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Key Points:

- Isotope-based metrics evidenced low evaporation to inflow (*E/I*) ratios (<5%)
- The water balance revealed seasonal water residence times of 0.61 (wet) - 1.08 (dry) years under steady-state conditions
- Estimates of groundwater input indicated an annual contribution of 61.3 ± 8.1% of total inflow

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Tracing Groundwater-Surface Water Interactions in a Volcanic Maar Lake Using Stable Isotopes and ^{222}Rn

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Abstract Isotope hydrological studies to understand groundwater-surface water interactions in tropical, high-elevation catchments are limited. These interactions are important in controlling lake water residence time, aqueous biogeochemistry, and water availability for downstream communities and ecosystems. To better comprehend the complexity of spatio-temporal variations in the aquifer-lake domain in tropical volcanic regions, a multi-tracer approach including water and inorganic carbon stable isotopes (δ^2H, δ^{18}O, $\delta^{13}C_{DIC}$), hydrochemistry, and ^{222}Rn was applied in Lake Hule, northern Costa Rica. Seasonal isotope mass balance calculations using lake, stream, precipitation, and groundwater compositions were supplemented with local hydrometeorological information. Evaporation to inflow ratios (*E/I*) revealed a small variability between the dry (December–April) and wet seasons (May–November), with relatively low evaporation losses, 2.9 ± 1.0 % and 3.2 ± 1.8 %, respectively. Bayesian end-member analysis indicated that annual inputs from groundwater, precipitation, and runoff represented 61.3 ± 8.1%, 24.4 ± 8.4, and 14.3 ± 5.9% of total lake inflow, respectively. Temporal variations of $\delta^{13}C_{DIC}$ confirmed the key role volcanic carbonate buffering plays in this lake and indicated greater CO_2 degassing from groundwater sources in the wet season. This tracer-aided assessment in a volcanic lake maar of northern Costa Rica provides evidence of previously unknown groundwater-surface water interactions and illustrates the application of isotopic tools for estimating water balances and seasonal variability of groundwater discharge into natural lakes across the volcanic front of Central America.

Plain Language Summary This study analyzed the interactions between groundwater and surface water at Lake Hule, a volcanic maar lake located in northern Costa Rica. The results showed that evaporation losses were relatively similar and low in both dry (December–April) and wet (May–November) seasons and that most of the total inflow to the lake was related to groundwater inputs. The study also revealed the key role of carbon dioxide (CO_2) dissolution in the lake water chemistry, with greater volcanic CO_2 inputs in the wet season. This study reveals previously unknown groundwater-surface water interactions regarding groundwater discharge into natural lakes across the volcanic front of Central America.

1. Introduction

Understanding the relationship between lacustrine and groundwater systems is key for assessing the impact of climate change and human activities on these water sources. Information about these interactions is also crucial for monitoring and managing water quality in lakes and aquifers. Moreover, it can also be used to determine sustainable water extraction without competing with natural replenishment rates (May et al., 2021; Vasistha & Ganguly, 2020). However, identification and quantification of groundwater-lake interactions are challenging in lacustrine systems, given the intricate relationships between water chemistry, mass, and energy fluxes, and the local hydrogeology of these landscapes (Jian et al., 2020; Ortega et al., 2015).

Isotope techniques are useful for identifying and tracing water sources across regional/local and temporal scales (De Freitas et al., 2019; Ortega et al., 2022; Pierchała et al., 2022). Stable isotopes, such as oxygen-18 and deuterium, can provide insights into the origin and flow paths of groundwater discharge (Balagizi et al., 2022; Jian et al., 2020; Sánchez and Birkel, 2016; Sánchez-Murillo et al., 2022a; Wu et al., 2021). Additionally, radon-222

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(hereafter ^{222}Rn), a naturally occurring radioactive gas, serves as a tracer for groundwater discharge due to its high solubility in water and relatively short half-life (∼3.87 days). Monitoring ^{222}Rn activities in lake water can reveal areas where groundwater input is substantial, aiding in quantifying groundwater fluxes into lakes (Cook et al., 2008; Dabrowski et al., 2020). Together, stable isotopes and ^{222}Rn offer valuable information for understanding the dynamics of lacustrine groundwater discharge, which is essential for managing water resources and ecosystems in lake environments (Luo et al., 2018; Petermann et al., 2018).

Lakes serve as essential freshwater reservoirs, supporting biodiversity and providing water for agriculture, drinking, and hydroelectric power. In tropical regions, like Costa Rica, lakes are abundant and represent multiple lake formation processes, including volcanic activity, fluvial dynamics, glaciation, and landslides (Horn, 2017; Horn & Haberyan, 2016). Overall, volcanic lakes or maars can be classified into (a) high-activity lakes, affected by inputs of hydrothermal-magmatic fluids (e.g., high temperature and hyper-acidic), and (b) low-activity lakes, characterized by CO_2-dominated fluid inputs at a relatively low rate from sub-lacustrine fluid discharge (Cabassi et al., 2014; Rouwet et al., 2014). Lakes in the vicinity or within maar structures usually present intriguing hydrological processes as interactions between subsurface waters (e.g., aquifers and hydrothermal activity) and the critical zone can play a significant role in shaping water fluxes and solute transport. The convergence of these components establishes a dynamic equilibrium governing water levels, biogeochemical compositions, and ecology within lake ecosystems (Aguilar et al., 2023; Cabassi et al., 2014; Silva-Aguilera et al., 2022). The implementation of protecting and preserving actions for these lakes is critical for maintaining ecological connectivity and sustaining livelihoods in downstream communities and ecosystems.

Historically, the application of hydrochemical and isotope tracers for evaluating interactions between lakes (e.g., maars) and the underlying groundwater systems in Central America has been limited mainly to hydropower reservoirs (López et al., 2004) In this work, we present a seasonal isotopic and hydrochemical characterization of Lake Hule, one of the major volcanic lakes in Costa Rica. This study aims to evaluate groundwater-lake interactions and estimate the isotope mass balance of Lake Hule by combining water and inorganic carbon stable isotopes (δ^2H, $\delta^{18}O$, $\delta^{13}C_{DIC}$) and ^{222}Rn measurements. Specifically, our contribution addresses the following research questions: (a) How do hydrochemistry and isotope tracers vary in Lake Hule and the lake catchment over different seasonal conditions (i.e., dry vs. wet season)? (b) Do ^{222}Rn gradients between groundwater and lake water indicate lacustrine-aquifer interactions in Lake Hule? and (c) What is the annual contribution of precipitation, runoff, and groundwater to the Lake Hule water budget based on the isotope mass balance approach? We anticipate that our findings may serve to improve water management strategies in tropical lakes under changing climatic conditions (e.g., intensified evaporation conditions) and complex catchment-lake interactions (e.g., inputs of CO_2-rich fluids through the lake bottom).

2. Materials and Methods

2.1. Study Area

The Hule maar basin is situated ∼11 km north of Poas volcano on the Caribbean slope of the Central Cordillera of Costa Rica (Latitude: 10.2951°, Longitude: −84.2117°, 750 m asl, Figure 1). It is situated in a protected area, namely the Bosque Alegre National Wildlife Refuge. The climate of this region is classified as tropical humid (Köppen-Geiger code cf., Esquivel-Hernández et al., 2017). The lake system is part of the headwaters of the Rio Tercero basin, which has an area of 24.7 km^2, an average slope of 11.2%, and mean annual precipitation (MAP) of 4,235 mm/yr (1985–2019, Arcienega-Esparza et al., 2022). Meteorological records for the period 2022–2023 (Figure 2) indicated an annual precipitation of 4,283 mm with most of the rainfall falling during the wet season (3,297 mm or 77%). The area is characterized by relatively high humidity, with an average value of 90.9% and minimum and maximum values of 74.2% and 99.5%, respectively. Daily solar radiation averaged 153.1 ± 66.5 and 135.1 ± 54.1 W/m^2 during the dry and wet seasons, respectively.

