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Hydrochemical Indicators Dynamic in Surface Water of Ukraine – Border Areas with Poland and Slovakia Case Study

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ABSTRACT

This study assesses the hydrochemical dynamics of surface waters in Ukraine's border regions with Poland and Slovakia over a 15-year period. Key water quality parameters, including sulfates (SO_4^{2-}), biochemical oxygen demand (BOD_5), dissolved oxygen (DO), and total suspended solids (TSS), were analysed to determine the ecological state of these transboundary water bodies. The results indicate that sulfate concentrations remain below the maximum permissible concentrations (MPC) for both household and fishery water use. BOD_5 and DO levels generally comply with environmental standards, though localized areas show signs of organic pollution. TSS concentrations remain within acceptable limits, likely influenced by natural erosion and occasional anthropogenic activities. Pearson correlation analysis revealed significant relationships between nitrogen and nitrates ($r = 0.814$), underscoring the role of agricultural runoff in nutrient dynamics. Negative correlations between DO and several pollutants suggest that organic and chemical contamination affects oxygen availability. These findings emphasize the need for continued monitoring and transboundary collaboration to safeguard water quality in the region.

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

INTRODUCTION

The quality of water in rivers is an important environmental indicator that affects the health of the population, ecosystems [Zhou et al., 2024] and the economic development of regions [Babuji et al., 2023; Chidiac et al., 2023; Chigor et al., 2012; Durkowski and Jarnuszewski, 2015; Gaagai et al., 2023; Giri, 2021; Kale et al., 2021; Kothari et al., 2021; Nayak et al., 2024; Olatinwo and Joubert, 2024; Zhang et al., 2018]. The study of water quality in the rivers of Ukraine, especially in the territories bordering Poland and Slovakia [Gopchak et al., 2020], s an urgent task, since these waters can be affected by both natural and anthropogenic factors [Babuji et al., 2023].

Studies show that anthropogenic sources of pollution, such as agricultural fertilizers, sewage, and industrial emissions [Bernatska et al., 2023; Dzhumelia and Spodaryk, 2022; Kothari et al., 2021; Mahinoor Islam Tonmoy, 2024; Mokryi et al., 2023; Pohrebennyk and Dzhumelia, 2020; Qadem et al., 2024], significantly affect water quality. For example, in studies [Chowdury et al., 2019; Uddin et al., 2022] found that 57% of groundwater in the Ganges basin is of poor quality due to geogenic and anthropogenic sources. This also indicates the need to monitor and control the quality of water in the rivers passing through the border areas.

Natural factors such as bank erosion, stormwater runoff and geological features can also affect water quality. Studies show that natural sources of pollution can account for a significant portion of total water pollution, as found in studies where eight sources of pollution were responsible for 77.1% of the variation in water quality.

The study of water quality in the rivers of Ukraine in the border areas with Poland and Slovakia requires a comprehensive approach, which includes statistical analysis, monitoring of anthropogenic and natural factors [Durkowski and Jarnuszewski, 2015; Dzhumelia and Spodaryk, 2022; Kale et al., 2021; Kieu and Quoc, 2024; Mokryi et al., 2023; Phan et al., 2024]. This will allow not only to assess the current state of water resources, but also to develop recommendations for improving water quality and preserving ecosystems.

For a comprehensive and effective study of surface water quality, it is necessary to carry out detailed monitoring of water quality in rivers in border areas, use modern statistical methods for data analysis. This will help in developing a water resources management strategy taking into account the influence of both natural and anthropogenic factors.

Statistical methods, such as the Shapiro-Wilk test and the Kruskal-Wallis test, are used to detect statistically significant differences in the values of water quality parameters [Beyaitan Bantin et al., 2020; Garg, 2018; Havrys et al., 2023; Havrysh et al., 2017; Jannat et al., 2019; Kachan et al., 2018; Kieu and Quoc, 2024]. For example, in studies [Durkowski and Jarnuszewski, 2015; Phan et al., 2023; Phan et al., 2024] revealed strong correlations between the hydrochemical composition of surface and groundwater, which emphasizes the importance of an integrated approach to water quality analysis.

The main purpose of the work was assessment of the state of Ukrainian water bodies in Volyn, Lviv, Zakarpattia regions near Poland and Slovakia by integrated hydrochemical parameters and their correlation analysis. In order to achieve the goal, there was a need for a detailed study of the characteristics of water basins study area. In this research water parameters for 15 year were analysed.

