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GEOSCIENCES

Assessment of River-Aquifer Interaction and Nitrogen Contamination in an Agricultural Zone Located in the Guarani Aquifer System Outcrop Area

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Abstract: The excessive use of nitrogen fertilizers is responsible for an increase in nitrate concentrations in water bodies, which in the future could led to an irreversible contamination compromising the water resource quality. In this way, understand the water movement within a watershed and evaluate the impacts related to agricultural practices is relevant for water management, especially in an environmental fragile region, such as the outcrop area of the Guarani Aquifer. Water samples from a small watershed located at the Guarani Aquifer region in São Paulo state, representing surface water and groundwater discharge in riverbeds from two creeks, as well as groundwater (springs and wells) were collected for isotopic ratios ($\delta^{18}O$ e $\delta^{2}H$) and nitrate determination. The results indicated that the river flow is mostly supplied by groundwater discharge, and despite the observed concentrations of nitrate in groundwater reaching the creeks, the current scenario indicate contamination in the surface water, above the regulatory levels. Therefore, the expansion in sugarcane production increases the possibility that the released nitrate reaches high levels in the future in this watershed.

Key words: Contamination, Guarani Aquifer System, Nitrate, River-Aquifer Interaction, Water Resource

INTRODUCTION

The global demands on food and bioenergy require the implementation of more efficient agricultural practices regarding the crop's productivity, which has led to an increase in the use of nitrogen fertilizers (Bordonal et al. 2018, Liu et al. 2015). These current practices have impacted and contaminated numerous surface water bodies and aquifers by nitrate, above the acceptable concentrations for human consumption (Abascal et al. 2022, Galloway et al. 2004, Matiatos et al. 2021).

The complexity of water flow paths in small agricultural watershed associated to the excess of nitrogen-based fertilizer application and sources associated to manure from livestock production, produces different paths for nitrate contamination reach streams both via overland (runoff) or subsurface (groundwater) flows (Browne & Guldan 2005, Gilmore et al. 2016, Richards et al. 2021).

One of the many techniques used to increase the efficiency of the nitrogen fertilizers is the fertigation technique. Largely used in sugar cane production in Brazil, fertigation differs from conventional fertilizer application because it is applied to the crop through irrigation water. Many are the advantages of fertigation, such as: (i) increase the Nitrogen stock in the soil; (ii) accelerate the cycle of nutrients used in the crop; (iii) reduces labor and machinery costs; (iv) constitute a good option regarding the reduction of water footprint in bioenergy productions systems (Bordonal et al. 2018, Coelho et al. 2010).

However, if the soil has high drainage and infiltration capacity, fertigation may represent a risk regarding environmental aspects, because it can accelerate the arrival of contaminants to groundwater and surface water bodies through leaching (Jadoski et al. 2010). The nitrogen loads end up being carried away and temporarily stored in the upper portions of aquifers below agricultural lands and can reach the surface water connected to them (Puckett et al. 2011).

The interaction between the surface and groundwater represents a key point in the water management, playing an important role in the water availability and quality in rivers and aquifers (Kennedy et al. 2007). Since in tropical regions the groundwater normally discharges toward the rivers, therefore it is important to monitor their quality and degradation level (Resende 2002). The evaluation of surface water quality is essential to assess two critical issues: the present and the future impacts of groundwater discharge on surface water (Gilmore et al. 2016). In this way, knowledge of the water origin, the path it had taken and the time it remains in the watershed are key points to carry out a good hydrological study.

In areas where the application of nitrogen fertilizers has produced high nitrate concentrations, contaminated groundwater may be transported to streams (Gilmore et al. 2016). There is a need to study this phenomenon in regions where the connection between the surface and groundwater is already known, such as the Guarani Aquifer outcrop area in São Paulo state, Brazil (Batista et al. 2018).

Since nitrate concentrations in water becomes a concern in many parts of the world, several studies analyze the quality of groundwater related to nitrate contamination, some still look for its source (Egbi et al. 2020, Gilmore et al. 2016, Lee et al. 2020, Nejatijahromi et al. 2019). The nitrogen fluxes management has been a key step in determining whether the aquifer is contaminated, and the quantification of such fluxes becomes relevant to estimate the quantify of nitrogen is transferred from groundwater to surface water, mainly in rivers and recharge areas located in agricultural regions (Böhlke 2002, Gilmore et al. 2016, Spruill et al. 2004).

Temporal and spatial variations on stable isotopes ratios of water ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) have been used as a tool for water movement studies (Clark & Fritz 1997, Eastoe et al. 2018, Kendall & McDonnell 1998, Lachniet & Patterson 2009, Winnick et al. 2014), including those related to the aquifer-river interaction and recharge processes (Batista et al. 2018, Sánchez-Murillo et al. 2015, Santarosa et al. 2021), as well as to determine the origin of nitrate contamination in agricultural watersheds (Böhlke & Denver 1995). When comparing the isotopic compositions of surface water, groundwater, and precipitation from a study area, it is possible to understand how the water has behaved within this watershed (Martinelli et al. 2009, Batista et al. 2017, 2018, Gastmans et al. 2021).

The Upper Jacaré-Pepira Sub-Basin, located in the central portion of São Paulo state, is characterized by an intense agricultural active and it drains an important recharge area of the Guarani Aquifer. In this area the conversion of the land use to sugar cane cultivation is being observed in recent years (Projeto MapBiomas 2021), leading to the increase in using vinasse for soil fertilization purposes (Scarpe et al. 2016).

Despite the regional low level of nitrate concentration in surface water, locally high nitrate concentrations have been finding, indicating possible source of recent anthropic contamination and/or associated with agricultural activities (Batista & Gastmans 2015). Due to this scenario, it becomes necessary to know how agriculture is affecting or not the water of this watershed, and a scientific support is required to assess the flow of nitrogen towards the rivers by the groundwater discharge, that can be potentialized due to the increase in sugar cane crops area and the lack of control in vinasse application by the producers.

Therefore, the general purpose of this paper is to understand the river-aquifer interaction and quantify nitrate concentrations in the water of a small watershed inserted into Upper Jacaré-Pepira Sub-Basin, in the State of São Paulo in Brazil. Our results contribute to introduce a new approach to assess nitrogen contamination derived from fertigation in agricultural region on surface and groundwater, integrating different tracers (isotopic and chemical).

