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SPECIAL FEATURE: ISOSCAPES

Strontium isotopes in tap water from the coterminous USA

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Abstract. Strontium isotope analysis has proven useful in geo-location investigations of organic and inorganic materials and may complement the region-of-origin information provided by hydrogen and oxygen stable isotope analysis. In this study, we analyzed 99 drinking (tap) water samples collected from 95 municipal water systems across the USA to investigate the potential that $^{87}Sr/^{86}Sr$ can be used to provenance samples from managed hydrological systems. Results from a leaching and exchange experiment demonstrated that non-ideal storage conditions did not prohibit Sr isotope analysis of previously archived water samples stored in glass. Tap water samples were analyzed via multi-collector inductively coupled plasma mass spectrometry, which was preceded by a novel, automated, in-line Sr purification method. Measured tap water $^{87}Sr/^{86}Sr$ was compared to expected $^{87}Sr/^{86}Sr$ for collection location, which was predicted using four published isotope landscape (isoscape) models: age of bedrock (bedrock model), age plus major and minor lithology of bedrock (major bedrock model), weathering of Sr from rock (local water model), and surface fluxes within watershed (catchment model). The geologic history of the geographic regions represented by collected tap waters was diverse and we therefore expected significant covariation in measured and modeled $^{87}Sr/^{86}Sr$ values. Tap water exhibited large ranges in both Sr concentration (0–1.9 mg/L) and $^{87}Sr/^{86}Sr$ (0.7037–0.7320). Measured tap water $^{87}Sr/^{86}Sr$ ratios were significantly and positively correlated with predictions based on bedrock and catchment models. However, these bedrock and catchment models explained relatively little of the tap water Sr isotopic variation (~10% and 17%, respectively), suggesting that the factors affecting drinking water $^{87}Sr/^{86}Sr$ are complex and more numerous than the variables included in current water models. This could be due to the reliance of some municipal water systems on groundwater, rather than surficial water sources; the natural movement of water across distinct geologic gradients; and/or the managed transport of water from source to point-of-use. Although published isoscape models for predicting Sr isotopic variation within the continental USA are reasonable approaches for estimating surface water $^{87}Sr/^{86}Sr$, additional efforts are needed to develop a prediction model specifically for tap water $^{87}Sr/^{86}Sr$.

Key words: $^{87}Sr/^{86}Sr$; automated Sr purification column chemistry; drinking water; Isoscapes Special Feature; isotope landscapes; isotope ratio analysis; multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS); municipal water supply; tap water.

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Introduction

There is growing curiosity in stable isotope applications to understand the origins of goods, materials, and organisms; this interest is demonstrated by the recent publication of several reviews of the analytical technique for source investigation (e.g., Hobson 1999, Kelly et al. 2005, West et al. 2006, Ehleringer et al. 2010, Oulhote et al. 2011). Most geo-location research using stable isotope analysis has focused on predictable, spatially dependent variations in the hydrogen (δ^2H) and oxygen (δ^{18}O) stable isotope ratios of water and the transfer of those isotopic variations through ecological systems and into plant and animal tissues (see Bowen 2010, Ehleringer et al. 2010 and references therein). Yet the analysis of other elements, such as strontium (Sr), may also prove useful for geo-location (Aggarwal et al. 2008) and could complement the region-of-origin information provided by hydrogen and oxygen isotopes. This is because the relative abundances of Sr isotopes in the environment vary spatially and are largely dependent upon local geology (Åberg 1995, Bentley 2006).

There are four natural isotopes of Sr, 3 non-radiogenic (^{84}Sr, ^{86}Sr, and ^{88}Sr) and 1 radiogenic, the product of radioactive decay. The radiogenic isotope, ^{87}Sr, is formed through the β-decay of ^{87}Rb, which has a half-life of 48.8×10^9 years. By convention, measured Sr isotope ratios are reported as ^{87}Sr/^{86}Sr and calculated as

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{T2} = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{T1} + \left(\frac{^{87}\mathrm{Rb}}{^{86}\mathrm{Sr}}\right)(e^{\lambda t} - 1),$$

where $T1$ and $T2$ denote points of time in the geologic past and present, respectively; λ is 1.42×10^{-11}/year, the decay constant for ^{87}Rb; and t is defined as $T1 - T2$, in years. Measured ^{87}Sr/^{86}Sr of any material is therefore dependent upon the initial ^{87}Sr/^{86}Sr and Rb/Sr ratios of the material and its age. Due to the long half-life of ^{87}Rb, significant variations in measured ^{87}Sr/^{86}Sr are generally observed when geological materials are tens of millions of years old or older. Young materials with low Rb concentrations, such as modern volcanic basalts, are typically characterized by low ^{87}Sr/^{86}Sr (i.e., 0.702 to 0.706) whereas old and Rb-rich materials, such as Paleozoic granites, have higher ^{87}Sr/^{86}Sr (i.e., 0.710 and greater) (Capo et al. 1998, Beard and Johnson 2000). Unaltered limestones spanning the Phanerozoic eon (~540 Ma to present) have intermediate ^{87}Sr/^{86}Sr values ranging from 0.7068 to 0.7092, reflecting the Sr isotopic composition of seawater as a mixture of radiogenic and non-radiogenic Sr sources (McArthur and Howarth 2004).

Capitalizing on variability in the geologic ages of different geographic regions, Beard and Johnson (2000) developed a model for predicting ^{87}Sr/^{86}Sr within the continental USA. This spatial representation of predicted Sr isotopic variation across the landscape ('isoscape' model) was built upon the premise that bedrock age was the principal determinant of ^{87}Sr/^{86}Sr within ecosystems (Beard and Johnson 2000) and was used to investigate human birth place and subsequent movements from place of birth. Due to similarities in charge and atomic radius, Sr substitutes for calcium (Ca) in biological systems (Åberg 1995) and thus both primary producers and higher-level consumers record information about local geology in the ^{87}Sr/^{86}Sr of their tissues. Some of the most well documented examples of using ^{87}Sr/^{86}Sr for geo-location are the analysis of tooth enamel and bone apatite from human remains to reconstruct movements of historic (Price et al. 2002, Hodell et al. 2004, Bentley 2006, Montgomery 2010, Price et al. 2011) and modern (Aggarwal et al. 2008, Juarez 2008) populations. More recently, measurements of ^{87}Sr/^{86}Sr have been used to investigate the regions-of-origin of foods and drugs consumed by humans, including coffee (Rodrigues et al. 2010, Rodrigues et al. 2011), dairy products (Rossmann et al. 2000, Crittenden et al. 2007), juice (Rummel et al. 2010), heirloom vegetables (Swoboda et al. 2008), wine (Almeida and Vasconcelos 2004), and marijuana (West et al. 2009). Measured ^{87}Sr/^{86}Sr has also proven useful in reconstructing the movements of non-human animals, most especially birds (Chamberlain et al. 1997, Font et al. 2007, Sellick et al. 2009) and fish (Ingram and Weber 1999, Kennedy et al. 2000, Barnett-Johnson et al. 2008).

The Beard and Johnson (2000) isoscape model is a valuable tool for understanding general patterns in predicted ^{87}Sr/^{86}Sr at large geographic scales. Nevertheless, two constants in this age-based model complicate its application: (1) a uniform Rb/Sr ratio for the earth's crust, and (2) a fixed initial ^{87}Sr/^{86}Sr for parent material regard-

less of actual bedrock lithology. (Because the model authors discuss these assumptions in detail [Beard and Johnson 2000], we will not describe the ramifications of the presumptions here.) At smaller geographic scales, additional variables such as lithology, surface weathering rates, exogenous Sr deposition, and even fertilizer application (Vitòria et al. 2004) may play a substantial role in determining ecosystem $^{87}Sr/^{86}Sr$.