STUDY AREA

The study was conducted in the border regions of Ukraine, adjacent to Poland and Slovakia, focusing on the surface waters of in this area (Fig. 1, Table 1). This region is of significant environmental interest due to its transboundary nature, where water systems cross multiple countries, creating shared responsibilities for water quality management. The study primarily covers sections of rivers that flow through the Volyn, Lviv and Zakarpattia regions of Ukraine, which are located

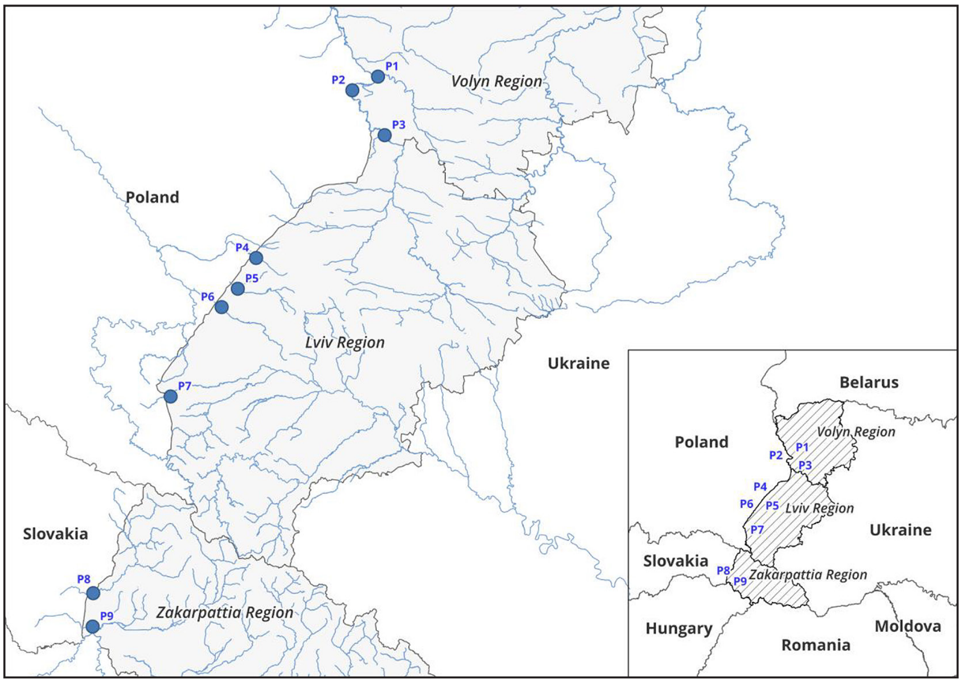

Figure 1. The study area and observation posts

Table 1. Water observation posts

No	Observation post	Region	Basin	Neighbouring Country
1.	The Western Bug River, 569 km, Ustyluh city, 500 m below the confluence of the Ustyluh river	Volyn	Vistula	Poland
2.	The Western Bug River, 583.5 km, village Ambukiv, 500 m below the confluence of the Khuchva River	Volyn	Vistula	Poland
3.	The Western Bug River, 631 km, village Lytovezh, the bridge of the Novovolynsk-Chervonograd highway	Lviv	Vistula	Poland
4.	The Zavadivka River, 12 km, village Hrushiv, Yavorivsky district	Lviv	Vistula	Poland
5.	The Shklo River, 66 km, village Krakovets, under the road bridge, city of Lviv – Krakovets village	Lviv	Vistula	Poland
6.	The Vyshnia River, 37 km, Chernevo village, under the road bridge Mostyska city – Krakovets village	Lviv	Vistula	Poland
7.	The Strviazh River, 83 km, Terlo village, under the bridge on the Khyriv – Smilnytsia road	Lviv	Dniester	Poland
8.	The Uzh River, 32 km, village Storozhnytsia, Uzhhorodskyi district	Zakarpattia	Danube	Slovakia
9.	The Latorytsia River, 65 km, Chop city, drinking water intake	Zakarpattia	Danube	Slovakia

in the basins of the Dniester, Danube, Vistula, and Western Bug rivers.

The Dniester River Basin covers a large area in Eastern Europe, flowing through Ukraine and Moldova. It consists of several sub-basins, each contributing to the river's hydrology. The Upper Dniester Basin originates in the Carpathian Mountains in western Ukraine, where the river flows through mountainous terrain with a fast current, encompassing cities like Lviv, Stryi, and Drohobych. In the middle part of the basin, the river flows through the Podolian Upland, where its flow slows down and the valley widens. This area is characterized by more agricultural land and reservoirs, with important cities including Ivano-Frankivsk, Ternopil, and Khmelnytskyi. The Lower Dniester Basin extends through Moldova and southwestern Ukraine, where the terrain flattens, leading to the formation of wetlands and floodplains. The river flows into the Dniester Liman before reaching the Black Sea. Key cities in this part include Tiraspol in Moldova and Odesa in Ukraine, near the estuary. Major tributaries of the Dniester include the Stryi, Zbruch, and Răut rivers. The Dniester Basin plays a crucial role in local ecosystems, agriculture, and water supply, making water quality monitoring essential for effective resource management.

