Research paper

Sr isotopes as tracers of anthropogenic influences on stream water in the Austin, Texas, area

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ABSTRACT

The impact of urbanization on streams is multifold and affects both stream flow and stream-water quality. These impacts can lead to either 1) a decrease in stream base flow via increased runoff to streams and reduced diffuse recharge caused by the burial of soil by impervious cover, or 2) an increase in stream base-flow via addition of anthropogenic water sources. Identifying the sources of inputs to urbanized streams is essential to addressing this issue. In the Austin, Texas area, we find a strong contrast in Sr isotope composition between municipal water and stream water in relatively undeveloped watersheds. Dissolved Sr in stream water from eight watersheds in Austin has a wide range of Sr isotope compositions, from $^{87}Sr/^{86}Sr = 0.70778$ to 0.70918. The mean $^{87}Sr/^{86}Sr$ value of stream water in each of the eight watersheds correlates highly to both 1) a variety of indices of the degree of urbanization within the watersheds, such as amount of impervious cover, and 2) mean stream-water concentrations of dissolved ions of anthropogenic origin, such as F, Cl, NO_3, Na, and K. These $^{87}Sr/^{86}Sr$ values can be accounted for by the mixing of two endmembers: 1) the lowest values are similar to those for Cretaceous marine limestones that comprise nearly all of the bedrock in the Austin-area watersheds, and 2) the highest values are similar to Austin municipal water that is taken from the Colorado River of Texas. These relationships enable the novel application of Sr isotopes as a proxy for municipal water contributions to stream base-flow. In the more urbanized watersheds, Sr-isotope mass balance indicates that ~90% of base flow is composed of water from anthropogenic sources. Sr isotopes may also be applied to identify thresholds in the extent of urbanization, above which stream-water flow and quality is impacted.

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1. Introduction

The impact of urbanization on streams is multifold, including impairment or loss of stream habitat for a range of species, reduction of water quality, and alteration of stream flow (e.g., Wang et al., 2001; Walsh et al., 2005). Complicating the study of urbanized streams is the observation that most of the effects on streams in urban environments are of non-point-source origin and difficult to identify (Marsalek and Ng, 1989). The impact of urbanization on stream-water quality has been monitored in earlier studies by determining concentrations of various dissolved components of anthropogenic origin (e.g. F, heavy metals, caffeine, pharmaceuticals, PAHs; Beasley and Kneale, 2002; Kolpin et al., 2002). The concentrations of dissolved chemical species in stream water, however, can be affected by a variety of environmental processes, including evaporation, dilution, mineral precipitation or dissolution, mixing of water masses, oxidation, and ion-exchange or sorption processes in soils. These processes impede both the identification of the sources and the quantification of the amounts

of impacts. The use of naturally occurring isotope tracers can reduce many of these uncertainties. Although low-temperature chemical and biological processes can significantly fractionate elemental concentrations and light, stable isotope ratios (e.g. C, H, O, N, S), natural fractionation of the isotope compositions of relatively heavy elements such as Sr, Nd, and Pb, is negligible (Gosz et al., 1983; Banner and Kaufman, 1994; Blum et al., 2000). Heavy-element isotope compositions are instead primarily controlled by the balance of inputs from the sources of the dissolved constituents to the stream. Isotope compositions can be diagnostic of specific environmental reservoirs, both natural and anthropogenic. This study focuses on Sr isotopes because there are substantial isotopic differences between natural and anthropogenic Sr sources in the Austin, Texas area.

The impact of urbanization on streams can affect both stream flow and stream-water quality. These impacts can lead to either an increase or decrease in stream flow. Increased impervious cover can result in flashy discharge during storms, increased runoff to streams and reduced diffuse recharge via reduced infiltration through soils, which may lead to a decrease in base flow (e.g. Schueler, 2000; McClean, 2000). On the other hand, addition of anthropogenic water to a watershed may increase groundwater levels and stream base-flow above natural levels (e.g. Savini and Kammerer, 1961; Hutchinson and Woodside, 2002; Garcia-Fresca and Sharp, 2005; Wiles and Sharp,

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2008; Sharp, 2010). Stream base-flow may be increased and water quality decreased in urban streams by a variety of processes, including urban infrastructure leakage and over-irrigation. Estimates of water lost from water distribution systems can exceed 50% worldwide, although the U.S. average is 16% (Garcia-Fresca and Sharp, 2005). A survey of water losses in 1997 from the largest cities across Texas and some smaller communities within central Texas recorded losses between 8% and 37%, while water losses within the city of Austin ranged from 8 to 14% between 1997 and 2007 (Austin American-Statesman, 1998, 2009; City of Austin, 2009a). This value does not, however, include leakage between water meters and buildings (Garcia-Fresca and Sharp, 2005). Consequently, this value is likely a conservative estimate. Moreover, leakage increases with the age of the system (e.g. Eiswirth et al., 2001). Loss from sewage systems in developed countries is conservatively considered to be approximately 5% (Garcia-Fresca and Sharp, 2005).

Municipal water for the city of Austin has been taken from the Colorado River of Texas since 1871 (City of Austin, 2009b). The Colorado River watershed contains an outcrop of 1.1 Ga Precambrian granitic basement in the Llano Uplift region, approximately 100 km upstream of Austin. Average whole-rock $^{87}Sr/^{86}Sr$ values for gneisses and granites from the region are 1.00 (n = 23) and 0.86 (n = 24), respectively (Richmann, 1977; Garrison et al., 1979; Bland, 1991; Rougvie, 1993). Weathering of these rocks contributes dissolved Sr with high $^{87}Sr/^{86}Sr$ values to the Colorado River. The $^{87}Sr/^{86}Sr$ value of a sample from the Llano River, a tributary of the Colorado that drains the Llano Uplift, is 0.7102. Consequently, the Colorado River in Austin also has a relatively high average $^{87}Sr/^{86}Sr$ value of 0.7091 (n = 4). In contrast, natural stream-water in the smaller, Austin-area watersheds, which are eroded into Cretaceous limestone bedrock, has lower $^{87}Sr/^{86}Sr$ values, approaching those of Cretaceous seawater (~0.7074; cf. Burke et al., 1982). These isotopic differences indicate that Sr may be a useful tracer of urban water inputs into natural streams in the Austin area. As the population of Austin has increased, the city has expanded into an increasing number of small watersheds. Today, watersheds in the Austin area are characterized by a wide range in the extent and timing of urbanization.

In the present study of Austin-area watersheds, we find large Sr isotope differences between municipal water and stream water in the less urbanized watersheds. We also find a strong correlation between stream-water Sr isotope composition and the extent of watershed urbanization. We apply these results as a means to independently constrain the quantities of municipal water inputs to area watersheds. This application of Sr isotopes may also provide a novel means to reconstruct historical records of urbanization impacts on stream-water flow and quality.

2. Study area

Eight watersheds in the Austin, Texas, area were investigated: Barton, Bull, West Bull, Onion, Shoal, Slaughter, Waller, and Williamson Creeks (Fig. 1). These watersheds are characterized by ephemeral and perennially flowing streams with base-flow discharge typically less than 10 cfs (0.28 m^3/s; Table 1). Stream channels are incised into limestone, which comprises 95% of the bedrock that is not covered by alluvium within the study area. Mudstone and shale comprise the remaining 5%. Terrace deposits of the Colorado River occur in the Shoal, Waller, and the most downstream part of the Onion Creek watersheds, and include detritus eroded from the Llano Uplift, which has relatively high $^{87}Sr/^{86}Sr$ values. Adjacent to the streams and overlying the bedrock are small flood plains with typical soil thicknesses of 0.25 to several meters (Werchan et al., 1974). Soil thicknesses diminish on the uplands to a few tens of centimeters or less. Savanna and woodlands are the dominant ecosystems; riparian woodlands are present along some streams. These watersheds have similar bedrock types, primarily composed of Cretaceous marine limestone with minor occurrences of shale and mudstone, but exhibit a range in the amount and timing of urbanization. Previous studies
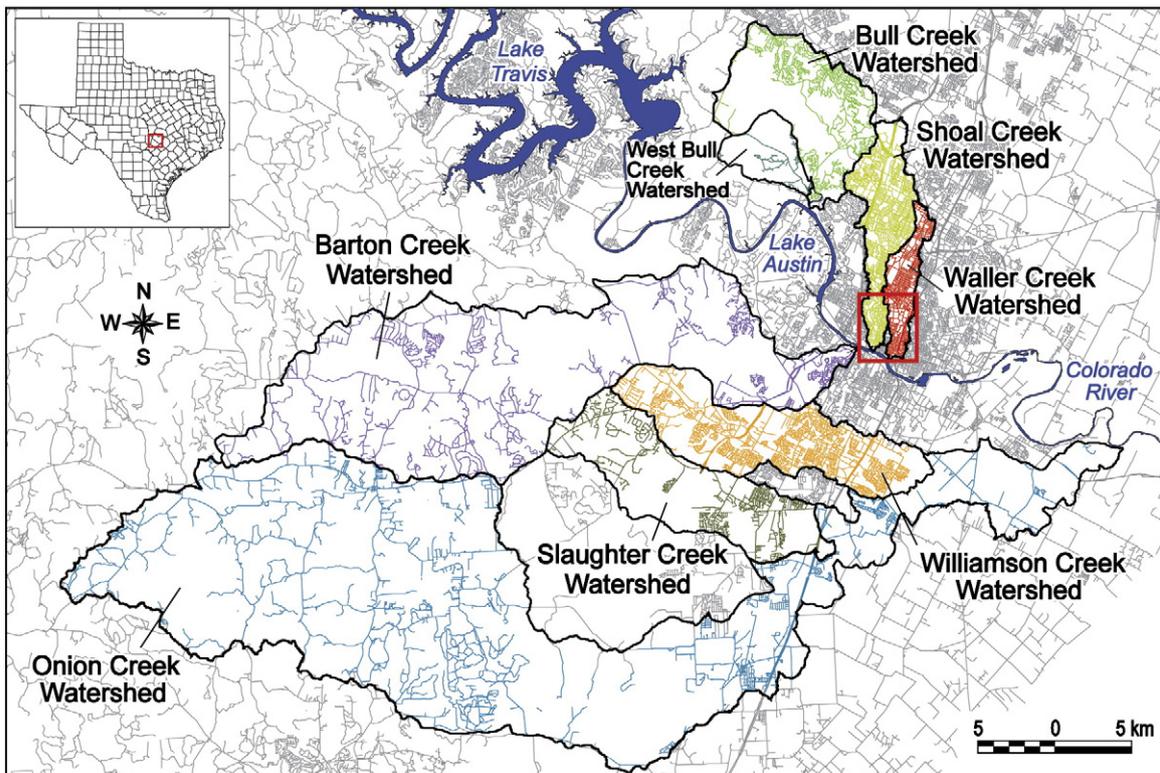

Fig. 1. Watersheds studied in the Austin, Texas area. Also shown are road densities (designated by the fainter lines, colored within the watersheds). Road density is one measure used in this study to assess the degree of watershed urbanization. The location of downtown Austin is indicated by the red rectangle.

