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SI STABLE ISOTOPES IN HYDROLOGICAL STUDIES

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Insight into the stable isotopic composition of glacial lakes in a tropical alpine ecosystem: Chirripó, Costa Rica

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Abstract

Tropical high-elevation lakes are considered sentinels of global climate change. This work characterizes the hydrological conditions of tropical alpine glacial lakes located in the highlands of Chirripó, Costa Rica, using a unique data set of water stable isotopes (δ^2 H and δ^{18} O) in precipitation, stream water, and lake water between September 2015 and July 2017. A combined dataset of bathymetric, hydrometric, and isotope data collected between July 2016 and July 2017 on Lake Ditkevi was used to calculate the annual water balance of the lake. Evaporation to inflow ratios from three lake systems was estimated using a linear resistance model, the experimentally estimated local evaporation line of Chirripó, and the first glacial lake water evaporation lines in the region. The temporal isotopic variations (δ^{18} O, *d*-excess, and lcexcess) confirm variations in the dry and wet season evaporative conditions for the glacial lakes and consistently average annual low evaporation to inflow (E/I) ratios in the range of 2.0 \pm 0.8% and 18.1 \pm 12.2%. Lake Ditkevi's water balance indicates annual steady-state conditions, with an estimated evaporation loss of 650 mm/year $(10.0 \pm 5.0\% \text{ of inflow})$, a high-water contribution to the catchment (90% of inflow), a residence time of 0.53 \pm 0.27 years, and a catchment scale (0.289 km²) water yield or depth equivalent run-off of 278 mm/yr. These results provide novel information about water balance and evaporation losses in tropical alpine glacial lakes, which can serve as baseline information for future isotope-based hydro-climate research in high-elevation regions in the tropics and elsewhere.

KEYWORDS

Chirripó, evaporation to inflow ratios, glacial lakes water balance, isotope mass balance, Páramo, water stable isotopes

1 | INTRODUCTION

Stable isotopes of water (δ^2 H and δ^{18} O) are valuable components of lake water hydrological studies as integrative proxies of the lake water balance (Gat, 1996; Gibson & Edwards, 2002; Gibson, Edwards, Bursey, & Prowse, 1993; Gibson & Reid, 2014; Mayr et al., 2007). Improved hydrological balance calculations for lakes require the isotopic composition of inputs (i.e., direct precipitation, stream, and groundwater inflow) and outputs (i.e., evaporation, stream, and groundwater outflow), as well as a measure of changes in storage; the influence of headwater conditions (e.g., catchment area and slope); rainfall seasonality; and atmospheric feedbacks (Cui, Tian, Biggs, & Wen, 2017; Dincer, 1968; Gibson, Birks, & Yi, 2016; Gonfiantini, 1986; Jonsson, Leng, Rosqvist, Seibert, & Arrowsmith, 2009; Lachniet & Patterson, 2002).

A key feature to evaluate the water balance of lakes is the quantification of evaporation as a fraction of inflow (E/I), which can be calculated using water stable isotopes and models of isotopic

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fractionation during evaporation (Gibson, Birks, & Yi, 2016; Jasechko, Gibson, & Edwards, 2014; Kang, Yi, Yanwei, Baiqing, & Yulan, 2017). The *E/I* ratios obtained from this isotope mass balance approach can be used in combination with hydrometric data (e.g., precipitation records and water level measurements) to make volumetric estimates of vapour loss from surface water bodies (e.g., lakes and wetlands; Sacks, Terrie, & Swancar, 2014; Skrzypek et al., 2015).

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In low-latitude regions, evaporation rates are constant throughout the year, and precipitation is in isotopic equilibrium with local water vapour (Gibson, Birks, & Edwards, 2008; Gibson, Birks, & Yi, 2016). As a result, humidity does not significantly affect the slope of the local evaporation line (LEL) but tends to limit the overall offset from the local meteoric water line (LMWL) along the LEL (Cui et al., 2017; Gibson, Birks, & Yi, 2016). That is, lake waters plotting on the LMWL are isotopically similar to the precipitation of the study region, whereas lake waters that plot below the LMWL (i.e., plotting in a LEL with different gradient than the LMWL) indicate isotopic fractionation due to evaporation. Effects of evaporation result in progressive isotopic enrichment of the residual lake water (Jonsson et al., 2009; Wu et al., 2017). Thus, the comparison of the isotopic composition of lake water to the LMWL can give useful information about the lake's hydrological conditions and seasonal changes in the water balance (Biggs et al., 2015; Gibson, Birks, & Yi, 2016; Jasechko et al., 2014).

The influence of evaporation in lakes can also be inferred using secondary isotope-derived parameters such as the deuterium excess (hereafter d-excess, Dansgaard, 1964). The d-excess reflects precipitation seasonality and the dominant sources of moisture in precipitation, stream, and groundwater in the lake catchment (Biggs et al., 2015; Froehlich et al., 2008; Mayr et al., 2007). Recently, another isotopederived parameter called the line-conditioned excess (hereafter lcexcess; Landwehr & Coplen, 2006) has been used to improve the understanding of evaporation within catchments based on the $\delta^2 H$ and $\delta^{18}O$ deviations of surface waters from the original isotopic composition of precipitation. This dual-isotope parameter is more advantageous than the simple and direct analysis of $\delta^2 H$ or $\delta^{18} O$ because it can distinguish the influence of the variations in the isotopic composition of precipitation inputs and subsequent isotopic enrichment due to evaporation of stream water (Sprenger, Tetzlaff, Tunaley, Dick, & Soulsby, 2017).

Past glaciation landform investigations in the Central American land bridge, which encompasses the study area, have focused on the collection of glacial geomorphology and sedimentary lacustrine data (e.g., past glacial extent, glacial altitude estimations, and stable carbon and hydrogen isotope analyses) to identify past long-term climate variations (Lachniet & Vazquez-Selem, 2005; Lane, Horn, Mora, Orvis, & Finkelstein, 2011; Lane & Horn, 2013; Orvis & Horn, 2000). However, research in Costa Rican glacial lakes so far has been restricted to basic morphometric and limnologic surveys (Göcke, Lahmann, Rojas, & Romero, 1981; Haberyan, Horn, & Umaña, 2003; Horn, Orvis, & Haberyan, 2005; Jones, Lohman, & Umaña, 1993; Löffler, 1972), with very little attention given to the lakes water balance, storage, and supply. At Chirripó, for example, Lachniet and Patterson (2002) included the isotopic composition of three lake water samples and one precipitation sample in their study. Therefore, the Chirripó system of glacial lakes presents an important need not only to conduct a baseline characterization of the hydrologic lake conditions (e.g., evaporation to inflow ratios) based on the isotopic characterization of surface and atmospheric waters but also to provide valuable input data for the reconstruction of past hydrologic conditions.

This study presents a systematic characterization of the isotopic composition of glacial lakes located in the highlands of Chirripó, Costa Rica. Our specific objectives were to establish the first water isotope framework for Chirripó, to estimate the water fluxes contributing to the water balance of the lakes and to estimate the annual water balance of one of the Chirripó glacial lake systems using a stable isotope approach. A range of precipitation, stream, and lake water samples were collected in the lake district of this region between September 2015 and July 2017. It is postulated that the seasonal variations of the lake water isotopic composition are controlled by precipitation inputs and evaporation conditions throughout the year in Chirripó, with evaporation to inflow ratios reflecting the high elevation climatic conditions of the Páramo.

