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Key Points:

- Surface water isotope values of small watersheds in the Snake River basin vary primarily with longitude, latitude, and elevation
- Accounting for evaporative effects on Snake River isotope values illustrates how contributing area and evaporation vary with flow dynamics
- Source water isotope values are elevated when the flow is high, reflecting contributions from a larger, more western portion of the basin

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

G. Windler,
gwindler@email.arizona.edu

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Climate Impacts on Source Contributions and Evaporation to Flow in the Snake River Basin Using Surface Water Isoscapes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$)

Grace Windler¹ , J. Renée Brooks² , Henry M. Johnson³ , Randy L. Comeleo², Rob Coulombe⁴, and Gabriel J. Bowen⁵ 

¹Department of Geosciences, University of Arizona, Tucson, AZ, USA, ²Pacific Ecological Systems Division, Center for Public Health and Environmental Assessment Office of Research and Development, U.S. Environmental Protection Agency, Corvallis, OR, USA, ³U.S. Geological Survey, Oregon Water Science Center, Portland, OR, USA, ⁴CSS, Inc., Corvallis, OR, USA, ⁵Department of Geology and Geophysics and Global Change and Sustainability Center, University of Utah, Salt Lake City, UT, USA

Abstract Rising global temperatures are expected to decrease the precipitation amount that falls as snow, causing greater risk of water scarcity, groundwater overdraft, and fire in areas that rely on mountain snowpack for their water supply. Streamflow in large river basins varies with the amount, timing, and type of precipitation, evapotranspiration, and drainage properties of watersheds; however, these controls vary in time and space making it difficult to identify the areas contributing most to flow and when. In this study, we separate the evaporative influences from source values of water isotopes from the Snake River basin in the western United States to relate source area to flow dynamics. We developed isoscapes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) for the basin and found that isotopic composition of surface water in small watersheds is primarily controlled by longitude, latitude, and elevation. To examine temporal variability in source contributions to flow, we present a 6-years record of Snake River water isotopes from King Hill, Idaho, after removing evaporative influences. During periods of low flow, source water values were isotopically lighter indicating a larger contribution to flow from surface waters in the highest elevation, eastern portion of the basin. River evaporation increases were evident during summer likely reflecting climate, changing water availability, and management strategies within the basin. Our findings present a potential tool for identifying critical portions of basins contributing to river flow as climate fluctuations alter flow dynamics. This tool can be applied in other continental-interior basins where evaporation may obscure source water isotopic signatures.

1. Introduction

The timing and nature of precipitation are projected to change under rising global temperatures. Warmer winter temperatures are expected to decrease mountain snowpack in regions where the water supply is dominated by snowmelt and shift the timing of peak snowpack earlier in the spring (Barnett et al., 2005; Li et al., 2017; Stewart et al., 2005). Much of the western United States relies heavily on mountain snowpack for water supply, but as temperatures rise less precipitation will fall as snow, thus reducing snowpack and increasing early runoff to streams (Mote, 2003; Mote et al., 2005; Stewart et al., 2005). Earlier snowmelt reduces streamflow during the dry season leading to water scarcity, groundwater overdraft, and increased fire potential (Adam et al., 2009; Gergel et al., 2017; Li et al., 2017). A need exists to understand how large river basins function and which portions of the basin are important for supplying water on an interannual basis (Bales et al., 2006; Gergel et al., 2017).

A primary control on streamflow sensitivity to temperatures within a basin is the amount and timing of snowpack; however, the amount and type of total precipitation, evapotranspiration, and catchment properties controlling storage and drainage also affect streamflow (Safeeq et al., 2013; Tague & Grant, 2009; Tague et al., 2013). For example, streams in basins with low-permeable bedrock generally have less late-summer baseflow compared to basins underlain by more permeable geologic materials that promote infiltration of precipitation (Tague & Grant, 2009). Warmer summer temperatures will increase evapotranspiration, potentially causing additional decreases in summer streamflow (Tague & Grant, 2009). During the dry season after spring snowmelt, groundwater is the dominant source of streamflow in most montane catchments,

which spatiotemporally varies depending on the groundwater recharge rate and the underlying lithology (Blumstock et al., 2015; Nickolas et al., 2017; Sánchez-Murillo et al., 2015; Segura et al., 2019). These controls on streamflow vary not only spatially across the geologically and topographically complex western United States, but also temporally with interannual changes in temperature and precipitation. This variability results in considerable differences in streamflow sensitivity to rising temperatures among western United States basins, making it difficult to understand which areas contribute the most to flow and when. Tools to address this issue include hydrologic models and classification strategies, both of which are limited by model parameterization or the restricted spatial coverage and length of available data records (Adam et al., 2009; McGuire & McDonnell, 2006; Tague et al., 2013).

Water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) are useful for tracing spatiotemporal changes in source water contributions within a basin or catchment. Rivers are points of integration within their watersheds, so the isotopic value of river water is an integration of all values of upstream water that reached the river. The values of precipitation $\delta^2\text{H}$ and $\delta^{18}\text{O}$ vary systematically according to patterns of water vapor transport, convective processes, and temperature (Dansgaard, 1964; Rozanski et al., 1993). As a water vapor parcel moves inland, the gradual rainout results in the remaining pool of vapor being depleted in the heavy isotope. The same process occurs when water vapor orographically lifts and cools, instigating precipitation and more isotopic depletion of the residual vapor. Stream water isotope values reflect the integrated isotopic composition of precipitation falling across all contributing areas in the catchment, including direct precipitation, rainfall runoff, snowmelt runoff, and groundwater discharge. Isoscapes, or maps of isotopic variation, can be used to predict the spatial distribution of precipitation, surface water, and groundwater isotopes within a basin, thus providing valuable information on water source, upstream transport processes, or local fractionation (Bowen, 2010; Bowen & Good, 2015; Bowen & Wilkinson, 2002; Dutton et al., 2005; Stahl et al., 2020). Several water isotope studies from western United States basins have found elevation to be a primary predictor of surface water isotope variability under average flow conditions; however, the importance of elevation varies between basins with windward basins having stronger elevation influences (Brooks et al., 2012; McGill et al., 2020; Segura et al., 2019). Climatic conditions, such as drought or changes in the proportion of rain and snow, can also affect elevation as a predictor of isotopic variability when high elevation snowpack contributes less to overall flow (Blumstock et al., 2015; Nickolas et al., 2017; Segura et al., 2019).

Stream water evaporation along its course can change the original isotopic composition of surface water, which presents a potential problem when developing an isoscape meant to explore surface water values at the source. Lighter isotopes, ^1H and ^{16}O , preferentially evaporate leaving the remaining water isotopically heavier than its integrated meteoric water value (Craig & Gordon, 1965; Gat, 1996). The kinetic effects of evaporation cause systematic offsets of the residual surface water from a characteristic meteoric water line (MWL—the linear relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ with a slope of eight for the Global MWL), resulting in the isotopic values of evaporated water evolving along an evaporation line (EL) with a lower dual isotope slope than the MWL. A common approach to inferring source water values from evaporated samples is to find the point of intersection between the EL and a characteristic MWL (Clark & Fritz, 1997), which typically represents an integrated source value. ELs are not fixed in time and space; therefore, the method used to estimate an EL slope, either a regression or theoretical modeling, must be appropriate for the spatiotemporal scale of the study. Bowen et al. (2018) provided a framework for theoretical modeling of EL slopes and inferring isotopic values of source water for evaporated samples ($i\text{SW}_E$) that also quantitatively assesses uncertainty. A mixing model implementation of $i\text{SW}_E$ has been developed and allows estimation of the fractional contribution of two or more sources (e.g., sub-watersheds) to a sampled location while accounting for (and quantifying) evaporation effects during transport from source to sampling point (Bowen et al., 2018). This latter property may be important in continental-interior basins where evaporative demand and potential for evaporative modification of source-water isotope signatures is high. The Snake River basin is a good example. High elevation snowpack contributes most of the streamflow in the river throughout the year with little contribution from the drier eastern lowlands, which receive only 8–10 inches of precipitation annually (Clark et al., 1998). The Snake River system is highly managed for irrigated agriculture. Evaporation occurring during water storage, distribution, and irrigation could obscure the isotopic signature of source water, but it also contains useful information about flow path and water management.

