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Temporal and Spatial Dynamics of Carbon, Nitrogen, and Phosphorus in a Subtropical Urban River (Tamanduateí River, São Paulo, Brazil)

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Abstract: Water quality in urban streams often reflects the broader environmental challenges posed by dense population centers, where pollution from untreated sewage and runoff can significantly degrade ecosystems. This study examines the spatial and temporal variations of carbon, nitrogen, and phosphorus concentrations in the Tamanduateí River, which runs through the Metropolitan Region of São Paulo, Brazil. Data were sourced from the annual reports of the Environmental Company of the State of São Paulo (CETESB) covering the period from 2011 to 2022. Between 2011 and 2017, carbon and phosphorus concentrations declined, likely due to sanitation improvements. However, since 2017, these concentrations have been rising again, indicating renewed pollution inputs, primarily from untreated sewage. Nitrogen levels remained consistently high, with elevated concentrations observed upstream, linked especially to domestic effluent discharges. The recent increase in phosphorus levels is also of concern. The absence of spatial variation in phosphorus suggests diffuse pollution from urban areas, while nitrogen decreases downstream, possibly due to biological assimilation. The study underscores the pressing need for enhanced sewage management. Drawing from the successful revitalization of the Cheonggyecheon stream in Seoul, implementing nature-based solutions and regular maintenance could effectively reduce nutrient pollution and improve water quality, facilitating the restoration of the Tamanduateí River.

Keywords: neotropics; urbanization; pollution; eutrophication

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Citation: Souza, F.H.B.; Morilla, M.; Guedes-Pereira, B.; Lemes, K.; Taniwaki, R.H. Temporal and Spatial Dynamics of Carbon, Nitrogen, and Phosphorus in a Subtropical Urban River (Tamanduateí River, São Paulo, Brazil). *Limnol. Rev.* **2024**, *24*, 557–567. https://doi.org/10.3390/limnolrev24040032

Academic Editor: Prosper K. Zigah

Received: 19 September 2024
Revised: 4 November 2024
Accepted: 11 November 2024
Published: 13 November 2024

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1. Introduction

Rivers are fundamental components of the urban landscapes and play an essential role in the development of ecological relationships and the conservation of freshwater biodiversity. In urban landscapes, rivers not only support local biodiversity but also provide essential ecosystem services, such as water purification, flood regulation, and temperature moderation [1,2]. Despite the pressures of urbanization, these waterways act as ecological corridors, connecting fragmented habitats and offering critical resources to both aquatic and terrestrial species [3]. Furthermore, the presence of healthy river systems within cities contributes to improved air and water quality, as well as offering recreational and aesthetic benefits for residents, thereby enhancing overall urban livability [4]. The monitoring and recovery of freshwater has been further highlighted by actions such as the Sustainable Development Goals (SDGs), set by the United Nations (UN) related to clean water and sanitation (SDG n. 6) and life below water (SDG n. 14) [5]. These goals are intended to try to recover the damage in freshwaters caused mainly by anthropogenic actions that are advancing, such as urbanization. With the advance of urbanization, rivers suffer various impacts that profoundly affect their physical morphology and dynamics. Among the problems triggered by urbanization are the degradation and depletion of water resources, flooding, erosion, siltation, and contamination from waste disposal [6–8].

Consequently, with increased concentrations of nutrients and contaminants, there is a reduction in aquatic biodiversity, indicating a decrease in water quality [9,10]. These global concerns are also reflected locally, as exemplified by the impact of urbanization in São Paulo, Brazil, where the largest metropolis in the country has faced significant challenges in water quality management.

Studies indicate that in tropical and subtropical regions, urban landscapes are the land use that most impacts water quality, especially regarding nutrient enrichment and eutrophication [11–13]. As the Metropolitan Region of São Paulo is the largest metropolis in Brazil, it is understood that its irregular growth has had a negative impact on the region's water bodies, including the Tamanduateí River Basin Complex. The Tamanduateí River's main source is in an environmental protection area in Mauá city (São Paulo state, Brazil) and flows into the Tietê River [10]. Inserted in the middle of São Paulo's urban sprawl, the Tamanduateí River has suffered serious anthropic interventions during the development of the city, which is still experiencing serious environmental problems today [14–16]. Due to the high level of contamination from several anthropogenic sources, the rivers and streams of Brazil's metropolitan regions have been gradually polluted as these regions have expanded without proper planning [15–17].

