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EVALUATION OF CHEMICAL INDICATORS OF ANTHROPOGENIC INFLUENCE IN THE LOWER DANUBE BASIN

The article explores the nature and trends of hydrochemical parameter connection and changes in the Lower Danube basin. The research examines nitrogen and phosphorus compounds, dissolved oxygen, and biochemical oxygen demand as indicators of anthropogenic influence and surface water quality alterations. The study was conducted between 2015 and 2023 at three sampling points: the Reni and Vilkovo water intakes on the Danube River and the Yalpuh Reservoir, which is connected to the Danube. The study employed mathematical statistics approaches. The research established changes in annual median values, investigated correlation links between chemical components by Spearman correlation, and implemented factor analysis by minimizing residuals. A spatiotemporal analysis of chemical components indicative of anthropogenic impact on the Lower Danube surface water revealed notable changes in the basin during 2019-2021. These changes were manifested as a sharp increase in ammonium concentrations and phosphate growth since 2020-2021, an abnormal decrease in dissolved oxygen concentration in 2019, a decrease in BOD within Yalpuh to the Danube BOD level, and a shift in trends from decreasing to increasing for nitrites. The water quality class also changed. Currently, the Danube River water is of the third quality class for nitrates, phosphates, and ammonium. In the Yalpuh Reservoir, it is of the 2nd class for nitrogen compounds and the 3rd class for phosphates. Two principal groups of chemical components are identified based on their underlying causes and sources, as revealed by correlation and factor analysis. A consistent relationship is observed between ammonium and phosphates across all monitoring sites, suggesting their role as pollutants entering surface waters via wastewater discharge and agricultural runoff and representing the main anthropogenic impact factor. The Danube River displays a specific relationship between nitrates and dissolved oxygen, reflecting the seasonal fluctuations in their concentrations and their underlying causes of changes, which stem from both anthropogenic and natural processes.

Keywords: *Lower Danube, anthropogenic impact, biochemical components, nitrogen, phosphates, dissolved oxygen, spatiotemporal, Spearman correlation, factor analysis*

Introduction. The continuous impact of human activities during the Anthropocene has made the question of river and basin evolution critically important on a global scale [25]. In many cases, this impact affects changes in river flow [5], the connectivity between rivers and their basins, and the increasing accumulation of pollutants in surface waters [11].

The Danube's water regime has undergone significant changes since the early 1960s. Over the period from 1960 to 1990, nitrogen discharge into the Danube basin experienced a fivefold increase, while anthropogenic phosphorus inputs doubled [19].

The observed changes in this world's largest transboundary water system, which encompasses 19 countries and covers 10% of continental Europe, have been subjected to international control [4]. Implementing the EU Water Policy [8,9] and establishing the International Commission for the Protection of the Danube River (ICPDR), with the participation of most basin countries, has led to a decrease in the discharge of biogenic and hazardous substances into the Danube River. Although water pollution levels have been decreasing in some areas of the Danube, the river still suffers from degradation, especially downstream of large cities and in several key tributaries [11,19].

The Lower Danube basin in Ukraine is subject to the combined influence of all countries upstream along the river's course [2]. The Lower Danube Basin within Ukraine covers an area of 6,400 square kilometers and includes 29 reservoirs and 88 ponds. The five largest reservoirs in the basin are the most significant, with the Yalpuh - Kugurlui Reservoir being one of the largest [17]. Analysis of water pollution chemical indicators at Ukrainian monitoring stations may reveal both local and basin-wide patterns of change. Understanding change dynamics leads to better water resources management, including the identification of protection and restoration strategies.

The assessment of anthropogenic influence on water bodies relies heavily on the analysis of nitrogen and phosphorus compounds as well as dissolved oxygen concentration. Anthropogenic nitrogen and phosphorus compounds discharged from point and diffuse sources

as a result of industrial and domestic wastewater and agricultural runoff disrupt the ecological balance of aquatic organisms and cause eutrophication [18,7]. Dissolved oxygen levels and their utilization rates influence the self-purification capabilities of water bodies [20].

The problem of biogenic pollution indicators in the Lower Danube basin is addressed in foreign and Ukrainian studies not as a standalone topic, but as part of a broader analysis of water quality assessment and coefficient selection for surface water quality assessment at the basin scale [3,10,14,23]. The relationships, redistribution, and spatiotemporal changes of nitrogen and phosphorus compounds and dissolved oxygen in the Lower Danube basin remain poorly understood.

This publication aims to shed light on the distribution, relationships, and spatiotemporal changes of anthropogenic pollutants in the Lower Danube basin's surface water between 2015 and 2023 by a comprehensive analytical approach, contributing to a more holistic understanding of the basin's water pollution dynamics.

