

# Water Resources Research

# **RESEARCH ARTICLE**

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#### **Key Points:**

- We document the geochemical evolution of infiltrating municipal water (via leakage and/or irrigation) within a semiurbanized watershed
- Geochemical modeling results indicate stream and spring water consists of 50–90% municipal water within urban areas
- Our geochemical modeling approach estimates subsurface flow paths and relative groundwater residence times of infiltrating municipal water

#### **Supporting Information:**

- Supporting Information S1
- Figure S1

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# Stream and Spring Water Evolution in a Rapidly Urbanizing Watershed, Austin, TX

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**Abstract** Quantifying urban development impacts on fresh water quality and quantity is critical, especially as growing populations concentrate in urban centers and with climate change projections of increased hydrologic extremes. We investigate geochemical processes through which municipal supply and waste water, carbonate bedrock, and soils impact stream and spring water compositions within the Bull Creek watershed (Austin, Texas). This watershed exhibits a sharp geographic divide between urban and rural land. Urban and rural waters were assessed to quantify relative influences of municipal water on stream and spring water elemental compositions and <sup>87</sup>Sr/<sup>86</sup>Sr values. Higher <sup>87</sup>Sr/<sup>86</sup>Sr for samples from urban sites relative to rural sites can be accounted for by two processes: (1) water leakage from municipal infrastructure and/or irrigation or (2) ion exchange as precipitation infiltrates through soils with varying <sup>87</sup>Sr/<sup>86</sup>Sr. Irrigated soils have higher <sup>87</sup>Sr/<sup>86</sup>Sr than unirrigated soils, indicating that irrigated municipal water resets soil compositions and that process (1) is a dominant driver of urban stream and spring water evolution. Geochemical modeling results indicate that urban waters consist of 50% to 95% municipal water. Geochemical modeling further demonstrates the evolution of municipal water as it infiltrates as groundwater and undergoes water-rock interaction. These results are compared with groundwater compositions on a regional scale to infer local flow paths and relative groundwater residences times of municipal water. This study provides a geochemical modeling framework that quantifies both the significance of municipal water on urban stream water and soil compositions and the role of municipal water within urbanized watersheds and aquifers.

# 1. Introduction

Documenting urban development impacts on fresh water resources is critical for ensuring resiliency of both the quality and quantity of fresh water, which will become increasingly important with rapid population growth (United Nations, Department of Economic and Social Affairs, Population Division, 2017) and climate change projections of increased hydrologic extremes for the 21st century (Intergovernmental Panel on Climate Change, 2014). The global population is projected to increase from 6.9 billion in 2010 to 9.8 billion in 2050 (United Nations, Department of Economic and Social Affairs, Population Division, 2015; United Nations, Department of Economic and Social Affairs, Population Division, 2017) with 66% of this growth concentrated in urban areas. Thus, the provisioning (e.g., quantity, quality, and distribution) of fresh water will be an acute challenge in many regions (McDonald et al., 2011). The study of urban hydrology has increased in recent decades to address current and growing challenges for management of sustainable water quantity and quality (e.g., Abbott et al., 2019). These studies have highlighted the urban hydrology phenomena, including increased runoff amounts and flashy discharge due to impervious cover (e.g., Leopold, 1968; Boyd et al., 1993; Glick, 2009; Ragab et al., 2003; Shuster & Pappas 2011), the physical and chemical effects of storm water routing to streams via subsurface drainage systems (Hamel et al., 2013, Reynolds & Barrett, 2003), and shifts in aquatic ecosystem dynamics and vulnerability (e.g., Schueler, 1994; Walsh et al., 2005). Other studies have sought to understand the connection between treated water and natural surface and groundwater. These studies have highlighted urbanization effects on local to regional groundwater recharge (e.g., Berg et al., 1996; Garcia-Fresca & Sharp, 2005; Sharp, 2010) and have documented the increase in anthropogenic constituents in natural surface water and groundwater compositions due to water main leakage, irrigation, or wastewater (e.g., Reynolds & Barrett, 2003; Tang et al., 2004; Pu et al., 2014; Lim





**Figure 1.** The distribution of urbanization and key features within the study area. (a) Map of northcentral Austin, Texas, area watersheds showing road densities (gray and black lines). The Bull Creek watershed is outlined with a thick black line. (b and c) Sampled rural and urban (red and blue, respectively) stream and spring water sites. (b) The distribution of geologic units throughout the watershed, and (c) the four dominant soils. (d) A schematic cross section showing the three major hydrostratigraphic units in of the Bull Creek watershed and approximate location of the local groundwater table. Geologic data were obtained from the Bureau of Economic Geology, The University of Texas at Austin (Geology of the Austin area; 1:62,500 scale). Soil data were obtained from the U.S. Department of Agriculture-Natural Resources Conservation Service (NRCS) Geospatial Data Gateway.

et al., 2017; Roehrdanz et al., 2017; Lesser et al., 2018; Burri et al., 2019). In karst systems, groundwater is especially susceptible to contamination due to the high permeability and dual-porosity nature of the rock (White, 1988). That is, diffuse (i.e., matrix) and conduit (i.e., fractures, joints, and dolines) flow paths make karst aquifers particularly vulnerable to contaminated recharge that can infiltrate rapidly (hours to days; e.g., Mahler & Massei, 2007; Katz et al., 2009; Panno et al., 2019). Tracking the geochemical evolution of infiltrating contaminants (e.g., municipal water) in karst systems, which constitutes about a quarter of the world's drinking water resources (Ford & Williams, 2007), is critical for protecting groundwater quality through the 21st century.

In urbanized watersheds, municipal water may be an important contributor to the urban hydrologic cycle. Here we quantify the nature and geochemical evolution of infiltrating water to inform fluid mixing processes and their endmembers, the interaction between local and regional hydrogeologic units, subsurface flow paths, and relative groundwater residence times (e.g., Wong et al., 2014) within a semiurbanized karst watershed. We seek to specifically quantify (1) the extent that infiltrating municipal (supply and waste) water mixes with natural groundwater and stream water and its interaction with carbonate bedrock, (2) the relative depths to which municipal water infiltrates, and (3) the relative groundwater residence time of infiltrating municipal water with respect to regional phreatic and vadose groundwater. We assess the relative impact of municipal (supply and waste) water on the stream and spring waters using major ion and isotope geochemistry. Geochemical endmembers are determined by their distinct elemental and/or isotopic (<sup>87</sup>Sr/<sup>86</sup>Sr) compositions. The extent to which municipal (supply and waste) water (1) mixes with rural (i.e., natural) groundwater and/or (2) interacts with the carbonate rocks of the watershed/aquifer is quantified using spatial variations of stream and spring water composition in the semiurbanized watershed. We then apply elemental and isotopic (<sup>87</sup>Sr/<sup>86</sup>Sr) tracers and models to assess the geochemical evolution of urban stream and spring water and to estimate the relative extents of water-rock interaction between infiltrating municipal water and carbonate bedrock. We compare our local watershed results to those for the regional groundwater system for which previous research delineates the geochemical and physical relationship between short, intermediate, and long groundwater residence times. This allows us to infer relative groundwater flow paths and residence times for different components of the local urban watershed system.

