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Research Article

Spatio - Temporal Distribution of Nitrate and Phosphate in Serayu Watershed, Central Java, Indonesia

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Abstract

The Serayu Watershed is a vital area in Indonesia, where agricultural runoff contributes to nutrient enrichment in rivers. This study offers novelty as it is the first to analyze the spatiotemporal distribution of nitrate and phosphate in the Serayu River over a three-year period (2021–2023). The research aims to support sustainable watershed management by examining nutrient dynamics and their correlation with environmental parameters such as dissolved oxygen (DO), pH, total suspended solids (TSS), and chemical oxygen demand (COD). Water sampling was conducted at 15 stations across the upstream, midstream, and downstream segments. Data were analyzed using Microsoft Excel and PAST 4.03, applying Principal Component Analysis (PCA) and biplot methods. Results showed nitrate levels were highest downstream in 2021, but shifted upstream in 2022–2023, likely due to organic matter decomposition. Phosphate remained highest midstream throughout the period, linked to domestic activity and land use. Nitrate levels fluctuated seasonally, especially during the rainy season, while phosphate levels were relatively stable. Spatial mapping highlighted dynamic nitrate changes in Banjarnegara and Cilacap, with phosphate distribution remaining more uniform. Correlation analysis revealed nitrate was related to TSS and COD in 2021, had no significant correlation in 2022, and was linked with pH in 2023. Phosphate consistently correlated with COD and pH. These findings emphasize that both natural and human-induced factors drive nutrient variability in the Serayu watershed, underlining the urgency of integrated watershed management to control nutrient pollution and protect water quality.

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1. Introduction

Watersheds play a critical role in maintaining ecological stability and supporting human livelihoods, yet they are increasingly threatened by anthropogenic pressures. Common anthropogenic activities occurring around the river area include the indiscriminate disposal of domestic waste and agricultural practices. Residues from agricultural activities, such as fertilizers and pesticides, are often carried into the river system through surface runoff during rainfall events, contributing to the degradation of water quality (Hu, 2018). The Serayu River Basin (SRB), one of the major watersheds in Central Java, Indonesia, flows through five regencies and is subject to escalating environmental stress, particularly nutrient pollution (Bhagawati *et al*., 2013). Likewise, the Teteriv River in Ukraine has experienced increased nutrient concentrations from anthropogenic activities, leading to heightened eutrophication risks (Tsyhanenko-Dziubenko *et al*., 2023). The excessive use of fertilizers in agriculture, coupled with domestic wastewater discharges, has led to increased concentrations of nitrate and phosphate in the river system. These nutrients degrade water quality, promote eutrophication, and pose risks to aquatic biodiversity (Xu *et al*., 2022).

Globally, nutrient pollution in freshwater systems has become a major challenge. Recent studies have shown that agricultural runoff is a dominant source of nitrogen and phosphorus compounds, often leading to oxygen depletion and algal blooms (Li *et al*., 2024; Yin *et al*., 2024). Household detergents also contribute significantly to phosphate loading in urban rivers (Wu *et al*., 2023). In Vietnam, Giao *et al.* (2022) documented how agricultural intensity affects seasonal nutrient variation. Similar findings have been reported in China (Li *et al*., 2023; Wang *et al*., 2023), India (Ramalingam *et al*., 2021), Algeria (Ounissi and Bouchareb, 2013), and Indonesia (Elvania *et al*., 2019; Handayani *et al*., 2023; Lestari *et al*., 2023; Lukmanulhakim *et al*., 2023; Pratama *et al*., 2020).

Although the effects of nitrate and phosphate on water quality have been widely reported, most studies focus on single-point observations or general trends in major rivers. Very few have analyzed the spatiotemporal distribution of these nutrients in mid-sized tropical river basins, especially in Indonesia. Furthermore, the relationship between these nutrients and multiple environmental indicators such as dissolved oxygen (DO), pH, total suspended solids (TSS), and chemical oxygen demand (COD) remains not well understood, making it difficult to identify pollution hotspots and predict ecological risk under varying seasonal and land-use conditions. This study addresses this gap by conducting a multi-year spatiotemporal assessment combined with PCA analysis, linking nutrient dynamics to key environmental parameters (pH, TSS, and COD) in a tropical watershed context. The lack of integrated assessments in tropical contexts represents a critical research gap, and addressing it remains a major challenge for effective watershed management. This study specifically addresses that gap by conducting a long-term spatiotemporal analysis of nitrate and phosphate distribution in a mid-sized tropical river, the Serayu River in Indonesia, where such assessments have not previously been conducted. The findings are expected to support science-based recommendations for integrated river water quality management.

Therefore, this study aims to map nitrate/phosphate distribution, analyse correlations with DO/pH/TSS/COD, and identify pollution hotspots. The outcome of this research is expected to contribute to more effective watershed management by identifying pollution hotspots and clarifying the interactions between nutrient pollution and environmental conditions. Ultimately, this work will enrich our understanding of nutrient behaviour in tropical river systems, which presently remains a major challenge in aquatic science.

2. Materials and Methods

2.1 Materials

2.1.1 The equipment

2.5 L water jerry cans, Erlenmeyer flasks, measuring cylinders, hotplates, pipettes with volumes of 2 mL, 5 mL, and 10 mL, test tubes, cuvettes, and COD reactors (Hach DRB200). For nutrient analysis, a nitrate test kit (Hanna Instruments HI781) and a phosphate test kit (Hanna Instruments HI736) were utilized. Additional instruments included a pH meter (Ohaus Starter 3100 series), a water quality checker (WQC), desiccators, an oven, Whatman No. 41 filter paper, petri dishes, tweezers, 100 mL measuring cylinders, labels, markers, tissue paper, latex gloves, general stationery, and documentation tools.

2.1.2 The materials

The materials used in this study included water samples collected from the Serayu River Basin, trash bags, and various chemical reagents for nutrient and chemical oxygen demand (COD) analyses. These reagents consisted of 0.0511 g potassium dichromate ($K_2Cr_2O_7$), 8.35 mL sulfuric acid solution (H_2SO_4), 1.655 g mercuric sulfate ($HgSO_4$), 1.012 g silver sulfate (Ag_2SO_4), 100 mL sulfuric acid reagent, digestion solution reagents, and phosphate low-range (LR) reagents. For nitrate analysis, marine nitrate low-range reagents A (4 mL), B, and C were also used.

2.1.3 Ethical approval

This study does not require ethical approval because it does not use experimental animals.

2.2 Methods

This study employed a purposive sampling method to select 18 sampling stations along the Serayu River Basin, representing upstream, midstream, and downstream sections. Each sampling station was analyzed for nitrate and phosphate concentrations to assess their spatiotemporal distribution. The collected data were then analyzed using Principal Component Analysis (PCA) to determine the relationship between nutrient levels and environmental parameters.

