Nitrogen

Article

Spatiotemporal Dynamics of Carbon and Nitrogen in Subtropical Urban Streams (Santo André, SP, Brazil)

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Abstract: Urban sprawl poses a significant threat to urban stream water quality due to impermeabilization, reduced vegetation cover, and the release of diffuse pollutants. This study evaluates water quality in seven catchments in Santo André, SP, considering seasonality. Nutrient concentrations and in situ measurements were taken during both dry and rainy seasons. Comparisons were made using Kruskal–Wallis and Mann–Whitney tests. Streams showed significant differences in relation to water quality parameters. The Carapetuba, Jundiaí, and Apiaí streams were most adversely affected, underscoring the need for urgent water quality intervention (water conductivity above 500 µS/cm, dissolved oxygen below 2 mg/L, total dissolved carbon above 50 mg/L, and total dissolved nitrogen above 25 mg/L). Significant differences were observed across seasons. The dry season showed elevated temperatures (above 25 °C) and increased total dissolved carbon (above 50 mg/L) and nitrogen concentrations (above 30 mg/L), indicating reduced dilution effects from rainfall and heightened organic contamination. Conversely, the wet season demonstrated lower nutrient concentrations, emphasizing seasonal dynamics. Sustained, long-term monitoring of urban streams in Santo André and the implementation of sewage collection and treatment in irregular settlements are recommended. These measures are essential to mitigate the adverse impacts of urban expansion on water quality.

Keywords: water quality; nutrients; land use; catchments; sustainable cities

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1. Introduction

The ongoing phenomenon of urban expansion exerts substantial pressure on the water quality of urban streams, and this environmental strain is anticipated to escalate in the future as a direct consequence of the continual growth of the population in urban areas. The release of pollutants [1] and soil impermeabilization [2] are the primary factors degrading water quality in urban streams. Examples of this include increased concentrations of nutrients such as nitrogen, phosphorus, and carbon, as well as hydrocarbons and pharmaceuticals [1]. Additionally, other sources of degradation, such as deforestation that can intensify soil erosion and sedimentation [2,3] and changes in hydrology [4], can be observed, especially in urban impermeable watersheds. The detrimental impacts mentioned earlier stand in direct contradiction to the fundamental principles endorsed by sustainable cities, wherein the provision of clean water and sanitation serves as an integral component essential for achieving and maintaining overall sustainability.

The aforementioned impacts are evident in the water bodies within the Metropolitan Region of São Paulo (MRSP), representing the largest urbanized region in Brazil. This area grapples with significant challenges concerning water quality, primarily stemming from heightened urbanization. The conversion of native vegetated areas into residential zones, commercial establishments, and industrial facilities, coupled with the release of untreated sewage into rivers, streams, and reservoirs, contributes substantially to the serious issues surrounding water quality in the region. In addition, changes in several environmental laws in Brazil have fostered urban expansion over natural areas, such as the changes to the Native Vegetation Protection Law (Law n. 12651/2012) [5] that reduces the riparian buffers and the creation of the Law n. 14285/2021 [6] that allows the regularization of buildings on the margins of watercourses in urban areas. The now-urbanized streams in the region may exhibit characteristics of Urban Stream Syndrome, as elucidated by Walsh et al. [7].

Urban Stream Syndrome manifests through various symptoms, with altered water flow being one of the consequences of soil impermeabilization, leading to decreased rainfall water infiltration and, consequently, increased surface runoff [8]. This phenomenon significantly contributes to increased water volume during the wet season and altered flow patterns in streams, especially for stream flashiness. In addition to this aspect, Urban Stream Syndrome also encompasses the issue of the inadequate discharge of untreated sewage and polluted surface runoff into the streams, further exacerbating the situation [8]. Furthermore, other symptoms such as an increase in toxic substances, nutrients like nitrogen, carbon, and phosphorus, and higher water temperature are associated with this syndrome, which may cause several alterations to the biogeochemical cycles in these environments [7]. Additionally, changes in morphology, particularly the reduction in channel complexity, are relevant, considering that habitat heterogeneity is an important factor for freshwater biodiversity.

The study conducted by Araújo et al. [9] demonstrated that urban streams within less anthropized watersheds, predominantly covered by native vegetation, have better water quality compared to urban streams belonging to watersheds more affected by urbanization. In highly urbanized streams, higher concentrations of carbon, nitrogen, and phosphorus are prominent, while dissolved oxygen levels are lower. Increased nutrient concentrations are linked to eutrophication and pollution processes, leading to a decline in dissolved oxygen levels. Consequently, this reduction in oxygen levels contributes to decreased biodiversity and the presence of polluted waters in ecosystems situated near residential areas. Such conditions have the potential to pose risks to freshwater biodiversity [10].