Here, we aim to separate the evaporative influences on Snake River water isotopes to understand changes to flow contribution areas of the Snake River over time, the underlying causes, and how contributing area relates to flow dynamics. First, we developed surface water isoscapes for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the Snake River basin using the isotopic values of surface water samples collected across the basin to understand what drives spatial variation in surface water isotopes of small watersheds. Second, using a 6-year time series of Snake River water isotopes collected from King Hill, Idaho, we separate the evaporative component from the isotopic values using $i\text{SW}_E$ to infer integrated source values for the King Hill samples. Third, comparing the temporal variance at King Hill to our surface water isoscapes and river discharge data, we illustrate how the Snake River basin changes in the potential contributing area over 6 years when discharge varies by orders of magnitude.

2. Materials and Methods

2.1. Study Area

We selected the Snake River basin in the western United States as a case study to determine changes in contributing areas through time. The Snake River is the largest tributary to the Columbia River and flows through four northwestern states: Wyoming, Idaho, Oregon, and Washington. The river is highly managed, with several reservoirs contributing to a total storage capacity of nearly 18 billion m^3 drained from over 258,000 km^2 of watershed (M. McGuire et al., 2006; VanRheenen et al., 2003). Snake River water is overwhelmingly used in agricultural irrigation, but is also an important source of electricity, drinking water, and recreation for millions of people in the greater Pacific Northwest area (Clark et al., 1998; Idaho Department of Water Resources, 1997). Spring snowmelt is an important source of streamflow in the Snake River. Streamflow typically peaks during May/June (McGuire et al., 2006) and declines to a minimum during late summer when stream water is sourced from groundwater and reservoir release. In a warmer climate with less snow and an earlier melting season, the water supply would rely on reservoir storage and groundwater for a longer period of time, potentially causing water scarcity; therefore, identifying source areas within the basin and how climatological controls affect water availability is crucial for understanding future streamflow in the Snake River.

2.2. Sample Collection and Small Watershed Characteristics

To characterize spatial differences in surface water isotopes across the Snake River basin, 178 samples were collected from small streams and tributaries distributed across the basin (Figure 1). Sample collection occurred during three separate trips: October (late summer, low flow conditions) 2013 and June (early summer, high flow conditions) of 2014 and 2015 to account for seasonal differences. Selected locations covered the range of elevation, latitude, and longitude across the basin, but sampling was limited to accessible sites to maximize the number of samples collected during each trip. Locations were resampled, when possible, to account for interannual variation. Samples were collected within the main thalweg of the stream or as close as safely possible. A total of 124 small watersheds were delineated using ArcGIS geographic information systems software (Environmental Systems Research Institute, 2014). The upslope contributing area to each sampling location (Figure 1) was determined using a flow direction raster created from the National Elevation Data set (NED), a 30 m resolution digital elevation model (U.S. Geological Survey, 2017). To characterize temporal variability of source areas along the Snake River, an additional 89 water samples were collected from the river at King Hill, Idaho, (Figure 1) between July, 2013 and October, 2019. These samples were collected by USGS field staff as part of an ongoing water-quality sampling effort. River samples were depth- and width-integrated to ensure they were representative of the river at this location.

Characteristics for the 124 small watersheds were determined as potential explanatory variables for surface water isotope values (Table 1). Latitude, longitude, elevation, and precipitation amount are known to influence spatial patterns of modern precipitation isotopes (Bowen & Revenaugh, 2003; Bowen & Wilkinson, 2002; Dansgaard, 1964). We consider watershed area, mean temperature, aquifer/soil permeability, and classes of climate/season, terrain, and hydrologic landscape (HL) as additional potential variables affecting either the integration of precipitation isotopes into stream water, or evaporation of surface waters. HLs are a classification scheme meant to generalize broad scale hydrologic attributes of a region based on

