



# Assessment of the changes in contributions from water sources to streamflow induced by urbanization in a small-sized catchment in Southeastern Brazil using the dual stable isotopes of water ( $^{18}\text{O}$ and $^2\text{H}$ )

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Received: 28 June 2021 / Accepted: 5 April 2022 / Published online: 12 April 2022  
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**Abstract** Urban growth often results in changes in the urban hydrological cycle, causing impacts on water availability in densely populated regions. The water isotopologues can provide relevant information about the origin of water under different hydrogeological scenarios, aiding to implement better strategies for water conservation in coupled natural-urbanized environments. In this study, the isotopic compositions of multiple water sources were assessed in a pristine (Ipanema National Forest, FLONA) and an urbanized (Lavapés catchment, SOR) watershed located in the

Sorocaba River basin (State of São Paulo, Southeastern Brazil), seeking to understand the causes of isotopic variability and to determine the relative contribution from different sources to streamflow, using the Bayesian mixing model approach. Differences in isotopic composition were observed, as FLONA yielded the most depleted water (*ca.*  $-7.5\text{‰}$   $\delta^{18}\text{O}$  for surface and groundwater and *ca.*  $+11.0\text{‰}$  *d*-excess), while SOR yielded the most enriched water (*ca.*  $-5.5\text{‰}$   $\delta^{18}\text{O}$  for surface and groundwater and  $-3.8\text{‰}$   $\delta^{18}\text{O}$  for the water supply system), with evidence of evaporation (*ca.*  $+8.2\text{‰}$  *d*-excess). The differences observed in isotopic compositions are related to a combination of different factors, such as geological framework, groundwater recharge, and evaporation associated with the Itupararanga water reservoir. Both

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10661-022-10040-9>.

**Key points** Dual stable isotopes of water ( $^{18}\text{O}$  and  $^2\text{H}$ ) identify possible water source contributions to natural and urbanized watersheds.

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in FLONA and SOR, groundwater discharge is the most important factor that regulates streamflow. However, in SOR, losses from the water supply system were almost constant along the year, representing an important contribution. The results presented here highlight the use of isotope hydrology techniques to solve problems related to urban hydrology.

**Keywords** Stable isotopes · Urban hydrology · Bayesian mixing model · Streamflow

## Introduction

Despite the importance of pristine environments and natural landscapes to understand natural conditions of water circulation along the water cycle, most of the challenges resulting from changes in water circulation are related to increasing urban demands. The use of stable isotopes as a tracer of water movement can be helpful to solve problems associated with water supply and water dynamics in urban environments (Ehleringer et al., 2016; Jameel et al., 2016; Li et al., 2019).

Urbanization creates impervious surfaces by sealing soils and expanding surface runoff, therefore decreasing evapotranspiration and infiltration in urban catchments (Shuster et al., 2005). The combination of these processes has led to important modifications in urban streamflow, directing most of the surface runoff to urban river channels with an apparent decrease in the contribution from groundwater, due to the reduced recharge of aquifers, whereas contributions from utilities (e.g., drainage, water supply and sewage systems) seem to be more relevant to urban catchments (Barron et al., 2013; Bonneau et al., 2018; Gabor et al., 2017; Lerner, 2002; Li et al., 2019; Shuster et al., 2005). A better understanding of these processes in tropical urban regions is required, in view of the impacts of extreme events associated with climate changes.

Contrarily to urban environments, streamflow in natural catchments has been largely studied, taking into account different climatic scenarios (Batista et al., 2018; Gan & Luo, 2013; Lachniet & Patterson, 2009; Sánchez-Murillo et al., 2015; Santarosa et al., 2021; Schulte et al., 2011; Soulsby et al., 2011; Tetzlaff & Soulsby, 2008; Zhang et al., 2017). The contribution of groundwater to streamflow has been found to be

variable and directly related to environmental parameters, such as geological and geomorphological frameworks and soil types (Berhanu et al., 2015; Betancur et al., 2020; Carlier et al., 2018; Cheng et al., 2012; Price, 2011; Soulsby et al., 2004, 2011; Zhang et al., 2017).

The use of stable isotopes as tracers of the water origin and flow represents an important tool to understand the hydro-climatic factors that affect water resources at distinct spatial and temporal scales, including water flow in watersheds and the connections between precipitation, surface, and groundwater (Aggarwal et al., 2012, 2016; Jouzel et al., 2013; Kendall & Coplen, 2001; Rozanski et al., 1993), as well as the modification induced by anthropogenic activities, such as irrigation in agricultural areas (Cherry et al., 2020).

Urbanization promotes important changes in urban streamflow, having direct impacts on the water isotopic composition. These impacts are mostly related to modifications implemented in the urban subsurface that can result in adjustments of the processes related to water flow (infiltration, surface runoff, and evaporation), as well as changes in the contributions from different sources (including losses from the water supply system and sewage discharge). In addition to the vast literature focusing on isotope hydrology applied to the investigation of catchment processes and water balance in quasi-undisturbed or undisturbed basins (Bonneau et al., 2018; Darling, 2011; Li et al., 2019; Santarosa et al., 2021; Unnikrishnan & Praveen, 2012), urban hydrology studies have recently incorporated the dual stable isotopes of water to evaluate the effects of urbanization on hydrological processes, such as runoff distribution and transit times (Dimitrova-Petrova et al., 2020; Soulsby et al., 2014), the contribution of different water sources to urban streamflow (Jasechko, 2019; Jefferson et al., 2015), and the origin of the water distributed by an underground water supply network (Ehleringer et al., 2016).

The middle Sorocaba River basin (hereafter SRb) is located in the central-eastern portion of the State of São Paulo, which is one of the most developed regions of the state, being in a very advanced stage of land occupation and containing few natural and preserved areas. At present, the estimated SRb population is 1.5 million inhabitants, mostly living in Sorocaba, the largest SRb city that encompasses an

important industrial park and has reached high levels of urbanization and sanitization (FAT & FABH-SMT, 2016).

Sorocaba presents one of the highest rates of population growth of the State of São Paulo, starting from *ca.* 70 thousand inhabitants in the 1940s to almost 700 thousand inhabitants nowadays (Gonçalves et al., 2014; IBGE, 2021). This increase in population has led to fast urbanization that, despite land-use planning, has taken place in a disordered way, leading to hydrological and hydrogeological problems (FABH-SMT, 2020). About 65% of the SRb population's water demand is supplied by the Itupararanga reservoir, located 20 km southeast of Sorocaba city (Fernandes et al., 2016).

