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Spatial distribution of $\delta^{18}\mathrm{O}$ in rainwater and groundwater to identify areas of recharge in the Colombian Northwest

Distribución espacial del $\delta^{18}\mathrm{O}$ en agua lluvia y subterránea para identificar áreas de recarga en el Noroeste de Colombia

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ABSTRACT: The understanding of the spatiotemporal variability of the water molecule stable isotopes $(\delta^{18}\mathrm{O}$ and $\delta^{2}\mathrm{H})$ in rain and groundwater has been used in hydrogeology to validate recharge zones. In this study, we analyzed the recharge of four aquifer systems located in northwestern Colombia. This region is characterized by highly complex topography, as the Andes Mountain range splits into three branches, two of them included in the study area. The relation in the variation of values of the $\delta^{18}\mathrm{O}$ between Precipitation (P) and groundwater (GW) was analyzed through the arithmetic expression P/GW; when P/GW is equal or larger than 1, the recharge is direct, and values less than 1 indicate recharge from regional flows. For the purposes of this research, according to statistics criteria, values between 0.98 and 1.02 are considered as 1. It was found that on Bajo Cauca, Occidente and Urabá, the phreatic aquifers are recharged directly with rainwater or after slight evaporation processes, while the recharge of deep aquifers occurs through regional flows. The Valle de Aburrá´s phreatic aquifer is also recharged from distant areas; this occurs because the surface has been impermeabilized by urban processes. The P/GW ratio seems to be useful in identifying recharge processes in regions with higher elevation gradients. In low-lying areas, the applicability of this method should be restricted.

RESUMEN: La comprensión de la variación espacial y temporal de los isótopos estables $(\delta^{18}\mathrm{O}$ and $\delta^{2}\mathrm{H})$ en la lluvia y el agua subterránea ha sido usada en la hidrogeología para validar zonas de recarga. En este estudio, se realiza un análisis de la recarga para cuatro sistemas acuíferos localizados en el noroeste de Colombia. Esta región se caracteriza por una alta complejidad topográfica, debido a que es cruzada por dos de las tres bifurcaciones de los Andes Colombianos. Se usaron isoscapes para caracterizar mayor la variabilidad espacial de la composición isotópica de las aguas lluvias y subterráneas. La variación del $\delta^{18}\mathrm{O}$ de las aguas subterráneas (GW) fue analizada respecto a la variación de la precipitación a través de la relación P/GW, cuando el resultado de esta relación es 1 indica recarga directa y valores menores a 1 indican recarga de flujos regionales, para los propósitos de esta investigación, de acuerdo con criterios estadísticos, los valores entre 0.98 y 1.02 son considerados como 1. Se encontró que la mayoría de los acuíferos libres se recargan directamente con agua de lluvia o luego de leves procesos de evaporación mientras que en acuíferos profundos y áreas urbanas ocurre a través de flujos regionales. La relación P/GW parece ser útil para identificar procesos de recarga en las regiones con mayores gradientes de elevación. En áreas bajas, la aplicabilidad de este método estaría restringida.

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1. Introduction

Environmental isotopes are a tool for the interpretation of hydrological processes related to the superficial and underground environments [1–3]. In the groundwater subsystem, environmental isotopes of the water molecule $(\delta^{18}\mathrm{O}$ and $\delta^{2}\mathrm{H})$ have been used for validating conceptual hydrogeological models, allowing the identification of recharge areas, transit and discharge zones. Additionally, they have been used to determine interactions with other water systems and for the establishment of the residence time of water in hydrogeological units [4, 5].

The variation in the isotopic composition of water is determined by fractionation processes [6], which take place in the meteoric environment and are closely associated with water state changes. This is how the stable isotopes of the water molecule become tracers in the underground environment, since their relationship remains constant during the time that the water is in the aquifer, independent of the mineralogical characteristics of the geological formations. The use of the water molecule isotopes $(^{1}\delta^{18}\mathrm{O}$ y $\delta^{2}\mathrm{H})$ allows the evaluation of different water routes in the hydrological cycle. Their use in hydrogeology is based on the fact that different isotopic compositions can be obtained according to the recharge environment. Many factors allow the interpretation of recharge processes, regional flow patterns and the distribution of hydrogeological units, including: i) the relation of isotopes between surface water and groundwater, ii) the similarity in the composition of water from precipitation and from the aquifer, and iii) the altitudinal relation and the similarity among waters from neighboring formations [6, 7].

Considering the water cycle, spatial and temporal variations that are present in a study area are related to the climate. This spatiotemporal variability can be analyzed with the representation of the isotopic composition through maps (isoscapes mapping), which allows us to understand the dynamics of precipitation and its relationship with groundwater from recharge. The isoscape models highlight the fractionation processes [8–11], and results obtained from isoscape maps can be used to answer research questions such as: What is the source of water vapor in the rain? Where is the recharge area from the aquifer? [12], What is the climate environment in a specific ecosystem? What is the migration route of a bird? [13]. This concept of "isoscapes" is a relatively recent term; it has been used to describe the mapping of large-scale spatial and temporal distributions of stable isotope relationships in rain, oceans, rocks, plants and animals [13]. For example, it has been recently used in ecology to identify migratory routes [13], in anthropology to identify migrations and interactions of past human societies [14–16], and to understand local, regional or global climatic and hydrological processes [7, 12, 17–19], such as the implications of seasonal infiltration, precipitation/evapotranspiration relationships, or the hydrology of the basin, including recharge processes [7, 9, 10].

In the tropics, isoscapes are a low-cost and effective tracer technique to understand precipitation dynamics and groundwater recharge mechanisms [9]. Using isoscapes, possible recharge areas can be determined with the arithmetic ratio between precipitation and groundwater (P/GW): if this ratio is less than 1 (because groundwater is more impoverished than local rainfall), it suggests that the recharge zones are located at higher elevations than where the measurement is taken; if the ratio is equal to 1, it means that the recharge water comes from local rain, registering a direct recharge; and if the ratio is greater than 1 (because groundwater is more enriched than local rainfall), it indicates that evaporation processes are present or that the recharge occurred in different climatic conditions [20]. However, this tool needs to be improved and adapted to regional and local scales, because of natural factors (such as topography) that interfere with the results, and invoke more sampling efforts to capture spatiotemporal variations, particularly in mountainous landscapes due to their inherent environmental complexity [9, 21].

Colombia covers an area of 1,143,000 km^{2} and approximately 75% of its territory presents favorable conditions for groundwater storage. However, less than 15% of the territory has been explored for establishing adequate water balances and conceptual hydrogeological models. Currently, 61 hydrogeological systems of interest have been identified, but only 16 of them have detailed studies [22]. The relationship between precipitation and groundwater flow has been studied in the country to understand their interaction with wetlands [23], and to identify regional flow systems. Hydrogeochemical analyzes have been used to validate hydrogeological models in regions such as Bajo Cauca and the Gulf of Morrosquillo [24]. In addition, isotopic techniques have been implemented in hydrodynamic studies [25–28] to identify flow lines in tunnels [29] and recharge zones [25, 30].

The northwestern area of Colombia presents highly complex climate systems, as it is situated in the Intertropical Convergence Zone (ITCZ), and there are patterns of ocean-mainland atmospheric circulation determined by thermal and pressure gradients. Additionally, the orographic variability of the Western and Central Mountain ranges determines special circulation systems characteristic of Valley-Mountain areas and microclimate conditions in inter-Andean areas [31]. The sum of these circumstances makes the territory of Antioquia a complex system, in which there are several fronts of atmospheric humidity [22, 32] combined with the orographic gradients and the isotopic fractionation effects that occur according to the distance to the sea [33].

The objective of this work is to identify possible aquifer recharge areas in northwestern Colombia (Antioquia), using information from stable isotopes $\left(^{18}\mathrm{O}\text{ and }^{2}\mathrm{H}\right)$ of rain and groundwater, through the construction of $\delta^{18}\mathrm{O}$ isoscapes. The spatial modeling of rain is based on the definition of altitudinal gradients; the spatial modeling of the isotopic composition of the groundwater is carried out by spatial interpolation, and the ratio between both allows the location of the possible recharge altitude.