GENERAL SETTINGS

The study area is located in the central region of São Paulo state (Brazil), constituted by a small watershed located in the right side of the Jacaré-Pepira River (Figure 1), within the Brotas municipality. The Upper Jacaré-Pepira

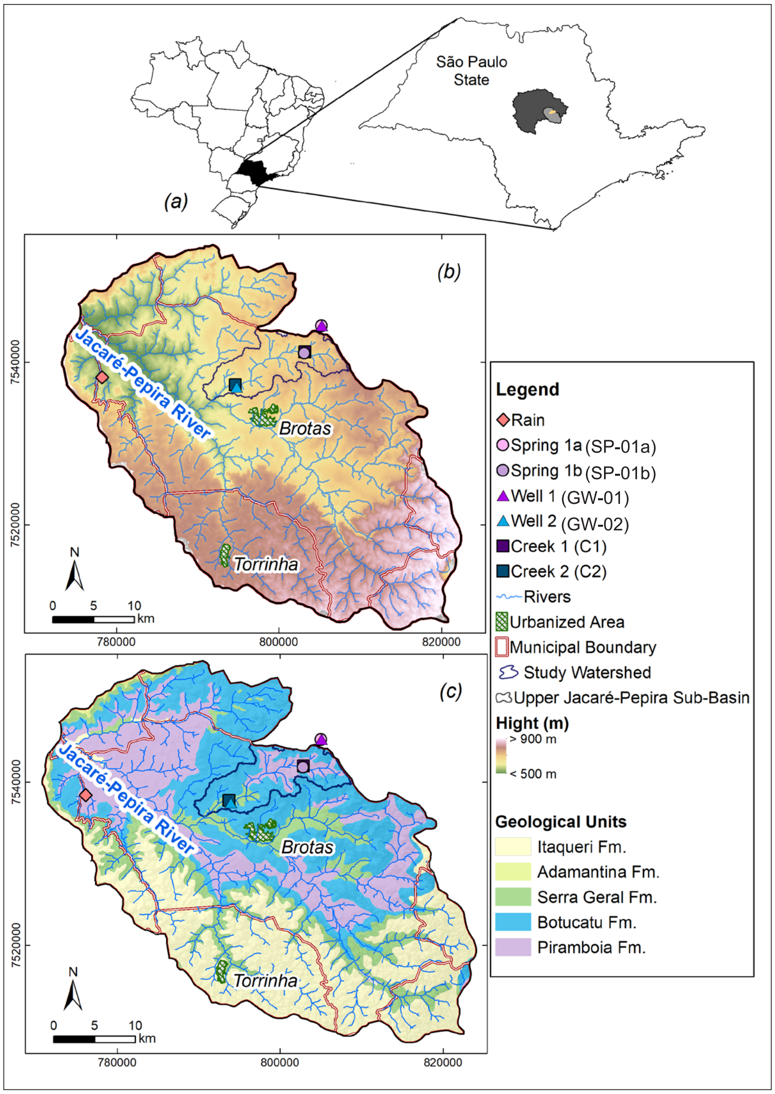

Figure 1. (a) Map showing the location of the Tietê-Jacaré Basin, Upper Jacaré-Pepira Sub-Basin and the small watershed studied, in the São Paulo state and Brazilian territory (b) Digital elevation model of the Upper Jacaré-Pepira Sub-Basin, showing the study area and the location of the sampled points (creeks, wells, springs and rain). (c) Geological map (extracted from DAEE-UNESP, 1980) of the Upper Jacaré-Pepira Sub-Basin showing the same information of the previous map.

encompass seven municipalities (São Pedro, Torrinha, Brotas, Dourado, Dois Córregos, Ribeirão Bonito and Itirapina) with a total population estimated up to 140,000 inhabitants (CBH – TJ 2018).

The economic activities developed in this zone are quite diversified, including agriculture and few transformation industries, as well as general services related to agricultural activities. The main crops are sugarcane, citrus and pasture areas for cattle and swine farming (CBH – TJ 2018, IPT 2006). It is also important to highlight the recent growing of the touristic activity at the city of Brotas, based on the Jacaré-Pepira River (Barrocas 2005, Silva 2006).

The increase in sugarcane production in the region is responsible by an intense conversion of the soil use over the last 50 years. Portions of land that were originally occupied by pastures and natural Savana vegetation are now occupied by sugar cane and orange crops, as well as by eucalyptus plated forests (Valezio & Perez Filho 2017).

The climate in the region is subtropical humid (Cwa), according to Köppen-Geiger classification (Peel et al. 2007), characterized by a rainy summer from October to March (rainy season), and a dry winter from April to September (dry season). The annual average precipitation is about 1,500 mm, while the annual average temperature is about 22°C, with the higher average temperature observed in January (about 30°C) and the lowest average temperature in July (about 12°C) (IPT 2006).

The Piramboia and Botucatu Formations, that constitute the geological framework of the Guarani Aquifer System (GAS), are the most important geological units outcropping in the watershed, making this region an important recharge area for the aquifer (Figure 1) (Gastmans et al. 2012a). The Piramboia Formation is composed by fine to medium aeolian and fluvial sandstones, with reddish to whitish color (Caetano-Chang 1997, IPT 2006). The contact with the overlying unit, Botucatu Formation is characterized by a sudden change in color and texture of the sediments (Gastmans et al. 2012b). The Botucatu Formation is composed by fine to coarse aeolian sandstones, with reddish color (Andrade & Soares 1971, Scherer 1998). A detailed description of these units can be found in Gastmans et al (2012a).

MATERIALS AND METHODS

Water samples from surface and groundwater were collected from October/2019 to July/2020 (Figure 1). Two points along the selected watershed (thereafter C-01 and C-02), were chosen to be representative for fluxes contributions within this small watershed. Samples from the surface water were collected about 15cm depth in the middle of the river channel from each point (thereafter SW-01 and SW-02, respectively), while samples representative from the aquifer discharge to the river were collected from the riverbed, about 30 cm depth using a piezomanometer designed by Kennedy et al. (2007) (thereafter DW-01 and DW-02). Samples were collected on monthly basis.