Table 1
Physical characteristics of Austin-area watersheds.

Watershed	Area[a] (km^2)	Stream Length[b] (km)	Typical Base Flow [c] (m^3/s)	Categories of Land Use[a] (% of total watershed area)			Percent Impervious cover[d]	Population Density[a,e] (persons/km^2)
				Undeveloped (Includes Parks)	Developed Road-ways	(Business + Civic + Residential)		
Barton	281	77	0.01	89	2	8	7.6	130
Bull	64	17	0.06	52	9	39	22	680
West Bull	18	8	<0.03[f]	79	5	16	9.8	140
Onion	547	127	0.06	92	3	5	6.2	60
Shoal	34	17	<0.03	8	24	68	44	1800
Slaughter	79	27	0.003	64	8	28	15	420
Waller	15	12	<0.1[g]	5	26	70	43	2200
Williamson	80	29	0.03	43	14	43	29	1200

[a] City of Austin (2009c).
[b] City of Austin (1997).
[c] Gauging stations: Barton (Lost Creek Blvd.); Bull (Loop 360); Onion (US Hwy. 183); Shoal (W 12th St); Slaughter (FM 2304); Waller (UT campus); Williamson (Jimmy Clay Rd.). An example data source is United States Geological Survey (2009) for the Bull (Loop 360) station.
[d] Percent impervious cover determined by R. Botto using locally-derived relationship between land use and impervious cover, and the City of Austin's 2003 parcel-based land use layer and impervious cover polygon layer (R. Botto, City of Austin, pers. comm.).
[e] Population in year 2000.
[f] Visual estimate.
[g] City of Austin WPDR database.

provide additional geochemical and Sr isotopic data for water, limestone and soil in the region (Oetting et al., 1996; Sharp and Banner, 1997, 2000; Musgrove and Banner, 2004).

South of the Colorado River, the Williamson Creek watershed is extensively urbanized, containing 57% developed land (DL), and it has similar bedrock geology to the less-urbanized Slaughter (36% DL), Barton (11% DL) and Onion Creek watersheds (8% DL; Table 1). North of the Colorado River, the Waller, Shoal, Bull, and West Bull Creek watersheds have a range of urbanization (95, 92, 48, and 21% DL, respectively). These eight watersheds also exhibit a range in the average age and timing of the onset of urbanization, which for Waller and Shoal Creeks began by 1880, for Williamson Creek by 1950, and for Onion, Barton, Bull, and West Bull Creeks by the latter part of the 20th century (Garcia-Fresca, 2004). Mean building ages within the more urbanized watersheds (e.g. Shoal, Waller, and Williamson Creeks) range from 1964 to 1985, while the less developed watersheds (e.g. Slaughter, Bull, West Bull, Barton, and Onion Creeks) range between 1988 and 1991 (United States Census Bureau, 2000). Moreover, the municipal water infrastructure serving Austin, Texas has grown correspondingly through the decades in order to meet increasing water demand. Austin had 132 km of municipal water mains and 121 km of sewer mains citywide in 1917 (Anonymous, 1917), while at the time of this study, these infrastructure networks had grown to 2670 km (municipal) and 1764 km (sewer) within the study area watersheds alone. The density of urban development in each watershed is shown in Fig. 1, and physical characteristics and land use in each watershed are summarized in Table 1.

3. Methods

Stream-water samples (n = 174) were collected from 79 sites in the eight Austin-area watersheds over a 17 month period that extended from April 2001 through September 2002 (Fig. 2). Several locations in Waller and Onion Creeks were re-sampled in 2008. Individual watersheds were sampled within one to seven day intervals, during base-flow conditions, and at least three days following a precipitation event. Stream-water samples were collected (1) toward the middle of the stream, (2) in areas of flowing water, and (3) upstream of any impediments where practical. Water samples were filtered in the field through acid-cleaned 0.45 μm polypropylene (PP) filter disks on acid-cleaned PP syringes. Two samples were filtered through acid-cleaned 0.2 μm polypropylene (PP) filter disks

for comparison. Cation and Sr-isotope samples were stored in acid-cleaned high-density polyethylene (HDPE) bottles; anion samples were stored in non-acid-cleaned HDPE bottles. Municipal-water samples from private residences were collected in 2002–2003, and in 2008, by allowing municipal tap water to flow for at least one minute prior to sampling. These samples were not filtered. Cation and Sr-isotope samples were preserved with ultrapure HNO_3 to a concentration of 0.1% following return to the laboratory.

Cation concentrations were measured by quadrupole ICP-MS (Perkin Elmer/Sciex Elan 5000 at The University of Minnesota; Micromass Platform and Agilent 7500ce at The University of Texas at Austin). Those samples measured at The University of Texas at Austin were analyzed across four separate sample runs with a total of 12 analyses of the NIST 1640 standard. Sample size was approximately one ml, and the dilution factor was 20:1. Analytical uncertainty is element- and concentration-dependent. Estimated 2-sigma uncertainties (based on replicate analyses of the NIST standard and samples from this study) range from <4% for Na, Mg, Ca, Sr, and Ba to 31% for Zn. Anion concentrations were measured on a Dionex Ion Chromatography System at the University of Minnesota, except for alkalinity, which was determined by titration with 0.1 N H_2SO_4 at The University of Texas at Austin. Alkalinity analyses were measured either by manual titration or with an S M Titrino 702 autotitrator on 25 ml of sample. Two-sigma analytical uncertainty for anions is <4% for most species in most samples. For low concentrations of NO_3, and for PO_4, the uncertainty is 10–20%. Charge balance analysis shows that 90% of the sample analyses are within 5% of neutral; only 3% of the samples differed by more than 10%.

The different Sr isotope analyses, described below, were designed to simulate in the laboratory the environmental processes to which the many natural and anthropogenic Sr reservoirs are subjected, in order to determine the isotopic composition of the Sr which is potentially released to the streams. We analyzed the dissolved Sr in stream water, municipal tap water and sewage; the water-soluble fractions of dust and brick; the acetic-acid-soluble fraction of dust and limestone; the ammonium-exchangeable cations in soils, shales, concrete, brick, and asphalt; the nitric-acid-soluble fraction of concrete, brick, and asphalt; and the HF-soluble Sr in dust and road metal. Limestone samples were dissolved in 4% acetic acid for 10 min, and the solution centrifuged to remove insoluble residue (e.g. Montanez et al., 1996). Approximately 4 cm^3 of the soil samples, and 0.75 cm^3 of crushed samples of the Del Rio and Eagle Ford
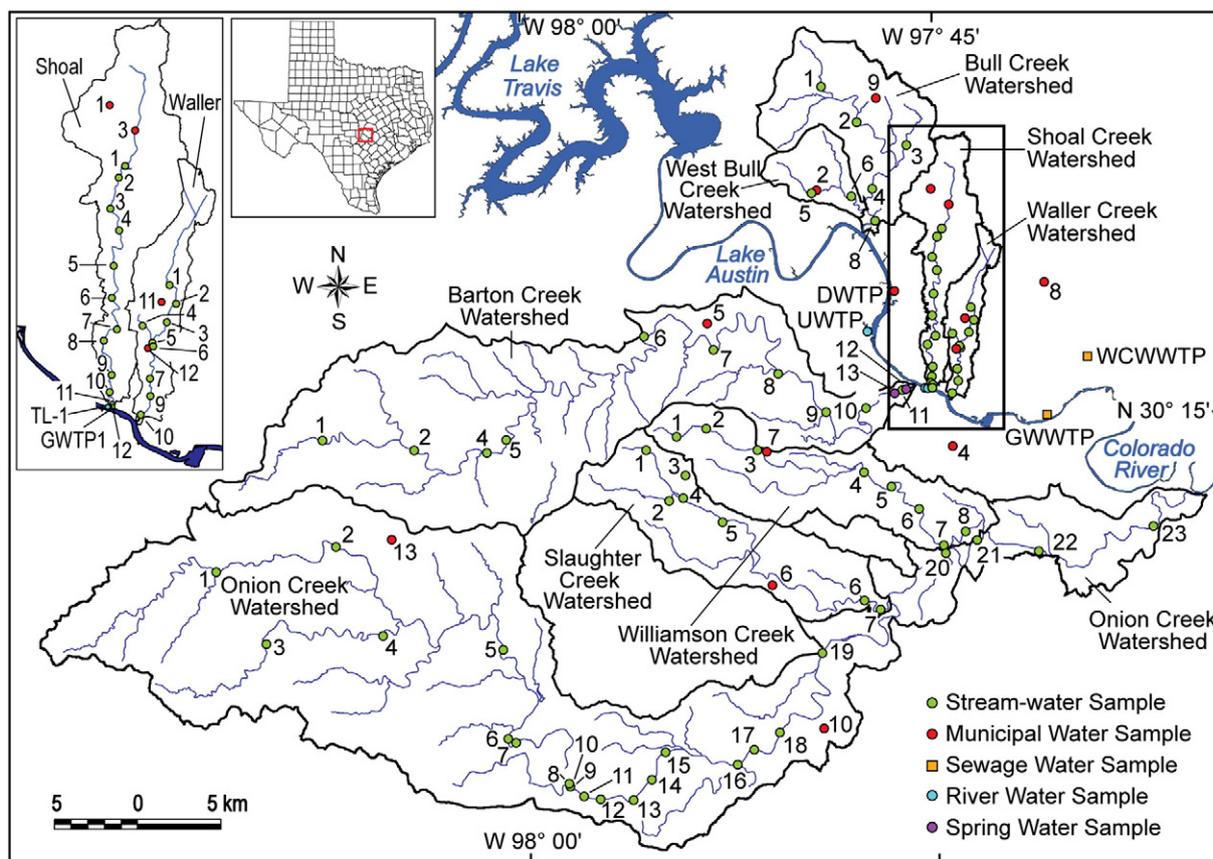
Fig. 2. Location of stream, municipal, sewage, river and spring water samples collected in the Austin, Texas area. The sample site numbering system increases in the downstream direction and is reflected in the sample numbering system included in the online data repository. Water treatment facilities sampled include two sewage treatment plants: 1) Walnut Creek Wastewater Treatment Plant (WCWWTP) and 2) Govalle Wastewater Treatment Plant (GWWTP; since decommissioned) and three municipal water treatment plants: 1) Davis Water Treatment Plant (DWTP), 2) Green Water Treatment Plant (GWTP; since decommissioned) and 3) Ullrich Water Treatment Plant (UWTP).

