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Qualitative assessment in river and phreatic aquifer water in a rural watershed in the Atlantic Forest biome

Comportamento qualitativo da água de rio e aquífero freático de bacia hidrográfica rural do bioma Mata Atlântica

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ABSTRACT

Watersheds have different water compartments (surface, subsurface, and underground) connected by the soil-water interface. In order to be able to relate these compartments, monitoring data are necessary, such as the case of the Ribeirão Concórdia watershed, in Lontras, Santa Catarina (SC). This study aimed to evaluate the behavior and the correlation between rainfall-runoff and phreatic surface levels with chemical species concentrations in surface and groundwaters in a rural watershed. Data of 3 piezometers installed in the hydrographic basin were used: PZ2127, PZ3, and PZMC. The piezometers are equipped with hydrostatic level sensors. A fluviometric station is located adjacent to PZ2127 (near the catchment outlet). Concentrations of anions and carbon forms were analyzed in water samples (river and piezometers) taken every 2-3 weeks, from January 14, 2012, to December 23, 2016, totaling 103 samples. Correlations between daily data were verified using Pearson's correlation coefficient (ρ). The river presented a dilution effect, while the adjacent piezometer had the highest average concentrations of chemical species. Precipitation and chemical species concentration showed no seasonal pattern, with events/peaks throughout the year. Higher concentrations of carbon forms were found in the summer, while lower concentrations were observed in the winter. Positive correlations between concentrations of anions and carbon forms in surface and groundwaters were obtained.

Keywords: hydrographic basin; water quality; surface water; groundwater.

RESUMO

Bacias hidrográficas apresentam diferentes compartimentos de água (superficial, subsuperficial e subterrâneo) que estão ligados pela interface solo-água. Para conseguir relacionar esses compartimentos são necessários dados de monitoramento, como é o caso da bacia hidrográfica do Ribeirão Concórdia, em Lontras (SC). Este estudo avaliou o comportamento e a correlação entre o escoamento fluvial e a elevação da superfície freática, com concentrações de espécies químicas, em águas superficiais e subterrâneas em uma bacia hidrográfica rural. Utilizaram-se dados referentes a três piezômetros instalados na bacia hidrográfica: PZ2127, PZ3 e PZMC. Estes são equipados com sensores de nível hidrostático. Adjacente ao PZ2127 (próximo ao exutório), existe uma estação de monitoramento fluviométrico (R). Amostras de concentrações de ânions e formas de carbono foram coletadas no rio e nos piezômetros em uma frequência de 2–3 semanas, entre 14 de janeiro de 2012 e 23 de dezembro de 2016, totalizando 103 amostras. Correlações de dados diários foram verificadas por meio do coeficiente de correlação de Pearson (ρ). O rio apresentou menores concentrações das espécies químicas analisadas, enquanto o piezômetro adjacente apresentou as maiores concentrações médias dessas espécies. Precipitação e concentração das espécies químicas não exibiram padrão sazonal, com ocorrência de eventos/picos ao longo do ano. Formas de carbono apresentaram maiores concentrações nas coletas no verão e menores no inverno. Obteve-se correlação positiva entre as concentrações de ânions e das formas de carbono da água do rio e dos piezômetros.

Palavras-chave: bacia hidrográfica; qualidade da água; água superficial; água subterrânea.

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Introduction

Groundwater management requires an in-depth understanding of hydrological processes. Aquifers, for example, are influenced by meteorological conditions, runoff processes, human interventions, and geological characteristics at different spatial and temporal scales (Winter et al., 1998). The interactions of these water reservoirs play a decisive role in the quality of water bodies, and understanding them can provide information on sources and transport of pollutants in rivers and aquifers in watersheds (Guggenmos et al., 2011; Martinez et al., 2015).

Rural experimental hydrographic basins are environmental research observatories that enable enlightening hydroclimatic processes and the impact of human activities on water resources. Given the ever-expanding Brazilian agribusiness, it is vital to develop agricultural activities strategically, ensuring adequate quality and quantity of water for its various uses. Inadequate land use management and anthropogenic activities degrade aquatic systems, reducing the availability and quality of water resources (Santos et al., 2019). Pollution of these environments in rural areas occurs by contaminants resulting from agricultural activities, specifically pesticide and fertilizer application, and the risk of water contamination is usually associated with rainfall and the consequent transport of these substances (Soares et al., 2020). In this scenario, water quality can become limiting for sustainable development. Therefore, monitoring the qualitative parameters of this resource represents a crucial indicator to formulate public policies and apply control actions (Azevedo et al., 2016). Brazil has an excellent water potential; however, according to Santos and Hernandez (2013), it lacks sufficient quali-quantitative monitoring to support the expansion of knowledge about the dynamics of aquatic systems.