Samples representing groundwater were collected from wells (thereafter GW-01 and GW-02) and springs (thereafter SP-01a and SP-01b, collected once during the period, respectively in January and July/2020), used for domestical supply purposes, and before sampling, water flow was maintained for about 15-20 minutes to ensure the renewal of the water and make sure the sample represents the groundwater stored in the aquifer. The well GW-01 has 345 meter depth and GW-02 has 50 meter depth, chosen for representing respectively deeper and shallow portions of the Guarani Aquifer System in the watershed.

Samples for stable isotopes determination were filtered on site using a 0.45µm syringe filter, and due to the required sample volume and the presence of particulate material, samples for nitrate determination were filtered in laboratory the day after sampling using a PDPF 0.45µm filter. After collecting samples were stored under refrigeration (about 4°C), until the laboratory. Samples were collected for stable isotopes and nitrate determination, except for precipitation, which only have been taken for isotopic determination. It should be mentioned that due to the restrictions imposed by the COVID-19 pandemic samples were not taken in April and May/2020.

Precipitation has been collected in the Jacaré Pepira since 2016, however seeking the purposes stablished for this study only nineteen rain samples were evaluated. These samples were collected between October/2019 to July/2020 on weekly basis during the study period using a PALMEX rain collector (Gröning et al. 2012), especially designed to avoid evaporation. Samples were filtered through a 0.45 µm filter and immediately stored in 25 mL PEAD bottles capped with seal and cap to prevent fractionation. As reference the Rio Claro/SP meteoric water line was used a Local Meteoric Water Line (LMWL). Data were obtained from Global Network of Isotopes Precipitation (GNIP) (access by: http://www-naweb.iaea.org/napc/ih/IHS_resources_isohis.html), with monthly rainfalls collected (February 2013 to December 2018). The LMWL, calculated using the Ordinary Least Squares Regression (OLSR) method, used is:

$$\delta^{2}H = 8.35 \pm 0.13 * \delta^{18}O + 14.51 \pm 0.66 \qquad \text{Eq. 01}$$

Ground meteorological parameters (temperature, relative humidity and precipitation) were collected using a meteorological station (ATMOS 41) during the period of the study, installed at the same location where the rain sampler was installed, close to the Brotas city area. The data has been used to assist the local climate analysis.

The nitrate concentrations were determined just before the filtering procedures using a HACH DR 2800 spectrophotometer. Results are expressed in NO_3--N mg L^{-1}, and the limit of determination was stablished in 0.1 NO_3--N mg L^{-1}. These analyzes were conducted at the Center of Environmental Studies/UNESP Rio Claro laboratories.

The water stable isotope determination was part performed at the Hydrogeology and Hydrogeochemistry Laboratory of the Department of Applied Geology IGCE/UNESP Rio Claro and the isotopic ratios were measured using a cavity ring laser spectroscopy method and the results were expressed in relation to VSMOW (Vienna Standard Mean Ocean Water). The secondary standards were USGS-45 ($\delta^{2}H$ = -10.30‰, $\delta^{18}O$ = -2.24‰), USGS-46 ($\delta^{2}H$ = -236,0‰, $\delta^{18}O$ = -29.80‰) and river water (Cachoeira de Emas-CE); $\delta^{2}H$ = -36.1‰, $\delta^{18}O$ = -5.36‰). USGS standards were used to normalize the results to the VSMOW-SLAP2 scale, whereas CE was used as an internal quality control and drift control standard.

The nitrate and stable isotopes data were processed in Microsoft Excel 365, in which calculations of mean, minimum value, maximum value and standard deviation performed, as well as graphs and tables, were performed.

The evaluation of changes in land use due to the agricultural grow in the region, were carried out using data from MapBiomas Project (mapbiomas.org). Information about land use of the state of São Paulo in 1989, 1999, 2009 and 2019 was acquired to assess changed along studied region. All MapBiomas data are produced from pixel-by-pixel classification (30 x 30 m) of Landsat satellite images (30 m resolution), that are processed through a toolkit available to download on the Google Earth Engine platform. Later, the map was constructed using GIS software ArcMap 10.8 in UTM (SIRGAS 2000, Zone 22S) projection system.

RESULTS

Assessment on Land Use Changes

Changes in land use within the Brotas municipality was marked by a significant increase in agricultural crops between 1989 and 2019, directly associated to the economic growing observed in the region, mostly based on agricultural commodities. Sugarcane was the most outstanding crop during this period, especially after 1999 when the increasing is visibly noticeable (Figure 2). It had increased of almost 5 times in the planted area (Table 1), replacing areas that was occupied before with pastures.