2 | DATA AND METHODS

2.1 | Study area

The lake district of Chirripó comprises approximately 30 lakes of glacial origin, situated in the Chirripó National Park (Latitude: 9.46°, Longitude: -83.49°; hereafter Chirripó), a protected area with an extension of ~104 km², belonging to La Amistad-Pacífico Conservation Area (Figure 1a). This region is covered by the most extensive area of Páramo in Costa Rica, a grass- or shrub-dominated ecosystem that occupies the cool and wet upper slopes of tropical mountains, with alpine elevations above the timber or tree line and below the perpetual snow limit (Hofstede, Segarra, & Mena, 2003; Kappelle & Horn, 2016). The climate of this Costa Rican high-elevation region is controlled by the northeast trade winds (i.e., alisios); the latitudinal migration of the Intertropical Convergence Zone; cold continental outbreaks (i.e., northerly winds); and the seasonal influence of Caribbean cyclones (Waylen, 1996). These circulation processes produce two rainfall maxima, one in May and one in October, which are interrupted by a relative minimum between July and August known as the mid-summer drought (i.e., intensification of the trade winds over the Caribbean Sea (Durán-Quesada, Gimeno, & Amador, 2017; Magaña, Amador, & Medina, 1999). Historical rainfall records for the Páramo located in the Talamanca range of Costa Rica show that ~89% of the rainfall falls between May and November (wet season), and as a result, a welldefined dry season is established from December to April (Kappelle & Horn, 2016).

Three main lake systems can be found in the highlands of Chirripó: the Morrenas lakes, Lake Ditkevi, and the Chirripó lakes (Figure 1 and Table 1). The Morrenas lakes are located on the Caribbean slope of Chirripó, in the so-called Valle de las Morrenas, one of three glaciated valleys that are situated around the Cerro Chirripó, the highest elevation mountain peak in Costa Rica (3,820 m a.s.l.). This lake system comprises five main lakes, which are interconnected and drain to the Caribbean Sea as headwaters of the Río Chirripó-Atlántico. Lake Ditkevi is also located on the Caribbean slope of Chirripó. Lake Ditkevi's



FIGURE 1 (a) Location of La Amistad-Pacífico Conservation Area (ACLA-P) and the Chirripó National Park in the Talamanca range of Costa Rica. (b) Geographic situation of the main three glacial lakes systems (i.e., Morrenas lakes, Chirripó lakes, and Lake Ditkevi) in the Chirripó National Park. Sampling sites included a rainfall collector (yellow square), lakes (green triangles), and streams (red circles). The location of the Lake Morrenas 1 (labelled as 1) and Lake Chirripó (labelled as 2) are also shown. The blue lines correspond to surface waters, namely, the lakes and streams in Chirripó. The black polygon shows the limits of the Lake Ditkevi basin

TABLE 1 Characteristics of the three main lake systems located in the Chirripó National Park

Lake system	Number of major lakes	Latitude (decimal degrees)	Longitude (decimal degrees)	Elevation (m a.s.l.)	Area (m²)	Maximum depth (m)	Relation to water divide	pН	Temperature (°C)	EC (μS/cm)
Morrenas Lakes	5	9.49	-83.48	3,490	5.2 × 10 ⁴	8.3	Caribbean slope	7.87	14.6	20.0
Chirripó Lakes	3	9.48	-83.50	3,506	7.8×10^{4}	22	Pacific slope	8.09	12.5	4.5
Lake Ditkevi	1	9.47	-83.48	3,520	1.66×10^{4}	8.2 ^a	Caribbean slope	7.71	13.6	17.3

Note. Area and Maximum depth values correspond to Lake Morrenas 1 and Lake Chirripó. EC: Electrical conductivity.

^aThe maximum depth reported for Lake Ditkevi was measured in study.

outflow drains into the Río Telire basin. The Chirripó lakes are situated on the Pacific slope, in the so-called Valle de los Lagos. This lake system comprises three interconnected glacial lakes, which are also the headwaters of the Río Chirripó-Pacífico. The two largest glacial lakes in Chirripó are the 22-m-deep Lake Chirripó in the Valle de los Lagos and the 8.3-m-deep Lake Morrenas in the Valles de las Morrenas (Horn et al., 2005). In general, these lakes have low temperatures (~10–15°C); are dilute and polymictic (i.e., nonstratified); and have very clear water due to the low productivity that accompanies their low nutrient levels (Horn, 2017; Kappelle & Horn, 2016).

2.2 | Sampling design and data collection

Three types of water samples were collected between September 2015 and July 2017 in Chirripó, namely, precipitation, stream, and lake water samples. Precipitation samples (N = 166) were collected at the Base Crestones shelter (3,400 m a.s.l.; Figure 1b) on the Pacific slope of Chirripó using a passive collector (Palmex Ltd., Croatia; Gröning et al., 2012). Samples were collected manually on every rainy day at 07:00 hr (-06:00 GMT). Lake water samples were collected at Lake Chirripó (located on the Pacific slope) and Lake Ditkevi (situated on the Caribbean slope) following a roughly biweekly sampling plan. These lakes were selected to collect isotopic information of lake

waters located on both sites of the continental divide of Chirripó. At Lake Chirripó, samples were collected on the east bank of the lake (N = 31), whereas at Lake Ditkevi, samples were collected on the north bank of the lake (N = 39) as shown in Figure 1b. Additionally, eight field trips (i.e., two field trips per season or every 3 months) were organized to collect stream water (N = 29) and to collect samples at the Morrenas lakes (N = 24; Figure 1). Stream water was only collected at sites where surface water was flowing into the lakes. Lake samples of the Morrenas lakes, Lake Ditkevi, and the Chirripó lakes were manually collected from about 20 cm below the surface and ~25 m away from surface stream inlets (Cui et al., 2017). Samples were collected in 30-ml high-density polyethylene vials and stored at 5°C until analysis. To ensure that the isotopic composition at the sampling points selected in the three lake systems was representative of their vertical and horizontal heterogeneity, additional samples (N = 5) were collected from the near-shore and outlet during the dry and wet seasons. The average isotopic composition of these additional samples was compared with the lake average isotopic composition at the sampling points in order to verify that they were the same. Temperature and electrical conductivity (EC) of water samples were recorded at each lake using a field portable tester during the study period (Hanna Instruments, USA). During the study period, water temperatures of Lake Chirripó and Lake Ditkevi were relatively constant with mean

values of 12.5 \pm 2.0°C (1 σ) and 13.6 \pm 2.5°C (1 σ), respectively, whereas mean EC for these lakes was 4.5 \pm 7.4 (1 σ) μ S/cm and 17.3 \pm 9.3 (1 σ) μ S/cm, respectively (Table 1).

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Meteorological variables (relative humidity, air temperature, and precipitation amount) were recorded at 2 m height using an LW301 weather sensor kit (Oregon Scientific, USA) installed at the Base Crestones shelter (Figure 1b). The available meteorological data were used to estimate average daily evaporation using the Penman equation (Penman, 1948). At Lake Ditkevi, water temperature was recorded at 15-min intervals by an Onset HOBO water temperature data logger installed at the west bank. From July 2016 to July 2017, water temperature and water pressure were simultaneously recorded at 30-min intervals by an Onset HOBO water-level data logger installed at this same location. In July 2016 and September 2016, a bathymetric survey at Lake Ditkevi was conducted using a handheld sonar sensor (Hawkeye, USA). A total of 118 depth records were registered, which were manually geo-referenced using a GPS. These records were used to construct a depth profile using interpolations performed in ArcGIS 10.4 (ESRI, USA) based on an ordinary kriging algorithm.

A pan evaporation experiment was conducted at the Base Crestones shelter on April–May 2016 to calculate the LEL under the high-elevation conditions of Chirripó, using the methodology described by Corrales, Sánchez-Murillo, Esquivel-Hernández, Herrera, and Boll (2016). A stainless steel cylindrical pan (diameter = 24.9 cm) was filled with 2.4 L of local stream water ($\delta^{18}O = -11.64$, $\delta^2H = -84.87$ ‰). The pan was exposed to the climatic conditions of Chirripó for 136 hr. A 2-ml sample was taken from the pan every 6 hr (N = 21) from 8:00 am until 05:00 pm. The samples were sealed with parafilm and stored at 5°C until analysis. The water temperature, relative humidity, water isotope data, and the LEL constructed using the data recorded at the Base Crestones shelter were used as input for the *E/I* ratio calculations.