Water quality, where human actions exert great influence, is an increasingly recurrent issue due to the growth in demand, increased pollution, and the reduction of natural areas (Freitas, 2020). Monitoring water quality is a complex activity and requires a large number of resources. In Brazil, a growing number of actions to monitor surface and underground water has been currently observed, which expands the knowledge of the spatiotemporal dynamics of water quality in these reservoirs. Nevertheless, studies dealing with the qualitative behavior of these aquatic systems with a long period of monitoring and high frequency are scarce. For instance, regarding rural watersheds with family farming management, the scientific discussion lacks adequate information for establishing spatiotemporal standards in surface and groundwater quality. Analyses of the qualitative behavior of water from rivers and aquifers were developed by Guggenmos et al. (2011), Martinez et al. (2015), Kumar et al. (2017), Li et al. (2018), and Park et al. (2018). However, these studies generally have short monitoring periods and few samples, which hampers the temporal and exploratory interpretation of chemical species concentrations in water. Monitoring data enable the establishment of water quality indices (WQI) that aim to synthesize monitored parameters providing weights to the most important ones in a given region, helping the general public to interpret the data.

In this study, we investigated the behavior of chemical species concentrations in the interaction between piezometers and rivers, in a rural watershed in the Atlantic Forest biome, southern Brazil, in order to identify patterns and characteristics related to the use and occupation of the local land (small properties).

Material and Methods

Study area

The study was carried out in the Ribeirão Concórdia hydrographic basin, located in Lontras, Santa Catarina, Brazil. The hydrographic basin has its catchment outlet at 27°10’54.19” S latitude and 49°31’37.28” W longitude (Figure 1). It has an area of 30.93 km^2, with approximately half of it occupied by agricultural activities (Piazza et al., 2014). The distribution of land use and occupation is shown in Figure 1. Rural properties have a good distribution along the watershed and are characterized as small and medium-sized properties (Lubitz et al., 2013). In the region, practices of direct planting, minimum cultivation, and conventional planting with soil management are adopted. The main crops produced are maize, beans, irrigated rice, tobacco, tomato, and cabbage. The planted forests are composed of eucalyptus and pine, and the areas destined for pasture are characterized by perennial crops with the constant presence of cattle.

According to Strahler, the climate is subtropical with hot, humid summers and cold, dry winters. The average annual temperature and precipitation are 20°C and 2,000 mm, respectively. The climate is classified as Cfa, with an average temperature in the coldest month below 18°C and an average temperature in the warmest month above 22°C (Alvares et al., 2013). The hydrographic basin presents altitudes that vary between 300 and 900 m in relation to the sea level, and it is found, for the most part, above the Taciba unit (Paleozoic). The head area is located at the Rio Bonito (Paleozoic) unit (Piazza, 2019). The hydrographic basin belongs to the Itararé geological formation group, with intrusive granitic suites. One of its subgroups, located in the lower portion of this formation, is from the Rio do Sul formation, with dark gray shales and argillites. Above them, there are grayish diamictites, with a sandy matrix interspersed with very fine sandstones. These are covered by shales, usually varvites, argillites, rhythmites, and siltstones (EMBRAPA, 2004). The soils are derived from this geological formation and have the following distribution in percentage area:

- Cambisols: 62.2%;
- Argisols: 32.9%;
- Gleisols: 0.9% (Piazza et al., 2014).

Data

Phreatic level

Groundwater level data referring to 3 monitoring piezometers installed in the hydrographic basin were used. The piezometers were installed according to the different uses and occupations of the land, positions relative to the watershed, depths of impermeable soil layers, and distances from the river in order to assess the possible influence of these factors on the phreatic surface elevation and chemical species concentrations in groundwater. PZ2127 and PZ3 are located in pasture areas, while PZMC is located in an area covered by a riparian forest. PZ2127 is located close to the watershed catchment outlet (Figure 1). PZ2127, PZ3, and PZMC have depths of 5.1, 3.8, and 2.6 m and are located 35, 60, and 3 m away from the river, respectively. Their altimetric dimensions are 367, 372, and 433 m, respectively. The piezometers are equipped with hydrostatic level sensors connected to dataloggers, and groundwater levels were recorded every 15 min. The characterization of land use around the piezometers can be seen in Figure 2.

Fluviometric quota

Quota data were obtained from the fluviometric station (R) installed in the cross-section of the river, adjacent to PZ2127. This section features an automatic level sensor with a float-operated axis encoder, which recorded this data at 1-h intervals in a datalogger.

