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SI STABLE ISOTOPES IN HYDROLOGICAL STUDIES

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Isotope hydrology of a tropical coffee agroforestry watershed: Seasonal and event-based analyses

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Abstract

Stable isotope variations are extremely useful for flow partitioning within the hydrologic cycle but remain poorly understood throughout the tropics, particularly in watersheds with rapidly infiltrating soils, such as Andisols in Central America. This study examines the fluctuations of stable isotope ratios ($\delta^{18}O$ and $\delta^{2}H$) in the hydrologic components of a tropical coffee agroforestry watershed (~1 km^2) with Andisol soils in Costa Rica. Samples were collected in precipitation, groundwater, springs, and stream water over 2 years. The local meteoric water line for the study site was $\delta^2H = 8.5\ \delta^{18}O + 18.02$ ($r^2 = 0.97$, $n = 198$). The isotope ratios in precipitation exhibited an enriched trend during the dry season and a notable depletion at the beginning of the wet season. The $\delta^{18}O$ compositions in groundwater (average = −6.4‰, σ = 0.7) and stream water (average = −6.7‰, σ = 0.6) were relatively stable over time, and both components exhibited more enriched values in 2013, which was the drier year. No strong correlation was observed between the isotope ratios and the precipitation amount at the event or daily time-step, but a correlation was observed on a monthly scale. Stream water and base flow hydrograph separations based on isotope end-member estimations showed that pre-event water originating from base flow was prevalent. However, isotope data indicate that event water originating from springs appears to have been the primary driver of initial rises in stream flow and peak flows. These results indicate that isotope sampling improves the understanding of water balance components, even in a tropical humid location, where significant variations in rainfall challenge current modelling efforts. Further research using fine-scale hydrometric and isotopic data would enhance understanding the processes driving spring flow generation in watersheds.

KEYWORDS

Costa Rica, groundwater-base flow connectivity, isotope hydrology, springs

1 | INTRODUCTION

Temporal changes in watershed hydrology occur through varying precipitation regimes and evapotranspiration amounts (Bruijnzeel, 2004; Cadol, Kampf, & Wohl, 2012). These changes reflect the impacts of climate change, management, and land use change on other hydrologic components (e.g., overland flow and base flow) and the availability of spring water, according to the size of groundwater reservoirs (Bruijnzeel, 2004; Tang, Yang, Hu, & Gao, 2011). Hydrologic processes in the tropics have been studied less (Goldsmith et al., 2012) and differ greatly from those in temperate regions, which experience relatively unstable air surface temperatures year-round and precipitation regimes that can vary greatly between seasons (Bruijnzeel, 2004;

Seasonal isotope hydrology of a tropical coffee agroforestry watershed: Separating groundwater, springs, and stream flow

Lachniet & Patterson, 2002). Seasonal isotope variations in watersheds are increasingly being investigated (Kendall, 1998), including more recently in the tropical region of Central America (Lachniet, Patterson, Burns, Asmerom, & Polyak, 2007; Lachniet, 2009; Sánchez-Murillo & Birkel, 2016; Sánchez-Murillo, Birkel, et al., 2016).

One technique for assessing temporal changes in watershed hydrology is through a dual isotope approach of oxygen-18 ($\delta^{18}O$) and deuterium ($\delta^{2}H$) in different hydrological components. Stable isotopes have been used in a variety of applications, including identifying water sources (Burns et al., 2001; Rhodes, Guswa, & Newell, 2006), water flow pathways (de Jesús-Crespo & Ramírez, 2011; Genereux & Hooper, 1998; Genereux, Jordan, & Carbonell, 2005; Goldsmith et al., 2012; Goller et al., 2005; Rodgers, Soulsby, Waldron, & Tetzlaff, 2005), and mean transit times within a watershed (McGuire, Dewalle, & Gburek, 2002; Sánchez-Murillo, Brooks, Elliott, & Boll, 2015; Turner, Macpherson, & Stokes, 1987). Mean transit times estimate how fast water travels through the watershed, the dynamics of storage processes, and types of water origins (de Jesús-Crespo & Ramírez, 2011; McGuire & McDonnell, 2006). In precipitation, deuterium excess, or *d*-excess, is a measure of the deviation of local samples from the global meteoric water line (Craig, 1961; Froehlich, Gibson, & Aggarwal, 2002) and is influenced by the physical conditions (e.g., relative humidity, sea surface temperature, and wind speed) of the moisture source, as well as the conditions along the route of the air masses (Froehlich et al., 2002; Merlivat & Jouzel, 1979). When examined in surface waters in relation to the deviation to the local meteoric water line (LMWL), *d*-excess is influenced by the local processes of re-evaporation of intercepted water, thus affecting the compositions of throughfall, stemflow, and soil evaporation (Landwehr & Coplen, 2006).

Several studies have examined the isotopic variations in precipitation between seasons and storm events in the tropical Americas (see Salati, Dall'Olio, Matsui, & Gat, 1979; Gat & Matsui, 1991; Vuille, Bradley, Werner, Healy, & Keimig, 2003; Vuille & Werner, 2005; Poveda, Waylen, & Pulwarty, 2006; Rhodes et al., 2006; Guswa, Rhodes, & Newell, 2007; Scholl, Shanley, Zegarra, & Coplen, 2009; Sánchez-Murillo et al., 2013; Sánchez-Murillo, Birkel, et al., 2016). Spatial and temporal variations in stable isotope ratios of precipitation help explain regional and local isotope variations in other hydrologic components, such as base flow, soil water, and spring flow (Araguás-Araguás & Froehlich, 1998; Dewalle, Edwards, Swistock, Aravena, & Drimmie, 1997; Froehlich et al., 2002; Lachniet & Patterson, 2002; Rozanski, Araguás-Araguás, & Gonfiantini, 1992). Among the many factors that influence stable isotope ratios in precipitation, a correlation with the precipitation amount, known as the "amount effect," has been widely used to explain isotope variations in the tropics (Araguás-Araguás, Froehlich, & Rozanski, 2000; Dansgaard, 1964; Risi, Bony, & Vimeux, 2008; Rozanski et al., 1992; Rozanski, Araguás-Araguás, & Gonfiantini, 1993; Sánchez-Murillo et al., 2013; Scholl et al., 2009). However, this correlation is primarily seen at a monthly time scale and is not as strong when examined on an event or daily-basis (Vimeux, Gallaire, Bony, Hoffmann, & Chiang, 2005; Risi et al., 2008; Wu et al., 2010; Wu, Xinping, Xiaoyan, Li, & Huang, 2014; Sánchez-Murillo, Esquivel-Hernández, et al., 2016).

Spring flow is often a significant component of water transport in watersheds (Frisbee, Phillips, White, Campbell, & Liu, 2013), but its origin and behaviour is not always clearly understood. In particular, despite the prevalence of temporary springs worldwide, few isotope studies exist that examine the influence of springs in watershed hydrology (Buttle et al., 2012; Frisbee et al., 2013). In one isotope study on spring flow in French Polynesia, the springs were sampled and found to correspond to elevational differences in precipitation, suggesting localized recharge (Hildenbrand et al., 2005). In general, however, little information about the physical processes of spring flow generation and the role of subsurface flow in tropical watersheds exists, and the processes appear difficult to characterize. Goller et al. (2005) found that precipitation in three tropical catchments in Ecuador generally infiltrated vertically during normal conditions; but during storm events shallow lateral subsurface flow became a predominant pathway. We hypothesized that deep and shallow groundwater systems in watersheds have different behaviours that influence watershed hydrology. Deeper groundwater systems contribute to base flow and often are more stable, whereas shallow groundwater systems contribute to spring flow and fluctuate more based on precipitation inputs.

