Journal of Hydrology 388 (2010) 144–156

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Springwater geochemistry at Honey Creek State Natural Area, central Texas: Implications for surface water and groundwater interaction in a karst aquifer

M. Musgrove [a,b,*], L.A. Stern [a,c], J.L. Banner [a]

[a] *Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, TX 78712, United States*
[b] *US Geological Survey, Texas Water Science Center, 1505 Ferguson Lane, Austin, TX 78754, United States*
[c] *Federal Bureau of Investigation Laboratory – CFSRU, 2501 Investigation Parkway, Quantico, VA 22135, United States*

ARTICLE INFO

Article history:
Received 15 June 2009
Received in revised form 30 March 2010
Accepted 24 April 2010

This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Sheng Yue, Associate Editor

Keywords:
Strontium isotopes
Edwards aquifer
Water–rock interaction
Hydrogeochemistry

SUMMARY

A two and a half year study of two adjacent watersheds at the Honey Creek State Natural Area (HCSNA) in central Texas was undertaken to evaluate spatial and temporal variations in springwater geochemistry, geochemical evolution processes, and potential effects of brush control on karst watershed hydrology. The watersheds are geologically and geomorphologically similar, and each has springs discharging into Honey Creek, a tributary to the Guadalupe River. Springwater geochemistry is considered in a regional context of aquifer components including soil water, cave dripwater, springwater, and phreatic groundwater. Isotopic and trace element variability allows us to identify both vadose and phreatic groundwater contributions to surface water in Honey Creek. Spatial and temporal geochemical data for six springs reveal systematic differences between the two watersheds. Springwater Sr isotope values lie between values for the limestone bedrock and soils at HCSNA, reflecting a balance between these two primary sources of Sr. Sr isotope values for springs within each watershed are consistent with differences between soil compositions. At some of the springs, consistent temporal variability in springwater geochemistry (Sr isotopes, Mg/Ca, and Sr/Ca values) appears to reflect changes in climatic and hydrologic parameters (rainfall/recharge) that affect watershed processes. Springwater geochemistry was unaffected by brush removal at the scale of the HCSNA study. Results of this study build on previous regional studies to provide insight into watershed hydrology and regional hydrologic processes, including connections between surface water, vadose groundwater, and phreatic groundwater.

1. Introduction

Surface water features such as springs, streams, and rivers interact with groundwater in diverse environments and complex processes (Winter et al., 1998). Karst systems are often characterized by substantial groundwater–surface water connections via processes such as aquifer recharge by losing streams, fracture and conduit connections between surface water and groundwater, and spring flow contributions to surface water (e.g., Katz et al., 1997). In spite of these connections, a thorough understanding of surface and groundwater interactions in karst settings is lacking, including with respect to the geochemical mixing of surface water and groundwater and the differential reactivity of geochemically distinct waters with the aquifer host rock.

Karst aquifer systems often respond rapidly to changes in environmental and climatic conditions (e.g., Malard and Chapuis, 1995; Mahler and Massei, 2007). Temporal variations in geochemical parameters such as strontium isotopes, stable isotopes, and anthropogenic contaminants have been observed in karst systems in response to variations in flow and recharge (Lakey and Krothe, 1996; Boyer and Kuczynska, 2003; Barbieri et al., 2005). An understanding of temporal variability in karst systems provides insight into hydrologic processes and aquifer structure, water-use management, and aquifer vulnerability to contaminants.

Woody plant encroachment in semiarid landscapes is a developing issue in ecohydrology (Archer et al., 1995; Van Auken, 2000; Huxman et al., 2005) and may impact groundwater recharge and streamflow (Wilcox, 2002; Wilcox and Thurow, 2006). Ashe juniper (*Juniperus ashei*), a native woody plant species, has substantially increased in coverage of central Texas grasslands in the last century (Smeins and Fuhlendorf, 1997). Selective removal of ashe juniper from the uplands of one watershed (“treatment” watershed) occurred during this study, while the second watershed was left as a control (“control” watershed), in order to evaluate the potential effects of brush clearing on watershed hydrology and springwater geochemistry.

Previous work in the Edwards aquifer of central Texas provides a framework of understanding for regional scale controlling

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* Corresponding author at: US Geological Survey, Texas Water Science Center, 1505 Ferguson Lane, Austin, TX 78754, United States. Tel.: +1 512 927 3522.
E-mail address: mmusgrov@usgs.gov (M. Musgrove).

0022-1694/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.jhydrol.2010.04.036

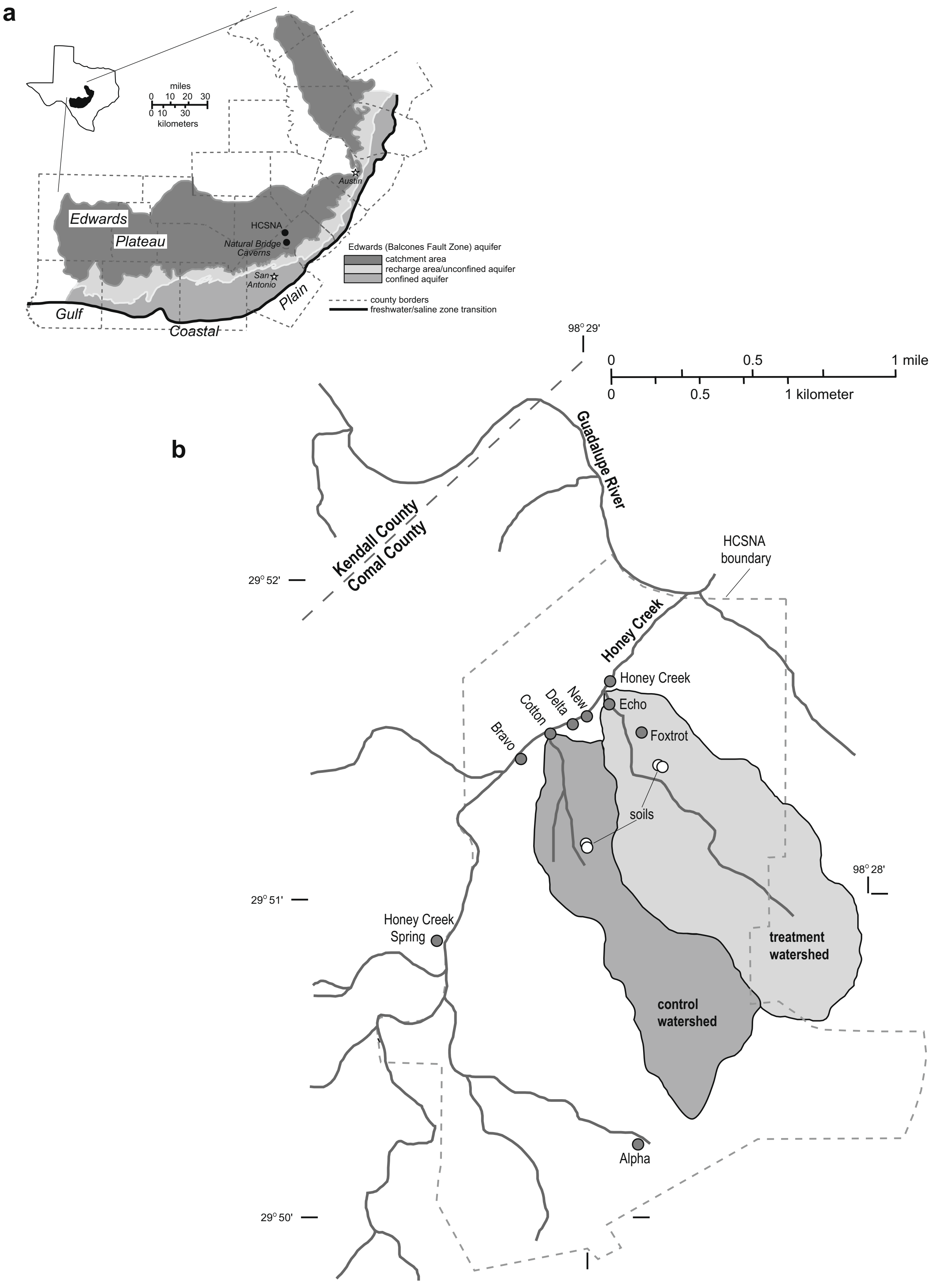

Fig. 1. Map of region and HCSNA field area. (a) Location map of the Edwards Plateau and hydrologic components of the Edwards aquifer within the state of Texas, and the location of HCSNA and Natural Bridge Caverns (NB). Locations of vadose cave dripwater samples from cave NB in Musgrove and Banner (2004). The freshwater/saline zone transition defines the down-dip limit of potable water (1000 mg/L total dissolved solids) in the aquifer. Regional aquifer map after Burchett et al. (1986) and Brown et al. (1992). (b) Detail of HCSNA showing control and treatment watersheds, spring locations and sample collection locations for springs, surface water, and soils.

