Prepared in cooperation with the Texas Commission on Environmental Quality

Recent (2008–10) Water Quality in the Barton Springs Segment of the Edwards Aquifer and Its Contributing Zone, Central Texas, with Emphasis on Factors Affecting Nutrients and Bacteria

Scientific Investigations Report 2011–5139

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

Front cover: Barton Springs pool, Austin, Texas (photograph courtesy of Nelson Guda, University of Texas).

Back cover:

Top, A U.S. Geological Survey hydrologist collects a sample from Onion Creek, near Driftwood, Texas.

Bottom, Barton Creek in flood, at the bridge at Lost Creek Boulevard, Austin, Texas.

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KEN SALAZAR, Secretary

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
mile, nautical (nmi)	1.852	kilometer (km)
	Volume	
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
gallon (gal)	3.785	cubic decimeter (dm^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
	Volume	
milliliter (mL)	0.035	ounce, fluid (fl. oz)
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
	Flow rate	
cubic meter per second (m^3/s)	70.07	acre-foot per day (acre-ft/d)

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

$$°F=(1.8×°C)+32$$

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

$$°C=(°F-32)/1.8$$

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

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

Recent (2008–10) Water Quality in the Barton Springs Segment of the Edwards Aquifer and Its Contributing Zone, Central Texas, with Emphasis on Factors Affecting Nutrients and Bacteria

By Barbara J. Mahler,[1] MaryLynn Musgrove,[1] Thomas L. Sample,[1] and Corinne I. Wong[2]

Abstract

The Barton Springs zone, which comprises the Barton Springs segment of the Edwards aquifer and the watersheds to the west that contribute to its recharge, is in south-central Texas, an area with rapid growth in population and increasing amounts of land area affected by development. During November 2008–March 2010, an investigation of factors affecting the fate and transport of nutrients and bacteria in the Barton Springs zone was conducted by the U.S. Geological Survey (USGS), in cooperation with the Texas Commission on Environmental Quality. The primary objectives of the study, described herein, were to characterize occurrence of nutrients and bacteria in the Barton Springs zone under a range of flow conditions; to improve understanding of the interaction between surface-water quality and groundwater quality; and to evaluate how factors such as streamflow variability and dilution affect the fate and transport of nutrients and bacteria in the Barton Springs zone. The USGS collected and analyzed water samples from five streams (Barton, Williamson, Slaughter, Bear, and Onion Creeks), two groundwater wells (the Marbridge well [YD–58–50–704] and the Buda well [LR–58–58–403]), and the main orifice of Barton Springs in Austin, Texas. During the period of the study, during which the hydrologic conditions transitioned from exceptional drought (the dry period, November 1, 2008 to September 9, 2009) to wetter than normal (the wet period, September 10, 2009 to March 31, 2010), water samples were collected routinely (every 3 to 4 weeks) from the streams, wells, and spring and, in response to storms, from the streams and spring. All samples were analyzed for major ions, nutrients, the bacterium *Escherichia coli*, and suspended sediment. During the dry period, the geochemistry of groundwater at the two wells and at Barton Springs was dominated by flow from the aquifer matrix and was relatively similar and unchanging at the three sites. At the onset of the wet period, when the streams began to flow, the geochemistry of groundwater samples from the Marbridge well and Barton Springs changed rapidly, and concentrations of most major ions and nutrients and densities of *Escherichia coli* became more similar to those of samples from the streams relative to concentrations and densities during the dry period. Geochemical modeling indicated that the proportion of Barton Springs discharge composed of stream recharge increased from about 0–8 percent during the dry period to about 80 percent during the wet period. The transition from exceptional drought to wetter-than-normal conditions resulted in a number of marked changes that highlight factors affecting the fate and transport of nutrients and bacteria and the strong influence of stream recharge on water quality in the Barton Springs segment of the Edwards aquifer. The transition from exceptional drought to wetter-than-normal conditions had a pronounced effect on the fate of nitrogen species. Organic nitrogen loaded to and stored in soils during the dry period was nitrified to nitrate when the soils were rewetted, resulting in elevated concentrations of nitrate plus nitrite in streams as these constituents were progressively leached during continued wet weather. Estimated mean monthly loads of organic nitrogen and nitrate plus nitrite in stream recharge and Barton Springs discharge, which were relatively low and constant during the dry period, increased during the wet period. Loads of organic nitrogen, on average, were about six times greater in stream recharge than in Barton Springs discharge, indicating that organic nitrogen likely was being converted to nitrate within the aquifer. Loads of total nitrogen (organic nitrogen plus ammonia and nitrate plus nitrite) in stream recharge (162 kilograms per day) and in Barton Springs discharge (157 kilograms per day) for the period of the investigation were not significantly different. Dilution was not an important factor affecting concentrations of nitrate plus nitrite in the streams or in Barton Springs during the period of this investigation: Concentrations of nitrate plus nitrite did not decrease in streams with increasing stream discharge, and nitrate plus nitrite concentrations measured at Barton Springs during the period of this investigation were positively correlated with spring discharge. Dilution or another mechanism, such as deposition or filtration, decreased densities of

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coli from stream recharge to spring discharge during the wet period but not during the dry period. There were relatively few correlations between concentrations of nutrients or densities of *Escherichia coli* and the explanatory variables of suspended-sediment concentration and discharge, indicating that these variables are poor predictors of nutrient and bacteria occurrence. The results of this investigation demonstrate that climatic conditions and streamflow variability have a marked effect on the fate and transport of nutrients and bacteria from stream recharge to Barton Springs discharge.

Introduction

The Barton Springs zone, which comprises the Barton Springs segment of the Edwards aquifer (hereinafter, Barton Springs segment) and the watersheds to the west contributing to its recharge (the contributing zone), is in south-central Texas (fig. 1), an area that is undergoing rapid growth in population (1.1 percent per year during 2003–08 [Combs, 2010]) and in land area affected by development (City of Austin, 1995). There is interest, therefore, in monitoring surface-water and groundwater quality in the Barton Springs zone under a range of aquifer flow conditions in order to establish a baseline against which potential future changes in water quality related to increasing urbanization and associated wastewater production can be compared. Such a baseline is necessary to evaluate the potential effects of the discharge of treated wastewater on the water quality of the aquifer. Also necessary is an understanding of the factors affecting the fate and transport of nutrients and bacteria from the point of recharge to the point of discharge. During November 2008–March 2010, an investigation of factors affecting the fate and transport of nutrients and bacteria in the Barton Springs zone was conducted by the U.S. Geological Survey (USGS), in cooperation with the Texas Commission on Environmental Quality. The primary objectives of the study described herein were to characterize occurrence of nutrients and bacteria in the Barton Springs zone under a range of flow conditions; increase the understanding of the interaction between surface-water quality and groundwater quality; and evaluate how factors such as streamflow variability and dilution affect the fate and transport of nutrients, bacteria, and suspended sediment in the Barton Springs zone.

Barton Springs, located in Austin, Tex., is the main discharge point of the Barton Springs segment, and water quality at the springs and in the Barton Springs segment are of interest for several reasons. The spring system supplies a 750-foot (ft)-long swimming pool visited by more than 400,000 people each year (City of Austin, 2010b), provides a part of the City of Austin's municipal water supply (Slade and others, 1986), and is the only known habitat for the Barton Springs Salamander (*Eurycea sosorum*), a federally listed endangered species that is extremely vulnerable to changes in water quality (U.S. Fish and Wildlife Service, 1997). Additionally, the Barton Springs segment has been designated a Sole Source Aquifer by the U.S. Environmental Protection Agency (2006).

The Barton Springs segment is karst, meaning that most groundwater flow is through voids formed by dissolution of the host rock. Because voids can be as large as a foot or more in diameter (conduits or caves), transport times in karst from the point of recharge to discharge can be extremely rapid (White, 1988). Transport through large voids offers little opportunity for filtration or sorption; therefore, karst aquifers are considered to be very vulnerable to contamination (White, 1988). Dye traces have demonstrated that traveltimes through the Barton Springs segment are rapid and variable and that the direct-line velocity increases with higher spring discharge rates (Hunt and others, 2006a). Following storms, surface runoff recharges through stream recharge features and streambeds, delivering runoff-associated contaminants to Barton Springs (Mahler and others, 2006). When aquifer flow conditions are low, storm-associated recharge moves rapidly through the conduit system and undergoes relatively little dilution before discharging at the springs; when aquifer flow conditions are high, much of the storm-associated recharge goes into temporary storage (Mahler and others, 2006).

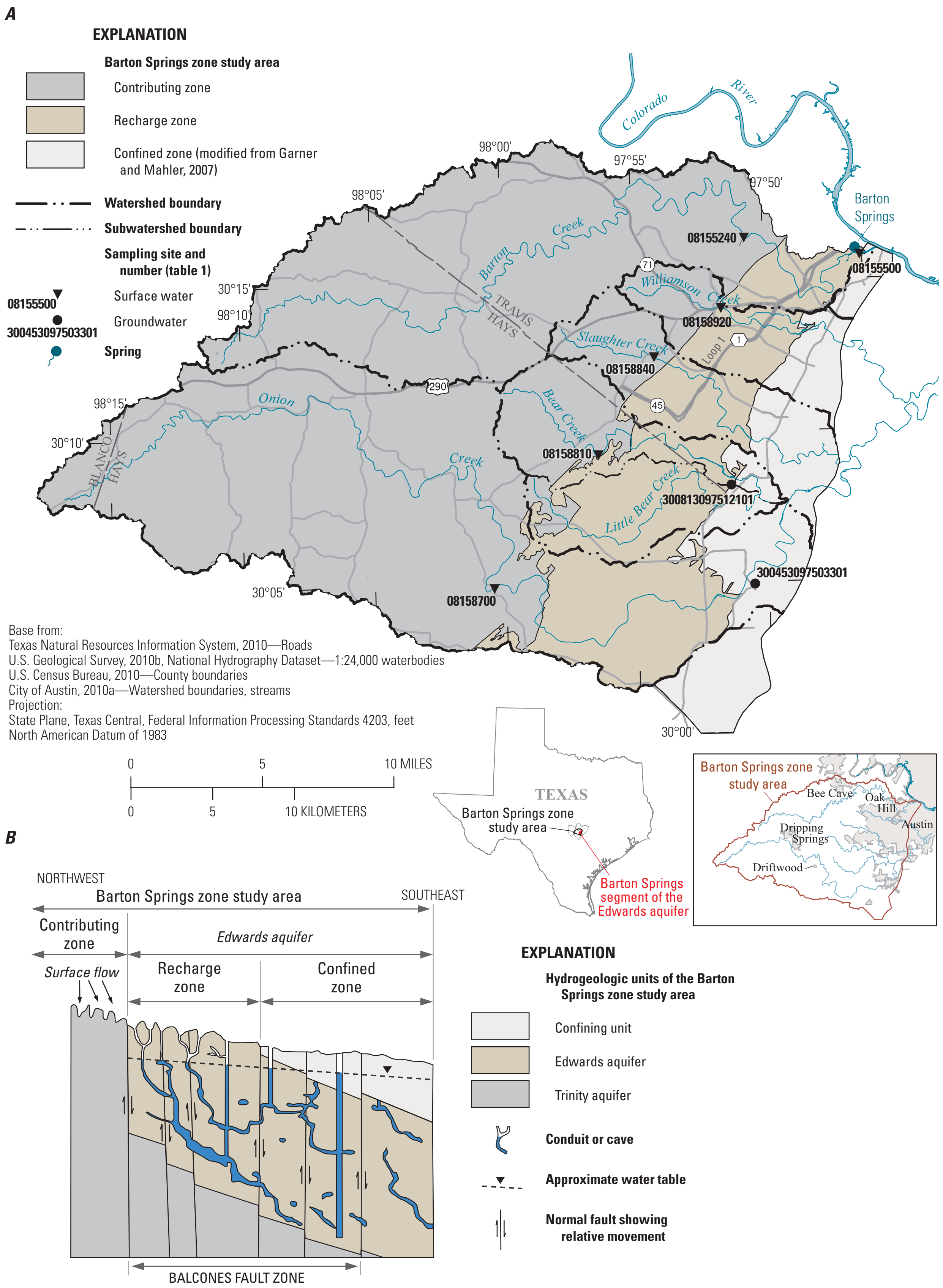
During the course of this investigation, hydrologic conditions changed from exceptional drought (U.S. Drought Monitor, 2011) to wetter than normal. Between November 1, 2008, and September 9, 2009 is referred to as the dry period. Between September 10, 2009, and March 31, 2010 is referred to as the wet period. Rainfall and runoff during the period of the investigation are described in detail in the Climatic and Hydrologic Conditions During the Period of Study section of this report. Constituents of interest were monitored under a wide range of aquifer flow conditions, providing an opportunity to investigate the response of water quality in a karst system to different hydrologic conditions. The results of this investigation will provide a baseline against which future potential changes in water quality in the Barton Springs zone can be compared and will enhance understanding of geochemical and hydrologic processes within the aquifer that affect spatial and temporal variations in nutrient concentrations and bacterial densities.

Purpose and Scope

The purpose of this report is to

1. Describe recent (November 2008–March 2010) water quality (major ion and nutrient chemistry and bacterial content) in five streams recharging the Barton Springs segment, in groundwater in two wells with contrasting hydrogeologic properties, and in Barton Springs discharge in response to climatic changes and in response to storms during November 2008–March 2010.

2. Evaluate changes in water chemistry in Barton Springs and in groundwater sampled from wells during the dry and wet periods relative to changes in water chemistry in the streams during the dry and wet periods.



Base from:
Texas Natural Resources Information System, 2010—Roads
U.S. Geological Survey, 2010b, National Hydrography Dataset—1:24,000 waterbodies
U.S. Census Bureau, 2010—County boundaries
City of Austin, 2010a—Watershed boundaries, streams
Projection:
State Plane, Texas Central, Federal Information Processing Standards 4203, feet
North American Datum of 1983

Figure 1. Barton Springs zone study area, south-central Texas. *A*, Map of the study area. *B*, Schematic cross section of the study area (modified from Slade and others, 1986).

3. Synthesize the findings to evaluate processes affecting fate and transport of nutrients and bacteria in the Barton Springs zone, including effects of hydrologic and climatic conditions, mixing, and dilution.

Hydrogeologic Setting

The Barton Springs segment is a hydrologically isolated section of the karstic Edwards aquifer of south-central Texas. The segment is bounded on the north by the Colorado River, on the south by a groundwater divide, on the west by the fault-controlled outcrop of the Trinity aquifer, and on the east by a zone of low permeability containing saline water (greater than 1,000 milligrams per liter [mg/L] dissolved solids concentration) known as the saline zone (Abbott, 1975; Slade and others, 1986; Sharp and Banner, 1997). The hydrogeology is substantially controlled by the Balcones fault zone, a zone of en echelon normal faults that dip generally southeastward and strike southwest-northeast across the study area.

The rocks of the Barton Springs segment consist of the Edwards Group and the Georgetown Formation of Lower Cretaceous age (Rose, 1972; Maclay, 1995; Small and others, 1996; Sharp and Banner, 1997). The Barton Springs segment is underlain by the Glen Rose Limestone, which composes the upper part of the generally less permeable Trinity aquifer, and is overlain by the Del Rio Clay, an upper confining unit (fig. 1*B*). Miocene Epoch tectonic activity produced the Balcones fault zone; uplift associated with this tectonic activity increased surface erosion rates and helped establish a “through-flow” system in the aquifer, which allows for enhanced transmission of groundwater.

Barton Springs is the main discharge point for the Barton Springs segment. The long-term median discharge is about 50 ft^3/s, with historical (1917–82) minimum and maximum flows of 10 and 166 ft^3/s, respectively (Slade and others, 1986). Other discharge points include smaller springs and groundwater supply wells. About 1,230 operational wells drilled into the aquifer withdrew an estimated 2.3 billion gallons of water in 2006, equivalent to a constant withdrawal rate of about 9.8 ft^3/s (Hunt and others, 2006b).

Slade and others (1986) estimated that about 85 percent of the aquifer recharge is provided by the six major streams that cross the recharge zone: Barton, Williamson, Slaughter, Bear, Little Bear, and Onion Creeks (fig. 1). Although this estimate has been debated (Hauwert, 2009), it is generally agreed that most recharge to the aquifer occurs as focused recharge through swallets and fractures in streambeds and that the geochemistry of the streams providing the recharge water has a strong control on the geochemistry of the water discharging from Barton Springs (Mahler and others, 2006). Additional sources of recharge, minor in comparison to streambed recharge on a volumetric basis, include infiltration of recharge water through interstream sinkholes and soil zones (Hauwert, 2009), leaking municipal water-supply and sewer pipes (St. Clair, 1979; Sharp and Banner, 1997; Garcia-Fresca Grocin, 2004), and cross-formational flow from adjacent hydrostratigraphic units (Slade and others, 1986; Smith and Hunt, 2004; Garner and Mahler, 2007). These additional sources of recharge are not characterized in this report. Throughout this report, “stream recharge” refers to recharge occurring through the streambeds of Barton, Williamson, Slaughter, Bear, and Onion Creeks. Recharge from Little Bear Creek was not considered because there is no streamflow-gaging station on Little Bear Creek.

Groundwater flow in the Barton Springs segment generally follows the northeastward strike of the Balcones fault zone toward Barton Springs, although direction varies somewhat with changes in aquifer flow condition (Slade and others, 1986). Precise understanding of the flow system is confounded by the presence of karst conduits, which can transport water in a direction different from that of the larger scale hydraulic gradient (Hauwert and others, 2004). Dye-tracing studies have verified the general direction of flow and have identified several probable conduit flow paths. Hauwert and others (2004) found that straight-line groundwater traveltimes under some conditions exceeded 6 miles (mi) per day. The dye-tracing studies indicated that one prominent aquifer flow path is near the saline zone boundary, which results in elevated sodium, chloride, and sulfate concentrations in water along that flow path relative to concentrations along other flow paths (Hauwert and others, 2004), affecting the aqueous geochemistry at Barton Springs (Herrington and others, 2005).

Discharge from Barton Springs reflects aquifer flow conditions and water-level altitudes. When water-level altitudes in the aquifer are high, spring discharge is high; as water-level altitudes drop, spring discharge decreases. Mahler and others (2006) defined low aquifer flow conditions as those during which Barton Springs discharge was 40 ft^3/s or less, average flow conditions as those during which discharge was from 40 to 89 ft^3/s, and high aquifer flow conditions as those during which discharge was 90 ft^3/s or greater.

Previous Water-Quality Studies

Properties and constituents characterizing water quality have been measured in the Barton Springs zone since the 1970s, with a few constituents such as nitrate measured as early as 1937 (City of Austin, 1997; Turner, 2000). Mahler and others (2006) provided a review of water-quality studies in the Barton Springs segment prior to 2005. They also presented the results of a multiyear investigation of water quality (2003–05), conducted during above-average flow conditions, that included analysis of major ions, nutrients, soluble pesticides, and volatile organic compounds in the four orifices of Barton Springs under both routine and storm-influenced conditions. They reported that Barton Springs was affected by persistent low concentrations of atrazine (an herbicide), chloroform (a drinking-water disinfection byproduct), and tetrachloroethene (a solvent). Increased recharge from the major recharging streams resulted in increased calcium, sulfate, atrazine, simazine, and tetrachloroethene concentrations, and in decreased concentrations of most other major ions, nitrate, and chloroform at one or more of the spring orifices. Their results demonstrated the influence of water quality in recharging streams on water quality at the springs even during nonstorm flow conditions.

The contribution of recent recharge to spring discharge was further investigated by Mahler and Garner (2009), who used nitrate as a conservative tracer to quantify the contributions of aquifer water and recent recharge to spring discharge. Differentiation between these two endmembers (aquifer water and recharge water) was possible because they had different nitrate concentrations: 1.5 mg/L in the aquifer-water endmember and 0.17–0.25 mg/L for the recharge endmember (the range in values for this endmember represents nonstorm flow [0.17 mg/L] and stormflow [0.25 mg/L]) . Mahler and Garner (2009) reported that recharge water contributed from 0 to 55 percent of spring discharge during nonstorm flow.

Additional investigation of nutrients in the Barton Springs zone and in Austin has been done by the City of Austin (COA). Herrington and Scoggins (2006) used field and laboratory experiments to determine the limiting nutrient that controlled algae growth in Bear Creek and in Barton Springs. They reported that the stream and the spring were highly oligotrophic and that algae growth was phosphorus limited. COA also has measured nitrate and phosphorus concentrations in rain in the Austin area (Turner, 2003). The median concentrations of nitrate at a rural site and at an urban site were 0.47 and 0.78 mg/L, respectively, and median concentrations of total phosphorus at a rural site and at an urban site were 0.05 and 0.09 mg/L, respectively.

Most recently, Mahler and others (2011) characterized concentrations of nitrate and wastewater compounds in the Barton Springs zone and their potential relation to wastewater sources in the contributing zone. They reported that concentrations of nitrate measured during November 2008–March 2010 were elevated relative to those measured during 1990–2008 for similar flow conditions. Concentrations of wastewater compounds were very low (at or below the laboratory reporting level), as was the frequency of detection (one or more compounds were detected in 3 percent of routine samples and 9 percent of storm-associated samples). The elevated concentrations and loads of nitrate were attributed to minimal leaching from soils during drought conditions and maximal leaching following the onset of rains, coupled with increased loading of nitrogen species to the watersheds. The isotopic composition of the nitrate in many of the samples indicated that the origin of the nitrate included a contribution with a human or animal waste (or both) origin. There was no indication that denitrification was occurring within the aquifer. An evaluation of changes in areally weighted numbers of septic systems, rates of land application of treated wastewater, and numbers of domesticated dogs and cats in the contributing zone indicated that a rapid increase in numbers of septic systems and volume of land-applied wastewater during 2000–10 likely contributed to increased loading of nitrogen species to the Barton Springs system (Mahler and others, 2011).

Chemical Species and Contaminants of Interest

Chemical species and contaminants investigated in this report include major ions, nutrients, and bacteria. Concentrations of major ions provide information on geochemical processes occurring in soils and streams and within the aquifer. Evaluating the fate and transport of nutrients and bacteria is a principal focus of this report.

Major ions make up the majority of constituents in natural waters. Major ions are those commonly present in concentrations exceeding 1.0 mg/L (Hem, 1992). In this report, the minor ions strontium, fluoride, bromide, and boron are included in all discussions of major ions. The study area consists of carbonate terrain; in carbonate terrains, the constituents in water are mostly the ions calcium, magnesium, and bicarbonate because these constituents are readily weathered from carbonate minerals such as calcite and dolomite; strontium also is associated with carbonate minerals (Hem, 1992). Noncarbonate constituents such as the ions sodium, chloride, and sulfate have several possible sources in carbonate terrains, including overlying silicate soils; noncarbonate minerals incorporated in the bedrock, such as evaporite and clay minerals; contribution of allogenic groundwater with high noncarbonate concentrations; and anthropogenic contributions such as fertilizers, road salt, treated drinking water, septic tanks, and wastewater effluent. Some constituents are useful tracers of sources or processes. For example, fluoride, bromide, and boron can provide information regarding potential sources of water. Fluoride is present at low levels in sedimentary rock (Hem, 1992) and in fluoridated municipal water; it also occurs naturally in saline zone groundwater (Mahler, 2008). Boron and bromide are present at low levels in bedrock, and boron is associated with wastewater (Hem, 1992).

Nutrients are those elements that are important to plant growth and survival; elevated concentrations of the nutrients nitrogen (N) or phosphorus (P) in surface water can cause excessive growth of algae and other nuisance aquatic plants (a condition known as eutrophication) (Dubrovsky and others, 2010). These plants can clog water-supply intake pipes and interfere with recreational activities such as fishing, swimming, and boating. Decomposition of the algae consumes dissolved oxygen, and can result in the death of other aquatic life (Ansari and others, 2010).

There are numerous natural and anthropogenic sources of N species to water. They include fertilizers (manure, organic fertilizers, and synthetic fertilizers); human and animal waste (animal feces, treated wastewater effluent, and septic-system drainage); decaying plant debris; runoff from fertilized residential lawns, golf courses, and construction sites; vehicle exhaust; and precipitation. Nitrogen has several chemical forms, and the process by which it is converted from one form to another is called the nitrogen cycle. In aquatic systems, an important process is the conversion of organic nitrogen to nitrate, the principal form of nitrogen in water. Organic nitrogen from the decomposition of plants and in animal waste is converted, in the presence of oxygen, to ammonia (NH_3) by bacteria and fungi, a process called ammonification, and in water forms the ammonium ion (NH_4^+). The positively charged ammonium ion adsorbs strongly to mineral surfaces, such as those in soils, and is released by cation exchange (Hem, 1992). When ammonium ion is released, it is oxidized by bacteria, in the presence of oxygen, to nitrite and then to nitrate, a process called nitrification. The conversion of organic nitrogen to nitrate in groundwater consumes dissolved oxygen. The occurrence of organic nitrogen and nitrite in water generally is an indication of contamination from disposal of sewage or organic waste; the presence of nitrate might also indicate such contamination but at a location and time more removed from the sampling point (Hem, 1992). National background concentrations of nitrate have been estimated to be 0.24 mg/L for streams and 1.0 mg/L for groundwater (Dubrovsky and others, 2010).

The initial source of P species is the weathering of rocks, and P cycles through soils, plants, animals, and water. Phosphorites are a common source of P in carbonate rocks, and limestones are, on average, 0.04 percent phosphorus pentoxide (P_2O_5) (Blatt, 1982). Anthropogenic sources of P to water include fertilizers, sewage, and detergents. In rocks and waters near the Earth's surface, P occurs primarily as the anion PO_4^{3-}, which is referred to as orthophosphate (hereinafter, orthoP) (Hem, 1992). Background concentrations of orthoP have been estimated as 0.010 mg/L for streams and 0.030 mg/L for groundwater (Dubrovsky and others, 2010). Other forms of P include organic P, which is mostly from plant material and usually bound to sediment (Dubrovsky and others, 2010). Phosphorus availability generally is the critical factor controlling eutrophication, as it frequently is the nutrient in most limited supply in aquatic systems (Hem, 1992). Dissolved P tends to combine with calcium, iron, and aluminum as sparingly soluble minerals and tends to sorb on surfaces of other minerals (Hem, 1992). As a result, much of the P transported by streams is associated with suspended sediment (Litke, 1999).

The presence of some species of bacteria is interpreted as an indicator of contamination from human and (or) animal waste. *Escherichia coli* (hereinafter, *E. coli*) is one of the most commonly used bacterial indicator species. The presence in water of *E. coli* generally is interpreted as evidence of fecal contamination from warm-blooded animals. A few strains of *E. coli* are pathogenic, such as *E. coli* O157:H7, but most strains are not (Myers and others, 2007).

Methods of Investigation

Study Design

For this study, the geochemistry of water samples collected routinely (every 3 to 4 weeks) and in response to storms (storm samples) were used to evaluate the geochemistry of water from Barton Springs and the streams that provide much of its recharge. Samples were collected from the main orifice of Barton Springs, from five streams that recharge the Barton Springs segment, and from two groundwater wells (fig. 1; table 1). Complete data for all analyses are available in USGS annual water data reports for 2008, 2009, and 2010 (U.S. Geological Survey, 2010a). Quality assurance (QA) procedures were an integral part of the study design. QA procedures and quality control sample results are documented in appendix 1.

Samples were collected routinely every 3 weeks from November 2008 through November 2009 and monthly from

Table 1. Sampling sites for water-quality characterization in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[USGS; U.S. Geological Survey; FM, Farm Road; --, not applicable]

USGS station number (fig. 1)	USGS station name	Site identifier	Site type	State well number
08155240	Barton Creek at Lost Creek Blvd. near Austin, Tex.	Barton	Stream	--
08158920	Williamson Creek at Oak Hill, Tex.	Williamson	Stream	--
08158840	Slaughter Creek at FM 1826 near Austin, Tex.	Slaughter	Stream	--
08158810	Bear Creek below FM 1826 near Driftwood, Tex.	Bear	Stream	--
08158700	Onion Creek near Driftwood, Tex.	Onion	Stream	--
300813097512101	Marbridge	Marbridge	Groundwater well	YD–58–50–704
300453097503301	City of Buda 1	Buda	Groundwater well	LR–58–58–403
08155500	Barton Springs at Austin, Tex.	Barton Springs	Spring	--

November 2009 through March 2010 (fig. 2; table 2) without regard to hydrologic conditions, such as rising, falling, or stable streamflow or spring discharge (hereinafter, “routine” samples). Routine samples were collected from five of the six major streams that recharge the aquifer (Barton, Williamson, Slaughter, Bear, and Onion Creeks, and excepting Little Bear Creek) at USGS water-quality sampling sites less than 2 mi upstream from the recharge zone or on the upstream part of the recharge zone (fig. 1), provided that there was flow at the site. Because these streams frequently have no flow, the presence of flowing water in the creeks generally resulted from recent rainfall and should not be assumed to represent base flow. Routine samples also were collected from two groundwater wells: the Marbridge well (USGS station number 300813097512101, State well number YD–58–50–704) and the Buda well (USGS station number 300453097503301, State well number LR–58–58–403) (fig. 1). These two wells were selected on the basis of historical data (U.S. Geological Survey, 2010a) that indicate that the Marbridge well likely receives some conduit flow, whereas the Buda well likely receives mostly matrix flow. Finally, routine samples were collected from Barton Springs. Routine samples were analyzed for a suite of major ions and nutrients, suspended-sediment concentration (SSC), and *E. coli* (table 3). The objective of the routine sample collection was to evaluate temporal variation and similarities and differences in water quality at stream, groundwater, and spring sites under nonstorm conditions.

To characterize changes in water quality in response to storms, samples were collected from the five major recharging streams and the main orifice of Barton Springs in response to three major storms (fig. 2; table 2). At the stream sites, flow-weighted composite samples were collected over the storm hydrograph. At Barton Springs, one grab sample was collected just prior to the storm, and eight grab samples were collected at closely spaced intervals (hours to days) following the storm. All storm samples were analyzed for major ions,

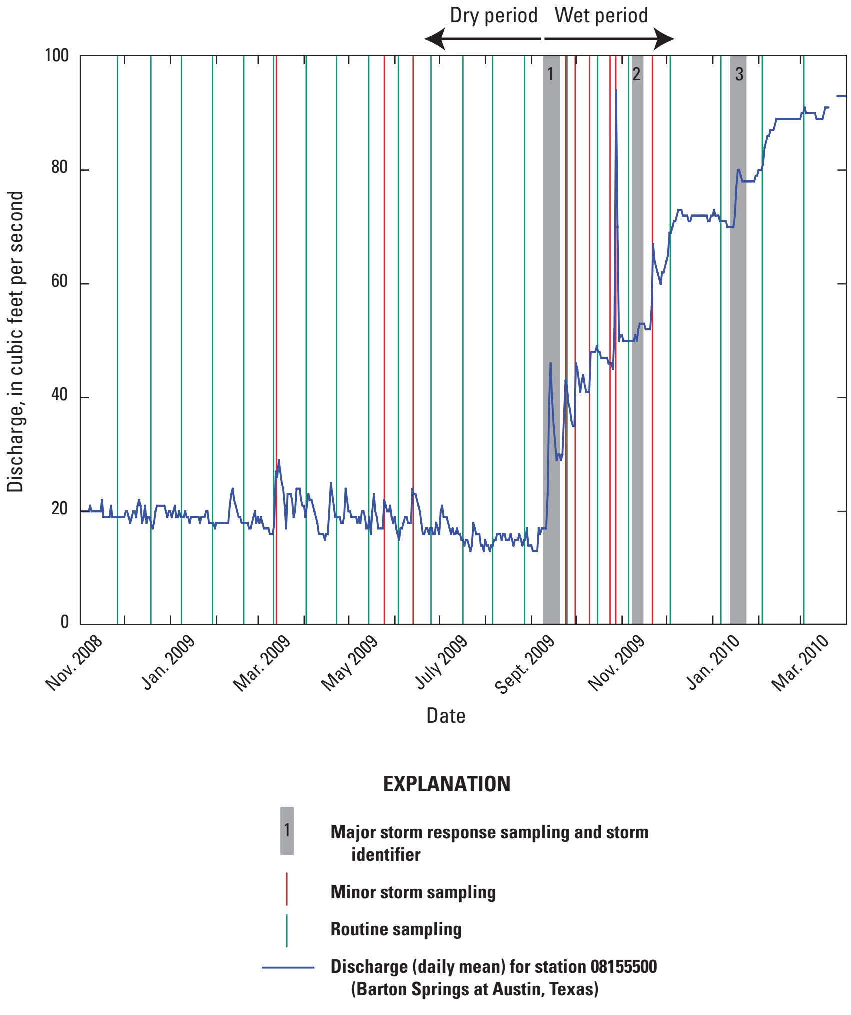


Figure 2. Time series of Barton Springs discharge (daily mean for U.S. Geological Survey station no. 08155500 Barton Springs at Austin, Tex.) and timing of collection of major-storm, minor-storm, and routine samples at sites in the Barton Springs zone, south-central Texas (November 2008–March 2010).

Table 2. Summary of number of samples analyzed, Barton Springs zone, south-central Texas (November 2008–March 2010).

[*E. coli*, *Escherichia coli*; FM, Farm Road]

USGS station number (fig. 1)	USGS Station name	Number of routine samples		Number of storm samples		
		Dry period	Wet period	Minor storm	Major storm[1]	Major storm (*E.coli*)
08155240	Barton Creek at Lost Creek Blvd. near Austin, Tex.	13	6	4	4	9
08158920	Williamson Creek at Oak Hill, Tex.	2	6	5	6	10
08158840	Slaughter Creek at FM 1826 near Austin, Tex.	0	6	2	4	6
08158810	Bear Creek below FM 1826 near Driftwood, Tex.	4	6	5	6	9
08158700	Onion Creek near Driftwood, Tex.	0	6	2	4	7
300813097512101	Marbridge (State well number YD–58–50–704)	13	0	0	0	0
300453097503301	City of Buda 1 (State well number LR–58–58–403)	13	0	0	0	0
08155500	Barton Springs at Austin, Tex.	14	7	6	27	27

[1] Storms 1–3 (fig. 2).

