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Stable isotope ratios of tap water in the contiguous United States

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[1] Understanding links between water consumers and climatological (precipitation) sources is essential for developing strategies to ensure the long-term sustainability of water supplies. In pursing this understanding a need exists for tools to study and monitor complex human-hydrological systems that involve high levels of spatial connectivity and supply problems that are regional, rather than local, in nature. Here we report the first national-level survey of stable isotope ratios in tap water, including spatially and temporally explicit samples from a large number of cities and towns across the contiguous United States. We show that intra-annual ranges of tap water isotope ratios are relatively small (e.g., <10‰ for δ^{2}H) at most sites. In contrast, spatial variation in tap water isotope ratios is very large, spanning ranges of 163‰ for δ^{2}H and 23.6‰ for δ^{18}O. The spatial distribution of tap water isotope ratios at the national level is similar to that of stable isotope ratios of precipitation. At the regional level, however, pervasive differences between tap water and precipitation isotope ratios can be attributed to hydrological factors in the water source to consumer chain. These patterns highlight the potential for monitoring of tap water isotope ratios to contribute to the study of regional water supply stability and provide warning signals for impending water resource changes. We present the first published maps of predicted tap water isotope ratios for the contiguous United States, which will be useful in guiding future research on human-hydrological systems and as a tool for applied forensics and traceability studies.

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1. Introduction

[2] Planning for and maintaining sustainable drinking water resources is a major challenge for human societies. As human populations grow and exert more powerful and widespread influence on their environment, this challenge will be multiplied through factors such as increased demand, heightened potential for contamination, and changes in the characteristics and distribution (both spatial and temporal) of supplies. Understanding and managing supplies requires routine monitoring and predictive modeling of the forces exerted by these factors on hydrological systems. Factors such as population growth and infrastructure for water diversion have increasingly transformed local shortfalls in supply into regional water management problems. Thus there is an increasing need for research programs that use spatial data to identify and characterize regional water resource issues that have the potential to severely impact large sectors of society in the coming decades.

[3] The light stable isotope ratios of water (δ^{2}H, δ^{18}O) are parameters that can be easily and routinely measured for almost any water sample and which can preserve information on the climatological source (i.e., the location, time, and phase of precipitation) and postprecipitation history of water. Environmental water resources, including river, ground, and lake water, derive their H and O isotopic composition primarily from the meteoric precipitation that supplies them [*Gat*, 1981; *Kendall and Coplen*, 2001; *Smith et al.*, 2002; *Dutton et al.*, 2005]. Natural or artificial mixing of waters from different sources and of different ages and overland or subsurface flow will mix and propagate the isotopic "signatures" of source water, preserving an integrated signal of the precipitation sources contributing to water supplies. Other postprecipitation processes such as evaporation and chemical interaction with minerals in soils and rock have the potential to modify stable isotope ratios of water, and can commonly be distinguished through consideration of coupled δ^{2}H/δ^{18}O data. Given the potential wealth of information available and the relative ease of δ^{2}H and δ^{18}O measurements of water, these parameters have already featured prominently in climatological and hydrological monitoring networks [*Rozanski et al.*, 1993; *Kendall and Coplen*, 2001] and could contribute greatly to future networks focused on the human/hydrological system.

[4] Here we present results from the first national-scale spatiotemporal survey of stable isotopes in tap water. The new data show that tap water samples exhibit high levels of spatially coherent isotope ratio variation that can be related to commonality in patterns of water source and postprecipitation history for water resources in different parts of the

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country. A strong relationship exists between tap water isotope ratios and those of annually averaged local precipitation (as estimated by geostatistical modeling), but robust differences between tap water and precipitation isotope ratios also exist in many parts of the United States. These patterns can be related to regional tendencies in water resource selection and water history, including patterns likely related to high-altitude dominated sources, seasonally biased recharge, and evaporative loss from natural or artificial surface reservoirs. Our data provide the first evidence that large, spatially distributed isotope sampling networks offer the potential to identify and characterize the magnitude and regional relevance of such processes within complex human-hydrological systems. Our goal is to demonstrate these capabilities in order to promote and guide future network-based data gathering and spatial analysis efforts that will increase the level of scientific understanding and security of climatically sensitive, regionally important water resources. We synthesize our data as a set of predictive tap water isotope ratio maps that, when interpreted with respect for the limitations of the underlying data, should benefit future water resources research efforts as well as fields such as ecology and forensic sciences where understanding of large-scale patterns of hydrological isotope ratio variation is increasingly important.

2. Methods

2.1. Sample Acquisition

[5] Tap water samples for spatial characterization of U.S. tap water isotope ratios were collected between December 2002 and August 2003 through a volunteer network consisting of professors at academic institutions and water managers. Sample sites were selected to obtain a relatively complete geographic coverage, particularly with respect to known variability in precipitation isotope ratios within the United States, and to represent inhabited areas ranging from large cities to small rural communities. Participants who conducted sampling were instructed to obtain cold tap water from a local source by running the tap for ~10 s before filling, capping, and sealing (with parafilm) a clean 2-dram vial (poly-lined cap [e.g., *Clark and Fritz*, 1997]). Sample vials were returned to the Stable Isotope Ratios for Environmental Research (SIRFER) lab at the University of Utah, where they were prepared for analysis within a few weeks to a few months of receipt. Samples were stored in a cool, dark environment between the time of receipt and analysis, and before analysis vials were visually inspected for signs of leakage or evaporation, including water seepage from around the cap or the presence of large air bubbles in the sample.

[6] An additional set of samples was collected for characterization of seasonal variations in tap water isotope ratios through a volunteer network. Individuals in 43 cities and towns in the United States and southern Canada were chosen to provide samples from one or more location within their city/town. Sample sites were again chosen to cover known gradients in natural water isotope ratios in the United States and to include a range of small towns to large cities in a range of physiological and climatological settings. Volunteers collected samples from one or more taps (e.g., home tap, office or laboratory tap) once per month from January 2005 to January 2006. These samples were received, stored, and checked for quality assurance using the same protocols as for the spatial characterization samples. The overall sampling return rate was 91%, and data from the 47 taps in 38 cities with returns for more than 8 months during the 13 month period are considered here.

