



Seasonal variations of the isotopic ratios for oxygen and deuterium in the groundwater of the Serra Geral Aquifer System in the northeast region of the state of Rio Grande do Sul, Brazil

Taison Anderson Bortolin¹ · Pedro Antonio Roehe Reginato² · Franciéle Schwanck Carlos² · Gustavo Barbosa Athayde³ · Marcos Imério Leão² · Luis Henrique Mancini⁴ · Vania Elisabete Schneider¹

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Abstract

This paper presents the results of the monitoring of oxygen (^{18}O) and deuterium (^2H) isotopes in groundwater of the Serra Geral Aquifer System (SGAS) in the region of Carlos Barbosa, Rio Grande do Sul. Rainwater, and water from 12 tubular wells of the SGAS was collected monthly (from April to November). The results indicated that groundwater originates from meteoric water. For rainwater, values were found to be between -11.73 and -3.25‰ V-SMOW for $\delta^{18}\text{O}$ and -61.56 and -8.63‰ V-SMOW for $\delta^2\text{H}$. The air masses simulated by the HYSPLIT model revealed that retro-trajectories for depleted rainfall ($d^{18}\text{O} < -7.5\text{‰}$) are mostly influenced by moisture transported from Antarctica, through the Atlantic Polar mass (April, October, and November months). For enriched rainfall, the Atlantic Ocean appears as a more important moisture source, with most of the trajectories coming from this region. This moisture transport pattern occurred mainly during winter, when the South Atlantic Subtropical Anticyclone is closer to the continent. For groundwater, the monthly average values of all wells ranged from -9.02 to -5.06‰ V-SMOW for $\delta^{18}\text{O}$ and from -43.32 to -27.27‰ V-SMOW for $\delta^2\text{H}$ and indicated a similar trend in rainwater. Thus, the results show the different climatic conditions that occur over the months, influence of recharge processes, and isotopic ratios of groundwater.

Keywords Hydrochemical · Groundwater quality · Serra geral aquifer

✉ Taison Anderson Bortolin
tabortol@ucs.br

Pedro Antonio Roehe Reginato
pedro.reginato@ufrgs.br

Franciéle Schwanck Carlos
franschwanck@gmail.com

Gustavo Barbosa Athayde
gustavo.athayde@ufpr.br

Marcos Imério Leão
imerio@iph.ufrgs.br

Luis Henrique Mancini
lmancini@unb.br

Vania Elisabete Schneider
veschnei@ucs.br

¹ University of Caxias Do Sul (UCS), St. Francisco Getulio Vargas, Caxias do Sul 1130, Brazil

² Federal University of Rio Grande Do Sul (UFRGS), Porto Alegre, Brazil

³ Federal University of Paraná (UFPR), Curitiba, Brazil

⁴ University of Brasília (UnB), Brasília, Brazil

Introduction

The use of oxygen (^{18}O) and deuterium (^2H) isotopes in hydrogeologic studies has increased in recent years facilitating the assessment of the origin and circulation of groundwater (Clark Fritz 1997; Porowski 2014; Nunes et al. 2017; Regan et al. 2017, Wright e Novakowski, 2019). According to Drever (1997), fractionation of water leads to different isotopic ratios that can be used in studies of the evolution of waters in a region. Besides that, the meteoric isotopic ratio is influenced by factors such as temperature, evaporation, quantity, altitude, latitude and continentality (Dansgaard et al. 1973; Clark and Fritz 1997; Geyh 2000; Maldaner 2010; Porowski 2014). Thus, assessments of groundwater isotopic ratios should consider those variations that may occur in rainwater and that will be reflected in groundwater.

The first isotopic studies performed in Brazil took place in the late 1960s within the Amazon and the northeast regions (Silveira and Silva Junior 2002), and several studies in others regions in the last decade. Stradioto and Kiang (2010)

evaluated the groundwater in the municipality of Rio Claro (São Paulo) and identified that these waters had the same isotopic characteristics as rainwater and a low residence time. Teramoto et al. (2018) developed studies on fissural aquifers in the Itabuna region of northeastern Brazil with results indicating the impacts of local atmospheric conditions on isotopic fluctuations. These studies demonstrate that climatic conditions have an influence and relationship with the isotopic content of groundwater.

Studies were developed in the Serra Geral Aquifer System (SGAS) with the objective of evaluating the isotopic characteristics and patterns, whose works present different values for the waters that circulate in this aquifer system. Minardi et al. (2008) identified values of -7.5‰ to -6.9‰ for $\delta^{18}\text{O}$ and -50.6‰ to -44.7‰ for δH , as well as an average impoverishment of -0.43‰ for every 100 m of altitude, both in groundwater and in precipitation for groundwater in the Bauru and Serra Geral aquifers in the municipality of Araguari. Gastmans et al. (2016) studied the geochemical evolution of groundwater in the Serra Geral Aquifer System in the state of São Paulo, Brazil, with variations in isotopic ratios (-61.3 to -37.8‰V-SMOW from $\delta^2\text{H}$ e -8.9 to -5.7‰V-SMOW from $\delta^{18}\text{O}$). In the southern region of Brazil, Nanni (2013) identified the occurrence of variations in isotopic ratios of SGAS waters, which are related to recharge processes, and the possibility of the occurrence of water mixing between the Guarani and Serra Geral Aquifer System. These works present general values for SGAS not evaluating the influence of seasonal variations in groundwater.

Spatial and seasonal variations in the isotopic content of rainwater can also influence groundwater. Gastmans et al. (2017) evaluated the spatial and seasonal variations of the isotopic composition of rainwater in different regions of Brazil, and the results indicated that the interactions between air masses from the Atlantic Ocean, the Amazon region, the convergence zone of the South Atlantic, and the intertropical convergence zone are the main drivers of the isotopic composition in these regions. Griebler Junior (2018) carried out a study on the origin of rainfall that occurs in Rio Grande do Sul through isotopic analysis. They showed that the occurrence of extreme precipitation events influences the monthly values of $\delta^{18}\text{O}$. In addition, seasonal variations were identified, caused by the occurrence of air mass inflows from different atmospheric systems, which caused changes (depletion or enrichment) in the isotopic ratios.

Studies already developed for the SGAS do not involve the assessment of the occurrence of seasonal variations in the isotopic content of groundwater and rain, to identify possible correlations. In general, ranges of values are presented for the isotopic ratios, and considerations are made about the probable influence of the precipitation processes, but monitoring data that can prove this influence are not presented. Thus, to assess the seasonal behavior of the SGAS

groundwater isotopic composition, monitoring was carried out in tubular wells that capture water from this system in the northeast region of the state of Rio Grande do Sul. The results presented in this paper show the occurrence of variations in isotopic content relate these variations to changes in precipitation conditions and recharge processes. Although the study was carried out in a region located in the south of Brazil, the results are important for the entire SGAS, because they show the occurrence of seasonal variations in the isotopic content, which can occur in other parts of this system. Studies with the objective of evaluating the isotopic content of the waters of the SGAS should consider data from monthly monitoring, since there is variation in the isotopic content influenced by the conditions of precipitation.

Overview of the study region

The study area is located in the municipality of Carlos Barbosa, at an altitude of 618 m, coordinates $29^{\circ}18'$ South latitude and $51^{\circ}30'$ West longitude, in the northeast region of Rio Grande do Sul (Fig. 1).

The area is part of the geomorphological unit Planalto dos Campos Gerais, which is part of the Planalto das Araucárias region (IBGE, 2003). The climate of the study area is characterized by Rossato (2011) as subtropical IV, with characteristics of high humidity, presenting cold winters and mild summers, with average temperatures ranging from 14 to 17 °C and annual precipitation ranging from 1700 to 2000 mm well distributed between 130 and 150 days of the year.

