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Hydrogeological responses in tropical mountainous springs

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ABSTRACT

This study presents a hydrogeochemical analysis of spring responses (2013–2017) in the tropical mountainous region of the Central Valley of Costa Rica. The isotopic distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in rainfall resulted in a highly significant meteoric water line: $\delta^2\text{H} = 7.93 \cdot \delta^{18}\text{O} + 10.37$ ($r^2 = 0.97$). Rainfall isotopic composition exhibited a strong amount-dependent seasonality. The isotopic variation ($\delta^{18}\text{O}$) of two springs within the Barva aquifer was simulated using the FlowPC program to determine mean transit times (MTTs). Exponential-piston and dispersion distribution functions provided the best-fit to the observed isotopic composition at Flores and Sacramento springs, respectively. MTTs corresponded to 1.23 ± 0.03 (Sacramento) and 1.42 ± 0.04 (Flores) years. The greater MTT was represented by a homogeneous geochemical composition at Flores, whereas the smaller MTT at Sacramento is reflected in a more variable geochemical response. The results may be used to enhance modelling efforts in central Costa Rica, whereby scarcity of long-term data limits water resources management plans.

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1. Introduction

In the Central America region, between 50 and 90% of the total water used for public supply comes from groundwater sources [1]. For example, it is estimated that 88% of the water used in Costa Rica is extracted from wells or spring systems [1,2]. This large dependence of groundwater extraction may be explained by the current surface water pollution status [3,4] and the great hydrogeological aptitude of Costa Rican territory where, according to Astorga and Arias [5], 76% of the land is classified as suitable for the formation of a shallow aquifer, with the central and northern regions being the areas with the greatest groundwater potential. In addition, groundwater from volcanic aquifers commonly does not require expensive purification treatments and water distribution (i.e. either from springs or wells) is often done by gravity [2,6].

In the Central Valley of Costa Rica, a multilayer volcanic aquifer system known as the Barva-Colima system supplies about 65% of the water used in the Great Metropolitan Area (GMA) [2,3]. This aquifer system is being threatened by high population density,

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increased water demand, and a large degree of surface water contamination that results in high water resources vulnerability in the Central Valley of Costa Rica [4,7].

Environmental tracers such as stable isotopes of water (^{18}O , ^2H) have helped understand subsurface water generation, movement, storage, recharge, and mixing processes [8–10]. Particularly, these naturally occurring tracers have commonly been used in hydrogeology studies to understand rainfall processes and moisture origin [11–17], surface and groundwater interaction and to determine mean transit times (MTTs) [18–23]. The MTT is defined as the time a meteoric water molecule or tracer spends travelling along subsurface flow pathways to the stream network [19,24,25]. MTT is a fundamental hydraulic descriptor that provides useful information about water sources and mixing processes, potential flow pathways, and storage capabilities within a particular catchment [26–30].

The main objectives of this study were to: (a) describe the temporal hydrogeochemical variations in the discharge of Sacramento and Flores springs; (b) establish a local meteoric water line (LMWL) and its relationship with long-term spring isotopic composition, and (c) determine the MTTs and the distribution function (RTD) for each spring system. This hydrogeological information is crucial to better understand these highly variable spring systems under a changing climate.

2. Study area

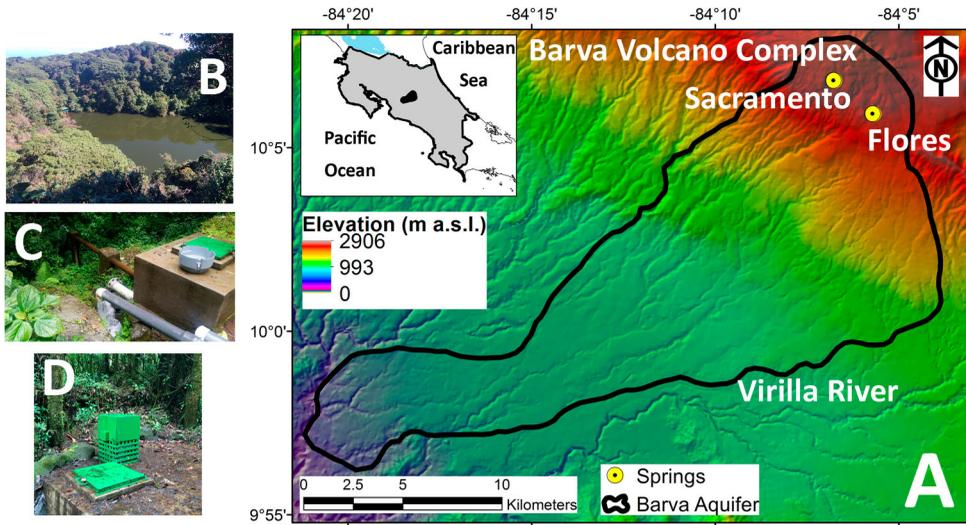
Costa Rica (52,100 km²) is located in the Central American Isthmus. A mountainous range system extends from northwest to southeast dividing the territory into two main regions: the Caribbean and the Pacific slopes [31]. The Central Valley of Costa Rica is limited to the north by the Central Cordillera, to the east by the Talamanca Cordillera, to the west by the Aguacate formation, and to the south by the Escazú mountain range [32,33].

