Vegetation source water identification using isotopic and hydrometric observations from a subhumid mountain catchment

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Abstract
This study coupled long-term hydrometric and stable water isotope data to identify links between subsurface water storage and vegetation in a subhumid mountain catchment in Arizona, USA. Specific observations included catchment-scale hydrologic fluxes and soil water storage and stable water isotopes from stream water, soil water, groundwater, and sap water from Arizona pine (Pinus arizonica) and Douglas fir (Pseudotsuga menziesii) individuals. Here, we find that tightly bound soil water was sufficient to meet dry period vegetation water demand when the former was defined in terms of field capacity as opposed to a matric tension threshold. This water was a mixture of summer and winter precipitation that predominates in both shallow and deep soil waters, and contributed significantly to streamflow. We also identified a less common mobile water type that did not contribute significantly to streamflow and was related to infiltration during isotopically depleted precipitation events. Although each water type was used by both Arizona pine and Douglas fir vegetation, the second water type was dominant in Douglas fir sap water. Therefore, we conclude that Arizona pine and Douglas fir can occupy different ecohydrological niches at this subhumid mountain location. Further, a lack of isotopic distinction between tightly bound
INTRODUCTION

Mountainous catchments are often regarded as the “water towers for humanity” (Viviroli, Dürr, Messerli, Meybeck, & Weingartner, 2007) as they provide critical water and ecosystem services for increasingly arid regions downstream (Klein et al., 2019; Mekonnen & Hoekstra, 2016). Yet our knowledge of the hydro-biogeochemical functioning of high-elevation systems has remained relatively limited, largely due to the lack of observations in remote mountain ranges with extreme climatic and topographic gradients. Therefore, fundamental questions pertinent to mountain catchment hydrology remain, most notably: what are the source waters that support seasonal vegetation activity in high elevation forested landscapes?

At present, there is significant uncertainty as to the source waters that support vegetation across various ecosystem types. For example, several recent studies suggest that the water used by vegetation is mainly immobile, “tightly bound” soil water that is not available to streamflow (Brooks, Barnard, Coulombe, & McDonnell, 2009; Evaristo et al., 2015; Evaristo et al., 2016; Goldsmith et al., 2012; McDonnell, 2014). However, Evaristo and McDonnell (2019) proposed a geoclimatic conceptual model in which vegetation uses the same water that supports streamflow. Therefore, in the context of catchment-scale water balance research, a better understanding of the definition and role of tightly bound immobile soil water across a range of landscapes and ecosystem types is required.

Identification of distinct subsurface vegetation source waters or of the water-use strategies of different plant species is a challenging task from a catchment-scale water balance perspective. Various studies have shown that stable water isotopes are useful for making such distinctions (Allen, Kirchner, Braun, Siegwolf, & Goldsmith, 2018; Dawson & Ehleringer, 1991; Goldsmith et al., 2012; Silvertown, Araya, Gowing, & Cornell, 2015; Szutu & Papuga, 2019). As a result, we used stable water isotopes in this work from various potential vegetation source waters such as precipitation, soil water at various depths, stream water, and deep groundwater to identify differences in subsurface water-use strategy by vegetation type.

A better understanding of how transient, spatially heterogeneous subsurface water storage controls water allocations to various ecosystem components is urgently needed (Evaristo & McDonnell, 2019; McDonnell et al., 2018; Oerter & Bowen, 2019; Oshun, Dietrich, Dawson, & Fung, 2016). For example, Evaristo and McDonnell (2019) reported that the total water yield of a forested watershed responds to management practices such as deforestation or forest harvesting in ways that are highly dependent on those management practices. Additionally, a global synthesis of paired catchment studies noted that the role of subsurface storage in supporting forested ecosystems is not well understood due to a lack of long-term observations of soil and deep groundwater storages, transient water table data, and stable water isotopes (Evaristo & McDonnell, 2019). Recent studies (Oerter & Bowen, 2019; Oshun et al., 2016) have also reported heterogeneity not only in subsurface water storage but also in the stable water isotopic signatures of various subsurface water storage reservoirs, for example, soil layers, soil, saprolite, and weathered and fresh bedrock. These studies further note that local-scale variations in the stable water isotope signatures of storage reservoirs can complicate attempts to uniquely identify the source waters of various ecosystem components. Accordingly, the current study utilizes spatially distributed long-term hydrometric and soil water storage and stable water isotope data to provide a better understanding of subsurface water storage and its use by a forest ecosystem.

The overarching goal of this work was to identify vegetation source waters, their seasonal dynamics, and their mechanisms of generation in the Santa Catalina Mountains, Arizona, USA. The specific objectives were to (a) determine the adequacy of tightly bound soil water to meet dry period vegetation water demand at the catchment scale; (b) identify vegetation source waters and their origins using stable water isotopes; and (c) improve the understanding of subsurface water storage and its contribution to various ecohydrological components of a subhumid mountain ecosystem. To meet these objectives, we used both long-term catchment-scale hydrologic fluxes and stable water isotope data from precipitation, stream water, soil water (at various depths), xylem waters from two local vegetation types, and deep groundwater. Application of these results indicates that identification of various subsurface water storages in terms of ecohydrological water source separation (EWSS), or the “two water worlds” hypothesis (Brooks et al., 2009; McDonnell, 2014), is inevitably complicated by lack of agreement about the identification of immobile and tightly bound soil waters. As a result, we highlight that clear definition and justification for the use of these terms are essential to meaningful interpretation of ecohydrological source water identification.

