In cooperation with the City of Dallas Water Utilities Division

Bromide, Chloride, and Sulfate Concentrations and Loads at U.S. Geological Survey Streamflow-Gaging Stations 07331600 Red River at Denison Dam, 07335500 Red River at Arthur City, and 07336820 Red River near DeKalb, Texas, 2007–09

Scientific Investigations Report 2010–5120

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

Cover: Red River downstream from Denison Dam on Lake Texoma in Texas, February 2008.

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Conversion Factors, Datum, and Water-Quality Units

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
acre-foot (acre-ft)	0.001233	cubic hectometer (hm^3)
	Flow rate	
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
ton, short (2,000 pounds)	0.9072	megagram (Mg)
ton per day (ton/d)	0.9072	metric ton per day

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

$$°F=(1.8 \times °C)+32$$

Datum

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

Water-Quality Units

Concentrations are reported in metric units. Chemical concentrations are reported in milligrams per liter (mg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight of solute (milligrams) per unit volume (liter) of water. For concentrations less than 7,000 mg/L, the numerical value of milligrams per liter is equivalent to the concentration in parts per million.

Specific conductance is reported in microsiemens per centimeter at 25 degrees Celsius (μS/cm).

Bromide, Chloride, and Sulfate Concentrations and Loads at U.S. Geological Survey Streamflow-Gaging Stations 07331600 Red River at Denison Dam, 07335500 Red River at Arthur City, and 07336820 Red River near DeKalb, Texas, 2007–09

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Abstract

The U.S. Geological Survey, in cooperation with the City of Dallas Water Utilities Division, did a study to characterize bromide, chloride, and sulfate concentrations and loads at three U.S. Geological Survey streamflow-gaging stations on the reach of the Red River from Denison Dam, which impounds Lake Texoma, to the U.S. Highway 259 bridge near DeKalb, Texas. Bromide, chloride, and sulfate concentrations and loads were computed for streamflow-gaging stations on the study reach of the Red River. Continuous streamflow and specific conductance data and discrete samples for bromide, chloride, sulfate, and specific conductance were collected at three main-stem streamflow-gaging stations on the Red River: 07331600 Red River at Denison Dam near Denison, Texas (Denison Dam gage), 07335500 Red River at Arthur City, Texas (Arthur City gage), and 07336820 Red River near DeKalb, Texas (DeKalb gage). At each of these streamflow-gaging stations, discrete water-quality data were collected during January 2007–February 2009; continuous water-quality data were collected during March 2007–February 2009. Two periods of high flow resulted from floods during the study; floods during June–July 2007 resulted in elevated flow during June–September 2007 and smaller floods during March–April 2008 resulted in elevated flow during March–April 2008.

Bromide, chloride, and sulfate concentrations in samples collected at the three gages decreased downstream. Median bromide concentrations ranged from 0.32 milligram per liter at the Denison Dam gage to 0.19 milligram per liter at the DeKalb gage. Median chloride concentrations ranged from 176 milligrams per liter at the Denison Dam gage to 108 milligrams per liter at the DeKalb gage, less than the 300-milligrams per liter secondary maximum contaminant level established by the Texas Commission on Environmental Quality. Median sulfate concentrations ranged from 213 milligrams per liter at the Denison Dam gage to 117 milligrams per liter at the DeKalb gage, also less than the 300-milligrams per liter secondary maximum contaminant level. Kruskal-Wallis analyses indicated statistically significant differences among bromide, chloride, and sulfate concentrations at the three gages.

Regression equations to estimate bromide, chloride, and sulfate loads were developed for each of the three gages. The largest loads were estimated for a period of relatively large streamflow, June–September 2007, when about 50 percent of the load for the study period occurred at each gage. Adjusted R-squared values were largest for regression equations for the DeKalb gage, ranging from .957 for sulfate to .976 for chloride. Adjusted R-squared values for all regression equations developed to estimate loads of bromide, chloride, and sulfate at the three gages were .899 or larger.

Introduction

Regional planning groups in Texas have proposed increasing the transfer of water from the Red River to meet municipal water-supply needs for the rapidly growing Dallas metropolitan area and other cities in north Texas. These supplies could be withdrawn from points in a reach of the Red River from Lake Texoma, impounded by Denison Dam, to several miles downstream at a point on the Red River north of DeKalb, Tex., at the U.S. Highway 259 bridge crossing (fig. 1). Municipal water suppliers, such as the City of Dallas Water Utilities Division, are increasingly concerned about the possibility of bromate concentrations in finished water supplies because of bromide in the raw water. When the raw water contains bromide, bromate (a known carcinogen) can form during disinfection processes that oxidize the water to kill pathogens (Singer, 2006; Agus and others, 2009). The oxidation of bromide to bromate during ozonation is influenced by factors such as the concentration of bromide, pH of the source water, and reaction time of the ozone used to disinfect the water (State of New York, Department of Health, 2006). Bromate concentrations in finished drinking water are

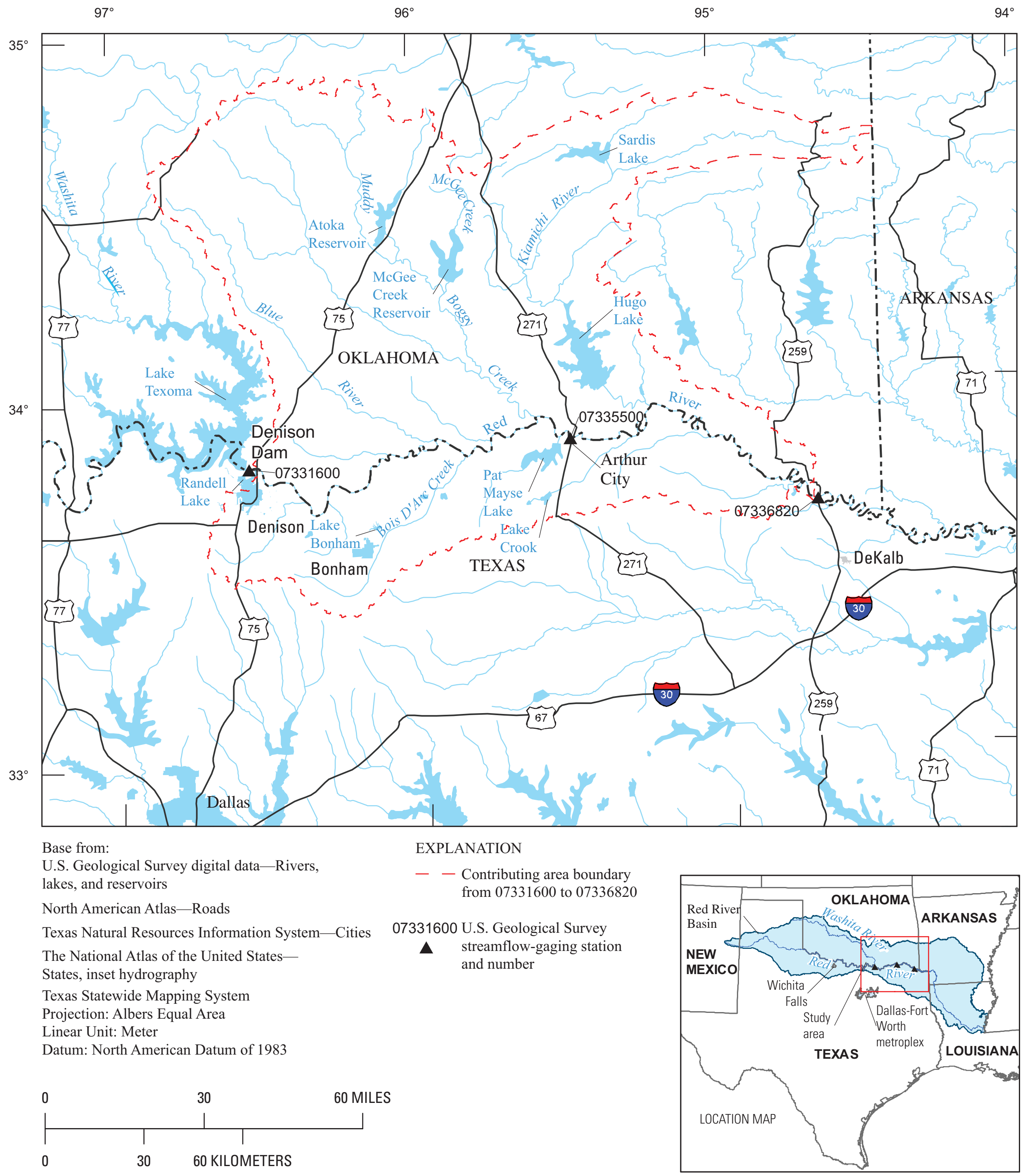

Figure 1. Contributing area for reach of the Red River from Denison Dam to DeKalb, Texas, and location of U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas.

regulated by the Texas Commission on Environmental Quality at a maximum contaminant level of 0.01 milligram per liter (mg/L) (Texas Administrative Code, 2009). The U.S. Environmental Protection Agency (2006a) has developed a Stage 2 disinfectants and disinfection byproducts (DBP) rule to improve drinking-water quality and provide additional protection from DBP.

Concentrations of bromide and other salinity-related constituents and physical properties in Lake Texoma were characterized by the U.S. Geological Survey (USGS) in a previous report (Baldys, 2009). Median bromide concentrations ranged from 0.28 mg/L in the Washita arm of Lake Texoma to 0.60 mg/L in the Red River arm of the lake. Median concentrations of chloride ranged from 122 mg/L in the Washita arm of Lake Texoma to 431 mg/L in the Red River arm of the lake. Because elevated concentrations of salinity-related constituents, including chloride and sulfate, have been measured in Lake Texoma (Atkinson and others, 1999; Baldys, 2009), there is a concern that chloride and sulfate concentrations in the reach of the Red River downstream from Lake Texoma to DeKalb, Tex., might at times exceed applicable secondary maximum contaminant levels (SMCLs) of the "Texas Surface Water Quality Standards" for drinking water (Texas Commission on Environmental Quality, 2003).

As a companion to the study summarized in Baldys (2009), the USGS, in cooperation with the City of Dallas Water Utilities Division, did a study to characterize bromide, chloride, and sulfate concentrations and loads at three USGS streamflow-gaging stations on the reach of the Red River from Denison Dam, which impounds Lake Texoma, to the U.S. Highway 259 bridge near DeKalb, Tex. Discrete water-quality data collected during January 2007–February 2009 and continuous water-quality data collected during March 2007–February 2009 were evaluated at USGS streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Tex.; 07335500 Red River at Arthur City, Tex.; and 07336820 Red River near DeKalb, Tex. Little information is available regarding bromide, chloride, and sulfate concentrations and loads in that reach of the Red River. Specific conductance measured in 25 discrete water-quality samples and measured continuously at the three gages were used in load calculations. In addition to water released from Lake Texoma through Denison Dam, tributaries contribute a large part of the flow in the reach of the Red River from Denison Dam to near DeKalb. Because of tributary inflows, the water quality of the Red River in this reach might differ from the water quality of Lake Texoma. In addition to Lake Texoma, there are numerous reservoirs in the contributing area for the reach. Bromide, chloride, and sulfate concentrations and loads also could vary in the reach because of reservoir releases and changes in hydrologic conditions.

Purpose and Scope

This report describes bromide, chloride, and sulfate concentrations and loads and specific conductance at three USGS streamflow-gaging stations on the main stem of the Red River between Denison Dam at Lake Texoma in Texas and Oklahoma and the U.S. Highway 259 bridge near DeKalb, Tex.: USGS streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Tex. (hereinafter Denison Dam gage); 07335500 Red River at Arthur City, Tex. (hereinafter Arthur City gage); and 07336820 Red River near DeKalb, Tex. (hereinafter DeKalb gage). At each gage, discrete water-quality data collected during January 2007–February 2009 and continuous water-quality data collected during March 2007–February 2009 were evaluated. The 25 discrete environmental samples collected at each gage were analyzed for selected dissolved constituents (bromide, calcium, magnesium, potassium, sodium, carbonate, bicarbonate, chloride, and sulfate) and physical properties (specific conductance, pH, temperature, dissolved oxygen, and alkalinity). Bromide, the primary constituent of concern, and chloride, sulfate, and specific conductance, of secondary concern, are evaluated in light of the amount of streamflow associated with each sample. This report also documents the techniques used to collect and analyze the discrete water-quality samples collected every 2 to 6 weeks during January 2007–February 2009 at the three gages.

The spatial and temporal variability of bromide, chloride, sulfate, and specific conductance is described using summary statistics and boxplots. A Kruskal-Wallis test was used to determine if there were statistically significant differences among the bromide, chloride, and sulfate concentrations measured at each gage. Results for chloride and sulfate are compared with applicable SMCLs. Estimates of bromide, chloride, and sulfate loads were developed for March 2007–February 2009 using continuously measured streamflow and water-quality properties (specific conductance, water temperature) as well as discrete water-quality samples analyzed for bromide, chloride, sulfate, and specific conductance.

Description of Study Area

The study area is the reach of the Red River from Denison Dam, which impounds Lake Texoma on the Texas-Oklahoma border, to the U.S. Highway 259 bridge on the Red River near DeKalb (hereinafter the Denison Dam-DeKalb reach) and the contributing area to this reach (fig. 1). During January 2007–February 2009, releases from Lake Texoma accounted for 44 percent of the streamflow measured at the DeKalb gage. During periods of drought, most of the flow in the Denison Dam-DeKalb reach measured at the three streamflow-gaging stations (see table on next page) along this reach consists of releases from Lake Texoma (U.S. Army Corps of Engineers, 2009; U.S. Geological Survey, 2009). During wet periods, releases from Lake Texoma can vary greatly depending on reservoir management needs; the U.S. Army Corps of Engineers releases water from Lake Texoma to generate power and manage inflows. The hydrology and climatology of the drainage basin upstream from Lake Texoma, which has a major effect on the quantity and quality of flows released through Denison Dam, are described in Baldys (2009).

Description of U.S. Geological Survey streamflow-gaging stations on Denison Dam-DeKalb reach of Red River.

Station number (fig. 1)	Station name	Latitude (degrees, minutes, seconds)	Longitude (degrees, minutes, seconds)
07331600	Red River at Denison Dam near Denison, Tex.	33°49'08"	96°33'47"
07335500	Red River at Arthur City, Tex.	33°52'30"	95°30'06"
07336820	Red River near DeKalb, Tex.	33°41'02"	94°41'39"

In addition to outflows from Lake Texoma, streamflow in the Denison Dam-DeKalb reach of the Red River is mostly from tributaries in Oklahoma. Tributaries in a small part of Texas also confluence with the Red River and provide inflows to the Denison Dam-DeKalb reach (fig. 1). Annual rainfall increases from about 38 inches (in.) at Denison to about 46 in. at DeKalb (National Weather Service Weather Forecast Office, Dallas/Fort Worth, 2009).

Measured in miles upstream from the mouth of the Red River where it empties into marshlands surrounding the Mississippi and Atchafalaya Rivers, the Denison Dam gage is at river mile 725.5 and the DeKalb gage is at river mile 556.9; the Denison Dam-DeKalb reach is 168.6 river miles (U.S. Geological Survey, 1987). Perennial tributaries to the Red River in this reach include the Blue River, Muddy Boggy Creek, and Kiamichi River from Oklahoma. The ephemeral Bois D'Arc Creek is the largest tributary in Texas that contributes flow (fig. 1).