The Danube is the second longest river in Europe after the Volga, flowing through ten countries and serving as a vital waterway for Central and Eastern Europe. The river originates in Germany's Black Forest and empties into the Black Sea, forming the Danube Delta, which spans Romania and Ukraine. The Danube River Basin covers over 800,000 km^2 and plays a crucial role in water supply, agriculture, transport, energy, and ecology. It can be divided into three sections: the Upper Danube, which flows through Germany and Austria, marked by a fast current and mountainous terrain; the Middle Danube, which passes through Slovakia, Hungary, Croatia, and Serbia, characterized by slower flow through the plains of the Pannonian Basin; and the Lower Danube, which flows through Romania, Bulgaria, Moldova, and Ukraine, featuring wide floodplains and culminating in the Danube Delta before reaching the Black Sea. The delta is a UNESCO biosphere reserve and one of the largest and most diverse ecosystems in Europe. The Danube provides water to millions of people and is a key component in the regional ecosystems and economies of many countries.

The Vistula River Basin is the largest river basin in Poland, covering approximately 194,000 km^2. The Vistula (Wisła) is the longest river in Poland, flowing entirely within the country before emptying into the Baltic Sea. The basin is divided into several sub-basins, with numerous tributaries contributing to the overall hydrology. The Vistula River Basin primarily lies within Poland; however, its influence extends into Ukraine through several tributaries. While the Vistula itself does not flow through Ukraine, the basin is relevant due to the Dniester and the Southern Bug rivers, which are significant rivers in Ukraine that contribute to the broader hydrological system connected to the Vistula. The Vistula Basin in Ukraine includes the western part of the country, particularly in the regions of Lviv and Ivano-Frankivsk. Here, various small rivers and streams feed into the tributaries of the Vistula. The rivers in this area are generally characterized by hilly terrain, lush forests, and agricultural lands. The main tributaries related to the Vistula that flow from Ukraine include the San River, which originates in the Ukrainian Carpathians and flows into Poland, eventually joining the Vistula. The basin's ecosystem is diverse, with rich biodiversity in wetlands and floodplains, providing habitats for various species. The region's hydrology is essential for local agriculture, providing irrigation and water supply. Additionally, the Vistula Basin's ecological health affects water quality and the overall environmental balance in both Poland and Ukraine, making it vital for cooperative water management efforts between the two countries.

The Western Bug is an important river basin in Eastern Europe, primarily located in Poland and Ukraine. The Western Bug River (Bug Zachodni) originates in the western part of Ukraine and flows northwest, forming part of the border between Poland and Ukraine before eventually merging with the Vistula River. The basin covers approximately 21,500 km^2, with the river's length being around 772 km. Its tributaries include the Horyn, Zbrucz, and Styr rivers. The basin is characterized by a diverse landscape, including forests, wetlands, and agricultural lands. In Ukraine, the Western Bug basin is primarily located in the Lviv and Volyn regions. The river serves as a vital resource for local communities, providing water for drinking, irrigation, and industry. The basin's ecosystems support a rich diversity of flora and fauna, making it important for conservation efforts. The Western Bug is also significant for regional hydrology, as it influences water quality and resource availability in both Poland and Ukraine. Managing the basin is essential for addressing issues like pollution, flooding, and sustainable resource use, requiring cooperation between the two countries to ensure the ecological health of the river and its surrounding areas.

These river basins play a vital role in providing water for drinking, agriculture, and industry, as well as maintaining biodiversity in the region. However, due to the proximity to agricultural areas, industrial zones, and urban settlements, these water bodies are subject to various sources of pollution, both natural and anthropogenic. The cross-border nature of the rivers increases the importance of cooperation between Ukraine and neighbouring countries to ensure effective monitoring and mitigation of water quality issues.

The river basins in this region are characterized by diverse geological and hydrological features, including mountainous terrain and valleys, which influence the hydrodynamic and chemical properties of the water. Seasonal variations in precipitation, snowmelt, and temperature also contribute to fluctuations in water quality parameters.

