Prepared in cooperation with Yavapai County Water Advisory Committee and Arizona Department of Water Resources

Analysis of Stable Isotope Ratios ($\delta^{18}O$ and $\delta^{2}H$) in Precipitation of the Verde River Watershed, Arizona, 2003 through 2014

Open-File Report 2016–1053

U.S. Department of the Interior
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COVER PHOTO
Convective rainstorm near Flagstaff, Arizona, on June 15, 2015. Photograph by Brandon Forbes, U.S. Geological Survey.

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
	Volume	
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m3)
gallon (gal)	3.785	cubic decimeter (dm3)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Volume	
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in3)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
°F=(1.8×°C)+32

Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88)
Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83)

Analysis of Stable Isotope Ratios ($\delta^{18}O$ and $\delta^{2}H$) in Precipitation of the Verde River Watershed, Arizona, 2003 through 2014

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Abstract

Stable isotope delta values ($\delta^{18}O$ and $\delta^{2}H$) of precipitation can vary with elevation, and quantification of the precipitation elevation gradient can be used to predict recharge elevation within a watershed. Precipitation samples were analyzed for stable isotope delta values between 2003 and 2014 from the Verde River watershed of north-central Arizona. Results indicate a significant decrease in summer isotopic values over time at 3,100-, 4,100-, 6,100-, 7,100-, and 8,100-feet elevation. The updated local meteoric water line for the area is $\delta^{2}H = 7.11\ \delta^{18}O + 3.40$. Equations to predict stable isotopic values based on elevation were updated from previous publications in Blasch and others (2006), Blasch and Bryson (2007), and Bryson and others (2007). New equations were separated for samples from the Camp Verde to Flagstaff transect and the Prescott to Chino Valley transect. For the Camp Verde to Flagstaff transect, the new equations for winter precipitation are $\delta^{18}O = -0.0004z - 8.87$ and $\delta^{2}H = -0.0029z - 59.8$ (where z represents elevation in feet) and the summer precipitation equations were not statistically significant. For the Prescott to Chino Valley transect, the new equations for summer precipitation are $\delta^{18}O = -0.0005z - 3.22$ and $\delta^{2}H = -0.0022z - 27.9$; the winter precipitation equations were not statistically significant and, notably, stable isotope values were similar across all elevations. Interpretation of elevation of recharge contributing to surface and groundwaters in the Verde River watershed using the updated equations for the Camp Verde to Flagstaff transect will give lower elevation values compared with interpretations presented in the previous studies. For waters in the Prescott and Chino Valley area, more information is needed to understand local controls on stable isotope values related to elevation.

Introduction

The Verde River watershed is located in north-central Arizona and includes Great Basin, Semidesert, Great Basin Conifer, and Montane Conifer biomes (Arizona Game and Fish, 2015) where the climate is dominated by separate winter and summer precipitation periods (fig. 1). Stable isotope ($\delta^{18}O$ and $\delta^{2}H$) precipitation elevation gradients and local meteoric water lines were originally published for the Verde River watershed in north-central Arizona using data collected between 2003 and 2005 (Blasch and others, 2006; Blasch and Bryson, 2007; Bryson and others, 2007). Stable isotope delta values of precipitation can vary with elevation, and quantification of the precipitation elevation gradient can be used to predict recharge elevation within a watershed. Additional precipitation data were collected at elevations of 3,100 to 8,100 feet from 2003 through 2014 and the comprehensive dataset was analyzed. This report uses that analysis to update the precipitation elevation gradients and local meteoric water line equations originally published by Blasch and others (2006), Blasch and Bryson (2007), and Bryson and others (2007).

Methodology

Samples were collected from precipitation buckets (described below) at 10 sites ranging in elevation from 3,100 to 8,100 feet to represent precipitation in 1,000-foot increments along two north-south transects, one from Camp Verde to Flagstaff (Camp Verde-Flagstaff transect) between 2003 and 2014 and the other from near Prescott to Chino Valley (Prescott-Chino transect) between 2003 and 2009 (fig. 2). Precipitation samples were collected in 5-gallon plastic buckets generally twice a year to obtain a composite summer precipitation sample and a composite winter precipitation sample. The precipitation samples collected for this study included a mixture of some spring and some fall precipitation in both the summer and winter samples (see Appendix tables 1, 2, and 3 for sample locations and durations).

The bottoms of the buckets were each coated with a fresh layer of mineral oil after sample collection to minimize the effect of evaporation (Blasch and Bryson, 2007). Buckets were capped with screens to limit contamination and three sites (at 6,100-, 7,100-, and 8,100-feet elevation) had funnels in the bucket lids (installed in October 2009) to help avoid overflow of water from the buckets. Buckets were removed and sampling was discontinued along the Prescott-Chino transect in April 2009, and after October 2010 buckets only remained at 3,100-, 6,100-, and 7,100-foot-elevation sites along the Camp Verde-Flagstaff transect.