Four reservoirs on tributaries in Oklahoma to the Denison Dam-DeKalb reach have conservation pool capacities of more than 100,000 acre-feet (acre-ft) (U.S. Geological Survey, 2009): (1) Atoka Reservoir (conservation pool capacity 123,500 acre-ft); (2) McGee Creek Reservoir (conservation pool capacity 108,004 acre-ft); (3) Hugo Lake (conservation pool capacity 109,560 acre-ft); and (4) Sardis Lake (conservation pool capacity 274,333 acre-ft) (fig. 1). Atoka Reservoir, constructed in 1959, and McGee Creek Reservoir, constructed in 1978 (U.S. Geological Survey, 2009), are on the upper reaches of the Muddy Boggy Creek tributary. The Blue River and Muddy Boggy Creek enter the Red River upstream from the Arthur City gage (fig. 1). Although the water quality of Muddy Boggy Creek has not been assessed for public water-supply use by the State of Oklahoma or U.S. Environmental Protection Agency (2006b), historically the chemical quality of the surface water of Muddy Boggy Creek Basin was deemed sufficient for domestic, irrigation, and most industrial purposes; concentrations of dissolved solids were 100 to 500 mg/L (Westfall and Cummings, 1963). The U.S. Environmental Protection Agency (2006b) also has not assessed the water quality of McGee Creek for municipal water-supply uses; historically the surface waters of McGee Creek contained concentrations of dissolved solids less than 100 mg/L (Westfall and Cummings, 1963). The drainage area for the Arthur City gage is 44,531 square miles (mi^2), of which 5,936 mi^2 are probably noncontributing (U.S. Geological Survey, 2009).

Hugo Lake, located on the Kiamichi River, was constructed in 1974 and has a drainage area of 1,709 mi^2 (U.S. Geological Survey, 2009). Sardis Lake, located on a tributary to the Kiamichi River upstream from Hugo Lake, was constructed in 1982 and has a drainage area of 275 mi^2. The Kiamichi River confluences with the Red River downstream from the Arthur City gage and upstream from the DeKalb gage (fig. 1). According to Laine and Cummings (1963), the water of the Kiamichi River Basin is of excellent quality for municipal, agricultural, and most industrial uses. On the basis of data collected from the Kiamichi River during December 1998–September 2001, the Oklahoma Water Resources Board (2010) assigned a supported rating for water used for the designated beneficial use for public and private water supply. The drainage area at the DeKalb gage is 47,348 mi^2, of which 5,936 mi^2 are probably noncontributing (U.S. Geological Survey, 2009).

In addition to a relatively large reservoir near Arthur City (Pat Mayse Lake, capacity 122,000 acre-ft [Texas Water Development Board, 2009]), several relatively small reservoirs are in the contributing area to the Denison Dam-DeKalb reach on the Texas side of the Red River, including Randell Lake (conservation pool capacity 5,400 acre-ft [Handbook of Texas Online, 2009]), Lake Bonham (conservation pool capacity 12,022 acre-ft [Texas Water Development Board, 2009]), and Lake Crook (conservation pool capacity 9,106 acre-ft [Texas Water Development Board, 2009]). Compared with releases from Lake Texoma and releases from reservoirs with conservation pool capacities of more than 100,000 acre-ft in the contributing area to the Denison Dam-DeKalb reach, releases from the smaller reservoirs likely have little effect on the water quality of the Red River in the Denison Dam-DeKalb reach (fig. 1).

A summary report by the Red River Authority of Texas (2009) states "water resources within the Red River Basin are generally good and support a hearty and robust aquatic life with respect to stream standards. However, only 12 of the 30 classified stream segments have been designated as useable for public water supply [because of] naturally occurring [large] concentrations of salt." Analyses by the Red River Authority of Texas (2009) also indicated chloride, chlorophyll *a*, sulfate, and pH levels were increasing over time, however, only values for chlorophyll *a* exceeded State standards (Texas Commission on Environmental Quality, 2003).

Data-Collection and Regression Methods

During March 1, 2007–February 28, 2009, the USGS continuously monitored selected water-quality properties, including specific conductance, at the three streamflow-gaging stations on the main stem of the Red River, the Denison Dam, Arthur City, and DeKalb gages (fig. 1). During January 31, 2007–February 19, 2009, discrete water-quality samples also were collected every 2 to 6 weeks at these gages and analyzed for selected dissolved constituents, including bromide, chloride, and sulfate concentrations, and for specific conductance. The Denison Dam gage is 1,800 feet (ft) downstream from the Denison Dam powerhouse. The Arthur City gage is located on U.S. Highway 271 bridge in Arthur City and the DeKalb gage is located on U.S. Highway 259 bridge, 13 miles (mi) north of DeKalb. Continuous water-quality data included hourly measurements of water temperature and specific conductance. All data from the discrete environmental samples, including results for quality-control samples, were published in the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2009). Samples were collected at the Denison Dam gage by wading when possible, or from the cableway or at the U.S. Highway 69/75 bridge 1 mi downstream from the gage when the flow was too deep to wade. Samples were collected at the Arthur City and DeKalb gages from the U.S. Highway 271 and 259 bridges, respectively. All samples at the DeKalb gage were collected from the U.S. Highway 259 bridge. Bromide, chloride, and sulfate concentrations and specific conductance measured in discrete environmental samples and quality-control samples are listed in appendix 1. Instantaneous streamflow measured at the time water-quality samples were collected is also listed in appendix 1. All dissolved constituent and physical property data are stored in NWIS (U.S. Geological Survey, 2009).

Streamflow

"Streamflow" is the discharge that occurs in a natural channel (U.S. Geological Survey, 2008). Methods used to measure streamflow (discharge) amounts are described in detail by Rantz and others (1982) and summarized by Olson and Norris (2005). Streamflow measurements were made about every 2 months during the study at each streamflow-gaging station. Stage, or gage height, is measured every 60 minutes at the three gaging stations using a pressure transducer or radar equipment. The gage height represents the elevation of the water surface referenced to an arbitrary elevation datum. The gage height data are transmitted through a satellite system to a downlink site and then to the USGS Oklahoma Water Science Center, Oklahoma City, Okla., where the gage height information is used to determine streamflow from an established stage-discharge relation called a rating curve (Rantz and others, 1982). Rating curves are developed and updated for each station using gage height and discharge volume measurements made periodically at each gage. The gage height and streamflow information are stored in NWIS (U.S. Geological Survey, 2009).

Streamflow measured at the Denison Dam gage was characterized by two flow regimes. During cycles of normal daily electrical power generation at Denison Dam, streamflow varied from small base flows (periods of no power generation) of about 60 cubic feet per second (ft^3/s), with average depths less than 1.0 ft and velocities less than 1 foot per second (ft/s), to large flows (periods of power generation) of 15,000 to 33,000 ft^3/s, with average depths 8 to 12 ft and velocities more than 6 ft/s. The transition between the two flow regimes was usually abrupt. Two periods of high flow in the Denison Dam-DeKalb reach (figs. 2–4) resulted from floods during the study. Floods during June–July 2007 resulted in elevated flow during June–September 2007; smaller floods during March–April 2008 resulted in elevated flow during March–April 2008. Water flowed over the spillway at Denision Dam in July 2007 for only the third time since Denison Dam was constructed. The maximum daily mean streamflows measured at the Denison Dam gage during the 2007 and 2008 floods were 38,400 ft^3/s on July 16, 2007, and 21,300 ft^3/s on April 20, 2008 (U.S. Geological Survey, 2009). Twelve of the 25 discrete samples at the Denison Dam gage were collected when mean instantaneous streamflow ranged from 77 ft^3/s (November 4, 2008) to 480 ft^3/s (February 26, 2008) (appendix 1). Four samples were collected during the elevated streamflow associated with the 2007 floods; mean instantaneous streamflow for the four samples ranged from about 30,000 to 34,000 ft^3/s.

Streamflow patterns at the Arthur City gage during the study were generally similar to streamflow patterns at the Denison Dam gage. The lowest base flows sampled varied from about 300 to about 700 ft^3/s; these periods of low flow occurred in March 2007 and again during October 2008–January 2009 (fig. 3). The maximum daily mean streamflows at the Arthur City gage during the 2007 and 2008 floods were 80,800 ft^3/s on July 12, 2007, and 70,000 ft^3/s on March 20, 2008 (U.S. Geological Survey, 2009). The large increases in streamflow in the Red River from the Denison Dam gage to the Arthur City gage during the 2007 and 2008 floods largely resulted from reservoir releases on tributaries downstream from Denison Dam.

Samples collected at the DeKalb gage in November and December 2008 were collected when some of the lowest daily mean streamflows were measured during the entire sample collection period (fig. 4). In contrast to the relatively small instantaneous streamflows of 5,110 ft^3/s or less measured for 12 discrete samples, mean instantaneous streamflow for four samples collected during the elevated streamflow associated with the 2007 and 2008 floods ranged from about 40,000 to 69,000 ft^3/s (appendix 1). Maximum daily mean streamflow measured at the DeKalb gage during the 2007 and 2008 floods were 83,500 ft^3/s on July 14, 2007, and 97,800 ft^3/s on March 21, 2008 (U.S. Geological Survey, 2009). The large range of streamflow in the Denison Dam-DeKalb reach during the study made it possible to collect samples representing a wide range of hydrologic conditions.

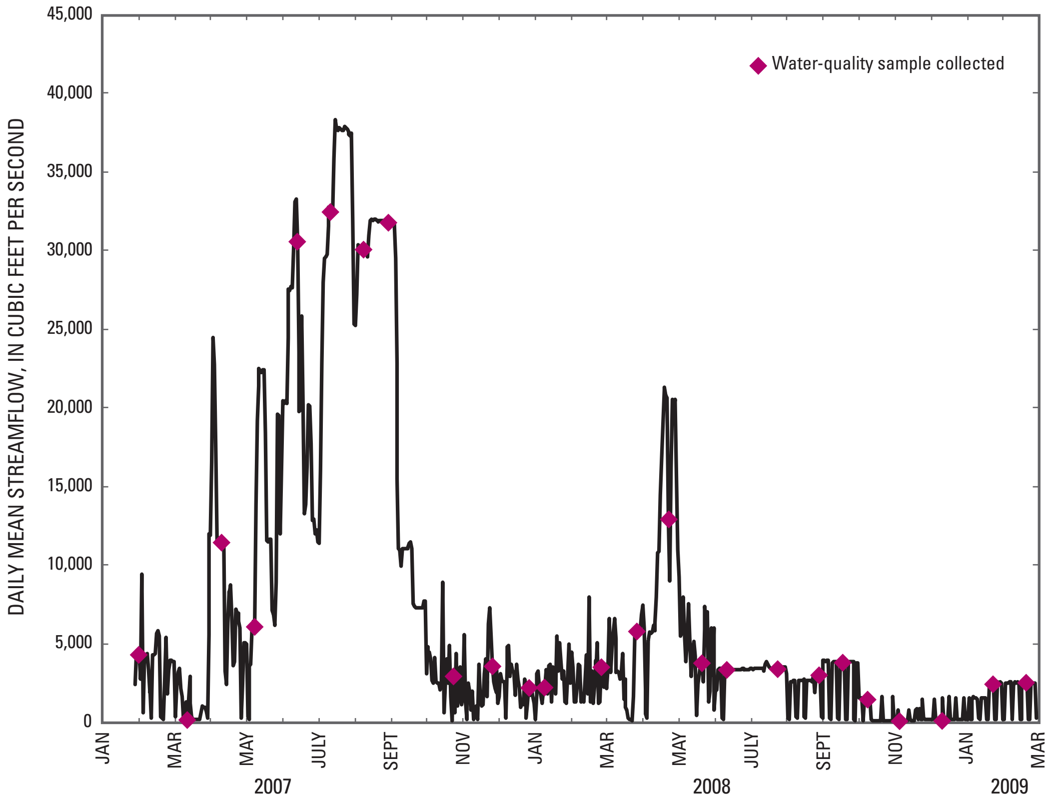

Figure 2. Hydrograph showing streamflow at U.S. Geological Survey streamflow-gaging station 07331600 Red River at Denison Dam near Denison, Texas, 2007–09.

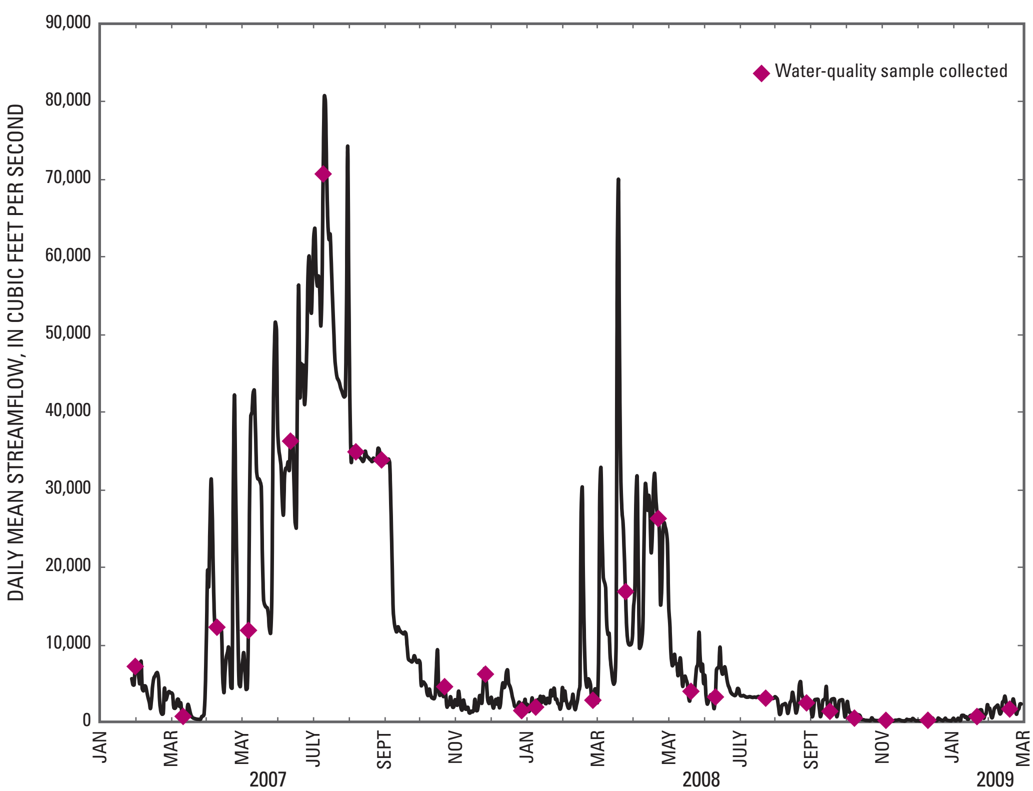

Figure 3. Hydrograph showing streamflow at U.S. Geological Survey streamflow-gaging station 07335500 Red River at Arthur City, Texas, 2007–09.

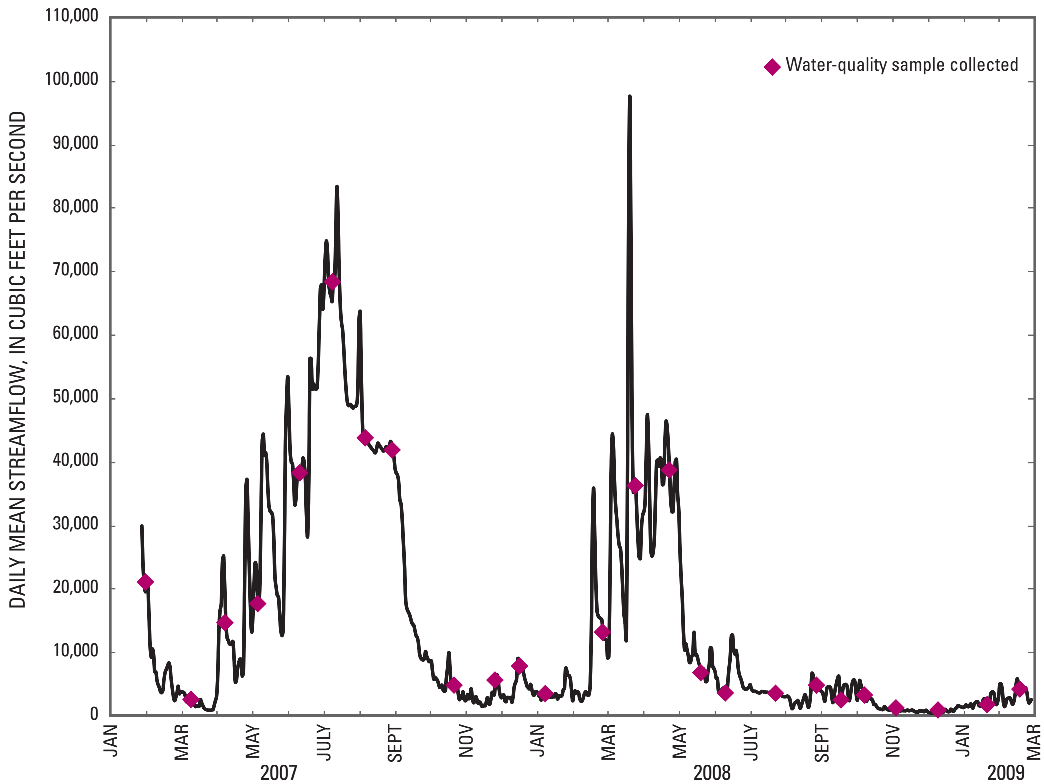

Figure 4. Hydrograph showing streamflow at U.S. Geological Survey streamflow-gaging station 07336820 Red River near DeKalb, Texas, 2007–09.

