



Application of hydrogeochemistry and isotopic characterization for the assessment of recharge in a volcanic aquifer in the eastern region of central Costa Rica

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ABSTRACT

In the eastern region of central Costa Rica, land use in the sub-basins of the Maravilla-Chiz and Quebrada Honda rivers (47 km²) is dominated by agricultural and livestock production, while groundwater resources constitute the main drinking water supply. This study aimed to (a) evaluate the location of groundwater recharge areas and groundwater flow paths, and (b) provide a characterization of the hydrochemistry and possible anthropic impacts. Groundwater was collected from 20 sites during the dry and rainy seasons and analysed for major ions, water stable isotopes and ²²²Rn. Approximated recharge areas were estimated through a local altitudinal line based on isotopic compositions in springs. The hydrochemical and isotopic characterization of groundwater showed that the main recharge areas occur in the upper part of the basin, except for springs in the middle part of the basin probably due to a certain hydraulic disconnection from the upper part that facilitates local recharge processes. In the lower basin, groundwater exhibited greater transit times and longer flow paths. Low nitrate, chloride and sulphate concentrations found in groundwater indicate low leaching of fertilizers or urban wastewaters. Our results are focused to improve water resources and agricultural management plans in a dynamic tropical landscape.

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1. Introduction

In highly dynamic tropical landscapes, knowledge of groundwater dynamics, including potential recharge elevations, flow directions, and the recognition of natural and anthropic hydrogeochemical impacts is an imperative task to enhance water resources management, i.e. in terms of water quality and quantity [1]. The Maravilla-Chiz and Quebrada Honda sub-basins, located in the eastern part of central Costa Rica, are

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dominated by agricultural activities, in which a lack of knowledge about recharge areas and location of river and spring protection areas have been identified as the main concerns [2].

Several tools allow the analysis of the hydrogeochemical and isotope evolution of aquifers of a volcanic nature [3,4]. The use of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in groundwater and precipitation allows the assessment of groundwater flows [5,6]. In Costa Rica, the use of isotopes as tracers of the hydrological cycle has been mainly focused on the western part of the Central Valley. A study on recharge areas of the Barva-Colima aquifer system, which serves as a water source for about 20 % of the country's population, was conducted by Reynolds-Vargas and Fraile [7]. Moreover, Sánchez-Murillo et al. [8] performed an analysis of historical isotope data on precipitation in Costa Rica, using the Global Network of Isotopes in Precipitation database [9], and the meteoric line was determined for Costa Rica: $\delta^2\text{H} = 7.61 \delta^{18}\text{O} + 7.40$ ($r^2 = 0.98$). In another study [10], a national-wide and high spatial resolution isoscapes of rainfall, groundwater, and surface water (100 × 100 grid) was proposed and large-scale groundwater recharge mechanisms across the country were inferred. A similar approach has been recently applied to the Pacific slope of Central America [11].

The objectives of this research were to: (a) evaluate groundwater recharge areas and elevations, and (b) provide a characterization of the hydrogeochemistry and possible anthropic impacts. The combination of environmental tracers and techniques in this study provides a baseline for future hydrological and hydrogeochemical studies in the Maravilla-Chiz sub-basins, as it generates information on solutes transport and improves knowledge on the main groundwater flow paths and the priority recharge areas, required for the protection of groundwater for human supply.

2. Materials and methods

2.1. Study area

The study area comprises the sub-basins of the Maravilla-Chiz and Quebrada Honda rivers (46.8 km²) and is located on the Caribbean slope of central Costa Rica, in the northeast of the province of Cartago (Figure 1). Altitude ranges from 2000 to 650 m a.s.l., with an average topographic gradient of 12 % reaching up to 30 % in the lower part of the sub-basins. The study area is characterized by a bimodal pattern of precipitation with peaks during the rainy season in May–June and September–October and two dry periods, between July and August, known as Mid-Summer Drought (MSD) [12] and from December to April. Average annual precipitation is 2500 mm in the middle and lower parts of the basin and 3000 mm in the upper part [13], although during the year of study (2016) a considerable decrease in precipitation was registered, with a value of 1810 mm due to the presence of El Niño/Southern Oscillation warm phase in the first leg of the year. The average annual air temperature is 19.0 °C. About 70 % of the study area is covered by sugarcane, coffee, vegetable crops and livestock activities, about 25 % by forests and the rest by small urban areas without sewerage system [2]. Vegetable crops, which demand more pesticides and fertilizers [14], are located in the upper part of the basin, while coffee and sugar cane crops, in the middle and lower parts, demand an intermediate amount of fertilizers [15].

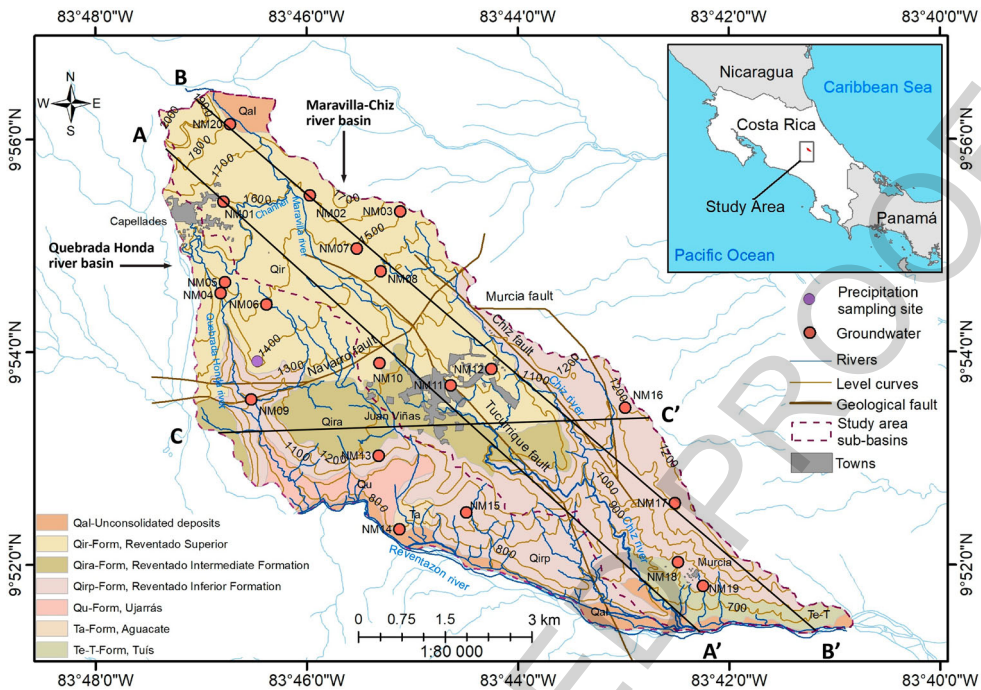


Figure 1. Geological map of the Maravilla-Chiz and Quebrada Honda river basins (modified from [20]), location of groundwater sampling sites, rainfall sampling site and, A–A', B–B', and C–C' geological transects).

