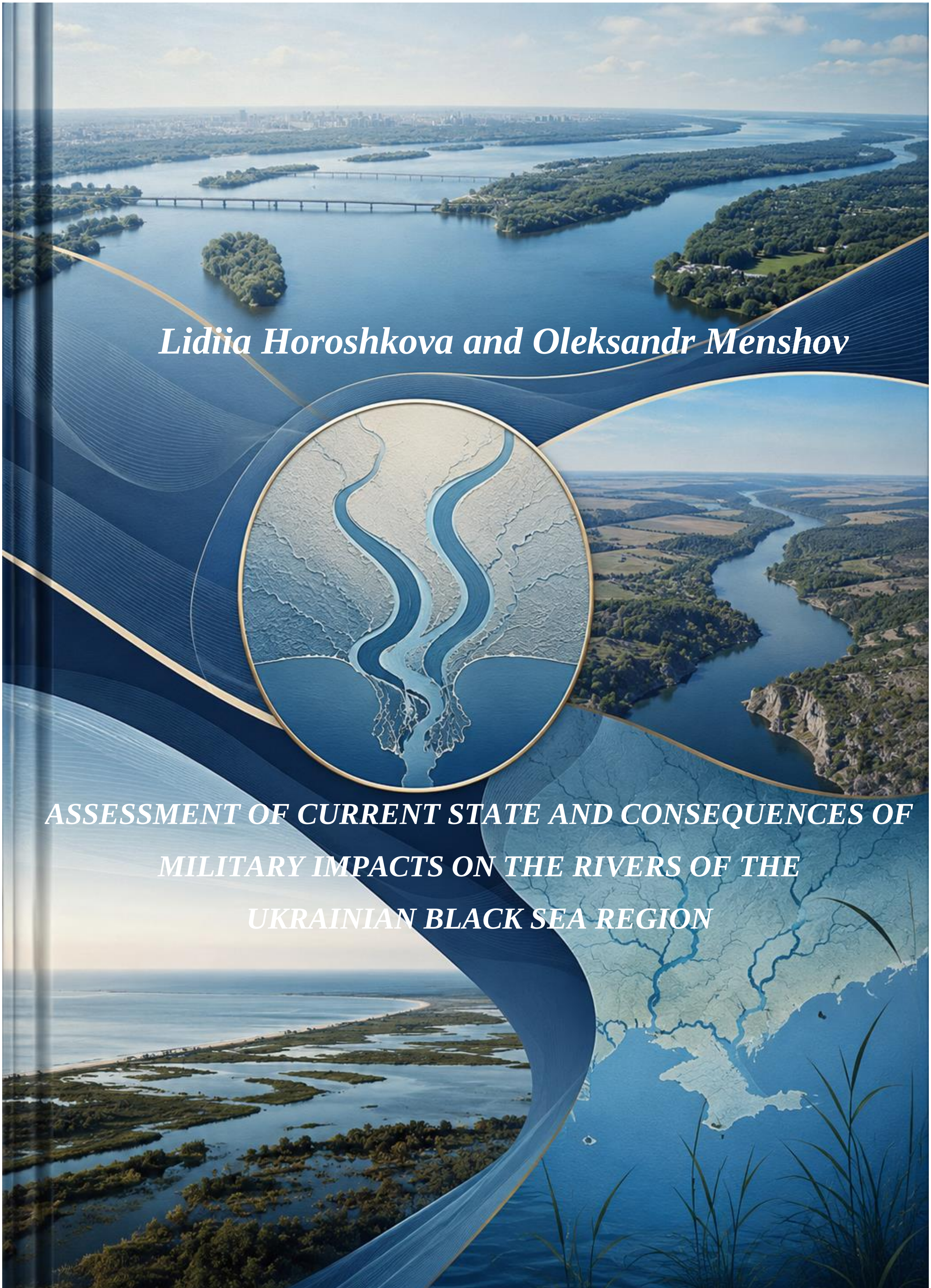
Lidiia Horoshkova and Oleksandr Menshov
ASSESSMENT OF CURRENT STATE AND CONSEQUENCES OF
MILITARY IMPACTS ON THE RIVERS OF THE
UKRAINIAN BLACK SEA REGION

*Lidiia Horoshkova and Oleksandr Menshov*

# *ASSESSMENT OF CURRENT STATE AND CONSEQUENCES OF MILITARY IMPACTS ON THE RIVERS OF THE UKRAINIAN BLACK SEA REGION*

**MONOGRAPH**

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This monograph is devoted to a comprehensive assessment of the hydrochemical and ecological state of surface waters in the Lower Dnipro, the Southern Bug, and the Ukrainian section of the Lower Danube River. The study is based on long-term monitoring data and focuses on the main water quality indicators, including nutrients, major ions, organic matter parameters, dissolved oxygen, and suspended solids. The research considers spatial and temporal variability of hydrochemical characteristics within different river sections and hydrological conditions. The monograph also examines the influence of natural hydrological processes, long-term anthropogenic pressure, and military-related impacts on the formation of water quality in the studied river systems.

**CONTENT**

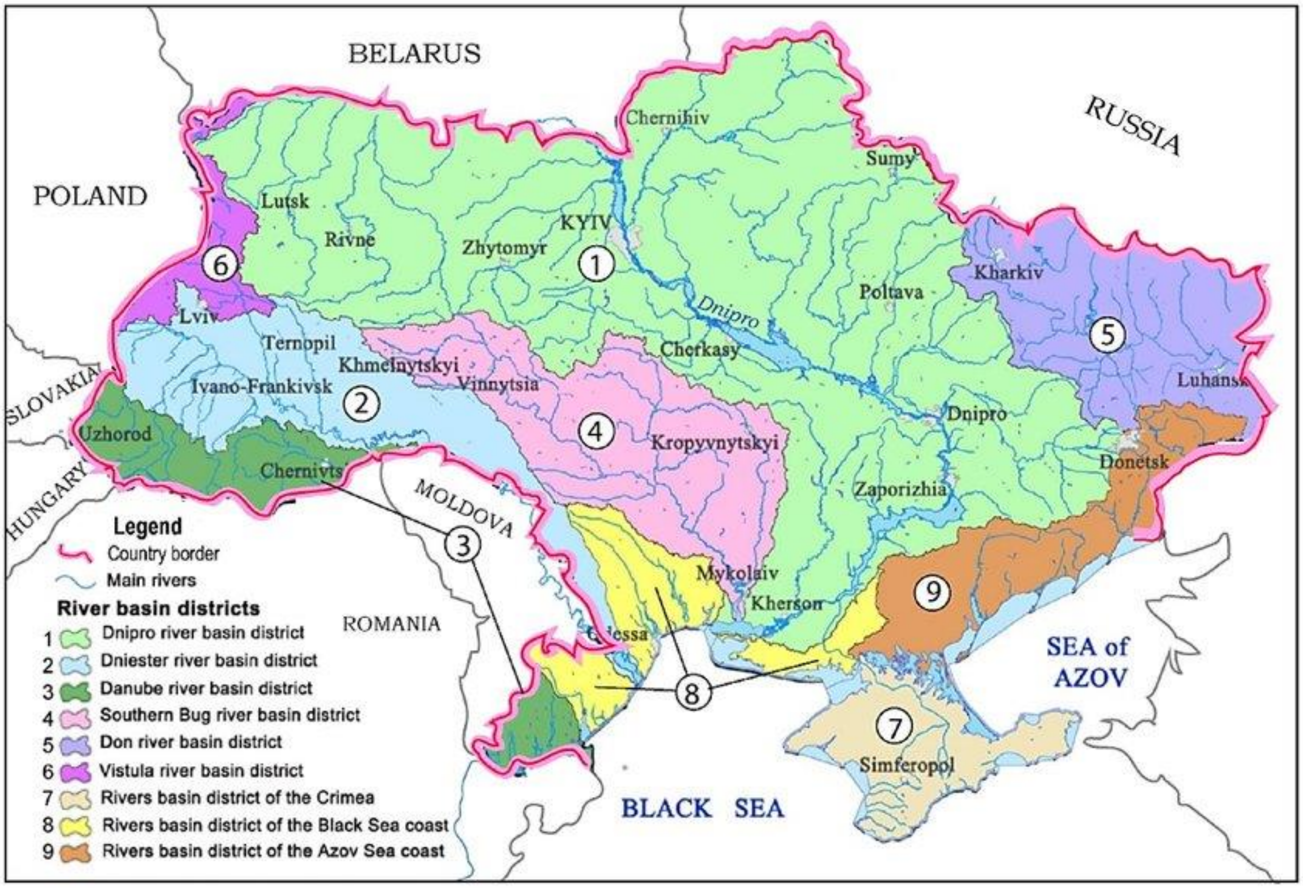
## *Introduction*

The rivers of the Ukrainian Black Sea region, including the Lower Dnipro, Southern Bug, Danube Delta tributaries, and smaller coastal river systems, represent a critical component of the region’s freshwater resources, ecological stability, and socio-economic development. These river systems sustain biodiversity-rich wetlands, support agriculture and water supply for населення, and maintain hydrological connectivity between inland ecosystems and the Black Sea. In recent decades, however, their ecological condition has been influenced by a combination of natural variability, long-term anthropogenic pressure, and accelerated environmental change.

Since the onset of large-scale military actions in Ukraine, the pressure on river ecosystems in the Black Sea basin has intensified significantly. Military activities have introduced both direct and indirect stressors, including physical destruction of riverbanks and hydraulic infrastructure, contamination from fuel, explosives, and heavy metals, disruption of water management systems, and increased risk of accidental or deliberate pollution events. In addition, restricted access to monitoring sites has created substantial gaps in environmental observation, complicating the assessment of real-time water quality and ecological status.

This monograph aims to assess the current ecological state of rivers in the Ukrainian Black Sea region and to analyze the consequences of military impacts on their hydrological and chemical characteristics. Special attention is given to changes in water quality parameters, sediment contamination, ecosystem resilience, and long-term risks for aquatic environments. The study integrates available monitoring data, remote observations, and previous baseline assessments to provide a comprehensive overview of ongoing transformations and to support the development of post-conflict environmental recovery strategies.

***General Characteristics of the Lower Dnipro, Southern Bug and the Ukrainian Section of the Lower Danube River Basins***




Map of hydrographic zoning of the territory of Ukraine (2016). River basin district: 1 – Dnipro; 2 – Dniester; 3 – Danube; 4 – Southern Bug; 5 – Don; 6 – Vistula; 7 – Rivers of the Crimea; 8 - Rivers of the Black Sea coast; 9 - Rivers of the Azov Sea coast [1]

The river basins of the Lower Dnipro, Southern Bug, and the Ukrainian part of the Lower Danube constitute the principal hydrological framework of the Northern Black Sea coastal region. These systems play a key role in sustaining regional water balance, ecological connectivity between inland and marine environments, and socio-economic stability. Despite their geographical proximity, each basin exhibits distinct geomorphological structures, hydrological regimes, and levels of anthropogenic transformation, shaped by differences in catchment size, climate gradients, and historical development of land and water use. Together, they form a complex transitional zone between continental Eastern Europe and the Black Sea coastal ecosystem, where natural hydrological processes are strongly modified by human activity, including river regulation, agriculture, industrial development, and more recently, military impacts.

The Lower Dnipro basin represents one of the most heavily transformed fluvial systems in Eastern Europe. Its hydrological structure is dominated by a cascade of large reservoirs constructed along the main channel, which significantly altered natural discharge variability, sediment transport, and floodplain connectivity. The lower reaches of the river are characterized by a wide, regulated channel, reduced natural flow dynamics, and strong dependence on upstream reservoir management.

A defining feature of the basin is its high degree of flow regulation, which has led to a decrease in sediment delivery to the Dnipro-Bug estuarine system and changes in deltaic processes. These modifications have had cascading ecological consequences, including the simplification of aquatic habitats and alteration of spawning conditions for native fish species. The Lower Dnipro also serves as a key water source for agriculture, industry, and urban settlements, which increases pressure on water abstraction and quality.

Recent studies indicate that the Lower Dnipro is highly sensitive to hydrological disturbances and extreme events, particularly under conditions of climatic variability and infrastructure disruption. In addition, the estuarine zone acts as a critical interface where freshwater discharge mixes with saline Black Sea waters, forming a dynamic transitional ecosystem highly dependent on riverine inflow regimes .

The Southern Bug basin is unique among large Ukrainian rivers in that it lies entirely within the national territory, which simplifies integrated basin-scale management and monitoring strategies. The basin is characterized by a heterogeneous geological structure, combining crystalline Ukrainian Shield formations in the upper reaches with sedimentary landscapes downstream. This results in spatial variability in runoff formation, water chemistry, and ecological productivity.

Hydrologically, the Southern Bug exhibits a pronounced seasonal flow regime typical of temperate continental rivers, with spring snowmelt peaks and relatively low summer discharges. Climate-driven variability increasingly influences the river's hydrological stability, with observed trends indicating shifts in seasonal runoff distribution and reduced ice-cover duration in winter periods .

From a water quality perspective, the basin is affected by agricultural runoff, urban wastewater discharges, and localized industrial pollution. Ecological assessments based on phytoplankton structure demonstrate that the river maintains moderate ecological status in some sections, although eutrophication processes are evident in more anthropogenically loaded reaches . The Southern Bug thus represents a transitional system where natural processes still dominate in upstream areas, while downstream sections are increasingly shaped by human activity.

The Ukrainian part of the Lower Danube basin is situated within a highly dynamic deltaic environment characterized by a dense network of distributaries, wetlands, floodplain lakes, and marshes. This region is one of the most ecologically valuable areas in Europe due to its high biodiversity and its role as a key migratory corridor for aquatic and avian species.

Hydrologically, the Lower Danube is strongly influenced by upstream flow regulation across multiple countries, which affects discharge variability, sediment load, and nutrient transport. The Ukrainian section is particularly sensitive to changes in upstream hydropower operations and climatic variability, which directly impact wetland hydrodynamics and estuarine mixing processes.

The ecological structure of the basin is defined by its high productivity and strong connection between riverine and marine systems. Floodplain inundation dynamics play a central role in sustaining wetland ecosystems and maintaining habitat diversity.

However, anthropogenic pressures, including land reclamation, navigation infrastructure, and pollution inputs, have significantly altered natural flood regimes and reduced the extent of periodically inundated areas.

In recent years, the Lower Danube–Black Sea interface has also demonstrated increased sensitivity to extreme hydrological events, where large freshwater discharges can rapidly alter salinity gradients and influence coastal marine ecosystems .

Although the Lower Dnipro, Southern Bug, and Lower Danube basins differ in scale and morphological complexity, several common features can be identified. All three systems are located within the steppe and forest-steppe zones, where evapotranspiration processes significantly influence water balance. Additionally, each basin is affected by intensive agricultural land use, which contributes to nutrient loading and diffuse pollution.

A key distinguishing factor is the degree of hydrological regulation. The Lower Dnipro is the most heavily regulated system, with extensive reservoir cascades that fundamentally alter natural flow regimes. The Southern Bug remains partially regulated but retains more natural hydrological variability, especially in its upper and middle reaches. The Lower Danube, in contrast, is an international transboundary system where hydrological conditions are governed by upstream management decisions and cross-border water governance frameworks.

Ecologically, the Danube basin exhibits the highest biodiversity due to its extensive wetland complexes, while the Southern Bug reflects intermediate ecological conditions, and the Lower Dnipro shows the most pronounced signs of ecosystem simplification due to long-term regulation and industrial pressure. These differences are critical for understanding basin-specific vulnerability to environmental stressors, including climate change and anthropogenic disturbances.

The Lower Dnipro, Southern Bug, and Lower Danube basins form an interconnected hydrological system of the Northern Black Sea region, yet each demonstrates distinct structural and functional characteristics. Their current ecological state reflects a combination of natural hydrological variability and long-term human transformation, with increasing importance of climatic fluctuations and extreme events.

Understanding the comparative structure and functioning of these basins is essential for developing integrated water resources management strategies, particularly in the context of environmental degradation risks and ongoing geopolitical and climatic pressures. Future research should focus on improving monitoring networks, enhancing transboundary cooperation, and assessing long-term ecosystem resilience under changing hydrological regimes.

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# 1 SURFACE WATER CONDITIONS OF THE DNIPRO RIVER

The Lower Dnipro River Basin represents the downstream section of the Dnipro River system, extending from the Kakhovka Reservoir area (historically) to the Dnipro–Bug Estuary and the northwestern part of the Black Sea coastal zone. The basin is entirely located within Ukraine and constitutes one of the most hydrologically and economically significant river corridors of Eastern Europe. Its area is commonly estimated at approximately 100,000 km² within the lower and middle-lower sub-basin system, depending on delimitation approaches used in hydrological zoning studies (Shakirzanova et al., 2018; Chornomorets et al., 2023) [1].

The Lower Dnipro is strongly influenced by a cascade of large reservoirs constructed along the river during the 20th century, including the Kremenchuk, Kamianske, and (formerly) Kakhovka reservoirs. These artificial water bodies fundamentally transformed the natural fluvial system into a regulated cascade, significantly altering discharge patterns, sediment transport, floodplain connectivity, and ecological continuity (Hryha et al., 2024; Morozov et al., hydrological synthesis studies) [2].

The hydrological regime of the Lower Dnipro is characterized by strong anthropogenic regulation combined with natural climatic variability. Flow is primarily controlled by upstream reservoir management, seasonal snowmelt contribution from the upper basin, and precipitation variability across the Dnipro catchment. Recent studies highlight that the lower reaches exhibit reduced natural buffering capacity and weakened self-purification processes due to flow regulation and pollutant accumulation (Hruzdieva et al., 2025) [3].

Geomorphologically, the Lower Dnipro Basin is located within the Black Sea Lowland and is characterized by wide floodplains, alluvial terraces, and extensive anthropogenic reshaping due to reservoir inundation. Historically, the region included large floodplain ecosystems (e.g., the “Velykyi Luh” area), which were largely submerged after dam construction but are now undergoing partial ecological re-naturalization following the destruction of the Kakhovka dam in 2023.

The hydrographic network of the Lower Dnipro includes the main channel of the river and numerous tributaries such as the Inhulets and lower reaches of smaller steppe rivers. The system also interacts strongly with large reservoir-lake complexes, which dominate the hydrological storage capacity of the basin. These reservoirs play a key role in water supply, irrigation, hydropower production, and navigation, but simultaneously cause fragmentation of aquatic habitats and changes in sediment deposition patterns (Chornomorets et al., 2023) [4].

The climate of the Lower Dnipro Basin is temperate continental with strong aridization tendencies toward the south. Mean annual precipitation ranges from approximately 350–500 mm, while evaporation significantly exceeds precipitation during the warm period. These conditions result in frequent droughts, increased water stress, and reduced ecological resilience of aquatic ecosystems. Climate-driven hydrological variability is further amplified by reservoir regulation and land-use transformation (Shakirzanova et al., 2018) [1].

Ecologically, the Lower Dnipro Basin contains a mosaic of floodplain forests, steppe ecosystems, deltaic wetlands, and reservoir ecosystems. Despite strong anthropogenic transformation, the region remains an important habitat for migratory birds, fish spawning areas, and riparian biodiversity. However, long-term monitoring shows significant ecological stress, including eutrophication, oxygen depletion, and accumulation of organic and industrial pollutants in sediments and water columns (Hryha et al., 2024) [2].

Socio-economically, the Lower Dnipro Basin is one of Ukraine’s key industrial and agricultural regions. It hosts large urban centers (Dnipro, Zaporizhzhia, Kherson region influence zone) and critical infrastructure, including hydropower stations, irrigation systems, and water supply networks. The river is intensively used for energy production, navigation, irrigation, fisheries, and municipal water supply, making it a strategic water resource for national security and economic stability (Chornomorets et al., 2023) [4].

The ecological condition of the Lower Dnipro Basin is determined by the combined influence of hydrological regulation, industrial pollution, agricultural runoff, and climate change. Recent studies indicate increased biochemical oxygen demand (BOD), reduced dissolved oxygen levels, and declining self-purification capacity in several sections of the river, particularly in reservoir zones and urbanized reaches (Hryha et al., 2024) [2].

In addition, the destruction of the Kakhovka dam in 2023 has introduced a new phase of morphological and ecological transformation in the Lower Dnipro system. This event led to rapid drainage of the reservoir, exposure of former floodplain areas, and initiation of large-scale natural rewilding processes. At the same time, concerns remain regarding contamination of sediments and long-term water quality impacts.

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## 1.1 ECOLOGICAL ASSESSMENT AND FORECASTING OF SURFACE WATER CONDITIONS IN THE DNIPRO RIVER IN ZAPORIZHZHIA

The issue of preserving water resources in river basins, particularly their rational utilization, is extremely relevant under current conditions. Since the beginning of the war, Ukraine's water resources have experienced additional anthropogenic impact, thus necessitating continuous monitoring of surface water conditions. Among the rivers affected by this additional impact is the Dnipro. Therefore, there is a need to conduct a comprehensive analysis of the ecological state of the Dnipro River basin to identify the most pressing problems requiring immediate solutions. As is known, the surface waters of the Dnipro River are of key importance for water supply in Ukraine. At the same time, the Dnipro's aquatic ecosystem is under constant anthropogenic pressure, causing gradual and persistent deterioration of its ecological state. To improve the quality of surface waters in the Dnipro basin, it is necessary to implement a reliable and effective model for forecasting the state of the ecosystem, including accounting for the impact of war.

To assess the impact of anthropogenic load, including war impact on the surface water conditions in the Dnipro River in Zaporizhzhia, a study was conducted on the water quality of the Dnipro River using data from the Water Monitoring Laboratory of the Basin Department for Water Resources of Azov Rivers. Comparative analysis was carried out for the monitoring station: Dnipro River, 328 km, Zaporizhzhia, upper tailrace of the Dnipro HPP, drinking water intake of Zaporizhzhia (DWS No. 1) (47°81'80" N, 35°10'00" E) during 2015-2024.

The ecological state of the Dnipro River has long attracted attention, as it is the country's main waterway, but remains under constant anthropogenic pressure [1-4]. Considering the changing situation, there is a need for continuous monitoring of its surface water quality in the context of main pollutants, which include phosphate and ammonium ions, sulfates and chlorides, and others, as well as assessing the ratio of $BOD_5$ to dissolved oxygen concentration.

Phosphates play a key role in the functioning of biota and hydroecosystems in general. Under optimal concentration conditions, they contribute to increased ecosystem productivity and influence the species composition of aquatic organisms. However, exceeding the maximum permissible limits of phosphates changes the trophic status of water bodies, stimulating the development of organisms that release harmful metabolites, negatively affecting other inhabitants of the water body and deteriorating water quality. Phosphate levels in aquatic environments vary seasonally, related both to their sources (weathering and dissolution of rocks, application of phosphorus fertilizers and detergents) and biological processes (life activities and death of organisms). The main sources of anthropogenic phosphate pollution are considered to be agricultural runoff, wastewater from treatment facilities, and industrial enterprises [5-7].

Ammonium ions are one form of nitrogen naturally present in the environment. They are primarily concentrated in the upper layers of the hydrosphere, where intensive decomposition of protein substances from aquatic organisms and accumulation of their metabolic products occur. In this context, ammonium acts as a natural element of the aquatic environment, involved in the nitrogen cycle in the biosphere. At the same time, its concentration must remain within permissible levels, as excessive content can cause serious ecological consequences. Specifically, elevated $NH_4^+$ levels in surface waters promote the development of eutrophication [4, 9], which harms biodiversity: this phenomenon stimulates excessive growth of certain algae species, which reduce dissolved oxygen content in the water. As a result, the water bodies' ability to self-purify is significantly impaired.

Sulfates are the most common anions present in aquatic ecosystems. The main factors for increasing their concentration in water bodies are the processes of organism death, oxidation of substances, and influx from groundwater [10, 11]. Sulfate ions

($SO_4^{2-}$) enter natural waters primarily through dissolution of sulfur-containing minerals such as gypsum, as well as through oxidation of sulfur and sulfides. Additionally, a significant portion consists of sulfur released during the decomposition of plant and animal remains, as well as from wastewater.

Chlorides enter surface waters from mineral fertilizers containing chlorine-containing potassium compounds, as well as from domestic and industrial effluents. Due to high solubility, chlorides are poorly adsorbed by suspended matter and are hardly assimilated by aquatic organisms. Their concentration plays an important role in forming non-carbonate water hardness. Chloride ion ($Cl^-$) also enters water bodies through dissolution of chlorine-containing minerals. An additional source is atmospheric transport from marine and oceanic areas to continental water bodies. The significant increase in chloride concentrations in recent years is associated with increased impact of industrial and municipal wastewater [11].

The biochemical oxygen demand (BOD) indicator shows how much oxygen is required for complete oxidation of organic substances in a water body. During the oxidation and decomposition of organic matter, BOD values decrease. Simultaneously with consumption, oxygen enters surface waters from the atmosphere and water saturation with dissolved oxygen occurs. This diffusion compensates for oxygen losses during decomposition of organic matter in water. This relationship is described by the well-known Streeter-Phelps model, which allows evaluation of the balance between oxygen consumption in water due to organic matter decomposition and its recovery through atmospheric diffusion. This, in turn, allows assessment of water quality and its capacity for natural self-purification [12, 13].

When monitoring surface waters, it is important not only to determine the content of substances in them, but also to compare the obtained data with maximum permissible concentrations, which are indicators of the safe level of harmful substances per unit volume or mass in the aquatic environment that has minimal impact on human health [14, 15].

The research object was the surface water condition of the Dnipro River within the monitoring station: Dnipro River, 328 km, Zaporizhzhia, upper tailrace of the Dnipro HPP, drinking water intake of Zaporizhzhia (DWS No. 1) (47°81'80" N, 35°10'00" E). The study covered the period 2013-2024 and was conducted for the following parameters: phosphate ions, ammonium ions, sulfate ions, chloride ions, $BOD_5$, and dissolved oxygen.

Figure 1.1 presents the results of analysis of phosphate and ammonium ion dynamics in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

Analysis of phosphate and ammonium ion dynamics in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024 revealed clear changes that are both seasonal and anthropogenically induced. During 2017-2020, indicators for both ions demonstrated relative stability with typical fluctuations caused by surface runoff from agricultural lands and domestic discharges.

Since 2021, there has been a trend toward decreased phosphate concentration, reaching a minimum in mid-2022. Simultaneously, in July 2022, an abnormally high spike in ammonium ion concentration was observed, exceeding 0.8 $mg/dm^3$. This may be a result of local discharges or increased mineralization of organic matter under conditions of reduced flow, high temperature, and dissolved oxygen deficit.

In 2023-2024, ammonium content gradually decreases, indicating activation of nitrification processes. In the presence of oxygen, ammonium is oxidized to nitrites (by bacteria of the genus Nitrosomonas) and further to nitrates (Nitrobacter), indicating improved water body aeration and stabilization of ecosystem processes. Phosphates during this period demonstrate gradual growth with individual sharp peaks (September-October 2024), likely related to mobilization of phosphates from bottom sediments under anaerobic conditions or through the influence of organic matter decomposition (SPAR).

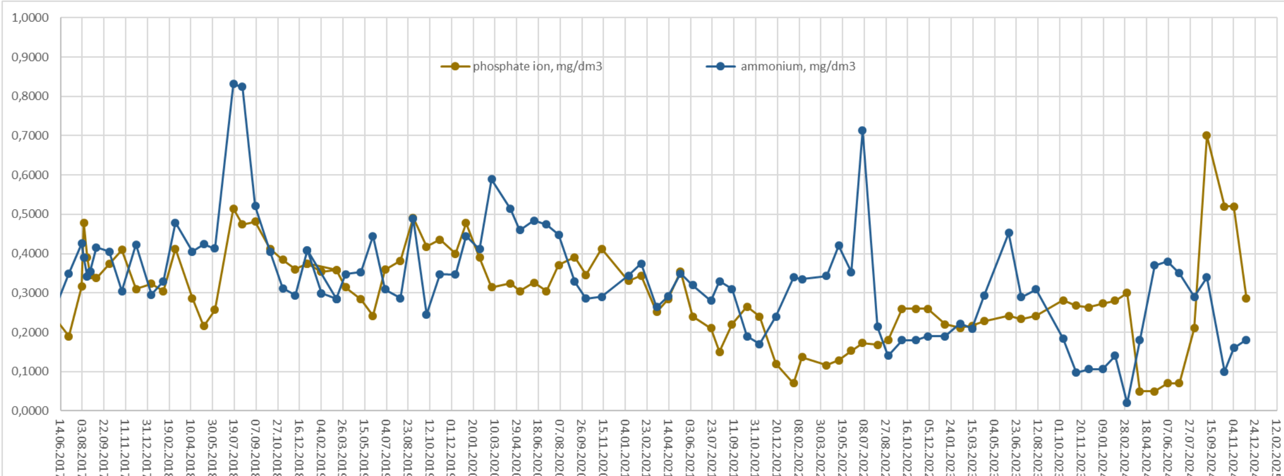


Fig. 1.1 Dynamics of phosphate and ammonium ion content in Dnipro River surface waters in Zaporizhzhia during 2017-2024

Overall, a complex interaction of chemical and biogeochemical processes is observed - reduced anthropogenic load decreased phosphate and ammonium influx, while changes in hydrodynamics, particularly through HPP damage, affected flow, oxygen regime, and remobilization of compounds from bottom sediments.

Figure 1.2 presents the results of analysis of sulfate and chloride ion dynamics in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

The graph demonstrates fluctuations in sulfate and chloride ion concentrations in river water, which are indicators of mineralization, degree of anthropogenic load, and hydrochemical stability of the aquatic environment.

Throughout the entire period, sulfate concentrations (blue line) fluctuate within 30-90 mg/dm³, with notable peaks in certain months (e.g., 05.2021, 10.2021, 09.2022, 11.2023, 11.2024). Such anomalous increases may be related to local wastewater discharges or active oxidation of organic matter during changes in hydrochemical regime. Increased sulfates may also result from microbiological decomposition of biota, particularly during periods of algae death, or active sulfate reduction with subsequent release of sulfur-containing compound oxidation products.

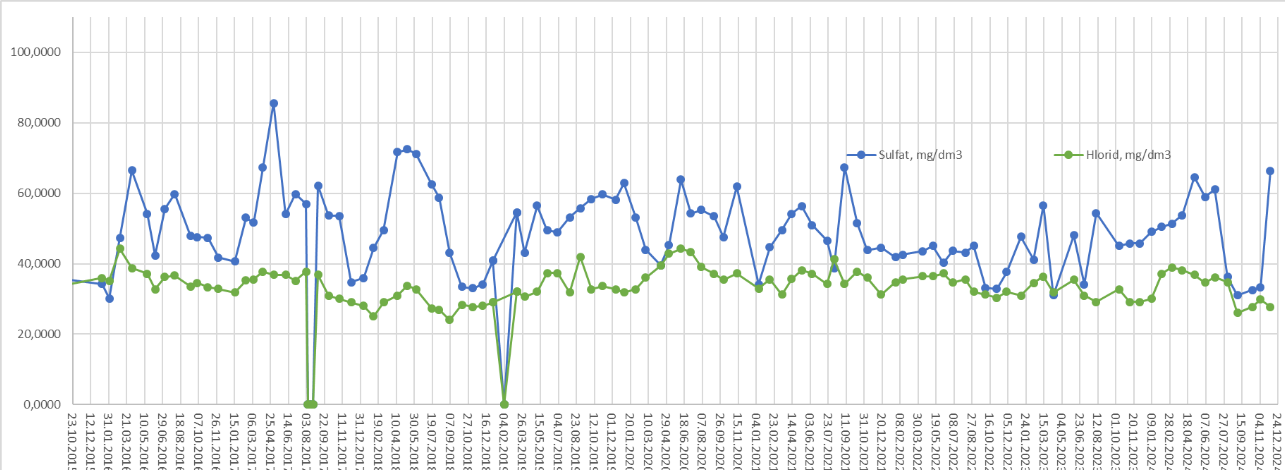


Fig. 1.2 Dynamics of sulfate and chloride ion content in Dnipro River surface waters in Zaporizhzhia during 2017-2024

Characteristically, sulfate ions demonstrate higher variability, which is typical for ions that can actively come from anthropogenic sources - industrial enterprises, storm and domestic runoff. Particularly sensitive fluctuations are observed in 2022-2023, which may reflect the impact of military actions and disruption of wastewater treatment facilities.

Unlike sulfates, chloride ions (green line) have more stable concentration, maintained in the range of 25-40 mg/dm³. This corresponds to the nature of chlorides as conservative ions that are not actively involved in biogeochemical processes and have high solubility. However, short-term decreases (e.g., in 07.2021 and 04.2022) may result from technical errors or local water dilution, for example, after severe floods or increased water exchange.

Overall, comparison of dynamics for both ions indicates increased reactivity of sulfates in the river water system, while chlorides remain a stable indicator of overall mineralization level. Increased sulfates with unchanged chloride levels may indicate activation of biochemical processes - particularly, oxidation of SPAR or hydrogen sulfide formation with subsequent oxidation to $SO_4^{2-}$ under variable oxygen regime conditions.

Figure 1.3 presents the results of analysis of dissolved oxygen concentration dynamics and biochemical oxygen demand over 5 days in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

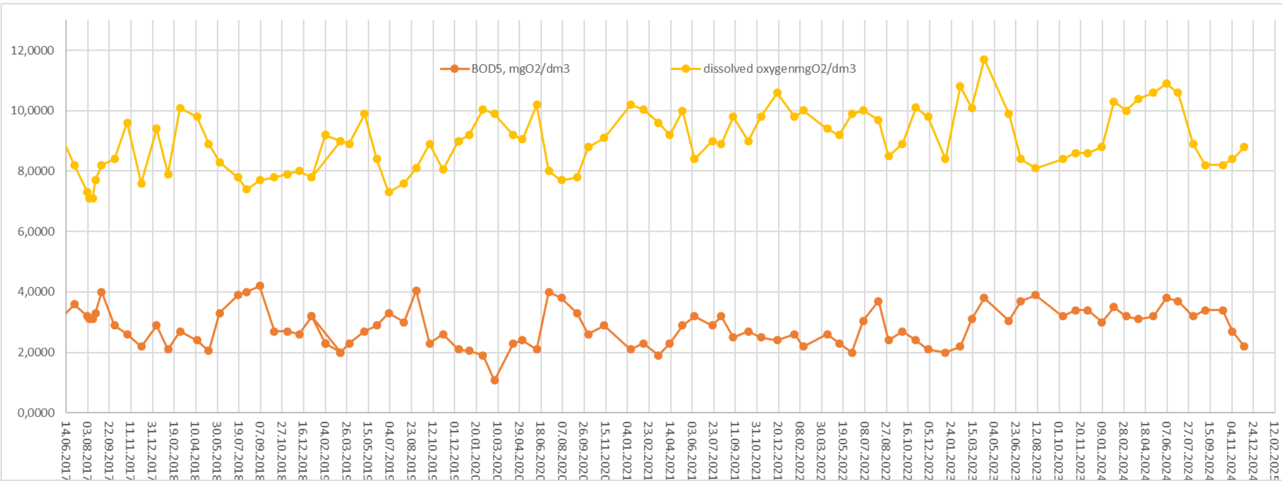


Fig. 1.3 Dynamics of dissolved oxygen concentration and biochemical oxygen demand over 5 days in Dnipro River surface waters in Zaporizhzhia during 2017-2024

The graph depicts the dynamics of two key indicators of aquatic environment condition: dissolved oxygen concentration and biochemical oxygen demand over 5 days ($BOD_5$). Both parameters are closely related to the intensity of biochemical processes and are primary markers of water body self-purification and its ecological state.

During the period from 2017 to 2022, typical seasonal dynamics are observed; in summer, dissolved oxygen levels decrease, which is due to reduced solubility at elevated water temperatures and activation of microbiological decomposition of organic matter. During this time, $BOD_5$ values increase, as elevated temperature and organic load stimulate metabolic activity of aerobic bacteria, increasing oxygen consumption. In autumn and winter, conversely, there is an increase in dissolved oxygen concentration and decrease in $BOD_5$ - the result of slowed biochemical processes and improved oxygen solubility.

However, beginning in 2023, this clear seasonal rhythm is disrupted. The graph shows a significant decrease in dissolved oxygen during the summer and autumn period of 2023, while $BOD_5$ values remain relatively stable, without corresponding growth. This may indicate oxygen deficit caused by hydrological regime disruption due to destruction of the Kakhovka HPP (06.2023) and reduced flow velocity, limiting water mixing and oxygen saturation from the atmosphere.

Continued organic matter decomposition under conditions of limited oxygen access in 2023-early 2024 explains the low DO level with relatively unchanged $BOD_5$ - available organic substances decompose with slowing, and oxygen access is limited. During the summer period of 2024, increased DO indicates partial restoration of aeration, possibly through improved weather conditions or reduced anthropogenic load (particularly organic matter), which is also evidenced by stability or even slight decrease in $BOD_5$.

Overall, the graph confirms the effect of "biochemical paradox": when high dissolved oxygen levels correspond to low $BOD_5$ (ecosystem capable of self-purification), and its decrease without accompanying $BOD_5$ growth indicates disruption of natural organic matter oxidation due to reduced flow and decreased atmospheric diffusion. Such changes demonstrate reduced adaptive potential of the aquatic ecosystem under the influence of hydrotechnical and climatic factors.

For overall assessment of anthropogenic load levels from pollutants and their impact on $BOD_5$ levels and dissolved oxygen concentration, distribution histograms were constructed for the period 2015-2024.

Figure 1.4 presents a histogram of phosphate ion concentration distribution in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

The distribution histogram of phosphate ion concentrations in Dnipro River water demonstrates an asymmetric (right-skewed) character with a modal interval of 0.36-0.44 mg/dm$^3$, indicating predominance of moderate phosphate loading levels.

Approximately 80% of values are concentrated within 0.22-0.50 mg/dm³ - typical for water bodies with regular impact from wastewater and agricultural runoff.

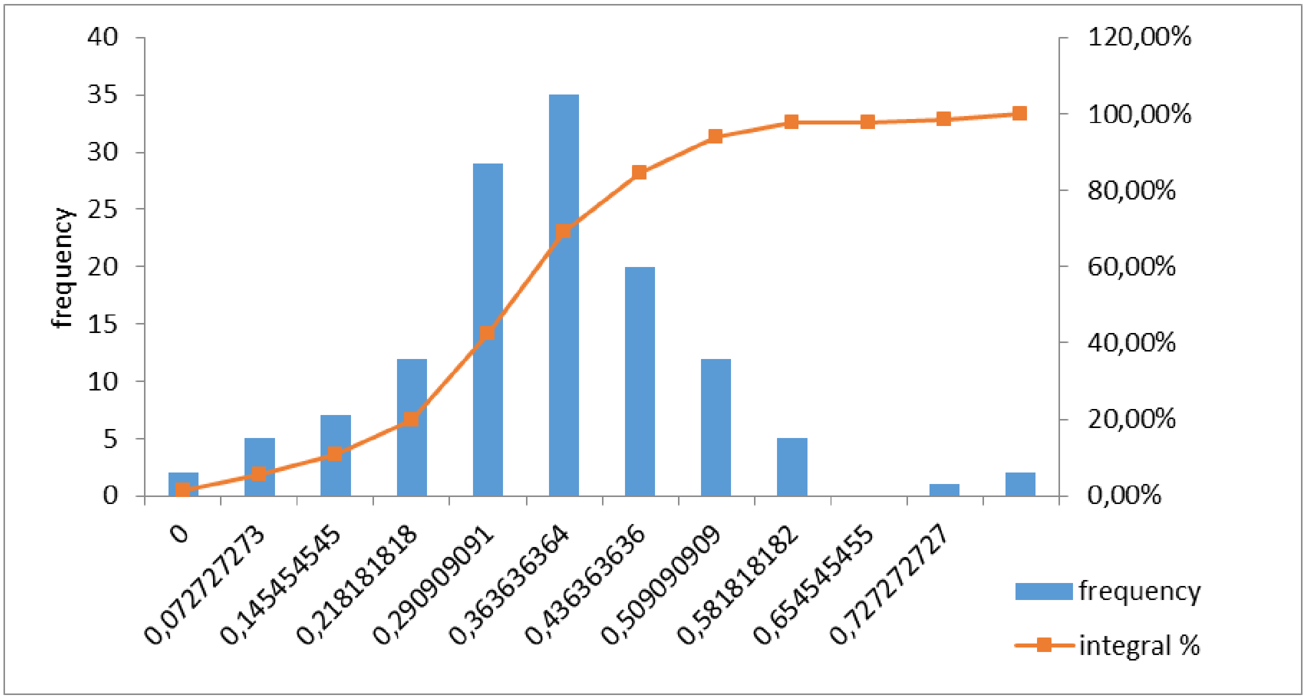


Fig. 1.4 Distribution histogram of phosphate ion concentrations in Dnipro River surface waters in Zaporizhzhia during 2017-2024

Such concentrations can support increased aquatic ecosystem productivity but promote phytoplankton biomass accumulation, especially during summer periods, increasing the risk of eutrophication development. Individual high values (>0.65 mg/dm³) are likely related to local unauthorized discharges or episodic fertilizer washout, and indicate disruption of the water body's buffer capacity. This distribution profile indicates the need for systematic monitoring and ecological control of phosphate loading sources.

Figure 1.5 presents a histogram of ammonium ion concentration distribution in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

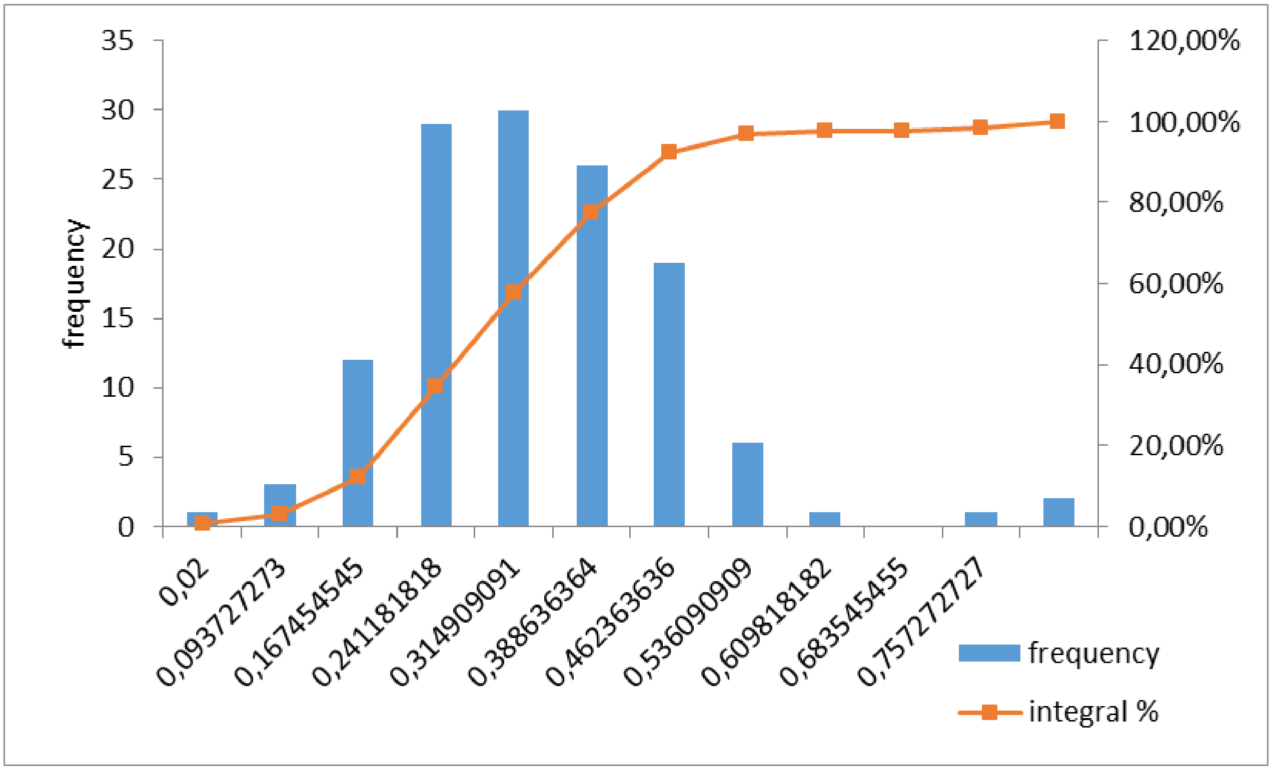


Fig. 1.5 Distribution histogram of ammonium ion concentrations in Dnipro River surface waters in Zaporizhzhia during 2017-2024

The histogram demonstrates frequency distribution of ammonium ion concentrations, which has a pronounced right-skewed distribution with a maximum in the 0.31-0.39 mg/dm³ range. The main portion of values (over 80%) is concentrated within 0.24-0.53 mg/dm³, indicating the presence of a persistent ammonium pollution source, likely of domestic or agricultural origin. The cumulative curve (integral %) confirms predominance of average values, characteristic of aquatic systems with regular anthropogenic load but still capable of self-purification. Ammonium is an intermediate product of organic matter mineralization and an important indicator of oxygen regime. With sufficient dissolved oxygen levels, $NH_4^+$ undergoes nitrification to nitrites and further to nitrates, so this distribution form indicates relatively aerobic conditions. At the same time, individual emissions with concentrations above 0.60 mg/dm³ (outliers on the right) indicate episodic overloads or reduced aeration - likely due to local discharges or flow reduction due to hydrotechnical changes (e.g., dam destruction or seasonal low water). This distribution profile is typical for waterways affected by anthropogenic factors but still maintaining buffer capacity for self-purification. At the same time, the presence of even occasional high concentrations requires enhanced control, as $NH_4^+$ is toxic to aquatic biota under high pH and temperature conditions characteristic of summer periods.