Data and Methods. The article presents an analysis of the long-term monitoring results of the Danube River Basin, which were obtained within the framework of state surface water monitoring programs conducted by the Water Monitoring Laboratory of the Black Sea and Lower Danube River Basin Water Resources Management Agency and provided by the State Water Agency of Ukraine. The article highlights the results of processing and analyzing monthly measurements of ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), dissolved oxygen (DO), biochemical oxygen demand (BOD) and phosphate (PO_4^{3-}), utilizing robust statistical methods to ensure data accuracy and reliability. Data analysis was performed for the sampling points of the Reni (S1) and Vilково (S2) water intakes within the Danube River and the Bolhrad water intake within Yalpuh Reservoir (S3) (Fig. 1). The sampling points of Reni and Vilково are located at varying distances from the Danube Delta margin. Reni is located 136 kilometers away, on the border with Romania and Vilково is 20 kilometers away from the delta margin. The Yalpuh sampling point is located on the northern shore of Yalpuh Reservoir, which is connected to the Danube River via the Kugurlui. The selection of monitoring points S1, S2, and S3 was based on the availability of virtually continuous monthly measurements of pollutants over 9-year period (January 2015 to December 2023).

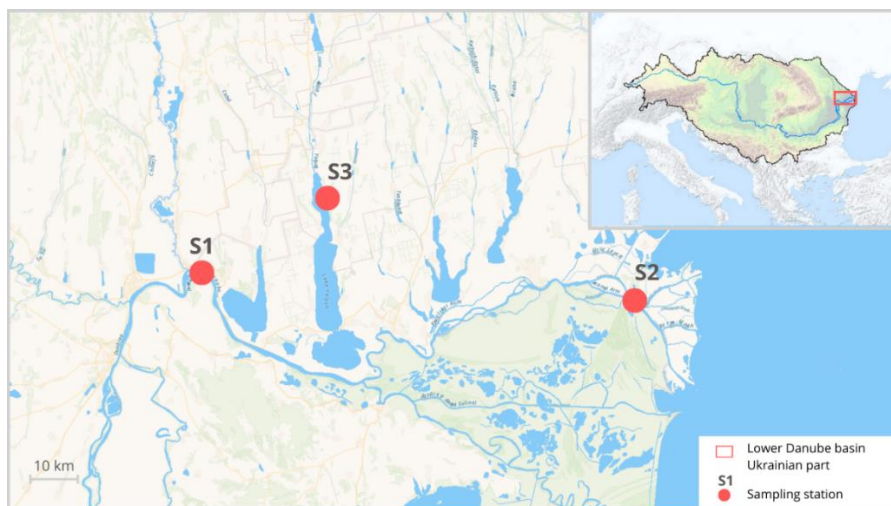


Fig. 1. Distribution of sampling points (stations). Site 1 (S1) – Reni, Site 2 (S2) – Vilково, Site 3 (S3) – Yalpuh

The application of mathematical and statistical processing methods to the research results allowed for the identification of several distinct approaches to the analysis of the obtained data. This methodological framework provides a systematic basis for interpreting the findings and drawing meaningful conclusions from the study.

Data analysis was performed using the Python programming language and the pandas, matplotlib, seaborn, and numpy libraries and exploratory factor analysis module.

The analysis of temporal changes in the data for 2015-2023 involved the calculation of annual median values based on monthly measurements. The median is the value separating the higher half from the lower half of a data sample of distribution. For a data set, it may be thought of as "the middle" value. This approach was chosen over the calculation of mean values due to the robustness of medians to extremely large or small values, which ensures a more accurate representation of the data distribution [6,26].

The study employed Spearman's rank correlation analysis to investigate the associations between nitrogen compounds, phosphates and dissolved oxygen at each sampling station. This non-parametric approach was selected in favor of the widely-used Pearson's correlation analysis due to its robustness to non-linearity in data distribution, which was evident in certain data sets [19,20].

The exploratory factor analysis (EFA) was conducted using the minimum residual method (Minres) with varimax rotation. Minres, introduced by Harman [12,13], is an analytic procedure that minimizes the sum-of-squares of the off-diagonal residuals of the correlation matrix. Varimax, developed by Kaiser, is a criterion for analytic rotation in exploratory factor analysis and principle component analysis [16]. It is a method for transforming the original solution (factor loadings) to a pattern that is easier for inspection and interpretation. The obtained factor matrix with varimax-rotated factor loadings provides a more comprehensive understanding of the underlying mechanisms of the relationship between chemical components [15].

