Water balance model for mean annual hydrogen and oxygen isotope distributions in surface waters of the contiguous United States

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[1] The stable H and O isotope composition of river and stream water records information on runoff sources and land-atmosphere water fluxes within the catchment and is a potentially powerful tool for network-based monitoring of ecohydrological systems. Process-based hydrological models, however, have thus far shown limited power to replicate observed large-scale variation in U.S. surface water isotope ratios. Here we develop a geographic information system–based model to predict long-term annual average surface water isotope ratios across the contiguous United States. We use elevation-explicit, gridded precipitation isotope maps as model input and data from a U.S. Geological Survey monitoring program for validation. We find that models incorporating monthly variation in precipitation-evapotranspiration (P-E) amounts account for the majority (>89%) of isotopic variation and have reduced regional bias relative to models that do not consider intra-annual P-E effects on catchment water balance. Residuals from the water balance model exhibit strong spatial patterning and correlations that suggest model residuals isolate additional hydrological signal. We use interpolated model residuals to generate optimized prediction maps for U.S. surface water δ^2H and δ^{18}O values. We show that the modeled surface water values represent a relatively accurate and unbiased proxy for drinking water isotope ratios across the United States, making these data products useful in ecological and criminal forensics applications that require estimates of the local environmental water isotope variation across large geographic regions.

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1. Introduction

[2] The stable isotopic composition (δ^2H and δ^{18}O) of environmental water varies widely and systematically across the continents due to isotopic fractionation accompanying the transport of water within the global hydrological cycle [*Craig*, 1961; *Dansgaard*, 1964; *Kendall and Coplen*, 2001; *Rozanski*, 1985; *Rozanski et al.*, 1993]. As water transits between any two points in a hydrological system, changes in its isotopic composition integrate information on processes it incurs, e.g., mixing with water of contrasting isotopic composition (positive or negative change in isotopic composition following a linear mixing relationship), evaporative loss (increasing the δ^2H and δ^{18}O values of residual water), or loss due to transpiration or infiltration (producing a loss of water with no change in isotopic composition). As a result, isotopic measurements, in the context of appropriate models for their interpretation, provide a powerful tool for observing and quantifying the spatially integrated effects of water cycle processes within watersheds and air sheds [e.g., *Bowen et al.*, 2007b; *Brooks et al.*, 2010; *Gat et al.*, 1994; *Gibson and Edwards*, 2002; *McGuire et al.*, 2005; *Worden et al.*, 2007]. Recent work has also demonstrated that hydrological isotope effects can be traced into human-managed hydrological and biological systems, providing information on the geographic and hydrological context of samples from such systems [*Bowen et al.*, 2005b, 2007a; *Ehleringer et al.*, 2008; *O'Brien and Wooller*, 2007].

[3] The use of stable isotopes to study integrated hydrological processes within catchments requires (1) that the isotopic composition of water entering and leaving the study system is known and (2) that models are available to describe the transit of water through the system and the isotopic effect of processes occurring during this transit. For most surface water systems, the ultimate source of water is precipitation incident within the catchment. The mechanisms controlling spatial and temporal variation in the isotopic composition of precipitation have been extensively studied, based largely on the long-term monitoring efforts of the Global Network for Isotopes in Precipitation [*International Atomic Energy Agency*, 1992], and are well understood

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from a theoretical perspective [*Gat*, 1996]. This understanding has been developed into a range of predictive statistical models for precipitation isotope ratios at global to subcontinental scales [*Bowen*, 2010] and incorporated into dynamical models of the atmospheric water cycle [*Noone and Sturm*, 2010]. Among the dominant large-scale patterns in precipitation δ^2H and δ^{18}O values are decreases in values with increasing latitude, elevation, and distance from the ocean coasts. Relatively few systematic attempts have been made to measure stream and river water isotopic composition over large geographic areas. One such contribution, on which we focus here, was a program to monitor and interpret spatial and temporal changes in the isotopic composition of streams and rivers sampled by the United States Geological Survey's National Stream Quality Accounting Network and Hydrological Benchmark Network (NASQAN/HBN) over a 4 year period during the mid-1980s [*Kendall and Coplen*, 2001].

[4] Two previous studies have applied spatially explicit modeling to investigate the relationship between precipitation isotope ratios and the NASQAN/HBN stream water data set. *Dutton et al.* [2005] developed statistical models, incorporating geographic and physiographic parameters (latitude and altitude), for U.S. precipitation and stream water δ^{18}O data sets. Although their work did not explicitly model the hydrological processes linking precipitation and stream waters, they demonstrated that both data sets were described well by models of identical form, with differences in model parameter values (e.g., stream water δ^{18}O values decreased more rapidly with altitude) that could be related to properties of the hydrological systems (e.g., change in mean catchment elevation as a function of sampling site elevation). *Fekete et al.* [2006] applied a process-based distributed hydrology model to simulate the isotopic composition of river discharge globally. Through a range of sensitivity tests the authors were able to identify the modeled expression of a number of large-scale hydrological processes (evapotranspiration, seasonality of runoff generation) on the isotopic composition of hydrological fluxes and reservoirs. In a final analysis of model closure, involving comparison of the modeled results for sites within the United States to the NASQAN/HBN network data, the model performed relatively poorly, particularly in cooler and higher-elevation regions.

[5] In this study we adopt an approach of intermediate complexity, using standard geographic information system (GIS) tools to develop a simple, "steady state," water balance model for surface water isotopic composition. Our approach differs fundamentally from that of *Dutton et al.* [2005] in that we explicitly model surface water discharge within catchments and river systems. Although the model we apply is not as comprehensive as that used by *Fekete et al.* [2006], it offers a number of advantages relative to that study; among them are the following: (1) we use a model of precipitation δ^2H and δ^{18}O values that represents elevation effects, improving the estimation of incident precipitation in mountainous catchments; (2) we are able to conduct our simulation at much higher spatial resolution (1 km^2); (3) the simple model formulation allows us to easily and unambiguously isolate key hydrological processes and assess their modeled isotopic expression relative to the observational data set; and (4) we consider an additional observational data set for U.S. municipal tap waters, extending our analysis to evaluate isotopic relationships between surface water and drinking water across the contiguous United States.

[6] We begin by developing the water balance model and describing its predictions. We then evaluate the model results relative to the NASQAN/HBN monitoring data, interpret processes leading to differences between the modeled and observed surface water values, and consider how these differences might be used to quantify regional variation in large-scale hydrological fluxes. We propose a residual correction scheme for developing an optimized GIS map of mean annual surface water isotope ratios across the United States, and finally compare the residual-corrected map values with observed isotopic values for tap waters to assess if and where the modeled surface water values provide an accurate approximation for the isotopic composition of human-consumed drinking water.

2. Methods

[7] Five data sets were used in the analysis: (1) gridded, long-term average mean annual and mean monthly δ^2H and δ^{18}O values for global precipitation, developed using an updated database of precipitation isotope ratio monitoring data from the period 1960–2000 and previously published methods (Figure 1a; http://waterisotopes.org) [*Bowen and Revenaugh*, 2003; *Bowen et al.*, 2005a]; (2) the Hydro 1K hydrology-corrected North American digital topography at 1 km spatial resolution (http://edc.usgs.gov/products/elevation/gtopo30/hydro/namerica.html); (3) North American Regional Reanalysis (NARR) annual and monthly climatological (1979–2002) precipitation and actual evapotranspiration amounts at 32 km spatial resolution (Figure 1b; http://www.esrl.noaa.gov/psd/data/gridded/data.narr.monolevel.html) [*Mesinger et al.*, 2006]; (4) observed river water δ^2H and δ^{18}O values for U.S. rivers from the period 1984–1987 [*Kendall and Coplen*, 2001]; and (5) measured tap water δ^2H and δ^{18}O values from cities and towns in the contiguous United States during the period 2002–2003 [*Bowen et al.*, 2007b]. All data were imported into ArcGIS 9.3 and gridded data were projected onto the Lambert Azimuthal Equal Area projection for North America. Where necessary, data were resampled on the ~1 km Hydro 1K grid using cubic convolution and clipped to extract values within a spatial domain that encompassed all catchments within Canada and Mexico draining into the contiguous United States. Data quality and temporal coverage varies for each source as described in the references given, and is discussed below where directly relevant to the analysis.