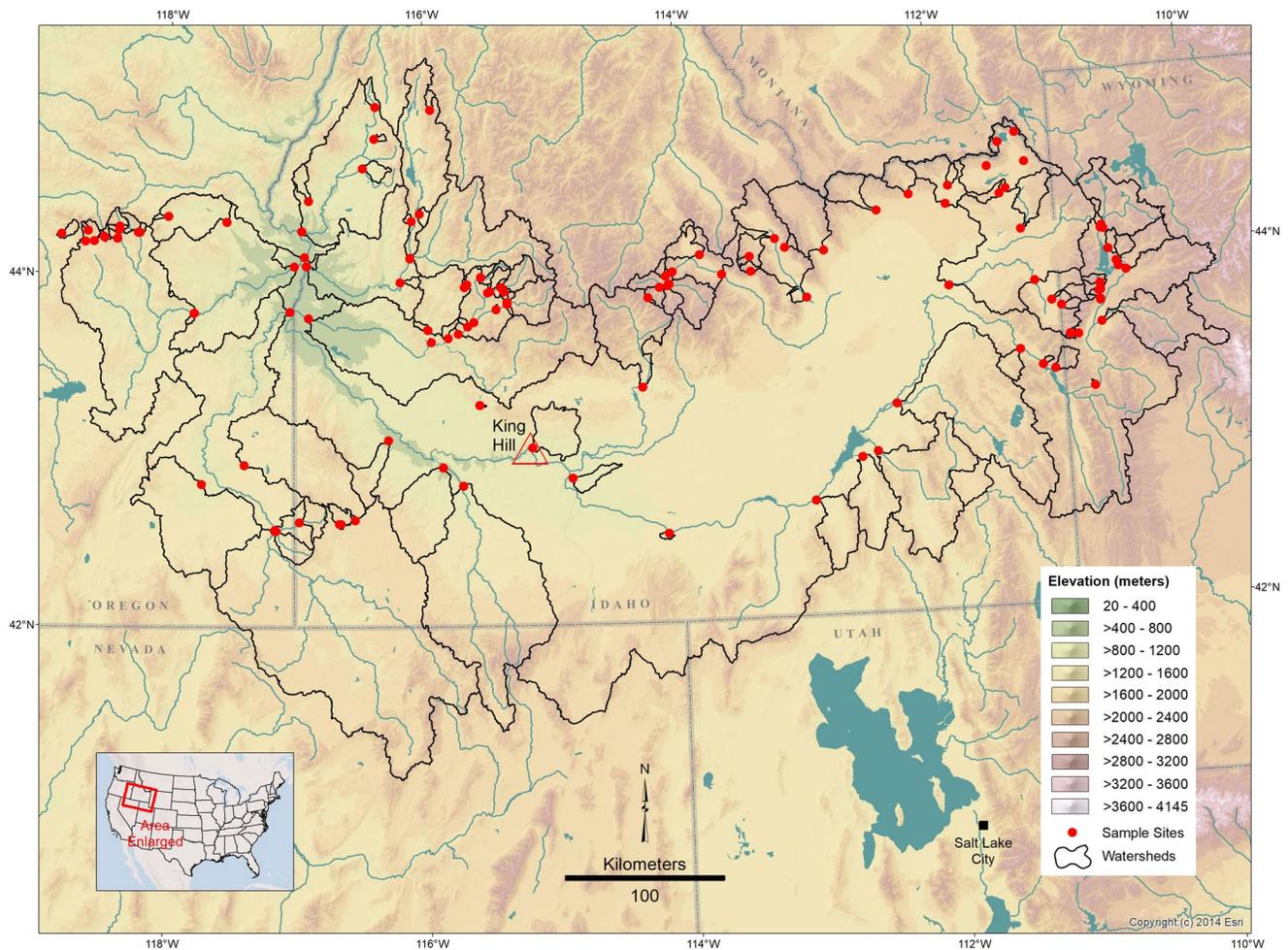


Figure 1. Sampling locations and corresponding watersheds in the Snake River basin. Black lines delineate the 124 small watersheds for each collection site (red dots). Red triangle marks the USGS sampling location on the Snake River at King Hill.

characteristics of the terrain, geology, soil, aquifers, or annual climate into similarly functioning units (Leibowitz et al., 2016; Wigington et al., 2013; Winter, 2001).

All small watershed characterization metrics were calculated using ArcGIS. Mean annual temperature and precipitation were determined using the 30 years averaged (1971–2000) climate data products derived from 400 m resolution Parameter-elevation Regressions on Independent Slopes Model data from Climate Source, Inc. (Daly et al., 2008). Mean elevation was calculated using the NED (U.S. Geological Survey, 2017). The following watershed metrics were calculated using the data and methods described in Wigington et al. (2013). Relief is the difference between maximum and minimum elevation within each watershed. The dominant climate class for each watershed was designated as dry, semiarid, moist, wet, or very wet. The dominant water seasonality class was designated as spring, summer, or fall/winter. The dominant terrain class for each watershed was designated as flat, transitional, or mountainous. Aquifer and soil permeability were designated as high, medium, or low based on the highest percentage of their occurrence within each watershed following the methodology of Wigington et al. (2013), by applying the gridded aquifer permeability map of the Pacific Northwest developed by Comeleo et al. (2014). Last, the dominant HL class, which combines relief, climate, seasonality, terrain, and permeability as described by Wigington et al. (2013), was determined for each watershed.

Table 1
Characteristics for Small Watersheds in the Snake River Basin

Variable	Units/Classes	Watershed characteristic	Data source
Latitude	Decimal degrees	Centroid latitude	
Longitude	Decimal degrees	Centroid longitude	
Area	km ²	Area	NED DEM (USGS, 2017)
Elevation	m	Mean elevation	NED DEM (USGS, 2017)
Relief	m	Elevation max. – min.	NED DEM (USGS, 2017)
Flat land	%	Percentage of flat land (slope < 1%)	NED DEM (USGS, 2017)
Precipitation	mm/yr	30 yr mean precipitation	PRISM (Daly et al., 2008)
Temperature	°C	30 yr mean temperature	PRISM (Daly et al., 2008)
Aquifer	High, moderate, low	Dominant aquifer permeability class	Comeleo et al. (2014)
Soil	High, moderate, low	Dominant soil permeability class	Wigington et al. (2013)
Climate	Arid, semiarid, moist, wet, very wet	Dominant climate class	Wigington et al. (2013)
Seasonality	Spring, summer, fall/winter	Dominant seasonality class	Wigington et al. (2013)
Terrain	Flat, transitional	Dominant terrain class	Wigington et al. (2013)
Hydrologic landscape	HL class	Dominant hydrologic landscape class	Wigington et al. (2013)

2.3. Analysis of Water Isotopes

All water samples were collected in 20 mL polypropylene bottles with polyseal cone caps to prevent evaporation, stored capsid down, and analyzed within six months of collection. All samples were analyzed for water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) using a Laser Absorption Water-Vapor Isotope Spectrometer (Los Gatos Research [LGR]—Model 908-0004) at the Integrated Stable Isotope Research Facility of the Pacific Ecological Systems Division of the EPA (Corvallis, Oregon). All isotope values are expressed in ‰ notation relative to Vienna-Standard Mean Ocean Water (V-SMOW):

$$\delta^2\text{H or } \delta^{18}\text{O} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1,000$$

where R is the ratio of heavy to light atoms of the sample or the standard V-SMOW. Each analytical run of the LGR was calibrated with three internal standards that ranged from -134‰ to -1.9‰ for $\delta^2\text{H}$ and -18.4‰ to -1.8‰ $\delta^{18}\text{O}$, which were calibrated to internationally certified standards at least annually. A fourth internal standard not used for calibration (QA standard) was used to assess the accuracy of the instrument and duplicate study samples to assess the precision of each run. Precision (1σ) of the Laser Spectrometer between 22 duplicate sample measurements was 0.2‰ $\delta^2\text{H}$ and 0.1‰ $\delta^{18}\text{O}$. Accuracy based on 17 QA standards was $0.1 \pm 0.2\text{‰}$ (σ) for $\delta^2\text{H}$ and $0.02 \pm 0.1\text{‰}$ for $\delta^{18}\text{O}$. Deuterium-excess (d -excess) was calculated as an index for the effect of evaporation on the isotopic value of each surface water sample (Clark & Fritz, 1997; Dansgaard, 1964):

$$d - \text{excess} = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$$

2.4. Statistical Analyses

All statistical analyses, as described below, were conducted in the R programming language version 4.0.4 (R Core Team, 2021) unless otherwise stated.

2.4.1. Isoscape Development

To understand how surface water isotopes vary across the Snake River basin, we used the spatially distributed data set (Figure 1, red circles) to develop an isoscape for surface water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ using generalized linear models (GLMs) that best explain the spatial variation of surface water values.

Linear modeling is a reasonable approach for predicting the spatial variance in water isotopes due to the systematic fractionation of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ during rainout (Dansgaard, 1964; Rozanski et al., 1993) and has been successfully used to develop precipitation and surface water isoscapes at the global and continental scale (Bowen & Wilkinson, 2002; Dutton et al., 2005). We developed GLMs for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ separately using isotope data from the spatially distributed sites using the “leaps” package in R (<https://cran.r-project.org/web/packages/leaps/index.html>). Using “leaps,” we performed an automated search for the best predictor variables in a regression using the Akaike Information Criterion (AIC; Akaike, 1974). We used the calculated small watershed characteristics (Table 1) as potential explanatory variables in the analysis. The package cycles through all possible combinations of predictors that result in the best linear regression, specifically, that with the lowest AIC and residual values (see Table S1 for a list of the top 15 performing models). Our selection goal was to identify the simplest (low order), high-performing model (low AIC) with consistent predictor variables between $\delta^2\text{H}$ and $\delta^{18}\text{O}$. To measure the accuracy of the models we used a bootstrap resampling approach, which consisted of randomly selecting a subset of 75% of the original data, using that subset to evaluate the model, and repeating this process 10,000 times to measure the variance in model performance.