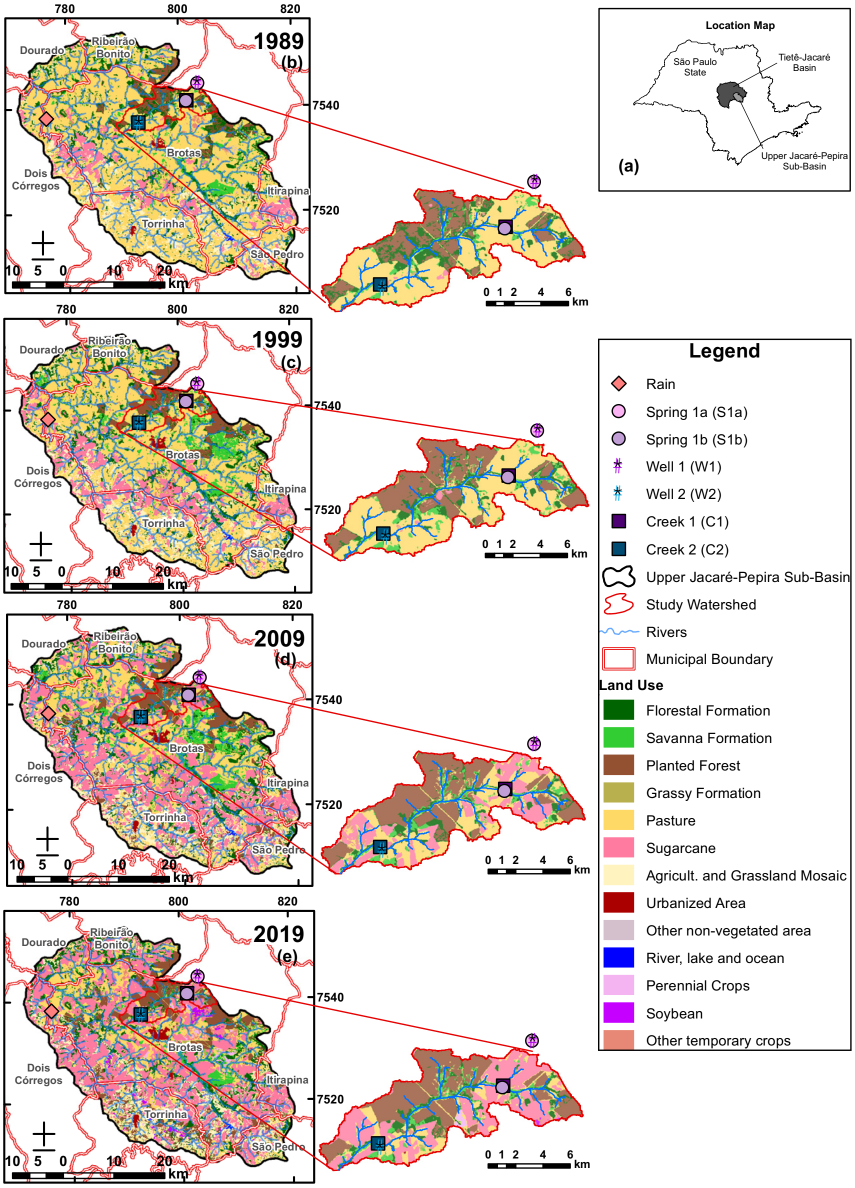

Figure 2. (a) Map showing the location of the Tietê-Jacaré Basin, Upper Jacaré-Pepira Sub-Basin and the small watershed studied, in the São Paulo state and Brazilian territory. (b, c, d and e) Upper Jacaré-Pepira Sub-Basin land use map, showing the land use in 1989, 1999, 2009 and 2019, respectively, with the studied watershed highlighted. Location of the sampled points (creeks, wells, springs and rain) are presented.

Perennial crops (coffee and citrus plantation and soybeans also had an increase within the analyzed period. Crops of soybean began to appear in 2000 and, like perennial crops, it gradually gained ground. However, they do not stand out in the region as much as the sugarcane crop.

With the increase in agriculture crops, the pasture areas, that were once prominent throughout the region were losing area. In 1989, forests (forest and savanna formations) occupied 20.79% of the total area, with the advance of agriculture, this area decreased to 15.78%, mostly replaced by sugarcane crops.

The watershed studied were mostly occupied by pasture areas in the beginning of the time series evaluated by MapBiomas project (1989). By 2019, these pasture areas were mostly transformed into sugarcane crops, especially in the lower portion of the watershed.

Climate Analysis

Climate in the area, during the studied period, is clearly marked by a dry season (from April to September) and a rainy season (from October to March), that concentrate most than 85% of the total precipitation observed during the period. The observed seasonality reflects on a large variation on daily precipitation rates, that ranged from no rain to 88.5 $mm.day^{-1}$ (mean 3.7±5.8 $mm.day^{-1}$).

These changes also were corroborated by variations on the relative humidity (RH), that ranged from 50.7 to 100% (mean 77.6±8.0%). A decrease in RH was observed during the dry winter season, while higher values were coincident with the summer season, when an increase in precipitation occurs. The average temperature during the studied period was 21.8±3.1°C, with maximum temperature about 28.1°C and minimum of 10.8°C. Compared with precipitation and RH, temperature showed little variation, with higher temperatures observed during the wet season and lower temperatures during the dry season, characterizing the arrival of autumn and winter (Figure 3).

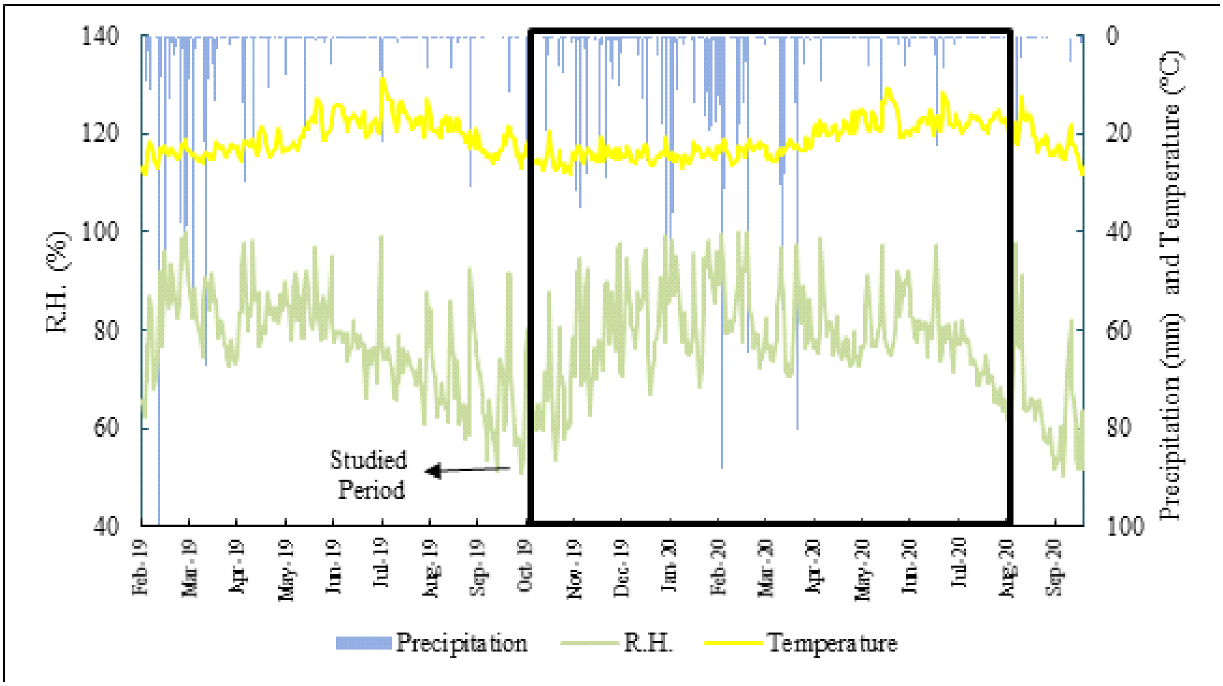

Figure 3. Daily rainfall, RH and temperature data with emphasis on the studied period.

