In cooperation with the City of Austin, City of Dripping Springs, Barton Springs/Edwards Aquifer Conservation District, Lower Colorado River Authority, Hays County, and Travis County

Recent (2008–10) Concentrations and Isotopic Compositions of Nitrate and Concentrations of Wastewater Compounds in the Barton Springs Zone, South-Central Texas, and Their Potential Relation to Urban Development in the Contributing Zone

Scientific Investigations Report 2011–5018

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

Front cover:

Top left, Algal bloom in Bear Creek, Austin, Texas (photograph courtesy of Andrew Clamann, City of Austin).

Top right, Barton Creek, Austin, Texas, upstream from Barton Springs pool (photograph courtesy of Nelson Guda, University of Texas).

Lower right Barton Creek, Austin, Texas, downstream from the bridge at Lost Creek Boulevard.

Back cover:

Top photo, Barton Springs pool, Austin, Texas (photograph courtesy of Nelson Guda, University of Texas).

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

Recent (2008–10) Concentrations and Isotopic Compositions of Nitrate and Concentrations of Wastewater Compounds in the Barton Springs Zone, South-Central Texas, and Their Potential Relation to Urban Development in the Contributing Zone

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Conversion Factors, Datums, Water-Quality Units, and Explanation of Isotope Units

Inch/Pound to SI

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.4047	hectare (ha)
	Volume	
gallon (gal)	3.785	liter (L)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)

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

$$°F=(1.8×°C)+32$$

Datums

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

Water-Quality Units

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

Explanation of Isotope Units

The δ values for stable-isotope ratios discussed in this report are referenced to the following standard materials:

Element	R	Standard
Nitrogen	Nitrogen-15/nitrogen-14	Nitrogen in air
Oxygen	Oxygen-18/oxygen-16	Vienna Standard Mean Ocean Water (VSMOW) (Casciotti and others, 2002)

Recent (2008–10) Concentrations and Isotopic Compositions of Nitrate and Concentrations of Wastewater Compounds in the Barton Springs Zone, South-Central Texas, and their Potential Relation to Urban Development in the Contributing Zone

By Barbara J. Mahler,[1] MaryLynn Musgrove,[1] Chris Herrington,[2] and Thomas L. Sample[1]

Abstract

During 2008–10, the U.S. Geological Survey, in cooperation with the City of Austin, the City of Dripping Springs, the Barton Springs/Edwards Aquifer Conservation District, the Lower Colorado River Authority, Hays County, and Travis County, collected and analyzed water samples from five streams (Barton, Williamson, Slaughter, Bear, and Onion Creeks), two groundwater wells (Marbridge well [YD–58–50–704] and Buda well [LR–58–58–403]), and the main orifice of Barton Springs in Austin, Texas, with the objective of characterizing concentrations and isotopic compositions of nitrate and concentrations of wastewater compounds in the Barton Springs zone. The Barton Springs zone is in south-central Texas, an area undergoing rapid growth in population and in land area affected by development, with associated increases in wastewater generation. Over a period of 17 months, during which the hydrologic conditions transitioned from dry to wet, samples were collected routinely from the streams, wells, and spring and, in response to storms, from the streams and spring; some or all samples were analyzed for nitrate, nitrogen and oxygen isotopes of nitrate, and wastewater compounds. The median nitrate concentrations in routine samples from all sites were higher in samples collected during the wet period than in samples collected during the dry period, with the greatest difference for stream samples (0.05 milligram per liter during the dry period to 0.96 milligram per liter for the wet period). Nitrate concentrations in recent (2008–10) samples were elevated relative to concentrations in historical (1990–2008) samples from streams and from Barton Springs under medium- and high-flow conditions. Recent nitrate concentrations were higher than historical concentrations at the Marbridge well but the reverse was true at the Buda well. The elevated concentrations likely are related to the cessation of dry conditions coupled with increased nitrogen loading in the contributing watersheds. An isotopic composition of nitrate (delta nitrogen-15) greater than 8 per mil in many of the samples indicated there was a contribution of nitrate with a biogenic (human and or animal waste, or both) origin. Wastewater compounds measured in routine samples were detected infrequently (3 percent of cases), and concentrations were very low (less than the method reporting level in most cases). There was no correlation between nitrate concentrations and the frequency of detection of wastewater compounds, indicating that wastewater compounds might be undergoing removal during such processes as infiltration through soil. Three potential sources of biogenic nitrate to the contributing zone were considered: septic systems, land application of treated wastewater, and domesticated dogs and cats. During 2001–10, the estimated densities of septic systems and domesticated dogs and cats (number per acre) increased in the watersheds of all five creeks, and the rate of land application of treated wastewater (gallons per day per acre) increased in the watersheds of Barton, Bear, and Onion Creeks. Considering the timing and location of the increases in the three sources, septic systems were considered a likely source of increased nitrate to Bear Creek; land application of treated wastewater a likely source to Barton, Bear, and Onion Creeks; and domestic dogs and cats a potential source principally to Williamson Creek. The results of this investigation indicate that baseline water quality, in terms of nitrate, has shifted upward between 2001 and 2010, even without any direct discharges of treated wastewater to the creeks.

Introduction

The Barton Springs zone, which comprises the Barton Springs segment of the Edwards aquifer (hereinafter, Barton Springs segment) and the watersheds contributing to its recharge (the contributing zone), is in south-central Texas

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[1] U.S. Geological Survey.

[2] City of Austin.

(fig. 1A), an area 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). Increases in population result in an increase of wastewater generated. Indirect sources of wastewater to the Barton Springs zone include leaking sewer lines (primarily over the recharge zone), land application of treated wastewater, and septic systems. Although currently (November 2010) there are no discharges of treated wastewater into the streams that recharge the Barton Springs segment, one discharge permit had been approved (Texas Commission on Environmental Quality, 2009). There is interest in establishing a baseline against which potential future changes in water quality related to increasing urbanization and associated wastewater production can be compared. The primary objectives of the investigation described here were to characterize concentrations of nitrate and wastewater compounds in the Barton Springs zone in surface water, groundwater, and Barton Springs discharge, and to evaluate potential sources of nitrate using nitrogen (N) and oxygen (O) isotopes of nitrate and detections of wastewater compounds, and the spatial and temporal distribution of potential sources of biogenic (animal- or human-waste origin, or both) nitrate.

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 inches to feet or more in diameter (conduits or caves), transport times in karst from the point of recharge to discharge can be extremely rapid (on the order of days). Transport through large voids offers little opportunity for filtration or sorption, thus karst aquifers are vulnerable to contamination (White, 1988). Dye traces have demonstrated that travel times through the aquifer are rapid and variable, and that the direct-line velocity increases with higher discharge rates at Barton Springs (Hunt and others, 2006). Following storms, surface runoff recharges through interstream recharge features and streambeds, delivering runoff-related contaminants to Barton Springs (Mahler and others, 2006).

To provide understanding of occurrence of nitrate and wastewater compounds in the Barton Springs zone, the U.S. Geological Survey (USGS), in cooperation with the City of Austin (COA), the City of Dripping Springs, the Barton Springs/Edwards Aquifer Conservation District, the Lower Colorado River Authority, Hays County, and Travis County, conducted a study that monitored concentrations of nitrate in streams, wells, and Barton Springs routinely and in response to three storms. In addition, nitrogen and oxygen isotopes of nitrate and wastewater compounds were measured in selected samples to provide information regarding nitrate sources.

Purpose and Scope

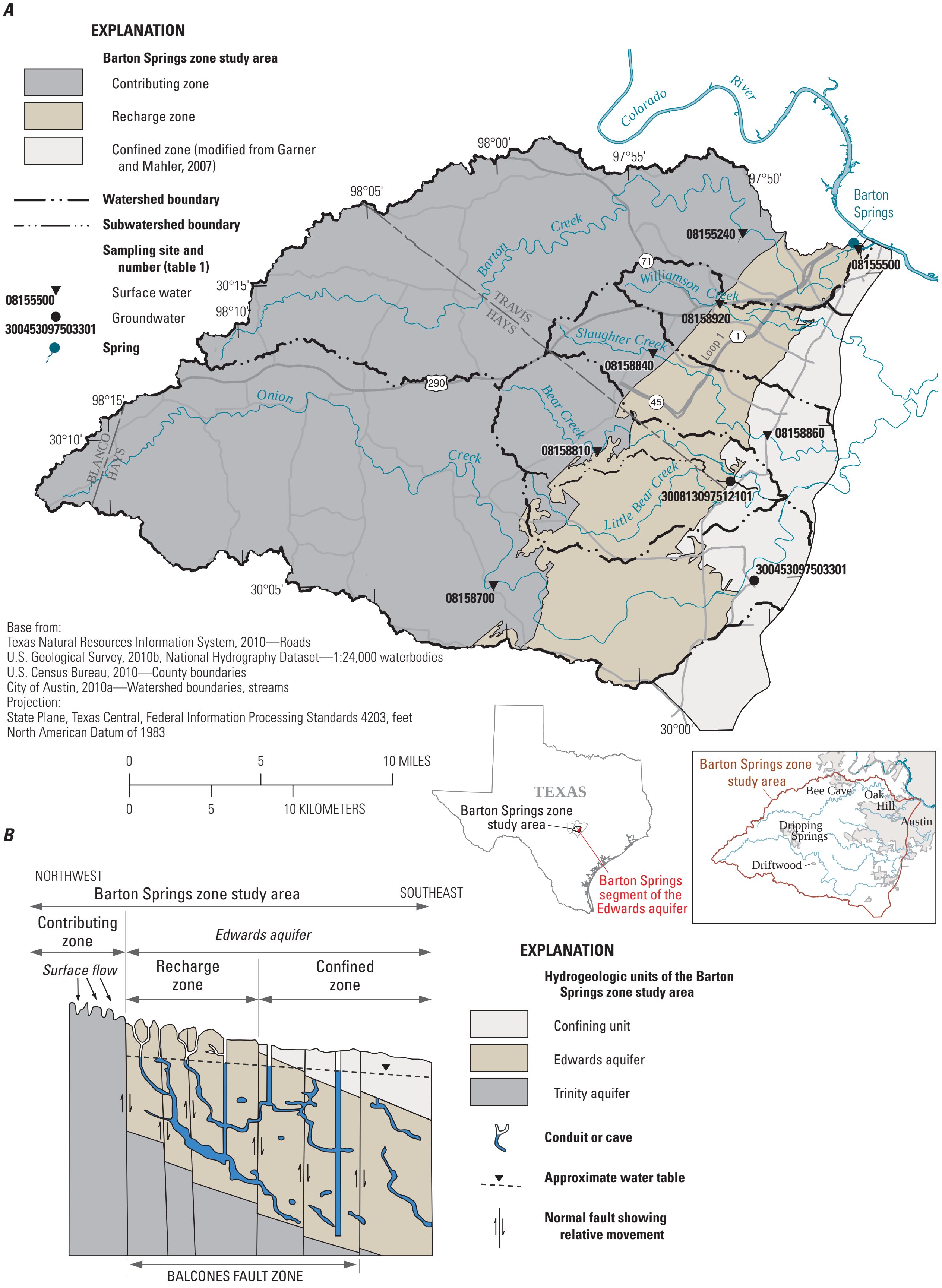
The purpose of this report is to

1. Describe the concentrations and isotopic compositions of nitrate and the concentrations of wastewater compounds in five streams recharging the Barton Springs segment, in two wells with contrasting hydrogeologic properties, and in Barton Springs discharge over an annual cycle and in response to storms during November 2008–March 2010.
2. Compare dissolved nitrate concentrations measured during November 2008–March 2010 to those measured by the USGS at the same sites prior to this investigation (1990–2007).
3. Infer potential sources of nitrate from nitrate isotopic compositions.
4. Compare concentrations of nitrate to concentrations and frequency of detection of wastewater compounds measured during November 2008–March 2010.
5. Interpret any changes in nitrate concentrations relative to historical concentrations in the context of changes in number of septic systems, volume of land application of treated wastewater, and number of domesticated dogs and cats in the watersheds of the five recharging streams.

Hydrogeologic Setting

The Barton Springs segment is a hydrologically isolated section of the karstic Edwards aquifer of south-central Texas (fig. 1A). The Barton Springs 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) (fig. 1A). The hydrogeology is substantially controlled by a zone of en-echelon normal faults that dip generally southeastward and strike southwest-northeastward across the study area.

Surface water flows generally from west to east across the contributing zone; when it crosses onto the recharge zone, it infiltrates into the karstic Edwards aquifer (fig. 1B), then follows the trend of the Balcones fault zone to the north-northeast toward Barton Springs. Slade and others (1986) estimated that about 85 percent of aquifer recharge is provided by the six major streams that cross the recharge zone: Barton, Williamson, Slaughter, Bear, Little Bear, and Onion Creeks (fig. 1A). The combined watersheds of these six streams upstream from the recharge zone is referred to as the contributing zone (fig. 1A). In this report, the contributing zone and the Barton Springs segment together are referred to as the Barton Springs zone. Although the estimated amount of recharge from the six major streams reported by Slade and others (1986) 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



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).

Springs (Mahler and others, 2006). Focused recharge through karst features in streambeds can rapidly provide large volumes of water to the aquifer. Additional sources of recharge, likely minor in comparison to streambed recharge on a volumetric basis, include infiltration of water through soils and karst features such as sinkholes in interstream areas (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). Dye traces have demonstrated that flow infiltrating through the bed of Barton Creek upstream from where it is traversed by Loop 1 (fig. 1A) does not discharge from Barton Springs, but rather from 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 the bed of Barton Creek downstream from Loop 1 discharges from Barton Springs. Therefore, flow at Barton Creek measured during periods of little rainfall, during which all creek flow has infiltrated before it reaches Loop 1, likely makes little to no contribution to Barton Springs discharge.

Barton Springs is the main discharge point for the Barton Springs segment. Barton Springs discharge reflects aquifer flow conditions: 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 cubic feet per second (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 higher. The long-term mean discharge from Barton Springs is about 50 ft^3/s.

Chemical Species and Contaminants of Interest

Nitrate

Nitrate (NO_3^-) is the principal form of the nutrient nitrogen (N) dissolved in surface water and groundwater (Dubrovsky and others, 2010). Nutrients are those elements that are important to plant growth and survival; elevated nitrate concentrations in surface water can cause excessive growth of algae and other nuisance aquatic plants (a process known as eutrophication) (Dubrovsky and others, 2010). Algae and other nuisance aquatic plants can clog pipes and interfere with recreational activities such as fishing, swimming, and boating. Decomposition of the algae consumes dissolved oxygen, and low dissolved oxygen concentrations can result in the death of other aquatic life that depend on dissolved oxygen for respiration. Potential concerns for human health related to elevated nitrate in drinking water include methemoglobinemia (also known as blue baby syndrome), adverse reproductive outcomes such as stillbirths and premature births, and cancer (Dubrovsky and others, 2010). The Federal drinking-water standard for nitrate (maximum contaminant level, or MCL), set by the U.S. Environmental Protection Agency (2011), is 10 mg/L as N. Natural background concentrations of nitrate are estimated to be 0.24 mg/L in U.S. streams and 1.0 mg/L in U.S. groundwater (Dubrovsky and others, 2010, p. 52). Background concentrations of nitrate in samples collected from springs in undeveloped areas of the Barton Springs segment, however, are about 0.25 mg/L (Chris Herrington, City of Austin, written commun., 2010).

Nitrate is formed when nitrogen from ammonia or other sources combines with oxygenated water, a process known as nitrification and facilitated by bacteria. There are numerous sources of nitrogen, both natural and anthropogenic, to surface water and groundwater. They include fertilizers (manure, organic fertilizers, and synthetic fertilizers); human and animal waste (treated wastewater effluent, septic-system drainage, and animal feces); decaying plant debris; runoff from fertilized residential lawns, golf courses, and construction sites; vehicle exhaust; and precipitation (Reynolds and others, 1992; Dubrovsky and others, 2010).

Nitrogen and Oxygen Isotopes of Nitrate

Isotopes of a particular element have the same number of protons in the atomic nucleus but different numbers of neutrons, resulting in different atomic masses. Ratios of the isotopes of nitrogen and oxygen in nitrate often are useful for determining sources of nitrate in surface water and groundwater. There are two stable isotopes of nitrogen: nitrogen-14 (^{14}N) and nitrogen-15 (^{15}N), of which ^{15}N occurs as a very small proportion (less than 1 percent) of the total N. Similarly, oxygen (O) has three stable isotopes, oxygen-16 (^{16}O), oxygen-17 (^{17}O), and oxygen-18 (^{18}O), of which ^{17}O and ^{18}O occur as a very small proportion of the total O. All reservoirs of nitrogen and oxygen compounds contain all the isotopes of the element, but the isotopes are incorporated into compounds in different proportions depending on the nature of the reactions that produce the compounds. For example, during processes such as evaporation, microbial denitrification, and algal nitrate assimilation, the amount of an isotope remaining in the nitrate reservoir might be enriched or depleted. As a result, different sources or reservoirs of nitrate have characteristic isotopic “signatures” (^{15}N relative to ^{14}N and ^{18}O relative to ^{16}O) that reflect the source of the nitrate (fig. 2). The boundaries of the source regions as indicated on fig. 2 are not absolute, and different interpretations of the ranges of isotopic compositions corresponding to a source type exist in the scientific literature. Additionally, the isotopic composition of the nitrate in a water sample might reflect either a single source or a mix of sources with different isotopic compositions. An evolution of the isotopic composition of a water sample from a single site might represent a change in the proportion of nitrate contributed by different sources. The isotopic signature also can be modified by biogeochemical processes, such as denitrification (fig. 2). Detailed information on nitrogen and oxygen isotopes

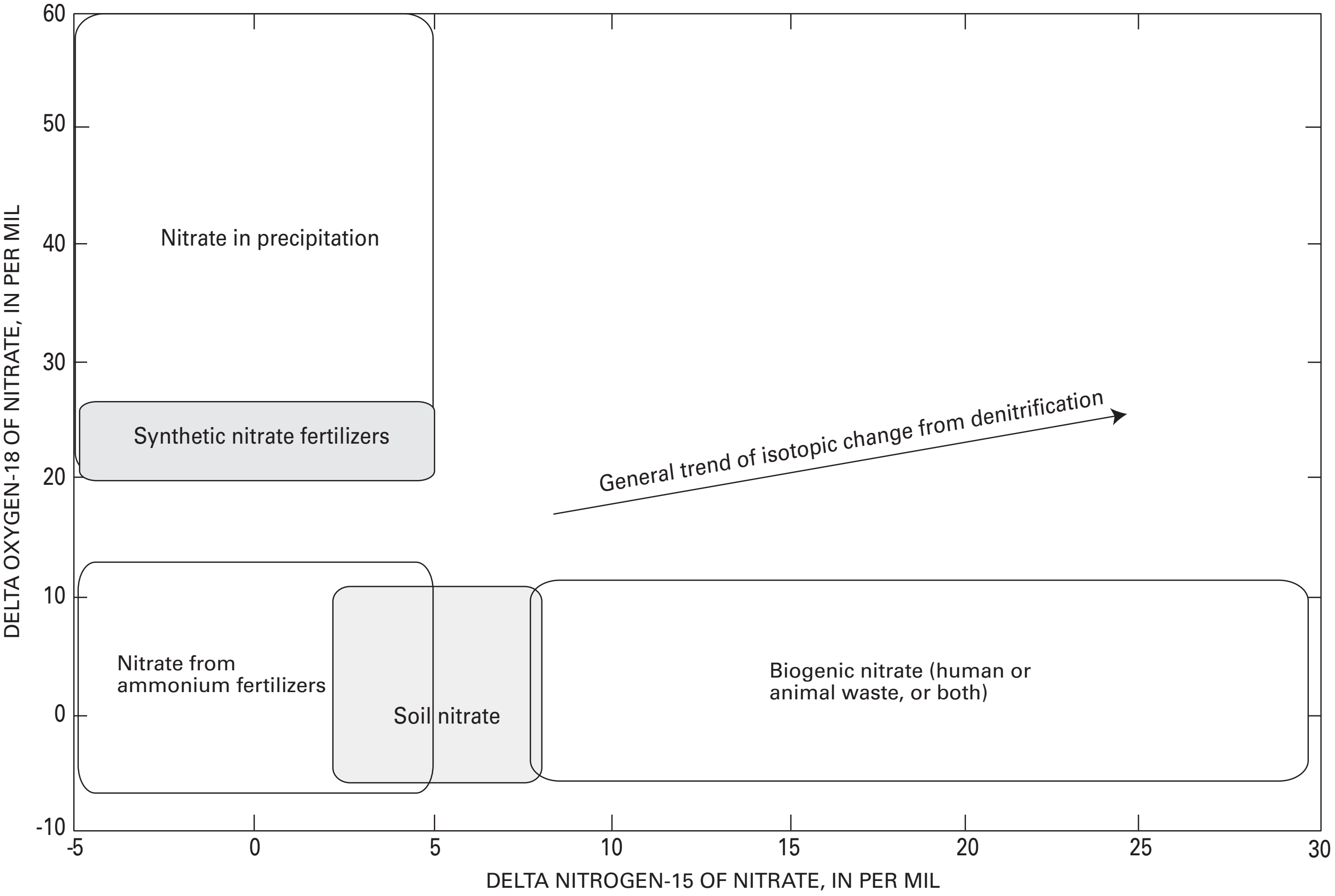


Figure 2. Common source fields of delta nitrogen-15 and delta oxygen-18 of nitrate from precipitation, synthetic nitrate fertilizers, ammonium fertilizers (including urea), soil, and human and animal waste; arrow indicates general trend of isotopic change from denitrification (modified from Silva and others, 2002).

in hydrological systems is given by Kendall and McDonnell (1998).

