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RESEARCH ARTICLE

Geochemical evolution of municipal water in a natural hydrologic system and implications for urban watershed resilience

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Abstract

Austin, Texas is among the most rapidly urbanizing regions in the U.S., posing challenges to the resilience of its water resources. Geochemical differences between stream water from relatively pristine (rural) and impacted (urban) watersheds indicate several distinct controls on stream water compositions, including extent of urbanization, extent of failure of the city's municipal water infrastructure, and differences in bedrock composition and permeability. We focus here on the largely unstudied evolution of municipal water once it leaves the infrastructure and enters the natural hydrologic system as groundwater and/or surface water. We use the distinct Sr isotope values ($^{87}Sr/^{86}Sr$) and other compositional differences between municipal waters, natural stream and spring water, limestone bedrock, and soils as tracers of the sources of and processes by which four Austin-area streams and springs acquire their dissolved constituents. These processes include 1) fluid-mixing between municipal and natural surface water and groundwater, 2) multiple mineral-solution reactions, including dissolution and water-rock interaction (WRI) processes of precipitation, incongruent dissolution, and recrystallization, and 3) varying groundwater residence times. Stream water in two urbanized watersheds have high $^{87}Sr/^{86}Sr$ values and ion compositions close to values for municipal water, whereas stream and spring water in two rural watersheds have compositions close to natural stream water. Urbanized stream water compositions can be accounted for by models of municipal water contributions followed by dissolution of bedrock minerals. By contrast, rural stream water compositions are consistent with a model sequence of dissolution followed by extensive WRI with limestone. The results of this study indicate significant contributions to streams from the municipal infrastructure. We find that the evolution of this municipal water in the natural hydrologic system comprises multiple fluid-mixing processes and mineral-solution reactions, which are influenced by differences in bedrock geology. This composite evolution advances our understanding of the complexities of "Urban Stream Syndrome".

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Introduction

Maintaining water quality and availability in urban watersheds in the 21st Century will be challenging with increasing urbanization and climate change. The population of Texas is projected to reach 47.3 million people by the year 2050 (more than double the population in 2010), with most growth concentrated in major cities [1]. This will result in widespread increases in urbanization—particularly in central Texas, home to 7 of the 15 fastest growing cities in the U.S. [2]. Additionally, prolonged climatic extremes are projected to increase water stress in this region over the 21st century [3,4]. Indications that significant amounts of water from municipal infrastructure from leakage and irrigation are transmitted to streams in this region (Christian, 2011, Beal et al. 2020, Banner et al. 2024) underscore the need to understand this contribution if we are to develop and use increasingly limited water resources in a resilient manner. In our study of the transmission of water from municipal water networks into natural hydrologic systems, we refer to total municipal water as 'municipal water,' supply, tap, or drinking water as 'municipal supply,' and municipal wastewater as 'waste'. Non-revenue water (NRW) is the difference between the volume of municipal supply (e.g., tap water) put into to the distribution network and the volume of water charged to customers [5].

Geochemical differences observed between rural and urban stream waters indicate varying degrees of anthropogenic impacts from municipal supply and wastewater networks due to infrastructure leakage or failure. Previous studies in Austin-area watersheds have found that NRW and leaked wastewater comprise a large fraction (up to 90%) of water at some sites in urbanized streams [6,7]. Whereas the loss of water from municipal infrastructure is widely recognized in previous research [8–12], relatively little is known about the geochemical evolution of municipal water once it is transmitted to the natural hydrologic system as ground water and surface water. This study aims to address the gap in understanding this evolution and its governing processes, to help inform the sustainable development of water resources that serve urban centers.

Urban stream syndrome and resilience of urban watersheds

"Urban stream syndrome" is used to describe the common effects on streams where urbanization degrades stream ecology. Symptoms of urban stream syndrome include diminished water quality due to nutrient loading and anthropogenic pollutants, flashy and increased discharge during storms, and changes in stream geomorphology and bank stability [13–15]. Elevated nutrient and bacteria concentrations are ubiquitous in urban stream environments, particularly in areas where wastewater, animal waste, fertilizers, and herbicides can be transmitted to the stream through point source and nonpoint source processes [16]. Infrastructure leakage and irrigation with reclaimed water contribute anthropogenic pollutants to streams as point source processes [15,17] while storm runoff from roadways and de-icing applications applied to roads contribute as nonpoint processes. As water networks age and begin to fail, municipal supply and wastewaters leak into the subsurface and eventually discharge into a nearby stream through vadose or phreatic flow paths [7].

Riparian vegetation plays a crucial role in mitigating the effects of urbanization on stream ecosystems and evapotranspiration by riparian vegetation can reduce the urban heat island effect [18–21]. Clearing of trees not only eliminates these ecosystem services but this also has been shown to increase gas exchange between the land and atmosphere and decrease atmospheric moisture content [22]. Urban watershed studies often focus on aquatic habitat or species degradation [23–26] and less on how municipal water leakage affects riparian vegetation and ecosystem resilience. A recently recognized impact on riparian vegetation resilience is municipal water leakage, which may buffer vegetation against water-stressed conditions during periods of drought [27]. Although urbanization can increase channel incision, municipal water leakage may offset the resultant lowered water table to benefit riparian vegetation [28].

Evolution of municipal water

Although the impacts of urban stream syndrome are well described, processes of municipal water inputs to natural streams remain unclear. Understudied controls on urban hydrology include: 1) the geochemical evolution of municipal water once it enters streams and aquifers and the consequences for water quality, and 2) the hydrogeologic flowpaths (e.g., conduit or diffuse) municipal water takes in the subsurface as a function of bedrock lithology.

To characterize watershed hydrogeologic processes as a function of urbanization, our results include published and unpublished stream and spring water analyses collected at various intervals from 2001–2020 across four Austin-area watersheds (Fig 1), in addition to municipal supply, wastewater, soil, and watershed bedrock samples. The City of Austin takes its drinking water from the Colorado River, which drains a tributary that flows through

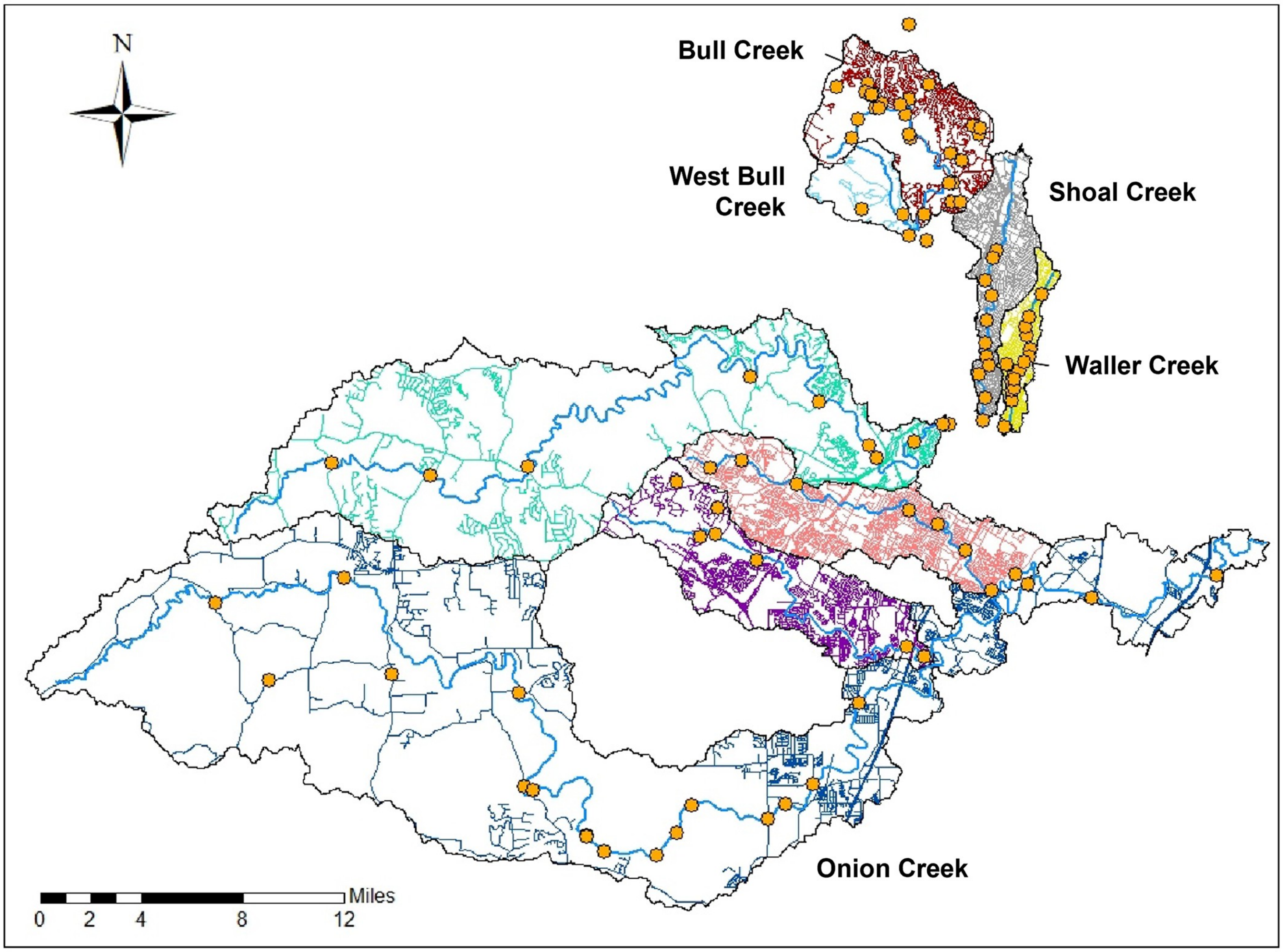

Fig 1. Stream and spring water sample locations. Sampling sites of stream and spring water samples from this study, Christian et al. [6], and Beal et al. [7] underlain by lines of road density for 2021 from the Texas Dept. of Transportation [34]. GIS data for creeks and watershed boundaries are from the City of Austin [35].

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Precambrian granite and other geologic units of the Llano uplift. This results in distinct Sr-isotope ratios between municipal water (relatively high $^{87}Sr/^{86}Sr$) and the local Lower Cretaceous carbonate bedrock (low $^{87}Sr/^{86}Sr$) of Austin-area watersheds. These distinct isotope ratios is used as a tracer to identify municipal water leakage in natural streams [6,7]. This study uses $^{87}Sr/^{86}Sr$ values of Austin-area stream waters to identify municipal supply and wastewater contributions across watersheds with varying degrees of urbanization. Stream water Na, Cl, F, NO_3, and SO_4 concentrations are commonly used to identify anthropogenic inputs in urban streams [6,7,29–33]. We use these elemental concentrations of stream waters to delineate between municipal waste and municipal supply water contributions to Austin streams. We define the 'natural endmember' as stream waters from the least-developed portions of rural watersheds. This endmember has a low Sr-isotope ratio and low Na, Cl, F, NO_3, and SO_4 concentrations. Stream, spring, and municipal water elemental ratios, cation, and anion concentrations, mineral saturation indices, and $^{87}Sr/^{86}Sr$ variations are used to understand and model the extent of fluid mixing and water-rock interaction (WRI) processes (i.e., dissolution and recrystallization) in urban and rural watersheds.

Here we apply elemental and isotope geochemistry to Austin-area watersheds that have a range of extents of urbanization, to identify and infer the relative importance of fluid-mixing processes and mineral-solution reactions in the evolution of stream and spring water. We address the following questions: 1) What are the dominant hydrogeologic processes by which Austin-area stream waters evolve? 2) How does municipal water evolve once it enters the natural system? And 3) How does watershed bedrock composition influence stream water chemistry? We find that stream water comprises varying amounts of municipal water and that there is a distinct control of bedrock composition on stream-water chemistry. We also find that a watershed's bedrock type and permeability impart a flowpath control on groundwater residence time and extent of WRI processes. These mixing processes and hydrogeologic characteristics of a watershed's bedrock control the evolution of municipal water in the natural system at the interface between engineered and natural water systems.

Hydrogeologic setting

In addition to municipal water contributions to the natural hydrologic cycle, the underlying bedrock can influence stream water chemistry through WRI. In Austin, stream waters flow over lower Cretaceous carbonate bedrock that is subject to dissolution and recrystallization. Within the Cretaceous bedrock there are compositional differences between hydrostratigraphic units that may control the geochemical evolution of stream water.

