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The Seasonal Characterization and Temporal Evolution of Nitrogen, Phosphorus and Potassium in the Surface and Groundwater of an Agricultural Hydrographic Basin in the Midwestern Brazilian Savanna

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Abstract: The Brazilian savanna (*Cerrado* Biome) is one of the most important regions in the world in terms of food production, with the use of fertilizers based on nitrogen, phosphorus and potassium (NPK). When not applied properly, fertilizers can alter and affect water quality. The objective of this study was to evaluate the presence of these compounds in surface and groundwater in the Upper Jardim River Hydrographic Unit, Federal District, thus characterizing seasonal variations during the dry and rainy seasons in two periods. A total of 207 groundwater samples and 23 surface water samples were collected in the years 2014, 2015, 2019 and 2020. The parameters analyzed were pH and nitrate, nitrite, ammonium, phosphate and potassium ions. In groundwater samples, pH values were significantly higher and ion levels lower in samples collected during the early years (except for nitrate), and the ammonium concentrations were lower in the dry season than the rainy (in 2014 and 2019). In surface samples, total phosphorus levels were significantly higher in the rainy/2019 compared to the rainy/2020 season, while this tendency was inverted for potassium during the dry season. The use of NPK-based fertilizers has increased considerably in recent years in the region due to the expansion of the agricultural area, and although the results of the study show that concentrations in water are much lower than the maximum values allowed by Brazilian legislation, continuous monitoring is necessary to guarantee water quality.

Keywords: fertilizers; NPK; water quality; aquatic contaminants; Federal District

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1. Introduction

The Brazilian savanna covers around 25% of the country, making up an area that exceeds 2 million km^2, part of it located in Brazil's Midwestern region [1]. The soils of this biome are highly weathered, with a high content of iron and aluminum oxides, low pH and low amounts of nutrients, mainly nitrogen and phosphorus [2]. Even with all these characteristics, this biome is one of the main producers of agricultural commodities in Brazil, with strategic importance for the country's economy [3]. Its excellent performance is due to the combination of technologies such as mechanization, genetic improvement and the use of limestone, pesticides and chemical fertilizers, leading to higher productivity [4].

The main function of fertilizers is to overcome low crop yield due to the lack of nutrients in the soil and to replace elements in the soil that are removed in each harvest, in order to maintain or even expand productive potential [5]. Absorbed by plants in large quantities, macronutrients such as nitrogen (N), phosphorus (P) and potassium (K) are normally supplied to plants in the form of NPK mixture [6].

Worldwide, inorganic fertilizer use in 2020 was 201 million tons, 49% more than in 2000, of which 56% was N, 24% P (P_2O_5) and 20% K (K_2O) [7]. Brazil is one of the four major food producers, ranking fourth in inorganic fertilizer use, responsible for about 8% of global consumption, behind China, India and the United States [8].

Over the last 60 years, the Federal District, located in the savanna of the Midwestern region of Brazil, has experienced an increased demand for vegetables and fruit, in addition to a significant increase in grain production [9]. NPK-based chemical fertilizers are a major agricultural input, with over 64,000 tons used in the region in 2017 [10]. Despite the increase in productivity, the use of the land by the agricultural sector can have consequences for the hydrological and biogeochemical watershed cycles, leading to changes in the quantity and quality of water resources, in addition to negative effects on the soil, such as acidification and the accumulation of heavy metals, among other elements [11–13]. Furthermore, damage to the atmosphere can also be seen during the production, transport and use of fertilizers, contributing to the increase in global greenhouse gas emissions [14].

Nutrients such as N, P and K can also reach surface and groundwater, from runoff and leaching, which can lead to eutrophication and, consequently, the loss of biodiversity and ecosystem services [15]. Another impact from the use of fertilizers is a high nitrate content in water for human consumption, which may cause methemoglobinemia in infants [16]. Savanna soils have high permeability that allows soil recharge through the infiltration of rainwater [11], which can contribute to the leaching of compounds that alter the natural characteristics of groundwater [17].

The effects of fertilizer use on water quality evolve slowly, requiring time to be identified [18]. The objective of the present work was to evaluate the seasonal presence and temporal evolution of compounds linked to the NPK group in surface and groundwater in the Upper Jardim River Hydrographic Unit (HU-35) and possible changes in water quality over time. HU-35 was chosen due to its representativeness of the savanna biome in terms of geoenvironmental conditions and because it is located in the main agricultural region of the Federal District, in Brazil's Midwestern savanna. To the best of our knowledge, this is the first published study that investigates the impact of NPK fertilizer use on groundwater quality in the region.