Among the main sources of contamination in the Tamanduateí River are the domestic and industrial sewage from the surrounding metropolis, which is discharged into the river's flow. This waste significantly alters the river's biodiversity and impacts its physical and chemical water parameters, including concentrations of phosphorus, nitrogen, and organic matter. Monitoring the temporal and spatial dynamics of these nutrients is crucial, as it allows for a better understanding of how contamination levels fluctuate over time and across different areas of the river. In particular, nitrogen and phosphorus are key indicators of water quality in urban rivers because of their high concentrations in wastewater and their potential to cause environmental harm, such as freshwater contamination and eutrophication [18–20]. Tracking changes in these compounds can help identify critical periods and zones where interventions are most needed. Additionally, total organic carbon (TOC), an indicator of organic matter content, is another essential parameter for water quality assessment. In wastewater, TOC can reach concentrations of up to 1000 mg/L, while surface water typically ranges from 1 to 20 mg/L. A sudden increase in TOC levels may signal the introduction of a new pollutant source, such as untreated sewage or industrial effluents, further reinforcing the need for continuous and spatially distributed monitoring [21].

Despite the importance of the Tamanduateí River in one of the biggest metropolitan regions of Latin America, the evaluation of the spatial and temporal characteristics of water quality has never been assessed. In this sense, this study can contribute to the preservation and recovery of the quality of the Metropolitan Region of São Paulo's urban water resources by evaluating how and when the water quality in the river has improved or degraded. We focus on two main questions: how the water quality in the Tamanduateí River has changed over the past 11 years and which areas of the river require special attention for water quality management. In addition, we discuss some cases of success of urban river restoration and how they could be applied in the region.

2. Materials and Methods

2.1. Study Area

The Tamanduateí River runs through a stretch extending from the municipality of Mauá to São Paulo, crossing a large area of the São Paulo Metropolitan Region (Southeast Brazil) (Figure 1). The São Paulo Metropolitan Region has a climate characterized by two distinct periods of rain and drought, corresponding to summer and winter, respectively [22], and is classified as humid subtropical, type Cwa—the summer is hot and rainy and the winter is mild and dry—by Köppen's classification. According to the National Institute of Meteorology (INMET, Brazil), the maximum and minimum average temperatures in São Paulo between the period of 1991–2020 were 27 °C and 20 °C, respectively, based on

climatological normals, which indicates the average climatic characteristics in a location based on 30 years of data.