calcareous mudstones and shales, were leached with 1 M ammonium acetate (pH 8) for approximately 30 min and centrifuged. One duplicate soil sample from the Waller Creek watershed was leached with deionized water for 1 day and centrifuged. Crushed concrete, brick, and asphalt samples were rinsed in water to remove fines. The brick sample was leached in water overnight. The concrete, brick, and asphalt samples were leached with 0.5 M ammonium acetate, then leached with 1 N HNO$_3$ (cf. Graham et al., 2000). The road-metal sample was dissolved in HF following leaching in warm 3 N HCl.

Sr was isolated from all samples using Eichrom Sr-specific resin. Over 95% of the samples were loaded onto Ta filaments and their ^{87}Sr/^{86}Sr values were measured on a Finnigan MAT 261 thermal-ionization mass spectrometer, operated in dynamic multi-collection mode. The water samples collected in 2008 were analyzed using Re filaments on a Thermo Triton TI thermal-ionization mass spectrometer, operated in static multi-collection mode. Both instruments are located in the Department of Geological Sciences, The University of Texas at Austin. During the periods of analysis, the mean ^{87}Sr/^{86}Sr value measured for the NIST SRM 987 Sr standard was 0.710266 for the MAT 261 and 0.710249 for the Triton. Analytical uncertainty for the MAT 261 measurements, based on the 2-sigma external reproducibility of the NIST standard, is +/−0.000014 (n = 82). For the Triton measurements, analytical uncertainty is +/−0.000020 (n = 32). To adjust for instrument bias, 0.000017 was added to the measurements made on the Triton. No correction has been made to account for offset between the measured value for the NIST standard and an accepted value. Five field water-sample-collection blanks were determined, and were between 7 and 55 pg of Sr. Laboratory processing blanks were <17 pg of Sr. These blanks are negligible relative to the size of the samples analyzed, which was typically greater than 1 μg of Sr.

Filtration did not significantly affect measured Sr isotope compositions. Filtered-unfiltered pairs of samples were collected at nine of the sampling locations on Onion Creek. In all cases, the filtered (0.45 μm) and unfiltered samples are analytically indistinguishable, with the average difference in ^{87}Sr/^{86}Sr equal to 0.000005, which is smaller than the analytical uncertainty of 0.000014. Moreover, for one sample locality in Williamson Creek, the measured ^{87}Sr/^{86}Sr values from an unfiltered sample, a sample filtered through a 0.45 μm filter, and a sample filtered through a 0.20 μm filter differed by only 0.000006. Similarly, Sr concentrations for the same samples in this filtration analysis varied from 302 to 304 ppb. This difference is also within the analytical uncertainty.

One soil sample from the Waller Creek watershed was analyzed by leaching with both ammonium acetate and deionized water. The ^{87}Sr/^{86}Sr value for the deionized water-leached sample was 0.70907 compared with the slightly higher ammonium acetate-leached value of 0.70913. This difference is greater than the analytical uncertainty, which may imply that ammonium acetate is a more aggressive leaching technique that represents the total extractable as opposed to the total exchangeable reservoir. This was also observed by Jenne and Wahlberg (1968).

Fluid-mixing model calculations follow the method of Banner et al. (1989) for isotopic compositions. Aquachem 2010.1 was used to determine model component ion concentrations.

4. Results

Physical measurements and chemical and isotopic compositions for all of the samples analyzed as part of this study are presented in an online data repository table.

4.1. Representativeness of stream-water samples

In order to assess the extent to which short-term temporal variability might control stream-water composition, we collected stream-water samples from two watersheds in three different years. We selected the most urbanized (Waller Creek) and least urbanized (Onion Creek) watersheds. For six Onion Creek localities that were initially sampled in 2001 or 2002, we resampled the same sites in 2002 or 2008. Stream-water sampled from an individual site in different years varies in $^{87}Sr/^{86}Sr$ value by an average of 0.000017. Of these six localities, only one differed by an amount (0.000035) outside of analytical uncertainty. For the most highly urbanized watershed, Waller Creek, there was greater variability between samples collected in 2001, 2002 and in 2008, although the overall downstream trend was similar. One sampling locality differed in $^{87}Sr/^{86}Sr$ value by 0.00012; the average difference for four other localities was 0.00005. One sampling locality on Waller Creek was also sampled on a near-weekly basis from August 2001 until September 2002, resulting in 42 samples collected under base-flow conditions (Fig. 3). In addition to the aforementioned sampling that addresses temporal variability, along-stream variability was addressed by collecting between 7 and 23 water samples along the length of each of the eight studied streams (except for the smaller West Bull Creek tributary, from which only two samples were collected). With the exception of the highly urbanized Shoal Creek, the sample compositions produce relatively consistent downstream trends (Fig. 4). We conclude that the samples collected for this study are representative of consistent interannual conditions within each watershed, rather than ephemeral events.

4.2. Natural Sr reservoirs

We consider here the most significant potential contributors of Sr to the streams. Natural streams in the Austin area are characterized by predominantly Ca–Mg–HCO$_3$ waters. Ca–Na–HCO$_3$–Cl waters typify the more urbanized streams (Waller and Shoal). Nearly all of the stream water samples collected during this study were supersaturated with respect to calcite. Stream-water Sr isotope compositions range from 0.70778 to 0.70918 (Table 2), and Sr concentrations range from 140 to 1940 ppb. Average Austin-area rainwater has an $^{87}Sr/^{86}Sr$ value of 0.70833 (Table 3). However, because the Sr concentration is so low (6 ppb), rainwater is a negligible source of Sr. Phreatic
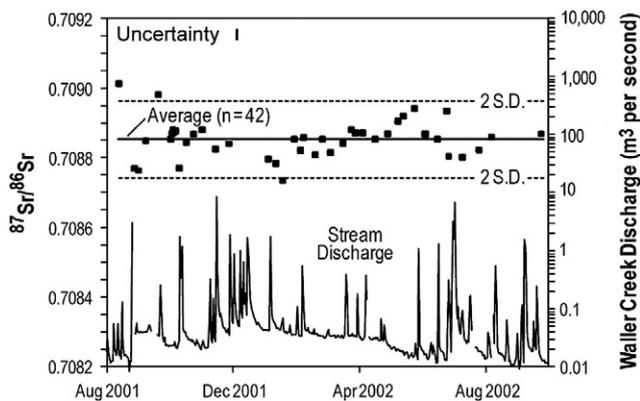

Fig. 4. Downstream trends in $^{87}Sr/^{86}Sr$ for four watersheds. The upstream distance of each sampling location was normalized to total stream length in order to portray both Onion Creek (stream length = 127 km) and Waller Creek (stream length = 12 km) on the same figure. Urbanized watersheds (e.g. Waller, Shoal) have higher $^{87}Sr/^{86}Sr$ values, more downstream variability in $^{87}Sr/^{86}Sr$, and larger downstream increases in $^{87}Sr/^{86}Sr$ than do the less-urbanized Onion and Barton Creeks. The most upstream portions of these creeks do not maintain perennial base flow and were not sampled. The increase in the $^{87}Sr/^{86}Sr$ value of Onion Creek at ~35% upstream distance coincides with an increase in the amount of urbanization in the watershed and with the confluences of more-urbanized streams (e.g. Slaughter and Williamson Creeks) with Onion Creek (Fig. 1). The four watersheds illustrated are representative of the most- and least-urbanized watersheds based on classifications used in this study. The other four watersheds were not plotted for clarity.

groundwater from less-urbanized watersheds typically has $^{87}Sr/^{86}Sr$ values between 0.7076 and 0.7082 (n = 20; Garcia-Fresca, 2004; State of Texas, 2010; N. Hauwert, personal communication). Barton Springs (in the Barton Creek watershed) $^{87}Sr/^{86}Sr$ is typically 0.7079 (Oetting, 1995; Garner, 2005; City of Austin, 2011; this study). The saline water or "badwater" zone (>1000 ppm total dissolved solids) in the Edwards aquifer in the Austin area has $^{87}Sr/^{86}Sr$ values ranging from 0.7086 to 0.7095 (n = 6; Oetting et al., 1996).

Trees alongside Austin-area streams contain about 10 ppm Sr (relative to the weight of dry wood and have $^{87}Sr/^{86}Sr$ values similar to those of the adjacent stream (Mack et al., 2008). The $^{87}Sr/^{86}Sr$ values of the water and acetic-acid-soluble fractions of a dust sample from the Austin area are 0.7079 (Table 2); the HF-soluble fraction (silicate minerals) is 0.7123.