2.3 | Stable isotope analysis

The ²H and ¹⁸O isotopic composition of water samples was determined using a Cavity Ring Down Spectroscopy water isotope analyser L2120-i (Picarro, USA) with an analytical long-term uncertainty of ±0.5‰ (1 σ) for δ^{2} H and ± 0.1‰ (1 σ) for δ^{18} O. Stable isotope compositions are presented in delta notation δ (‰, per mil), relating the ratios (R) of ¹⁸O/¹⁶O and ²H/¹H relative to Vienna Standard Mean Ocean Water. Two isotope-derived parameters were calculated: the *d*-excess and lc-excess. The *d*-excess is the intercept of the global meteoric water line following Dansgaard (1964):

$$d - excess = \delta^2 H - 8x \delta^{18} O. \tag{1}$$

The lc-excess was calculated using the LMWL as a reference to identify water that experienced evaporation losses and subsequent fractionation (Sprenger et al., 2017). The lc-excess is defined as follows:

$$lc - excess = \delta^2 H - ax \delta^{18} O - b, \qquad (2)$$

where a and b represent the slope and intercept, respectively, of the LMWL at Chirripó.

Simple linear regression analysis was used to construct the LMWL, the LEL, and $\delta^{18}O-\delta^2H$ plots of isotopic signatures of stream and lake water of Chirripó. A Kruskal–Wallis non-parametric one-way analysis of variance on ranks (Kruskal & Wallis, 1952) was used to investigate if the isotopic signatures (i.e., $\delta^{18}O$, *d*-excess, and Ic-excess) of one lake system stochastically dominates the other lakes and the input waters (i.e., precipitation or streams) during the study period. A pairwise multiple comparison procedure was applied using the Dunn's method (Dunn, 1961) for those groups having a significant difference in $\delta^{18}O$, *d*-excess, and Ic-excess in order to isolate the stochastic dominance of the group or groups that differ from the others.

2.4 | Evaporation conditions analysis

The evaporation to inflow ratios (*E*/*I* ratios) of Lake Chirripó, Lake Ditkevi, and Morrenas lakes were estimated using the stable isotope balance approach described by Gibson, Birks, and Yi (2016); Gibson, Birks, Yi, Moncur, and McEachern (2016). The calculations were done for the dry and wet seasons of Chirripó in order to take into account the seasonal precipitation variations. For each season, an average *E*/*I* ratio was calculated for the three lake systems. In this approach, the evaporation (*E*) from the lakes as a fraction of inflow are estimated based on the linear resistance model developed by Craig and Gordon (1965) for free-surface evaporation. Calculations were done using the Hydrocalculator software that provides robust estimations of evaporation based on the isotopic composition of water (Skrzypek et al., 2015). The *E*/*I* ratios were calculated using the following equation:

$$\frac{E}{I} = \frac{1 - h}{h} x \frac{\delta_{lake} - \delta_{rain}}{\delta^* - \delta_{lake}},$$
(3)

where *h* is the average local relative humidity during the dry and wet season (expressed as a fraction), δ_{rain} is the average dry and wet season isotopic composition of precipitation, δ_{lake} is the average dry and wet season isotopic composition of lake water, and δ^* is the limiting isotope composition enrichment. The further estimations of δ^* were conducted using the following expression:

$$\delta^{*} = \frac{h \times \delta_{vapor} + \varepsilon}{h - \frac{\varepsilon}{1000}},$$
(4)

where ε is the total isotope fractionation and δ_{vapor} is the isotopic composition of atmospheric water vapour. The total isotope fractionation is defined as

$$\varepsilon = \frac{\varepsilon^+}{\alpha^+ + \varepsilon_k},\tag{5}$$

where ε^+ is the equilibrium isotope fractionation factor, ε_k is the kinetic isotope fractionation factor, and α^+ is the equilibrium isotope fractionation factor. ε^+ values are temperature dependent, with $\varepsilon^+ = (\alpha^+ - 1) \times 1,000$. The α^+ values were computed using the following equations for hydrogen and oxygen, respectively (Horita & Wesolowski, 1994):

$$\begin{aligned} &10^3 \text{xln}(\alpha^+) = 1,158.8 \text{x} \text{T}^3 \text{x} 10^{-9} - 1,620.1 \text{x} \text{T}^2 10^{-6} \\ &+ 794.84 \text{x} \text{T} \text{x} 10^{-3} - 161.04 + 2.9992 \text{x} \text{T}^{-3} 10^9, \end{aligned} \tag{6}$$

$$\begin{split} 10^{3} \textit{xln}(\alpha^{+}) &= -7.685 \\ &+ 6.7123 \textit{x} \textit{T}^{-1} 10^{3} - 1.6664 \textit{x} \textit{T}^{-2} \textit{x} 10^{6} - 0.35041 \textit{x} \textit{T}^{-3} 10^{9}, \end{split}$$

where T (K) is the temperature, estimated using the lake water surface temperature (usually close to the air-water mean temperature, Gibson, Birks, & Yi, 2016). The ε_k values were approximated using the following equation:

$$\varepsilon_k = (1 - h) x C_k, \tag{8}$$

where C_k is the kinetic fractionation constant, 12.5‰ for δ^2 H and 14.2‰ for δ^{18} O (Gonfiantini, 1986).

The δ_{vapor} was estimated using local records of precipitation and their stable isotope composition (δ_{rain}) during the dry and wet season, corrected using the LEL, and based on the following equation:

$$\delta_{vapor} = \frac{\delta_{rain} - X x \epsilon^{+}}{1 + X \epsilon^{+} x 10^{-3}}.$$
 (9)

The X term in Equation (9) is a correction factor that is assigned to values between 0.6 and 1.0, and it is adjusted to minimize the difference between the calculated slope of LEL by Hydrocalculator software and the actually observed slope of LEL obtained from the evaporation pan experiment (Skrzypek et al., 2015).

The probable error range (PER) of *E/I* ratios was estimated using the root mean square method (Topping, 1972), where the relative error estimates for the individual calculation components, estimated as one standard deviation, were combined using the following expression:

$$\frac{\mathsf{PER}_{E/l}}{\frac{E}{l}} = \sqrt{\left(\frac{\sigma_{T}}{T}\right)^{2} + \left(\frac{\sigma_{h}}{h}\right)^{2} + \left(\frac{\sigma_{\delta_{rain}}}{\delta_{rain}}\right)^{2} + \left(\frac{\sigma_{\delta_{lake}}}{\delta_{lake}}\right)^{2}}, \quad (10)$$

where σ_T , σ_h , $\sigma_{\delta rain}$, and $\sigma_{\delta lake}$ are the standard deviations of *T*, *h*, δ_{rain} , and δ_{lake} , respectively, and $PER_{E/l}$ is the *PER* value of *E/l*. This expression includes the input parameters that have a dominant contribution to the calculation of *E/l* values of a lake and that have been previously identified using sensitivity analysis, namely, the water temperature; air humidity; input water isotope (e.g., precipitation); and lake water isotope (Cui et al., 2017; Gibson et al., 1993; Mayr et al., 2007).

2.5 | Lake water balance

For Lake Ditkevi, a stable isotope approach was used to calculate an annual water balance after confirming if this glacial lake was at steady-state conditions (i.e., that the water level remains constant as evaporation from the pool was compensated by inflow that equalled or exceeded evaporation; Gibson et al., 1993; Gibson, Birks, & Yi, 2016). Hydrometric measurements (i.e., water levels) were used to estimate the change in the lake storage and to confirm steady-state conditions. Under steady-state conditions, the annual balance of the lake was then defined as

$$I = O + E, \tag{11}$$

$$\delta_I I = \delta_O O + \delta_E E, \tag{12}$$

where *I*, *O*, and *E* are the lake inflow, lake outflow, and evaporation fluxes (m³/yr), respectively, and δ_{I} , δ_{O} , and δ_{E} are the isotopic

composition of the lake inflow, lake outflow, and evaporation fluxes (‰), respectively (Gibson, Birks, Yi, Moncur, & McEachern, 2016). For a well-mixed and headwater stagnant water body such as Lake Ditkevi, the isotopic composition of lake water (δ_{lake}) is roughly equal to the lake water outflow (δ_O), and the isotopic composition of lake inflow is approximately close to that of precipitation (δ_{rain} ; Gibson, Birks, & Yi, 2016). Water input to Lake Ditkevi may have included some subsurface water from the bottom layers of Páramo soils (e.g., Histosols and Andosols). We assumed that these were very small, as they are mostly restricted to flow depths <1 m in soil layers above bedrock (Buytaert, Iñiguez, & De Bièvre, 2007; Correa et al., 2017).