2.2. Analysis

[7] Samples were analyzed for their δ^2H and δ^{18}O values using either "traditional" (spatial survey) or "online" (seasonal survey) preparation methods, with all sample values reported using δ notation (where $\delta = (R_{sample}/R_{standard} - 1)*1000$, $R = {}^2H/{}^1H$ or ${}^{18}O/{}^{16}O$) and normalized on the VSMOW – VSLAP standard scale. For "traditional" analyses, hydrogen and oxygen isotope ratios were determined from separate aliquots of the sample. Hydrogen isotope ratios were determined by analysis of H_2 gas produced via the reduction of 2 μL of water on 100 mg of Zn reagent at 500°C [modified from *Coleman et al.*, 1982]. Oxygen isotope ratio determination was made by analysis of CO_2 equilibrated with sample water using the method of *Fessenden et al.* [2002]. For analysis via the "online" method, a single small (1 μL) aliquot of water was injected onto a column of glassy carbon held at 1400° C to produce H_2 and CO gases. These were separated chromatographically in a helium carrier gas stream and introduced sequentially into the ion source of an IRMS (Delta +XL, ThermoFinnigan) for isotope ratio determination. Samples were analyzed in duplicate, with average precision of 1.5‰ for δ^2H and 0.2‰ for δ^{18}O (1σ) for replicate analyses. All data obtained by either method were normalized to the VSMOW-SLAP scale through repeated analysis of 2 calibrated laboratory working standards [*Coplen*, 1996]. Analyses previously reported by *Bowen et al.* [2005] demonstrate that isotope ratio data generated using the 2 different preparation techniques in the SIRFER lab are comparable across a wide range of values.

2.3. Spatial Analysis

[8] We analyze the tap water data in the context of maps of mean annual precipitation isotope ratios created using the method of *Bowen and Revenaugh* [2003]. The method involves fitting parameters of a nonlinear model including latitude, altitude, and spatial weighting effects to a database of isotope ratio measurements. The model is then applied to a georeferenced grid, using the isotope data and ancillary elevation data, to produce a prediction surface of precipitation isotope ratios. Data for North America were compiled from the Global Network for Isotopes in Precipitation (GNIP) database (International Atomic Energy Agency, http://isohis.iaea.org/GNIP.asp) and literature sources [*Friedman et al.*, 1992, 2002; *Welker*, 2000; *Kendall and Coplen*, 2001, and references therein], giving a total of 78 δ^2H data and 84 δ^{18}O data for the contiguous United States and adjacent areas of Canada and Mexico (see auxiliary material).[1] The precipitation data were reduced to precipitation amount-weighted, annually averaged values as described previously [*Kendall and Coplen*, 2001; *Bowen and Wilkinson*, 2002] (see auxiliary material). The North American data were added to a global database of precip-

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[1] Auxiliary materials are available at ftp://ftp.agu.org/apend/wr/2006wr005186.

itation isotope ratios (GNIP database) and used to create a global mean annual map using elevation data from the ETOPO5 digital elevation model [*National Geophysical Data Center*, 1998]. All precipitation isotope ratio values referenced in this manuscript are estimated values derived from these maps.

[9] The predictions used here provide imperfect but relatively accurate estimates of the regional patterns of precipitation isotope ratio variation across most of the contiguous United States. For example, based on previous statistical analyses of equivalent maps the average 2 standard deviation uncertainty for these predictions is approximately 8 and 1.0‰ (δ^2H and δ^{18}O, respectively) for sites within the United States [*Bowen and Revenaugh*, 2003]. One significant exception occurs along the Pacific coast in northern California and Oregon, where our database does not include sufficient spatial sampling to document the strong isotopic gradients known to exist between coastal and inland regions [e.g., *Ingraham and Taylor*, 1991]. As a result, we do present tap water isotope ratio data and predictions for this part of the United States, but do not focus on interpretation of the tap water data in the context of mapped precipitation isotope ratio estimates in this region.

[10] Additional analysis of spatial patterns in the tap water isotope data were conducted in ArcGIS 9.1 (ESRI; Redlands, CA; all calculations conducted using grids in U.S. contiguous states Albers equal area conic projection). Identification of robust spatial patterns in the data was accomplished using Morans I (Spatial Statistics Toolbox, ArcGIS 9.1) to quantify spatial autocorrelation. These calculations were conducted using unstandardized weights derived from squared inverse Euclidean distances between data points. Additional quantification of spatial coherence and the quality of tap water isotope ratio predictions made by spatial interpolation was accomplished through ordinary Kriging of the raw, spatial survey tap water data using the Geostatistical Analyst extension in ArcGIS 9.1 and cross validation (i.e., prediction at each sampling site based on a kriging of a resampled data set excluding data from that site). For further data analysis and to create prediction maps of average tap water isotope ratios, differences were calculated between measured isotope ratios and mapped precipitation isotope ratios at each tap water collection site. Tap minus precipitation difference surfaces for δ^2H, δ^{18}O, and d were generated by ordinary kriging. All kriging of raw data and tap-precipitation data used a spherical semivariogram with nugget. No strong spatial anisotropy was observed in any of the data sets or incorporated in any of the interpolations. The δ^2H and δ^{18}O prediction maps were created by summing the interpolated U.S. precipitation isotope layer for each element and the corresponding Kriged tap minus precipitation difference layer. The d map was calculated from the tap water H and O isotope prediction maps by the equation $d = \delta^2H - 8 \times \delta^{18}O$. Cross-validation of the Kriged difference layers using Geostatistical Analyst was used to estimate prediction errors (root mean square error) for the tap water δ^2H and δ^{18}O maps.

3. Results

[11] Five hundred and ten tap water samples for spatial characterization were obtained from 496 towns and cities within the contiguous United States (Figure 1). Samples were obtained from each of the 48 contiguous States, with few sampling gaps greater than ~100 km in radius. Notable exceptions include sparse sampling in eastern Oregon, central Nevada, central Texas, and eastern Montana.

[12] The raw data values measured in this study are embargoed by the federal government, but are presented here graphically. Readers are encouraged to contact the authors for guidance in the use and application of the data. The stable isotope ratios of these samples (Figures 1 and 2) span a large range of values from −152 to +11‰ (δ^2H) and −19.4 to +4.2‰ (δ^{18}O). Average values for the sample set are −66‰ for δ^2H and −8.9‰ for δ^{18}O. For each element the data distribution is somewhat bimodal, with a dominant mode similar to the lumped average and a minor mode near −118‰ (δ^2H) and −16‰ (δ^{18}O). The tap water data cluster near the Global Meteoric Water Line ($\delta^2H = \delta^{18}O \times 8 + 10$ [*Craig*, 1961]) characterizing average global precipitation, but most samples lie below this line. Deuterium excess (d, $d = \delta^2H - \delta^{18}O \times 8$) values for the sample set range from −22.2 to 22.4‰, with an average value of 5.5‰.

[13] The spatial distribution of tap water stable isotope ratios is nonrandom (Figure 1; Moran's I for raw tap water isotope ratio data = 0.68 and 0.59, Z = 7.9 and 6.8, $p < 0.01$ and 0.01 for δ^2H and δ^{18}O, respectively). The lowest δ^2H and δ^{18}O values (< −110‰ and < −14‰, respectively) occur throughout the northern Rocky Mountain states (primarily Idaho, Montana, Utah, and Wyoming), and samples from this region comprise the lower, minor mode of the hydrogen and oxygen isotope ratio distributions shown in Figure 2. The highest δ^2H and δ^{18}O values for U.S. tap water samples (> 0‰ for each element) represent samples from a relatively restricted region of north central Texas and south central Oklahoma. Other samples with relatively high values were obtained throughout the Gulf Coast states. The general pattern of spatial variation for isotope ratios of each element is one of decreasing values from low-latitude, low-elevation coastal regions toward inland, high-latitude, and mountainous areas. In contrast to the H and O isotope ratio values, d values for the U.S. tap water samples show no clear, overarching spatial pattern in their distribution, and values of d between 5 and 10‰ occur throughout the contiguous United States. Extreme values of d, however, appear to be limited to certain regions, with the highest d values (> 16‰) found in the northeastern United States (e.g., New England) and the lowest (< −10‰) concentrated in southern California and along the lower Colorado River, along the Missouri River, and in north central Texas and south central Oklahoma.