2. Materials and Methods

2.1. Study Area

The water samples were collected from the Upper Jardim River Hydrographic Unit (HU-35), located in the eastern zone of the Federal District, in the Midwestern region of the country (Figure 1) and where Brasília, the Brazilian capital, is located. The Unit has an area of 104.86 km^2 and is responsible for most of the grain production in the Federal District, mainly soybean and corn, using central pivot irrigation and the exploitation of underground water resources through drilled wells [19,20]. The hydrographic basin has several humid areas, springs and streams that drain into the Preto River and subsequently into the Paracatu River (MG), the main tributary on the left bank of the São Francisco River basin, one of the most important watercourses in Brazil and South America [20,21].

Groundwater samples were collected from 26 piezometric wells and 1 artesian well (PT), previously installed in HU-35. Surface water samples were collected at six points close to agricultural areas and to the piezometric wells (Figure 1). The geographic location of each sampling point is shown in Table S1 (Supplementary Materials).

The Federal District has an AW (dry winter) climate according to the Köppen–Geiger classification [21]. The rainfall dynamics are well defined and distinct: the dry winter, from May to October, is characterized by almost total absence of rain, low air humidity, which can be below 15%, a high evaporation rate and temperatures ranging from 12 to 26 °C; and the rainy summer is between November and April, with an average annual precipitation ranging from 1000 mm to 1700 and temperatures normally from 17 to 29 °C [19,20,22].