North of the Colorado River in Austin, the Shoal Creek watershed is comprised of multiple major rock units, described here following Young [36] in Table 1 and S1 Fig. The Georgetown Formation is characterized by faulting and a fine-grained to marly limestone lithology. Above the Georgetown lies the Del Rio Clay—a claystone composed of montmorillonite, kaolinite, and illite—and the Buda Limestone above that, which is a soft to hard nodular, fossiliferous limestone. Shoal Creek exposes the top of the South Bosque Member of the Eagle Ford Shale, which is primarily composed of calcite and montmorillonite. The oldest member of the Austin Chalk, the Atco Member, outcrops in the northern part of Shoal Creek and is composed of marly chalk, limestone, and small amounts of shale. Waller Creek flows over the Vinson Member of the Austin Chalk, which lies above the Atco, and Quaternary terrace deposits from the Colorado River and its tributaries. The Atco and Vinson members are both characterized by chalky limestone, fossils, and small amounts of shale but differ in the Vinson having more chalk and thinner shale bedding [36]. We collected Austin Chalk samples at six locations within Shoal and Waller Creeks to determine if chalk geochemical compositions vary spatially

Table 1. Urbanization and geologic characteristics of watersheds studied.

Watershed	% Impervious cover[a]	Population density[b] (persons/ km^2)	Major rock units	Major soil series
Waller	61	2,363	Austin Chalk, Quaternary	Urban
Shoal	55	1,753	Georgetown, Del Rio, Buda, Eagle Ford, Austin Chalk, Quaternary	Urban, Tarrant
Bull	32	683	Glen Rose, Walnut, Comanche Peak, Edwards	Brackett, Tarrant
Onion	6.8	60	Glen Rose, Edwards, Quaternary	Brackett, Comfort, Lewisville

Percent impervious cover and population density by watershed. Major rock units described by Young [36] and soil series listed by Mauceri and Banner [38] are listed for each watershed. As described in text and Fig 2, all units are lower Cretaceous marine deposits, except for Quaternary alluvium.

[a] Percent impervious cover determined by using City of Austin's 2023 impervious cover polygon layer.

[b] [39].

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and/or stratigraphically in these watersheds and if these compositions differ from Cretaceous limestone units in other Austin-area watersheds (Fig 2).

Bull Creek's watershed comprises lower Cretaceous Trinity and Edwards Groups (Table 1). While the Glen Rose limestone is considered a low-permeability unit [40,41] it has high matrix permeability (~1–100 mD) [42] relative to the Austin Chalk (0.03–1.27 mD) [43]. The Glen Rose is made up of dolomite, limestone, and marl [40] within the Trinity Group. The overlying Walnut Formation is medium-grained and fossiliferous, and the Comanche Peak Limestone is fine-grained, fossiliferous, and contains marl and shale within limestone bedding [40]. Above the Comanche Peak lies the Edwards Limestone, which primarily comprises fossiliferous, chert-rich dolomitic limestone characterized by abundant solution formations including dolines, caverns, and fractures. The Edwards Limestone serves as a major aquifer for central Texas and supplies municipal water to San Antonio and other cities in central Texas.

Watershed urbanization and infrastructure influence

We use extent of impervious cover and population density as proxies for urbanization (Table 1) [38,39]. Our study watersheds range from 6.8% to 61% impervious cover. Watersheds with high population density and extent of impervious cover that overlie the Edwards aquifer may contribute anthropogenic pollutants (via aging infrastructure, runoff, point-source pollutants, etc.) to this central Texas water resource.

As subsurface infrastructure ages, municipal pipes are more likely to fail and leak supply and wastewater into the groundwater, which then discharge into nearby streams. Water mains, pumps, wells, reservoirs, and septic tanks are all part of the municipal water system and are subject to failure based on materials used, construction practices, pipe diameter, soil type, and infrastructure age [44]. Some of these failures can result in a sizable economic and energy loss since underground infrastructure leakage is difficult to detect. Municipal water leaked into the subsurface will flow down the hydraulic gradient, eventually discharging into streams. This transfer of municipal water to the natural system by water main leakage has been estimated to contribute around 5–6% of total recharge for the Barton Springs segment of the Edwards aquifer during average recharge conditions [45]. Municipal leakage contributions vary widely monthly from <1% to almost 100% of total recharge. NRW losses in Austin were around 12% from 2001–2002 [46] and rose to about 16% in 2022 [47], which is close to the typical range of 20–25% for municipal systems globally [10,48].

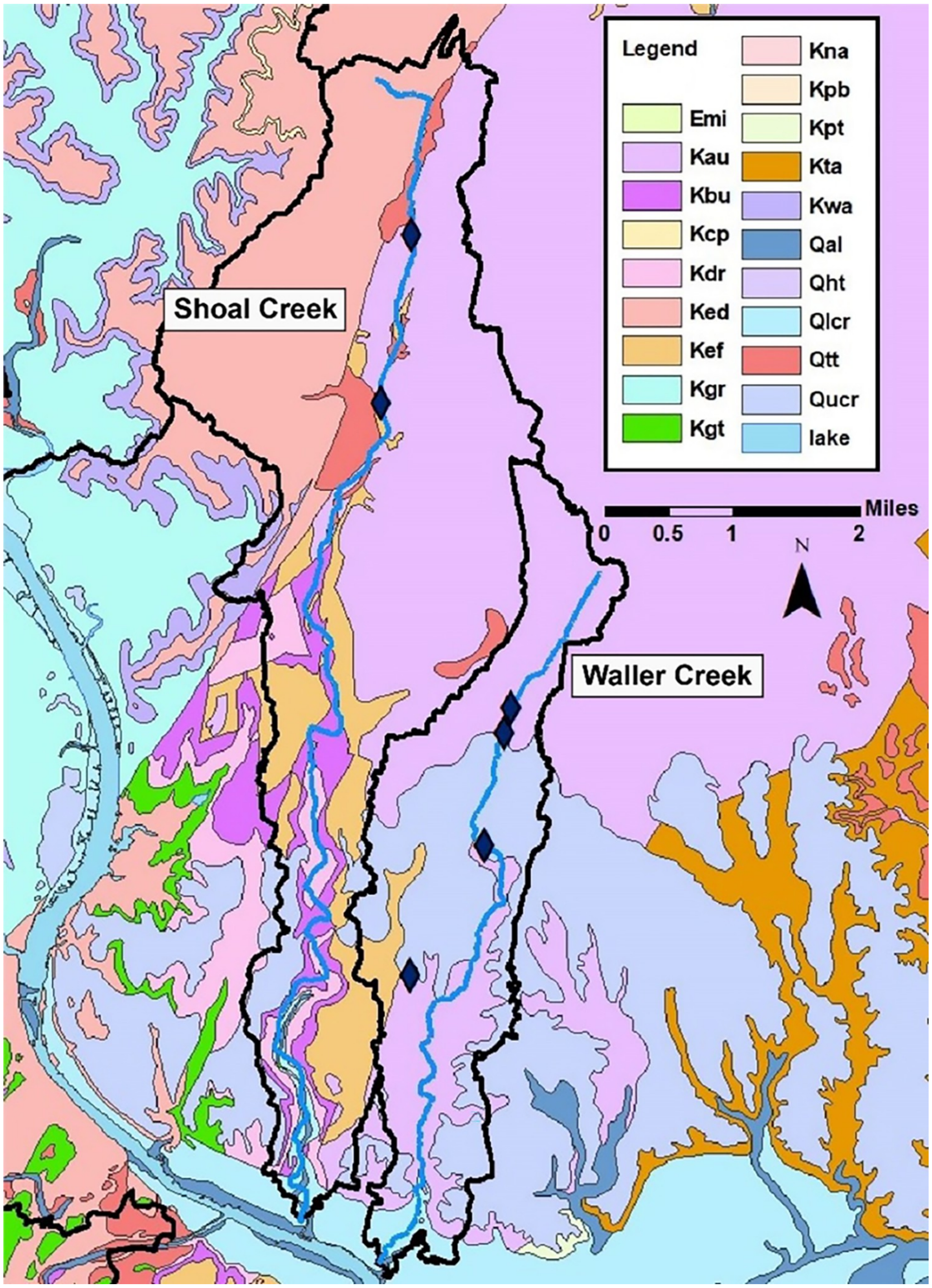

Fig 2. Geologic map and Austin Chalk sample locations. Geologic map of Shoal and Waller Creek watersheds (outlined in black) showing Austin Chalk sampling sites, indicated by black diamonds. Stream and watershed boundary GIS data are from the City of Austin [35] and geologic data are from the Bureau of Economic Geology, The University of Texas at Austin [37].

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Methods and data sources

Stream and spring waters were sampled from seven Austin-area watersheds during baseflow conditions following USGS protocol [49] from 2001 to 2020. An antecedent dry period (no more than 0.1 inches of rainfall within 24 hours) of at least five days or a return to baseflow conditions (based on monthly average stream discharge) was used to designate baseflow conditions. We determined the average rainfall from at least three rain gauges and stream discharge from at least two stream gauge stations in the watershed of interest using LCRA Hydromet (https://hydromet.lcra.org/). Sampling at baseflow conditions is necessary to determine how hydrogeologic processes and municipal water contributions influence stream water compositions without dilution by storm water. Water sample collection procedures for cation, anion, and $^{87}Sr/^{86}Sr$ analysis followed those of Beal et al. [7]. Samples were collected in cleaned HDPE Nalgene bottles and aliquoted into acid cleaned HDPE vials for cation and $^{87}Sr/^{86}Sr$ analysis and cleaned vials for anion analysis using a cleaned 0.45-micron polypropylene filter and syringe. For samples collected during this study, filters and syringes were not acid cleaned. Filtered and unfiltered stream water replicate concentrations for cations and anions are within 1% of each other for 58% of replicate pairs (n = 14), and within 6% for all replicates, except for one bicarbonate value with a 13% difference (S1 Table). This indicates that particulates in the stream water samples do not affect the analytical results. Replicate pair analyses for cation concentrations (n = 11; S2 Table) are typically (6 of 11 samples) within 5–6% of each other for all analytes, and anion replicates (n = 15; S3 Table) are within 5–9%. Detection limits for ICP-Q-MS and IC analyses are listed in S4 Table.

Carbonate bedrock samples were prepared following a method modified from Montañez et al. [50], using ammonium acetate to remove exchangeable ions from noncarbonate minerals and then dissolving the carbonates in 4% acetic acid. Carbonate bedrock geochemistry was analyzed to determine the influence of local watershed bedrock composition on stream water chemistry. Waters and bedrock collected during this study (2018–2020) were analyzed for cation concentrations and $^{87}Sr/^{86}Sr$ at the University of Texas at Austin, Department of Geological Sciences (UT DGS). Cation concentrations were measured using an Agilent 7500ce inductively coupled plasma quadrupole mass spectrometer (ICP-Q-MS). Stream and spring waters were analyzed for anion concentrations using ion chromatography at the Department of Civil, Architectural, and Environmental Engineering at UT Austin. Alkalinities were determined by manual titration. We calculate saturation indices for calcite (SI_c) and the partial pressure of CO_2 (P_{CO2}) using Geochemist's Workbench [51].

Field blanks (n = 10) for anion and cation concentrations are below the detection limits for all elements at all sites (S4 Table), except for three Waller and Onion blanks with NO_3 values from 0.07–0.08 mM. The U.S. EPA anion analytical method recommends a maximum holding time (time between collection and analysis date) of 28 days for most anion analytes except for nitrate, nitrite, and phosphate, for which 48 hours is recommended [52]. To investigate the potential of fluctuating anion concentrations in samples collected in this study and stored beyond the EPA recommended holding times, we analyzed 15 stream water replicates as aliquots from a single bottle of water collected at one site on Onion Creek and analyzed three replicates at a time with increasing holding time over a 93-day period for select anions (S5 Table and S2 Fig). Stream water sample concentrations increased on average with increasing holding time for NO_2, NO_3, and SO_4. These results indicate significant concentration changes for most constituents after 26 days. Charge balances for all stream water replicates are calculated in S6 Table. The ICP-Q-MS average analytical uncertainty (twice the standard error of replicate internal standard analyses) is within 3% for Sr, Ca, Mg, Na, and K and is listed in S7 Table. Sample anion concentrations reported in S8 and S9 Tables are adjusted for analytical blanks, and approximately 11% of stream water data required these blank corrections. Charge balance calculations for stream, spring, and municipal water samples with cation, anion, and alkalinity analyses in this study show that 84% of sample analyses are within 5% of neutral, another 14% of data are within 5–10%, and all data are within 11% of neutral (S8 and S9 Tables).

