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Changes in sources and storage in a karst aquifer during a transition from drought to wet conditions

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SUMMARY

Understanding the sources and processes that control groundwater compositions and the timing and magnitude of groundwater vulnerability to potential surface-water contamination under varying meteorologic conditions is critical to informing groundwater protection policies and practices. This is especially true in karst terrains, where infiltrating surface water can rapidly affect groundwater quality. We analyzed the evolution of groundwater compositions (major ions and Sr isotopes) during the transition from extreme drought to wet conditions, and used inverse geochemical modeling (PHREEQC) to constrain controls on groundwater compositions during this evolution. Spring water and groundwater from two wells dominantly receiving diffuse and conduit flow (termed diffuse site and conduit site, respectively) in the Barton Springs segment of the Edwards aquifer (central Texas, USA) and surface water from losing streams that recharge the aquifer were sampled every 3–4 weeks during November 2008–March 2010. During this period, water compositions at the spring and conduit sites changed rapidly but there was no change at the diffuse site, illustrating the dual nature (i.e., diffuse vs. conduit) of flow in this karst system. Geochemical modeling demonstrated that, within a month of the onset of wet conditions, the majority of spring water and groundwater at the conduit site was composed of surface water, providing quantitative information on the timing and magnitude of the vulnerability of groundwater to potential surface-water contamination. The temporal pattern of increasing spring discharge and changing pattern of covariation between spring discharge and surface-water (steam) recharge indicates that that there were two modes of aquifer response—one with a small amount of storage and a second that accommodates more storage.

1. Introduction

Karst groundwater systems are dynamic and can respond rapidly to changes in meteorologic conditions (Hess and White, 1988; Ford and Williams, 1989). Alternation of drought and wet conditions occurs commonly in semi-arid and arid regions and is predicted to intensify with ongoing climate change (Banner et al., 2010; Seager et al., 2007). Understanding the controls on groundwater compositions and vulnerability of groundwater to potential surface-water contamination during dry and wet conditions and transitions between such conditions is critical to informing land management practices and policies concerned with protecting water quality.

Variations in spring discharge and spring water compositions (referred to herein as spring responses) have been used to characterize karst systems and investigate the processes that control groundwater quality. Such studies have been used to: (i) characterize the general nature of karst systems along the spectrum of diffuse- vs. conduit-dominated groundwater flow (Massei et al., 2007), (ii) separate recharging surface water from spring baseflow following storm events (Lakey and Krothe, 1996; Mahler and Garner, 2009; Herman et al., 2009), and (iii) investigate exchange between conduit- and matrix-flow routes (Martin and Dean, 2001; Bailly-Comte et al., 2010; Gulley et al., 2011). For clarification, diffuse flow refers to flow in the matrix pore space and micro-joints or fractures of the aquifer bedrock, and conduit flow refers to flow moving through solution-widened joints, fractures, and conduits. An integrated investigation of recharging surface water, spring discharge, and groundwater can yield a more comprehensive understanding of the surface and groundwater sources, processes, and variations in flow type that control spring and groundwater compositions than can be gained by considering only spring responses (Moore et al., 2009).

Many studies have investigated dynamics of karst systems by interpreting spring response to short-lived events (e.g., storm or flood) to develop a conceptual understanding of how surface water

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and groundwater move through karst systems (e.g., Smart, 1988; Desmarais and Rojstaczer, 2002; Birk et al., 2004; Florea and Vacher, 2007) and demonstrate the vulnerability of karst groundwater to surface-water contamination (e.g., Andrews, 1984; Ryan and Meiman, 1996; Mahler and Massei, 2007; Pronk et al., 2007; Heinz et al., 2009). To our knowledge, there are no studies that have assessed the geochemical response of karst groundwater to a long-term transition from drought to wet conditions and quantified the timing and magnitude of groundwater vulnerability to potential surface-water contamination during such a transition. This study investigates how the controls on groundwater compositions in a karst system evolve during the transition from a prolonged extreme drought (as defined by the Palmer Drought Severity Index; Palmer, 1965) to above-average flow conditions. Groundwater geochemistry (major ions and Sr isotopes) was monitored monthly in the Barton Springs segment of the Edwards aquifer at a well receiving predominantly diffuse flow, a well receiving predominantly conduit flow, and Barton Springs, a spring receiving both types of flow, during several months of extreme drought and during the recovery from that drought. Surface water from losing streams that provide the majority of recharge to the aquifer (surface-water recharge) also was monitored to determine the potential geochemistry of aquifer recharge. Geochemical variations, statistical analysis, and geochemical modeling were used to identify controls on groundwater compositions and quantify their evolution.

2. Hydrogeologic setting

The study site is the Barton Springs segment of the Edwards aquifer (BSE). The Edwards aquifer is developed in the extensively karstified, Cretaceous-age carbonates of the Edwards Group (Rose, 1972). The strata of the Edwards Group have been buried, diagenetically altered during this process, and re-exposed (Rose, 1972), making it a telogenetic karst system (vs. eogenetic) as defined by Vacher and Mylroie (2002). Telogenetic systems are characterized by secondary porosity that generally consists of conduits and fractures, and differ from younger eogenetic (pre-burial) systems, which have secondary porosity consisting of macro-void pathways throughout the matrix (Vacher and Mylroie, 2002). The hydraulic response of telogenetic systems to recharge events typically is restricted to the conduit network, and spring discharge responds immediately to discrete recharge events. In contrast, the void space of the matrix in eogenetic systems, which is enhanced relative to that of telogenetic systems, causes dampening (or even muting) of spring discharge to discrete storm events (Supplementary data Fig. S1; Florea and Vacher, 2006).

The BSE extends southwest from Austin, Tex., and is bounded by the Colorado River to the north and a groundwater divide to the south (Fig. 1A). The Trinity aquifer underlies the BSE and extends to the south and west where strata of the Edwards Group have been removed by erosion (Rose, 1972). Barton Springs, in Austin, is the principal discharge point for the BSE, and is a culturally and historically important recreational site that is habitat for endemic and endangered species (Slade et al., 1986). The contributing zone consists of the watersheds to the west of the recharge zone (Fig. 1A); the majority of rainfall runoff that occurs in this zone drains via five creeks to the recharge zone (from north to south, Barton, Williamson, Slaughter, Bear, and Onion Creeks, Fig. 1A) (Slade et al., 1986). A saline zone bounds the aquifer along the eastern part of the BSE (Fig. 1A; Abbott, 1975). The downdip limit of freshwater in the aquifer is the approximate surface defined by the 1000-mg/L dissolved solids concentration (Perez, 1986).

2.1. Sources of recharge

The majority (~70–85%) of recharge to the BSE is surface water from losing streams (Barton, Williamson, Slaughter, Bear, and Onion) that cross the recharge zone (Fig. 1A), where the Edwards formation outcrops at the surface and is heavily faulted and fractured (Slade et al., 1986; Barrett and Charbeneau, 1997; Hauwert, 2009). Other sources of recharge include diffuse recharge through the soil zone and direct recharge into karst features (e.g., sinkholes and solution crevices; Fig. 1B). These have been estimated to account for ~15–30% of total recharge (Hauwert, 2009). Surface-water recharge along conduit flow routes has been deduced by correlations between groundwater specific conductance values and Barton Spring discharge and between groundwater specific conductance values and estimated stream-loss recharge to the BSE (Garner and Mahler, 2007). Dye traces have delineated major conduit flow routes that allow rapid (up to 12 km/day) transport of surface water to Barton Springs (Hauwert, 2009). Recharge during storms contributes pesticides such as atrazine and simazine to spring discharge (Mahler and Massei, 2007). As much as 55% of Barton Springs discharge following storms could be accounted for by recharging water from losing streams that has been rapidly (2–4 days) transported to the spring (Mahler and Garner, 2009). Previous studies have demonstrated that Edwards aquifer groundwater compositions also can be affected by mixing with water from the adjacent and underlying Trinity aquifer (Senger and Kreitler, 1984) and from the saline zone (Oetting et al., 1996).

2.2. Sr isotope tracers of hydrologic processes

Groundwater Sr isotope ($^{87}Sr/^{86}Sr$) values in the BSE generally are lower than those measured in surface water (Oetting et al., 1996; Garner, 2005; Christian et al., 2011), and can potentially be

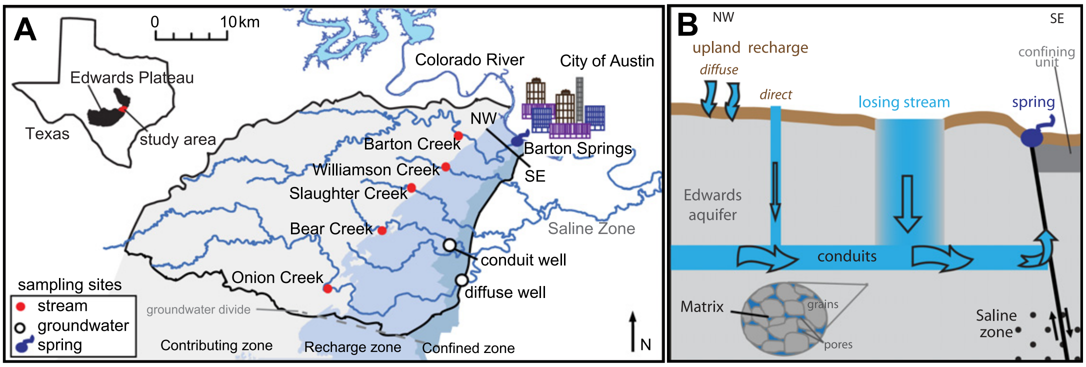

Fig. 1. The Barton Springs segment of the Edwards aquifer and sampling site locations. (A) "NW–SE" indicates line of a conceptual cross-section shown in B. (B) Conceptual cross-section of the hydrogeologic setting illustrating possible recharge and groundwater flow sources that affect groundwater compositions.

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used to quantify mixing between surface and groundwater. Water acquires its initial Sr isotope signature ($\sim$0.7090) from interaction with silicate minerals in soils overlying the BSE (Musgrove and Banner, 2004; Wong et al., 2011). As water interacts with the underlying carbonate bedrock, $^{87}Sr/^{86}Sr$ progressively decreases, becoming more similar to that of the Cretaceous limestone bedrock ($^{87}Sr/^{86}Sr \sim 0.7076$) (Musgrove and Banner, 2004; Christian et al., 2011). Longer groundwater residence times and more extensive water–rock interaction with aquifer host rocks result in lower $^{87}Sr/^{86}Sr$ values (Oetting et al., 1996; Garner, 2005). Mixing of municipal water from leaking infrastructure and irrigation runoff with stream water also can result in higher surface water $^{87}Sr/^{86}Sr$ values relative to those in groundwater, because municipal water has a higher Sr isotope signature ($^{87}Sr/^{86}Sr \sim 0.7090$) than does the Cretaceous limestone; mixing of municipal and natural water has been demonstrated to control $^{87}Sr/^{86}Sr$ values in some Austin-area streams (Christian et al., 2011).