The northern and central regions of the Central Valley were formed in the Quaternary by lahars and ashes deposition, filling the depression between the mountain range and the Miocene volcanism [34,35]. The largest urban areas form the GMA which houses 2,653,430 inhabitants, corresponding to 54.25% of Costa Rica's total population, within 3.8% of the national territory (i.e. 1700 km²) [36,37].

This study focuses on two main spring systems within the Barva aquifer (Central Valley of Costa Rica): Sacramento and Flores (Figure 1). Flores is located at 2239 m a.s.l. (–84.0595 W, 10.0993 N), whereas Sacramento is located at 2401 m a.s.l. (–84.1127 W, 10.1138 N). The geological formations within the Central Valley are formed by fractured and brecciated materials with primary and secondary porosities, allowing the formation of a multilayer volcanic aquifer systems (with high permeability), known as the Barva-Colima system [34,38]. The Barva aquifer overlies the Colima formation and is located northwest of the Central Valley, limiting towards north with the continental divide [39]. The Barva aquifer comprises 275 km² and supplies water to approximately 500,000 inhabitants [36] (Figure 1).

2.1. Hydrogeological characteristics

The Barva aquifer is mostly constituted by andesitic lavas and andesitic-basaltic lava flows, which are high in potassium, similar to lavas of recent stratovolcanoes, suggesting that the aquifer was formed during the last evolution stage of Barva volcano [34,39] (Figure 1).



Formation	Member	Geology	Thickness (m)
Barva	Los Ángeles- Los Bambinos	Lavas	0-35
	Carbonal	Tuff and clays	0-50
	Bermúdez	Lavas	0-85
Tiribí	Tiribí	Tuff and ignimbrites	0-100
Colima	Libertad-Colima Superior	Lavas	0-185
	Puente Mulas	Tuff and ignimbrites	0-35
	Colima Inferior	Lavas	20-190

Figure 1. (A) Study area within the Barva volcano complex, including the elevation gradient (m a.s.l.), spring locations (Sacramento and Flores), and the Barva aquifer boundary (bold line). The inset shows the location of the Barva aquifer in central Costa Rica. (B) Aerial photograph of Barva volcano crater and surrounding primary and secondary forest. (C) and (D) Photographs of Sacramento and Flores springs, respectively. The chart shows a stratigraphy summary of the aquifer system [40].

Aquifer thickness ranges from 10 up to 80 m with ash and lapilli intercalations [40]. The aquifer is divided into several hydrogeological members: (a) Bermudez member is constituted by fractured andesitic lavas divided by tuffs, known as Barva Inferior. It is the most extensive, old member and is buried by new lavas [35,41]. Porrosatí and Carbonal members are formed by pyroclastic of several ages, thick volcanic sands and weathered argillaceous tuffs, allowing the establishment of aquitards [38,42]. Los Angeles and Los Bambinos members include upper lavas allowing the formation of small, discontinuous

and perched aquifers [41]. The Crater member is constituted by recent pyroclastics covering the Barva aquifer to some extent [38,40].

Aquifer permeability ranges between 1 and 10 m d⁻¹, the saturated thickness varies from 50 to 100 m, transmissivity values range from 100 up to 500 m² d⁻¹, and the storage coefficient corresponds to 0.10 [39,40,42].

2.2. Climate characteristics

Four regional air circulation processes predominantly control the climate of Costa Rica: northeast trade winds (i.e. alisios), the latitudinal migration of the Intertropical Convergence Zone (ITCZ), cold continental outbreaks (i.e. northerly winds or nortes), and sporadic influence of Caribbean cyclones [32,43]. These circulation processes produce two rainfall maxima, one in May and June and another one in September and October, with a relative minimum between July and August known as the mid-summer drought (MSD) (i.e. intensification of the trade winds over the Caribbean Sea) [44,45]. In addition to these circulation processes, the continental divide (i.e. a mountainous range that extends from the NW to the SE) also influences precipitation patterns across the country dividing the territory into the Caribbean and Pacific drainage basins. Both basins exhibit distinct rainfall regimes in terms of magnitude and timing [46]. In general, annual precipitation in Costa Rica varies from ~1500 mm in the drier northwestern region, ~2500 mm in the Central Valley, and up to ~7000 mm on the Caribbean side of the Talamanca range. Temperature seasonality is low throughout the country (<2°C). The mean annual temperature on the coastal lowlands is about 27°C, 20°C in the Central Valley and below 10°C at the summits of the highest mountain range (3820 m a.s.l., Chirripó peak).