Samples were prepared for $^{87}Sr/^{86}Sr$ analysis following methods from Beal et al. [7], Banner and Kaufman [53], and Musgrove and Banner [54] using a Thermo Scientific Triton Thermal Ionization Mass Spectrometer (TIMS). This study compiles data from Christian et al. [6], Beal et al. [7], and Senison [55] in addition to data collected for the present study, as labeled in S8 and S9 Tables. Sr-isotope NBS-987 standard measurements averaged 0.710261 across all datasets, and Sr isotope data displayed in figures have been normalized to the mode of NBS-987 values ($^{87}Sr/^{86}Sr = 0.710264$), whereas data presented in S8 and S9 Tables have not been adjusted for the values measured for the NBS-987 standard, which are also given in S8 and S9 Tables. The analytical uncertainty for $^{87}Sr/^{86}Sr$ measurements is +/- 0.000012, based on 2-sigma of the population of NBS-987 standard analyses, and +/- 0.000019 based on the mean deviation of sample replicates (n = 6). Analytical uncertainties and NBS-987 $^{87}Sr/^{86}Sr$ values across all datasets are reported in S8 and S9 Tables. Laboratory and field filtration blanks were 4–12 pg and 130 pg of Sr, respectively, which are negligible compared to the minimum amount of Sr analyzed (2 μg).

Surface, groundwater, and municipal water data from the City of Austin [35], the Texas Water Development Board [56], Musgrove and Banner [54], Musgrove et al. [57] and Wong et al. [58] supplement this primary dataset. Carbonate bedrock compositions from this study and from references [57,59–62] are presented in S10 Table.

Mass balance models for fluid mixing, WRI, and calcite dissolution are used in this study to analyze the geochemical evolution of natural and municipal waters, following the methods of Musgrove and Banner [54], Banner et al. [63], Banner and Hanson [64], and Banner et al. [65]. Fluid mixing between endmembers is calculated by mass balance using $^{87}Sr/^{86}Sr$ values and Sr, F, and Cl concentrations. The dissolution of calcite is calculated using mass-balance to calculate Ca and Sr concentrations as dissolution progressively increases. WRI models simulate the progressive dissolution and re-precipitation of a given mineral (i.e., calcite in the present study) and are calculated using iterative mass-balance of $^{87}Sr/^{86}Sr$, Sr, Ca, and Sr/Ca between soil water (represented by soil leachate analyses) or municipal waters and carbonate bedrock. During each iteration, it is assumed that the water reaches equilibrium with calcite. Reaction progress for both WRI and dissolution processes are designated on model curves by increasing values for mmol or mg of calcite reacted per liter of water.

Results

Stream water and endmember water isotope variations

We use $^{87}Sr/^{86}Sr$ values for samples of stream and spring water, pipe discharge water, municipal waters, and Cretaceous limestones (Fig 3) to determine endmember and stream water Sr isotope variations across seven Austin-area watersheds with varying degrees of urbanization. From most urbanized to rural, the watersheds are ordered as follows: Waller Creek, Shoal Creek, Williamson Creek, Bull Creek Urban (i.e., the urbanized part of Bull Creek with high road density; Fig 1), Slaughter Creek, Bull Creek Rural (i.e., the rural part of Bull Creek with low road density; Fig 1), Barton Creek, and Onion Creek. Municipal supply water Sr isotope values range from 0.7088–0.7095, which are high relative to local Cretaceous limestones, which span values of 0.7074–0.7077 (Fig 3). Municipal wastewater has a larger range of $^{87}Sr/^{86}Sr$ than supply water, from 0.7079 to 0.7090. Stream and spring waters in the most rural watersheds—Onion, Barton, and Bull Rural—have low Sr isotope averages similar to the $^{87}Sr/^{86}Sr$ values of the underlying Cretaceous limestone and represent a natural stream water endmember. As the degree of urbanization increases, the range and average $^{87}Sr/^{86}Sr$ value of a watershed's stream water increase, particularly in Bull Urban (0.7077–0.7087), Shoal

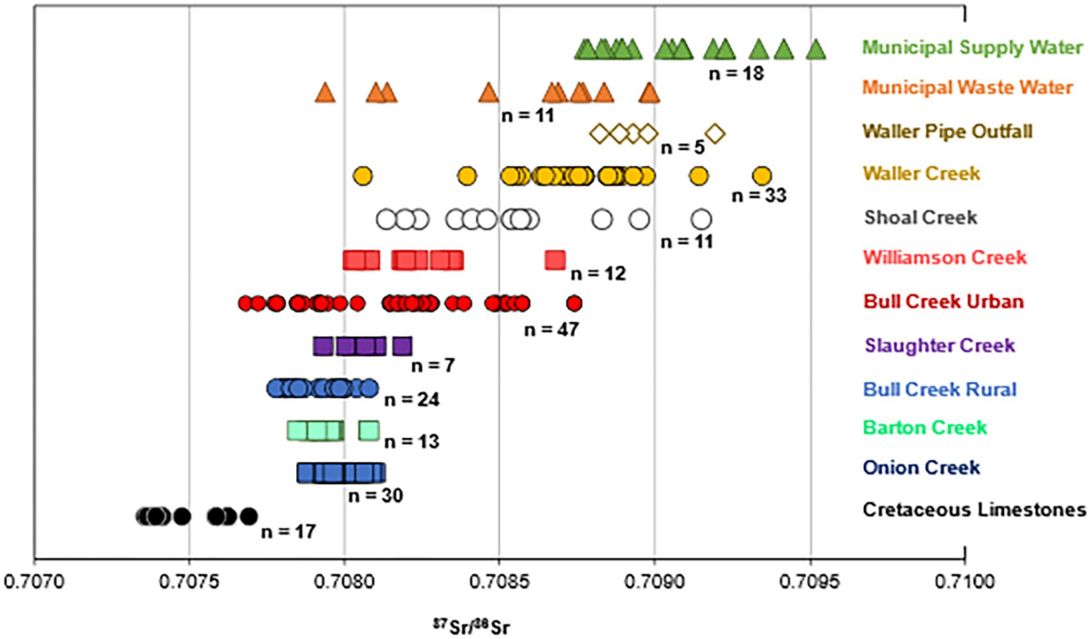

Fig 3. Distribution of ^{87}Sr/^{86}Sr values. Distribution of ^{87}Sr/^{86}Sr values for municipal waters, pipe discharge (or outfall), stream waters, and Cretaceous limestones in the Austin area. All stream waters plot between two endmembers (i.e., low ^{87}Sr/^{86}Sr Cretaceous limestones and high ^{87}Sr/^{86}Sr municipal water). The analytical uncertainty for Sr isotope measurements is +/- 0.000012, which is smaller than the size of the symbols. Sr isotope averages are as follows: Municipal supply = 0.7091, municipal waste = 0.7086, Waller pipes = 0.7090, Waller = 0.7088, Shoal = 0.7085, Williamson = 0.7082, Bull Urban = 0.7082, Slaughter = 0.7081, Bull Rural = 0.7079, Barton = 0.7079, Onion = 0.7080, and Cretaceous limestones = 0.7075. Sr isotope data from this study is presented with published data [6,7].

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(0.7081–0.7092), and Waller Creek (0.7081–0.7094), which have values within the municipal supply and wastewater ranges (Fig 3). Pipe discharges that contribute directly to Waller Creek have a narrow range of 0.7088–0.7092, which is elevated on average relative to Waller Creek stream water, and within the range of municipal water. The pipes studied are storm water pipes that have perennial flow, likely from the leakage of municipal supply and/or wastewater infrastructure.

Piper diagram variations show that municipal wastewaters are sodium-chloride type, municipal supply waters are calcium-chloride type, and stream waters are primarily calcium-bicarbonate type waters (S3 Fig). Municipal wastewaters decouple from supply water in the cation and anion Piper sub-triangles and have elevated Na + K, Cl, and SO_4 concentrations compared to supply waters. While most Austin-area stream waters are calcium-bicarbonate type, Waller Creek waters trend towards sodium-potassium type (S3 Fig). Waller stream and spring waters also span the greatest range of Ca, Cl, and SO_4 concentrations compared to other stream waters. Several Waller stream waters have Cl concentrations that trend towards wastewater, and two samples have Cl concentrations greater than wastewaters. A few Waller and Shoal stream waters trend towards calcium-chloride type as do Waller Creek pipe discharges, suggesting that the input from pipe discharges may influence stream water chemistry by increasing chloride concentrations in urban watersheds. Concentrations of Na + K, Cl, and SO_4 for natural stream water endmembers Bull Rural and Onion Creek are lower than densely urbanized Waller and Shoal Creek (S3 Fig). Bull Urban stream waters have intermediate concentrations that plot between the most rural (Onion) and urban (Waller) watershed data.

Key elemental constituents

Municipal wastewater contains high concentrations of Na and Cl, which have been used in previous studies as indicators of wastewater contributions to urbanized stream waters [7,66]. Waller Creek stream waters span a large range of Na vs. Cl concentrations along a 1:1 concentration line compared to rural waters from Onion and Bull Creek Rural (Fig 4). These results are similar to the densely urbanized Shoal Creek and semi-urbanized Bull Creek Urban. Concentrations of Na and Cl are low in municipal supply water but are elevated in wastewaters (Fig 4). The natural stream water endmember has Na and Cl concentrations lower than municipal supply water samples. Stream waters that have low concentrations of these constituents are also low in other anthropogenic tracers such as F, NO_3, and SO_4 (Fig 5). Samples from

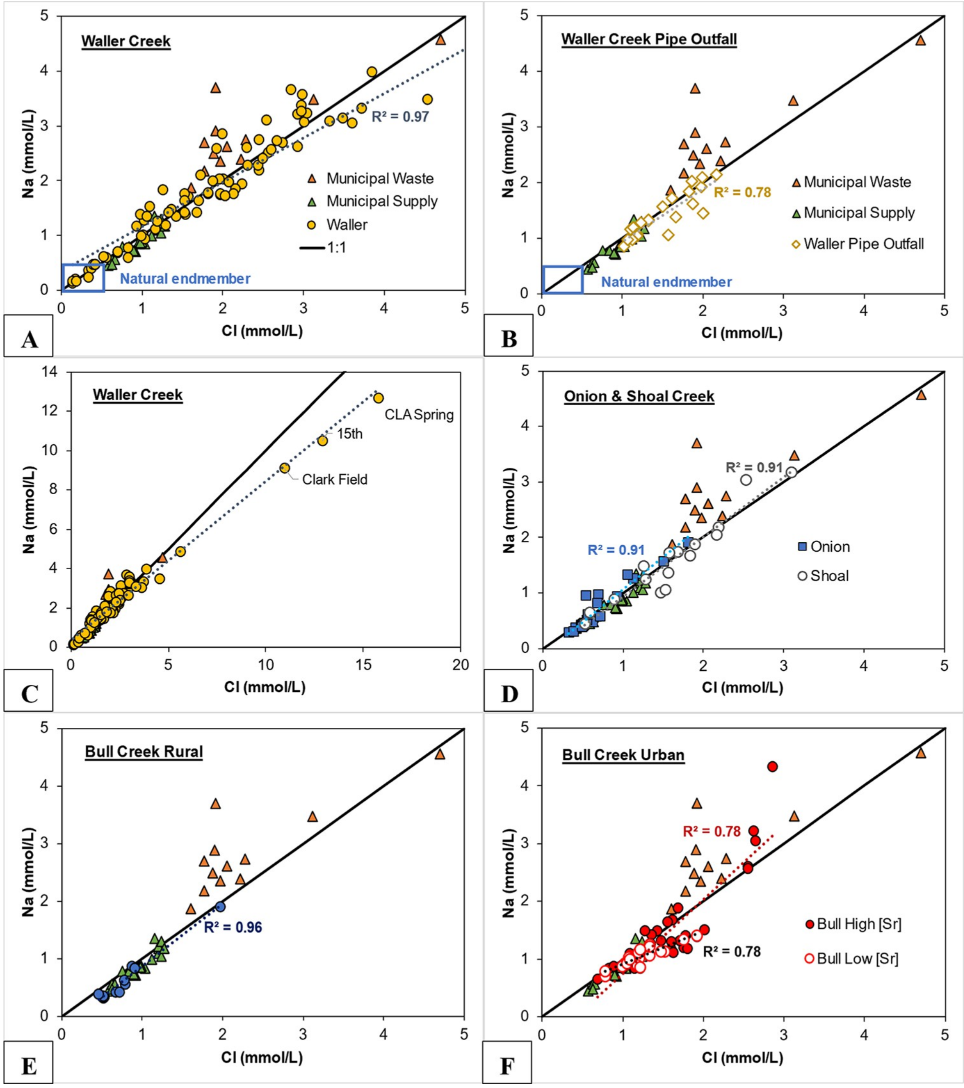

Fig 4. Chloride versus sodium concentrations. Chloride versus sodium concentrations up to 5 mmol/L for municipal supply, waste, pipe discharge, and stream waters for Austin-area watersheds with a 1:1 concentration line. The natural endmember outlined in a blue box is defined by low Na and Cl (i.e., less than any municipal water concentrations). Most stream water samples show elevated Na and Cl relative to the natural endmember, and this trend is more pronounced for the more urbanized Waller, Bull Creek Urban, and Shoal watersheds than for Onion and Bull Creek Rural.

