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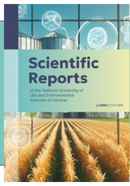

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Biogenic pollution of the Unava River waterbody

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Abstract. Biogenic pollution of Ukraine's waterbodies is a systemic issue requiring continuous monitoring due to its impact on water quality and its role in driving anthropogenic eutrophication. This study aimed to assess the Unava River waterbody to determine the level of biogenic pollution and identify the predominant contamination type (nitrogen- or phosphorus-based). The findings indicate that the concentration of biogenic substances in the Unava River affects water quality, depending on its intended use and the functioning of the aquatic biota (aquatic ecosystem). Specifically, nitrite nitrogen concentrations (0.006-0.306 mg$N$/dm^3 in 2022; 0.006-0.051 mg$N$/dm^3 in 2024) are critical for the aquatic ecosystem. Ammonium nitrogen levels impact recreational and domestic uses (1.21-1.83 mgNH_4^+/dm^3 in 2022; 1.16-5.88 mgNH_4^+/dm^3 in 2024) as well as drinking water supply and the aquatic ecosystem as a whole (0.814-6.84 mg$N$/dm^3 in 2022; 0.3644.56 mg$N$/dm^3 in 2024). Phosphorus concentrations also influence the aquatic ecosystem (0.062-0.196 mg$P$/dm^3 in 2022; 0.333-0.597 mg$P$/dm^3 in 2024). Calculations of the degree of correlation between the variables revealed a negative (inverse) correlation between air temperature and phosphate levels (r = -0.07), nitrate nitrogen (r = -0.69), and nitrite nitrogen (r = -0.10). Conversely, a positive correlation was observed between water temperature and mineral nitrogen ($rNH_4^+ = 0.38$; $rNO_3^- = 0.79$; $rNO_2^- = 0.46$) as well as phosphorus ($rPO_4^{3-} = 0.52$). Calculations based on the *Redfield Ratio* (*RR*) demonstrated that in 2022 (*RR* = 29.42-108.64), mineral phosphorus ions were the limiting biogenic substance, while mineral nitrogen ions were in excess, leading to predominant nitrogen pollution, potentially promoting the growth of green algae. In 2024

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(*RR* = 6.32-18.71), mineral nitrogen ions became the limiting factor, whereas phosphorus ions were in excess under these conditions, resulting in predominant phosphorus pollution, which could facilitate the proliferation of cyanobacteria

Keywords: nutrients; eutrophication; water quality; nitrogen; phosphorus; Redfield Ratio

Introduction

According to research by L.V. Voitenko (2019), the primary substances contributing to biogenic pollution are phosphorus compounds (phosphate ions) and mineral nitrogen (ammonium ions, nitrate ions, and nitrite ions). In line with the Resolution of the Cabinet of Ministers of Ukraine No. 1134-r (2022), leading up to 2050, nitrogen and phosphorus compounds, along with other pollutants, are recognised as key components of both point-source and diffuse pollution in surface waters. Research conducted by V. Strokal *et al*. (2023) indicated that in Ukraine, phosphorus pollution is largely attributed (up to 80%) to point sources. These include the discharge of untreated or inadequately treated wastewater from municipal and industrial facilities, as well as the presence of cesspits in private households lacking centralised water supply and sewage systems. Conversely, diffuse sources, particularly agricultural activities, account for up to 80% of nitrogen pollution in surface waters. These activities involve the introduction of nitrogen compounds into waterbodies through water and wind erosion due to the ploughing of riparian zones, the presence of cultivated agricultural fields near waterbodies, uncontrolled storage of organic fertilisers on farms, and the application of organic and mineral fertilisers for plant nutrition. All of the aforementioned pollution sources have a detrimental effect on the quality of aquatic ecosystems. This, in turn, leads to biogenic pollution of waterbodies and, potentially, to accelerated eutrophication processes. Therefore, it is essential to monitor the quality of surface waterbodies to identify key pollution indicators and minimise their impact on aquatic ecosystems.

Researchers V.S. Kapsalis & I.K. Kalavrouziotis (2021) have highlighted that eutrophication, driven by high concentrations of nutrients in water, is a global issue that must be addressed in all strategies for conserving river ecosystems. M. Devlin & J. Brodie (2023) investigated the input of biogenic substances into river waterbodies. Their research identified nitrogen and phosphorus compounds as the main biogenic substances entering surface waters through both diffuse (river discharges with fertiliser losses from fields, terrestrial runoff) and point sources (wastewater treatment plant discharges). The researchers emphasised in their studies that these substances have a destructive impact on the entire aquatic ecosystem.

The research of I. Micella *et al.* (2024) asserts that agriculture and urbanisation are the two primary sources of nutrients (nitrogen, phosphorus), chemical, macro- and microplastic pollution in natural waters. The authors noted that biogenic substances (nutrients) from agricultural activities frequently enter rivers through runoff from fertilised fields and via wastewater from treatment plants.

This study aimed to assess the Unava River waterbody to determine the level of biogenic pollution and to establish the ratio of phosphates to nitrates, thereby identifying the limiting nutrient and predicting the dominant type of pollution.

To achieve this aim, the study pursued the following objectives:

- evaluate the water quality of the Unava River to determine the level of biogenic pollution based on phosphate ion concentrations and mineral nitrogen levels (ammonium ions, nitrate ions, and nitrite ions);
- establish the correlation between changes in meteorological parameters (air and water temperature at the time of water sampling) and biogenic substance concentrations;

- determine the limiting biogenic substance using the *Redfield Ratio* (RR) for the Unava River ecosystem and, based on the obtained data, substantiate anthropogenic eutrophication of the Unava River waterbody.

The scientific novelty of the results lies in the fact that this is the first comparative assessment of the Unava River waterbody's quality at the point of established biogenic pollution. This includes the identification of the limiting biogenic substance using the stoichiometric *Redfield Ratio*.

Materials and Methods

Ecological investigations were conducted during 2022 and 2024. Water samples from the Unava River waterbody were collected in September 2022 and early November 2024. Water sampling was carried out following DSTU ISO 5667-6:2009 (2009). Each observation point included three water sampling locations. Sampling began at the river's mouth (1st observation point) and concluded at the point where the Unava River flows into the Irpin River (10th observation point). In total, there were 10 observation points, three of which encompassed reservoirs on the Unava River (Table 1, Fig. 1).

The Unava River aquatic ecosystem is a transformed hydro-ecosystem, altered by intensive agricultural development and urbanisation. The Unava River is located within the Kyiv and Zhytomyr regions of Ukraine. Approximately 80% of its riparian zone consists of arable land and private garden plots. Three reservoirs are situated along the Unava River (Popilnia pond farm), serving recreational needs and sport fishing. One reservoir is located within the city of Fastiv (Kyiv Region) and is used for domestic water supply, sport fishing, and recreation. Additionally, grain elevators and livestock stables are present in the riparian zones. The river is notably marshy, with shrubs and diverse vegetation along its banks (Ministry of Environmental…, 2021).

The assessment of the Unava River's water quality, to determine the level of biogenic pollution based on phosphate ion concentrations and mineral nitrogen levels (ammonium ions, nitrate ions, and nitrite ions), was conducted by comparing the actual biogenic substance concentrations from 2022 and 2024 with the regulatory (optimal) values for these indicators across different water use categories (Tables 2-3).