Figure 1.6 presents a histogram of sulfate ion concentration distribution in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

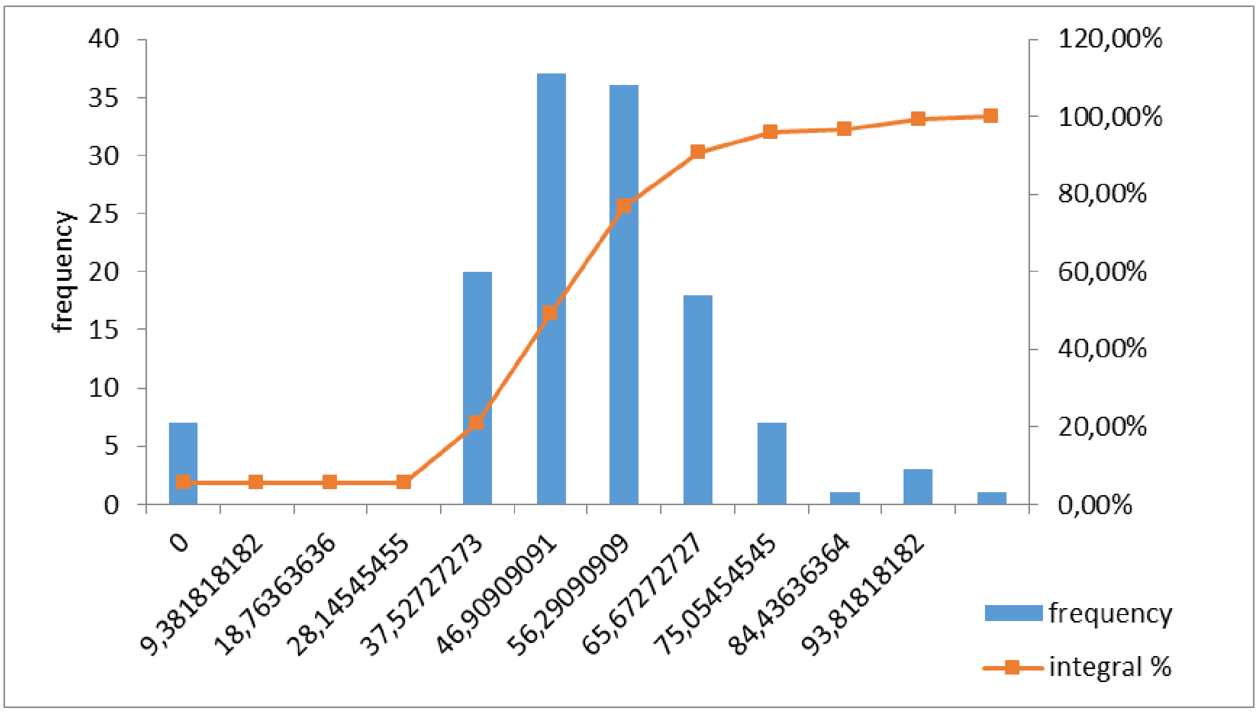


Fig. 1.6 Distribution histogram of sulfate ion concentrations in Dnipro River surface waters in Zaporizhzhia during 2017-2024

The distribution of sulfate concentrations has a normal distribution character with a maximum within 56-66 mg/dm³, corresponding to the natural mineralization level for large river systems with moderate technogenic load. The main mass of values (over 80%) is concentrated in the 46-75 mg/dm³ range, confirmed by the smooth cumulative curve. This indicates a stable source of sulfate influx - particularly from natural minerals (gypsum, sulfides), as well as from domestic and industrial wastewater.

Sulfates are indicators of the water body's oxidative regime, and high values may indicate active organic matter decomposition processes or influx of sulfur-containing compounds. Individual cases of concentrations above 84 mg/dm³ may result from local pollution, desorption processes from bottom sediments, or atmospheric runoff impact.

This distribution profile is typical for river systems experiencing seasonal changes and having both natural and anthropogenic sources of $SO_4^{2-}$ influx. High concentrations at low oxygen levels can also serve as a substrate for sulfate reduction with hydrogen sulfide ($H_2S$) formation, which is potentially toxic to aquatic biota.

Figure 1.7 presents a histogram of chloride ion concentration distribution in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

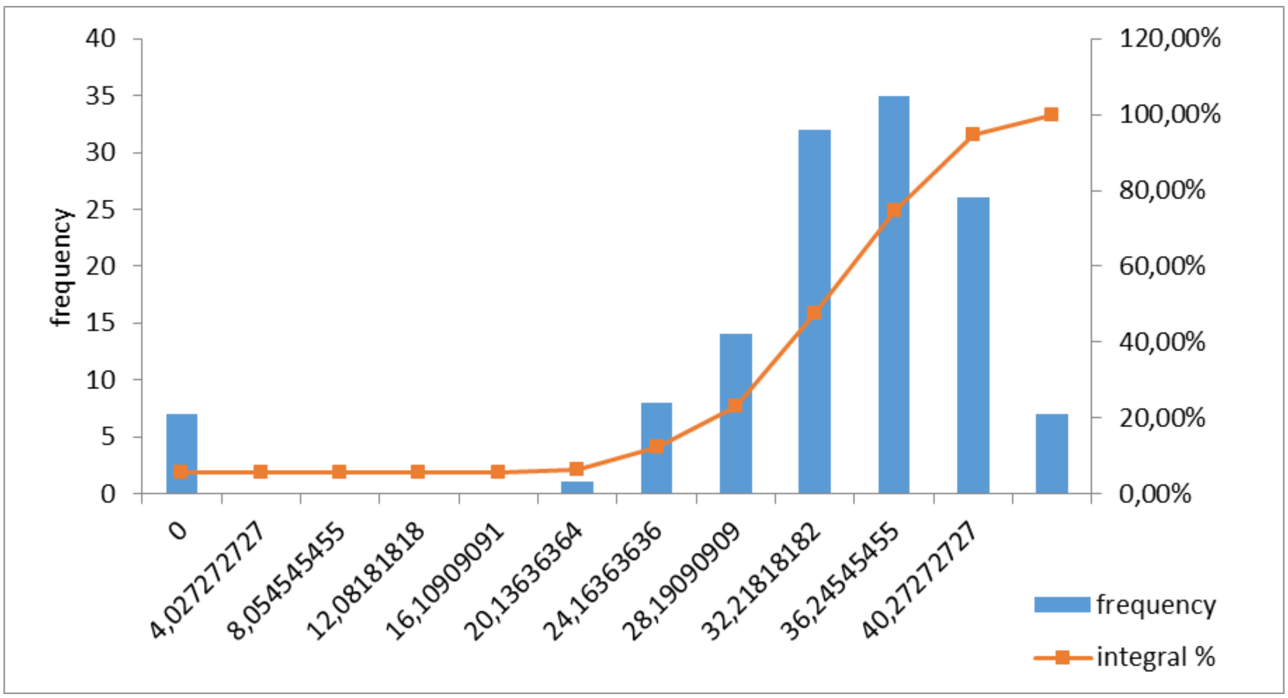


Fig. 1.7 Distribution histogram of chloride ion concentrations in Dnipro River surface waters in Zaporizhzhia during 2017-2024

The chloride ion distribution histogram is characterized by left-skewed asymmetry with a modal class in the 36.2-40.3 mg/dm³ range, indicating predominance of moderate mineralization levels. Over 80% of observations are concentrated within 28-44 mg/dm³, typical for freshwater river systems with background hydrogeochemical regime and minimal anthropogenic load.

Chlorides, as inert conservative ions, do not participate in the biogeochemical cycle and are not adsorbed by bottom sediments, so their distribution serves as a marker of hydrochemical background stability. The absence of pronounced extreme values in the right tail of the distribution indicates minimal influence of point pollution sources - particularly domestic or industrial effluents characteristic of urbanized territories.

The presence of individual low values in the left part of the histogram (below 12 mg/dm³) may result from water dilution by flood or atmospheric precipitation or seasonal reduction in mineralization.

Thus, $Cl^-$ distribution reflects hydrochemical stability and can be used as an indicator of background conditions when assessing changes in more reactive aquatic environment components.

Figure 1.8 presents a histogram of $BOD_5$ value distribution in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

The distribution of $BOD_5$ values has an asymmetric form with a maximum in the 2.7-3.1 $mgO_2/dm^3$ range, indicating predominance of moderate organic pollution. Most values (≈80%) are within 2.3-3.8 $mgO_2/dm^3$, corresponding to the level of weak to moderate anthropogenic load according to water quality ecological assessment classification. This profile is typical for water bodies with biodegradable organic matter of domestic and agricultural origin. The $BOD_5$ indicator is an integral biochemical indicator characterizing the oxygen requirement of aerobic microorganisms for oxidation of dissolved organic matter. Stable peak position in the medium range indicates conditions for natural self-purification and relatively aerobic environment. The presence of individual high values (>3.8 mg/dm³) indicates periodic local organic matter influx, likely from effluents without proper treatment. The cumulative percentage distribution curve (integral %) confirms uniform transition from background to elevated values, indicating absence of sharp anthropogenic emissions.

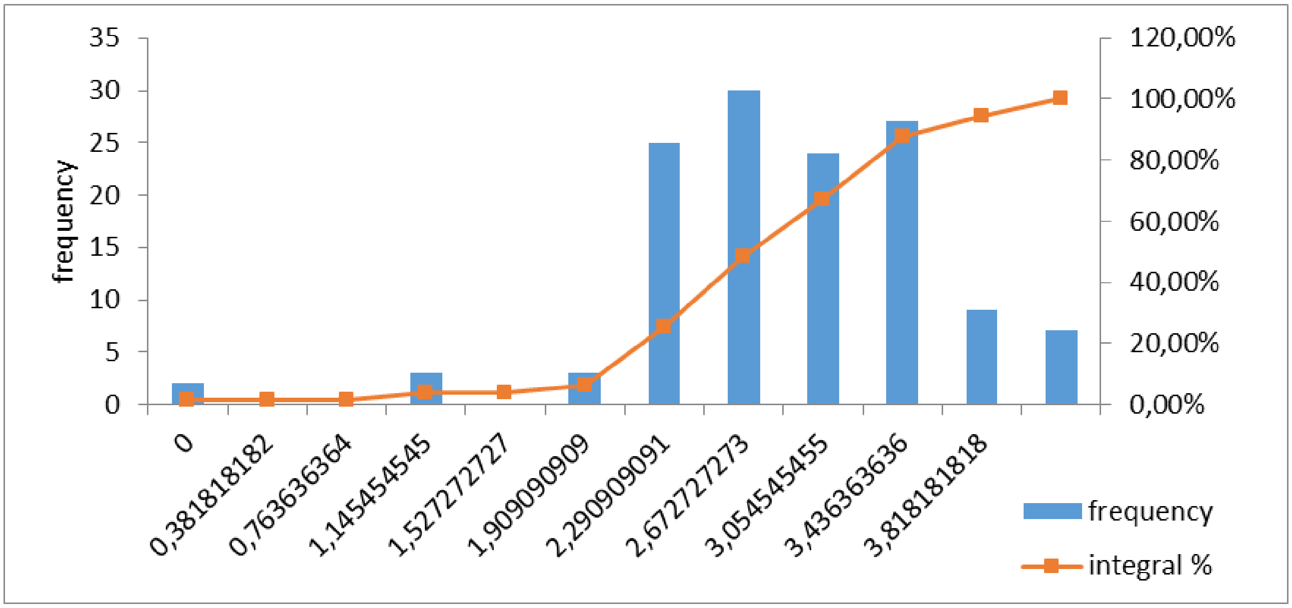


Fig. 1.8 Distribution histogram of $BOD_5$ values in Dnipro River surface waters in Zaporizhzhia during 2017-2024

Figure 1.9 presents a histogram of dissolved oxygen concentration distribution in the surface waters of the Dnipro River in Zaporizhzhia during 2017-2024.

The distribution of dissolved oxygen concentrations has a clearly defined modal interval of 9.7-10.4 $mgO_2/dm^3$, where the largest number of observations are concentrated. Over 80% of all values are within 8.2-11.2 $mgO_2/dm^3$, indicating the aerobic nature of the environment, favorable for aquatic biota functioning.

This level of oxygen saturation corresponds to good ecological conditions, characteristic of water bodies with moderate organic loading and active oxygen diffusion from the atmosphere. It also indicates effective self-purification through aerobic oxidation of organic matter. The presence of a small number of values above 12 $mgO_2/dm^3$ may be related to intensive photosynthetic activity of algae during daytime, especially in summer. At the same time, the absence of a significant number of low values (<7 $mg/dm^3$) indicates stable oxygen regime and absence of critical phenomena related to oxygen deficit (hypoxia), usually observed in reservoirs with reduced flow or excessive eutrophication. The obtained distribution is an indicator of stable hydrobiological state, allowing maintenance of natural self-purification mechanisms and providing conditions for aerobic transformation of organic and inorganic pollutants.

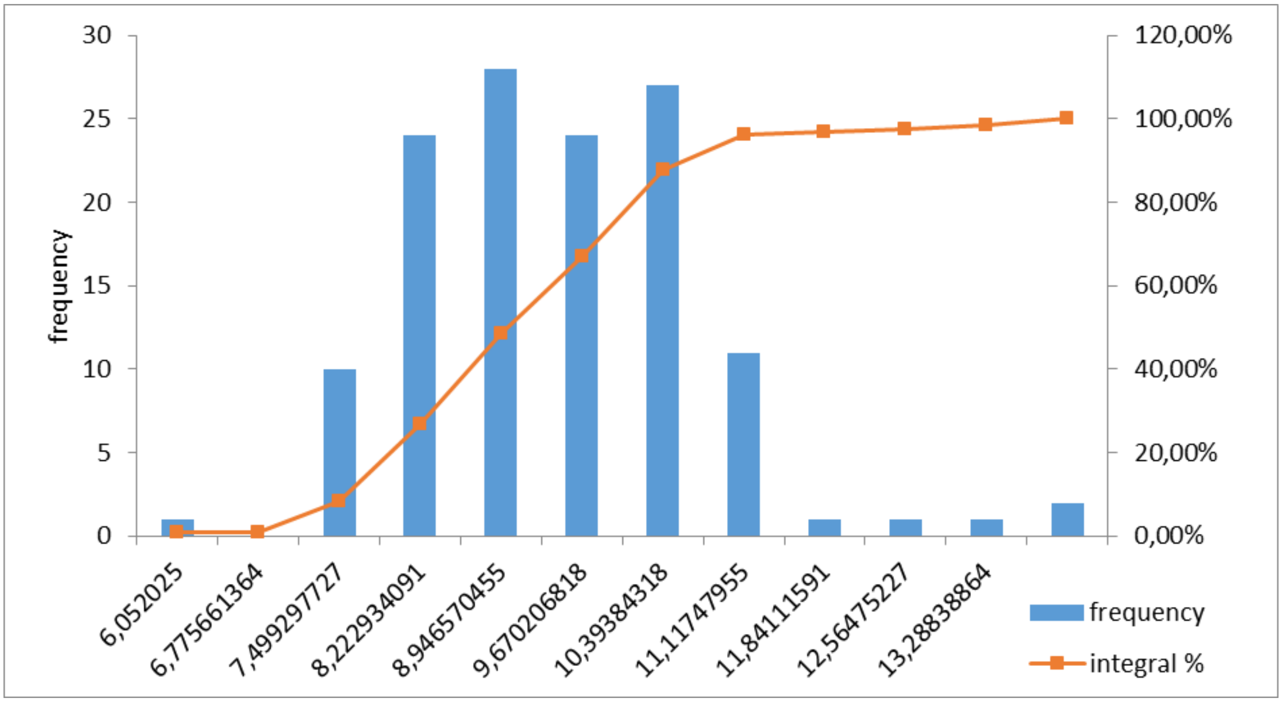


Fig. 1.9 Distribution histogram of dissolved oxygen concentrations in Dnipro River surface waters in Zaporizhzhia during 2017-2024

To determine dynamics of anthropogenic load level changes on Dnipro River surface waters (DWS-1 station) and subsequent forecasting in the context of individual pollutants, corresponding regression equations were constructed. Annual average values of harmful substance emissions were used in their construction (i.e., seasonality of pollution was leveled).

Figure 1.10 presents the dynamics of phosphate and ammonium ion concentration changes in water during 2013-2024 and corresponding approximating curves.

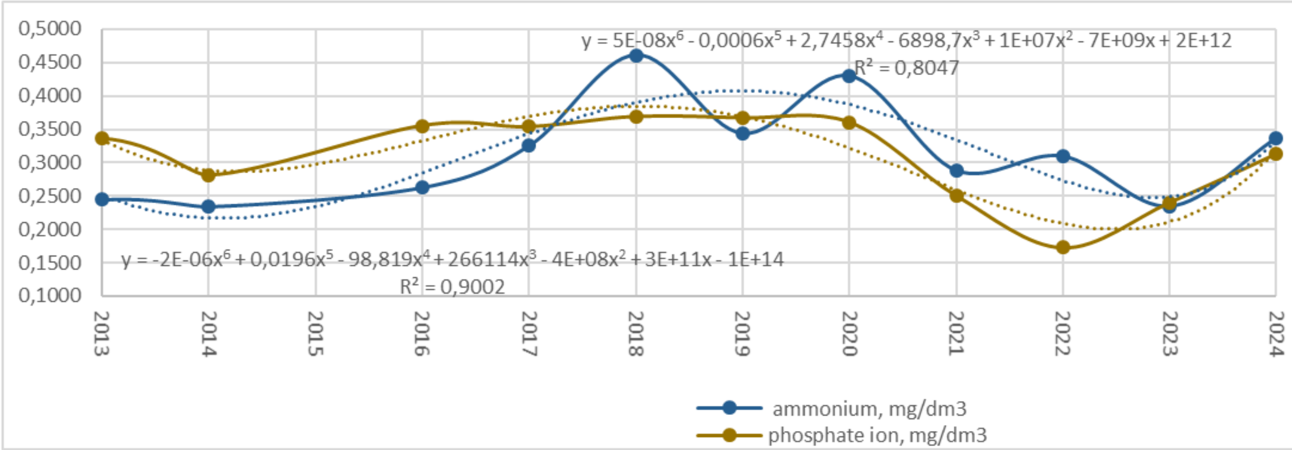


Fig. 1.10 Dynamics of phosphate and ammonium ion concentration changes in water during 2013-2024 and corresponding approximating curves

Regression equation of the identified dependence for phosphate ions: $y = 5 \times 10^{-8}x^6 - 6 \times 10^{-4}x^5 + 2.7458x^4 - 6.89987 \times 10^3x^3 + 1 \times 10^7x^2 - 7 \times 10^9x + 2 \times 10^{12}$, approximation reliability – $R^2 = 0.8047$.

The identified dependencies indicate that phosphate ion content reduction in water occurs periodically, namely being minimal in 2014 and in 2022.

Regression equation of the identified dependence for ammonium ions: $y = -2 \times 10^{-6}x^6 + 1.96 \times 10^{-2}x^5 - 98.819x^4 + 2.66114 \times 10^5x^3 - 4 \times 10^8x^2 + 3 \times 10^{11}x - 1 \times 10^{14}$, approximation reliability – $R^2 = 0.9002$.

The identified dependencies indicate that ammonium ion content reduction in water also occurs periodically, being at low levels during 2013-2015, and then in 2019, 2021, and in 2023.

This provides grounds to confirm the assumption regarding the main impact factor - fertilizer application, as reduction in application of some fertilizers is compensated by others. Additionally, from 2016 to 2021, general situation deterioration was observed, as average content of phosphate and ammonium ions in water increased.

After situation improvement during 2022-2023 (due to reduced fertilizer application), in 2024 there was a return to previous trends.

Figure 1.11 presents the dynamics of sulfate and chloride ion concentration changes in water during 2013-2024 and corresponding approximating curves.

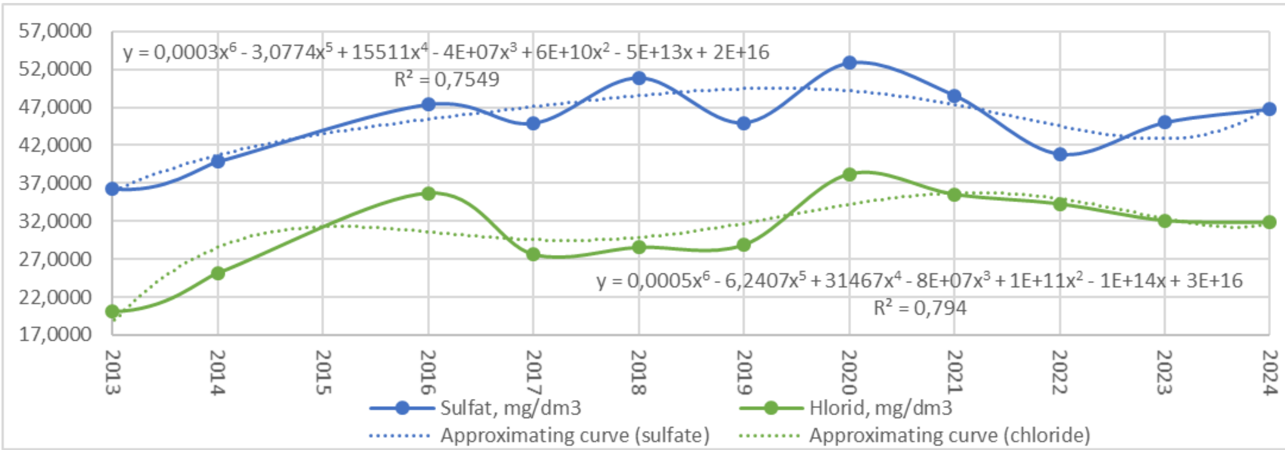


Fig. 1.11 Dynamics of sulfate and chloride ion concentration changes in water during 2013-2024 and corresponding approximating curves

Regression equation of the identified dependence for sulfate ions: $y = 3 \times 10^{-4}x^6 - 3.0774x^5 + 1.5511 \times 10^4x^4 - 4 \times 10^7x^3 + 6 \times 10^{10}x^2 - 5 \times 10^{13}x + 2 \times 10^{16}$, approximation reliability – $R^2 = 0.7549$.

Regression equation of the identified dependence for chloride ions: $y = 5 \times 10^{-4}x^6 - 6.2407x^5 + 3.1467x^4 - 8 \times 10^7x^3 + 1 \times 10^{11}x^2 - 1 \times 10^{14}x + 3 \times 10^{16}$, approximation reliability – $R^2 = 0.794$.

The identified dependencies indicate that chloride ion content changes in water are also insignificant.

As can be seen, sulfate and chloride ion content during 2013-2016 increased, while in subsequent years it fluctuates around a certain average level.

Figure 1.12 presents the dynamics of $BOD_5$ and dissolved oxygen concentration changes during 2013-2024 and corresponding approximating curves.

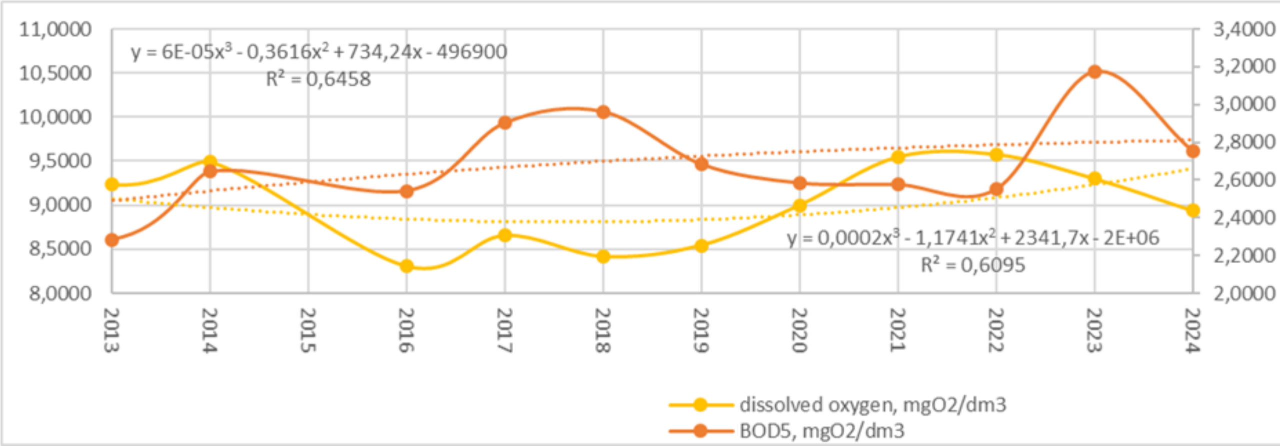


Fig. 1.12 Dynamics of $BOD_5$ and dissolved oxygen concentration changes in water during 2013-2024 and corresponding approximating curves

Regression equation of the identified dependence for $BOD_5$: $y = 6 \times 10^{-5}x^3 - 0.3616x^2 + 7.3424 \times 10^2x - 4.969 \times 10^5$, approximation reliability – $R^2 = 0.6458$. The identified dependencies indicate that maximum indicator levels were in 2017-2018 and in 2023 (significant increase) with practically unchanged level in other years.

Regression equation of the identified dependence for dissolved oxygen: $y = 2 \times 10^{-4}x^3 - 1.1741x^2 + 2.3417 \times 10^3x - 2 \times 10^6$, approximation reliability – $R^2 = 0.6095$.

The identified dependencies indicate that minimum indicator levels were in 2016-2019 and in 2024, with maxima observed in 2014 and during 2021-2022.

Therefore, opposite trends exist for $BOD_5$ and dissolved oxygen, as should be expected. The obtained results provide grounds to confirm the assumption about the existence of self-purification capacity despite existing anthropogenic influences.

*Conclusions.* The work conducted an analysis of anthropogenic load impact on surface water conditions in the Dnipro River in Zaporizhzhia. The study covered the period 2013-2024 and was conducted in the context of the following indicators: phosphate ions, ammonium ions, sulfate ions, chloride ions, $BOD_5$, and dissolved oxygen. It was established that the main anthropogenic load is created by industry, agriculture, and municipal enterprises. The consequences of war were also assessed, namely the destruction of the Kakhovka HPP dam (destruction of the Kakhovka Reservoir) and cessation of Dnipro HPP operations. Considering that indicators of surface water ecological state are $BOD_5$ and dissolved oxygen level, special attention was given to these indicators. It was established that during 2017-2022, typical seasonal dynamics of indicators were observed. Since 2023, the clear seasonal rhythm changed due to disruption of hydrological regime through destruction of the Kakhovka HPP (06.2023) and reduced flow velocity, limiting water mixing and oxygen saturation from the atmosphere. Nevertheless, reduced pollution levels by phosphate and ammonium ions since the beginning of war has provided the possibility for self-purification of Dnipro River surface waters. For overall assessment of anthropogenic load levels from pollutants and their impact on $BOD_5$ levels and dissolved oxygen concentration in Dnipro River surface waters, distribution histograms were constructed for the period 2015-2024. Forecasting of anthropogenic load levels for main pollutants was carried out using regression equations, and predicted levels of $BOD_5$ and dissolved oxygen concentration in Dnipro River surface waters were determined.

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## 1.2 STUDY OF THE INFLUENCE OF WAR ON HYDROCHEMICAL INDICATORS SURFACE WATERS OF THE DNIPRO RIVER WITHIN THE BOUNDARIES OF THE CITY OF ZAPORIZHYA AND ZAPORIZHYA DISTRICT

The Dnipro River is one of the largest river systems in Europe and a key source of surface water in Ukraine, which ensures the functioning of industrial, communal and agricultural water management complexes. Within Zaporizhzhia and Zaporizhzhia District, the river system is subject to the cumulative impact of many years of anthropogenic load caused by the high concentration of the metallurgical, energy, and chemical industries, as well as significant flow regulation due to the functioning of the cascade of Dnipro reservoirs. This forms a complex multicomponent hydrochemical regime with pronounced spatio-temporal heterogeneity of water quality indicators. At the same time, since 2022, the functioning of the Dnipro basin has been affected by an additional extreme factor - military actions, which significantly changed the structure and intensity of anthropogenic impacts on water ecosystems.

Despite a significant number of studies devoted to the assessment of the quality of surface waters of the Dnipro, in modern conditions there is a need to apply complex approaches to the interpretation of changes in hydrochemical indicators, taking into account the simultaneous action of hydrodynamic, industrial and military factors. In this regard, the study of the hydrochemical parameters of the surface waters of the Dnipro River within the boundaries of the city of Zaporizhzhia and the Zaporizhzhia district under the conditions of war is an urgent scientific task aimed at establishing modern laws of the transformation of the water ecosystem, identifying the key factors of water quality changes, and clarifying the mechanisms of the formation of the hydrochemical regime under the conditions of increased anthropogenic pressure in the conditions of war.

The purpose of this study is a comprehensive assessment of the modern hydrochemical state of the surface waters of the Dnipro River within the city of Zaporizhzhia and the Zaporizhzhia district under conditions of increased anthropogenic and military influence, as well as the identification of the main patterns of spatio-temporal variability of key hydrochemical indicators (in particular, suspended substances, biogenic elements, indicators of organic pollution and oxygen regime).

Within the scope of the goal, identification and quantification of changes in the hydrochemical characteristics of the water environment under the influence of extreme anthropogenic factors of military origin, establishment of their role in the transformation of the self-cleaning processes of the river system and disruption of the natural hydrochemical balance are envisaged.

The analysis was based on data from the Water Monitoring Laboratory of the Basin Water Resources Management of the Azov Rivers and covered the period from 2015 to 2026 in the context of the following indicators: phosphate ions, ammonium ions, sulfate ions, chloride ions, nitrates, nitrites, $BOD_5$, suspended solids and dissolved oxygen.

Methods of comparison, computer-based statistical data processing using correlation analysis of the results, as well as modeling and forecasting using regression analysis, were applied.

The problem of anthropogenic impacts on the state of surface waters is a global one. That is why scientists pay considerable attention in their research both to the analysis of the hydrochemical regime of aquatic systems and to the search for ways to restore and stabilize aquatic ecosystems. The results of recent studies on surface waters in different countries are presented in articles [1–11].

This issue also remains in the focus of attention of researchers studying the condition of the surface waters of the Dnipro River and the sources of anthropogenic impacts that degrade its state [12-22].

The problem of surface water quality of the Dnipro River is one of the key issues in the ecological security system of Ukraine, since this river provides a significant part of the domestic and drinking water supply and functions under conditions of long-term anthropogenic load. The formation of the quality of Dnipro water is determined by a combination of natural-climatic, hydrological, hydrochemical and economic factors, and its assessment requires a comprehensive analysis of biogenic, organic, salt and oxygen indicators. A spatio-temporal approach to water quality assessment makes it possible to identify long-term trends in the deterioration of the state of water ecosystems, associated with the accumulation of biogenic substances, heavy metals and the weakening of the river's ability to self-clean [12].

A significant contribution to the study of the Dnipro basin was made in the works devoted to the retrospective analysis of hydrochemical indicators and the modeling of the oxygen regime. It is shown that among the most informative indicators of the ecological state of river waters are the ratio between $BOD_5$ and dissolved oxygen, as well as the content of phosphates and ammonium, which characterize the organic and biogenic load [13-14]. For the Dnipro basin, a trend towards a steady deterioration of the ecological state under the influence of man-made factors has been established, and for forecasting changes in the oxygen regime, it is proposed to use models of the Streeter-Phelps type, which describe the balance between oxygen consumption during the oxidation of organic substances and its supply from the atmosphere. Such approaches create a theoretical basis for the analysis of ecological risks in water bodies, where the state of the oxygen regime directly reflects the level of disruption of self-cleaning processes [15].

A separate area of research is related to the assessment of the salinity of the surface waters of the Dnipro within the city of Zaporizhzhia. For the water intake areas of the city, it is shown that the sum of ions, chlorides and sulfates remain important indicators of anthropogenic transformation of the water environment. Ecological assessment by block of salinity revealed a relatively stable, but not background state of the waters, which is characterized as moderately polluted. This indicates the need to take into account not only biogenic and oxygen indicators, but also mineralization characteristics, since changes in the salt regime determine the ecological stability of the water body and the general hydrochemical stability of the river system in an urbanized environment [16].

With the beginning of a full-scale war, the problem of surface water quality gained new relevance. In modern works, it is emphasized that military operations affect aquatic ecosystems due to the fall into the water of explosion products, fuel and lubricants, fragments of equipment, the destruction of industrial and communal facilities, damage to sewage treatment plants, as well as due to changes in the structure of production and displacement of the population. For the Dnipro River within Zaporizhzhia, according to monitoring data, differences in the behavior of the main indicators of water quality before and after the start of the full-scale war were revealed, in particular for ammonium, $BOD_5$, dissolved oxygen, phosphates, sulfates and chlorides. The influence of war does not always manifest itself in the form of linear dependencies, since weather, hydrological, agrarian and man-made factors are simultaneously imposed on the state of water, but the war itself became a factor that significantly changed the nature of the dynamics of indicators and the structure of connections between them [17].

The further development of this direction is connected with the consideration not only of direct military pollution, but also of the long-term consequences of the destruction of hydrotechnical infrastructure. Research on the suspended sediments of the Dnipro and the Danube shows that the full-scale war caused a transformation of the hydrological and hydrochemical regime of the flow of large rivers, which, in turn, affects sedimentation and lithodynamic processes. The destruction of the Kakhovka Reservoir is considered as one of the largest factors of ecological restructuring of the river system, which changes the transport of suspended matter, the accumulation of pollutants and the conditions of long-term monitoring. In this regard, qualitative and quantitative characteristics of suspended sediments are beginning to be considered as an important addition to traditional hydrochemical indicators, as they reflect the accumulative effect of military and anthropogenic influence [18].

For the immediate Zaporizhzhia section of the Dnipro, modern research has formed a separate body of knowledge about the change in the hydrochemical regime under the influence of the war. In the works that analyzed the state of surface waters in the upper basin of the Dnipro HPP, the main attention was focused on the dynamics of $BOD_5$, dissolved oxygen, phosphates and ammonium. It is shown that the oxygen regime is one of the most sensitive indicators of changes in the river ecosystem, and the use of the Streeter-Phelps model makes it possible to estimate the balance between biochemical oxygen consumption and its atmospheric recovery. After the beginning of the war, and especially after the destruction of the Kakhovka HPP, the seasonal rhythms of the behavior of individual indicators changed, and the reduction of phosphate and ammonium concentrations at certain stages contributed to the improvement of self-cleaning conditions. At the same time, such a trend does not mean complete stabilization, since in the event of a return to the pre-war level of pollution, the risks of deterioration of water quality will increase again [6].

This issue is most systematically revealed in works where a comprehensive ecological assessment and forecasting of the state of surface waters of the Dnipro in Zaporizhzhia was carried out for the period 2013-2024. In these studies, it is emphasized that phosphates and ammonium have a pronounced seasonal and anthropogenic nature of fluctuations, sulfates are characterized by high variability of natural and man-made origin, while chlorides are a more stable indicator of general mineralization. Special attention is paid to the violation of the seasonal dynamics of $BOD_5$ and dissolved oxygen after 2023, which is associated with the destruction of the Kakhovka dam and the change in the hydrological regime. At the same time, it was concluded that the partial ability of the river to self-recovery is preserved under the conditions of reducing the load of phosphates and ammonium [19].

The use of comparative methodological schemes tested on other river systems of Ukraine is also important for the development of research. In the works devoted to the Southern Bug, a combination of comparative analysis, correlation analysis, and regression forecasting was used to study the dynamics of phosphates, ammonium, sulfates, chlorides, $BOD_5$, and dissolved oxygen under wartime conditions. It is emphasized that the combination of these indicators makes it possible to simultaneously assess biogenic load, organic pollution, water mineralization and hypoxia risks. Methodologically, such works are important for the study of the Dnipro within Zaporizhzhia, as they demonstrate the possibility of integrating retrospective monitoring and predictive models into a single scheme for analyzing war-related changes in surface waters [20].

In the broader regional context, the study of bottom sediments and soils of the territories adjacent to the Dnipro, in particular the island of Khortytsia and the drained lakes formed after the destruction of the Kakhovka Reservoir, is also important for the Zaporizhzhya region. Significant excesses in the content of certain heavy metals, high values of magnetic susceptibility and complex relationships between lithogenic and technogenic components were revealed. Although such studies are not directly related to the hydrochemical indicators of the water column, they significantly expand the understanding of the general geoecological state of the Dnipro coastal-channel system in the Zaporizhzhia region and confirm that the military impact has a multi-component nature and is manifested not only in water, but also in bottom sediments and adjacent landscapes [21-22].

The existing mass of scientific works gives reason to assert that the study of the impact of the war on the hydrochemical indicators of the surface waters of the Dnipro River within the boundaries of the city of Zaporizhzhia and the Zaporizhzhia District is based on several complementary directions: spatio-temporal analysis of the quality of the Dnipro waters, modeling of the oxygen regime, ecological assessment of the salt composition, military-ecological analysis of monitoring series, the study of the consequences of the destruction of the Kakhovka Reservoir and forecasting of changes in aquatic ecosystems in the war and post-war periods

In order to achieve the stated aim of the study, we selected two monitoring points for the surface waters of the Dnipro River within the city of Zaporizhzhia and Zaporizhzhia District: 1) Dnipro River, 328 km, Zaporizhzhia, municipal drinking water intake (DVS No. 1) (47°81′80″ N, 35°10′00″ E); 2) Dnipro River, 0 km, drinking water intake of the Bilenke Municipal Enterprise, Bilenkivska Territorial Community, Zaporizhzhia District (47°62′04″ N, 35°05′10″ E).

The first monitoring point is located in the upper pool of the Dnipro Hydroelectric Power Station (Dnipro Reservoir), while the second is below the Dnipro Hydroelectric Power Station within the Kakhovka Reservoir (the channel of the Old Dnipro).

Fig. 1.13 shows the results of the analysis of changes in $BOD_5$, dissolved oxygen, COD, and suspended solids at monitoring point DVS-1 during 2015-2026.

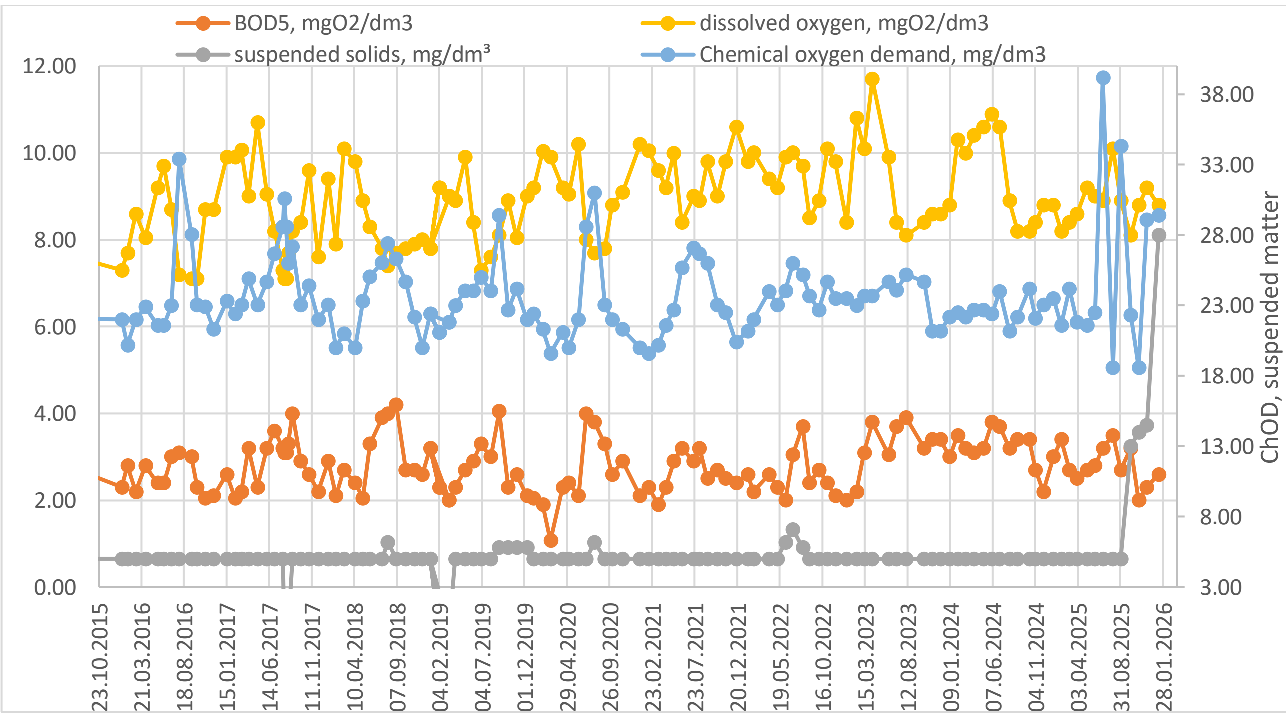


Fig. 1.13 Dynamics of changes in $BOD_5$, dissolved oxygen, COD, and suspended solids at monitoring point DVS-1 during 2015-2026 (January)

Analysis of the dynamics of changes in the value of $BOD_5$ shows that it varies in the range of 2.0-4.0 $mgO_2/dm^3$. The COD indicator constantly exceeds $BOD_5$ and is approximately in the range of 5.5-8.0 $mgO_2/dm^3$, which is expected, since it characterizes the total content of both biodegradable and oxidation-resistant organic substances. This may indicate the presence of hard-to-oxidize organic or certain inorganic components in surface waters.

The concentration of dissolved oxygen has a pronounced seasonal character: in the cold period it increases (up to 9-11 $mgO_2/dm^3$) due to the increased solubility of gases and a decrease in biological activity, while in the warm season it decreases (to 7-8 $mgO_2/dm^3$) due to the increase in water temperature and the activation of microbiological oxidation of organic matter.

As for COD, a significant increase in this indicator has been noted since July 2025 (with the exception of August and November). At the same time, the situation is atypical, because against the background of the increase in COD, the values of $BOD_5$ remain almost unchanged, only a slight summer increase is observed, which does not exceed the levels of previous years. The concentration of dissolved oxygen also maintains the trends characteristic of the previous period.

Another anomaly has been recorded since November 2025 - a sharp increase in the content of suspended solids from the traditional level of about 5 $mg/dm^3$ to 13 $mg/dm^3$, with further increases in the following months. It is worth noting that during the entire period of observation, no such deviations were detected, previously the maximum value was reached only once at the level of 6 $mg/dm^3$.

Fig. 1.14 shows the results of the analysis of changes in phosphate and ammonium ions at monitoring point DVS-1 during 2017-2026 (January).

Concentrations of ammonium $NH_4^+$ vary in a fairly wide range (0.1-0.8 $mg/dm^3$). The most noticeable maxima are observed in 2018 (up to ~0.8 $mg/dm^3$) and in 2022 (about 0.7 $mg/dm^3$). After 2022, there is a certain decrease with periodic short-term increases. In 2024, minimum values are recorded (in places close to 0.1 $mg/dm^3$), after which moderate growth is again observed in 2025-2026.

The content of phosphate ions $PO_4^{3-}$ also varies between 0.2-0.5 $mg/dm^3$ in 2017-2023. Starting from 2024, more pronounced maxima appear - in 2024-2025, concentrations rise to 0.6-0.75 $mg/dm^3$, which are the maximum values for the entire observation period. After the peak values, there are sharp declines, which indicates the instability of phosphate supply. In 2024-2025, there is a certain asynchrony: phosphate content increases, while ammonium ions often remain at lower levels or fluctuate without sharp maxima at this time. The increase in ammonium may be related to the processes of decomposition of organic matter or additional pollution, while the increase in phosphate, especially in 2024-2025, may indicate an increase in anthropogenic influence.