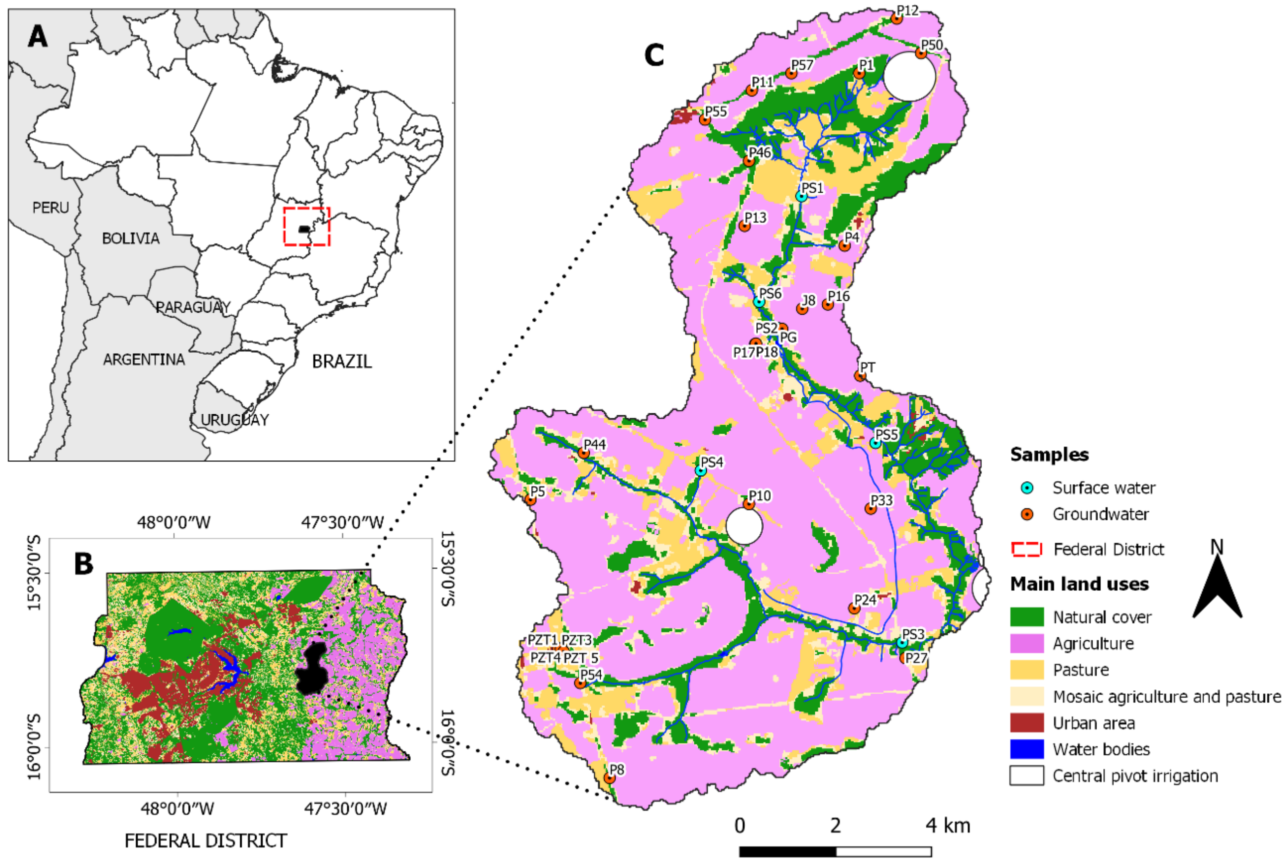

Figure 1. (**A**) Brazil and Brazilian Federal District in South America. (**B**) Location of the Upper Jardim River Hydrographic Unit (HU-35) in the Brazilian Federal District. (**C**) Water sampling points. Prepared using MAPBIOMAS [23] and SIEG [24].

In this region, the rainy season promotes hydrological processes and groundwater recharge [20]. As precipitation is characterized by marked seasonality, the maximum elevation of the water table of the HU-35 piezometric wells varies considerably, ranging between 1.8 m and 8.5 m [20]. The region is situated on a terrain that varies from flat to markedly undulating, with low slopes almost throughout the entire basin, ranging from 0.0 to 4.83 degrees in most of the area [25]. The soil is predominantly composed of ferrosols (76.4%), with clay content varying between 67% and 75%, followed by cambisol (16.7%), plintosol (2.5%), gleisol (2.4%), quartzarenic neosol (2.1%) and a small portion of rocky outcrops (0.24%) [21,25].

2.2. Sample Collection and Analytical Methods

Water samples were collected in two different periods: 4 campaigns in 2014/2015 (groundwater only); and 8 campaigns in 2019/2020 (4 groundwater and 4 surface water). Samples were collected during the dry (June and September) and rainy (December and February) seasons of each period, totaling 12 sampling campaigns. A total of 230 water samples were collected, 207 from groundwater and 23 from surface water (Table 1). Groundwater samples were collected using a bailer-type polychloroethene sampler (3 cm diameter, 100 cm high, opening at 50 cm) attached to a 20 m nylon string inserted in a 6 cm piezometric tube (Figure S1), and surface water samples were collected manually by dipping 350 mL polyethylene bottles, approximately 15 to 30 cm deep, or using a van Dorn-type collector in areas where access was difficult [26].

Table 1. Samples collected in Upper Jardim River Hydrographic Unit (HU-35), Federal District, Brazil.

Sample Type	Season	Sampling Date	Number of Samples
Groundwater	Dry	September 2014	27
Groundwater	Dry	June 2015	26
Groundwater	Dry	September 2019	25
Groundwater	Dry	September 2019	25
Groundwater	Rain	December 2014	26
Groundwater	Rain	February 2015	26
Groundwater	Rain	December 2019	26
Groundwater	Rain	February 2020	26
Surface water	Dry	September 2019	6
Surface water	Rain	December 2019	6
Surface water	Rain	February 2020	5
Surface water	Dry	June 2020	6
	Total groundwater samples		207
	Total surface water samples		23

The samples were stored in a thermal box protected from light and sent for analysis to the Water Analytical Chemistry Laboratory of the Brazilian Agricultural Research Corporation (Embrapa Cerrados, Planaltina, Brazil).

The pH analyses were carried out on the day of collection, using an Orion Star A211 pH meter from Thermo Scientific® (Waltham, MA, USA). Total phosphorus (TP) was determined by the ascorbic acid/colorimetric method (APHA, 2018 [27]), using a Shimadzu UV/Vis spectrophotometer at 882 nm, model UV-1800 (Kyoto, Japan).

To determine the levels of NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and K^+ ions, the samples were filtered with microfibers PTFE 0.45 µm (Millipore ®, Darmstadt, Germany) and analyzed by ion chromatography using the 761 Compact IC chromatograph, from Metrohm (Herisau, Switzerland) [28,29]. For anion analysis, a Metrosep A Supp 5 column and a mobile phase of buffer solution (pH 10.5) prepared with 3.2 mM sodium carbonate and 1.0 mM Merck sodium hydrogen carbonate (Darmstadt, Germany) were used, followed by a suppressant solution of water:100 mM sulfuric acid (50:50). For cation analysis, a Metrosep C4 ion exchange column was used, with a mobile phase of a buffer solution (pH 3.6) prepared with 4.0 mM tartaric acid and 0.75 mM analytical grade 2,6-pyridinedicarboxylic acid (Carlo Erba; Milan, Italy).