3. Materials and methods

3.1. Spring instrumentation

Water column levels were continuously monitored (15-minute resolution) with a pressure transducer coupled to a Sigma 900 MAX autosampler (HACH, USA). Weekly spring discharges were conducted to develop appropriate rating curves since October 2014.

In situ parameters were weekly measured using a multi-parameter sonde Hanna Instruments (HI 98194) since August 2014 at each spring system, including electrical conductivity (EC) ($\mu\text{S cm}^{-1}$), temperature (°C), pH, oxidation–reduction potential (ORP in mV). Additionally, at Sacramento spring, continuous EC and temperature were measured using a HOBO sensor U24 Conductivity logger (U24-001) at 15-minute resolution since June 2015.

Rainfall amounts were continuously monitored using a weather station (Davis Instruments, USA) at 30-minute resolution since October 2015. The weather station was located at the Barva volcano summit (2906 m a.s.l.).

3.2. Stable isotopes analysis

Stable isotope data of precipitation is composed of weekly samples ($N = 158$, sampling period: April 2013–September 2017). Samples were collected at Sacramento (2400 m

a.s.l.), using a traditional mineral oil-based collector, which consisted of a plastic funnel coupled with a filter mesh to prevent external contamination. The funnel was connected to 4 L high-density polyethylene (HDPE) container. A 2 cm layer of mineral oil was added prior collection to prevent fractionation according to standard sampling protocols [47]. The mineral oil was later separated using a 250–500 mL separatory funnel. Oil-free samples were stored at 5°C in HDPE bottles of 30 mL hermetically sealed until analysis. Routinely quality control inspections guaranteed no organic contamination in the spectral analysis (Chemcorrect software verification). The analytical long-term uncertainty was: ± 0.5 (‰) (1σ) for $\delta^2\text{H}$, ± 0.1 (‰) (1σ) for $\delta^{18}\text{O}$.

Spring isotope data are composed of weekly and daily (sampling period: October 2014–September 2017) samples ($N = 906$). Daily samples were collected using a Sigma 900 MAX autosampler (HACH, USA). All samples were filled with no head space in 30 mL HDPE bottles to avoid exchange with atmospheric moisture and were stored at 5°C hermetically sealed until analysis.

Stable isotope analyses were conducted at the Stable Isotope Research Group facilities of the Universidad Nacional (Heredia, Costa Rica) using a cavity ring down spectroscopy (CRDS) water isotope analyser L2120-i (Picarro, USA) and a LWIA-45-EP water isotope analyzer (Los Gatos, USA). The secondary standards were: Moscow Tap Water, MTW ($\delta^2\text{H} = -131.4\text{‰}$, $\delta^{18}\text{O} = -17.0\text{‰}$), Deep Ocean Water, DOW ($\delta^2\text{H} = -1.7\text{‰}$, $\delta^{18}\text{O} = -0.2\text{‰}$), and Commercial Bottled Water, CAS ($\delta^2\text{H} = -64.3\text{‰}$, $\delta^{18}\text{O} = -8.3\text{‰}$). MTW and DOW standards were used to normalize the results to the VSMOW2-SLAP2 scale, while CAS was used as a quality control and drift control standard. Stable isotope compositions are presented in delta notation δ (‰), relating the ratios (R) of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$, relative to Vienna Standard Mean Ocean Water (V-SMOW).

3.3. Determination of MTT and RTD for the spring systems

MTT and RTD were estimated using a lumped-parameter model approach proposed by Maloszewski and Zuber [48]. In this method, the system investigated is considered closed, homogeneous, stable, and with constant flow [26,49]. In the case of steady flow, the MTT is defined by Equation (1) as:

$$\tau = \frac{V}{Q}, \quad (1)$$

where V is the volume of mobile water in the system (*volume unit*), Q is the volumetric flow rate (*volume per time*) [50,51]. The MTT of a tracer is defined by Equation (2) [19,27,52] as:

$$\tau_t = \frac{\int_0^\infty t C_i(t) dt}{\int_0^\infty C_i(t) dt}. \quad (2)$$

In the lumped-parameter approach for stable isotopes, the output composition can be related to the input composition using the following convolution integral (Equation (3)):

$$\delta_{out}(t) = \int_0^\infty g(\tau) \delta_{in}(t - \tau) d\tau, \quad (3)$$

where $\delta_{in}(t)$ and $\delta_{out}(t)$ are the input and output tracer contents at any time t , respectively, $g(\tau)$ is the weighting function describing the RTD for tracer molecules in the system, and τ is the MTT of the tracer [48,51,53]. The MTT of the water infiltrated (τ) is equal to the MTT of the tracer (t_t) only if the tracer is conservative, ideal, injected, and measured proportionally to the volumetric flow rate [48,49].