Table 3. Analytes measured and associated sample processing for samples in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[mL, milliliter; µm, micrometers; HNO_3, nitric acid; <, less than; N, nitrogen; P, phosphorus; H_2SO_4, sulfuric acid; Teflon® DuPont]

Constituent	Filter	Collection bottle material	Shipping container	Sample volume (mL)	Preservative
Major ions (including strontium, fluoride, and boron)					
Cations	0.45-µm versapor membrane	Teflon or polyethylene	Polyethylene	250	HNO_3 to pH <2
Anions	0.45-µm versapor membrane	Teflon or polyethylene	Polyethylene	250	None
Nutrients					
Ammonia, as N	0.45-µm cellulose	Teflon or polyethylene	Polyethylene	125	None
Ammonia + organic nitrogen, as N	None	Teflon or polyethylene	Polyethylene	125	H_2SO_4
Nitrite, as N	0.45-µm cellulose	Teflon or polyethylene	Polyethylene	125	None
Nitrite + nitrate, as N	0.45-µm cellulose	Teflon or polyethylene	Polyethylene	125	None
Phosphorus, dissolved, as P	0.45-µm cellulose	Teflon or polyethylene	Polyethylene	125	None
Orthophosphate, as P	0.45-µm cellulose	Teflon or polyethylene	Polyethylene	125	None
Phosphorus, total	None	Teflon or polyethylene	Polyethylene	125	H_2SO_4
Escherichia coli	None	Polycarbonate	Polycarbonate	100	Sodium thiosulfate, ice
Suspended sediment	None	Polyethylene	Polyethylene	250	None

nutrients, *E. coli*, and SSC. Additionally, composite or grab samples were collected from some of the surface-water sites following some storms that resulted in flow in only one or two of the streams (minor storms); for one of these minor storms, samples were also collected from Barton Springs (March, 2009) (table 2). Two of the routine samples (Williamson and Bear Creeks, March 13, 2009) were collected within 24 hours of rainfall, and these two samples are included in the discussion of minor-storm results. One date for collection of routine samples (September 23, 2009) coincided with rainfall that resulted in flow in three streams (Barton, Williamson, and Bear Creeks); samples collected from these three sites are included in the discussion of minor-storm results, and samples collected from Barton Springs and the groundwater well sites are included in the discussion of routine samples.

In this report, samples from the five major recharging streams are referred to as “surface water” or “stream water.” Samples from the two wells are referred to as “groundwater,” and samples from Barton Springs are referred to as “spring water” or “spring flow.” Barton Springs is the main discharge point of the aquifer and, as such, integrates all of the inputs and processes that occur along flow paths in the Barton Springs segment (Quinlan, 1989). Groundwater samples collected from wells integrate inputs and processes that occur along flow paths supplying water to those individual wells and, as such, might represent more local influences affecting individual wells that may not be representative of aquifer-wide processes.

Sample Collection

Samples were collected from recharging streams (surface water), groundwater wells (groundwater), and the main orifice of Barton Springs (spring water). At the stream sites, routine samples were collected by immersing bottles below the water surface near the centroid of flow (grab samples), avoiding contact with the atmosphere (Wilde and others, 1999). Following the storms, samples were collected over the duration of the storm hydrograph by autosampler, which was triggered to begin sampling when discharge in the creek reached a preset threshold. The autosampler was equipped with seven 9-liter (L) polyethylene carboys lined with polytetrafluoroethylene (PTFE) (Teflon® DuPont) bags. For each stream, the discrete samples were combined into a rising-limb flow-weighted composite and a falling-limb flow-weighted composite. For smaller storms, resulting in flow in one or two of the streams, grab samples were collected. At the groundwater sites, the well was purged until water temperature, dissolved oxygen, pH, and specific conductance stabilized (Wilde, variously dated). Samples were collected after the purging was completed. Samples were collected directly from the well discharge and did not undergo any treatment (filtration, chlorination, and so on) prior to collection. Samples from Barton Springs were collected by immersing bottles below the water surface into or near the spring orifice, avoiding contact with the atmosphere and standing surface water. Reusable bottles, bags, and sampling equipment were cleaned with Liquinox soap, hydrochloric acid, methanol, and deionized water prior to use (Wilde, 2004).

All samples were stored on ice in coolers following collection and during transport to the Lower Colorado River Authority (LCRA) laboratory and to the USGS Texas Water Science Center. At the LCRA laboratory, samples were analyzed for *E. coli*. At the Center, samples were filtered, dispensed into shipping bottles, and preserved as required for the various analyses (table 3). Samples for analysis of nutrients and major ions were maintained at 4 degrees Celsius (°C) or less and shipped to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., for analysis. Samples for analysis of SSC were shipped to the USGS Kentucky Water Science Center Sediment Laboratory in Louisville, Ken. Physicochemical properties (specific conductance, turbidity, water temperature, pH, and dissolved oxygen) were measured at Barton Springs (USGS station number 08155500) at 15-minute intervals by using a multiparameter water-quality monitor installed in the orifice. Data collected at Barton Springs are available in real time on the USGS Web site (http://waterdata.usgs.gov/tx/nwis/uv/?site_no=08155500).

Analytical Methods

Alkalinity titrations were done at the USGS Texas Water Science Center. Alkalinity was determined by titration of 50 milliliters (mL) of filtered sample with 1.6-normal sulfuric acid to a pH of less than 4.0 and computed by using the inflection point method (Rounds, 2006). All samples had negligible hydroxide and carbonate concentrations; thus, these ions were not considered in this report. Suspended-sediment concentrations were measured by the USGS Kentucky Water Science Center Sediment Laboratory by using procedures described in Guy (1969) and Mathes and others (1992). *E. coli* was analyzed at the LCRA laboratory in Austin, Tex. The bacterium was analyzed as the most probable number per 100 milliliters (MPN/100 mL) by using the Colilert method (Standard Methods 9223-B) (American Public Health Association, 2005), a chromogenic coliform substrate test. Samples with more than a 6-hour hold time were reported as qualified. When transport conditions necessitated delays in delivery longer than 6 hours, the hold time was extended and the samples processed within 48 hours. Analyses of major ions (except bicarbonate) and nutrients were done by the NWQL by using published USGS analytical methods. Concentrations of major dissolved cations were measured by using inductively coupled plasma-mass spectrometry (ICP/MS), and concentrations of anions (except bicarbonate) were measured by using ion-exchange chromatography (Fishman, 1993). Nitrate plus nitrite (NO_3+NO_2) and nitrite (NO_2) were reported by the NWQL. Organic N plus ammonia (org N+NH_3) was measured by a Kjeldahl digestion method and an automated photometric finish (Patton and Truitt, 2000), and total P was measured by a Kjeldahl digestion method and an automated colorimetric finish (Patton and Truitt, 1992). Quantifiable concentrations less than the laboratory reporting level (LRL) were flagged as estimated by the NWQL and are considered herein at the estimated level. All N species concentrations are reported and discussed as N, and all P species concentrations are reported and discussed as P.

Streamflow Measurement and Stream Recharge Estimation

Streamflow is the volume of water passing an established reference point in a stream at a given time. Methods used to determine streamflow (discharge) are described in Buchanan and Somers (1969). Stage, or gage height, was measured every 15 minutes by using submersible pressure transducers to the nearest 0.01 foot at the surface-water sampling sites. A stage-discharge relation has been developed by the USGS for these sites on the basis of streamflow measurements and the stage of the stream at the time of measurement (Kennedy, 1984). These unique relations are used to compute a continuous record of streamflow (Kennedy, 1983) from the stage recorded at each site. Continuous measurements of stream discharge are available for the sampling sites on the USGS National Water Information System (NWIS) website (U.S. Geological Survey, 2011).

Recharge, as estimated for this report, was computed as the sum of the streamflows measured at gaging stations near the upstream end of the recharge zone for the five major recharging streams (fig. 1), up to the maximum rate (R_{max}) for each stream as determined by Barrett and Charbeneau (1996). Barrett and Charbeneau (1996) demonstrated that discharge exceeding R_{max} for each stream passes across the recharge zone without recharging the aquifer. This approach was used for Onion, Slaughter, Bear, and Williamson Creeks. For Barton Creek, the algorithm of Barrett and Charbeneau (1996) developed for R_{max} was used; this algorithm uses a third-order polynomial to relate the discharge to recharge. Use of this algorithm is necessary because Barton Creek can be either a gaining or a losing stream depending on aquifer flow conditions. Recharge estimates were computed as daily mean values, except for the three major storms, for which mean recharge estimations were calculated for the rising and falling limbs by using 15-minute values of discharge. This estimate does not include recharge that originates as precipitation over the recharge zone and flows as storm runoff into the streams along the reaches over the recharge zone and, thus, underestimates recharge resulting from storms. Additionally, recharge computed on the basis of streamflow does not account for other possible recharge sources, such as upland or interstream recharge, which is the recharge occurring over the recharge zone in the areas between the channels of the five creeks. This recharge occurs through internal drainage sinkholes or as diffuse recharge through soils and has been estimated to contribute from 15 percent of total recharge (Slade and others, 1986) to 27–36 percent of total recharge (Hauwert, 2009); it occurs during and shortly after rain events when humidity is high and evapotranspiration is low (Hauwert, 2009). Recharge from other sources such as leaking municipal water-supply pipes and cross-formation flow from adjacent hydrostratigraphic units also are not included in the recharge estimate.

Recharge from Barton Creek might have been overestimated during the first months of the study when flow was very low. Dye traces have demonstrated that flow infiltrating through Barton Creek upstream from where it is traversed by Loop 1 (fig. 1) does not discharge from Barton Springs but rather at a spring system that is isolated from the Barton Springs segment (Barton Springs/Edwards Aquifer Conservation District, 2003). The dye traces also demonstrated that flow infiltrating through Barton Creek downstream from Loop 1 discharges from Barton Springs. When discharge at the Barton Creek stream site (USGS station number 08155240) is less than 15 ft^3/s, all creek flow infiltrates before it reaches Loop 1 and likely contributes little or no flow to Barton Springs discharge. As a result, the recharge relation for Barton Creek, which was developed for Barton Creek prior to the dye traces and used in the estimate of total recharge in this report, likely overestimates the contribution from Barton Creek to aquifer recharge and, correspondingly, to Barton Springs discharge, particularly during low-flow conditions.

Load Estimation and Geochemical Numerical Models

Two models, LOADEST and PHREEQC, were used in this investigation. LOADEST (Runkel and others, 2004) was used to estimate mean monthly loads of org N+NH_3 and NO_3+NO_2 in streams and in Barton Springs, and PHREEQC (Parkhurst and Appelo, 1999) was used to calculate equilibrium concentrations of chemical species in solution and to simulate reactions and processes occurring in the aquifer.

LOADEST uses a time series of streamflow and measured constituent concentrations to develop a regression model for the estimation of constituent load. LOADEST is not a watershed-scale model, and it does not infer processes affecting loads or evaluate sources of water-quality impairment. For this investigation, the adjusted maximum likelihood estimation (AMLE) method was chosen from the three estimation methods offered in LOADEST because the constituent concentrations included censored data; the AMLE eliminates the first-order bias usually exhibited by model coefficients when the data are censored (Runkel and others, 2004). A simple regression model with a single explanatory variable, log streamflow, was used. Concentrations of NO_3+NO_2 measured in routine and storm samples and estimated rates of recharge for each stream and of discharge for Barton Springs were used for model calibration. Recharge rates for streams were estimated as described in the section “Streamflow Measurement and Stream Recharge Estimation.” An average daily load was calculated for each month for the entire sampling period. The total load in recharge was estimated as the sum of the loads for Barton, Williamson, Slaughter, and Bear, and Onion Creeks; it does not include any load contributed from Little Bear Creek.

PHREEQC was used to calculate cation-anion charge balances, for speciation modeling, and for inverse modeling. Charge balance, a comparison of the sum of positive and negative charges in a water sample, provides an independent assessment of the accuracy of major-ion analysis. Differences of up to +/-5 percent are generally accepted as reasonably accurate within analytical uncertainties (Appelo and Postma, 2005). Speciation modeling determines the potential for mineral dissolution or precipitation to occur in natural waters by calculating the saturation index (SI) for specified minerals and phases. The precipitation or dissolution of mineral phases can be an important control on fluid composition. In a carbonate aquifer, such as the Barton Springs segment, the dissolution or precipitation of minerals such as calcite and dolomite, which comprise the aquifer rocks, will add or remove carbonate constituents (calcium, magnesium, strontium, and bicarbonate). The dissolution or precipitation of common trace minerals in carbonate rocks, such as celestite or gypsum, can also influence fluid composition. SI values were calculated for aragonite, calcite, celestite, chalcedony, dolomite, fluorite, gypsum, quartz, and strontianite, and for carbon dioxide and dissolved oxygen gas phases. An SI value of 0 indicates equilibrium conditions, a value greater than 0 indicates saturation with respect to a phase and the potential for precipitation, and a value less than 0 indicates undersaturation with respect to a phase and the potential for dissolution.

Inverse modeling accounts for the chemical evolution in observed water compositions by (1) identifying geochemical reactions and associated mass transfers of specified sources and sinks of major dissolved constituents and (2) quantifying mixing proportions. For this investigation, inverse modeling was used to approximate mixing proportions of selected endmember water compositions and plausible geochemical reactions along a hypothetical flow path. An initial water composition was allowed to mix with saline-zone groundwater and matrix groundwater. A final water composition was designated. Reactions along the flow path with selected mineral and gas phases were allowed, and results were constrained by the concentrations of selected major ions (calcium, magnesium, strontium, sodium, potassium, chloride, and sulfate) and alkalinity. All models contained phases for calcite, celestite, dolomite, gypsum, quartz, carbon dioxide, dissolved oxygen, and for calcium and sodium cation exchange. Celestite, dolomite, and gypsum phases were constrained to allow for only dissolution reactions (no precipitation). Dissolved oxygen was constrained to allow for only precipitation reactions; that is, loss or consumption of dissolved oxygen. Resulting mixing-reaction models are valid within the constraints of available thermodynamic data.

Statistical Methods

Nonparametric statistical tests were used for data interpretation. A nonnormal distribution is a common characteristic of water-resources data, and nonparametric tests usually are better suited to evaluate water-resources data than are traditional parametric methods, which require a normal distribution (Helsel and Hirsch, 2002). The Kendall's tau coefficient is a nonparametric, rank-based test used to measure the strength of the monotonic relation between x and y (linear and nonlinear) and is resistant to the effects of outliers (Helsel and Hirsch, 2002). The tau coefficient ranges from -1 to 1; a value of 0 indicates no correlation, and values approaching -1 or 1 indicate an increasing strength of negative or positive correlation, respectively. The tau coefficient values generally will be lower than values of traditional correlation coefficients for linear associations of the same strength; for example, a strong linear correlation of greater than or equal to 0.9 corresponds to a tau value of greater than or equal to about 0.7 (Helsel and Hirsch, 2002). Kendall's tau was used in this investigation to test the significance of correlations. The Mann–Whitney U test, a nonparametric test for comparing two independent groups of data, was used to test for differences between populations. For all tests reported here, statistical results with p-values less than 0.05 ($p < 0.05$) are considered statistically significant and are reported.

Climatic and Hydrologic Conditions During the Period of the Study

Central Texas is prone to climatic and hydrologic extremes (Griffiths and Strauss, 1985; Jones, 1991), and droughts lasting from many months to years have been documented in the region since the earliest settlers began keeping records (Texas State Historical Association, 2009). Climatic and hydrologic conditions during the period of the study covered a large range: from exceptional drought conditions (as defined by the U.S. Drought Monitor [2011]) to wetter-than-normal conditions. The U.S. Drought Monitor—a product of the U.S. Department of Agriculture, the National Oceanic and Atmospheric Administration, and the National Drought Mitigation Center—integrates meteorological, agricultural, and hydrological drought indices (National Weather Service, 2008). In south-central Texas, the range of hydrologic conditions varied from drought conditions (characterized by sustained low amounts of precipitation, surface-water flow, and Barton Springs discharge) to wetter-than-normal conditions with regularly occurring rainfall, continuous surface-water flow, and above-average Barton Springs discharge (for example, fig. 2; table 2). When sampling began in November 2008, 6 months of dry conditions had already occurred, during which discharge from Barton Springs had decreased from 110 to 19 ft^3/s. Dry conditions persisted until early September 2009. Between November 1, 2008, and September 9, 2009 (the dry period), spring discharge ranged from 13 to 29 ft^3/s, and there was sustained low flow in only Barton Creek and, to a lesser extent, Bear Creek. The infrequent rainfall that did occur resulted in ephemeral flow in only one or two of the five streams. When possible, composite or grab samples of ephemeral flow were collected between November 1, 2008, and September 9, 2009. Beginning September 10, 2009, storms occurred more frequently, and 32 inches of rain fell between September 10, 2009, and March 31, 2010 (the wet period) (Lower Colorado River Authority, 2010). The total of 32 inches of rain during the wet period is an areally weighted mean based on Lower Colorado River Authority rainfall data collected in the study area at LCRA site numbers 4517, 4519, 4593, 4594, 4595, and 4596 (Lower Colorado River Authority, 2010).

Between September 2009 and March 2010, samples were collected from streams and from Barton Springs following three storms of sufficient magnitude to result in flow in three or more of the five recharging streams (major storms): storm 1 (September 10–12, 2009), storm 2 (November 8, 2009), and storm 3 (January 14–15, 2010) (table 4). The largest amount of rainfall occurred during storm 1, but the largest response in stream discharge occurred in response to storm 3.

Stream recharge estimates indicate that the amount of recharge from each stream varied through the period of the investigation, and for each stream was markedly higher during the wet period than during the dry period (fig. 3*A*). During the dry period, the small amount of estimated stream recharge was predominately from Barton Creek, with some recharge contributed by Bear and Williamson Creeks (fig. 3*B*). In contrast, during the wet period, Onion Creek contributed the largest amount to total estimated stream recharge. The contribution to total estimated stream recharge during the wet period decreased from Onion Creek (40 percent), to Barton Creek (30 percent), to Bear Creek (20 percent), to Slaughter Creek (7 percent), to Williamson Creek (3 percent). Barton and Onion Creeks dominated estimated stream recharge contributions throughout the wet period (fig. 3*B*), but the proportional contribution from Onion Creek increased during the wet period while that from Barton Creek decreased (fig. 3*B*).

The three major storms evaluated for this investigation varied in size, antecedent moisture conditions, and resulting stream and spring discharge response (fig. 4*A*–*C*; table 4). Storm 1 occurred following the driest antecedent moisture conditions, had the greatest rainfall amount, was accompanied by the smallest discharge response in the streams, and resulted in the largest discharge response at Barton Springs. Only Bear and Williamson Creeks had flow at the sampling sites in response to storm 1. Storm 2 occurred following the wettest antecedent moisture conditions, had the smallest rainfall amount, and resulted in the smallest discharge response at Barton Springs. Storm 3 was intermediate with respect to antecedent moisture conditions, rainfall amount, and discharge response at Barton Springs, but resulted in the largest discharge response in the streams. Runoff from storms 2 and 3 resulted in flow at all stream sampling sites. The estimated proportion of recharge by stream varied for each of the three storms. Stream recharge in response to storms 1, 2 and 3 was predominately from Bear Creek, Barton Creek, and Onion Creek, respectively (fig. 5). A minor storm in March 2009 resulted in small increases in flow at Barton, Williamson, and Bear Creeks (fig. 4*D*; table 4). Flow was sufficient to trigger the autosampler at the Barton Creek site, but a subsequent malfunction prevented sample collection. Grab samples were collected at Williamson and Bear Creeks following a second small rain that resulted in increased flow (fig. 4*D*).

Water Quality of the Barton Springs Segment of the Edwards Aquifer and Its Contributing Zone (November 2008–March 2010)

Stream and spring discharge, physicochemical properties, concentrations of major ions, nutrients, and suspended sediment, and bacterial densities were measured at the five stream sites, two groundwater wells, and Barton Springs from November 2008 to March 2010. Samples were collected over a range of hydrologic conditions (fig. 2). Geochemical responses to climatic changes were investigated by analysis of samples collected at routine intervals (every 3 or 4 weeks) at each site. Geochemical responses to storms were investigated by analysis of samples collected directly following storms. Of particular interest for this investigation were differences in geochemistry between stream, groundwater (well), and spring sites; the influence of aquifer flow conditions, recharge, mixing, and dilution on geochemistry; and the factors that influence fate and transport of nutrients and bacteria.

Continuous Discharge and Physicochemical Measurements at Barton Springs

Continuous measurements of discharge and physicochemical properties (water temperature, dissolved oxygen, specific conductance, and turbidity) were recorded at Barton Springs at 15-minute intervals (fig. 6). These Barton Springs data, available from the USGS NWIS website at http://waterdata.usgs.gov/tx/nwis/uv/?site_no=08155500, are used as interpretative aids throughout this report. During the dry period, temperature and dissolved oxygen remained relatively constant, but small variations in discharge and larger variations in specific conductance occurred in response to small amounts of rainfall, and turbidity was low and constant with the exception of responses to rains. During the wet period, temperature decreased and concentrations of dissolved oxygen increased as discharge increased; variations in specific conductance in response to rain were similar in magnitude to those during the dry period, but variations in turbidity were more marked. Discharge, concentrations of dissolved oxygen, and turbidity were lower during the dry period than during the wet period, and temperature and specific conductance were higher; the differences were statistically significant. Summary statistics for discharge and physicochemical properties from surface water (streams), groundwater (wells), and Barton Springs are shown in table 5.

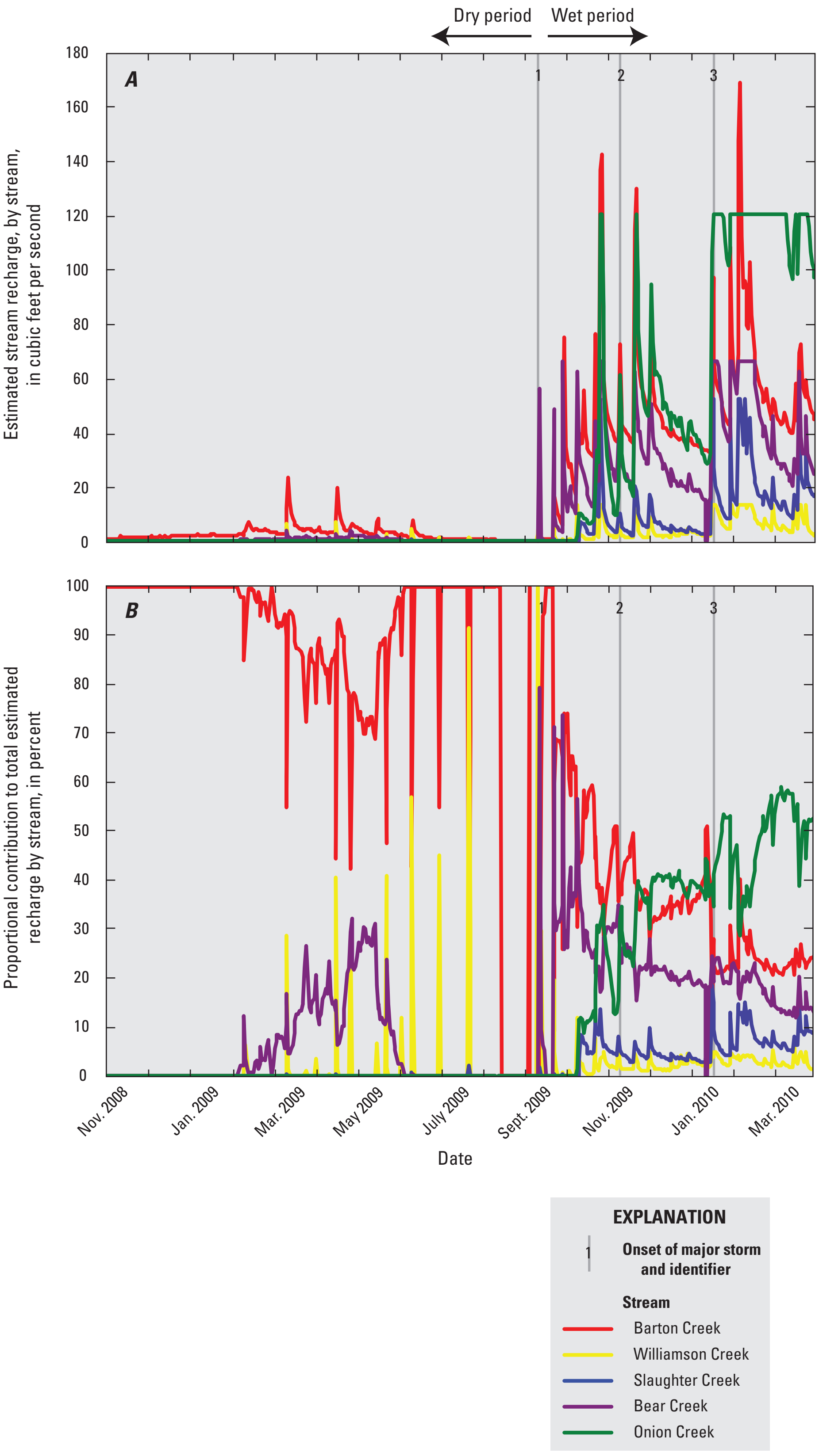


Figure 3. Time series of estimated stream recharge to the Barton Springs segment, by stream, for the five major streams recharging Barton Springs, Austin, Tex. (November 2008–March 2010). *A*, Recharge rate. *B*, Proportion of total recharge volume.

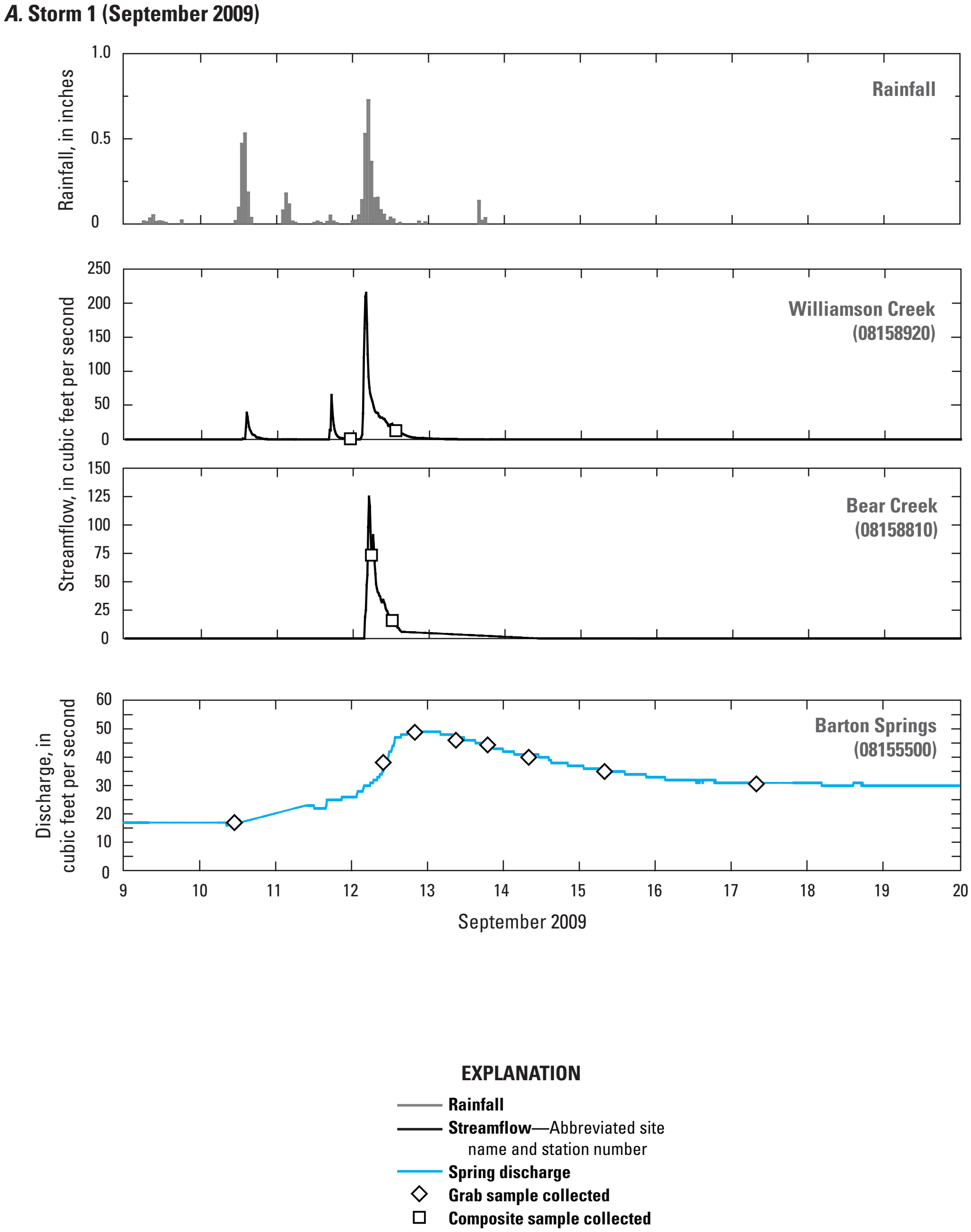


Figure 4. Rainfall hyetograph (Lower Colorado River Authority, 2010; areally weighted means for sites 4517, 4519, 4593, 4594, 4595, and 4596), hydrographs for recharging streams, and timing of collection of stream samples (start of autosampler for rising and falling storm limbs) and Barton Springs (grab) samples for storms in the Barton Springs zone, south-central Texas, 2009–10. *A*, Storm 1 (September 2009). *B*, Storm 2 (November 2009). *C*, Storm 3 (January 2010). *D*, A minor storm (March 2009).

B. Storm 2 (November 2009)

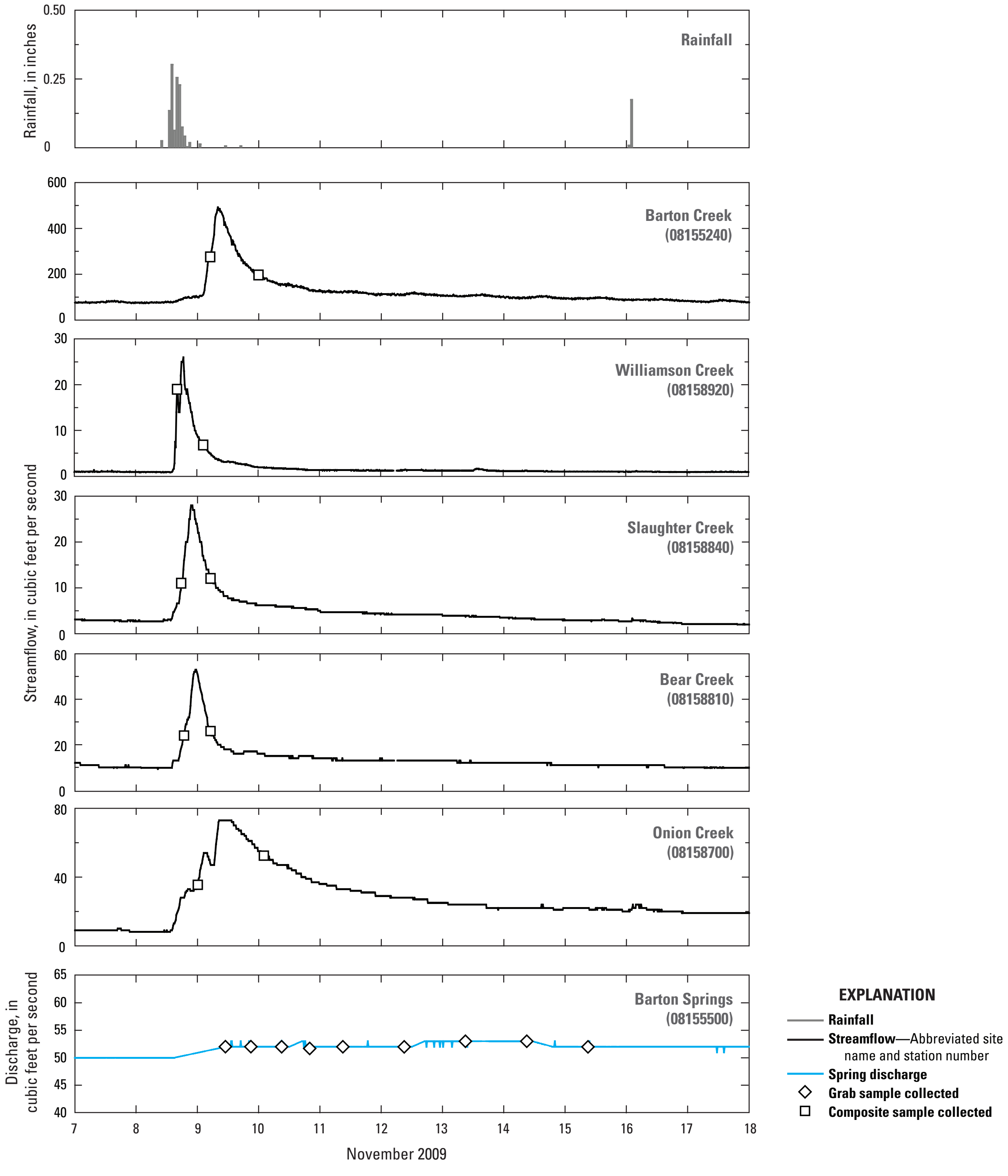


Figure 4. Rainfall hyetograph (Lower Colorado River Authority, 2010; areally weighted means for sites 4517, 4519, 4593, 4594, 4595, and 4596), hydrographs for recharging streams, and timing of collection of stream samples (start of autosampler for rising and falling storm limbs) and Barton Springs (grab) samples for storms in the Barton Springs zone, south-central Texas, 2009–10. *A*, Storm 1 (September 2009). *B*, Storm 2 (November 2009). *C*, Storm 3 (January 2010). *D*, A minor storm (March 2009). —Continued.