processes on groundwater evolution (e.g., Oetting, 1995; Sharp and Banner, 1997; Musgrove and Banner, 2004; Wong, 2008). Temporal variations in groundwater geochemistry in the region have been previously interpreted to record changes in environmental, climatic, and hydrologic conditions (Musgrove and Banner, 2004; Wong et al., 2007; Wong, 2008). A two and a half year study of spring and streamwater geochemistry for two adjacent watersheds was conducted at Honey Creek State Natural Area (HCSNA), located on the Edwards Plateau in central Texas (Fig. 1). The two watersheds are between 400 and 500 acres with similar geologic and geomorphic features, including springs and ephemeral streams that discharge into Honey Creek. We evaluate spatial and temporal variability in geochemical and isotopic constituents in spring and surface water (Mg/Ca and Sr/Ca, and $^{87}Sr/^{86}Sr$), fluid evolution processes, and surface water–groundwater interactions. We also evaluate the effect of brush clearing on springwater geochemistry. Results for springwaters are compared to previously published data for vadose dripwater and soils from Natural Bridge Caverns (NB), a nearby cave, and regional phreatic groundwater to provide a regional hydrologic context.

2. Hydrogeologic setting

The approximately 2300 acre HCSHA is located in western Comal County in the Edwards Plateau region of central Texas (Fig. 1). The Edwards Plateau is a physiographic region characterized by distinctive climatic, vegetational, geologic, and pedogenic characteristics (Kastning, 1983; Abbott and Woodruff, 1986). The region consists of Cretaceous limestone that is extensively karstified and contains caves, sinkholes and springs. The Edwards aquifer provides extensive municipal, commercial, and agricultural water resources to the area. HCSNA is undeveloped; surrounding land use is rural and dominated by livestock ranching and recreation in the adjacent Guadalupe River State Park. The study area includes the watersheds for two ephemeral streams that contribute streamflow and runoff to the main channel of Honey Creek, a tributary of the Guadalupe River, which is an important regional water resource. The two watersheds were designated the “control” and “treatment” watersheds for the purposes of juniper clearing studies. Honey Creek, a perennial, south-to-north flowing stream, is sourced by a large spring, Honey Creek spring, which is located on private land just outside HCSNA (Fig. 1). Given the karstic nature of the study area, it is not definitive that the contributing areas for the two ephemeral streams are represented by their surface watersheds, though this is assumed for interpreting the study results. Multiple springs and seeps discharge along or near Honey Creek on the northwest side of HCSNA, which contribute to creek flow. The largest and most accessible of these springs were sampled for this study (Fig. 1).

HCSNA is underlain by the Glen Rose Limestone, Hensel Sand, and Cow Creek Limestone, as well as Quaternary terrace deposits (Collins, 2000). Surface stratigraphy is dominated by the lower member of the Glen Rose Limestone, except along Honey Creek, where the Hensel Sand and Cow Creek Limestone are exposed. The exposed Hensel unit is a glauconitic sandy limestone (White, 2005). The Cow Creek limestone is a fossiliferous dolomitic limestone with interbedded sands and shales (Barnes, 1983). The Glen Rose Limestone contains interbedded limestone, marl, dolomite, and clay (Kastning, 1983; Elliott and Veni, 1994; Veni, 1997). NB is largely formed within the upper member of the Glen Rose Limestone. The topography of HCSNA is influenced by karstification and fracture orientation, and is characterized as a gently rolling landscape that is dissected by steep and narrow drainages (White, 2005). Elevation at HCSNA ranges from approximate 320 m along Honey Creek in the vicinity of the springs, to 370 m in the upland area near Alpha spring.

Dry and cool winters, and hot summers characterize the region. Climatic and hydrologic extremes are common (Griffiths and Strauss, 1985; Jones, 1991). Average annual precipitation over the region encompassing HCSNA ranges from 790 to 860 mm (Larkin and Bomar, 1983). Approximately 85–90% of precipitation in the area is lost through evapotranspiration (Maclay, 1995; Burchett et al., 1986), which accounts for low effective moisture (defined herein as precipitation less evapotranspiration). Meteorologic conditions were generally wetter than average during the study (relative to the historical mean), based on monthly flow data for the Guadalupe River at Honey Creek. The first half of 2002, and the period of May, 2003 through February, 2004, during which Guadalupe River flow was less than the historical mean, are exceptions to these conditions. July, 2003, June, 2004, and November, 2004 experienced especially higher than average monthly rainfall amounts of approximately 14, 12, and 10 in., respectively (data from National Climatic Data Center for Spring Branch, TX, located adjacent to HCSNA). Characteristic of the Edwards Plateau, soils at HCSNA are calcareous and typically thin, particularly on the upland areas (Godfrey et al., 1973; Batte, 1984). Ashe juniper and live oak vegetation dominate the upland areas with minor grasses, and the surrounding area is primarily cedar elm and ashe juniper vegetation (Texas Parks and Wildlife Department, 2006).

3. Methods

Water samples from multiple springs that contribute to Honey Creek, as well as Honey Creek streamwater samples, were collected periodically (generally every 3–8 weeks) between February 2003 and August 2005 (Fig. 1). The springs sites are designated as Alpha, Bravo, Cotton, Delta, Echo, and Foxtrot. An additional spring was sampled during 2005 (New spring). Bravo, Cotton, Delta, and New springs discharge directly along Honey Creek in the control watershed. In the treatment watershed, Echo spring is located slightly upland from Honey Creek and Foxtrot spring is located in the uplands of the watershed. Alpha spring, an ephemeral seep, is located within HCSNA but outside of the paired watersheds. All of the springs are ephemeral and experienced both dry and variable flow conditions during the course of the study. Alpha spring was dry during most of the study and thus was not sampled frequently. Soil samples ($n = 10$) were collected prior to ashe juniper clearing from four augered soil profiles (Fig. 1). Ashe juniper in the treatment watershed was cleared throughout 2004. Land-use differences between the two watersheds, aside from the ashe juniper clearing, are negligible.

Springwater was sampled directly at the spring orifices. Samples from Honey Creek were collected directly downstream from Echo spring. During the initial part of the study (i.e., prior to March 2004) water samples were not filtered. Data collected from September 2004 onward reflect analyses of samples filtered at the time of collection. For samples collected in March, May, and July of 2004, analyses of both field filtered and unfiltered samples were performed for several of the springs. Samples were filtered using 0.45 μm polypropylene syringe filters, pre-cleaned with 10% HNO_3 and deionized water. Water samples for Sr isotope and elemental analyses (excluding alkalinity) were acidified with ultrapure HNO_3 and stored below 4 °C. Soil samples were leached with 1 M NH_4Ac and the leachates analyzed to determine the composition of the exchangeable fraction (Suarez, 1996).

Strontium isotope values were measured at the University of Texas at Austin, mostly using a Finnigan-MAT 261 thermal ionization mass spectrometer (TIMS) following methods of Banner and Kaufman (1994). Results were normalized for fractionation to

$^{86}Sr/^{88}Sr = 0.1194$ using an exponential fractionation law. Analyses of the NIST-SRM-987 standard conducted during the course of this study yielded a mean $^{87}Sr/^{86}Sr$ value of 0.710268 ± 8 ($n = 46$; external $2\sigma = 0.00002$). Soil samples from HCSNA and some of the springwaters collected in the early part of the study were analyzed for $^{87}Sr/^{86}Sr$ values using an Isoprobe multicollector ICP mass spectrometer (ICP–MS). ICP–MS analyses were corrected for fractionation using the first-order mass bias correction, based on the Generalized Power Law, as described by Albarede et al. (2004). Eimer and Amend (E and A) Sr was used as the primary standard to calibrate mass fractionation each day, and fractionation parameters were adjusted to give a value for E and A of $^{87}Sr/^{86}Sr = 0.708031$ (relative to $^{86}Sr/^{88}Sr = 0.1194$). NBS-987 was run as a secondary standard; six analyses of NBS-987 gave a mean $^{87}Sr/^{86}Sr$ value of 0.710252 ± 0.000016 (external 2σ) over the course of these analyses. Comparative measurements of the same samples by TIMS and ICP–MS yielded a mean deviation (absolute value) of 0.00006 ($n = 6$).