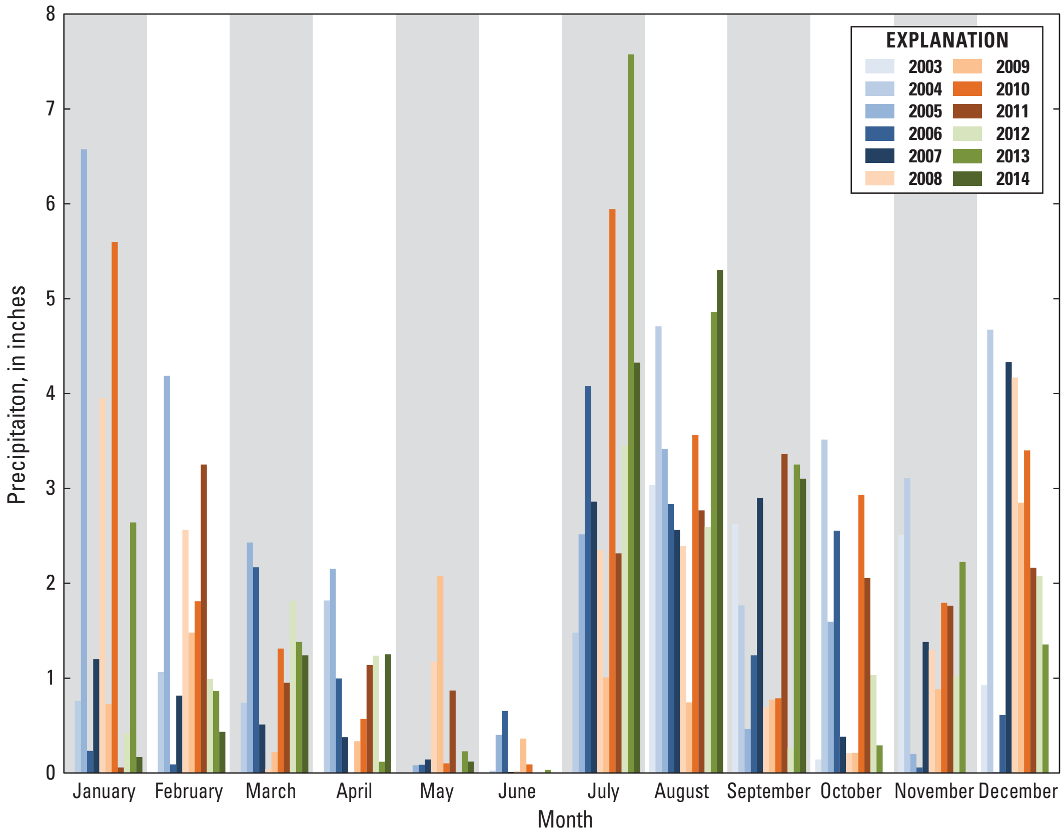


Figure 1. Graph of monthly precipitation data for the Flagstaff Pulliam Airport meteorological station from September 2003–September 2014. Data from National Oceanic and Atmospheric Administration (2015).

The volume of rainwater collected was measured to the nearest 1/32 of an inch, using a stainless steel ruler to determine the water depth in standard-size buckets with 11-inch inner diameters. Samples were collected from the precipitation buckets using a plastic baster. The tip of the baster was placed underneath the mineral oil layer, the samples were extracted, and then the baster was rinsed three times prior to discharging the water samples into 60 mL glass bottles with polyseal caps.

Stable isotope delta values ($\delta^{18}O$ and $\delta^{2}H$) were measured at the University of Arizona (UA) Environmental Isotope Laboratory in Tucson using a gas-source isotope ratio mass spectrometer (Finnigan Delta S). For hydrogen, samples were reacted at 750 °C with Cr metal using a Finnigan H/Device coupled to the mass spectrometer. For oxygen, samples were equilibrated with CO_2 gas at approximately 15 °C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials, Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation. Precision is 0.9 per mil or better for $\delta^{2}H$ and 0.08 per mil or better for $\delta^{18}O$ on the basis of repeated internal standards. Some samples were analyzed at the U.S. Geological Survey (USGS) Reston Stable Isotope Laboratory (RSIL) (following methods by Révész and Coplen, 2008a,b) and delta values were reported relative to VSMOW.