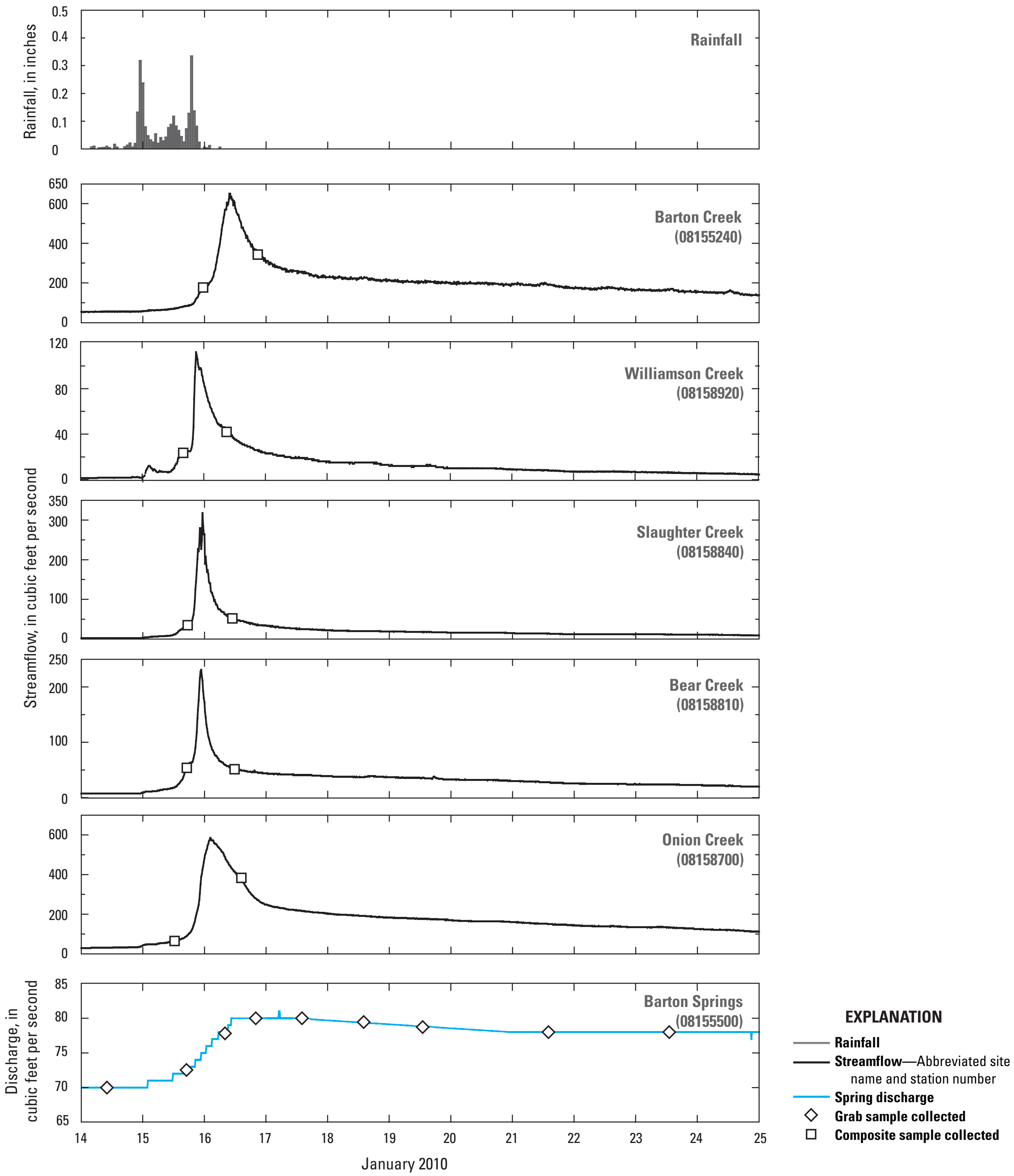
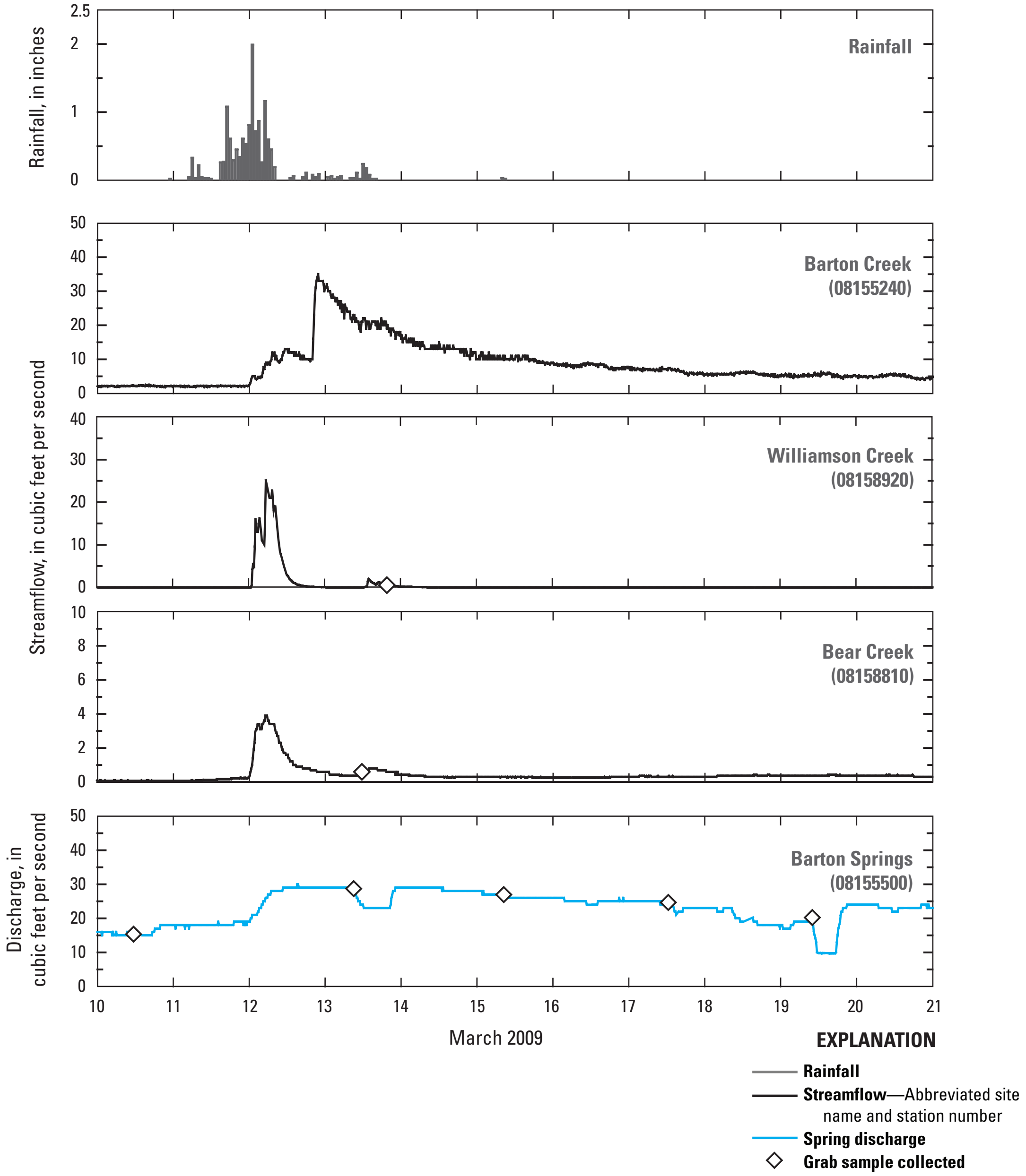

***C.* Storm 3 (January 2010)**

Figure 4. Rainfall hyetograph (Lower Colorado River Authority, 2010; areally weighted means for sites 4517, 4519, 4593, 4594, 4595, and 4596), hydrographs for recharging streams, and timing of collection of stream samples (start of autosampler for rising and falling storm limbs) and Barton Springs (grab) samples for storms in the Barton Springs zone, south-central Texas, 2009–10. *A*, Storm 1 (September 2009). *B*, Storm 2 (November 2009). *C*, Storm 3 (January 2010). *D*, A minor storm (March 2009). —Continued.



D. Minor storm (March 2009)

Figure 4. Rainfall hyetograph (Lower Colorado River Authority, 2010; areally weighted means for sites 4517, 4519, 4593, 4594, 4595, and 4596), hydrographs for recharging streams, and timing of collection of stream samples (start of autosampler for rising and falling storm limbs) and Barton Springs (grab) samples for storms in the Barton Springs zone, south-central Texas, 2009–10. *A*, Storm 1 (September 2009). *B*, Storm 2 (November 2009). *C*, Storm 3 (January 2010). *D*, A minor storm (March 2009). —Continued.

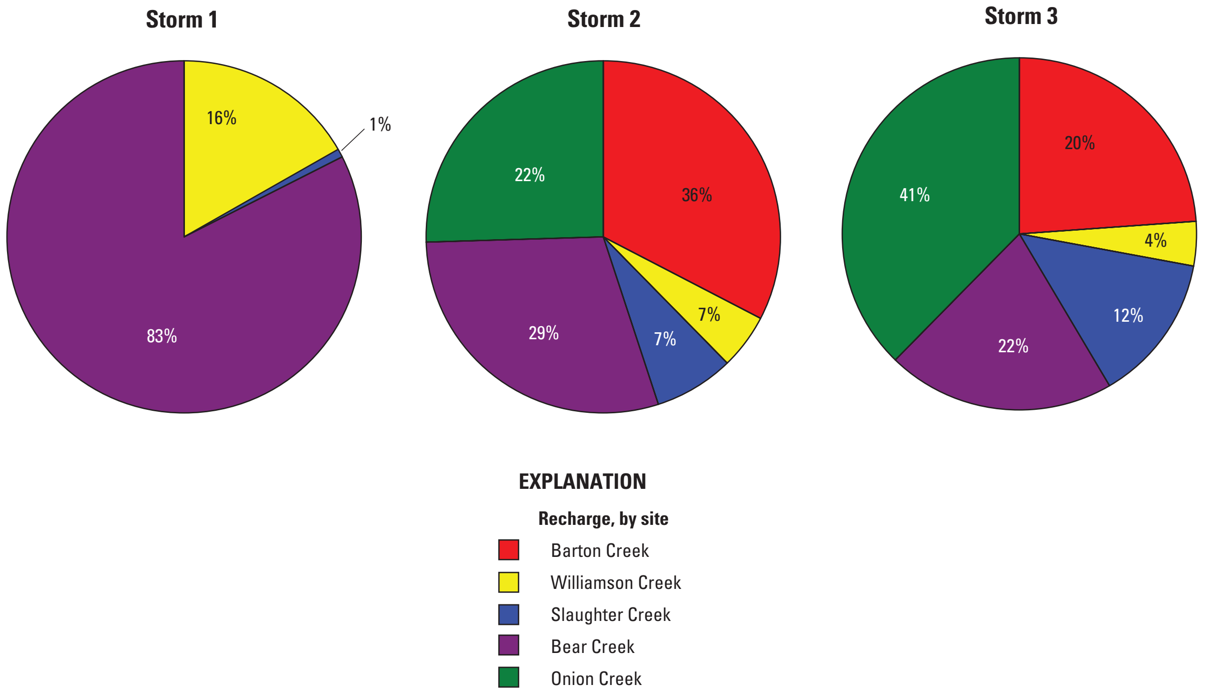


Figure 5. Estimated proportion, in percent, of total stream recharge contributed by Barton, Williamson, Slaughter, Bear, and Onion Creeks for storm 1 (September 2009), storm 2 (November 2009), and storm 3 (January 2010) in the Barton Springs zone, south-central Texas.

Physicochemical properties were measured at the streams and wells when routine samples were collected (table 5) and varied between the dry and wet periods and among site types. Median values for specific conductance were higher in the streams and in Barton Springs than in the groundwater at the two wells for all hydrologic conditions. Median specific conductance values in the streams and in Barton Springs were similar to each other during both dry and wet periods but were higher during the dry period than during the wet period. During the dry period, median values of dissolved oxygen in the streams and Barton Springs discharge were similar and were lower than those in groundwater. During the wet period, median dissolved oxygen values in the streams and Barton Springs discharge were similar but were higher than during the dry period and were higher than those in the groundwater at the two wells (table 5). Median turbidity values were low (< 2.5 formazin nephelometric units [FNU]) at all sampling sites during both dry and wet periods but increased in the streams and in Barton Springs discharge during the wet period (table 5). Surface-water temperature was higher during the dry period than during the wet period, reflecting seasonal differences of surface air temperature.

Geochemical Responses to Climatic Changes

Concentrations of major ions, nutrients, and suspended sediment (SSC) and densities of bacteria were measured at the five stream sites, the two groundwater wells, and Barton Springs in routine samples collected during November 2008–March 2010 (fig. 2). Geochemical changes during this period reflect a transition from exceptional drought to wetter-than-normal conditions.

Major Ion Geochemistry

Surface Water

Evaluation of the effect of the climatic transition on geochemistry of the streams is complicated by the fact that, during the dry period, Barton and Bear Creeks were the only streams with some sustained flow. A golf course upstream from the sampling site on Barton Creek is irrigated with treated wastewater (Chris Herrington, City of Austin, oral commun., 2010); return flow from this irrigation might have been the source of much of the low but sustained flow in Barton Creek through most of the dry period. Through the dry period, concentrations of calcium and sulfate decreased slightly at Barton Creek and more markedly at Bear Creek; concentrations of sodium, chloride, bromide, and boron at Barton Creek increased during the second part of the dry period (during which time there was no flow at Bear Creek) (fig. 7). Comparison of constituent concentrations measured in routine samples between the wet and dry periods is limited to Barton and Bear Creek because of the small number of samples collected during the dry period.

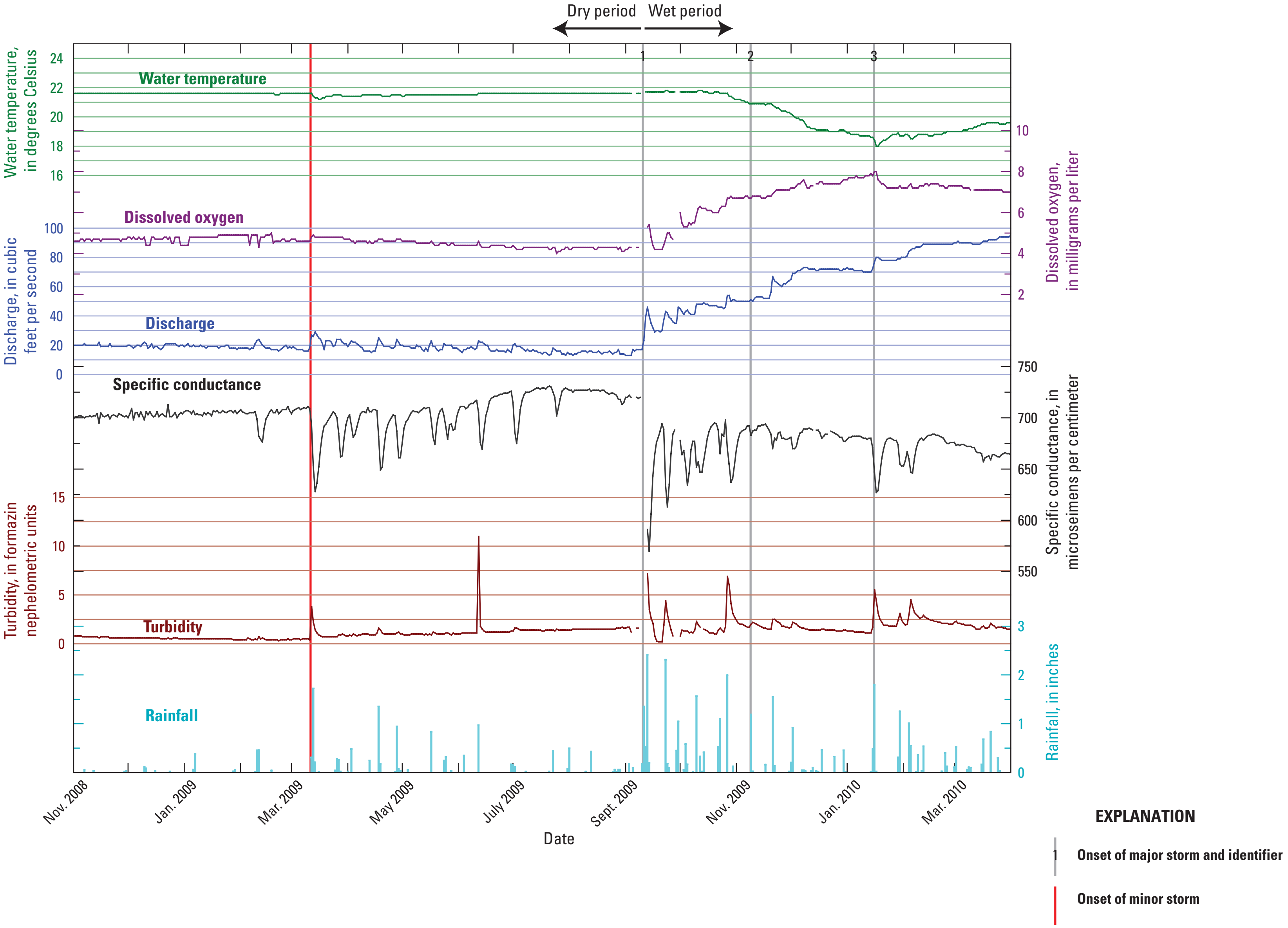


Figure 6. Time series (November 2008–March 2010) of water temperature, dissolved oxygen concentration, discharge, specific conductance, and turbidity at Barton Springs (daily means for U.S. Geological Survey station no. 08155500 Barton Springs at Austin, Tex.), and rainfall (Lower Colorado River Authority, 2010; areally weighted daily means for sites 4517, 4519, 4593, 4594, 4595, and 4596) in the Barton Springs zone, south-central Texas.

Table 4. Characteristics of storms sampled, antecedent moisture conditions, and system response in the Barton Springs zone, south-central Texas (2009–10).

[ft³/s, cubic feet per second]

Storm description				Antecedent moisture conditions[1]		System discharge response	
Storm	Date	Total (inches)	Temporal distribution	Rainfall in prior 3 months (inches)[1]	Days since last storm[1]	Barton Springs (ft³/s)	Stream (ft³/s)
Minor	March 11, 2009	2.30	1.9 inches (83 percent of total rainfall) fell from 1500 on March 11 to 0800 on March 12.	1.58	318	18–30	Barton: 2–33; Bear: 0.2–4; Williamson 0–25
1	September 10–12, 2009	4.66	80 percent of total rainfall fell in two episodes: 1.34 inches (29 percent of total rainfall) between 1000 and 1700 on Sept. 10 and 2.39 inches (51 percent) between 0000 and 1700 on Sept. 12.	3.42	500	13–50	Bear: 0–125; Williamson 0–215
2	November 8, 2009	1.36	1.12 inches (82 percent of total rainfall) fell between 1300 and 2100 on Nov. 8.	17.8	13	50–53	Barton: 77–485; Williamson: 1–26; Slaughter: 3–30; Bear: 10–53; Onion: 3–57
3	January 14–15, 2010	2.46	2.30 inches (94 percent of total rainfall) fell from 2200 on Jan. 14 to 2200 on Jan. 15.	9.98	43	70–84	Barton: 54–650; Bear: 10–231; Onion: 25–597; Slaughter: 2–318: Williamson: 1–112

[1] Rainfall data from Lower Colorado River Authority (2010) (sites 4517, 4519, 4593, 4594, 4595, and 4596).

At Barton and Bear Creeks, concentrations of carbonate constituents and sulfate measured in routine samples at Barton and Bear Creeks were similar during the dry and wet periods or slightly higher during the wet period than during the dry period (fig. 7). Concentrations of most noncarbonate constituents measured in routine samples were lower during the wet period than during the dry period (fig. 7). During the wet period, there were few consistent geochemical patterns among sites (fig. 7), with the exception of concentrations of boron, which decreased through the wet period similarly at all sites. Major, minor, and unsampled storm events occurred between routine sampling events, which likely affected the chemical composition of routine samples.

Groundwater

During the dry period, concentrations of most major ions in groundwater at the Buda and Marbridge wells were similar, with the exception of strontium and sulfate (fig. 8): Concentrations of strontium were 22 times higher and concentrations of sulfate in groundwater at the Buda well were 2 times higher than in groundwater at the Marbridge well. Concentrations of most major ions in groundwater at the Buda and Marbridge wells varied little during the dry period, with the exception of concentrations of calcium, which varied similarly at the wells, and bicarbonate, which was more variable at the Marbridge well than at the Buda well (fig. 8). During the wet period, concentrations of major ions at the Buda well were similar to those measured during the dry period. In contrast, concentrations of most major ions at the Marbridge well were different and more variable during the wet period than during the dry period. Concentrations of carbonate constituents (except calcium) in the Marbridge well decreased at the beginning of the wet period and remained at concentrations lower than those of the dry period; concentrations of sodium, chloride, and sulfate increased at the beginning of the wet period to maximum concentrations in December 2009 and January 2010 and then decreased back to near-initial concentrations. Initial changes in concentrations of carbonate constituents and sulfate at the Marbridge well preceded those in concentrations of sodium and chloride by one routine sampling period (about 3 weeks), and the timing of the occurrence of maximum and minimum concentrations of these constituents did not coincide (fig. 8), indicating contributions from multiple sources with different traveltimes or the influence of different geochemical processes.

Concentrations of some carbonate constituents (calcium and magnesium) measured in routine samples were similar

Table 5. Summary statistics for discharge and physicochemical properties from surface water (streams), groundwater (wells), and Barton Springs in the Barton Springs zone, south-central Texas, during dry and wet hydrologic conditions (November 2008–March 2010).

[--, not applicable; <, less than]

Discharge or physicochemical property	Hydrologic condition	Streams[1]			Wells[2]			Barton Springs[3]		
		Median	25th percentile	75th percentile	Median	25th percentile	75th percentile	Median	25th percentile	75th percentile
Discharge	Dry period[4]	0	0	0	--	--	--	18	16	20
	Wet period[5]	14	4	67	--	--	--	72	50	87
Temperature	Dry period[4]	21.4	17.1	21.6	21.9	21.6	22.0	21.6	21.5	21.6
	Wet period[5]	18.7	13.2	21.3	21.6	18.5	21.9	19.5	18.9	21.2
Dissolved oxygen	Dry period[4]	4.7	4.4	7.4	5.7	4.4	6.0	4.6	4.4	4.7
	Wet period[5]	7.6	6.7	10.2	5.8	4.7	7.0	7.2	6.7	7.4
Specific conductance	Dry period[4]	710	689	717	587	584	608	705	701	714
	Wet period[5]	666	606	707	606	590	608	678	665	684
Turbidity	Dry period[4]	1.1	<1	1.4	<1	<1	<1	.9	.6	1.2
	Wet period[5]	1.8	1.1	2.3	1.2	<1	1.7	1.7	1.4	2.1

[1] Stream discharge recorded at 15-minute intervals; physicochemical data measured at time of routine sample collection.

[2] Physicochemical properties for wells measured at time of routine sample collection.

[3] Data for Barton Springs are continuously measured at 15-minute intervals.

[4] Dry period: November 1, 2008, through September 9, 2009.

[5] Wet period: September 10, 2009, through March 31, 2010.

in surface water and groundwater, whereas others (bicarbonate and strontium) generally were higher in groundwater than in surface water. In contrast, concentrations of noncarbonate constituents, with the exception of fluoride, generally were higher in surface water than in groundwater (figs. 7 and 8). Specific conductance values were generally higher in routine samples (and some storm samples) of surface water than in routine samples of groundwater (fig. 9). Elevated specific conductance and noncarbonate constituent concentrations in surface water relative to groundwater might indicate a larger contribution from sources of noncarbonate constituents such as soils, municipal water leaking from pipes or used for landscape irrigation, treated wastewater effluent, septic leakage, and influxes of groundwater from the Trinity aquifer (Garner and Mahler, 2007). Following the onset of the wet period, concentrations of carbonate constituents, except calcium, were lower and noncarbonate constituents (except fluoride and boron) higher at the Marbridge well than at the Buda well (fig. 8). Overall, following the onset of the wet period, the geochemical composition of the groundwater at the Marbridge well became more similar to that of surface water, whereas that of groundwater at the Buda well did not change (figs. 7 and 8). This pattern is consistent with the hypothesis that the Marbridge well likely receives some conduit flow, whereas the Buda well likely receives mostly matrix flow.

Barton Springs

Temporal patterns in concentrations of major ions in routine samples collected from Barton Springs during the dry period were different from those during the wet period. During the latter part of the dry period, concentrations of carbonate and noncarbonate constituents, with the exception of calcium and bicarbonate, gradually increased. The gradual increase in concentrations of many of these constituents likely reflects an increasing contribution of groundwater from the saline zone as conditions became progressively drier and aquifer levels decreased, but the increase in concentrations might also reflect stream recharge (fig. 3*B*). Concentrations of many major ions decreased abruptly immediately following the onset of the wet

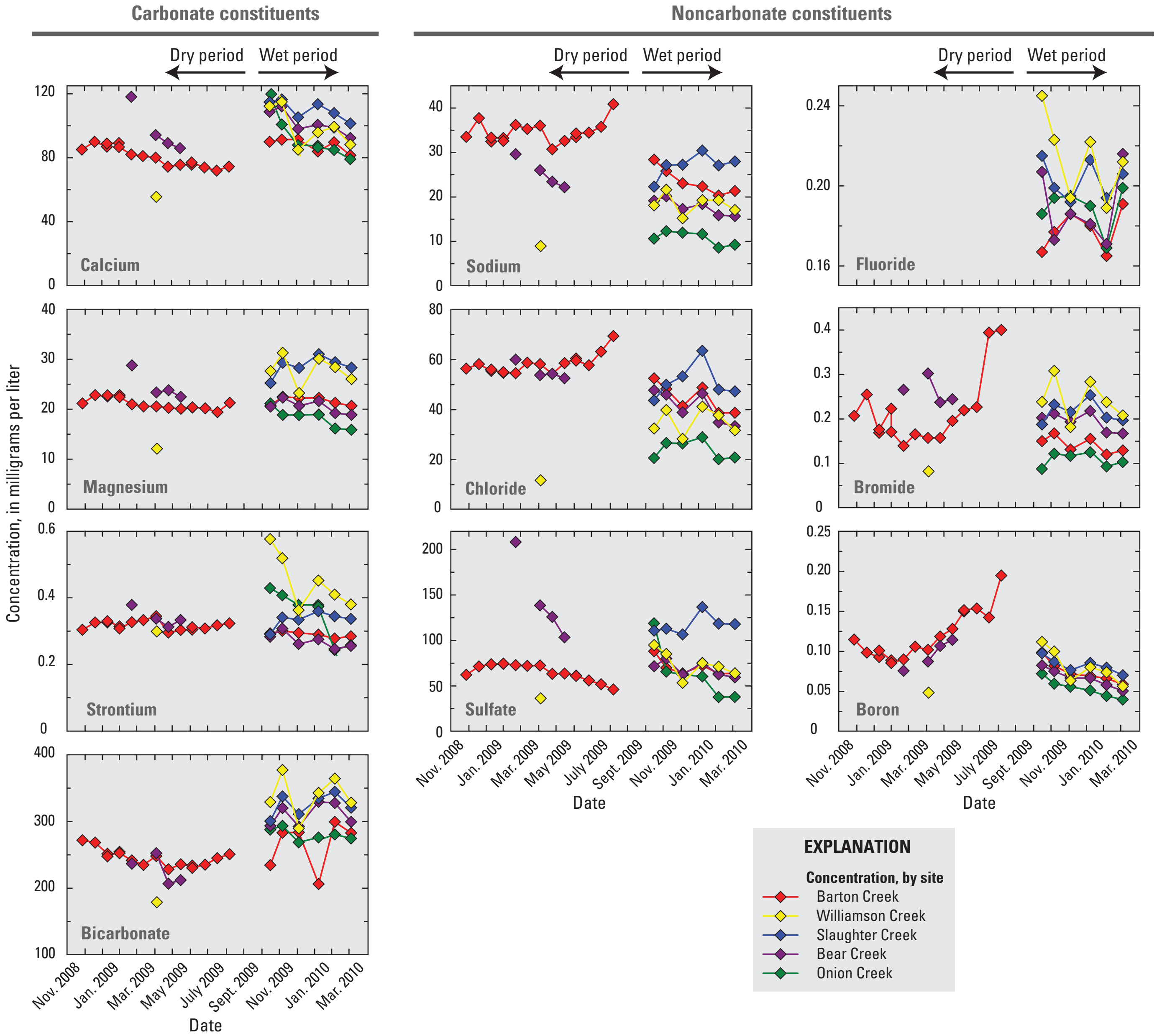


Figure 7. Time series of major-ion concentrations (carbonate and noncarbonate constituents) from the five stream sites during routine sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas.

period, likely reflecting dilution by recharging surface water, and then either decreased more gradually throughout the wet period or remained constant at, or slightly higher than, the lowest concentration (fig. 8). Concentrations of calcium and sulfate increased following the onset of the wet period and decreased during the second half of the wet period; the peak in concentrations of calcium preceded that in concentrations of sulfate by about 6 weeks. Overall, concentrations of most carbonate and noncarbonate constituents were lower during the wet period than during the dry period, with the exception of calcium and sulfate concentrations, which were higher, and bicarbonate concentrations, which were similar.

Concentrations of most major ions at Barton Springs were intermediate between concentrations at stream and groundwater sites during the dry period and became more similar to those at stream sites during the wet period (figs. 7 and 8). For example, after the onset of the wet period, concentrations of strontium and fluoride at Barton Springs decreased and concentrations of calcium and sulfate increased, becoming more similar to concentrations at all of the stream sites. These results are consistent with results of previous studies that have documented the influence of surface-water recharge from streams on water quality at Barton Springs whenever there is flow in the streams (Mahler and others, 2006, 2011; Mahler

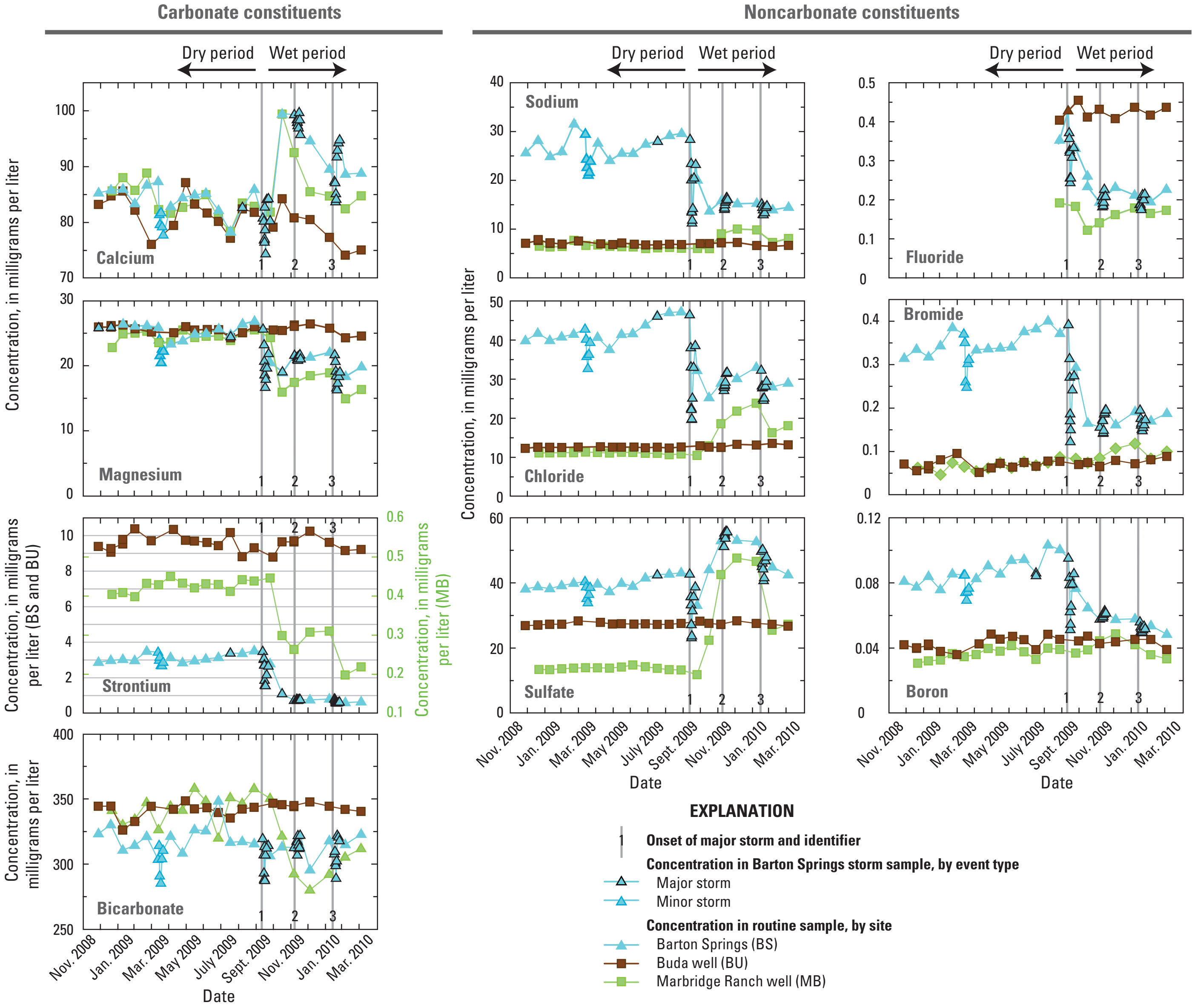


Figure 8. Time series of major-ion concentrations (carbonate and noncarbonate constituents) for the two groundwater (well) sites and Barton Springs during routine and storm (Barton Springs) sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas.

and Massei, 2007; Mahler and others, 2008; Mahler and Garner, 2009. Concentrations of magnesium, sodium, chloride, and bromide, however, decreased to concentrations lower than those measured at all of the stream sites except Onion Creek (figs. 7 and 8). This pattern indicates that, during the latter part of the wet period, the proportion of stream recharge contributed from Onion Creek was greater than that from the other streams and is consistent with recharge estimations (fig. 3*B*).

Nutrient Geochemistry

For this investigation, N species were measured in routine samples as org N+NH_3, NH_3, NO_3+NO_2, and NO_2 and are reported and discussed as mg/L as N. Phosphorus species were measured as total P, dissolved P, and orthoP and are reported and discussed as mg/L as P.