Between three and nine soil samples were collected from each of the eight watersheds. The Sr isotope compositions of the cation-exchangeable fractions of these soils vary between 0.70786 and 0.70986 (Table 2). The range of these values is greater than that reported by Musgrove and Banner (2004) for soils from an area overlying Cretaceous carbonate bedrock about 40 km north of Austin. The higher values are found in the most urbanized watersheds (mean values for Shoal and Waller Creek watersheds are 0.70856 and 0.70895). Sr isotope compositions of Cretaceous marine limestone bedrock in the study area range from 0.70742 to 0.70804 and average 0.7076 (Table 2; data repository). This range is similar to that observed by Koepnick et al. (1985) for central Texas Cretaceous carbonates. Exchangeable Sr fractions of two argillaceous units in the Upper Cretaceous section, the Eagle Ford Formation and the Del Rio Clay, range from 0.70811 to 0.70843. These units comprise <9% by thickness of the Cretaceous stratigraphic section in the area (Young, 1977) and crop out primarily within the Shoal Creek watershed and in watersheds south of the Colorado River. Deposits of Colorado River sediment occur in the middle and downstream portion of the Waller Creek watershed, the downstream third of the Shoal Creek watershed, and in the lowermost Onion Creek watershed. One analysis from a soil profile developed on this material immediately to the east of the Waller Creek watershed has an exchangeable $^{87}Sr/^{86}Sr$ value of 0.7130.

Fig. 3. Temporal variability in base-flow $^{87}Sr/^{86}Sr$ from one sampling locality along the highly urbanized Waller Creek. Stream discharge is also shown. Base-flow samples were collected at least three days after a storm event. There is a poor correlation (r^2 = 0.18) between the $^{87}Sr/^{86}Sr$ value of base flow and the volume of base flow. The 'Uncertainty' bar in all figures represents the 2-sigma analytical uncertainty for individual $^{87}Sr/^{86}Sr$ analyses. Average and 2 S.D. for the entire data set are also shown.
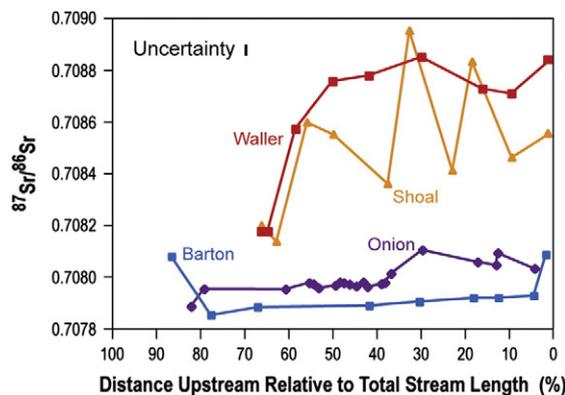
Table 2
Streamwater and other watershed component $^{87}Sr/^{86}Sr$ data.

Watershed	Percent urbanized[a]	Number of samples	$^{87}Sr/^{86}Sr$ mean	$^{87}Sr/^{86}Sr$ range	Downstream increase in $^{87}Sr/^{86}Sr$ per km	Standard deviation about regression
Barton	10	9	0.70793	0.70785–0.70809	3E−7	9E−5
Bull	48	5	0.70801	0.70778–0.70824	1E−5	2E−4
West Bull	21	2	0.70781	0.70778–0.70783	2E−5	
Onion	8	21	0.70798	0.70788–0.70810	2E−6	3E−5
Shoal	92	10	0.70853	0.70814–0.70896	2E−5	2E−4
Slaughter	36	7	0.70806	0.70794–0.70819	−9E−7	9E−5
Waller	95	65	0.70879	0.70818–0.70918	7E−5	2E−4
Williamson	57	8	0.70822	0.70803–0.70870	1E−5	2E−4
Municipal water	17		0.70897	0.70878–0.70917		
Waste water	2		0.70839	0.70810–0.70867		
Colorado River	4		0.70910	0.70886–0.70939		
Limestone bedrock	11		0.70760	0.70742–0.70804		
Soil exchangeable Sr	35		0.70850	0.70786–0.70986		
Dust	1		0.70795 [b]	0.70792 [c] 0.71226 [d]		
Concrete [e,f]	1		0.70785 [g]	0.70815 [h]		
Asphalt [e,i]	1		0.70753 [g]	0.70790 [h]		
Brick [e,j]	1		0.70939 [g]	0.70907 [h] 0.70926 [b]		
Road metal [e, k]	1		0.70352			
Lawn fertilizer [e]	1		0.70839			

Mean and range for Sr isotope values presented here. All individual sample Sr isotope and elemental data are presented in the online data repository. Stream-water samples were collected under base flow conditions.

- [a] Based on percent developed land, as in Table 1.
- [b] Water-soluble fraction.
- [c] 4% acetic-acid-soluble fraction.
- [d] HF-soluble fraction.
- [e] Samples collected in the Waller Creek watershed.
- [f] Analysis of two pooled samples.
- [g] 1 M HNO_3-soluble fraction.
- [h] NH_4-exchangeable Sr.
- [i] Analysis of five pooled samples.
- [j] Analysis of eight pooled samples collected from the Waller Creek bedload.
- [k] Used as the aggregate in seal-coat treatment on older roads.

4.3. Anthropogenic Sr reservoirs

Austin municipal water has a high $^{87}Sr/^{86}Sr$ value relative to stream water from non-urbanized watersheds. During the course of this study, the Sr isotope composition of Austin tap water varied, both temporally and spatially, from 0.70878 to 0.70918 (n = 16). Sr concentration of tap water averaged 140 ppb. Austin water treatment procedures have used lime (CaO) since 1925 (City of Austin, 2009b). One sample of this lime, collected in 2002, had an $^{87}Sr/^{86}Sr$ value of 0.70759. We attribute most of the temporal variability in Sr isotope composition of tap water to variation in $^{87}Sr/^{86}Sr$ of the Colorado River water, which for locations near the intakes for Austin municipal water has ranged from 0.70886 in 2002 to 0.70939 in 2008. Two sewage samples were collected from two sewage treatment plants (one per plant) in 2002 and have $^{87}Sr/^{86}Sr$ values of 0.70810 and 0.70867. A third sewage sample collected in 2006 from an interceptor tunnel in the Slaughter Creek watershed had a value of 0.70781 (City of Austin, 2011). The degree to which these values are representative of the incoming sewage is not well understood, however, because of the addition of treatment chemicals and additional water prior to sampling. Groundwater from wells and springs from urbanized watersheds has $^{87}Sr/^{86}Sr$ values that range from 0.70792 to 0.70962 (Garcia-Fresca, 2004; DeMott, 2007; this study).

The exchangeable-cation and nitric-acid-soluble fractions (considered to be the most environmentally mobile) of two concrete and five asphalt samples have $^{87}Sr/^{86}Sr$ values similar to those of local Cretaceous limestone bedrock (Table 2). Aggregate used in new seal-coat treatments on older roadways in Austin is quarried from Cretaceous volcanic/intrusive rock near Uvalde, Texas (R. Koehn, personal communication). One sample analyzed has a very low $^{87}Sr/^{86}Sr$ value (0.70352), within the range reported by Wittke and Mack (1993) for the

Uvalde rocks. The water-soluble, exchangeable-cation, and nitric-acid-soluble fractions of brick range from 0.7091 to 0.7094 (Table 2). Sr concentrations of crushed-brick leachates are 14 ppb for a water leach, 390 ppb for a 0.5 M ammonium acetate leach, and 3.5 ppm for a 1 M HNO_3 leach. The Sr isotope composition of lawn fertilizer (NPK 23-3-5) used at The University of Texas at Austin (Waller Ck. watershed) is 0.70839, which is similar to the average exchangeable Sr fraction of local soils. Although not analyzed as part of this study, much of the building stone used in this area is quarried from Cretaceous limestone (e.g. Ellison and Jones, 1984) and consequently is expected to have $^{87}Sr/^{86}Sr$ values similar to those measured in our limestone bedrock samples (~0.7076; Table 2).

4.4. Quantity of anthropogenic water

In 2009, 50 billion gallons (1.9×10^8 m^3) of water were supplied to the City of Austin's water distribution system, while only 32 billion gallons (1.2×10^8 m^3) were processed by its wastewater facilities (City of Austin, 2010a). This difference represents water lost from the system and added to the environment as one of the following: 1) leakage from the sewage system, 2) leakage from the water supply system, or 3) irrigation (e.g. lawns and gardens). These are collectively referred to as 'anthropogenic water' herein. Accounting for differences in the number of connections served by the two utilities, we estimate that this difference between supply and sewage is approximately 16 billion gallons (6.1×10^7 m^3), or 32% of the total municipal supply that was distributed in Austin. This estimate is probably conservative because during intense rainfall events storm-water may infiltrate the sewage system and contribute to the volume of processed sewage. Leakage from sewer pipes (loss 1 above) is estimated to comprise about 2 billion gallons (3.8×10^6 m^3), or 13% of the anthropogenic water delivered to

Table 3
Water isotopic and elemental geochemistry (Concentrations in ppm).

	Municipal Water[a]	Sewage[b]	Non-urbanized Stream[c]	Highly urbanized Stream[d]	Rain water[e]
$^{87}Sr/^{86}Sr$	0.70897	0.70839	0.70794	0.70881	0.70833
TDS	190	450	440	610	n/a
Cl	35	67	18	88	1.8
F	0.81	n/a	0.22	0.47	n/a
NO_3	0.16	0.9	<0.1	1.2	1.1
SO_4	27	17	37	88	2.8
PO_4	0.11	12	<0.02	0.09	n/a
Alkalinity	67	220	270	240	n/a
Ba	0.009	0.005	0.035	0.075	n/a
Ca	13	28	73	98	3.4
Cu	<0.00008	0.004	0.0005	0.01	n/a
Fe	0.011	0.16	0.045	0.032	n/a
K	3.3	13	1.1	6.5	0.2
Mg	15	15	22	13	0.2
Na	19	62	10	70	0.8
Pb	0.0002	0.0004	0.00035	0.0007	n/a
Sr	0.14	0.14	0.28	0.43	0.006
Zn	0.007	0.02	0.0008	0.012	n/a
Ba/Mg (molar)	1.3 E−4	6 E−5	2.7 E−4	1.1 E−3	n/a
Number of Samples	9 (17)	2	4	4	4

Notes:

n/a = Not Analyzed.