In this study, we examined the temporal variations of stable isotopes in a small tropical watershed and used stable isotopes to characterize subsurface processes seasonally and event-based. Therefore, the objectives of this study were to determine how (a) seasonality influences the isotope ratios of precipitation, (b) the isotope ratios of hydrologic components compare with the seasonal patterns observed in precipitation, and (c) isotopes can explain subsurface flow influences on stream flow in watershed hydrology. We analysed the temporal variations in isotopic and hydrometric data for precipitation, stream water, groundwater, and springs in a coffee agroforestry watershed (~1 km^2) in Costa Rica over the course of 2 years (2012 and 2013) with contrasting precipitation regimes.

2 | STUDY SITE

2.1 | Climatology and isotope seasonality of precipitation in Costa Rica

This study was conducted in Costa Rica, in the Mejías Creek microwatershed, which is part of the Turrialba watershed and the larger Reventazón watershed (Figure 1). The mean annual precipitation of Costa Rica ranges from less than 1,500 to 8,500 mm depending on the area of the country (Sánchez-Murillo et al., 2013). Located across the Continental Divide, the region experiences a rainy season dominated by continental winds originating from the Pacific Ocean (Sánchez-Murillo et al., 2013). The Intertropical Convergence Zone (ITCZ) shifts throughout the year and significantly impacts the dual seasonality in this region (Lachniet & Patterson, 2002; Poveda et al., 2006). A transitional period occurs from November to January, followed by the dry season, which is dominated by the trade winds from the Caribbean Sea (Waylen & Caviedes, 1996). Isotopically depleted events generally occur after the ITCZ heads north in mid-May, whereas isotopically enriched events are frequent during the dry season (Sánchez-Murillo et al., 2013). This shift in climate patterns over the course of the year produces a variable pattern of stable isotope compositions in precipitation (Sánchez-Murillo & Birkel, 2016).

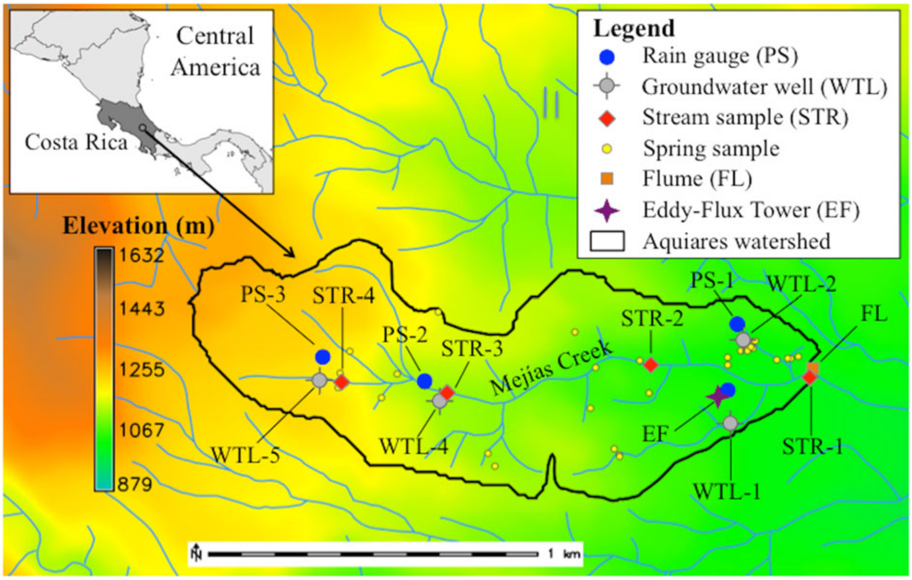

FIGURE 1 The experimental set-up of the Mejías Creek microwatershed study site, showing the study site location within Costa Rica (inset)

2.2 | Mejías Creek watershed

The Mejías Creek watershed is located near the town of Aquiares, Cartago province, and lies on the southern slope of Turrialba Volcano in the Central Caribbean region of the country. This single land use watershed is situated within a coffee agroforestry system on the Aquiares Farm, one of the largest coffee farms in Costa Rica (~700 ha). The dominant land cover is *Coffea arabica* at a planting density of 6,300 plants/ha interspersed with large, unpruned *Erythrina poeppigiana* shade trees (Goméz-Delgado et al., 2011). Coffee plants are deeply rooted, down to 4 m (Defrenet et al., 2016). Coffee leaf area index varies seasonally between 2.4 and 4.4 m^2 m^{-2} and approximately 0.67 m^2 m^{-2} for the shade trees (Taugourdeau et al., 2014).

Elevation within the watershed ranges from approximately 1,018 to 1,280 m.a.s.l., and slopes average 20% with steeper slopes of 80% in the upper portions of the watershed. The soils within the study region are classified as Andisols, using the United States Department of Agriculture soil taxonomy. This soil order is characterized as having at least 60% andic soil properties in the upper 60 cm of the soil profile (United States Department of Agriculture, 1999), with high levels of soil organic content (Kinoshita et al., 2016). Andisols in the study region tend to have very high infiltration capacity, therefore resulting in almost no overland run-off (Benegas, Ilsted, Roupsard, Jones, & Malmer, 2013; Gómez-Delgado et al., 2011; Spaans et al., 1989). In addition, macropores enhance rapid water movement by preferential flow through subsurface soils (Benegas et al., 2013; Spaans et al., 1989).

The study site is a tropical humid location with precipitation events throughout the year. The mean annual precipitation for the site was 2,706 mm during the period when this study was conducted (2,974 mm in 2012 and 2,006 mm in 2013, which was a particularly dry year). The greatest amount of precipitation falls during the rainy season from May to October. In Costa Rica, the "dry" season occurs from February to April, although in our study site we would characterize these months as more of a "drier" season relative to the rainy season. Due to the tropical humid climate of our study site, rainfall did occur during the dry season (precipitation amounts in the dry season were 633 mm for 2012 and 420 mm for 2013), but less than during the rainy season (1431 mm for 2012 and 1231 mm for 2013).

3 | METHODOLOGY

3.1 | Hydrometric measurements

Rainfall was recorded every 10 min using four ARG100 tipping buckets (R.M. Young Company, USA) distributed throughout the watershed. An eddy-flux tower at the site recorded climate and meteorological variables every 30 min. Tower instrumentation included a net radiation sensor (NR-Lite, Kipp and Zonen, the Netherlands), a temperature and relative humidity probe (HMR45C, Campbell-Scientific, USA), and a 03001 R.M Young Wind Sentry Set (USA) to measure wind speed and direction. Actual evapotranspiration data were collected at the eddy-flux tower at a reference height of 26 m, that is, above the shade trees (Gómez-Delgado et al., 2011).

Stream flow was measured with a 3.9-m long steel flume located at the watershed outlet. Water levels were measured every 10 min with a pressure transducer (PDCR-1830, Campbell-Scientific, USA) placed in a stilling well connected to the flume.