2. Study area

Antioquia is located in northwestern Colombia and has an extension of $63,612Km^2$ (Figure 1). The area has a significant topographic and geomorphological complexity because it is crossed by two of the three mountain ranges of the Colombian Andes: The Western and Central Cordilleras. Two of the most important rivers in Colombia, the Cauca River and the Magdalena River, flow through them with average regional flows of $1,184m^3/s$ in the municipality of Tarazá for the former, and $2,361m^3/s$ in Puerto Berrío for the latter [22]. The climate is determined by the topography and weather phenomena such as the Chocó low-level jet and the ITCZ. These characteristics favour a great diversity of ecosystems that range from Coastal to Paramo ecosystems [30].

In Antioquia, there are metamorphic, igneous, and sedimentary rocks, whose ages have been assigned from the Proterozoic to the Recent [34]. The rocks of the Precambrian and Paleozoic ages were intruded by various plutonic bodies, from the Paleozoic to the Cretaceous. At that time (Cretaceous), there was a deposition of sediments and products of oceanic volcanism to the west of the Central Cordillera, along with the magmatic activity. These rocks were attached by tectonic effects to the continent in the Mesozoic. The Cauca River basin, Lower Cauca and the Urabá region are characterized by the presence of sedimentary rocks originated during the Tertiary period. The Cenozoic is marked by some magmatic intrusion events, especially to the west, and the development of intense volcanism in the western flank of the Central Cordillera. The erosive processes of the Quaternary allowed the formation of alluvial, lake, marine and slope deposits.

The study of the hydrogeological potential in Antioquia has been developed through cooperation programs between the University of Antioquia and Environmental Authorities. In four regions of the Antioquia department, the hydrogeological studies have included isotopic analysis: Bajo Cauca [24, 25], Western Antioquia [27], Valle de Aburrá [28] and Urabá Antioquia [31]. Table [1] presents some characteristics of interest of these regions for the purpose of this study.

The rocks present in the Bajo Cauca (Figure 2a) include an igneous and metamorphic basement, and rocks and sedimentary deposits from the Tertiary and Quaternary periods. The latter are those of greatest hydrogeological interest. The Cerrito Formation (Ngce) is composed of sediments from a shallow to the continental marine environment and is divided into three members: 1) Upper Member: formed by intercalations of sand and clay, with calcareous sandstone levels and some coal mantles, with thicknesses of up to 300 m; 2) Middle Member: it has layers of silt and clay and some layers of calcareous sand, with thicknesses of up to 850 m; 3) Lower Member, made up of sandstones, conglomerates and limestone, with a thickness of 400 m. The most important alluvial deposits (Qal) are associated with the floodplains of the Cauca, Nechí and Man rivers, and the terraces (Qt) are associated with the Cauca River (6 in total), and the Nechí and Man rivers (3 levels in each). Three main hydrogeological units were defined for Bajo Cauca: a phreatic aquifer over Recent Sedimentary deposits and Upper Member of the Cerrito Formation; an aquitard over the Middle Member of the Cerrito Formation and a confined aquifer related to the Lower Member of the same geological formation [25, 27].

The region named Occidente de Antioquia (Figure 2b) is geologically located in the intramontane depression of the Western and Central Mountain ranges of the Colombian Andes, along with the Cauca - Romeral faults system. The Western Cordillera is mainly composed of oceanic rocks accreted from the western margin of South America during the Mesozoic and early Cenozoic, later affected by intrusions from the Tertiary. The Cordillera Central is composed of a basement that includes oceanic and continental rocks, intruded by several Mesozoic and Cenozoic plutons. The geological framework closes with the Tertiary units, corresponding to the Amagá Formation (Pgai: Miembro Inferior, Pgam: Miembro Medio and Ngas: Miembro Superior) and the Combia Formation (Ngc). In this environment, alluvial (Qal) and slope deposits (Q2v) have been deposited during the Quaternary. A phreatic aquifer related to the alluvial deposits of the Cauca River and its tributaries have been identified.

The geological environment of the Valle de Aburrá (Figure 2c) is formed by rocks from the Paleozoic, intrusive of different ages and recent sediments. A more detailed description was made within the seismic microzoning project [34]. In the Valle de Aburrá, there are 3 hydrogeological units: the phreatic aquifer, the semi-confined aquifer -both of them laying over Quaternary sedimentary deposits (Qal)-, and the Dunita de Medellín (Kium) aquifer, associated with rocks with

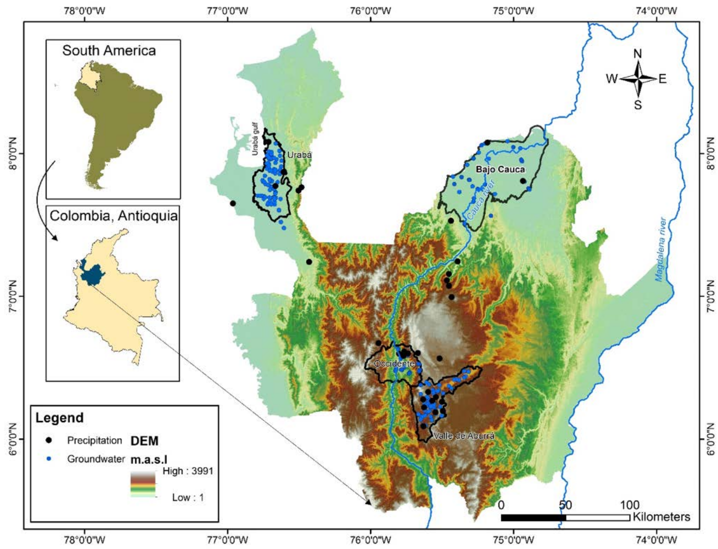

Figure 1 Location of the study area

Table 1 Characteristics of the study area

Region and aquifers	Area	Altitude range (m.a.s.l) temperature (°C)	Average annual multi-year precipitation (mm)	multi-year	Annual cycle
Bajo Cauca: An unconfined aquifer and a confined aquifer.	3,273	30 to 1,400	28	2,800	A dry period between December and March and a wet period between April and November
Valle de Aburrá: An unconfined aquifer.	1,152	1,500 to 3,100	16-29	1,500	A dry period between December and March and a wet period between April and November
Golfo de Urabá: An unconfined aquifer and a multilayer. confined aquifer	1,206	0 to 1,729	28	2,100	A dry period from December to March and a humid period from April to November
Occidente: An unconfined aquifer.		600 to 2,800	28	850 to 2,200	A drier period from December to March

secondary porosity [26, 35].

Urabá (Figure 2d) is a flat region, located in the coastal area. In this region, there are Neogene sedimentary rocks–on an older basement–, including the Pavo Formation (Ngpv), the Arenas Monas Formation (Ngam) and the Corpa Formation (Ngco), and alluvial (Qal), fluvio-lacustrine (Q2fl), fluviomarine and marine deposits of the Quaternary. The aquifer units are associated with the Corpa Formation and alluvial deposits. The Corpa Formation (Ngco) was divided by INGEOMINAS into three subunits, informally designated as T2A, T2B and T2C. T2A is made up of fine to medium-grain sandstones, with a thickness that reaches 165 m. The T2B subunit has layers of sandstone and conglomerate and reaches a thickness of 210 meters. T2C is made up of mudstones, interspersed with discontinuous layers of conglomerates, with a thickness of 115 meters. The Quaternary in the study region is formed by alluvial terraces related to the Chigorodó, Carepa, Apartadó, Grande, and Currulao rivers, by the plain floods of El Tres and Turbo rivers, and by the Mutatá-Turbo alluvial plain. The hydrogeological system of the study area comprises an unconfined aquifer and a confined multilayer system consisting of an alternating series of permeable, semipermeable, and impermeable layers [36].

3. Data source and methodology

Data used for this study were obtained from previous studies conducted in the four described areas, including the analysis of new samples collected between March and September, 2017. For rainwater, 678 samples were collected in 32 control stations, and 390 samples were collected for groundwater. All data are included in the supplementary material, and Table 2 summarizes the data used for this research.