The δ_{vapor} calculated using Equation (9) was used to approximate the average isotopic composition of the evaporation fluxes under the climatic conditions of Chirripó. It is expected that evaporation in our study area occurs consistently throughout the year with atmospheric moisture in equilibrium with precipitation because of its location in a tropical region (Gibson, Birks, & Yi, 2016). Therefore, the dry and wet season *E/I* values calculated for each lake system using Equation (3) were compared with estimate the influence of the precipitation input variations on the evaporation conditions of the lakes. The isotopic composition of the evaporation fluxes was then calculated using the expression defined by Craig and Gordon (1965):

$$\delta_{E} = \frac{\left((\delta_{lake} - \varepsilon^{+}) / (\alpha^{+} - hx\delta_{vapor} - \varepsilon_{k}) \right)}{\left(1 - h + 10^{-3}x\varepsilon_{k} \right)},$$
(13)

where the input variables were previously defined.

The water inflow to the lake (i.e., *I* in Equation 11) was estimated using the annual *E* calculated using the Penman method and the average annual E/I value (Equation 3) of Lake Ditkevi using the following expression:

$$I = \frac{E}{\overline{E}}.$$
 (14)

The ungauged run-off inflow contribution (*R*) to Lake Ditkevi was estimated as R = I-P, where *P* is the precipitation on the lake surface using Equation (15).

$$R = \frac{E}{\overline{E}} - P \tag{15}$$

Using the above-calculated R (in m³), the water yield (W_y), or depth-equivalent run-off, of the Lake Ditkevi catchment was estimated using the following expression:

$$W_{\rm y} = \frac{R}{W_{\rm A}} \times 1,000. \tag{16}$$

where W_A is the catchment area (in m²). The catchment area was estimated using ArcGIS performing a delineation of upstream and surrounding area of the lake based on the hydrographic and elevation data available for Chirripó. The planimetric area of the catchment polygon was calculated in the ArcGIS software based on the equal area projection. Based on the bathymetric data recorded for Lake Ditkevi, the lake water residence time (τ) was calculated using the

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following expression:

$$\tau = \frac{\frac{E}{I}xV}{E}$$
(17)

that uses the estimated volume V (m^3). This calculation takes into account the catchment run-off and precipitation contributions to the lake (Gibson, Birks, Yi, Moncur et al., 2016).

3 | RESULTS

3.1 | Isotopic temporal variations in precipitation and lake water

Between September 2015 and July 2017, mean monthly ambient temperature was $15.0 \pm 1.5^{\circ}$ C (1 σ) and varied between 12.7 $^{\circ}$ C and 18.4 $^{\circ}$ C. The maximum precipitation was recorded in May 2017 (385 mm/month, Figure 2a), and the minimum precipitation was

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registered in January 2016 and February 2017 (5 mm/month, Figure 2a). Mean precipitation during the dry season and wet season was 50 mm/month and 195 mm/month, respectively. The isotopic variations (δ^{18} O and *d*-excess) of precipitation showed greater average changes at the beginning of the dry season in November–December (range: -20.67‰ to -4.32‰, mean value: -11.51‰; Figure 2b) and at the end of the dry season in April–May (range: -14.81‰ to -4.52‰, mean value: -10.24‰; Figure 2b). Increased *d*-excess values (up to +27.94‰) were also registered at the beginning and end of the dry seasons in November–December and April–May, respectively. Low *d*-excess values (up to -1.63‰) were registered during the most intense rainy periods (November 2015, May 2016, and October 2016; Figure 2b).

No significant differences were found in the average δ^{18} O values of precipitation between the wet seasons of 2015 and 2016 (mean value $\pm 1\sigma$: $-11.74 \pm 4.01\%$ and $-11.55 \pm 2.6\%$, respectively) and between the dry seasons of 2015–2016 and 2016–2017 (mean value $\pm 1\sigma$: $-5.53 \pm 2.00\%$ and $-6.51 \pm 2.90\%$, respectively). The



FIGURE 2 Time series of (a) mean monthly precipitation (blue bars, mm/month) and ambient temperature (red circles, °C). (b) δ^{18} O (‰) composition and (c) *d*-excess (‰) for precipitation (blue circles), Lake Chirripó (red squares), and Lake Ditkevi (green triangles). (d) lc-excess (‰) for Lake Chirripó (red squares) and Lake Ditkevi (green triangles)

corresponding mean *d*-excess values also were similar between the dry and wet seasons. The mean *d*-excess values in the wet seasons of 2015 and 2016 were $10.43 \pm 3.43\%$ and $11.72 \pm 3.50\%$, respectively, whereas the *d*-excess value observed in the dry season of 2016–2017 was $18.41 \pm 4.41\%$ and $13.85 \pm 2.64\%$ during the dry season 2015–2016.

The isotopic variations (δ^{18} O) in Lake Chirripó (range: -16.90%) to -8.33‰, mean: -9.57‰) and in Lake Ditkevi (range: -11.57‰ to -5.77‰, mean: -8.52‰) were similar but attenuated in comparison with those in precipitation (Figure 2c,d). The temporal changes in δ18O were more noticeable in Lake Ditkevi than in Lake Chirripó, especially during the dry season (December-April), due to a reduction in precipitation (up to 5 mm/month; Figure 2a), the smaller volume of Lake Ditkevi, and thus the smaller residence time of water in this lake. For example, dry season δ^{18} O values in Lake Ditkevi varied between -10.35‰ and -5.77‰ (mean value: -7.81‰), whereas in Lake Chirripó, these values fluctuated between -10.27‰ and -8.33‰ (mean: -9.05%). The observed dry season variations in δ^{18} O coincided with a simultaneous decrease in the *d*-excess values of Lake Ditkevi and Lake Chirripó. In Lake Ditkevi, d-excess was in the range 2.33-10.42‰ (mean: 5.97‰), and in Lake Chirripó, d-excess changed between 2.71‰ and 8.90‰ (mean: 6.28‰). The lowest d-excess values occurred in April-May and November-December (up to -0.36‰ and 2.71‰, respectively). Ic-excess values were also systematically low in Lake Chirripó and Lake Ditkevi during the dry season (Figure 2c,d). In Lake Ditkevi, the Ic-excess varied between -11.86‰ and -2.43‰ (mean: -7.81‰), and in Lake Chirripó, the corresponding Ic-excess values were between -10.89‰ and -4.40‰ (mean: -7.05‰). During the wet season, and in response to the input of precipitation, relative increments in both the *d*-excess and lc-excess were observed. In Lake Ditkevi, the highest d-excess and Ic-excess were +11.54‰ and -1.69%, respectively, whereas in Lake Chirripó, these values were +16.71‰ and +6.27‰, respectively. These increments in the *d*-excess and lc-excess also coincided with low δ^{18} O values in Lake Ditkevi and Lake Chirripó (up to -11.57‰ and -16.90‰, respectively).

The average isotopic composition (δ^{18} O) of Lake Chirripó showed no significant variations between the seasons (i.e., the wet seasons of 2015 and 2016 and the dry seasons of 2015-2016 and 2016-2017). The mean isotopic compositions in the wet seasons of 2015 and 2016 were $-9.88 \pm 0.26\%$ and $-9.10 \pm 0.32\%$ (1 σ), respectively, whereas for the dry seasons of 2015-2016 and 2016-2017, these values were -9.01 ± 0.56‰ and -9.18 ± 0.66‰, in that order. Unlike Lake Chirripó. Lake Ditkevi showed variations in the average δ^{18} O values between the wet seasons of 2015 and 2016. The average δ^{18} O value was greater in the wet season of 2015 than that of 2016 (-10.01 ± 0.76‰ vs. -8.94 ± 0.68‰). However, no difference was found between the dry seasons of 2015-2016 and 2016-2017 (from -8.35 ± 1.45‰ to -7.59 ± 1.44‰). For Lake Ditkevi, dry season isotopic compositions were also significantly different from wet season compositions. These isotopic variations were also evident in the dexcess and Ic-excess. These secondary isotope-derived parameters decreased in 2016 with respect to 2015, from 10.03 ± 0.92‰ to 5.32 ± 2.53‰ and from -2.95 ± 0.96‰ to -8.19 ± 2.92‰, respectively.