2.3. Regional climate

The climate in the area is sub-tropical-sub-humid to semi-arid (Larkin and Bomar, 1983) with average annual rainfall of 860 mm and a range of 390–1370 mm (1856–2010; National Weather Service, 2012). Soils are generally thin (<20 cm) and silicate rich (Cooke et al., 2007). Meteorologic conditions in Texas tend to oscillate between extremes of wet and dry (Griffiths and Ainsworth, 1981), and the linkage of the hydrologic system to these oscillations is demonstrated by the covariation between Barton Springs discharge and the regional drought index (National Climate Data Center, 2012) (Fig. 2). Projections of future climate for this region predict intensification of climate extremes (Banner et al., 2010; Seager et al., 2007).

2.4. Transition from dry to wet conditions

The data collection interval spanned 17 months from November 2008 through March 2010, during which the Palmer Drought Severity Index (PDSI) for Texas ranged from −4.4 during a period of prolonged extreme drought to 3.2 during an extended period of well-above average rainfall (National Climate Data Center, 2012; Fig. 2). During November 2008–August 2009 (hereinafter the dry interval), which was preceded by 6 months of dry conditions, there was 330 mm of rainfall. Flow was intermittent or absent in the five principal recharging streams, and discharge at Barton Springs decreased from 0.82 m^3/s (29 ft^3/s) to 0.37 m/s (13 ft^3/s), approaching the historic low of 0.28 m^3/s (10 ft^3/s; U.S. Geological Survey, 2012) measured during the 1950s drought of record. During September 2009–March 2010 (hereinafter the wet interval), there was 800 mm of rainfall, and conditions generally became increasingly wetter during September 2009–March 2010. Within a month of the onset of wet conditions, the five streams flowed continuously through the end of the sampling interval and discharge from Barton Springs rebounded to average discharge 1.42 m^3/s (50 ft^3/s). Discharge from Barton Springs reached 2.7 m^3/s (95 ft^3/s) prior to the end of the study (Fig. 3).

Results are discussed in the context of four time intervals: first (November 2008–May 2009) and second (June–August 2009) parts of the dry interval and first (September–October, 2009) and second (November 2009–March 2010) parts of the wet interval (Fig. 3). Dry and wet intervals were divided on the basis of geochemical modeling results (see Section 4.5) and changes in temporal patterns of spring discharge (see Section 4.1), respectively.

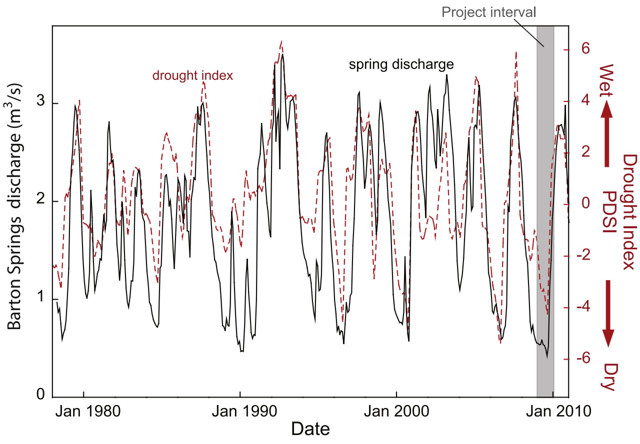

Fig. 2. Monthly average discharge at Barton Springs (solid black line) and the 3-month Palmer Drought Severity Index for Texas (dashed red line; PDSI) from 1978 to 2011. The gray bar indicates the interval during which sampling occurred. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Methods

3.1. Hydrologic measurements

Daily mean rainfall was calculated as a weighted average of rainfall measured at six rain gages within the contributing zone of the BSE (Lower Colorado River Authority, 2011; sites 4517, 4519, 4593, 4594, 4595, 4596). Stream and spring discharge data (15-min and daily mean) was obtained from the U.S. Geological Survey (USGS) National Water Information System (U.S. Geological Survey, 2012). Following several storms, flooding of surface water over the orifice of Barton Springs precluded determination of spring discharge (Supplementary material Table S1). During these intervals, the USGS estimated daily mean spring discharge by linear interpolation (oral communication, John Snatic, U.S. Geological Survey, 2011).

Daily mean total surface-water recharge to the BSE was estimated from stream flow measured at USGS streamflow-gaging stations immediately upstream from the recharge zone as described by Mahler et al. (2011). Total recharge was computed as the sum of recharge from the five streams, up to a maximum rate for Williamson, Slaughter, Bear, and Onion Creeks and using an algorithm relating stream flow to recharge for Barton Creek (Barrett and Charbeneau, 1997).

3.2. Sampling

To investigate the evolution of groundwater compositions during the project interval, groundwater from different parts of the aquifer and water from the five losing streams was sampled. Groundwater samples were collected from two wells: one that was hypothesized to receive predominantly diffuse flow (USGS station number 300453097503301; hereinafter the diffuse site) and one hypothesized to receive predominantly conduit flow (USGS station number 300813097512101; hereinafter the conduit site). The groundwater wells were so characterized on the basis of historical data that showed the absence of a correlation between groundwater specific conductance and estimated surface-water recharge at one well (diffuse site) and presence of a correlation at the other (conduit site) (Garner and Mahler, 2007). Water collected from these two wells was pumped from similar depths in the aquifer and from similar stratigraphic units. Spring water was collected from the main spring orifice of Barton Springs (USGS station 08155500), the principal discharge point of the BSE (Slade et al., 1986) (hereinafter the spring site). The principal discharge point

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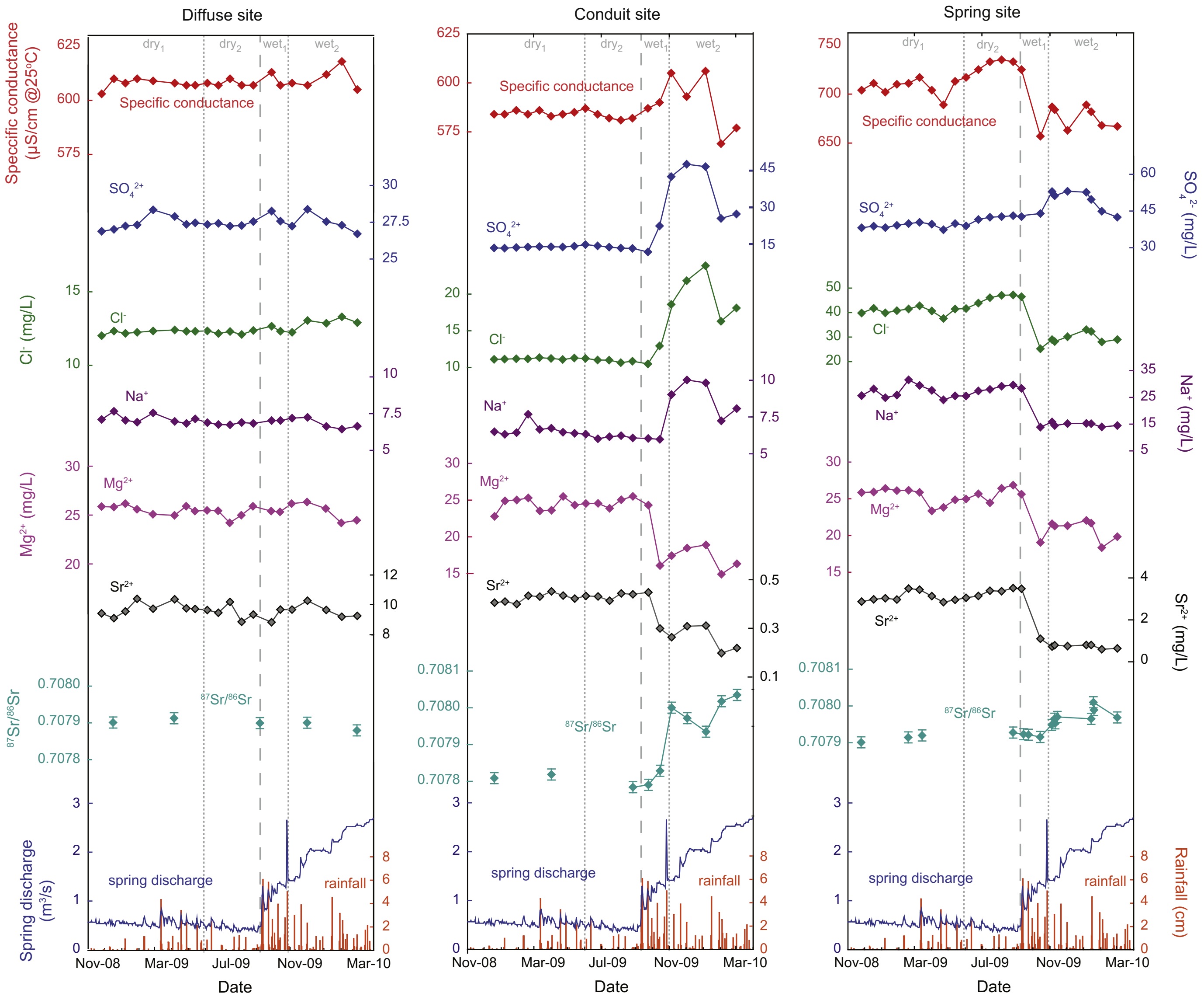

Fig. 3. Groundwater and spring specific conductance values, major-ion concentrations, $^{87}Sr/^{86}Sr$ values, spring discharge, and daily rainfall for the project interval. Dashed vertical gray lines mark division between the dry and wet interval. Dotted vertical lines mark the division between the first and second parts of the dry and wet intervals. Note differences in *y*-axis scales among sites for specific conductance and some major ions.

of an aquifer segment integrates all the inputs and processes that occur along the aquifer flow paths (Quinlan, 1989), and Barton Springs, therefore, represents the integrated response of the aquifer system to changing meteorologic conditions. Stream water (surface-water) was collected from the five losing streams at USGS streamflow-gaging stations immediately upstream from the recharge zone (Fig. 1).

Samples were collected every 3–4 weeks during November 2008–March 2010. Routine collections of discrete samples were collected from spring stream sites by submerging bottles beneath the water surface at the centroid of flow (Wilde and others, 1999). Samples at wells were collected prior to any filtration, chlorination, or other treatment. Wells were purged prior to sample collection, as determined by stable readings of water temperature, pH, conductivity, dissolved oxygen, and turbidity measured by a multi-parameter sonde (Wilde and others, 1999). All samples for anions ($Br^-, Cl^-, F^-, NO_2^- + NO_3^-, SO_4^{2-}$), cations ($Ca^{2+}$, Mg^{2+}, K^+, Na^+, Sr^{2+}), B, Si, alkalinity, and Sr isotope analysis were filtered using a 0.45-μm disc filter. While B, Br^-, and F^- are not commonly sampled in karst settings, these constituents can be useful indicators of urban influence and therefore are potentially useful in delineating groundwater mixing with stream water influenced by urbanization (Christian et al., 2011; Barrett et al., 1999). Samples for analysis of cations and Sr isotopes were acidified with HNO_3. Alkalinity was determined by manual titration and the inflection point method (Rounds, 2006).