[8] Our analysis workflow is documented in Figure 2. For each 1 km^2 grid cell, runoff of incident precipitation (m^3/Q, month or/yr) was estimated as the larger of precipitation minus evaporation (P-E) (Figure 1a) or 0.01 × P. This formulation represents a somewhat arbitrary simplifying assumption allowing us to account for the contribution of dry season and dry region events to runoff: it minimizes the contribution of runoff from grid cells and time periods where there is no excess P while acknowledging that these conditions can lead to some runoff. The formulation is also not consistent with a strictly closed water budget at each cell; however, the water balance represented by the NARR data products is not itself closed and the deviation imposed here

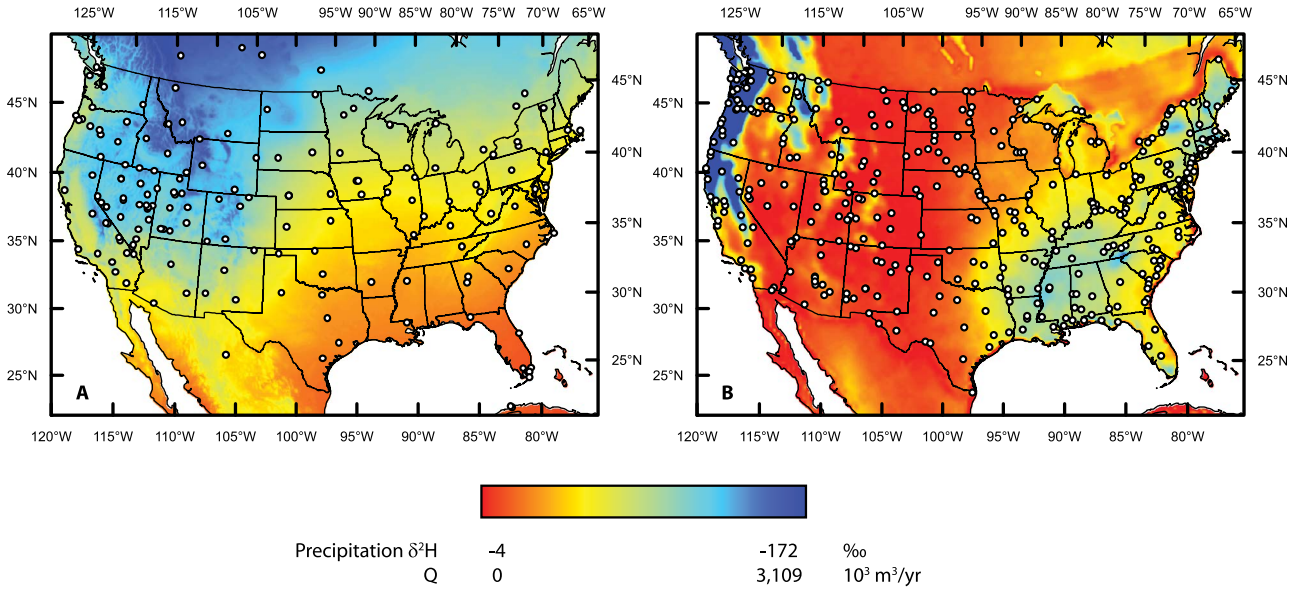

Figure 1. Input data sets used to model surface water isotope ratios. (a) Gridded, long-term mean annual average precipitation δ^2H values, interpolated from a global database of monitoring station data. Station locations within the study domain are shown. (b) Estimated climatological mean annual runoff (Q) based on North American Regional Reanalysis precipitation and evapotranspiration data. Points show the location of 372 National Stream Quality Accounting Network and Hydrological Benchmark Network (NASQAN/HBN) surface water monitoring sites. See section 2 for information on data sources.

is minimal in comparison with the imbalance inherent to the input data [e.g., *Kumar and Merwade*, 2011]. In addition to runoff amount, we calculated the "isotopic flux" associated with grid cell discharge (δQ) for each cell in two different ways:

$$\delta Q_a = (P_a - E_a) \times \delta_a, \tag{1}$$

and

$$\delta Q_m = \sum[(P_i - E_i) \times \delta_i], \tag{2}$$

where δ is the H or O stable isotopic composition of precipitation falling in a given grid cell (all isotope values are reported in ‰ units relative to the Vienna SMOW standard), a indicates annual average values, and the monthly weighted

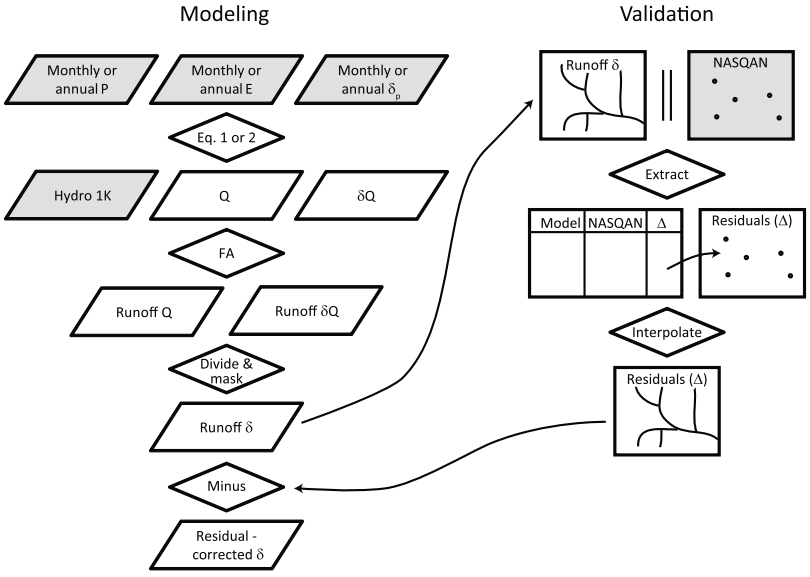

Figure 2. Workflow for geographic information system–based modeling and analysis of surface water isotope distributions. Trapezoids indicate raster data sets; diamonds are operations. Shaded entries are input data sets. P, precipitation; E, evaporation; δ_P, isotopic composition of precipitation; FA, flow accumulation; Q and δQ, as described in section 2 of the text.

value (m) is calculated by summing across all monthly values (i). The first approach, which we will hereafter refer to as the spatially weighted water balance model, effectively assumes that runoff is an unbiased average of the precipitation falling on a grid cell, whereas the second (the spatiotemporally weighted water balance model) allows for seasonal variation in the contribution of precipitation to runoff driven by intra-annual changes in evapotranspiration rates. Because the value of δ varies systematically throughout the seasonal cycle at most sites [*Bowen*, 2008] the spatiotemporally weighted model accounts for biases in the isotopic flux due to temporal covariance of Q and δ, and differences between the models should be reflective of the predicted significance and pattern of seasonal variation in grid cell water balance.

[9] Flow direction (indicating which of the 8 adjacent cells receives discharge from each grid cell) was calculated for each grid cell within the contiguous United States and adjacent, hydrologically connected areas of Canada and Mexico. Values of Q and δQ were then summed throughout the runoff networks defined by grid cell flow directions (using the flow accumulation tool, Spatial Analyst toolbox). Modeled estimates of the surface water isotopic composition at each grid cell in the river networks were calculated as accumulated upstream δQ values divided by accumulated Q. After calculation of surface water δ values at all grid cells, the resulting raster grid was masked to generate a stream network by excluding grid cells with accumulated flows of <1000 m^3/yr or total drainage areas <9 km^2. These criteria were subjectively chosen to achieve our goal of masking "nonriver" cells with little accumulated runoff while representing the range of catchment areas and discharge amounts sampled in the NASQAN/HBN data set.

[10] The model employed here does not include any seasonal water balance effects other than those represented by the P-E input data, for example water storage as snowpack and soils or variation in partitioning of runoff and infiltration throughout the seasonal cycle. These effects will contribute strongly to the intra-annual isotope dynamics of many catchments, but with the exception of cases in which they significantly alter the fraction of seasonal precipitation lost to evapotranspiration they are unlikely to have a large impact on the long-term (multiyear) isotope flux. The model also does not account for the influence of isotope fractionation during evaporation on the isotope runoff flux. Evaporative fractionation is well understood from a theoretical perspective [*Craig and Gordon*, 1965], but its incorporation in predictive land surface hydrology models is complex because fractionation is dynamic and can vary strongly over time and between different land surface systems (e.g., canopy intercepted water, soil water, and open water evaporation). In fact, significant uncertainty remains as to what extent each of these modes of evaporation impacts the isotopic composition of runoff [e.g., *Brooks et al.*, 2010; *Gat*, 1996]. In this study we treat evaporative fractionation as an unknown, but probe the results of the water balance model with the goal of identifying if and under what circumstances the isotopic effects of evaporation can be revealed in the comparison of model predictions with observational data.

[11] Modeled values were compared with long-term annual average stream water isotopic compositions, derived from the data set of *Kendall and Coplen* [2001], in order to evaluate the performance of the water balance model and identify areas of systematic disagreement between the model and data (Figure 2, right). Samples from 372 sites were available within the study domain, representing a wide range of catchment areas (mean area ≈8,000 km^2), and all data from all sites were included in the analysis. Sampling was conducted throughout the year with minimal seasonal bias. On average 12.25 samples were analyzed per site (5.25 per site per yr) during the study period. We base our analysis on the flow-weighted annual average values calculated by *Kendall and Coplen* [2001].