Investigators typically assume there is little or no mass-dependent fractionation of Sr during biological, chemical, and ecological processes (Åberg 1995, Capo et al. 1998) and $^{87}Sr/^{86}Sr$ of a collected specimen directly reflects that of Sr available in the local ecosystem. However, the Sr isotopic composition of some materials, such as water, does not necessarily reflect total $^{87}Sr/^{86}Sr$ of local bedrock. Instead, water $^{87}Sr/^{86}Sr$ reflects that of the Sr available for exchange (i.e., 'mobile' or 'weatherable' Sr) (Stewart et al. 1998, Shand et al. 2009) and the degree to which different minerals are susceptible to weathering may therefore disproportionately affect $^{87}Sr/^{86}Sr$ of a water sample. For instance, $CaCO_3$ in limestones has a much greater impact on water $^{87}Sr/^{86}Sr$ than Ca-silicates from other rock types.

In order to more accurately describe variations in water $^{87}Sr/^{86}Sr$ at large geographic scales, Bataille and Bowen (2012) recently built upon the work of Beard and Johnson (2000) to generate a series of new Sr isoscape models for the continental USA. The authors first accounted for major and minor lithology and Sr concentration in addition to bedrock age to predict $^{87}Sr/^{86}Sr$ in a 'major bedrock' model. The major bedrock model was further modified with Sr transfer and weathering rates to predict $^{87}Sr/^{86}Sr$ that would be leached at each map point in a 'local water' model. To geographically expand the local water $^{87}Sr/^{86}Sr$ predictions, the authors then estimated the flux of surface waters through each map point to generate a flow-weighted model and finally integrated these flow-weighted estimates within watersheds to build a 'catchment' model. We refer the reader to Bataille and Bowen (2012) for a complete description of the models and simply note here that the variables used as the foundation for model construction—bedrock age, major and minor lithology, and Sr concentration—are more numerous than those used in the Beard and Johnson (2000) model, which accounted only for bedrock age while assuming that parent lithology was constant across the landscape.

Methods and models for predicting water $^{87}Sr/^{86}Sr$ like those published by Beard and Johnson (2000) and Bataille and Bowen (2012) are important because of the diverse uses of Sr isotopic variation in natural waters to understand ecosystem processes (Capo et al. 1998, Shand et al. 2009). Examples include the application of $^{87}Sr/^{86}Sr$ measurements to elucidate marine chronostratigraphy (Veizer 1989, McArthur and Howarth 2004), mineral weathering (Åberg et al. 1989, Clow et al. 1997, Horton et al. 1999), surface water and groundwater interactions (Négrel and Petelet-Giraud 2005, Vengosh et al. 2007), and water source mixing (Hogan et al. 2000, Land et al. 2000). Recent publications have demonstrated that $^{87}Sr/^{86}Sr$ is useful for understanding the provenance of water (Evans et al. 2009, Voerkelius et al. 2010, Frei and Frei 2011), which has forensic implications for sourcing individuals (Rauch et al. 2007) or for investigating the origin of waters with particular properties (i.e., natural mineral waters) (Montgomery et al. 2006). While published studies on water origin have focused on bottled and surface waters, Sr isotope analysis may also be useful for understanding the processes impacting waters subjected to intense human management, such as drinking (tap) waters.

In this study, we used tap water collected from municipal water systems to investigate patterns in Sr isotopic variation within the coterminous USA. We hypothesize that local bedrock age and lithology will generally be good predictors of tap water $^{87}Sr/^{86}Sr$ and that published Sr isoscape models (Beard and Johnson 2000, Bataille and Bowen 2012) can be successfully used to estimate tap water $^{87}Sr/^{86}Sr$. We expect disagreements in measured and modeled $^{87}Sr/^{86}Sr$ only in areas where the geology of the tap water source is drastically different from that underlying the town or city of its collection, as when water is transported long distances (e.g., water conveyance through canals and aqueducts in southern California) or when water crosses abrupt geological boundaries, such as the transition from mountain ranges in the Rocky Mountains to the high plains.

Methods

Sample acquisition and storage

Ninety-nine samples from municipal water supplies (tap water) were analyzed for this study. The tap water samples were collected in 95 municipalities of the coterminous USA, located in 29 states and the District of Columbia (Fig. 1, Supplement). The majority ($n = 77$) were collected during a cross-country sampling effort in summer 2004 (Ehleringer et al. 2008); the remaining water samples were collected between 2005 and 2011 (Supplement). Water samples were initially procured for hydrogen and oxygen stable isotope measurements and collected in 1- or 3-dram borosilicate glass vials. Since original collection date, vials were stored capped and sealed (Parafilm M laboratory film; Pechiney Plastic Packaging, Menasha, Wisconsin, USA) at room temperature and in the dark.

To quantify the potential effect of storage in glass containers on measured Sr concentration and $^{87}Sr/^{86}Sr$, we conducted a leaching and exchange experiment. Visually clean glass vials similar to those used for sample collection as well as 30-mL acid-cleaned low-density polyethylene (LDPE) bottles were filled with both filtered and unfiltered stream water (Dry Creek, near the University of Utah campus in Salt Lake City, Utah, USA) and with tap water collected from five separate residences within the Salt Lake Valley, Utah, USA. No acid was added to the glass vials; 10 drops of concentrated ultra pure HNO_3 was added to waters in LDPE bottles (~3% total acid). To generate analytical 'blanks', three glass vials and one acid-cleaned LDPE bottle were filled with ultra pure Milli-Q water (Millipore, Billerica, Massachusetts, USA) and the water in the LDPE bottle was subsequently acidified. We note that the LDPE collection scheme is the method typically recommended for collecting water samples for elemental analysis (Capo et al. 1998). Filled vials and bottles were capped, sealed, and allowed to sit undisturbed at room temperature and in the dark. From August to November 2011, sub-samples were collected from filled vials and bottles monthly for Sr concentration analysis ($n = 4$ per container). A final sub-sample of all tap waters and the filtered Dry Creek water was collected March 2012 for $^{87}Sr/^{86}Sr$ analysis.

Sample analysis

Due to limited material, 0.1 mL aliquots of the collected USA tap waters were filtered (0.45 mm) and then diluted with 1.0 mL 2.4% ultrapure HNO_3. In contrast, 1 mL sub-samples collected during the leaching and exchange experiment were filtered and then diluted with 3 mL 2.4% ultrapure HNO_3. Filtered, acidified water samples were spiked with a 10 ppb In internal standard and Sr abundance was measured via inductively coupled plasma quadrupole-mass spectrometry using an Agilent 7500ce instrument (Agilent Technologies, Santa Clara, California, USA) at the ICP-MS Metals Lab in the Department of Geology & Geophysics at the University of Utah, Salt Lake City, Utah, USA. The USGS standard reference solution T-205 was measured as an external standard at least five times within each analytical run. Four tap water samples (collected in Byron, Illinois; Rolla, Missouri; Chadds Ford, Pennsylvania; and Kerrville, Texas) had measured Sr contents too low for subsequent isotope analysis (i.e., <5 μg/L Sr). The $^{87}Sr/^{86}Sr$ ratios of the remaining 95 tap water samples and the March 2012 sub-samples from the leaching and exchange experiment were measured via multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using a Thermo Scientific Neptune (Bremen, Germany).