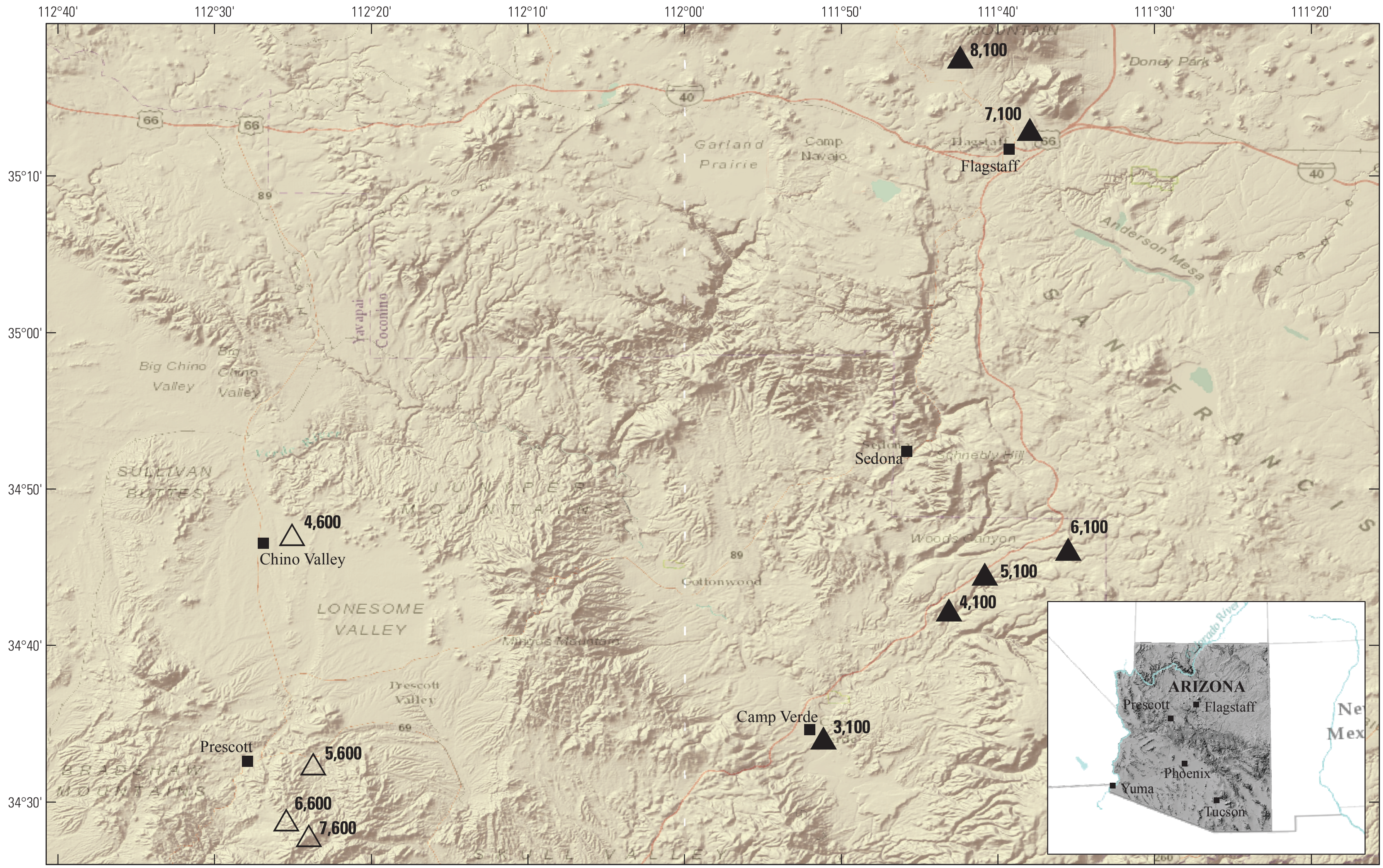
Sixteen replicate sample pairs were sent to both laboratories to understand the variability between the labs (Appendix table 4), which was quantified by taking the average of the standard deviation of the sample and replicate pairs and using it to determine a 95-percent confidence interval range for sample values (table 1). Eight replicate pairs were sent to the RSIL and the variability from that lab is quantified in table 1. One replicate was also sent to the UA laboratory where it had the same value for $\delta^{2}H$ and was different by 0.2 for $\delta^{18}O$ (Appendix table 5).

Table 1. Replicate sample variability.

[RSIL, USGS Reston Stable Isotope Laboratory; UA, University of Arizona Environmental Isotope Laboratory]

Type of replicate pair	95-percent confidence Interval	
	$\delta^{2}H$ (per mil)	$\delta^{18}O$ (per mil)
RSIL and UA	±1.30	±0.26
RSIL	±1.56	±0.22

Stable isotope delta values for each elevation were averaged using a volume weighting to determine a single value for each season based on the volume of water measured in the buckets during collection (samples that had a funnel added in 2009 were adjusted by multiplying the water depth by 1.46, which is the ratio of the open bucket diameter [11 inches] to the funnel diameter [7.5 inches]).



Base is World Terrain Basemap from ESRI. Map is intellectual property of ESRI and is used herein under license. Copyright © 2014 ESRI and its licensors. All rights reserved
Data from U.S. Geological Survey National Water Information System, 2015
North American Datum of 1983

Figure 2. Map of precipitation sample locations. Filled triangles represent the Camp Verde to Flagstaff transect and open triangles represent the Prescott to Chino Valley transect. Numbers adjacent to triangles indicate the elevation of the precipitation sample locations in feet.