Studies evaluating water quality in urban streams within the Metropolitan Region of São Paulo (MRSP) are limited, leaving these ecosystems more susceptible to threats and impeding progress toward achieving urban sustainability. Therefore, prioritizing the preservation of water resources, with a specific emphasis on urban streams, becomes paramount for guiding cities toward sustainability. In this regard, the present study aimed to analyze water quality in seven watersheds in the municipality of Santo André—SP, located in the Metropolitan Region of São Paulo, considering that the streams in the region may exhibit intrinsic characteristics of Urban Stream Syndrome. The specific objectives of this study were as follows: (i) to identify the streams with the greatest anthropogenic impact and (ii) to assess whether seasonality influences nitrogen and carbon concentrations in urban streams. We hope that the results of this study will aid decision-makers in identifying priority areas for urban stream restoration, conservation, and the implementation of wastewater treatment in the municipality of Santo André.

2. Materials and Methods

2.1. Study Area

The municipality of Santo André is situated within the Metropolitan Region of São Paulo (MRSP), in the state of São Paulo, Brazil, forming part of the southeast region of Brazil. Encompassing a total land area of around 176 square kilometers, it is home to a population of 748,919 inhabitants. The municipality exhibits a population density of 4.260 people per square kilometer and a per capita Gross Domestic Product (GDP) of BRL 40.812 [11]. This municipality plays a significant role in the MRSP and, as an urbanized region, is directly and indirectly dependent on the ecosystem services provided by preserved areas. However, environmental degradation has been increasing in parallel with urban expansion.

The municipality of Santo André—SP is situated at an average elevation of 760 m above sea level [12]. According to the Köppen climate classification, the region's climate is categorized as Cfa (subtropical climate with hot summers). The average annual temperature is approximately 19 °C. The hottest month (February) has an average temperature of 23 °C, while the coldest month (July) has an average of 16 °C. The highest temperature ever recorded in the city was 35 °C and the lowest was −3 °C. The month with the lowest precipitation is August, recording around 70 mm. In contrast, January records the highest precipitation, with an average value of 345 mm. The dominant vegetation in the municipality is the Atlantic Forest, which is considered a biodiversity hotspot, primarily found in parks and areas designated for environmental preservation. However, there are also small patches of the Araucaria moist forest at elevations above one thousand meters, although it has been largely depleted [13].

Seven urbanized catchments draining headwater streams were selected for this study (Figure 1). All the analyzed catchments are part of the sub-basin of the Tamanduateí River, an important river that crosses the Metropolitan Region of São Paulo and discharges into Tietê River, one of the most polluted rivers in Brazil. The Tamanduateí sub-basin is part of the Alto Tietê hydrographic watershed, which represents one of the most complex watersheds in terms of water management because it is the most populated watershed in the state and has the most urbanized region of the country. The territory of Alto Tietê watershed encompasses a significant portion of the MRSP, housing approximately 99.5% of the local population. With a total area of 5.868 square kilometers, the majority of the urban region is situated on sedimentary land from the Cenozoic era and more recent Quaternary alluvial deposits. These characteristics developed along the major river courses that drain the area [14].

Information regarding the total urbanized area and vegetation cover was calculated for the seven catchments (Table 1). The catchments with the highest percentages of urbanization were Ribeirão Jundiaí, Comprido, Apiaí, Beraldo, and Guaixaya, respectively. Catchments with the highest percentages of public green areas were Carapetuba and G.E. In general, all sampling points were located within areas surrounded by residences, businesses, and industries, with an absence of riparian vegetation. They also exhibited concrete structures along their banks and beds and were all channelized. The Guaixaya, Ribeirão Jundiaí, and G.E. streams are situated near urban parks.

Table 1. Total area and the percentages of land use categories in each catchment and location of each sampling station in the sampled streams in the Santo André municipality, located in the Metropolitan Region of São Paulo, Brazil.

Catchments	Coordinates	Industrial (%)	Urban (%)	Green (%)	Total Area (km²)
Comprido	23°38′29.7″ S 46°31′18.3″ W	0.00	98.06	1.94	2.47
Guxaixaya	23°37′53.5″ S 46°30′11.5″ W	0.00	96.68	3.32	2.67
Jundiaí	23°37′52.7″ S 46°31′45.1″ W	0.16	99.03	0.81	2.87
Beraldo	23°38′28.6″ S 46°32′16.2″ W	0.76	96.39	2.85	1.93
G. E	23°38′44.1″ S 46°32′07.0″ W	1.08	90.32	8.60	0.99
Carapetuba	23°39′59.4″ S 46°31′55.6″ W	0.03	84.03	15.94	2.83
Apiaí	23°40′35.0″ S 46°31′10.1″ W	0.00	97.75	2.25	2.96