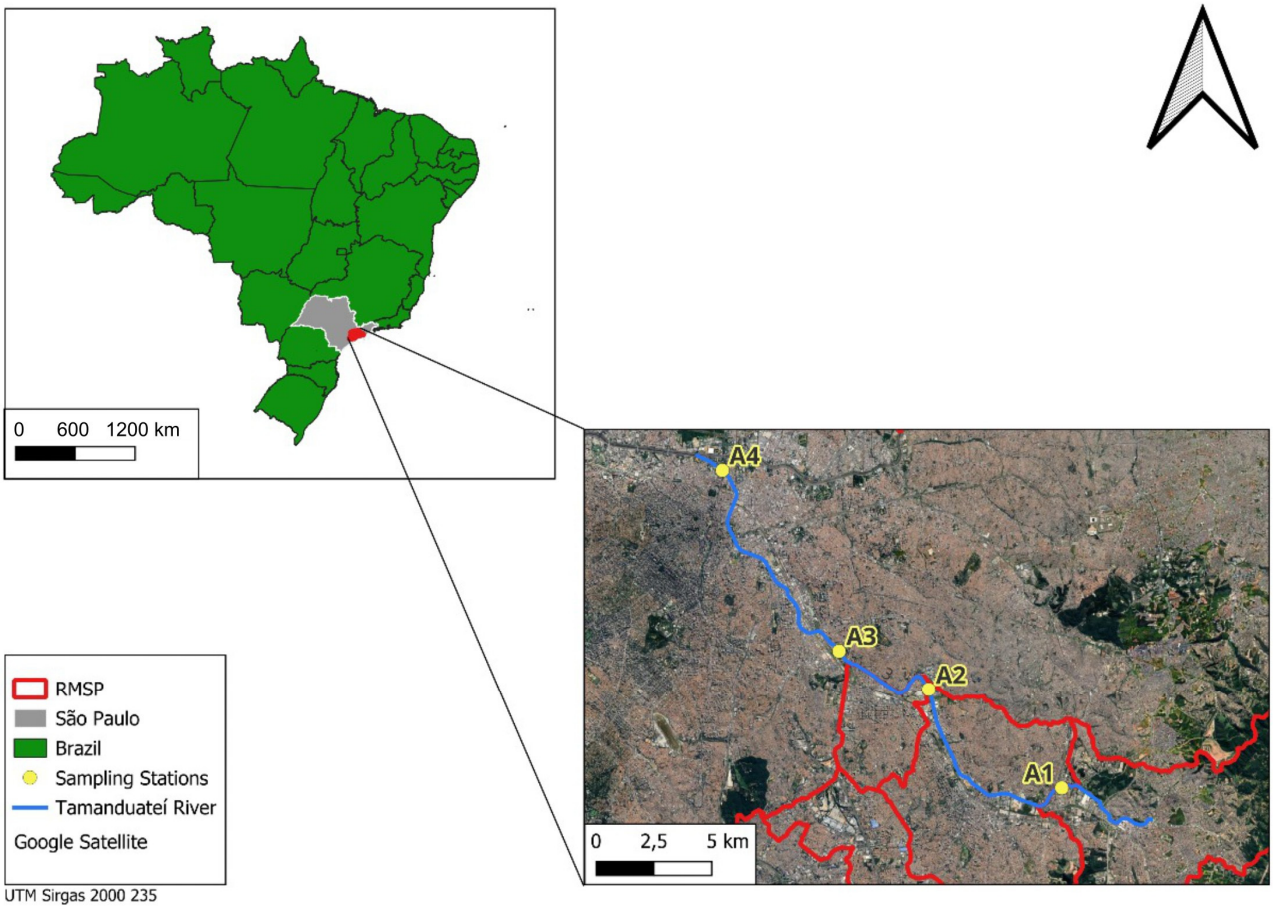

Figure 1. Sampling stations of the study, collected by the Environmental Company of the State of São Paulo (CETESB). RMSP = municipalities of the Metropolitan Region of São Paulo.

The water samples were collected in the cities of Mauá, São Caetano, and São Paulo along the course of the Tamanduateí River by the Environmental Company of the State of São Paulo (CETESB) (Figure 1). These data are made available annually in the "Report on the Quality of Inland Waters of the State of São Paulo" [23]. For this study, the sampling points along the Tamanduateí River were separated, extracting data of total nitrogen, total phosphorus, and total organic carbon (TOC) between the years 2011 and 2022 (last available report) [23]. The sampling areas (Ax) were classified as follows: A1: CETESB sampling point TAMT 04250, located in the municipality of Mauá; A2: CETESB sampling point TAMT 04500, located in the municipality of São Caetano do Sul; A3: CETESB sampling point TAMT 04600 and A4: CETESB sampling point TAMT 04900, located in the municipality of São Paulo.

2.2. Data Collection and Analysis Methodology by CETESB

The analytical methodology used for the analysis of total phosphorus was optical emission spectrophotometry with argon plasma (ICP/OES), as described by the United States Environmental Protection Agency (USEPA)—Method 6010C and SW 846 Compendium. After collection, the sample was preserved in a plastic bottle by adding sulfuric acid until reaching the pH below 2.0 to prevent the precipitation of phosphorus-containing compounds. The sample then underwent an acid digestion process to convert all forms of phosphorus, whether organic or inorganic, into orthophosphate, which is detected by ICP/OES. After digestion, the sample was nebulized and introduced into the argon

plasma of the ICP-OES. The total phosphorus concentration was determined based on the light intensity relative to a calibration curve built with phosphorus standards of known concentration.

For the analysis of total organic carbon (TOC) concentrations, the methodology from the Standard Methods for the Examination of Water and Wastewater was used [24]. For TOC analysis, CETESB uses two methods, 5310-B and 5310-C. The 5310-B method was used for samples with higher TOC loads. It is carried out through combustion oxidation at high temperatures using a total organic carbon analyzer (TOC). The sample is homogenized and diluted if necessary, and a portion is injected into a heated reaction chamber with an oxidative catalyst, which can be cobalt oxide, platinum group metals, or barium chromate. The water in the sample is vaporized, and the organic carbon is oxidized into CO_2 and H_2O. The CO_2 obtained from the oxidation of organic and inorganic carbon is transported by a carrier gas flow and measured by a non-dispersive infrared detector. The 5310-C method was used for samples with low TOC levels. Organic carbon is oxidized to carbon dioxide (CO_2) through persulfate in the presence of heat or ultraviolet light. The CO_2 is purged from the sample, dried, and transferred by carrier gas flow to a non-dispersive infrared detector and then titrated colorimetrically or separated from the liquid flow by a specific membrane that allows the passage of CO_2 into high-purity water, where the change in conductivity is measured and related to the passage of CO_2 through the membrane [24].