2.1.1. Geology

The major part of the study area is composed of volcanic rocks of Tertiary and Quaternary age [16]. From bottom to roof, the following geological units are found (Figure 1 and Figure S1, Supplementary Material):

- Tuis Formation: it is composed of sandstones interspersed with shales and breccias of Palaeocene–Middle Eocene age [17,18].
- Aguacate Group: includes all volcanic lithologies prior to the formation of the volcanoes of the current volcanic front, from the Miocene to the Pliocene–Pleistocene [19].
- Ujarrás Formation: it is composed of conglomerates of metric clasts and local breccias not very consolidated, interspersed with sandstone and shale facies [18].
- Reventado Formation: emerges in almost all of the basin and includes the most important volcanic lithologies corresponding to the late Pleistocene eruptions of the Irazú Volcano [20]. This formation has been divided into three members:
 - Inferior Member: lava flows formed by basaltic andesites (lava flows and laharc flows in smaller proportions interspersed), due to a calcic character of the plagioclase and the presence of augite, olivine and, bronzite in the matrix. It is estimated that it reaches a thickness of 170 m and outcrops in the southeastern zone of the basin.
 - Intermediate Member: this is a thin (15 m thick in the thickest sections) layer of highly weathered ash, with the potential presence of a paleosol of a clay nature, and which

presents a lenticular and discontinuous morphology which is mostly in the western and central part in the middle of the basin (Figures 1 and 2(a)).

- Superior Member: these are superficial layers of ash, lahar flows and lava flows (formed by basaltic andesites) of decametric thickness that are superimposed in a discordant manner on the Intermediate Member. It emerges in the upper part of the basin with 600 m of thickness.
- Finally, in the upper part of the lithological column there are outcrops of unconsolidated deposits formed by the action of gravity or by water dragging.

In recent years, significant volcanic phenomena have been observed in the region; among them, the eruptive and seismic activities of the Irazú and Turrialba volcanoes, located to the north of the basin under study [21]. This activity has caused gas release, through degassing, towards the superficial layers of the crust [21]. Some of these gases include CO₂ which is integrated as a hydrogeochemical component in the groundwater. From a tectonic point of view, the study area is a complex and active zone [22], with two fault systems (Figure 1): the Navarro fault, which presents a W–E direction and a slight tectonic subsidence of the northern block of the basin (Figures 1 and 2(a,b)), while the Tucurrique, Chiz and Murcia faults present a predominance of NW–SE direction and, due to the normal displacement component of the Chiz and Murcia faults, the eastern sector of the basin is uplifted (Figure 2(c)). The most visible faults have been represented in Figure 1, although the orographic complexity and the vegetation cover make it difficult to follow these tectonic features.

2.1.2. Hydrogeology

The predominant lithology and the abundance of springs throughout the basin indicate that groundwater flows preferentially in highly fractured volcanic rocks of the Superior

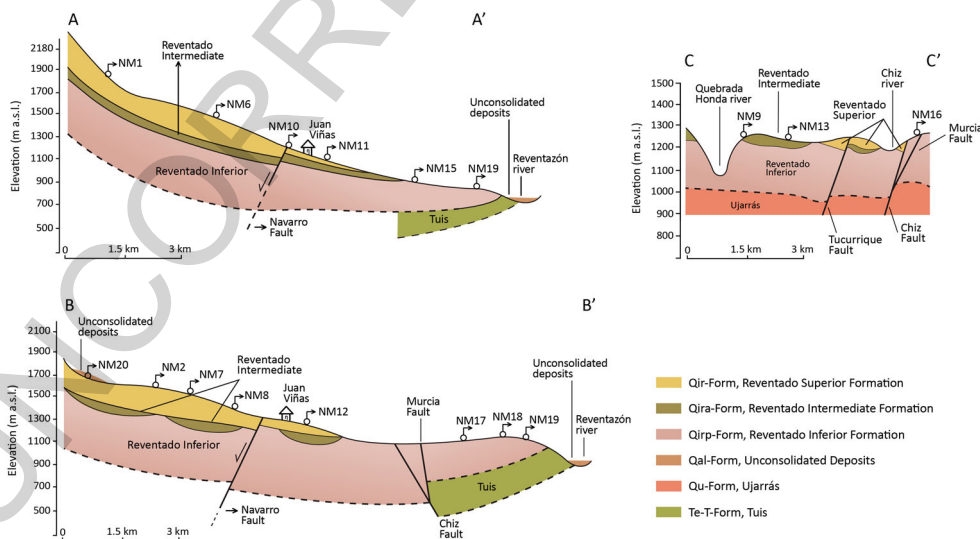


Figure 2. Idealized geological transects of the Maravilla-Chiz and Quebrada Honda river basins: (a) transect A–A', (b) transect B–B' and (c) transect C–C'.

and Inferior members of Reventado Formation [23]. Further, drilling of production or research wells has not been developed in the area; therefore, the description of the characteristics is based on the information provided by the springs, whose position within the basin is mainly due to geomorphological conditions and, to a lesser extent, to the presence of intercalations of a clay nature [23]. On the other hand, the important deformation of the study area has strong implications from the hydrogeological point of view, since it modifies the geometric characteristics of the possible aquifers.

In the sub-basin of Maravilla-Chiz rivers (Figure 1), the direction of the groundwater flows is mainly from the northwest towards the Reventazón River [24] in the southeast, while in the Quebrada Honda sub-basin river, the important geomorphological changes produce that groundwater flow to be directed towards this river. All these groundwater flows are likely to occur through a unique aquifer more than multilayer aquifer, since the lenticular and discontinuous structure of the pyroclastic deposits of Intermediate Member of Reventado Formation results in a low degree of confinement and a hydrogeological continuity between the Superior and Inferior Members of Reventado Formation, especially in the eastern sector of the basin (Figures 1 and 2(b)), although this continuity is also partly due to the tectonic uplift of this basin sector (Figures 1 and 2(c)). In contrast, in the middle part of the basin, the tectonic contact of the Navarro fault, together with the presence and continuity of Intermediate Member of Reventado Formation, especially in the western and central sectors (Figures 1 and 2(a)), might produce a certain hydraulic disconnection between the fractured andesitic lavas of the Superior and Inferior Reventado Formations. Furthermore, in the lower part of the study area (Figure 1), the eastern hydrogeological boundary does not coincide with the basin limit, and groundwater flows may occur from the north-eastern sector, but of lesser importance than those described above due to the smaller recharge area. As for the use of water resources of the study area, the main water supply to the population (11,500 inhabitants) [25] comes from the springs captured, while surface water is regulated through concessions for agricultural use, according to the database of the Water Directorate of the Ministry of Environment and Energy in 2019 [26].