All the records of $\left(\delta^{18}\mathrm{O}\right.$ and $\left.\delta^{2}\mathrm{H}\right)$ were subjected to quality tests, and all the records with excess deuterium below 6 were discarded because they were considered

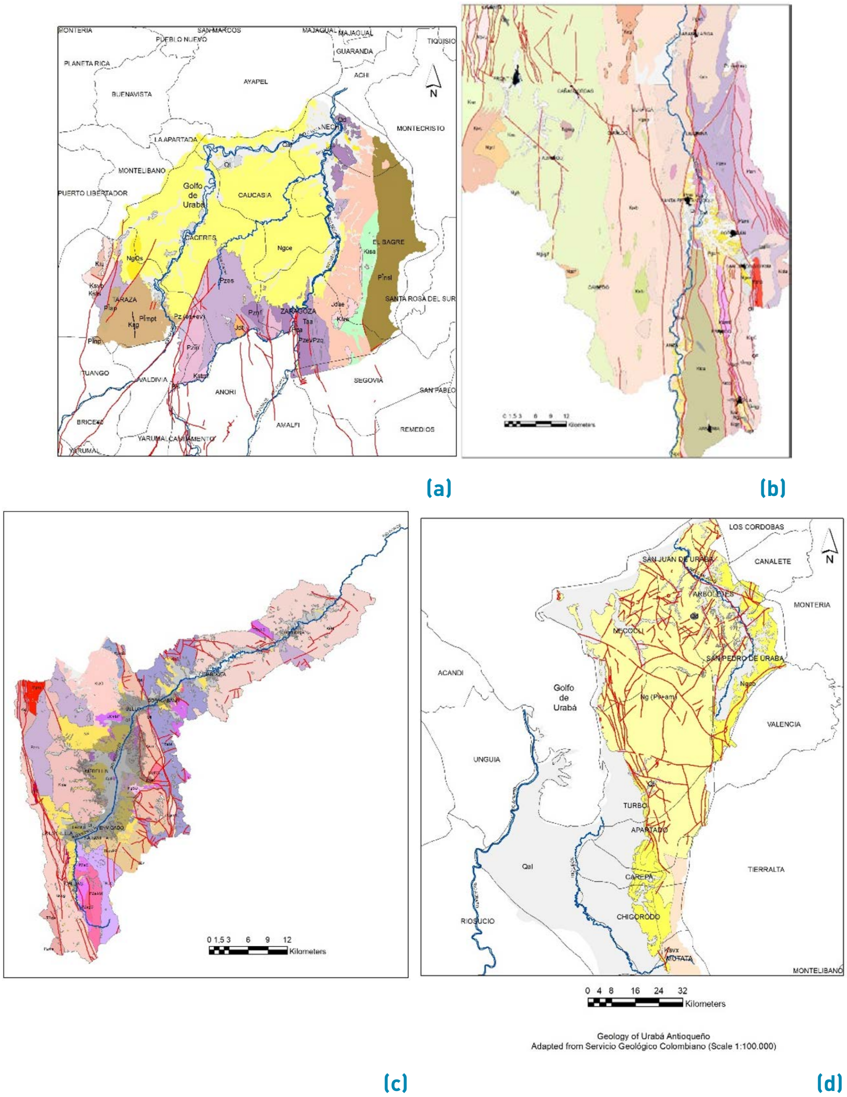

Figure 2 Geology of the study area. (a) Geology of Bajo Cauca, (b) Geology of Occidente, (c) Geology of Valle de Aburrá, and (d) Geology of Urabá.

incorrect, or that the samples could have been subjected to evaporation processes.

The evaluation of the existing isotopic relationship between precipitation and groundwater was carried out for each hydrogeological system. In addition, a precipitation isoscape was obtained for Antioquia by integrating the information on a regional scale.

For each considered area, weighted calculations were made with the amount of rainfall in each sample based on the isotopic composition data; then, the corresponding local meteoric lines were obtained. In the same way, all the data was taken to estimate a Regional Meteoric Line called the Meteoric Line of Antioquia.

In Bajo Cauca, Occidente de Antioquia, and Valle de Aburrá, the construction of the precipitation isoscapes was achieved from the linear relationship found between the rain height and the isotopic composition (altitudinal effect). These isoscapes were developed based on a digital elevation model with a cell size of 12.5 * 12.5 meters, obtained from the ALOS PALSAR satellite. Due to the physiographic conditions of the Urabá region (heights between 0 and 100 m.a.s.l), there is not an altitudinal effect. In this case, the spatial variability of $\delta^{18}\mathrm{O}$ was achieved through the Inverse Distance Weighting -IDW- interpolation method, using a cell size of 12.5 * 12.5 meters.

The results of the 32 stations located in the four study zones were compiled to find an altitudinal gradient for the Department of Antioquia, which allowed to obtain not only a local spatial representation of the spatial variation

Table 2 Description of available data

Study area	Type	Quantity	Monitoring period
Bajo Cauca	Rainwater	8 stations (98 samples)	Jul-2005 to Jun-2006
	Groundwater	55 samples in 32 stations	Mar-2005, Nov-2005 and Mar-2005
Occidente de Antioquia	Rainwater	7 stations (77 samples)	Jul 2005 to May 2005
Antioquia	Groundwater	31 samples in 31 stations	Jun 2006 and Oct 2006
Urabá	Rainwater	8 stations (355 samples)	Mar 2008 to Dec 2016 (1 station) May 2011 to May 2012 (2 stations) May 2011 to Dec 2016 (1 station) Feb 2013 to Dec 2016 (2 stations) Jan 2011 to Dec 2012 (1 station) Jan 2011 to Dec 2016 (1 station)
	Groundwater	124 samples in 84 stations	2008-2016
Valle de Aburrá	Rainwater	9 stations (148 samples)	Mar 2011 to Aug 2013 (5 stations) Mar 2017 to Aug 2017 (4 stations)
	Groundwater	180 samples	October 2011, January 2012, August 2013.

of $\delta^{18}\mathrm{O}$, but also a regional representation based on the above-described digital elevation model.

To obtain groundwater isoscapes of the four aquifer systems, several interpolation methods were evaluated to identify the best representation. To obtain the first approximation to the determination of recharge areas, the arithmetic ratio between the isotopic nature of precipitation (P) and the isotopic nature of groundwater (GW) (P / GW) was estimated [9]. For this ratio, values higher than one indicate that the isotopic composition of groundwater is more enriched than the amount-weighted isotopic composition of precipitation. This suggests three possible situations: i) that rainwater has been evaporated before entering the aquifer, ii) that the recharge took place under weather conditions different from those of the rainwater monitoring date, or iii) that groundwater is the result of mixing rainwater and surface water. If the ratio is one, it follows that the isotopic composition of groundwater matches the amount-weighted isotopic composition of rainwater, which is an indicator of direct recharge. Finally, values lower than one indicate that the isotopic composition of groundwater is more depleted than the isotopic composition of rainfall; in this case, groundwater would be considered from regional fluxes. For the purposes of this research, values between 0.98 and 1.02 are considered as 1. This interval was obtained from statistical and sensitivity analyses of the precipitation isoscapes of Antioquia, considering mean values, extreme values, standard deviation, and elevation gradient.

4. Results

From previous studies [24, 26–29] and supplementing with new information, the following local meteoric lines for the study regions were obtained: Bajo Cauca: $\delta^2\mathrm{H} = 8.05\delta^{18}\mathrm{O} + 11.7$; Occidente de Antioquia: $\delta^2\mathrm{H} = 8.01\delta^{18}\mathrm{O} + 9.5$; Valle de Aburrá: $\delta^2\mathrm{H} = 8.23\delta^{18}\mathrm{O} + 12.2$; and Urabá: $\delta^2\mathrm{H} = 8.03\delta^{18}\mathrm{O} + 10.3$ The regional meteoric line of Antioquia corresponds to the expression $\delta^2\mathrm{H} = 8.09\delta^{18}\mathrm{O} + 10.9$. In all cases, meteoric lines had a correlation coefficient R^2 equal to 0.99. The slope of these lines corresponds to the Global Meteoric Water Line. The intercept shows slight variations, with the most significant occurring in the Valle de Aburrá, the region with the highest climatic variability [23, 26].