KEYWORDS
ecohydrological niche, mountains, plant water dynamics, soil water, stable water isotopes, subsurface storage
2 | BACKGROUND

2.1 | Study site

This study was conducted in the Marshall Gulch catchment (MGC), a subhumid (aridity index between 0.5 and 0.65) headwater catchment (Figure 1) located within the Santa Catalina Mountains Critical Zone Observatory near Tucson, Arizona, in the south-western United States. The annual average precipitation at MGC was ~920 mm from 1981 to 2010 (PRISM Climate Group, 2018) but declined to 654 mm during the study period (2008–2017). Of the total precipitation, 43% fell during the winter season (October 1 through May 20), 3% during the dry season (May 21 through June 30), and 54% during the summer monsoon season (July 1 through September 30). The surface elevation at MGC varies from 2,285 to 2,632 m above sea level (asl), with a mean of 2,428 m asl and a mean slope of ~22°. The instrumentation and sampling locations within and around the field site are shown in Figure 1a.

At upper elevations, vegetation is Rocky Mountain aspen forest and woodland (~32%) and Madrean upper montane conifer-oak forest and woodland (~28%); at lower elevations, vegetation is mainly Madrean pine-oak forest and woodland (~40%; Figure 1b; GIS data source: NatureServe, 2004). Common plant species include Douglas fir (Pseudotsuga menziesii), Arizona pine (Pinus arizonica), oak (Quercus gambelli), quaking aspen (Populus tremuloides), Engelmann spruce (Picea engelmannii), Ponderosa pine (Pinus ponderosa), and white fir (Abies concolor). The bedrock in MGC is granite at upper elevations and muscovite schist at lower elevations (Dickinson, Hirschberg, Pitts, Stephen, & Bolm, 2002). The soil is mostly sandy loam (Holleran, 2013), with soil depth varying from 0 to 1.5 m (Pelletier & Rasmussen, 2009). Soils overlying schist tend to be deeper, and with higher clay content, than those overlying granite (Heidbüchel, Troch, & Lyon, 2013; Holleran, 2013; Heidbuchel, Personal Communication, 2016). A significant area (~64%) of MGC was affected by the Aspen wildfire in 2003 (https://www.mtbs.gov; accessed on April 20, 2018).

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**FIGURE 1** (a) Map of Marshall Gulch catchment (MGC boundary in green) and the surrounding area, showing existing instrumentation, sampling locations for deep groundwater (Pigeon spring, Mount Lemmon Water District well, Sabino well, and Wilson point). (b) Areas of vegetation types in MGC. (c) Location of MGC in south-eastern Arizona, USA. The digital elevation model is from U.S. Geological Survey (2018).
2.2 Data used and methods

2.2.1 Hydrometric observations

Measurements of hydrologic fluxes and storages, including long-term catchment-scale daily observations of precipitation (P), streamflow (Q), soil water storage, and actual evapotranspiration (AET), were collected by the Santa Catalina Mountains Critical Zone Observatory from water year (WY) 2008 through WY 2017 (Figure 2; see Section S1 in the Supporting Information for more details). Note that due to the observed annual patterns in soil water storage, a water year \( n \) in this study is defined as an annual period from July 1 of a calendar year \( n - 1 \) through June 30 of year \( n \) (see Figure S21). The AET data were obtained from the Mt. Bigelow eddy covariance (flux) tower located approximately 1.5 km from the MGC weir (Brown-Mitic et al., 2007).

2.2.2 Soil water parameters

Genuchten (1980) soil model parameters for unsaturated MGC soils (Holleran, 2013) were derived from Guardiola-Claramonte (2005), with values as follows: porosity = 0.45 cm³/cm³, residual water content = 0.08 cm³/cm³, parameter \( \alpha \) = ~0.027 1/cm, and \( N = 1.445 \) (dimensionless). The field capacity and permanent wilting points occurred at matric tensions of 10 kPa (equivalent to volumetric soil water content of 0.30 cm³/cm³) and 1.5 MPa (equivalent to volumetric soil water content of 0.11 cm³/cm³), respectively. These parameters were obtained from a model calibration based on field observations before the Aspen fire in 2003. Because wildfires may cause hydrophobicity in top soil (Guardiola-Claramonte, 2005, and references therein), Guardiola-Claramonte reduced soil hydraulic conductivity by 10% during the postfire period but left all other parameters unchanged.

2.2.3 Stable water isotope data

Precipitation

The precipitation isotope dataset represents observations collected from (a) bulk samplers located at the Schist, Fern Valley, and Granite sites, the Palisades Ranger Station (PRS), and Mt. Bigelow and (b) autosamplers located at Mt. Lemmon and the MG-Weir ISCO site (Figure 2a; see also Section S1.1.2 in the Supporting Information for more details). The PRS station data (Wright, 2001, and Wright, unpublished data) included both daily samples and weekly to biweekly composites from 1995 through 2004; the Mt. Bigelow data are biweekly aggregates from 2014 through 2016 (Hamann, 2018). The data from the Schist, Fern Valley, and Granite bulk samplers represent composite samples collected approximately weekly between 2007 and 2017, and samples from Mt. Lemmon and the MG-Weir ISCO site represent daily precipitation collections from 2007 to 2017. At all five stations, the data density decreased after 2012 for logistical reasons.