Selected GLMs were used to generate surface water isoscapes, which predict the average isotopic values of surface water entering the river network from small hydrologic units across the basin. To do so, we used aggregated NHDPlusV2 (McKay et al., 2012) catchments to define 2,653 hydrologic assessment units for the Snake River basin using ArcGIS, following the method described in Leibowitz et al. (2016). Hydrologic assessment units based on NHD catchments partition the entire drainage area for a given stream without the units being nested. The explanatory variables necessary to predict isotopic values and estimate precipitation-weighting in subsequent analyses were calculated for each hydrologic assessment unit, including latitude and longitude of the centroid, area, mean elevation, and mean precipitation (Table 1). We then applied the best GLM for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ individually to each of the assessment units, resulting in two surface water isoscapes for the Snake River basin.

2.4.2. Separating Evaporative Effects From Source Water Variation

The isotopic values of river water at King Hill were likely enriched in ^2H and ^{18}O relative to the contributing source(s) due to in-stream evaporation and evaporation from diverted water that re-joins the river. To separate this evaporative effect and examine how areas contributing to flow in the Snake River vary temporally, we used the $i\text{SW}_E$ mixing model analysis to estimate the fractional contribution of catchments represented in our isoscapes to water samples collected at King Hill (Bowen et al., 2018). We utilized the *mixSource* function available in the “isoWater” package in R (<https://spatial-lab.github.io/isoWater/>), which is an updated version of the $i\text{SW}_E$ mixing analysis developed by Bowen et al. (2018). This function uses Markov Chain Monte Carlo (MCMC) sampling to estimate the distribution of parameters in a mixing-evaporation model that is conditioned on the observed water sample's isotopic values.

Prior distributions—or the probability distributions of the model parameters—must be provided for the isotopic composition of each source, the fractional contribution of each source, and the slope of the EL. Since 1,247 out of the 2,653 hydrologic assessment units used in the isoscape are located upstream from King Hill, the number of sources used in the analysis had to be reduced. To do so, we used the hydrologic unit codes (HUC) in the Watershed Boundary Data set (U.S. Geological Survey, 2020b) for units located upstream from King Hill. We calculated the isotopic values of each HUC10 watershed ($n = 181$), using the latitude and longitude of the centroid and elevation to apply the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ GLMs. In addition to the mean $\delta^2\text{H}$ and $\delta^{18}\text{O}$, *mixSource* requires estimates of uncertainty in the source values, which we approximated by aggregating the data from the HUC10 to HUC8 level, calculating the precipitation-weighted mean of all HUC10 watersheds within a given HUC8 ($n = 26$), the standard deviation of each isotopic system, and their covariance for the HUC10 units within each HUC8 watershed. We used the total area-integrated precipitation amount for each HUC8 source watershed as the mixing ratio prior.

We estimated EL slopes for each water year of our sampling period following the theoretical approach of Craig and Gordon (1965), using the methodology outlined by Bowen et al. (2018) (R code: <http://github.com/SPATIAL-Lab/watercompare/tree/master>). Briefly, monthly EL slope rasters for the continental United States were calculated based on Equation 7 from Gat and Bowser (1991):

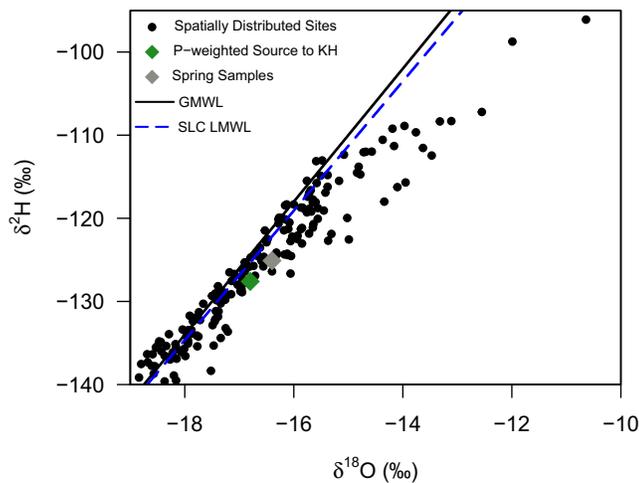


Figure 2. Dual isotope scatterplot of samples collected across the Snake River basin. Green diamond indicates the area-integrated precipitation-weighted source value calculated for King Hill (Section 3.2). Gray diamond represents the median values of the four spring samples collected near King Hill (Section 4.2). Solid black line represents the GMWL: $\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10$. Dashed blue line represents the Salt Lake City (SLC) LMWL: $\delta^2\text{H} = 7.78 \cdot \delta^{18}\text{O} + 5.4$ (Figure S1).

$$\text{EL slope} = \frac{\left[\delta_{\text{atm}} - \delta_{\text{precip}} + \left(\varepsilon + \varepsilon_k \times \theta \right) / h \right]_{2\text{H}}}{\left[\delta_{\text{atm}} - \delta_{\text{precip}} + \left(\varepsilon + \varepsilon_k \times \theta \right) / h \right]_{18\text{O}}}$$

The equilibrium fractionation factors (ε) of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ were calculated using gridded monthly air temperature data from the NCEP North American Regional Reanalysis (NARR) (NOAA/OAR/ESRL PSL, 2020). The kinetic fractionation factors (ε_k) were found using monthly NARR values of relative humidity (h). We used rasters of monthly precipitation isotopes (δ_{precip}) for the United States, updated from Bowen and Revenaugh (2003) (<https://waterisotopesDB.org>). Isotopic ratios of atmospheric water vapor (δ_{atm}) were calculated assuming an equilibrium state with precipitation. The evaporation weighting term (θ) was set to 0.5, which is appropriate for surface waters under natural conditions (Gat, 1996). Gridded monthly EL slope values were then aggregated into evaporation-weighted annual rasters for the water years corresponding to sample collection dates and appropriate EL slope values for King Hill were extracted for each sample.

We ran the *mixSource* function for each King Hill observation to iteratively estimate the isotopic composition of the source water mixture, the fractional contribution of each source, and the evaporation component (the difference between the sample $\delta^{18}\text{O}$ and the inferred source mixture, $\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{\text{source}}$), which provides a relative measure of how much evaporation has occurred. Analyses used three MCMC chains, each run

to a length of 500,000 samples. Convergence was assessed by the Rhat statistic (median Rhat = 1.002, 95% of Rhat < 1.012) and effective sample size (median = 3,100, 95% of effective sample size > 390 out of a possible 7,500) for each output variable, indicating good convergence in the analyses.

3. Results

3.1. Surface Water Isotope Variation in the Snake River Basin

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of surface water from small spatially distributed watersheds ranged from -139.6‰ to -96.1‰ and -18.84‰ to -10.64‰ , respectively (Figure 2). The d -excess values ranged from -11.0‰ to $+13.2\text{‰}$. To characterize precipitation isotopes near the Snake River basin, we used the volume-weighted LMWL from precipitation isotope measurements in Salt Lake City (SLC), Utah, (Figure 1) that fell between October, 2012 and February, 2020 (Waterisotopes Database (2021), <https://waterisotopesDB.org>, Figure S1). The slope and intercept of the SLC MWL are statistically different from the Global MWL (t test, $p < 0.05$, Figure 2).