As part of a previous study, four groundwater wells placed throughout the watershed (Figure 1) were used to measure water table levels (WTL) with pressure transducers (Micro-Divers, Schlumberger Water Services, USA; see Gómez-Delgado, 2010; Gómez-Delgado et al., 2011). Wells were installed to a depth of 4 m and data were collected every half hour between 2009 and 2010. In two of the wells, the groundwater table fluctuated by more than 1.5 m between events or seasons (wells WTL-01 and WTL-04), whereas in the other two wells (WTL-02 and WTL-05) the signal was much smoother (0.5 m maximum fluctuation). These data were used as background for improved understanding of groundwater behaviour through isotopes as part of this study. More details are available in Gómez-Delgado et al. (2011) and Gómez-Delgado (2010).

Within the study watershed, 28 spring locations (see Figure 1) were recorded, all possibly contributing to stream flow, particularly during high flow and long duration events in the rainy season. Springs were surveyed systematically within the watershed and sampled at the point where water emerged from the hillslope. Of the 28 springs, 15 were continuous and 13 were ephemeral.

3.2 | Field sampling

Field sampling for stable isotopes in the study watershed is outlined in Table 1, and locations are shown on Figure 1. Precipitation samples were collected for stable isotopes on an event-basis at three locations at elevations 1,040 (PS-1), 1,128 (PS-2), and 1,210 (PS-3) m.a.s.l., corresponding with three of the rain gauges. The lowest collector was in operation from September 2011, and two additional collectors were added in November 2011 and December 2011. These passive collectors consisted of a 10-cm diameter plastic funnel equipped with a fine metal mesh atop the funnel to prevent external contamination from debris. The funnel drained via plastic tubing to a 0.5 or 1 L high-density polyethylene container. A 2-cm layer of mineral oil was placed inside the container to prevent evaporation and fractionation, according to standard sampling protocols (International Atomic Energy Agency, 2012). The collection container was placed inside a plastic shield to protect the samples from sunlight and extreme temperature variations. Precipitation samples were manually collected from the field following storm events and transported to the laboratory, where the mineral oil was separated from the water with a 500 ml separation funnel.

In the watershed, groundwater samples were collected weekly between December 2011 and December 2013 at the four-well locations proximate to the rain gauges (Figure 1). Samples were collected according to the standard protocol of purging the well prior to sampling. Manual stream water samples were collected on a weekly basis between November 2011 and December 2013 at four locations throughout the watershed (Figure 1), from the lowest elevation to the highest: STR-1 (flume), STR-2 (lower), STR-3 (middle), and STR-4 (upper), each in relative proximity to the groundwater wells. Additionally, samples were collected at the flume (see Table 1) during the rainy season on an hourly basis between November 26 and December 3, 2012 to capture variability in precipitation regimes and meteorological conditions. Samples were collected hourly during the day, hourly the first night, and every 2 hr for remaining nights (8 p.m.–6 a.m.).

A full sampling campaign of all 28 springs occurred when all springs were flowing on March 29, 2013, and three additional samples were collected at six of the main springs during the rainy season between September and November 2013. All samples were collected in 30-ml high-density polyethylene bottles, covered with parafilm to prevent evaporation, and stored upside down. Samples were refrigerated at 5 °C until laboratory analysis.

The total collection consisted of 275 precipitation samples representing 149 storm events, 327 groundwater samples, 56 spring samples, and 380 stream water samples.

3.3 | Stable isotope analyses

Stable isotope analyses of hydrogen (δ^2H) and oxygen ($\delta^{18}O$) were conducted in the Idaho Stable Isotopes Laboratory at the University of Idaho in Moscow, Idaho using a Cavity Ring-Down Spectroscopy water isotope analyser L1120-i (Picarro, USA) for samples collected in 2011. For samples collected in 2012 and 2013, analyses were conducted at the Stable Isotope Research Group facilities at the National University (UNA) in Heredia, Costa Rica using a Cavity Ring-Down Spectroscopy water isotope analyser L2120-i (Picarro, USA). The same primary and secondary standards were used at both locations to ensure comparison between laboratories. The secondary standards were Moscow tap water ($\delta^{18}O$ = −17.0‰, δ^2H = −131.4‰), deep ocean water ($\delta^{18}O$ = −0.2‰, δ^2H = −1.7‰), and Commercial Bottled Water (CAS, $\delta^{18}O$ = −8.3‰, δ^2H = −64.3‰). Moscow tap water and deep ocean water standards were used to normalize the results to the Vienna Standard Mean Ocean Water–Standard Light Antarctic Precipitation scale, whereas CAS was used as a quality control and

TABLE 1 Information on field sampling conducted for stable isotopes at the study site

Hydrologic component sampled	Sampling period	Frequency of sampling	Location(s)/elevations
Precipitation	Sept. 2011–Dec. 2013 (upper two elevations sampled after Dec. 2011)	Event-basis	PS-1 (1,040 m.a.s.l.) PS-2 (1,128 m.a.s.l.) PS-3 (1,210 m.a.s.l.)
Groundwater	Dec. 2011–Dec. 2013	Weekly	WTL-1 (1,029 m.a.s.l.) WTL-2 (1,032 m.a.s.l.) WTL-4 (1,122 m.a.s.l.) WTL-5 (1,204 m.a.s.l.)
Stream water	Nov. 2011–Dec. 2013	Weekly	Flume–STR-1 (1,018 m.a.s.l.) STR-2 (1,042 m.a.s.l.) STR-3 (1,120 m.a.s.l.) STR-4 (1,191 m.a.s.l.)
	Nov. 1, 2011	Hourly	Flume
	Nov. 26–Dec. 3, 2012	Hourly during the day; every 2 hr at night	Flume
	Dec. 9–13, 2013	Hourly from 4 a.m. to 8 p.m. plus one sample at midnight	Flume
Overland flow	Nov. 9, 2012	Once	Random grab samples where observed
Spring flow	Mar. 29, 2013 Sept.–Nov. 2013	Once Three times	28 springs in watershed 6 main springs

Note. PS = precipitation sample; WTL = groundwater sample; STR = stream water sample.

drift control standard. The analytical long-term uncertainty was ±0.1‰ (1σ) for $\delta^{18}O$ and ± 0.5‰ (1σ) for $\delta^{2}H$. Stable isotope compositions are presented in delta notation (‰, per mil) with the ratios (R) of $^{18}O/^{16}O$ and $^{2}H/^{1}H$, relative to Vienna Standard Mean Ocean Water (Dansgaard, 1964). *D*-excess was calculated for all samples for a comparison of the proportions of $\delta^{2}H$ to $\delta^{18}O$ in water samples as *d*-excess = $\delta^{2}H - 8 \times \delta^{18}O$ (Dansgaard, 1964).

We calculated the mean transit time (τ), or the approximate time for a water molecule to travel through the watershed to a certain point, for various hydrologic components, as $\tau = c^{-1*}\sqrt{\left[(D)^{-2}-1\right]}$, where *c* is the radial frequency constant (2π/365) in rad per degree and *D* is equal to the standard deviation of all sample point stable isotope values (either stream or groundwater) divided by the standard deviation of all precipitation sample values (McGuire, 2004; Sánchez-Murillo et al., 2015). We used this τ model because the observed data exhibit a W-shaped pattern, and the model, therefore, is primarily a preliminary descriptor of the mean transit time for the watershed. We calculated the error (ε) of τ by estimating +/−0.2‰ due to instrument and sampling errors assuming a normally distributed error function.

