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Research papers

Elevation and spatial structure explain most surface-water isotopic variation across five Pacific Coast basins

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1. Introduction

Isoscapes are a framework that describe the spatial patterns in isotopic ratios across a landscape and are useful for addressing a variety of basic and applied research questions (West et al., 2010; Bowen and Good, 2015). Stable isotopes of oxygen and hydrogen can be harnessed to determine source-water contributions to streamflow on a range of spatial and temporal scales (Rock and Mayer, 2007; Koeniger et al., 2009; Wang et al., 2009; Mountain et al., 2015), estimate mean transit times (McGuire et al., 2005; McGuire and McDonnell, 2006; Jasechko et al., 2016), delineate animal migration paths (Chamberlain et al., 1997; Hobson and Wassenaar, 1997), and understand hydrologic flow paths (Rodgers et al., 2005; Singh et al., 2016; Nickolas et al., 2017). Despite the widespread use of water isotope ratios in research and their potential application for predicting future flows under a changing climate or for identifying likely areas of cool water for fisheries management, few studies have compared drivers of variation in isotopic ratios at the basin scale or across basins.

The generation of accurate isoscapes is possible in part because water stable isotope ratios exhibit systematic spatial and temporal variation resulting from the process of isotope fractionation that accompanies water cycle phase changes and diffusion. Isotope fractionation is the primary force acting to produce variations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (both spatially and temporally) in water sources across the globe (Gat, 1996; Araguás-Araguás et al., 2000). An example of this process is the Rayleigh rainout effect, wherein progressive isotopic depletion of a vapor cloud occurs as it moves along its storm trajectory. Rayleigh rainout occurs because heavy isotopes preferentially fall as

precipitation (Dansgaard, 1964; Clark and Fritz, 1997). As a result, both precipitation and surface water isotopic ratios of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are highly correlated with changes in elevation, latitude, and longitude (Yonge et al., 1989; Ingrahm and Taylor, 1991; Dutton et al., 2005; Lechler and Niemi, 2011), although the strength and presence of these relationships can vary among river basins due to local processes such as evaporation (Bowen and Good, 2015).

Although broad-scale patterns in water isotopic ratios are well documented, when generating isoscapes for use in water resource management, basin-scale factors that may affect isotope distributions must be incorporated. Previous studies have shown consistent relationships between elevation and surface water stable isotopes at the basin scale (Biggs et al., 2015; Peng et al., 2015; Vespasiano et al., 2015; Fan et al., 2016). When the elevation-isotope relationship is clear and consistent, water isoscapes can be a valuable tool for assessing the proportion of water that comes from high elevation, climate sensitive snowmelt that may be critical for sustaining summer baseflow in mountainous regions (Barnett et al., 2005; Brooks et al., 2012). However, within certain regions, the elevation-isotope relationship is weak, absent, or inverse (Wassenaar et al., 2009; Lechler and Niemi, 2011; Bershaw et al., 2012), suggesting that local atmospheric or hydrologic mechanisms are overriding the elevation effect within these regions. Basins in close geographic proximity can have fundamentally different relationships between surface water isotope ratios and elevation (Brooks et al., 2012; Nickolas et al., 2017); therefore, cross-basin analyses are needed to describe the variation in the landscape covariates that are highly correlated with surface water isotope ratios in order to identify where and how isotopic variation can be leveraged to identify

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distinct water sources within a river basin.

Previous studies have predominately generated water isoscapes in two-dimensional space. Such models may be appropriate for estimating terrestrial, oceanic, or atmospheric conditions such as precipitation over the continental United States or the surface of the Atlantic Ocean (Vachon et al., 2010; McMahon et al., 2013). The movement of stream surface water, however, is constrained by the topology of the dendritic stream network, which strongly affects the distribution of surface water stable isotopes that are conserved as water moves downstream (Clark and Fritz, 1997). To date, isoscapes of stream networks have largely relied on interpolation using Euclidean distance (the straight-line distance between two sites) and have been restricted to predicting inputs from the local catchment (Brooks et al., 2012; Katsuyama et al., 2015). Although Bowen et al. (2011) modeled continuous river water isotope values by accumulating elevation-explicit, gridded precipitation isotope maps downstream and correcting them with model residuals, no explicit statistical method was used to partition the effects of downstream transport versus landscape predictors such as geology. Given that typical two-dimensional models do not account for the branching structure of stream networks, longitudinal connectivity, or flow direction, they may be inappropriate for use on river networks.

Ver Hoef et al. (2010) developed a class of geostatistical models, spatial stream network models (SSNMs), which account for spatial dependencies across stream networks. SSNMs are similar to conventional linear mixed models in that the deterministic mean of the dependent variable is modeled as a linear function of explanatory variables; however, the assumption of independent errors is relaxed and an autocovariance model is used to account for spatial autocorrelation in the errors (Ver Hoef et al., 2006; Peterson and Ver Hoef, 2010; Ver Hoef and Peterson, 2010). The autocovariance model can be specified using any combination of tail-up, tail-down, or Euclidean autocovariance functions. Tail-up and tail-down functions use hydrologic rather than Euclidean distance, and, in the tail-up model, spatial autocorrelation is restricted to flow-connected locations (i.e., water flows from an upstream location to a downstream location). SSNMs have been applied to answer a broad suite of questions, in each case improving model fit by explicitly modeling spatial autocorrelation in the data (Isaak et al., 2014; Brennan et al., 2016; Filipe et al., 2017). Application of these models to water isotopes might provide information on the relative influence of environmental versus spatial processes on isotope distribution, improve estimation of the covariate-isotope relationships absent confounding spatial autocorrelation, and generate more robust predictions of isotope values at unmeasured sites.

In this study, we compare the spatial patterns of surface water isotopes across five basins within Washington and southeastern Alaska to quantify and compare local controls on isotopic variability of surface water and to explore the utility of applying simple elevation regressions models for estimating water source across river basins. We also compare the performance of models with and without network-based spatial autocorrelation. Specifically, the objectives of our study are (1) to compare the strength with which isotope ratios vary by mean watershed elevation (MWE) across five river basins, (2) to assess and compare whether additional landscape predictors improve models of isotope ratios across basins, and (3) to explore where SSNMs might be used to improve river water isoscape generation.

2. Methods

2.1. Study sites

We selected five climatically and geographically distinct watersheds across Washington and Alaska (Fig. 1). The Washington river basins (Snoqualmie, Skagit, Green, and Wenatchee) are within the Cascade Range with the Wenatchee River draining to the east (leeward), and the other three rivers draining to the west (windward). Western Washington has a Mediterranean climate with dry summers and wet, mild

winters influenced by its proximity to the Pacific Ocean. Eastern Washington has a Continental climate with warmer summers, colder winters, and comparatively less precipitation (Mote and Salathé, 2010). The Alaska river basin, Cowee Creek, has a Temperate Rain Forest climate characteristic of higher latitudes with cold, wet winters and cool, wet summers. Precipitation in all regions occurs predominately from October to March and falls as snow or rain, depending on latitude, elevation, and proximity to the Pacific Ocean. Precipitation within all basins originates from vapor coming from the Pacific Ocean. Average climate and physical characteristics for each basin are displayed in Table 1.

The Snoqualmie River begins as three distinct forks in the Mt. Baker-Snoqualmie National Forest and drains 1793 km² on the west side of the Cascade Range, Washington. The three forks originate in forested public land before converging and flowing through a mix of agricultural, residential, and commercial land use. On one major tributary, the Tolt River, a dam and a large reservoir provide drinking water for the City of Seattle.

The Green River drains a 1185 km² watershed on the west side of the Cascade Range, Washington. During the 19th and 20th centuries, there was extensive railroad and logging activity in the upper Green River valley; however, it has now become a gated water supply for the city of Tacoma via damming of the river at the Howard Hansen Dam. The lower portion of the river flows through downtown Seattle and is heavily modified and urbanized.

The Skagit River drains 8163 km² of the western Cascade Range before emptying into Puget Sound. It originates from headwaters in southwestern British Columbia and flows southwest before meeting up with the Sauk River, which flows northwest and drains the North Cascades. Five major hydropower projects are present on the Upper Skagit and its tributaries. The river experiences year-round glacial influence from numerous mountains, including Mount Baker and Glacier Peak, both of which exceed 3200 m.

The Wenatchee River drains 3440 km² of the eastern Cascades before flowing into the Columbia River. Land use is similar to that of other basins, wherein the headwaters originate in forested public lands before flowing through a mix of agricultural, residential, and commercial land use. As described above, the climate on the east side of the Cascades is drier than that of the west side; however, the prevailing westerly winds, which cross the Cascades, create temperature and precipitation patterns that vary widely across the Wenatchee basin. For example, annual precipitation on the crest of the mountains averages over 2900 mm, the majority of which falls as snow, whereas eastward and at only 780 m, the city of Wenatchee averages less than 235 mm of annual precipitation.