All individual analyses presented in the online data repository.

[a] Collected at residential and university laboratory faucets. Sr isotope value is mean for 17 samples; elemental concentrations are means for nine samples.

[b] Collected at waste treatment plants.

[c] Average of two most upstream samples from both Onion and Barton Creeks.

[d] Average of two samples each from Shoal and Waller Creeks (WAC 6 and 10; SHC 6 and 12).

[e] Rainwater collected in the Austin area. Concentration data from Oetting (1995). Average $^{87}Sr/^{86}Sr$ value for analyses from Oetting (1995; n = 3) and this study (n = 5).

the environment. This estimate is based on losses in the wastewater distribution system reported in Garcia-Fresca and Sharp (2005). The municipal water supply component that was lost during transmission (loss 2) was estimated to be 8% of the total municipal water supply in 2007 (City of Austin, 2009a). This component comprises about 4 billion gallons (1.5×10^7 m^3), or 25% of the anthropogenic water volume. The remaining 9.9 billion gallons (3.7×10^7 m^3), or 62% of the anthropogenic water, is attributed to irrigation (loss 3).

For the Waller Creek watershed, we estimate that the amount of anthropogenic water added to the environment is at least 2.5 cfs (0.07 m^3/s). This calculation uses the total water input into the city's distribution system (see above) and estimates of the proportion of customers in the watershed relative to total City of Austin customers served. The calculation does not factor in the expected increased leakage from the older infrastructure, however, making this a conservative estimate. This volume is greater than the typical base flow of the creek, which averaged 1.0 cfs (0.028 m^3/s) in 2001–2002 (Fig. 3). We assume that evapotranspiration accounts for the difference between predicted and observed flow.

4.5. Correlation of stream-water $^{87}Sr/^{86}Sr$ with indices of urbanization

The Sr isotope composition of stream water from Austin-area watersheds ranges from relatively low $^{87}Sr/^{86}Sr$ values (e.g., Onion, Barton, and West Bull Creeks), close to those for Cretaceous limestones that comprise most of the bedrock in the region, to much higher $^{87}Sr/^{86}Sr$ values (e.g., Waller and Shoal Creeks), which are close to those for Austin municipal water. Those higher $^{87}Sr/^{86}Sr$ stream-water values are found in the more urbanized watersheds and are correlative with many parameters that can be used to represent the degree of urbanization (Table 4). These include categories of land usage, percentage of impervious cover (which includes structures and roadways), density of population and roadways (cf. Fig. 1), and total length of municipal and sewage pipes within a watershed. In the Austin area, seven indices of urbanization are highly correlated to stream-water mean $^{87}Sr/^{86}Sr$ values, with r^2 values greater than 0.86 (Table 4, Fig. 5). Stream-water $^{87}Sr/^{86}Sr$ values are also highly correlated (r^2 = 0.95) to the timing of urbanization within the watershed (Fig. 6).

4.6. Relationship of stream-water $^{87}Sr/^{86}Sr$ to anthropogenically-derived elements in stream water

There are a number of chemical indicators of urban stream-water quality, two of which, F and Cl, are also useful as conservative tracers. In the Austin-area, four of the least-urbanized streams (Onion, Barton, Bull and West Bull Creeks) have F concentrations that average 0.18 ppm, and a F concentration measured for the Colorado River at Austin is 0.15 ppm. These values are typical of natural stream water (e.g. Fleischer and Robinson, 1963; Sugawara, 1967). Fluoride has been added to municipal water in most cities throughout the United States, including Austin, since 1973 (City of Austin, 2010b). The fluoridation process elevates the fluoride concentration to approximately 1 ppm for the purpose of reducing tooth decay (e.g. Lennon, 2006). Fluoride concentrations measured in nine samples of municipal water collected from locations across Austin ranged from 0.613 ppm to 1.08 ppm with a mean concentration of 0.815 ppm. Chloride concentrations in pristine streams can be less than 10 ppm, depending on the bedrock within the watershed (Livingstone, 1963). However, slightly higher values occur in groundwater from marine sedimentary rocks. Twenty ppm Cl is typical for groundwater from limestone terrains (White et al., 1963). In the Austin area, the least urbanized streams average 18 ppm Cl, and the Colorado River contains 19 ppm. In the more urbanized Austin-area streams, both F and Cl concentrations, and $^{87}Sr/^{86}Sr$ values, are elevated, attaining values as high as 0.65 ppm, 161 ppm, and 0.70935, respectively. Strong positive correlations (r$^2 \geq$ 0.90) exist between average watershed $^{87}Sr/^{86}Sr$ values and fluoride and chloride concentrations in Austin-area streams (Fig. 7). Similarly, average watershed $^{87}Sr/^{86}Sr$ values correlate highly to concentrations of other dissolved chemical species (Table 5), particularly K, Cl, NO_3, Ba, and Cu. Phosphate concentrations are generally below detection limits (20 ppb, 2-sigma) except in the highly urbanized Waller Creek (the watershed with the highest mean $^{87}Sr/^{86}Sr$ value), in which the average concentration is 150 ppb, with a maximum of 450 ppb.

Table 4
Correlations between mean stream-water $^{87}Sr/^{86}Sr$ values and various indicators of urbanization for each watershed. Mean watershed values were calculated for eight watersheds and used to determine r^2 values.

Urbanization indicator	r^2
1. Categories of Land Use	
Percent urbanized area [a]	0.95
Percent urbanized area [b]	0.97
2. Other Urban Parameters [c]	
Population density	0.93
Median structure age	0.95
Roadway index [d]	0.95
Municipal-water pipe index [d]	0.86
Sewage pipe index [d]	0.86
Percent impervious cover	0.86

Data sources:

[a] City of Austin, 2001. No data were available for portions of Barton and Onion Creek watersheds outside of Travis County. Therefore the r^2 values were calculated using only the remaining six watersheds.

[b] United States Geological Survey, 1990. The r^2 values were calculated using data from all eight watersheds.

[c] Derived from miscellaneous U. S. Census Bureau and City of Austin data sets.
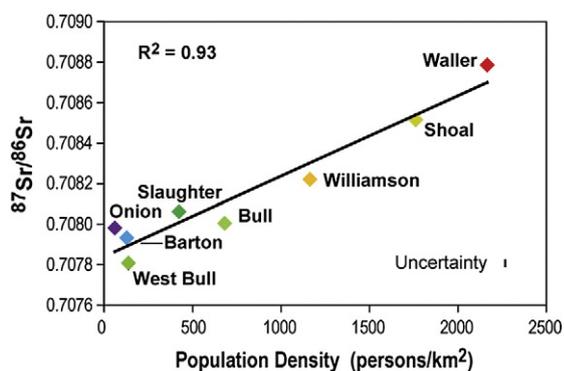
[d] Index is total length divided by watershed area.

Fig. 5. Variation in stream-water $^{87}Sr/^{86}Sr$ relative to population density for the eight Austin-area watersheds studied. Other urbanization indices exhibit similar high correlations to stream-water $^{87}Sr/^{86}Sr$ values (Table 4). $^{87}Sr/^{86}Sr$ values are mean values for each watershed.

4.7. Downstream trends

All of the watersheds, with the exception of Slaughter Creek, exhibit a downstream increase in $^{87}Sr/^{86}Sr$ (Table 2; Fig. 4). In most of the watersheds, the degree of urbanization also increases downstream (Fig. 1). Overall $^{87}Sr/^{86}Sr$ values are higher, and the downstream $^{87}Sr/^{86}Sr$ increase is more pronounced in the more urbanized watersheds (Waller and Shoal Creeks; Fig. 4, Table 2). The more urbanized streams also display greater downstream variability in $^{87}Sr/^{86}Sr$ values (Table 2; Fig. 4).

4.8. Temporal variability

In addition to exhibiting greater downstream variability in $^{87}Sr/^{86}Sr$, the more urbanized streams also exhibit greater variation in $^{87}Sr/^{86}Sr$ over time. $^{87}Sr/^{86}Sr$ values for one sampling locality on the less-urbanized portion of Onion Creek differ by 0.00002 for three base-flow samples collected in 2001, 2002, and 2008. This difference is similar to the analytical uncertainty. In contrast, for the highly urbanized Waller Creek, base-flow $^{87}Sr/^{86}Sr$ values from one locality have differed by as much as 0.00025 within a period of 18 days (Fig. 3; 8/13/01-9/1/01). However, over a period of one year for this site, one standard deviation of 42 base-flow $^{87}Sr/^{86}Sr$ values is 0.00006. The $^{87}Sr/^{86}Sr$ value of municipal water has also varied temporally. In 2002–2003, the mean value was 0.70889 (n = 10; 1sd = 0.00009). In 2008, the mean value was 0.70911 (n = 5; 1sd = 0.00009).
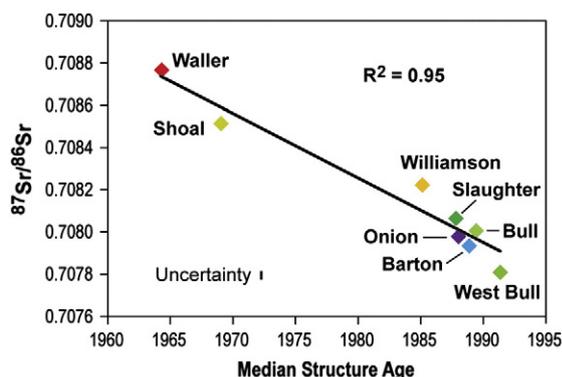

