	0	0	0	0	0	0	.04
Ethylan, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Methoxychlor, in µg/L	<.01	<.01	<.01	<.01	<.01	<.01	.01
Parathion, in µg/L	<.024	<.024	<.024	<.024	<.024	<.024	<.024
Phorate, in µg/L	<.076	<.076	<.076	<.076	<.076	<.076	<.076
Prometon, in µg/L	<.22	<.22	<.22	<.22	<.22	<.22	.6
Prometryn, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Propachlor, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	.12
Propazine, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	.10
Silvex, in µg/L	0	0	0	0	0	.01	.14
Simazine, in µg/L	.056	.08	.08	.1	.20	.34	1.1
Simetryn, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	.13
Terbacil, in µg/L	<.2	<.2	<.2	<.2	<.2	<.2	.27
Toxaphene, in µg/L	<1	<1	<1	<1	<1	<1	1
Tribufos, in µg/L	<.01	<.06	<.06	<.06	<.06	<.06	<.06
Trifluralin, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	.80
Vernolate, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Organics, other							
Polychlorinated biphenyls, in µg/L	0	0	0	0	0	0	3
Total organic carbon, in mg/L	1.90	6.90	7.80	9.60	12.1	17.3	52
Phenolic compounds, in µg/L	0	0	.5	3	5.5	9	28
Polychlorinated naphthalenes, in µg/L	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Radiochemical							
Potassium-40 radioactive isotope, in picocuries per liter	4.6	5.4	7.5	8.2	9.0	9.0	9.7
Sediment							
Suspended sediment particle diameter, in percent smaller than .0625 millimeters	21	33	55	68	77	88	94
Suspended sediment, in mg/L	12	31	39	68	146	456	2,000
Suspended sediment discharge, in tons/day ¹	3.2	10.8	15.6	47.6	142	909	18,522

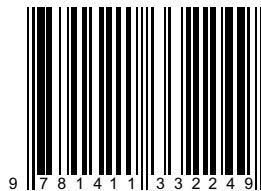
Appendix 2. Summary statistics of water-quality data from the North Canadian River near Harrah, Oklahoma, streamflow-gaging station, 1968–2009.—Continued

[mg/L, milligrams per liter; µg/L, micrograms per liter; L, liter; <, less than; >, greater than; --, not determined; e, natural exponent; ln, natural logarithm; hardness, hardness in mg/L; CCC, Criteria Continuous Concentration (U.S. Environmental Protection Agency, 2010a); all constituents analyzed in unfiltered samples unless identified as “dissolved” or “filtered”]

Constituent name	CCC	Percent of samples in which measurement exceeded CCC	Date of first sample (month/year)	Date of last sample (month/year)	Number of samples	Number of samples with detected measurements	Percent of samples with detected measurements
Organics, pesticides—Continued							
<i>p,p'</i> -Dichlorodiphenyldichloroethylene (DDE), in µg/L	--	--	5/1973	8/2009	117	2	1.7
<i>p,p'</i> -Dichlorodiphenyltrichloroethane (DDT), in µg/L	0.001	2.5	5/1973	8/2009	118	6	5.1
Ethylan, in µg/L	--	--	11/1988	5/2000	46	0	.0
Methoxychlor, in µg/L	.03	.0	11/1988	8/2009	84	1	1.2
Parathion, in µg/L	.013	.0	5/1973	8/2009	164	5	3.0
Phorate, in µg/L	--	--	8/1989	8/2009	123	1	.8
Prometon, in µg/L	--	--	8/1988	8/2009	85	10	11.8
Prometryn, in µg/L	--	--	8/1988	8/2009	85	0	.0
Propachlor, in µg/L	--	--	2/1991	8/2009	75	1	1.3
Propazine, in µg/L	--	--	8/1988	8/2009	85	3	3.5
Silvex, in µg/L	--	--	5/1973	8/2009	117	13	11.1
Simazine, in µg/L	--	--	8/1988	8/2009	85	62	72.9
Simetryn, in µg/L	--	--	8/1988	8/2009	85	3	3.5
Terbacil, in µg/L	--	--	2/1991	8/2009	75	2	2.7
Toxaphene, in µg/L	.0002	1.0	5/1974	8/2009	103	1	1.0
Tribufos, in µg/L	--	--	8/1989	8/2009	126	0	.0
Trifluralin, in µg/L	--	--	8/1988	8/2009	85	4	4.7
Vernolate, in µg/L	--	--	2/1991	8/2009	75	0	.0
Organics, other							
Polychlorinated biphenyls, in µg/L	.014	7.6	5/1973	8/2009	118	9	7.6
Total organic carbon, in mg/L	--	--	10/1977	8/2009	103	103	100
Phenolic compounds, in µg/L	--	--	5/1973	6/1996	92	69	75.0
Polychlorinated naphthalenes, in µg/L	--	--	3/1976	5/2000	47	0	.0
Radiochemical							
Potassium-40 radioactive isotope, in picocuries per liter	--	--	11/1980	5/1981	17	17	100
Sediment							
Suspended sediment particle diameter, in percent smaller than .0625 millimeters	--	--	10/1982	3/1986	65	65	100
Suspended sediment, in mg/L	--	--	10/1982	3/1986	65	65	100
Suspended sediment discharge, in tons/day ¹	--	--	10/1982	3/1986	65	65	100

¹ (Instantaneous discharge in cubic feet per second)*(Sediment concentration in mg/L)*(0.00269 second*L*tons/d*cubic feet*mg).

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