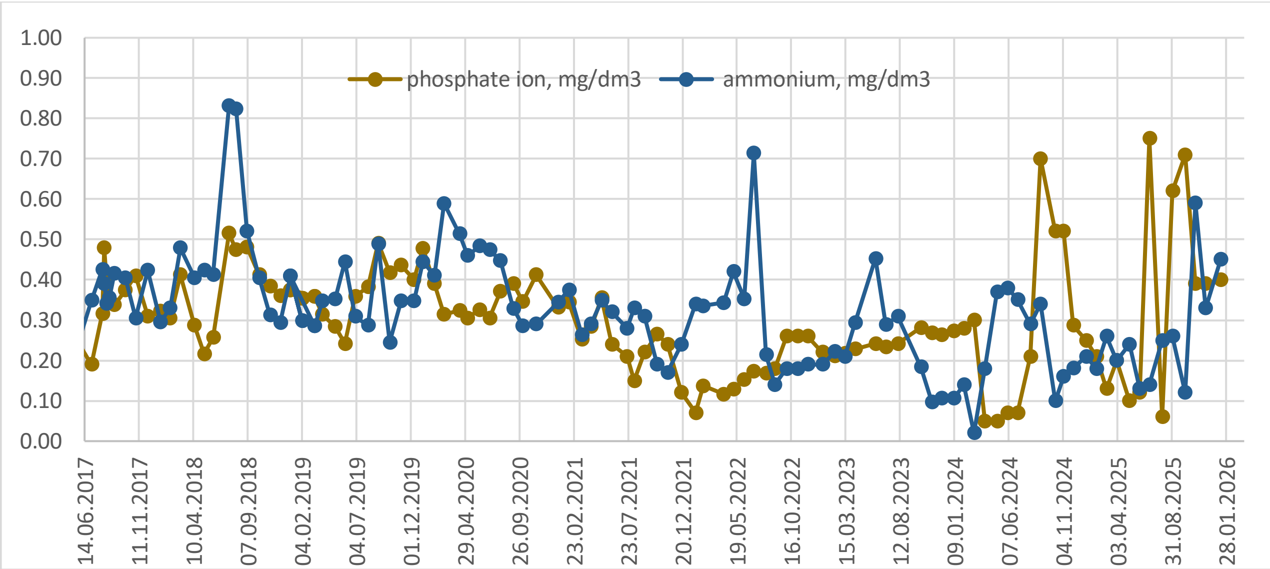


Fig. 1.4 Dynamics of changes in phosphate and ammonium ion content at monitoring point DVS-1 during 2017-2026 (January)

Fig. 1.15 presents the temporal dynamics of nitrite ($NO_2^-$) and nitrate ($NO_3^-$) concentrations in water for the period 2015-early 2026.

The content of nitrites $NO_2^-$ throughout the period remains mainly low and stable - about 0.02-0.05 mg/dm³. At the same time, sharp peaks that significantly exceed the background values are recorded. The most pronounced surge is observed at the beginning of the period (about 0.33 mg/dm³), as well as separate increases in 2021-2022 (up to ~0.1 mg/dm³) and in 2024 (up to ~0.2 mg/dm³). Such short-term growth may indicate episodic disturbances of nitrification processes or the arrival of fresh organic pollution.

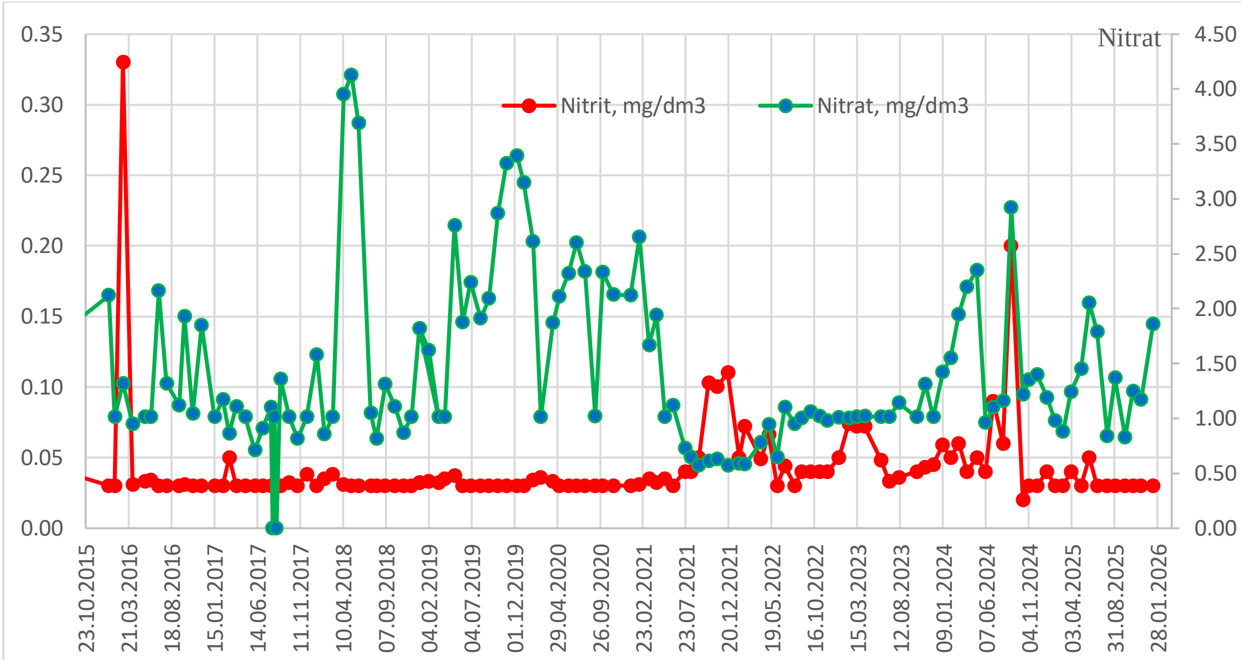


Fig. 1.15 Dynamics of changes in nitrite ($NO_2^-$) and nitrate ($NO_3^-$) concentrations in water for the period 2015-early 2026

Concentrations of nitrates $NO_3^-$ vary in a much wider range (approximately 0.5-4.0 mg/dm³) and are characterized by more pronounced variability. The highest values were recorded in 2018 (more than 3-4 mg/dm³), as well as in 2019-2020 (about 2-3 mg/dm³). In 2021-2022, there is a decrease to minimum levels (~0.5-1.0 mg/dm³), after which in 2023-2024 there is a gradual increase with individual peaks (up to ~2-3 mg/dm³). In 2025-2026, the values remain moderate, with fluctuations within 1-2 mg/dm³.

Nitrites are an intermediate form in nitrification processes, so their concentrations are usually much lower than nitrates, which is confirmed by the given data.

The maxima of nitrite content, as a rule, do not coincide with the maximum values of nitrates, which indicates the short-term nature of $NO_2^-$ accumulation and its rapid oxidation to $NO_3^-$.

During periods of increased nitrates (for example, 2018-2020), nitrites remain at a low level, which indicates the effective flow of nitrification processes.

The dynamics of nitrogen forms reflect the variability of biogeochemical processes in the water body. High concentrations of nitrates can be associated with both external input (flushing from the catchment, anthropogenic influence) and active nitrification. Episodic increases in nitrites indicate short-term disturbances in redox conditions or the arrival of fresh pollution. In general, the system is characterized by relative stability, but with periodic anomalies.

Fig. 1.16 presents the dynamics of sulfate ion ($SO_4^{2-}$) and chloride ion ($Cl^-$) concentrations in surface waters for the period 2015-early 2026.

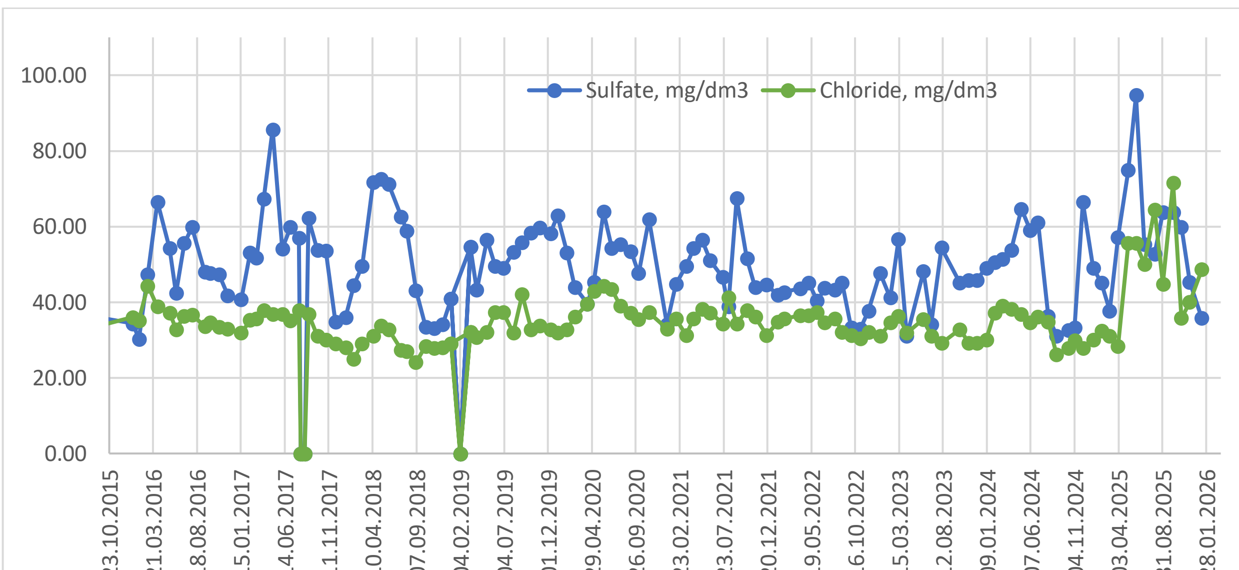


Fig. 1.16 Dynamics of changes in sulfate ion ($SO_4^{2-}$) and chloride ion ($Cl^-$) concentrations in surface waters for the period 2015-early 2026.

Sulfate concentrations varied between 40-65 mg/dm³, with periodic increases. The most notable maxima are observed in 2017 (up to ~85 mg/dm³) and especially in 2025, where values reach maximum levels for the entire period (~90-95 mg/dm³). In

2018-2022, the dynamics are relatively stable, although fluctuations of average amplitude persist. After 2023, there is an upward trend with sharp short-term spikes.

The chloride content is more stable over a long period of time and is usually in the range of 30-40 mg/dm³. In 2015-2023, minor fluctuations are observed without sharp anomalies. Starting from 2024, a tendency to increase concentrations is noted, and in 2025, sharp peaks (up to ~60-70 mg/dm³) are recorded, which are atypical for the previous period.

During the entire period, the content of sulfates was greater than the content of chlorides. Sulfates had a larger amplitude of oscillations and a more pronounced reaction to changing conditions. In 2025, there is a simultaneous increase in both indicators, which may indicate a common source of income or a change in the hydrochemical regime.

The dynamics of sulfates and chlorides reflects both natural processes (mineralization of water, hydrological conditions) and possible anthropogenic influence. A sharp increase in the content of both ions in 2025, especially after a long period of relative stability, may indicate an increase in man-made load.

Fig. 1.17 shows the dynamics of changes in $BOD_5$, dissolved oxygen, and suspended solids from January 2024 to March 2026 at the monitoring point - the drinking water intake in the village of Bilenke.

Throughout the studied period, the $BOD_5$ concentration fluctuates between 2.0 and 3.5 mg $O_2/dm^3$, which indicates a moderate level of organic pollution. In 2024, this indicator is relatively stable with minor fluctuations, with a short-term decrease in early 2025, followed by a gradual increase in the second half of 2025 to peak values at the end of the year. The content of dissolved oxygen throughout the period remains quite high and varies between 8.5-10.5 mg $O_2/dm^3$. In 2024, the values are consistently high, in the first half of 2025 there is a slight decrease, and at the end of 2025 - an increase again, which in general indicates favorable conditions of the oxygen regime of the water environment.

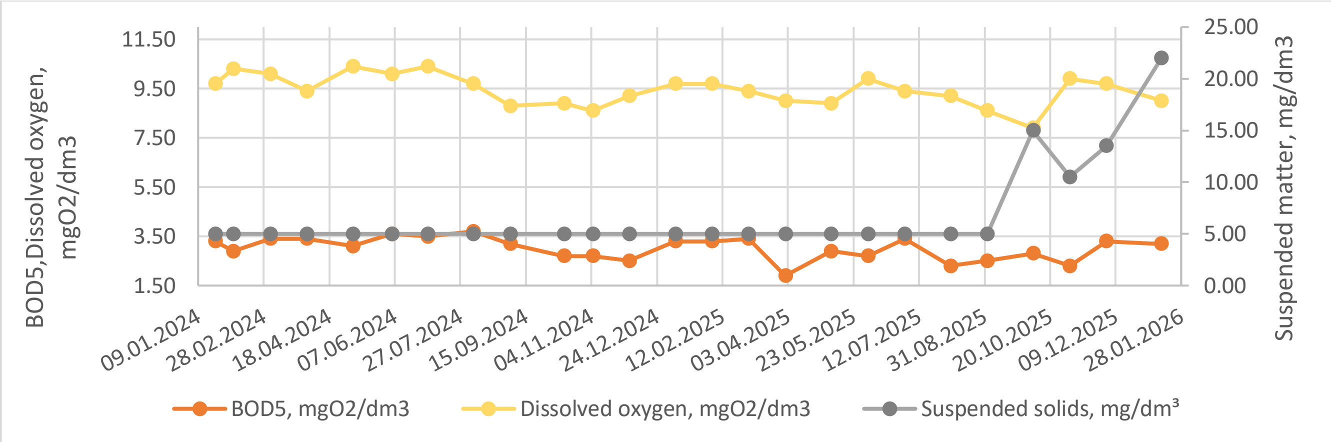


Fig. 1.17 Dynamics of changes in $BOD_5$, dissolved oxygen, and suspended solids from January 2024 to January 2026 at the monitoring point - the drinking water intake in the village of Bilenke.

The most pronounced changes are characteristic of suspended solids: during 2024 and most of 2025, their concentration remains almost constant at the level of about 4-5 mg/dm³, but from the fall of 2025, there was a sudden increase to maximum values of more than 20 mg/dm³ at the end of the studied period. Such dynamics may indicate the influence of short-term but intense factors, in particular hydrological processes or increased anthropogenic load. In general, there is a stable organic and oxygen water regime against the background of a sharp and abnormal change in the content of suspended matter at the end of the observation period.

Fig. 1.18 shows the change in ammonium and phosphate ion concentrations in surface waters from January 2024 to January 2026.

The ammonium content fluctuates within the range of approximately 0.05-0.45 mg/dm³ throughout the entire time. At the beginning of 2024, its values are relatively low, after which there is an increase in the spring and early summer to a maximum of about 0.4-0.43 mg/dm³. In the second half of 2024, the concentration of ammonium decreases and continues to be mainly at a moderate level with minor fluctuations. Throughout 2025, there were ups and downs, with local increases in the middle and end of the year, and at the beginning of 2026, the values stabilize at around 0.25-0.27 mg/dm³.

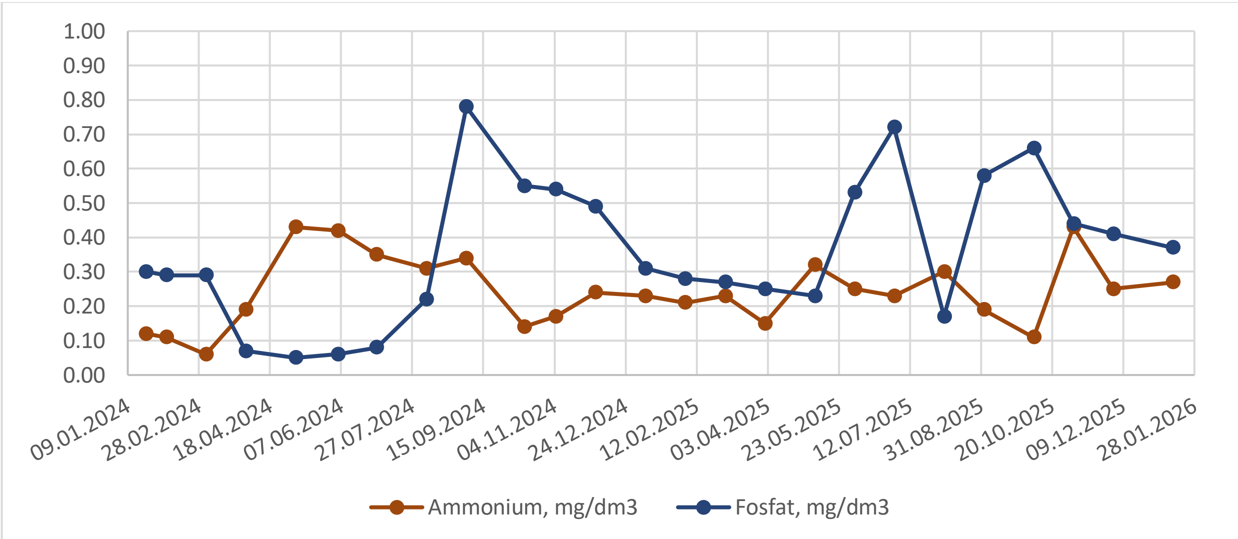


Fig. 1.18 Dynamics of changes in ammonium and phosphate ion concentrations in surface waters from January 2024 to January 2026.

The concentration of phosphates changes more sharply and in a wider range - from 0.05 to 0.8 mg/dm³. At the beginning of 2024, the content of phosphates was at the level of 0.3 mg/dm³, in the spring there is a decrease to minimum values, after which a sharp peak of almost 0.8 mg/dm³ is recorded in September 2024. In the future, the values gradually decrease at the end of 2024 - the beginning of 2025, but in the summer and autumn of 2025 significant fluctuations are again observed with several pronounced rises above 0.6-0.7 mg/dm³. In general, the graph shows more stable dynamics of ammonium and much more variable dynamics of phosphate content, which may indicate the periodic influence of certain natural or anthropogenic factors on the phosphate regime of water.

Fig. 1.19 presents the dynamics of nitrate and nitrite concentrations in surface waters in the period from January 2024 to January 2026.

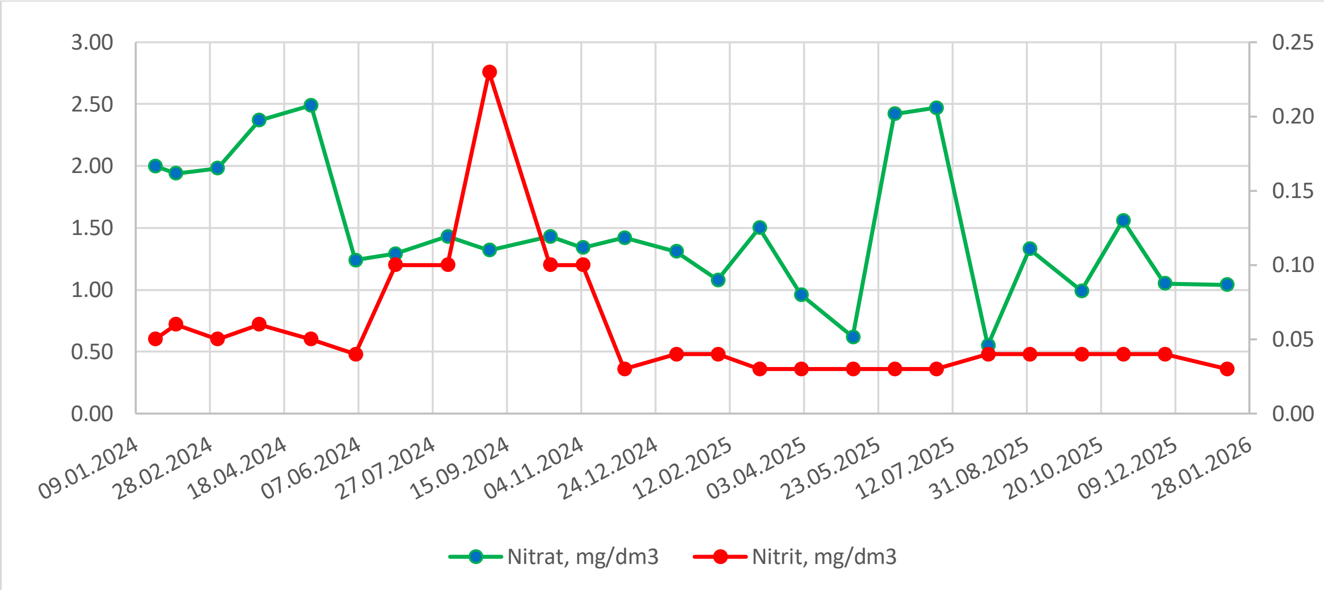


Fig. 1.19 Dynamics of changes in nitrate and nitrite concentrations in surface waters in the period from January 2024 to January 2026

During the entire period, the nitrate content is characterized by moderate variability with fluctuations in the range from 1.0 to 2.5 mg/dm³. In early 2024, nitrate levels are relatively stable and fairly high, increasing to local maxima in the spring, followed by a marked decline in the early summer. In the second half of 2024, the concentration of nitrates fluctuates around the average values. In the spring of 2025, a decrease to the minimum values for the studied period is noted, while in the summer months a sharp increase of nitrates to a level of more than 2.4 mg/dm³ is recorded. In the future, the nitrate content will decrease and at the end of 2025 - at the beginning of 2026 will stabilize at the level of about 1.0-1.1 mg/dm³.

The concentration of nitrites in the water during the entire period is significantly lower, but it is characterized by sharper and more uneven dynamics. In the first half of 2024, nitrite values mostly do not exceed 0.07 mg/dm³, after which there is a pronounced sharp peak in August-September 2024 with an increase to almost 0.25 mg/dm³. After that, the concentration decreases rapidly and during most of 2025 is kept at a relatively low and stable level, around 0.03-0.05 mg/dm³, with minor fluctuations.

At the end of 2025, no significant increases in nitrites are observed, and at the beginning of 2026, the values remain low. In general, the obtained data indicate a more stable nitrate water regime and episodic, short-term spikes in nitrite content, which may be associated with temporary disturbances of nitrification processes or external input of nitrogen-containing compounds.

Fig. 1.20 shows the change in sulfate and chloride concentrations in water for the period from January 2024 to January 2026.

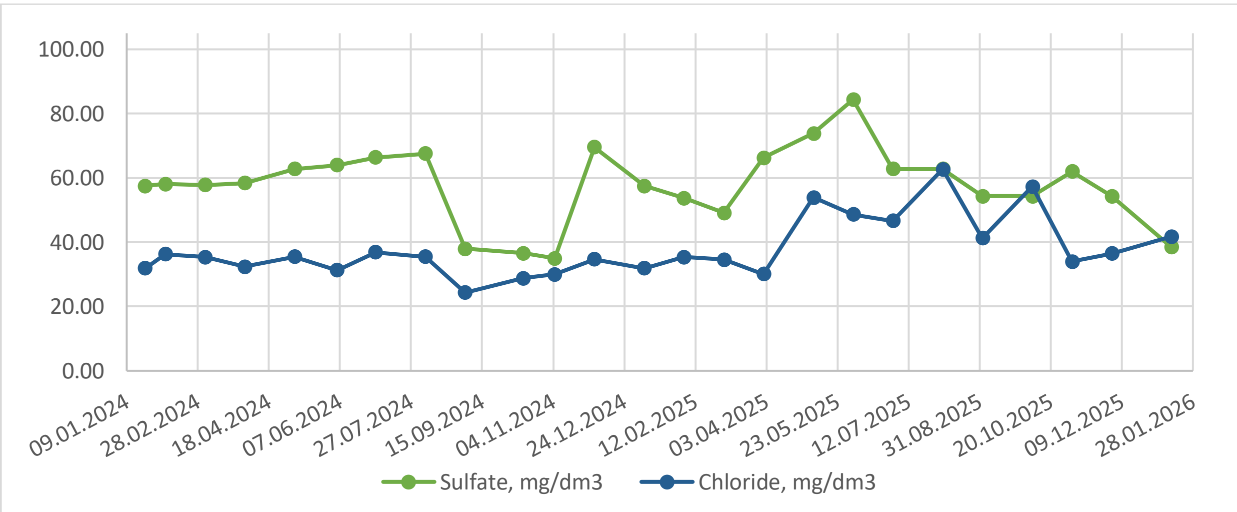


Fig. 1.20 Dynamics of changes in sulfate and chloride concentrations in water for the period from January 2024 to January 2026.

The content of sulfates during the entire period is higher than the concentration of chlorides and is characterized by noticeable variability. At the beginning of 2024, sulfate values are around 55-60 mg/dm³, with a gradual increase to 65-67 mg/dm³ in the spring and early summer, followed by a sharp drop to around 35-40 mg/dm³ in September. At the end of 2024, the concentration of sulfates increases sharply to a local maximum of about 70 mg/dm³, and at the beginning of 2025 it decreases again. In mid-2025, the highest level for the entire monitoring period is recorded — more than 80 mg/dm³, after which the values gradually decrease and approach 40 mg/dm³ by the beginning of 2026. Chloride concentration varies in a narrower range - from 25 to 65 mg/dm³. In 2024, the chloride content was in the range of 30-37 mg/dm³ with a short-term decrease to minimum values in autumn. In 2025, an increase is observed in the spring, and a maximum of about 60-65 mg/dm³ was recorded in the summer. At the end of 2025, the concentration of chlorides decreases, and at the beginning of 2026, it stabilizes at the level of about 40 mg/dm³.

A comparative analysis of hydrochemical indicators of surface waters at monitoring points DVS-1 (the upper pool of Dnipro HPP in the city of Zaporizhzhia) and the village of Bilenke, located downstream, indicates the formation of a cascade spatio-temporal response of the water system to anthropogenic and wartime impacts. Given that the city of Zaporizhzhia is subjected to more intense shelling, DVS-1 serves as the zone of primary formation of hydrochemical anomalies, whereas the water intake in the village of Bilenke is the site of their subsequent transformation and accumulation.

In the upper pool, a relatively stable oxygen and organic regime is generally observed: $BOD_5$ fluctuates within moderate values, and dissolved oxygen remains high. At the same time, COD shows a sharp increase in 2025 without a corresponding rise in $BOD_5$, which indicates the appearance of organic or technogenic compounds resistant to biochemical oxidation. In Bilenke, these processes manifest themselves differently: COD rises more gradually and persistently, without sharp peaks, which indicates not direct pulse impacts but the accumulation and transformation of pollutants carried by the current.

The most indicative difference is the dynamics of suspended solids. At monitoring point DVS-1, their increase is local and impulsive in nature, associated with direct physical disturbances of the hydrosystem, whereas in Bilenke, in 2025, a sharp and substantial increase in their concentration to more than 20 mg/dm³ was recorded after a long period of stability. This indicates that material mobilized in the upper sections accumulates downstream, and that the additional involvement of bottom sediments in resuspension processes is also possible. At the same time, the absence of a sharp decrease in dissolved oxygen content in surface waters at both sites indicates the predominantly mineral or weakly biologically active nature of the suspended particles.

Biogenic elements show complex spatial differentiation. In the area of DVS-1, the content of ammonium and phosphate ions is characterized by sharp short-term peaks, which reflects pulsed inflows of pollution and disruption of the stability of biogeochemical processes.

In Bilenke, these same indicators display a smoother but more prolonged dynamics, which points to their gradual transport and secondary redistribution in the aquatic environment.

The nitrate content in both reaches changes relatively consistently; however, in the lower pool these fluctuations are less abrupt, which reflects the equalization of concentrations along the flow. Nitrite content remains low, but episodic peaks, more characteristic of DVS-1, indicate short-term disturbances of nitrification precisely in the zone exposed to more intense impacts.

Mineral components also show clear spatial differentiation. Sharp fluctuations of sulfates and chlorides are observed at DVS-1, especially in 2025, which reflects direct man-made influence and disturbance of the hydrochemical regime.

In Bilenke, these changes appear as a smoother but coordinated increase in both ions, which indicates their transport and accumulation in the lower part of the flow.

Summarizing, it is possible to note a fundamental difference between the two monitoring points (sections of the Dnipro River). At DVS-1, where the impact of military actions is more intense, hydrochemical indicators react quickly, sharply and impulsively, forming local anomalies.

In Bilenke, certain transformations do occur, yet persistent changes are present that reflect the processes of transport, mixing, and accumulation. Thus, the river system performs the function of a natural integrator of impacts, where the upper pool is the zone of generation of hydrochemical disturbances and the lower pool is the zone of their accumulation and partial transformation. In the context of intensified shelling of

Zaporizhzhia, this means that the upper section forms the primary ecological risks, while in the lower section they spread spatially and become fixed in the form of an altered hydrochemical background.

*Conclusions.* The analysis of hydrochemical indicators at the DVS-1 monitoring point for the period 2015-2026 indicates a generally relatively stable state of the water environment with periodic phases of destabilization, which are especially clearly manifested after 2024.

The organic load, reflected by $BOD_5$ and COD, has a moderate level in most of the period. At the same time, an atypical situation is recorded in 2025: the level of COD increases significantly (since July), while $BOD_5$ remains relatively stable. This is an anomaly that indicates an increase in the proportion of hard-to-oxidize organic or even inorganic reducing agents (for example, humic substances, man-made products), without a corresponding increase in biologically available organic substances.

The level of dissolved oxygen has seasonal dynamics: high values in the cold period and a decrease in the warm period. Its inverse relationship with $BOD_5$ and COD confirms the active use of oxygen in the processes of oxidation of organic matter. At the same time, the absence of a sharp drop in oxygen content even during periods of increased COD (especially in 2025) indicates sufficient aeration of water or the fact that a significant part of the substances that form COD is not involved in intensive biochemical oxidation.

The content of suspended solids remains stable for a long time (~5 $mg/dm^3$), which is typical for conditions of a relatively stable hydrological regime. However, a sharp increase at the end of 2025 (up to 13 $mg/dm^3$ and above) is an anomaly. Unlike previous years, when similar values did not exceed 6 $mg/dm^3$ and increases were episodic in nature, this increase is long-lasting. It is probably related to local anthropogenic influence. It is important that this increase is accompanied by an increase in COD, which is consistent with the adsorption of organic substances on suspended particles. Therefore, suspended substances act as a carrier of organic load and additionally affect the oxygen regime, worsening the aeration conditions.

The dynamics of biogenic elements (ammonium and phosphate ions) reflects the variability of both internal processes and external inputs. Ammonium content is characterized by sharp but short-term peaks, which are a typical sign of the influx of fresh organic pollution or the activation of mineralization processes. The decline in ammonium after the peaks is usually associated with its oxidation to nitrites and nitrates. This is confirmed by the behavior of nitrates, which show a smoother but much broader amplitude of changes (up to 3-4 mg/dm$^3$), with maxima in 2018-2020 and renewed growth in 2023-2024.

Nitrites, as an intermediate form, remain at a low level, but with episodic sharp spikes (especially at the beginning of the period, in 2021-2022 and 2024). Such peaks are an indicator of short-term nitrification disturbances or local oxygen deficiency in microzones. It is important that these spikes do not coincide with nitrate maxima, which indicates the rapid conversion of $NO_2^-$ to $NO_3^-$ and, in general, the effective flow of nitrification processes in the system.

The content of phosphate ions is unstable, especially after 2024, when their concentrations reach maximum values (0.6-0.75 mg/dm$^3$). Unlike ammonium, their increases are of a longer duration and are often not synchronized with nitrogen forms. This indicates a different origin.

The mineral composition (sulfates and chlorides) generally reflects the background hydrogeochemical conditions, but also reacts to external influences. The content of sulfates has a larger amplitude of fluctuations and shows sharp peaks (2017 and especially 2025 — up to 90-95 mg/dm$^3$), which can be associated with both natural processes (oxidation of sulfur-containing compounds) and technogenic influence. The content of chlorides remains stable for a long time, but from 2024 their concentration increases, and in 2025 sharp peaks are recorded (up to 60-70 mg/dm$^3$). Synchronous growth of sulfates and chlorides in 2025 indicates a common source of income.

The impact of the war on the recorded dynamics of hydrochemical indicators at DVS-1 is indirect, but can be clearly traced through a set of anomalies that intensify after 2022 and especially in 2024-2025. It is important to understand that the war does not create "new" processes in the water environment, but sharply changes the intensity and balance of already existing ones - hydrological, biogeochemical, and anthropogenic.

Under conditions involving the use of Shahed-type strike drones and missiles, various substances may enter water bodies, simultaneously causing an increase in suspended solids and a rise in chemical oxygen demand (COD). The sources of such pollution include both explosion products and the components of the technical devices themselves, as well as materials from destroyed infrastructure.

First of all, a significant contribution is made by products of detonation of explosive substances containing organic compounds. During the explosion, partially oxidized organic residues, nitro compounds and finely dispersed solid particles, in particular soot, are formed. These components increase COD as chemically oxidizable substances and at the same time form the fraction of suspended substances in water.

An important source is also fuel and lubricants - liquid hydrocarbon fuels, lubricating oils and hydraulic fluids, which can enter the water due to equipment damage. They are characterized by a high content of organic carbon, which leads to the growth of COD, and are also able to form emulsions or adsorb on solid particles, indirectly increasing the concentration of suspended substances.

A separate role is played by the debris of the hulls and structures of drones and missiles. Particles of metals, polymers, composites, rubber and insulating materials enter the water. In a finely dispersed state, they directly increase the content of suspended substances, and organic components of polymers with partial degradation can additionally affect the growth of COD.

Combustion products accompanying explosions and fires also have a significant impact. These include soot, polycyclic aromatic hydrocarbons and other partially oxidized organic compounds. They are simultaneously components of suspended substances and a source of increased COD.

In addition, construction materials that enter the water due to the destruction of structures make a significant contribution to pollution. These are cement dust, particles of concrete, bricks, silicates, as well as paints and coatings. Mineral components increase the content of suspended solids, while organic additives and coatings can increase COD.

In addition, heavy metals, electronic components, and electrolytes may appear in the water, which, although they do not always have a direct effect on COD, are capable of suppressing microbiological processes, changing the general nature of the transformation of pollutants.

The increase in ammonium-ion content in surface waters under wartime conditions may be associated with the thermal destruction of nitrogen-containing materials during explosions and fires, as well as with the decomposition of organic and technical substances containing nitrogen. Under normal conditions, ammonium in water undergoes nitrification with the formation of nitrites and nitrates, which is accompanied by oxygen consumption; however, under wartime conditions this process is often suppressed because of the toxic effect of impurities, high water turbidity, and disruption of the functioning of microbiocenoses. As a consequence, ammonium can accumulate in the aquatic environment without a significant effect on $BOD_5$ and without a noticeable decrease in dissolved oxygen.

Phosphate ions enter the water mainly as a result of the destruction of building materials, washing of dust from man-made surfaces, damage to infrastructure, as well as the release of compounds from soils and man-made deposits. The simultaneous increase of ammonium and phosphate ions at a stable level of dissolved oxygen and the absence of $BOD_5$ growth indicates the dominance of pulsed man-made input of substances and suppression of natural processes of nitrogen and phosphorus cycles. Under such conditions, the water system accumulates mineral forms of nitrogen and phosphorus without effective biological transformation, while changes in COD and suspended matter reflect the parallel arrival of organic and mechanical degradation products.

The increase in the content of sulfates can be associated with the oxidation of sulfur-containing compounds that are formed during fuel combustion and explosive processes. In particular, sulfur dioxide entering the atmosphere during combustion is oxidized to sulfuric acid in an aqueous environment and further transforms into the form of sulfate ions. An additional source is the destruction of building materials, in particular gypsum and cement components, which contain sulfate compounds. Industrial objects and dust aerosols of mineral origin can also contribute.

Chlorides can enter the water as a result of the burning of polymeric materials, especially those containing chlorine, such as polyvinyl chloride. During the thermal destruction of such materials, hydrogen chloride is formed, which transforms into chloride ions in an aqueous medium. In addition, the source of chlorides can be technical fluids, electrolytes, cooling mixtures and products of the destruction of engineering infrastructure. Chlorides are conservative ions, they do not decompose and are practically not removed from water by natural processes, therefore they tend to accumulate.

The overall dynamics of changes in hydrochemical indicators in the water of the Dnipro River (the village of Bilenke) in 2024-early 2026 indicate a relatively stable state of the oxygen and organic regimes against the background of more dynamic and, in places, anomalous changes in biogenic and mineral components.

Indicators of $BOD_5$ and dissolved oxygen show an inverse relationship typical for relatively clean or moderately polluted waters. During most of the period, $BOD_5$ is maintained at the level of 2.0-3.5 mg $O_2/dm^3$, while the concentration of dissolved oxygen remains high (8.5-10.5 mg $O_2/dm^3$). This indicates the balance of biochemical oxidation processes and sufficient water aeration. A slight decrease in oxygen in the first half of 2025 is accompanied by a relative stabilization or even a decrease in $BOD_5$, which is atypical and may indicate not so much an increase in organic load, but the influence of the temperature factor (decrease in oxygen solubility in the warm period) or hydrobiological processes (increased respiration of hydrobionts). Further growth of $BOD_5$ in the second half of 2025 is logically consistent with an increase in the supply of organic matter (for example, during the summer-autumn development of phytoplankton or the washing of organic matter from the catchment).

At the same time, a sharp increase in the concentration of suspended solids in the fall of 2025 (over 20 mg/dm$^3$) against the background of their long-term stability (4-5 mg/dm$^3$) is abnormal. This phenomenon is probably of anthropogenic origin. It is important that this growth is not accompanied by a sharp increase in $BOD_5$ or a decrease in oxygen, which indicates the predominantly mineral nature of the suspended particles. At the same time, the increase in suspended solids could contribute to the adsorption of phosphates and temporary changes in their concentrations.

The content of ammonium ions increases in the spring (2024), which may be associated with flushing from the catchment and mineralization of organic matter, while the subsequent decrease is due to active nitrification. This is confirmed by the behavior of nitrates: their increase in spring and summer reflects intensive oxidation of ammonium. At the same time, the sharp increase in nitrates in the summer of 2025 after the spring minimum is an indicator of either increased inflow from the basin (agricultural runoff) or activation of nitrification processes under favorable temperature conditions.

Nitrites, as an unstable intermediate form, show episodic peaks, the most pronounced of which was recorded in August-September 2024. Such a surge is a classic sign of an imbalance between nitrification stages (oxidation of $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) or local oxygen deficiency in microzones, even if the total content of dissolved oxygen remains high. This may be due to the arrival of fresh organic matter or local pollution.

Phosphate-ion content is the most variable indicator. Maxima, especially in September 2024 and in the summer-autumn period of 2025, indicate short-term inputs, most likely from wastewater and agricultural runoff. Importantly, these peaks are not always accompanied by a proportional increase in $BOD_5$, which may indicate rapid phosphate uptake by phytoplankton or their binding to suspended particles. The relationship between maxima of phosphate content and suspended solids at the end of 2025 may indicate intense resuspension processes in bottom sediments, where phosphorus accumulates in a bound form.

Mineral components (sulfates and chlorides) reflect both natural and anthropogenic factors. The sulfate content has peaks (up to more than 80 $mg/dm^3$ in 2025), which may be related to industrial discharges or oxidation of sulfur-containing compounds. The content of chlorides does not have sharp maxima, but its increase in 2025 (up to 60-65 $mg/dm^3$) indicates an increase in anthropogenic influence (domestic sewage, man-made load). Concordant chloride and nitrate maxima in 2025 may indicate a common source.

For the water intake in the village of Bilenke, the influence of wartime factors likewise manifests itself not as a simultaneous deterioration of all indicators, but as a disruption of the stability of the hydrochemical regime, the appearance of sharp impulse changes, and atypical combinations of indicators, especially in 2024-2025.

First of all, this is visible against the background of a generally stable oxygen and organic regime. $BOD_5$ throughout the period remains within moderate values, and dissolved oxygen is high. This means that there was no mass influx of easily oxidizable organic matter (for example, large volumes of domestic sewage). At the same time, such "normality" is somewhat misleading, since other indicators show significant disturbances. That is, the war is manifested here not because of classic organic pollution, but because of another type of influence - hydrological and man-made.

The most telling is the sharp increase in suspended solids in the fall of 2025 (more than 20 $mg/dm^3$ after a long-term level of 4-5 $mg/dm^3$). Such a change has the characteristics of a military or related influence. It is important that this increase is not accompanied by a proportional increase in $BOD_5$ and a drop in oxygen, that is, suspended substances are mainly of mineral or weakly bioavailable origin. This is a typical indicator of mechanical (rather than organic) disruption of the system, which corresponds well with the consequences of military actions.

Thus, in the area of the drinking water intake in the village of Bilenke, the influence of the war manifests itself as a sharp increase in suspended solids without deterioration of the oxygen regime; pulse-like inputs of pollutants, including peaks in phosphate and nitrite content; changes in water mineralization, including the synchronous increase in sulfate and chloride content; and so forth.

Importantly, unlike DVS-1, where the technogenic component is more clearly manifested through COD, in Bilenke the hydrological-geochemical effect predominates - that is, the impact exerted through changes in the physical state of the system (channel, bottom sediments, runoff), and not solely through direct chemical pollution.

Thus, comparing the hydrochemical data with periods of intensified shelling of the city of Zaporizhzhia makes it possible to interpret the recorded changes as a consequence of short-term but intense inputs of destruction and combustion products into the river system. This is manifested in the form of increasing COD and suspended solids under a relatively stable oxygen regime, which is characteristic of an impact type of pollution rather than of a prolonged organic load. In addition, in our opinion, one may also speak of a cumulative effect of previous impacts which, under conditions of intensified shelling of the city, manifested themselves in the form of the anomalies under study.

In sum, it is more appropriate to speak not of a catastrophic deterioration in water quality, but of the system's transition to an unstable state, in which, even under normal average values, the frequency and amplitude of anomalies increase sharply, which is a characteristic sign of the influence of wartime factors on aquatic ecosystems.

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# 2 ECOLOGICAL ASSESSMENT AND FORECASTING OF SURFACE WATER CONDITIONS IN THE SOUTHERN BUG RIVER IN THE TERRITORY OF MYKOLAIV REGION

The Southern Bug River basin is one of the major hydrological systems of Ukraine, located entirely within the country and covering a diverse range of natural and socio-economic landscapes. The river originates in the Podolian Upland and flows southeastward for approximately 700 km before emptying into the Black Sea via the Dnipro–Bug estuary. The basin area is characterized by a combination of upland, forest-steppe, and steppe zones, which strongly influences its hydrological regime, water balance, and ecological conditions.

Hydrologically, the Southern Bug is a moderately regulated river system with a predominance of natural flow characteristics in its upper and middle reaches, while the lower reaches are more affected by hydraulic structures, water abstraction, and local anthropogenic modification. Seasonal discharge variability is significant, with high spring floods caused by snowmelt and rainfall, and low-flow conditions during summer and early autumn. This seasonal instability plays a key role in shaping sediment transport, water quality dynamics, and ecosystem functioning throughout the basin.

The geological and geomorphological structure of the basin is diverse, consisting mainly of crystalline rocks in the upper reaches and sedimentary formations in the middle and lower parts. This diversity determines the chemical composition of surface waters, contributing to the presence of bicarbonates, calcium, and magnesium as dominant ions. The river's catchment is also influenced by loess soils, which are highly susceptible to erosion, especially under intensive agricultural use. As a result, diffuse pollution and sediment inflow represent important components of the basin's environmental load.

Land use in the Southern Bug basin is dominated by agriculture, which significantly shapes both hydrological and hydrochemical processes. Fertilizer application, pesticide use, and soil erosion contribute to elevated concentrations of nutrients such as nitrogen and phosphorus compounds in surface waters. In addition, urban wastewater discharge from settlements and industrial zones introduces organic matter and various pollutants, affecting dissolved oxygen levels and increasing biochemical oxygen demand ($BOD_5$) in certain sections of the river.

Despite anthropogenic pressure, the Southern Bug retains relatively high ecological resilience compared to heavily regulated river systems. Its partially natural flow regime supports self-purification processes, including dilution, sedimentation, and biological degradation of organic substances. However, this capacity is not uniform along the river and is significantly reduced in areas with high population density, intensive agriculture, and industrial activity.