Table 1. *Characteristics of observation points on the Unava River waterbody*

Point	Location
1	Horodyshche Village, Andrushivska District, Zhytomyr Region River mouth
2	Velyki Lisivtsi Village, Popilnia District, Zhytomyr Region
3	Kvitneve Village, Popilnia District, Zhytomyr Region (Unava River reservoir)
4	Yerchyky Village, Zhytomyr District, Zhytomyr Region (Unava River reservoir)
5	Koshliaky Village, Popilnia District, Zhytomyr Region
6	Pivni Village, Fastiv District, Kyiv Region
7	Volytsia Village, Fastiv District, Kyiv Region
8	Fastiv City, Kyiv Region Fastiv Reservoir on the Unava River
9	Between Mala Ofirna and Velyka Ofirna villages
10	Vasylkiv District, Kyiv Region. Towards the Pereviz Village, between Chornohorodka and Dzvinkove villages Unava River flows into the Irpin River

Source: compiled by the authors based on the conducted research

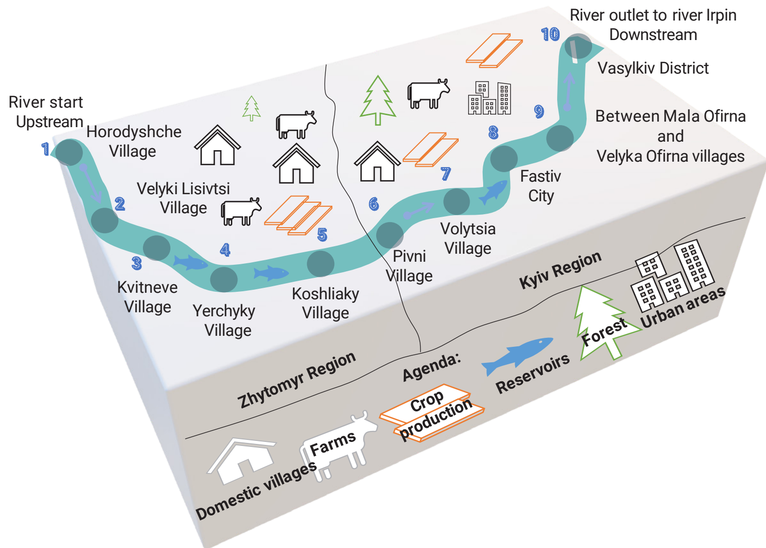


Figure 1. *Projection of observation and water sampling points, including key anthropogenic sources impacting the Unava River aquatic ecosystem*

Source: compiled by the authors based on the conducted research

Table 2. *Regulatory (optimal) values of key biogenic substances for potable and recreational water use, as well as for fishery waterbodies*

Water quality indicator	Regulatory (optimal) values for water use from rivers														
	For fishery water bodies (FWB)**		For waterbodies used for potable (centralised/decentralised supply), domestic, recreational, and other public needs												
	SOU		Ministry of Health of Ukraine dated 02 May 2022 No. 721			SOU 05.01-37-385:2006		DSTU 7525:2014			DSTU 4808:2007				
											Centralised water supply				
											Water quality classes				
	Unit	Category – carp	Unit	The first category (drinking)	The second category (recreation, etc.)	Unit	For drinking water (tap water)	Unit	Centralised water supply	Decentralised water supply	Unit	1 – excellent	2 – good	3 – satisfactory	4 - moderate, LP
Phosphates –PO_4^{3-}	mgP/dm³	≤0.5	mgPO_4^{3-}/dm³	3.5	3.5	mgrPO_4^{3-}/dm³	≤3.5	mgPO_4^{3-}/dm³	≤3.5	-*	mgP/dm³	<0.3	0.3-0.5	0.6-1.0	>1.0
Ammonium nitrogen – NH_4^+	mgN/dm³	≤1.0	mgNH_4^+/dm³	2.0	2.0	mgNH_4^+/dm³	0.5-2.6	mgNH_4^+/dm³	0.5-2.6	-*	mgN/dm³	-*	0.05-0.50	0.51-2.00	>2.00
Nitrate nitrogen – NO_3^-	mgN/dm³	≤2.0	mgNO_3^-/dm³	45.0	45.0	mgNO_3^-/dm³	≤50.0	mgNO_3^-/dm³	≤50.0	≤ 5.0	mgN/dm³	<5.0	5.0-7.0	7.1-10.0	>10.0
Nitrite nitrogen – NO_2^-	mgN/dm³	≤0.1	mgNO_2^-/dm³	3.3	3.3	mgNO_2^-/dm³	≤0.5	mgNO_2^-/dm³	≤0.5	≤ 0.02	mgN/dm³	<0.05	0.05-0.50	0.51-1.00	>1.00

Note: First category – centralised and decentralised potable water supply; Second category – water used for domestic needs, health resorts, recreation, and sports; LP (Limitedly potable) – water of limited suitability for use; * – indicates that the parameter should be absent in water; **FWB – fishery water body

Source: developed by the authors based on regulatory data SOU 05.01-37-385:2006 (2006), DSTU 4808:2007 (2007), Order of the Ministry of Health of Ukraine No. 400 (2010), DSTU 7525:2014 (2014), Order of the Ministry of Health of Ukraine No. 721 (2022)

Table 3. *Regulatory (optimal) values for key biogenic substances for waterbody assessment (surface waters)*

Water quality indicator	Methodology for ecological assessment of surface water quality by relevant categories, Approved by the Ministry of Environmental Protection No. 44 order dated 31 January								
	Ecological classification of surface water quality								
	Unit	Quality class	I	II		III		IV	V
		Quality category	1	2	3	4	5	6	7
Phosphates – PO_4^{3-}	mg*P*/dm³		<0.015	0.015-0.030	0.031-0.05	0.051-0.10	0.101-0.20	0.201-0.300	>0.30
Ammonium nitrogen – NH_4^+	mg*N*/dm³		≤0.1	0.10-0.20	0.21-0.30	0.31-0.50	0.51-1.00	1.01-2.50	>2.50
Nitrate nitrogen – NO_3^-	mg*N*/dm³		<0.20	0.20-0.30	0.31-0.50	0.51-0.70	0.71-1.00	1.00-2.50	>2.50
Nitrite nitrogen – NO_2^-	mg*N*/dm³		<0.002	0.0020.005	0.0060.01	0.011-0.02	0.021-0.05	0.051-0.10	>0.10
Characteristics of water quality classes and categories Quality category General information		Quality class	Excellent	Very good	Good	Satisfactory	Moderate	Poor	Very poor
		Very clean	Clean	Fairly clean	Slightly polluted	Moderately polluted	Dirty	Highly polluted	
			The waterbody is xeno- or oligo-saprobic. A diverse range of organisms inhabit the water, but their numbers are low (e.g., *Vorticella*, *Daphnia longispina*, diatom alga *Synedra*). Eutrophication processes are practically absent		The waterbody is mesosaprobic. Contains numerous planktonic organisms that mineralise organic matter. Green and diatom algae may develop.		The waterbody is polysaprobic. Inhabited by numerous colourless flagellates, fungi (*Sewage fungus*), certain ciliates, saprobacteria, filamentous bacteria (*Sphaerotilus*), and others. Eutrophication processes are intensified and highly active.		

Source: developed by the authors based on the established methodology by V.D. Romanenko *et al*. (1998), V.P. Strokal & A.V. Kurovska (2024)

Given the presence of reservoirs on the Unava River, the optimal water quality values for fishing (fishery water bodies) and recreation (cultural-domestic and recreational needs) were considered. Furthermore, the city of Fastiv, located on the Unava River, relies on a reservoir within its boundaries for its water supply. Therefore, regulatory water quality values for potable and domestic needs were also taken into account. Historically, the Unava River waterbody was used for crop irrigation. During field sampling trips, irrigation channels were observed, now completely overgrown with shrubs and various vegetation. Due to active agricultural practices and the ploughing of riparian zones, the Unava River has become a low-flow river with sections containing minimal water. Consequently, optimal water quality values for irrigation were not included in this study. For fishery water bodies, the regulatory (optimal) values for the carp family were applied, as they are prevalent in the Unava River reservoirs.