[12] Monitoring station locations were manually screened and relocated onto the gridded stream network where geographic discrepancies existed due to the generalization inherent in the digital elevation model (DEM)–based drainage geometry; accuracy was checked by comparing the United States Geological Survey–reported catchment areas and those derived from the digital topography (ordinary least squares regression: slope = 0.991, R^2 = 1.000). Modeled isotopic compositions were then extracted from each grid cell corresponding to an observation site and the differences between modeled and observed values were calculated. The resultant residual values were used for evaluation of the model results, and spatial patterns in the residuals were analyzed using the Moran's I test (Spatial Analyst Extension, inverse Euclidean distance model [*Moran*, 1950]) to test for spatial autocorrelation. In all cases spatial clustering was observed, and residual values were interpolated onto a 1 km grid by ordinary kriging [*Cressie*, 1993] using the Geostatistical Wizard (Geostatistical Analyst Extension) in ArcGIS 9.3. Interpolated residual values were subtracted from the modeled surface water isotope grids to produce optimized surface water prediction maps (Figure 2).

[13] We compared the optimized map values with an independent data set of tap water isotope ratios from 490 sites in the contiguous United States [*Bowen et al.*, 2007b]. These values represent individual grab samples from a wide range of domestic use water sources nationwide. They have not been screened on the basis of water supply type or other hydrological or environmental variables; nonetheless *Bowen et al.* [2007b] showed pervasive spatial patterns in this data set and in the differences between tap water and local precipitation isotope ratios that were suggested to result from hydrological factors such as seasonal biases in runoff generation and transport in rivers. In order to compare tap water isotope ratios with modeled values for nearby surface water sources we created a circular buffer with a 50 km radius around each tap water sampling site and summed the modeled Q and δQ values for all river grid cells within the buffer zone. We then divided these values to give a flow-weighted average value for river grid cells within a 50 km radius of the tap water sampling site. The choice of buffer radius and the Q-weighted calculation method was subjective, but provided a self-consistent, GIS-based method for estimating the isotopic composition of the most abundant and proximal surface water sources at a large number of locations for this exploratory analysis.

3. Results and Discussion

3.1. Input Data

[14] The gridded precipitation isotope ratio maps used here are in most respects similar to those previously published

by the authors [*Bowen and Revenaugh*, 2003; *Bowen et al.*, 2005a], but are based on a larger data set amassed from published and unpublished sources (see auxiliary material).[1] In all cases (δ^2H and δ^{18}O, monthly and annual maps) the modeled values vary widely across the study domain, with relatively high values occurring along the Gulf Coast, intermediate values throughout the northeastern and southwestern United States, the midcontinent, and the Pacific Coast, and low values in the northern Rocky Mountain interior (Figure 1a). All of the precipitation maps explicitly represent the effect of altitude on precipitation isotope ratios through the use of elevation as an ancillary variable in interpolation [*Bowen and Revenaugh*, 2003], which is of particular importance in the calculation of runoff-modeled surface water isotope ratios in areas of high topographic relief. 169 precipitation isotope monitoring stations area located within the study domain, and the global gridded maps provide an accurate representation of these data (e.g., representing 93% and 87% of the variance in the station mean annual δ^2H and δ^{18}O values, respectively).

[15] One problematic element of the input data used here is the existence of significant edge effects in the climatological P-E layer used in the calculation of grid cell runoff amounts (Figure 1b). These effects are introduced in the NARR precipitation amount layers, and derive from the use of different data assimilation methods for the United States and adjacent countries in the reanalysis (http://www.emc.ncep.noaa.gov/mmb/rreanl/faq.html#cat-rain) [*Mesinger et al.*, 2006]. The effect of this artifact on the modeled surface water isotope ratios within the contiguous United States should be minimal and limited to border-crossing streams and rivers. We have explored other potential input data sets for P-E (e.g., National Center for Environmental Prediction/National Center for Atmospheric Research reanalysis) but for our analysis we prefer the NARR layers given that they provide both variables from a unified analysis and offer relatively high spatial resolution combined with comprehensive spatial coverage for the study region.

3.2. Water Balance Model

3.2.1. Spatial and Spatiotemporal Weighting

[16] Modeled surface water δ^2H and δ^{18}O values at the 372 NASQAN/HBN monitoring sites range from −134 to −15‰ (average = −73‰) and −17.3 to −3.2‰ (average = −10.2‰), respectively, using spatially weighted runoff values (equation (1)), and from −163 to −17‰ (average = −89‰) and −21.2 to −3.4‰ (average = −12.3‰) when the isotope composition of runoff is spatiotemporally weighted (equation (2)). The distribution of modeled values is similar to that of the observed data, which range from −168 to −4‰ (average = −70‰) for δ^2H and from −21.8‰ to −1.1‰ (average = −9.9‰) for δ^{18}O, with the spatiotemporally weighted model better approximating the low end of the observed ranges and the spatially weighted model better reproducing the observed means. Comparison of measured and modeled values at individual sites (Figure 3) shows that with the exception of two outliers (which will be discussed separately below) both versions of the simple runoff model explain a large fraction of the variance in the observational data (91–92% for δ^2H, 89% for δ^{18}O). The relative strength of the simple model is perhaps surprising given that studies employing more comprehensive models have demonstrated much poorer ability to reproduce the same NASQAN/HBN data set [*Fekete et al.*, 2006, Figure 8c]. To a large degree this contrast may reflect the use of higher-resolution routing schemes and input grids as well as the use of elevation-explicit precipitation isotope grids in our study, but it may also reflect inaccuracies in the representation of hydrological or isotope fractionation processes in the more complex models. At a minimum, our result demonstrates the importance of precipitation amount distributions as a control on the spatiotemporal distribution of runoff generation within catchments.

[17] Despite the general strength of the water balance model in reproducing the observed isotopic data, strong and systematic deviations between the modeled and observed values exist. The spatially weighted model tends to overestimate (i.e., positive residuals) surface water δ values at sites with very low δ^2H and δ^{18}O (Figures 3a and 3b). These sites are situated primarily in the western interior of the United States (Figures 4a and 4b), and comprise 36% of sites based on δ^2H values and 38% based on δ^{18}O values. Previous studies of large-scale environmental water isotope distributions in the United States have observed that surface and groundwater δ^2H and δ^{18}O values within the western interior are notably lower than those of measured or modeled mean annual precipitation from the same location [*Bowen et al.*, 2007b; *Dutton et al.*, 2005; *Fekete et al.*, 2006; *Kendall and Coplen*, 2001; *Smith et al.*, 2002]. In most cases, this pattern has been attributed to the high topographic relief of the region and the fact that high-elevation precipitation, which is relatively ^{2}H and ^{18}O depleted, is the predominant source of water in most streams and many aquifers [e.g., *Manning and Solomon*, 2003; *Viviroli et al.*, 2003]. In the current analysis, the incorporation of elevation-explicit precipitation isotope grids and a flow accumulation model should largely account for catchment elevation effects on surface water isotope ratios. In fact, although the magnitude of the bias is lower than that observed in studies not incorporating elevation effects, the spatially weighted version of our model retains a systematic tendency to predict values higher than the observations across this region.

[18] The number of sites with positive δ^2H or δ^{18}O residual values is much lower when spatiotemporal weighting was used in the water balance model (3% for δ^2H, 4% for δ^{18}O). Moreover the systematic overprediction bias for stations with low-δ values is essentially eliminated, as reflected in regression slopes for the spatiotemporally weighted model/observation relations that approach 1 (Figures 3c and 3d). The difference between the two model versions stems from the asymmetry of estimated runoff efficiency (Q/P) for summer and winter months, which are characterized by relatively high-δ and low-δ precipitation, respectively. Across most of the contiguous United States, and particularly at high elevations within the western interior, along the Pacific coast, and throughout the eastern United States, the NARR climate layers give substantially higher runoff efficiency for the winter months than for summer (Figure 5a). This pattern can be attributed to a number of factors, including efficient generation of runoff from melting snowpack and high summer season evapotranspiration. The impact of this

[1] Auxiliary materials are available in the HTML. doi:10.1029/2010jg001581.