The study area for this approach is the Bull Creek watershed in the area of Austin, Texas, which exhibits a sharp geographic divide (i.e., steep gradient) between urban development and undeveloped rural land. This range of land use provides an ideal setting to assess endmember (e.g., municipal water) processes that may be obscured in watersheds with less delineated distributions of urban and rural land use (Figure 1). Previous

studies within the same watershed have characterized, in response to urbanization, (1) an increase in stream water nutrients (Ging & Bennett, 1994; Duncan et al., 2010), (2) temporal shifts in the geochemical composition of spring discharge toward that of municipal water (DeMott et al., 2006), and (3) declines in an endangered salamander population within the urbanized areas (Bendik et al., 2014). Geochemical and isotopic variations in stream water, spring water, municipal supply water and municipal waste water, and soils and carbonate bedrock are assessed to quantify the evolution of stream and spring water compositions sampled across the watershed's urban and rural land (Figure 1). Strontium (Sr) isotope values provide a novel tool for tracing the origin and controlling processes of water composition in this watershed. The utility of Sr isotopes (<sup>87</sup>Sr/<sup>86</sup>Sr) as a tracer of water sources and controlling processes of fluid evolution have been previously demonstrated in this (Musgrove & Banner, 2004) and other carbonate systems (e.g., Banner et al., 1994; Dogramaci & Herczeg, 2002; Katz & Bullen, 1996) and is likely to yield insight to analogous processes in other rural and urbanized watersheds. We further evaluate the application of endmember <sup>87</sup>Sr/<sup>86</sup>Sr values through a comparative study of soils across the urbanization gradient.

# 2. Study Area

# 2.1. Regional Setting

Regional demographic projections in central Texas indicate rapid urbanization has occurred and will continue in the coming decades (Texas Demographic Center, 2019). Understanding the geochemical evolution of stream and spring water in this semiurbanized watershed will provide insight into the impacts to fresh water quality and may aid in defining the urban hydrologic cycle as development continues. The population of Austin increased from 576,000 in 1990 to 790,000 in 2010 and is expected to reach 2 million by 2050 (Texas Demographic Center, 2019; U.S. Census Bureau, 1990). Population growth in urban centers, coupled with climate change projections of an intensifying hydrologic cycle (Hayhoe, 2014; Swain & Hayhoe, 2015), poses significant challenges to water resource (e.g., Banner et al., 2010; Breyer et al., 2018) and habitat management (e.g., Bendik et al., 2014; Schueler, 1994; Walsh et al., 2005) that requires a dynamic understanding of the altered quantity and quality of water within the urban hydrologic cycle. Austin area municipal system losses (i.e., leakage) and irrigation demands account for 12% and 21%, respectively, of the annual city water production. Losses are based on the difference between pumpage from water treatment plants and the annual billable consumption (Joe Smith, City of Austin, personal communication, November 29, 2018).

#### 2.2. Spatial and Land Use Setting

The Bull Creek watershed occupies 82 km<sup>2</sup> of northwest Austin (Figure 1). The catchment area is considered semiurbanized, with urban development (largely single-family homes) in about half of the watershed (55%), specifically to the north of the main stream channel (Figures 1b and 1c). The urbanized region of the watershed has experienced increased urban development over the past two decades, and the population is projected to increase from 44,000 in 2000 to 70,000 by 2030 (City of Austin, 2001)). The undeveloped region of the watershed is protected from urbanization to maintain habitat for endangered species and to preserve the quality and quantity of spring discharge along the tributary canyon walls that provide perennial habitat for sensitive aquatic organisms and migratory birds (Balcones Canyonlands Preserve, 1996).

#### 2.3. Hydrogeologic Setting

The Bull Creek watershed consists of the Cretaceous-aged Trinity and Fredericksburg Groups, with carbonate bedrock including (from oldest to youngest) the Glen Rose Formation, Walnut Formation, Comanche Peak Limestone, and Edwards Limestone (Figures1b and 1d). The Edwards Limestone composes the principal aquifer for much of central Texas—the Edwards aquifer—and provides drinking water for cities both north and south of Austin; in contrast, Austin's water supply is primarily sourced from the Colorado River (Figure 1a), which is geochemically distinct from the Edwards aquifer (Christian et al., 2011). The Edwards aquifer is extensively karstified; its strata have undergone burial and diagenetic alteration and exposure (i.e., telogenetic karst system; Vacher & Mylroie, 2002). The Edwards Limestone outcrops in the study area (60–100 m thick), consisting of chert-rich, rudist-bearing, dolomitic limestone. The presence of vugs, solution collapse zones, caverns, and fracture networks makes the Edwards Limestone highly transmissive, both locally and regionally. The underlying geologic units locally vary between the thin (6 m) Comanche Peak Limestone and the Walnut Formation (up to 40 m thick). The Comanche Peak Limestone is a fine-grained fossiliferous limestone with interbedded marl and shale (Brune & Duffin, 1983) that pinches out in the northeastern region of the Bull Creek watershed (Figure 1c). The Walnut Formation is a thick medium-grained fossiliferous limestone that underlies the Edwards Limestone through much of the watershed. The Walnut Formation is considered a confining unit, although the presence of permeable shell beds may transmit groundwater (Brune & Duffin, 1983). The Glen Rose Formation (Trinity Group) is a thick (200 m) argillaceous package of alternating limestone, dolomite, and marl beds (Brune & Duffin, 1983). The Glen Rose limestone is considered a low-permeability unit that yields small amounts of fresh to slightly saline water (Brune & Duffin, 1983; Wong et al., 2014). The Glen Rose limestone is considered an aquitard in some Austin area watersheds (Wong et al., 2014), but we do not find evidence of this in the Bull Creek watershed. That is, seeps and springs are observed throughout the Edwards, Walnut, and Glen Rose outcrops in the Bull Creek watershed. These seeps and springs provide baseflow to tributary channels throughout the watershed (Geismar, 2001). The local phreatic water table is estimated between 5 and 68 m below ground surface, based on observation well data (n = 24; City of Austin-Watershed Protection Department personal communication, June 19, 2019) through the Fredericksburg Group (Figures 1b and 1d). Regional groundwater recharge (Hauwert, 2016; Smith et al., 2015) occurs through precipitation and losing streams that intersects outcrops of the Edwards Limestone (Figure 1b). The Edwards Aquifer Recharge Zone (e.g., unconfined Edwards Limestone) underlies much of the city of Austin (294 km<sup>2</sup>), making groundwater particularly susceptible to urbanization-related contamination (e.g., storm water runoff and sewage) via conduit flow paths (Wong et al., 2012).

The topography within the Bull Creek watershed varies from 5% to 15% rolling slopes (Geismar, 2001) to 100 m deep canyons. There are four primary soils that overlay the carbonate bedrock—Brackett, Speck, Tarrant, and Volente soils (Figure 1c). Brackett and Tarrant soils cover 89% of the watershed. Both soil types are thin (0–50 cm), well-drained, gravelly clay loam and stony clay material. Volente soils are well drained, thick (55–130 cm), and range from silty clay to silty clay loam that occurs adjacent to stream channels (Figure 1c; Soil Survey of Travis County, 1974). The Speck soil occurs in 2% of the watershed near the northern boundary and is considered a moderately thick (45 cm) clay loam. It should be noted that "Urban Land" soils (e.g., highly altered and obscured; Soil Survey of Travis County, 1974) occur in other Austin area watersheds but are not documented within the Bull Creek watershed. Recent field observations, however, show unconformities within soil profiles where landscaping is prevalent.

# 3. Methods

The extent of urban development associated with each sample site was delineated based on calculated subwatershed areas; these were determined following the methods of Maidment (2002) and calculated spatial extents for impervious cover and road density (from City of Austin, 2010, Land Use geodata). Sampling sites were classified as urban or rural as follows: Urban sites had either greater than 25% impervious cover or greater than 0.002 m<sup>-1</sup> road density within the subwatershed; rural sites had less than 25% impervious cover and 0.002 m<sup>-1</sup> road density within the subwatershed. The difference between urban and rural sites is based on Schueler (1994), who documented the relationship between impervious cover and stream quality.