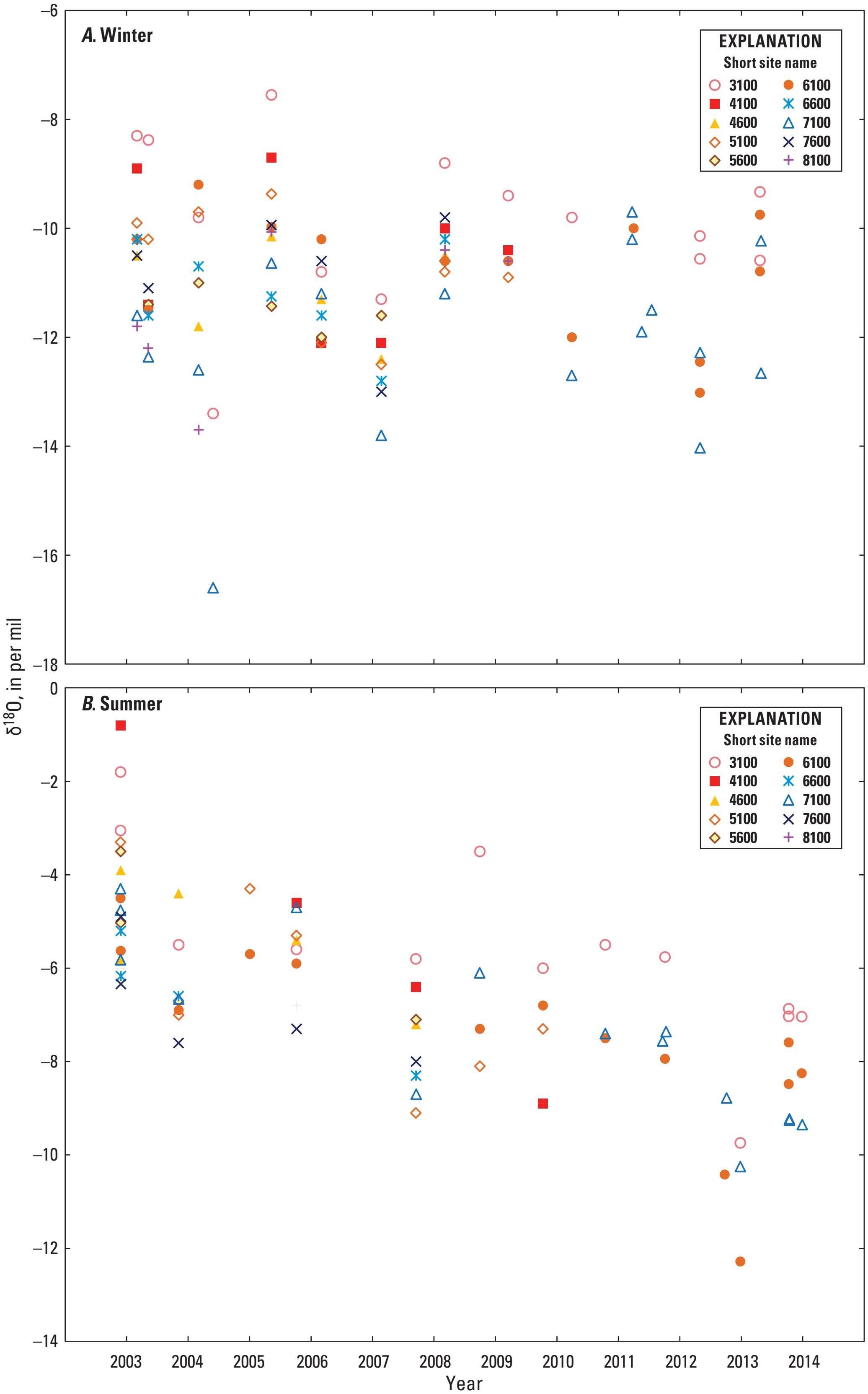


Figure 3. Graph of stable isotope delta values of $\delta^{18}O$ over time for A, winter and B, summer.

Table 2. Correlation statistics for stable isotope delta values of $\delta^{18}O$ over time.

[Text in bold indicates a significant value of Kendall's tau at a 95-percent confidence level (p-value <0.05)]

Elevation (feet)	USGS site ID	Season	Kendall's tau	P-value	Date range	Number of samples
3,100	343404111510801	Winter	-0.22	0.27	2003 to 2014	14
		Summer	**-0.69**	**0.001**		13
4,100	344214111430601	Winter	-0.19	0.54	2003 to 2010	7
		Summer	**-1**	**0.04**		4
4,600	344704112250101	Winter	-0.09	0.76	2003 to 2009	7
		Summer	-0.53	0.21	2003 to 2008	5
5,100	344432111404901	Winter	-0.35	0.22	2003 to 2010	8
		Summer	-0.52	0.10		7
5,600	343224112234201	Winter	-0.33	0.29	2003 to 2009	7
		Summer	-0.91	0.07	2003 to 2008	4
6,100	344608111352801	Winter	-0.26	0.22	2003 to 2014	13
		Summer	**-0.73**	**0.0003**		14
6,600	342848112252401	Winter	-0.25	0.44	2003 to 2009	7
		Summer	-0.91	0.07	2003 to 2008	4
7,100	351256111375801	Winter	0.04	0.80	2003 to 2014	17
		Summer	**-0.73**	**0.0002**		15
7,600	342749112235801	Winter	0.07	0.85	2003 to 2009	6
		Summer	-0.74	0.08	2003 to 2008	5
8,100	351735111422301	Winter	0.2	0.57	2003 to 2010	6
		Summer	**-0.92**	**0.005**		7