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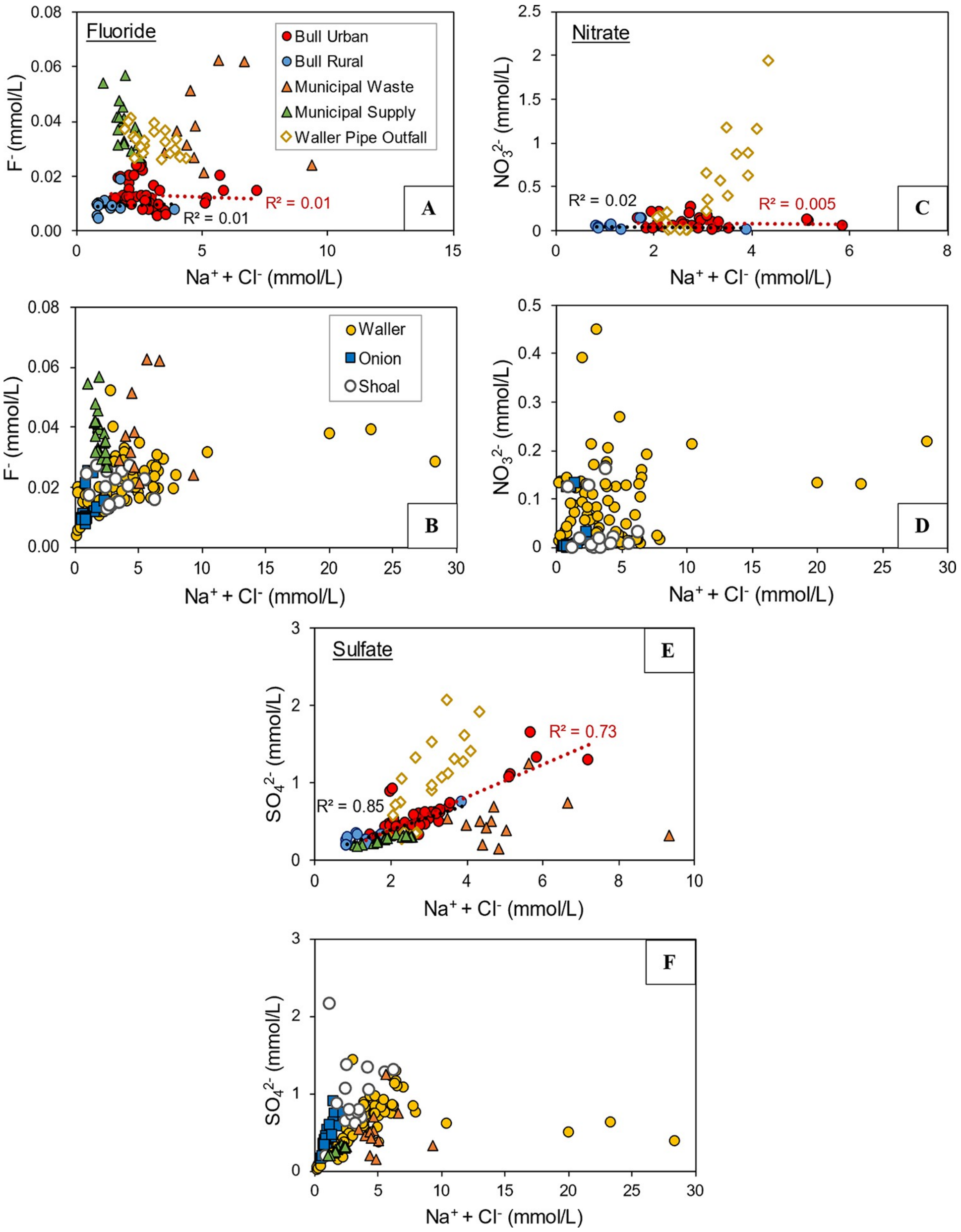

Fig 5. Fluoride, nitrate, and sulfate concentrations. F (A and B), NO_3 (C and D), and SO_4 (E and F) concentrations plotted against Na + Cl of stream waters from Waller (yellow circles), Shoal (open grey circles), Bull Urban (red circles), Bull Rural (blue circles), and Onion (dark blue squares) and pipe discharge from Waller Creek (open yellow diamonds). Municipal supply and waste waters are represented by green and orange triangles, respectively.

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pipe outfalls are high in both SO_4 and NO_3. These results indicate that municipal wastewater contributions to the natural hydrologic cycle may be identified in both urban and rural watersheds using Na and Cl variations.

Fluid mixing and bedrock dissolution

Covariations between (F + Cl) concentrations and $^{87}Sr/^{86}Sr$ indicate that compositions of stream waters in densely urbanized watersheds, such as Waller Creek, are influenced by

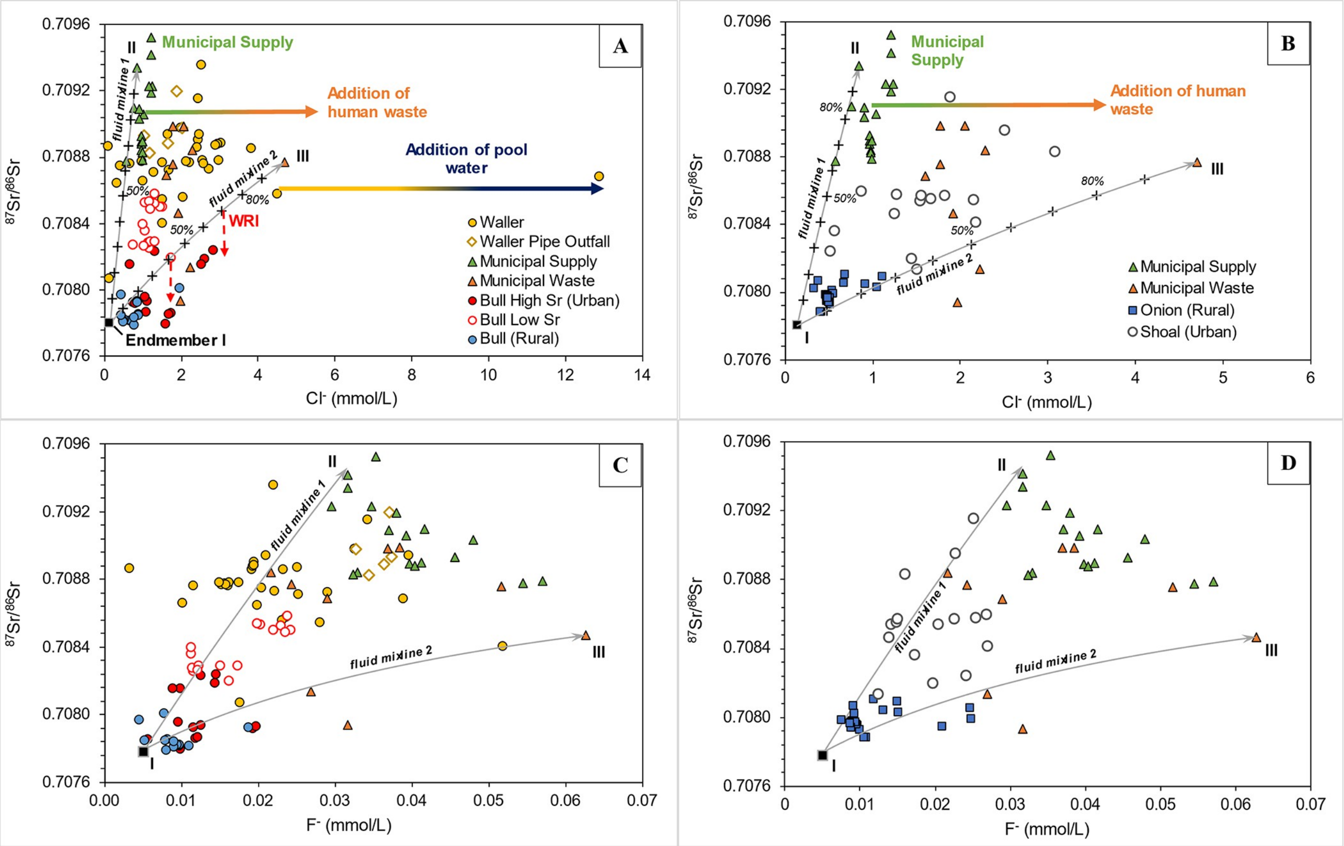

Fig 6. Chloride and fluoride concentrations versus ^{87}Sr/^{86}Sr. Chloride (top) and fluoride (bottom) concentrations versus ^{87}Sr/^{86}Sr for municipal supply, waste, and stream waters from (A & C) Waller, Bull, (B & D) Onion, and Shoal Creek. The fluid mixing line between endmembers I & II (fluid mix line 1) represents mixing between natural stream water (I) and municipal supply water (II) with crosses at 10% increments. The fluid mixing line between endmembers I & III (fluid mix line 2) represents a mixture between natural stream water (I) and municipal wastewater (III). The green and orange arrow represents a mixture of municipal supply water with the addition of human waste, which results in a municipal wastewater composition elevated in Cl concentration but relatively unchanged in ^{87}Sr/^{86}Sr compared to supply water. This mixture may leak into stream waters through underground infrastructure and produce stream water compositions such as those circled in red on A. Similarly, the addition of swimming pool water results in highly elevated Cl concentrations with unchanged ^{87}Sr/^{86}Sr as represented by a yellow and blue arrow on A. Red dashed arrows below mixing line III represent model pathways for WRI processes.

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municipal water (Fig 6). Austin-area watershed stream water geochemistry closely corresponds to the modeled dissolution of local bedrock. Waller and Shoal stream waters have positive Sr vs. Ca correlations ($R^2 = 0.87$ and 0.27, respectively), and the slope of these data is distinct from the trend of these constituents for Bull Creek stream waters (Fig 7). Bull Creek stream water Sr and Ca concentrations exhibit two trends; one that follows a calcite dissolution pathway and another that follows a calcite recrystallization pathway (Fig 7C). However, Waller and Shoal stream waters correspond only with the dissolution trend. These results are used in the following section to interpret and constrain stream and municipal water evolution.