Results and Discussion. Spatiotemporal distribution of components characterizing anthropogenic impact on surface waters of the Lower Danube.

The annual median values calculated from monthly data for each sampling point between 2015 and 2023 were summarized in the Table 1. Analysis of these indicators yielded a series of significant conclusions regarding the spatiotemporal distribution patterns and trends of nitrogen compounds, phosphates, dissolved oxygen, and BOD, providing valuable insights into the dynamics of these parameters within the study area (Fig. 2).

Table 1. The annual median concentration (MC) of nitrogen compounds, phosphate, DO, and BOD for 2015-2023

MC (mg/dm ³)	2015	2016	2017	2018	2019	2020	2021	2022	2023
NH ₄ ⁺ (S1)	0,07	0,05	0,04	0,10	0,14	0,17	0,43	0,25	0,52
NH ₄ ⁺ (S2)	0,07	0,08	0,04	0,11	0,11	0,10	0,57	0,30	0,42
NH ₄ ⁺ (S3)	0,13	0,10	0,19	0,14	0,15	0,38	0,38	0,36	0,30
NO ₃ ⁻ (S1)	5,24	4,77	4,08	4,57	3,85	3,30	3,19	4,50	3,60
NO ₃ ⁻ (S2)	4,80	4,45	4,69	4,33	4,18	4,65	3,86	3,40	2,86
NO ₃ ⁻ (S3)	0,58	0,51	0,56	0,60	0,45	0,64	1,06	0,75	1,10
NO ₂ ⁻ (S1)	0,06	0,06	0,05	0,06	0,04	0,04	0,05	0,04	0,05
NO ₂ ⁻ (S2)	0,06	0,08	0,05	0,07	0,03	0,04	0,02	0,04	0,09
NO ₂ ⁻ (S3)	0,02	0,03	0,02	0,02	0,01	0,01	0,00	0,00	0,01
PO ₄ ³⁻ (S1)	0,13	0,17	0,16	0,17	0,17	0,24	0,23	0,18	0,25
PO ₄ ³⁻ (S2)	0,14	0,14	0,15	0,12	0,15	0,29	0,25	0,26	0,25
PO ₄ ³⁻ (S3)	0,05	0,03	0,04	0,05	0,07	0,26	0,08	0,18	0,18
DO (S1)	9,2	8,9	9,9	9,5	8,0	10,3	10,3	10,5	9,8
DO (S2)	8,7	9,3	9,8	9,7	8,2	9,8	10,5	10,5	10,1
DO (S3)	9,0	9,4	8,5	11,3	7,0	9,6	10,7	10,6	9,5
BOD (S1)	1,4	2,4	3,0	2,3	2,5	2,5	2,0	2,3	2,3
BOD (S2)	1,6	1,8	1,8	2,0	2,0	2,1	2,0	2,1	2,4
BOD (S3)	3,9	5,5	5,2	4,9	3,4	2,3	2,0	2,6	3,0

Ammonium concentrations in surface waters of the Lower Danube basin show increasing trends (Fig. 2). For monitoring points within the Danube River, a sharp increase in concentrations was observed in 2021 from 0.17 mg/dm³ to 0.43 mg/dm³ for Reni and from 0.10

mg/dm³ to 0.57 mg/dm³ for Vilkovovo. In 2023, a similar jump in concentrations was repeated for Reni. Now it has the highest annual median concentrations compared to other monitoring points, reaching 0.52 mg/dm³. For the monitoring point within Yalpuh Reservoir, a sharp increase occurred in 2020 from 0.15 mg/dm³ to 0.38 mg/dm³ with a slight decrease in 2023. Until 2020, ammonium concentrations in the reservoir were higher than in the Danube River, now it is the opposite.