The Hule maar is within a subcircular volcanic depression or crater, with a major axis of 2.3 km and a minor axis of 1.8 km, for a total area of ∼3.5 km^2. Horn (2001) reported an age of 2,950 (calibrated) years B.P. for the Hule maar. The lake system is currently formed by three lakes (∼750 m asl, Figure 1): Lake Hule (54.7 ha, ∼23 m deep), Lake Congo (14.9 ha, ∼15 m), and Lake Bosque Alegre (<1 ha, ∼5 m deep) (Alvarado et al., 2011; Horn & Haberyan, 1993). A secondary pyroclastic cone and a lava flow separate Lake Hule from Lake Congo. Lake Congo mainly flows into Lake Bosque Alegre during the wet season, but no evidence of water flowing from Lake Bosque Alegre into Lake Hule has been reported. The outflow of Lake Hule drains into the Hule river via a small

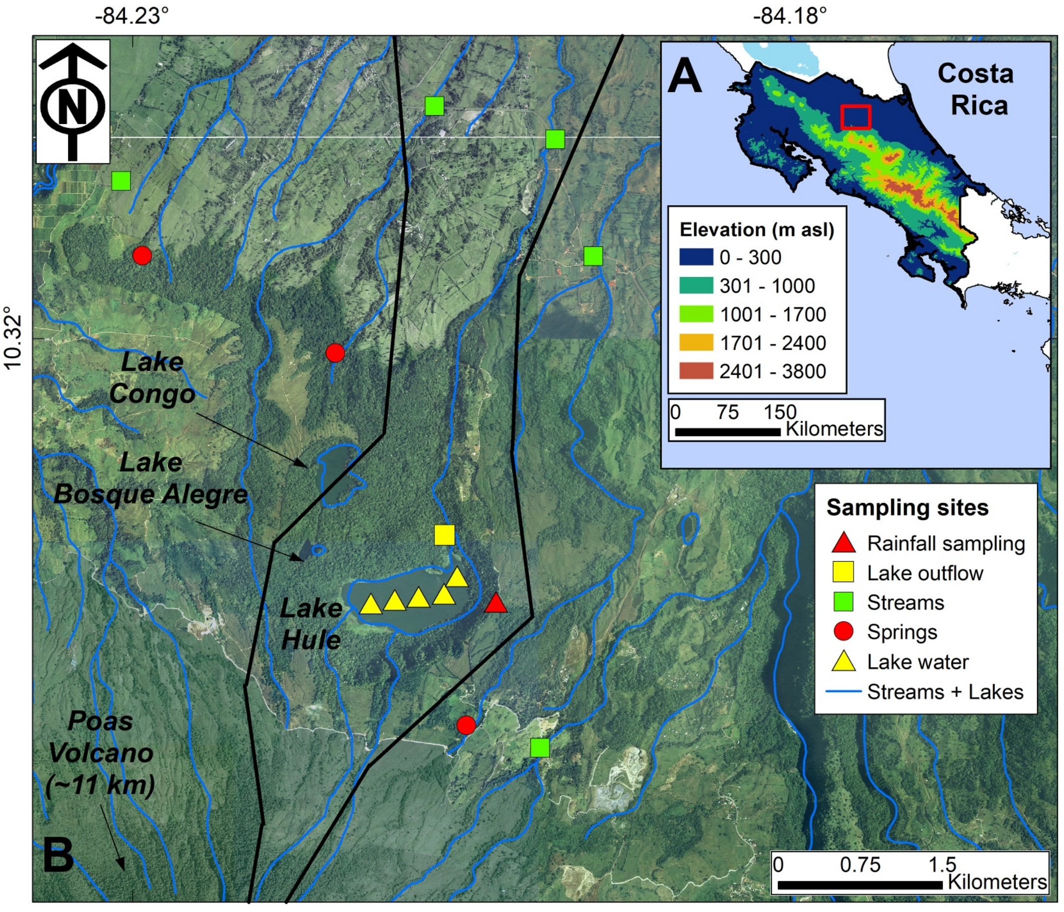

Figure 1. (a) Location of the Hule lake system in the northern region of Costa Rica. (b) Distribution of the three lakes of the Hule lake system (i.e., Lake Congo, Lake Bosque Alegre, and Lake Hule) within the Bosque Alegre National Wildlife Refuge. Sampling sites included Lake Hule (yellow triangles), streams (green squares), and springs (red circles). The lake outflow (Yellow Square) and the rainfall precipitation collector (red triangle) are also indicated. The blue lines correspond to surface waters, namely, the lakes and streams in the study area. The limits of the Rio Tercero basin are also shown as a black line.

channel with a cross-section area of 1.93 m^2 located on its northeast shore (Figure 1). The lake area is characterized by high caldera walls (~200 m above the lake water level) and steep slopes (up to 45°). Haberyan and Horn (1999) and Umaña (1993) reported that Lake Hule is thermal stratified with water temperature of ~20°C in the hypolimnion and ~25°C in the surface and has also elevated CO_2 levels at the bottom. A weak thermocline was identified in Lake Hule, with the absolute depletion of O_2 occurring between 10 and 12 m depth (Cabassi et al., 2014; Göcke, 1997; Umaña, 1993). The stratigraphic analysis of the Hule maar revealed that it is mainly formed by pyroclastic surges, silica-rich andesitic pumice flows, air-fall deposits, ballistic blocks, and reworked deposits. Basal organic debris also overlies the regional, well-developed, thick orange-to-brown soils (Alvarado et al., 2011; Horn, 2001). The petrochemistry of Hule maar is related to juvenile tephras formed by andesites (showing blocky grains with very small crystals of plagioclase), mafic minerals (amphibole) and minor amounts of magnetite. The chemical composition of rocks was mainly classified as low to medium in K in the calc-alkaline series and with an average content of CaO and MgO of 8.6% and 4.5% (Alvarado et al., 2011 and references herein).

Macías et al. (2016) estimated flow parameters for the volcanic fractured phreatic area surrounding the Hule maar (i.e., saturated hydraulic conductivity, effective porosity, and Darcy's flux) using salt tracer methods. The values reported by these authors are in the lower of range end of values described in the literature for other fractured aquifers with volumetric flow in the range of 8–19 L/s (Salas-Navarro et al., 2018). Overall, there are no easily accessible boreholes or wells in the study area. Groundwater is mostly available from springs like Pata Gallo (in

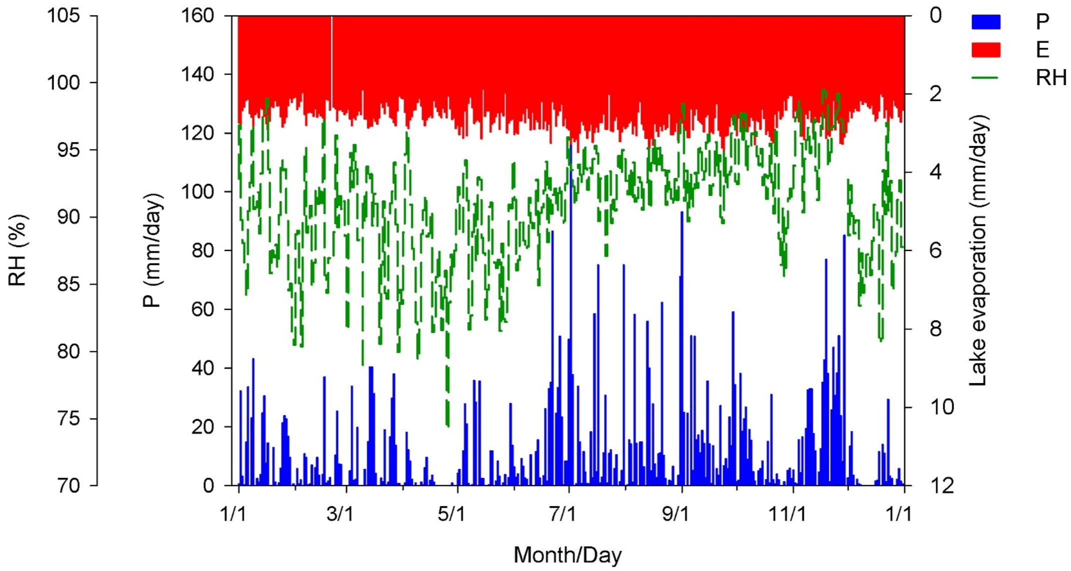

Figure 2. Time series showing average meteorological conditions for the study area and Lake Hule (2022–2023): precipitation (blue bars in mm/day, left *y*-axis), relative humidity (green dashed line in percentage, left offset *y*-axis), and lake evaporation (red bars in mm/day, right *y*-axis).

the southern area of the lake) and Rio Cuarto and Crucero (situated on the northern side of the lake system, Figure 1). Lake Hule is also reported to be fed by three permanent streams that flow from the south and above the caldera walls (Cabassi et al., 2014). There are also several streams in the Rio Tercero catchment (e.g., Maria Aguilar, Sardinal, Tercero, and Rio Cuarto; Figure 1). The area is also characterized by low-to-moderate hydrothermal activity and CO_2 inputs to the lake that is probably related to hydrothermal fluid circulation from the Poas Volcano activity (Alvarado et al., 2007; Cabassi et al., 2014). We calculated the lake catchment area using ArcGIS 10.4 (ESRI, USA) by performing a delineation of the upstream and surrounding area of the lake based on the hydrographic and elevation data available for Rio Tercero basin (Arcienega-Esparza et al., 2022). We estimated the lake basin area at 3.57 km^2, corresponding to 14% of the Rio Tercero basin area.