To determine the isotopic signature of nitrate, the proportions of the N and O isotopes are expressed relative to their proportions in a standard, which for N and O are air and Vienna Standard Mean Ocean Water (VSMOW), respectively (Sigman and others, 2001; Casciotti and others, 2002; Révész and Casciotti, 2007):

$$\delta^{15}N_{[nitrate]} = ([^{15}N/^{14}N]_{sample}/[^{15}N/^{14}N]_{standard} - 1) \times 1{,}000, \quad (1)$$

$$\delta^{18}O_{[\mathrm{nitrate}]} = ([^{18}O/^{16}O]_{sample}/[^{18}O/^{16}O]_{standard} - 1) \times 1{,}000. \quad (2)$$

The delta (δ) values are reported in parts per thousand (per mil; ‰). A sample containing nitrate that is isotopically enriched in ^{15}N relative to ^{14}N or in ^{18}O relative to ^{16}O will have a higher delta value relative to samples in which ^{15}N or ^{18}O are less enriched.

Wastewater Compounds

Wastewater compounds are those that occur frequently or principally in wastewater, although they might also have other sources. Examples of wastewater compounds include selected fragrances, surfactants, flame retardants, plasticizers, pharmaceuticals, and sterols. These compounds can enter the wastewater stream in several ways, including being flushed down toilets or washed down residential or industrial drains. Beginning in the late 1990s, when analytical methods were first developed to measure these wastewater compounds at low concentrations (less than 1 microgram per liter [µg/L]), the occurrence of wastewater compounds has been documented in surface water and groundwater across the United States (Barnes and others, 2008; Focazio and others, 2008). In the United States, regulatory standards do not currently exist for the occurrence of most of these chemicals in the environment (Focazio and others, 2008).

Methods of Investigation

Study Design

For this investigation, routine sampling and storm-targeted sampling were used to evaluate the occurrence of nitrate and wastewater compounds in 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, and from two groundwater wells (fig. 1A; 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).

To characterize seasonal changes in water quality, routine samples were collected every 3 weeks from November 2008 through November 2009 and monthly from November 2009 through March 2010 (fig. 3). 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 miles upstream from the recharge zone or on the upstream part of the recharge zone (fig. 1A), 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

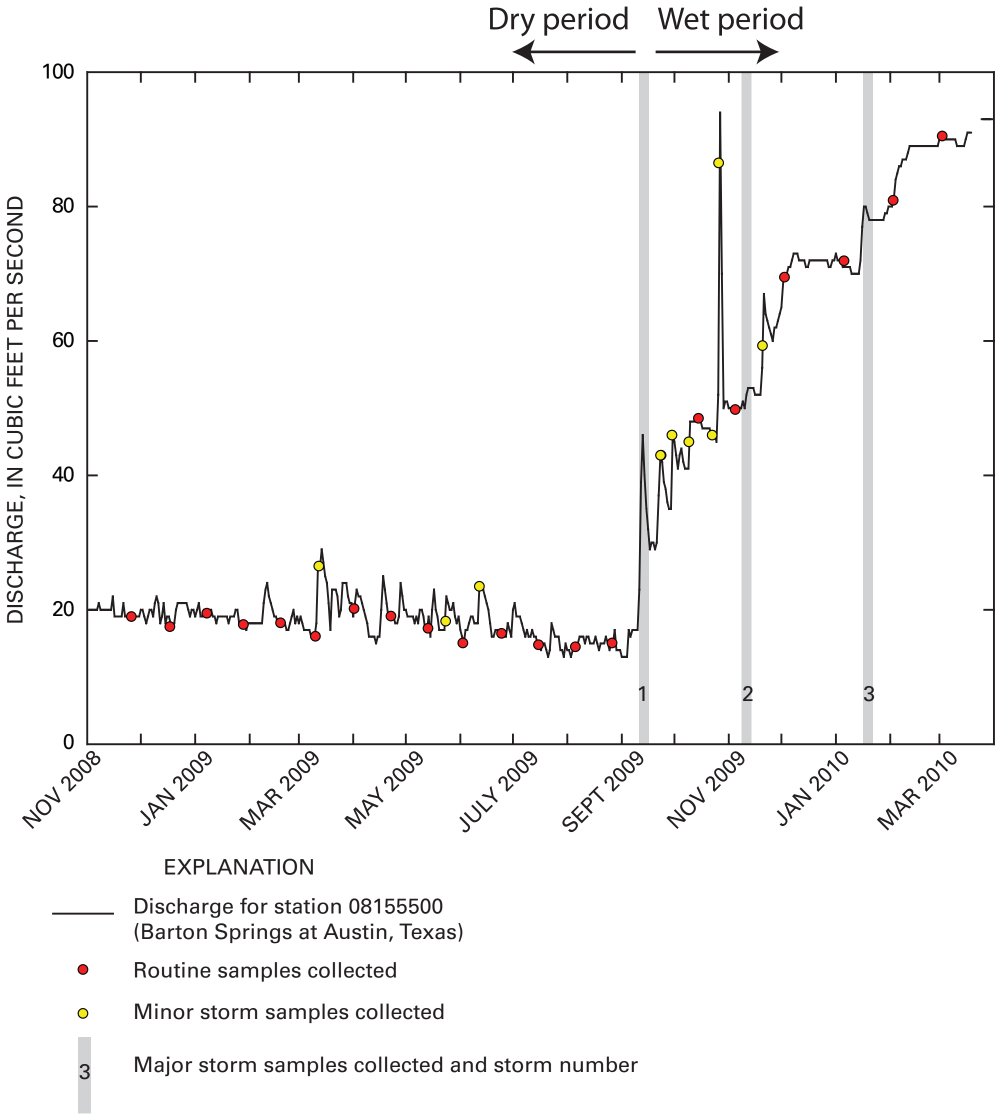


Figure 3. Time series of Barton Springs discharge (daily mean for station 08155500 Barton Springs at Austin, Texas) and timing of collection of routine, minor storm, and major storm samples at sites in the Barton Springs zone, south-central Texas, November 2008–March 2010.

Table 1. Sampling sites for water-quality characterization of the Barton Springs zone, south-central Texas, 2008–10.

[--, not applicable; FM, Farm Road]

U.S. Geological Survey station number (fig. 1)	Site name	Site identifier	Site type	State well number
08155240	Barton Creek at Lost Creek Blvd. near Austin, Tex.	Barton Creek	Stream	--
08158920	Williamson Creek at Oak Hill, Tex.	Williamson Creek	Stream	--
08158840	Slaughter Creek at FM 1826 near Austin, Tex.	Slaughter Creek	Stream	--
08158860	Slaughter Creek at FM 2304 near Austin, Tex.	Slaughter 2304	Stream	--
08158810	Bear Creek below FM 1826 near Driftwood, Tex.	Bear Creek	Stream	--
08158700	Onion Creek near Driftwood, Tex.	Onion Creek	Stream	--
300813097512101	Marbridge Ranch well	Marbridge well	Groundwater well	YD–58–50–704
300453097503301	Buda well	Buda well	Groundwater well	LR–58–58–403
08155500	Barton Springs at Austin, Tex.	Barton Springs	Spring	--

YD–58–50–704) and the Buda well (USGS station number 300453097503301, State well number LR–58–58–403) (fig. 1A). Finally, routine samples were collected from the main orifice of Barton Springs. Nitrate was measured in all routine samples, and N and O isotopes of nitrate and wastewater compounds were measured in a subset of those samples (table 2) representing a range of flow conditions. 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 non-storm 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 following three major storms. 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 nitrate and its isotopes and wastewater compounds. Additionally, composite or grab samples were collected from some of the surface-water sites and from Barton Springs following some storms that resulted in flow in only one or two of the streams (minor storms). 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 discussions of minor storm results. All minor storm samples were analyzed for nitrate and a subset was analyzed for N and O isotopes of nitrate and wastewater compounds.

Hydrologic Conditions

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 (hereinafter the dry period), spring discharge ranged from 13 to 29 ft^3/s, and there frequently was no flow in the streams; the infrequent rainfall that did occur resulted in ephemeral flow in only one or two of the five streams. Composite or grab samples of ephemeral flow were collected during November 2008–September 2009 when possible. Beginning in September 2009, storms occurred more frequently and 32 inches of rain fell between September 10, 2009, and March 31, 2010 (hereinafter the wet period) (Lower Colorado River Authority, 2010; sites 4517, 4519, 4593, 4594, 4595, and 4596).

Aquifer flow conditions (Barton Springs discharge) were characterized by low-flow conditions (40 ft^3/s or less) during the dry period. After the onset of the wet period, aquifer flow conditions (Barton Springs discharge) increased steadily from 17 ft^3/s on September 10, 2009, to 90 ft^3/s on March 2, 2010, the day the final routine sample was collected (fig. 3). For this report, low aquifer flow conditions are defined as those during which Barton Springs discharge was less than 40 ft^3/s, average flow conditions as those during which discharge was from 40 to 69 ft^3/s, and high aquifer flow conditions as those during which discharge was 70 to 100 ft^3/s. These definitions of average and high flow are more narrow than those defined

Table 2. Summary of analytes and number of samples analyzed for water-quality characterization of the Barton Springs zone, south-central Texas, 2008–10.

[FM, Farm Road; --, not sampled for]

U.S. Geological Survey station number (fig. 1)	Site name	Number of routine samples for indicated analytes			Number of storm samples for indicated analytes		
		Nitrate	Nitrogen and oxygen isotopes of nitrate	Wastewater compounds	Nitrate	Nitrogen and oxygen isotopes of nitrate	Wastewater compounds
08155240	Barton Creek at Lost Creek Blvd. near Austin, Tex.	19	6	3	10	4	2
08158920	Williamson Creek at Oak Hill, Tex.	7	4	1	15	6	4
08158840	Slaughter Creek at FM 1826 near Austin, Tex.	6	5	2	[1]10	[2]5	[2]3
08158810	Bear Creek below FM 1826 near Driftwood, Tex.	10	2	1	14	6	4
08158700	Onion Creek near Driftwood, Tex.	6	6	2	8	4	2
300813097512101	Marbridge Ranch well (YD–58–50–704)	21	4	3	0	--	--
300453097503301	Buda well (LR–58–58–403)	20	3	3	0	--	--
08155500	Barton Springs at Austin, Tex.	21	10	4	32	31	27

[1] Includes two samples collected at 08158860 (Slaughter Creek at FM 2304 near Austin, Tex.)

[2] Includes one sample collected at 08158860 (Slaughter Creek at FM 2304 near Austin, Tex.)

in Mahler and others (2006) and were chosen so that comparisons could be made relative to the range of conditions that occurred during the period of sampling.

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, 2009), storm 2 (November 8, 2009), and storm 3 (January 14, 2010) (table 3). The largest amount of rainfall occurred for storm 1, but the largest response in stream discharge occurred for storm 3. No flow occurred at USGS station 08158840 Slaughter Creek at Farm Road (FM) 1826 near Austin, Tex. (hereinafter Slaughter Creek site), as a result of storm 1, but a large amount of stormwater runoff (daily mean discharge of 724 ft^3/s on September 12, 2009) occurred at USGS station 08158860 Slaughter Creek at FM 2304 near Austin, Tex. (hereinafter Slaughter 2304 site), downstream from the Slaughter Creek site. For storm 1, samples from Slaughter Creek were collected at the Slaughter 2304 site.

Sample Collection and Processing

Polytetrafluoroethylene (PTFE) (Teflon) or polyethylene bottles were used to collect water for nitrate analysis, and glass bottles were used to collect water for analysis of wastewater compounds. A 60-milliliter (mL) polyethylene syringe was used to collect water for analysis of N and O isotopes of nitrate. At the surface-water sites, routine samples were collected by immersing the bottle or syringe below the water surface near the centroid of flow (grab samples), avoiding contact with the atmosphere (Wilde and others, 1999). Storm-related surface-water samples from streams were collected over the duration of the storm hydrograph by an autosampler that was triggered to begin sampling when discharge in the creek reached a pre-set threshold. The autosampler was equipped with seven 9-liter (L) polyethylene carboys lined with PTFE bags. For each stream, the discrete samples were combined into a flow-weighted composite. For minor storms resulting in flow in one or two of the streams, composite or grab samples were collected. At the groundwater sites, the well was purged until temperature, dissolved oxygen, pH, and specific conductance stabilized. Samples were not collected until the purging was completed. Samples were collected directly from the well discharge and did not undergo any treatment (for example, filtration, chlorination) prior to collection. Samples from Barton Springs were collected by immersing the bottle or syringe below the water surface into or near the spring orifice, avoiding contact with the atmosphere and

Table 3. Characteristics of major storms sampled, antecedent moisture conditions, and system response for three major storms, Barton Springs zone, south-central Texas, September 2009–March 2010.

[in., inches; ft^3/s, cubic feet per second]

Storm description				Antecedent moisture conditions[1]		System discharge response (ft^3/s)	
Storm	Date	Total rainfall (in.)	Temporal distribution	Rainfall in prior 3 months (in.)	Days since last storm	Barton Springs	Stream
1	Sept. 10, 2009	4.66	80 percent of total rainfall fell in two episodes: 1.34 in. (29 percent of total rainfall) between 1000 and 1700 on Sep. 10 and 2.39 in. (51 percent) between 0000 and 1700 on Sep. 12	3.42	500	13–50	Bear: 0–125; Williamson: 0–215
2	Nov. 8, 2009	1.36	1.12 in. (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	Jan. 14, 2010	2.46	2.30 in. (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).

standing surface water. Reusable bottles, bags, and sampling equipment were cleaned with Liquinox soap, hydrochloric acid, methanol, and deionized water prior to use (Horowitz and Sandstrom, 1998). Samples for analysis of N and O isotopes of nitrate were filtered onsite by injecting water from the syringe through a 0.2-micrometer (µm) pore-size disk filter into a field-rinsed 125-mL brown polyethylene bottle, and a potassium hydroxide (KOH) pellet was added for preservation.

All samples were stored on ice in coolers following collection and during transport to the USGS Texas Water Science Center office in Austin, Tex., where samples for the analysis of nitrate were filtered through a 0.45-µm pore-size capsule filter into a 125-mL brown polyethylene bottle. Samples for the analysis of wastewater compounds were filtered through a 0.7-µm pore-size glass fiber filter into a baked 1-L amber glass bottle. Samples for analysis of nitrate and wastewater compounds 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 N and O isotopes of nitrate were shipped to the USGS Stable Isotope Laboratory in Reston, Va.

Analytical Methods

Nitrate and wastewater compounds were measured by the NWQL, and N and O isotopes of nitrate were measured by the USGS Stable Isotope Laboratory. In brief, nitrate plus nitrite (NO_3+NO_2) and nitrite were measured using ion-exchange chromatography (Fishman, 1993); nitrate was computed as the difference between those two and reported as N (NO_3-N) in milligrams per liter. Where nitrite was not detected above the method reporting level (MRL) of 0.002 mg/L as N, nitrate is reported as the NO_3+NO_2 value. Sixty-two wastewater compounds (table 4) were measured by capillary-column gas chromatography/mass spectrometry following polystyrene-divinylbenzene solid-phase extraction (Zaugg and others, 2002). N and O isotopes of nitrate were measured by continuous-flow isotope ratio analysis with sample preparation by freeze-drying, ion exchange, and conversion to carbon monoxide with a thermal combustion/elemental analyzer system (Révész and Casciatti, 2007). Quantifiable concentrations less than the MRL were flagged as estimated by the NWQL and are reported here at the estimated level.

Statistical Methods

Nonparametric statistical methods were used to analyze the geochemical data, except for the comparison of slopes, for which a parametric method was used (Helsel and Hirsch, 1992). Nonparametric methods commonly are used when the dataset is non-normally distributed or contains censored data (nondetections), or both. Nondetections are ranked equally and lower than all detections. Estimated values (less than the MRL) were considered at the estimated concentration.

Table 4. Wastewater compounds measured, method reporting level, and type or typical use of compound, or both.