From an ecological perspective, the basin is characterized by moderate to high vulnerability, particularly due to the combined effects of climate variability, land degradation, and increasing human pressure. Periodic low-water conditions exacerbate pollution concentrations, while extreme weather events intensify erosion and pollutant transport. In recent years, additional stress has been associated with broader regional disturbances, including indirect impacts of military activities, which have affected infrastructure stability and environmental monitoring capacity.

Overall, the Southern Bug River basin represents a dynamic and sensitive freshwater system where natural hydrological processes interact closely with long-term anthropogenic influences. Sustainable management of the basin requires integrated water resource planning, improved wastewater treatment, soil conservation practices, and strengthened environmental monitoring to ensure the preservation of its ecological functions and water quality.

In Ukraine's water supply system, surface waters play an important role, accounting for approximately 80% of the demand. However, at the same time, the country is among those with limited reserves of freshwater. The problem of water scarcity is particularly acute in the south, especially in the Mykolaiv region. In terms of specific water reserves per area and per capita, the region is among the least provided for among all regions of the country.

The issues of water supply and water security have become more urgent in Ukraine under wartime conditions. Considering that Ukraine has an extensive water infrastructure, which includes large multipurpose reservoirs, hydroelectric power station dams, cooling systems for nuclear power plants, etc., the impact of the war is already environmentally hazardous and catastrophic. In addition, during military aggression, surface and groundwater, as well as atmospheric air, are subjected to direct military influence. This impact is noticeable for major rivers such as the Dnipro, Southern Bug, Inhul, Siverskyi Donets, and Danube, as well as for smaller rivers, natural and artificial reservoirs, and coastal areas of the Azov and Black Seas [1–20].

Therefore, the study of anthropogenic influence, including during military actions, is especially relevant for the Southern Bug River, which is a vital strategic resource for the ecological, social, and economic development of the Mykolaiv region of Ukraine.

The main source of water supply for most settlements in the Mykolaiv region is surface water, particularly the Southern Bug, Syniukha, and Inhul rivers. In rural areas and district centers, however, underground aquifers are more commonly used.

The rivers within the Southern Bug basin are actively used to meet the needs of industry and the agricultural sector, and they also serve as a source for the replenishment of underground water reserves and play an important role in maintaining the natural ecosystems of the region.

Despite the fact that the ecological state of the Southern Bug basin has already been the subject of scientific research in various fields [1–16], the issues of monitoring and analyzing the quality of surface waters in this area remain extremely relevant.

Therefore, the main objective of the conducted study was to assess the anthropogenic and military impact on the surface waters of the Southern Bug River within the Mykolaiv region, which are used for the drinking water supply of the city of

Yuzhnoukrainsk, in order to forecast the development of the ecological situation and to formulate measures for its improvement during the post-war recovery of the country.

The study was conducted based on data from the Laboratory of Water and Soil Monitoring of the Regional Office of Water Resources (ROVR) in the Mykolaiv region and covered the period from 2003 to 2024 in the context of the following indicators: phosphate ions, ammonium ions, sulfate ions, chloride ions, $BOD_5$, and dissolved oxygen.

Methods of comparison, computer-based statistical data processing using correlation analysis of the results, as well as modeling and forecasting using regression analysis, were applied.

The basin of the Southern Bug River is considered one of the oldest drainage areas on the territory of Ukraine. Its formation is closely linked to tectonic processes that occurred within the Ukrainian Shield – one of the key structural elements of the East European Platform. The geological foundation of the basin is represented by massive formations of crystalline rocks of Archean and Proterozoic age, whose age ranges from 2.5 to 3.0 billion years. The foundation consists of granites, gneisses, quartzites, and amphibolites, which have a complex block structure with pronounced fracturing [1,2].

In the middle section of the river – from Haivoron to Pervomaisk – ancient crystalline rocks are exposed, forming unique granite rapids. This region, known as the «Buzkyi Gard», has exceptional geomorphological and environmental significance and represents an interaction between tectonic movements and contemporary erosional-accumulative processes [3,4].

In terms of relief, the basin is structurally complex, encompassing territories of three geographical zones: the Volhynian-Podolian and Dnipro Uplands, as well as the Black Sea Lowland. In the upper reaches of the Southern Bug, deep valleys with a dense network of gullies and ravines developed on loess soils are formed. The middle course is characterized by rocky outcrops of magmatic rocks that form canyons, waterfalls, and rapids. The lower part of the river has wide, weakly incised valleys with alluvial and deluvial deposits, where floodplains, oxbow lakes, deltas, and limans are formed [2].

Tectonic uplifts and subsidences were key factors in the development of the basin, altering the erosion base and contributing to the formation of numerous tributaries, gullies, and ravines. This led to the uneven development of the Southern Bug's valley network. In the lower course, the Pliocene and Pleistocene transgressions of the Black Sea had a significant impact, resulting in the accumulation of thick layers of marine sediments – clays, sandy loams, sands with shell fragments. These deposits are highly permeable and influence the hydrogeochemical regime [2].

The chemical properties of the water are determined by the geological foundation. The water of the Southern Bug is predominantly of hydrocarbonate-calcium composition. This is due to the dissolution of carbonate rocks and secondary salinization of alluvial layers. In the middle and lower courses, mineralization can reach 600–1000 mg/dm$^3$, which significantly affects both aquatic biota and the suitability of water for technical use. Fracturing of the crystalline rocks ensures stable underground inflow to the river during low-water periods, supporting the base flow [6].

Paleogeographic research indicates that the geological structure of the area significantly influenced the settlement of the basin even in prehistoric times. As early as the Mesolithic, the river served as an important transport artery, source of water, and food resources for early communities. Numerous archaeological sites have been discovered near the cities of Pervomaisk, Voznesensk, and Mykolaiv, attesting to continuous human occupation of this region [2].

In recent decades, anthropogenic pressure on the Southern Bug basin has intensified, associated with the development of cities, industrial facilities, agriculture, and a decline in the effectiveness of environmental control. The main sources of pollution include industrial effluents, domestic wastewater, urban stormwater runoff, and agrochemicals – nitrates, phosphates, pesticides, and herbicides washed off from fields [7,8].

The most polluted areas are zones around Khmelnytskyi, Vinnytsia, Pervomaisk, Voznesensk, and Mykolaiv, where the river flows into the Buh Estuary. High concentrations of heavy metals (Cu, Zn, Pb, Ni, Cd), petroleum products, phenols, and surfactants are recorded in the water. This negatively affects benthic ecosystems and the overall ecological condition of the river. Thanks to geoinformation analysis, ecological risk maps have been created [9].

A separate threat is eutrophication, which arises due to excessive input of phosphorus and nitrogen, causing rapid development of blue-green algae. The most vulnerable is the middle course in the Podillia region, where more than 70% of land is used for agriculture. Eutrophication leads to oxygen depletion, reduced water transparency, and decreased biodiversity [10,11].

An increase in the content of phosphates, nitrites, organic matter, and ammonium is observed in the water, causing the ecosystem to shift into a stable eutrophic or hypertrophic state. At the same time, the composition of the ichthyofauna changes – valuable fish species are displaced by less demanding or invasive ones. The number of mollusks and zooplankton decreases, disrupting food chains [8].

Additional harm is caused by thousands of small water bodies – over 3,500 ponds, reservoirs, and dams – that slow down the flow, reduce aeration, and contribute to the formation of anaerobic zones. Under such conditions, toxic compounds such as methane and hydrogen sulfide are formed, which further deteriorate the state of the aquatic environment.

The Southern Bug is the second-longest river located entirely within Ukraine. Its basin covers an area of over 64,000 km$^2$ and includes seven regions, with a population of about 3 million people. The total length of its tributaries exceeds 13,000 km; the largest among them are the Buzhok, Ikva, Syniukha, and Chychykliia [12].

The seasonal dynamics of water flow are clearly expressed: in spring (March–April), during snowmelt, up to 60% of the annual runoff is formed. In summer and autumn, water levels decrease due to lack of precipitation, increased evaporation, and active water abstraction. In dry years, the average discharge in the lower reaches can drop to 60–70 $m^3/s$ [13].

Over 3,000 artificial water bodies operate in the basin territory, significantly altering the natural distribution of water, affecting temperature, aeration, and self-purification processes. This disrupts fish migration, reduces the productivity of floodplain zones, and changes the hydrological regime [14].

In the Mykolaiv region, water withdrawal during the summer period reaches 8–10 million $m^3$, while only up to 20% is returned. This causes runoff deficits, drying of small tributaries, and degradation of the coastal ecosystem [13].

Water quality remains problematic. Exceedances of ammonium nitrogen, phosphates, and $BOD_5$ levels are frequently recorded. In the lower course, especially near the estuary, mineralization reaches 800–1000 $mg/dm^3$, making it difficult to use for drinking purposes [15].

Compliance with the EU Water Framework Directive is a current task. The existing monitoring system is mostly focused on chemical indicators, while bioindication is rarely applied. This hinders an adequate assessment of the state of water bodies [11].

Under conditions of climate change, prolonged drought periods, and the risk of desertification in certain regions, it is necessary to implement integrated water resource management: modernization of treatment facilities, ecological restoration of rivers, creation of buffer zones, and optimization of water abstraction regimes [15].

In order to achieve the stated objective, an analysis of the chemical composition of water was conducted at the drinking water intake site in the city of Yuzhnoukrainsk, Mykolaiv region: the Southern Bug River, 153 km mark, near the village of Oleksiivka (village of Pankratove), (47°86′87″ N, 31°11′97″ E) (Fig. 2.1).

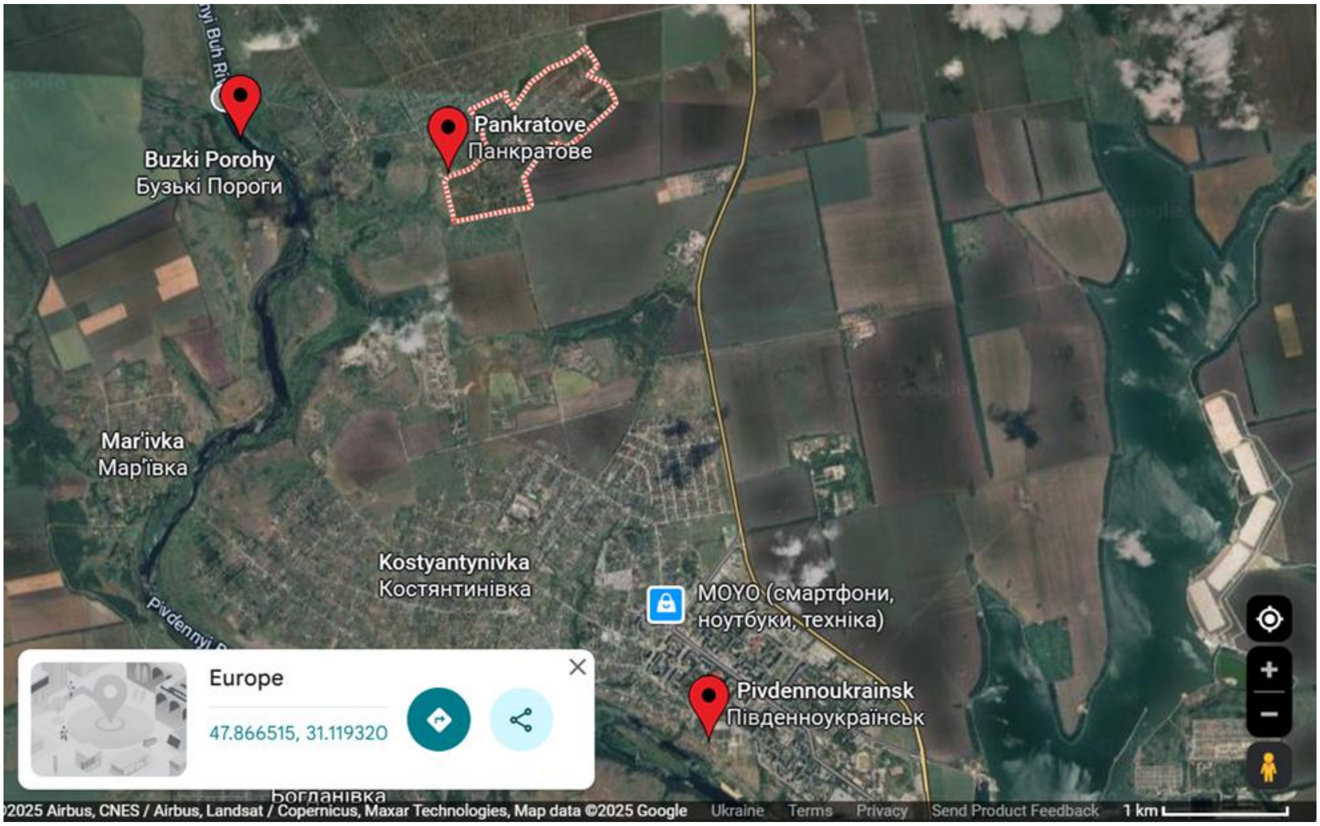


Fig. 2.1 Drinking water intake site (village of Pankratove) of the city of Yuzhnoukrainsk

The catchment basin of the Southern Bug River has a shape close to pear-shaped but with irregular contours. From a tectonic perspective, the majority of the basin is located within the territory of the Ukrainian Crystalline Shield. Only the river's sources lie within the Volhynian-Podolian Plate, while the mouth section belongs to the Black Sea Depression. The upper and middle courses pass through the Volhynian-Podolian and Dnipro Uplands, while the lower part is situated in the Black Sea Lowland.

According to physical-geographical zoning, the basin partially covers the broad-leaved forest zone and fully includes the forest-steppe and steppe zones. Within the administrative division of the territory, the Southern Bug River and its tributaries flow through the Khmelnytskyi, Vinnytsia, Kirovohrad, Mykolaiv, Cherkasy, and partially the Odesa and Kyiv regions.

Along the river's course, three sections are distinguished, which differ significantly from one another: Upper, Middle, and Lower Pobuzhzhia. The studied section of the river belongs to the Middle Pobuzhzhia (from Vinnytsia to the village of Oleksandrivka in the Voznesensk district of the Mykolaiv region). The valley here is wider than in the previous section and ranges from 1 to 2 km. The channel is also different – unlike the previous section with small rapids, here there are many rapids, and the banks are steep, rocky, and elevated in certain segments. The flow velocity in this section is higher than in the previous one and reaches 3–4 m/s.

The basin of the Southern Bug River belongs to one of the key agro-industrial regions of Ukraine, where both agricultural and industrial activities are intensively developed. Among the sectors contributing the largest volumes of discharges into surface waters of the basin, agriculture leads (44.1%), followed by municipal utilities (31.9%) and industry (23.6%).

After treatment at municipal treatment facilities, wastewater is discharged into the Southern Bug or its first- and second-order tributaries. However, most treatment systems are worn out, and the volumes of wastewater often exceed the design capacities, leading to the discharge of insufficiently treated wastewater into water bodies.

The majority of the territory is under significant agricultural influence: agricultural lands occupy about 81% of the total basin area, and in certain sub-catchments this figure ranges from 74% to 90%.

Within the Mykolaiv region, the main sources of pollution are: MKP «Mykolaivvodokanal» (Mykolaiv city), KP «Olshanske» (urban-type settlement of Olshanske), KP «Pervomaisk City Water Utility» (Pervomaisk city), KP «Prybuzke» (Nova Odesa city), «City Water Utility» (Bashtanka city), as well as the South Ukraine Nuclear Power Plant. It is worth noting that MKP «Mykolaivvodokanal» discharges already treated wastewater directly into the Southern Bug Estuary.

Thus, the main types of economic activity that create anthropogenic pressure on the water resources of the Southern Bug River basin include the housing and utilities sector, industrial production, agriculture along with fisheries, hydropower, and flood control measures.

The natural conditions of the Southern Bug River basin, along with the impact of economic activity, form specific features of its hydrochemical regime. The river is characterized by increased water mineralization, which intensifies closer to the mouth – this is explained by the geological characteristics of the territory. At the same time, the waters of the Southern Bug are saturated with dissolved oxygen, which can be attributed to the presence of rapids where active mixing of water masses occurs.

Our general assessment of the pollution level shows that throughout the entire observation period there is high variability in total nitrogen, ammonium ($NH_4^+$), nitrite ($NO_2^-$), and nitrate ($NO_3^-$) ions. The highest concentrations were recorded in 2005–2008, 2013, 2020, and after 2022, which indicates regular inflows of anthropogenic organic matter. Probable sources include sewage discharges, fertilizer leaching from agricultural lands, and accidental pollution.

The content of phosphate ions ($PO_4^{3-}$) remained stable during 2003–2019, but since 2020 a gradual increase has been observed, which may be associated with the use of phosphate-containing detergents or mineral fertilizers.

Chemical oxygen demand (COD) and biochemical oxygen demand over 5 days ($BOD_5$) show similar trends with multiple peaks in 2007, 2010, 2015, and 2023. This indicates regular periods of organic matter inflow into the river. Such peaks coincide with decreases in dissolved oxygen levels, which is a sign of reduced self-purification capacity of the water body.

Permanganate oxidizability, as a general indicator of the presence of organic substances, also shows periodic increases, especially in 2020–2024, indicating a persistent organic load.

Dissolved oxygen is generally maintained at the level of 6–9 $mgO_2/dm^3$, which is acceptable for most aquatic ecosystems. However, in certain periods (2016, 2020, 2023), a decline in concentration is observed, associated with increased organic load or changes in the hydrodynamic regime. Such oxygen deficits pose risks to aquatic fauna and the microbiocenosis.

The content of sulfate ions ($SO_4^{2-}$) depends on seasonality and shows interannual fluctuations with a tendency to increase after 2018. Peaks in 2020 and 2023 are the result of erosion processes, leaching of agricultural lands, or the use of sulfur-containing fertilizers.

The content of chloride ions ($Cl^-$) increases steadily throughout the entire period. A particularly sharp rise is recorded after 2020, indicating reduced water flow, prolonged evaporation, and the impact of sewage discharges.

Synthetic surfactants are generally at low levels; however, since 2022 a gradual increase has been observed. Atrazine and simazine, as herbicides of agricultural origin, are present in the water at a consistently low level. Their presence indicates chronic influence of the agricultural sector on water quality.

Suspended solids show uneven dynamics with periodic increases, particularly in 2013–2015, 2020, and 2024.

Phytoplankton is recorded in moderate concentrations, indicating relative stability of the trophic status of the water body; however, its increase after 2022 signals the development of eutrophication.

The aquatic system of the Southern Bug River in the area of the village of Oleksiivka (village of Pankratove) demonstrates a stable biogenic-organic load, intensified during 2020–2024. The increase in nitrogen, phosphate, surfactants, and herbicides content indicates systematic influence of domestic and agricultural pollution sources. The COD/$BOD_5$ trends, combined with a decline in dissolved oxygen, point to a reduction in aeration potential and a risk of hypoxia.

We will now conduct a more detailed analysis in the context of the following indicators: phosphate ions, ammonium ions, sulfate ions, chloride ions, $BOD_5$, and dissolved oxygen.

Figure 2.2 shows the results of the analysis of the dynamics of changes in the content of ammonium ($NH_4^+$) and phosphate ($PO_4^{3-}$) ions in the water during the period from 2003 to 2024.

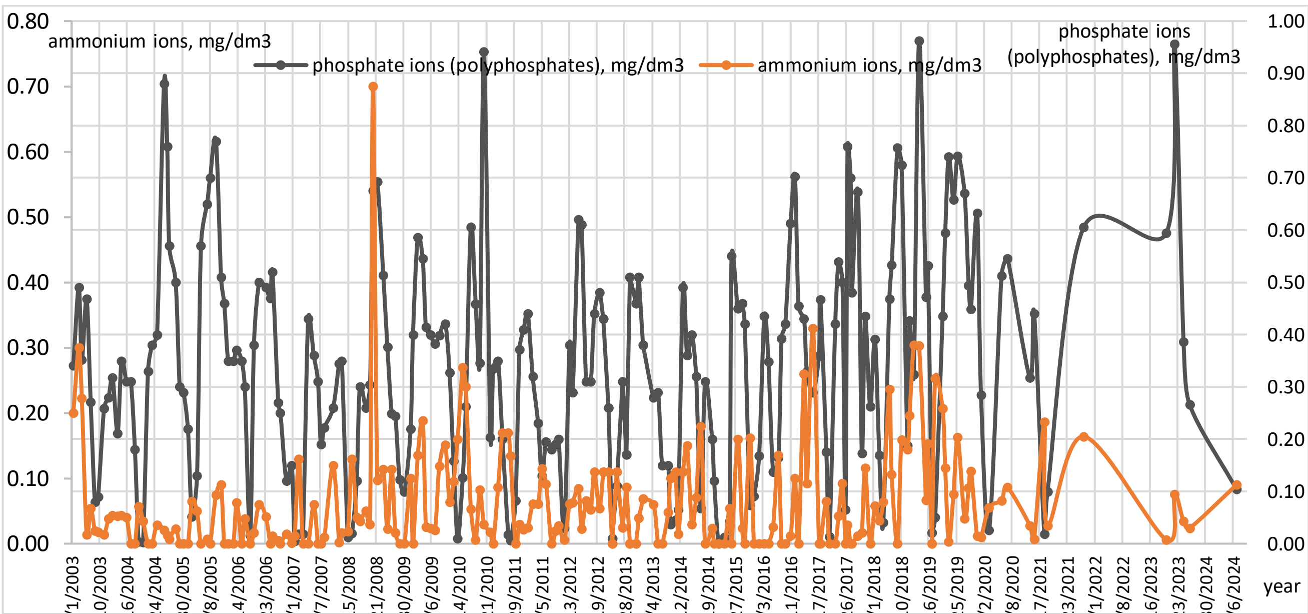


Fig. 2.2 Dynamics of ammonium and phosphate ion concentrations in the water of the Southern Bug River (village of Oleksiivka, drinking water intake of the city of Yuzhnoukrainsk) in 2003–2024.

The data indicate significant interannual variability, especially during the period from 2003 to 2012, when frequent peak discharges of both indicators were observed. This is likely related to irregular discharges of untreated or insufficiently treated wastewater, particularly from domestic and agricultural sources. In the period from 2013 to 2019, a certain stabilization of ammonium concentrations is observed; however, periodic spikes indicate recurring episodes of anthropogenic impact. The content of phosphate ions during this period is variable, with some anomalous increases (for example, in 2016 and 2019).

After 2020, a general decrease in the content of phosphates and ammonium in the Southern Bug River is noted, which potentially indicates a reduction in pollution sources or improvements in water treatment systems. At the same time, in 2023–2024, a sharp increase in phosphates and a decrease in ammonium levels are observed.

These trends can be explained as follows. First, there was a significant reduction in the amount of mineral fertilizers applied by agricultural producers in the Mykolaiv region. Thus, while 194 kg of mineral fertilizers (in active substance) per hectare were applied for the 2021 crop, this figure decreased to 138 kg/ha in 2022, and in the following years, 2023–2024, it amounted to 82 kg/ha and 98 kg/ha, respectively. This is due to the fact that with the onset of the war, the ability of farmers to use mineral fertilizers changed. Ukraine ceased supplies of fertilizers such as urea, UAN (urea-ammonium nitrate), ammonium sulfate, NPK fertilizers, and potassium chloride from Belarus. As a result of rising European prices for these fertilizers, their import into Ukraine became more difficult for agricultural producers. Due to the shutdown of major nitrogen fertilizer producers in Ukraine since the beginning of the war, prices for them increased, which reduced their use by agricultural producers and, consequently, led to a decrease in the content of ammonium ions in the Southern Bug River. Based on the obtained data, it can be concluded that the underuse of nitrogen fertilizers was compensated by the use of phosphate fertilizers, which led to an increase in the amount of phosphate ions in the water of the Southern Bug.

Secondly, unfortunately, domestic wastewater remains, which contains residues of detergents and, accordingly, pollutes surface waters with phosphates.

The inverse trends between $NH_4^+$ and $PO_4^{3-}$ in certain years indicate competition for biogenic uptake (for example, during algal blooms); oxygen degradation, during which phosphates settle into bottom sediments; or differences in the sources of input (organic wastewater – ammonium, detergents – phosphates).

Figure 2.3 shows the results of the analysis of the dynamics of sulfate ($SO_4^{2-}$) and chloride ($Cl^-$) ion concentrations, as indicators of mineralization and hydrochemical stability of river waters.

During the period from 2003 to 2020, the concentrations of both ions fluctuated within a wide range (chlorides: 30–70 mg/dm³, sulfates: 80–120 mg/dm³), reflecting both natural seasonal variations and the influence of anthropogenic sources – particularly domestic and industrial wastewater.

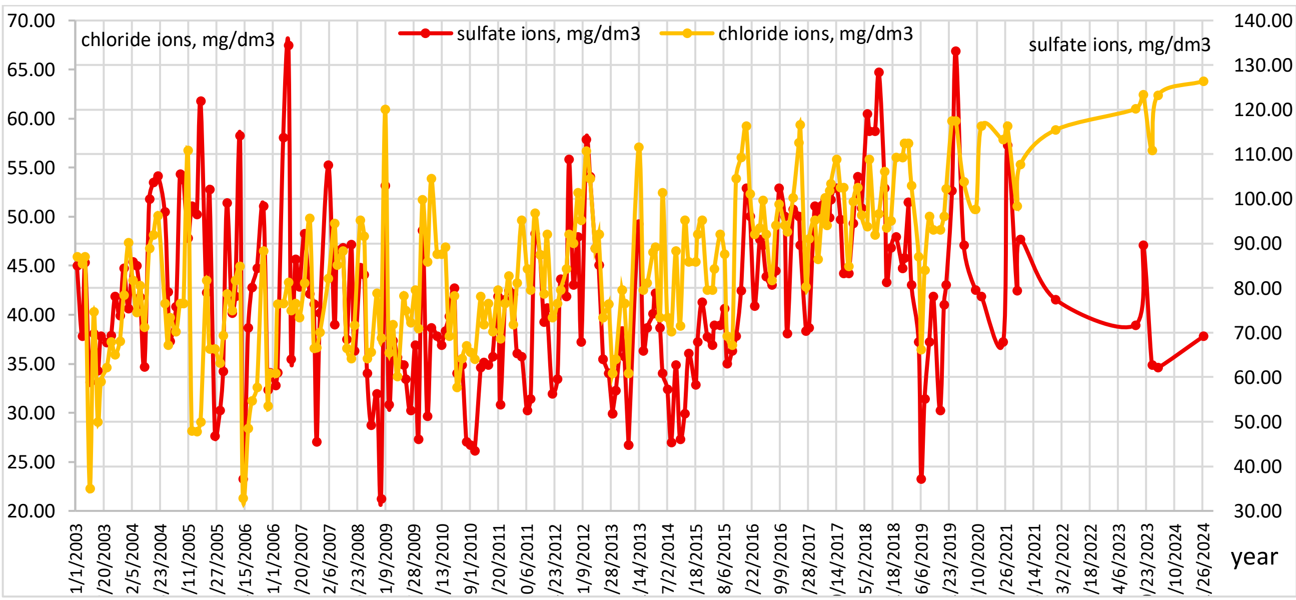


Fig. 2.3 Dynamics of changes in sulfate and chloride ion concentrations in the water of the Southern Bug River (village of Oleksiivka, drinking water intake of the city of Yuzhnoukrainsk) in 2003–2024

After 2020, a clear divergence in the behavior of the indicators is observed: the chloride level stabilizes at a lower level, while the concentration of sulfates rises sharply and remains elevated in 2022–2024. This indicates an increased load from sources related to detergents, agriculture, or the oxidation of sulfur-containing organic residues under conditions of reduced oxygen availability.

The increase in sulfates without a corresponding rise in chlorides indicates the activation of biogeochemical processes in the aquatic environment, particularly sulfate reduction and the influx of technogenic sulfate sources. Such dynamics are a sign of ecological imbalance.

Figure 2.4 presents the results of the analysis of the relationship between the level of dissolved oxygen (DO) and biochemical oxygen demand over five days ($BOD_5$) during the period from 2003 to 2024, which are key indicators of the degree of organic pollution and the self-purification capacity of the water body.

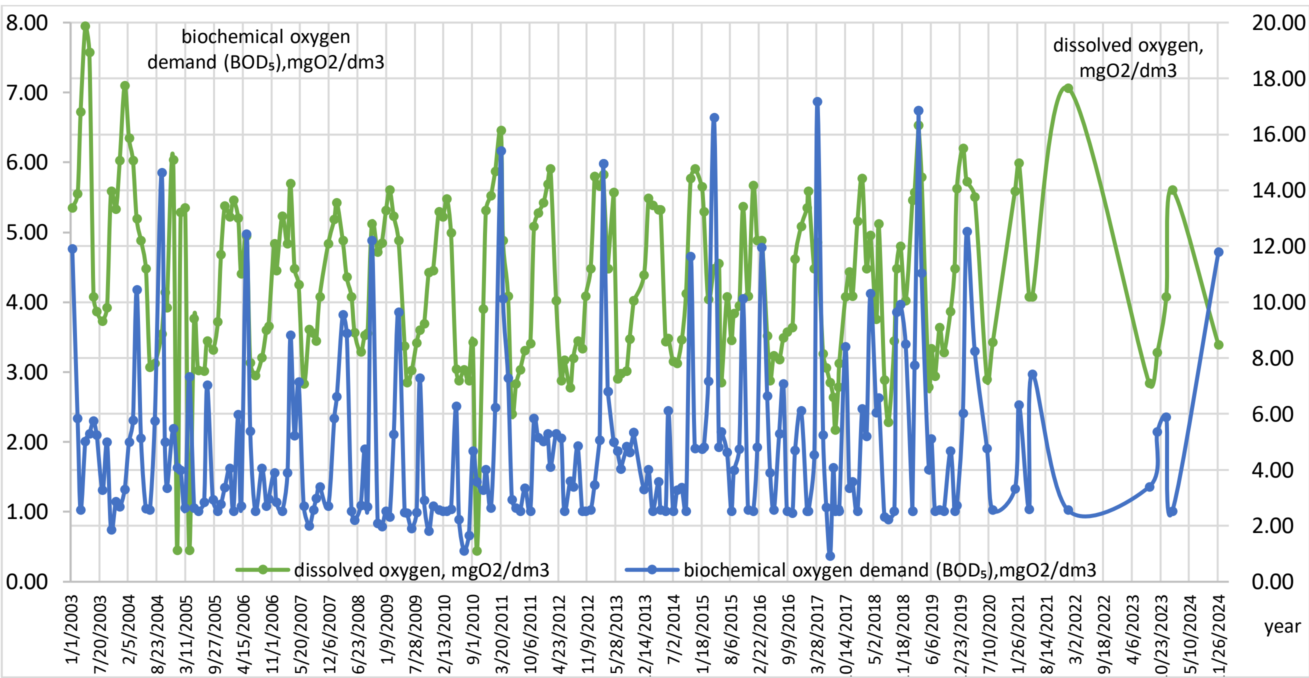


Fig. 2.4 Dynamics of dissolved oxygen concentration and biochemical oxygen demand ($BOD_5$) in the water of the Southern Bug River (village of Oleksiivka, drinking water intake of the city of Yuzhnoukrainsk) in 2003–2024

Throughout the entire observation period, a typical inverse relationship between these two parameters is observed. In years with elevated $BOD_5$ values (for example, 2006, 2009, 2015, 2020–2021), the level of dissolved oxygen decreases. This indicates intensive oxygen consumption by microorganisms decomposing organic pollutants.

At the same time, during periods with relatively low $BOD_5$ levels (2007, 2012, 2018), an increase in DO is observed, which indicates a reduction in organic load and improved aeration conditions.

Starting from 2020, an increase in the amplitude of fluctuations in both indicators is observed, which is associated with the instability of sources of organic pollution or changes in the hydrological regime of the river. Particularly notable is the drop in dissolved oxygen concentration in August 2023, which can be explained by a certain increase in $BOD_5$; thus, oxygen was consumed for the oxidation of organic substances in the water. In addition, the maximum permissible concentration (MPC) for $BOD_5$ was exceeded in December 2024 for the first time since 2020, under conditions of low dissolved oxygen levels. This indicates pollution of surface waters and oxygen consumption for the oxidation of organic contaminants.

Overall, the data confirm the sensitivity of the river ecosystem to organic loading. $BOD_5$ values above 3–4 $mgO_2/dm^3$, in combination with reduced DO, indicate an increased risk of aquatic environment degradation.

Figure 2.5 presents the results of statistical analysis of the dynamics of changes in the values of the studied indicators during the period from 2003 to 2024. For visualization, «box-and-whisker» diagrams were used to show the distribution of surface water indicators of the Southern Bug River, including minimum and maximum values, first and third quartiles, as well as the median.

As we can see, the interquartile range, which indicates dispersion, for dissolved oxygen, phosphate, sulfate, and chloride ions demonstrates a moderate level of variation. Exceptions are ammonium ions and $BOD_5$, for which the spread is more significant.

Table 2.1 presents a comparison of the average values of the studied indicators with their median values.

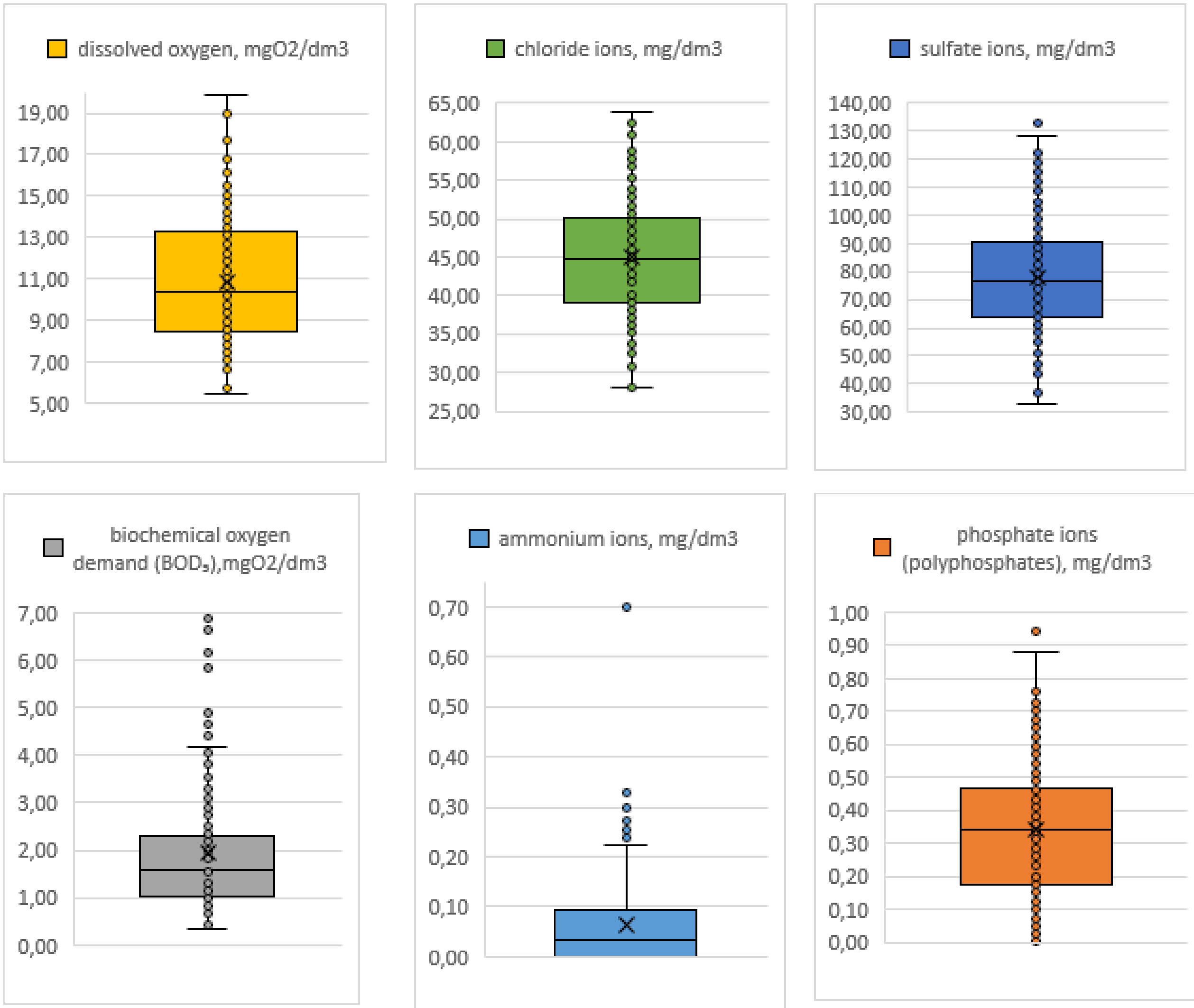


Fig. 2.5 Statistical analysis of pollution dynamics indicators of the Southern Bug River

As observed, the median and arithmetic mean values are practically the same for most indicators, except for ammonium ions and $BOD_5$. This indicates the presence of anomalous values (either low or high) during the period 2004–2024. Other indicators exhibited more stable trends over the years. The median, as is well known, is a more robust measure of central tendency, less sensitive to such outliers, and better reflects the typical value in a dataset. However, in this case, both the arithmetic mean and the median values do not exceed the maximum permissible concentrations (MPC). This gives reason to conclude that, despite the presence of occasional instances of increased surface water pollution in the Southern Bug River, the river demonstrates a capacity for self-purification.

In order to determine the relationship between different pollutants in the surface waters of the Southern Bug River, correlation matrices were constructed for two periods – from 2003 to 2024 and from 2016 to 2024. It was established that for the first period, there is a positive correlation between sulfate and chloride ions (0.48841), and a negative correlation between phosphate ions and $BOD_5$ (–0.33761).

*Table 2.1*

Comparative analysis of arithmetic mean and median values of pollutant concentration indicators

| | ammonium ions, mg/dm3 | phosphate ions, mg/dm3 | biochemical oxygen demand ($BOD_5$), mgO2/dm3 | dissolved oxygen, mgO2/dm3 | sulfate ions, mg/dm3 | chloride ions, mg/dm3 |
|---|---|---|---|---|---|---|
| MPC (Maximum Permissible Concentration) | 0,5 | 3,5 | 3,00 | 4,00 | 100,00 | 350,00 |
| Arithmetic mean value | 0,0625 | 0,3395 | 1,9618 | 10,8035 | 77,5747 | 44,9376 |
| Median value | 0,0350 | 0,3410 | 1,6000 | 10,3600 | 76,8000 | 44,9000 |

An increase in the concentration of sulfate ions ($SO_4^{2-}$) in surface waters may be accompanied by a rise in chloride ion ($Cl^-$) concentration for several reasons related to pollution sources, hydrochemical processes, and anthropogenic impact. Industrial effluents often contain a complex of salts, including both sulfates and chlorides. Agro-industrial complexes (fertilizers, pesticides) may also contain both types of ions. In urban areas, especially in winter, de-icing agents (salt mixtures) may include NaCl, $CaCl_2$, and $MgSO_4$, leading to the simultaneous input of $Cl^-$ and $SO_4^{2-}$ into water bodies.

During low-flow periods or increased evaporation, the concentration of all dissolved ions increases, including chlorides and sulfates.

The negative correlation between phosphate ions ($PO_4^{3-}$) and biochemical oxygen demand over 5 days ($BOD_5$) means that as phosphate concentration increases, $BOD_5$ decreases. This may seem illogical, as phosphates usually promote eutrophication. However, there are several possible explanations. For example, a reduction in organic pollution may occur if the source of phosphates is mineral fertilizers rather than organic discharges. Such trends were periodically observed during the study period. During rainfall or snowmelt, phosphate levels (from fields) may increase, but at the same time, organic matter is diluted and $BOD_5$ decreases.

For the second period, positive correlations were identified between chloride ions and the level of dissolved oxygen (0.44174), and negative ones between phosphate ions and $BOD_5$ (–0.45908).

In order for the level of dissolved oxygen in surface waters to increase, even despite the rise in chloride ion concentrations, compensatory or enhancing factors must be present to outweigh the negative effects of chlorides. Wind-induced mixing, river currents, and rapids – all of which contribute to oxygenation from the atmosphere – can play a significant role. Such a situation is present at the studied section of the Southern Bug River. Upstream (above the drinking water intake) lie the most well-known rapids in Mykolaiv region – the Myhiia rapids, located near the village of Myhiia in the Pervomaisk district. This is a narrow rocky canyon formed by outcrops of the Ukrainian crystalline shield. It consists of two main sections: the upper rapid ( «Mlynovyi») and the lower rapid ( «Integral» or «Red Gates»). They are part of the Buzkyi Gard National Nature Park.

From 2022 to 2024, along with the increase in chlorides, biochemical oxygen demand ($BOD_5$) decreased, which led to an overall reduction in oxygen consumption and a subsequent increase in its level. This situation may have arisen due to a reduction in organic discharges, which could be explained by the start of the full-scale invasion of the Russian Federation in 2022. In the Mykolaiv region, the beginning of the war resulted in population decline due to migration, as well as reduced volumes of industrial (shutdowns, suspensions, and relocation of enterprises) and agricultural production. These processes led to a reduction in water consumption volumes and, accordingly, a reduction in wastewater discharge.

For example, in 2021, the volume of fresh water used in the Mykolaiv region amounted to 169 million cubic meters, while in 2022, it dropped significantly to 95 million cubic meters. Similar trends are observed for total wastewater discharge – it decreased from 95 million cubic meters in 2021 to 51 million cubic meters in 2022. The gradual increase in chloride ion concentrations in the surface waters of the Southern Bug River (despite the reduction in water abstraction and wastewater discharge) can be explained by the fact that treatment facilities were practically not renewed during this time.

The negative correlation between phosphate ion ($PO_4^{3-}$) levels and $BOD_5$ remained and became even more pronounced during 2022–2024. This may be explained by the increased use of phosphate fertilizers (instead of ammonium fertilizers) following the start of the war, as mentioned above. Additionally, improved wastewater treatment or a reduction in its quantity (as noted earlier), combined with increased water flow, may also have had an effect. There is reason to believe that this is due to a decrease in water abstraction since the beginning of the war (increased water availability) and a reduction in wastewater volumes.

For pollutants that showed significant correlation relationships, scatter plots were constructed to visually assess the relationship between the two indicators (Figures 2.6–2.9).

The obtained results allow us to conclude that, since $BOD_5$ and dissolved oxygen levels in surface waters are key indicators of their quality, the ecological state of the water in the Southern Bug River can be improved by reducing discharges of chloride and phosphate ions.