The best performing GLMs used to generate $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isoscapes of the basin include average watershed elevation, longitude, and latitude as predictor variables, accounting for about 61% and 64% of the surface water isotope variance within the basin for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively (Table 2). Using AIC for model selection, additional variables, such as watershed area, temperature, and precipitation, did not improve the power of prediction and would overcomplicate the calculation (higher order) (Table S1). Longitude, latitude, and elevation thus provide a relatively simple model for such a large area. Residuals from the GLMs ranged from -17.7‰ to $+21.7\text{‰}$ ($\pm 5.4\text{‰}$ σ) $\delta^2\text{H}$ and -3.02‰ to $+4.46\text{‰}$ ($\pm 0.86\text{‰}$) $\delta^{18}\text{O}$ and were evenly distributed across the data range (Figure S2). Some of the largest residuals are located in the western half of the basin where the climate is more arid, but are not consistently positive or negative (Figures S3 and S4).

Surface water $\delta^2\text{H}$ values are inversely related to longitude (Table 2), demonstrated by the distinct longitudinal gradient in the isoscape with the heaviest values in the western portion of the basin and the lightest values to the east near the headwaters in the Teton Mountain Range, Wyoming (Figure 3). Mean elevation of the hydrologic assessment units in the isoscape ranges from 653 to 3,481 m. Most of the Snake River main stem lies in a lowland basin surrounded by mountainous regions of northwest Wyoming and central/southern Idaho (Figure 1). High elevations of the surrounding mountains create differences in surface water

Table 2
Surface Water Isotope GLMs

Isotope	Adj. R^2 (%)	RMSE (‰)	MAE (‰)	Variable	Coefficient	Units
$\delta^2\text{H}$	61.0	5.48	3.93	Intercept	-225.8	
				Longitude	-1.672	Decimal degrees
				Latitude	-1.766	Decimal degrees
				Elevation	-0.006522	m
$\delta^{18}\text{O}$	63.7	0.878	0.619	Intercept	-18.99	
				Longitude	-0.2404	Decimal degrees
				Latitude	-0.5130	Decimal degrees
				Elevation	-0.001281	m

Note. Includes adjusted R^2 (Adj. R^2) value as a percentage as well as the root mean square error (RMSE) and mean absolute error (MAE) from bootstrap resampling (Section 2.4.1).
Abbreviation: GLMs, generalized linear models.

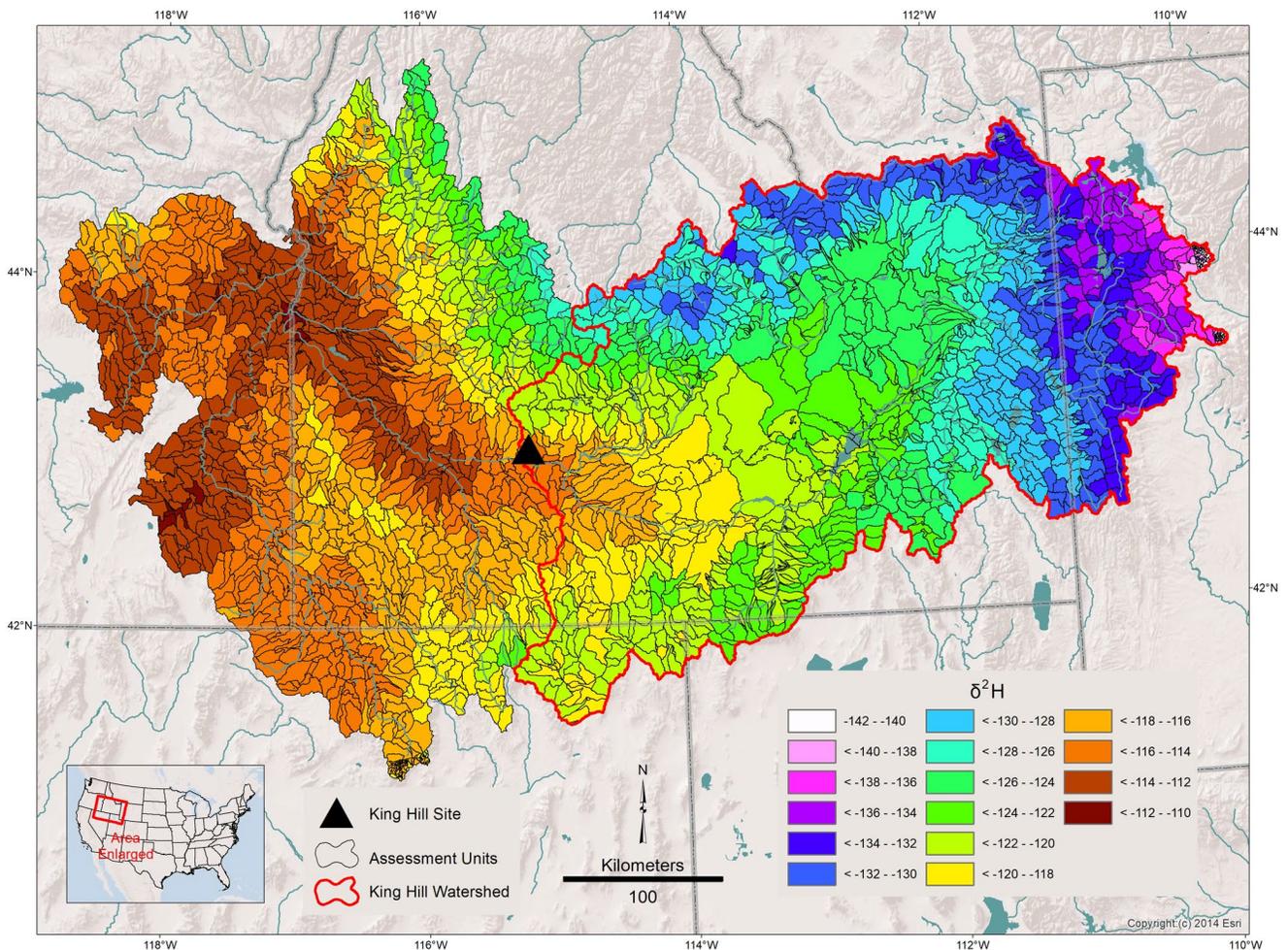


Figure 3. Isoscape of average surface water $\delta^2\text{H}$ in the Snake River basin. Black triangle indicates the King Hill sampling location. The area upstream from King Hill is outlined in red.

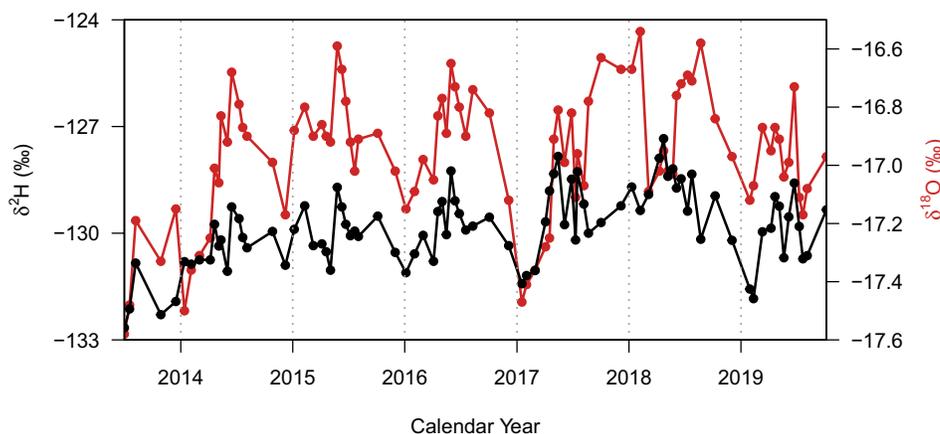


Figure 4. Isotope measurements from Snake River water at King Hill collected between July, 2013 and October, 2019. Black line represents $\delta^2\text{H}$ and the red indicates $\delta^{18}\text{O}$. Dotted gray lines mark the start of each calendar year.

isotope values along longitudinal and latitudinal lines. For example, the Idaho/Oregon state line (Figure 1) lies along a gradient with the heaviest surface waters in a low-lying region to the north and lighter values in the slightly higher elevation region to the south near Nevada (Figure 3). Surface water variation is similar in the $\delta^{18}\text{O}$ isoscape (Figure S5).