Elemental analyses were determined at the University of Texas at Austin by ICP mass spectrometry (Micromass Platform Quadrupole) using standard analytical methods. Differences between replicate analyses ($n = 17$) averaged 7% or less for all major and trace elements, excluding trace metals such as Fe and Mn, which ranged up to mean differences of approximately 20%. Alkalinity, assumed as HCO_3^-, was determined by autotitration within 48 h of sample collection on samples stored below 4 °C in glass vials.

4. Results

Table 1 summarizes the HCSNA data and compares mean elemental and isotopic values with vadose cave dripwater from cave NB and regional phreatic groundwater (based on data from Musgrove and Banner, 2004). Springwater as well as Honey Creek streamwater are dilute $Ca–HCO_3$ waters of meteoric origin, similar to cave dripwater and preatic groundwater from previous studies in the region (Harmon, 1970; Oetting, 1995; Veni, 1997; Musgrove and Banner, 2004). Soil leachate and vadose cave dripwater (NB), and regional phreatic groundwater data discussed in the text are from Musgrove and Banner (2004), and also include other unpublished data (e.g., Mihealsick et al., 2004). Sr isotope values for Cretaceous carbonate rocks are from Koepnick et al. (1985) and Oetting (1995), adjusted to a value for NIST-SRM-987 = 0.710252.

4.1. Filtered-unfiltered comparisons

A comparison of filtered and unfiltered water samples indicates that particulate matter in the unfiltered samples may affect geochemical compositions. Measured differences between filtered and unfiltered samples for carbonate-rock-derived constituents focused on herein such as HCO_3, Ca, Mg, Sr, and $^{87}Sr/^{86}Sr$ were generally small, but quite variable. Elemental differences for filtered-unfiltered comparisons were on average 2% or less for HCO_3, Ca, Mg, and Sr ($n = 13$, except for HCO_3, where $n = 12$). The average difference between filtered-unfiltered comparisons for $^{87}Sr/^{86}Sr$ is 0.00004, which is slightly larger than the analytical uncertainty. For some individual samples, however, maximum differences were 5–13% for elemental analyses (HCO_3, Ca, Mg, and Sr), and 0.00017 for $^{87}Sr/^{86}Sr$. Filtered samples consistently have lower concentrations of elements such as Fe that may be associated with clay or oxide particulates (Fe concentrations range from 60% to 90% higher in unfiltered samples ($n = 13$)). Subsequent to regular filtering of all samples, spatial variations in the geochemistry of springwaters and Honey Creek decreased, revealing generally similar characteristics. For example, Honey Creek streamwater $^{87}Sr/^{86}Sr$ dropped to lower values, which consistently mirror values for many of the springwaters (Bravo, Cotton, Delta, and New springs), beginning in late 2003 and early 2004. This corresponds to the timing of the transition to filtered sample collection and suggests that elevated and fluctuating $^{87}Sr/^{86}Sr$ values measured for Honey Creek in the early part of the study reflect the contribution of particulates associated with unfiltered samples. This is in contrast to cave dripwater samples for which filtering does not generally affect geochemical compositions of parameters such as Sr isotopes or major elements (Musgrove, 2000).

4.2. Soil-spring comparisons

Although strontium isotope values for soil samples are limited ($n = 10$), results indicate differences among soils from the two watersheds, as well as between soils and springwaters. Soil leachate $^{87}Sr/^{86}Sr$ values range from 0.70822 to 0.70906 with a mean value of 0.70848 (standard deviation = 0.0003). Soil leachate $^{87}Sr/^{86}Sr$ values, however, are distinct between the control and treatment watersheds: soil samples from the control watershed have a lower Sr isotope composition (range = 0.70822–0.70829, mean = 0.70825, $n = 6$, standard deviation = 0.00003) than soils from the treatment watershed (range = 0.70867–0.70906, mean = 0.70883, $n = 4$, standard deviation = 0.00002). X-ray diffraction analyses of soils at NB indicate that soils in the area are composed of variable mixtures of calcite, clay, and quartz (Musgrove and Banner, 2004).

Soil leachates tend to have higher $^{87}Sr/^{86}Sr$ values than the springwaters (Fig. 2). The mean springwater $^{87}Sr/^{86}Sr$ value (including Honey Creek stream) is 0.70807 ($n = 111$, standard deviation = 0.0002), which is lower than the mean soil leachate value of 0.70848. For the treatment watershed (Echo and Foxtrot springs), the mean springwater $^{87}Sr/^{86}Sr$ value is 0.70811; for the control watershed (Bravo, Cotton, Delta, and New springs) the mean springwater $^{87}Sr/^{86}Sr$ value is 0.70780. Sr isotope values for the springwaters generally fall between more radiogenic values for soil leachates and less radiogenic values for the host limestones (mean = 0.7076). This pattern is consistent within each watershed: Sr isotope values for the treatment watershed soil leachates and springwater are higher relative to the equivalent materials in the control watershed (Fig. 2). Mg/Ca values for springwater samples from the control watershed (mean = 0.160) are similar to values from Echo spring (mean = 0.121), but considerably lower than values for Foxtrot spring (mean = 0.223; Table 1). Springwater samples from the control watershed have higher Sr/Ca ratios (mean values, for treatment and control watersheds are 0.502×10^3 and 1.695×10^3, respectively; Table 1).

4.3. Spring comparisons

A comparison of geochemical data for the springs and Honey Creek reveals both spatial and temporal differences and similarities between individual springs and between groups of springs associated with the two watersheds (Table 1). Springs in the control watershed (Bravo, Cotton, Delta, and New) were geochemically similar to each other and to surface-water values for Honey Creek for most of the study period (Fig. 3) (unfiltered samples from Honey Creek were more variable). Samples from the two upland springs in the treatment watershed (Echo and Foxtrot springs) were similar to each other, but distinct from the control watershed springs. A limited number of samples from Alpha spring are geochemically distinct from the other springs and likely reflect a different hydrology given this spring's location outside of the two watersheds. Given its location and limited sample availability, data from Alpha spring is not considered in the following discussion. A comparison of other aquifer components with HCSNA springwater suggests a continuum of geochemical variability from soil water, to

Table 1
Mean spring water and groundwater geochemistry.