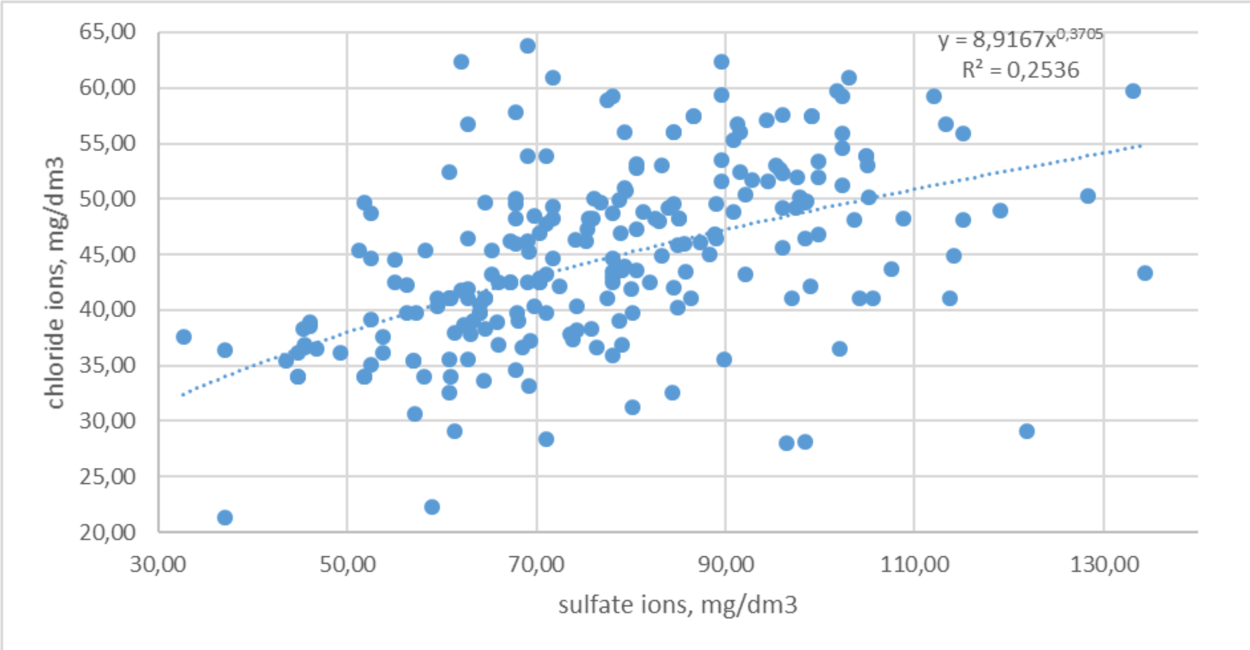


Fig. 2.6 Scatter plot of sulfate and chloride ion pollution levels during 2003–2024

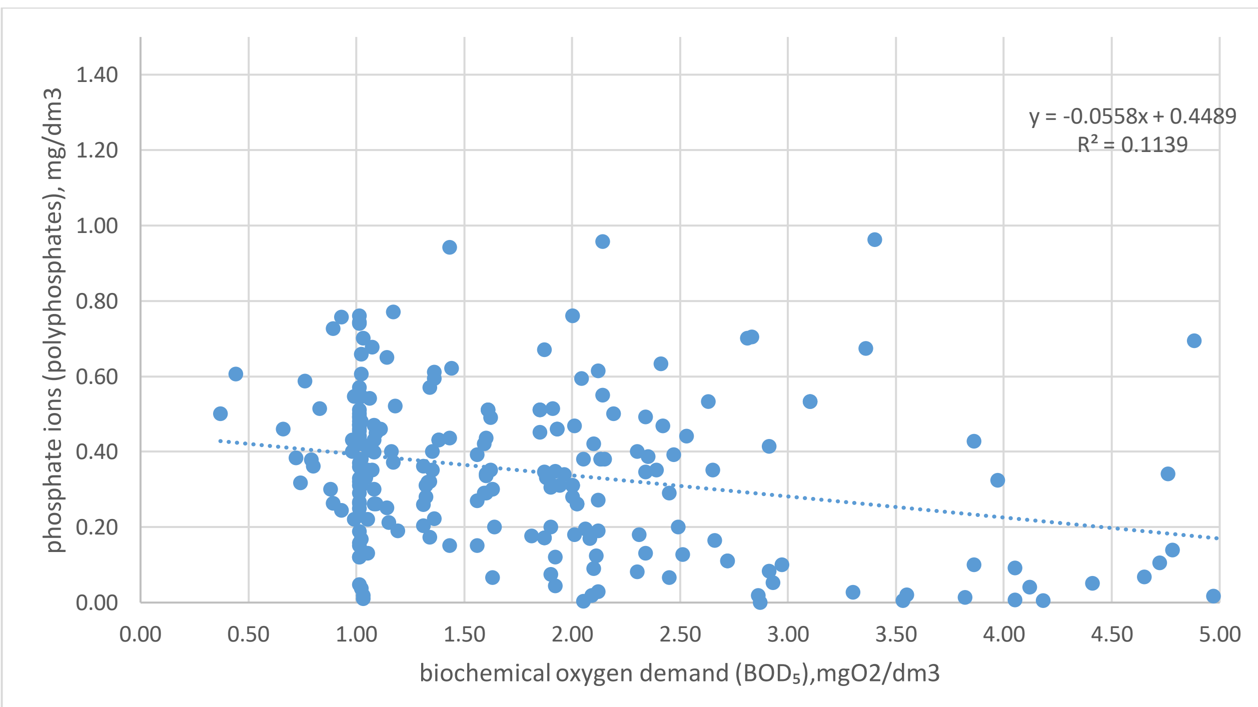


Fig. 2.7 Scatter plot of phosphate ion and $BOD_5$ pollution levels during 2003–2024.

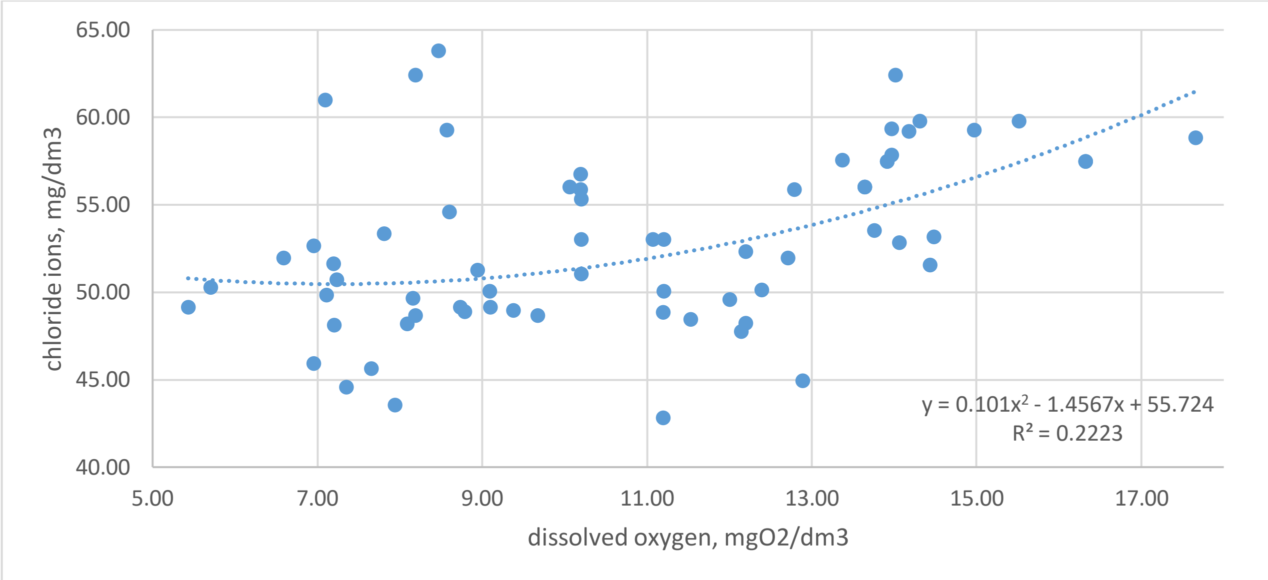


Fig. 2.8 Scatter plot of chloride ion and dissolved oxygen pollution levels during 2016–2024.

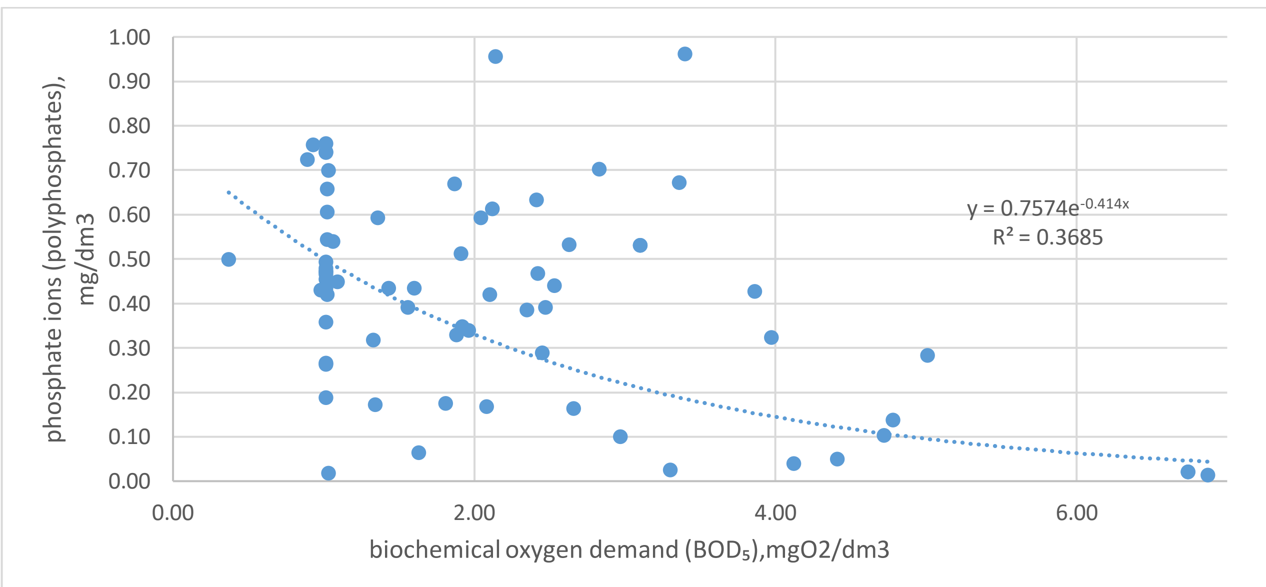


Fig. 2.9 Scatter plot of phosphate ion and $BOD_5$ pollution levels during 2016–2024.

Figure 2.10 presents the results of the analysis of averaged indicators (arithmetic mean) of changes in the concentrations of ammonium ions ($NH_4^+$, orange line) and phosphate ions ($PO_4^{3-}$, dark gray line) in the water during 2003–2024.

Approximating curves have been constructed to illustrate the general long-term trends in the concentration changes of two key biogenic components – mineral nitrogen and phosphorus. As previously shown, the arithmetic mean values are sufficiently close to the median values, and therefore the use of arithmetic means is entirely acceptable.

The approximation equation for ammonium ions ($NH_4^+$): $y = -3\times10^{-6}x^6 + 0.0255x^5 - 102.76x^4 + 2.0681\times10^5x^3 - 2\times10^8x^2 + 8\times10^{10}$, with a coefficient of determination $R^2 = 0.3607$.

Maximum concentrations of ammonium were observed in 2008, 2018, and 2022, which is associated with the inflow of domestic wastewater and a decrease in nitrification efficiency due to reduced dissolved oxygen.

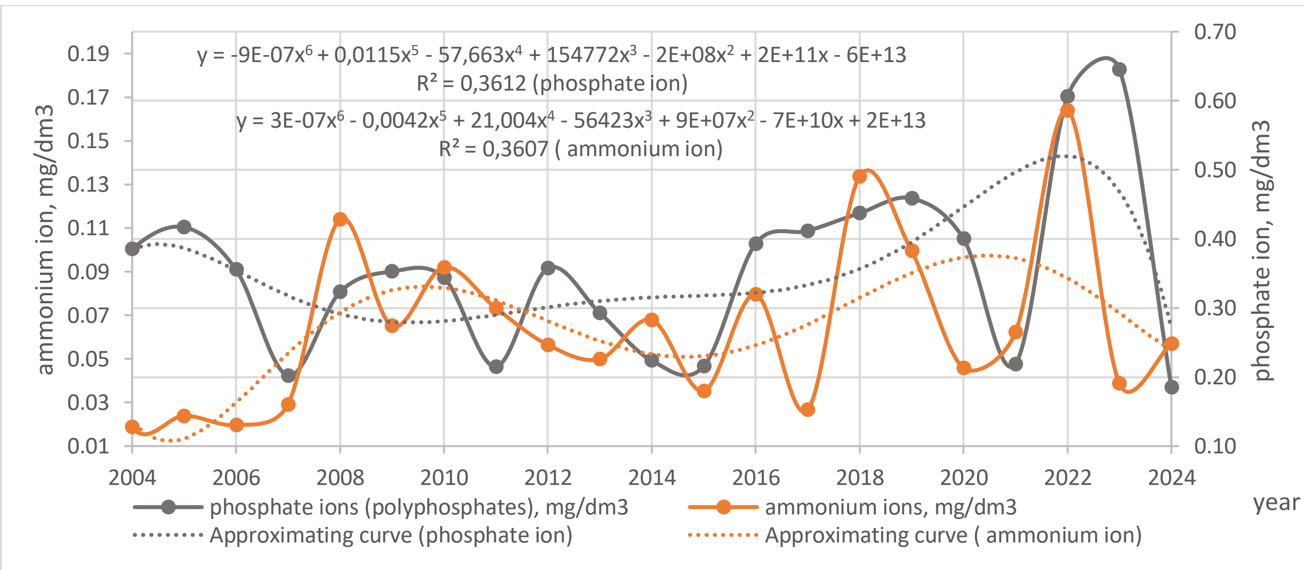


Fig. 2.10 Dynamics of changes in phosphate and ammonium ion concentrations in the water of the Southern Bug River (village of Oleksiivka, drinking water intake of the city of Yuzhnoukrainsk) in 2004–2024 with approximation curves

The approximation equation for phosphate ions ($PO_4^{3-}$): $y = -9\times10^{-7}x^6 + 0.0115x^5 - 57.663x^4 + 1.54772\times10^3x^3 - 2\times10^8x^2 + 2\times10^{11}x - 6\times10^{13}$, with a coefficient of determination $R^2 = 0.3612$.

Phosphate ions show clear maxima in 2005, 2013, 2019, and 2023, with minima in 2010, 2016, and 2024. This indicates an uneven inflow of phosphorus compounds, originating from detergents or agricultural sources.

The overall dynamics indicate that during the studied period there was a periodic increase in the concentrations of both components, with certain asynchronous fluctuations. This confirms the complexity of the biogeochemical interaction between nitrogen and phosphate compounds in the aquatic environment, driven both by anthropogenic influence and internal transformation processes (biogenic uptake, desorption, anoxic release).

Figure 2.11 presents the results of the analysis of the averaged concentrations of sulfate ($SO_4^{2-}$) and chloride ions ($Cl^-$) in the surface waters of the Southern Bug River during 2003–2024. These values represent the arithmetic means of the respective ion concentrations. Such averaging levels out seasonal variability but allows for modeling with the construction of polynomial approximation curves, making it possible to identify general trends in mineralization over the period 2004–2024.

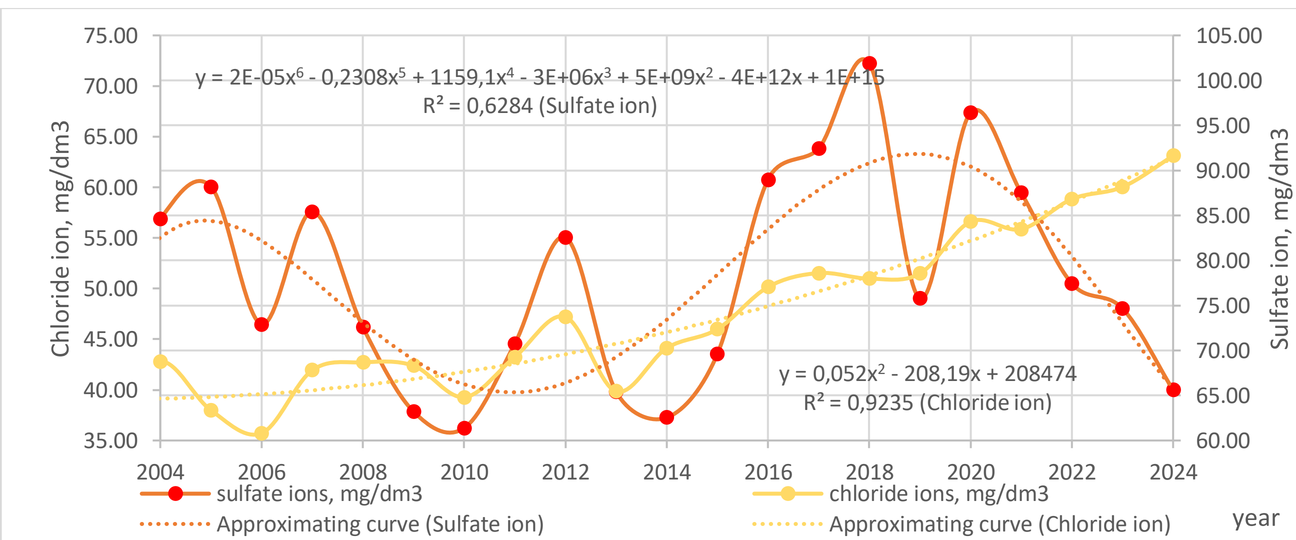


Fig. 2.11 Dynamics of changes in sulfate and chloride ion concentrations in the water of the Southern Bug River (village of Oleksiivka, drinking water intake of the city of Yuzhnoukrainsk) in 2004–2024 with approximation curves

Approximation equation for sulfate ions ($mg/dm^3$): $y = 2\times10^{-5}x^6 - 0.2308x^5 + 1159.1x^4 - 3\times10^6x^3 + 5\times10^9x^2 - 4\times10^{12}x + 1\times10^{15}$, coefficient of determination $R^2 = 0.6284$, which indicates acceptable model reliability.

Approximation equation for chloride ions ($mg/dm^3$): $y = 0.052x^2 - 208.19x + 208474$, coefficient of determination $R^2 = 0.9235$, which indicates a high degree of model fit to the actual data.

In the early years of the analyzed period (2004–2010), the concentrations of both ions fluctuated with periodic decreases, which is associated with changes in the water balance or limitations in the sources of mineral pollution. Starting from 2012, chloride concentrations show a clear and steady increase, which is related to the influence of agricultural activities or the accumulation of salts in the water body due to reduced flow.

The reasons for such an increase include the presence of domestic wastewater, as a significant amount of insufficiently treated effluents enters the surface waters of the Southern Bug River. In addition, additional anthropogenic pressure may result from fertilizer runoff – specifically potassium chloride – from agricultural lands. Furthermore, a common issue for the Southern Bug, as well as many rivers in southern Ukraine, is the gradual reduction in water flow.

Sulfates, in turn, reached peak values in 2018–2020, after which their levels began to decline. This indicates both changes in pollution sources and chemical reactions in the aquatic environment associated with shifts in pH or the formation of sediment deposits.

The overall trend confirms a tendency toward increasing water mineralization, especially due to the growth in chloride levels, which is an indicator of salt accumulation in the system and potential deterioration of water quality.

Figure 2.12 presents the results of the analysis of averaged values of biochemical oxygen demand over 5 days ($BOD_5$, blue line) and dissolved oxygen concentration (green line) in the water during the period 2004–2024, along with the corresponding approximation curves that illustrate the general trends in the changes of these indicators.

Approximation equation for $BOD_5$ ($mgO_2/dm^3$): $y = 6\times10^{-7}x^6 - 0.0077x^5 + 39.553x^4 - 1.0791\times10^5x^3 + 2\times10^8x^2 - 1\times10^{11}x + 5\times10^{13}$, coefficient of determination $R^2 = 0.3889$, which indicates low reliability of the model describing the trend of this indicator.

Approximation equation for dissolved oxygen ($mgO_2/dm^3$): $y = 5\times10^{-6}x^6 - 0.0568x^5 + 285.69x^4 - 7.66601\times10^3x^3 + 1\times10^9x^2 - 9\times10^{11}x + 3\times10^{14}$, coefficient of determination $R^2 = 0.4155$, which indicates considerable variability in dissolved oxygen concentrations during the period.

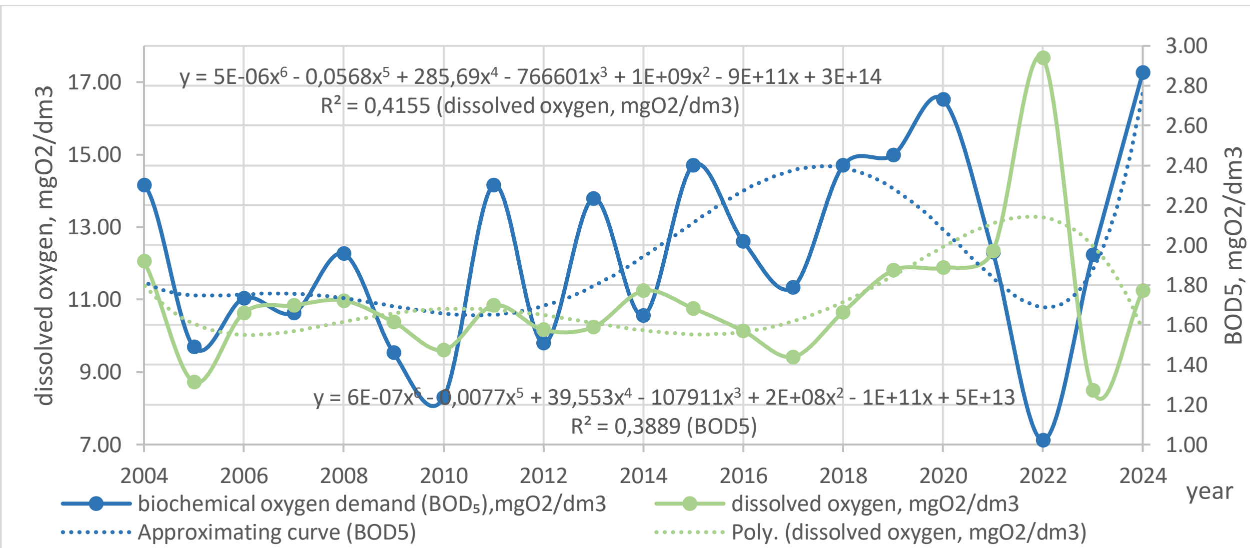


Fig. 2.12 Dynamics of changes in biochemical oxygen demand ($BOD_5$) and dissolved oxygen concentration in the water of the Southern Bug River (village of Oleksiivka, drinking water intake of the city of Yuzhnoukrainsk) in 2004–2024 with approximation curves

During 2004–2012, $BOD_5$ values remained relatively stable, but starting from 2015 a trend of gradual increase is observed, reaching peak values in 2020–2024. This indicates growing organic load associated with intensified anthropogenic impact.

High concentrations of dissolved oxygen were recorded in 2004, 2010, 2018, and 2022, while significant declines indicating hypoxic conditions were observed in 2006, 2009, 2015, and 2023.

Thus, during the period from 2003 to 2021, there were years when a classical inverse relationship between $BOD_5$ and dissolved oxygen was observed, i.e., increased organic load (higher $BOD_5$) was accompanied by a decrease in oxygen content. However, there were also periods when this relationship was disrupted.

During 2022–2024, a classical pattern re-emerged – an increase in dissolved oxygen was accompanied by a decrease in $BOD_5$. A decrease in $BOD_5$ means there are fewer organic substances in the water that require decomposition, and therefore less oxygen is consumed in the process. Taking into account that in these very years the levels of sulfate and ammonium ions decreased, there is reason to believe that these ions represent the main anthropogenic load on the surface waters of the Southern Bug River.

The gradual increase in chloride content and the periodic (point-source) increases in phosphate ions had a negative impact, but it was not catastrophic in nature.

*Conclusions***.** The obtained analysis results allow us to conclude that the aquatic system of the Southern Bug River in the area of the village of Oleksiivka (village of Pankratove) – the drinking water intake for the city of Yuzhnoukrainsk – experiences a stable biogenic-organic load, which intensified in 2020–2024. Increases in nitrogen, phosphates, surfactants, and herbicides indicate systematic influence from domestic and agricultural pollution sources. Trends in COD/$BOD_5$ combined with decreased dissolved oxygen suggest a decline in aeration potential and an increased risk of hypoxia.

It was found that during 2003–2012, irregular discharges of untreated or insufficiently treated wastewater were observed. In 2013–2019, some stabilization in ammonium concentrations was noted, although periodic spikes indicated recurring episodes of anthropogenic impact. During this period, phosphate ion levels fluctuated with individual anomalous increases. After 2020, a general decline in phosphate and ammonium content in the Southern Bug River was recorded, potentially indicating a reduction in pollution sources or improvements in water treatment systems. At the same time, in 2023–2024, a sharp increase in phosphates and a decrease in ammonium levels were observed, associated with a shift in the types of fertilizers used in agriculture – from ammonium-based to phosphate-based.

An analysis of the dynamics of sulfate ($SO_4^{2-}$) and chloride ($Cl^-$) ion concentrations – as indicators of mineralization and hydrochemical stability of river waters – showed that during 2003–2020, the concentrations of both ions varied within a wide range. This was associated both with natural seasonal changes and the influence of anthropogenic sources – in particular, domestic and industrial wastewater. After 2020, the main pollution sources were linked to detergents, agriculture, or the oxidation of sulfur-containing organic residues under low-oxygen conditions.

The results of the analysis of the relationship between dissolved oxygen (DO) levels and biochemical oxygen demand over five days ($BOD_5$) during 2003–2024 showed an inverse interaction between these two parameters. Since 2020, the amplitude of fluctuations in both indicators has increased, which is associated with the instability of organic pollution sources or changes in the river's hydrological regime.

A statistical analysis of the dynamics of changes in the studied indicators during 2003–2024 was conducted and visualized using box-and-whisker plots.

To identify relationships between different pollutants in the surface waters of the Southern Bug River, correlation matrices were built for two periods – 2003 to 2024 and 2016 to 2024. It was found that in the first period there was a positive correlation between sulfate and chloride ions, and a negative one between phosphate ions and $BOD_5$. In the second period, a positive correlation was observed between chloride ions and dissolved oxygen levels, and a negative one between phosphate ions and $BOD_5$.

Forecasting of anthropogenic load levels based on key pollutants was conducted using regression equations, and projected levels of phosphate ions, ammonium ions, sulfate ions, chloride ions, $BOD_5$, and dissolved oxygen in the surface waters of the Southern Bug River were determined.

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# 3 SURFACE WATER CONDITIONS OF THE DANUBE RIVER

The Ukrainian part of the Lower Danube Basin is located in the southwestern part of Odesa Oblast and represents the downstream section of the international Danube River Basin within Ukraine. Although Ukraine occupies less than 1% of the total Danube Basin area, this region is of exceptional hydrological, ecological, and economic importance because it includes the Kiliya branch of the Danube Delta, extensive floodplain wetlands, numerous floodplain lakes, and the transitional waters of the northwestern Black Sea. The Ukrainian sub-basin covers approximately 6,400 $km^2$ and constitutes the country's only direct connection to the Danube Delta and the Lower Danube wetlands (Vyshnevskyi et al., 2020; Negm et al., 2022).

The Ukrainian reach of the Danube extends from the vicinity of Reni to the Black Sea and comprises approximately 170 km of the river, including the deltaic distributaries. The Kiliya branch carries nearly 60–70% of the total Danube discharge entering the delta and therefore plays the dominant role in maintaining the hydrological regime of Ukrainian floodplains and wetlands. The river provides a stable water supply for domestic consumption, irrigation, navigation, fisheries, and industrial activities while simultaneously sustaining internationally important ecosystems (Negm et al., 2022).

Hydrologically, the Ukrainian Lower Danube is characterized by a relatively stable flow regime compared with many Eastern European rivers because its runoff integrates climatic conditions across the entire Danube Basin, which extends over nineteen European countries. Mean annual discharge near the delta exceeds 6,000 $m^3 s^{-1}$, while seasonal fluctuations are mainly controlled by snowmelt in the Alps and Carpathians together with precipitation throughout Central and Southeastern Europe. This large upstream catchment buffers local climatic variability, producing comparatively moderate interannual variations in discharge (Schiller et al., 2010; Zaharia et al., 2022).

The hydrographic network of the Ukrainian sub-basin includes numerous floodplain lakes and small rivers hydraulically connected with the Danube. Among the largest lakes are Yalpug, Kugurlui, Katlabukh, Kahul, and Kytai, which perform essential hydrological and ecological functions by regulating water storage, supporting fisheries, and maintaining regional biodiversity. These lakes are also important sources of freshwater for irrigation and municipal water supply, although many experience increasing eutrophication and periodic cyanobacterial blooms during warm seasons (Vyshnevskyi et al., 2020).

The region is characterized by a temperate continental climate with strong Black Sea influence. Annual precipitation generally ranges between 350 and 450 mm, whereas potential evaporation substantially exceeds precipitation during summer months. Consequently, the Lower Danube constitutes the principal freshwater resource for agriculture and human water use in southwestern Ukraine. Climate change has increased the frequency of droughts, heat waves, and hydrological extremes, thereby enhancing pressure on regional water resources and aquatic ecosystems (Bănăduc et al., 2020).

Geomorphologically, the Ukrainian Lower Danube consists predominantly of recent alluvial deposits forming an extensive floodplain-delta complex. The Kiliya Delta contains numerous distributary channels, islands, reed beds, marshes, and shallow lakes, creating one of Europe's largest continuous wetland systems. These habitats support exceptionally high biodiversity and provide spawning, feeding, and migration areas for numerous fish species and migratory birds. Most of these ecosystems are protected within the Danube Biosphere Reserve, which forms part of the UNESCO World Network of Biosphere Reserves and internationally important Ramsar wetlands (Vadineanu et al., 2003).

The Ukrainian Lower Danube also possesses considerable socio-economic significance. The ports of Reni, Izmail, and Ust-Dunaisk constitute strategic transport hubs connecting Ukraine with the European inland waterway network. Following the disruption of Black Sea shipping after 2022, the importance of the Danube transport corridor increased substantially, resulting in intensified navigation and cargo handling. Although these developments enhanced the strategic role of the region, they also increased anthropogenic pressure on aquatic ecosystems through dredging, shipping activities, accidental pollution risks, and shoreline modification (Negm et al., 2022).

The ecological condition of the Ukrainian Lower Danube is determined by the combined influence of natural processes and anthropogenic activities occurring throughout the international Danube Basin. The principal environmental pressures include nutrient enrichment, organic pollution, heavy metals, sediment transport alteration, invasive species, hydromorphological modifications, and climate change. In recent years, additional environmental challenges have emerged due to the consequences of the Russian military aggression against Ukraine, including increased navigation intensity, risks associated with military activities near river infrastructure, and growing pressures on the Danube Delta ecosystems. These factors highlight the necessity of integrated transboundary monitoring and adaptive river basin management consistent with the principles of the European Union Water Framework Directive (Afanasyev & Liashenko, 2006; Romanenko et al., 2012).

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## 3.1 ECOLOGICAL ASSESSMENT OF SURFACE WATER CONDITIONS OF THE DANUBE RIVER

The Danube River, as one of Europe's major transboundary watercourses, plays a critical ecological, hydrological, and socio-economic role in the region. Its lower reach within Ukraine encompasses the dynamic and biologically rich Danube Delta, a UNESCO Biosphere Reserve that supports high biodiversity and essential ecosystem services. However, this area faces increasing environmental pressure from agricultural runoff, municipal discharges, industrial activities, and intensified navigation.

In recent years, the ecological integrity of the Danube has been further challenged by hydromorphological alterations, climate variability, and, since 2022, the environmental consequences of military conflict. These factors have altered the river's water quality, disrupted natural flow regimes, and increased the load of pollutants.

A comprehensive assessment of hydrochemical indicators is essential to evaluate the current ecological status of surface waters in the Ukrainian section of the Danube. Such analysis forms the basis for understanding pollution dynamics, identifying priority risks, and developing effective environmental management and forecasting strategies in the context of both peace and crisis conditions.

To assess the ecological state of surface waters and the impact of anthropogenic pressures-including industrial activity, navigation, and military-related factors—on the Danube River, a hydrochemical study was conducted using long-term monitoring data from the Ukrainian section of the river (Reni–Izmail–Vylkove). Data were obtained from the Water Monitoring Laboratory of the Lower Danube Basin Department and included observations collected between 2010 and 2024.

Monitoring focused on key water quality parameters: ammonium, phosphates, sulfate and chloride ions, biochemical oxygen demand over five days ($BOD_5$), and dissolved oxygen. These indicators were analyzed at observation points near the cities of Kiliya and Vylkove, as well as in the river delta, with particular attention to areas of drinking water intake and ecological sensitivity.

The research employed statistical analysis, frequency distribution assessment, and regression modeling to identify trends, determine pollution patterns, and evaluate the river's capacity for self-purification under varying anthropogenic loads. This approach provides a scientific basis for forecasting environmental risks and supporting sustainable water resource management in the Danube basin.

*1. Physical-Geographical and Hydrological Characteristics of the Danube River Basin*

The Danube River is one of the main water arteries of Europe, encompassing the territories of ten countries, including Ukraine. Its lower course, particularly the delta, is located in the southwest of the country and plays an important role in the region's water, ecological, and economic balance. This section is characterized by a complex natural structure, diverse wetland ecosystems, and a high level of biological diversity. The Ukrainian section of the river extends for approximately 174 km and includes a branched delta with numerous arms, lakes, and floodplains. The territory is predominantly flat, with minimal elevation above sea level, which contributes to regular flooding and the formation of marshy landscapes. The Danube Delta is one of the youngest geomorphological formations in Europe and continues to actively change due to sedimentation processes. The climatic conditions of the region are generally moderately continental, with relatively mild winters and hot, dry summers. The level of precipitation is low—within the range of 350–400 mm per year, while evaporation exceeds this value twofold. Such a water deficit affects runoff formation and the ecological state of water bodies. The hydrological regime of the Danube is quite variable and depends on both climatic factors and flow regulation in the upper course. The lower section experiences annual floods lasting from several weeks to several months. Water levels can rise by several meters, influencing the formation of the delta's hydrological cycle and causing changes in the channel network [1].

According to estimates, the average annual water discharge near the city of Kiliya is about 6460 $m^3/s$, but in some years these values may significantly deviate—from historical minimums to extreme maximums. These fluctuations are associated with changes in precipitation, snowmelt in the upper course, as well as economic activities, in particular, the operation of hydraulic structures and land reclamation systems [2].

In addition to natural factors, changes in the Danube's hydrology are intensified by human intervention: engineering restructuring of channels, expansion of navigation routes, deforestation, and draining of wetlands [3]. At the same time, numerical modeling results show that Danube runoff significantly affects water quality and hydrodynamic processes in the adjacent marine area—particularly in the vicinity of Snake Island. This confirms the importance of considering the complex "river–sea" dynamics when assessing the condition of the lower river course [4].

Based on long-term observations of water levels and discharges in the Reni–Izmail section, a general trend of a slight increase in average and maximum levels has been identified, especially pronounced in recent decades. At the same time, seasonal phases—spring floods and autumn low water—remain stable, although peak flow discharges are increasingly shifting to late spring months [5].

*2. Hydrochemical Characteristics and Water Quality Assessment of the Danube River*

Water quality assessment is a key stage of hydroecological monitoring, especially under conditions of significant anthropogenic pressure. For the Danube River, which is used as a source of drinking water, recreational and industrial needs, the issue of water chemical purity is a priority in terms of sustainable water resource management. The mineralization of water in the Reni–Izmail section has shown a steady decline during the period from 1981 to 2015. This process is associated with an increase in the proportion of fresh meltwater and rainwater in the runoff structure, especially during spring floods. In high-water years, mineralization decreases to 368 mg/dm$^3$, while in low-water periods its level can exceed 425 mg/dm$^3$ [5].

Hydrochemical analysis of water at observation posts in Kiliya and Vylkove indicates regular exceedances of maximum allowable concentrations for parameters such as biochemical oxygen demand ($BOD_5$), ammonium nitrogen, nitrite nitrogen, as well as chemical oxygen demand (COD). In some months, the Water Pollution Index (WPI) reached 19.35, corresponding to class VII water quality—"extremely polluted water." A positive fact is that the level of dissolved oxygen in water in the summer months was quite high—8.4–9.8 mg/dm$^3$, which facilitated effective natural self-purification of the ecosystem. However, the presence of pollutants such as nitrites, petroleum products, and phenols, even in low concentrations, requires additional control due to their toxicity [6].

One of the most common integral indicators for assessing surface water is the Water Pollution Index (WPI). It allows the combination of various pollution parameters into a single numerical value and assigns the corresponding quality class. The WPI takes into account six main parameters: $BOD_5$, dissolved oxygen, ammonium, nitrites, petroleum products, and phenols. According to the classification, water with WPI > 10 is considered extremely polluted, and with WPI < 0.3—very clean [7].

In most sources, particularly in the study by Romanchuk M.Ye. and Veslohuzova Z.H., generalized water quality assessment also used integral quality indices based on the average values of several groups of indicators (organoleptic, toxicological, general sanitary). Based on these indices, the water of the Danube River in 2022 in the Kiliya area was classified within the second–third quality classes—"satisfactory," "slightly polluted" [8].

An important problem noted in modern studies is the discrepancy between Ukrainian and European water quality assessment standards. European approaches, which are increasingly being integrated into Ukrainian practice, focus not only on chemical parameters but also on biological and morphological indicators, allowing a comprehensive assessment of the ecological state of water bodies [6].

*3. Anthropogenic Impact on the Condition of the Danube River Surface Waters*

The lower course of the Danube, flowing through the territory of Ukraine, experiences significant anthropogenic pressure caused by both industrial and agricultural use of water, as well as urban wastewater discharge. This leads to changes in hydrochemical parameters, disturbances of aquatic ecosystems, accumulation of toxic substances, and degradation of the aquatic environment. The reduction of suspended sediment runoff over the past 30 years has been recorded as a result of the construction of hydraulic structures, water intake for irrigation and industrial needs. The most noticeable decline occurred during 1990–2015. This may lead to reduced silting of channels connecting the Danube lakes with the river and, consequently, to improved water exchange quality between them [5].

The main sources of water pollution in the Danube basin are municipal treatment facilities, which are mostly outdated and overloaded. In 2020, municipal sources discharged over 785 tons of organic substances in terms of $BOD_5$, and nearly 2000 tons in terms of COD. At the same time, the design capacities of treatment facilities were significantly exceeded, which led to the discharge of insufficiently treated or even untreated effluents into the river [6]. An additional threat is posed by food and paper industry enterprises. According to observations, the organic load from these sectors amounted to 9.1 tons for $BOD_5$ and 98.9 tons for COD, while the contribution from point agricultural sources is relatively minor. Accidental pollution caused by industrial facility malfunctions also poses a separate danger. For example, in 2000, a large volume of wastewater with high cyanide and heavy metal content entered the Danube due to an accident in Romania. Such situations not only disrupt the local state of the waters but also pose a transboundary ecological threat [6].

Prolonged load results in significant changes in the hydrochemical characteristics of water. Harmful compounds such as heavy metals and pesticides accumulate in the delta waters, along with increasing mineralization and changes in pH. All of this threatens aquatic flora and fauna, disrupts biodiversity, and may lead to eutrophication of water bodies [3].

Anthropogenic pressure also alters the river’s morphological structure—dam and canal construction changes flow hydrodynamics, hinders migration of aquatic organisms, and reduces the river’s self-purification capacity [6]. Since 2022, due to armed aggression, the number of potentially environmentally hazardous situations has increased—including the destruction of hydraulic structures, pollution by petroleum products, ammunition, and other toxicants. This is particularly relevant for the southern region of Ukraine, where the Danube Delta is located. Research confirms that the war has not only immediate but also long-term impacts on the hydroecological condition of water bodies [6].

*4. The Influence of the Danube River on the Ecosystem of the Black Sea*

The Danube is the main source of fresh water for the northwestern shelf of the Black Sea. The river's runoff transports water masses that influence salinity, temperature, and chemical composition of marine water through advection and diffusion processes. In high-water years, the area of Danube runoff distribution covers a significant part of the shelf, substantially altering its hydrodynamic characteristics.

Modeling confirms that the river runoff affects marine waters not only by changing salinity but also by transporting pollutants. In particular, in the coastal zone near Snake Island, reduced water transparency, fluctuations in oxygen content, and increased levels of biogenic elements are observed [4].

As a result of intensive input of nitrogen, phosphorus compounds, and organic matter with river runoff, eutrophication is observed in the northwestern part of the Black Sea. This leads to rapid algal growth, reduced transparency, and oxygen depletion in bottom layers. Hypoxic conditions resulting from algal blooms negatively affect the flora and fauna of the marine zone. In such conditions, oxygen-depleted zones may form, causing mass mortality of aquatic organisms and destabilization of the ecosystem [3].

*5. The Importance of the Danube River for Economy and Navigation*

The Danube River water is widely used to supply the population with drinking water, especially in Kiliya and Vylkove. However, hydrochemical analysis indicates frequent exceedances of maximum permissible concentrations for $BOD_5$, nitrites, ammonium, and COD. This threatens the quality of drinking water supply and requires improvement of treatment systems. According to the study, in some years, water from the control site at 48 km was classified as extremely polluted (class VII), indicating a high health risk for consumers [6, 8].

The Danube performs an important transport function as part of the international water corridor. However, intensive navigation leads to several environmental problems: shoreline erosion, wave generation, pollution by petroleum products, and mechanical damage to benthic biocenoses [6].

In addition, port and canal infrastructure (e.g., the Danube–Black Sea Canal) changes current speeds and sediment structure, degrading the condition of aquatic ecosystems in the estuarine zone [3]. Particular attention is drawn to the implementation of the deep-water navigation route "Danube–Black Sea" through the Bystre mouth, which since the early 2000s has been the subject of international discussion. The main goal is to restore navigation in the Ukrainian part of the delta, creating an alternative to the Romanian Sulina Canal. The project is viewed as Ukraine's attempt to strengthen its presence on the Pan-European Transport Corridor VII. At the same time, the construction of the route has faced opposition from Romania and a number of international environmental organizations emphasizing its potential impact on the Danube Biosphere Reserve, part of which is located in the Bystre estuary. Nevertheless, the Ukrainian side insists that the project complies with international standards and considers it technically and logistically advantageous due to its shorter length and economic feasibility [9].

An important institutional mechanism for international navigation regulation on the Danube is the Danube Commission—an intergovernmental organization established under the Belgrade Convention of 1948. Its structure and authority aim to ensure free, safe, and equitable navigation for all Danube countries. In recent years, the commission has undergone significant updates due to the need to adapt to technological progress in navigation, new standards (ES-TRIN, PLATINA 3), and challenges associated with Russia's military aggression. In 2022, the Danube Commission suspended Russia's powers, condemning violations of navigation freedom and the safety of Ukraine's port infrastructure. The Commission plays a coordinating role in standardizing navigation dimensions, hydraulic engineering works, and integrating the

Danube into the European TEN-T transport network. Some of its projects (e.g., Green Deal, GRENDEL, RIS COMEX) are aimed not only at improving navigation conditions but also at ensuring the ecological safety of the river environment. This integrated approach makes the commission a key link in the sustainable development of Danube navigation [10].

In order to assess the impact of anthropogenic pressure, including the intensification of navigation and the war, on the condition of surface waters in the Danube River, an analysis was conducted of water quality indicators at the monitoring station: Danube River, 163 km, Reni city, border with Romania (45°46′72″ N, 28°22′95″ E). The data used were obtained from the Water Monitoring Laboratory of the Basin Department for Water Resources of the Black Sea and Lower Danube Rivers. The study focused on the following parameters: phosphate ions, ammonium ions, sulfate ions, chloride ions, biochemical oxygen demand over five days ($BOD_5$), and dissolved oxygen.

Figure 3.1 presents the results of the analysis of phosphate and ammonium ion dynamics in the surface waters of the Danube River during the period from 2004 to 2024.

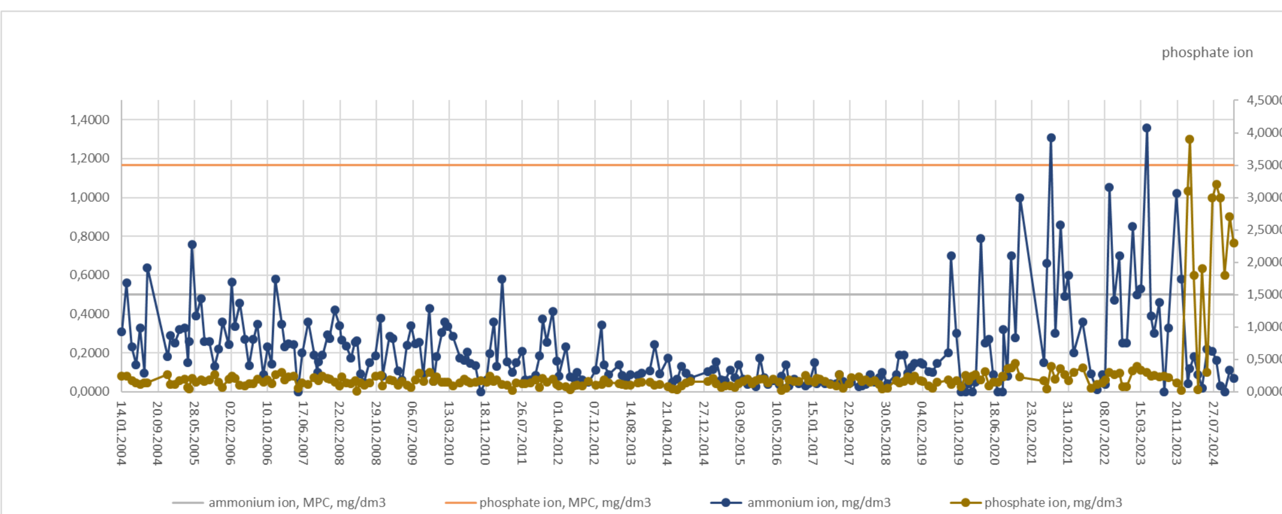


Fig. 3.1 Dynamics of Ammonium and Phosphate Ion Concentrations in Aquatic Environment Compared to Maximum Permissible Concentrations (MPC) (2003–2024)

The graph illustrates the long-term dynamics of ammonium ($NH_4^+$) and phosphate ($PO_4^{3-}$) ion concentrations in surface waters from 2004 to 2024. A noticeable upward trend in concentrations, especially after 2020, may indicate increased anthropogenic pressure such as discharges of untreated or insufficiently treated wastewater, agricultural runoff, and urban development. The orange and gray lines represent the maximum permissible concentrations (MPCs) for phosphate (1.1 mg/dm³) and ammonium (0.39 mg/dm³), respectively. Frequent exceedances of these limits signal ecological degradation, deterioration of water quality, and heightened risk of eutrophication, posing a threat to aquatic biodiversity.