Contrasting with this intense urbanization, the Ipanema National Forest (FLONA), located about 20 km northwest of Sorocaba, is one of the few preserved areas in SRb (Fig. 1). FLONA is an environmental conservation unit established in 1992, with the purpose of preserving fragments of the semi-deciduous forest (Atlantic Forest) and the savannah (Cerrado), as well as the rich historical site located in the area, where the first iron foundry was installed in Brazil in the 1800s (de Silva & Mazine, 2016).

This study adopted the paired-catchment approach, focusing on two small watersheds of SRb: (i) the Ferro micro-basin (hereafter FLONA), located in a pristine region of the Ipanema National Forest, and (ii) the Lavapés catchment (hereafter SOR), located in the Sorocaba urban zone. Our main purpose was to investigate the origin of water and the influence of the urban water supply network on the urbanized watershed, in order to quantify the contributions of different water sources using stable isotopes ( $^2\text{H}$  and  $^{18}\text{O}$ ) as tracers and the Bayesian mixing model approach. The following questions were made to guide this study: (i) How does urbanization impact streamflow in urban catchments? (ii) Can river water isotopic compositions be used to identify and quantify different water sources in urban and pristine watersheds? (iii) Are the water isotopic compositions in different watersheds related to the geological framework? The answers to these questions will (i) inform us about the temporal and spatial variations of the water sources in both watersheds and (ii) provide the basis for the use of the dual stable isotopes of water to identify losses in the water supply network, as monitoring programs

can help the water management agencies implement programs to reduce such water losses.

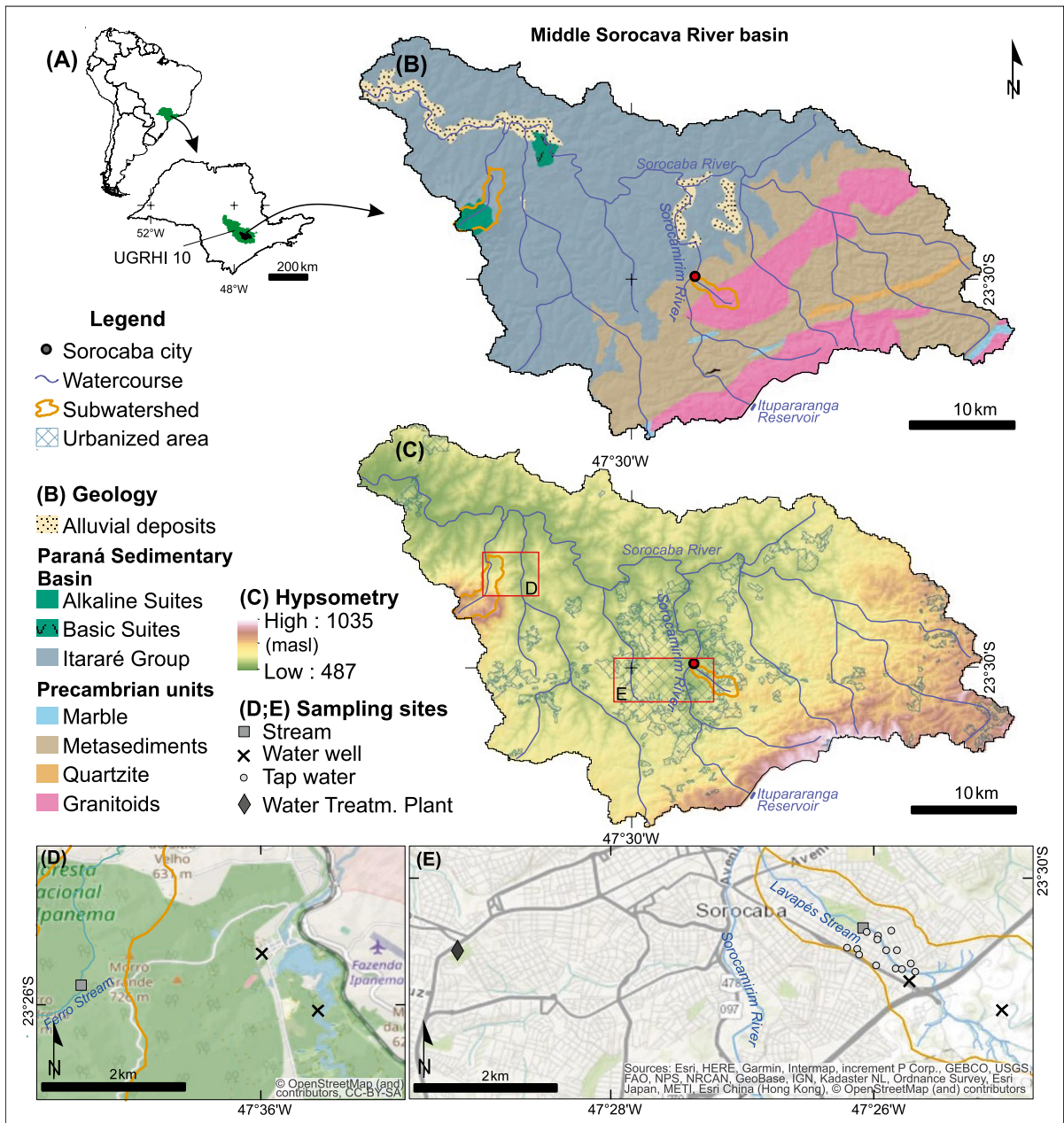
## General settings

The two watersheds selected for this study (SOR and FLONA) are located in SRb, which is in turn situated in the central-southern portion of the State of São Paulo. SRb is part of the Middle Tietê-Sorocaba UGRHI-10, which is one of the 21 water resources management units of the state. Draining an area of about 5,300 km<sup>2</sup>, SRb totally or partially comprises 18 municipalities, supplying water for about 1.5 million inhabitants (FAT & FABH-SMT, 2016).

Two climate types predominate in SRb, according to the Köppen–Geiger climate classification (Peel et al., 2007): subtropical (Cwa) and humid subtropical (Cfa). The mean temperature is 21.4 °C and the mean annual rainfall is about 1,300 mm and mostly concentrated in the summer, which lasts from October to March, while the period from April to September is characterized by a dry and cold climate (Silva & Silva, 2016).

SRb drains two distinct geological compartments. The eastern portion of the basin, where Sorocaba city is located, is dominated by phyllites, quartzites, and metasedimentary rocks of the São Roque Group and granitic rocks of the Embu Complex (Godoy et al., 1996). The western portion, where FLONA is located, is inserted in the Paraná Sedimentary Basin, predominating outcrops of the Itararé Group and basic and alkaline igneous rocks related to the Serra Geral Formation (DAEE, 2005; Petri et al., 1996) (Fig. 1). The two main aquifers of the study area are the fractured aquifer or Precambrian Aquifer System (hereafter PAS), developed in crystalline rocks of the SRb eastern portion, and the porous aquifer or the Tubarão Aquifer System (hereafter TAS), encompassed by the Itararé Group.

