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HYDROCHEMICAL ANALYSIS OF SURFACE WATER PARAMETERS DYNAMICS IN THE RIKA AND TEREBLIA RIVER (UKRAINE)

Vladyslav Dzhumelia, Elvira Dzhumelia ✉

Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013, Ukraine
elvira.a.dzhumelia@lpnu.ua

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Abstract. This study assesses the hydrochemical dynamics of the Rika and Tereblia Rivers in Ukraine to evaluate water quality trends. Key water quality parameters, including biological oxygen demand, dissolved oxygen, total suspended solids, ammonium, nitrate, nitrite, phosphate, and sulphate, were analysed over a 1 0-year monitoring period. Statistical tools, such as Pearson correlation and regression analysis, were applied to determine relationships among these parameters and identify pollution sources. Results show that nutrient loading from agricultural activities, natural processes, erosion, and occasional industrial discharge contribute to water quality variability, impacting dissolved oxygen levels and increasing the risk of eutrophication. The results underscore the need for integrated water management practices to mitigate nutrient and organic matter influx and maintain the ecological health of these river systems.

Keywords: water quality, ecological monitoring, ecological safety, hydrochemical analysis, correlation analysis, regression analysis.

1. Introduction

Hydrochemical analysis of surface water parameters dynamics is essential for understanding the ecological state of rivers and addressing pressing environmental challenges (Behmel et al., 2016; Durkowski & Jarnuszewski, 2015; Kieu & Quoc, 2024; Matovelle et al., 2024; Nayak et al., 2024; Nguyen & Huynh, 2022).

According to the Cabinet of Ministers of Ukraine's Resolution No. 1100, dated September 11, 1996, "On approval of the Procedure for the development of standards for the maximum permissible discharge of pollutants into water bodies and the list of pollutants whose discharge into water bodies is regulated", a set of regulated pollutants has been established, including: ammonium nitrogen, organic substances (measured by biological oxygen demand (BOD_5) and chemical oxygen demand (COD)), total suspended solids, petroleum products, nitrates, nitrites, sulphates, phosphates, chlorides.

Monitoring the hydrochemical dynamics of water bodies allows researchers to track fluctuations in key water quality indicators, such as nutrient levels, dissolved oxygen (Sánchez et al., 2007), and concentrations of pollutants, which are critical for maintaining healthy aquatic ecosystems (Fisher et al., 2009; Kale et al., 2021; Pandey & Umamahesh, 2024). Such analysis is particularly important for mountain rivers of Ukraine, which are known for their relatively clean water but are increasingly threatened by anthropogenic factors.

The pollution of rivers, including mountain rivers, poses significant environmental concerns. Industrial discharges, agricultural runoff, and deforestation contribute to the degradation of water quality. In mountain regions, the steep terrain and rapid water flow can exacerbate these issues, as pollutants are quickly transported downstream, affecting broader ecosystems. Mountain rivers (Chen et al., 2024; Lenart-Boroń et al.,

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2022; Yu et al., 2022; Zhang et al., 2023; Zhao et al., 2024; Zhou et al., 2019) are also sensitive to changes in hydrological regimes, particularly due to the construction of reservoirs and hydropower plants, which can alter natural water flow and impact the surrounding environment.

Effective hydrochemical monitoring is important for early detection of pollution and for the development of strategies to mitigate its impact. However, the challenges in conducting consistent and widespread monitoring, especially in remote mountainous areas, often hinder timely responses. Addressing these issues requires improved monitoring systems, stricter regulations, and sustainable practices to protect the vital water resources that mountain rivers provide.

Statistical methods, such as descriptive statistics, the Shapiro-Wilk test, the Kruskal-Wallis test (Phan et al., 2024), correlation and regression analysis (Kothari et al., 2021; Phan et al., 2023), as well as principal component analysis, play a crucial role in assessing water quality parameters by revealing patterns and evaluating relationships among various hydrochemical indicators (Dzhumelia & Spodaryk, 2022; Gopchak et al., 2020; Kale et al., 2021; Olatinwo & Joubert, 2024; Phan et al., 2024). The application of these methods provides objective conclusions that aid in decision-making for ecological management and the preservation of water resources.

Regression analysis is an important tool for predicting water parameters, as it helps identify and assess relationships between various environmental variables. This aids in developing effective water resource management strategies, particularly in the context of water quality preservation and wastewater management. The use of regression models enhances the accuracy of predictions, which is critical for planning in agriculture and ecology (Pandey & Umamahesh, 2024).