A base flow hydrograph separation was conducted using an end-member isotope mixing approach to gain further insight into the processes driving stream flow and subsurface water contributions. We followed the methodology outlined by Sklash and Farvolden (1979) and relied on previously identified assumptions that the isotope ratios of pre-event and event water differ significantly, the isotope composition of both pre-event and event water remains relatively constant, soil water input is not significant, and surface storage inputs to stream flow are not significant (Buttle, 1994; Klaus & McDonnell, 2013; Moore, 1989).

Historic data of monthly precipitation composite samples were analysed from the Global Network of Isotopes in Precipitation (GNIP) database, maintained by the International Atomic Energy Agency and the World Meteorological Organization. This dataset was analysed to determine if similar patterns were observed prior to the study years. Data were recorded (n = 28) for Turrialba, Costa Rica, approximately 10 km from the project site, from February 2002 to January 2004.

3.4 | Statistical analysis

We applied a simple linear regression between $\delta^{18}O$ and $\delta^{2}H$ ratios in precipitation to calculate the LMWL for the study site. A Pearson correlation was calculated to determine potential relationships between the observed isotope ratios in observed hydrologic components and surface meteorological data at the study site. We assessed the correlations between $\delta^{18}O$, $\delta^{2}H$, and *d*-excess in precipitation, stream water, and groundwater; month of year; and meteorological parameters. All statistical analyses were conducted with the statistical package R, version 3.1.0.

4 | RESULTS

4.1 | Seasonal variation of isotopes in precipitation

On an annual time scale, the amount of precipitation in 2013 (2,006 mm) was approximately two-thirds of the amount in 2012 (2,974 mm). During all seasons, less rain fell in 2013 than in 2012. The seasonal and annual precipitation totals along with stable isotope data are presented in Table 2. The average event size for the rainy season in 2013 was 11 mm, which was the lowest for all seasons during the study period. December 2013 yielded 102 mm of precipitation, significantly less than during December 2012, when 301 mm were recorded.

The isotope compositions varied from 2012 to 2013, with a depletion of the annual $\delta^{18}O$ and $\delta^{2}H$ compositions and a decrease in the average annual *d*-excess value in 2013. The LMWL of the Aquiares study site was $\delta^{2}H = 8.5\ \delta^{18}O + 18.0$ (r^2 = 0.97, N = 198; Figure 2a), revealing that both the slope and intercept are greater than the GWML. The LMWL for each sample year is provided in Table 2. For comparison, the LMWL of Turrialba derived from GNIP data (2002–2004) was $\delta^{2}H = 8.6\ \delta^{18}O + 16.5$ (r^2 = 0.99), consistent with our finding. The average $\delta^{18}O$ composition in precipitation during the study period was −6.1‰ (σ = 3.6), with a range of −18.5‰ to −0.3‰ (see Figure 2b for seasonal variation of the $\delta^{18}O$ compositions). The average $\delta^{2}H$ composition in precipitation was

TABLE 2 Seasonal precipitation data throughout the study period comparing precipitation amount, $\delta^{18}O$ ratios, $\delta^{2}H$ ratios, *d*-excess, and LMWL

Dates		Nov. 2011–Jan. 2012	Feb.–Apr. 2012	May–Oct. 2012	Nov. 2012–Jan. 2013	Feb.–Apr. 2013	May–Oct. 2013	2012	2013
Season		Transition	Dry	Rainy	Transition	Dry	Rainy	Annual	Annual
Precipitation	Total amount (mm)	855	633	1,431	790	420	1,231	2,974	2006
	Average event size (mm)	13	15	13	15	13	11	16	14
	Maximum event size (mm)	69	118	182	54	85	52	182	113*
$\delta^{18}O$ (‰)	Average	−6.74	−2.27	−8.96	−3.37	−2.90	−6.90	−5.53	−6.13
	Minimum	−13.95	−4.52	−18.52	−8.33	−15.49	−15.76	−18.52	−15.76
	Maximum	−2.08	−1.16	−3.93	−1.00	−0.45	−0.29	−1.16	−0.29
	σ	3.68	0.85	3.92	1.79	3.87	3.41	3.99	3.53
$\delta^{2}H$ (‰)	Average	−39.0	0	−56.5	−7.1	−1.5	−42.6	−27.0	−34.72
	Minimum	−99.5	−20.8	−136.4	−49.9	−114.2	−117.8	−136.42	−117.8
	Maximum	9.3	11.4	−12.1	13.7	13.1	13.4	11.44	13.66
	σ	32.78	8.95	33.3	15.79	34	27.44	34.13	30.21
d-excess (‰)	Average	14.88	18.2	15.18	19.91	21.68	12.56	17.28	14.34
LMWL	Slope	8.9	9.9	8.4	8.5	8.6	8	8.5	8.4
	Intercept	20.7	22.6	18.5	21.6	23.5	12.2	19.9	17

Note. Annual data are presented for 2012 and 2013. ANOVA for $\delta^{18}O$ ratios in precipitation by season: F = 6.157, p < .0001. LMWL = local meteoric water line.

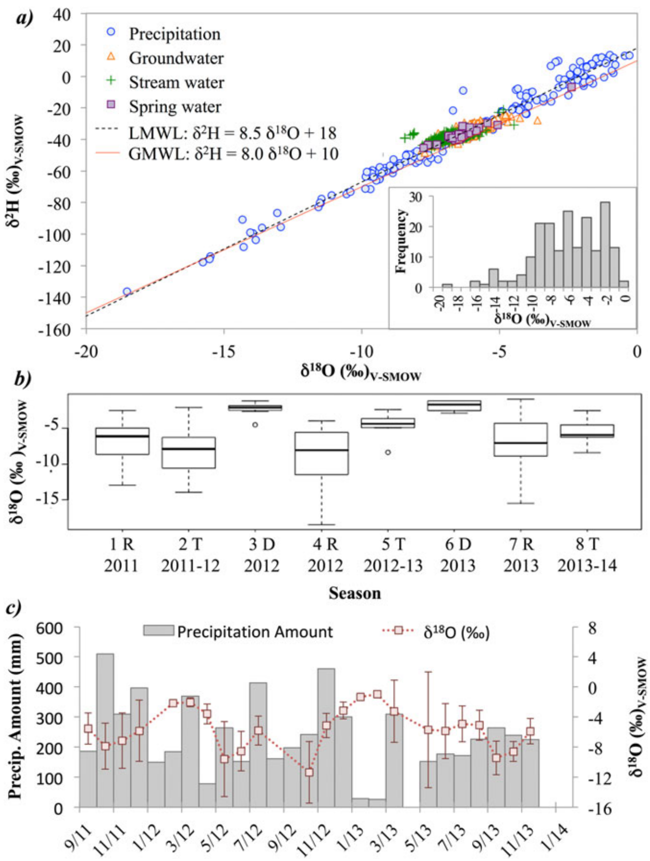

FIGURE 2 (a) LMWL for Aquiares study site with GMWL (Craig, 1961) for comparison in red. Inset shows distribution of δ^{18}O ratios. (b) Temporal variation of average δ^{18}O ratios in precipitation by season during the sampling period. The labels are preceded by a unique number; a letter denoting the season (R = rainy, T = transitional, and D = dry), and the year. (c) Monthly integrated δ^{18}O ratios in precipitation compared with average monthly precipitation amounts from historic Global Network of Isotopes in Precipitation data. LMWL = local meteoric water line; GMWL = global meteoric water line

−33.4‰ (σ = 31.1), with a range of −136.4‰ to +13.7‰. The average *d*-excess value during the study period was +15.0‰ (σ = 5.3).