Samples were analyzed via MC-ICP-MS after employing a novel Sr purification method (Mackey and Fernandez 2011) that automates the purification of Sr from liquid samples by utilizing a peristaltic pump, a pair of 6-way valves, an in-line separation column, and a SC-2 DX autosampler with a FAST2 valve block (Elemental Scientific, Omaha, Nebraska, USA). Briefly, a water sample is loaded by the autosampler into a column packed with Sr resin (Eichrom Technologies, Lisle, Illinois, USA) and then washed directly from the column into the instrument spray chamber. Variable speed settings on the peristaltic pump allow samples to be rapidly loaded into the purification column where Sr is trapped while all other elements are rinsed away; purified Sr is then slowly eluted from the column into the spray chamber. Each sample (or standard) is followed by a blank to monitor the condition of the purification column. Ideally samples and standards should contain less than 250 μg/L total Sr to avoid saturating the

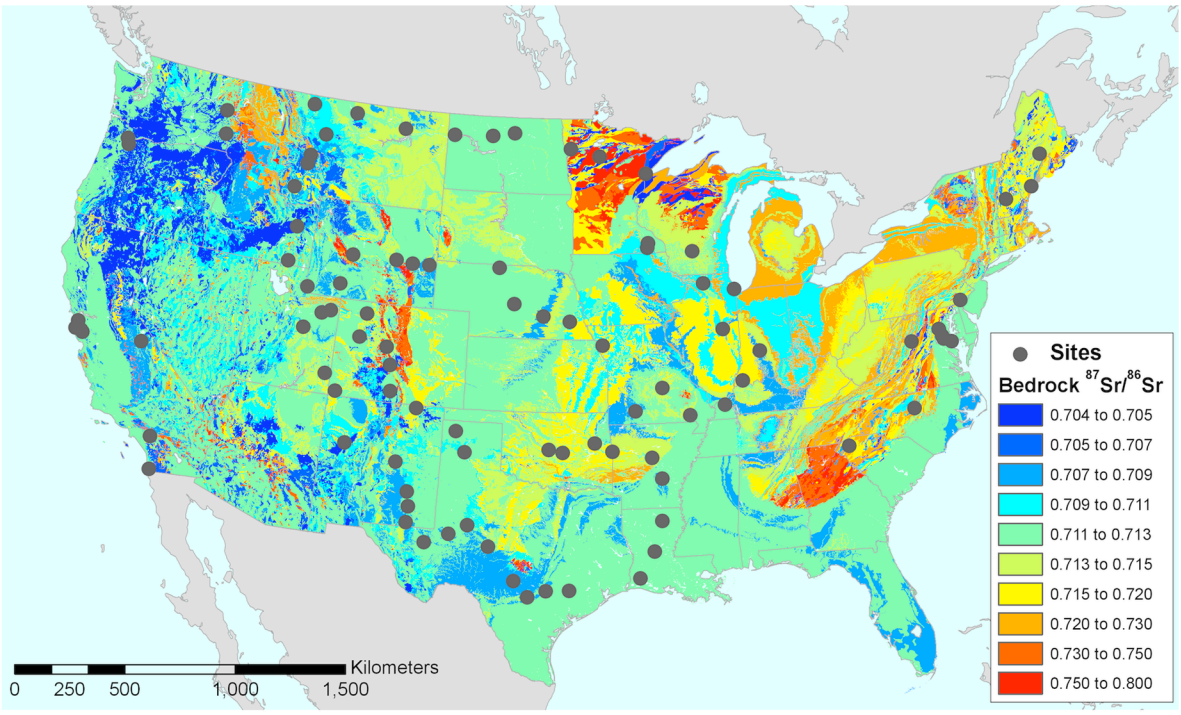

Fig. 1. Sites of tap water sample collection (gray circles), displayed on an isoscape of predicted $^{87}Sr/^{86}Sr$ variation in the coterminous USA. Isoscape from Bataille and Bowen (2012) and based on the bedrock age model of Beard and Johnson (2000).

column and instrument detectors. Sample/standard + blank pairs require approximately 30 minutes for analysis; using the automated Sr purification method, 24 sample + blank pairs and 11 standard + blank pairs can be analyzed per day. Sr data for the samples and standards were blank- and interference-corrected and then normalized for instrumental mass discrimination using a defined $^{86}Sr/^{88}Sr$ of 0.1194.

Solutions of the international Sr standard reference material SRM 987 (NIST; www.nist.gov) were analyzed alongside water samples. Within-run reproducibility of SRM 987 ranged from ± 0.00002 (2σ, $n = 22$) when analyzed at a concentration of 150 μg/L to ± 0.00018 (2σ, $n = 11$) when analyzed at a concentration of 20 μg/L. The long-term mean $^{87}Sr/^{86}Sr$ of SRM 987 analyzed using the automated purification method and MC-ICP-MS at concentrations of 10–200 μg/L is 0.71027 ± 0.00010 (2σ, $n = 239$).

Statistical analysis

Predictions for $^{87}Sr/^{86}Sr$ were extracted from four published Sr isoscape models using GIS and the coordinates for sample collection sites (Supplement), which were assigned as the municipality center using the Global Gazetteer (www.fallingrain.com/world). Tested isoscapes included the bedrock model of Beard and Johnson (2000) as well as the major bedrock, local water, and catchment models of Bataille and Bowen (2012). Predictions from the Beard and Johnson (2000) bedrock model were extracted as 'epsilon' ($\varepsilon^{87}Sr$) and converted to $^{87}Sr/^{86}Sr$ as

$$^{87}Sr/^{86}Sr = \left[\left(\frac{\varepsilon^{87}Sr}{10,000}\right) + 1\right] \times (^{87}Sr/^{86}Sr)_{bulk},$$

where $(^{87}Sr/^{86}Sr)_{bulk}$ is defined as 0.7045 for bulk earth. Measured $^{87}Sr/^{86}Sr$ ratios for tap water samples were compared to $^{87}Sr/^{86}Sr$ predicted from each model by calculating the coefficient of determination (r^2). Statistical analyses were completed using Prism version 5.0c (GraphPad Software, La Jolla, California, USA) and Microsoft Excel 2008 for Mac.

Results

Leaching and exchange experiment

Sub-samples of water from the glass vials and LDPE bottles used in the leaching and exchange experiment were collected and analyzed for Sr concentration mid-month from August to November 2011. Sub-samples of Milli-Q water collected from glass in August 2011 were not analyzed. Sub-samples from all other containers were collected and analyzed for Sr concentration 4 times during the experiment. A final collection of tap water and filtered Dry Creek water was completed in mid-March 2012; these sub-samples were analyzed for $^{87}Sr/^{86}Sr$.

The Sr concentration of the acidified ultra pure Milli-Q water stored in a LDPE bottle was below detection limit at all sub-sampling time points. On the contrary, Sr concentration in the Milli-Q water stored in glass was high enough for detection at all sub-sampling intervals, except the final time point for one vial (mean = 1.0 μg/L, $1\sigma = 0.5$ μg/L, $n = 8$; data not shown). There was no trend in concentration changes for Milli-Q water stored in glass vials during the course of the experiment.

The Sr concentrations measured for Milli-Q water stored in glass were several orders of magnitude smaller than the concentrations measured for the six natural water samples used in the experiment, which ranged from ~0.2 mg/L for tap water to >1 mg/L for creek water (Table 1). There were no trends in concentration change of the natural waters during the 4 months of storage in either glass vials or LDPE bottles. Using the mean Sr concentration measured for Milli-Q water stored in vials as baseline, the contribution of glass storage containers to the total measured Sr concentrations of the creek or Salt Lake Valley tap waters was ≤0.5%. Since the concentration of Sr for Milli-Q water stored in a LDPE bottle with acid for 4 months was below detection limit, we assume no exogenous contribution of Sr to the natural waters stored in plastic bottles during the leaching and exchange experiment. A paired *t*-test comparison (with $\alpha = 0.05$) of filtered creek, unfiltered creek, and tap water samples stored in glass vials and in LDPE bottles found no significant difference in measured Sr concentrations between the two types of storage containers ($P = 0.63$).

There was a significant difference in measured $^{87}Sr/^{86}Sr$ between Salt Lake Valley tap and filtered creek waters stored in glass vials and those stored in LDPE bottles with acid, based on a paired *t*-test comparison ($t = 4.599$, df = 5, $P = 0.0058$; Table 2). Measured $^{87}Sr/^{86}Sr$ was higher for the water samples stored in glass than in LDPE. The mean ($\pm 1\sigma$) difference in $^{87}Sr/^{86}Sr$ between storage containers was 0.00045 (±0.00004) for Salt Lake Valley tap waters with a measured Sr concentration of ~0.2 mg/L ($n = 3$), 0.00020 (±0.00003) for Salt Lake Valley tap waters containing ~0.5 mg/L Sr ($n = 2$), and 0.00010 for the filtered creek water (Tables 1 and 2).

Based on the results of this leaching and exchange experiment, $^{87}Sr/^{86}Sr$ is reported with 4 significant figures (i.e., 0.7113 rather than 0.71128) throughout the remainder of the text. The uncertainty for measured $^{87}Sr/^{86}Sr$ is 0.0004, defined as the mean difference between Salt Lake Valley tap waters stored in glass versus LDPE bottles with acid.