4.1 Isoscapes

Precipitation isoscapes

The analysis of variation in the isotopic composition of rainwater in each of the study areas allowed the identification of a marked orographic effect [29] in the regions of Bajo Cauca, Occidente de Antioquia and Valle de Aburrá. For this reason, the spatial representation of $\delta^{18}\mathrm{O} = -0.002\,\mathrm{h}$ variability in rainwater in these three regions was carried out by means of the equations found for the elevation gradient (Table 3).

To produce the precipitation isoscape for the Bajo Cauca region (Figure 3a), the equation $\delta^{18}\mathrm{O} = -0.002\,\mathrm{h} - 7.6211$ was used with a correlation coefficient of $R^2 = 0.94$ [23]. This gradient indicates a variation of the isotopic composition of rainwater of -0.2‰ per 100 meters. The variation rate for this precipitation isoscape ranges from -8.48‰ for the highest elevations in the southern area, to -7.60‰ for the lowest elevations in the northern area, resulting in a total variation of $\delta^{18}\mathrm{O}$ in rainwater of 0.88‰.

For Occidente de Antioquia (Figure 3b), the elevation gradient is $\delta^{18}\mathrm{O} = -0.0006\,\mathrm{h} - 7.621$, with a correlation coefficient $R^2 = 0.80$. This gradient indicates a variation rate of $\delta^{18}\mathrm{O}$ in rainwater of -0.06 per 100 meters. The variation for this precipitation isoscape ranges from

Table 3 Characteristics of δ18O on precipitation

Study area	Gradient Line*/meteoric line	R^2	isotopic gradient (‰ per 100 meters)	variation rate for precipitation isoscape (‰)
Bajo Cauca	$\delta^{18}\mathrm{O} = -0.002\,\mathrm{h} - 7.6211^{*}$	0.94	-0.2	-7.60 to -8.48
Occidente de Antioquia	$\delta^{18}\mathrm{O} = -0.0006\,\mathrm{h} - 7.621^{*}$	0.80	-0.06	-10.69 to -12.69
Valle de Aburrá	$\delta^{18}\mathrm{O} = -0,0014\,\mathrm{h} - 8.887^{*}$	0.75	-0.14	-9.94 to -12.18
Urabá	$\delta^{2}\mathrm{H} = 8.03\delta^{18}\mathrm{O} + 10.3$	0.96	Not Determined	-7.57 to -6.14
Regional for Antioquia	$\delta^{2}\mathrm{H} = 8.09\delta^{18}\mathrm{O} + 10.9$	0,99	-0.17	-14.67 to -7.89

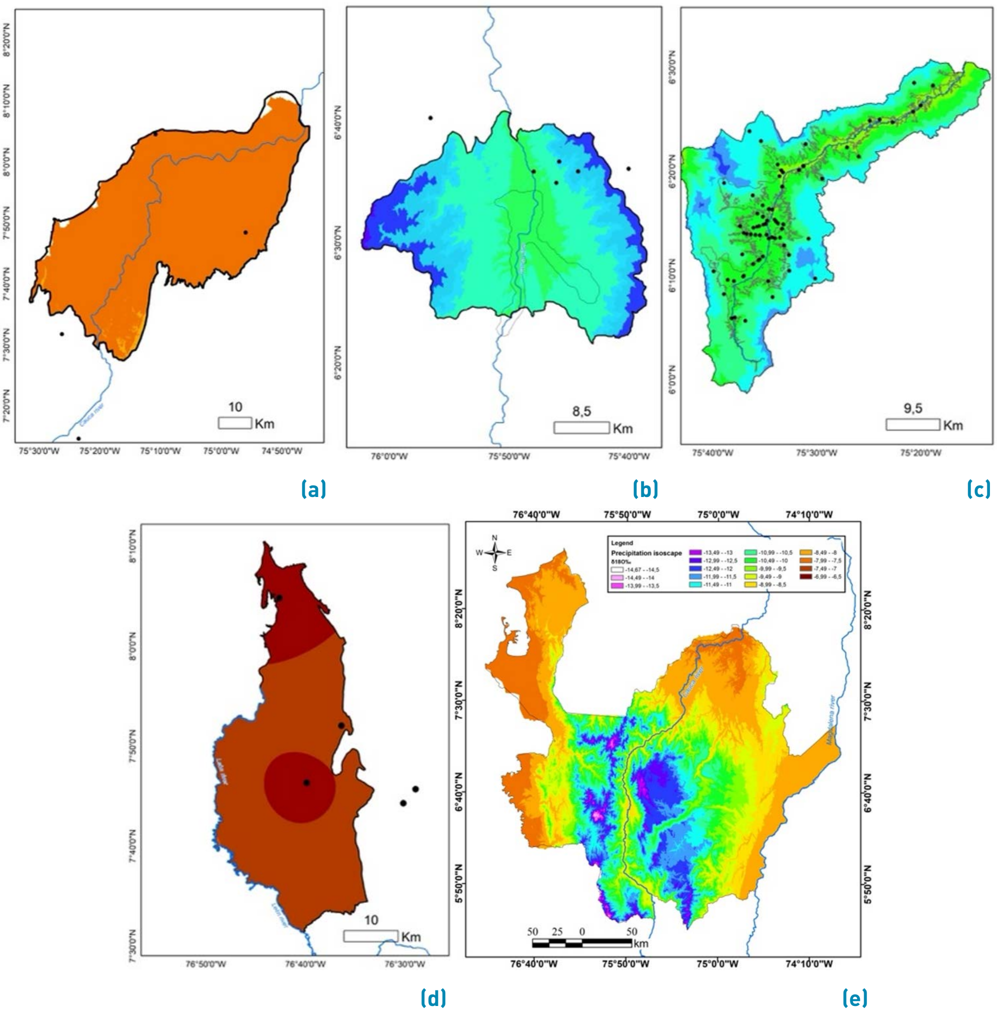

Figure 3 Precipitation Isoscapes: (A) Bajo Cauca, (B) Occidente de Antioquia, (C) Valle de Aburrá, (D) Urabá, and (E) Antioquia.

-12.69‰ for the highest elevations to -10.69‰ for the lowest elevations, for a total variation of 2‰.

Figure 3c represents the precipitation isoscape for Valle de Aburrá. In this case, the expression $\delta^{18}\mathrm{O} = -0,0014\,\mathrm{h} - 8.887$ describes the elevation gradient, with a correlation coefficient $R^2 = 0.75$. This ratio indicates a depletion rate of $\delta^{18}\mathrm{O}$ in rainwater of -0.14‰ per 100 meters. The variation in this precipitation isoscape ranges from -12.18 for the highest elevations to -9.94‰ for the lowest elevations, for a total variation of the isotopic composition of rainwater ($\delta^{18}\mathrm{O}$) of 2.24‰.

The gradients found for these three regions fall within the typical values for mountainous zones [37, 38]. In the Urabá region, variations obtained by applying an IDW spatial modeling algorithm range from -7.57‰ to -6.14‰, for a total variation of $\delta^{18}\mathrm{O}$ in rainwater of 1.43‰ (Figure 3d).

By aggregating all the information on $\delta^{18}\mathrm{O}$ in precipitation, a regional orographic effect was identified according to the equation $\delta^{18}\mathrm{O} = -0.0017\,\mathrm{h} - 7.889$, with correlation coefficient R^2 = 0,81. Based on this equation, the creation of the precipitation isoscapes of Antioquia was possible (Figure 3e). Variations of δ^{18}O in these precipitation isoscapes range from -14.67‰ on the highest areas to -7.89‰ on the lowest areas, at sea level.

Groundwater isoscapes

For each identified aquifer, isoscapes allow obtaining a representation of the spatial variability of the isotopic content in groundwater. (Table 4).

In the Bajo Cauca region, δ^{18}O isoscapes were modeled for the shallow and deep levels of the system. For the shallow level of the Bajo Cauca aquifer, there is a total variation of δ^{18}O of 2.87‰ (Figure 4a), with values ranging from -9.01‰ to -6.14‰. Regarding the spatial distribution of δ^{18}O in the deep level of the Bajo Cauca aquifer (Figure 4b), the values range from -10.09‰ to -7.22‰, for a total variation of 2.87‰. However, it is important to note that there is a great predominance of δ^{18}O in the range from -8.29‰ to -7.94‰.