Monthly averaged data for δ^{18}O collected from this study and from the GNIP data both exhibited a seasonal W pattern corresponding to the time of the year, with a δ^{18}O enrichment during the dry season and a depletion during the wet season, particularly in May to June and September to October (Figure 2c). Pearson correlations conducted on δ^{18}O, δ^{2}H, *d*-excess, and surface meteorological parameters showed a correlation between precipitation amount and δ^{18}O on a monthly scale (p = .0001) but not on an event-basis (p = .44; see Figure 3).

4.2 | Seasonal variations of isotopes in groundwater

Groundwater isotope compositions were significantly enriched in 2013 compared with 2012 (p < .05 for δ^{18}O and p < .10 for δ^{2}H; Table 3). All data plot closely along the LMWL (Figure 2a) and indicate only slight enrichment compared to precipitation isotope ratios after infiltration and evaporation processes. Isotopes were more noticeably enriched during the 2013 rainy season, which was the drier year (Table 4). Wells WTL-1 and WTL-4 were more enriched than WTL-2 and WTL-5 during the course of the year, particularly during the rainy season (see Figure 4a). Wells WTL-1 and WTL-4 also have experienced more fluctuating groundwater levels and a faster response to precipitation events than wells WTL-2 and WTL-5 (Gómez-Delgado et al., 2011). The approximate mean transit times (τ) of groundwater wells WTL-1 and WTL-4 (less than a year) also were shorter than of wells WTL-2 and WTL-5 (approximately 1 year, see Table 3), which could correspond to the difference in these observed responses. Isotopic compositions were significantly correlated between all wells (p < .01). The Pearson product–moment correlations indicate a correlation between both δ^{18}O and δ^{2}H ratios in groundwater and the month of the year (p < .01). No correlation was noted between δ^{18}O ratios and any meteorological parameters measured on site.

4.3 | Seasonal variations of isotopes in stream water

The isotope ratios of stream water averaged −6.7‰ (σ = 0.6) with a range of −8.4‰ to −4.5‰ for δ^{18}O and −38.3‰ (σ = 0.3) with a range of −45.9‰ to −21.2‰ for δ^{2}H (Table 4). Isotope ratio data also plotted along the LMWL (Figure 2), which reveals that little enrichment occurred during the hydrological processes. In the stream samples, the elevation was correlated with the isotopic ratios of the water (p < .10; see Table 5). The τ value for all stream water samples was calculated to be approximately 1.0 year, which is similar to the τ values for groundwater.

Stable isotope ratios collected from weekly stream water samples over the course of the study are shown in Figure 4b. Consistent with groundwater, the isotope ratios in the stream were more enriched in 2013 than in 2012 (p < .05 for δ^{18}O). For the stream water, the means of δ^{18}O at the four sample locations were not statistically significantly different (ANOVA, p < .05). The means of the δ^{18}O compositions between the stream samples and the proximate groundwater wells also were not statistically significantly different (t test, p < .05; Figure 4a). However, one exception existed at the highest groundwater well (WTL-5) and the upper sample point (STR-4; t test, p = .37). Pearson correlations between stream water ratios and other parameters reveal a significant correlation between isotope ratios and the month of the year (p < .01).

4.4 | High-frequency isotope sampling in stream water

Hourly δ^{18}O compositions in stream water from November 26 to December 1, 2012 closely mirrored the stream flow at the flume location, and both responded rapidly to precipitation (see Figure 5a,b). End-member base flow separation using these δ^{18}O compositions over the course of three storm events indicates that the majority of water entering the stream was pre-event water, except during the stream flow peaks when event water contributed most of the flow (see Figure 5c). The base flow separation included the stream peaks on November 28–30, 2012 with the largest peaks in precipitation at 21:00, 15:00, and 2:00, respectively. The δ^{18}O composition for pre-event water was taken at 10:00 November 27, when the δ^{18}O