The results of NO_3^-, NO_2^- and NH_4^+ are expressed as nitrogen (NO_3^--N, NO_2^--N and NH_4^+-N), by applying factors of 0.226, 0.304 and 0.774 [30], respectively, in accordance with the Brazilian Directive from the National Environmental Council (CONAMA), which provides a classification of surface and groundwater, as well as environmental guidelines [31,32]. The method's limits of detection (LOD) are 0.006 mg L^{-1} for NO_2^--N and 0.001 mg L^{-1} for NO_3^--N, NH_4^+-N, TP, PO_4^{3-} and K^+.

2.3. Data Processing and Statistical Analysis

Statistical analyses were conducted using GraphPad Prism software version 10.2.3. Data for all parameters in all campaigns showed a non-normal distribution (Shapiro–Wilk test), and a Kruskal–Wallis test (non-parametric) was used to compare the mean levels found between the seasons and sampling periods. The statistical analyses for ion concentration considered levels below the LOD as zero.

3. Results and Discussion

3.1. Groundwater Samples

The results for each parameter analyzed in the water samples are presented in Table S1. The pH was below 7.0 in all 207 groundwater samples, with the exception of two samples in the rainy season. The means and the lowest pH values from both seasons were higher in 2014/2015 (means of 6.0; from 5.3 to 7.1) compared to 2019/2020 (means of 5.4 and 5.2, from

4.2 to 7.1). Figure 2A compares the pH of samples collected from all campaigns; significance between the means was checked between seasons within the same year and between the years for the same season. pH values were not significantly different between the seasons for each year ($p > 0.05$), but pH in the dry 2014 and 2015 seasons was significantly higher than that of dry 2019 and 2020 (Figure 2A). Similarly, the pH in the rainy 2014 season was higher than that of rainy 2019 and 2020 ($p < 0.01$). These results are comparable to the data obtained in other studies conducted in the same region, which reflects the natural acidity of the soils of the savanna biome [33,34]. The reason for the higher pH during the 2014/2015 period is not clear. Although higher NH_4^+ levels in the water could lead to higher pH, they were lower in 2014/2015 compared to 2019/2020, as will be discussed further. Brazilian legislation does not set pH standards for groundwater samples [31].