The average thickness of the TAS in outcrop area is of about 300 m that increases significantly westwards (Ezaki et al., 2020). Due to the multi-layering and interfingering of the sedimentary layers, the TAS is one of the most complex hydrogeological units of the Paraná Basin. Despite groundwater flow is preferentially controlled by the primary porosity of the sedimentary rocks that constitute TAS, structural discontinuities can also



**Fig. 1** (A) Location of the Sorocaba River basin (SRb) in South America, in the State of São Paulo and in the Middle Tietê-Sorocaba basin. (B) Simplified geological map (modified after DAEE & UNESP, 1980). (C) Digital Elevation map (m a.s.l.) extracted from the Digital Shuttle Radar Topography

Mission (SRTM) Data Elevation Model (available at: <http://dds.cr.usgs.gov/srtm/>). Red rectangles indicated in this map represent the FLONA area (D) and the SOR area (E). (D) Detail of the FLONA area and location of sampling points. (E) Detail of the SOR area and location of sampling points

influence water movement throughout the unit. These discontinuities are associated with lithological heterogeneity and layering, which attribute

anisotropy characteristics to TAS and create semi-confinement and/or confinement conditions (DAEE, 2005; Ezaki et al., 2020).

This geological compartmentation has consequences on the geomorphology of the study area. The western portion is characterized by the Atlantic Plateau landforms, with altitudes ranging from 800 to 1,000 m a.s.l., mainly comprising convex hill tops and very eroded valleys, with slopes dipping more than 20%. The SRb eastern compartment is encompassed by the Paulista Peripheral Depression, where the relief is flatter, constituted by tabular and large convex hill tops, with altitudes about 650 m a.s.l., and slopes dipping less than 10% (Ross, 1997) (Fig. 1).

The Lavapés catchment (SOR) is located south-east of Sorocaba (Fig. 1). It is divided in two urban compartments by the Raposo Tavares highway, which connects Sorocaba to São Paulo city. The SOR upper portion is characterized by low urban occupation, isolated reforested fragments, and intense mineral activity (granite exploitation), while the SOR lower portion is occupied by a high-density residential zone. The soil in this portion is predominantly impervious, as a result of urban occupation. Granitic and meta-sedimentary rocks predominate in the SOR upper and lower portions, respectively (Fig. 1).

The Ferro micro-basin (FLONA) is located *ca.* 20 km northwest of Sorocaba. The Ipanema National Forest is an Environmental Conservation Unit created in 2000. It is covered by one of the most important Atlantic Forest remaining vegetation in the State of São Paulo, occupying an area of about 50 km<sup>2</sup> (Fávero et al., 2004). The upper and lower Ferro micro-basin drains alkaline rocks and the Itararé Group sedimentary rocks, respectively (Fig. 1).

## Methods

Precipitation data obtained from meteorological stations located in Sorocaba (WMO Code: 83,851) and in the Ipanema National Forest (INMET Code: A713-Sorocaba) were used to assess 2019 and historical (1994 to 2020) trends (data available on: <https://bdmep.inmet.gov.br/>).

River water samples were collected biweekly from January to December 2019, both in SOR and FLONA (Fig. 1). These samples were preferentially collected in the middle of the river channels about 30 cm depth, to avoid stagnant water at the margins. Two groundwater samples representing TAS were collected in January 2019 from 120 m-deep wells

(PA03FL and PA04FL) drilled in FLONA, yielding flow rates of *ca.* 20 m<sup>3</sup>.h<sup>-1</sup>. Other two groundwater samples representing PAS were collected from 100 m-deep wells (PA01SOR and PA02SOR) drilled in SOR, yielding flow rates of *ca.* 30m<sup>3</sup>.h<sup>-1</sup>, respectively in November and December 2019 (Fig. 1). Two samples from the Sorocaba treatment plant (one at the entrance and the other at the exit of the treatment system) and 14 tap water samples were collected in SOR in November 2019 to characterize the isotopic composition of the Sorocaba water supply system (Itupararanga reservoir and water supplied to the population).

All samples were filtered in the field using a 0.45- $\mu$ m cellulose acetate syringe filter and stored in 25 mL HDPE bottles. In order to prevent isotope fractionation, air headspace was avoided, and the bottles were stored at 5 °C.

Isotopic determinations were conducted at the Environmental Isotopes Laboratory (LIA) of the Groundwater Research Center (CEPAS) of the Geoscience Institute of São Paulo University, and at the LabEcoh/INPE in São José dos Campos (Brazil), using a Cavity Ringdown Spectrometer L2130i Isotopic H<sub>2</sub>O (Picarro), and results reported as ‰ relative to the Vienna Standard Mean Ocean Water (VSMOW). To avoid memory effect, seven injections were made for each sample, and the three initial injections were discarded. The secondary standards SP1 ( $\delta^2\text{H}$ : -2.20 ‰ and  $\delta^{18}\text{O}$ : -1.43 ‰), SP2 ( $\delta^2\text{H}$ : -26.70 ‰ and  $\delta^{18}\text{O}$ : -4.39 ‰), and SP3 ( $\delta^2\text{H}$ : -70.40 ‰ and  $\delta^{18}\text{O}$ : -9.88 ‰) were used to normalize the results to the VSMOW2-SLAP2 scale. The results were treated using the software LIMS for Laser (IAEA & USGS, 2016). The analytical precision was:  $\pm 0.9$  ‰ (1 $\sigma$ ) for  $\delta^2\text{H}$  and  $\pm 0.09$  ‰ (1 $\sigma$ ) for  $\delta^{18}\text{O}$ .

Deuterium excess (hereafter *d*-excess) was calculated according to Eq. (1), as defined by Dansgaard (1964):

$$d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O} \quad (1)$$

The *d*-excess was used to assess sample storage protocols such as evaporation losses and ensure the quality of the isotopic determination. This check allowed to discard from the analysis the sample SOR (FEB-1) that has presented a very low value of *d*-excess (+0.5‰).

Rainwater seasonal isotopic variations were analyzed on the basis of monthly rainfalls collected in Rio Claro city (hereafter RC) (February 2013 to December 2018), available in the Global Network of Isotopes in Precipitation (GNIP) database (access by: [http://www-naweb.iaea.org/napc/ih/IHS\\_resources\\_isohis.html](http://www-naweb.iaea.org/napc/ih/IHS_resources_isohis.html)). The local meteoric line used is the available in the GNIP database:

$$\delta^2H = 8.35 \pm 0.13 * \delta^{18}O + 14.51 \pm 0.66 \quad (2)$$

The reference values used in this study are calculated based on the available GNIP data set, encompassing samples collected between 2013 and 2018: (i) annual weighted mean:  $-5.9 \text{ ‰}$  for  $\delta^{18}O$  and  $-32.8 \text{ ‰}$  for  $\delta^2H$ ; (ii) rainy season (October–March) weighted mean:  $-7.7 \text{ ‰}$  for  $\delta^{18}O$  and  $-44.9 \text{ ‰}$  for  $\delta^2H$ ; (iii) dry season (April–September) weighted mean:  $-4.6 \text{ ‰}$  for  $\delta^{18}O$  and  $-21.3 \text{ ‰}$  for  $\delta^2H$ .