Table 1. Sr concentration (mg/L) data for waters collected in August 2011 and stored in either glass or plastic containers for 4 months.

	August 2011		September 2011		October 2011		November 2011	
Water sample	Glass	LDPE	Glass	LDPE	Glass	LDPE	Glass	LDPE
Dry Creek, filtered	1.117	1.098	0.930	0.976	1.071	1.042	0.914	0.981
Dry Creek, unfiltered	1.106	1.076	0.929	0.924	1.058	1.122	0.945	0.904
Salt Lake Valley tap 1	0.229	0.229	0.201	0.206	0.228	0.231	0.202	0.205
Salt Lake Valley tap 2	0.214	0.207	0.185	0.187	0.208	0.210	0.191	0.192
Salt Lake Valley tap 3	0.488	0.482	0.424	0.431	0.462	0.485	0.426	0.439
Salt Lake Valley tap 4	0.216	0.212	0.187	0.190	0.216	0.211	0.194	0.197
Salt Lake Valley tap 5	0.455	0.450	0.397	0.401	0.451	0.456	0.402	0.407

Notes: LDPE = low density polyethylene bottles, which had been acid-cleaned prior to use. Water stored in LDPE bottles was acidified with HNO_3 (~3% total acid). Salt Lake Valley tap water samples were collected from 5 separate residences.

Table 2. $^{87}Sr/^{86}Sr$ data for waters collected in August 2011 and stored in either glass or plastic containers until March 2012.

Water sample	Measured $^{87}Sr/^{86}Sr$ Glass	Measured $^{87}Sr/^{86}Sr$ LDPE	Difference, Glass − LDPE Δ
Dry Creek, filtered	0.70831	0.70822	+0.00010
Dry Creek, unfiltered	...	...	...
Salt Lake Valley tap 1	0.70984	0.70939	+0.00045
Salt Lake Valley tap 2	0.71023	0.70974	+0.00049
Salt Lake Valley tap 3	0.70947	0.70925	+0.00022
Salt Lake Valley tap 4	0.71038	0.70996	+0.00042
Salt Lake Valley tap 5	0.71262	0.71244	+0.00018

Notes: Abbreviations and sample descriptions are as in Table 1. Difference (Δ) was calculated as $^{87}Sr/^{86}Sr$ of water in glass minus $^{87}Sr/^{86}Sr$ of the water in LDPE.

Tap water samples

Measured Sr concentrations for the 99 tap waters collected across the USA ranged from essentially 0 μg/L to 1.9 mg/L (Table 3). The most concentrated sample was collected in Andover, New Hampshire from a household that relied on well water. Three tap water samples contained no detectable Sr: Rolla, Missouri; Chadds Ford, Pennsylvania; and Kerrville, Texas. Measured $^{87}Sr/^{86}Sr$ for water samples with Sr contents >5 μg/L ($n = 95$) ranged from 0.7037 to 0.7320 (Table 3), with a mean of 0.7112 ± 0.0038 (1σ), and were not normally distributed (D'Agostino and Pearson omnibus normality test: $K^2 = 27.0$, $P < 0.0001$; Fig. 2). The lowest $^{87}Sr/^{86}Sr$ was measured for tap water collected in Beavercreek, Oregon whereas the highest was measured for the sample collected in Spokane, Washington.

We analyzed three independent water samples collected from separate locations within two cities, Duluth, Minnesota and Valentine, Nebraska. The mean Sr content (±1σ) was 20 (±3) μg/L and 127 (±20) μg/L for Duluth and Valentine replicates, respectively ($n = 3$ for each city). Mean measured $^{87}Sr/^{86}Sr$ (±1σ) for the Duluth replicates was 0.7165 (±0.0001) and for the Valentine replicates was 0.7099 (±0.0000). We note that Table 3 presents data for only one water sample per city.

Comparisons of modeled and measured tap water $^{87}Sr/^{86}Sr$

The range of predicted $^{87}Sr/^{86}Sr$ was largest for the Bataille and Bowen (2012) major bedrock model (max. − min. = 0.0573). This was due to $^{87}Sr/^{86}Sr$ estimated for Bemidji, Minnesota (0.7614; Table 3), which was the highest prediction of any of the four tested isoscape models. Predictions from the Beard and Johnson (2000) bedrock model as well as the Bataille and Bowen (2012) local water and catchment models generally ranged from 0.704 to 0.738 (Table 3). Because of the conversion of $\varepsilon^{87}Sr$ derived from rock type categories to $^{87}Sr/^{86}Sr$, Beard and Johnson (2000) model predictions were categorically distributed (see Fig. 3). Predictions from the Bataille and Bowen (2012) major bedrock, local water, and catchment models were not normally distributed (major bedrock: $K^2 = 147.4$, local water: $K^2 = 86.9$, and catchment: $K^2 = 131.4$; $P < 0.0001$ for all). Approximately 50% (49 of 95) of $^{87}Sr/^{86}Sr$ ratios predicted from the major bedrock and local water models were 0.7113 since parent rocks with missing information (i.e., an unconsolidated lithology) were assigned Rb/Sr = 0.24.

Measured tap water $^{87}Sr/^{86}Sr$ ratios were significantly positively correlated with $^{87}Sr/^{86}Sr$ predicted from the Beard and Johnson (2000) bedrock model ($P = 0.0023$, df = 89) and from the Bataille and Bowen (2012) catchment model ($P < 0.0001$, df = 89), although the fraction of variance in measured $^{87}Sr/^{86}Sr$ explained by predicted $^{87}Sr/^{86}Sr$ was relatively low for both models ($r^2 = 0.10$ and 0.17, respectively). The slope of the relationship between measured and modeled water $^{87}Sr/^{86}Sr$ was closest to 1 for the catchment predictions (0.42). We note that Duluth, Minnesota had the highest $^{87}Sr/^{86}Sr$ estimated from the catchment model (0.7383; Table 3, Fig. 3) and removal of this data point increased the correlation and slope between measured and modeled data to 0.24 and 0.81, respectively. Measured tap water $^{87}Sr/^{86}Sr$ ratios were not significantly correlated with $^{87}Sr/^{86}Sr$ predicted from either

Table 3. Measured and modeled Sr data for tap water samples collected in 95 municipalities across the coterminous USA.