The correlation between meteorological variables (air and water temperature at the time of water sampling) and biogenic substance concentrations was established by calculating the linear correlation coefficient (r). The degree of correlation can range from -1 to +1. A positive (direct) correlation indicates that high values of one variable correspond to high values of another; a negative (inverse) correlation indicates that high values of one variable correspond to low values of another. The general classification indicates that a correlation is strong (or close) when $r \geqslant 0.7$; moderate when $0.5 \leqslant r \leqslant 0.7$; moderate when $0.3 \leqslant r \leqslant 0.5$; weak when $0.2 \leqslant r \leqslant 0.3$; and very weak when $r < 0.2$ (Strokal & Kurovska, 2024).

The limiting biogenic substance was determined using the stoichiometric *Redfield Ratio* (*RR*) for the Unava River ecosystem, based on the analysed data from the first objective. The Redfield Ratio (*RR*) allowed for tracking the balance of nitrates and phosphates in the river's surface waters (Rudenko & Dzenzerska, 2015; Bedunkova & Kaletnik, 2017). It also indicated the degree of limitation of phytoplankton production processes (Voitenko, 2019) and the excess or deficiency of nitrogen or phosphorus in the waterbody (Bedunkova & Kaletnik, 2017). Given that visible eutrophication processes were observed in the studied river during field trips, the application of the Redfield Ratio (*RR*) is particularly relevant. It allowed for the determination of the limiting factor influencing anthropogenic eutrophication in the Unava River waterbody. It is important to note that mineral forms of nitrogen (ammonium ions – NH_4^+, nitrate ions – NO_3^-, nitrite ions – NO_2^-) and phosphorus in the water were used for the *RR* calculation.

The stoichiometric Redfield Ratio (*RR*) was determined using the following formula (Voitenko, 2019):

$$RR_{at}(N/P) = 1.53*((1.35*[NO_2^-] + [NO_3^-] + 3.44*[NH_4^+]/[PO_4^{3-}]), \quad (1)$$

where the ion concentrations are expressed in μg/dm³. If RR_{at} $(N/P) > 16$, the limitation of phytoplankton primary production can be attributed to mineral phosphorus (meaning that mineral phosphorus ions are the limiting biogenic substance, and mineral nitrogen ions are in excess, indicating a dominance of nitrogen pollution in the waterbody). Conversely, if RR_{at} (N/P) < 16, the limitation is attributed to nitrogen (meaning that mineral nitrogen ions are the limiting biogenic substance, phosphorus ions are in excess, and consequently, phosphorus pollution is the dominant factor).

Results

The hydrological regime of the river is deteriorating annually due to anthropogenic impacts, which have led to the transport of erosion products (along with biogenic substances – nutrients) into the waterbody. This is compounded by the effects of climate change, resulting in river shallowing, and the impact of war, which has introduced higher concentrations of toxic substances into the waterbody.

The assessment of the Unava River waterbody's quality for recreational and domestic water supply needs was conducted by considering the concentration of water quality indicators (biogenic substances) in mg*PO*/dm³, mg*NO*/dm³, or mg*NH*/dm³. For other uses and types of water consumption, such as fisheries and potable water, as well as for assessing the aquatic ecosystem itself, the comparison of water quality indicator concentrations (biogenic substances) with optimal values was performed in mg*P*/dm³ or mg*N*/dm³. This is due to the units of measurement used in the regulatory standards (Tables 2-3).

It is crucial to understand the pathways through which biogenic (nutrient) substances enter waterbodies. Phosphorus and nitrogen ions can enter waterbodies via rainfall runoff through storm sewer systems and discharges of municipal and industrial wastewater (Tyagniy *et al*., 2022). Generally, the concentration of pollutants in rainfall runoff depends on the time elapsed since the last rainfall. The longer the period without rain, the more dust, debris, and associated pollutants accumulate on streets and pavements, which are then washed into the river during rainfall (Stepova *et al*., 2022). The biogenic salt content of nitrogen and phosphorus in rainwater is approximately 5-6 mg/dm³ and 0.7-1.2 mg/dm³, respectively. Domestic wastewater contains about 50% of its nitrogen in the ammonium form, 30% as organic compounds, and 20% as nitrates and nitrites (Stepova *et al*., 2022).

Based on analytical studies of phosphate ion concentrations in the Unava River water, it was determined that their concentration in 2022 was lower than that in the 2024 water samples (Figs. 2a, 2b). Water samples were collected during the autumn period in both years. It should be noted that, particularly in spring and autumn, silty deposits in waterbodies can release an average of 27 mg/m² of ammonium and 0.7 mg/m² of phosphorus per day (Pichura, 2021).

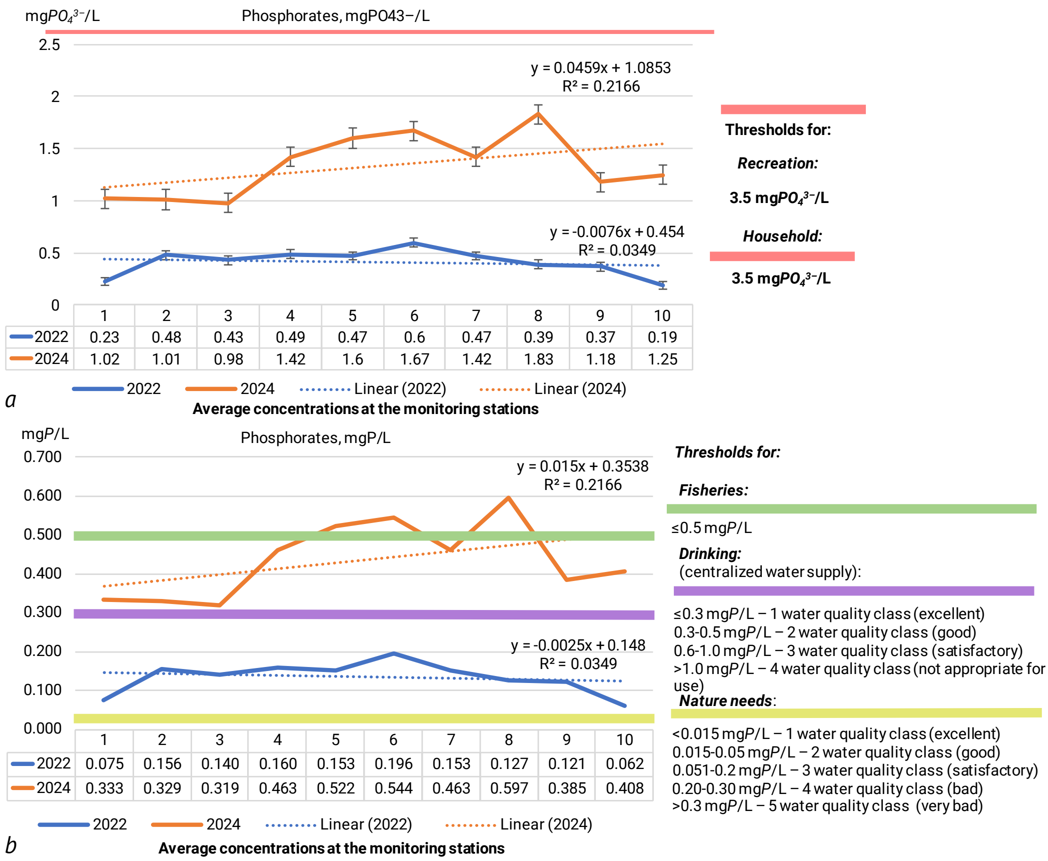


Figure 2. *Weighted average concentrations of phosphate ions for 2022 and 2024 (n = 3 at each observation point) compared to the optimal PO_4^{3-} concentration values for use*