2.2. Sample collection and analyses

Twenty springs were sampled (Figure 1), selected according to their spatial distribution, use for public supply, permanent condition of the springs and accessibility. Groundwater samples were collected: (a) during April 2016, for water stable isotope analysis only, (b) during June 2016, for water stable isotopes, ^{222}Rn , and major ions, and (c) during April 2017, for major ion analysis only. The sampling surveys during April 2016 and 2017 were considered representative of the conditions of the dry season, while the June survey, of the first month of the rainy season. Samples were organized according to their location in the upper, middle and lower zones, considering their similarities in the hydrochemical compositions; the presence of the Navarro fault, which induces a certain discontinuity on the groundwater flow paths from the upper to the middle zones, was also used as a geological and geomorphological criterion. At the time of sampling, electrical conductivity (EC in $\mu\text{S}/\text{cm}$), temperature (T in $^{\circ}\text{C}$), dissolved oxygen (DO in mg/L), pH, total dissolved solids (TDS in mg/L) and redox potential (ORP in mV) were measured in all groundwaters in the field with a multiple electrode model HI98311 for EC, TDS and T ; a

multiple electrode model HI98121 for pH and ORP and a DO sensor model HI 9147 (Hanna Instruments, USA).

Groundwater samples were collected in HDPE bottles pre-treated according to the specifications of method 1060C of the Standard Methods for Examination of Water and Wastewater [27] and stored in cold (4°C) until analysis. Calcium, magnesium, potassium, sodium, chloride, nitrate, sulphate were analysed by ion chromatography (Dionex Thermo Scientific ICS 5000), according to the method 4110 [27], silica by spectrophotometry according to the 4500-SiO₂ C method [27] and, in the case of alkalinity, by volumetric analysis according to the method 2310B [27]. The percentage error of the ion balance in all samples was less than 5 %.

Precipitation amount was measured, from March 2016 to December 2017, by using a Davis Vantage Pro Plus 2 weather station, while rain samples for isotope analysis were collected weekly with a passive sampler [28]; precipitation measurements and rain isotope samples were collected in the central part of the study area (Figure 1), at 1400 m a.s.l. Samples were stored in 50 mL vials (HDPE) and preserved (5 °C) until the stable isotopic analyses. Stable isotope analyses in rain and groundwater were performed by laser spectroscopy using an analyzer model L2120-I (Picarro Inc., USA) and an LWIA-45EP analyzer (Los Gatos, USA). Calibrated secondary standards were used to normalize the results as well as to assess quality and drift control procedures. ¹⁸O/¹⁶O and ²H/¹H ratios are presented in the established delta notation (δ, ‰), with reference to the VSMOW-SLAP scale. Deuterium excess was calculated as $d\text{-excess} = \delta^2\text{H} - 8 \delta^{18}\text{O}$. The laboratory precision was ±0.5 ‰ (1σ) for δ²H and ±0.1 ‰ (1σ) for δ¹⁸O.

To estimate the characteristic isotope value of the local recharge water, assigning more weight to the stable isotope values of higher rainfall amounts, seasonal and annual amount-weighted mean isotope values were calculated by using the weekly rainfall isotope value and the corresponding weekly measured amount of precipitation, p_w , as follows:

$$\text{Mean amount weighted } \delta_{mw} = \frac{\sum_{i=1}^n p_w \delta_w}{\sum_{i=1}^n p_w}$$

To determine radon activity, samples were collected in 250 mL glass bottles. The bottles were completely filled, without the presence of air bubbles and hermetically sealed on site. The activity of ²²²Rn dissolved in water was determined in the laboratory within 8–12 h of sample collection using a RAD7 field equipment (DurrIDGE Inc., USA). RAD7 converts alpha radiation directly to an electrical signal, using alpha spectrometry. Statistical and graphical analysis was performed using the open source statistical R language and packages [30]. Hydrogeochemistry and graphical editing software were used to represent the data. The cartography and spatial analysis were performed using Arcmap v.10.5 (ESRI, USA).

3. Results

3.1. Hydrochemistry

In general, groundwater collected during both sampling surveys exhibited low mineralization (EC < 342 μS/cm), temperatures between 17.0 and 23.2 °C, while pH remained in a range between 5.8 and 8.6 (Table S1, Supplementary Material). Bicarbonate ranged

between 18.6 and 198.6 mg/L, calcium below 44.1 mg/L and silica from 15.0 to 123.6 mg/L. More than half of the samples presented silica concentrations greater than 50 mg/L. Sulphate remained below 4.7 mg/L, while chloride was found below 4.6 mg/L, both parameters presented greater concentrations in springs near population centres. Nitrate remained below 15.4 mg/L (as NO_3^-), with the greatest concentrations in springs NM01, NM05, NM09 and NM14, near vegetable, sugarcane and coffee crops and population centres without sanitary sewage. Most of the groundwater samples were classified as calcium–magnesium bicarbonate facies (Figure S2, Supplementary Material), while biplot diagrams including silica, bicarbonate, calcium and magnesium indicate a relatively moderate spatial hydrogeochemical evolution (Figure 3). In the middle zone of the basin, ion concentrations were lower compared to most of springs in the upper zone, especially bicarbonate, silica, and calcium (Figure 3 and Table S1, Supplementary Material), resulting