[14] Five hundred and sixty-eight water samples were collected and analyzed as a part of the monthly water survey effort. The spatial density of the monthly water survey sampling sites is much lower than that of the spatial characterization sampling sites, but the distribution of these sites still encompasses much of the physiographic and climatological variation present in the lower 48 States (Table 1). These samples represent cities and towns in 22 of the contiguous United States and the province of Alberta. Sampling density was lowest through the Great Plains and the south central states. Although no explicit accounting of specific water sources is attempted here, we note that the monthly tap water samples represent water sources ranging

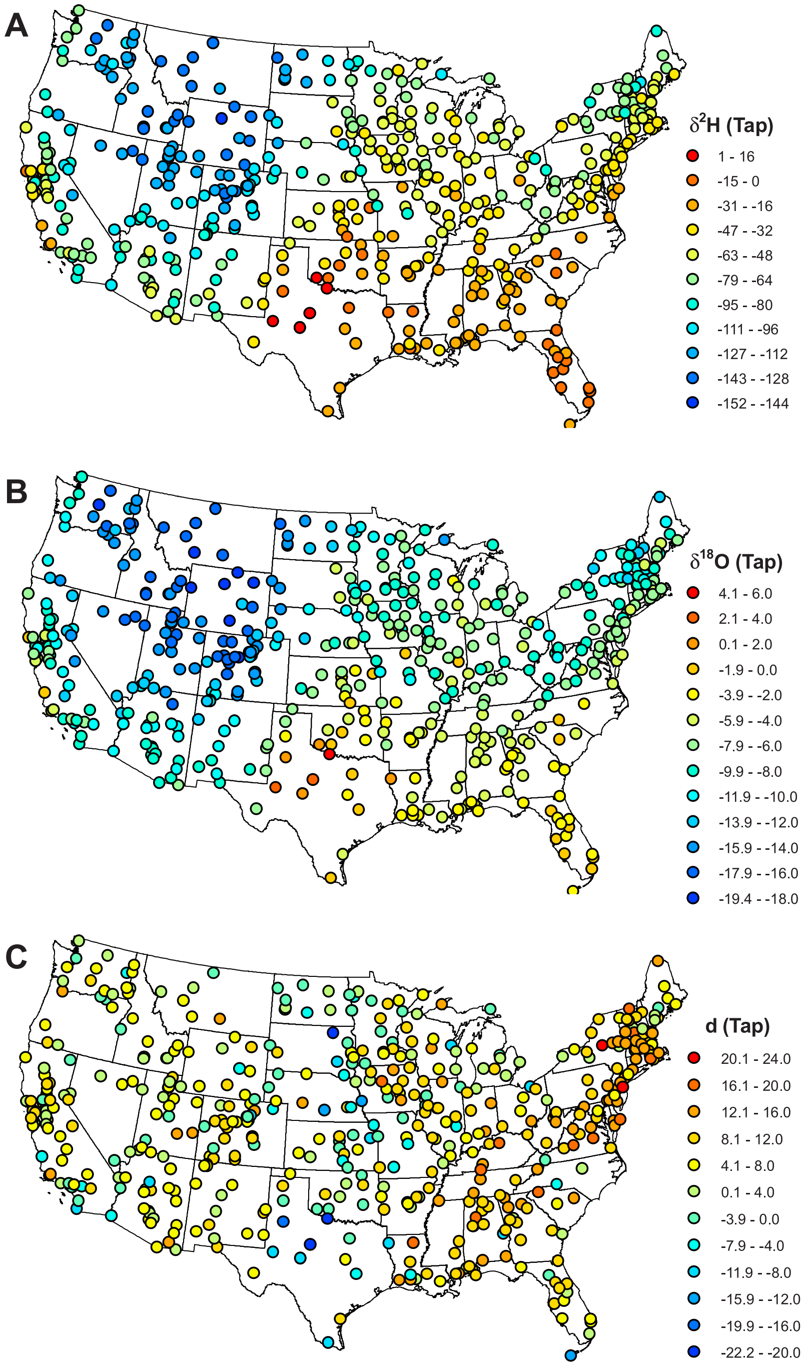

Figure 1. Observed isotope ratios for tap water samples in the spatial data set: (a) δ^2H, (b) δ^{18}O, and (c) deuterium excess. All values in ‰ relative to the VSMOW standard.

from single-home wells to municipally distributed water from small towns (e.g., Durham, NH) through major US cities (e.g., Houston, TX).

[15] The isotope ratios of tap water from the monthly sample set range from −144 to +4‰ for δ^2H (average = −61‰) and from −18.9‰ to +1.2‰ for δ^{18}O (average = −8.4‰). Annual average δ^2H and δ^{18}O values for the monthly sampling locations (calculated as unweighted averages of the monthly samples) range from −135 to −4‰ (average = −60‰) and from −17.3 to −0.5‰ (average = −8.2‰), respectively (Table 1). Tests of the mean and variance of these distributions suggest that the distribution of monthly survey δ^2H and δ^{18}O values is not statistically different than that of the spatial characterization data set (F test for variance, $p = 0.49$ and 0.51; T test for means, $p = 0.28$ and 0.33 for δ^2H and δ^{18}O, respectively;