Geochemical parameter	Alpha spring	Bravo spring	Cotton spring	Delta spring	Echo spring	Foxtrot spring	New spring	Honey creek	Natural bridge Caverns; vadose cave dripwaters	Regional phreatic groundwaters
	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)	Mean (*n*) *range* (*standard deviation*)
$^{87}Sr/^{86}Sr$	0.7088 (*3*) *0.7081–0.7081* (*0.00001*)	0.7079 (*25*) *0.7078–0.7081* (*0.00006*)	0.7079 (*15*) *0.7079–0.7081* (*0.00006*)	0.7079 (*25*) *0.7078–0.7081* (*0.00007*)	0.7082 (*21*) *0.7081–0.7083* (*0.00005*)	0.7085 (*16*) *0.7085–0.7085* (*0.00002*)	0.7079 (*6*) *0.7078–0.7081* (*0.00008*)	0.7080 (*19*) *0.7078–0.7083* (*0.00014*)	0.7088 (*61*) *0.7083–0.7091* (*0.0002*)	0.7079 (*49*) *0.7076–0.7086* (*0.0002*)
Mg/Ca	0.084 (*9*) *0.073–0.091* (*0.007*)	0.163 (*24*) *0.079–0.219* (*0.036*)	0.153 (*18*) *0.081–0.207* (*0.034*)	0.162 (*27*) *0.077–0.237* (*0.041*)	0.121 (*23*) *0.069–0.259* (*0.036*)	0.223 (*19*) *0.120–0.281* (*0.031*)	0.160 (*5*) *0.100–0.201* (*0.037*)	0.144 (*21*) *0.080–0.227* (*0.035*)	0.118 (*81*) *0.015–0.359* (*0.071*)	0.326 (*27*) *0.119–0.752* (*0.163*)
Sr/Ca	0.50×10^{-3} (*9*) [*0.45–0.53* (*0.03*)] $\times 10^{-3}$	1.72×10^{-3} (*24*) [*0.74–2.33* (*0.50*)] $\times 10^{-3}$	1.60×10^{-3} (*18*) [*0.75–2.40* (*0.54*)] $\times 10^{-3}$	1.74×10^{-3} (*24*) [*0.71–2.72* (*0.57*)] $\times 10^{-3}$	0.57×10^{-3} (*23*) [*0.44–1.17* (*0.15*)] $\times 10^{-3}$	0.42×10^{-3} (*19*) [*0.38–0.50* (*0.03*)] $\times 10^{-3}$	1.70×10^{-3} (*5*) [*0.75–2.15* (*0.55*)] $\times 10^{-3}$	1.33×10^{-3} (*19*) [*0.58–2.45* (*0.60*)] $\times 10^{-3}$	0.26×10^{-3} (*82*) [*0.08–0.57* (*0.08*)] $\times 10^{-3}$	2.07×10^{-3} (*27*) [*0.58–5.8* (*1.1*)] $\times 10^{-3}$
HCO_3 (mg/l)	295 (*7*) *218–332* (*36*)	313 (*21*) *251–349* (*26*)	292 (*15*) *256–344* (*24*)	322 (*26*) *258–363* (*27*)	334 (*22*) *197–366* (*37*)	439 (*15*) *342–484* (*48*)	348 (*5*) *336–367* (*13*)	312 (*23*) *237–362* (*27*)	261 (*42*) *152–413* (*66*)	230 (*27*) *110–377* (*50*)
Ca (mg/l)	109 (*9*) *89–134* (*13*)	109 (*24*) *100–115* (*4*)	110 (*18*) *101–120* (*5*)	109 (*27*) *102–116* (*4*))	116 (*23*) *54–128* (*15*)	135 (*19*) *105–153* (*14*)	107 (*5*) *103–108* (*2*)	108 (*21*) *101–119* (*6*)	91 (*84*) *38–320* (*35*)	80 (*27*) *54–150* (*23*)
Mg (mg/l)	5.5 (*9*) *4.3–6.1* (*0.7*)	10.8 (*24*) *5.5–14.4* (*2.2*)	10.1 (*18*) *5.5–13.4* (*2.2*)	10.7 (*27*) *5.3–15.0* (*2.6*)	8.3 (*23*) *4.6–11.0* (*1.6*)	18.3 (*19*) *8.2–21.4* (*2.9*)	10.3 (*5*) *6.6–12.8* (*2.3*)	9.4 (*21*) *5.5–14.5* (*2.1*)	5.7 (*81*) *1.1–10.0* (*2.0*)	17.5 (*27*) *7.2–54* (*9.7*)
Sr (mg/l)	0.12 (*9*) *0.10–0.13* (*0.01*)	0.41 (*24*) *0.18–0.55* (*0.11*)	0.38 (*18*) *0.18–0.56* (*0.12*)	0.41 (*24*) *0.17–0.62* (*0.13*)	0.14 (*23*) *0.11–0.17* (*0.02*)	0.12 (*19*) *0.11–0.14* (*0.01*)	0.39 (*5*) *0.18–0.50* (*0.12*)	0.31 (*19*) *0.15–0.56* (*0.13*)	0.05 (*82*) *0.03–0.07* (*0.01*)	1.43 (*27*) *0.09–3.2* (*0.57*)
Ba (mg/l)	0.03 (*9*) *0.02–0.03* (*0.004*)	0.03 (*22*) *0.03–0.04* (*0.003*)	0.03 (*15*) *0.03–0.04* (*0.001*)	0.03 (*24*) *0.03–0.04* (*0.001*)	0.03 (*21*) *0.03–0.04* (*0.002*)	0.04 (*17*) *0.04–0.06* (*0.006*)	0.03 (*5*) *0.03–0.03* (*0.001*)	0.03 (*19*) *0.03–0.04* (*0.003*)	0.03 (*82*) *0.02–0.05* (*0.007*)	0.04 (*27*) *0.03–0.15* (*0.02*)
Na (mg/l)	4.42 (*9*) *3.5–5.3* (*0.7*)	7.92 (*24*) *5.2–9.1* (*0.8*)	8.08 (*18*) *5.1–9.2* (*1.0*)	7.67 (*24*) *5.0–8.9* (*0.9*)	4.95 (*23*) *3.2–6.2* (*0.7*)	5.17 (*29*) *2.6–6.3* (*0.8*)	7.68 (*5*) *6.7–8.2* (*0.6*)	7.40 (*21*) *5.2–8.4* (*0.8*)	5.25 (*82*) *3.0–19.9* (*2.1*)	11.73 (*27*) *4.5–96.0* (*17.5*)
K (mg/l)	0.44 (*9*) *0.36–0.48* (*0.04*)	1.18 (*24*) *1.00–1.30* (*0.07*)	1.17 (*18*) *0.99–1.30* (*0.08*)	1.13 (*27*) *0.97–1.26* (*0.07*)	0.88 (*23*) *0.78–1.02* (*0.07*)	1.04 (*19*) *0.47–3.06* (*0.51*)	1.10 (*5*) *0.97–1.16* (*0.07*)	1.14 (*21*) *1.01–1.33* (*0.07*)	0.44 (*71*) *0.08–3.3* (*0.44*)	1.36 (*27*) *0.70–3.4* (*0.64*)
Si (mg/l) mg/l	4.6 (*9*) *3.7–5.8* (*0.7*)	5.3 (*22*) *4.5–5.9* (*0.5*)	5.2 (*15*) *4.5–5.8* (*0.5*)	5.1 (*27*) *4.2–5.7* (*0.4*)	5.6 (*21*) *4.7–6.4* (*0.5*)	6.9 (*17*) *4.8–8.6* (*1.0*)	5.0 (*5*) *4.6–5.4* (*0.3*)	5.0 (*19*) *4.3–5.9* (*0.5*)	4.5 (*69*) *3.7–5.8* (*0.4*)	12.41 (*27*) *10.0–22.0* (*2.1*)
U (μg/l)	0.55 (*9*) *0.47–0.65* (*0.06*)	0.81 (*22*) *0.56–0.95* (*0.08*)	0.77 (*15*) *0.58–0.91* (*0.08*)	0.80 (*24*) *0.61–0.94* (*0.09*)	0.90 (*21*) *0.55–1.15* (*0.15*)	1.6 (*17*) *0.80–2.11* (*0.38*)	0.83 (*5*) *0.73–0.89* (*0.06*)	0.77 (*19*) *0.49–0.95* (*0.14*)	0.44 (*35*) *0.29–0.61* (*0.08*)	1.4 (*1*) –
Rb (μg/l)	0.41 (*9*) *0.27–0.86* (*0.17*)	0.79 (*22*) *0.62–0.95* (*0.85*)	0.77 (*15*) *0.63–0.89* (*0.09*)	0.78 (*24*) *0.61–1.0* (*0.10*)	0.60 (*21*) *0.46–0.75* (*0.07*)	0.54 (*17*) *0.22–1.47* (*0.26*)	0.77 (*5*) *0.63–0.84* (*0.09*)	0.72 (*19*) *0.60–0.90* (*0.09*)	*0.48* (*35*) *0.26–1.82* (*0.29*)	NA

Data for Natural Bridge Caverns (NB) vadose cave dripwaters and regional preatic groundwaters from Musgrove and Banner (2004) and Gandara and Barbie (1998). Number in parentheses (*n*) following mean value = number of samples in mean calculation. Numbers following mean value (*n*) = range of values used in mean calculation and standard deviation. NA = not analyzed (in parentheses). Element ratios are molar concentrations.

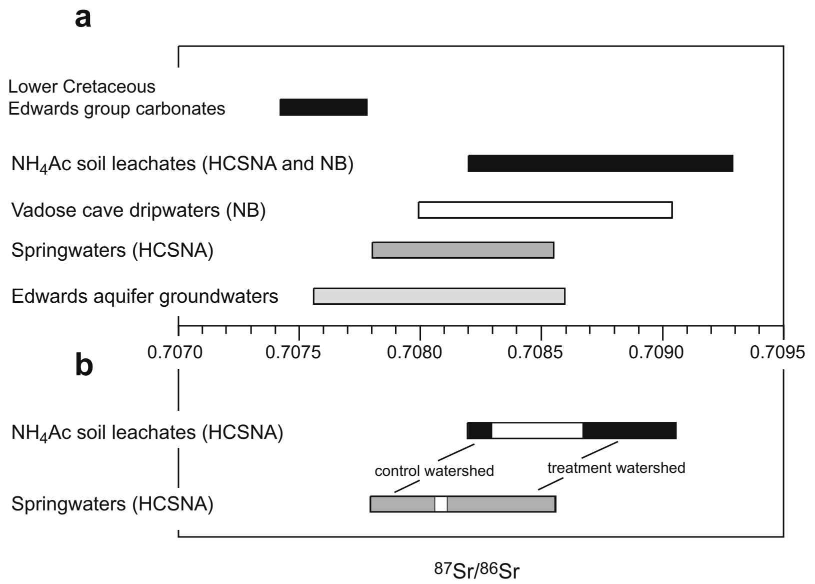

Fig. 2. Strontium isotope values for HSCNA soils and springwaters and regional Edwards aquifer components. Soil leachate data represents exchangeable Sr in soils. (a) Range for Edwards group carbonates includes whole rock $^{87}Sr/^{86}Sr$ values for lower cretaceous carbonates and evaporites from Koepnick et al. (1985; $n = 18$) and Oetting (1995; $n = 2$). Strontium isotope variations in regional Edwards aquifer system components, including springwaters from HCSNA (this study), soil leachates from HCSNA and NB ($n = 21$), cave dripwaters from several caves across the Edwards Plateau ($n = 100$), and phreatic groundwaters from the Edwards aquifer across the region ($n = 49$). Soil leachate data from Musgrove and Banner (2004) for NB ($n = 4$), subsequent unpublished data for NB ($n = 7$), and HCSNA ($n = 10$). Cave dripwater and regional groundwater data from Musgrove and Banner (2004). (b) Soil leachate and springwater data from HCSNA for control and treatment watersheds. Modified from Musgrove and Banner (2004), with data for HCSNA springwaters added.

