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2 **Stream and spring water evolution in a rapidly urbanizing watershed, Austin, TX**

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4 Lakin Beal ^a, Jeffrey Senison ^b, Jay Banner ^{a,c}, MaryLynn Musgrove ^c, Lindsey Yazbek ^d, Nathan
5 Bendik ^e, Christopher Herrington ^e, and Daniel Reyes ^f

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7 Affiliations: ^a Department of Geological Sciences, The University of Texas at Austin; ^b
8 Occidental Petroleum Corporation; ^c Environmental Science Institute, The University of Texas at
9 Austin; ^d The Department of Geology, Kent State University; ^e City of Austin - Watershed
10 Protection Department; ^f Texas Water Development Board

11 **Key Points**

- 12 • We document the geochemical evolution of infiltrating municipal water (via leakage
13 and/or irrigation) within a semi-urbanized watershed
- 14 • Geochemical modeling results indicate stream and spring water consists of 50% - 90%
15 municipal water within urban areas
- 16 • Our geochemical modeling approach estimates subsurface flow paths and relative
17 groundwater residence times of infiltrating municipal water

18
19 **Abstract**

20 Quantifying urban development impacts on fresh water quality and quantity is critical,
21 especially as growing populations concentrate in urban centers and with climate change
22 projections of increased hydrologic extremes. We investigate geochemical processes through
23 which municipal supply and waste water, carbonate bedrock, and soils impact stream and spring
24 water compositions within the Bull Creek watershed (Austin, Texas). This watershed exhibits a

25 sharp geographic divide between urban and rural land. Urban and rural waters were assessed to
26 quantify relative influences of municipal water on stream and spring water elemental
27 compositions and $^{87}\text{Sr}/^{86}\text{Sr}$ values. Higher $^{87}\text{Sr}/^{86}\text{Sr}$ for samples from urban sites relative to rural
28 sites can be accounted for by two processes: (1) water leakage from municipal infrastructure
29 and/or irrigation, or (2) ion exchange as precipitation infiltrates through soils with varying
30 $^{87}\text{Sr}/^{86}\text{Sr}$. Irrigated soils have higher $^{87}\text{Sr}/^{86}\text{Sr}$ than unirrigated soils, indicating that irrigated
31 municipal water resets soil compositions, and that process (1) is a dominant driver of urban
32 stream and spring water evolution. Geochemical modeling results indicate that urban waters
33 consist of 50% to 95% municipal water. Geochemical modeling further demonstrates the
34 evolution of municipal water as it infiltrates as groundwater and undergoes water-rock
35 interaction. These results are compared with groundwater compositions on a regional scale to
36 infer local flow paths and relative groundwater residence times of municipal water. This study
37 provides a geochemical modeling framework that quantifies both the significance of municipal
38 water on urban stream water and soil compositions, and the role of municipal water within
39 urbanized watersheds and aquifers.

40 **Introduction**

41 Documenting urban development impacts on fresh water resources is critical for ensuring
42 resiliency of both the quality and quantity of fresh water, which will become increasingly
43 important with rapid population growth (United Nations, Dept. of Economic and Social Affairs,
44 2017) and climate change projections of increased hydrologic extremes for the 21st century
45 (Intergovernmental Panel on Climate Change, 2014). The global population is projected to
46 increase from 6.9 billion in 2010 to 9.8 billion in 2050 (United Nations, Dept. of Economic and
47 Social Affairs, 2017; United Nations, Dept. of Economic and Social Affairs, 2015) with 66% of

48 this growth concentrated in urban areas. Thus, the provisioning (e.g., quantity, quality, and
49 distribution) of fresh water will be an acute challenge in many regions (McDonald et al., 2011).
50 The study of urban hydrology has increased in recent decades to address current and growing
51 challenges for management of sustainable water quantity and quality (e.g., Abbott et al., 2019).
52 These studies have highlighted the urban hydrology phenomena, including increased runoff
53 amounts and flashy discharge due to impervious cover (e.g., Leopold, 1968; Boyd et al. 1993;
54 Glick, 2009; Ragab et al., 2003; Shuster et al., 2011), the physical and chemical effects of storm
55 water routing to streams via subsurface drainage systems (Hamel et al., 2013, Reynolds et al.,
56 2003), and shifts in aquatic ecosystem dynamics and vulnerability (e.g., Walsh et al., 2005;
57 Schueler, 1994). Other studies have sought to understand the connection between treated water
58 and natural surface and groundwater. These studies have highlighted urbanization effects on
59 local to regional groundwater recharge (e.g. Berg et al., 1996; Garcia-Fresca, 2004; Garcia-
60 Fresca and Sharp, 2005; Sharp, 2010), and have documented the increase in anthropogenic
61 constituents in natural surface water and groundwater compositions due to water main leakage,
62 irrigation, or wastewater (e.g., Reynolds and Barrett, 2003; Tang et al., 2004; Pu et al., 2014;
63 Lim et al., 2017; Roehrdanz et al., 2017; Lesser et al., 2019; Burri et al., 2019). In karst systems,
64 groundwater is especially susceptible to contamination due to the high permeability and dual-
65 porosity nature of the rock (White, 1988). That is, diffuse (i.e., matrix) and conduit (i.e.,
66 fractures, joints, and dolines) flow paths make karst aquifers particularly vulnerable to
67 contaminated recharge that can infiltrate rapidly (hours to days; e.g. Mahler and Massei, 2007;
68 Katz et al., 2009; Panno et al., 2019). Tracking the geochemical evolution of infiltrating
69 contaminants (e.g., municipal water) in karst systems, which constitutes about a quarter of the

70 world's drinking water resources (Ford and Williams, 2007), is critical for protecting
71 groundwater quality through the 21st century.

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

93 The study area for this approach is the Bull Creek watershed in the area of Austin, Texas,
94 which exhibits a sharp geographic divide (i.e., steep gradient) between urban development and
95 undeveloped rural land. This range of land use provides an ideal setting to assess endmember
96 (e.g., municipal water) processes that may be obscured in watersheds with less delineated
97 distributions of urban and rural land use (Fig. 1). Previous studies within the same watershed
98 have characterized, in response to urbanization, 1) an increase in stream water nutrients (Ging,
99 1994; Duncan et al., 2010), 2) temporal shifts in the geochemical composition of spring
100 discharge toward that of municipal water (DeMott, 2006), and 3) declines in an endangered
101 salamander population within the urbanized areas (Bendik et al., 2014). Geochemical and
102 isotopic variations in stream water, spring water, municipal supply water and municipal waste
103 water, and soils and carbonate bedrock are assessed to quantify the evolution of stream and
104 spring water compositions sampled across the watershed's urban and rural land (Fig. 1).

105 Strontium (Sr) isotope values provide a novel tool for tracing the origin and controlling processes
106 of water composition in this watershed. The utility of Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) as a tracer of water
107 sources and controlling processes of fluid evolution have been previously demonstrated in this
108 (Musgrove and Banner, 2004) and other carbonate systems (e.g. Banner et al., 1994; Katz and
109 Bullen, 1996; Dogramaci and Herczeg, 2002) and is likely to yield insight to analogous
110 processes in other rural and urbanized watersheds. We further evaluate the application of
111 endmember $^{87}\text{Sr}/^{86}\text{Sr}$ values through a comparative study of soils across the urbanization
112 gradient.