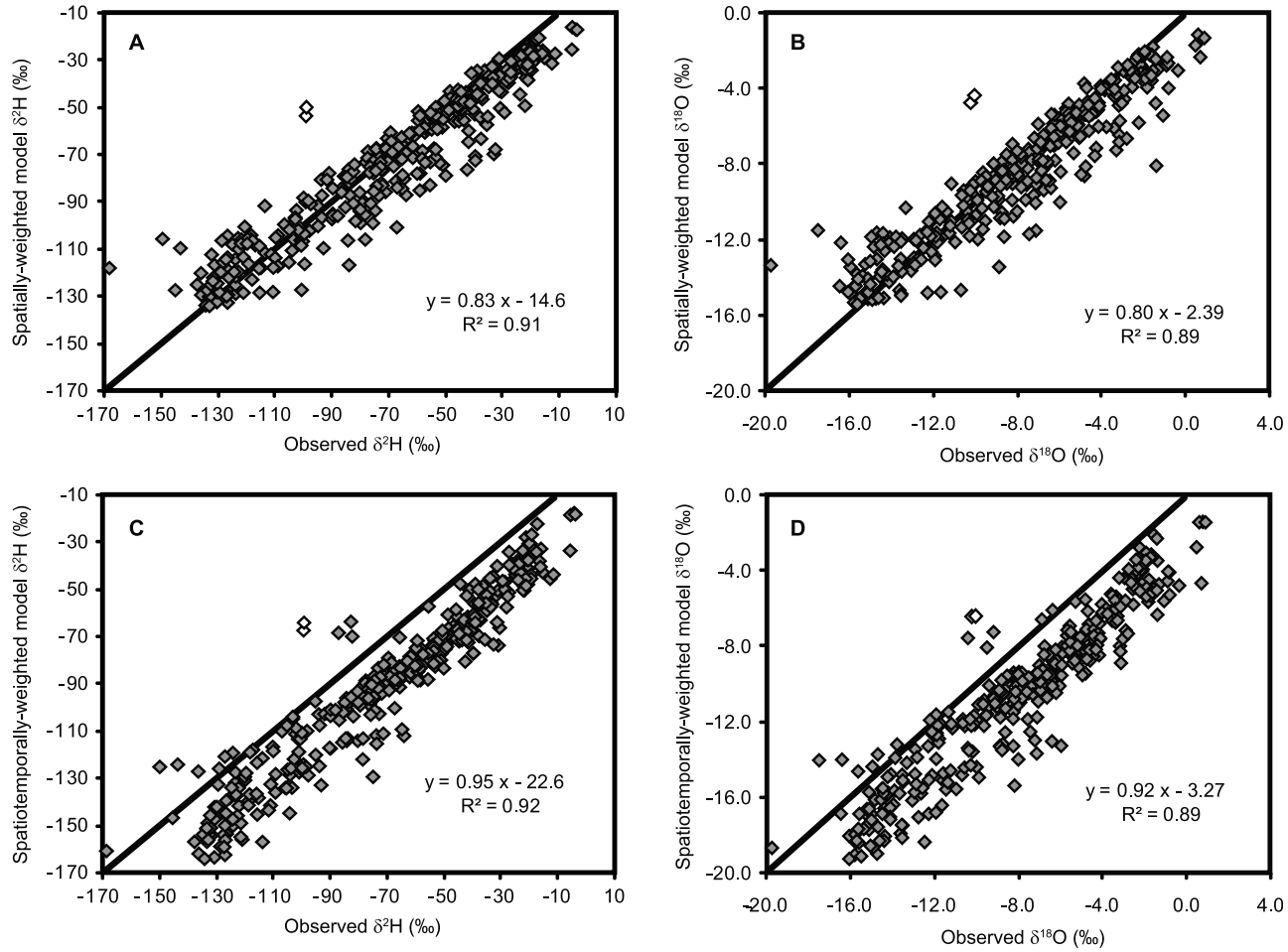

Figure 3. Comparison of measured mean annual isotope ratios for NASQAN/HBN surface water sites [*Kendall and Coplen*, 2001] with (a, b) predicted values from the spatially weighted and (c, d) spatiotemporally weighted water balance model. Bold lines show the 1:1 relationship, and the two outlier data points (open symbols) lying above the 1:1 line show data from the Alamo and New Rivers, California, which are not reflected in the least squares regression line equation.

variation on the spatiotemporally weighted isotope predictions can be seen in catchments where winter season runoff efficiency is high (Figure 5b), and is strongest in catchments with high-elevation headwaters within the western interior, where seasonal differences in precipitation δ^2H and δ^{18}O values are also maximal [*Bowen*, 2008].

[19] Despite the elimination of positive prediction bias for sites in the western interior, less spurious overestimation persists at a handful of sites in the spatiotemporally weighted model (Figures 3c and 3d). These sites are spatially clustered (Figure 5b) and occur in regions where the climate input layers indicate discrete variation in the seasonal asymmetry of runoff efficiency, including the northwestern Great Plains, New Mexico, and Isle Royale National Park (Michigan). In the Great Plains and New Mexico cases, the streams and rivers in question have mountain headwaters in areas where winter snowpack likely contributes disproportionately to runoff, but this effect is not represented in the NARR data due to their limited spatial resolution (Figure 5a). The impact of this inaccuracy in the climate data is exacerbated by the strong contrast in seasonal runoff efficiency between high and low elevations in these regions. Isle Royale, situated in Lake Superior, is in a region where even stronger contrasts in seasonal runoff efficiency are predicted between the Great Lakes and adjacent land areas. In this case the island area is not represented in the NARR physiography. Although the addition of monthly weighting of runoff values reduces the overestimation bias and improves the linearity of the water balance model/observation relationship overall, these examples demonstrate some of the inaccuracies associated with the current analysis and in particular highlight the potential improvements that could be obtained through the use of more accurate, higher-resolution climate forcing data.

3.2.2. Other Effects

[20] With the exception of the results for the sites just discussed, the water balance model has a general tendency to predict δ^2H and δ^{18}O values that are lower than the observed values (Figure 3). For the spatially weighted model, this "underestimation" tendency is dominant for all but the lowest-δ sites, whereas the spatiotemporally weighted model produces nearly ubiquitous underestimation at sites across the range of observed δ values. Sites where the isotopic composition of surface water is most severely

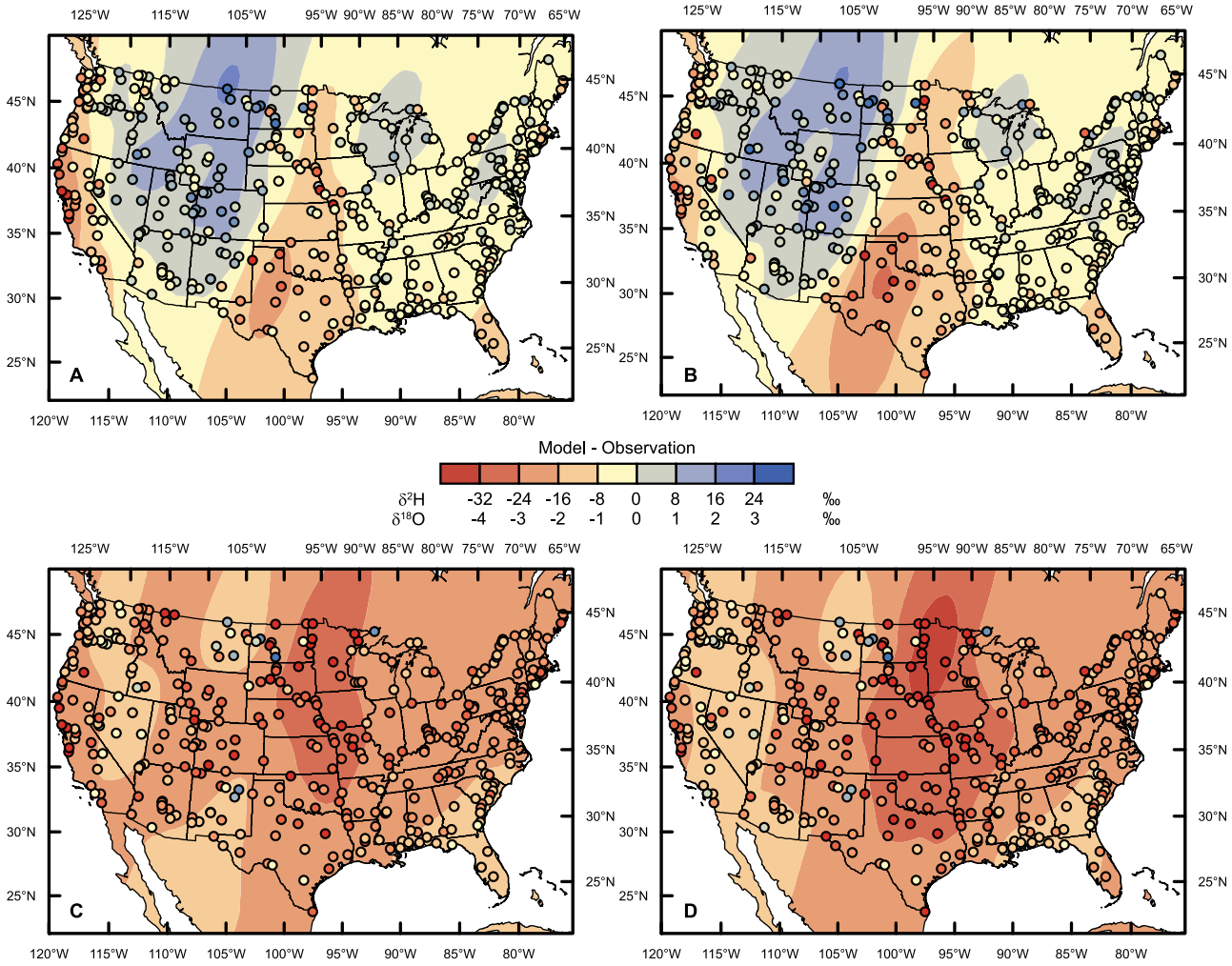

Figure 4. Spatial distribution of residuals from the (a, b) spatially weighted and (c, d) spatiotemporally weighted water balance model for surface water δ^2H (Figures 4a and 4c) and δ^{18}O (Figures 4b and 4d) values. Data points show residual values for individual surface water sites, and the background color field shows interpolated residual values, with the same color scale used for both the points and color fields.

underestimated by both versions of the model are concentrated in the Great Plains (Figure 4).