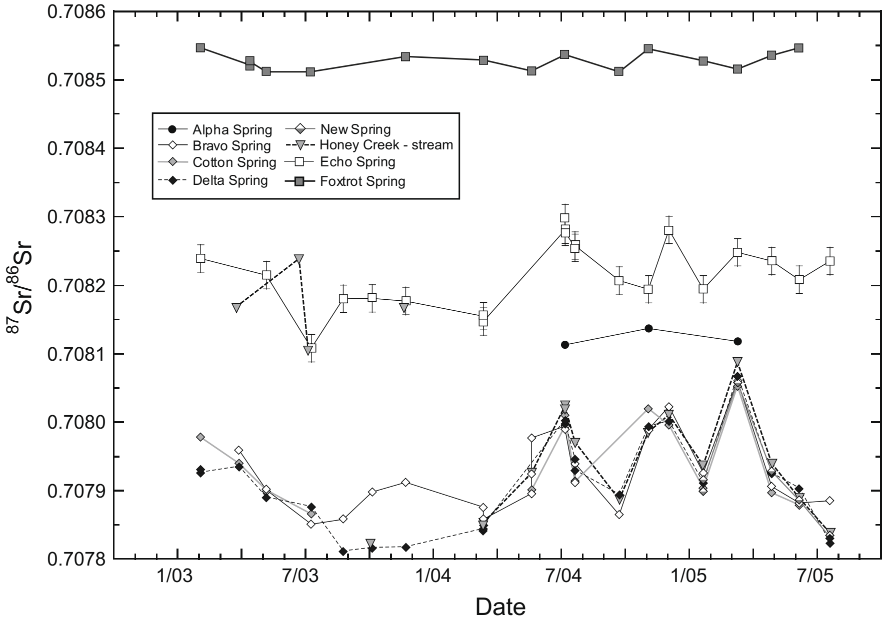

Fig. 3. Temporal variations in $^{87}Sr/^{86}Sr$ values for HCSNA springwaters and streamwater for 2003 through 2005.

vadose cave dripwater (NB), to springwater (HCSNA), to deeper regional phreatic groundwater (Fig. 2).

In addition to differences in spatial variability, the geochemistry of most of the springs varies temporally (Fig. 3). The control watershed springs (Bravo, Cotton, Delta, and New) and Honey Creek show similar temporal changes. Values for Echo spring, while offset from values from the control watershed, follow a similar pattern of temporal changes (Figs. 3 and 4). The geochemistry of Foxtrot spring, and limited results for Alpha spring, shows little temporal variability (Fig. 3).

5. Discussion

5.1. Effects of woody plant clearing on springwater geochemistry

Ashe juniper in the treatment watershed was cleared throughout 2004; we assess potential effects on spring and surface water geochemistry during and after the clearing. Results suggest that the removal of ashe juniper woody plants does not significantly affect fluid geochemistry at the spatial and temporal (~1 year of data post-clearing) scale of this study. Distinct geochemical changes are

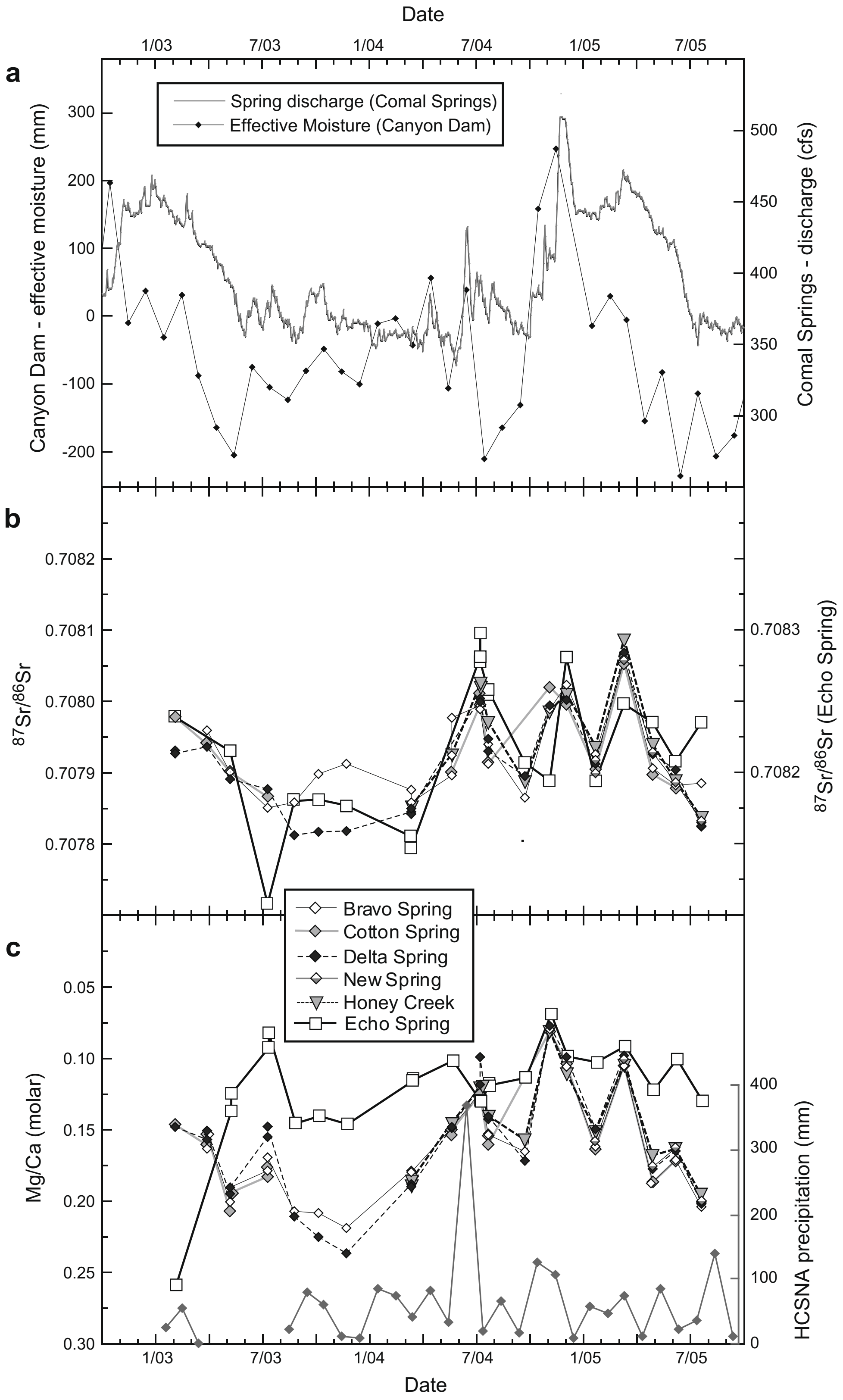

Fig. 4. Temporal variability (2003–2005) in (a) springflow at Comal springs, TX and effective moisture (precipitation minus evaporation) at Canyon Dam, TX; (b) ^{87}Sr/^{87}Sr values for select HCSNA springwaters. Echo spring is plotted on a separate *Y* axis to allow for better comparison of ^{87}Sr/^{86}Sr values; (c) Mg/Ca ratios for select HCSNA springwaters. Note that Mg/Ca ratios are plotted on an inverted scale. Precipitation at HCSNA, when available, is also shown in (c). Precipitation values are the monthly mean for USGS monitoring sites 08167347, 08167350, and 08167353 at HCSNA (http://tx.usgs.gov/). Historical record for Comal Springs daily average discharge (cfs = cubic feet/s) from US Geological Survey archives for station number #08168710 (http://waterdata.usgs.gov/tx/nwis). Monthly average rainfall and evaporation data used to calculate effective moisture from the National Climatic Data Center (http://www.ncdc.noaa.gov) archive for Canyon Dam, TX (National Weather Service Cooperative Station Network – COOP ID# 411429). Effective moisture values range to negative values, which may reflect pan evaporation values used to calculate effective moisture, that are not necessarily representative of ground evapotranspiration.

not observed in springwater samples from the treatment watershed before and after ashe juniper clearing (Fig. 3). These results are consistent with other studies that suggest the potential hydrologic impact of woody plants in the region may not be significant (for example, Heilman et al., 2009). A concurrent study of temporal changes in vadose dripwater geochemistry at cave NB in response to brush clearing noted no discernible changes in drip rate or geochemistry up to 1 year after clearing (Wong and Banner, submitted for publication). It is possible, however, that over longer timescales, permitting the maturation of new vegetation cover, or different hydrologic conditions (e.g., extreme drought or prolonged wet conditions) this conclusion may not remain valid. Previous results of vadose cave dripwater geochemistry suggest that geochemical impacts may be more significant during extreme climatic and hydrologic conditions (Musgrove and Banner, 2004). It is commonly assumed that removal of woody plant cover may increase water yield and water recharge in arid and semiarid areas (e.g., Wilcox et al., 2005). Vegetation-hydrologic-climatic relationships, however, are complex (Wilcox, 2002) and, as with this study, results may not be conclusive. Monitoring of springflow, in addition to springwater geochemistry may provide additional insights into hydrologic impacts of woody plants.