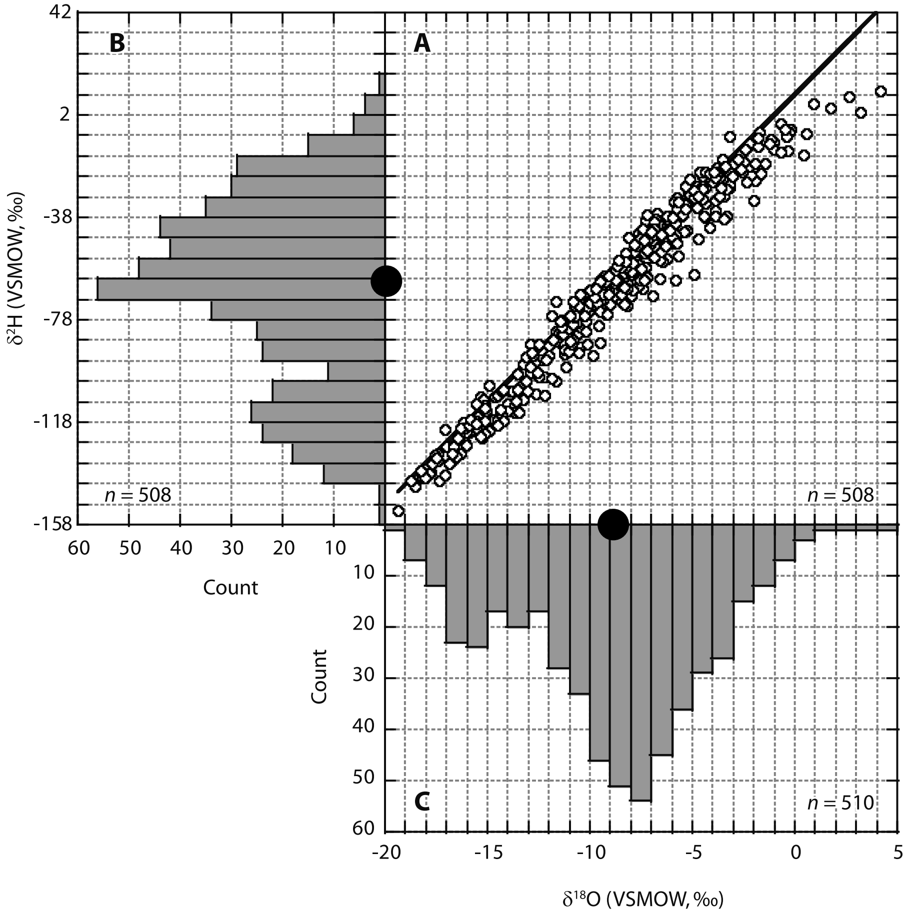

Figure 2. Stable H and O isotope ratios for spatial data set tap water samples. (a) Covariation of δ^2H and δ^{18}O values. The thick line represents the global meteoric water line (δ^2H = δ^{18}O × 8 + 10). (b and c) Frequency distributions for the individual isotope ratios. The large circles show the mean values for each isotope ratio for the entire data set.

calculations made using the Analysis toolpack for Microsoft Office Excel 2003). Intra-annual variation in tap water isotope ratios was calculated as the standard deviation of isotope ratios for the monthly samples, and ranges from 1 to 10‰ for δ^2H and from 0.1 to 1.7‰ for δ^{18}O (Figure 3). The average 1σ value across all sites is 4‰ and 0.6‰ for δ^2H and δ^{18}O, respectively, or ~2.3% of the range of values measured in the spatial characterization survey for each element. Interannual variation (1σ) in tap water d values ranges from 0.9 to 5.4‰, with an average value of 2.2‰, or approximately 5% of the total range observed for all tap water samples.

[16] The interannual variability of tap water isotope ratios exhibits relatively weak spatial coherence, although some spatial patterns may be expressed in the data set. Most areas of the country include some sampling locations that exhibit low (i.e., < 5 and 0.6‰, 1σ, for δ^2H and δ^{18}O, respectively) interannual variability. Sample locations with the highest interannual variability (e.g., >7‰ for δ^2H) occur almost exclusively in the southwestern United States (California, Nevada) and the northeastern and north central United States (e.g., Minnesota, New York, Ohio, northern Virginia). In contrast, sampling locations in the northwestern, Rocky Mountain, Great Plain, and Gulf Coast states are almost all characterized by low interannual variability < 5 and 0.6‰ (1σ, δ^2H and δ^{18}O, respectively).

4. Temporal Isotopic Variability of Tap Water and the Fidelity of the Spatial Data

[17] Temporal variability in tap water isotope ratios at the local level can be assessed from data collected for the monthly water sampling project. This is important because the timing (i.e., month) of sample collection for the spatial tap water survey sampling was not prescribed, and as a result it is difficult to say with absolute certainty how representative these single samples are of the average tap water isotope ratios at the sampling sites. In general, interannual variability of tap water isotope ratios was found to be low relative to the range of variation across the spatial sample set and relative to the major spatial patterns discussed below. Although we allow that a single year of sampling is probably not sufficient to provide a comprehensive picture of seasonal tap water isotope ratio variability, the seasonal survey data currently available suggest that in more than half of all cases, a sample taken at a random time during the year will be similar to the annual average value of tap water to within

Table 1. Average Isotope Ratios and Interannual Variability for Monthly Tap Water Survey

			Average		1σ	
City	State/Province	N	δ^2H	δ^{18}O	δ^2H	δ^{18}O
Lethbridge	Alberta	13	−135	−17.3	4	0.6
Tempe	AZ	11	−75	−9.4	6	0.7
Tucson	AZ	10	−62	−8.3	2	0.1
Tucson	AZ	12	−62	−8.2	2	0.2
Berkeley	CA	12	−83	−11.4	9	1.3
Buena Park	CA	10	−71	−9.2	9	0.8
Davis	CA	11	−56	−8.0	2	0.2
Davis	CA	11	−52	−7.4	3	0.3
Fullerton	CA	12	−77	−9.7	2	0.2
Pasadena	CA	12	−65	−8.5	8	0.8
San Diego	CA	11	−78	−9.5	4	0.5
San Diego	CA	11	−78	−9.5	6	0.7
Boulder	CO	14	−116	−15.4	5	1.1
Coral Gables	FL	8	−4	−0.8	1	0.1
Tallahassee	FL	13	−11	−1.8	2	0.2
Tallahassee	FL	10	−16	−2.8	2	0.1
Tallahassee	FL	10	−16	−2.9	3	0.2
Athens	GA	13	−25	−4.3	2	0.3
Watkinsville	GA	12	−28	−5.2	2	0.2
Boise	ID	12	−129	−16.8	3	0.3
Chicago	IL	9	−44	−5.8	2	0.2
Westmont	IL	9	−45	−5.8	2	0.2
Evansville	IN	12	−50	−7.5	5	1.0
Lawrence	KS	13	−28	−4.0	7	1.0
Manhattan	KS	12	−37	−5.4	2	0.4
Rockville	MD	12	−49	−7.5	3	0.4
Minneapolis	MN	11	−58	−7.5	9	1.1
Minneapolis	MN	12	−57	−7.4	10	1.2
Wykoff	MN	13	−63	−9.3	2	0.4
Durham	NH	11	−56	−8.5	5	0.9
Albuquerque	NM	13	−97	−13.0	1	0.3
Las Vegas	NV	13	−97	−11.8	1	0.3
Reno	NV	13	−110	−14.7	1	0.1
Reno	NV	12	−89	−11.5	9	1.7
Ithaca	NY	13	−71	−10.3	8	1.2
Columbus	OH	10	−54	−8.0	7	1.3
Eugene	OR	12	−75	−10.4	2	0.2
Eugene	OR	12	−83	−11.7	3	0.3
Portland	OR	13	−69	−9.9	4	0.5
University Park	PA	13	−60	−9.2	1	0.2
Austin	TX	11	−17	−2.4	1	0.2
Dallas	TX	11	−4	−0.3	6	1.1
Houston	TX	13	−12	−2.1	4	0.9
Houston	TX	13	−13	−2.2	5	1.0
Salt Lake City	UT	12	−120	−15.9	2	0.3
Great Falls	VA	12	−47	−7.8	1	0.1
Herndon	VA	8	−46	−7.3	4	0.6

4‰ for δ^2H and 0.6‰ for δ^{18}O, with values for even extreme months falling within ~12‰ and 1.8‰ of the average values.