Correlation analysis is a crucial tool in studying water quality, as it helps identify and assess the relationships between various hydrochemical parameters. This analysis enhances our understanding of how changes in one parameter can affect others, which is key to developing effective water resource management strategies. It enables the detection of statistically significant links between parameters such as dissolved oxygen, nitrates, ammonium, and phosphates. For instance, a strong correlation between nitrate and phosphate concentrations may indicate a common origin related to agricultural runoff. Additionally, correlation analysis allows for evaluating the impact of anthropogenic factors, such as wastewater discharge and fertilizer use, on water quality. Recognizing these relationships aids in the development of pollution control measures. Furthermore, it is essential for monitoring the ecological status of rivers and water bodies, enabling the identification of quality changes due to seasonal fluctuations, climatic conditions, or human influences.

For instance, study (Phan et al., 2023) have identified strong correlations between the hydrochemical compositions of surface and groundwater, highlighting the importance of an integrated approach to water quality analysis. Ultimately, correlation analysis provides valuable insights for making informed decisions in ecological management, contributing to sustainable water resource management and ecosystem preservation.

The aim of this work is to assess long-term water quality trends in the Rika and Tereblia rivers (Ukraine), identifying key natural processes and anthropogenic influences and pollutant interactions to support effective water management and ecosystem preservation.

2. Experimental Part

2.1. Study Area

The study was conducted in the Rika and Tereblia rivers in the Zakarpattia region (Ukraine), focusing on the surface waters in this area (Table, Fig. 1). The Rika and Tereblia rivers are important watercourses in the Zakarpattia region, playing a significant role in both the natural environment and the economic development of the area. The Rika River, approximately 92 km in length, originates in the northern part of the Carpathians, flows through the Khust district, and discharges into the Tysa (Tisza) River near the town of Khust. It exhibits the fast-flowing characteristics typical of mountain rivers, making it a critical source of water supply for local communities and industrial facilities. A key feature of the Rika River is its use in electricity generation. The most notable hydroelectric power plant in the region is the Tereblia-Rika Hydro Power Plant (HPP), which utilises the waters of both the Tereblia and Rika rivers for power generation.

Water observation posts

No	Observation post
P1	Repynka River, 1 km, village Repynne, 1 km, village Repynne, Mizhhiria district, road bridge
P2	Rika river, 1 km, Khust city, mouth, bridge
P3	Tereblia river, 1 km, village Bushtyno, 1 km, village Bushtyno, Tyachiv district, road bridge
P4	Tereblia river, 1 km, village Bushtyno, mouth
P5	Tereblia River, 54 km, village Meryshor, Khust district, road bridge
P6	Umnozhanskyi stream, 0 km, 2 km above Mizhhiria, drinking water intake
P7	Tereblia-Rika HPP, 52 km, village Vilshany, Khust district, dam

The Tereblia-Rika HPP is a vital energy facility in the region. Its uniqueness lies in the fact that water from the Tereblia River is transported through a 3.7 km tunnel to a reservoir, from where it is directed into the Rika River for electricity production. This hydroelectric power plant supplies a significant portion of Zakarpattia's energy demands, and the interconnection of the two rivers ensures high efficiency in the energy system.

The Tereblia River, 91 km in length, is also a mountain river that originates on the southern slopes of the Vododil Range. Flowing through the Tiachiv district, it traverses picturesque forests and mountains, providing water to local communities and industrial enterprises. In addition to its role in energy production, the river serves as a valuable natural resource, supporting the region's ecosystems.

The ecological condition of the Rika and Tereblia rivers warrants special attention. These rivers are known for their relatively clean water, owing to their mountainous origin and natural filtration through forest ecosystems. However, anthropogenic factors, including industrial pollution, intensive agriculture, and deforestation, can pose significant threats to the ecological balance of these water bodies. For instance, alterations to the natural hydrological regime due to reservoirs and hydroelectric infrastructure can negatively affect local flora and fauna, particularly fish populations that rely on the natural water cycle. The ecological status of these rivers necessitates continuous monitoring, as anthropogenic pressures, such as industrial discharges and modifications to the hydrological regime caused by hydroelectric power stations, present serious challenges to the maintenance of their natural balance.