Discussion

The isotopic and elemental variability of Austin-area stream waters are used to identify and quantify municipal water contributions to streams in urban and rural watersheds. We also use the geochemistry and hydrogeologic properties of each watershed's bedrock to assess the evolution of municipal water once it leaves the infrastructure and enters the watershed. We

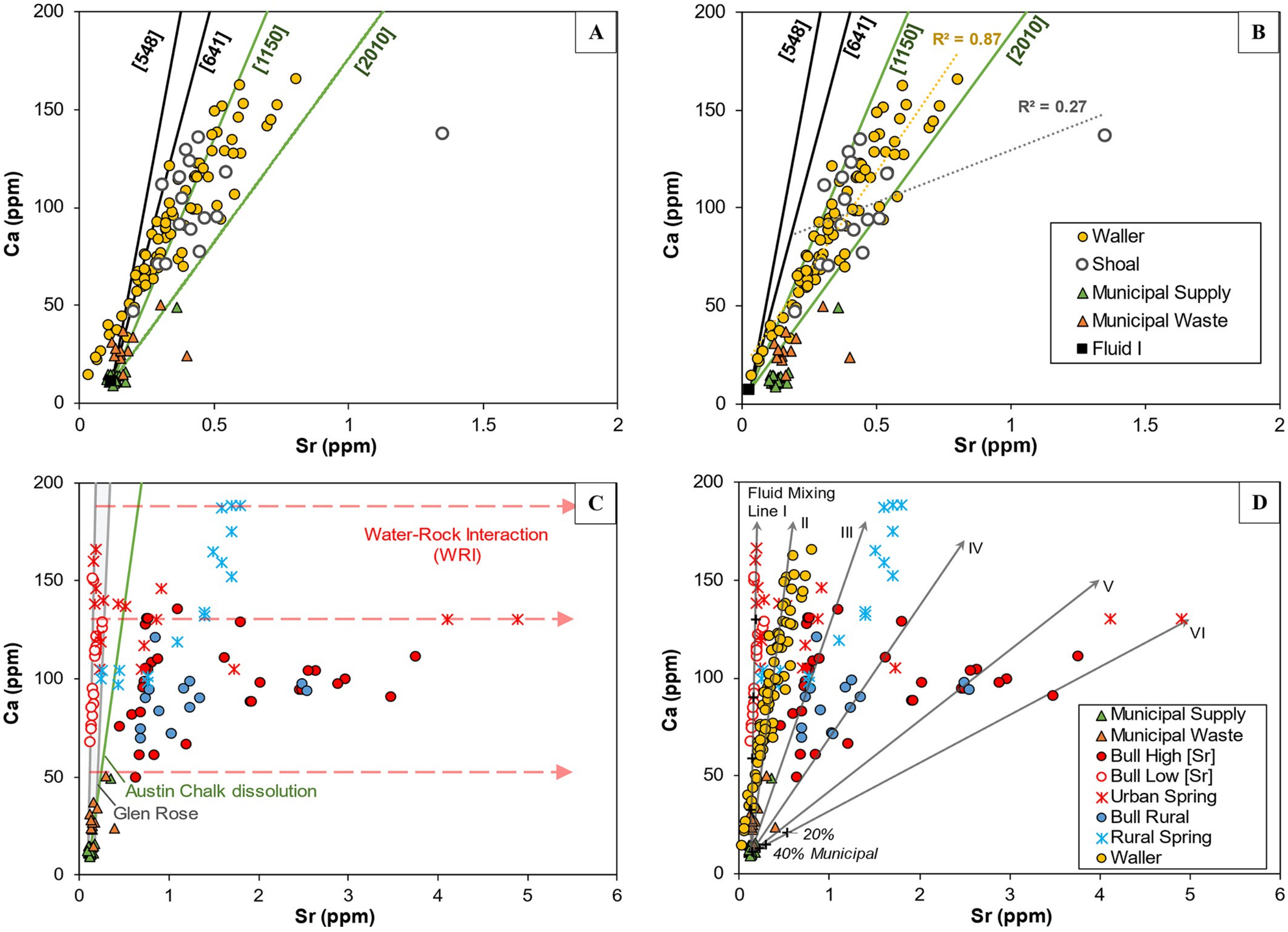

Fig 7. Sr versus Ca concentrations for stream and spring waters. Sr vs Ca concentrations for stream and spring waters from Waller and Shoal Creeks (A, B). Waller Creek (yellow circles) and Bull Creek (C) with calcite dissolution models for the Austin Chalk (black and green lines) and Glen Rose limestone (grey lines) compositions and a starting fluid composition (black square) or municipal water (green and orange triangles). Starting fluid compositions are modeled from starting soil leachate fluids using Sr isotope ratios and Sr/Ca concentrations in Fig 6 of Beal et al. [7]. Numbers in brackets represent the Sr concentration of the mineral dissolved corresponding to each line. The dissolution models in (C) use Sr concentrations of 1150 ppm for the Austin Chalk and 170 and 200 ppm for the Glen Rose Formation. Austin Chalk dissolution lines in black use rock compositions from Waller Creek bedrock samples, and lines in green use published compositions of Austin Chalk from central Texas [59]. Stream, spring, and municipal water data are from this study and Christian et al. [6] and Beal et al. [7].

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integrate these results, models, and interpretations to develop a schematic model of urban hydrology in Austin-area watersheds.

To determine the major geochemical processes occurring in urban and rural watersheds in this study, we compare measured stream water data to modeled fluid mixing and WRI processes (i.e., dissolution and recrystallization). We also analyze stream water saturation indices with respect to calcite and P_{CO2} values to evaluate the tendency of the waters to dissolve or precipitate.

Fluid mixing processes

In order to track potential municipal water sources contributions to stream waters, we examine F, NO_3, and SO_4 variations (Fig 5), of which SO_4 and NO_3 can provide an indication of wastewater sources [67]. NO_3 and SO_4 concentrations are elevated in Waller Creek pipe discharge waters, which may indicate wastewater leakage to subsurface infrastructure such as storm water discharge pipes. Stream waters in both urban and rural watersheds display variable concentrations of F, NO_3, and SO_4, suggesting municipal water contributions in watersheds with different urbanization settings.

In addition to using $^{87}Sr/^{86}Sr$ to identify endmembers and the total contribution of municipal water to streamflow, we couple Sr isotope ratios with F and Cl concentrations to distinguish between municipal supply and wastewater contributions to natural stream waters (Fig 6). Fluoride is commonly added to city tap water for dental health and has been used as a tracer of supply main leakage in the natural environment [6,7,12]. Austin municipal supply waters have high $^{87}Sr/^{86}Sr$ values (0.7088–0.7095) and a narrow range of Cl and F concentrations (0.58–1.24 mM and 0.029–0.057 mM, respectively) compared to municipal wastewaters with variable $^{87}Sr/^{86}Sr$ (0.7079–0.7089) and Cl and F (1.61–4.70 mM and 0.021–0.063 m). The covariations of Cl and F concentrations vs. $^{87}Sr/^{86}Sr$ variations of stream waters in densely urbanized watersheds indicate that these waters comprise up to 90% municipal water (Fig 6). Stream waters from urbanized sites such as Waller, Bull Urban (Fig 6A and 6C), and Shoal (Fig 6B and 6D) span or exceed the range of isotopic values and elemental concentrations between municipal supply and wastewater. This is consistent with municipal waters comprising most of the stream waters in urbanized watersheds. The elevated isotopic values of Waller Creek pipe discharge (0.7088–0.7092) are consistent with their serving as one means of transmission of leaked municipal water to streams (Fig 6A and 6C). Compiled Waller Creek stream water data from this study, Christian et al. [6], and Beal et al. [7] exhibit relatively consistent elemental concentrations and lack any seasonal or interannual fluctuations from 2001 to 2020. As the Bull Creek watershed has become increasingly urbanized over the past decade, we have tracked spring water Sr-isotope measurements annually to identify trends. Annually increasing Sr-isotope ratios are observed in Bull Creek spring waters and travertine calcite collected from 1996–2007 [68].

The natural stream water endmember ('endmember I' in Fig 6) has low $^{87}Sr/^{86}Sr$ values and low elemental concentrations, similar to the least urbanized watersheds—Onion (Fig 6B and 6D) and Bull Rural (Fig 6A and 6C). Municipal supply water (endmember II) has high $^{87}Sr/^{86}Sr$ values and lower elemental concentrations compared to wastewater. Finally, municipal wastewater (endmember III) has elevated $^{87}Sr/^{86}Sr$ values and high elemental concentrations. Model fluid mixing curves are displayed for mixing between 1) natural stream water (endmember I) and municipal supply water (endmember II) and 2) municipal supply water and municipal wastewater (endmember III). These mixing processes account for a large portion of the variability in the stream water data (Fig 6). Bull Creek waters with low [Sr] and high $^{87}Sr/^{86}Sr$ values (0.7081–0.7085) form a continuum towards high [Sr] waters with low $^{87}Sr/^{86}Sr$ (0.7077–0.7082). These compositions can be accounted for by WRI processes that decrease stream water $^{87}Sr/^{86}Sr$ to values closer to those for Cretaceous limestone, increase Sr concentrations, and not affect Cl concentrations (Fig 6A). In this scenario, samples with values below the fluid mixing line between endmembers I and III are hypothesized to evolve through WRI processes, which will follow a vertical trend in $^{87}Sr/^{86}Sr$ vs. Cl space (Fig 6A).

Fluid mixing and water-rock interaction processes

The high Sr-isotope variability among wastewaters is likely due to mixing with natural groundwaters that have evolved through WRI processes. Municipal waste subsurface infrastructure is not pressurized, and therefore groundwater can leak into the network and mix with wastewater in route to a wastewater treatment plant (Fig 8). Shoal and Waller Creek stream water and pipe discharge compositions are primarily constrained by mixing lines I & II (Fig 6A and 6C).

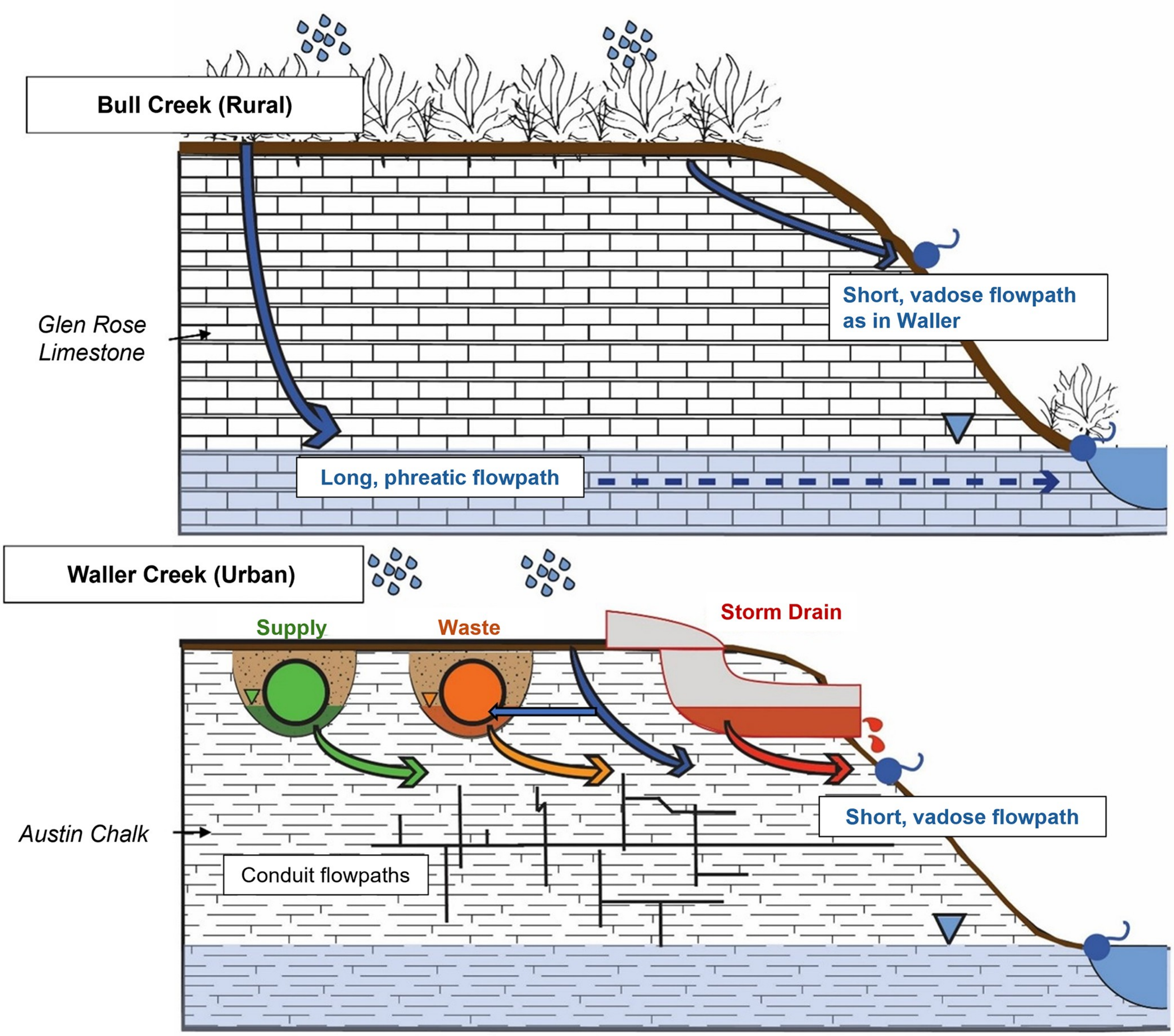

Fig 8. Cross-section conceptual diagrams. Cross-section conceptual diagrams of a rural watershed (e.g., Bull Creek) with Glen Rose limestone bedrock (top) and an urban watershed (e.g., Waller Creek) with Austin Chalk bedrock (bottom) modified from Beal et al. [7]. In the rural watershed, precipitation infiltrates a thick soil and vegetation layer and groundwater (blue arrows) either takes a shallow or deep flowpath before discharging via springs (solid blue circles). Waller Creek stream water is influenced by contributions from supply (green arrow), waste (orange arrow), storm drain outfall (red arrow), and natural waters. As indicated by a thinner blue arrow than in the rural setting, less precipitation can infiltrate the subsurface of Waller Creek due to the higher extent of impervious cover. Municipal and natural waters spend relatively little time in the subsurface and are restricted to shallow, vadose flow through conduit flowpaths resulting from fractures in the otherwise low-permeability Austin Chalk.