113 **Study Area**

114 *Regional setting*

115 Regional demographic projections in central Texas indicate rapid urbanization has
116 occurred and will continue in the coming decades (Texas Demographic Center, 2019).
117 Understanding the geochemical evolution of stream and spring water in this semi-urbanized
118 watershed will provide insight into the impacts to fresh water quality and may aid in defining the
119 urban hydrologic cycle as development continues. The population of Austin increased from
120 576,000 in 1990 to 790,000 in 2010 and is expected to reach 2 million by 2050 (U.S. Census
121 Bureau 1990; Texas Demographic Center, 2019). Population growth in urban centers, coupled
122 with climate change projections of an intensifying hydrologic cycle (Hayhoe, 2014; Swain and
123 Hayhoe, 2015), pose significant challenges to water resource (e.g., Banner et al, 2010; Breyer et
124 al., 2018) and habitat management (e.g., Bendik et al., 2014; Walsh et al., 2005; Schueler, 1994)
125 that requires a dynamic understanding of the altered quantity and quality of water within the
126 urban hydrologic cycle. Austin area municipal system losses (i.e., leakage) and irrigation
127 demands account for 12% and 21%, respectively, of the annual city water production. Losses are
128 based on the difference between pumpage from water treatment plants and the annual billable
129 consumption (Joe Smith, City of Austin, personal comm., 2018).

130 *Spatial and land use setting*

131 The Bull Creek watershed occupies 82 km² of northwest Austin (Fig. 1). The catchment
132 area is considered semi-urbanized, with urban development (largely single-family homes) in
133 about half of the watershed (55%), specifically to the north of the main stream channel (Fig. 1B ,
134 C). The urbanized region of the watershed has experienced increased urban development over
135 the past two decades, and the population is projected to increase from 44,000 in 2000 to 70,000
136 by 2030 (City of Austin – Watershed Protection Department – WPD Masterplan, 2001). The
137 undeveloped region of the watershed is protected from urbanization to maintain habitat for

138 endangered species, and to preserve the quality and quantity of spring discharge along the
139 tributary canyon walls that provide perennial habitat for sensitive aquatic organisms and
140 migratory birds (Balcones Canyonlands Preserve, 1996).

141 *Hydrogeologic setting*

142 The Bull Creek watershed consists of the Cretaceous aged Trinity and Fredericksburg
143 Groups, with carbonate bedrock including (from oldest to youngest) the Glen Rose Formation,
144 Walnut Formation, Comanche Peak Limestone, and Edwards Limestone (Fig. 1B, D). The
145 Edwards Limestone composes the principal aquifer for much of central Texas — the Edwards
146 aquifer— and provides drinking water for cities both north and south of Austin; in contrast,
147 Austin’s water supply is primarily sourced from the Colorado River (Fig. 1A), which is
148 geochemically distinct from the Edwards aquifer (Christian et al., 2011). The Edwards aquifer is
149 extensively karstified; its strata have undergone burial and diagenetic alteration, and exposure
150 (i.e., telogenetic karst system; Vacher and Mylroie, 2002). The Edwards Limestone outcrops in
151 the study area (60-100 m thick), consisting of chert-rich, rudist-bearing, dolomitic limestone. The
152 presence of vugs, solution collapse zones, caverns, and fracture networks make the Edwards
153 Limestone highly transmissive, both locally and regionally. The underlying geologic units
154 locally vary between the thin (6 m) Comanche Peak Limestone, and the Walnut Formation (up to
155 40 m thick). The Comanche Peak Limestone is a fine-grained fossiliferous limestone with
156 interbedded marl and shale (Brune and Duffin, 1983) that pinches out in the northeastern region
157 of the Bull Creek watershed (Fig. 1C). The Walnut Formation is a thick medium-grained
158 fossiliferous limestone that underlies the Edwards Limestone through much of the watershed.
159 The Walnut Formation is considered a confining unit, although the presence of permeable shell
160 beds may transmit groundwater (Brune and Duffin, 1983). The Glen Rose Formation (Trinity

161 Group) is a thick (200 m) argillaceous package of alternating limestone, dolomite, and marl beds
162 (Brune and Duffin, 1983). The Glen Rose limestone is considered a low-permeability unit that
163 yields small amounts of fresh to slightly saline water (Brune and Duffin, 1983; Wong et al.,
164 2014). The Glen Rose limestone is considered an aquitard in some Austin area watersheds
165 (Wong et al., 2014), but we do not find evidence of this in the Bull Creek watershed. That is,
166 seeps and springs are observed throughout the Edwards, Walnut, and Glen Rose outcrops in the
167 Bull Creek watershed. These seeps and springs provide baseflow to tributary channels
168 throughout the watershed (Geismar, 2001). The local phreatic water table is estimated between 5
169 and 68 meters below ground surface, based on observation well data (n = 24; City of Austin -
170 Watershed Protection Department personal comm., 2019) through the Fredericksburg Group
171 (Fig. 1B, D). Regional groundwater recharge (Smith et al., 2015; Hauwert, 2016) occurs through
172 precipitation and losing streams that intersects outcrops of the Edwards Limestone (Fig. 1B). The
173 Edwards Aquifer Recharge Zone (e.g., unconfined Edwards Limestone) underlies much of the
174 city of Austin (294 km²), making groundwater particularly susceptible to urbanization related
175 contamination (e.g., storm water runoff, sewage) via conduit flow paths (Wong et al., 2012).

176 The topography within the Bull Creek watershed varies from 5-15% rolling slopes
177 (Geismar, 2001) to 100 m deep canyons. There are four primary soils that overly the carbonate
178 bedrock—Brackett, Speck, Tarrant, and Volente soils (Fig. 1C). Brackett and Tarrant soils cover
179 89% of the watershed. Both soil types are thin (0-50 cm), well-drained, gravelly clay loam and
180 stony clay material. Volente soils are well-drained, thick (55-130 cm), and range from silty clay
181 to silty clay loam that occurs adjacent to stream channels (Fig. 1C; U.S. Department of
182 Agriculture, 1974). The Speck soil occurs in 2% of the watershed near the northern boundary
183 and is considered a moderately thick (45 cm) clay loam. It should be noted that “Urban Land”

184 soils (e.g., highly altered and obscured; U.S. Department of Agriculture, 1974) occur in other
185 Austin area watersheds, but are not documented within the Bull Creek watershed. Recent field
186 observations, however, show unconformities within soil profiles where landscaping is prevalent.

187 **Methods**

188 The extent of urban development associated with each sample site was delineated based
189 on calculated subwatershed areas; these were determined following the methods of Maidment
190 (2002) and calculated spatial extents for impervious cover and road density (from City of Austin,
191 2010, Land Use geodata). Sampling sites were classified as urban or rural as follows: urban sites
192 had either greater than 25% impervious cover or greater than 0.002 m⁻¹ road density within the
193 subwatershed; rural sites had less than 25% impervious cover and 0.002 m⁻¹ road density within
194 the subwatershed. The difference between urban and rural sites are based on Schueler (1994),
195 who documented the relationship between impervious cover and stream quality.