MTTs were estimated using the lumped parameter computer program FLOWPC 3.2 (http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html) [54] at the two spring systems. FLOWPC has been widely applied to estimate MTTs in several hydrologic applications [26,55–58]. Model parameters ($\tau, \eta, D/vx$) for the different models (exponential model (EM), exponential-piston model (EPM), dispersion model (DM), lineal model (LM), and lineal piston model (LPM)) were obtained by trial and error in order to fit measured output isotope ratios. In FLOWPC, the goodness of fit is determined as:

$$\Sigma = \frac{\sqrt{\sum_{i=0}^n (C_m - C_p)^2}}{n}, \quad (4)$$

where C_m and C_p are the measured and predicted tracer compositions, n is the number of observations.

In order to complement the evaluation of the simulations in FLOWPC, other authors [26,59] have suggested the incorporation of the following goodness of fit criteria: root mean square error (RMSE) and the mean absolute error (MAE), both of them quantify the simulation error in ‰ [60]. Based on Legates and McCabe [61] $RMSE \geq MAE$ and the degree to which RMSE exceeds MAE is an indicator of the extent to which outliers exists in the data. The coefficient of efficiency (E) ranged between $-\infty$ to 1, where highest values represent a perfect fit. Efficiency lower than zero means that the average value of observed data should have been a better predictor than the model [62]. The coefficient of determination (r^2) describes how much of the observed dispersion is explained by the prediction, ranging between 0 (no correlation) and 1 (prediction equal to observation) [63]. The index of agreement (d) was proposed by Willmott [60] to overcome the insensibility of r^2 and E , representing the grade in which the prediction is error-free. It lies between 0 and 1, where 0 means no correlation and 1 means a perfect fit [63,64]. In both spring systems, a deeper groundwater reservoir with a constant isotopic composition was considered: at Sacramento simulations included a mix of 60% stored water ($\delta^{18}O = -9.0\text{‰}$) and at Flores a mix of 70% stored water ($\delta^{18}O = -5.5\text{‰}$). These deep reservoir percentages were obtained by trial and error after multiple iterations. The isotopic values were extracted from previously published high-resolution groundwater isoscapes of Costa Rica [31], which correspond to the isotopic variability observed in the Central Valley of Costa Rica, previously reported by Sánchez-Murillo et al. [39].

4. Results

4.1. Spring hydrogeochemical characteristics

During the sampling period, weather conditions at Barva volcano exhibited rainfall amounts ranging between 3300 and 3500 mm. Figure 2 shows daily precipitation amounts, where the wet months within the northern mountainous region of the Central Valley of Costa Rica corresponding to May and June (1st rainfall maxima) and September