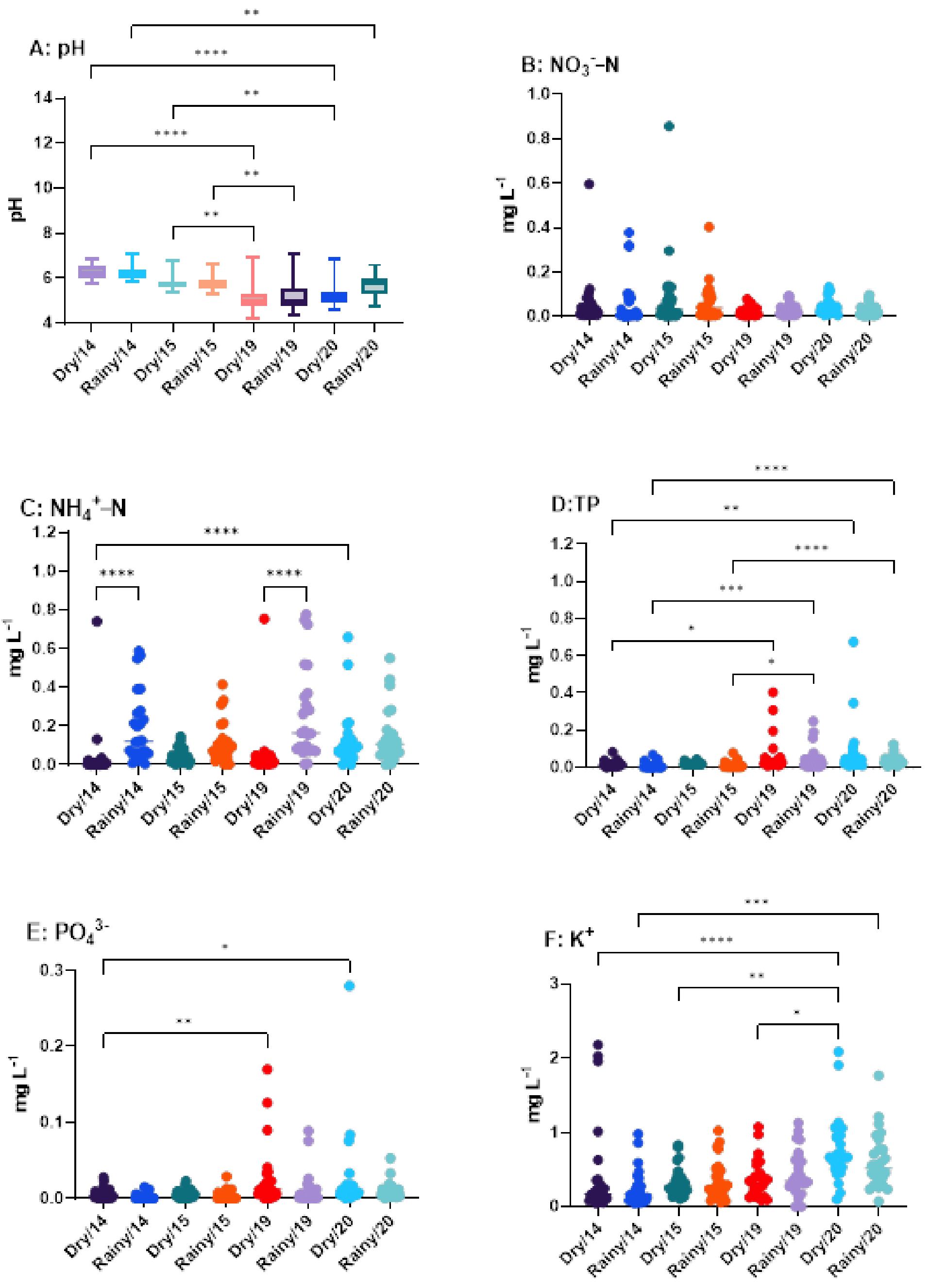

Figure 2. pH and ion concentration ranges in groundwater samples collected from the Upper Jardim River Hydrographic Unit (HU-35) during the dry and rainy seasons of 2014, 2015, 2019 and 2020. Kruskal–Wallis test (non-parametric, n = 25–27); * < 0.05; ** < 0.01; *** < 0.001; **** < 0.0001.

Figure 2B–F show the levels of NO_3^--N, NH_4^+-N, PO_4^{3-}, TP and K^+ in groundwater samples, indicating any significant differences ($p < 0.05$) between the seasons within one sampling period or during the same season between sampling periods. Although some higher NO_3^--N levels were found in 2014/2015 (up to 0.857 mg L^{-1}), no significant differences were found between the means of the sampling campaigns (Figure 2B). In general, NH_4^+-N mean levels were lower during the dry season, with significant differences compared to the rainy season in 2014 (mean of 0.039 × 0.185 mg L^{-1}) and 2019 (0.050 × 0.258 mg L^{-1}); the levels in dry/2014 samples were also significantly lower than in dry/2020 (Figure 2C). This is probably due to the low monthly precipitation during the dry season (from 0 to 8 mm; Figure S2).

TP levels did not significantly change between the seasons within the same year, but samples from dry/2014 had significantly lower mean levels (0.017 mg L^{-1}) compared to dry/2019 (0.062 mg L^{-1}) and dry/2020 (0.079 mg L^{-1}; Figure 2D). Similarly, significant lower mean levels were found in rainy 2014 and 2015 (0.010 and 0.012 mg L^{-1}) compared to rainy 2019 and 2020 (0.061 and 0.026 mg L^{-1}). Significant lower mean levels of PO_4^{3-} were also found in dry/2014 (0.039 mg L^{-1}) compared to dry/2019 (0.050 mg L^{-1}) and dry/2020 (0.126 mg L^{-1}) (Figure 2E). Finally, mean K^+ levels during dry/2014, 2015 and 2019 campaigns (0.303 to 0.429 mg L^{-1}) were significantly lower than the levels of dry/2020 (0.777 mg L^{-1}), and the mean rainy/2014 level was lower than rainy/2020 (Figure 2F).

The lower ion mean levels in 2014/2015 compared to 2019/2020 found in this study may be a consequence of increased agricultural activity, with consequent increase in fertilizers, in the later years.

3.2. Surface Water Samples

According to Brazilian legislation, the pH for surface water (salinity < 0.005%) should range from 6 to 9 [30]. In this study, pH values in the 23 samples collected during the dry and rainy seasons of 2019/2020 ranged from 5.17 to 6.92, with about 61% of the samples with values below 6.0 (Table S1). These levels are within the same range as those of the groundwater samples and confirm the acidic characteristic of the soil in the region. Similar to the groundwater samples, no significant differences were found in pH values during the campaigns of 2019/2020 (Figure 3A).