Cowee Creek drains 118 km² of the United States Forest Service Héén Latinee Experimental Forest located in the Tongass National Forest, Alaska. The watershed is approximately 15% glaciated and experiences substantial influence from three alpine glaciers (18.2-km²) and extensive perennial snowfields. The glaciers are rapidly diminishing and loss of the cool summer discharge from glacial melt is a concern in fish habitat management. Cowee Creek is characteristic of the thousands of moderately sized watersheds that drain the Coast Mountains of Alaska and British Columbia, and in addition to perennial snowfields, encompasses alpine meadows, spruce-hemlock forests, and extensive valley-bottom wetlands.

2.2. Data collection and processing

We collected between 31 and 58 spatially distributed water samples within each of our five basins in Summer, 2017 during baseflow (Fig. 1). Sampling sites within each basin were selected to include a mix of mainstem and tributary locations and to span the geographic and elevation range found within each basin. Water samples were collected within wading distance from the stream edge, but in flowing current. Samples were collected in 20 ml vials with conical plastic cap inserts to

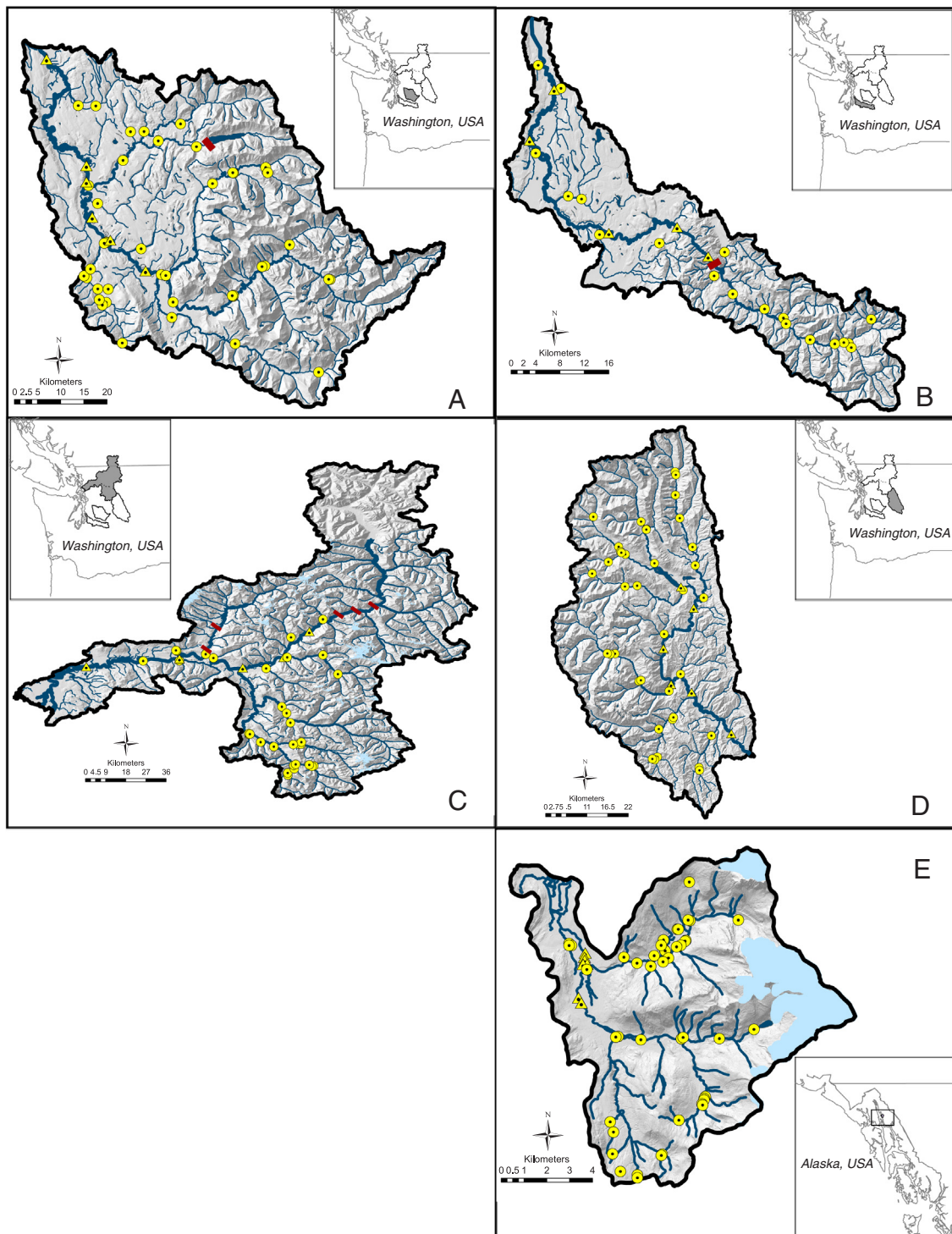


Fig. 1. Geographic locations of study basins, the Snoqualmie (A), Green (B), Skagit (C), and Wenatchee (D) Rivers in Washington and Cowee Creek (E) in southeastern Alaska. Between 31 and 58 water samples were collected within each basin ($n_{\text{Snoqualmie}} = 58$, $n_{\text{Green}} = 31$, $n_{\text{Skagit}} = 38$, $n_{\text{Wenatchee}} = 44$, $n_{\text{Cowee}} = 38$) and are shown in yellow. Red points indicate a major dam and blue shading indicates an ice mass. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

prevent evaporation, and duplicates were collected for every 20th sample.

Watersheds for each sampling point were delineated and landscape variables describing the watersheds were derived from commonly available geostatistical products (Table 2). We chose candidate covariates that were known to influence water isotope fractionation in some basins, e.g., elevation and longitude (Dansgaard, 1964; Clark and Fritz, 1997), as well as those that had some mechanistic basis for

influencing isotopic ratios, e.g., aquifer and soil permeability (Tauge and Grant, 2009; Nickolas et al., 2017). Covariates examined include catchment area, MWE, latitude, longitude, mean annual precipitation (MAP), mean annual air temperature (MAT), aquifer permeability, and soil permeability (Table 2).

Water isotopes were analyzed on a Laser Absorption Water-Vapor Isotope Spectrometer (Model 908-0004, Los Gatos Research, Mountain View, CA) located at the Integrated Stable Isotope Research Facility at

Table 1
Climate and physical characteristics for each basin.

		Snoqualmie	Green	Skagit	Wenatchee	Cowee
Mean Annual Temperature (C°)	Mean	8.16	8.25	6.36	6.15	1.76
	Maximum	11.55	11.84	10.68	11.13	5.09
	Minimum	1.77	4.04	-0.22	-0.12	-0.38
Mean Annual Precipitation (mm)	Mean	2435	1810	2154	1210	3568
	Maximum	4304	2727	4948	2940	4792
	Minimum	1102	925	711	232	1792
Elevation (m)	Mean	629	580	946	1087	638
	Maximum	1876	1500	3283	2390	1791
	Minimum	8	5	1	194	1
Basin Size (km ²)		1793	1185	8163	3440	118

the Western Ecology Division of the Environmental Protection Agency, Corvallis Oregon. Oxygen and Hydrogen isotope ratios are reported as delta (δ) values and presented in parts per thousand (‰) deviation from the adopted standard representing mean isotopic composition of the global ocean (Vienna Standard Mean Ocean Water). Measurement precision estimates (± 1 standard deviation) were determined on repeated measures of both field and lab duplicates and were 0.12‰ for $\delta^{18}\text{O}$ and 0.17‰ for $\delta^2\text{H}$. Deuterium excess (d-excess = $\delta^2\text{H} - 8 \delta^{18}\text{O}$; Dansgaard, 1964) is a measure of the evaporative influence on water isotopes. The global meteoric water line (GMWL) has a d-excess value of 10‰ but precipitation events vary around this value. Based on d-excess variance in a 14-year record of precipitation isotopes collected in Corvallis OR, we considered samples with d-excess values below 5‰ to have been influenced by evaporation since falling as precipitation and we removed those values from our analyses.

2.3. Data analysis

In all five basins, we first conducted exploratory and mapping analyses to understand and display the spatial distribution of landscape covariates (Table 2). We examined maps of and correlations between landscape covariates to understand the distribution of and relationships between predictor variables within and across watersheds. The goal of these exploratory analyses was to understand underlying collinearity between covariates that might hinder our ability to interpret statistical models.

We then examined relationships between landscape covariates and isotope values using exploratory single variable analyses and explanatory multiple regression models. As $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are highly correlated (Clark and Fritz, 1997), all regression analyses considered only $\delta^{18}\text{O}$ values. We used ordinary least squares regression to fit a linear model to each basin independently; the model explained variation in isotope ratios as a function of a single landscape characteristic (for the exploratory analyses) or suites of landscape characteristics (for the explanatory models). For each univariate model, we conducted a *t*-test to test whether or not the regression coefficient was statistically different from zero. An alpha level of 0.001 was chosen to

indicate a significant relationship. A conservative cutoff was chosen because of the large quantity of statistical tests necessary to explore all potential predictors.