[µg/L, micrograms per liter; PAH, polycyclic aromatic hydrocarbon]

Wastewater compound	Method reporting level (µg/L)	Compound type or typical use, or both
Cotinine	0.8	nicotine metabolite
4-tert-Octylphenol diethoxylate (OP2EO)	1	surfactant degradate
4-tert-Octylphenol monoethoxylate (OP1EO)	1	surfactant degradate
5-Methyl-1H-benzotriazole	1.2	deicer
Anthraquinone	.16	laxative, dye production
Acetophenone	.4	fragrance
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	1	fragrance
Anthracene	.01	PAH
1,4-Dichlorobenzene	.02	disinfectant, urinal cakes, moth balls
Benzo[a]pyrene	.018	PAH
Benzophenone	.08	fragrances, soaps
Bromacil	.36	landscape herbicide
Bromoform	.1	disinfection byproduct
3-tert-Butyl-4-hydroxyanisole (BHA)	.6	food preservative
Caffeine	.06	coffee
Camphor	.044	pharmaceutical
Carbaryl	.16	insecticide
Carbazole	.03	PAH derivative in coal tar
Chlorpyrifos	.16	insecticide
Cholesterol	2	lipid with dietary origin
3-beta-Coprostanol	1.8	human feces
Isopropylbenzene	.3	refined oil, paint thinner
N,N-diethyl-meta-toluamide (DEET)	.06	insect repellent
Diazinon	.16	insecticide
Triethyl citrate (ethyl citrate)	.16	food additive
Tetrachloroethylene	.12	solvent
Fluoranthene	.024	PAH
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	.052	fragrance
Indole	.08	fragrance
Isoborneol	.08	essential oils
Isophorone	.032	solvent
Isoquinoline	.08	ingredient in antihypertension, antifungal, disinfectant, vasodilator
d-Limonene	.08	citrus oil used in household cleaners
Menthol	.32	local anesthetic, sore throat lozenges
Metalaxyl	.12	fungicide (used on tobacco, in cigarettes)
Metolachlor	.028	herbicide
Naphthalene	.04	PAH in mothballs
1-Methylnaphthalene	.022	metabolite of naphthalene
2,6-Dimethylnaphthalene	.06	metabolite of naphthalene
2-Methylnaphthalene	.036	metabolite of naphthalene

Table 4. Wastewater compounds measured, method reporting level, and type or typical use of compound, or both—Continued.

Wastewater compound	Method reporting level (µg/L)	Compound type or typical use, or both
4-Nonylphenol diethoxylate (sum of all isomers) (NP2EO)	5	detergent surfactant
p-Cresol	.08	disinfectant, fragrance
4-Cumylphenol	.06	detergent metabolite
para-Nonylphenol (total) (branched)	2	detergent metabolite
4-n-Octylphenol	.06	detergent metabolite
4-tert-Octylphenol	.14	detergent metabolite
Phenanthrene	.016	cigarette smoke, steroid framework
Phenol	.16	antiseptic, oral anesthetic, used in production of many drugs and cosmetics
Tributyl phosphate	.16	plasticizer, foaming agent in detergent, fire retardant
Triphenyl phosphate	.12	plasticizer, fire retardant
Tris(2-butoxyethyl)phosphate	.8	flame retardant in plastics
Tris(2-chloroethyl)phosphate	.1	flame retardant in plastics
Prometon	.12	herbicide
Pyrene	.042	PAH, in dyes, plastics
Methyl salicylate	.044	liniments, flavoring agent, fragrance
3-Methyl-1(H)-indole (Skatole)	.036	feces, fragrance
beta-Sitosterol	4	steroid; natural in many foods, cholesterol and other health treatments
beta-Stigmastanol	2.6	steroid
Triclosan	.2	disinfectant
Tris(dichlorisopropyl)phosphate	.16	flame retardant

Standard statistical methods were used to compute medians and percentiles. The statistical significance of differences between populations of data was evaluated using the Mann-Whitney U test, which is the nonparametric equivalent of the parametric two-sample *t*-test. Correlations between two populations and the statistical significance of trends were assessed using the Kendall's tau test, which measures the degree of correspondence between the rankings of two sets of data (in the case of temporal trends between date and concentration). The difference between slopes of the relation between discharge and instantaneous nitrate load (the product of concentration and instantaneous discharge) was evaluated using the parametric Student's *t*-test. For all statistical tests, the criterion used for statistical significance was a p-value less than .05 ($p < .05$).

Quality Assurance and Quality Control

Quality-control (QC) data were collected to assess sample-collection procedures and laboratory analyses. QC consisted of analysis of field- and equipment-blank samples, laboratory deionized (DI) water, field- and laboratory-replicate samples, and laboratory-surrogate samples. Blank samples were collected to evaluate if 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. 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 Texas Water Science Center laboratory did not contain measurable quantities of the constituents of interest, and was collected from the DI tap. After collection, the blank and DI samples received the same treatment as environmental samples. Field-replicate samples were collected in the same way as and immediately after the associated environmental sample. One laboratory replicate (for the analysis of N- and O-isotopes of nitrate only) consisted of analyses of two aliquots of the same sample. The deviation between the replicate sample and environmental sample, computed in those cases where the analyte of interest was reported at a concentration higher than the MRL for both samples, was expressed as the relative percent difference (RPD), with the equation

$$RPD = |C_1 - C_2|/((C_1 + C_2)/2) \times 100, \qquad (3)$$

where

C_1 is the constituent concentration, in milligrams per liter, from the environmental sample; and

C_2 is the constituent concentration, in milligrams per liter, from the replicate sample.

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 MRL. Cases for which the analyte in both of the samples either was not detected or was detected at a concentration less than the MRL were defined as in agreement. Cases for which the analyte was detected at a concentration equal to or greater than the MRL in one of the samples and not detected or detected at a concentration less than the MRL were defined as in non-agreement. This distinction was necessary because of the large number of instances in which a wastewater compound was not detected or was detected at a concentration less than the MRL. RPDs of 10 percent or less indicate good agreement between paired results when the concentrations are sufficiently large relative to their associated MRL; however, RPDs for replicates with small concentrations are often large, but do not necessarily indicate a lack of laboratory precision.

Surrogate compounds added to samples are analyzed to assess the consistency of the analytical method. Surrogate compounds have chemical properties similar to those of some of the compounds being measured in environmental samples, but are not expected to be present naturally. Surrogates were added at the NWQL for each sample submitted for analysis of wastewater compounds, and recovery was expressed as a percentage.

Nitrate

Twenty-three QC samples were analyzed for nitrate (NO_3+NO_2): 10 field blanks, 1 equipment blank, 1 DI water sample, and 11 field replicates. NO_3+NO_2 was detected at a concentration exceeding the MRL in 1 of the 10 field blanks. This concentration represents 1.5 percent of the environmental response range. The concentration detected (0.036 mg/L as N) is 7 and 33 times lower than the minimum and mean nitrate concentration reported for environmental samples, respectively. In a second field blank, NO_3+NO_2 was reported at an estimated concentration (less than the MRL) of 0.0124 mg/L as N. NO_3+NO_2 was not detected in either the equipment blank or the DI water.

The median RPD for 11 field replicate pairs was 0.58 percent. The RPDs for eight of the replicate pairs of NO_3+NO_2 were less than 5 percent; one replicate pair had an RPD of 6.3 percent. Two had a high RPD, but the concentrations of NO_3+NO_2 were close to the MRL, and the actual concentration variations represented were very small (<0.1 mg/L).

Nitrogen and Oxygen Isotopes of Nitrate

Analysis of N and O isotopes of nitrate requires that a sufficient concentration of nitrate is present. For this reason, no blank samples were analyzed for nitrogen or oxygen isotopes.

Six replicate samples were analyzed for N and O isotopes of nitrate: five field-replicate samples and one laboratory-replicate sample. The mean RPD for $\delta^{15}N$ for the six pairs was 2.6 percent with a maximum of 4.2 percent, and the mean RPD for $\delta^{18}O$ was 2.9 percent with a maximum of 8.1 percent. The 8.1-percent result was the only instance where a calculated RPD value for either $\delta^{15}N$ or $\delta^{18}O$ exceeded 5 percent. The analytical precision for N and O isotopes of nitrate at the USGS Stable Isotope Laboratory is about 0.5 per mil.

Wastewater Compounds

Nine QC samples were analyzed for wastewater compounds: four field-blank samples, one equipment-blank sample, and four field-replicate samples. Among the field-blank samples, there were 228 nondetections of an analyte, 6 detections of an analyte at a concentration less than the MRL and flagged as estimated, and 3 detections of an analyte at a concentration higher than the MRL. The six estimated detections occurred in the same sample and were for benzophenone, camphor, N,N-diethyl-meta-toluamide (DEET), isophorone, menthol, and methyl salicylate. The three detections with concentrations that exceeded the MRL all occurred in different samples and were all for phenol. The concentrations detected were 0.18, 0.23 and 0.30 µg/L; the MRL is 0.16 µg/L. For the equipment blank sample collected from the autosampler, there were estimated detections of four analytes (benzophenone, DEET, menthol, and methyl salicylate) at concentrations less than the MRL and no detections of analytes at concentrations that exceeded the MRL.

Four field-replicate samples were analyzed for wastewater compounds. Two of the replicates were collected in association with routine samples, one in association with a minor storm grab sample, and one in association with a storm-composite sample. Of the 240 cases (60 analytes and four replicate pairs) there were measurable RPDs for only three cases. In both samples of one replicate pair, caffeine was detected at concentrations higher than the MRL and had an RPD of 4.3 percent. Phenol was detected in both samples of a second different replicate pair and had an RPD of 57.8 percent. DEET was detected in both samples of a third replicate pair and had an RPD of 5.7 percent. For all other pairs the results were in agreement.

Surrogate recovery was measured for all environmental and QC samples in which wastewater compounds were measured. Three surrogates were added to each sample before analysis. Each of the surrogate recoveries associated with the samples analyzed was compared to the historical surrogate recoveries for all samples analyzed from November 2008 through March 2010; 73.3 percent of all recoveries were within 1 standard deviation of the mean recovery, 95.6 percent were within 2 standard deviations, and all were within 3 standard deviations. In summary, the QC results for all analytes are acceptable with the exception of phenol. Phenol is considered a chronic blank contaminant (detected in more than 10 percent of laboratory blanks at the NWQL) (Zaugg and Leiker, 2006) and therefore is excluded from discussion in this report.

Concentrations and Isotopic Composition of Nitrate and Concentrations of Wastewater Compounds in the Barton Springs Zone

Samples were collected from five creeks that recharge the Barton Springs segment, two wells, and Barton Springs and analyzed for concentrations and isotopic composition of nitrate and concentrations of wastewater compounds. Concentrations of nitrate were compared to those measured historically (1990–2008) by the USGS, and the isotopic composition of nitrate was compared to that measured historically (1990–94) by the COA. Concentrations of wastewater compounds were summarized and evaluated in relation to occurrence of nitrate.

Concentrations of Nitrate and Comparison to Historical Data

Concentrations of nitrate in samples of surface water, groundwater, and spring water were summarized for the dry and wet periods and compared between the two periods. Nitrate concentrations measured in samples collected following minor and major storms were evaluated for systematic patterns among storms and among sites and relative to routine samples. Nitrate concentrations measured for this investigation were compared to those measured by the USGS during January 1990–October 2008 (“historical”) at the same sites.

Nitrate Concentrations

Nitrate was quantified in every sample from every site with the exception of three samples collected at the Bear Creek site during the dry period (November 2008 through September 8, 2009), for which concentrations were less than the MRL. During the dry period, Barton Creek was the only site of the five surface-water sites with sustained flow. Nitrate concentrations measured in routine samples collected during the dry period from the Barton Creek site peaked in early April 2009 and were lower and more variable than nitrate concentrations measured contemporaneously in samples collected from the two wells and the spring site (fig. 4). The nitrate concentration in the single sample that could be collected from the Williamson Creek site during the dry period was similar to that measured in a sample collected at the Barton Creek site on the same date (April 2, 2009). Nitrate concentrations at the Bear Creek site during the dry period were low compared to those measured at all other sites and varied little. Nitrate concentrations measured during the dry period in routine samples from the two wells and Barton Springs varied little; concentrations at Barton Springs were consistently higher than those at all other sites, and concentrations at the wells were intermediate between those at the stream sites and at Barton Springs. Once the wet period began on September 9, 2009, nitrate concentrations at the surface-water sites became both more elevated and more variable, as did concentrations at the Marbridge well, where they peaked in October 2009. In contrast, there was little temporal variation at the Buda well throughout the entire period of the investigation. These findings are consistent with the hypothesis that the geochemistry of the groundwater at the Marbridge well is controlled by conduit flow that receives rapid recharge, and that the groundwater at the Buda well is controlled by matrix flow, the chemistry of which over the short term is relatively unaffected by recharge (Atkinson, 1977; Toran and Roman, 2006). Nitrate concentrations at Barton Springs also increased following the onset of the wet period, peaking in November 2009 at concentrations similar to those measured in Bear Creek and Marbridge well and lower than that measured in Onion Creek on the same day.

For routine samples, descriptive statistics (median, 25th percentile, and 75th percentile) were computed for nitrate concentrations by site type (stream, well, spring) and by individual site for the entire 17 months of sampling, the dry period, and the wet period (September 2009–March 2010) (fig. 5; table 5). For all sites combined, all site types, and all individual sites (Slaughter and Onion Creeks excluded, as there was no flow during the dry period), the median nitrate concentration measured in routine samples collected during the wet period exceeded that of samples collected during the dry period. The difference in nitrate concentrations was statistically significant for all sites combined, all well samples combined, all stream samples combined, and samples from Barton Creek, Bear Creek, and the Marbridge well. Among site types, the change was greatest for the streams (table 5), for which the median nitrate concentration increased from 0.04 to 0.96 mg/L; among individual sites, the change was greatest for Bear Creek, for which the median nitrate concentration increased from 0.02 to 1.34 mg/L, which was the highest median concentration of the five stream sites during the wet period.

Nitrate was measured in samples collected from streams and Barton Springs following minor and major storms (fig. 6). There were no systematic patterns in nitrate concentrations across the three storms, nor were there systematic patterns

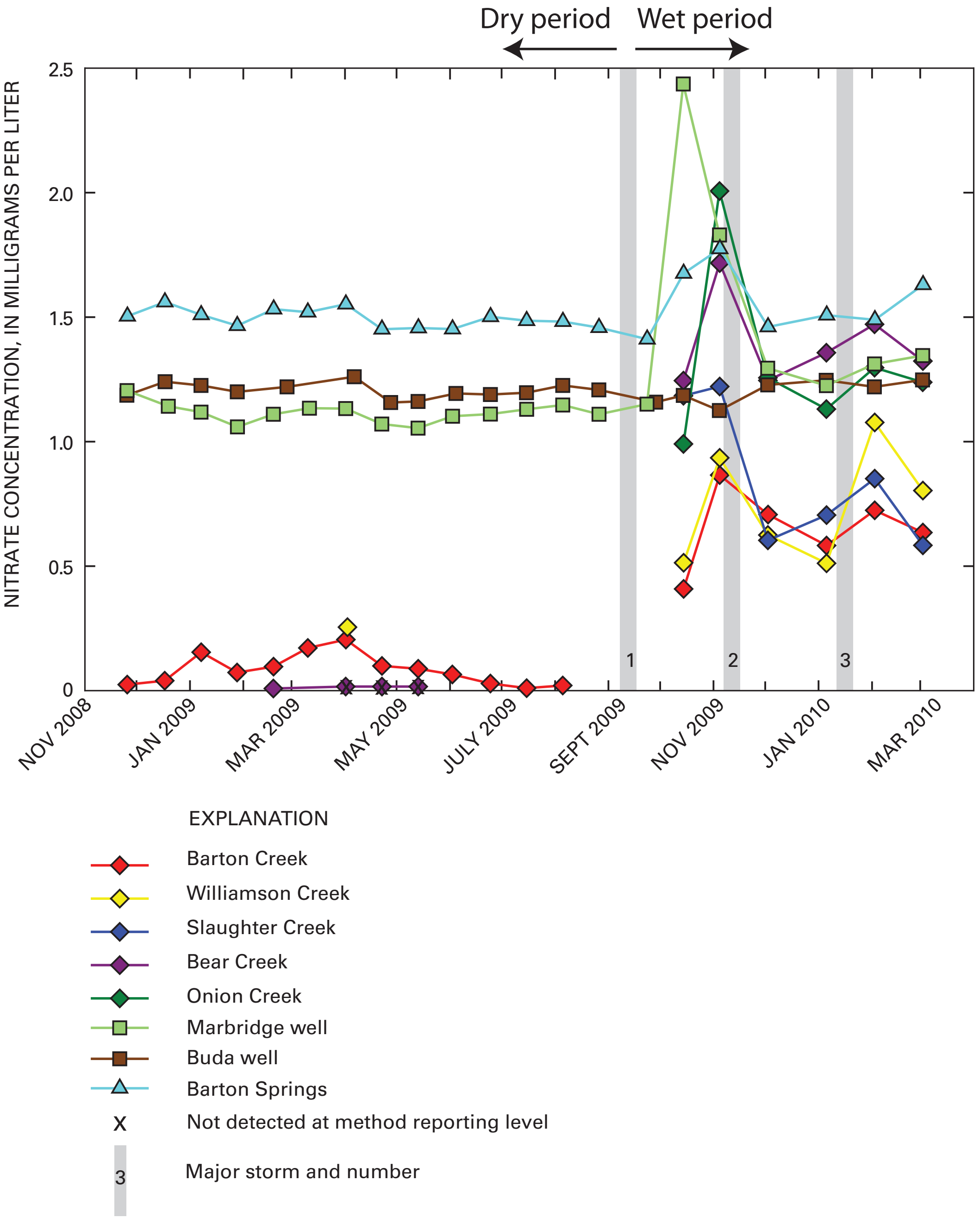


Figure 4. Time series of nitrate concentrations in routine samples from sites in the Barton Springs zone, south-central Texas, November 2008–March 2010.

in nitrate concentrations for minor storms relative to major storms, although in general, concentrations tended to be lower for minor storms than major storms. The range of nitrate concentrations in storm samples at each site was similar to that for routine samples collected during the wet period, with the exception of samples from the Bear Creek site. A nitrate concentration of 0.03 mg/L was measured at the Bear Creek site in response to a minor storm (March 13, 2009) that occurred during the dry period. This concentration was similar to those measured in routine samples collected at this site during the dry period. Nitrate concentrations collected at the Bear Creek site in response to four subsequent minor storms that occurred during the wet period (September and October 2009) increased over the course of the four storms to about 1 mg/L. With the exception of nitrate at Bear Creek during storm 1, nitrate concentrations in storm samples at the surface-water sites were lower than those at Barton Springs (fig. 6).