Fig. 6. Variation in stream-water $^{87}Sr/^{86}Sr$ relative to median structure age for the eight Austin-area watersheds studied. Structure age is used as a proxy for the age of the associated municipal water and sewer pipe infrastructure. Increasing age is associated with increased leakage in municipal water systems. $^{87}Sr/^{86}Sr$ values are mean values for each watershed. Age data from 2000 Census (United States Census Bureau, 2000).
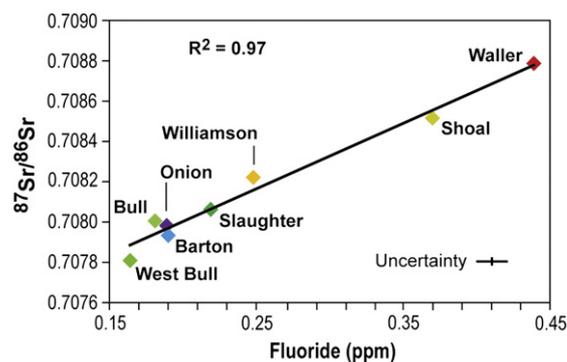

Fig. 7. Co-variation of $^{87}Sr/^{86}Sr$ and F concentration in Austin-area watersheds. Values are means for the different watersheds. Similar correlations are observed between $^{87}Sr/^{86}Sr$ values and concentrations of Cl, NO_3, Na, and K (Table 5).

4.9. Correlation of stream-water $^{87}Sr/^{86}Sr$ with soil Sr

In the Austin-area watersheds, the mean stream-water $^{87}Sr/^{86}Sr$ values covary with the mean $^{87}Sr/^{86}Sr$ values of the exchangeable Sr from soil samples ($r^2 = 0.74$). Across the study area, the range of soil ammonium-acetate exchangeable $^{87}Sr/^{86}Sr$ values (0.70786 to 0.70986) is similar to the range of values of individual stream-water samples (0.70778 to 0.70918).

5. Discussion

The range of stream-water $^{87}Sr/^{86}Sr$ values may be controlled by input from a variety of sources, both natural and anthropogenic. Anthropogenic sources of Sr include municipal water (tap water) and sewage, building stone, brick, concrete, road metal, and fertilizer. Natural sources of Sr include bedrock, soil, dust, rain, groundwater, and vegetation. Because of the low Sr concentrations of central Texas rain water and similarity in Sr isotope composition between riparian vegetation and associated stream water, these sources have negligible potential to affect the $^{87}Sr/^{86}Sr$ values of stream water (Mack et al., 2008; Table 3). The more likely Sr sources are evaluated in this study.

5.1. Natural controls: groundwater, geologic units and atmospheric deposition

In the Austin area, springs contribute phreatic groundwater to some watersheds. However, potentiometric-surface data from water wells in the Austin area (State of Texas, 2010) indicate that contribution of deeper groundwater from the Trinity and Edwards

Table 5
Correlation between stream-water $^{87}Sr/^{86}Sr$ values and other dissolved constituents. Mean watershed values were calculated for eight watersheds and used to determine r^2 values.

Component	r^2
TDS	0.59
Cl	0.90
F	0.97
NO_3	0.82
SO_4	0.58
Alkalinity	−0.01
Ba	0.80
Ca	0.37
Cu	0.81
Fe	0.06
K	0.91
Mg	−0.69
Na	0.78
Pb	0.43
Zn	0.49
Zn	0.49

aquifers to watersheds north of the Colorado River (except in the Bull Creek watershed) is unlikely. Moreover, nearly all samples of phreatic groundwater in the Austin area have much lower $^{87}Sr/^{86}Sr$ values (Oetting, 1995; Garner, 2005; N. Hauwert, pers. comm.; State of Texas, 2010; this study) than those observed in the urban streams and cannot therefore be a significant source of the elevated $^{87}Sr/^{86}Sr$ values in urban streams. In contrast, higher $^{87}Sr/^{86}Sr$ values are observed in the badwater zone of the Edwards aquifer (Oetting et al., 1996), which underlies the eastern-most part of the study area. However, there is no known discharge of this water into the studied watersheds except a small contribution (<10%) to Barton Springs (N. Hauwert, pers. comm.). Moreover, the major-element composition of badwater (Oetting et al., 1996) precludes it from being a dominant source of the anthropogenic elements in the more-urbanized watersheds. Similarly, addition of groundwater from the Trinity aquifer (Oetting et al., 1996) cannot produce the observed elemental and Sr isotope composition of the urban streams.

Atmospheric dust deposited in the Austin area contains a component of marine limestone, which buffers the $^{87}Sr/^{86}Sr$ value of the most reactive fractions of the dust (water-soluble, NH_4-exchangeable, and acetic-acid-soluble) to values between 0.7079 and 0.7085 (Table 2; S.I. Dworkin, pers. comm.). The silicate fraction of dust has elevated $^{87}Sr/^{86}Sr$ values, but this Sr is considered to be less mobile due to lower solubilities of most silicate minerals relative to calcite. Moreover, deposition of dust should affect all watersheds similarly because of the relatively small geographic area involved. Consequently, dust is unlikely to be the source of the elevated $^{87}Sr/^{86}Sr$ values that are only observed in the more urbanized watersheds.

Over 95% of the bedrock in the Austin area is Cretaceous limestone, which has $^{87}Sr/^{86}Sr$ values that are too low to produce the elevated $^{87}Sr/^{86}Sr$ values in the most urbanized watersheds (Table 2). $^{87}Sr/^{86}Sr$ values of ammonium acetate leachates from the more argillaceous units (n = 4; Del Rio Clay and Eagle Ford Fm.) range up to 0.7084. However, these units comprise <9% of the stratigraphic section in the area, and we observe no correlation between stream-water $^{87}Sr/^{86}Sr$ values and the outcrop area of these units in the watershed. In addition, the Sr isotope composition of the exchangeable Sr from these units is not sufficiently radiogenic to produce the elevated values observed in the more-urbanized streams.

Alluvium derived from within a given watershed is generally more abundant downstream. The downstream increase in both alluvium and stream-water $^{87}Sr/^{86}Sr$ values suggests that discharge of shallow alluvial groundwater to streams may be a control on stream-water $^{87}Sr/^{86}Sr$. The lithologic composition of the locally-derived alluvium, however, is similar to that of the downstream bedrock, precluding substantial differences in $^{87}Sr/^{86}Sr$ value.

5.2. Natural controls: soils

Soil likely affects $^{87}Sr/^{86}Sr$ of stream water via ion-exchange processes as rainfall infiltrates through soils. The most pristine stream water in the study area (uppermost Onion and Barton, and West Bull Creeks, Table 3) has $^{87}Sr/^{86}Sr$ values that are slightly higher than the Sr in local limestone bedrock (0.7079, compared with average limestone value of ~0.7076; Table 2). Soils are the most likely source of this elevated $^{87}Sr/^{86}Sr$ because soil leachates have high $^{87}Sr/^{86}Sr$ values compared with $^{87}Sr/^{86}Sr$ in the limestone and because there are few anthropogenic sources in the upper reaches of these watersheds. Soils developed on Colorado River terrace deposits in the Waller Creek watershed have exchangeable Sr ratios as high as 0.7099. More typical soil values are 0.7079 to 0.7085 (Table 2).

The correlation ($r^2 = 0.74$) between streamwater $^{87}Sr/^{86}Sr$ and exchangeable Sr from the soils (within the different watersheds) suggests that soil Sr is the dominant control on stream-water $^{87}Sr/^{86}Sr$. There are several lines of evidence, however, that are not consistent with this hypothesis. A soil control on stream-water

composition cannot account for the close correspondence between $^{87}Sr/^{86}Sr$ and concentrations of anthropogenic-elements, such as Na, F, Cl, and NO_3, in stream water among all watersheds. The Na/Ca ratio of exchangeable cations from the soils is very low (~0.004) compared to this ratio in stream water in the urbanized streams (~ 0.45), requiring that Na in urban stream water have a different source. Furthermore, Ba/Mg ratios of stream water are not consistent with a dominant soil control on the stream-water composition. Because of the greater affinity of exchange sites in the soil for Ba (e.g. Capo et al., 1998; Evangelou, 1998), the stream-water Ba/Mg ratios should diminish with increasing dominance by soil. The opposite is observed, with stream-water Ba/Mg ratios ranging from 3 to 10 times greater in the watersheds with the higher $^{87}Sr/^{86}Sr$ values (more urbanized watersheds; Table 3). Lastly, the downstream increases in stream-water $^{87}Sr/^{86}Sr$ (Fig. 4) that correspond with downstream increases in urbanization cannot be accounted for by changes in soil $^{87}Sr/^{86}Sr$. For example, in the Waller Creek watershed, the two soil samples having the most-elevated exchangeable $^{87}Sr/^{86}Sr$ values are in the upstream portion of the watershed where the stream-water $^{87}Sr/^{86}Sr$ is lowest. We conclude that, although soils do contribute dissolved Sr and other elements to the stream water, soils are not the dominant source of elevated $^{87}Sr/^{86}Sr$ values. The observed correlation between soil and stream-water Sr isotope values may be a consequence of soil $^{87}Sr/^{86}Sr$ values in the more urbanized watersheds having already been shifted toward that of municipal water by contact with anthropogenic water from long-term leakage or irrigation because Sr is preferentially sorbed to exchange sites in soil relative to Ca or Mg (e.g. Capo et al., 1998; Evangelou, 1998).