According to the Brazilian Directive (CONAMA n. 357/2005), the Maximum Allowable Value (VMP) of N levels for surface water depends on the water use, with the most restrictive values for water for human consumption (after treatment) and for recreation: 10 mg L^{-1} (NO_3^--N), 1.0 mg L^{-1} (NO_2^--N) and 3.7 mg L^{-1} (NH_4^+-N for pH < 7.5), respectively [30]. NO_2^- was found in only one surface water sample (0.039 mg L^{-1}; rainy/2019) and PO_4^{3-} only in three samples at very low concentrations (0.001–0.002 mg L^{-1}; dry/2020).

Figure 3B–E compare the ion levels (NO_3^--N, NH_4^+-N, TP and K^+) between the seasons within the same year and between the years for the same season. In general, the levels were lower than those found in groundwater samples (Figure 3) but with a much higher rate of positive samples (only one sample had TP < LOD). No significant differences were found for NO_3^- and NH_4^+ in the various campaigns, although NH_4^+ levels in the rainy seasons were higher (means of 0.005–0.007 mg L^{-1} vs. 0.044 mg L^{-1}; $p = 0.17$ and 0.09 for 2019 and 2020, respectively).

The pollution of water bodies by nitrogen has been a concern over the years due to agricultural intensification in the 20th century [35]. In this study, the levels of N species in groundwater and surface water are much lower than the Brazilian VMP values, which is expected as the main crop cultivated in the study area is soybean (~52% of the agricultural area) [36]. In Brazil and other countries, N fertilizers are not used in soybean cultivation, and the seed is instead inoculated with rhizobia for nitrogen fixation [36]. The second most cultivated crop in the region is maize (~30%), for which N fertilizer application ranges from 40 to 180 kg/ha, depending on the expected productivity [36]. Fertilizer application starts for both crops in the rainy season, which may explain the higher NH_4^+ levels in groundwater (Figure 2C) and in surface water samples during the rainy season, although, in this case, the difference was not significant (Figure 3C).