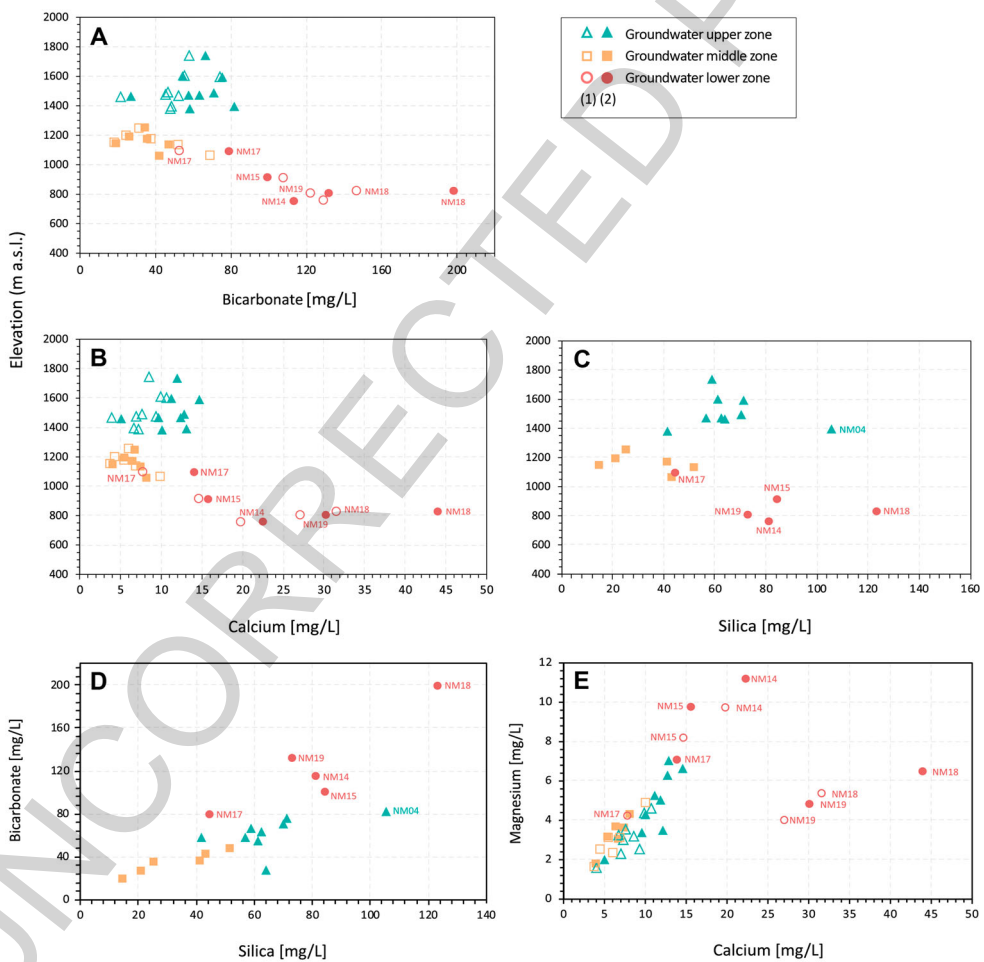


Figure 3. Relations of (a) bicarbonate vs. elevation, (b) calcium vs. elevation, (c) silica vs. elevation, (d) silica vs. bicarbonate and (f) calcium vs. magnesium in groundwater within Maravilla-Chiz and Quebrada Honda river basins. Numbers in brackets refer to the sampling surveys of April (1) (open symbols) and June (2) (solid symbols).

in an inverse hydrochemical evolution (Figure 4). In terms of the temporal variation, most of the spring samples collected during the second sampling survey exhibited higher bicarbonate, calcium, silica and magnesium concentrations, which was more evident in the springs located in the lower zone (Figure 3).

In the study area, mainly composed of basaltic and andesitic volcanic rocks, bicarbonate can be originated from the weathering of silicates and feldspars, and from the dissolution of CO_2 into groundwater; CO_2 can be supplied through the rain, oxidation of organic matter in the soil, wastewaters or degasification due to volcanic activity in the region. However, the major source of CO_2 in the groundwater is CO_2 degassing [31,21] due to recent volcanic activity in the area. The CO_2 reacts with water to produce carbonic acid, which dissociates releasing carbonates and bicarbonates.

The carbonic acid released enhances the dissolution of other minerals through weathering of rocks [32]. Sulphate dissolves into groundwater through the oxidation of sulphide in volcanic rocks, leaching of fertilizers and waste waters and atmospheric deposition; however, most samples showed low concentrations (below 4.7 mg/L). Low concentrations of chloride (below 4.6 mg/L) results from low occurrence of this ion in volcanic rocks; in addition, a weak correlation of 0.62 in both sampling surveys was found between nitrate and chloride (Table S2, Supplementary Material), suggesting a less important origin of chloride from wastewaters; therefore, the main origin might be meteoric. In contrast to chloride, groundwater samples received an important contribution of calcium and, to a lesser extent, of silica [29] and magnesium through the weathering of the plagioclases, mainly anorthite (containing elevated amounts of calcium and lower concentration of

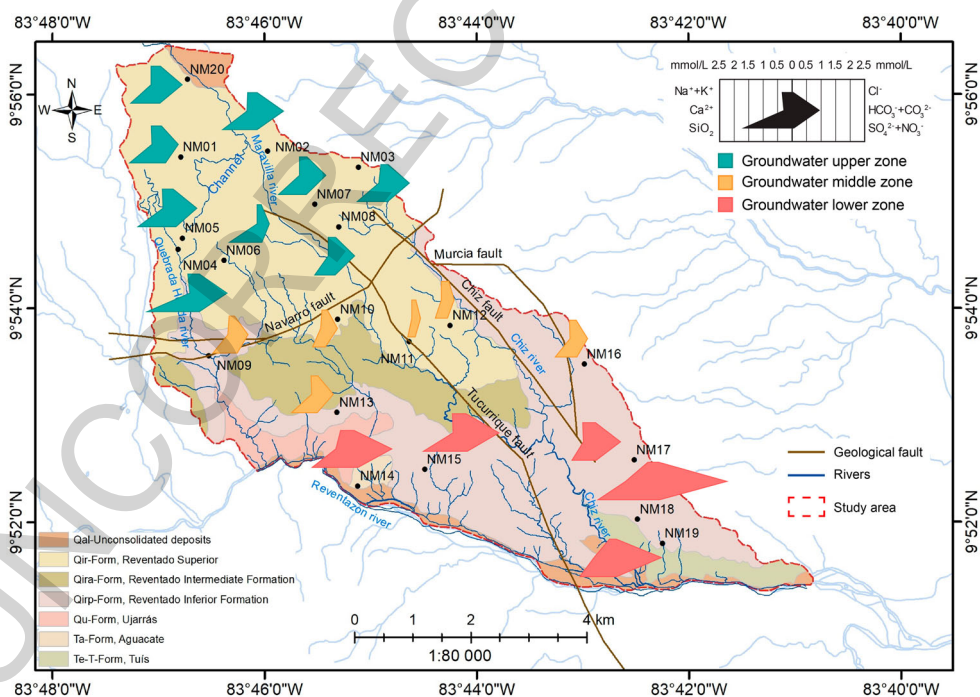


Figure 4. Modified stiff diagrams showing silica, sodium, potassium, calcium, chloride, sulphate, nitrate and bicarbonate (mmol/L) in groundwater within Maravilla-Chiz and Quebrada Honda river basins.

silica), immersed in a ferromagnesian matrix, from the andesitic and basaltic rocks of the Reventado Superior and Inferior Formations. Strong positive correlations were found between calcium–magnesium, calcium–bicarbonate and magnesium–bicarbonate (Table S2, Supplementary Online Material), indicating mineralization process as the main source, strongly influenced by the presence of CO₂ and bicarbonate.

