In cooperation with the Texas Commission on Environmental Quality

Recent (2003–05) Water Quality of Barton Springs, Austin, Texas, With Emphasis on Factors Affecting Variability

Scientific Investigations Report 2006–5299

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

Cover.
Top left: Main Spring of Barton Springs (photograph courtesy of David Johns, City of Austin).

Top right: Eliza Spring of Barton Springs (photograph courtesy of David Johns, City of Austin).

Bottom right: Upper Spring of Barton Springs (photograph by Greg Stanton, U.S. Geological Survey).

Bottom left: Old Mill Spring of Barton Springs (photograph by Brad Garner, U.S. Geological Survey).

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By Barbara J. Mahler, Bradley D. Garner, MaryLynn Musgrove,
Amber L. Guilfoyle, and Mohan V. Rao

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U.S. Geological Survey, Reston, Virginia: 2006
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Suggested citation:

Mahler, B.J., Garner, B.D., Musgrove, M., Guilfoyle, A.L., and Rao, M.V., 2006, Recent (2003–05) water quality of Barton Springs, Austin, Texas, with emphasis on factors affecting variability: U.S. Geological Survey Scientific Investigations Report 2006–5299, 83 p., 5 appendixes.

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Conversion Factors, Abbreviations, and Datum

Inch/Pound to SI

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer (km)
	Volume	
gallon (gal)	0.003785	cubic meter (m^3)
	Flow rate	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
inch per hour (in/hr)	25.4	millimeter per hour (mm/hr)

SI to Inch/Pound

Multiply	By	To obtain
	Length	
	micrometer (µm)	3.937 x 10^{-5}inch (in.)
	Mass	
gram (g)	0.03527	ounce avoidupois (oz advp))
kilogram (kg)	2.205	pound avoidupois (lb advp)
	Volume	
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.034	fluid ounce (fl oz)

Temperature in degrees Celsius (ºC) may be converted to degrees Fahrenheit (ºF) as follows:

ºF = 1.8 ºC + 32

Abbreviations:

microgram per liter, µg/L

microsiemens per centimeter at 25 ºC, µS/cm

milligram per liter, mg/L

nephelometric turbidity unit, NTU

Datum

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Recent (2003–05) Water Quality of Barton Springs, Austin, Texas, With Emphasis on Factors Affecting Variability

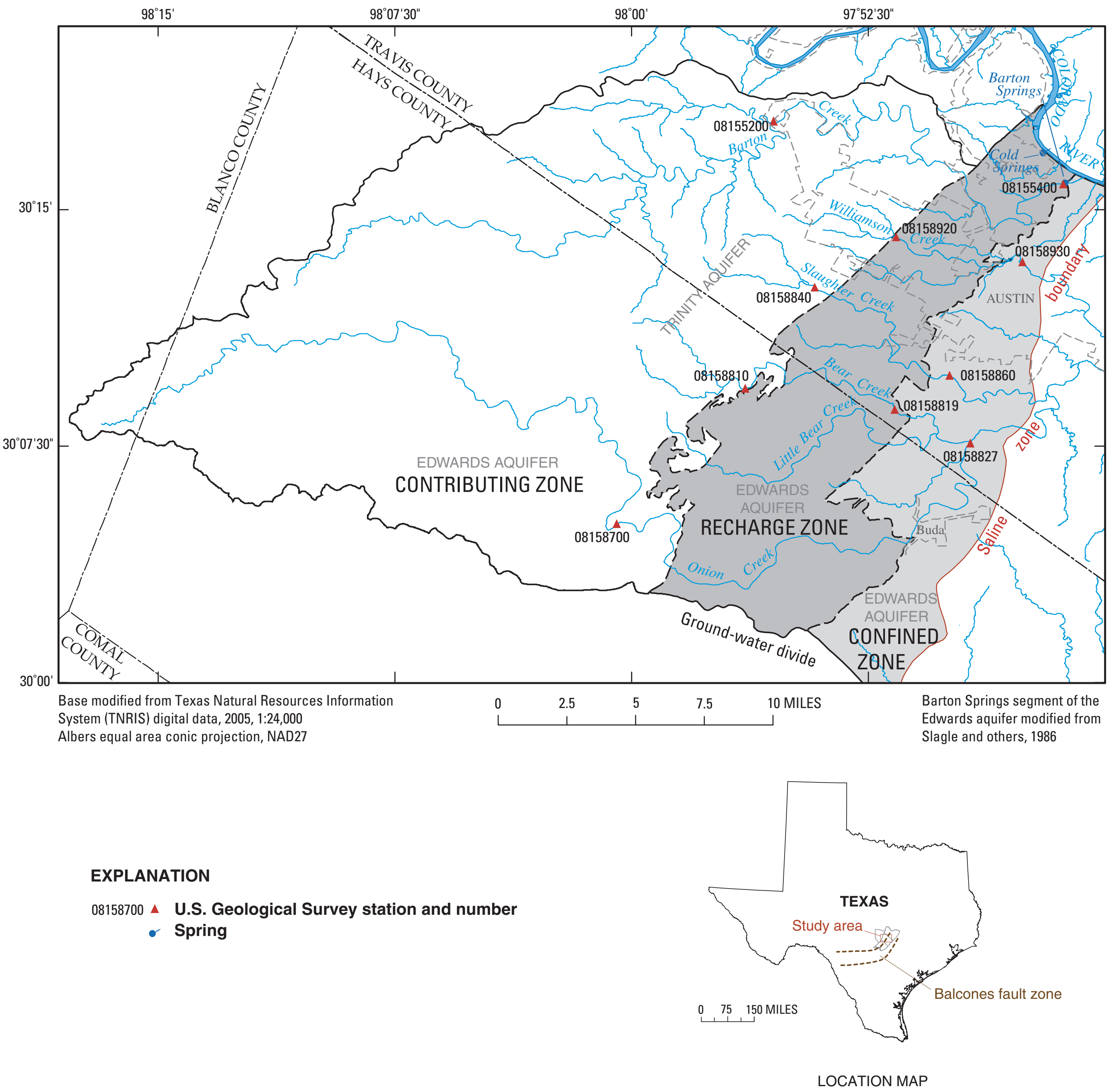
Barbara J. Mahler, Bradley D. Garner, MaryLynn Musgrove, Amber L. Guilfoyle, and Mohan V. Rao

Abstract

From 2003 to 2005, the U.S. Geological Survey, in cooperation with the Texas Commission on Environmental Quality, collected and analyzed water samples from the four springs (orifices) of Barton Springs in Austin, Texas (Upper, Main, Eliza, and Old Mill Springs), with the objective of characterizing water quality. Barton Springs is the major discharge point for the Barton Springs segment of the Edwards aquifer. A three-pronged sampling approach was used: physicochemical properties (including specific conductance and turbidity) were measured continuously; samples were collected from the four springs routinely every 2 weeks (during August–September 2003) to 3 weeks (during June 2004–June 2005) and analyzed for some or all major ions, nutrients, trace elements, soluble pesticides, and volatile organic compounds; and samples were collected from the four springs at more closely spaced intervals during the 2 weeks following two storms and analyzed for the same suite of constituents. Following the two storms, samples also were collected from five of the six major streams that provide recharge to Barton Springs. Spring discharge during both sample collection periods was above average (60 cubic feet per second or greater). Barton Springs was found to be affected by persistent low concentrations of atrazine (an herbicide), chloroform (a drinking-water disinfection by-product), and tetrachloroethene (a solvent). Increased recharge from the major recharging streams resulted in increased calcium, sulfate, atrazine, simazine, and tetrachloroethene concentrations and decreased concentrations of most other major ions, nitrate, and chloroform at one or more of the springs. These changes in concentration demonstrate the influence of water quality in recharging streams on water quality at the springs even during non-stormflow conditions. The geochemical compositions of the four springs indicate that Upper Spring is more contaminated and is influenced by a contributing flow path that is separate from those leading to the other springs under all but stormflow conditions. Main, Eliza, and Old Mill Springs share at least one common flow path that contributes contaminants to the three springs. Old Mill Spring, however, is less affected by anthropogenic contaminants than the other springs and receives a greater component of water from a flow path whose geochemistry is influenced by water from the saline zone of the aquifer. At Main Spring, atrazine, simazine, chloroform, and tetrachloroethene concentrations increased following storms, describing breakthrough curves that peaked 2 days following rainfall; at Upper Spring, atrazine and simazine concentrations described breakthrough curves that peaked 1 day following rainfall. At both Main and Upper Springs, additional anthropogenic compounds were detected following storms. The geochemical response of the springs to recharge indicates that much of the transport occurs through conduits. When there is no flow in the recharging streams, ground water advects from the aquifer matrix into the conduits and is transported to the springs. When there is flow in the streams, recharge through the streambeds directly enters the conduit system and is transported to the springs. Following storms, surface runoff recharges through both interstream recharge features and streambeds, delivering runoff-related contaminants to Barton Springs.

Introduction

The Barton Springs segment of the Edwards aquifer (fig. 1) is in Central Texas, an area undergoing rapid growth in population and in land area affected by development (City of Austin, 1995). Barton Springs, located in Zilker Park, Austin, Tex., is the main discharge point of the Barton Springs segment of the aquifer. A question of interest to stakeholders and water managers is, to what extent are increases in population and urban land use affecting water quality at Barton Springs. Water



Base modified from Texas Natural Resources Information System (TNRIS) digital data, 2005, 1:24,000
Albers equal area conic projection, NAD27

Barton Springs segment of the Edwards aquifer modified from Slagle and others, 1986

Figure 1. Map showing the study area—Barton Springs segment of the Edwards aquifer, Austin, Texas, and its contributing zone.

quality at Barton Springs is of interest for a number of reasons: Water from the springs supplies a 750-foot (ft)-long swimming pool visited by more than 350,000 people each year, provides a part of the City of Austin's municipal water supply (Slade and others, 1986), and provides the only known habitat for the Barton Springs salamander (*Eurycea sosorum*), a federally-listed endangered species that is extremely vulnerable to changes in water quality (U.S. Fish and Wildlife Service, 1997). Moreover, the Barton Springs segment of the Edwards aquifer has been designated a sole source aquifer by the U.S. Environmental Protection Agency (USEPA) (2006b).

Barton Springs comprises four spring orifices: Upper Spring, Main Spring, Eliza Spring, and Old Mill Spring (fig. 2). The Barton Springs salamander has been found at all four orifices. Dye-tracing studies have demonstrated that several preferential ground-water flow paths lead to the springs and that the four springs do not all receive water from the same flow paths (Barton Springs/Edwards Aquifer Conservation District,

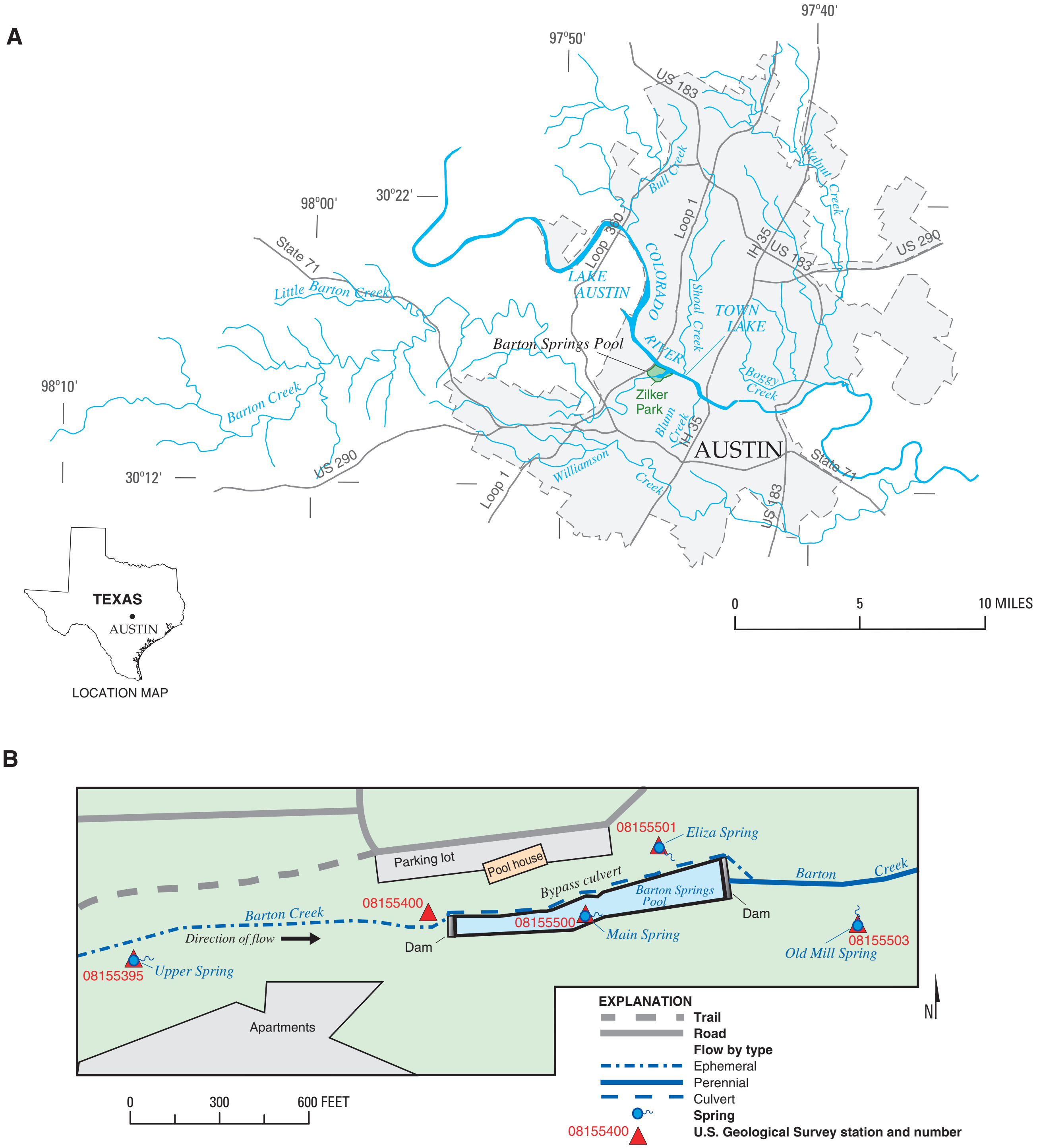


Figure 2. Location of (A) Zilker Park and (B) the four springs of Barton Springs, Austin, Texas.

2003; Hunt and others, 2006); this has been corroborated by differences in chloride and sulfate concentrations between water discharging from the different spring orifices (City of Austin, 1997; Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004). Dye-tracing study results also have demonstrated that travel times through the aquifer are rapid and variable and that the direct-line velocity increases with higher spring discharge.

Table 1. Sampling sites for water-quality characterization of Barton Springs, Austin, Texas (2003–05).

[USGS, U.S. Geological Survey; SH, State Highway; FM, Farm Road]

USGS station number (fig. 1 or 2)	Abbreviated site name	Station name	Site type
08155200	Barton 71	Barton Creek at SH 71 near Oak Hill, Tex.	Creek (upstream)
08155400	Barton Above	Barton Creek above Barton Springs at Austin, Tex.	Creek (downstream)
08158700	Onion Driftwood	Onion Creek near Driftwood, Tex.	Creek (upstream)
08158810	Bear 1826	Bear Creek below FM 1826 near Driftwood, Tex.	Creek (upstream)
08158819	Bear Brodie	Bear Creek near Brodie Lane near Manchaca, Tex.	Creek (downstream)
08158827	Onion Twin Creeks	Onion Creek at Twin Creeks Road near Manchaca, Tex.	Creek (downstream)
08158840	Slaughter 1826	Slaughter Creek at FM 1826 near Austin, Tex.	Creek (upstream)
08158860	Slaughter 2304	Slaughter Creek at FM 2304 near Austin, Tex.	Creek (downstream)
08158920	Williamson Oak Hill	Williamson Creek at Oak Hill, Tex.	Creek (upstream)
08158930	Williamson Manchaca	Williamson Creek at Manchaca Road, Austin, Tex.	Creek (downstream)
08155395	Upper Spring	Upper Barton Springs at Austin, Tex.	Spring
08155500	Main Spring	Barton Springs at Austin, Tex.	Spring
08155501	Eliza Spring	Eliza Spring at Austin, Tex.	Spring
08155503	Old Mill Spring	Old Mill Spring at Austin, Tex.	Spring

The Barton Springs segment of the Edwards aquifer is karst, meaning that most ground-water flow is through voids formed by dissolution of the host rock (usually carbonate). Because voids can be several feet or more in diameter (caves or conduits), transport times in karst from the point of recharge to the point of discharge can be extremely rapid. Because transport through large voids offers little opportunity for filtration or sorption, karst aquifers are considered very vulnerable to contamination (White, 1988).

Previous reports on the water quality of Barton Springs have focused on indicators that are relatively easy and inexpensive to collect, such as bacteria, nitrate (nitrogen), dissolved oxygen, organic carbon, and major ions (Barrett and Charbeneau, 1996; City of Austin, 1997; Slade and others, 1986; Turner, 2000). Other contaminants with a clearer anthropogenic source, such as pesticides and solvents, have been detected at low concentrations during routine sampling of spring water (for example, Aragon Long and others, 2005; Gandara, 2002, 2003, 2004). To improve understanding of the water quality of Barton Springs, the U.S. Geological Survey (USGS), in cooperation with the Texas Commission on Environmental Quality (TCEQ), conducted a study that involved continuous monitoring of physicochemical properties of Barton Springs discharge. Additionally, concentrations of major ions, nitrate, and anthropogenic compounds were measured routinely (as often as every 2 weeks) and at more closely spaced intervals after two storms resulting in streamflow.

Purpose and Scope

The purpose of this report is to

1. Describe recent water quality of Barton Springs on the basis of chemistry of water samples collected from the four spring orifices during 2003–05.
2. Describe the major ion and contaminant chemistry of water from the four Barton Springs orifices over an annual cycle and the temporal variability in that chemistry, and identify possible reasons for spatial and temporal variability.
3. Describe the response of the major ion and contaminant chemistry of water from the four Barton Springs orifices to rainfall that results in storm runoff into recharging streams, and identify possible reasons for similarity and variability.
4. Synthesize the findings to identify factors that influence water-quality variability, including ground-water flow paths, sources of water to the aquifer, and aquifer flow conditions (with high aquifer flow conditions represented by relatively high water-table altitudes and low aquifer flow conditions represented by relatively low water-table altitudes).

Samples were collected every 2 weeks from the four springs (table 1) during August–September 2003 (Phase 1), and every 3 weeks during June 2004–June 2005 (Phase 2). Phase 1 was a relatively dry period during which spring discharge decreased gradually from 87 to 61 cubic feet per second (ft^3/s). During Phase 2, samples also were collected from the four springs over the 2 weeks following two storms that resulted in flow in the major streams (creeks) that contribute recharge to the aquifer. For the same two storms, samples were collected from five of the six major streams recharging the Barton Springs segment of the Edwards aquifer at the downstream end of the aquifer recharge zone (samples were collected from Barton, Onion, Slaughter, Bear, and Williamson Creeks; Little Bear Creek is not included in this study, except for historical data). The spring- and stream-water samples were selectively analyzed for major ions, nutrients (nitrogen and phosphorus compounds), trace elements (metals), soluble pesticides, and volatile organic compounds (VOCs). In addition, selected samples from Main Spring were analyzed for pharmaceutical compounds. This report presents data for these analyses and interprets the results in the context of potential sources of water, ground-water flow paths, and travel times. Additionally, historical (1974–2003, with a few exceptions) data on occurrence of pesticides and VOCs in samples from wells and streams in the Barton Springs segment of the Edwards aquifer are reviewed and presented as supplementary material in appendix 1 (Review of Historical [1974–2003] Water-Quality Data) and appendix 2 (Historical Data) for comparative purposes with the objectives of this report.

Overview of Karst Systems

In karst systems, dissolution of the rock matrix (usually carbonate) is the dominant factor controlling the geomorphology (White, 1988). This feature gives rise to the unique characteristics of karst aquifers in which most of the transport of water occurs through a system of interconnected solution cavities, which can range in size from bedding-plane partings to conduits that are several feet in diameter (White, 1988). This low-storage, high-transmissivity network of cavities is embedded in a high-storage, low-transmissivity matrix (Atkinson, 1977; Desmarais and Rojstaczer, 2002; Martin and Screaton, 2001). Most of the storage occurs within the matrix, but most of the transport occurs within the conduits.

Recharge to karst aquifers occurs both as relatively uniformly distributed diffuse infiltration into the rock matrix (diffuse recharge) and as direct infiltration into karst features such as fractures, cave openings, and swallow holes (focused recharge). Although diffuse and focused recharge might occur simultaneously, their relative volumetric proportions can vary greatly depending on many variables including rainfall intensity, vegetative cover, soil thickness, and surface permeability. During periods when there is little to no surface recharge, water in the matrix advects into the conduits, resulting in a potentiometric trough in the area near the conduits (Worthington, 2003). During periods when there is a large amount of focused recharge through karst features, for example following storms, the head within the conduit can be sufficiently great to result in a reversal of the gradient, causing recently recharged water to advect into the matrix, similar to the concept of bank storage in surface-water systems (Fetter, 1988; Vaute and others, 1997).

Because conduit networks can occur at different altitudes within the aquifer, variations in the level of the water table can result in conduits being saturated during some periods of the year and drained during others, with a resulting change in overall transmissivity of the aquifer (Larocque and others, 1998). When conduits are drained, they do not transport advection from the matrix to the spring outlet, but they can transport focused recharge from the surface to the spring outlet (Mahler and Massei, 2007). In this conceptual model of an unconfined karst ground-water system, water-table altitude, which reflects aquifer flow conditions (with high aquifer flow conditions represented by relatively high water-table altitudes and low aquifer flow conditions represented by relatively low water-table altitudes), affects the speed and efficiency of transport through the conduits, as well as the quantity of water and contaminants going into storage in the matrix (fig. 3).

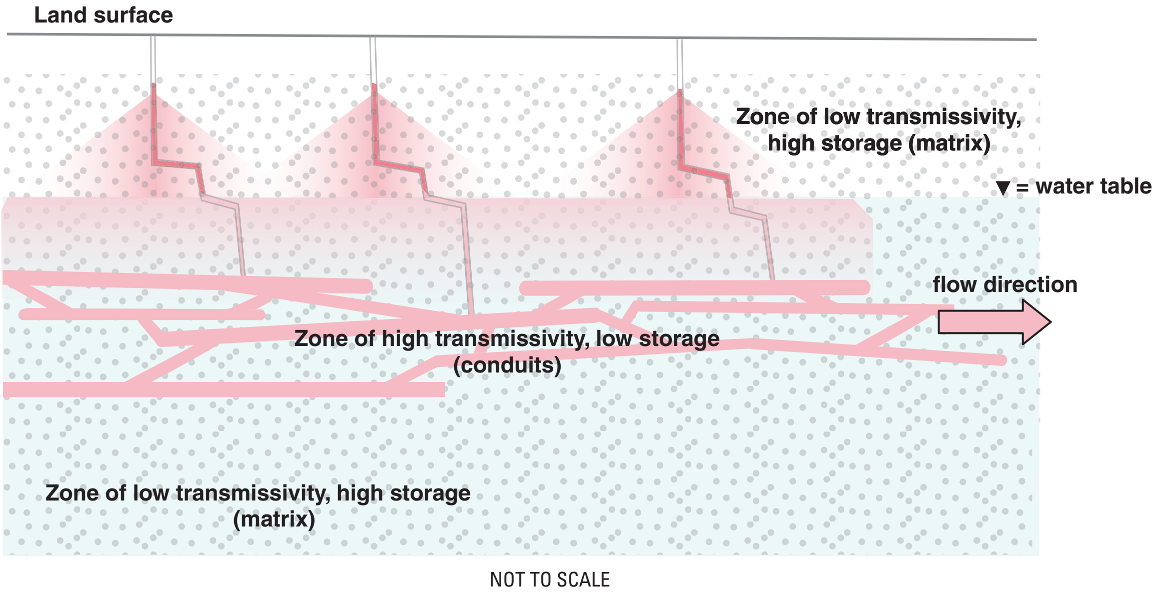
One of the most striking characteristics of karst aquifers is their extreme spatial and temporal heterogeneity. Wells in proximity might show very different hydrogeologic and geochemical characteristics (Garner and Mahler, 2007; Long and Putnam, 2004; Malard and Chapuis, 1995). The aqueous geochemistry and quality of water at a single site can change rapidly (on the scale of minutes to hours) if focused recharge is moving through the system. In response to rainfall, in a matter of hours spring discharge can become turbid, specific conductance can undergo large changes (Andrews and others, 1984), and concentrations of anthropogenic contaminants (Mahler and Van Metre, 2000) or bacteria (Andrews and others, 1984; Ryan and Meiman, 1996) can increase.

Karst springs are ideal sites for studying aquifer-wide processes, as they are the integrators of the inputs and processes occurring along all flow paths supplying water to them (Quinlan, 1989). Fluctuations in spring characteristics such as discharge (Felton and Currens, 1994), hardness and calcium/magnesium ratios (Shuster and White, 1971), specific conductance (Bakalowicz, 1977), major ion concentrations (Pinault and others, 2001), and turbidity (Massei and others, 2002) have been used to investigate karst aquifer functioning, including characterization of degree of karstification, mechanisms of generation of “quick flow” and “slow flow,” and water source.

Study Area Description and Previous Studies

The Barton Springs segment of the Edwards aquifer (hereinafter, Barton Springs segment) is a hydrologically isolated section of the karstic Edwards aquifer of Central and South Texas. The Barton Springs segment is bounded on the north by the Colorado River (Town Lake in Austin); on the south by a ground-water 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

A. High aquifer flow conditions—conduits are saturated and some initial recharge goes into matrix storage



B. Low aquifer flow conditions—conduits are dewatered and initial recharge moves rapidly through the conduits

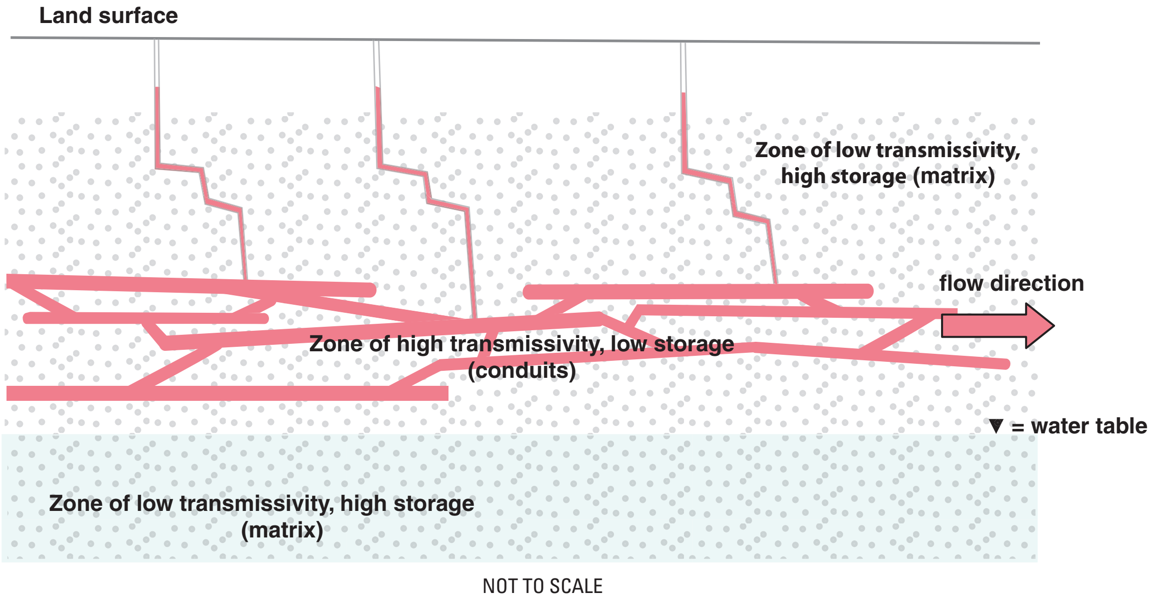


Figure 3. Schematic diagram of hypothesized aquifer functioning of the Barton Springs segment of the Edwards aquifer, Austin, Texas, in response to recharge during (A) high aquifer flow conditions and (B) low aquifer flow conditions (modified from Mahler and Massei, 2007).

1,000 milligrams per liter [mg/L] dissolved solids concentration) known as the saline zone (Abbott, 1975; Sharp and Banner, 1997; Slade and others, 1986) (fig. 1). The hydrogeology is substantially controlled by the Balcones fault zone, a zone of en-echelon normal faults that dip generally southeastward and strike southwest-northeastward across the study area.

Geologic Setting

The rocks of the Barton Springs segment consist of the Edwards Group and the Georgetown Formation of Lower Cretaceous age (Maclay, 1995; Rose, 1972; Sharp and Banner, 1997; Small and others, 1996) (fig. 4). The Del Rio Clay, a upper confining unit, overlies the Barton Springs segment. The Glen Rose Limestone, which composes the upper part of the generally less permeable Trinity aquifer, underlies the Barton Springs segment.

Miocene Epoch tectonic activity produced the Balcones fault zone (Rose, 1972). Maximum total displacement in the direction of dip across the fault zone is about 1,700 ft (Woodruff and Abbott, 1979), and the large Mount Bonnell fault became the western boundary of the Barton Springs segment. Uplift associated with this tectonic activity increased surface erosion rates and helped establish a “through-flow system” in the aquifer, which allows for enhanced transmission of ground water (Abbott, 1975; Woodruff and Abbott, 1979).

Sources of Recharge

Slade and others (1986) estimated that about 85 percent of aquifer recharge is provided by the six major surface streams that cross the recharge zone: Barton Creek, Onion Creek, Slaughter Creek, Bear Creek, Little Bear Creek, and Williamson Creek (fig. 1). Although this percentage might be revised somewhat on the basis of ongoing research (N.M. Hauwert, City of Austin, oral commun., 2006), it is generally agreed that most recharge to the aquifer occurs through sinkholes, swallow holes, and fractures in the streambeds; these sources of focused recharge can rapidly provide large volumes of water to the aquifer. Additional sources of recharge, minor in comparison to streambed recharge on a volumetric basis, include infiltration of recharge water through interstream sinkholes and soil zones (N.M. Hauwert, City of Austin, unpub. data, 2006), leaking municipal water-supply pipes and sewer pipes (Garcia-Fresca Grocin, 2004; St. Clair, 1979; Sharp and Banner, 1997), and cross-formational flow from other hydrostratigraphic units adjacent to those of the Barton Springs segment (Slade and others, 1986; Smith and Hunt, 2004; Garner and Mahler, 2007).

Discharge From the Aquifer

Barton Springs is the main discharge point for the Barton Springs segment. Barton Springs discharges water at a long-term average of about 50 ft^3/s (measured as the combined flow from Main, Eliza, and Old Mill Springs [fig. 2]), with historical (1917–82) minimum and maximum flows of 10 and 166 ft^3/s (Slade and others, 1986). Discharge from these springs accounts for more than 90 percent of natural (non-pumped) discharge from the aquifer (Hauwert and Vickers, 1994).

Other discharge points include smaller springs and wells used for ground-water supply. Cold Springs (fig. 1) has a discharge of about 4 ft^3/s or less (Hauwert and Vickers, 1994), and discharges water from a relatively small subbasin that apparently is not connected to the larger part of the aquifer (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004). About 970 active wells drilled into the aquifer withdrew an estimated 2.5 billion gallons of water in 2004 (Smith and Hunt, 2004), equivalent to a constant withdrawal rate of about 10 ft^3/s.

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. During 1978–2005, the median flow was about 66 ft^3/s, the 75th percentile of flow (the flow exceeded 75 percent of the time) was about 40 ft^3/s, and the 25th percentile of flow (the flow exceeded 25 percent of the time) was about 89 ft^3/s. For this report, therefore, low aquifer flow conditions are defined as those during which Barton Springs discharge was 40 ft^3/s or less, average aquifer flow conditions as those during which discharge was from 40 to 89 ft^3/s, and high aquifer flow conditions as those during which discharge was 90 ft^3/s or greater.

General Ground-Water-Flow Direction

Ground-water flow in the Barton Springs segment (fig. 4) generally follows the north-northeastward strike of the Balcones fault zone toward Barton Springs. Direction of flow varies somewhat with changes in aquifer flow conditions (Slade and others, 1986). The general flow direction indicated by potentiometric surface maps has been confirmed by several digital computer models (Barrett and Charbeneau, 1996; Scanlon and others, 2003; Slade and others, 1985). Precise, smaller-scale understanding of the flow system is confounded by the presence of karst conduits, which can transport water in a direction different from that of the larger-scale hydrologic gradient (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004).

Dye-tracing studies have provided striking evidence of the rapid movement of water through conduits in the Barton Springs segment, as well as identification of several potential flow paths. Hauwert, Johns, and others (2004) and Hauwert, Samson, and others (2004) found that straight-line ground-water travel times under some conditions exceeded 6 miles per day. They used the dye-tracing results to delineate three ground-water basins within the Barton Springs segment, each with a network of flow paths. They also identified a flow path along the eastern side of the Barton Springs segment, parallel to the saline zone. The general direction of flow was eastward and then north toward Barton Springs. Those authors hypothesized

HYDROGEOLOGIC UNIT	STRATIGRAPHIC UNIT	
Upper confining unit	Del Rio Clay	
Edwards aquifer, Barton Springs segment	Georgetown Formation	
	Edwards Group	Cyclic and marine members
		Leached and collapsed members
		Regional dense member
		Grainstone member
		Kirschberg evaporite and dolomitic members
		Basal nodular member
Trinity aquifer	Glen Rose Limestone	

Correlation between hydrogeologic and stratigraphics units associated with the Barton Springs segment of the Edwards aquifer (modified from Maclay, 1995, fig. 11)

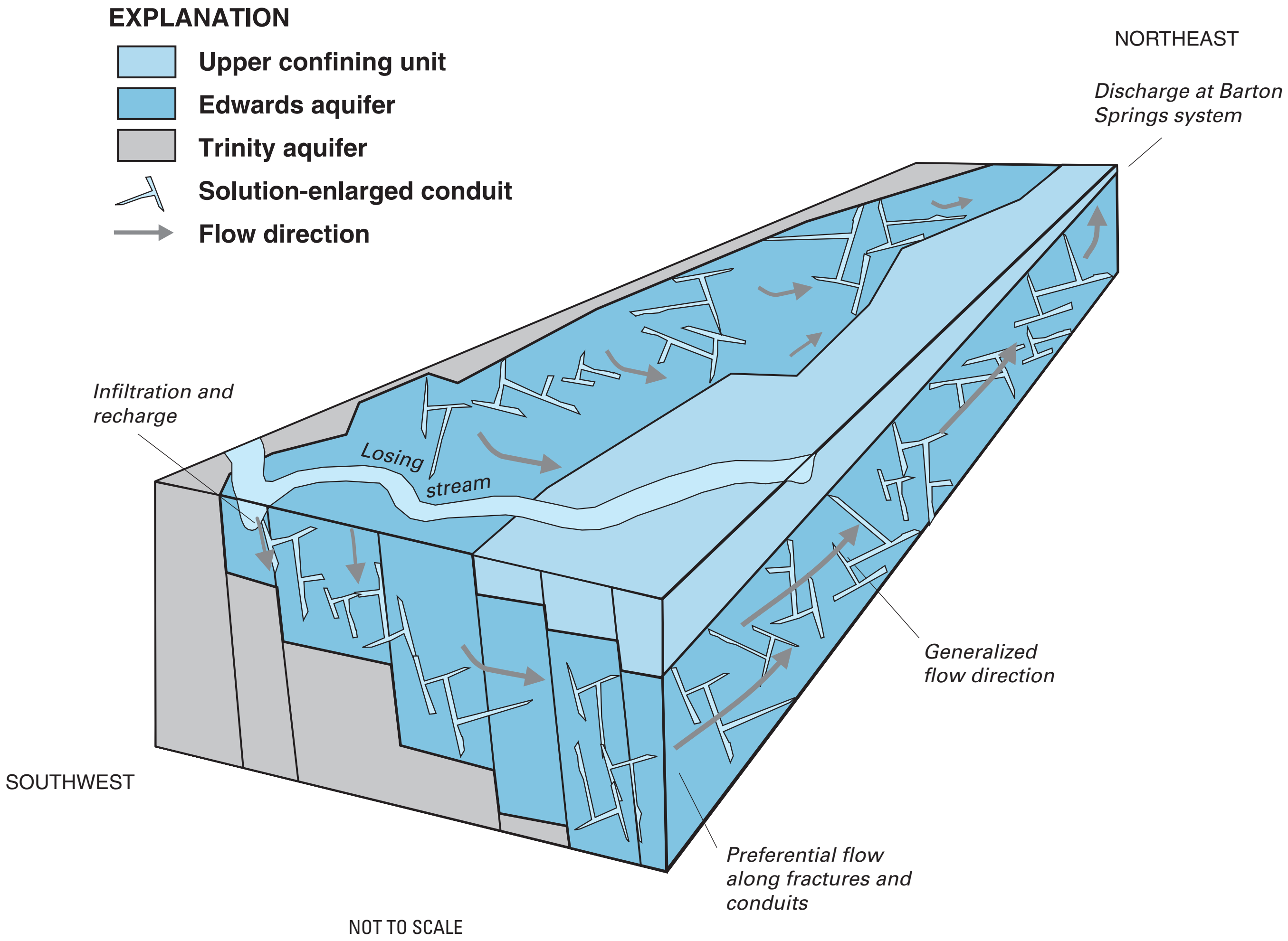


Figure 4. Idealized block diagram of the Barton Springs segment of the Edwards aquifer, Austin, Texas.

that the different springs receive water from some shared flow paths and some individual flow paths.

Saline Zone Boundary

The saline zone constitutes the eastern boundary of the Barton Springs segment. The saline zone is more deeply buried than the adjacent freshwater confined zone of the aquifer. The rocks of the saline zone are thought to have relatively low permeability and to have undergone very little meteoric diagenesis compared with rocks in the freshwater zone (Deike, 1987; Small and others, 1996). Saline zone ground water has dissolved solids concentrations greater than 1,000 mg/L, and sodium and chloride are the dominant ions (Sharp and Clement, 1988). The location of the saline zone boundary might be related to the hypothesized prominent conduit system that follows the strike of the Balcones fault zone (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004; Woodruff and Abbott, 1979).

Dye-tracing studies have indicated that one prominent aquifer flow path is near the saline zone boundary, which results in elevated sodium, chloride, and sulfate concentrations in water along that flow path relative to concentrations along other flow paths (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004). On the basis of the major ion chemistry of the four springs of Barton Springs, Hauwert, Johns, and others (2004) and Hauwert, Samson, and others (2004) concluded that Old Mill Spring receives most of its water and Main Spring receives some of its water from the saline-zone-influenced flow path, and that Upper and Eliza Springs receive water from other flow paths. Recent interpretation of the dye-tracing data, however, supports the hypothesis that a saline zone flow path influences Eliza Spring, as well as Main and Old Mill Springs (D.A. Johns, City of Austin, written commun., 2006).

Water Quality in the Barton Springs Segment of the Edwards Aquifer

Water in the Barton Springs segment has been analyzed for properties and constituents characterizing water quality since the 1970s, with a few constituents such as nitrate analyzed as early as 1937 (City of Austin, 1997; Turner, 2000).

Slade and others (1986) analyzed samples from streams, wells, and springs for nutrients, physicochemical properties, indicator bacteria, major ions, trace elements, and pesticides. They concluded that “the quality of water [mid-1980s] in the Edwards aquifer generally is very good” and that “no regional contamination problems [were] identified by this water-quality sampling program.”

The Barton Springs/Edwards Aquifer Conservation District (2006) has analyzed samples from wells for pesticides, dissolved solids, and petroleum hydrocarbons intermittently since 1990. Wells thought to intersect major flow paths were chosen for sampling. From 1990 through 1994, samples from 37 wells and springs were analyzed for a wide range of constituents (Hauwert and Vickers, 1994). Pesticides detected at one well (YD–58–50–201) included 2,4-D, 3,5-dichlorobenzene, dichloroprop, and bromacil. No pesticides were detected in samples from Old Mill Spring, the only spring sampled for the study.

From 1993 through 1996, the City of Austin monitored ground water in the Barton Creek watershed to determine, among other purposes, the effects of urbanization on water quality during both base-flow and stormflow conditions and to identify water-quality characteristics in Barton Springs and throughout the Barton Springs segment (City of Austin, 1997). The compounds measured included nutrients, trace elements, and major ions. The City documented the effect of discharge variation on the aqueous geochemistry of the springs, finding an inverse relation between concentrations of nitrate, several major ions, and discharge, and a positive relation between concentrations of suspended solids and bacteria and discharge. The City also found that changes in physicochemical properties at the springs were correlated with flow in Barton Creek following stormwater runoff. The City did not detect any trends in nutrients or trace elements in Barton Springs but noted that tetrachloroethene was detected at Main Spring and that petroleum hydrocarbons were detected at Old Mill Spring.

In 2000, the City of Austin analyzed trends in a number of properties and constituents measured since the 1970s or 1980s at Main Spring (Turner, 2000). Statistically significant upward trends were identified for specific conductance, sulfate, turbidity, and total organic carbon; a statistically significant downward trend was identified for dissolved oxygen. The City noted that these trends might be a result of increasing urbanization. A more recent analysis of trends (D.A. Johns, City of Austin, written commun., 2006) indicates a statistically significant increase in suspended solids and total nitrate but not in dissolved nitrate.

Also in 2000, the USGS monitored pesticides in discharge from Main Spring during 1 week following a storm (Mahler and Van Metre, 2000). The storm occurred when aquifer flow conditions were low (Barton Springs discharge of about 17 ft^3/s). The herbicides atrazine and simazine, the atrazine degradate deethylatrazine (DEA), and the insecticides carbaryl and diazinon were detected in three or more of the nine samples. Concentrations of all five compounds described breakthrough curves, that is, a relatively rapid increase and decrease in concentration over time. The peak atrazine concentration (0.57 microgram per liter [μg/L], in a sample collected 4 days after the storm) was about 75 times higher than the atrazine concentration in the first sample collected after the storm.

Major ions, nutrients, pesticides, and VOCs have been measured by the USGS, in cooperation with the City of Austin, in samples from wells, springs, and recharging streams intermittently since the 1970s. Those data are reviewed in appendix 1, subsequently listed in appendix 2, and summarized here.

Twenty-eight soluble pesticides were detected in historical samples from springs, streams, and wells. Atrazine, carbaryl, diazinon, prometon, and simazine accounted for 74 percent of all detections. The highest frequency of detections in well samples was from wells in the northern one-third of the Barton Springs segment. More pesticides were detected in samples

Chemical Species and Contaminants of Interest

Three principal groups of compounds or contaminants measured for this study are nutrients, pesticides, and VOCs. Many of the compounds in these groups are relatively soluble and therefore are likely to be dissolved in ground water if a source is present.