2.2.1 Study area

This study was conducted within the Serayu River Basin Area (DAS Serayu), located in Central Java, Indonesia. The data collection focused on six key water quality parameters: nitrate, phosphate, pH, total suspended solids (TSS), dissolved oxygen (DO), and chemical oxygen demand (COD). These data were collected over a three-year period: 2021, 2022, and 2023. Primary data for the year 2023 were obtained through field sampling conducted in October 2023. The data for 2021 and 2022 were obtained from secondary sources, specifically from the Serayu-Citanduy Water Resources Management Center (Balai Pengelolaan Sumber Daya Air-BPSDA Serayu-Citanduy). The sampling locations are distributed as follows (Figure 1).

2.3 Analysis Data

The collected data were analyzed using Microsoft Excel and statistical software, including PAST version 4.03. To evaluate the patterns and relationships among water quality parameters, specifically nitrate and phosphate, Principal Component Analysis (PCA) was employed. This multivariate analysis technique was used to reduce data dimensionality while retaining the essential variation in the dataset. PAST version 4.03 was selected due to its accessibility as free software and its user-friendly interface, making it suitable for performing multivariate statistical analyses commonly used in ecological and environmental studies. Meanwhile, Microsoft Excel was used for preliminary data organization and descriptive analysis, as it provides appropriate tools for tabulating and visualizing basic trends in water quality parameters.

Principal Component Analysis (PCA) was used in this study by considering its basic assumptions, namely the existence of correlation between variables, interval or ratio scale data, and the relevance of dimension reduction to simplify complex data. In this context, several water quality parameters, such as nitrate, phosphate, and total suspended solids (TSS), showed a correlated relationship. In addition, environmental conditions such as community agricultural activities in the river basin also affect the values of these parameters. Therefore, PCA is considered appropriate to identify the main patterns in the spatial and temporal distribution of water quality in the study area. A biplot analysis was then generated using PAST 4.03 to visualize the grouping patterns of sampling points and to identify correlations among environmental variables such as nitrate, phosphate, dissolved oxygen (DO), pH, total suspended solids (TSS), and chemical oxygen demand (COD). The biplot aids in interpreting how these variables contribute to spatial and temporal variability and in determining potential clustering among observation sites within the Serayu River Basin. It is important to note that the analysis is based on secondary data collected during 2021-2022, which may contain some inconsistencies or gaps due to variations in data collection methods and environmental factors. These potential biases should be considered when interpreting the results.

3. Results and Discussion

3.1 Results

3.1.1 Concentration of nitrate and phosphate

Industrial, domestic, and agricultural activities often influence the concentration of nitrate and phosphate in river water. Anthropogenic inputs, such as fertilizer runoff, significantly contribute to nitrogen enrichment (Shuler *et al*., 2017; Ramalingam *et al*., 2021), which can lead to water contamination and promote excessive algal growth (Ding *et al*., 2019). Therefore, monitoring nitrate levels is crucial for the sustainability of aquatic ecosystems. Observations from 2021 to 2023, as shown in Figure 2, provide an overview of nitrate distribution in the Serayu watershed.

From 2021 to 2023, phosphate concentrations were consistently highest in the midstream area (Figure 3). The high concentration of phosphate in the middle of the river is caused by community activities, such as washing with detergents containing phosphate (Masykur *et al*., 2018; Larasati *et al*., 2021; Setiawati and Ariani, 2021). This phosphate accumulation can trigger phytoplankton blooms, which have a negative impact on water quality and fish metabolism (Rifal, 2013; Ebeling *et al*., 2006).

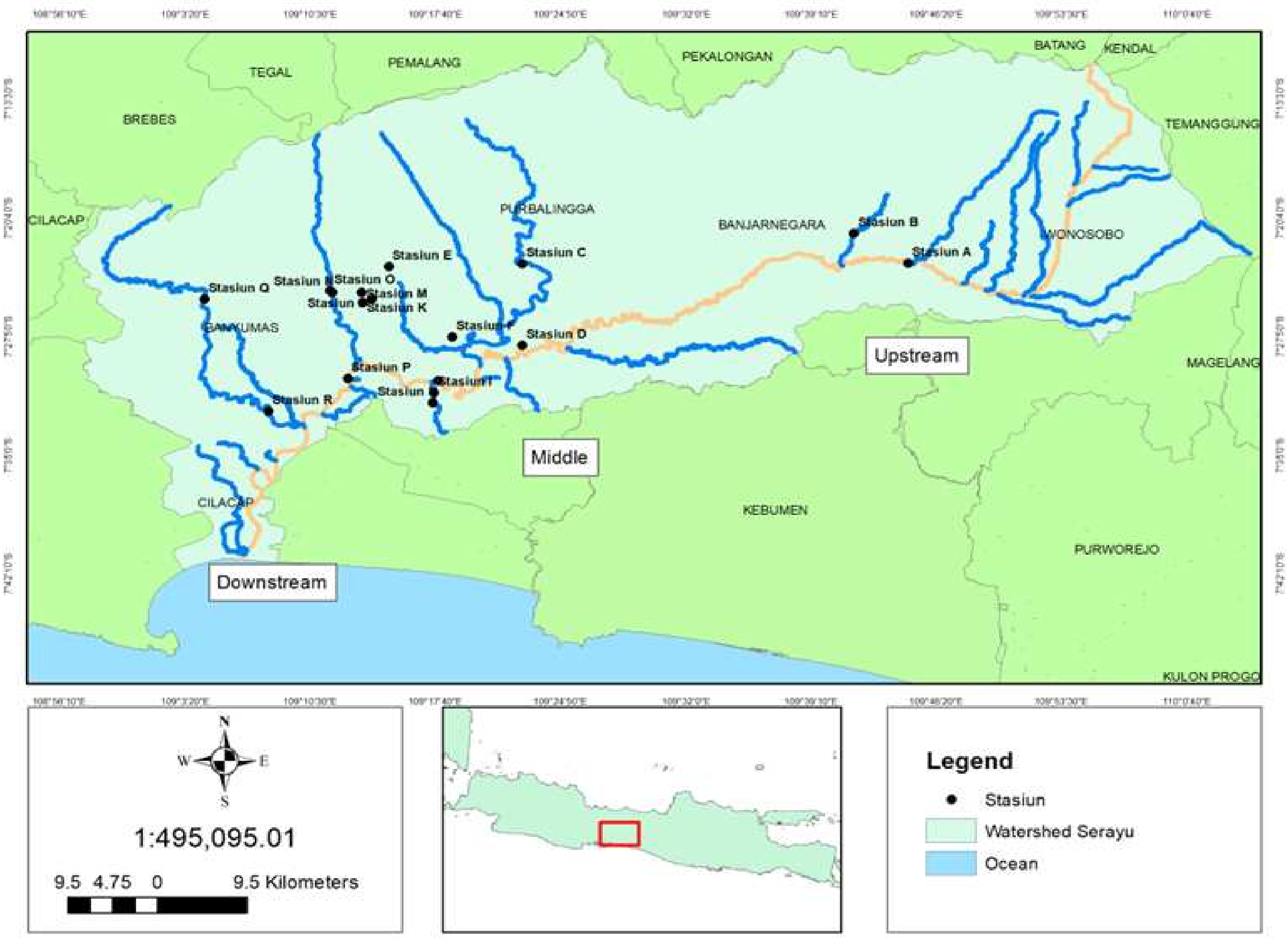

Figure 1. Sampling locations.