3.2. Isotope hydrology

Figure 5 shows the local meteoric line for the intramountainous region of Juan Viñas, Cartago ($N = 90$). The slope greater than 8 is due to the influence of samples with high values of d -excess during the cold front period, which occurs due to the influence of north-easterly trade winds during the northern hemisphere winter, approximately from December to March. Similarly, the value of the intercept greater than 10 (equilibrium conditions) refers to the addition of local moisture from evapotranspiration in the mountainous region. The temporal distribution of the isotopic composition presents a bimodal pattern with enriched samples between -6.0 and $+0.15$ ‰ during the dry season and another group of depleted samples during the rainy season between -14.9 and -6.0 ‰; groundwater sampling surveys were developed during these seasons. d -excess ranged from -2.6 to 20.5 ‰, with an average of 13.0 ± 4.4 ‰ (1σ), indicating strong conditions of local moisture recycling in the generation of precipitation. Most of the groundwater samples present an isotopic composition close to the Global Meteoric Water Line

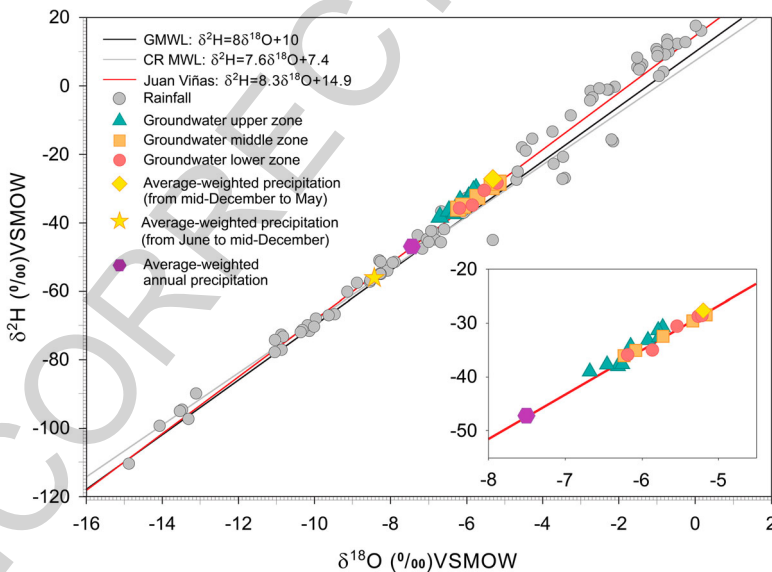


Figure 5. Local meteoric water line for the intermountainous region of Maravilla-Chiz and Quebrada Honda river basins, Cartago. Weekly rain samples at Juan Viñas and the amount-weighted mean isotope values of precipitation are included: (a) from mid-December to the end of May (yellow rhomboid), (b) from June to mid-December (yellow star) and (c) annual (purple hexagon). The Global (GMWL; black) and Costa Rica (grey) meteoric water lines are included as a reference, as well as the local water meteoric line of this study (red).

(GMWL), which indicates a meteoric origin and, due to the lack of irrigation, no recharge by returns of agricultural areas. The most depleted spring samples correspond to higher elevations, while samples in the middle and lower zones exhibited both isotopically enriched (e.g. NM10, 12, 16 and 19) and depleted compositions (NM13, 14, 15, 17 and 18) (Figure 6, Table 1).

Three amount-weighted mean isotopic compositions of precipitation were calculated: (a) annual, (b) from mid-December to the end of May, comprising enriched samples from dry season and depleted samples from the first events of early rainy season, and (c) from June to mid-December (with depleted samples from rainy season events). The three values are located along the local water meteoric line (Figure 5). Stable isotopic signature of groundwater collected during April (dry season) and June (first month of the rainy season) are located between these values.

3.2.1. Approximation of groundwater flow paths by using hydrochemistry and isotopic compositions

Furthermore, to obtain a better understanding of the groundwater flow paths and recharge areas, a principal component analysis (PCA), including hydrochemical and isotope data, was developed (Figure 7). The variables that showed factor loadings higher than 0.65 in at least one of the two first principal components were selected, while correlated variables were excluded. Table S3 (Supplementary Material) shows the two principal components, describing 82.1 % of the cumulative variance. Figure 7 shows the variation of loadings for each variable within the two main factors, F1 and

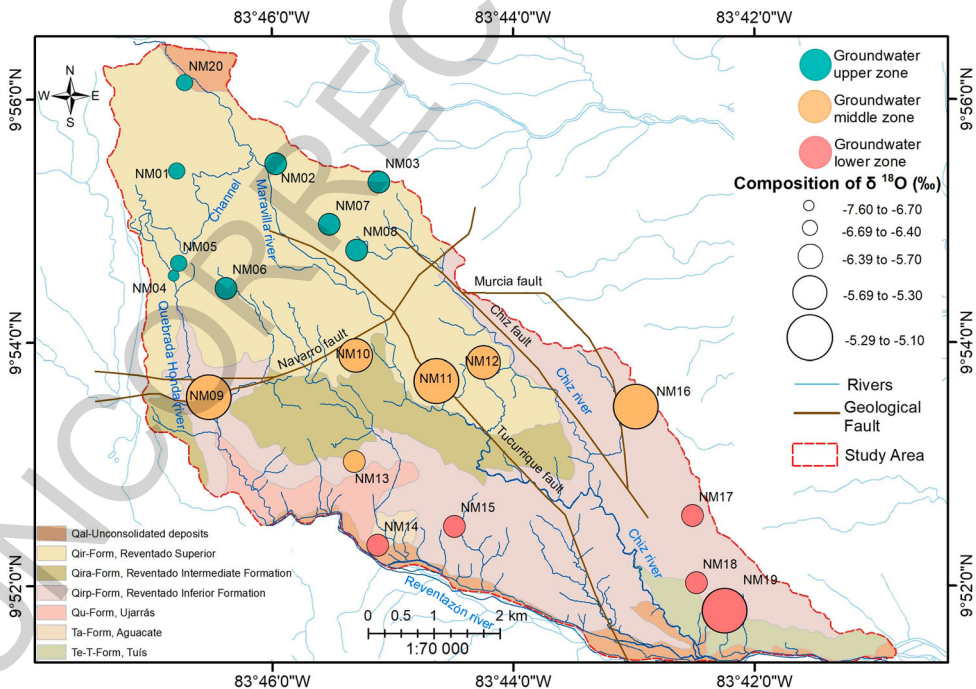


Figure 6. Spatial variability of $\delta^{18}\text{O}$ in groundwater within Maravilla-Chiz and Quebrada Honda river basins.

Table 1. Isotopic composition of groundwater collected during April (S1) and June (S2) sampling surveys, elevation of sampling site, approximated recharge area and difference in elevation (m) between the minimum and maximum approximated elevation in each spring within Maravilla-Chiz and Quebrada Honda river basins.