Nutrients

Nutrients are those elements that are important to plant growth and survival; the primary mineral nutrients are nitrogen, phosphorous, and potassium. In ground water, these nutrients generally occur as nitrate (NO_3^-), phosphate (PO_4^{3-}), and potassium (K^+) ions; of these three, nitrate is the most soluble and phosphate the least (Hem, 1992). An excess of nutrients in waterways promotes algal blooms (eutrophication). Decomposition of the algae consumes dissolved oxygen, causing other organisms to die.

Nutrients in water can come from many sources. Some sources are natural and include animal wastes and decomposing plants. There also are many anthropogenic sources of nutrients, including fertilizers in agricultural, lawn, and golf course runoff and infiltration; sewage; and soil erosion.

More information on nutrients can be found at
http://toxics.usgs.gov/definitions/eutrophication.html
http://www.epa.gov/waterscience/criteria/nutrient/
http://www.policyalmanac.org/environment/archive/water_nonpoint_source.shtml

Pesticides

Pesticides are toxic compounds designed to kill or control plants (herbicides), insects (insecticides), fungus (fungicides), or other organisms. Many pesticides commonly used before the 1970s were persistent and insoluble (for example, chlordane, DDT); as a result they degraded slowly but generally were not detected or were detected in very low concentrations in water. Since the 1970s, less persistent and more easily degradable pesticides have been developed. Although these degrade more quickly than their predecessors, they are more soluble and frequently are detected in water (Gilliom and others, 2006). Although agricultural use of pesticides is greater than nonagricultural use, nonagricultural use has been increasing since 1998 (Gilliom and others, 2006).

The herbicides or herbicide degradates most commonly detected in urban streams in the United States are atrazine, prometon, and simazine, and those most commonly detected in urban ground water are atrazine, DEA, and prometon. The insecticides most commonly detected in urban streams are carbaryl, chlorpyrifos, and diazinon, and those most commonly detected in urban ground water are carbaryl, diazinon, and dieldrin (Gilliom and others, 2006). Atrazine, DEA, prometon, and simazine were detected in samples collected for this study from one or more springs of Barton Springs.

Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds. Although atrazine is considered an agricultural herbicide (primarily used on corn and soybeans), it has some urban uses, such as on turf grass (residential lawns) and ornamentals (Sipcam Agro USA, Inc., 2006). Atrazine is the active ingredient in some “weed and feed” products. It is slightly to moderately toxic to humans and other animals and has been found to affect the sexual development of amphibians at environmentally relevant concentrations (as low as 0.1 μg/L) (Hayes, 2004). The USEPA maximum contaminant level (MCL) in drinking water for atrazine concentrations is 3 μg/L. Atrazine is persistent in soils with a half-life of 60 to more than 100 days (Extension Toxicology Network, 1996a) and is persistent in water, showing no degradation in Sacramento River water over the duration of 34- to 37-day experiments (Starner and others, 1999).

DEA is one of the three degradation products of atrazine and is formed by the dealkylation of atrazine by microbes. Because microbial populations generally are much higher in the soil than in surface or ground water, this degradation is much more likely to occur in soils than in water. The atrazine/DEA ratio thus has been used as an indicator of residence time in the soil; the highest atrazine/DEA ratios in water tend to occur just after atrazine application, and lower atrazine/DEA ratios indicate a longer soil residence time (Gilliom and others, 2006). Less is known about the toxicity of degradates than the parent compounds, but recent research has indicated that DEA has a toxicity similar to or less than atrazine (Sinclair and Boxall, 2003).

Prometon is a non-selective triazine herbicide primarily used for bare-ground weed control around buildings, fences, roadways, and rights-of-way (Gilliom and others, 2006). Prometon is not registered for agricultural use. It is slightly toxic to aquatic invertebrates and fish, and the principal exposure health effect is liver damage. There is no MCL for prometon. Prometon is highly soluble and mobile in water but is much more persistent than either atrazine or simazine, with a soil half-life of 932 days (Gilliom and others, 2006).

Simazine is a selective triazine herbicide used to control broadleaf weeds and grasses. It is considered a nonagricultural herbicide (Gilliom and others, 2006), and its urban uses include weed control for turfgrass and ornamentals, and non-selective weed control (Extension Toxicology Network, 1996b). Simazine has low to no toxicity (Extension Toxicology Network, 1996b), but exposure health effects include blood changes, damage to testes, kidneys, and thyroid, and cancer. The MCL for simazine is 4.0 μg/L. Like prometon, simazine is highly soluble and mobile in water (Gilliom and others, 2006). Similar to atrazine, simazine is moderately persistent in soils (average soil half-life of 60 days) and is persistent in water, showing no degradation in Sacramento River water over the duration of 34- to 37-day experiments (Starner and others, 1999).

Additional information on these and other pesticides can be found on the following Web sites:
http://www.epa.gov/pesticides/about/index.htm
http://www.pesticideinfo.org/Index.html
http://extoxnet.orst.edu/
http://www.scorecard.org/chemical-profiles/

Volatile Organic Compounds

VOCs are carbon-based compounds that have a vapor pressure exceeding 0.08 inch (in.) of mercury, causing them to volatilize (evaporate) readily. Because of their volatility, VOCs are not usually detected in aerated surface water; because they are fairly soluble they can leach from the soil into ground water, where they can be persistent. Groups of VOCs include trihalomethanes (THMs); benzene, toluene, ethylbenzene, and xylene (BTEX compounds); industrial solvents; and other industrial compounds.

THMs are methane molecules that have a halogen atom (chloride or bromide) substituted for one or more of the hydrogen atoms. A principal source of THMs is the disinfection of drinking water by chlorination, during which added chlorine reacts with the natural organic matter in the water to create disinfection by-products, including THMs. Use of chloramination for drinking-water disinfection, which includes both chlorine and small amounts of ammonia that react to form chloramine, greatly reduces the production of THMs (Guay and others, 2005). Chloramination is the current (2006) disinfection process used by the City of Austin. THMs in drinking water are of concern because they have been linked to cancer and to heart, lung, kidney, liver, and central nervous system damage (Capece, 1998). The USEPA MCL for total THMs is 80 µg/L.

BTEX compounds are in gasoline and other petroleum products. Benzene is a known carcinogen, ethylbenzene and toluene are designated as “not classifiable as to human carcinogenicity,” and there is insufficient information to determine whether xylene is carcinogenic (Agency for Toxic Substances and Disease Registry, 2006). The MCLs for benzene, toluene, ethylbenzene, and xylene are 5, 1,000, 700, and 10,000 µg/L, respectively.

Industrial solvents are another group of VOCs. Solvents for degreasing, cleaning, metal fabrication, and other industrial uses include tetrachloroethene (also called tetrachloroethylene, perchloroethene, perchloroethylene, or PERC), trichloroethene (also called trichloroethyelene or TCE), and 1,1,1-trichloroethane. Tetrachloroethene primarily is used in dry cleaning and metal degreasing. Once present in ground water, chemical and biological degradation of tetrachloroethene is very slow (Spectrum, 2003a). Trichloroethene is a degradation product of tetrachloroethene and also is an industrial solvent. Trichloroethene mainly is used as a metal or glass degreaser, although it is in many household products, including paint and spot removers. Degradation of trichloroethene in ground water is very slow (Spectrum, 2003b). The MCL for both tetrachloroethene and trichloroethene is 5 µg/L. 1,1,1-trichloroethane is used as a metal degreaser, in textile processing, in dyeing, and in aerosols (U.S. Environmental Protection Agency, 2006a). The MCL for 1,1,1-trichloroethane is 200 µg/L.

Other industrial VOCs in ground water include1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) and carbon disulfide. Freon 113 is a refrigerant, dry-cleaning solvent, and degreaser. Carbon disulfide is an industrial VOC commonly used in the manufacture of other industrial compounds such as regenerated cellulose and carbon tetrachloride and is used as a fumigant insecticide. It also is produced naturally by several types of soil, sediment, and aquatic microorganisms (Environment Canada, 2006). There is no MCL for either Freon 113 or carbon disulfide.

Additional information on these and other VOCs can be found at the following Web sites.

http://www.agen.ufl.edu/~wq/thm/
http://toxics.usgs.gov/definitions/btex.html
http://www.speclab.com/compound
http://www.epa.gov/OGWDW/hfacts.html
http://www.ec.gc.ca/substances/ese/eng/esehome.cfm

from streams than in samples from wells or springs, particularly in those samples collected from streams following storms.

Nineteen VOCs were detected in historical samples from wells and eight VOCs in samples from springs. Data collected after the mid-1990s, when a method with low-level reporting levels began to be used, provide most of the information about VOC occurrence. The most frequently detected VOCs in samples from wells were chloroform (a drinking-water disinfection by-product), toluene (a constituent of gasoline), and tetrachloroethene (a solvent). Wells located in the northern one-third of the Barton Springs segment study area had the highest number of VOC detections per sample. Tetrachloroethene was the most frequently detected VOC in samples from springs.

Data from streams and wells indicate that contaminant concentrations are not spatially distributed evenly across the Barton Springs segment but instead are elevated in some areas relative to others (appendixes 1, 2). Samples from several wells (SVE, SVN, SVS, and SVW) (appendix 1, figs. 1.6, 1.7) had more detections of contaminants and at higher concentrations than samples from other wells. These wells are in the Williamson Creek watershed, which has a greater proportion of urban land use than the other watersheds (Bio-West, 2002).

Acknowledgments

The authors thank Wayne Lapham and Phillip Hays, U.S. Geological Survey, and David Johns, City of Austin, for their helpful reviews of this report.

Methods

Study Design

For this study, a three-pronged approach was used to evaluate the water quality of Barton Springs. Aquifer (spring) discharge and recharge were monitored continuously, and selected physicochemical properties were measured continuously at the

Table 2. Phase 1 and Phase 2 sample schedules for Barton Springs, Austin, Texas (2003–05).

[--, not sampled for]

Constituents sampled for	Period of sample collection							
	Phase 1				Phase 2			
	August–September 2003 sampling period				June 2004–June 2005 sampling period			
	Upper Spring	Main Spring	Eliza Spring	Old Mill Spring	Upper Spring	Main Spring	Eliza Spring	Old Mill Spring
Major ions	2 weeks	2 weeks	2 weeks	2 weeks	3 weeks	3 weeks	3 weeks	3 weeks
Full suite of nutrients (including nitrite plus nitrate nitrogen)	2 weeks	2 weeks	2 weeks	2 weeks	quarterly	quarterly	quarterly	quarterly
Nitrite plus nitrate nitrogen only	--	--	--	--	3 weeks	3 weeks	3 weeks	3 weeks
Trace elements	2 weeks	2 weeks	2 weeks	2 weeks	--	--	--	--
Soluble pesticides	2 weeks	2 weeks	2 weeks	2 weeks	3 weeks	3 weeks	quarterly	quarterly
Volatile organic compounds	2 weeks	2 weeks	2 weeks	2 weeks	3 weeks	3 weeks	quarterly	quarterly

four springs. Routine samples were collected from the four spring orifices every 2 weeks during a pilot period (Phase 1) and then every 3 weeks throughout an annual cycle (Phase 2), and analyzed for natural and anthropogenic compounds. Stormflow samples were collected from the four spring orifices at closely spaced intervals following two storms that resulted in surface-water flow in contributing watersheds.

Continuous monitoring of discharge, estimates of recharge, and measurements of physicochemical properties were recorded at 15-minute intervals (“continuously”) from July 2003 through June 2005. Discharge and recharge were computed to provide general hydrologic variables against which other water-quality constituents could be compared. Physicochemical properties were used to characterize long-term and short-term changes in Barton Springs water chemistry; similar to discharge and recharge, physicochemical properties provided a general context for other measured water-quality constituents.

To characterize seasonal changes in aqueous geochemistry, routine sampling was done in two phases. During these two phases, a total of 22 samples (five during Phase 1 and 17 during Phase 2) were collected from each orifice. The pilot part of the routine sampling (Phase 1), carried out during August– September 2003, was designed to assess water quality at the four spring orifices under base-flow conditions (defined as conditions during which there was little to no recharge). The objective was to evaluate temporal variation as well as similarities and differences in water chemistry and quality at the four spring orifices under base-flow conditions. Samples were collected from the four spring orifices every 2 weeks and analyzed for natural and anthropogenic compounds, including major ions, nutrients (nitrogen and phosphorus compounds), trace elements, soluble pesticides, and VOCs.

The second part of routine sampling (Phase 2) began about 8 months after the end of Phase 1 and was designed on the basis of the results from Phase 1. For Phase 2, samples were collected from the four spring orifices during June 2004–June 2005, and the interval between the collection of routine samples was increased to 3 weeks. On the basis of results from Phase 1, the suite of analytes (major ions, nutrients, soluble pesticides, VOCs, and trace elements) measured at the four sites was modified for Phase 2 (table 2). Samples from Upper and Main Springs were analyzed for major ions, nitrate, soluble pesticides, and VOCs. Samples from Eliza and Old Mill Springs were analyzed every 3 weeks for major ions and nitrate and quarterly for soluble pesticides and VOCs. In addition, selected samples from Main Spring were analyzed for pharmaceutical compounds. Because concentrations of all nutrients except nitrite plus nitrate either were not detected or were detected at estimated concentrations below the laboratory reporting level (LRL; including nitrite), nitrite plus nitrate was assumed to consist exclusively of nitrate. Therefore, only nitrite plus nitrate was analyzed routinely during Phase 2, and the full nutrient suite was analyzed quarterly. Because soluble pesticide and VOC concentrations measured in Eliza and Old Mill Springs during Phase 1 were similar to those in Main Spring, pesticides and VOCs in Eliza and Old Mill Springs were analyzed quarterly during Phase 2. Because trace element concentrations measured during Phase 1 either were not detected or were very low, analysis of trace elements was not continued at any site in Phase 2. Quality assurance (QA) procedures were an integral part of the study design. QA procedures and results are documented in appendix 3.

During routine sampling, samples were collected at regular intervals rather than in response to a storm. These samples therefore are interpreted as representing the expected variation in aqueous geochemistry of Barton Springs over the course of a year during average to high aquifer flow conditions. However, the results should not be interpreted as representing base-flow conditions, as sample collection might have coincided with a period during which focused recharge was moving through the aquifer. The sample collected on November 24, 2004, following a period of very heavy rainfall beginning November 16, 2004, is an extreme case of this condition, and is discussed in the section "Response of Barton Springs to Stormflow." Constituent concentrations in samples collected during Phase 1 most closely reflect base-flow conditions, as recharge was 2.9 ft^3/s or less for each of the five sampling events. The sampling event on September 16, 2003, however, was preceded by recharge of 5.4 ft^3/s on September 12 and 14, 2003.

During Phase 2 of routine sampling, the four spring orifices were sampled at closely spaced intervals following two storms (Storm 1, October 2004; Storm 2, May 2005). Nine samples were collected from each of the four spring orifices at intervals ranging from 12 hours (directly after the storm) to several days for 2 weeks following each storm. Samples from all four springs were analyzed for major ions and nitrate, and samples from Upper and Main Springs also were analyzed for pesticides and VOCs; selected samples from Main Spring collected following the second storm were analyzed for pharmaceutical compounds and a full suite of nutrients.

For the same two storms, samples were collected from the major streams that recharge the aquifer at the water-quality sampling stations at the downstream end of the recharge zone (fig. 1; table 1). At each sampling station, multiple samples were collected over the duration of the storm hydrograph and combined into a flow-weighted composite sample for each stream for each storm. At Onion Creek (Storm 1) and Slaughter Creek (Storm 2), an additional sample was analyzed to provide more thorough coverage of the storm hydrograph. The sample analyzed from Onion Creek was a grab sample, and the sample analyzed from Slaughter Creek was a flow-weighted composite. An average concentration for the entire storm event was computed by weighting the concentration of the samples analyzed by the proportion of the total volume of flow represented by each. Stream-water samples were analyzed for nitrate, soluble pesticides, and, for the second storm, pharmaceutical compounds.

Discharge Measurements

Barton Springs discharge, as referred to in this report, is the combined discharge of Main, Eliza, and Old Mill Springs. It does not include discharge from Upper Spring, which is estimated to represent less than 10 percent of the total discharge. Barton Springs discharge is computed on the basis of a stage-discharge relation developed between the water level in a nearby well and manual discharge measurements (Slade and others, 1986); discharge at the spring has been monitored continuously in this way and reported by the USGS since 1978. The stage-discharge relation is verified periodically by manual measurements. During this study, an acoustic Doppler velocity meter placed within the orifice of Main Spring was used to estimate discharge when the stage-discharge relation was not applicable (Asquith and Gary, 2005), for example during flooding or when the water level in Barton Springs Pool is lowered for pool cleaning by opening the gates of the downstream dam.

Recharge Estimation

Recharge, as estimated for this report, was computed as the sum of the streamflows measured at gaging stations at the upstream end of the recharge zone for five recharging streams (fig. 1), up to the maximum rate (R_{max}) for each stream as determined by Barrett and Charbeneau (1996). Maximum recharge through streambeds might have been low during high aquifer flow conditions, and thus computed recharge might have been overestimated during high aquifer flow conditions (N.M. Hauwert, City of Austin, oral commun., 2006). Recharge computed on the basis of streamflow does not account for recharge from interstream areas. Interstream recharge presently (2006) cannot be quantified but has been estimated as 15 percent of total recharge (Slade and others, 1986). In 2006, research was ongoing to quantify interstream recharge (N.M. Hauwert, City of Austin, oral commun., 2006).

During non-stormflow conditions, recharge from each creek was assumed to equal flow at the upstream gage (Q_{US}) up to R_{max}, as determined by Barrett and Charbeneau (1996), at which point any additional flow passes the downstream gage (Q_{DS}) without recharging the aquifer. This approach was used for Onion, Slaughter, Bear, and Williamson Creeks. For Barton Creek, the algorithm of Barrett and Charbeneau (1996) developed for R_{max} was used; this algorithm uses a third-order polynomial to relate Q_{US} to recharge. Use of the algorithm was necessary because Barton Creek can be either a gaining or a losing stream depending on aquifer flow conditions. Recent dye-tracing studies have indicated that some recharge from Barton Creek flows to Cold Springs rather than Barton Springs (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004), but this recharge was assumed to be negligible for this study.

During stormflow conditions, recharge computations were considerably more complex. If there was overland flow in the recharge zone, then R_{max} might have been reached for a stream even when Q_{US} measured less than R_{max}. Conversely, a non-zero value for Q_{DS} did not necessarily imply that R_{max} had been reached for a stream. To account for conditions when both Q_{US} and Q_{DS} were greater than zero, recharge computations for each stream were divided into three cases:

1. Hydrograph rising limb, when Q_{US} is greater than Q_{DS}. Recharge was assumed equal to Q_{US}, up to R_{max}.
2. During peak stormflow, when Q_{US} is less than Q_{DS}. Recharge was computed as the greater of Q_{US} or $(Q_{DS}/Q_{channelfull})*R_{max}$. $Q_{channelfull}$ is the discharge (streamflow) corresponding to channel-full conditions as determined from cross-sectional surveys at the

downstream gaging station (R.A. Samuelson, U.S. Geological Survey, oral commun., 2005). Underlying this equation were the assumptions that R_{max} was achieved only under channel-full conditions and that non-channel-full conditions allowed recharge in direct proportion to the water level in the stream channel.

3. Hydrograph falling limb, when Q_{DS} is less than hydrograph recession breakpoint (change in slope). Recharge was assumed to equal zero, as Q_{DS} was assumed to entirely reflect discharge from localized epikarst (rather than the regional water table).

This approach yields only a rough estimate of total recharge, and the associated uncertainty cannot be quantified. However, because the maximum recharge most likely was reached throughout most of a storm event, and because the same approach was used for all monitored storms, comparison of the relative amounts of recharge between the storms is considered appropriate and informative.

Physicochemical Property Measurements

Physicochemical properties (specific conductance, turbidity, temperature, pH, and dissolved oxygen) were measured at Main Spring at 15-minute intervals using a multiparameter water-quality monitor installed in the orifice. Data collected at Main Spring are available in real time on the USGS Website http://waterdata.usgs.gov/tx/nwis/uv/?site_no=08155500

Physicochemical properties also were measured at 15-minute intervals at Old Mill Spring by USGS staff, and at Upper and Eliza Springs by City of Austin staff, using the same method as at Main Spring. Data from these springs are used in this report for the purpose of comparison with Main Spring, particularly during storm sampling.

Water-Quality Sample Collection

Samples were collected from each of the four spring orifices at Barton Springs and from the recharging streams (figs. 1, 2; table 1). Samples from the springs were collected by immersing bottles below the water surface into or near the spring orifice, avoiding contact with the atmosphere and standing surface water (Wilde and others, 1999). Samples for analysis of major ions, nutrients, and alkalinity were collected in either a 3-liter (L) polytetrafluoroethylene (PTFE) (Teflon) bottle or polyethylene bottles. Samples for analysis of trace elements, soluble pesticides, and pharmaceutical compounds were collected in a 3-L PTFE (Teflon) bottle. Samples for analysis of VOCs were collected in 40-milliliter (mL) baked amber glass bottles following the methods of Shelton (1997). Any reusable bottles and sampling equipment were cleaned with Liquinox soap, hydrochloric acid, and deionized water prior to use (Horowitz and Sandstrom, 1998).

Stormflow composite samples were collected from streams following two storms. Discrete samples were collected over the duration of the storm hydrograph either in seven 9-L polyethylene carboys lined with Teflon bags or in twelve 1-L glass bottles. For each stream, the discrete samples were combined into a single flow-weighted composite sample. Samples were composited on the basis of volume of flow represented by each discrete sample as measured at the gaging station (Fisk and others, 1994). The concentration of an analyte in the composite sample is assumed to represent the event mean concentration. Teflon bags and glass bottles were cleaned using the same protocol as that used for cleaning the spring sampling equipment.

All samples were stored on ice in coolers following collection and during transport to the USGS Texas Water Science Center. At the Center, most samples were filtered, dispensed into shipping bottles, and either preserved as required for the various analyses or not preserved (table 3). Samples for ammonia nitrogen, phosphorous, and VOC analysis were not filtered (table 3). Samples were maintained at 4 degrees Celsius (°C) or less, and shipped to the USGS National Water Quality Laboratory (NWQL) for analysis.

Analytical Methods

Analyses of major ions (except bicarbonate), nutrients, trace elements, soluble pesticides, VOCs, and pharmaceutical compounds were done by the NWQL using published USGS analytical methods. Concentrations of major dissolved cations were measured using inductively coupled plasma-mass spectrometry (ICP/MS), and concentrations of anions (except bicarbonate) were measured using ion-exchange chromatography (Fishman, 1993). Alkalinity was determined by titration of 50 mL of filtered sample with 1.6-normal sulfuric acid to a pH of less than 4.0 and computed using the inflection point method (Rounds and Wilde, 2001). All samples had negligible hydroxide and carbonate concentrations, thus these ions were not considered in this report. Ammonium plus organic nitrogen was measured by a Kjeldahl digestion method and an automated photometric finish (Patton and Truitt, 2000), and total phosphorous was measured by a Kjeldahl digestion method and an automated colorimetric finish (Patton and Truitt, 1992). Dissolved trace elements (metals) (cadmium [Cd], chromium [Cr], copper [Cu], nickel [Ni], lead [Pb], zinc [Zn], and the metalloid arsenic [As]) were measured either by ICP/MS (Cd, Cu, Ni, Pb, and Zn) (Faires, 1993) or collision/reaction cell ICP/MS (As and Cr) (Garbarino and others, 2006). Concentrations of soluble pesticides and pesticide degradates were quantified by solid-phase extraction and capillary-column gas chromatography/mass spectrometry (GC/MS) (Zaugg and others, 1995). VOCs were quantified using purge and trap GC/MS (Connor and others, 1998). Pharmaceutical compounds were quantified using solid-phase extraction followed by high-performance liquid chromatography-electrospray ionization mass spectrometry (Cahill and others, 2004).

Table 3. Sample collection and processing equipment for sampling of Barton Springs, Austin, Texas (2003–05).

[mL, milliliters, µm, micrometer; HNO_3, nitric acid; <, less than; H_2SO_4, sulfuric acid; HCl, hydrochloric acid]

Constituent	Filter	Collection bottle material	Shipping container	Sample volume (mL)	Preservative
Major Ions					
Cations	0.45-µm cellulose	Teflon or polyethylene	Polyethlyene	250	HNO_3 to pH <2
Anions	0.45-µm cellulose	Teflon or polyethylene	Polyethlyene	250	None
Nutrients					
Nitrate nitrogen	0.45-µm cellulose	Teflon or polyethylene	Polyethylene	125	None
Ammonia nitrogen, phosphorus	None	Collected directly	Polyethylene	125	H_2SO_4
Trace elements	0.45-µm capsule	Teflon	Polyethylene	250	HNO_3 to pH <2
Soluble pesticides	0.7-µm glass fiber	Teflon	Baked amber glass	1,000	None
VOCs	None	Collected directly	Baked amber glass	40	HCl to pH <2
Pharmaceuticals	0.7-µm glass fiber	Teflon	Baked amber glass	1,000 (x 2 bottles)	None

Water Quality of Barton Springs (2003–05)

Continuous Discharge and Physicochemical Measurements

Continuous measurements of discharge and physicochemical properties (specific conductance, turbidity, temperature, pH, and dissolved oxygen) were recorded at Main Spring at 15-minute intervals. These measurements were used to characterize both long-term and short-term changes in water quality and quantity for Barton Springs. Monitoring occurred throughout Phases 1 and 2, as well as the time between these two sampling phases and for 1 month before Phase 1—thus, continuous monitoring data are available from July 2003 through June 2005. These data are used as interpretive aids throughout other sections of this report and are summarized here.

Spring Discharge

The long-term mean Barton Springs discharge is 54 ft^3/s, based on data from 1917 through 2005. This mean was computed using data from Slade and others (1986) and from real-time discharge recorded continuously for Barton Springs after 1982. On the basis of data from 1978, when the current (2006) system of measuring discharge was put into place, through 2005, the long-term mean discharge for 1979–2005 is 65 ft^3/s.

Barton Springs discharge ranged from 36 to about 130 ft^3/s from the beginning of Phase 1 (August 2003) to the end of Phase 2 (June 2005); the lowest values occurred, however, during the period between Phases 1 and 2 (October 2003–May 2004), and the discharge during Phases 1 and 2 always exceeded 60 ft^3/s (fig. 5). Maximum discharges are likely to be underestimated, as measurement accuracy is less when Barton Creek floods into Barton Springs Pool (Asquith and Gary, 2005). The lowest discharge was recorded in February 2004, coincident with the end of a period of low rainfall. The highest discharge was recorded in March 2005, coincident with the end of a period of high rainfall. Mean discharges during Phases 1 and 2 (76 and 93 ft^3/s, respectively), when samples were collected, were higher than the long-term mean discharge. Therefore, the findings of this report reflect water-quality conditions during above-average aquifer flow conditions.

Specific Conductance

Specific conductance is a physical measurement of the amount of electrical current that water can transmit and is a direct reflection of the ionic strength, or total amount of dissolved solids in the water (Hem, 1992). Rain has very low specific conductance (Herczeg and Edmunds, 2000); surface water has higher specific conductance resulting from chemical reactions with the land surface, soils, and the streambed; ground water typically has a higher specific conductance than surface water resulting from the dissolution of the rock matrix of the aquifer. Specific conductance can act as a tracer of recently infiltrated surface water as it flows through a karst aquifer. Specific conductance at Main Spring has been observed to decrease in response to rainfall as recently recharged meteoric water moves through the system (Andrews and others, 1984; David Johns, City of Austin, unpub. data, 1999–2002). Specific conductance at Main Spring has been observed to increase when the dam at the downstream end of the pool is removed (a “drawdown” event), lowering the water level in the pool and consequently decreasing the head over the spring. The decrease in head results in an increase in discharge; the increase in specific conductance has been attributed to an inflow of water from the saline zone resulting from a reduction in karst conduit pressure (Mahler, 1997).

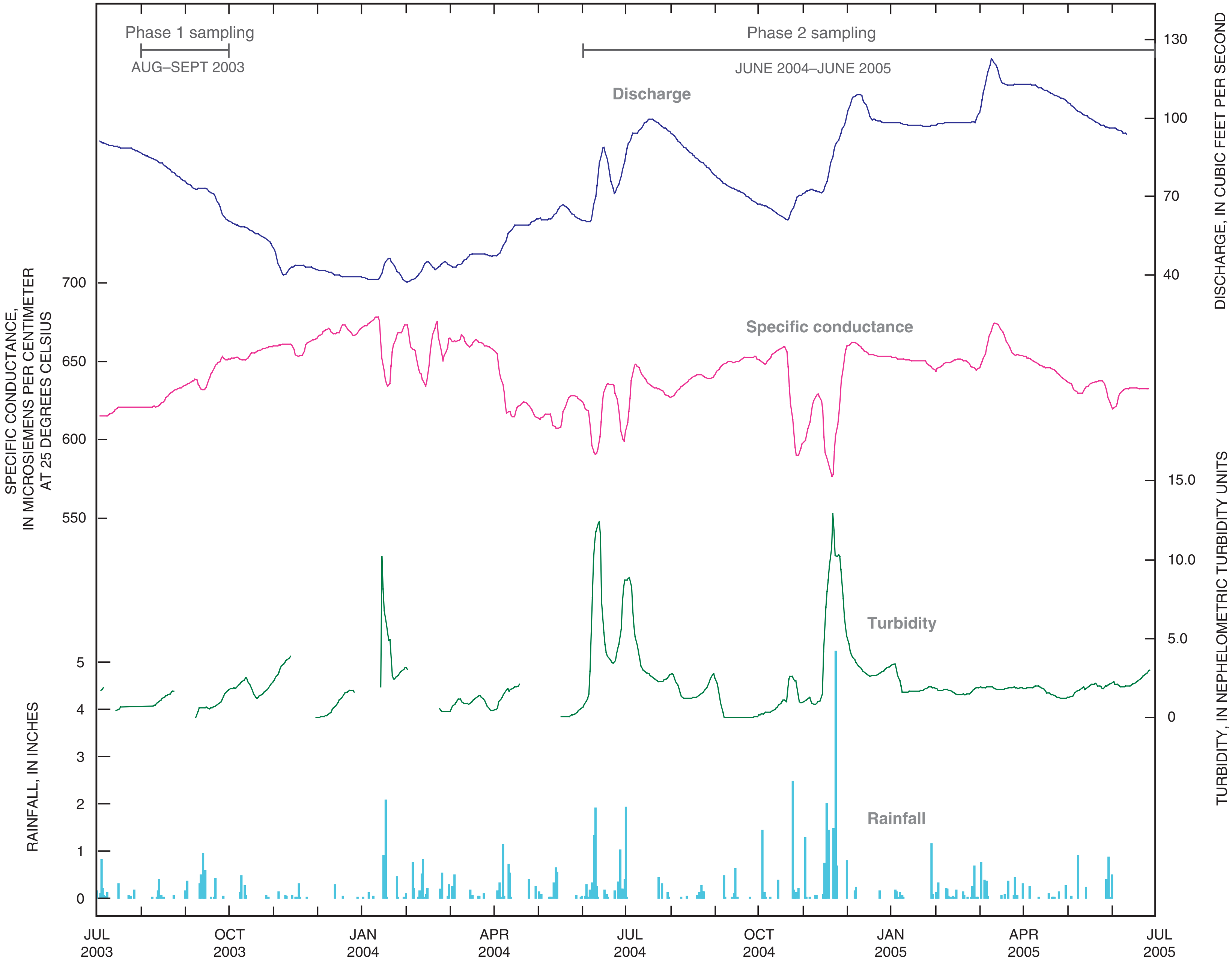


Figure 5. Time series of discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.), specific conductance, and turbidity from Main Spring, Austin, Texas, and weekly rainfall (based on areally-weighted average for as many as 10 rain gages in study area) (2003–05). (Turbidity and specific conductance series are moving 7-day means.)

Table 4. Summary statistics for continuously measured spring discharge and physicochemical properties from Main Spring, Austin, Texas (2003–05).

[ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; NTU, nephelometric turbidity unit; °C, degrees Celsius; mg/L, milligrams per liter]

Property (units)	Minimum	Maximum	Median	5th percentile	95th percentile	Data availability (percent)
Barton Springs discharge[1] (ft^3/s)	36	130	76	39	112	100
Specific conductance (µS/cm)	464	683	647	608	673	95
Turbidity (NTU)	0	74	1.7	0	5.7	75
Temperature (°C)	20.0	22.3	21.1	20.2	22.1	96
pH (standard units)	6.8	7.3	7.1	7.0	7.3	71
Dissolved oxygen (mg/L)	5.5	7.9	6.6	5.8	7.3	68

[1] Combined discharge measurement of Main, Eliza, and Old Mill Springs; station 08155500 Barton Springs at Austin, Tex.

Specific conductance of Main Spring varied from a minimum value of 464 to a maximum value of 683 microsiemens per centimeter at 25 °C (µS/cm) during this study (table 4); moving 7-day mean values are shown in figure 5. The maximum conductance occurred in January 2004, coinciding with the end of a period of low rainfall. The minimum conductance occurred in November 2004, coincident with a period of near-record high rainfall.

Rainfall events and the draining of Barton Springs Pool are the principal causes of rapid changes in specific conductance. The most rapid decreases in specific conductance, as much as 43 µS/cm per hour, occurred within hours following large rainfall events, indicating that storm-related recharge can rapidly alter the water chemistry of Main Spring. This characteristic is described in detail in this report in the section "Response of Barton Springs to Stormflow, Variation in Physicochemical Properties in Response to Storms."

For more than 95 percent of the study period, the absolute rate of change of specific conductance was less than 1 µS/cm per hour. Most periods of slow change were characterized by a decrease in Barton Springs discharge, very little or no rainfall (less than 1 in. per day) and a gradual increase in specific conductance. Slow and gradual increases in specific conductance (fig. 5) likely result from increasing ground-water residence times (resulting in more water-rock interaction) and decreasing recharge from streams (resulting in less dilution by low-specific-conductance water). During three periods (July 2004, December 2004–January 2005, and April 2005), however, discharge and specific conductance decreased simultaneously; these periods occurred exclusively when discharge was greater than 95 ft^3/s and appear to have been related to large volumes of recharge from streams. This characteristic is described in the section "Water Quality Over an Annual Cycle, Major Ions, Temporal Variability in Major Ions and Relation to Recharge and Discharge."

Turbidity

The Barton Springs segment contains a karst conduit network that can transport suspended sediment through the aquifer (Mahler, 1997; Mahler and Lynch, 1999; Mahler and others, 1998). Sediment from the surface (allochthonous) enters the conduit system through focused recharge from streambeds and karst features such as caves, sinkholes, and swallow holes, and travels through conduits toward discharge points (wells and springs). Sediment derived within the aquifer (autochthonous) can be eroded or resuspended by ground water flowing through conduits. Turbidity, an indirect measurement of suspended sediment using reflected light, is used as a proxy for suspended-sediment concentration.

Turbidity of Main Spring varied from a minimum of zero to an estimated maximum of 74 nephelometric turbidity units (NTU) (table 4); moving 7-day mean values are shown in figure 5. Ninety-five percent of all turbidity measurements were less than 5.7 NTU. Turbidity measurements greater than 5.7 NTU occurred exclusively after large rainfall events in January 2004, June 2004, July 2004, and November 2004. The association of increased turbidity with stormflow conditions is a phenomenon that has been documented at Main Spring for more than 20 years (Andrews and others, 1984; City of Austin, 1997; Garner, 2005; Mahler and Lynch, 1999; Slade and others, 1986) and is common in many other karst springs (Mahler and others, 2000; Massei and others, 2002; Massei and others, 2003; Ryan and Meiman, 1996; Valdes, 2005).

Temperature

There is a significant nonparametric correlation between water temperature of Main Spring and air temperature (fig. 6). Water temperatures over time generally are an attenuated version of air temperatures over time. Water temperature variability was greater after April 2004 than before; the post April 2004

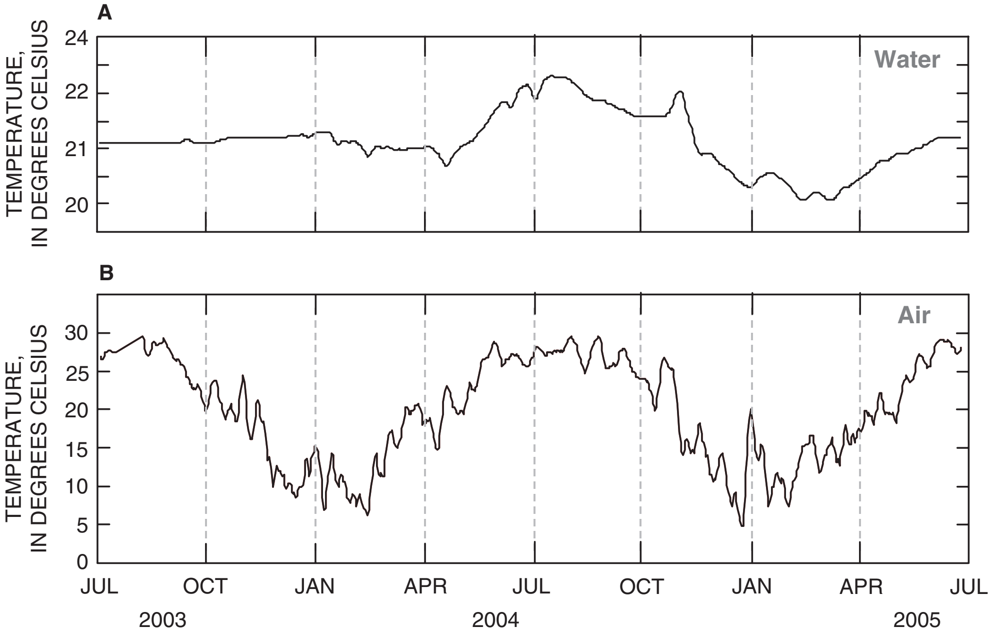


Figure 6. Time series of moving 7-day means of temperature of (A) discharge (water) from Main Spring, Austin, Texas (station 08155500 Barton Springs at Austin, Tex.), and (B) air at Austin-Bergstrom International Airport, Austin, Texas (National Climatic Data Center, 2005) (2003–05).

period coincided with the onset of a period of increased rainfall and aquifer recharge. The most rapid change in water temperature coincided with record rainfalls during November 2004, indicating that large inflows of recharge-affected spring-water temperature on a short time scale.

Spring-water temperature can be simulated as a function of air temperature, recharge, and discharge (aquifer flow condition), using two end-member mixing equations (similar to mixing approaches discussed in Freeze and Cherry, 1979; Lakey and Krothe, 1996):

$$Q_{MIX} = Q_{SURFACE} + Q_{MATRIX}, \quad (1)$$

$$Q_{MIX}\, T_{MIX} = Q_{SURFACE}\, T_{SURFACE} + Q_{MATRIX} T_{MATRIX}, \quad (2)$$

$$Q_{SURFACE} = \alpha\, R_{STREAMS}, \quad (3)$$

where

Q_{MIX} =Main Spring + Eliza Spring + Old Mill Spring discharge;

$Q_{SURFACE}$ = surface-water component of spring discharge (assumed equal to a constant [α] times computed recharge from streams [$R_{STREAMS}$]);

T_{MIX} =temperature of water (Main Spring);

$T_{SURFACE}$ = temperature of surface water (assumed equal to temperature of air [T_{AIR}]); and

T_{MATRIX} =temperature of ground water (assumed equal to median temperature of spring water, July 2003– June 2005, 21.1 °C).

Solving this system of equations for spring-water temperature yields

$$T_{MIX} = 21.1 + (\alpha\, R_{STREAMS}\, (T_{AIR} - 21.1))\, /\, Q_{MIX}. \quad (4)$$

Using daily mean values of recharge, discharge, and air temperature, and an empirically derived α value ($\alpha = 0.05$), simulated water temperature generally matches measured water temperature (fig. 7). The model is a substantial simplification of Barton Springs behavior and contains many assumptions. For example, no spatial component is in the model; therefore, transit time and temperature differences among streams are not accommodated. Also, α represents all unknown phenomena and most likely is not constant through time. The model underpredicts water temperature in July and November 2004, possibly because high aquifer flow conditions caused recharge to enter the aquifer in a different manner than during average flow conditions. Despite these shortcomings, this simple model generally predicts water temperature, indicating that water temperature is mostly a function of air temperature, recharge, and aquifer flow conditions.