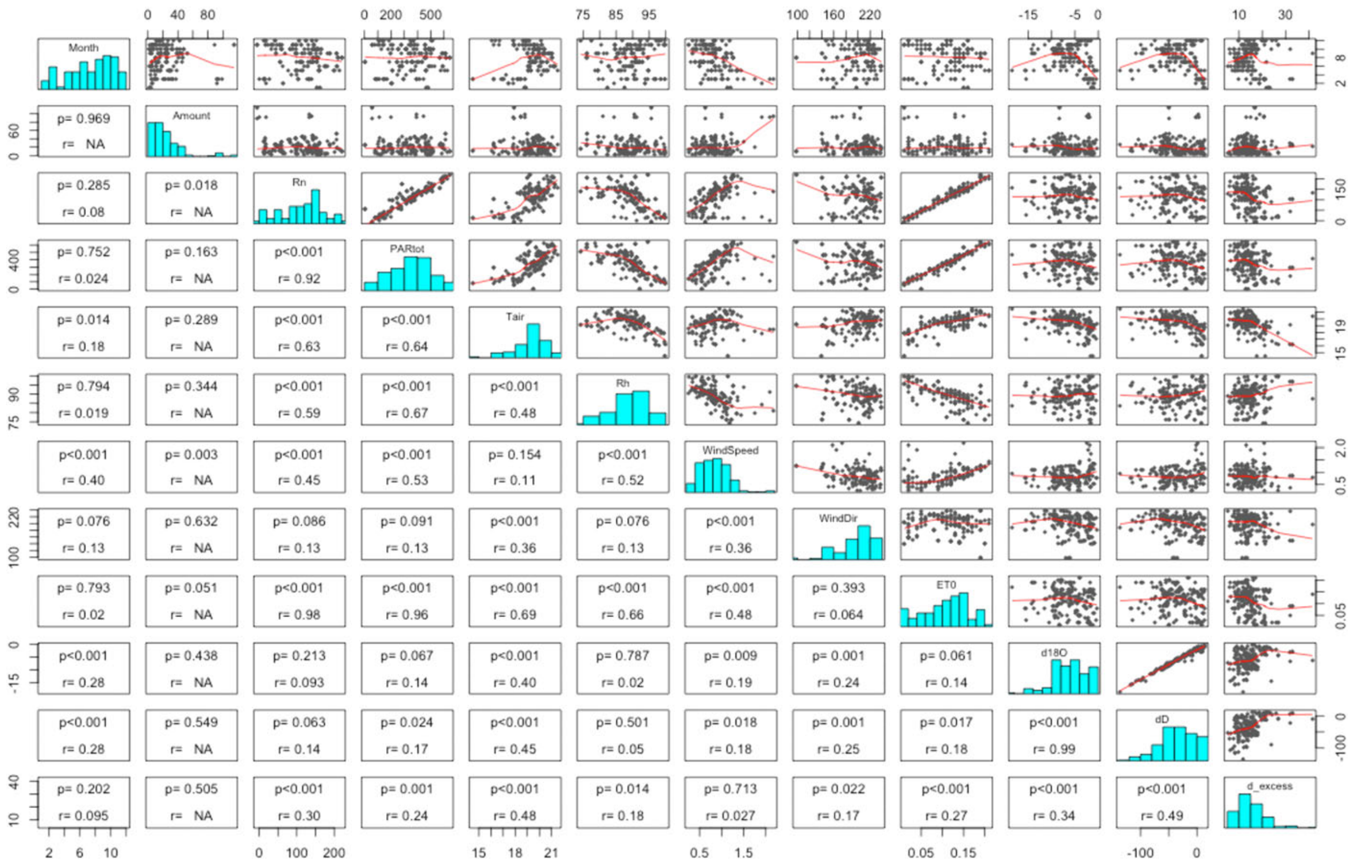

FIGURE 3 Correlation matrix of meteorological factors and stable isotope (δ^{18}O and δ^{2}H) ratios in precipitation. The lower panel contains Pearson coefficients and associated *p* values, and histograms show distribution of data. Only factors that were correlated with δ^{18}O, δ^{2}H, or *d*-excess are included in this matrix. Month = calendar month of precipitation sample; amount = precipitation amount; Rn = net radiation; PARtot = photosynthetically active radiation total; Tair = surface air temperature; Rh = relative humidity; WindSpeed = wind speed; WindDir = wind direction; ET0 = potential evapotranspiration; d18O = δ^{18}O value, dD = δ^{2}H value, *d*-excess = deuterium excess

composition was relatively stable. During peak flows, the maximum percent of event water was at 91.5% of total water at 22:00 on November 28.

4.5 | Spring flow

Stable isotope ratios for spring water averaged −6.8‰ (σ = 0.32) for δ^{18}O and −36.5‰ (σ = 1.64) for δ^{2}H. One additional sampling campaign was conducted on six of the primary perennial springs from November 27 to 29, 2013. On November 27, a preliminary sample was conducted of all six springs (δ^{18}O average was −5.4‰, σ = 1.6, with a range of −6.7‰ to −2.4‰). On November 28, sampling was conducted at the beginning and middle of a significant precipitation event (114.9 mm). Post-event sampling was conducted on November 29. As the springs increased in flow, at the beginning of the event during the rising limb of the hydrograph, samples

TABLE 3 Data for groundwater wells at the study site, including elevation, mean transit time (τ), and average isotope ratios for 2012 and 2013 with standard deviations in parentheses

Groundwater well	Elevation (m)	τ (days)*	2012			2013		
			δ^{18}O mean (‰)	δ^{2}H mean (‰)	*d*-excess (‰)	δ^{18}O mean (‰)	δ^{2}H mean (‰)	*d*-excess (‰)
WTL-1	1,029	345	−6.60 (0.55)	−36.6 (4.39)	16.26 (1.30)	−5.96 (0.47)	−33.7 (3.00)	13.90 (2.69)
WTL-2	1,032	367	−6.77 (0.21)	−37.4 (1.84)	16.76 (1.68)	−6.23 (0.48)	−36.1 (2.52)	13.67 (2.84)
WTL-4	1,122	279	−6.54 (0.60)	−35.8 (4.68)	16.49 (1.42)	−5.64 (0.55)	−30.1 (2.93)	14.97 (2.39)
WTL-5	1,204	374	−7.22 (0.56)	−41.0 (3.83)	16.74 (2.11)	−6.71 (0.44)	−38.8 (1.73)	14.86 (2.98)
WTL-1 & WTL-4			−6.57 (0.57)	−36.2 (4.52)	16.37 (1.36)	−5.82 (0.53)	−31.9 (3.44)	14.58 (2.59)
WTL-2 & WTL-5			−6.99 (0.48)	−39.2 (3.49)	16.76 (1.89)	−6.50 (0.51)	−37.6 (2.49)	14.46 (2.94)
All wells			−6.78 (0.57)	−37.6 (4.30)	16.56 (1.64)	−6.17 (0.62)	−34.8 (4.11)	14.52 (2.77)

Note. ANOVA results for each well series: F = 31.78, p < .0001. WTL = water table levels.

*ε ranged from −25 to +16 days.

TABLE 4 Seasonal isotope ratios for groundwater and stream water at the study site for the sampling period with standard deviation in parentheses

			Groundwater		Stream water	
Season	Months	Year	$\delta^{18}O$ average (‰)	δ^2H average (‰)	$\delta^{18}O$ average (‰)	δ^2H average (‰)
Dry	Feb.–Apr.	2012	−7.36 (0.27)	−41.9 (2.21)	−6.83 (0.54)	−38.1 (4.57)
Rainy season	May.–Oct.	2012	−6.79 (0.51)	−38.0 (3.96)	−7.17 (0.42)	−39.7 (1.71)
Transition	Nov.–Jan.	2012–2013	−6.50 (0.56)	−35.0 (3.63)	−6.90 (0.61)	−38.4 (3.20)
Dry	Feb.–Apr.	2013	−6.39 (0.55)	−34.8 (4.17)	−7.00 (0.39)	−38.6 (2.84)
Rainy season	May.–Oct.	2013	−5.99 (0.61)	−34.6 (4.54)	−6.35 (0.33)	−37.5 (1.67)
Transition	Nov.	2013	−6.04 (0.39)	−34.9 (2.69)	−6.30 (0.24)	−37.3 (1.32)
Dry	Feb.–Apr.	All	−6.90 (0.59)	−37.8 (4.79)	−6.91 (0.48)	−38.3 (3.84)
Rainy	May–Oct.	All	−6.31 (0.69)	−36.0 (4.62)	−6.68 (0.55)	−38.4 (2.01)
Transition	Nov.–Jan.	All	−6.35 (0.55)	−35.0 (3.34)	−6.69 (0.59)	−38.1 (2.75)
Annual		2012	−6.77 (0.57)	−37.6 (4.30)	−6.97 (0.48)	−38.9 (0.70)
Annual		2013	−6.14 (0.62)	−34.7 (4.11)	−6.46 (0.70)	−37.6 (3.53)
All data			−6.42 (0.67)	−36.0 (4.41)	−6.72 (0.55)	−38.3 (2.66)

*ε ranged from −35 to +10 days.

