Spatial and temporal variability in the isotope signatures of two California streams

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ENVS 190

15 December 2016

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Abstract

Stable isotopes of hydrogen and oxygen are becoming increasingly useful for many applications in addition to hydrological studies. A need exists for spatial predictions of the isotope signatures of surface waters, though making predictions on finer scales is complicated by many factors. We monitored the stable isotope abundance ($\delta^2$H and $\delta^{18}$O) and electrical conductivity of water in two tributaries of the Sacramento-San Joaquin River Delta, the American River and Putah Creek. Each stream has spatial differences in the distance inland and elevation of its source as well as temporal differences in the phase and timing of precipitation that supplies its source. We sampled similar post dam reaches of each stream to determine the scale at which variability in the water’s isotope signature occurs, comparing within reach variability (fine scale) to between reach variability (coarse scale) over space and time.

Substantial spatial differences were observed between streams with $\delta^2$H, $\delta^{18}$O, and electrical conductivity consistently higher in Putah Creek. Overall seasonal differences in $\delta^2$H and $\delta^{18}$O were not observed in Putah Creek, though wet season rain events decreased average $\delta^2$H and $\delta^{18}$O and increased variability. The American River was most affected by season, with decreased $\delta^2$H and $\delta^{18}$O during the dry season as its source shifts from lower elevation rain to melting snowpack. Putah Creek’s low seasonal variability allows representative samples to be collected year round as long as storms are avoided, and the seasonal shift in the American river should be adequately captured by sampling at even intervals throughout the year. The seasonal pattern of the American River’s isotope signature reveals possibilities for monitoring water resources, as the Sierra Nevada snowpack is an important component of California’s water storage.
Introduction

The development of water system models using light stable isotopes has become increasingly common in hydrological studies (Pereira et al. 2014, Litt et al. 2015, Candel et al. 2016). Stable isotopes provide clues to source dynamics of surface and ground waters and the processes that impact water quality, in addition to broader applications in the fields of forensics and ecology. Accurately predicting changes in a water system’s source dynamics and water quality will become increasingly useful as climate change impacts water sources by altering average temperatures, snowpack, and the timing and amount of precipitation. The projected diminishing Sierra Nevada snowpack will narrow the gap between water supply and water demand in California (Pagan et al. 2016), as much of California’s water storage is dependent on delayed release of melting snowpack during its dry season. Models of California’s water resources using light stable isotopes will provide much of the information necessary to adapt to climate induced changes in water sources.

Isotope Hydrology

Isotopes are variants of an element with unique mass resulting from a different number of neutrons in the nucleus of the atoms of that element. Isotopes are notated by their mass, where $^A_X$ is an element with mass $A$. The elements that comprise the water molecule, hydrogen and oxygen, have a number of stable (non-radioactive) isotopes. The most abundant isotope of hydrogen, $^1$H, contains no neutrons and has an atomic mass of 1. Hydrogen has one stable heavy isotope, $^2$H, also called deuterium. Oxygen has a number of light and heavy isotopes in addition to its most abundant isotope, $^{16}$O. However, only two heavy isotopes, $^{17}$O and $^{18}$O, are abundant enough to be useful as tracers (Gat 2010).
Water molecules contain different combinations of the stable isotopes of hydrogen and oxygen. These different combinations have different physical and chemical properties and behave differently in chemical reactions because of the difference in mass that results from their isotopic composition. As a result, the stable isotopes of hydrogen and oxygen are unequally distributed as water undergoes physical and chemical processes throughout the hydrologic cycle. Processes that result in changes in isotope abundance are called fractionation processes, as isotopes are partitioned, or fractionated, into different abundances among different phases or chemical species.

Fractionation results in either increasing or decreasing the concentration of stable isotopes in a water body, and the results of fractionation are described in terms of depletion and enrichment of the uncommon stable isotopes. Stable isotopes are measured in precipitation, surface, and groundwater by measuring the ratio (R) of uncommon to common isotopes in a sample compared to the ratio in a standard that represents the average stable isotope abundance of freshwater. The ratios are converted to delta (δ) values to make comparisons in units of per mil (‰). \[ \delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \] (Bowen et al. 2007). Negative δ values are depleted and positive δ values are enriched relative to the standard.