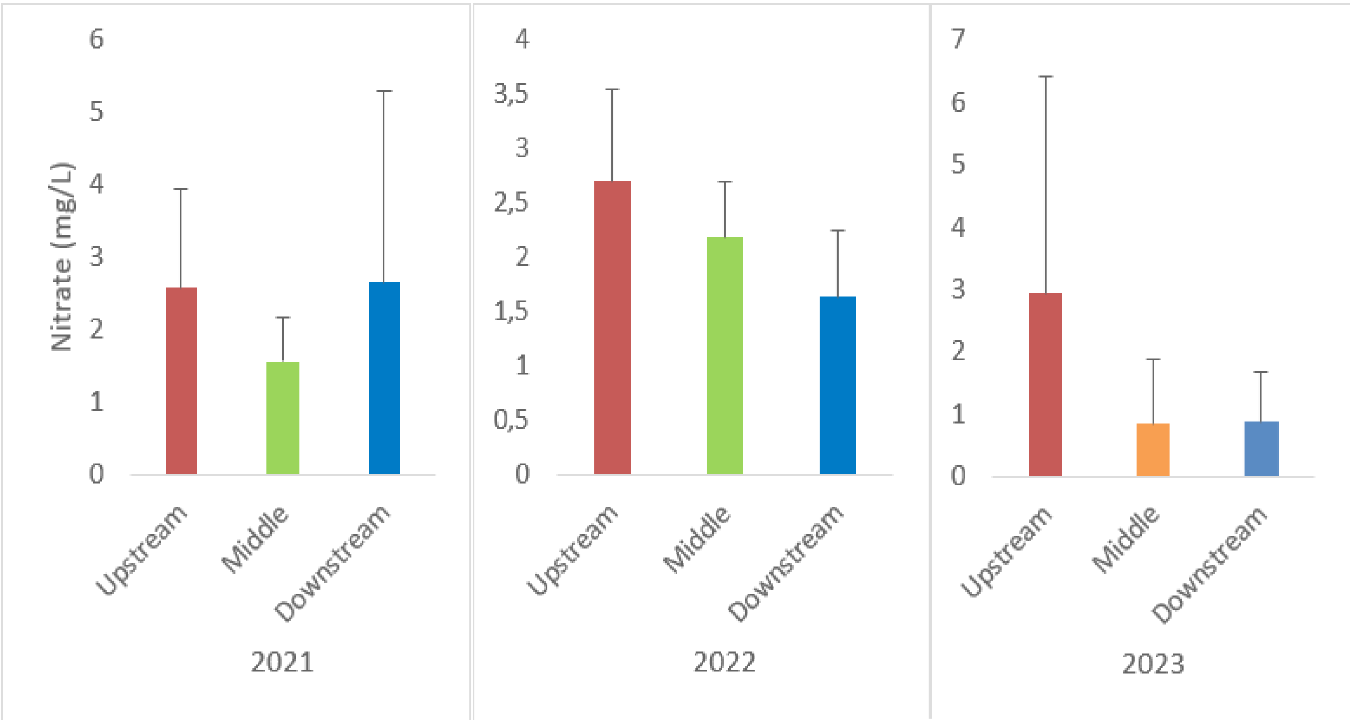

Figure 2. Average concentration of nitrate in water in Serayu Watershed.

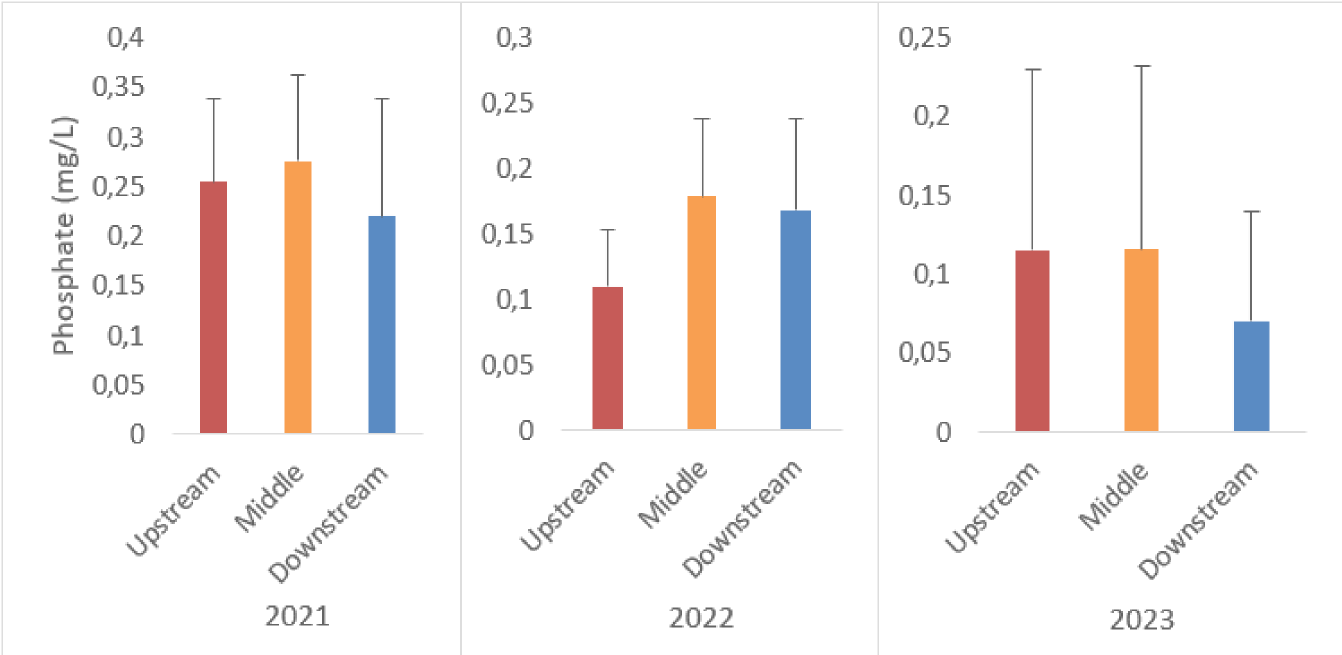

Figure 3. Average concentration of phosphate in water in Serayu Watershed.

3.1.2 Spatio-temporal distribution of nitrate and phosphate in Watershed Serayu

3.1.2.1 Nitrate

Nitrate is the predominant form of nitrogen in natural waters and serves as a key nutrient for the growth of algae and aquatic plants. However, elevated nitrate levels exceeding the quality standards may signal water pollution, typically resulting from anthropogenic sources such as domestic waste, industrial discharge, agricultural runoff, and livestock activities (Yogafanny, 2015). Therefore, understanding the spatial and temporal distribution of nitrate is essential for effective watershed management. This study evaluated the distribution of nitrate concentrations across the Serayu watershed from 2021 to 2023, as illustrated in Figure 4.