City	State	Sr (μg/L)	$^{87}Sr/^{86}Sr$ Measured tap water	Bedrock model†	Major bedrock model‡	Local water model‡	Catchment model‡	Difference, Tap − Catchment Δ
Conway	AR	24	0.7151	0.7080	0.7132	0.7150	0.7139	0.0012
Fort Smith	AR	34	0.7138	0.7080	0.7194	0.7181	0.7103	0.0035
Pine Bluff	AR	235	0.7093	0.7049	0.7113	0.7113	0.7094	−0.0001
Chula Vista	CA	285	0.7071	0.7054	0.7113	0.7113	0.7083	−0.0012
Half Moon Bay	CA	58	0.7078	0.7049	0.7114	0.7114	0.7091	−0.0014
Mammoth Lakes	CA	104	0.7074	0.7059	0.7113	0.7113	0.7096	−0.0022
Palo Alto	CA	45	0.7067	0.7049	0.7113	0.7113	0.7104	−0.0037
Riverside	CA	332	0.7139	0.7059	0.7113	0.7113	0.7093	0.0045
San Francisco	CA	58	0.7070	0.7073	0.7113	0.7113	0.7112	−0.0042
Sunnyvale	CA	133	0.7074	0.7049	0.7113	0.7113	0.7104	−0.0031
Alamosa	CO	68	0.7099	0.7049	0.7115	0.7115	0.7080	0.0019
Craig	CO	39	0.7132	0.7059	0.7113	0.7113	0.7132	0.0000
Leadville	CO	39	0.7149	0.7080	0.7113	0.7113	0.7112	0.0036
Rifle	CO	441	0.7110	0.7054	0.7113	0.7113	0.7106	0.0005
Salida	CO	260	0.7135	0.7242	0.7113	0.7113	0.7112	0.0022
Towaoc	CO	173	0.7101	0.7059	0.7150	0.7144	0.7133	−0.0032
Washington	DC	127	0.7112	0.7059	0.7113	0.7113	0.7109	0.0004
Malad	ID	175	0.7126	0.7087	0.7113	0.7113	0.7096	0.0030
Osgood	ID	288	0.7091	0.7049	0.7113	0.7113	0.7053	0.0038
Byron	IL	1	...	...	...	...	...	...
Chicago	IL	100	0.7100	0.7091	0.7104	0.7100	0.7100	0.0000
Mahomet	IL	296	0.7095	0.7091	0.7221	0.7223	0.7093	0.0002
Bloomington	IN	37	0.7136	0.7091	0.7089	0.7089	0.7090	0.0046
Evansville	IN	214	0.7109	0.7080	0.7195	0.7182	0.7155	−0.0046
Paducah	KY	69	0.7110	0.7059	0.7113	0.7113	0.7109	0.0001
Alexandria	LA	24	0.7110	0.7049	0.7113	0.7113	0.7113	−0.0003
Lake Charles	LA	306	0.7083	0.7049	0.7113	0.7113	0.7113	−0.0030
Monroe	LA	38	0.7111	0.7049	0.7113	0.7113	0.7113	−0.0001
California	MD	87	0.7093	0.7049	0.7113	0.7113	0.7130	−0.0037
Dentsville	MD	27	0.7101	0.7049	0.7113	0.7113	0.7115	−0.0014
White Plains	MD	10	0.7122	0.7049	0.7113	0.7113	0.7115	0.0007
Newport	ME	247	0.7147	0.7091	0.7143	0.7144	0.7097	0.0049
Portland	ME	15	0.7121	0.7045	0.7092	0.7092	0.7106	0.0015
Bemidji	MN	37	0.7178	0.7320	0.7614	0.7360	0.7207	−0.0029
Chatfield	MN	63	0.7096	0.7101	0.7094	0.7096	0.7103	−0.0007
Crookston	MN	160	0.7170	0.7320	0.7048	0.7057	0.7120	0.0050
Duluth	MN	24	0.7165	0.7172	0.7059	0.7056	0.7383	−0.0217
Wykoff	MN	70	0.7106	0.7101	0.7094	0.7096	0.7103	0.0003
Ozark	MO	11	0.7123	0.7080	0.7089	0.7089	0.7091	0.0031
Poplar Bluff	MO	26	0.7137	0.7049	0.7143	0.7139	0.7115	0.0022
Rolla	MO	0	...	...	...	...	...	...
St. Joseph	MO	253	0.7091	0.7080	0.7192	0.7093	0.7092	−0.0001
Boulder	MT	175	0.7087	0.7059	0.7113	0.7113	0.7080	0.0007
Cut Bank	MT	152	0.7129	0.7059	0.7091	0.7076	0.7087	0.0041
Dillon	MT	531	0.7108	0.7049	0.7113	0.7113	0.7086	0.0022
Glasgow	MT	376	0.7096	0.7059	0.7113	0.7113	0.7129	−0.0033
Great Falls	MT	189	0.7119	0.7059	0.7113	0.7113	0.7079	0.0040
Havre	MT	216	0.7096	0.7059	0.7119	0.7120	0.7113	−0.0018
Helena	MT	92	0.7096	0.7059	0.7056	0.7056	0.7074	0.0022
Chapel Hill	NC	71	0.7076	0.7101	0.7097	0.7097	0.7113	−0.0037
Minot	ND	71	0.7088	0.7054	0.7113	0.7113	0.7113	−0.0025
Rugby	ND	52	0.7089	0.7059	0.7113	0.7113	0.7113	−0.0024
Williston	ND	146	0.7095	0.7054	0.7113	0.7113	0.7113	−0.0018
Broken Bow	NE	222	0.7097	0.7049	0.7115	0.7114	0.7114	−0.0017
Grand Island	NE	487	0.7119	0.7059	0.7077	0.7077	0.7078	0.0042
Lincoln	NE	257	0.7107	0.7059	0.7122	0.7130	0.7092	0.0015
Valentine	NE	150	0.7099	0.7049	0.7115	0.7114	0.7097	0.0002
Andover	NH	1918	0.7163	0.7091	0.7171	0.7166	0.7105	0.0058
Artesia	NM	7	0.7143	0.7049	0.7113	0.7113	0.7089	0.0054
Carlsbad	NM	263	0.7075	0.7080	0.7100	0.7084	0.7084	−0.0009
Grants	NM	691	0.7134	0.7080	0.7113	0.7113	0.7081	0.0053
Raton	NM	232	0.7096	0.7059	0.7113	0.7113	0.7082	0.0014

Table 3. Continued.

City	State	Sr (μg/L)	$^{87}Sr/^{86}Sr$ Measured tap water	Bedrock model†	Major bedrock model‡	Local water model‡	Catchment model‡	Difference, Tap − Catchment Δ
Roswell	NM	934	0.7077	0.7049	0.7113	0.7113	0.7084	−0.0006
Vaughn	NM	713	0.7123	0.7080	0.7115	0.7115	0.7089	0.0034
Muskogee	OK	144	0.7102	0.7080	0.7194	0.7181	0.7102	0.0000
Sayre	OK	468	0.7088	0.7080	0.7113	0.7113	0.7102	−0.0014
Shawnee	OK	106	0.7129	0.7080	0.7192	0.7179	0.7102	0.0026
Beavercreek	OR	19	0.7037	0.7049	0.7040	0.7040	0.7062	−0.0025
Portland	OR	9	0.7039	0.7049	0.7113	0.7113	0.7058	−0.0019
Chadds Ford	PA	0	...	...	...	...	...	...
Easley	SC	12	0.7150	0.7101	0.7156	0.7156	0.7133	0.0017
Amarillo	TX	1063	0.7092	0.7049	0.7113	0.7113	0.7091	0.0001
Big Spring	TX	1513	0.7087	0.7059	0.7114	0.7114	0.7078	0.0009
Columbus	TX	643	0.7082	0.7049	0.7113	0.7113	0.7088	−0.0006
Dalhart	TX	789	0.7089	0.7049	0.7113	0.7113	0.7091	−0.0001
Kerrville	TX	0	...	...	...	...	...	...
Luling	TX	282	0.7083	0.7054	0.7090	0.7092	0.7075	0.0007
Odessa	TX	1726	0.7086	0.7049	0.7113	0.7113	0.7090	−0.0004
Pecos	TX	1326	0.7086	0.7049	0.7113	0.7113	0.7086	0.0000
San Angelo	TX	1903	0.7085	0.7080	0.7113	0.7113	0.7075	0.0010
San Antonio	TX	640	0.7080	0.7054	0.7113	0.7113	0.7076	0.0004
Monticello	UT	116	0.7082	0.7059	0.7113	0.7113	0.7126	−0.0044
Price	UT	251	0.7112	0.7059	0.7139	0.7134	0.7085	0.0027
Roosevelt	UT	370	0.7109	0.7054	0.7113	0.7113	0.7107	0.0002
Vernal	UT	27	0.7130	0.7059	0.7113	0.7113	0.7094	0.0036
Stanley	VA	1077	0.7127	0.7101	0.7240	0.7219	0.7108	0.0019
Pullman	WA	157	0.7103	0.7049	0.7040	0.7040	0.7083	0.0020
Spokane	WA	41	0.7320	0.7049	0.7113	0.7113	0.7186	0.0135
Baraboo	WI	50	0.7112	0.7101	0.7146	0.7119	0.7116	−0.0004
Casper	WY	416	0.7123	0.7059	0.7139	0.7132	0.7097	0.0026
Douglas	WY	306	0.7159	0.7054	0.7113	0.7113	0.7093	0.0066
Evanston	WY	48	0.7162	0.7054	0.7113	0.7113	0.7091	0.0071
Lander	WY	13	0.7244	0.7073	0.7113	0.7113	0.7099	0.0145
Lusk	WY	5	0.7155	0.7049	0.7088	0.7082	0.7096	0.0059
Rock Springs	WY	263	0.7114	0.7059	0.7113	0.7113	0.7101	0.0013
Summary statistics								
Minimum		0	0.7037	0.7045	0.7040	0.7040	0.7053	−0.0217
Maximum		1918	0.7320	0.7320	0.7614	0.7360	0.7383	0.0145
Median		146						
Mean		282	0.7112					0.0008
1σ		406	0.0038					0.0041

Notes: State names presented as official 2-letter U.S. Postal Service abbreviations. Difference (Δ) was calculated as measured tap water $^{87}Sr/^{86}Sr$ minus catchment-modeled $^{87}Sr/^{86}Sr$. A cell containing an ellipsis (···) indicates the tap water sample contained no measureable Sr.