To identify the suite of landscape characteristics most closely associated with $\delta^{18}\text{O}$ values, we constructed a best fit multiple regression model for each basin. We selected variables in our final best-fit models using a modified forward stepwise regression where we always included MWE, if significant in the univariate model, as the first term in the models. Only predictors significant at the univariate level were additionally considered for inclusion. We did not include landscape predictors highly correlated with predictors already in the model (pairwise correlation greater than 0.8). To constrain the number of statistical tests, total size of each model was limited to four covariates and only main effects were examined. Covariates were individually added to the model if they reduced the root mean squared error more than other potential covariates, were significant at the univariate level, and increased the overall coefficient of determination (R^2). For each best-fit model, we calculated the R^2 and the root mean squared prediction error (RMSPE) using leave one out cross validation (LOOCV). To quantify variable importance in models with more than one covariate, we calculated the independent effect of each covariate by comparing the fit of all models containing a particular covariate to the fit of all nested models lacking that covariate, through the process of hierarchical partitioning (Murray and Conner, 2009; Walsh and MacNally, 2013). The resulting independent effect weights represent the average contribution of each covariate to the variance in $\delta^{18}\text{O}$ values over all possible models, and are an estimate of the proportion of variance in $\delta^{18}\text{O}$ values explained by each covariate.

In the Snoqualmie and Wenatchee basins, we further modeled the spatial relationship of $\delta^{18}\text{O}$ values using semivariograms and SSNMs. We chose to test the use of spatial tools in the Snoqualmie and Wenatchee as these basins are similar in size and network configuration but differ in the amount of isotopic variation explained by covariates. Semivariograms depict how the semivariance, or average variation between measurement values separated by some distance, changes in relation to the distance separating them. Semivariograms are useful for visualizing patterns of spatial autocorrelation in the measured data and

Table 2
Covariates considered for inclusion in each model. Here, “watershed” indicates the upstream area draining to a sample.

Covariate	Abbreviation	Description	Unit	Data Source
Elevation	MWE	Mean watershed elevation	m	NED DEM model
Mean Annual Precipitation	MAP	Mean watershed 30-year average (1981–2010) annual normal precipitation	mm	PRISM Climate Group, EPA StreamCat (Hill et al. 2015)
Mean Average Air Temperature	MAT	Mean watershed 30-year average (1981–2010) annual mean air temperature	C°	PRISM Climate Group, EPA StreamCat (Hill et al. 2015)
Area	Area	Log transformed watershed area	log(km ²)	NED DEM model
Latitude	Lat	Latitude of watershed centroid	degree	
Longitude	Lon	Longitude of watershed centroid	degree	
Soil Permeability	SoilPerm	Mean watershed soil permeability	cm/hour	STATSGO, StreamCat (Hill et al. 2015)
Aquifer Permeability	AqPerm	Mean watershed aquifer permeability	dimensionless; 1–7 based on lithology	USGS Hydrologic Landscape Regions (Wolock et al. 2004)

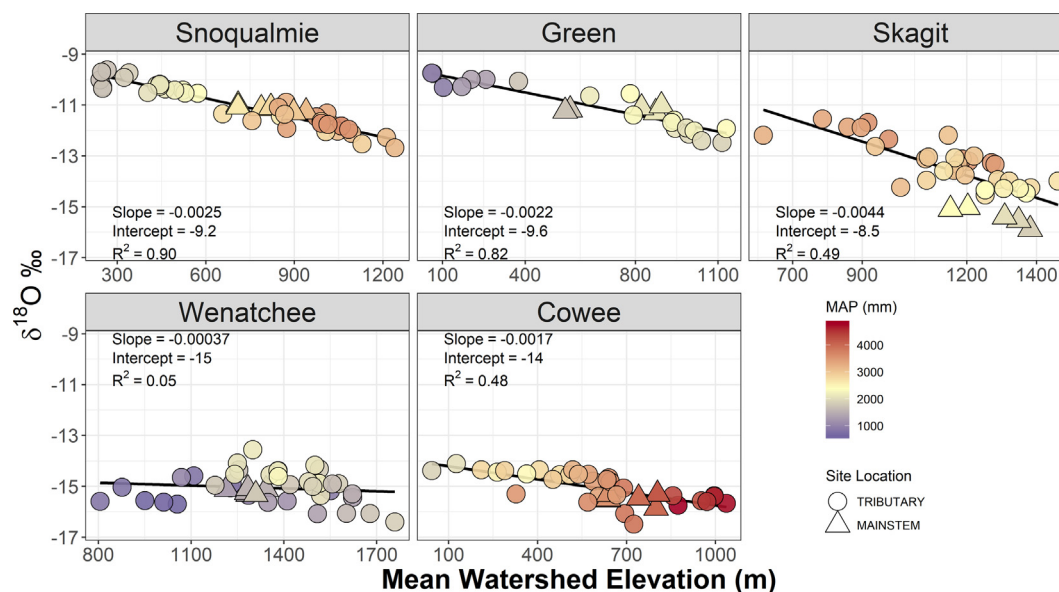


Fig. 2. Regressions of $\delta^{18}\text{O}$ values with MWE for samples collected during summer low flow for each basin. Lines represent the least squares relationships. Triangle symbols are mainstem sites and circle symbols are tributary sites. Symbols are colored according to the mean annual precipitation (MAP) within the upstream watershed.

model residuals. Low semivariance values indicate that sample pairs within some distance are similar, whereas high values indicate dissimilar sample pairs. If positive autocorrelation occurs within a data set, the semivariance values are smallest at short distance lags and increase with distance. We displayed and compared two measures of distance between points: flow-connected distance (a network-based measure) and Euclidean distance (a straight-line measure). Semivariograms of the network-based distance consider only the topological distance between sites and illustrate relationships between sites when flow-connectedness is taken into account. Semivariograms of Euclidean distance reveal interactions or lateral connectivity between the stream network and the landscape. Semivariance was calculated using the robust estimator (Cressie, 1993). We estimated the semivariogram at lag distances whose bins contained greater than 10 site-pairs and that were less than half the maximum flow-connected distance between sites (Zimmerman and Ver Hoef, 2017). We examined semivariograms to visualize dependencies in both raw $\delta^{18}\text{O}$ values and residuals from the best-fit linear models and SSNMs. Semivariograms were compared to one another to identify scales of spatial autocorrelation (McGuire et al., 2014; Brennan et al., 2016).

The SSNMs described in Ver Hoef and Peterson (2010) extend the standard linear model as:

$$Y = X\beta + z_{TD} + z_{TU} + z_{EUC} + \varepsilon$$

where Y is a vector of the response (i.e. isotope ratios), X is a matrix of predictors (i.e. covariates from Table 2), β is a vector of estimated coefficients, z_{TD} , z_{TU} , and z_{EUC} are the tail-down, tail-up, and Euclidean autocovariance models, and ε is a vector of independent normally distributed random errors. We followed a two-step procedure in fitting the SSNMs (Peterson and Ver Hoef, 2010). First, we selected fixed effects while maintaining a constant spatial component consisting of exponential tail-up and exponential Euclidean spatial autocovariance functions. Fixed effects in our final SSNMs were selected independently of the linear model approach, but were selected according to the same process described above for best-fit linear models. Second, we used Akaike Information Criterion (AIC) to select a covariance structure while maintaining the fixed effect(s) selected in the first step. We considered models having four possible spatial components: an exponential tail-up and Euclidean covariance structure, an exponential covariance structure alone, an exponential tail-up covariance structure

alone, and a nugget-only model (i.e. assuming no spatial autocorrelation). We examined the predictive accuracy using LOOCV, and calculated the R^2 , AIC, and RMSPE. We also decomposed the variation explained in each model into the proportion explained by the predictors and by the covariance structure in order to examine how each component contributed to model fit. Although the SSNM framework can include a mixture of autocovariance models based on tail-up, tail-down (i.e., based on network distance of flow-unconnected sites), and Euclidean distance, we chose to consider only tail-up and Euclidean (Steel et al., 2016; Steel et al., 2018). We elected to do this as isotopes move in a downstream direction and we had no reason to believe that any explanatory power achieved by using a tail-down covariance structure would reflect the underlying mechanism. All data analyses were conducted in R (<http://cran.r-project.org>) using the Spatial Stream Network (SSN) package (Ver Hoef et al., 2014) and Spatial Tools for the Analysis of River Systems (STARS) toolbox in ArcGIS 10.6 (Peterson and Ver Hoef, 2014).

3. Results

3.1. General description and relationships with MWE

The measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in stream water samples ranged from -16.50‰ to -9.37‰ (mean = -12.85‰) and from -119.93‰ to -66.33‰ (mean = -92.42‰) respectively. In general, the highest values were found in the Snoqualmie and Green Rivers and the lowest values in the Wenatchee River. Only three samples in our analysis had d-excess values less than 5‰. All of these samples were collected in the Snoqualmie basin from streams that drained small, stagnant ponds and were removed from further analyses. After their removal, the measured d-excess values in stream water samples ranged from 5.01‰ to 15.43‰ (mean = 10.28‰).