Stream and spring water samples were collected under baseflow conditions in August 2010, April 2011, and quarterly from July 2012 to June 2013, spanning 21 urban and 7 rural sites (Figures 1b and 1c). Samples were collected in precleaned HDPE Nalgene bottles and decanted with 0.45 micron polypropylene syringe filters into precleaned HDPE vials for anion analysis and acid-cleaned vials for cation and <sup>87</sup>Sr/<sup>86</sup>Sr analysis. Samples for cation and <sup>87</sup>Sr/<sup>86</sup>Sr analysis were acidified to pH 4.5 with concentrated ultrapure HNO<sub>3</sub>. Soil samples (n = 20) were collected for <sup>87</sup>Sr/<sup>86</sup>Sr analysis using precleaned plastic trowels from 5 to 15 cm depth and were classified as irrigated (i.e., urban) or unirrigated (i.e., natural) based on field-observed irrigation systems and surveying of landowners. Soil samples were leached using ammonium acetate to extract exchangeable ions from grain surfaces, which simulated the natural interaction of infiltrating water with soils. Carbonate bedrock samples (n = 9) were treated with acetic acid. Both soil and carbonate bedrock leaching of noncarbonate minerals and then dissolved with acetic acid. Both soil and carbonate bedrock leachate extractions followed a method modified from Montañez et al. (1996).

Water samples collected for major ion geochemistry in 2010 and 2011 were analyzed by the Lower Colorado River Authority, in partnership with the City of Austin's Watershed Protection Department. Municipal



Table 1	L
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Range of Geochemical Concentrations (mg/L) and <sup>87</sup>Sr/<sup>86</sup>Sr Values for the Measured Waters

		High-Sr urban $(n = 17)$	Low-Sr urban $(n = 25)$	Rural $(n = 14)$	Municipal supply $(n = 7)$	Municipal waste $(n = 9)$	Rural endmember (n = 2)	Municipal supply endmember (n = 2)	Municipal waste endmember (n = 1)
				Range (mean)					
(mg/L)	Ca	75–146 (112)	67–166 (116)	85-104 (96)	11-12 (11)	15-37 (27)	90, 100	11, 11	25
	Mg	16-29 (23)	11-33 (20)	16-26 (19)	14-18 (16)	16-21 (18)	16, 19	15, 18	16
	Na	15-74 (35)	11-41 (25)	7-11 (9)	18-31 (24)	43-105 (64)	9,10	18, 28	63
	Κ	0.4-4 (2.2)	0.9-4.4 (2.4)	0.5-1.3 (0.8)	3.2-4.9 (4.1)	BDL-26 (15)	0.5, 0.8	3.2, 4.4	18
	Cl	28-93 (58)	19-88 (46)	16-26 (19)	27-44 (39)	57-167 (80)	16, 19	27, 43	81
	HCO <sub>3</sub>	250-456 (337)	245-481 (351)	308-359 (336)	60-76 (67)	94-166 (139)	312, 353	68, 76	165
	NO <sub>3</sub> as	0.3-16.6 (5.4)	0.8-28.7 (8.2)	BDL-3.5 (1.2)	0.5-2.0(1)	BDL-2.1 (0.4)	1.8, 1.8	0.8, 1.1	BDL
	$NO_3$								
	Sr	0.46-4.9 (1.6)	0.13-0.44 (0.2)	0.24-2.6 (1.1)	0.11-0.13 (0.1)	0.12-0.4 (0.1)	0.24, 0.75	0.11, 0.12	0.15
(-)	<sup>87</sup> Sr/ <sup>86</sup> Sr	0.7077-0.7082	0.7079-0.7087	0.7078-0.7081	0.7091-0.7095	0.7079-0.7090	0.7078,	0.7091, 0.7095	0.7088
		(0.7079)	(0.7084)	(0.7079)	(0.7093)	(0.7086)	0.7081		

*Note.* Values in parentheses represent the standard deviation of measured concentrations. Below detection limit (BDL) indicates samples that were below the analytical detection limits.

supply water samples (n = 7) were collected from residents and businesses within the Bull Creek watershed (Figures 1b and 1c), while municipal waste water samples (n = 9) were collected by the City of Austin's Watershed Protection Department from city-wide treatment plants. Water, soil, and bedrock samples collected in 2012 and 2013 were analyzed at The University of Texas at Austin, Department of Geological Sciences, and the respective analytical methods are summarized herein. Stream and spring water Cl, SO<sub>4</sub>, and NO<sub>3</sub> concentrations were determined using Waters 501 High Performance Liquid Chromatograph (Tables 1 and S2 in the supporting information). F was measured using a  $LaF_3$  Ion Selective Electrode (Table S2). The percent difference between replicate samples (n = 23) for Cl, SO<sub>4</sub>, NO<sub>3</sub>, and F were within 10%, with one exception, for which  $NO_3$  had an anomalous uncertainty of 25%. Cation concentrations were analyzed using an Inductively Coupled Plasma Quadrupole-Mass Spectrometer (Tables 1 and S1). Analytical uncertainty for Ca, Mg, Na, and Sr was 0.13, 0.04, 0.04, and 0.02 mg/L, respectively, based on twice the standard error of sample replicate analyses of the internal standard. The mean percent difference between replicate samples (n = 7) for Ca, Mg, Na, and Sr was within 4%. Detection limits for anions and cations were 1 to 5 orders of magnitude below sample elemental concentrations. Charge balances for stream and spring water samples ranged from  $\pm 0.8\%$  to  $\pm 10.3\%$ , with most (89%) less than  $\pm$ 5%. Water, soil leachate, and carbonate bedrock <sup>87</sup>Sr/<sup>86</sup>Sr values (Table S3) were measured following the methods of Banner and Kaufman (1994) and Musgrove and Banner (2004) using a Triton Thermal Ionization Mass Spectrometer. The analytical uncertainty is  $\pm 0.000015$  for reported  ${}^{87}$ Sr/ ${}^{86}$ Sr values, based on 2-sigma ( $2\sigma$ ) standard NBS-987 measurements (0.710271). Field and laboratory blank analyses contained 130 and 4 to 12 pg of Sr, respectively, which are negligible relative to the minimum amount of analyzed Sr (2 µg).

The geochemical and isotopic evolution of stream and spring waters via endmember mixing and water-rock interaction is modeled following Banner et al. (1989), Banner and Hanson (1990), Banner et al. (1994), and Musgrove and Banner (2004). We consider fluid mixing between representative municipal supply water, municipal waste water, and rural water endmembers (e.g., samples with the highest and lowest <sup>87</sup>Sr/<sup>86</sup>Sr values) by mass balance of <sup>87</sup>Sr/<sup>86</sup>Sr values and Sr concentrations. Water-rock interaction is modeled based on mass-balance relationships between endmember (e.g., Cretaceous limestone and municipal supply water) elemental and isotopic values. We model two distinct geochemical processes for municipal water interacting with calcite and dolomite using iterative mass-balance calculations: (1) dissolution and (2) recrystallization (i.e., dissolution and reprecipitation). The dissolution model simulates incremental increases of Ca and Sr from limestone into solution. The recrystallization model (hereafter "water-rock interaction model") simulates a given volume of water passing through progressively increasing increments of carbonate bedrock. In the recrystallization model, we assume that during each iteration, the volume of





**Figure 2.** Na and Cl (mmol/L) variations for municipal supply (green triangles) and waste (orange triangles) water, rural stream and spring water (blue circles), and urban stream and spring water (red circles). Line shows the 1:1 molar ratio of Na:Cl concentrations.

water attains equilibrium with the calcite and dolomite in the carbonate bedrock (Banner et al., 1989, 1994; Musgrove & Banner, 2004).