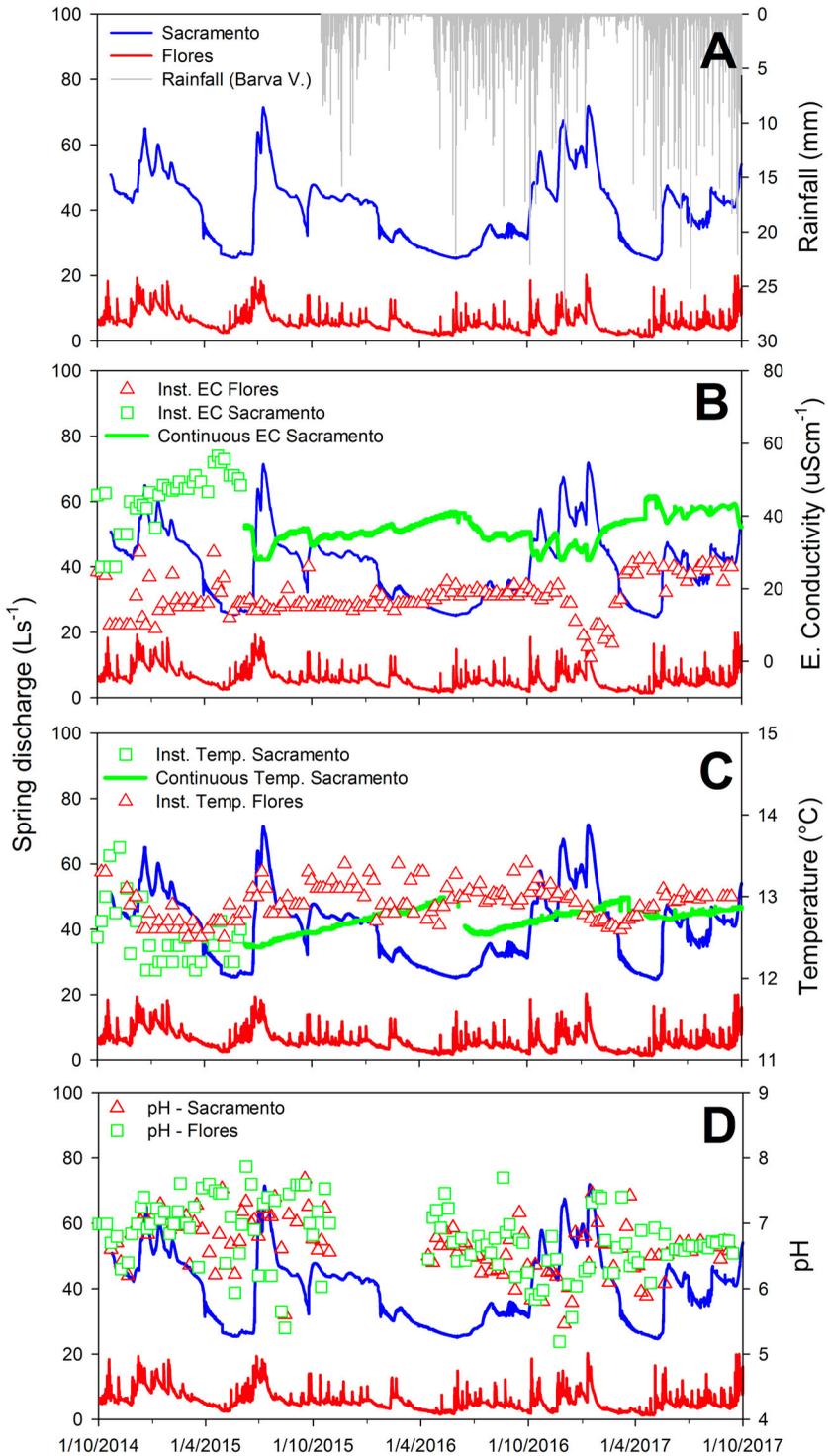


Figure 2. Spring discharge ($L s^{-1}$) relationship with (A) rainfall (mm), (B) electrical conductivity ($\mu S cm^{-1}$), (C) water temperature ($^{\circ}C$), and (D) pH, from October 2014 to October 2017.

and October (2nd rainfall maxima) (Figure 2(a)), according to the wet season from May to November which is interrupted by a relative minimum between July and August (known as the MSD). On the other hand, the driest months corresponded to January and February, according to the dry season from December to April.

Figure 2(a) shows the time series of volumetric discharge for both springs compared to the rainfall. Sacramento's volumetric discharge ranged from 24.6–71.9 L s⁻¹, whereas Flores' volumetric discharge varied from 1.3–20.0 L s⁻¹. The lowest discharge values for both spring systems were observed between April and May corresponding to the baseflow period at the end of the dry season. The greatest discharge values were observed between December and January at the end of the wet season and during the period of the cold influence over central Costa Rica. During July and August, discharge decreased due to effect of the MSD.

Figure 2(b) shows the EC time series for both springs compared to the changes in discharge. The mean EC value for Sacramento was 52.2 μS cm⁻¹ and ranged from 42.1 up to 61.7 μS cm⁻¹ with a clear inverse relationship to discharge. For Flores spring, EC ranged from 5.5 up to 30.0 μS cm⁻¹ with a mean value of 17.9 μS cm⁻¹; despite the discharge changes EC values were close to the mean EC value during the sampling period.

Figure 2(c) shows temperature time series for each spring system compared to the volumetric discharge. At Sacramento water temperature ranged from 12.1°C up to 14.2°C and at Flores spring, water temperature ranged from 12.4°C up to 13.9°C. Figure 2(d) shows the pH time series compared to the volumetric discharge for each spring system. At Sacramento pH varied from 5.46 to 8.05, and at Flores pH ranged from 5.19 to 8.66. The mean ORP values for Sacramento and Flores were 218.7 and 188.7 mV, respectively.

4.2. Isotopic variations

4.2.1. δ²H and δ¹⁸O in precipitation

The linear regression of δ²H and δ¹⁸O ratios of precipitation collected at Sacramento (*N* = 158) is presented in Figure 3 and compared to the GMWL [65] and the Costa Rica MWL [17]. The δ²H and δ¹⁸O values of precipitation ranged from -124.8 to +14.5‰ and from -17.1 to -0.2‰, respectively (see Supplementary Material S1). An ordinary least squares regression resulted in a highly significant LMWL: δ²H = 7.93δ¹⁸O + 10.37 (*r*² = 0.97, Figure 3), with a mean annual weighted value for δ²H and δ¹⁸O -54.1 and -8.2‰, respectively. Previous studies have explained high intercepts and slopes as a result of moisture recycling processes, such as localized strong convective events fed by evapotranspiration fluxes (e.g. forested areas within the Central Valley) [39,41,66].

δ¹⁸O values exhibited a bimodal pattern throughout the year (Figure 4). Isotope ratios in the dry season (December–April) rainfall are mostly related to enriched events. By mid-May to November, when the ITCZ reaches Costa Rica, a sharp depletion in isotope ratios was observed. One important factor controlling isotopic variations in the tropics is the 'amount effect', and a moderate negative correlation of -1.6‰ δ¹⁸O/100 mm (*r*² = 0.52) on historic monthly composite samples from GNIP has been reported by Sánchez-Murillo et al. [17].