Changes in nitrate concentration as a result of four storms were evaluated at Barton Springs: a minor storm on March 11, 2009 (which resulted in little streamflow in any of the streams

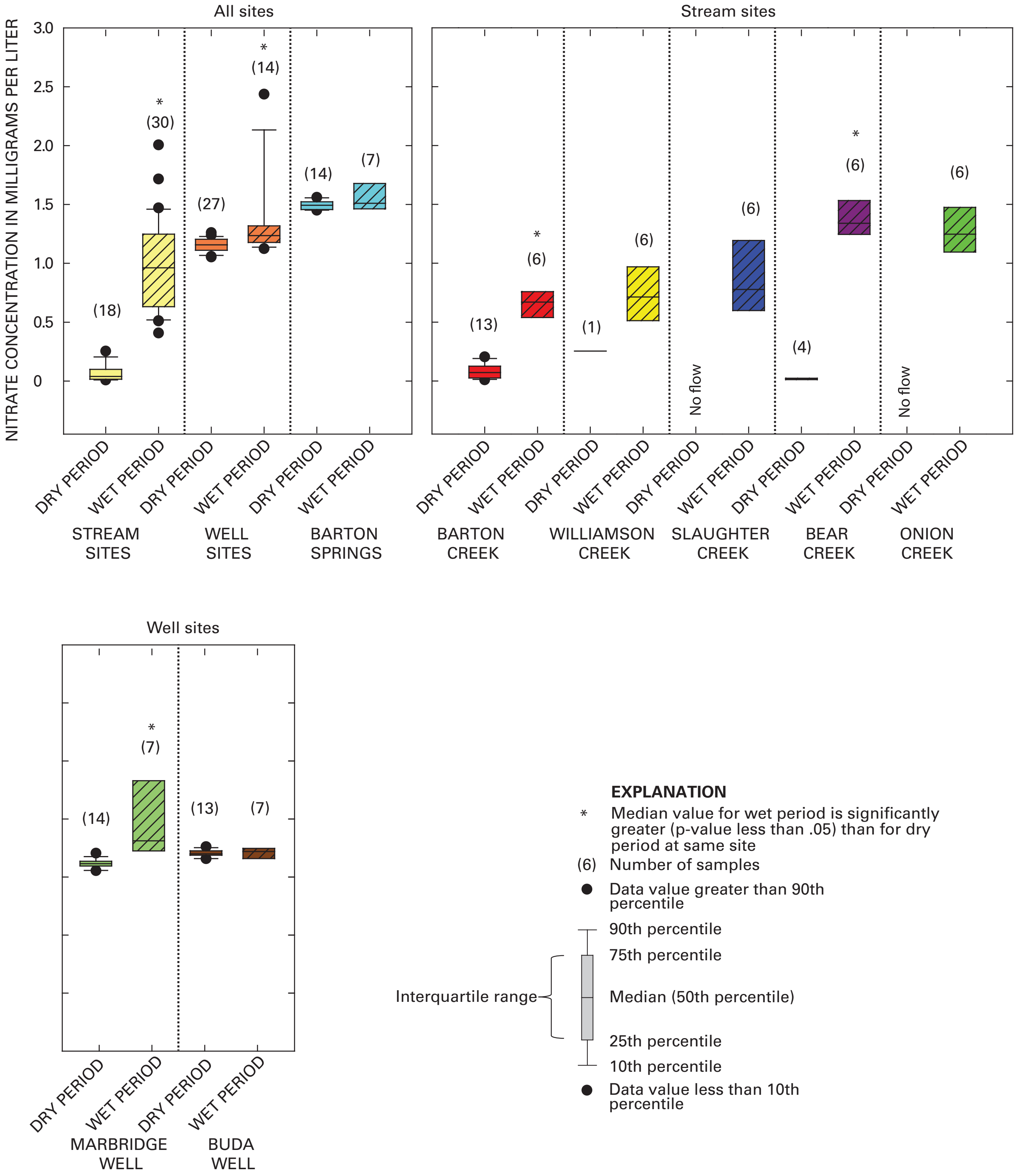
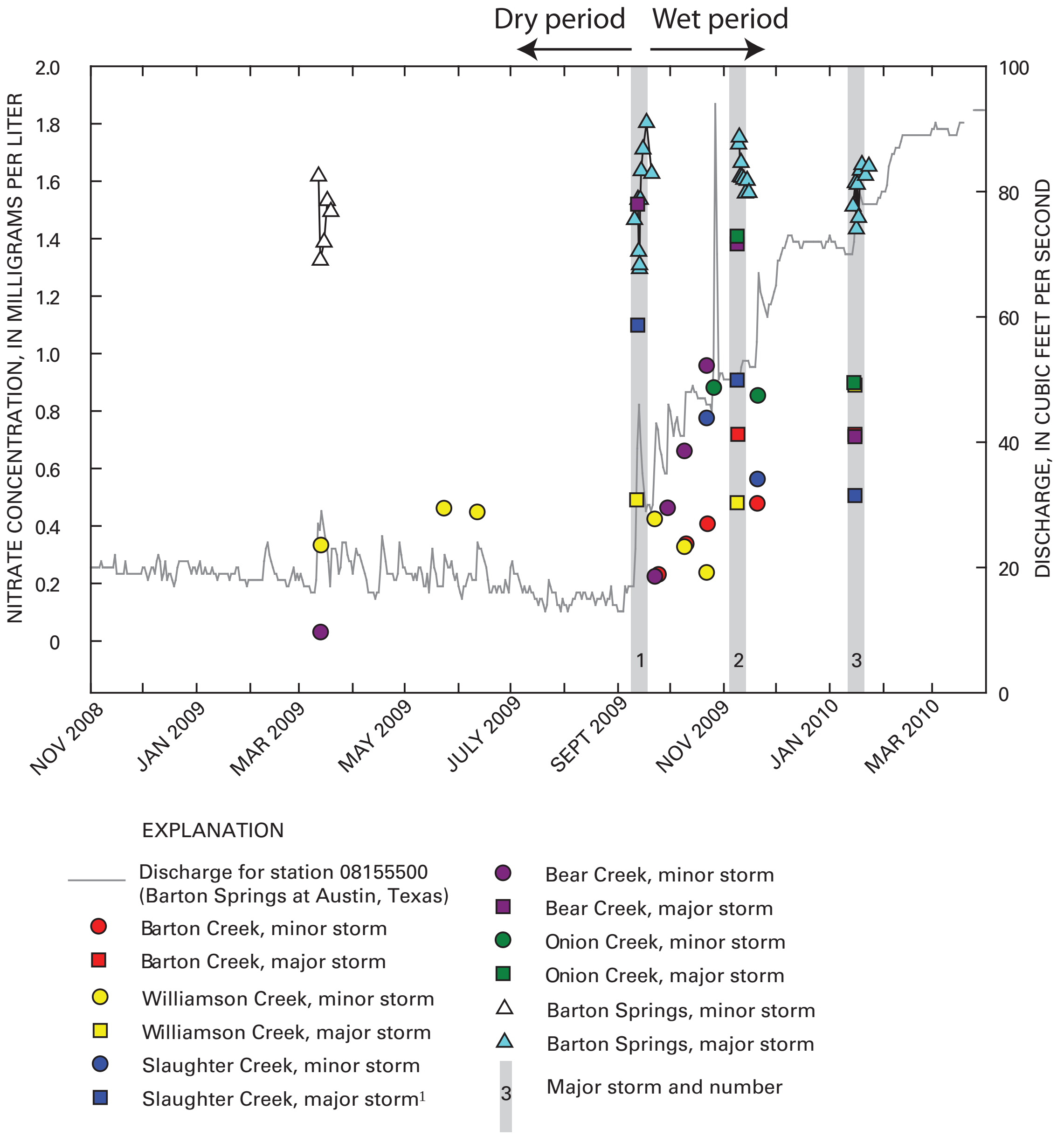


Figure 5. Nitrate concentrations in routine samples from sites in the Barton Springs zone, south-central Texas, November 2008–September 2009 (dry period) and September 2009–March 2010 (wet period).



[1] Storm 1 sample collected at Slaughter 2304.

Figure 6. Nitrate concentrations in storm samples collected from Barton, Williamson, Slaughter, Bear, and Onion Creeks and from Barton Springs, Barton Springs zone, south-central Texas, 2008–10.

that recharge the Barton Springs segment [fig. 8A–E]), and storms 1–3 on September 10, 2009, November 8, 2009, and January 14, 2010, respectively (fig. 7). Mahler and others (2006) reported a decrease in nitrate concentration at Barton Springs in response to storms occurring in 2004 and 2005. During the storms sampled for this study, however, a decrease in nitrate occurred only in response to the minor storm on March 11, 2009, and to storm 2. In response to storms 1 and 3, an initial decrease in nitrate 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 nitrate concentration peaked 8 days after rainfall at a concentration about 0.3 mg/L higher than the initial concentration.

Comparison of Recent (2008–10) and Historical (1990–2008) Nitrate Concentrations

Nitrate concentrations measured for this investigation during November 2008–March 2010 ("recent") were compared to historical concentrations. The sample collected at the Slaughter 2304 site during storm 1 of this investigation is not included in the comparison because it consists of only one data point. The historical data consist of nitrate

Table 5. Selected statistics of nitrate concentrations in routine samples from sites in the Barton Springs zone, south-central Texas, 2008–10.

[Nitrate concentrations in milligrams per liter; n, number of samples]

Sampling period	All stream sites				All groundwater sites				Barton Springs			
	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile
Nov. 2008–Mar. 2010	48	0.61	0.09	1.16	41	1.19	1.13	1.23	21	1.50	1.46	1.53
Dry period[1]	18	.04	.02	.10	27	1.16	1.11	1.20	14	1.49	1.46	1.52
Wet period[2]	30	.96	.63	1.25	14	1.24	1.19	1.31	7	1.51	1.46	1.68

Sampling period	Stream sites																			
	Barton Creek				Williamson Creek				Slaughter Creek				Bear Creek				Onion Creek			
	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile
Nov. 2008–Mar. 2010	19	0.10	0.04	0.58	7	0.67	0.51	0.93	6	0.78	0.60	1.18	10	1.25	0.02	1.36	6	1.25	1.13	1.30
Dry period[1]	13	.07	.03	.10	1	.25	.25	.25	0	no flow			4	.02	.01	.02	0	no flow		
Wet period[2]	6	.67	.58	.72	6	.71	.51	.93	6	.78	.60	1.18	6	1.34	1.25	1.47	6	1.25	1.13	1.30

Sampling period	Groundwater sites							
	Marbridge well				Buda well			
	n	Median	25th Percentile	75th Percentile	n	Median	25th Percentile	75th Percentile
Nov. 2008–Mar. 2010	21	1.13	1.11	1.22	20	1.20	1.19	1.23
Dry period[1]	14	1.11	1.10	1.13	13	1.20	1.19	1.23
Wet period[2]	7	1.31	1.22	1.83	7	1.22	1.16	1.25

[1] Nov. 1, 2008–Sept. 8, 2009.

[2] Sept. 9, 2009–Mar. 30, 2010.

concentrations measured in filtered water samples collected by the USGS during all flow conditions at the same sites as sampled in this investigation and are published in the USGS National Water Information System (NWIS) (U.S. Geological Survey, 2010c). The starting date of 1990 was chosen for the historical data because it was the first year that nitrate was measured in a filtered, rather than unfiltered, water sample at these sites; it was decided to compare only data for filtered samples for consistency with methods used in this study. The hydrologic conditions during the periods when historical and recent data were collected are mostly similar (fig. 8, left graph for creeks and spring), with relatively small discharges of 20 ft^3/s or less at Barton Springs during 1990, 1996, 2000, 2006, and 2008. However, the maximum Barton Springs discharge measured during the collection of the recent samples (94 ft^3/s) was less than the maximum discharge measured during the collection of the historical samples (130 ft^3/s).

For each stream or spring site, the nitrate data were evaluated as concentration relative to time, concentration relative to discharge at the time of sample collection, and as instantaneous load relative to discharge at the time of sample collection (fig. 8A–E, H). Recent nitrate concentrations ranged from <0.008 to 2.17 mg/L, and historical nitrate concentrations ranged from 0.01 to 1.80 mg/L. The transition between the mostly lower concentrations measured historically and mostly higher concentrations measured recently appears to have occurred gradually since 2005 in Barton and Williamson Creeks (fig. 8A–B), and more abruptly at Slaughter, Bear, and Onion Creeks (fig. 8C–E).

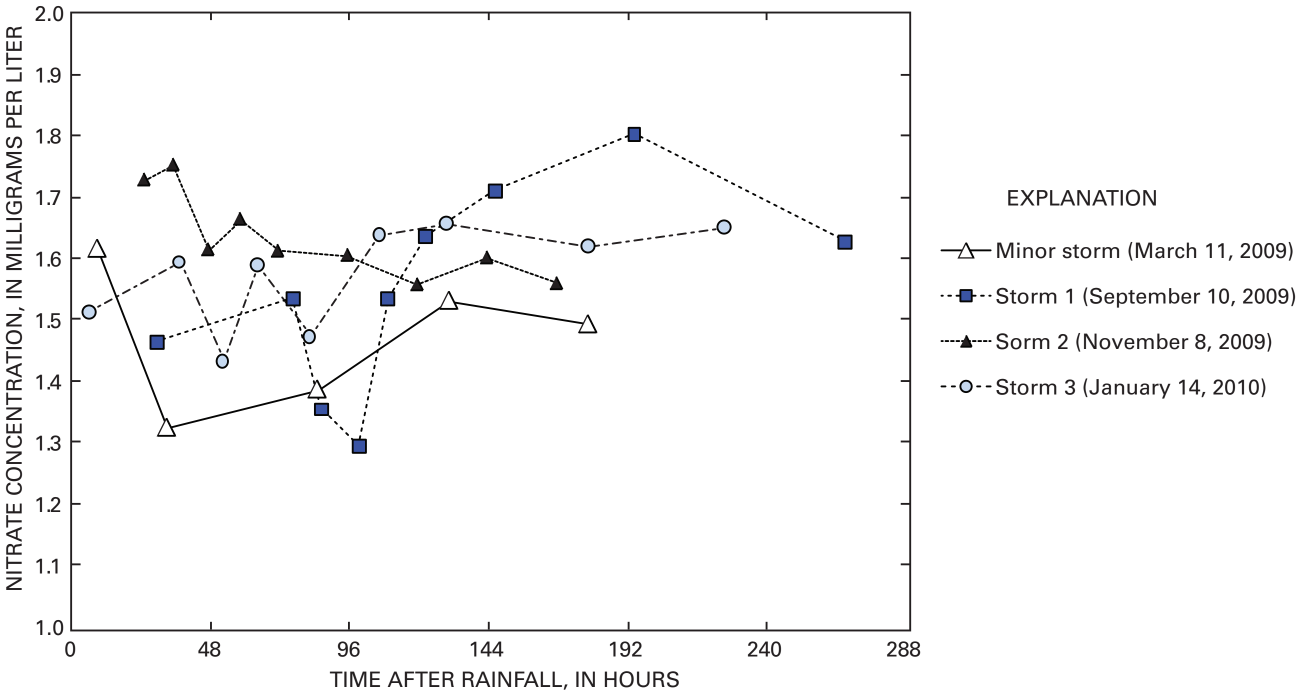


Figure 7. Nitrate concentrations in samples collected at Barton Springs in response to four storms in the Barton Springs zone, south-central Texas, 2008–10.

Because stream discharge can be related to concentrations of many constituents, nitrate concentrations were evaluated relative to discharge at the sites at the time of sample collection. On the basis of the Kendall's tau test for trends, there was no significant relation between nitrate concentration and discharge at any of the stream sites except Barton Creek, where concentration increased with increasing flow (fig. 8A). Historical and recent nitrate concentrations at each stream site were compared for low (1 to less than 10 ft^3/s), medium (10 to less than 100 ft^3/s), and high (100 to less than 1,000 ft^3/s) flow categories (table 6). For all stream sites and all flow categories, the median nitrate concentration for recent samples exceeded that for historical samples except for the low-flow category for Bear Creek (table 6). In those cases for which data were sufficient for statistical analysis, there was no significant difference in nitrate concentrations during low-flow conditions except at Slaughter Creek. During medium- and high-flow conditions, however, nitrate concentrations were significantly higher for recent samples than for historical samples at all stream sites. In four cases a statistical comparison could not be done because there was only one or no measured value for either the historical or the recent data. The largest increases in median nitrate concentration from the historical to the recent data occurred at Slaughter Creek (low-flow conditions) and Onion Creek (medium-flow conditions) (table 6).

A comparison of instantaneous nitrate loads (mass of nitrate per time at the moment that the sample was collected) relative to discharge indicates that, for a given discharge, the nitrate loads during the investigation period were significantly greater than those measured historically at all stream sites except Williamson Creek (fig. 8A–E). Because the slope is the ratio between load (the product of concentration and discharge) and discharge, it is another way to express the average concentration, which here is different between the two periods.

The striking difference between historical and recent concentrations and loads of nitrate at the stream sites likely is related, at least in part, to the transition from dry to wet conditions. The large increase in concentrations occurred subsequent to the beginning of the wet period (mid-September 2009). Increases in nitrate concentrations in streams following the transition from dry to wet conditions have been reported elsewhere (Burt and others, 1988; Reynolds and Edwards, 1995). This increase has been ascribed to suppression of mineralization and nitritification in soils during dry conditions, followed by an enhancement of those processes following rewetting (Lucey and Goolsby, 1993; Reynolds and Edwards, 1995). The change in concentrations coupled with minimal leaching during dry conditions and maximal leaching following the onset of rains results in a large contrast in nitrate loads between dry and wet conditions (Burt and others, 1988). However, periods of extended dry weather occur regularly in south-central Texas, as reflected in the hydrograph for Barton Springs (fig. 8H). During the period of historical data collection (1990–2008), discharge at Barton Springs decreased to 20 ft^3/s or less in January 1990 (15 ft^3/s), August 1996 (18 ft^3/s), October 2000 (17 ft^3/s), and September 2006 (20 ft^3/s). Although in some cases nitrate concentrations measured at the

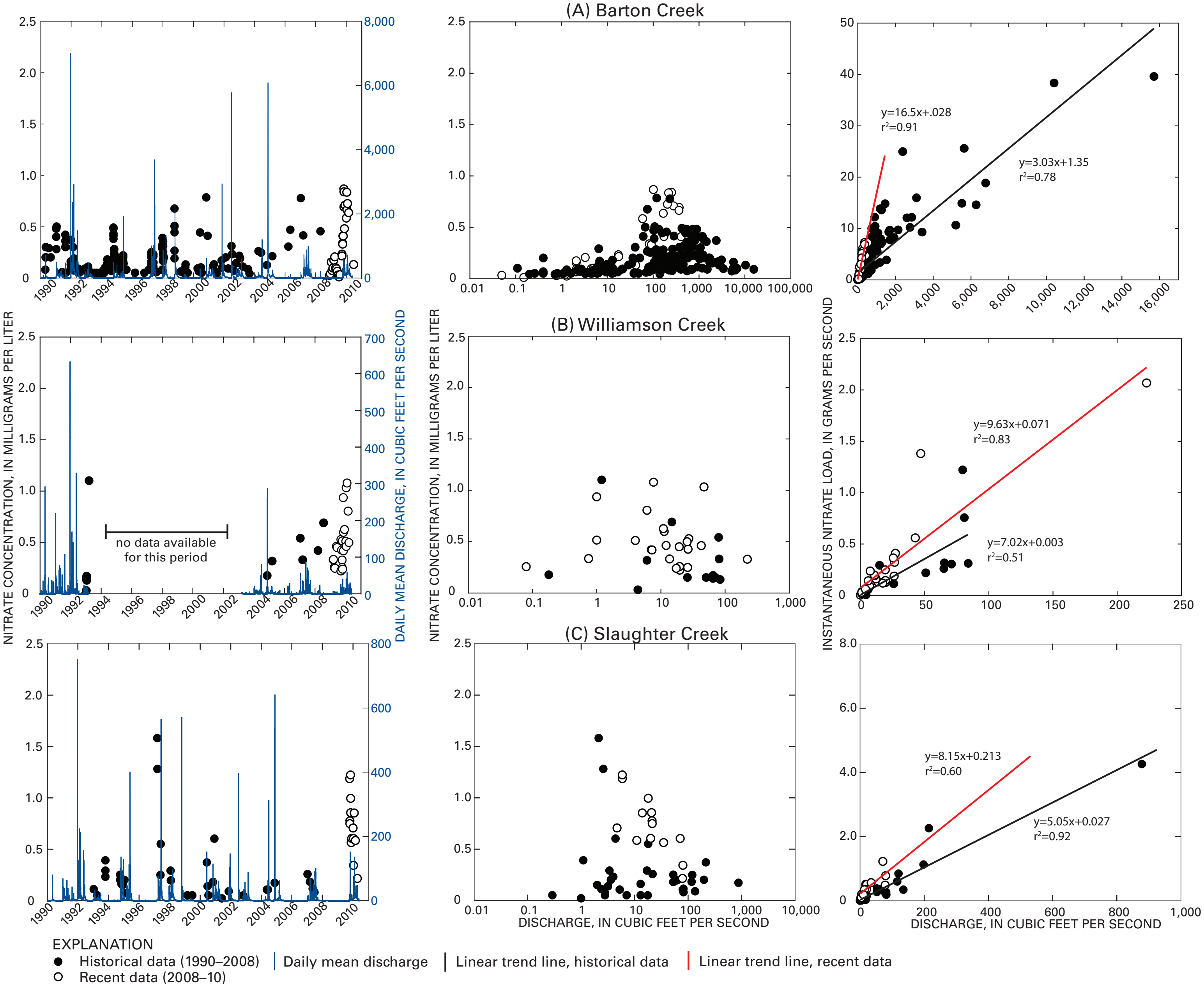


Figure 8. Comparison of historical (1990–2008) and recent (2008–10) nitrate concentrations from sites in the Barton Springs zone, south-central Texas, (A) Barton Creek, (B) Williamson Creek, (C) Slaughter Creek, (D) Bear Creek, (E) Onion Creek, (F) Marbridge well, (G) Buda well, and (H) Barton Springs. (Left graph: Nitrate concentrations relative to time; middle graph: nitrate concentrations relative to discharge; and right graph: nitrate load relative to discharge.)