Precipitation data obtained from a meteorological station located at the *Centro de Análise e Planejamento Ambiental*, São Paulo State University at Rio Claro ( $22^\circ 23'S$ ,  $47^\circ 32'W$ ) were used as reference for rainwater isotopic composition. Historical precipitation data include the period from 1994 to 2020, and the Kruskal–Wallis (Kruskal & Wallis, 1952) non-parametric test was applied to test statistical differences ( $p$ -value:  $<0.05$ ) when comparing Rio Claro, FLONA, and SOR data, in order to validate the use of isotopic ( $\delta^{18}O$ ,  $\delta^2H$  and  $d$ -excess) data.

### The isotope mixing model

In this study, the Bayesian mixing model approach was used to identify proportional contributions from water sources to streamflow. This model allows to identify proportional contributions, account for uncertainties and the use of isotope data from multiple sources (Gokool et al., 2018; Ma & Song, 2016). Estimations were performed using the stable isotope mixing model package in R (simmr), developed to solve mixing equations for stable isotope data using a Bayesian statistical framework (Parnell, 2019; Parnell et al., 2013).

To determine the proportional contributions from water sources, the model requires three sets of input data as a minimum. In this study,  $\delta^2H$  and  $\delta^{18}O$  values for all river water samples and the mean values (considering the standard deviation) for rain- and groundwater.

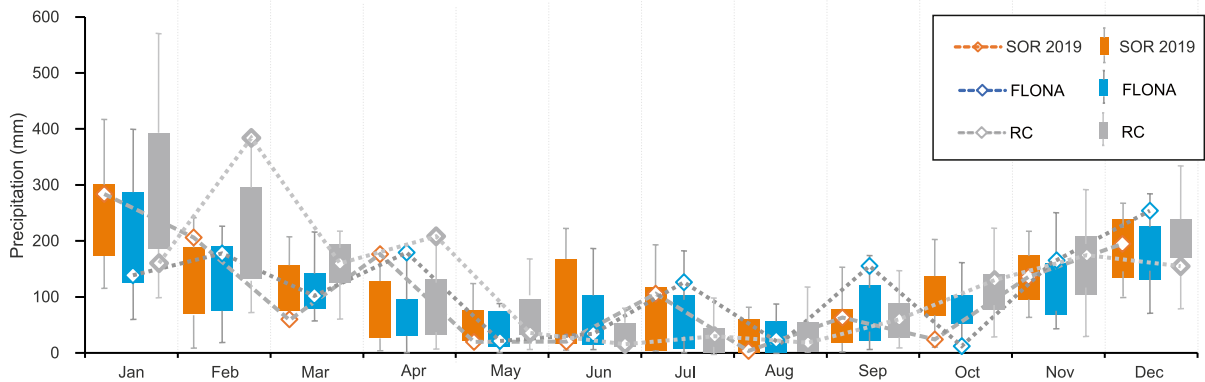
The proportional contributions of each source to streamflow were subsequently determined using a Markov Chain Monte Carlo function (MCMC) to estimate the proportions of the various water sources (Parnell, 2019). In the Bayesian context, MCMC repeatedly assesses water proportion values and estimates the values that best fit the data representing different sources. The simulations produce plausible contributions of rain and groundwater (in terms of proportions) to streamflow and return a posterior distribution representing a true probability density of data (Brum et al., 2019; Parnell et al., 2013).

## Results

### Precipitation

The monthly precipitation data at FLONA and SOR watersheds during 2019 yielded an evident seasonal distribution, following the pattern observed for a long-term monthly precipitation (Fig. 2). The rainy season (October to March) encompassed about 65% of the annual precipitation, reaching 1,391 mm at FLONA and 1,293 mm at SOR, which are values comparable to the historical annual precipitation (1,191 mm at FLONA and 1,345 mm at SOR). Precipitation in April and July reached values higher than the average values; however, the precipitation rate was closer to the third quartile values (126.3 and 105 mm, against 55 and 60 mm for FLONA and SOR, respectively).

This clear division in wet and dry season is associated with two main climatological features: the South American Convergence Zone (SACZ) that represents an area of greater convective activity, with a wide range of cloud cover, humidity, and heavy rainfall during the Brazilian summer (Kodama, 1993), and the South America Summer Monsoon system (Liebmann & Marengo, 2001; Marengo et al., 2012; Reboita et al., 2010). These regional meteorological features also act in RC, resulting precipitation during 2019 with a seasonal distribution similar to the observed in FLONA and SOR, despite the higher total amount of 1,487 mm, when compared to FLONA and SOR values. The Kruskal–Wallis test revealed no statistical differences in precipitation ( $p$ -value=0.8863 for the historical data, and  $p$ -value=0.9538 for the 2019 precipitation). The



**Fig. 2** Comparison between the historical (bars) and 2019 (dashed lines) monthly precipitation data at Rio Claro (grey), FLONA (blue), and SOR (orange)

combination of the statistical test and the influence of the same climatological system indicate that the adoption of the isotopic composition observed in RC (ca. 150 km far from SRb) was valid.

During 2019, the RC rainwater isotopic composition ranged from  $-9.39$  to  $-0.56$  ‰ (mean  $-5.09 \pm 2.60$  ‰ and weighted mean  $-6.36$  ‰) for  $\delta^{18}\text{O}$ , from  $-60.3$  to  $+12.6$  ‰ (mean  $-24.8 \pm 22.4$  ‰ and weighted mean  $-35.9$  ‰) for  $\delta^2\text{H}$ , and  $d$ -excess from  $+12.2$  to  $+22.1$  ‰ (mean  $+12.2 \pm 2.4$  ‰ and weighted mean  $+15.9$  ‰), exhibiting a seasonal distribution similar to the historical data, i.e., more depleted rainwater during the wet season and more enriched rainwater during dry season. However, when compared to the historical data, a more enriched rainwater was observed in January 2019 and a more depleted rainwater during the late summer and early winter of 2019 (Fig. 3A). Isotopic composition aligns along the local meteoric water line (LMWL) (Eq. (2), Fig. 3B).