# 4. Results

#### 4.1. Key Elemental Constituents

Chemical indicators of municipal (supply and/or waste) water interacting with natural surface water and groundwater include Na, Cl, and NO<sub>3</sub>. Na and Cl are particularly useful conservative tracers because the aqueous concentrations do not change with water-rock interaction processes (e.g., precipitation and dissolution of limestone). In this study, the range of both Na and Cl concentrations are elevated in both the municipal waste water (43–105 and 57–167 mg/L, respectively) and urban water samples (11–74 and 19–93 mg/L, respectively), relative to municipal supply water (18–31 and 27–44 mg/L, respectively) and rural water samples (7–11 and 16–26 mg/L, respectively) (Figure 2 and Table 1). The Na and Cl concentrations for urban water samples span the range between the lowest concentrations in the rural samples and the highest concentrations in the municipal waste water samples (Figure 2). Municipal waste water has a higher range of Na concentrations relative to Cl concentrations, such that

many of the samples lie above the 1:1 molar ratio (Na:Cl) line (Figure 2). NO<sub>3</sub> concentrations in the urban samples (0.3–28.7 mg/L NO<sub>3</sub> as NO<sub>3</sub>) are elevated with respect to both the measured municipal supply (0.5–2 mg/L) and municipal waste water (<2.1 mg/L; Table 1).

In contrast to municipal water indicators, the key constituents associated with rural groundwater interacting with carbonate host rock are Ca,  $\text{HCO}_3$ , and Sr (Table 1). These major (Ca and  $\text{HCO}_3$ ) and trace (Sr) element concentrations are used, in conjunction with  $^{87}\text{Sr}/^{86}\text{Sr}$  values, throughout this study to quantify geochemical interaction processes between municipal water and rural water and municipal water interaction with the carbonate host rock. That is, elevated concentrations of Ca,  $\text{HCO}_3$ , and Sr in the rural stream and spring water samples (85–104, 308–359, and 0.24–2.60 mg/L, respectively) relative to municipal supply (11–12, 60–76, and 0.11–0.13 mg/L, respectively) and waste water (15–37, 94–166, and 0.12–0.40 mg/L, respectively) samples are used to distinguish between different geochemical mechanisms such as fluid mixing and water-rock interaction. This quantitative geochemical modeling approach is then used to assess the origin and evolution of urban stream and spring waters.

#### 4.2. Water Types and Endmembers

In Austin area watersheds, distinct isotopic ( ${}^{87}$ Sr/ ${}^{86}$ Sr) and elemental differences exist between rural groundwater and municipal (supply and waste) water. Here we assess these geochemical differences among sampled waters and soil leachates to identify endmember geochemical compositions. We then use these endmember compositions to quantify the altered isotopic ( ${}^{87}$ Sr/ ${}^{86}$ Sr) and elemental composition of stream and spring waters within the urbanized region of the Bull Creek watershed. The endmember waters described herein represent distinct  ${}^{87}$ Sr/ ${}^{86}$ Sr values and/or elemental compositions.

#### 4.2.1. Urban Stream and Spring Waters

The Ca-HCO<sub>3</sub> type water that occurs within the urbanized region of the watershed has  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  values that range from 0.7077 to 0.7087 (Table 1 and Figure 3). We identify endmember waters from among the (1) rural stream and spring water, (2) municipal supply water, and (3) municipal waste water compositions and apply these to understand the origin of urban stream and spring water ("urban waters" hereafter).

# 4.2.2. Rural Stream and Spring Waters

In the Austin area, rural water <sup>87</sup>Sr/<sup>86</sup>Sr values (mean <sup>87</sup>Sr/<sup>86</sup>Sr = 0.7079; Christian et al., 2011) are similar to values for Cretaceous seawater (0.7072–0.7080; Koepnick et al., 1985), reflecting Sr sourced by carbonate bedrock. These Ca-HCO<sub>3</sub> type rural waters have a local range of <sup>87</sup>Sr/<sup>86</sup>Sr values from 0.7078 to 0.7081 (Table 1 and Figure 3). We consider two endmember samples local to Bull Creek rural stream and spring waters ("rural waters" hereafter), which represent (1) the lowest <sup>87</sup>Sr/<sup>86</sup>Sr value (0.7078) and (2) the highest <sup>87</sup>Sr/<sup>86</sup>Sr value (0.7081; Figure 3) within this range.





**Figure 3.** Distribution of <sup>87</sup>Sr/<sup>86</sup>Sr values for Bull Creek stream and spring water, soils, municipal (supply and waste) water, and Cretaceous limestone in the Bull Creek watershed. Hypothesized geochemical processes (dashed arrows) are inferred for the evolution of water and soils from starting compositions (circles at start of dashed arrows). Uncertainty symbol shows representative analytical uncertainty for <sup>87</sup>Sr/<sup>86</sup>Sr analysis.

#### 4.2.3. Municipal Supply Water

The City of Austin's municipal supply water is sourced from the Colorado River and has high <sup>87</sup>Sr/<sup>86</sup>Sr values across the Austin area (mean <sup>87</sup>Sr/<sup>86</sup>Sr = 0.7090; Christian et al., 2011) relative to the Austin area rural ground-water (mean <sup>87</sup>Sr/<sup>86</sup>Sr = 0.7079; Christian et al., 2011). The high <sup>87</sup>Sr/<sup>86</sup>Sr values of Austin's municipal supply water reflect the contribution of Sr from Precambrian granitic and metamorphic rocks (Christian et al., 2011) that outcrop approximately 100 km upstream of Austin in the Llano uplift region. The Mg-HCO<sub>3</sub> type municipal supply water has local (i.e., within the Bull Creek watershed) <sup>87</sup>Sr/<sup>86</sup>Sr values that range from 0.7091 to 0.7095, which is the narrowest endmember range (Table 1 and Figure 3). We consider two endmember samples of the measured municipal supply: (1) the lowest <sup>87</sup>Sr/<sup>86</sup>Sr value (0.7091) and (2) the highest <sup>87</sup>Sr/<sup>86</sup>Sr value (0.7095). Differences in elemental compositions between municipal supply and rural water (e.g., Ca, Na, Cl, and HCO<sub>3</sub>; Table 1) are also considered.

#### 4.2.4. Municipal Waste Water

The Na+K-HCO<sub>3</sub> type municipal waste water has a broad range of  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  values, from 0.7079 to 0.7090 (Table 1 and Figure 3) throughout

the Austin area. We consider municipal waste water as an elemental endmember for conservative ions (e.g., Na and Cl) but not for  ${}^{87}$ Sr/ ${}^{86}$ Sr values or carbonate constituents (e.g., Ca and HCO<sub>3</sub>) due to its highly variable composition that spans the range of both municipal supply water and rural water (Table 1). **4.2.5. Soils** 

Additional sources of high  ${}^{87}$ Sr/ ${}^{86}$ Sr values (e.g.,  ${}^{87}$ Sr/ ${}^{86}$ Sr > 0.7090) to Austin stream and spring water have been hypothesized to include soils with high  ${}^{87}$ Sr/ ${}^{86}$ Sr values (Christian et al., 2011). Our results show a distinct increase in soil leachate  ${}^{87}$ Sr/ ${}^{86}$ Sr values from unirrigated soil (0.7079–0.7084) to soils irrigated (0.7085–0.7091) with municipal supply water (Figure 3). Notably, the unirrigated soils do not span the range of  ${}^{87}$ Sr/ ${}^{86}$ Sr values measured in the urban water samples (0.7077–0.7087), discounting unirrigated soils as a source of high  ${}^{87}$ Sr/ ${}^{86}$ Sr values to the urban waters. Thus, we do not consider soils as an endmember hereafter.

#### 4.2.6. Rain Water

The low concentration of Sr in local rainwater (mean Sr = 0.006 mg/L; Christian et al., 2011) is negligible relative to the other endmembers and is not considered further as it is unlikely to contribute measurable Sr to the watershed.