Total Kjeldahl Nitrogen is the sum of organic nitrogen and ammoniacal nitrogen, and CETESB analyzes it using two methods, one developed by APHA [24] and the other by the International Organization for Standardization (ISO) [25]. The APHA-AWWA-WEF method (4500-N) contains two forms of analysis, differing by concentration and number of samples. The analysis is performed in the presence of H_2SO_4, potassium sulfate (K_2SO_4), and cupric sulfate ($CuSO_4$) catalyst, where the amino nitrogen in organic materials is converted into ammonium, as is free ammonia. After the addition of a base, ammonia is distilled from an alkaline medium and absorbed into boric or sulfuric acid. Ammonia can be determined colorimetrically, which is used to determine organic nitrogen levels below 5 mg/L, by an ammonia-selective electrode or by titration with mineral acid, with both methods used to determine a wide concentration of organic nitrogen.

2.3. Statistical Analysis

In order to identify points in a time series data set where there is a significant change in the underlying data structure, we employed the breakpoints function from the "strucchange" package [26] in R (version 4.3.1) [27] to detect structural changes in phosphorus concentrations over time. The analysis involved fitting a piecewise linear model to the data, allowing us to visualize the fitted values alongside the observed data points. Vertical dashed lines were used to indicate the identified breakpoints, which represent moments of significant shifts in phosphorus, carbon and nitrogen levels. By incorporating these breakpoints into our graphical representations, we provided a clearer understanding of temporal trends.

3. Results

3.1. Temporal Variation of Carbon, Nitrogen, and Phosphorus Concentrations in the Tamanduateí River

The concentrations of carbon, nitrogen, and phosphorus in the Tamanduateí River exhibited temporal variations from 2011 to 2022 (Figure 2). Phosphorus concentrations showed breakpoints in 2013 and 2018, with an increase followed by a decrease and then stability of the elevated concentrations until 2022. The nitrogen concentrations did not show any breakpoints, with the concentrations being high during the entire analyzed period. Carbon concentrations displayed a downward trend from 2011 to 2016, with average concentrations around 50 mg/L in 2011 and 22 mg/L in 2022.