Stable Isotopes

Isotopic composition of rain for δ^{18}O ranged from -11.84‰ to +0.18‰ VSMOW (mean of -5.73±3.54‰ VSMOW and weighted average mean -6.78‰ VSMOW), while δ^{2}H ranged from -79.7‰ to +16.7‰ VSMOW (mean of -33.6±27.3‰ VSMOW and weighted average mean -42.10‰ VSMOW), and *d*-excess ranged from +4.09‰ to +16.99‰ VSMOW (mean of 12.26±3.74‰ VSMOW and weighted average mean 12.16‰ VSMOW).

It was observed a clear seasonality and the isotopic ratios follows the precipitation volumes, confirmed by the weighted average values, biased by the highest volumes of precipitation. An enrichment on isotopic composition is observed during the dry season and when the precipitation volume increased, during summer season, it is observed a depletion in the isotopic values (Figure 4a). Despite the observed seasonality the amount effect is not clearly characterized. The calculated correlation factor between precipitation and δ^{18}O is -0.31, however the value is not significant (p-value = 0.15).

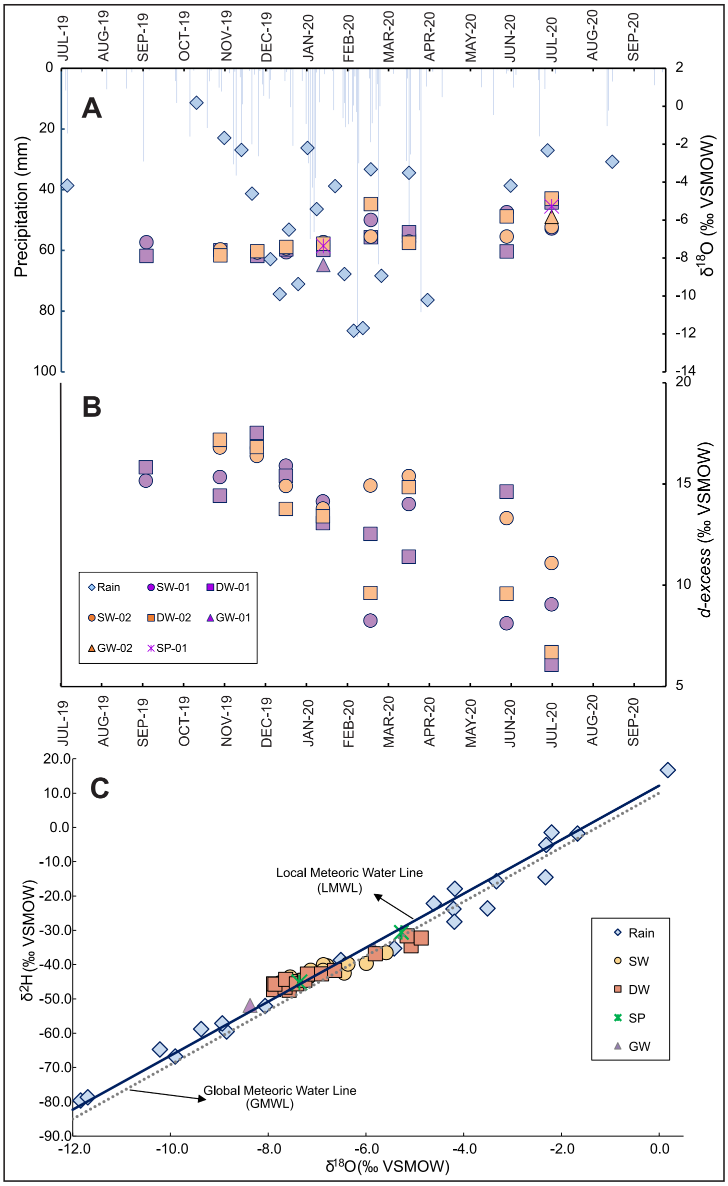

Figure 4. **(a) Daily precipitation rates (blue bars) and temporal variation of δ^{18}O for rain (blue diamonds), surface water (circles), riverbed discharge (squares), groundwater wells (triangles) and springs (cross mark). Sampling points are distinguished by colors (orange refers to C1 and purple to C2). (b) Temporal variation of *d*-excess values for surface water and riverbed discharge (symbology and colors are the same of previous figure). (c) Dual diagram δ^{18}O x δ^{2}H for surface water (circles), riverbed discharge (squares), groundwater wells (triangle) and springs (cross mark) from the two studied creeks, as well as rain samples (diamonds) collected during the studied period. For comparison the GNIP Local Meteoric Water Line (LMWL) from Rio Claro and the Global Meteoric Water Line (GMWL) are presented.**

Surface water (SW) in both sampling points showed a narrow range for the isotopic composition. It was observed an enrichment tendency during the second half of the monitored period, from March 2020 (Figure 4a). Isotopic compositions are similar in the upper (SW-01) and lower (SW-02) portion of the watershed. $\delta^{18}O$ ranged in SW-01 from -7.76 to -5.58‰ VSMOW (mean of -6.93±0.8‰ VSMOW) and in SW-02 from -7.71 to -6.37‰ VSMOW (mean of -7.14±0.4‰ VSMOW), while for $\delta^{2}H$ ranged from -45.7 to -36.5‰ VSMOW (mean of -42.4±3.1‰ VSMOW – SW-01) and from -45.3 to -39.8‰ VSMOW (mean of -42.6±2.1‰ VSMOW – SW-02). The *d*-excess values for SW presented a tendency to decrease along the studied period (Figure 4b) and ranged from 8.1 to 16.8‰ VSMOW (mean of 12.9±3.5‰ VSMOW – SW-01) and from 11.1 to 16.8‰ VSMOW (mean of 14.6±1.8‰ VSMOW – SW-02).