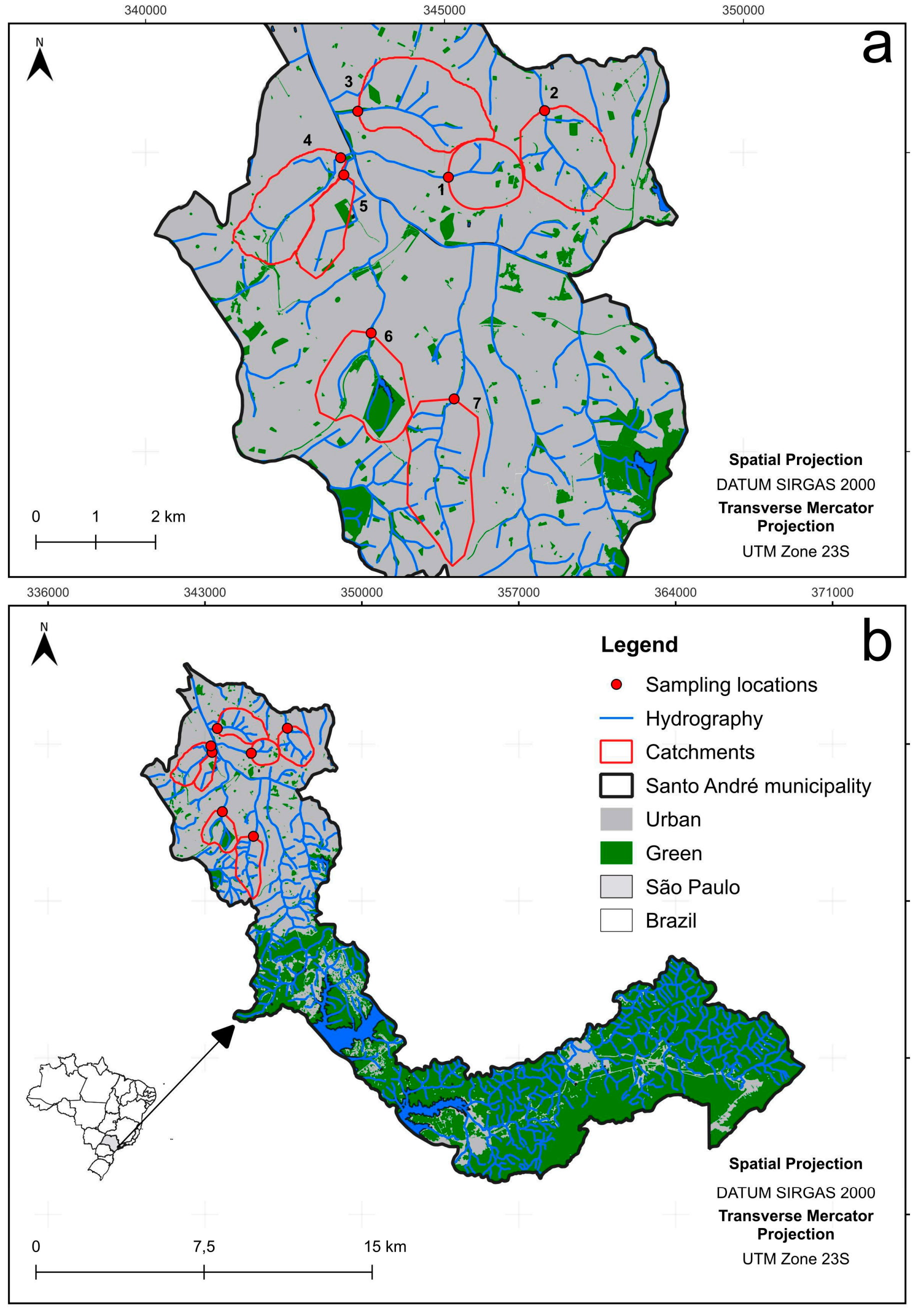

Figure 1. (**a**) Location of the seven selected catchments (highlighted in red) belonging to the Santo André municipality: (1) Córrego Comprido, (2) Córrego Guaixaya, (3) Ribeirão Jundiaí, (4) Córrego Beraldo, (5) Córrego da G.E., (6) Córrego Carapetuba e, and (7) Córrego Apiaí. (**b**) Location of Santo André municipality and the main land uses.