3.2. Source Contributions to King Hill, Idaho

The time series of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ from Snake River water samples collected at King Hill, Idaho, ranged from -132.7‰ to -127.3‰ and -17.58‰ to -16.54‰ , respectively (Figure 4). The two isotope systems follow the same general patterns of change at this location over time (Figure 4). The d -excess varied from $+2.5$ to $+9.2\text{‰}$. The lowest isotope values generally occurred during the winter just after the new calendar year, whereas the highest values each year occurred during early summer (Figure 4). To interpret temporal patterns, we separated the source and evaporative contributions to the King Hill isotope variation using the $i\text{SW}_E$ analysis. The median source $\delta^2\text{H}$ values ranged from -132.6‰ to -127.8‰ (Figure 5a) and the median evaporation component ($\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{\text{source}}$) ranged from $+0.05\text{‰}$ to $+0.66\text{‰}$ (Figure 5b). The highest evaporative effect detected during each calendar year regularly occurred in the summer from 2014 to 2016, but shifted to later in the year during 2017 and 2018. No seasonal evaporative increase was observed in 2019 (Figure 5b). The $i\text{SW}_E$ source $\delta^{18}\text{O}$ results follow the same temporal pattern as $\delta^2\text{H}$ (Figure S6).

Daily discharge of the Snake River at King Hill (U.S. Geological Survey, 2020a) m^3/s (median = $206 \text{ m}^3/\text{s}$). Large peaks in flow occurred during the early months of 2017, 2018, and 2019 (Figure 5). The 2017 and 2018 periods of high flow at King Hill coincide with the most isotopically enriched source values (Figure 5a) and low values of evaporation (Figure 5b).

To put temporal variability of Snake River isotopic values at King Hill into the broader context of the basin, we calculated the area-integrated, precipitation-weighted isotope values for the hydrologic units located upstream from King Hill. In other words, if all units contributed to streamflow proportional to the precipitation volume they receive, then water sampled from King Hill would have expected values of -127.6‰ $\delta^2\text{H}$ and -16.8‰ $\delta^{18}\text{O}$ (green diamond and dashed line in Figures 2 and 5a). This value represents the isotopic composition resulting from a perfectly proportioned mixing ratio of upstream sources to King Hill, based on our isoscape, which is a useful benchmark for gauging when the $i\text{SW}_E$ inferred source values reflect a mixing ratio that was more evenly distributed among the potential sources. The inferred mixed source values of King Hill water only approached this benchmark value during the periods of high discharge in 2017 and 2018 (Figure 5a). At other times with less discharge, inferred median source values were more ^2H - and ^{18}O -depleted than the idealized precipitation-weighted values from the isoscapes, indicating that areas with more depleted isotopic values are contributing more to Snake River flow.

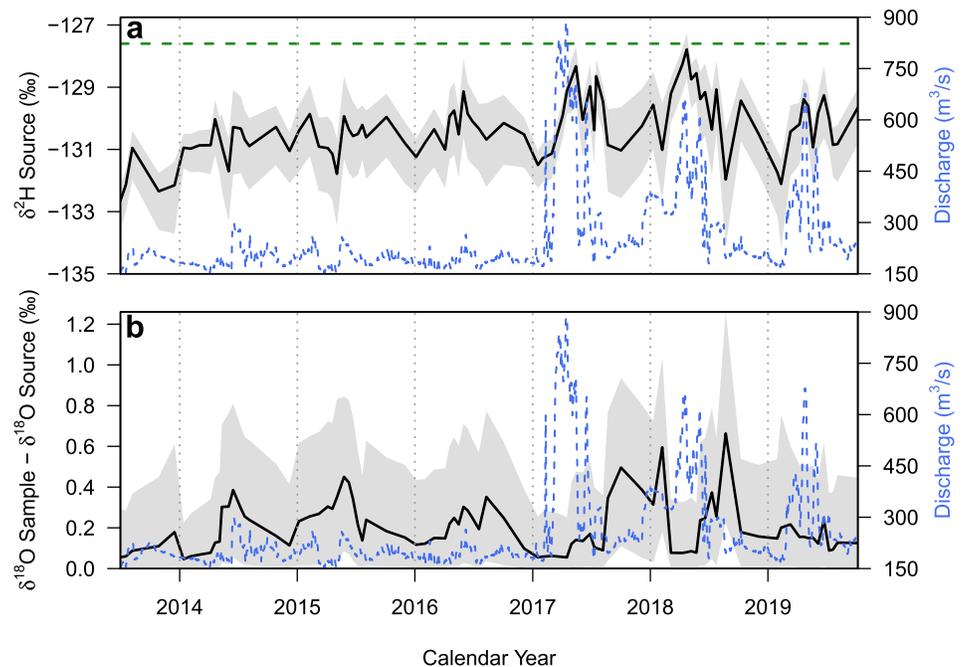


Figure 5. King Hill (a) inferred mixed source $\delta^2\text{H}$ values and (b) evaporative component ($\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{\text{source}}$). Solid black lines represent the median of the $i\text{SW}_E$ values and gray shading indicates the 95% confidence interval of the model. Dashed blue line represents daily Snake River discharge at King Hill. Dashed green line (panel a) represents the expected $\delta^2\text{H}$ value of Snake River water at King Hill (-127.6‰), assuming all upstream hydrologic units contribute to streamflow proportional to their area-integrated average precipitation inputs (Section 3.2).

4. Discussion

4.1. Understanding the Surface Water Isoscape

Surface water isotopes in the Snake River basin vary primarily by longitude, latitude, and mean elevation of the watersheds (Table 2), which can be explained by the process known as rainout (Clark & Fritz, 1997; Dansgaard, 1964; Gat, 1996). The primary source of moisture to the basin is the Pacific Ocean. As storm tracks move inland from the Pacific Ocean, heavy isotopes are lost to rainout, resulting in regions farther from the coast and higher in elevation having more ^2H - and ^{18}O -depleted surface waters than locations closer to the coast. For example, streams in the Teton Range in Wyoming are isotopically lighter than streams draining the western portion of the Snake River basin (Figures 3 and S5). Surface water isotope values within a watershed may reflect post-precipitation fractionation processes, such as evaporation from reservoirs and streams or snowpack sublimation. The samples collected from the small watersheds across the Snake River basin primarily plot below the SLC MWL indicating varying amounts of post-precipitation evaporation (Figure 2). Since the isoscape GLMs were generated using these data (Table 2), the isoscapes (Figures 3 and S5) reflect the likely isotopic values of water as it leaves a particular unit including its evaporative effect. Evaporative effects (quantified as more negative d -excess values) were more evident in samples with heavier isotope values. For example, stream water flowing out of hydrologic units in the Teton Range on the eastern side of the basin (dark blue to pink in Figure 3) would be closer to the MWL and more depleted in heavy isotopes relative to water that would flow from a lowland area downstream (yellow to green in Figure 3).