#### Isotopic composition—FLONA

The isotopic composition of the FLONA surface waters was very stable along 2019, ranging from  $-6.38$  to  $-7.51$  ‰ (mean  $-7.27 \pm 0.22$  ‰) for  $\delta^{18}\text{O}$ , from  $-37.6$  to  $-47.0$  ‰ (mean  $-45.3 \pm 1.8$  ‰) for  $\delta^2\text{H}$ , and  $d$ -excess from  $+12.4$  to  $+14.1$  ‰ (mean  $+12.9 \pm 0.4$  ‰). No tendency of enrichment or depletion was observed during that year, despite the local  $\delta^{18}\text{O}$  enrichment observed for the sample collected in July 2019, probably related to the rain that fell before sampling, and the  $d$ -excess variations during the first half of the sampling period (Fig. 4).

The isotopic composition of the groundwater collected from the two wells at FLONA (representing the porous aquifer TAS) yielded values similar to the average value for surface water:  $\delta^{18}\text{O}$  of  $-7.78$  and  $-7.28$  ‰,  $\delta^2\text{H}$  of  $-50.3$  and  $-46.9$  ‰, and  $d$ -excess of  $+11.9$  and  $+11.3$  ‰, respectively, for wells PA03FL and PA04FL.

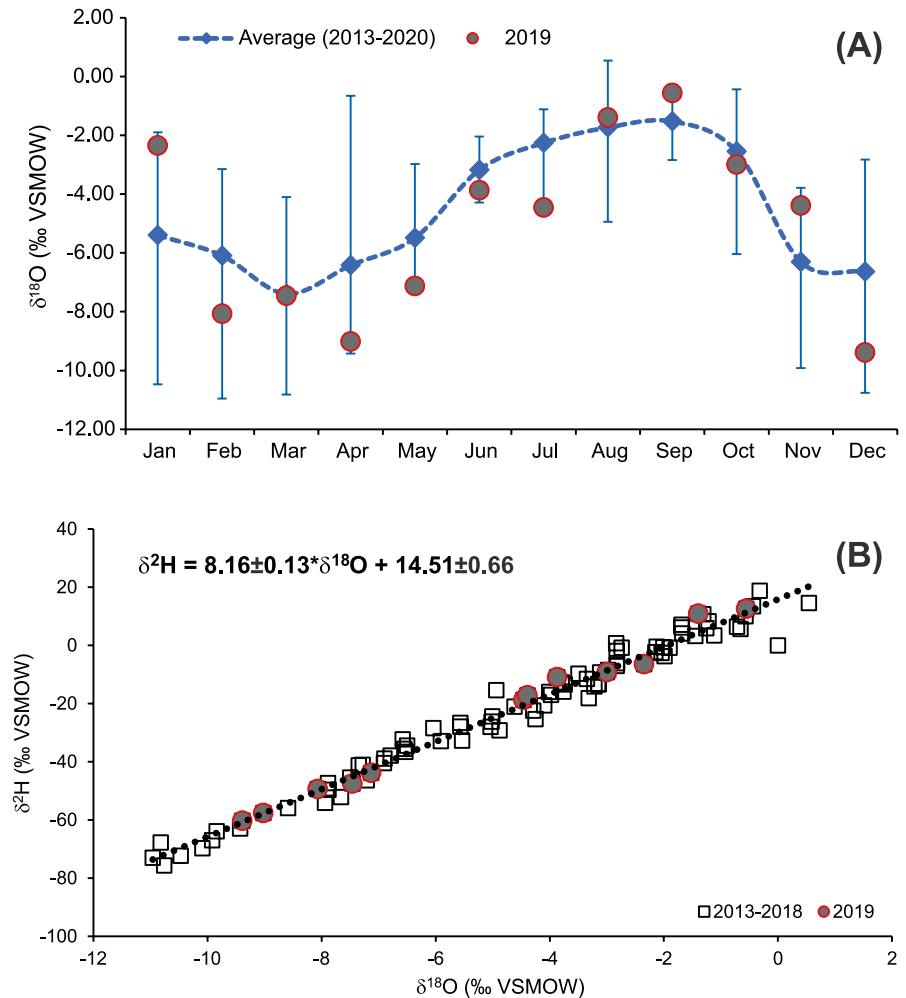
The application of the Bayesian mixing model indicated that the proportional contributions of rain- and groundwater to the Ferro streamflow (FLONA) are, respectively,  $14.1 \pm 11.2\%$  and  $85.9 \pm 11.2\%$  (Fig. 5). Despite the model could not depict the influence of individual rain events, it represents an average picture of the contributions along the year, indicating the great influence and connection between groundwater and surface water in FLONA.

#### Isotopic composition—SOR

The isotopic composition of SOR surface waters was more enriched than that of FLONA and varied considerably during the sampling period, with  $\delta^{18}\text{O}$  values ranging from  $-5.33$  to  $-3.88$  ‰ (mean  $-5.02 \pm 0.38$  ‰),  $\delta^2\text{H}$  values ranging from  $-34.4$  to  $-23.9$  ‰ (mean  $-31.2 \pm 2.4$  ‰), and  $d$ -excess ranging from  $+7.1$  to  $+10.2$  ‰ (mean  $+8.9 \pm 1.0$  ‰) (Fig. 4). A little tendency of progressive depletion was observed for  $\delta^{18}\text{O}$  associated with an increase in  $d$ -excess, which exhibited a strong inverse correlation with  $\delta^{18}\text{O}$  ( $r = -0.80$  and  $p$ -value  $< 0.01$ ).

The isotopic composition of the groundwater collected from two wells in SOR (representing the fractured aquifer PAS) was more depleted than surface

**Fig. 3** (A) Comparison between the rainwater historical monthly isotopic composition (line and bars indicating the variation) and 2019 isotopic compositions (red circles). (B) Dual isotope diagram for the rainwater isotopic composition (squares) and 2019 values (red circles). Dotted black line represents LMWL available at GNIP data base ( $\delta^2\text{H} = 8.35 \pm 0.13 * \delta^{18}\text{O} + 14.51 \pm 0.66$ )



water, but more enriched than the porous aquifer TAS, with  $\delta^{18}\text{O}$  of  $-5.90$  and  $-5.98$  ‰,  $\delta^2\text{H}$  of  $-34.4$  and  $-37.3$  ‰, and  $d$ -excess of  $+12.5$  and  $+10.1$  ‰, respectively, for wells PA01SOR and PA02SOR.