Precipitation

Rainfall series recorded in eight pluviographs (seven tipping-bucket rain gauges and one weighing rain gauge) installed in the hydrographic basin were used. The tipping-bucket and weighing rain gauges are installed at 1.5 m and 0.5 m from the ground surface, respectively. These devices performed readings every 5 min. Data were stored in dataloggers.

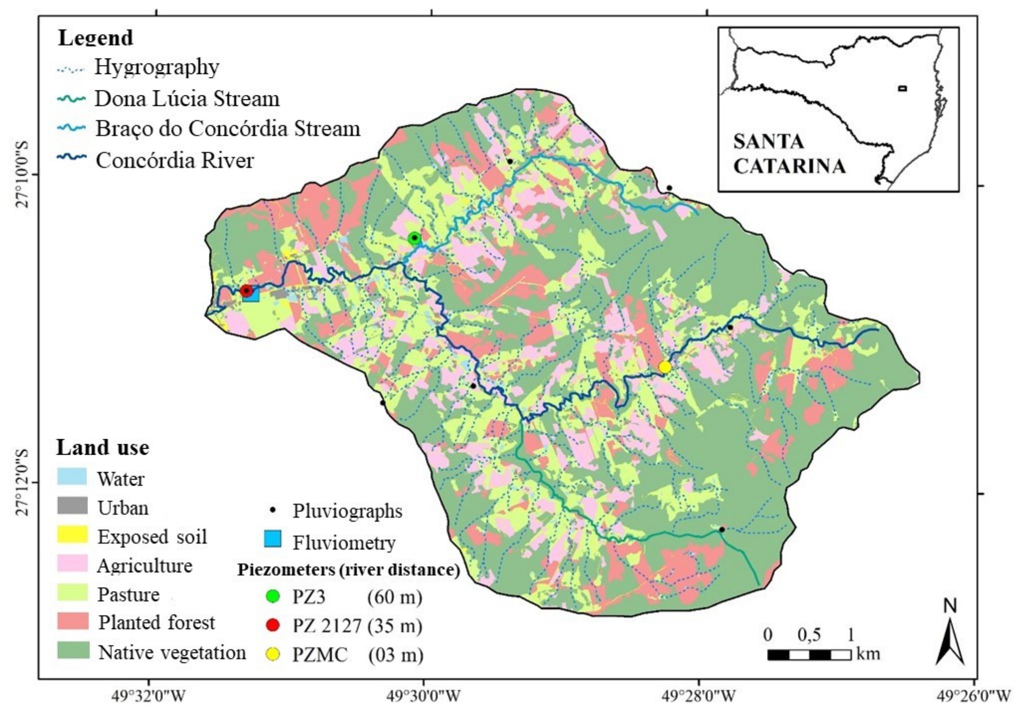

Figure 1 – Location of piezometers and land use and occupation distribution in the Ribeirão Concórdia watershed, Lontras, Santa Catarina, Brazil.

Figure 2 – Characterization of land use around the piezometers.

Chemical species concentrations in water

Chemical species concentrations in surface and groundwater were taken from sampling in the river (in the fluviometry measurement section - R) and piezometers (Figure 1). The collections respected the national standard established by NBR 9898 (ABNT, 1987) and took place every 2-3 weeks, totaling 103 samples. Collections in R were performed manually, and the samples were placed in polyethylene bottles. A syringe connected to a silicone tube was used to collect 100 mL water samples from the piezometers. After suction, the samples were also stored in polyethylene bottles (Figure 3). The first sample of each collection was discarded to clean the vials.

The concentrations of chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}) anions, and total organic carbon (TOC) and inorganic carbon (IC) were determined. The anions were analyzed using the Dionex AG4A ion-exchange chromatograph (DIONEX, 2010), and the carbon forms were quantified using the SHIMADZU TOC - V CPH Carbon Analyzer.

Data analysis

Groundwater levels, fluviometric quotas, precipitation, and chemical species concentrations in the water from January 1, 2012 to December 31, 2016 were used.

Temporal and exploratory analysis

A temporal analysis of monthly precipitation data and chemical species concentrations per compartment was performed, that is, for R, PZ2127, PZ3, and PZMC. An exploratory analysis of concentrations was carried out to understand the data set and significant variations thereof. Arithmetic mean and standard deviation were used. The means were subjected to analysis of variance (ANOVA) and compared using the Tukey test, with a significance level of 5%. Statistical tests were performed using PAST software (version 3.25). Calculations were performed on a monthly basis.

Figure 3 – Collection of water samples in the river using a piezometer.