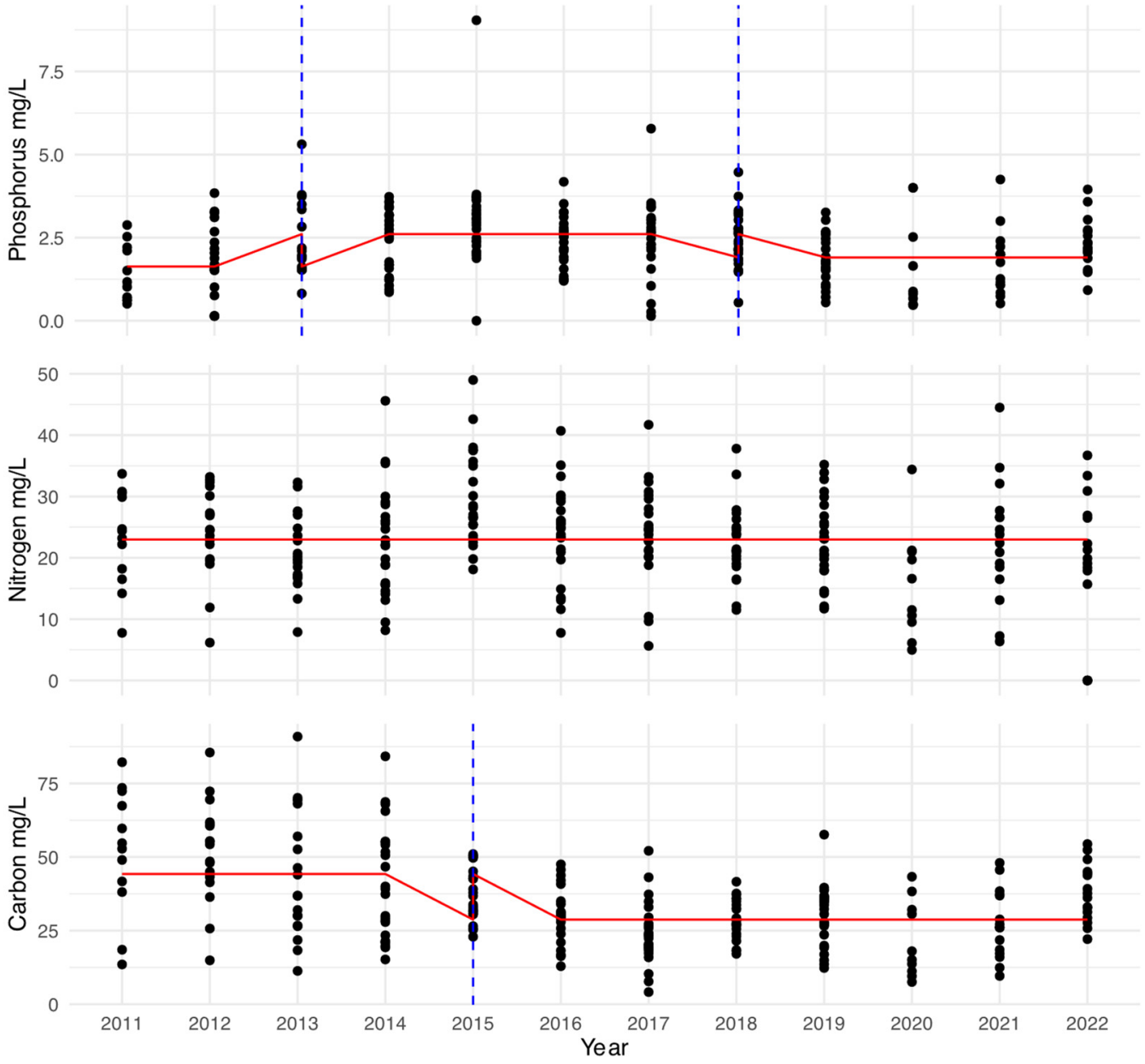

Figure 2. Temporal variation of each analyzed nutrient by the Environmental Company of the State of São Paulo (CETESB). The red line represents the fitted piecewise linear model to the data, to visualize the fitted values alongside the observed data points. Vertical dashed lines were used to indicate the identified breakpoints, which represent moments of significant shifts in phosphorus, carbon, and nitrogen concentrations.

3.2. Spatial Variation of Carbon, Nitrogen, and Phosphorus Concentrations in the Tamanduateí River

The concentrations of nutrients evaluated in this study revealed distinct spatial patterns (Figure 3). Phosphorus levels showed stable concentrations among the river segments, with the highest concentrations in the upstream region in Mauá municipality. Nitrogen concentrations were higher, especially at the upstream region, in Mauá municipality. However, no temporal changes were observed in the different segments of the river. For carbon concentrations, a decreasing trend can be observed in all river segments since 2014.