196 Stream and spring water samples were collected under baseflow conditions in August
197 2010, April 2011, and quarterly from July 2012 to June 2013, spanning 21 urban and 7 rural sites
198 (Fig. 1B, C). Samples were collected in precleaned HDPE Nalgene bottles and decanted with
199 0.45 micron polypropylene syringe filters into precleaned HDPE vials for anion analysis, and
200 acid-cleaned vials for cation and ⁸⁷Sr/⁸⁶Sr analysis. Samples for cation and ⁸⁷Sr/⁸⁶Sr analysis
201 were acidified to pH 4.5 with concentrated ultrapure HNO₃. Soil samples (n = 20) were collected
202 for ⁸⁷Sr/⁸⁶Sr analysis using precleaned plastic trowels from 5 –15 cm depth, and were classified
203 as irrigated (i.e., urban) or unirrigated (i.e., natural) based on field-observed irrigation systems
204 and surveying of landowners. Soil samples were leached using ammonium acetate to extract
205 exchangeable ions from grain surfaces, which simulated the natural interaction of infiltrating
206 water with soils. Carbonate bedrock samples (n = 9) were treated with ammonium acetate to

207 minimize trace element leaching of noncarbonate minerals, then dissolved with acetic acid. Both
208 soil and carbonate bedrock leachate extractions followed a method modified from Montañez et
209 al. (1996).

210 Water samples collected for major ion geochemistry in 2010 and 2011 were analyzed by
211 the Lower Colorado River Authority, in partnership with the City of Austin's Watershed
212 Protection Department. Municipal water samples (n = 7) were collected from residents and
213 businesses within the Bull Creek watershed (Fig. 1B, C), while municipal waste water samples
214 (n = 9) were collected by the City of Austin's Watershed Protection Department from city-wide
215 treatment plants. Water, soil, and bedrock samples collected in 2012 and 2013 were analyzed at
216 The University of Texas at Austin, Department of Geological Sciences, and the respective
217 analytical methods are summarized herein. Stream and spring water Cl, SO₄, and NO₃
218 concentrations were determined using Waters 501 High Performance Liquid Chromatograph
219 (HPLC). F was measured using a LaF₃ Ion Selective Electrode. The percent difference between
220 replicate samples (n = 23) for Cl, SO₄, NO₃, and F were within 10%, with one exception, for
221 which NO₃ had an anomalous uncertainty of 25%. Cation concentrations were analyzed using an
222 Inductively Coupled Plasma Quadrupole - Mass Spectrometer. Analytical uncertainty for Ca,
223 Mg, Na, and Sr was 0.13, 0.04, 0.04, and 0.02 mg/L, respectively, based on twice the standard
224 error of sample replicate analyses of the internal standard. The mean percent difference between
225 replicate samples (n = 7) for Ca, Mg, Na, and Sr was within 4%. Detection limits for anions and
226 cations were one to five orders of magnitude below sample elemental concentrations. Charge
227 balances for stream and spring water samples ranged from ±0.8% to ±10.3%, with most (89%)
228 less than ±5%. Water, soil leachate, and carbonate bedrock ⁸⁷Sr/⁸⁶Sr values were measured
229 following the methods of Banner and Kaufmann (1994) and Musgrove and Banner (2004) using

230 a Triton Thermal Ionization Mass Spectrometer. The analytical uncertainty is ± 0.000015 for
231 reported $^{87}\text{Sr}/^{86}\text{Sr}$ values, based on 2-sigma (2σ) standard NBS-987 measurements (0.710271).
232 Field and laboratory blank analyses contained 130 pg and 4 to 12 pg of Sr, respectively, which
233 are negligible relative to the minimum amount of analyzed Sr (2 μg).

234 The geochemical and isotopic evolution of stream and spring waters via endmember
235 mixing and water-rock interaction is modeled following Banner et al. (1989), Banner and
236 Hanson (1990), Banner et al. (1994), and Musgrove and Banner (2004). We consider fluid
237 mixing between representative municipal supply water, municipal waste water, and rural water
238 endmembers (e.g., samples with the highest and lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values, respectively) by mass
239 balance of $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr concentrations. Water-rock interaction is modeled based on
240 mass-balance relationships between endmember (e.g., Cretaceous limestone, municipal supply
241 water) elemental and isotopic values. We model two distinct geochemical processes for
242 municipal water interacting with calcite and dolomite using iterative mass-balance calculations:
243 1) dissolution and 2) recrystallization (i.e., dissolution and re-precipitation). The dissolution
244 model simulates incremental increases of Ca and Sr from limestone into solution. The
245 recrystallization model (hereafter “water-rock interaction model”) simulates a given volume of
246 water passing through progressively increasing increments of carbonate bedrock. In the
247 recrystallization model, we assume that during each iteration the volume of water attains
248 equilibrium with the calcite and dolomite in the carbonate bedrock (Banner et al., 1989; Banner
249 et al., 1994; Musgrove and Banner, 2004).

250 **Results**

251 *Key elemental constituents*

252 Chemical indicators of municipal (supply and/or waste) water interacting with natural
253 surface water and groundwater include Na, Cl, and NO₃. Na and Cl are particularly useful
254 conservative tracers because the aqueous concentrations do not change with water-rock
255 interaction processes (e.g., precipitation and dissolution of limestone). In this study, the range of
256 both Na and Cl concentrations are elevated in both the municipal waste water (43 - 105 mg/L
257 and 57 - 167 mg/L, respectively) and urban water samples (11 - 74 mg/L and 19 - 93 mg/L,
258 respectively), relative to municipal supply water (18 - 31 mg/L and 27 - 44 mg/L, respectively)
259 and rural water samples (7 - 11 mg/L and 16 - 26 mg/L, respectively) (Fig. 2 and Table 1). The
260 Na and Cl concentrations for urban water samples span the range between the lowest
261 concentrations in the rural samples and the highest concentrations in the municipal waste water
262 samples (Fig. 2). Municipal waste water has a higher range of Na concentrations relative to Cl
263 concentrations, such that many of the samples lie above the 1:1 molar ratio (Na : Cl) line (Fig.
264 2). NO₃ concentrations in the urban samples (0.3 - 28.7 mg/L NO₃ as NO₃) are elevated with
265 respect to both the measured municipal supply (0.5 - 2 mg/L) and municipal waste water (< 2.1
266 mg/L; Table 1).

267 In contrast to municipal water indicators, the key constituents associated with rural
268 groundwater interacting with carbonate host rock are Ca, HCO₃, and Sr (Table 1). These major
269 (Ca, HCO₃) and trace (Sr) element concentrations are used, in conjunction with ⁸⁷Sr/⁸⁶Sr values,
270 throughout this study to quantify geochemical interaction processes between municipal water
271 and rural water, and municipal water interaction with the carbonate host rock. That is, elevated
272 concentrations of Ca, HCO₃, and Sr in the rural stream and spring water samples (85 - 104 mg/L,
273 308 - 359 mg/L, and 0.24 - 2.60 mg/L, respectively) relative to municipal supply (11 - 12 mg/L,
274 60 - 76 mg/L, and 0.11 - 0.13 mg/L, respectively) and waste water (15 - 37 mg/L, 94 - 166

275 mg/L, and 0.12 – 0.40 mg/L, respectively) samples are used to distinguish between different
276 geochemical mechanisms such as fluid mixing and water-rock interaction. This quantitative
277 geochemical modeling approach is then used to assess the origin and evolution of urban stream
278 and spring waters.