RESEARCH METHODS

The first stage of the research involved the collection, systematization, and processing of available initial hydrochemical data on water quality within the cross-border section of Ukraine near Poland and Slovakia. Experts conducted water quality monitoring to assess pollution levels in surface waters at various monitoring points as part of the state water quality control program.

According to the resolution of the Cabinet of Ministers of Ukraine dated September 11, 1996 N 1100 "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" [Cabinet of Ministers of Ukraine, 1996] established a list of pollutants whose discharge into water bodies is regulated:

- ammonium nitrogen,
- organic substances (according to indicators: Biological oxygen demand (BOD_5) and chemical oxygen demand (COD),
- total suspended solids,
- petroleum products,
- nitrates,
- nitrite,
- sulfates,
- phosphates,
- chlorides.

It were analysed sulfates, dissolved oxygen, biological oxygen demand and total suspended solids in our research.

The study was conducted based on those hydrochemical parameters from 2009 to 2023. The results of systematic hydroecological observations on the river water quality were performed by the analytical control and monitoring services of the Ministry of Ecology and Natural Resources of Ukraine, State Agency of Water Resources of Ukraine.

The monitoring stations used in the study were distributed along several key points in the rivers near the borders with Poland and Slovakia. 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.

During the year, water samples were taken from 3 to 12 times a year. Using statistical analysis methods to assess the state of surface waters, the distribution of sulfates, biochemical oxygen demand, dissolved oxygen, and total suspended solids was analysed based on results over a period of 15 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.

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.

RESULTS AND DISCUSSION

Sulfate naturally forms in water as a result of leaching from gypsum and other common minerals. The discharge of industrial waste and domestic sewage tends to increase their concentration [WHO, 2023]. In this studied area, the values of this parameter in the studied waters are very diverse, as can be seen in the Figure 2. They vary between 0 and 58 mg/dm^3. According to the Order of the Ministry of Environmental Protection and Natural Resources of Ukraine "On Approval of Methodological Recommendations for the Development of Standards for Maximum Permissible Discharge of Pollutants into Water Bodies with Return Waters" [Ministry of Environmental Protection and Natural Resources of Ukraine, 2021] MPC (maximum permissible concentration) of sulfates in water for fishing purposes is 100 mg/dm^3, in water for household purposes it is 500 mg/dm^3.

In Ukraine, the maximum permissible concentration (MPC) of dissolved oxygen (DO) in water is regulated by relevant environmental and sanitary standards. The main requirements for water quality are established by the State Sanitary Rules and Regulations (DSanPiN) and are regulated for various types of water bodies, such as reservoirs intended for fishing, drinking and recreational purposes. MPS of DO is not less than 6 mg O_2/dm^3 for reservoirs for fishing purposes, is not less than 4 mg O_2/dm^3 for household use water.

Biochemical oxygen consumption in 5 days (BOD_5) is an indicator that determines the amount of oxygen consumed by microorganisms to decompose organic substances in water during five days under certain conditions (usually at a temperature of 20 °C). This indicator is important for assessing the level of water pollution by organic compounds. A high BOD^5 level indicates the presence of a large amount of organic matter in the water, which can lead to a decrease in dissolved oxygen (DO) levels and negatively affect aquatic ecosystems.

For fresh water bodies, maximum permissible concentration BOD_5 is 3 O_2/dm^3. For wastewater, acceptable BOD_5 values can vary depending on the type of wastewater, but often do not exceed 25–30 mg/dm^3. Total suspended solids (TSS) is an indicator that determines the total mass of solid particles that are suspended in water and do not settle quickly under the influence of gravity. TSS is often used to assess water quality, as this indicator affects water clarity, light availability for aquatic plants, and can also indicate the presence of pollutants.

High levels of TSS can lead to reduced water clarity, which affects photosynthesis in algae and plants by reducing light availability. In Ukraine, MPC for TSS is 15 mg/dm^3. There are sources of suspended solids:

- Natural sources: soil erosion, organic residues, algae, microorganisms;
- Anthropogenic sources: sewage, industrial emissions, activities on construction sites, agriculture (soil and fertilizer washing).

High concentrations of suspended solids can block fish gills and reduce dissolved oxygen (DO) levels, which can be harmful to aquatic life. Suspended matter can carry pollutants, particularly heavy metals and pathogens, that settle in water bodies. The results of the analysis of the presented box-plots (Figure 2–5) and Pearson correlation (Figure 6) provide important conclusions regarding the quality of surface waters of Ukraine in the border areas with Poland and Slovakia.