The isoscape is useful for mapping source contributions to the Snake River if it represents average conditions over time. Repeated sampling of the small watersheds during different collection trips was designed to account for interannual variability of surface water isotope values at the same location. Collection occurred in either June, during high flow conditions, or October, during the low flow of late summer, to account for seasonal differences. The mean standard deviation among sites with repeat samples ($n = 52$) is 1.44‰ $\delta^2\text{H}$ and 0.20‰ $\delta^{18}\text{O}$ and among sites sampled in different months ($n = 44$) is 1.49‰ $\delta^2\text{H}$ and 0.18‰ $\delta^{18}\text{O}$, indicating that interannual and interseasonal variability is relatively small within a hydrologic unit. This small

Table 3
Snow Telemetry Data for the Snake River Basin

Date	Snow water equivalent (% Median)	Total precipitation (% Average)
Apr 1, 2013	80	92
Sep 30, 2013		95
Apr 1, 2014	113	100
Sep 30, 2014		100
Apr 1, 2015	56	87
Sep 30, 2015		89
Apr 1, 2016	107	110
Sep 30, 2016		98
Apr 1, 2017	125	146
Sep 30, 2017		132
Apr 1, 2018	100	101
Sep 30, 2018		96
Apr 1, 2019	116	102
Sep 30, 2019		108

Note. Listed as percentage of median or average values for 1981–2010. Data accessed from the USDA NRCS SNOTEL update report for the Snake River basin.

Abbreviation: SNOTEL, snow telemetry.

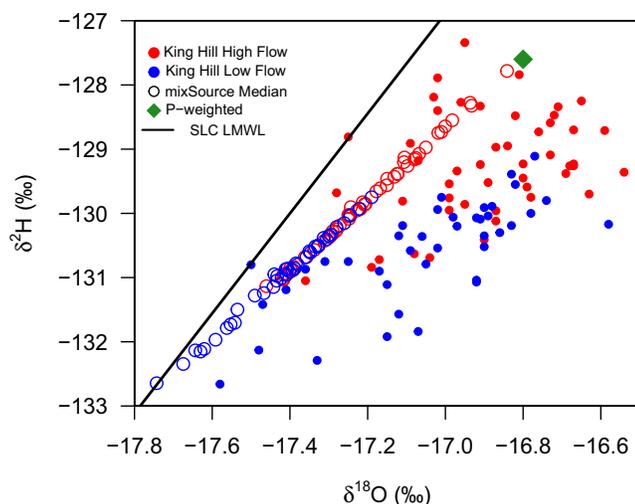


Figure 6. Dual isotope scatterplot of King Hill samples. Red points indicate samples taken when discharge was above the median value ($206 \text{ m}^3/\text{s}$). Blue points indicate samples taken when discharge was below the median. Black line is the Salt Lake City meteoric water line. Open circles indicate the median $i\text{SWE}$ predicted source values. Large green diamond represents the expected isotopic value of King Hill water, assuming all upstream watersheds contribute equally to streamflow and reflects the mean of the mixing fractions used as the prior in our analysis.

variability suggests that the area-integrated precipitation within a unit is isotopically similar to the baseflow discharging to the stream draining that unit; therefore, small hydrologic units serve to spatially and temporally integrate precipitation falling within them. For example, despite dry conditions in the Snake River basin during 2015 (Table 3), which caused several small streams to dry out, sample collection year did not significantly alter the dual-isotope relationship across the basin (not shown: t -tests for all regressions had $p > 0.05$), suggesting that the collected data set represents the time-averaged spatial distribution of surface waters. We argue that the isotope data collected for this study adequately represents temporal variance of surface water values within the Snake River basin, making the isoscape representative of average conditions.

4.2. Changing Source Contributions With Flow Conditions

Snake River water samples collected at King Hill were isotopically distinct between periods of high- and low-flow (Figure 6). When discharge in the river was above the median value ($206 \text{ m}^3/\text{s}$), the river water was more enriched in ^2H and ^{18}O relative to water collected when discharge was below the median (z -tests: $z < -3$, $p < 0.05$); where sample points overlap on Figure 6, discharge was close to the median value. This difference in isotope values between high- and low-flow was seen in both the observations and the $i\text{SWE}$ output (Figure 6). In other words, the $i\text{SWE}$ estimated mixture for the Snake River at King Hill has a greater contribution from sources with lighter isotopic values during periods of low flow. In contrast, the isotopic composition of water at King Hill during high flows was more reflective of all basin precipitation inputs (green diamond in Figure 6), including larger contributions of isotopically heavier sources (see Figure S7 for a break down of source contributions). The most ^2H -depleted surface waters in the isoscape were located in the high elevation, eastern portion of the basin (Figure 3); therefore, when discharge at King Hill was low, these hydrologic units in the east contributed the majority of water that eventually traveled downstream to King Hill. Conversely, when river discharge at King Hill was high, the entire basin was contributing to the river, relative to precipitation inputs.

Snake River discharge at King Hill rarely exceeded the median value from 2013 to 2016, but 2017–2019 all had periods of high discharge rates exceeding $600 \text{ m}^3/\text{s}$ (Figure 5). The high discharge in 2017 and 2018 with their elevated isotopic values occurred when snowpacks within the basin were particularly high. According to Snow Telemetry (SNOTEL) data from the USDA Natural Resources Conservation Service, on April 1, 2017 the entire Snake basin had 125% of the snow-water equivalent (SWE) and 146% of the average precipitation for the period 1981–2010 (Table 3; USDA/NRCS, 2020). The large increases in snowpack and total precipitation in 2017 supports the $i\text{SWE}$ mixed source results that more hydrologic units within the basin contributed to flow resulting in the large discharge rates reflecting a greater contribution from lower elevation and more western hydrologic units (Figures 3 and S7). In contrast to the highest flows in 2017, the lowest Snake River flows during our observation period occurred in 2015 when SWE and total precipitation in the basin were 56% and 87% of the mean values on April 1, 2015, respectively (Table 3). Snake River the mixed source values ($\sim -132\text{‰}$ $\delta^2\text{H}$) were relatively ^2H -depleted (Figure 5a), reflecting a larger fractional contribution from hydrologic units in the eastern portion of the Snake River basin (Figures 3 and S7).

Changes in the isotopic composition of precipitation in the Snake River basin might influence the values of river water sampled from King Hill, rather than changes in source contributions. To explore this possibility we evaluated the volume-weighted average isotope values of SLC precipitation during our sampling period (Figure S1). Precipitation isotope values in SLC became lighter after 2016 (Figures S1b and S1d), which is the opposite response of the water at King Hill during high discharge in 2017 and 2018 (Figure 5a); therefore, precipitation isotope variability was not likely driving the isotopic changes in river water recorded at King Hill.

The isotopic composition of groundwater may also influence the values of river water sampled at King Hill. The Snake River Plain Aquifer underlies the lowland area in south-central Idaho, including the area upstream from King Hill (Figure 1). The aquifer consists of two types of groundwater: (a) isotopically lighter groundwater sourced from high-elevation areas during winter recharge (Stahl et al., 2020) and (b) isotopically heavier (relative to the natural recharge values) groundwater resulting from evaporative effects in Snake River water diverted for irrigation (Plummer et al., 2000). The age of shallow groundwater in the Snake River Plain Aquifer is generally 10 years old or less (Plummer et al., 2000); therefore, groundwater contributions to flow integrate relatively recent upstream sources and would likely be isotopically stable over time. We collected four samples from springs in June, 2014 near Twin Falls, Idaho ($\sim 42.5^{\circ}\text{N}$, 114.5°W), upstream from King Hill. The median $\delta^2\text{H}$ value of the springs was -125.1‰ ($\pm 3.0\sigma$) (Figure 2), which was lower than the local surface water according to the isoscape (light orange color ranging from -118‰ to $-116\text{‰} \pm 4$ MAE in Figure 3), but higher than both the eastern high elevation surface waters (blue to white colors ranging from -142‰ to $-130\text{‰} \pm 4$ MAE in Figure 3) and the expected upstream input if it matched the distribution of precipitation (green diamond in Figure 2). The median $\delta^{18}\text{O}$ ($-16.4\text{‰} \pm 0.5\sigma$) of our spring samples was also within the range of previously measured groundwater values near Twin Falls, Idaho (Plummer et al., 2000).