The model indicates that water temperature might serve as a conservative tracer of recharge through the system but has several important limitations: First, temperature generally varies only on an annual scale, and the changes are minor relative to the mean, which limits sensitivity. Second, during some periods of the year recharge temperature might not be appreciably different than ground-water temperature. Third, the rocks of the aquifer buffer temperature, the net effect of which is controlled

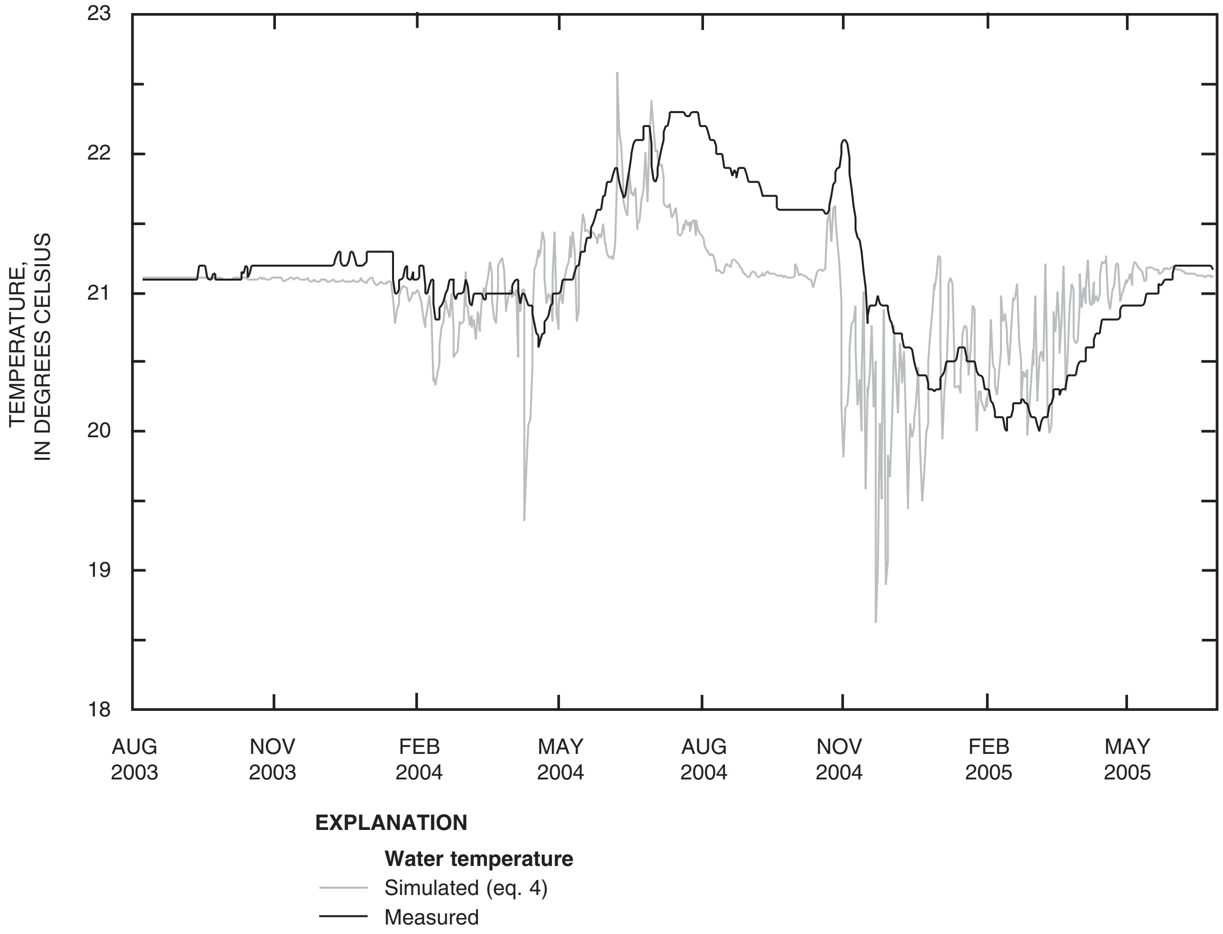


Figure 7. Time series of simulated and measured temperature of discharge (water) from Main Spring, Austin, Texas (station 08155500 Barton Springs at Austin, Tex.) (2003–05).

by a complex set of factors including geological structure, vertical depth and geothermal gradient, and conduit geometry (Leutscher and Jeannin, 2004). Specific conductance thus provides a simpler, more reliable, and conservative tracer of short-term recharge, as described in the section "Response of Barton Springs to Stormflow."

pH

The pH of Main Spring ranged from 6.8 to 7.3 standard units (table 4). Fifty percent of all measurements were within the limits of analytical uncertainty, as indicated by an interquartile range of 0.1. Thus, actual pH variability was small, which might result from the high alkalinity of the ground water of the Barton Springs segment. One period with measurable pH variability was from October 2004 through November 2004, during which pH decreased to the lowest recorded value of 6.8, approximately coinciding with the two largest rainfall events during the study period. This indicates that large rainfall events can cause a slight and temporary decrease in pH, likely a result of low-ionic-strength, mildly acidic meteoric water entering the aquifer and reducing ground-water alkalinity. The low pH values also indicate that the time scale of transport of recharge water through the aquifer is sufficiently rapid to limit buffering of pH by way of water-rock (limestone) interaction.

Dissolved Oxygen

Dissolved oxygen concentration in Main Spring ranged from 5.5 to 7.9 mg/L (table 4), however, the data were affected by instrument reliability and environmental factors. The data show that spring discharge was always aerobic. Dissolved oxygen had the lowest data availability of all continuously monitored properties, and the data are considered to be of fair t o poor quality (see appendix 3, Quality-Assurance/Quality-Control Data); such problems often occur with remotely or continuously monitored dissolved oxygen measurements because of the labor-intensive and technically difficult requirements of maintaining these instruments. The lowest dissolved oxygen concentrations, in December 2003, coincided with the lowest spring discharge during the study, which indicates that longer ground-water residence times might allow for more oxidation of organic and inorganic material within the aquifer and result in consumption of dissolved oxygen. From October 2004 through November 2004, dissolved oxygen concentrations varied in response to rainfall events (see the section "Response of Barton Spring to Stormflow, Variation in Physicochemical Properties in Response to Storms"), indicating that high recharge resulted in a larger component of oxygen-rich water discharging from Main Spring.

Water Quality Over an Annual Cycle

Major Ions

The 22 sets of samples collected from Main Spring were analyzed for major ions, and 20 of the 22 sets of samples collected from Upper, Eliza, and Old Mill Springs were analyzed for major ions (appendix 4). Major ion concentrations can be interpreted individually and collectively to provide information about water source and geochemical processes. Of particular interest for this study is the difference in aqueous geochemistry between sites (previous geochemical investigations primarily have focused on Main Spring only) and the influence of aquifer flow condition and recharge on spring-water geochemistry.

Differences in Geochemistry Among Spring Orifices

Concentrations of several major ions were systematically different at the four spring orifices (figs. 8, 9). For example, sodium and chloride concentrations were consistently highest at Old Mill Spring and consistently lowest at Upper Spring. To more clearly summarize these differences and interpret the underlying processes, the aqueous geochemistry of the four springs was investigated using principal components analysis (PCA). PCA is a statistical technique that transforms a set of variables into a new set (the principal components, or factors) that are linear combinations of the original variables (Davis, 2002). The transformation maximizes the amount of variability explained by the first new variable, with decreasing amounts explained by the following variables. In aqueous geochemistry, the constituents that are most heavily weighted in a factor sometimes indicate a water source or process (Christophersen and Hooper, 1992; Johnson and others, 1997; Meharg and others, 2003). For this analysis, the data were standardized and weighted by $1/n$, where n is the number of samples collected at each site. The major ion concentrations from the four spring orifices were input as variables, and total recharge was input as a supplementary variable.

The first three factors identified by the PCA explain about 80 percent of the variance in the data (fig. 10A, B). The first factor (Factor 1) is very heavily weighted on sodium, chloride, and sulfate (all weights negative) and is interpreted as representing the influence of the saline zone. The second factor (Factor 2) is most heavily weighted on magnesium, bicarbonate, and silica (all weights negative) and is interpreted as representing an intrinsic geochemical signature of the aquifer matrix. The third factor is most heavily weighted on calcium (positive), recharge (positive), and strontium (negative) and is interpreted as representing the effect of recent recharge on calcium and strontium concentrations. The negative relation between strontium and recharge in Factor 3 likely is the result of dilution of strontium concentrations in ground water by water (with a lower strontium concentration) infiltrating from streams. The mean base-flow strontium concentration in water from Upper Spring is 0.46 mg/L and ranges from 0.80 to 0.94 mg/L in water from the three other spring orifices, whereas the average strontium concentration in historical samples collected from recharging streams ranges from 0.16 mg/L at station 08158810 Bear Creek below FM 1826 to 0.30 mg/L at station 08158700 Onion Creek near Driftwood. An increase in recharge thus yielded a linear decrease in strontium concentration in spring water (fig. 11), resulting from dilution. The increase in calcium in spring water with increasing recharge cannot be explained by a similar process, as surface water is less enriched in calcium than ground water. Water-rock interaction processes, including calcite dissolution, might result in higher calcium concentrations. The mixing of surface water with karst ground water might result in a solution that is undersaturated with respect to calcite; mixing of two water types in equilibrium with calcite but with different partial pressures of carbon dioxide might yield increased dissolution of the limestone matrix and a corresponding increase in calcium concentrations (Bogli, 1971; Dreybrodt, 1981; Kaufmann, 2003).

The geochemistry of the four spring orifices can be compared on the basis of their separation along different factors (fig. 10C, D). Old Mill Spring is the most heavily negatively weighted and Upper Spring is the most heavily positively weighted on Factor 1, indicating that the saline zone has the most influence on the geochemistry of water from Old Mill Spring and the least on water from Upper Spring. Factor 2 has a range of weights across all four spring orifices, but Old Mill and Upper Springs group together and are more heavily negatively weighted, and Main and Eliza Springs group together and are more heavily positively weighted; the interpretation of this is less clear but could be related to soil zone processes or carbonate equilibria processes, or both. Water-rock interaction with carbonate aquifer minerals and silicate minerals present in soils and as impurities in the limestone can influence Factor 2 weights. Factor 3 has a range of weights for all four springs, indicating that the aqueous geochemistry of all four springs is affected by recharge. The similar weightings on Main and Eliza Springs for all three factors indicate that these two spring orifices have similar geochemical compositions and are subject to similar geochemical processes or a shared flow path(s), or both. If the influence of the saline zone (Factor 1) is removed, it appears that Upper and Old Mill Springs have similar geochemical compositions (fig. 10D). All four springs have heavy weightings on Factor 3 for those samples collected when aquifer flow conditions were high, but discharge, recharge, sulfate concentration, and specific conductance all were decreasing.

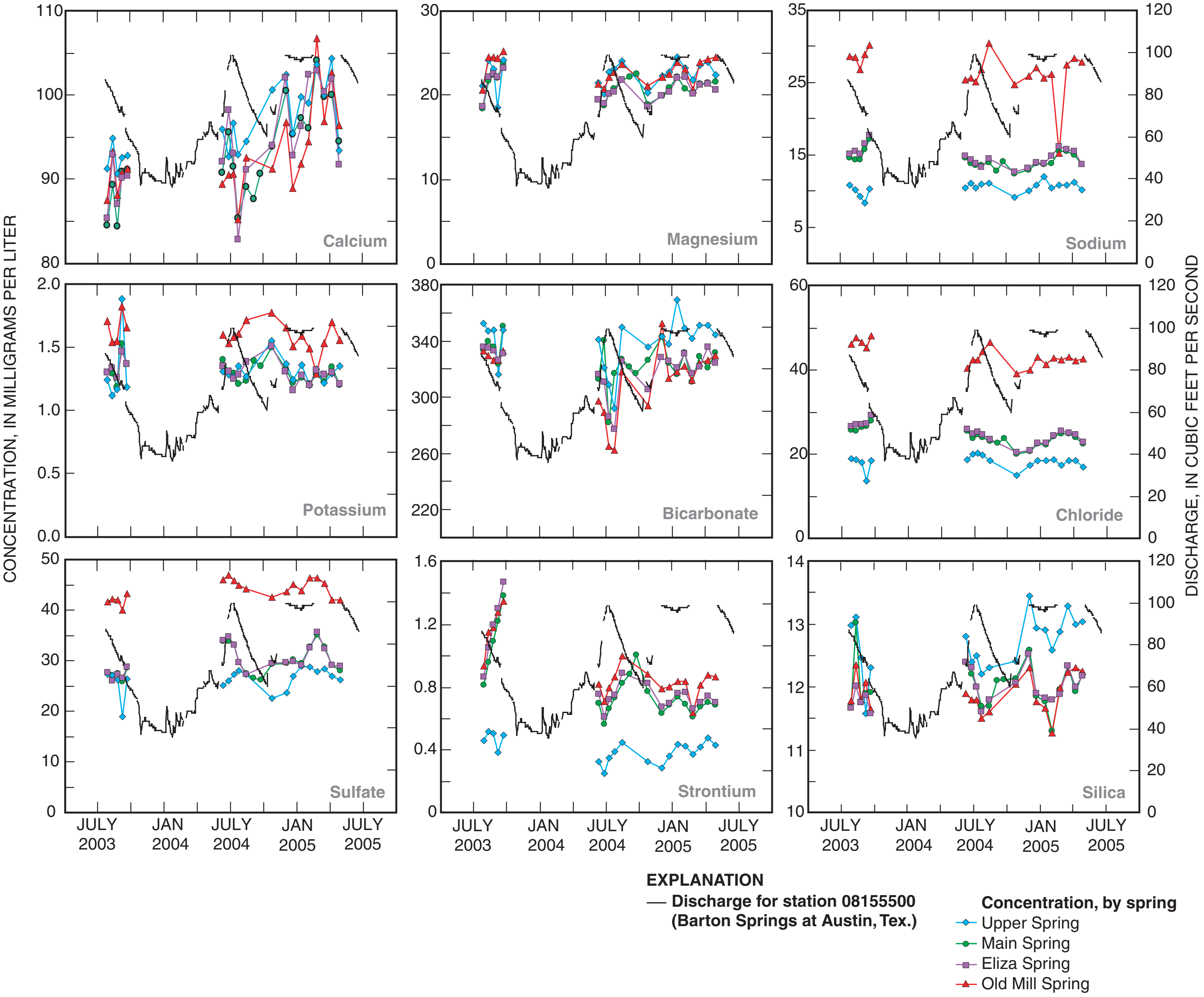


Figure 8. Time series of major ion concentrations from the four spring orifices of Barton Springs, Austin, Texas, and discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.) during routine sampling (2003–05).

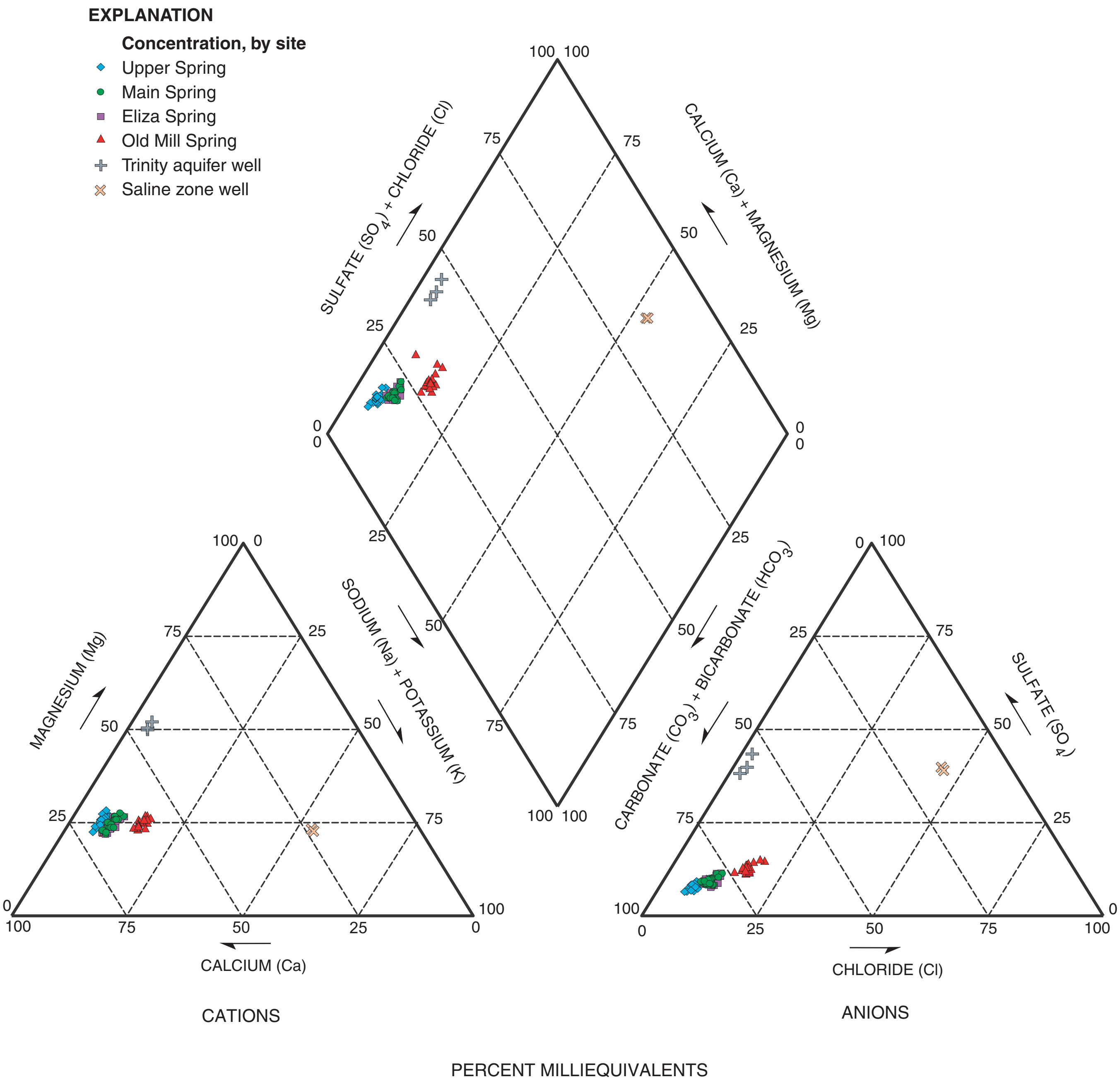
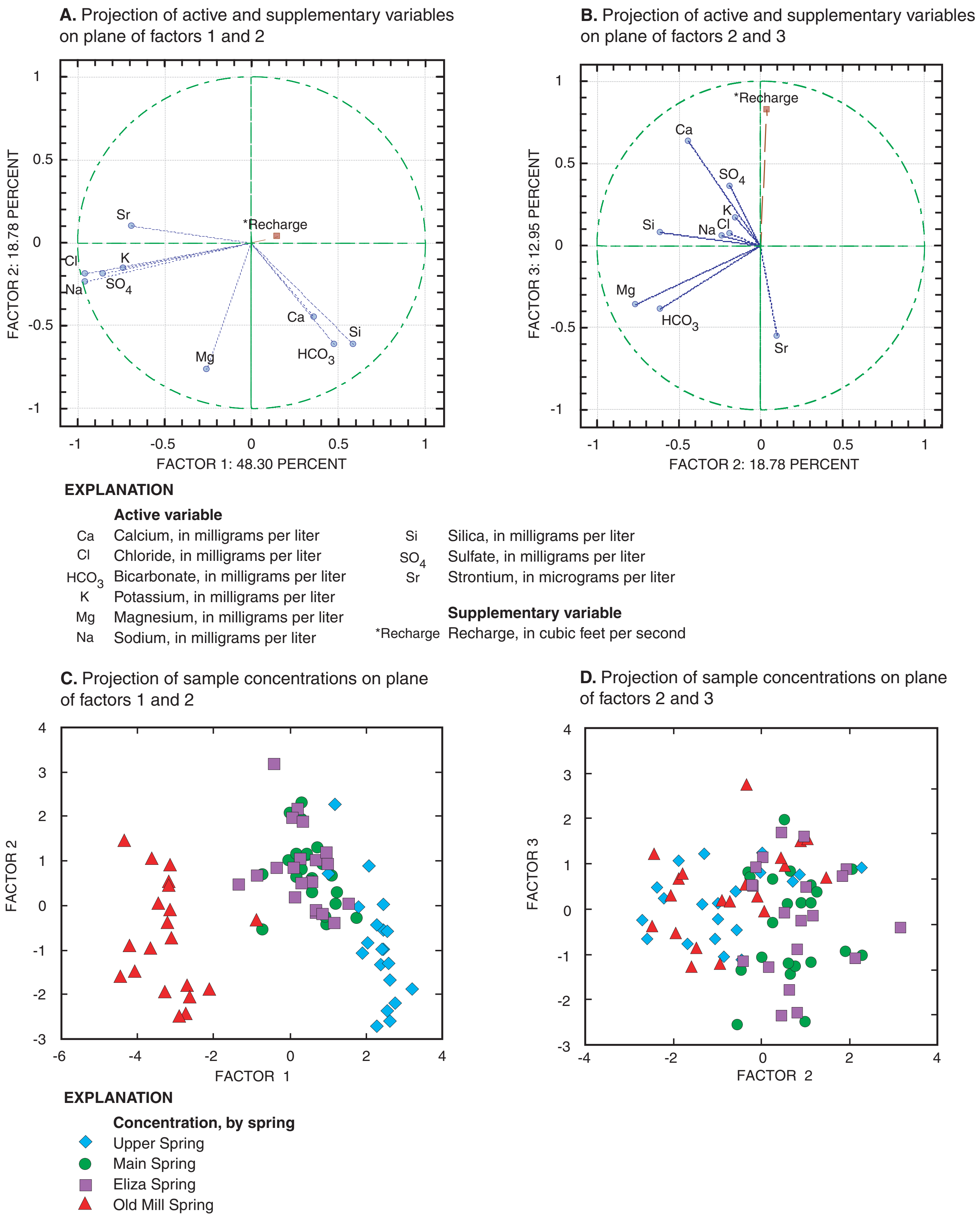


Figure 9. Piper diagrams showing geochemical composition of samples from the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05), and selected wells in the study area for comparison.

Temporal Variability in Major Ion Concentrations and Relation to Recharge and Discharge

Major ion concentrations at all four spring orifices varied at the time scale of the routine sampling (figs. 8, 9). The most variation was for strontium (median coefficient of variation [C_V] [ratio of standard deviation to mean] for the four springs of 0.23), and the least for silica (median C_V for the four springs of 0.03). To investigate controls on major ion concentration variability, the linear relation between major ion concentrations at each spring and Barton Springs recharge, and between major ion concentrations at each spring and discharge were assessed. The discharge and recharge associated with the sampling events were only weakly related to each other (coefficient of determination [r^2] = .23).



A. Projection of active and supplementary variables on plane of factors 1 and 2

B. Projection of active and supplementary variables on plane of factors 2 and 3

C. Projection of sample concentrations on plane of factors 1 and 2

D. Projection of sample concentrations on plane of factors 2 and 3

Figure 10. Summary of principal components analysis of major ion concentrations of samples from the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05).

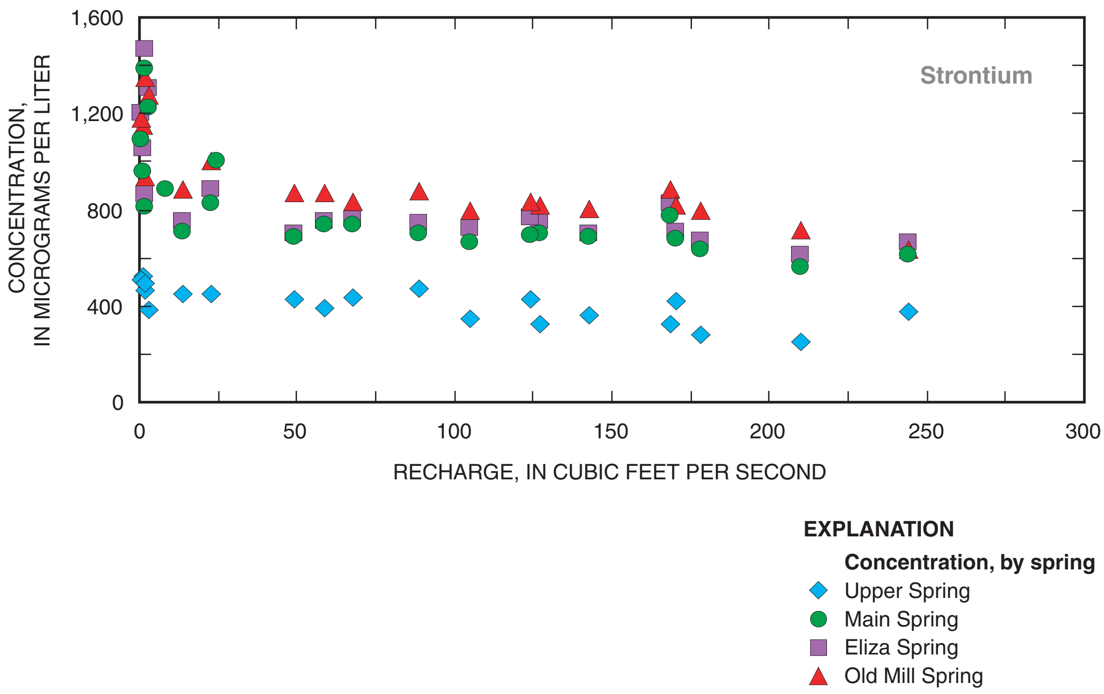


Figure 11. Relation between recharge (daily mean) and strontium concentrations of samples from the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05).

Recharge from streams exerts a stronger influence on major ion concentrations in spring discharge than does aquifer flow condition during the average-to-high flow conditions encountered during this study. Major ion concentrations at a spring orifice and recharge had a significant linear relation in 17 of a possible 36 cases, and the relations are relatively strong (median $r^2 = .51$) (table 5). Correlations between calcium and sulfate concentrations and recharge are positive at all sites where they are significant, and correlations between the other major ions and recharge are negative at all sites where they are significant.

Variability in major ion concentrations is not well explained by Barton Springs discharge. There is a significant linear correlation (p-value < .05) between a major ion concentration at a spring orifice and discharge for 13 of a possible 36 cases, and those relations generally are weak (median $r^2 = .30$) (table 5). The strongest relation is a negative correlation between strontium concentration and discharge ($r^2 = .49$ to .56), which is significant at all of the spring orifices except Upper Spring. Thus, aquifer flow condition (as reflected by discharge), at the range of discharges for the sampling dates during 2003–05 (61 to 120 ft^3/s; fig. 12), exerts a relatively weak influence on major ion concentrations in spring flow except for strontium. The historical data indicate, however, that at low discharges (less than 40 ft^3/s) aquifer flow condition exerts a stronger influence on some of the major ion concentrations, in particular sodium, chloride, and sulfate (appendixes 1, 2), which likely reflects the greater influence of the saline zone under low aquifer flow conditions. Because this study was done during a period of average to high flow, the influence of flow condition on ion concentrations over longer time scales that encompass low-flow conditions is beyond the scope of this report.

Elemental ratios of magnesium to calcium (Mg/Ca) and strontium to calcium (Sr/Ca) are strongly correlated with recharge and discharge for some of the springs (table 5), all with negative correlations. In carbonate aquifers, Mg/Ca and Sr/Ca ratios have been used as indicators of residence time and provide insight into water-rock interaction processes including carbonate dissolution and recrystallization (Musgrove and Banner, 2004; Plummer, 1977). The application of elemental ratios as geochemical tracers in Barton Springs is discussed in Garner (2005). A significant correlation between Mg/Ca and Sr/Ca ratios with both recharge and discharge likely reflects a combination of water-rock interaction processes, carbonate equilibria, and mixing of recharge waters with more geochemically evolved water in the aquifer.

Surface water generally has a lower ionic concentration than ground water, because it has undergone less water-rock interaction. However, the water in the recharging streams has flowed across the soils and rock of the contributing zone (fig. 1), and thus bears to some degree the imprint of a geochemical signature from the contributing zone. On the basis

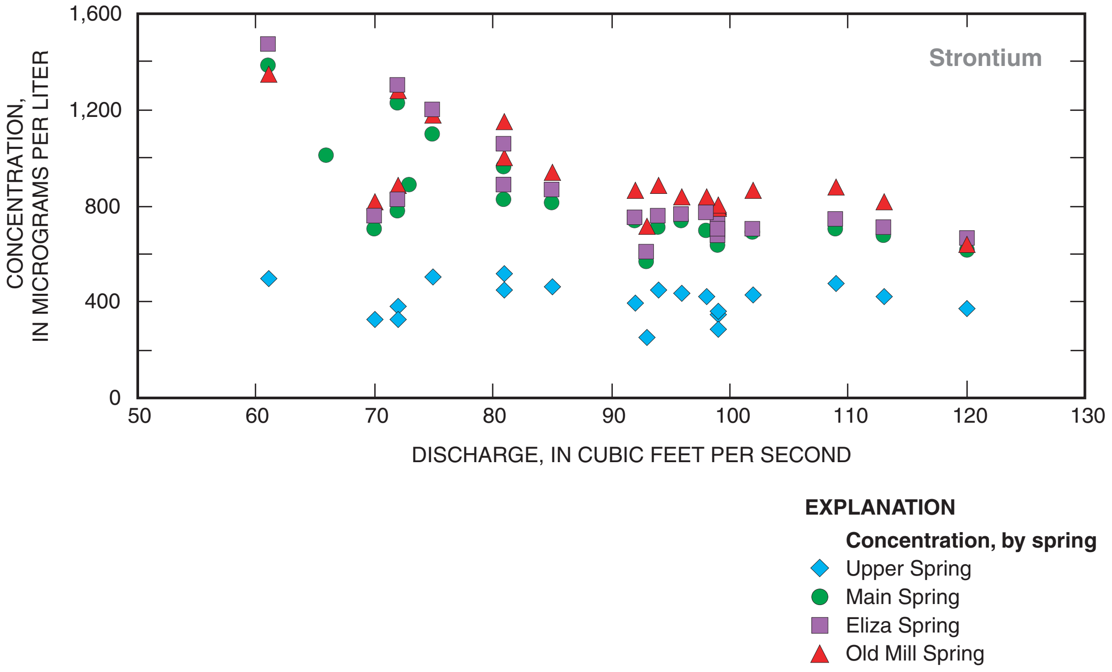


Figure 12. Relation between discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.) and strontium concentrations of samples from the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05).

of historical data, as recharging streams enter the recharge zone, water in the streams has lower concentrations of many of the major ions (fig. 13), indicating a geochemical signature different from that of spring discharge.

Calcium concentrations in spring water increase with increasing recharge. When little to no recharge is occurring (base-flow conditions), the calcium concentration in discharge was between 84 and 95 mg/L (2003–05). The mean calcium concentration in stream samples collected at the upstream boundary of the recharge zone when the recharging streams are flowing is 73 mg/L (appendix 2), thus the increase in calcium in discharge cannot be attributed to the mixing of recharge water with ground water unless accompanied by geochemical processes resulting in an increase in calcium. When recharging surface water mixes with ground water, a solution that is undersaturated with respect to calcite might result (as discussed in the section “Water Quality Over an Annual Cycle, Major Ions, Differences in Geochemistry Among Spring Orifices”), leading to increased dissolution of the limestone matrix and an increase in calcium concentration.

Sulfate concentration in spring water also increases with increasing recharge. The recharging streams have sulfate concentrations that in some cases are elevated relative to concentrations in the spring orifices. Under base-flow conditions (2003–05), the sulfate concentration in water from Main and Eliza Springs is 27 mg/L; the Old Mill Spring base-flow concentration is 42 mg/L. The average sulfate concentration in historical samples collected from recharging streams ranged from 29 mg/L for station 08158920 Williamson Creek at Oak Hill to 75 mg/L for station 08155240 Barton Creek at Lost Creek Blvd., Austin (appendix 2). Sulfate concentrations for Main and Eliza Springs are strongly correlated with recharge and for Old Mill Spring to a lesser degree (table 5); thus, recharging water might contribute some sulfate to spring discharge. Water-rock interaction with calcite and minor amounts of gypsum in the aquifer rocks is another possible mechanism that could increase calcium and sulfate in spring discharge. Gypsum commonly is a trace mineral in carbonate rocks (Jacobson and Wasserburg, 2005); Garner (2005) suggests that ground water in Barton Springs might be reacting with gypsum.

Strontium concentration generally decreases linearly at all four spring orifices with increasing recharge (fig. 11), and reflects a range of values when there is no recharge (base-flow conditions). The range of strontium concentrations in water from each spring orifice under base-flow conditions might reflect variations in residence time and water-rock interaction in the aquifer, with longer residence times resulting in higher strontium concentrations; as water-rock interaction with carbonate rocks progresses, strontium will partition into the water phase (Banner, 1995).

Most of the statistically significant decreases in concentrations of other ions with an increase in recharge occur at Old Mill Spring, which is enriched in sodium, potassium, chloride, and sulfate relative to the other spring orifices. Thus when recharging water from streams, which has low concentrations of these four ions, mixes with water along the flow path leading to Old Mill Spring, the concentrations in the ground water are diluted (fig. 13; table 5).

Table 5. Statistical relations for major ions with recharge and spring discharge, Barton Springs, Austin, Texas (2003–05).

[ns, not significant based on α < p-value = .05; na, not applicable]

Constituent	Upper Spring		Main Spring		Eliza Spring		Old Mill Spring	
	r^2	Sign	r^2	Sign	r^2	Sign	r^2	Sign
Relations with recharge								
Calcium	.43	+	.60	+	.52	+	.23	+
Magnesium	ns	na	.38	-	.33	-	.44	-
Sodium	ns	na	ns	na	ns	na	.51	-
Potassium	ns	na	ns	na	ns	na	.25	-
Bicarbonate	ns	na	ns	na	ns	na	ns	na
Chloride	ns	na	ns	na	ns	na	.56	-
Sulfate	ns	na	.69	+	.68	+	.49	+
Strontium	.56	-	.48	-	.54	-	.62	-
Silica	ns	na	ns	na	ns	na	ns	na
Magnesium/calcium (molar)	.34	-	.79	-	.75	-	.65	-
Strontium/calcium (molar)	.69	-	.58	-	.59	-	.66	-
Relations with discharge								
Calcium	.24	+	.34	+	.28	+	.26	+
Magnesium	ns	na	ns	na	ns	na	ns	na
Sodium	.26	+	ns	na	ns	na	ns	na
Potassium	ns	na	.31	-	.42	-	ns	na
Bicarbonate	ns	na	ns	na	ns	na	ns	na
Chloride	ns	na	ns	na	ns	na	ns	na
Sulfate	.22	+	.19	+	ns	na	ns	na
Strontium	ns	na	.55	-	.56	-	.49	-
Silica	.30	+	ns	na	ns	na	ns	na
Magnesium/calcium (molar)	ns	na	.35	-	.23	-	.11	-
Strontium/calcium (molar)	ns	na	.59	-	.59	-	.58	-

Nutrients

During Phase 1, several forms of nitrogen and phosphorous were analyzed in samples collected from the four springs under base-flow conditions, allowing determination of concentrations of ammonia nitrogen, organic nitrogen, nitrite nitrogen, nitrate nitrogen, orthophosphate phosphorus (inorganic phosphorus), dissolved phosphorus, and particulate phosphorus (table 6, at end of report). Complete data are listed in appendix 4. At all four spring orifices, all of these compounds, except nitrate, either were not detected or were detected at concentrations less than the LRL of 0.015 mg/L and therefore identified as "estimated." Nitrite was detected in one sample only, at an estimated concentration of 0.005 mg/L; thus, all nitrite plus nitrate measurements in this study were assumed to have a negligible nitrite component and to be essentially a measure of nitrate (similar to Andrews and others [1984]). Because of the low detection rates of the nutrients analyzed except nitrate, during Phase 2 only nitrite plus nitrate was measured routinely, and the full suite of nutrients was measured quarterly.

Differences in Nitrate Concentrations Among Spring Orifices

Nitrate concentrations in samples from Main, Eliza, and Old Mill Springs were very similar (fig. 14). During Phase 1, nitrate concentrations in samples from these three springs were within 5 percent of one another, and during Phase 2, they were within 12 percent of one another.

The mean nitrate concentration during this study (2003–05) in samples from Upper Spring (2.05 mg/L) was 65 to 72 percent higher than those at the other spring orifices (1.24, 1.19, and 1.21 mg/L at Main, Eliza, and Old Mill Springs, respectively). For comparison, well BPS, a well in the Barton Springs segment that is assumed to be representative of background ground-water composition, has a mean nitrate concentration of 1.3 mg/L; this well, which is frequently sampled, has shown little geochemical variability during 26 years of measurement (Garner and Mahler, 2007). Nitrate concentrations at Upper Spring were more variable than those of the other spring orifices, with a C_V of 0.21 compared to C_V values of 0.15, 0.16, and 0.16 at Main, Eliza, and Old Mill Springs, respectively. The elevated nitrate concentration in Upper Spring relative to the three other spring orifices indicates that there might be an anthropogenic source, or sources, of nitrate to the part of the aquifer that contributes to Upper Spring, or that Upper Spring might receive more nitrate leached from the soil zone, or a combination of the two. Dye-tracing results and land-use studies show that the area that supplies recharge to Upper Spring is largely urbanized (Bio-West, 2002; Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004).

Temporal Variability in Nitrate Concentrations and Relation to Recharge and Discharge

Nitrate concentrations in Main, Eliza, and Old Mill Springs are related to recharge conditions. The maximum nitrate concentration in samples from these three spring orifices was 1.5 mg/L, which was attained during periods with little recharge (fig. 15; for example, during Phase 1). Samples collected from major recharging streams following two storms during the study period had a median nitrate concentration of 0.39 mg/L. This indicates that recharge from streams is diluting concentrations of nitrate in ground water. In general, as the rate of recharge decreases over the months following a large storm, nitrate concentrations in spring water increase, approaching a maximum value of 1.5 mg/L (figs. 15, 16). Historical data for nitrate in samples from Main Spring (appendixes 1, 2) are consistent with this hypothesis: Since 1984, a concentration of 1.5 mg/L has been exceeded in only one of 55 samples (1.6 mg/L in a sample collected on Aug. 10, 1994), but a concentration of 1.5 mg/L has been measured in 12 of 55 samples (22 percent). Although some samples collected before 1984 had nitrate concentrations that exceeded 1.5 mg/L, these samples were not filtered before analysis, so the concentration includes nitrate associated with particulates.

The average difference between the nitrate concentrations in samples from Main, Old Mill, and Eliza Springs collected on the same day (2003–05) increases as recharge increases (p-value = .005, $r^2 = .3$), indicating different degrees of dilution by recharge water. This is additional evidence that these three springs receive their water from different flow paths (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004) and indicates that the entire aquifer has a fixed baseline nitrate concentration of about 1.5 mg/L, which is diluted to different degrees along the different flow paths. These findings are consistent with recent data (Garner and Mahler, 2007), which show that nitrate concentrations greater than 1.5 mg/L in samples from wells in the Barton Springs segment occur only in isolated instances. Other wells that yielded samples with lower nitrate concentrations were hypothesized to intersect major flow paths, resulting in dilution of baseline nitrate concentration. This baseline nitrate concentration might result from the long-term leaching of nitrate from soils into the matrix porosity of the aquifer.

At Upper Spring, nitrate concentrations varied around a mean of 2.10 mg/L, rather than approaching a maximum that was not exceeded, and did not have a significant relation with total recharge or the recharge from individual streams. The elevated nitrate concentrations for Upper Spring relative to the other spring orifices, and the lack of relation to recharge, indicate that the dynamics controlling nitrate concentrations at Upper Spring are different from the dynamics controlling nitrate concentrations at the three other spring orifices. As noted in the previous section, the elevated nitrate concentration at Upper Spring relative to the concentrations at the three other spring orifices might indicate the presence of an additional anthropogenic source of nitrate.

Trace Elements

During Phase 1, dissolved trace metals (cadmium, chromium, copper, lead, nickel, zinc, and the metalloid arsenic) were analyzed in samples from all four spring orifices. Cadmium was not detected in any sample (LRL of 0.037 µg/L); chromium was detected in three samples (15 percent), lead in two samples (10 percent), and zinc in 10 samples (50 percent) of the 20 samples analyzed; copper, nickel, and arsenic were detected in every sample (table 7, at end of report).

Copper, nickel, and arsenic were detected at very low concentrations in every sample. The mean arsenic concentration for all sites combined was 0.45 µg/L; the USEPA MCL for arsenic is 10 µg/L. The mean arsenic concentrations at Old Mill and Upper Springs were substantially higher than those at Eliza and Main Springs, possibly a result of natural geochemical variations in the host rock or overlying soils. The mean copper concentration was 0.59 µg/L, which is about 1,000 times less than the USEPA action level (the level that might trigger requirements for monitoring, treatment, and education) of 1.3 mg/L. The mean nickel concentration was 1.7 µg/L; there is no MCL or action level for nickel. The lowest nickel concentrations were measured in samples collected at all four spring orifices on September 16, 2003, following a period of rain. This characteristic for nickel concentrations indicates a natural geologic source that is diluted by recharging surface water following rain and infiltration of runoff. There were no notable differences among sites for either copper or nickel.

Chromium, lead, and zinc were detected infrequently and at very low concentrations. Chromium was detected in one sample each from Upper, Eliza, and Old Mill Springs. All three chromium detections were in samples collected on September 16, 2003, following a period of rain. This might indicate an anthropogenic source for chromium, which could be entering the aquifer with recharging stormwater. Chromium concentrations were very low: The detections were flagged as "estimated" and the concentrations were about one-half the NWQL LRL of 0.8 µg/L. Lead was detected in two samples, one from Upper Spring and one from Eliza Spring, collected on different

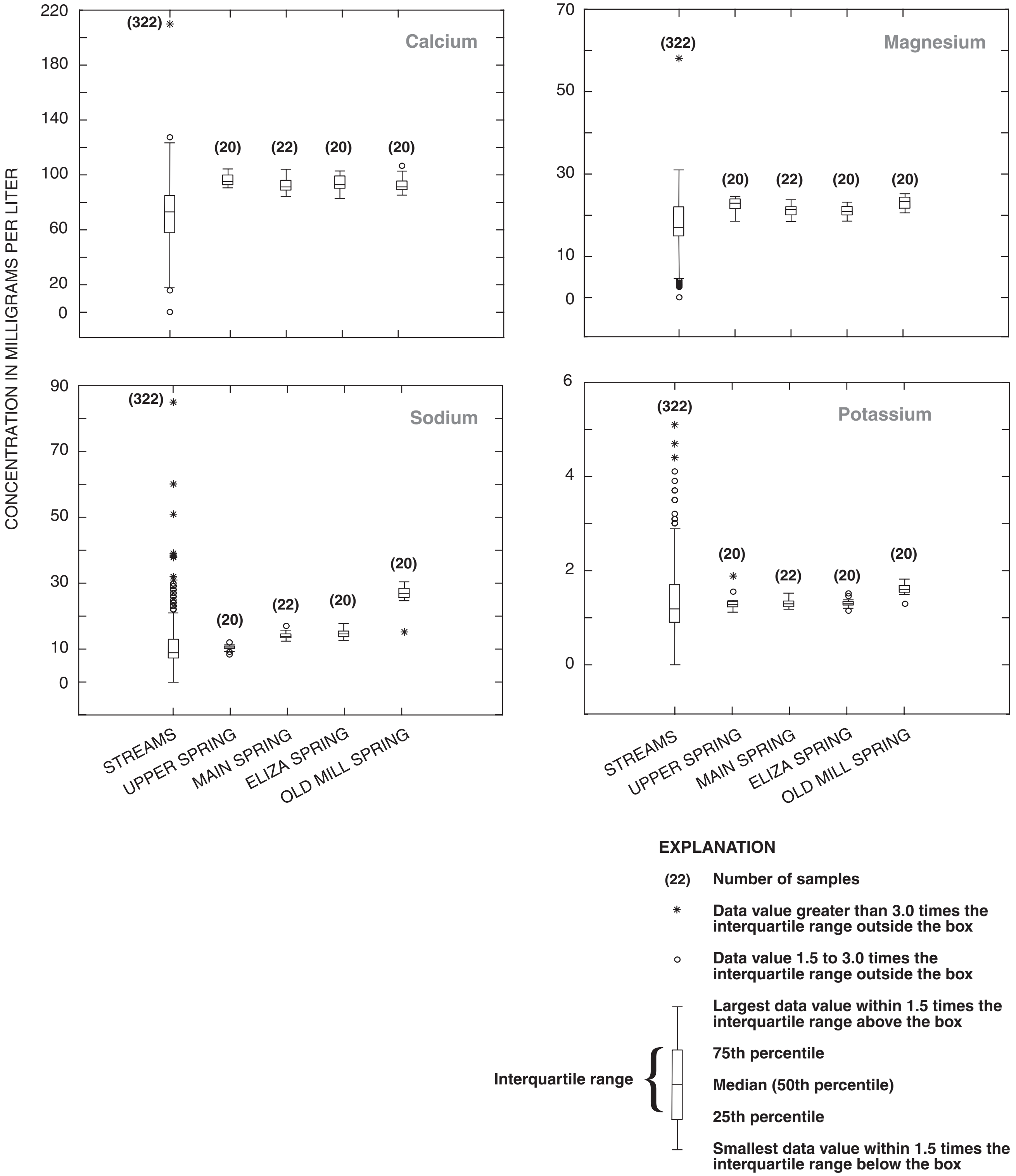


Figure 13. Distribution of major ions in historical samples from streams at the upstream boundary of the recharge zone of the Barton Springs segment of the Edwards aquifer and in samples (2003–05) from the four spring orifices of Barton Springs, Austin, Texas.