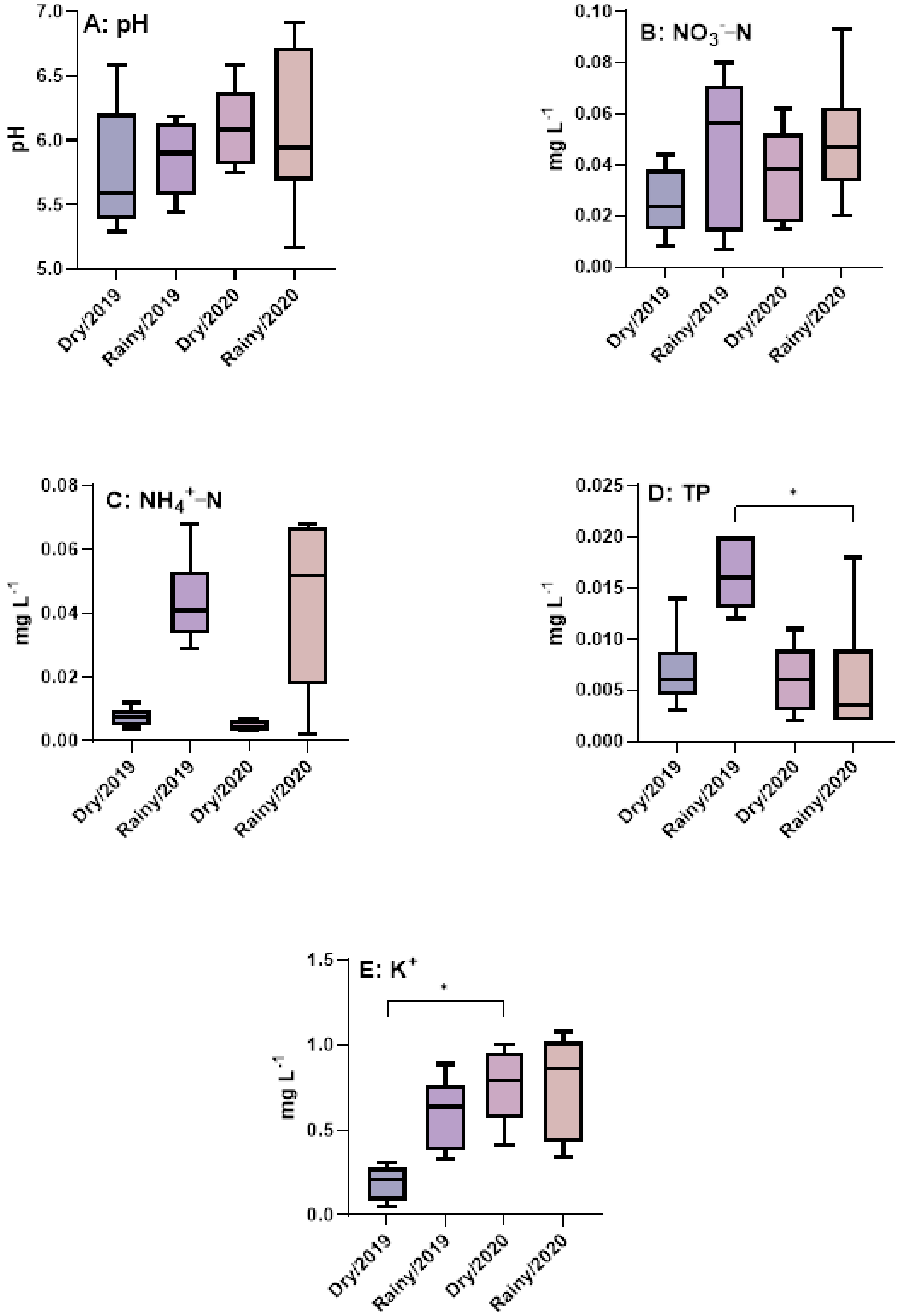

Figure 3. pH and ion concentrations in surface samples collected from the Upper Jardim River Hydrographic Unit (HU-35) during the dry and rainy seasons of 2019/2020. Kruskal–Wallis test (non-parametric, n = 5–6); * < 0.05.

Despite the growing environmental concern about changes in nutrient cycles in water bodies, the influence of agricultural activities on the concentration of PO_4^{3-} is not well known [37], and the fate of K^+ from fertilizers has also received less attention than nitrogen and phosphorus [38]. An increase in the concentration of potassium in groundwater in agricultural areas can be expected, as a consequence of the leaching of the nutrient, which can cause water salinization, especially in arid and semi-arid regions [39–41]. In this study, TP was quantified in all but one surface water sample, at levels up to 0.020 mg L^{-1} (rainy/2019), much lower than the VMP set by the Brazilian directive, which depends on water flow (lotic, intermediate or lentic) and pH and ranges from 0.2 to 0.15 mg L^{-1} [31]. Significantly higher levels were found in the rainy/2019 samples compared to rainy/2020 (Figure 3D). The levels of K^+ ranged from 0.048 (dry/2019) to 1.077 mg L^{-1} (dry/2020), with levels significantly lower in the dry/2019 season compared to dry/2020 (Figure 3E).

Table 2 summarizes the NPK levels found in this and other studies conducted in HU-35 (surface water) and in other countries. No studies that analyzed groundwater samples collected in HU-35 were found in the literature. In the two studies conducted in the Rio Jardim River, samples were collected monthly at three sampling points for one year [33,34]. In the study conducted in 2012/2013 [34], the levels of NO_3^--N were similar to those found in the surface samples of the present study (2019/2020), whereas the levels of NO_3^--N and of NH_4^+-N found by Passos et al. [33] in 2016/2017 were much higher, with monthly means reaching 0.413 and 2.392 mg L^{-1}, respectively (Table 2). As in the present study, NO_2^--N and PO_4^{3-} were detected in only a few samples, and TP and K^+ levels were within the same range.

In two studies conducted in intensive agricultural areas in India [41,42], NO_3^--N levels in surface and/or groundwater were much higher than what was found in this study (Table 2). K^+ levels in groundwater reached 118 mg L^{-1} (mean of 6.20 mg L^{-1}), which was attributed mainly to potassium feldspars, in addition to potassium fertilizers [43]. In China, a long-term monitoring study of the country's second largest reservoir showed low ammonia concentration (0.0139–0.15 mg L^{-1}), which was attributed to the use of fertilizers, with the variation mainly due to the reservoir water level [43].

Table 2. Summary of the results of NPK ions found in this and other studies conducted in the Upper Jardim River Hydrographic Unit (HU-35) and other countries.