2.2. Sampling Strategy

We collected water samples of Lake Hule, springs, and streams between March 2022 and September 2023 ($N = 129$). Our sampling period was characterized by La Niña conditions between March 2022 and January 2023 (sea surface temperature anomalies up to −1.05 in El Niño 3.4 region), neutral conditions in the period February-June 2023, and El Niño conditions from July–September 2023 (sea surface temperature anomalies up to +1.53 in El Niño 3.4 region, http://www.cpc.ncep.noaa.gov/data/indices/sstoi.indices). Despite the good availability of stable isotope hydrological data for the Caribbean domain of Costa Rica (e.g., Sánchez-Murillo et al., 2020), we decided to estimate and update the local meteoric water line (LMWL) for the study area. For this purpose, we installed a passive collector (Palmex Ltd., Croatia; Gröning et al., 2012) in July 2022 above the caldera wall on the east side of Lake Hule (Latitude: 10.2951°, Longitude: −84.2033°, 875 m asl, Figure 1). Samples were collected manually on every rainy day in the morning (7–8 a.m.) from July 2022 to September 2023 ($N = 248$). To better characterize the groundwater system in the lake basin, we collected water samples from three springs, namely Pata Gallo (982 m asl), Rio Cuarto (651 m asl), and Crucero (617 m asl). Samples were collected manually every week in the periods of March–October 2022 and March–September 2023 ($N = 66$). Water samples of streams, namely Maria Aguilar river (736 m asl), Sardinal river (453 m asl), Hule river (418 m asl), and Rio Cuarto river (417 m asl) were collected during sampling campaigns in March 2022 March 2023, and September 2023 ($N = 24$). At Lake Hule, samples were also collected in March 2022 March 2023, and September 2023 at five sites located along a transect in the west-east direction ($N = 39$, Figure 1). We collected surface samples (∼1 m below the surface) and bottom samples (in the last 1 m of the water column and as close as possible to the lake floor). The depth at which Lake Bottom samples were collected was in the range of 10–20 m. Lake water samples were collected using a 2.2 L Niskin bottle sampler (Wildco, USA). At each sampling site, we measured the water depth using a using a handheld sonar sensor (Erchang, China). We also manually measured the water level at the lake outlet for each sampling campaign. The sites were also manually geo-referenced using a GPS.

Samples for water stable isotope analysis were collected in 30-mL high-density polyethylene vials and stored at 5°C until analysis. We also collected samples for stable isotope analysis of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and ion chemistry (i.e., major ions, $N = 28$). These samples were filtered using 0.45 μm syringe membranes in the field and stored in dark and frozen conditions until analysis. Samples for ^{222}Rn analysis were also manually collected using 250 mL glass bottles with septum caps (with no headspace). These samples were only recovered from the lake bottom to identify the groundwater inputs to the lake ($N = 18$). We measured the hydrogen potential (pH), temperature, and oxidation-reduction potential (ORP) at each site (i.e., lake, springs, and streams) using a field portable tester during the study period (Hanna Instruments, USA). A portable tester (Hanna Instruments HI775, USA) was also used to measure the total alkalinity in the field and to control the quality of alkalinity estimations carried out at the laboratory (see details in Section 2.3.). Hourly meteorological variables (relative humidity, air temperature, solar radiation, wind speed and direction, and precipitation amount) were recorded at 2 m height using a Vantage Pro2 weather station (Davis Instruments, USA), which was installed next to the precipitation collector.

2.3. Laboratory Analysis

The stable isotope composition of lake, springs, streams, and precipitation samples was analyzed at the Stable Isotopes Research Group laboratory at the Universidad Nacional (Heredia, Costa Rica) using an IWA-45EP water analyzer (Los Gatos Research, Inc., California, USA) with a precision of ±0.5‰ for δ^2H and ±0.1‰ for $\delta^{18}O$ (1σ, $N = 5$). Calibrated secondary standards MTW (Moscow, Idaho tap water) ($\delta^2H = -130.3$ ‰, $\delta^{18}O = -16.7$‰), USGS45 ($\delta^2H = -10.3$‰, $\delta^{18}O = -2.2$‰), and PGW (local groundwater) ($\delta^2H = -52.6$ ‰, $\delta^{18}O = -8.4$‰) were used to normalize the results and to assess the quality and drift control procedures. $^{18}O/^{16}O$ and $^2H/^1H$ ratios are presented in delta notation δ (‰), relative to the VSMOW-SLAP scale.

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and total alkalinity of filtered aliquots (0.45 μm PTFE) were analyzed using an automated DIC sample preparation system (Picarro AutoMate FX system, USA). A detailed explanation of the analytical procedure is described in Sánchez-Murillo et al. (2022b). Calibration was done using the following standards: University of McGill, Canada: CO_2 mixing ratio: 1553 ppmv, $\delta^{13}CO_2 = -43.15$‰, Heredia's compressed air: CO_2 mixing ratio: 419.1 ppmv, $\delta^{13}CO_2 = -10.09$‰, NOAA gas standard: CO_2 mixing ratio: 394.85 ppmv, $\delta^{13}CO_2 = -8.292$‰. $^{13}C/^{12}C$ ratios in DIC are presented in delta notation δ (‰), relative to the VPDB scale (Craig, 1957). The corresponding uncertainty for $\delta^{13}C$ in DIC is ±0.1‰ (1σ).

Ion chromatography (Thermo Scientific ICS-5000+, CA, USA) was used to analyze ammonium, sodium, potassium, magnesium, calcium, chloride, nitrite, nitrate, and sulfate. The detection limits for these ions are (in mg/L): 0.02, 0.041, 0.05, 0.05, 0.07, 0.06, 0.07, 0.24, and 0.17, respectively. Blanks and recovery standards were also included in each batch of samples to ensure the quality of the analysis. The alkalinity of each sample (reported as mg/L $CaCO_3$) was also calculated from the average CO_2 concentration measured during the isotope analysis. The CO_2 concentration measured by the CRDS was standardized against Na_2CO_3 solutions (Sigma Aldrich, >99.0%, 5–200 mg/L). These standard solutions were analyzed following the same procedure described above. Only those water samples with alkalinity >10 mg/L $CaCO_3$ were quantified due to the small volume of sample that is analyzed by this method.

The ^{222}Rn activity was measured in lake, groundwater, and stream water samples using a RAD7 detector (Durridge Co., USA). Samples were collected in 250 mL glass bottles and were analyzed in the laboratory using the accessories to measure radon in grab samples (RAD H_2O kit). Samples were analyzed within 24 hr after collection in the field. The activities are expressed in Bq/m^3 with an analytical uncertainty of ±2σ at a 95% confidence interval (Ortega et al., 2015, 2022; Sánchez-Murillo et al., 2016). The uncertainty or standard error for this method was ∼20%. The ^{222}Rn activity in the water samples was corrected for decay using the following equation:

$$^{222}Rn_i = {}^{222}Rn_t x e^{\left(\frac{t}{132.4}\right)} \tag{1}$$

where $^{222}Rn_i$ is the ^{222}Rn activity in the water sample, $^{222}Rn_t$ is the ^{222}Rn activity measured at the lab after time t, and t is the time elapsed since the water was collected in the field and the analysis at the laboratory. To better interpret the ^{222}Rn activities measured at Lake Hule and the local water system, we compared our data with the radon activities reported by Sánchez-Murillo et al. (2016) for the Central Valley of Costa Rica (Barva volcano southern slope), namely spring water ($N = 43$) and groundwater samples from wells ($N = 21$). We also compared the ^{222}Rn activities of lake water and stream water samples with surface water samples collected near hydrothermal sources across the volcanic range of Costa Rica ($N = 7$, unpublished data). We also estimated the atmospheric evasion of radon (F_{atm}) for dry and wet season conditions using the concentration gradient across the air-water interface and the surface transfer as follows:

$$F_{atm} = kx(C_{water} - \alpha x C_{air}) \tag{2}$$

Here, k is the is the gas transfer velocity, C_{water} and C_{air} are the radon activities in water and the air, respectively, and α is the partitioning coefficient Schubert et al. (2012). Given the absence of ^{222}Rn measurements in air at Lake Hule, we used a C_{air} value of 5 Bq/m_3 as a reference value for our calculations. To estimate k, the empirical relationship reported by MacIntyre et al. (1995) was applied:

$$k_{600} = 0.45xu_{10}^{1.6} \tag{3}$$

where k_{600} is the transfer velocity (cm/hour) for wind speed u_{10} (m/s) at 10 m height above the water surface. The transfer velocity is reported for a Schmidt number (S_c or the ratio of kinematic viscosity to molecular diffusivity) of 600 which is the value estimated for CO_2 in freshwater at 20°C (Dulaiova & Burnett, 2006).

2.4. Evaporation Conditions Analysis

We estimated annual and seasonal evaporation-to-inflow ratios (*E/I*) for Lake Hule using oxygen-18 and deuterium data in the period December 2022- April 2023 (dry season) and May– September 2023 (wet season). Overall, this approach has been demonstrated to be useful for estimating water balance parameters of lakes around the world (e.g., Jasechko et al., 2013; Vystavna et al., 2021), and it is comprehensively described in Gibson et al. (1993, 2008, 2016), Gibson and Edwards (2002), and Gibson and Reid (2014). We have also applied this approach to estimate water balance calculations for glacial lakes in the Chirripó National Park, southeastern Costa Rica (Esquivel-Hernández et al., 2018Esquivel-Hernández et al., 2018, 2022).