3.3. Analytical methods

Anion and cation analyses were performed by the USGS National Water Quality Lab in Denver, Colo., using ion-exchange chromatography and inductively coupled plasma-mass spectrometry, respectively (Fishman, 1993). The median percent difference of 11 replicate analyses was less than 2.3% for each constituent. The absolute difference between cations and anions was <5% for all samples. Field blank measurements ($n = 12$) were below method reporting limits for all constituents except $Ca^{2+}, NO_2^- + NO_3^-$, and Si, which each had a single blank detection of 0.01, 0.04, and 0.04 mg/L, respectively (Mahler et al., 2011). Concentrations of constituents in blank samples were 2–3 orders of magnitude less

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than concentrations measured in environmental samples (Mahler and others, 2011, pp. 59–65).

Sr isotope values ($^{87}Sr/^{86}Sr$) were measured following the methods of Banner and Kaufman (1994) using a multi-collector Thermo Scientific Triton Thermal Ionizing Mass Spectrometer in the Department of Geological Sciences at the University of Texas at Austin ($2\alpha = 0.000015$, where α is the standard error). The mean for all the measurements of $^{87}Sr/^{86}Sr$ made using the National Institute of Standards and Technology Strontium Carbonate Isotopic Standard 987 (National Institute of Standards and Technology, 2012) during the project interval was 0.710256 ($2\alpha = 0.000012$, $n = 59$). Replicate analyses of four unknown samples were within 0.000009. Samples were analyzed in four sets. Sr mass in blank values associated with the first set ($n = 36$) was 15 pg ($n = 2$). Sr mass in blank values associated with the second ($n = 12$) and third ($n = 34$) sets was 430 and 23–170 pg ($n = 2$), respectively. The highest blank value was $\leqslant$ 5% of the mass of sample Sr used (800 ng–40 μg) for analysis in spring and groundwater samples. For stream-water analysis, the highest blank value was $\leqslant$16% of the mass of sample Sr loaded (~4 mL; 800 ng–2 μg depending on concentration). The high blank values in stream-water samples were tracked to incompletely cleaned sample vials. A fourth set of analyses was done to measure replicate values ($n = 5$) of samples measured in the second and third sets. Replicate values were within analytical uncertainty, which indicates that high blank values had a negligible impact on the measured values. The blank value associated with this fourth set of samples was 6 pg.

3.4. Statistics and principal components analysis

Correlation coefficients (Pearson r) and p-values were used to evaluate the strength of linear correlations between geochemical measurements. Results with p-values less than 0.05 were considered statistically significant.

Interrelations among constituent concentrations were investigated using principal components analysis (PCA). PCA is a statistical technique that creates a new set of variables (the principal components, or factors) that are linear combinations of the original variables. New factors are created on the basis of the common variance among the original variables, with the first factor explaining the most variance and each subsequent variable explaining less variance (Davis, 2002). The advantage of PCA is that the majority of the variance is encapsulated into one to three variables, which facilitates graphical visualization and interpretation. Input data were the major-ion concentrations in spring and groundwater samples for the project interval and the concentrations of major ions in stream-water composite samples from the wet interval (surface-water recharge was minimal to absent during the dry interval). Major-ion geochemistry of stream-water composite samples was determined on the basis of the proportion that each stream contributed to estimated total recharge. Concentration data were standardized prior to input; specific conductance (also standardized) was input as a supplementary variable.

3.5. Geochemical modeling

Inverse modeling was done using the geochemical modeling program PHREEQC (Parkhurst and Appelo, 1999), which simulates a wide variety of end-member mixing and low-temperature aqueous geochemical reactions and processes. In inverse modeling, PHREEQC calculates combinations of end-member proportions and amounts (i.e., moles) of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits. For this study, PHREEQC was used to account for evolving spring and groundwater compositions during the transition from dry to wet conditions. Each inverse model run derived multiple possible scenarios of end-member mixing and geochemical processes that could account for user-specified (sampled) final water compositions. Models with the minimal number of mineral and gas phases (termed minimal models) were identified. Five geochemical interactions were included: (i) dissolution and precipitation of calcite; (ii) dissolution of dolomite, gypsum, and celestite; (iii) consumption or loss of CO_2; (iv) loss of O_2; and (v) ion exchange of Ca^{2+} and Na^{+}.

Possible end members (initial solutions) considered in the model were fresh Edwards groundwater, Edwards groundwater from the saline zone, recharging stream-water composites, and upland recharge. The composition of fresh Edwards groundwater (herein referred to as Edwards groundwater) was represented by groundwater collected from the conduit site at the peak of the dry interval (August 5, 2009) when no recharge was occurring. Under such conditions, water pressure in the conduit is less than that in the surrounding matrix (White, 1999), and conduits receive groundwater draining from the aquifer matrix. The composition of Edwards groundwater from the saline zone (herein referred to as saline-zone groundwater) was represented by two groundwater samples previously inferred to be predominantly influenced by saline-zone groundwater (well D-1 sampled March 19, 1993, Oetting et al., 1996; Saint Albans well about 4 km east of the study area, sampled July 13, 2009, Wierman et al., 2010). Recharging stream water was represented by the compositions of stream-water composite samples collected throughout the project interval in the five major streams that recharge the BSE. Upland recharge, surface water that directly recharges the aquifer in the recharge zone by infiltration through karst features, such as caves and sink holes, was represented by the composition of overland runoff entering a sinkhole in the Bear Creek watershed, collected as discrete samples and analyzed by the City of Austin (http://www.ci.austin.tx.us/wrequery/query_form.cfm) during May–September 2007. The area surrounding the sinkhole is undisturbed and is protected as part of a municipal groundwater-quality protection program. Median concentrations of each constituent in all the runoff samples ($n = 26$) were used to define the geochemistry of the upland recharge. The variability in concentrations in upland runoff was small (standard deviation/mean <0.25 for all major ions, except K^{+}) relative to the variation in concentrations between end members and variations within spring-water and groundwater samples. For modeling purposes, Edwards groundwater, saline-zone groundwater, and upland recharge end members were assumed to be constant throughout the period of sample collection (i.e., the same compositions were used for all models). Changes in stream water compositions, however, were incorporated into the modeling (i.e., spring and groundwater compositions were modeled using surface water compositions measured in samples collected on the same day as the spring and groundwater samples).

Upland-recharge samples had the lowest specific conductance of all the end members, and saline-zone samples had the highest (Table 1). Upland recharge, Edwards groundwater, and stream water are Ca-HCO_3-type waters with similar Ca^{2+} and HCO_3^- concentrations. Concentrations of K^{+}, Cl^{-}, Na^{+}, and SO_4^{2-} increase from upland recharge to Edwards groundwater to stream water. The saline zone is characterized by Na–Cl-type water, and has higher concentrations of Na^{+}, Cl^{-}, and SO_4^{2-} relative to the other sources (Table 1).

For each site, the available geochemical reactions were the same, but the combinations of end members were different. Groundwater at the diffuse site was modeled as a possible mixture of Edwards groundwater, saline-zone groundwater, and recharging water from upgradient streams (Bear and Onion). Groundwater at the conduit site was modeled as a possible mixture of Edwards groundwater, recharging water from upgradient streams (Bear and Onion), and upland recharge. Spring water was modeled as a

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Table 1

Median (and minimum and maximum) concentrations and isotopic compositions for spring, groundwater, and stream water composites and model source water inputs.

		Specific conductance (µs/cm @ 25 °C)	HCO_3^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Sr^{2+} (mg/L)	Si (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	$NO_3^- + NO_2^-$ (mg/L)	F^- (mg/L)	B (mg/L)	Br^- (mg/L)	$^{87}Sr/^{86}Sr$
Observed spring, groundwater, and stream water composite compositions																
Spring																
Dry	*n* = 15[a](4)	711 (689–735)	320 (304–348)	84 (78–87)	25 (23–27)	3.1 (2.8–3.5)	12 (11–12)	1.7 (1.6–1.8)	27 (24–32)	40 (37–43)	42 (38–47)	1.5 (1.5–1.6)	0.35[b]	0.087 (0.076–0.10)	0.35 (0.31–0.40)	0.70792 (0.70790–0.70792)
Wet	*n* = 7[a](15)	667 (656–689)	312 (296–323)	92 (80–99)	20 (18–22)	1.01 (0.60–2.8)	10 (10–11)	1.5 (1.2–1.8)	16 (14–20)	46 (33–53)	30 (25–33)	1.5 (1.4–1.8)	0.24 (0.19–0.33)	0.060 (0.048–0.077)	0.19 (0.16–0.29	0.70796 (0.70791–0.70801)
Diffuse site (groundwater)																
Dry	*n* = 13[a](2)	608 (603–610)	341 (326–349)	82 (76–87)	26 (24–26)	9.6 (8.8–10.4)	11 (10–12)	1.2 (1.2–1.3)	7.0 (6.7–7.7)	27 (27–28)	12 (12–12)	1.2 (1.2–1.3)	0.40[b]	0.043 (0.036–0.049)	0.07 (0.05–0.10)	0.70791 (0.70791–0.70791)
Wet	*n* = 7[a](3)	608 (605–618)	344 (340–348)	79 (74–84)	25 (24–26)	9.5 (8.8–10.2)	11 (11–12)	1.2 (1.2–1.3)	6.9 (6.4–7.2)	28 (27–28)	13 (12–13)	1.2 (1.1–1.2)	0.43 (0.41–0.46)	0.044 (0.039–0.047)	0.08 (0.06–0.09)	0.70789 (0.70788–0.70790)
Conduit site (groundwater)																
Dry	*n* = 13[a](3)	584 (581–587)	342 (320–358)	84 (78–89)	25 (23–26)	0.43 (0.40–0.45)	12 (10–13)	0.9 (0.9–1.0)	6.5 (6.0–7.7)	14 (13–15)	11 (11–11)	1.1 (1.1–1.2)	0.19[b]	0.036 (0.031–0.041)	0.07 (0.05–0.09)	0.70781 (0.70778–0.70782)
Wet	*n* = 7[a](7)	590 (587–606)	308 (280–350)	87 (82–99)	18 (15–24)	0.29 (0.20–0.45)	10 (8.7–12)	1.1 (0.9–1.4)	8.0 (6.0–10)	32 (12–48)	17 (10–24)	1.3 (1.2–2.4)	0.16 (0.12–0.18)	0.040 (0.033–0.049)	0.09 (0.07–0.12)	0.70794 (0.70778–0.70804)
Stream composites																
Dry	*n* = 12[a](12)[c]	701 (602–736)	247 (201–272)	75 (67–90)	21 (18–23)	0.32 (0.27–0.33)	10 (7–17)	2.5 (2.0–3.2)	33 (27–41)	63 (46–77)	56 (50–69)	0.06 (<0.02–0.17)		0.11 (0.089–0.20)	0.21 (0.14–0.40)	0.70806 (0.70796–0.70814)
Wet	*n* = 7[a](35)[c]	588 (458–634)	247 (148–267)	80 (52–85)	18 (13–19)	0.26 (0.23–0.30)	8 (6–8)	1.6 (1.1–2.5)	16 (13–22)	59 (48–78)	36 (26–42)	0.89 (0.20–0.98)	0.16 (0.14–0.19)	0.058 (0.045–0.095)	0.14 (0.11–0.15)	0.70803 (0.70793–0.70818)
Model source water inputs																
Saline zone[d]		2944	282	175	106	14	15	13	342	491	512	<0.02	3.7	–	–	–
Saline zone[e]		3280	220	143	87	21	15	15	393	596	533	<0.02	3.8	–	–	–
Upland recharge[f]		472	240	87	10.5	0.05	–	0.33	2.5	5.43	2.8	0.75	0.05	0.03	0.15	–
Edwards groundwater[g]		581	347	83	25	0.44	12.18	0.90	6.2	13	11	1.15	0.19	0.04	0.09	–

[a] *n* = number of major ion samples (number of $^{87}Sr/^{86}Sr$ samples).