#### 4.3. Geochemical Modeling

Fluid mixing and water-rock interaction models are used to assess geochemical processes that account for the variations observed in Bull Creek stream and spring water compositions. First, we simulate mixing between three sets of endmembers (rural water, municipal supply, and municipal waste water) to portray the range of water compositions that may result from fluid mixing. The chemical constituents considered in the fluid mixing models (Figure 4) are selected to represent carbonate (Sr; Figure 4a) and municipal (Cl; Figure 4b) water. Variations in measured elemental (Sr and Cl) compositions and <sup>87</sup>Sr/<sup>86</sup>Sr values are then used to quantify possible fluid mixing between endmember waters. Fluid Mixing Lines I and III (Figures 4a and 4b) represent mixing between the highest <sup>87</sup>Sr/<sup>86</sup>Sr endmember compositions of rural and municipal supply water, whereas Fluid Mixing Lines II and IV represent mixing between the lowest <sup>87</sup>Sr/<sup>86</sup>Sr endmember compositions of rural and municipal supply water (Figures 4a and 4b). In contrast, Fluid Mixing Line V (Figure 4b) uses an endmember mixture between municipal waste water and a 90%:10% composition of rural:municipal supply water, respectively.

Using the contrasting elemental and isotopic covariability within the urban waters (Figure 4), we identify two distinct urban stream and spring water groups. These urban water groups are differentiated by low Sr concentration (<0.27 mg/L; hollow red circles in Figure 4) (hereafter "low-Sr-urban-waters") and high Sr concentration (>0.44 mg/L; solid red circles in Figure 4) (hereafter "high-Sr-urban-waters"). The geochemical distinction between the two urban water groups becomes increasingly apparent with additional modeling





**Figure 4.** Geochemical models portraying fluid mixing between (a, b) rural and municipal supply water and (b) a mixture of rural and municipal supply (90%:10%, respectively) water with municipal waste water. Each tick represents a 10% change in the proportion of municipal (supply and/or waste) water in the modeled fluid mixture. (a) Gray dashed lines depict inferred geochemical processes including limestone dissolution or water-rock interaction. (b) Multicolored lines depict two processes that, when combined, can account for the measured municipal waste water geochemical composition: (1) the addition of human waste to municipal supply water and (2) rural water and waste water mixing (via nonwatertight pipes). Red dashed lines illustrate inferred water-rock interaction model trajectories that results in low <sup>87</sup>Sr/<sup>86</sup>Sr values in the high-Sr-urban-waters relative to the low-Sr-urban-waters.

(presented herein). The low-Sr-urban-waters have distinctly higher <sup>87</sup>Sr/<sup>86</sup>Sr values (>0.7082) than either rural or high-Sr-urban-waters and consist of 50% to 95% municipal supply water (Fluid Mixing Lines I and II). In contrast, the high-Sr-urban-waters have distinctly lower  ${}^{87}$ Sr/ ${}^{86}$ Sr values (<0.7082), and mixing results show a notably smaller municipal supply component (<50%; Fluid Mixing Lines I and II). The geochemical composition of municipal waste water is also accounted for by fluid mixing between rural water and municipal supply water (Fluid Mixing Lines I and II in Figure 4a). Fluid mixing with respect to Cl, a distinctive municipal water component, and <sup>87</sup>Sr/<sup>86</sup>Sr indicates that the majority (93%) of urban waters cannot be accounted for by the rural and municipal supply water mixing model (Fluid Mixing Lines III and IV; Figure 4b). In this view, thelow-Sr-urban-waters lie along the endmember mixture with municipal waste water (Fluid Mixing Line V in Figure 4b). Both the low- and high-Sr-urban-waters have elevated Cl concentrations (19-88 and 28-93 mg/L, respectively) with respect to rural and municipal supply water (e.g., Table 1), but the <sup>87</sup>Sr/<sup>86</sup>Sr values are distinctly different between the two urban water groups (Figures 4a and 4b). We note that approximately half (55%) of the urban waters are not accounted for the by the rural and municipal supply water mixing models in Figure 4a (Fluid Mixing Lines I and II), particularly for samples with compositions that fall above Fluid Mixing Line I or below Fluid Mixing Line II. Moreover, the high-Sr-urban-waters are not accounted for by Fluid Mixing Lines III, IV, or V (Figure 4b). We describe below additional geochemical processes to account for the urban water samples that are not constrained by fluid mixing models.

To assess additional geochemical processes that may account for urban water geochemical compositions, we consider the covariability between measured Sr and Ca concentrations with respect to limestone dissolution (black line in Figure 5). Sr and Ca concentrations vary widely in rural and urban waters (Figure 5) but are notably low by comparison for municipal supply and waste water (Figure 5). Both the high- and low-Sr-urban-waters have a relatively large range of Ca concentrations (75–146 and 67–166 mg/L, respectively; Figure 5) but exhibit contrasting Sr concentrations ranges (high-Sr-urban-waters Sr = 0.44-4.9 mg/L; low-Sr-urban-waters Sr = 0.13-0.27 mg/L; Figure 5). The rural water compositions are low in Ca (85–104 mg/L) compared to both urban stream and spring water groups, with a somewhat high range of Sr concentrations (0.24-2.6 mg/L; Figure 5). The limestone dissolution pathway (black line in Figure 5) represents a mass balance calculation of municipal supply water infiltrating and dissolving Glen Rose Formation, which is the dominant carbonate bedrock that Bull Creek and its tributaries incise. The range and covariability of Sr and Ca concentrations in the low-Sr urban-waters are accounted for by the limestone dissolution pathway (Figure 5), but the high-Sr-urban-waters are not. It should be noted that the water-rock interaction line (red dashed line in Figure 5) is inferred, as opposed to the calculated limestone dissolution line. Below we quantify these water-rock interaction processes by first examining models that explain regional





**Figure 5.** Geochemical model for dissolution (black line) of the Glen Rose Limestone by interaction with municipal supply water (green triangles). Numbers along the dissolution line represent the amount of limestone dissolved into solution (in units of mmol/L). Measured municipal supply and waste water (green and orange triangles, respectively) and low-Sr-urban stream and spring waters (hollow red circles) plot along this line, while the rural (blue circles) and high-Sr-urban (solid red circles) stream and spring waters exhibit an increased Sr concentration relative to Ca.

groundwater processes (e.g., Musgrove et al., 2010; Musgrove & Banner, 2004; Wong et al., 2014). We then use these models to reassess the urban waters at the local setting (this study).

Water-rock interaction models (e.g., Figure 6) that quantify the recrystallization of calcite and dolomite have been applied regionally to assess the geochemical processes controlling groundwater composition in central Texas (e.g., Musgrove et al., 2010; Musgrove & Banner, 2004; Wong et al., 2014). Regional groundwater (Musgrove et al., 2010; Musgrove & Banner, 2004) sampled from cave dripwaters (i.e., vadose zone; hollow circles in Figure 6a), springs (gray circles in Figure 6a), and phreatic groundwater wells (black circles in Figure 6a) reflect increasing extents of water-rock interaction and thus increasing relative groundwater residence times ( $\tau$  in Figure 6). Relatively low Sr/Ca ratios and high <sup>87</sup>Sr/<sup>86</sup>Sr values in the vadose zone waters (Sr/Ca = 0.0003–0.001, <sup>87</sup>Sr/<sup>86</sup>Sr = 0.7084–0.7092) compared to those for the phreatic zone waters (Sr/Ca = 0.0004–0.009, <sup>87</sup>Sr/<sup>86</sup>Sr = 0.7076–0.7086) illustrate the increase in reaction progress, respectively, between the infiltrating water and Cretaceous limestone (Figure 6a).