In the environment, Org N is converted to NH_3 and then to NO_2 or NO_3 through the process of nitrification in a matter of days under warm, moist conditions (van Handel and van der Lubbe, 2007). Org N+NH_3 are N species that have not yet been nitrified to NO_2 or NO_3 and thus represent either recent (within days) inputs of N or N that has been in conditions not conducive to nitrification (for example, dry or cold conditions). NH_3 was not detected at the LRL of 0.02 mg/L or was measured at an estimated concentration less than the LRL in all samples from all sites except for five samples

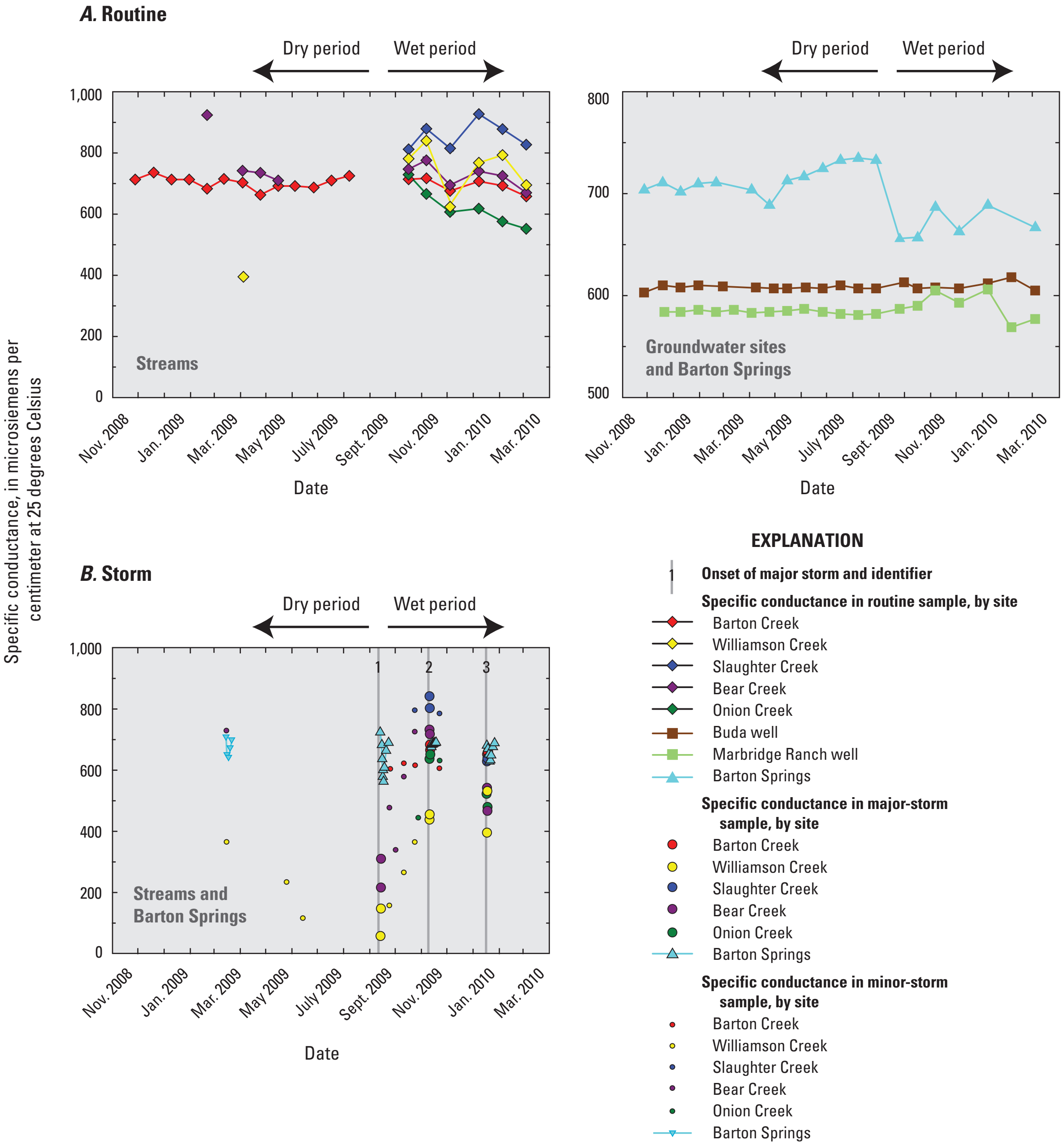


Figure 9. Time series of specific conductance values for samples from the five stream sites, the two groundwater (well) sites, and Barton Springs collected during *A*, routine, and *B*, storm sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas.

collected during the second part of the dry period at Barton Creek (May–August 2008) and one sample collected from the Marbridge well during the wet period (December 2009). Where NH_3 concentrations were reported, they constitute from 4 to 14 percent of org $N+NH_3$. Thus, org $N+NH_3$ consists mostly of organic N and is referred to throughout this section as "organic N." NO_3 and NO_2 are N species that have undergone nitrification. NO_2 is unstable in aerated water and generally constitutes a small fraction of dissolved N species (Dubrovsky and others, 2010). NO_2 either was measured at low concentrations (≤ 0.01 mg/L; for stream sites and two samples at the Buda well) or was not detected at the LRL of 0.002 mg/L (for Barton Springs and all groundwater samples except two noted above at the Buda well). Where NO_2 was detected, it constituted from 0.09 to 9 percent of NO_3+NO_2.

Phosphorus species were measured as total phosphorus, dissolved P, and orthoP and are reported and discussed here in mg/L as P. Total P and dissolved P either were not detected or were estimated at a concentration less than the LRL of 0.02 mg/L in all routine samples from all sites, and their concentrations in routine samples are not discussed further in this report. The LRL for orthoP was substantially lower (0.008 mg/L) compared to the LRL for total P, and orthoP was quantified in all but 13 of 111 routine samples. Median concentrations of orthoP in routine samples among stream sites (0.005 mg/L), groundwater sites (0.010 mg/L), and Barton Springs (0.013 mg/L) were significantly different (table 6).

Surface Water

Organic N was detected in all routine samples from streams. Organic N represented the majority of total N during the dry period (median of 79 percent) and a small fraction of total N during the wet period (median of 18 percent). Concentrations of organic N increased at the Barton Creek site through the dry period. Sustained flow in Barton Creek throughout most of the dry period is possibly attributable to irrigation with treated wastewater of a nearby golf course (Chris Herrington, City of Austin, oral commun., 2010). Treated wastewater is a potential source of organic N, as is the decay of biomass (Hem, 1992; Clark and Fritz, 1997). Organic N concentrations at all stream sites generally decreased through the wet period, interrupted by a slight increase in organic N at all stream sites in February 2010 coincident with a period of increased rain and stream discharge (fig. 10*A*). This temporal pattern is consistent with accumulation of organic N in soils during the dry period followed by leaching from soils during the wet period.

Nitrate plus nitrite was detected in every sample at every stream site with the exception of three samples collected at Bear Creek during the dry period (fig. 10*A*). During the dry period, concentrations of NO_3+NO_2 at those streams where samples could be collected (Barton, Williamson, and Bear Creeks) were low relative to concentrations at the same sites during the wet period and were lower than NO_3+NO_2 concentrations during the dry period at the groundwater and spring sites. During the dry period, concentrations of NO_3+NO_2 at Barton Creek peaked in April 2009 and then decreased into the summer months, whereas concentrations at Bear Creek were near or less than the LRL and varied little (only one sample could be collected from Williamson Creek during the dry period). During the wet period, concentrations of NO_3+NO_2 in Barton and Bear Creeks were elevated relative to the dry period; concentrations at Williamson, Slaughter, and Onion Creeks could not be compared between the dry and wet periods because of a lack of flow during the dry period. Concentrations of NO_3+NO_2 at all streams were consistently greater than the national background concentration for streams of 0.24 mg/L (Dubrovsky and others, 2010). The temporal pattern in NO_3+NO_2 concentration among the five creeks was similar, with maximum concentrations occurring in early November 2009 and February 2010 (fig. 10*A*), and coinciding with periods of high discharge. This pattern is similar to that for organic N, except that concentrations of NO_3+NO_2 in streams peaked about 1 month later than did concentrations of organic N. This response is consistent with leaching of N species loaded to and stored in soils during the dry period. Boron was included among the analytes measured for this investigation as a potential tracer of wastewater; however, there were no consistent correlations between boron and NO_3+NO_2 or organic N in samples from streams.

Concentrations of orthoP in routine samples collected from the streams were low (median concentration 0.005 mg/L [table 6]) and similar (fig. 10*A*) and were less than the national background concentration of 0.010 mg/L for streams (Dubrovsky and others, 2010), with the exception of one sample collected from Williamson Creek during the dry period (April 2, 2009). During the wet period, concentrations of orthoP in Barton and Bear Creeks were similar to those during the dry period; concentrations at Williamson, Slaughter, and Onion Creeks could not be compared because of a lack of flow during the dry period. There was no significant difference in orthoP concentrations among stream sites. Although transport of P in surface water generally is associated with suspended sediment (Litke, 1999), there were insufficient detections of total P (which includes the fraction associated with particulates) for evaluation of a statistical correlation between particulate-associated P (the difference between concentrations of P in filtered and unfiltered samples) and SSC in routine samples or in storm samples from stream sites. There were, however, sufficient detections in storm samples from Barton Springs to do this analysis. There was a positive correlation between particulate-associated P and SSC for storm 1 samples (Kendall's tau of 0.48), no significant correlation for storm 2 samples, and a negative correlation for storm 3 samples (Kendall's tau of -0.63). There thus was not conclusive evidence that suspended sediment transport is an important mechanism for transport of P through the aquifer.

Groundwater

In the samples collected from the two groundwater wells during the dry period, organic N was not detected or was detected at a concentration less than the LRL of 0.1 mg/L (fig. 10*B*). Following the onset of the wet period, organic N was detected at a concentration above the LRL in only one sample from a well (Buda well, October 14, 2009). At the Marbridge well, however, concentrations of organic N increased during the first part of the wet period, reaching a maximum in early November 2009, with a secondary peak in February 2010.

Concentrations of NO_3+NO_2 at the two groundwater wells during the dry period were similar, varied little, and were higher than those measured at the stream sites during the same period (fig. 10*A*, *B*). After the onset of the wet period, however, concentrations of NO_3+NO_2 at the wells followed different temporal patterns (fig. 10*B*). Nitrate plus nitrite concentrations at the Buda well varied little throughout the entire period of the investigation. At the Marbridge well, in contrast, concentrations of NO_3+NO_2 increased rapidly in October 2009 to a concentration about twice that measured

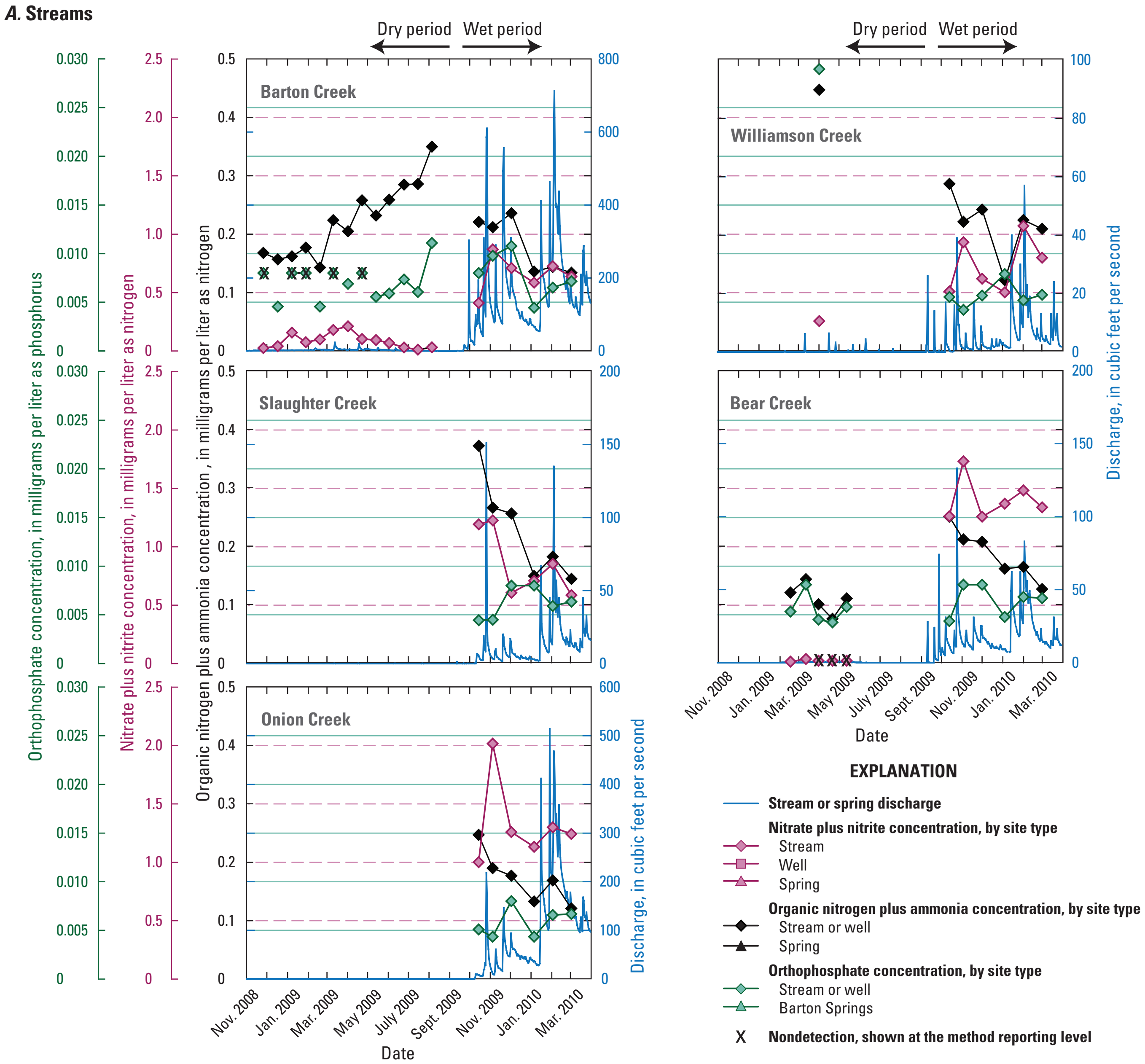


Figure 10. Time series of nutrient concentrations from *A*, the five stream sites, *B*, the two groundwater (well) sites, and *C*, Barton Springs during routine sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas.

in September 2009, decreased over the following 2 months to a concentration slightly higher than that measured during the dry period, and then increased slightly through the final 3 months of the investigation (January–March 2010) (fig. 10*B*). Concentrations of NO_3+NO_2 at both wells consistently exceeded the national background concentration for groundwater of 1.0 mg/L (Dubrovsky and others, 2010) during both the dry and wet periods.

Concentrations of ortho P at the two groundwater wells during the dry period generally were similar (fig. 10*B*), and concentrations were consistently less than the national background concentration of 0.030 mg/L (Dubrovsky and others, 2010). Concentrations of orthoP in routine samples from the wells were about twice those of routine samples from streams (table 6), indicating that the orthoP might have a geologic source. At the Marbridge well, however, concentrations of orthoP were more variable during the wet period than during the dry period and, relative to concentrations at the Buda well, decreased to a minimum (0.005 mg/L) in December 2009 before increasing again during the second part of the wet period. OrthoP generally followed the same temporal pattern as did NO_3+NO_2 at the Marbridge well (fig. 10*B*), indicating the effects of stream recharge containing lower concentrations of orthoP.

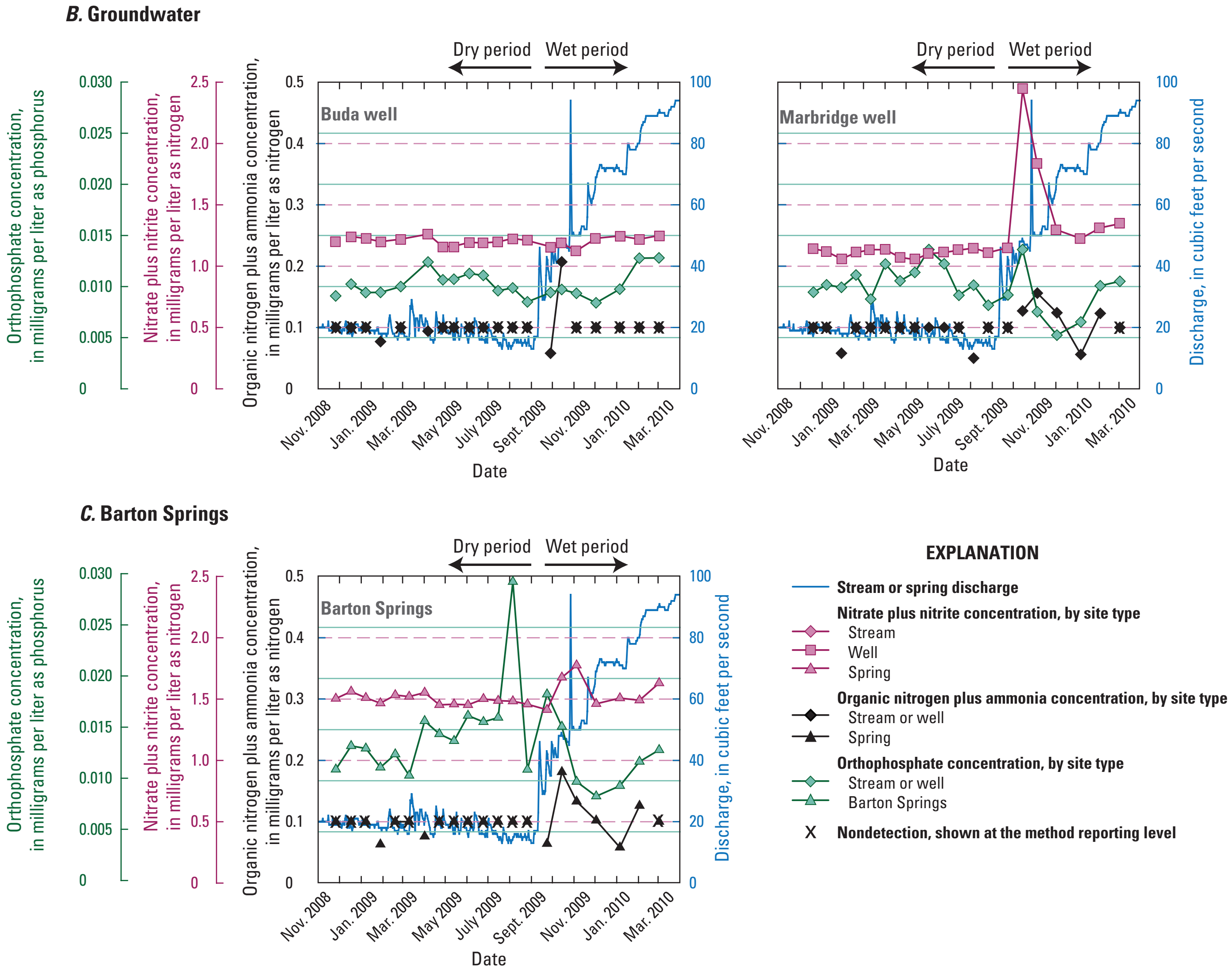


Figure 10. Time series of nutrient concentrations from *A*, the five stream sites, *B*, the two groundwater (well) sites, and *C*, Barton Springs during routine sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas. —Continued

Barton Springs

The temporal pattern of concentrations of organic N at Barton Springs was similar to that at the Marbridge well (fig. 10*B*, *C*). Organic N was not detected or was detected at a concentration less than the LRL throughout the dry period. Concentrations were more variable during the wet period and peaked in October 2009, 1 month earlier than peak concentrations at the Marbridge well, which might reflect a difference in traveltimes.

Concentrations of NO_3+NO_2 at Barton Springs varied little during the dry period and were higher than those at the streams and the wells (fig. 10). During the wet period, the temporal pattern in concentrations at Barton Springs was similar to that at the Marbridge well. Following the onset of the wet period in early September 2009, concentrations of NO_3+NO_2 increased in October and peaked in November 2009 at a concentration about 20 percent higher than that during the dry period, then decreased back to a concentration similar to that measured during the dry period, and then increased again slightly in March 2010. There thus was about a 1-month lag time between the peak concentrations in NO_3+NO_2 measured at the stream sites (October 2009 and February 2010) and those measured at Barton Springs (November 2009 and March 2010). Concentrations of NO_3+NO_2 at Barton Springs were consistently greater than the national background concentration for groundwater of 1.0 mg/L (Dubrovsky and others, 2010).

Concentrations of orthoP at Barton Springs were variable (fig. 10*C*) but consistently less than the national background concentration for groundwater of 0.030 mg/L (Dubrovsky and others, 2010), with the exception of one sample (0.029 mg/L on August 5, 2009). Concentrations of orthoP in routine samples from Barton Springs were slightly higher than those

Table 6. Summary statistics for nutrient species for routine and storm samples of surface water (streams), groundwater (wells), and Barton Springs in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[mg/L, milligram per liter; <, less than; NA, not applicable]

Constituent	Sampling condition	Streams			Wells			Barton Springs		
		Median [mg/L]	25th percentile [mg/L]	75th percentile [mg/L]	Median [mg/L]	25th percentile [mg/L]	75th percentile [mg/L]	Median [mg/L]	25th percentile [mg/L]	75th percentile [mg/L]
Organic nitrogen + ammonia	Routine	0.19	0.14	0.24	<0.1	<0.1	0.05	<0.1	<0.1	0.06
	All storms	.43	.29	.58	NA	NA	NA	.10	.08	.12
	Major storms	.39	.26	.58	NA	NA	NA	.11	.09	.13
	Minor storms	.46	.33	.69	NA	NA	NA	<.1	<.1	<.1
Nitrate + nitrite	Routine	.61	.09	1.13	1.19	1.13	1.23	1.50	1.46	1.53
	All storms	.66	.42	.89	NA	NA	NA	1.60	1.50	1.64
	Major storms	.84	.61	1.09	NA	NA	NA	1.61	1.54	1.64
	Minor storms	.46	.33	.67	NA	NA	NA	1.49	1.39	1.53
Total phosphate	Routine	<.02	<.02	<.02	<.02	<.02	<.02	.01	<.02	<.02
	All storms	.03	.01	.06	NA	NA	NA	<.02	<.02	<.02
	Major storms	.02	<.02	.05	NA	NA	NA	<.02	<.02	<.02
	Minor storms	.04	.01	.07	NA	NA	NA	<.02	<.02	<.02
Dissolved phosphate	Routine	<.02	<.02	<.02	<.02	<.02	.011	.011	<.02	.015
	All storms	<.02	<.02	.03	NA	NA	NA	<.02	<.02	.012
	Major storms	<.02	<.02	.03	NA	NA	NA	<.02	<.02	<.02
	Minor storms	<.02	<.02	.03	NA	NA	NA	<.02	<.02	<.02
Orthophosphate	Routine	.005	<.008	.006	.010	.009	.011	.013	.011	.016
	All storms	.006	.005	.021	NA	NA	NA	.013	.011	.016
	Major storms	.006	.005	.020	NA	NA	NA	.012	.011	.017
	Minor storms	.006	.005	.021	NA	NA	NA	.015	.014	.015

in routine samples from the wells and more than twice those in samples from the streams (table 6), indicating that a geologic source is likely. Variations in orthoP at Barton Springs were similar to those at the Marbridge well. Similarities in concentrations of organic N, NO_3+NO_2, and orthoP at Barton Springs and the Marbridge well during the wet period indicates that groundwater at both sites was affected by stream recharge.

OrthoP has been measured by the USGS at the five stream sites, the two groundwater (well) sites, and Barton Springs intermittently since 1990 (U.S. Geological Survey, 2007). Median concentrations of orthoP measured during this investigation, however, could not be compared to those measured during 1990–2008 because the median concentration measured during 1990–2008 at all sites except Williamson Creek was reported as less than the LRL, which varied from 0.01 to 0.02 mg/L. Because the median concentrations measured during this investigation are less than 0.02 mg/L, a statistical comparison with the data from 1990–2008 would not be meaningful.

Bacterial Densities and Suspended Sediment Geochemistry

Surface Water

For stream sites where samples could be collected during both the dry and wet period, densities of *E. coli* in routine samples were higher and more variable during the wet period than during the dry period (fig. 11*A*). During the dry period, densities of *E. coli* generally were low (<100 MPN/100 mL) at Barton and Bear Creeks, the two stream sites with some

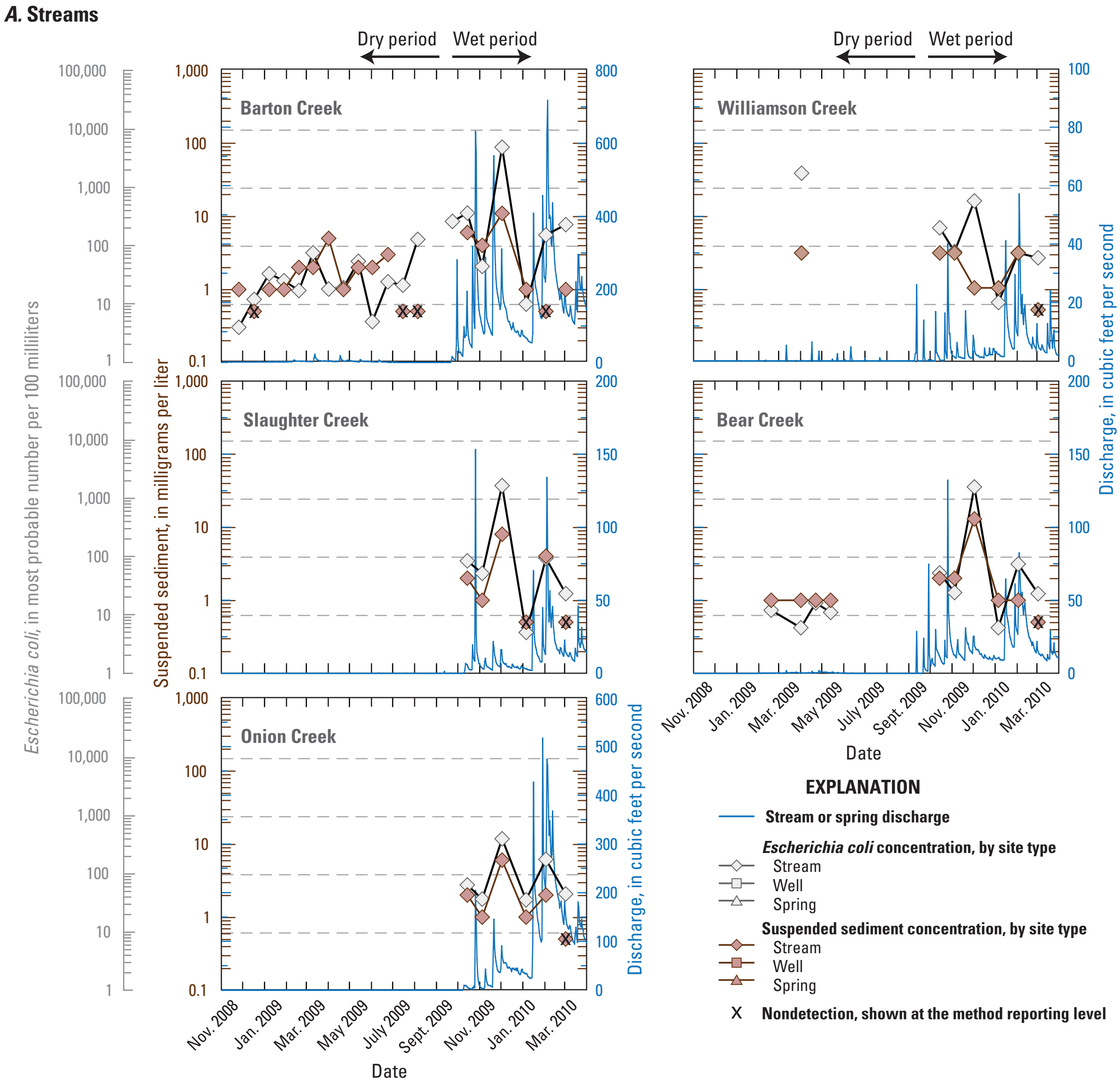
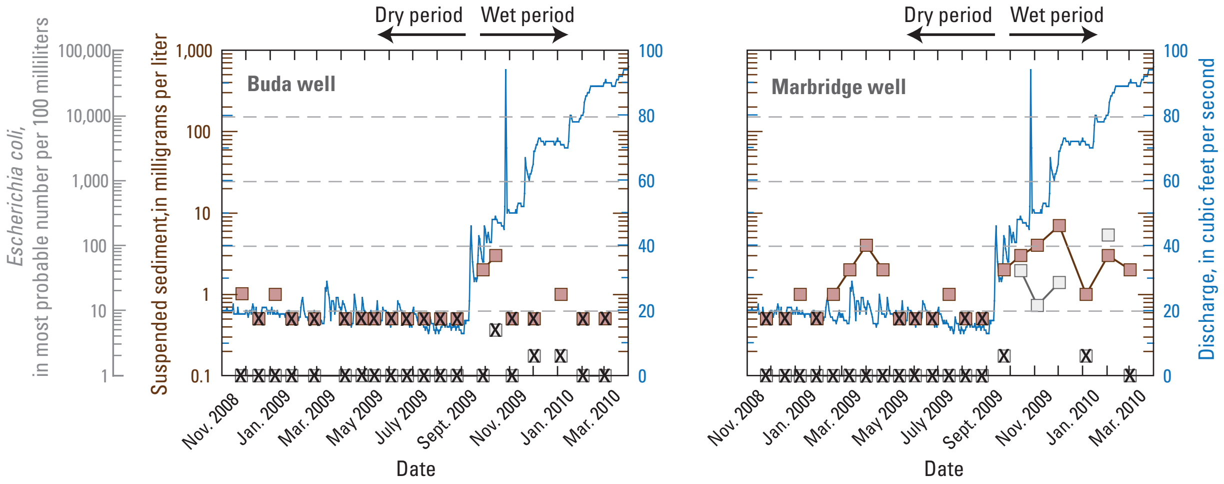


Figure 11. Time series of densities of *Escherichia coli* and concentrations of suspended sediment from *A*, the five stream sites, *B*, the two groundwater (well) sites, and *C*, Barton Springs during routine sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas.

sustained flow. During the wet period, densities of *E. coli* in routine samples varied from less than 10 to 4,800 MPN/100 mL. There was no consistent temporal pattern in densities of *E. coli* through the wet period, and it is likely that major and minor storms that occurred between routine sampling events influenced densities in routine samples. Maximum and median densities of *E. coli* varied among sites. The maximum densities of *E. coli* at Barton, Williamson, Slaughter, and Bear Creeks were higher than those at Onion Creek (fig. 11*A*). In contrast, median densities at Williamson, Slaughter, and Onion Creeks (54–74 MPN/100 mL) were about twice as high as those at Barton and Bear Creeks (29 and 20 MPN/100 mL, respectively). There were no significant correlations between densities of *E. coli* and discharge at any of the creeks except for Barton Creek during the wet period (positive correlation), although the absence of correlations might be the result of the relatively small number of samples.

Suspended sediment concentrations in routine samples collected from stream sites generally were low (<10 mg/L) during the entire period of the investigation (fig. 11*A*). Concentrations were similar among all stream sites, and there were no correlations between SSC and discharge, except at Barton Creek during the dry period. There were no significant correlations between SSC and densities of *E. coli* measured

***B.* Groundwater**



***C.* Barton Springs**

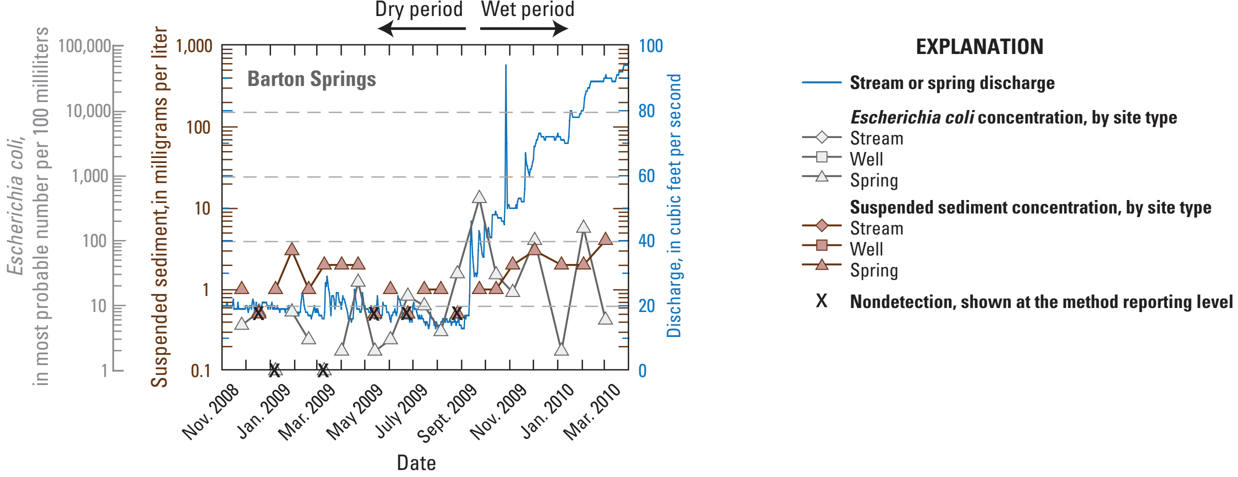


Figure 11. Time series of densities of *Escherichia coli* and concentrations of suspended sediment from *A*, the five stream sites, *B*, the two groundwater (well) sites, and *C*, Barton Springs during routine sampling (November 2008–March 2010) in the Barton Springs zone, south-central Texas. —Continued

in routine samples, although maximum concentrations of SSC were coincident with maximum densities of *E. coli* at all streams sites except Williamson Creek.

Groundwater

Densities of *E. coli* were less than the LRL of 1 MPN/100 mL at both groundwater (well) sites during the dry period (fig. 11*B*). During the wet period, densities were less than the LRL at the Buda well and low but quantifiable at the Marbridge well. Densities of *E. coli* were variable at the Marbridge well throughout the wet period, and there was no consistent temporal pattern (fig. 11*B*). Major and minor storms that occurred between sampling events likely affected counts in routine samples at the Marbridge well, which is consistent with the hypothesis that the Marbridge well receives some conduit flow. Densities of *E. coli* in samples from the wells were lower than densities in streams during both the dry and wet periods (table 7). Concentrations of suspended sediment were significantly higher during the wet period than during the dry period at the Marbridge well, but there was no significant difference at the Buda well. There was a significant correlation between SSC and densities of *E. coli* in samples from the Marbridge well (Kendall's tau of 0.54), but there was no correlation at the Buda well.

Barton Springs

Densities of *E. coli* in routine samples from Barton Springs were low (<30 MPN/100mL) during the dry period and were higher and more variable during the wet period (2–450 MPN/100 mL). There was no consistent temporal pattern in densities of *E. coli* (fig. 11*C*), and it is likely that major and minor storms that occurred between routine sampling events affected densities of *E. coli* in samples from Barton Springs. Median and maximum densities of *E. coli* were about an order of magnitude higher during the wet period than during the dry period, and densities of *E. coli* in Barton Springs were higher than those in groundwater and similar to or less than in those the streams during both the dry and wet periods

Table 7. Summary statistics for suspended sediment and *Escherichia coli* for routine and storm samples in surface water (streams), groundwater (wells), and Barton Springs in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[mg/L, milligrams per liter; NA, not applicable; MPN/100 mL, most probable number per 100 milliliters]

Constituent	Sampling condition	Streams			Wells			Barton Springs		
		Median	25th percentile	75th percentile	Median	25th percentile	75th percentile	Median	25th percentile	75th percentile
Suspended sediment (mg/L)	Routine	1	1	2	1	1	2	1	1	2
	All storms	16	6	49	NA	NA	NA	2	1	4
	Major storms	17	6	36	NA	NA	NA	2	1	3
	Minor storms	16	5	49	NA	NA	NA	3	2	4
Escherichia coli (MPN/100 mL)	Routine	25	10	84	1	1	1	8	3	23
	All storms	480	138	4,839	NA	NA	NA	52	14	189
	Major storms	333	83	1,840	NA	NA	NA	71	16	213
	Minor storms	819	271	4,839	NA	NA	NA	15	6	56

(table 7). There was no correlation, however, between densities of *E. coli* in Barton Springs and Barton Springs discharge.