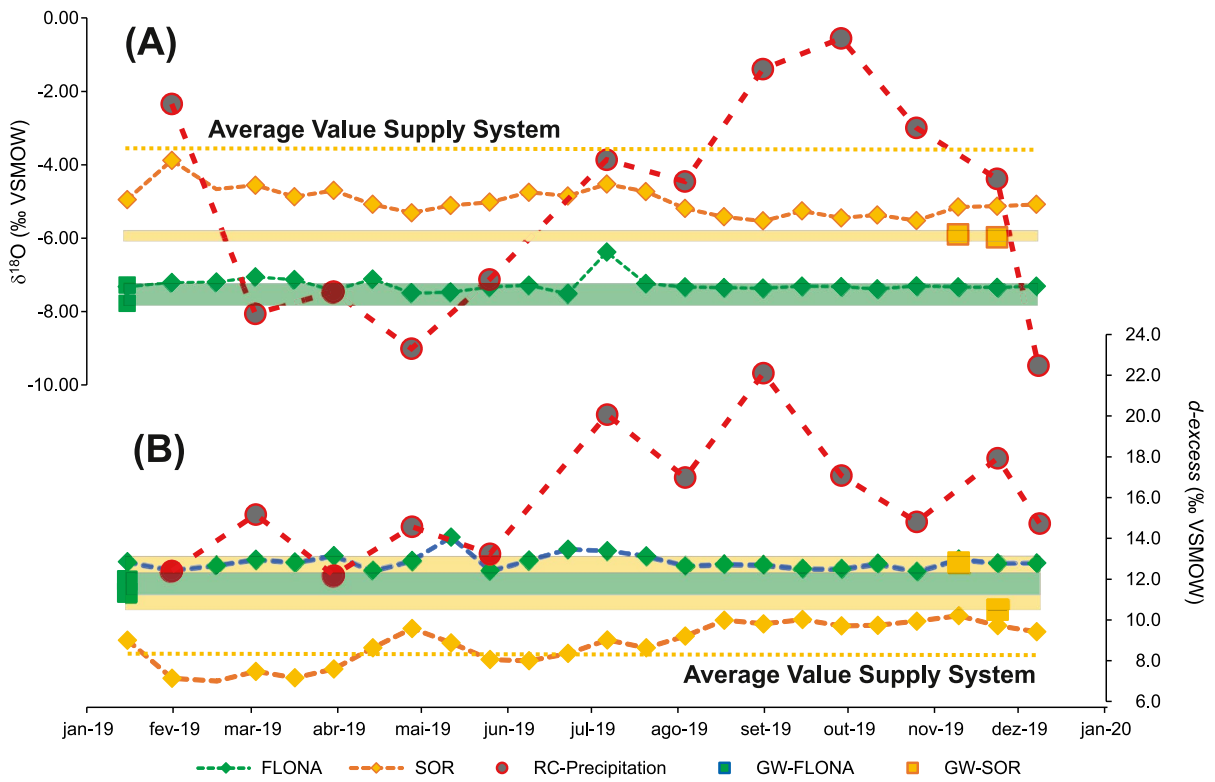
Samples collected at the entrance and exit of the Sorocaba treatment plant yielded the following isotopic compositions:  $\delta^{18}\text{O}$  of  $-3.82$  and  $-3.74$  ‰,  $\delta^2\text{H}$  of  $-23.01$  ‰ and  $-22.88$  ‰, and  $d$ -excess of  $+7.6$  and  $+7.0$  ‰, respectively. Similar values were also observed for tap water ( $n = 14$ ) collected in residences located in SOR.  $\delta^{18}\text{O}$  ranged from  $-3.86$  to  $-3.72$  ‰ (mean  $-3.81 \pm 0.03$  ‰),  $\delta^2\text{H}$  from  $-22.99$  to  $-21.89$  ‰ (mean  $-22.37 \pm 0.31$  ‰), and  $d$ -excess from  $+7.97$  to  $+8.5$  ‰ (mean  $+8.1 \pm 0.2$  ‰) (Fig. 4).

Contributions to SOR streamflow estimated using the Bayesian mixing model approach indicated the highest contribution from groundwater

( $47.1 \pm 10.9\%$ ), when compared to precipitation ( $16.9 \pm 12.1\%$ ) and losses from the water supply network ( $35.9 \pm 3.8\%$ ) (Fig. 5). Despite the SOR stream water isotopic composition varied a little more than in FLONA, the contributions from precipitation throughout the year seem to be quite similar, whereas the contribution from leakages complements that from groundwater in SOR.

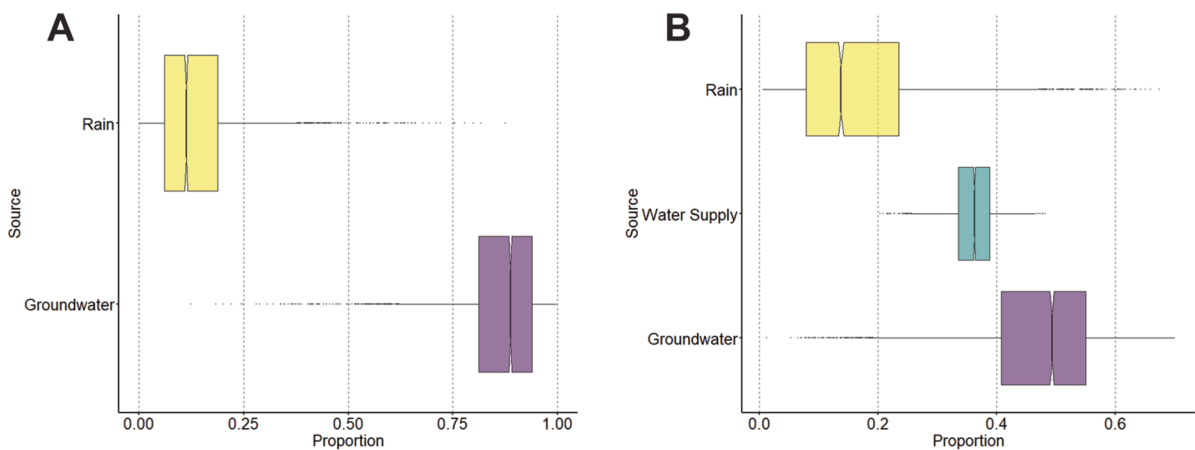
## Discussion

The seasonal pattern observed in the rainwater isotopic composition is directly related to the atmospheric system acting over the study area, as recognized in other sites in Southeastern Brazil (Gastmans et al., 2017). The characteristic depletion observed



**Fig. 4** Temporal variation of  $\delta^{18}O$  (A) and  $d$ -excess (B) in precipitation (red dots and line), surface water at FLONA (green diamonds and line), and SOR (orange diamonds and lines). Individual values of groundwater isotopic composition for the two watersheds are presented (green squares for FLONA and

orange squares for SOR). Orange lines represent the mean value for water from the water supply network (treatment plant and residences) for the SOR watershed. Empty rectangles (green for FLONA and orange for SOR) represent the range of values obtained for groundwater



**Fig. 5** Multiple-source (groundwater, rain, and water supply system) contributions to streamflow according to the Bayesian mixing model based on (A) FLONA and (B) SOR isotopic compositions

during the rainy season is associated with the establishment of the South Atlantic Convergence Zone (SACZ) and the transport of vapor emanating from the Amazonian Forest, which also causes  $d$ -excess values higher than the GMWL. On the other hand, the most enriched rainwater is observed during the driest months and is related to the period of scarce humidity coming from the Atlantic Ocean and to the decrease in evapotranspiration in the Amazonian Forest, coupled with lower continental surface temperatures and incursions of cold fronts (Santos et al., 2019a, b). These changes in moisture sources and transport pattern could be responsible for the higher  $d$ -excess values observed during the dry season.