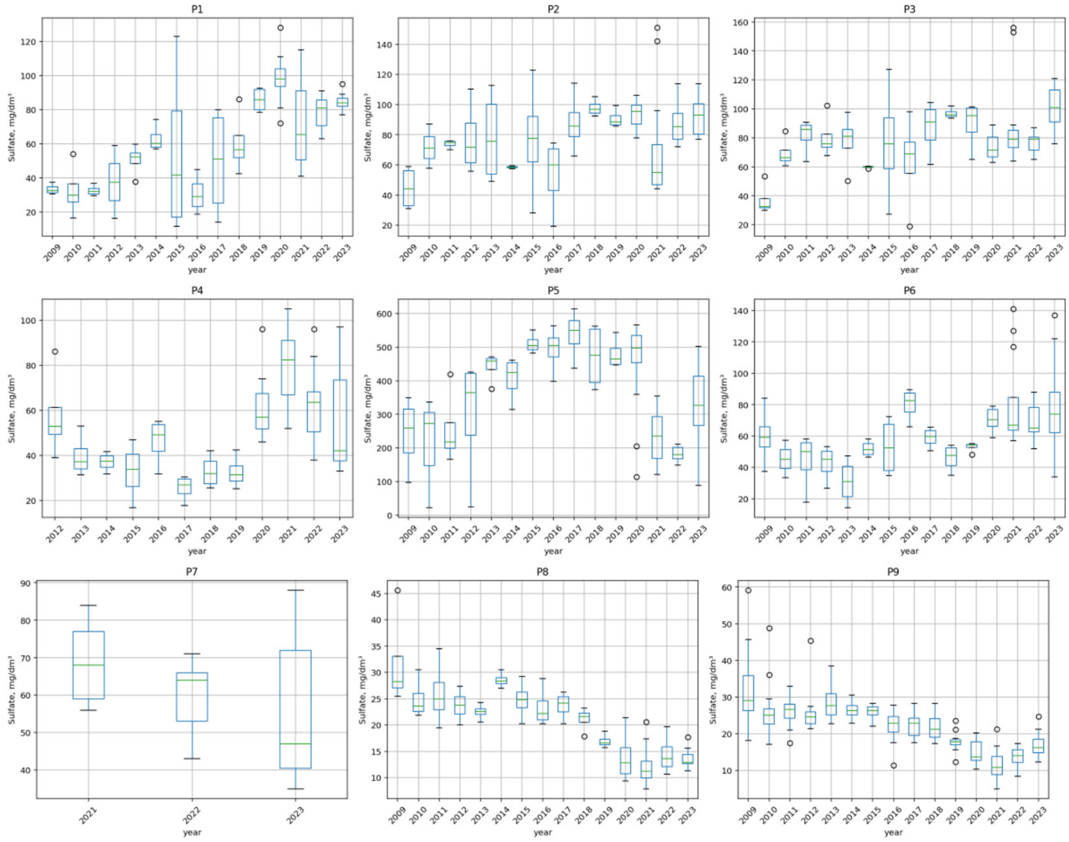

Figure 2. The boxplot showing the distribution of sulfates

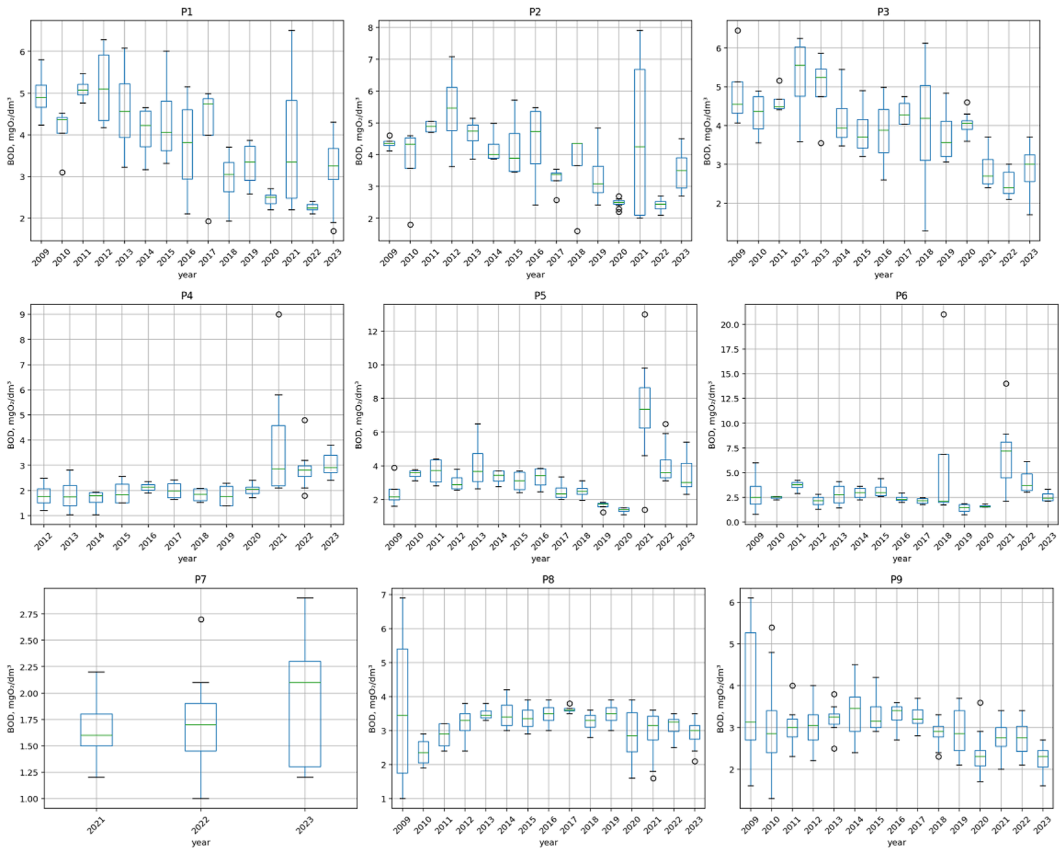

Figure 3. The boxplot showing the distribution of BOD_5

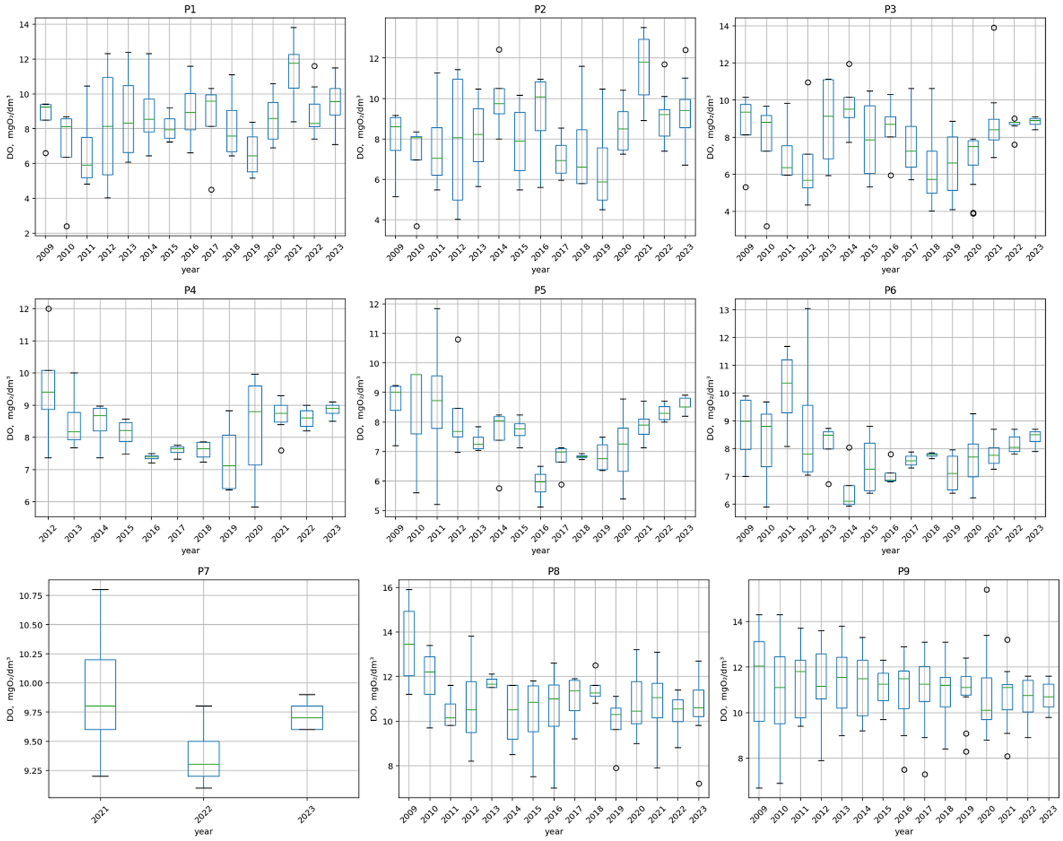

Figure 4. The boxplot showing the distribution of DO

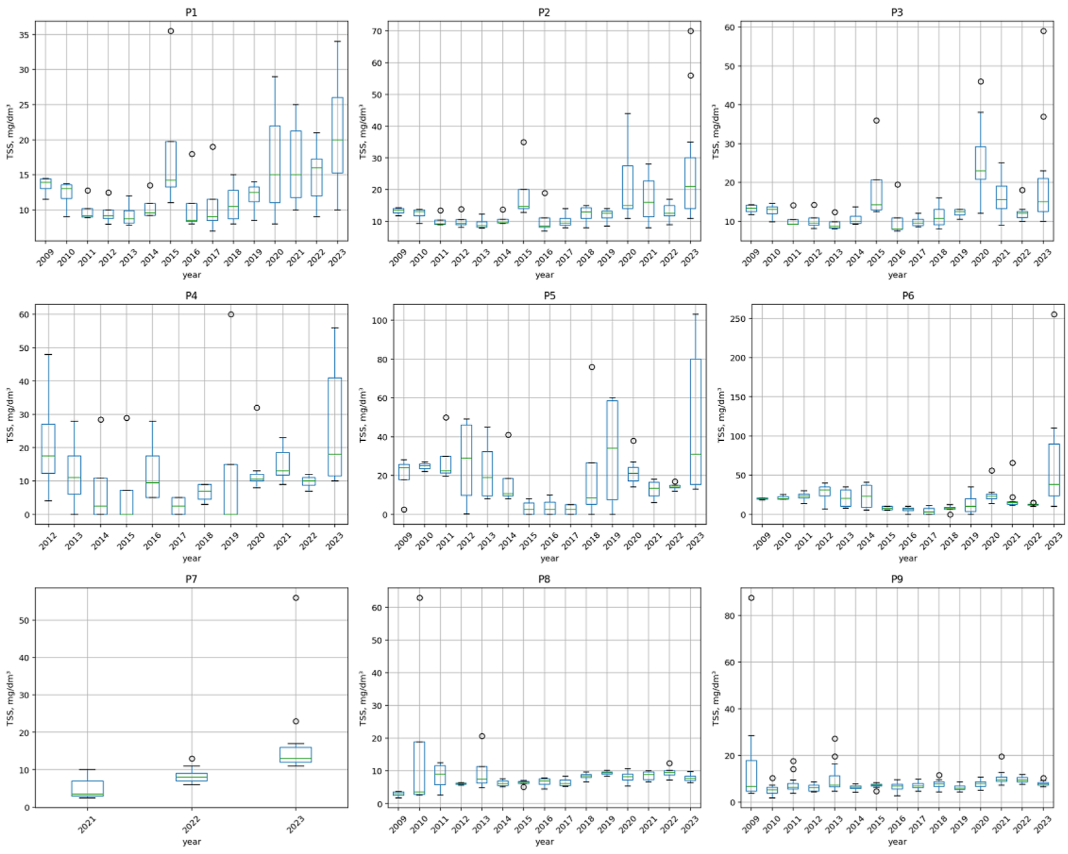

Figure 5. The boxplot showing the distribution of TSS

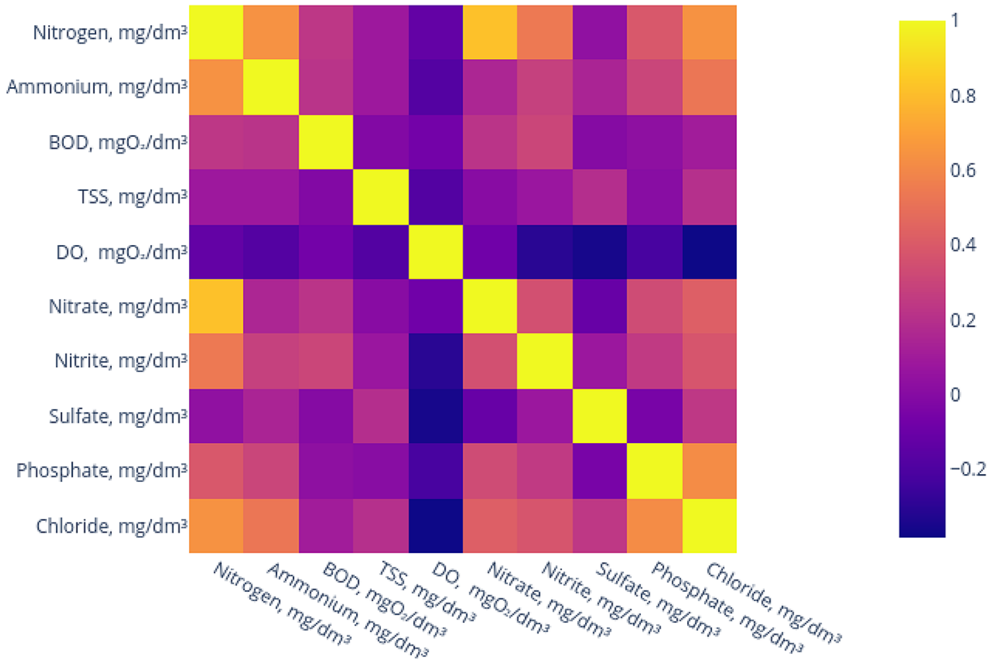

Figure 6. Correlation matrix of the hydrochemical properties at the observed points

Sulfate concentrations range from 0 to 58 mg/dm³, showing significant variation. According to the standards for water bodies designated for fishing, the maximum permissible concentration (MPC) of sulfates is 100 mg/dm³, and for household use water, it is 500 mg/dm³. Thus, all measured values are below the established limits, indicating the absence of significant anthropogenic sources of sulfate pollution or that the parameter is primarily of natural origin. Elevated levels may result from industrial discharges or wastewater.

BOD_5 is an important indicator of organic pollution in water. High BOD_5 levels indicate the presence of significant organic matter that requires oxygen for decomposition. In the studied area, BOD_5 values vary considerably, but most are within acceptable limits for water bodies designated for fishing (up to 3 mg O_2/dm³). This suggests that ecosystems are generally stable, though certain areas may have anthropogenic sources of organic pollution.