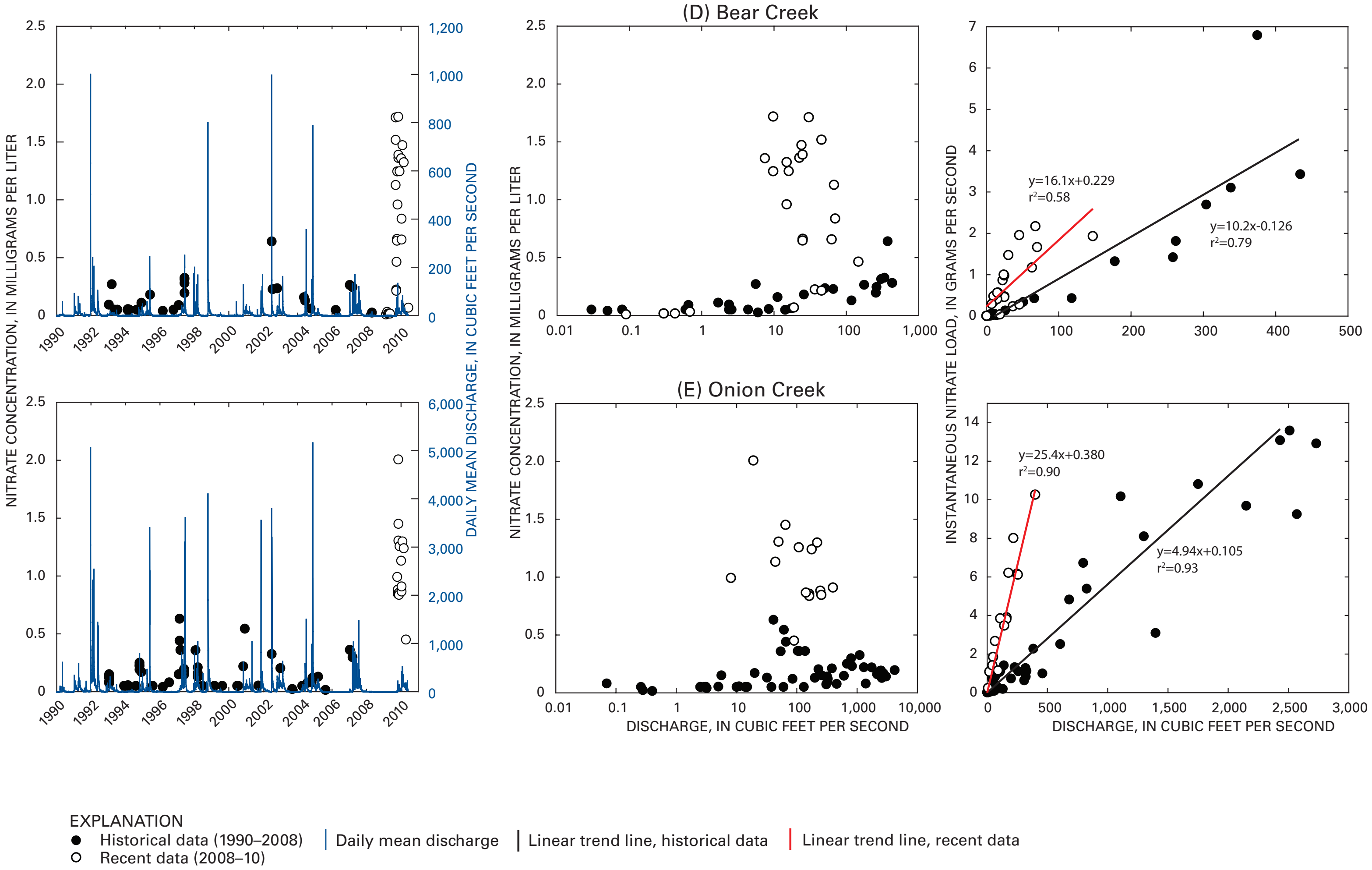


Figure 8.—Continued.

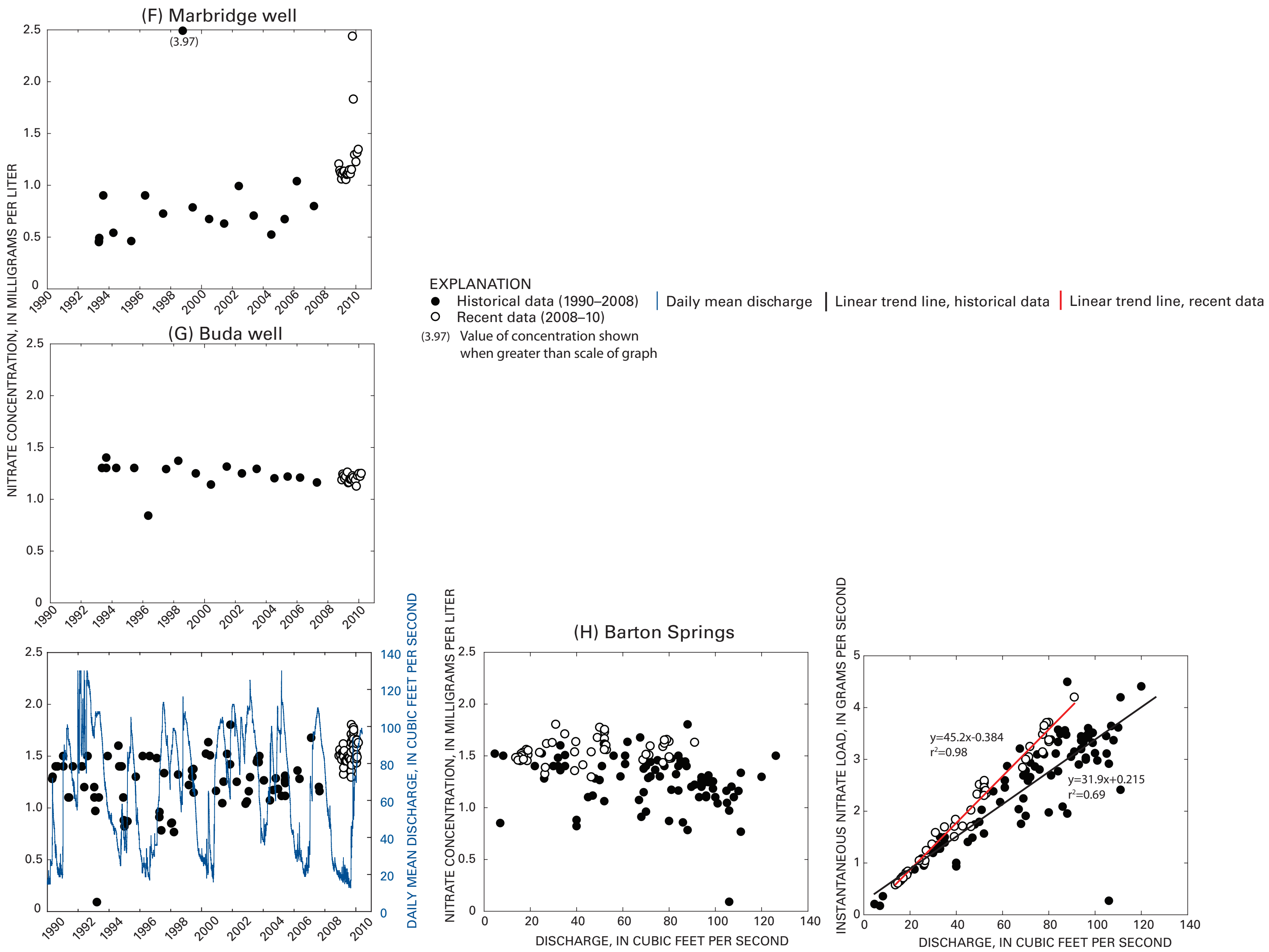


Figure 8.—Continued.

Table 6. Comparison of historical (1990–2008) and recent (2008–10) median nitrate concentration, by flow category, for sites in the Barton Springs zone, south-central Texas.

[mg/L, milligrams per liter; n, number of samples; ft^3/s, cubic feet per second; <, less than; --, no data or not applicable]

Site identifier		Median nitrate concentration, mg/L (n)					
		Historical (1990–2008)			Recent (2008–10)[1]		
	Flow range (ft^3/s)[2]	1–<10	10–<100	100–<1,000	1–<10	10–<100	100–<1,000
Barton Creek		0.06 (35)	0.12 (29)	0.22 (69)	0.07 (13)	**0.33 (5)**	**0.69 (11)**
Williamson Creek		.32 (5)	.15 (9)	-- (0)	.51 (7)	**.45 (14)**	*.33 (1)*
Slaughter Creek		.15 (17)	.17 (12)	.19 (6)	**1.18 (3)**	**.60 (11)**	-- (0)
Bear Creek		.05 (14)	.17 (6)	.27 (8)	.02 (8)	**1.13 (15)**	*.46 (1)*
Onion Creek		.05 (12)	.12 (13)	.15 (17)	*.99 (1)*	**1.38 (4)**	**.88 (9)**
Marbridge well	--		.69 (18)			**1.13 (21)**	
Buda well	--		**1.29 (17)**			1.20 (20)	
	Discharge (ft^3/s)	<40	40–<70	70–<100	<40	40–<70	70–<100
Barton Springs		1.44 (14)	1.27 (18)	1.26 (40)	1.50 (26)	**1.61 (15)**	**1.59 (12)**

[1] Values in bold are significantly greater than corresponding value in historical or recent dataset (Mann-Whitney U test, $p < .05$); values in italics did not have enough data for statistical analysis.

[2] Low flow defined as 1 to <10 ft^3/s; average flow defined as 10 to <100 ft^3/s; high flow defined as 100 to <1,000 ft^3/s.

stream sites in response to rains following an extended period of dry weather have been elevated relative to those measured during wetter periods (fig. 8A–E), those values are included in the analysis of the historical data, and are lower than those measured during the period of this investigation. Although the 2008 dry period was slightly more extreme, as reflected by a minimum Barton Springs discharge of 13 ft^3/s, than the dry periods that occurred during 1990–2008, the durations were similar. For example, during 2005–06, there were 527 contiguous days during which discharge in Onion Creek was less than 1 ft^3/s, and during 2008–09 there were 502 contiguous days during which discharge in Onion Creek was less than 1 ft^3/s. This indicates that the high nitrate concentrations and loads measured during the period of this investigation likely occurred as the result of climatic conditions coupled with an additional factor, such as higher nitrogen loading in the watersheds.

At the two wells, comparison of recent nitrate concentrations and historical data yielded contrasting results (fig. 8F–G). At the Buda well, nitrate concentrations during 1990–2008 varied little, and the median historical nitrate concentration (1.29 mg/L) was significantly higher than the median recent nitrate concentration (1.20 mg/L) (table 6). In contrast, the median nitrate concentration (1.13 mg/L) for the recent (2008–10) samples collected at the Marbridge well was significantly higher than the median historical (1990–2008) concentration (0.69 mg/L). Furthermore, the concentration of nitrate measured in every sample at the Marbridge well during this investigation was higher than those measured historically (with the exception of a single high outlier of 3.97 mg/L measured on April 22, 1998). There was no significant upward trend in nitrate concentrations at the Marbridge well during 1990–2008, which indicates that a step increase in nitrate concentrations occurred at this site around 2008 similar to the increase that occurred at the stream sites. The difference between the nitrate concentrations in samples from the two wells is consistent with the hypothesis that the Buda well intersects only the aquifer matrix, whereas the Marbridge well intersects a fracture or conduit, because it responds rapidly to changes in nitrate concentrations in recharging surface water.

At Barton Springs, nitrate concentrations in recent samples were higher than those measured in historical samples (fig. 8H), and the relation between nitrate concentrations and spring discharge, previously inverse, reversed during the period of this investigation. Because Barton Springs discharge is related to concentrations of many constituents (Mahler and others, 2006), nitrate concentrations were evaluated for low (less than 40 ft^3/s), average (40 to less than 70 ft^3/s), and high (70 to less than 100 ft^3/s) discharges. For medium- and high-discharge categories, the median nitrate concentration for recent data was significantly higher than that for historical data (table 6). The correlation between nitrate concentration in samples from Barton Springs and spring discharge was assessed statistically for the historical data and the recent data. Nitrate concentrations measured during 1990–2008 at Barton Springs are inversely related to spring discharge, consistent with the findings of Mahler and others (2006). In contrast, nitrate concentrations measured during 2008–10 are positively related to spring discharge. In other words, prior to this investigation, nitrate concentrations decreased with increasing spring discharge, but in 2008 this relation reversed, and during 2008–10, nitrate concentrations increased with increasing spring discharge. This change is consistent with the recent increase in nitrate concentrations in the five recharging streams relative to historical conditions.

Nitrate concentration at the stream sites and at Barton Springs also was assessed for historic and recent data as the slope of the linear trend line fitted to instantaneous loads (units of mass per time) relative to discharge at the site (fig. 8A–E, H). The relation between instantaneous load and discharge (the slope of the fitted line, which is an overall measure of concentration) for the recent and historical data was significantly different for all sites except Williamson Creek. This indicates that nitrate in aquifer recharge from streams during both routine and stormflow conditions is elevated relative to concentrations prior to 2008, and that recharge no longer substantially dilutes the nitrate concentration in groundwater.

Isotopic Composition of Nitrate as an Indicator of Nitrate Source and Comparison to Historical Data

Isotopic Composition of Nitrate

N and O isotopes of nitrate were measured in selected routine samples from all sites and in storm samples from all stream sites (one flow-weighted composite sample per site during storms 1–3 and one composite or grab sample from selected streams during minor storms) and from Barton Springs (four samples for one minor storm and nine samples for each of storms 1–3). Routine samples for analysis were selected to represent a range of aquifer flow conditions. To identify potential nitrate sources, the isotopic signatures of the elements in nitrate—nitrogen and oxygen—were examined as $\delta^{15}N$ and $\delta^{18}O$.

Isotopic compositions of nitrate in routine samples from streams span a wide range of values, with $\delta^{15}N$ ranging from 3.28 to 29.28 per mil and $\delta^{18}O$ from 6.27 to 35.96 per mil (fig. 9). Surface-water samples collected during the dry period have isotopic signatures that are different from those collected during the wet period. Samples collected from Barton Creek during the dry period have elevated values of both $\delta^{15}N$ and $\delta^{18}O$. This isotopic signature likely indicates a contribution of biogenic nitrate (animal- or human-waste origin, or both) that has undergone some denitrification, elevating both $\delta^{15}N$ and $\delta^{18}O$ in the direction indicated by the arrow on fig. 9. A sample collected from Williamson Creek during the dry period has a low value of $\delta^{15}N$ and a value of $\delta^{18}O$ greater than 20 per mil, indicating that the likely nitrate source is the atmosphere (rain or vehicle exhaust, or both [Fang and others, 2010]). In contrast, the isotopic compositions of most samples from all streams collected during the wet period are relatively similar, with a signature indicating a biogenic source of nitrate with some contribution from soil nitrate to the compositions of some samples from Onion and Bear Creeks.

Routine samples from the two wells have isotopic compositions indicating soil nitrate as a principal source (fig. 9). The isotopic compositions of samples collected at the Buda well are all similar, whereas isotopic compositions at the Marbridge well are more variable, consistent with the hypothesis that groundwater from the Buda well is dominated by matrix flow which changes in composition relatively slowly, and groundwater from the Marbridge well is dominated by conduit flow, which can change in composition relatively rapidly (Atkinson, 1977).

The isotopic signature of routine samples from Barton Springs is intermediate between that of the groundwater samples and that of the stream samples collected during the wet period (fig. 9). The isotopic composition of samples collected during the dry and wet periods is similar and indicates that the source of the nitrate is mostly from soils, but the three samples collected during the latter part of the wet period have relatively elevated $\delta^{15}N$ values (8.84, 7.70, and 8.20 per mil for samples collected on Jan. 5, Feb. 2, and March 2, 2010, respectively), indicating an increased contribution of biogenic nitrate. This change in nitrate sources likely results from greatly increased recharge from streams, which have elevated $\delta^{15}N$ values, relative to values for Barton Springs, during the wet period compared with the dry period.

The general relation between $\delta^{15}N$ and $\delta^{18}O$ values for samples collected from Barton Springs zone sites during the wet period (fig. 9) is similar to that which might be interpreted as indicating denitrification (Kendall and McDonnell, 1998). Denitrification, however, is not likely to be a dominant process within the Edwards aquifer near Barton Springs for several reasons. First, denitrification requires a dissolved oxygen concentration less than 0.5 mg/L, at most, and ideally less than 0.2 mg/L (van Haandel and van der Lubbe, 2007); the minimum dissolved oxygen concentration measured in any sample collected during this investigation was 3.92 mg/L. Second, the progression of samples from the lowest $\delta^{15}N$ and $\delta^{18}O$ values to the highest (fig. 9) is opposite that which would be expected: denitrification generally occurs in geochemical space from recharge (high dissolved oxygen, low $\delta^{15}N$ and $\delta^{18}O$ values) to groundwater (decreasing dissolved oxygen and increasing $\delta^{15}N$ and $\delta^{18}O$ values along the flow path). However, in this case, it is the oxygenated surface water (median dissolved oxygen concentration of 9.61 mg/L) with the highest $\delta^{15}N$ and $\delta^{18}O$ values, and the groundwater and spring water (median dissolved oxygen concentration of 5.26 mg/L) with the lowest $\delta^{15}N$ and $\delta^{18}O$ values.

Although denitrification is not indicated as a dominant process affecting the groundwater and spring samples, some of the surface-water samples might be affected by denitrification.