Measured waters within the Bull Creek watershed are modeled with respect to the regional groundwater system (Figure 6b). That is, modeled water-rock interaction with Fluids I and II (gray lines in Figure 6) are applied to both the regional (Musgrove et al., 2010; Musgrove & Banner,

2004) and local (this study) systems to determine relative extents of water-rock interaction between infiltrating water and the Cretaceous limestone. The results from the measured Bull Creek waters (Figure 6b) are then compared to regional vadose and phreatic groundwater compositions in central Texas (Figure 6a; Musgrove & Banner, 2004; Musgrove et al., 2010) to provide additional insight into urban water flow paths and relative groundwater residence times of infiltrating municipal water. Sr/Ca values are highest in the rural and high-Sr-urban-waters (Sr/Ca = 0.001-0.013 and 0.001-0.018, respectively) with lower overall <sup>87</sup>Sr/<sup>86</sup>Sr values (Figure 6b). Rural water <sup>87</sup>Sr/<sup>86</sup>Sr values (0.7078-0.7081) are within the range for Cretaceous limestone (0.7072-0.7080; Christian et al., 2011; Koepnick et al., 1985), whereas high-Srurban-water values are higher (0.7077–0.7082; Figure 6a). The range of both rural and high-Sr-urban-water compositions (Figure 6b) is within the range measured for regional spring water and/or phreatic groundwater (Figure 6a). In contrast to the rural and high-Sr urban waters, the low-Sr urban waters exhibit relatively low Sr/Ca ratios (0.001-0.0005) and high <sup>87</sup>Sr/<sup>86</sup>Sr values (0.7082-0.7087) compared to the rural and high-Sr-urban-waters (Figure 6b). The low-Sr urban waters (Figure 6b) are within the range of regional spring and/or vadose groundwater compositions (Figure 6a). Fluid Endmembers I and II (Figures 6a and 6b) represent values for soil leachates above a central Texas cave (Natural Bridge Cavern; Musgrove & Banner, 2004), which are within the same geologic setting as the present study. Fluid III (Figure 6b) represents municipal supply water, which has the highest <sup>87</sup>Sr/<sup>86</sup>Sr value (present study).

# 5. Discussion

# 5.1. Controls on Urban Stream and Spring Water Elemental Composition

Elevated concentrations of major ions in the urban water samples relative to rural water samples (Table 1) are indicative of an additional, more saline component in stream and spring water from the urban sites, which we hypothesize is consistent with a significant contribution from municipal supply and waste water. Relatively high Na and Cl concentrations are commonly associated with municipal water sources (e.g., Barrett et al., 1999; Leopold, 1968; Porras et al., 2016), which is consistent with the urban water compositions measured in this study (Table 1 and Figure 2). The magnitude by which stream and spring water Na and Cl concentrations are elevated (Figure 2) may be attributed to the degree of urbanization and/or infrastructure age for a sample's subwatershed (e.g., Christian et al., 2011). NO<sub>3</sub> concentrations in the urban stream and spring waters (0.3–28.7 mg/L, NO<sub>3</sub> as NO<sub>3</sub>) were generally elevated relative to endmember concentrations (e.g., municipal waste water; less than 2.1 mg/L) as well as estimated national background concentrations





A Regional Groundwater Data and Models

**Figure 6.** <sup>87</sup>Sr/<sup>86</sup>Sr values versus Sr/Ca molar ratios for (a) regional phreatic, spring, and vadose zone groundwater from Musgrove et al. (2010) and soil leachates (Musgrove et al., 2010; Christian et al., 2011; this study) and (b) Bull Creek waters and soil leachates. Short, intermediate, and long  $\tau$  indicate relative groundwater residence times. Modeled Water-Rock Interaction (WRI) curves shows the evolution of initial fluids (I–III) through progressive increases in recrystallization (i.e., dissolution and reprecipitation) of calcite and dolomite. That is, the modeled WRI III curve (b) shows the incremental increase in Sr/Ca and decrease in <sup>87</sup>Sr/<sup>86</sup>Sr values as Fluid III (municipal supply water) undergoes increased water-rock interaction with calcite (solid black line) and dolomite (dashed black line). Modeled WRI I and II curves (gray) represent the range (i.e., widths) of recrystallization expected for calcite and dolomite starting at Fluids I and II, respectively. Arrows indicate increasing molar concentrations of dissolved bedrock for each modeled curve (incremental amounts of calcite and dolomite reported along each curve in mmol/L). Fluids I and II are the range of soil leachates presented in Musgrove et al. (2010) and were sampled above a central Texas cave (Natural Bridge Caverns, located about 70 mi south-southwest of Austin). Fluid III (b) is the measured municipal supply water sample (this study) with greatest <sup>87</sup>Sr/<sup>86</sup>Sr value (0.7095).



of 1.1 and 4.4 mg/L, respectively, for streams and groundwater (Dubrovsky et al., 2010). Measured stream and spring water  $NO_3$  concentrations were as much as an order of magnitude higher than other studies in the area that have investigated natural and anthropogenic sources of  $NO_3$ , which may reflect influence from fertilizer, human, and/or animal waste (Ging et al., 1996; Musgrove et al., 2016).

#### 5.2. Tracing Hydrologic Endmembers With Sr Isotopes

Previous studies in the Edwards aquifer have applied <sup>87</sup>Sr/<sup>86</sup>Sr values to constrain sources of dissolved constituents to groundwater and to assess geochemical evolution processes (e.g., Musgrove & Banner, 2004; Oetting et al., 1996). The varying distribution of <sup>87</sup>Sr/<sup>86</sup>Sr values in different components of the Bull Creek watershed provides a unique tracer of contributing water sources (Figure 3). We use the isotopic composition in conjunction with elemental differences in endmember waters (i.e., rural and municipal) to quantify the effects of urbanization on stream and spring water composition. Our results are consistent with previous studies in Austin area watersheds where hydrogeologically (and isotopically) distinct endmembers were identified (DeMott et al., 2006; Christian et al., 2011; Senison et al., 2013). That is, elevated <sup>87</sup>Sr/<sup>86</sup>Sr values in Austin area urban stream waters correspond to increases in urban development (Christian et al., 2011). We also address here an alternative hypothesis to account for the high <sup>87</sup>Sr/<sup>86</sup>Sr values in urban stream and spring water—that these high <sup>87</sup>Sr/<sup>86</sup>Sr values might result from natural variability in soil <sup>87</sup>Sr/<sup>86</sup>Sr values (Christian et al., 2011).

Unirrigated (i.e., natural) soil <sup>87</sup>Sr/<sup>86</sup>Sr values (0.7079–0.7084) cannot account for the full range of values observed in the urban stream and spring waters, which range notably higher (0.7077–0.7095; Figure 3). Additionally, the range of irrigated soil <sup>87</sup>Sr/<sup>86</sup>Sr values (0.7085–0.7091) is distinctly higher than that of unirrigated soils, with significantly different median values (p < 0.0001), which can account for the higher <sup>87</sup>Sr/<sup>86</sup>Sr values of the urban stream and spring waters (Figure 3). These consistent results discount the natural variability of soils as a source of high <sup>87</sup>Sr/<sup>86</sup>Sr to stream and spring waters and indicate that municipal leakage and/or irrigation water are likely an important contribution to urban stream and spring waters. The higher <sup>87</sup>Sr/<sup>86</sup>Sr values of irrigated soil relative to unirrigated soil, and the similarly higher range of values for irrigated soils and municipal water, suggest that soils in the urbanized parts of the watershed evolve toward municipal water <sup>87</sup>Sr/<sup>86</sup>Sr values via ion exchange as a consequence of extensive irrigation with municipal water.