The modulation observed in the rainwater isotopic composition was not recognized in the surface water isotopic composition in FLONA and SOR, despite the large differences observed between the watersheds, for both surface and groundwater. FLONA surface water yielded depleted values when compared to SOR (mean  $\delta^{18}\text{O}$  of  $-7.3$  and  $-5.0$  ‰, respectively) (Figs. 4 and 6). Despite the differences in isotopic compositions, the importance of groundwater discharge to streamflow in both watersheds is highlighted (Fig. 5).

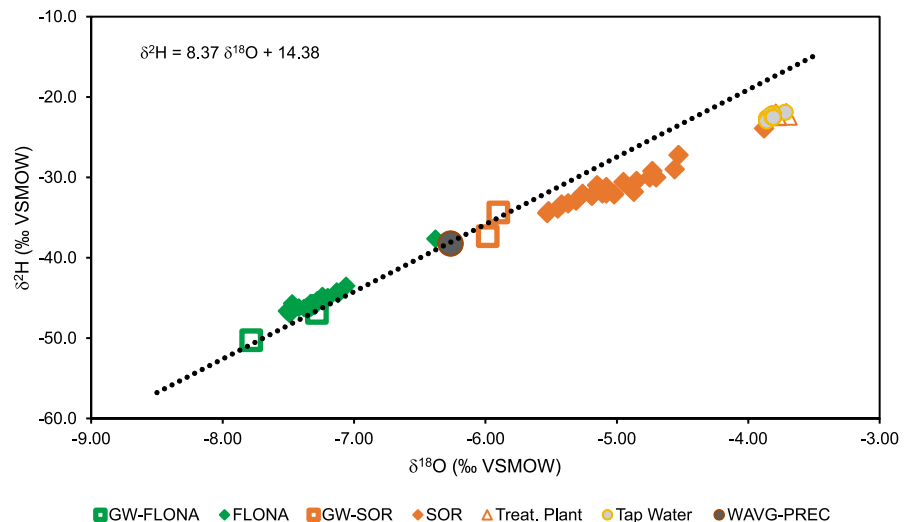
Differences observed in groundwater isotopic compositions seem to be most related to the hydrogeological framework of the watersheds, which is reflected in the aquifer recharge and water flow through the aquifer. Despite the differences in FLONA and SOR headwater elevation (900 versus 600 m a.s.l.,

respectively), altitude effect is not the most plausible explanation for the depletion observed in groundwater from FLONA (about  $-1.5$  ‰ for  $\delta^{18}\text{O}$ ) that represents an altitude gradient higher than the observed in other tropical regions, 0.5 ‰/100 m in this case against 0.1–0.2 ‰/100 m in Costa Rica, for example (Sánchez-Murillo et al., 2017).

The FLONA groundwater isotopic composition ( $\delta^{18}\text{O}$  of ca.  $-7.5$  ‰) is similar to that observed by Ezaki et al. (2020) in the TAS upper portion, characterized by Ca- $\text{HCO}_3$  types and with residence time of up to 10,000 years. According to these authors, recharge is biased by intense rainfalls occurring during the wet season, in a mechanism similar to that proposed by Jasechko and Taylor (2015). These values are in agreement with the rainwater isotopic composition observed during the summer in Rio Claro (Fig. 4) (Santos et al., 2019b, c), and were directly related to the humidity recycled from the Amazonian Forest and the influence of the convective activity related to SACZ, which explains the more  $\delta^{18}\text{O}$  depleted rainwater in the recharge zones in most part of the sedimentary aquifers from Southeastern portion of Brazil (Chang et al., 2020).

However values of  $d$ -excess in groundwater was lower than surface water in FLONA and from the precipitation in RC during the wet period, that can reveal an old groundwater, recharged under a little different climatic conditions, meanwhile in accordance with the residence time obtained for TAS upper portion groundwater.

**Fig. 6** Dual-isotope ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) diagram for the SOR and FLONA watersheds, encompassing all collected samples. LMWL (dotted line) was included as reference



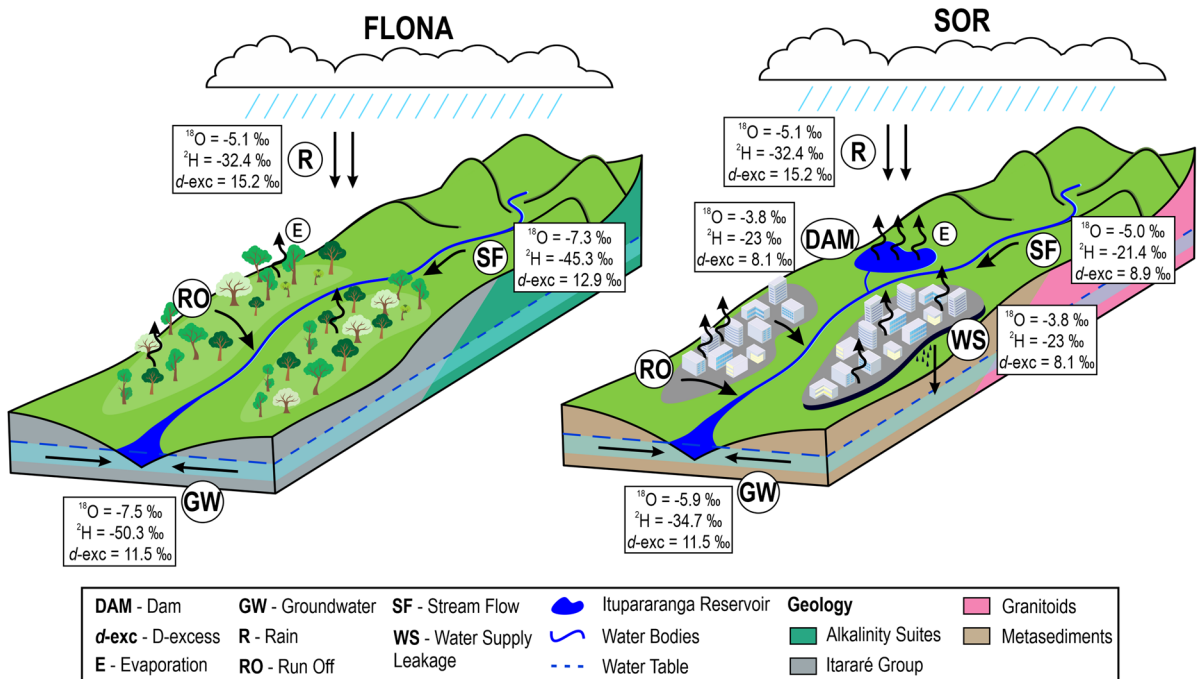
On other hand, the isotopic composition of the SOR groundwater stored in PAS is similar to that measured in the same aquifer and samples from wells located north of SOR by Santarosa (2020). This composition is also very close to the mean value obtained for the rainwater isotopic composition (Fig. 6). This similarity reflects the contribution of precipitation along the year, associated with the fast circulation of water in fractured aquifers (Clark & Fritz, 1997; Jasechko, 2019). In both PAS and TAS, the position of the groundwater relative to LMWL and the *d*-excess values (about + 12.0 ‰) indicate no evaporation during recharge, as well as no contamination due to leakages from the water supply network.