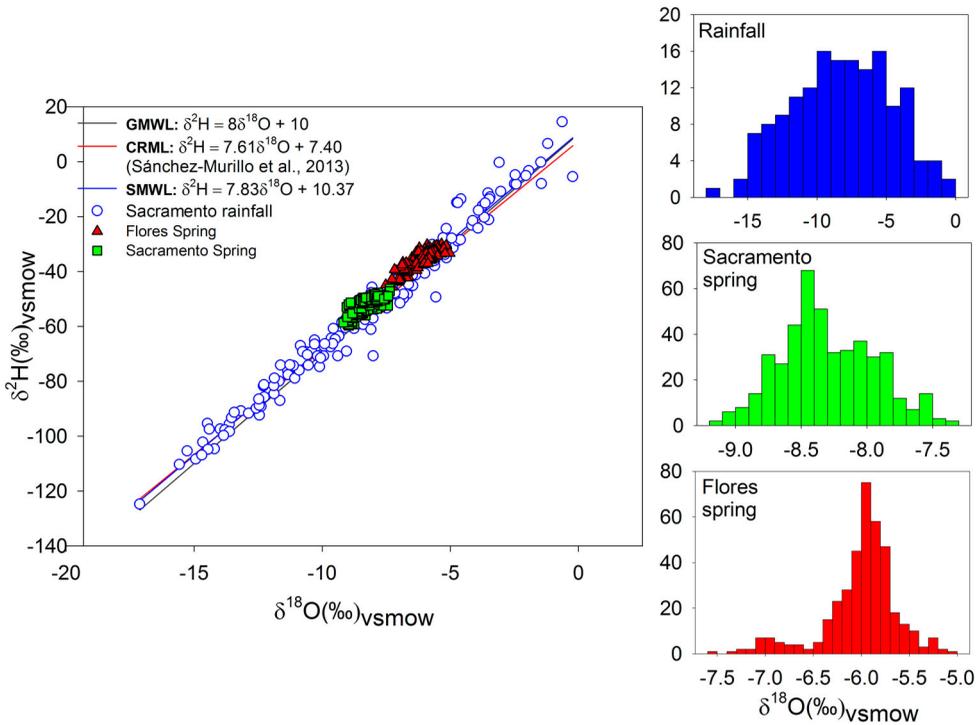


Figure 3. Dual isotope diagram including Sacramento rainfall and both springs (Sacramento and Flores). The GMWL and the Costa Rican MWL are plotted as references. Histograms show the $\delta^{18}\text{O}$ distribution in precipitation and spring water.

4.2.2. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the springs

The relationship of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values at each spring system is presented in Figure 3 along with the Sacramento meteoric water line as a reference (see Supplementary Material S2). Spring $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in Sacramento ranged from -9.2 to -7.4‰ (mean = -8.30‰) and from -59.8 to -46.3‰ (mean = -52.2‰), respectively. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in Flores spring ranged from -7.5 to -5.0‰ (mean = -6.0‰) and from -45.8 to -30.0‰ (mean = -34.5‰), respectively. Overall, the spring isotopic composition exhibited a clear damping effect, which is represented by the cluster of data points along the LMWL. However, both springs presented a distinct isotopic range, Flores spring is more enriched compared to Sacramento ($\sim 3\text{‰}$) (Figure 3).

The difference in the isotopic composition between rainfall and the springs is also reflected by the standard deviations. In rainfall, standard deviations ranged from 0.25 – 4.89‰ in $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Standard deviations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the springs ranged from 0.01 – 0.48‰ (Flores) and from 0.02 – 0.64‰ (Sacramento), respectively (Figure 4).

4.3. MTT and RTD for the spring systems

Table 1 shows the MTTs at each spring and goodness of fit metrics for each model (EM, EPM, DM, LM, and LPM). In Sacramento the best model fit ($\sigma = 0.034\text{‰}$ and $r^2 = 0.68$) with the observed $\delta^{18}\text{O}$ values was exhibited by the DM, which resulted in an MTT of 1.27 years