In the study area, basic and acidic volcanic rocks from the Serra Geral Formation exist (CPRM, 2010; Viero e Silva, 2010). In the structures associated with these rocks, there are fractured aquifers that form the Serra Geral Aquifer System (SGAS). The main conditioning structures that facilitate aquifers in this system are tectonic fractures and, secondarily, primary structures that are generated by the cooling of volcanic rocks or by contacts between lava flows (Reginato et al. 2015). According to Bortolin (2018), the recharge in the SGAS occurs through rainwater that infiltrates the soils and fractures in the rocks. Soils have an important role in the recharge processes, because depending on their characteristics, there will be more or less infiltration with possibility of storage and circulation of water through these layers. Thus, only a part of the water that infiltrates the soil will reach the fractures and recharge the fractured aquifer. This reflects a faster initial change in the recharge of the aquifer located in the soil, with part of this water contributing to the recharge of the fractured one and another portion being discharged into the river.

In the Carlos Barbosa area, the SGAS is characterized by fractured aquifers that occur in cracks that cut acid rock lava

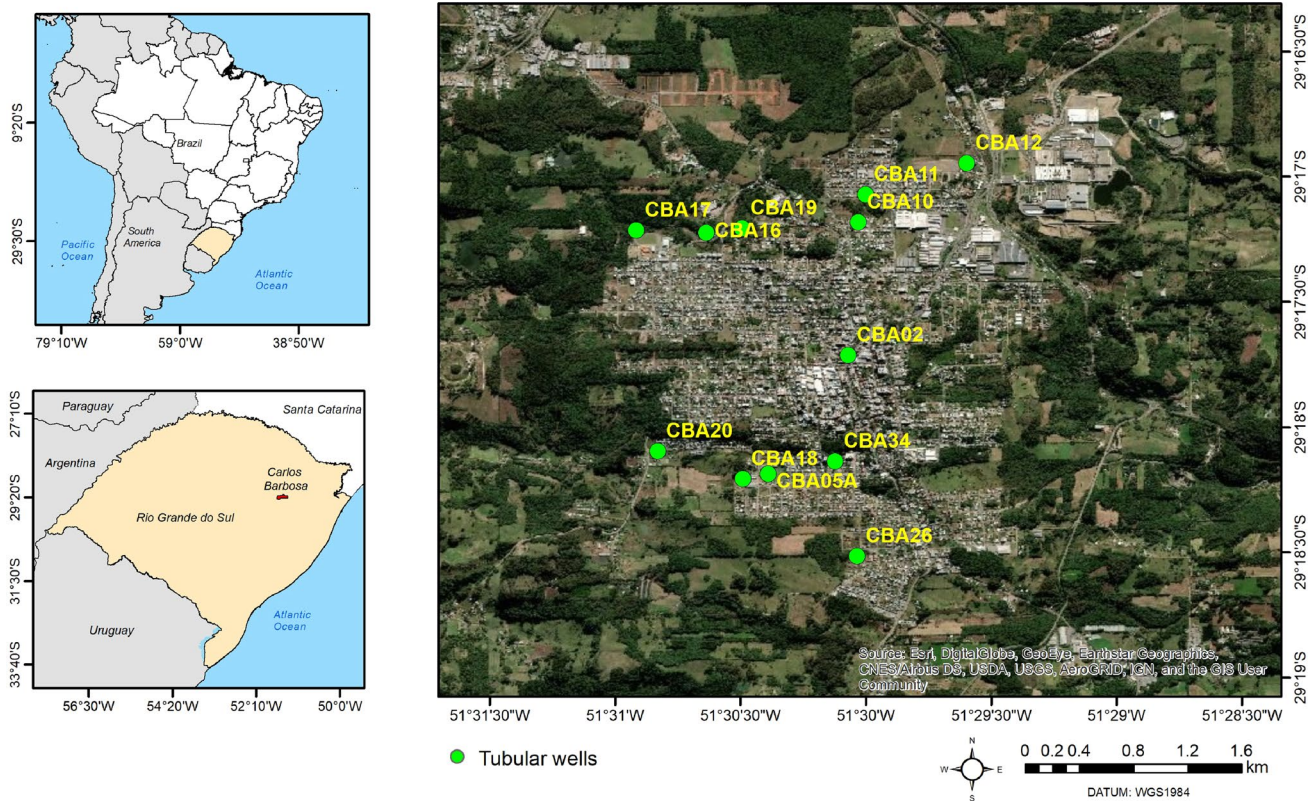


Fig. 1 Location of the study area

flows from the Serra Geral Formation (Bortolin et al. 2016). In this study, the authors identified variations in the physical–chemical composition of groundwater, the same being related to the depth of occurrence of fractures that were intercepted by the wells. In addition, the results indicated that the waters of this region have a low degree of mineralization and a short aquifer residence time.

There are two principal soil groups in the study area: Ultisol and Cambisol (Flores et al. 2007). First group is deeper and well-drained soils that have a clayey subsurface horizon, occurring in areas of smooth to undulating reliefs. The second group is shallow, poorly developed, clayey to sandy soils with the occurrence of rock fragments, generally associated with more steep reliefs. Reginato and Strieder (2006) comment that the soils condition the existence of fractured aquifers, because the recharge depends on the infiltration capacity associated with the characteristics of the soils.

Data and methods

Monitoring, sampling and analysis of isotopic ratios

For the development of this study, activities were carried out related to the selection and obtaining data from the water

sample points, monitoring and collection of water samples, analysis of the isotopic content, and interpretation of the results. Twelve tubular wells were selected from Companhia Riograndense de Saneamento (CORSAN) having different depths and water interception inlets located at varying depths (Table 1).

The monitoring of the 12 wells was carried out monthly over 8 months (April to November 2013), with collections at the end of each month at all points.

Samples for isotope analysis were collected in 10-mL amber glass bottles, washed three times with the sample, and were filtered without the addition of preservatives. To avoid fractionation of the samples, the flasks were completely filled without the formation of air bubbles and immediately plugged after collection. In the wells, the collection was carried out at the pipe outlet that was connected to the submerged pump after the well had been pumping for at least 20 min. To assess the isotopic content of rainwater, samples were collected monthly in a rain gauge located in the CORSAN laboratory in Carlos Barbosa.

The isotopic analyses to determine the $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios were performed at the Stable Isotope Laboratory of the Geosciences Institute of the University of Brasília (LAIS/IG/UnB), using the Picarro L2120-i Analyzer equipment with Vaporization Module A0211 and Autosampler PAL

Table 1 Data from wells monitored

Wells	CBA 02	CBA 05	CBA 10	CBA 11	CBA 12	CBA 16	CBA 17	CBA 18	CBA 19	CBA 20	CBA 26	CBA 34
Well depth (m)	74.8	216	90	98	86	114	141.5	150	122	140	150	180
Water inlet (m)	52.7	40	14.3	14 and 22	21 and 61	53 to 59	101	56 and 80	34 and 112	74	70	48, 60 and 71
Static level (m)	30.3	6.3	1.9	1.3	10	1.36	0.15	2.5	2.44	0.1	5.8	7.0
Flow (m ³ .h ⁻¹)	13.7	12	32.15	20	20	25.35	24	13.31	50	20	10	12

HTC-xt (Cavity Ringdown Spectrometer) with precision for $\delta^2\text{H} = 1\text{‰}$ and $\delta^{18}\text{O} = 0.2\text{‰}$. The ratios were expressed as the difference between the ratios measured in the sample and the ratios of a reference standard, using the delta (δ) notation. The values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are expressed in parts per thousand (‰), in relation to V-SMOW (Vienna Standard Mean Ocean Water).