Correlations

The correlations between phreatic levels and fluviometric quotas, both in daily frequency, with chemical species concentrations, and the correlations between concentrations per compartment were verified using the Pearson correlation coefficient (ρ). Statistical tests were performed using PAST software (version 3.25).

Results and Discussion

Temporal and exploratory analysis

The temporal variations in precipitation and chemical species concentrations in water from the river and piezometers (Figure 4) presented no seasonal pattern, with the occurrence of events/peaks throughout the year. None of the chemical species were correlated with precipitation. Carbon forms showed higher concentrations in summer collections and lower values in those conducted in the winter. Average TOC concentrations were 4.14, 2.85, 1.99, and 3.11 mg L^{-1} for summer, autumn, winter, and spring, respectively. As for CI concentrations, average values were 10.09 mg L^{-1} for the summer, 8.95 mg L^{-1} for the autumn, 7.34 mg L^{-1} for the winter, and 7.97 mg L^{-1} for the spring. According to Nascimento and Barbosa (2005), higher IC concentrations in the summer are related to intense precipitation, which carries a greater flow of particles from the surface to aquifers and rivers. Likewise, Kaufmann et al. (2009) assessed the Ribeirão Concordia watershed and found higher concentrations of IC and TOC in the summer, related to intense rainfall as well. However, higher soil temperature and moisture may also have benefited microbial activity and, consequently, contributed to higher concentrations of CI (Bayer et al., 2012).

The highest chemical species concentration peaks were observed in PZ2127, while the lowest values were found in R. The greater concentrations in PZ2127 can be explained by the larger drainage area, accumulating nutrient input. Feitosa and Manoel Filho (2000) also detected higher concentrations of chemical species near the watershed catchment outlet, justified by the slow characteristic of water movement and accumulation of chemical species in the flow direction. Another trait observed in the monitored watershed was the occurrence of lower chemical species concentrations in the river section compared to the piezometers. This result was expected since in free aquifers or with local recharge, the up and down movements in the unsaturated zone favor

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rock leaching and the transport of products present on the surface to the interior of the soil, contributing to higher concentrations of nutrients in groundwater (Silva and Migliorini, 2014). Another factor to be considered when explaining the differences in chemical species concentrations is the influence of the riparian zone in regulating the supply of nutrients from the saturated zone of the soil into surface water bodies, acting on nutrient absorption (Martí et al., 2000) and inducing the occurrence of biogeochemical transformations.

Table 1 shows the mean concentrations and standard deviations of chemical species in the river and piezometers. The values followed by the same letter for different compartments do not differ significantly from each other, according to ANOVA and Tukey post-hoc test with a significance level of 5%. For most parameters, river concentrations are statistically similar to those of the PZMC piezometer. On the other hand, the concentrations in piezometers PZ3 and PZ2127 present, for most parameters, statistically different concentrations from those measured in the river, with higher values. The PZMC piezometer located near the surface watercourse is directly influenced by it. The other two piezometers are far from the river. Thereby, their waters may not be affected by the river flow during a flood wave passage. The water quality of these two piezometers is influenced by land use in their contributing area.

Average Cl^- concentrations in the hydrographic basin were below 14.6 mg L^{-1}. Park et al. (2018), in an area with intensive agricultural activity, obtained average concentrations of 98.9 and 297.0 mg L^{-1} in surface water and 623.0 and 464.0 mg L^{-1} in groundwater. In a region with similar characteristics, Li et al. (2018) obtained an average Cl^- concentration of 219.7 mg L^{-1} in groundwater.

Regarding NO_3^- concentration in the Ribeirão Concórdia watershed, values varied from 2.94 to 15.86 mg L^{-1}. In an area of ag-