Concentrations of suspended sediment in routine samples from Barton Springs were consistently low (<10 mg/L) during both the dry and wet periods (fig. 11*C*) but were significantly higher during the wet period (median of 2 mg/L) than during the dry period (median of 1 mg/L). There was a significant correlation between spring discharge and SSC (Kendall's tau of 0.50) if the entire period of sampling was considered, although there was no significant correlation if the dry and wet periods were considered individually. There was no correlation between densities of *E. coli* and SSC.

Geochemical Response to Storms

Samples were collected at the stream and spring sites in response to three major storms (storms 1–3) that occurred during the wet period and in response to several minor storms that occurred during the dry and wet periods.

Major Ion Geochemistry

Surface Water

Surface water (stream) samples collected in response to storms 1–3 were combined into a rising-limb flow-weighted composite sample and a falling-limb flow-weighted composite sample. Concentrations of major ions in rising-limb and falling-limb storm composites were similar for most constituents at all sites, except for Bear Creek in response to storm 1, for which concentrations of most major ions in the rising-limb composite sample were lower than those in the falling-limb composite sample. For other sites and storms, slight offsets between rising-limb and falling-limb constituent concentrations were not systematic between sites, storms, or type of constituent.

Concentrations of most major ions at some stream-sampling sites were lower in storm samples than in routine samples, and concentrations in storm samples were lower for storms 1 and 3 than for storm 2 (fig. 12). Concentrations of major ions in the storm samples were significantly lower than those in routine samples at Williamson, Slaughter, and Bear Creeks, with the exception of bicarbonate, for which there was no significant difference. The differences between concentrations of major ions in routine and storm-sample were greatest at Williamson Creek (median reduction of 68 percent in storm samples compared to routine samples), less at Bear Creek (median reduction of 28 percent), and least at Slaughter Creek (median reduction of 16 percent). At Barton and Onion Creeks, concentrations of major ions in storm samples were not significantly different from those in routine samples. The lowest concentrations of major ions were measured following storm 1 at Bear and Williamson Creeks, the two sites where there was sufficient flow to trigger sampling. Concentrations in samples from storm 3 generally were lower than in samples from storm 2. Concentrations of major ions in samples collected in response to minor storms generally were similar to or less than concentrations in storm 2 samples, with some exceptions for samples from Barton and Bear Creeks.

Barton Springs

Concentrations of major ions in samples collected at Barton Springs in response to storms overall were lower than

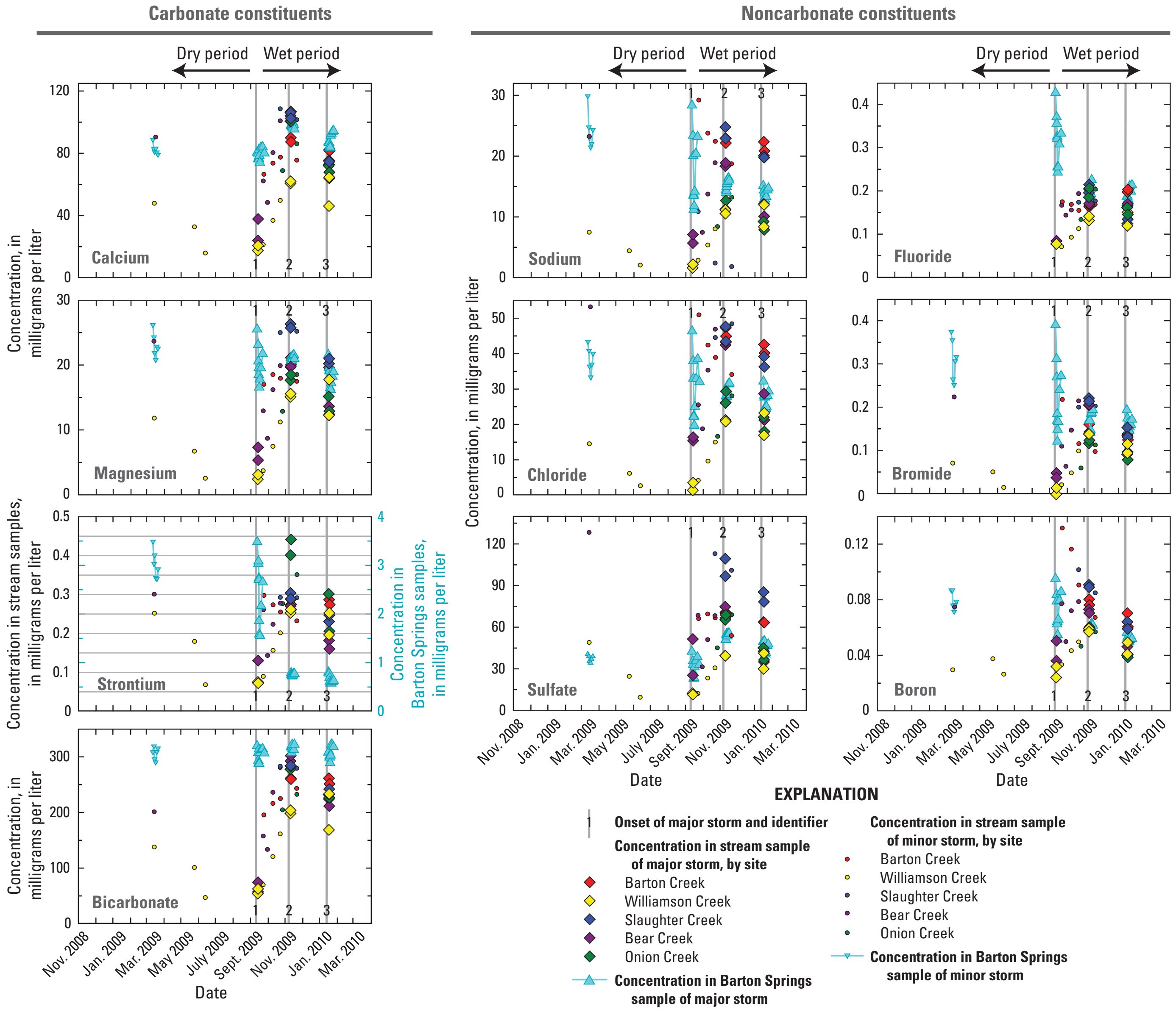


Figure 12. Time series of major-ion concentrations (carbonate and noncarbonate constituents) for the five stream sites and Barton Springs in response to major and minor storms (2009–10), Barton Springs zone, south-central Texas. The time series for major-ion concentrations for Barton Springs in response to each storm is shown in figure 13.

those in routine samples collected prior to the storms, and the magnitude of change in concentrations of most constituents following each storm was largest when antecedent moisture conditions were driest (storm 1) (table 4). Concentrations of major ions, with the exception of calcium, in storm samples generally decreased following the collection of the initial storm sample (fig. 13). There were significant negative correlations for storm samples from Barton Springs between total stream recharge and all constituent concentrations (Kendall's tau from -0.34 to -0.74), except those of bicarbonate, calcium, and sulfate. There also were significant negative correlations (Kendall's Tau from -0.35 to -0.73) between spring discharge and all constituent concentrations, again except bicarbonate, calcium, and sulfate. All three major storms resulted in a decrease in calcite and dolomite saturation index (SI) values relative to those for routine samples. A decrease in calcite SI values in response to the storms indicates that Barton Springs discharge was not fully equilibrated with calcite, in contrast to conditions indicated by SI values for routine samples, reflecting a shorter residence time in response to storm recharge.

Changes in concentration of individual major ions in response to the minor storm (March 2009) and to storms 1 and 3 were similar, but changes in concentration in response to

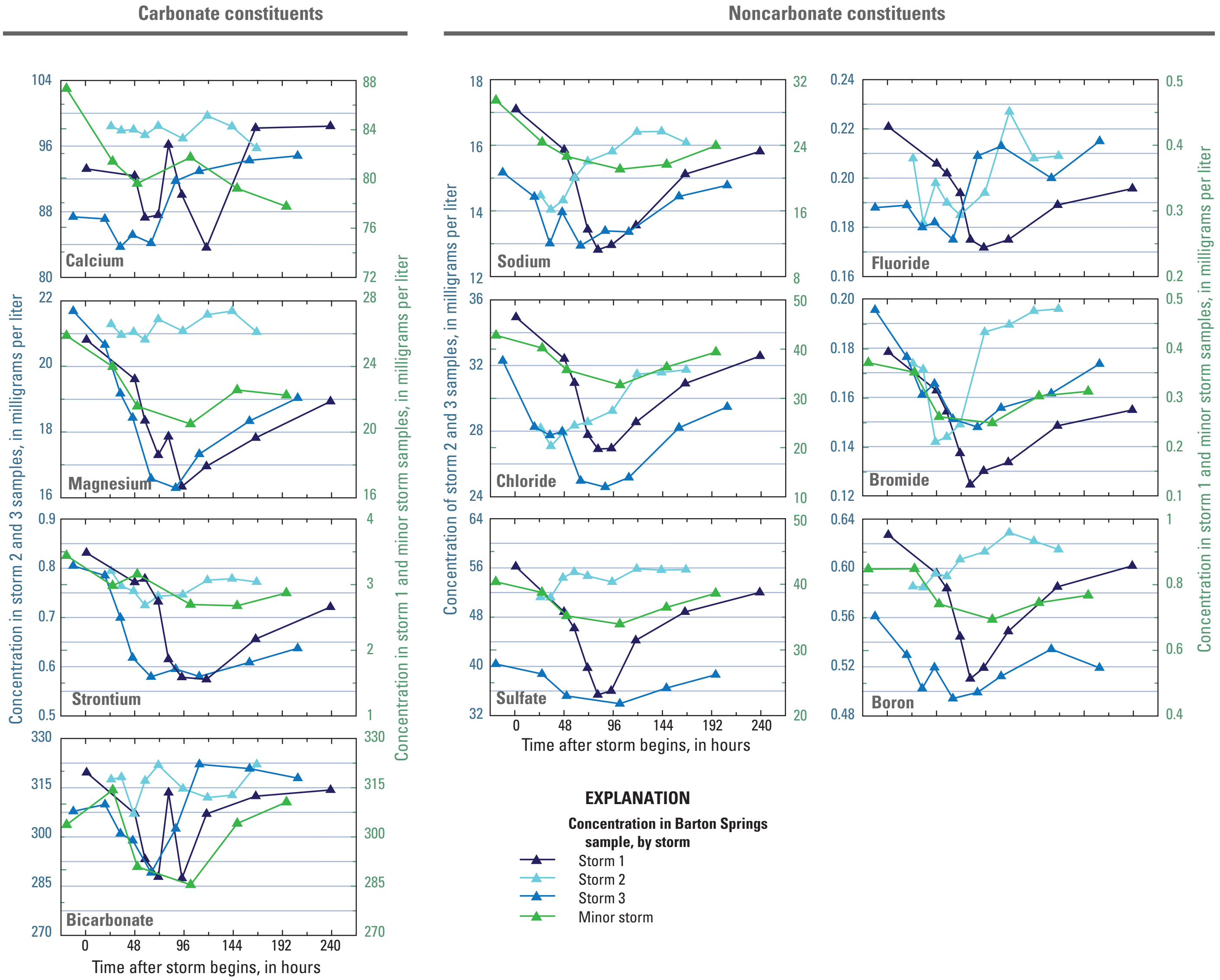


Figure 13. Time series of major-ion concentrations (carbonate and noncarbonate constituents) for Barton Springs in response to storm 1 (September 2009), storm 2 (November 2009), storm 3 (January 2010), and a minor storm (March 2009), Barton Springs zone, south-central Texas.

storm 2 for which antecedent moisture conditions were wettest, were different (fig. 13). For the minor storm and storms 1 and 3, concentrations of most major ions decreased to a minimum value and had begun to return to pre-storm concentrations before the final sample was collected. In contrast, concentrations of many major ions following storm 2 remained constant or increased. Several major ions had a single sample "spike" in concentration that interrupted a pattern of decreasing concentration. The time elapsed between the start of the storm and the geochemical response was shorter for the minor storm and storm 3, which might reflect differences in temporal distribution of rainfall (fig. 4*C*, *D*).

The relation between stream and spring water constituent concentrations is nonlinear and reflects the evolution of stream and spring water compositions with changing antecedent moisture conditions. Of the different storm sampling events (storms 1–3), the lowest major ion concentrations in streams were measured in storm-1 samples (fig. 12); dilution of Barton Springs water in response to storm 1 is consistent with groundwater mixing with recharging stream water. In response to storm 2, concentrations of noncarbonate constituent in Barton Springs discharge increased (fig. 13), and concentrations of most major ions and specific conductance at Barton Springs were intermediate between higher major-ion concentrations at Barton, Slaughter, and Bear Creeks and lower major-ion concentrations at Williamson and Onion Creeks (figs. 9 and 12). Recharge estimates for storm 2 indicate that the majority of stream recharge (72 percent) was supplied by Barton, Slaughter, and Bear Creeks, resulting in the increase in major-ion concentrations measured at Barton Springs (fig. 5). Major-ion concentrations at Barton Springs decreased in response to storm 3 and, along with values of specific conductance, were intermediate between or similar to higher concentrations at Barton and Slaughter Creeks and lower concentrations at Williamson, Bear, and Onion Creeks (figs. 9 and 12). Recharge estimates for storm 3 indicate that the majority (67 percent) of stream recharge was supplied by Williamson, Bear, and Onion Creeks, resulting in the decrease in major-ion concentrations measured at Barton Springs. The dynamic relation between major-ion concentrations of streams and Barton Springs indicates that the influence of recharging surface water on the geochemical composition of Barton Springs varies as a function of antecedent moisture conditions and specific sources of recharge.

Nutrient Geochemistry

N and P species were measured in samples collected at the five stream sites and at Barton Springs in response to the three major storms and several minor storms. In most cases where total and dissolved P were both quantified (23 of 27 samples), concentrations of total P exceeded those of dissolved P, indicating that some of the P was associated with suspended sediment. In a few cases (4 of 23 samples), concentrations of dissolved P exceeded those of total P, likely because of analytical uncertainty at concentrations close to the LRL.

Surface Water

For each storm sampling event (storms 1–3), the samples were combined into a rising-limb flow-weighted composite sample and a falling-limb flow-weighted composite sample. For all nutrient species measured, there was no systematic difference between concentrations representing the rising and falling limbs of the stream hydrograph by site, by storm, or by constituent.

Organic N plus ammonium was detected at a concentration above the LRL (0.1 mg/L) in all of the major and minor storm samples from streams (fig. 14*A*) (NH_3 either was not detected or was estimated at a concentration less than the LRL of 0.02 mg/L; therefore, org N+NH_3 is referred to as “organic N” throughout this section). There was not a significant difference between the median concentrations of organic N in stream samples for major and minor storms. The median concentration for all storms was significantly greater than that for routine samples (table 6), and concentrations of organic N in all storm samples exceeded the concentration in any of the routine samples collected from streams with the exception of one sample collected from Williamson Creek (April 2, 2009) (figs. 10 and 14*A*). Concentrations of organic N were highest for storm 1 and lowest for storm 2. This temporal pattern was similar to that during the routine sampling during the wet period (fig. 10*A*), for which the highest concentrations occurred at the onset of the wet period in September 2009, followed by a decrease and then by another increase in February 2010.

Nitrate plus nitrite was measured at concentrations above the LRL in all major and minor storm samples collected from all five streams (fig. 14*A*). NO_2 was detected at a concentration above the LRL of 0.002 mg/L in only two of the major and minor storm samples from streams. Where NO_2 was detected, it constituted only from 0.2 to 7 percent of NO_3+NO_2. The median concentration of NO_3+NO_2 in major-storm samples from streams was about twice that of the median concentration in minor-storm samples from streams (table 6), and the difference was statistically significant. The median concentration of NO_3+NO_2 for storm samples, however, was not significantly different from that for routine samples. There was no systematic pattern in concentrations of NO_3+NO_2 among the three major storms (fig. 14*A*). There was no correlation between organic N and SSC at any stream site, with the exception of Bear Creek, where organic N and SSC were positively correlated (Kendall’s tau of 0.47).

Total or dissolved P, or both, were detected at a concentration above the LRL of 0.02 mg/L in one or more storm samples from all five streams (fig. 14*B*). OrthoP was detected in all storm samples from all five streams with the exception of one minor storm sample (Bear Creek) and three major storm samples (Williamson Creek [one] and Onion Creek [two]) (fig. 14*B*), although in many cases the result was reported as estimated at a concentration less than the LRL (0.008 mg/L). Concentrations of P species were highest in samples from Williamson and Bear Creeks; in contrast to routine samples, concentrations of orthoP in storm samples from these streams frequently were greater than the national background concentration for streams of 0.010 mg/L (Dubrovsky and others, 2010) and were greater than concentrations in Barton Springs. This indicates that, during stormflow, recharge from these streams is a source of orthoP to groundwater, and the concentrations contributed by recharge from Williamson and Beer Creeks in response to storms are diluted within the aquifer. Median concentrations of orthoP in major storm samples collected from Williamson (0.023 mg/L) and Bear Creeks (0.018 mg/L) were about 3 and 5 times greater than those in routine samples (0.004 for Williamson Creek and 0.006 for Bear Creek), respectively, indicating that the excess orthoP might have an anthropogenic source. OrthoP in samples from the other three stream sites in most cases was not detected or was reported as estimated at a concentration less than the LRL. Median concentrations of P species in stream samples were not significantly different for major and minor storms, but the median concentration of P species measured in storm samples was significantly greater than that for routine samples (table 6). Among the three major storms, concentrations of P species were highest and most variable for storm 1 and similar for storms 2 and 3 (fig. 14*B*).

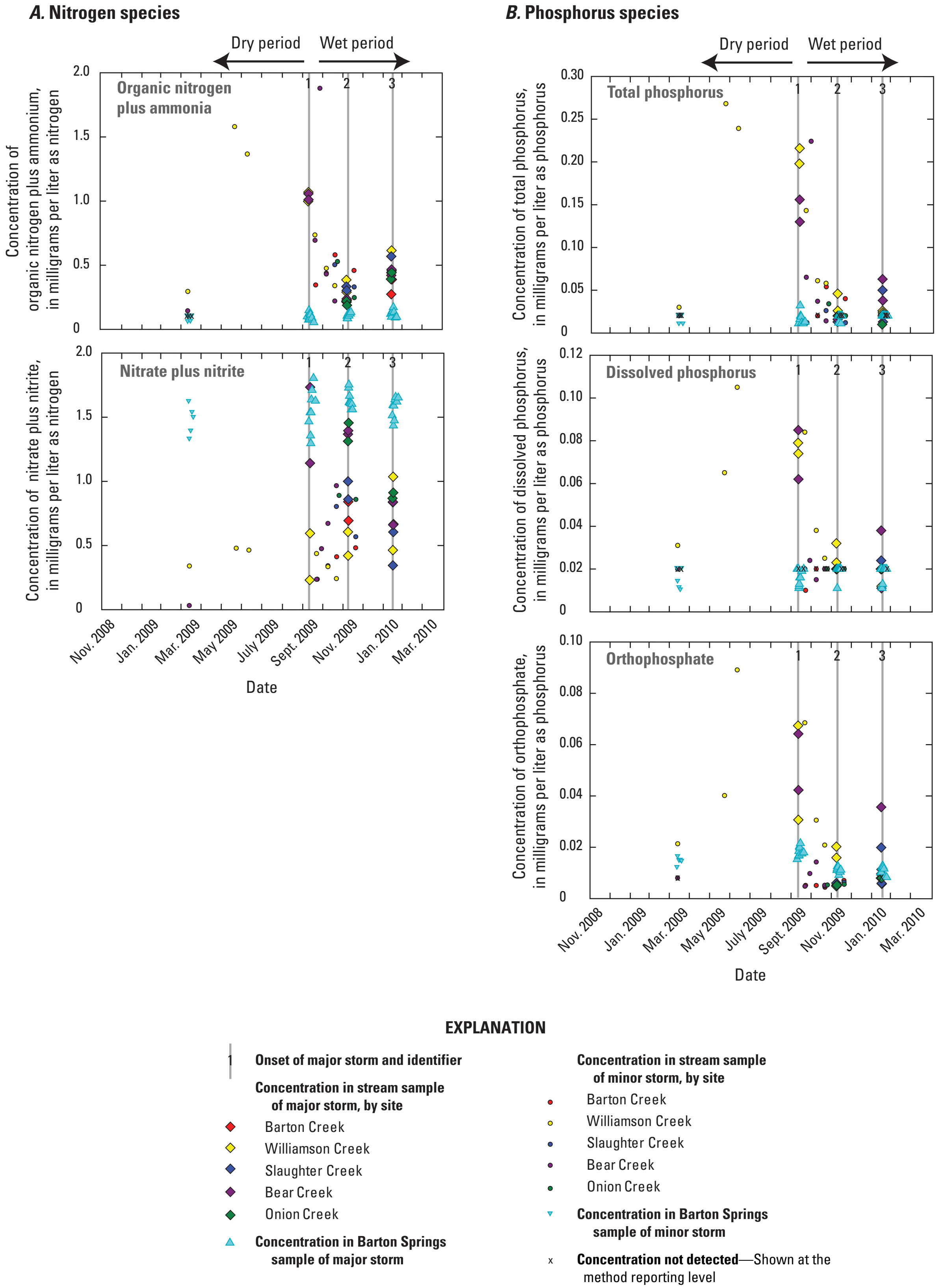


Figure 14. Time series of concentrations of *A*, nitrogen species, and *B*, phosphorus species for the five stream sites and Barton Springs in response to major and minor storms (2009–10), Barton Springs zone, south-central Texas. The time series for nutrient concentrations for Barton Springs in response to each storm is shown in figure 15.

Barton Springs

Concentrations of organic N, measured as org $N+NH_3$ in mg/L as N, in samples collected from Barton Springs in response to the three major storms and the one minor storm (March, 2009) were in all cases lower than concentrations in all samples collected from streams in response to the same storms (figs. 10 and 14*A*). In all major and minor storm samples from Barton Springs, NH_3 was not detected at the LRL of 0.02 mg/L; thus, org $N+NH_3$ consisted almost entirely of organic N and is referred to as "organic N" throughout this section. Concentrations of organic N at Barton Springs were similar for the minor storm and three major storms. The median concentration of organic N in storm samples (major and minor combined) from Barton Springs was significantly greater than that measured in routine samples (table 6).

Nitrate plus nitrite was detected at a concentration greater than the LRL in all minor and major storm samples collected from Barton Springs. Concentrations of NO_3+NO_2 in these samples collected from Barton Springs were in all cases higher than the concentrations in samples collected from streams in response to the same storms with the exception of one sample collected at Bear Creek for storm 1 (figs. 10 and 14*A*). In all major and minor storm samples collected from Barton Springs, NO_2 was not detected at the LRL of 0.002 mg/L. The median concentration of NO_3+NO_2 for storm samples from Barton Springs was significantly higher than the median concentration for routine samples (table 6). Concentrations of NO_3+NO_2 at Barton Springs were similar for the minor storm and three major storms but were most variable for storm 1 (fig. 14*A*).

The temporal pattern of organic N and NO_3+NO_2 concentrations measured at Barton Springs varied among storms, and there was no relation between the concentrations of the two N species (fig. 15*A*). Differences in concentration in response to storms might partly result because organic N is measured in unfiltered water and thus the measurement might include some N associated with the solid phase. At Barton Springs, there was a weak correlation between organic N and SSC (Kendall's tau of 0.29) if all storm samples were considered together, but there was no significant correlation for any individual storm.

In response to the storms sampled during this investigation, a decrease in NO_3+NO_2 occurred only for the minor storm and for storm 2. In response to storms 1 and 3, an initial decrease in NO_3+NO_2 concentration was followed by an increase to a concentration exceeding that of the initial concentration. This response was most marked for storm 1, for which NO_3+NO_2 concentration peaked 8 days after rainfall at a concentration about 0.3 mg/L higher than the initial concentration. Nitrate plus nitrite concentrations measured from 1990 to 2008 at Barton Springs were inversely correlated with spring discharge, but those measured during the investigation described in this report were positively correlated with spring discharge (Mahler and others, 2011). This change likely is related to an increase in concentrations of NO_3+NO_2 in the five recharging streams relative to historical conditions (Mahler and others, 2011), which has decreased the degree of dilution of NO_3+NO_2 in groundwater by stream recharge. The transition from mostly undeveloped watersheds to a mix of land uses including urban areas in the watersheds of the Barton Springs contributing zone is likely causing higher nitrate concentrations in the recent stormwater runoff documented in this report compared to concentrations documented in 1990–2008 stormwater runoff.

At Barton Springs, total and dissolved P in minor and major storm samples were measured at concentrations at or above the LRL in only two samples, both of which were for storm 1. In all other samples, total and dissolved P either were not detected or were reported as estimated at a concentration less than the LRL of 0.02 mg/L. OrthoP was detected at a concentration greater than the LRL in all storm samples. There was no significant difference between median concentrations of any P species for storm samples and routine samples collected from Barton Springs. Among storms, concentrations of P species were higher and more variable for storm 1, similar to the temporal pattern in streams, with substantially fewer nondetections of dissolved and total P for storm 1 than for storms 2 and 3 (fig. 15*B*). In response to storm 1 there was a breakthrough curve (that is, a relatively rapid increase and then decrease in concentration over time) for total P and orthoP, but concentrations of P species did not describe breakthrough curves in response to storms 2 or 3 (fig. 15*B*).

Bacterial Densities and Suspended Sediment Geochemistry

E. coli and SSC were measured in samples collected from the streams and from Barton Springs in response to the three major storms and several minor storms (fig. 16). Densities of *E. coli* in the streams were measured in one sample collected at the beginning of the storm hydrograph by autosampler and in one to three grab samples collected along the rest of the storm hydrograph. Suspended sediment was measured in rising-limb and falling-limb flow-weighted composite samples from the streams.

Surface Water

Densities of *E. coli* in storm samples collected from Barton, Williamson, and Bear Creeks were elevated relative to those in routine samples collected at the same sites (figs. 11*A* and 16*A*). Densities in samples collected during the rising and falling limbs of the hydrograph were similar at all sites, and slight differences in *E. coli* densities between rising- and falling-limb samples were not systematic between sites or storms. Densities of *E. coli* generally were higher in response to storm 1 than in response to storm 2 or 3 (fig. 16*A*). The only correlation between densities of *E. coli* and creek discharge was for samples from Onion Creek (Kendall's tau of 0.66).

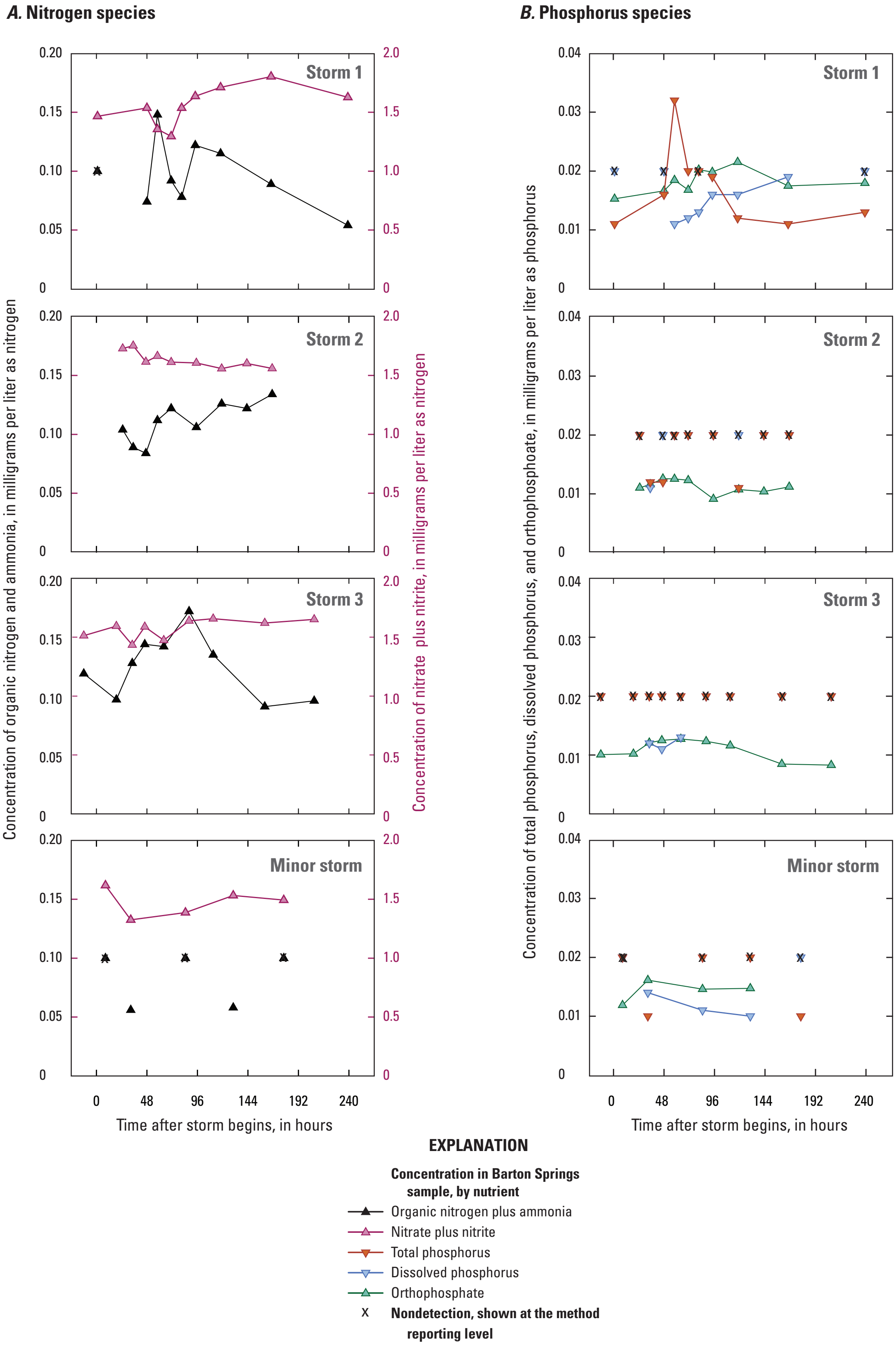
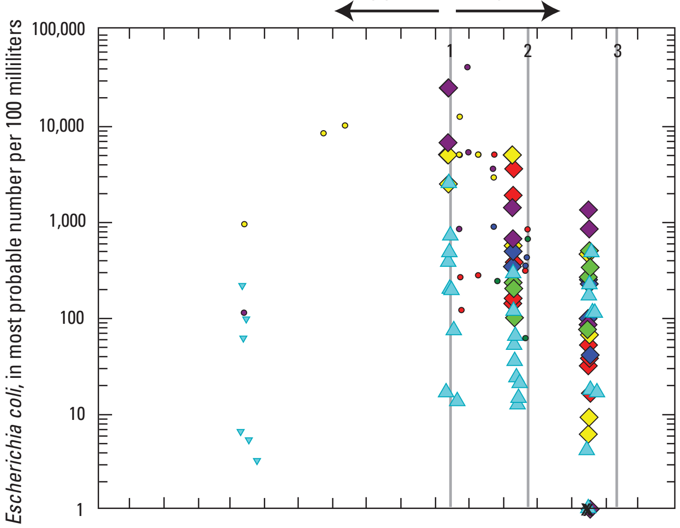


Figure 15. Time series of concentrations of *A*, nitrogen species, and *B*, phosphorus species for Barton Springs in response to storm 1 (September 2009), storm 2 (November 2009), storm 3 (January 2010), and a minor storm (March 2009), Barton Springs zone, south-central Texas.

A. Escherichia coli



***B.* Suspended sediment**

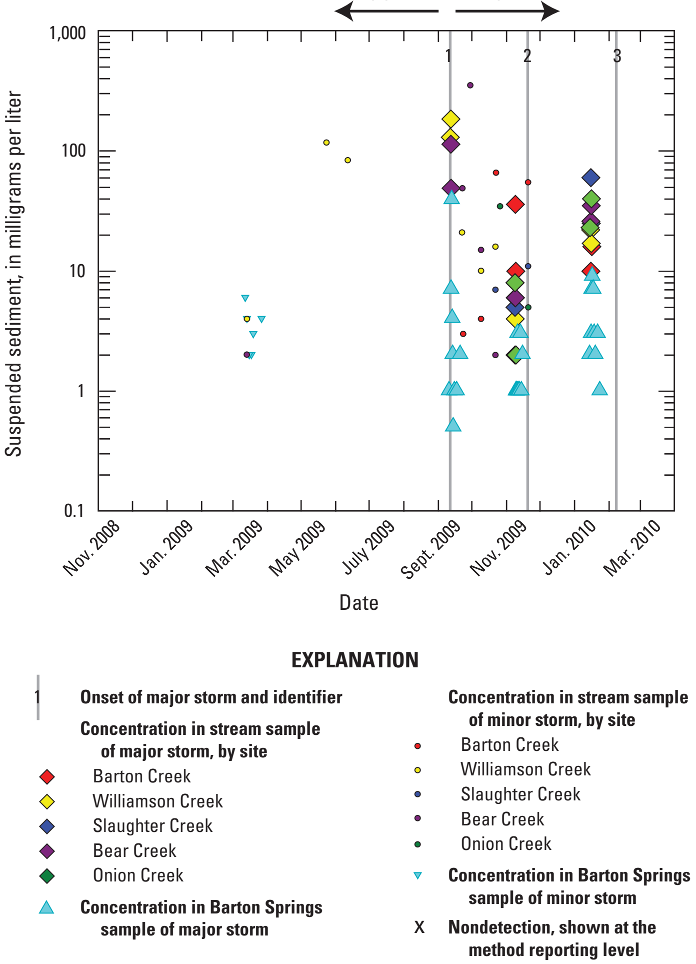


Figure 16. Time series of *A*, densities of *Escherichia coli*, and *B*, concentrations of suspended sediment from the five stream sites and from Barton Springs in response to major and minor storms (2009–10), Barton Springs zone, south-central Texas.