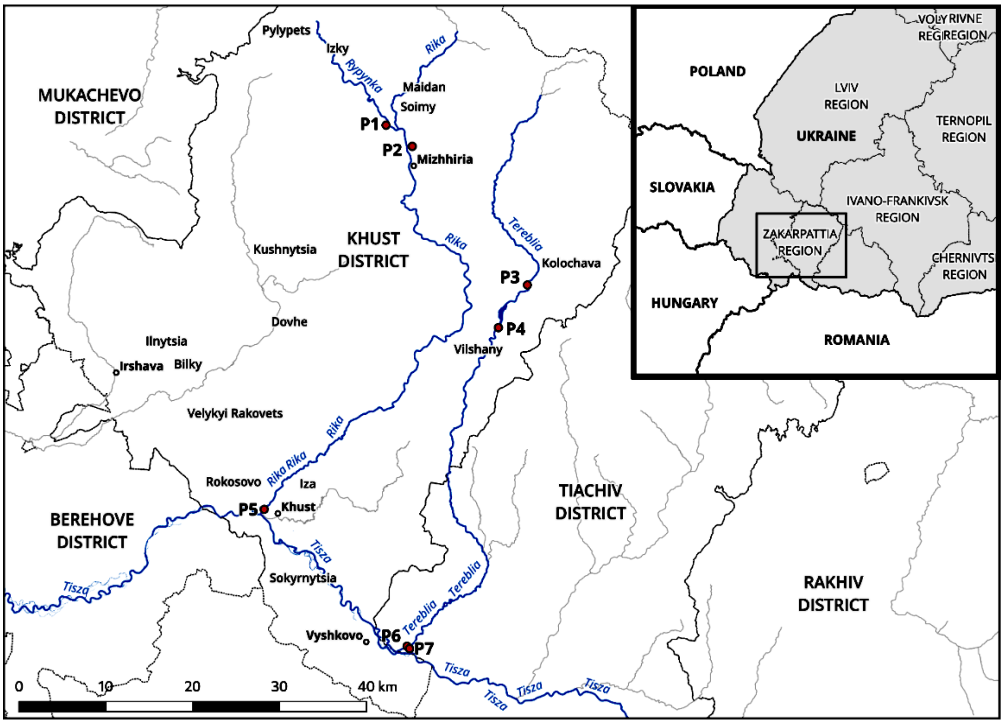

Fig. 1. The study area and observation posts

2.2. Research Methods

The initial phase of this research involved collecting, organizing, and processing available hydrochemical baseline data on water quality. Specialists of the State Agency of Water Resources of Ukraine conducted water quality monitoring to evaluate pollution levels in surface waters at various monitoring points along the Rika and Tereblia rivers as part of the national water quality control program.

The study was conducted based on those hydrochemical parameters from 2014 to 2023. The results of hydroecological observations on the river water quality were performed by the analytical control and monitoring services of the State Agency of Water Resources of Ukraine.

The monitoring stations used in the study were distributed along several key points in the Rika and Tereblia rivers. Data collection involved regular sampling and analysis of hydrochemical indicators, which provided valuable insights into the long-term dynamics of water quality in the region. The primary focus was on assessing levels of pollutants such as nitrates, phosphates, suspended solids, and heavy metals, which are indicative of both natural processes and human activities.

Using statistical analysis methods to assess the state of surface waters, the distribution of sulphates, phosphates, biochemical oxygen demand, dissolved oxygen, and total suspended solids was analysed based on results over a period of 10 years.

To analyse the data, statistical methods were applied, including the calculation of descriptive statistics (mean, range, standard deviation) and the generation of box plots to visualize the distribution of each parameter.

To identify the most significant parameter of water quality and its correlation with other parameters correlation matrix studies were done. The correlation method in the Pandas library in Python was used for the computation the Pearson correlation between water parameters. This allowed for the identification of significant correlations between pollutants. The use of Plotly Express for regression analysis, combined with descriptive statistics and correlation studies, provided a comprehensive approach to understanding the hydrochemical dynamics of the Rika and Tereblia rivers.

3. Results and Discussion

For waters designated for fishery purposes in Ukraine, the maximum permissible concentration (MPC) of chlorides is set at 300 mg/dm³. Elevated chloride levels in such waters can negatively affect fish and other aquatic organisms by altering osmotic balance and reducing habitat suitability.