†Predicted from a model by Beard and Johnson (2000); see *Introduction* for model description.

‡Predicted from a model by Bataille and Bowen (2012); see *Introduction* for model description.

the major bedrock or local water models of Bataille and Bowen (2012) ($P > 0.05$ for both comparisons).

Positing the Bataille and Bowen (2012) catchment model as the most accurate of the published methods for predicting tap water $^{87}Sr/^{86}Sr$, calculated differences between measured and modeled $^{87}Sr/^{86}Sr$ (Tap-Catchment Δ) ranged from −0.0217 (Duluth, Minnesota) to +0.0145 (Lander, Wyoming), with a mean (±1σ) of 0.0008 (±0.0041; Table 3). Mean Tap-Catchment Δ was not significantly different from 0 based on a paired *t*-test with a significance level of 0.05. Differences between measured and catchment-modeled $^{87}Sr/^{86}Sr$ are presented spatially by collection site in Fig. 4.

Discussion

As expected based on the diversity of bedrock types present within the continental USA (Beard and Johnson 2000), there was significant variation in Sr concentration and $^{87}Sr/^{86}Sr$ measured for 99 tap waters collected in 29 states and in the

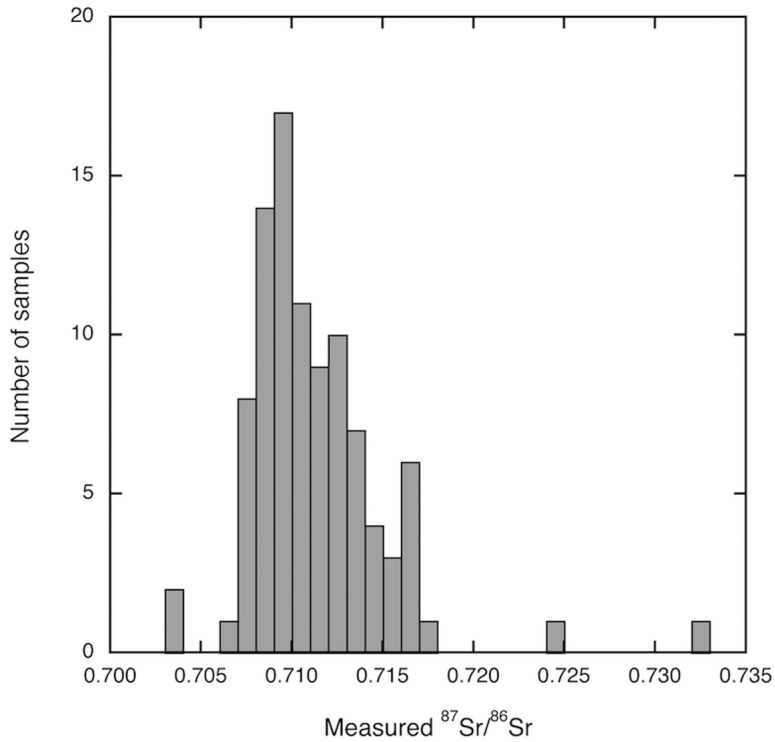

Fig. 2. Histogram of measured $^{87}Sr/^{86}Sr$ for collected USA tap water samples containing >5 μg/L Sr ($n = 95$).

District of Columbia. The variation was large, despite the potential of Sr leaching from or Sr exchange with sample storage containers. An experiment conducted with containers similar to those used for sample collection demonstrated that storage in glass had no statistically significant impact on the concentration of Sr in natural stream and tap waters when compared to storage in LDPE bottles with acid. However, storage in glass did significantly impact measured $^{87}Sr/^{86}Sr$ in tap waters, with higher values observed relative to samples stored in LDPE bottles with acid (Table 2).

For tap waters with naturally low Sr contents, the effect of leaching due to storage conditions would be detrimental if final concentrations were too low for analysis or if the storage containers contributed a significant amount of Sr (with a significantly different $^{87}Sr/^{86}Sr$) to the sample. Only 4 of the 99 tap water samples collected in this survey had Sr contents less than 5 μg/L and contained too little Sr for subsequent $^{87}Sr/^{86}Sr$ measurement. The mean concentration of Sr leached into ultra pure water stored in glass over 4 months was 1.0 μg/L. This would amount to 10% of the Sr signal in a water sample naturally containing 9 μg/L Sr, a worst-case scenario that may have impacted <8% (7 of 99) of the USA tap waters.

On the other hand, we observed that storage for 8 months in glass did significantly impact $^{87}Sr/^{86}Sr$ of Salt Lake Valley tap and creek waters that contained ≥200 μg/L, most likely due to exchange of Sr in the water with Sr in the borosilicate vials. Since ~60% (60 of 99) of the samples collected in our study contained <200 μg/L of Sr, these results suggest that measured $^{87}Sr/^{86}Sr$ of some USA tap waters could have changed during storage. The impact of exchange was smaller in waters with higher concentrations of Sr (Tables 1 and 2), suggesting the pool of Sr available for exchange from the glass was limited. The difference between Salt Lake Valley tap waters stored in glass versus LDPE was relatively small (mean glass-LDPE $\Delta = 0.0004$) and comparable in order of magnitude to the reproducibility of SRM 987 measurements. Thus, results from the experiment also suggest it may

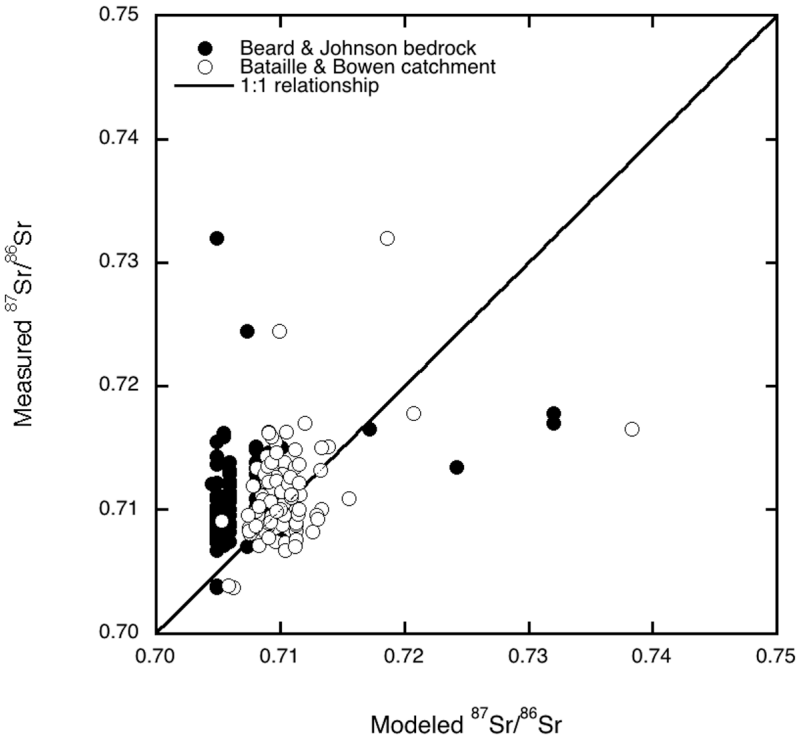

Fig. 3. Measured tap water $^{87}Sr/^{86}Sr$ versus modeled $^{87}Sr/^{86}Sr$. Predictions were generated using the bedrock model of Beard and Johnson (2000), denoted by black circles, and the flux-weighted catchment model of Bataille and Bowen (2012), denoted by white circles. The diagonal line represents the 1:1 relationship between measured and modeled $^{87}Sr/^{86}Sr$.

be possible to analyze previously collected water samples for Sr concentration and $^{87}Sr/^{86}Sr$ and still gain valuable information related to broad patterns in Sr variation, despite imperfect storage conditions. In recognition of the uncertainty related to Sr exchange during storage in glass containers we have presented $^{87}Sr/^{86}Sr$ for USA tap waters with 4 significant figures throughout the text.