Because there are limited combinations of heavy and common isotopes that form the water molecule, and only a few of these combinations commonly occur, δ^{18}O and δ^2H in precipitation are covariant. The relationship between the abundances of the isotopes in precipitation is depicted by the global meteoric water line (GMWL) (Craig 1961, Rozanski et al. 1993). There is a linear relationship between hydrogen and oxygen isotopes in precipitation, with global average isotope abundances falling along the line \( \delta^2H = 8 \delta^{18}O + 10\% \). Changes in
latitude, altitude, and distance inland on continents will result in precipitation that is enriched or depleted in stable isotopes, but will maintain the linear relationship between δ²H and δ¹⁸O. Post precipitation processes can alter this relationship by disproportionately enriching or depleting ²H or ¹⁸O. Surface water in arid regions experiences more evaporation and will deviate from the GMWL with decreased slope (Gat 2010). ²H and ¹⁸O are enriched unevenly during surface evaporation because of the difference in mass resulting from ¹⁸O in water molecules. As a result, surface water becomes less enriched in ²H than would be predicted by the GMWL. Deviations from the GMWL in surface waters can also occur as a result of the relative mass difference between heavy and light isotopes of hydrogen and oxygen. Generally, light isotopes form weaker chemical bonds and are more easily utilized in chemical reactions, such as photosynthesis in plants or reactions with minerals. This can shift the line by affecting oxygen and hydrogen isotope abundance.

Fractionation processes leave a signature, or evidence that the process occurred in the altered stable isotope abundance. The altitude effect, latitude effect, and continental effect act in combination to change the stable isotope abundance in precipitation (Coplen et al. 1999). ²H and ¹⁸O abundance decreases with increasing altitude and latitude as a result of increasing rainout. Precipitation of water in the liquid phase favors ²H and ¹⁸O, resulting in water vapor becoming increasingly depleted as it moves away from the equator and releases moisture. The continental effect is related to rainout but occurs on a smaller scale. Water vapor becomes more depleted as it moves inland from the ocean as a result of orographic lifting. ²H and ¹⁸O are lost in the rain events nearer to the coast and the depleted moisture moves inland containing lower concentrations of ²H and ¹⁸O. As a result, coastal precipitation is enriched in ²H and ¹⁸O and becomes increasingly depleted as it moves inland.
The isotope signature of surface water is evidence of all the processes that acted upon the water, from the vapor that formed in the ocean to precipitation that falls inland, and all the post precipitation processes that may have acted upon it as surface and groundwater. This provides useful information for hydrological studies as well as many other fields.

Applications of Isotope Hydrology

Stable isotopes are used in hydrological studies as a simple and cost effective way to measure flows, mass balance, and source of surface and ground waters. Water samples for isotopes are easily collected and stored, and stable isotope analysis can be mostly automated. Because of this, isotopes are often used in conjunction with other water quality and flow measurements to study water systems. Isotopes have been used to create models of evaporation in surface reservoirs to quantify water balance without the need to continuously monitor flows (Gibson et al. 1993). Isotopes can also be used to identify temporal changes in the sources of water systems that may occur because of seasonal differences in the elevation of the source and the type of precipitation at the source (Brooks et al. 2012). The isotope signature of surface water reflects the changes in source from lower elevation rain and groundwater inflow to higher elevation snowmelt through seasonal changes in temperature and precipitation.

Farther afield from the more direct applications of isotope hydrology, isotopes can be used in forensics and ecology as organisms retain the isotope signature of the water they consume in their tissues. Isotopes can be used to study animal diets, trophic structure, and nutrient transfers in ecological studies (West et al. 2006). Forensic applications include determining the geographic origin of meat (Camin et al. 2016), cheese (Necemer et al. 2016), wine (Roßmann et al. 1999), and determining the residence of individuals based on the isotope
signature of tap water in residential areas and the isotope signature preserved in human hair (Mant et al. 2016).