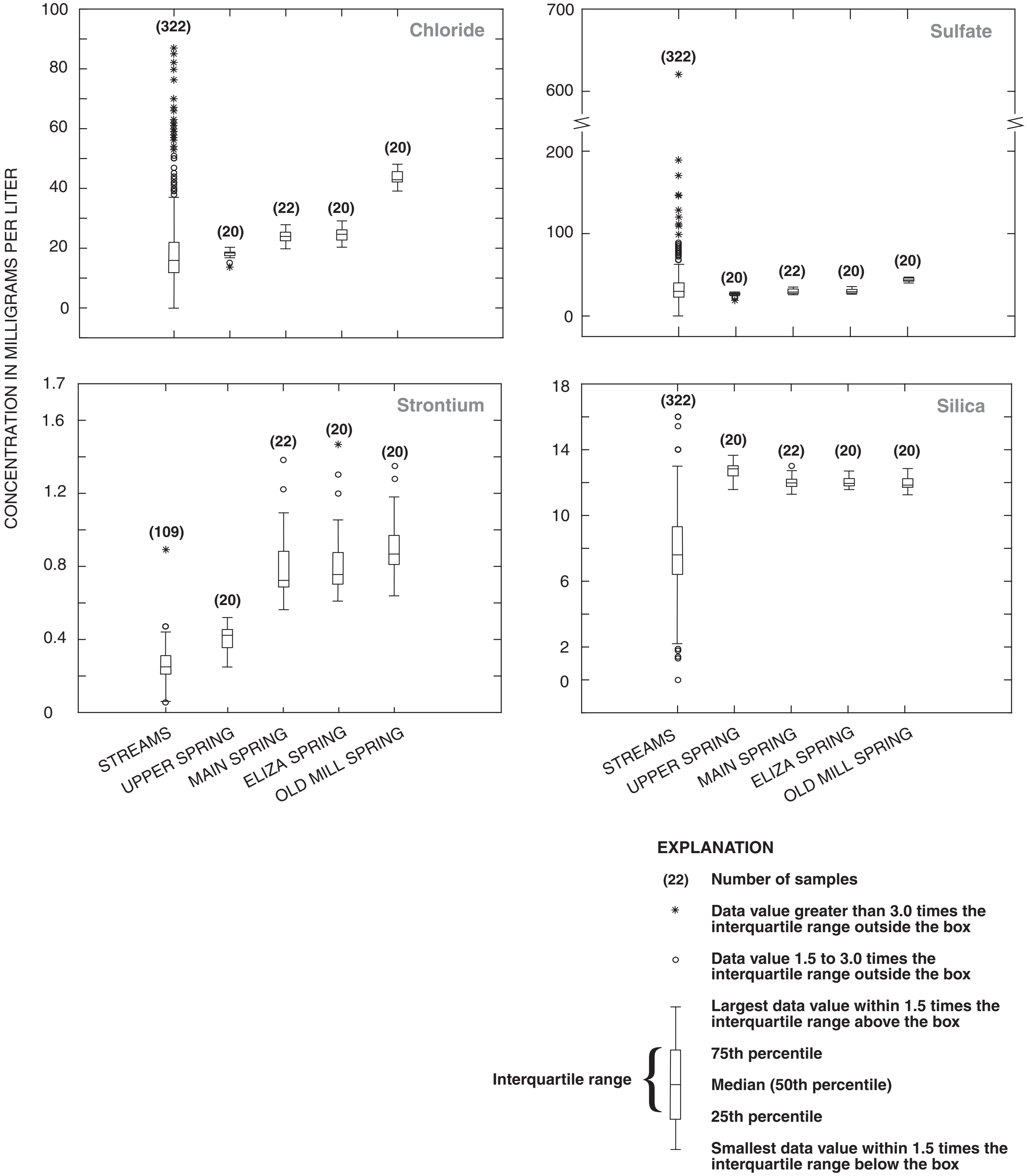


Figure 13. Continued.

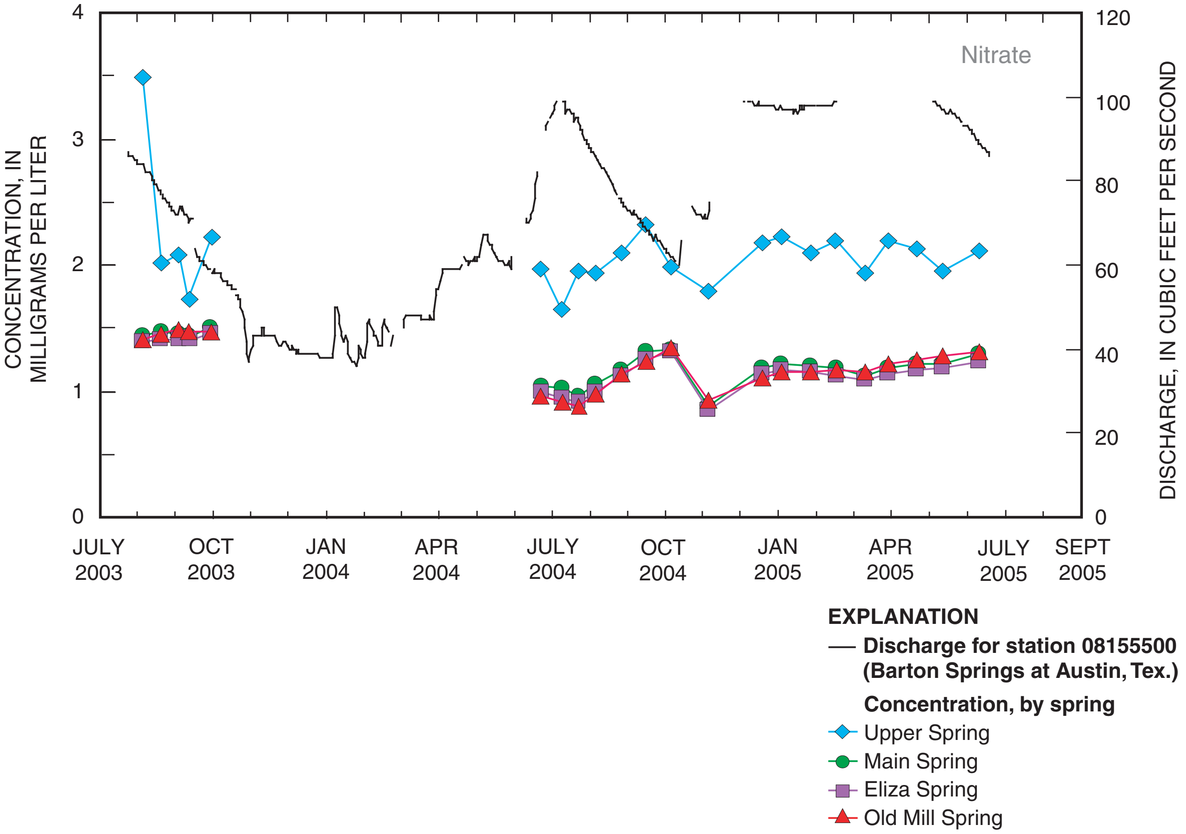


Figure 14. Time series of nitrate nitrogen concentrations in samples from the four spring orifices of Barton Springs, Austin, Texas, and discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.) during routine sampling (2003–05).

dates. The maximum lead concentration detected (0.11 µg/L) is about 150 times less than the USEPA action level of 15 µg/L. Zinc was detected in two to three of the five samples collected from each spring orifice. In about one-half of the cases the zinc concentration was less than the LRL of 1.0 µg/L and was flagged as "estimated." The maximum concentration (2.0 µg/L) was detected in a sample from Eliza Spring on September 16, 2003. There is no MCL or action level for zinc. Because trace elements either were not detected or were detected at very low concentrations in samples from all four springs, they were not analyzed during Phase 2. The results of the Phase 1 sampling, however, do indicate that chromium and zinc concentrations might increase following recharge events.

Soluble Pesticides

Routine samples collected from the four springs during Phases 1 and 2 (quarterly samples only for Eliza and Old Mill Springs during Phase 2; table 2) were analyzed for a suite of 52 soluble pesticides (appendix 4). Four herbicide compounds were detected: atrazine, the atrazine degradate DEA, prometon, and simazine (table 8, at end of report). No insecticides or fungicides were detected during the routine sampling.

Detection Frequencies and Concentrations

Atrazine and DEA were the most frequently detected pesticides at all four spring orifices (fig. 17). DEA was detected in 53 of 60 samples analyzed (88 percent), and atrazine was detected in 51 of 60 samples analyzed (85 percent). The highest atrazine concentration detected was about 0.08 µg/L in a sample from Upper Spring, about 40 times less than the USEPA MCL of 3.0 µg/L. The atrazine/DEA ratio in samples ranged from 0.37 to 5.0; because atrazine degrades to DEA in soils, a high atrazine/DEA ratio (10 or greater) is an indicator of recently applied atrazine (M.T. Meyer, U.S. Geological Survey, oral commun., 2005).

Simazine was detected in 19 of 60 samples (32 percent), and prometon was detected in 13 of 60 samples (22 percent). The highest simazine concentration detected was 0.016 µg/L in a sample from Upper Spring. All detections of prometon excluding one were in samples from Upper Spring; all prometon detections were at concentrations below the LRL and were reported as estimated.

Differences in Pesticide Concentrations Among Spring Orifices

Pesticides concentrations at Main, Eliza, and Old Mill Springs during routine sampling were very similar (fig. 18).

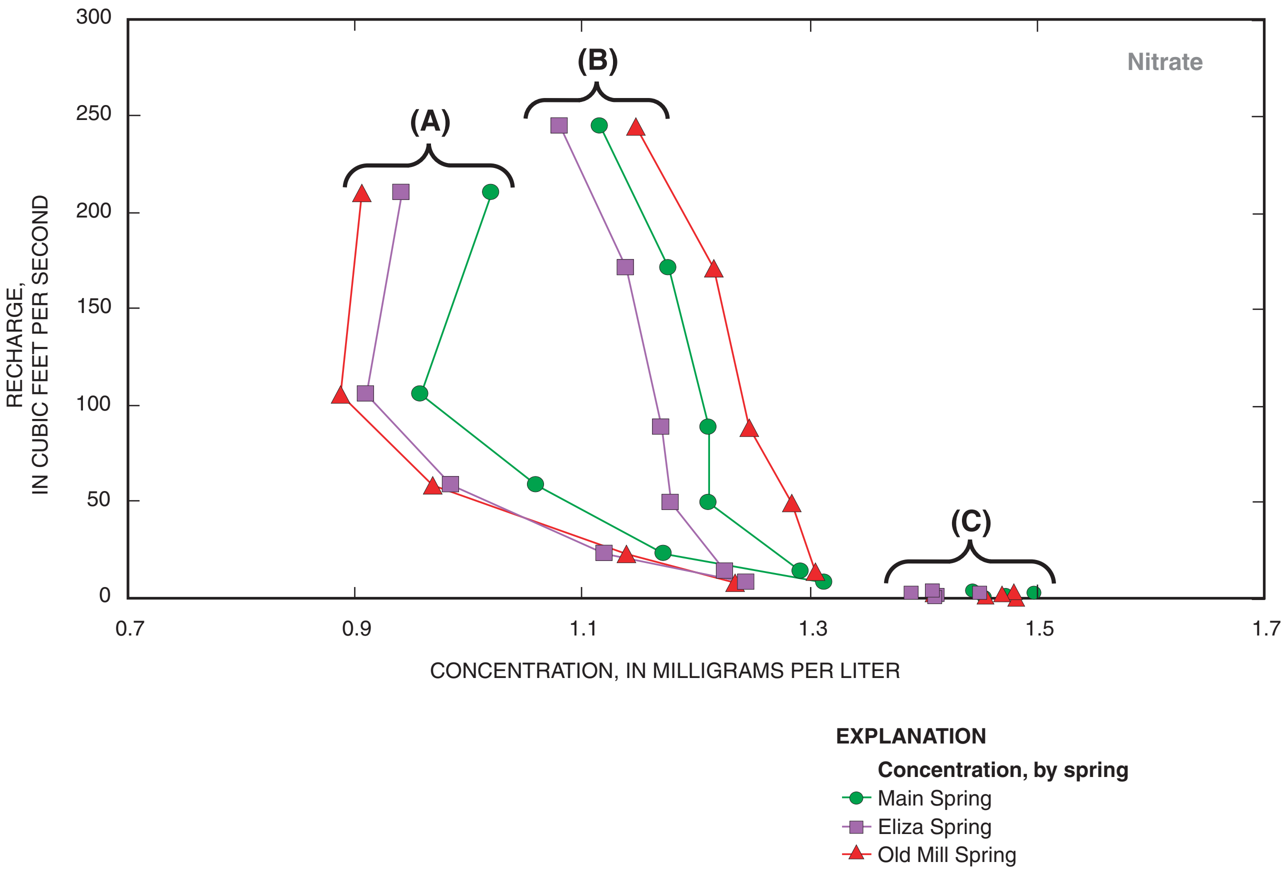


Figure 15. Relation between nitrate nitrogen concentrations in samples from three of the four spring orifices of Barton Springs, Austin, Texas (Main, Eliza, and Old Mill Springs) and recharge (daily mean) during two periods of recharge (A and B) and one period of no recharge (C).

Concentrations at these sites during Phase 1 were all either below the LRL or not detected. Because of the similarity of compounds and concentrations detected, samples from Old Mill and Eliza Springs were analyzed during Phase 2 on a quarterly basis. The concentrations in the quarterly samples collected during Phase 2 also were similar, with the exception of the sample collected on March 9, 2005, for which Old Mill Spring had an atrazine concentration about two-thirds those of Eliza and Main Springs. The similarity of compounds and concentrations detected indicates that Main, Eliza, and Old Mill Springs receive flow from the same sources under non-storm conditions, which might reflect a shared flow path or contribution from a baseline concentration in the aquifer matrix. Old Mill Spring, however, might receive additional water from a less-contaminated source when recharge occurs, resulting in lower concentrations than those detected at Main and Eliza Springs.

Pesticides were detected more frequently in Upper Spring than at the three other spring orifices, and in most cases at higher concentrations. In particular, atrazine and DEA were detected in every sample from Upper Spring, and at higher concentrations than in samples from the three other springs; the atrazine concentration measured in a sample collected from Upper Spring was on average 2.5 times higher than the concentration measured in a sample collected from Main Spring on the same day. In most cases, simazine concentrations measured in samples from Upper Spring were higher than those collected from the other springs on the same day, and, with the exception of one sample, prometon was detected only in Upper Spring. The atrazine/DEA ratio at Upper Spring was consistently similar to or less than those at the other spring orifices (fig. 19). The median atrazine/DEA ratio was lowest in Upper Spring (0.82) and highest in Main and Eliza Springs (1.44 and 1.48, respectively). A lower atrazine/DEA ratio at Upper Spring indicates that the atrazine discharging from this orifice has had a longer residence time in the soil zone than atrazine from the three other spring orifices; correspondingly, atrazine discharging from Main and Eliza Springs has had the shortest residence time in the soil zone (Kolpin and others, 2004).

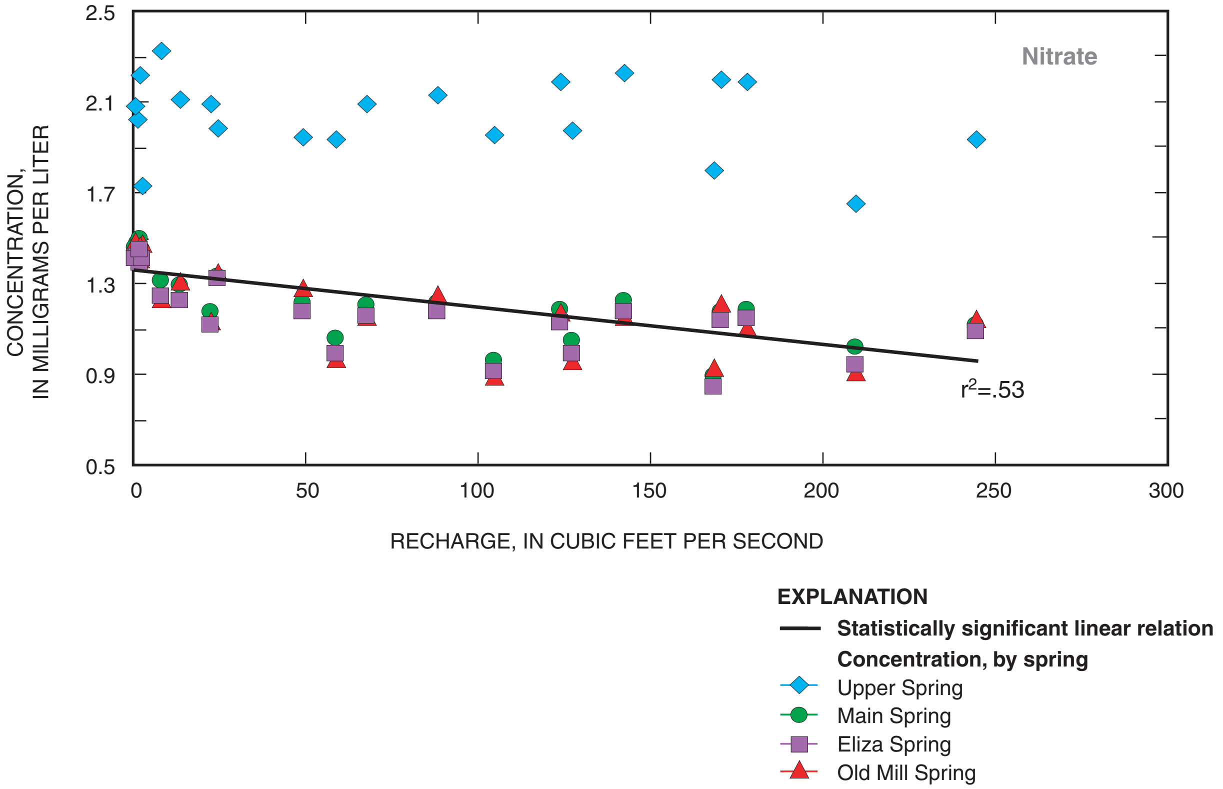


Figure 16. Relation between nitrate nitrogen concentrations in samples from the four spring orifices of Barton Springs, Austin, Texas, and recharge (daily mean) during routine sampling (2003–05).

Temporal Variability in Pesticide Concentrations and Relation to Recharge and Discharge

The relations among concentrations of pesticides—atrazine, prometon, simazine, and atrazine/DEA from Upper and Main Springs—and recharge and discharge were analyzed statistically. Because the data contained censored results (nondetections), they were analyzed using a parametric survival analysis method (StatSoft, Inc., 2004), which efficiently uses the information available in multiply-censored data as part of the analysis (Helsel, 2005). Using the survival analysis method, linear regression was applied to the logarithms of the multiply-censored data; a statistically significant relation was identified as one for which p-values are < .05. The strength of the relation is reported as the likelihood-r^2, analogous to the coefficient of determination (r^2) in linear regression. As with r^2, the likelihood-r^2 varies from 0 to 1, with a value close to 1 indicating that there is a high likelihood of producing the observed pattern when the relation between variables is taken into consideration (Helsel, 2005).

There was a significantly positive but weak relation ($r^2 = .22$) between atrazine and recharge at Upper Spring and a significantly positive but weak relation between simazine and recharge at Main Spring ($r^2 = .29$). These weak relations indicate that recharge might affect concentrations of these pesticides in these spring orifices but that most of the variability is attributable to other processes; the relation is sufficiently weak to indicate that recharge is not a good predictor of the concentrations. The lack of a strong relation between recharge and concentration of any pesticide likely is because concentrations of pesticides in runoff are temporally variable; in particular, they might be highest in the initial runoff following a storm. Temporal variations in pesticide concentrations in recharge, however, have not been investigated in the major recharging streams of the Barton Springs segment. Although pesticide concentrations in Upper and Main Springs varied over time, there were no statistically significant relations between spring discharge and pesticide concentrations or atrazine/DEA ratios.

Volatile Organic Compounds

Routine samples collected from the four springs during Phases 1 and 2 (quarterly samples only for Eliza and Old Mill Springs during Phase 2; table 2) were analyzed for a suite of 85 VOCs (appendix 4). Nine VOCs (table 9, at end of report) were detected in one or more samples: two drinking-water disinfection by-products (chloroform and bromodichloromethane), one gasoline compound (toluene), four solvents

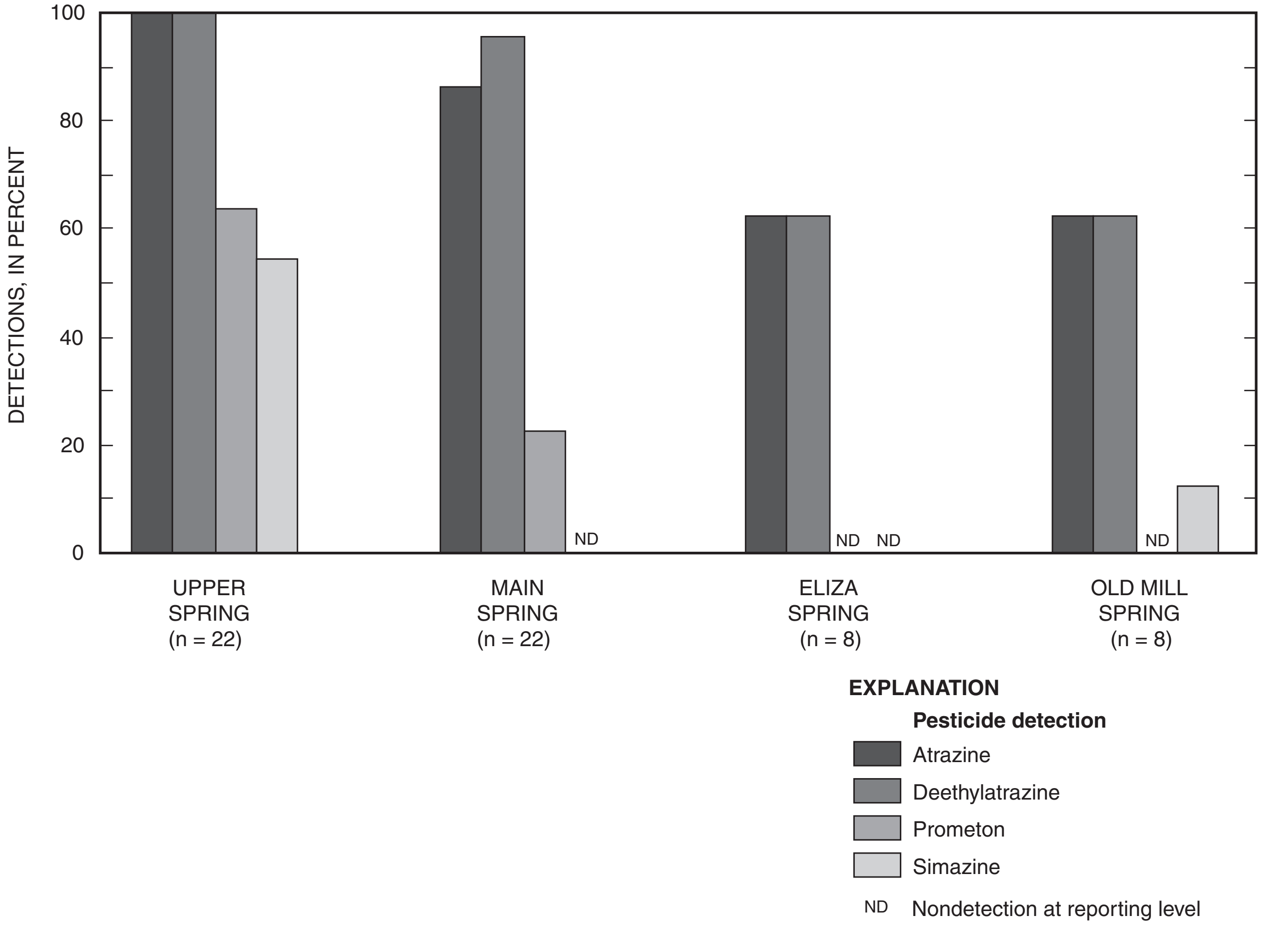


Figure 17. Percentage of detections of four selected pesticides in samples from the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05).

(1,1,1-trichloroethane, *cis*-1,2-dichloroethene, tetrachloroethene, and trichloroethene), and two other industrial VOCs (carbon disulfide and 1,1,2-trichloro-1,2,2-trifluoroethane [Freon 113]).

Detection Frequencies and Concentrations

Chloroform and tetrachloroethene were detected in all routine samples collected from the four spring orifices (figs. 20, 21). Chloroform concentrations ranged from 0.024 to 0.15 µg/L with a mean concentration of 0.059 µg/L. Tetrachloroethene concentrations ranged from 0.017 to 0.34 µg/L with a mean concentration of 0.062 µg/L (fig. 20).

Other VOCs were detected much less frequently than chloroform and tetrachloroethene (fig. 21) but were detected relatively frequently at specific springs. Bromodichloromethane was detected in 11 of 22 samples (50 percent) from Upper Spring. Carbon disulfide was detected in three of eight samples (38 percent) from Old Mill Spring. Trichloroethene, a solvent and a degradate of tetrachloroethene, was detected in eight of 22 samples (36 percent) from Main Spring.

Differences in Volatile Organic Compound Concentrations and Detection Frequencies Among Spring Orifices

Patterns of VOC contamination were different among the four spring orifices. A similar number of VOCs was detected per sample from the four orifices (mean number of detections per sample of 2.5 [Main Spring] to 2.9 [Old Mill and Eliza Springs]), but the concentrations and compounds detected differed. In general, both tetrachloroethene and chloroform concentrations were similar at Main, Eliza, and Old Mill Springs, whereas tetrachloroethene concentrations were lower and chloroform concentrations were higher at Upper Spring. However, the tetrachloroethene concentrations at all four orifices were similar when little or no recharge was occurring (Phase 1), from about 0.04 to 0.06 µg/L. Chloroform concentrations at Upper Spring were always higher than at the three other spring orifices and were highest during Phase 1, when there was little recharge. Bromodichloromethane was detected only at Upper Spring, in all cases at very low concentrations (reported as estimated). The relatively frequent detection of bromodichloromethane and the elevated chloroform concentrations at Upper Spring relative to

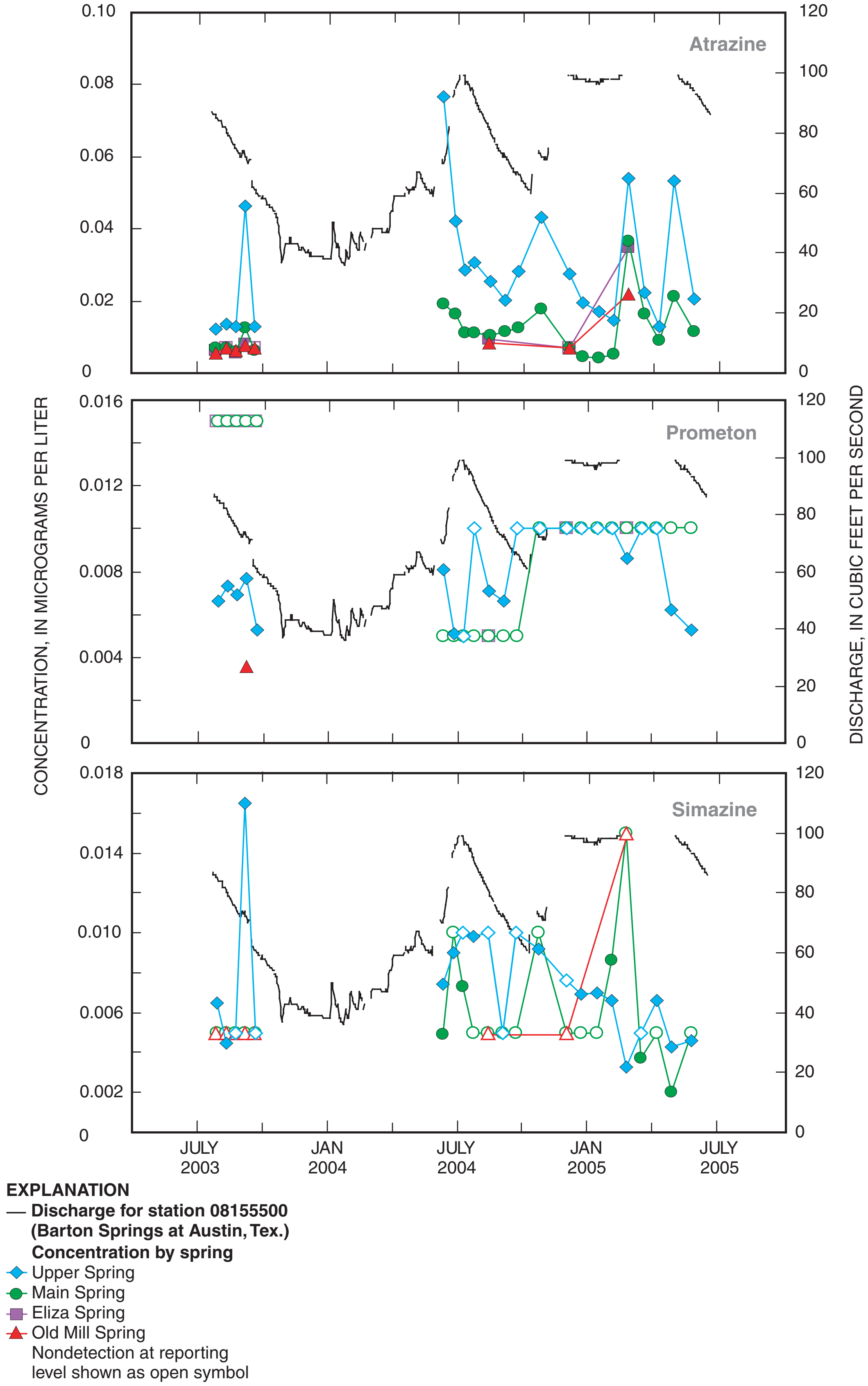


Figure 18. Time series of selected pesticide concentrations in samples from the four spring orifices of Barton Springs, Austin, Texas, and discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.) during routine sampling (2003–05).

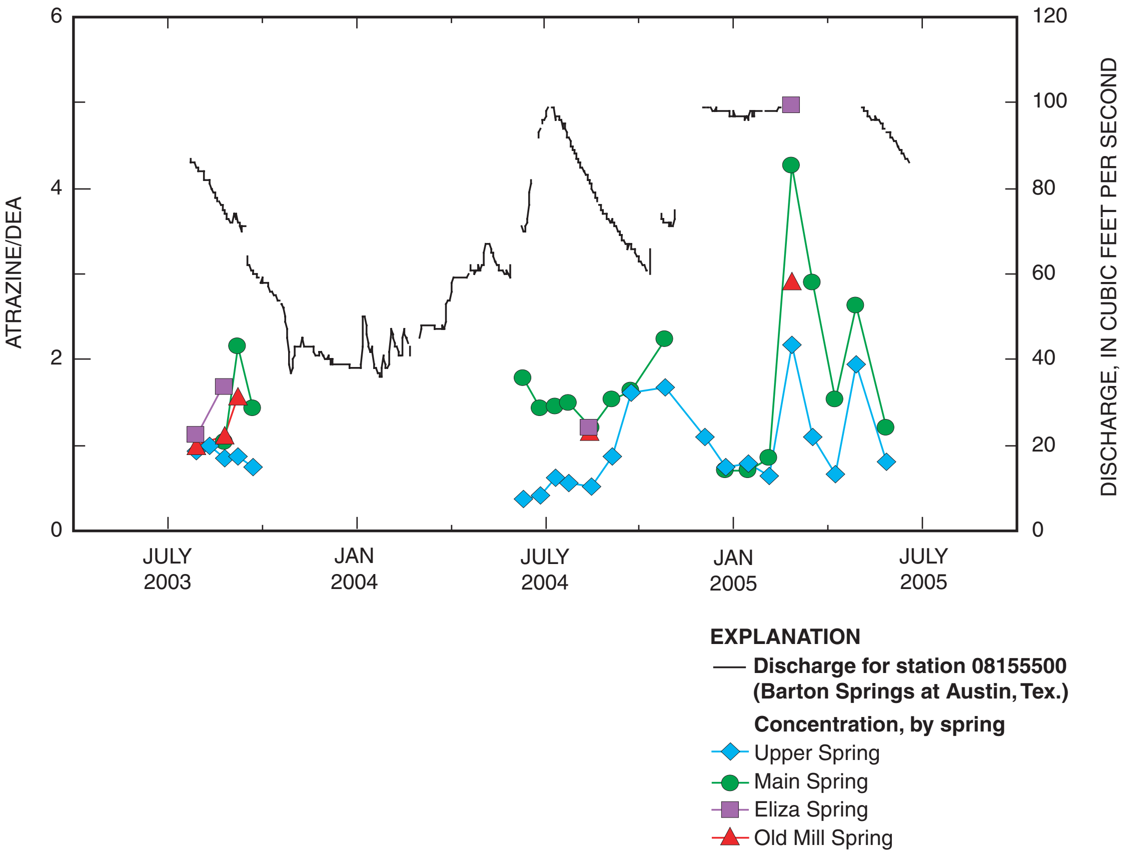


Figure 19. Time series of atrazine/deethylatrazine (DEA) ratios in samples from the four spring orifices of Barton Springs, Austin, Texas, and discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.) during routine sampling (2003–05).

those at the other spring orifices indicate that Upper Spring is particularly vulnerable to contamination from drinking-water disinfection by-products. Trichloroethene was detected at Main, Eliza, and Old Mill Springs but not at Upper Spring. When trichloroethene was detected, its concentration was strongly correlated to that of tetrachloroethene in the same sample ($r^2 = .85$), indicating that the trichloroethene source, or sources, at these three spring orifices are likely the breakdown of tetrachloroethene rather than an independent source.

Temporal Variability in Volatile Organic Compound Concentrations and Relation to Recharge and Discharge

Relations among chloroform and tetrachloroethene concentrations in Upper and Main Springs and recharge and discharge provide an indication of source. No significant relation to Barton Springs discharge was observed for chloroform or tetrachloroethene concentration at either site. Tetrachloroethene concentration was positively correlated with recharge at Main Spring and negatively correlated with recharge at Upper Spring (fig. 22), which indicates that recharge flowing to Main Spring contains tetrachloroethene but recharge flowing to Upper Spring does not. Tetrachloroethene concentrations at Main and Eliza Springs were very similar in all samples (fig. 20). Concentrations at Old Mill Spring were similar to those at Main and Eliza Springs when concentrations were low (little recharge). However, with increasing amounts of recharge, tetrachloroethene concentrations in Main, Eliza, and Old Mill Springs increased, but concentrations in Old Mill Spring increased to a lesser degree. This indicates that all three springs receive water from a flow path containing tetrachloroethene, but that Old Mill Spring also receives water from a less-contaminated or uncontaminated flow path when recharge is occurring. It is unlikely that the source of the tetrachloroethene is surface water because of the volatility of tetrachloroethene. If, however, tetrachloroethene is perched somewhere in the unsaturated zone, it might be dissolving into recharging surface water as the water passes through a zone containing tetrachloroethene, resulting in concentrations at the springs that are correlated with recharge.

Chloroform in samples from Upper Spring have a significant negative correlation with recharge, but only for recharge of less than about 25 ft^3/s (fig. 22): Chloroform concentration decreases as recharge increases to about 25 ft^3/s, then stabilizes at a concentration of about 0.09 µg/L for recharge greater than 25 ft^3/s. It is not known why the relation with recharge is limited to recharge less than about 25 ft^3/s, a condition that does not occur for tetrachloroethene at this spring.

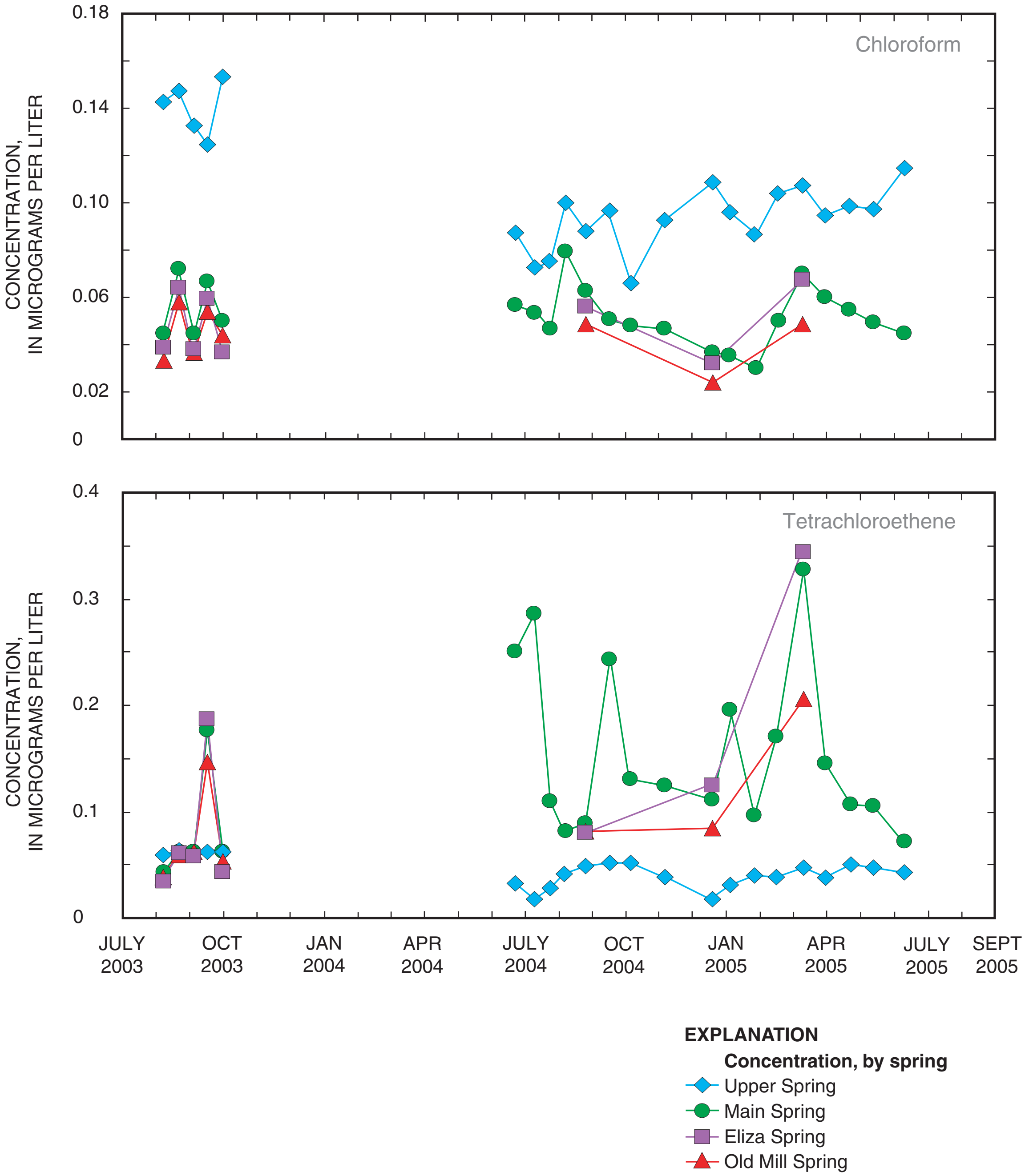


Figure 20. Time series of the drinking-water disinfection by-product chloroform and the solvent tetrachloroethene in the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05).

Comparison of Pesticide and Volatile Organic Compound Concentrations in Spring Waters and Ground Waters

A comparison of pesticide data for the springs (table 8) with historical data for ground-water wells (appendixes 1, 2) reveals many similarities. Atrazine in ground-water wells has been detected at concentrations of 0.01 to 0.02 µg/L (wells SVE, SVN, SVS; appendixes 1, 2), which is similar to the range of atrazine concentrations detected at Main Spring. Atrazine concentrations at Upper Spring are slightly higher, as much as about 0.08 µg/L. DEA is detected in many of the same locations that atrazine is detected and also is detected at concentrations similar to those of DEA in the springs, with detections in several wells of about 0.01 µg/L. Both atrazine and DEA concentrations, however, are higher in one ground-water well

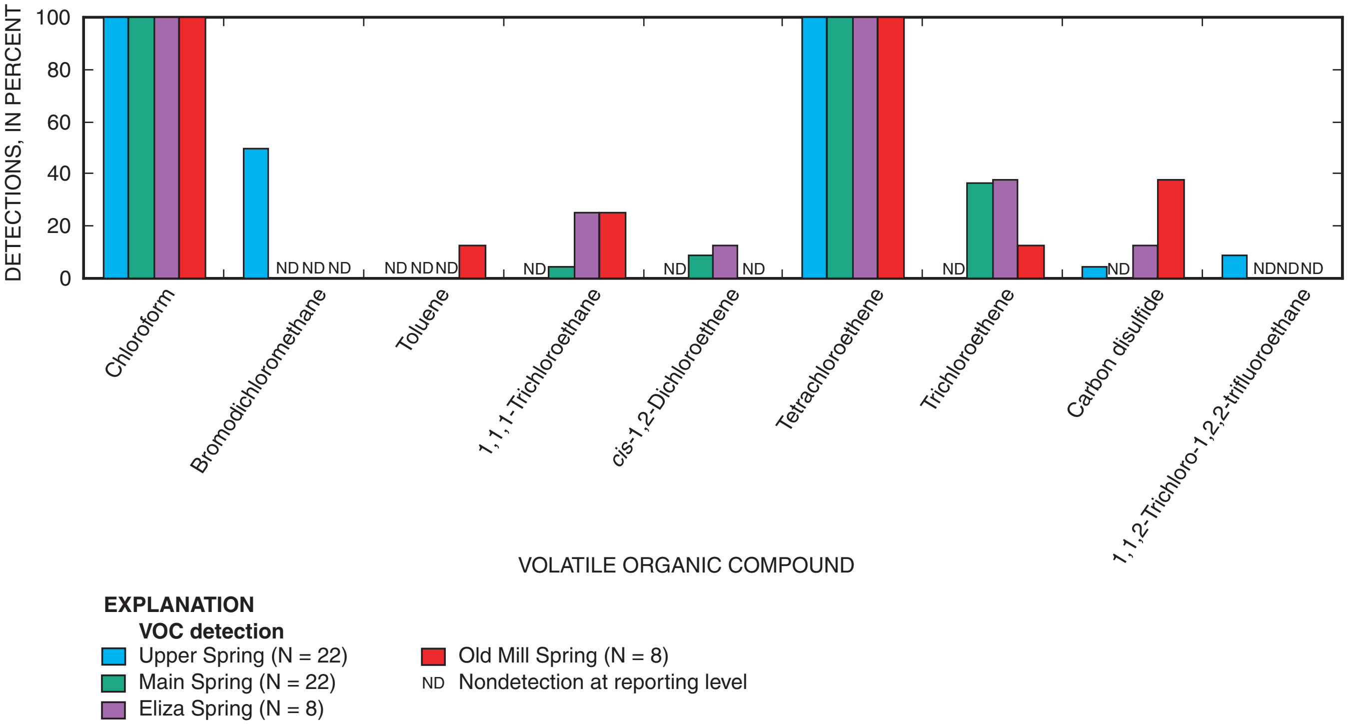


Figure 21. Percentage of detections of nine selected volatile organic compounds (VOCs) in samples from the four spring orifices of Barton Springs, Austin, Texas, during routine sampling (2003–05).