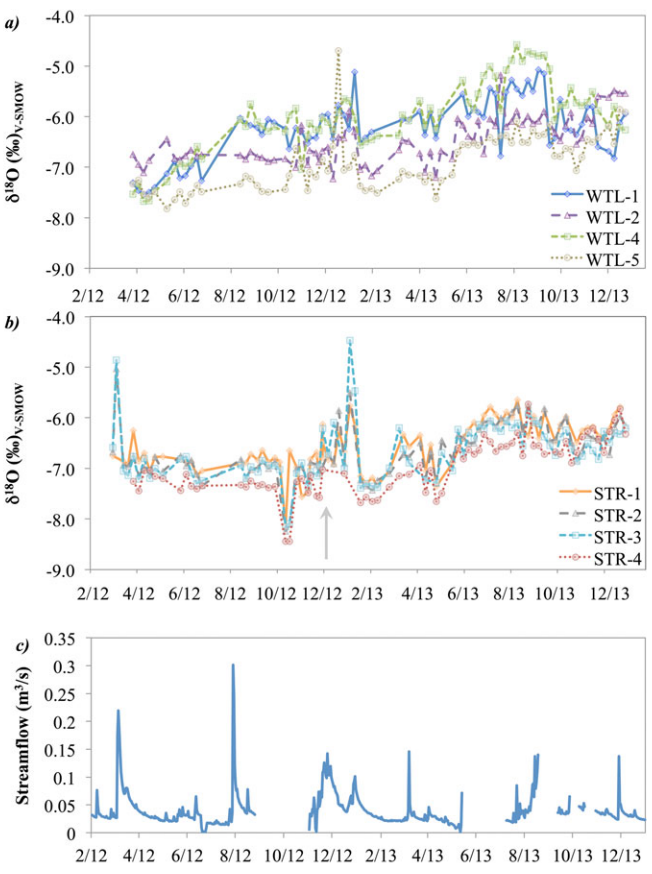

FIGURE 4 Comparison of (a) $\delta^{18}O$ ratios in groundwater, collected weekly between March 2012 and December 2013, (b) $\delta^{18}O$ ratios in stream water, collected between February 2012 and December 2013 (grey arrow indicates timing of event featured in Figure 5), and (c) stream flow measured at the flume

became more depleted in $\delta^{18}O$ and δ^2H relative to the pre-event samples. As flow started to subside, samples became more enriched, and in the day after the event, samples were more enriched than during the storm.

5 | DISCUSSION

5.1 | The influence of seasonality on the isotope ratios of precipitation

Stable isotope studies related to precipitation within Costa Rica were studied by Sánchez-Murillo et al. (2013), who determined the LMWL for the Central Caribbean region to be δ^2H = 8.17 $\delta^{18}O$ + 12.3, compared to a LMWL of δ^2H = 8.5 $\delta^{18}O$ + 18.0 for our project site. Watersheds on the Caribbean slopes of Costa Rica are influenced predominantly by the transport of moisture from the Caribbean Sea to the lowlands. Within this region of Costa Rica, the absence of significant orographic barriers and abundant vegetation results in isotopically enriched precipitation in comparison with precipitation over the Pacific slope (Sánchez-Murillo & Birkel, 2016).

During the sampling period, varying precipitation characteristics exhibited an annual and a seasonal influence on the stable isotope compositions. Less precipitation in 2013 corresponded with a depletion in the average annual isotope ratios, contrary to what was observed on a seasonal scale. Sánchez-Murillo, Birkel, et al. (2016) also found climate anomalies throughout Costa Rica with less precipitation volume in 2013 than in previous years. The regression slopes were similar for both years in our study, but the lower LMWL intercept and average *d*-excess value for 2013 characterize the drier year. The overall high LMWL slopes (>8) observed at the study site were due to the sample ratios with high *d*-excess values during the dry season and potentially an artefact introduced due to small precipitation events. Others also determined that enhanced moisture recycling processes, including strong localized convective events due to evapotranspiration fluxes, resulted in high LMWL intercepts and slopes, whereby *d*-excess increased as a result (Froehlich et al., 2002; Gat & Matsui, 1991). Therefore, the increases in the *d*-excess value that we observed during the dry and transitional seasons are likely indicative of increased continental moisture recycling (Froehlich et al., 2002;

TABLE 5 Key data for stream sample locations at the study site including elevation of sample locations, mean transit time (τ), and average isotope ratios for duration of sampling period

Stream location	Elevation (m)	τ (days)*	2012			2013		
			$\delta^{18}O$ mean (‰)	$\delta^{2}H$ mean (‰)	*d*-excess (‰)	$\delta^{18}O$ mean (‰)	$\delta^{2}H$ mean (‰)	*d*-excess (‰)
Flume (STR-1)	1018	425	−6.82	−38.4	16.16	−6.35	−36.6	14.14
Lower (STR-2)	1042	367	−6.93	−38.1	17.33	−6.48	−37.8	14.01
Middle (STR-3)	1120	384	−6.85	−38.2	16.58	−6.44	−37.2	14.31
Upper (STR-4)	1191	388	−7.40	−41.6	17.53	−6.74	−39.6	14.36

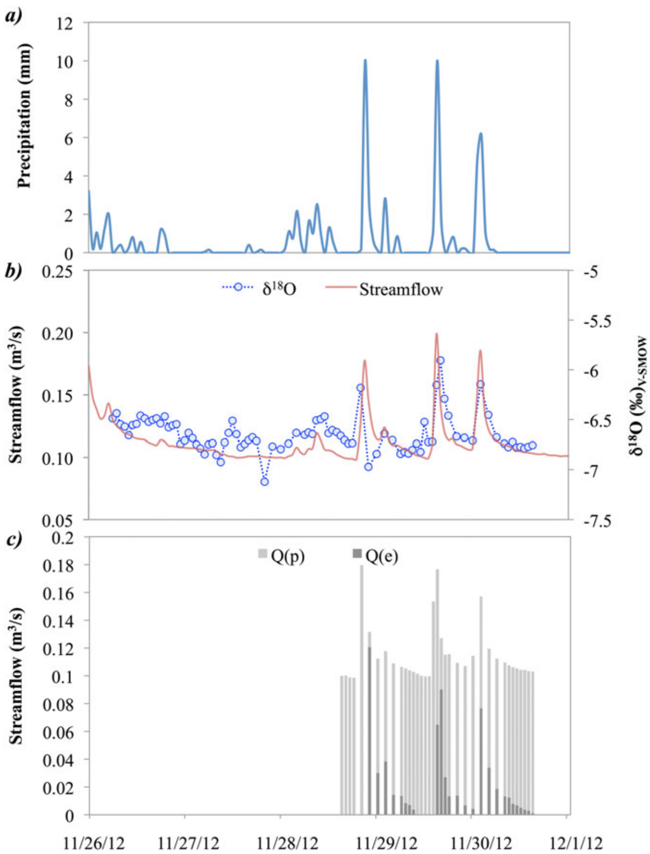

FIGURE 5 Comparison of (a) precipitation amount in the Aquiares watershed, (b) stream flow at the flume compared with hourly $\delta^{18}O$ ratios in stream water, and (c) base flow separation from November 26 to December 1, 2012. Q(p) is pre-event water and Q(e) is event water

Gat, Bowser, & Kendall, 1994; Sánchez-Murillo et al., 2017). The average *d*-excess value (+15.0‰) we observed confirms that moisture recycling is an important component of the local hydrology in this region.

Seasonality influenced the $\delta^{18}O$ values in precipitation, when examining the distribution of values in precipitation by month (Figure 2b). Depletion during the rainy season relative to the dry season is evident. As observed in Figure 2c, the isotope ratios in the precipitation events occurring during the dry season (December to April) corresponded to small, enriched events. When the ITCZ travels north over Costa Rica in mid-May, a strong isotopic depletion was observed. This depletion has been attributed to the considerable increase in precipitation amounts (Sánchez-Murillo et al., 2013; Sánchez-Murillo, Birkel, et al., 2016). The shift of the ITCZ, combined with midsummer drought conditions (Magaña, Amador, & Medina, 1999) across Central America, result in greater variability of isotopes during the wet season, compared to the dry season.