Note: a – for recreational and domestic needs; b – for fishery needs, drinking needs, and the aquatic ecosystem

Source: developed by the authors based on their own analytical research results

Comparing the obtained phosphate ion concentrations in the Unava River water with optimal values for various uses reveals that, for recreational and domestic needs, the PO_4^{3-} concentration in the water was within the normal range in both 2022 and 2024 (Fig. 2a). However, for fisheries (Figure 2b), the PO_4^{3-} concentration in the water increased in 2024 by 15-35% (depending on the points), and consequently, in some observation points, the PO_4^{3-} concentration exceeds the optimal values (observation points No. 5-6, 8). When assessing the Unava River ecosystem as a whole, the PO_4^{3-} concentration at all observation points in 2022 and 2024 was outside the optimal range (the actual concentration ranged from 0.075 to 0.597 mg*P*/dm³). This indicates that according to the methodology (Romanenko *et al*., 1998), the aquatic ecosystem corresponds to quality class 3 (2022) – satisfactory quality, and quality classes 4-5 (2024) – poor and very poor water quality. For drinking water needs, all observation points in 2024 had phosphate ion concentrations exceeding the normal range, compared to the phosphate ion content in 2022 (Fig. 2b). This situation could be caused by various anthropogenic factors (point and diffuse sources) in the Unava River basin, including the input of biogenic substances by rainwater, along with the transport of these biogenic substances from ploughed agricultural areas (diffuse input) located directly on the riverbank. Also, at observation point 8, an important factor is both storm runoff (diffuse input) and wastewater from municipal and domestic facilities in the Fastiv area (point input).

The situation regarding nitrate ion concentrations in the studied water is less critical than that of phosphate ions (Fig. 3).

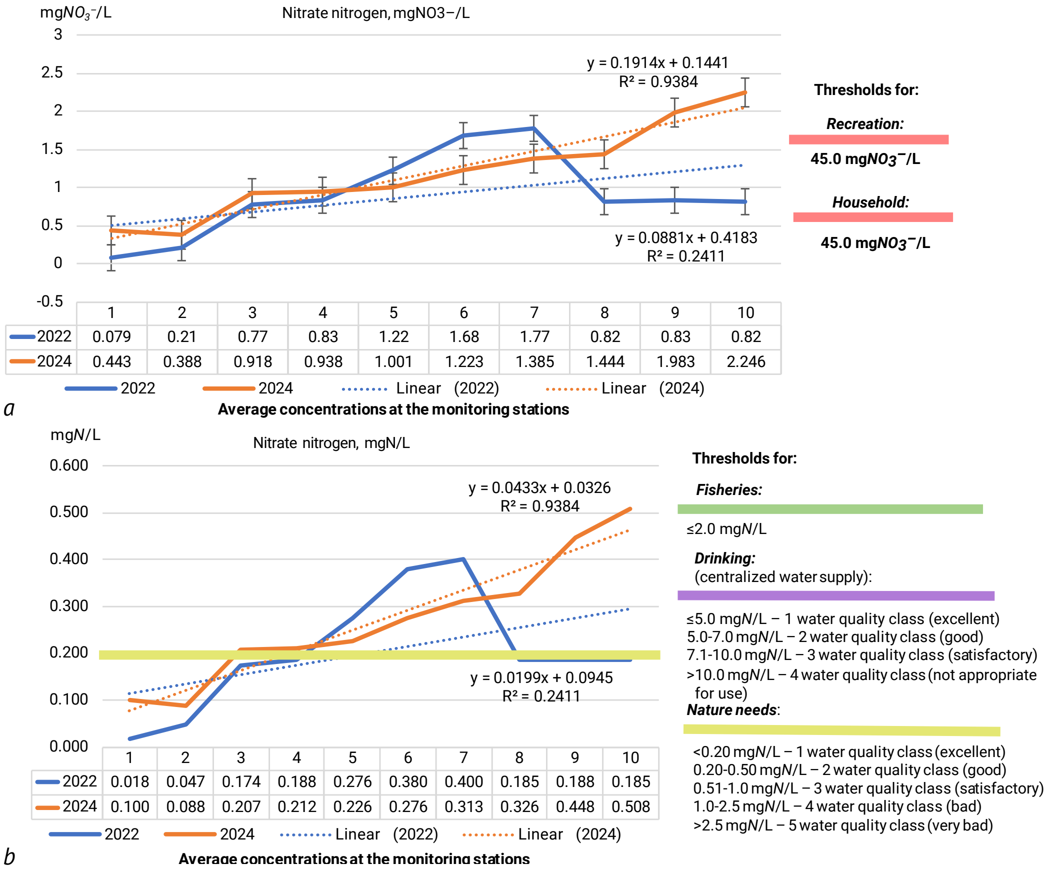


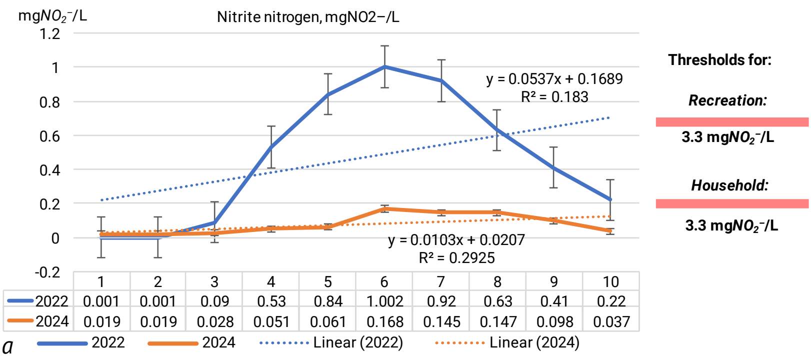
***Figure 3.** Weighted average concentrations of nitrate ions for 2022 and 2024 (n = 3 at each observation point) compared to the optimal NO_3^- concentration values for use*

Note: a – for recreational and domestic needs; b – for fishery needs, drinking needs, and the aquatic ecosystem

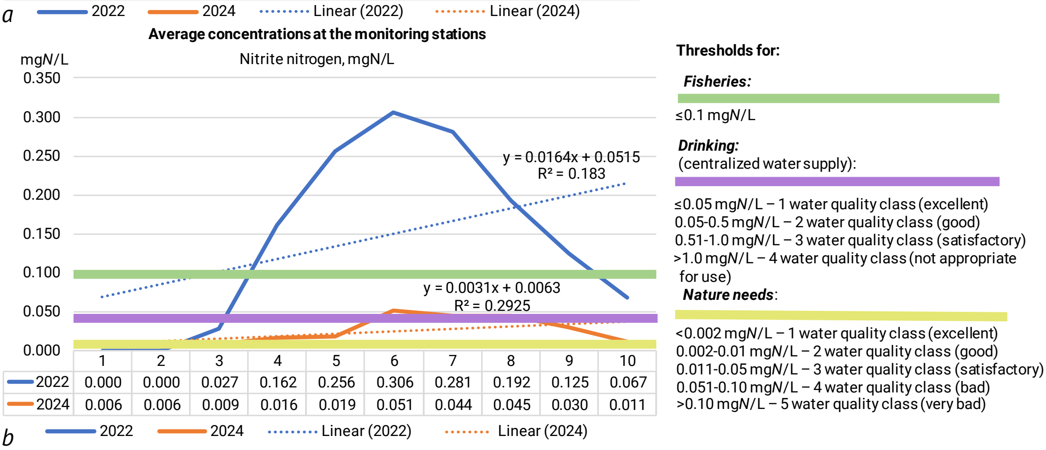
Source: developed by the authors based on their own analytical research results