Precipitation data were obtained from the Meteorological Database for Teaching and Research (BDMEP), of the National Institute of Meteorology (INMET). Daily data (mm of precipitation) recorded at the station located in the city of Bento Gonçalves (station 83,941) were used.

HYSPLIT analysis

To explore possible sources of the observed stable isotopes rates, air mass backward trajectories were simulated over the Bento Gonçalves weather station (29°09'00.0" S and 51°30'36.0" W, 640-m altitude). Retro-trajectory simulations were performed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, developed by the NOAA Air Resources Laboratory (Draxler et al. 2010) in conjunction with the global reanalysis datasets from the National Centers for Environmental Prediction (NCEP) and the National Center for Atmospheric Research (NCAR), known as NCEP/NCAR reanalysis model (NCEP1) (Kalnay et al. 1996; Kistler et al. 2001).

Calculations in HYSPLIT are based on a hybrid combination of Eulerian and Lagrangian frameworks (Draxler et al. 1998). Eulerian models focus on a specific location in space and calculate both advection and diffusion on a fixed spatial grid while Lagrangian models are applied to an air parcel moving through space, therefore, calculating advection and diffusion separately (Draxler et al. 1998). The most basic meteorological inputs required to operate HYSPLIT include U and V wind components, temperature, height or pressure, and surface pressure (Draxler et al. 1998). NCEP/NCAR Reanalysis model meteorology was used as input for the HYSPLIT simulations presented here. The NCEP/NCAR Reanalysis project produces a globally gridded dataset through a combination of

numerical weather prediction models and assimilation of observational data (Kalnay et al. 1996). Global Reanalysis data are available at 6 h (0Z, 6Z, 12Z, 18Z), daily, and monthly time resolution with continuous coverage from January 1948 through the present.

Five-day (120 h) retro-trajectories were simulated every 6 h over the Bento Gonçalves weather station from 01 April 2013 to 30 November 2013, reaching a total of 984 retro-trajectories. To obtain information on circulation patterns, cluster analysis was applied to the database of individual retro-trajectories for each month analyzed. The cluster analysis algorithm of the HYSPLIT model groups the trajectories by minimizing the spatial variability between them within a defined number of clusters (Draxler, 1999). For the retro-trajectories presented here, it was determined that five clusters are sufficient to capture monthly variability during the period.

Results and discussion

Analysis of precipitation data

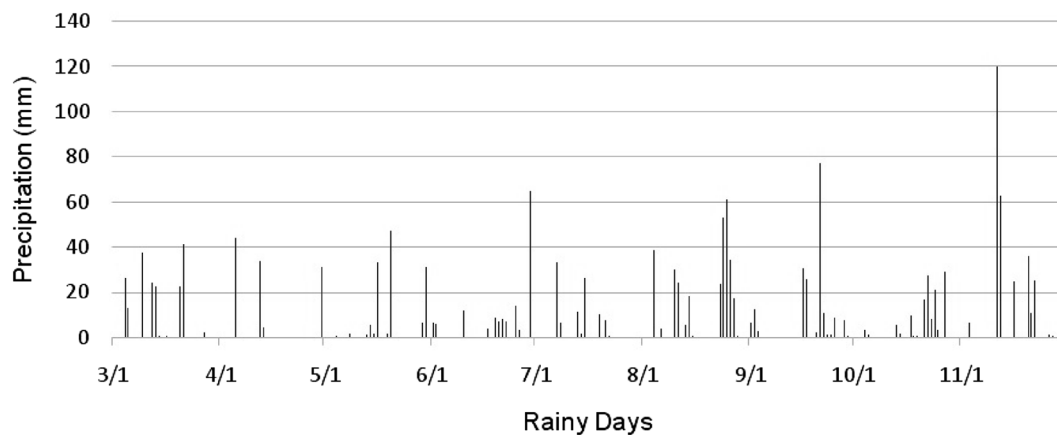
The rainfall data analyzed corresponds to the interval between March and November 2013, with results shown in Table 2 and Fig. 2.

Table 2 and Fig. 2 show that the accumulated values varied between 97.9 (July) and 312 mm (August), and in the months of March, August, September, and November the highest accumulated values were recorded. Maximum daily rainfall with values greater than 50 mm was observed during the months of June (65.2 mm), August (61.2 mm), September (77.3 mm), and November (120.1 mm).

Precipitation volumes and rainy occurrence are related to the geographic location of Rio Grande do Sul, which is influenced by atmospheric low-pressure systems that come from middle to high latitudes (Griebler Junior, 2018). Thus, air masses from the tropical and polar regions have an influence on the climatic characteristics of the state. As a result, precipitation can occur in large quantities, as well as over several days, as observed in the study area.

Table 2 Precipitation data

Month/2013	Accumulated monthly (mm)	Rainy days	Rainy days < 10 mm	Rainy days 10–20 mm	Rainy days 20–50 mm	Rainy days > 50 mm
March	191.8	11	4	1	6	0
April	114.1	6	3	0	3	0
May	131.7	11	8	0	3	0
June	143.5	17	14	2	0	1
July	97.9	8	4	2	2	0
August	312	15	6	2	5	2
September	187.7	15	10	2	2	1
October	128.4	13	9	1	3	0
November	288.5	10	4	1	3	2

**Fig. 2** Daily and monthly record of rainfall in the region

Retro-trajectory simulation

The cluster analysis of the simulated individual retro-trajectories for the period from April 1, 2013 to November 30, 2013 are shown in Figs. 3 and 4.

We identified two clusters with dominant southwestern circulation and fast movement (long trajectory) in all months analyzed (marked in dark blue in Figs. 3 and 4), one southwest/southeast cluster, depending on the month, that includes slower-moving retro-trajectories (shown in light blue), and a slow-moving cluster (short trajectories) that encompasses most of the retro-trajectories. This group has the greatest variation in circulation, being predominantly from the southeast during warm months (April, May, and November) and with oceanic influence (marked in light green), while during the cool months (June and July) circulation is from the west to northwest and with continental influence (shown in orange). During the other months, the predominant flow is southwest and the influence is mixed between ocean and continent (marked in yellow). Last, a continental group of slow moving with

predominant circulation coming from the north of the country with a variable direction from northwest to northeast (in red).

The frequency distribution of the clusters for the studied period shows a distinct seasonality between the warm months (April, May, October, and November) in relation to the cool months (June, July, August, and September). This shows a change in circulation patterns during different seasons, as well as different origins for rainfall in the south of Brazil.

Isotopic analysis of rainwater

The results of isotopic analyses of oxygen and deuterium from rainwater samples are shown in Table 3.

The values of $\delta^{18}\text{O}$ e $\delta^2\text{H}$ varied between -11.73 and -3.25 ‰ and from -61.56 to -8.63 ‰, respectively. In addition, during the months of April, October, and November, the values are more depleted, while the month of July presents a more enriched value for oxygen and deuterium.