5.2. Spatial variability in HCSNA and regional aquifer geochemistry

Strontium isotopes and trace element ratios (Mg/Ca and Sr/Ca) have been shown to be useful tracers of fluid evolution processes, sources of dissolved constituents, and/or residence times in carbonate groundwaters (e.g., Banner et al., 1994; Katz and Bullen, 1996; Plummer, 1977; Langmuir, 1971; Cowell and Ford, 1980; Trudgill et al., 1980; Fairchild et al., 1996). These tracers have been previously applied in central Texas to assess water–rock interaction processes and groundwater geochemical evolution (e.g., Oetting, 1995; Oetting et al., 1996; Sharp and Banner, 1997; Musgrove, 2000; Musgrove and Banner, 2004; Wong, 2008).

Sr isotope values for HCSNA springwaters (0.7078–0.7085) generally fall between values for HCSNA soil leachates (0.7082–0.7091) and regional phreatic groundwaters (0.7071–0.7084; Fig. 2). Values for regional phreatic groundwaters approach those of the host aquifer rocks, yet range to higher values. Sr isotope values for soil leachates in central Texas are consistently higher than aquifer host rocks (Oetting, 1995; Musgrove and Banner, 2004; this study). Soils may derive their radiogenic/silicate component from weathering of a formerly overlying but now eroded clay, along with minor insoluble residue from underlying carbonate rocks, and airborne dust (Cooke et al., 2007).

As discussed in Banner et al. (1996) and Musgrove and Banner (2004), water compositions that fall between soil leachates and host rocks suggest that fluids acquire Sr from interaction with these two isotopically distinct endmember sources, the relative contributions of which can be influenced by factors such as flowpaths, water residence time, antecedent hydrologic conditions, stratigraphy, and soil type and thickness. Interaction with Cretaceous carbonate rocks is a likely source of Sr to groundwater and the influence of carbonate aquifer rocks on groundwater geochemistry in the region is well-documented (e.g., Clement and Sharp, 1988; Oetting et al., 1996). This process of waters evolving to Sr isotope compositions akin to values for the host limestones has been observed in other carbonate aquifer systems (e.g., Banner et al., 1994; Katz and Bullen, 1996; Dogramaci and Herczeg, 2002). In central Texas, this progression is reflected by lower Sr isotope compositions, approaching those of Edwards group carbonates, resulting from increasing water–rock interaction with host limestones relative to contributing soils (Fig. 3). Waters with lower Sr isotope compositions that have undergone greater extents of water–rock interaction with aquifer host rocks are inferred to have experienced longer residence time.

Processes of fluid evolution operate at a continuum of scales from local (e.g., at a cave) to regional (e.g., aquifer-wide) (Musgrove and Banner, 2004). Here we specifically include the intermediate watershed scale as exhibited at HCSNA (Fig. 3). Mg/Ca and Sr/

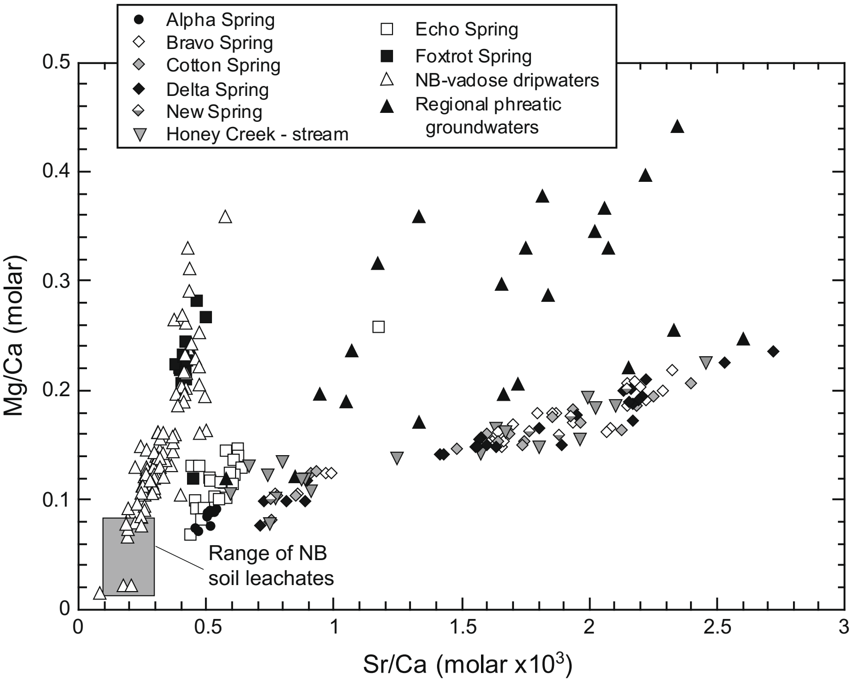

Fig. 5. Mg/Ca vs. Sr/Ca ($\times 10^3$) molar ratios for regional aquifer components including springs and streamwater samples at HCSNA, dripwater samples from cave NB, and regional phreatic groundwaters. Values for several phreatic groundwater samples lie off the scale shown, with higher Mg/Ca and Sr/Ca ratios. Regional phreatic groundwater data from Oetting (1995), Gandara and Barbie (1998), and Musgrove and Banner (2004). Cave NB cave dripwater data from Musgrove and Banner (2004).

Ca values for regional aquifer components, including HCSNA spring and streamwaters covary (Fig. 5). The range of Mg/Ca and Sr/Ca values for soil leachates is low relative to those for cave dripwater, HCSNA springwater, and regional phreatic groundwater. Note that soil leachate Mg/Ca and Sr/Ca values shown on Fig. 5 are from cave NB. HCSNA soils were not analyzed for soil mineralogy or elemental concentrations, but based on the proximity of the study area to cave NB, similar geology, stratigraphy, soil classifications, and regional soil relationships as noted in Musgrove and Banner (2004), soils at HCSNA are inferred to be geochemically similar to soils from nearby cave NB. The trend toward higher Mg/Ca and Sr/Ca values shown in Fig. 5 is consistent with a model of increasing water–rock interaction. Progressive water–rock interaction processes, including calcite recrystallization and incongruent dissolution of dolomite and calcite (Wigley, 1973; Lohmann, 1988), in conjunction with partitioning behavior of Mg and Sr (Banner et al., 1994; Oomori et al., 1987), result in higher water Mg/Ca and Sr/Ca ratios associated with increasing groundwater residence time.