[18] Sample collection times for the spatial survey were not random, however, with 63% of samples having been collected during the months of December 2002 and March 2003, and it is possible that the isotope ratio data could reflect biases related to the timing of collections. Because the analyses presented in this paper focus on regional patterns supported by data from many sample sites, these biases would be of concern primarily if the data set included spatial clusters of data biased due to nonrandom collecting times. Analysis of sample collection dates within the spatial sample set, however, indicates that no significant spatial autocorrelation exists for the date of sample collection (Moran's I for sample collection dates = −0.0047, Z = −0.031, $p \gg 0.1$). Thus, although it is possible that measured values from single sites may differ from representative annually averaged values at that location due to the timing of sample collection, spatial patterns supported by multiple data stations are likely to be representative due to spatial averaging of collecting biases, a conclusion further supported by the high spatial coherence of the tap water data.

5. Discussion: Comparative Analysis of Tap Water and Precipitation Isotope Ratio Data

[19] As noted above, the tap water data show spatially coherent variability. Cross validation of tap water isotope ratio predictions generated by ordinary kriging of the raw isotope data, for example, indicates that approximately 87% of δ^2H and 83% of δ^{18}O variation within the data set can be explained in terms of the isotope ratios of tap water from adjacent sample sites alone. This implies that aspects of water source and history that vary continuously across space exert a dominant control on tap water isotope ratios, an observation that is perhaps surprising given the great potential for discrete factors (e.g., catchment boundaries, artificial diversion) to impact water isotope ratio patterns.

[20] Spatial variation in the isotope ratios of precipitation represents a source of spatially continuous variability that exerts strong influence on the distribution of stable isotopes in meteoric waters [e.g., *Kendall and Coplen*, 2001; *Dutton et al.*, 2005]. The overall patterns of variation in the precipitation maps (Figure 4) and the tap water data are similar, with the lowest values occurring in the high-altitude continental regions of the northern Rocky Mountain interior, and the highest values in low-latitude and altitude areas of the south central to southeastern United States. Across the entire tap water data set, strong correlation exists

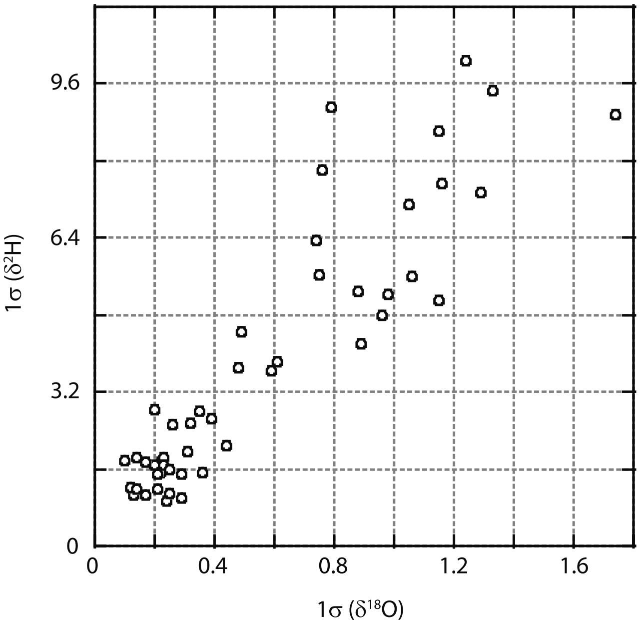

Figure 3. Variability of H and O isotope ratios at sites sampled in the seasonal survey. Values shown are 1 standard deviation (in ‰) for all single-month values at each site.

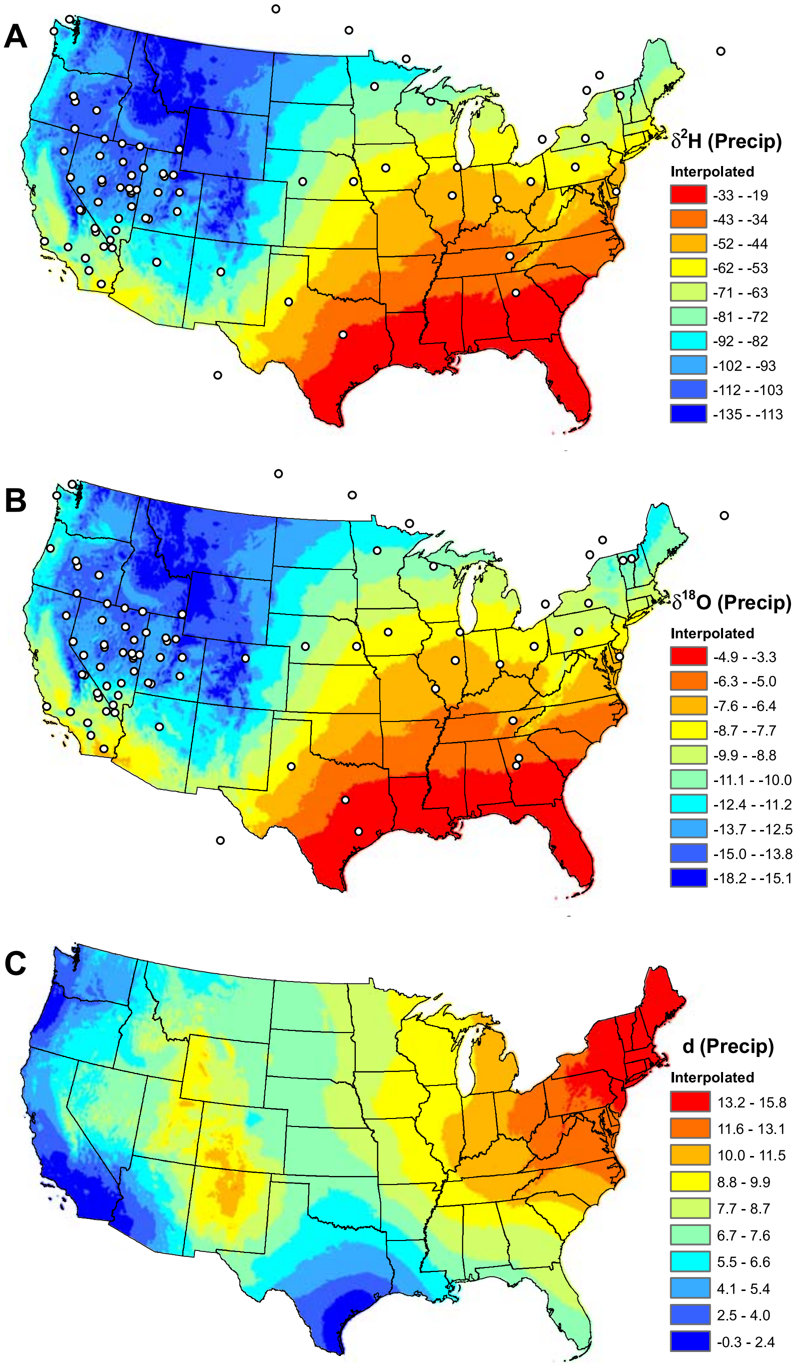

Figure 4. Interpolated (a) δ^2H, (b) δ^{18}O, and (c) deuterium excess of annually averaged precipitation across the contiguous United States (see section 2). The locations of data stations within and adjacent to the contiguous United States are shown in Figures 2a and 2b. All values are in ‰ relative to the VSMOW standard.