5.3. Anthropogenic controls

The addition of anthropogenic water appears to control the elevated $^{87}Sr/^{86}Sr$ values of the most urbanized streams. Relative to natural stream water, anthropogenic water (both tap water and sewage) contains elevated concentrations of chemical species such as Na, K, F, Cl, and NO_3 that are also present at elevated concentrations in stream water from the most urbanized watersheds (Table 3). Elevated concentrations of these species are commonly attributed to anthropogenic sources (Barrett et al., 1999; Meybeck, 2004; Lennon, 2006). The mean $^{87}Sr/^{86}Sr$ value in each Austin-area watershed is highly correlated to the mean concentrations of these chemical species (Fig. 7; Table 5). Additionally, the downstream increase in stream-water $^{87}Sr/^{86}Sr$ in the urban streams (Fig. 4) coincides with an increase in the amount of urbanization and/or the age of urbanization within the watershed (Fig. 1), and with increased concentrations of the anthropogenic elements. These results are consistent with an anthropogenic origin for the elevated $^{87}Sr/^{86}Sr$ values and permit the use of Sr isotopes as indicators of the degree of anthropogenic impact to surface-water systems in the Austin, Texas area.

Elevated concentrations of some chemical species such as Na, Cl, and NO_3 suggest sewage as a component to the stream water. The N and O isotope composition of dissolved nitrate in the two most urbanized watersheds (Waller and Shoal) also indicates a sewage component in those two streams (Ging et al., 1996). Other dissolved elements such as F could be derived from either municipal water or sewage. Because municipal water initially comprises a large volume of sewage, the sewage begins with an aqueous $^{87}Sr/^{86}Sr$ value close to that of municipal water. Therefore, the elevated Sr isotope signal may result from either or both municipal water and sewage, such that this geochemical tracer is indicative of the integrated urban water input to a watershed. Mass-balance mixing models that consider two end member water masses, natural stream water and municipal water, can be used to assess the hypothesis that Austin-area stream water is a mixture of natural stream flow and urban water. Model results indicate that this two endmember mixing process can account for much of the variation in chemical composition of Austin-area stream
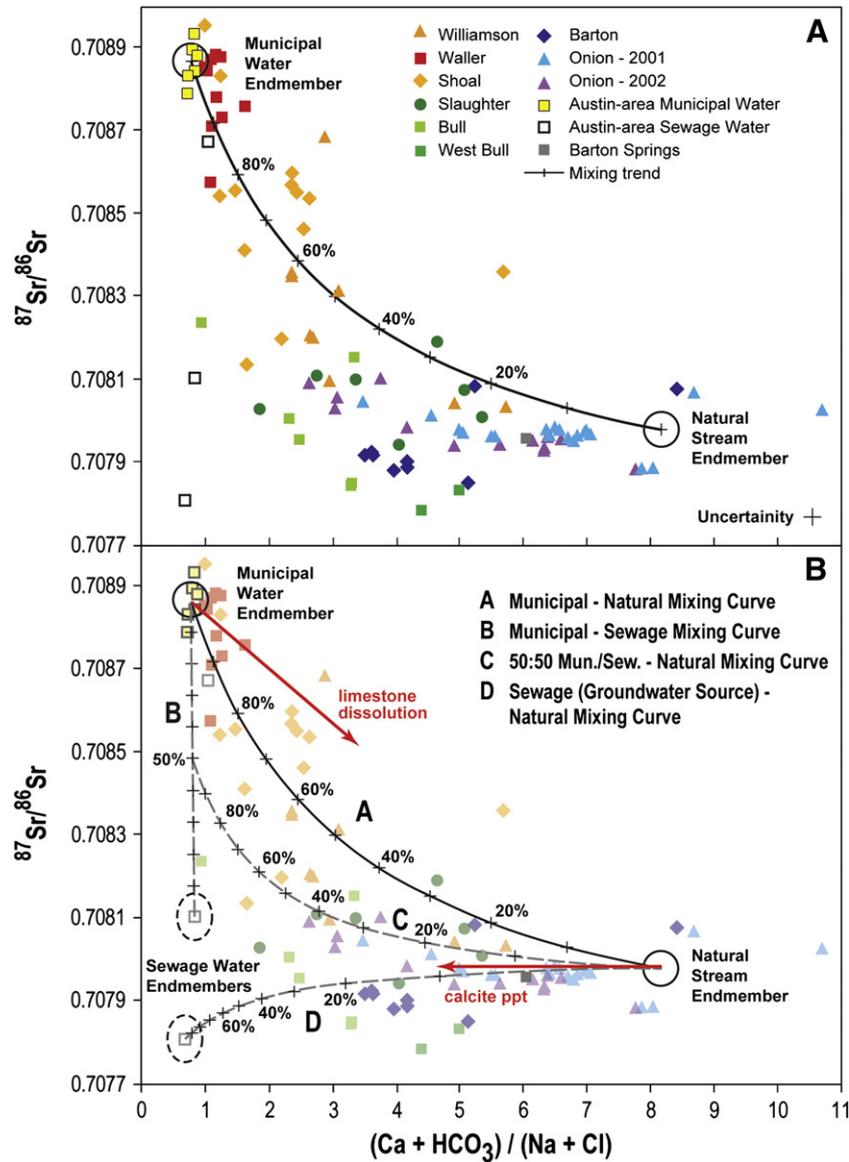
Fig. 8. A. Relationship between $^{87}Sr/^{86}Sr$ and $(Ca + HCO_3)/(Na + Cl)$ in Austin-area streams. Ca and HCO_3 are the dominant ions in natural stream water in the Austin-area. The addition of sewage increases the concentrations of Na and Cl in natural stream water. Water softening treatment reduces the concentrations of Ca and HCO_3 relative to Na and Cl in Austin municipal water. The fluid-mixing curve between the natural streamwater and municipal water endmembers is calculated using compositions in Table 3 and the online data repository table. Percentages shown along the mixing curve are the amount of municipal water in the two-component mixture. X-axis values are molar quantities. B. The same data set and principal mixing curve (Curve A) is illustrated as in (A), with additional model processes. These processes include 1) fluid mixing involving municipal water and a sewage endmember (Curve B), natural streamwater and a 50:50 mixture of municipal water and sewage (Curve C), and natural streamwater and a groundwater-sourced sewage endmember (Curve D); and 2) mineral-solution reactions involving limestone dissolution and calcite precipitation (calcite ppt).

water (Fig. 8a). Based on this mixing model, more than 50%, and as much as 95%, of the water in the more urbanized watersheds is derived from municipal water. Scatter of the stream-water samples about the mixing curve requires varying contributions from other environmental reservoirs (e.g., sewage or soils) to the stream water, or other processes (e.g., sorption, calcite dissolution or precipitation), as illustrated in Fig. 8b. Many of the stream-water samples that lie below or to the left of the principal mixing curve (Curve A) are from developing watersheds (Fig. 8a). Use of septic tanks, which discharge nearly all the water they receive to shallow groundwater, is common in these areas. It is reasonable to conclude, therefore, that much of the anthropogenic water being discharged into streams, whether diffuse or point source inputs, is composed of a combination of municipal (leakage, irrigation) and sewage water (leakage, septic tank effluent; Fig. 8b, Curve B). A mixing curve between a 50:50 municipal water–sewage mix and the natural stream-water endmember (Curve C), for

example, lies in the center of the field defined by many of those points that lie below the principal mixing curve. Additionally, some small communities in the "undeveloped" and developing watersheds (e.g. Onion Creek) obtain municipal water from the underlying limestone aquifers. One such sample of groundwater-derived municipal water was collected in the city of Buda (Edwards aquifer, E. Conner, pers. comm.) and had a $^{87}Sr/^{86}Sr$ value of 0.70791. Addition of sewage (high Na and Cl) with such relatively low $^{87}Sr/^{86}Sr$ values will shift water compositions to the left of mixing curve A (Fig. 8b, Curve D). In summary, the high isotopic variability of sewage compositions leads to higher uncertainties in models using sewage relative to models using municipal water or natural stream water.

An additional process that may drive water compositions to the left of mixing curve A is the precipitation of calcite from the supersaturated stream waters (Fig. 8b). This process would remove Ca and HCO_3 from solution and leave Na and Cl concentrations and Sr

isotope compositions unchanged. The predicted effect of soils on the concentrations of cations in anthropogenic water is to increase Na relative to Ca (Capo et al., 1998; Evangelou, 1998), thereby shifting values to the left of the mixing curve (Fig. 8b). The $^{87}Sr/^{86}Sr$ value of the water interacting with the soil may be shifted either higher or lower, depending upon the watershed involved.

The range of fluid mixing processes, sources, and mineral-solution reactions illustrated in Fig. 8 can account for much of the geochemical variability in Austin-area stream waters. The high stream-water Ca concentrations in the more developed watersheds relative to the less developed watersheds and municipal water (Table 4), in contrast, are not readily explained by these processes and sources. This indicates that in the more developed watersheds there may be a greater influence of a process such as evapotranspiration, or an additional source of dissolved ions to streams. Such a source would likely be one with 1) higher $^{87}Sr/^{86}Sr$ and/or higher Ca/Sr values than those for the local limestones, which would lower the Sr isotope values of the stream water, and 2) more widespread occurrence in the developed watersheds. Of the anthropogenic reservoirs analyzed in this study, only brick has a sufficiently high $^{87}Sr/^{86}Sr$ value (Table 2), but it remains to be determined if bricks in the region weather to a significant enough extent or contain enough calcium to produce the observed trend (Elert et al., 2003; Scolforo and Browne, 1996). A high Ca/Sr source may be one or more components not analyzed in detail in the present study, such as rooftop materials and concrete, which are indicated to have significant input in urbanized watersheds (van Metre and Mahler, 2003; Bain et al., 2010). This issue may be further addressed through a more detailed analysis of 1) the effects of evapotranspiration, and 2) the range of anthropogenic materials in the Austin-area watersheds, in terms of their range of elemental and isotopic compositions, areal distributions, and susceptibility to weathering.