Results

Winter precipitation samples did not show a significant directional trend of stable isotope delta values over time at any of the 10 sites. Summer precipitation samples at five sites (at 3,100-, 4,100-, 6,100-, 7,100-, and 8,100-feet elevation), however, showed a significant decrease in stable isotope delta values over time (fig. 3 and table 2). Figure 3 and table 2 show the oxygen isotope trends. The hydrogen isotope data are not shown on a figure because they exhibit the same patterns between summer and winter and the same sites have significant trends as determined by a Kendall's tau coefficient test (table 2, Appendix tables 2 and 3).

An updated local meteoric water line equation was developed using the volume-weighted average value for each sample elevation for winter and summer values (fig. 4).

(1) $$\delta^2H = 7.11\delta^{18}O + 3.40$$

where δ^2H is the hydrogen isotopic delta value of the water relative to the standard VSMOW, and

$\delta^{18}O$ is the oxygen isotopic delta value of the water relative to the standard VSMOW.

The slope of the updated equation is similar to the local meteoric water line (LMWL) equation published in Bryson and others (2007) ($\delta^2H = 7.48\ \delta^{18}O + 9.15$, referred to in this paper as LMWL-2), which was based on a subset of the data in this report from 2003 to 2005. The equation in Blasch and others (2006) of $\delta^2H = 6\ \delta^{18}O - 14$ (referred to in this paper as LMWL-1) was based on International Atomic Energy Agency (IAEA) (2016) precipitation data collected in Flagstaff between 1961 and 1974 and is not similar to the recent precipitation data. The global meteoric water line (GMWL) equation is $\delta^2H = 8\ \delta^{18}O + 10$ and is shown on figure 4 (Craig, 1961).

The IAEA data indicate a four-season distribution with distinct stable isotopic delta values for spring (March, April, and May), summer (June, July, and August), fall (September and October), and winter (November, December, January, and February) (fig. 5; Blasch and others, 2006). The current study, however, primarily separated precipitation into two seasons. It should be noted that the half-year cumulative samples collected for the current study combine spring and fall precipitation with winter and summer precipitation and this may account for some of the difference between these results and previous patterns reported for the area.

Stable isotopic delta values in precipitation along elevation gradients showed different trends for the Camp Verde-Flagstaff transect (fig. 6) and the Prescott-Chino transect (fig. 7), and the different seasonal equations are given in table 3. For the Camp Verde-Flagstaff transect, a decrease in stable isotopic delta values with increasing elevation has good correlation for the winter data and fair and poor correlation for $\delta^{18}O$ and δ^2H respectively in the summer data (fig. 6). For the summer data, the 8,100-foot sample-site precipitation showed