In the Rika and Tereblia rivers, chloride concentrations were generally within permissible limits, indicating minimal anthropogenic pollution. Natural processes, such as soil leaching and mineral dissolution, are likely the primary sources of chloride in these waters. The absence of exceedances suggests that industrial discharges or other human sources have a limited impact on chloride levels in this region.

The dissolved oxygen (DO) concentration is regulated by sanitary standards, with MPCs set at a minimum of 6 mg O_2/dm³ for fishery waters and 4 mg O_2/dm³ for domestic water use.

Biochemical oxygen demand over five days (BOD_5) represents the oxygen microorganisms need to decompose organic matter at 20 °C, providing insight into organic pollution levels. High BOD_5 levels indicate significant organic presence, potentially reducing DO and harming aquatic ecosystems. For freshwater bodies, the BOD_5 limit is 3 mg O_2/dm³, while for wastewater it typically should not exceed 25-30 mg/dm³.

Total suspended solids (TSS) reflect the mass of solid particles suspended in water, impacting clarity and plant photosynthesis. In Ukraine, the MPC for TSS is 15 mg/dm³. These solids stem from both natural sources (e. g., erosion) and human activities (e. g., sewage, construction). Elevated TSS levels can hinder fish gill function and reduce DO, affecting aquatic life and transporting pollutants such as heavy metals.

Sulphates occur naturally in water from gypsum and mineral leaching; however, industrial and domestic waste can increase their concentration significantly. According to Ukraine's environmental standards, as specified in the 2021 Order of the Ministry of Environmental Protection and Natural Resources, the maximum permissible sulphate concentration for fishing water is 100 mg/dm³, while for household use it is 500 mg/dm³.

The data presented in Figs. 2–8 in our study provides an in-depth examination of water quality parameters in the Rika and Tereblia Rivers, focusing on critical hydrochemical indicators and their interactions. Fig. 2's boxplot, displaying biological oxygen demand, dissolved oxygen, ammonium, chloride, nitrate, nitrite, and sulphate concentrations, reveals that BOD levels generally fall within acceptable limits for aquatic ecosystems designated for fishery purposes. However, occasional elevations in BOD suggest localized organic pollution, potentially linked to agricultural runoff or urban wastewater. Dissolved Oxygen levels, while largely compliant with standards necessary to support aquatic life, show notable reductions at sites with elevated BOD, underscoring an inverse relationship where organic material decomposition intensifies oxygen demand, thereby lowering DO availability. Ammonium concentrations exhibit spatial variability, with heightened levels at particular monitoring sites, indicative of inputs potentially associated with agricultural or municipal wastewater sources, which, through nitrification, contribute to decreased oxygen levels.

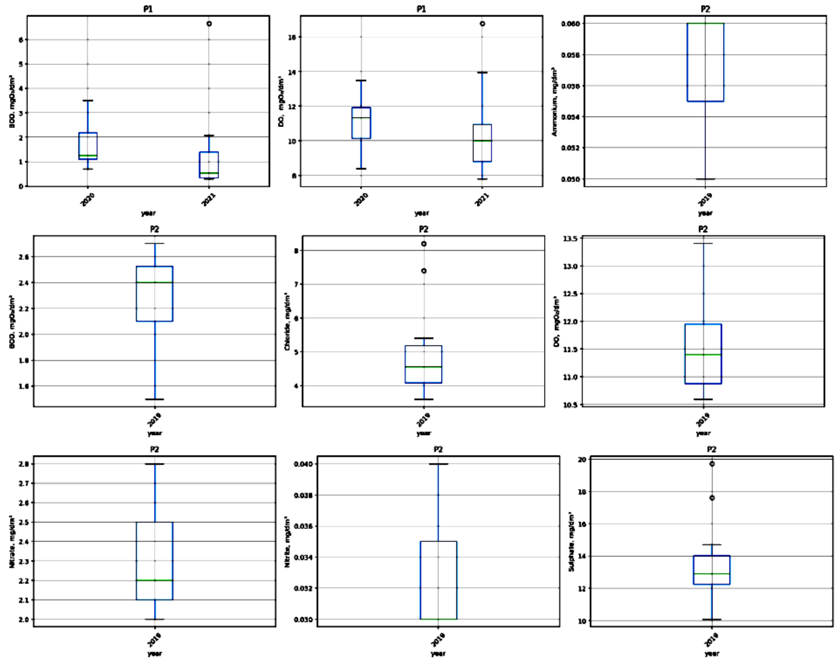

Fig. 2. The boxplot showing the distribution of BOD, DO, ammonium, chloride, nitrate, nitrite, sulphate in the observed points

Fig. 3 further emphasizes the inverse relationship between BOD and DO, highlighting the impact of organic pollution on ox ygen consumption. As organic matter decomposes, microbial activity elevates oxygen demand, consequently reducing DO levels, especially in areas of concentrated organic contamination.