The regression models between MWE and isotopic signature displayed an inverse relationship for all basins except the Wenatchee River, which displayed no relationship (Fig. 2). The $\delta^{18}\text{O}$ -MWE slopes for the regression models using both mainstem and tributary sites were $-2.5 \pm 0.13\text{‰ km}^{-1}$ ($R^2 = 0.90$) for the Snoqualmie River, $-2.2 \pm 0.20\text{‰ km}^{-1}$ ($R^2 = 0.82$) for the Green River, $-4.4 \pm 0.66\text{‰ km}^{-1}$ ($R^2 = 0.49$) for the Skagit River, and $-1.7 \pm 0.28\text{‰ km}^{-1}$ ($R^2 = 0.48$) for Cowee Creek. For the

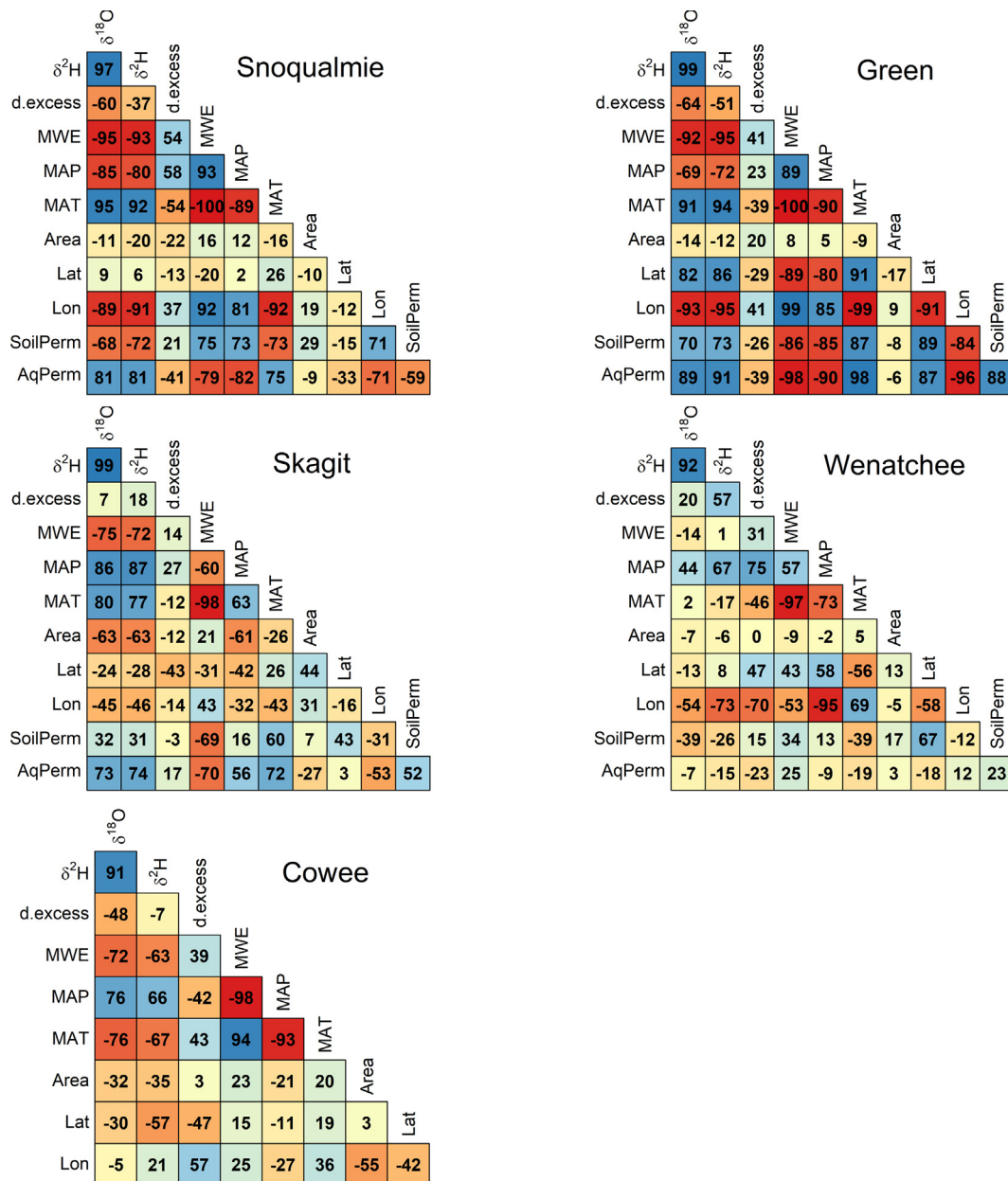


Fig. 3. Correlation matrices for the Snoqualmie, Green, Skagit, and Wenatchee Rivers, and Cowee Creek. Both isotope metrics and landscape covariates are included. Red indicates a negative correlation between two variables, and blue indicates a positive correlation. The darker the color, the stronger the correlation. See Table 2 for a description of covariates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Wenatchee River, the R² value was 0.05 and the δ¹⁸O-MWE slope was $-0.4 \pm 0.41\text{‰ km}^{-1}$. In four basins, tributaries and mainstem samples fall together on the same regression but, in the Skagit River, mainstem samples have lower isotopic values for a given MWE than smaller tributaries.

3.2. Landscape covariates

The structure of landscape covariates differed dramatically across basins and impacted our ability to model δ¹⁸O values as a function of landscape covariates (Fig. 3). In the Snoqualmie and the Green basins, most landscape predictors were highly correlated with one another. For example, in the Snoqualmie basin, MWE had a correlation coefficient greater than or equal to 0.75 with all landscape predictors except area and latitude. Similarly, in the Green basin MWE had a correlation coefficient greater or equal to 0.69 with all landscape predictors except

area. In the Skagit, Wenatchee and Cowee basins, correlation among landscape predictors existed, but was less extreme. In the Skagit basin, no correlation among predictors exceeded 0.75, with the exception of MAT and MWE, which were almost perfectly correlated (-0.98). Additionally, the Skagit is the only basin in which MAP and MWE were negatively correlated (Fig. 3). The Wenatchee basin displayed the lowest average correlation among landscape predictors. Only longitude was moderately correlated (greater than 0.40) with all landscape covariates except soil and aquifer permeability. In Cowee basin, there was a tight coupling among MWE, MAP, and MAT where all correlations exceeded 0.92; however, beyond these relationships no correlation exceeded 0.55.

3.3. Univariate and best-fit linear models

The direction and magnitude of relationships between δ¹⁸O and δ²H

Table 3

Best fit linear models from the Snoqualmie, Green, Skagit, Wenatchee, and Cowee basins. The independent effect weight is the percentage of variance explained by each covariate.

Basin	Covariates	Covariate Coefficient (SE)	Independent Effect Weight (%)	R ²	RMSPE
Snoqualmie	MWE	-0.0025 (0.00013)	100	0.90	0.26
Green	MWE	-0.0022 (0.00020)	100	0.82	0.35
Skagit	MWE	-0.0018 (0.00051)	21	0.87	0.38
	MAP	0.00095 (0.00021)	33		
	Area	-0.00015 (0.000041)	26		
	Aquifer Permeability	0.40 (0.14)	20		
Wenatchee	Longitude	-2.99 (0.44)	70	0.47	0.42
	MWE	-0.0016 (0.00034)	30		
Cowee	MWE	-0.0017 (0.00028)	100	0.48	0.41

values and landscape covariates varied across basins (Fig. 3). For example, in the Snoqualmie and Green basins, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were highly negatively correlated with mean annual precipitation (MAP) (-0.85, -0.69 for $\delta^{18}\text{O}$ and -0.80, -0.72 for $\delta^2\text{H}$), whereas in the Skagit, Wenatchee and Cowee basins this relationship was reversed (0.86, 0.44, 0.76 for $\delta^{18}\text{O}$ and 0.87, 0.67, 0.66 for $\delta^2\text{H}$). We note again that the high collinearity of landscape predictors within basins made it difficult to parse some effects.

Best-fit models for all basins included MWE but displayed clear differences in both level of complexity and predictive accuracy. In the Snoqualmie, Green and Cowee basins, best-fit models included only MWE (Table 3). Calculated R² values were 0.90 for the Snoqualmie, 0.82 for the Green, and 0.48 for Cowee. The RMSPE for these models was 0.26, 0.36 and 0.42‰, respectively. In the Skagit and Wenatchee basins, on the other hand, incorporating additional predictors beyond MWE increased the amount of variance explained in our isotope data. Additional covariates included in the Skagit model were MAP, area, and aquifer permeability, whereas the only additional covariate included in the Wenatchee model was longitude (Table 3). The Skagit River, similar to other west side basins, displayed high predictive accuracy (R² = 0.87; RMSPE = 0.41‰) whereas the Wenatchee River displayed low predictive accuracy (R² = 0.47; RMSPE = 0.42‰). Independent effect weights for the Skagit model show a relatively even partitioning of variance among all predictors ($I_{\text{elev}} = 21\%$, $I_{\text{precip}} = 33\%$, $I_{\text{area}} = 26\%$, $I_{\text{perm}} = 20\%$), whereas in the Wenatchee model the majority of variation in $\delta^{18}\text{O}$ values is explained by longitude ($I_{\text{lon}} = 70\%$, $I_{\text{elev}} = 30\%$).