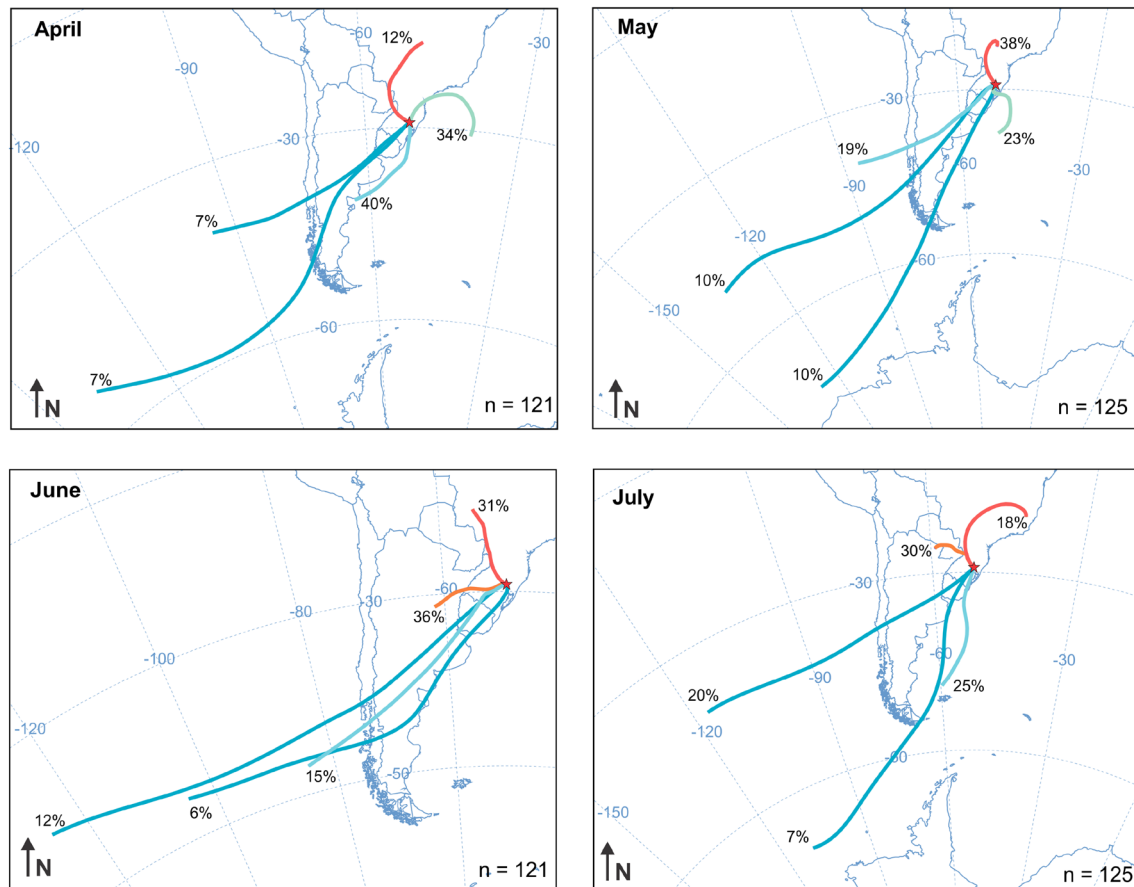


Fig. 3 Monthly clusters of the 5-day retro-trajectories for April, May, June, and July 2013. Blue tones mark the clusters with oceanic influence, and earth tones identify clusters with continental influence

To characterize the origin of the air masses, retro-trajectory simulations were performed for the largest precipitation events (four events) during the 2 months with the greatest isotopic variation (July with more enriched values and October with more depleted values).

The simulations were carried out for 240 h (10 days) ending at the Bento Gonçalves weather station. Figures 5 and 6 show the variation in the pattern of movement of air masses between July and October for the chosen precipitation events.

Analyzing the simulations, it is possible to observe that during winter precipitation has a greater influence from the high-pressure system known as the Atlantic Tropical mass (ATm). Its center of origin is the South Atlantic Subtropical Anticyclone (SASA), which is a warm semi-stationary anticyclone (Ito and Ambrizzi, 2000). The ATm maintains the characteristics of the anticyclone but changes as it enters the continent (Borsato and Collischonn, 2017). During the winter, the SASA approaches the continent and the air mass dominates the weather conditions throughout the southeast, midwest, part of the northeast, and south Brazil; this domain can be clearly seen in the first three plots in Fig. 5.

On the other hand, for the precipitation that occurred during the month of October (Fig. 6), there is a predominance of the advance of the polar masses. The Atlantic Polar mass (APm) is a cold and wet high-pressure system that originates in the Atlantic Ocean between the South Pole and Patagonia. The APm advances over south Brazil and sometimes divides into two segments, one advancing along the Rio da Prata River channel reaching the center-south of Brazil and the other following the coast (Monteiro 1969).

The moisture transport of air masses simulated by the HYSPLIT model revealed that retro-trajectories for depleted rainfall ($\delta^{18}\text{O} < -7.5\text{‰}$) are mostly influenced by moisture transported from Antarctica, through the APm. For enriched rainfall, the Atlantic Ocean appears as a more important moisture source, with most of the trajectories coming from this region (35°W ; 15°S) and passing over the northeastern region of Brazil. This moisture transport pattern occurred mainly during winter, when the SASA is closer to the continent.

Another factor that needs to be considered is the effect of kinetic fractionation (Rayleigh fractionation) during the transport of the moisture. During long-distance transport,

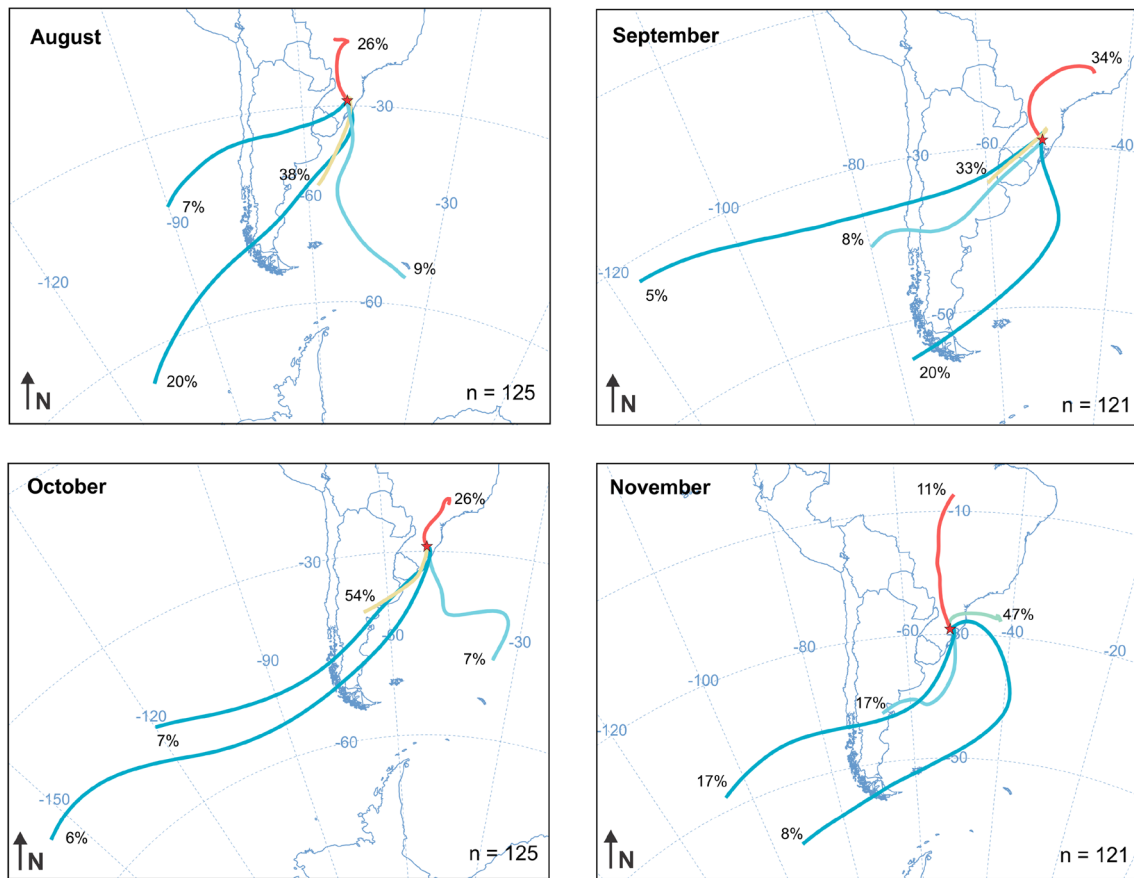


Fig. 4 Monthly clusters of the 5-day retro-trajectories for August, September, October, and November 2013. Blue tones mark the clusters with oceanic influence, and earth tones identify clusters with continental influence