DO is a key indicator for maintaining aquatic ecosystems, as it reflects the availability of sufficient oxygen for aquatic life. In the studied water bodies, DO levels mostly comply with the standards for fishery water bodies (not less than 6 mg O_2/dm³), which indicates favourable conditions for aquatic fauna. However, some areas show reduced oxygen levels, which may be due to organic pollution or other factors affecting the water environment. TSS is a key indicator of water quality, as high levels can reduce water clarity, hinder photosynthesis in aquatic plants, and negatively affect aquatic organisms. In the studied region, TSS levels vary but generally remain within acceptable limits (MPC = 15 mg/dm³). High concentrations may be linked to soil erosion or wastewater discharges.

The Pearson correlation table shows several significant relationships between water quality parameters. There is a strong positive correlation between nitrogen and nitrates ($r = 0.814$), suggesting that rising nitrogen levels are likely associated with an increase in nitrate concentrations, typically due to the impact of fertilizers. Chlorides also show strong correlations with nitrates ($r = 0.420$) and phosphates ($r = 0.618$), indicating possible anthropogenic pollution sources, such as wastewater or fertilizers. Dissolved oxygen (DO) exhibits negative correlations with several parameters, including nitrites ($r = -0.305$), sulfates ($r = -0.354$), and chlorides ($r = -0.381$), which may indicate decreased oxygen levels due to organic pollution or elevated levels of these contaminants.

The study results indicate that surface waters in the investigated regions generally meet environmental safety standards. However, some areas exhibit elevated levels of organic and chemical substances, suggesting the influence of anthropogenic factors. The correlation analysis highlights several important relationships between water quality parameters, forming the basis for further studies and the development of water management strategies in cross-border areas.

CONCLUSIONS

The study of hydrochemical indicators in surface waters of Ukraine's border areas with Poland and Slovakia (in Volyn, Lviv, Zakarpattia regions) over a 15-year period provides valuable insights into the dynamics of water quality. The results of the analysis indicate that sulfates (SO_4^{2-}) levels were consistently below the maximum permissible concentration for both fishery and household purposes, suggesting minimal anthropogenic impact in most areas. It is established that biochemical oxygen demand and dissolved oxygen measurements generally met environmental standards, though localized instances of elevated BOD_5 and reduced DO point to potential organic pollution sources.

Total suspended solids were within acceptable limits, indicating stable sediment loads, with higher concentrations likely due to natural processes such as erosion or occasional wastewater discharges. The correlation analysis revealed significant relationships between key water quality parameters, such as the strong positive correlation between nitrogen and nitrate levels, suggesting that agricultural runoff plays a role in nutrient dynamics. Negative correlations between dissolved oxygen and several pollutants emphasize the impact of organic and chemical contaminants on oxygen availability in aquatic ecosystems.

These findings highlight the need for continuous monitoring and targeted management interventions to address localized pollution sources and ensure the sustainable use of transboundary water resources. The study provides a foundation for future research and cross-border cooperation in water quality management, promoting the ecological safety of these shared water bodies.

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