[b] *n* = 1.

[c] *n* for all stream water $^{87}Sr/^{86}Sr$ analyses.

[d] Data from Oetting et al. (1996) (well D-1 sampled March 19, 1993).

[e] Data from Saint Albans well sampled July 13, 2009 (Wierman et al., 2010).

[f] Data from City of Austin (http://www.ci.austin.tx.us/wrequery/query_form.cfm).

[g] Groundwater sampled from conduit site (USGS station 300813097512101) on August 5, 2009; F^- value from water sampled on August 26, 2009.

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possible mixture of Edwards groundwater, saline-zone groundwater, and stream water from all five streams.

The user-assigned uncertainty (global uncertainty) for the final water composition and each source-water composition was 5%. In the cases where the model could not produce a result, global uncertainty was increased by integer increments up to 10%. In the rare case that model results could not be produced with a 10% global uncertainty, the uncertainty of all source-water inputs was increased by integer increments until model results could be produced.

4. Results

4.1. Recharge and spring discharge

During the dry interval, surface-water recharge and spring discharge rates were low, although intermittent and short-lived increases following rainfall events occurred; spring discharge and surface-water (stream) recharge increased markedly during the wet interval (Figs. 3 and 4). During the first part (September–November, 2009) of the wet interval, surface-water recharge and spring discharge covaried (Fig. 4). Once spring discharge surpassed ~1.5 m^3/s (~50 ft^3/s), spring discharge increased in discrete steps following recharge pulses (Figs. 3 and 4). With the exception of the first month of the wet period (September 2009), specific conductance in spring water decreased by about 16–44 $\mu s/cm$ following recharge pulses (Supplementary material Table S2).

4.2. Major ion compositions

Stream, spring, and groundwater samples were Ca-HCO_3-type waters with pH values ranging from 6.3 to 8.0 (Supplementary material Table S3). Stream-water composite samples generally had high concentrations of Ca^{2+}, Cl^-, Na^+, and SO_4^{2-} and low concentrations of Mg^{2+} and Sr^{2+} relative to groundwater (Table 1). Concentrations of constituents (except Sr^{2+}) measured in samples collected from the diffuse site were similar to or slightly higher than those collected from the conduit site during the dry interval and similar to or lower than those at the spring site, and varied little throughout the dry and wet intervals (Fig. 3). Concentrations of constituents at the conduit site varied little throughout the dry interval, and gradually evolved towards those of surface water during the wet interval. Concentrations of most constituents in spring-water samples increased slightly over the dry interval, and were similar to those of surface-water samples collected during the wet interval (Fig. 3).

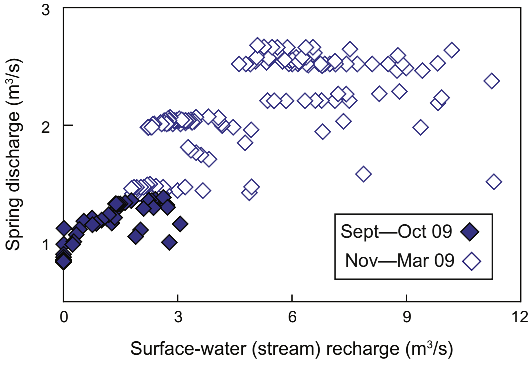

Fig. 4. The relation between surface-water (stream) recharge and spring discharge for the first (September–October 2009) and second (November 2009–March 2010) parts of the wet interval.

4.3. Sr isotope compositions

$^{87}Sr/^{86}Sr$ values in spring discharge and groundwater ranged from 0.70778 to 0.70804 (Table 1), which are between values measured for the Edwards Group (0.7075–0.7080; Koepnick et al., 1985; Christian et al., 2011) and surface water (0.70793–0.70818; this study). Values at the diffuse site (0.70788–0.70791) varied little throughout the transition from the dry interval to the wet interval (Fig. 3), and there was no correlation between Sr concentrations and $^{87}Sr/^{86}Sr$ values ($n = 5$).

At the conduit site, $^{87}Sr/^{86}Sr$ values varied little and were low (0.70778–0.70782) relative to the diffuse site during the dry interval, and gradually increased (from 0.70778 to 0.70804) during the wet interval to values similar to those measured in surface water. There was a strong negative correlation ($r = -0.90$, $n = 10$) between Sr concentrations and $^{87}Sr/^{86}Sr$ values at the conduit site. Spring water $^{87}Sr/^{86}Sr$ values also varied little during the dry interval and values (0.70790–0.70792) were similar to those measured at the diffuse site. As at the conduit site, $^{87}Sr/^{86}Sr$ values at the spring increased (from 0.70791 to 0.70801) during the wet interval toward values similar to those measured in surface water. There was a negative correlation ($r = -0.70$, $n = 15$) between Sr concentrations and $^{87}Sr/^{86}Sr$ values in spring samples, and the correlation was stronger ($r = -0.85$, $n = 9$) when only samples collected a month or more after the onset of wet conditions (October 2009–March 2010) were considered.

4.4. Principal components analysis

The first two factors identified by the PCA explain 70% of the variance in major-ion compositions measured in spring water, groundwater, and stream-water-composite samples (Fig. 5a). The first factor explains 46% of the variance, and is heavily weighted on B, Br^-, Cl^-, HCO_3^-, K^+, Na^+, and SO_4^{2-} (all positive except for HCO_3^-). The second factor explains 24% of the variance, and is heavily weighted on HCO_3^-, Mg^{2+}, and Si (all negative). Two constituent groupings are evident: (i) B, Br^-, Cl^-, K^+, and Na^+, and (ii) HCO_3^-, Mg^{2+}, and Si. SO_4^{2-} did not group with any other variables, and Ca^{2+}, NO_3^-, and Sr^{2+} did not strongly influence Factors 1 or 2 (Fig. 5a).

Three vertices are apparent when surface water, spring water, and groundwater geochemistry are viewed on the Factors 1–2 plane (Fig. 5b). The vertices are defined by (i) groundwater sampled at the diffuse site during both the dry and wet interval and at the conduit site during the dry interval only; (ii) spring water sampled during the dry interval; and (iii) stream-water composites sampled during the wet interval. During the wet interval, the geochemistry of conduit-site groundwater, spring water, and stream-water composites converged towards similar scores on Factors 1 and 2 (Fig. 5b).

4.5. Geochemical modeling using PHREEQC

Most groundwater compositions at the diffuse site could be modeled with varying amounts of Edwards and saline-zone groundwater or stream water along with specified mineral solution reactions. The amount of saline-zone (<1%) or stream-water (0–19%) contribution to groundwater was temporally inconsistent, and most models could not balance K^+ with global uncertainty less than 9% (Table 2).

Groundwater compositions at the conduit site could be modeled with varying amounts of Edwards groundwater, recharging stream water, and upland recharge along with specified mineral solution reactions. During the dry interval, groundwater compositions could be modeled without any surface water contribution (i.e., upland recharge and stream loss) when recharge was not

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Table 2
Geochemical model results.

Diffuse	% of Groundwater comprised of			Calcite (mols)	Dolomite (mols)	Gypsum (mols)	Ca^{2+} exchange (mols)	Na^+ exchange (mols)	Celestite (mols)	Minimal, total models	Global model uncertainty (%)	Constituents requiring uncertainty increase	Stream recharge bear and onion (m^3/s)
	Edwards groundwater	Saline zone	Stream (bear and onion)										
Dry interval													
28-Jan-2009	99.2	0.8	–	−1.32e−4	9.3e−6	0	4.3e−5	−8.6e−5	1.1e−4	1, 6	10	K^+	0.00
6-April-2009	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]		10	K^+	0.01
27-April-2009	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]		10	K^+	0.05
13-May-2009	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]		10	K^+	0.01
5-Aug-2009	99.4	0.6	–	−3.14e−5	0	0	4.0e−5	−8.1e−5	9.4e−5	1, 8	9	K^+	0.00
Wet interval													
23-Sep-2009	86–87	0	12–14	0 to 3.9e−6	0 to 1.1e−4	0 to 2.4e−5	0 to 6.6e−7	−1.3e−6 to 0	9.6e−5	4, 94	5		0.68
14-Oct-2009	89–90	0	10–11	−7.1e−5 to 0	0 to 3.2e−5	0	0 to 1.4e−5	−2.8e−5 to 0	9.6e−5	9, 16	9	K^+	0.53
4-Nov-2009	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	10	K^+	0.46
2-Dec-2009	81–85	0	14–19	−9.1e−5 to 9.6e−5	0 to 8.4e−5	0	0 to 2.5e−5	−5.9e−5	1.1e−4	30, 42	9	K^+	0.98
5-Jan-2010	99.3	0.7	0	−3.8e−5 to 0	0 to 1.1e−5	0	4.7e−5	−9.4e−5	1.0e−4	3, 9	10	K^+	1.23
2-Feb-2010	99.2	0.08	0	−6.4e−5	0	0	6.7e−5	−1.2e−4	9.8e−5	3, 5	9	K^+	4.16
2-Mar-2010	85–99	0.7–0.9	0–14	−4.7e−5 to 2.9e−5	0	0	4.5 to 5.1e−5	−1.0e−4 to −8.9e−5	9.9e−5	7, 14	10	K^+	3.84
Conduit	% of groundwater comprised of			Calcite (mols)	Dolomite (mols)	Gypsum (mols)	Ca^{2+} exchange (mols)	Na^+ exchange (mols)	Celestite (mols)	Minimal, total models	Global model uncertainty (%)	Constituents requiring uncertainty increase	Stream recharge bear and onion (m^3/s)
	Edwards groundwater	Upland Recharge	Stream (bear and onion)										
Dry interval													
28-Jan-2009	100	–	–	3.5e−5	0	2.7e−6	−4.5e−6	9.0e−6	–	1, 16	6	SO_4^{2-}, Sr^{2+}	0.00
12-Mar-2009	96	3	1	−5.0e−5	0	0	−8.9e−6	−1.8e−5	–	1, 44	5		0.05
22-April-2009	100	0	0	−3.5e−5	1.8e−5	0	−3.4e−6	−6.7e−6	–	1, 48	5		0.01
13-May-2009	94	5	1	1.0e−4	0	0	−2.5e−6	5.0e−6	–	1, 119	5		0.01
15-July-2009	100	–	–	3.3e−5	0	4.2e−6	1.6e−6	−3.2e−6	–	1, 16	5		0.00
Wet interval													
23-Sep-2009	98	2	–	2.29e−5	0	0	2.3e−6	−4.7e−6	–	1, 7	6	All	0.67
14-Oct-2009	46	33	21	0 to 9.5e−5	0	0	0 to 2.3 e−5	0 to −4.6e−5	–	4, 4	9	K^+	0.53
4-Nov-2009	10	30	60	0 to −1.2e−4	0 to 7.6e−7	0	0 to 1.8e−5	0 to −3.5e−5	–	8, 8	5		0.46
2-Dec-2009	27–30	12–14	58–59	−2.0e−4 to 0	–	4.6 to 6.9e−5	2.4 to 3.0e−5	−6.1 to −4.8e−5	–	4, 4	6	K^+	0.98
5-Jan-2010	13–26	11–19	63–69	−9.7e−5 to 0	–	–	0 to 1.3e−5	−2.5e−5 to 0	–	14, 20	5		1.23
2-Feb-2010	8–13	32–34	56–60	−9.8 to 1.2e−5	0	0	−4.1e−6 to 0	0 to 8.3e−6	–	8, 8	5		1.46
2-Mar-2010	7–15	21–25	63–69	0 to 9.1e−5	0 to 4.2e−5	0	−4.7e−6 to 0	0 to 9.4e−6	–	9, 13	5		3.84