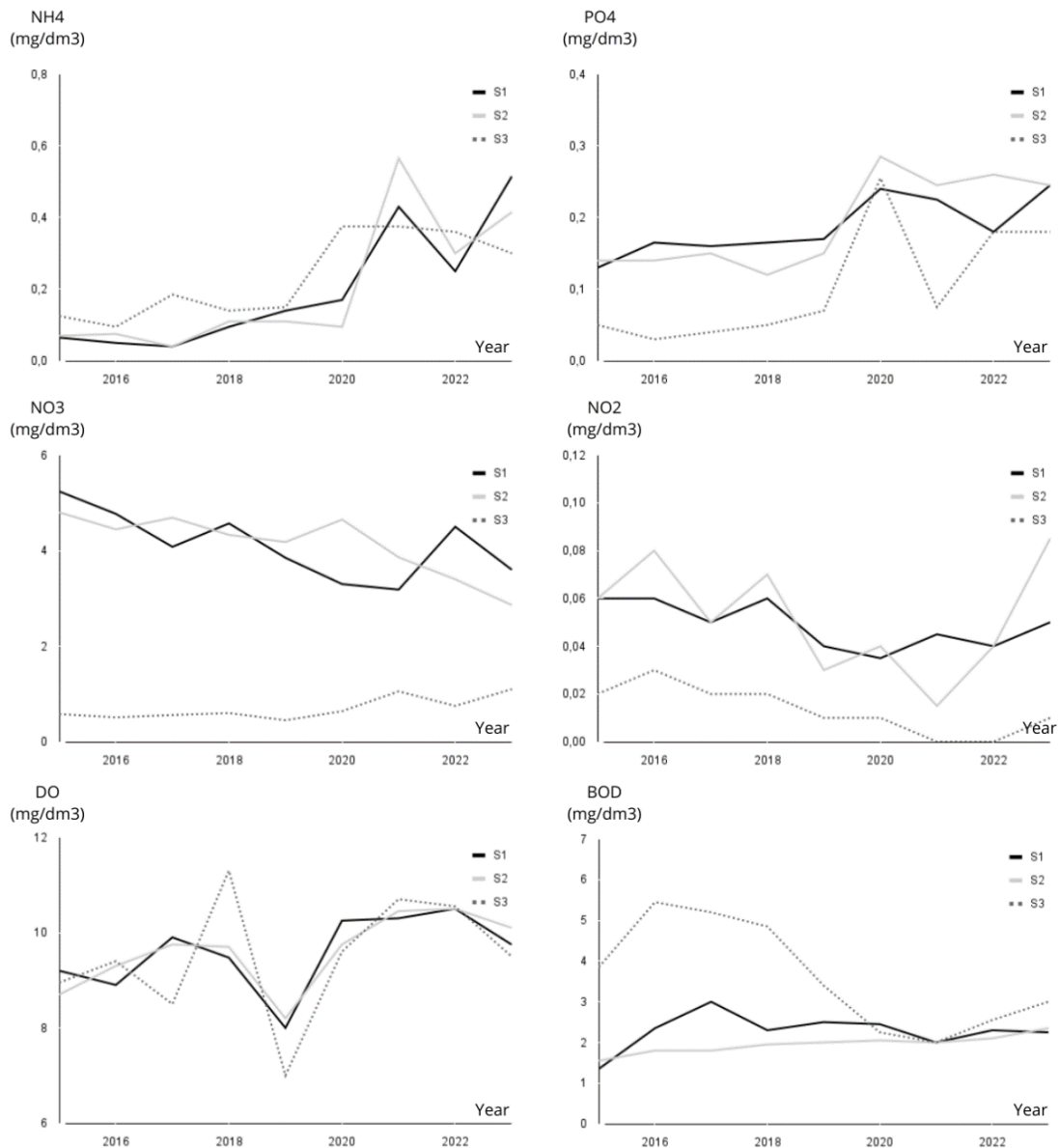


Fig. 2. Variation of annual median concentrations of ammonium (NH₄), phosphate (PO₄), nitrate (NO₃), nitrite (NO₂), DO and BOD on S1, S2, S3 sampling points

Similar to ammonium, phosphate concentrations also exhibit increasing trends at all monitoring stations (Fig. 2). The most gradual increase is observed at the Reni monitoring station located on the border with Romania. For Vilkovovo and Yalpuh, a sharp increase in concentrations was observed in 2020 from 0.15 mg/dm³ to 0.29 mg/dm³ and from 0.07 mg/dm³ to 0.26 mg/dm³, respectively. From 2015 to 2020, the phosphate concentrations in Yalpuh Reservoir were the lowest, while in Reni they were the highest. Since 2020, Vilkovovo has been demonstrating the highest annual median concentrations.

Nitrate concentrations demonstrate diverse trend patterns across different monitoring stations (Fig. 2). Danube stations predominantly exhibit a decreasing trend in concentrations.

Vilkovo shows a distinct annual decline since 2020, with a decrease from 4.65 mg/dm³ to 2.86 mg/dm³ in 2023. In Reni, the decline continued until 2021, reaching a minimum of 3.19 mg/dm³, followed by fluctuations and sharp changes in concentrations in subsequent years. Yalpuh Reservoir exhibits significantly lower annual median nitrate concentrations compared to the Danube, with an average 5-fold difference, and shows slight increasing trends.