Median and maximum densities of *E. coli* were about an order of magnitude higher at Williamson and Bear Creeks than at Barton, Slaughter, and Onion Creeks.

Concentrations of suspended sediment in streams were higher in storm samples relative to routine samples and, similar to densities of *E. coli*, at most sites were highest in response to storm 1 (figs. 11*A* and 16*B*). Concentrations of suspended sediment in rising- and falling-limb composites were similar at all sites, and slight differences between concentrations in rising- and falling-limb samples were not systematic between sites or storms. Concentrations of suspended sediment were positively correlated with stream discharge at all sites (Kendall's tau of 0.60–0.74) except at Williamson Creek. Also similar to densities of *E. coli*, maximum SSC in storm samples were 6 and 10 times higher at Williamson (170 mg/L) and Bear (300 mg/L) Creeks, respectively, than at Barton, Slaughter, and Onion Creeks. The cause of elevated *E. coli* densities and SSC at Williamson and Bear Creeks is not known.

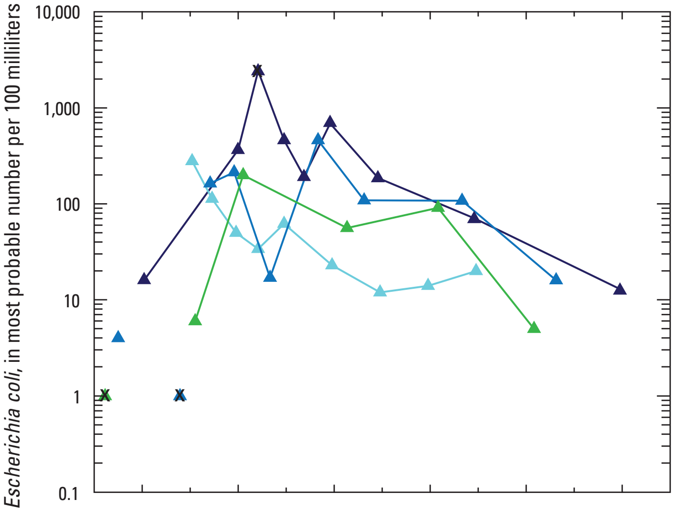
Barton Springs

Densities of *E. coli* and SSC in Barton Springs were significantly higher in storm samples than in routine samples. Maximum densities or concentrations were highest in response to storm 1, lower in response to storm 3, and lowest in response to storm 2 and the minor storm (fig. 17). Densities of *E. coli* and SSC at Barton Springs varied similarly in response to storms 1 and 3 and the minor storm, and then returned to pre-storm values. In contrast, densities of *E. coli* decreased at Barton Springs in response to storm 2, and there was no change in SSC. There were no correlations between densities of *E. coli* or SSC and Barton Springs discharge. Densities of *E. coli* in storm samples from Barton Springs generally were lower than or similar to those in storm samples from streams for storms 1 and 2, and similar to those in streams for storm 3 (fig. 16*A*).

Interaction Between Surface Water and Groundwater

The interaction between surface water and groundwater can have a large influence on the fate and transport of constituents in the system because surface water is a source of many constituents and because recharge can dilute or add to concentrations of constituents in groundwater. Interaction between the streams recharging Barton Springs and the Barton Springs segment is manifested as changes in discharge at Barton Springs and as changes in water quality (Barrett and Charbeneau, 1996; Mahler and others, 2006; Mahler and Massei, 2007; Mahler and Garner, 2009). This section focuses on loads of N species in stream recharge and in Barton Springs and on the geochemical processes of mixing, dissolution, precipitation, and water-rock interaction occurring within the aquifer as a result of interaction between surface water and groundwater.

A. Escherichia coli



***B.* Suspended sediment**

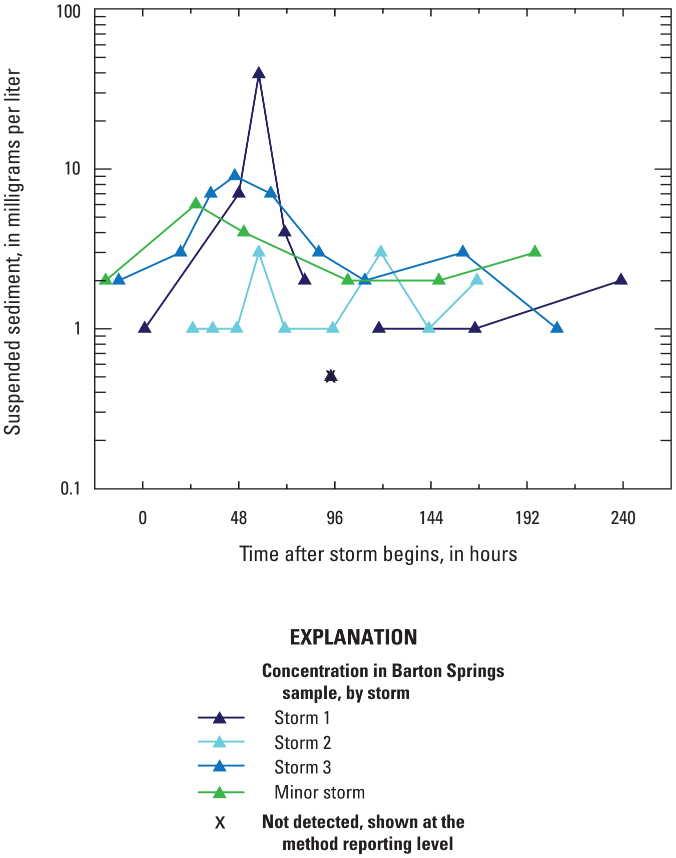


Figure 17. Time series of *A*, densities of *Escherichia coli*, and *B*, concentrations of suspended sediment for Barton Springs in response to storm 1 (September 2009), storm 2 (November 2009), storm 3 (January 2010), and the minor storm (March 2009), Barton Springs zone, south-central Texas.

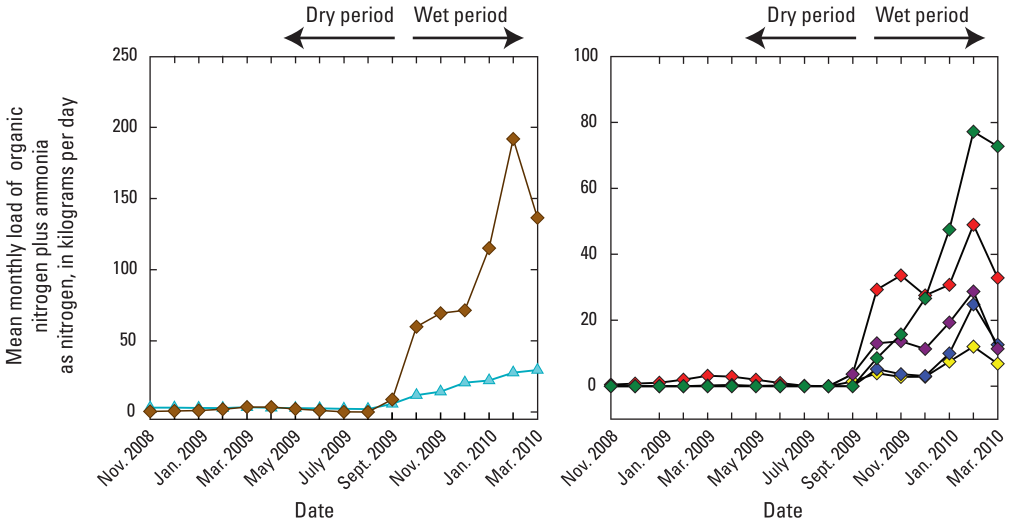
Loading of Nitrogen Species

Quantifying the loads of organic N and NO_3+NO_2 recharging and discharging from the Barton Springs segment provides information regarding the fate and transport of N species from recharge to discharge. Of particular interest is the contribution of each recharging stream to loading organic N, NO_3+NO_2, and total N (the sum of the two) and a comparison of the load recharged by streams and the load discharged from Barton Springs. Mean monthly loads of organic N and NO_3+NO_2 in stream recharge and Barton Springs discharge were estimated with LOADEST (Runkel and others, 2004), a model that estimates loads on the basis of flow rate and measured concentrations. In this specific application, because loads were computed on a monthly basis, the dry period refers to November 2008–August 2009 and the wet period refers to September 2009–March 2010. The results of the load estimation highlight the important contribution of stream recharge to water quality in the Barton Springs segment and provide insight into geochemical processes occurring that affect concentrations of N species in the aquifer.

Estimated mean monthly loads of organic N both in stream recharge and in Barton Springs discharge were much lower during the dry period than during the wet period (fig. 18*A;* table 8). During the dry period, the mean monthly load of organic N in stream recharge was low and similar to that in Barton Springs discharge. During the wet period, mean monthly loads of organic N in stream recharge and in Barton Springs discharge increased, but loads in stream recharge on average were about six times greater than those in Barton Springs discharge. During the first part of the wet period, Barton Creek contributed the greatest loads of organic N; during the second part of the wet period, Onion Creek contributed the greatest loads of organic N. This pattern is consistent with the distribution of estimated recharge from the creeks (fig. 3*B*), which was greatest from Barton Creek during the early part of the wet period and greatest from Onion Creek during the latter part of the wet period. The loading of organic N from the Bear Creek watershed likely is greater than estimated here because this estimate does not include the contribution from Little Bear Creek.

The large excess load of organic N in stream recharge relative to that in Barton Springs discharge during the wet period (fig. 18*A*) indicates that removal of organic N is occurring within the aquifer. A likely removal mechanism is conversion of organic N to nitrate by ammonification and nitrification. Conversion of organic N to nitrate occurs in oxic conditions (water with greater than 0.5 mg/L dissolved oxygen [Dubrovsky and others, 2010]), consuming dissolved oxygen in the process. Concentrations of dissolved oxygen in the streams, two groundwater wells, and Barton Springs were oxic during the entire period of the investigation; the minimum dissolved oxygen concentration measured was 3.92 mg/L. Concentrations of dissolved oxygen were significantly lower in Barton Springs discharge than in streams during the wet period (table 5), consistent with consumption of dissolved

***A.* Mean monthly loads of organic nitrogen plus ammonia**



***B.* Mean monthly loads of nitrate plus nitrite**

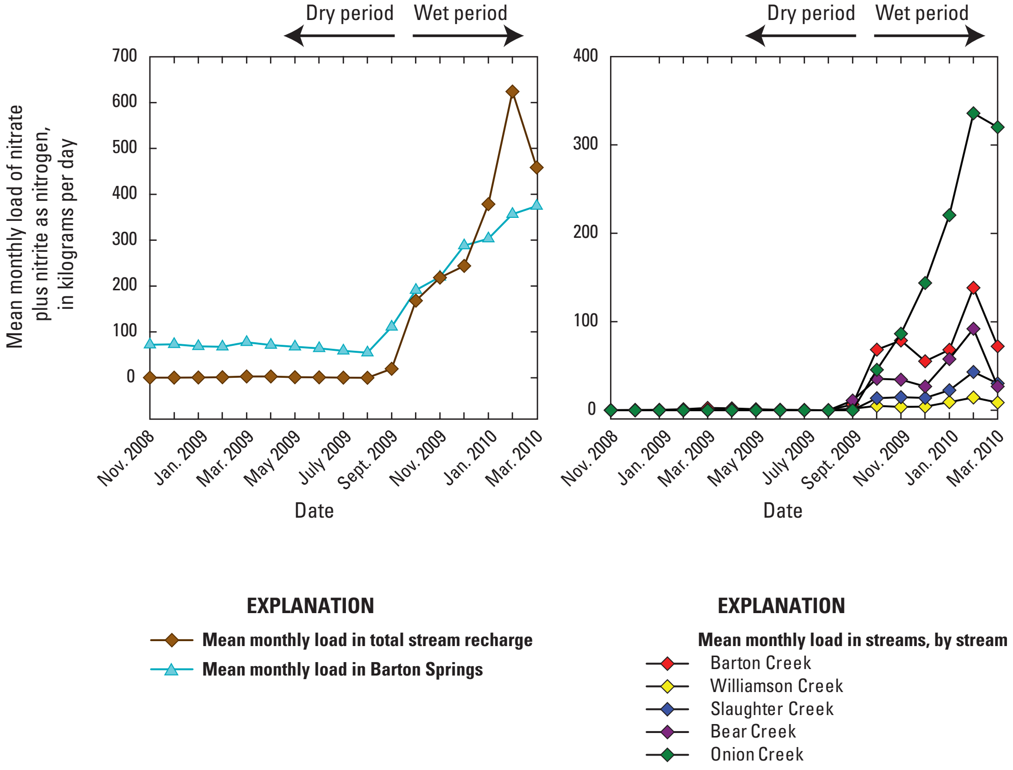


Figure 18. LOADEST model (Runkel and others, 2004) results for the Barton Springs zone, south-central Texas (November 2008–March 2010). Estimated mean monthly loads of *A*, organic nitrogen plus ammonia, and *B*, nitrate plus nitrite in total stream recharge and Barton Springs discharge, and in the five major streams recharging the Barton Springs segment.

Table 8. Loads of nitrogen species in estimated recharge from surface water (streams) and discharge from Barton Springs in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[kg/d, kilograms per day]

Constituent	Sampling condition	Streams mean daily load (kg/d)	Barton Springs mean daily load (kg/d)
Organic nitrogen + ammonia, as N	Study period[1]	39	9.4
Nitrate + nitrite, as N		123	142
Total nitrogen species, as N		162	157
Organic nitrogen + ammonia, as N	Dry period[2]	1.5	2.8
Nitrate + nitrite, as N		1.0	67
Total nitrogen species, as N		2.4	70
Organic nitrogen + ammonia, as N	Wet period[3]	93	19
Nitrate + nitrite, as N		301	263
Total nitrogen species, as N		395	282

[1] Study period: November 2008 through March 2010.

[2] Dry period: November 1, 2008, through September 9, 2009; because loads were computed by month, however, load estimates for the dry period were computed for November 2008 through August 2009.

[3] Wet period: September 10, 2009, through March 31, 2010.

oxygen within the aquifer. Additional verification of the conversion of organic N to nitrate would require additional analytical work, such as the measurement of oxygen isotopes of dissolved oxygen (Daniel Doctor, U.S. Geological Survey, oral commun., 2011). The conversion of organic N in stream recharge to nitrate within the aquifer might account for the higher concentrations of NO_3+NO_2 that have been measured historically in Barton Springs discharge and in groundwater than in streams (U.S. Geological Survey, 2010a).

During the dry period, the load of NO_3+NO_2 in stream recharge was low and less than that in Barton Springs discharge; during the wet period, loads of NO_3+NO_2 in stream recharge and Barton Springs discharge increased, and NO_3+NO_2 loads in stream recharge were similar to or exceeded those in Barton Springs discharge (fig. 18*B*; table 8). During the first part of the wet period, loads of NO_3+NO_2 in stream recharge from Barton, Bear, and Onion Creeks were similar and were greater than those in stream recharge from Williamson and Slaughter Creeks; during the latter part of the wet period, as flow and the estimated recharge contribution from Onion Creek increased, loads of NO_3+NO_2 were greatest in stream recharge from Onion Creek (fig. 18*B*). As with estimates for organic N, loading of NO_3+NO_2 from the Bear Creek watershed likely is greater than estimated here because this estimate does not include the contribution from Little Bear Creek.

The estimated total load of NO_3+NO_2 in stream recharge and Barton Springs discharge (fig. 19; table 8) for the entire period of the investigation were similar. It is not known whether this has been the case historically. Mahler and others (2011) reported that instantaneous NO_3+NO_2 loads (mass

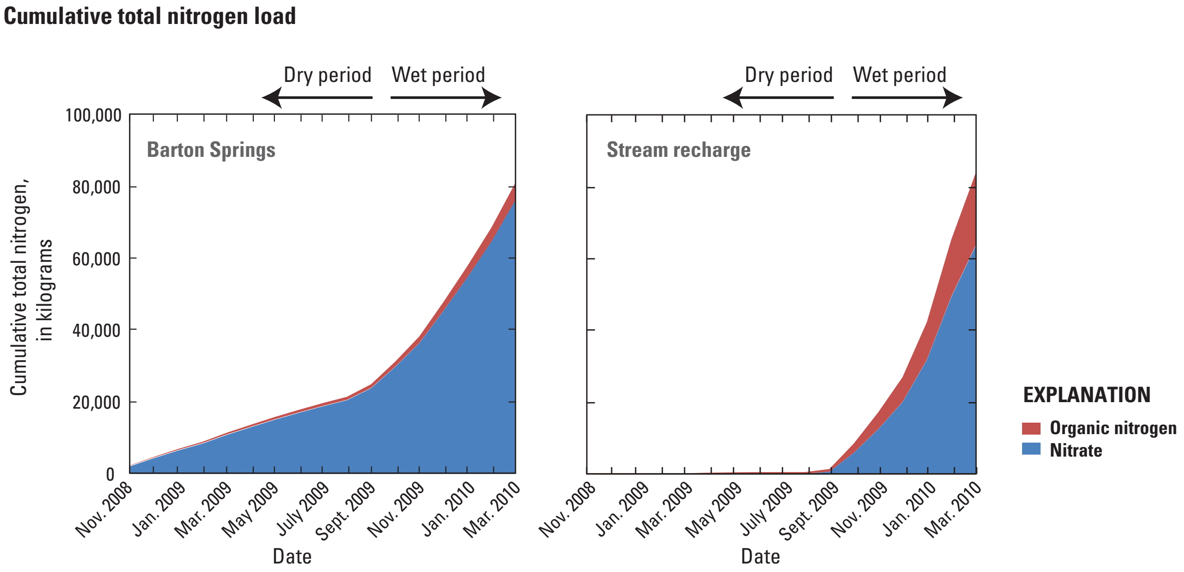


Figure 19. Cumulative total nitrogen load (shown as the sum of organic nitrogen plus ammonia and nitrate plus nitrite) in Barton Springs discharge and stream recharge, Barton Springs zone, south-central Texas, estimated by using the LOADEST model (Runkel and others, 2004).

of NO_3+NO_2 per time at the moment that the sample was collected) relative to flow rates during this investigation (September 2008–March 2010) were significantly greater ($p < 0.05$) than those measured during 1990–2008 at Barton Springs and at all stream sites except Williamson Creek, but the net difference between loads in recharge and discharge were not quantified. There are insufficient data for NO_3+NO_2 in the streams during 1990–2008 for a robust LOADEST (Runkel and others, 2004) estimation of monthly loads.

The loading of total N (organic N + NO_3+NO_2) over the course of the investigation in stream recharge (162 kilograms per day [kg/d]) and in Barton Springs discharge (157 kg/d) were not significantly different. The timing of the loading, however, was variable, with virtually all of the loading of total N to the aquifer by stream recharge occurring during the wet period (fig. 19; table 8). During the wet period, discharge from Barton Springs increased (fig. 2) as the water-level elevation in the aquifer increased rapidly, indicating storage of recharge and the N it contained within the aquifer. The relation between nitrogen loading to the aquifer and nitrogen load discharging from the aquifer is not linear: over the period of the drought cycle investigated here, nitrogen previously loaded to and stored in the aquifer discharged during the dry period when stream recharge was very low or zero; during the wet period nitrogen was recharged to the aquifer, with much of it going into storage.

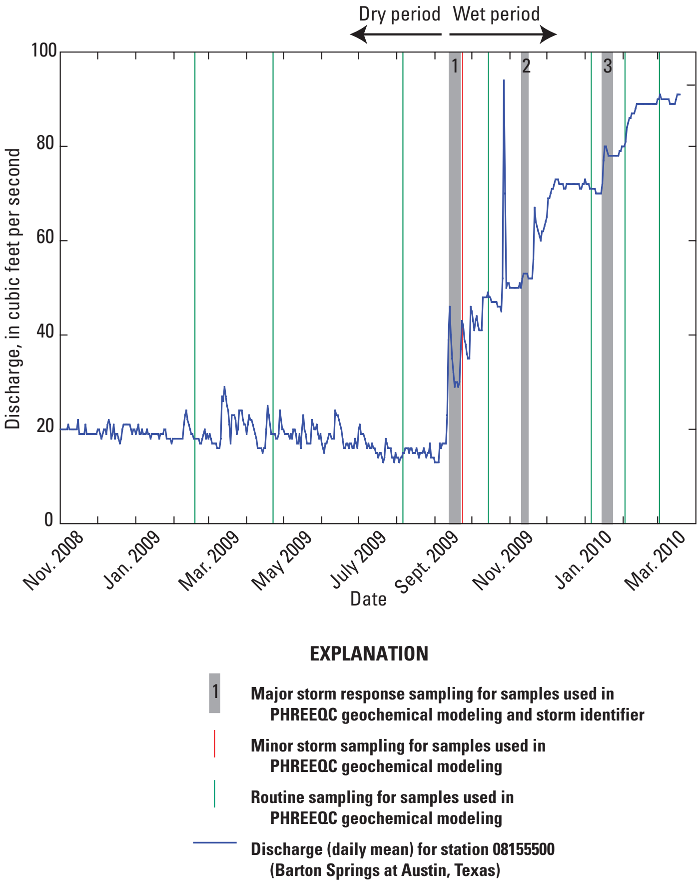


Figure 20. Time series of Barton Springs discharge (daily mean for U.S. Geological Survey station no. 08155500 Barton Springs at Austin, Tex.) and timing of sample collection used for PHREEQC (Parkhurst and Appelo, 1999) geochemical modeling.

Geochemical Modeling

Results of inverse modeling (table 9) provide insight into interactions between surface water and groundwater and aquifer processes under different hydrologic conditions and demonstrate the important effect of water quality in recharging streams on water quality of discharge from Barton Springs. Inverse modeling with the geochemical model PHREEQC (Parkhurst and Appelo, 1999) was used to approximate mixing proportions of endmember water compositions (matrix groundwater, saline-zone groundwater, and stream recharge) and mass-transfer processes that could feasibly produce the concentrations of constituents measured in the groundwater samples.

Inverse modeling was done for a range of hydrologic conditions (dry, wet, and storm conditions) (fig. 20). For routine and storm conditions, inverse modeling was used to mix matrix groundwater, stream recharge, and saline-zone groundwater to approximate the composition of Barton Springs discharge. The composition of the sample collected from the Marbridge well on August 5, 2009, was used to represent matrix groundwater (the Buda well was not used because of its high strontium concentrations, which are discussed in more detail below in this section). The geochemistry of groundwater from the Marbridge well during the dry period was relatively unchanging and was thus considered to be a reasonable proxy for matrix groundwater. The composition of samples collected from a well located in the saline zone east of the Barton Springs zone (State well number YD–58–50–840) was used to represent saline-zone groundwater. The saline zone has multiple distinct hydrochemical facies throughout the regional extent of the Edwards aquifer (Clement, 1989; Oetting and others, 1996), and the composition of groundwater at State well number YD–58–50–840 is hypothesized to be representative of the saline zone to the east of the Barton Springs zone (Garner, 2005; Garner and Mahler, 2007). Stream recharge was represented by integrating recharge estimates with the measured geochemical composition for each of the recharging streams. PHREEQC was used to estimate the composition of the total resulting stream recharge by proportionally mixing the composition of water from each stream. The resulting composition was used to represent stream recharge in inverse modeling. For two of the dates during the dry period, the composition of stream recharge was approximated with and without a contribution from Barton Creek (table 9) to account for possible overestimation of recharge from Barton Creek during the dry period.

For major storms, the geochemical composition of the rising-limb samples for each stream were combined proportionately to represent stream recharge. Rising-limb samples were assumed to represent the initial pulse of recharge moving through the aquifer and discharging at Barton Springs. Physicochemical properties such as temperature and dissolved oxygen were not measured in those storm samples that were collected from streams by autosamplers. These values, required for the modeling, were estimated on the basis of values measured for the routine samples collected from the same sites before and after the storm. Three samples collected from Barton Springs over each storm hydrograph, each with a characteristic that might be representative of discharge associated with a large pulse of surface water, were modeled for each storm response: (1) the third sample collected (typically 24–36 hours after the storm began, estimated to coincide with the timing of discharge of the largest pulse of surface water [Mahler and Massei, 2007]), (2) the sample with the lowest specific conductance, and (3) the sample associated with the highest daily mean discharge for Barton Springs.

For routine samples and the minor storm sample, results of inverse modeling with PHREEQC indicate that the proportion of stream recharge in Barton Springs discharge generally increased as hydrologic conditions became wetter (table 9). The proportion of Barton Springs discharge composed of stream recharge was lowest (0–8.3 percent) during the dry period and increased to as much as 81.3 percent during the wet period. There was a significant positive correlation between Barton Springs discharge and the proportion of that discharged composed of stream recharge (Kendall's tau = .80) (fig. 21). Inverse modeling results for routine samples also indicate that Barton Springs discharge includes a small component of saline groundwater (0–5.8 percent; table 9). The contribution of saline-zone groundwater to Barton Springs discharge decreased during the wet period when considered as a proportion, but it was less variable when considered as a rate, ranging from 0 to 1.2 ft^3/s over all modeled hydrologic conditions.

For the storms, results of inverse modeling with PHREEQC indicated that the proportion of Barton Springs discharge that was composed of stream recharge generally increased as hydrologic conditions became wetter (table 9), similar to results for routine samples. The modeled proportion of Barton Springs discharge composed of stream recharge for storm 1 was the least well constrained, ranging from 17.7 to 38.1 percent depending on how the initial water compositions were proportioned in the model (table 9). The daily mean discharge at Barton Springs increased by nearly a factor of 3 (from 17 to 46 ft^3/s) in response to storm 1. The decrease in specific conductance in response to storm 1 (fig. 9*B*) indicates that the likely source of the increase in discharge was stream recharge and not a pulse of matrix groundwater. As a result, it is implausible that matrix groundwater contributed as much as 78.4 percent of flow at Barton Springs, as indicated by inverse model results. To address this inconsistency, the composition of Barton Springs discharge for storm 1 also was modeled using only stream recharge and saline-zone groundwater as initial water compositions. Results for this model indicated that the composition of Barton Springs in response to storm 1 could also be accounted for almost exclusively (about 99 percent) by stream recharge undergoing geochemical reactions with mineral and gas phases. This result is more hydrologically plausible. Overall, results of PHREEQC modeling for storm 1 do not tightly constrain the potential mixture of water sources needed to account for the composition of Barton Springs discharge.

For storms 2 and 3, results of inverse modeling indicate that the endmember representing the composition of stream recharge accounts for more than half of the discharge from Barton Springs (table 9), with storm 2 ranging from 56.4–72.2 percent, and storm 3 ranging from 53.5–82.0 percent. For all three of the storms, inverse modeling results indicated that the water quality of recharging streams is an important control on the composition of discharge at Barton Springs. All three storms resulted in a decrease in calcite and dolomite saturation index (SI) values for Barton Springs discharge. A decrease in calcite SI values as a result of storms indicates that the storm response at Barton Springs included a component of water from the streams that had moved rapidly through the aquifer to Barton Springs and had not fully equilibrated with calcite and contrasts with equilibrium conditions during routine sampling conditions.

Inverse modeling was used to investigate the composition of samples collected from the Buda well. Groundwater from the Buda well has high concentrations of strontium relative to the Marbridge well and other wells in the Barton Springs zone (Garner and Mahler, 2007). The composition of groundwater from the Buda well cannot be accounted for by mixing of matrix and saline-zone groundwater. Oetting (1995) identified examples of fresh groundwater with high strontium concentrations in a narrow "transition" zone very near the down-dip limit of the aquifer and proposed that water-rock interaction with strontium-rich minerals (celestite or strontianite, or both) along fault contacts between Edwards aquifer and Glen Rose carbonates might account for these transitional compositions. The Buda well is located very close to the eastern side of the Barton Springs zone (fig. 1), where the transition to the saline zone occurs, and the geochemical composition of groundwater at this well is consistent with Oetting's (1995) description of a transitional water.

Synthesis of Factors Affecting Nutrients and Bacteria

Collection of routine and storm-associated samples from streams, wells, and Barton Springs over 17 months provided an opportunity to investigate the fate and transport of nutrients and *E. coli*, as well as other constituents, in surface water and groundwater during drought conditions and in response to a transition to wetter-than-normal conditions. The wide range of hydrologic conditions that occurred during this investigation had, in particular, a strong effect on processes affecting fate and transport of N species.

Table 9. Summary of PHREEQC (Parkhurst and Appelo, 1999) inverse modeling results in the Barton Springs zone, south-central Texas (2009–10).

[ft^3/s, cubic feet per second; do., ditto; --, not included in model]

Sample date	Hydrologic condition (dry period or wet period)	Barton Springs discharge (ft^3/s) mean daily value	Total estimated stream recharge (ft^3/s) for sample date or storm total (for storms: rising limb, falling limb)	Estimated recharge by stream as a percentage of total estimated stream recharge for sample date or storm total (recharge during rising limb of the storm-runoff hydrograph plus recharge during the falling limb of the storm-runoff hydrograph)				
				Barton Creek	Williamson Creek	Slaughter Creek	Bear Creek	Onion Creek
			Routine sampling					
2/18/09	dry	16.8	4.0	97.0	0	0	3.0	0
2/18/09	dry	16.8	4.0	97.0	0	0	3.0	0
4/22/09	dry	18.7	5.2	90.0	0	0	10.0	0
4/22/09	dry	18.7	5.2	90.0	0	0	10.0	0
8/5/09	dry	13.7	.03	100	0	0	0	0
9/23/09	wet (directly after storm 1)	43	22.0	59.9	4.9	0	35.2	0
10/14/09	wet (between storm 1 and 2)	49.8	94.1	58.4	.9	6.5	25.5	8.7
1/5/10	wet (between storm 2 and 3)	71.3	93.8	37.0	2.3	3.1	19.2	38.4
2/10/10	wet	80.0	309.2	25.6	3.9	10.4	21.4	38.8
3/2/10	wet	91.0	224.1	22.6	2.9	6.7	14.3	53.5
			Storm sampling					
9/12/09	storm 1 (9/10/09–9/20/09)	39 (storm range: 17–46)	133.6 (79.6, 54.0)	0	16.7 (16.3, 24.1)	.8 (.8, 1.1)	82.5 (82.9, 74.8)	0
9/13/09	do.	46 (storm range: 17–46)	do.	do.	do.	do.	do.	do.
9/14/09	do.	40 (storm range: 17–46)	do.	do.	do.	do.	do.	do.
9/14/09	do.	40 (storm range: 17–46)	do.	do.	do.	do.	do.	do.
11/9/09	storm 2 (11/9/09–11/15/09)	51 (storm range: 50–53)	389.1 (185.3, 203.8)	32.7 (35.7, 30.9)	5.0 (6.9, 4.5)	7.3 (6.7, 7.4)	29.5 (28.6, 30.0)	25.5 (22.1, 27.2)
11/10/09	do.	52 (storm range: 50–53)	do.	do.	do.	do.	do.	do.
11/13/09	do.	53 (storm range: 50–53)	do.	do.	do.	do.	do.	do.
1/16/10	storm 3 (1/14/10–1/23/10)	78 (storm range: 70–80)	632.7 (249.8, 337.9)	23.9 (20.5, 27.2)	4.1 (4.4, 3.8)	13.6 (12.0, 13.9)	20.7 (22.4, 19.5)	37.7 (40.7, 35.5)
1/17/10		80 (storm range: 70–80)	do.	do.	do.	do.	do.	do.
1/18/09	do.	80 (storm range: 70–80)	do.	do.	do.	do.	do.	do.

Table 9. Summary of PHREEQC (Parkhurst and Appelo, 1999) inverse modeling results in the Barton Springs zone, south-central Texas (2009–10).—Continued

[ft^3/s, cubic feet per second; do., ditto; --, not included in model]

Sample date	PHREEQC model details[1-5]	Model results, proportion of initial water (percent)			Models found, minimal models found	Maximum fractional uncertainty in model (element concentrations)	Portion of Barton Springs discharge from saline-zone endmember (ft^3/s
		Saline-zone groundwater	Surface water (stream recharge)	Matrix groundwater			
	Routine sampling						
2/18/09	Initial: matrix, saline, and surface water (Barton Creek only)	5.0	0–0.8	94.2–95.0	6, 1	0.07	0.8
2/18/09	Initial: matrix, saline, and surface water (Bear Creek only)	5.0	0	95.0	4,1	.07	.8
4/22/09	Initial: matrix, saline, and surface water	4.1–4.5	4.1–8.3	87.6–91.4	13, 1	.08	.8
4/22/09	Initial: matrix, saline, and surface water (Bear Creek only)	5.5	0	94.5	8, 1	.08	1.03
8/5/09	Initial: matrix and saline water	5.8	--	94.2	16, 1	.07	.8
9/23/09	Initial: matrix, saline, and surface water	1.8	24.8–25.2	73.0–73.4	12, 2	.07	.8
10/14/09	Initial: matrix, saline, and surface water	0	51.6	48.4	9, 1	.10	0
1/5/10	Initial: matrix, saline, and surface water	0–0.8	61.1–72.6	27.4–38.0	14, 4	.03	0–.6
2/10/10	Initial: matrix, saline, and surface water	0	81.3	18.6	6, 2	.07	0
3/2/10	Initial: matrix, saline, and surface water	.7–1.3	63.0–69.8	29.4–36.0	12, 2	.04	.6–1.2
	Storm sampling						
9/12/09	Initial: matrix, saline, and surface water. Final: sample 3 of 9 over storm hydrograph	3.4–3.5	17.7–25.4	70.2–78.4	12, 2	.07	1.4
9/13/09	Initial: matrix, saline, and surface water. Final: sample 5 of 9 over storm hydrograph (associated with highest discharge)	1.4	22.7–22.8	75.8–75.9	8, 1	.05	0.6
9/14/09	Initial: matrix, saline, and surface water. Final: sample 6 of 9 over storm hydrograph (lowest specific conductance sample)	1.2–2.0	37.4–38.1	60.0–61.4	12, 2	.07	.5–.8
9/14/09	Initial: saline and surface water. Final: sample 6 of 9 over storm hydrograph (lowest specific conductance sample)	.7–.8	99.2–99.3	--	2, 2	.10	.3
11/9/09	Initial: matrix, saline, and surface water. Final: sample 2 of 9 over storm hydrograph; (lowest specific conductance sample)	0–.3	56.4–63.2	36.8–43.3	12, 1	.04	0–2
11/10/09	Initial: matrix, saline, and surface water. Final: sample 3 of 9 over storm hydrograph	0–.1	58.5–65.4	34.6–41.4	12, 3	.03	.1
11/13/09	Initial: matrix, saline, and surface water. Final: sample 7 of 9 over storm hydrograph (associated with highest discharge)	0–.6	62.1–72.2	27.8–37.3	16, 4	.03	0–3
1/16/10	Initial: matrix, saline, and surface water. Final: sample 3 of 9 over storm hydrograph	.9	53.5–53.8	45.3–45.6	16, 1	.09	.1
1/17/10	Initial: matrix, saline, and surface water. Final: sample 5 of 9 over storm hydrograph (lowest specific conductance sample)	0	76.6–82.0	18.0–23.4	3, 1	.05	0
1/18/09	Initial: matrix, saline, and surface water. Final: sample 6 of 9 over storm hydrograph (associated with highest discharge)	0	80.2	19.8	2, 1	.05	0

[1] Initial = initial water composition(s); matrix = matrix groundwater composition (on the basis of the sample collected from Marbridge well on 08/05/2009); saline = saline zone groundwater based on composition of well YD–58–50–840.