For the aquifer in Occidente de Antioquia (Figure 4c), the ^{18}O variation is relatively low: the most enriched value is -9.74‰, and the most depleted value is -10.81‰, for a total variation of 1.07‰. The most depleted values of δ^{18}O occur in the Valle de Aburrá aquifer, with values of -11.90‰ (Figure 4d). This is also the region with the highest variations of δ^{18}O, with records ranging from -11.90‰ to -8.66‰ for a total variation of 3.24‰.

The most enriched data of δ^{18}O is present in the superficial level of the Urabá aquifer, with values ranging from -6.69‰ to -4.70‰ (Figure 4e). For the deep level of the Urabá aquifer (Figure 5f), the existence of a depletion of the value of the isotopic deviation in the west-east direction is detected, with δ^{18}O variations ranging from -6.14‰ to -8.65‰.

4.2 P/GW ratio

The P/GW ratio was used to identify the recharge zones of the four aquifer systems. Initially, the results corresponding to the recharge of the phreatic aquifers are described. For the Bajo Cauca aquifer, the ratio is shown in Figure 5a, obtained from the ratio between P (Figure 3a) and GW (Figure 4a). For the aquifer in Occidente, the ratio is given in Figure 5d, with the results from P (Figure 3b) and GW (Figure 4c). For the shallow level of the Valle de Aburrá aquifer, the P/GW ratio is shown in Figure 5d, obtained from the precipitation isoscape (Figure 3c) and groundwater (Figure 4d). The ratio for Urabá is presented in Figure 5e, where P comes from Figure 3d and GW from Figure 4e.

According to these results, it is observed that for the Bajo Cauca, Occidente de Antioquia, and Urabá regions, the P/GW ratio generally indicates that the isotopic composition of groundwater is slightly more enriched than the isotopic composition of rainwater, thus indicating that the recharge of these levels occurs directly, with minor processes of evaporation. On the other hand, for the shallow level of the Valle de Aburrá aquifer, the P/GW ratio indicates that recharge comes mostly from regional fluxes, because values P/GW are lower than 1.0 in most parts of the aquifer. However, it is also important to highlight that, to a lesser extent, the ratio indicates that direct recharge is prevailing for the southern area of the aquifer.

For the confined aquifers of Bajo Cauca and Urabá, the P/GW ratio permits the following inferences in terms of recharge: in the Bajo Cauca region, the P/GW ratio (Figure 5b) indicates a recharge from regional fluxes, as the results give values lower than one for most of the region. Likewise, for the deep level of the Urabá aquifer, the P/GW ratio (Figure 5e) indicates that the isotopic composition of groundwater is more depleted than the isotopic composition of rainwater, which means, in principle, that recharge at this level occurs through regional fluxes or form other climate conditions [31, 33], different from the actual climate.

5. Discussion

In all cases, local meteoric lines obtained from the available data depict a slope equal to that of the Global Meteoric Water Line (GMWL). Regarding the intercept, substantial variation is reported from the above-mentioned GMWL for the Valle de Aburrá and Bajo Cauca regions (12.2 and 11.7‰, respectively). 22.4% of rainwater samples from Valle de Aburrá and 25.51% from Bajo Cauca show an excess of deuterium higher than 13‰. This condition possibly reveals the existence of more rain as an effect of recycling [37], something that would explain the condition of these local meteoric lines.

Isotopic gradients associated with an elevation variation in the northern and central parts of Antioquia fall within the typical values for mountainous regions [37, 39]. The western region presents a different pattern, with a difference of at least 0.08‰ as compared to the central and northern regions. This region is governed by a marked climatic contrast that shows variations in temperature (between 28 and 12 °C) and precipitation (between 600 and 2600 mm / year) from the bottom of the valley of the Cauca River to the highest elevations of the western mountain range. However, this is not enough to explain this anomalous behavior in the spatial variability of the isotopic brand. Additional information is needed to understand this case, as we only have data for 11 months.

Table 4 δ^{18}O variability in groundwater

Aquifer	Range of δ^{18}O	variation of δ^{18}O
Unconfined Bajo Cauca	-9.01‰ to -6.14‰	2.87‰
Confined Bajo Cauca	-10.09‰ to -7.22‰ (-8.29‰ to -7.94‰),	2.87‰ (0.35)
Occidente	-9.74‰ to -10.81‰	1.07‰
Valle de Aburrá	-11.90‰ to -8.66‰	3.24‰
Unconfined of Urabá	-6.69‰ to -4.70‰	1.99
Multilayer confined of Urabá	-8.65‰ to -6.14‰	5.51

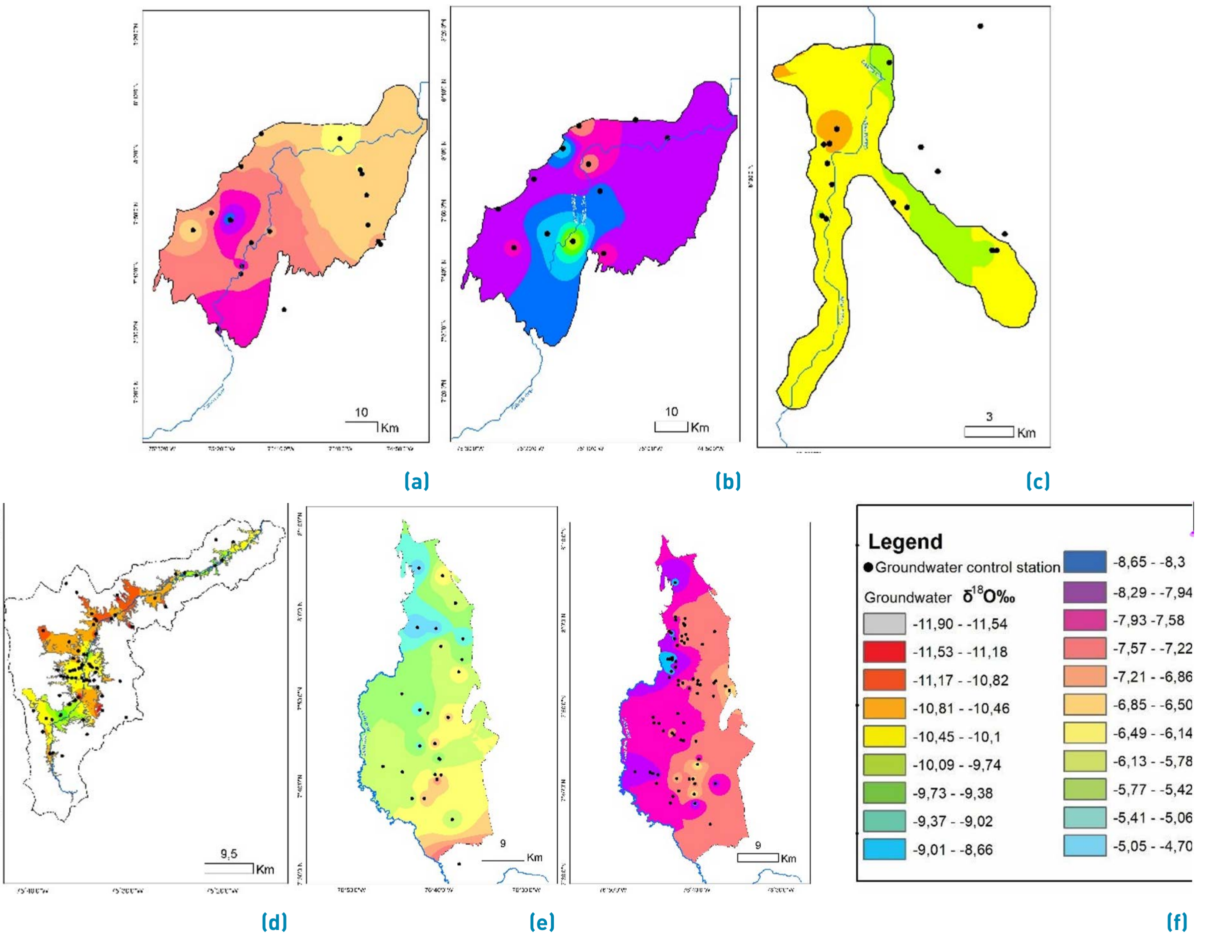

Figure 4 Groundwater Isoscapes: (a) Bajo Cauca shallow level, (b) Bajo Cauca deep level (c) Western Antioquia, (d) Valle de Aburrá, (e) Urabá shallow level, (f) Urabá deep level.