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Spring	% of groundwater comprised of			Calcite (mols)	Dolomite (mols)	Gypsum (mols)	Ca^{2+} exchange (mols)	Na^{+} exchange (mols)	Celestite (mols)	Minimal, total models	Global model uncertainty (%)	Constituents requiring uncertainty increase	Stream recharge (m^3/s)	Spring discharge (m^3/s)	Recharge/discharge (%)
	Edwards ground-water	Saline zone	Stream (bear and onion)												
Dry interval															
17-Dec-2008	90	5	5	2.6e−6	0	0	−1.0e−4	2.1e−4	2.1e−5	1,4	6	SO_4^{2-}	0.03	0.54	5.8
7-Jan-2009	85	4	11	−6.0e−5	0	0	−2.8e−5	5.6e−5	2.3e−5	1, 2	7	SO_4^{2-}	0.05	0.54	9.5
28-Jan-2009	88	5	8	−9.5e−5	0	0	−4.0e−5	8.0e−5	2.1e−5	1,2	5		0.05	0.51	10
18-Feb-2009	84	4	12	5.9e−5	0	0	−1.3e−4	2.6e−4	2.8e−5	1, 4	7	SO_4^{2-}	0.11	0.48	24
1-April-2009	74	3	23	−1.5e−5 to 0	0	0	−.4e−4	2.3e−4	2.6e−6	4, 4	8	SO_4^{2-}	0.10	0.54	19
22-April-2009	49	0	51	1.1e−4	0	0	1.2e−4	2.4e−4	2.5e−5	1, 29	9	$K^{+}SO_4^{2-}$	0.15	0.54	27
13-May-2009	81	4	16	0 to 1.3e−4	0	0	−6.7e−5	1.3e−4	2.2e−5	7, 10	5		0.08	0.45	17
2-June-2009	57–67	1–2	30–42[b]	0 to 1.0e−4	0	0	−7.0 to −5.0e−5	1.0 to 1.4 e−5	2.7e−5	2, 22	5		0.05	0.45	11
	95	5	–	−1.2e−4	0	0	−6.3e−6	1.2e−5	−1.9e−5	1, 16	8	Mg^{2+}, SO4^{2-}	0.00		
24-June-2009	71	3	25[b]	2.2e−4	0	0	−6.4e−5	1.3e−4	2.6e−5	1, 22	5		0.02	0.45	4.8
	95	5	–	3.5e−5	0	0	−2.2e−5	4.5e−5	1.9e−5	1, 32	7	Mg^{2+}, SO4^{2-}			
15-July-2009	69	3	28[b]	−2.3e−5	0	0	−6.3e−5	1.3e−4	2.9e−5	1, 8	5		0.003	0.42	0.7
	94	6	–	−2.1e−4	0	0	1.5e−5	−3.1e−5	2.1e−5	1, 8	10	Mg^{2+}, SO4^{2-}			
5-Aug-2009	69–84	4–5	11–27[b]	−4.2 to 0	0	0	−5.5e−5 to 0	0 to 1.1e−4	2.5 to 2.8e−5	3, 14	5		0.001	0.40	0.2
	94	6	–	−1.6e−4	0	0	−4.9e−5	9.7e−5	2.2e−5	1,8	7	SO_4^{2-}			
Wet interval															
23-Sep-2009	67	1	32	0 to 7.2e−5	0	0	−7.5e−5	1.5e−4	2.6e−5	2,6	8	SO_4^{2-}, Sr^{2+}	0.76	1.22	63
14-Oct-2009	49	0	51	−9.9e−5 to 8.0e−5	0	0	0 to 3.2e−5	−6.4e−5 to 0	8.6e−6	12, 12	10	Mg^{2+}	2.63	1.67	160
4-Nov-2009	41–48	0	53–60	0 to 7.6e−5	0	0 to 8.8e−5	−7.9e−6 to 1.8e−5	−3.6e−5 to 1.6 e−5	4.1e−6	32, 32	5		2.10	1.47	140
2-Dec-2009	24–47	0–1	52–76	0 to 2.0e−4	0 to 4.2e−5	0 to 9.9e−5	−2.2 to 4.3e−5	−8.6e−5 to 4.3e−5	2.0 to 4.2e−6	34, 37	5		6.80	1.78	380
5-Jan-2009	26–53	0–1	45–73	0 to 2.7e−4	0 to 7.8e−5	0 to 7.2e−5	−2.5 to 2.5e−5	−4.9e−5 to 5.0e5	2.6 to 5.1e−6	38, 42	5		2.66	2.01	130
2-Feb-2010	11–16	0	83–88	0 to 7.2e−5	0	0	−2.1e−5 to 0	0 to 4.2e−5	3.6e−6	8, 8	5		7.22	2.24	320
2-Mar-2010	29–37	1	66–71	0 to 1.6e−4	0	0 to 6.2e−7	0 to 2.0e−5	−4.0e−5 to 0	1.6 to 2.3e−6	9, 9	5		6.37	2.58	250

"–" Not included in model.

[a] Could not be modeled.

[b] Exceeds percentage of recharge relative to discharge.

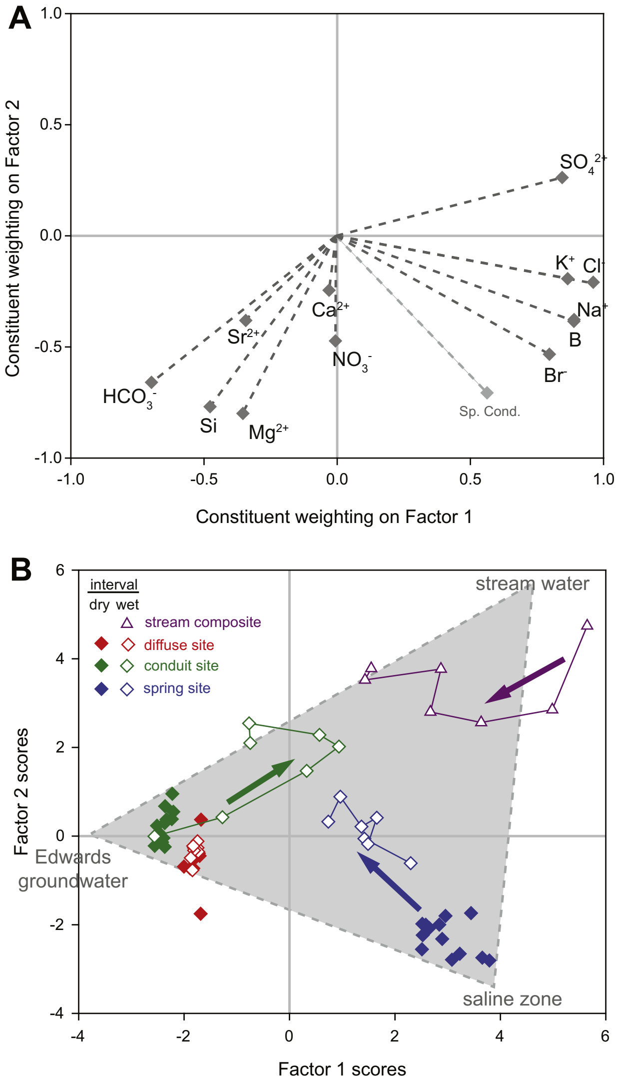

Fig. 5. Results from principal component analysis. (A) Physical property or constituent weighting on Factors 1 and 2 scores for each constituent. (B) Evolution during the wet and dry periods of Factors 1 and 2 scores (arrows indicate direction of change).

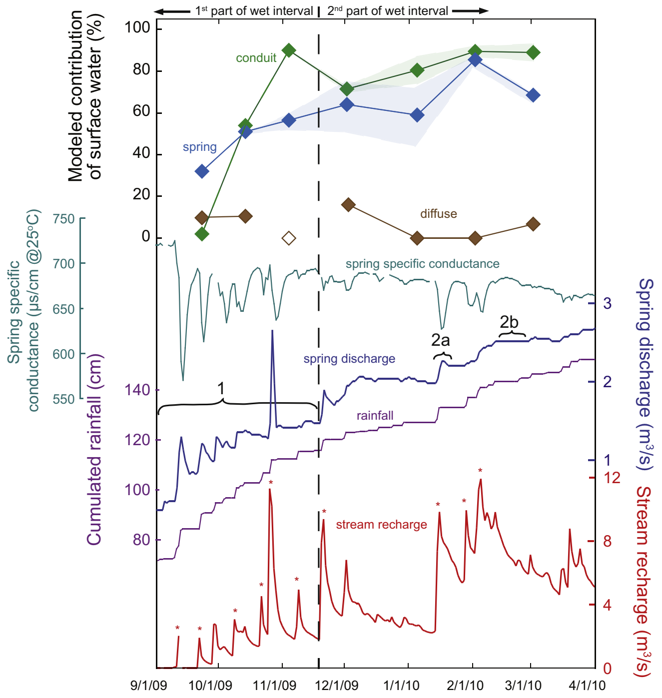

Fig. 6. Time series for modeled surface-water contribution (solid diamond symbols represent the median; shaded area, the range) to spring and groundwater (empty diamond symbol represents a composition that could not be modeled), spring water specific conductance, spring discharge, cumulative daily rainfall, and estimated surface-water (stream) recharge for the wet period. Labeled parts of spring discharge are detailed in Fig. 7. Asterisks indicate recharge pulses for which peak was estimated by linear interpolation because flooding precluded making a discharge measurement.

occurring, but required small contributions (0–6% of total) of recharging surface water, including both upland recharge and losing stream water, when recharge was occurring. The modeled proportional contribution of recharging surface water to groundwater at the conduit site increased rapidly during the first 3 months of the wet interval, and more gradually during the remainder of the wet interval (Fig. 6).