In this approach, the evaporation (E) from the lakes, as a fraction of inflow (I), is calculated based on the linear resistance model developed by Craig and Gordon (1965) for free-surface evaporation. Calculations were done using the Hydrocalculator software, which serves to estimate evaporation based on the isotopic composition of precipitation and lake water (Skrzypek et al., 2015). The *E/I* ratios were calculated using the following equation:

$$\frac{E}{I} = \frac{1-h}{h} x \frac{\delta_{lake} - \delta_{rain}}{\delta^* - \delta_{lake}} \tag{4}$$

where h is the average local relative humidity (expressed as a fraction), δ_{rain} is the amount weighted isotopic composition of precipitation, δ_{lake} is the average isotopic composition of lake water, and δ^* is the limiting isotope composition enrichment. The calculation of δ^* is described in detail by Skrzypek et al. (2015). Estimating δ^* requires the stable isotope composition of the moisture in the ambient air (δ_A). We estimated δ_A in the Hydrocalculator software from the local records of precipitation stable isotope compositions corrected using the local evaporation line (LEL) method. The calculated slope of LEL by Hydrocalculator software was corrected using the observed slope of LEL obtained from an evaporation pan experiment carried out at Cocos Island, a region with similar weather conditions as the Hule maar (mean surface air temperature and relative humidity of 26.2°C and 83.2 %, Corrales et al., 2016). 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. We included error contributions from water temperature, air humidity, input water isotope (e.g., precipitation), and lake water isotope. These are the input parameters that have a strong error contribution to the calculation of *E/I* values of tropical lakes and that have been previously identified using sensitivity analysis (Abba et al., 2023; Esquivel-Hernández et al., 2017; Vallet-Coulomb et al., 2001).

We applied an energy budget formulation to estimate the water vapor flux from the lake (Brutsaert, 2015). The average daily evaporation was estimated based on a Penman evaporation model (Linacre, 1977; Penman, 1948) and the available meteorological data for the study area. We estimated an average evaporation value of 2.66 ± 0.31 mm/day (1σ) with a maximum value of 3.49 mm/day (Figure 2). We also calculated the water residence time (τ) as described by Gibson et al., 2016. To estimate the annual and seasonal water residence times, we used the following equation:

$$\tau = \frac{\frac{E}{I}xV}{E} \tag{5}$$

This residence time considers the catchment runoff, groundwater, and precipitation contributions to the lake. In Equation 5, we used the lake volume (in m^3) reported by Umaña (1993).

2.5. End-Member Analysis Modeling

We applied a Bayesian mixing isotope model (R package Simmr; Parnell & Inger, 2016) to better constrain the water inputs to Lake Hule during the study period. Overall, the annual balance of the lake under steady-state conditions can be defined as:

$$I = O + E \tag{6}$$

$$\delta_I I = \delta_O xO + \delta_E xE \tag{7}$$

where I, O, and E are the lake inflow, lake outflow, and evaporation fluxes (mm/yr), respectively, and δ_I, δ_O, and δ_E are the isotopic composition of the lake inflow, lake outflow, and evaporation fluxes (‰), in that order (Gibson et al., 2016). The input of water to Lake Hule includes precipitation on the lake surface (P_L), ungauged runoff (I_R), groundwater (I_{GW}), and streams (I_U):

$$I = P_L + I_R + I_{GW} + I_U \tag{8}$$

Thus, the stable isotopic composition of these water source endmembers (δ_P, δ_R, and $\delta_{GW,}$ δ_U) could be useful to separate their relative contributions to the lake water budget. Even though two permanent streams are reported to feed Lake Hule from the north, our field explorations in the Hule Lake basin indicated no channelized water inflow to Lake Hule during our study period and $I_U = 0$ in Equation 8. Given the inherent complexity of tropical and fractured volcanic aquifer systems (Sánchez-Murillo et al., 2022a) and the lack of hydrogeological data for the study area, the good availability of precipitation data (i.e., rainfall amount and weighted-average isotopic composition) can be used to constrain the contributions of groundwater and runoff better as follows:

$$\delta_L = \left(\delta_P x \frac{P_L}{I}\right) + \left(\delta_R x \frac{I_R}{I}\right) + \left(\delta_{GW} x \frac{I_{GW}}{I}\right) \tag{9}$$

Here, the isotopic composition of lake water (δ_L) reflects the relative contribution of P_L, I_R, and I_{GW}, namely P_L/I, I_R/I, and I_{GW}/I, and their isotopic composition (i.e., δ_P, δ_R, and δ_{GW}). We used the Simmr with uninformative priors and 10,000 Markov Chain Monte-Carlo (MCMC) iterations (5,000 burn-in) to evaluate the contribution of water sources (known as the endmembers) to the lake water (known as the mixture). To estimate the relative errors of these calculations, we accounted for the isotopic compositions of lake water, the isotopic compositions from springs, streams and precipitation (i.e., the endmembers), and the standard deviations of the isotopic compositions of the endmembers. These calculations were performed for dry and wet season conditions. Moreover, Gelman-Rubin diagnostic (Gelman & Rubin, 1992) was performed to test model convergence using the isotopic compositions of each endmember. The Gelman–Rubin diagnostic evaluates MCMC convergence by analyzing the difference between multiple Markov chains. All selected runs exhibited good model convergences (Gelman-Rubin value equal 1 at $p < 0.05$).

Table 1
A Comparative Summary of Field Parameters, Stable Isotopes (Water and Dissolved Inorganic Carbon), and ^{222}Rn for Dry Season and Wet Season Conditions in the Study Area

Water system	Water temperature (°C)	pH	EC (μS/cm)	ORP (mV)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	$\delta^{13}C$ (‰)	^{222}Rn (Bq/m^3)
Lake Hule	26.6 ± 1.7 (26.4 ± 0.9)	6.32 ± 0.34 (6.16 ± 0.41)	129.8 ± 35.6 (143.7 ± 50.4)	−8.67 ± 77.9 (3.38 ± 131.3)	−5.92 ± 1.76 (−5.33 ± 0.65)	−36.39 ± 12.79 (−25.82 ± 4.39)	−6.5 ± 2.0 (−0.7 ± 1.8)	98.3 ± 48.6 (71.1 ± 79.0)
Springs	22.3 ± 1.1 (22.1 ± 0.8)	6.46 ± 0.70 (6.01 ± 0.21)	137.0 ± 21.0 (144.0 ± 20.3)	161.0 ± 35.5 (176.0 ± 31.5)	−4.19 ± 1.72 (−5.19 ± 1.34)	−18.66 ± 13.04 (−27.40 ± 10.51)	−11.1 ± 5.3 (−7.6 ± 7.7)	20,130 ± 8,645 (27,810 ± 13,459)
Streams	22.9 ± 1.3 (23.5 ± 1.1)	7.11 ± 0.63 (6.63 ± 0.35)	193.4 ± 61.4 (134.8 ± 34.4)	128.0 ± 20.3 (114.2 ± 14.2)	−2.73 ± 2.06 (−4.85 ± 0.57	−7.08 ± 15.08 (−25.77 ± 5.75)	−4.1 ± 1.9 (−3.2 ± 3.8)	577 ± 502 (847 ± 1666)

Note. Values are reported as average ±SD (i.e., one standard deviation or 1σ). The values shown in parentheses correspond to the May–November period (i.e., wet season).

We applied the Kruskal-Wallis one-way analysis of variance (ANOVA) on Ranks followed by Dunn's method to assess spatial and temporal differences in the isotopic and chemical variables. Statistical analyses ($\alpha = 0.05$) were done using SigmaPlot software 11.0.

3. Results

3.1. Isotope Composition of Precipitation, Springs, Streams, and Lake Water

We confirmed that there are seasonal variations in the isotopic composition of precipitation, springs, streams, and lake water (Table 1). During the dry season, the $\delta^{18}O$ values of precipitation and streams were significantly higher ($p < 0.05$) compared to the corresponding isotopic values of lake water and springs (Figure 3a). The median values for the $\delta^{18}O$ of precipitation and streams were −0.94‰ and −0.48‰, respectively, while for lake water and springs they were −5.30‰ and −4.71‰, respectively. However, during the wet season, there were no statistically significant differences between the $\delta^{18}O$ values of these four types of water collected in the study area (Figure 3b). We only found two dry-season water samples that were significantly different than the median value for that period, whereas no significant differences between the wet-season samples were identified.

The local meteoric water line (LMWL) of the Hule maar basin was calculated as $\delta^2H = 8.40*\delta^{18}O + 15.14‰$ ($r^2 = 0.986$, $p < 0.001$, $N = 248$). We found a slight variation in the slope of LMWL for dry and wet season conditions from 7.52 to 8.20 but similar intercepts of ∼14‰ (Figures 4a and 4b), reflecting the predominant moisture source from the Caribbean Sea (Sánchez-Murillo & Birkel, 2016). As for lake water, the dry season evaporation line (EL) of Lake Hule was estimated as $\delta^2H = 3.55*\delta^{18}O – 6.21‰$ ($r^2 = 0.702$, $p < 0.001$, Figure 4a), whereas the wet season EL was calculated as $\delta^2H = 7.04*\delta^{18}O + 5.64‰$ ($r^2 = 0.935$, $p < 0.001$, Figure 4b). Springs exhibited similar conditions for dry and wet seasons, with slopes of ∼7 and intercepts of ∼12 (Figures 4a and 4b). As for streams, however, we found notable season variations between dry and wet seasons, with a slope greater than 8 and an intercept with a value of ∼18‰ for the wet season (Figures 4a and 4b). Overall, the slope of lake water reflects stronger evaporation effects in the dry season than in the wet season but also greater evaporative losses than the springs and streams. We estimated amount-weighted $\delta^{18}O$ and δ^2H values in precipitation of −1.84‰ and +0.87‰ (dry season) and 4.51‰ and −25.45‰ (wet season), respectively (Figures 4a and 4b).