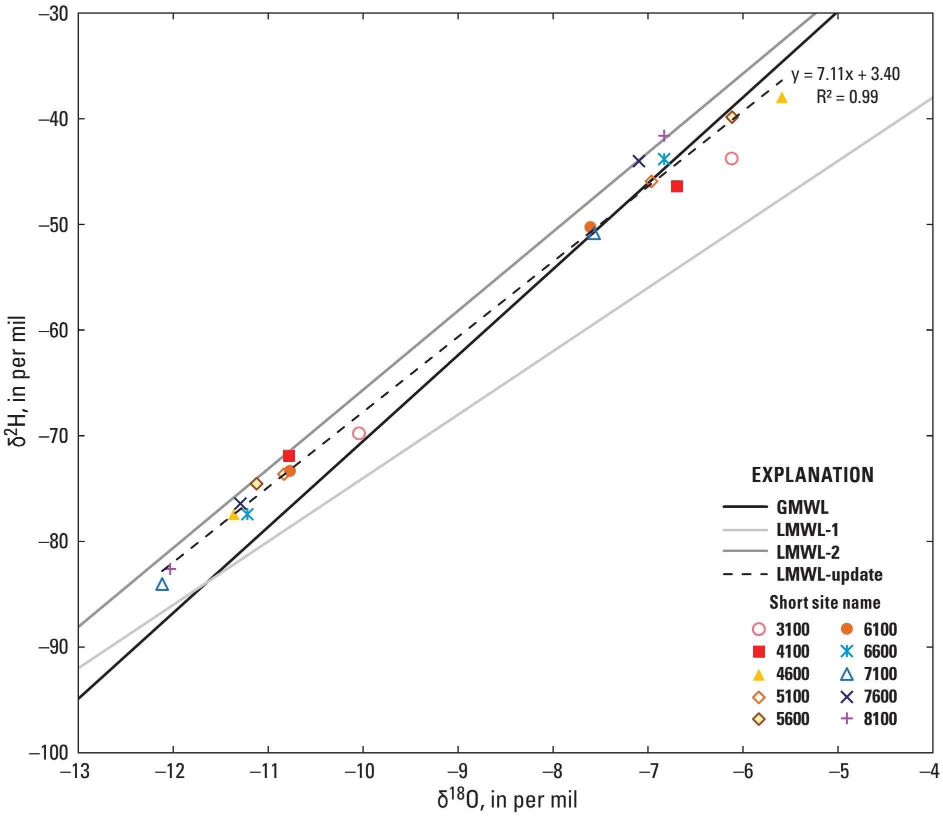


Figure 4. Graph of volume-weighted stable isotope delta values of $\delta^{18}O$ versus $\delta^{2}H$. LMWL, local meteoric water line; GMWL, global meteoric water line. LMWL-1 from Blasch and others (2006), LMWL-2 from Bryson and others (2007), and GMWL from Craig (1961).

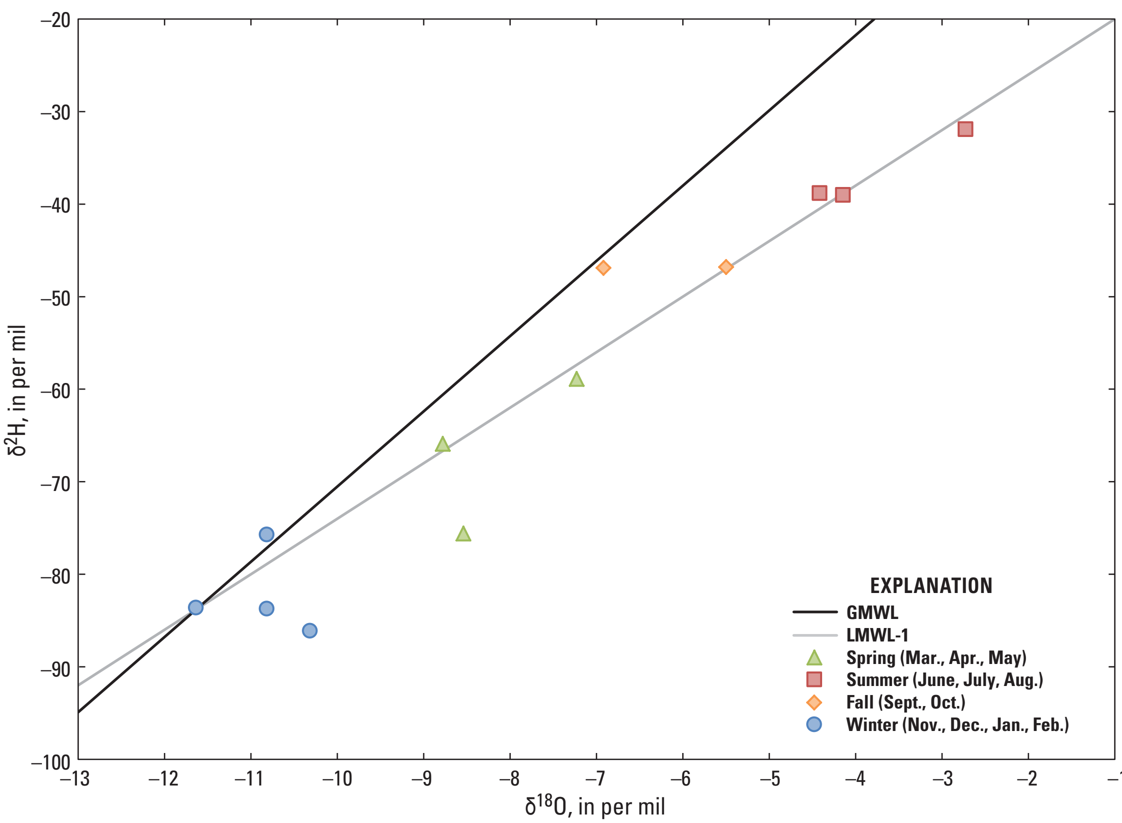


Figure 5. Graph of monthly average stable isotope values from precipitation collected by the International Atomic Energy Agency (2016) between 1961 and 1974 in Flagstaff. LMWL, local meteoric water line; GMWL, global meteoric water line. LMWL-1 from Blasch and others (2006) and GMWL from Craig (1961).

Table 3. Regression equations for stable isotope delta values relative to elevation.