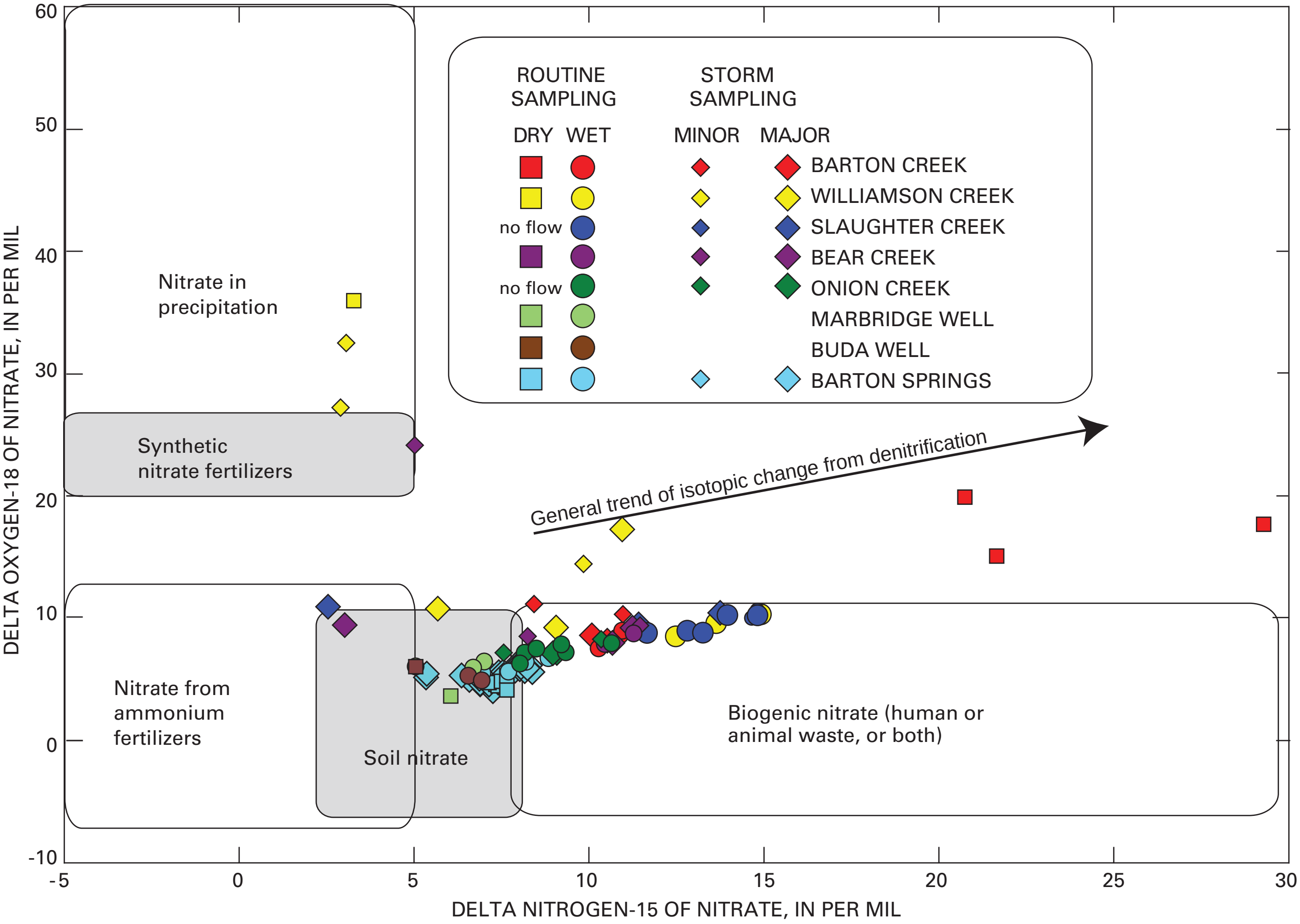


Figure 9. Isotopic compositions of nitrate in routine and storm samples from sites in the Barton Springs zone, south-central Texas, November 2008–March 2010 (common source fields of delta nitrogen-15 and delta oxygen-18 of nitrate modified from Silva and others, 2002).

The samples that appear to be most affected by denitrification were collected from Barton Creek during the dry period. Barton Creek is the only site with a significant inverse relation between δ^{15}N and nitrate concentrations (fig. 10) (Kendall's tau -0.47), which is commonly associated with denitrification (Kendall and McDonnell, 1998). Although dry soil conditions have been shown to restrain both nitrification and denitrification processes (Ohte and others, 1997), some denitrification might be occurring in the soils during dry conditions, when creek flow likely has a component of seepage from shallow soils. Although some data indicate that samples of soil water from Barton Creek are oxygenated (Oetting, 1995), denitrification can occur intermittently in anaerobic microsites within an oxygenated soil, sediment, or water body (Koba and others, 1997). The samples collected from Barton Creek during the dry period that had elevated δ^{15}N and δ^{18}O values (indicating potential denitrification) had lower dissolved oxygen concentrations (median 8.10 mg/L) than samples collected during the wet period (median 10.14 mg/L), which is consistent with this hypothesis, although the difference is not statistically significant. Alternatively, if the source of the small amount of flow in Barton Creek during the dry period consists largely of return flows from irrigation with treated wastewater, the isotopic signature of the samples might represent denitrication that occurred during secondary treatment of wastewater (James M. Montgomery Consulting Engineers, 1985) or in holding ponds, where anoxic conditions might occur (Picot and others, 2009).

The isotopic composition of nitrate in storm samples from streams was more variable than that in routine samples (fig. 9). Most storm samples have an isotopic composition of nitrate indicating some contribution of biogenic N (δ^{15}N >8 per mil). Two samples collected at Williamson Creek in response to minor storms that occurred during the dry period have isotopic compositions similar to that of a routine sample collected at the same site during the dry period (low δ^{15}N value and high δ^{18}O value), which indicates a contribution of nitrate to streamflow from the atmosphere. Samples collected following storm 1 at Bear Creek and Slaughter 2304 had isotopic compositions of nitrate that

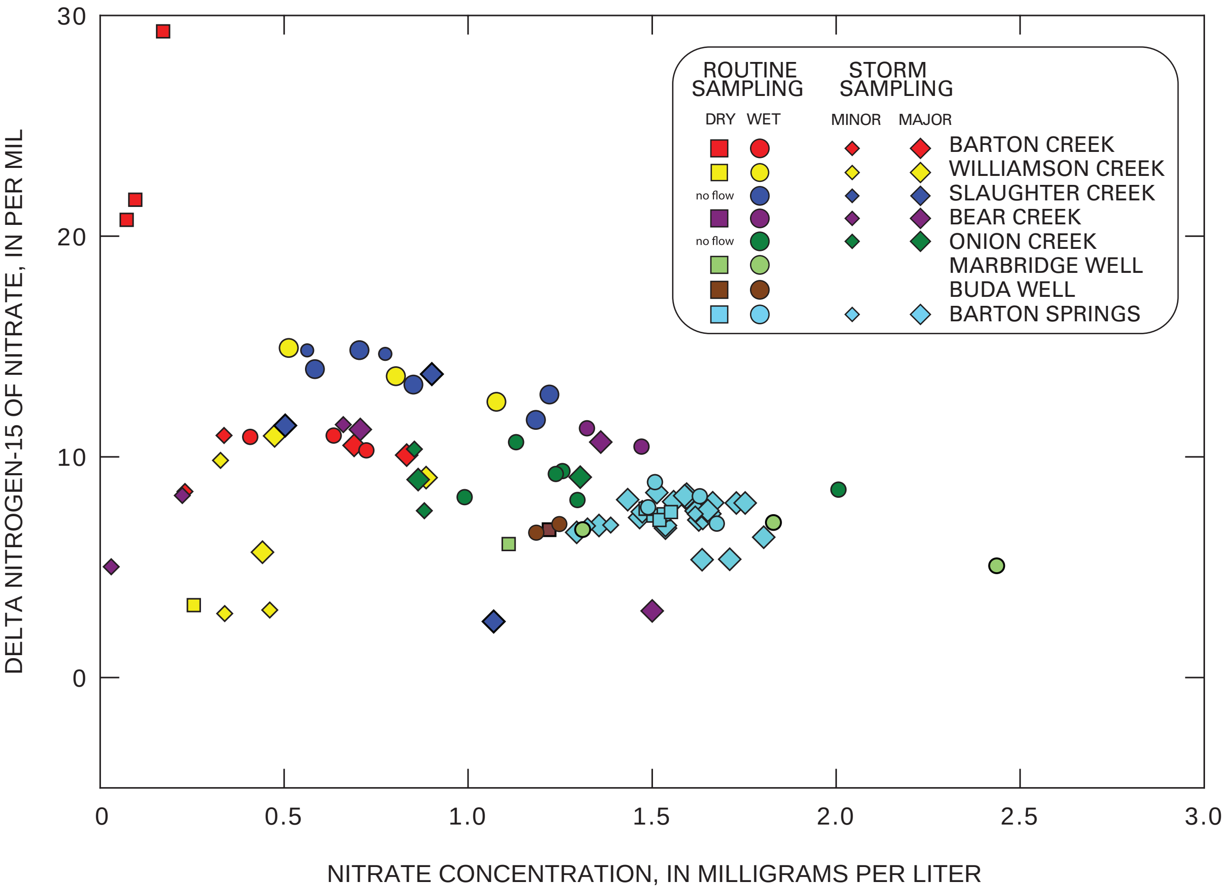


Figure 10. Values of delta nitrogen-15 of nitrate relative to nitrate nitrogen concentrations in routine and storm samples from sites in the Barton Springs zone, south-central Texas, November 2008–March 2010.

indicate a potential contribution from ammonium fertilizer ($\delta^{15}N$ <5 per mil). Overall, the greater variability of isotopic compositions for storm samples indicates that they might represent a greater mix of nitrate sources than do the routine samples.

The isotopic composition of nitrate in samples from Barton Springs collected in response to one minor storm (March 2009) and three major storms (storms 1–3) is similar to that of the routine samples (fig. 9). However, the shift toward a higher value of $\delta^{15}N$ indicates a greater contribution of biogenic nitrate during storms 2 and 3 relative to the minor storm and storm 1. This likely reflects a contribution from recharging surface water, as $\delta^{15}N$ values were higher for storms 2 and 3 than for storm 1 at those streams that had sufficient flow to sample for storm 1 (Williamson Creek, Slaughter Creek, and Bear Creek).

Comparison of Recent (2008–10) Isotopic Composition of Nitrate to Historical Data (1990–94)

Previous to this investigation, the USGS had not measured the isotopic composition of nitrate at the sites included in this investigation. However, between 1990 and 1994, the COA measured the N isotopes of nitrate in water samples from Barton Creek, from some tributaries and small springs that contribute flow to Barton Creek near the USGS sampling site, from the Buda well, and from Barton Springs. The samples were analyzed for $\delta^{15}N$ of nitrate by Coastal Laboratories in Austin, Tex., using a methodology (capture of ammonia in an acid trap, Kjeldahl digestion to convert to nitrate, followed by combustion and continuous flow into a mass spectrometer, per Richard Anderson, Coastal Laboratories, oral communication, 2010) different from that used by the USGS Stable Isotope Laboratory; $\delta^{18}O$ of nitrate was not measured. These early measurements of $\delta^{15}N$ of nitrate (City of Austin, 2010b) are compared to those measured for this investigation to investigate changes in wastewater sources to these sites during the previous 20 years, however, because inter-laboratory and inter-method comparisons have not been made, the results should be interpreted with caution. The highest $\delta^{15}N$ reported by the COA (21.0 and 22.4 per mil for samples collected in 1990 and 1992, respectively) was for a pond holding wastewater effluent 1,300 feet upstream from the Barton Creek sampling site (station 08155240) and used to irrigate a golf course, also upstream from the Barton Creek sampling site. Values for $\delta^{15}N$ of nitrate reported by the COA and measured in samples collected during 1990–94 from springs and tributaries

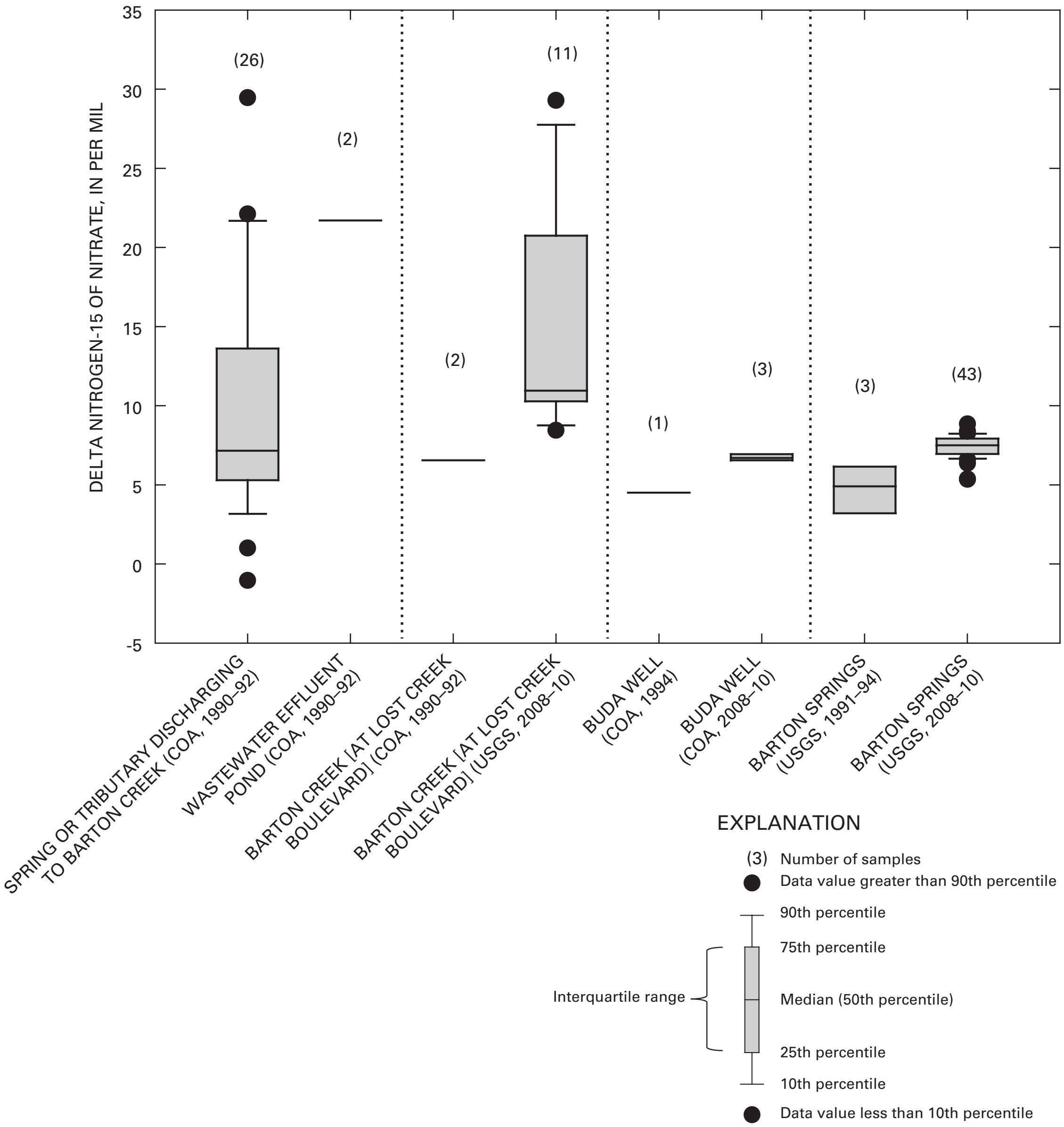


Figure 11. Delta nitrogen-15 of nitrate in samples from sites in the Barton Springs zone, south-central Texas, collected by the City of Austin (COA), 1990–94, and by the U.S. Geological Survey (USGS), 2008–10.

flowing into Barton Creek upstream or just downstream from the Barton Creek sampling site spanned a wide range, from less than 0 (indicating a ratio of ^{15}N to ^{14}N less than that of the standard) to 29 per mil (fig. 11). Among the samples from springs and tributaries, the highest δ^{15}N value was measured in the sample from a small spring that flows into Barton Creek about 300 feet downstream from the Barton Creek sampling site, and is consistent with the δ^{15}N values reported in the literature for wastewater effluent (Heaton, 1986) (fig. 2). The two δ^{15}N values measured in samples from Barton Creek by the COA are less than all of those measured in all of the samples from Barton Creek collected for this study except for one, but the difference between sample populations is not statistically significant (p-value equal to .06), likely because the small number of measurements made by COA is not sufficient for a robust analysis. Similarly, although the difference in δ^{15}N values at the Buda well cannot be compared statistically because δ^{15}N was measured by the COA in only one sample, that value is less than all three measured during this study by a substantial amount (more than 2 per mil). The δ^{15}N values measured in samples from Barton Springs for this investigation are significantly higher than those reported by the COA. The tendency toward higher δ^{15}N values in samples collected during 2008–10 relative to those collected during 1990–94 indicates the potential for a greater contribution from biogenic N sources.

Concentrations of Wastewater Compounds

Wastewater compounds were measured in selected routine samples from all sites and in storm samples for all stream sites (one flow-weighted composite sample per site per major storm and a composite or grab sample from selected streams during smaller storms) and for Barton Springs (nine samples per major storm). The wastewater compounds analysis suite consisted of 60 analytes (table 4), one of which (3-tert-butyl-4-hydroxyanisole [BHA]) was reported for less than one-half of the samples submitted for analysis. Excluding phenol, the remaining 58 analytes were reported consistently. The results for 59 analytes are discussed in this report and summarized in table 7.

Concentrations of wastewater compounds measured in routine samples collected for this investigation were very low: All concentrations were estimated at a concentration less than the MRL. For that reason, the evaluation of occurrence of wastewater compounds in routine samples focuses on frequency of detection rather than concentration.

Twelve of the 59 wastewater compounds measured were detected in at least one routine sample, and the overall frequency of detection for routine samples was 3 percent (35 of 1,113 cases). The five wastewater compounds most frequently detected were DEET (8 of 19 samples; 42 percent), caffeine (4 of 19 samples; 21 percent), camphor (4 of 19 samples; 21 percent), isophorone (4 of 19 samples; 21 percent), and tetrachloroethene (4 of 19 samples; 21 percent). Of these five, DEET, camphor, and isophorone were detected at concentrations less than the MRL in one (isophorone) or two (DEET and camphor) of the QC blank samples. With the exception of one measurement of camphor that was at a concentration higher than the MRL, concentrations in the environmental samples were similar to those in the QC blank samples, indicating that their detection might not have any environmental relevance.

For routine samples, wastewater compounds were most frequently detected in samples collected from Barton Springs (10 of 235 cases; 4 percent), less frequently detected in routine samples collected from the five streams (17 of 526 cases; 3 percent), and least frequently detected in routine samples collected from the two wells (8 of 352 cases; 2 percent). Of the stream sites, wastewater compounds were most frequently detected in routine samples collected from Williamson Creek (3 of 58 cases; 5 percent). Samples were collected at Williamson and Bear Creeks on March 13, 2009, after a minor storm during the dry period. The frequency of detection for the minor storm samples from both of these sites (25 percent

Table 7. Summary of wastewater compound detections and statistics for most frequently detected compounds in samples (routine and storm samples combined) from sites in the Barton Springs zone, south-central Texas, 2008–10.