Site code	Elevation (m a.s.l.)	$\delta^{18}\text{O}$ (‰)		$\delta^2\text{H}$ (‰)		Recharge area (m a.s.l.)	
		S1	S2	S1	S2	Min	Max
<i>Groundwater in the upper zone</i>							
NM01	1604	-6.45	-6.59	-37.7	-39.0	1600	1800
NM02	1597	-6.15	-6.14	-34.1	-35.2	1600	1700
NM03	1472	-5.92	-5.91	-33.1	-33.6	1500	1600
NM04	1395	-6.68	-6.74	-39.0	-40.3	1600	1900
NM05	1491	-6.26	-6.45	-37.5	-38.9	1500	1800
NM06	1464	-5.78	-5.83	-32.5	-33.7	1500	1600
NM07	1474	-5.79	-5.96	-31.3	-32.8	1500	1600
NM08	1383	-5.73	-5.73	-30.8	-32.5	1400	1500
NM20	1739	-6.31	-6.53	-38.0	-38.3	1750	1800
<i>Groundwater in the middle zone</i>							
NM09	1059	-6.24	-5.28	-36.0	-30.0	1300	1700
NM10	1249	-5.17	-5.31	-28.4	-29.7	1250	1300
NM11	1146	-5.72	-5.14	-32.4	-28.8	1150	1300
NM12	1193	-5.34	-5.36	-29.5	-30.4	1200	1300
NM13	1133	-6.09	-5.96	-35.0	-34.3	1300	1700
NM16	1172	-5.28	-5.28	-28.7	-30.1	1200	1300
<i>Groundwater in the lower zone</i>							
NM14	754	-5.86	-6.12	-35.0	-35.9	1300	1700
NM15	909	-6.19	-6.27	-35.7	-36.6	1400	1700
NM17	1091	-5.55	-5.77	-30.6	-32.0	1200	1600
NM18	825	n.d.	-5.72	n.d.	-31.2	1300	1500
NM19	803	-5.21	-5.25	-28.5	-27.7	1100	1400

F2. The F1 exhibits three variables with strong factor loadings: calcium, magnesium, and EC, corresponding to water-rock interaction and groundwater mineralization processes. Groundwater samples in the lower zone (NM14, 15, 17, 18 and 19) are related to bicarbonate, calcium, magnesium, and EC, indicating greater mineralization and, probably, flows of greater length and longer transit times, which is more evident in sample NM18. The F2 shows two variables with strong factors loadings in temperature and $\delta^{18}\text{O}$. Springs in the upper zone are positioned both in the negative and positive parts of F2 (Figure 7), and opposed to EC, calcium, magnesium, temperature, and $\delta^{18}\text{O}$, representing samples with low mineralization and depleted isotopic compositions (Figure 6), which might indicate local recharge, local flows, short transit times and, therefore, the presence of a shallow groundwater system. Groundwater samples in the middle zone are located in the positive sector of F2, opposed to major ions and EC and related to temperature and $\delta^{18}\text{O}$, indicating lower mineralization and isotopically enriched groundwater, compared to the upper zone (Figure 6). This might reveal local recharge in the middle zone of the basin, short flow paths and short transit times. Samples in the middle zone also present, in average, similar temperatures compared to samples at lower elevations (Table S2, Supplementary Material), probably due to the influence of the Navarro fault dividing the upper and middle zones, although Tukurrique fault may also be conditioning the water temperature of any of these springs, e.g. NM11, given possible groundwater flows at higher temperature rising to surface (springs), in favour of these faults.

In general, spring samples collected in the upper and middle zones might indicate conditions of local recharge, shallow flow paths and short residence times, with a certain

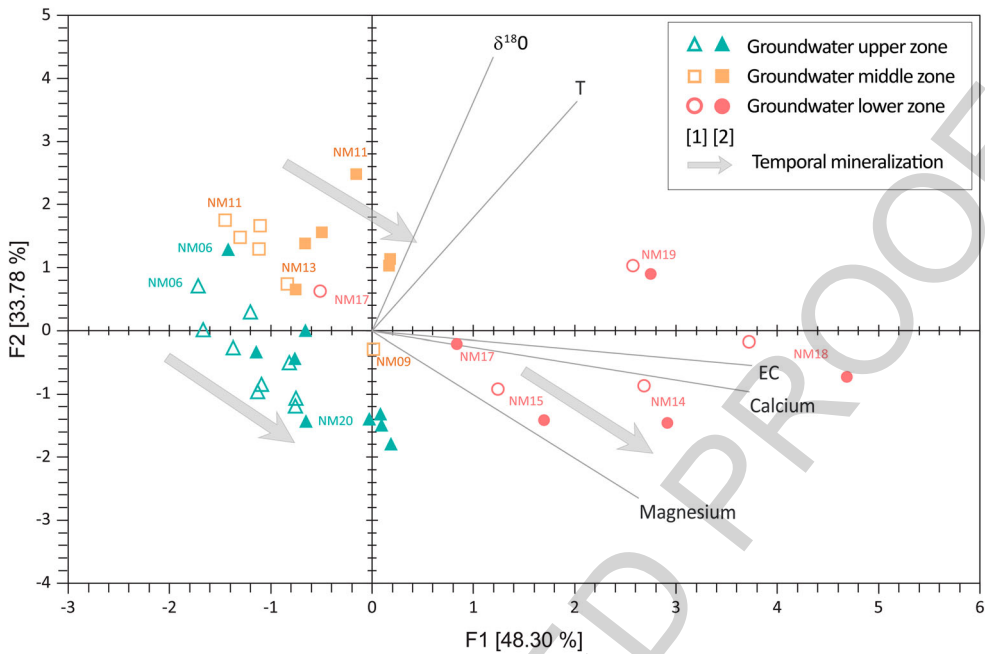


Figure 7. Multivariate statistical analysis for the composition of groundwater samples within Maravilla-Chiz and Quebrada Honda river basins. Numbers in brackets refer to the sampling surveys of April (1) (open symbols) and June (2) (solid symbols).

hydraulic disconnection between the flow paths circulating from the upper to the middle zones of the basin.