3.4. Semivariograms and spatial stream network models

The Snoqualmie and Wenatchee basins showed spatial dependencies for raw $\delta^{18}\text{O}$ values (Fig. 4). For the Snoqualmie basin raw $\delta^{18}\text{O}$ values, semivariance for Euclidean distance (i.e. the straight line distance between all sites) increased rapidly and linearly before leveling off around 35 km. This change in semivariance suggests that sites beyond 35 km apart were uncorrelated, whereas sites closer together were more highly correlated with one another. Semivariance for flow-connected sites (i.e. the network distance between sites that share flow) for raw $\delta^{18}\text{O}$ values was generally much smaller and increased slowly with distance. Furthermore, semivariance of raw $\delta^{18}\text{O}$ values between flow-connected sites never leveled off, suggesting the presence of an unmodeled trend such as MWE. Similar patterns of semivariance were apparent in the Wenatchee basin raw $\delta^{18}\text{O}$ values, although overall values and the difference between the magnitude of Euclidean and flow-connected semivariance were both smaller. In addition, the semivariance for the Euclidean distance leveled off at around 25 km in the Wenatchee basin.

We compared model fit and variance decomposition for SSNNMs with four distinct autocovariance models (Table 4; Fig. 5; Fig. 6). For the Snoqualmie basin, similar to the best-fit linear model, only MWE was selected as a fixed effect, capturing between 81 and 90 % of the

variance in $\delta^{18}\text{O}$ values (Table 4; Fig. 6). When spatial autocorrelation was explicitly accounted for by including a covariance structure in the model, the total variance explained was greater than the non-spatial model; however, between 3 and 9 % of the variance previously explained by the covariates was shifted onto the covariance structure (Table 4; Fig. 6). The SSNNM with a tail-up covariance structure outperformed all others and had the lowest AIC, RMSPE and R². RMSPE decreased from 0.26‰ in the linear model to 0.16‰, similar to analytical precision (0.12‰), and R² increased from 0.90 in the linear model to 0.96 (Table 4). Adding a Euclidean covariance structure did not improve prediction accuracy as much as the tail-up model.

For the Wenatchee basin, longitude and MWE were again selected as fixed effects, explaining 45–47% of the variation in $\delta^{18}\text{O}$ values, significantly less variation than in the Snoqualmie models. Spatial autocorrelation explained an additional 14–26% of the variance not explained by covariates. Contrary to the Snoqualmie basin, models that included a Euclidean covariance structure outperformed all others and had the lowest AIC, RMSPE, and R², suggesting that network structure was less important in this basin (Table 4; Fig. 6). Including both tail-up and Euclidean covariance structures improved the R² and RMSPE over the simple Euclidean model (0.71 vs 0.67 and 0.31‰ vs 0.33‰, respectively), but resulted in a nearly identical AIC value (51.67 vs. 51.24, respectively). Although the models are comparable, we selected the model with both a tail-up and Euclidean covariance structure to move forward with further analyses.

Semivariograms of spatial and linear model residuals displayed a reduction in semivariance as compared to the raw data for both basins and distance measures (Fig. 4). This reduction suggests that by accounting for spatially structured covariates such as MWE and longitude, regression models remove some spatial autocorrelation. The decrease in semivariance between raw data and linear residuals was more pronounced for the Snoqualmie basin, whereas the decrease in semivariance between linear and spatial residuals was more pronounced for the Wenatchee basin. For both the Snoqualmie and Wenatchee basins, semivariance of spatial model residuals is relatively flat. This pattern suggests that accounting for spatial structure through SSNNMs removes the majority of spatial autocorrelation in the $\delta^{18}\text{O}$ values.

4. Discussion

4.1. MWE gradient

Although we expected MWE to be the main determinant of isotopic variation in surface water, our analysis revealed differences in surface water MWE- $\delta^{18}\text{O}$ slopes between basins based on basin size, shape and location on the windward versus leeward sides of mountains. The strong elevation gradient observed in western Washington basins and Cowee Creek, all of which drain windward mountainsides, can be attributed to the rainout effect, or Rayleigh distillation (Dansgaard, 1964; Clark and Fritz, 1997). Storms bringing precipitation to western Washington and coastal Alaskan basins originate from the Pacific Ocean

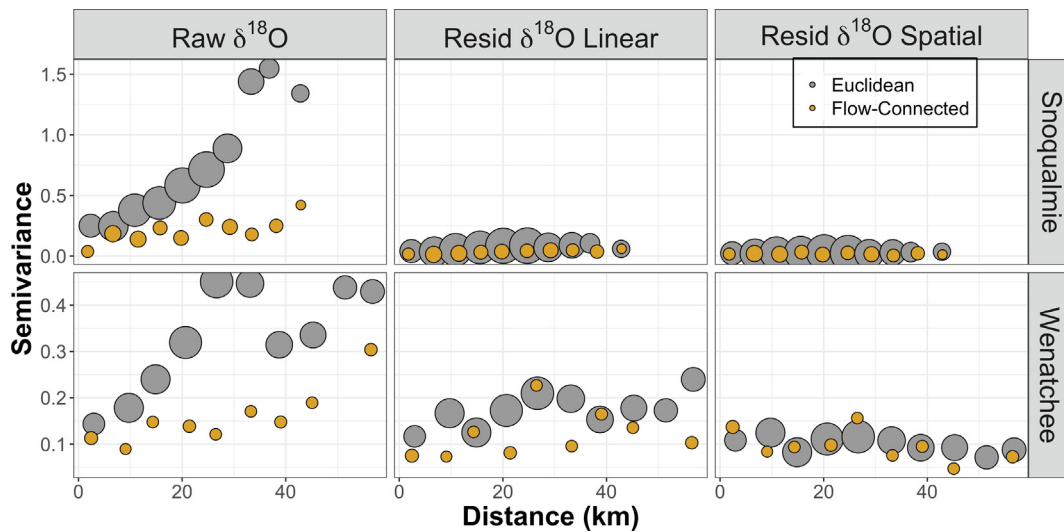


Fig. 4. Semivariograms for raw $\delta^{18}\text{O}$ values, residual $\delta^{18}\text{O}$ values from the best-fit linear models, and residual $\delta^{18}\text{O}$ values from the best-fit SSNNMs for the Snoqualmie and Wenatchee basins. Circles are proportional to the number of sites used to estimate each bin value.

and move eastward. Continued rainout produces isotopically-depleted precipitation at higher elevations, with the most depleted precipitation found at the crest. Close proximity to the Pacific Ocean exacerbates the rainout process. As the warm, wet air mass travels up the Cascade and Alaskan Coast Mountains, it experiences orographic lifting and adiabatic cooling, resulting in increased precipitation and the observed elevation trends. Similar to most other studies globally, our observed $\delta^{18}\text{O}$ -MWE relationship is close to linear over the sampled elevation range for windward basins (Poage and Chamberlain, 2001). The combination of processes dominantly responsible for isotopic distillation during rainout behave linearly over much of the world; however, basin specific processes such as mixing of baseflow sources from differential geologies may contribute to differences in $\delta^{18}\text{O}$ -MWE slopes and proportion of isotopic variation explained by MWE across basins.

Several studies have found global average isotopic-elevation relationships, or lapse rates, for precipitation, snow, and river water between -2.1‰ km^{-1} and 2.9‰ km^{-1} , except at latitudes greater than 70° where isotopic lapse rates are higher (Poage and Chamberlain, 2001; Bowen and Wilkinson, 2002; Dutton et al., 2005). In our study, the Snoqualmie and Green basin $\delta^{18}\text{O}$ -MWE slopes fall within this range ($-2.5 \pm 0.13\text{‰ km}^{-1}$ and $-2.2 \pm 0.20\text{‰ km}^{-1}$, respectively). The similar $\delta^{18}\text{O}$ -MWE slopes of the Green and Snoqualmie Rivers are likely due to the close geographic proximity of the basins and similar orientation with respect to incoming coastal weather. Additionally, MWE

explains most of the variation in isotope ratios for the Snoqualmie and Green Rivers, indicating that elevation-induced rainout is the greatest control on $\delta^{18}\text{O}$ values. The higher $\delta^{18}\text{O}$ -MWE slope of the Skagit River is surprising, given its close proximity to the Green and Snoqualmie basins, but this basin has unique attributes discussed in the next section. Our observed $\delta^{18}\text{O}$ -MWE slope for Cowee Creek was lower ($-1.7 \pm 0.28\text{‰ km}^{-1}$) than windward Washington basins even though MWE was the only significant driver. However, Cowee basin is small and glaciated and samples were collected over several months. This is further discussed in the next section. Even though MWE was a strong driver of isotopic variance, each windward basin responded uniquely, reiterating the importance of basin specific isoscapes.

We did not observe a large $\delta^{18}\text{O}$ -MWE slope in the Wenatchee basin, which is located on the leeward side of the Cascade Range. For leeward basins, if precipitation results from continued rainout of air masses as they traverse topographic barriers, then continued Rayleigh distillation on the leeward slope should produce an inverse relationship with altitude. Although less prevalent in the literature than windward, orographically induced rainout (Poage and Chamberlain, 2001), inverse or ambiguous $\delta^{18}\text{O}$ -elevation relationships have been reported from leeward slopes in the Sierra Nevada (Friedman and Smith, 1970) and the Canadian Rockies (Grasby and Lepitzki, 2002; Moran et al., 2007) for precipitation isotopes, and from the Oregon Coast Range for stream water isotopes (Brooks et al., 2012; Nickolas et al., 2017). Potential

Table 4

Model fit statistics from SSNNMs in the Snoqualmie and Wenatchee basins. Variance component values are the percentage of variance explained by fixed effects (covariates) and spatial error. Models in bold were selected as the best fit models.