The Unava River exhibits optimal values for recreational (Fig. 3a), domestic, and drinking water needs (Fig. 3b), as well as for fishery water bodies (for the carp family, Fig. 3b), with actual water concentrations ranging from 0.018 to 0.4 mg$N$/dm^3 in 2022 and 0.08 to 0.5 mg$N$/dm^3 in 2024. When assessing the aquatic ecosystem according to the methodology (Romanenko *et al.*, 1998), observation points 3-7 (in 2022) and 3-10 (in 2024) show elevated nitrate ion concentrations in the studied water. Accordingly, on average, the waterbody corresponds to quality class 2 (good) in 2022 and class 3 (satisfactory) in 2024. A trend of increasing nitrate ion concentrations in the Unava River is observed along the observation points. This indicates a correlation between the distance from the river's mouth (point 1), where nitrate ion concentrations are within optimal conditions for the entire aquatic ecosystem and various water use needs (observation points 1-3), and an increase towards point 7 (Volytsia Village) in 2022, and towards point 10 (confluence with the Irpin River) in 2024. This situation is indicative of active agricultural activity in the Unava River basin, particularly in the areas of these observation points. It is also worth noting that elevated nitrate ion concentrations indicate pollution that occurred in past years or seasons.

Elevated concentrations of nitrite and ammonium ions indicate nitrogen pollution caused by recent anthropogenic factors. Based on the analytical results, the actual concentration of nitrite ions (NO_2^-) in the studied water at the observation points (Fig. 4a) is within optimal ranges for recreational and domestic needs (0.01-1.01 mgNO_2^-/dm^3 with a standard of 3.3 mgNO_2^-/dm^3). For fisheries (Fig. 4b), the results are within optimal ranges for 2024 (0.06-0.051 mg$N$/dm^3 with a standard of 0.1 mg$N$/dm^3) and within acceptable ranges for 2022 (0.001-0.306 with a standard of 0.1 mg$N$/dm^3). For drinking water needs (Fig. 4b), the water quality at the studied observation points corresponded to quality class 1 (2024) and quality class 2 (2022). The Unava River waterbody's quality, according to the methodology (Romanenko *et al.*, 1998), was also assessed as quality class 2-3 (2024) and quality class 4-5 (2022). A trend of decreasing actual nitrite ion (NO_2^-) concentrations is observed in 2024 compared to 2022 (by 25-40%). It is important to consider that these indicators may have been influenced by temperature conditions (which were lower in 2024 than in 2022 during water sampling) and the presence of precipitation.



	1	2	3	4	5	6	7	8	9	10
2022	0.001	0.001	0.09	0.53	0.84	1.002	0.92	0.63	0.41	0.22
2024	0.019	0.019	0.028	0.051	0.061	0.168	0.145	0.147	0.098	0.037



	1	2	3	4	5	6	7	8	9	10
2022	0.000	0.000	0.027	0.162	0.256	0.306	0.281	0.192	0.125	0.067
2024	0.006	0.006	0.009	0.016	0.019	0.051	0.044	0.045	0.030	0.011

Figure 4. *Weighted average concentrations of nitrite ions for 2022 and 2024 (n = 3 at each observation point) compared to the optimal NO_2^- concentration values for use*

Note: a – for recreational and domestic needs; b – for fishery needs, drinking needs, and the aquatic ecosystem

Source: developed by the authors based on their own analytical research results

The concentration of ammonium nitrogen (NH_4^+) (Fig. 5) in the water samples from 2022 and 2024 revealed the following situation:

➤ for recreational and domestic needs (Fig. 5a) – in 2024, the Unava River exhibited elevated ammonium nitrogen concentrations exceeding the standard at points 4-5 and 8-9 (2.215.88 mgNH_4^+/dm^3 with a standard of 2.0 mgNH_4^+/dm^3). In 2022, exceedances were observed at points 28 (2.06-8.83 mgNH_4^+/dm^3 with a standard of 2.0 mgNH_4^+/dm^3). The concentration of this indicator was lower in 2024 (25-30% lower) compared to the 2022 studies;

➤ for fishery water bodies (Fig. 5b) – The Unava River at all observation points (except point 1 – the river mouth) was characterised by elevated ammonium nitrogen (NH_4^+) concentrations, indicating pollution at the time of water sampling and creating unfavourable conditions for aquaculture development;

➤ for drinking water needs (Fig. 5b) – The waterbody is of limited suitability for consumption, as the indicator concentration exceeds the first quality class. Specifically, in 2024, it ranged from 0.9 to 4.5 mg*N*/dm^3, and in 2022, from 0.9 to 6.8 mg*N*/dm^3, with a standard of 0.05 mg*N*/dm^3. Water with an NH_4^+ concentration > 2.0 mg*N*/dm^3 is considered unsuitable;

➤ assessing the aquatic ecosystem based on this indicator (Fig. 5b), it can be characterised as belonging to quality classes 4-5 (poor and very poor) for both 2022 and 2024.

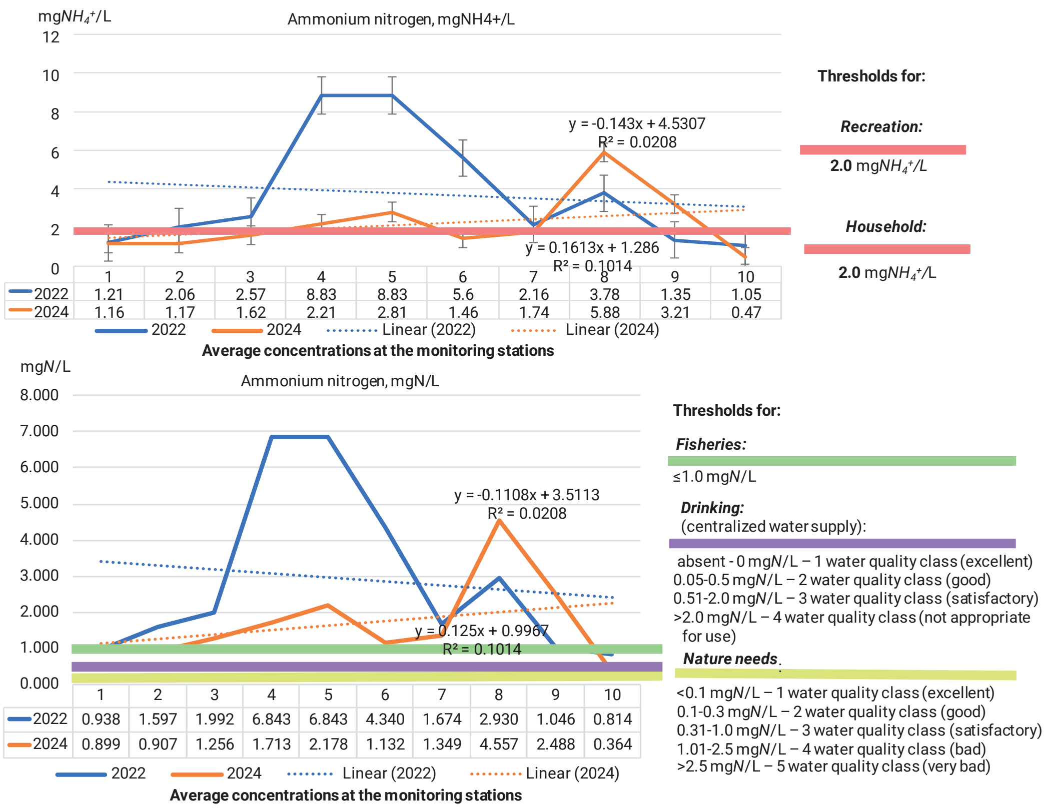


Figure 5. *Weighted average ammonium nitrogen (NH_4^+) concentrations for 2022 and 2024 (n = 3 at each observation point) compared to the optimal NH_4^+ concentration values for use*