279 *Water types and endmembers*

280 In Austin area watersheds, distinct isotopic ($^{87}\text{Sr}/^{86}\text{Sr}$) and elemental differences exist
281 between rural groundwater and municipal (supply and waste) water. Here we assess these
282 geochemical differences among sampled waters and soil leachates to identify endmember
283 geochemical compositions. We then use these endmember compositions to quantify the altered
284 isotopic ($^{87}\text{Sr}/^{86}\text{Sr}$) and elemental composition of stream and spring waters within the urbanized
285 region of the Bull Creek watershed. The endmember waters described herein represent distinct
286 $^{87}\text{Sr}/^{86}\text{Sr}$ values and/or elemental compositions.

287 Urban stream and spring waters: The Ca-HCO₃ type water that occurs within the
288 urbanized region of the watershed has $^{87}\text{Sr}/^{86}\text{Sr}$ values that range from 0.7077 – 0.7087 (Table 1,
289 Fig. 3). We identify endmember waters from among the 1) rural stream and spring water, 2)
290 municipal supply water, and 3) municipal waste water compositions and apply these to
291 understand the origin of urban stream and spring water (urban waters hereafter).

292 Rural stream and spring waters: In the Austin area, rural water $^{87}\text{Sr}/^{86}\text{Sr}$ values (mean
293 $^{87}\text{Sr}/^{86}\text{Sr} = 0.7079$; Christian et al., 2011) are similar to values for Cretaceous seawater (0.7072–
294 0.7080; Koepnick et al., 1985), reflecting Sr sourced by carbonate bedrock (Fig. 3). These Ca-
295 HCO₃ type rural waters have a local range of $^{87}\text{Sr}/^{86}\text{Sr}$ values from 0.7078 – 0.7081 (Table 1, Fig.
296 3). We consider two endmember samples local to Bull Creek rural stream and spring waters

297 (“rural waters” hereafter), which represent 1) the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.7078) and 2) the
298 highest $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.7081; Fig. 3) within this range.

299 Municipal Supply: The city of Austin’s municipal supply water is sourced from the
300 Colorado River, and has high $^{87}\text{Sr}/^{86}\text{Sr}$ values across the Austin area (mean $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7090,
301 Christian et al., 2011) relative to the Austin area rural groundwater (mean $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7079;
302 Christian et al., 2011). The high $^{87}\text{Sr}/^{86}\text{Sr}$ values of Austin’s municipal supply water reflects the
303 contribution of Sr from Precambrian granitic and metamorphic rocks (Christian et al., 2011) that
304 outcrop approximately 100 km upstream of Austin in the Llano uplift region. The Mg- HCO_3 type
305 municipal supply water has local (i.e., within the Bull Creek watershed) $^{87}\text{Sr}/^{86}\text{Sr}$ values that
306 range from 0.7091 – 0.7095, which is the narrowest endmember range (Table 1, Fig. 3). We
307 consider two endmember samples of the measured municipal supply: the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ value
308 (0.7091) and 2) the highest $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.7095). Differences in elemental compositions
309 between municipal supply and rural water (e.g., Ca, Na, Cl, and HCO_3 ; Table 1) are also
310 considered.

311 Municipal Waste: The Na+K- HCO_3 type municipal waste water has a broad range of
312 $^{87}\text{Sr}/^{86}\text{Sr}$ values, from 0.7079 – 0.7090 (Table 1, Fig. 3) throughout the Austin area. We consider
313 municipal waste water as an elemental endmember for conservative ions (e.g., Na and Cl), but
314 not for $^{87}\text{Sr}/^{86}\text{Sr}$ values or carbonate constituents (e.g., Ca and HCO_3) due to its highly variable
315 composition that spans the range of both municipal supply water and rural water (Table 1).

316 Soils: Additional sources of high $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$ > 0.7090) to Austin
317 stream and spring water have been hypothesized to include soils with high $^{87}\text{Sr}/^{86}\text{Sr}$ values
318 (Christian et al., 2011). Our results show a distinct increase in soil leachate $^{87}\text{Sr}/^{86}\text{Sr}$ values from
319 unirrigated soil (0.7079 – 0.7084) to soils irrigated (0.7085 – 0.7091) with municipal supply

320 water (Fig. 3). Notably, the unirrigated soils do not span the range of $^{87}\text{Sr}/^{86}\text{Sr}$ values measured
321 in the urban water samples (0.7077 – 0.7087), discounting unirrigated soils as a source of high
322 $^{87}\text{Sr}/^{86}\text{Sr}$ values to the urban waters. Thus, we do not consider soils as an endmember hereafter.

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

326 *Geochemical modeling*

327 Fluid mixing and water-rock interaction models are used to assess geochemical processes
328 that account for the variations observed in Bull Creek stream and spring water compositions.

329 First, we simulate mixing between three sets of endmembers (rural water, municipal supply, and
330 municipal waste water) to portray the range of water compositions that may result from fluid
331 mixing. The chemical constituents considered in the fluid mixing models (Fig. 4) are selected to
332 represent carbonate (Sr; Fig. 4A) and municipal (Cl; Fig. 4B) water. Variations in measured
333 elemental (Sr and Cl) compositions and $^{87}\text{Sr}/^{86}\text{Sr}$ values are then used to quantify possible fluid
334 mixing between endmember waters. Fluid Mixing Lines I and III (Fig. 4A, B) represent mixing
335 between the highest $^{87}\text{Sr}/^{86}\text{Sr}$ endmember compositions of rural and municipal supply water,
336 whereas Fluid Mixing Lines II and IV represent mixing between the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ endmember
337 compositions of rural and municipal supply water (Fig. 4A, B). In contrast, Fluid Mixing Line V
338 (Fig. 4B) uses an endmember mixture between municipal waste water and a 90% : 10%
339 composition of rural : municipal supply water, respectively.

340 Using the contrasting elemental and isotopic co-variability within the urban waters (Fig.
341 4) we identify two distinct urban stream and spring water groups. These urban water groups are
342 differentiated by low Sr concentration (< 0.27 mg/L; hollow red circles in Fig. 4) (hereafter

343 “low-Sr-urban-waters”), and high Sr concentration (> 0.44 mg/L; solid red circles in Fig. 4)
344 (hereafter “high-Sr-urban-waters”). The geochemical distinction between the two urban water
345 groups becomes increasingly apparent with additional modeling (presented herein). The low-Sr-
346 urban-waters have distinctly higher $^{87}\text{Sr}/^{86}\text{Sr}$ values (> 0.7082) than either rural or high-Sr-urban-
347 waters and consist of 50% to 95% municipal supply water (Fluid Mixing Lines I and II). In
348 contrast, the high-Sr-urban-waters have distinctly lower $^{87}\text{Sr}/^{86}\text{Sr}$ values (< 0.7082) and mixing
349 results show a notably smaller municipal supply component ($< 50\%$; Fluid Mixing Lines I and
350 II). The geochemical composition of municipal waste water is also accounted for by fluid mixing
351 between rural water and municipal supply water (Fluid Mixing Lines I and II in Fig. 4A). Fluid
352 mixing with respect to Cl, a distinctive municipal water component, and $^{87}\text{Sr}/^{86}\text{Sr}$ indicates that
353 the majority (93%) of urban waters cannot be accounted for by the rural and municipal supply
354 water mixing model (Fluid Mixing Lines III and IV, Fig. 4B). In this view, the low-Sr-urban-
355 waters lie along the endmember mixture with municipal waste water (Fluid Mixing Line V in
356 Fig. 4B). Both the low- and high-Sr-urban-waters have elevated Cl concentrations (19 – 88 mg/L
357 and 28 - 93 mg/L, respectively) with respect to rural and municipal supply water (e.g., Table 1),
358 but the $^{87}\text{Sr}/^{86}\text{Sr}$ values are distinctly different between the two urban water groups (Fig. 4A and
359 B). We note that approximately half (55%) of the urban waters are not accounted for the by the
360 rural and municipal supply water mixing models in Fig. 4A (Fluid Mixing Lines I and II),
361 particularly for samples with compositions that fall above Fluid Mixing Line I or below Fluid
362 Mixing Line II. Moreover, the high-Sr-urban-waters are not accounted for by Fluid Mixing Lines
363 III, IV, or V (Fig. 4B). We describe below additional geochemical processes to account for the
364 urban water samples that are not constrained by fluid mixing models.