In order to reduce the potential for evaporative enrichment, mineral oil was added to all water samples prior to 2015 (Hamann,
2018; Lyon, Desletes, & Troch, 2009; Wright, 2001). However, for the water samples collected from Fern Valley, Schist, Granite, and the Mt. Lemmon and ISCO autosampling locations, mineral oil was not added after mid-2015 to ensure that the water samples could be analysed for additional solutes. Samples were transported to the University of Arizona, Department of Hydrology and Atmospheric Sciences laboratory, within a few hours after collection where they were stored in a refrigerator at 4°C; there was no indication of evaporative enrichment in samples without addition of mineral oil.

Samples from Schist, Fern Valley, Granite, and the Mt. Lemmon and the MG-Weir ISCO site were analysed using a DLT-100 laser spectrometer, Los Gatos Research, Inc., Model 908-0008 (Lyon et al., 2009), with an analytical precision (1σ) of ±0.37‰ and ±0.12‰ for δ²H and δ¹⁸O, respectively. Samples from PRS were analysed for δ¹⁸O using the CO₂ equilibration method and a Finnigan Delta S mass spectrometer with an analytical precision (1σ) of ±0.1‰ (Wright, 2001). For samples collected from 1996 to 1998, δ²H was measured using the zinc reduction method on a modified VG-602C mass spectrometer with a precision of ±2‰; samples collected after 1998 were measured using the chromium reduction method on a Finnigan Delta S mass spectrometer with a precision of ±1‰ (Wright, 2001). Data from the Mt. Bigelow station were measured on a L2120-I cavity ring-down spectrometer, Picarro, Inc., with analytical precision of ±0.20‰ for δ¹⁸O and ±0.7‰ for δ²H (Johnson et al., 2017). All measurements after 1995 were standardized relative to international standards VSMOW and SLAP (Coplen, 1993); prior measurements were standardized relative to SMOW.

Stream water
Stream water samples were collected using (a) an autosampler installed at the MG-Weir site from 2006 through 2012 and (b) stream water grab samples after 2012 (Figure 2b). Water collected in the autosampler was protected from evaporation using mineral oil. Grab samples were capped tightly on collection to prevent evaporation. All stream water samples were analysed using the DLT-100 laser spectrometer (see above).

Xylem or sap water
Arizona pine xylem water samples were collected between 1995 and 2004 by Wright (2001) and Wright (unpublished data). The samples were analysed by the vacuum distillation method (Pendall, 1997; Wright, 2001) using the VG-602C and Finnigan Delta S mass spectrometers (see above). Douglas fir xylem water samples were collected biweekly between July 16, 2014, and October 1, 2016, and were measured using the L2130-I cavity ring-down spectrometer (Hamann, 2018). For this instrument, Hamann (2018) followed the protocol of Johnson et al. (2017) who reported that errors arising from spectral interference from organic compounds could be reduced by treating samples with activated charcoal.

Soil water
Samples were obtained from soil suction lysimeters (seven in the Granite subcatchment and eight in the Schist subcatchment; see Figures 1a and S16) by applying a vacuum of 60 to 70 kPa (see Heidbüchel et al., 2013, for details). Suction lysimeter samples were analysed with the DLT-100 laser spectrometer (see details above). Other soil water samples were collected using the cryogenic vacuum distillation method (see also Pendall, 1997) and analysed using the VG-602C and Finnigan Delta S mass spectrometers (see above; Wright, 2001) or using an induction heating technique and cavity ring-down spectrometer (see above; Hamann, 2018). The cryogenic vacuum and induction extraction methods are considered to extract all water from soil samples (Johnson et al., 2017).

Deep groundwater
Groundwater samples were collected between 2017 and 2018 from Pigeon and Wilson Point springs and from the Mt. Lemmon Water District and Sabino wells (Figure 1). A single sample from Pigeon Spring (June 1, 2017) showed evaporative enrichment of isotopes and was therefore excluded from consideration. All groundwater samples were analysed using the DLT-100 laser spectrometer (see above). It is important to note that the present study relies heavily on long-term stable water isotope datasets from various previous site-specific studies. To ensure data quality and data reliability and promote consistency between the various data sources, all sample collections and analyses for stable water isotope tracers were performed following standard sampling and analysis protocols (Hamann, 2018; Heidbüchel, Troch, Lyon, & Weiler, 2012; Wright, 2001) to prevent evaporative enrichment of the collected samples (see Sections S1.1.2, S1.2.2, S1.3.2, and S1.4 in the Supporting Information for details).

2.2.4 Local meteoric water line

The local meteoric water line (LMWL) was determined from precipitation samples collected from WYs 1996 through 2017 (see Section S1.1.2) at the stations listed above. The data were subsequently reduced to seasonal, that is, winter and summer monsoon, amount-weighted averages. An amount-weighted LMWL was calculated using the regression method of Hughes and Crawford (2012) in order to minimize the effects dry conditions.

2.2.5 Line-conditioned excess

The line-conditioned excess (lc-excess) was calculated following Landwehr and Coplen (2004) using Equation (1). Note that if the lc-excess is negative, it suggests evaporative enrichment. The slope (A) and intercept (B) in Equation (1) are the slope and intercept of the LMWL.

\[
\text{lc-excess} = \delta^2H - A\delta^{18}O - B
\]

Because soil water samples at all depths showed significant isotopic variability (related to the isotopic variability of precipitation water; Figures S4 and S17), the depth-averaged (in 10-cm increments) lc-
excess values of soil water were used for estimating the evaporation penetration depth.