The strong enrichment observed in the isotopic composition of the Sorocaba treatment plant and tap water (i.e., the SOR water supply system) is also evidenced by the *d*-excess values (mean *d*-excess of + 8.1 ‰), which reflects the primary effect of evaporation occurring in the Ituparanga reservoir (Fig. 1). This isotopic fingerprint persists throughout the water distribution system and represents a consistent tracer to assess the impact on streamflow in the urban zone

caused by the insertion of a new source in the hydrological system.

The urbanization that led to the impermeabilization of the soil surface and the construction of an underground water supply network modified streamflow in the urbanized watershed, by complementing the contribution of groundwater discharge with contributions associated with losses in the water network (Jameel et al., 2016, 2018). Isotopic compositions measured in SOR surface water corroborate this hypothesis. The acceleration of the water flow caused by urbanization, as previously estimated by Soulsby et al. (2014), as well as changes of the soil structure due to the installation of pipelines, created preferential pathways for water originated from leakage of distribution network that discharge directly in the river channels.

Considering the variations in isotopic compositions observed in different water sources and the processes related to these variations, a conceptual model was developed for both watersheds, which is synthesized in Fig. 7. In FLONA, the main water source for the Ferro stream is groundwater, characterized by a depleted isotopic composition caused by the aquifer



**Fig. 7** Conceptual model summarizing streamflow contributions and hydrological processes for the FLONA and SOR watersheds. The isotopic composition presented in the figure is the mean of values measured in each contributing source

recharge biased by more intense rainfalls, with no evidence of evaporation.

In SOR, groundwater represents the most important source for maintaining the Lavapés streamflow. The groundwater isotopic composition is more enriched when compared to that of the FLONA groundwater, reflecting the fractured aquifer recharge (PAS) along the year. The contribution from the water supply system is attested by the lowest *d*-excess values, associated with the evaporation of surface water stored in the Itupararanga reservoir.

## Conclusions

This study attests the functionality of the dual stable isotopes of water to trace and quantify different water source contributions to streamflow in urban and pristine watersheds. It also shows that the hydrogeological framework plays an important role in the hydrological processes and in water isotopic compositions, controlling aquifer recharge and storage of water that can be released to rivers. Also the contribution from leakage of water distribution networks in urbanized areas is unquestionable.

The importance of groundwater discharge to maintain streamflow is indubitable, and the headwater preservation, avoiding the soil impermeabilization caused by urbanization processes, as observed in the SOR watershed, seems to indicate that the upstream areas represent important contribution zones for the Lavapés stream. On the other hand, the lower SOR receives an important and constant contribution from the water supply system losses. The contribution associated with water evaporation in the Itupararanga reservoir is attested by isotopic data.

The low contribution from rainwater estimated by the Bayesian mixing model may be due to sampling frequency that was not able to capture the influence of individual rain events and does not reflect the observed seasonality of the rainwater isotopic signature, especially in the pristine (FLONA) watershed. The results indicate the necessity of another sampling strategy to capture the real influence of runoff due to extreme and concentrated rain events, in both watersheds, as well as the implementation of a river gauging network to measure the discharge on the rivers and contribute with data to supply hydrological models, that can estimate the proportions of

surface runoff, interflow (or leakage from water supply network) and base flow, serving as a comparison for the isotopic measurements. On the other hand, it could be observed that the introduction of a third water source discharging in rivers, represented by the losses of water distribution system, introduces a large variability in the water isotopic composition in urban environments.

The results presented here allowed to identify an effect of urbanization on streamflow in urban zones: the impact of leakage from the underground water supply system, which represents *circa* 35% of the contribution to streamflow along the year in SOR. The approach involving the dual stable isotopes of water and monitoring network in a coupled natural-anthropogenic and peri-urban watersheds allow the water managers and policy makers to have insights into the potential human impacts on water cycle, providing consistent information about possible water sources and contributions to stream flow maintenance, as well as making possible to estimate losses from water supply network.

**Author contribution** VGL designed and conducted field work, interpreted the data, and wrote and revised the MS. LVS preformed the Bayesian Modeling and revised the MS. LNG interpreted the data, wrote and revised the MS. LSB performed the isotopic analysis. CSQ interpreted the data and wrote and revised the MS. VTSM performed the isotopic analysis DG coordinated the project, designed field work, interpreted the data, and wrote and revised the MS.

**Funding** This research was funded by the São Paulo Research Foundation (FAPESP -Process 2018/06666-4), and by the International Atomic Energy Agency, grant CRP-19747, under the initiative “Stable isotopes in precipitation and paleoclimatic archives in tropical areas to improve regional hydrological and climatic impact models”, and CRP-F31006, under the initiative “Isotope Variability of Rain for Assessing Climate Change Impacts”. L.V.S. thanks FAPESP for the scholarship grant (Process 2017/13576-9), and L.N.G. and C.S.Q. thank the National Council for Technological and Scientific Development (CNPq) for providing M.Sc. scholarships (Processes 134432/2019-3 and 130944/2019-0).

**Data availability statement** Isotopic data set used in this research is available as a Supplementary Material submitted with this MS. Complementary information regarding precipitation rates and isotopic composition was cited in the MS.

## Declarations

**Conflict of interest** The research reported in the accompanying manuscript represents original work and presents results not previously published or under consideration for publication

and will not be submitted for publication elsewhere while under analysis of Environmental, Monitoring and Assessment. There are no conflicts of interest to disclose. All authors of the manuscript are aware of and approve the content and submission of the manuscript to Environmental, Monitoring and Assessment.

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