Riverbed discharge (DW) presented a variation similar to the observed in SW samples (Figure 4A), with the same enrichment tendency, and similar variations comparing the upper (DW-01) and lower (DW-02) portions of the watershed. $\delta^{18}O$ ranged in DW-01 from -7.89 to -5.08‰ VSMOW (mean of -7.20±0.9‰ VSMOW) and in DW-02 from -7.86 to -4.87‰ VSMOW (mean of -6.65±1.2‰ VSMOW), while for $\delta^{2}H$ ranged from -47.5 to -34.5‰ VSMOW (mean of -44.2±4.1‰ VSMOW – DW-01) and from -45.7 to -31.6‰ VSMOW (mean and standard deviation of -40.5±5.9‰ VSMOW – DW-02). The *d*-excess values for DW also showed a tendency to decrease along the studied period (Figure 4B) and ranged from 6.06 to 17.52‰ VSMOW (mean of 13.4±3.3‰ VSMOW – DW-01) and from 6.7 to 17.2‰ VSMOW (mean of 12.7±3.7‰ VSMOW – SW-02).

Groundwater represented by springs (SP-01) had presented values for $\delta^{18}O$ -7.36 and -5.27‰ VSMOW, for $\delta^{2}H$ values observed were, respectively -45.20, -30.61‰ VSMOW, while *d*-excess were 13.68‰ and 11.58‰, indicating a clear tendency of enrichment previously observed in SW and DW samples for C-01. Groundwater collected in wells (GW-01 and GW-02) presented, respectively, the following isotopic composition: for $\delta^{18}O$ -8.37 and -5.83‰ VSMOW, for $\delta^{2}H$, values observed were, respectively -51.90 and -35.74‰ VSMOW, while *d*-excess were 15.06‰ for GW-01 and 10.87‰ VSMOW for GW-02.

Nitrate Concentration

Nitrate concentrations have presented little variation in both portions of the studied watershed, with concentrations below the regulatory quality limits (<5.0 NO_3--N mg L^{-1}) (Figure 5). Nitrate concentrations in surface water from the upper portion of the watershed (SW-01) ranged from 0.4 to 0.8 NO_3^--N mg L^{-1}. The lowest concentrations were found in December/2019 and February/2020 (0.4 NO_3--N mg L^{-1}), while the highest concentrations were found in two samples (0.8 NO_3--N mg L^{-1}) collected in October/2019 and January/2020. These values were slightly below those founded by Batista and Gastmans (2015), at the same location. Slight lower concentrations were found in the lower portion of the watershed (SW-02), that ranged from 0.2 to 0.6 NO_3^--N mg L^{-1}, showing a tendency to increase along the studied period. The observed concentration is similar to the reported by Batista and Gastmans (2015) in samples collected in the same location (0.6 NO_3^--N mg L^{-1}).

Nitrate concentrations in riverbed discharge samples in the upper portion of the watershed (DW-01) ranged from 0.1 to 0.6 NO_3^--N mg L^{-1}. The concentration increased from the beginning of sampling period until January/2020 (that is also the month that started the rainfall increase), reaching the higher concentration (0.6 NO_3^--N mg L^{-1}), before and after that, the samples did

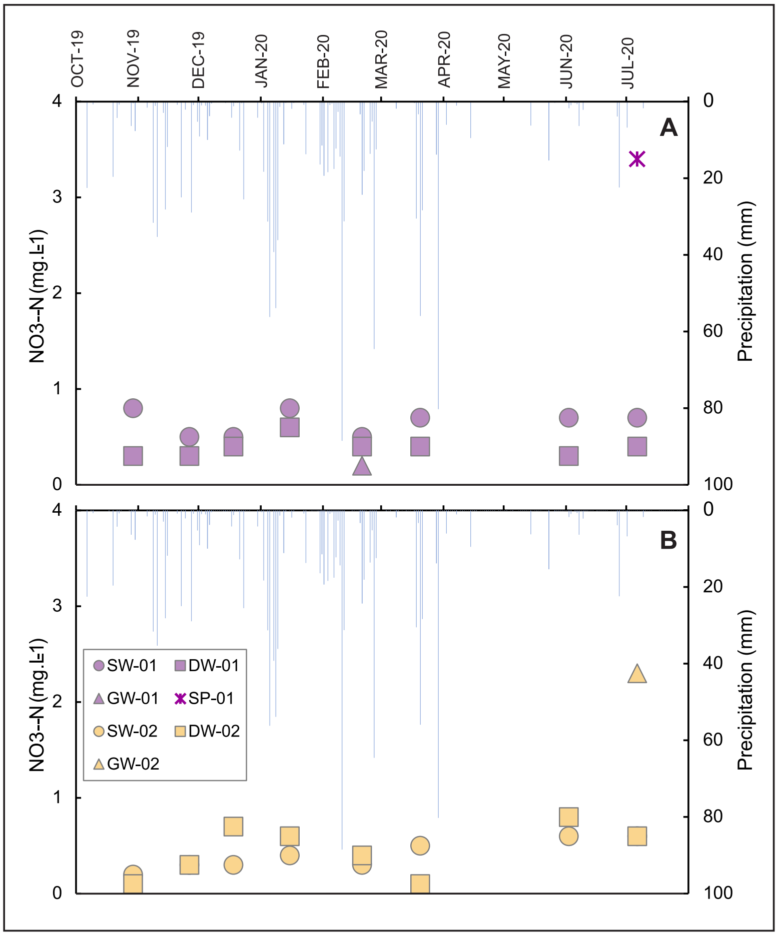

Figure 5. (a) Nitrate concentration in surface water (circles), riverbed discharge (squares), groundwater well (triangles) and springs (cross mark) and daily precipitation (bars in the upper portion of the graph) in C-01. **(b)** Nitrate concentration in surface water (circles), riverbed discharge (squares) and groundwater well (triangles) and daily precipitation (bars in the upper portion of the graph) in C-02. Sampling points are distinguished by colors (orange refers to C-01 and purple to C-02).