[Equations from Blasch and Bryson (2007) and Bryson and others (2007) were converted to units of feet for comparison. Text in bold indicates a significant relationship, p<0.05; z, elevation; NA, not available]

Source	Season	Equation	R^2 value	Equation Number
Camp Verde-Flagstaff (this study)	Summer	$\delta^{18}O = -0.0002z - 5.87$ $\delta^{2}H = -0.0002z - 45.4$	0.42 0.01	2 3
Prescott-Chino Valley (this study)	**Summer**	**$\delta^{18}O = -0.0005z - 3.22$** **$\delta^{2}H = -0.0022z - 27.9$**	**0.97** **0.91**	4 5
Camp Verde-Flagstaff (this study)	**Winter**	**$\delta^{18}O = -0.0004z - 8.87$** **$\delta^{2}H = -0.0029z - 59.8$**	**0.83** **0.81**	6 7
Prescott-Chino Valley (this study)	Winter	$\delta^{18}O = 1E-05z - 11.3$ $\delta^{2}H = 2E-05z - 76.5$	0.018 0.0002	8 9
Blasch and others, 2006	Winter	$\delta^{18}O = -0.0007z - 6.01$ $\delta^{2}H = -0.005z - 44.6$	NA NA	10
Blasch and Bryson, 2007; Bryson and others, 2007	Winter	$\delta^{18}O = -0.00079z - 5.36$ $\delta^{2}H = -0.00579z - 39.04$	NA NA	11

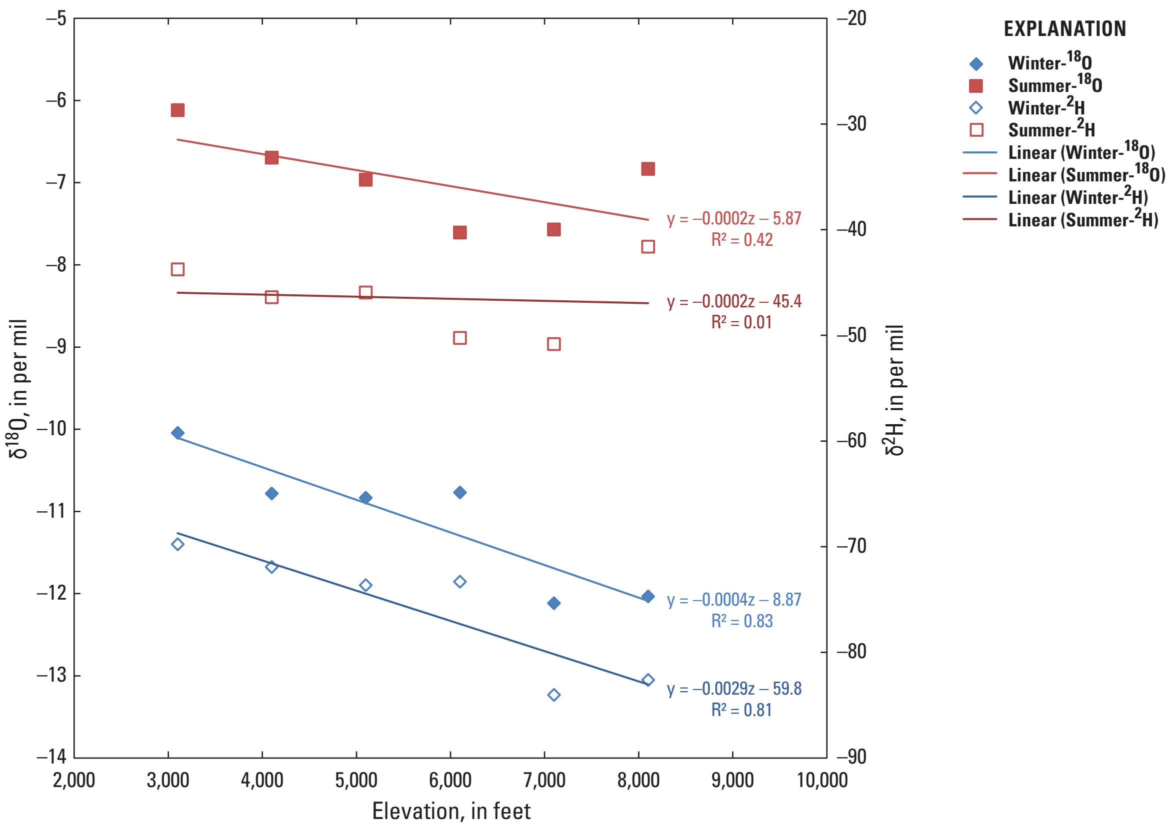


Figure 6. Graph of volume-weighted stable isotopic delta values versus elevation for Camp Verde to Flagstaff transect.