Figure 3.2 presents the results of the analysis of the dynamics of sulfate and chloride ion concentrations in the surface waters of the Danube River during the period from 2003 to 2024.

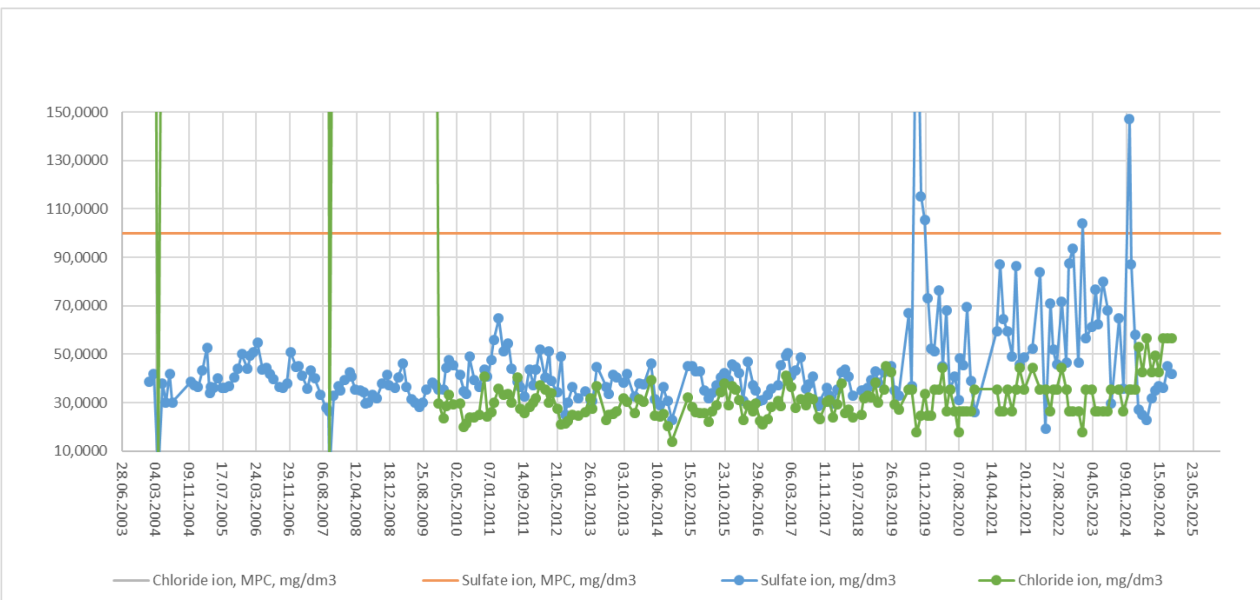


Fig. 3.2 Assessment of Chloride and Sulfate Ion Concentration Variability in Surface Waters in the Context of Environmental Safety (2003–2024)

The graph shows the fluctuations in sulfate ($SO_4^{2-}$) and chloride ($Cl^-$) ion concentrations in surface waters from 2003 to 2025. The maximum permissible concentration (MPC) for sulfate is marked with an orange line (100 mg/dm³), while values for chloride appear to reference regulatory thresholds (green). Recurrent exceedances of sulfate levels, especially in recent years, may reflect increased industrial discharge, mine drainage, or agrochemical runoff. Chloride levels are more stable, but their accumulation can indicate secondary salinization. These chemical shifts in aquatic environments affect aquatic organisms, disrupt ecosystems, and emphasize the need for enhanced environmental monitoring and pollution mitigation strategies.

Figure 3.3 presents the results of the analysis of the dynamics of dissolved oxygen concentration and five-day biochemical oxygen demand ($BOD_5$) in the surface waters of the Danube River during the period from 2004 to 2024.

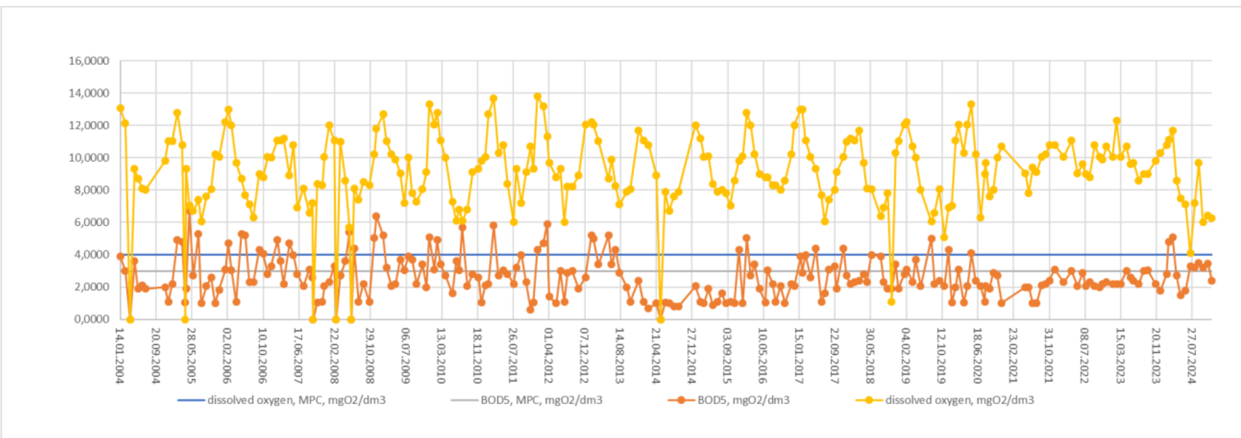


Fig. 3.3 Monitoring of Dissolved Oxygen and Biochemical Oxygen Demand ($BOD_5$) in Aquatic Ecosystems: Indicators of Aeration and Organic Pollution (2004–2024)

The graph shows the fluctuations of dissolved oxygen (DO, yellow line) and biochemical oxygen demand over 5 days ($BOD_5$, orange line) in surface waters from 2004 to 2024. The blue line represents the maximum permissible concentration (MPC) for dissolved oxygen (4.0 $mgO_2/dm^3$), while the gray line marks the $BOD_5$ threshold (approximately 3.0 $mgO_2/dm^3$).

Dissolved oxygen is a critical ecological indicator: drops below the MPC can lead to hypoxia and threaten aquatic life. $BOD_5$ reflects the level of organic pollution — higher values indicate increased oxygen consumption for decomposition. Repeated $BOD_5$ exceedances along with low oxygen episodes point to anthropogenic pressure such as wastewater discharge and organic contamination, signaling a risk of eutrophication and ecosystem degradation.

For a general assessment of the level of anthropogenic pressure from pollutants and their impact on $BOD_5$ levels and dissolved oxygen concentration, distribution histograms were constructed for the period 2003–2024.

Figure 3.4 presents the histogram of the distribution of phosphate ion concentrations in the surface waters of the Danube River during the period from 2004 to 2024.

The histogram shows the frequency distribution of phosphate ($PO_4^{3-}$) concentrations in water. The vast majority of samples (over 90%) fall within the 0.1–0.5 $mg/dm^3$ range, indicating a low level of eutrophication pressure. However, a few samples exceed 1.0 $mg/dm^3$, which may point to localized pollution from domestic wastewater, detergents, or fertilizers.

Figure 3.5 presents the histogram of the distribution of ammonium ion concentrations in the surface waters of the Danube River during the period from 2004 to 2024.

This histogram displays the frequency distribution of ammonium ion ($NH_4^+$) concentrations in water. Over 80% of the samples show concentrations below 0.5 $mg/dm^3$, indicating generally low pollution levels, typical for waters with limited organic input. However, the presence of samples exceeding 1.0 $mg/dm^3$ may indicate localized sources of contamination, such as domestic or agricultural wastewater discharges. Ammonium is a sensitive indicator of recent organic pollution, and elevated levels require attention through environmental monitoring.

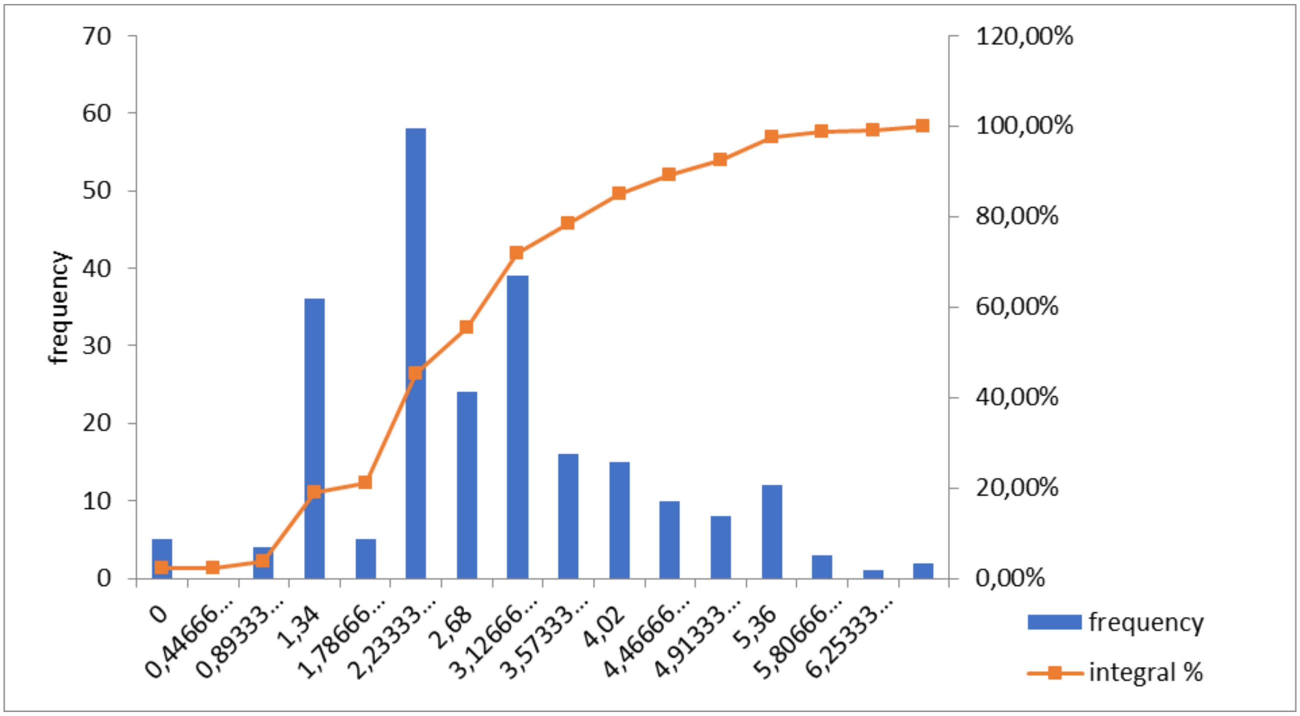


Fig. 3.4 Distribution histogram of Phosphate Concentrations in Water with Cumulative Percentage Analysis (2004–2024)

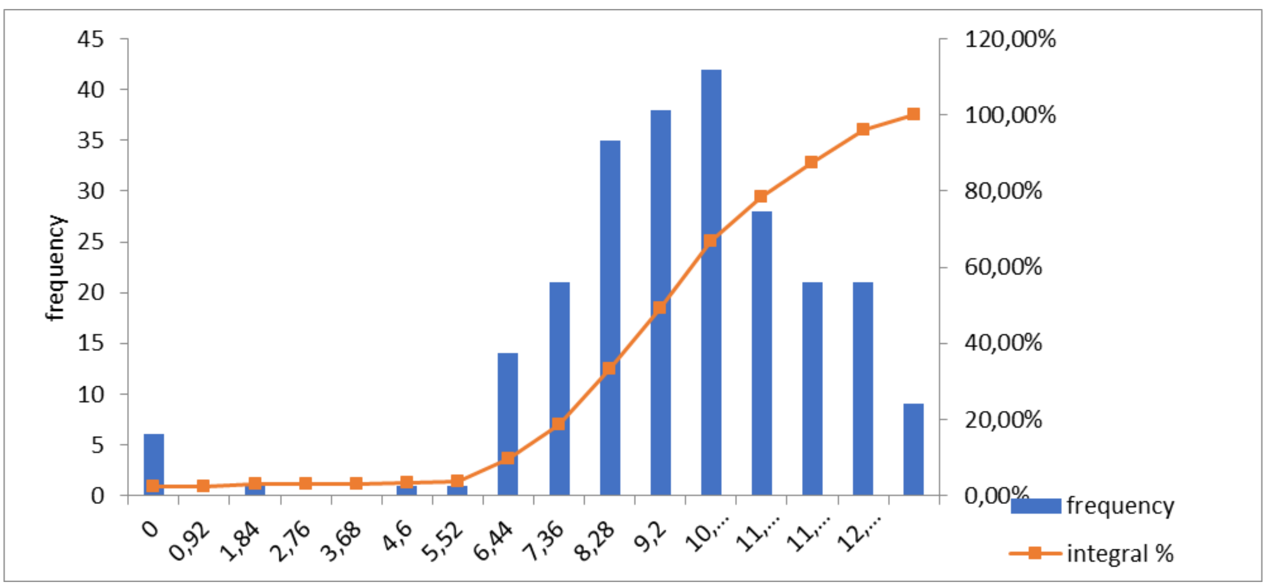


Fig. 3.5 Distribution histogram of Ammonium Ion Concentrations in Water with Cumulative Frequency Analysis (2004–2024)

Figure 3.6 presents the histogram of the distribution of sulfate ion concentrations in the surface waters of the Danube River during the period from 2004 to 2024.

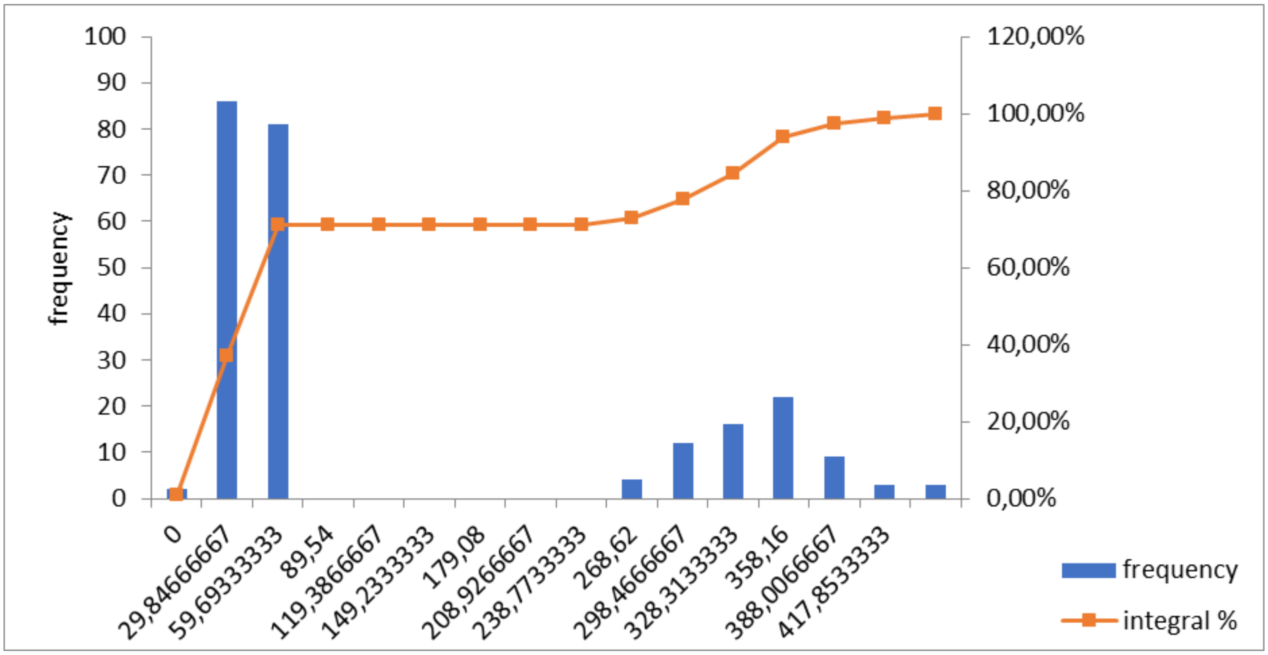


Fig. 3.6 Distribution histogram of Sulfate Concentrations in the Aquatic Environment with Cumulative Frequency Analysis (2004–2024)

The distribution of sulfate concentrations shows peaks within the range of 40–60 mg/dm³, which corresponds to the natural level of mineralization for large river systems experiencing moderate anthropogenic pressure. The majority of values (over 80%) are concentrated within the 45–50 mg/dm³ range. This indicates a stable source of sulfate input — particularly from natural minerals (such as gypsum and sulfides), as well as from domestic and industrial wastewater. Isolated instances of higher concentrations may result from localized pollution, desorption processes from bottom sediments, or the influence of atmospheric runoff. Such a distribution profile is typical for river systems subject to seasonal variability and influenced by both natural and anthropogenic sources of $SO_4^{2-}$. High concentrations in combination with low oxygen levels may also provide a substrate for sulfate reduction with the formation of hydrogen sulfide ($H_2S$), which is potentially toxic to aquatic biota.

Figure 3.7 presents the histogram of the distribution of chloride ion concentrations in the surface waters of the Danube River during the period 2004–2024.

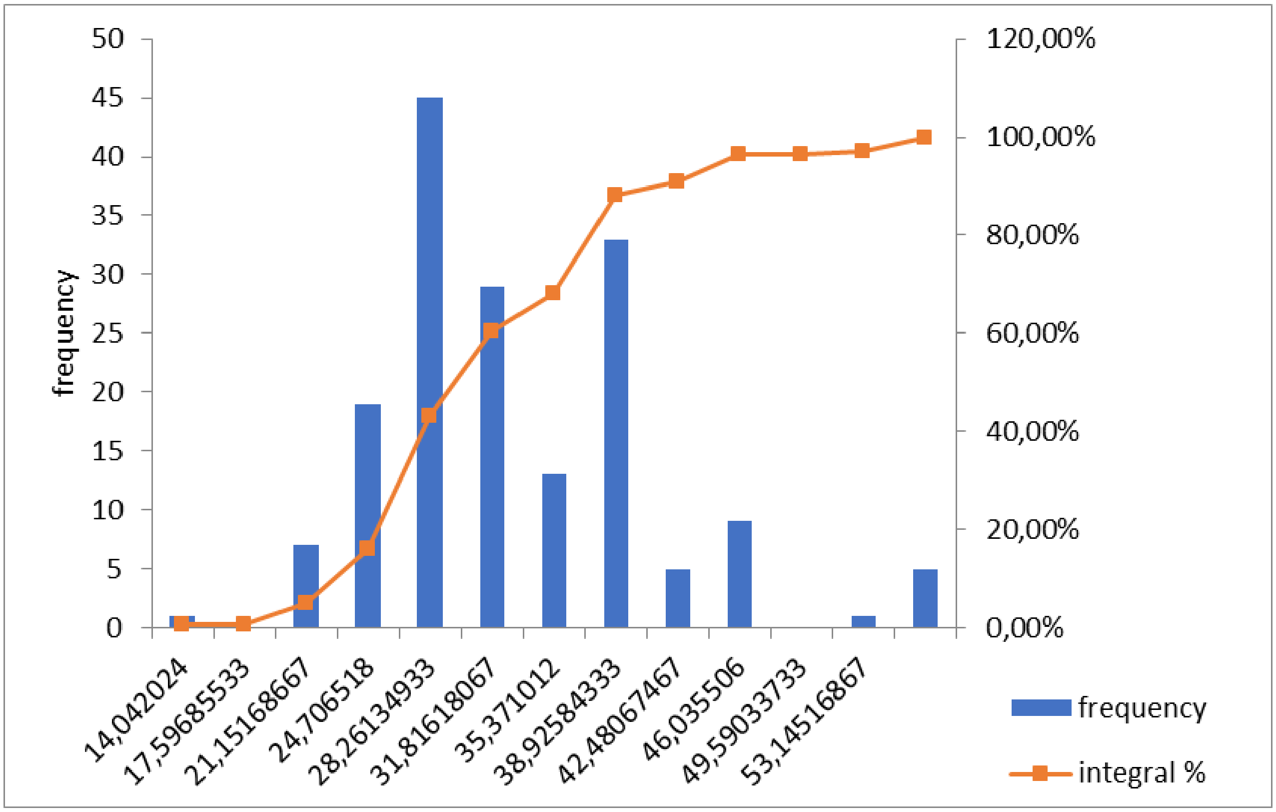


Fig. 3.7 Distribution histogram of Chloride Ion Concentrations in Water with Cumulative Percentage Assessment (2004 – 2024)

The histogram illustrates the frequency distribution of chloride concentrations in the water. As shown, the frequency distribution of chloride pollution levels is heterogeneous. The majority of samples (over 80%) have concentrations up to 90 mg/dm³, indicating a relatively low level of chloride pollution. However, the right side of the chart shows a smaller but noticeable number of samples with concentrations exceeding 200 mg/dm³. Data on chloride ion concentrations indicate that prior to 2010, the level of chloride pollution was significantly higher and substantially decreased after 2010. Thus, in the context of chloride ion concentration frequencies, it is appropriate to conduct a separate analysis starting from 2010. The results of this analysis are presented in Figure 3.8.

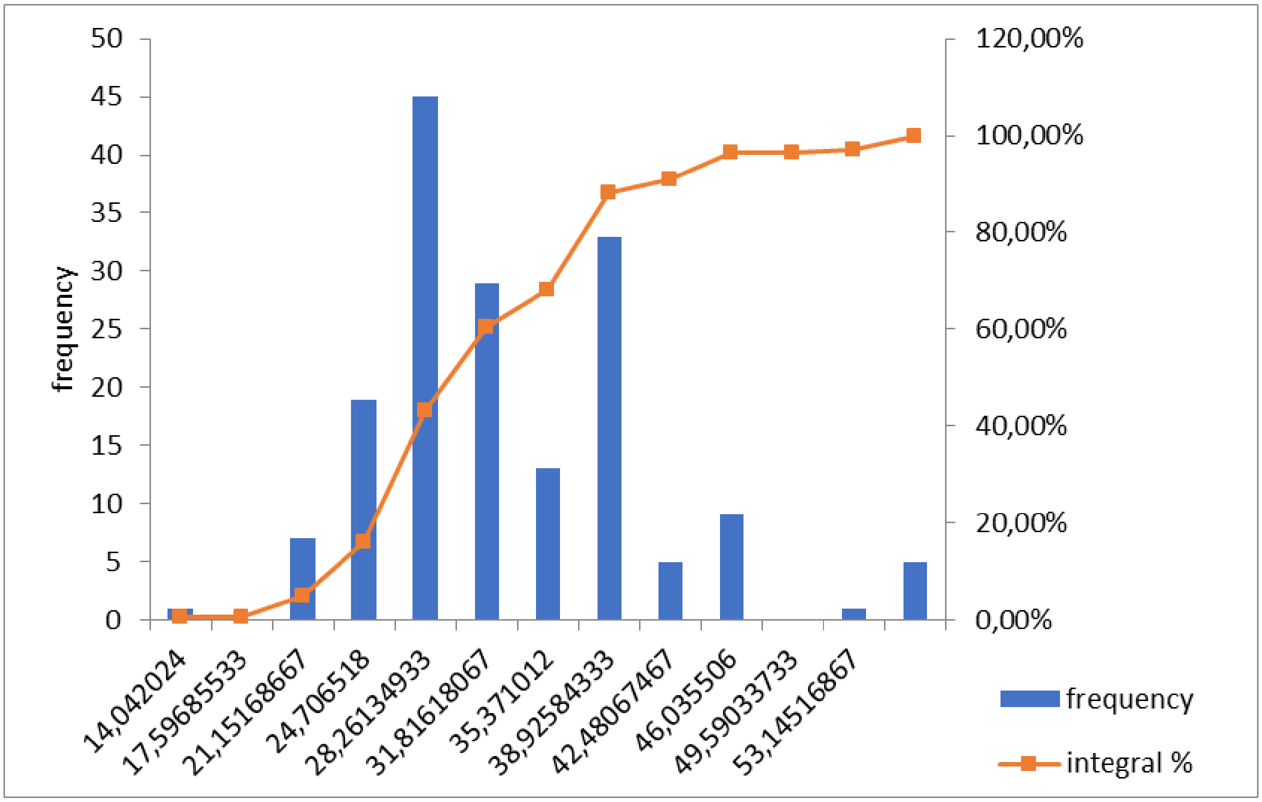


Fig. 3.8 Distribution histogram of Chloride Ion Concentrations in Water with Cumulative Percentage Assessment (2010 – 2024)

The histogram shows the frequency distribution of chloride ion ($Cl^-$) concentrations in water. The majority of samples (over 80%) fall within the 25–45 $mg/dm^3$ range, indicating a moderate and stable level of mineralization, typical for natural freshwater systems. However, a few values exceed 50 $mg/dm^3$, suggesting possible local sources of elevated chloride input, such as municipal or industrial discharges, road de-icing agents, or soil salinization.Elevated chloride levels can adversely affect aquatic ecosystems by disrupting the osmotic balance of organisms, reducing biodiversity, and degrading drinking water quality.

A comparison of the two histograms indicates that since 2010, the level of chloride pollution in the surface waters of the Danube has decreased. This is most likely associated with a reduction in anthropogenic pressure due to decreased use of inorganic fertilizers, such as potassium chloride, and improvements in the quality of municipal wastewater.

Figure 3.9 presents the histogram of the distribution of $BOD_5$ values in the surface waters of the Danube River over the period 2004–2024.

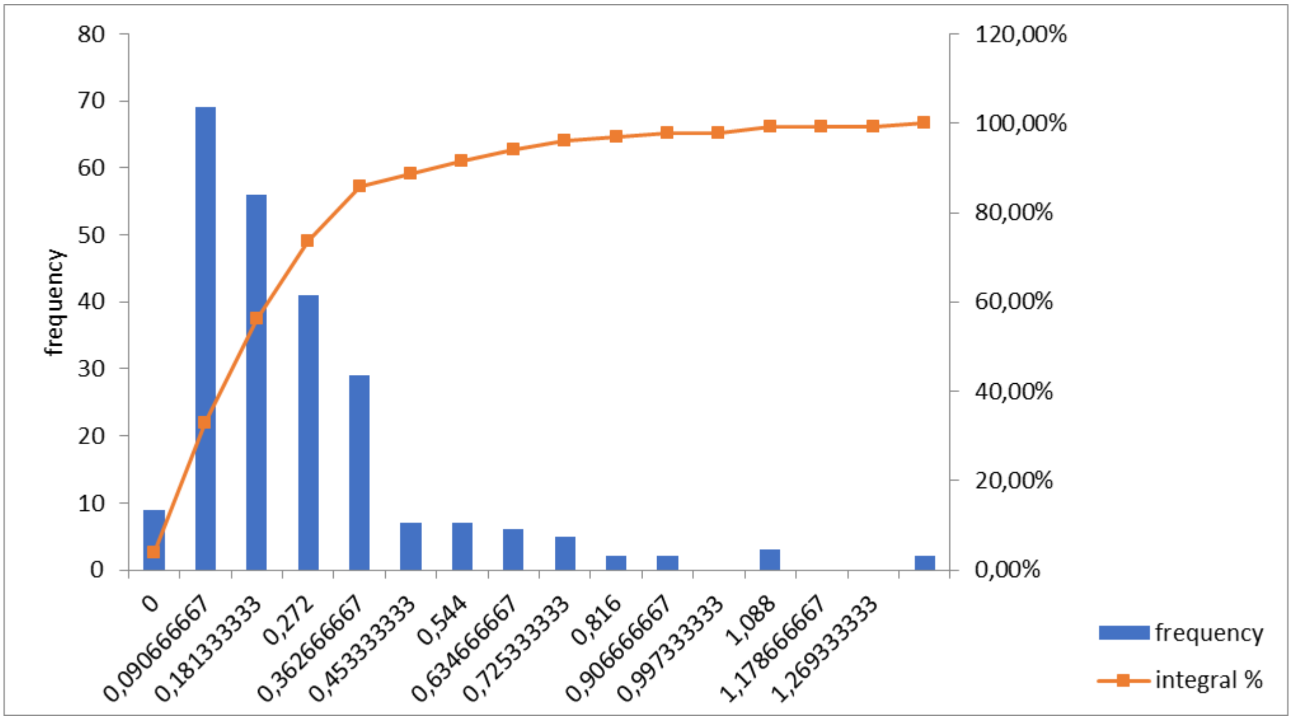


Fig. 3.9 Distribution histogram of $BOD_5$ values and cumulative percentage: assessment of organic pollution in aquatic environments (2004 – 2024)

This histogram shows the distribution of $BOD_5$ (Biochemical Oxygen Demand over 5 days), an indicator of organic pollution in water. Most samples fall within the 2.2–2.7 $mgO_2/dm^3$ range, indicating moderate contamination. However, about 20% of values exceed 4.0 $mgO_2/dm^3$ — the threshold where negative effects on aquatic organisms can occur. This suggests the presence of organic pollution sources that may lead to decreased dissolved oxygen, eutrophication, and overall deterioration of the water body's ecological condition.

Figure 3.10 presents the histogram of the distribution of dissolved oxygen concentrations in the surface waters of the Danube River over the period 2004–2024.

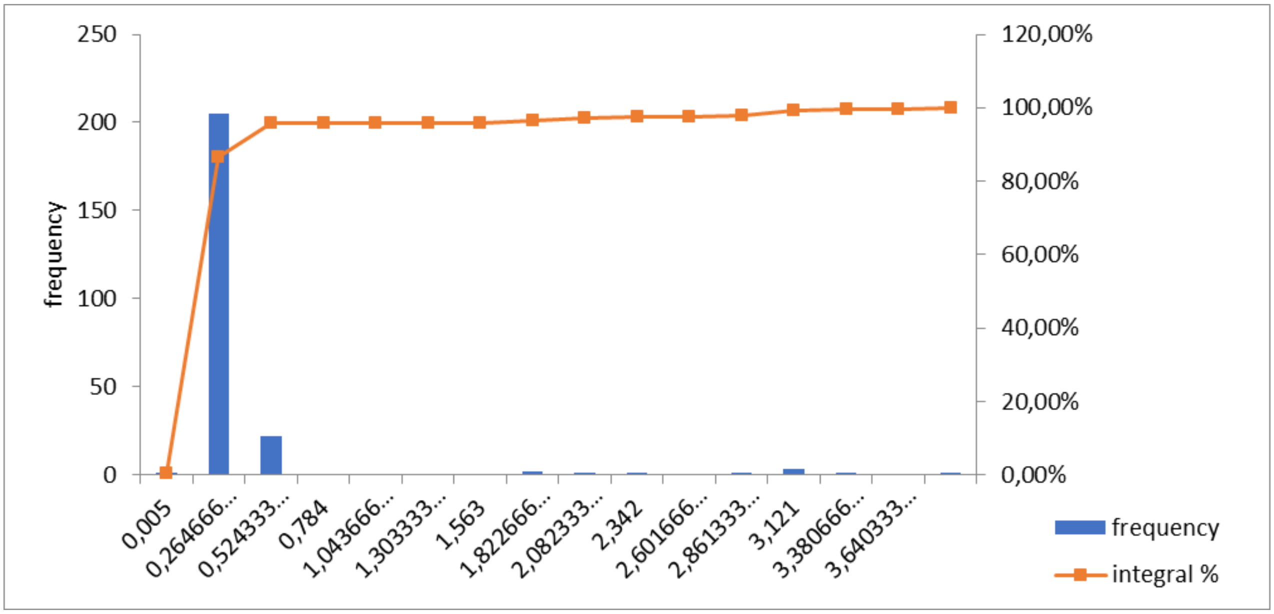


Fig. 3.10 Distribution histogram of Dissolved Oxygen Concentrations in Water and Cumulative Sample Percentage (2004 – 2024)

This histogram shows the frequency distribution of dissolved oxygen levels in the aquatic environment. Most samples fall within the 9–11 $mgO_2/dm^3$ range, indicating a well-oxygenated ecosystem that supports aquatic life. Approximately 90% of the samples exceed 7 $mgO_2/dm^3$, suggesting a stable ecological condition of the water body. Lower oxygen values are rare but should be monitored to prevent hypoxia and associated risks to biodiversity.

In order to determine the dynamics of changes in the level of anthropogenic pressure on the surface waters of the Danube River (Reni station) and to further forecast in the context of specific pollutants, appropriate regression equations were constructed.Annual average values of harmful substance discharges were used in their construction (thus smoothing the seasonality of pollution).

Figure 3.11 shows the dynamics of changes in phosphate and ammonium ion concentrations in the water during 2004–2024, along with the corresponding approximating curves.

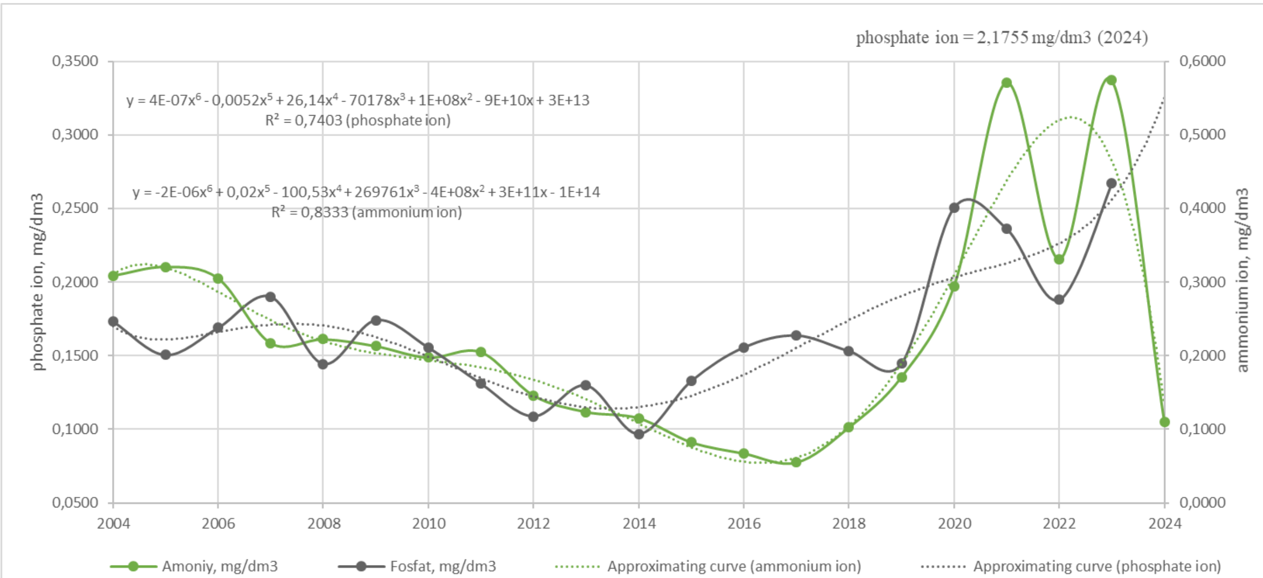


Fig. 3.11 Dynamics of phosphate and ammonium ion concentrations in water from 2004 to 2024 and the corresponding approximating curves (2004-2024)

The regression equation of the identified dependence for phosphate ions is: $y = 4 \times 10^{-7}x^6 - 5.2 \times 10^3x^5 + 26.14x^4 - 7.0178 \times 10^4x^3 + 1 \times 10^8x^2 - 9 \times 10^{10}x + 3 \times 10^{13}$, approximation reliability – $R^2 = 0.7403$. The identified dependencies indicate that a decrease in phosphate ion content in the water is observed periodically, but starting from 2014 the overall level began to increase. When constructing the regression equation, the data for 2024 were not taken into account because they significantly differ from previous years (the average value of the indicator increased to 2.1755 mg/dm³).

The regression equation of the identified dependence for ammonium ions is: $y = -2 \times 10^{-6}x^6 + 0.02 \times 10^2x^5 - 100.53x^4 + 2.69761 \times 10^5x^3 - 4 \times 10^8x^2 + 3 \times 10^{11}x - 1 \times 10^{14}$, approximation reliability – $R^2 = 0.8333$.

The identified dependencies indicate that a decrease in ammonium ion content in water is also observed periodically with a general downward trend. However, starting from 2017, the indicators began to rise sharply and significantly decreased to the previous level only in 2024.

Figure 3.12 presents the dynamics of changes in sulfate and chloride ion concentrations in water from 2013 to 2024 and the corresponding approximating curves.

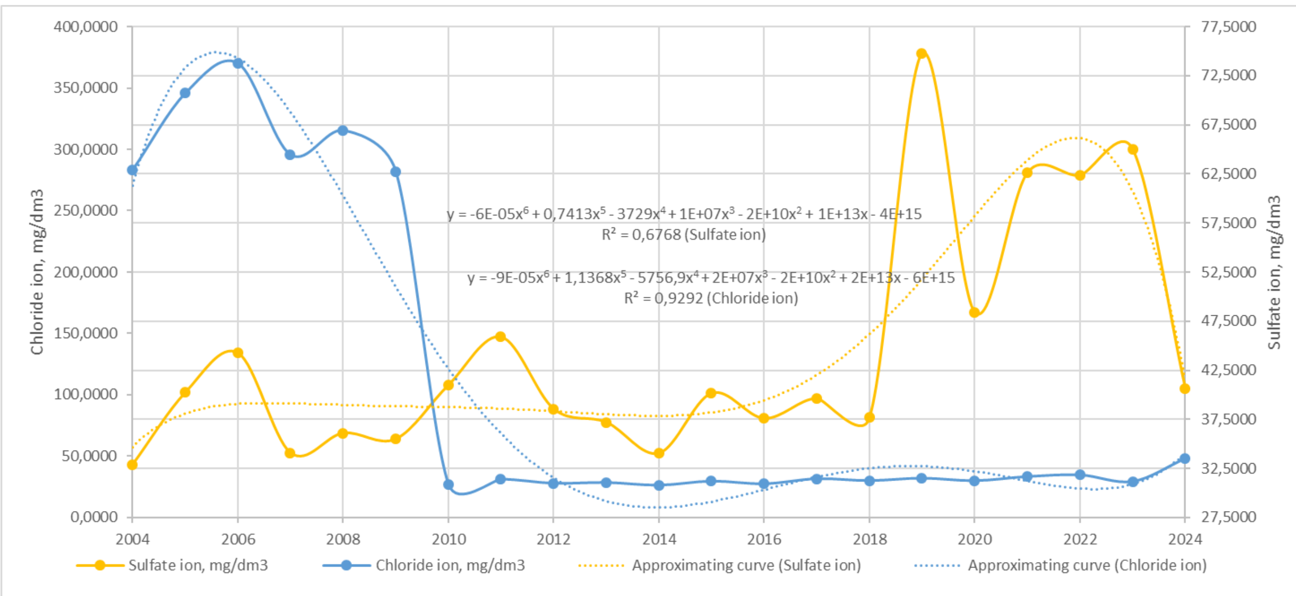


Fig. 3.12 Dynamics of sulfate and chloride ion concentrations in water from 2004 to 2024 and the corresponding approximating curves (2013-2024)

The regression equation of the identified dependence for sulfate ions is: $y = -6 \times 10^{-5}x^6 + 0.7413x^5 + 1 \times 10^7x^4 - 3.729 \times 10^3x^3 + 1 \times 10^7x^2 + 1 \times 10^{13}x - 6 \times 10^{15}$, approximation reliability – $R^2 = 0.6768$. The regression equation of the identified dependence for chloride ions is: $y = -9 \times 10^{-5}x^6 + 1.1368x^5 - 5.75569x^4 + 2 \times 10^7x^3 - 2 \times 10^{13}x^2 + 2 \times 10^{13}x - 6 \times 10^{15}$, approximation reliability – $R^2 = 0.794$. The identified dependencies indicate that the changes in the content of chloride ions in water are also relatively minor. As observed, the content of sulfate ions from 2004 to 2018 fluctuated around the average level, increased significantly during 2019–2023, and decreased again in 2024. Regarding chloride ions, their content was high until 2010. However, starting from 2011, it significantly decreased and only increased again in 2024. Therefore, we conducted an additional analysis of the situation from 2010 to 2024 to refine the regression equation. Figure 3.13 presents the dynamics of changes in the concentrations of sulfate and chloride ions in the water during the period 2010–2024, along with the corresponding approximating curves.

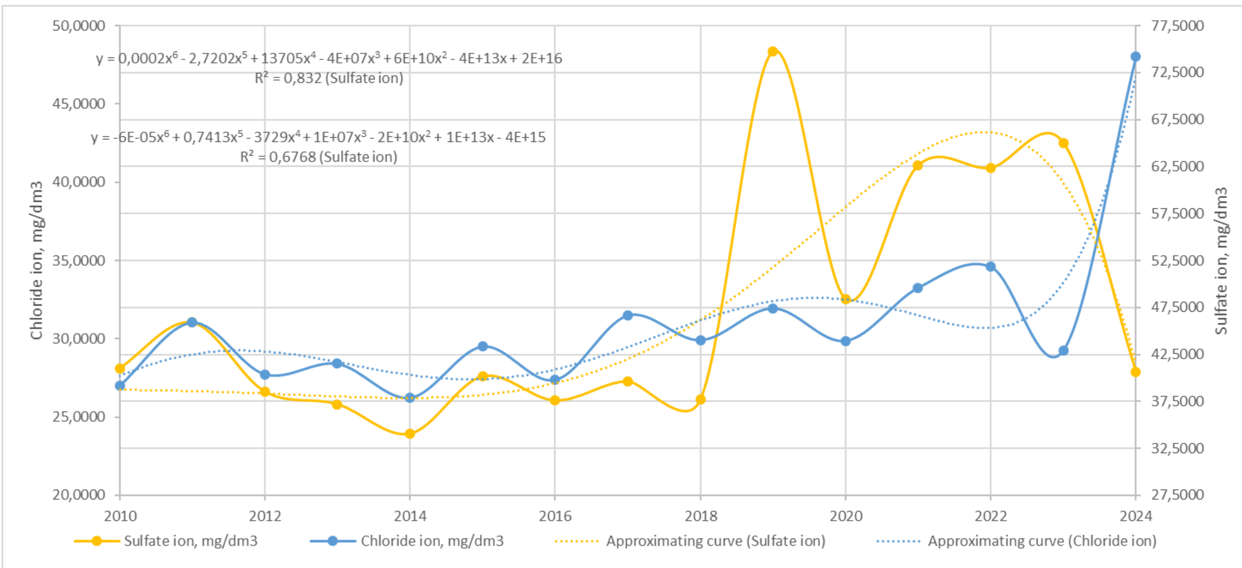


Fig. 3.13 Dynamics of sulfate and chloride ion concentrations in water from 2010 to 2024 and the corresponding approximating curves (2010-2024)

The regression equation of the identified dependence for sulfate ions is: $y = 2 \times 10^{-4}x^6 - 2.7202x^5 + 1.3705 \times 10^4x^4 - 4 \times 10^7x^3 + 6 \times 10^{10}x^2 - 4 \times 10^{13}x + 2 \times 10^{16}$,

with an approximation reliability of $R^2 = 0.832$.The regression equation of the identified dependence for chloride ions is: $y = -6 \times 10^{-5}x^6 + 0.7413x^5 - 3.729 \times 10^4x^4 + 1 \times 10^7x^3 - 2 \times 10^{10}x^2 + 1 \times 10^{13}x - 4 \times 10^{15}$, with an approximation reliability of $R^2 = 0.6768$.

Figure 3.14 presents the dynamics of changes in $BOD_5$ (Biochemical Oxygen Demand over 5 days) and dissolved oxygen concentrations during the period 2013–2024, along with the corresponding approximating curves.