Country	Sample	Sampling	Range of Values (Mean), mg L^{-1}					
			NO_3^-–N	NO_2^-–N	NH_4^+–N	TP	PO_4^{3-}	K^+
This study Brazil (HU-35)	Groundwater N = 207	2014, 2015 2019, 2020	<LOD–0.857 (0.048)	0.076, 0.054	<LOD–0.776 (0.119)	<LOD–0.675 (0.033)	<LOD–0.280 (0.011)	0.002–2.178 (0.448)
	Surface N = 23	2019, 2020	0.008–0.093 (0.040)	0.040	0.002–0.72 (0.055)	0.002–0.020 (0.009)	0.001, 0.002	0.048–1.077 (0.573)
Brazil (HU-35) [34] [a]	Surface N = 36	2012, 2013	0.0002 0.081	na	na	na	na	0.001–0.660
Brazil (HU-35) [33] [a,b]	Surface N = 36	2016, 2017	0.018–0.413	<LOD	1.316–2.379	0.002–0.018	0.090	0.320–0.580
India [41]	Groundwater	2005	0.01–4.56 (0.67)	na	na	na	na	na
	Surface		0.57–3.12 (1.13)	na	na	na	na	na
India [42] [a]	Groundwater N = 100	2015	0.009–132.2, (0.255)	na	na	na	na	1–118 (6.20)
China [44] [a]	Reservoir, Surface	2004 to 2018	na	na	0.039–0.155	na	na	na

[a] original data expressed as NO_3^- and/or NH_4^+, conversion factors are ×0.226 and ×0.774, respectively. [b] range of 12-month period means at three sampling points. na = not analyzed.

In addition to agriculture, sewage systems of rural residences and livestock farming can be important sources of water pollution. In a 5-year monitoring study of a Chinese canal, agriculture and livestock contributed to 43.3% of the total phosphorus in the rainy season and livestock to 52.9% in the dry season [44]. Domestic sewage, surface runoff and unknown sources contributed to 67.4% of the total nitrogen in the rainy season [44]. HU-35 is an agricultural area with few residences, so the contribution of domestic sewage to the nitrogen and phosphorus levels in groundwater and surface water can be considered irrelevant.

Pollution in surface and groundwater due to the use of fertilizers generally reflects current and past applications of fertilizers, as a large part of the applied portion remains in the soil's organic reservoir, where it is mineralized and absorbed by plants and/or is lost through leaching over several years [41]. Fertilizers can reach surface water by rain runoff from the field and reach groundwater when not totally absorbed by the soil particles, leaching out from the root zone [42]. Although rainwater runoff is expected to be a driving mechanism for agricultural pollution, this relationship could not be found in this study for surface water, probably due to the low precipitation before sampling (203–234 mm, Figure S2). For groundwater, this impact was only found for NH_4^+.

A major limitation of this study is the lack of surface water samples collected during the years 2014/2015 and the low number of samples collected in the later period, which compromised the conclusions about the NPK levels in surface water and their comparison with groundwater.

4. Conclusions

In summary, the pH of groundwater samples from the 2014/2015 seasons was higher than in 2019/2020, while the NPK levels were higher during the 2019/2020 campaigns, probably due to greater agricultural activity over time. The season only impacted NH_4^+ groundwater levels, which were lower during the dry seasons of 2014 and 2019.

The levels of NPK ions found in the water samples were much lower than the limits established by Brazilian standards, which indicates that the use of fertilizers in the region did not impact water quality during the evaluated periods. However, longer-term monitoring is necessary to corroborate these results, because surface water (springs, rivers and reservoirs) and groundwater (cisterns and water wells) are important sources for human consumption and crop irrigation in the region.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16177659/s1, Table S1: Location of sampling points of groundwater and surface water collected at HU-35 and the results found for each evaluated parameter; Figure S1: (A) P26GW sampling point. (B) Polychloroethene bailer sampler. (C,D) Groundwater sample collection in the piezometric well in Upper Jardim River Hydrographic Unit (HU-35); Figure S2: Monthly values of total accumulated precipitation (mm) from August 2014 to July 2015 and August 2019 to July 2020 obtained from the *Águas Emendadas* monitoring station (A045/coordinates S-15°60′62.5″; W-47°63′84.2″). Source: INMET, 2024. Reference [45] is cited in Supplementary Materials.

Author Contributions: N.L.P.: original draft preparation, conceptualization, formal analysis, investigation. D.H.d.F.M.: formal analysis, conceptualization, review. L.S.d.A.: formal analysis, conceptualization, investigation. J.E.F.W.L.: funding acquisition, supervision, project administration, conceptualization. R.A.T.G.: supervision, project administration, conceptualization. E.D.C.: data curation, supervision, writing, reviewing and editing. E.C.O.-F.: funding acquisition, supervision, project administration, writing, reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: Authors Daphne Heloisa de Freitas Muniz, Jorge Enoch Furquim Werneck Lima and Eduardo Cyrino Oliveira-Filho are employed by the Brazilian Agricultural Research Corporation. The remaining author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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