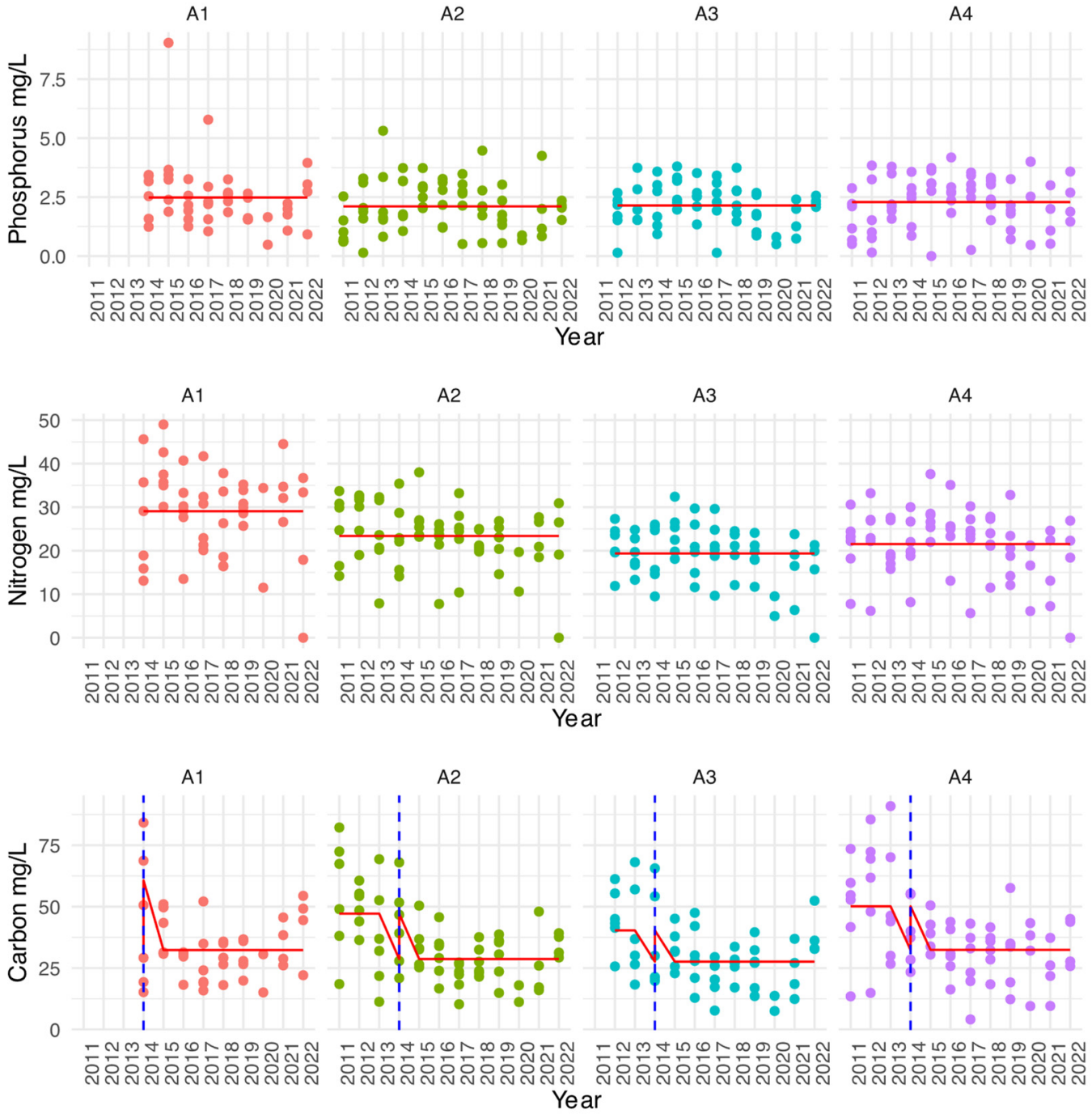

Figure 3. Spatial variation of nutrient concentrations in each sampling station from Environmental Company of the State of São Paulo (CETESB). The red line represents the fitted piecewise linear model to the data to visualize the fitted values alongside the observed data points. Vertical dashed lines were used to indicate the identified breakpoints, which represent moments of significant shifts in phosphorus, carbon, and nitrogen concentrations.

4. Discussion

This study aimed to evaluate the spatial and temporal fluctuations of carbon, nitrogen, and phosphorus concentrations in the Tamanduateí River, an important river that runs through Brazil's largest metropolis. Regarding temporal variations, significant oscillations in nitrogen carbon and phosphorus concentrations were found. Phosphorus concentrations displayed an increase in average levels after 2013 and a decrease after 2018. Nitrogen concentrations were high and stable. In contrast, carbon concentrations exhibited a de-

creasing trend over the analyzed years. The decreased concentration of carbon is possibly related to the sanitation works carried out since 2011, primarily aimed at reducing the direct discharge of domestic sewage into the rivers. From 2007 to 2015, the São Paulo ABC region received the Growth Acceleration Program—Urbanization of Precarious Settlements (PAC-UAP), launched by the federal government in partnership with state and municipal governments. PAC-UAP was developed to fund urbanization projects in precarious settlements, including sanitation works, which were likely responsible for the reduction in carbon concentrations in the Tamanduateí River [28]. Despite stabilization, nitrogen concentrations remain consistently high. This is likely due to the high rate of domestic and, primarily, industrial effluent discharge in upstream areas near the border between the municipalities of Mauá and Santo André [29]. As for phosphorus, concentrations remained above the limit of 0.15 mg/L for Class III rivers, as set by Brazilian legislation in CONAMA Resolution No. 357/05 [30]. However, for Class IV, where the river is currently classified, there is no defined phosphorus concentration limit, and to improve the classification, a reduction of about 1070% from the concentration found in 2019 would be necessary [30]. Studies conducted in another municipality in the state of São Paulo also show phosphorus concentration levels exceeding CONAMA resolution standards in an urban stream, even at its lowest concentration in 2013, because of local urbanization [31,32]. In this context, it is essential to continue implementing sanitation projects to prevent further degradation of the Tamanduateí River and to improve its water quality.