Spring-water compositions were accounted for by varying amounts of Edwards groundwater, saline-zone groundwater, and recharging stream water, and mineral-solution reactions. During the first part of the dry interval (November 2008–May 2009), with the exception of one sample, the modeled contribution of recharging stream water to spring discharge was similar to the ratio of surface-water recharge to spring discharge (on the basis of measured stream and spring discharge), but was higher than that ratio during the second part of the dry interval (June–August 2009) (Table 2). Models with a mixture of only Edwards groundwater and a small component of saline-zone groundwater (5–6%) were geochemically feasible during this latter interval, but required higher global uncertainties to balance Mg^{2+} and SO_4^{2-} (Table 2). During the wet interval, the modeled saline-zone contribution was small ($\leqslant 1\%$), and an increasing amount of recharging stream water was required to account for spring-water compositions as the wet interval progressed (Table 2 and Fig. 6).

In addition to mixing, groundwater and spring water compositions were modeled with varying amounts of calcite dissolution or precipitation and Ca^{2+} and Na^{+} ion exchange (Table 2). Models rarely involved the dissolution of dolomite and gypsum. Celestite dissolution was involved in all of the models of spring water and groundwater at the diffuse site. There were no temporal patterns in the amount of mineral dissolution (or precipitation) or ion exchange at any of the sites.

5. Discussion

5.1. Controls on spring-water and groundwater compositions under dry and wet conditions

Each site had a unique combination of controls that dictated geochemical compositions under dry and wet conditions. During the dry interval, groundwater compositions at the conduit site were dominated by mineral-solution reactions, whereas the compositions at the diffuse and spring sites were dominated by mixing of Edwards groundwater with other groundwater sources. During the wet interval, mixing of Edwards groundwater with recharging surface water was the dominant control at the conduit and spring sites, while the controls at the diffuse site were the same as during the dry interval.

During the dry interval, the geochemistry of groundwater at the conduit site was consistent with mineral-solution reactions with carbonate minerals. Concentrations of $Cl^{-}, Na^{+}, SO_4^{2-}$, and Sr^{2+} at

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the conduit site were low relative to those at the diffuse and spring sites, and concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- and values of $^{87}Sr/^{86}Sr$ were static and consistent with extensive and relatively uniform interaction with Edwards aquifer bedrock (Wong and Banner, 2010). This supports the hypothesis that, during the dry interval, water was draining from the aquifer matrix into conduits.

Elevated concentrations of Cl^-, Na^+, SO_4^{2-}, and Sr^{2+} and higher values of $^{87}Sr/^{86}Sr$ at the diffuse and spring sites relative to those at the conduit site during the dry interval indicate that groundwater at these sites is a mix of Edwards groundwater and an additional source(s) or chemical reaction(s). A contribution of groundwater from the saline zone, hypothesized to occur when spring discharge is low (Senger and Kreitler, 1984; Mahler et al., 2006), can account for elevated concentrations of Cl^-, Na^+, and SO_4^{2-}. High Sr^{2+} concentrations, although sometimes coincident with saline-zone influence, are not characteristic of the saline zone, and indicate an additional source to or geochemical reaction at the diffuse site. This additional source might also have contributed, to a lesser extent, to groundwater at the spring site, which had concentrations of Sr^{2+} that were much lower than those at the diffuse site but higher than those at the conduit site (Fig. 3 and *Table* S3). $^{87}Sr/^{86}Sr$ values at the spring and diffuse sites were similar, indicating that the source of the Sr^{2+} at the two sites likely was the same. A potential source is "transitional" saline-zone groundwater containing dissolved celestite ($SrSO_4$), or strontianite ($SrCO_3$) associated with fault zones, which previously has been hypothesized to be a source of high Sr^{2+} concentrations in fresh groundwater (<500 μs/cm) in the Edwards aquifer (Oetting, 1995), or both.

Geochemical modeling supports the hypothesis that additional uncharacterized sources of groundwater contributed to discharge at the diffuse and spring sites during the dry interval. At the diffuse site: (i) all geochemical models required the dissolution of celestite, (ii) models using a mix of Edwards, saline-zone groundwater, and stream water required large global uncertainties ($\geqslant$9%), (iii) some compositions could not be modeled (Table 2), and (iv) there was no temporal pattern to the groundwater compositions or to the contributions of either of the three sources (Table 2, Fig. 3). Thus, saline-zone groundwater and stream water likely were not sufficient end members to constrain groundwater compositions, indicating either the influence of additional end members or occurrence of more complex mineral–solution interactions than those included in the modeling. At the spring, it was necessary to include celestite dissolution in geochemical models as well as contributions of saline zone groundwater, indicating that an additional end member likely is needed to account for spring water Sr concentrations. Another uncharacterized source (e.g., municipal recharge) might have been contributing to groundwater at the spring during the second part of the dry interval (June–August 2009). Geochemical models of spring water during the second part of the dry interval either required an unrealistically high stream-water contribution (i.e., exceeding the amount of surface-water recharge occurring), or high global uncertainties (7–10%) to balance Mg^{2+} and SO_4^{2-}. The saline-zone contribution to the spring varied little during the dry interval and was greater than its contribution to the diffuse site (Table 2), even though the spring is farther from the saline zone than is the diffuse site (Fig. 1). The relatively large saline-zone contribution to the spring likely is associated with a major conduit flow route that is affected by the saline zone, as demonstrated by dye traces (Hauwert et al., 2004).

During the wet interval, the geochemistry of groundwater at the conduit and spring sites reflected the large contribution from recharging stream water. The major-ion geochemistry and scores for groundwater compositions on PCA Factors 1 and 2 at the diffuse and conduit sites, which were similar during the dry interval, diverged during the wet interval, with concentrations of major ions and PCA scores at the diffuse site remaining static and concentrations and PCA scores at the conduit site becoming more similar to those of stream water (Figs. 3 and 5). The contrasting geochemical dynamics at the diffuse and conduit sites are consistent with the initial hypothesis that one site receives dominantly diffuse flow and the other receives dominantly conduit flow. Concomitantly, the major-ion geochemistry and PCA scores for spring-water samples, initially different from those at the conduit site, converged with those of groundwater at the conduit site and of stream water (Figs. 3 and 5). Concentrations of Sr^{2+} at the conduit and spring sites, initially higher than that of stream water, decreased during the wet interval, and values of $^{87}Sr/^{86}Sr$ at the conduit and spring sites, initially lower than that of stream water, increased. The strong negative linear correlation between Sr^{2+} concentrations and $^{87}Sr/^{86}Sr$ values at the two sites is an additional indication that surface water was mixing with groundwater. The use of Sr^{2+} concentrations and $^{87}Sr/^{86}Sr$ values in identifying the influence of surface water recharge on spring and groundwater demonstrate a novel use of Sr isotopes in this system.

5.2. Timing of vulnerability of groundwater to contamination

The quantification of the contribution of recharging stream water to groundwater is a useful descriptor of the timing and magnitude of the vulnerability of groundwater in the conduit network to contamination from the land surface. Under dry conditions, the ratio of surface-water recharge to spring discharge is a reasonable approximation of the proportional stream water contribution to spring discharge, as indicated by geochemical modeling estimates (Table 2). The approximation, however, is not appropriate under wet conditions, as surface-water recharge exceeded spring discharge for the majority of the wet interval but the contribution of surface water to spring discharge was less than 100% (Fig. 6).

Within a month of the onset of the wet interval, surface water composed more than 50% of groundwater at the conduit and spring sites (Fig. 6). This high contribution—which modeling indicated could be as high as 90% for some samples—continued throughout the wet interval, indicating that stream water was the dominant control on the quality of groundwater and spring discharge, not just during the storm response but also during non-storm flow conditions. By using geochemical modeling to quantify the surface-water influence on groundwater, we also quantify the vulnerability of groundwater in the conduit network to contamination from surface water.

5.3. Nature of the matrix and the conduit network

The response of the aquifer system to the transition from drought to wet conditions and the quantification of surface-water contributions to spring and groundwater at each site enable interpretations about how surface water recharges the aquifer and the connection between the matrix and conduit parts of the aquifer. The lack of geochemical response at the diffuse site to the transition from drought to wet conditions indicates either that geochemical changes within the aquifer were limited to the conduit network, or that the amount of recent recharge that entered the matrix was negligible relative to the amount of water in storage. There is evidence that exchange occurs between the aquifer matrix and conduit network in this karst system (e.g., Mahler et al., 2006) and others (e.g., Martin and Dean, 2001; Bailly-Comte et al., 2010). The results presented here indicate that water from the conduits did not flow, to a substantial extent, into the matrix in the area of the diffuse site. Alternatively, flow from the conduit to the matrix, if occurring, had a negligible effect on the matrix water geochemistry on the time scale of this study. This is consistent with previous modeling using matrix porosity, hydraulic conductivity, and specific storage values from this and other karst aquifers that

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has indicated that the distance to which flow from conduits penetrates the matrix is small (10^{-2} and 10^{-4} m for high and low hydraulic conductivity aquifers, respectively) and that less than 0.1% of solute moves from conduits to the matrix (Peterson and Wicks, 2005). Although this study focuses on recharge originating from stream loss, the static geochemical nature of the diffuse site indicates that the amount, or the geochemical effect, of diffuse recharge to the aquifer also was negligible with respect to the area supplying water to the diffuse site.

Filling of the conduit network with recent recharge was neither spatially uniform nor complete. The proportion of spring discharge and groundwater at the conduit site composed of surface-water recharge, as determined by geochemical modeling, did not increase at the same rate or follow the same temporal pattern (Fig. 6). These differences might result from (i) a non-uniform spatial distribution of recharge, (ii) a difference in size of the recharge area contributing to the sites, (iii) differences in groundwater travel times, or (iv) a combination of these. Further, at no time was the conduit network filled entirely with recharging stream water. Even though estimated recharge exceeded spring discharge from October 2009 to the end of the study, geochemical modeling indicated that some component of Edwards groundwater was needed to account for spring water and conduit site groundwater compositions throughout the wet interval (Fig. 6). The persistence of Edwards groundwater in the conduit network might result from variations in conduit geometry (Raeisi et al., 2007) or the occurrence of eddies in flow through irregular and rough fractures and conduits (Cardenas et al., 2007). Regardless of the mechanism, the persistence of Edwards groundwater indicates that complete piston flow is not occurring, i.e., recharging water does not push all existing water in the conduits ahead and out through the spring orifice.