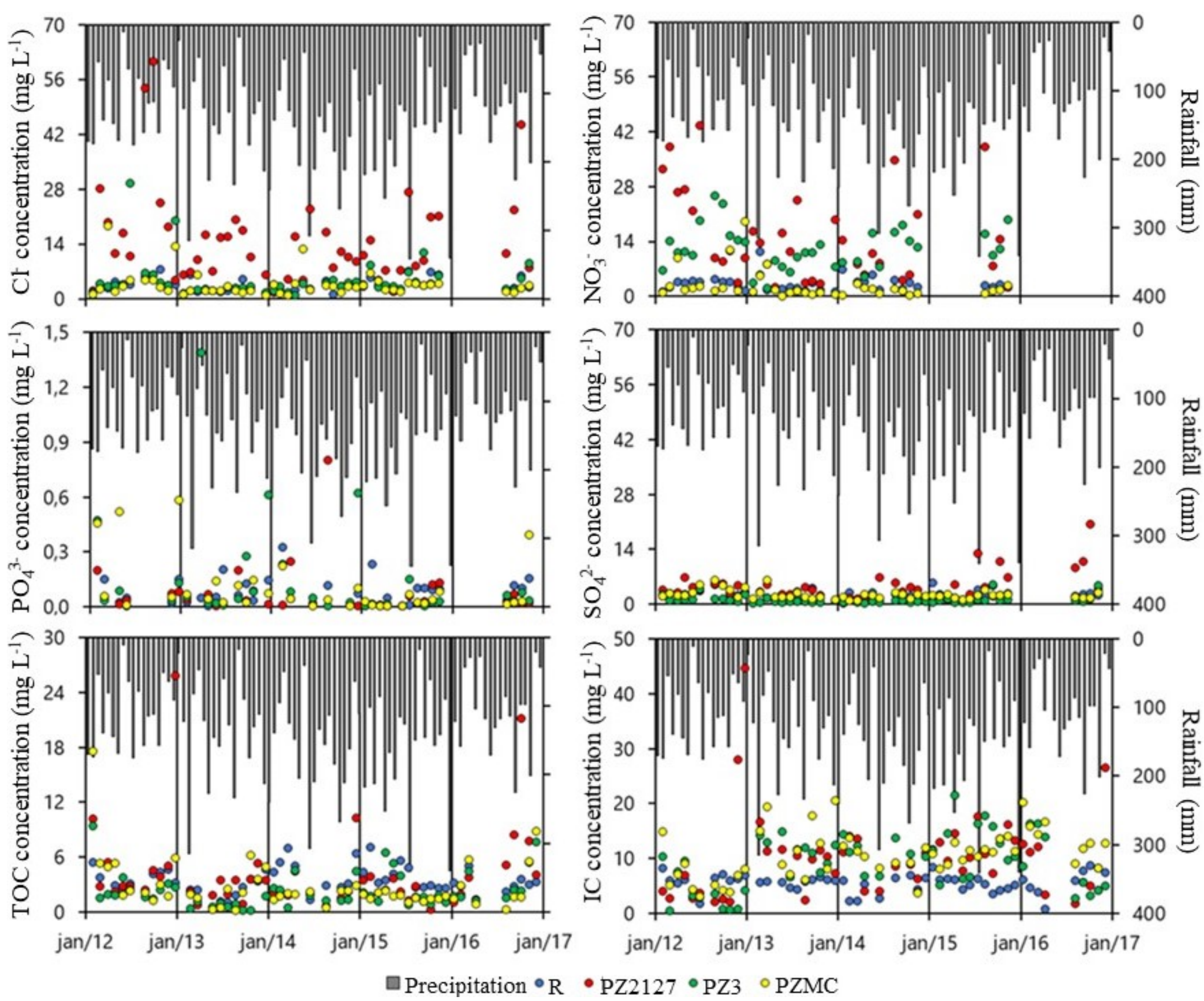

Figure 4 – Temporal variations of precipitation and chemical species concentrations in river water and piezometers.

ricultural intensification, Guggenmos et al. (2011) found average concentrations of NO_3^- around 46.00 mg L^{-1} in groundwater. Park et al. (2018), also in an area intended for agricultural activities, obtained average NO_3^- concentrations of 25.9 and 118.0 mg L^{-1} in surface water, and 575.0 and 265.0 mg L^{-1} in groundwater.

Average concentrations of PO_4^{3-} in the Ribeirão Concordia watershed were below 0.13 mg L^{-1}. Kumar et al. (2017) obtained average PO_4^{3-} concentrations of 4.90 and 4.80 mg L^{-1} in surface and groundwater, respectively.

The average concentrations of SO_4^{2-} did not exceed 4.11 mg L^{-1}. Park et al. (2018) found SO_4^{2-} concentrations of 53.00 and 164.00 mg L^{-1} for surface water, and 127.00 and 110.00 mg L^{-1} for groundwater. Guggenmos et al. (2011) and Li et al. (2018) obtained concentrations of 7.00 and 152.97 mg L^{-1} on average for groundwater, respectively.

The discrepancies between the average concentrations of Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} obtained in this study and those presented by other studies can be explained by the fact that the Ribeirão Concordia watershed has a predominance of extensive agricultural and livestock systems, unlike the other evaluated areas, characterized by the predominance of intensive agricultural activity.

In an overview (surface x underground), it is observed that the surface compartment (river) had lower average concentrations of Cl^- and IC, compared to piezometers, an effect resulting from the regulation of the riparian zone and the transport of products from the surface and interior of the soil to the groundwater, as

Table 1 – Mean concentrations and standard deviations of chemical species in river water and piezometers (mg L^{-1}).