2.2.6 Identification of source water isotopic signatures for evaporatively enriched samples

Stream, soil, and sap waters commonly show stable isotope signatures indicative of evaporation to some degree (Benettin et al., 2018; Bowen et al., 2018). In order to estimate the true source water isotopic composition of evaporated samples, we followed the protocol of Benettin et al. (2018). Accordingly, each evaporated sample was projected along a postulated linear evaporation trend line. In the case of MGC, the slope of this line was 3.8, which is typical of southern Arizona ecosystems at both high and low elevations (Eastoe & Towne, 2018; C. Eastoe, unpublished data).

2.2.7 Statistical hypothesis testing between regression models

The method of Kleinbaum and Kupper (1978) was used to evaluate statistical equivalence between pairs of linear regression models to describe mixing between water types (e.g., shallow and deep soil waters or stream and deep soil waters). In each case, the null hypothesis \( H_0 \) was that the two models were statistically indistinguishable, and the alternative hypothesis \( H_a \) was that they were statistically significantly different at the 95% confidence level.

2.2.8 Method for examination of the EWSS hypothesis

Following Dawson and Simonin (2011) and McDonnell et al. (2018), stable water isotope data from precipitation, streamflow, deep and shallow soil waters, deep groundwater, and sap water from the two tree species were used, along with catchment-scale daily hydrometric observations from WY 2008 through WY 2017 (Figure 2). Hydrologic fluxes and storage data for WY 2010 were excluded because precipitation during WY 2010 was significantly under-reported and required adjustment (these values are shown in red in Figure 2a). A detailed description of the methods for preparing the daily hydrologic time series data without gaps and the stable water isotope data series is presented in Section S1 of the Supporting Information. We considered tightly bound soil water in this work as that which is retained at field capacity (Definition 1), as in other studies (Berry et al., 2018; Evaristo et al., 2019). An alternative definition (Definition 2) of tightly bound soil water as water held in soil pores at a matric tension of 65 kPa (the average of the applied matric tension range for the MGC soil lysimeter

![Figure 3](image-url)  
**FIGURE 3** (a) Daily precipitation and mean daily streamflow and (b) mean values of actual evapotranspiration, streamflow, and catchment-scale soil water storage. (c) A soil water characteristic curve for sandy loam soil type, showing the two “routes” representing two soil water storage options based on different definitions of tightly bound soil water during the dry period. WY is water year.
samples) or higher, that is, the soil moisture outside the lysimeter sampling domain (Berry et al., 2018), is also considered below.

3 | RESULTS

3.1 | Annual patterns of hydrologic fluxes and storages

Annual patterns of daily precipitation and mean daily streamflow followed a seasonal distribution with peaks in both summer and winter (Figure 3a). Daily soil water storage, expressed in area-normalized units, generally followed the same pattern as precipitation, but the increase in soil water storage was higher during the late winter than during the summer monsoon (Figure 3b). Isolated peaks in mean daily soil water storage at other times (e.g., mid-October) can be attributed to either isolated precipitation events or lateral groundwater flow from upper-gradient locations. Overall, soil water storage decreased monotonically between March 15 and June 30. The mean daily AET was lowest during the late winter, increased with the onset of the spring season, peaked during the monsoon, and decreased rapidly thereafter at approximately the same rate as soil water storage (Figure 3b). From March 15 to June 30, daily streamflow was either very low or non-existent, and therefore, this period is referred to as the dry period. We refer to the remainder of the year as the wet period. During the dry period, the mean cumulative water loss due to AET was 132 ± 35 mm (Figure 3b).

3.2 | Dry period soil water storage

According to Definition 1 of tightly bound soil water (Section 2.2.8), the potentially available tightly bound soil water storage was slightly higher (by ~20%) than cumulative AET during the dry period. However, it was significantly lower (by ~53%) than cumulative AET following Definition 2. As a result, two different “routes” were examined to assess the potential available soil water storage that could sustain vegetation water demand during the dry period. Along Route 1 (Figure 3c), which is based on Definition 1 of tightly bound soil water, conditions changed from a soil matric tension of 10 kPa (the field capacity point) to 1.5 MPa (Point 3 in Figure 3c, suggested as the permanent wilting point for a soil by Kirkham, 2005). Note that Kirkham (2005, p. 105), Brantley et al. (2017), and Rose, Graham, and Parker (2003) suggest that the wilting point of a soil is not a constant but a dynamic quantity that depends on multiple factors relating to plant-soil relationships. Along Route 2, which is based on Definition 2 of tightly bound soil water, conditions changed from a matric tension of 65 kPa to 1.5 MPa, the wilting point.

Our results demonstrate that the dry period cumulative AET demand (both mean and mean plus one standard deviation) can be met with soil thicknesses of 0.85 m or greater following Route 1 (Table 1), which is within the variability of soil thicknesses at MGC (mean thickness = 0.80 m, median thickness = 0.72 m, and standard deviation = 0.36 m). In contrast, the dry period cumulative AET demand cannot be met by following Route 2 even when using the maximum soil thickness across the whole catchment (Table 1). Thus, the dry period AET water demand at MGC can only be supported by tightly bound soil water as defined in terms of field capacity.

3.3 | Isotopes in stream and soil waters

3.3.1 | Amount-weighted LMWL

The equation of the amount-weighted LMWL was δ²H = 6.86 δ¹⁸O + 3.39 with an R² value of 0.96 (Figure 4), differing only slightly from the LMWL determined by Wright (2001) (δ²H = 6.82 δ¹⁸O + 2.4; R² = 0.91) between 1995 and 2005 for the nearby PRS. The overall amount-weighted seasonal means of δ²H and δ¹⁸O values at MGC were higher in summer than in winter by 19.2‰ and 2.9‰, respectively (Figure 4).