Many applications of isotope hydrology depend on data collected to establish the typical isotope signature of surface water and precipitation in a geographic area to make a comparison. Spatial data of stable isotopes have been used to create isoscapes, spatial predictions of isotope abundance of surface and municipal water as well as precipitation. Several isoscapes have been created for different regions of the United States at various resolutions, although certain areas remain under represented. Bowen et al. (2007) mapped stable isotopes of tap water on a national scale, finding that the isotope signature of tap water was associated with the isotope signature of local precipitation throughout most of the United States. The coarse resolution of this study, the contiguous United States, limits its application to regional and watershed scale issues. Isoscapes are more difficult to measure at a finer resolution, as spatial and temporal changes within water bodies complicate sampling. Certain areas of the country are more difficult to measure because of local geography, climate, and water system infrastructure, such as reservoirs, canals, and groundwater pumping. The arid West, and California in particular, contains many of the features that confound collecting spatial data of stable isotopes at fine resolutions.

*California Isoscapes*

California’s geography and climate create conditions that complicate measuring isotopes in surface water. The north to south orientation of the Coast Range and the Sierra Nevada result in strong altitude and continental effects as water vapor moves inland from the Pacific Ocean, and the Mediterranean climate creates the potential for strong seasonal variability in isotope abundance. A complex water system has been developed to cope with the long dry season, and most surface water bodies contain water that originated far from the point of use. Surface water
is mixed with wastewater, which results from municipal water that is pumped from groundwater or surface water that is often conveyed great distances through canals. All of these factors complicate finding an isotope signature of surface waters, as water bodies vary temporally and spatially in their stable isotope abundance.

To begin to characterize the variability in stable isotope abundance of California streams, we selected a reach from two streams, Putah Creek and the American River, that have differences in their sources, such as elevation, distance inland, and the phase and timing of precipitation. The stream reaches are similar in that they are both post dam reaches of similar distance. Understanding the variability in stable isotope abundance in these stream reaches both temporally and spatially at coarse and fine resolutions will help us in future isoscape mapping projects.

Methods

Study Area

The American River and Putah Creek are both tributaries of the Sacramento-San Joaquin River Delta. The area has a Mediterranean climate, with hot, dry summers and cool, wet winters. The area surrounding Putah Creek consists of a mixture of oak woodland, agricultural land, and urban development. The land surrounding the reach of the American River sampled in this study consists almost entirely of urban development, though riparian forests are found adjacent to the river along much of the reach. Each stream contains a reservoir that impounds the flow upstream of the study area.

Although each stream flows through areas with similar climate and land use, their sources differ. The headwaters of Putah Creek are in the Mayacamas Mountains, part of California’s Coastal Range. The range’s highest point is Cobb Mountain, elevation 4721 feet. Precipitation
falls mostly as rain, and Putah Creek’s annual flow consists of a mixture of precipitation runoff and groundwater inflow from this area. The American River has three forks that originate in the Sierra Nevada mountains. The headwaters of these forks are located at elevations of 9000 feet and greater, where most precipitation falls as snow. The Sierra Nevada snowpack contributes to the American River’s flow during the dry season after it begins to melt in the spring.

**Experimental Design**

Five sample sites were selected along each stream reach, spanning 43 and 37 Km for the American River and Putah Creek, respectively (Table 1). Samples were collected within each reach five times during the wet and dry season to observe variation between the stream reaches (variation resulting from water source), variation along each stream reach (variation resulting from post precipitation processes) and seasonal variation. During the dry season, sampling dates were selected at even intervals of three weeks. During the wet season, sampling dates were planned around rain events to see how storms influenced isotope signatures.

Samples were collected at each site by wading into the stream to mid-stream or knee depth and rinsing the bottle several times with stream water before filling the bottle. At sites where wading was impossible or unsafe, a Van Dorn sampler was used. Water samples were collected and stored in 60mL glass bottles with airtight conical plastic lid liners. The bottles were filled completely and capped under water to prevent evaporation and exchange with water vapor in the air during storage.