Basin	Model	Covariate	Covariate Coefficient (SE)	RMSPE	AIC	R ²	Variance Component	
							Fixed effects (%)	Spatial error (%)
Snoqualmie	Nugget	MWE	-0.0025 (0.00013)	0.26	25.80	0.90	90	-
	Tail-up	MWE	-0.0026 (0.00015)	0.16	-5.97	0.96	87	9
	Euclid	MWE	-0.0025 (0.00017)	0.23	19.35	0.89	83	6
	Euclid + Tail-up	MWE	-0.0026 (0.00019)	0.17	-4.18	0.96	81	15
Wenatchee	Nugget	Longitude	-2.99 (0.44)	0.42	61.07	0.47	47	-
		MWE	-0.0016 (0.00034)					
	Tail-up	Longitude	-3.24 (0.52)	0.37	53.29	0.61	45	16
		MWE	-0.0016 (0.00037)					
	Euclid	Longitude	-3.22 (0.58)	0.33	51.24	0.67	42	24
		MWE	-0.0013 (0.00033)					
	Euclid + Tail-up	Longitude	-3.73 (0.62)	0.31	51.67	0.71	45	26
	MWE	-0.0015 (0.00034)						

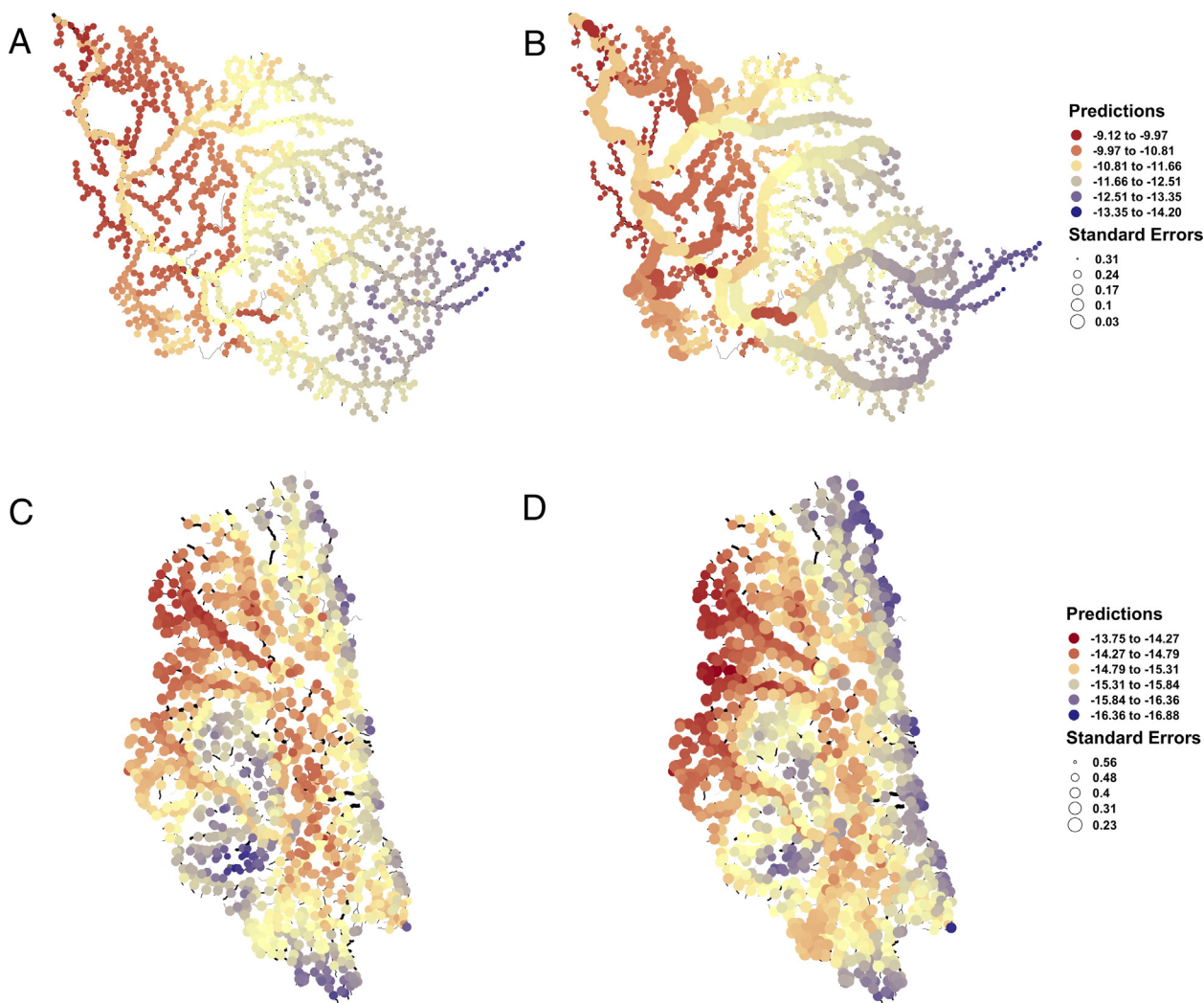


Fig. 5. Isoscapes from the Snoqualmie best-fit linear model (A), Snoqualmie best-fit SSNM (B), Wenatchee best-fit linear model (C), and Wenatchee best-fit SSNM (D). Colors represent predicted $\delta^{18}\text{O}$ values and the size of each point is inversely proportional to the prediction standard error.

reasons for the ambiguous $\delta^{18}\text{O}$ -MWE relationship in the Wenatchee basin are threefold. First, the amount of precipitation falling in the Wenatchee basin is lower than in west side basins (e.g. Snoqualmie MAP is 2435 mm/year and Wenatchee MAP is 1210 mm/year). Within this drier climate, local evaporation of surface water could add to the atmospheric vapor or subcloud evaporation could be influential, which

would negate isotope depletion from the rainout effect. Previous studies have documented this dampened rainout effect (Ingraham and Taylor, 1991; Guan et al., 2009; Wassenaar et al., 2009; Bershaw et al., 2012). However, we did not see the changes in d-excess expected if subcloud evaporation were significant in the Wenatchee basin. Second, although the Wenatchee samples show no systematic relationship with MWE

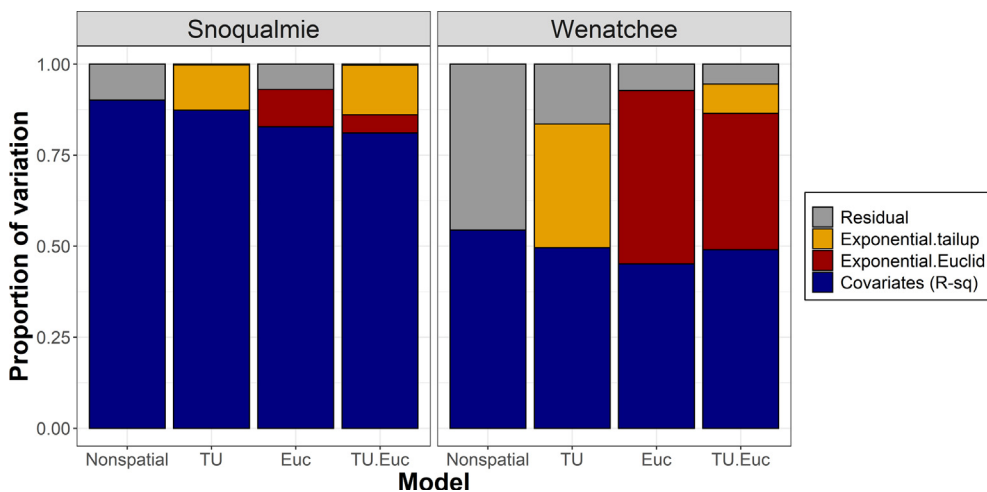


Fig. 6. Variance decomposition into the proportion of variation explained by covariates (blue), tail-up covariance structure (yellow), Euclidean covariance structure (red), and the nugget (gray) for each of the SSNMs (categories on the x-axis) in the Snoqualmie and Wenatchee basins. TU = tail-up; Euc = Euclidean; TU.Euc = tail-up and Euclidean. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

alone, when longitude, which is a proxy for distance inland, and MWE are included together in the best-fit model, a $\delta^{18}\text{O}$ -MWE slope similar to windward basins emerges, although longitude was still the most important variable within the model. The Wenatchee basin is oriented north to south and shares a long border with the Cascade crest (Fig. 1). Consequently, the heaviest precipitation occurs near the crest. As a vapor cloud moves eastward along the typical storm trajectory, precipitation becomes more depleted as a result of rainout. Rainout with increasing distance from the Pacific Coast may counteract the less pronounced elevation gradient. Lastly, turbulent atmospheric mixing of air masses as they are forced up and over the Cascade crest may contribute to the lack of an observable $\delta^{18}\text{O}$ -MWE slope (Moran et al., 2007). More research is needed into leeward basins to distinguish among these three potential factors.