# 5.3. Delineating Geochemical Processes and Groundwater Flow Pathways

Fluid mixing and water-rock interaction modeling results quantify the extent of geochemical evolution for infiltrating rural and municipal water. These results are then used, in the context of the regional groundwater setting, to constrain flow paths and relative groundwater residence times of municipal water within the Bull Creek watershed. Endmember mixing between rural and municipal supply water is considered with respect to geochemical constituents representative of both carbonate (e.g., Sr) and municipal water (e.g., Cl; Figure 4). Fluid mixing model results yield insight to the geochemical evolution of (1) municipal waste water and (2) urban stream and spring water compositions. The observed decrease in municipal waste water Sr concentration and <sup>87</sup>Sr/<sup>86</sup>Sr values relative to municipal supply water (Fluid Mixing Lines I and II in Figure 4a) may represent infiltration and exfiltration of rural groundwater and waste water, respectively, within nonwatertight infrastructure pipes (e.g., Goebel et al., 2004). The marked increase in municipal waste water Cl concentrations relative to municipal supply water (Figure 4b) is inferred to occur through the addition of human waste. Fluid mixing model results indicate that urban stream and spring water samples consist of 50% to 95% municipal supply water (Fluid Mixing Lines I and II in Figure 4a) and/or municipal waste water (Fluid Mixing Line V in Figure 4b) relative to rural water. We propose that mixing models based on <sup>87</sup>Sr/<sup>86</sup>Sr values and Sr concentrations may underestimate the influence of municipal water on the high-Sr urban waters (e.g., <50% in Figure 4a) due to additional geochemical processes (e.g., higher extents of water-rock interaction with the carbonate bedrock, as discussed below). This is supported by mixing models based on <sup>87</sup>Sr/<sup>86</sup>Sr and Cl concentrations, which demonstrate the influence of municipal (supply and/or waste) water on both the high- and low-Sr-urban-waters (Figure 4b). In this view, the mixture of rural and municipal supply (90%:10%, respectively) water with municipal waste water constrains Cl concentrations for both the high- and low-Sr-urban-waters. The measured decreases in the high-Sr-urban-water <sup>87</sup>Sr/<sup>86</sup>Sr values relative to the low-Sr-urban-waters can again be accounted for by additional geochemical processes (e.g., water-rock interaction). These mixing model results indicate that municipal water infiltration via pipe network leakage (supply and waste) and/or irrigation (supply) is a significant source of water in the local urban hydrologic cycle. We document that additional geochemical evolution of this infiltrating municipal (supply and waste) water occurs as it enters and interacts with the natural groundwater system and carbonate bedrock.

Sr, Ca, and <sup>87</sup>Sr/<sup>86</sup>Sr variations in the rural and urban waters lie along a continuum of geochemical evolution within the regional carbonate groundwater system (Figures 5 and 6). Low-Sr urban water has compositions that can be accounted for by limestone dissolution (0.5–2 mmol/L; Figure 5), as opposed to recrystallization (which would yield higher Sr concentrations, since Ca is preferentially incorporated into the crystal lattice). We infer that limestone dissolution occurs as municipal water interacts with the limestone host rock along vadose zone flow paths (e.g., Figure 6). Increasing reaction progress between the water and carbonate bedrock is evident throughout the Bull Creek watershed, as evidenced by increasing Sr/Ca values and decreasing <sup>87</sup>Sr/<sup>86</sup>Sr values that approach those of the Cretaceous limestone bedrock (Musgrove et al., 2010; Musgrove & Banner, 2004 ; Wong et al., 2014) via increasingly long groundwater residence times.

The vadose zone waters in Figure 6a are cave dripwaters from two caves in the region (Musgrove & Banner, 2004; Wong et al., 2014) and represent rainwater infiltrated through the unsaturated (vadose) zone. These vadose zone waters are the least geochemically evolved (i.e., relatively low Sr/Ca and high <sup>87</sup>Sr/<sup>86</sup>Sr values) due to lesser extents of interaction with the carbonate host rock, which is a result of relatively short ground-water residence times. Samples from several springs in the region, mostly small local springs (Musgrove et al., 2010; Wong et al., 2014) and Bull Creek watershed springs (this study; Figure S1), represent intermediate groundwater residence times. That is, spring waters are more geochemically evolved than vadose waters but less so than relatively deep phreatic groundwater (Musgrove & Banner, 2004). Low Sr/Ca and high <sup>87</sup>Sr/<sup>86</sup>Sr values in the low-Sr-urban-water (Figure 6b) is associated with regional vadose zone and intermediately evolved (i.e., shallow) groundwater, which corresponds with relatively short to intermediate groundwater residence times (i.e., lesser extents of water-rock interaction).

These regional geochemical models are applied at the local watershed scale (this study) to further assess the geochemical and physical evolution of the infiltrating municipal water (i.e., urban waters). We show that both the rural and high-Sr urban waters have higher Sr/Ca values and lower <sup>87</sup>Sr/<sup>86</sup>Sr values than regional vadose zone water (Figure 6a) and the low-Sr urban waters (Figure 6b). Moreover, the rural and high-Srurban-water <sup>87</sup>Sr/<sup>86</sup>Sr values are relatively low, and the rural waters are within the range of Cretaceous limestone (0.7072-0.7080; Christian et al., 2011; Koepnick et al., 1985). Water-rock interaction results for the rural and high-Sr urban waters (Figure 6b) indicate that these waters have relatively long groundwater residence times (i.e., more geochemically evolved), similar to regional phreatic groundwater compositions (Figure 6a). We note that the variability in the high-Sr-urban-water <sup>87</sup>Sr/<sup>86</sup>Sr values are larger than that observed in the rural waters, which is likely a result of the geochemical evolution process of infiltrating municipal water (relatively high <sup>87</sup>Sr/<sup>86</sup>Sr; i.e., Fluid III in Figure 6b) (1) mixing with rural groundwater and/or (2) interacting with the carbonate bedrock (relatively low <sup>87</sup>Sr/<sup>86</sup>Sr). The majority of measured urban waters do not fall along the modeled line for water-rock interaction with Fluid III (i.e., municipal water; green triangle in Figure 6b) and instead fall to its left, suggesting that a combination of fluid mixing and water-rock interaction occurs as municipal water infiltrates as groundwater. Our water-rock interaction model results are consistent with geochemical evolution models developed from regional phreatic and vadose groundwater in central Texas (Figure 6; Musgrove et al., 2010; Musgrove & Banner, 2004; Wong et al., 2014), allowing us to link the geochemical evolution observed in the Bull Creek watershed urban stream and spring waters (both high- and low-Sr-urban-waters) to physical flow paths. That is, infiltrating municipal (supply and/or waste) water may take vadose zone flow paths (high <sup>87</sup>Sr/<sup>86</sup>Sr and low Sr/Ca values in low-Sr urban waters; Figures 6a and 6b) or phreatic flow paths (low <sup>87</sup>Sr/<sup>86</sup>Sr and high Sr/Ca in high-Sr urban waters; Figures 6a and 6b).

#### 5.4. Conceptual Framework for the Urban Hydrologic Cycle

Studies that have documented natural groundwater flow paths in central Texas show that recharge may take shallow (i.e., vadose zone), deep (i.e., phreatic zone), or mixed flow paths (e.g., Musgrove et al., 2010; Musgrove & Banner, 2004; Smith et al., 2015; Wong et al., 2014), depending on antecedent moisture conditions and the density of carbonate dissolution features (e.g., Wong et al., 2012). Urban development,