The behavior of the spatial distribution of the δ^{18}O isotopic ratio for the regions under consideration is coherent with their geographic and climatic conditions. Precipitation isoscapes for each area present values more enriched for the Urabá region (-6.14 to -8.40‰ o δ^{18}O) in the flat coastal area (minor elevation differences close to the sea). The Bajo Cauca region reflects the transition from a coastal environment to a continental one, with influence from orographic patterns that can reach elevations of up to 2,400 m.a.s.l.. The isotopic composition of the Valle de Aburrá (-9.94 to -12.80‰ δ^{18}O) and Occidente de Antioquia (10.69 to -12.69‰) presents the most depleted values, possibly as a result of the humidity, pressure and temperature conditions of inter-Andean valleys [38–40].

The isoscape of isotopic variation of Antioquia, with a gradient of -0.17‰ δ^{18}O, spatially reproduces the regional orographic effect, resulting in a variation range of -7.89 to -14.67‰ δ^{18}O. The difference between this regional model and local models shows that the characteristics measured in the Urabá region do not fall within the ranges defined by the elevation effect. A similar

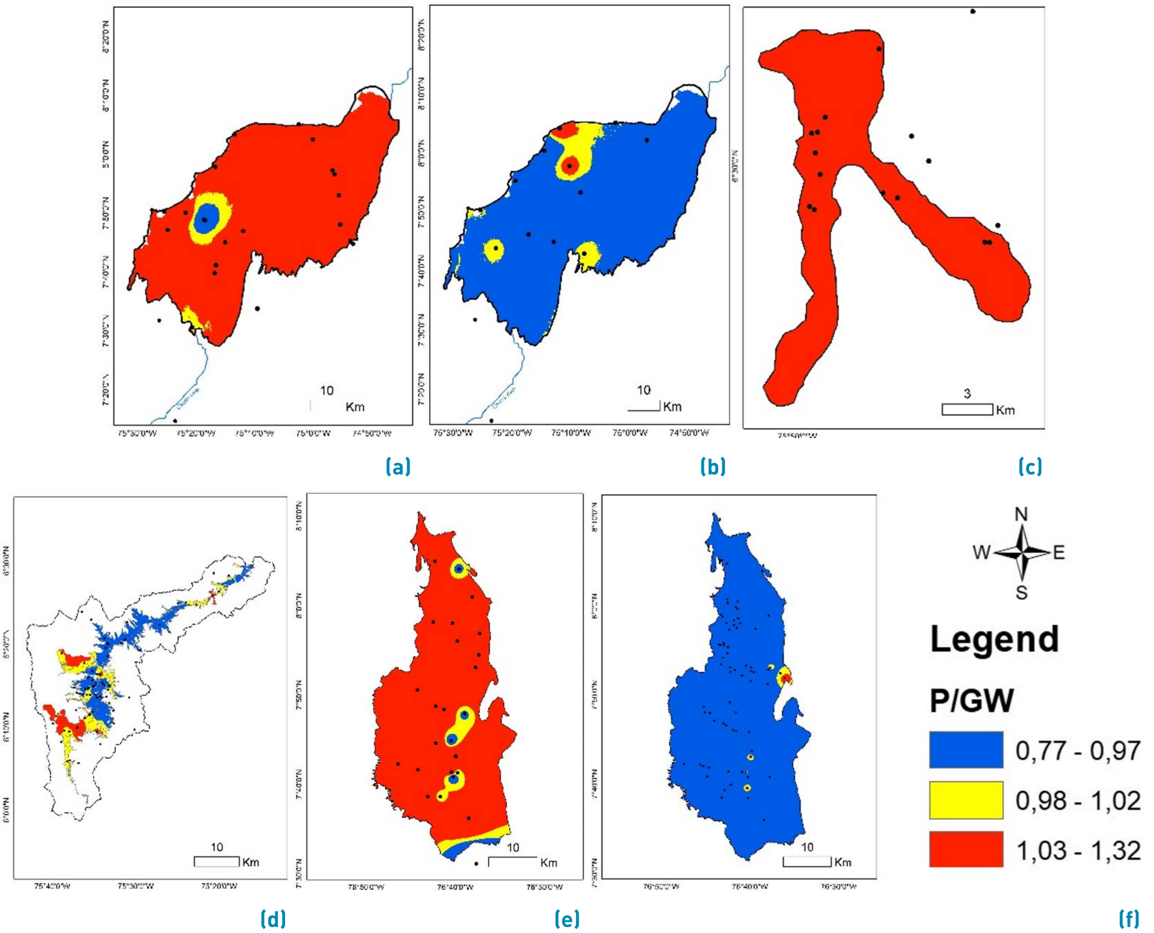

Figure 5 P/GW ratio and a first approximation to the hydrogeological flow routes in some aquifer systems of Antioquia: (a) Bajo Cauca shallow level, (b) Bajo Cauca deep level (c) Western Antioquia, (d) Valle de Aburrá, (e) Urabá shallow level, (f) Urabá deep level.

situation is found for the plains of the foothills of the Bajo Cauca region. This suggests that geospatial modeling with isoscapes could be limited in low-lying areas [41].

The P/GW ratio allowed us to identify areas of recharge in the aquifers of Antioquia: i) direct recharge occurs in the phreatic aquifers of Bajo Cauca, Occidente de Antioquia and the Gulf of Urabá, and ii) the recharge to the confined aquifers of Bajo Cauca and Uraba occurs from rains at higher altitudes.

The δ^{18}O isotopic composition of the groundwater in Bajo Cauca Antioqueño and in the Uraba region reveals, in both cases, a more depleted composition in confined aquifers. According to those, different sources of water recharge to the unconfined and confined aquifers can be inferred. Figure 6 shows the more depleted value of δ^{18}O in the groundwater of the Bajo Cauca confined aquifer (-10,1 ‰ δ^{18}O) and Gulf of Urabá (-9,1 ‰ δ^{18}O). These values correspond with rain occurring at locations 950 meters and 500 meters above. The above-mentioned P/GW ratio, grounded both in local and regional spatial models, clearly shows that in inter-Andean conditions, the occurrence of lateral contributions of groundwater would correspond to what is called regional fluxes [27].

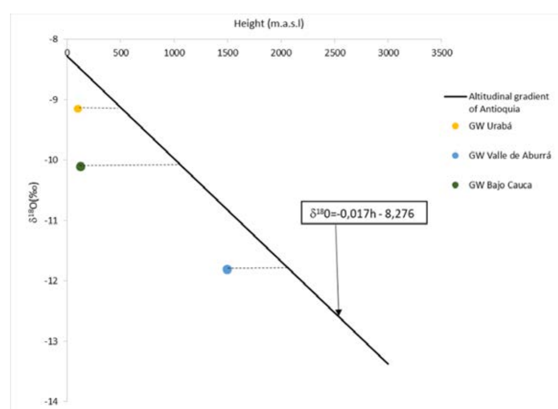

Figure 6 More deflected groundwater values of δ^{18}O vs height and gradient water line

For the specific case of the Valle de Aburrá region (-11,8

‰ δ^{18}O), the result indicating recharge areas associated with precipitation at higher altitudes (2.100 m.a.s.l) is especially significant, as the direct recharge zone is not permeable by the effects of development and urban expansion.

Even though the validity of the precipitation distribution map is limited due to the lack of data uniformly distributed across the territory, this first exercise of comparing rainwater and groundwater isoscapes is a general indicator of the behavior of direct recharge and the existence of regional fluxes, that are the basis for the sustainability of groundwater levels and reservoirs. The importance of expanding the regional monitoring network is evident.