Information regarding the total urbanized area and vegetation cover was calculated for the seven catchments. The catchments were demarcated through GIS (Geographic Information System). The Universal Transverse Mercator (UTM) projection, Zone 23S, and the SIRGAS 2000—INPE (Instituto Nacional de Pesquisas Espaciais) datum were employed. Catchments were delineated using the QGIS software (version 3.34.8), utilizing shapefiles of hydrography, municipal delineation, and land use and occupation obtained from the IBGE website. Additionally, shapefiles of land use in the urban macrozone of the Santo André Municipality Geographic Information System were also utilized (Table 1). The catchments with the highest percentages of urbanization were Ribeirão Jundiaí, Comprido, Apiaí, Beraldo, and Guaixaya, respectively. Catchments with the highest percentages of public green areas were Carapetuba and G.E. In general, all sampling points were located within areas surrounded by residences, businesses, and industries, with an absence of riparian vegetation. They also exhibited concrete structures along their banks and beds and were all channelized. The Guaixaya, Ribeirão Jundiaí, and G.E. streams are situated near urban parks. The municipality of Santo André advertises 100% sewage collection and treatment coverage in all regular areas of the city. However, numerous irregular settlements are scattered throughout the city.

Two field campaigns were conducted, one during the dry season and one during the rainy season, in the stream waters of seven selected catchments draining headwater streams over the course of a year, resulting in a total of forty-two samples. Samples were collected in triplicate under baseflow conditions and took place on the following dates: 16 and 26 June 2021; 3 July 2021; during the dry season, and on 1, 2, and 15 March 2022. The sampling stations were selected based on accessibility, and the sampling dates were selected by the availability of field equipment. In situ measurements of water temperature (Temp), dissolved oxygen (DO), pH, and electrical conductivity (EC) were taken using a HANNA I9829 multiparameter probe. Samples were collected using a bucket and rope, filtered through 0.45 µm pore size fiberglass filters, stored in 50 mL Falcon tubes, and placed in refrigerated coolers. Falcon tubes were rinsed with hydrochloric acid and deionized water before the sampling procedures.

Following sampling, the samples were frozen at −20 °C for storage and later thawed for the analysis of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total dissolved carbon (TDC), and total dissolved nitrogen (TDN) using a TOC-L Shimadzu instrument in the laboratory facilities of the Federal University of ABC. The method for analyzing dissolved organic carbon, dissolved inorganic carbon, and total carbon followed the catalytic combustion (680 °C) and nondispersive infrared detection (NDIR) methods. For total nitrogen, thermal decomposition/chemiluminescence detection was used, employing the TNM-1 module [15].

2.2. Statistical Analysis

To verify the presence of significant differences between streams and seasonal periods, an in-depth analysis of water quality data was conducted employing the Mann–Whitney and Kruskal–Wallis tests, and the results were visually represented through the creation of box plots. Following this, a comprehensive Principal Component Analysis (PCA) was conducted to establish correlations between water quality parameters, the various streams under consideration, and the distinct seasons they represent. All these analyses were carried out using the software R (version 4.3.1) and executed in the RStudio environment (version 2024.04.1+748).

3. Results

3.1. Spatial Comparisons

Figure 2 presents the outcomes of the sampling results, facilitating a comparison across different streams. Notably, only temperature exhibited no significant differences between the streams, fluctuating within the range of 18 to 25 °C. The Comprido stream displayed the lowest average pH (6.4 ± 0.1), while Apiaí (7.2 ± 0.08) and Carapetuba (7.2 ± 0.06) showcased higher values. Dissolved oxygen levels varied from 0.55 to 3.99 mg/L, with Carapetuba registering the lowest and Guaixaya recording the highest levels. Concerning electrical conductivity, Ribeirão Jundiaí exhibited the highest average (774.8 µS/cm ± 105), whereas Guaixaya displayed the lowest (185.7 µS/cm ± 41). In terms of nutrient concentrations, all analyzed parameters demonstrated significant differences ($p < 0.05$) among the streams. Carapetuba presented the highest average concentration of total organic carbon (89.77 mg/L ± 23.11) and total carbon (119.89 mg/L ± 24.69). Conversely, Apiaí exhibited the highest average concentration of inorganic carbon (33.8 mg/L ± 1.63). In contrast, Comprido displayed the lowest average concentration for total organic carbon (17.99 mg/L ± 6.72), inorganic carbon (13.6 mg/L ± 2.86), and total carbon (31.59 mg/L ± 9.57).

The total nitrogen concentrations varied, with Ribeirão Jundiaí registering the highest average (48.38 mg/L ± 17.44) and the G.E. stream recording the lowest average (17.62 mg/L ± 6.64).