Chemical species	Measurement	Compartments			
		R	PZ2127	PZ3	PZMC
Cl^-	Mean	3.3a	14.6b	4.5a	3.5a
	Standard deviation	1,7	12.2	4.8	3.2
NO_3^-	Mean	2.9a	15.9b	11.7b	2.6a
	Standard deviation	1,9	12.2	5.4	3.8
PO_4^{3-}	Mean	0.091a	0.131a	0.098a	0.072a
	Standard deviation	0.097	0.267	0.151	0.140
SO_4^{2-}	Mean	2.189a	4.111b	1.006c	2.359a
	Standard deviation	1.046	3.589	1.035	1.206
TOC	Mean	3.415ab	3.943a	2.294b	2.711ab
	Standard deviation	1.481	4.562	1.911	2.776
IC	Mean	5.451a	10.473b	9.803b	8.973b
	Standard deviation	1.662	4.262	7.511	5.190

described above. The same results were found by Piazza (2019) at the same sites. The location factor of the piezometers suggests that it influences the concentrations of anions and carbon forms. The installation of piezometers in places with different total depth and unsaturated soil zones, distances from the river and watershed catchment outlet, and land uses proved essential for verifying different water quality behaviors among these sites and in relation to the river water. PZ2127 had the highest average concentrations of chemical species, except for PO_4^{3-}, also obtained by Piazza (2019). This result may be due to the larger drainage area of PZ2127 compared to other piezometers and because groundwater increases the concentrations of dissolved substances along its path. The greater depth of PZ2127 may also have contributed to greater nutrient dissolution along the water path (Silva and Migliorini, 2014). Piazza (2019) did not find statistically significant differences between the concentrations of carbon forms in river water and piezometers, unlike this study.

What was observed with the analysis by compartment is in line with what was found in areas with agricultural activities by Vega et al. (1998) in north-central Spain, by Palácio et al. (2008) in the state of Ceará, and by Piazza (2019) at the same site of this study. The dynamics of Cl^-, NO_3^-, and SO_4^{2-} concentrations were related to the location and human intervention around the piezometer. For example, the proximity of residences in PZ2127 (Figure 2) justifies higher average Cl^-, NO_3^-, and SO_4^{2-} concentrations due to the possibility of contamination via septic tanks and infiltration into surface areas of animal husbandry. The location of the piezometer can strongly influence the geochemical behavior of water. Observing the standard deviations, it can be seen that Cl^-, NO_3^-, and IC presented greater data variability around the averages, which suggests the possible association of the concentrations of these chemical species with surrounding anthropogenic factors through precipitation.

Despite the different lad uses, the studied hydrographic basin presents low concentrations of the analyzed chemical species. The little significant impact on the quality of surface and underground water can be explained by the characteristics of the properties (small and medium) and the agricultural activities carried out in them (low to medium intensity). Nevertheless, it is worth highlighting the accumulation of chemical species in the direction of the hydrographic basin drainage, that is, close to its catchment outlet. According to Fernandes et al. (2014), solute concentrations tend to increase with increasing distance from the preserved forest sampling point, similar to what is observed in the studied hydrographic basin.

Moreover, it is worth highlighting the role of vegetation in physical, chemical, and biological processes in the surface drainage system. The occurrence of lower concentrations in surface water than in groundwater demonstrates that the effects of nutrient absorption by channel vegetation, sedimentation of chemical species adhered to sediments, biochemical transformations of nitrogen, carbon, and phosphorus compounds, reduce the mass in the surface drainage system. The river channel works as a reactor to reduce the load of chemical species transported by the river flow, which is especially important for minimal flows. For flood wave runoff conditions, the surface runoff can generate dilution of chemical species introduced by the underground runoff.

Correlations

Figure 5 shows the Pearson correlation coefficients (ρ) between the fluviometric quota and phreatic levels with chemical species concentrations and the correlation coefficients per compartment. The blue or red circles represent positive or negative correlations, and the size of the circles indicates how close they are to the maximum variation (1), according to a significance of $p < 0.05$ (gray background).

Specific behaviors related to water quality were verified, considering the physiography of the watershed, soil type and texture, hydroclimatological variables, land use, and agricultural practices.