**Data Analysis**

Stable isotopes were measured with a Los Gatos Research isotope analyzer. Quality control measures are built into the process the machine uses to analyze the samples. Each sample is analyzed over several runs. The machine monitors errors that may occur during each run,
flagging runs where errors may have occurred. The successful runs are averaged to obtain a result for each water sample. Precision within runs was within 0.3‰ for $\delta^2$H and within 0.1‰ for $\delta^{18}$O. Electrical conductivity was measured with a handheld meter from the remaining sample after the isotope analysis.

The averaged runs were used in repeated measures analysis of variance (ANOVA) to compare sites and dates (using Stata 14 software). Sites were compared with a repeated measures ANOVA. To compare dates, ANOVA blocked by site was used. Delta values were compared to electrical conductivity using a linear regression model for each stream reach.

Results

In the one hundred samples collected (fifty from each stream), $\delta^{18}$O values ranged from -11.24 to -2.40‰ and $\delta^2$H values ranged from -78.87 to -24.71‰. American River delta values fell along the GMWL ($R^2=0.924$, slope=9.107, $D$-excess=-22.5) but were clustered according to season (Figure 1). Putah Creek samples plotted along an evaporation line ($R^2=0.956$, slope=3.379, $D$-excess=-16.44), with samples collected on rainy days falling closer to the GMWL intersection.

Electrical conductivity of the samples ranged from 49 to 520 µS/cm. In the American River, electrical conductivity was positively correlated with $\delta^2$H values and $\delta^{18}$O values (Figure 2). Electrical conductivity was higher than expected at the Effie Yeaw site on two days during the dry season. In Putah Creek, there was no relationship between $\delta^2$H or $\delta^{18}$O and electrical conductivity ($p=0.5732$ and $p=0.5954$ for comparing slope to zero).

Spatial variability

Delta values and electrical conductivity values in Putah Creek were greater than the American River in both seasons (Figure 1, Figure 2). $\delta^2$H and $\delta^{18}$O were more variable among
sites in Putah Creek overall, with the greatest site variability after rain events (Figure 3). $\delta^2$H and $\delta^{18}$O variability among sites in the American River was low relative to Putah Creek in both seasons.

**Temporal variability**

Seasonal variation was stronger on the American River reach. Average delta values from dry season dates were significantly different from average wet season dates, with both greater $\delta^2$H and $\delta^{18}$O during the wet season (Figure 3). Delta values varied less by season in Putah Creek. Three of five wet season dates were not significantly different from the dry season dates in either $\delta^2$H or $\delta^{18}$O, though variability among sites within dates was greater during the wet season. Abrupt decreases in $\delta^2$H and $\delta^{18}$O occurred after rain storms (Figure 3).

**Discussion**

We observed substantial coarse scale differences between each stream reach. The American River delta values fell along the GMWL in two distinct clusters, one containing the dry season samples and the other containing the wet season samples. This indicates that equilibrium processes, such as rainout, altitude, and continental effects, are the dominant fractionation processes that influence the isotope signature of this reach of the American River. Putah Creek delta values fell along an evaporation line, with a decreased slope and D-excess relative to the GMWL. This indicates that non equilibrium processes, such as surface evaporation, have a greater effect on the isotope signature of Putah Creek than the American River. Each stream reach has unique conditions that result in spatial and temporal variability in isotope signatures.
Spatial variability

The overall difference in delta values between Putah Creek and the American River can be explained by each reach’s source location. Putah Creek’s source in the coastal mountains receives precipitation that is relatively enriched due to continental and altitude effects. The American River’s source is further inland and higher in elevation than Putah Creek, and therefore receives relatively depleted precipitation. This pattern of increasing depletion from west to east is well documented in precipitation (Ingraham and Taylor 1991, Friedman et al. 1992) and surface and groundwater (Ingram et al. 1996, DeCarvalho 2012) in California.