The spatial patterns of nutrient concentrations analyzed in this study reveal distinct nutrient patterns along the Tamanduateí River. Regarding phosphorus concentrations, the results indicate higher concentrations in the upstream region in Mauá municipality. The absence of spatial variation in the middle stretches of the river may be associated with diffuse sources, such as highly urbanized zones with predominant impervious surfaces, which reduce infiltration and increase surface runoff. This dynamic homogenizes phosphorus distribution along urban rivers [33]. On the other hand, nitrogen concentrations showed a distinct spatial pattern, with higher levels observed at the upstream point of the river, located in the municipality of Mauá. This increase may be attributed to point or diffuse sources of nitrogen situated upstream, such as domestic effluent discharges, which may introduce significant amounts of nitrogen into the fluvial system [9,13]. The decreases in concentration downstream may indicate biological assimilation or dilution processes along the river or the presence of retention zones where nitrogen is partially removed [29]. Regarding carbon, the gradual reduction in concentrations between 2011 and 2022 at all sampling points without spatial distinction suggests a temporal trend of decreasing carbon availability in the water. This behavior may result from sanitation actions implemented in the region influencing the organic matter load in the river and by decomposition processes [34]. However, starting in 2018 in the downstream region, a gradual increase in carbon concentrations was observed, possibly related to the lack of periodic maintenance of domestic and industrial effluent pipelines, contributing to increased organic matter and, consequently, total organic carbon [35]. The same trend can be observed for the nitrogen concentrations. Therefore, special attention should be directed to the downstream region, where high concentrations have begun to be observed.

Urban river interventions in São Paulo began in the 1980s, with a focus on sustainability and revitalization of settlement infrastructure surrounding the river. By the late 2000s, new intervention proposals were advanced but still faced socio-environmental challenges in achieving real river recovery [36]. In addition to the Tamanduateí River, another significant urban river in São Paulo with similar variations is the Pinheiros River, which underwent a revitalization process costing over BRL 3 billion [37]. This project faced challenges similar to those of the Tamanduateí River, particularly regarding the spatial variation of nutrient concentrations [38]. One of the greatest challenges still faced today is the discharge of partially or untreated sewage into water bodies, particularly in areas with irregular settlements, where homes are often built along streambanks and where there is no

sewage collection due to the difficulty in connecting homes to the state collection network, regulatory problems, and the costs associated with the connection [29].

When it comes to alternatives for reducing nutrient levels in rivers, one option is the use of nature-based solutions, which offer various benefits for both territorial management and environmental quality improvement. These technologies range from interventions in stream infrastructure to the implementation of bioretention structures capable of mitigating the dispersion of nutrients in urban rivers. Bioretention systems are an excellent sustainable alternative, as they provide continuous action and are capable of controlling pollutant loads at the source with high efficiency in containing diffuse pollution loads [39]. An example of an urban stream that experienced extreme degradation and later underwent revitalization is the Cheonggyecheon stream in South Korea. With the rapid and disordered growth of the city of Seoul during the 20th century, various interventions were carried out along the stream, resulting in significant environmental degradation and the reduction of its natural area. In the 1970s, the stream was completely buried to make way for urban road expansion, almost eliminating its presence in the urban environment [40,41]. As part of efforts to improve local river sustainability, in 2002, the Seoul city government began infrastructure works to reopen the channel and expand the stream's banks [41], with the construction of parks and green areas (such as bioretention systems). With public approval, the stream is now an important landscape feature of Seoul and a model for urban river revitalization in large cities.

When comparing the Cheonggyecheon stream in South Korea with the Tamanduateí River, some similarities can be observed in terms of location and environmental challenges. Both rivers are in densely urbanized areas, with channelized stretches and high levels of pollution (in the past of Cheonggyecheon and nowadays in the Tamanduateí). In the case of the Tamanduateí River, the main problem to be solved is the implementation of sewage collection and treatment in the entire river basin. In addition, the proper maintenance of its streams and pipeline systems, along with the expansion of riverbanks through bioretention installations, could drastically reduce nutrient loads, such as those of nitrogen and phosphorus [39]. The installation of bioretention systems would be effective in mitigating pollution, improving water quality, and contributing to the environmental recovery of surrounding urban areas [42]. This alternative is common in some countries and is being applied in some regions of Brazil, but it still lacks regulatory and normative processes for widespread use in urban river treatment [39].