365 To assess additional geochemical processes that may account for urban water
366 geochemical compositions, we consider the co-variability between measured Sr and Ca
367 concentrations with respect to limestone dissolution (black line in Fig. 5). Sr and Ca
368 concentrations vary widely in rural and urban waters (Fig. 5), but are notably low by comparison
369 for municipal supply and waste water (Fig. 5). Both the high- and low-Sr-urban-waters have a
370 relatively large range of Ca concentrations (75 - 146 and 67 - 166 mg/L, respectively; Fig. 5), but
371 exhibit contrasting Sr concentrations ranges (high-Sr-urban-waters Sr = 0.44 - 4.9 mg/L; low-Sr-
372 urban-waters Sr = 0.13 - 0.27 mg/L; Fig. 5). The rural water compositions are low in Ca (85 -
373 104 mg/L) compared to both urban stream and spring water groups, with a somewhat high range
374 of Sr concentrations (0.24 - 2.6 mg/L; Fig. 5). The limestone dissolution pathway (black line in
375 Fig. 5) represents a mass balance calculation of municipal supply water infiltrating and
376 dissolving Glen Rose Formation, which is the dominant carbonate bedrock that Bull Creek and
377 its tributaries incise. The range and co-variability of Sr and Ca concentrations in the low-Sr-
378 urban-waters are accounted for by the limestone dissolution pathway (Fig. 5), but the high-Sr-
379 urban-waters are not. It should be noted that the water-rock interaction line (red dashed line in
380 Fig. 5) is inferred, as opposed to the calculated limestone dissolution line. Below we quantify
381 these water-rock interaction processes by first examining models that explain regional
382 groundwater processes (e.g., Musgrove and Banner, 2004; Musgrove et al., 2010; Wong et al.,
383 2014). We then use these models to re-assess the urban waters at the local setting (this study).

384 Water-rock interaction models (e.g., Fig. 6) that quantify the recrystallization of calcite
385 and dolomite have been applied regionally to assess the geochemical processes controlling
386 groundwater composition in central Texas (e.g., Musgrove and Banner, 2004; Musgrove et al.,
387 2010; Wong et al., 2014). Regional groundwater (Musgrove and Banner, 2004; Musgrove et al.,

388 2010) sampled from cave dripwaters (i.e., vadose zone; hollow circles in Fig. 6A), springs (grey
389 circles in Fig. 6A), and phreatic groundwater wells (black circles in Fig. 6A) reflect increasing
390 extents of water-rock interaction and thus increasing relative groundwater residence times (τ in
391 Fig. 6), respectively. Relatively low Sr/Ca ratios and high $^{87}\text{Sr}/^{86}\text{Sr}$ values in the vadose zone
392 waters (Sr/Ca = 0.0003 – 0.001, $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7084 – 0.7092) compared to those for the phreatic
393 zone waters (Sr/Ca = 0.0004 – 0.009, $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7076 – 0.7086) illustrate the increase in
394 reaction progress, respectively, between the infiltrating water and Cretaceous limestone (Fig.
395 6A).

396 Measured waters within the Bull Creek watershed are modeled with respect to the
397 regional groundwater system (Fig. 6B). That is, modeled water-rock interaction with Fluids I and
398 II (grey lines in Fig. 6) are applied to both the regional (Musgrove and Banner, 2004; Musgrove
399 et al., 2010) and local (this study) systems to determine relative extents of water-rock interaction
400 between infiltrating water and the Cretaceous limestone. The results from the measured Bull
401 Creek waters (Fig. 6B) are then compared to regional vadose and phreatic groundwater
402 compositions in central Texas (Fig. 6A ; Musgrove and Banner, 2004; Musgrove et al., 2010) to
403 provide additional insight into urban water flow paths and relative groundwater residence times
404 of infiltrating municipal water. Sr/Ca values are highest in the rural and high-Sr-urban-waters
405 (Sr/Ca = 0.001 - 0.013 and 0.001 - 0.018, respectively) with lower overall $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig.
406 6B). Rural water $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.7078-0.7081) are within the range for Cretaceous limestone
407 (0.7072 - 0.7080; Christian et al., 2011; Koepnick et al., 1985), whereas high-Sr-urban-water
408 values are higher (0.7077 - 0.7082; Fig. 6A). The range of both rural and high-Sr-urban-water
409 compositions (Fig. 6B) are within the range measured for regional spring water and/or phreatic
410 groundwater (Fig. 6A). In contrast to the rural and high-Sr-urban-waters, the low-Sr-urban-

411 waters exhibit relatively low Sr/Ca ratios (0.001 - 0.0005) and high $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.7082 -
412 0.7087) compared to the rural and high-Sr-urban-waters (Fig. 6B). The low-Sr-urban-waters
413 (Fig. 6B) are within the range of regional spring and/or vadose groundwater compositions (Fig.
414 6A). Fluid endmembers I and II (Fig. 6A, B) represent values for soil leachates above a central
415 Texas cave (Natural Bridge Cavern; Musgrove and Banner, 2004), which are within the same
416 geologic setting as the present study. Fluid III (Fig. 6B) represents municipal supply water,
417 which has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ value (present study).

418 **Discussion**

419 *Controls on urban stream and spring water elemental composition*

420 Elevated concentrations of major ions in the urban water samples relative to rural water
421 samples (Table 1) are indicative of an additional, more saline component in stream and spring
422 water from the urban sites, which we hypothesize is consistent with a significant contribution
423 from municipal supply and waste water. Relatively high Na and Cl concentrations are commonly
424 associated with municipal water sources (e.g., Barrett et al., 1999; Leopold, 1968; Porras et al.,
425 2016), which is consistent with the urban water compositions measured in this study (Table 1;
426 Fig. 2). The magnitude by which stream and spring water Na and Cl concentrations are elevated
427 (Fig. 2) may be attributed to the degree of urbanization and/or infrastructure age for a sample's
428 subwatershed (e.g., Christian et al., 2011). NO_3 concentrations in the urban stream and spring
429 waters (0.3 – 28.7 mg/L, NO_3 as NO_3) were generally elevated relative to endmember
430 concentrations (e.g., municipal waste water; less than 2.1 mg/L) as well as estimated national
431 background concentrations of 1.1 and 4.4 mg/L, respectively, for streams and groundwater
432 (Dubrovsky et al., 2010). Measured stream and spring water NO_3 concentrations were as much
433 as an order of magnitude higher than other studies in the area that have investigated natural and

434 anthropogenic sources of NO₃, which may reflect influence from fertilizer, human and/or animal
435 waste (Ging et al., 1996; Musgrove et al., 2016).