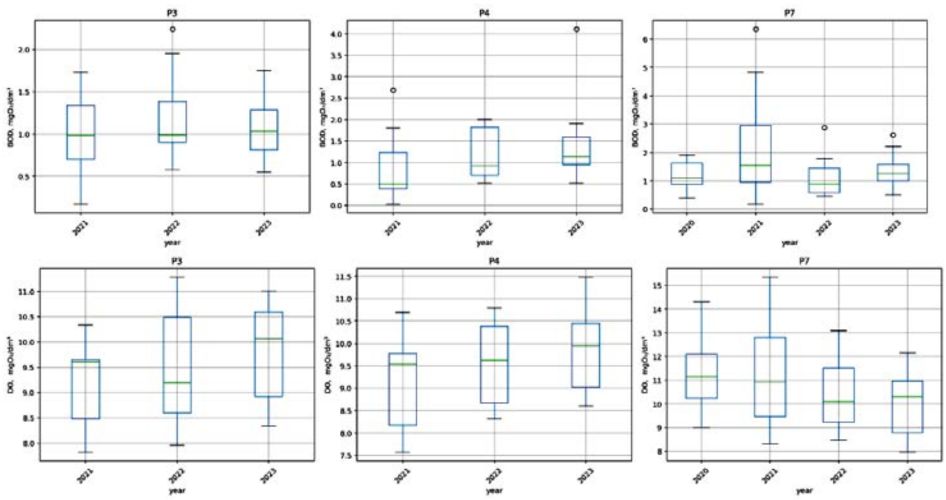

Fig. 3. The boxplot showing the distribution of BOD, DO in the observed points

Figs. 4 and 5 extend the analysis by including total suspended solids and phosphate along with the previously examined indicators, providing a more comprehensive perspective on pollution sources. Elevated TSS levels at some observation points suggest erosion, construction activities, or wastewater discharge as contributors to suspended particle concentrations, which impair water transparency and potentially disrupt photosynthetic processes, imposing stress on aquatic organisms. Elevated phosphate levels further suggest nutrient enrichment likely stemming from agricultural fertilizer use, a phenomenon often observed in tandem with higher ammonium and TSS levels, signifying the impact of agricultural practices on nutrient loading and subsequent eutrophication risks.

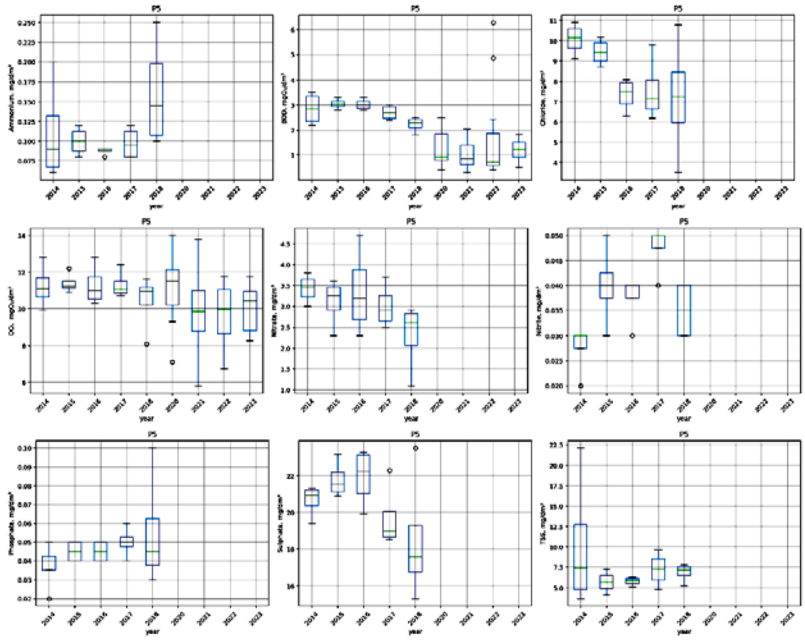

Fig. 4. The boxplot showing the distribution of BOD, DO, TSS, phosphate, ammonium, chloride, nitrate, nitrite, sulphate in the observed points