FIGURE 3 (a) Graph of δ^{18} O versus δ^2 H in precipitation (blue circles) used to calculate the local meteoric water line (LMWL). The local evaporation line (LEL) was calculated using the pan evaporation data (red squares). The calculated mean isotopic composition of water vapour (black diamond) is also shown. Error bars represent ±1 σ . (b) Evaporation lines calculated for stream waters (green triangles), Lake Ditkevi (blue squares). The global meteoric water line (GMWL) is included as reference in both panels a and b

TABLE 2 $\delta^2 H$ versus $\delta^{18} O$ relationships in precipitation, streams, lakes, and the pan evaporation experiment at Chirripó between September 2015 and July 2017

	$\delta^2 H$ versus $\delta^{18} O$ relationship	r ²
LMWL	$\delta^2 H = 8.37^* \delta^{18} O + 16.7\%$	0.98
LEL	$\delta^2 H = 5.21^* \delta^{18} O - 22.3\%$	0.96
Streams	$\delta^2 H = 8.01^* \delta^{18} O + 11.4\%$	0.93
EL Lake Ditkevi	$\delta^2 H = 6.49^* \delta^{18} O - 6.43\%$	0.96
EL Lake Chirripó	$\delta^2 H = 6.61^* \delta^{18} O - 7.01\%$	0.97
EL Morrenas Lakes	$\delta^2 H = 6.07^* \delta^{18} O - 10.5\%$	0.95

Note. EL: lake water evaporation line; LEL: local evaporation line; LMWL: local meteoric water line. r^2 = determination coefficient (p < 0.001).

3.2 $~\mid~ \delta^2 H$ and $\delta^{18} O$ relationships in precipitation, stream, and lake waters

The LMWL of Chirripó was $\delta^2 H = 8.37^* \delta^{18} O + 16.7\%$ ($r^2 = 0.98$, N = 166, p < 0.001; Figure 3 and Table 2). For stream water, the

 δ^2 H versus δ^{18} O relationship was δ^2 H = 8.01* δ^{18} O + 11.4‰ $(r^2 = 0.93, N = 29, p < 0.001;$ Figure 3 and Table 2). The LEL for Chirripó estimated from the pan evaporation experiment (red circles in Figure 3) was $\delta^2 H = 5.21^* \delta^{18} O - 22.3\%$ ($r^2 = 0.96$, N = 21, p < 0.001; Figure 3 and Table 2). During the pan evaporation data-collection period, the average temperature and humidity at Chirripó were 14.0 ± 2.7 °C (1 σ) and 0.79 \pm 0.56 (1 σ), respectively. During the completion of the experiment (136 hr), an enrichment of ~9‰ for δ^{18} O (from -11.67‰ to -4.06% for δ^{18} O) was registered with a mean evaporation rate of 5.0 ± 2.2 mm/day (~42% of the initial water volume). Additionally, the calculated mean isotopic composition of atmospheric water vapour (black diamonds; Figure 3) was -149.91% for δ^2 H and of -20.74% for δ^{18} O. As shown in Table 2, there is little variation among the slopes of the ELs of the three lakes (6.07–6.61). These slopes of ~6 are greater than the slopes of the LEL but resemble the LEL in the negative intercepts (-10.5‰, -7.01‰, and -6.43‰) as a result of evaporation effects. A comparison between the intercepts for precipitation and stream water (+16.7‰ and +11.4‰, respectively) indicate that stream water in Chirripó is also somewhat affected by evaporation, but to a much lesser degree than the lake water (Clark & Fritz, 1997).

Using the Kruskal-Wallis non-parametric one-way analysis of variance on ranks, statistically significant differences were found between the median δ^{18} O, *d*-excess, and lc-excess values of precipitation, stream, and lake waters shown in Table 3 (p < 0.001, Figure 4a-c). No significant differences were found between the median $\delta^{18}O$ values of precipitation and stream water (-10.77‰ and -10.60‰, respectively; p > 0.05). Nevertheless, the median δ^{18} O values of the lakes (Lake Ditkevi, -8.54‰; Lake Chirripó, -9.34‰; and Morrenas lakes, -9.36‰) were significantly greater than the corresponding median δ^{18} O of precipitation and stream water (p < 0.001). No significant differences were found between the median d-excess values of the lakes (Lake Ditkevi, 6.25%; Lake Chirripó, 5.77%; and Morrenas lakes, 7.86‰, p > 0.05). However, these values were significantly lower than the median *d*-excess of precipitation and stream water (12.11‰ and 10.77‰, respectively; p < 0.05). The median lc-excess values of the lakes (Lake Ditkevi, -7.40%; Lake Chirripó, -7.39%; and Morrenas lakes, -5.19‰) were significantly lower than the median value for stream water (-1.90‰, p < 0.05), but not significantly different among the lake waters (p > 0.05). Overall, the mean isotopic composition of the lakes shown in Table 3 is slightly greater than the δ^{18} O values (-14.5‰ to 12.2‰) and *d*-excess (+11.4‰ to +16.0‰) reported by Lachniet and Patterson (2002) for one precipitation sample and three lake water samples they collected at Chirripó.

3.3 | Evaporation to inflow ratios

The *E/I* ratios calculated for the dry seasons (December–April) of 2015–2016 and 2016–2017 and for the wet seasons (May–November) of 2015 and 2016 are isotope-based estimates expressed in percentage (Figure 5). Based on the stable isotope water balance approach, *E/I* ratios of the lakes were greater during the dry season than during the wet season. For the dry season of 2015–2016, the estimated seasonal *E/I* ratios and the corresponding PER_{E/I} values for Lake Chirripó, Lake Ditkevi, and Morrenas lakes were 8.5 ± 4.5%, 10.7 ± 6.0%, and 18.1 ± 12.2%, respectively, whereas during the dry

	summary	/ statisti	cs of the Is	otopic data	a Irom wate	er samples	collected at		ndəc uəəmə	ember 201	ז אוחר מחה כ							
				δ ¹⁸ Ο ((°%			δ ² H ((%)			d-excess	(%o) (%)			lc-exces	s (%o)	
Water samples		z	Median	Max	Min	SD	Median	Max	Min	SD	Median	Мах	Min	SD	Median	Мах	Min	SD
Precipitatio	۲	166	-10.77	-3.32	-20.67	3.94	-72.41	-10.55	-155.45	33.29	12.11	27.94	-1.63	4.75				
Pan experii	nent	21	-7.75	-4.06	-11.64	2.18	-60.44	-48.59	-84.87	11.64	1.46	8.26	-16.10	6.58				
Streams		29	-10.60	-6.41	-13.02	1.17	-73.82	-38.10	-93.65	9.69	10.78	17.17	7.15	2.48	-1.90	4.50	-5.77	2.52
Lake Ditke	/i	41	-8.57	-5.77	-11.57	1.47	-63.39	-41.90	-82.12	9.77	6.71	11.54	-0.36	2.85	-6.89	-1.69	-14.15	3.31
Lake Chirri	ЭÓ	31	-9.34	-8.33	-16.90	1.48	-67.90	-58.03	-118.49	9.93	5.77	16.71	2.71	2.64	-7.39	6.27	-10.89	3.08
Morrenas L	akes	24	-9.36	-1.88	-11.51	2.42	-66.83	-26.14	-80.01	15.06	7.86	13.03	-11.08	5.78	-5.20	0.60	-27.05	6.52
:			:	-	-	-	:											

200

c

Note. Max: maximum; Min: minimum; N: number of samples; SD: standard deviation.