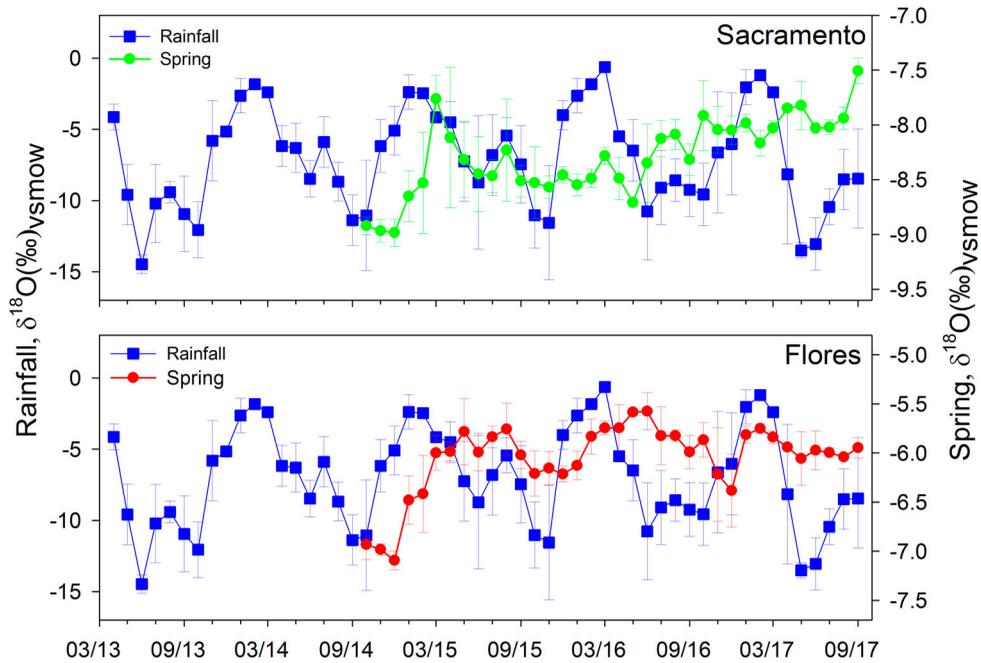


Figure 4. Monthly rainfall (Sacramento) and spring water (Sacramento and Flores) $\delta^{18}\text{O}$ (‰) from March 2013 to October 2017.

($D_p = 0.1$). Similarly, in Flores the best model fit was described by EPM ($\eta = 1.4$; $\sigma = 0.044\%$ and $r^2 = 0.47$), which translates in an MTT of 1.42 years. Figure 5 shows the observed isotopic composition compared to best-fit simulated isotopic composition at each spring system.

5. Discussion

5.1. Groundwater isotopic composition in the study area

As others authors have evidenced [19,35,41], the Barva aquifer is directly recharged by seasonal rainfall, whereby the mean isotopic composition of precipitation ($\delta^{18}\text{O} = -8.24\%$) is

Table 1. MTTs of Sacramento and Flores springs and the goodness of fit metrics for each evaluated distribution models.

Model	Goodness of fit metrics					MTT (years)	
	σ (‰)	RSME(‰)	MAE(‰)	D	E		r^2
Sacramento							
EM	0.044	0.20	0.14	0.87	0.39	0.52	1.92
EPM	0.045	0.23	0.18	0.89	0.45	0.41	1.23
DM	0.034	0.18	0.15	0.94	0.68	0.68	1.27
LM	0.040	0.16	0.15	0.91	0.38	0.44	2.12
LPM	0.039	0.21	0.17	0.89	0.49	0.41	1.67
Flores							
EM	0.063	0.38	0.28	0.59	-0.16	0.01	2.17
EPM	0.044	0.20	0.17	0.87	0.36	0.47	1.42
DM	0.064	0.27	0.23	0.74	-0.18	0.57	2.33
LM	0.061	0.36	0.26	0.56	0.06	0.03	7.83
LPM	0.058	0.27	0.23	0.76	-0.09	0.48	2.42

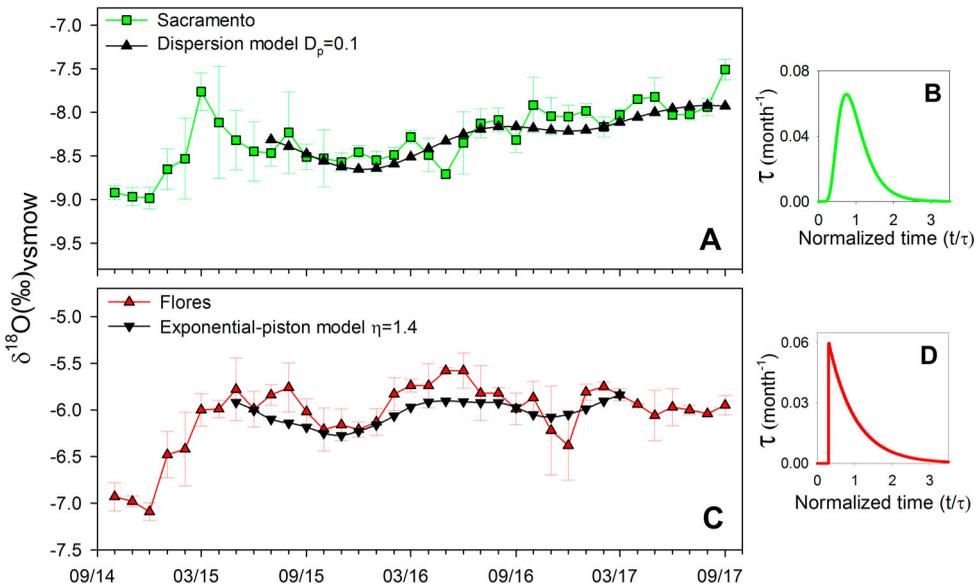


Figure 5. Observed and best-fit simulated $\delta^{18}\text{O}$ (‰) at each spring using the FlowPC program. (A) and (B) Sacramento spring (dispersion model). (C) and (D) Flores spring (exponential-piston model).