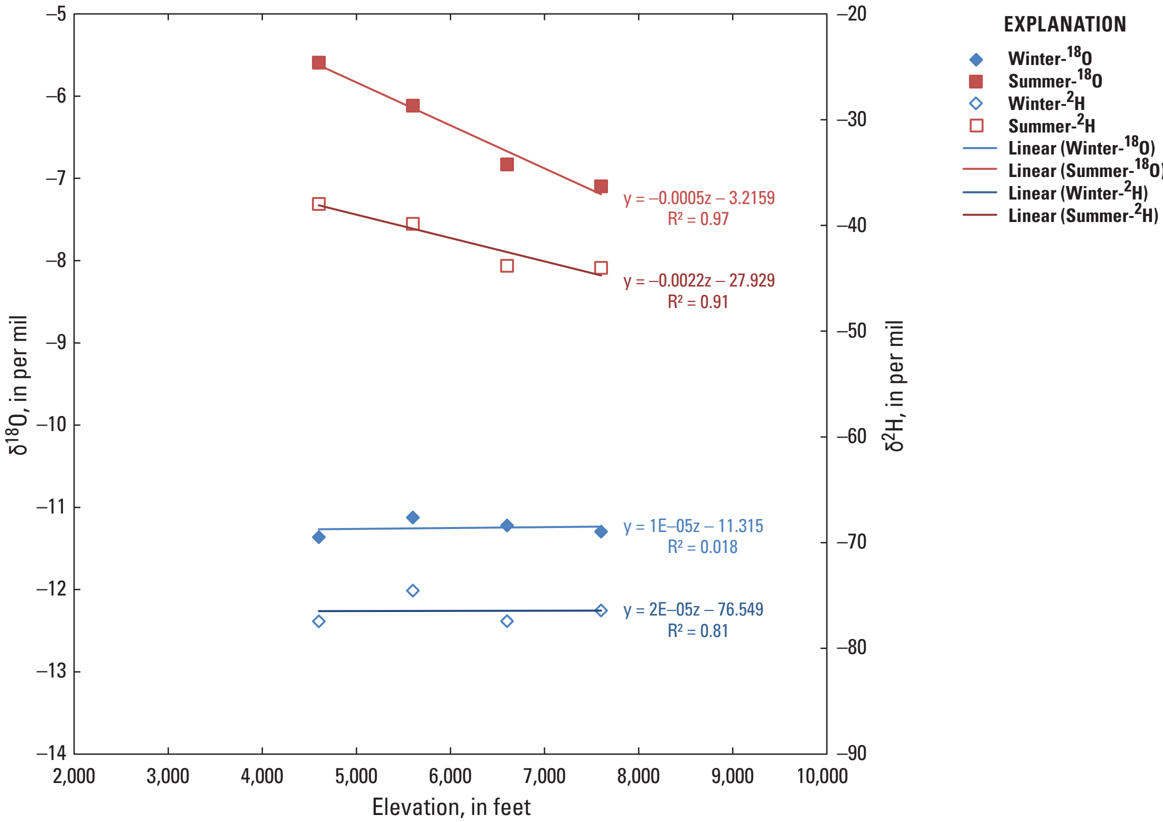


Figure 7. Graph of volume-weighted stable isotopic delta values versus elevation for Prescott to Chino Valley transect.

an increase over time in delta values compared with lower elevations, which likely contributed to the weak correlation (fig. 3).

For the Prescott-Chino Valley transect there was good correlation between a decrease in stable isotopic delta values and increasing elevation for the summer data but little to no change in stable isotopic delta values with increasing elevation for the winter data (fig. 7).

The Camp Verde-Flagstaff transect increases in elevation from the south to the north whereas the Prescott-Chino transect decreases in elevation from the south to the north. Summer storms may follow different trajectories compared with winter storms in this area and further investigation is needed to understand the differences between the elevation gradients for each transect. The updated winter equations for the Camp Verde-Flagstaff transect have gradients that are almost half and have slightly lower intercept values compared to the previously published equations by Blasch and others (2006), which only reported winter regression equations.

Conclusions

The updated local meteoric water line, using 10 additional years of volume-weighted average precipitation stable isotope delta values, was similar to the previously published equation of Bryson and others (2007). Summer precipitation stable isotope values decreased from 2003 to 2014 while winter values did not show a directional trend over the same time period.

The updated precipitation stable isotope delta values versus elevation equations predict more negative stable isotope delta values for winter precipitation along the Camp Verde to Flagstaff transect compared with previously published equations (Blasch and others, 2006; Blasch and Bryson, 2007; Bryson and others, 2007). Interpretation of stable isotope delta values in the Verde River watershed surface and groundwater using the new updated equations gives lower recharge source elevations than do the equations of the previous studies noted above. In addition, one equation was previously used to estimate recharge source elevation for the entire Verde River watershed; this may not accurately represent all areas of the watershed, however (such as in the vicinity of the Prescott-Chino transect). Precipitation samples from additional locations within the Verde River watershed (such as a transect increasing in elevation from Chino Valley north to Big Black Mesa) may provide valuable information about localized seasonal differences in precipitation isotopic gradients that would contribute to a greater understanding of recharge source locations and the greater hydrologic system.

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Appendix

Appendix tables are available online at http://dx.doi.org/10.3133/ofr20161053.

Table 1. Precipitation sample locations.

Table 2. Winter season precipitation data.

Table 3. Summer season precipitation data.

Table 4. Laboratory comparison data.

Table 5. Laboratory replicate data.

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