Note: a – for recreational and domestic needs; b – for fishery needs, drinking needs, and the aquatic ecosystem

Source: developed by the author based on their own analytical research results

Thus, based on the assessment of biogenic substance content in the waterbody, it can be concluded that nitrite ion and ammonium ion concentrations have the greatest impact on the aquatic ecosystem. These substances indicate pollution that occurred shortly before the water sampling period. Phosphorus loading, according to the research results, negatively affects the water quality of the Unava River, particularly for the aquatic ecosystem, while its concentration in the studied water is optimal for recreational, domestic, and drinking needs.

During the 2024 research, a correlation between changes in meteorological parameters (water and air temperature measured at the time of water sampling at the observation points) and biogenic substances was established (Tables 4 and 5). This allowed for confirming the hypothesis that biogenic substance concentrations are significantly dependent on temperature conditions.

Table 4. *Initial data for calculating the correlation dependency*

Indicator/ Point	Concentration of biogenic substances in the studied water				t_{Air}, ℃	t_{Water}, ℃
	Phosphates, mgPO_4^{3-}/dm^3	Ammonium nitrogen, mgNH_4^+/dm^3	Nitrate nitrogen, mgNO_3^-/dm^3	Nitrite nitrogen, mgNO_2^-/dm^3		
1	1.02	1.16	0.443	0.019	6.0	11.4
2	1.01	1.17	0.388	0.019	6.0	10.4
3	0.98	1.62	0.918	0.028	7.0	10.8
4	1.42	2.21	0.938	0.051	6.0	10.9
5	1.6	2.81	1.001	0.061	6.0	11.6
6	1.67	1.46	1.223	0.168	6.0	12.1
7	1.42	1.74	1.385	0.145	6.0	12.0
8	1.83	5.88	1.444	0.147	6.0	13.9
9	1.18	3.21	1.983	0.098	5.0	12.2
10	1.25	0.47	2.246	0.037	5.0	14.0

Source: developed by the authors based on their own analytical research results

Table 5. *Dependency of biogenic substances in the water on air and water temperature*

Indicator	Coefficient of linear correlation *r*		Justification
	t_{Air}, ℃	t_{Water}, ℃	
Phosphates, mgPO_4^{3-}/dm^3	-0.07	0.52	Medium correlation with t_{Water}; inverse correlation with t_{Air}
Ammonium nitrogen, mgNH_4^+/dm^3	0.01	0.38	Weak correlation with t_{Water}; very weak correlation with t_{Air}
Nitrate nitrogen, mgNO_3^-/dm^3	-0.69	0.79	Strong correlation with t_{Water}; inverse correlation with t_{Air}
Nitrite nitrogen, mgNO_2^-/dm^3	-0.10	0.46	Medium correlation with t_{Water}; inverse correlation with t_{Air}

Source: developed by the authors based on their own analytical research results

The correlation between meteorological variables (air and water temperature at the time of water sampling) and biogenic substances was established by calculating the linear correlation coefficient (*r*). Calculations revealed a negative (inverse) correlation between air temperature and phosphate, nitrate nitrogen, and nitrite nitrogen levels. Conversely, a positive correlation was found between water temperature and all biogenic indicators. The inverse (negative) correlation may be attributed to the intensification of various microbiological processes during temperature increases or decreases. The direct (positive) correlation with water temperature is justified because elevated water temperatures stimulate microbiological processes within the waterbody, which can significantly influence nitrogen and phosphorus concentrations. This is particularly evident in the nitrate nitrogen indicator, which exhibits a strong correlation with water temperature (Table 5).

Based on the objectives outlined above, the stoichiometric Redfield Ratio (*RR*) for the Unava River ecosystem was calculated (Fig. 6) to determine the limiting factor, which demonstrates the dominant type of pollution (mineral phosphorus or mineral nitrogen).

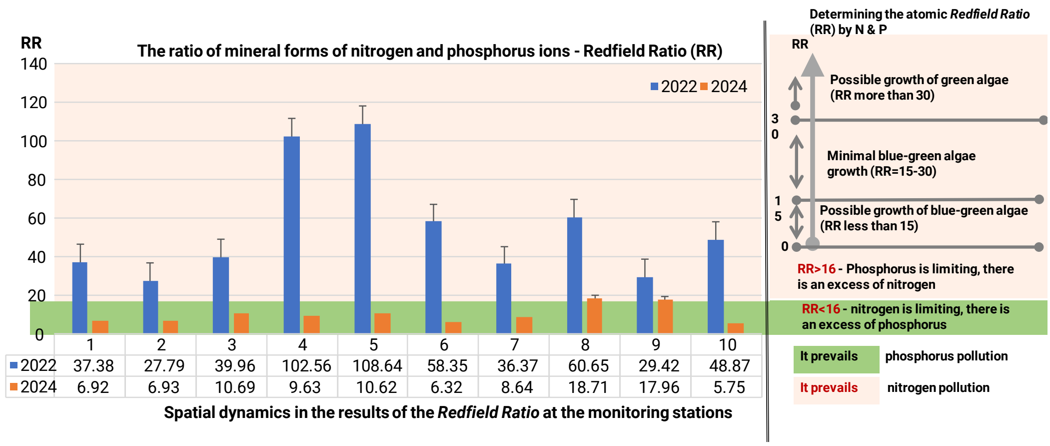


Figure 6. *Calculation of the stoichiometric Redfield Ratio (RR) based on nitrogen and phosphorus ion forms in the Unava River, showing the changes across the 2022 and 2024 study period*
Source: developed by the authors based on their own analytical research results

According to the calculated *RR*, the dominant type of pollution in 2022 was nitrogen. As the *RR* during this period ranged from 29.42 to 108.64, this indicated that mineral phosphorus ions were the limiting biogenic substance, while mineral nitrogen ions were in excess. This signifies that nitrogen pollution was dominant in the waterbody, potentially favouring the growth of green algae.

The 2024 results differ significantly. The *RR* during this period ranged from 6.92 to 18.71, indicating that mineral nitrogen was the limiting factor, and phosphorus ions were in excess. Consequently, this indicates a shift towards dominant phosphorus pollution in the water. Under these conditions, blue-green algae may proliferate in the waterbody. This is consistent with the previously described analysis of biogenic substances. In particular, based on the assessment of phosphate ions in the studied water, the waterbody was classified as quality class 3 (satisfactory) in 2022 and quality class 5 (very poor) in 2024. This indicates a substantial increase in phosphate ion concentrations compared to 2022.

Therefore, anthropogenic eutrophication of the Unava River waterbody has been actively occurring and continues to do so. Biogenic substances play a significant role in intensifying these processes, as evidenced by the biogenic substance levels in the studied water for 2022 and 2024.

Overall, the Unava River is experiencing shallowing in most of its length and is overgrown with shrubs. There is a considerable amount of unauthorised waste along the riverbanks. Throughout the Unava River basin, there are ploughed agricultural lands, animal stables, and active fishing in the Unava River reservoirs. There is also significant siltation at the bottom of the Fastiv reservoir (observation point 8).