remarkably similar to Sacramento mean isotopic composition ($\delta^{18}\text{O} = -8.30\text{‰}$), providing a strong evidence of the seasonal recharge. Nevertheless, Flores spring isotopic composition is more enriched with a mean value of $\delta^{18}\text{O} = -6.0\text{‰}$. This overall $\sim 2.3\text{‰}$ difference cannot be explained by a simple isotopic lapse rate, since the elevation difference between the two springs is only ~ 250 m. Sánchez-Murillo et al. [19] have reported a lapse rate of -0.2‰ per 100 m in the study area. Based on this isotopic lapse rate, the overall isotopic difference between the two springs should be in the order of $\sim -0.4\text{‰}$. Sánchez-Murillo and Birkel [31] reported significant differences on the isotopic composition of rainfall, groundwater, and surface water of Costa Rica within the mountainous regions, which appear to be related with the type of precipitation (i.e. convective versus stratiform) within the Caribbean and Pacific slopes. Air masses travelling mainly from the Caribbean Sea experienced a strong orographic effect resulting in a notable depletion in rainfall and consequently in groundwater–surface water isotope ratios across the mountainous range. Recharge areas relying on Caribbean-type (more convective activity) parental moisture show an enrichment trend. The combination of high relief topography and rainfall type dynamics is translated in the distinct isotopic spatial patterns within the study area [39,41,66].

5.2. Spring MTTs

The Barva aquifer is described as a shallow aquifer, constituted of volcanic and fissured rock [38–41]; based on those characteristics the water MTT was expected to be between months and few years [67]. Figure 5 shows Flores and Sacramento best-fit simulated isotopic compositions. The best-fit simulation for both spring systems confirmed the presence of a large stored groundwater reservoir. Exponential-piston and dispersion distribution functions

provided the best-fit to the observed isotopic composition at Flores and Sacramento springs, respectively. MTTs corresponded to 1.23 ± 0.03 (Sacramento) and 1.42 ± 0.04 (Flores) years (Table 1). In line with the relative age estimates aforementioned, Sacramento spring presented a more dynamic hydrogeochemical composition, whereas Flores with a greater MTT, presented a more homogenous hydrogeochemical composition.

Flores spring simulated isotopic composition was weakly correlated (Table 1) with almost all weighting functions compared to Sacramento simulations. At Flores a large discrepancy was found between the observed isotopic composition and the simulated isotopic values ($E < 0$), which points out that the mean observed value is a better prediction than the simulated model [62,63].

According to Clark [67] the water age estimate increases due to the dispersion effects, diffusion, and hydrodynamic mixing. For Sacramento spring, the dispersion parameter ($D_p = 0.1$) describes the relationship of dispersion to advection [68]. The dispersion parameter usually varies between 0.05 and 0.5, the higher the value of this parameter, the wider and more asymmetric the distribution of transit times [54]. Kreft and Zuber [69] demonstrated that as the dispersion parameter tends to zero (i.e. $D/Vx \rightarrow 0$), the system gets closer to piston-like flow conditions indicating a dominance of the advection flow process [19,70]. Therefore, the smaller D_p value suggests that piston flow or advection processes were more dominant mechanism at Sacramento spring so a smaller MTT was obtained.

For Flores spring, η (ratio of the total volume to the volume with the exponential distribution) was selected as 1.4 [68]. The EPM describes the condition where the new water fraction initially has no effect on the output water source [19,71]. In the EPM, when $\eta=1$, it means that the model tends to the EM distribution and for greater η values, involves a DM distribution with a low value of D_p [49,54]. By the definition of η , the time distribution function is lagged by an amount proportional to $\left[1 - \frac{1}{\eta}\right]$ [19,71]. For Flores spring, $\eta = 1,4$ means that 29% of the total volume was piston-like [70].

6. Conclusions

Isotope ratios in the northern mountainous region of the Central Valley of Costa Rica showed an amount-dependent seasonality with a regional meteoric line of: $\delta^2\text{H} = 7.93 \delta^{18}\text{O} + 10.37$ ($r^2 = 0.97$). Despite the observed isotopic variation in precipitation, the $\delta^{18}\text{O}$ composition of springs exhibited a large damping effect. Spatial isotopic differences in the study area highlight the contribution of two distinct rainfall generation types in combination with strong orographic effects. The strong similarity between the mean isotopic composition of precipitation and spring water at Sacramento highlights the recharge seasonality dependence of Barva aquifer.

Relative short MTTs for Sacramento and Flores springs were determined using the FlowPC program: 1.27 and 1.42 years, respectively. The best-fit simulation for both spring systems confirmed the presence of a large stored groundwater reservoir. Hydrogeochemical coevolution at each spring supported the relative water age estimates. At Flores with a greater MTT, geochemical characteristics were more homogenous, whereas in Sacramento with a shorter MTT, the geochemical variations were more dynamic. This hydrogeological information is crucial to better understand these highly variable spring systems under a changing climate.

Disclosure statement

No potential conflict of interest was reported by the authors.

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