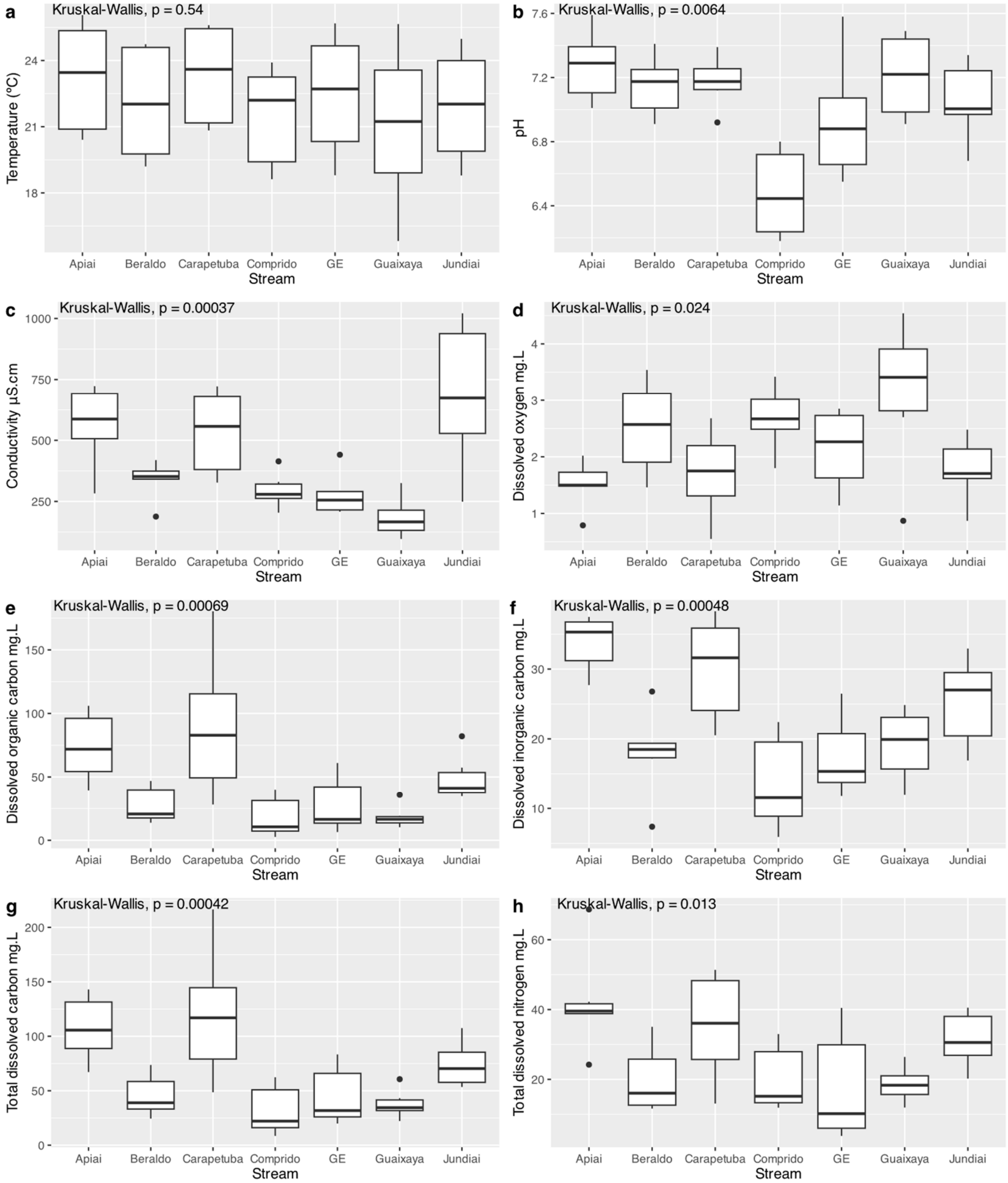

Figure 2. Boxplots representing the water quality parameters between the sampled streams in the Santo André municipality (São Paulo, Brazil) and the comparisons between the sampled streams. (**a**) Water temperature, (**b**) pH, (**c**) water conductivity, (**d**) dissolved oxygen, (**e**) dissolved organic carbon, (**f**) dissolved inorganic carbon, (**g**) total dissolved carbon, and (**h**) total dissolved nitrogen. Outliers are represented by the black dots.

3.2. Seasonal Comparisons

During the dry season, water temperature, dissolved organic carbon, total dissolved carbon, and total dissolved nitrogen exhibited significant increases (Figure 3). Conversely, other water quality parameters showed no discernible differences between the dry and wet seasons.