4.1. Potential Effects of Climate Change on Nutrient Concentrations of Tamanduateí River

Climate change plays a significant role in influencing nutrient concentrations in rivers by altering hydrological cycles, temperature, and ecological interactions [43]. Rising global temperatures can boost microbial activity, accelerating the decomposition of organic matter and potentially increasing carbon and nitrogen levels in water bodies [34]. In the Tamanduateí River, while recent trends have shown decreases in carbon concentrations due to past sanitation efforts, warmer conditions could reverse this pattern by enhancing organic matter breakdown. Additionally, elevated temperatures may drive algal blooms that initially reduce nutrient levels through uptake but later release them upon die-off, creating cycles of nutrient variability [44]. Changes in precipitation also contribute to nutrient dynamics, as intensified rainfall can elevate surface runoff [6], transporting nitrogen and phosphorus from urban and industrial areas, such as those upstream in Mauá. This leads to increased nutrient loading, while periods of drought may concentrate pollutants due to reduced water flow.

Erosion and land-use changes triggered by climate change further exacerbate these nutrient fluctuations [8]. Heavy rainfall can wash more sediments and associated phosphorus into rivers, potentially explaining high phosphorus concentrations in urban stretches and contributing to eutrophication risks [6]. The increased carbon concentrations observed downstream post-2018 could be linked to climate-related stresses such as flooding, which strain existing sanitation infrastructure and allow for greater discharge of organic matter.

Effective river management must therefore integrate climate change resilience by reinforcing wastewater treatment systems and adopting adaptive measures, such as nature-based solutions like bioretention systems. These strategies can help mitigate nutrient dispersion and sustain water quality improvements amid changing environmental conditions.

4.2. Study Limitations

A key limitation of this study lies in the reliance on secondary data provided by the Environmental Company of the State of São Paulo (CETESB), which may not capture all potential pollution sources or account for variations in monitoring frequency and precision over the study period. Additionally, the study's temporal scope (2011–2022) may not fully reflect longer-term trends in nutrient concentrations, especially given the potential for unmonitored pollution events or infrastructural changes. The spatial analysis was also constrained by the available sampling points, which may not adequately represent the entire river system, particularly in identifying localized pollution hotspots. Furthermore, while the study highlights the impact of sanitation improvements and irregular discharges, it does not incorporate direct measurements of sewage or industrial effluent inputs, making it difficult to definitively attribute observed changes in nutrient concentrations to specific sources. Lastly, the study does not assess the ecological impacts of nutrient fluctuations on aquatic life, which would provide a more comprehensive understanding of the river's health.

5. Conclusions

The Tamanduateí River, located in the Metropolitan Region of São Paulo, suffers from severe pollution, particularly from phosphorus, carbon, and nitrogen. Although carbon concentrations have historically declined, they remain high, and recent years have shown an upward trend. The most critically polluted areas within the Tamanduateí watershed include the headwaters, where nitrogen and phosphorus levels are highest. Sewage discharge is identified as the primary issue needing resolution, especially in irregular settlements. Future studies in the Tamanduateí River could evaluate the combined effects of urbanization, irregular settlements, and climate change on water quality, focusing on how these factors contribute to nutrient loading, pollution patterns, and overall ecosystem health. Addressing this essential challenge in Latin America's largest metropolitan area could pave the way for applying restoration strategies similar to those used in the Cheonggyecheon stream in South Korea.

Author Contributions: Conceptualization, R.H.T.; methodology, R.H.T.; software, R.H.T.; formal analysis, R.H.T.; investigation, F.H.B.S., M.M., B.G.-P. and K.L.; resources, R.H.T.; writing—original draft preparation, F.H.B.S., M.M., B.G.-P. and K.L.; writing—review and editing, F.H.B.S., M.M., B.G.-P., K.L. and R.H.T.; supervision, R.H.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—CAPES, grant number 001.

Data Availability Statement: The data used in this study are available at: https://cetesb.sp.gov.br/catalogo-de-dados-abertos (accessed on 1 February 2024).

Acknowledgments: We are grateful to Companhia Ambiental do Estado de São Paulo—CETESB, who made the data of water quality in the state of São Paulo available.

Conflicts of Interest: The authors declare no conflicts of interest.

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