5.4. Two modes of aquifer response

The spring hydrograph transitioned from one characteristic of a telogenetic karst system to that characteristic of an eogenetic system as the wet interval progressed from the first part to the second, indicating a change in mode of aquifer response to increasingly wetter conditions. In the first mode (spring discharge <~1.5 m^3/s; 50 ft^3/s), spring discharge was correlated with surface-water recharge (Fig. 4), indicating that increasing amounts of surface-water recharge resulted in increasing hydrostatic pressure and greater spring discharge. There were discrete responses in spring discharge shortly following recharge events, which is characteristic of telogenetic karst systems (Supplementary Fig. S1; Florea and Vacher, 2006). Because recharge events occurred frequently, however, recharged water did not completely empty from the system before the next event, and there was an overall gradual increase in spring discharge (Fig. 6).

The second mode (spring discharge >~1.5 m^3/s; 50 ft^3/s) of aquifer response was characterized by greater storage of recharging water, which resulted in a hydrograph that was characteristic of a eogenetic karst system (Supplementary Fig. S1; Florea and Vacher, 2006). Spring discharge responded to discrete recharge events, but recessions were shortened when spring discharge plateaued in December 2009–January 2010 and in March–April 2010 (Fig. 6). Stepped increases and plateaus in spring discharge and a lack of covariation between spring discharge and surface-water recharge during each of these steps (Figs. 4 and 6) indicates that: (i) large pulses of recharge resulted in discrete increases in hydrostatic pressure that were maintained at a constant level until another pulse of recharge entered the system, and (ii) there was greater storage of recharging water during the second mode relative to the first.

Florea and Vacher (2006) demonstrated how spring response hydrographs vary between aquifer systems on the basis of physical properties (e.g., porosity and permeability) inherent to the formation of the karst system (i.e., eogenetic vs. telogenetic). The transition of the BSE from a mode characteristic of a telogenetic system to one characteristic of a eogenetic system indicates that spring response hydrographs can vary within the same aquifer on the basis of changes in hydrologic conditions. Such a transition within an aquifer has not, to the knowledge of the authors, been previously discussed. This transition could reflect an enhancement of commu-

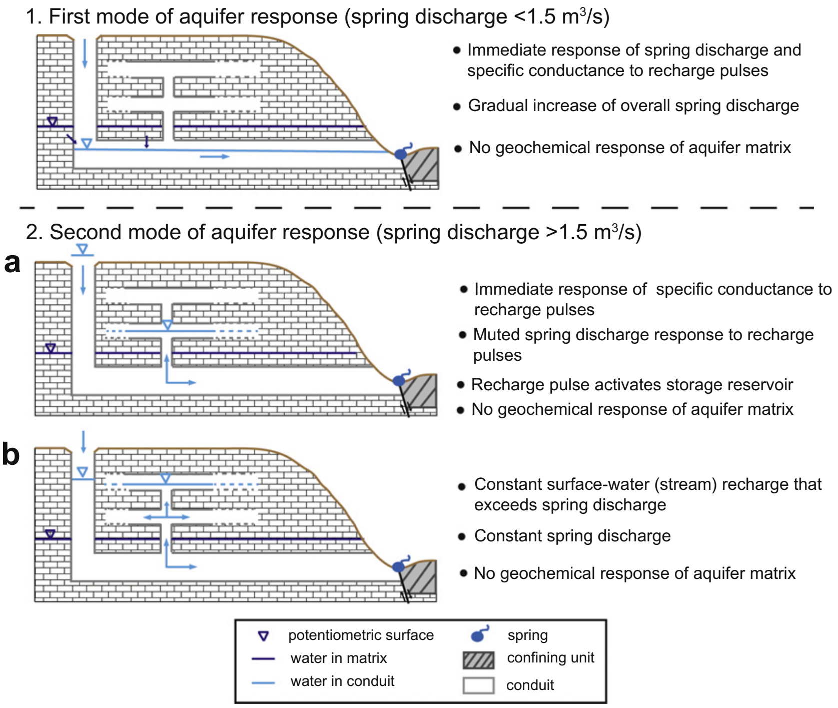

Fig. 7. Conceptual diagram illustrating the first and second modes of aquifer response. 1, 2a, and 2b refer to different parts of the spring discharge hydrograph labeled in Fig. 6. Diagram is not drawn to scale.

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nication between matrix and conduit parts of the aquifer (i.e., a more eogenetic-like porosity and permeability system) at higher aquifer water levels. The chemostatic nature of the matrix demonstrated in this study (Fig. 3) and a previous study (Garner and Mahler, 2007), however, suggests that the contribution of recharging surface water to the matrix part of the aquifer is negligible. Furthermore, recharging surface water would have to enter the matrix in a way that did not substantially affect hydrostatic head pressure as long intervals (up to 4 weeks) of constant spring discharge were observed.

A series of perched, restricted reservoirs could result in intervals of nearly constant spring discharge despite the occurrence of recharge consistently entering the system at rates that exceed spring discharge. Previous numerical modeling of conduit flow in aquifers with reservoirs illustrates that input to a reservoir drained by conduits that are small relative to the reservoir (Fig. 7) results in just this phenomenon: an immediate increase in spring discharge followed by a gradual, nearly zero-slope decline (Halihan and Wicks, 1998) and a hydrograph similar to that recorded by this study during the second mode of aquifer response. Alternatively, spring hydrograph plateaus could result from the activation of overflow routes; plateaus in a well hydrograph have previously been deduced to result from the piracy of water from the primary conduit (Ray, 1997). If water was pirated from the spring, then surface-water recharge should grossly exceed spring discharge on long (multiple years) time scales. Slade et al. (1986) reported a long-term balance between recharge from streams and spring discharge for the BSE, which indicates that piracy is likely not occurring.

Although the aquifer likely has two modes of physical response to changing meteorologic conditions, it is less evident that there are different modes of geochemical response. The decrease of spring-water specific conductance following recharge pulses (*Table* S2 and Fig. 6) indicates that the spring discharge responses resulted, in part, from the rapid transit of recently recharged surface water, as opposed to resulting solely from a pressure pulse associated with increases in hydrostatic pressure, and that this occurred during both modes of aquifer response. The decrease of specific conductance of spring water was similar throughout most of the wet interval (Supplementary material Table S2 and Fig. 6), with the exception of the first month of the wet interval (September 2009). A high amount of dilution during this first month, relative to those during the remainder of the wet period, likely reflects the combined effects of a conduit network that initially was relatively empty and low stream-water specific conductance during the first month of the wet interval (September 2009) relative to that during the rest of the wet interval (Supplementary material Table S3). The contribution of surface water to spring water increased gradually throughout the entire wet interval, although the rate of increase was constant during the first mode and fluctuated during the second mode (Fig. 6). These differences could reflect differences in the modes of aquifer responses, or sampling that did not occur at sufficient frequency to capture temporal variations in response.

6. Conclusions

A 17-month study of groundwater geochemistry in the Barton Springs segment of the Edwards aquifer during the transition from a prolonged and extreme drought (PDSI = −4.4) to an extended period of well-above average rainfall (PDSI = 3.2) provides insight into the geochemical and physical response of this karst system to changes in meteorologic extremes. A striking divergence of geochemical compositions in response to changing meteorologic conditions at groundwater sites receiving conduit and diffuse flow provides a clear illustration of the dual nature of groundwater flow in a karst system. Quantification of the contribution of surface water to spring discharge demonstrates that the majority of spring water and groundwater was composed of surface water within a month of the onset of wet conditions, and provides an improved understanding of the timing and magnitude of vulnerability of groundwater quality to surface-water quality. The documentation of the physical aquifer response to extreme changes in meteorologic conditions was key to identifying two modes of aquifer response: a first mode (spring discharge $<\sim 1.5$ m^3/s; 50 ft^3/s) with a spring discharge hydrograph that is characteristic of telogenetic systems, and a second mode with enhanced storage (perhaps in a series of perched, constricted reservoirs) resulting in a spring discharge hydrograph characteristic of eogenetic systems. These conclusions were enabled by the use of a comprehensive set of approaches (real-time monitoring, Sr isotopes, PCA, and geochemical modeling), and integration of the results from multiple sites representing different parts of the aquifer.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2012.08.030.

References

Abbott, P.L., 1975. On the hydrology of the Edwards Limestone, south-central Texas. J. Hydrol. 24, 251–269.
Andrews, F.L., 1984. Effects of Storm-Water Runoff on Water Quality of the Edwards Aquifer Near Austin, Texas. Water Research Investigation, Report 84–4124.
Bailly-Comte, V., Martin, J.B., Jourde, H., Screaton, E.J., Pistre, S., Langston, A., 2010. Water exchange and pressure transfer between conduits and matrix and their influence on hydrodynamics of two karst aquifers with sinking streams. J. Hydrol. 386, 55–66.
Banner, J.L., Kaufman, J., 1994. The isotopic record of ocean chemistry and diagenesis preserved in non-luminescent brachiopods from Mississippian carbonate rocks, Illinois and Missouri. Geol. Soc. Am. Bull. 106, 1074–1082.
Banner, J.L., Jackson, C.S., Zong-Liang, Y., Hayhoe, K., Woodhouse, C., Gulden, L., Jacobs, K., North, G., Leung, R., Washington, W., Jiang, X., Casteel, R., 2010. Climate change impacts on Texas water: a white paper assessment of the past, present and future and recommendations for action. Texas Water J. 1, 1–19.
Barrett, M.E., Charbeneau, R.J., 1997. A parsimonious model for simulating flow in a karst aquifer. J. Hydrol. 196, 47–65.
Barrett, M.H., Hiscock, K.M., Pedley, S., Lerner, D.N., Tellam, J.H., French, M.J., 1999. Marker species for identifying urban groundwater recharge sources: a review and case study in Nottingham, UK. Water Resour. 33, 3083–3097.
Birk, S., Liedl, R., Sauter, M., 2004. Identification of localized recharge and conduit flow by combined analysis of hydraulic and physicochemical spring responses (Urenbrunnen, SW-Germany). J. Hydrol. 286, 179–193.
Cardenas, M.B., Slottke, D.T., Ketcham, R.A., Sharp, J.M., 2007. Navier–Stokes flow and transport simulations using real fractures shows heavy tailing due to eddies. Geophys. Res. Lett. 34, L14404.
Christian, L.N., Banner, J.L., Mack, L.E., 2011. Sr isotopes as tracers of anthropogenic influences on stream water in the Austin, Texas, area. Chem. Geol. 282, 84–97.
Cooke, M.J., Stern, L.A., Banner, J.L., Mack, L.E., 2007. Evidence for the silicate source of relict soils on the Edwards Plateau, central Texas. Quatern. Res. 67, 275–285.
Davis, J.C., 2002. Statistics and Data Analysis in Geology. Wiley, New York, 638p.
Desmarais, K., Rojstaczer, S., 2002. Inferring source waters from measurements of carbonate spring response to storms. J. Hydrol. 260, 118–134.