436 *Tracing hydrologic endmembers with Sr isotopes*

437 Previous studies in the Edwards aquifer have applied ⁸⁷Sr/⁸⁶Sr values to constrain sources
438 of dissolved constituents to groundwater and to assess geochemical evolution processes (e.g.,
439 Oetting et al., 1996; Musgrove and Banner, 2004). The varying distribution of ⁸⁷Sr/⁸⁶Sr values in
440 different components of the Bull Creek watershed provide a unique tracer of contributing water
441 sources (Fig. 3). We use the isotopic composition in conjunction with elemental differences in
442 endmember waters (i.e., rural and municipal) to quantify the effects of urbanization on stream
443 and spring water composition. Our results are consistent with previous studies in Austin area
444 watersheds where hydrogeologically (and isotopically) distinct endmembers were identified
445 (DeMott, 2006; Christian et al., 2011; Senison et al., 2013). That is, elevated ⁸⁷Sr/⁸⁶Sr values in
446 Austin area urban stream waters correspond to increases in urban development (Christian et al.,
447 2011). We also address here an alternative hypothesis to account for the high ⁸⁷Sr/⁸⁶Sr values in
448 urban stream and spring water — that these high ⁸⁷Sr/⁸⁶Sr values might result from natural
449 variability in soil ⁸⁷Sr/⁸⁶Sr values (Christian et al., 2011).

450 Unirrigated (i.e., natural) soil ⁸⁷Sr/⁸⁶Sr values (0.7079-0.7084) cannot account for the full
451 range of values observed in the urban stream and spring waters, which range notably higher
452 (0.7077 - 0.7095; Fig. 3). Additionally, the range of irrigated soil ⁸⁷Sr/⁸⁶Sr values (0.7085 -
453 0.7091) is distinctly higher than that of unirrigated soils, with significantly different median
454 values ($p < 0.0001$), which can account for the higher ⁸⁷Sr/⁸⁶Sr values of the urban stream and
455 spring waters (Fig. 3). These consistent results discount the natural variability of soils as a source
456 of high ⁸⁷Sr/⁸⁶Sr to stream and spring waters, and indicate that municipal leakage and/or

457 irrigation water are likely an important contribution to urban stream and spring waters. The
458 higher $^{87}\text{Sr}/^{86}\text{Sr}$ values of irrigated soil relative to unirrigated soil, and the similarly higher range
459 of values for irrigated soils and municipal water, suggest that soils in the urbanized parts of the
460 watershed evolve toward municipal water $^{87}\text{Sr}/^{86}\text{Sr}$ values via ion exchange as a consequence of
461 extensive irrigation with municipal water.

462 *Delineating geochemical processes and groundwater flow pathways*

463 Fluid mixing and water-rock interaction modeling results quantify the extent of
464 geochemical evolution for infiltrating rural and municipal water. These results are then used, in
465 the context of the regional groundwater setting, to constrain flow paths and relative groundwater
466 residence times of municipal water within the Bull Creek watershed. Endmember mixing
467 between rural and municipal supply water is considered with respect to geochemical constituents
468 representative of both carbonate (e.g., Sr) and municipal water (e.g., Cl; Fig. 4). Fluid mixing
469 model results yield insight to the geochemical evolution of 1) municipal waste water and 2)
470 urban stream and spring water compositions. The observed decrease in municipal waste water Sr
471 concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ values relative to municipal supply water (Fluid Mixing Lines I and
472 II in Fig. 4A) may represent infiltration and exfiltration of rural groundwater and waste water,
473 respectively, within non-watertight infrastructure pipes (e.g., Goebel et al., 2004). The marked
474 increase in municipal waste water Cl concentrations relative to municipal supply water (Fig. 4B)
475 is inferred to occur through the addition of human waste. Fluid mixing model results indicate that
476 urban stream and spring water samples consist of 50% to 95% municipal supply water (Fluid
477 Mixing Lines I and II in Fig. 4A) and/or municipal waste water (Fluid Mixing Line V in Fig. 4B)
478 relative to rural water. We propose that mixing models based on $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr
479 concentrations may underestimate the influence of municipal water on the high-Sr-urban-waters

480 (e.g., < 50 % in Fig. 4A) due to additional geochemical processes (e.g., higher extents of water-
481 rock interaction with the carbonate bedrock discussed below). This is supported by mixing
482 models based on $^{87}\text{Sr}/^{86}\text{Sr}$ and Cl concentrations, which demonstrate the influence of municipal
483 (supply and/or waste) water on both the high- and low-Sr-urban-waters (Fig. 4B). In this view,
484 the mixture of rural and municipal supply (90% : 10%, respectively) water with municipal waste
485 water constrains Cl concentrations for both the high- and low-Sr-urban-waters. The measured
486 decreases in the high-Sr-urban-water $^{87}\text{Sr}/^{86}\text{Sr}$ values relative to the low-Sr-urban-waters can
487 again be accounted for by additional geochemical processes (e.g., water-rock interaction). These
488 mixing model results indicate that municipal water infiltration via pipe network leakage (supply
489 and waste) and/or irrigation (supply) is a significant source of water in the local urban hydrologic
490 cycle. We document that additional geochemical evolution of this infiltrating municipal (supply
491 and waste) water occurs as it enters and interacts with the natural groundwater system and
492 carbonate bedrock.

493 Sr, Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in the rural and urban waters lie along a continuum of
494 geochemical evolution within the regional carbonate groundwater system (Fig. 5 and Fig. 6).
495 Low-Sr-urban-water has compositions that can be accounted for by limestone dissolution (0.5 –
496 2 mmol/L; Fig. 5), as opposed to recrystallization (which would yield relatively higher Sr
497 concentrations, since Ca is preferentially incorporated into the crystal lattice). We infer that
498 limestone dissolution occurs as municipal water interacts with the limestone host rock along
499 vadose zone flow paths (e.g., Fig. 6). Increasing reaction progress between the water and
500 carbonate bedrock is evident throughout the Bull Creek watershed, as evidenced by increasing
501 Sr/Ca values and decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ values that approach those of the Cretaceous limestone

502 bedrock (Musgrove and Banner 2004; Musgrove et al., 2010; Wong et al., 2014) via increasingly
503 long groundwater residence times.

504 The vadose zone waters in Fig. 6A are cave dripwaters from two caves in the region
505 (Musgrove and Banner, 2004; Wong et al., 2014) and represent rainwater infiltrated through the
506 unsaturated (vadose) zone. These vadose zone waters are the least geochemically evolved (i.e.,
507 relatively low Sr/Ca and high $^{87}\text{Sr}/^{86}\text{Sr}$ values) due to lesser extents of interaction with the
508 carbonate host rock, which is a result of relatively short groundwater residence times. Samples
509 from several springs in the region, mostly small local springs (Musgrove et al., 2010; Wong et
510 al., 2014) and Bull Creek watershed springs (this study; Supplemental Fig. S1) represent
511 intermediate groundwater residence times. That is, spring waters are more geochemically
512 evolved than vadose waters but less so than relatively deep phreatic groundwater (Musgrove and
513 Banner, 2004). Low Sr/Ca and high $^{87}\text{Sr}/^{86}\text{Sr}$ values in the low-Sr-urban-water (Fig. 6B) is
514 associated with regional vadose zone and intermediately evolved (i.e., shallow) groundwater,
515 which corresponds with relatively short to intermediate groundwater residence times (i.e., lesser
516 extents of water-rock interaction).