Continuous Water Quality

Water temperature and specific conductance data were collected hourly at the three streamflow-gaging stations using multiprobe sondes encased in flow-through wells (Wagner and others, 2006) suspended in the stream. The flow-through well at the Denison Dam gage was mounted on the south bank, whereas the flow-through wells at the Arthur City and DeKalb gages were suspended in the main thalweg of the stream from the bridge on which each of these gages is installed. Field procedures, calibration of the continuous water-quality monitors, and record computation and review methods followed Wagner and others (2006).

Sampling

Water-quality samples were collected at each gage following guidelines documented in the USGS "National Field Manual for the Collection of Water-Quality Data" (U.S. Geological Survey, variously dated). Samples were collected every 2 to 6 weeks using isokinetic depth-integrated sampling and non-isokinetic sampling methods (Lane and others, 2003). Discrete samples were generally collected within a span of 24 hours at all three gages. Three types of samplers were used for the study—an isokinetic depth-integrator sampler (US D–95) for streamflow velocities exceeding 1.7 ft/s, a hand-held weighted-bottle sampler for streamflow velocities less than 1.7 ft/s and depths too deep to wade, and an open-mouth bottle for depths too shallow to use either the isokinetic or the hand-held weighted-bottle sampler. Teflon bottles were used with the three types of samplers. For the isokinetic sampling, aliquots (small volumes of water; for this study, about 1 liter) were collected from stream verticals selected by dividing the stream into equal segments known as equal-width increments (EWI). Non-isokinetic sampling with a weighted-bottle sampler also was used to collect sample aliquots from stream segments determined by EWI. Using the EWI selection process, the width of the stream typically was divided into a minimum of 10 equal increments. Field measurements were made in each increment, and a water sample was withdrawn from the increment and placed in a polyethylene churn for compositing with waters withdrawn from the other sections. Once water from all sections was placed in the churn, the water was mixed (composited) and aliquots were withdrawn for analysis by the USGS National Water Quality Laboratory (NWQL), Denver, Colo. The EWI method for isokinetic and non-isokinetic sampling methods allowed a representative sample to be collected at each of the three gaging stations and accounted for tributary inflows which were not 100-percent mixed with the upstream flow of the Red River.

Sample Analysis

Water samples were sent to the NWQL for analyses to determine concentrations of common ions including dissolved bromide, chloride, and sulfate. The analytical method used for these constituents was ion chromatography (Fishman and Friedman, 1989; Fishman, 1993). Preparation and pretreatment of the samples by the NWQL followed guidelines documented in Fishman and Friedman (1989). Bromide, chloride, and sulfate analyses were done on filtered water samples that were not acidified.

Quality Assurance

Quality-assurance procedures outlined in Wagner and others (2006) were followed in the collecting and processing of continuous water-quality data for temperature and specific conductance. The temperature probe on each sonde was checked by comparing its temperature readings to those from a National Institute of Standards and Technology (NIST) certified thermometer. Specific conductance probes were calibrated with standards traceable to NIST electrolytic conductivity standard reference solutions. Data from cross-sectional surveys made at the time of sample collection indicated that the monitor sondes were placed at locations representative of flows in the stream cross section.

Quality-assurance procedures outlined in the "National Field Manual for the Collection of Water-Quality Data" (U.S. Geological Survey, variously dated) were followed for collecting and processing water-quality samples. Quality-control samples were collected to evaluate potential bias and variability or contamination introduced during sample collection, processing, or laboratory analysis. Three samples of deionized (DI) water used to clean sampling equipment (DI samples) were submitted to the NWQL and analyzed for dissolved bromide and selected constituents. DI samples were submitted for associated environmental samples collected on December 4, 2007, June 19, 2008, and January 23, 2009. Dissolved bromide concentrations measured in the three DI samples were less than the laboratory reporting level of 0.02 mg/L. Major ion data were evaluated to ensure the cation-anion balances were consistently within 5 percent. On May 8, 2007, a field-equipment blank was collected with the environmental sample at the Arthur City gage; bromide, chloride, and sulfate concentrations measured in the field-equipment blank were less than their applicable laboratory reporting levels (appendix 1). Bromide, chloride, and sulfate concentrations in field-replicate samples were similar to concentrations in environmental samples; percent differences of less than 5 percent were measured for field-replicate samples collected on February 26 and July 24, 2008, at the Denison Dam gage, on May 8, 2007, at the Arthur City gage, and on January 21, 2009, at the DeKalb gage (appendix 1).

Development of Regression Equations to Estimate Constituent Concentrations

Using hourly streamflow and specific conductance measurements and discrete water-quality data collected every 2 to 6 weeks and analyzed for bromide, chloride, and sulfate concentrations and for specific conductance, regression equations were derived to estimate daily mean bromide, chloride, and sulfate concentrations. The daily mean concentrations in turn were used to compute daily loads of bromide, chloride, and sulfate. Keller and others (1988) describes specific conductance as "a measure of the ability of a water to conduct an electrical current and thus it is related to the types and concentrations of major ions in solution . . . consequently, specific conductance can be used for approximating the concentrations of dissolved solids and major ions dissolved in water." Keller and others (1988) computed loads for chloride, sulfate, and dissolved solids for October 1970–April 1988 at selected streamflow-gaging stations in the Red River Basin upstream from Lake Texoma for the Red River Chloride Control Project, using the same multi-variable regression equations used in this study. The same methods also were used to compute loads for chloride, sulfate, and dissolved solids for many sites published in the USGS Texas Water Science Center annual water-data reports (U.S. Geological Survey, 1987–2002). The Texas Water Science Center developed a load computation program (F.L. Andrews, U.S. Geological Survey, written commun., 2000) to automate the computation procedure used for sites in Texas.

Daily mean values of streamflow and estimated instantaneous (hourly) constituent concentrations derived from the relation of instantaneous (hourly) specific conductance values to concentrations of bromide, chloride, and sulfate measured in discrete samples were used to compute monthly loads of bromide, chloride, and sulfate.

Whereas daily mean streamflow data were available from continuous streamflow records, periodic (rather than daily) constituent concentration data were available from the discrete samples collected every 2 to 6 weeks. Because bromide, chloride, and sulfate concentrations were highly correlated with specific conductance and continuous specific conductance data were generally available for the three streamflow-gaging stations, it was possible to develop regression equations that relate constituent concentrations to specific conductance to obtain estimates of daily mean constituent concentrations.

Using methods described in Keller and others (1988), linear regression equations derived for each gage are of the form:

$$C_i = B_0 + B_1(SC_i) + B_2(SC_i)^2, \tag{1}$$

where

C_i = instantaneous constituent concentration, in milligrams per liter;

SC_i = instantaneous specific conductance, in microsiemens per centimeter at 25 degrees Celsius; and

B_0, B_1, B_2 = regression coefficients computed from data collected at the three gaging stations during March 2007–February 2009.

In a linear regression analysis, the R-squared (R^2), adjusted R^2, and standard error of regression are useful statistics for evaluating the goodness of fit, that is, how well the regression equation fits the data. The R^2 value is the coefficient of determination, and it is used to describe the proportion of the total sample variability in the response explained by the regression model. The adjusted R^2 statistic compensates for this by assessing a "penalty" for the number of explanatory variables in the model; adding additional explanatory variables increases the value of the adjusted R^2 only when the predictive capability of the model increases. The standard error of regression is an estimate of the predictive accuracy of the regression equation; choosing a model with the highest adjusted R^2 value is equivalent to choosing a model with the lowest mean standard error (Helsel and Hirsch, 2002; Iman and Conover, 1983).

Bromide, Chloride, and Sulfate Concentrations and Specific Conductance

Discrete water-quality samples were collected every 2 to 6 weeks at the Denison Dam, Arthur City, and DeKalb gages and analyzed for bromide, chloride, and sulfate concentrations and for specific conductance. The results for the 25 discrete samples collected at each gage, including streamflow measured at the time the samples were collected, are listed in appendix 1.

Bromide

The distribution of bromide data collected at each gage is summarized by boxplots (fig. 5). Boxplots provide visual summaries of the center of the data (median), the variation or spread (interquartile range), the skewness (relative size of box halves), and presence or absence of extreme values (Helsel and Hirsch, 2002). The median bromide concentration for the 25 samples collected at each gage in the Denison Dam-DeKalb reach decreased from upstream to downstream. Median bromide concentrations at the Denison Dam, Arthur City, and DeKalb gages were 0.32, 0.26, and 0.19 mg/L, respectively (table 1). Not only did the median bromide concentration measured at each gage decrease in the downstream direction, but the overall spread of bromide concentrations at each gage decreased as well (fig. 5). The Kruskal-Wallis test is a nonparametric test that can be used to determine the general equivalence of groups of data (Helsel and Hirsch, 2002). A Kruskal-Wallis test was used to determine if there were statistically significant differences among the bromide concentrations measured at the Denison Dam, Arthur City, and DeKalb gages. The null hypothesis of no statistically significant

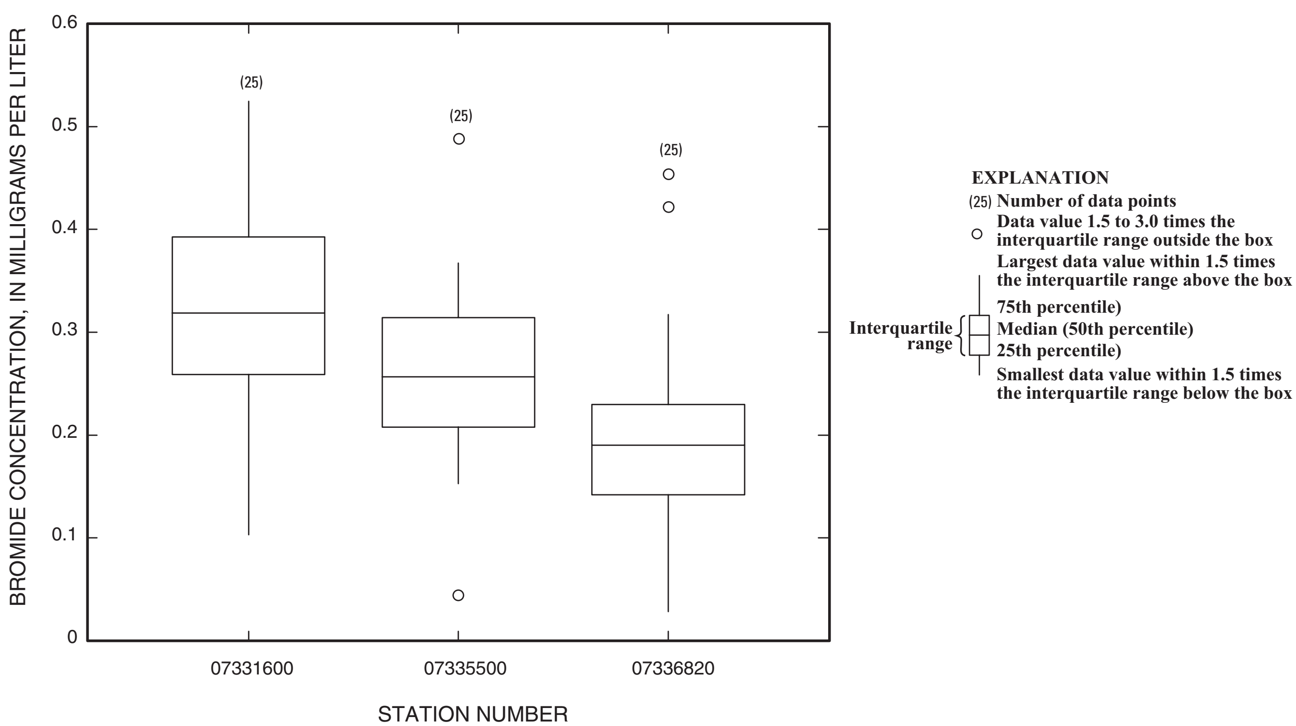

Figure 5. Distribution of bromide concentrations at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

Table 1. Selected statistics for bromide, chloride, and sulfate concentrations and specific conductance at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

[Bromide, chloride, and sulfate concentrations in milligrams per liter; specific conductance in microsiemens per centimeter at 25 degrees Celsius]

Constituent or physical property[1]	07331600				07335500				07336820			
	Maximum	Minimum	Mean	Median	Maximum	Minimum	Mean	Median	Maximum	Minimum	Mean	Median
Bromide	0.52	0.10	0.33	0.32	0.49	0.05	0.26	0.26	0.45	0.03	0.20	0.19
Chloride	464	103	230	176	431	9.80	165	137	400	5.37	120	108
Sulfate	293	95.1	213	213	268	20.7	154	155	250	11.7	119	117
Specific conductance	2,190	780	1,370	1,250	2,030	230	1,090	1,020	1,940	145	847	814

[1] For all values, n = 25.

difference among the bromide concentrations measured at the three gages was rejected; the difference among the bromide concentrations from each of the three gages was statistically significant (p <.01).

The maximum bromide concentration of 0.52 mg/L (table 1) was in the January 31, 2007, sample at the Denison Dam gage, the first sample collected for the study; instantaneous streamflow was 4,500 ft^3/s (appendix 1). The minimum bromide concentration for a discrete sample was 0.03 mg/L, first measured in a sample collected at the DeKalb gage on February 1, 2007, when instantaneous streamflow was 20,800 ft^3/s. A bromide concentration of 0.03 mg/L was measured again in the March 26, 2008, sample at the DeKalb gage, when instantaneous streamflow was 36,900 ft^3/s. The largest instantaneous streamflows measured at the time the discrete water-quality samples were collected all occurred during the June–July 2007 floods. At the Denison Dam gage, the bromide concentration was 0.36 mg/L in the sample collected on June 14, 2007, when instantaneous streamflow was 33,600 ft^3/s. At the Arthur City gage, the bromide concentration was 0.15 mg/L in the sample collected on July 11, 2007, when instantaneous streamflow was 72,400 ft^3/s. At the DeKalb gage, the bromide concentration was 0.14 mg/L in the sample collected on July 11, 2007, when instantaneous streamflow was 69,100 ft^3/s. Changes in bromide concentrations in the Denison Dam-DeKalb reach were evident (appendix 1) after the June–July 2007 floods, which resulted in large releases from Denison Dam. The daily mean streamflow on the day when a sample was collected at each gage in July 2007 was 32,500 ft^3/s at Denison Dam gage (fig. 2), 70,800 ft^3/s at the Arthur City gage (fig. 3), and 68,600 ft^3/s at the DeKalb gage (fig. 4). Prior to July 2007, the most recent daily mean streamflow greater than 30,000 ft^3/s was recorded at the Denison Dam gage on March 10, 2001 (32,400 ft^3/s). Daily mean streamflows of 70,000 ft^3/s or more were recorded on 4 days (July 11–14) in July 2007 at the Arthur City gage. Prior to July 2007, daily mean streamflow most recently approached 70,000 ft^3/s at the Arthur City gage on January 4, 2005 (65,400 ft^3/s). Prior to July 2007, the most recent large streamflow recorded at the Arthur City gage was 42,400 ft^3/s on January 15, 2007.