[All concentrations in micrograms per liter; n, number of samples analyzed; %, percent; <, less than; --, no data]

	Surface-water samples		Groundwater samples	Barton Springs samples	
	Routine	Storm	Routine	Routine	Storm
Number of compounds detected	8	27	6	4	29

Most frequently detected compounds[1]	Detection frequency % (n), median, maximum concentration	Detection frequency, % (n), median, maximum concentration	Detection frequency, % (n), median, maximum concentration	Detection frequency, % (n), median, maximum concentration	Detection frequency, % (n), median, maximum concentration
N,N-diethyl-meta-toluamide (DEET)	22% (9)	100% (15)	33% (6)	100% (4)	37% (27)
	<.06, .037	.055, .34	<.06, .026	.015, .029	<.06, .048
Caffeine	44% (9)	80% (15)	0 (6)	0 (4)	44% (27)
	<.06, .069	.035, .46	--	--	<.06, .042
Tetrachloroethene	0 (9)	0 (15)	0 (6)	100% (4)	89% (27)
	--	--	--	.017, .1	.035, .17
Camphor	44% (9)	67% (15)	0 (6)	0 (4)	4% (27)
	<.044, .031	.03, .12	--	--	<.044, .0061
Isophorone	22% (9)	69% (15)	33% (6)	0 (4)	19% (27)
	<.032, .01	.012, .043	<.032, .0086	--	<.032, .014

[1] Most frequently detected compounds are those detected in more than 20 percent of samples.

and 7 percent, respectively) was higher than those for the routine samples, indicating that detectable concentrations of wastewater compounds in streams might occur more frequently following storms, particularly those that occur during droughts. Of the two wells, wastewater compounds were more frequently detected at the Buda well (7 of 176 cases; 4 percent) than at the Marbridge well (1 of 176 cases; less than 1 percent).

Wastewater compounds were measured in samples collected from each of the streams and from Barton Springs in response to storms 1–3. The only samples for analysis of wastewater compounds collected in response to a minor storm were those at Bear and Williamson Creeks on March 13, 2009, and described in the previous paragraph. The sample for storm 1 for Slaughter Creek was collected at the downstream end of the recharge zone at the Slaughter 2304 site (fig. 1). The frequency of detections in storm samples at concentrations equal to or greater than the MRL was low (13 of the 2,453 cases; 0.5 percent), but exceeded that for routine samples. Four compounds (caffeine, camphor, DEET, and triclosan) were detected at a concentration equal to or greater than the MRL. All other detections were reported as estimated at a concentration less than the MRL. For that reason, the evaluation of occurrence of wastewater compounds in storm samples focuses on frequency of detection rather than concentration.

Forty-three of the 59 wastewater compounds were detected in at least one storm sample, and the overall frequency of detection for storm samples was 9 percent (221 of 2,453 cases), about twice that for routine samples. The five wastewater compounds most frequently detected in storm samples were tetrachloroethene (24 of 42 samples; 57 percent), DEET (25 of 42 samples; 60 percent), caffeine (24 of 42 samples; 57 percent), isophorone (15 of 42 samples; 36 percent), and hexahydrohexamethylcyclopentabenzopyran (HHCB) (11 of 42 samples; 26 percent). The greater frequency of detection of wastewater compounds at all concentrations and the greater frequency of detections at concentrations equal to or exceeding the MRL in storm samples relative to routine samples indicate that there likely was a greater contribution of wastewater to samples collected in response to storms than to those collected routinely.

Wastewater compounds were more frequently detected in storm samples collected at streams (129 of 877 cases; 15 percent) than at Barton Springs (92 of 1,576 cases; 6 percent). At stream sites, as for routine samples, wastewater compounds were most frequently detected in storm samples collected at Williamson Creek (57 of 234 cases; 24 percent). The frequency of detection for storm samples collected at the other stream sites was much lower: the stream site with the next highest frequency of detection was Slaughter Creek, which had a detection frequency of 14 percent (24 of 175 cases). The frequency of detection was similar for storms 1–3, but was lowest for storms 1 (54 of 701 cases; 8 percent) and 2 (67 of 822 cases; 8 percent) and highest for storm 3 (80 of 812 cases; 10 percent).

At Barton Springs, nine storm samples were collected during a period of 1 to 2 weeks following each of the three storms. None of the wastewater compounds, with the exception of tetrachloroethene, showed breakthrough curves in response to any of the storms. Tetrachloroethene concentrations peaked at 86 (storm 1), 35 (storm 2), and 37 (storm 3) hours after the storm began. Breakthrough curves have been reported for tetrachloroethene for storms in the past (Mahler and others, 2006; Mahler and Massei, 2007), and the source has been hypothesized to be a point source, such as a spill, rather than a nonpoint source, such as wastewater (Mahler and Massei, 2007). In this investigation, tetrachloroethene was detected only at Barton Springs, an additional indication that wastewater is not the source of this compound in the Barton Springs zone.

Evaluation of the Relation Between Occurrence of Nitrate and Wastewater Compounds

The occurrence of nitrate above background concentration, the isotopic composition of nitrate, and the detection of wastewater compounds are all indicators of a potential contribution to environmental waters from wastewater sources. To determine whether occurrences of nitrate and wastewater compounds during this study were giving consistent indications of potential wastewater inputs, the correlation between nitrate concentrations and the frequency of detection of wastewater compounds in routine and storm samples was tested statistically. Those samples with an isotopic composition of nitrate indicating a biogenic source ($\delta^{15}N$ value greater than 8 per mil [Silva and others, 2002]) were included in the analysis. All samples were tested together, and Barton Springs samples and stream samples were tested separately as two groups. In no case was there a statistically significant relation between the concentration of nitrate and the frequency of detection of wastewater compounds.

There is an apparent inconsistency between the occurrence of nitrate with an isotopic composition indicating a potential biogenic source and the infrequent occurrence of wastewater compounds. Nitrate concentrations at Barton Springs and in the five recharging creeks have increased relative to historical (1990–2008) samples, and the isotopic composition of nitrate in many of the samples, particularly those from streams, indicates a biogenic source, for which wastewater is a potential source. However, during this investigation, wastewater compounds were detected in Barton Springs and at stream and groundwater sites in the Barton Springs zone only at very low concentrations (less than the MRL in more than 99 percent of cases), and the frequency of detection was not correlated to nitrate concentrations. This apparent inconsistency might arise if nitrate and wastewater compounds have the same source (for example, wastewater) but react differently to environmental fate processes. This was proposed by Katz and others (2009) in a report of an investigation of the karstic Floridan aquifer. They reported elevated nitrate concentrations at groundwater and spring sites downgradient from land application of treated wastewater; the isotopic composition of the nitrate was similar to that of the sprayfield effluent and different from that of water at other groundwater sites unaffected by infiltration from the sprayfield. Numerous wastewater compounds were detected in the sprayfield effluent, but at concentrations less than the MRLs; few compounds were detected at the groundwater sites affected by infiltration from the sprayfield. Katz and others concluded that the wastewater compounds were removed from the treated effluent during infiltration through the relatively thin layer of permeable sand overlying the aquifer. In contrast, nitrate is, under aerobic conditions, both soluble and conservative (Hem, 1992), and is not expected to be removed during infiltration.

Urban Development in the Barton Springs Contributing Zone and Potential Relation to Nitrate Concentrations

The abrupt increase in nitrate concentrations that occurred between 2004 and 2008 in the five principal creeks of the Barton Springs zone at the upstream end of the recharge zone and in Barton Springs indicates that urban development and associated activities in the Barton Springs zone, and in particular the contributing zone, might be a contributing factor. The isotopic composition of the nitrate and the historical changes in that isotopic composition are consistent with an increased contribution of nitrate from a biogenic source. Changes since 2000 in the Barton Springs zone in the density of three potential sources of such wastes in the area are evaluated here: two types of wastewater disposal facilities (septic systems and land application of treated wastewater) and domesticated dogs and cats. The analysis was limited to the contributing zone, as the five stream sampling sites, where changes in nitrate have been greater than those at the wells or at Barton Springs, are located near the upstream end of the recharge zone (fig. 1A). Septic systems, land application of treated wastewater, and domesticated dogs and cats in the watershed of Little Bear Creek were not included in the analysis as the confluence of Bear and Little Bear Creeks is downstream of the Bear Creek sampling site.

Currently (November 2010), all wastewater disposal in the Barton Springs zone is done by individual on-site sewage facilities (OSSF), commonly referred to as septic systems, or by land application of treated wastewater under the Texas Land Application Permit (TLAP) system (Texas Commission on Environmental Quality, 2011). In 2009, Hays County Water Control and Improvement District 1, serving the Belterra Subdivision, was granted the first wastewater discharge permit in the contributing zone of the aquifer, but as of November 2010 direct discharge of wastewater to streams had not begun. OSSFs and land application of treated wastewater do not involve intentional discharge to surface water, but overloaded OSSF drain fields will flood discharging sewage to the ground surface (U.S. Environmental Protection Agency, 2005), and runoff can occur from land application facilities if the infiltration capacity of the soil is exceeded (Alberta Environment, 2000). Additionally, infiltration from both septic systems and land application can affect groundwater, which in turn can discharge into streams during base flow conditions (Stelzer and others, 2010).

An increase in population is accompanied by an increase in domesticated animals, in particular dogs and cats, whose feces are a source of fecal pathogen contamination (U.S. Environmental Protection Agency, 2001) and, potentially, nitrate (Tota-Maharaj and Scholz, 2010). Additionally, dog urine contains much higher concentrations of urea, which is transformed to nitrate in soils, than does the urine of humans.

Leaking wastewater-collection-system infrastructure for centralized sewage treatment is a potential source of nutrients to surface water and groundwater but is limited in the contributing zone to the Williamson Creek watershed. Much of the wastewater line was installed relatively recently—the length-weighted average date of wastewater-line installation in the Williamson Creek watershed is 1996—and therefore the amount of leakage likely is small. For these reasons, centralized wastewater infrastructure was not included in this report in the analysis of potential nitrate sources to the contributing zone streams.

Although urban development over the Barton Springs zone has increased since 2000 (Naismith Engineering, 2005), agricultural land use, including livestock, has decreased. From 2002 to 2007, the area of farmed land in Travis and Hays Counties decreased by 12 and 15 percent, respectively (U.S. Department of Agriculture, 2009). The potential agricultural land-use area (defined as undeveloped and agricultural land combined) is estimated to have decreased in the Barton Springs zone from 87 percent in 1995 to 40 percent in 2003, and in the contributing zone from 90 percent in 1995 to 54 percent in 2003 (City of Austin, 2005). Therefore, although animal wastes either from livestock-feeding operations or used as agricultural fertilizer are a potential source of nitrate to surface water and groundwater, livestock operations are assumed not to be increasing in the Barton Springs zone or contributing zone. As livestock operations therefore are unlikely to be the source of increases in nitrate concentrations that occurred after 2005, they are not further evaluated here.

Changes in Septic System Density

Septic-system density was determined on the basis of OSSF permits granted by Travis County, Hays County, the City of Austin, and the Village of Bee Cave (Herrington and others, 2010), which together comprise more than 97 percent of the jurisdictional area in the Barton Springs zone. Although the City of Dripping Springs also issues OSSF permits, they do not maintain electronic records of permits and the data are not included in those considered here. The City of Dripping Springs has issued about 80 OSSF permits since 2006 (Kyle Dayheart, City of Dripping Springs, oral commun., 2010), and in 2008 took about 300 OSSFs off line and replaced them with a centralized land-application system (Susan Zachos, City of Dripping Springs, oral commun., 2010).

Currently (November 2010) there are 7,608 OSSF permits issued for the contributing zone, of which 6,217 (83 percent) were issued from 2001 through 2010 (fig. 12). The annual number of OSSF permits issued peaked in 2001, and more permits were issued between 2001 and 2005 than existed in 2000 or were issued from 2006 to 2010 (fig. 13A). The most permits were issued for properties in the Barton and Onion Creek watersheds, and the fewest in the Williamson and Slaughter Creek watersheds. However, the density of OSSFs (number of OSSFs per acre) is greatest for the Bear Creek watershed (fig. 13A), and density generally has a greater effect than the number of OSSFs on water quality (Canter and Knox, 1985). In the Barton, Bear, and Onion Creek watersheds, the density of OSSFs increased more rapidly from 2001 to 2005 than from 2006 to 2010; in the Williamson and Slaughter Creek watersheds, the increase in the density of OSSFs from 2001 to 2010 was relatively steady.

Changes in Land Application of Treated Wastewater

The volume of treated wastewater used for land application was determined on the basis of the permitted discharge volume on the TLAPs issued by the Texas Commission on Environmental Quality (TCEQ) (information on obtaining permits available from *http://www.tceq.state.tx.us/adminservices/data/fileroom.html*) and the phase of the project at which the facility is operating (available from the U.S. Environmental Protection Agency permit compliance web site at *http://www.epa.gov/enviro/html/pcs/pcs_query_java.html*) (Herrington and others, 2010), and on the reported volume of land application of treated wastewater in Dripping Springs (about 40,000 gallons per day; Susan Zachos, City of Dripping Springs, oral commun., 2010). Permitted irrigation volumes were determined by summing permitted volumes for the phase (interim or final) of operation for each facility. There were 28 active TLAP facilities in the Barton Springs zone in 2010, 26 of which are on the contributing zone and two of which are on the recharge zone. TLAP facilities use either surface (spray) irrigation or subsurface drip irrigation of treated effluent. TLAP facilities generally are operated at less than 75 percent of permitted flow, because the operator is required to contact the TCEQ when flow volumes exceed 75 percent of the permitted volume for 3 consecutive months. The estimate of effluent irrigation volume generated from permit files therefore likely overestimates the actual irrigation volume.

Currently (November 2010), there is a total permitted final-phase wastewater irrigation volume for TLAP facilities in the contributing zone of 5,300,000 gallons per day, 5,000,000 gallons per day of which (95 percent) were for TLAP facilities permitted from 2001 to 2010. Because most of the facilities have multiple phases or are in an interim phase, the permitted volume of irrigated flow is 3,300,000 gallons per day (fig. 13B). The volume of new permitted irrigation by year peaked in 2005; the volume permitted in 2005 was about 2.5 times that permitted either from 2001 through 2005 or from 2006 through 2010 (fig. 13B). Both the highest irrigation volume and rate (volume per day per area) are in the Barton Creek watershed, where they increased most rapidly from 2004 to 2005 (fig. 13B). Irrigation rate in the Bear and Onion Creek watersheds also increased rapidly from 2004 to 2005. The irrigation rate in the Bear Creek watershed increased again between 2008 and 2009.

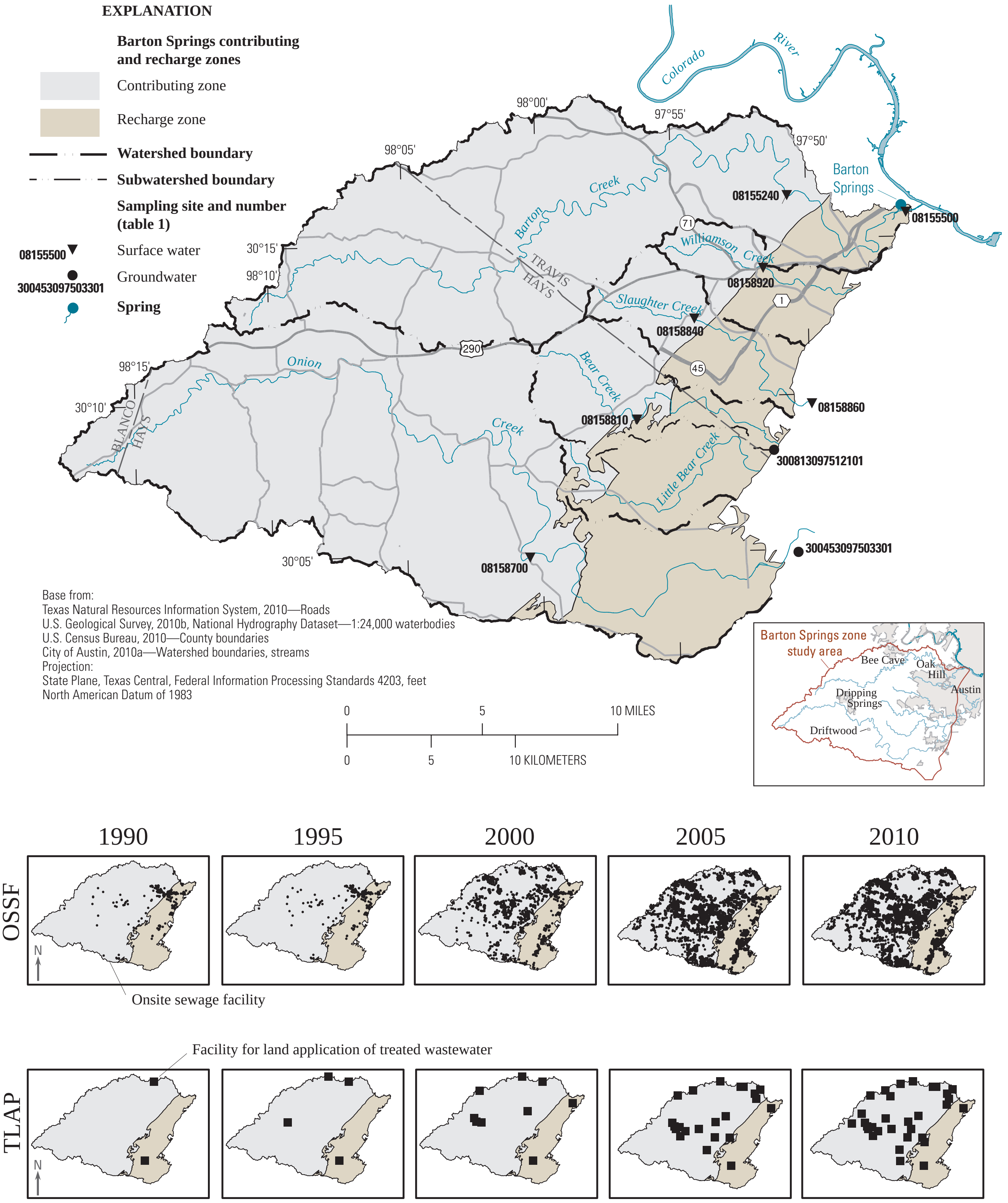
Changes in Numbers of Domesticated Dogs and Cats

Populations of domesticated dogs and cats were estimated using a demographic approach based on the number of estimated households in each watershed and national data on pet ownership. The number of household units in the watersheds of the contributing zone was estimated from household demographics reported for 2000, 2005, 2008, and 2010 by the Capital Area Metropolitan Planning Organization (2010). Data on the percentage of households with dogs and cats and the average number of dogs and cats owned per pet-owning household from the American Veterinary Medical Association (2007) were combined with the estimates of the numbers of households to estimate the number of domesticated dogs and cats in the contributing zone.

In contrast to the increase in the number of OSSFs and the volume of land application of treated wastewater, the number of domesticated dogs and cats estimated to be in the watersheds prior to 1991 is similar to the estimated number added since that time (fig. 13C). On the basis of the demographics data, the number of domesticated dogs and cats in the contributing zone increased by 30 percent during 2001–05, and by another 3 percent during 2006–10. The highest density of domesticated dogs and cats and the most rapid increase in their density during 2000–10 was in the Williamson Creek watershed (fig. 13C), with a density by 2010 about 3.5 times greater than that in the Slaughter Creek watershed, the watershed with the next highest density.