Fishman, M.J., 1993. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments: U.S. Geological Survey Open-File Report 93–125, 217p.

Florea, L.J., Vacher, H.L., 2006. Springflow hydrographs: eogenetic vs. telogenetic karst. Ground Water 44, 352–361.

Florea, L.J., Vacher, H.L., 2007. Eogenetic karsty hydrology: Insights from the 2004 hurricanes, peninsular Florida. Ground Water 45, 439–446.

Ford, D.C., Williams, P.W., 1989. Karst Geomorphology and Hydrology. Unwin Hyman, London, 601p.

Garner, B.D., 2005. Geochemical Evolution of Ground Water in the Barton Springs Segment of the Edwards Aquifer. Dissertation. The University of Texas at Austin, 317p.

Garner, B.D., Mahler, B.J., 2007. Relation of Specific Conductance in Ground Water to Intersection of Flow Paths by Wells, and Associated Major Ion and Nitrate Geochemistry, Barton Springs Segment of the Edwards Aquifer, Austin, Texas, 1978–2003: U.S. Geological Survey Scientific Investigations Report 2007–5002, 39p.

Griffiths, J.F., Ainsworth, G., 1981. One Hundred Years of Texas Weather 1880–1979. Texas A&M Univ., Office of the State Climatologist, College Station, 205p.

Gulley, J., Martin, J.B., Screaton, E.J., Moore, P.J., 2011. River reversals into karst springs: a model for cave enlargement in eogenetic karst aquifers. Geol. Soc. Am. Bull. 123, 457–467.

Halihan, T., Wicks, C.M., 1998. Modeling of storm responses in conduit flow aquifers with reservoirs. J. Hydrol. 208, 82–91.

Hauwert, N.M., 2009. Groundwater Flow and Recharge within the Barton Springs Segment of the Edwards Aquifer, Southern Travis County, Texas. Dissertation. The University of Texas at Austin, 328p.

Hauwert, N.M., Johns, D.A., Aley, T.J., Sansom, J.W., 2004. Groundwater Tracing Study of the Barton Springs Segment of the Edwards Aquifer, Southern Travis and Northern Hays Counties, Texas. Report by the Barton Springs/Edwards Aquifer Conservation District and City of Austin Watershed Protection and Development Review Department, 110p.

Heinz, B., Birk, S., Liedl, R., Geyer, T., Straub, K.L., Andresen, J., Bester, K., Kappler, A., 2009. Water quality deterioration at a karst spring (Gallusquelle, Germany) due to combined sewer overflow: evidence of bacterial and mirco-pollutant contamination. Environ. Geol. 57, 797–808.

Herman, E.K., Toran, L., White, W.B., 2009. Quantifying the place of karst aquifers in the groundwater to surface water continuum: a time series analysis study of storm behavior in Pennsylvania water resources. J. Hydrol. 376, 307–317.

Hess, J.W., White, W.B., 1988. Storm response of the karstic carbonate aquifer of south central Kentucky. J. Hydrol. 99, 235–252.

Koepnick, R.B., Burke, W.H., Denison, R.E., Hetherington, E.A., Nelson, H.F., Otto, J.B., Waite, L.E., 1985. Construction of the seawater ^{87}Sr/^{86}Sr curve for the Cenozoic and Cretaceous: supporting data. Chem. Geol. 58, 55–81.

Lakey, B., Krothe, N.C., 1996. Stable isotopic variation of storm discharge from a perennial karst spring, Indiana. Water Resour. Res. 32, 721–731.

Larkin, T.J., Bomar, G.W., 1983. Climatic Atlas of Texas: Texas Department of Water Resources, Limited Printing Report LP–192, 151p.

Lower Colorado River Authority, 2011. <http://hydromet.lcra.org/full.aspx>.

Mahler, B.J., Garner, B.D., 2009. Using nitrate to quantity quick flow in a karst aquifer. Ground Water 47, 350–360.

Mahler, B.J., Massei, N., 2007. Anthropogenic contaminants as tracers in an urbanizing karst aquifer. J. Contam. Hydrol. 91, 81–106.

Mahler, B.J., Garner, B.D., Musgrove, MaryLynn, Guilfoyle, A.L., Rao, M.V., 2006. Recent (2003–2005) Water Quality of Barton Springs, Austin, Texas, with Emphasis on Factors Affecting Variability. U.S. Geological Survey Scientific Investigations Report 2006–5299, 83p.

Mahler, B.J., Musgrove, M., Sample, T.L., Wong, C.I., 2011. Recent (2008–10) Water Quality in the Barton Springs Segment of the Edwards Aquifer with Emphasis on Factors Affecting Nutrients and Bacteria. U.S. Geological Survey Scientific Investigation, Report 2011–5139.

Martin, J.B., Dean, R.W., 2001. Exchange of water between conduits and matrix in the Floridan aquifer. Chem. Geol. 179, 145–165.

Massei, N., Mahler, B.J., Bakalwicz, M., Fournier, M., Dupont, J.P., 2007. Quantitative interpretation of specific conductance frequency distributions in karst. Ground Water 45, 288–293.

Moore, P.J., Martin, J.B., Screaton, E.J., 2009. Geochemical and statistical evidence of recharge, mixing, and controls on spring discharge in an eogenetic karst aquifer. J. Hydrol. 376, 443–455.

Musgrove, M., Banner, J.L., 2004. Controls on the spatial and temporal variability of vadose dripwater geochemistry: Edwards Aquifer, central Texas. Geochim. Cosmochim. Acta 68, 1007–1020.

National Climate Data Center, 2012. <http://lwf.ncdc.noaa.gov/temp-and-precip/time-series/> (accessed 23.05.12).

National Institute of Standards and Technology, 2012. Standard Reference Materials—SRM987 – Strontium Carbonate Isotopic Standard <https://www-s.nist.gov/srmors/view_detail.cfm?srm=987> (accessed 23.05.12).

National Weather Service, 2012. <http://www.srh.noaa.gov/ewx/?n=austinmabryclidata.htm> (accessed 23.05.12).

Oetting, 1995. Evolution of Fresh and Saline Groundwaters in the Edwards Aquifer, Central Texas: Geochemical and Isotopic Constraints on Processes of Fluid–Rock Interaction and Fluid Mixing. Dissertation. The University of Texas at Austin, 203p.

Oetting, G.C., Banner, J.L., Sharp, J.M., 1996. Regional controls on the geochemical evolution of saline groundwaters in the Edwards aquifer, central Texas. J. Hydrol. 181, 251–283.

Palmer, W.C., 1965. Meteorological Drought. Research Paper No. 45. U.S. Weather Bureau, Washington, DC, 58p.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (ver. 2)—A Computer Program for Speciation, Reaction-Path, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations 99–4259, 312p.

Perez, Roberto, 1986. Potential for Updip Movement of Salinewater in the Edwards Aquifer, San Antonio, Texas: U.S. Geological Survey Water-Resources Investigations Report 86–4032, 21p.

Peterson, E.W., Wicks, C.M., 2005. Fluid and solute transport from a conduit to the matrix in a carbonate aquifer system. Math. Geol. 37, 851–867.

Pronk, M., Goldscheider, N., Zopfi, J., 2007. Particle-size distribution as indicator for fecal bacteria contamination of drinking water from karst springs. Environ. Sci. Technol. 41, 8400–8405.

Quinlan, J.F., 1989. Ground-Water Monitoring in Karst Terranes—Recommended Protocols and Implicit Assumptions. U.S. Environmental Protection Agency EPA 600/X–89/050.

Raeisi, E., Groves, C., Meiman, J., 2007. Effects of partial and full pipe flow on hydrochemographs of Logsdon river, Mammoth Cave Kentucky USA. J. Hydrol. 337, 1–10.

Ray, J.A., 1997. Overflow conduit systems in Kentucky: a consequence of limited underflow capacity. In: Engineering Geology and Hydrogeology of Karst Terrains 6th Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst, Springfield, MO, pp. 69–67.

Rose, P.R., 1972. Edwards Group, Surface and Subsurface, Central Texas. Report of Investigations. Bureau of Economic Geology, No. 74. University of Texas at Austin, Austin.

Rounds, S.A., 2006. Alkalinity and Acid Neutralizing Capacity (ver. 3.0): U.S. Geological Survey Techniques of Water-Resources Investigations (Book 9, Chapter A6, section 6.6). <http://pubs.water.usgs.gov/twri9A6>.

Ryan, M., Meiman, J., 1996. An examination of short-term variations in water quality at a karst spring in Kentucky. Ground Water 34, 23–30.

Seager, R., Ting, M., Held, I., Kushnier, Y., Lu, J., Vecchi, G., Huang, H.P., Harnik, N., Leetmaa, A., Lau, N.C., 2007. Model projections of an imminent transition to a more arid climate in southwestern North America. Science 316, 1181–1184.

Senger, R.K., Kreitler, C.W., 1984. Hydrogeology of the Edward Aquifer, Austin Area, Central Texas. Report of Investigations. Bureau of Economic Geology, The University of Texas at Austin.

Slade, R.M., Jr., Dorsey, M.E., Stewart, S.L., 1986. Hydrology and Water Quality of the Edwards Aquifer Associated with Barton Springs in the Austin Area, Texas. U.S. Geological Survey Water-Resources Investigations Report 86–4036, 117p.

Smart, C.C., 1988. Artificial tracer techniques for the determination of the structure of conduit aquifers. Ground Water 26, 445–453.

U.S. Geological Survey National Water Information System, 2012. <http://waterdata.usgs.gov/tx/nwis>.

Vacher, H.L., Mylroie, J.E., 2002. Eogenetic karst from the perspective of an equivalent porous medium. Carbonat. Evap. 17, 182–196.

White, W.B., 1999. Conceptual models for karstic aquifers. In: Palmer, A.N., Palmer, M.V., Sasowsky, I.D. (Eds.), Karst Modeling, vol. 5. Karst Waters Institute Special Publication, pp. 11–16.

Wierman, D.A., Broun, A.S., Hunt, B.B., 2010. Hydrogeologic atlas of the Hill Country Trinity Aquifer, Blanco, Hay, and Travis Counties, Central Texas. Hays-Trinity Groundwater Conservation District.

Wilde, F.D., Radtke, D.B., Gibs, J., Iwatsubo, R.T., 1999. National Field Manual for the Collection of Water-Quality Data—Collection of Water Samples: U.S. Geological Survey Techniques of Water-Resources Investigations, pp. 49–52 (Book 9, Chapter A4).

Wong, C., Banner, J.L., 2010. Response of cave air CO_2 and drip water to brush clearing in central Texas: implications for recharge and soil CO_2 dynamics. J. Geophys. Res. 115, 1–13.

Wong, C., Banner, J.L., Musgrove, M., 2011. Seasonal dripwater Mg/Ca and Sr/Ca variations driven by cave ventilation: implications for and modeling of speleothem paleoclimate records. Geochim. Cosmochim. Acta 75, 3514–3529.

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