Releases from Lake Texoma and other reservoirs in the study area for management of floodwaters from the two large streamflow events had pronounced effects on bromide concentrations during the study period. Bromide concentrations measured at the Denison Dam gage were 0.47 to 0.52 mg/L for samples collected during January 31–May 9, 2007, before the June–July 2007 floods. After the sample collected on May 9, 2007, bromide concentrations of 0.40 mg/L or greater were not measured again until one of the last samples for this study was collected on January 22, 2009. During July–August 2007, bromide concentrations at the Denison Dam gage ranged from 0.10 to 0.25 mg/L. Although the March–April 2008 floods had little effect on bromide concentrations measured in releases from Denison Dam, the lowest bromide concentrations in samples collected at the Arthur City and DeKalb gages were measured during the March–April 2008 floods (appendix 1). The March–April 2008 floods had a relatively greater effect on reservoir releases and hydrologic conditions in the contributing area to the Denison-DeKalb reach downstream from Lake Texoma than on reservoir releases from Lake Texoma, resulting in measurable changes in bromide concentrations at the Arthur City and DeKalb gages compared with concentrations at the Denison Dam gage. Bromide concentrations in samples collected at the three streamflow-gaging stations do not appear to vary seasonally.

Chloride

The distribution of chloride data collected at each gage is summarized by boxplots (fig. 6). The median chloride concentration for the 25 samples collected at each gage

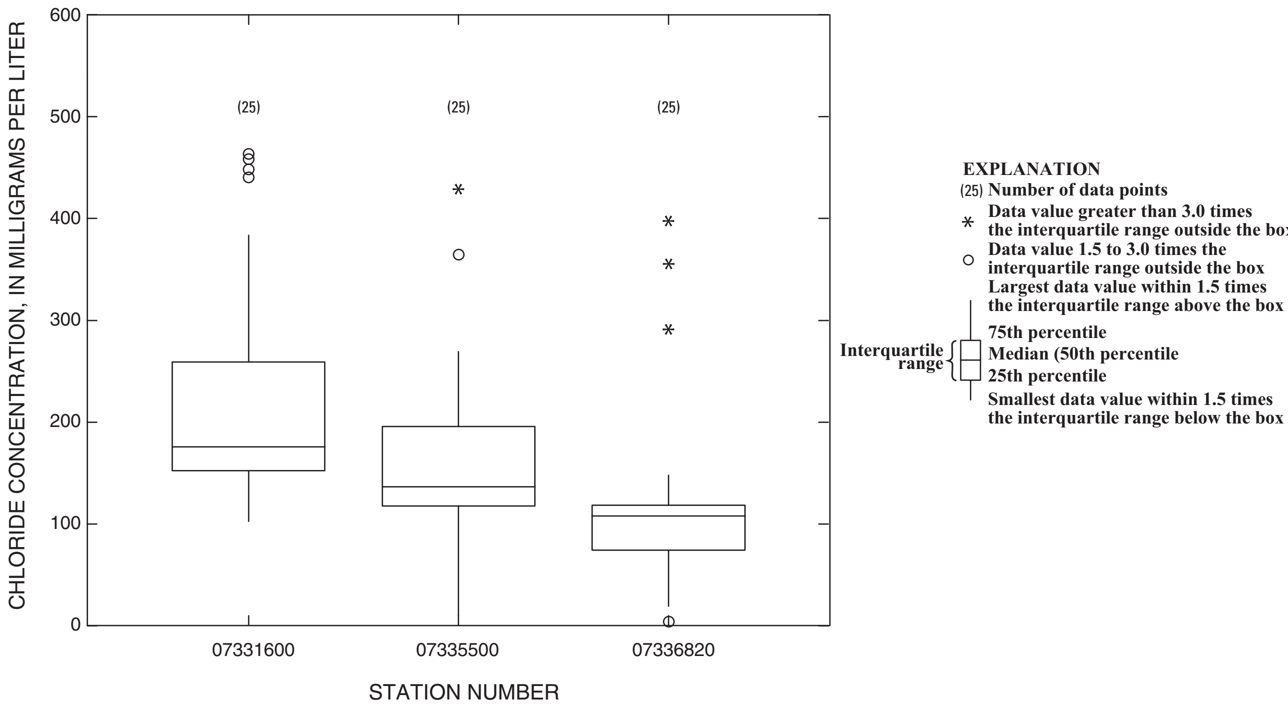

Figure 6. Distribution of chloride concentrations at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

decreased from upstream to downstream, from 176 mg/L at the Denison Dam gage, to 137 mg/L at the Arthur City gage, to 108 mg/L at the DeKalb gage (table 1) and were less than the SMCL of 300 mg/L (Texas Commission on Environmental Quality, 2003). Similar to the medians, the spread of chloride concentrations measured at each gage decreased downstream (fig. 6). A Kruskal-Wallis test of chloride concentrations indicated a statistically significant (p <.01) difference among the chloride concentrations measured at each of the three gages.

The maximum chloride concentration of 464 mg/L (table 1) was in the March 13, 2007, sample at the Denison Dam gage; instantaneous streamflow was 168 ft^3/s (appendix 1). The minimum chloride concentration was 5.37 mg/L at the DeKalb gage on March 26, 2008; instantaneous streamflow was 36,900 ft^3/s. The chloride concentration associated with the largest instantaneous streamflow measurement (72,400 ft^3/s) was 126 mg/L in the July 11, 2007, sample at the Arthur City gage.

Chloride concentrations for the first four samples collected at the Denison Dam gage before the June–July 2007 floods were more than 440 mg/L, exceeding the SMCL of 300 mg/L for chloride (Texas Commission on Environmental Quality, 2003). After the June–July 2007 floods, chloride concentrations ranged from 103 to 138 mg/L in samples collected at the Denison Dam gage during August 2007–January 2008. Despite steadily increasing during the last 11 months of data collection (April 2008–February 2009), chloride concentrations at each gage were still less than 300 mg/L at the end of the data-collection period. During the March–April 2008 floods, chloride concentrations decreased at the Arthur City and DeKalb gages, then steadily increased until the end of the data-collection period. Chloride concentrations at the Denison Dam gage after the March–April 2008 floods did not decrease as much as concentrations at the two downstream gages. Chloride concentrations in the Denison Dam-DeKalb reach varied as a result of reservoir releases and changing hydrologic conditions; seasonal variations in chloride concentrations were not apparent.

Sulfate

Similar to bromide and chloride concentrations, the median sulfate concentration at each gage decreased downstream, from 213 mg/L at the Denison Dam gage, to 155 mg/L at the Arthur City gage, to 117 mg/L at the DeKalb gage (table 1) and were less than the SMCL of 300 mg/L (Texas Commission on Environmental Quality, 2003). Not only did the median sulfate concentration measured at each gage decrease downstream, the spread of sulfate concentrations at each gage also decreased downstream (fig. 7). A Kruskal-Wallis test of sulfate concentrations indicated a statistically significant (p <.01) difference among the sulfate concentrations measured at each of the three gages.

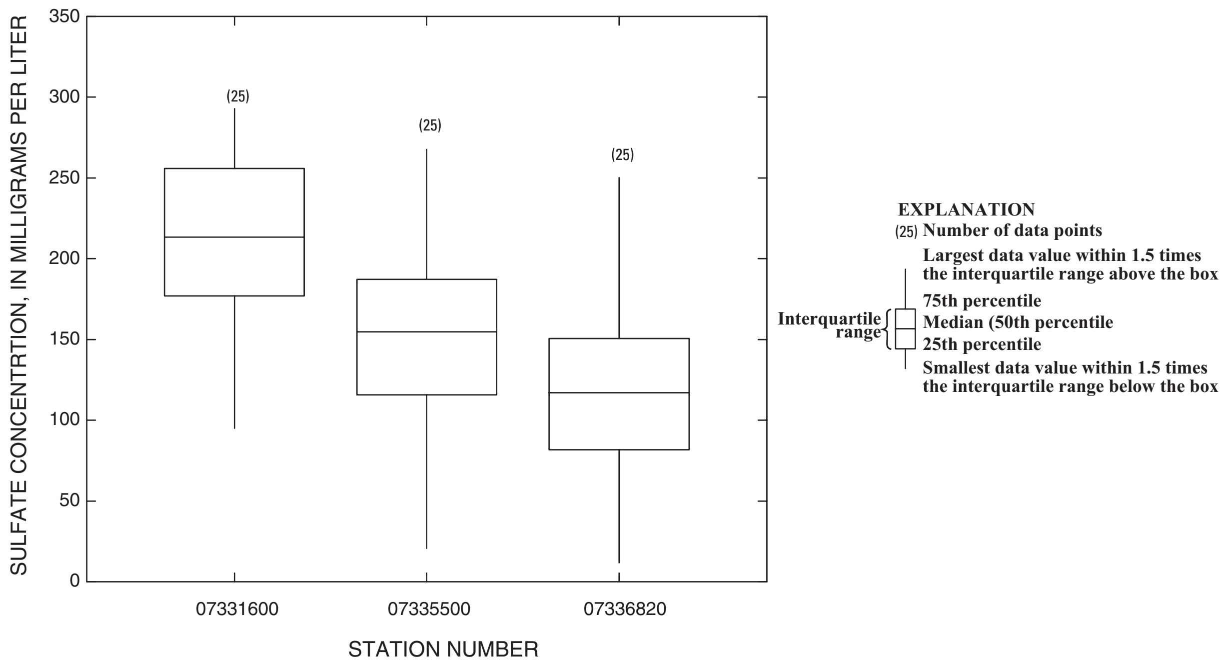

Figure 7. Distribution of sulfate concentrations at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

The maximum sulfate concentration was 293 mg/L (table 1), less than the SMCL of 300 mg/L for sulfate (Texas Commission on Environmental Quality, 2003). The sulfate concentration of 293 mg/L was measured in the March 13, 2007, sample at the Denison Dam gage; instantaneous streamflow was 168 ft^3/s (appendix 1). The minimum sulfate concentration was 11.7 mg/L in the March 26, 2008, sample at the DeKalb gage; instantaneous streamflow was 36,900 ft^3/s. The sulfate concentration associated with the largest instantaneous streamflow measurement (72,400 ft^3/s) was 94.2 mg/L in the July 11, 2007, sample at the Arthur City gage (appendix 1).

The effect of the June–July 2007 and March–April 2008 floods on sulfate concentrations in the Denison Dam-DeKalb reach was similar to the effect of these floods on bromide and chloride concentrations. The June–July 2007 floods resulted in smaller sulfate concentrations in samples at the Denison Dam gage; concentrations decreased by more than 50 percent, from 235 to 293 mg/L measured during January–June 2007 prior to the floods, to 95.1 mg/L measured on August 30, 2007, after the floods. Decreases in sulfate concentrations after the June–July 2007 floods also were observed in samples collected at the Arthur City and DeKalb gages. The March–April 2008 floods affected sulfate concentrations measured in samples collected at the Arthur City and DeKalb gages more than the floods affected the sulfate concentrations measured in samples collected at the Denison Dam gage. Changes in streamflow, including large floods and subsequent releases from the reservoirs, likely caused most of the variability in sulfate concentrations; sulfate concentrations did not appear to vary seasonally during the study period.

Specific Conductance

Median specific conductance in the Denison Dam-DeKalb reach decreased from upstream to downstream, from 1,250 microsiemens per centimeter at 25 degrees Celsius (µS/cm) at the Denison Dam gage, to 1,020 µS/cm at the Arthur City gage, to 814 µS/cm at the DeKalb gage (table 1). The spread of specific conductance values measured at each gage also decreased downstream (fig. 8). A Kruskal-Wallis test of specific conductance values indicated a statistically significant ($p < .01$) difference among the specific conductance values measured at each of the three gages.

The maximum specific conductance was 2,190 µS/cm (table 1) at the Denison Dam gage on January 31, 2007; instantaneous streamflow was 4,500 ft^3/s (appendix 1). The minimum specific conductance was 145 µS/cm at the DeKalb gage on March 26, 2008; instantaneous streamflow was 36,900 ft^3/s. The specific conductance associated with the largest instantaneous streamflow measurement (72,400 ft^3/s) was 775 µS/cm in the July 11, 2007, sample at the Arthur City gage. Similar to bromide, chloride, and sulfate concentrations,

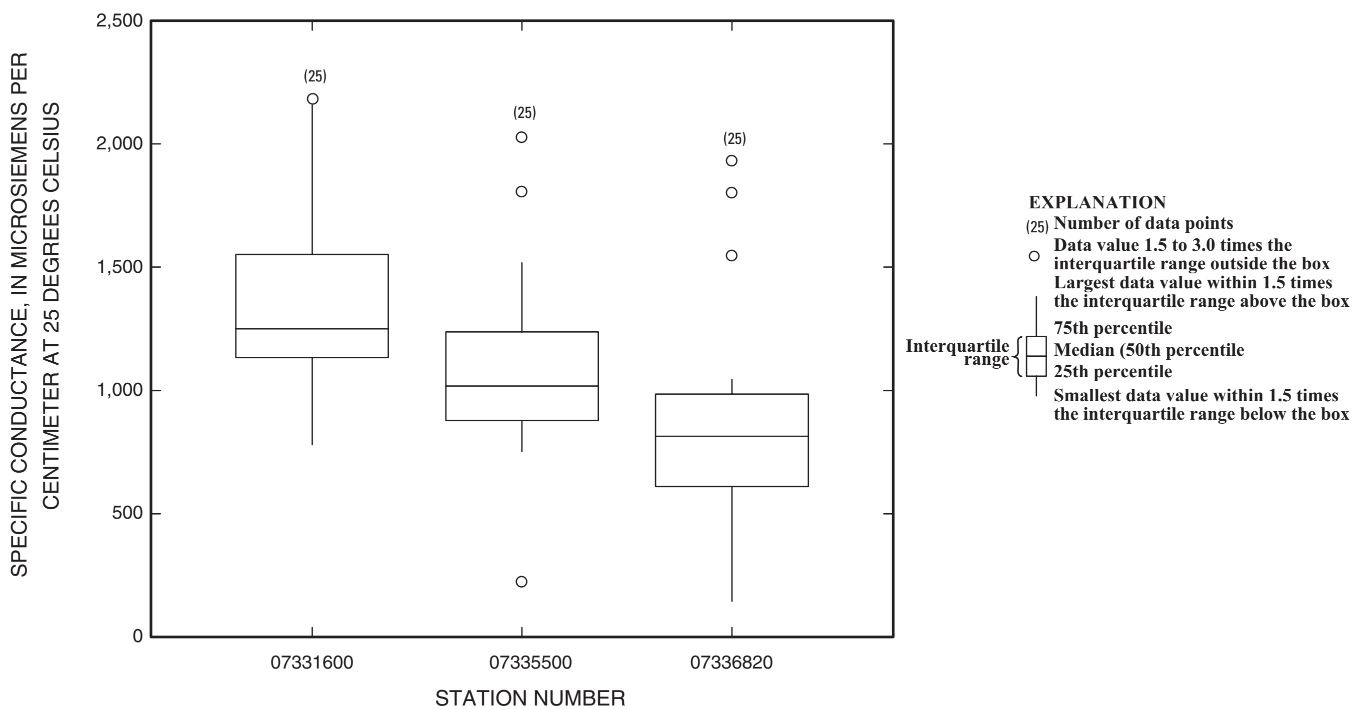

Figure 8. Distribution of specific conductance at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

specific conductance values were affected by reservoir releases. Some of the smallest specific conductance values were measured during April–September 2007 when large reservoir releases occurred. Specific conductance values did not appear to vary on a seasonal basis (fig. 9).