3.1.2.2 Phosphate

Phosphate is an essential nutrient that plays a key role in supporting aquatic productivity and influencing water fertility. However, its concentration in aquatic systems can vary significantly depending on the form of the compound and the surrounding environmental conditions. Under certain scenarios, phosphate levels may exceed safe thresholds, especially in waters influenced by anthropogenic activities. The increasing input of nutrients, particularly from urban and agricultural sources, has raised concerns about their ecological impacts on freshwater systems (Wang *et al*., 2024). Thus, an analysis of the spatio-temporal distribution of phosphate in the Serayu River Basin is necessary to assess the dynamics and potential risks, as illustrated in Figure 5.

3.1.3 Relationship between nitrate and phosphate with environmental factors using principal component analysis (PCA)

Principal Component Analysis (PCA) is a multivariate statistical technique used to identify patterns in data and explore relationships among several interrelated variables. PCA is particularly effective in environmental studies to determine correlations among water quality parameters by reducing data dimensionality while retaining most of the variation present in the dataset (Chamidy *et al*., 2020). In this study, PCA was applied to analyze the relationship between nitrate and phosphate with other environmental factors such as Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD) for the years 2021 and 2022, and with Dissolved Oxygen (DO), pH, TSS, and COD for 2023. This analysis utilized a biplot representation to interpret the relationships between parameters, where the angles between vectors indicate the nature and strength of their correlation (Kristiana *et al*., 2020). An acute angle (<90°) suggests a positive correlation, a right angle (~90°) indicates no correlation, and an obtuse angle (>90°) indicates a negative correlation (Ikhtifari and Prasetyo, 2020). Additionally, vectors pointing in the same direction represent parameters that vary similarly across sampling stations. The PCA biplot for 2021 is displayed in Figure 6. Furthermore, the 2022 PCA biplot graph is presented in Figure 7.

The PCA biplot for 2023, presented in Figure

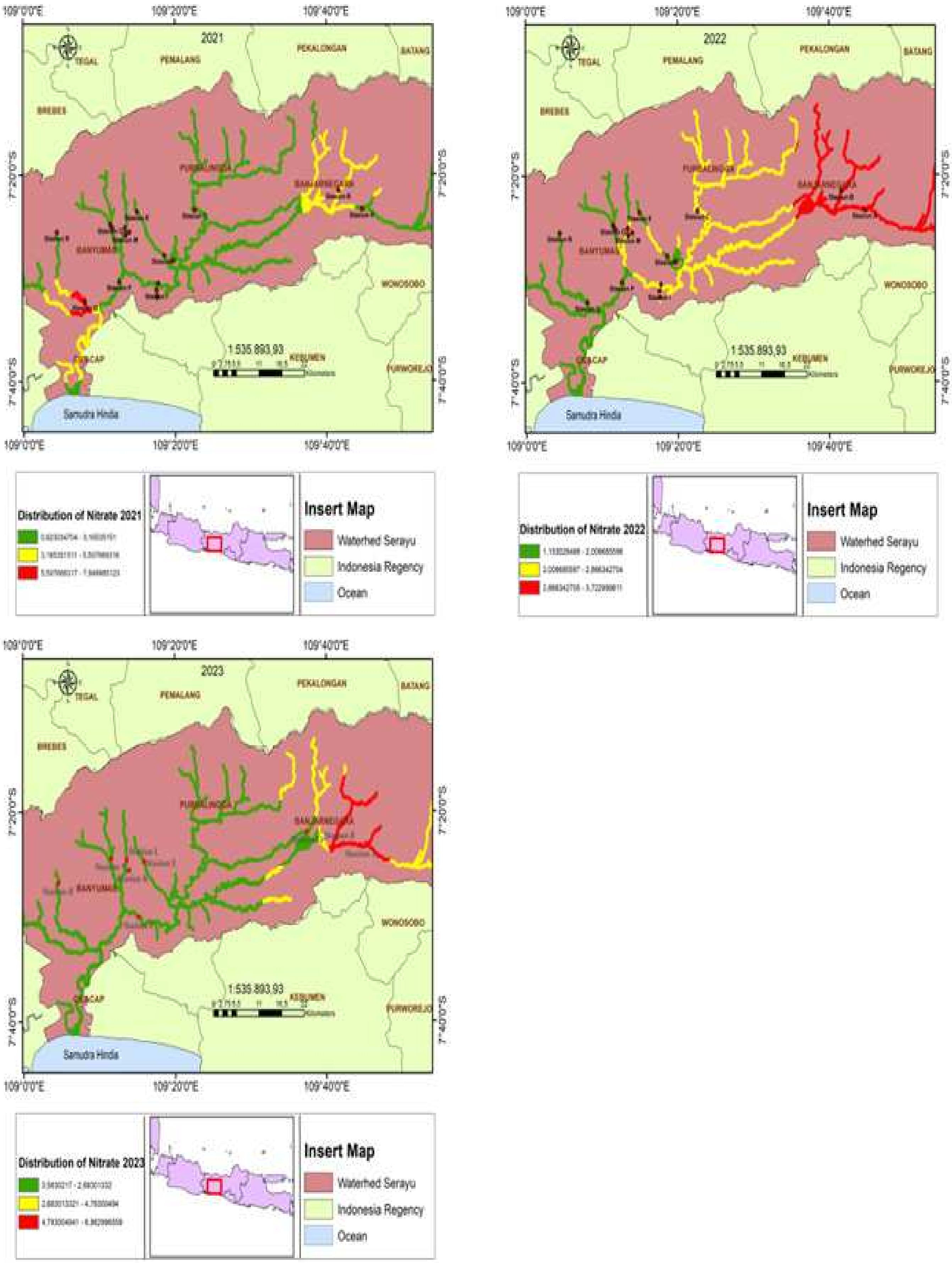

Figure 4. Distribution of nitrate in Serayu Watershed 2021-2023.