FIGURE 4 Box plots of (a) δ^{18} O (‰) and (b) *d*-excess (‰) in precipitation, Lake Chirripó, Lake Ditkevi, Morrenas lakes, and streams. (c) lc-excess (‰) in Lake Chirripó, Lake Ditkevi, Morrenas lakes, and streams. The grey box indicates the 25th and 75th percentiles with the median in middle. The error bars indicate the minimum and maximum values. The black circles indicate outliers (1.5 times the central box)

season of 2016–2017, the analogous mean values were $5.2 \pm 3.1\%$, 10.8 ± 6.9%, and 6.1 ± 4.2%, respectively (Figure 5a). For the wet season of 2015, these *E/I* ratios were 2.6 ± 1.0%, 2.0 ± 0.8%, and 2.7 ± 1.0%, in that order, and for the wet season of 2016, the corresponding ratios were 4.9 ± 1.6%, 5.7 ± 1.9%, and 3.7 ± 1.2%, respectively. Using these seasonal estimates in 2015, the average *E/I* ratios were estimated as 5.5%, 6.4%, and 10.4%, respectively, whereas in 2016, these values were 5.3%, 8.6%, and 8.2%.

3.4 | Lake Ditkevi

The major morphometric characteristics used to estimate the water levels of Lake Ditkevi are shown in Table 4 and Figure S1 (bathymetric depth profile). In the time period from July 2016 to July 2017, a decrease in the water level of 19 mm in Lake Ditkevi was recorded which corresponds to a variation of ~0.5% in the mean lake volume. The lake water temperature and air humidity are shown in Figure 6a. The observed *h* (as defined in Equation 3) at Lake Ditkevi varied between 38.5% and 98.5%, with a mean of 71.8% ± 18.5% (1 σ), whereas the mean lake water temperature at ~1.25 m depth was 12.0°C ± 1.3°C, with minimum and maximum values of 8.5°C and



FIGURE 5 (a) Dry season and (b) wet season estimates of evaporation to inflow ratios (*E*/*I*, in %) for Lake Chirripó, Lake Ditkevi, and Morrenas lakes. Error values were calculated as the probable error range by combining the relative error estimates of water temperature, air humidity, isotopic composition of precipitation, and lake water

15.0°C, respectively. A mean water level of 3,509.1 m a.s.l. was estimated for Lake Ditkevi (Figure 6b), equivalent to a mean depth of 3.5 m and a volume of 5.77×10^4 m³ (Table 4).

In general, the mean daily changes in water level showed a relatively stable level between July and November 2016, with sporadic increases between December 2016 and mid-January 2017 (up to 3,509.5 m a.s.l.) caused by relatively large precipitation events (up to 50 mm/day). In February and parts of April 2017, a constant decrease in the water level (down to 3,508.9 m a.s.l.) was recorded, followed by slight increases in water levels due to precipitation events of up to ~30 mm/day between March and April 2017. After May 2017, when the wet season was re-established at Chirripó, another increase in water level was observed. As shown in Figure 6c, there was a clear effect of the dry season (from December to April) on the isotopic composition of the lake water. The greatest changes in water level and lcexcess were observed during the dry season when E/I ratios in the lakes tend to increase as result of decreased precipitation in Chirripó (December-April; Figure 6c). This results in a systematic reduction in Ic-excess was observed (down to -14.1%), but also a high response to precipitation inputs that rapidly increased Ic-excess, especially at the beginning of the wet season. Overall, the water-level data

TABLE 4 Major morphometric characteristics, annual water balance components, and isotope-based estimates of evaporation/inflow (*E/I*) and residence time (τ) for Lake Ditkevi between July 2016 and July 2017

Major morphometric parameters	
Lake area (×10 ⁴ m ²)	1.66
Mean volume (×10 ⁴ m ³)	5.77
Maximum depth (m)	8.2
Mean depth (m)	3.5
Annual water balance components	
Precipitation (mm)	1,682
δ ¹⁸ Ο (‰)	-10.41
δ ² Η (‰)	-68.96
Lake evaporation (mm)	650
δ ¹⁸ Ο (‰)	-33.42
δ ² Η (‰)	-178.47
Lake outflow (O, mm)	5,874
Δ Lake level (mm)	-19
Basin area (×10 ⁵ m ²)	2.89
Water yield or depth-equivalent run-off, (W_y, mm)	278
Isotope-based estimates	
E/I (%)	10.0 ± 5.0
τ (years)	0.53 ± 0.27

recorded in Lake Ditkevi confirm that on an annual time step, it can be assumed that the lake was at steady state.

Using the available meteorological data at Chirripó and the Penman equation, the average daily evaporation from the lakes of Chirripó varied from 1.2 mm/day in May to 4.6 mm/day in February (average value: 2.3 \pm 0.9 mm/day). Annual *E* from the lakes was 823 mm/yr. Tanny et al. (2008) reported that daily evaporation using five evaporation models (which included Penman-based equations) was about 1.27 times greater than the evaporation measured using eddy covariance methods. Therefore, *E* from the lakes of Chirripó calculated using meteorological data and the Penman equation are equal to 650 mm/ yr, after applying a correction factor of 1.27 to the 823 mm/year value. The average daily evaporation of 5.0 \pm 2.2 mm/day measured using the pan experiment at Chirripó corrected using a pan coefficient of 0.65 (Tanny et al., 2008), gives a reference value of 3.25 mm/day equivalent to the mean daily evaporation of 3.3 mm/day in April at Chirripó based on the Penman method.

From July 2016 to July 2017, the average annual *E/I* ratio was 10.0 \pm 5.0%, which yields an annual inflow of 6,524 mm/year (or 1.1×10^5 m³/year) for Lake Ditkevi, with a relative contribution of precipitation and ungauged run-off of 26% and 74%, respectively. The run-off ratio was estimated as the ratio of the lake outflow (5,874 mm/ year or 9.8 $\times 10^4$ m³/year; Table 4) to precipitation over the catchment area ($P \times W_A$ or 4.9×10^5 m³/year), which is equivalent to 20.0%. This run-off ratio is smaller than the run-off ratios reported for the Marianza and Huagrahuma Páramo catchments (0.84 and 2.58 km², respectively) located in southern Ecuador (Cuenca) of 53–73%, correspondingly (Buytaert et al., 2007). However, Poulenard, Podwojewski, Janeau, and Collinet (2001) reported run-off ratios lower than 25% for undisturbed Páramo sites located in northern Ecuador. The water residence time estimated for Lake Ditkevi was calculated as 0.53 \pm 0.27 years. This result

also means that most of the water input (~90%) to Lake Ditkevi is lost either by surface outflow (mostly ungauged run-off) or, possibly, infiltration processes through the Páramo soils. Based on the catchment area of Lake Ditkevi ($2.89 \times 10^5 \text{ m}^2$ or 0.289 km²) and the ungauged run-off estimation, the first isotope-based water yield or depth-equivalent run-off (W_y) is 278 mm/year for the Páramo of Chirripó, which can be considered equivalent to the average run-off contribution from the catchment to the lake expressed as annual depth equivalent (Table 4). In general, the Lake Ditkevi catchment is characterized by steep slopes that promote rapid hydrological responses such as the fast water-level changes shown in Figure 6b (Kang et al., 2017). For example, precipitation events registered during the dry season caused a fast response in lake levels (Figure 6b).

4 | DISCUSSION

4.1 | Seasonal controls on the isotopic composition of lake water

The precipitation records (shown in Figure 2a) are in agreement with the historical precipitation pattern reported by Kappelle and Horn (2016), with 82% of the rainfall registered between May and November during the study period. Lake-water temperature measurements are also in agreement with the temperature values reported by Horn et al. (2005). EC measurements confirm the low concentrations of dissolved substances in Lake Chirripó reported by Göcke et al. (1981) and Jones et al. (1993), which reflect the type of parent material in this watershed (i.e., volcanites and plutonic materials).