[21] Previous analysis of the NASQAN/HBN water data demonstrated evidence for the strong influence of evaporative water loss on stream water isotope ratios in many regions [*Kendall and Coplen*, 2001]. Evaporation produces a progressive, preferential loss of light isotopes to vapor, leaving the residual water enriched in ^{2}H and ^{18}O. Evaporative isotope effects, which are not included in the runoff model, likely contribute to the higher-than-modeled δ values of surface waters observed at many NASQAN/HBN sites, as supported by the high frequency of these sites across the Great Plains where E/P is ubiquitously high (Figure 1b). Kinetic isotope fractionation during evaporation also leads to a progressive decrease in the deuterium excess value ($d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$) of residual water [*Craig and Gordon*, 1965], providing an independent metric for the impact of evaporation on surface water isotope ratios. For both spatially and spatiotemporally weighted models, residuals (model minus observation) for δ^2H and δ^{18}O values are strongly, inversely correlated with d residuals (F test, $p = 0.03$ for spatially weighted δ^2H versus d, $p < 0.001$ for all other comparisons). This relationship is strongest for δ^{18}O values, for the spatiotemporal model, and for relatively large catchments (Figure 6), as might be expected for evaporation-driven effects given that (1) the spatiotemporal model has been shown to better account for other nonevaporation effects, (2) O isotopes are more strongly fractionated (relative to their natural range of variation) than H isotopes during evaporation, and (3) longer reaches can integrate more in-channel evaporation. The spatial distribution of model residuals for deuterium excess also closely mimics that of δ^2H and δ^{18}O across the central and eastern United States, with a regional maximum across the Great Plains (Figure 7).

[22] Taken together, these results indicate that underestimation of δ values and overestimation of d values likely reflects variation in the magnitude of evaporative isotope effects among catchments. This suggests that isotopic signals recording the evaporative component of catchment water balance could be extracted from first-order distributed hydrology models such as that used here. Such tools may be

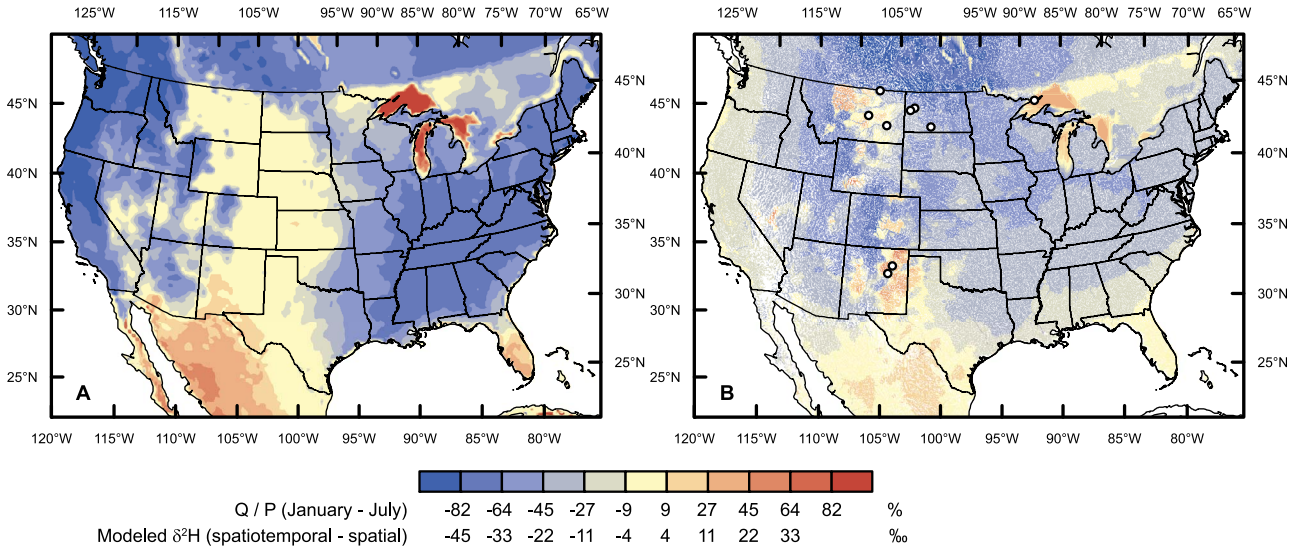

Figure 5. Comparison of forcings and results for the spatially and spatiotemporally weighted water balance models. (a) Seasonal asymmetry of runoff efficiency (estimated monthly runoff/monthly precipitation) based on the North American Regional Reanalysis monthly climatology data. (b) Difference between surface water δ^2H values predicted by the spatiotemporally and spatially weighted models. Points show the locations of nine stations where observed δ^2H values were more that 5‰ lower than the spatiotemporally weighted model predictions.

useful for studying and monitoring large-scale trends and short-term perturbations in regionally integrated land-atmosphere water fluxes within and among catchments. A refined and more comprehensive analysis is needed to further explore this possibility and identify optimal methods for considering factors such as water residence time and evaporation-transpiration ratios in such analyses.

[23] The inverse relationship between δ and d model residual values does not hold along the Pacific coast, where the water balance model significantly underestimates both δ and d values (Figures 4 and 7), suggesting an alternative control on model residuals in this region. A factor that may contribute to the underestimation of δ values for Pacific coastal sites is the tendency of the global precipitation model to underestimate precipitation isotope ratios in this region, a previously observed phenomenon [*Bowen et al.*, 2007b] that persists in the current version of the model. Improvements in the prediction of precipitation values, which will likely be possible in the near future given new data sets, geostatistical models, and regional modeling capabilities currently under development [*Bowen*, 2010], will greatly increase the power of regional water isotope studies in this part of the United States.

[24] Two outlier sites apparent across all model output (Figure 3), at which measured isotopic values are between 32 and 49‰ (δ^2H) lower than the modeled values, are located on the Alamo and New Rivers in southern California. Discharge in these rivers is primarily derived from agricultural runoff in the Imperial Valley, where Colorado River water diverted through the All American Canal system comprises the dominant source of irrigation water [*Michel and Schoeder*, 1994]. Given that the DEM-based drainage network does not represent the artificial diversion of water, and that the isotope ratios of lower Colorado River water (δ^2H ≈ −100‰ at the outflow of the Imperial Dam on the California/Arizona border [*Guay et al.*, 2006]) are much lower than those of modeled local precipitation in the vicinity of the Alamo and New Rivers (δ^2H ≈ −55‰), it is not surprising that the model does not accurately reproduce

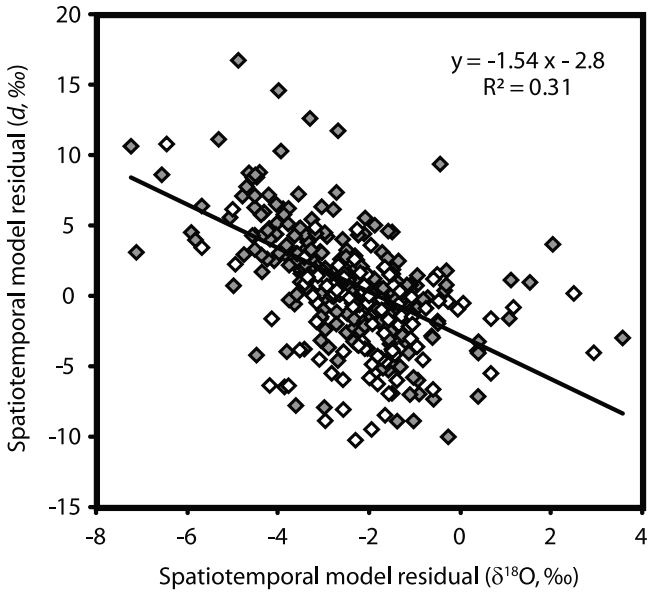

Figure 6. Comparison of model deuterium excess (d) and δ^{18}O residual values (spatiotemporally weighted model) at 370 NASQAN/HBN monitoring sites. Shaded symbols represent sites with catchment areas >2,000 km^2 (n = 266). Open symbols represent sites with catchments smaller than 2,000 km^2. The line and equation show the least squares regression for data from the large catchments; for the small catchments the relationship is significant (p = 0.005) but weak (R^2 = 0.07).