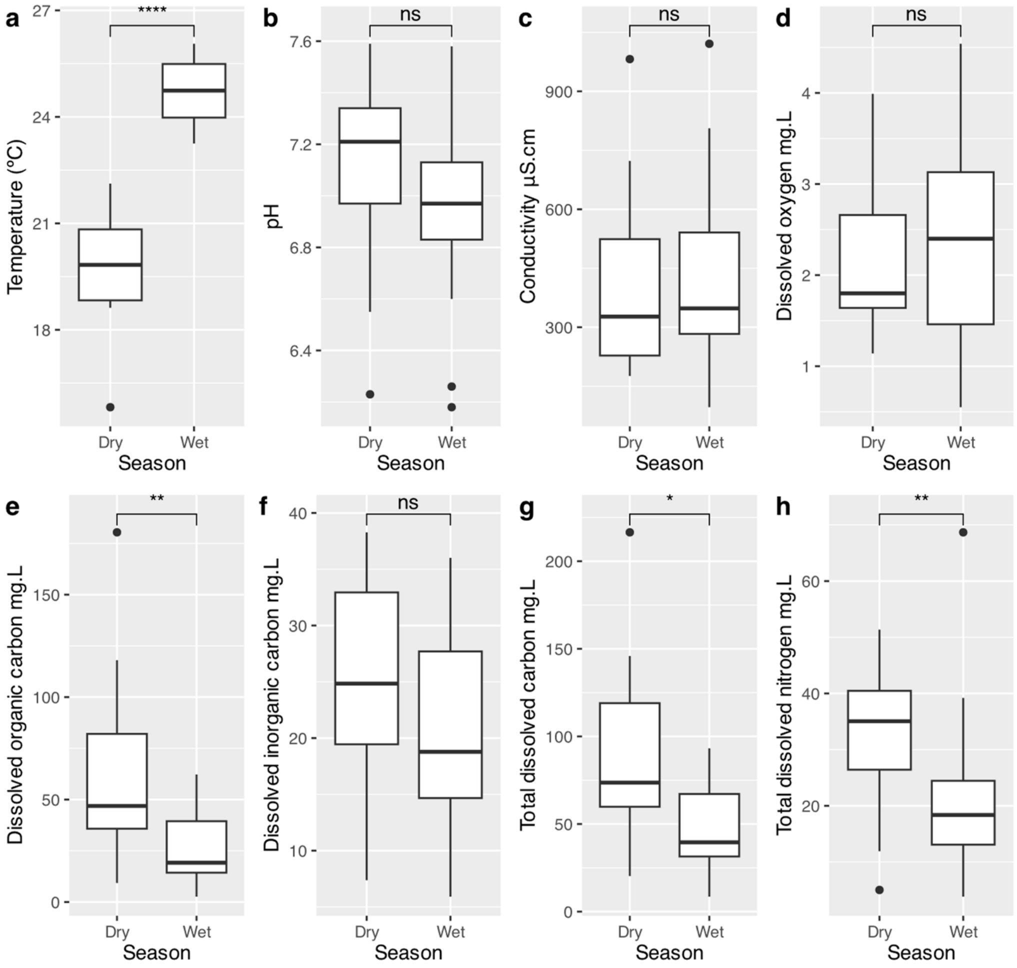

Figure 3. Boxplots representing the water quality parameters between dry and wet seasons in the Santo André municipality (São Paulo, Brazil) and the comparisons between seasons. * $p < 0.05$; ** $p < 0.01$; **** $p < 0.0001$. (**a**) Water temperature, (**b**) pH, (**c**) water conductivity, (**d**) dissolved oxygen, (**e**) dissolved organic carbon, (**f**) dissolved inorganic carbon, (**g**) total dissolved carbon, and (**h**) total dissolved nitrogen. Outliers are represented by the black dots.

3.3. Seasonal and Spatial Correlations between Water Quality Parameters

A Principal Component Analysis (PCA) was conducted to examine the correlation between the parameters and nutrient concentrations assessed in this study and the different streams and seasons. The parameters considered included water temperature, pH, electrical conductivity, dissolved oxygen concentration, as well as nutrients such as dissolved organic carbon, dissolved inorganic carbon, total dissolved carbon, and total nitrogen.

The PCA depicted in Figure 4a revealed that temperature, electrical conductivity, pH, and nutrient levels exhibited a direct correlation as opposed to the concentration of dissolved oxygen (mg/L). The higher concentrations of nutrients and higher values of pH and water conductivity were associated with the Carapetuba, Apiaí, and Jundiaí streams. The PCA depicted in Figure 4b showed that the nutrient concentrations, water conductivity, and pH were associated with the dry season in the streams.