3.2. Hydrochemistry and Carbon Isotope Composition of Springs, Streams, and Lake Water

We observed no clear variations in the ion chemistry of springs, streams, and lake water during the study period. We found that the sum of $Na^+ + K^+$ was significantly higher ($p < 0.05$) in stream water in the dry season and spring water in the wet season than in lake water (Figure 5). The median values for the sum of $Na^+ + K^+$ were 0.322 meq/L and 0.335 meq/L, respectively. However, the sum of $Cl^- + SO_4^{2-}$ and $Ca^{2+} + Mg^{2+}$ in these three types of water were not significantly different ($p > 0.05$) during both dry and wet season conditions. Median values of $Cl^- + SO_4^{2-}$ were in the range of 0.123–0.220 meq/L and median values of $Ca^{2+} + Mg^{2+}$ varied between 0.724 and 1.142 meq/L (Figure 5). Overall, the ion chemistry of Lake Hule reflects the contributions from the volcanic minerals (i.e., CaO and MgO dissolution) but higher concentrations in stream water than in spring and lake waters. As shown in Table 1, pH and EC values were also relatively similar in the three types of

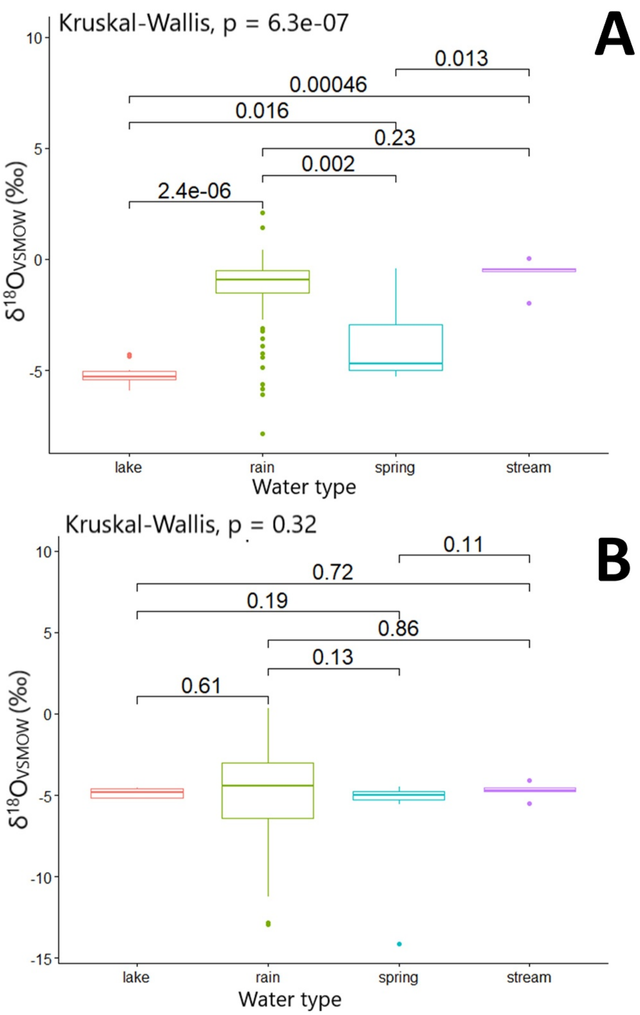

Figure 3. Box plots of $\delta^{18}O$ in precipitation, lake water, springs, and streams calculated for (a) dry and (b) wet season conditions. Box plots include the 25th percentile, 75th percentile, median value, and outliers. We also report the p-values for the comparison of the median values of each water type. Those p-values <0.05 indicate a significant difference between water types.

water during the dry and wet seasons (Table 1). Calcium-magnesium bicarbonate water is the dominant type in the lake (Figure 5).

We also did not find differences in the $\delta^{18}O$ values of the lake for the dry and wet seasons. Median values of $\delta^{18}O$ of lake water were −4.63‰ and −5.30‰, respectively. Average lake alkalinity in the entire water column was also very similar in the dry and wet seasons with values of 71.2 ± 45.9 and 65.1 ± 26.1 mg/L $CaCO_3$. However, we found that alkalinity was significantly greater in the lake hypolimnion (<10 m depth) than in the epilimnion with values up to 203.9 mg/L $CaCO_3$ in the dry season and up to 126.2 mg/L $CaCO_3$ in the wet season. Even though no variations were observed in the ion composition of Lake Hule, we registered clear seasonal changes in the isotopic composition of inorganic carbon in this lake (Figure 6). Based on a Mann-Whitney Rank Sum Test, we confirmed that $\delta^{13}C_{DIC}$ values were statistically significantly lower in the dry season (median value: −4.6‰) than in the wet season (median value: −1.4‰). The isotopic composition of inorganic carbon of springs and streams was also very similar in the dry and wet seasons (Table 1).

3.3. ^{222}Rn Activities in Lake Hule

We used ^{222}Rn activities and the isotope composition of near-bottom water to identify groundwater inputs into Lake Hule during the dry and wet seasons. During our sampling campaigns at Lake Hule, we confirmed that: (a) Lake Hule was stratified with ORP values up to −115 mV below 10 m depth and (b) the hypolimnion of Lake Hule showed relatively steady ^{222}Rn activities with median values of 58.0 Bq/m^3 and 16.7 Bq/m^3 in the dry and wet seasons, respectively. Overall, ^{222}Rn values were systematically higher near the lake outlet in the dry season, with a maximum activity of 146.6 ± 31.0 Bq/m^3. In turn, this area of Lake Hule showed the lowest isotopic values of lake water with a minimum of −5.91‰. In the wet season, however, the highest ^{222}Rn activity of 163.3 ± 39.5 Bq/m^3 was registered near the lake's west bank. Interestingly, the isotope composition of lake water in this area showed the highest isotopic value of −4.53‰, contrasting with our observation during the dry season sampling.

The median ^{222}Rn activity (292.4 Bq/m^3) in the streams near the Lake Hule catchment was significantly greater ($p < 0.05$) compared to the corresponding ^{222}Rn activity of lake water (82.1, Figure 6a). We found, however, that the median ^{222}Rn activity was not significantly lower ($p > 0.05$) than the ^{222}Rn activity of 146 Bq/m^3 measured at surface water samples collected near hydrothermal activity (Figure 6a). As for springs and groundwater samples, the median ^{222}Rn activity of the springs surrounding the Lake Hule basin of 16,761 Bq/m^3 was significantly greater ($p < 0.05$) than the median ^{222}Rn activity of 6,754 Bq/m^3 reported by Sánchez-Murillo et al. (2016) for spring located at the northern region of the Central Valley in Costa Rica (Figure 6b). However, it was not greater ($p > 0.05$) than the median value of 14,916 Bq/m^3 estimated for groundwater samples collected from wells located in the central mountainous region of Costa Rica (Figure 6b).

3.4. Evaporation Conditions at Lake Hule

We estimated evaporation low evaporation-to-inflow ratios (*E/I*) of 2.9 ± 1.0% (wet season) and 3.2 ± 1.8% (dry season) for Lake Hule. The annual *E/I* value was estimated at 3.0 ± 1.3% (Table 2). Our field observations of the water level at Lake Hule ratified steady-state conditions with water level variations at the outlet of the lake <1 m from March (lowest water level) to October (highest water level). During the dry season (January to April), we observed no outflow from Lake Hule to the Hule river. We estimated an annual water residence of 0.39 ± 0.17 years (~4.7 months) based on an annual evaporation loss of 967 mm (Table 2). However, seasonal estimates were 1.07 years for the dry season and 0.60 years for the wet season. Bayesian mixing isotope modeling

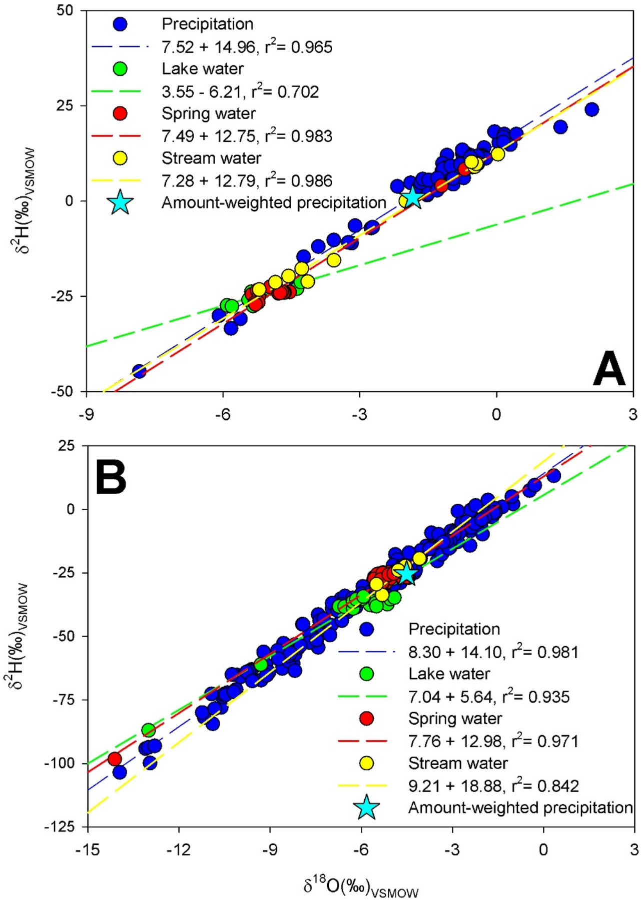

Figure 4. Dual plot of $\delta^{18}O$ versus $\delta^{2}H$ in precipitation (blue circles), lake water (green circles), springs (red circles), and streams (yellow circles) for (a) dry season and (b) wet season conditions. The local meteoric water line (LMWL) for each season (blue dashed line) is also included in the graph. The evaporation line (EL) for Lake Hule is represented by the green dashed lines whereas the best linear trends for springs and stream waters are also represented by the red and yellow dashed lines, respectively. The amount weighted isotopic composition of precipitation for each season is indicated by the cyan star.