The changes in δ^{18} O values of precipitation depict a systematic depletion due to convective precipitation reaching Chirripó and are linked to the passage of the Intertropical Convergence Zone over Costa Rica (Rhodes, Guswa, & Newell, 2006; Sánchez-Murillo et al., 2016). The observed positive variations in *d*-excess were due to the influence of re-evaporated/recycled moisture fluxes (Sánchez-Murillo et al., 2013), whereas the negative changes in this second-order parameter were related to precipitation formed under high humidity conditions of the Talamanca range of Costa Rica (Pfahl & Sodemann, 2014). The isotopic composition of lake water may change due to the timing of precipitation, surface and subsurface inflows, and evaporation loss from the lake surface (Cui et al., 2017). Overall, the attenuation effect observed in Lake Chirripó and Lake Ditkevi most likely resulted from the relatively long residence times of precipitation, stream, and subsurface water. A similar effect was observed in highelevation Páramo catchments in southern Ecuador by Mosquera et al. (2016b). Such catchments were fed by wetlands where water resides for long periods in the hydrologic system, with catchments with more attenuated isotopic compositions showing the longest water residence times. Despite these attenuations in the isotopic compositions of the lake waters, these compositions still preserve the observed seasonality in the isotopic composition of precipitation (Figure 2b). This indicates that the input of water to these glacial lakes is mostly controlled by the seasonal inputs of rainfall, which mix up with stream and subsurface waters at Chirripó (Mayr et al., 2007; Yi, Brock, Falcone, Wolfe, & Edwards, 2008). The larger variation in the isotopic composition of Lake Ditkevi may reflect its smaller lake



FIGURE 6 Time series graphs constructed for Lake Ditkevi between July 2016 and July 2017 showing (a) mean daily water temperature (blue squares) and mean daily relative humidity (*h* in %, green circles). (b) Daily precipitation (mm/day, blue bars) and mean daily water level (in m). The mean water elevation was estimated as 3,509.1 m (dashed red line), with an equivalent mean lake volume of 5.77×10^4 m³. (c) Mean weekly water level (red squares) and Ic-excess (green triangles)

volume (5.77 × 10^4 m³; Table 1) in comparison with Lake Chirripó (4.45 × 10^5 m³; Göcke et al., 1981), which resulted in a larger isotopic enrichment due to evaporation in this lake. Similar findings have been reported by Gibson et al. (1993) and Gibson, Birks, Yi, Moncur, et al. (2016) in lake systems of Canada located in the Districts of Mackenzie and Keewatin, and in Alberta, respectively.

Terrestrial surface waters with *d*-excess values <10 are presumed to have undergone evaporation, and lower *d*-excess values in lakes generally indicate more evaporation (Brooks et al., 2014). Therefore, the low *d*-excess values recorded in lake waters of Lake Chirripó and Lake Ditkevi (median: 5.77‰ and 6.71‰, respectively; Table 3) with respect to the precipitation of Chirripó (median: 12.11‰; Table 3) indicate net evaporation from these lakes (Cui et al., 2017). These evaporation effects were also evident in the lc-excess changes found in the lakes of Chirripó, which are in agreement with the observed variations in the lc-excess recorded in a peatland drainage network in Scotland during dry periods and related with lower discharge rates and greater potential evapotranspiration (Sprenger et al., 2017). Overall, the constantly low *d*-excess and lc-excess values (i.e., *d*-excess <10 and lc-excess <0; Figure 2c,d) recorded in Lake Chirripó and Lake Ditkevi throughout the study period demonstrate that these secondary isotope variables can provide better evidence of evaporation effects controlling the isotopic composition of the lake waters than the single isotopic composition (i.e., δ^{18} O) that is more variable and is mostly controlled by the seasonal inputs of rainfall.

4.2 | Evaporation effects on the isotopic composition of lake water

In general, the isotopic composition of water that has undergone evaporation diverges from the LMWL of the study region. The variations of δ^2 H and δ^{18} O values in surface waters are systematic because of mass-dependent fractionation that occurs during isotopic enrichment (Yi et al., 2008). Because of this isotopic enrichment, the slope of ELs usually varies between 4 and 6 (Gibson, Birks, & Yi, 2016) with lower values commonly associated with stronger evaporation effects (Brooks et al., 2014). Therefore, the slope of ELs calculated for Lake Ditkevi, Lake Chirripó, and Morrenas lakes can be compared with

12 WILEY the slope of the LMWL of Chirripó and gualitatively describe the evaporation losses in these lakes systems (Gibson & Reid, 2014). The LMWL of Chirripó compares well with the LMWL estimated for the montane cloud forest of Monteverde, Costa Rica (~1,500 m a.s.l.), which was $\delta^2 H = 8.6^* \delta^{18} O + 14.3\%$ (Rhodes et al., 2006). An intercept greater than +10% reflects the influence of re-evaporated/ recycled moisture arriving at Chirripó similar to other Páramo sites (e.g., Mosquera et al., 2016a). The LMWL and the δ^2 H versus δ^{18} O relationship for stream water share similar slope values (~8), although the smaller intercept of 11.4‰ for the stream water may indicate the influence of evaporation as indicated above (Clark & Fritz, 1997). The estimated slope of the LEL for Chirripó is consistent with the isotopic enrichment observed in $\delta^2 H$ versus $\delta^{18} O$ space for evaporating water under 75% humidity, for which a slope of 5.2 has been reported (Clark & Fritz, 1997; Gonfiantini, 1986). The slope of the LEL in Chirripó is also in agreement with values reported for nonseasonal systems (i.e., with evaporation occurring consistently throughout the year with atmospheric moisture in equilibrium with precipitation), for which slope values are typically in the range 4 to 5 (Bouchez et al., 2016; Gibson et al., 2008). As the isotopic composition of atmospheric water

vapour plots practically along the LMWL of Chirripó, it is likely that evaporation conditions at Chirripó are characterized by the input from precipitation that is in isotopic equilibrium with local water vapour (Gibson & Reid, 2014; Skrzypek et al., 2015). Therefore, the isotopic reference value provided by the pan evaporation experiment (i.e., LEL of Chirripó) seems to be a realistic reference value to be applied in the E/I calculations using the Hydrocalculator software (Skrzypek et al., 2015) because the isotopic fractionation in the pan was controlled by the actual meteorological conditions that prevailed at Chirripó during the experiment.

The slopes of the ELs for Lake Ditkevi, Lake Chirripó, and Morrenas lakes (Table 2) reflect the high-altitude climatic conditions of Chirripó as these $\delta^2 H$ versus $\delta^{18} O$ relations for these lakes have slopes >5, as previously reported for high elevation regions in Canada (Gibson et al., 2008; Gibson, Birks, & Yi, 2016) and the Andes of Bolivia (South America) at ~4,400 m a.s.l. (Abbott, Wolfe, Aravena, Wolfe, & Seltzer, 2000; Wolfe, Edwards, Beuning, & Elgood, 2001). As the slopes of the ELs are similar among these lake systems, these results suggest that lake water isotopic compositions are similarly affected by evaporation regardless of their position across the continental divide. These findings may be explained by the strong influence of the trade winds blowing from the Caribbean Sea and across the Caribbean side of the Talamanca range (Durán-Quesada et al., 2017). This wind influence is enhanced during the dry season and causes kinetic isotopic fractionation and mass transfer of liquid lake water to the atmospheric boundary layer above the lakes' surfaces (Feng, Lauder, Posmentier, Kopec, & Virginia, 2016; Gonfiantini, 1986).

The results of the non-parametric one-way analysis of variance are in agreement with the analyses of the lake water ELs. As the isotopic composition of precipitation and stream water is statistically different than the lake water, this finding provides further evidence that the isotopic composition of the lake waters in this study is strongly influenced by evaporation. In addition, the distinct isotopic composition of the different water cycle components of Chirripó (i.e., precipitation, stream, and lake waters) demonstrate the feasibility to separate the components of the lake water balance quantitatively using isotope-based estimates of E/I ratios in tropical montane glacial lakes, as has been previously evaluated in other environments by Gibson, Birks, and Yi (2016).