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One Waller stream sample has elevated chloride and fluoride concentrations (460 ppm, total), which could be due to fluid mixing between natural water and concentrated wastewaters and/or anthropogenic contaminants (e.g., pool water).

Model results for fluid mixing are portrayed in 1/[Sr] versus $^{87}Sr/^{86}Sr$ space to further assess the degree to which municipal water influences urban stream water geochemical and isotopic compositions (Fig 9). Stream waters in the densely urbanized Waller Creek are distinguished by high $^{87}Sr/^{86}Sr$ values as previously noted except for one outlier. Most Waller stream waters

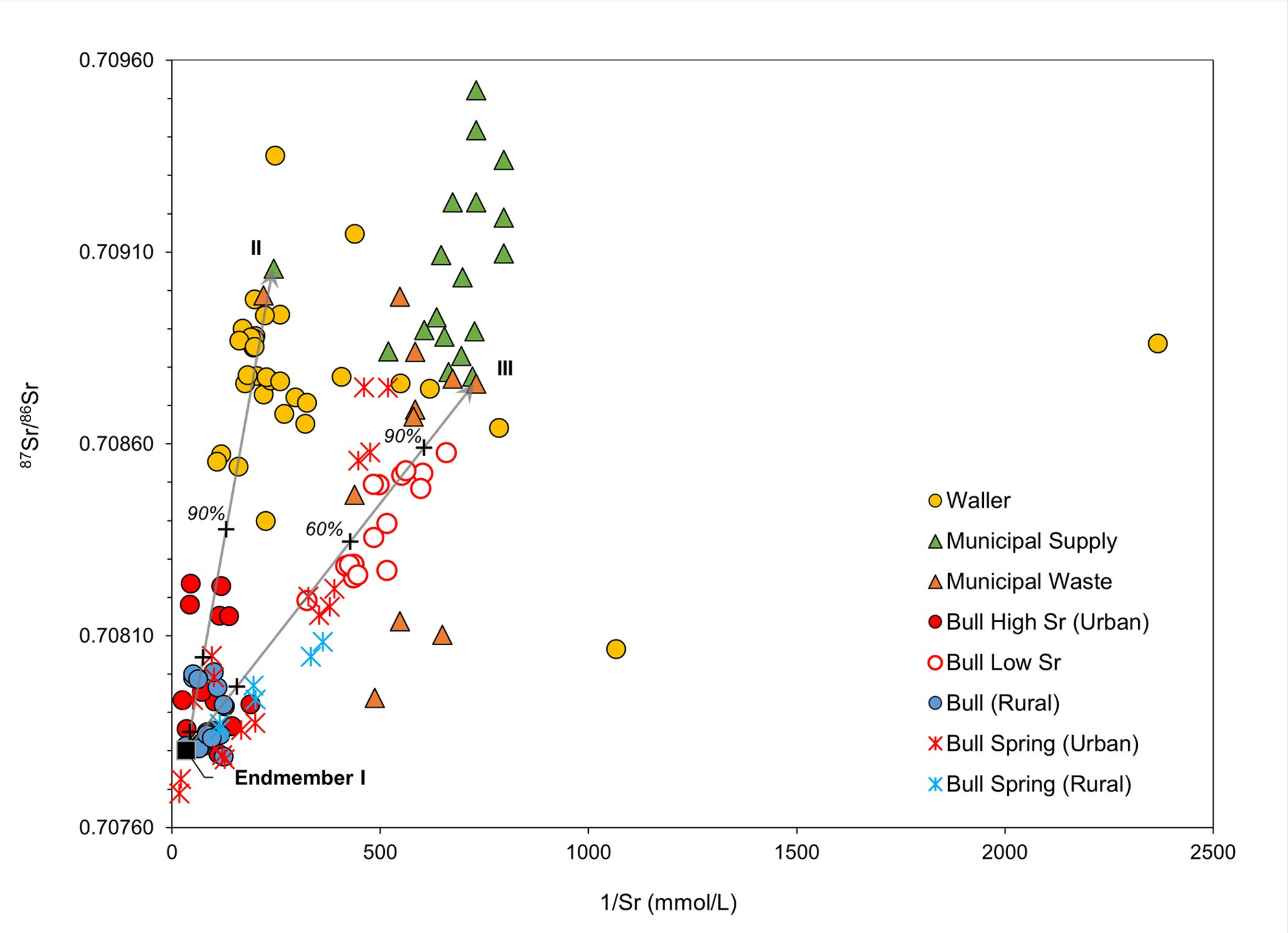

Fig 9. 1/Sr concentrations versus $^{87}Sr/^{86}Sr$. 1/Sr concentrations versus $^{87}Sr/^{86}Sr$ for municipal supply, waste, and stream waters from Waller and Bull watersheds. The fluid mixing line between endmembers I & II (fluid mix line 1) represents mixing between a natural stream water endmember (I) and municipal supply water endmember (II) with crosses at 30% increments. The fluid mixing line between endmembers I & III (fluid mix line 2) represents a mixture between natural stream water (endmember I) and municipal wastewater (endmember III). Rural and municipal endmember compositions are the same as in Figs 6 and 7.

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plot along the rural-municipal supply model mixing lines, with higher Sr concentrations relative to Bull Low [Sr] waters and most municipal supply and wastewaters. Bull Low [Sr] waters plot along or to the right of the rural-wastewater model mixing line, while Bull High [Sr] waters are within the range of all fluid mixtures. Municipal waters are variable in $^{87}Sr/^{86}Sr$ values and Sr concentrations and span the range between high Sr Waller waters and Bull Low [Sr] waters. Comparison of the model results with stream water data (Fig 9) supports the hypothesis that more densely urbanized watersheds (Waller and Bull Urban) have greater contributions of municipal water compared to rural watersheds (Onion and Bull Rural). Beal et al. [7] uses geochemical models to infer that dissolution processes drive water compositions below the mixing line with endmember III (which would account for Bull Low [Sr] waters), whereas WRI processes drive water compositions to the left of the mixing line with endmember II (accounting for Bull High [Sr] waters). While this model-data comparison supports the hypothesized multiple evolution processes of both dissolution and recrystallization in Bull Creek, our findings for Waller Creek portray stream water evolution primarily via dissolution.

Based on the fluid mixing model results (Fig 9), we also infer a significant contribution of municipal water to the stream waters in the urbanized watersheds of Waller and Shoal Ck.

Evolution of municipal water in the natural hydrologic system

We compare stream and spring water geochemical compositions with modeled processes of dissolution of watershed bedrock by an endmember water (Figs 7 and 10). Bedrock compositions for dissolution models of the Austin Chalk and Glen Rose limestone are based on both previously published and newly presented geochemical data (S10 Table). Stream water Sr vs. Ca concentration variations in Waller and Shoal Creeks closely correspond with the modeled dissolution trend of the Austin Chalk (Fig 7A and 7B). Bull Creek (Fig 7C) stream and spring waters also correspond with a limestone dissolution trend, using the Glen Rose Limestone, but unlike Waller and Shoal waters, a group of Bull samples have high Sr concentrations that lie to the right of the dissolution pathways. The Austin Chalk has a large range of Sr concentrations (264–2010 ppm; S10 and S11 Tables) compared with the Glen Rose Fm. (166–225 ppm; S10 Table) and therefore the dissolution models for the chalk span a larger range of modeled stream water Sr concentrations than the dissolution model for the Glen Rose (Fig 7C). The chalk dissolution pathways with the closest fit to observed stream data are modeled using published Austin Chalk compositions from the central Texas area, while the steeper slope pathways are modeled from Austin Chalk collected in Waller and Shoal Creek watersheds by Beal et al. [7] and this study (S11 Table). Waller and Shoal Creek water chemistry may not follow the local Austin Chalk dissolution models as closely as that of central Texas chalk models due to elevated Sr concentrations in stream waters from municipal water mixing with elevated $^{87}Sr/^{86}Sr$. Waller stream waters exhibit a systematic Sr vs Ca concentration trend ($R^2 = 0.86$) (Fig 7A and 7B). The Austin Chalk dissolution models that originate from municipal supply or wastewater compositions are close approximations to the majority of Waller and Shoal Creek stream data (Fig 7A), but they do not account for the lowest Sr and Ca concentrations—below 0.2 and 50 ppm, respectively. These few data points may be a natural endmember represented by a soil water composition in a densely urbanized watershed. Bull Creek Low [Sr] stream waters are well-approximated by the Glen Rose dissolution models, while Bull Creek High [Sr] and spring waters deviate from the dissolution models (Fig 7C). Fig 7D shows six model fluid mixing trends (I–VI) between a natural endmember and six urban endmembers that account for the range of the observed data in the absence of WRI processes. It is unlikely that such fluid mixing processes account for the stream water data, as this would involve six different urban endmember water compositions. Instead, we posit that dissolution followed by recrystallization/WRI processes is a more realistic model to account for the observed stream water variations (Fig 7C).

To better constrain the dissolution and recrystallization processes in the subsurface, we compare regional phreatic and vadose zone groundwater data and spring water data with the modeled dissolution of the Glen Rose limestone (Fig 10). The Glen Rose dissolution model results have similar Sr and Ca concentration ranges to vadose drip waters from Natural Bridge Caverns in central Texas [54,57,60], and drip waters have a lower and narrower range of Sr concentrations relative to spring and phreatic waters. Deep, phreatic groundwaters are high in Sr relative to Ca concentrations, which reflects the progressive dissolution and recrystallization of calcite.

The relatively high concentrations of Sr observed in spring and phreatic groundwaters compared to vadose drip waters in the central Texas region (Fig 10) are similar to the high Sr concentrations produced by the WRI model represented in Fig 7C. Spring waters and phreatic groundwaters typically have long aquifer residence times relative to vadose drip waters in

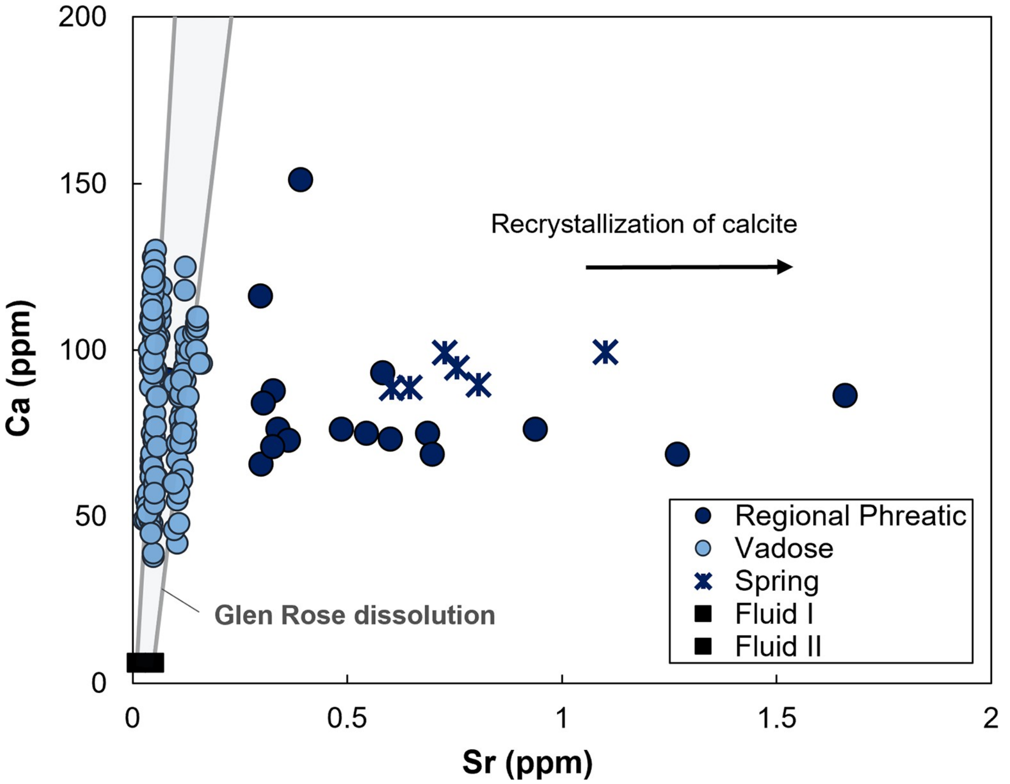

Fig 10. Groundwater Sr versus Ca concentrations. Regional phreatic groundwaters (dark blue circles; n = 18) from central Texas and vadose drip waters (light blue circles; n = 164) from Natural Bridge Caverns, San Antonio, TX [33,54]. Spring water data (dark blue asterisks; n = 6) from Barton Springs, Austin, TX [58]. Dissolution of the Glen Rose limestone by Fluids I and II (black squares) is modeled and represented by grey lines.