4.2. Other drivers of observed isotope patterns

The Skagit basin was unique among the windward basins in that the best-fit model included MAP, watershed area, and aquifer permeability as covariates in addition to MWE. Orientation with respect to storm path alignment and topographic features of each basin likely drive differences in the strength and slope of river $\delta^{18}\text{O}$ -MWE slopes observed in windward basins and resulted in the inclusion of MAP in the Skagit best-fit model (Scheihing et al., 2018). The Green and Snoqualmie Rivers flow northwest. The Skagit River generally flows west; however, the largest tributary to the Skagit, the Sauk, flows northwest (Fig. 1; Fig. S1). Due to the rain-shadowing effects of Mt. Rainier and the Olympic mountains, southwestern Puget Sound watersheds like the Green and Snoqualmie tend to receive maximum precipitation during westerly air flow, whereas watersheds in the northwest Puget Sound, like the Skagit, tend to receive maximum precipitation during west-southwesterly air flow (Neiman et al., 2011; Siler et al., 2013). As a result, precipitation and elevation gradients largely align in the Green and Snoqualmie basins, with the greatest amount of precipitation occurring at high elevations leading to strong covariation (Fig. 3). In contrast, the greatest amount of precipitation in the Skagit basin occurs at mid elevations on the western side of the basin, including in headwaters of the Sauk and Baker Rivers (Fig. S1). East of the mainstem Skagit dams, at some of the highest elevations in the basin, precipitation amount declines substantially due to a rain shadow effect produced by the high peaks of the Skagit Crest within the basin (Fig. S1). Storms approaching the Skagit basin on a west-southwesterly track reach the Sauk basin first as they move inland. As they progress along their trajectory, continued rainout results in progressively more isotopically depleted precipitation. The influence of complex precipitation patterns in the Skagit basin was reflected in our data. Samples collected from the Sauk basin were systematically more isotopically enriched than samples collected from the upper Skagit basin, even at identical elevations. Additionally, in our best-fit model, MAP was positively related to $\delta^{18}\text{O}$ values, indicating that in areas of high MAP isotope ratios were more enriched. High MAP at mid elevations likely contributes to the high $\delta^{18}\text{O}$ -MWE slope observed in the Skagit basin.

Basin attributes not examined within our modeling framework may influence isotope ratios. Within the Skagit River, mainstem samples displayed the lowest isotope ratios, likely indicating that the mainstem of the Skagit is fed by higher elevation source water than small tributaries (Fig. 2). The negative relationship between watershed area and $\delta^{18}\text{O}$ values in the Skagit best-fit model reflects this, indicating that in large watersheds isotope ratios were more depleted. Glaciation in the Skagit River points to the importance of high elevation glacial and snowpack melt as a significant source of summer baseflow. Riedel and Larrabee (2016) found that surface melt from glaciers contributes 6–12% of the Skagit River's total summer runoff, and roughly twice that fraction in August and September. This same study also noted that glacial meltwater is concentrated in the tributaries Thunder Creek, White Chuck River, Suiattle River, Baker River, and Cascade River (Fig.

S1). Our Skagit River water samples showed $\delta^{18}\text{O}$ values below the average $\delta^{18}\text{O}$ -MWE regression line for the outlets of the White Chuck and Suiattle Rivers and isotope ratios above the average $\delta^{18}\text{O}$ -MWE regression line for the Baker and Cascade River outlets. We would expect samples to fall below the line if a greater proportion of flow originated from high-elevation glacial meltwater. The presence of glacial meltwater and snowmelt may have skewed the high elevation watersheds to lower isotopic ratios and may have contributed to the high $\delta^{18}\text{O}$ -MWE slope observed in the Skagit basin.

Although the Cowee Creek basin is heavily glaciated, we did not observe the same pattern of highly depleted mainstem isotope ratios present in the Skagit basin and watershed area was not included in our best-fit model. This was surprising, as previous studies have found seasonal patterns in $\delta^{18}\text{O}$ at the outflow of Cowee Creek that are consistent with an increase in the proportion of streamflow derived from $\delta^{18}\text{O}$ -depleted snow and glacial melt in higher elevation watersheds from late May into August (Fellman et al., 2014; Fellman et al., 2015). Fellman et al. (2015) found an average $\delta^{18}\text{O}$ ratio of -14.5‰ at the outflow of Cowee Creek across summer months (May – August) with $\delta^{18}\text{O}$ ratios below -15.0‰ through most of August, reflecting the contribution of glacial meltwater (average $\delta^{18}\text{O} = -16.4\text{‰}$) as the winter snowpack is typically ablated by early summer. At the lowest site on Cowee Creek in our study, samples collected in late May already had values (-15.5‰) that were as low as those measured in late August during the Fellman et al. (2015) study. The weak $\delta^{18}\text{O}$ -MWE relationship in Cowee Creek could be because high elevation, glacial sources of water dominated the flow in most tributaries sampled during our study. Higher resolution temporal sampling of the area is necessary to parse these mechanisms.

Within the Snoqualmie and Green basins, all water isotope samples fell upon a similar MWE gradient, regardless of whether it was a small tributary, or mainstem samples that aggregate the entire basin (Fig. 2). The isotopic composition of river water samples is determined by water isotopes in precipitation infiltrating into mountain blocks. The subsequent stream water is a mixture of groundwater baseflows with different transit times. The tight $\delta^{18}\text{O}$ -MWE coupling suggests summer baseflow derives from inputs more evenly dispersed throughout the basin, potentially because of shallow groundwater influx (i.e., as opposed to deep groundwater flowpaths or snowmelt sources). The isotopic composition of shallow groundwater does not deviate significantly from the mean weighted annual composition of precipitation in temperate climates in areas without seasonal or spatial bias in recharge (Clark and Fritz, 1997; Bowen et al., 2011). In the Snoqualmie and Green basins, nearly all precipitation falls within the winter months, and previous studies have not found significant seasonal differences in precipitation isotope ratios in the Pacific Northwestern USA (Brooks et al., 2012). Several studies find similar patterns for summer baseflow (Yeh et al., 2014; Singh et al., 2016; Rautio and Korkka-Niemi, 2015). In contrast, Brooks et al. (2012) found that the mainstem Willamette River, and outlets of other large rivers feeding the Willamette had isotopic values that were lower than the predicted elevation gradient relationship estimated from small watersheds, which we also found in the Skagit River. They interpreted this difference as a bias towards high elevation water sources dominating the flow within the river, likely due to deep groundwater flowpaths within the Oregon High Cascades. This suggests that the Green and Snoqualmie Rivers are much less dependent on high elevation snowmelt for summer baseflow as compared to the Cascade rivers in Oregon, and the Skagit River. Future studies should more explicitly consider the geologic context of each basin in order to understand the interaction between potentially complex ground and surface water flowpaths.

Dams, reservoirs, and lakes are pervasive across our study basins and have the potential to alter water storage and transport, thus impacting our interpretation of isotope values below these structures. In our data, we found small differences when examining isotope ratios above and below the Howard Hansen Reservoir and Lake Wenatchee.

The Howard Hansen Reservoir on the Green River and the Tolt Reservoir, a similar hydropower structure in the Snoqualmie River, are operated for flood control in the winter, flow augmentation in the summer, and provide drinking water year-round. The reservoirs fill in the late winter and spring, potentially holding back winter precipitation and high elevation snowmelt and releasing it during summer low flow. However, in our data, isotope ratios of water sampled above the Howard Hansen Reservoir ($\delta^{18}\text{O} = -11.92\text{‰}$ and $d\text{-excess} = 10.33$) were only slightly more depleted than those sampled at the outflow ($\delta^{18}\text{O} = -11.03\text{‰}$ and $d\text{-excess} = 7.24$). Conversely, isotope ratios of water sampled at the Lake Wenatchee outflow ($\delta^{18}\text{O} = -15.32\text{‰}$ and $d\text{-excess} = 11.29$) were more depleted than ratios from both the inflowing Little Wenatchee ($\delta^{18}\text{O} = -14.09\text{‰}$ and $d\text{-excess} = 11.47$) and White Rivers ($\delta^{18}\text{O} = -14.94\text{‰}$ and $d\text{-excess} = 10.16$), which join together to form Lake Wenatchee. The isotopic signature of Lake Wenatchee likely reflects the long-term average of river water input which may be more depleted than isotope ratios of September river flows due to a large influx high-elevation snowmelt in Spring. Previous studies have found muted temporal isotopic variation below artificial impoundments and natural lakes, reflecting extended retention times and elevated river water mixing (Kendall and Coplen, 2001; Wassenaar et al., 2011; Brooks et al., 2012; Trinh et al., 2017). Although the retention time of water within impoundments is an important consideration when interpreting downstream isotope ratios, our results illustrate that despite the presence of extensive hydrologic modification within our basins, isotopes can preserve signals of mainstem source water dynamics.