In the river, significant correlations were obtained between total carbon concentration (TC) and TOC (0.73), IC and TC (0.67), SO_4^{2-} and Cl^- (0.49), PO_4^{3-} and NO_3^- (0 .24), TC and fluviometric quota (-0.23), and IC and NO_3^- (-0.29). The significant negative correlation between CT and the fluviometric level is considered weak, but it can be explained by the increase in the river flow and the consequent dilution effect, described by Torres et al. (2011). The negative correlation between IC and NO_3^-, although weak, indicates the different behaviors of carbon forms and NO_3^-. According to Bruland et al. (2008), NO_3^- is related to fertilization and soil prepa-

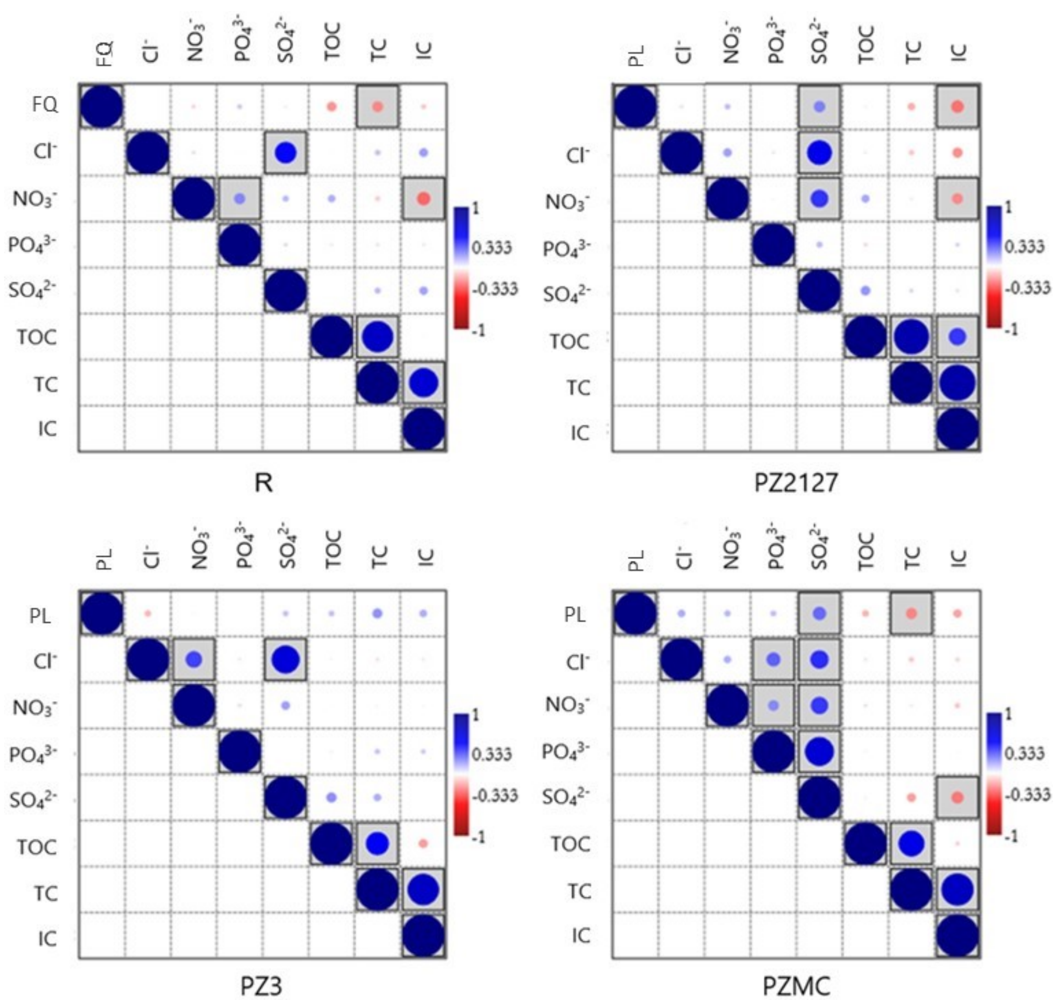

Figure 5 – Pearson correlation coefficients (ρ) between fluviometric quota (FQ), phreatic level (PL), and chemical species concentrations in the river and piezometer water.

ration, that is, the effect of land use. On the other hand, the concentrations of carbon forms can be influenced by biological activity, temperature, edaphic factors, vegetation cover, and terrain slope. The significant positive correlations between TOC and CI with CT, strong and moderate, respectively, are explained by the fact that these two carbon forms compose CT, which was previously found by Kaufmann et al. (2009) in the Ribeirão Concórdia hydrographic basin. The correlation between TOC and CI with CT occurred for all compartments, except for PZ2127, which also showed a TOC/CI correlation.