Table 3 Isotopic ratios determined for rainwater samples

Month	Sampling date	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
April	30/04	-9.56	-61.19
May	23/05	-6.22	-34.74
June	25/06	-7.17	-40.30
July	24/07	-3.25	-8.63
August	30/08	-7.72	-37.42
September	18/09	-7.88	-41.27
October	25/10	-11.73	-61.56
November	27/11	-8.89	-43.85

the condensate is continuously removed from the system in the form of precipitation, thus, the δ value of the remaining vapor becomes progressively depleted in the heavy isotope (Dansgaard, 1964). In this way, it can be interpreted that the retro-trajectories influenced by the Polar air mass (and also longer ones) are associated with more depleted rainfall while rains formed on the coast of Brazil (i.e., short retro-trajectories) will be more enriched.

The relationship between monthly precipitation values (Table 2) and isotopic ratios (Table 3), shows that in periods of less precipitation there are more enriched values than in the period of greater precipitation. This quantity effect, observed initially by Dansgaard (1964) and more recently by the other authors such as Andreo et al. (2004), Yang et al. (2019), and Wright and Novakowski (2019), results in higher $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values during short precipitation events and lower isotopic rates in long rain events.

However, there is no direct relationship between the amount of precipitation and the depletion of isotopic ratios, since the most depleted values were found in October when a 128.4 mm precipitation event took place. The isotopic signature of rainfall from this event was different to 312 mm that took place in August that had less depleted values. These variations indicate an influence of seasonality, a fact already observed by Griebler Junior (2018) who demonstrated that, for the winter and spring seasons, there is a tendency of enrichment in isotopic values, while during summer and autumn there is a tendency for impoverishment. In addition, the author identified that extreme precipitation events have a direct influence on the values of isotopic ratios.

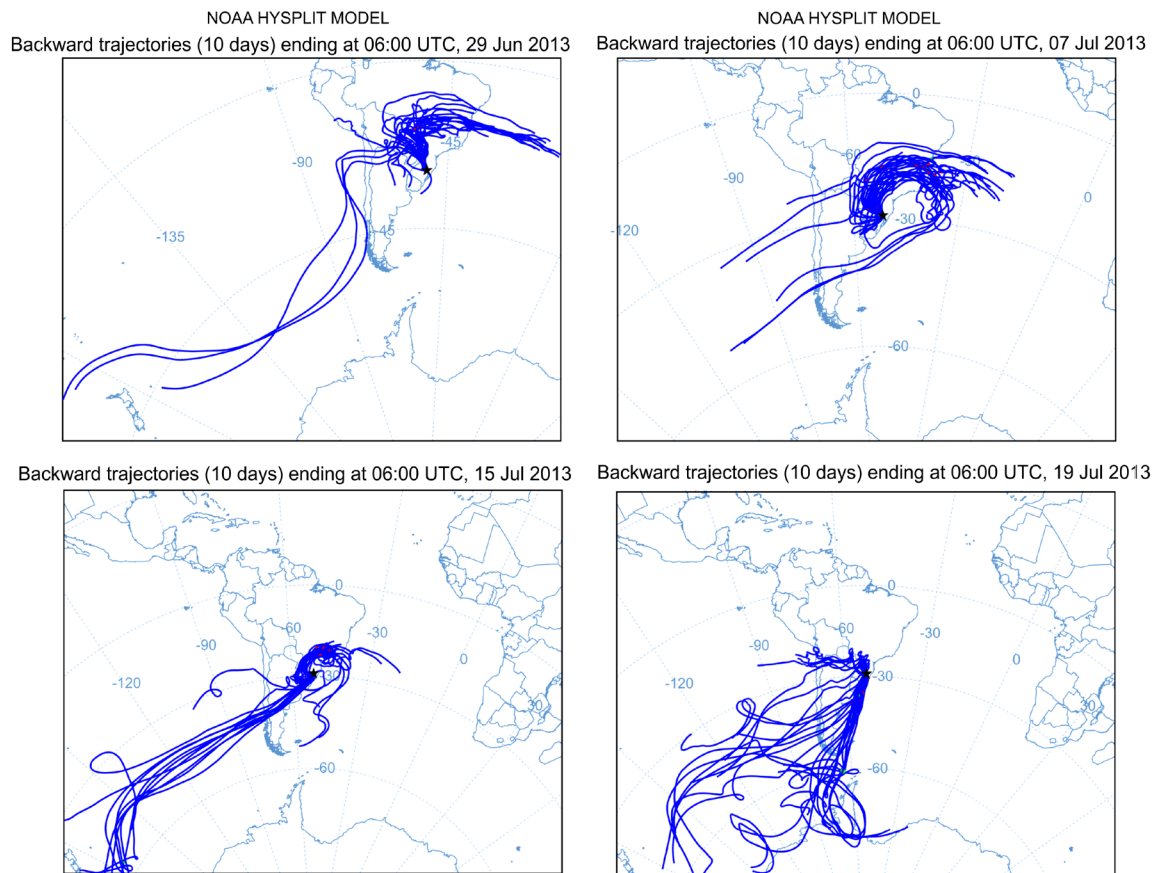


Fig. 5 Retro-trajectory simulation for the largest precipitation events that occurred in July

Isotopic analysis of SGAS groundwater

Table 4 presents the results of the isotopic analyses of oxygen and deuterium for groundwater samples collected monthly in the 12 tubular wells.

The results show that there are variations in the isotopic ratios of each well, as well as during each month of collection. The mean of the well data indicated a range of -8.09 to -6.66 ‰ for $\delta^{18}\text{O}$ and of -38.47 to -34.58 ‰ for $\delta^2\text{H}$. These values are similar to those found by Gastmans et al. (2016), who indicated that the waters of the SGAS tend to present values between -5.8 and -7.5 ‰ for $\delta^{18}\text{O}$, these variations being related to the recharge processes that occur under different climatic conditions.

The analysis of month averages (Table 4) indicates an increasing tendency of the isotopic ratio impoverishment from April to November (with the exception for the month of July). This behavior is better demonstrated when the monthly results obtained for each well and for rainwater are evaluated, represented in Fig. 7.

Figure 7 shows an impoverishment behavior from April to November, with greater variations in the isotopic oxygen

ratios in each well from April to June, while between August and November these variations are smaller. Figure 8 presents the relationship between isotopic signals and the dry (months with accumulated volume less than 150 mm) and wet seasons (months with large accumulated volumes, over 150 mm). This figure shows that the isotopic ratios of depletion of deuterium and oxygen appear more frequently in the wet period. In drier periods, the volume of water that infiltrates into the aquifer tends to be lower, and considering that before reaching the fractures, the water circulates through the soil, where evaporation occurs with potential reflection in the isotopic signal.