not show significant variations (Figure 5A). In the lowest portion of the watershed (DW-02) nitrate concentration ranged from 0.1 to 0.8 NO_3^--N mg L^{-1}. The samples showed two peaks, one with 0.7 NO_3^--N mg L^{-1} and the other with 0.8 NO_3^--N mg L^{-1}, in December/2019 and June/2020, respectively. The lowest concentration reached from DW at this point was 0.1 NO_3^--N mg L^{-1} in October/2019 (Figure 5B). It should be noticed the decrease in the nitrate concentration in the riverbed discharge water during the rainy months (January to March), and an increase in the dry months (June and July). At the end of the rainy season (March/2020), there is an inversion, where the SW had a higher concentration than DW, while for the upper portion the concentration observed in the SW samples were higher than the DW samples during all the studied period (Figure 5b).

The nitrate concentrations in groundwater have presented a large variation. GW-01 presented the lowest concentration (0.2 NO_3^--N mg L^{-1}), associated to the deepest, and most protected against anthropogenic contamination, portion of the aquifer, while in samples collected in GW-02 and SP-01, that represent the shallow portions of the aquifer, nitrate concentrations were 2.3 and 3.4 NO_3^--N mg L^{-1}, respectively (Figure 5).

DISCUSSION

Seasonal variations observed in isotopic composition of precipitation are directly associated to the main large scale climatic features acting over the central portion of São Paulo state. Depleted isotopic rainfall observed to occur during the wet season (October to March) are associated to the excess of moisture available in the atmosphere, as a result of the vapor re-evaporation originated from the Amazon basin. Due to the heating of the continental surface that increase the convective activity, Amazon moisture related to the convection generating the South Atlantic Convergence Zone (SACZ), while enriched rains observed during dry season were associated to periods of lower moisture availability from the Atlantic Ocean and an important decrease of evapotranspiration flux from the Amazonia Basin. Lower continental surface temperatures decrease the convective activity, resulting in rainfall that occurs by strong incursions of cold fronts (dos Santos et al. 2019a, b, 2022).

Isotopic composition of groundwater, represented here by samples collected in wells and springs, ranged in the same averaged values of precipitation observed during the wet season, indicating that the replenishment of the system is probably biased by these intense rainfall period, as observed in many other tropical regions (Jasechko & Taylor 2015, Jasechko 2019), however a temporal variation in isotopic composition of shallow portions of the aquifer is observed. Samples from SP-01, which was observed to be more depleted in January-2020 than in July-2020, respectively rainy and dry season (Figure 4A and C). It should be noticed that despite the increase in isotopic composition in July-2020, values do not reach the correspondent isotopic composition of precipitation during the dry period. This could be explained due to the amount of water stored in the aquifer, much higher compared to recharge rates, as well as the low rain rates observed during this season or the lag of time during the infiltration in the vadose zone.

Isotopic composition of surface water and riverbed discharge samples presented an enrichment along the period studied, and consequently, a decrease of *d*-excess (Figure 4a and b). The groundwater and surface water connection can be corroborated by the small differences between isotopic composition of SW and DW samples, especially during the dry season, when flows in the river are mainly maintained by groundwater discharge (Figure 4a). Between October and December/2019 and just after the rain season (March/2020) $\delta^{18}O$ values were very similar. This connection between groundwater and river discharge in the region was previously described and discussed by Batista et al. (2018).

Nitrate concentrations measured in SW and DW samples presented a similar behavior throughout the analyzed period, however it should be observed that nitrate concentrations observed at the lower portion of the watershed (Figure 5b), during specific periods of the year, during the rainy season, presented higher concentration of nitrate in the riverbed discharge than in the surface water. On other hand in the higher portion of the watershed (Figure 5A) the DW has presented nitrate concentrations lower than the SW. The possible explanations for these different behaviors can be related to the relative position of the sampling points, associated to the land coverage, because sugarcane crops are mostly concentrated in the downstream portion of the watershed (Figure 2E). The period of increasing nitrate concentration in DW samples can be associated to the vinasse application in the soil, that normally occurs just after the harvest (May to October). The lag time to nitrate contamination appears in the discharge is about one month, that is explained due to the sandy and highly permeable soil characteristic (Oliveira et al. 2021, Rocha et al. 2019). This hypothesis is corroborated due to the gradual decrease in the nitrate concentration observed in the following months (Figure 5b).

It is noticeable the changes in land use, especially during last 10 years, when sugarcane crops increased, mostly in the lower portion of the watershed. These changes in land use should modify the hydrological cycle. Changes in flow paths and infiltration rates were associated to the implementation of monocultures, that changes the path taken by water causing a decrease in infiltration rates, leading to a lowering of the water table in addition to modifying the frequency of transpiration and the hydrological flows of the site, transforming these areas, where monocultures have increased, more vulnerable to hydroclimatic and ecological disturbances (Levia et al. 2020). These changes could explain the previously observed pulses of nitrate concentrations in the river, as pointed out by Batista & Gastmans (2015), despite the forest and savanna coverage near the creeks had not a significant reduction since 1989 (Figure 2).

Considering this scenario of land uses changes and the impacts on water flow paths, connectivity between groundwater and river represents the main process responsible for the inputs of nitrogen in the water stream in the study area, because of the higher nitrate concentration observed in groundwater. A conceptual model was created (Figure 6) that shows the interaction between rivers and groundwater flows in the studied watershed. The model is a representation of the sampled points in this study (surface water, groundwater discharge, deep well, shallow well, springs and precipitation), the sugarcane crop that is remarkable in the region, as well as the variation of isotopic ratios and nitrate concentrations. The model is not represented in real scale, only in visual scale.