(well SVW), with concentrations as much as 0.06 µg/L for both compounds. Prometon, with all but one detection at Upper Spring, also has been detected in wells SVS and SVW at similar concentrations (about 0.01 µg/L).

Similar to the comparison of pesticide data, a comparison of VOC data for the springs (table 9) with historical ground-water well data (appendixes 1, 2) also reveals similarities. Chloroform concentrations in Main Spring ranged from about 0.04 to 0.07 µg/L, regardless of recharge. These concentrations are similar to, or slightly higher than, those measured in ground-water samples from wells SVE and SVN (appendixes 1, 2). Chloroform concentrations at Upper Spring (0.13 to 0.15 µg/L when little to no recharge was occurring) were higher than at Main Spring. Upper Spring chloroform concentrations are more similar to those in well SVW, which range from 0.17 to 0.41 µg/L in samples collected since 1998 (appendix 2.5). Freon 113 was detected in all samples from well SVS collected during 2001–05 and in two samples from Upper Spring, but in no other wells or springs. The occurrence of chloroform and Freon 113 in wells SVW and SVS, respectively, and at Upper Spring might indicate the existence of a flow path between the wells and the spring. The existence of a flow path between well SVW and Upper Spring is consistent with dye-tracing results by Hauwert, Johns, and others (2004) and Hauwert, Samson, and others (2004).

Pesticide and VOC concentrations are generally similar at springs and in historic ground-water well data. This generalization, however, is tempered by measurements of higher concentrations in some ground-water wells (such as SVS and SVW) (appendixes 1, 2), which indicate that pesticide and VOC contaminants are not uniformly distributed in the aquifer, but that localized regions with relatively greater contamination exist. Hydrologic connections, or flow paths, between areas of higher contaminant concentration and the springs might allow for enhanced transport of pesticide and VOC contaminants to the springs.

Pharmaceuticals

Three pharmaceutical compounds were detected at least twice in seven samples collected from Upper and Main Springs during Phase 2 (appendix 4). Cotinine (a nicotine metabolite) was detected at both springs on March 9, 2005. Acetaminophen and caffeine were detected twice at Main Spring and once at Upper Spring. The maximum concentration of each of these compounds was about 0.1 and 0.05 µg/L, respectively. Fifteen pharmaceutical compounds were detected in one sample from Main Spring on March 9, 2005—about 7 times the number of detections in any other sample. Cotinine, acetaminophen, and

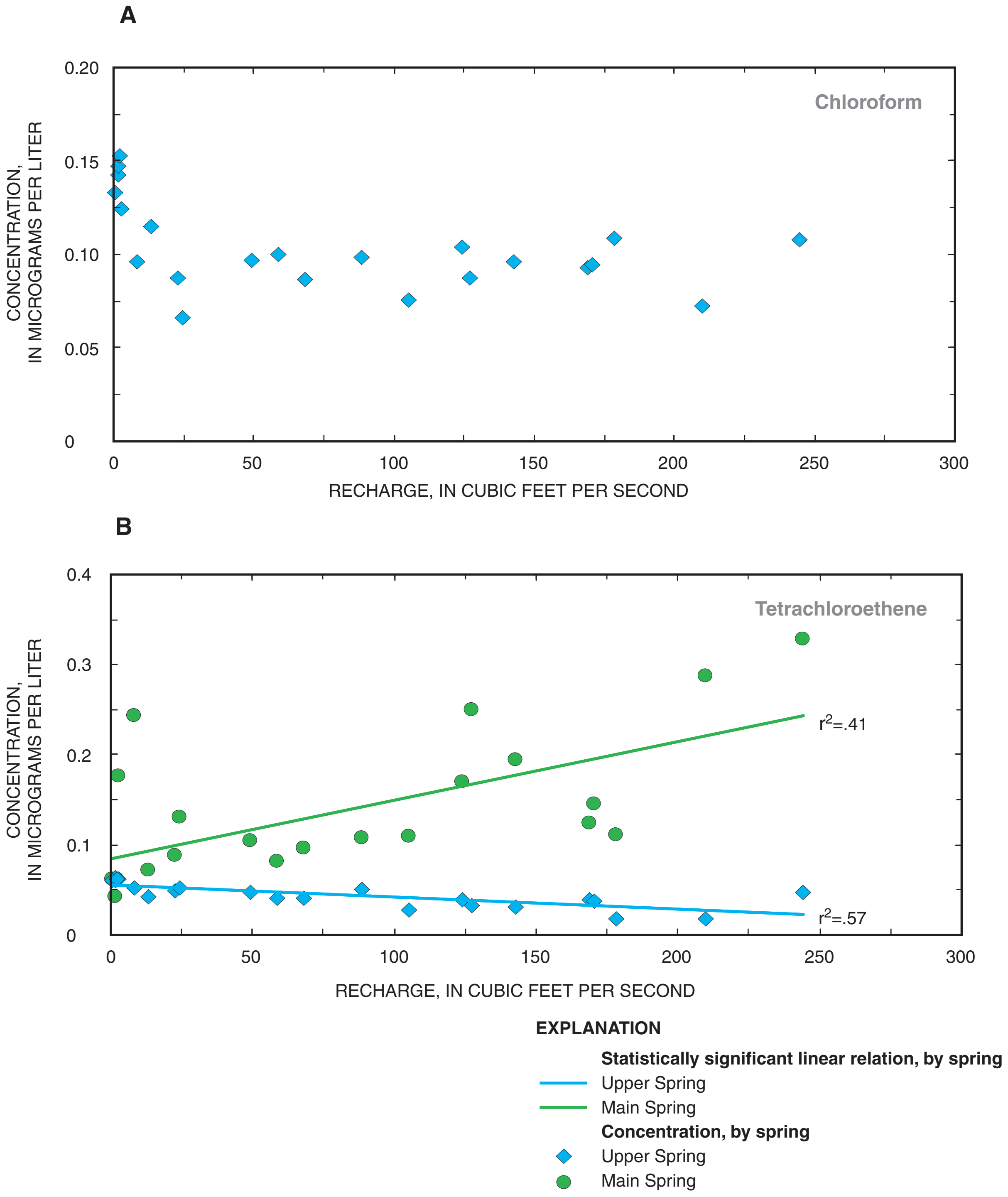


Figure 22. Relation during routine sampling between recharge (daily mean) and (A) chloroform concentration in samples from Upper Spring, Austin, Texas, and (B) tetrachloroethene concentration in samples from two of the four spring orifices of Barton Springs, Austin, Texas (Main and Upper Springs) (2003–05).

caffeine were detected, as well as cimetidine, ranitidine, trimethoprim, diltiazem, fluoxetine, warfarin, sulfamethoxazole, dehydronifedipine, thiabendazole, diphenhydramine, erythromycin, and miconazole. Concentrations ranged from 0.005 µg/L for caffeine, cimetidine, and sulfamethoxazole to 0.122 µg/L for acetaminophen. It is unknown why so many compounds were detected in this single sample; hydrologic conditions on this date were not unusual.

Annual Loads of Ubiquitous Contaminants

Assessment of contaminant loads (mass of contaminant per unit time) provides valuable information for water-resource management. A comparison of contaminant loads during non-storm and storm conditions is useful in assessing the potential effect or importance of contaminants, or both, on the hydrologic system. Total annual loads of the most ubiquitous contaminants (atrazine, chloroform, and tetrachloroethene) estimated to discharge from Main, Eliza, and Old Mill Springs under non-storm conditions were computed using routine sample concentrations from Main Spring and daily spring discharge (concentrations in Eliza and Old Mill Springs were assumed to be the same as in Main Spring). Loads were computed as the product of the concentration in a sample and the discharge volume corresponding to the sample. Discharge volume was computed as the sum of daily discharge volumes from the midpoints in time between preceding and following sampling events. The total annual load estimated to discharge during routine sampling conditions (based on the June 2004–June 2005 sampling period) is 1.1 kilograms (kg) of atrazine, 4.2 kg of chloroform, and 12 kg of tetrachloroethene.

Response of Barton Springs to Stormflow

To investigate the effect of an influx of recent runoff (that is, recharge from storms) on water quality at the four spring orifices, spring-water samples were collected for 2 weeks following two storms (October 2004 [Storm 1] and May 2005 [Storm 2]) on a variable time interval (several hours to days). The sampling objective was to determine how concentrations of different chemical constituents vary in response to a storm-generated recharge influx and to quantify the timing and magnitude of the response. Samples from the four spring orifices were analyzed for major ions (appendix 5) and selected nutrients (tables 10, 11, at end of report). Samples from Upper and Main Springs were analyzed for pesticides (tables 12, 13, at end of report) and VOCs (tables 14, 15, at end of report). For Storm 2, samples from Main Spring also were analyzed for a suite of nutrients and pharmaceutical compounds. In addition, results for a single sample collected on November 24, 2004, are discussed. Although this sample was collected as part of the routine sampling during November 13–23, 2004, 12.4 in. of rain occurred in the study area, much of which (5.2 in.) fell on November 22. This sample therefore represents extreme stormflow conditions (table 16, at end of report), and the results are compared here to those for Storms 1 and 2.

Flow-weighted composite samples were collected from recharging streams (Barton, Onion, Slaughter, Bear, and Williamson Creeks) at the downstream end of the recharge zone and analyzed for pesticides. The concentrations in the surface water were used in conjunction with streamflow to estimate the load of pesticides entering the aquifer with recharge. VOCs were not sampled in surface water, as it was assumed that because of their volatility, streamflow is not an important transport mechanism. Rainfall was computed as the areally weighted average on the basis of rainfall recorded at as many as 10 rain gages in the watersheds of the recharging streams.

Storms 1 and 2 were similar in some respects and different in others. The storms represent contrasting initial flow conditions—about average for Storm 1 (though above the median flow), and high for Storm 2 (table 17, at end of report). Both storms were preceded by 4 weeks or longer with no rainfall exceeding 0.1 in., and there was generally little to no flow in the recharging streams prior to the storms. Although total rainfall for each of the two storms was roughly the same magnitude (3.0 in. for Storm 1 and 2.1 in. for Storm 2), temporal rainfall distributions were different (fig. 23). The single sample collected on November 24, 2004, as part of routine sampling, followed an extremely wet period: the rainfall of 16.8 in. during the previous month represents about one-half the annual average for the Austin area.

Concentrations of several natural and anthropogenic constituents in spring discharge changed rapidly in response to Storms 1 and 2, in some cases describing breakthrough curves and in other cases describing “anti”-breakthrough curves (demonstrating constituent dilution by recharge). The recharging stream hydrographs, changes in specific conductance of the four springs, and changes in concentrations of major ions and anthropogenic compounds in the four springs were compared to determine potential source waters, sources of anthropogenic contaminants, and travel times.

Variation in Physicochemical Properties in Response to Storms

Streamflow and Spring Discharge

In response to Storms 1 and 2, streamflow in the recharging streams greatly increased in the reach between the upstream and downstream boundaries of the recharge zone (figs. 24, 25), indicating that most of the rainfall and runoff occurred over the recharge zone rather than over the upstream contributing zone. The hydrographs were generally sharp for all streams except Barton Creek (in some cases extremely so, for example, Bear Creek during Storm 1 and Slaughter Creek during Storm 2), and the streams rapidly returned to low-flow or no-flow conditions after the storms. For Storm 2, flow was not sufficient to activate the autosamplers at Barton or Bear Creeks and no samples were collected from those streams.

Spring discharge responded differently to the two storms (fig. 24, 25). In response to Storm 1, discharge began to increase within 30 minutes after the onset of rainfall from about 60 ft^3/s to a maximum of 72 ft^3/s twenty-four hours later; throughout the remainder of the storm sampling period, discharge remained above 70 ft^3/s. Discharge did not change in response to Storm 2, but instead very gradually decreased from 96 to 94 ft^3/s during the following 2 weeks. These differences in storm response likely reflect differences in antecedent conditions, such as aquifer flow condition and water levels, as well as

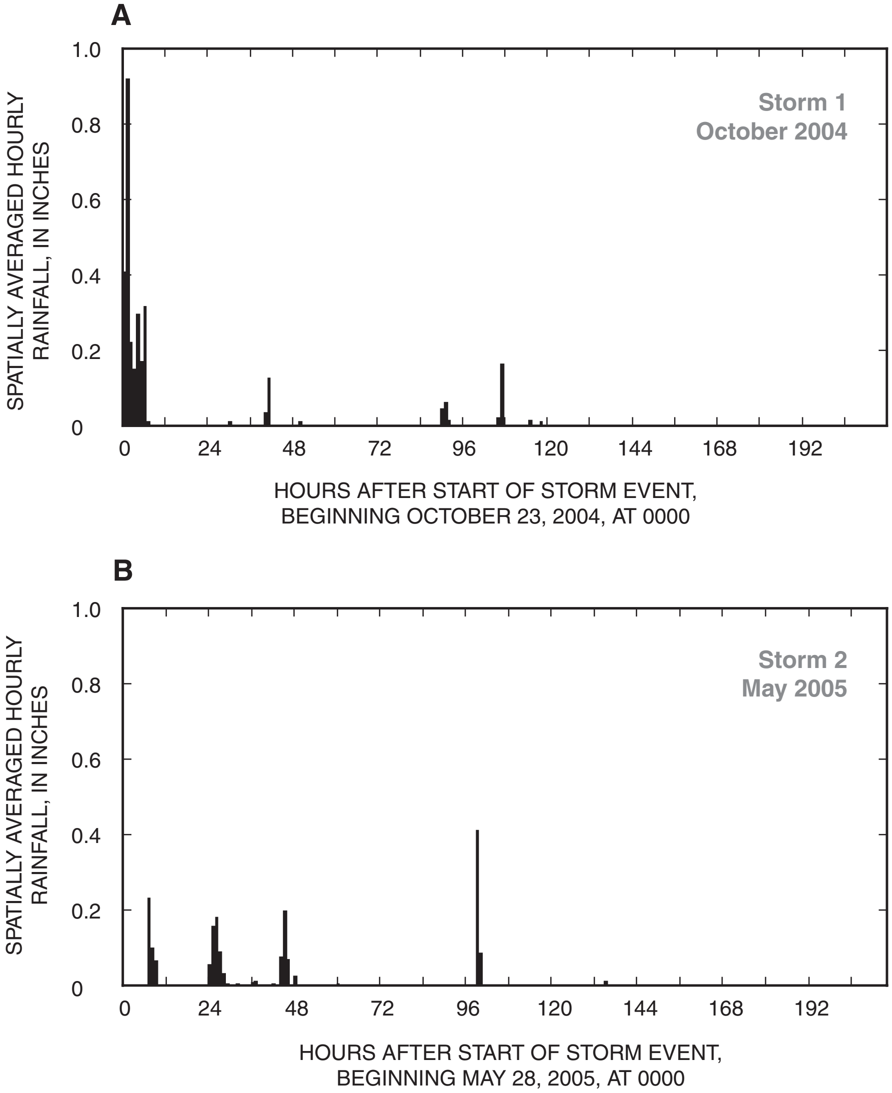


Figure 23. Rainfall hyetographs for (A) Storm 1 (October 23, 2004) and (B) Storm 2 (May 30, 2005).

differences in patterns of rainfall and corresponding recharge to the aquifer. Spring discharge was lower at the beginning of Storm 1 than for Storm 2, and the temporal rainfall distribution for Storm 2 was more spread out than for Storm 1.

Specific Conductance and Turbidity

Specific conductance of spring discharge decreased in response to both storms, reflecting pulses of low-ionic-strength recharge water moving through the aquifer (fig. 26). This pattern of specific conductance behavior is typical of karst aquifer behavior (Desmarais and Rojstaczer, 2002; Dreiss, 1989; Hess and White, 1988; Lakey and Krothe, 1996; Liu and others, 2004; Ryan and Meiman, 1996). For each storm, the pattern of decrease in specific conductance at Main and Eliza Springs was similar, although with subtle differences (fig. 26). Patterns of specific conductance maxima and minima observed at Main and Eliza Springs also were observed at Old Mill Spring, but at Old Mill Spring the magnitude of change was less and the timing was delayed by about 5 hours. These observations indicate that Old Mill Spring is less responsive to focused recharge and also are consistent with the hypothesis of Hauwert, Johns, and others (2004) and Hauwert, Samson, and others (2004) that a flow path bifurcation results in delayed transport to Old Mill Spring.

The pattern of decrease in specific conductance was very different at Upper Spring than the patterns at the three other springs (fig. 26; data are only available for Storm 1 for Upper Spring). At Upper Spring (Storm 1), rather than having several local minima, following rainfall there was a very large trough in specific conductance preceded by a small spike. This pattern occurred twice: On October 23 and again on

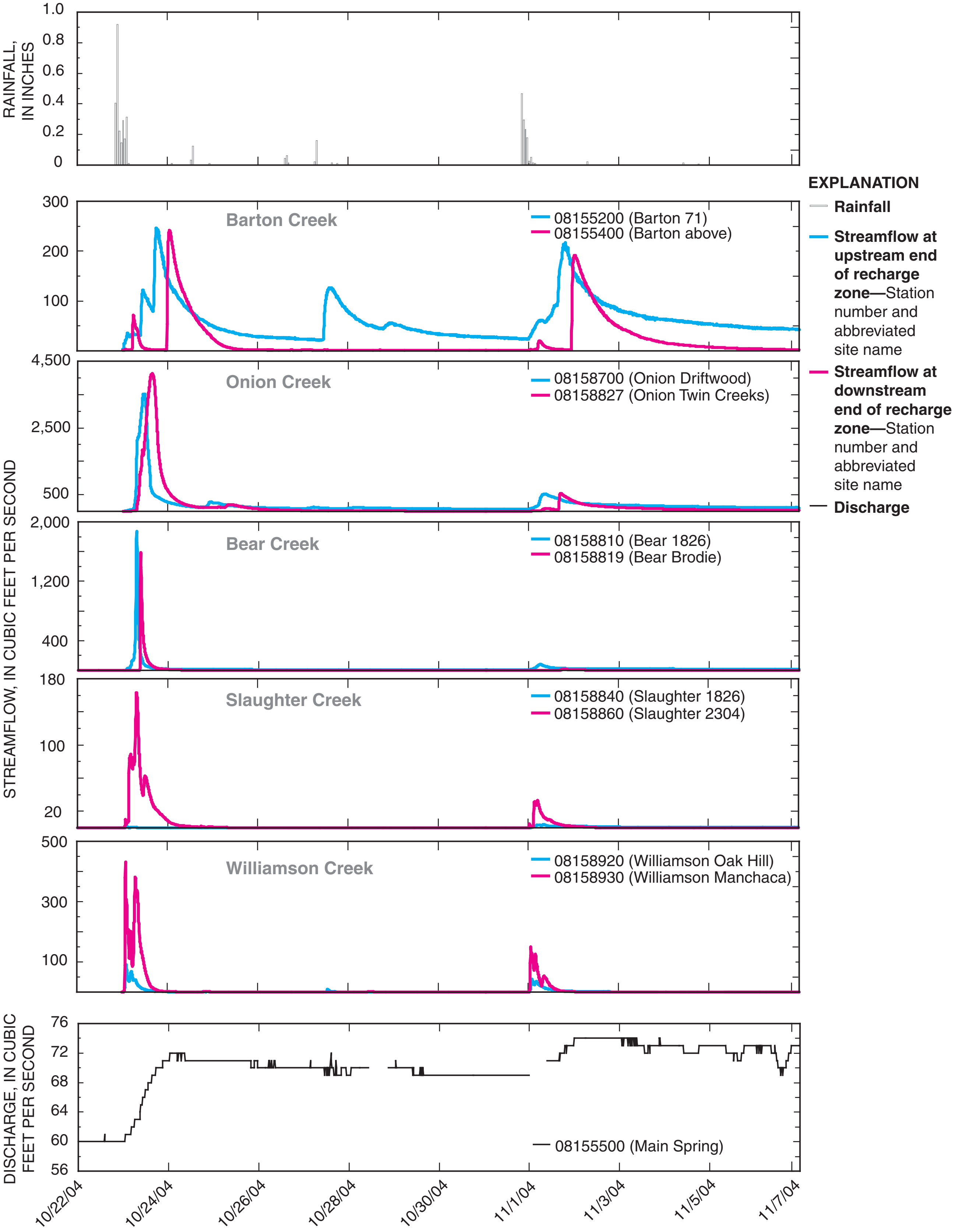


Figure 24. Rainfall hyetograph, storm hydrographs for the five major streams recharging Barton Springs, Austin, Texas, and discharge (station 08155500 Barton Springs at Austin, Tex.) for Storm 1 (October 2004).

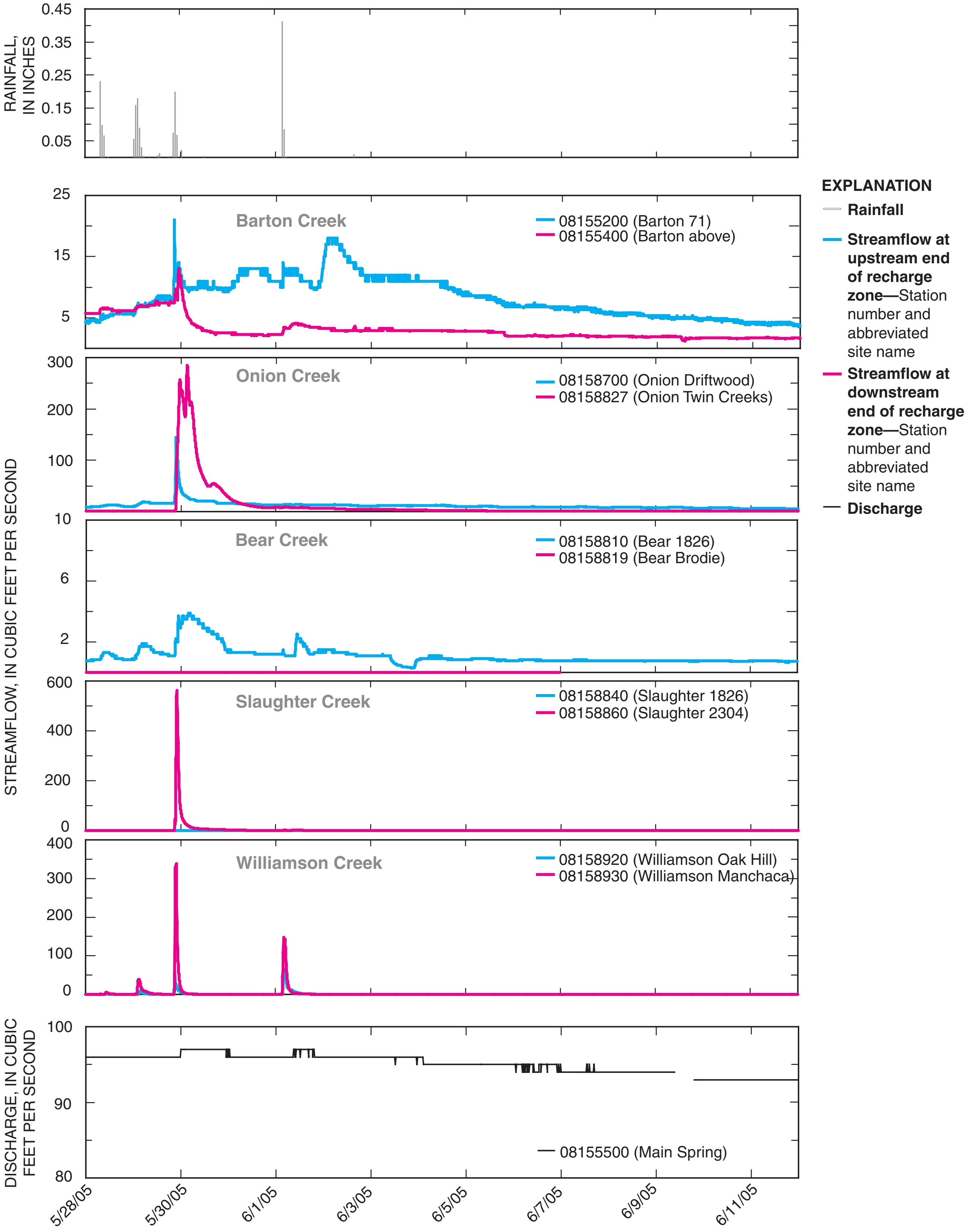


Figure 25. Rainfall hyetograph, storm hydrographs for the five major streams recharging Barton Springs, Austin, Texas, and discharge (station 08155500 Barton Springs at Austin, Tex.) for Storm 2 (May 2005).

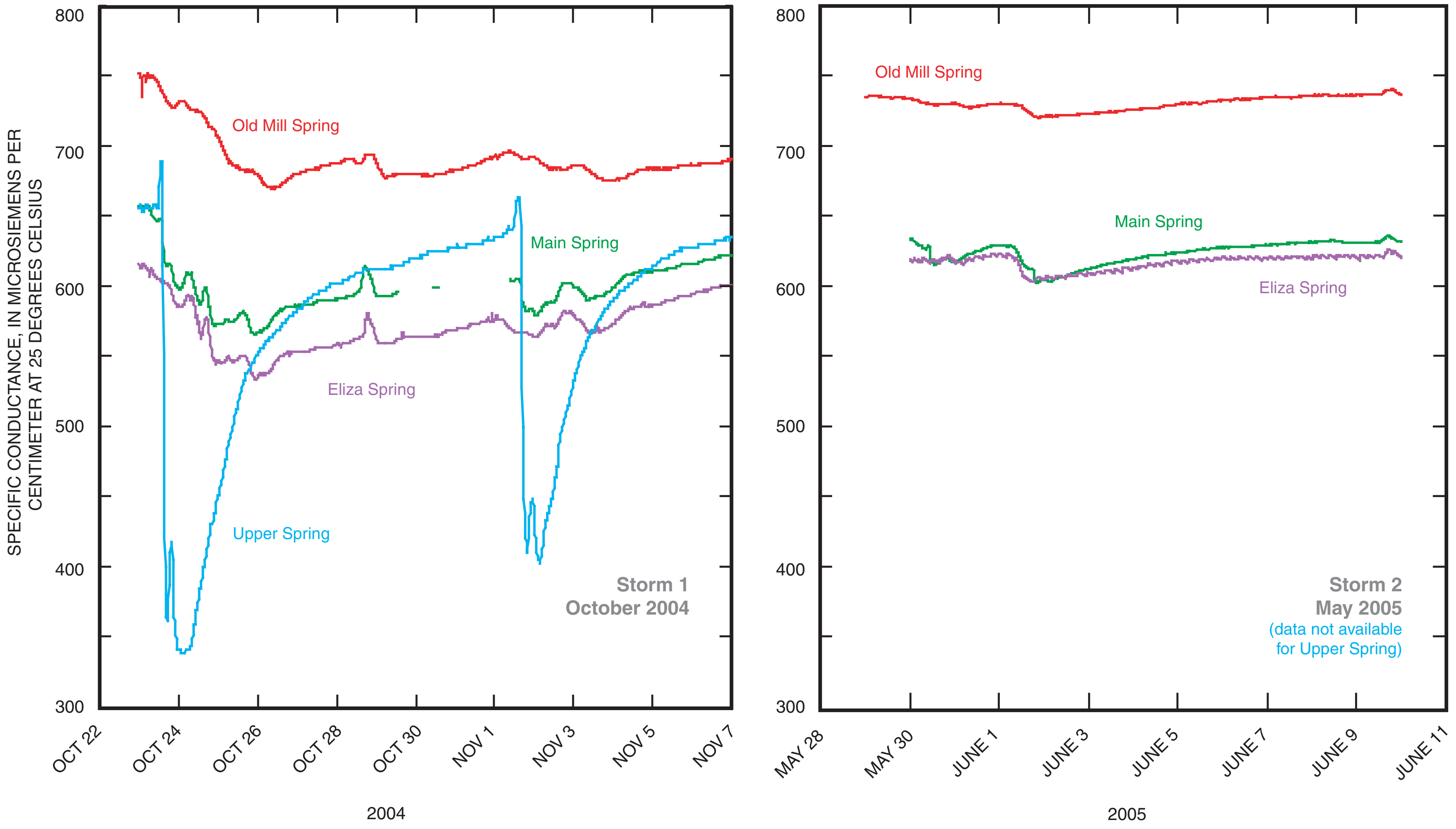


Figure 26. Time series of specific conductance of the four spring orifices of Barton Springs, Austin, Texas, for Storms 1 (October 2004) and 2 (May 2005).

November 1, about 1 week following Storm 1. The first large trough is associated with rainfall and streamflow on October 23, and the second trough is associated with rainfall and streamflow on November 1 that resulted in an increase in flow in all of the streams (fig. 24). This second trough coincided with a less-pronounced decrease in specific conductance at Main Spring (decrease at Upper Spring about 3 times greater), and small decreases at Eliza and Old Mill Springs. Each of the large troughs recorded at Upper Spring had two minima, which occurred 13 and 8 hours apart in the first and second troughs, respectively. The specific conductance at Upper Spring began returning to baseline about 48 hours before the minimum value occurred at Main Spring. The less complex but more extreme response of specific conductance at Upper Spring to rainfall relative to the three other springs might indicate that Upper Spring is receiving focused recharge from a smaller number of sources, but that discharge for a period of 8 to 16 hours after the storm consists largely of recently recharged surface water.

Removal of the gates at the downstream end of Barton Springs Pool on October 28 led to a rapid increase in specific conductance at Main, Eliza, and Old Mill Springs, but no response at Upper Spring. This phenomenon has been observed previously (Mahler and Lynch, 1999) and is interpreted as an inflow of water from the saline zone because of lower karst conduit pressure. The lack of response at Upper Spring is interpreted as further evidence that the saline zone does not contribute to Upper Spring.

Storm-related recharge is widely accepted as the cause of rapid specific conductance and turbidity changes in Barton Springs (Andrews and others, 1984; City of Austin; 1997; Garner, 2005; Mahler and others, 1998; Slade and others, 1986). Turbidity and specific conductance values are usually higher and lower, respectively, in surface-water stormflow than in non-stormflow ground water. Particle-load transport to Main Spring differs from dissolved-load transport. The general spring orifice response to infiltration following a storm is an increase in turbidity (particle-load transport) and a decrease in specific conductance (dissolved-load transport). The precise timing of specific conductance and turbidity changes, however, is not simultaneous on the basis of data for large rainfall events in January, April, June, and October 2004 and May 2005 (fig. 27). These rainfall events all generally exhibit a turbidity change of at least 8 NTU and a single large rainfall pulse (although the May 2005 storm included several small rainfall pulses). In most cases, in response to rainfall and infiltration, the decrease in specific conductance preceded the increase in turbidity, but the timing of the turbidity maximum preceded the timing of the specific conductance minimum. This might indicate that the primary source of the turbidity is resuspension of autocthonous sediment by the infiltration pressure pulse, that the first flush of infiltration is more turbid than the infiltration that follows, or that there are multiple sources of infiltration of which the first is the most turbid.

The turbidity response at Upper Spring for Storm 1 was quite different than that at Main Spring. This response is interpreted as additional evidence that Upper Spring receives water from different flow paths. During Storm 1, Upper Spring is characterized by an initial small though unusual increase in specific conductance, and a very substantial and unusual increase in turbidity—the maximum value of 518 NTU is 7 times higher than any value ever measured at Main Spring (fig. 28). Turbidity data for Upper Spring is not available for Storm 2 for comparison, and no storm turbidity data is available for Eliza or Old Mill Springs.

The early increases in both specific conductance and turbidity responses at Upper Spring for Storm 1 could be accounted for by the following conceptual model of stormflow unplugging a clogged conduit (fig. 29). In this conceptual model, a conduit becomes blocked by sediment, and ground water accumulates in the conduit upgradient from the blockage. As the water is in contact with the aquifer rocks for some extended period of time, it therefore has an elevated specific conductance relative to recharge water. When recharge enters the conduit after rainfall, pressure increases until the clog fails. When the clog fails, a mixture of high specific conductance water and sediment enters the conduit network and travels to Upper Spring. Support for this model and additional insight into the behavior of this spring would require additional storm monitoring at Upper Spring.

Major Ions

The response of major ion concentrations to the two storms varied between sites, between ions, and between storms (figs. 30, 31, 32). In general, the patterns of major ion concentration variations at Main, Eliza, and Old Mill Springs are similar to each other and distinct from those at Upper Spring. Variations in concentrations of most of the major ions were greater at Upper Spring than at the three other springs.

At Upper Spring, magnesium, sodium, strontium, chloride, sulfate, and silica concentrations were diluted by recharging surface water after Storms 1 and 2 (figs. 30, 31). Calcium concentrations initially decreased, indicating the arrival of surface water with lower calcium concentrations. Calcium concentrations at Upper Spring then increased to a concentration exceeding that of the three other springs. Calcium concentrations at Upper Spring during routine sampling are also on average slightly higher than at the three other springs. At Main, Eliza, and Old Mill Springs, magnesium, sodium, strontium, bicarbonate, and chloride concentrations decreased within about the first 48 hours following Storm 1, but the decreases were much more subdued than those at Upper Spring. In contrast, little change was observed at Main, Eliza, and Old Mill Springs following Storm 2, whereas decreases in most major ion concentrations at Upper Spring tracked decreases in specific conductance (figs. 26, 30, 31).

The only major ion that increased in concentration in response to the storms was potassium. Potassium concentrations increased in all four springs following Storm 1 and in Upper Spring following Storm 2 (fig. 30). Similar responses

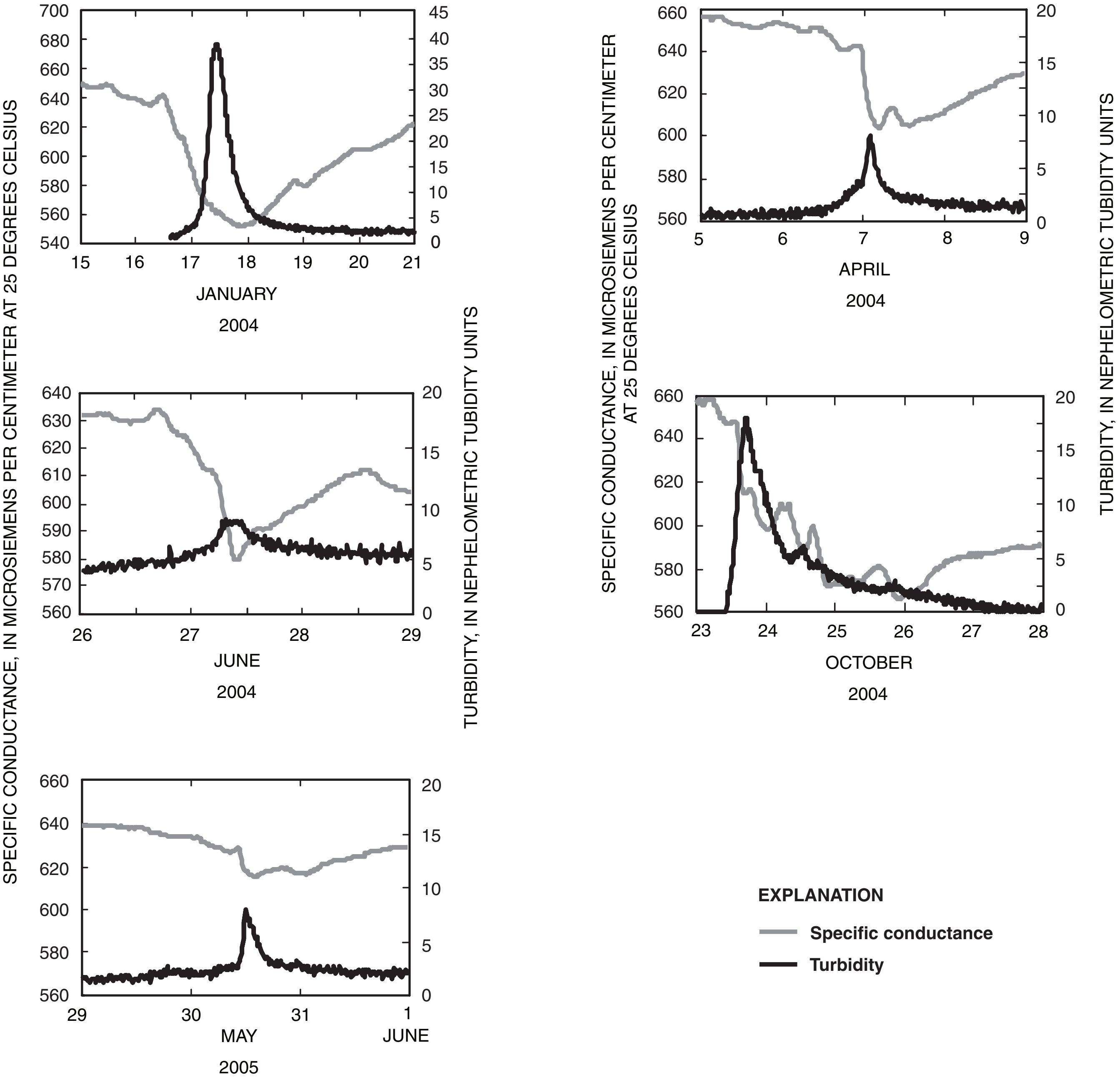


Figure 27. Response of specific conductance and turbidity of Main Spring, Austin, Texas, to five rainfall events (2004–05).

have been observed in numerous karst springs in Normandy, France (Valdes, 2005). Potassium concentrations during routine sampling never exceeded 2.0 mg/L, and routinely exceeded 1.5 mg/L only at Old Mill Springs. An increase in potassium concentration was observed, however, at all four springs in the Phase 1 sample collected within a few days after a storm. In response to Storm 1, concentrations of potassium at all four springs orifices increased to 1.8 mg/L or higher; at Upper Spring, the maximum potassium concentration was 2.7 mg/L. Historical data indicate that some of the recharging streams have elevated potassium concentrations at the downstream end of the recharge zone; on the basis of historical data (appendix 2) the average potassium concentration exceeded 2.0 mg/L at station 08158800 Onion Creek at Buda, station 08158825 Little Bear Creek at FM 1626 near Manchaca, station 08158860 Slaughter Creek at FM 2304 near Austin, station 08158922 Williamson Creek at Brush Country Blvd., Oak Hill, and station 08158970 Williamson Creek at Jimmy Clay Rd., Austin. Potential sources of potassium include weathering of silicate minerals in soils and aquifer sediments. However, a lack of

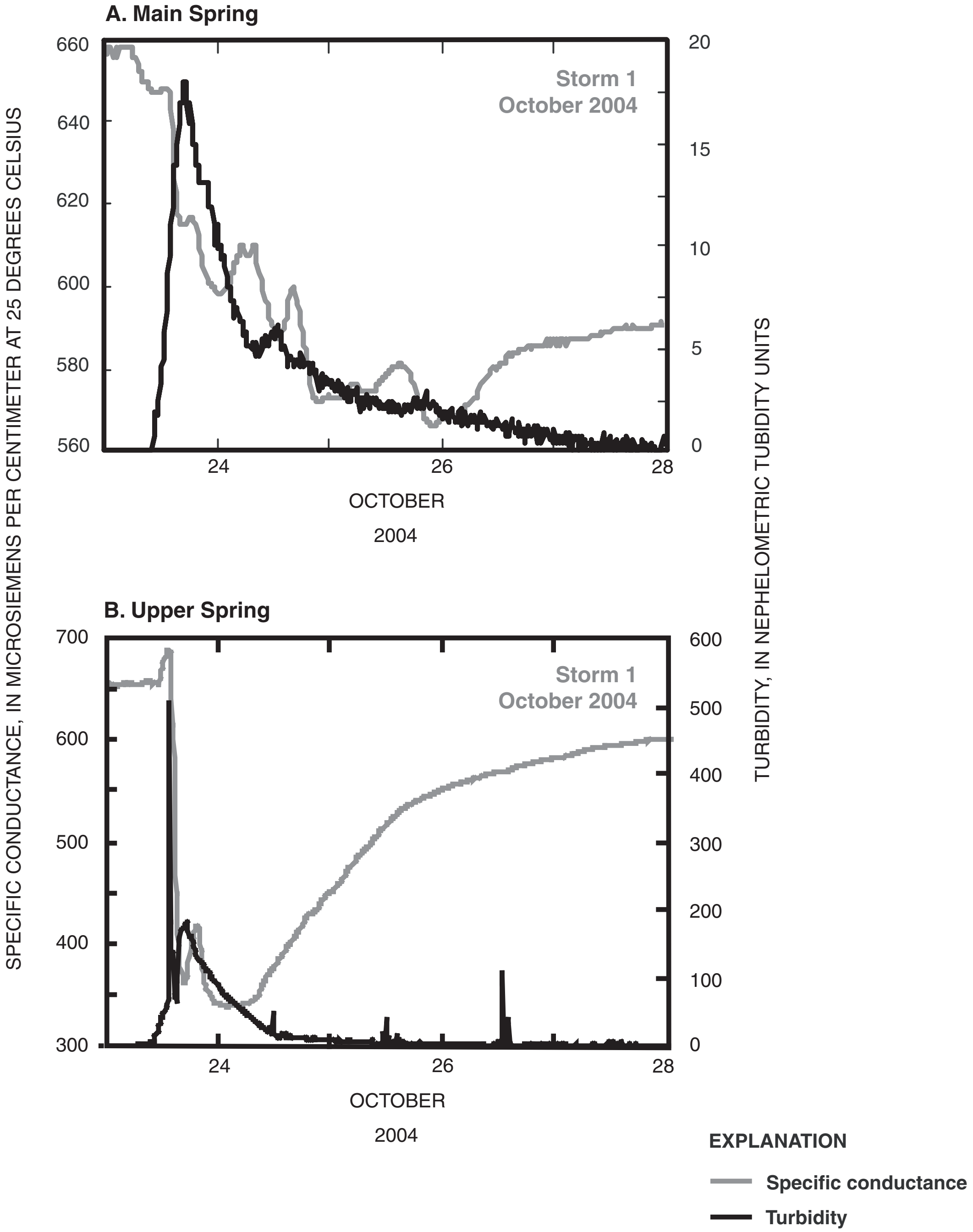


Figure 28. Response of specific conductance and turbidity for (A) Main Spring and (B) Upper Spring, Austin, Texas, for Storm 1 (October 2004).

positive covariance between silica and potassium suggests that weathering processes are not the source of increasing potassium in spring discharge. One process that might explain increased potassium concentrations in spring discharge after storms is mobilization of fertilizer constituents by storm runoff. If so, the increased potassium concentrations in spring discharge are caused by storms and corresponding flow across the recharge zone, and the source of potassium is anthropogenic. Potassium does not leach from soils as easily as nitrate (Broschat, 1995; Incitec Pivot, 2005; Schulte and Kelling, 2005) and might remain at the surface while nitrate more readily leaches into the ground with diffuse infiltration; following rainfall, potassium might be washed into the aquifer with focused recharge along with other anthropogenic compounds.