Figure 9 shows the distribution of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic ratios for all wells in relation to the meteoric lines of local (Carlos Barbosa), regional (Porto Alegre), and global. The isotopic data of rainwater from the meteorological line in the region of Carlos Barbosa (RS) located just above the global and Porto Alegre meteoric lines. This may be related to the location of the municipality of Carlos Barbosa, which is located more than 100 km from Porto Alegre, at altitudes above 600 m. Therefore, variations in isotopic ratios, in addition to seasonal influence, may be

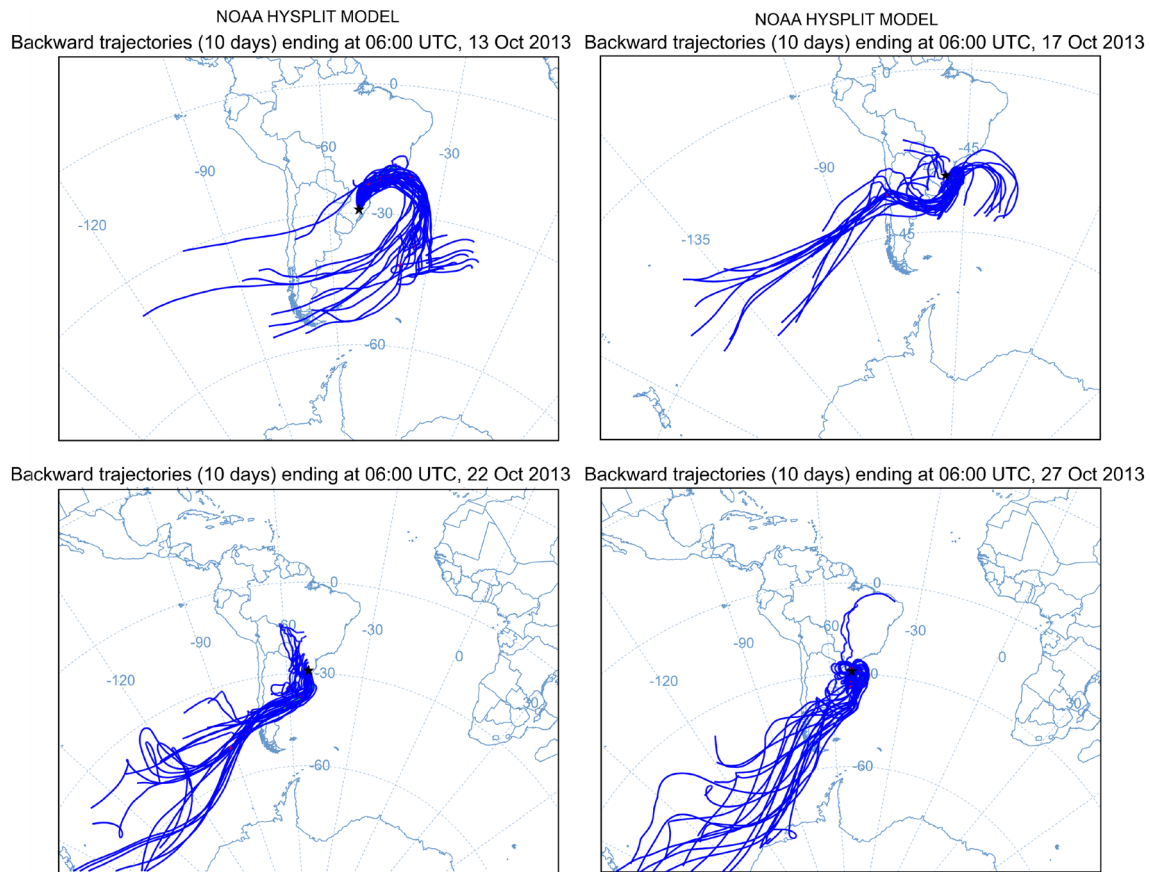


Fig. 6 Retro-trajectory simulation for the largest precipitation events that occurred in October

related to altitude and continentality (distance from the coast).

The figure demonstrates that all wells have isotopic values similar those of precipitation, indicating that groundwater originates from rainwater, which infiltrates the soil and through fractures, recharging the fractured aquifers that form the SGAS.

The distribution of the isotopic ratio values (Fig. 10) for each month and its relationship with the local meteorological line (Carlos Barbosa) indicates that during the months of April to July, there are variations in the isotopic ratios in each well. In the months of August to November, there is a greater impoverishment with closer values between the wells, represented by the grouping of monthly results.

Variations in the isotopic ratios of groundwater are related to recharge, which is affected by precipitation and infiltration, circulation, groundwater storage in the soil, and fractures in volcanic rocks. The recharge is also influenced by the storage conditions and characteristics of the soil and the rock matrix. This determines the recharge rates and their relationship to precipitation. Bortolin et al. (2016) observed that the waters of the SGAS, in the study region, have low

concentrations of cations and anions and low values of pH, EC and total dissolved solids that can be associated with a short residence time and fast recharge. In addition, the authors identified that in the wells where deeper fractures occurred, the waters showed a higher concentration for cations and anions, and higher values of pH, EC and TDS.

Thus, the monthly variations found for the groundwater isotopic ratios can be explained based on the infiltration and recharge processes, as well as the water flow that occurs through the structures in the rocks. The predominant soil types in the region (Ultisols and Cambisols) show differences in thickness and infiltration conditions, with the region of occurrence of ultisols tending to favor the infiltration and water storage processes in the soil. From the geological profiles of the wells, it can be identified that the thickness of the mantle of alteration in each well is variable, with values between 1 and 20 m (average of 6.5 m, but with a predominance of thicknesses below 5 m—67%). These characteristics explain different infiltration and recharge conditions in each region where the wells are located, with the possibility of evaporation processes of the water that is stored in the soil, causing changes in the isotopic signal.