4.3 Evaporation conditions in the lakes of Chirripó

The estimated E/I ratios for Chirripó are relatively low compared with other lakes in the tropics, such as in Uganda-Congo (~50%; Russell & Johnson, 2006); the Tibetan Plateau (24.1-27.3%, Cui et al., 2017); southern Patagonia (50-58%, Mayr et al., 2007); and Alberta, Canada (18-136%, Gibson, Birks, Yi, Moncur, et al., 2016). These low E/I ratios of the Páramo of Chirripó showed differences between the lake systems that can be related to different lake morphologies, inflow rates, and wind exposure (Mayr et al., 2007). Overall, the higher E/I ratios found during the dry season with respect to the wet season are associated with the seasonal variations in the precipitation of Chirripó. For example, during the dry seasons of 2015-2016 and 2016-2017. cumulative precipitation amounts in Chirripó were 202 and 295 mm, respectively, whereas during the wet seasons of 2015 and 2016, these values were 922 and 1,359 mm, in that order. However, the year-toyear seasonal variations observed in the three lakes systems indicate that the contribution of evaporation to the lake water balance could vary across different periods. Therefore, E/I data need to be further validated by long-term isotopic monitoring of the different natural sources (Gibson et al., 2008; Wu et al., 2017).

The average smaller E/I ratio for Lake Chirripó compared with Lake Ditkevi and the Morrenas lakes appear to be related to the greater lake heat storage (Andreasen, Rosenberry, & Stannard, 2017) of Lake Chirripó, which has an area of 7.8×10^4 m² and a mean depth of 8.2 m (Göcke et al., 1981). The lake system located in Valle de las Morrenas, for example, has an area of $\sim 1.2 \times 10^5$ m², but a smaller mean depth of 5.2 m (Horn et al., 2005), which reduces the heat storage and enhances evaporation. The observed water temperature in Lake Chirripó is also in agreement with greater heat storage in this lake. For example, the average water temperature in Lake Chirripó was 12.5°C, whereas the average water temperature in the Morrenas lakes was 14.6°C (Table 1). Generally, lakes with smaller water volumes are subject to gradual volume reduction as a result of evaporation (e.g., Giadrossich, Niedda, Cohen, & Pirastru, 2015; Mayr et al., 2007), which could lead to overestimation in the mean E/I ratios because of the enhanced isotopic enrichment in the reservoir (Gibson et al., 1993). However, the estimated E/I ratios were more sensitive to the variations in δ_{rain} and *h* (with mean relative uncertainty values of ~28% and ~17%, respectively) than to those in T and δ_{lake} . For example, in the Morrenas lakes (which had the greatest variations in E/I ratios during the dry season), variations in δ_{rain} of ±3.5% for δ^{18} O in the calculation of the E/I values result in differences of ~5% in the E/I ratios, whereas variations of ±15% in h show changes in E/I values of ~10%. Therefore, the E/I ratios were not subject to overestimation introduced by high δ_{lake} values, as they were more sensitive to the δ_{rain} and *h* values. Additionally, because the δ_{rain} and *h* parameters were measured in situ, no assumption errors were introduced in the calculations of the E/I ratios due to these parameters.

4.4 | Lake Ditkevi hydrological status

The annual water balance results for Lake Ditkevi are representative of steady-state conditions. Overall, the water level of Lake Ditkevi appears to be controlled by seasonal increases of precipitation amount and run-off, which is a characteristic of headwater lakes without channelized inflow from upstream lakes (Gibson, Birks, & Yi, 2016). However, deep subsurface water contributions from a groundwater pool could be present as has been observed in the Páramo of northern Ecuador associated with water flowing through permeable morainic deposits (Favier et al., 2008). The relative contributions of subsurface/groundwater water entering and leaving Lake Ditkevi could not be guantified with the available data. A strong reduction in the precipitation amounts during the dry season was associated with a strong reduction in the stream water flow in Chirripó (Figures 2a and 6b). Field observations also revealed that from January to mid-April, the contribution of subsurface water to streams-and to the lakes potentially-was absent because the stream channels were totally dried up. These observations indicate that the contribution of groundwater to the lake systems was minimal, as was previously found in the wetlands of the Andean Páramo in southern Ecuador (Correa et al., 2017: Mosquera et al., 2016a; Mosquera et al., 2016b). As a result, the observed decreasing water levels in Lake Ditkevi during the dry season may reflect both the absence of precipitation, stream, and subsurface/groundwater contributions flowing to the lake (Figure 6b). These observations are in agreement with the fast water-level response to precipitation, which further indicate that Lake Ditkevi is mostly fed by precipitation and run-off.

The relatively low E/I ratios estimated for the lakes of Chirripó using the isotope-based approach may be explained by (a) the relatively high humidity recorded throughout the year at Chirripó (71.8% $\pm 18.5\%$, 1σ) that tends to limit the mass transfer of liquid lake water and atmospheric vapour at the lake surface; (b) the polymictic (i.e., nonstratified) characteristic of the lakes of Chirripó that mix frequently, keeping a relatively low and uniform water temperature in the lakes; and (c) the relatively high ungauged run-off estimated for the Lake Ditkevi catchment that results in a high throughflow in the lake and in a relatively fast transit time (~6 months), reducing the amount of water lost by evaporation. Similar evaporation conditions were identified using *d*-excess values (with mean values ranging from 10.7‰ to 11.6‰) in the wetlands of Zhurucay (southern Ecuador), where surface and soil water were not strongly evaporated as humidity remained relatively high year-round (usually >90%, Mosquera et al., 2016b). These wetlands are located at the valley bottoms near the streams and connected to the slopes mostly during the wet season (Correa et al., 2017), which are characteristics similar to those found in the Lake Ditkevi catchment. For these wetlands, estimated mean transit times were similar to the residence times calculated for Lake Ditkevi (0.64-0.84 years; Mosquera et al., 2016a). Finally, as Lake Ditkevi was found to be at steady-state during the study period and the lakes of Chirripó are well-mixed lakes (Göcke et al., 1981; Horn et al., 2005), the steady isotope mass balance model appears to provide accurate estimates of the E/I ratio for this lake (Gibson, Birks, & Yi, 2016; Mayr et al., 2007) and the isotopic compositions of evaporation fluxes in Table 4 are controlled by the isotopic atmospheric water WILEY <u>13</u>

vapour and the climate conditions of Chirripó (Gibson et al., 2008). As mentioned above, most of the water input to Lake Ditkevi is lost either by surface outflow or, possibly, by infiltration processes. As this physical outflow does not cause isotopic fractionation (Yi et al., 2008), the lake outflow is isotopically equal to lake water (i.e., $\delta_{lake} = \delta_0$), and relatively small temporal changes are observed in the isotopic composition of the lake water as shown in Figure 2B.

5 | CONCLUSIONS

The stable isotopic characterization of precipitation, streams, and lake waters has provided insights into the evaporation and water balance conditions of the tropical glacial lakes of Chirripó, Costa Rica. These findings reveal that (a) evaporation conditions in Chirripó are highly influenced by input from precipitation that is in isotopic equilibrium with local water vapour, (b) lake water undergoes low evaporation to inflow ratios (< 20%), and (c) the residence time of water in one of the investigated lakes is around 0.53 years. These findings and the isotope mass balance indicate that these lakes can be considered a reliable source of water for surrounding and lowland areas as ~90% of the water input to these lakes is available as surface outflow or, possibly, infiltration to the catchment. The stable isotope approach applied in the Páramo of Chirripó provides the first characterization of present-day surface water and lake conditions, which are valuable baseline for future studies on hydrology and climate including the reconstruction of past hydrologic conditions in other montane catchment in the tropics and elsewhere. Overall, tropical high-elevation lakes may be considered sentinels of global climate change because of their position near the equator that results in limited seasonal variation in temperature and, hence, a weak thermal stratification. Therefore, long-term monitoring of lake water temperature, level, and isotopic composition can be used to identify changing climatic conditions related to El Niño Southern Oscillation and, specifically, to changes in air temperature and seasonal cloud cover variations. Continuous lake surveys should also aim to update the limnological and trophic status of these lakes to provide novel information about the inputs of organic matter and nutrients from the catchment (e.g., dissolved organic carbon). Opportunities for future research also include the evaluation of the contribution of subsurface and groundwater components to lakes of glacial formation. Hence, these findings for Chirripó can serve as a baseline for the evaluation of lake conditions in other high-elevation tropical environments, such as in the glacial lakes of the Páramo of southern Ecuador, where limnological and trophic status analyses have been recently conducted, but the evaluation of lake water balance remains unknown.

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

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