Nitrite concentrations generally showed decreasing trends across all sampling stations during specific periods: 2015-2020 for Reni, 2016-2022 for Yalpuh Reservoir, and with fluctuations until 2021 for Vilkovo (Fig. 2). In recent years, the trends have shifted towards an increase at all stations. This is most noticeable in Vilkovo, where concentrations have increased from 0.04 mg/dm³ to 0.09 mg/dm³ between 2021 and 2023. The nitrite concentration in Yalpuh Reservoir is on average 5 times lower compared to the Danube stations.

Dissolved oxygen concentrations exhibited a dramatic increase in 2019 across all monitoring stations (Fig. 2). Reni experienced a change from 9.5 mg/dm³ to 8 mg/dm³, Vilkovo from 9.7 mg/dm³ to 8.2 mg/dm³, and Yalpuh Reservoir the most significant change, from 11.3 mg/dm³ to 7 mg/dm³. Notably, 2020 witnessed a recovery to levels even higher than pre-decline values. The trends and concentrations of dissolved oxygen are nowadays remarkably similar at all three stations. Currently, the concentrations hover around 10 mg/dm³.

Biochemical oxygen demand (BOD) indicators from 2015 to 2020 were the lowest for Vilkovo and the highest for Yalpuh Reservoir. In 2020, the indicators became very close. For all monitoring points in 2021, they were 2 mg/dm³. It should be noted that the situation changed the most for Yalpuh Reservoir, where the indicator concentrations were 1.5-2 times higher and began to decrease since 2019, reaching the Danube level the following year (Fig. 2).

Time series plots of monthly concentrations were constructed for biogenic components that exhibited anomalously elevated annual median values over the past years (Fig. 3).

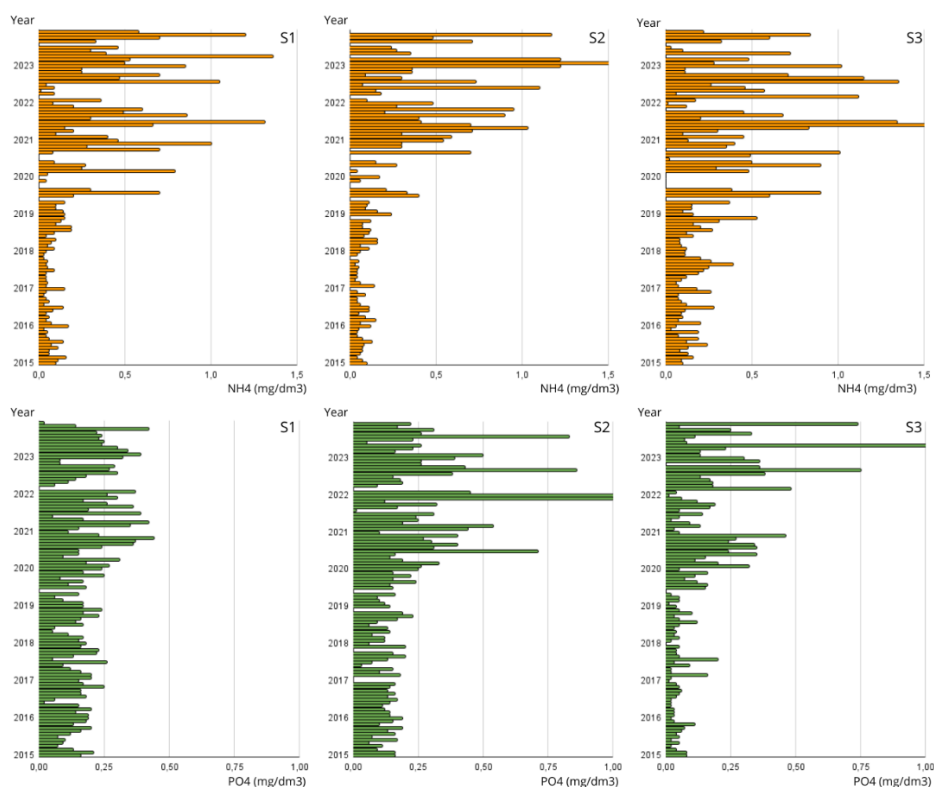


Fig. 3. Variation of month concentrations of ammonium (NH₄) and phosphate (PO₄) on S1, S2, S3 sampling points

The plots reveal a consistent increase in ammonium concentrations for all three monitoring stations. Notably, both the maximum and minimum ammonium values have increased. The maximum values now exceed 0.6 mg/dm³ in most cases, reaching up to 1.5

mg/dm³, while the minimum values have increased to 0.2-0.3 mg/dm³. Phosphate concentrations also show an increasing trend at all three stations. In VilkoVo and Yalpuh the increase sometimes reaches 0.75-1 mg/dm³. In Reni, the increase in phosphate concentrations is less pronounced but still reaches 0.3-0.4 mg/dm³. The upward trend in concentrations of ammonium and phosphates is conclusively established.