6. Conclusion

Taking into account the altitude gradients to δ^{18}O (local and regional for Antioquia) in the isotopic behavior of the rain, maps of isoscapes were obtained to be compared with the isotopic characteristics of groundwater. Groundwater isoscape maps were obtained by spatial interpolation, using the Inverse Distance Square method. By aggregating all the information on δ^{18}O in precipitation, a regional orographic effect was identified according to the equation $\delta^{18}\mathrm{O} = -0.0017\,\mathrm{h} - 7.889$. Variations of δ^{18}O in these precipitation isoscapes range from -14.67‰ in the highest areas and to -7.89‰ in the lowest areas, at sea level.

The P / GW ratio allowed us to identify sources of direct recharge and regional flows in the aquifers in Antioquia: i) direct recharge occurs in the phreatic aquifers of El Bajo Cauca, Western Antioquia, and the Gulf of Urabá, and ii) the recharge to the confined aquifers of Bajo Cauca and Urabá occurs from rains at higher altitudes.

Regarding the Valle de Aburrá aquifer, the comparison between groundwater and its elevation gradient suggests that local direct recharge should be taking place. However, the isotopic composition of groundwater is more depleted than the isotopic composition of rainwater, which indicates that recharge comes mostly from regional fluxes, associated twith rain above 1,500 m.a.s.l. and up to 2,200 m.a.s.l.. For the Valle de Aburrá, the direct recharge zone is waterproofed by urban expansion.

7. Declaration of competing interest

We declare that we have no significant competing interests including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.

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10. Author contributions

Juliana Ossa Valencia: monitoring and data collection, compile isotopic information, data analysis, information synthesis, elaboration of maps and figures, writing, discussion of results.
Teresita Betancur Vargas: monitoring and data collection, secondary information review, selection of study area, data analysis, information synthesis, writing, discussion of results.
Ana Karina Campillo Pérez: monitoring and data collection, data analysis, information synthesis, writing, discussion of results.

11. Data availability statement

The data used for this study was obtained from previous studies conducted in the four described areas and includes the analysis of new samples collected between March and September of 2017. f

References

[1] P. Négrel, E. Petelet-Giraud, and R. Millot, "Tracing water cycle in regulated basin using stable δ^{18}o–δ^{2}h isotopes: The ebro river basin (spain)," *Chemical Geology*, vol. 422, Mar. 2016. [Online]. Available: https://doi.org/10.1016/j.chemgeo.2015.12.009

[2] P. Ala-aho, C. Soulsby, O. S. Pokrovsky, S. N. Kirpotin, J. Karlsson, and *et al.*, "Using stable isotopes to assess surface water source dynamics and hydrological connectivity in a high-latitude wetland and permafrost influenced landscape," *Journal of Hydrology*, vol. 556, Jan. 2018. [Online]. Available: https://doi.org/10.1016/j.jhydrol.2017.11.024

[3] S. He and K. Richards, "Stable isotopes in monsoon precipitation and water vapour in nagqu, tibet, and their implications for monsoon moisture," *Journal of Hydrology*, vol. 540, Sep. 2016. [Online]. Available: https://doi.org/10.1016/j.jhydrol.2016.06.046

[4] M. Kumar, A. L. Ramanathan, S. Ranjan, V. Bahadur-singh, N. Kumar, and *et al.*, "Groundwater evolution and its utility in upper ganges-yamuna alluvial plain of northern india, india: Evidence from solute chemistry and stable isotopes," *Groundwater*

for Sustainable Development, vol. 7, Sep. 2018. [Online]. Available: https://doi.org/10.1016/j.gsd.2018.07.001

[5] S. Prada, J. Virgilio-Cruz, and C. Figueira, "Using stable isotopes to characterize groundwater recharge sources in the volcanic island of madeira, portugal," *Journal of Hydrology*, vol. 536, May. 2016. [Online]. Available: https://doi.org/10.1016/j.jhydrol.2016.03.009

[6] I. D. Clark and P. Fritz, *Environmental Isotopes in Hydrogeology*, 1st ed. Boca Ratón, NY: CRC Press, 1997.

[7] A. G. West, E. C. February, and G. J. Bowen, "Spatial analysis of hydrogen and oxygen stable isotopes ("isoscapes") in ground water and tap water across south africa," *Journal of Geochemical Exploration*, vol. 145, Oct. 2014. [Online]. Available: https://doi.org/10.1016/j.gexplo.2014.06.009

[8] T. Keesari, D. A. Sharma, M. S. Rishi, D. Pant, H. V. Mohokar, and *et al.*, "Isotope investigation on groundwater recharge and dynamics in shallow and deep alluvial aquifers of southwest punjab," *Applied Radiation and Isotopes*, vol. 129, Nov. 2017. [Online]. Available: https://doi.org/10.1016/j.apradiso.2017.07.022

[9] R. Sánchez-Murillo and C. Birkel, "Groundwater recharge mechanisms inferred from isoscapes in a complex tropical mountainous region," *Geophysical Research Letters*, vol. 43, no. 10, May. 11, 2016. [Online]. Available: https://doi.org/10.1002/2016GL068888

[10] G. J. Bowen and J. B. West and J. Hoogewerff, "Isoscapes: Isotope mapping and its applications," *Journal of Geochemical Exploration*, vol. 102, no. 3, 2009. [Online]. Available: https://doi.org/10.1016/j.gexplo.2009.05.001

[11] G. J. Bowen, "Isoscapes: Spatial pattern in isotopic biogeochemistry," *Annual Review of Earth and Planetary Sciences*, vol. 38, May. 30, 2010. [Online]. Available: https://doi.org/10.1146/annurev-earth-040809-152429

[12] L. I. Wassenaar, S. L. Van-Wilgenburg, K. Larson, and K. A. Hobson, "A groundwater isoscape (δd, δ^{18}o) for mexico," *Journal of Geochemical Exploration*, vol. 102, no. 3, Jan. 24, 2009. [Online]. Available: https://doi.org/10.1016/j.gexplo.2009.01.001

[13] H. B. Vander-Zanden, D. M. Nelson, M. B. Wunder, and T. J. Conkling, "A groundwater isoscape (δd, δ^{18}o) for mexico," *Biological Conservation*, vol. 228, Dec. 2018. [Online]. Available: https://doi.org/10.1016/j.biocon.2018.10.019

[14] K. M. Hedman, P. A. Slater, M. A. Fort, T. E. Emerson, and J. M. Lambert, "Expanding the strontium isoscape for the american midcontinent: Identifying potential places of origin for cahokian and pre-columbian migrants," *Journal of Archaeological Science: Reports*, vol. 22, Dec. 2018. [Online]. Available: https://doi.org/10.1016/j.jasrep.2018.09.027

[15] L. M. Kootker, R. J. V. Lanen, H. Kars, and G. R. Davies, "Strontium isoscapes in the netherlands. spatial variations in ^{87}sr/^{86}sr as a proxy for palaeomobility," *Journal of Archaeological Science: Reports*, vol. 6, Apr. 2016. [Online]. Available: https://doi.org/10.1016/j.jasrep.2016.01.015

[16] H. Wlhelmson and T. D. Price, "Migration and integration on the baltic island of Öland in the iron age," *Science: Reports*, vol. 12, Apr. 2017. [Online]. Available: https://doi.org/10.1016/j.jasrep.2017.01.031

[17] C. Birkel, R. Helliwell, B. Thornton, S. Gibbs, P. Cooper, and *et al.*, "Characterization of surface water isotope spatial patterns of scotland," *Journal of Geochemical Exploration*, vol. 194, Nov. 2018. [Online]. Available: https://doi.org/10.1016/j.gexplo.2018.07.011

[18] S. E. Hollins, C. E. Hughes, J. Crawford, D. I. Cendón, and K. T. Meredith, "Rainfall isotope variations over the australian continent – implications for hydrology and isoscape applications," *Science of The Total Environment*, vol. 645, Dec. 2018. [Online]. Available: https://doi.org/10.1016/j.scitotenv.2018.07.082

[19] V. Raidla, Z. Kern, J. Parn, A. Babre, K. Erg, and *et al.*, "A δ^{18}o isoscape for the shallow groundwater in the baltic artesian basin," *Journal of Hydrology*, vol. 542, Nov. 2016. [Online]. Available: https://doi.org/10.1016/j.jhydrol.2016.09.004