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central Texas karst systems. Spring and groundwater Sr-Ca-^{87}Sr/^{86}Sr compositions are consistent in that longer residence time waters are expected to attain more evolved compositions [7,54,57,69]. Applying this process to the Austin-area stream waters, regional vadose drip waters with short-residence times closely correspond to the modeled dissolution of the Glen Rose limestone (Fig 10) and are thus analogous to the Austin-area stream waters that follow the high-slope Austin Chalk and Glen Rose dissolution trends (Waller, Shoal, Bull Low [Sr], Fig 7). Further, the regional phreatic and spring waters with longer-residence times (Fig 10) are analogous to the Austin-area stream waters that are accounted for by the WRI trends (Bull High [Sr], Fig 7).

This comparison of regional water compositions has implications for groundwater residence times, as we infer that the decreased geochemical evolution indicates a shorter time that the water spends interacting with bedrock. The close correspondence between the stream water data and the model trends, as well as the distinct trends of the different model processes, demonstrate that 1) small differences in limestone bedrock composition may control measurable differences in stream water compositions, and 2) watershed bedrock hydrogeologic properties may control stream water geochemical evolution processes.

Saturation indices, pH, and PCO2

To determine the factor(s) that may drive dissolution versus recrystallization processes in urban and rural watersheds, we consider pH and P_{CO2} covariations with calcite saturation

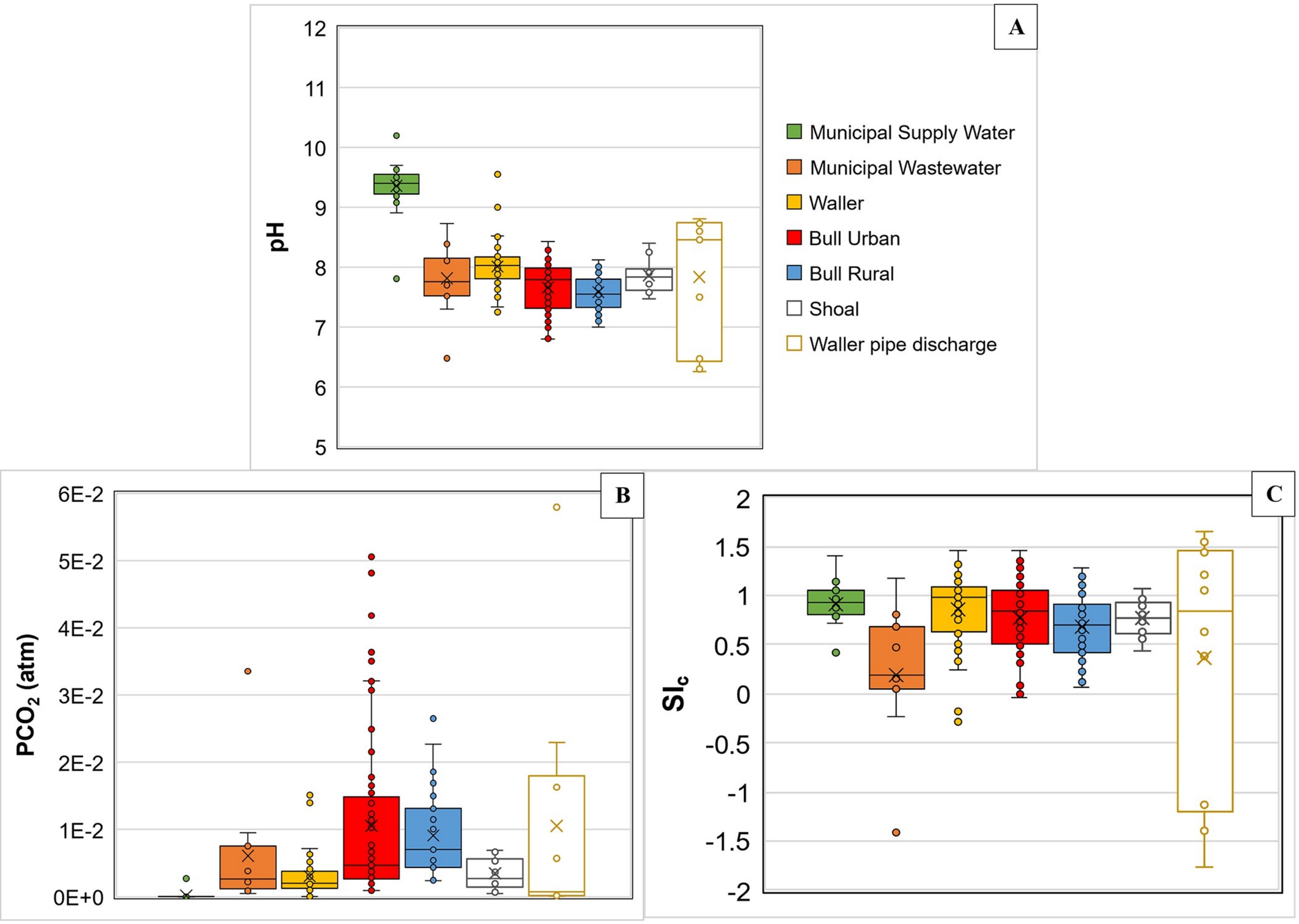

Fig 11. Box and whisker plots. Box and whisker plots of pH (A), PCO_2 (B), and saturation indices with respect to calcite (SI_c) (C) for stream waters from Waller (yellow), Bull Urban (red), Bull Rural (blue), and Shoal (gray border) watersheds as well as municipal supply (green) and wastewater (orange) and Waller Creek pipe discharge (gold border). Box and whisker represent the median of the datasets and minimum/maximum percentiles. Mean values are shown with an 'x'. Water chemistry data from this study is supplemented with data from Christian et al. [6], Beal et al. [7], and municipal water data from the City of Austin.

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indices (SI_c) for stream, municipal supply, and waste waters (Fig 11). When spring waters discharge into a stream, they typically outgas excess CO_2, which will increase SI_c and in turn may drive the precipitation of calcite [70]. Stream waters will trend towards equilibrium with atmospheric CO_2 ($10^{-3.4}$ atm) and continue to precipitate if supersaturated, or waters will dissolve bedrock if CO_2 is higher than atmospheric or waters are undersaturated. The mostly positive SI_c values for municipal waters (Fig 11) indicate that municipal waters are likely to precipitate calcite, or, that they have dissolved calcite. Most SI_c for all waters are positive, that is, supersaturated, suggesting precipitation as a dominant process, but experimental studies show that precipitation occurs at rates several orders of magnitude slower than dissolution processes due to the slow reaction kinetics of calcite precipitation [71,72].

Municipal supply waters are treated by raising the pH to make waters slightly supersaturated with respect to calcite to prevent pipe corrosion [73], which is consistent with our results showing increased SI_c and pH of supply waters (Fig 11A). Stream waters, wastewaters, and pipe discharge waters also follow this positive relationship between SI_c and pH but generally have lower pH values compared to supply waters. Municipal wastewaters, Waller stream waters, and Waller pipe discharge waters span the greatest range of SI_c and pH values compared to Shoal, Bull, and supply waters.

High PCO_2 values compared to atmospheric will undersaturate solutions and increase their potential to dissolve calcite, while low PCO_2 will increase their potential to precipitate calcite. Since municipal supply waters are treated to produce supersaturation, they have low PCO_2 values compared to untreated, undersaturated municipal wastewaters with high PCO_2 (Fig 11B). Stream water SI_c values that range from -2 to 0.07 in waters also have high PCO_2 values (10^{-4} to 10^{-2} atm). Some Waller Creek stream and pipe discharge PCO_2 values (10^{-6} to 10^{-5} atm) are as low as municipal supply water PCO_2 (10^{-7} to 10^{-5} atm), which may indicate an influence of supply water on Waller Creek stream water and pipe discharge water geochemistry. This may also be the case for high Waller Creek PCO_2 values similar to those for municipal wastewater. While dissolution is a primary control on stream water evolution, natural stream water mixing with wastewater may account for the two undersaturated Waller Creek waters that have not yet undergone dissolution (Fig 11C). Stream waters with the potential to precipitate calcite, or waters with high SI_c, likely have groundwater contributions via seeps or springs like in Bull Creek watershed. Our results indicate PCO_2 is a determinant for driving 1) dissolution processes, in the case of increased PCO_2 values in urbanized stream waters, and 2) precipitation processes as a result of decreased PCO_2.

Tracing the municipal water component in Austin-area watersheds

Natural stream water in Austin reflects the Sr isotope composition of local Cretaceous limestone while the Sr isotope composition of municipal water, derived from the Colorado River, is influenced by older Phanerozoic and Precambrian rocks of the Llano Uplift (Fig 3). Stream waters in rural watersheds such as Onion Creek and parts of Bull Creek have Sr-isotope compositions similar to the watersheds' Cretaceous limestone bedrock, consistent with mineral-solution reactions with limestone producing the dominant dissolved Sr load in the stream waters. Higher stream water $^{87}Sr/^{86}Sr$ values that range up to values equivalent to that for municipal water in extensively urbanized watersheds such as Waller, Shoal, and Williamson Creeks can be accounted for by natural stream water mixing with municipal water [6,7].

We additionally consider an alternative hypothesis, that natural soils might provide significant Sr to the stream dissolved load to account for the elevated $^{87}Sr/^{86}Sr$ in the urbanized watersheds. $^{87}Sr/^{86}Sr$ analyses of leachate of Austin soils (n = 97) from Mauceri and Banner [38] and Beal et al. [7] are used to represent soil contributions to streams to test this hypothesis. Results show that irrigated soil $^{87}Sr/^{86}Sr$ values across seven watersheds are distinctively higher compared to unirrigated soils, closer to the Sr isotope range of municipal supply waters. These results do not support the hypothesis that unaltered, unirrigated soils are a source of high $^{87}Sr/^{86}Sr$ in urban stream waters.

Variations in the concentrations of (Na + K), Cl, and SO_4 allow us to constrain potential municipal wastewater components in stream waters. The more urbanized watershed stream waters (Waller and Shoal) and pipe discharge contain elevated (Na + K), Cl, and SO_4 compared to rural watershed streams (Bull Rural and Onion; S3 Fig). Concentrations of these elements for stream waters from the semi-urbanized (Bull Urban) watershed span the range between urbanized and rural stream water concentrations. These results indicate that urban stream water geochemistry is distinct from semi-urbanized and rural watershed geochemistry and is strongly influenced by municipal supply and wastewater (S3 Fig).