Variation in delta values among sites on the same date was greatest in Putah Creek in both the wet and dry season. This within reach spatial variation could be a result of Putah Creek’s relatively low flow. Surface and groundwater inflow during storms, wastewater discharge, and post precipitation isotope fractionation processes could have a greater effect on the average delta values of the stream water. The American River showed little variation between sites. This could be a result of its relatively greater flow, as the effects of stormwater inflow and fractionation processes are dampened by mixing with a greater amount of water than in Putah Creek. The American River also does not receive any municipal wastewater in the sampled reach, although it is unclear if this is responsible for some of the difference in variability between reaches because we do not know when wastewater was discharged into Putah Creek, or if it was discharged at all during the sampled dates.

Temporal variability

Both stream reaches were affected by changing seasons, but in different ways. The American River did not increase in within reach variability, instead average delta values shifted to a more enriched signature during the wet season overall. The American River’s source
alternates between high elevation inland snowpack during the dry season and lower elevation rainfall during the wet season. This results in a more depleted isotope signature during the dry season due to the altitude and continental effects. The effect of mixing in Folsom Lake, the reservoir upstream of the sampled reach of the American River, did not appear to dampen the seasonal fractionation effects. This could be explained by the low water level in the reservoir during the sampling period. However, Brooks et al. (2012) observed similar seasonal shifts in streams with high elevation sources even though some of the streams were dammed. The effect of mixing in reservoirs seems to cause a gradual change in isotope signature between seasons instead of a strong decrease during the spring as snow begins to melt in high elevation sources. We may have observed a more gradual decrease between the wet and dry season in the American River if we had collected samples continuously throughout the year.

There was little overall seasonal difference in the isotope signatures of Putah Creek samples. Putah Creek’s source is derived from low elevation rainfall near the coast. Rainfall during the wet season and groundwater inflow combined with water released from Lake Berryessa should have similar levels of isotope enrichment. Unlike the American River, there was no observed seasonal shift in source elevation. Additionally, mixing in the reservoir upstream of the sampled stream reach could dampen seasonal variability in precipitation. Despite the lack of overall seasonal change in isotope signature, within reach variability greatly increased during the wet season on rainy days.

Putah Creek sites varied the most during rain events with relatively more depleted delta values compared to other wet and dry season dates. During storms, the reach receives a greater amount of inflow from local precipitation. Local precipitation would be expected to be more depleted as the sampled reach is well inland of Putah Creek’s mountain source. Changes in
reservoir releases and increased storm and sanitary sewer discharges associated with storms further contribute to the potential for increased variability in both delta values and electrical conductivity (Ingraham and Taylor 1991).

The effect of increased local inflows to Putah Creek during rain events may explain why we found no relationship between electrical conductivity and isotope enrichment. A pattern of increasing EC downstream is consistent with within reach surface evaporation, which appears to occur in Putah Creek based on its evaporation line (Figure 1), though it is unclear if the evaporation line results from evaporation within the sampled reach of Putah Creek or upstream in Lake Berryessa. We did not observe isotope enrichment that would be expected to occur if surface evaporation were taking place. Rain events resulted in a more depleted isotope signature due to the increased inflows from local precipitation, though increased inflows may also increase electrical conductivity. Ingraham and Taylor (1991) found similar patterns of increased electrical conductivity during storms in the San Francisco Bay, as high electrical conductivity stormwater and wastewater from developed areas mixed with water in the bay. Storm flows in Putah Creek may have increased electrical conductivity and resulted in a depleted isotope signature. This confounds the association between increased electrical conductivity and isotope enrichment that we would expect from surface evaporation.

**Conclusion**

Based on the variability in delta values we observed, representative samples could be collected all year for both streams as long as sampling during certain conditions is avoided. The seasonal variation in the American River is best captured by sampling at intervals throughout the year because the delta values plot along the GMWL, shifting between depletion and enrichment.
The variability in Putah Creek could be captured by sampling at any time of the year outside of periods of increased flows due to storms or reservoir releases.

The results obtained should generally apply to other surface water bodies in California, and they highlight the differences between water bodies with high and low elevation sources and high and low flows. The seasonal shift in the American River’s isotope signature is particularly interesting, and has implications for future studies on source dynamics of other streams that originate in the Sierra Nevada. A better understanding of source dynamics could be useful for water supply monitoring as water storage in the Sierra Nevada snowpack becomes less reliable due to climate change.
Table 1. Location and description of sample sites on both stream reaches.