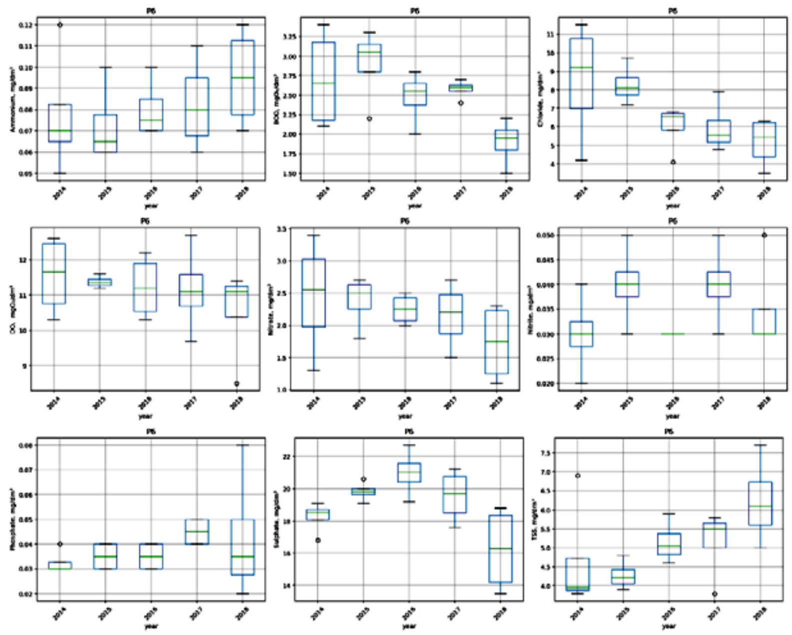

Fig. 5. The boxplot showing the distribution of BOD, DO, TSS, ammonium, chloride, nitrate, nitrite, sulphate, phosphate in the observed points

Pearson's correlation analysis is a preliminary descriptive technique to estimate the degree of association among multiple variables involved in the study. Therefore, a correlation matrix was computed which shows the degree of a linear association between any two of the parameters, and measured by the degree of correlation as a coefficient (*R*). *R*-value is used to identify the highly correlated and interrelated water quality parameter and that may influence the water quality of the area. The value of *R* ranges from –1 to +1; *R* =+1, or near to one indicates a strongest positive linear correlation between two parameters compared and *R* =–1 or near to –1 reveals strongest negative linear correlation (Kothari et al., 2021).

The correlation analysis (Fig. 6) of water quality parameters in the Rika and Tereblia rivers provides insight into the interrelationships between various indicators of water health:

1. There is a moderate positive correlation (*r* = 0.568) between BOD and nitrate levels, suggesting that higher levels of organic pollution are associated with elevated nitrate concentrations. This may be due to the decomposition of organic matter, which releases nitrogen compounds into the water.

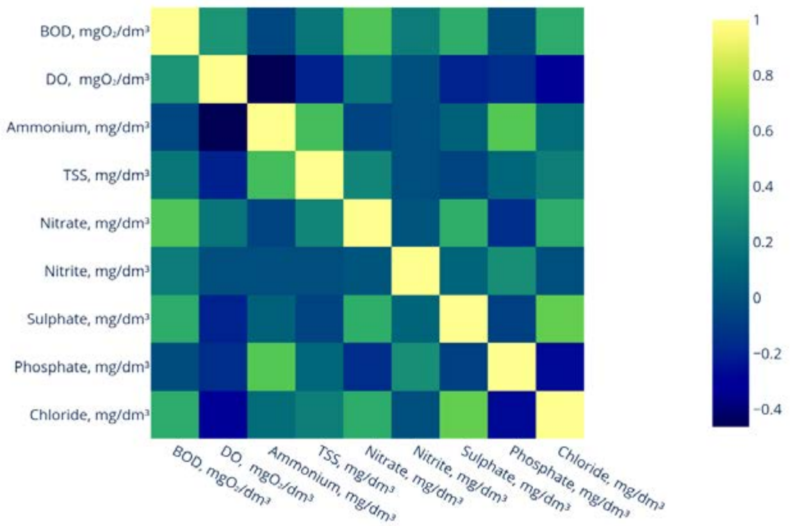

Fig. 6. The Pearson correlation matrix of the hydrochemical properties at the observed points the Rika and Tereblia rivers

2. A moderate negative correlation (*r* = –0.463) exists between DO and ammonium, indicating that as ammonium levels increase, DO tends to decrease. This relationship could be due to oxygen consumption during nitrification processes, where ammonium is converted to nitrate, a process that requires oxygen.