Daily Mean Bromide, Chloride, and Sulfate Concentrations

Regression equations that relate constituent concentrations to specific conductance were used to obtain estimates of daily mean constituent concentrations. Data collected at the three gaging stations during March 2007–February 2009 were used in equation 1 to develop the regression equations (table 2). The regression equations derived from discrete (every 2 to 6 weeks) and continuous (hourly) measurements of specific conductance and discrete measurements of constituents of concern (bromide, chloride, and sulfate) were used to estimate daily mean bromide, chloride, and sulfate concentrations. The daily mean bromide, chloride, and sulfate concentrations then were used with daily mean streamflow to compute estimated bromide, chloride, and sulfate loads for each of the three gages.

Bromide, chloride, or sulfate concentration relative to specific conductance and the adjusted R^2 value (Helsel and Hirsch, 2002, p. 313) for the best-fit regression equation for each constituent at each gage are shown in figures 10–18. Adjusted R^2 values were largest for regression equations for the DeKalb gage, ranging from .957 for sulfate to .976 for chloride (table 2). Adjusted R^2 values for all regression equations were .899 or larger, indicating that the equations explained 89.9 percent or more of the variance in the data for each constituent at each gage, one indicator of the goodness-of-fit of the best-fit regression equation. The F-test, used to determine whether all independent variables together significantly contribute to the prediction of the dependent variable, yielded statistically significant F-statistics for each constituent at each gage for the best-fit models (table 2) (Kleinbaum and Kupper, 1978). A large adjusted R^2 or significant F-statistic does not guarantee that the data have been fitted well (Helsel and Hirsch, 2002). Residual plots (Weisberg, 2005) used to graphically depict goodness-of-fit and additional diagnostics (not shown) were used to confirm the goodness-of-fit of the regression equations. Although all regression equations fit the data well, the adjusted R^2 and F-statistic (table 2) indicate that the equations for data collected at the DeKalb gage describe the data slightly better compared with the equations for data collected at the Denison Dam and Arthur City gages.

Much of the variability in the Denison Dam gage data for bromide, chloride, and sulfate resulted from samples collected during June–August 2007, which coincided with some of the largest discharge releases from Denison Dam during the study

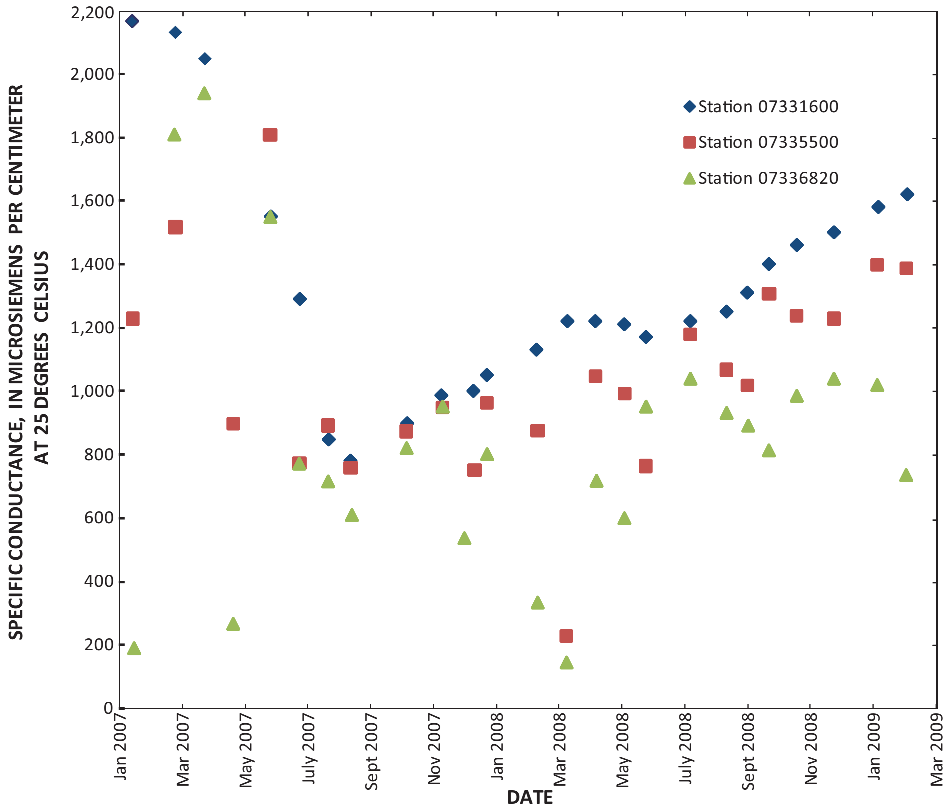

Figure 9. Specific conductance at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

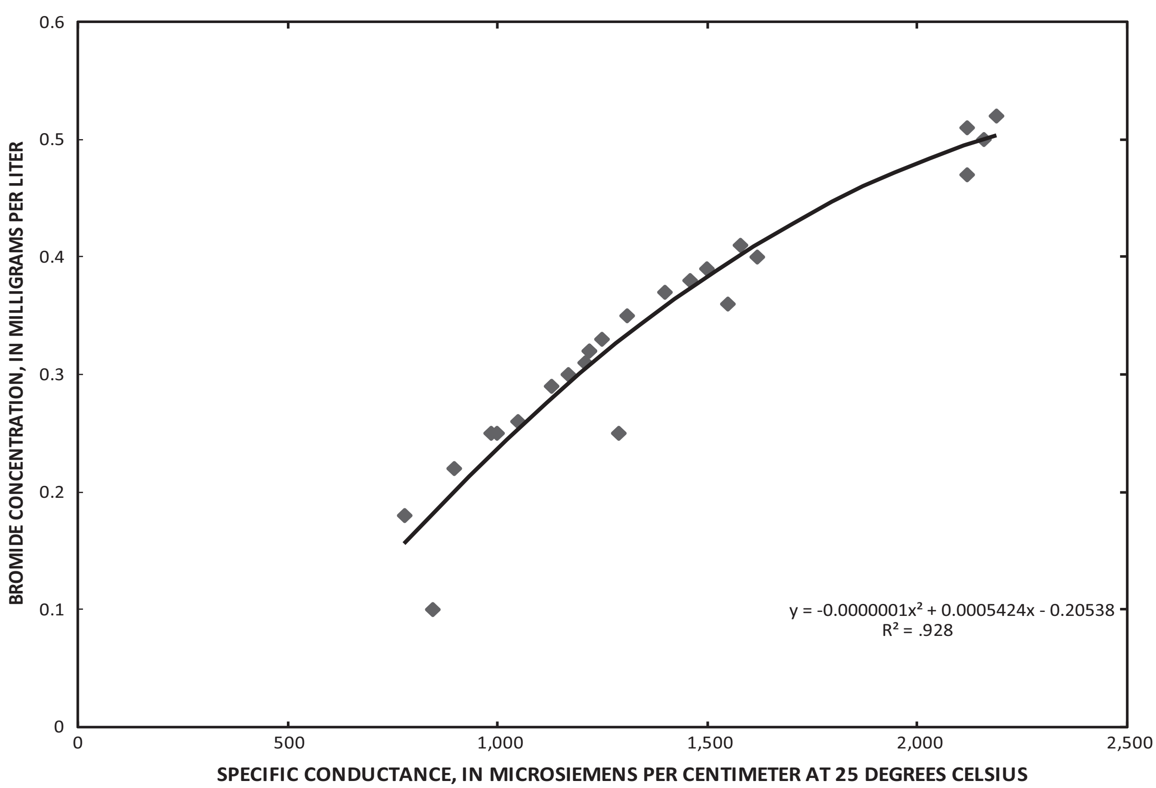

Figure 10. Bromide concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07331600 Red River at Denison Dam near Denison, Texas, 2007–09.

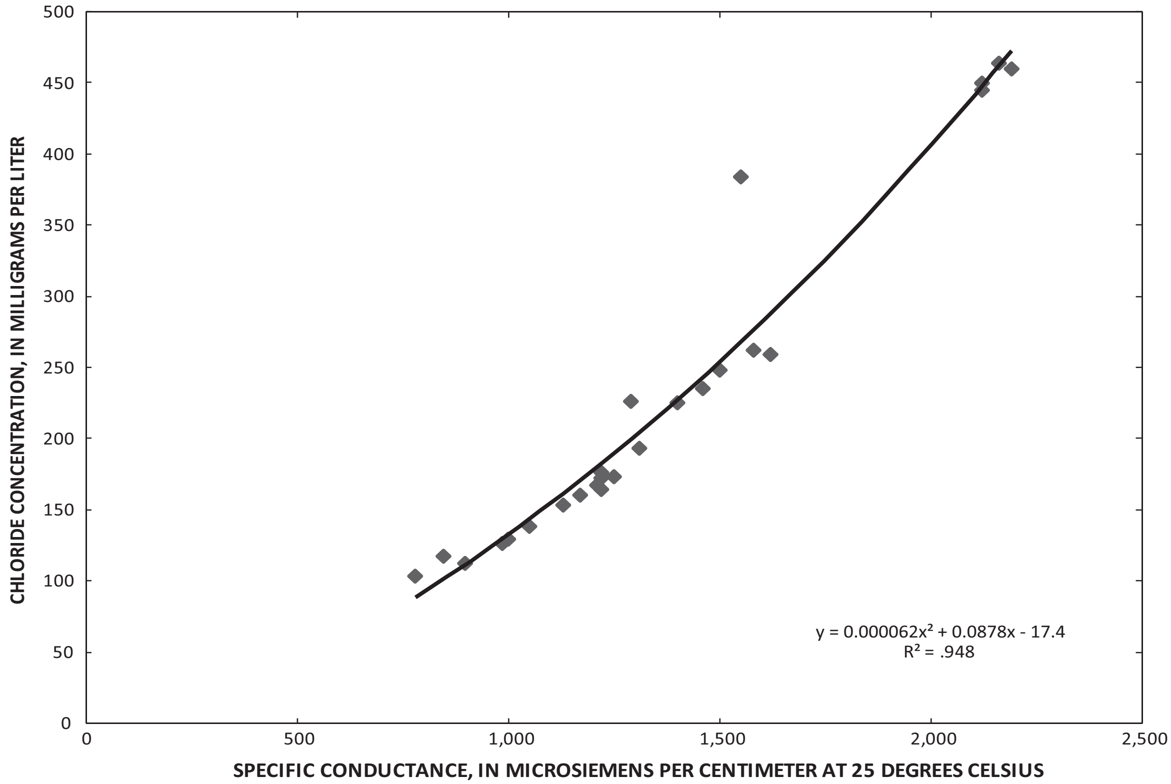

Figure 11. Chloride concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07331600 Red River at Denison Dam near Denison, Texas, 2007–09.

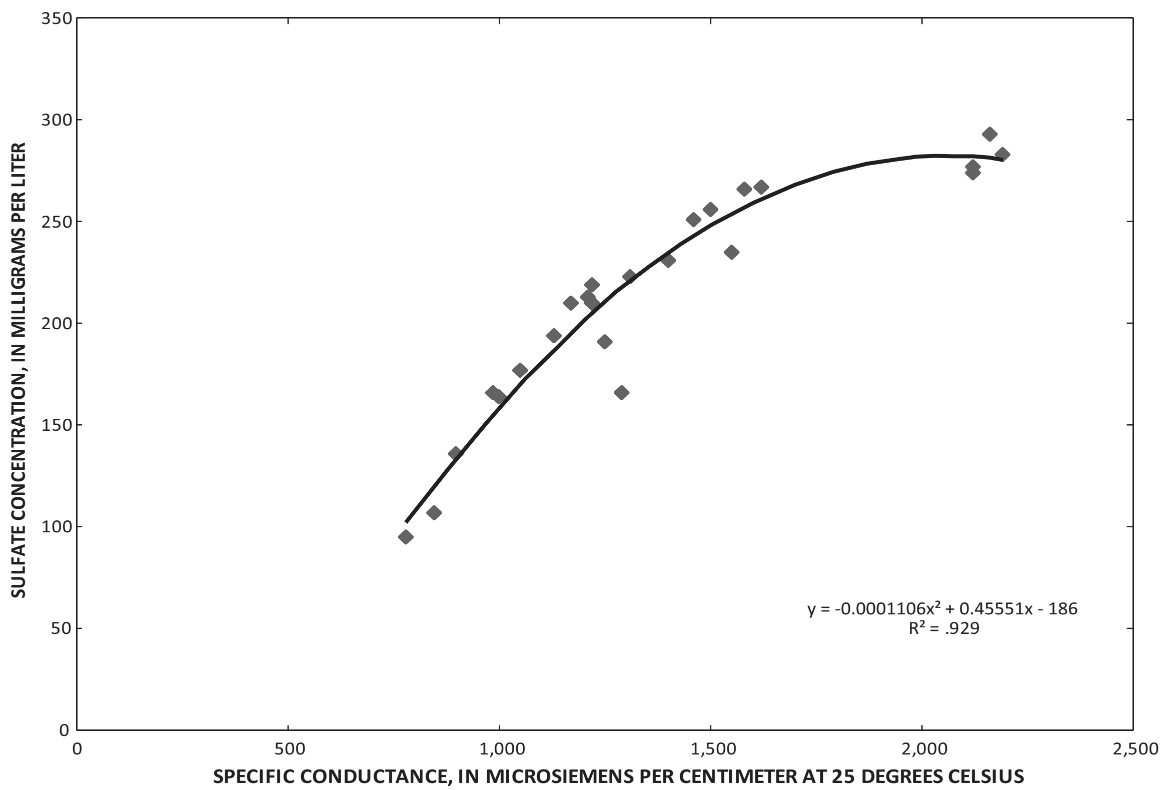

Figure 12. Sulfate concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07331600 Red River at Denison Dam near Denison, Texas, 2007–09.

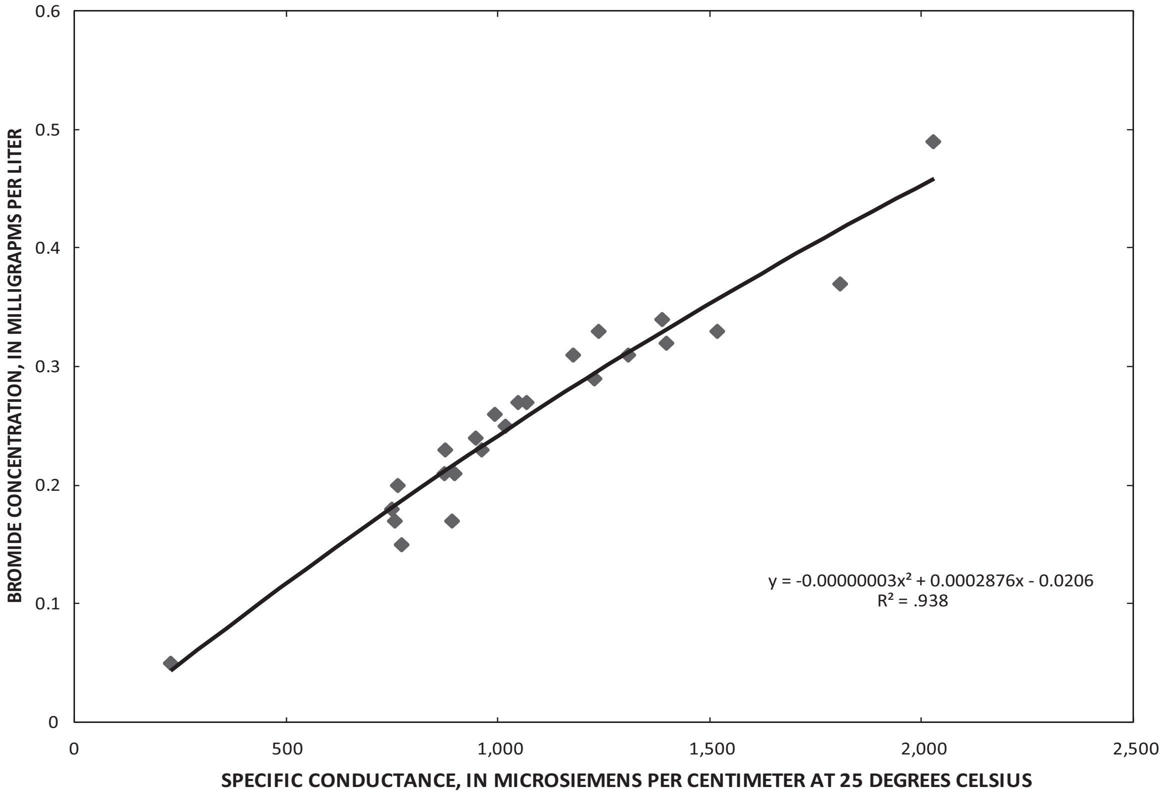

Figure 13. Bromide concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07335500 Red River at Arthur City, Texas, 2007–09.