517 These regional geochemical models are applied at the local watershed scale (this study) to
518 further assess the geochemical and physical evolution of the infiltrating municipal water (i.e.,
519 urban waters). We show that both the rural and high-Sr-urban-waters have higher Sr/Ca values
520 and lower $^{87}\text{Sr}/^{86}\text{Sr}$ values than regional vadose zone water (Fig. 6A) and the low-Sr-urban-
521 waters (Fig. 6B). Moreover, the rural and high-Sr-urban-water $^{87}\text{Sr}/^{86}\text{Sr}$ values are relatively low,
522 and the rural waters are within the range of Cretaceous limestone (0.7072 - 0.7080, Christian et
523 al., 2001; Koepnick et al., 1985). Water-rock interaction results for the rural and high-Sr-urban-
524 waters (Fig. 6B) indicate that these waters have relatively long groundwater residence times (i.e.,

525 more geochemically evolved), similar to regional phreatic groundwater compositions (Fig. 6A).
526 We note that the variability in the high-Sr-urban-water $^{87}\text{Sr}/^{86}\text{Sr}$ values are larger than that
527 observed in the rural waters, which is likely a result of the geochemical evolution process of
528 infiltrating municipal water (relatively high $^{87}\text{Sr}/^{86}\text{Sr}$; i.e., Fluid III in Fig. 6B) 1) mixing with
529 rural groundwater and/or 2) interacting with the carbonate bedrock (relatively low $^{87}\text{Sr}/^{86}\text{Sr}$). The
530 majority of measured urban waters do not fall along the modeled line for water-rock interaction
531 with fluid III (i.e., municipal water; green triangle in Fig. 6B), and instead fall to its left,
532 suggesting that a combination of fluid mixing and water-rock interaction occurs as municipal
533 water infiltrates as groundwater. Our water-rock interaction model results are consistent with
534 geochemical evolution models developed from regional phreatic and vadose groundwater in
535 central Texas (Fig. 6; Musgrove et al., 2010; Musgrove and Banner, 2004; Wong et al., 2014),
536 allowing us to link the geochemical evolution observed in the Bull Creek watershed urban stream
537 and spring waters (both high- and low-Sr-urban-waters) to physical flow paths. That is,
538 infiltrating municipal (supply and/or waste) water may take vadose zone flow paths (high
539 $^{87}\text{Sr}/^{86}\text{Sr}$ and low Sr/Ca values in low-Sr-urban-waters; Fig. 6A, B) or phreatic flow paths (low
540 $^{87}\text{Sr}/^{86}\text{Sr}$ and high Sr/Ca in high-Sr-urban-waters; Fig. 6A, B).

541 *Conceptual framework for the urban hydrologic cycle*

542 Studies that have documented natural groundwater flow paths in central Texas show that
543 recharge may take shallow (i.e., vadose zone), deep (i.e., phreatic zone), or mixed flow paths
544 (e.g., Smith et al., 2015; Musgrove et al., 2010; Musgrove and Banner, 2004; Wong et al., 2014),
545 depending on antecedent moisture conditions and the density of carbonate dissolution features
546 (e.g., Wong et al., 2012). Urban development, however, complicates the controls on these flow
547 paths due to the alteration of both surface (e.g., impervious cover) and subsurface (e.g.,

548 municipal pipe networks) characteristics. We present a conceptual framework based on
549 geochemical modeling results to illustrate the altered flow paths between rural and urban settings
550 (Fig. 7). We consider the watershed holistically, comparing rural and urban water samples and
551 processes rather than individual hydrogeologic units. Geochemical evolution modeling for Bull
552 Creek watershed samples indicate varying groundwater residence times. This also suggests there
553 are varying flow paths followed by municipal leakage and/or irrigation water, which are distinct
554 and include: 1) shallow to intermediate vadose zone flow (low-Sr-urban-waters, hollow red
555 arrow in Fig. 7B) and 2) deeper phreatic groundwater flow (high-Sr-urban-waters, solid red
556 arrow in Fig. 7B). Relatively long groundwater residence times and extensive water-rock
557 interaction can account for the composition of both rural and high-Sr-urban-water (Fig. 6),
558 whereas the low-Sr-urban-water has compositions consistent with lower extents of water-rock
559 interaction and relatively shorter groundwater residence times (Fig. 6). Here we show increased
560 municipal water mixing (50% to 95%) for the low-Sr-urban-waters (hollow red line in Fig. 7B)
561 relative to rural settings (thick blue lines in Fig. 7B). In this case, shallow municipal leakage
562 dominates the geochemical signature, likely as a result of artificial recharge. This may occur
563 through one or both of the following processes: 1) a high volume of municipal water mutes the
564 geochemical signature of naturally infiltrating precipitation or 2) dense impervious cover limits
565 the amount of naturally infiltrating precipitation and artificial recharge dominates the shallow
566 groundwater system. Moreover, the municipal water geochemical signature within the urban
567 phreatic groundwater system (e.g., high-Sr-urban-waters; solid red arrow in Fig. 7B) may evolve
568 toward natural water geochemical compositions due to greater extents of water-rock interaction
569 and/or the volume of natural phreatic groundwater with which the municipal water mixes. Both
570 processes are consistent with the interpretation of relatively long groundwater residence times.

571 Based on observation well data (n = 24; City of Austin Department of Watershed Protection,
572 personal comm., 2019) in the Bull Creek watershed, the phreatic water table ranges from 5 to 68
573 meters below ground surface, but antecedent moisture conditions (e.g., Wong et al., 2012) and
574 topography influence the travel time and path that infiltrating water takes to the water table. This
575 conceptual framework, based on evidence of geochemically evolving municipal water, is
576 consistent with the findings of Musgrove et al. (2010), who demonstrate the geochemical
577 evolution of natural water as residence time and the extent of water-rock interaction increases.
578 That is, vadose zone flow is the least geochemically evolved hydrologic component and deep
579 regional phreatic groundwater is the most evolved hydrologic component; other groundwater
580 may be intermediate depending on residence time, length of flow path, and extent of water-rock
581 interaction (Fig. 6B).

582 *Implications*

583 Our results provide a quantitative framework for understanding how municipal water
584 impacts natural water geochemical compositions and interacts with the hydrologic cycle as a
585 function of urbanization. Physical hydrologic modeling that previously estimated the volume of
586 artificial recharge (e.g., Garcia-Fresca and Sharp, 2005; Sharp, 2010; Bhaskar and Welty, 2012;
587 Passarello et al., 2012; Bhaskar et al., 2016; Minnig et al., 2018) may be advanced by estimates
588 of relative extents of mixing and groundwater residences time of municipal water. This
589 identification of the evolution of municipal water as it enters bedrock adds a novel diagnostic
590 approach to quantifying the urban hydrologic cycle. The geochemical approach presented in this
591 study can be applied within or across watersheds with varying degrees of urban development
592 (e.g., Fig. 1) to quantify regional alterations to the urban hydrologic cycle, particularly locations
593 with chemically or isotopically distinct municipal and natural groundwater or stream water

594 sources (e.g., Chesson et al., 2012). Considering specifically Sr isotopes, for example, the
595 municipal water supply for St. Louis, Missouri is from the Mississippi and Missouri Rivers
596 ($^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7095 and 0.7010, respectively; Goldstein and Jacobsen, 1987; Christian et al.,
597 2011), whereas the city overlies Paleozoic marine carbonate rocks ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7085; Christian
598 et al., 2011); Spokane, Washington, receives municipal water from the Spokane Valley-
599 Rathdrum Prairie Aquifer ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7320; Chesson et al., 2012), which is markedly distinct
600 from the city's underlying Columbia River Basalts ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7186; Bataille and Bowen,
601 2012). We expect that many cities worldwide exhibit isotopic distinctions between watershed
602 geology and municipal water (e.g., Chesson et al., 2012 for U.S. cities). Thus, the integration of
603 geochemical and isotopic tools presented herein may have wide application to delineate the
604 impacts of urbanization on the hydrologic cycle.