for annual conditions revealed that the relative water contributions to Lake Hule were 61.3 ± 8.1%, 24.4 ± 8.4, and 14.3 ± 5.9% of groundwater, precipitation, and runoff, respectively (Figures 7a and 7b). Despite the evaporation loss during the dry season, water outflow from Lake Hule may be connected with subsurface flow paths, given the absence of surface outflow into the Hule River during this period. During the wet season, outflow from Lake Hule is formed by evaporation, groundwater, and water discharge into the Hule River. In September 2022, we measured the volumetric discharge of the channel that connects Lake Hule with the Hule River. Our average estimated discharge was ~0.20 m^3/s (20 L/s). If we assume that this channelized outflow is mostly present from May to November, the average outflow from Lake Hule is estimated at 168 mm during the wet season.

4. Discussions

4.1. Water Isotope Framework of Lake Hule

The water isotope balance for Lake Hule showed that the isotopic composition consistently reflected the input of groundwater (i.e., lacustrine groundwater discharge), contributing 61.3 ± 8.1% of the annual water budget. Cabassi et al. (2014) reported the most recent isotopic values of lake water for Lake Hule when they conducted a biogeochemical study in March 2010. They noted water samples plotted near the Global Meteoric Water Line (GMWL, Craig, 1961) and Costa Rica surface water line, and concluded that the main water source of Lake Hule was meteoric. However, we consider that this finding indicates that (a) lake water is indeed not subject to strong evaporation and (b) ^{18}O exchange with silicates from hydrothermal fluids is not significantly influencing the isotopic composition of lake (Ramírez-Leiva et al., 2017). In general, our isotopic data agreed with the dual isotopic space (i.e., $\delta^{18}O$–$\delta^{2}H$ plot) reported by Cabassi et al. (2014) but were also useful to provide further insights into the regional hydrology of Lake Hule and the relevance of groundwater recharge processes for the water budget of this volcanic lake. Jasechko and Taylor (2015) recognized that mean groundwater $\delta^{18}O$ values are lower than the amount-weighted precipitation $\delta^{18}O$ across the globe. In tropical areas like Central America, where volcanic lithologies are common, isotopic data also showed that groundwater recharge is mostly biased to intensive rainfall with precipitation to groundwater ratios (P/GW) $\delta^{18}O$ ratios >1. The corresponding P/GW ratios for the Lake Hule catchment were calculated at 3.2 and 1.2 for dry and wet season conditions, respectively. These values also agreed with the P/GW isotope ratios close to and greater than 1 reported by Sánchez-Murillo and Birkel (2016) for the northern and Caribbean lowlands of Costa Rica, an indication of rapid groundwater recharge. Thus, especially during the dry season when Lake Hule experienced a significant reduction in the precipitation input (~24% of the annual mean precipitation fell between December and April), the isotopic composition of lake water was still very similar to the isotopic composition of springs, indicating water inputs from the local aquifers.

Our estimations of evaporative losses assumed a steady state for both the dry and wet seasons. However, the lake level varied slightly during the year, with a maximum level change of <1 m. In general, lake evaporative losses were relatively steady during the dry and wet seasons due to the high relative humidity and constant lake water season temperature and solar radiation recorded during the study period. The low evaporation estimated for the Lake Hule catchment is also in agreement with the high transpiration (T) estimates reported by Iraheta et al. (2021) for the Caribbean lowlands of Costa Rica, with transpiration-to-precipitation (T/P) ratios of ~80%. Overall, the hypotheses of steady state and lake water homogeneity can be considered as a first order estimates devoted to sensitivity testing (Abba et al., 2023; Gibson et al., 2016). On this regard, given the small variations in h (Equation 4), we consider that our E/I values for Lake Hule were not subject to estimation errors due to strong changes in the ambient humidity (Figure 2). Thus, the next main parameter with a strong influence on the model

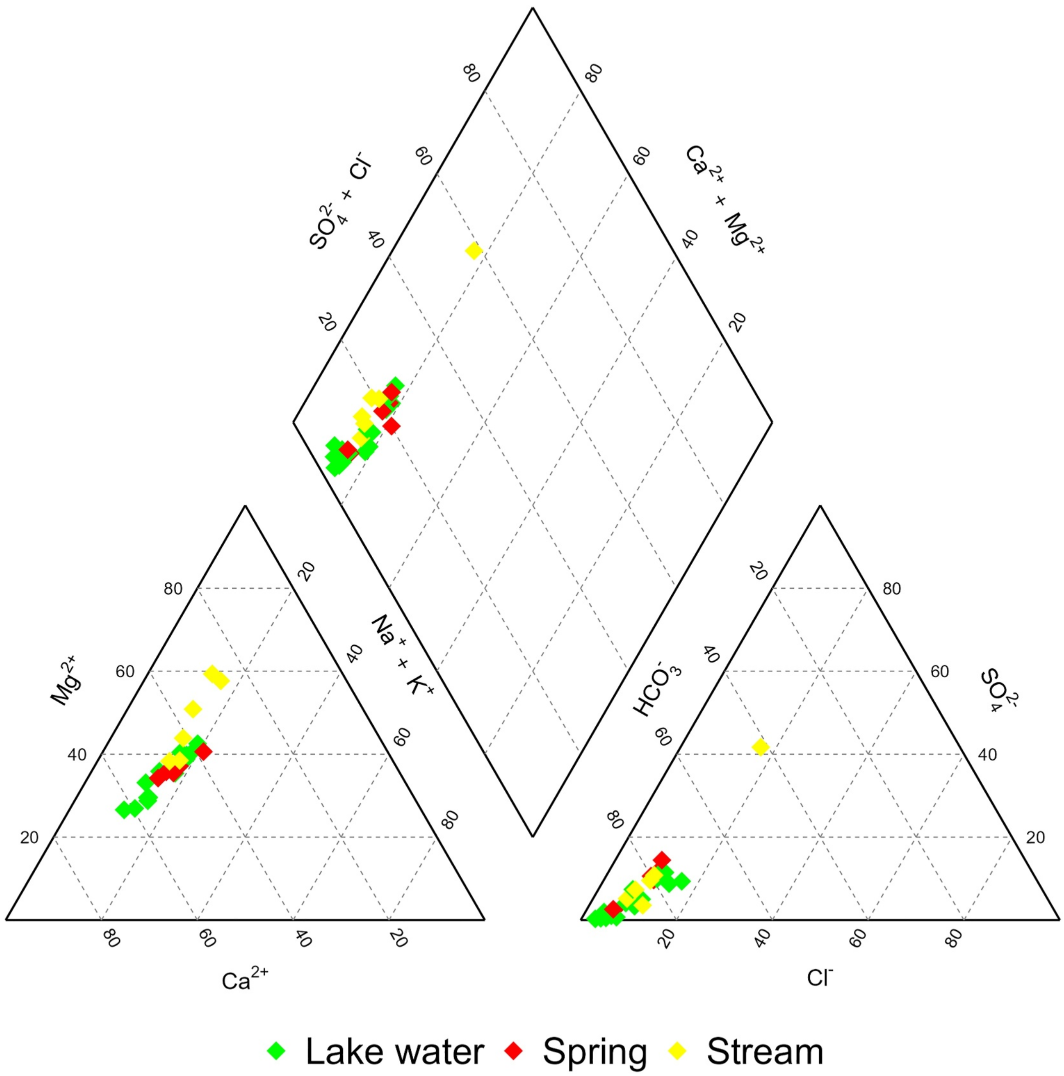

Figure 5. Piper diagram showing the distribution of the main cations and anions in lake water (green diamonds), springs (red diamonds), and streams (yellow diamonds).

results should be δ_A (Abba et al., 2023). However, we also found that the calculated isotopic composition δ_A during the dry and wet season, namely −10.88‰ δ^{18}O and −13.50‰ δ^{18}O, respectively, were at equilibrium with respect to the amount weighted δ_{rain} (−1.84‰ δ^{18}O and −4.51‰ δ^{18}O, in that order). Moreover, as both the δ_{rain} and *h* parameters were measured in situ, the relative uncertainties of the *E/I* values may be considered as valid estimates of the calculation errors.