between tap water isotope ratios and predicted mean annual precipitation isotope ratios (Figure 5), with more that 74% of the variation in each isotope system correlated with predicted local precipitation isotope ratios. Values of *d* for tap water are more poorly correlated with those of predicted local precipitation (r^2 = 0.14; not shown). Despite the large number of intervening processes, the dominant control on tap water isotope ratios at the national level appears to be the H and O isotope ratios of climatological water sources near the location of water use.

[21] Despite the overarching control of spatial precipitation isotope ratio patterns on the δ^2H and δ^{18}O values of tap water, strong and systematic differences exist between the two data sets. For both elements, the distribution of tap water isotope ratios is significantly broader than that of estimated precipitation (i.e., the standard deviation of tap water isotope ratios is 45–50% greater than that of precip-

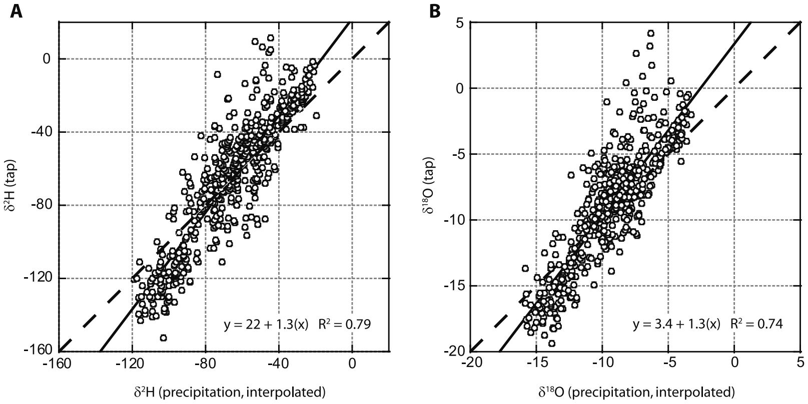

Figure 5. Regression relationships between observed tap water isotope ratios and interpolated precipitation isotope ratios at the sites of tap water collection: (a) δ^2H and (b) δ^{18}O (‰ relative to VSMOW). The empirical least squares regression (equation given) is shown as a solid line, and a 1:1 relation is given as a dashed line.

itation). This can be seen in Figure 5 as a tendency for tap water δ^2H and δ^{18}O values to be higher than predicted local precipitation values at sites with relatively high water isotope ratios, and lower than predicted precipitation values at the more ^{2}H and ^{18}O depleted sites. Visual inspection suggests that the deviation from a 1:1 relation between tap water and modeled precipitation values is similar for both elements at low isotope ratios, but that the effect is stronger for δ^{18}O than for δ^2H at high values.

[22] Our data set demonstrates a high degree of spatial coherence in the distribution of differences between tap water and predicted annual average precipitation isotope ratios (Moran's I for tap - precipitation differences = 0.40, 0.29, 0.2; Z = 4.7, 3.4, 2.6; $p < 0.01$, 0.01, 0.01 for δ^2H, δ^{18}O, and *d*, respectively; Figure 6), implying that spatially autocorrelated processes dominate postprecipitation isotopic modification. This spatially coherent variation allows us to create interpolated representations of the tap - precipitation isotope ratio differences that represent 74, 68, and 43% of the variability for δ^2H, δ^{18}O, and *d* offsets at the national level (Figure 6). On the basis of our kriged maps we distinguish two contrasting patterns in the tap - precipitation isotope ratio offsets that, we argue, reflect different dominant postprecipitation processes affecting water resources in the contiguous United States.

5.1. "Light" Water Regions

[23] Stable hydrogen and oxygen isotope ratios of tap water are much lower than those of modeled local precipitation across most of the western interior of the United States and along the Colorado, Missouri, and Ohio River valleys. We believe that the low tap water isotope ratios in these areas can be attributed to three factors. First, the stable isotope ratios of H and O in precipitation are strongly correlated with altitude [e.g., *Poage and Chamberlain*, 2001; *Bowen and Wilkinson*, 2002], and tap water derived from sources recharged with high-elevation water could have lower isotope ratios than those characteristic of precipitation at the site of water use. Second, in regions characterized by temperate, continental climates, the stable isotope ratios of precipitation exhibit strong seasonality [*Rozanski et al.*, 1993] and tap water derived from sources recharged primarily with winter season water might have isotope ratios that reflect the relatively low δ^2H and δ^{18}O values of winter precipitation. Third, the stable isotope ratios of many pre-Holocene groundwaters, particularly those recharged during end Pleistocene deglaciation, are much lower than those of younger groundwater or precipitation [e.g., *Fritz et al.*, 1974; *Fontes et al.*, 1991; *Grasby and Betcher.*, 2002; *Zuber et al.*, 2004], and tap water derived from these old groundwaters may have atypically low δ^2H and δ^{18}O values.

[24] It is likely that within the light water regions described here all three factors contribute to the low stable isotope ratios of tap water, and based on the current data set we do not attempt to distinguish among the factors. The impact of high-elevation water on water resources in the western United States, for example, has been documented in data sets of river water isotope ratios [*Kendall and Coplen*, 2001; *Dutton et al.*, 2005] and in groundwater studies [e.g., *Manning and Solomon*, 2003]. Within this region, elevation and seasonality factors are commonly linked, and the concentrated release of winter season water during spring and summer melting of high-elevation snowpack provides an important opportunity for recharge of groundwater and surface water reservoirs [*Wilson and Guan*, 2004]. Evidence for the impact of pre-Holocene recharge on the isotope ratios of groundwater within the region has been provided by *Smith et al.* [2002] based on regional data sets of isotope ratios of groundwater and precipitation in the Great Basin. Although the low tap water isotope ratios defining our light water regions may primarily reflect one of theses factors, without site-specific hydrological and water management information it is not possible to demonstrate this using our current data set representing a static time slice of tap water isotope distributions.