[2] Final water composition for all inverse models was Barton Springs discharge.

[3] Surface-water composition calculated (with PHREEQC) based on estimated recharge portion from each creek, unless otherwise noted; surface-water composition for storms based on proportional mix of rising-limb samples.

[4] Mineral and gas phases included for all models: calcite, celestite, dolomite, gypsum, quartz, carbon dioxide (gas), oxygen (gas), CaX_2 (calcium) exchange site), NaX (sodium exchange site).

[5] Phase transfer option for celestite, dolomite, and gypsum included only dissolution

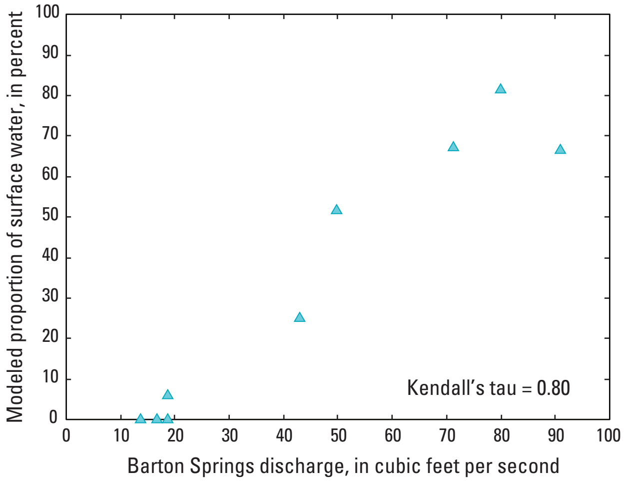


Figure 21. Relation between Barton Springs discharge (daily mean for U.S. Geological Survey station no. 08155500, Barton Springs at Austin, Tex.) and the modeled proportion of Barton Springs discharge that is composed of stream recharge based on PHREEQC (Parkhurst and Appelo, 1999) inverse model results (detailed in table 9). For model results that included a range of stream proportions, the midpoint is shown and used for statistical analysis.

Effects of Changes in Hydrologic Conditions on Geochemistry

This investigation provided the opportunity to examine the geochemical responses of surface water, groundwater, and Barton Springs to drought conditions and to the wetter-than-normal post-drought conditions that followed. The results highlight the strong influence of surficial processes on the geochemistry of stream water that recharges the aquifer and the geochemistry of groundwater in the Barton Springs segment and provide information on factors affecting the fate and transport of nutrients and bacteria at the surface and within the aquifer. Stream chemistry during the dry period was assessed primarily at Barton Creek. As a consequence of the drought, geochemistry at this site through the dry period reflected a decrease in nitrification in soils (see the section Factors Affecting Fate and Transport of Nutrients and Bacteria) and possibly an increase in the component of irrigation return flow. Specific conductance of water in Barton Creek was higher than that in groundwater at the Buda and Marbridge wells and similar to that at Barton Springs; concentrations of sodium, chloride, bromide, and boron increased between May 2009 and the onset of the wet period (fig. 7), consistent with an irrigation return-flow source, which generally is concentrated in salts (Richter and Kreitler, 1991). Concentrations of organic N in Barton Creek, for which return flow from irrigation with treated wastewater is a potential source (Hem, 1992), also increased through the dry period. As a result of low stream discharge (mostly less than 5 ft^3/s), however, the estimated load of organic N in recharge was small (fig. 18*A*). Because there was little rainfall resulting in runoff during the dry period, densities of *E. coli* and concentrations of suspended sediment were low and varied relatively little (fig. 11*A*).

During the dry period, the influence of the chemistry of surface water on that of groundwater was minimal because there was little to no flow in the streams and thus little to no recharge. The geochemistry of the water in the wells and in Barton Springs discharge during the dry period therefore reflects principally water from aquifer storage. The results of the geochemical modeling are consistent with this assumption (table 9). The geochemistry of the water at the groundwater wells varied little during the dry period (fig. 8), reflecting a minimal amount of stream recharge. Concentrations of suspended sediment below the LRL in samples from wells also were consistent with no contribution from stream recharge. *E. coli*, however, was detected at the Marbridge well during March–May 2009, a period during which there was some intermittent rainfall (fig. 6), which might indicate a source of bacterial contamination associated with locally recharging water.

The geochemistry of Barton Springs discharge during the dry period reflects an increasing proportional contribution from the saline zone, or from recharge from streams, or both. During the dry period, proportions of Barton Springs discharge composed of stream recharge (0–8.3 percent) and saline-zone water (4.1–5.8 percent) estimated from geochemical modeling were similar (table 9). An increase in concentrations of several major ions (magnesium, strontium, sodium, chloride, sulfate, bromide, and boron) in samples from Barton Springs through the latter part of the dry period (fig. 8) might indicate that, as Barton Springs discharge decreased through the dry period, the proportion of discharge composed of water from the saline zone increased. However, temporal patterns in concentrations of sodium, chloride, bromide, and boron during the latter part of the dry period were similar to those at Barton Creek and also might indicate that some recharge from Barton Creek was reaching Barton Springs, despite reports that recharge from this site goes to a local aquifer rather than to the Barton Springs segment (Barton Springs/Edwards Aquifer Conservation District, 2003). Low but detectable concentrations of suspended sediment at Barton Springs during the dry period (fig. 11*C*) might indicate that Barton Springs was receiving a small contribution of suspended sediment from stream or interstream recharge. Alternatively, concentrations of these ions in Barton Creek might reflect processes occurring in soils across the contributing zone during the dry period.

Rainfall and streamflow signaling the end of the drought resulted in changes in the aqueous geochemistry of water in the streams, wells, and Barton Springs. Water chemistry continued to change throughout the wet period, highlighting the influence of the quality of surface water on that of groundwater. Geochemical modeling indicated that the proportion of stream recharge in Barton Springs discharge increased through the wet period (table 9), reaching a maximum of about 80 percent of Barton Springs discharge in February 2010.

At the onset of the wet period, wetting of soils that were desiccated during the drought affected the geochemistry of water in the streams. During drought, constituents associated with weathering products are concentrated in soils by evaporation (Worrall and others, 2006). Constituents concentrated in soils are leached out when the soils become saturated (Richter and Kreitler, 1991). However, concentrations of sodium, chloride, bromide, and boron in Barton Creek—the major ions that increased during the latter part of the dry period—decreased immediately following the onset of the wet period (fig. 7). This pattern is consistent with irrigation return flow as the source of the elevated concentrations that were then diluted with meteoric water following the drought. Concentrations of orthoP in streams during the wet period were similar to those during the dry period (fig. 10*A*), indicating that leaching of soils likely is not a source of orthoP.

The increase in streamflow following the transition to the wet period resulted in increased loads of organic N and NO_3+NO_2 in stream recharge. At Barton Creek, the concentration of organic N decreased in response to the onset of the wet period (fig. 10*A*), likely as a result of resumption of nitrification in soils (see the section Factors Affecting Fate and Transport of Nutrients and Bacteria). The load of organic N in Barton Creek recharge increased (fig. 18*A*), however, because the decrease in concentration was more than offset by the increase in streamflow. Similarly, loads of organic N in the other streams (which were near zero or zero during the dry period), and therefore in total stream recharge, increased as well (fig. 18*A*). In the case of NO_3+NO_2, concentrations and recharge from streams were much less during the dry period than during the wet period (figs. 3 and 10*A*). Consequently, the transition from dry to wet conditions resulted in a large increase in the load of NO_3+NO_2 in stream recharge, which continued to increase during most of the wet period (fig. 18*B*).

In general, during the wet period, concentrations of major ions in samples from the Marbridge well and from Barton Springs became more similar to those in samples from the streams, consistent with the large contribution of recharge from streams to Barton Springs discharge, which was estimated by geochemical modeling to have reached about 80 percent by February 2010 (table 9). Many of the changes in geochemistry at the Marbridge well and at Barton Springs were similar, whereas the geochemistry at the Buda well was relatively unchanging, consistent with conduit control of the first two and matrix control of the latter (much of the water issuing from Barton Springs is reported to reach the springs through conduit flow paths [Barton Springs/Edwards Aquifer Conservation District, 2003; Mahler and Massei, 2007]). At the onset of the wet period, specific conductance and concentrations of those major ions that increased during the latter part of the dry period (sodium, chloride, bromide, and boron) in Barton Springs decreased rapidly to concentrations more similar to those in water from the Marbridge well (figs. 8 and 9). These changes are consistent with dilution of those constituents as a result of the rapid infiltration of recharge from reactivated streamflow. Specific conductance and concentrations of those major ions at the Marbridge well and Barton Springs then varied similarly during the remainder of the wet period (figs. 8 and 9). Densities of *E. coli* and concentrations of suspended sediment generally were higher and more variable in samples from wells and from Barton Springs during the wet period than during the dry period (fig. 11*C*) and are additional evidence of the influence of stream recharge on groundwater when streams are flowing.

Factors Affecting Fate and Transport of Nutrients and Bacteria

The fate and transport of N species and *E. coli* in surface water and groundwater were affected by hydrologic and climatologic conditions and geochemical processes occurring in the soils and in the aquifer. Processes and factors affecting fate and transport of N and P species and *E. coli* occur at the surface and within the aquifer and potentially include nitrification, surface runoff, dilution, filtration, residence time, and deposition and resuspension.

Effects of hydrologic and climatologic conditions and geochemical processes on the fate and transport of N species were manifested in two ways: (1) the geochemical processes in soils that affect N speciation and (2) the amount of recharge to and discharge from the aquifer, which affects loads of N species. During the dry period, lack of rainfall and the transition from winter to summer temperatures resulted in progressive desiccation of soils. During drought conditions, enhanced evaporation concentrates soil-water solutes (Reynolds and Edwards, 1995), and vegetation can be damaged by stress, which reduces uptake of nutrients (Reynolds and others, 1992). These combined processes result in an accumulation of nitrogen in the soil and large increases in soil-water nitrate (Reynolds and Edwards, 1995) but do not necessarily result in an increase in nitrate concentrations in surface water because of a lack of leaching and runoff (Burt and others, 1988). Additionally, when soils become very dry, nitrification of organic nitrogen to nitrate may be limited because of moisture stress (Wetselaar, 1968; Reynolds and Edwards, 1995), causing an accumulation of organic nitrogen in the soils. The result of these processes was observed in the concentrations of nutrients in samples collected from Barton Creek during the dry period, the only creek with sustained flow during most of the dry period. Increasingly reduced soil moisture inhibited the bacterial activity involved in nitrification of organic N to nitrate: concentrations of organic N exceeded those of nitrate and increased through the latter half of the dry period as temperatures increased. Concentrations of NO_3+NO_2, which were relatively low, peaked in April 2009 and then decreased through the remainder of the dry period (fig. 10*A*) in response to increasing inhibition of nitrification. Although such changes were not observed for the other streams because there was no flow, similar processes likely were occurring in the soils of all the watersheds.

During the dry period, organic N was not detected at the groundwater wells or at Barton Springs, because of the small amount of stream recharge, or because of nitrification of organic N within the aquifer, or both. Concentrations of NO_3+NO_2 at the three sites varied little and were similar in water at the two wells and slightly higher (about 0.2 mg/L) at Barton Springs (fig. 10*B*, *C*). During the dry period, loads of organic N in stream recharge were very small (fig. 18*A*), and any NO_3+NO_2 produced by nitrification likely was sufficiently small that it did not affect NO_3+NO_2 concentrations in the aquifer.

Frequent rainfall began in September 2009, rewetting soils and greatly affecting N dynamics. Rewetting of soils following a drought results in a flush of nitrification (Lucey and Goolsby, 1993; Reynolds and Edwards, 1995), which has been reported to be proportional to the length of the preceding dry period, the dryness of the soils, and the drying temperature (Birch, 1960) (the summer of 2009 was the ninth warmest on record for the State of Texas [National Oceanic and Atmospheric Administration, 2011]). As a consequence, during the immediate post-drought period, runoff and soil leachate contains elevated concentrations of nitrate, and elevated concentrations of nitrate in soil water can persist for months (Reynolds and others, 1992; Lucey and Goolsby, 1993) or even years (Burt and others, 1988) following a drought. Nitrogen dynamics in the Barton Springs zone following the onset of the wet period conformed to these patterns. Concentrations of organic N in samples from streams generally decreased through the wet period (fig. 10*A*) as a result of reactivation of nitrification, or depletion of organic N stored in soils by leaching, or both. Concentrations of NO_3+NO_2 in all of the streams during the wet period were elevated relative to the dry period (fig. 10*A*) and to historical concentrations for similar stream discharges (Mahler and others, 2011), and the elevated concentrations persisted throughout the wet period (fig. 10*A*). The magnitude of the increases in NO_3+NO_2 concentrations was unprecedented relative to increases that occurred following similar historical extended periods of dry weather (Mahler and others, 2011). The high NO_3+NO_2 concentrations measured in streams during this investigation therefore likely occurred as the result of climatic conditions coupled with an additional factor, such as greater nitrogen loading in the watersheds, as described by Mahler and others (2011). This study investigated only a single cycle of drought to post-drought conditions, but similar nitrogen response likely would occur for similar conditions in the future. Prolonged periods of elevated N concentrations following droughts might become more frequent if N loading to the watersheds continues to increase or if climate change results in more frequent or more severe drought cycles, as has been forecast for Texas (Banner and others, 2010).

Processes within the aquifer also affected the fate of N species. Water in the Barton Springs segment is oxic (the minimum dissolved oxygen concentration of any sample collected during this investigation was 3.92 mg/L), and oxic conditions are required for the nitrification of organic N to nitrate. During the wet period, estimated mean monthly loads of organic N in stream recharge were greater than those in Barton Springs, and dissolved oxygen concentrations in Barton Springs discharge were significantly less than those in stream recharge (table 5), consistent with nitrification within the aquifer. Organic N in storage in the aquifer would also likely undergo nitrification in oxic aquifer conditions. Nitrification involves the oxidation of organic N to NO_3 and the reduction of dissolved oxygen, consuming dissolved oxygen in the process. The consumption of dissolved oxygen has biological relevance in this system because survival of the Barton Springs salamander (*Eurycea sosorum*) is compromised below a dissolved-oxygen concentration of 3.4 mg/L (Woods and others, 2010). Oxic conditions within the Barton Springs segment preclude denitrification, which is the principal process attenuating nitrate in groundwater (Dubrovsky and others, 2010). Denitrification requires a dissolved oxygen content less than 0.5 mg/L at most and ideally less than 0.2 mg/L (van Haandel and van der Lubbe, 2007).

Concentrations of NO_3+NO_2 in Barton Springs are, under most conditions, higher than those in surface water (Mahler and others, 2011); when no recharge is occurring, concentrations historically have been about 1.50 mg/L (Mahler and others, 2006; Mahler and Garner, 2009). During the period of this investigation, however, concentrations of organic N in samples from streams exceeded those in samples from Barton Springs. The mass balance of total N loads estimated from modeling indicated that the total load of total N (the sum of organic N and NO_3+NO_2) recharging the aquifer and the total load discharging from Barton Springs during the period of the investigation (fig. 19; table 8) were not significantly different. Differences in the timing of recharge and discharges of loads were marked, however: loads discharging from Barton Springs during the dry period exceeded those entering as stream recharge, and those entering as stream recharge during the wet period exceeded those discharging from Barton Springs (fig. 19; table 8). This pattern indicates that total N entering the aquifer during periods of high recharge likely goes into storage and then discharges gradually as water-level altitudes in the aquifer decrease. The proportion of total N in recharge as organic N is greater than that in spring discharge (fig. 19; table 8) and is hypothesized to nitrify to NO_3 within the aquifer, accounting for higher concentrations of NO_3+NO_2 in Barton Springs discharge than in stream recharge. This investigation did not assess all potential sources of recharge to the Barton Springs segment, and other sources, such as diffuse recharge through soils and stream recharge originating downstream from the sites where samples were collected for this investigation, are additional sources of N species.

Dilution was not an important factor affecting NO_3+NO_2 concentrations in the streams or in Barton Springs during the period of this investigation. There was not an inverse relation between stream discharge and NO_3+NO_2 concentration measured in samples collected from any of the five streams, which means that NO_3+NO_2 in the streams was not diluted as flow rate increased. Indeed, the load of NO_3+NO_2 in the streams and Barton Springs increased substantially through the wet period (fig. 18*B*), during which discharge from Barton Springs increased steadily (fig. 2). Nitrate in the Barton Springs segment has been shown, based on samples collected as recently as 2005, to be diluted by stream recharge (Mahler and others, 2006; Mahler and Garner, 2009). This dilution was manifested by an inverse correlation between nitrate concentrations measured from 1990 to 2008 at Barton Springs and spring discharge (Mahler and others, 2011). Nitrate plus nitrite concentrations in streams during the period of this investigation, however, were elevated relative to concentrations measured during 1990–2008 for similar streamflows, and NO_3+NO_2 concentrations measured at Barton Springs during the period of this investigation were positively correlated with spring discharge (Mahler and others, 2011). The maximum concentration measured during the wet period (1.77 mg/L), when recharge was greatest, exceeded that during the dry period (1.56 mg/L), when recharge was minimal, indicating that recharge from streams was not effective at diluting NO_3+NO_2 concentrations. Concentrations of NO_3+NO_2 at Barton Springs during the period of this investigation also were higher, relative to discharge, than they were during 1990–2008 (Mahler and others, 2011). The effect of higher concentrations of NO_3+NO_2 in recharge also is evident in the response of NO_3+NO_2 concentrations in Barton Springs to storms, for which stream recharge provided little dilution (fig. 15*A*).

The effect of dilution on P species in the aquifer was affected by flow conditions. In routine samples, concentrations of orthoP in samples from Barton Springs and the two groundwater wells exceeded those in stream samples (table 6), indicating a likely geologic source for the orthoP and dilution of orthoP concentrations in groundwater by stream recharge. Following storms, however, orthoP concentrations at the Williamson Creek and Bear Creek sites were elevated relative to those from other streams and those in Barton Springs, indicating a likely anthropogenic source and dilution or sorption of P within the aquifer. Elevated concentrations of all P species measured in storm samples from streams relative to those in routine samples indicates that storm runoff is a likely transport mechanism for P.

Dilution, deposition and resuspension, filtration, and bacterial die-off are fate processes that depend on flow condition and might be affecting densities of *E. coli* in the Barton Springs segment. During the dry period, densities of *E. coli* at Barton Springs and the Marbridge well were similar to those at Barton Creek, indicating little dilution of the bacteria during transport. In contrast, the very low (1 MPN or not detected) densities of *E. coli* at the Buda well indicate that, under low-flow conditions, these bacteria likely are filtered out or die off before reaching this site. During the wet period, however, median densities of *E. coli* were about 9 times as high at the stream sites (480 MPN/100 mL) than at Barton Springs (52 MPN/100 mL (table 7), indicating that dilution, die-off, or settling, or a combination of those, affected the fate and transport of the bacteria from recharge to discharge at Barton Springs. The gradual increase in *E. coli* densities in Barton Springs discharge throughout the wet period (fig. 11*C*), in contrast to the more variable patterns of densities in the streams (fig. 11*A*), indicates that bacteria in stream recharge might be going into storage within the aquifer when aquifer levels are low and resuspended and transported as Barton Springs discharge increases. Densities of *E. coli* were greater at the Marbridge well where much of groundwater flow is likely through conduits than at the Buda well where much of the groundwater flow is likely through the aquifer matrix; these differences in *E. coli* density likely are a result of filtration processes and longer transit times conducive to bacterial die-off associated with matrix flow at the Buda well compared to the transit times at the Marbridge well.

There were relatively few correlations between concentrations of nutrients or densities of *E. coli* in samples from streams, wells, and Barton Springs and the explanatory variables of SSC and discharge during either routine or storm conditions. SSC was positively correlated with organic N at one stream site (storm samples only) and with *E. coli* at one well site. There were no positive correlations between SSC and orthoP. Discharge was positively correlated with concentrations of suspended sediment for storm samples from all streams except Williamson Creek but was not correlated with suspended-sediment concentrations at Barton Springs. Discharge was positively correlated with densities of *E. coli* at two stream sites but under different conditions (routine samples during the wet period at one site and storm samples at the other). SSC and *E. coli*, although often reported as associated (for example, Mahler and others, 2000; Characklis and others, 2005; and Flynn and others, 2008), were correlated at only the Marbridge well—not at any of the stream sites or at Barton Springs. The only correlation for these constituents noted for Barton Springs was a positive correlation between discharge and SSC for routine samples. The low number of correlations indicates that discharge and SSC are poor predictors of nutrient and bacteria occurrence in the Barton Springs zone.

Interactions Between Surface Water and Ground Water

Streams in five principal watersheds contribute stream recharge to the Barton Springs segment, but the proportion of recharge contributed and the geochemistry of recharge varied temporally and among streams. During the period of this investigation the only stream with nearly continuous flow was Barton Creek, which likely was receiving irrigation return flow. If urban development of the contributing zone increases, then other watersheds might receive sufficient irrigation return flow that they will contribute recharge to the Barton Springs segment during drought conditions. The quality of stream recharge during low-flow conditions might have a large effect on groundwater and Barton Springs water quality.

When conditions were wet and there was flow in the streams, the proportion of total stream recharge contributed by each creek, and thus its influence on water quality at Barton

Springs, varied temporally (fig. 3*B*). The onset of the wet period triggered continuous flow in only Barton and Bear Creeks, and continuous flow in all five streams did not occur until a full month later. During the first part of the wet period, Barton and Bear Creeks contributed the largest proportion of stream recharge, but during the second part of the wet period stream recharge was dominated by recharge from Onion Creek. Because there are geochemical differences among the five streams (figs. 7, 10, and 11), differences in the proportion of recharge contribution from each stream affect water quality in the aquifer. For example, during the latter part of the wet period, when Onion Creek was contributing the largest estimated proportion of stream recharge (fig. 3*B*), concentrations of magnesium, sodium, chloride, and bromide in Barton Springs were intermediate between those at Onion Creek and those at the other four stream sites (figs. 7 and 8), evidence of the large influence of Onion Creek on Barton Springs geochemistry. Concentrations of NO_3+NO_2 in samples from Onion Creek during the latter part of the wet period (median concentration of 1.24 mg/L for January–March 2010) were about twice those in samples from Barton Creek (median concentrations of 0.64 mg/L for the same period) and dominated the loading of NO_3+NO_2 to the aquifer (fig. 18*B*).

The proportional contribution of each stream to estimated stream recharge in response to storms varied among storms (fig. 5) as well as during routine sampling conditions. Virtually all of the estimated stream recharge that occurred as a result of storm 1 was from Bear and Williamson Creeks (fig. 5), which had elevated storm-associated concentrations of P species (fig. 10*A*; fig. 14*B*), *E. coli* densities (fig. 11*A*; fig. 16*A*), and SSC (fig. 16*B*) for storm 1 relative to other sites and other storms; concentrations of these constituents at Barton Springs were elevated following storm 1 relative to the other two storms. In contrast, recharge from Barton, Bear, and Onion Creeks dominated estimated stream recharge following storms 2 and 3. These results indicate that the water quality of Barton Springs, which changes rapidly in response to storms (Mahler and others, 2006; Mahler and Massei, 2007), is affected by the location of the rainfall (different stream watersheds) and whether antecedent moisture conditions are such that they trigger streamflow.

This investigation evaluated whether there were qualitative differences in water quality associated with the rising limb and with the falling limb of the hydrograph. There were no systematic differences among samples associated with the rising limb and falling limb by site, by storm, or by constituent. This indicates that, for the constituents measured for this investigation, there was no pronounced first-flush effect. This conclusion, however, cannot be extended to those constituents that were not measured, such as soluble pesticides and volatile organic compounds.

The geochemical response of groundwater in the two wells sampled for this investigation differed greatly, although both wells are in the Barton Springs segment. When no recharge was occurring, the geochemistry of the groundwater at the two wells was similar (fig. 8). Following the onset of recharge, however, the geochemistry of groundwater at the Marbridge well became quite variable and more similar to that of the streams and Barton Springs, whereas the geochemistry of groundwater at the Buda well varied little (fig. 8). These contrasting responses illustrate how interception of a conduit or conduits by a well can affect the geochemistry of the groundwater at a site, likely increasing its susceptibility to contamination.

The concentrations of most geochemical constituents at Barton Springs generally were intermediate between those of groundwater and those of the streams. This is in contrast to the usual conceptualization of groundwater geochemistry, in which there is an evolution of groundwater from the point of recharge (streams) to the point of discharge (springs). During the dry period, discharge from Barton Springs was dominated by flow from the aquifer matrix, and its geochemistry was relatively unchanging; however, with the onset of stream recharge, the geochemistry of Barton Springs discharge changed rapidly, becoming more similar to that of the streams. The water quality at Barton Springs therefore is influenced by climatic and hydrologic conditions; the water quality changes as the climate becomes drier or wetter and streamflow in the contributing zone decreases or increases. Climatic and hydrologic conditions (table 4) also affect the way in which the geochemistry of Barton Springs discharge changes in response to a storm. Changes in concentrations of major ions, nutrients, and suspended sediment and densities of *E. coli* were consistently the greatest for storm 1, the least for storm 2, and intermediate for storm 3. Storm 1 had the highest amount of rainfall and driest antecedent moisture conditions, yet resulted in flow sufficient to sample in only two of the streams (Williamson and Bear). Storm 2 was the first storm to result in flow in all five streams in more than 2 years, yet the geochemical response was relatively subdued, likely because of the relatively wet antecedent moisture conditions. These results indicate that the geochemical response of streams and groundwater to storms is not a simple linear response to rainfall amount but rather is a complex response that is affected by several factors, chief among them antecedent moisture conditions.

Summary

The Barton Springs zone, which comprises the Barton Springs segment of the Edwards aquifer and the watersheds to the west contributing to its recharge (the contributing zone), is in south-central Texas, an area that is undergoing rapid growth in population and in land area affected by development. There is interest, therefore, in establishing a baseline against which future potential changes in water quality related to increasing urbanization and associated wastewater production can be compared and in improving understanding of the factors affecting the fate and transport of nutrients and bacteria from the point of recharge to the point of discharge.

During November 2008–March 2010, a study to provide understanding of nutrients and bacteria in the Barton Springs zone was conducted by the U.S. Geological Survey (USGS), in cooperation with the Texas Commission on Environmental Quality. The primary objectives of the study were to characterize occurrence of nutrients and bacteria in the Barton Springs zone under a range of flow conditions; to improve understanding of the interaction between surface-water quality and groundwater quality; and to evaluate how factors such as streamflow variability and dilution affect the fate and transport of nutrients and bacteria in the Barton Springs zone.

During the course of this investigation, hydrologic conditions underwent a transition from exceptional drought to wetter than normal. Between November 1, 2008, and September 9, 2009 is referred to as the dry period. Between September 10, 2009, and March 31, 2010 is referred to as the wet period. This investigation therefore offered an opportunity to monitor constituents under a wide range of aquifer flow conditions and to investigate the response of water quality in a karst system to different hydrologic conditions.

The geochemistry of water samples collected routinely (every 3 to 4 weeks) and in response to storms were used to evaluate the geochemistry of surface water in five streams that provide much of the recharge to the Barton Springs zone (Barton, Williamson, Slaughter, Bear, and Onion Creeks), of groundwater at two wells (the Marbridge well [YD–58–50–704] and the Buda well [LR–58–58–403]), and of discharge from the main orifice of Barton Springs in Austin, Tex. (hereinafter referred to as "Barton Springs"). Physical properties, major ions, nutrients (nitrogen and phosphorus species), suspended-sediment concentration (SSC), and *Escherichia coli* (*E. coli*) density were measured in all samples.

Concentrations of major ions in samples collected from some sites changed following the onset of the wet period. Concentrations of major ions could not be compared between dry and wet periods for most stream samples because Barton and Bear Creeks were the only streams with some sustained flow during the dry period. In samples collected from these two sites, concentrations of most noncarbonate constituents measured in routine samples were higher during the wet period than during the dry period. During the dry period, concentrations of major ions in groundwater at the Buda and Marbridge wells were similar and varied little. During the wet period concentrations of most major ions at the Buda well were similar to those measured during the dry period, but concentrations of most major ions at the Marbridge well were different and more variable than during the dry period and the geochemical composition of groundwater at the Marbridge well became more similar to that of water from the streams. Concentrations of most major ions at Barton Springs were intermediate between concentrations at stream and groundwater sites during the dry period, and became more similar to those at stream sites during the wet period.

Nitrogen (N) and phosphorus (P) species responded differently to the change in climatic conditions from dry to wet. Organic N represented the majority of total N in routine samples from streams during the dry period (median of 79 percent) but represented a much smaller fraction of total N during the wet period (median of 18 percent). During the dry period, concentrations of nitrate plus nitrite (NO_3+NO_2) at those streams where samples could be collected (Barton, Williamson, and Bear Creeks) were low relative to concentrations at the same sites during the wet period and were lower than NO_3+NO_2 concentrations during the dry period at the groundwater and spring sites. Temporal patterns in concentrations of organic N and NO_3+NO_2 in streams were consistent with loading of N species to soils during the dry period followed by leaching during the wet period. In contrast, concentrations of orthophosphate (orthoP) in streams were similar and low (median concentration 0.005 milligrams per liter [mg/L]) throughout the period of the investigation. Concentrations of NO_3+NO_2 at the two groundwater wells during the dry period were similar and varied little. Nitrate plus nitrite concentrations at the Buda well varied little throughout the entire period of the investigation, but NO_3+NO_2 concentrations at the Marbridge well increased following the onset of the wet period and then decreased to a concentration slightly higher than that measured during the dry period. Concentrations of orthoP in routine samples from the wells (median concentration 0.010 mg/L) were about twice those of routine samples from streams, indicating that the orthoP might have a geologic source. Concentrations of orthoP at the Marbridge well became more variable following the onset of the wet period and generally followed the same temporal pattern as NO_3+NO_2 at that site. At Barton Springs, temporal patterns of concentrations of N species and orthoP were similar to those at the Marbridge well, indicating that water at both sites is affected by stream recharge.

Densities of *E. coli* generally were low (less than [<] 100 most probable number per 100 mL [MPN/100 mL]) at Barton and Bear Creeks during the dry period. During the wet period, densities of *E. coli* in routine samples collected from streams varied from less than 10 to 4,800 MPN/100 mL. Densities of *E. coli* were less than the LRL (1 MPN/100 mL) at both groundwater well sites during the dry period. During the wet period, densities were less than the LRL at the Buda well and low but quantifiable at the Marbridge well. Densities of *E. coli* in routine samples from Barton Springs were low (<30 MPN/100mL) during the dry period and were higher and more variable during the wet period (2–450 MPN/100 mL).

Concentrations of major ions at stream sites and Barton Springs responded to different degrees to three major storms (storms 1–3). Concentrations of most major ions at some stream-sampling sites were lower in storm samples than in routine samples, and concentrations in storm samples were lower for storms 1 and 3 than for storm 2. Concentrations of major ions in samples collected at Barton Springs in response to storms overall were lower than those in routine samples collected prior to the storms, and the magnitude of change in concentrations of most constituents following each storm was largest when antecedent moisture conditions were driest (storm 1).

Concentrations of nutrients at stream sites and Barton Springs responded to different degrees to the three major storms. The median concentration of organic N in storm samples from streams was significantly greater than that for routine samples; concentrations were highest for storm 1 and lowest for storm 2. The median concentration of NO_3+NO_2 for storm samples from streams, however, was not significantly different from that for routine samples, and there was no systematic pattern in concentrations of NO_3+NO_2 among the three major storms. Concentrations of orthoP in storm samples from Williamson and Bear Creeks were about 3 and 5 times greater than those in routine samples, respectively, but orthoP in samples from the other three stream sites in most cases was not detected or was reported as estimated at a concentration less than the LRL. Concentrations of organic N in storm samples collected from Barton Springs were lower than concentrations in storm samples collected from streams in response to the same storms, but were higher than those measured in routine samples from Barton Springs. Concentrations of NO_3+NO_2 in storm samples from Barton Springs were generally higher than the concentrations in samples collected from streams in response to the same storms. The median concentration of NO_3+NO_2 for storm samples from Barton Springs was significantly higher than the median concentration for routine samples. A decrease in NO_3+NO_2 at Barton Springs in response to major storms occurred in response to storm 2, but not in response to storm 1 or storm 3. There was no significant difference between median concentrations of any P species for storm samples and routine samples collected from Barton Springs.

Densities of *E. coli* at stream sites and Barton Springs responded to different degrees to the three major storms. Densities of *E. coli* at most stream sites were elevated in storm samples relative to routine samples. Densities were highest in response to storm 1 and lowest in response to storm 2. Maximum densities of *E. coli* in storm samples from Williamson and Bear Creeks were about an order of magnitude higher than those in storm samples from Barton, Onion, and Slaughter Creeks. Densities of *E. coli* at Barton Springs also were elevated in storm samples relative to routine samples, and were lower than or similar to those in storm samples from the streams, indicating that some dilution or deposition, or both, is occurring.

Quantifying loads of organic N and NO_3+NO_2 recharging and discharging from the Barton Springs segment provided information on the fate and transport of N species from recharge to discharge. Mean monthly loads of organic N and NO_3+NO_2 in stream recharge and Barton Springs discharge were estimated with the model LOADEST. Estimated mean monthly loads of organic N both in stream recharge and in Barton Springs discharge were much lower during the dry period than during the wet period. During the wet period, mean monthly loads of organic N in stream recharge on average were about 6 times greater than those in Barton Springs discharge, indicating removal of organic N is occurring within the aquifer, likely by ammonification and nitrification. The conversion within the aquifer of organic N in stream recharge to nitrate might account for the higher concentrations of NO_3+NO_2 that have been measured historically in Barton Springs discharge and in groundwater than in streams. The loading of total N over the course of the investigation in stream recharge (162 kilograms per day [kg/d]) and in Barton Springs discharge (157 kg/d) were not significantly different. The timing of the loading, however, was variable, with virtually all of the loading of total N to the aquifer by stream recharge occurring during the wet period. The relation between nitrogen load in recharge to the aquifer and nitrogen load discharging from the aquifer is not linear: nitrogen previously loaded to and stored in the aquifer discharged during the dry period when stream recharge was very low or zero; during the wet period nitrogen was recharged to the aquifer, with much of it going into storage.