According to the ecological classification of surface water quality of land and estuaries based on ecology-sanitary criteria [24] and calculated median annual values of chemical components of 2015, 2019, and 2023 years, the following trends can be noted (Table 2). In 2023, the Danube waters within Reni and VilkoVo are classified as the third quality class – satisfactory, polluted waters for ammonium and nitrates. The Yalpuh Reservoir is classified as the second quality class – good, clean waters. All three are classified as the third quality class for phosphate concentration. Compared to 2015 and 2019, there is a deterioration of water quality by one class or more for ammonium and phosphates. For nitrates, the Danube shows an improvement by one class compared to 2019 and 2015. Water pollution classes are established as follows: 1 – very good, 2 – good, 3 – satisfactory, polluted, 4 – bad, polluted, 5 – very bad, polluted.

Table 2. The water quality classes based on classification of surface water quality of land and estuaries based on ecology-sanitary criteria

	2015	2019	2023		2015	2019	2023		2015	2019	2023
NH ₄ ⁺ (S1)	1	2	3	NO ₃ ⁻ (S1)	4	3	3	PO ₄ ³⁻ (S1)	2	3	3
NH ₄ ⁺ (S2)	1	3	3	NO ₃ ⁻ (S2)	4	4	3	PO ₄ ³⁻ (S2)	2	3	3
NH ₄ ⁺ (S3)	2	2	2	NO ₃ ⁻ (S3)	1	1	2	PO ₄ ³⁻ (S3)	2	2	3

Spearman's correlation analysis was used to identify the relationships between nitrogen compounds, phosphates, and dissolved oxygen. The results are presented in the form of heatmaps, where the correlation coefficients between the components are represented in color (Fig. 4). According to the Spearman's correlation analysis for the Reni site (Fig. 4a), strong connections are found between dissolved oxygen and nitrates, with correlation coefficients reaching 0.51. Additionally, positive correlation links are observed between ammonium and phosphates, nitrates and nitrites, and phosphate and dissolved oxygen. Several other relationships below the significance level are also present, primarily negative, between nitrates and ammonium, and nitrates and phosphates. The significance of the correlation coefficient defines the critical values below which the correlation matrix values are considered insignificant [21]. For the given data distributions and an alpha level of 0.5, the critical values are 0.16 for the Reni and Yalpuh sampling points, and 0.17 for VilkoVo.

VilkoVo site exhibits similar patterns to the Reni site, with the strongest correlation observed between nitrates and dissolved oxygen (correlation coefficient of 0.52) (Fig. 4b). Correlation links are also present between ammonium and phosphates, as well as between ammonium and dissolved oxygen. Negative relationships on the border of critical values are observed between ammonium and nitrates, and between nitrites and phosphates.

Yalpuh site (Fig. 4c) demonstrates the highest correlation coefficients for phosphates and ammonium, reaching 0.32. Positive correlations between nitrates and dissolved oxygen and nitrates and ammonium are observed near the critical values level. No significant negative correlations were detected.

Therefore, the correlation analysis revealed relationships between oxygen and nitrate concentrations and ammonium and phosphate concentrations for all observation stations. The strongest correlations exist between oxygen and nitrates for the Danube observation points (Reni and VilkoVo).

The factor analysis conducted for all sampling points using the Minres varimax rotation method helped to determine the factors that combine different indicators of anthropogenic impact and clarify the specifics and sources of their relationships (Fig. 4). For the Reni site (S1), three factors are distinguished, indicating three main types of relationships between studied components and three types of their sources.

The first factor combines the indicators of nitrates and dissolved oxygen with factor loadings of 0.73 and 0.72, respectively (Fig. 4). This factor aligns with the observed trends of maximum correlation between oxygen and nitrates in Reni and signifies simultaneous changes in their concentrations during specific time intervals. The seasonal variations in oxygen levels, typical in the sampling point and shown in studies [20], in this case, are also characteristic of the seasonal fluctuations in nitrate levels with summer minimum and winter maximum concentrations. The low summer concentration of nitrates may be caused by weak nitrification due to a lack of dissolved oxygen. Seasonal variations can be caused by both anthropogenic and natural impacts.