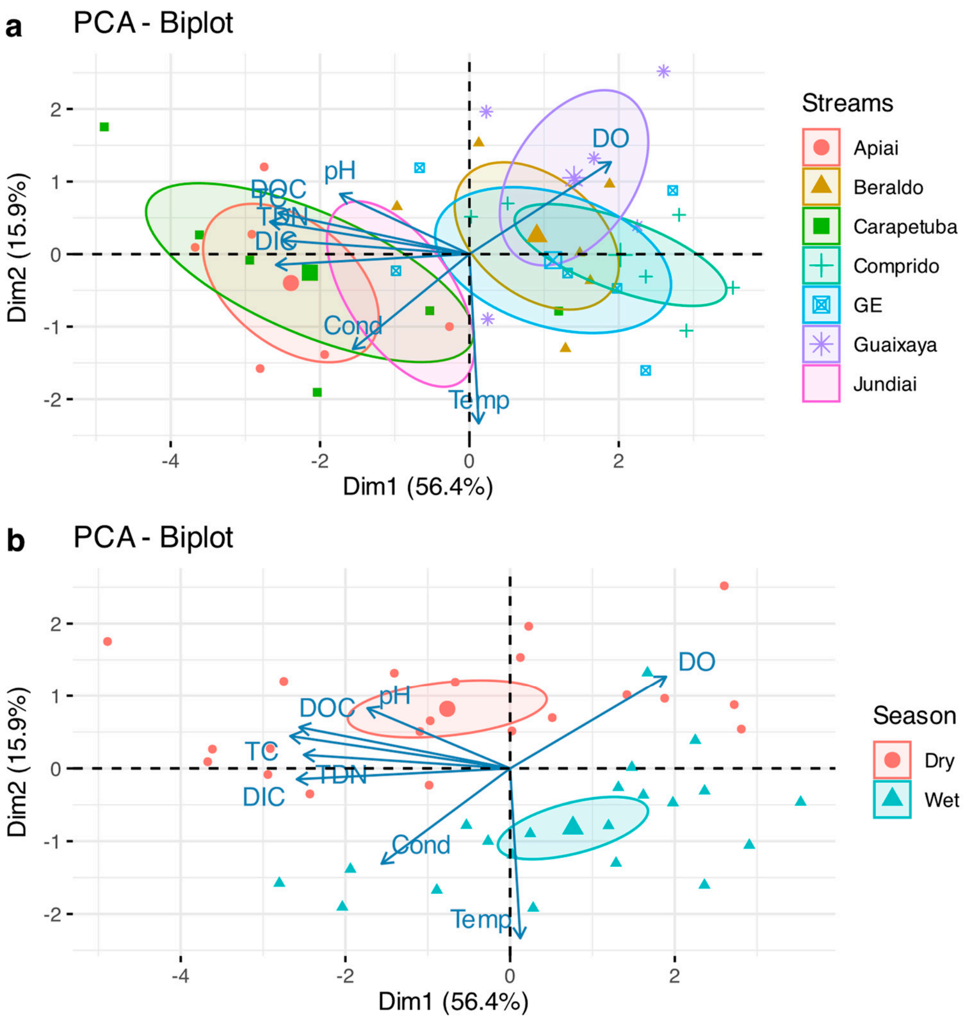

Figure 4. Principal Component Analysis correlating results from water quality between streams (**a**) and between seasons (**b**).

4. Discussion

The first objective of this study was to identify the streams with the greatest anthropogenic impact in the municipality of Santo André. The results demonstrated that the most impacted streams are the Apiaí, Carapetuba, and Jundiaí streams. The Apiaí stream showed higher concentrations of dissolved inorganic carbon and total dissolved nitrogen, indicating that this stream possibly receives untreated sewage and other organic and inorganic pollutants that may also come from surface runoff during rain events. The Carapetuba stream showed higher concentrations of dissolved organic carbon and total dissolved carbon, indicating that the main pollution source is organic, probably untreated sewage and other organic sources. The Jundiaí stream showed higher values of electrical conductivity, indicating the main pollution source in this stream is related to salts and other inorganic pollution sources that alter water conductivity. The Carapetuba and Jundiaí streams are in the central region, between the Santo Antônio and Santa Teresinha neighborhoods, respectively. According to the Municipal Decree No. 17,165 of 1 March 2019, [16] the Carapetuba stream underwent channelization works carried out by SEMASA, which diverted sewage for treatment at the Effluent Treatment Plant (ETE) ABC in accordance with the Sewer Master Plan of RMSP. Additionally, the Guaixaya stream and part of the Beraldo stream catchment also underwent channelization works and are now completely channelized. The studies conducted by Daniel et al. [17], Andrade et al. [18], and Kaushal et al. [19] contributed to the analysis of the influence of urbanization on carbon concentrations in streams and has indicated that untreated sewage can be one of the most important components for organic pollution in urban streams. Peninno et al. [20] addressed the increase in nitrogen levels because of increases in urbanization. Among other researchers, Manning et al. [21], Morgan et al. [22], Tromboni and Dodds [23], Couceiro et al. [24], and Bega et al. [25] stand out for their significant investigations in this field. Excessive nutrients can alter ecological processes in water bodies such as nitrogen and carbon, which can reduce oxygen concentrations in the water due to algal blooming and, consequently, eutrophication due to organic matter decomposition [26].