[25] Data from continued stable isotope ratio monitoring, however, could provide clear warning signals of future supply stability problems related to these hydrological factors, particularly when analyzed in the context of data on climate and water supply infrastructure. Subnetworks designed to target water supplies drawing from deep, shallow, and surface reservoirs could monitor for potential supply changes in each type of hydrological system. In aquifer-supplied systems consuming old groundwater, sta-

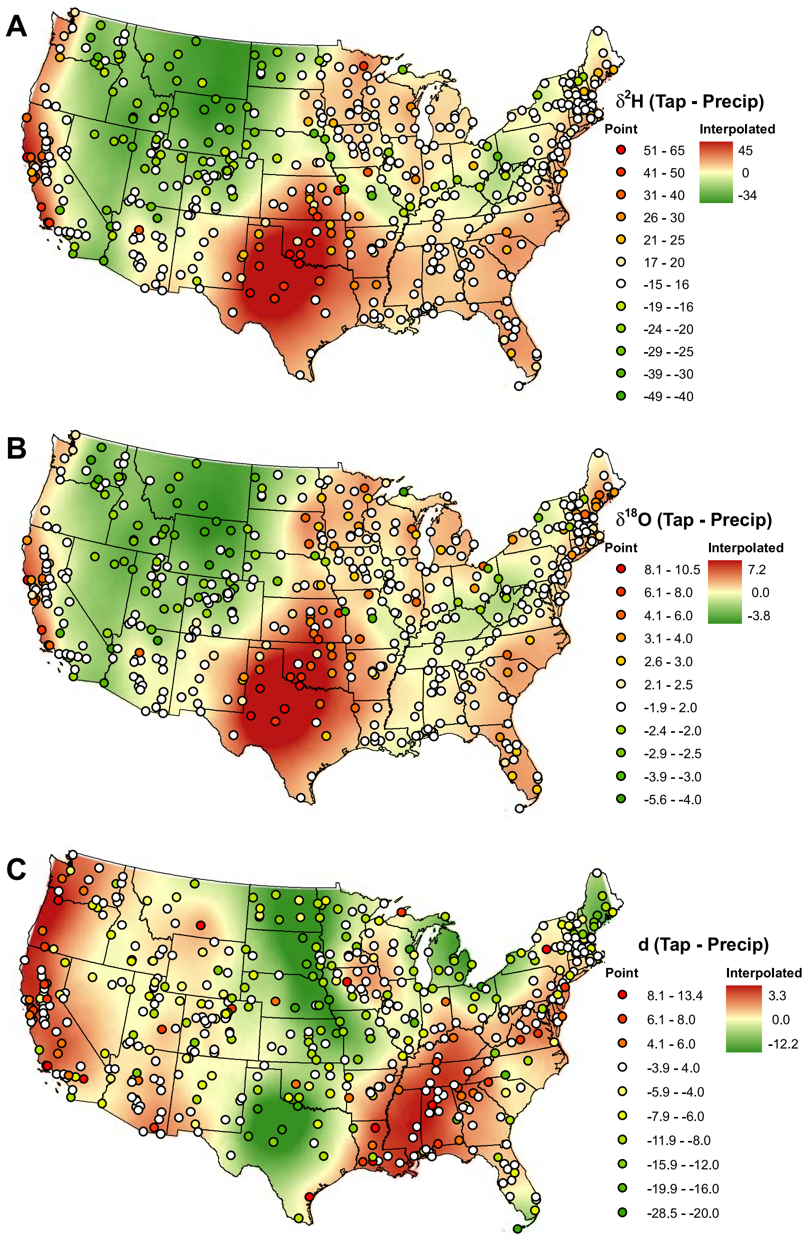

Figure 6. Differences between observed tap water isotope ratios ((a) δ^2H and (b) δ^{18}O) or (c) deuterium excess and interpolated values for annual average precipitation (Figure 4). Values for individual data collection sites are given as points, which are color coded by the size of the difference between tap water and precipitation values. In each case, values that are close to zero (i.e., within 16‰ for δ^2H, 2‰ for δ^{18}O, or 4‰ for d) are grouped and shown as white symbols. Background color fields show regional patterns of the difference between tap water and precipitation values interpolated by ordinary kriging using a spherical semivariogram (see section 2). All values are in ‰ units.

ble isotope monitoring might identify the early stages of changes in aquifer status, for example depletion of old water stocks and replacement by younger recharge. Perhaps more important, however, monitoring of active surface- and shallow groundwater-supplied systems might provide a means of detecting the early impacts of hydroclimatological change on regionally important sources and supplies of water. As longer-term data sets are developed, spatial analysis to determine common trends and relate them to climatological and hydrological forcing factors may lead to improved understanding of the water supply impacts of factors such as changes in mountain snowpack [*McCabe et al.*, 2004; *Mote et al.*, 2005].

5.2. Low Deuterium Excess Regions

[26] Across most of the contiguous United States, tap water d values are dominantly either similar to or slightly less than those predicted for precipitation and only scattered single sites give values that are significantly different (Figure 6c). Throughout much of the Great Plains and the