In PZ2127, significant correlations were obtained between the concentrations of SO_4^{2-} and phreatic level (0.25), SO_4^{2-} and Cl^- (0.57), SO_4^{2-} and NO_3^- (0.40), TC and TOC (0.82), IC and phreatic level (-0.27), IC and NO_3^- (-0.23), IC and TOC (0.39), and IC and TC (0.85). The significant positive correlation between SO_4^{2-} and the phreatic level, although weak, may be associated with the infiltration of this compound into the soil during periods of higher precipitation. SO_4^{2-} results from the leaching of sulfated compounds; it is also present in precipitation, decomposition of organic matter, and sulfated fertilizers (Feitosa and Manoel Filho, 2000; Midões et al., 2001). Considering the physiographic characteristic of the site, the lower slope and the soil texture, PZ2127 may be favoring the infiltration of SO_4^{2-}. The moderately significant positive correlation between SO_4^{2-} and NO_3^- may indicate the impact of domestic sewage discharges or the misuse of fertilizers, factors that cause the input of these chemical species (Moura et al., 2010; Esteves, 2011). A significant negative correlation between IC and the phreatic level was also found by Torres et al. (2011).

In PZ3, significant correlations were obtained between the concentrations of NO_3^- and Cl^- (0.37), SO_4^{2-} and Cl^- (0.65), TC and TOC (0.53), and IC and TC (0.73). The moderately significant positive correlation between NO_3^- and Cl^- can be explained by the high solubility and stability of these chemical species in groundwater and by the distance between this piezometer and the river, which gives a longer permanence for these chemical water constituents (Silva and Borges, 2009). Another factor that may explain this correlation is pasture fertilization in this location (manure and chemical fertilization).

In PZMC, significant correlations were obtained between the concentrations of PO_4^{3-} and Cl^- (0.21), PO_4^{3-} and NO_3^- (0.22), SO_4^{2-} and the phreatic level (0.28), SO_4^{2-} and Cl^- (0.30, SO_4^{2-} and NO_3^- (0.38), SO_4^{2-} and PO_4^{3-} (0.67), TC and the phreatic level (-0.24), TC and TOC (0.59), IC and SO_4^{2-} (-0.26), and IC and TC (0.75). The greatest significant positive correlations between anions occurred in this compartment, the place with the shortest distance from the watercourse (soil x water interface). As was observed between TC and the fluviometric quota, a weak significant negative correlation was identified between TC and the phreatic level in PZMC, also resulting from the dilution effect, since the elevation of levels indicates a greater volume of water in this reservoir (Torres et al., 2011).

The significant positive correlations between SO_4^{2-}, Cl^-, and NO_3^- in the PZ2127 and PZMC piezometers can be explained by the common origin of these anions, possibly agricultural inputs (Fernandes et al., 2014). Especially in PZMC, the correlation between SO_4^{2-} and NO_3^- can originate from the occurrence of nitrification and denitrification processes, once that a strip of riparian forest protects the surroundings of the site.

The temporal and exploratory analysis and the correlations between chemical species concentrations carried out in this study allow a better understanding of the variations in groundwater quality in points with different characteristics of the hydrographic basin and with different factors that influence them. In addition, comparison with surface water concentrations proved to be of great value for understanding the different qualitative behaviors of these compartments and expanding knowledge about them.

Conclusions

The results presented contribute to understanding processes related to water quality at the surface, subsurface, and underground interfaces (soil x water interface). However, the sources of contamination still lack a concrete identification since land uses and their impacts on these reservoirs did not have a spatial pattern. In addition, seasonality was not identified in the variations of quality peaks, which occurred throughout the year.

The river had lower chemical species concentrations than groundwater. Effects of nutrient absorption by vegetation in the surface drainage system, adsorption to particles and plants, and biochemical transformations contribute to reducing the drained mass. Higher average chemical species concentrations were found in PZ2127 (near the catchment outlet and R).

The present study, combining a surface water sampling point and 3 groundwater sampling points, allowed a comprehensive assessment of the system's characteristics, integrating qualitative and quantitative water information (fluviometric quota and phreatic level).

It is recommended to continue the intensive monitoring carried out in the hydrographic basin, in addition to expanding the number of monitoring points for surface and underground water in order to broaden knowledge of the spatial and seasonal dynamics of chemical species and the relationships between them and hydroclimatological variables. Furthermore, monitoring the phreatic levels in each of these piezometers and the fluviometric levels could provide information on the underground discharge to the river with regard to the amount of water and nutrient input.

Contribution of authors:

Melo, M.N.V.: Conceptualization, Methodology, Data Curation, Formal Analysis, Writing — Review and Editing. Piazza, G.A.: Data Curation, Formal Analysis, Writing — Review and Editing. Pinheiro, A.: Conceptualization, Methodology, Writing — Review and Editing, Supervision, Project Administration. Torres, E.: Data Curation, Formal Analysis. Kaufmann, V.: Data Curation, Formal Analysis; Supervision.

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