Almost all wastewaters trend towards higher Na concentrations than rural stream waters. Samples from all watersheds show an increase in Na above the 1:1 Na:Cl line (Fig 4), indicating inputs of some wastewater into all watershed streams. High Na and Cl concentrations are more common in more extensively urbanized watersheds such as Bull, Waller, and Shoal Creek. An increase in Na/Cl above the 1:1 line can be produced by the weathering of minerals or mixing with fluids that have undergone WRI. These processes can account for Bull Urban High [Sr] data that have elevated Na concentrations, while Bull Urban Low [Sr] data plot at or below the 1:1 line. Data below the 1:1 line may reflect the dissolution of host rock and Na—Ca cation exchange with mineral surfaces. Additionally, waters with Na/Cl ratios below the 1:1 line are commonly found in human and animal waste as well as municipal wastewaters [74–76] due to higher Cl intake compared to Na. In any case, elevated Na and Cl concentrations relative to natural stream waters are indicative of a wastewater contribution. Our results are consistent with the hypothesis that wastewater constituents are elevated in watersheds with a higher degree of urbanization and increased infrastructure age, such as Waller and Shoal Creeks [6]. These constituents are also elevated in semi-urbanized watersheds such as Bull [7] and Slaughter Creeks [6] compared to stream waters from rural watersheds.

Calculated fluid mixing lines between natural and municipal endmembers from Figs 6 and 9 are used to estimate municipal supply and wastewater contributions to the studied watersheds. Municipal supply and wastewater contributions to stream water samples compositions are estimated to be as high as 95% in Waller and Shoal Creeks, 90% in Bull Creek, and 30% in Onion Creek (Figs 6 and 9). Further research involving other wastewater indicators, such as bacteria analyses, is required to unravel the relative contributions of waste and supply water.

Geologic controls on mineral-solution reactions and stream water chemistry

Stream water data correspond to the dissolution model for each respective watershed's bedrock composition (Fig 7). This reveals a subtle but distinct control of bedrock geochemistry on stream water evolution (Fig 7). The calcite dissolution trends originating from a municipal water endmember can account for the covariations of Sr and Ca concentrations in stream waters (Fig 7A–7C). We infer from this that municipal water evolves via dissolution of limestone in the Waller and Shoal Creek urban watersheds (Fig 7A and 7B). The majority of Waller and Shoal Creek stream waters closely correspond to the Austin Chalk dissolution pathways originating from municipal water and suggest limited recrystallization or other chemical evolution processes beyond dissolution.

Stream water compositions that plot in a horizontal trend to the right of these model pathways in Fig 7, such as Bull High [Sr] samples, can be accounted for by the recrystallization of calcite. The recrystallization process will discriminate against the incorporation of Sr relative to Ca into the recrystallized calcite, leading to an increase in the remaining solution's Sr relative to Ca concentration [57,64]. This process drives a horizontal evolution path for recrystallization that is distinct in slope from the near-vertical linear trend of calcite dissolution (Fig 7C). Bull Creek stream water Sr-Ca variability exhibits both dissolution and recrystallization processes, with the Bull Low [Sr] group stream waters following the Glen Rose dissolution model and the High [Sr] group stream waters deviating significantly from the dissolution model [7]. The models in this study use rock compositions that are specific to the hydrostratigraphic units in each watershed, and though all are lower Cretaceous marine limestones, there are distinct trace element concentration ranges for the different units (S10 and S11 Tables). In contrast to these models, in order to account for the range of data by fluid mixing processes, five or more endmembers would need to be involved in the mixing processes, as represented in Fig 7D. A more likely explanation for the range of samples with high Sr concentrations is a sequence of mineral-solution reactions comprising 1) calcite dissolution by municipal water, followed by 2) WRI processes (represented by dashed arrows in Fig 7C), including the recrystallization of calcite. Waller and Shoal Creek samples compositions do not reflect the second-stage recrystallization processes, indicating that Waller and Shoal stream waters are less chemically evolved than those from the other five watersheds.

Municipal water evolution and the modified hydrologic cycle

The Austin Chalk in central Texas is characterized by relatively high fracture permeability (7,100–286,000 mD) [77] and low matrix permeability (0.03–1.27 mD) [43] relative to the matrix permeability of the Glen Rose limestone (~1–100 mD) [42]. The more limited geochemical evolution of Waller Creek waters described previously (Fig 7 and associated discussion) may be a result of fracture-flow dominating over matrix flow in the Austin Chalk, leading to decreased groundwater residence times prior to discharge to Waller Creek. By contrast, the greater matrix permeability and lower extent of fractures associated with the Glen Rose would engender longer groundwater residence times, thereby resulting in more geochemically evolved groundwaters that then discharge to Bull Creek (Fig 7).

In watersheds comprised of Austin Chalk, we infer that both municipal and natural water spend relatively little time in the subsurface before discharging into a stream. This is based on stream water data from Shoal and Waller Creek that can be accounted for by calcite dissolution only, no indication of WRI processes typically associated with longer residence times (Fig 7), and the high fracture permeability of the Austin Chalk. In watersheds with relatively high matrix permeability Glen Rose bedrock, municipal or natural water likely have longer groundwater residence times compared to watersheds with Austin Chalk. To illustrate the multiple impacts that both hydrogeology and extent of urbanization have on groundwater flow paths, we present a cross-sectional schematic that integrates our observations and inferences using stream water compositions and geochemical models (Fig 8). The more rural watersheds, such as Bull and Onion Creek, are primarily influenced by natural water that infiltrates into the subsurface, and that may follow vadose and/or phreatic flow paths within Glen Rose bedrock. Waller Creek, which is the most densely urbanized watershed in this study, is influenced by supply, waste, and storm pipe discharge with conduit-dominated flow paths based on inferred short groundwater residence times within the low matrix permeability and high fracture permeability Austin Chalk.

Implications

The results of this study constrain the sources of stream water dissolved constituents in Austin-area watersheds and address how leaked and irrigated municipal water evolves once it is transmitted from infrastructure to the natural environment. Understanding the hydrogeologic processes in an altered, urban hydrologic cycle has implications for water quality degradation and contaminant transport in the subsurface. This becomes especially important in highly urbanized watersheds and as urbanization encroaches on rural watersheds and sensitive aquifer recharge zones. We identify dissolution as a key geochemical process in less chemically evolved stream waters and infer that these waters have relatively short groundwater residence times. In this way, municipal waste or supply waters spend less time interacting with the surrounding host rock, and thus enter the stream with elevated $^{87}Sr/^{86}Sr$ values and high concentrations of anthropogenic constituents such as SO_4, NO_3, Cl, Na, and F. Stream waters that exhibit greater extents of geochemical evolution indicate longer groundwater residence times, and we can infer that municipal water introduced into the subsurface is more likely to be naturally filtered through WRI and/or ion exchange and sorption processes before discharging into surface waters compared with shorter residence time waters in Austin's urbanized watersheds.

Stakeholders such as taxpayers, city planners, developers, environmental protection entities, and local governments can play important roles in preserving watershed ecosystems to the benefit of aquatic species and public health. City planners will gain a better (i.e., more specialized and geochemical evidence based) understanding of how anthropogenic contaminants enter streams to inform city planning and development, depending on both watershed hydrogeology and the transfer of water from the municipal infrastructure to the natural hydrologic system. Our results indicate that municipal water can comprise a large portion of urban stream baseflow at a given site (up to 90%; Fig 9). Knowing the processes and extent to which municipal water influences stream water geochemistry may provide planners with a more comprehensive foundation to design and regulate (and/or retrofit) better subsurface infrastructure that is less likely to fail with age and prevent water main leakage that may be difficult to detect. It is also important to account for potential unintended positive consequences of infrastructure failure, such as improving the resiliency of riparian vegetation against water-stress [27].

Conclusions

This study examines a commonly overlooked part of the hydrologic cycle in urban and rural watersheds by assessing the evolution of municipal water once it is transmitted to the natural hydrologic system by infrastructure failure and irrigation. The key conclusions are:

1. There is a significant contribution of water from the municipal infrastructure in the Austin area based on the amounts of stream water comprised of municipal water. This contribution includes both supply water, from leakage and irrigation, and wastewater from leakage.
2. We delineate the fluid-mixing and mineral-solution reaction evolution pathways of municipal water during its transmission through watershed bedrock.
3. There is a subtle but distinct control of bedrock composition on stream water chemistry resulting from dissolution and WRI processes.
4. Watershed hydrostratigraphy and permeability impart a flowpath control on residence time and extent of WRI processes.

Cation, anion, and Sr-isotope compositions indicate contributions from supply and/or wastewater to stream waters, which demonstrates a significant input from the municipal infrastructure, by leakage, failure, and irrigation. The extent of this contribution is quantified using fluid mixing models. Our results are consistent with Christian et al. [6] and Beal et al. [7] in that up to 90% municipal water has been identified in some urban stream water samples. However, we note that our range of values lead to uncertainty (up to ~40% in highly urbanized watersheds) in quantifying supply and wastewater endmember contributions in stream waters using covariations in F and Cl concentrations and ^{87}Sr/^{86}Sr values. We find that wastewater contributions to urban and rural watersheds are potentially higher than municipal supply water contributions. A future research prospect is to address how the range and variability of municipal supply and wastewater contributions are related to changes in hydrologic conditions.

We identity a control of bedrock composition via dissolution processes and watershed urbanization on stream water chemistry. Small differences in Sr concentrations between two lower Cretaceous marine limestone hydrostratigraphic units can account for the differences in stream water evolution pathways between watersheds. Additional research may focus on addressing the differences between Sr concentrations in Austin area stream waters and the modeled dissolution of Austin Chalk samples from within the study area. Geologic and permeability variations between watersheds impart a flowpath control on residence time and extent of WRI processes. The degree of urbanization also influences stream water chemistry, with increased contributions of municipal supply and wastewater following increased degrees of urbanization. In watersheds underlain by the low matrix permeability, high fracture permeability Austin Chalk, we infer that municipal water has relatively short groundwater residence times before discharging into the stream. In watersheds underlain by Glen Rose bedrock, which is dominated by matrix permeability, we infer that leaked or irrigated municipal water has longer groundwater residence times relative to watersheds comprising Austin Chalk. Hydrogeology and bedrock geochemistry, specific mineral-solution reactions, and extent of urbanization have a significant influence on the hydrologic system and yield insight into the evolution of municipal water upon its transmission to the natural environment.

Supporting information

S1 Fig. Geologic map of Austin-area watersheds. Geologic map of Austin-area watersheds with stream and watershed boundary GIS data from the City of Austin [35] and geologic data from the Bureau of Economic Geology, The University of Texas at Austin [37].
(TIF)

S2 Fig. Anion holding times vs stream water chemistry. (A) Onion Creek anion replicate concentrations plotted against sample holding times from S5 Table, and (B) stream water charge balances plotted against holding times from S6 Table.
(TIF)

S3 Fig. Piper diagram of municipal and stream waters. Piper diagram of municipal supply (green triangles), waste (orange triangles), Waller Creek stream waters (solid yellow circles), Waller Creek pipe discharge (open yellow diamonds), Shoal Creek (open grey circles), Onion Creek (open blue squares), Bull Creek Rural (solid blue circles), and Bull Creek Urban (solid red circles) Creek stream waters. Stream waters are mostly calcium bicarbonate waters, and stream waters from more urbanized watersheds have variably elevated concentrations of SO4, Na + K, and Cl. Data from this study is combined with data from Christian et al. [6], Beal et al. [7], and municipal water compositions from the City of Austin.
(TIF)

S1 Table. Filtered and unfiltered replicates.
(DOCX)

S2 Table. Cation replicates. Stream water cation replicates and percent differences listed from original samples presented in S9 Table.
(DOCX)

S3 Table. Anion replicates for stream waters. Percent differences listed from original samples presented in S9 Table.
(DOCX)

S4 Table. Field blank replicates. Cation and anion concentrations for field blank replicates from this study and instrument detection limits.
(DOCX)

S5 Table. Anion holding time concentrations. Anion concentrations analyzed at different holding times for replicates collected at one site on Onion Creek.
(DOCX)

S6 Table. Anion holding time charge balances.
(DOCX)

S7 Table. Cation analytical uncertainty. Cation concentrations for ICP-Q-MS standard replicate averages with standard deviations from NIST 1643f standard accepted values.
(DOCX)

S8 Table. Municipal water chemical data.
(DOCX)

S9 Table. Stream and spring water chemical data. Data compiled from multiple sources.
(DOCX)

S10 Table. Bedrock chemical compositions. Chemical concentrations of local to regional carbonates from unpublished and published studies.
(DOCX)

S11 Table. Austin Chalk concentrations and Sr isotope values.
(DOCX)

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