3.3.2 | Evaporation penetration depth

The evaporation penetration depth, that is, the maximum depth for the kinetic fractionation of pore water (Barnes & Allison, 1988; Sprenger, Leistert, Gimbel, & Weiler, 2016), was approximately 35 cm below the ground surface (bgs; Figure 5a), which is close to the reported value (30 cm) from a global analysis of soil pore waters (Sprenger et al., 2016). The lc-excess values were consistent below 35 cm but more negative above that depth (Figure 5a), and soil water samples at depths greater than 35 cm also showed lc-excess values

| TABLE 1 | Dry period AET water demand and potentially available soil water storages |
|----------------|-------------------------|----------------------------------|
| Item                        | Demand or availability (mm) | Comments                              |
| Cumulative AET water demand | 132 ± 35 | Dry period: March 15 through June 30 |
| Total potentially available soil water storage | | |
| Route 1 (field capacity to wilting point) | 158 | Using the average soil depth = 0.80 m |
| Route 2 (65 kPa to wilting point) | 62 | Using the average soil depth = 0.80 m |
| Route 1 (field capacity to wilting point) | 296 | Using the maximum soil depth = 1.5 m |
| Route 1 (field capacity to wilting point) | 168 | Using soil thickness = 0.85 m |
| Route 2 (65 kPa to wilting point) | 116 | Using the maximum soil depth |

Abbreviation: AET, actual evapotranspiration.
that were closer to those of deep groundwater samples (blue point markers in Figure 5a). Consistent with the above interpretation, soil water samples from depths >35 cm bgs were located closer to the LMWL than those from depths ≤35 cm bgs (Figure 5b). About 1% of deep soil water samples, collected during the summer monsoon, were also located far from the LMWL. Linear regression trends of δ²H versus δ¹⁸O for soil water samples from ≤35 cm bgs and from >35 cm bgs were statistically different (Table 2), but the trend for the deep soil water samples was not statistically different from the LMWL (Table 2). As a result, soil water samples from ≤35 cm bgs are subsequently referred to as shallow soil water, and those from >35 cm bgs as deep soil water.
Results of the statistical tests for significant (evaluated at 95% confidence level) differences in fitted linear regression models between pairs of water types for dry (March 15 through June 30) and wet (all other) periods

<table>
<thead>
<tr>
<th>Hypothesis test for slope</th>
<th>Hypothesis test for intercept</th>
<th>Period</th>
<th>Category 1</th>
<th>Category 2</th>
<th>Z statistic for slope</th>
<th>Z statistic for intercept</th>
<th>p value</th>
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<td>Shallow soil water</td>
<td>Deep soil water</td>
<td>4.30</td>
<td>0.20</td>
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<td>Intercept: Shallow soil water</td>
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<td>3.82</td>
<td>0.15</td>
<td>5.35</td>
</tr>
</tbody>
</table>

Note: (a) For each test, the null hypothesis (H0) is that the two slopes (or intercepts) are the same, and the alternative hypothesis (Ha) is that they are different; (b) the Z statistic is used for statistical comparison of two regression models if sample sizes are large; (c) the critical statistic for slope (or intercept) is 1.96; and (d) all required data for performing statistical tests are presented in Table S3.

Abbreviation: LMWL, local meteoric water line.

3.3.3 Isotopic signatures of stream and soil waters during dry and wet periods

Dry period
During the dry period, the stream water isotope data formed a single evaporation trend line on a δ²H versus δ¹⁸O plot with a regression slope that was not significantly different from that for shallow soil water but was statistically different from the regression slopes of the LMWL and deep soil water (Table 2). During the dry period, stream waters were less variable in isotope composition than during the wet period.

Wet period
In contrast to the dry period, stream water was not significantly different from the LMWL or deep soil water during the wet period but was significantly different from shallow soil water (Table 2). Likewise, shallow soil water was statistically distinct from both the LMWL and deep soil water. Whereas statistical comparison of stream and deep and shallow soil waters was possible using the existing dataset, the equivalent comparison with xylem water was not feasible because of the small sample size, low correlation coefficient, and the high variance of the linear regression coefficients for the xylem water data (see Table S3).

3.4 Seasonality in source waters

3.4.1 Stream source waters

The wet period stream water was more variable in isotope composition than the dry period stream water, reflecting both the presence of direct run-off after precipitation events during the wet period and the greater likelihood of base flow during the dry period (Figure 6). In both cases, however, winter precipitation was the dominant water source, evidenced by samples that were located closer to the long-term winter season evaporation trend line on a δ²H versus δ¹⁸O plot with a regression slope of 3.8 (see Section 2.2.6), source waters, and unevaporated sources for samples outside this zone are referred to as Type A source waters, and unevaporated sources for samples outside this zone are referred to as Type B source waters. Using the Benettin et al. (2018) protocol to identify the pre-evaporation isotopic composition of any evaporated sample by translating the sample along an evaporation trend line with a slope of 3.8 (see Section 2.2.6), source waters were located along a segment of the LMWL (Figure 7). Type A source waters may thus be explained as various combinations of seasonal amount-weighted mean precipitation. In contrast, Type B source waters were located at −23 < δ¹⁸O < −15‰ on the LMWL and appear to be related to low-δ¹⁸O rain events. This distinction is relevant to the discussion of soil and xylem waters below.
3.4.2 Soil waters

Most source waters (98% for deep soil water and 61% for shallow soil water) at MGC were of Type A. Because the Type B source waters require infiltration from low-δ²H rain events and little or no mixing with water from precipitation events with δ¹⁸O > −15‰, the presence of a large number of Type B waters in shallow soil is problematic because precipitation events with δ¹⁸O < −15‰ are rare in summer and are not the largest winter events.