605 Continued research to quantify urbanization impacts may bolster how we manage fresh
606 water resources in the 21st century and may reveal both advantages and disadvantages of such
607 impacts on the urban hydrologic cycle. That is, infiltrated municipal water (via leakage and/or
608 irrigation) quantified in this study may provide consistent water availability for vegetation and
609 sensitive aquatic ecosystems, especially under the increased frequency of drought conditions
610 projected for central Texas in the 21st century (Banner et al., 2010; Hayhoe, 2014; Swain and
611 Hayhoe, 2015). The Lower Colorado River Authority manages water supplies for both the city of
612 Austin and Gulf Coast rice growing operations, but only the city's municipal water supply is
613 guaranteed (Lower Colorado River Authority, 2015). When reservoir levels persisted at just 30%
614 from 2011 - 2015, the water provisioned to Gulf Coast rice growing operations was interrupted
615 (2012 - 2015) and city irrigation was curtailed (2009-present) to mitigate against decreases in
616 Austin's municipal water supply (Lower Colorado River Authority, 2015; Breyer et al., 2018). In

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

626 **Conclusions**

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

636 The geochemical compositions of stream and spring water from urban sites within the
637 watershed are significantly influenced by fluid mixing between rural (i.e., natural) and municipal
638 (supply and/or waste) water (50% to 95% municipal water in mixture). The quantification of
639 municipal water influence on stream and spring water composition demonstrates that municipal

640 water can be a significant source of hydrologic recharge, even when a watershed is only partly
641 urbanized. Water-rock interaction models indicate that when municipal water infiltrates into the
642 carbonate bedrock, it evolves as groundwater along diagnostic Sr-Ca- $^{87}\text{Sr}/^{86}\text{Sr}$ pathways. Water-
643 rock interaction model results are then used to infer relative groundwater residence times and
644 flow paths. This approach portrays infiltrating municipal water as having short to intermediate
645 (i.e., vadose zone) or long (i.e., phreatic zone) residence times prior to stream or spring
646 discharge. The contribution of municipal water to watersheds (via leakage and/or irrigation)
647 demonstrated here may provide consistently available water for vegetation and sensitive aquatic
648 ecosystems during drought conditions, but it may also affect long-term water availability and
649 energy costs for both municipality and agricultural operations. Municipal (supply and/or waste)
650 water may enter the vadose and/or phreatic zone, with risks to long-term surface and/or
651 groundwater water quality.

652

653 **Figure and Table Captions**

654 Figure 1. The distribution of urbanization and key features within the study area. (A) Map of
655 northcentral Austin, Texas, area watersheds showing road densities (grey and black lines). The
656 Bull Creek watershed is outlined with thick black line. (B and C) Show sampled rural and urban
657 (red and blue, respectively) stream and spring water sites. (B) Shows the distribution of geologic
658 units throughout the watershed, and (C) shows the four dominant soils. (D) A schematic cross
659 section showing the three major hydrostratigraphic units in of the Bull Creek watershed and
660 approximate location of the local groundwater table. Geologic data was obtained from the
661 Bureau of Economic Geology, The University of Texas at Austin (Geology of the Austin area;

662 1:62,500 scale). Soil data was obtained from the U.S. Department of Agriculture - Natural
663 Resources Conservation Service Geospatial Data Gateway.

664

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

668

669 Table 1. Range of geochemical concentrations (mg/L) and $^{87}\text{Sr}/^{86}\text{Sr}$ values for the measured
670 waters. Values in parentheses represent the standard deviation of measured concentrations. BDL
671 (below detection limit) indicates samples that were below the analytical detection limits.

672

673 Figure 3. Distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ values for Bull Creek stream and spring water, soils, municipal
674 (supply and waste) water, and Cretaceous limestone in the Bull Creek watershed. Hypothesized
675 geochemical processes (dashed arrows) are inferred for the evolution of water and soils from
676 starting compositions (circles at start of dashed arrows). Uncertainty symbol shows
677 representative analytical uncertainty for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis.

678

679 Figure 4. Geochemical models portraying fluid mixing between (A, B) rural and municipal
680 supply water and (B) a mixture of rural and municipal supply (90% : 10%, respectively) water
681 with municipal waste water. Each tick represents a 10% change in the proportion of municipal
682 (supply and/or waste) water in the modeled fluid mixture. (A) Grey dashed lines depict inferred
683 geochemical processes including limestone dissolution or water-rock interaction. (B) Multi-
684 colored lines depict two processes that, when combined, can account for the measured municipal

685 waste water geochemical composition: 1) the addition of human waste to municipal supply
686 water, and 2) rural water and waste water mixing (via non-watertight pipes). Red dashed lines
687 illustrate water-rock interaction model trajectories that results in low $^{87}\text{Sr}/^{86}\text{Sr}$ values in the high-
688 Sr-urban-waters relative to the low-Sr-urban-waters.

689

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

697

698 Figure 6. $^{87}\text{Sr}/^{86}\text{Sr}$ values vs Sr/Ca molar ratios for (A) regional phreatic, spring, and vadose zone
699 groundwater from Musgrove et al. (2010) and soil leachates (Musgrove et al., 2010; Christian et
700 al, 2011; this study), and (B) Bull Creek waters and soil leachates. Short, Intermediate, and Long
701 τ indicate relative groundwater residence times. Modeled Water-Rock Interaction (WRI) curves
702 shows the evolution of initial fluids (I, II, & III) through progressive increases in recrystallization
703 (i.e., dissolution and re-precipitation) of calcite and dolomite. That is, the modeled WRI III curve
704 (in B) shows the incremental increase in Sr/Ca and decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ values as Fluid III
705 (municipal supply water) undergoes increased water-rock interaction with calcite (solid black
706 line) and dolomite (dashed black line). Modeled WRI I & II curves (grey) represent the range
707 (i.e., widths) of recrystallization expected for calcite and dolomite starting at Fluids I & II,

708 respectively. Arrows indicate increasing molar concentrations of dissolved bedrock for each
709 modeled curve (incremental amounts of calcite and dolomite reported along each curve in
710 mmol/L). Fluids I and II are the range of soil leachates presented in Musgrove et al. (2010) and
711 were sampled above a central Texas cave (Natural Bridge Caverns, located about 70 miles south-
712 southwest of Austin). Fluid III (in B) is the measured municipal supply water sample (this study)
713 with greatest $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.7095).

714

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

725

726 Supplemental Figure S1. A modified version of Fig. 6 showing spring water compositions for the
727 Bull Creek watershed.

728

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739

740

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