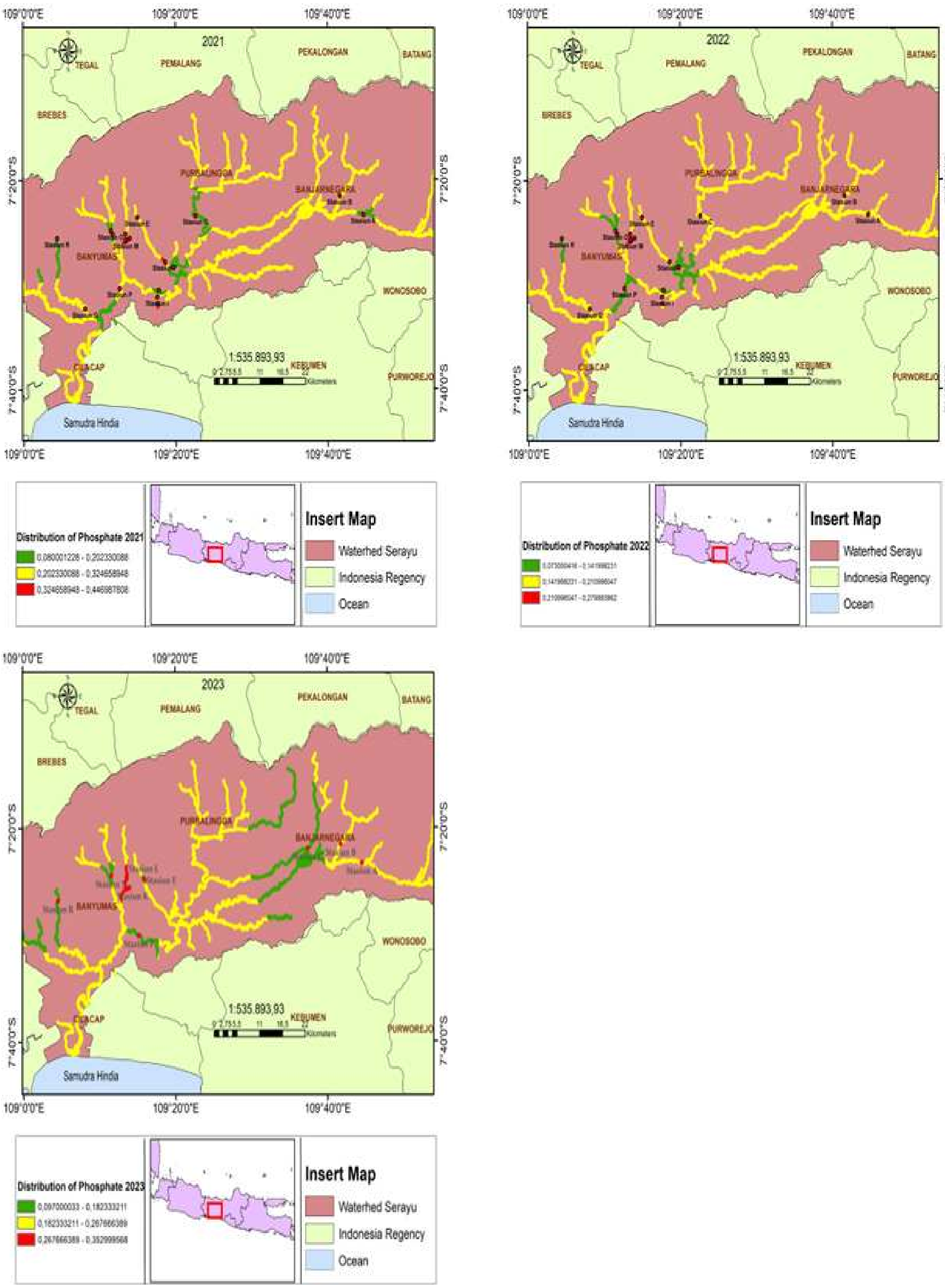

Figure 5. Distribution of phosphate in Serayu Watershed 2021-2023.

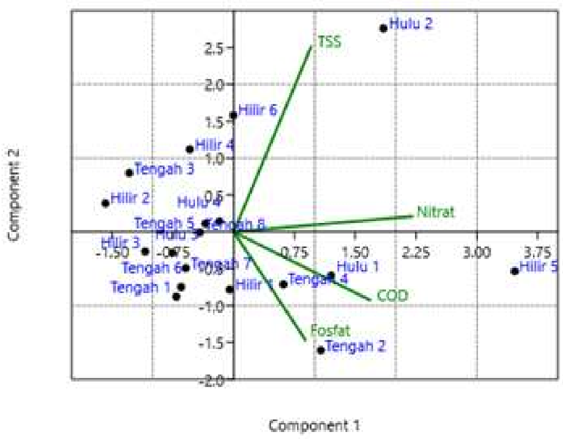

Figure 6. PCA biplot graph 2021.

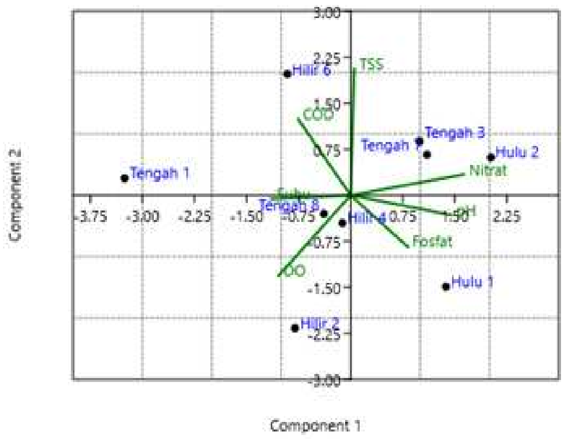

Figure 7. PCA biplot graph 2022.

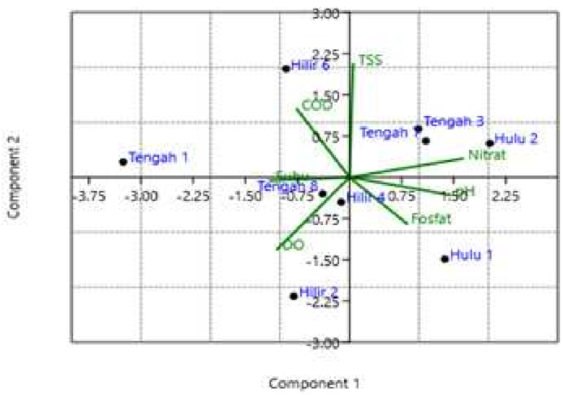

Figure 8. PCA biplot graph 2023.

8, shows a cumulative covariance of 59.247%, indicating that the two principal components account for a considerable proportion of the variance in the dataset.

3.2 Discussion

3.2.1 Concentration of nitrate and phosphate

3.2.1.1 Nitrate

In 2021, the highest nitrate concentrations were recorded in the downstream region, while in 2022 and 2023, concentrations were highest in the upstream areas. Elevated nitrate levels upstream are not solely attributed to anthropogenic waste but are also linked to the decomposition of organic matter from aquatic plants (Yanti, 2017; Kumar *et al.*, 2024). Furthermore, microbial degradation of phytoplankton in bottom waters under hypoxic conditions contributes to increased nutrient concentrations (Shulkin *et al.*, 2018). The upstream area of the Serayu River remains relatively natural, with minimal infrastructure development, allowing for the growth of diverse plant species (Nugroho *et al.*, 2021). Field observations confirmed the presence of substantial vegetation in the upstream region, particularly at the Serayu Tengah station, where decaying plant matter contributes to nutrient enrichment (Karina *et al.*, 2022).

In 2022, nitrate concentrations showed fluctuations from upstream to downstream. These variations may result from the denitrification process, which is influenced by dissolved oxygen levels. Low DO in downstream areas can promote nitrate reduction into gaseous nitrogen forms through sequential microbial processes (Arnanda, 2023). Additionally, accumulation of nitrate from upstream, combined with downstream anthropogenic activities such as domestic waste disposal and agricultural runoff, contributes to elevated concentrations in lower river segments (Hu, 2018; Hidayati *et al.*, 2022). Ultimately, the accumulated nutrients are transported to the river mouth and into the sea, potentially influencing marine primary production, as nitrogen acts as a limiting nutrient in marine environments (Correll, 1996).