3.4.3 Vegetation source waters

The use of subsurface water sources differed between both Douglas fir and Arizona pine and between wet and dry periods for each species.
However, there was no evidence for isotope fractionation during water uptake by either species (Section S2 in the Supporting Information). During wet and dry periods, Arizona pine utilized soil water derived from both Type A and Type B source waters, whereas Douglas fir utilized both Type A and Type B source waters during the wet period but primarily Type B waters during the dry period.

### 3.5 Comparison of mobile water and tightly bound soil waters

Both Type A and Type B source waters contributed to tightly bound soil waters, regardless of sampling depth (Figure 9). For this study, mobile soil water was considered to have the same isotopic composition as stream water during the wet period on days with no

**FIGURE 8** (a) Wet period and (b) dry period Arizona pine and Douglas fir source waters in dual isotope space. The blue and orange boxes represent Type A and Type B source water types. The broken lower boundary for the Type B source water type box is an arbitrary boundary.

**FIGURE 9** δ²H versus δ¹⁸O plot showing mobile, shallow, and deep tightly bound soil water samples. The blue and orange boxes represent Type A and Type B source water types. The broken lower boundary for the Type B source water type box is an arbitrary boundary. LMWL, local meteoric water line.
precipitation (see Section ). Accordingly, mobile soil water also originated as Type A source water. Tightly bound soil water was subject to greater evaporative enrichment at shallower depths.

4 | DISCUSSION

Our results suggest that the dry period AET water demand at MGC can be supported by tightly bound soil water when it is defined in terms of field capacity and, in a broader sense, that there are two dominant subsurface soil water storage types, termed Type A and Type B. Although Arizona pine and Douglas fir vegetation each utilized both source water types, Douglas fir’s predominant use of Type B waters during dry periods suggests that these two species may occupy distinct ecohydrological niches in terms of dry season subsurface water use. In the following, we evaluate the influence of alternative definitions of tightly bound water on interpretation of vegetation source water data, as well as the potential mechanisms for generating isotopically different vegetation source water types. Finally, we propose an improved ecohydrological conceptual model based on the identification of vegetation and stream source waters. This model contributes to an improved understanding of how and when subsurface water storage supports various ecohydrological components of the mountain critical zone.

4.1 | Catchment-scale AET water demands and potential water sources

Vegetation water demand is best considered during the dry period when AET is most likely to be limited by water availability. In contrast, soil water is more abundant during the summer monsoon, and water demand is lower when plants are dormant in winter.

4.1.1 | Availability and mobility of tightly bound soil water during the dry period

Tightly bound soil water is defined in a variety of ways (Berry et al., 2018; Evaristo et al., 2019; Oshun et al., 2016). Two possible cases have been proposed here. If tightly bound soil water is defined in terms of field capacity, that is, Definition 1, then it was sufficient to supply vegetation demand during the dry period at MGC. However, if defined in terms of the maximum matric tension applied to lysimeters, that is, Definition 2, it was insufficient to meet dry period vegetation water demand at MGC. Previous work has concluded that tightly bound or immobile soil water was insufficient to maintain vegetation during protracted dry periods in semi-arid ecosystems (Bowling, Schulze, & Hall, 2017; McCutcheon, McNamara, Kohn, & Evans, 2017; Oerter, Siebert, Bowling, & Bowen, 2019). Similarly, Berry et al. (2018) argued that immobile soil water, once consumed by vegetation, would have to be replenished during dry periods from mobile water, in order to continue supporting vegetation.

The following three important notes should be considered with respect to the above discussion. First, a single soil water characteristic curve (SWCC) was used to determine potentially available soil water drawdown for a vegetation water source. However, an SWCC can depend on soil depth and spatio-temporal variations in soil texture and soil physical properties (Warren, Meinzer, Brooks, & Domec, 2005) and also on the wetting and drying cycles, that is, hysteresis effects (Bear, 1972; Furbish, 1997; Jury & Horton, 2004). As a result, we justify the use of a single SWCC to examine potentially available soil water storage to sustain vegetation water demand during the dry period.

**FIGURE 10** Illustration of soil moisture movement between two control volumes (CVs) embedded in a vadose zone where both CVs have volumetric moisture content less than the field capacity. Note. Various parameters such as porosity ($\theta_s$), residual water content ($\theta_r$), field capacity ($\theta_{fc}$), wilting point ($\theta_{w}$), and Genuchten model parameters including $\alpha$ and $N$ are obtained from a site-specific study (Guardiola-Claramonte, 2005) that covers Marshall Gulch catchment. $\theta$ is volumetric moisture content.
only. Second, we primarily consider drainage conditions in the SWCC analysis, which are the conditions most often used to construct SWCCs. Third, the use of the SWCC was intended to determine how much the soil water column can be drained in a cumulative sense to meet the catchment-scale AET water demand for the whole dry period.