Groundwater associated to local flows, represented by springs, are more susceptible to anthropogenic contamination, whether by local agriculture or not, depending on how their area of contribution is located. If there was a higher contamination in the contribution area, the waters belonging to this flow will also present higher contamination. However, when this flow reaches the river, the level of this contamination is diluted, bring on the surface water a lower

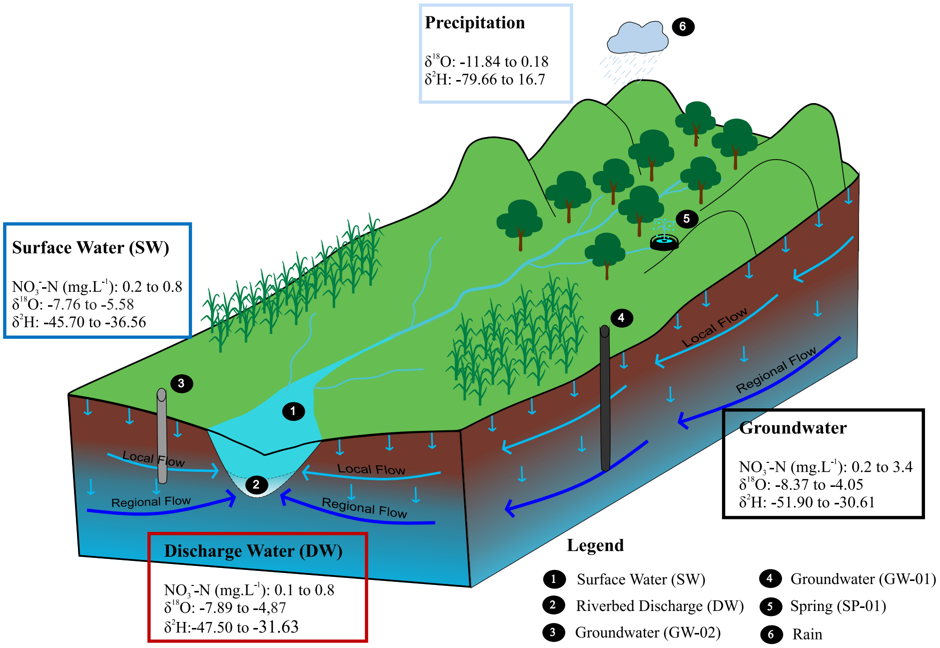

Figure 6. Conceptual model from the studied watershed with the representation of the sampled points. Surface Water, Discharge Water, Shallow Well, Deep Well and Spring, represents respectively SW, DW, GW-02, GW-01, SP-01 samples

concentration than the spring water and higher than the riverbed discharge. In this way, surface water represents a mixture of two end members: precipitation water and groundwater discharge.

Groundwater associated to regional flows paths are represented by wells and take a longer time to reach the river. Just like the recharge of this deep groundwater also takes a longer time to happen. The W1, being a deeper well, may represent water recharged in a past time and with different climatic conditions than the current ones, so its sample has lower concentration than the river and other groundwater samples.

The riverbed discharge represents a mixture of groundwater from local and regional subsurface flows. This mixture is confirmed by the isotopic ratios analysis (Figure 4A) where the concentrations of the groundwater discharge samples are presented with intermediate values between the surface and groundwater.

From the results it is possible to understand that the groundwater of the GW-02 has the highest concentration of nitrate because there is a time interval between this nitrate reaching the groundwater and then, through the regional flow, it reaches the river through its discharge. Therefore, it is believed that the regional flow, that is discharging into rivers, still represents water from a period prior to that found in the waters of the well. That is the reason to groundwater discharge has lower nitrate concentrations than the surface waters and the groundwater from GW-02 and SP-01.

The increase in nitrate concentrations observed in the DW-02, with two peaks in December/2019 and June/2020, probably were coincident with the flows generated by the vinasse application at the opening and before close the sugarcane crops. Which through leaching, the nitrate from the vinasse reaches the aquifer and through the local flow reaches the river a month before, as a contamination plume.

CONCLUSIONS

Our results show that the water flows in the watershed represents mixture of different sources as indicated by the water isotopologues, that highlighted the connection between groundwater and surface water, as well as the rain contributions for the total flows. Seasonality observed in isotopic ratios revealed the importance of groundwater discharge to maintain the fluxes in the channel, especially during the dry season when the volume of precipitation is lower.

Despite the nitrate concentration measured in the surface water and riverbed discharge did not show a currently nitrate contamination that exceeds the Brazilian regulatory, higher nitrate levels have been found in the shallow portions of the aquifer, which are directly connected to the river, that leads to the belief that this nitrate reached the aquifer in the past and is heading towards the creeks. Although the levels of nitrate in groundwater are not above the accepted limits for human consumption, it is recommendable a continuous monitoring in these levels.

With the agriculture activity enhance mainly based on the increase in production of sugarcane spreading through the region, shown by the land use data, in order to minimize the contamination risks for surface water, it is recommended the control over the applied nitrogen fertilizer load, following the norms of the fertigation. Because once in excess, the fertilizer components are not fully absorbed by the crop, so they can infiltrate into the water table and reach the groundwater, and/or being run off to surface waters.

Considering the small thickness of the vadose zone along the studied watershed, since the high numbers of springs observed and the existing connection between creeks and groundwater, this lag of time can be also attributed to a substantial amount nitrogen stored or moving slowly through the unsaturated zone above the water table.

Furthermore, in the case of a recharge area of an important aquifer system such as the Guarani Aquifer, must have even more care. Once this water is contaminated, the situation may become irreversible in the short term. A recommendation for future works refers to the importance to expand a network of monitoring wells, with samples analyzed periodically, to verify if the contamination in groundwater is increasing or not and, consequently, in surface waters. Therefore, carrying out a campaign to find out the residence time of water in this watershed could predict the arrival of this possible contamination.

Finally, this work reinforces the need to monitor all the waters in a watershed (surface waters and groundwater discharges), as well as aquifers, especially those located in agricultural regions in expansion. As seen, surface and groundwater are part of a set of waters, and when polluted or overexploited one of them, the other will also suffer the impact, and it may be shown in the present as well as in the future.

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CL has conducted the field and laboratory activities, interpretated the data and written the MS. LVB has reviewed the version of the MS. LNG has conducted the field and laboratory activities and made the maps. VS has reviewed the MS and discussed the isotopic data. CSQ has participated in the field and laboratory activities and reviewed the MS. DG has conduced the research, discussed the data, written and reviewed the MS