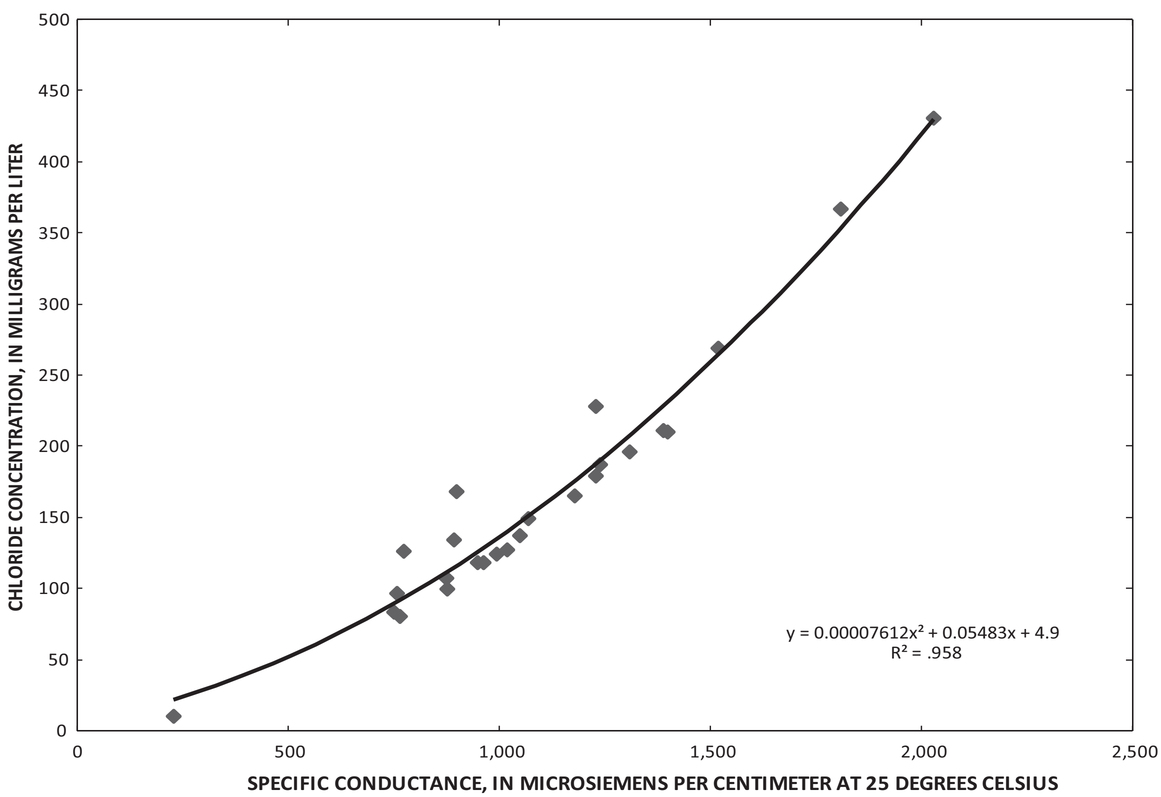

Figure 14. Chloride concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07335500 Red River at Arthur City, Texas, 2007–09.

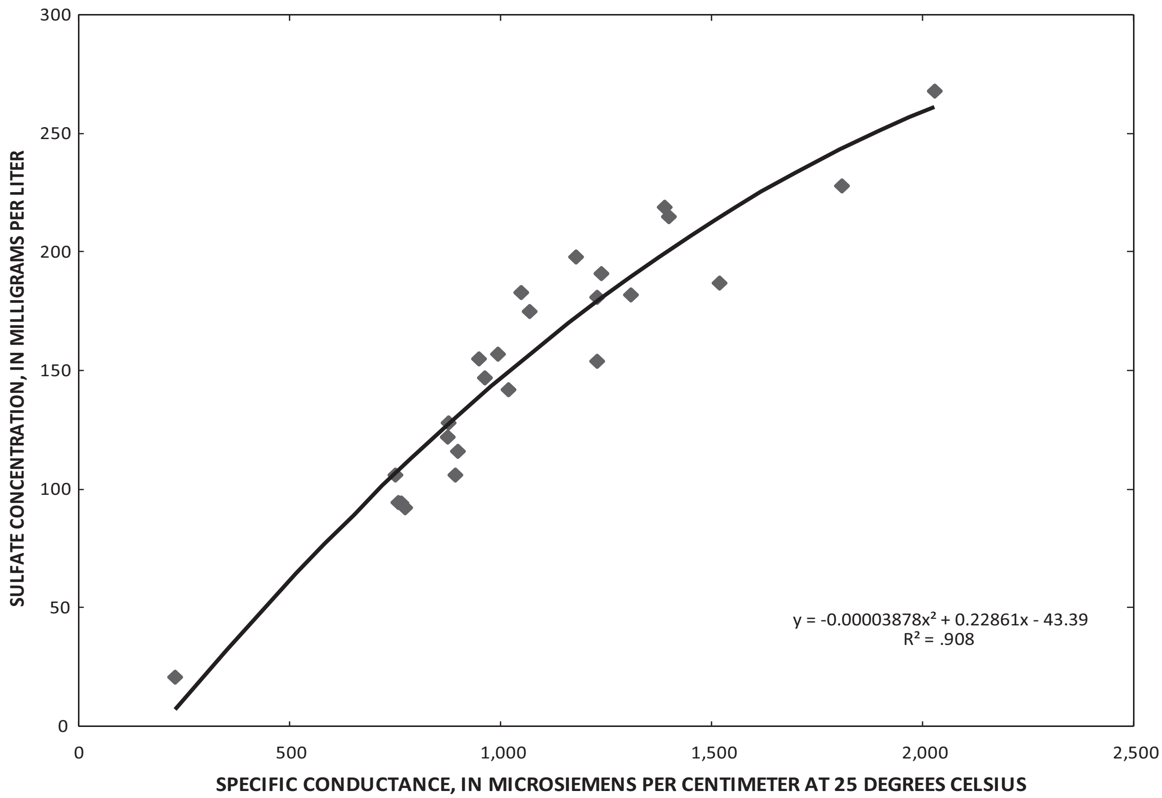

Figure 15. Sulfate concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07335500 Red River at Arthur City, Texas, 2007–09.

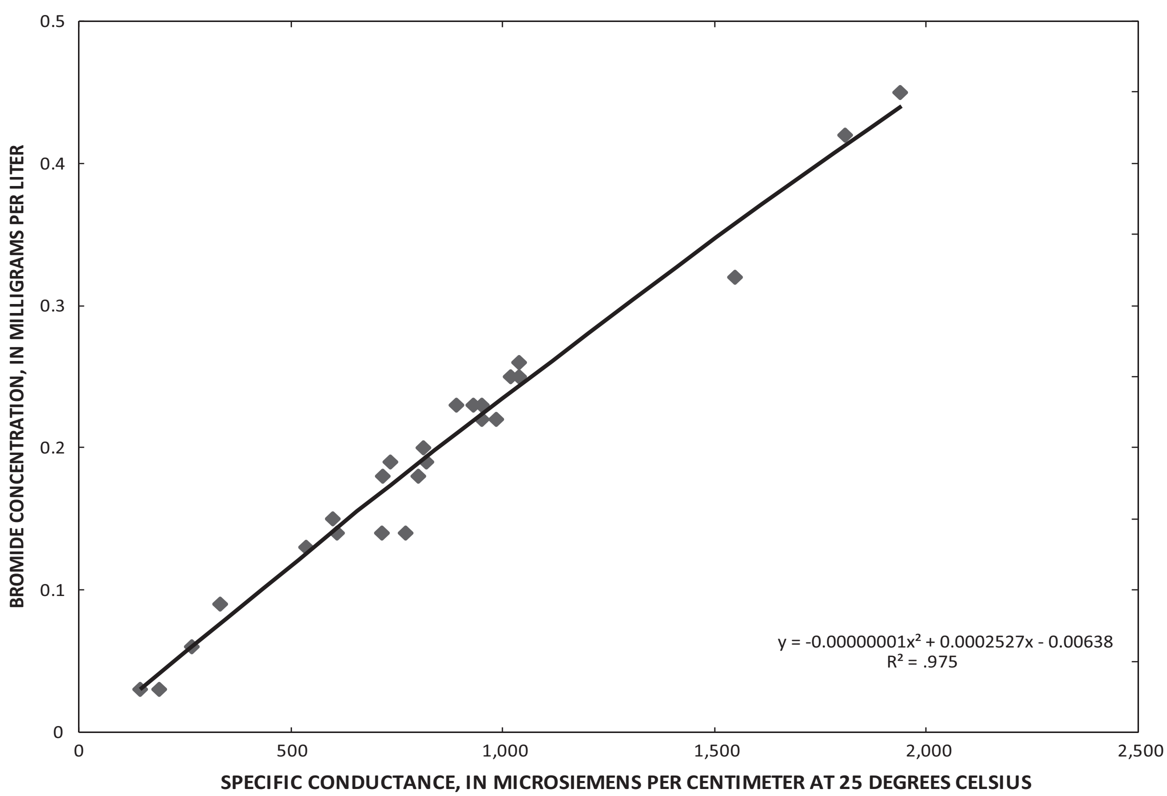

Figure 16. Bromide concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07336820 Red River near DeKalb, Texas, 2007–09.

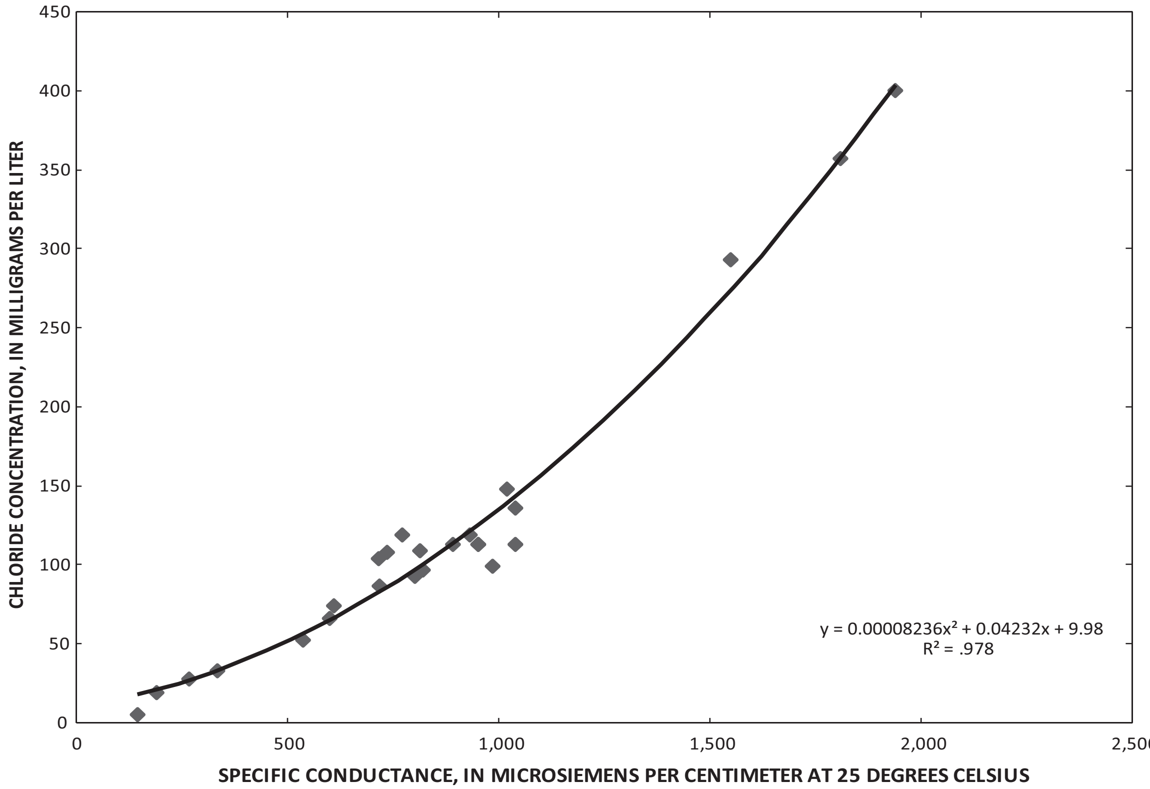

Figure 17. Chloride concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, U.S. Geological Survey streamflow-gaging station 07336820 Red River near DeKalb, Texas, 2007–09.

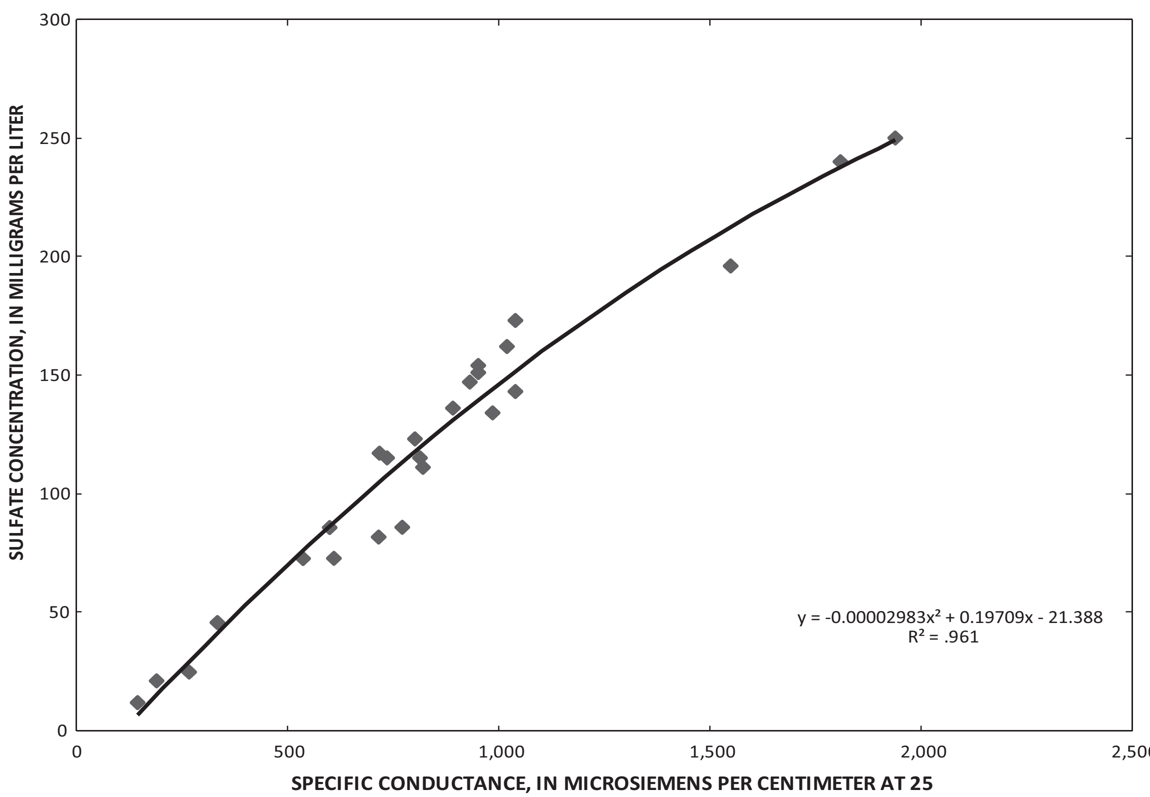

Figure 18. Sulfate concentration relative to specific conductance measured in 25 water-quality samples and best-fit regression line, at U.S. Geological Survey streamflow-gaging station 07336820 Red River near DeKalb, Texas, 2007–09.