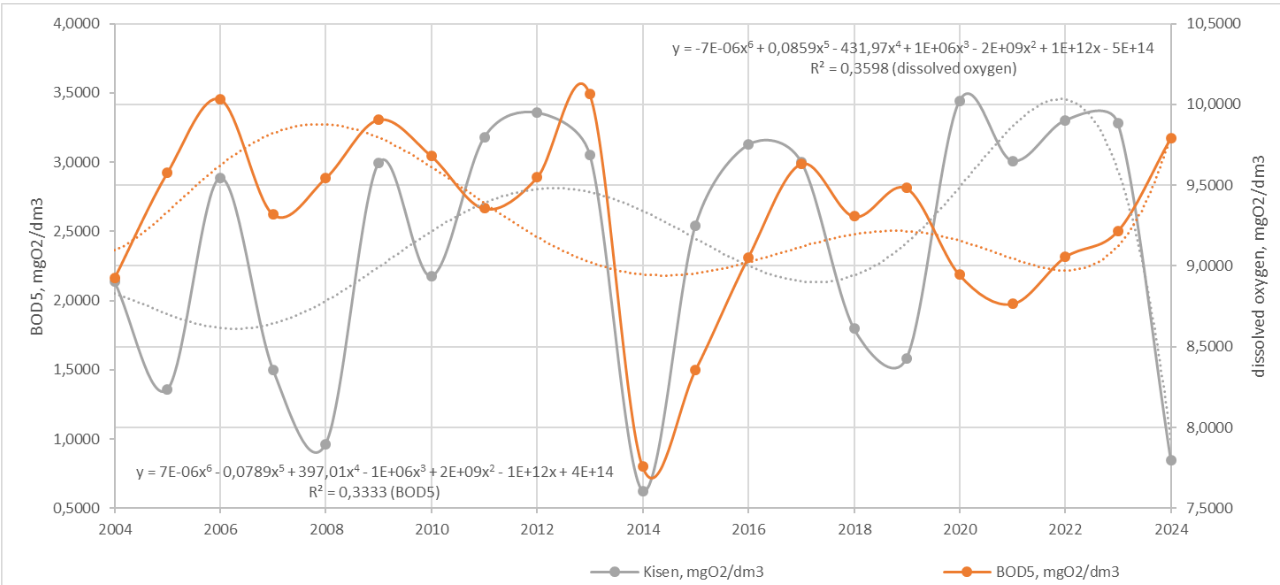


Fig. 3.14 Dynamics of $BOD_5$ and dissolved oxygen concentrations in water from 2013 to 2024 and the corresponding approximating curves (2013-2024)

The identified dependencies show that the lowest levels of this indicator were recorded in 2014 and 2024. Thus, there are opposite trends for $BOD_5$ and dissolved oxygen, as expected. The obtained results support the assumption of the presence of a self-purification capacity despite existing anthropogenic impacts.

*Conclusions.* This study conducted an analysis of the impact of anthropogenic pressure on the state of surface waters in the Danube River. The research covered the period from 2004 to 2024, with a focus on six key water quality indicators: phosphates, ammonium, sulfates, chlorides, biochemical oxygen demand over five days ($BOD_5$), and dissolved oxygen concentration.

It was established that phosphate and ammonium compounds exhibit seasonal fluctuations due to organic and agricultural discharges. Sulfate concentrations show high variability, influenced by both natural and anthropogenic sources, while chloride levels remain stable, indicating chronic exposure.

The analysis of $BOD_5$ and dissolved oxygen indicates a potential for self-purification, although episodes of oxygen depletion were recorded, particularly during periods of local organic overloading and disrupted hydrodynamics.

Developed regression models allowed for the identification of correlations between changes in water circulation, the intensity of port activity, and pollution levels.

The main environmental issues of the lower Danube were identified: organic and mineral pollution, eutrophication, oxygen regime deterioration, hydromorphological alterations, and threats posed by armed conflict. Despite these challenges, the river retains a capacity for partial self-recovery, especially under reduced anthropogenic pressure.

Restoration of ecological balance requires the implementation of systematic monitoring, modernization of treatment facilities, effective management of pollution sources, and Ukraine's active participation in international environmental regulatory mechanisms such as the Danube Commission. The modeling results can be used to forecast the state of the aquatic environment in both peacetime and post-war recovery scenarios.

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## 3.2 THE DEVELOPMENT OF DANUBE PORTS AMID WAR AND POST-WAR RECOVERY OF THE UKRAINE

One of the most important tasks today is the restoration of Ukraine, overcoming the consequences of hostilities on its territory, and addressing issues of national security and defense capability. This focus is emphasized in the developed Plan for the Recovery of Ukraine, presented in the EU. This document identifies three most important areas on which the future of the country and its national security depend: logistics, reconstruction of infrastructure, and energy. Therefore, it is possible to solve logistical and infrastructure tasks by expanding the use of water (sea and river) transport and its infrastructure. Emphasizing the Danube River is important given the limitations of using traditional waterways.

An analysis of the main publications shows that the issue of river logistics development is considered by many researchers. For example, studies by Krčum, M., Plazibat V., Gorana J. M., Wójcikiewicza R., Kaupb M., Nowakowski T., Kulczyk J., Skupień E. & Tubis A., Kolář J. & Stopka, O., Krile S. focus on solving specific issues in the context of individual countries, such as the Croatian transport system and directions for integrating sea and river ports [1], the specifics of the operation of inland water transport in Szczecin (Poland) [2], the determinants of the transformation of the Lower Vistula river ports [3], the search for the location of a multimodal logistics center at the port on the Labe (Elbe) River [4], the development of the inland water transport market, and the strengthening of European cooperation in the field of inland water transport [5]. Problems of river transport and logistics development are also considered by a number of domestic scientists [6-12], among others.

In the research process, both general scientific methods (analysis and synthesis, induction and deduction, analytical grouping) and specialized methods (abstraction, modeling, etc.) were utilized for studying economic phenomena and processes. The object of the study is the Danube river ports.

The Danube River is one of the most important transport routes in Europe: it not only crosses ten countries but also connects with the Black Sea. The Danube has significant economic importance for all Danube countries. The river is navigable for 2500 km from the mouth. To improve navigation conditions, a network of canals has been constructed, the fairway has been deepened in some sections, and bank revetments have been carried out, among other things. The Danube is connected by canals with the basins of the Rhine, Elbe, Odra, and the Black Sea (Danube-Black Sea Canal).

In recent years, access to the Black Sea through the Ukrainian part of the Danube has gradually lost its significance. The only acceptable through route to the Black Sea via the Danube for a long time has been the Romanian canals - the Sulina and the Chornavoda-Constanta. Previously, more than 1 million tons of cargo were annually transported through the Ukrainian ports of Ust-Danube, Izmail, and Reni to the ports of the Mediterranean and back. However, these positions of Ukraine have gradually been lost. With the start of the war, due to the impossibility of using traditional sea transportation through the Black Sea, the importance of Danube logistics has increased.

If we analyze the volume of cargo transportation through Ukrainian ports in recent years, it has decreased by 2,6 times in 2022 compared to 2021. In 2023, Ukrainian ports increased cargo handling by 5% year on year - up to 62 million tons. This result was achieved thanks to the opening of a temporary maritime corridor. As a result, 430 ships were accepted through the corridor under loading, and 400 ships were sent, exporting 12,8 million tons of cargo.

However, the dynamics of cargo handling by ports compared to 2022 is ambiguous. Thus, the port of Odessa saw an increase of 9% to 84 million tons; the port of Chornomorsk saw a decrease of 3% to 11,4 million tons; and the port of Pivdenny saw a decline of 34% to 10,1 million tons.

The most dynamic increase in handling is observed in the Danube ports (Izmail, Reni, and Ust-Danube). By the end of 2023, the total cargo turnover in these ports almost doubled - to 32 million tons in 2022 - tripled to 16,5 million tons from 5,5 million tons in 2021. In particular, last year the volume of handling in the port of Izmail amounted to 202 million tons (an increase of 2,3 times compared to 2022), in Reni – 10,1 million tons (+47% year on year).

Cargo transportation through these ports was carried out using the routes shown in Figures 3.15 and 3.16.

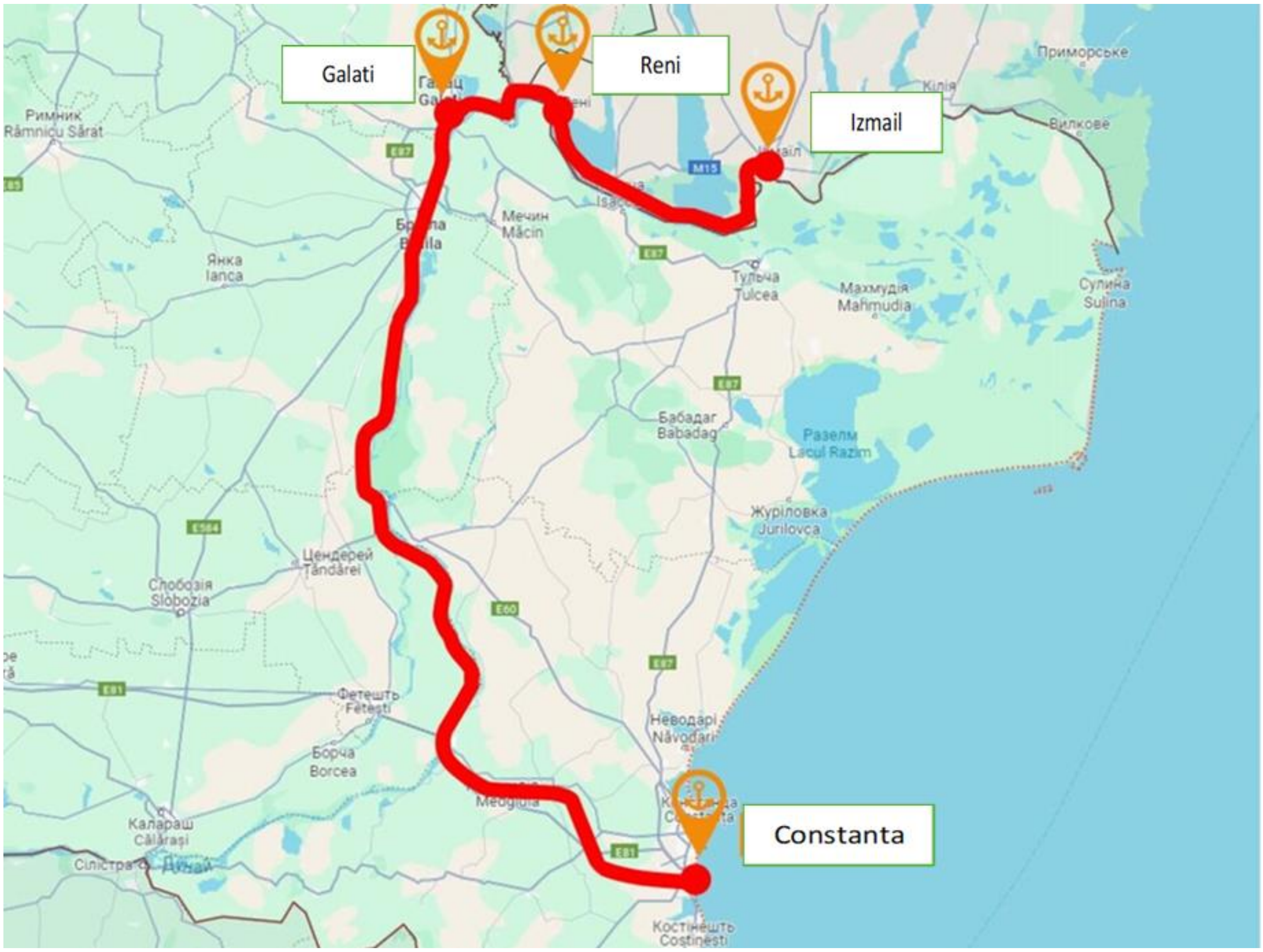


Fig. 3.15 Danube route to the port of Constanta

Source: https://uga.ua/meanings/sergij-kalkutin-pro-osvoyennya-dunajskih-marshrutiv-eksport-ukrayinskoyi-agroproduktsiyi-cherez-konstantsu-osoblivosti-richkovoyi-logistiki-nyuansi-tsinoutvorennya-ta-bezpekovi-riziki-dlya-ukrayinskog/

Under such conditions, there are all reasons to pay special attention to navigation on the Danube. Due to the periodic blocking of Ukraine's western border with Poland, increasing cargo transportation to Europe via the Danube is becoming important.

Today, the Ukrainian Danube Shipping Company (UDSC) has proposed to redirect cargo that was transported to EU countries by trucks to river transport. The UDSC has developed three lines for barge caravans:

1. Ukraine - Galati. The fastest route for transferring cargo through the western border to EU countries. Given the long distance, the river caravan can make 5-7 trips to Galati per month. So the delivery time of containers is only a few days.

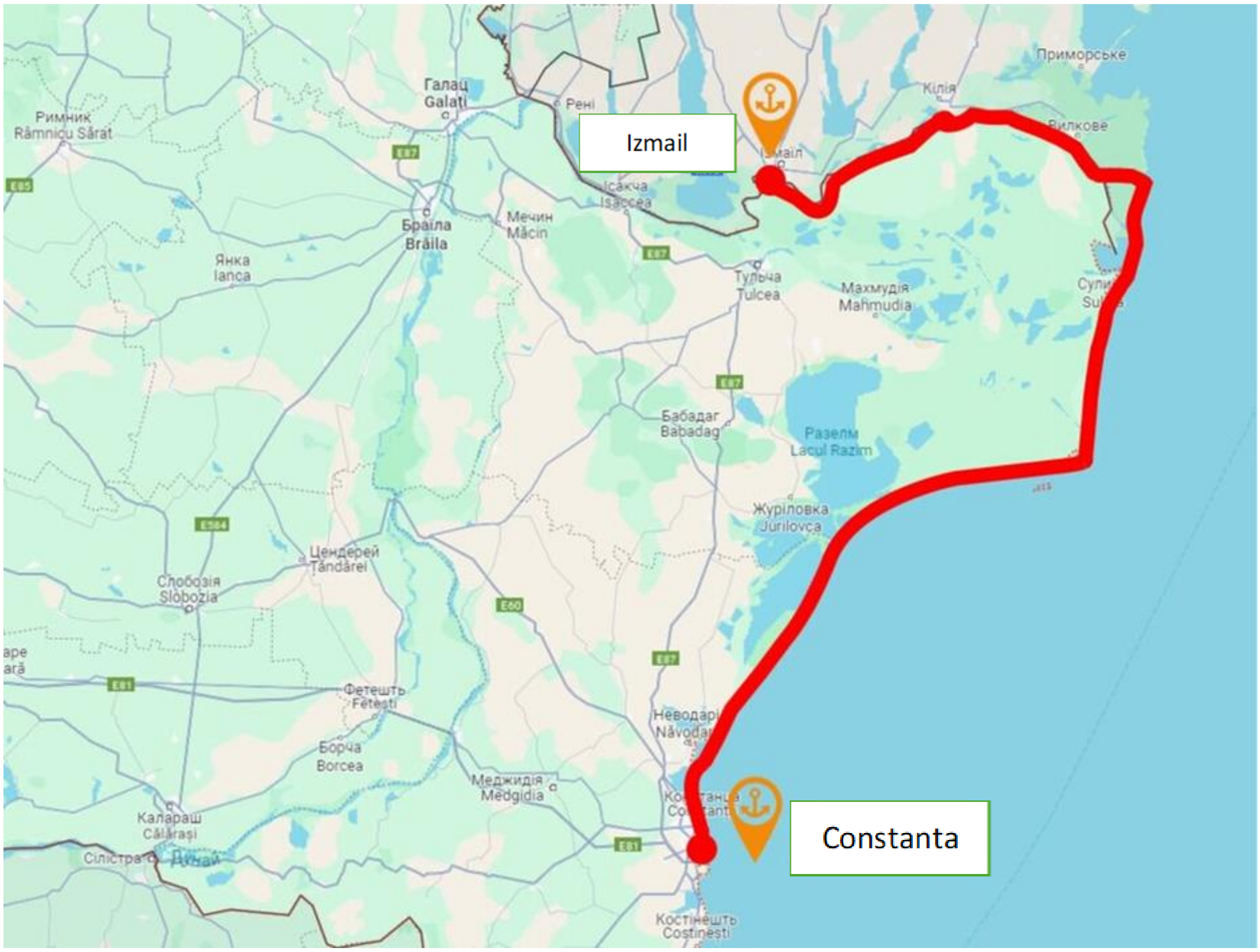


Fig. 3.16 Danube-Black Sea route to the port of Constanta

Source: https://uga.ua/meanings/sergij-kalkutin-pro-osvoyennya-dunajskih-marshrutiv-eksport-ukrayinskoyi-agroproduktsiyi-cherez-konstantsu-osoblivosti-richkovoyi-logistiki-nyuansi-tsinoutvorennya-ta-bezpekovi-riziki-dlya-ukrayinskog/

2. Ukraine - Regensburg. The route allows delivery of cargo to Germany to the closest point to the main market for Ukrainian exports. Or to any port on the Middle and Upper Danube. However, the duration of the trip is longer than in the case of delivery to Galati.

3. Ukraine - Constanta. Delivery of cargo to one of the largest European seaports with the possibility of further export to any point in the world.

In this context, it should be understood that such transportation has both advantages and disadvantages, including risks.

There is indeed a threat of a seasonal drop in the water level in the Danube, which may affect transportation. There are cases when caravans on the Middle Danube get stuck: while loading, the water level dropped, and it cannot pass through the shallow. And then they have to wait for the water level to rise again. Last year, 2023, the water level fell to a critical level. All operations on the Middle (Slovakia, Serbia, and Hungary) and Upper (Austria and Germany) Danube were closed. But there were opportunities to use the Lower Danube (Romania, Bulgaria, and Ukraine). The loading of barges fell by 30% - instead of 1,5 thousand tons, they loaded 1,1 thousand tons. But the caravans were running. There is no problem stated in the year 2024. The water level fell, but much less than last year. Currently, some cities in Europe are experiencing a critical rise in the water level.

But there are far more advantages. The Danube, for a very long time in 2022-2023, replaced the lack and significant limitations of Ukrainian Black Sea ports. And the route through the Danube naturally began to be used less after the blockade of the ports of Odessa was lifted thanks to the actions of the Armed Forces of Ukraine. The route through Poland is not a replacement for the Danube and Odessa, it is an additional route for the implementation of a small amount of products. Moreover, grain is not exported to Poland; it transits mainly to the Baltic countries and Germany. Delivery of cargo to one of the largest European seaports with the possibility of further export to any point in the world.

According to the UDSC's plans, it is planned to install additional barge caravans on container lines, which will ensure the delivery of 2?1 thousand TEU per month to Regensburg (Germany) or 5?9 thousand TEU to Constanta (Romania). The UDSC can work with TEU/FEU containers as well as reefer containers.

River transportations only by the UDSC fleet are an alternative to 2-5 thousand trucks, which has additional environmental significance. In general, the increase in the turnover of road transport compared to rail and sea transport is not a positive trend since, as you know, the average $CO_2$ emissions per ton-kilometer in road transport amount to 139.8 g, while in rail transport - only 15.6 g. Water transport is more environmentally friendly.

Replacing road transport with river transport will significantly reduce the specific weight of $CO_2$ emissions by freight road transport. Instead of transporting large volumes of cargo by roads, river transport can become a more environmentally sustainable option. For example, diesel fuel consumption for transporting 1 ton of cargo by river over a distance of 400 km is 3,95 kg/t. The same transportation by road transport requires 7,73 kg/t. As we can see, fuel savings will be 3,78 kg.

Reorienting transport flows to river transport can be a profitable strategy in terms of reducing the specific weight of $CO_2$ emissions by freight road transport. This will not only reduce fuel consumption but also contribute to reducing carbon dioxide emissions and improving the environmental condition.

Thus, the emphasis on the use of rail and water transport is the most effective way to integrate the domestic transport system into the European one, including taking into account environmental standards.

It is quite understandable that water transport also creates a certain environmental burden, namely: increased noise (both above water and underwater), possible oil and wastewater spills, exhaust gas emissions ($CO_2$, carbon monoxide, sulfur oxides, nitrogen oxides, particulate matter).

However, modern river transport is the most environmentally friendly, along with rail and road transport, which significantly enhances its competitiveness given the latest trends in EU greening and the implementation of relevant standards. According to research by Delft University of Technology (Netherlands), $CO_2$ (carbon dioxide) emissions from inland water transport are approximately three times lower (per 1 ton/km) than those from road transport.

The possibility of installing particulate filters on river vessels allows for a reduction of up to 90% in NOX (nitrogen oxide) emissions, which are responsible for smog formation and the greenhouse effect, and a reduction of up to 98% in PM10 particulate matter levels. River transport enables the transportation of large volumes of cargo. For example, a barge with a carrying capacity of 900 tons can replace 18 railcars or 45 twenty-ton trucks.

To substantiate the ecological and economic advantages of the aforementioned transportations along the Danube, we will conduct appropriate analytical assessments. Figure 3.17 shows the possibilities of transportation within the Danube countries-participants of the Danube Commission.

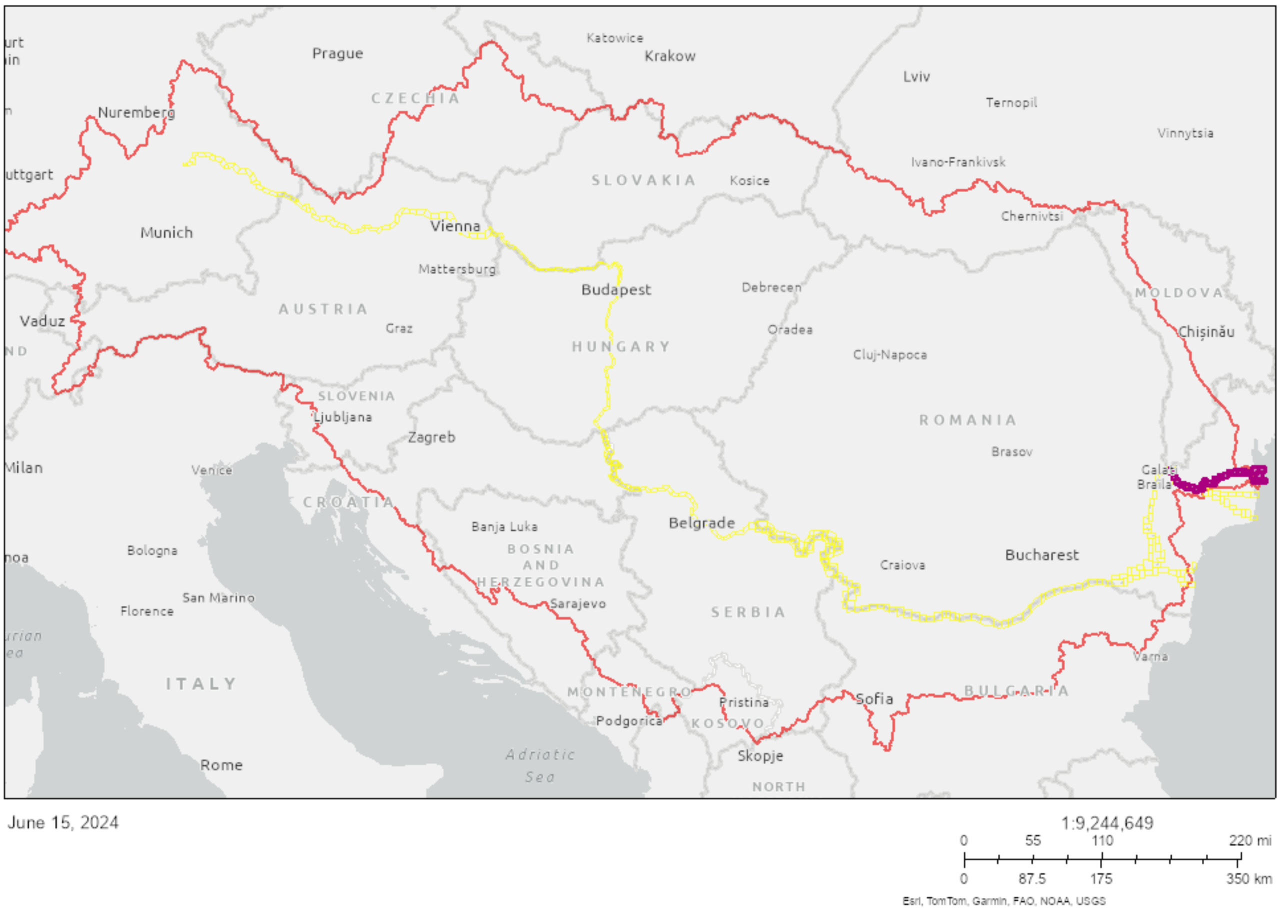


Fig. 3.17 Objects from Danube Commission's hydrological database

Source: https://danubecommission.maps.arcgis.com/apps/View/index.html?appid=4c9e7f38b65541deb9c8d974b9ab2923&extent=7.9149,39.0323,32.9638,51.3481

Figure 3.18 shows the results of the analysis of cargo turnover of the ports of Danube countries.

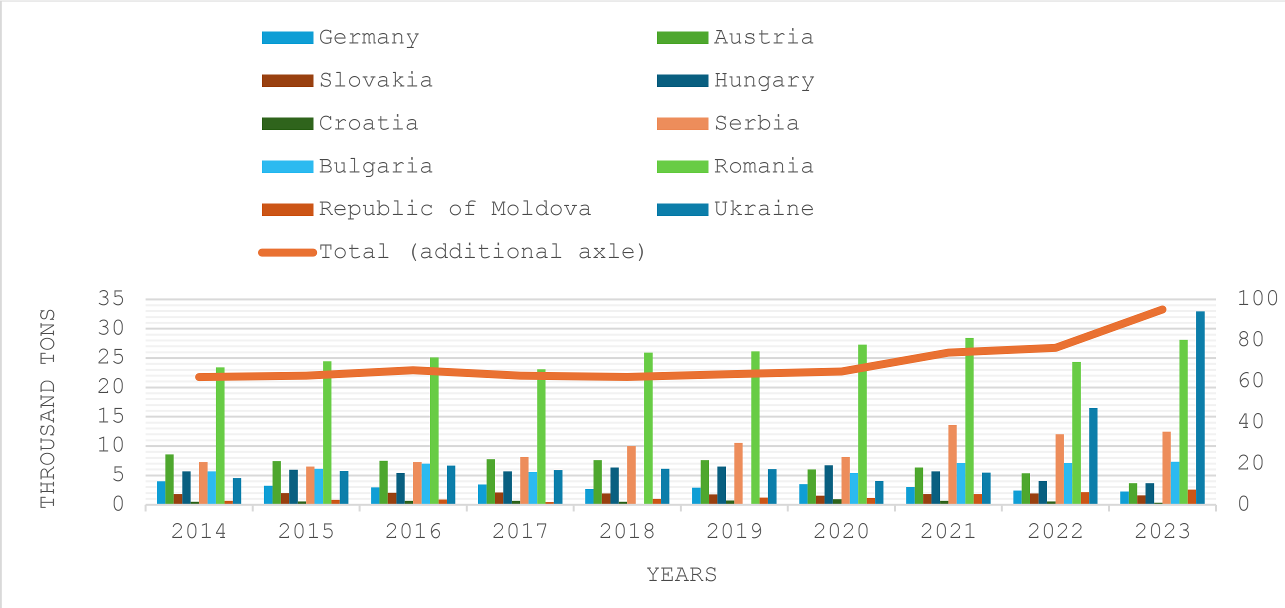


Fig. 3.18 Cargo turnover volumes in different countries over the years

In most countries, there is an increase in cargo transportation volumes over the study period.

Germany: cargo transportation volumes significantly decreased from 4.031 thousand tons in 2014 to 2.283 thousand tons in 2023. The lowest figure was recorded in 2022 - 241 thousand tons.

Austria: after minor fluctuations in 2014-2017, cargo transportation volumes began to gradually decrease from 7,604 thousand tons in 2018 to 3.688 thousand tons in 2023.

Slovakia: the cargo turnover remains stable with slight fluctuations, from 1.8 thousand tons in 2014 to 1.619 thousand tons in 2023. The peak was in 2015 with 2.009 thousand tons.

Hungary: the volume of transportation increased from 5.673 thousand tons in 2014 to 6.742 thousand tons in 2020, after which it decreased to 3.664 thousand tons in 2023.

Croatia: the cargo transportation indicators are relatively stable with minor fluctuations. The lowest indicator was in 2018 (0.521 thousand tons), and the highest was in 2017 (0.6827 thousand tons).

Serbia: there has been a significant increase in the volume of cargo transportation, from 7.27 thousand tons in 2014 to 12.440 thousand tons in 2023. Notably, there was a sharp increase in 2022 to 12.023 thousand tons.

Bulgaria: the data for the study period is incomplete, but there is an increase from 5.689 thousand tons in 2014 to 7.357 thousand tons in 2023.

Romania: the indicators remain high, from 23.406 thousand tons in 2014 to 28.129 thousand tons in 2023. There has been steady growth since 2020.

Republic of Moldova: the volume of cargo transportation increased from 0.678 thousand tons in 2014 to 2.605 thousand tons in 2023, with a noticeable increase after 2019.

Ukraine: there has been significant growth in the volume of cargo transportation from 4.547 thousand tons in 2014 to 32.940 thousand tons in 2023. A particularly sharp increase was recorded in 2022 (16.505 thousand tons).

The total cargo transportation volume increased from 62.196 thousand tons in 2014 to 95.090 thousand tons in 2023, with a noticeable increase after 2021.

Among the Danube countries, Romania has the largest transportation volumes, followed by Serbia. With the start of the war, Ukraine's transportation volumes have significantly increased due to the possibility of using the ports of Reni, Izmail, and Ust-Danube (Figure 3.19).

Regarding Izmail, from 2014-2016, cargo turnover increased, reaching a peak in 2016 (5.682 thousand tons). From 2017-2020, there is a decrease to the lowest level in 2020 (3.245 thousand tons). From 2021-2023, there is a significant increase, especially in 2022 and 2023, with the highest volume of 202 thousand tons in 2023.

Regarding Reni, from 2014-2016, there are minor fluctuations with a peak in 2014 (1.4648 thousand tons). From 2017-2020, relatively stable volumes with slight fluctuations. From 2021 to 2023, there was a sharp increase in 2022 and 2023, reaching 10.1 thousand tons in 2023.

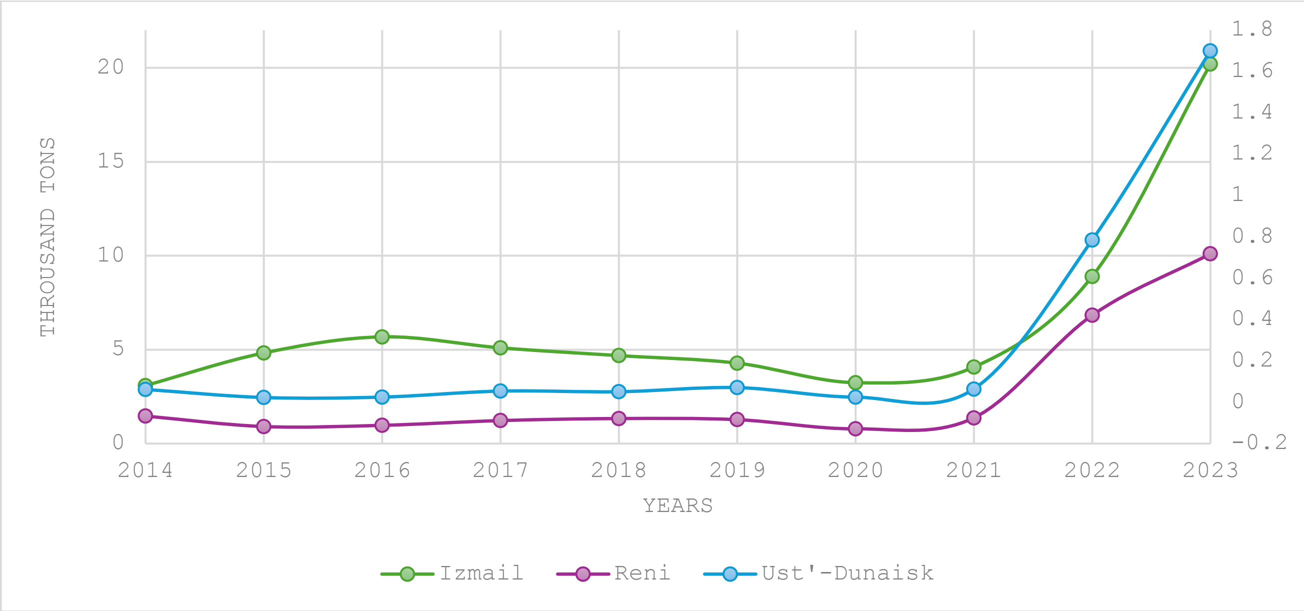


Fig. 3.19 Cargo turnover volumes through the channels Izmail, Reni, Ust-Danube from 2014 to 2023

Regarding Ust-Danube, from 2014-2020, cargo turnover is relatively stable and low with minor fluctuations. From 2021-2023, there is a significant increase, especially in 2022 and 2023, with the highest volume of 1,7 thousand tons in 2023.

Izmail has the highest cargo turnover volumes among the three channels, especially since 2022. Reni, in turn, is second in terms of volumes with significant growth in 2022 and 2023.

Ust-Dunaisk has the lowest cargo turnover volumes but also shows growth in 2022 and 2023. All three ports demonstrate sharp increases in 2022 and 2023.

The greatest increase is observed in Izmail, where cargo turnover volumes more than doubled in 2023 compared to 2022. All three channels show significant growth in 2022 and 2023. Izmail consistently has the highest cargo turnover figures, indicating its crucial role in regional transportation.

To analyze the situation in the Romanian Danube ports.

Figure 3.20 presents the analysis results of cargo transportation volumes through the Danube-Black Sea canal from 2012 to 2023. It includes three types of shipments: combined cargo turnover, international transportation, and domestic transportation.

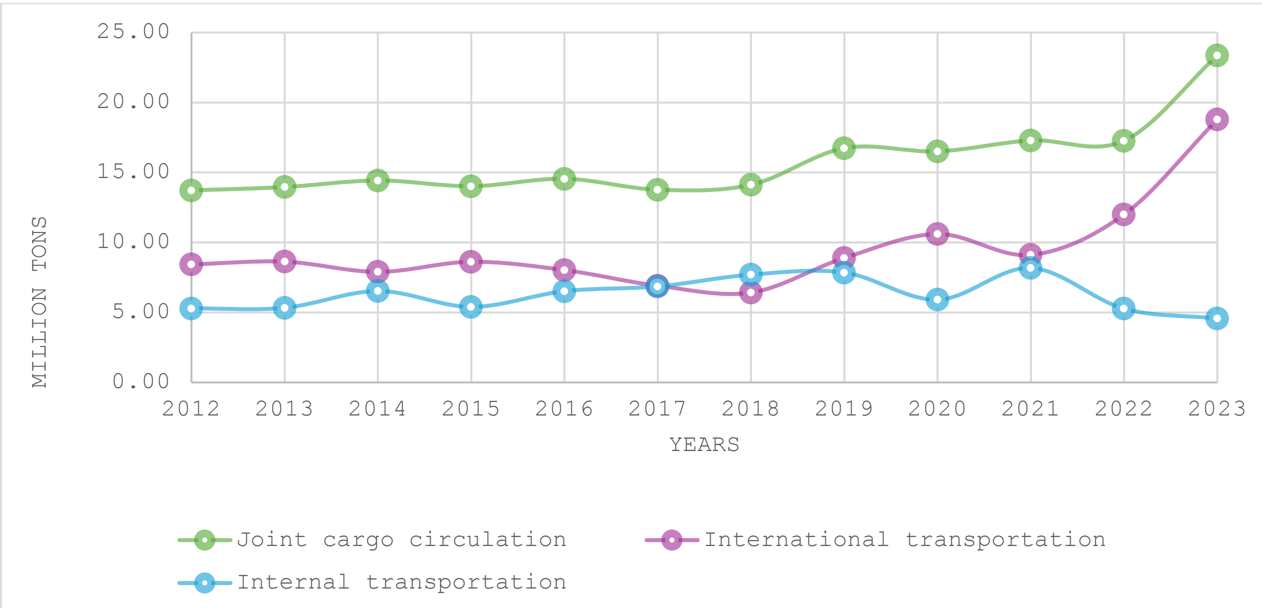


Fig. 3.20 Cargo volumes through the Danube-Black Sea canal over the years

The volumes of cargo transportation through the Danube-Black Sea canal during 2012-2023 showed steady growth. During this period, joint cargo turnover almost doubled from 1.372 million tons in 2012 to 2.336 million tons in 2023. International transportation during 2012-2023 accounted for the majority of joint cargo turnover. Their share in total transportation volumes from 2012 to 2023 ranged from 46% to 78%.

The analysis of cargo turnover through the Sulina port is shown in Figure 3.21.

The volumes of cargo transportation through the Sulina canal during 2018-2023 showed steady growth. During this period, cargo turnover increased more than three times. Transportation in the direction of "Danube-Sea" during 2015-2023 accounted for the majority of cargo turnover. Their share in total transportation volumes from 2015 to 2023 ranged from 63% to 78%. During 2015-2023, the volumes of cargo transportation through the canal showed steady growth, indicating its growing role in the global transportation system.

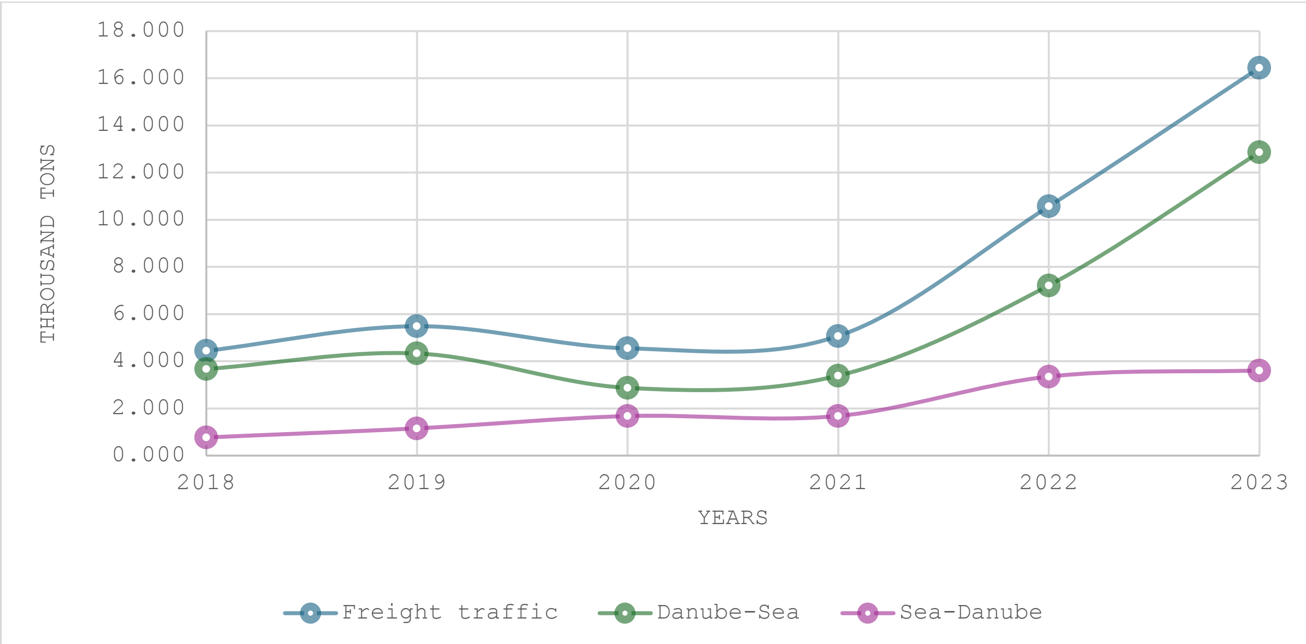


Fig. 3.21 Cargo volumes through the Sulina canal over the years.

The port of Galati holds significant importance in the transportation market along the Danube River. Figure 3.22 shows the volumes of cargo turnover by river and sea vessels to the port of Galati from 2015 to 2023.

Regarding cargo turnover by river vessels, from 2015-2019, there is relatively stable cargo turnover with fluctuations ranging from 2,961-3,287 thousand tons. In 2020, there is a slight decrease to 2.831 thousand tons. In 2021, there is an increase to the highest level of 3.350 thousand tons. In 2022, there is a slight decrease to 3.054 thousand tons. In 2023, there is a significant decrease to 0.915 thousand tons, which may be the result of significant changes in economic conditions and other factors.

Regarding cargo turnover by sea vessels, from 2015-2019, there is relatively stable cargo turnover with fluctuations ranging from 3,821-4,072 thousand tons. In 2020, there is a slight increase to 4,252 thousand tons. In 2021, there is an increase to the highest level of 4,635 thousand tons. In 2022, there is a slight decrease to 4470 thousand tons. In 2023, there is a significant decrease to 2,784 thousand tons, which may also be the result of significant changes in economic conditions and other factors.

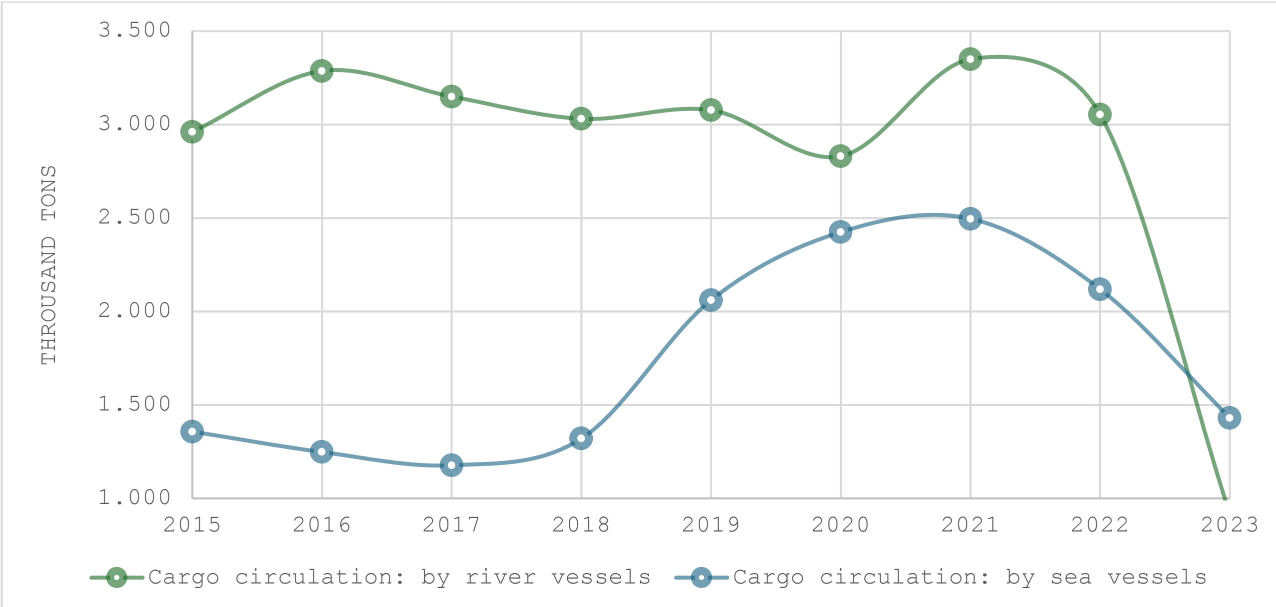


Fig. 3.22 Cargo turnover by river and sea vessels to the port of Galati from 2015 to 2023

Regarding cargo turnover by sea vessels, there was a consistent decline from 1.357 million tons in 2015 to 1.177 million tons in 2017. From 2018 to 2019, there was an increase, particularly sharp in 2019 to 2.061 million tons.

From 2020 to 2021, this growth continued to 2.496 million tons in 2021. There was a slight decrease in 2022 to 2.119 million tons. However, in 2023, there was a significant decrease to 1.431 million tons.

Therefore, regarding river cargo turnover, the figures remained relatively stable with minor fluctuations between 2015 and 2019. The year 2021 was the most successful with a volume of 3.350 million tons. However, there was a significant decrease in 2023 to 0.915 million tons. As for maritime cargo turnover, there was a gradual decrease until 2017, followed by stable growth until 2021. The peak volume was reached in 2021 at 2.496 million tons. There was a decrease in 2023 to 1.431 million tons.

River cargo turnover demonstrates more stable figures throughout the period from 2015 to 2019, while maritime cargo turnover shows more pronounced fluctuations. Both types of cargo turnover reached their peak values in 2021, but river cargo turnover exhibited a sharper decline in 2023. Both types of cargo turnover show a trend of growth until 2021, after which both decrease, though maritime cargo turnover remains more stable compared to river cargo.