3.2.2. Local altitudinal recharge line by using stable isotopes in springs

Due to the absence of precipitation isotope data at different elevations in the basin, the $\delta^{18}O$ in springs, whose altitude might represent the local recharge elevation, was applied. This enabled the development of a preliminary local altitudinal line to approximate the range of recharge elevations for the other springs sampled in the study area. Moreover, Tazioli et al. [33] and Lambán Jiménez et al. [34] concluded that this approach is appropriate in areas with high spatial and temporal variability of the isotopic composition in the precipitation. The springs in the upper zone, and several springs in the middle zone (NM10, 11, 12 and 16), were selected to construct the local altitudinal line, since they exhibited hydrochemical characteristics of shallow flows, local recharge, short transit times and enriched isotope content, similar to the amount-weighted mean isotope value of precipitation from mid-December to May (Figure 8). The results show that groundwater samples in the upper zone might recharge at an elevation between 1400 and 1900 m a.s.l., with the possibility of some groundwater recharging at higher elevations (Table 1). The main recharge areas for the springs in the middle zone are located between 1100 and 1300 m a.s.l., approximately from the Navarro fault to the southeast, except for NM09 and 13, whose recharge might be originated in the upper zone, between 1300 and 1700 m a.s.l. Finally, in the lower zone, springs NM14, 15, 17 and 18 springs may have their main recharge areas at the upper zone of the basin,

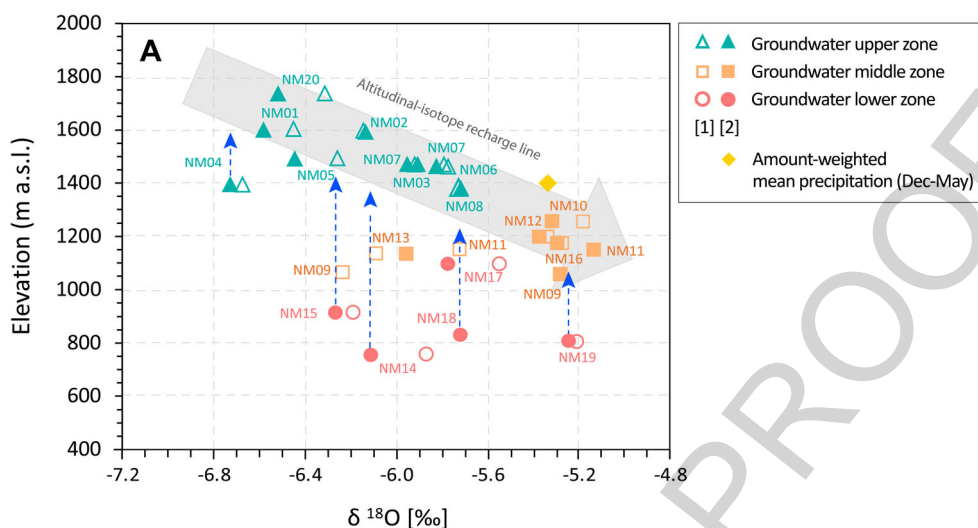


Figure 8. Relation of $\delta^{18}\text{O}$ versus elevation in groundwater within Maravilla-Chiz and Quebrada Honda river basins. Numbers in brackets refer to the sampling surveys of April (1) (open symbols) and June (2) (solid symbols).

between 1200 and 1700 m a.s.l., while the NM19 spring probably recharges at lower elevations, in the middle zone, from 1100 to 1400 m a.s.l, approximately.

3.2.3. Radon activities in springs

The ²²²Rn activities in groundwater were relatively low (below 55.2 Bq/L). Most of the spring samples exhibiting compositions above 10 Bq/L were located in the upper and middle zones (Figure S3 and Table S2, Supplementary Material). Major ²²²Rn were observed near geological faults, probably as a result of the movement of thermal gases through the geological formations and new conduits formed during the ascent of fluids [35,27]; no relation between ²²²Rn and elevation was observed (Figure S3). In the upper zone, spring samples showed compositions between 6.0 and 53.2 Bq/L, from 2.3 and 55.2 Bq/L in the middle zone, while ²²²Rn decreased in the lower basin (0.8 to 12.1 Bq/L).

4. Discussion

In Maravilla-Chiz and Quebrada Honda rivers basins, similar isotopically enriched compositions were found in the springs in the middle and lower basin, complying with the altitudinal effect by orographic fractionation. The temporal variability of the isotopic composition, with enriched samples during the dry season and depleted samples during the rainy season, might induce relatively enriched groundwater samples compared to the amount-weighted annual mean isotopic composition of precipitation in the study area. In a study in the western part of the Central Valley, Reynolds-Vargas and Fraile [7] found that groundwaters in the northeast of the aquifer are more enriched than the rest due to the recharge from enriched rainfall from the Caribbean, particularly during the cold front period. In other studies, Sánchez-Murillo and Birkel [10] and Sánchez-Murillo et al. [11] demonstrated that: (a) in the high elevation catchments along the

main mountain range of Costa Rica and during the cold fronts period (December–March) substantial rainfall is received with a particular enriched compositions; therefore, it is possible to find enriched compositions in wells and springs, even at high elevations; (b) by mid-May and September–October when the Intertropical Convergence Zone (ITCZ) is over Costa Rica a notable depletion in the isotopic composition is also observed.

These enriched and depleted incursions might explain that the isotope signature of the groundwater samples collected during dry season and the first month of rainy season fall, along the local weather line, between the amount-weighted mean isotope value of rainfall from mid-December to late May (comprising enriched events during the dry season and the depleted events from the first month of the rainy season) and the amount-weighted mean isotope value of rainfall from June to mid-December (including depleted events from the rainy season) (Figure 6).

Springs in the upper zone exhibited moderate mineralization, as a result of local flows, short transit times and, therefore, local recharge. This coincides with depleted ^{18}O contents obtained during April and June sampling surveys (with an average of -6.16 ± 0.35 ‰) (Figures 7 and 8). In the middle zone, the lowest compositions in major ions and enriched ^{18}O contents (-5.51 ± 0.38 ‰) indicate that, in most of the springs, the main recharge area might be located at a lower elevation (Figure 8) and, consequently, might present shorter transit times and shallow flow lines [36]. These characteristics suggests the existence of a hydraulic discontinuity from the upper to the middle sector, probably induced by the presence of the Reventado Intermediate Formation (the ash layer) in the central and western part of the middle basin, in combination with the Navarro fault (Figure 2(a)). Thus, at least on a preliminary basis, the upper and middle zones could represent two different systems with a certain hydrogeological connection (Figure 9).

Moreover, the geological structure in the eastern sector of the basin might facilitate the circulation of groundwater flows from the upper to the lower zone (Figures 2(b) and 9). Considering the hydrogeological knowledge that could be deduced from the study area – the depleted ^{18}O content (with an average in $\delta^{18}\text{O}$ of -6.23 ± 0.14 ‰) and the increase in the ions concentrations – it can be concluded that the main recharge in NM14, 15, 17 and 18 springs occurs in the upper zone (Figure 8). The groundwater in NM19 spring might recharge in the middle zone, possibly following the Navarro fault, as it has a higher $\delta^{18}\text{O}$ value (-5.3 ‰), similar to the sites in this area (-5.4 ± 0.31 ‰) (Figure 8). The higher ion concentrations in these springs (Figure 3) suggests greater transit times and longer flow paths, although recharge along the flow path and local recharge may not be discarded.

Low nitrate, chloride and sulphate compositions in groundwater indicate low leaching of fertilizers or urban wastewaters. Higher nitrate concentrations (but always below 15.4 mg/L as NO_3^-) were found in four springs, near vegetables crops and urban areas in the upper and middle zone. The low concentrations of sulphate (below 3.0 mg/L) and chloride (below 4.6 mg/L) in springs in the upper and middle basin, confirms the presence local flow paths through volcanic silicate rocks, which naturally present low contents of these anions [37], while higher sulphate concentrations in springs of the lower zone can be related to longer flow paths, basically from the Reventado Formation.