Table 4 Results of isotopic ratios of oxygen and deuterium

Well	Month	04 (April)	05 (May)	06 (June)	07 (July)	08 (August)	09 (September)	10 (October)	11 (November)	Average well	Standard Deviation Well
CBA 02	$\delta^{18}O$ (‰)	-5.96	-7.07	-7.43	-5.27	-7.77	-8.06	-8.93	-8.75	-7.41	1.28
	δ^2H (‰)	-32.07	-36.07	-40.2	-29.11	-40.93	-39.59	-41.9	-39.82	-37.46	4.63
CBA 05	$\delta^{18}O$ (‰)	-3.41	-6.0	-6.81	-6.85	-7.95	-7.84	-9.07	-8.95	-8.09	1.83
	δ^2H (‰)	-24.81	-33.34	-37.87	-32.94	-40.6	-38.59	-42.51	-41.16	-36.48	5.86
CBA 10	$\delta^{18}O$ (‰)	-5.19	-6.09	-6.84	-6.55	-7.98	-8.06	-8.82	-8.97	-7.31	1.35
	δ^2H (‰)	-30.29	-33.47	-38.63	-30.43	-39.57	-38.60	-41.03	-41.85	-36.73	4.65
CBA 11	$\delta^{18}O$ (‰)	-6.66	-4.74	-6.97	-6.59	-7.76	-7.77	-8.78	-8.94	-7.28	1.36
	δ^2H (‰)	-33.51	-28.53	-37.25	-30.84	-39.26	-38.35	-41.13	-41.2	-36.26	4.77
CBA 12	$\delta^{18}O$ (‰)	-4.94	-7.08	-6.65	-5.76	-8.09	-7.81	-8.91	-9.07	-7.29	1.46
	δ^2H (‰)	-29.26	-35.77	-38.95	-26.92	-40.2	-37.32	-42.12	-40.65	-36.40	5.53
CBA 16	$\delta^{18}O$ (‰)	-4.51	-5.04	-6.47	-7.08	-8.18	-7.95	-8.92	-8.67	-7.10	1.65
	δ^2H (‰)	-27.94	-29.86	-38.07	-30.41	-39.95	-38.34	-41.87	-40.13	-35.82	5.48
CBA 17	$\delta^{18}O$ (‰)	-4.28	-6.08	-6.17	-5.16	-7.78	-7.76	-9.13	-8.77	-6.89	1.74
	δ^2H (‰)	-27.91	-32.60	-37.50	-25.9	-40.14	-36.96	-42.91	-40.67	-35.57	6.18
CBA 18	$\delta^{18}O$ (‰)	-4.81	-5.03	-7.42	-4.35	-7.95	-7.69	-9.34	-8.91	-6.94	1.94
	δ^2H (‰)	-29.46	-29.97	-39.46	-23.87	-39.37	-36.51	-49.71	-41.58	-36.24	8.18
CBA 19	$\delta^{18}O$ (‰)	-4.21	-5.75	-5.78	-4.99	-7.35	-7.87	-9.15	-8.82	-6.74	1.82
	δ^2H (‰)	-28.12	-30.22	-35.54	-26.05	-38.04	-36.48	-45.70	-40.96	-35.14	6.67
CBA 20	$\delta^{18}O$ (‰)	-3.84	-4.90	-5.83	-5.66	-7.39	-7.78	-9.21	-8.66	-6.66	1.89
	δ^2H (‰)	-26.55	-29.05	-34.05	-27.15	-37.89	-37.34	-44.33	-40.27	-34.58	6.51
CBA 26	$\delta^{18}O$ (‰)	-6.86	-7.32	-6.87	-6.22	-8.0	-8.17	-9.18	-8.98	-7.70	1.06
	δ^2H (‰)	-34.84	-36.13	-40.45	-29.41	-40.29	-39.10	-44.42	-43.11	-38.47	4.86
CBA 34	$\delta^{18}O$ (‰)	-6.04	-7.02	-7.6	-6.41	-7.94	-7.93	-8.82	-9.01	-7.60	1.06
	δ^2H (‰)	-32.48	-35.75	-40.73	-30.66	-39.85	-38.2	-42.18	-41.81	-37.31	4.34
Average month	$\delta^{18}O$ (‰)	-5.06	-6.01	-6.74	-5.91	-7.85	-7.89	-9.02	-8.88	-7.60	1.06
Standard deviation month	δ^2H (‰)	-27.27	-33.64	-38.23	-28.64	-39.67	-37.95	-43.32	-41.10	-37.31	4.34
	$\delta^{18}O$ (‰)	1.11	0.95	0.60	0.84	0.25	0.15	0.18	0.14	0.14	0.14
	δ^2H (‰)	2.98	2.94	1.99	2.64	0.93	1.01	2.46	0.91	2.46	0.91

Fig. 7 Monthly variations in the isotopic ratio of oxygen in the waters of tubular wells and rain

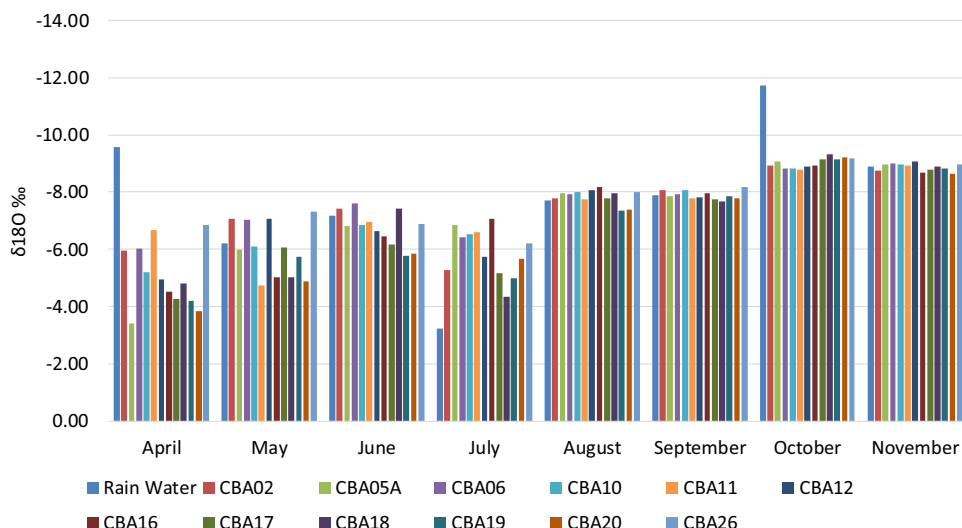
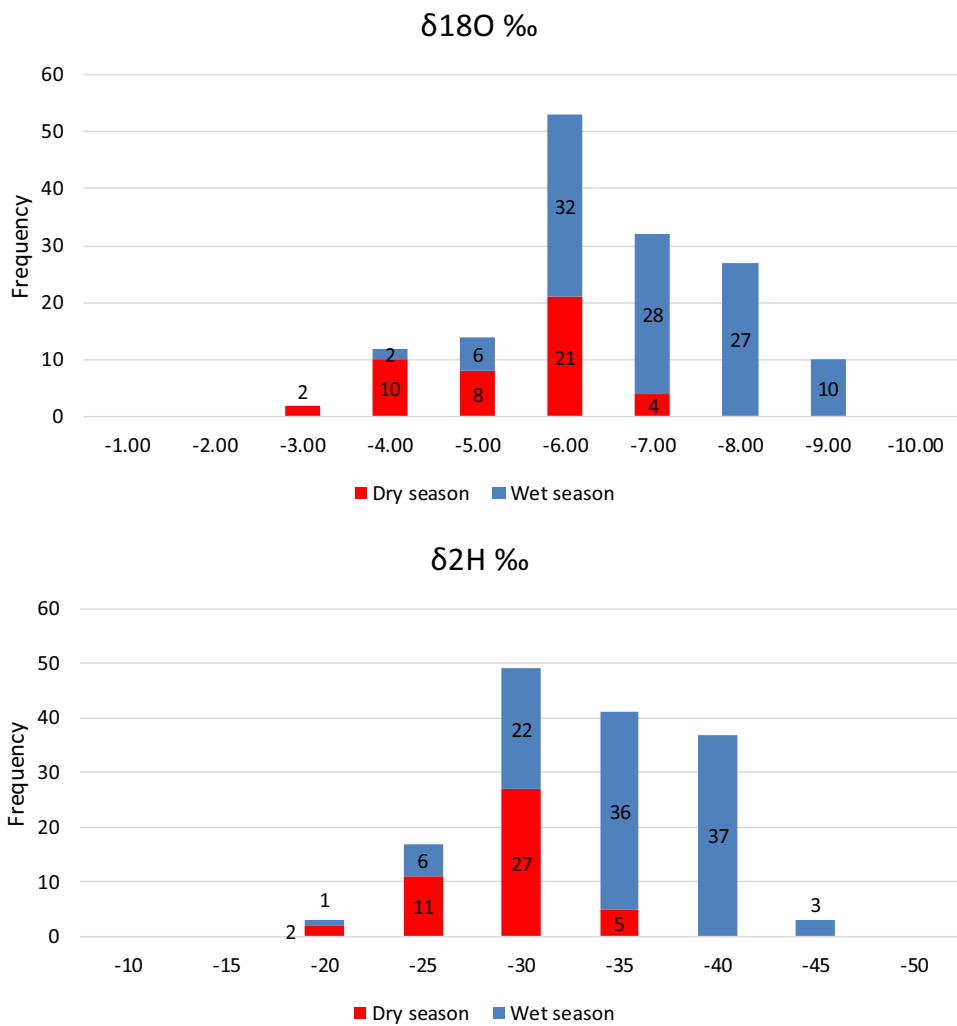