A comparison of the isotopic composition of groundwater and runoff with the precipitation isotope composition also confirmed that precipitation still has a strong influence on the water input into the lake because the δ^{18}O and δ^{2}H ratios of both groundwater and runoff plotted on the LMWL of the study site (Figure 4; Gibson et al., 2016; Jones et al., 2005). Overall, for stratified lakes like Lake Hule, it could be necessary to separately evaluate the epilimnion and hypolimnion water volumes and exchanges to explore if these two water layers have distinct isotopic compositions. The incomplete mixing in stratified lakes may also increase the error of calculations like the water residence time (Gat, 1970; Gibson et al., 2002). At Lake Hule, the epilimnion and hypolimnion water exhibited similar isotopic compositions, which decreased the potential bias in residence time calculations due to stratified isotopic compositions. Thus, despite the limited availability of historical research on groundwater-lake interactions and mass balance calculations for maar lakes, it is worthwhile to compare the evaporation loss and groundwater contribution estimated for Lake Hule with other studies. In Australia, Turner et al. (1984) estimated

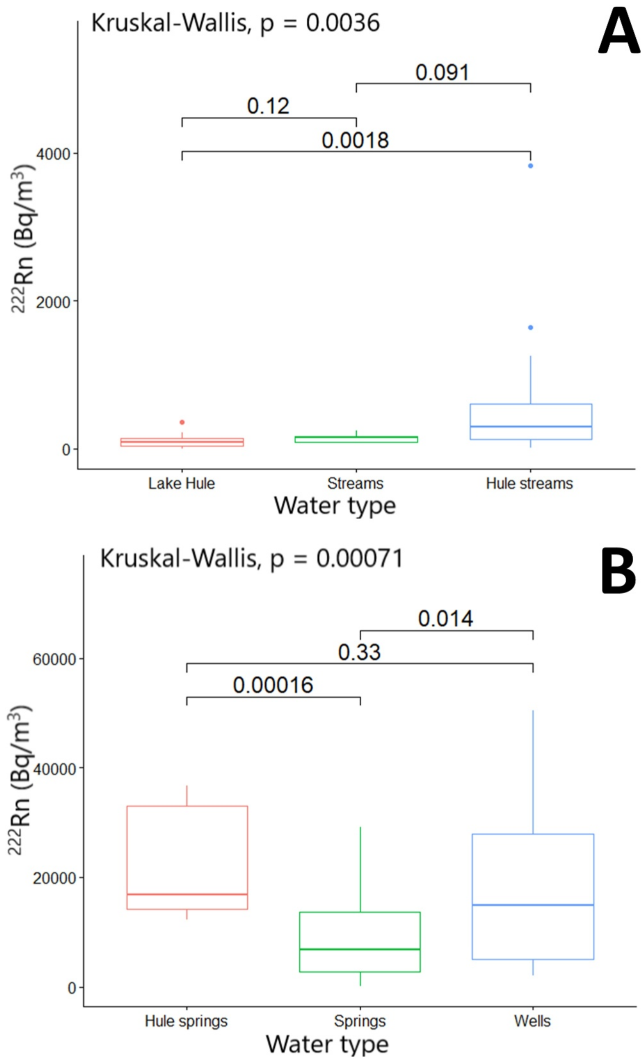

Figure 6. Box plots of ^{222}Rn in (a) surface waters (lake water, Costa Rican streams near hydrothermal systems, and streams near Lake Hule) and (b) in groundwater (springs near Lake Hule and springs and wells samples collected at the Central Valley of Costa Rica). Box plots include the 25th percentile, 75th percentile, median value, and outliers. We also report the p-values for the comparison of the median values of each water type. Those p-values <0.05 indicate a significant difference between water types.

the water budget of a maar lake, Blue Lake, using stable isotopes and tritium. They estimated an average *E/I* value of 13% and found that the lake was predominantly fed by groundwater (~90% of the inflow). In Mexico, Silva-Aguilera et al. (2022 and references herein) also assessed the hydrogeology and hydrogeochemistry of groundwater in the vicinity of a maar lake, Lake Alchichica. They found that the water budget was dominated by evaporation ($E/I = 117\%$) with a groundwater contribution of 34.5% of the inflow. In other maar lakes, like Lake Tana in Ethiopia, there is a very low groundwater inflow because the presence of a thick clay layer at the bottom of the lake that prevents groundwater inflow into the lake and low hydraulic gradients. The average *E/I* value of this maar lake was estimated in 67% (Alemu et al., 2020). Overall, the previously published data indicates that the evaporative losses at Lake Hule are indeed low but the groundwater input is comparable to the contributions estimated for other maar lakes. The evaporative enrichment in Lake Hule is also low (Figure 4). This finding is in agreement with the small area of Lake Hule (<10 km^2) and the short lake water residence time 0.39 ± 017 years. Thus, the fast hydrological cycle is controlled by the precipitation inputs and catchment-scale processes like evapotranspiration and groundwater discharges (Gibson & Edwards, 2002; Vystavna et al., 2021).

4.2. Groundwater Interactions in the Lake Hule Catchment

The availability of other tracers like $\delta^{13}C_{DIC}$, ^{222}Rn, and hydrochemistry also evidenced groundwater inputs to the lake in addition to the water isotopes-based observations. The ion composition of lake water confirmed that CO_2 dissolution played an important role in the water chemistry, with HCO_3^- as the major ion in dissolution (Figure 5). At the average pH of ~6 recorded at Lake Hule, the lake alkalinity was also mainly controlled by HCO_3^-. The bicarbonate formation can occur during the CO_2 dissolution from groundwater discharge or due to the incorporation of geogenic CO_2 through the bottom of the lake, as previously reported for Lake Hule (Cabassi et al., 2014). Thus, the input of CO_2-rich water to Lake Hule contributed to the DIC budget and reacts to form HCO_3^- via the following reaction:

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad (R1)$$

Besides this acid-base reaction, it is important to consider methanogenetic processes like CO_2 reduction Equation R2 and the degradation of organic matter through acetate fermentation at the bottom of the lake and the hypolimnion Equarion R3:

Table 2
Summary of Bayesian End-Member Analysis and Isotope-Based Calculations for Annual Balance Components of Lake Hule

Water balance components and isotope-based estimations	Annual estimates
P_L (mm)	4,284
E (mm)	967
I_{GW} (%)	61.3 ± 8.1
I_R (%)	14.3 ± 5.9
I_P (%)	24.4 ± 8.4
E/I (%)	3.0 ± 1.3
τ (years)	0.39 ± 0.17

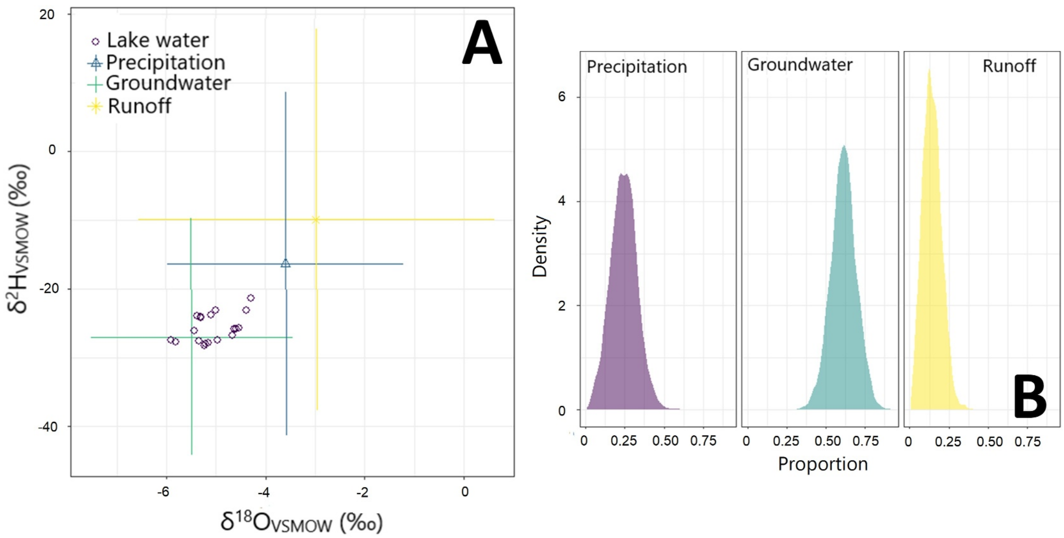

Figure 7. Annual water contributions to Lake Hule. (a) Dual isotope diagrams for lake water (gray empty circles) and mean values (error bars) of three endmembers: precipitation (purple), groundwater (cyan), and Maria Aguilar river (as proxy of the upper basin runoff, yellow). (b) Source contribution (as proportion) density plots for groundwater, precipitation, and runoff.