3. Ammonium and phosphate show a moderate positive correlation (*r* = 0.589), implying that they may originate from similar sources, such as agricultural runoff. The presence of both nutrients in elevated concentrations suggests potential nutrient loading from fertilizers or wastewater discharges.

4. The high positive correlation (*r* = 0.624) between sulphate and chloride indicates that these ions may have common sources, possibly geological (natural mineral dissolution) or anthropogenic, such as industrial discharges. Elevated levels of both ions could be a sign of industrial or urban influences on water quality.

5. The moderate positive correlation (*r* = 0.537) between TSS and ammonium suggests that suspended particles in the water may contribute to ammonium levels, possibly due to organic matter attached to these particles that releases ammonium upon decomposition.

6. There is also a moderate positive correlation (*r* = 0.305) between phosphate and nitrite, suggesting common sources of nutrient enrichment, such as wastewater or agricultural runoff. Elevated levels of these nutrients can lead to eutrophication, negatively impacting water quality and aquatic life.

Figs 7 and 8, which employ linear regression analyses, illustrate temporal trends in BOD and DO concentrations. The observed upward trend in BOD levels suggests a gradual increase in organic pollution, possibly attributable to intensified agricultural and urban activities, which augments the demand for oxygen and places additional stress on aquatic ecosystems. In contrast, the downward trend in DO levels corresponds with the rising BOD, reflecting how escalating organic pollutants progressively reduce available oxygen. This trend is of ecological concern, as declining DO levels are associated with adverse impacts on biodiversity and the stability of aquatic ecosystems.