Seasonal isotopic variability is also evident when comparing the data by the Costa Rican seasons identified by Solano and Villalobos (2000) (Table 2). The slope and intercept of the LMWL for each season show the shifting dynamics of isotope ratios in precipitation between seasons. Both the slope and intercept were lowest in the rainy season, increased in the transitional season and were greatest during the dry season. Goldsmith et al. (2012) explained similar seasonal differences in Mexico due to similar physical processes that we experienced at our site; higher *d*-excess compositions in the dry season could be due to isotopically enriched precipitation events originating from the northeast that experienced moisture recycling. Westerly sourced events that occurred during the rainy season resulted in more depleted precipitation compared to the dry season. Additionally, the seasonal variation could be explained by the source of the air mass (i.e., the Caribbean Sea to the east or the Pacific Ocean to the west), which changes by season with the shifting ITCZ and the influence of the trade winds. Our results confirm these previous findings.

We did not see any amount effect when data were analysed on an event or daily basis, similar to Sánchez-Murillo, Birkel, et al. (2016), suggesting that other meteorological factors were influencing the isotope variations within the precipitable water column.

5.2 | The seasonality of other hydrologic components

Similar to precipitation, the isotope ratios in groundwater changed seasonally. However, unlike precipitation, where samples were more enriched in the dry season, groundwater samples were more enriched during the wet season and appeared relatively more stable (see Figure 4a and Table 3), suggesting a delay in response to precipitation ratios and possible mixing with subsurface water sources (i.e., springs or deeper groundwater). The τ on the order of approximately 1 year indicates this delayed response of precipitation in groundwater. However, groundwater and stream water had more enriched compositions at the end of 2013, during the rainy season, when compared to the same time period in 2012. This suggests that precipitation of the same year was an important contributor to groundwater and stream water components in the watershed. In addition, we observed a faster response to precipitation when examining the water levels in WTL-1 and WTL-4 over the course of the year, although these fluctuations were not represented in the τ that was calculated for both locations.

The stream water samples became progressively more enriched moving downstream. These ratios were influenced directly by the isotope ratios in precipitation, ratios in the shallow subsurface possibly changed by evaporation processes, and ratios of water residing in the watershed longer. In addition, these observations may be influenced by a higher rate of foliage re-evaporation of intercepted rainfall and surface soil water evaporation in the bottom of the watershed, possibly due to a higher temperature and potential evapotranspiration (the elevation gradient in the watershed is approximately 300 m). Pearson correlations between $\delta^{18}O$, $\delta^{2}H$, and *d*-excess in stream water and meteorological parameters reveal a significant correlation between isotope ratios and the month of the year, as was also noted in precipitation and groundwater. Additionally, we observed a correlation between the isotope ratios in stream water and the precipitation amount, despite no significant correlation between the isotope ratios in precipitation and the precipitation amount. This observation could be due to the result that with more precipitation, the stream composition changed as new event water recharged the shallow and deep groundwater systems. Therefore, as old water flowed into the stream, more enriched isotopic ratios of the stream water occurred. The τ values for stream water were similar to those of groundwater. Overall, the strong correlation observed between stream locations and proximate groundwater locations indicates a strong influence of subsurface contributions to the stream.

5.3 | The role of subsurface flow in the watershed

Spring flow sampling provided insight into the influence of precipitation on springs, and thus the streams. The placement of the spring water isotope ratios along the LMWL indicates that the springs are representative of local precipitation and therefore originate from within the watershed. These ratios and the response shown in the event sampling provide evidence that the source of spring water is a perched water table system with a fast connection to local precipitation rather than a seasonal, deeper groundwater system possibly connected beyond the watershed boundaries. These results are similar to those in French Polynesia by Hildenbrand et al. (2005), who determined that springs originated from local precipitation in their study watershed.

The slight depletion of isotope ratios in spring water during the sampled storm event is likely due to the input of precipitation, as the precipitation isotope ratios for that event were depleted (−8.4‰ for $\delta^{18}O$) compared to spring water. As flow started to subside, samples became more enriched, and in the day after the event, samples remained enriched compared to the storm. This response of the isotope ratios in the spring water reveals the rapid influence that precipitation had on spring flow. The springs did not appear to significantly influence the stream water signal during regular flow but did influence the storm flow (i.e., peak flow) signals.

Results from high frequency stream water sampling (Figure 5) provided further insight into the role of subsurface flow in the watershed. These samples reveal a strong connectivity between stream water and precipitation, where shallow subsurface flow (i.e., springs) contribute to peak flows. The initial peak exhibited an approximate 1-hr lag in event water. This lag is not compatible with overland flow, which would be nearly immediate, nor with the groundwater system feeding the stream, which has a τ on the order of a year. Therefore, the likely explanation for this lag is via springs, consisting primarily of event water, contributing to the water level and isotope peaks. After the initial rain event, the second two rain events resulted in an event water contribution that mirrored the stream water peaks.

Gómez-Delgado et al. (2011) and Welsh et al. (in preparation) partitioned the water balance at this site using independent methods and found that the majority of stream flow (64% and 60%, respectively) consists of base flow and 20% of subsurface lateral flow, with the remainder being flow originating from compacted areas. Studies in temperate upland regions have shown that pre-event water typically contributes at least 50% of storm flow water (Buttle, 1994). Pre-event water appears to be the primary driver of stream water levels, whereas event-water with the precipitation signal contributes to peak flow. In our study, this influence was most likely due to the effects of spring flow, as perennial springs flow more significantly with increased precipitation inputs and ephemeral springs, consisting primarily of event water, begin flowing after a rise in the groundwater levels (Buttle, 1994). However, the τ values calculated for the stream water did not appear to capture the dynamic nature of event-driven subsurface contributions to stream water.

6 | CONCLUSIONS

By examining the influences of seasonality on precipitation, we found strong evidence that seasonality does influence isotopic ratios of precipitation in this region of Costa Rica. While this region exhibits weak rainfall seasonality, stable isotopes in precipitation were more enriched during the dry season than during the rainy season. The general climate patterns of Costa Rica and the shifting ITCZ had significant seasonal influence on isotope compositions. The source of the air mass yielding the precipitation event had the largest influence on isotope compositions in precipitation. We noted a correlation with the amount effect on the monthly time scale but not on an event basis. These results provide baseline information about isotope seasonality at the study site, and variations in the future can show how El Niño-Southern Oscillation influences precipitation in the region.

In this system, isotope data contributed to our understanding of flow pathways and the proportion of base flow versus storm flow. Based on the results of this study, we conclude that this watershed is a base flow driven system. While springs contributed a small proportion of the total flow to streams, they greatly influenced the isotopic signal of peak flow as event water. Seasonal effects had a mean transit time on the order of 1 year, whereas storm flow effects had a lag time of approximately 1 hr. The hydrograph separation method we used did not capture the signals of these rapid event-driven subsurface contributions to the stream water. Future work combining the dual isotope approach with mass balance modelling would help quantify the hydrologic response of the watershed and to confirm the subsurface flow paths that we suggest based on isotope data. Additional data collection would allow use of other hydrograph separation methods that have greater sensitivities to capture the dynamic nature of event-driven subsurface contributions to surface water. Logistical challenges existed in this study for collecting high-resolution samples simultaneously with precipitation, spring water, and stream water. However, matching the high-resolution hydrometric data with isotopic data would enhance understanding of the timing and flow processes that occur during storm events. A lack of information on spring flow exists in the literature, and further study on the seasonal variations of spring flows in tropical and temperate regions is necessary, considering their social and economical importance.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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