The current study raises the following question: Is tightly bound soil water really immobile when defined in the sense of field capacity (see also Bowen et al., 2018; Goldsmith et al., 2012; McDonnell, 2014; Oerter & Bowen, 2019)? To address this question, we performed a conceptual experiment considering the behaviour of soil water in amounts less than field capacity (Yeh, Khaleel, & Carroll, 2015), rather than as precluded soil water mobility under dry conditions as a response to an energy gradient (or gradient of energy/weight), which is comparable with the matric potential gradient in the present case, would cause soil moisture to move from CV1 to CV2 by capillary action. Although this thought experiment may appear simplistic, it demonstrates the potential for mobility of tightly bound soil water in a saturation state below field capacity, and the results are consistent with findings from numerous field and modelling investigations related to vadose zone soil reservoirs under wet and dry conditions (Figure 7), and both water types evolve in isotopic composition through evaporation within soil. However, Type A and Type B soil waters may be used differently by Arizona pine and Douglas fir tree species, where Type B waters are especially prominent in Douglas fir sap water. To understand this, we took a closer look at the characteristics of each sample. The Douglas fir sap samples were collected between 2014 and 2016, during and after a 5-month period of unusually low δ18O and δ2H in rain. During this period, August 25, 2014, to February 1, 2015, the weighted-averages for δ18O and δ2H in precipitation were −10.5‰ and −67.5‰, respectively. However, these values and the subsequent amount-weighted seasonal precipitation means are not low enough to explain the Douglas fir sap water data (Figure 8). During the Douglas fir sap water sampling period, there were 37 measurable rain events, of which four had δ18O values ranging from −19.2‰ to −15‰, accounting for ~19% of the rain volume during that period. There was no significant correlation between precipitation amount and δ18O value; hence, the Douglas fir sap water is responding to the low-δ18O events in an unexplained way. Nonetheless, our results are consistent with other studies that reported separation in vegetation source waters based on stable water isotopes (see tables 1 through 3 in Silvertown et al., 2015, and references therein).

At MGC, Type A source waters represent various combinations of seasonally averaged winter and summer season precipitation (Figure 7). In contrast, Type B source waters are precipitation that is isotopically lighter than average winter precipitation (Figure 7), which infiltrates saturated bedrock in sufficient quantity to appear in spring discharge at elevations below 2,000 m asl on the Santa Catalina Mountains (Cunningham et al., 1998).

Suggested explanations for the isotope composition of nonevaporated, isotopically light Type B water at MGC include the following:

(a) Preferential infiltration of precipitation with very low δ2H and δ18O values. Precipitation events with δ18O < −15‰ occur in the Santa Catalina Mountains in both winter and summer (Figure 4) and represented ~3.5% of all observed precipitation events between 1995 through 2016. In the 3 years prior to October 2016, which brackets the collection of the Douglas fir sap water, these events specifically constituted ~11% of precipitation events and ~19% of precipitation volume. Overall, soil water samples with a Type B source composed only 4.4% of the soil waters measured for this study, but Douglas fir sap water with a Type B source made up 71% of wet-season samples and 92% of dry-season samples (Figure 8). Type B source waters are thus over-represented as Douglas fir source waters relative to their occurrence in precipitation and soil. However, preferential infiltration of low-δ18O precipitation is problematic. In winter, infiltration of water with δ18O < −15‰ is unlikely at altitudes above 2,000 m asl, because a snowpack typically accumulates that eventually yields meltwater with δ18O values representing multiple snow events. In summer, low-δ18O precipitation constitutes only ~3.4% of the total summer monsoon precipitation events or 5.3% of the total precipitation volume, mainly in late July and late September.

4.1.2 The ecohydrologic role of groundwater in weathered and fractured bedrock

In addition to soil water storage, physical evidence suggests that vegetation in the Santa Catalina Mountains can access groundwater in weathered or fractured bedrock (Pelletier et al., 2013; Wright, 2001). Such access has also been demonstrated in Mediterranean and other climatic settings where long dry periods are characteristic in summer (Bornyasz, Graham, & Allen, 2005; Dralle et al., 2018; Egerton-Warburton, Graham, & Hubbert, 2003; Hahn et al., 2017; Hubbert, Beyers, & Graham, 2001; Rose et al., 2003; Stemberg, Anderson, Graham, Beyers, & Tice, 1996; Witty, Graham, Hubbert, Doi, & Wald, 2003). Access to bedrock groundwater could be facilitated by mycorrhizal fungal hyphae extending from roots in bedrock fractures to the surrounding weathered bedrock (Bornyasz et al., 2005; Egerton-Warburton et al., 2003; Witty et al., 2003).

4.2 Potential mechanisms for generating isotopically different vegetation source waters

At MGC, isotope data suggest two varieties of soil water, termed Type A and Type B above. Both are present in deep and shallow soil water
(b) Isotope fractionation in the vadose zone as a result of matric potential and/or atmospheric effects. Previous work showed that for clayey sand (resembling the loam at MGC), increasing soil tension generated a linear trend with a slope of 2 on a plot of $\delta^2$H versus $\delta^{18}$O and higher slopes for mixtures with less clay (Gaj & McDonnell, 2019). However, at MGC, a trend line with a slope of 2 drawn through the soil water isotope plot (EL 4 in Figure 7) does not alleviate the need for source waters with very low $\delta^2$H and $\delta^{18}$O values. A further objection to this explanation is the presence of Type B waters under both wet (soil saturated) and dry (vadose) conditions.