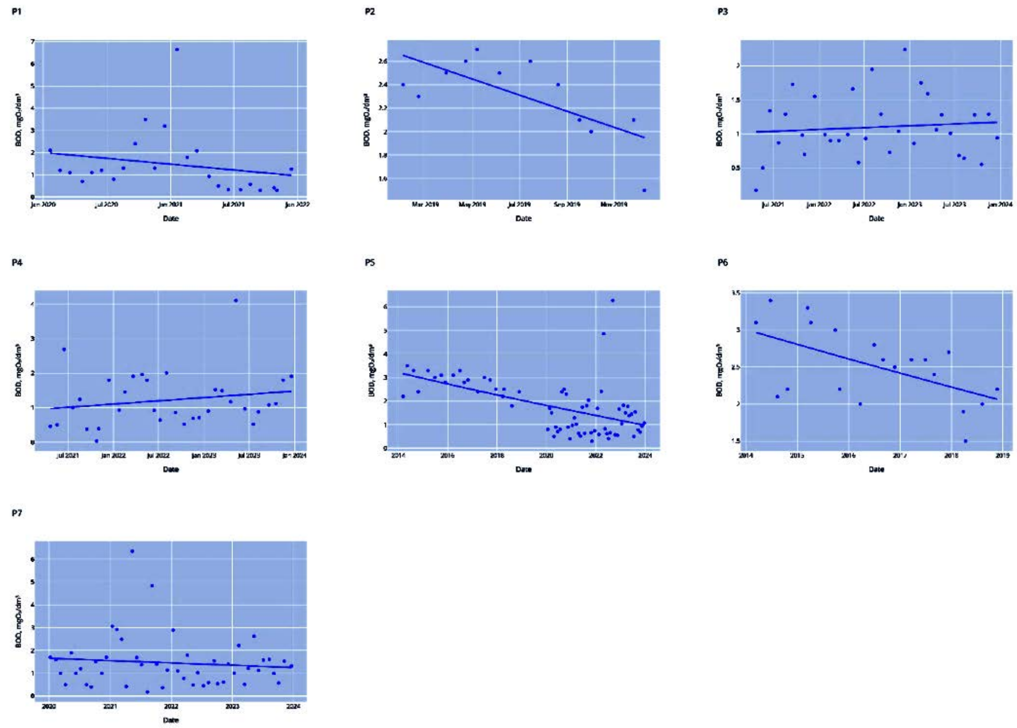

Fig. 7. Linear regression of BOD_5

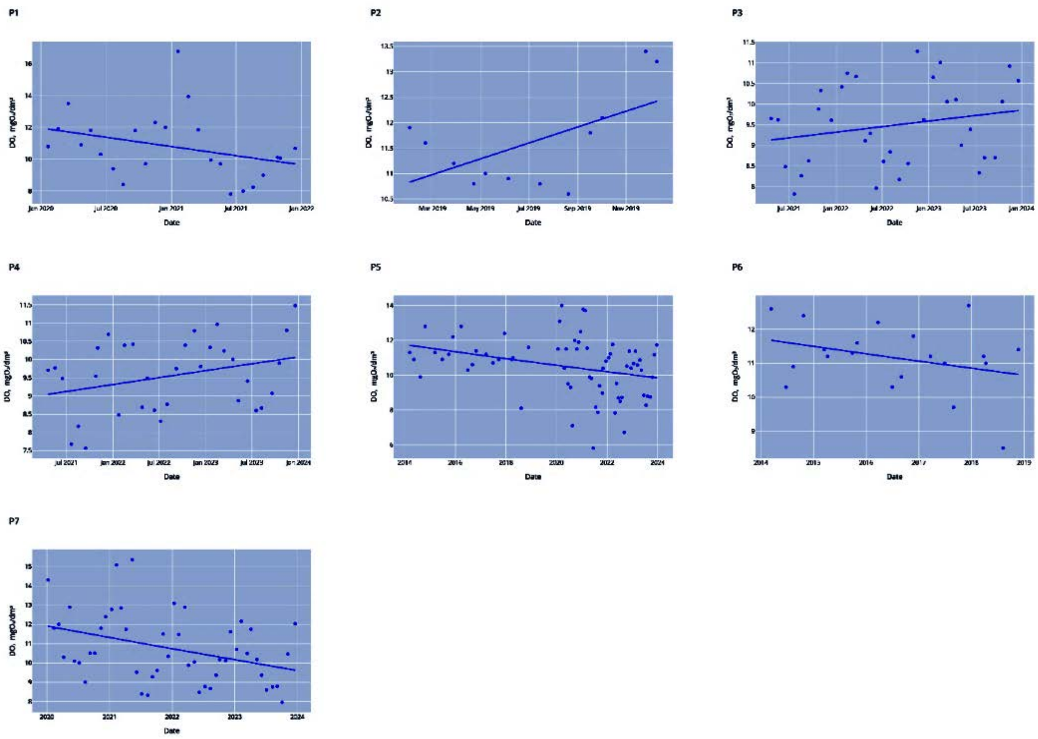

Fig. 8. Linear regression of DO

This analysis highlights the need for integrated water management strategies that target nutrient and organic pollution control. By addressing these key pollutants, such strategies would help maintain the ecological balance of the Rika and Tereblia Rivers, preserving their health and resilience in the face of ongoing anthropogenic pressures. Hydrochemical analysis of water quality is crucial for understanding the ecological health of river systems and informing water management strategies. However, the main issue lies in the unsystematic and irregular approach to data collection, reflecting broader challenges within the state system for ecological monitoring of water bodies. This lack of consistency in monitoring hinders both accurate assessments and timely responses to water quality issues, limiting the effectiveness of management efforts aimed at preserving the ecological integrity of rivers such as the Rika and Tereblia. Addressing these challenges requires a more standardized and continuous data collection framework to support reliable long-term analysis.

4. Conclusions

This study demonstrates that the Rika and Tereblia Rivers are subject to natural processes and anthropogenic influences, particularly from agricultural runoff and localized industrial discharge, which affect their hydrochemical profiles.

Elevated BOD values in certain areas indicate organic pollution, likely due to agricultural and urban inputs, which correlates with reduced DO levels and increased oxygen demand.

Ammonium, nitrate, and phosphate levels show a pattern consistent with agricultural runoff, while elevated TSS concentrations suggest additional inputs from erosion and construction activities. These factors contribute to nutrient loading, increasing eutrophication risks.

Pearson correlation analysis highlights significant relationships, such as the inverse association between DO and ammonium, and positive correlations among BOD, nitrate, and sulphate, indicating shared pollution sources.

The data emphasize the need for enhanced water quality monitoring and management strategies to control nutrient and organic pollution to ensure sustainable ecological balance in these rivers. Addressing these challenges is essential to preserving water quality due to increasing anthropogenic pressures.

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