There are very few published datasets to which the USA tap water samples can be directly compared. The available Sr concentration data include German tap waters published by Birke et al. (2010) and drinking water for Argentinean beef cattle analyzed by Baroni et al. (2011). The median Sr concentration measured for the 99 USA tap water samples (146 μg/L; Table 3) was comparable to the median concentration published for German tap waters (207 μg/L; Birke et al. 2010). In contrast, the mean Sr concentration of the USA tap water samples (282 μg/L) was lower than concentrations observed for water from three regions of Argentina, which ranged from 699 to 781 μg/L (Baroni et al. 2011). Comparison with published bottled water datasets reveals that the Sr concentration range for the USA tap waters (0 μg/L to 1.9 mg/L, $n = 95$; Table 3) was smaller than the ranges observed for large collections of German bottled waters (6 μg/L to 26.9 mg/L, $n = 908$; Birke et al. 2010) and other European mineral waters (0.2 μg/L to 22.8 mg/L, $n = 650$; Voerkelius et al. 2010) but larger than a small collection of British mineral waters (4–620 μg/L, $n = 32$; Montgomery et al. 2006).

The USA tap water with the lowest measured $^{87}Sr/^{86}Sr$ was collected in Beavercreek, Oregon where the underlying sediment is primarily Plio-Pleistocene alluvial deposits and basalts. These geologically young rocks are predicted to have relatively low $^{87}Sr/^{86}Sr$ and, as seen in Table 3, $^{87}Sr/^{86}Sr$ of water collected from the area was indeed low (see also Portland, Oregon). The

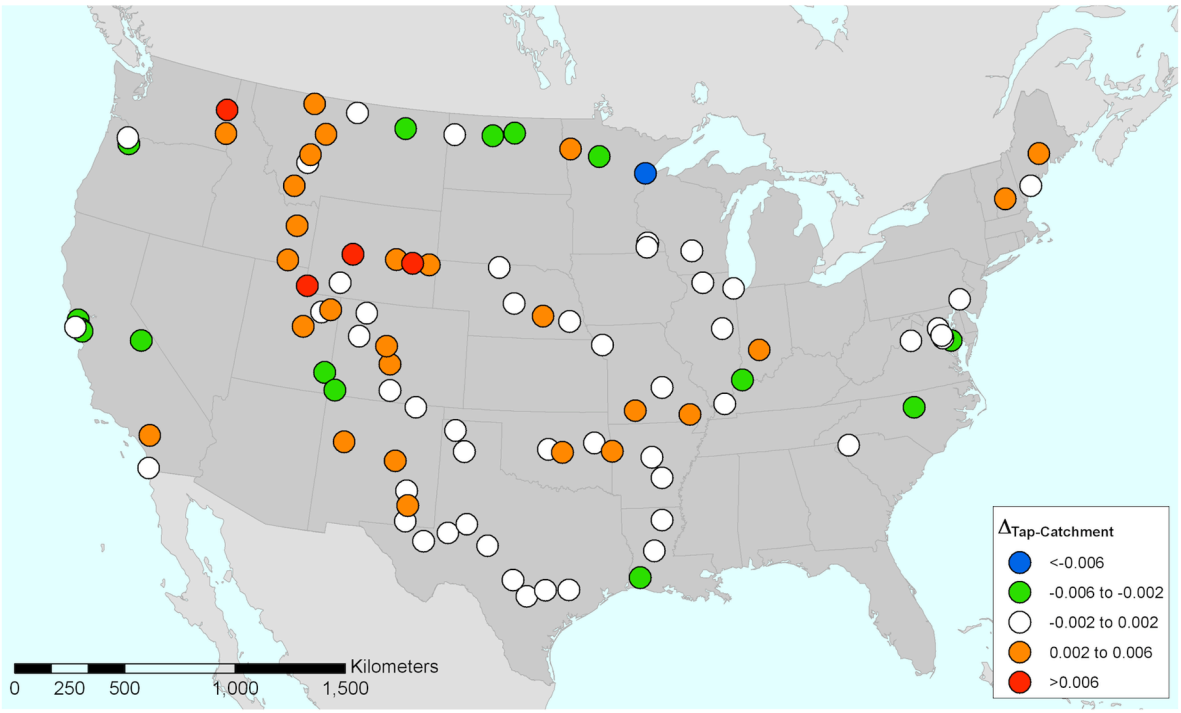

Fig. 4. Differences between measured and catchment-modeled $^{87}Sr/^{86}Sr$ (Tap − Catchment Δ), displayed at the sites of tap water sample collection within the coterminous USA.

collected sample with the highest measured $^{87}Sr/^{86}Sr$ was from Spokane, Washington where the underlying bedrock is relatively young (<2.5 Ma) and consists primarily of Columbia River basalts with some consolidated deposits of Quaternary sediments. These rock formations are also predicted to have relatively low $^{87}Sr/^{86}Sr$ and a large mismatch was observed between measured and modeled $^{87}Sr/^{86}Sr$ for the Spokane water sample (Table 3). The mismatch is likely related to the geology of Spokane's drinking water source, the Spokane Valley-Rathdrum Prairie Aquifer, which is composed of large-grained clastic sediments deposited from Glacial Lake Missoula flood events and is recharged predominately from runoff of the Bitterroot Mountains to the east of Spokane, in the state of Idaho.

As hypothesized, predicted $^{87}Sr/^{86}Sr$ of bedrock modeled as a function of age (Beard and Johnson 2000) was significantly and positively correlated with tap water $^{87}Sr/^{86}Sr$, although the explanatory power of bedrock age for the Sr isotopic composition of water was overall low (i.e., ~10%). Using calculated coefficient of determination to evaluate model performance, the Beard and Johnson (2000) bedrock model predictions of $^{87}Sr/^{86}Sr$ explained more variation in measured tap water $^{87}Sr/^{86}Sr$ than predictions from a newer major bedrock model that included additional lithology and Sr concentration variables and a local water model that accounted for the flux of Sr from rock ($r^2 < 0.10$ for both models; Bataille and Bowen 2012). Weighting modeled local water $^{87}Sr/^{86}Sr$ using catchment flow increased the coefficient of determination between predictions and observations, especially after the removal of a single data point (Duluth, Minnesota; $r^2 = 0.24$). We therefore conclude that the flux-weighted catchment model of Bataille and Bowen (2012) is the most accurate of the four methods tested in this study to predict tap water $^{87}Sr/^{86}Sr$ within the USA. This corroborates the conclusion drawn by the model authors themselves when they tested the accuracy of model predictions using 68 previously published watershed data points and 93 marijuana samples analyzed by West et al. (2009).

Yet the catchment model of Bataille and Bowen (2012) did not robustly predict tap water $^{87}Sr/^{86}Sr$ across the entire continental USA and there may be a geographic component to model performance, as seen in Fig. 4. For example, most Tap-Catchment Δ values calculated for samples collected in the Midwest and in western states of the Southern region (i.e., Louisiana, Oklahoma, and Texas) were ~0 (white points in Fig. 4). Surface bedrock and aquifers in these regions of the USA generally contain limestones rich in $CaCO_3$ and limestone carbonate would thus have the largest influence on $^{87}Sr/^{86}Sr$ of collected tap water. The relationship between weathering and mineral dissolution is well understood in limestones as opposed to other rock types. The agreement between measured and modeled $^{87}Sr/^{86}Sr$ for tap water collected from these regions indicates the Bataille and Bowen (2012) catchment model works well for predicting water Sr isotopic composition in carbonate-dominated areas, especially areas where both surficial and aquifer lithology is similar.