The contribution of groundwater to river flow is expected to be the greatest at low flow. The lowest discharge rates during our study—March, 2015 (Figure 5)—occurred during a year when dry conditions prevailed across the Snake River basin (Table 3). During this time, the mixed-source isotope values of Snake River water were lower than our measured spring water and the preceding water during slightly higher flows (Figure 5a), suggesting a larger surface water contribution from high elevation areas in the eastern portion of the basin (Figure 3). While we are unable to isolate the groundwater from the surface water signals in this study, the integrated isotopic values of groundwater likely buffered the surface water signal, suggesting that the isotopic variation observed at King Hill are likely reflecting changes in surface water contributions.

The annual increases of evaporatively enriched Snake River water at King Hill (Figure 5b) were likely related to climatic drivers, water use, and water management, including irrigation and reservoir storage/release. Spring snowmelt is stored in reservoirs along the river for later use during the dry months of summer (Clark et al., 1998; Idaho Department of Water Resources, 1997; McGuire et al., 2006). The increases of the evaporative component in 2014–2016 occurred during the summer when evaporative demand and crop irrigation were high and correspond to peak water storage in each year, according to historical data from the upper Snake River basin (Figure 7). The timing of evaporation maxima shifts to later in the year in 2017 and 2018, when water storage remained high (Figure 7) due to increased snowpack and wet conditions across the basin (Table 3), but flow in the river drops indicating the end of the snowpack pulse to the system. The higher and prolonged evaporation signal in 2017 could reflect greater surface area of water exposed to evaporation across the basin after the higher-than-average precipitation. In addition to reservoirs remaining full, wetlands and irrigation canals throughout the basin would also have contained more water than in other years. The increases in the evaporation signal could be reflecting the integration of water isotopes stored in the system over time before being released into the river. A similar, but shorter evaporative signal was detected in 2018, but none was detected in 2019 (Figures 5b and 7). While the precipitation and snowpack data were similar for these 2 years (Table 3) and river flow was also higher than it was from 2014 to 2016, the $i\text{SW}_E$ source mixture prediction for 2019 was more like the earlier low-flow years, indicating a greater contribution from the more eastern and high elevation portions of the watershed relative to 2017 and 2018. It could be that the influence of the high snowpack in 2017 took several years to drain from the system. Additionally, a prolonged cold season in early 2019 may have shifted the timing of the initial snowmelt and

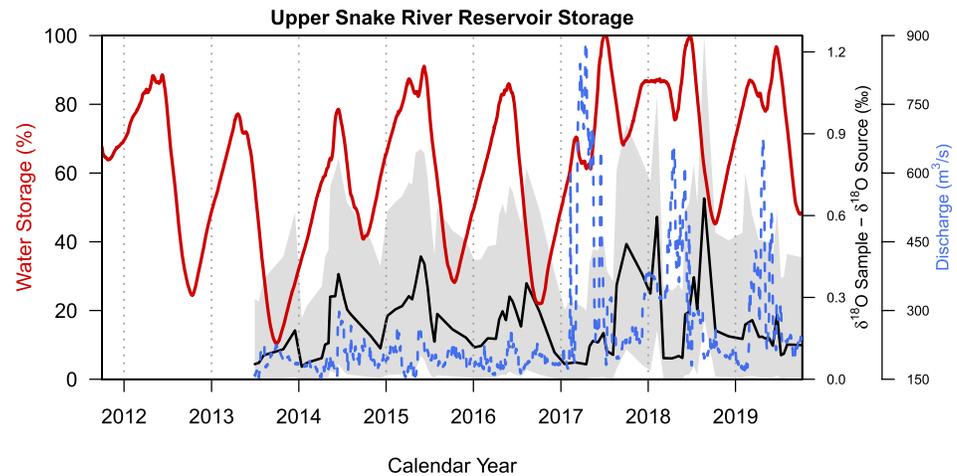


Figure 7. Water storage in the upper Snake River reservoir system as a percentage of total storage capacity (red line). The upper Snake River system is the combination of the major reservoirs: Jackson Lake, Palisades, Ririe, Grassy Lake, Island Park, American Falls, and Lake Walcott. Historical water storage data are publicly available for each of these locations from the Bureau of Reclamation: <https://www.usbr.gov/pn/hydromet/burtea.html>. Water storage is plotted with the evaporative component of iSW_E and discharge from King Hill (Figure 5b).

lowered evaporation that year. A longer time series of stable isotope data could help better understand these dynamics of the timing and duration of Snake River flows.

5. Conclusions

We have presented new surface water isotope (δ^2H and $\delta^{18}O$) data from the Snake River basin and used it to model their spatial variation. We used GLMs to generate δ^2H and $\delta^{18}O$ isoscapes for the Snake River basin and found that surface water isotope values vary with longitude, latitude, and elevation, with the lightest isotope values located in the highest elevation regions of the eastern portion of the basin near the headwaters of the Snake River. Isotope measurements of water samples collected from the Snake River at King Hill demonstrated the dynamic connection between contributing area and flow within the river. Generally, the eastern high-elevation hydrologic units contribute a greater proportion of surface water to river flow than the more western, lower elevation hydrologic units; however, this pattern shifted with flow dynamics of the river. During periods of high flow and above-average snowpack, the isotopic source values from the Snake River at King Hill became more enriched in 2H and ^{18}O , indicating a greater contribution of surface water from a wider variety of elevations in more western hydrologic units. Groundwater inputs and water management practices in the Snake River basin, such as reservoir storage and irrigation pumping, likely have a buffering effect on changes in the isotopic value of Snake River water at King Hill due to the relative contribution of eastern and western sources of streamflow. Separating source variations from evaporative effects using iSW_E allowed us to detect consistent river evaporation during summer dry periods. Both evaporation within source watersheds and in-stream evaporation within the Snake River vary systematically, suggesting there is potential to isolate these two different evaporation components in future studies.

This surface water isoscape provides a framework for identifying areas that contribute the most water to Snake River flow and how flow dynamics change with climatic conditions. The isoscape model is a potential tool for water managers to target water conservation efforts in areas that will become increasingly vital for water supply as temperatures rise and mountain snowpack and summer streamflow decline. Periods of low flow are likely to become more frequent as warming progresses, so surface water that supplies the Snake River will become increasingly restricted to the eastern region of the basin. The approach from this study provides a structure for using surface water isotopes to characterize flow dynamics within other mountainous, continental-interior river basins in which evaporative enrichment of surface waters is likely.

Data Availability Statement

The Snake Basin isotope and watershed characteristics data generated for this study are available on the U.S. Environmental Protection Agency ScienceHub (<https://doi.org/10.23719/1520442>). The isotope data are also available on <https://waterisotopesDB.org>.

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