4.3. In-stream and landscape processes shape isotope values

Ours is one of the first studies to use a class of geostatistical models, Spatial Stream Network Models (SSNM), to model stream water isotope ratios (but see Segura et al., 2019). The SSNM approach also allowed us to model spatial correlation explicitly, taking advantage of the unique topology of stream networks. Similar to studies of other ecological phenomena (Isaak et al., 2014; Brennan et al., 2016; Filipe et al., 2017), water isotopic ratios on stream networks showed substantial autocorrelation and predictive accuracy was improved by spatial models compared to non-spatial models (Bowen et al., 2011; Table 4; Fig. 5). Inherent covariation in river basins can hinder statistical efforts to identify mechanistic links between landscape gradients and features of aquatic ecosystems and result in negative consequences such as inflated goodness-of-fit metrics and inflated error terms on key coefficients that may undermine model building (Lucero et al., 2011). Linear regression assumes that each measurement is independent from others and contains non-redundant information. If measurements are spatially autocorrelated, standard error estimates will be artificially small, tests of statistical significance will be too liberal, and estimates of R^2 will be too large (Dale and Fortin, 2009; Isaak et al., 2014). SSNMs explicitly model spatial autocorrelation and therefore provide better estimates of the effect of landscape covariates on isotope ratios.

For the Snoqualmie River, incorporating an autocovariance function accounting for the branching river network structure resulted in modest improvements to model performance. Most variation in $\delta^{18}\text{O}$ values was already explained by MWE, which is spatially-structured, resulting in little residual variation or autocorrelation (Table 4; Fig. 4); however, the best-fit model did include a tail-up component, illustrating the importance of passive longitudinal transport of water isotopes along stream networks. The dominance of MWE in the model likely occurs in part due to the structure of landscape covariates in the Snoqualmie River. Most landscape predictors were highly correlated with one another, and the influence on isotope ratios aligned in the same direction (e.g. MWE and longitude were positively correlated). In basins such as the Snoqualmie, where landscape descriptors covary strongly and the subsequent relationship between water isotopes and landscape descriptors is simple, spatial models only slightly improve our

understanding of river water isoscapes.

In the Wenatchee River, on the other hand, incorporating spatial structure in Euclidean space dramatically improved model performance. The role of covariates in the Wenatchee models were limited, with fixed-effects explaining only 47% of variation in non-spatial models and 45–49% of variation in spatial models. Approximately two-thirds of the variance in the best-fit SSNM could be attributed to fixed effects and one-third to spatial structure in the Wenatchee model residuals (Table 4). The strong Euclidean component in the Wenatchee best-fit model, illustrated by the large proportion of variation explained in Fig. 6, suggests that linear relationships with longitude and MWE were insufficient to describe landscape processes influencing stream water isotope values (McGuire et al., 2014; Zimmerman and Ver Hoef, 2017). Landscape features affecting isotope ratios could include local geological features associated with groundwater upwelling, beyond the general descriptor of aquifer permeability. Previous studies have shown that geologic features, such as porous lava flows, sandstone, and earthflows as well as hillslope characteristics (e.g. slope and roughness) can influence baseflow isotopic composition (Nickolas et al., 2017; Singh et al., 2016; Segura et al., 2019). Furthermore, in the Wenatchee basin landscape covariates display little correlation with one another and often align in opposing directions (e.g. MWE and longitude were negatively correlated). These competing forces likely work against each other to create a complex isotopic landscape that is difficult to model using standard linear models. In basins such as the Wenatchee, where the influence of covariates on isotope signature is weak and covariates display little correlation with one another, including spatial structure provides insight about the presence of key structuring processes that would be unaccounted for in covariate selection.

4.4. Study limitations

As in any study, our ability to generalize results and make inferences about other watersheds is limited by our sampling design, dataset, and the models considered. In this study, water sample collection locations were limited to areas easily accessed by roads, and collection of samples across a large portion of the Upper Skagit basin into Canada did not occur. Increased spatial coverage would improve predictions of drivers of isotope ratios and allow us to consider a greater number of predictors in our analyses. Additionally, although we considered five basins across a single sampling season (summer low flow, 2017), only one basin was located on the leeward side of mountains.

Although our snapshot in time provides a picture of drivers of the isotope ratios during baseflow, it does not give insight into temporal variation in drivers of isotope signature. Several studies have found differences in drivers of isotope patterns across time (Liu et al., 2004; Payn et al., 2012), and therefore our results should not be generalized to other seasons or years. It should also be noted that while sampling of the Washington basins took place over no more than two weeks, Cowee Creek was sampled over the course of three months due to logistical challenges in accessing its remote sites by aircraft. Lastly, it is important to recognize that SSNMs are an extension of linear regression and both methods predict at unsampled locations using smoothed averages. Therefore, when we generated isoscapes features not included in our sampling design (e.g. local point sources of groundwater) were not included.

4.5. Management implications

Our study summarizes current knowledge of basin factors driving variability in surface-water isotope ratios and provides a foundation for future monitoring work as well as for leveraging the isotopic signature of surface water in river basins and fisheries management. We observed a strong MWE gradient across all rivers draining windward basins. Furthermore, in the Snoqualmie and Green basins, MWE was highly correlated with other parameters known to drive isotopic ratios. In

these basins, simple MWE-based relationships permit easy interpretation of isotope data. Future work could harness the information they contain for river basin management, such as predicting the contribution of climate sensitive, high-elevation snowmelt to summer baseflow.

Changes to climate and hydrology are expected across the Pacific Northwest. Climate models predict substantial winter warming, leading to increased precipitation falling as rain and decreased snowpack, translating to increased winter river runoff and reduced summer baseflow discharge (Elsner et al., 2010). Measuring water stable isotopes would be a simple method for monitoring these changes over time.

Impacts of global change will be heterogeneous both within river basins and across the region, and understanding how high elevation water contributes to stream discharge across basins will be a valuable tool (Steel et al., 2018). For example, all basins in this study host populations of ESA-listed salmonids, which are limited by high summer temperatures and low flows. Resource managers could easily access and plot covariate data such as MWE, longitude, and MAP to identify other basins in which these covariates are correlated, suggesting an easy to interpret isotope-MWE relationship. The same simple isotope-MWE relationship could also be applied to other midlatitude mountain ranges with prevailing westerly winds and a north-south orientation, such as the Sierra Nevada, the southern Alps, and the southern Andes (Siler et al., 2013).

For Cowee Creek and the Skagit River, interpretation of water isotope monitoring within the basins becomes more challenging. In the Cowee basin the $\delta^{18}\text{O}$ -MWE slope was much lower than expected. Temporal isotopic variance at the outlet may indicate the dominance of glacial sources over time, and we sampled over a period of high glacial output; however, additional sampling over a more condensed time period would be necessary for accurate interpretation. In the Skagit Basin, interpretation of isotopic variation is difficult, as the orographic rainout process becomes complicated by the complex topography and sampling in the upper basin was limited. In basins with similar accessibility issues, accurate isoscapes could help in monitoring the proportion of streamflow derived from glacial and snowmelt and relieve some of the burden of expensive field campaigns.

Our results provide guidance for future monitoring or research on stable isotopes in surface waters. In the basins described above, with expected simple and strong relationships between MWE and isotope values, fewer samples may be necessary to create customized and effective models or management tools. In larger basins or in areas where complex local atmospheric or hydrologic processes occur, greater temporal and spatial sampling may be necessary in order to partition water sources in ways that are both isotopically distinct and environmentally relevant.

Our study also provides guidance for understanding the types, advantages, and disadvantages of methods for stream isoscape generation. We found that in basins where correlation between covariates and isotope ratios is weak, spatial models can improve predictions and demonstrate evidence of landscape level patterns not captured by non-spatial models. We also found that in basins where covariates known to influence isotope signature correlate strongly with one another and are themselves highly spatially structured, spatial models do little to improve predictions. The choice to use spatial or non-spatial models should be determined by data availability and the relevant questions. Our results provide insight as to where the additional effort to build these models may be a particularly good investment.

5. Conclusions

In this study we demonstrated that elevation was the dominant predictor of isotope ratios across five Pacific Northwest basins, but the importance of elevation varied between basins and depended on geographic location, landscape attribute configuration, and basin size. Elevation explained a range of isotopic variation in surface water across

the five basins, but the nature of this relationship ($\delta^{18}\text{O}$ -MWE slope, other covariates) was different even between adjacent basins. Incorporating spatial structure through the SSNM framework captured aspects of water isotopic variation even in basins where variance explained by covariates was high. Spatial structure was particularly important to consider in the Wenatchee, our leeward side basin, where covariates explained the least of the isotopic variation. Our results illustrate that basin-specific models that include spatial structure improve accuracy of surface-water isoscapes for understanding hydrologic function, interpreting source contributions downstream, or assisting in basin management.

CRedit authorship contribution statement

L.M. McGill: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **E.A. Steel:** Conceptualization, Methodology, Writing - review & editing, Supervision. **J.R. Brooks:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision. **R.T Edwards:** Investigation, Writing - review & editing. **A.H. Fullerton:** Software, Investigation, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2020.124610>.

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