3.2.1.2 Phosphate

Related to the phosphate concentrations, the pattern is closely linked to dense residential zones and intensive domestic activities, including the use of phosphate-based detergents (Mahyudin *et al.*, 2015; Masykur *et al.*, 2018; Setiawati and Ariani, 2021). If unmanaged, these sources can increase phosphate concentrations in surface waters, leading to eutrophication and degradation of aquatic ecosystems (Wu *et* *al*., 2023). Additionally, phosphate pollution has been associated with metabolic disruption in fish and broader ecological impacts (Ebeling *et al*., 2006).

Community activities that result in the direct discharge of phosphate-containing waste into rivers are significant contributors to nutrient enrichment and eutrophication (Chen *et al*., 2019; Chen *et al*., 2020; Guo *et al*., 2021; Li *et al*., 2021). Phosphate, as a limiting nutrient in many freshwater systems, plays a critical role in regulating the growth of primary producers such as algae and aquatic plants. When phosphate input increases beyond the assimilation capacity of the ecosystem, it stimulates excessive algal growth, which can alter ecological balance, reduce water quality, and deplete dissolved oxygen through subsequent decomposition processes (Kesena, 2015).

Sources of phosphate in riverine environments are primarily linked to household waste, particularly from detergents, dishwashing agents, and human waste. In densely populated areas along riverbanks, continuous input of domestic waste into the water body creates persistent nutrient loading. This long-term enrichment, if unmanaged, accelerates eutrophication, characterized by murky waters, fish kills, and biodiversity loss (Correll, 1996).

3.2.2 Spatio-temporal distribution of nitrate and phosphate in Watershed Serayu

3.2.2.1 Nitrate

In 2021, the highest nitrate concentration was recorded at Station B (Merawu) with 4.230 mg/L, followed by Station P (Tajum Hulu). These values represent the average concentrations obtained from sampling in March, September, and November. The elevated nitrate levels at Station B coincided with high concentrations of total suspended solids (TSS) at 3.67 mg/L and chemical oxygen demand (COD) at 90.65 mg/L at nearby Station P. The catchment surrounding the Merawu River is characterized by extensive plantations and dense residential settlements, which contribute organic and nutrient-rich waste to the river. Similar findings were reported in previous studies (Rizki *et al*., 2015; Lee *et al*., 2020), indicating that mixed land uses such as agriculture and settlements significantly contribute to nitrate loading in river systems.

The lowest nitrate concentration in 2021 was at station J (Upstream Banjaran), with a concentration of 0.823 mg/L, and K (Downstream Banjaran) of 0.903 mg/L, and N (Logawa) of 0.823 mg/L. The low nitrate concentration in the Banjaran River may be due to the still low use of agricultural land (Jarvie *et al*., 2018). The still low concentration in the Logawa River also indicates little contribution from land activities, such as household waste disposal, mining activities, and livestock waste disposal, which are usually sources of nitrate pollution in waters (Ramalingam *et al*., 2021).

Conversely, the lowest nitrate concentrations in 2021 were observed at Station J (Upstream Banjaran), Station K (Downstream Banjaran), and Station N (Logawa), with values ranging from 0.823 to 0.903 mg/L. These relatively low concentrations are most likely attributed to the limited anthropogenic pressure in these areas. The Banjaran River segment, particularly in its upstream and downstream stretches, traverses regions with sparse agricultural activity, minimal residential development, and low levels of industrial or livestock operations. As a result, there is reduced input of nitrogen-rich substances such as fertilizer residues, untreated domestic wastewater, and organic livestock waste, which are commonly known contributors to nitrate enrichment in aquatic ecosystems (Ramalingam *et al*., 2021). Additionally, these stations may benefit from natural buffer zones, such as riparian vegetation and forested catchments, which serve important ecological functions in mitigating nutrient runoff (Mayer *et al*., 2007). Vegetative buffers can trap and utilize nitrogen before it enters the river, thus acting as a natural filter. The hydrological characteristics of these segments, such as slower surface runoff, higher infiltration rates, and lower erosion potential, may further support the retention of nitrate within soils rather than allowing it to leach into water bodies.

In 2022, the spatial distribution of nitrate across Stations A to Q indicated that the highest concentration occurred at Station A (Upstream Serayu) with 3.06 mg/L, followed closely by Station B (Merawu) at 3.723 mg/L. Total Suspended Solids (TSS) were also consistently high across most sampling locations, with an average of 0.93 mg/L, reflecting potential sediment and nutrient runoff. The recurrent elevation of nitrate levels at these two upstream stations suggests persistent and significant nutrient input from surrounding land use, particularly agricultural plantations (Xu *et al*., 2022). These areas are known for intensive farming activities, which often involve the liberal use of nitrogen-based fertilizers such as urea and NPK. The relationship between upstream agricultural practices and elevated nutrient concentrations is well documented, where fertilizers not absorbed by plants are susceptible to leaching and surface runoff, especially during rainfall events. These excess nutrients are eventually transported into adjacent water bodies, contributing to eutrophication and water quality degradation (Zhang *et al*., 2015). Such conditions are exacerbated in sloped agricultural landscapes, as found in parts of the upper Serayu catchment, where erosion and rapid runoff accelerate nutrient loss.

Historical monitoring data support these findings. For instance, nitrate concentrations at the Serayu Movable Dam in 2016 averaged 17.54 mg/L, highlighting the chronic nutrient stress affecting the watershed (Arinda *et al*., 2023). The persistence of high nitrate concentrations over the years emphasizes the need for improved land management strategies, such as buffer strips, controlled fertilizer application, and soil conservation practices, to mitigate nutrient transport from agricultural zones.

The 2023 data revealed an even higher nitrate concentration at Station A (4.85 mg/L) and Station B (6.883 mg/L), while Station N (Logawa) again recorded the lowest concentration. Sampling conducted in March, July, and October consistently showed that Stations A and B remained nitrate hotspots. This recurring pattern suggests the presence of stable and significant sources of nitrate in these areas. In the Merawu catchment, extensive agricultural land, particularly potato farming, is prominent (Wulandari, 2007; Prastia, 2015). Potato cultivation in the upper Serayu region often relies heavily on fertilizers such as urea and NPK, which, if not managed using conservation principles, increase nitrate leaching into nearby water bodies (Sutrisna and Surdianto, 2014). These findings are consistent with reports indicating that intensified fertilizer application directly elevates nitrate concentrations in aquatic systems, leading to water quality deterioration (Chen *et al*., 2021).

Spatial distribution maps across the three years highlighted color-coded changes, particularly in Banjarnegara and Cilacap regencies. In Banjarnegara, areas ranged from green to yellow in 2021 but turned red in 2022 and 2023, indicating a significant increase in nitrate concentration. Cilacap exhibited fluctuation from yellow-green to red in 2021, green in 2022, and remained green in 2023. These temporal shifts align with seasonal agricultural cycles, especially during the rainy season, when fertilizer application and runoff intensify (Wu *et al*., 2023). Rainfall acts as a key driver for nutrient transport, with intensive farming combined with high rainfall accelerating nitrogen leaching and distribution in river systems (Xie *et al*., 2021).