Table 2. Regression equation[1] coefficients, adjusted R-squared values, and F-statistic results for bromide, chloride, and sulfate at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

[<, less than]

Station number (fig. 1)	Constituent	B_0	B_1	B_2	R-squared	Adjusted R-squared	Standard error of regression	F-statistic	F-statistic attained significance (*p*-value)[2]
07331600	Bromide	-0.20538	0.0005424	-0.0000001	0.928	0.921	0.029	141.35	<.01
	Chloride	-17.4	.0878	.000062	.948	.943	27.972	200.27	<.01
	Sulfate	-186	.45551	-.0001106	.929	.923	14.895	144.79	<.01
07335500	Bromide	-.0206	.0002876	-.00000003	.938	.932	.023	165.72	<.01
	Chloride	4.9	.05483	.00007612	.958	.954	19.217	251.12	<.01
	Sulfate	-43.39	.22861	-.00003878	.908	.899	17.178	108.07	<.01
07336820	Bromide	-.00638	.0002527	-.00000001	.975	.972	.017	425.12	<.01
	Chloride	9.98	.04232	.00008236	.978	.976	14.856	482.76	<.01
	Sulfate	-21.388	.19709	-.00002983	.961	.957	12.691	268.8	<.01

[1] $C_i = B_0 + B_1(SC_i) + B_2(SC_i)^2$,

where

C_i = instantaneous constituent concentration, in milligrams per liter;

SC_i = instantaneous specific conductance, in microsiemens per centimeter at 25 degrees Celsius; and

B_0, B_1,B_2 = regression coefficients.

[2] *p*-values less than or equal to .05 are considered statistically significant.

period (figs. 2–4). The amount of variability in the data at the Arthur City and DeKalb gages downstream was less than the amount of variability in the data collected at Denison Dam gage. Cation-anion balances for the samples collected at the Denison Dam gage during the June–August 2007 period of elevated streamflow are within 3 percent, indicating that chloride and sulfate concentrations for these samples are acceptable for inclusion in the regression analysis. Bromide concentrations measured in samples collected at the Denison Dam gage during this time included several low concentrations, including the lowest concentration (0.10 mg/L in the August 9, 2007, sample). These low concentrations do not warrant exclusion from regression analyses as outliers; there is nothing to indicate they resulted from errors introduced during sample collection or analysis. On the contrary, the low concentrations are consistent with dilution resulting from a large influx of runoff to Lake Texoma. Baldys (2009) documented decreases in bromide concentrations throughout Lake Texoma after the large inflows that began in late June 2007. Constituent concentrations from samples collected during the period of elevated streamflow resulting from the March–April 2008 floods were similar compared with concentrations measured in samples collected during the months before and after the flooding occurred. The March–April 2008 floods resulted in less inflow to Lake Texoma compared with the June–July 2007 floods. During the June–July 2007 floods, inflows to Lake Texoma measured at gaging stations 07316000 Red River near Gainesville, Tex. (725,040 ft^3/s) and 07331000 Washita River near Dickson, Okla. (532,920 ft^3/s) totaled 1,257,960 ft^3/s; inflows resulting from the March–April 2008 floods measured at stations 07316000 (68,101 ft^3/s) and 07331000 (144,375 ft^3/s) totaled 212,476 ft^3/s (U.S. Geological Survey, 2009).

Bromide, Chloride, and Sulfate Loads

Daily mean bromide, chloride, and sulfate concentrations were used with streamflow in daily load computations. Dissolved bromide, chloride, and sulfate loads during March 1, 2007–February 28, 2009, were computed for the Denison Dam, Arthur City, and DeKalb gages in a two-step process. Using equation 2 (Keller and others, 1988), daily loads for the constituents of interest were computed from daily mean streamflow, instantaneous concentration for constituent of interest as the estimated daily mean concentration (from equation 1), and a conversion factor:

$$L_i = Q_i \times C_i \times K, \qquad (2)$$

where

L_i = daily constituent load, in tons per day;

Q_i = daily mean streamflow, in cubic feet per second;

C_i = instantaneous concentration, in milligrams per liter, computed from equation 1 (assumption is made that instantaneous concentration is satisfactory estimate of daily mean concentration); and

K = 0.0027, a units conversion factor, in tons per day per cubic foot per second-milligrams per liter.

Monthly bromide, chloride, and sulfate loads for each site (table 3) were computed by summing the individual daily loads computed from equations 1 and 2. Bromide loads were larger at the Arthur City gage compared with those measured at either the upstream Denison Dam gage or the downstream DeKalb gage. During March 2007–February 2009, the total bromide loads computed at the Denison Dam, Arthur City, and DeKalb gages were 4,186, 5,044, and 4,963 tons, respectively. The smaller total bromide load computed at the DeKalb gage compared with the total bromide load computed at the Arthur City gage was a result of lower bromide concentrations at the DeKalb gage compared with concentrations at the Arthur City gage, despite larger streamflow at the DeKalb gage compared with streamflow at the Arthur City gage. The computed loads were largest (fig. 19) for those periods when streamflow in the Red River was relatively large (figs. 2–4). At the Denison Dam and Arthur City gages, 53 percent of the total bromide load during March 2007–February 2009 was recorded during just 4 months, June–September 2007, compared with 50 percent at the DeKalb gage.

Chloride and sulfate loads at the three streamflow gages followed the same pattern observed for bromide loads, with the largest loads at the Arthur City gage (figs. 20–21). During March 2007–February 2009, total chloride loads computed at the Denison Dam, Arthur City, and DeKalb gages were 2,912,000, 3,213,000, and 2,830,000 tons, respectively (table 3). The total sulfate loads computed for the Denison Dam, Arthur City, and DeKalb gages during March 2007–February 2009 were 2,639,000, 3,023,000, and 2,954,000 tons, respectively (table 3). Similar to the computed bromide loads, computed chloride and sulfate loads were largest for those time periods when streamflow in the Red River was relatively large. About 50 percent of the total chloride and sulfate loads computed at each of the gages during March 2007–February 2009 occurred during June–September 2007.

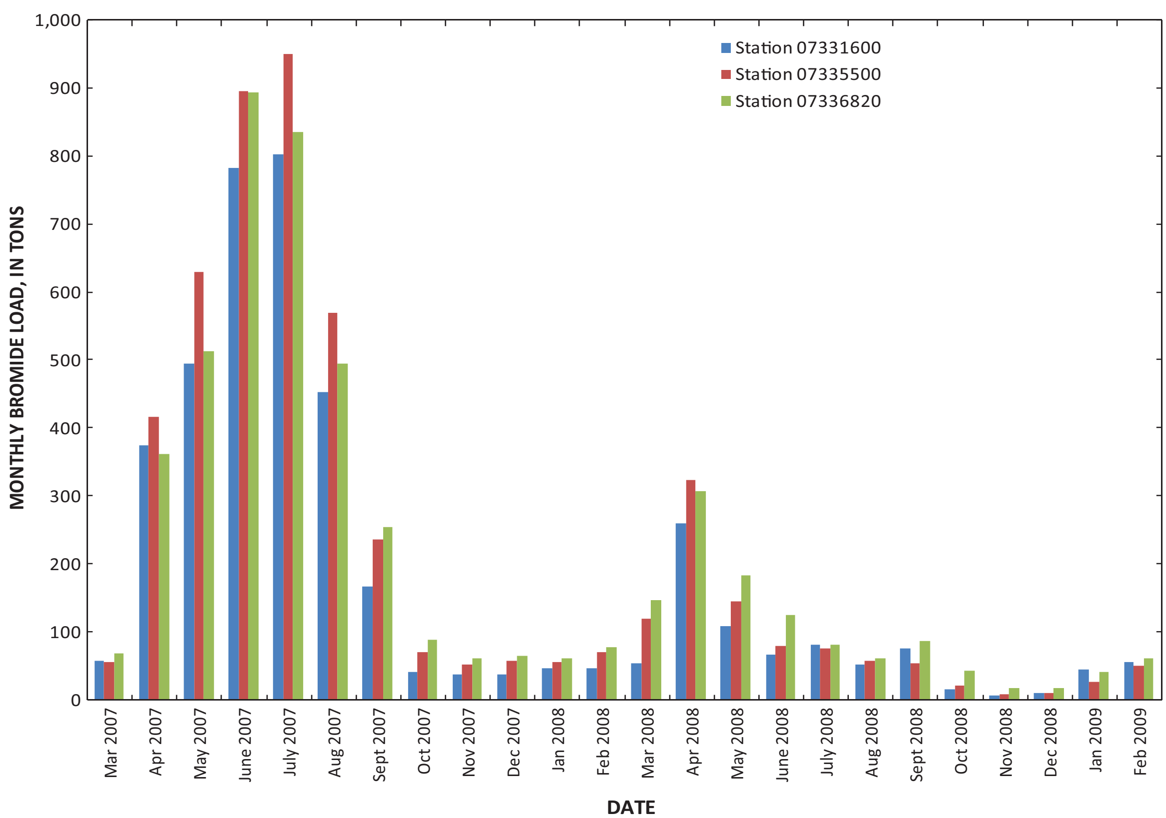

Figure 19. Monthly dissolved bromide loads at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River near Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

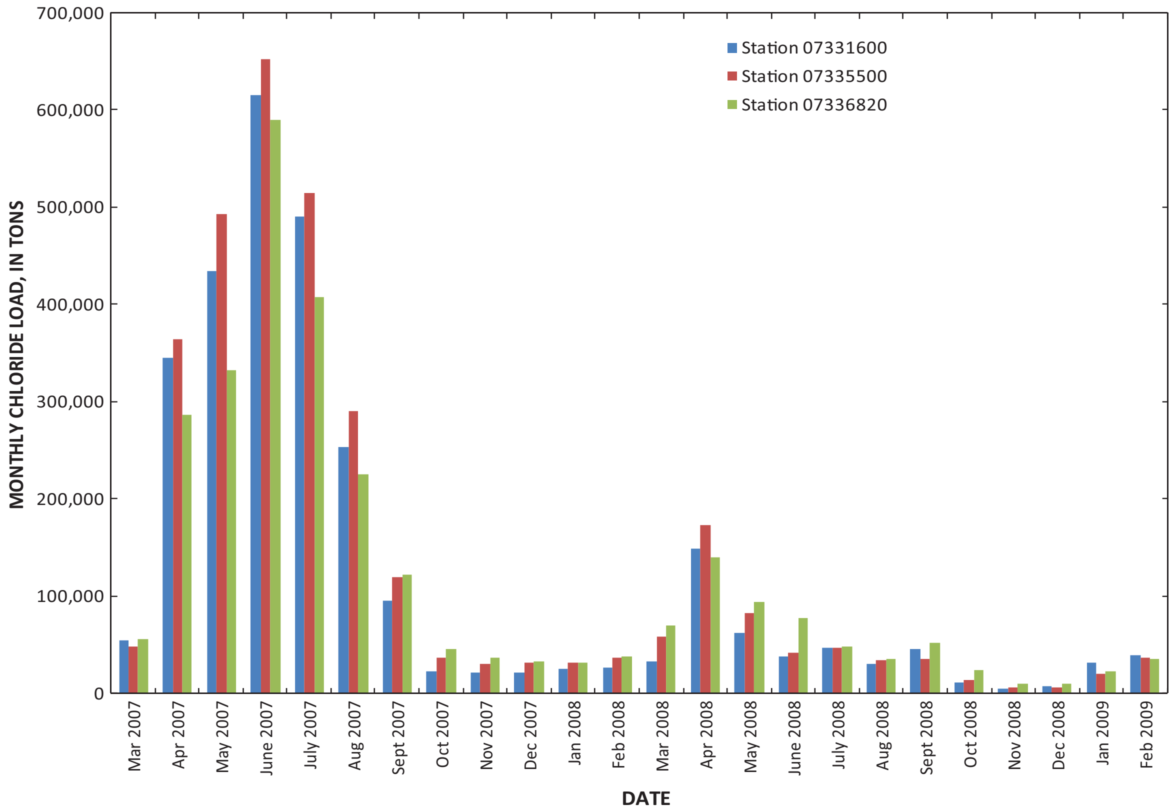

Figure 20. Monthly dissolved chloride loads at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River near Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

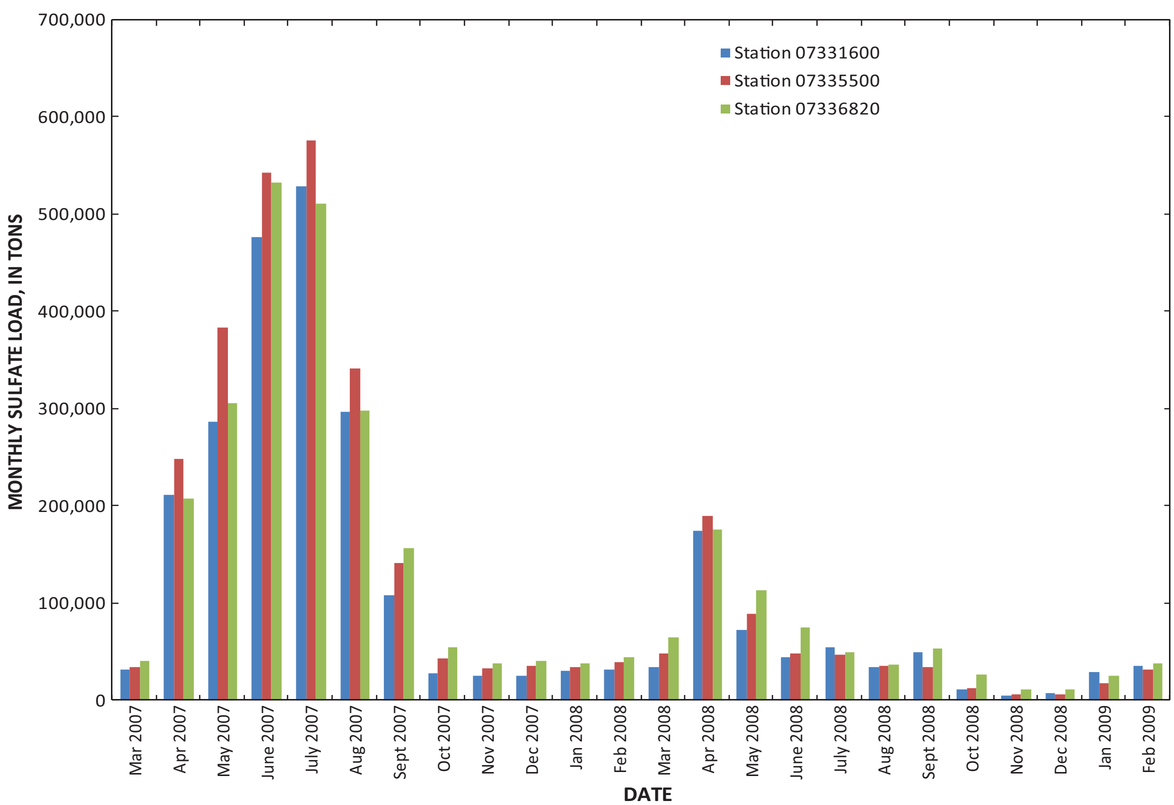

Figure 21. Monthly dissolved sulfate loads at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River near Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