Potential Relations Between Changes in Urban Development and Nitrate Concentrations

The temporal patterns of the densities of the three sources of human or animal waste, or both, associated with urban development—OSSFs, TLAP facilities, and domesticated dogs



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 12. Changes in number of on-site sewage facilities (OSSFs) (septic systems) and permitted facilities for land application of treated wastewater (Texas Land Application Permit [TLAP] system) in the contributing and recharge zones of the Barton Springs zone, south-central Texas, 1990–2010.

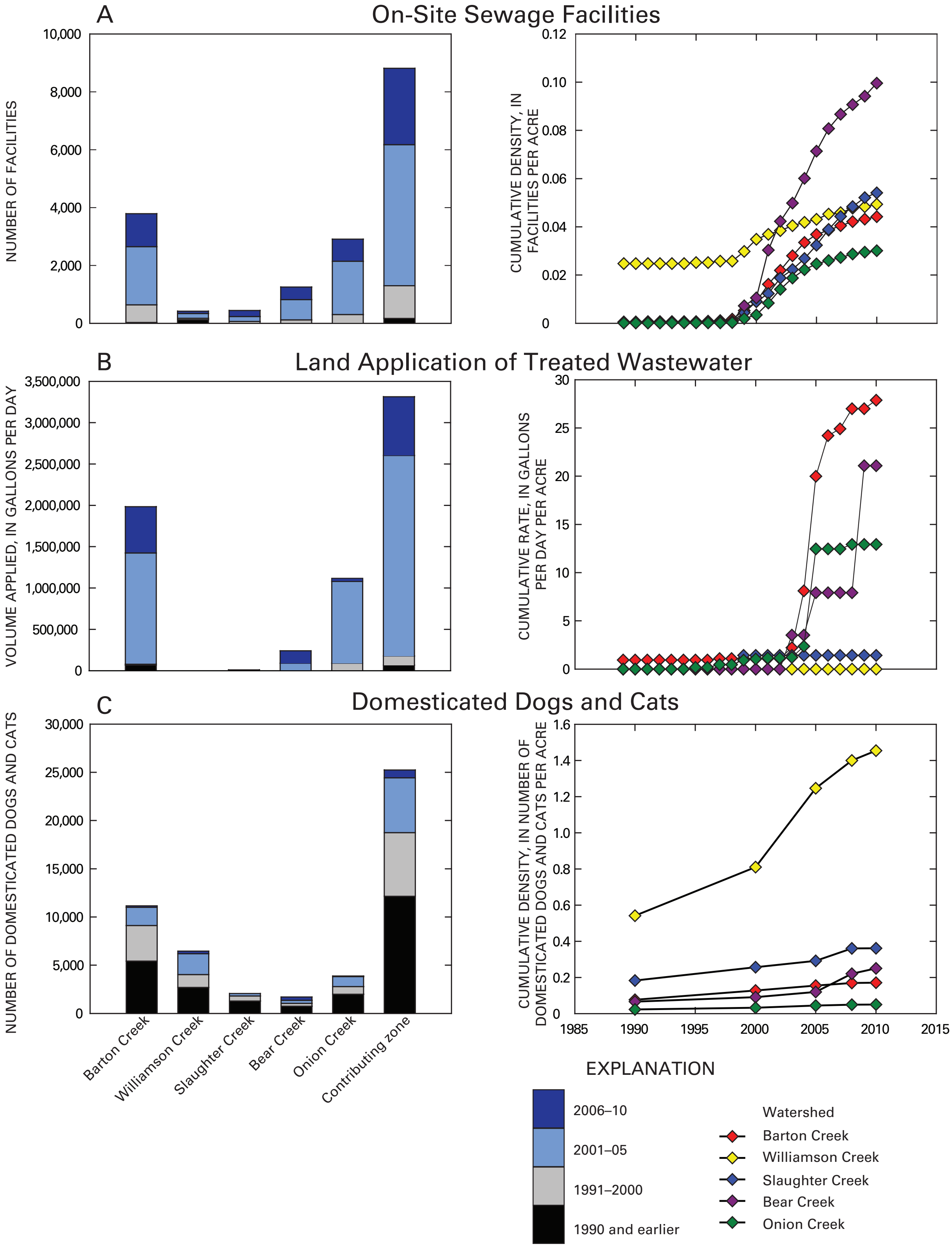


Figure 13. Changes by watershed in (A) number and density of on-site sewage facilities (septic systems), (B) volume and rate of land application of treated wastewater, and (C) estimated number and density of domesticated dogs and cats in the contributing zone of the Barton Springs zone, south-central Texas, 1990–2010.

and cats—were considered and provide information regarding potential sources of the documented increase in nitrate concentrations in streams crossing the contributing zone. As discussed in the section "Comparison of Recent (2008–10) and Historical (1990–2008) Nitrate Concentrations," increases in nitrate occurred beginning in about 2005 in Barton and Williamson Creeks and in 2008 in Slaughter, Bear, and Onion Creeks; the increases were most pronounced for Bear and Onion Creeks and, to a lesser extent, Slaughter Creek (fig. 8A–E).

The density of OSSFs increased in the watersheds of all five creeks from 2001 through 2010 (fig. 13A). The number of OSSFs permitted per year in each watershed peaked in 2001 or 2002; if OSSFs are related to increasing nitrate concentrations in the streams, a delay of several years would occur between the time that the permit was issued and increased nitrate concentrations were measured. Such a delay might be the result of the time required for nutrient saturation of the drainfield, migration of leachate into groundwater flow paths, or system malfunction. The increase in permitted OSSFs was most rapid in the Slaughter and Bear Creek watersheds and least rapid in the Onion Creek watershed. The increased density of OSSFs is more consistent with increasing nitrate concentrations in Bear Creek than the other streams, but increasing density of OSSFs cannot be ruled out as a source of the increasing nitrate to any of the five streams.

The irrigation rate (volume per unit area per time) of treated wastewater effluent increased rapidly in the watersheds of Barton, Bear, and Onion Creeks from 2004 through 2010 (fig. 13B). The maximum increase in rate in the Barton and Onion Creek watersheds occurred from 2004 to 2005, and in the Bear Creek watershed from 2008 to 2009. This temporal pattern is consistent with the increase in nitrate concentrations documented in those creeks. Because there are no TLAP facilities in the Williamson Creek watershed and because no new TLAP facilities have been installed in the Slaughter Creek watershed since 1997, it is unlikely that land application of treated wastewater effluent is associated with the increase in nitrate measured in those two streams.

The density of domesticated dogs and cats, estimated on the basis of demographics, increased in the watersheds of all five creeks during 2001–10 (fig. 13C), but to much less of an extent than the increase in OSSFs and TLAPs. The greatest density and the most rapid increase in density of domesticated dogs and cats occurred in the watershed of Williamson Creek and were much greater than in the other watersheds. However, nitrate concentrations measured in samples collected from Williamson Creek for this investigation are not higher than concentrations measured in samples collected contemporaneously from the other four streams, and the change in nitrate concentrations and loads in Williamson Creek is less than those at the other stream sites (fig. 8B; table 6). Domesticated dog and cat waste therefore might be a principal source of the increase in nitrate concentrations in Williamson Creek, but is unlikely to be a principal source in Barton, Slaughter, Bear, and Onion Creeks.

The nitrate and wastewater compound results in combination indicate that land application of treated wastewater might be the source of the measured increases in nitrate concentration. The low concentrations of wastewater compounds measured (less than the MRL in more than 99 percent of cases) and the lack of correlation with nitrate are consistent with removal of the wastewater compounds from the treated effluent during infiltration through the soil. A similar process was reported as occurring at sprayfields irrigating with treated municipal wastewater from Tallahassee, Fla., which resulted in increased nitrate concentrations at Wakulla Springs Basin in northern Florida (Katz and others, 2009). The marked increase in nitrate concentrations following the onset of the wet period (fig. 4) also is consistent with land application as a source, as nitrogen from land application would be expected to build up in the soils during the dry period and then leach out once the wet period began.

One of the objectives of this investigation was to establish a current (2010) baseline against which future potential changes in water quality related to increasing urbanization and associated wastewater production can be compared. The results of this investigation indicate that the baseline, in terms of nitrate, shifted upward between 2001 and 2010. The increase in nitrate in samples collected from the five streams, Marbridge well, and Barton Springs is noteworthy given that at the time of the investigation (2008–10), direct discharges of treated wastewater effluent to streams in the Barton Springs zone had not yet occurred. Neither OSSFs nor TLAPS involve intentional discharge to surface water, yet even without any intentional discharges the concentration of nitrate in the streams crossing the contributing zone increased relative to similar flow conditions by a factor of 3 (Barton Creek, medium-flow conditions) to 11 (Onion Creek, medium-flow conditions). One wastewater discharge permit in the Barton Springs zone has been issued, allowing a discharge of up to 350,000 gallons per day of treated wastewater effluent into the upper end of Bear Creek (Texas Commission on Environmental Quality, 2009), but no discharge yet has been released. Water-quality models have demonstrated that the proposed discharge would increase the loading of nitrate to Bear Creek and to Barton Springs (Herrington, 2008a, b) above current levels; the increase in the average daily load of nitrate in Bear Creek at the upstream boundary of the recharge zone was estimated to be 4.5 kilograms per day. An investigation of small streams on the nearby Edwards Plateau (central Texas) demonstrated that those streams receiving wastewater effluent had relatively high nutrient concentrations and had become eutrophic, characterized by excessive amounts of nutrients and low dissolved oxygen concentrations relative to historical nutrient concentrations and dissolved oxygen levels (Mabe, 2007).

Summary

The Barton Springs zone is in an area of south-central Texas undergoing rapid growth in population and in land area affected by development, with associated increases in population and wastewater disposal. An investigation to provide understanding of occurrence of nitrate and wastewater compounds in the Barton Springs zone was conducted by the U.S. Geological Survey (USGS), in cooperation with the City of Austin, the City of Dripping Springs, the Barton Springs/Edwards Aquifer Conservation District, the Lower Colorado River Authority, Hays County, and Travis County. The primary objectives of the investigation described here were to characterize concentrations of nitrate and wastewater compounds in the Barton Springs zone in surface water, groundwater, and Barton Springs discharge and to evaluate potential sources of nitrate using measured nitrogen (N) and oxygen (O) isotopes of nitrate and detections of wastewater compounds.

Routine sampling and storm-targeted sampling were used to evaluate the occurrence of nitrate and wastewater compounds in water from Barton Springs and the streams that provide much of its recharge. Samples were collected at five stream sites (Barton, Williamson, Slaughter, Bear, and Onion Creeks), at two groundwater wells (Marbridge well [YD–58–50–704] and Buda well [LR–58–58–403]), and at the main orifice of Barton Springs. Nitrate was measured in all samples, and N and O isotopes of nitrate and wastewater compounds were measured in a subset of samples representing a range of flow conditions. The first 10 months (November 1, 2008–September 8, 2009) of the 17-month period of sample collection was a dry period characterized by infrequent storms, low flow or frequently no flow in streams, and low aquifer flow conditions (Barton Springs discharge was 40 ft^3/s or less). The dry period was followed by a 7-month wet period (September 9, 2009–March 31, 2010) characterized by frequent storms, continuous flow in the streams, and a transition from low to high aquifer flow conditions (Barton Springs discharge increased steadily from 17 to 90 ft^3/s).

The median nitrate concentration in routine samples from all sites collected during the wet period exceeded that in routine samples collected during the dry period. The difference was greatest for the streams, for which the median nitrate concentration increased from 0.04 mg/L (dry period) to 0.96 mg/L (wet period). Among individual sites, the difference was greatest for Bear Creek, for which the median nitrate concentration increased from 0.02 to 1.34 mg/L, the highest median concentration of the five stream sites during the wet period. The abrupt transition from low nitrate concentrations measured during the dry period to high concentrations measured during the wet period likely resulted from loading and storage of nitrogen compounds during the dry period and leaching of those compounds with the resumption of frequent rainfall.

Nitrate concentrations measured in all samples collected during November 2008–March 2010 (“recent”) were compared to 1990–2008 (historical) nitrate concentrations for samples collected and analyzed by the USGS at the same sites. During medium- and high-flow conditions, for those cases with sufficient data for statistical analysis, nitrate concentrations were significantly higher for recent samples than for historical samples at all stream sites. The largest increases in median nitrate concentration in recent samples compared to historical samples occurred for Bear and Onion Creeks. As a result, nitrate concentrations in aquifer recharge from streams during this study (2008–10) were considerably elevated relative to concentrations prior to 2008, and during the period of this study, aquifer recharge occurring through the beds of Barton, Williamson, Slaughter, Bear, and Onion Creeks did not provide substantial dilution of nitrate in groundwater.

Recent nitrate concentrations were higher than historical concentrations at the Marbridge well but the reverse was true at the Buda well. All recent nitrate concentrations at the Marbridge well were higher than historical concentrations, except for one high outlier. Differences in variability of nitrate concentrations at the two wells was consistent with the hypothesis that the geochemistry of the groundwater at the Marbridge well is controlled by conduit flow that receives rapid recharge from streams, and that the geochemistry of the groundwater at the Buda well is controlled by matrix flow whose chemistry is relatively unaffected over the short term by recharge from streams.

At Barton Springs, the median recent nitrate concentrations were significantly higher than historical concentrations for low, average, and high aquifer flow conditions. Nitrate concentrations measured during 1990–2008 are inversely related to spring discharge, but concentrations measured during 2008–10 are positively related to spring discharge, a change that is consistent with the recent increase in nitrate concentrations in the five recharging streams relative to historical conditions. Although the climatic conditions during 2008–10 (transition from dry to wet periods) likely caused elevated nitrate concentrations during the wet period relative to the dry period, similar climatic conditions also occurred during 1990–2008. Thus an additional factor, such as higher nitrogen loading in the watersheds, would have been required to produce the high nitrate concentrations and loads measured at the stream sites, Marbridge well, and Barton Springs during this investigation.

Isotopic compositions of nitrate provided information regarding the source of the nitrate. Most stream samples had an isotopic composition indicating a biogenic (animal- or human-waste, or both) source for the nitrate. Samples collected during the dry period from Williamson Creek, however, had an isotopic composition indicating the atmosphere (rain or vehicle exhaust, or both) as the nitrate source. Samples from the two wells had an isotopic composition indicating natural soil nitrate as a principal source. The isotopic composition of routine samples from Barton Springs was intermediate between that of the groundwater samples and that of the stream samples collected during the wet period. The composition at Barton Springs trended toward higher delta nitrogen-15 ($\delta^{15}N$) values in response to the second and third storms and during high aquifer flow conditions, indicating an increased contribution of biogenic nitrate. Values of $\delta^{15}N$ for samples from Barton Creek, the Buda well, and Barton Springs were compared to those measured at the same sites by the City of Austin in the early 1990s. In most cases, the recent $\delta^{15}N$ values were higher than those measured in the 1990s.

Wastewater compounds were measured in selected routine samples from all sites, in all major storm samples from stream sites and Barton Springs, and in two minor storm samples from stream sites. Wastewater compounds measured in routine samples were detected infrequently (3 percent of cases), and concentrations were very low (less than the method reporting level [MRL] in all cases). The compounds were detected most frequently in samples from Barton Springs and least frequently in samples collected at the wells. The five wastewater compounds most frequently detected were N,N-diethyl-meta-toluamide (DEET), caffeine, camphor, isophorone, and tetrachloroethene. However, because DEET, camphor, and isophorone were detected at similar concentrations in one or two of the quality-control blank samples, their detection in environmental samples might have little relevance.

Wastewater compounds were measured in all major and two minor storm samples (streams and Barton Springs), and the frequency of detection (9 percent) was more than twice that for routine samples. Concentrations of wastewater compounds in storm samples exceeded those in routine samples: The frequency of detections in storm samples at concentrations equal to or greater than the MRL (0.5 percent) exceeded that for routine samples. The six compounds most frequently detected in storm samples were DEET, caffeine, tetrachloroethene, isophorone, camphor, and hexahydrohexamethylcyclopentabenzopyran (HHCB). The detection of tetrachloroethene in samples collected from Barton Springs but not in samples from the stream sites during this investigation is consistent with the hypothesis proposed in previous studies that this compound has a point source rather than a nonpoint source such as wastewater. The greater frequency of detections at concentrations equal to or exceeding the MRL in storm samples relative to routine samples indicates that there likely was a greater contribution of wastewater to samples collected in response to storms than to samples collected routinely.

Although both nitrate and wastewater compounds might have wastewater as a source, there was no relation between the concentration of nitrate for those samples with a $\delta^{15}N$ value greater than 8 per mil (indicating a biogenic source) and the frequency of detection of wastewater compounds. Wastewater compounds might be removed from the treated effluent during infiltration through soil overlying the aquifer, as has been demonstrated for karst terrane in Florida, or by some other process. Nitrate, in contrast, is both soluble and conservative under aerobic conditions and is not expected to be removed or transformed during infiltration.

To evaluate whether the abrupt increase in nitrate concentrations that occurred between 2004 and 2008 in the five principal creeks of the Barton Springs zone at the upstream end of the recharge zone and in Barton Springs is related to wastewater disposal, changes since 2000 in the density of two types of wastewater disposal facilities (individual on-site sewage facilities [OSSFs] [septic systems] and Texas land-application permit [TLAP] facilities [land application of wastewater]) and changes in the number of domesticated dogs and cats in the contributing zone were considered. Livestock was not evaluated as a source because land available for agricultural uses in the contributing zone has decreased since 1995, and centralized wastewater infrastructure (sewer lines) was not evaluated as a source because, within the contributing zone, it exists only in the Williamson Creek watershed.

The density of OSSFs during 2001–10 increased in the watersheds of all five streams, and the number of OSSFs permitted per year in each watershed peaked in 2001 or 2002. Thus the timing of maximum permitting of OSSFs pre-dates the increase in nitrate in the streams and Barton Springs by several years. The increased density of OSSFs in the contributing zone is more consistent with increasing nitrate concentrations in Bear Creek than in the other streams, but increased density of OSSFs cannot be ruled out as a source of the increasing nitrate to any of the five streams. The timing of permitting for TLAP facilities, most of which occurred in or after 2005, is concurrent with the timing of the increase in nitrate concentrations. However, there are no TLAP facilities in the Williamson Creek watershed and no new TLAP facilities in the Slaughter Creek watershed since 1997. Thus TLAP facilities in the contributing zone are a potential source of increased nitrate to Barton, Bear, and Onion Creeks, but not to Williamson or Slaughter Creeks. The most rapid increase in density of domesticated dogs and cats during 2001–10 occurred in the watershed of Williamson Creek, with a density by 2010 exceeding that in any other watershed by a factor of about 3.5. Therefore, waste from domesticated dogs and cats might be a principal source of the increase in nitrate concentrations in Williamson Creek, but is unlikely to be a principal source in Barton, Slaughter, Bear, and Onion Creeks. Of the three potential sources considered—OSSFs, TLAP facilities, and domesticated dogs and cats—TLAP facilities are the nitrate source most consistent with the combined occurrence of nitrate and wastewater compounds. The lack of correlation between the frequency of detection of wastewater compounds and nitrate concentration might be explained by removal of the wastewater compounds from the treated effluent during infiltration through the soil.

One of the objectives for this investigation was to establish a current (2010) baseline against which future potential changes in water quality related to increasing urbanization and associated wastewater production can be compared. The results of this investigation indicate that the baseline, in terms of nitrate, shifted upward between 2001 and 2010. Even without any intentional discharges of treated wastewater, the concentration of nitrate in the principal contributing zone streams, Barton Springs, and Marbridge well have increased recently.

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