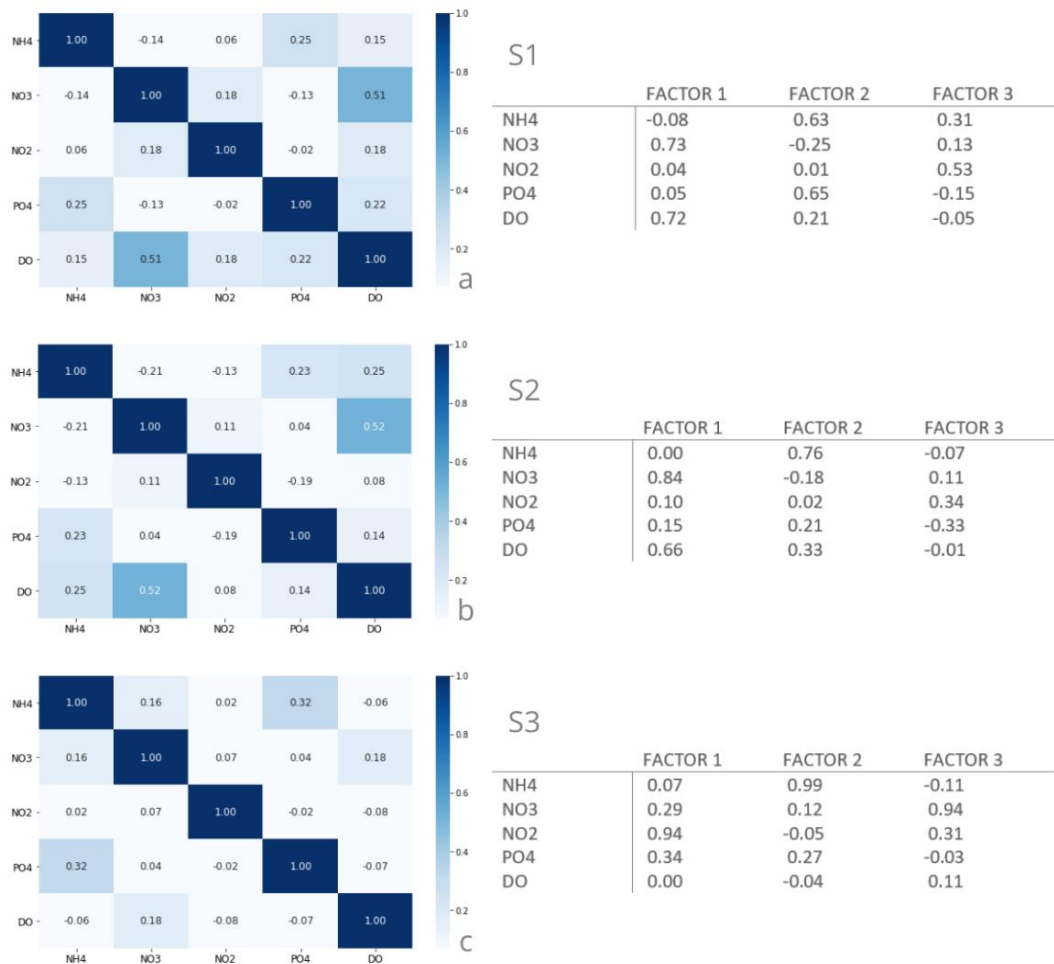


Fig. 4. Heat map of Spearman's correlation matrices and main factors by Minres factor analysis with rotation varimax of ammonium (NH4), phosphate (PO4), nitrate (NO3), nitrite (NO2), DO and BOD on S1, S2, S3 sampling points

The second factor is complex, encompassing ammonium and phosphates with factor loadings of 0.63 and 0.65, respectively, and, to a lesser extent, dissolved oxygen and, inversely, nitrates, into a unified system impacting the river's condition (Fig. 4). This factor aligns with the findings of the correlation analysis between ammonium and other indicators, highlighting the pivotal role of ammonium in this factor. The association between ammonium and phosphates suggests a shared source of their occurrence. Notably, these biogenic compounds primarily enter the Danube from agricultural runoff and wastewater discharge [2]. Consequently, the factor may point to typical Lower Danube anthropogenic influence on water bodies. The third factor mainly integrates ammonium and nitrites, potentially indicating peak simultaneous increases in these components during the deterioration of water body conditions.

Regarding the first two factors, the situation at the Vilково site (S2) is similar to that of Reni (Fig. 4). The difference lies in the lower contribution of phosphates to the second factor at Vilково, with a factor loading of 0.21 compared to three times higher values in Reni. At the same time, in Vilково, phosphates, together with nitrites, enter the third factor and are characterized by an inverse relationship. The nature of this type of relationship remains to be established.