5.4. Extent of urbanization

If anthropogenic water is indeed the primary influence on high $^{87}Sr/^{86}Sr$ values in Austin-area stream water, then one would expect strong correlations between mean $^{87}Sr/^{86}Sr$ stream water values by watershed and various indices of urbanization. The most generalized index of urbanization is that of land use patterns within the study area. Strong correlations are observed between mean stream water $^{87}Sr/^{86}Sr$ values and the percentage of urban land use relative to watershed area (two data sets: $r^2 = 0.95$ and $r^2 = 0.97$; Table 4). Comparisons of other urban indices such as impervious cover and roadway density with mean stream water $^{87}Sr/^{86}Sr$ values also yield strong correlations ($r^2 = 0.86$ and $r^2 = 0.95$, respectively). Although these correlations are strong, they are relatively general in that they either 1) do not reflect detailed information such as the density of development within the urban land use categories, or 2) are not direct comparisons of anthropogenic activities that would impact stream water compositions under base flow conditions. A comparison between watershed population densities and the mean stream water $^{87}Sr/^{86}Sr$ values yields an r^2 of 0.93. This correlation may be more reflective of the irrigation portion of anthropogenic water since this portion is primarily based upon human activity. An assessment of the other two portions of anthropogenic water (leakage from municipal and wastewater infrastructure) provides a more direct comparison of anthropogenic sources and stream water compositions. Correlations between municipal-water and sewage pipe densities with mean watershed stream water $^{87}Sr/^{86}Sr$ values are strong (both $r^2 = 0.86$), but lower than most of the previous comparisons. This correlation difference may result from infrastructure aging, which would be additive to the effects of variations in pipe density on stream water quality. Older but less dense pipe networks have the potential to input as much as, if not more, anthropogenic water than newer, more dense systems simply based on a lower transmittal efficiency.

5.5. Effects of age of urbanization

In the Austin area, the watersheds having the highest $^{87}Sr/^{86}Sr$ values are correspondingly those that have been urbanized for the longest periods of time. Although it is not possible to discriminate between the effects of age, or the extent of present-day urbanization on stream-water composition, older municipal water and sewage pipes are leakier (e.g. Eiswirth et al., 2001). In the absence of detailed water and sewage pipe infrastructure age data we use median structure age data available from the 2000 Census as a proxy for the age of infrastructure development. We use this approach because municipal infrastructure is typically constructed only shortly before real estate development, due primarily to the need for benefit realization from expensive infrastructure costs. Area-weighted mean structure age values by watershed in the Austin area are strongly correlated ($r^2 = 0.95$) to mean stream water $^{87}Sr/^{86}Sr$ values (Fig. 6; Table 4). We conclude that both age of infrastructure and extent of present-day urbanization impact the stream-water chemistry.

6. Implications and conclusions

6.1. Constraints on the quantity of urban water entering streams

We infer that there are two principal endmembers that control the Sr isotope composition of Austin-area stream water during base flow: 1) natural stream water having a low $^{87}Sr/^{86}Sr$ value governed by interaction with Cretaceous limestone bedrock and soil, and 2) anthropogenic water (i.e., municipal water and sewage) having a high $^{87}Sr/^{86}Sr$ signature inherited from Colorado River water (Fig. 8a; Table 2). Based on this inference and using mass-balance (Banner et al., 1989), the proportion of the two dominant endmembers present in a stream can be determined. In the highly urbanized Waller Creek watershed, for example, we calculate that approximately 90% of the base flow comes from anthropogenic sources. A similar calculation using F concentrations suggests that between 25% and 60% of Waller Creek water may be anthropogenic. The result depends on the fluoride concentration assumed for the municipal and natural water endmembers. Measured values for municipal water have varied from 0.6 to 1.1 ppm during the study (mean = 0.8). Regardless of the tracer considered, our results indicate that much of the water in the urban streams in Austin is of anthropogenic origin. Whereas mixing between the natural stream and urban water endmembers appears to be the primary control on Austin-area stream water, additional processes must operate to account for the observed range in compositions (Fig. 8). Advances in our understanding of the relative importance of the range of processes and sources discussed in this study will likely come from detailed analysis of individual watersheds.

6.2. Sensitivity

Using a Sr isotope analysis of stream water, a component of anthropogenic water as small as 5 vol.% of the total stream discharge can be detected in the Austin area. This value takes into account the differing Sr concentrations in the two waters (Table 3), and it depends on the $^{87}Sr/^{86}Sr$ value of the anthropogenic water, which has varied over time. This is comparable to the sensitivity using F concentrations (assuming 5% analytical uncertainty), but in contrast the Sr calculations are unaffected by processes such as evaporation, mineral precipitation and sorption because Sr isotope fractionation will be negligible during these processes (Banner and Kaufman, 1994). In localities having a greater contrast in $^{87}Sr/^{86}Sr$ values between municipal water and natural stream water, even smaller components of municipal water could be detected.
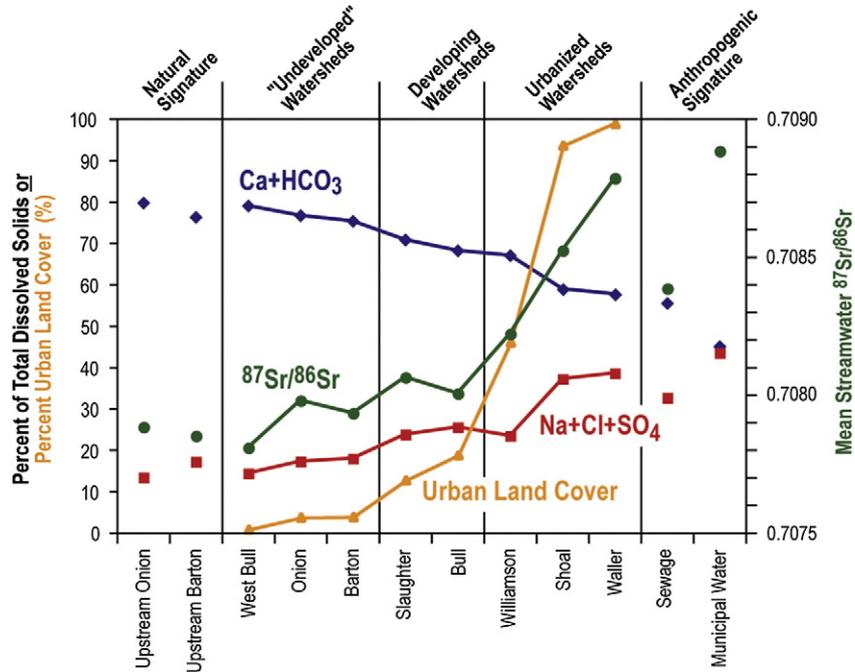
Fig. 9. Relationship between stream-water $^{87}Sr/^{86}Sr$, relative concentrations of $(Ca + HCO_3)$ and $(Na + Cl + SO_4)$, and percent urban land cover in Austin-area watersheds. Stream-water compositions can be accounted for by the addition of variable amounts of municipal water and sewage to natural stream water. The proportion of the anthropogenic water correlates with the degree of urbanization, as measured by percent urban land cover (Table 4). The individual r^2 values between $^{87}Sr/^{86}Sr$, $Ca + HCO_3$, and $Na + Cl + SO_4$ versus percent urban land cover are 0.97, −0.96, and 0.95, respectively. Stream-water composition begins to be discernibly affected when about 20% of the watershed is urbanized. Values are means for the different watersheds. Urban land cover data from United States Geological Survey (1990).

6.3. Effects of urbanization on recharge and base flow

The common assumption that urbanization, because of increased impervious cover leading to decreased recharge, reduces base flow in urban streams needs to be reconsidered for the Austin, Texas area (Wiles and Sharp, 2008; Sharp et al., 2009). The large addition of anthropogenic water to the more urbanized watersheds through irrigation and/or infrastructure leakage generally offsets the effects of increased impervious cover. One recent example of this is the change observed in a Bull Creek tributary, which shifted from an ephemeral to a perennial stream (Austin American-Statesman, 2008).

6.4. Critical threshold of urbanization

In watersheds that are undergoing urbanization, the Sr isotope method may be used to identify the threshold amount of urbanization, above which urbanization begins to affect the stream-water composition. For the Austin area, a modern "snapshot" suggests that stream-water composition ($^{87}Sr/^{86}Sr$, Na, Cl, and SO_4) is measurably affected when approximately 20% of the watershed has become urbanized (Fig. 9), although some parameters such as Ca and HCO_3 may exhibit increases even below 10% urban land cover. This does not take into account, however, the additional effect of age on infrastructure leakage. Because the changes to stream-water chemistry due to the age effect would be delayed, the actual urbanization threshold could be less than 20%. This value would also depend on other factors such as maintenance of water and sewage lines and watering restrictions.

6.5. Applicability to other municipal water resource systems

In regions where municipal water is isotopically distinct from local stream and/or ground water, there exists the potential to identify anthropogenic impacts on stream or ground water by the addition of municipal water (e.g. Butler and Verhagen, 1997). This condition may be satisfied in cities that use water from aquifers or from surface-water sources that are located in or drain terrains that are geologically distinct from that of the city. Although the application of Sr isotopes requires other geochemical and/or biological tracers such as F, NO_3, or bacteria to distinguish contributions from municipal supply vs. sewage, the Sr isotope signal can be a robust indicator of the total anthropogenic water input. An example of another city where this method should be applicable is St. Louis, MO. It is built upon marine carbonate rocks of Mississippian age, with $^{87}Sr/^{86}Sr$ values generally <0.7085 (Burke et al., 1982; Banner and Kaufman, 1994). The city derives its municipal water from both the Mississippi and Missouri Rivers (City of St. Louis, 2009) for which $^{87}Sr/^{86}Sr$ values for nearby locations are 0.70953 and 0.70998, respectively (Goldstein and Jacobsen, 1987).

6.6. Potential for temporal reconstruction of impacts of urbanization

Sr isotopes may be used as a proxy for reconstructing temporal changes in the impact of urbanization on stream water quantity and quality. This approach may be applicable in regions such as the Austin area using tree rings, fresh-water bivalves, and mineral deposits such as spring travertine (Mack et al., 2008; DeMott et al., 2006).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.chemgeo.2011.01.011.

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