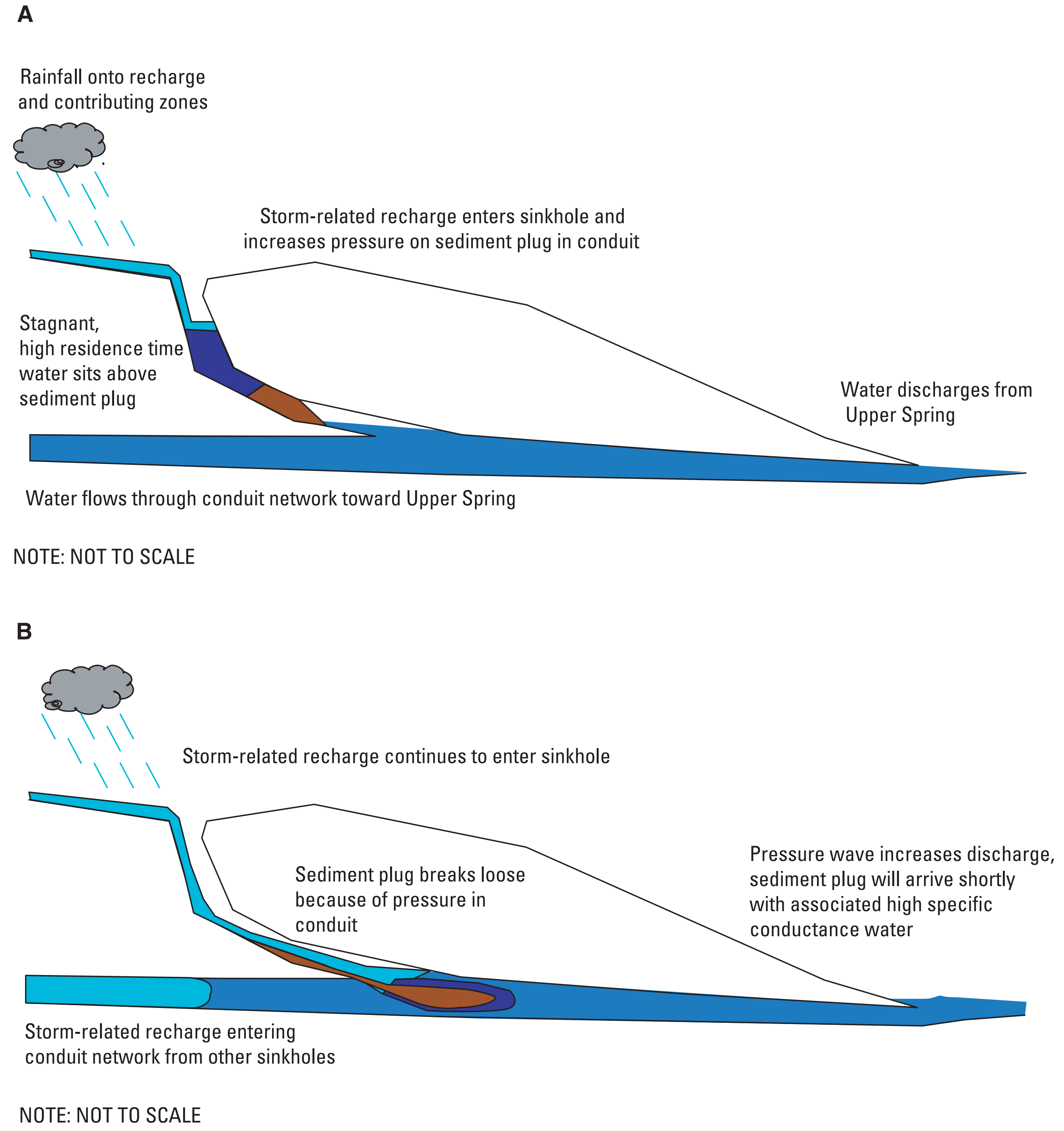


Figure 29. Schematic diagram showing a hypothesized mechanism for increases of specific conductance and turbidity at Upper Spring, Austin, Texas, shortly after rainfall.

Nutrients

Nitrite plus nitrate was analyzed for storm samples at all four spring orifices for both storms (appendix 5). At Main Spring, selected samples also were analyzed for a more complete suite of nutrients. Nitrite plus nitrate was detected in all but one sample at Main Spring and at concentrations greater than 0.9 mg/L; other nutrients were detected at very low concentrations (less than 0.15 mg/L and in most cases less than one-half that concentration), when detected at all. Nitrite was

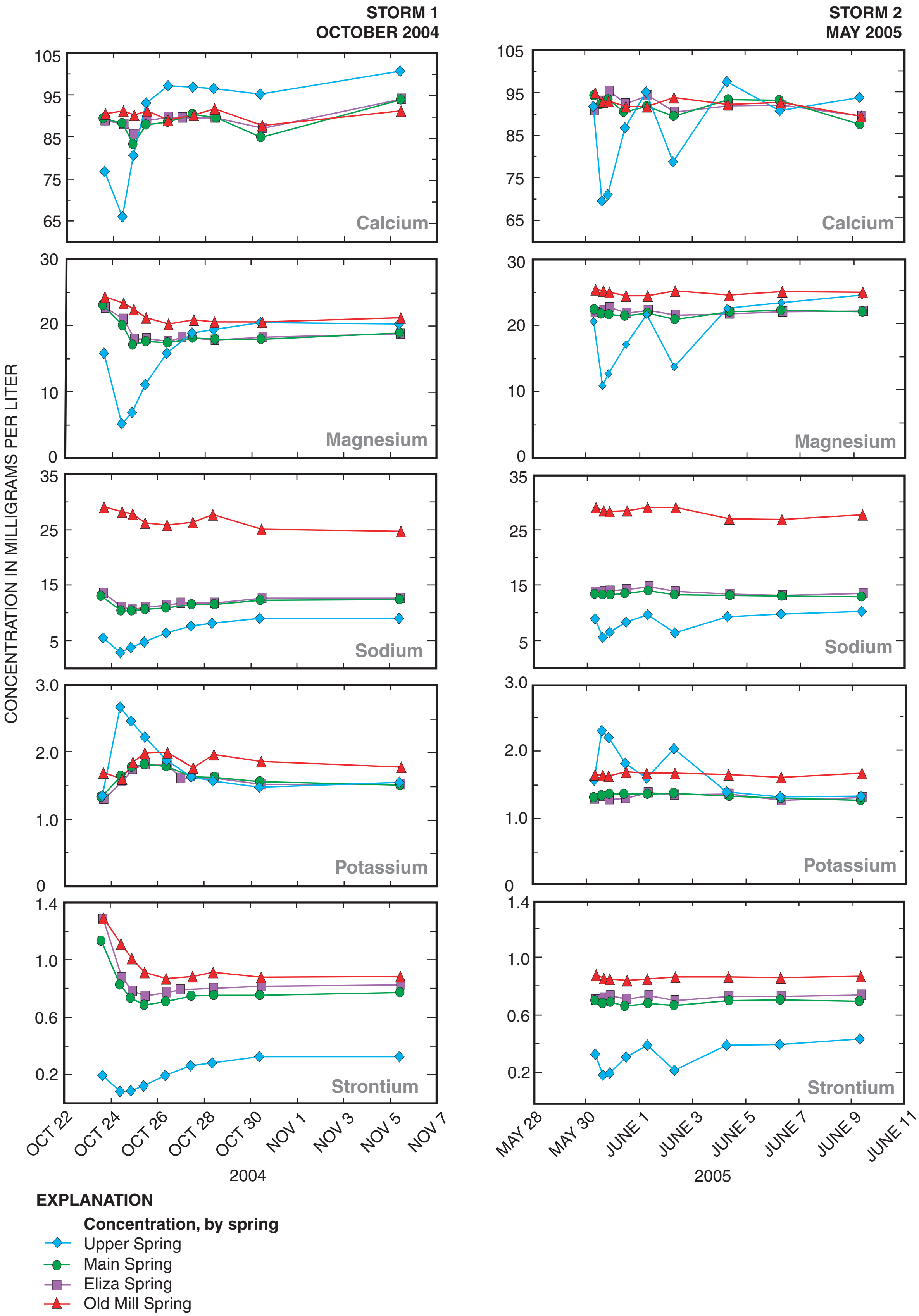


Figure 30. Time series of major ion concentrations (cations) of samples from the four spring orifices of Barton Springs, Austin, Texas, for Storms 1 (October 2004) and 2 (May 2005).

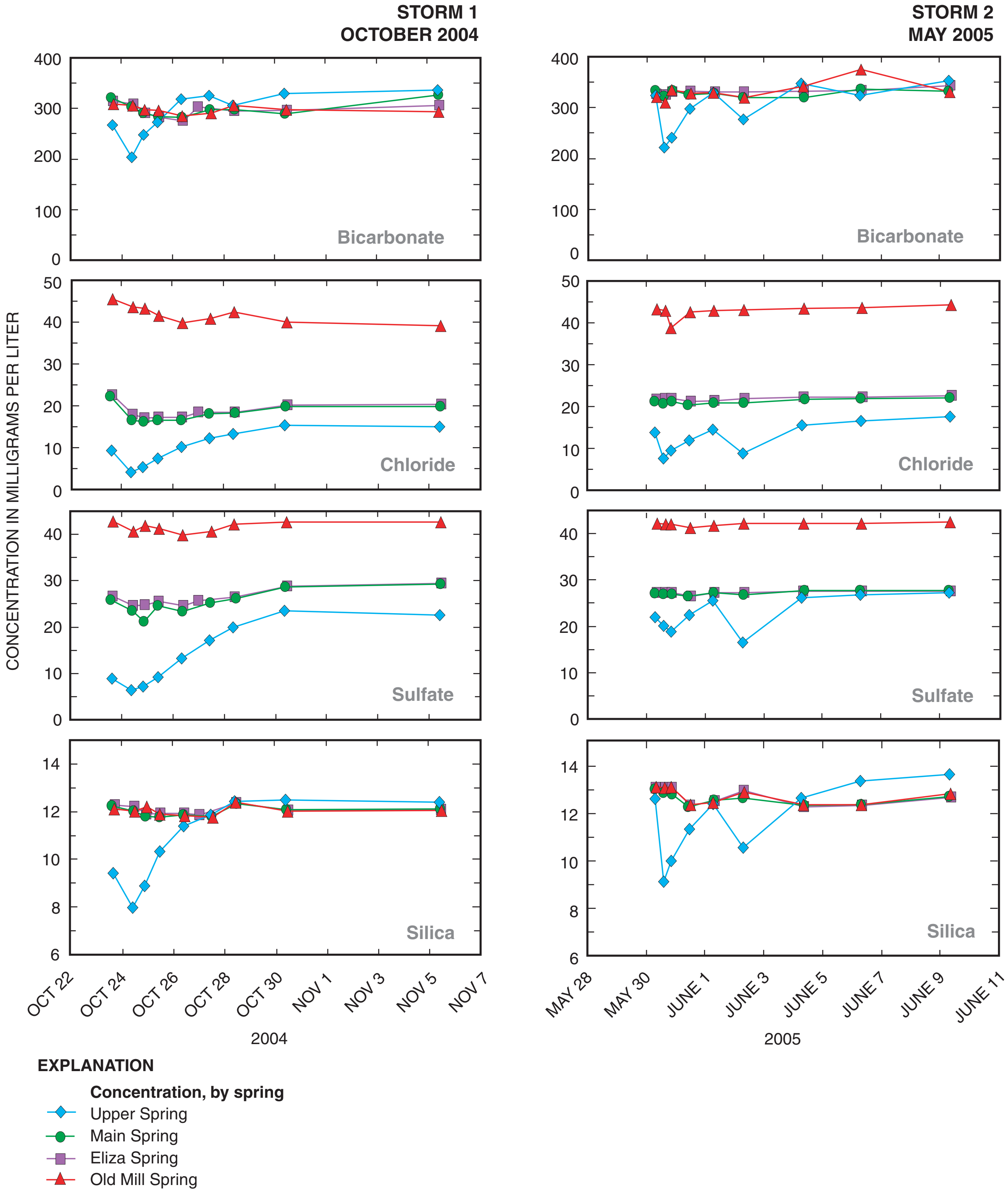


Figure 31. Time series of major ion concentrations (anions) of samples from the four spring orifices of Barton Springs, Austin, Texas, for Storms 1 (October 2004) and 2 (May 2005).

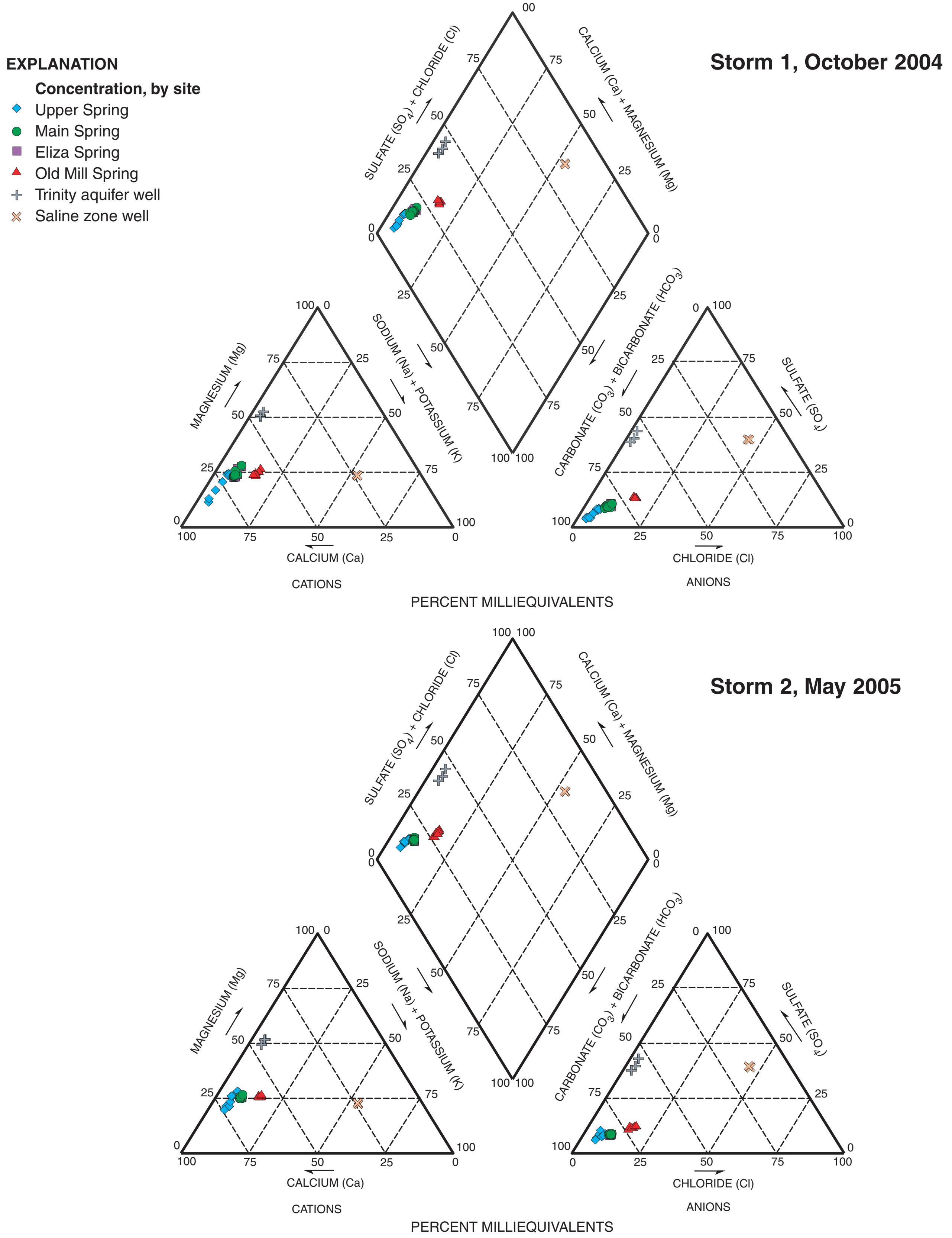


Figure 32. Piper diagrams showing geochemical composition of samples from the four spring orifices of Barton Springs, Austin, Texas, for Storms 1 (October 2004) and 2 (May 2005), and selected wells in the study area for comparison.

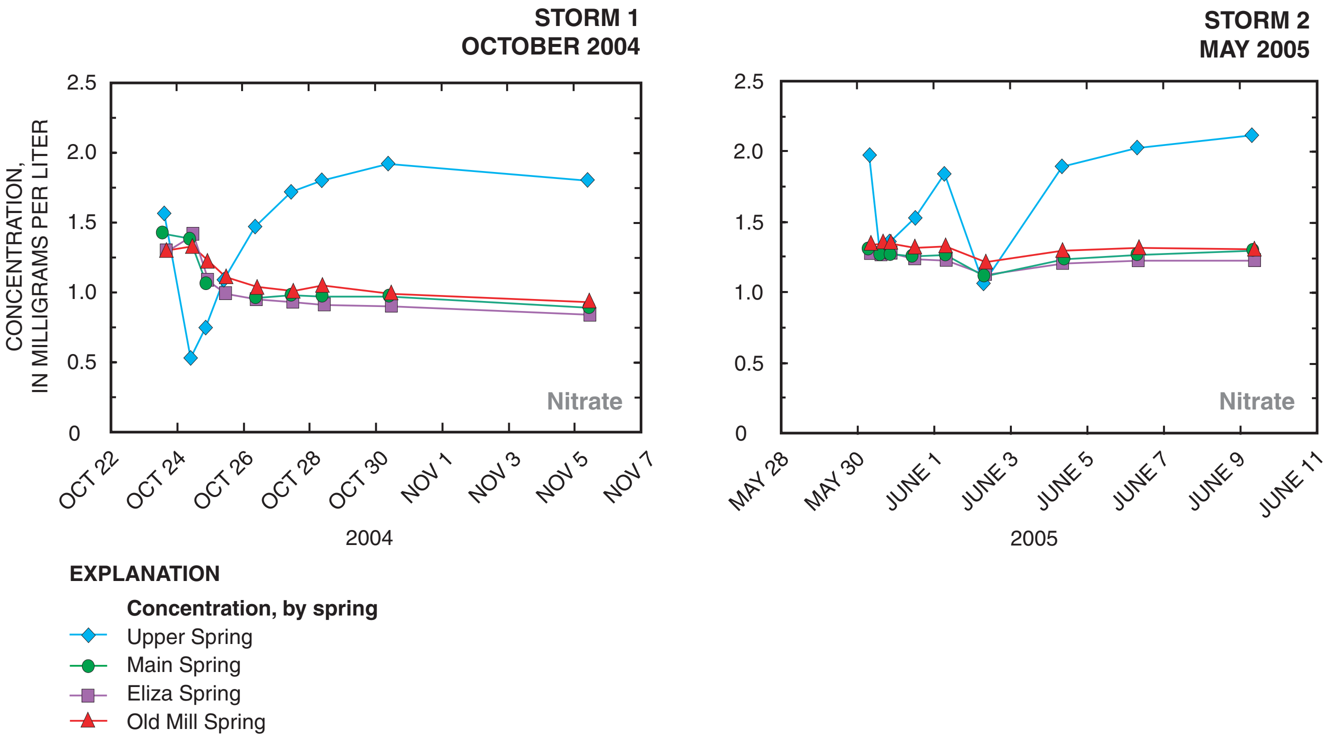


Figure 33. Time series of nitrate nitrogen concentrations of samples from the four spring orifices of Barton Springs, Austin, Texas, for Storms 1 (October 2004) and 2 (May 2005).

not detected (LRL 0.008 mg/L) in any samples, so concentrations of nitrite plus nitrate were assumed to be entirely nitrate. At the three other springs, nitrite plus nitrate was detected in all samples.

In response to Storm 1, nitrate concentrations at Main, Eliza, and Old Mill Springs decreased gradually over a period of about 48 hours and then continued to slightly decrease over the remainder of the sampling period (fig. 33). Concentrations of nitrate in Upper Spring rapidly decreased, coinciding with a rapid decrease in specific conductance that reflects the arrival of recent focused recharge. Nitrate concentrations subsequently increased rapidly and reached the probable pre-storm concentration within a week after the storm.

In response to Storm 2, nitrate concentrations at Main, Eliza, and Old Mill Springs decreased slightly (fig. 33), coinciding with minima in specific conductance. Concentrations of nitrate at Upper Spring decreased, rose, then decreased again. Although specific conductance data for Upper Spring for Storm 2 are not available, on the basis of the similar timing and the response of nitrate concentrations and specific conductance to rainfall, it is probable that specific conductance at Upper Spring behaved similarly to nitrate for the May 2005 storm. The coincidence of decreases in specific conductance and concentrations of nitrate at all four spring orifices indicates that recharge water was diluting ambient ground-water nitrate concentration.

In contrast, samples collected on November 24, 2004, following a month of heavy rainfall and 2 days after 5 in. of rainfall, had nitrate concentrations for Main, Eliza, and Old Mill Springs that were higher than in any other samples analyzed during this study (table 16); nitrate concentrations for Main and Eliza Springs were equivalent to the highest concentration measured historically (1.6 mg/L). These spring-water concentrations are similar to those in samples collected during periods of no recharge and indicate that during periods of extreme recharge, nitrate concentrations might be elevated rather than diluted, indicating more complex interactions with anthropogenic sources.

Soluble Pesticides

Nine samples for analysis of soluble pesticides were collected from Upper and Main Springs following Storms 1 and 2; the first sample was collected 12 to 24 hours after rainfall, and the final sample was collected about 2 weeks after rainfall. Flow-weighted composite samples also were collected at the water-quality stations at the downstream end of Barton, Williamson, Slaughter, Bear, and Onion Creeks (fig. 1) when streamflow was sufficient to activate autosamplers.

The three pesticide compounds detected at Main Spring during routine sampling (atrazine, DEA, and simazine) were detected in most of the storm samples; additionally, prometon, which was not detected during routine sampling, was detected in some of the storm samples. Changes in atrazine, DEA, and simazine concentrations following the storms all described breakthrough curves (fig. 34), with concentrations increasing over pre-storm concentrations within 32 hours after rainfall. At Upper Spring, the four pesticide compounds detected during routine sampling (atrazine, DEA, prometon, and simazine) were detected in most of the storm samples; additionally, four pesticide compounds not detected during routine sampling—carbaryl, diazinon, fipronil, and fipronil sulfone—were detected in several samples after one or both storms. Concentrations of atrazine at Upper Spring appeared to have already increased above pre-storm values when the first sample was collected. Peak storm concentration at Upper Spring in most cases arrived 12 to 24 hours prior to peak concentration at Main Spring. At Upper and Main Springs, concentrations of atrazine and simazine in the sample collected on November 24, 2004 (table 16), following a month of heavy rainfall, were similar to those in samples collected 3 to 5 days following Storm 1.

The atrazine/DEA ratio increased at both Upper and Main Springs in response to both storms (fig. 35). The atrazine/DEA ratio is an indicator of the residence time of atrazine in soils (Thurman and Fallon, 1996), thus the increase indicates an input of more recently applied atrazine, such as might be found in surface runoff. The peak atrazine/DEA ratio at Upper Spring exceeded that at Main Spring by a factor of about 2.3 after both storms, but for both springs was higher in response to Storm 1 relative to Storm 2. This indicates that recharge going to Upper Spring mixes with less aquifer water than that going to Main Spring; an atrazine/DEA ratio exceeding 10 at Upper Spring indicates that most of the water discharging from the spring was recent recharge (as also indicated by specific conductance).

Soluble pesticide compounds were measured in surface water for Storms 1 and 2 (tables 12, 13). Streamflow in Barton and Bear Creeks in response to Storm 2, however, was insufficient to trigger the autosamplers and no samples were collected. The same pesticides that were detected at the springs orifices were detected in the surface-water samples; additionally dacthal/DCPA and malathion were detected. Atrazine and carbaryl concentrations in Slaughter Creek exceeded by a factor of about 5 those concentrations in the springs and in the other streams for both storms, and concentrations of atrazine approached the MCL of 3.0 μg/L. Concentrations of prometon in Barton Creek exceeded by a factor of about 30 those at the springs and the other streams for Storm 1; no sample was collected for Storm 2. Fipronil and one or more of its degradates were detected in Slaughter and Williamson Creeks and at Upper Spring following Storm 2. These detections are the first incidence of fipronil detection in ground water of the Barton Springs segment.

Volatile Organic Compounds

Six VOCs were detected in samples collected from Upper or Main Spring following Storms 1 and 2 (tables 14, 15). Concentrations of tetrachloroethene and chloroform showed breakthrough curves at Main Spring following each storm, and showed “anti”-breakthrough or dilution curves at Upper Spring (fig. 36). These responses are consistent with data from routine sampling, which indicate that Main Spring receives recharge with elevated tetrachloroethene and chloroform concentrations relative to base-flow concentrations, but that Upper Spring does not. Instead, baseline concentrations of tetrachloroethene and chloroform at Upper Spring are diluted by recharge water that is less contaminated than the ground water. Similarly, another solvent—1,1,1-trichloroethane—and another THM—bromodichloromethane—were diluted by recharge water at Upper Spring following Storm 1. Trichloroethene, a degradation product of tetrachloroethene, described a breakthrough curve similar to that of tetrachloroethene in Main Spring following Storm 2; trichloroethene concentrations, however, were very low (less than the LRL, and about 10 times lower than concentrations of tetrachloroethene) in the first six samples collected and were not detected in the last three samples collected. The detected concentrations of trichloroethene are linearly related to concentrations of tetrachloroethene in Main Spring following Storm 2 ($r^2 = .75$), indicating that the trichloroethene likely is a by-product of the degradation of tetrachloroethene.

In the samples collected on November 24, 2005, following a month of heavy rain, five VOCs were detected in Upper Spring or Main Spring or both (table 16). Concentrations of chloroform and toluene were similar to those detected in samples collected following Storms 1 and 2. *cis*-1,2-Dichloroethene was detected at Main Spring but was not detected following Storms 1 or 2. The concentration on November 24, 2005, was about 50 percent higher than that detected in the two routine samples. Tetrachloroethene was detected at Main Spring at 0.80 μg/L, which is about 2.5 times higher than in any other sample (routine or storm). Similarly, trichloroethene also was detected at a concentration about 40 percent higher than in any other sample (routine or storm). In contrast, tetrachloroethene was detected in Upper Spring at a concentration lower than in any other sample. These results support the hypothesis that recharge delivers tetrachloroethene to Main Spring but dilutes tetrachloroethene at Upper Spring.

Pharmaceuticals

Five samples collected from Main Spring following Storm 2 were analyzed for a suite of 24 pharmaceutical compounds, which includes frequently used medications such as acetaminophen and ibuprofen and also caffeine (appendix 5). Only one compound, caffeine, was detected, at a concentration of 0.021 μg/L in only one sample. Samples from Onion, Slaughter, and Williamson Creeks also were analyzed for pharmaceutical compounds. Caffeine was detected in samples from these three

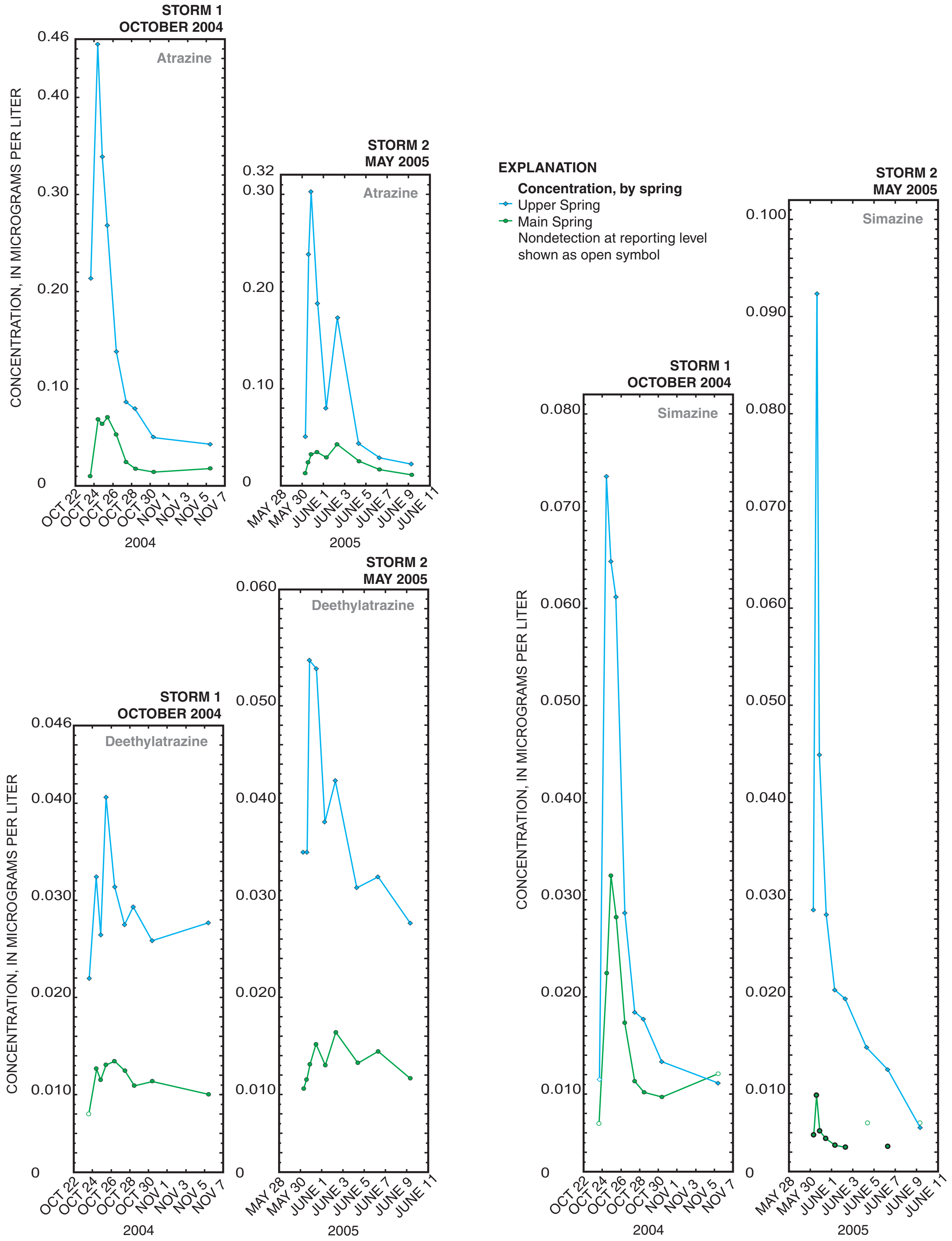


Figure 34A. Time series of concentrations of selected pesticides in samples from two of the four spring orifices of Barton Springs, Austin, Texas (Upper and Main Springs), for Storms 1 (October 2004) and 2 (May 2005) .

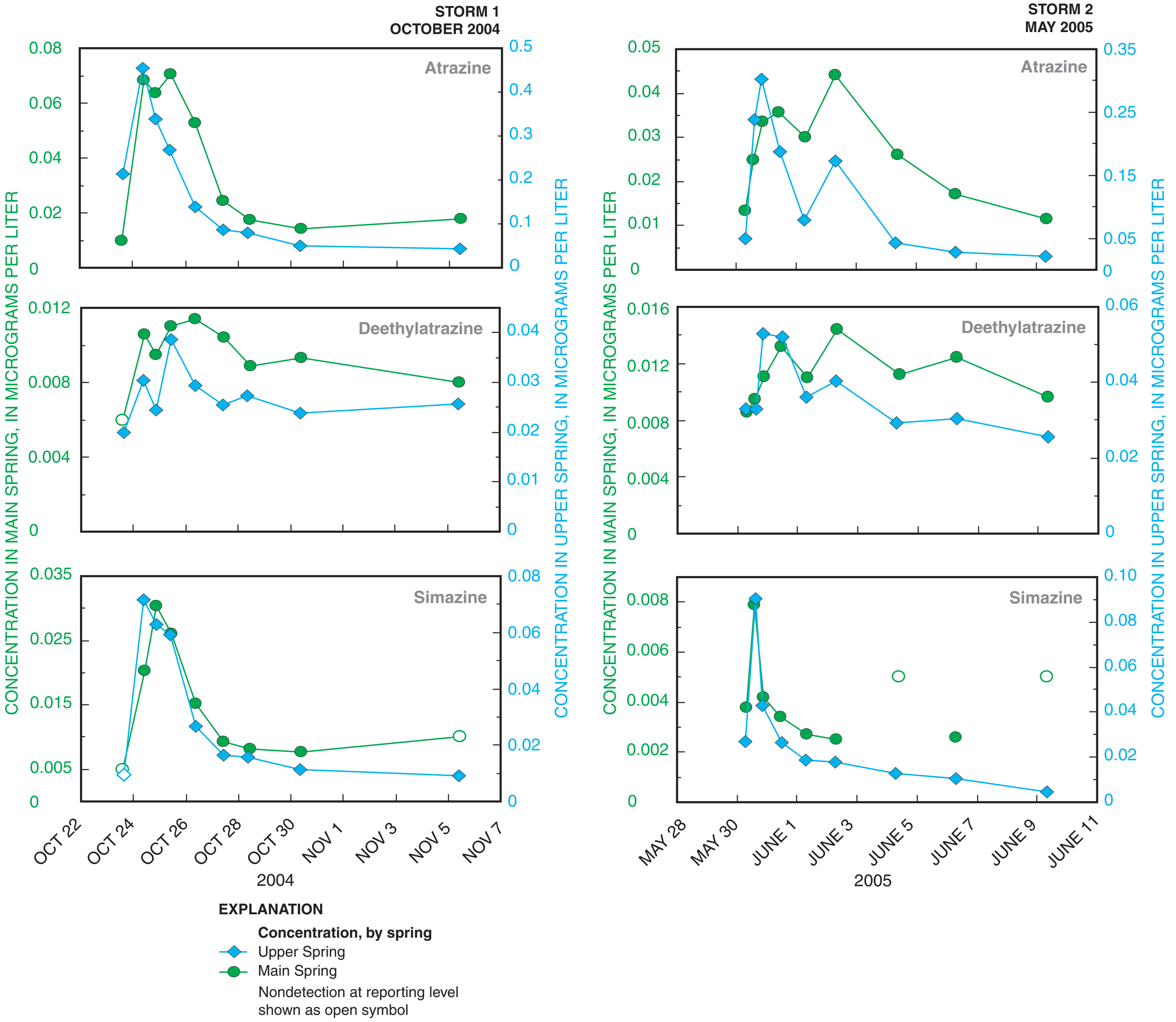


Figure 34B. Comparison of temporal patterns of variable-scaled concentrations of selected pesticides in samples from two of the four spring orifices of Barton Springs, Austin, Texas (Upper and Main Springs), for Storms 1 (October 2004) and 2 (May 2005).

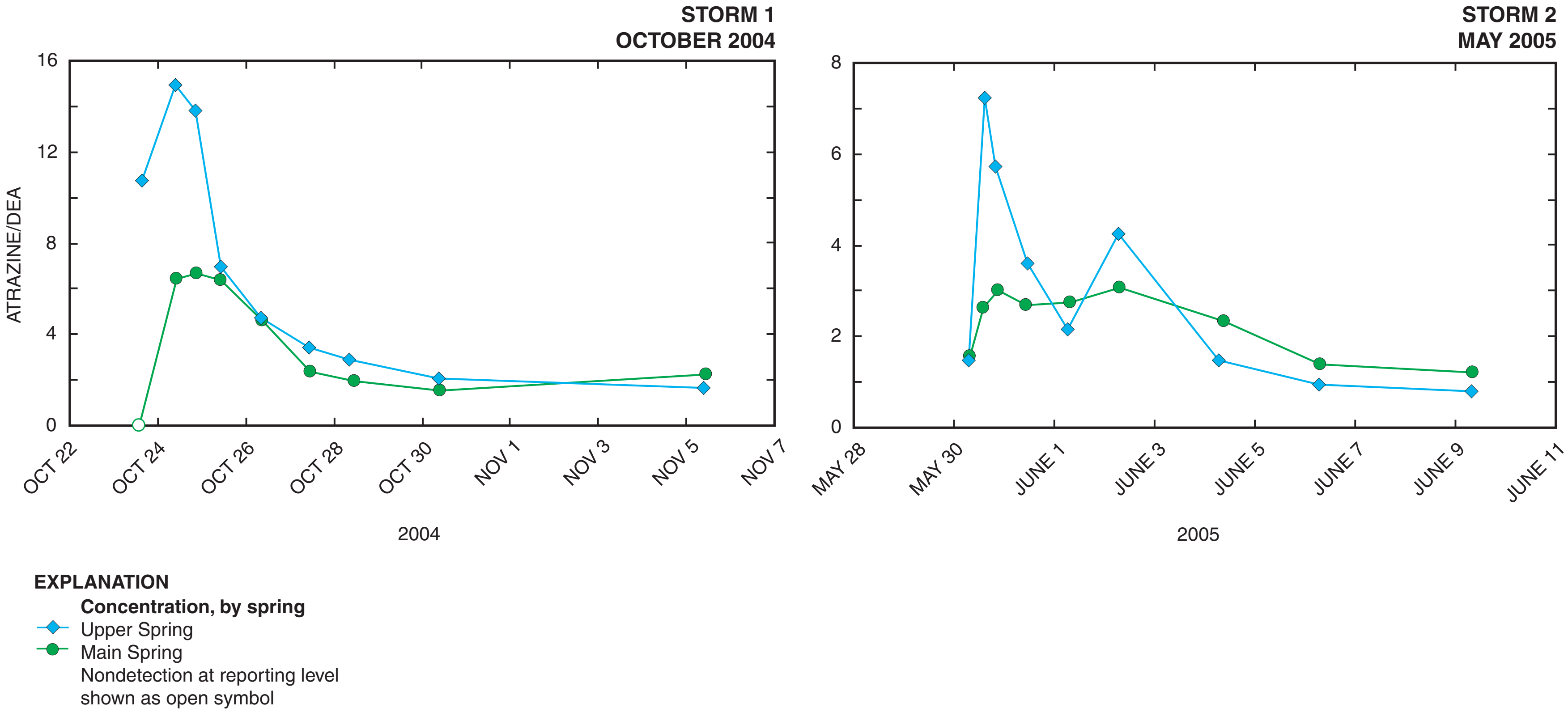


Figure 35. Time series of atrazine/deethylatrazine (DEA) ratios in samples from two of the four spring orifices of Barton Springs, Austin, Texas (Upper and Main Springs), for Storms 1 (October 2004) and 2 (May 2005).

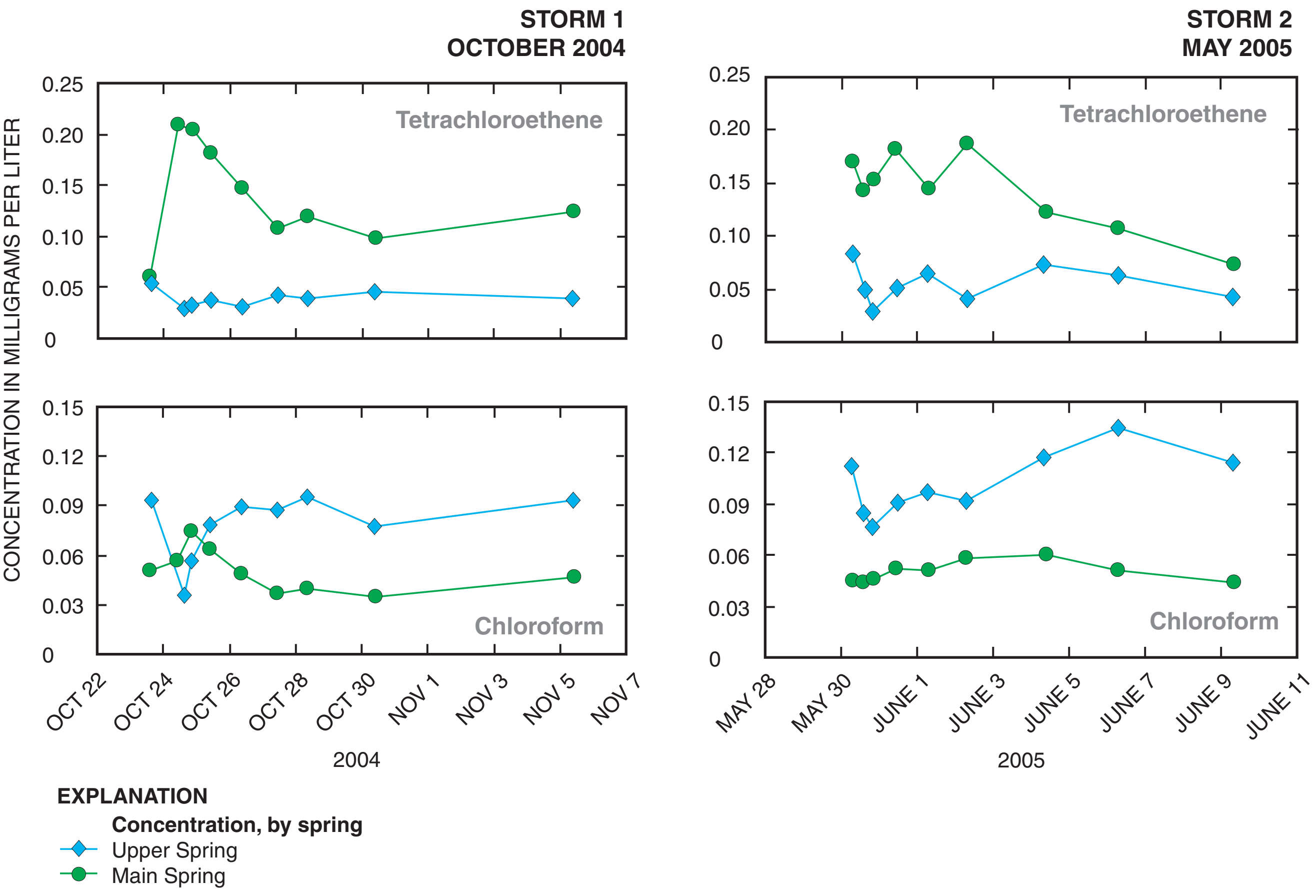


Figure 36. Time series of concentrations of selected volatile organic compounds (VOCs) in samples from two of the four spring orifices of Barton Springs, Austin, Texas (Upper and Main Springs), for Storms 1 (October 2004) and 2 (May 2005) .

streams at concentrations ranging from 0.028 µg/L in Onion Creek to 0.46 µg/L in Williamson Creek, but no other compounds were detected.