The Yalpuh site (S3) stands out in that nitrites emerge as the first factor with a factor loading of 0.94, accompanied by nitrates (0.29) and phosphates (0.34) (Fig. 4). Remarkably, this factor remained undetected by the correlation analysis. The clustering of these components within the first factor could be attributed to their distinctive changes over the past years, marked by rising annual average values and numerous spikes. The second factor depicts the association between ammonium and phosphates, with ammonium bearing the highest factor loading of 0.99. This factor is common to all three observation points, suggesting a universal source of biogenic compounds entering surface waters. The third factor characterizes the connection between nitrates and nitrites, which can coexist in a water body during nitrification processes.

Conclusions. A spatiotemporal analysis of chemical components indicative of anthropogenic impact on the Lower Danube surface water from 2015 to 2023 revealed notable changes in the basin during 2019-2021. These changes were manifested as a sharp increase in ammonium concentrations and phosphate growth since 2020-2021, an abnormal decrease in dissolved oxygen concentration in 2019, a decrease in BOD within Yalpuh to the Danube BOD level, and a shift in trends from decreasing to increasing for nitrites. The water quality class also changed. Currently, the Danube River water is of the third quality class for nitrates, phosphates, and ammonium. In the Yalpuh Reservoir, it is of the 2nd class for nitrogen compounds and the 3rd class for phosphates.

An analysis of chemical parameters using correlation and factor analysis identified the most significant correlations in the distribution of nitrates and dissolved oxygen, which are typical for the Danube River. These findings indicate that similar to oxygen, nitrates demonstrate long-term trends of seasonal variation and are affected by both anthropogenic activities and natural phenomena.

A common factor has been identified across all monitoring stations in the Lower Danube basin, which characterizes the relationship between ammonium and phosphates. It can be suggested that this factor represents anthropogenic influence on the Lower Danube since this combination of this biogenic components enters water bodies primarily through wastewater and agricultural runoff.

The aforementioned information illustrates the intricate and multifaceted impact on the Lower Danube basin. The research results indicate that the Lower Danube has undergone notable changes over the past 5 years. The observed changes necessitate further exploration and ongoing monitoring to prevent irreversible damage to the water system caused by human activities.

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Оцінка хімічних компонентів - індикаторів антропогенного впливу в басейні Нижнього Дунаю Грига М. Ю.

Стаття присвячена встановленню особливостей змін та зв'язків гідрохімічних показників в басейні Нижнього Дунаю. В рамках дослідження основний акцент зроблено на вивченні сполук азоту, фосфору, розчиненого кисню і біохімічного споживання кисню, як показників, що слугують індикаторами антропогенного впливу та змін якості поверхневих вод. Дослідження проводились для періоду 2015-2023 років в межах трьох пунктів спостереження – водозаборів Рені і Вілково на Дунаї та водосховищі Ялпуг в

басейні Нижнього Дунаю. Для дослідження використовувались математично-статистичні підходи. Були встановлені зміни медіанних річних показників, досліджені кореляційні зв'язки між хімічними компонентами за кореляційним аналізом Спірмена та реалізований дослідницький факторний аналіз. Просторово-часовий аналіз хімічних компонентів виявив значні зміни в басейні Нижнього Дунаю протягом 2019-2021 років. Вони проявились у різкому підвищенні концентрацій амонію та зростанні концентрацій фосфатів в 2020-2021 роках, аномальному зниженні концентрацій розчиненого кисню у 2019 році, зниженні БСК₅ у водосховищі Ялпуг до рівня БСК₅ Дунаю, та зміні трендів від зниження до підвищення для концентрацій нітритів. Також змінився клас якості води. Сьогодні вода Дунаю за вмістом нітратів, фосфатів та амонію відноситься до третього класу якості. У водосховищі Ялпуг вона 2-го класу за сполуками азоту і 3-го класу за фосфатами. За результатами кореляційного і факторного аналізу виділяються дві основні групи хімічних показників пов'язані причинами та джерелами виникнення. Для всіх пунктів спостереження встановлений зв'язок між амонієм і фосфатами, які забруднюють поверхневі води, потрапляючи зі стоками і через сільськогосподарську діяльність та є основним фактором антропогенного впливу на досліджувану територію. Для Дунаю нітрати характеризуються зв'язком з розчиненим киснем, що відображає спільну сезонність їх змін, викликану як антропогенними так і природними чинниками.

Ключові слова: Дунай; антропогенний вплив; біогенні компоненти; азот; фосфати; розчинений кисень; просторово-часові зміни; кореляційний аналіз Спірмена; факторний аналіз..

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