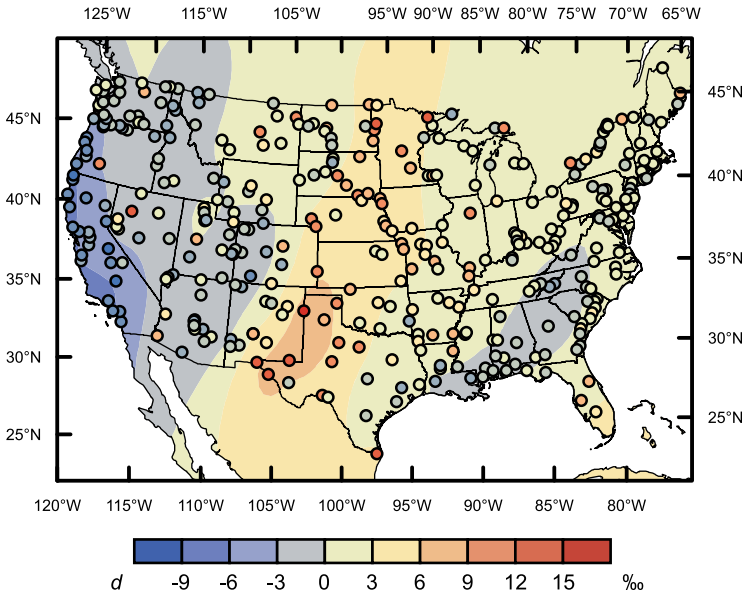

Figure 7. Spatial distribution of deuterium excess residuals from the spatiotemporally weighted surface water model. Symbols as in Figure 4.

the observed isotopic values. Such cases are likely to be restricted to relatively dry regions where water from large-scale water diversions contributes significantly to streamflow. They may be more common in other parts of the world where such conditions exist and water losses from diversion systems are large. These systems can be incorporated in forward models of surface water isotope ratios, but will need to be addressed on a case-by-case basis by manually modifying DEM drainage networks to represent diversions. Data from these sites are not incorporated in any of the following analyses.

3.3. Spatial Distribution of Model Residuals and Residual-Corrected Maps

[25] Model residuals for all isotopic parameters exhibited statistically significant spatial clustering (Table 1). As discussed above, this is consistent with the presence of regional environmental, hydrological and data quality controls on surface water isotope compositions. Although the residuals themselves represent only a relatively small amount of the total variance in U.S. surface water δ^2H and δ^{18}O values (8–11%), the strong spatial coherence of the residual values suggests that geostatistical modeling can be used to characterize regional trends in residuals and improve surface water isotope ratio predictions. We applied ordinary kriging to generate predication surfaces for the δ^2H, δ^{18}O, and d residual values from both model formulations (Figures 4 and 7). Based on data exploration using the ArcGIS Geostatistical Analyst package we implemented a spherical, anisotropic semivariogram model with nugget to describe the spatial correlation of residual values for each isotopic parameter. The semivariogram model parameters (major and minor range, partial sill, and nugget) were optimized on the observed residual values using the automated fitting program in the Geostatistical Wizard tool (Geostatistical Analyst). The resulting surfaces capture the large-scale trends in model residuals discussed in section 3.2, including the maximum for the spatially weighted model in the Rocky Mountain interior and minima over the west coast and Great Plains.

[26] In order to develop optimized prediction maps for surface water isotope ratios in the contiguous United States, we subtracted the interpolated residual value from the spatiotemporally weighted water balance model results at each river grid cell, producing a set of "residual-corrected" modeled river water isotope grids (Figure 8). Although both forms of the water balance model performed similarly with respect to the amount of the observed river water isotopic variance explained, we prefer the spatiotemporal form of the model because it offers an improved mechanistic basis for prediction in regions where runoff efficiency varies seasonally. Map-predicted river water isotope values for the contiguous United States average −63‰ for δ^2H (range −159 to +9‰) and −9.0 for δ^{18}O (range −20.5 to +0.5‰), with the lowest values occurring in small, high-elevation streams and larger, mountain-fed rivers, and the highest values found in small streams in the southeastern United States (Figure 8). Overall, the maps predict a similar distribution of to that observed across the NASQAN/HBN network (see section 3.2), but detailed comparisons are difficult to draw given that the NASQAN/HBN sites do not neces-

Table 1. Spatial Autocorrelation Statistics for Water Balance Model Residuals

	Spatial			Spatiotemporal		
Statistic	δ^2H	δ^{18}O	d[a]	δ^2H	δ^{18}O	d[a]
Moran's I[b]	0.52	0.33	0.44	0.31	0.24	0.46
z score[c]	4.92	3.17	4.19	2.93	2.32	4.38
P value[d]	$\ll$0.001	0.002	$\ll$0.001	0.003	0.020	$\ll$0.001

[a]Deuterium excess.
[b]A dimensionless measure of spatial autocorrelation for the given isotope parameter and model [*Moran*, 1950].
[c]The z test score for the given value of I.
[d]The p value expressing the probability level at which the test indicates significant spatial clustering.

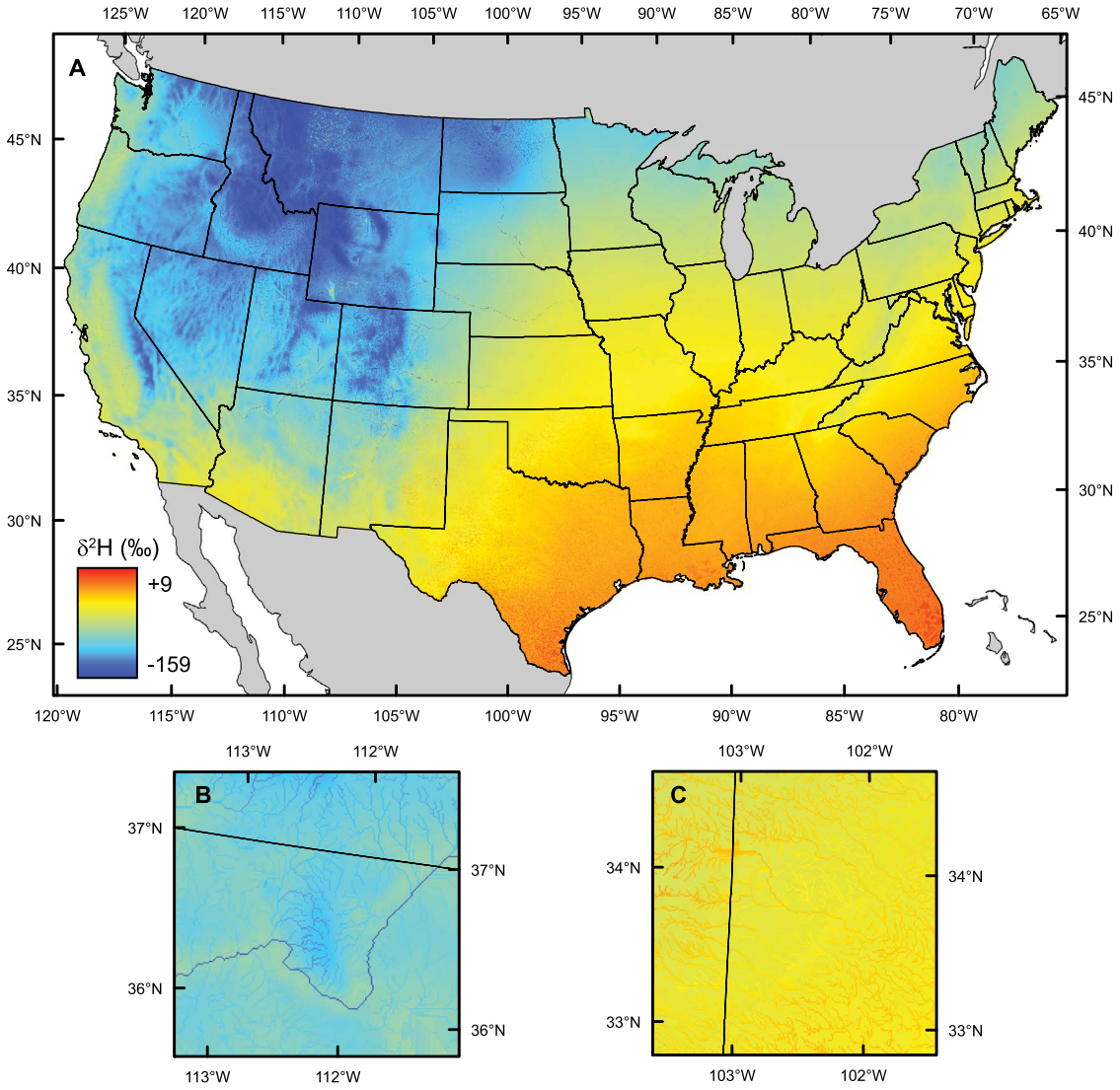

Figure 8. Predicted surface water δ^2H values from the residual-corrected, spatiotemporally weighted water balance model, superimposed on modeled precipitation δ^2H values. (a) Values for the contiguous United States. (b) Values for Grand Canyon of the Colorado River and tributaries in the vicinity of the Utah/Arizona border, showing the contrast between mountain-fed rivers (e.g., Colorado River water δ^2H ≈ −115‰) and local precipitation (δ^2H ≈ −80‰) in this region. (c) Values for low-order streams along the Texas/New Mexico border, showing the modeled effect of evaporative stream water ^{2}H enrichment (δ^2H ≈ −27‰) relative to precipitation (δ^2H ≈ −50‰).

sarily represent a randomized sample of the DEM-based surface water network (Figure 1b).