[20] J. Ossa, A. K. Campillo, C. Omar, and T. Betancur, "Representación espacial de zonas de recarga del agua subterránea a partir de mapas isotópicos de precipitación. caso de estudio: Valle de aburrá, colombia," *Boletín Geológio y Minero*, vol. 132, no. 1-2, 2021. [Online]. Available: https://doi.org/10.21701/bolgeomin.132.1-2.007

[21] G. J. Bowen and S. P. Good, "Incorporating water isoscapes in hydrological and water resource investigations," *Wiley Interdisciplinary Reviews*, vol. 2, no. 2, Feb. 16, 2015. [Online]. Available: https://doi.org/10.1002/wat2.1069

[22] IDEAM. (2014) Estudio nacional del agua. [Online]. Available: http://www.ideam.gov.co/web/agua/estudio-nacional-del-agua/-/document_library_display/hWSQik0LFPrw/view/125687715

[23] T. Betancur-Vargas, D. A. García-Giraldo, A. J. Vélez-Duque, A. M. Gómez, C. Flórez-Ayala, J. Patiño, and J. A. Ortíz-Tamayo, "Aguas subterráneas, humedales y servicios ecosistémicos en colombia," *Biota Colombiana*, vol. 18, no. 1, Jun. 30, 2017. [Online]. Available: https://doi.org/10.21068/c2017.v18n01a1

[24] D. P. Santa-Arango, D. C. Martínez-Franco, and T. Betancur-Vargas, "Uso de hidroquímica e isótopos ambientales para la evaluación de la conexión hidrológica entre el agua subterránea y el humedal ciénaga colombiana. (un primer acercamiento)," *Gestión y Ambiente*, vol. 11, no. 12, May. 01, 2008. [Online]. Available: https://revistas.unal.edu.co/index.php/gestion/article/view/13974/14772

[25] P. A. Palacio-B. and T. Betancur-Vargas, "Identificación de fuente y zonas de recarga a un sistema acuifero apartir de isótopos estables del agua. caso de estudio bajo cauca antioqueño," *Gestión y Ambiente*, vol. 10, no. 1, May. 2007. [Online]. Available: https://www.redalyc.org/pdf/1694/169419796014.pdf

[26] J. D. Taupin, L. E. Toro, and M. C. Vargas, "Etude géochimique et isotopique des aquifères dans la zone de maicao (colombie)," *Hydrological Sciences Journal*, vol. 54, no. 3, Dec. 19, 2009. [Online]. Available: https://doi.org/10.1623/hysj.54.3.538

[27] M. C. Vélez-O and R. L. R. G., "Determinación de la carga con isótopos ambientales en los acuíferos de santa fé de antioquia," *Boletín de Ciencias de la Tierra*, no. 24, Nov. 2008. [Online]. Available: http://www.scielo.org.co/scielo.php?pid=S0120-36302008000300005&script=sci_abstract&tlng=pt

[28] A. K. Campillo-Pérez, J. D. Taupin, N. Patris, and T. Betancur, "Uso de la geoquímica y de los isótopos estables del agua en el estudio de un sistema acuífero supercial en el complejo urbanizado andino (valle de aburrá, colombia)," *Revista Peruana Geo-atmosférica RPGA*, no. 4, 2015. [Online]. Available: http://www.scielo.org.co/scielo.php?pid=S0120-36302008000300005&script=sci_abstract&tlng=pt

[29] A. Piña, L. Donado, and T. Cramer, "Hydrogeochemical processes and isotopes analysis. study case: "La Línea Tunnel", colombia," in *19th EGU General Assembly, EGU2017, proceedings from the conference held 23-28 April*, Vienna, Austria, 2017. [Online]. Available: https://ui.adsabs.harvard.edu/abs/2017EGUGA..19.2675P/abstract

[30] J. E. Mariño-Martínez and A. Martínez-Sánchez, "Analysis of precipitation and recharge of aquifers in tota and ibagué (colombia) from stable isotopes (^{18}o and ^{2}h)," *Revista Facultad de Ingeniería, UPTC*, vol. 27, no. 47, 2018. [Online]. Available: https://revistas.uptc.edu.co/index.php/ingenieria/article/view/7752/6142

[31] Instituto de Hidrología, Meteorología y Estudios Ambientales (IDEAM), *Atlas climatológico de Colombia / Instituto de Hidrología, Meteorología y Estudios Ambientales (IDEAM)*, 1st ed. Bogotá, Colombia: Imprenta Nacional de Colombia, 2005. [Online]. Available: https://catalogo.sgc.gov.co/cgi-bin/koha/opac-detail.pl?biblionumber=46264

[32] S. Valencia, D. E. Marín, D. Gómez, N. Hoyos, J. F. Salazar, and J. C. Villegas, "Spatio-temporal assessment of gridded precipitation products across topographic and climatic gradients in colombia," *Atmospheric Research*, vol. 285, Feb. 05, 2023. [Online]. Available: https://doi.org/10.1016/j.atmosres.2023.106643

[33] P. Villegas, V. Paredes, T. Betancur, J. D. Taupin, and L. E. Toro, "Groundwater evolution and mean water age inferred from hydrochemical and isotopic tracers in a tropical confined aquifer," *Hydrological Processes*, vol. 32, no. 14, May. 17, 2018. [Online]. Available: https://doi.org/10.1002/hyp.13160

[34] Área Metropolitana del Valle de Aburrá, *Microzonificación y Evaluación del Riesgo Sísmico del Valle de Aburrá*. Medellín, Colombia: Prográficas Ltda, 2007.

[35] S. M. Patiño-Rojas, M. Jaramillo, C. Espinosa-Espinosa, and

M. F. Arias-López, "Preferential groundwater flow directions in a pseudokarst system in colombia, south america," *Journal of South American Earth Sciences*, vol. 112, no. 1, Sep. 20, 2021. [Online]. Available: https://doi.org/10.1016/j.jsames.2021.103572

[36] T. Betancur-Vargas, C. Martínez-Uribe, E. F. García-Aristizábal, and J. F. Escobar-Martínez, "Identificación y caracterización de flujos regionales de recarga de agua a un acuífero libre," *Revista Facultad de Ingeniería, Universidad de Antioquia*, no. 85, Oct-Dec 2017. [Online]. Available: https://doi.org/10.17533/udea.redin.n85a07

[37] W. Dansgaard, "Stable isotopes in precipitation," *Tellus*, vol. 16, no. 4, Dec. 15, 2016. [Online]. Available: https://doi.org/10.3402/tellusa.v16i4.8993

[38] S. Gómez, J. D. Taupin, and J. A. Rueda, "Estudio hidrodinámico, geoquímico e isotópico de las formaciones acuíferas de la región de bucaramanga (colombia)," *Revista Peruana Geo-Atmosférica RPGA*, no. 4, 2015. [Online]. Available: https://tinyurl.com/y3x87cw3

[39] G. Esquivel-Hernández, G. M. Mosquera, R. Sánchez-Murillo, A. Quesada-Román, C. Birkela, P. Crespo, and *et al.*, "Moisture transport and seasonal variations in the stable isotopic composition of rainfall in central american and andean páramo during el niño conditions (2015–2016)," *Hydrological Processes*, vol. 33, no. 13, Mar. 13, 2019. [Online]. Available: https://doi.org/10.1002/hyp.13438

[40] R. Gonfiantini, M. A. roche, J. C. Olivry, J. C. Fontes, and G. M. Zuppi, "The altitude effect on the isotopic composition of tropical rains," *Chemical Geology*, vol. 181, no. 1-4, Oct. 15, 2001. [Online]. Available: https://doi.org/10.1016/S0009-2541(01)00279-0

[41] R. Sánchez-Murillo, G. Esquivel-Hernández, J. L. Corrales-Salazar, L. Castro-Chacón, and A. M. Durán-Quesada, "Tracer hydrology of the data-scarce and heterogeneous central american isthmus," *Hydrological Processes*, vol. 34, no. 11, Apr. 08, 2020. [Online]. Available: https://doi.org/10.1002/hyp.13758