Fig. 8 Variations of the isotopic ratio in the dry and wet seasons



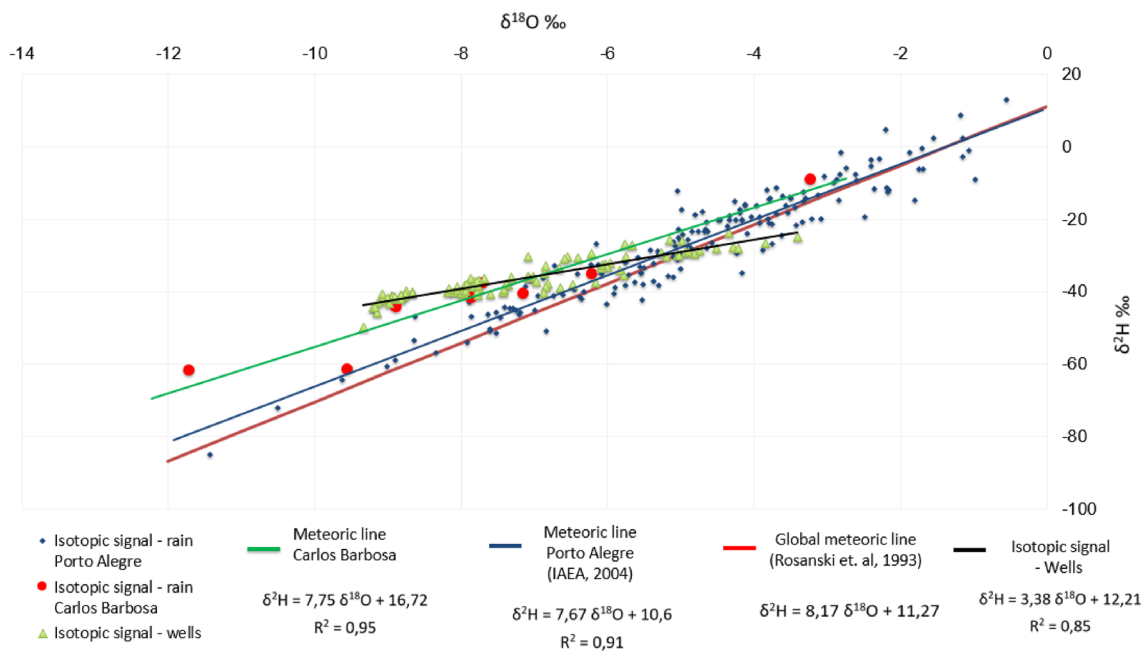


Fig. 9 Distribution of monthly isotopic ratios for all wells

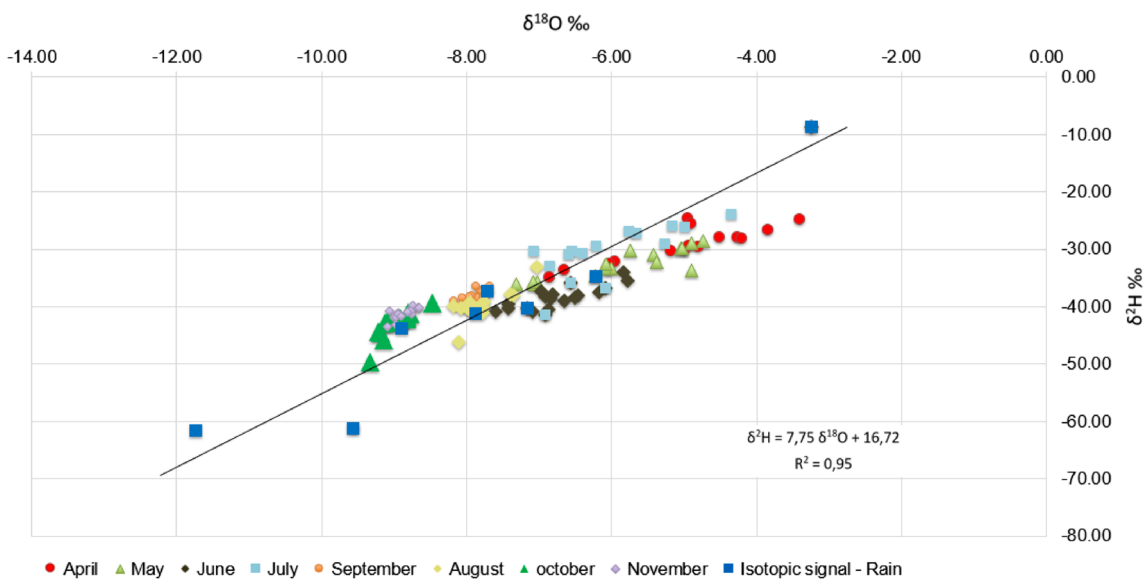


Fig. 10 Distribution of the isotopic ratios of the wells for each month monitored

In addition, when analyzing the occurrence of water ingress into the wells (fractures), it is observed that there are wells with either (CBA02, CBA05, CBA10, CBA17, CBA20 and CBA26) or more water inlets (CBA11, CBA12, CBA16, CBA18, CBA19 and CBA34) that are located at different depths, meaning they capture water from different horizons in the fractured rock aquifer. This ends up generating different flow conditions, influencing

the hydrochemical characteristics (as already identified by Bortolin et al. 2016) and, perhaps, the isotopic signature.

Such characteristics contribute to the occurrence of a different recharge and circulation of water. Therefore, when periods of less rainfall occur (April to July), a greater variation in the response of the isotopic ratios can be observed for each well. Under these conditions, the water takes longer to reach the fractures due to the smaller volumes that infiltrate,

as well as that the evaporation processes occur more easily. For periods where the specialty occurs in a greater number of days, with greater precipitated volumes, there will be a greater tendency for infiltration and recharge, with less evaporation of water from the soil, and for this reason the values of ionic ratios show fewer monthly variations between wells.

Conclusions

Groundwater of the SGAS in the study area originates from rainwater, since the isotopic ratios of the wells were located close to the local (Carlos Barbosa), regional (Porto Alegre), and global meteoric lines.

For rainwater, values were found between -11.73 and -3.25 ‰ for $\delta^{18}\text{O}$ and -61.56 and -8.63 ‰ for $\delta^2\text{H}$, with the months of greater precipitation having presented more depleted values. The origin of the air masses and their influence in the region were also well characterized by their isotopic variability. Months with the greatest ATm influence (June, July, August, and September) showed more enriched values in relation to the months where the APm was predominant (April, October, and November) and as a result the values found were more depleted.

In groundwater, the monthly average values of each well indicated a variation from -6.66 to -8.09 ‰ for $\delta^{18}\text{O}$ and from -34.58 to -38.47 ‰ for $\delta^2\text{H}$. The average values of the wells for each month varied between -5.06 and -9.02 ‰ for $\delta^{18}\text{O}$, and -27.27 and -43.32 ‰ for $\delta^2\text{H}$ indicating a trend of impoverishment. The analysis of rainwater showed similar results.

The variations in the isotopic ratio monthly results identified for groundwater show a greater variation between the wells for the months of April to July (lower precipitated volumes) and more similar values between the wells, but more depleted, for the months of August to November (highest amounts of precipitation).

The results of this study show that the conditions of occurrence of precipitation, different processes of infiltration, storage and evaporation of soil water, as well as recharge and circulation of water from the fractured aquifer, have an influence on the isotopic ratios of groundwater.

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