Vadose dripwater samples from cave NB fall on a different and steeper trend line relative to HCSNA springwater (Fig. 5), reflecting higher Mg/Ca relative to Sr/Ca ratios. Regional phreatic groundwaters fall along a more diffuse line generally bracketed by the NB and HCSNA trend lines (Fig. 5). Musgrove and Banner (2004) note distinct Mg/Ca–Sr/Ca ranges for dripwaters from different caves in the region and hypothesize that small differences in the soils

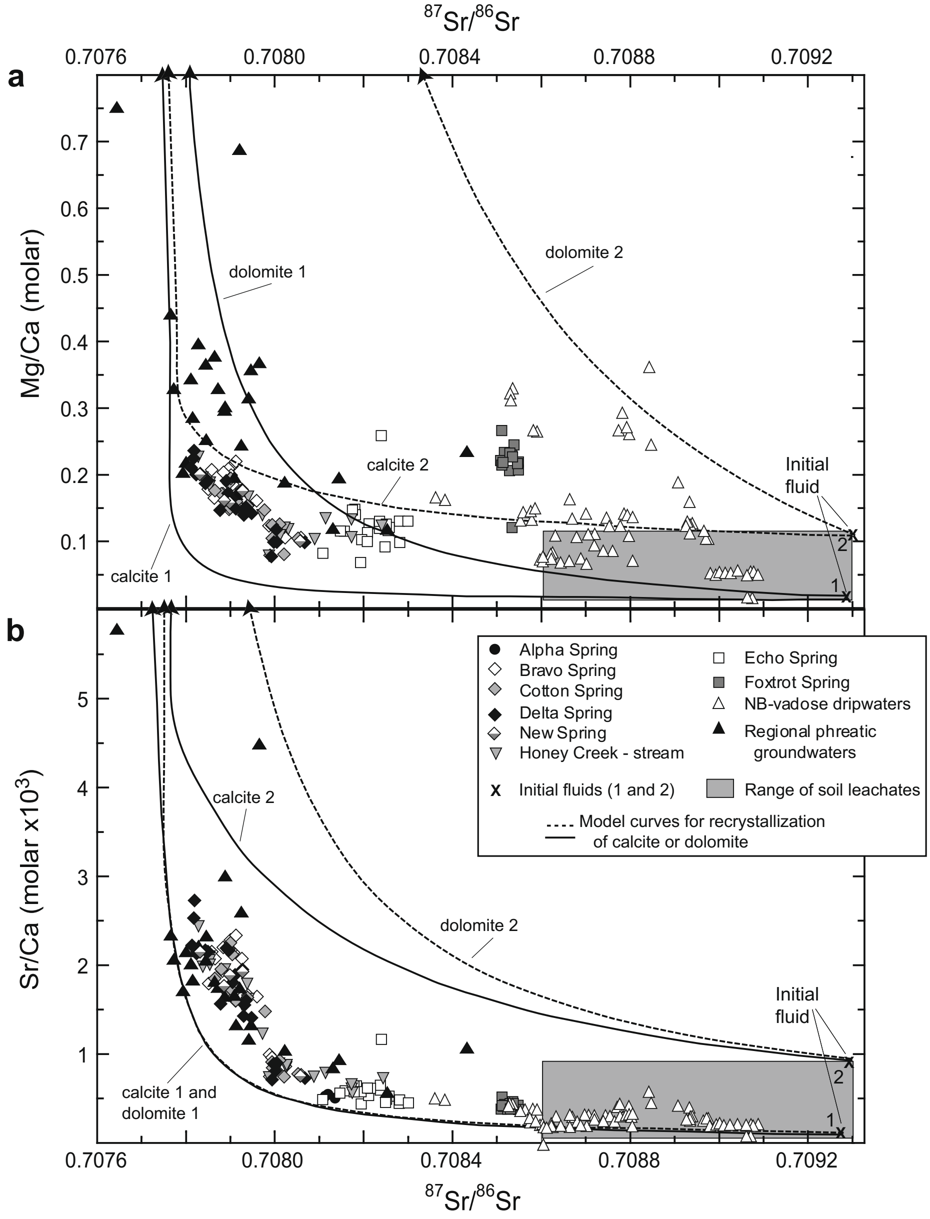

Fig. 6. (a) Mg/Ca molar ratios vs. $^{87}Sr/^{86}Sr$ and (b) Sr/Ca molar ratios vs. $^{87}Sr/^{86}Sr$ for HCSNA spring and streamwater samples, cave NB vadose dripwater samples, and regional phreatic groundwater. Regional phreatic groundwater data from Oetting (1995), Gandara and Barbie (1998), and Musgrove and Banner (2004). Cave NB dripwater data from Musgrove and Banner (2004). Shaded box represents range of values for exchangeable components of soils at HCSNA and NB. Model curves, using same parameters as Musgrove and Banner (2004), illustrate the evolution of $^{87}Sr/^{86}Sr$ and Mg/Ca (a), and $^{87}Sr/^{86}Sr$ and Sr/Ca (b) for a fluid that progressively recrystallizes either calcite or dolomite. Calculations for model curves follow Banner et al. (1989) and Banner and Hanson (1990). Model curves represent evolving compositions of two different initial fluids as they recrystallize calcite or dolomite (i.e., model curves labeled "calcite 1" and "dolomite 1" represent evolving composition of initial fluid 1; model curves labeled "calcite 2" and "dolomite 2" represent evolving composition of initial fluid 2). Initial fluid compositions are based on range of values measured for soil leachates and are detailed in Musgrove and Banner (2004). Element ratios are molar concentrations. Arrows indicate direction of increasing molar rock/water values.

may dictate the starting point of fluid geochemical evolution. This may also apply, in part, to explain differences in Mg/Ca–Sr/Ca trend line slopes for waters from cave NB relative to HCSNA (Fig. 5). Differences in mineralogy, stratigraphy, and specific mineral-solution processes, including prior precipitation of calcite along flowpaths may also contribute to differences in the relative trend lines for Mg/Ca–Sr/Ca variations (e.g., Wong et al., 2007; Wong, 2008). HCSNA and NB, 22 km apart, have similar geology and stratigraphy, but have different trend lines in Mg/Ca–Sr/Ca space (with the exception of samples from Foxtrot spring). These differences likely reflect geographic variations in soils, geology and stratigraphy and/or specific mineral-solution processes. The larger range of Mg/Ca and Sr/Ca results for regional phreatic groundwater relative to cave dripwaters (NB) and springwaters (HCSNA) is consistent with this hypothesis given the large geographic extent of aquifer groundwater represented by these samples.

5.3. Geochemical evolution models

Mg/Ca and Sr/Ca variations lie along a continuum of increasing values with decreasing Sr isotope values (Fig. 6). Mineral-solution reactions can be modeled using mass-balance calculations, values for Mg and Sr distribution coefficients (K_D), porosity, and mineral and water compositions (Banner et al., 1989; Banner and Hanson, 1990). We include HCSNA springwaters in models for regional $^{87}Sr/^{86}Sr$ versus Mg/Ca and Sr/Ca variations, using the approach and model parameters detailed in Musgrove and Banner (2004). Model results for the recrystallization of calcite and dolomite encompass regional groundwater data and demonstrate a progression with increasing mineral-solution reaction toward lower $^{87}Sr/^{86}Sr$ values and increasing Mg/Ca and Sr/Ca values (Fig. 6). HCSNA springwaters generally lie between cave NB vadose dripwaters (i.e., less geochemically evolved) and regional phreatic groundwaters (i.e., more geochemically evolved) within modeled pathways (Fig. 6). This indicates that HCSNA springwaters, while more geochemically evolved than vadose waters, are not dominantly supplied by deeper phreatic groundwater and instead represent an intermediate composition with respect to geochemical processes controlling regional groundwater compositions. Honey Creek streamwater results cover a large range, from more vadose-dominated treatment watershed springwaters to phreatic groundwaters (Fig. 6). This suggests that Honey Creek streamwater, while dominated by a composition most similar to springwater from the control watershed, represents a mix of water types.

5.4. Geochemical differences between the treatment and control watersheds

Springs associated with the control (Bravo, Cotton, Delta, and New) and treatment watersheds (Echo and Foxtrot) are geochemically different based on a number of geochemical constituents (e.g., $^{87}Sr/^{86}Sr$, Mg/Ca and Sr/Ca ratios). Sr isotope values for soil leachates and springwaters from HCSNA fall within two distinct groups (Fig. 2). Soil leachates and springwaters from the treatment watershed (Echo and Foxtrot springs) have higher $^{87}Sr/^{86}Sr$ values than soil leachates and springwaters from the control watershed (Fig. 2). We recognize that analyses of soil samples are limited ($n = 10$) and that inherent difficulties exist in characterizing representative soils in this landscape. Nonetheless, within each watershed, springwater has lower $^{87}Sr/^{86}Sr$ values relative to soil leachates (Fig. 2). This spatial variability in $^{87}Sr/^{86}Sr$ values at the scale of the two watersheds is consistent with results of Musgrove and Banner (2004), which detail distinct geochemical signatures associated with different caves across the region. HCSNA springwater from the two watersheds also reflect different Mg/Ca–Sr/Ca trend lines (Fig. 5). Springwater associated with the control watershed, and Honey Creek streamwater, have a broader range in Mg/Ca and Sr/Ca (Fig. 5). This local scale geochemical variability at HCSNA suggests that small-scale differences in geology, lithology, vegetation and/or weathering are reflected in corresponding soil compositions for each watershed.