[27] We tested the quality of the residual-corrected model results by conducting a partial cross-validation (pseudo cross-validation, in the sense of *Cressie* [1993]) against observed δ^2H, δ^{18}O, and d values at the NASQAN/HBN monitoring sites (Figure 9). This analysis was conducted within the ArcGIS 9.3 Geostatistical Wizard, and utilized the entire data set to fit the semivariogram model parameters before iterating through the data set, removing one data station at a time and predicting the value at that site using the remaining data. Very strong correlation was observed between modeled and observed isotope ratios, with the model predicting 94% and 92% of the variance in δ^2H and δ^{18}O values, respectively. Several of the "outlier" sites discussed above and shown in Figure 5b appear as anomalous in the cross-validation results, as well, and omitting these 9 values the model predicts 96% (δ^2H) and 94% (δ^{18}O) of the observed variance. The residual-corrected model performs less well in describing patterns of deuterium excess variation in surface waters of the contiguous United States, explaining 51% (52% omitting outliers) of the total variance in the observational data set (Figure 9c). This result likely reflects a number of factors, including the sensitivity of d values to evaporative isotope fractionation, which is incorporated only indirectly through our residual correction procedure, and the relatively small range of variation in d values relative to analytical and modeling uncertainty.

[28] Overall, the results suggest relatively high power to estimate the isotopic composition of unmeasured surface

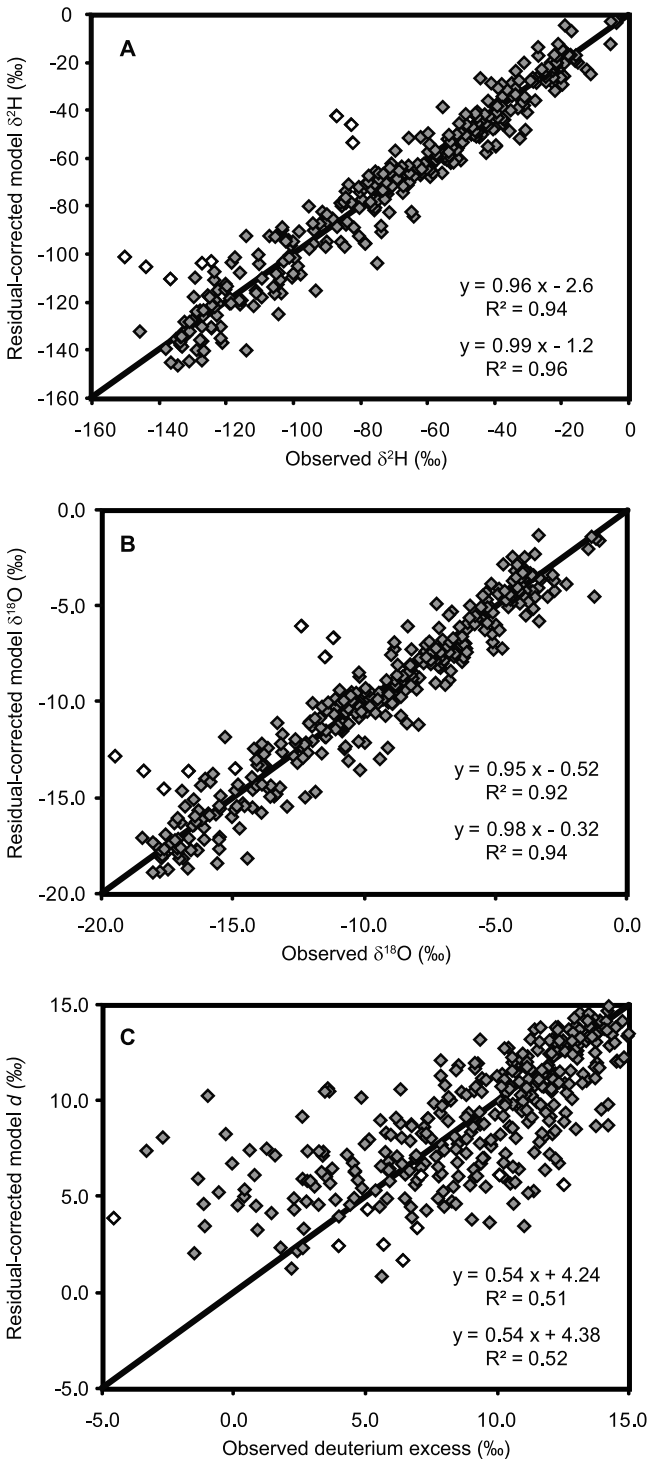

Figure 9. Partial cross-validation results (see text for details) for predictions of the residual-corrected, spatiotemporally weighted surface water isotope ratio model at 370 NASQAN/HBN monitoring sites. Shown are comparisons of model predictions and observations for (a) hydrogen isotopes, (b) oxygen isotopes, and (c) deuterium excess. Bold lines show the 1:1 relationship, and open symbols show 9 stations with δ^2H residuals >5‰ (see Figure 5). The upper regression equation applies to all sites and the lower excludes the high δ^2H residual sites.

waters using the continental-scale water balance model, with root mean squared errors (RMSE) of 9.2, 1.3, and 3.0‰ for δ^2H, δ^{18}O, and d values, respectively. Given the inaccuracies associated with the input data for particular regions such as the northwestern Great Plains and northern New Mexico, however, we caution that prediction accuracy is likely to be poorer in these areas. If we eliminate the 9 "outlier" sites from these regions and Isle Royale from the comparison the RMSE values improve to 7.7, 1.1, and 2.9‰.

3.4. Implications and Applications in Hydrological, Ecological, and Human Systems

[29] Our analysis confirms and extends on the results of previous work [*Kendall and Coplen*, 2001; *Dutton et al.*, 2005] demonstrating that spatial variation in precipitation isotopic composition is the dominant factor controlling variation in surface water isotope ratios across the contiguous United States. Although we focus on comparing data among catchments, one implication of this result is that stable isotope monitoring may provide an integrated signal of spatiotemporal shifts in runoff generation within large catchments. Comparison of models with and without the incorporation of monthly evapotranspiration effects on the water balance suggests that, even at the relatively large scale of our analysis, river water isotope budgets are sensitive to intra-annual variation in P-E, and could be used to help estimate one of these parameters if constraints on the other are available [e.g., *Karim and Veizer*, 2002; *Welp et al.*, 2005]. Although it represents a small fraction of the total variance in surface water δ^2H and δ^{18}O values, significant residual variation remains after accounting for the spatiotemporal distribution of runoff generation. A cursory analysis of this variance demonstrates that isotopic fractionation during evaporative water loss to the atmosphere is likely to be a significant contributor to this variation. With further consideration of regional variation in atmospheric, land surface, and waterway conditions, integration of monitoring data with simple hydrological models such as that introduced here may be a useful approach for developing comparative and/or quantitative assessments of catchment evaporation rates. For any of these applications, however, the availability of accurate and time-explicit isotope maps for precipitation is critical, and has been a limiting factor in previous analyses [e.g., *Fekete et al.*, 2006].