Concerning carbon, studies have found that changes in land use, such as urbanization, can also contribute to increased carbon concentrations in streams [19,27,28]. This increased carbon can trigger changes in the chemical properties of the water, exerting significant impacts on the ecosystem [29]. As highlighted in the study by Finlay [30], water pH can influence carbon dioxide (CO_2), causing effects on biotic communities. Another significant relationship between carbon forms and water pH is evident in our results. The stream with the lowest pH (Carapetuba) exhibited the lowest levels of dissolved inorganic carbon, probably because of the evasion in the form of CO_2 to the atmosphere [31]. Furthermore, according to Tundisi and Tundisi [10], in aquatic environments with high nutrient concentrations, such as phosphorus and nitrogen, some phytoplankton and aquatic plants may have a competitive advantage. These species can fix higher amounts of bicarbonate or carbonate, which are forms of inorganic carbon [26]. Therefore, the interaction between changes in land use, carbon concentrations, water chemistry, and other nutrients plays a crucial role in the dynamics of biogeochemical cycles in aquatic ecosystems [32,33], influencing the ecosystem's functions [34].

The second objective of this study was to assess whether seasonality influences the water quality parameters analyzed in the streams. The results showed that seasonality influenced the average water temperature, which was higher in the rainy season in all streams. In terms of nutrients, the season influenced the concentrations of dissolved organic carbon, total dissolved carbon, and total dissolved nitrogen, which were significantly higher during the dry season, as observed in the seasonal comparisons and in the Principal Component Analysis. These results can be associated with the diluting effects of rain during the wet season, which dilutes the untreated sewage and other pollutants, increasing the concentrations of these components during the dry season. The higher concentrations of carbon and nitrogen during the dry season can also be associated with the decomposition process of organic matter, which can be higher in low streamflow conditions [35]. Studies evaluating the seasonal effects on urban stream water quality found the same effects [17,18,25]. In another study, Bega et al. [25] observed that water quality parameters were worse in the morning, possibly due to a higher generation of pollutants before 8 a.m. and potential irregular sewage discharges. Hence, it is strongly advised to prioritize monitoring water quality in urban streams during dry seasons in the surveyed areas, recognizing the significant dilution impact during the wet season. Furthermore, we contend that similar effects might manifest in numerous cities across the Global South, given the shared challenges of untreated sewage disposal and extensively polluted surface runoff [8].

Finally, our study contributes some directions for the management of the studied catchments, considering that we were able to identify the most polluted streams draining urban catchments. The most polluted streams were the Carapetuba, Apiaí, and Jundiaí streams, which drained highly urbanized catchments. Despite the highest presence of green areas in the Carapetuba catchment (~15%), this amount of green area was not able to reduce nutrient concentrations. This result can be associated with the high loads of organic compounds in all seasons in the stream channel and the lack of hydrological connections between the stream water and groundwater in urban areas [7]. In addition, soil impermeabilization can enable the runoff of precipitation with a complex mixture of contaminants into streams and other water bodies, contributing to water degradation [36]. Furthermore, the channelization of streams can exacerbate the problem because straightening watercourses, along with the removal of riparian zones, which can act in the protection of these water bodies, can facilitate the transport of these contaminants [2]. In this regard, it is recommended that the monitoring of urban streams in the municipality of Santo André be carried out over the long term and specific legislation be developed for the conservation of urban streams, in addition to other measures that can be taken, such as improvements in wastewater treatment to remove nutrients from the water and the revitalization of vegetation, especially in the riparian zone, considering that all catchments have low vegetation cover.

5. Conclusions

Urban streams are among the most polluted freshwater ecosystems in tropical and subtropical regions. This study assessed the water quality in Santo André's urban streams, focusing on differences between catchments and seasons. The Apiaí, Carapetuba, and Jundiaí streams were the most polluted, with high water conductivity, total dissolved carbon, total dissolved nitrogen, and low dissolved oxygen, indicating that urgent management is needed. Seasonality significantly affected water quality, with higher nutrient concentrations in the dry season due to organic matter decomposition and reduced rainfall dilution. The key concerns were sewage disposal and organic contamination. The recommended actions include long-term monitoring, improved wastewater treatment, and riparian vegetation revitalization to preserve aquatic ecosystems amid urbanization.

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Data Availability Statement: The raw data with the concentrations of nutrients and water quality parameters are available at Mendeley Data with the DOI 10.17632/nvnghmcs4n.1.

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