Storm-Related Loads of Contaminants

The total load of contaminants discharging from Main, Eliza, and Old Mill Spring orifices was determined for each storm (fig. 37; table 18, at end of report) to assess the importance of contaminant storm-related loads in comparison to base-flow loads, as well as to provide constraints on the contribution of contaminants to matrix storage. Storm-related loads were computed by multiplying the concentration in each sample collected at Main Spring (and assumed to be representative of all three springs) by the discharge volume corresponding to the sample. Discharge volume was computed as the volume that discharged from the midpoints in time between preceding and following sampling events. Loads were computed for the three contaminants that were frequently detected under both storm and non-storm conditions: atrazine, chloroform, and tetrachloroethene (table 18).

The corresponding recharge loads were computed for atrazine, which was the only one of the three frequently detected contaminants (atrazine, chloroform, and tetrachloroethene) that was measured in surface-water samples (table 18). The load of atrazine recharging the aquifer for each sampled recharging stream was computed as the product of the estimated volume of recharge and the average atrazine concentration across the recharge zone. Loads from the recharging streams were summed for an estimate of the total recharge load.

The concentration of atrazine in recharge was estimated on the basis of the concentration measured at the downstream gage in each watershed multiplied by an adjustment factor. The adjustment factor was chosen on the basis of data for the two streams (Barton and Onion Creeks) for which samples have been analyzed for the same storm at both the upstream and downstream gages (Aragon Long and others, 2005; Gandara, 2002–04; Gandara and others, 2001). Atrazine concentrations were consistently larger at the downstream gages. The adjustment factor was determined by assuming that the concentration of each contaminant in each stream varies linearly across the recharge zone. For the five samples for which data are available, the mean of the upstream and downstream concentrations was

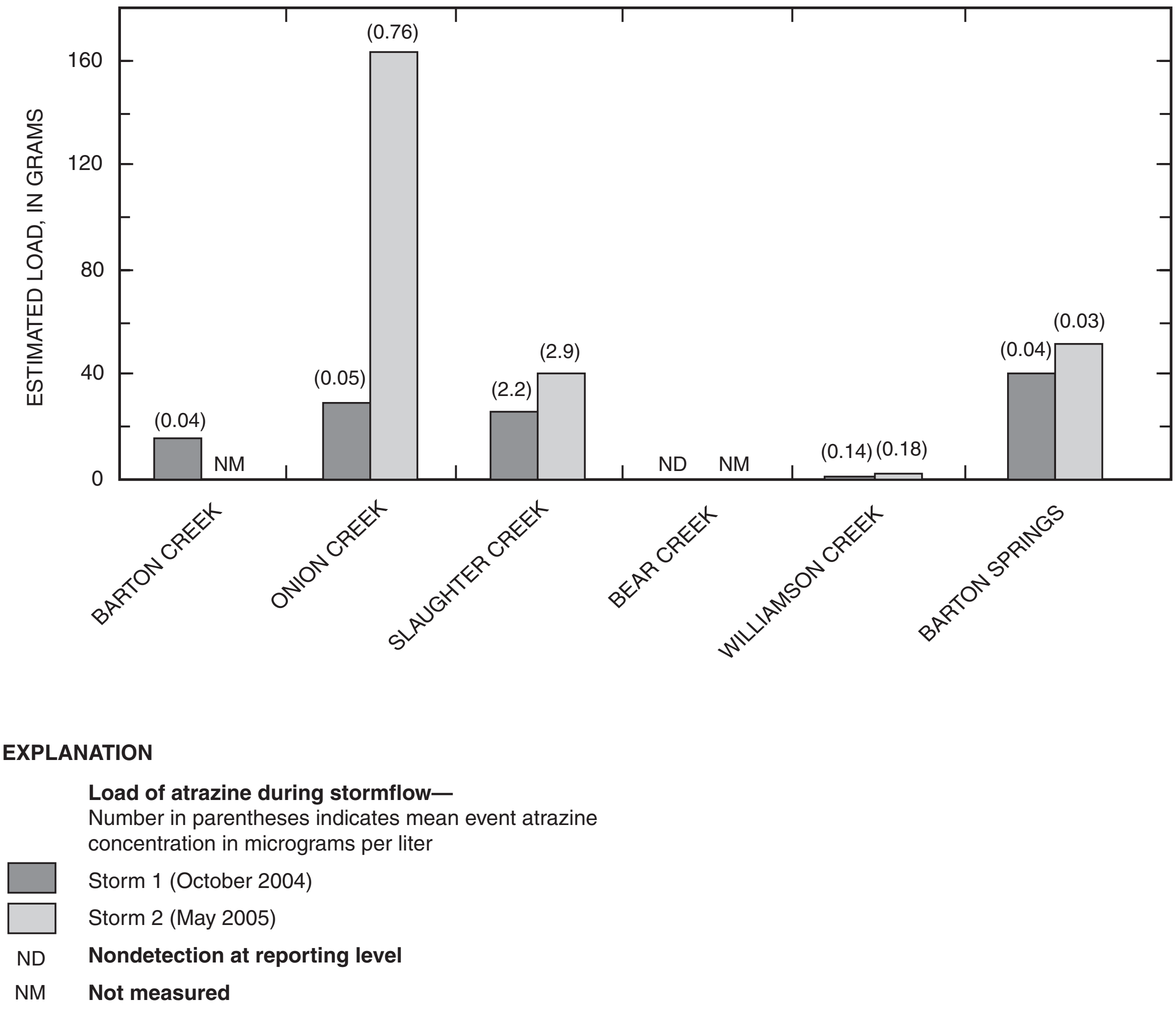


Figure 37. Estimated load of atrazine recharging the Barton Springs segment of the Edwards aquifer from streams and discharging from Barton Springs for Storms 1 (October 2004) and 2 (May 2005).

computed, and the ratio of that mean to the measured downstream concentration was computed. This ratio (0.57) was used as the adjustment factor.

Concentrations and loads of atrazine were higher in all of the streams sampled for Storm 2 (spring season) than for Storm 1 (autumn season) (fig. 37), consistent with increased application of herbicides such as atrazine in the spring. However, in Slaughter and Williamson Creeks the concentrations measured for Storm 2 were only about 30 percent higher than those measured for Storm 1, which indicates that application of atrazine occurs in these watersheds in the autumn as well as the spring. Concentrations measured in Slaughter Creek for Storms 1 and 2 (2.2 and 2.9 µg/L, respectively) approached the MCL of 3.0 µg/L, and were 4 times higher than the highest concentration measured in any other stream. The atrazine/DEA ratios for Storms 1 and 2 were 95 and 18, respectively, in Slaughter Creek and 12 and 8.3, respectively, in Williamson Creek. The elevated ratios (above 10) for both streams for Storm 1 further indicate that atrazine had been applied recently in the watershed.

Similar to atrazine concentration, the atrazine load recharged in each of the streams was greater following the spring storm than the autumn storm (fig. 37). In comparing the concentrations to the loads, the influence of watershed size on load is evident. The much larger watershed of Onion Creek results in higher flows; therefore, although the atrazine concentration in Onion Creek for Storm 2 is about 4 times less than that in Slaughter Creek, the atrazine load for Onion Creek recharge is about 4 times greater.

The computed load of atrazine recharging the aquifer exceeded the computed load discharging from the aquifer for both storms: It is estimated that about 64 percent of the atrazine in recharge was recovered at the spring orifices in the 2 weeks following Storm 1, but that only 23 percent of the atrazine in recharge was recovered at the spring orifices in the 2 weeks following Storm 2. This indicates that much of the atrazine and

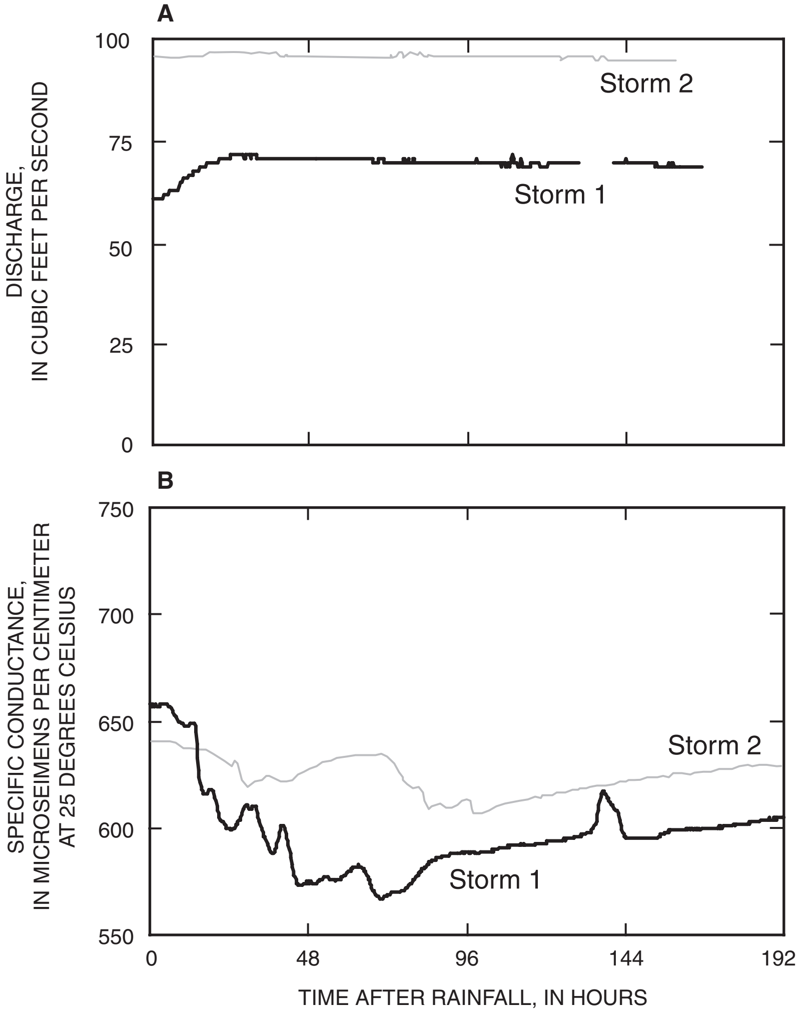


Figure 38. Response of (A) discharge (daily mean for station 08155500 Barton Springs at Austin, Tex.) and (B) specific conductance of Main Spring, Austin, Texas, for Storms 1 (October 2004; average aquifer flow conditions) and 2 (May 2005; high aquifer flow conditions).

other contaminants contained in recharging stormwater went into temporary storage following Storm 2, when aquifer flow conditions were high.

Synthesis—Factors That Affect Water-Quality Variability

Routine sampling of the four spring orifices and sampling of the spring orifices in response to storms provide information on water quality in Barton Springs. This information leads to an enhanced understanding of how the Barton Springs segment functions in terms of the complex relations between the four spring orifices, contributing ground-water flow paths, sources of water to the aquifer, and the effect of aquifer conditions on flow and transport. The information gained contributes to scientific understanding of some questions and also raises new questions.

Water Quality

The water quality of the Barton Springs segment is affected by persistent low levels and intermittent occurrence of higher levels of three anthropogenic compounds (atrazine, chloroform, and tetrachloroethene) and the intermittent occurrence of additional anthropogenic compounds. Atrazine was detected in one or more of the four orifices of Barton Springs every time the springs were sampled in 2003 and during 2004–05; chloroform and tetrachloroethene were detected in every sample from every spring orifice. Concentrations of contaminants in some cases rapidly increased in response to storms. The ubiquitous detection of these three contaminants in one or more spring orifices, even during conditions when there is no recharge from streams, indicates that they are present not only in focused recharge, but also within the aquifer matrix. These three contaminants also have been detected frequently in several wells in the Barton Springs segment.

Other pesticides (prometon, simazine), solvents (trichloroethene, 1,1,1-trichloroethane), and a drinking-water disinfection by-product (bromodichloromethane) were frequently detected in one or more of the spring orifices during routine sampling or storm sampling. The detection of additional contaminants in the four spring orifices in response to storms indicates that contaminants are present in or mobilized by focused recharge, and thus might be expected to diffuse or advect into the aquifer matrix over time, eventually resulting in occurrence of these contaminants at detectable concentrations in the water stored in the aquifer matrix. Numerous pesticides have been detected in the major streams recharging the Barton Springs segment at concentrations ranging from LRLs to near drinking-water MCLs.

Atrazine loads discharging from the spring orifices in response to storms made up only a small fraction (about 4 percent per storm) of the total annual load of atrazine discharging from the spring orifices (table 18). This indicates that contaminants both in stream water recharging under non-storm conditions (flow in the streams sometimes continues for days to months after storms) and in the aquifer matrix might be contributing to concentrations in discharge throughout the year. Computed contaminant load values indicate that although concentrations of some contaminants increase in response to storms, much of the annual contaminant load discharges under non-stormflow conditions.

The persistent occurrence of some contaminants and the intermittent occurrence of others is in contrast to previous results of Slade and others (1986), who stated that "no regional contamination problems [had] been identified by [their] water-quality sampling program" (p. 78). However, they did not measure VOCs, and the analytical methods for the detection of pesticides have improved greatly since 1986; LRLs have decreased by a factor of 10 or more. Additionally, numerous compounds have been added to the list of constituents measured. Thus, it is not known if contamination of Barton Springs has increased since the study of Slade and others, or if improved analytical methods have better enabled its identification.

Relation of Spring Geochemistry to Flow Paths

The geochemistry of samples collected from the four spring orifices provides information on their respective flow paths. Results of this study indicate that under most conditions, Upper Spring receives water from a different source or sources than the three other spring orifices, but following focused recharge shares a flow path with Main Spring; Main and Eliza Springs receive water from the same source or sources, except for immediately following storms, when Main Spring is fed by the flow path just described, shared with Upper Spring; Old Mill Spring receives water from the same sources feeding Main and Eliza Springs under non-recharge conditions and also receives water from an independent source when recharge is occurring. These results are both consistent with and complementary to the results of dye-tracing studies carried out by the Barton Springs/Edwards Aquifer Conservation District and the City of Austin (Barton Springs/Edwards Aquifer Conservation District, 2003; Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004; Hunt and others, 2006). Dye-tracing studies have identified four ground-water basins or flow paths: the Cold Springs flow path (which feeds only Cold Springs, not investigated for this study); the Sunset Valley flow path, which feeds Upper and Main Springs; the Manchaca flow path, which feeds Main and Eliza Springs and possibly Old Mill Spring; and a saline zone flow path, which feeds Old Mill Spring and, to some degree, also Main Spring (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004; Hunt and others, 2006).

The major ion and contaminant geochemistry at Main and Eliza Springs are almost indistinguishable, whereas Upper Spring has a very different geochemical and contaminant signature. In comparison to Main and Eliza Springs, Upper Spring has lower concentrations of several major ions (figs. 8, 9, 10), higher concentrations of nitrate and most contaminants (figs. 14, 17, 20), but lower concentrations of tetrachloroethene (fig. 20), indicating a shared flow path or flow paths for Main and Eliza Springs and a unique flow path for Upper Spring. However, dye-tracing study results have demonstrated that Upper and Main Springs share a flow path. In 1997 and 1999, dye injected into sinkholes in the Williamson Creek watershed was detected at Upper and Main Springs, but not in Eliza Spring or Old Mill Spring (Barton Springs/Edwards Aquifer Conservation District, 2003).

The apparent paradox between geochemical signatures and dye-tracing results might arise if there is an upper flow system that is activated only following storms. In both cases where dye was detected at Upper and Main Springs, the dye was injected into interstream sinkholes, rather than swallets in streambeds. Interstream recharge features only receive recharge immediately following storms. When the geochemical responses at Upper and Main Springs following storms are examined in detail, there is evidence of a flow path that feeds Upper and Main Springs following storms, but that does not feed Eliza Spring. A rapid decrease in specific conductance occurred simultaneously at the two springs following rainfall (fig. 26; Storm 1 on October 23 and again on November 1). The magnitude of the decrease was much greater at Upper Spring (decreases of about 35 and 15 μS/cm at Main Spring coinciding with decreases of about 300 and 200 μS/cm at Upper Spring on October 23 and November 1, 2004, respectively). A similar rapid decrease was observed at Main Spring for Storm 2 (decrease of 10 μS/cm on May 30); specific conductance data for Storm 2 are not available at Upper Spring. In no case was the decrease observed at Eliza Spring (fig. 26). Furthermore, the initial increase in concentrations of atrazine and simazine occurred simultaneously at Upper and Main Springs in response to Storms 1 and 2 (fig. 34). The peak concentration of atrazine at Upper Spring was about 6 times higher than that at Main Spring. The Upper Spring orifice exhibits much more pronounced responses in specific conductance and atrazine concentrations in comparison to Main Spring, which indicates that the shared flow path is a major flow path to the Upper Spring orifice but only a minor flow path to the Main Spring orifice. In addition, atrazine concentration peaked a second time for Main Spring and remained elevated for a longer period of time than at Upper Spring, indicating that Main Spring is fed by an additional flow path transporting atrazine. Finally, in response to storms, tetrachloroethene concentrations increase at Main Spring but decrease at Upper Spring (fig. 36).

The geochemistry of Main and Eliza Springs was extremely similar during the period of the study described here (figs. 10, 14, 17, 20), indicating that they are fed by the same source or sources of water under most conditions. In the 10 cases in which dye was detected at Eliza Spring, it also was detected at Main Spring (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004; Hunt and others, 2006). In four cases, dye was detected at Main Spring but not at Eliza Spring. In general, it appears that all of the flow paths feeding Eliza Spring also feed Main Spring, including the flow path contaminated with tetrachloroethene, but that there are one or more additional flow paths that feed only Main Spring. The very similar major ion and contaminant geochemistries at Main and Eliza Springs, however, indicate that any flow paths that they do not share are minor contributors to their respective flow volume.

Temporal trends in geochemistry at Old Mill Spring are similar to those at Main and Eliza Springs, but differences in concentrations of some major ions under all conditions and some contaminants under high recharge conditions indicate that there are additional sources of water to Old Mill Spring. Concentrations of major ions associated with the saline zone (sodium, potassium, chloride, and sulfate) are consistently higher at Old Mill Spring (figs. 8, 30, 31). Temporal patterns in major ion concentrations at Old Mill Spring in response to storms, however, are similar to those at Main and Eliza Springs (figs. 30, 31). Nitrate concentrations at Main, Eliza, and Old Mill Spring orifices are almost indistinguishable (fig. 14), although subtle differences indicate different amounts of dilution by recharge through streambeds (fig. 15). When little recharge is occurring (for example, July–September 2004), concentrations of pesticides and VOCs at Old Mill Spring are similar to those at Main and Eliza Springs, but different from those at Upper Spring (figs. 18, 20). The only exception is tetrachloroethene, concentrations of which are similar at all four springs when no recharge is occurring. During periods of recharge, concentrations of pesticides and VOCs at Old Mill Spring follow the same temporal patterns as those at Main and Eliza Springs, but have lower concentrations (figs. 18, 20). These patterns indicate that Old Mill Spring receives contaminants from the same flow paths as Main and Eliza Springs, but also is fed by one or more other flow paths that are less influenced by anthropogenic contaminants, resulting in some contaminant dilution. This hypothesis is consistent with the results of dye-tracing studies (Hauwert, Johns, and others, 2004; Hauwert, Samson, and others, 2004). Dye was detected in samples collected from Old Mill Spring following 10 of the 14 dye traces in which dye was detected at Main Spring; in all but one of these cases, the dye also was detected at Eliza Spring. However, in some cases the dye arrived at Old Mill Spring at a lower concentration or later than at Main and Eliza Springs; this behavior indicates dilution or bifurcation along a different flow path might be occurring.

Sources of Water to Barton Springs

An important source of water to Barton Springs is matrix water from the Barton Springs segment. When aquifer flow conditions are average to high and there is no recharge, spring discharge reflects this “Edwards aquifer” geochemistry, with concentrations of major ions and anthropogenic compounds that typify concentrations in the aquifer matrix (table 19, at end of report).

Recharge through the beds of major streams affects the geochemical composition and water quality of Main, Eliza, and Old Mill Springs. Such focused recharge continues for hours to months after rainfall, depending on the stream, the amount of rainfall, and antecedent conditions. Sulfate concentrations in Main, Eliza, and Old Mill Springs increase linearly with recharge, and magnesium and strontium concentrations (and sodium, potassium, and chloride concentrations at Old Mill Spring) decrease with recharge. No evidence for upward leakage from the underlying Trinity aquifer, which is a previously hypothesized source of elevated sulfate (City of Austin, 1997; Slade and others, 1986), was indicated by recent data. However, historical data indicate that water from the Trinity aquifer might affect major ion concentrations at some wells, particularly during high aquifer flow conditions (Garner and Mahler, 2006). Recharge affects the aqueous geochemistry of Upper Spring during storms, but its contribution during non-stormflow conditions is much less pronounced than at the three other springs. The major ion geochemistry of Upper Spring was unaffected by recharge except during about 1 week following the storms sampled, indicating that Upper Spring might be receiving recharge from one or more streams that are extremely ephemeral (that is, Slaughter or Williamson Creeks as opposed to Barton, Onion, or Bear Creeks) or from an interstream recharge feature. There is no evidence that quality of water in the other springs is more sensitive to the quality of streamflow from any one stream. Concentrations of nitrate in samples from Main, Eliza, and Old Mill Spring orifices decrease with increasing recharge, indicating that under all but extreme stormflow conditions the source of the nitrate to these three springs is the aquifer matrix, and thus might not be anthropogenic. In contrast, elevated concentrations of nitrate at Upper Spring relative to the three other springs indicates a potential anthropogenic source of nitrate to this spring. Recharge from major streams affects concentrations of some contaminants in the springs. There is a significant relation between recharge and concentrations of one VOC and two pesticides: At Main Spring, there is a significant and strongly positive relation between tetrachloroethene concentration and recharge and a significant but weakly positive relation between simazine concentration and recharge.

At Upper Spring, there is a significant and strongly negative relation between tetrachloroethene concentration and recharge and a significant but weakly positive relation between atrazine concentration and recharge.

Several lines of evidence indicate that water recharging Upper Spring under non-stormflow conditions might infiltrate through the soil zone rather than as focused recharge through streambeds. Upper Spring had concentrations of silica, nitrate, and arsenic that were elevated relative to concentrations at the other springs, which might indicate leaching from soils. Strontium isotope ratios (strontium-87/strontium-86) in samples from Upper Spring are more radiogenic than those in samples from the other springs, which indicates a greater contribution from soils (Garner, 2005). Finally, the median atrazine/DEA ratio at Upper Spring is less than that at the three other springs, which would result from a longer residence time in soils. All of these factors collectively suggest a greater soil influence on the spring-water geochemistry at Upper Spring. Although the hydrologic dynamics controlling recharge through the soil zone largely are unknown, factors such as surface geomorphology or the balance of recharge through interstream sinkholes compared to overland flow to streams might be contributing factors.

The geochemistry of water from Old Mill Spring has some similar characteristics to Upper Spring that are suggestive that water at this spring orifice might have recharged through the soil zone, although the geochemical evidence is less definitive than for Upper Spring. Strontium isotope ratios are more radiogenic at Old Mill Spring than those at Main and Eliza Springs, although less radiogenic than those at Upper Spring (Garner, 2005). Also, the median arsenic concentration and atrazine/DEA ratio at Old Mill Spring are intermediate between those of Upper Spring and Main and Eliza Springs. However, there are relatively strong relations between flow in recharging streams (represented by recharge) and major ion concentrations in samples from Old Mill Spring (table 5). Thus, the geochemistry at Old Mill Spring might be influenced both by focused recharge through streambeds and by recharge through the soil zone.

Aquifer Functioning in Response to Flow Conditions

The results of the investigation of Storms 1 and 2 are consistent with the conceptual understanding of karst aquifers presented in the “Introduction, Overview of Karst Systems” section, which implies that the concentrations and loads of contaminants delivered as focused recharge from the surface to Barton Springs are highest under low aquifer flow conditions. This likely results in part from decreased dilution by ground water. However, it also might result from a change in the way that the contaminants are transported through the conduit system. When the water table lies below the conduit system, the conduits are partially or fully drained, and focused recharge moves through them with little to no dilution and with limited loss to storage. In contrast, when aquifer flow conditions are high, the conduits are already saturated with water; focused recharge therefore is diluted by the water in the conduits, and peak concentrations of contaminants at the spring orifices are lower. Under these high aquifer flow conditions, much of the recharge and associated contaminants go into matrix storage. The results from Storms 1 and 2 are consistent with this conceptual model: the peak concentration of atrazine at the Main Spring orifice following Storm 1 (average aquifer flow conditions) was 0.070 μg/L and following Storm 2 (high aquifer flow conditions) was 0.044 μg/L, even though the atrazine concentrations in all of the recharging streams were higher for Storm 2 than for Storm 1. The peak atrazine concentration in Main Spring following a storm in June 2000, when aquifer flow conditions were extremely low (Barton Springs discharge of 17 ft^3/s), was 8 and 13 times higher than the peak concentrations for Storms 1 and 2, respectively (Mahler and Van Metre, 2000). Additionally, the amount of atrazine recovery decreased as flow increased, from 64 percent (Storm 1) to 23 percent (Storm 2), indicating that a greater proportion of the atrazine in recharge went into storage under high aquifer flow conditions. Contaminants that go into storage under high aquifer flow conditions are slowly released from the matrix into spring discharge as the aquifer drains, likely resulting in an increase in the concentration of contaminants in base flow over the long term. The potential for long-term storage and release of contaminants is demonstrated by tetrachloroethene. Intermittent detection of tetrachloroethene in Barton Springs discharge pre-dates 1989; its detection is now ubiquitous, and the minimum concentration measured at Main Spring during this study was 0.042 μg/L.

The contrasting response of spring discharge to the two sampled storms also is consistent with the conceptual model for aquifer functioning and indicates that during high aquifer flow conditions, more recharge goes into storage (fig. 38). Under high aquifer flow conditions (Storm 2), there was no change in spring discharge in response to the storm, indicating that most of the recharge went into storage. Under average flow conditions (Storm 1), spring discharge increased about 10 ft^3/s in response to the storm and then remained constant, consistent with a hypothesis that some of the recharge went into storage. In contrast, following the storm sampled in June 2000 under very low aquifer flow conditions, Barton Springs discharge initially increased in response to the storm and then decreased over a period of about 1 week, which might reflect the filling and subsequent draining of the conduit system with little recharge going into storage (Mahler and Massei, 2007).

Limitations of This Investigation

The results of this investigation provide a more detailed characterization of water quality in Barton Springs than previously existed and enhance understanding of aquifer functioning. However, in answering some questions, others are raised. First, aquifer flow conditions were average to high for the entire sample-collection period. The effect of low aquifer flow conditions on flow paths, saline zone influence, geochemical response to storms, and occurrence and concentration of anthropogenic compounds is largely unknown, although some insight was gained by analyzing the historic major ion geochemistry of Main Spring (appendixes 1, 2). Second, although a range of compounds was measured as part of this study, they were not measured at all springs and recharging creeks under a full spectrum of hydrologic conditions. The response of concentrations of anthropogenic compounds in Eliza and Old Mill Springs to stormflow was not investigated, and the response of concentrations of dissolved metals to stormflow is unknown. Other anthropogenic compounds that were not investigated in this study might or do occur in the Barton Springs segment (for example, wastewater indicators, bacteria, and other pesticides not measured as part of this study), but little is known of their behavior in Barton Springs. Temporal variability in contaminant concentrations in wells and streams in response to storms is not known. A study of combined dye-tracing of a storm event with sample collection at the springs has not been done, but might provide valuable information on contaminant sources. And finally, while results of the two monitored storms provide some understanding of how the aqueous geochemistry and water quality of Barton Springs change in response to storms, they represent only a very limited range of the types of storm conditions that occur.

Summary

The central Texas area is undergoing rapid population growth and land-use changes. The quality of ground water discharging from Barton Springs (comprised of four spring orifices: Upper, Main, Eliza, and Old Mill Springs) in Austin, Tex., is of interest to a wide range of stakeholders and water managers. Water quality at Barton Springs is of interest for a number of reasons: Barton Springs supplies a 750-ft-long swimming pool, is part of the City of Austin's municipal water supply, and is the only known habitat for the Barton Springs salamander (*Eurycea sosorum*). The Barton Springs salamander is a federally-listed endangered species and has been found at all four spring orifices.

About 85 percent of aquifer recharge is provided by major streams that cross the recharge zone. More than 90 percent of natural (non-pumped) discharge from the Barton Springs segment is from the four spring orifices that comprise Barton Springs, which has an average combined discharge of about 50 ft^3/s. Ground-water flow generally is to the north-northeast, although understanding of the flow system at a small scale is confounded by the presence of karst conduits and the heterogeneity of the system. Dye-tracing studies have provided insight into the behavior of the aquifer and the rapid water movement through conduits and have shown that the four spring orifices obtain water from one or more of several flow paths.

The focus of this investigation was a comprehensive characterization of water quality including the occurrence of anthropogenic compounds, such as pesticides and volatile organic compounds (VOCs). The purpose of this report is to (1) describe recent (2003–05) water quality of the four Barton Springs orifices; (2) describe the major ion and contaminant chemistry of Barton Springs over an annual cycle and identify possible reasons for spatial and temporal variability; (3) describe the response of major ion and contaminant chemistry of Barton Springs to rainfall that results in stormflow in major recharging streams and identify possible reasons for similarity and variability between the spring orifices; and (4) synthesize the information gained to identify factors that influence water quality, including aquifer flow paths, sources of water to the aquifer, and aquifer flow conditions.

For this investigation, carried out by the U.S. Geological Survey in cooperation with the Texas Commission on Environmental Quality, a three-pronged approach was used to characterize recent (2003–05) water quality in Barton Springs. Water-quality data included continuous 15-minute measurements of spring discharge and physicochemical properties at spring orifices; analysis of major ions, nutrients, trace elements, pesticides, VOCs, and pharmaceutical compounds in samples collected from the four springs every 2 weeks during August–September 2003 (Phase 1) and analysis of a combination of those compound groups in samples collected from the springs every 3 weeks during June 2004–June 2005 (Phase 2); and analysis of major ions and nitrate for the four spring orifices and of pesticides and VOCs for two of the spring orifices (Upper and Main Springs) in samples collected at closely-spaced intervals for 2 weeks following two storms.

Continuous measurement of Barton Springs discharge and of Main Spring physicochemical properties indicated variations in water quantity and characteristics during 2003–05. Discharge exceeded 60 ft^3/s during both Phase 1 and Phase 2, thus the results of the study represent water quality in the aquifer under average-to-high flow conditions. Specific conductance varied from 464 to 683 $\mu S/cm$; temporal changes mostly consisted of gradual increases punctuated by rapid changes (as much as 43 $\mu S/cm$ per hour) in response to storm events and draining of Barton Springs Pool. Turbidity varied from 0 to about 74 NTU; 95 percent of measurements were less than 5.7 NTU, and higher values occurred in response to storm events. Water temperature and pH varied little, highlighting both the physical and chemical buffering capacity of the aquifer rocks. Although measurement of dissolved oxygen was affected by instrument reliability, the data indicate that spring discharge is always aerobic and that large amounts of recharge might increase dissolved oxygen concentrations.

Major ion samples collected from the four springs showed systematic differences among spring orifices. Old Mill Spring had the highest concentrations of most major ions, Main and Eliza Springs had intermediate and very similar concentrations, and Upper Spring had lower concentrations of most major ions. On the basis of principal components analysis, 80 percent of the variability in major ion concentrations was explained by three factors, interpreted as representing (1) the influence of the saline zone, (2) an intrinsic geochemical signature of the aquifer matrix, and (3) the effect of recent recharge. Old Mill Spring was the most affected and Upper Spring was the least affected by the saline zone factor; Main and Eliza Springs were weighted

similarly for all three factors, indicating that they have very similar geochemical compositions.

Recharge exerts a strong influence on concentrations of several major ion concentrations: there were significant linear relations for 17 of 36 possible cases, and the relations were relatively strong (median $r^2 = .51$). There was a positive correlation between sulfate concentrations in spring samples and recharge, which might result from elevated sulfate concentrations in recharging stream water relative to ground water. A positive correlation between spring-water calcium and recharge might reflect carbonate water-rock interaction processes; water-rock interaction with minor amounts of gypsum might also contribute to the positive relation between recharge with both sulfate and calcium concentration. Significant correlations between other major ion concentrations and recharge were negative, indicating dilution of ions in ground water by recharging surface water. Variability in major ion concentrations is not well explained by Barton Springs discharge: except for strontium, the few significant relations were relatively weak (median $r^2 = .30$). However, historical data indicate that at spring discharge below about 40 ft^3/s (lower than discharge occurring during the periods when the samples for this study were collected), aquifer flow condition exerts a much stronger influence on major ion concentrations, in particular chloride, sodium, and sulfate.

Nitrate concentrations in Main, Eliza, and Old Mill Springs during the period of study were very similar, and were significantly negatively related to recharge. Recharging water from streams generally has concentrations of nitrate that are low relative to ground water. An upper limit of 1.5 mg/L for nitrate in samples from these three spring orifices was attained only when there was little to no recharge. The aquifer appears to have a baseline nitrate concentration of about 1.5 mg/L, which is diluted to different degrees by recharge along different flow paths, a hypothesis that is consistent with historical data. Nitrate concentrations in Upper Spring samples were higher and more variable than in samples from Main, Eliza, and Old Mill Springs, indicating that there might be an anthropogenic source contributing nitrate to Upper Spring. Nitrate concentrations in samples from Upper Spring were unrelated to recharge except immediately following storms.

Dissolved trace metals (cadmium, chromium, copper, lead, nickel, zinc, and arsenic) were analyzed in the spring samples during Phase 1. Copper, nickel, and arsenic were detected in all samples at very low concentrations; nickel and arsenic might have natural sources in the aquifer rock. Chromium was detected only in samples collected on one date following rainfall, indicating that anthropogenic chromium in surface runoff might discharge from the springs. Concentrations of all metals were well below U.S. Environmental Protection Agency maximum contaminant levels (MCLs) for drinking water.

A suite of 52 soluble pesticides was analyzed in all samples collected during Phase 1 and in samples from Main and Upper Springs collected during Phase 2. Atrazine (an herbicide) and deethylatrazine (DEA; a degradate of atrazine) were the most frequently detected pesticides (88 percent of samples), followed by simazine and prometon (32 and 22 percent of samples, respectively). In most cases pesticide concentrations were higher in samples from Upper Spring than in the other springs; atrazine was detected in every sample from Upper Spring, and prometon was detected only in samples from Upper Spring with one exception. Concentrations of pesticides measured during the study were very low relative to drinking-water standards; the maximum concentration measured was about 0.08 μg/L of atrazine (MCL 3.0 μg/L) in a sample from Upper Spring. There was a significant but weak positive relation between atrazine concentration and recharge for Upper Spring ($r^2 = .22$) and between simazine concentration and recharge for Main Spring ($r^2 = .29$).

A suite of 88 VOCs was analyzed in all samples collected during Phase 1 and in samples collected from Upper and Main Springs during Phase 2. Chloroform (a trihalomethane [THM] or drinking-water disinfection by-product) and tetrachloroethene (an industrial solvent) were detected in every sample analyzed. Other VOCs frequently detected included bromodichloromethane (a THM detected in 50 percent of samples from Upper Spring), carbon disulfide (an industrial VOC detected in 38 percent of samples from Old Mill Spring), and trichloroethene (an industrial solvent and a degradate of tetrachloroethene detected in 36 percent of samples from Main Spring). Concentrations of VOCs measured during the study were very low; the maximum concentration of tetrachloroethene was 0.34 μg/L, and the maximum concentration of chloroform was 0.15 μg/L; the MCLs for these VOCs are 5 μg/L (tetrachloroethene) and 80 μg/L (total THMs), respectively. Tetrachloroethene concentration was positively correlated with recharge at Main Spring and negatively correlated with recharge at Upper Spring, indicating a source of tetrachloroethene somewhere along the flow path leading to Main Spring, and likely also to Eliza and Old Mill Springs, as concentrations and patterns of tetrachloroethene contamination at those two springs are similar to those for Main Spring. There was a negative correlation between chloroform concentration and recharge at Upper Spring for recharge less than 25 ft^3/s.

Pharmaceutical compounds were analyzed four times for samples from Main Spring and three times for samples from Upper Spring during Phase 2. Cotinine (a nicotine metabolite), acetaminophen, and caffeine were each detected at least twice. Fifteen pharmaceutical compounds were detected in one sample collected from Main Spring; it is unknown why so many compounds were detected in this sample relative to other samples.

The total annual loads of the three most frequently detected contaminants—atrazine, chloroform, and tetrachloroethene—discharging under non-stormflow conditions from Barton Springs were computed on the basis of routine sample concentrations and daily spring discharge. The total annual loads were estimated to be 1.1 kg of atrazine, 4.2 kg of chloroform, and 12 kg of tetrachloroethene.

During Phase 2, samples were collected from the four spring orifices during the 2 weeks following two storms that resulted in flow in the major streams contributing recharge to the aquifer. Samples also were collected from the streams at the downstream end of the recharge zone during these storms. Most of the rainfall for both storms occurred over the recharge zone; for all streams except Barton Creek the rise in the hydrograph was sharp, and streamflow rapidly returned to low-flow or no-flow conditions. Barton Springs discharge response to the two storms was different. Following Storm 1 (October 2004), which occurred during average aquifer flow conditions, spring discharge increased by about 10 ft^3/s and then remained constant. Following Storm 2 (May 2005), which occurred during high aquifer flow conditions, spring discharge did not change. Changes in specific conductance at Main, Eliza, and Old Mill Springs were similar among the springs, with Old Mill being somewhat more muted, but the response to Storm 1 was greater than that to Storm 2. Numerous specific conductance minima indicated timing of individual pulses of recharge moving through the aquifer. The response of specific conductance at Upper Spring, available only for Storm 1, was very different from that at the other springs. The decrease in specific conductance at Upper Spring was about 3 times greater than that at Main Spring. Analysis of turbidity response at Upper and Main Springs for Storm 1 indicated that the sediment dynamics at Upper Spring were substantially different from those at Main Spring. At Upper Spring there was an early increase in specific conductance accompanied by a massive increase in turbidity: the maximum value of turbidity was about 7 times higher than that at Main Spring. This behavior might result from unplugging a blocked karst conduit.

The response of concentrations of major ions to the two storms varied among sites, among ions, and between storms. Variations in major ion concentrations at Main, Eliza, and Old Mill Springs were similar to each other and different from variations at Upper Spring. All springs showed dilution for most major ions, but dilution at Upper Spring was more rapid and more pronounced, indicating an initial large contribution of surface water. At the three other springs, dilution of major ion concentrations was more muted for Storm 2 than for Storm 1. One ion, potassium, increased in all four springs following Storm 1 and in Upper Spring following Storm 2; potassium increases in response to stormflow is hypothesized to result from infiltration of storm runoff containing fertilizer. Nitrate concentrations at the four springs were similar to patterns in specific conductance, indicating that recharge water is diluting ambient concentrations of nitrate in the ground water.

At Main and Upper Springs, concentrations of atrazine, DEA, simazine, and prometon (Upper Springs only) described breakthrough curves in response to the storms, with concentrations beginning to increase within less than 32 hours of rainfall. At Upper Spring, four pesticide compounds not detected during routine sampling—carbaryl, diazinon, fipronil, and fipronil sulfone—were detected in several samples after one or both storms. Concentrations of chloroform and tetrachloroethene described breakthrough curves at Main Spring following both storms and described anti-breakthrough, or dilution, curves at Upper Spring. Trichloroethene, a solvent and a degradation product of tetrachloroethene, described a breakthrough curve similar to that of tetrachloroethene in Main Spring following Storm 2, although the concentrations were very low. Of the pharmaceutical compounds analyzed in selected stormflow samples from Main Spring, only caffeine was detected.

The total load of atrazine, chloroform, and tetrachloroethene discharging from Main, Old Mill, and Eliza Springs was determined for each storm; the corresponding load in recharge was computed for atrazine, which was the only one of the three contaminants that was analyzed for in surface water. An estimated 64 and 23 percent of atrazine in recharge was exported as spring discharge in the 2 weeks following Storms 1 and 2, respectively, indicating that much of the atrazine and other contaminants contained in recharging stormwater entered temporary storage, later to discharge slowly during non-stormflow conditions. Concentrations and loads of atrazine were higher in all of the streams sampled for Storm 2 (spring) than for Storm 1 (autumn), but concentrations measured in Williamson and Slaughter Creeks for the two storms were similar, indicating year-round use of atrazine; concentrations measured in Slaughter Creek (2.2 and 2.9 μg/L for Storms 1 and 2, respectively) were near the MCL of 3.0 μg/L.

Existing information on the hydrogeology of Barton Springs, the routine sampling of the four spring orifices, and the sampling of the springs in response to storms can be synthesized to provide information on water quality in Barton Springs. The water quality of the Barton Springs segment is affected by persistent low levels of atrazine, chloroform, and tetrachloroethene, and the intermittent occurrence of higher levels of these and additional anthropogenic compounds. The ubiquitous detection of these contaminants in one or more spring orifices, even during conditions when there is little to no recharge occurring, indicates that they are present within the aquifer matrix as well as in storm recharge.

The detection of additional contaminants in the springs in response to storms indicates that the contaminants occur in focused recharge, and in time might also be expected to occur at detectable concentrations in the water stored in the aquifer matrix. Estimated values of contaminant loads indicate that even with increasing contaminant concentrations in response to storms, much of the total contaminant load discharges during non-stormflow conditions. Annual loads of atrazine discharging from the aquifer under non-stormflow conditions are about 25 times greater than the loads discharged following the two individual storms monitored.

Recharge from streams affects the major ion geochemical composition and water quality of Main, Eliza, and Old Mill Springs whenever there is surface-water flow, which can continue for days, weeks, or even months after rainfall. Historical samples collected from Main Spring indicate that the geochemical composition of spring water generally is calcium-magnesium-bicarbonate, and that much of the geochemical variability is related to aquifer flow conditions. When Barton Springs discharge is less than about 40 ft^3/s, concentrations of sodium, chloride, and sulfate are inversely proportional to discharge, indicating some influx of saline zone water into the springs. At discharge greater than 40 ft^3/s, this relation ceases.