3.2.2.2 Phosphate

In 2021, phosphate distribution patterns revealed the highest concentrations at several downstream stations. Specifically, Station F (Pelus downstream) recorded a concentration of 0.370 mg/L, Station H (Gawe upstream) at 0.433 mg/L, and Station M (Kranji downstream) at 0.447 mg/L. These values were derived from average measurements taken in March, September, and November. The elevated concentrations in downstream areas suggest that surface runoff, particularly from urban and agricultural zones, acts as a primary contributor to phosphate loading in these river segments (Contreras *et al*., 2024). Such runoff typically carries residues from fertilizers, household detergents, and untreated waste, which accumulate along the river course and lead to nutrient enrichment in lower catchment zones.

Conversely, the lowest phosphate concentrations were recorded in Station G (Central Serayu River) at 0.080 mg/L and Station D (Klawing downstream) at 0.090 mg/L. The low concentration in the central region of the Serayu River may be attributed to limited anthropogenic influence and minimal agricultural runoff, particularly from areas with less intensive land use. Reduced exposure to phosphorus-containing materials decreases the risk of eutrophication and helps maintain ecological balance. Moreover, minimal phosphate levels may indicate reduced accumulation of organic matter or waste residues that are commonly linked to the degradation of aquatic environments and the potential harm to aquatic biota (Elvania *et al*., 2019).

In 2022, phosphate data were collected during three sampling periods: March, July, and September. The results indicated that the highest phosphate concentration was recorded at Station M (Kranji downstream), with a value of 0.253 mg/L. Notably, this station also exhibited one of the highest Chemical Oxygen Demand (COD) values among all observed locations in 2022, reaching 49.09 mg/L. This finding suggests a potential positive correlation between phosphate and COD concentrations, which supports previous studies that link nutrient enrichment with increased organic pollutant loads in river systems (Lumaela *et al*., 2013). The presence of both high phosphate and COD levels often indicates input from untreated domestic waste or organic-rich agricultural runoff. Another area with elevated phosphate levels was Station J (Banjaran upstream). The high concentration at this station is likely influenced by its proximity to agricultural zones and residential settlements. Fertilizer use in agriculture and household waste disposal practices in the surrounding area contribute significantly to phosphate enrichment in the river.

The concentration recorded in Banjaran upstream aligns with findings from previous studies, such as Samudra *et al.* (2022), which reported an average phosphate level of 0.264 mg/L in similar environmental conditions. The persistent input of nutrient-rich runoff from these anthropogenic sources is a major factor in sustaining elevated phosphate levels in this section of the river. On the other hand, the lowest phosphate concentration in 2022 was observed at Station R (Serayu downstream), with an average value of 0.073 mg/L. This relatively low concentration is ecologically beneficial, as it supports the maintenance of aquatic ecosystem stability and reduces the likelihood of eutrophication (MacDonald and Bennett, 2009). Low phosphate levels contribute to balanced primary productivity, limit excessive algal growth, and help maintain dissolved oxygen levels crucial for aquatic life. The overall distribution pattern in 2022 emphasizes the strong influence of land use and wastewater input on phosphate levels in riverine environments. Upstream and agricultural areas are prone to higher phosphate input due to fertilizer application and human activities, while certain downstream sections may show signs of dilution or nutrient attenuation.

In 2023, the highest phosphate concentration was recorded at Station K (Kranji upstream) with an average value of 0.353 mg/L, followed by Station L (Banjaran downstream) with a concentration of 0.307 mg/L. These elevated values are visually represented by the red indicators on the spatial distribution map (Figure 4), which highlight zones with significant phosphate enrichment. The notably high phosphate concentrations in the Kranji and Banjaran Rivers are suspected to be strongly influenced by intensive community activities, particularly unregulated disposal of solid waste and domestic effluents. During the field sampling process, large amounts of garbage were visibly accumulated along both riverbanks, suggesting poor waste management practices in the surrounding settlements. This observation is consistent with earlier findings by (Nurnaningsih, 2000), which documented the use of these rivers as dumping grounds for household waste. Phosphates from domestic sources typically originate from detergents, food residues, and human waste (Ounissi and Bouchareb, 2013). When discharged directly into water bodies without adequate treatment, these substances contribute significantly to nutrient pollution. The sustained input of phosphate-rich waste not only increases the nutrient load in the river but also accelerates eutrophication, a condition characterized by excessive algal growth, reduced oxygen levels, and eventual degradation of aquatic ecosystems (Correll, 1996).

The spatial distribution of phosphate in the Serayu Watershed over the period of 2021 to 2023 shows a relatively stable pattern, with no significant year-to-year fluctuations in concentration. This suggests a degree of temporal uniformity in phosphate levels, where no extreme increases were observed in any particular year. The coloration on the distribution maps across the three years supports this observation, indicating consistent trends without drastic shifts. One station that consistently exhibited low phosphate concentrations was Station G (Central Serayu). This site recorded average concentrations of 0.08 mg/L in both 2021 and 2022, and 0.097 mg/L in 2023, remaining well below critical thresholds. The consistently low levels at this station are likely due to the limited application of phosphate-containing agricultural fertilizers in the surrounding areas. Unlike regions with intensive agriculture, this part of the watershed appears to have lower fertilizer runoff, resulting in reduced nutrient loading to the river system.

Low nutrient input in this area is beneficial for maintaining water quality and ecological balance. In contrast, excessive fertilizer use in other areas can lead to nutrient leaching during rainfall events, where phosphate is transported into water bodies and poses a threat to aquatic life by potentially causing eutrophication and oxygen depletion (Elvania *et al*., 2019). This preliminary conclusion emphasizes the importance of monitoring land use activities, especially agricultural practices, in relation to phosphate pollution, as well as identifying critical zones that require targeted watershed management interventions.

3.2.3 Relationship between nitrate and phosphate with environmental factors using principal component analysis (PCA)

The PCA biplot for 2021 shows distinct environmental characteristics across stations. Nitrate is strongly associated with TSS and COD, as indicated by vectors pointing in the same direction and forming acute angles. This correlation is particularly evident at Station B (Merawu), where high nitrate concentrations are accompanied by elevated TSS levels. This condition may be attributed to high water inflow mobilizing suspended particles and concurrently transporting nitrogen compounds (Paudel *et al*., 2019). Ecologically, this association suggests that areas with high nitrate and suspended solid concentrations are prone to increased turbidity and nutrient enrichment, which may promote phytoplankton blooms and subsequent oxygen depletion, adversely affecting aquatic organisms (Ramayanti and Amna, 2019).

Phosphate, on the other hand, is primarily correlated with COD, as shown by the acute angle between their respective vectors. This suggests that increases in phosphate concentrations are accompanied by increased organic matter, as reflected by COD values. Such conditions can elevate the risk of oxygen depletion in the water due to the decomposition of organic matter, potentially leading to hypoxic events that threaten fish populations and other aquatic life (Lumaela *et al*., 2013; Ramayanti and Amna, 2019).