Considering the isotope content of springs, the approximation of a local altitudinal line, the hydrochemistry of groundwater and the hydrogeological characteristics of the basin, the identification of two main recharge areas has been hypothesized (Figure 9): (a) upper area (between 1400 and 1900 m a.s.l.), where the local recharge of the springs in that zone is

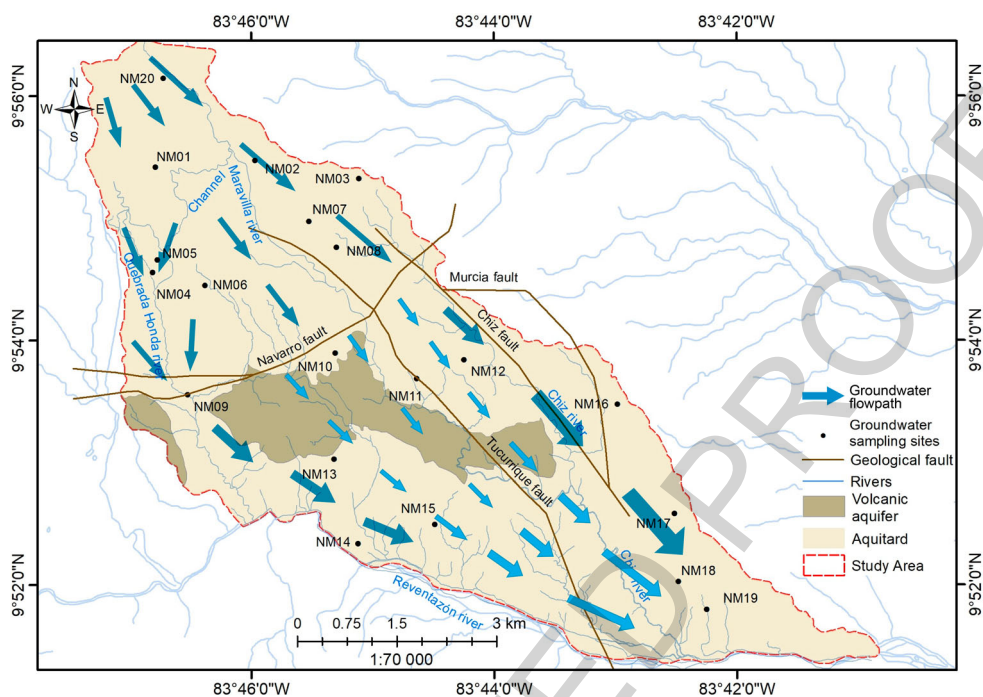


Figure 9. Idealized diagram showing the main groundwater flows within Maravilla-Chiz and Quebrada Honda river basins. The size of the arrows is proportional to the length of the flow path.

originated and, in addition, for some of the springs in the middle and lower parts of the basin; (b) middle zone (between 1100 and 1300 m a.s.l.), corresponding to the local recharge area for springs in the middle zone and the main recharge area for the NM19 spring and, to a lesser extent, for the rest of the springs in the lower zone of the basin.

Furthermore, the recharge of groundwater, due to the heavy rainfall events during the first month of the rainy season, may have induced an increased mineralization in most of the springs, especially in the lower part of the basin (Figure 3(a,b,e)). These recharge events cause an increase in the hydraulic head and might push the mineralized water, stored between the minor or secondary sizing fractures of the aquifer, during the dry season. This, in turn, might explain the increase in the EC, calcium, magnesium, and bicarbonate in most groundwater samples during the rainy season, which is more evident in NM18 and NM19 springs, characteristic of larger flow paths and longer residence times in the basin (Figure 5).

Contrary to expectations, low compositions of ^{222}Rn were found in the lower zone springs, even though these may have the longest transit times and flows, while the highest activities are observed near the fault lines in the upper and middle zones (Figure S3, Supplementary Material). The absence of contributing faults, radioactive decay [35,38] and the possible contribution of groundwater recharged locally might explain the low ^{222}Rn activities in springs NM13, 14, 15 and 19, at least during the first month of the rainy season. Similar results were obtained in Barva and Colima Superior volcanic aquifers, also in the Central Valley, Costa Rica [39]. Due to its low compositions, different sources and changes throughout the basin, the use of radon might introduce important uncertainties in the assessment of recharge areas and groundwater flow

paths, at least during the first month of the rainy season, especially in a volcanic setting. Consequently, to evaluate its potential use as a tracer in this basin, radon measurement is recommended during the dry season.

Finally, groundwater samples collected in this study represented, for the most part, shallow groundwater systems: (a) in the basin, all of the hydrogeochemistry of groundwater proves circulation through shallow flow paths, (b) the basin is relatively small, and thus groundwater circulates for a short time, regardless of whether it travels through shallow or deep flows, causing the mineralization process to be moderate, (c) the hydrogeological discontinuity may partially interrupt the continuity of the flows, preventing further mineralization at most springs, and (d) spring water is mixed with small fractions of shallow groundwater and with local recharge water at some of the sites. A possible deep flow system, although should not be neglected, is not strong enough to be confirmed.

5. Conclusions

Considering the hydrochemical and hydrogeological characterization, and the estimated local altitudinal line based on the isotope composition of groundwater, groundwater recharge is plausible occurring in the upper and middle zones. While the springs from the upper zones presented moderate concentrations in silica, calcium, bicarbonate and isotopic compositions indicating local recharge, local flow paths and short residence times, the springs in the lower zone showed the greatest mineralization, as a result of longer resident times and flow paths of groundwater through basaltic andesites of the Reventado Formation. Samples from the middle zone showed the lowest concentrations of these constituents; slight enrichment in ^{18}O in the middle zone indicates that the main source of water to the aquifer is through local recharge, since Navarro fault and the Reventado Intermediate Formation might represent a hydraulic discontinuity between the upper and the middle zones of the basin, especially in the western and central sectors. To enhance research for future assessment of largest and/or deep groundwater circulation, some dating tools should be applied, i.e. ^3H , $^3\text{H}/^3\text{He}$, SF_6 or CFCs. Finally, since the estimated recharge elevation areas for the springs in this study are located at upper and middle elevations in the basin, conservation efforts should be prioritized in these areas, where agriculture might impact groundwater quality. Therefore, agricultural management plans for the protection of water resources should be implemented.

Geolocation information

The study area is located in Central America, Costa Rica in Cartago province. The watershed coordinates are: $9^{\circ}52'13''$ to $9^{\circ}56'18''$ N and $83^{\circ}41'15''$ to $83^{\circ}47'22''$ W.

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