Tap water collected from cities in mountainous regions of the western USA (including the states of Montana, Idaho, Wyoming, Utah, and Colorado) displayed primarily positive differences between measured and catchment-modeled water $^{87}Sr/^{86}Sr$ (orange and red points in Fig. 4). Many of these regions rely in whole or in part on winter precipitation for drinking water and Sr from high elevations likely dominates local tap water $^{87}Sr/^{86}Sr$. Although the catchment model of Bataille and Bowen (2012) includes a weathering rate estimate, that variable may not account for the rates of weathering at high elevation, nor the disproportionate amount of water sourced from high elevations. In contrast, tap water collected in northern states bordering Canada had lower than expected $^{87}Sr/^{86}Sr$, as demonstrated by the green points in Fig. 4 within the states of Montana, North Dakota, and Minnesota. This area is characterized by Quaternary glacial till and older sedimentary basins; the glacial till is likely to be dominated by lithologies from the Canadian shield, a potential source of radiogenic Sr. However, due to the uncertainty in actual till source, almost all catchment model $^{87}Sr/^{86}Sr$ predictions for this area were 0.7113 (see Table 3). The measured $^{87}Sr/^{86}Sr$ of waters from this region are more consistent with typical limestone values, suggesting that aquifers within the sedimentary basins are the probable source of drinking water.

The distribution of sampling locations along the East Coast is too sparse to draw concrete conclusions about the performance of the Bataille and Bowen (2012) catchment model for predicting tap water $^{87}Sr/^{86}Sr$ in the Northeast and Southeast regions of the USA. The same may be true for samples from the West Coast, as well, but we also note that the state of California is known for its complex management of municipal water resources and its extensive use of transported water. For example, there is a large negative difference between measured and catchment-modeled $^{87}Sr/^{86}Sr$ of tap water collected in the San Francisco Bay area (Fig. 4, Table 3; see also Palo Alto and Half Moon Bay, California), suggesting the model over-predicts water $^{87}Sr/^{86}Sr$ at this coastal location. However, the actual source of ~85% of water used by the city of San Francisco is the Hetch Hetchy Reservoir, located ~200 miles east in the Sierra Nevada Mountains. Modeled $^{87}Sr/^{86}Sr$ predicted for the reservoir is ~0.707, much more similar to that of measured tap water from San Francisco (0.7070, Table 3) than predictions based on coordinates for the city itself (i.e., ~0.711, Table 3).

Notwithstanding San Francisco, an in-depth investigation of the difference between $^{87}Sr/^{86}Sr$ measured for each collected USA tap water and predicted by the catchment model is difficult without more detailed information on specific hydrologic resources used by different municipal water systems. Municipalities can draw water from groundwater supplies in addition to (or as opposed to) relying solely on hydrological sources at the planet's surface. If the mineral composition of an aquifer is vastly different from that of the surrounding surficial geology, predictions based on bedrock and weathering susceptibilities may not be the most appropriate for estimating tap water $^{87}Sr/^{86}Sr$. Considering that the content of many trace elements in groundwater is typically 1–2 orders of magnitude greater than the concentrations found in surface freshwaters (cf. Berner and Berner 1996), pairing elemental concentration measurements with $^{87}Sr/^{86}Sr$ could help in determining if the origin of municipal water was surficial or not. Even in areas where surface water is the predominant

component of drinking water, the water may have naturally moved through multiple distinct geologic regions with variable lithologies prior to use by the municipality, a scenario that would make it difficult to model $^{87}Sr/^{86}Sr$ without a thorough understanding of hydrogeology.

Human management practices often cause water to be unnaturally transported large distances, as when snowmelt from the Sierra Nevada Mountains is used to supply drinking water to the San Francisco Bay area 200 miles or more distant. This complex water management scenario is not confined to only metropolitan areas of California. Many urban population centers in the Western USA use transported water and rely on multiple water sources to provide a steady supply of tap water to residents throughout the year; examples include the cities of Phoenix and Tucson, Arizona and Salt Lake City, Utah. In addition, water needs within urban centers can fluctuate on a day-to-day basis and it is possible that in periods of high demands a municipality could exploit one water source to excess. As for the natural movement of water, the artificial movement of waters into cities would make it difficult to model $^{87}Sr/^{86}Sr$ without a thorough understanding of water transport dynamics.

Despite the unknowns related to original water source and its movement, this dataset of tap waters collected across the continental USA was useful for validating previously published Sr isoscape models and laying the groundwork for future research efforts. Although predictions from the catchment model of Bataille and Bowen (2012) were imperfect for describing all Sr isotopic variation in USA tap waters, we found $^{87}Sr/^{86}Sr$ modeled using major lithology, Sr content, weathering rates, and watershed-scale flow explained more variation than a previously published age-only model (Beard and Johnson 2000). This is presumably because ~60% of publically-supplied drinking water within the USA is derived directly from surface water (Hutson et al. 2004) and the flux-weighted catchment model of Bataille and Bowen (2012) is therefore a good first approach for predicting tap water $^{87}Sr/^{86}Sr$. However, the relatively low coefficient of determination between $^{87}Sr/^{86}Sr$ measured in USA tap water and predicted from the catchment model also suggests that the development of a specific tap water $^{87}Sr/^{86}Sr$ isoscape model that includes variables for the geography and geology of watersheds and aquifers as well as water transport is an important area of future focus.

Conclusions

As expected based on the diversity of geologic history in different regions of the country, we observed large variations in both Sr concentration and $^{87}Sr/^{86}Sr$ for 99 tap water samples collected from municipalities across the coterminous USA. Repeatability of observations was high based on two limited datasets where multiple samples were collected from the same city. Combined with the results of a storage container leaching and exchange experiment, the large variations in measured $^{87}Sr/^{86}Sr$ of USA tap water suggested that it might be possible for investigators to analyze previously collected water samples and generate useful data, despite less-than-ideal storage conditions. The Sr isotope analysis of USA tap water also demonstrated the applicability of a newly developed in-line Sr purification method for automating $^{87}Sr/^{86}Sr$ measurements using multi-collector inductively coupled plasma mass spectrometry.

Two of the four published Sr isoscape models (Beard and Johnson 2000, Bataille and Bowen 2012) tested in this study displayed significant predictability for tap water $^{87}Sr/^{86}Sr$ but neither captured all the factors that apparently impact Sr in the drinking water of citizens of the USA. Based on coefficient of determination, we determined that a flux-weighted catchment model (Bataille and Bowen 2012) performed best for predicting tap water $^{87}Sr/^{86}Sr$. In some areas of the continental USA, $^{87}Sr/^{86}Sr$ predicted using the catchment model closely matched $^{87}Sr/^{86}Sr$ of water collected in those areas, particularly in the state of Texas and regions south of the Great Lakes. Other regions of the continental USA were marked by large positive (e.g., high-elevation states) and negative (e.g., states bordering Canada) differences between measured and modeled $^{87}Sr/^{86}Sr$. While we could explain some of the differences with higher-than-expected Sr weathering rates and model assumptions, we conclude that bedrock age and lithology are not the sole best predictors of tap water $^{87}Sr/^{86}Sr$ in all areas

of the continental USA.

Investigating more completely the differences between measured and catchment-modeled $^{87}Sr/^{86}Sr$ of USA tap water will require additional efforts in the future. Collections from currently under-represented regions of the USA—for example, the Appalachian Mountains, states along the East Coast, and California—will provide additional validation of the Bataille and Bowen (2012) catchment model and can be used to further investigate mismatches between measurements and model predictions. It may be more appropriate in the future to compare measured tap water $^{87}Sr/^{86}Sr$ to predictions based on specific municipal watershed geography and the distance of water transport, an approach that would require a significant amalgamation of topographies and water system records from across the USA. Although the efforts represent a large investment of resources and time, the outcome would be invaluable in establishing how the isotopic composition of Sr from a particular geographic origin is recorded by the materials found in the area, such as tap water and the animals and plants that are reliant on that hydrologic resource.

Acknowledgments

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Supplemental Material

Supplement

Coordinates for sampled municipalities and the dates of tap water sample collection (*Ecological Archives* C003-008-S1).