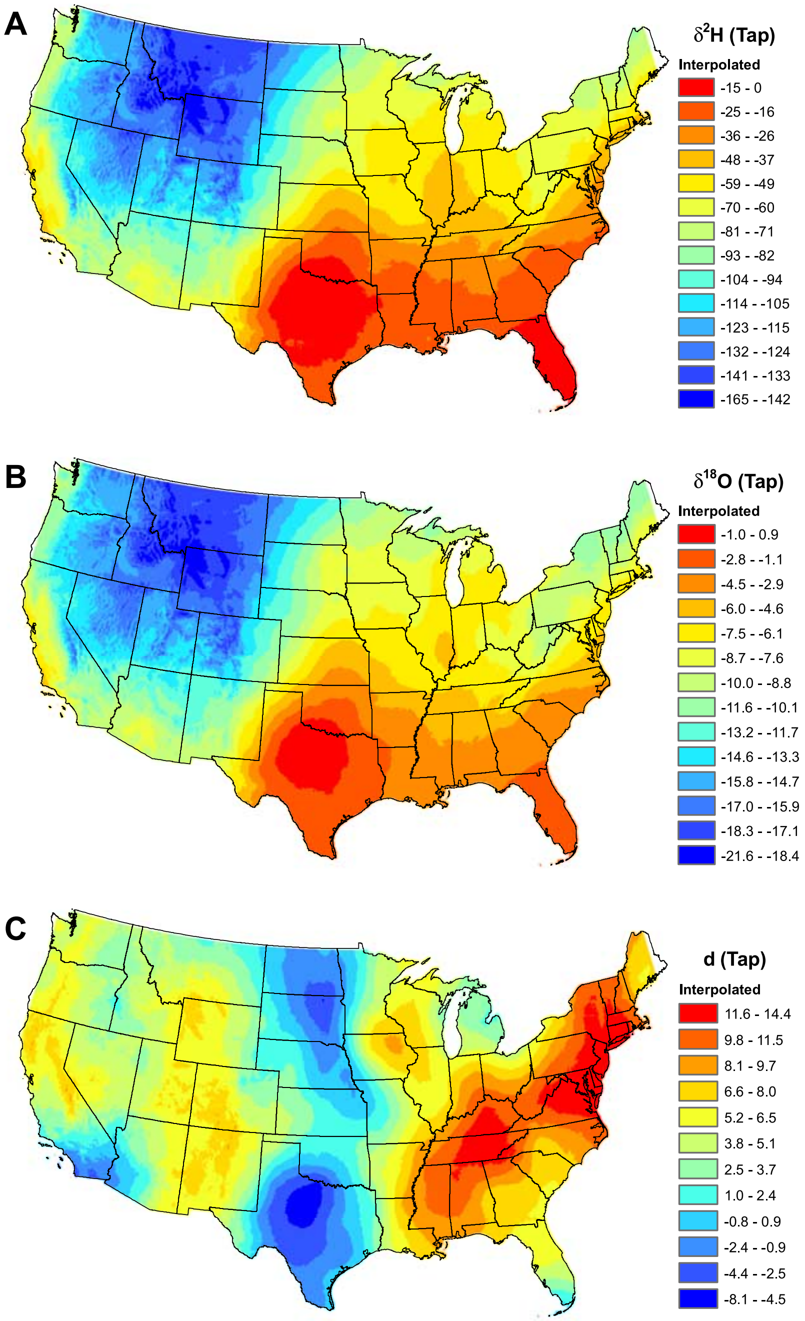

Figure 7. Prediction maps showing estimated isotope ratios ((a) δ^2H and (b) δ^{18}O) and (c) deuterium excess values for tap water in the contiguous United States. Isotope ratio maps were generated by summing interpolated precipitation isotope ratio layers (Figure 4) and interpolated differences between tap water and precipitation isotope ratios (Figure 6). The map of *d* values equals the difference of the δ^2H map and 8 times the δ^{18}O map (see section 2). All values are in ‰ relative to the VSMOW standard.

Great Lakes region, however, large concentrations of sampling sites are characterized by tap water *d* values that are much lower (i.e., >10‰) than local precipitation. In some of these areas, most notably the lower Great Plains, tap water isotope ratios are also much higher than those estimated for precipitation. Postprecipitation changes in *d* occur in response to evaporative loss of water, particularly under conditions of low relative humidity [*Gat*, 1981]. Evaporation also leads to an increase in the δ^2H and δ^{18}O values of the residual water, and the low *d* values and, in places, high stable isotope ratios of tap waters can be taken to indicate that a substantial degree of evaporation is typical of water stocks consumed in these areas.

[27] Surface reservoirs provide approximately 63% of all U.S. public supply water [*Hutson et al.*, 2004], and monitoring and planning for the stability of these water sources represents a major challenge for water managers. Evaporative water loss from reservoirs can significantly impact

water storage, and its effects on water resource stability, particularly under changing climatic conditions, can be difficult to incorporate in reservoir planning models [*Adeloye et al.*, 1999; *Montaseri and Adeloye*, 2004]. Network-based stable isotope data provide a means of monitoring rates of water loss and regional water resource sensitivity to evaporation. Although the isotopic evidence for evaporation clearly does not in itself provide a warning signal of water resource sensitivity, data collected over time and analyzed in combination with information on regional climate and hydrology could be used to characterize and monitor surface water resource susceptibility to climate change.

6. Conclusion: From Precipitation to Tap—A First Map of Tap Water Isotope Ratios

[28] Our results demonstrate that the distribution of δ^2H and δ^{18}O values of tap water across the contiguous United States is dominated by several levels of spatially patterned variability. Although they cannot always be directly or uniquely attributed to causal factors, the patterns can be described in terms of the stable isotope ratios of climatological water sources and postprecipitation processes affecting surface and groundwater resources. Continued isotope ratio monitoring of tap water through spatial networks such as that developed here offers a tool for monitoring the impacts of climatological and hydrological changes on water resource stability across large regions of the country.

[29] One unique contribution of our study has been to demonstrate that spatially coherent patterns in a tap water data set appear to reflect regionally pervasive features of water supply hydrology. We believe that by combining this type of spatial data analysis with collection of temporal sequences of samples the power of this approach will be greatly increased. In order to guide further development of these applications we have generated predictive maps of the estimated stable H and O isotope ratios and deuterium excess of tap water for the contiguous United States to serve as a baseline for future studies (Figure 7; see section 2). The creation of these maps follows the logic presented in our discussion: they incorporate both the national-scale similarity between isotope ratios of precipitation and tap water as well as regional offsets related to postprecipitation water source history. All three maps represented most of the observed variability in U.S. spatial tap water data (regression of predicted values against observations gives $r^2 = 0.93$ for δ^2H, 0.90 for δ^{18}O, and 0.57 for d), and root mean square errors for the map predictions (based on cross validation) are 12‰ for δ^2H and 1.8‰ for δ^{18}O (not available for d).

[30] The maps of tap water stable isotope ratios provide a tool and template for water resources research using H and O isotope ratios, but are also relevant to a wide and developing range of applications involving the use of stable isotope ratios for tracing the source of human-produced products. Recent studies of products ranging from foods [e.g., *Giménez-Miralles et al.*, 1999; *Bowen et al.*, 2005] to biological pathogens [*Kreuzer-Martin et al.*, 2004a, 2004b] have suggested that in many cases the δ^2H and δ^{18}O values of water used in the production of inorganic or organic products influences the H and O isotope ratios of the finished products in a predictable manner. As a result, analysis of the stable isotope ratios of products may be used to constrain the location of origin of samples if the spatial distribution of isotope ratios for relevant water sources is known. The tap water maps presented here will, in many cases, provide estimates of the spatial isotope ratio patterns relevant to understanding the origin of human-produced products, which may incorporate tap water directly (e.g., many bottled water products) or indirectly (e.g., through use of tap water in growth media for microbial cultures or irrigation of plants). The tap water maps are also highly relevant to a related category of applications in which the H and O isotope ratios of human body tissues, such as hair, nail, and tooth enamel, may be used to reconstruct the location of residence and/or travel history of individuals for purposes of archaeological and/or forensic investigation [*Fraser et al.*, 2006].

[31] Our maps represent a first attempt to depict the isotope ratios of tap water at the national scale, but do not capture the full dynamics controlling tap water isotope ratio distributions and should be used in awareness of their limitations. Tap water isotope ratios reflect a complex interplay of physical, chemical, and social processes, including both spatially continuous and discontinuous effects. Interpolation techniques, even when combined with spatial modeling of natural water sources as done here, cannot capture the full complexity of spatial tap water isotope ratio variation. A mechanistic, predictive model for tap water isotope ratios will require both improved understanding of the stable isotope ratios of water sources (including rivers, lakes, reservoirs, and naturally and anthropogenically recharged groundwater) and the development of models for the social and political processes that determine access to and selection of reservoirs as sources of water for consumption. The continuation of isotope ratio monitoring efforts focusing on a wide range of natural and human components of the hydrological cycle is therefore needed. These efforts will provide both an improved basis for stable isotope ratio mapping in human-hydrological systems and improved spatiotemporal data sets documenting the status and stability of regional water supplies.

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