Discussion

It is important to note that this study focuses on biogenic pollution of the waterbody by nutrients, specifically mineral compounds of nitrogen and phosphorus. The presence of these compounds in high concentrations leads to reduced oxygen saturation in the waterbody, the proliferation of bluegreen algae, for which these nutrients are a primary food source, and, as a final result in this chain, the intensification of anthropogenic eutrophication processes. Consequently, anthropogenic eutrophication of waterbodies deteriorates the ecological state of the waterbody itself, disrupts selfregulation and self-restoration processes within the aquatic ecosystem, leads to fish hypoxia, and worsens conditions for recreational needs.

The results of this study allow for the examination of biogenic pollution in surface waterbodies (rivers) by establishing the dominant type of pollution based on biogenic substances (nitrogen, phosphorus) using the stoichiometric Redfield Ratio. This is a key distinction from previous research by other authors. The use of this approach enables the prediction of pollution sources in waterbodies, both point and diffuse, and provides a basis for assessing the degree of their impact on the aquatic ecosystem. The significance of studying point and diffuse pollution sources in Ukrainian rivers is substantiated by the research of V.P. Strokal & A.V. Kurovska (2024). In their study, the authors elucidate the nature of nitrate pollution in the Dnipro River basin and demonstrate that nitrate pollution in rivers is closely linked to both diffuse and point pollution sources. The research of V.P. Strokal & A.V. Kurovska (2024) revealed that high concentrations of nitrogen compounds (nitrite, nitrate, and ammonium) in surface waters result from diffuse pollution. This type of pollution manifests through the introduction of nitrogen ions into waterbodies from ploughed agricultural fields (due to wind and water erosion, soil runoff enriched with nitrogen ions enters the waterbody) and ploughed riparian zones through the creation of additional arable land (leading to the direct input of nutrients from soils into waterbodies). A previous study by Strokal *et al.* (2023) confirms that phosphorus compounds, entering waterbodies through wastewater discharges from municipal and industrial facilities, constitute a significant portion of point source pollution in surface waters (rivers). In this context, urbanisation acts as the main pollution driver. Therefore, the current study adopts the previously outlined pollution types and predicts their occurrence in rivers.

Numerous scientific studies underscore the importance of researching and assessing biogenic pollution in rivers. Scientists A.K. Tiwari & D.B. Pal (2022) have demonstrated that the primary drivers of eutrophication in river systems are high concentrations of biogenic substances (nutrients) in the water. Their research indicates that along with the discharge of untreated industrial, urban, and agricultural runoff into waterbodies, large amounts of carbon, nitrogen, phosphorus, and many other pollutants are introduced. They also state that eutrophication is a natural process that enhances the growth of aquatic plants, such as algae, which in turn use excessive amounts of inorganic nutrients like nitrogen and phosphorus for their growth. The authors emphasised that eutrophication resulting from increased algal growth in a waterbody can lead to the formation of so-called “dead zones”, the death of aquatic animals, and the loss of the aquatic ecosystem.

The study of S. Bae & D. Seo (2021) analysed the impact of hydrodynamic changes in a large river on algal growth, which leads to eutrophication. They demonstrated that the response to algal blooms in water depends on the season, and this factor should be considered in research. The authors of the current article agree with their view that the season is an important factor in studying eutrophication processes in waterbodies. Consequently, the concentration of biogenic substances in water will also vary depending on the season. Temperature regimes (air and water temperature) and the amount of precipitation received during different seasons are key indicators that influence the concentration of biogenic substances in water. Therefore, one of the objectives of this article was to determine the correlation between nitrogen and phosphorus concentrations and air and water temperature. Future research should include additional monitoring studies for each season to establish the dominant type of pollution based on biogenic substances (nitrogen, phosphorus) in more detail, using the stoichiometric Redfield Ratio, and to determine whether these types differ depending on the season.

The scientific research of A. Ural-Janssen *et al.* (2024) indicates that the export of nitrogen (*N*) and phosphorus (*P*) compounds by rivers, as key indicators of coastal water eutrophication in Europe, will increase by 13-28% due to global climate change and technological advancements. Using the MARINA-Nutrients model, they calculated that to prevent future coastal eutrophication in European waterbodies, it is necessary to reduce nitrogen (*N*) compound inputs by up to 47% and phosphorus (*P*) compound inputs by up to 77%.

The results of scientists A.K. Sahu *et al.* (2024) confirmed that water resource pollution significantly affects drinking water quality and access, particularly for rural populations lacking centralised water supplies. They noted that, unlike groundwater, surface water sources such as small rivers, ponds, and lakes are most susceptible to elevated nutrient levels, which serve as food sources for eutrophic aquatic organisms (such as cyanobacteria). However, they argued that despite the toxic effects of cyanobacteria in water, they play a significant role as primary producers, nitrogen fixers, and organisms with high nutritional value. Complete eradication of cyanobacteria could disrupt the functioning of the aquatic ecosystem, especially in small rivers and ponds. Therefore, when researching small rivers (like the Unava River), particular attention must be paid to determining biogenic substance concentrations in the water and controlling eutrophication processes.

The research of E. Soana *et al.* (2024) indicates that the problem of waterbody eutrophication results from the presence of significant amounts of biogenic substances in the water and requires continuous monitoring. The scientists noted that all rivers worldwide suffer from nitrate pollution. Climate change exacerbates this problem for rivers, creating unexpected ecological consequences for aquatic ecosystems. This study examined nitrogen and phosphorus export in a seasonal pattern, along with correlations with water temperature. The research showed that despite the constant input of diffuse and point sources, a noticeable decrease (-20%) in nitrogen export, primarily in the form of nitrates, was recorded compared to the 1990s. However, the study did not show significant changes in phosphorus export. This indicates an increase in the proportion of point sources in river pollution.

The scientific article of I. Micella *et al.* (2024) confirmed that diffuse pollution sources contribute 95-100% of nitrogen (from agriculture) and macroplastics (from improper waste management), while point sources (wastewater) account for 40-95% of phosphorus and microplastics in global seas. Their research demonstrates riverine export of pollutants to seas, noting that the discharge of untreated wastewater and improper waste management are primary factors influencing the accumulation of biogenic substances in river waters. Additionally, the study of I. Zahoor & A. Mushtaq (2023) indicates that agricultural activities release chemicals and nutrients, such as phosphates and nitrates, into the water, leading to nutrient and chemical pollution. Accordingly, the authors emphasise the importance of controlling diffuse pollution sources.

The current research partially aligns with the studies of scientists V.I. Pichura & L.O. Potravka (2021), who assessed the ecological state of the Dnipro River, considering biogenic substances. Their study highlighted that a pressing issue for the Dnipro River cascade reservoirs is the deterioration of water properties due to eutrophication, which causes biological pollution of waterbodies, driven by the accumulation of biogenic compounds in the water mass. These scientists also examined other types of river pollution. For instance, the problem of anthropogenic pollution in the transboundary Siverskyi Donets River is addressed in the article of E.V. Vorobiev *et al.* (2021). They examined this type of pollution based on the composition of inorganic compounds (nitrates, nitrites, sulphates, chlorides, phosphates). Their research results showed that this type of river pollution occurs through both natural and anthropogenic pathways. It was also shown that nitrate pollution of the river occurs outside Ukraine, i.e., it is transboundary, while phosphate pollution occurs within Ukraine due to mine water discharges from the mining industry.