Station A (Serayu upstream) exhibits dominance of nitrate-related characteristics, while Station H (Gawe upstream) is characterized by higher phosphate levels. These findings support previous studies (Lumaela *et al*., 2013), which reported that increases in nitrate and phosphate are often accompanied by elevated COD levels due to their role in contributing to the organic and nutrient load in aquatic systems, which can significantly disrupt the ecological balance of freshwater habitats.

The PCA biplot for 2022 reveals important insights into the relationships between nutrient parameters and environmental variables. Phosphate shows a strong positive correlation with COD, as indicated by the acute angle (<90°) between their vectors. This pattern is consistent with previous findings (Lumaela *et al*., 2013), suggesting that an increase in phosphate concentrations is typically accompanied by higher COD values. Since COD reflects the amount of oxygen required to chemically oxidize organic substances in water, high COD levels imply high organic pollution (Indradewi *et al*., 2015). Ecologically, this relationship indicates that areas with simultaneous high phosphate and organic matter concentrations are at greater risk of experiencing oxygen depletion due to the decomposition of organic materials. This condition can result in hypoxic events, which negatively affect fish populations and other aquatic organisms, disrupt food webs, and degrade water quality (Ramayanti and Amna, 2019).

In contrast, both nitrate and phosphate exhibit a negative correlation with Total Suspended Solids (TSS), shown by the obtuse angle (>90°) between their respective vectors. This indicates that when TSS levels are high, nitrate and phosphate concentrations tend to be lower, and vice versa. Ecologically, this inverse relationship suggests that during periods of high sediment load such as during floods or land runoff nutrient concentrations in the water may be diluted or adsorbed onto suspended particles, potentially reducing the immediate risk of eutrophication but increasing sedimentation problems that can smother benthic habitats and reduce light penetration for aquatic vegetation (Paudel *et al*., 2019).

Stations characterized by high phosphate dominance include Banjaran upstream, Kranji upstream, and Kranji downstream. These areas are likely influenced by runoff from agricultural and domestic sources, contributing both nutrient loads and organic matter to the river system. The positive relationship between phosphate and COD has serious implications for aquatic health. Elevated COD levels can deplete dissolved oxygen, which is vital for sustaining aquatic life. Oxygen depletion may lead to hypoxic conditions, negatively affecting fish populations and aquatic vegetation (Ramayanti and Amna, 2019).

The nitrate parameter demonstrated the highest association with the following stations: Merawu River, Central Serayu, and Kranji upstream. These stations are located in areas with dense human activity, such as plantation areas (Kusnadi *et al*., 2023) and residential settlements, both of which are potential contributors to nutrient enrichment and water pollution (Rumanti *et al*., 2014). Based on the vector orientation in the biplot, nitrate shows a positive correlation with TSS, as indicated by the acute angle (<90°) between the two variables. This suggests that elevated nitrate concentrations tend to coincide with higher levels of suspended solids. Such a pattern could be explained by runoff carrying both nitrogen compounds and particulate matter into the river, particularly during periods of high flow (Paudel *et al*., 2019).

Meanwhile, phosphate and nitrate show no clear correlation with DO, temperature, or COD. Among these variables, temperature exhibits a negative correlation with both nitrate and phosphate, with the vectors forming obtuse angles (>90°). This inverse relationship may be attributed to the fact that high temperatures can accelerate the volatilization of nitrogen compounds, thereby reducing nitrate levels in the water (Kristiana *et al*., 2020). Furthermore, lower temperatures are generally associated with higher nutrient availability, creating favorable conditions for aquatic organisms (Yolanda *et al*., 2016).

The relationship between nitrate and phosphate with pH in 2023 exhibits a positive correlation, as indicated by the acute angle (<90°) formed between the variables on the PCA biplot. This correlation suggests that increasing pH levels, particularly in slightly alkaline conditions, may be associated with elevated concentrations of nitrate and phosphate in the water. This phenomenon can be explained by the behavior of nutrients under different pH conditions. According to Hindaryani *et al.* (2005), alkaline environments tend to enhance the concentration of nitrate in aquatic systems. Similarly, (Masduqi, 2004) reported that phosphate solubility and availability also increase under higher pH levels.

The underlying mechanism for nitrate involves the nitrification process, where ammonium (NH_4^+) is oxidized to nitrate (NO_3^-) through microbial activity. This process is highly pH-dependent. Putri *et al*. (2021) and Mita *et al.* (2016) found that pH levels between 8 and 9 are optimal for nitrification, leading to higher nitrate concentrations in water. Conversely, at pH levels below 6, the nitrification process tends to cease, resulting in lower nitrate accumulation. These findings underscore the importance of monitoring pH as a controlling factor in nutrient dynamics, as fluctuations in pH can significantly influence the biogeochemical cycles of nitrogen and phosphorus in freshwater ecosystems.

Ecologically, this positive relationship indicates that alkaline conditions not only facilitate the accumulation of nitrate and phosphate but may also promote phytoplankton blooms due to increased nutrient availability. Such nutrient enrichment can lead to eutrophication, potentially triggering oxygen depletion, harming aquatic organisms, and disturbing the ecological balance of freshwater systems (Ramayanti and Amna, 2019).

4. Conclusion

This study reveals the spatial-temporal dynamics of nitrate and phosphate in the Serayu River Basin (2021–2023) and their correlations with environmental parameters using PCA. Phosphate levels remained relatively stable over time but were consistently high in midstream and downstream stations, suggesting anthropogenic inputs such as agricultural runoff and domestic waste. Nitrate concentrations were elevated in stations near agricultural and residential areas, with hotspots like Kranji and Banjaran linked to dense settlements and poor waste management. PCA results showed nitrate positively correlated with TSS, while phosphate was associated with COD, and both nutrients with pH, indicating influences from suspended solids, organic pollutants, and alkaline conditions; temperature was inversely related to nitrate. While excess nutrients risk eutrophication, areas like Central Serayu showed low concentrations, implying better ecological balance. These findings highlight the importance of targeted nutrient management, regular monitoring, and community-based watershed governance to sustain river health.

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Authors' Contributions

All authors have contributed to the final manuscript. Nuning Vita Hidayati, research design and manuscript preparation; Ilma Azizah Arviani, data collection and data visualization; Sesilia Rani Samudra, data analysis; Agus Salim, data interpretation; Dewi Wisudyanti Budi Hastuti, data interpretation; Nabela Fikriyya, manuscript preparation; Abdul Malik Firdaus, statistical analysis; Tri Susanti, secondary data collection; Ghofar Ismail Putra, data collection; and El Mountassir El Mouchtari, critical revision of the article. All authors discussed the results and contributed to the final manuscript.

Conflict of Interest

The authors declare that they have no competing interests.

Declaration of Artificial Intelligence (AI)

The author(s) acknowledge the use of Quilboot for language refinement in preparing this manuscript. All AI-generated content was rigorously reviewed, edited, and validated to ensure accuracy and originality. Full responsibility for the manuscript's final content rests with the author(s). To ensure transparency and support the review process, a comprehensive delineation of the tool's application is furnished in the "all manuscript" in compliance with the publisher's ethical guidelines.

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