<table>
<thead>
<tr>
<th>Name</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Km from Dam</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>American River</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Negro Bar</td>
<td>38°40'56.2&quot;N</td>
<td>121°10'29.3&quot;W</td>
<td>3.2</td>
<td>Sampled near American River Trail foot bridge, located upriver of negro bar, deep water, high flow, infrequent foot traffic in sampled area, hike down to water</td>
</tr>
<tr>
<td>Sailor Bar</td>
<td>38°38'03.8&quot;N</td>
<td>121°13'51.4&quot;W</td>
<td>11.9</td>
<td>Riparian Riverside, boat launch, frequent foot traffic, sport fishing area, high water flow</td>
</tr>
<tr>
<td>Effie Yeaw</td>
<td>38°36'35.2&quot;N</td>
<td>121°18'24.9&quot;W</td>
<td>22.5</td>
<td>Nature Center in Sacramento. High flow area, frequent traffic, little vegetation, large gravel bed</td>
</tr>
<tr>
<td>Sacramento State</td>
<td>38°33'33.2&quot;N</td>
<td>121°24'47.1&quot;W</td>
<td>35.1</td>
<td>Sampled by city water pump. Frequent foot traffic, sampled in river, high flow, trail from Sacramento State</td>
</tr>
<tr>
<td>Jibboom Bridge</td>
<td>38°35'56.9&quot;N</td>
<td>121°30'21.9&quot;W</td>
<td>46.8</td>
<td>Bridge in Discovery Park. Frequent foot traffic, large canopy cover on banks, muddy sediment, sampled in river</td>
</tr>
<tr>
<td><strong>Putah Creek</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Putah Creek Fishing Access 2</td>
<td>38°30'56.59&quot;N</td>
<td>122°3'41.45&quot;W</td>
<td>4.0</td>
<td>Yolo County fishing access, infrequent foot traffic, fully shaded, narrow run, cobble-sized bed material, sampled just off bank</td>
</tr>
<tr>
<td>Winters Nature Park</td>
<td>38°31'14.6&quot;N</td>
<td>121°58'1.39&quot;W</td>
<td>15.8</td>
<td>City of Winters park, frequent foot traffic, some tree cover on south side, narrow run, gravel to small cobble-sized bed material, sampled close to mid-stream</td>
</tr>
<tr>
<td>Pedrick Road</td>
<td>38°31'36.47&quot;N</td>
<td>121°48'11.29&quot;W</td>
<td>31.7</td>
<td>UC Davis Riparian Reserve, infrequent foot traffic, narrow run, gravel-sized bed material, sampled close to mid-stream</td>
</tr>
<tr>
<td>Old Davis Road</td>
<td>38°31'1.58&quot;N</td>
<td>121°45'23.42&quot;W</td>
<td>36.2</td>
<td>UC Davis Riparian Reserve, frequent foot traffic, wide pool, tree cover on banks, fine sediment bed material, sampled from bank</td>
</tr>
<tr>
<td>Mace Road</td>
<td>38°38'8.03&quot;N</td>
<td>121°41'42.45&quot;W</td>
<td>41.7</td>
<td>City of Davis South Fork Preserve, infrequent foot traffic, right next to bridge, narrow run, fine sediment bed material (with some gravel and cobble), sampled from bank</td>
</tr>
</tbody>
</table>

Figure 1. $\delta^2$H as a function of $\delta^{18}$O for two California streams during wet (solid gray marker) and dry (open marker) seasons, compared to the global meteoric water line (solid). Triangles represent the American River and squares represent Putah Creek. Best fit lines for each season are shown as dashed lines.
Figure 2. $\delta^2$H and $\delta^{18}$O as a function of electrical conductivity in both stream reaches.
Figure 3. Mean (SD) $\delta^2$H and $\delta^{18}$O of all sites by date on each stream reach during wet (January-April) and dry (June-September) seasons. Points labeled with letters in common are not significantly different ($p > 0.05$).
References


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