[30] The analysis and surface water map product presented here also has significance to fields beyond hydrology. In particular, Figure 8 offers a previously unavailable assessment of isotopic heterogeneity in hydrological systems at the Earth's surface, and should be of use in many ecological and ecohydrological studies that capitalize on local or regional patterns of water isotope variability to determine the geographic locations and/or hydrological sources used by plants and animals [*Dawson and Ehleringer*, 1991; *Hobson and Wassenaar*, 2008; *Williams et al.*, 2005]. The map predicts a wide range of variation in the isotopic difference between precipitation (which in many cases has an isotopic composition similar to that of deep soil and shallow groundwater [*Gat*, 1996]) and surface waters, from areas where streams are 30‰ or more depleted in ^{2}H relative to precipitation to those where they are 20‰ or more enriched in ^{2}H (Figures 8b and 8c). This local-scale heterogeneity

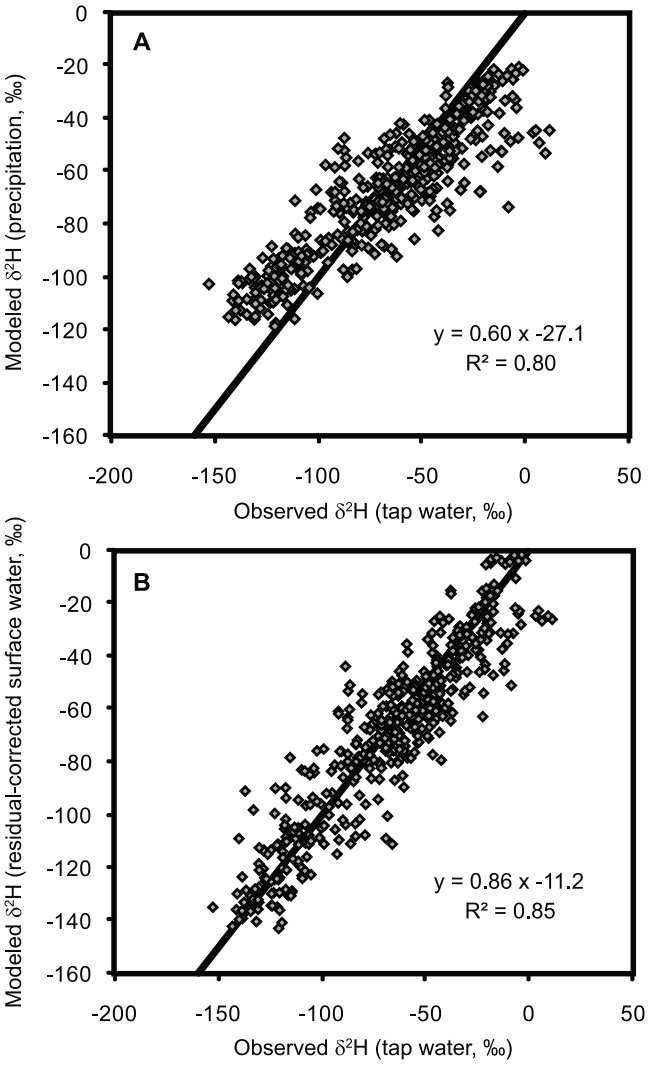

Figure 10. Comparison of measured tap water hydrogen isotope ratios at 490 sites in the contiguous United States with two independent proxies for tap water isotopic composition: (a) the modeled isotopic composition of precipitation at the location of tap water collection and (b) the flow-weighted average value of modeled surface water isotopic compositions (residual-corrected, spatiotemporally weighted model) for all rivers and streams within 50 km of the tap water collection location. Bold lines show a 1:1 relationship.

is both potentially advantageous and detrimental for ecological applications. The existence of large variation among water resource types in some regions provides a "source signal," which can be exploited to distinguish between water sources used by plants or animals, and the maps developed here provide a first-order guide to the potential strength of these signals in different regions. In contrast, for applications which seek to establish the geographic origin of migratory animals, local-scale isotopic heterogeneity in water resources may reduce the geographic specificity of water isotope tracers by increasing the variance of water isotope values in a local area relative to the variance across the animal's range. Numerous case studies clearly demonstrate that the application of H isotopes to the study of many migratory animals works well despite hydrological complexity such as that introduced here [e.g., *Hobson and Wassenaar*, 2008], but using the new maps of surface water isotope ratios this effect can now be considered explicitly in future work through the incorporation of local ranges of water isotope variation in statistical assignment models [e.g., *Wunder and Norris*, 2008].

[31] A similar suite of provenancing applications has been pursued in human-dominated systems for constraining the geographic source of products [e.g., *Bowen et al.*, 2005b; *Chesson et al.*, 2010; *Franke et al.*, 2008; *Iacumin et al.*, 2009] and people [e.g., *Ehleringer et al.*, 2008; *Kennedy et al.*, 2011; *Knudson et al.*, 2009; *Müller et al.*, 2003; *O'Brien and Wooller*, 2007; *Sharp et al.*, 2003]. In this case the hydrological source of interest is the tap water used and consumed by people. Over continental scales tap water isotope ratios covary with those of precipitation, but they often deviate strongly and systematically from precipitation values at local to regional scales level due to factors such as natural and human-managed transport of water in surface water and aqueduct systems and isotope fractionation during evaporation (Figure 10a) [*Bowen et al.*, 2007b]. As a result, predictive models for tap water isotopic composition are currently highly dependent on dense spatial sampling, limiting their usefulness in remote or otherwise poorly sampled regions.

[32] Surface water accounts for approximately 63% of public supply water in the United States [*Hutson et al.*, 2004], and many groundwater systems receive recharge from surface water systems and may be affected by hydrological isotope effects taking place in surface water systems. In order to determine whether the predicted surface water isotope distributions derived here represent an accurate proxy for tap water values, we compared tap water δ^2H data for the contiguous United States with modeled residual-corrected surface water values for rivers and streams within a 50 km radius of the sampled tap (Figure 10b). The surface water model not only explains more of the variance in tap water δ^2H values than does local precipitation isotopic composition (85 versus 80%), but also eliminates systematic deviations between tap water and proxy values for low- and high-δ^2H sites that have previously been attributed to catchment and evaporation effects [*Bowen et al.*, 2007b].

[33] The RMSE for estimation of the observed tap water δ^2H values from local surface water values is 14‰, which is similar to that for a geostatistical model incorporating a dense network of tap water isotope ratio observations (12‰ [*Bowen et al.*, 2007b]). The use of surface water values as a proxy, however, reduces the need for extensive tap water sampling and increases the potential applicability of the model in poorly sampled regions. In its current form, the surface water model introduced here still incorporates surface water isotope data for the correction of model residuals, but our analysis suggests that the predictive power of the model is only marginally reduced (e.g., still explaining 89–92% of observed variation) if this step is excluded. Moreover, the demonstration of systematic (and correctable) regional inaccuracies in the surface water model (Figure 5) and suggestion that environmental factors such as evaporative fractionation contribute to model error implies that improved models could be developed that accurately predict

surface and tap water isotope ratios without relying on data assimilation. Clearly exceptions will exist, e.g., where groundwater sources are used and have isotopic values distinct from those of surface waters or where complex, long-distance artificial transport systems are used to supply water to arid regions. The models should be validated against observations under a range of conditions and geographic locations, and extrapolation should be approached with caution, but our results suggest the potential to develop reasonably accurate predictive maps for first-order tap water isotope distributions over much of the Earth's surface without the development of new and extensive observational networks.

4. Conclusions

[34] We show that a simple water balance model for surface hydrology, when initiated with appropriate boundary conditions, closely reproduces observed continental-scale pattern of surface water isotope ratios across the contiguous United States. This result confirms that the spatiotemporal distribution of precipitation isotope ratios and runoff generation are the first-order determinants of surface water isotopic composition, and that the representation of these factors in distributed hydrology models can be validated using surface water isotope measurements. Model bias is of relatively small magnitude, but exists and is systematic. In a practical sense, this observation is encouraging in that it suggests that hydrological variables not included in the model, in particular the partitioning of evaporation and transpiration, are represented in the large-scale, time-averaged data set used here. To the degree that accurate precipitation isotope maps and climate data are available to represent the isotopic composition of water entering catchments, the application of simple hydrological models such as that presented here provides a way to isolate the isotopic signal associated with processes other than runoff generation.

[35] Our study also contributes to a growing literature on the predictability of environmental water isotope ratios over large geographic scale. We show that relatively accurate models for surface water isotope composition can be developed in the absence of densely distributed surface water monitoring data. Where monitoring data are available, these models can be improved through the incorporation of residual correction, but there is also promise for the further development of first principles models that do not rely on data assimilation. As demonstrated previously in local and regional studies, and emphasized in our analysis, the isotopic composition of surface water in many regions is widely different from that of other local environmental waters (e.g., precipitation and groundwater), and models such as the one presented here are necessary in order to accurately represent local variation in water δ^2H and δ^{18}O values in ecological and forensic studies. In order to facilitate their use in such studies, and promote the further development of process-based, isotope-enabled hydrology models, the map grids resulting from our work are freely available as GIS raster data sets at http://waterisotopes.org. As isotopic monitoring data sets grow, precipitation isotope maps are improved, and more comprehensive surface hydrology models are applied to the analysis of large-scale surface water isotope data sets, we anticipate that modeling approaches and data products of the type introduced here will support increasing powerful applications in global change research, macrosystems ecology, and forensic science.

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