Samples from Foxtrot spring (and to a lesser degree, Echo spring) suggest that treatment watershed springwater is less geochemically evolved relative to the control watershed, based on modeled fluid-evolution pathways hypothesized in Musgrove and Banner (2004) and described above (Fig. 6). Consistently higher $^{87}Sr/^{86}Sr$ values suggest that Foxtrot springwaters are dominated by interaction with soils, yet relatively invariant Sr isotope ratios through time (Fig. 3) suggest that this spring has a large component of diffuse/matrix flow. Higher $^{87}Sr/^{86}Sr$ values measured for Foxtrot spring may reflect locally more radiogenic soils.

Based on their more upland locations, treatment watershed springs may be surface-process dominated features that are more akin to cave dripwaters in their geochemical evolution relative to the other springs. Both Foxtrot and Echo springs have lower observed relative discharge rates than the other springs and Foxtrot spring is particularly ephemeral. Since Foxtrot and Echo springs are the only two springs associated with the treatment watershed, it is not certain if these differences reflect a different hydrology for these springs (i.e., more upland location, more surface dominated springs/seeps), or if they reflect differences between the two watersheds (i.e., differences in soil composition and geochemical evolution pathways). Sr isotope values for soils suggest that the two watersheds are different, even though land use and soil classifications are similar.

5.5. Temporal variability in springwater geochemistry

Similar to many karst systems, the Edwards aquifer responds rapidly (e.g., hours to days) to changes in precipitation and recharge. Temporal fluctuations in Edwards aquifer groundwater geochemistry has been previously attributed to the response of the aquifer system to changes in recharge and aquifer flow conditions (e.g., Bader et al., 1993; Mahler et al., 2006). Ogden and Collar (1990) discuss temporal variations in saturation states for central Texas spring discharge. Temporal variations in vadose cave dripwaters in central Texas are well-documented (Musgrove and Banner, 2004; Veni, 1997). These results are all indicative of processes that involve base flow (matrix/diffuse) and event flow (conduit) endmembers and differing residence times (e.g., Winston and Criss, 2004).

Temporal variability in karst water geochemistry suggests that processes controlling spatial variations in dripwater, springwater, and groundwater geochemistry, such as water–rock interaction, also vary in time. For example, dripwater, springwater, and groundwater from flow routes dominated by matrix/diffuse flow should exhibit less temporal variability than sites influenced by conduit flow. Changes in climatic and hydrologic variables such as rainfall, recharge and flow routing (as a result of event-driven flow) should influence the extent of water–rock interaction processes and associated fluid geochemistry.

We compare temporal variations in HCSNA springflow geochemistry with indicators of hydrologic variability: (1) Comal Springs discharge (Comal Springs is one of the major regional aquifer discharge points), which is broadly representative of regional hydrologic conditions, (2) effective moisture at Canyon Dam (approximately 24 km east of HCSNA), a local indicator that is representative of the scale of climatic variables likely to impact hydrology and geochemistry of HCSNA springs, and (3) HCSNA precipitation (Fig. 6). Canyon Dam is the closest location with records of both rainfall and evaporation data, used to calculate effective moisture. Temporal variability in HCSNA springwater geochemistry is consistent with changes in both regional discharge and local effective moisture (Fig. 6). For example, Comal Springs discharge and effective moisture at Canyon Dam both decrease during the first half of 2003; these decreases are accompanied by lower $^{87}Sr/^{86}Sr$ values for HCSNA springwaters. High Comal Springs discharge and effective moisture at Canyon Dam occur in mid to late 2004, accompanied by relatively low Mg/Ca ratios for HCSNA springwaters. These geochemical changes are consistent with the hydrologic model of groundwater geochemical evolution discussed in Musgrove and Banner (2004), wherein longer groundwater residence times associated with drier hydrologic conditions (indicated by decreased spring discharge and lower effective moisture) are associated with lower $^{87}Sr/^{86}Sr$ values and higher Mg/Ca ratios. The relationship between HCSNA springwater geochemistry and temporal variations in local rainfall is less apparent (Fig. 6c), which suggests that rainfall, while an important hydrologic input, is not the only factor influencing recharge and flow conditions.

HCSNA springwaters are not uniformly variable in time with respect to geochemistry (Fig. 3). Limited strontium isotope data from Alpha spring shows little variability, as does data from Foxtrot spring (treatment watershed). This contrasts with $^{87}Sr/^{86}Sr$ results for the control watershed springs and Echo spring (treatment watershed), which show considerable variability through time (Fig. 3). Samples from Bravo, Cotton, Delta, and New springs, as well as Honey Creek, are compositionally similar at any point in time and covary similarly throughout the study period with respect to $^{87}Sr/^{86}Sr$ and Mg/Ca (Figs. 3 and 4). This is also so for Sr/Ca variations (not shown). Although Echo spring (treatment watershed), is offset to higher $^{87}Sr/^{86}Sr$ values relative to the other springs (Fig. 3), the time-series variations are consistent with those exhibited by springs associated with the control watershed (Fig. 4). These results indicate that climatic and hydrologic processes are linked at multiple scales, from local to regional, and that temporal variability in springwater geochemistry is tied to changes in climatic and hydrologic conditions, including rainfall, effective moisture, and recharge.

5.6. Implications for surface water–groundwater interaction

Honey Creek streamwater is geochemically similar to HCSNA springs, but covers a large geochemical range that extends from vadose water (cave NB) to phreatic groundwater (Fig. 6). Surface water in Honey Creek is most geochemically similar to springwater from the control watershed (Bravo, Cotton, Delta, and New springs), in terms of both absolute values and temporal trends. These similarities indicate that extensive surface water–groundwater interaction affects HCSNA hydrology, and that springwater contributions dominate the composition of Honey Creek. Water transmission through karst occurs via a continuum from low-permeability diffuse flow pathways to high-permeability conduit flow pathways (Atkinson, 1977). A previously proposed model for central Texas vadose cave dripwater and groundwater links geochemical variability to changes in rainfall, resulting recharge, corresponding flow routing, and water–rock interaction processes (Musgrove and Banner, 2004). For example, an increase in high-permeability conduit flow will result in potentially shorter residence time and less mineral-solution interaction between fluids and host limestones. Fairchild et al. (2006) present a similar hydrologic routing model to account for evolution of fluid Mg/Ca and Sr/Ca ratios over multiple timescales.

For Edwards aquifer groundwater, including HCSNA springs and surface water, systematic changes in fluid geochemistry to lower $^{87}Sr/^{86}Sr$ (toward limestone values) and higher Mg/Ca and Sr/Ca values result from increasing extents of water–rock interaction as a result of increased low-permeability diffuse or matrix flow and longer residence time. Results of this study build on the model presented by Musgrove and Banner (2004) and provide empirical evidence for karst flowpath controlled geochemical evolution in the shallow phreatic part of the aquifer that supplies HCSNA springs. Springwaters represent an intermediate geochemical composition, and are more evolved than vadose water, but not as evolved as deeper phreatic groundwater. At HCSNA, groundwater-supplied springs control the surface water composition of Honey Creek. These surface water and groundwater connections result in a single, interactive, and temporally-dynamic flow system.

6. Conclusions

Groundwater evolution processes control the spatial and temporal variability observed in HCSNA springwater and Honey Creek streamwater, and document surface water–groundwater connections. Small-scale spatial variability in sources of dissolved constituents (e.g., soils, aquifer rocks), recharge characteristics, flow routes, and corresponding mineral-solution reactions contribute to the geochemical variability of HCSNA springwaters. Springwater falls on a geochemical continuum between soil water compositions and deeper phreatic Edwards aquifer groundwater. This geochemical variability serves to differentiate between vadose water and phreatic groundwater sources to surface water in Honey Creek and enables us to document a dominant groundwater contribution to this surface water. No discernible effect from ashe juniper clearing in the control watershed was evident in springwater geochemistry on the timescale of this study.

Mineral-solution reaction models indicate that groundwater with relatively low $^{87}Sr/^{86}Sr$ and high Mg/Ca and Sr/Ca values results from increased residence time and corresponding greater extents of water–rock interaction. A model of changes in fluid flow routes and corresponding changes in residence time and mineral-solution reactions as a function of rainfall and amount of recharge can account for both spatial and temporal variability in HCSNA springwater and Honey Creek streamwater. These results add an intermediate component (i.e., springs) to regional groundwater evolution processes proposed by previous studies, and provide insight into these processes at the watershed scale. HCSNA springwaters from multiple springs and from Honey Creek have similar temporal variability in geochemical parameters such as $^{87}Sr/^{86}Sr$, and Mg/Ca and Sr/Ca ratios, which suggests that common processes control fluid evolution, including surface water, in this area. Systematic differences in springwater geochemistry at the watershed are similar to differences in the soils between the control and treatment watersheds that may control the starting point of geochemical evolution processes.

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