Inverse modeling with the geochemical model PHREEQC was used to approximate mixing proportions of endmember water compositions (matrix groundwater, saline-zone groundwater, and stream recharge) and mass-transfer processes that could feasibly produce the concentrations of constituents measured in the groundwater samples. Results of inverse modeling with PHREEQC indicated that the proportion of stream recharge in Barton Springs discharge generally increased as hydrologic conditions became wetter. The proportion of Barton Springs discharge composed of stream recharge was lowest (0–8.3 percent) during the dry period and increased to as much as 81.3 percent during the wet period. There was a significant positive correlation between Barton Springs discharge and the modeled proportion of stream recharge in Barton Springs discharge. Results of PHREEQC inverse modeling for storm 1 did not tightly constrain the potential mixture of water sources needed to account for the composition of Barton Springs, but for storms 2 and 3, results of inverse modeling indicated that the proportion of stream recharge in Barton Springs discharge made up more than half of the discharge.

Stream geochemistry during the dry period, as assessed at Barton Creek, reflected a decrease in nitrification in soils and possibly an increasing proportion of irrigation return flow, both as a consequence of the drought. The influence of the chemistry of surface water on that of groundwater was minimal, however, because there was little to no flow in the streams and thus little to no recharge. The geochemistry of the water at the groundwater wells varied little during the dry period; the geochemistry of Barton Springs discharge during the dry period reflected an increasing proportional contribution from the saline zone, or from the small amount of recharge from streams (fig. 3*B*), or both. Rainfall and streamflow signaling the end of the drought resulted in changes in the aqueous geochemistry of water in the streams, wells, and Barton Springs. The transition from dry to wet conditions resulted in a large increase in the load of NO_3+NO_2 in stream recharge. During the wet period, concentrations of major ions in samples from the Marbridge well and from Barton Springs became more similar to those in samples from the streams, consistent with the large contribution of recharge from streams to Barton Springs discharge, which was estimated by geochemical modeling to have reached about 80 percent by February 2010.

The fate and transport of N species and *E. coli* in surface water and groundwater were affected by hydrologic and climatologic conditions and geochemical processes occurring in the soils and in the aquifer. During the dry period, increasingly reduced soil moisture inhibited the bacterial activity involved in nitrification of organic N to nitrate: concentrations of organic N in samples from Barton Creek exceeded those of nitrate and increased through the latter half of the dry period as temperatures increased. During the dry period, organic N was not detected at the groundwater wells or at Barton Springs, because of the small amount of stream recharge, or because of nitrification of organic N within the aquifer, or both. Concentrations of organic N in streams decreased through the wet period as a result of reactivation of nitrification, or depletion of organic N stored in soils by leaching, or both. Concentrations of NO_3+NO_2 in all of the streams during the wet period were elevated relative to the dry period and to historical concentrations for similar stream discharges; these concentrations persisted throughout the wet period. The elevated NO_3+NO_2 concentrations measured during this investigation likely occurred as the result of climatic conditions coupled with an additional factor, such as higher nitrogen loading in the watersheds. During the wet period, estimated mean monthly loads of organic N in stream recharge exceeded those in Barton Springs discharge, and dissolved oxygen concentrations in Barton Springs discharge were significantly less than those in stream recharge, indicating that nitrification likely was occurring within the aquifer. Conditions within the Barton Springs segment were oxic throughout the period of the investigation, precluding denitrification of nitrate.

Dilution was not a factor affecting NO_3+NO_2 concentrations in the streams or Barton Springs during the period of this investigation. Concentrations of NO_3+NO_2 in streams and in Barton Springs did not decrease as flow rate increased, and as a result the load of NO_3+NO_2 in the streams and Barton Springs increased substantially with increasing flow in the streams and discharge from Barton Springs. Concentrations measured at Barton Springs during the period of this investigation were positively correlated with spring discharge.

Dilution, deposition and resuspension, filtration, and bacterial die-off are fate processes that might be affecting densities of *E. coli* in the Barton Springs segment but depend on flow condition. During the dry period, there was little dilution of bacteria during transport to the Marbridge well site or to Barton Springs, but, filtration, or die-off, or a combination thereof, resulted in very low densities of *E. coli* at the Buda well. During the wet period, however, median densities of *E. coli* were about 9 times as high at the stream sites (480 MPN/100 mL) than at Barton Springs (52 MPN/100 mL), indicating that dilution, die-off, or settling, or a combination of those, affected the fate and transport of the bacteria from recharge to discharge at Barton Springs. The gradual increase in densities of *E. coli* at Barton Springs through the wet period indicates that bacteria might be stored within the aquifer when aquifer levels are low and might be resuspended and transported as Barton Springs discharge increases. Densities of *E. coli* were greater at the Marbridge well, where much of groundwater flow is likely through conduits, than at the Buda well, where much of groundwater flow is likely through the aquifer matrix; these differences in *E. coli* density likely are a result of filtration processes and longer transit times conducive to bacterial die-off associated with matrix flow. There were few correlations between concentrations of nutrients or densities of *E. coli* in samples from streams, wells, and Barton Springs and the explanatory variables of SSC and discharge during either routine or storm conditions. This indicates that these variables are poor predictors of nutrient and bacteria occurrence.

Interactions between surface water and groundwater have a strong control on groundwater geochemistry and quality. The proportion of recharge contributed to the Barton Springs segment and the geochemistry of recharge varied temporally and among streams. During the first part of the wet period, Barton and Bear Creeks contributed the largest proportion of stream recharge, but during the second part of the wet period stream recharge was dominated by recharge from Onion Creek. Because there are geochemical differences among the five streams, differences in the proportion of recharge contributed affected water quality in the aquifer. For example, concentrations of NO_3+NO_2 in samples from Onion Creek during the latter part of the wet period (median concentration of 1.24 mg/L for January–March 2010) were about twice those in samples from Barton Creek (median concentrations of 0.64 mg/L for the same period) and dominated the loading of NO_3+NO_2 to the aquifer. The proportional contribution of each stream to stream recharge in response to storms also varied among storms. Virtually all of the stream recharge that occurred as a result of storm 1 was contributed from Williamson and Bear Creeks, which consistently had the highest storm-associated concentrations of P species, SSC, and densities *E. coli*; concentrations of these constituents at Barton Springs were elevated following storm 1 relative to the other two storms. In contrast, recharge from Barton, Bear, and Onion Creeks dominated estimated stream recharge following storms 2 and 3. There were no systematic differences, however, between composite samples associated with the rising limb and composite samples associated with the falling limb of the hydrograph by site, by storm, or by constituent.

The concentrations of most geochemical constituents at Barton Springs generally were intermediate between those of groundwater and those of the streams. This is in contrast to the usual conceptualization of groundwater geochemistry, in which there is an evolution of groundwater from the point of recharge (streams) to the point of discharge (springs). During the dry period, discharge from Barton Springs was dominated by flow from the aquifer matrix, and its geochemistry was relatively unchanging; however, with the onset of stream recharge, the geochemistry of Barton Springs discharge changed rapidly, becoming more similar to that of the streams. The water quality at Barton Springs therefore is influenced by climatic and hydrologic conditions; the water quality changes as the climate becomes drier or wetter and streamflow in the contributing zone decreases or increases.

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Appendix. Quality Assurance and Quality Control

Quality-control (QC) data were collected to assess sample-collection procedures and laboratory analyses. QC samples were collected as described in the National Field Manual for the Collection of Water-Quality Data (Wilde, variously dated) and analyzed by the same laboratories and methods as the environmental samples. QC consisted of analysis of field- and equipment-blank samples, laboratory deionized (DI) water, and field-replicate samples (table 1.1). Blank samples were collected to evaluate whether sample collection, transport, and processing procedures introduced measurable amounts of the constituents of interest. Field-blank samples were collected by filling sample containers identical to those used to collect the environmental samples with laboratory-certified blank water at the field site. Field-blank samples were transported and processed in the same manner as were the environmental samples. The equipment blank was collected by drawing laboratory-certified organic-compound-free blank water through the collection line of an autosampler at one of the surface-water sites into containers identical to those used to collect the environmental samples. The DI water was analyzed to verify that the DI water at the U.S. Geological Survey Texas Water Science Center laboratory did not contain measurable quantities of the constituents of interest and was collected from the DI water tap at the center. After collection, the blank and DI water samples received the same treatment as did the environmental samples. Field-replicate samples were collected immediately after the associated environmental samples using the same sampling procedures.

The deviation between a replicate sample and environmental sample, computed in those cases where the analyte of interest was reported at a concentration greater than the laboratory reporting level (LRL) for both samples, was expressed as the relative percent difference (RPD) with the equation

$$RPD = |C_1 - C_2|/((C_1 + C_2)/2) \text{ x } 100, \tag{1}$$

where

C_1 is the constituent concentration, from the environmental sample; and
C_2 is the constituent concentration, in the same units, from the replicate sample.

Table 1.1. Summary of quality-control samples collected in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[QC, quality control]

Constituent or constituent group	Number of environmental samples	Number of field blanks	Number of equipment blanks	Number of laboratory deionized water blanks	Number of field replicates	Total number of QC samples
Nutrient	186	10	1	1	11	23
Major ions	186	10	1	1	11	23
Escherichia coli	220	10	0	0	8	18
Suspended sediment	189	10	1	0	9	20

An RPD was not computed in those cases where an analyte in one of the replicate sample pairs either was not detected or was detected at a concentration less than the LRL. Cases for which the analyte in both of the samples either was not detected or was detected at a concentration less than the LRL were defined as being in agreement. Cases for which the analyte was detected at a concentration equal to or greater than the LRL in one of the samples and not detected or detected at a concentration less than the LRL in the other were defined as in non-agreement. This distinction was necessary because of the large number of instances in which constituents were not detected or were detected at a concentration less than the LRL. RPDs of 10 percent or less indicate good agreement between paired results when the concentrations are sufficiently large relative to their associated LRL; however, RPDs for replicates with small concentrations are often large but do not necessarily indicate a lack of laboratory precision. For this investigation, constituents with large RPDs associated with small concentrations included nitrate, bromide, and *Escherichia coli* (*E. coli*), which are discussed in this section within the "Nutrients," "Major Ions," and "*Escherichia Coli*" subsections. In these instances, large RPDs indicated that low-level results should be evaluated qualitatively, rather than quantitatively.

Nutrients

All nitrogen (N) species concentrations are reported and discussed as milligrams per liter (mg/L) as N, and all phosphorus (P) species concentrations are reported and discussed as mg/L as P. Four types of QC samples were analyzed: field blanks, an equipment blank, a sample of DI water, and field replicates (table 1.1). There were no detections of nutrients in either the equipment blank or the DI water sample. For the field blanks, there were nine detections of nutrient constituents reported at an estimated concentration (quantifiable at a concentration less than the LRL) and two detections at a concentration exceeding the LRL (organic nitrogen plus ammonia [org N+NH_3] and nitrate plus nitrite [NO_3+NO_2]) (table 1.2). Org N+NH_3 was detected at 0.187 mg/L, which was about 10 percent of the response range observed in the environmental samples, and NO_3+NO_2 was detected at 0.036 mg/L, which was about 1.5 percent of the environmental response range (table 1.2).

Table 1.2. Summary of blank sample results for nutrients for quality-control samples collected in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[LRL, laboratory reporting level; mg/L, milligrams per liter; <, less than; ≥, greater than or equal to; wf, water filtered; wu, water unfiltered; NH_3, ammonia; org N, organic nitrogen; NO_3, nitrate; NO_2, nitrite; *, constituent not detected]

		Field blanks				Equipment blank				Laboratory deionized water			
Nutrient	LRL (mg/L)	Number of samples	Concentration maximum in blank samples (mg/L)	Number of detections < LRL	Number of detections ≥ LRL	Number of field blank samples	Concentration maximum in blank samples (mg/L)	Number of detections < LRL	Number of detections ≥ LRL	Number of field blank samples	Concentration maximum in blank samples (mg/L)	Number of detections < LRL	Number of detections ≥ LRL
Ammonia, wf	0.02	10	0.014	6	0	1	*	0	0	1	*	0	0
NH_3+orgN, wu	.1	10	.187	2	1	1	*	0	0	1	*	0	0
Nitrite, wf	.002	10	*	0	0	1	*	0	0	1	*	0	0
NO_3+NO_2, wf	.016	10	.036	1	1	1	*	0	0	1	*	0	0
Orthophosphate, wf	.008	10	*	0	0	1	*	0	0	1	*	0	0
Phosphorus, wf	.02	10	*	0	0	1	*	0	0	1	*	0	0
Phosphorus, wu	.02	10	*	0	0	1	*	0	0	1	*	0	0

Eleven field replicate pairs were collected (table 1.3). Results for all replicate pairs were reported for only NO_3+NO_2; for the remaining six nutrient constituents, those concentrations that were greater than the LRL generally were close in value to the LRL. As a result, several constituents had high RPD values, although the actual concentration variations represented were very small. For replicate pairs with concentrations that were reported as less than the LRL or quantified at a concentration below the LRL (qualified as estimated), RPDs were not calculated. Three replicate pairs for NO_3+NO_2 resulted in RPDs that exceeded 5 percent, two of which exceeded 10 percent. Because the detected concentrations were close in value to the LRL (fig. 1.1), however, the actual concentration variations represented were very small.

Major Ions

Twenty-three QC samples were analyzed for major ions: 10 field blanks, 1 equipment blank, 1 DI water sample, and 11 field replicates. There were three detections of major ions, all of which were in the DI water sample (table 1.4). Magnesium and strontium were detected in the DI water sample at concentrations below the LRL, and calcium was detected in the DI water sample at a concentration of 0.096 mg/L, about 4 times the LRL value of 0.022 mg/L. Concentrations of major ions detected in the DI water sample were negligible relative to the range of concentrations measured in environmental samples.

Eleven field replicate pairs were collected for major ions and analyzed for RPD (table 1.5). There was one instance each of an RPD greater than 5 percent for alkalinity, bicarbonate, sodium, fluoride, and boron. Four RPD values for bromide were greater than 5 percent (fig. 1.2); the maximum RPD of 27 percent represented a concentration difference of 0.052 mg/L. The

Table 1.3. Summary of field replicate results for nutrients for quality-control samples collected in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[LRL, laboratory reporting level; RPD, relative percent difference; mg/L, milligrams per liter; <, less than; ≥, greater than or equal to; wf, water filtered; wu, water unfiltered; NH_3, ammonia; orgN, organic nitrogen; NO_3, nitrate; NO_2, nitrite; --, not measured or not applicable]

Nutrient	Number of environmental and replicate sample pairs with detected concentrations > LRL and calculated RPDs	Number of environmental and replicate samples in agreement[1]	Number of environmental and replicate samples in non-agreement[2]	Replicate pairs with < 5 percent RPD	Replicate pairs with ≥ 5 percent RPD	Median RPD (percent)	Maximum RPD (percent)	Maximum concentration deviation (mg/L)
Ammonia, wf	1	10	0	1	0	3.2	3.2	0.037
NH_3+orgN, wu	5	3	3	1	4	7.0	33.0	.071
Nitrite, wf	5	6	0	4	1	1.2	5.9	.00037
NO_3+NO_2, wf	11	0	0	8	3	.6	56.0	.0735
Orthophosphate, wf	6	5	0	0	6	10.2	26.0	.0177
Phosphorus, wf	0	11	0	--	--	--	--	--
Phosphorus, wu	1	10	0	1	0	4.7	4.7	.0215

[1] Cases for which the analyte in both the environmental sample and the replicate sample was not detected or was detected at an estimated concentration < LRL.

[2] Cases for which the analyte was detected at a concentration ≥ LRL in one of the samples and not detected or < LRL in the other sample.

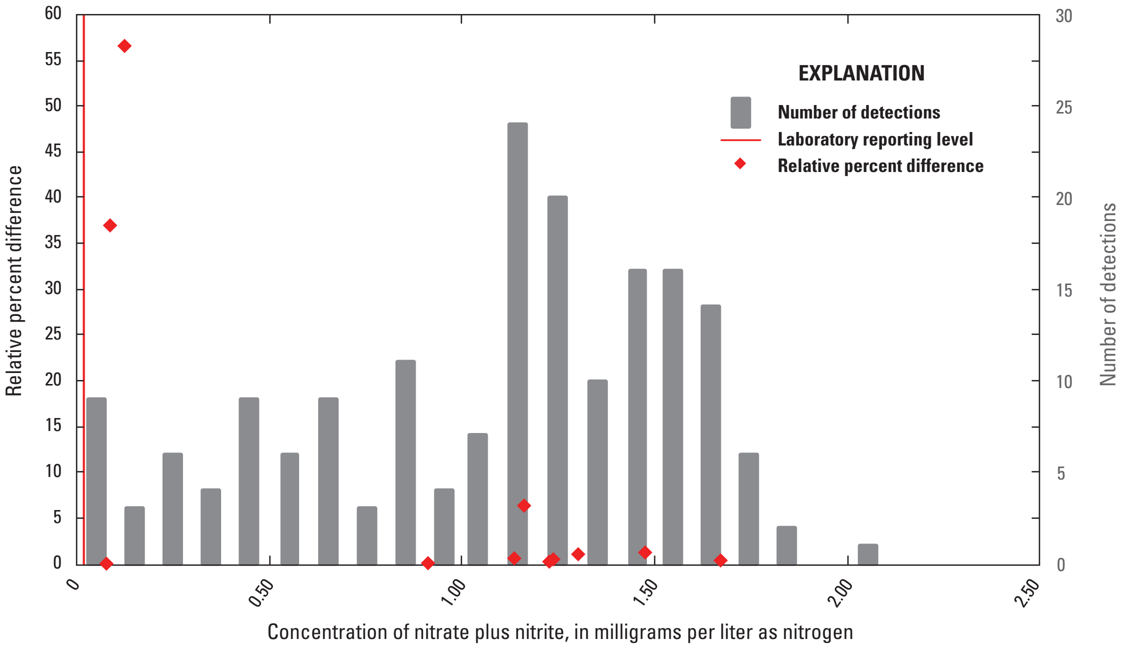

Figure 1.1. Bar graph showing the number of detections within a range of concentrations, relative percent difference for replicate pairs, and laboratory reporting level for nitrate plus nitrite analyses for quality-control samples, Barton Springs zone, south-central Texas (November 2008–March 2010).

Table 1.4. Summary of blank sample results for major ions for quality-control samples collected in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[LRL, laboratory reporting level; mg/L, milligrams per liter; <, less than; ≥, greater than or equal to; wf, water filtered; --, not sampled or not analyzed; *, constituent not detected

		Field blanks				Equipment blank				Laboratory deionized water			
Major ion	LRL (mg/L)	Number of blank samples	Maximum concentration in blank samples (mg/L)	Number of detections < LRL	Number of detections ≥ LRL	Number of blank samples	Maximum concentration in blank samples (mg/L)	Number of detections < LRL	Number of detections ≥ LRL	Number of blank samples	Maximum concentration in blank samples (mg/L)	Number of detections < LRL	Number of detections ≥ LRL
Alkalinity, wf	1	0	--	--	--	0	--	--	--	0	--	--	--
Bicarbonate,wf	1	0	--	--	--	0	--	--	--	0	--	--	--
Carbonate, wf	1	0	--	--	--	0	--	--	--	0	--	--	--
Calcium, wf	0.044	10	*	0	1	1	*	0	0	1	.096	0	1
Magnesium, wf	.016	10	*	1	1	1	*	0	0	1	.01	1	0
Strontium, wf	.4	10	*	0	1	1	*	0	0	1	.296	1	0
Sodium, wf	.12	10	*	0	0	1	*	0	0	1	*	0	0
Potassium, wf	.044	10	*	0	0	1	*	0	0	1	*	0	0
Chloride, wf	.12	10	*	0	0	1	*	0	0	1	*	0	0
Sulfate, wf	.18	10	*	0	0	1	*	0	0	1	*	0	0
Fluoride, wf	.08	6	*	0	0	1	*	0	0	1	*	0	0
Bromide, wf	.020	10	*	0	0	1	*	0	0	1	*	0	0
Boron, wf	2.0	10	*	0	0	1	*	0	0	1	*	0	0

Table 1.5. Summary of replicate sample results for major ions for quality-control samples collected in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[LRL, laboratory reporting level; RPD, relative percent difference; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; ≥, greater than or equal to; wf, water filtered; wu, water unfiltered]

Nutrient	Number of environmental and replicate sample pairs with detected concentrations > LRL and calculated RPDs	Number of environmental and replicate samples in agreement[1]	Number of environmental and replicate samples in non-agreement[2]	Replicate pairs with < 5 percent RPD	Replicate pairs with ≥ 5 percent RPD	Median RPD (percent)	Maximum RPD (percent)	Maximum concentration difference	Unit
Alkalinity, wf	11	0	0	10	1	1.5	5.5	15.2	mg/L
Bicarbonate,wf	11	0	0	10	1	1.5	5.6	18.90	mg/L
Carbonate, wf	11	0	1	10	0	0	0	0	mg/L
Calcium, wf	11	0	0	11	0	1.0	2.8	2.5	mg/L
Magnesium, wf	11	0	0	11	0	.8	1.8	.41	mg/L
Strontium, wf	11	0	0	11	0	1.1	2.7	260	µg/L
Sodium, wf	11	0	0	10	1	.9	5.7	.469	mg/L
Potassium, wf	11	0	0	11	0	1.1	2.9	.067	mg/L
Chloride, wf	11	0	0	11	0	.6	1.4	.826	mg/L
Sulfate, wf	11	0	0	11	0	.3	.7	.358	mg/L
Fluoride, wf	5	0	0	4	1	1.5	11	.027	mg/L
Bromide, wf	11	0	0	7	4	2.2	27	.052	mg/L
Boron, wf	11	0	0	10	1	1.9	8.3	8.05	µg/L

[1] Cases for which the analyte in both the environmental and replicate sample was not detected or was detected at an estimated concentration less than the LRL.

[2] Cases for which the analyte was detected at a concentration ≥ LRL in one of the samples and not detected or < LRL in the other sample.

mean RPD for bromide was 2.2 percent, which represented a deviation of less than 0.001 mg/L for the range of concentrations measured in environmental samples (<0.02 to 0.40 mg/L).

Escherichia Coli

Ten field blank samples (three of which had hold times exceeding the recommended hold time of 6 hours) were analyzed for *E. coli*, but there were no detections (table 1.6). Eight field replicate pairs were collected (table 1.7), four of which had hold times exceeding 6 hours. Densities of *E. coli* were analyzed as the most probable number per 100 milliliters (MPN/100 mL). *E. coli* densities for the replicate pairs ranged from less than 1 to 461 MPN/100 mL (fig. 1.3). Seven of the replicate pairs were

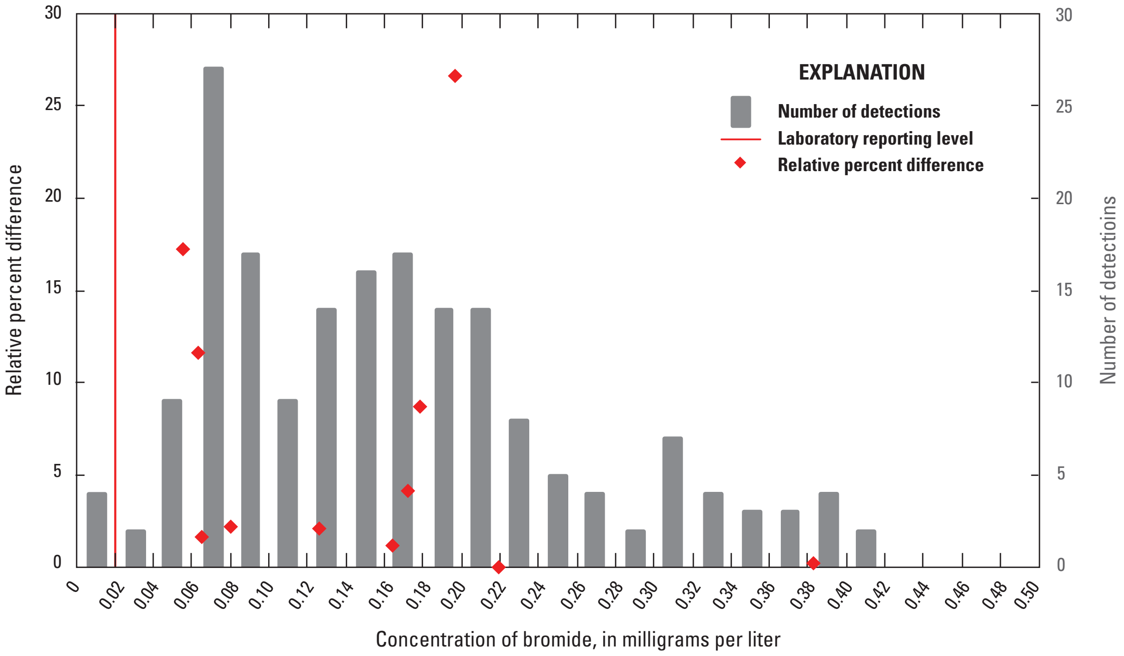

Figure 1.2. Bar graph showing the number of detections of bromide within a range of concentrations, relative percent difference for replicate pairs, and laboratory reporting level for bromide analyses for quality-control samples, Barton Springs zone, south-central Texas (November 2008–March 2010).

Table 1.6. Summary of blank sample results for *Escherichia coli* and suspended sediment for quality-control samples collected in the Barton Springs zone, south-central Texas, November 2008–March 2010.

[LRL, laboratory reporting level; MPN, most probable number; mg/L, milligrams per liter; <, less than; ≥, greater than or equal to; *, no detections; --, not measured]

		Field blanks				Equipment blank			
Constituent	**LRL**	**Number of blank samples**	**Maximum concentration in blank samples (MPN/100 mL [*Escherichia coli*]; mg/L [suspended sediment])**	**Number of detections < LRL**	**Number of detections ≥ LRL**	**Number of blank samples**	**Maximum concentration in blank samples (MPN/100 mL [*Escherichia coli*]; mg/L [suspended sediment])**	**Number of detections < LRL**	**Number of detections ≥ LRL**
Escherichia coli	1 MPN/100 mL	10	*	0	0	0	--	--	--
Suspended sediment	0.5 mg/L	10	2	0	5	1	*	0	0

Table 1.7. Summary of replicate sample results for *Escherichia coli* and suspended sediment for quality-control samples collected in the Barton Springs zone, south-central Texas (November 2008–March 2010).

[LRL, laboratory reporting level; RPD, relative percent different; MPN, most probable number; mL, milliliter; mg/L, milligrams per liter; <, less than; ≥, greater than or equal to]

Constituent	Number of environmental and replicate sample pairs with detected concentrations ≥ LRL and calculated RPDs	Number of environmental and replicate samples in agreement[1]	Number of environmental and replicate samples in non-agreement[2]	Replicate pairs with < 5 percent RPD	Replicate pairs with ≥ 5 percent RPD	Median RPD (percent)	Maximum RPD (percent)	Maximum concentration deviation
Escherichia coli	6	2	0	0	6	45	86	50 MPN/100 mL
Suspended sediment	5	1	3	2	3	7.2	67	3 mg/L

[1] Cases for which the analyte in both the environmental sample and the replicate sample was not detected or was detected at an estimated concentration < LRL.

[2] Cases for which the analyte was detected at a concentration ≥ LRL in one of the samples and not detected or < LRL in the other sample.

considered in agreement with densities of less than 50 MPN/100 mL, with a maximum deviation of 33 MPN/100 mL and a mean standard deviation of 8.3 MPN/100 mL. RPDs for these seven replicate pairs ranged from 9.0 to 86 percent. The eighth replicate pair had high *E. coli* densities (greater than 400 MPN/100 mL), with a deviation of 50 MPN/100 mL (table 1.7) and an RPD of 11.5 percent (fig. 1.3). RPD values less than 50 percent for *E. coli* are considered acceptable by the analyzing laboratory. Because many of them were collected on weekends or during the evening, 112 of the 220 environmental samples and 7 of the QC samples analyzed for *E. coli* had hold times exceeding 6 hours. For this investigation, *E. coli* densities below 50 MPN/100 mL were considered qualitatively rather than quantitatively.

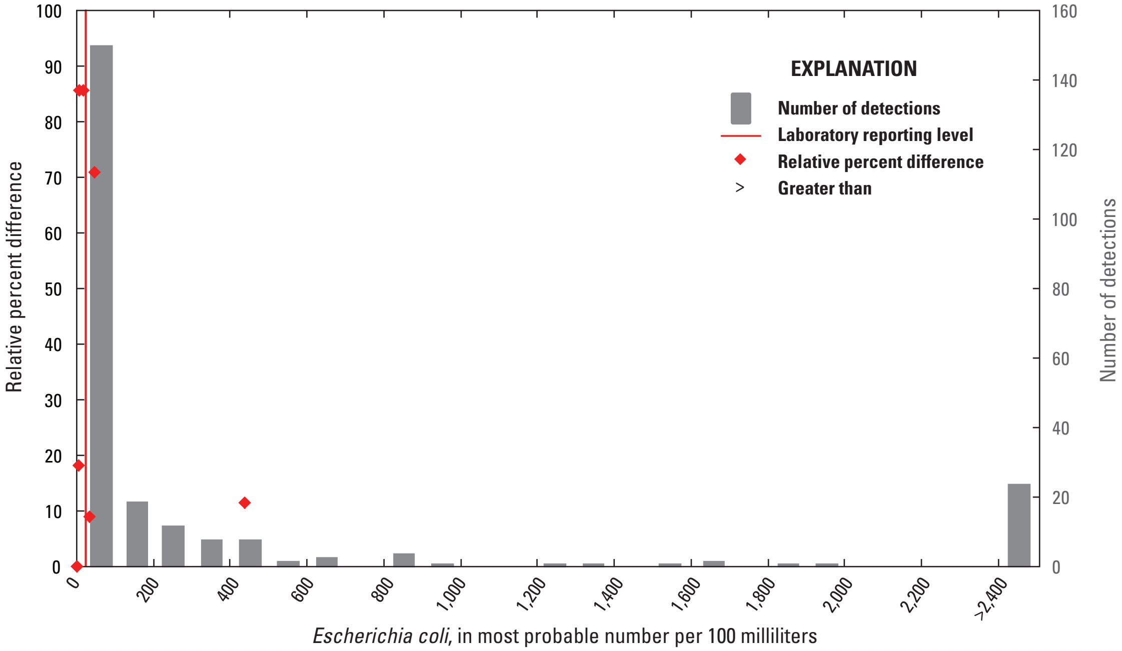

Figure 1.3. Bar graph showing the number of detections of *Escherichia coli* within a range of densities, relative percent difference for replicate pairs, and laboratory reporting level for quality-control samples, Barton Springs zone, south-central Texas (November 2008–March 2010).

Suspended Sediment

Suspended-sediment concentration was measured in 10 field blank samples and 1 equipment blank sample. Among the field blank samples, there were five nondetections and five detections below the LRL, the highest of which was 2 mg/L (table 1.6). Suspended sediment was not detected in the equipment blank.

Suspended-sediment concentration was measured in nine field replicate pairs. For replicate pairs with concentrations that were reported as less than the LRL or detected at a concentration less than the LRL (qualified as estimated), RPDs were not calculated. Five RPD values ranged from 0 to 67 percent, with a mean RPD of 19 percent. The detected concentrations associated with these replicate pairs were close to the LRL (fig. 1.4), therefore the actual concentration variations represented were small. The maximum concentration deviation between the nine replicate pairs was 3 mg/L (table 1.7), and the mean concentration deviation was less than 1 mg/L.

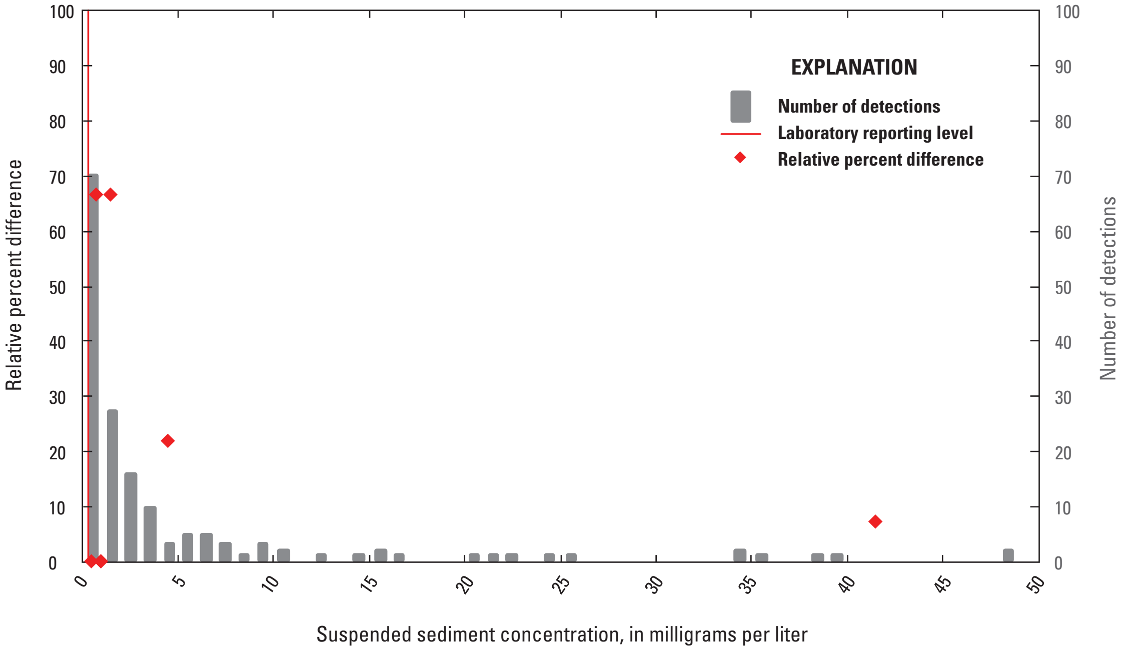

Figure 1.4. Bar graph showing the number of detections of suspended sediment within a range of concentrations, relative percent difference for replicate pairs, and laboratory reporting level for suspended sediment analyses for quality-control samples, Barton Springs zone, south-central Texas (November 2008–March 2010).

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