however, complicates the controls on these flow paths due to the alteration of both surface (e.g., impervious cover) and subsurface (e.g., municipal pipe networks) characteristics. We present a conceptual framework based on geochemical modeling results to illustrate the altered flow paths between rural and urban settings (Figure 7). We consider the watershed holistically, comparing rural and urban water samples and processes rather than individual hydrogeologic units. Geochemical evolution modeling for Bull Creek watershed samples indicates varying groundwater residence times. This also suggests there are varying flow paths followed by municipal leakage and/or irrigation water, which are distinct and include (1) shallow to intermediate vadose zone flow (low-Sr urban waters; hollow red arrow in Figure 7b) and (2) deeper phreatic groundwater flow (high-Sr urban waters; solid red arrow in Figure 7b). Relatively long groundwater residence times and extensive water-rock interaction can account for the composition of both rural and high-Sr-urban-water (Figure 6), whereas the low-Sr urban water has compositions consistent with lower extents of water-rock interaction and shorter groundwater residence times (Figure 6). Here we show increased municipal water mixing (50% to 95%) for the low-Sr urban waters (hollow red line in Figure 7b) relative to rural settings (thick blue lines in Figure 7b). In this case, shallow municipal leakage dominates the geochemical signature, likely as a result of artificial recharge. This may occur through one or both of the following processes: (1) A high volume of municipal water mutes the geochemical signature of naturally infiltrating precipitation or (2) dense impervious cover limits the amount of naturally infiltrating precipitation and artificial recharge dominates the shallow groundwater system. Moreover, the municipal water geochemical signature within the urban phreatic groundwater system (e.g., high-Sr urban waters; solid red arrow in Figure 7b) may evolve toward natural water geochemical compositions due to greater extents of water-rock interaction and/or the volume of natural phreatic groundwater with which the municipal water mixes. Both processes are consistent with the interpretation of relatively long groundwater residence times. Based on observation well data (n = 24; City of Austin Department of Watershed Protection, personal communication, 2019) in the Bull Creek watershed, the phreatic water table ranges from 5 to 68 m below ground surface, but antecedent moisture conditions (e.g., Wong et al., 2012) and topography influence the travel time and path that infiltrating water takes to the water table. This conceptual framework, based on evidence of geochemically evolving municipal water, is consistent with the findings of Musgrove et al. (2010), who demonstrate the geochemical evolution of natural water as residence time and the extent of water-rock interaction increases. That is, vadose zone flow is the least geochemically evolved hydrologic component, and deep regional phreatic groundwater is the most evolved hydrologic component; other groundwater may be intermediate depending on residence time, length of flow path, and extent of water-rock interaction (Figure 6b).

#### 5.5. Implications

Our results provide a quantitative framework for understanding how municipal water impacts natural water geochemical compositions and interacts with the hydrologic cycle as a function of urbanization. Physical hydrologic modeling that previously estimated the volume of artificial recharge (e.g., Bhaskar et al., 2016; Bhaskar & Welty, 2012; Garcia-Fresca & Sharp, 2005; Minnig et al., 2018; Passarello et al., 2012; Sharp, 2010) may be advanced by estimates of relative extents of mixing and groundwater residences time of municipal water. This identification of the evolution of municipal water as it enters bedrock adds a novel diagnostic approach to quantifying the urban hydrologic cycle. The geochemical approach presented in this study can be applied within or across watersheds with varying degrees of urban development (e.g., Figure 1) to quantify regional alterations to the urban hydrologic cycle, particularly locations with chemically or isotopically distinct municipal and natural groundwater or stream water sources (e.g., Chesson et al., 2012). Considering specifically Sr isotopes, for example, the municipal water supply for St. Louis, Missouri, is from the Mississippi and Missouri Rivers (<sup>87</sup>Sr/<sup>86</sup>Sr of 0.7095 and 0.7010, respectively; Goldstein & Jacobsen, 1987; Christian et al., 2011), whereas the city overlies Paleozoic marine carbonate rocks ( $^{87}$ Sr/ $^{86}$ Sr = 0.7085; Christian et al., 2011); Spokane, Washington, receives municipal water from the Spokane Valley-Rathdrum Prairie Aquifer ( ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.7320; Chesson et al., 2012), which is markedly distinct from the city's underlying Columbia River Basalts ( ${}^{87}$ Sr/ ${}^{86}$ Sr = 0.7186; Bataille & Bowen, 2012). We expect that many cities worldwide exhibit isotopic distinctions between watershed geology and municipal water (e.g., Chesson et al., 2012 for U.S. cities). Thus, the integration of geochemical and isotopic tools presented herein may have wide application to delineate the impacts of urbanization on the hydrologic cycle.





**Figure 7.** Conceptual model of hypothesized flow paths for rural (blue arrows) and municipal water (red arrows), from recharge to spring discharge (blue circles). (a) Rural site: Depicts rural water flow paths (phreatic and vadose zone). (b) Urban site: Depicts altered surface characteristics (e.g., unvegetated surface with impervious cover) and subsurface flow paths. Flow paths of municipal (supply water) leakage originate at the gravel packed trench and include (1) shallow flow with low groundwater residence time (hollow red arrow; i.e., vadose zone flow) and (2) deep flow with high groundwater residence time (solid red arrow; i.e., phreatic flow). Rural water originates from precipitation (in a and b) and is hypothesized to contribute to both phreatic and vadose zone flow. The contribution of infiltrating precipitation is inferred to be less in the urban site schematic (b) (depicted by smaller blue arrows than for the rural site schematic (a)).

Continued research to quantify urbanization impacts may bolster how we manage fresh water resources in the 21st century and may reveal both advantages and disadvantages of such impacts on the urban hydrologic cycle. That is, infiltrated municipal water (via leakage and/or irrigation) quantified in this study may provide consistent water availability for vegetation and sensitive aquatic ecosystems, especially under the increased frequency of drought conditions projected for central Texas in the 21st century (Banner et al., 2010; Hayhoe, 2014; Swain & Hayhoe, 2015). The Lower Colorado River Authority manages water supplies for both the city of Austin and Gulf Coast rice growing operations, but only the city's municipal water supply is guaranteed (Lower Colorado River Authority, 2015). When reservoir levels persisted at just 30% from 2011 to 2015, the water provisioned to Gulf Coast rice growing operations was interrupted (2012–2015), and city irrigation was curtailed (2009 to present) to mitigate against decreases in Austin's municipal water supply (Breyer et al., 2018; Lower Colorado River Authority, 2015). In watersheds where irrigation continued, the



watershed-scale drought severity decreased, resulting in increased resiliency of urban vegetation and stream flow to the impacts of drought (Breyer et al., 2018). The contribution of the city's municipal water to watersheds via water main leakage and/or irrigation demonstrated in the present study, however, may significantly affect the long-term availability and energy costs of both municipal and agricultural water supplies. The geochemical tools applied in this study can be used to assess the degradation of water quality via waste water leakage that poses risks to sensitive aquatic ecosystems, altered physical groundwater flow paths, and the quantity of water available to humans and vegetation as urbanization and climate change progresses.

# 6. Conclusions

The spatial variability of elemental and isotopic (<sup>87</sup>Sr/<sup>86</sup>Sr) compositions in stream and spring water samples in a rapidly urbanizing watershed in central Texas was assessed to delineate the influence of municipal (supply and waste) water. The watershed exhibits a pronounced spatial gradient of urbanization: 55% is developed, and 45% is undeveloped rural land. <sup>87</sup>Sr/<sup>86</sup>Sr values provide a robust geochemical tool to trace the influence of municipal water on natural stream and spring waters. Distinctly higher <sup>87</sup>Sr/<sup>86</sup>Sr values for irrigated soils relative to unirrigated soils suggest that municipal water resets soil compositions over time and that municipal water (via pipe network leakage and/or irrigation) is the source of high <sup>87</sup>Sr/<sup>86</sup>Sr values observed in streams, springs, and irrigated soils.

The geochemical compositions of stream and spring water from urban sites within the watershed are significantly influenced by fluid mixing between rural (i.e., natural) and municipal (supply and/or waste) water (50% to 95% municipal water in mixture). The quantification of municipal water influence on stream and spring water composition demonstrates that municipal water can be a significant source of hydrologic recharge, even when a watershed is only partly urbanized. Water-rock interaction models indicate that when municipal water infiltrates into the carbonate bedrock, it evolves as groundwater along diagnostic Sr-Ca-<sup>87</sup>Sr/<sup>86</sup>Sr pathways. Water-rock interaction model results are then used to infer relative groundwater residence times and flow paths. This approach portrays infiltrating municipal water as having short to intermediate (i.e., vadose zone) or long (i.e., phreatic zone) residence times prior to stream or spring discharge. The contribution of municipal water for vegetation and sensitive aquatic ecosystems during drought conditions, but it may also affect long-term water availability and energy costs for both municipality and agricultural operations. Municipal (supply and/or waste) water may enter the vadose and/or phreatic zone, with risks to long-term surface and/or groundwater water quality.

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