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O \quad (R2)$$

$$CH_3COOH \rightarrow CO_2 + CH_4 \quad (R3)$$

Therefore, we propose that the $\delta^{13}C$-DIC values at Lake Hule indicated a mixing of CO_2 sources, including those enriched in ^{13}C (e.g., mantle CO_2 with $\delta^{13}C$-CO_2 values ranging from ~ -10 to -5‰, Malowany et al., 2017) and those depleted in ^{13}C (e.g., soil CO_2 with $\delta^{13}C$-CO_2 values around ~ -25‰; Clark & Fritz, 1997; Pawellek & Veizer, 1994). Additionally, isotopic fractionation associated with acid-base reactions and methanogenesis (i.e., R1-3) also played a role. Recently, Winnick and Saccardi (2024) developed a quantitative framework for the role of carbonate/bicarbonate formation in the fluxes and patterns of CO_2 and the stable composition of DIC. Their results indicated that CO_2 hydration, namely the formation of HCO_3^- via R1, can effectively store dissolved CO_2 at levels above what would be predicted using gas solubility alone. Thus, the amount of CO_2 that can be "stored" via this reaction increases with increasing alkalinity, and there is systematic covariation between the alkalinity, pCO_2, and the isotopic composition of DIC during the initial CO_2 dissolution from groundwater leading to higher $\delta^{13}C_{DIC}$ values. During the wet season, we indeed observed a systematical increase in the $\delta^{13}C_{DIC}$ values (up to 2.8‰) in comparison to those values recorded in the dry season (Figure 6). Nonetheless, this observation may potentially indicate a greater contribution of sub-lacustrine fluids discharges enriched in ^{13}C during the rainiest period due to an enhanced dissolution of geogenic CO_2 and a higher phreatic level. Moreover, our results may also confirm the establishment of a more stable vertical stratification and accumulation of higher amounts of dissolved gases in the deep water layers during May–November than in December–April (Cabassi et al., 2014; Caracausi et al., 2013; Melián et al., 2021).

Our ^{222}Rn activity measurements provided insights into the hydrogeological context of the Lake Hule catchment. ^{222}Rn values indicated that groundwater inputs into the lake could be spatially distributed. The average ^{222}Rn activity in lake water was ~200 and 5 times smaller than the corresponding ^{222}Rn activity in the springs and streams near Lake Hule, respectively. The relatively high ^{222}Rn activities found in the streams near Lake Hule were also significantly higher than the activities measured in Lake Hule and other surface water samples collected at areas with hydrothermal activity across the volcanic front of Costa Rica. These results may indicate a rapid hydrological response of the local aquifer, with similar transit times in shallow spring as previously reported for the Barva aquifer (~1 year; Salas-Navarro et al., 2018). The local volcanic and fissured rock aquifer also shows a rapid response to heavy rainfall which is evident from the isotopic ratios of precipitation and groundwater as well as the ^{222}Rn activities that are distributed across the area (Figures 3 and 4). These ^{222}Rn activities are similar to those found in surface waters influenced by hydrothermal activity, as shown in Figure 6b.

Combined mass balance calculations based on stable water isotopes and radon have allowed groundwater discharge rates and water residence times estimations in different lacustrine scenarios (Arnoux et al., 2017; Luo et al., 2018; Petermann et al., 2018). In this first study, we decided only to implement an approach based on the mapping of ^{222}Rn activities and not to apply a radon mass balance to Lake Hule due to the complexity of the volcanic fractured phreatic area and the potential heterogeneity of groundwater discharge into the lake. However, it is worth discussing the potential implementation of a radon mass balance for Lake Hule in the future. Sediment equilibration experiments are needed to estimate the ^{222}Rn flux across the sediment-water interface (Arnoux et al., 2017; Kluge et al., 2012). Due to the complex biogeochemical transformations reported in the sediments of Lake Hule (Cabassi et al., 2014), we expect a significant degree of heterogeneity in the ^{222}Rn fluxes across the lake bottom. Thus, sediment experiments must be carried out using samples from representative lake locations to account for these spatial differences (e.g., sediment thickness and mineral composition). However, it is important to note that ^{222}Rn activities in local groundwater (i.e., springs) could be more representative of ^{222}Rn groundwater endmember than the lake bottom, given the high input of groundwater to the lake indicated by the isotope mass balance and the much higher ^{222}Rn activity found in spring than in lake water (Table 2). Still, the calculation of ^{222}Rn radon fluxes, such as the degassing flux at the lake surface, may be subject to high uncertainty. As high caldera walls and steep slopes characterize Lake Hule, wind speed is expected to be very low during some periods (e.g., wet season). As the ^{222}Rn evasion flux depends heavily on the wind speed over the lake surface, we expect that the low wind speed across the lake surface of Lake Hule limits the accurate calculation of the gas exchange at the lake surface (Kluge et al., 2012). Our first estimates of ^{222}Rn evasion for Lake Hule indeed indicate that average ^{222}Rn evasion is ~4 times greater during the dry season than in the wet season (7.6 ± 0.5 Bq/m^{2}day vs. 1.9 ± 0.1 Bq/m^{2}day). This difference reflects the wind speed variation during both seasons (0.82 m/s and 0.42 m/s, respectively). Moreover, the ^{222}Rn evasion values of Lake Hule are also lower than the average estimates reported for lakes in China (42.0 Bq/m^{2}day, Luo et al., 2018), in Germany (11.4 Bq/m^{2}day, Petermann et al., 2018), and in Alaska (~25 Bq/m^{2}day, Dabrowski et al., 2020). However, the weak stratification of Lake may also introduce additional uncertainty to the overall application of a radon mass balance. Given that the ^{222}Rn diffusion coefficient in water depends on the stratification of the water column (Kluge et al., 2012; Schubert et al., 2012), we consider that the application of a multilayer radon mass balance could be an interesting approach for Lake Hule (Arnoux et al., 2017). Moreover, the rapid hydrological response of the catchment and substantial input of groundwater to Lake Hule may also justify the analysis of the short-term variability in the groundwater discharge to this lake (e.g., monthly lake water sampling).

4.3. Implications for Future Hydrological Studies in Tropical Maar Lakes

Tropical maar lakes represent smaller and often shallow lakes that, due to relatively simple structure and limited size, make them ideal for studying hydroecological processes like interactions between groundwater and surface water, nutrient cycling, and the impacts of environmental changes (Awo et al., 2020; Haberyan & Horn, 1999; Melián et al., 2021). Despite the fact these lakes are generally less abundant and significant as water sources compared to larger and more integrated systems (e.g., rivers or aquifers), in particular local contexts, they can be highly relevant, especially where they represent one of the few available water sources. As recognized years ago, the protection and management of tropical lakes is still a difficult and exceedingly important problem to which scientists working at tropical latitudes can contribute (Horn, 2017; Lewis, 2000; May et al., 2021). Thus, we consider that the Lake Hule study case can provide useful guidelines for future research in tropical volcanic lakes. Our hydrological research reported on isotopic and water chemistry data on a seasonal basis for a lake in a protected area that can serve to assess the influence of external pollutants, such as agricultural runoff, sewage, or waste disposal. Our information can also be of interest to scientists working with biodiversity, like specialized and endemic species adapted to the specific environmental conditions in tropical lakes (e.g., oxic vs. anoxic conditions due to lake stratification). In tropical areas where maar lakes are used as a water source for consumption or agriculture (Alemu et al., 2020; Awo et al., 2020), the identification of interactions between groundwater and the lake may play a critical role in maintaining the hydrological balance and water quality of the lake because water over-extraction can alter the water level and chemistry, and then threaten the ecological functioning. Finally, our study case demonstrates the importance of carefully selecting natural tracers that meet criteria like conservative behavior, stability, measurable concentration levels, and distinct spatial or temporal variations. Overall, combining different environmental tracers may allow researchers to effectively study groundwater-lake interactions, gaining insights into the sources, flow paths, mixing processes, and water residence times in the interconnected systems.

5. Conclusions

Our study highlighted that the combination of water stable isotopes (δ^2H, $\delta^{18}O$) and ^{222}Rn measurements could be used as complementary tools for estimating groundwater inputs to volcanic lakes like Lake Hule despite the limnological and hydrogeological complexity of this type of lacustrine systems. Likewise, including other tracers, such as the isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and hydrochemistry, was also useful to confirm the major role CO_2 dissolution reactions play on the lake water chemistry of Lake Hule. Our isotopic sampling also confirmed that in areas where volcanic lithologies are predominant, groundwater recharge is mostly biased to intensive rainfall, and it may be an important component of the lake water budget. The selected tracers were also able to follow the seasonal dynamics of Lake Hule related to a comparatively greater geogenic CO_2 dissolution in groundwater during the wet season than in the dry season. Moreover, we confirmed that mapping ^{222}Rn activities across the lake area was also useful in identifying spatial variations in groundwater discharge to the lake. Overall, despite the seasonal variations in the water level of Lake Hule and its weak stratification, we consider our isotope mass balance calculations as good approximations of the lake water budget components because the groundwater discharge to the lake is much greater than the lake volume change and epilimnion and hypolimnion waters had similar isotopic compositions.

The results of our study provide valuable information for a better understanding of present water budgets and circulation patterns in volcanic lake catchments and their water resource management. We expect these new data to implement management strategies for both the lake and the surrounding groundwater resources and ensure that neither system is over-exploited. Moreover, our data is also useful to estimate how changes in precipitation patterns, evaporation rates, or groundwater levels could alter the water balance of the Lake Hule hydroecosystem but also to reconstruct paleohydrology in tropical lakes under the influence of global changes.

Data Availability Statement

The data sets presented in this study are accessible at Mendeley Data, https://data.mendeley.com/datasets/s87wf8zdgf/2 (Esquivel-Hernández et al., 2024).

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