Table 3. Monthly dissolved bromide, chloride, and sulfate loads at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

[cubic foot per second-days, volume of water represented by flow of 1 cubic foot per second for 24 hours times number of days in each month (1 cubic foot per second-day is 86,000 cubic feet; average flow in cubic feet per second for each month is volume of flow in cubic foot per second-days)]

Month	Year	Streamflow (cubic foot per second-days)	Dissolved bromide load (tons)	Dissolved chloride load (tons)	Dissolved sulfate load (tons)
07331600 Red River at Denison Dam near Denison, Texas (Denison Dam gage)					
Mar.	2007	42,253	58	55,409	31,867
Apr.	2007	278,363	375	345,316	211,448
May	2007	376,108	495	434,535	286,824
June	2007	640,177	783	616,211	476,367
July	2007	985,514	803	491,170	529,581
Aug.	2007	951,880	453	253,973	297,304
Sept.	2007	407,881	167	95,456	108,181
Oct.	2007	88,939	42	23,447	27,522
Nov.	2007	71,722	38	21,066	25,121
Dec.	2007	72,322	39	21,416	25,599
Jan.	2008	83,461	46	25,797	30,930
Feb.	2008	78,395	47	26,397	31,677
Mar.	2008	110,003	54	32,568	34,746
Apr.	2008	355,900	261	149,307	174,538
May	2008	153,621	109	62,035	73,125
June	2008	88,775	67	38,354	44,596
July	2008	106,377	82	47,757	54,917
Aug.	2008	64,060	52	30,862	34,857
Sept.	2008	85,112	76	46,487	50,342
Oct.	2008	17,518	17	10,897	11,177
Nov.	2008	7,644	8	5,171	5,085
Dec.	2008	11,045	12	7,761	7,481
Jan.	2009	42,601	46	31,562	29,511
Feb.	2009	50,762	56	39,298	35,770
TOTAL		5,170,431	4,186	2,912,252	2,638,567

Month	Year	Streamflow (cubic foot per second-days)	Dissolved bromide load (tons)	Dissolved chloride load (tons)	Dissolved sulfate load (tons)
07335500 Red River near Arthur City, Texas (Arthur City gage)					
Mar.	2007	54,097	56	49,004	33,943
Apr.	2007	443,376	417	364,529	249,119
May	2007	715,716	630	493,567	383,474
June	2007	1,186,351	896	652,648	542,584
July	2007	1,721,345	950	515,562	575,935
Aug.	2007	1,134,315	570	291,081	342,147
Sept.	2007	482,308	237	119,409	141,933
Oct.	2007	134,666	71	37,108	43,008
Nov.	2007	86,059	53	30,138	32,937
Dec.	2007	104,095	58	31,260	35,256
Jan.	2008	87,328	56	32,313	34,697
Feb.	2008	175,289	71	37,259	40,034
Mar.	2008	587,963	120	58,994	48,066
Apr.	2008	685,560	324	173,602	190,315
May	2008	235,459	145	82,631	89,261
June	2008	147,117	80	42,514	48,393
July	2008	106,272	76	46,542	46,936
Aug.	2008	85,352	58	34,696	35,630
Sept.	2008	71,478	55	35,921	34,225
Oct.	2008	25,661	21	14,657	13,198
Nov.	2008	13,520	10	6,236	6,160
Dec.	2008	14,129	11	6,658	6,536
Jan.	2009	31,928	28	20,305	17,434
Feb.	2009	57,704	51	36,702	31,489
TOTAL		8,387,087	5,044	3,213,336	3,022,709

Table 3. Monthly dissolved bromide, chloride, and sulfate loads at U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09—Continued.

Month	Year	Streamflow (cubic foot per second-days)	Dissolved bromide load (tons)	Dissolved chloride load (tons)	Dissolved sulfate load (tons)
7336820 Red River near DeKalb, Texas (DeKalb gage)					
Mar.	2007	69,497	70	56,160	40,349
Apr.	2007	433,530	363	287,434	208,106
May	2007	812,951	513	333,196	305,783
June	2007	1,343,790	895	590,054	533,336
July	2007	1,924,771	836	408,116	511,801
Aug.	2007	1,386,607	495	225,264	297,791
Sept.	2007	596,495	256	121,997	156,768
Oct.	2007	170,769	89	45,951	54,709
Nov.	2007	92,567	62	36,620	38,095
Dec.	2007	145,955	66	33,427	40,308
Jan.	2008	124,572	62	31,866	37,862
Feb.	2008	300,702	79	38,067	44,248
Mar.	2008	1,033,014	147	70,013	65,278
Apr.	2008	1,111,569	307	139,859	175,810
May	2008	369,877	185	94,912	113,768
June	2008	195,345	125	77,468	75,651
July	2008	119,423	81	48,397	49,956
Aug.	2008	98,121	61	35,092	37,583
Sept.	2008	127,857	88	52,289	53,750
Oct.	2008	74,659	44	24,047	26,970
Nov.	2008	29,157	18	10,211	11,200
Dec.	2008	30,444	18	10,458	11,320
Jan.	2009	69,821	41	23,025	25,462
Feb.	2009	99,608	62	35,853	37,709
TOTAL		10,761,099	4,963	2,829,778	2,953,614

Summary

The U.S. Geological Survey (USGS), in cooperation with the City of Dallas Water Utilities Division, did a study to characterize bromide, chloride, and sulfate concentrations and loads at three USGS streamflow-gaging stations on the reach of the Red River from Denison Dam, which impounds Lake Texoma, to the U.S. Highway 259 bridge near DeKalb, Texas.

During March 1, 2007–February 28, 2009, the USGS continuously monitored selected water-quality properties, including specific conductance, at three USGS streamflow-gaging stations on the main stem of the Red River: 07331600 Red River at Denison Dam near Denison, Texas (Denison Dam gage), 07335500 Red River at Arthur City, Texas (Arthur City gage), and 07336820 Red River near DeKalb, Texas (DeKalb gage). During January 31, 2007–February 19, 2009, discrete water-quality samples also were collected every 2 to 6 weeks at these gages and analyzed for selected dissolved constituents, including bromide, chloride, and sulfate concentrations, and for specific conductance. Two periods of high flow resulted from floods during the study; floods during June–July 2007 resulted in elevated flow during June–September 2007 and smaller floods during March–April 2008 resulted in elevated flow during March–April 2008.

Bromide, chloride, and sulfate concentrations in samples collected at the three gages decreased downstream. Median bromide concentrations ranged from 0.32 mg/L at the Denison Dam gage to 0.19 mg/L at the DeKalb gage. Median chloride concentrations ranged from 176 mg/L at the Denison Dam gage to 108 mg/L at the DeKalb gage and were less than the 300-mg/L secondary maximum contaminant level established by the Texas Commission on Environmental Quality. Median sulfate concentrations ranged from 213 mg/L at the Denison Dam gage to 117 mg/L at the DeKalb gage; these values also were less than the 300-mg/L secondary maximum contaminant level. Kruskal-Wallis analyses indicated statistically significant differences among the bromide, chloride, and sulfate concentrations measured at each gage.

During the study, bromide, chloride, and sulfate concentrations and loads and specific conductance values were affected by high flow during June–September 2007 and March–April 2008. Changes in bromide, chloride, and sulfate concentrations in the Denison Dam-DeKalb reach of the Red River were evident after the June–July 2007 floods, which resulted in large releases from Denison Dam. Bromide concentrations measured at the Denison Dam gage during January 31–May 9, 2007, were 0.47 to 0.52 mg/L. After the May 9, 2007 sample, bromide concentrations 0.40 mg/L or greater were not measured again until one of the last samples for this study was collected on January 22, 2009. During July–August 2007, bromide concentrations at the Denison Dam gage ranged from 0.10 to 0.25 mg/L.

Regression equations to compute bromide, chloride, and sulfate loads were developed for each of the three gages. The regression equations were developed using the same methods used by the Red River Chloride Control Project

and the USGS Texas Water Science Center to analyze data for previous reports. To aid in the evaluation of each regression equation, adjusted R-squared (R^2) and F-statistic values were computed. The regression equations for the DeKalb gage had the largest adjusted R^2 values for each regression equation, ranging from .957 for sulfate to .976 for chloride. Although all regression equations fit the data well, the adjusted R^2 and F-statistic values indicate that equations for data collected at the DeKalb gage describe the data slightly better compared with equations for data collected at the Denison Dam and Arthur City gages. Adjusted R^2 values for all regression equations developed to estimate loads were .899 or larger, indicating that the equations explained 89.9 percent or more of the variance in the data for each constituent at each gage.

Bromide loads were larger at the Arthur City gage compared with those measured at either the upstream Denison Dam gage or the downstream DeKalb gage. During March 2007–February 2009, the total bromide loads computed at the Denison Dam, Arthur City, and DeKalb gages were 4,186, 5,044, and 4,963 tons, respectively. The computed loads were largest for those periods when streamflow in the Red River was relatively large. At the Denison Dam and Arthur City gages, 53 percent of the total bromide load during March 2007–February 2009 was recorded during 4 months, June–September 2007, compared with 50 percent at the DeKalb gage. Chloride and sulfate loads at the three gages followed the same pattern observed for bromide loads, with the largest loads at the Arthur City gage. During March 2007–February 2009, total chloride loads computed at the Denison Dam, Arthur City, and DeKalb gages were 2,912,000, 3,213,000, and 2,830,000 tons, respectively, and total sulfate loads were 2,639,000, 3,023,000, and 2,954,000 tons, respectively.

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Appendix 1

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Appendix 1. Instantaneous streamflow measured at the time water-quality samples were collected and bromide, chloride, and sulfate concentrations and specific conductance measured in discrete water-quality samples collected from U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09.

[ft³/s, cubic feet per second; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; --, not measured; <, not detected at laboratory reporting level. Sample type: E, environmental; REP, field replicate; FBLK, field equipment blank]

Station	Sample collection date	Mean instantaneous discharge (ft³/s)	Bromide (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Specific conductance (µS/cm)	Sample type
07331600	1/31/2007	4,500	0.52	460	283	2,190	E
07331600	3/13/2007	168	.50	464	293	2,160	E
07331600	4/11/2007	11,500	.51	445	277	2,120	E
07331600	5/9/2007	310	.47	450	274	2,120	E
07331600	6/14/2007	33,600	.36	384	235	1,550	E
07331600	7/12/2007	32,800	.25	226	166	1,290	E
07331600	8/9/2007	30,400	.10	117	107	847	E
07331600	8/30/2007	32,100	.18	103	95.1	780	E
07331600	10/24/2007	2,780	.22	112	136	898	E
07331600	11/26/2007	340	.25	126	166	986	E
07331600	12/17/2007	150	.25	129	164	1,000	E
07331600	1/9/2008	450	.26	138	177	1,050	E
07331600	2/26/2008	480	.29	153	194	1,130	E
07331600	2/26/2008	480	.30	153	194	--	REP
07331600	3/27/2008	10,800	.32	172	210	1,220	E
07331600	4/23/2008	16,000	.32	164	219	1,220	E
07331600	5/21/2008	10,400	.31	167	213	1,210	E
07331600	6/11/2008	190	.30	160	210	1,170	E
07331600	7/24/2008	10,400	.32	176	210	1,220	E
07331600	7/24/2008	10,400	.31	176	211	--	REP
07331600	8/28/2008	260	.33	173	191	1,250	E
07331600	9/17/2008	170	.35	193	223	1,310	E
07331600	10/8/2008	120	.37	225	231	1,400	E
07331600	11/4/2008	77	.38	235	251	1,460	E
07331600	12/10/2008	124	.39	248	256	1,500	E
07331600	1/22/2009	1,300	.41	262	266	1,580	E
07331600	2/19/2009	10,700	.40	259	267	1,620	E
07335500	1/31/2007	6,700	.29	228	154	1,230	E
07335500	3/13/2007	1,060	.33	269	187	1,520	E
07335500	4/11/2007	11,900	.49	431	268	2,030	E
07335500	5/8/2007	12,700	.21	168	116	900	E
07335500	5/8/2007	12,700	.22	167	116	--	REP
07335500	5/8/2007	12,700	<.02	<.12	<.18	--	FBLK
07335500	6/13/2007	36,900	.37	367	228	1,810	E
07335500	7/11/2007	72,400	.15	126	92.2	775	E
07335500	8/8/2007	35,000	.17	134	106	894	E
07335500	8/30/2007	34,000	.17	96.3	94.4	759	E
07335500	10/23/2007	5,030	.21	107	122	876	E
07335500	11/27/2007	6,070	.24	118	155	950	E
07335500	12/18/2007	5,000	.18	83.1	106	752	E
07335500	1/9/2008	2,040	.23	118	147	964	E
07335500	2/27/2008	3,170	.23	99.4	128	878	E

Appendix 1. Instantaneous streamflow measured at the time water-quality samples were collected and bromide, chloride, and sulfate concentrations and specific conductance measured in discrete water-quality samples collected from U.S. Geological Survey streamflow-gaging stations 07331600 Red River at Denison Dam near Denison, Texas, 07335500 Red River at Arthur City, Texas, and 07336820 Red River near DeKalb, Texas, 2007–09—Continued.

Station	Sample collection date	Mean instantaneous discharge (ft^3/s)	Bromide (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Specific conductance (µS/cm)	Sample type
07335500	3/26/2008	16,700	0.05	9.79	20.7	230	E
07335500	4/23/2008	26,400	.27	137	183	1,050	E
07335500	5/21/2008	4,090	.26	124	157	995	E
07335500	6/11/2008	2,840	.20	80.1	94.2	766	E
07335500	7/24/2008	2,970	.31	165	198	1,180	E
07335500	8/28/2008	2,250	.27	149	175	1,070	E
07335500	9/17/2008	997	.25	127	142	1,020	E
07335500	10/8/2008	663	.31	196	182	1,310	E
07335500	11/4/2008	360	.33	187	191	1,240	E
07335500	12/10/2008	415	.29	179	181	1,230	E
07335500	1/21/2009	1,100	.32	210	215	1,400	E
07335500	2/18/2009	2,240	.34	211	219	1,390	E
07336820	2/1/2007	20,800	.03	19.3	20.9	190	E
07336820	3/12/2007	2,700	.42	357	240	1,810	E
07336820	4/10/2007	15,900	.45	400	250	1,940	E
07336820	5/8/2007	20,000	.06	27.9	24.6	267	E
07336820	6/13/2007	35,000	.32	293	196	1,550	E
07336820	7/11/2007	69,100	.14	119	85.7	772	E
07336820	8/8/2007	44,000	.14	104	81.6	716	E
07336820	8/31/2007	41,800	.14	74.2	72.6	610	E
07336820	10/23/2007	5,110	.19	96.8	111	821	E
07336820	11/27/2007	6,100	.23	113	151	952	E
07336820	12/18/2007	7,750	.13	52.5	72.5	537	E
07336820	1/9/2008	3,550	.18	92.8	123	802	E
07336820	2/27/2008	13,000	.09	33.1	45.5	334	E
07336820	3/26/2008	36,900	.03	5.37	11.7	145	E
07336820	4/24/2008	39,500	.18	86.7	117	718	E
07336820	5/21/2008	6,690	.15	66.2	85.6	600	E
07336820	6/11/2008	3,530	.22	113	154	952	E
07336820	7/24/2008	3,700	.26	136	173	1,040	E
07336820	8/28/2008	4,940	.23	119	147	932	E
07336820	9/18/2008	2,610	.23	113	136	892	E
07336820	10/8/2008	3,180	.20	109	115	814	E
07336820	11/4/2008	1,340	.22	99.2	134	986	E
07336820	12/10/2008	1,030	.25	113	143	1,040	E
07336820	1/21/2009	2,000	.25	148	162	1,020	E
07336820	1/21/2009	2,000	.25	147	161	--	REP
07336820	2/18/2009	4,300	.19	108	115	736	E

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