Nitrate concentrations rarely exceed 1.5 mg/L, although that concentration was measured in about 20 percent of samples.

The geochemistry of Barton Springs is consistent with and complementary to the results of dye-tracing studies carried out during 1997–2005. On the basis of the results of this investigation, under most conditions Upper Spring receives water from a different source or sources than the three other spring orifices, but following focused recharge Upper Spring shares a flow path with Main Spring. The origin of the water moving along this shared flow path is likely one or more interstream recharge features. With the exception of this additional source of water to Main Spring, Main and Eliza Springs share the same flow paths. Old Mill Spring receives water from the same sources feeding Main and Eliza Springs under non-recharge conditions, but receives water from additional, less contaminated sources when recharge is occurring.

Sources of water to Barton Springs include the matrix water from the Barton Springs segment, the recharging streams, and the soil zone. The proportional contribution of each of these depends on recharge and aquifer flow conditions. There are several lines of geochemical evidence indicating that Upper Spring, and to a lesser degree Old Mill Spring, might receive more recharge through the soil zone under non-storm conditions than do Main and Eliza Springs. Geochemical indicators for this include major ion, nitrate, and trace metal concentrations, strontium isotope ratios, and atrazine/DEA ratios.

Geochemical results are consistent with a conceptual model in which aquifer flow conditions affect the concentration and load of contaminants delivered to the springs following storms, as well as the amount of contaminants and recharge that go into storage. When aquifer flow conditions are low, some or all of the conduit network is drained; focused recharge entering the conduits is transported rapidly to the springs with little dilution or loss to storage. In contrast, when aquifer flow conditions are high, the conduit network is saturated with ground water advecting from the matrix. Focused recharge thus is diluted and retarded in the conduits, and much of the recharge and associated contaminants are stored within the matrix. The potential for long-term storage and release of contaminants is demonstrated by tetrachloroethene. The intermittent detection of tetrachloroethene in Barton Springs recharge pre-dates 1989; its detection now is ubiquitous in spring flow.

The results of this study provide a more detailed characterization of water quality in Barton Springs than existed previously and enhance understanding of aquifer functioning, but as questions are answered, others are raised. Future research might include investigation of: long-term temporal trends; water quality during low aquifer flow conditions; response of concentrations of anthropogenic compounds in Eliza and Old Mill Springs to storms; occurrence and behavior of other contaminants not analyzed during this study; and the effect of storm size, season, and concurrent aquifer flow conditions on contaminant response.

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Table 6. Concentrations of nutrients in routine samples, Barton Springs, Austin, Texas (2003–05).

[In milligrams per liter. E, estimated; <, nondetection; --, not sampled for]

Site	Date	Ammonia nitrogen	Ammonia plus organic nitrogen, total	Nitrite nitrogen	Nitrite plus nitrate nitrogen, dissolved	Ortho-phosphate phosphorus	Phosphorus, filtered	Phosphorus, total
Upper Spring	08/06/2003	E0.014	<0.1	<0.008	3.49	E0.013	<0.035	<0.04
	08/20/2003	E.009	<.1	<.008	2.02	E.015	<.035	<.04
	09/03/2003	E.008	E.053	<.008	2.08	<.018	<.035	<.04
	09/16/2003	E.011	E.056	<.008	1.73	<.18	E.024	E.027
	09/30/2003	E.01	<.1	<.008	2.22	E.01	<.035	<.04
	06/21/2004	--	--	--	1.97	--	--	--
	07/07/2004	--	--	--	1.65	--	--	--
	07/21/2004	--	--	--	1.95	--	--	--
	08/04/2004	--	--	--	1.94	--	--	--
	08/25/2004	<.01	<.1	<.008	2.09	<.018	E.022	<.04
	09/15/2004	--	--	--	2.32	--	--	--
	10/04/2004	--	--	--	1.98	--	--	--
	11/05/2004	--	--	--	1.80	--	--	--
	11/24/2004	--	--	--	.873	--	--	--
	12/14/2004	<.01	<.1	<.008	2.18	<.018	<.04	<.04
	01/03/2005	--	--	--	2.23	--	--	--
	01/26/2005	--	--	--	2.09	--	--	--
	02/16/2005	--	--	--	2.19	--	--	--
	03/09/2005	<.01	E.054	<.008	1.94	<.018	<.04	<.04
	03/30/2005	--	--	--	2.20	--	--	--
	04/20/2005	--	--	--	2.13	--	--	--
	05/11/2005	--	--	--	1.95	--	--	--
	06/09/2005	--	--	--	2.11	--	--	--
Main Spring	08/06/2003	E.012	<.1	<.008	1.45	<.018	<.035	<.04
	08/20/2003	<.015	<.1	<.008	1.47	E.009	<.035	<.04
	09/03/2003	<.015	E.079	<.008	1.46	<.018	<.035	<.04
	09/16/2003	E.008	<.1	E.005	1.44	<.18	E.019	<.04
	09/30/2003	E.008	<.1	<.008	1.50	<.018	<.035	<.04
	06/21/2004	--	--	--	1.05	--	--	--
	07/07/2004	--	--	--	1.02	--	--	--
	07/21/2004	--	--	--	.958	--	--	--
	08/04/2004	--	--	--	1.06	--	--	--
	08/25/2004	<.01	<.1	<.008	1.17	<.018	<.04	<.04
	09/15/2004	--	--	--	1.31	--	--	--
	10/04/2004	--	--	--	1.33	--	--	--
	11/05/2004	--	--	--	.886	--	--	--
	11/24/2004	--	--	--	1.65	--	--	--
	12/14/2004	<.01	<.1	<.008	1.18	<.018	<.04	<.04
	01/03/2005	--	--	--	1.22	--	--	--
	01/26/2005	--	--	--	1.20	--	--	--
	02/16/2005	--	--	--	1.18	--	--	--
	03/09/2005	<.01	E.075	<.008	1.12	<.018	<.04	<.04
	03/30/2005	--	--	--	1.18	--	--	--
	04/20/2005	--	--	--	1.21	--	--	--
	05/11/2005	--	--	--	1.21	--	--	--
	06/09/2005	<.01	<.1	<.008	1.29	<.018	<.04	<.04

Table 6. Concentrations of nutrients in routine samples, Barton Springs, Austin, Texas (2003–05)—Continued.

Site	Date	Ammonia nitrogen	Ammonia plus organic nitrogen, total	Nitrite nitrogen	Nitrite plus nitrate nitrogen, dissolved	Ortho-phosphate phosphorus	Phosphorus, filtered	Phosphorus, total
Eliza Spring	08/06/2003	E0.014	<0.1	<0.008	1.39	<0.018	<0.035	<0.04
	08/20/2003	E.009	<.1	<.008	1.41	<.018	<.035	<.04
	09/03/2003	<.015	E.063	<.008	1.41	<.018	<.035	<.04
	09/16/2003	E.009	<.1	<.008	1.41	<.18	<.035	<.04
	09/30/2003	E.008	<.1	<.008	1.45	<.018	<.035	<.04
	06/21/2004	--	--	--	.992	--	--	--
	07/07/2004	--	--	--	.942	--	--	--
	07/21/2004	--	--	--	.909	--	--	--
	08/04/2004	--	--	--	.985	--	--	--
	08/25/2004	<.01	<.1	<.008	1.12	<.018	<.04	<.04
	09/15/2004	--	--	--	1.24	--	--	--
	10/04/2004	--	--	--	1.32	--	--	--
	11/05/2004	--	--	--	.842	--	--	--
	11/24/2004	--	--	--	1.63	--	--	--
	12/14/2004	<.01	<.1	<.008	1.14	<.018	<.04	<.04
	01/03/2005	--	--	--	1.17	--	--	--
	01/26/2005	--	--	--	1.16	--	--	--
	02/16/2005	--	--	--	1.13	--	--	--
	03/09/2005	<.01	E.073	<.008	1.08	<.018	<.04	<.04
	03/30/2005	--	--	--	1.14	--	--	--
	04/20/2005	--	--	--	1.17	--	--	--
	05/11/2005	--	--	--	1.18	--	--	--
	06/09/2005	--	--	--	1.23	--	--	--
Old Mill Spring	08/06/2003	E.013	E.068	<.008	1.41	<.018	<.035	E.023
	08/20/2003	E.008	<.1	<.008	1.46	E.009	<.035	<.04
	09/03/2003	<.015	E.071	<.008	1.48	<.018	<.035	<.04
	09/16/2003	<.015	<.1	<.008	1.48	<.18	<.035	<.04
	09/30/2003	E.009	<.1	<.008	1.47	<.018	<.035	<.04
	06/21/2004	--	--	--	.960	--	--	--
	07/07/2004	--	--	--	.906	--	--	--
	07/21/2004	--	--	--	.887	--	--	--
	08/04/2004	--	--	--	.969	--	--	--
	08/25/2004	<.01	<.1	<.008	1.14	<.018	<.04	<.04
	09/15/2004	--	--	--	1.24	--	--	--
	10/04/2004	--	--	--	1.35	--	--	--
	11/05/2004	--	--	--	.933	--	--	--
	11/24/2004	--	--	--	1.50	--	--	--
	12/14/2004	<.01	<.1	<.008	1.10	<.018	<.04	<.04
	01/03/2005	--	--	--	1.15	--	--	--
	01/26/2005	--	--	--	1.16	--	--	--
	02/16/2005	--	--	--	1.17	--	--	--
	03/09/2005	<.01	E.069	<.008	1.15	<.018	<.04	<.04
	03/30/2005	--	--	--	1.22	--	--	--
	04/20/2005	--	--	--	1.25	--	--	--
	05/11/2005	--	--	--	1.28	--	--	--
	06/09/2005	--	--	--	1.31	--	--	--

Table 7. Concentrations of dissolved metals in routine samples, Barton Springs, Austin, Texas, Phase 1 sampling (2003).

[In micrograms per liter. <, nondetection; E, estimated]

Site name	Sample date	Cadmium, filtered	Chromium, filtered	Copper, filtered	Lead, filtered	Nickel, filtered	Zinc, filtered	Arsenic, filtered
Upper Spring	08/06/2003	<0.04	<0.8	0.6	E0.04	2.83	1.1	0.5
	08/20/2003	<.04	<.8	.4	<.08	3.21	<1	.5
	09/03/2003	<.04	<.8	.7	<.08	1.18	<1	.4
	09/16/2003	<.04	E.4	.7	<.08	.71	E.5	.5
	09/30/2003	<.04	<.8	.4	<.08	1.19	E1	.6
Main Spring	08/06/2003	<.04	<.8	.6	<.08	1.94	E1	.4
	08/20/2003	<.04	<.8	.4	<.08	3.12	<1	.4
	09/03/2003	<.04	<.8	.8	<.08	1.16	E.5	.4
	09/16/2003	<.04	<.8	.6	<.08	.58	<1	.4
	09/30/2003	<.04	<.8	.4	<.08	1.08	<1	.5
Eliza Spring	08/06/2003	<.04	<.8	.7	<.08	2.00	1	.4
	08/20/2003	<.04	<.8	.4	<.08	3.11	<1	.4
	09/03/2003	<.04	<.8	.7	<.08	1.06	<1	.3
	09/16/2003	<.04	E.4	1.1	.11	.70	2	.4
	09/30/2003	<.04	<.8	.4	<.08	1.27	<1	.5
Old Mill Spring	08/06/2003	<.04	<.8	.5	<.08	2.71	<1	.5
	08/20/2003	<.04	<.8	.5	<.08	3.05	E.6	.5
	09/03/2003	<.04	E.5	.7	<.08	1.02	<1	.5
	09/16/2003	<.04	<.8	.6	<.08	.67	1.1	.6
	09/30/2003	<.04	<.8	.5	<.08	1.21	1	.5

Table 8. Concentrations of pesticide compounds detected in routine samples, Barton Springs, Austin, Texas (2003–05).

[In micrograms per liter. E, estimated; <, nondetection; --, not sampled for]

Site	Date	Sample time	Atrazine	Deethyl-atrazine	Prometon	Simazine
Upper Spring	08/06/2003	1145	0.012	E0.013	E0.007	0.0065
	08/20/2003	0830	.014	E.012	E.007	E.0045
	09/03/2003	0800	.013	E.014	E.007	<.005
	09/16/2003	0730	.046	E.014	E.008	.016
	09/30/2003	0700	.013	E.016	E.005	<.005
	06/21/2004	1430	.077	E.033	.008	.0074
	07/07/2004	1300	.042	E.029	.005	.009
	07/21/2004	0730	.028	E.020	<.005	<.01
	08/04/2004	0800	.030	E.022	<.01	.0098
	08/25/2004	1000	.025	E.024	.007	<.01
	09/15/2004	0900	.020	E.014	.007	<.005
	10/04/2004	1200	.028	E.018	<.01	<.01
	11/05/2004	0930	.043	E.026	<.01	.0092
	12/14/2004	1500	.028	E.025	<.01	<.0076
	01/03/2005	0930	.021	E.026	<.01	.0069
	01/26/2005	0930	.017	E.022	<.01	.0070
	02/16/2005	0800	.015	E.023	<.01	.0066
	03/09/2005	0730	.054	E.025	E.009	E.0033
	03/30/2005	0800	.022	E.020	<.01	<.005
	04/20/2005	0730	.013	E.020	<.01	.0066
	05/11/2005	0800	.053	E.027	E.006	E.0043
	06/09/2005	0000	.021	E.026	E.005	E.0046
Main Spring	08/06/2003	1145	<.007	E.0055	<.015	<.005
	08/20/2003	0830	<.007	<.006	<.015	<.005
	09/03/2003	0800	E.0058	E.0056	<.015	<.005
	09/16/2003	0730	.012	E.0058	<.015	<.005
	09/30/2003	0700	E.0061	E.0043	<.015	<.005
	06/21/2004	1430	.019	E.011	<.005	E.0049
	07/07/2004	1300	.016	E.012	<.005	<.01
	07/21/2004	0730	.011	E.0077	<.005	.0073
	08/04/2004	0800	.011	E.0075	<.005	<.005
	08/25/2004	1000	.010	E.0086	<.005	<.005
	09/15/2004	0900	.012	E.0076	<.005	<.005
	10/04/2004	1200	.013	E.0078	<.005	<.005
	11/05/2004	1030	.018	E.008	<.01	<.01
	12/14/2004	1500	<.007	E.0068	<.01	<.005
	01/03/2005	0930	E.0047	E.0066	<.01	<.005
	01/26/2005	0930	E.0042	E.006	<.01	<.005
	02/16/2005	0800	E.0052	E.0062	<.01	.0086
	03/09/2005	0730	.037	E.0086	<.01	<.015
	03/30/2005	0800	.016	E.0057	<.01	E.0037
	04/20/2005	0730	.0089	E.0058	<.01	<.005
	05/11/2005	0800	.021	E.008	<.01	E.002
	06/09/2005	0000	.012	E.0096	<.01	<.005

Table 8. Concentrations of pesticide compounds detected in routine samples, Barton Springs, Austin, Texas (2003–05)—Continued.

Site	Date	Sample time	Atrazine	Deethyl-atrazine	Prometon	Simazine
Eliza Spring	08/06/2003	0000	E0.0062	E0.0056	<0.015	<0.005
	08/20/2003	0000	<.007	<.006	<.015	<.005
	09/03/2003	0000	E.0057	E.0034	<.015	<.005
	09/16/2003	0000	.008	<.006	<.015	<.005
	09/30/2003	0000	<.007	<.006	<.015	<.005
	08/25/2004	0000	.0093	E.0077	<.005	<.005
	12/14/2004	1500	<.007	E.0066	<.01	<.005
	03/09/2005	0730	.035	E.007	<.01	<.01
Old Mill Spring	08/06/2003	0000	E.0057	E.0058	<.015	<.005
	08/20/2003	0000	<.007	<.006	<.015	<.005
	09/03/2003	0000	E.0061	E.0055	<.015	<.005
	09/16/2003	0000	.0077	E.0049	E.004	<.005
	09/30/2003	0000	<.007	<.006	<.015	<.005
	08/25/2004	0000	.0083	E.0072	<.005	<.005
	12/14/2004	1500	<.007	<.006	<.01	<.005
	03/09/2005	0730	.022	E.0076	<.01	<.015

Table 9. Concentrations of volatile organic compounds detected in routine samples, Barton Springs, Austin, Texas (2003–05).

[In micrograms per liter. <, nondetection; E, estimated]

Site	Date	1,1,1-Trichloroethane	Carbon disulfide	Chloroform	*cis*-1,2-Dichloroethene	Tetrachloroethene	Trichloroethene	Bromodichloromethane	1,1,2-Trichloro-1,2,2-trifluoroethane	Toluene
Upper Spring	08/06/2003	<0.032	<0.070	0.14	<0.038	E0.060	<0.038	<0.048	<0.060	<0.050
	08/20/2003	<.032	<.070	.15	<.038	E.063	<.038	E.022	<.060	<.050
	09/03/2003	<.032	<.070	.13	<.038	E.061	<.038	<.048	<.060	<.050
	09/16/2003	<.032	<.029	.12	<.038	E.062	<.038	<.048	<.060	<.050
	09/30/2003	<.032	<.070	.15	<.038	E.062	<.038	<.048	<.060	<.050
	06/21/2004	<.032	<.038	E.087	<.024	E.032	<.038	E.022	<.038	<.050
	07/07/2004	<.032	<.038	E.073	<.024	E.018	<.038	<.028	<.038	<.050
	07/21/2004	<.032	<.038	E.076	<.024	E.028	<.038	<.028	<.038	<.050
	08/04/2004	<.032	<.038	.10	<.024	E.041	<.038	<.028	<.038	<.050
	08/25/2004	<.032	<.038	E.088	<.024	E.049	<.038	<.028	<.038	<.050
	09/15/2004	<.032	<.038	E.096	<.024	E.052	<.038	<.028	<.038	<.050
	10/04/2004	<.032	<.038	E.066	<.024	E.052	<.038	<.028	<.038	<.020
	11/05/2004	<.032	<.038	E.093	<.024	E.038	<.038	E.030	<.038	<.020
	12/14/2004	<.032	<.038	.11	<.024	E.017	<.038	<.028	<.038	<.020
	01/03/2005	<.032	<.038	E.096	<.024	E.031	<.038	E.035	E.013	<.020
	01/26/2005	<.032	<.038	E.086	<.024	E.040	<.038	E.029	E.015	<.020
	02/16/2005	<.032	<.038	.10	<.024	E.039	<.038	E.039	<.038	<.020
	03/09/2005	<.032	<.038	.11	<.024	E.047	<.038	E.038	<.038	<.020
	03/30/2005	<.032	<.038	E.094	<.024	E.038	<.038	E.036	<.038	<.020
	04/20/2005	<.032	<.038	E.099	<.024	E.051	<.038	E.034	<.038	<.020
	05/11/2005	<.032	<.038	E.097	<.024	E.047	<.038	E.039	<.038	<.020
	06/09/2005	<.032	<.038	.12	<.024	E.043	<.038	E.049	<.038	<.020
Main Spring	08/06/2003	E.011	<.070	E.044	<.038	E.042	<.038	<.048	<.060	<.050
	08/20/2003	<.032	<.070	E.072	<.038	E.062	<.038	<.048	<.060	<.050
	09/03/2003	<.032	<.070	E.045	<.038	E.062	<.038	<.048	<.060	<.050
	09/16/2003	<.032	<.070	E.067	<.038	.18	E.012	<.048	<.060	<.050
	09/30/2003	<.032	<.070	E.050	<.038	E.063	<.038	<.048	<.060	<.050
	06/21/2004	<.032	<.038	E.057	<.024	.25	E.017	<.028	<.038	<.050
	07/07/2004	<.032	<.038	E.053	E.019	.29	E.027	<.028	<.038	<.050
	07/21/2004	<.032	<.038	E.047	<.024	.11	<.038	<.028	<.038	<.050
	08/04/2004	<.032	<.038	E.079	<.024	E.081	<.038	<.028	<.038	<.050
	08/25/2004	<.032	<.038	E.062	<.024	E.089	<.038	<.028	<.038	<.050
	09/15/2004	<.032	<.038	E.051	<.024	.24	E.015	<.028	<.038	<.050
	10/04/2004	<.032	<.038	E.048	<.024	.13	<.038	<.028	<.038	<.020
	11/05/2004	<.032	<.038	E.046	<.024	.12	<.038	<.028	<.038	<.020
	12/14/2004	<.032	<.038	E.037	<.024	.11	<.038	<.028	<.038	<.020
	01/03/2005	<.032	<.038	E.035	<.024	.20	E.012	<.028	<.038	<.020
	01/26/2005	<.032	<.038	E.030	<.024	E.097	<.038	<.028	<.038	<.020
	02/16/2005	<.032	<.038	E.050	<.024	.17	E.014	<.028	<.038	<.020
	03/09/2005	<.032	<.038	E.070	E.018	.33	E.029	<.028	<.038	<.020
	03/30/2005	<.032	<.038	E.060	<.024	.14	E.012	<.028	<.038	<.020
	04/20/2005	<.032	<.038	E.055	<.024	.11	<.038	<.028	<.038	<.020
	05/11/2005	<.032	<.038	E.049	<.024	.10	<.038	<.028	<.038	<.020
	06/09/2005	<.032	<.038	E.044	<.024	E.073	<.038	<.028	<.038	<.020

Table 9. Concentrations of volatile organic compounds detected in routine samples, Barton Springs, Austin, Texas (2003–05) —Continued.

Site	Date	1,1,1-Trichloroethane	Carbon disulfide	Chloroform	*cis*-1,2-Dichloroethene	Tetrachloroethene	Trichloroethene	Bromodichloromethane	1,1,2-Trichloro-1,2,2-trifluoroethane	Toluene
Eliza Spring	08/06/2003	E0.011	<0.070	E0.039	<0.038	E0.035	<0.038	<0.048	<0.060	<0.050
	08/20/2003	<.032	<.070	E.064	<.038	E.060	<.038	<.048	<.060	<.050
	09/03/2003	<.032	<.070	E.038	<.038	E.057	<.038	<.048	<.060	<.050
	09/16/2003	E.012	E.030	E.059	<.038	.19	E.015	<.048	<.060	<.050
	09/30/2003	<.032	<.070	E.037	<.038	E.044	<.038	<.048	<.060	<.050
	08/25/2004	<.032	<.038	E.056	<.024	E.080	<.038	<.028	<.038	<.050
	12/14/2004	<.032	<.038	E.032	<.024	.12	E.012	<.028	<.038	<.020
	03/09/2005	<.032	<.038	E.068	E.018	.34	E.030	<.028	<.038	<.020
Old Mill Spring	08/06/2003	E.012	E.031	E.034	<.038	E.038	<.038	<.048	<.060	<.050
	08/20/2003	<.032	E.036	E.058	<.038	E.060	<.038	<.048	<.060	<.050
	09/03/2003	<.032	<.070	E.037	<.038	E.062	<.038	<.048	<.060	<.050
	09/16/2003	E.012	E.030	E.054	<.038	.15	<.038	<.048	<.060	<.050
	09/30/2003	<.032	<.070	E.044	<.038	E.054	<.038	<.048	<.060	E.011
	08/25/2004	<.032	<.038	E.049	<.024	E.081	<.038	<.028	<.038	<.050
	12/14/2004	<.032	<.038	E.024	<.024	E.084	<.038	<.028	<.038	<.020
	03/09/2005	<.032	<.038	E.049	<.024	.21	E.016	<.028	<.038	<.020

Table 10. Concentrations of nutrients detected in samples for Storm 1 (October 2004), Barton Springs, Austin, Texas.

[In milligrams per liter. --, sample not collected or sample not analyzed; <, nondetection; E, estimated]

Site	Date	Time	Ammonia nitrogen	Ammonia plus organic nitrogen, total	Nitrite nitrogen	Nitrite plus nitrate nitrogen, dissolved	Nitrite plus nitrate plus ammonia nitrogen	Orthophosphate phosphorus	Phosphorus, dissolved	Phosphorus, total
Upper Spring	10/23/2004	1500	--	--	--	1.56	--	--	--	--
	10/24/2004	0930	--	--	--	.531	--	--	--	--
	10/24/2004	2030	--	--	--	.746	--	--	--	--
	10/25/2004	1000	--	--	--	1.09	--	--	--	--
	10/26/2004	0830	--	--	--	1.47	--	--	--	--
	10/27/2004	1030	--	--	--	1.72	--	--	--	--
	10/28/2004	0830	--	--	--	1.80	--	--	--	--
	10/30/2004	0900	--	--	--	1.92	--	--	--	--
	11/05/2004	0930	--	--	--	1.80	--	--	--	--
Main Spring	10/23/2004	1400	--	--	--	1.43	--	--	--	--
	10/24/2004	1000	<0.04	0.11	<0.008	1.38	1.39	E0.01	E0.02	E0.021
	10/24/2004	2100	--	--	--	1.06	--	--	--	--
	10/25/2004	1030	E.005	.14	<.008	--	--	E.01	E.025	E.024
	10/26/2004	0900	--	--	--	.963	--	--	--	--
	10/27/2004	1100	--	--	--	.979	--	--	--	--
	10/28/2004	0900	--	--	--	.967	--	--	--	--
	10/30/2004	1000	--	--	--	.966	--	--	--	--
	11/05/2004	1030	--	--	--	.886	--	--	--	--
Eliza Spring	10/23/2004	1630	--	--	--	1.29	--	--	--	--
	10/24/2004	1130	--	--	--	1.41	--	--	--	--
	10/24/2004	2230	--	--	--	1.08	--	--	--	--
	10/25/2004	1130	--	--	--	.987	--	--	--	--
	10/26/2004	1000	--	--	--	.949	--	--	--	--
	10/27/2004	1230	--	--	--	.935	--	--	--	--
	10/28/2004	1030	--	--	--	.914	--	--	--	--
	10/30/2004	1200	--	--	--	.899	--	--	--	--
	11/05/2004	1130	--	--	--	.842	--	--	--	--
Old Mill Spring	10/23/2004	1600	--	--	--	1.31	--	--	--	--
	10/24/2004	1100	--	--	--	1.33	--	--	--	--
	10/24/2004	2200	--	--	--	1.23	--	--	--	--
	10/25/2004	1100	--	--	--	1.11	--	--	--	--
	10/26/2004	0930	--	--	--	1.04	--	--	--	--
	10/27/2004	1200	--	--	--	1.01	--	--	--	--
	10/28/2004	0930	--	--	--	1.06	--	--	--	--
	10/30/2004	1100	--	--	--	.992	--	--	--	--
	11/05/2004	1100	--	--	--	.933	--	--	--	--

Table 11. Concentrations of nutrients detected in samples for Storm 2 (May 2005), Barton Springs, Austin, Texas.

[In milligrams per liter. --, sample not collected or sample not analyzed; <, nondetection; E, estimated]

Site	Date	Time	Ammonia nitrogen	Ammonia plus organic nitrogen, total	Nitrite nitrogen	Nitrite plus nitrate nitrogen, dissolved	Orthophosphate phosphorus	Phosphorus, dissolved	Phosphorus, total
Upper Spring	05/30/2005	0700	--	--	--	1.97	--	--	--
	05/30/2005	1430	--	--	--	1.23	--	--	--
	05/30/2005	2000	--	--	--	1.36	--	--	--
	05/31/2005	1130	--	--	--	1.53	--	--	--
	06/01/2005	0630	--	--	--	1.84	--	--	--
	06/02/2005	0700	--	--	--	1.06	--	--	--
	06/04/2005	0800	--	--	--	1.90	--	--	--
	06/06/2005	0700	--	--	--	2.03	--	--	--
	06/09/2005	0730	--	--	--	2.11	--	--	--
Main Spring	05/30/2005	0730	0.011	E0.058	<0.008	1.31	<0.018	<0.04	<0.04
	05/30/2005	1400	<.01	E.055	<.008	1.26	<.018	<.04	<.04
	05/30/2005	2100	<.04	E.063	<.008	1.27	<.018	<.04	<.04
	05/31/2005	1030	<.01	<.1	<.008	1.26	<.018	<.04	<.04
	06/01/2005	0730	<.01	<.1	<.008	1.27	<.018	<.04	<.04
	06/02/2005	0730	<.01	<.1	<.008	1.11	<.018	<.04	<.04
	06/04/2005	0930	<.01	<.1	<.008	1.24	<.018	<.04	E.022
	06/06/2005	0730	<.01	<.1	<.008	1.26	<.018	<.04	<.04
	06/09/2005	0800	<.01	<.1	<.008	1.29	<.018	<.04	<.04
Eliza Spring	05/30/2005	0830	--	--	--	1.27	--	--	--
	05/30/2005	1600	--	--	--	1.27	--	--	--
	05/30/2005	2130	--	--	--	1.28	--	--	--
	05/31/2005	1230	--	--	--	1.23	--	--	--
	06/01/2005	0800	--	--	--	1.23	--	--	--
	06/02/2005	0830	--	--	--	1.13	--	--	--
	06/04/2005	0900	--	--	--	1.20	--	--	--
	06/06/2005	0830	--	--	--	1.22	--	--	--
	06/09/2005	0930	--	--	--	1.23	--	--	--
Old Mill Spring	05/30/2005	0830	--	--	--	1.34	--	--	--
	05/30/2005	1530	--	--	--	1.35	--	--	--
	05/30/2005	2030	--	--	--	1.35	--	--	--
	05/31/2005	1200	--	--	--	1.31	--	--	--
	06/01/2005	0700	--	--	--	1.32	--	--	--
	06/02/2005	0800	--	--	--	1.22	--	--	--
	06/04/2005	0830	--	--	--	1.30	--	--	--
	06/06/2005	0800	--	--	--	1.32	--	--	--
	06/09/2005	0830	--	--	--	1.31	--	--	--

Table 12. Concentrations of pesticides detected in samples for Storm 1 (October 2004), Barton Springs, Austin, Texas.

[In micrograms per liter. E, estimated; <, nondetection; --, not applicable]

Site	Date	Time	Atrazine	Deethyl-atrazine	Prometon	Simazine	Carbaryl	Diazanon	DCPA	Mala-thion
Upper Spring	10/23/2004	1500	0.21	E0.020	<0.01	<0.01	E0.034	<0.005	<0.003	<0.027
	10/24/2004	0930	.45	E.030	<.01	.072	E.025	.016	<.003	<.027
	10/24/2004	2030	.34	E.024	E.0043	.063	<.041	E.0037	<.003	<.027
	10/25/2004	1000	.27	E.039	.010	.059	<.041	E.0038	<.003	<.027
	10/26/2004	0830	.14	E.029	E.0087	.027	<.041	<.005	<.003	<.027
	10/27/2004	1030	.087	E.026	<.01	.016	<.041	<.005	<.003	<.027
	10/28/2004	0830	.079	E.027	E.0091	.016	<.041	<.005	<.003	<.027
	10/30/2004	0900	.050	E.024	E.0088	.011	<.041	<.005	<.003	<.027
	11/05/2004	0930	.043	E.026	<.01	.0092	<.041	<.005	<.003	<.027
Main Spring	10/23/2004	1400	<.01	<.006	<.01	<.005	<.041	<.005	<.003	<.027
	10/24/2004	1000	.068	E.011	<.01	.020	<.041	<.005	<.003	<.027
	10/24/2004	2100	.064	E.0095	<.01	.030	<.041	<.005	<.003	<.027
	10/25/2004	1030	.070	E.011	E.0066	.026	<.041	<.005	<.003	<.027
	10/26/2004	0900	.053	E.011	<.01	.015	<.041	<.005	<.003	<.027
	10/27/2004	1100	.024	E.010	<.01	.0092	<.041	<.005	<.003	<.027
	10/28/2004	0900	.017	E.0089	E.0059	.0082	<.041	<.005	<.003	<.027
	10/30/2004	1000	.014	E.0093	<.01	.0077	<.041	<.005	<.003	<.027
	11/05/2004	1030	.018	E.008	<.01	<.01	<.041	<.005	<.003	<.027
Barton Creek[1]	10/23/2004	--	.039	E.006	.32	.024	E.02	.022	<.003	.029
Onion Creek[1,2]	10/23/2004	--	.061	<.006	<.01	.019	<.041	<.005	.0004	.027
Slaughter Creek[1]	10/23/2004	--	2.2	E.023	E.01	.035	E.11	<.01	.003	E.015
Bear Creek[1]	10/23/2004	--	<.007	<.006	<.01	<.01	<.041	<.005	<.003	.027
Williamson Creek[1]	10/23/2004	--	.14	<.01	<.01	.11	.02	.012	<.003	.061

[1] Stormflow composite samples.

[2] Flow-weighted composite concentrations computed on basis of two sets of samples collected over storm hydrograph.

Table 13. Concentrations of pesticides detected in samples for Storm 2 (May 2005), Barton Springs, Austin, Texas.

[In micrograms per liter. E, estimated; <, nondetection; --, not applicable]

Site	Date	Time	Atrazine	Deethyl-atrazine	Prometon	Simazine	Carbaryl	Diazinon	Mala-thion	Fipronil or degradate[1]
Upper Spring	05/30/2005	0700	0.049	E0.033	0.016	0.027	<0.041	<0.005	<0.027	<0.094
	05/30/2005	1430	.24	E.033	.014	.090	E.066	<.005	<.027	E.015
	05/30/2005	2000	.30	E.053	.015	.043	E.049	<.005	<.027	E.009
	05/31/2005	1130	.19	E.052	E.009	.026	<.041	<.005	<.027	<.094
	06/01/2005	0630	.078	E.036	E.005	.019	<.041	<.005	<.027	<.094
	06/02/2005	0700	.17	E.041	E.008	.018	<.041	<.005	<.027	<.094
	06/04/2005	0800	.043	E.029	<.010	.013	<.041	<.005	<.027	<.094
	06/06/2005	0700	.028	E.031	E.005	.010	<.041	<.005	<.027	<.094
	06/09/2005	0730	.021	E.026	E.005	E.005	<.041	<.005	<.027	<.094
Main Spring	05/30/2005	0730	.013	E.009	E.002	E.004	<.041	<.005	<.027	<.094
	05/30/2005	1400	.025	E.010	<.010	.008	<.041	<.005	<.027	<.094
	05/30/2005	2100	.034	E.011	<.010	E.004	<.041	<.005	<.027	<.094
	05/31/2005	1030	.036	E.013	<.010	E.003	<.041	<.005	<.027	<.094
	06/01/2005	0730	.030	E.011	<.010	E.003	<.041	<.005	<.027	<.094
	06/02/2005	0730	.044	E.014	<.010	E.003	<.041	<.005	<.027	<.094
	06/04/2005	0930	.026	E.011	<.010	<.005	<.041	<.005	<.027	<.094
	06/06/2005	0730	.017	E.012	<.010	E.003	<.041	<.005	<.027	<.094
	06/09/2005	0800	.012	E.010	<.010	<.005	<.041	<.005	<.027	<.094
Onion Creek[2]	05/29/2005	--	.76	E.057	<.01	.006	E.093	<.005	E.02	<.094
Slaughter Creek[2,3]	05/29/2005	--	2.9	E.16	<.01	.012	E.26	.021	E.02	E.042
Williamson Creek[2]	05/29/2005	--	.18	E.022	E.01	<.005	.02	.032	.042	E.015

[1] Summation of fipronil, desulfinyl fipronil, desulfinylfipronil amide, fipronil sulfide, and fipronil sulfone.

[2] Stormflow composite samples.

[3] Composite concentrations calculated on basis of two sets of composite samples collected over storm hydrograph.

Table 14. Concentrations of volatile organic compounds detected in samples for Storm 1 (October 2004), Barton Springs, Austin, Texas.

[In micrograms per liter. <, nondetection; E, estimated]

Site	Date	Time	Carbon disulfide	Chloroform	Dichloro-methane	Tetrachloro-ethene	Trichloro-ethene	1,1,2-Trichloro-ethane
Upper Spring	10/24/2004	1500	<0.038	E0.093	<0.060	E0.053	<0.038	E0.033
	10/24/2004	0930	<.038	E.036	<.060	<.030	<.038	<.028
	10/24/2004	2030	<.038	E.056	<.060	E.032	<.038	<.028
	10/25/2004	1000	<.038	E.079	<.060	E.037	<.038	E.020
	10/26/2004	0830	<.038	E.089	<.060	E.031	<.038	E.029
	10/27/2004	1030	<.038	E.088	<.060	E.042	<.038	E.033
	10/38/2004	0830	<.038	E.095	<.060	E.040	<.038	E.031
	10/30/2004	0900	<.038	E.077	<.060	E.045	<.038	<.028
	11/05/2004	0930	<.038	E.093	<.060	E.038	<.038	E.030
Main Spring	10/23/2004	1400	<.038	E.051	<.060	E.061	<.038	<.040
	10/24/2004	1000	<.038	E.056	<.060	.21	<.038	<.040
	10/24/2004	2100	<.038	E.074	<.060	.20	E.017	<.040
	10/25/2004	1030	<.038	E.064	E.046	.18	<.038	<.040
	10/26/2004	0900	<.038	E.049	E.034	.15	<.038	<.040
	10/27/2004	1100	E.035	E.036	<.060	.11	<.038	<.040
	10/28/2004	0900	<.038	E.040	<.060	.12	<.038	<.040
	10/30/2004	1000	<.038	E.034	<.060	E.099	<.038	<.040
	11/05/2004	1030	<.038	E.046	<.060	.12	<.038	<.040

Table 15. Concentrations of volatile organic compounds detected in samples for Storm 2 (May 2005), Barton Springs, Austin, Texas.

[In micrograms per liter. <, nondetection; E, estimated]

Site	Date	Time	Carbon disulfide	Chloroform	Tetrachloro-ethene	Trichloro-ethene	Bromo-dichloro-methane	Toluene
Upper Spring	05/30/2005	0700	<0.038	0.11	E0.083	<0.038	E0.046	<0.020
	05/30/2005	1430	<.038	E.085	E.049	<.038	E.034	E.016
	05/30/2005	2000	E.016	E.076	E.029	<.038	E.036	<.020
	05/31/2005	1130	<.038	E.091	E.052	<.038	<.028	<.020
	06/01/2005	0630	<.038	E.097	E.065	<.038	E.036	<.020
	06/02/2005	0700	<.038	E.092	E.040	<.038	E.033	<.020
	06/04/2005	0800	E.024	.12	E.073	<.038	E.047	<.020
	06/06/2005	0700	<.038	.14	E.063	<.038	E.051	<.020
	06/09/2005	0730	<.038	.12	E.043	<.038	E.049	<.020
Main Spring	05/30/2005	0730	E.018	E.044	.17	E.011	<.040	<.035
	05/30/2005	1400	E.016	E.043	.14	E.009	<.040	<.035
	05/30/2005	2100	E.015	E.046	.15	E.012	<.040	<.035
	05/31/2005	1030	<.038	E.052	.18	E.013	<.040	<.035
	06/01/2005	0730	<.038	E.051	.14	E.010	<.040	<.035
	06/02/2005	0730	E.018	E.058	.19	E.014	<.040	<.035
	06/04/2005	0930	<.038	E.060	.12	<.038	<.040	<.035
	06/06/2005	0730	<.038	E.051	.11	<.038	<.040	<.035
	06/09/2005	0800	<.038	E.044	E.073	<.038	<.040	<.035

Table 16. Concentrations of nitrite plus nitrate nitrogen and selected pesticides and volatile organic compounds (VOCs) detected in samples collected November 24, 2004, Barton Springs, Austin, Texas.

[E, estimated ; <, nondetection]

Nitrite plus nitrate nitrogen, dissolved (milligrams per liter)		
Site	Date	Concentration
Upper Spring	11/24/2004	0.873
Main Spring	11/24/2004	1.65
Eliza Spring	11/24/2004	1.63
Old Mill Spring	11/24/2004	1.50

Pesticides (micrograms per liter)					
Site	Date	Time	Atrazine	Deethyl-atrazine	Simazine
Upper Spring	11/24/2004	1000	0.078	E0.019	0.040
Main Spring	11/24/2004	1100	.021	E.012	.015

VOCs (micrograms per liter)							
Site	Date	Time	Chloro-form	*cis*-1,2-Dichloro-ethene	Tetra-chloro-ethene	Trichloro-ethene	Toluene
Upper Spring	11/24/2004	1000	E0.034	<0.02	E0.017	<0.038	E0.015
Main Spring	11/24/2004	1100	E.061	E.03	.80	E.037	<.02

Table 17. Stormflow and rainfall conditions for Storms 1 (October 2004) and 2 (May 2005), Barton Springs, Austin, Texas.

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

Storm	Initial aquifer flow conditions		Onset of rainfall (date and time)	End of measurement period (date and time)	Total rainfall (in.)	Maximum rainfall intensity (in/hr)
	Barton Springs discharge (ft^3/s)	Percentile relative to period of record[1]				
1	74	60	10/23/2004 0100	10/31/2004 2359	3.0	1.02
2	95	80	05/29/2005 0800	06/08/2005 2359	2.1	.51

[1] Daily average discharge (1978–2005).

Table 18. Loads of common contaminants after Storms 1 and 2 and during non-stormflow conditions, Barton Springs, Austin, Texas.

[In grams except where noted, rounded to 2 significant figures. NM, not measured because of insufficient stormflow in stream; --, not applicable; ND, not detected in stormflow composite sample]

Stream or spring	Load		
	Storm 1 (October 2004)	Storm 2 (May 2005)	Annual (non-stormflow)
	Atrazine		
Barton Creek (input)	16	NM	--
Onion Creek (input)	29	160	--
Slaughter Creek (input)	26	41	--
Bear Creek (input)	ND	NM	--
Williamson Creek (input)	1.1	2.7	--
Total	71	210	--
Barton Springs (output)	45	47	1,100
Percent recovery	64 percent	23 percent	--
	Chloroform		
Barton Springs (output)	67	88	4,200
	Tetrachloroethene		
Barton Springs (output)	180	250	12,000

Table 19. Mean concentrations of major ions and selected organic compounds in spring flow for baseline conditions, Barton Springs, Austin, Texas (2003–05).

[Calculated based on values from routine sampling when little to no recharge occurred (recharge less than 25 cubic feet per second). mg/L, milligrams per liter, µg/L, micrograms per liter]

Major ion (units)	Mean concentration	Contaminant[1] (units)	Mean concentration
Calcium (mg/L)	90	Atrazine (µg/L)	0.0085
Magnesium (mg/L)	23	Chloroform (µg/L)	.05
Sodium (mg/L)	17	Tetrachloroethene (µg/L)	.088
Potassium (mg/L)	1.4		
Chloride (mg/L)	28		
Sulfate (mg/L)	30		
Strontium (µg/L)	.92		
Silica (mg/L)	12		
Nitrate nitrogen[1] (mg/L)	1.4		

[1] Values for Upper Spring excluded from calculation.