Additionally, the current research partially coincides with the concept of O.V. Stepova *et al.* (2022), who analysed diffuse pollution by biogenic elements (phosphorus, nitrogen) in the Vorskla River in Poltava. They analysed the main sources of biogenic substances entering the Vorskla River, establishing that rainwater entering the river contained elevated concentrations of biogenic substances and caused river pollution.

Scientists are paying particular attention to military activity as a source of pollution, which significantly affects the contamination of environmental components, including water resources. For example, the research of M. Matkivskyi & T. Taras (2024) shows that as a result of military actions in the Kharkiv Region, all rivers have high concentrations of ammonium nitrogen (exceeding the maximum permissible concentration (MPC) by 2 to 4 times) and correspondingly low levels of dissolved oxygen in the water (below the optimal level by 2 times). O.O. Dmitrieva *et al.* (2023) noted that military actions significantly intensify anthropogenic eutrophication processes.

In researching biogenic pollution in the Unava River, the ideas of the aforementioned scientists were considered to substantiate the problem of eutrophication and the pollution sources that cause the appearance of biogenic substances in the water. To establish the dominant type of pollution source, the stoichiometric Redfield Ratio method was used, which, in the authors' view, is appropriate and complements the aspects of assessing rivers at the time of biogenic pollution in waterbodies.

It is worth noting that in 2020, residents of Fastiv appealed to the mayor of the Fastiv City Council, Kyiv Region, with a request to designate the Unava River valley as an ecological disaster zone (petition No. HOO.1495.8 dated 16 July 2020). However, they received a response from the mayor stating that there were no grounds for this decision. The residents of Fastiv were concerned about the rapid shallowing of the river, which was turning into a swamp, and they noted that the river was becoming increasingly overgrown with reeds and algae each year.

Within the framework of the Program for Comprehensive Restoration of the Kyiv Region for 2023-2027, approved by the decision of the Kyiv Regional Council on 17 October 2023, No. 726-21-VIII, the Strategy for the Development of the Kyiv Region for 2021-2027, approved by the decision of the Kyiv Regional Council on 19 December 2019, 2019, No. 789-32-VII, was developed. As part of this strategy, in 2023, the project "Cleaning of the Channel, Restoration and Maintenance of the Hydrological Regime and Sanitary Condition of the Unava River" (project identifier DREAM-UA-041223-9528D395) was developed. This project aimed to restore the natural channel of the Unava River by eliminating unauthorised obstructions, clearing the channel from siltation, improving the hydrobiological regime and rehabilitating the river, and creating favourable conditions for the existence of flora, fauna, ichthyofauna, and biodiversity. This project is currently in the implementation stage.

Conclusions

In this study, according to the first objective, it was established that the concentration of biogenic substances (nutrients) in the Unava River water affects water quality depending on its intended use and the functioning of aquatic biota (aquatic ecosystem). Specifically, nitrite nitrogen concentrations (0.006-0.306 mg$N$/dm^3 in 2022, 0.006-0.051 mg$N$/dm^3 in 2024, assessed as quality classes 3 to 5) are critical for the aquatic ecosystem; ammonium nitrogen concentrations are critical for recreational and domestic needs (1.21-1.83 mgNH_4^+/dm^3 in 2022, 1.16-5.88 mgNH_4^+/dm^3

in 2024, with a standard of 2.0 mgNH_4^+/dm^3), for drinking water needs, and for the aquatic ecosystem as a whole (0.814-6.84 mg$N$/dm^3 in 2022, 0.364-4.56 mg$N$/dm^3 in 2024, assessing the waterbody as quality classes 3 and 4 for drinking water, and quality classes 4-5 for the aquatic ecosystem); phosphorus concentrations are critical for the aquatic ecosystem (0.062-0.196 mg$P$/dm^3 in 2022, 0.333-0.597 mg$P$/dm^3 in 2024, assessing the waterbody as quality classes 2-3 in 2022 and quality class 5 in 2024).

Based on the calculations of the correlation degree between variables (second objective), a negative (inverse) correlation was established between air temperature and phosphate (r = -0.07), nitrate nitrogen (r = -0.69), and nitrite nitrogen (r = -0.10) levels. Correspondingly, a positive correlation was found between water temperature and mineral nitrogen ($rNH_4^+ = 0.38$; $rNO_3^- = 0.79$; $rNO_2^- = 0.46$) and phosphorus ($rPO_4^{3-} = 0.52$).

The results of the third objective, which involved calculating the *Redfield Ratio* (*RR*), established that in the 2022 research period (*RR* = 29.42-108.64), the limiting biogenic substance was mineral phosphorus ions, while mineral nitrogen ions were in excess, indicating dominant nitrogen pollution in the waterbody, potentially leading to the growth of green algae. In 2024 (*RR* = 6.32-18.71), the limiting factor was mineral nitrogen ions, and phosphorus ions were in excess, indicating dominant phosphorus pollution in the water, potentially leading to the development of blue-green algae.

Future research directions involve assessing the water quality of the Unava River based on heavy metal concentrations and general hydrochemical indicators, which will allow for a more accurate conclusion regarding the ecological state of the Unava River and determine its suitability for specific water use needs.

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None.

Conflict of Interest

None.

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Біогенне забруднення водойми річки Унава

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Анотація. Біогенне забруднення водойм України є системною проблемою, яка потребує постійного моніторингу через його вплив на якість води та стимулювання антропогенної евтрофікації. Мета дослідження передбачала провести оцінювання водойми р. Унава для визначення рівня забруднення водойми біогенними речовинами та обґрунтування переважаючого типу забруднення (азотне/фосфорне). В ході дослідження визначено, що концентрація біогенних речовин у воді р. Унава впливає на якісний стан води залежно від потреб її використання та функціонування водної біоти (водна екосистема). Зокрема, концентрація азоту нітритного (0,006-0,306 мгN/дм^3 за 2022 р., 0,006-0,051 мгN/дм^3) у воді є критичною для водної екосистеми; азоту амонійного – для рекреаційних, господарсько-побутових потреб (1,21-1,83 мгNH_4^+/дм^3 за 2022 р., 1,16-5,88 мгNH_4^+/дм^3 за 2024 р.) для питних цілей й водної екосистеми в цілому (0,814-6,84 мгN/дм^3 за 2022 р., 0,364-4,56 мгN/дм^3 за 2024 р.); фосфору – водної екосистеми (0,062-0,196 мгP/дм^3 за 2022 р., 0,333-0,597 мгP/дм^3). За розрахунками ступеня кореляційного зв'язку між ознаками встановлено негативну кореляцію (обернену) між температурою повітря та показниками фосфатів (r = -0,07), азоту нітратного (r = -0,69) та азоту нітритного (r = -0,10). Відповідно, позитивну кореляцію виявлено між температурою води та мінеральним азотом (rNH_4^+ = 0,38; rNO_3^- = 0,79; rNO_2^- = 0,46) і фосфором (rPO_4^{3-} = 0,52). Проведені обрахунки за співвідношенням Редфільда (*Redfield Ratio – RR*) дозволили обґрунтувати, що у 2022 році досліджень (*RR* = 29,42-108,64) лімітуючою біогенною речовиною були іони мінерального фосфору, а іони мінерального азоту знаходилися в надлишку, переважаючим стало азотне забруднення водойми з можливим ростом зелених водоростей. У 2024 році (*RR* = 6,32-18,71) – лімітуючою ознакою були іони мінерального азоту, а іони фосфору в цих умовах перебували у надлишку, переважаючим стало фосфорне забруднення води з можливим розвитком синьо-зелених водоростей

Ключові слова: поживні речовини; евтрофікація; якість води; азот; фосфор; співвідношення Редфільда