(c) Isotopic fractionation between water and Ca–Mg smectite. Smectite is present in MGC soils (Holleran, Levi, & Rasmussen, 2015), and fractionation between water and smectite leads to depletion of heavy isotopes in the water phase (Oerter et al., 2014; Oshun et al., 2016). However, the efficacy of this possibility would be limited by the shallow soil profile at MGC where, over the long term, water is present in much larger quantities than clay and is therefore unlikely to undergo a significant isotope shift.

The apparent preferential uptake of Type B soil water by Douglas fir remains problematic, and we cannot offer a satisfactory explanation for the origin and role of Type B water in the soil-vegetation system at MGC. This unresolved problem (which can also be observed in the soil water datasets of Brooks et al., 2009; Bowling et al., 2017; McCutcheon et al., 2017; and Oerter et al., 2019) highlights the need for additional research incorporating high-density spatial and temporal sampling of soil and sap waters in order to promote comprehensive understanding of subsurface waters in complex critical zone systems.

4.3 Evaluation of the EWSS hypothesis at MGC

Our results, with a focus on the dry period, are equivocal in relation to the EWSS hypothesis (Brooks et al., 2009; McDonnell, 2014). The hypothesis is permissible at MGC insofar as tightly bound soil water is available in sufficient quantity to support AET demand during dry periods and can be tested in the MGC because there is no evidence for isotopic fractionation as a result of uptake of soil water by roots. However, the EWSS hypothesis supposes an isotopic distinction between mobile and tightly bound soil waters, and this is not generally applicable at MGC (Figure 9). Further, the isotopic composition of sap water falls within the range of the isotopic composition of soil water at MGC (Figures 7 and 8; see also Section S2 in the Supporting Information). For context, one of the few previous studies to have quantitatively evaluated the EWSS similarly reported no isotopic distinction between mobile and tightly bound soil waters in a semi-arid mountain ecosystem in Idaho, USA (McCutcheon et al., 2017). Another study (Oshun et al., 2016) reported differences in the isotopic signatures of mobile and chemically adsorbed waters for a actively uplifting, eroding, and weathering field site in California, USA.

The small sap water isotope dataset for the Santa Catalina Mountains indicates that Douglas fir used soil water that is distinctive in isotopic composition and could be classified as either mobile or tightly bound soil water. Accordingly, in the case of Douglas fir but not Arizona pine, a phenomenon akin to, but not strictly identical to, the EWSS hypothesis may thus be applicable. Given that discussion of the EWSS hypothesis is inevitably complicated by lack of agreement about the identification of immobile and tightly bound soil waters, clear definition and justification for the use of these terms are essential to meaningful interpretation of source water identification studies. Notwithstanding, on the basis of the totality of the results presented in this work, we conclude that vegetation has access to soil water of Type B origin. Such soil water is on average strongly evaporated (Figure 7) and does not contribute significantly to streamflow, in which it is undetectable in the isotope data or to mountain system recharge, in which Type B source water is unevaporated.

4.4 An improved understanding of subsurface water storages in the mountains

The results of this work contribute to an improved understanding of the role of subsurface water storages in supporting various components of the mountain critical zone. For example, previous local and regional studies (Hamann, 2018; Szutu & Papuga, 2019; Wright, 2001) have attempted to relate vegetation source waters to a two-layer model for soil water, that is, shallow and deep, whether implicitly or explicitly considered. The results of this work suggest that there is no consistent isotope distinction between shallow and deep soil storages, as demarcated by the penetration of evaporation. Further, the stream source waters identified in this study are consistent with a conceptual model for streamflow generation (Dwivedi et al., 2019) wherein the isotopic variability of stream water is storage dependent, such that there is more isotopic variability during wet periods than in dry periods (Figure 6). The current study also suggests that distinctive, albeit unexplained, subsurface water storage derived from the Type B source exists in both shallow and deep soil layers and that this storage can be important to supporting vegetation water demand. Considered together, the results of this work and the conceptual model of Dwivedi et al. (2019) represent a holistic interpretation of the various hydrological pathways and fluxes at MGC. Within the context of long-term monitoring, this type of integrated hydrometric and isotopic analysis contributes to a more thorough understanding of hydrological cycling and the role of subsurface storage in supporting mountain ecosystem services.

5 Conclusions

A catchment-scale water balance analysis at Marshall Gulch indicates that total tightly bound soil water storage is sufficient to meet dry period vegetation water demand when defined in terms of field capacity. Because tightly bound water is likely to be mobile under the influence of matric potential gradients during dry periods, this work further supports consideration of soil water mobility at conditions below field capacity in terms of an energy gradient. Most soil water, both shallow and deep and tightly bound, originates as mixtures of summer and winter precipitation with source isotope compositions that are in between the long-term average winter and summer precipitation
endmembers (termed Type A source water). Other soil waters that comprise 4% to 10% samples depending on the time interval of sampling originate as precipitation with δ18O and δ2H values below the long-term winter means (Type B source water). Although Type A and Type B soil waters were used by both Arizona pine and Douglas fir, the two species occupied distinctive ecohydrological niches during dry periods when waters of Type B origin dominated Douglas fir xylem water samples for reasons that remain unclear. Given that the identification of subsurface water storages and interpretation of their seasonal importance to mountain ecosystems are inevitably complicated by lack of agreement about the identification of immobile and tightly bound soil waters, the question of whether tightly bound soil water is sufficient to meet vegetation demand depends on how tightly bound water is defined. As a result, a clear definition and justification for the use of these terms are essential to meaningful interpretation of water source data within the context of plant water dynamics in Earth’s critical zone.

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CONFLICT OF INTEREST

The authors declare no financial conflict of interest.

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