Let's analyze the cargo turnover of the Port of Constanta (Figure 3.23). The majority share of the port's cargo turnover is provided by maritime transportation. However, the port also utilizes the capabilities of river transport facilities.

Regarding cargo turnover by river vessels, there was a decrease from 13.229 thousand tons in 2016 to 12.664 thousand tons in 2018. From 2019 to 2021, there was recovery and growth, reaching the highest volume of 15.863 thousand tons in 2021. From 2022 to 2023, there were minor fluctuations with a peak volume of 15.679 thousand tons in 2023.

As for cargo turnover by sea vessels, there was a slight decrease from 46.195 thousand tons in 2016 to 45.622 thousand tons in 2017. From 2018 to 2019, there was significant growth to 51.458 thousand tons in 2019. In 2020, there was a noticeable decrease to 45.506 thousand tons. From 2021 to 2023, there was steady growth to a peak volume of 76.821 thousand tons in 2023.

Cargo turnover of sea vessels has significantly increased, especially in 2022 and 2023, reaching 76.821 thousand tons in 2023. The cargo turnover of river vessels remains relatively stable with a slight increase to 15.679 thousand tons in 2023. Sea vessels handle significantly larger volumes of cargo compared to river vessels, which is a crucial indicator for international trade development.

Considering the viability of expanding cargo transportation through Danube River ports, it would be worthwhile to examine the situation in the context of the Port of Regensburg (Germany).

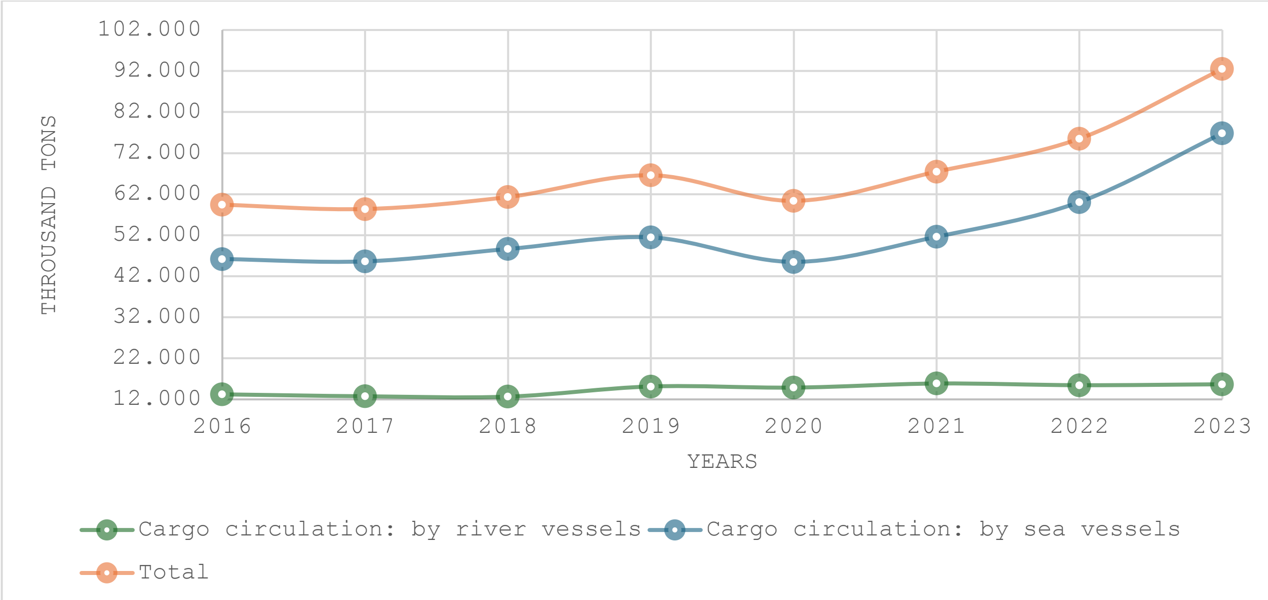


Fig. 3.23 Volume of cargo turnover by river and sea vessels at the Port of Constanta from 2016 to 2023

Figure 3.24 presents data on cargo transportation at the Port of Regensburg.

The cargo turnover of the Regensburg port shows significant fluctuations during the analyzed period. The highest volume was in 2020, after which there is a stable decline. The largest growth was observed in 2017 and 2020, with a peak in 2020 (1.553 thousand tons). Significant decline in 2018 and after 2020. The lowest level of cargo turnover was recorded in 2023 (1.021 thousand tons). From 2016-2017, cargo turnover increased by 11,3% from 1.350 thousand tons in 2016 to 1.502 thousand tons in 2017. However, from 2017 to 2018, there was a significant decrease by 22.2% to 1.169 million tons. From 2018 to 2019, there was a recovery with an increase of 18.6% to 1.387 million tons. From 2017-2019, cargo turnover decreased by 25% to 1.130 thousand tons. From 2020-2023, there is a decrease of 33% to 1.021 thousand tons.

The trends of recent years, as we can see, are negative, although there are positive examples in 2017 and 2020. Therefore, there are all reasons to expect that the expansion of navigation on the Danube will increase the cargo turnover volumes in the Regensburg port to its planned capacities.

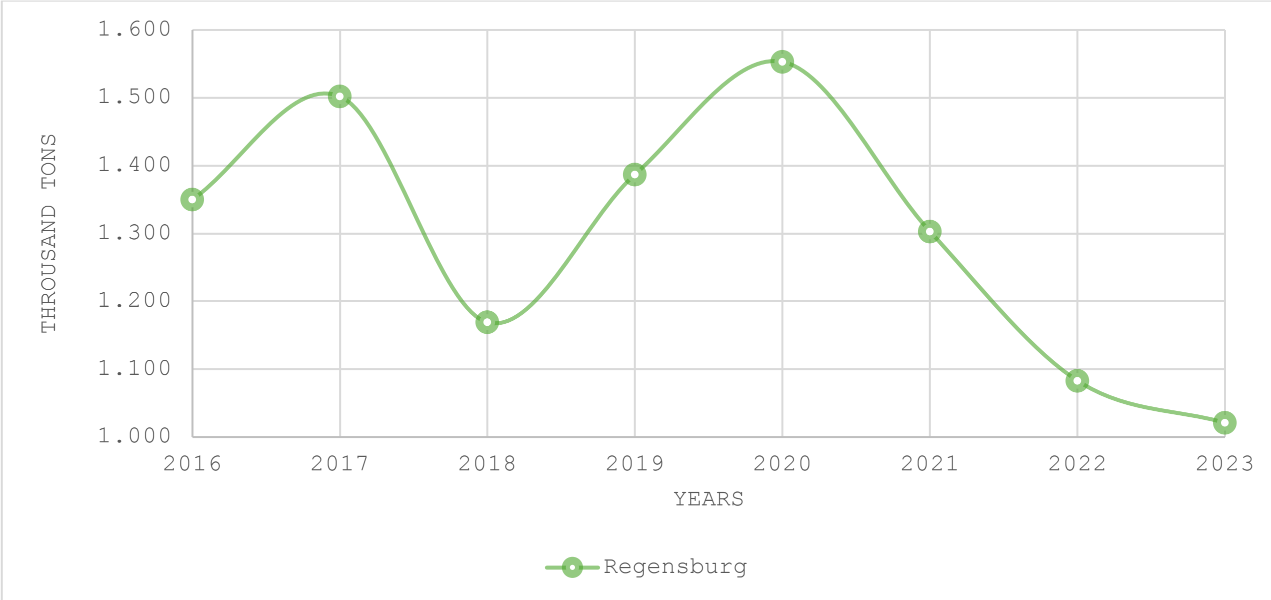


Fig. 3.24 Volume of cargo turnover at the Port of Regensburg from 2016 to 2023

*Conclusions.* The conducted analysis showed that in the conditions of war and the blockade of the ports of Greater Odessa, export transportation through the Ukrainian Danube ports of Reni, Izmail, and Ust-Danube has been activated. This was also facilitated by the dredging works in the Bystre estuary, which allowed its transport capabilities to be used for the passage of vessels with a draft of up to 6.5 meters, and not only the Romanian Sulina canal.

The analysis showed that, in addition to positive results for Ukrainian ports, there was also an increase in cargo handling volumes in Romanian ports, for example, the Sulina port has shown an increase in cargo movement volumes in recent years. Overall, if we compare the growth rates in the direction of Danube-Black Sea and in the opposite direction, the preference is given to the Danube-sea direction.

Regarding transportation through the Danube-Black Sea canal, recent years have also seen an increase in cargo transportation volumes, but this is mainly due to international transportation. Domestic transportation does not show similar dynamics. The Constanta port has also been increasing cargo handling volumes in recent years due to sea transportation, but river transportation is also growing, although not as significantly.

Unlike the mentioned ports, the Romanian port of Galati has been decreasing cargo handling volumes since 2021. The reason for this is that, among the two routes considered - the Danube and the Danube-Black Sea to the Constanta port, preference is given to the latter.

This gives reason to expect that the further expansion of navigation along the Danube using the routes Ukraine - Galati, Ukraine - Regensburg, and Ukraine-Constanta (via the Danube) will ensure the effectiveness of the mentioned ports and create additional conditions for the development of transport logistics in the Danube region as part of the security system for Ukraine, Europe, and the world as a whole.

An additional advantage of such decisions is their environmental orientation, since among all types of transport, water transport is the most environmentally friendly.

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## 3.3 ASSESSMENT OF THE IMPACT OF NATURAL AND ANTHROPOGENIC FACTORS ON THE STATE OF SURFACE WATERS IN THE UKRAINIAN SECTION OF THE DANUBE RIVER

The Danube River is one of Europe's largest transboundary rivers and plays a key role in shaping the hydrological regime, ensuring water-resource availability, and maintaining the region's ecological balance. The Ukrainian section of the Lower Danube is characterized by a complex network of branches, deltaic processes, and intense anthropogenic pressure, which makes the aquatic ecosystem highly sensitive to changes of both natural and technogenic origin.

Under current conditions, the hydrochemical regime of the Danube is affected both by natural factors (seasonal runoff fluctuations, flood processes, erosion, and sediment migration) and by anthropogenic pressures, among which navigation, dredging operations, and local impacts of port infrastructure are of particular importance. In recent years, the consequences of military actions on the territory of

Ukraine have become an additional significant factor, leading to further contamination of the aquatic environment and disruption of natural hydrochemical processes.

The relevance of the study is determined by the need for a comprehensive assessment of the current state of surface waters in the Ukrainian section of the Danube, taking into account the interaction of natural, transboundary, and military-anthropogenic factors, as well as the identification of spatio-temporal changes in the main hydrochemical indicators.

The aim of this study is to conduct a comprehensive analysis of the spatio-temporal dynamics of the hydrochemical condition of surface waters in the Ukrainian section of the Danube River, from the city of Reni to the city of Vylkove, on the basis of long-term monitoring data, and to identify the main patterns governing water-quality formation under the influence of natural, transboundary, and anthropogenic factors.

Within the scope of the study, it is envisaged to assess long-term changes in key hydrochemical indicators, in particular the content of dissolved oxygen, biochemical and chemical oxygen demand ($BOD_5$, COD), as well as the concentration of suspended solids, which are sensitive indicators of the state of aquatic ecosystems.

It is also envisaged to assess the impact of military actions on the state of surface waters, in particular through analysis of changes in port water areas and coastal sections, where products of infrastructure destruction, combustion products, and other pollutants may enter the aquatic environment. The study also seeks to identify spatial differences in water-quality changes between individual cross-sections of the studied area, determine the sections with the most pronounced anthropogenic pressure, and assess the processes of self-purification of surface waters in the Ukrainian part of the Danube River.

The study of the state of surface waters was conducted using data from monitoring stations for the surface waters of the Danube River in the cities of Reni, Izmail, Kiliia, and Vylkove. Long-term monitoring data from the Water Monitoring Laboratory of the Danube RBWR, the Water and Soil Monitoring Laboratory of the

Dniester BWR, and the Water Monitoring Laboratory of the Southern Region were used.

The methodological basis of the study consisted of the analysis of time series of hydrochemical indicators, followed by an assessment of their spatio-temporal dynamics. The study included the identification of long-term trends in the concentrations of dissolved oxygen, biochemical and chemical oxygen demand ($BOD_5$, COD), as well as suspended solids at different river cross-sections.

Microsoft Excel software was used for data processing and preliminary analysis, in particular methods of statistical generalization, construction of indicator-dynamics graphs, and comparative analysis between individual periods and monitoring cross-sections.

During the study, comparative analysis methods were applied to assess differences between river sections with varying levels of anthropogenic pressure, as well as the method of generalization to interpret the obtained results in the context of the influence of natural and technogenic factors.

The obtained results were interpreted with due regard to hydrological conditions, seasonal variability, and known extreme events in the Danube basin, which made it possible to comprehensively assess changes in surface-water quality.

The Danube River is the second-longest river in Europe and one of the most important transboundary water systems in the world. The Danube basin covers the territories of 19 countries and provides water resources for more than 80 million people. Owing to its geographical position and substantial anthropogenic pressure, the Danube is the subject of numerous hydrological, hydrochemical, ecological, and geoecological studies.

One of the most important directions in the study of the river is the assessment of water quality and its long-term trends. A synthesis of the results of long-term studies was carried out by Manoiu and Crăciun [1], who analysed more than four dozen scientific publications devoted to the state of the Danube's water resources. The following issues were examined: spatially related changes in water quality (the extent or location of the Danube section/sections subject to water-quality analysis) and temporally related changes in water quality over recent decades (1990–2018), with trends compared, where data were available, with the "decades of high pollution", namely 1960–1990. The authors established that, beginning in the 1970s, the construction of reservoirs, dams, and hydroelectric power plants had a significant impact on the river's hydrological regime. The study also showed that Danube water quality depends on a combination of natural processes and anthropogenic factors, including urbanization, agriculture, and industrial development.

Issues of monitoring and assessment of the ecological status of Danube waters were addressed in the work of Călmuc et al. [2]. The researchers summarized methodologies for determining the ecological status of water bodies in accordance with the requirements of the EU Water Framework Directive and showed that water-quality assessment should take into account not only physicochemical indicators but also biological indicators. The authors emphasize the need to use integrated water-quality indices for assessing the state of river ecosystems.

A considerable number of studies are devoted to the Lower Danube and its deltaic ecosystems. In the work of Topa et al. [3], a spatial-seasonal analysis of heavy-metal content in the waters of the Danube and adjacent delta areas was conducted. It was established that metal concentrations vary depending on season and local pollution sources, with the greatest impact observed near urbanized areas and transport corridors.

Particular attention has been paid to the Ukrainian part of the Danube Delta. The study "Integrated Assessment of Surface Water Quality in Danube River Chilia Branch" [4] carried out a comprehensive assessment of water quality in the Chilia branch. The results indicated a generally satisfactory ecological status of the water masses; however, elevated concentrations of nitrogen and phosphorus compounds were recorded at certain observation points, which is associated with the influence of agricultural activity and settlements.

A separate group of studies consists of works on microbiological monitoring. Kirschner et al. [5] conducted a large-scale study of bacterial pollution along the entire length of the Danube. It was established that the main sources of faecal contamination are large cities and insufficiently treated wastewater. The obtained results formed an important basis for international monitoring programmes in the Danube basin.

The study by Török et al. [6], devoted to the analysis of drinking-water quality within the Danube Delta Biosphere Reserve, is of considerable importance for assessing the state of water resources in the Danube Delta. The authors carried out a comprehensive assessment of the physicochemical indicators of water and established that the quality of water supply in individual settlements of the delta depends to a significant extent on local natural conditions and anthropogenic influence. Particular attention was paid to the content of mineral components and the compliance of indicators with sanitary standards. The results of the study underscore the need for continuous monitoring of drinking-water supply sources in deltaic ecosystems, which are particularly vulnerable to pollution.

A significant contribution to improving methods for assessing the state of river ecosystems was made by Muresan, Battes, and Momeu [7]. Their work examined the possibilities of applying various water-quality indices to determine the ecological status of the Danube. The authors showed that integrated indices make it possible to generalize a large body of hydrochemical data and provide a more transparent assessment of the ecological status of water bodies. It was established that the index-based approach is an effective tool for ecological monitoring, water-resource management, and the adoption of environmental protection decisions in the Danube basin.

An important direction of contemporary research is the study of new types of pollutants. In the work of Ene et al. [8], the content of heavy metals, nutrients, pharmaceuticals, endocrine disruptors, and bacterial contamination in the Lower Danube and the delta was investigated. The obtained results indicate the emergence of new anthropogenic pollutants in the aquatic environment, which may pose a threat to aquatic ecosystems and public health.

A comprehensive analysis of the problems of Danube basin management is presented in the work of Sommerwerk et al. [9]. The authors consider the Danube to be the world's most international river system, whose water resources are used by numerous states. The study analyses the main environmental challenges associated with water pollution, flow regulation, the development of navigation, biodiversity loss, and the impact of climate change. Particular attention is paid to the activities of the International Commission for the Protection of the Danube River (ICPDR) and to the implementation of integrated water-resource management in accordance with the requirements of the European Union Water Framework Directive. The authors emphasize that effective basin management is possible only under conditions of close international cooperation and harmonization of environmental policy among all countries of the basin.

The authors of [10] conducted a study of river sediments from the Danube River and its tributaries, namely the Sava, Tisa, Tamiš, and Timok. The results showed that geological origin has a strong influence on the heavy-metal content of river sediments, primarily with respect to Ni and Co concentrations. In addition, sediments of the Tamiš, Tisa, Sava, and Danube are subject to strong anthropogenic influence.

Article [11] analysed studies conducted during 2011–2021 on hydrocarbon pollution in the Romanian sector of the Danube. The articles included in this review were selected from three scientific platforms—Web of Science, ScienceDirect, and Google Scholar—using keywords, a dedicated search protocol, and various selection filters. It was demonstrated that the highest levels of hydrocarbon pollution in suspended solids and sediments were found in the Iron Gates–Călărași sector, while the main sources of pollution were industry, navigation, and wastewater discharges. The principal research methods included fluorescence analysis, the comet assay, the micronucleus test, complementary passive samplers, in vitro bioassays, a fugacity-based calculation model, sensors, oil-spill modelling, and others.

A number of studies are devoted to the investigation of heavy-metal pollution in the Danube River.

One of the studies [12] is based on the results of the Joint Danube Survey. As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were investigated in sediments and suspended solids along the entire length of the Danube. It was established that such pollution is recorded throughout the river's course, with the most critical contamination affecting not only surface waters but also bottom sediments.

The authors of [13] identified the main sources of heavy-metal pollution in the Danube and proposed solutions to reduce the amounts of these contaminating elements. The main object of the study was the Somova–Parcheș aquatic complex, which is considered representative in terms of contaminating elements. This area is located between Tulcea and Isaccea, in the pre-delta zone of the Danube Delta Biosphere Reserve.

The authors of [14] conducted a study of the Montenegrin part of the Black Sea and Danube River basin and identified the main pollutants: wastewater and solid waste from settlements.

Microplastics constitute another source of pollution in the Danube River. In recent years, the number of such studies has been increasing.

The results of study [15] on the Danube River and its tributaries during the Joint Danube Survey 4 (JDS4) expedition are presented. This study is a field investigation of 2,040 km of the Danube River in the context of microplastic pollution. It was established that this type of pollution is becoming increasingly critical for the state of the river's surface waters.

The authors of [16] demonstrated that microplastic (MP) pollution in river systems is becoming an increasingly serious environmental problem, especially in transboundary rivers such as the Danube. The authors assessed microplastic pollution in the Szigetköz section of the Danube and its main tributary, the Mosoni-Danube. The main research methods were Fourier-transform infrared spectroscopy (FTIR) combined with automated spectral evaluation. The results indicate that the tributary may constitute an important source of input to the main Danube channel in this section, while differences in polymer composition point to differing source characteristics within the study area.

An important research direction is the detection of emerging pollutants in the Danube basin. Ng et al. [17] conducted a large-scale screening of chemical substances using high-resolution mass spectrometry. In total, 2,362 chemical compounds were analysed, of which 586 substances were detected in the waters of the Danube basin. On the basis of the results obtained, 33 priority emerging pollutants were identified that require inclusion in future environmental monitoring programmes. The authors emphasize that traditional water-quality control systems do not always allow timely detection of new organic compounds of anthropogenic origin.

Bottom sediments play a significant role in shaping the ecological state of the river, as they act as accumulators of pollutants. Matić Bujagić et al. [18] studied the bottom sediments of the Đerdap Reservoir (Iron Gate I Reservoir). Accumulation of pesticides, pharmaceuticals, steroids, and perfluorinated compounds was established. The authors showed that the reservoir retains more than 50% of suspended solids and associated pollutants, which substantially affects the downstream transport of substances along the Danube.

Considerable attention is paid to the problem of eutrophication and nutrient inputs into the Black Sea. Kovacs and Zavadsky [19] analysed the long-term dynamics of nitrogen and phosphorus loads in the Danube basin. It was established that the maximum inputs of nutrients occurred in the late 1980s, causing large-scale eutrophication and hypoxia on the north-western shelf of the Black Sea. Owing to the implementation of environmental protection measures and the modernization of wastewater-treatment systems, nutrient concentrations gradually decreased. At the same time, the authors emphasize the need for further control of diffuse agricultural pollution sources.

Contemporary studies increasingly use artificial-intelligence methods to forecast water quality. Georgescu et al. [20] developed a forecasting system for the Water Quality Index (WQI) of the Danube River based on neural networks. Monitoring data for 2011–2017 and nineteen physicochemical water-quality parameters were used to construct the models. The results showed the high efficiency of cascade neural networks in short-term forecasting of the river's ecological state, creating prospects for the development of early-warning systems for deterioration in water-resource quality.

A comprehensive assessment of the state of Lower Danube waters was carried out by Radu et al. (2020) [21]. Based on the analysis of approximately 1,500 water samples collected in 2011–2017 at ten monitoring points, the researchers established that the waters of the Lower Danube are characterized as moderately polluted and correspond to Class III surface-water quality. Multivariate statistical analysis revealed the influence of both natural factors and anthropogenic pollution sources associated with navigation, industry, and municipal wastewater.

A separate direction of contemporary research is associated with the spread of antibiotic resistance in the aquatic environment. Schachner-Groehs et al. [22] monitored antibiotic-resistance genes along more than 2,300 km of the Danube channel. It was established that the main source of the spread of antibiotic-resistance genes is insufficiently treated municipal wastewater. A significant correlation was identified between concentrations of antibiotic-resistance genes and indicators of faecal contamination, underscoring the importance of modernizing sewerage and wastewater-treatment systems in the countries of the Danube basin.

The results of the authors' own studies of the state of the Danube River surface waters are presented in articles [23–24].

Thus, the analysis of scientific sources shows that contemporary studies of the Danube cover a wide range of issues: from the monitoring of physicochemical indicators and the microbiological state of waters to the assessment of the impacts of climate change, economic activity, and military actions. Studies of the Lower Danube and its delta remain particularly relevant, as they combine substantial anthropogenic pressure, intensive navigation, and high conservation value of the territories.

The analysis was conducted using data from the following monitoring stations for the status of surface waters of the Danube River in the cities of Reni, Izmail, Kiliia, and Vylkove:

1) Danube River, 163 km, Reni, border with Romania (45°46′72″ N, 28°22′94″ E). Monitoring data from the Water Monitoring Laboratory of the Danube Regional Office of Water Resources (from 2024 to 2026). The station is located upstream of the Reni Sea Commercial Port (Port of Reni, 130 rkm: 45°25′15″ N, 28°17′25″ E). The port is situated on the left bank of the Danube from 123.6 km to 128.3 km.

2) Danube River, 94 km, Izmail, municipal drinking-water intake (45°33′85″ N, 28°81′48″ E). Monitoring data from the Water Monitoring Laboratory of the Danube Regional Office of Water Resources (from 2004 to 2021). The station is located upstream of the Izmail Sea Commercial Port (Port of Izmail, 87–97 rkm: 45°20′20.8″ N, 28°47′50.5″ N). The Izmail Sea Commercial Port is situated within the water area of the Kiliia branch of the Danube River (85–95 rkm).

Official monitoring data for the period from 2021 to 2023 are unavailable. Monitoring was resumed in 2024 at the following point: Danube River, 94 km, Izmail (Kiliia branch) (45°33′58″ N, 28°79′38″ E). Monitoring data from the Water and Soil Monitoring Laboratory of the Basin Administration of Water Resources of the Black Sea Rivers and the Lower Danube.

3) Danube River, 89.9 km, Izmail (45°33′58″ N, 28°79′38″ E). Monitoring data from the Water and Soil Monitoring Laboratory of the Dniester Basin Administration of Water Resources. The monitoring station is located within the boundaries of the Izmail Sea Commercial Port.

4) Danube River, 48 km, Kiliia, municipal drinking-water intake (45°43′51″ N, 29°26′40″ E). Monitoring data from the Water Monitoring Laboratory of the Danube Regional Office of Water Resources.

5) Danube River, 32 km, Kiliia; 32.0 km of the Danube River; 13.0 km downstream of Kiliia (45°44′47″ N, 29°43′19″ E). Monitoring data from the Water Monitoring Laboratory of the Southern Region.

The Port of Kiliia (a port point of the Ust-Dunaisk Sea Commercial Port), 47 rkm (45°26′31.4″ N, 29°15′24.9″ E), is located in immediate proximity to the drinking-water intake of Kiliia.

6) Danube River, 20 km, Vylkove, municipal drinking-water intake (45°40′15″ N, 29°57′18″ E). Monitoring data from the Water Monitoring Laboratory of the Danube Regional Office of Water Resources.

The Ust-Dunaisk Sea Commercial Port, 19 rkm (45°28′01.2″ N, 29°42′42.8″ E), is located upstream of the monitoring point. In general, the Ust-Dunaisk seaport is situated in the southern part of Zhebriiany Bay of the Black Sea and adjoins the Ochakiv branch of the Danube River.

Figure 3.25 presents the dynamics of changes in the content of suspended solids, BOD5, and dissolved oxygen in the surface waters of the Danube River (Reni, 163 km).

During 2004–2023, the quality of surface waters was characterized by a relatively stable hydrochemical regime. The concentration of dissolved oxygen varied within 7–13 $mgO_2/dm^3$, exceeding the MPC of 4 $mgO_2/dm^3$ and indicating normal aeration of the water masses. During this period, BOD5 ranged from 1 to 5 $mgO_2/dm^3$, periodically exceeding the MPC of 3 $mgO_2/dm^3$. This dynamics of indicator changes may be explained by seasonal inputs of organic matter into the river, surface runoff from agricultural lands, and the specific features of the hydrological regime. As for suspended solids, their content fluctuated within 2–8 $mg/dm^3$, although occasional maximum increases to 100–150 $mg/dm^3$ were recorded.

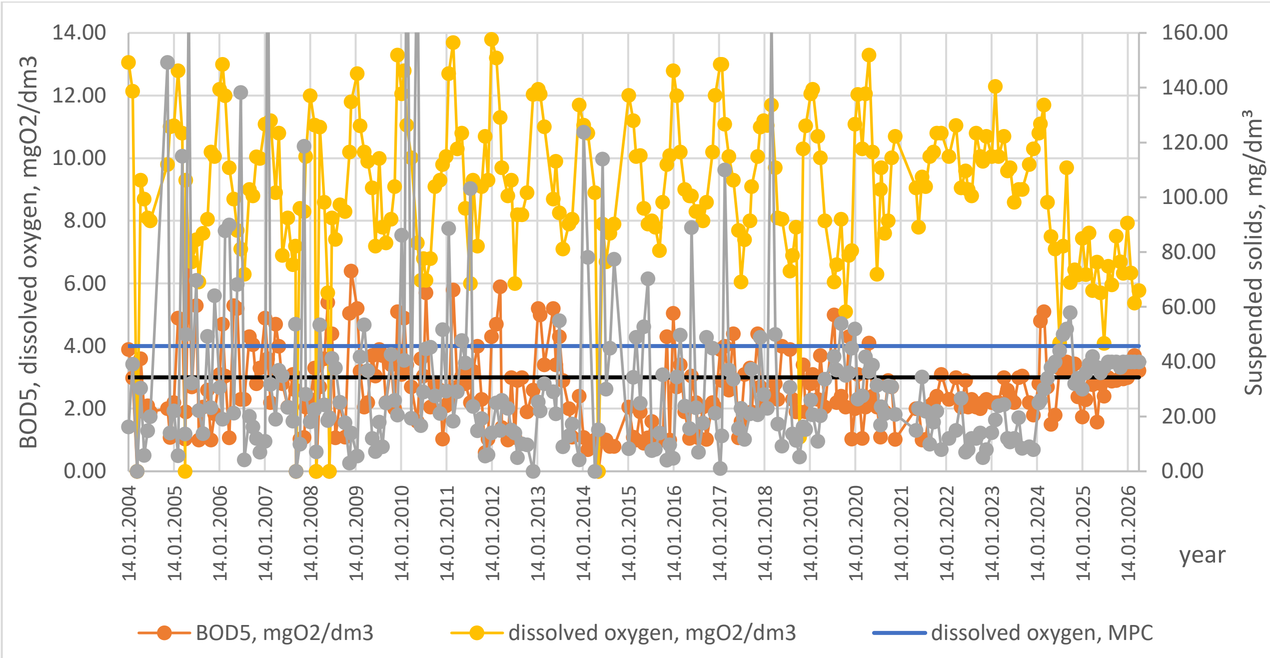


Fig. 3.25 Dynamics of changes in the content of suspended solids, BOD5, and dissolved oxygen in the surface waters of the Danube River (Reni, 163 km)

The situation changed from 2024 onward. A sustained increase in the level of suspended solids to 30–50 mg/dm3 occurred, and since 2025 the value has not fallen below 40 mg/dm$^3$. The dissolved oxygen level decreased slightly to 7–8 mgO$_2$/dm$^3$, although it remains above the MPC. During this period, BOD$_5$ quite frequently exceeds the MPC. These phenomena may be explained by the fact that this section is located on the border with Romania, and the observed changes are a consequence of transboundary impacts. In our view, these impacts include the effects of natural phenomena, namely first the summer drought and then Cyclone Boris in September 2024. As a result of the drought, dredging operations intensified in the Romanian ports of Galați and Brăila, which led to an increase in suspended solids downstream. The subsequent increase was caused by erosional runoff resulting from the washing of tons of sand, clay, and soils from countries located upstream along the Danube during the September flood. In addition, the flood activated the washout of silts previously retained by upstream hydropower plants. In previous years, these phenomena were not observed, since in

2024 there was a cumulative effect produced by the simultaneous action of natural phenomena and anthropogenic impacts of human activity. Moreover, microplastics are currently a significant pollutant of the Danube and also contribute to the increase in suspended solids in Reni. The decrease in dissolved oxygen during this period, as well as throughout 2025–2026 below the long-term level, indicates the accumulation in the border area of organic compounds and fine-grained sediments that continue to oxidize, thereby reducing oxygen levels.

Figures 3.26 and 3.27 present data on the dynamics of changes in suspended solids, BOD5, and dissolved oxygen in the surface waters of the Danube River at two sections: Izmail, 94 km, and Izmail, 89 km. The first section is located upstream of the Izmail Sea Port, while the second is located downstream.

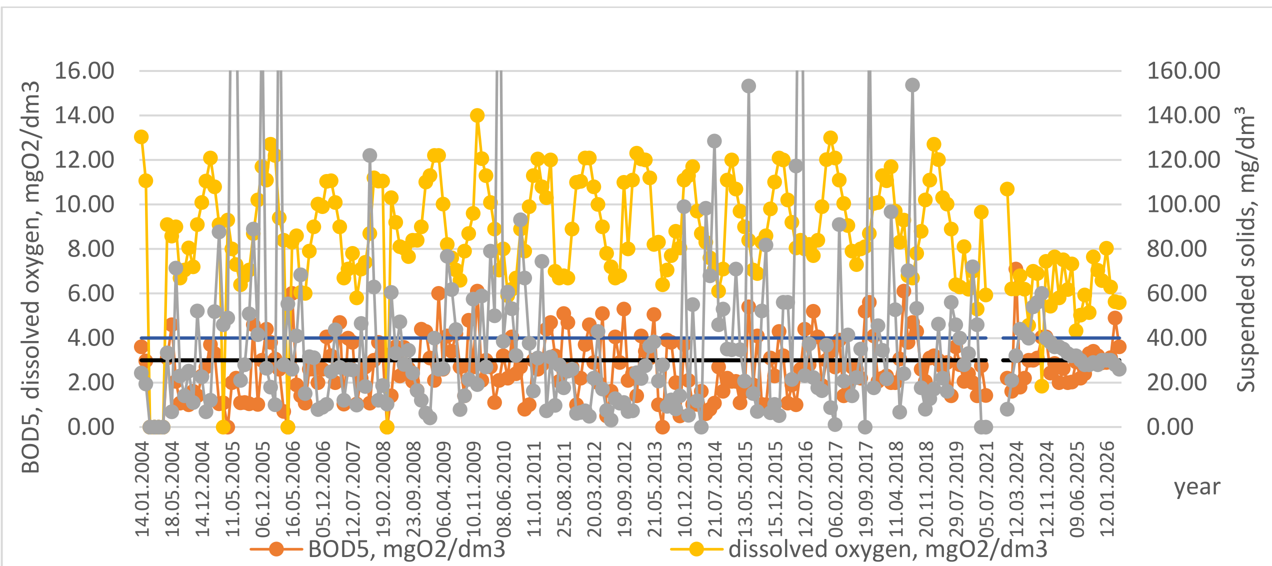


Fig. 3.26 Dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Izmail, 94 km)

The situation differs at the Izmail, 89 km section (Fig. 3.27).

Throughout the entire observation period, the concentration of dissolved oxygen was 6–13 $mgO_2/dm^3$, i.e. above the MPC, which indicates a favorable oxygen regime. For most of the period, BOD5 values ranged from 1 to 6 $mgO_2/dm^3$; that is, MPC exceedances occurred periodically, but they were short-lived. Their occurrence can be explained by periodic inputs of organic pollutants with runoff, the development of biological processes during the summer period, and changes in the river's hydrological regime.

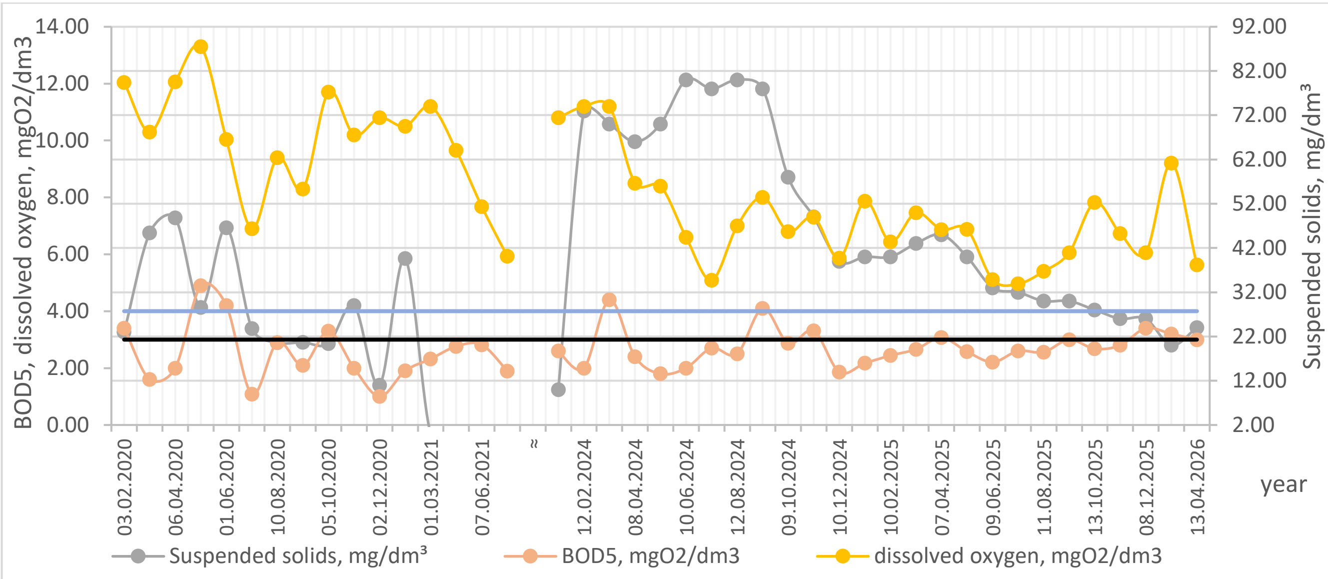


Fig. 3.27 Dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Izmail, 89 km)

Regarding suspended solids, episodic spikes up to 100–160 mg/dm$^3$ were observed, which may be explained by increased surface runoff after intense precipitation, bank erosion, redistribution of bottom sediments, and the specific features of the Danube River hydrological regime. During 2024–2026, this section of Izmail showed a slight and short-term increase in suspended solids to 40–60 mg/dm$^3$; however, a decrease in dissolved oxygen was accompanied by an increase in $BOD_5$. As for another important indicator of the consequences of anthropogenic pollution, COD, its value in this section ranged from 10 to 35 mg/dm3, and no substantial increase occurred alongside the rise in suspended solids; therefore, the existing pollution was predominantly of organic origin. The identified negative phenomena were short-lived, and their occurrence can be explained by surface-water runoff containing suspended solids (Reni).

During 2020–2026, the ecosystem remained in a relatively stable state with typical seasonal cyclicity. As regards dissolved oxygen, it remained at 6–12 $mgO_2/dm^3$ and did not fall below the MPC. $BOD_5$ fluctuated within 1–5 mgO2/dm3, periodically crossing the MPC level. The concentration of suspended solids increased substantially to 12 mg/dm3 in 2024, accompanied by a decrease in dissolved oxygen. In 2025, suspended solids gradually declined, but the concentration of dissolved oxygen in surface waters remained at 6–8 $mg/dm^3$, which is lower than the levels recorded, for example, in 2021. In 2026, a further decrease in suspended solids occurred while the concentration of dissolved oxygen remained practically unchanged. BOD5 values were at an almost unchanged level, with periodic minor exceedances of the MPC. As for COD, in 2020–2021 its level fluctuated between 8 and 12 $mg/dm^3$; data for 2022–2025 are unavailable, while in 2026 this indicator increased to 22–38 $mg/dm^3$.

Analysis of the situation in the Port of Izmail makes it possible to conclude that the increase in suspended solids in surface waters is a consequence of the war. In 2023–2024, shelling of the port, the largest on the Danube, intensified. It is known that in 2022 dredging operations were carried out in the Bystre mouth to increase depths to 7.2 m, which made it possible to use Ukrainian Danube ports for cargo transportation. In addition, dredging operations were also conducted in the ports of Reni, Izmail, and Ust-Dunaisk. As a result of shelling, the grain elevator, fuel terminals, and administrative buildings were repeatedly struck, and large-scale fires occurred. In our view, this was precisely what caused the increase in suspended solids, including those of organic origin. The improvement of the situation in 2025–2026, despite the continuation of shelling of the port, occurred because the increased depths ensured greater flow-through capacity and, consequently, the possibility of oxygen saturation of surface waters. Moreover, since 2025 the Ukrainian Danube ports have substantially changed their logistical approaches: they abandoned the accumulation of cargo in ports in favor of feeder container transportation. In other words, cargo is no longer stored in the port for subsequent transportation in large batches, but is instead loaded into small containers, which are placed on barges and dispatched. This "just-in-time" dispatch approach, rather than storage, has significantly reduced the amount of damaged cargo and, consequently, anthropogenic pollution of surface waters. The increase in COD in 2026 may indicate that the composition of suspended matter has changed; that is, as a result of shelling, substances of non-organic origin enter the surface waters.

Figure 3.28 presents the dynamics of changes in the content of suspended solids, BOD5, and dissolved oxygen in the surface waters of the Danube River (Kiliia, 48 km). This monitoring section is located 1 km from the Kiliia port point of the Ust-Dunaisk Port.

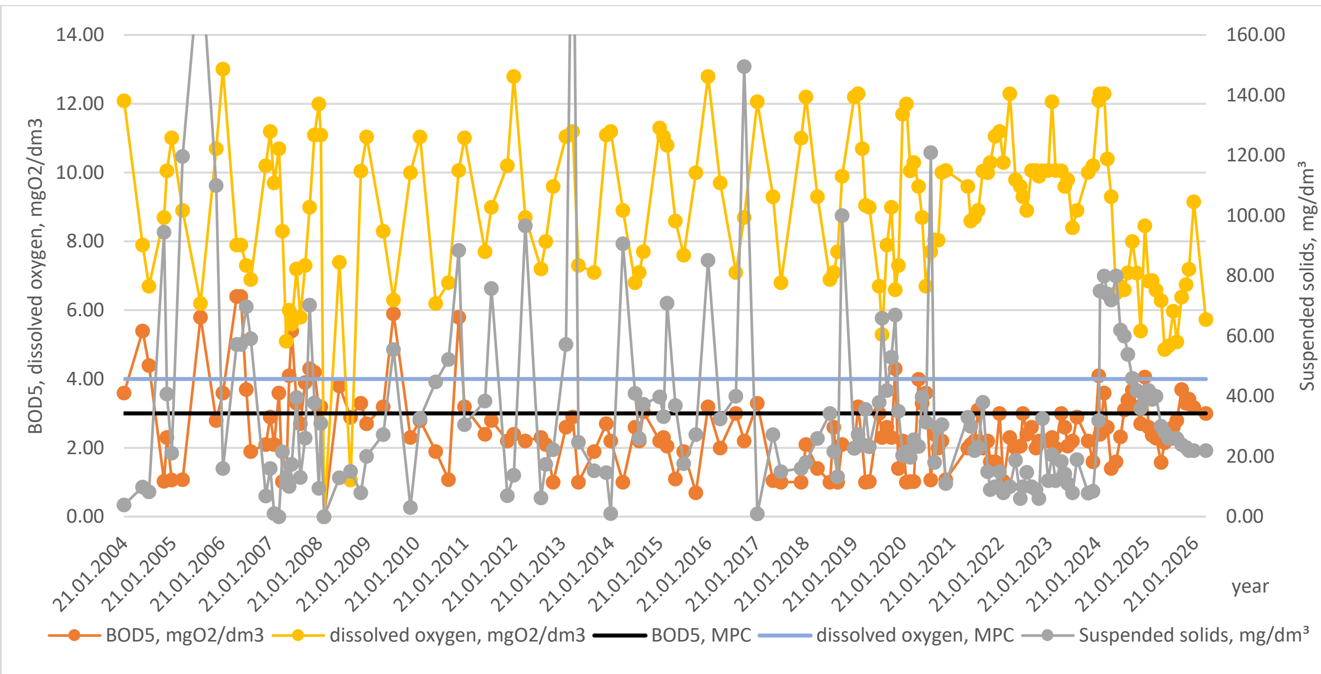


Fig. 3.28 Dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Kiliia, 48 km)

As can be seen, during 2004–2022 the dissolved oxygen content fluctuated from 5 to 12 $mgO_2/dm^3$, and the MPC was exceeded only once. As for $BOD_5$, as in the other sections, its level ranged within 2–4 $mgO_2/dm^3$, periodically exceeding the MPC. The content of suspended solids fluctuated within 20–40 mg/dm3, with periodic peaks up to 120 $mg/dm^3$ (several such peaks), but from 2022 it decreased to 15–20 $mg/dm^3$.

However, during 2024 its value increased substantially to 36–80 mg/dm$^3$, and in 2025–2026 it gradually decreased to 22 mg/dm$^3$. The COD value did not change significantly. The obtained results may be explained as follows. On the one hand, a higher concentration of sediments should be expected in Kiliia, since it is located closer to the delta; however, dredging operations, including those conducted at this port point, ensured greater flow-through capacity due to increased depths. The rise in suspended solids in 2024 may be explained by the transit nature of pollution: all organic pollutants from the destruction of cargo and port infrastructure in Reni and Izmail flowed here. The improvement of the situation upstream led to a decrease in suspended solids. However, the fact that this was accompanied by a decrease in dissolved oxygen and a simultaneous increase in $BOD_5$, while COD remained practically unchanged, indicates the settling of silt on the bottom of the Kiliia port and the oxidation of the organic components of pollution. Moreover, as can be seen, because the Port of Kiliia was practically not subjected to shelling, the situation differs substantially from the state of surface waters in the Port of Izmail.

Figure 3.29 presents the dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Kiliia, 32 km). This section is located downstream of the Port of Kiliia.

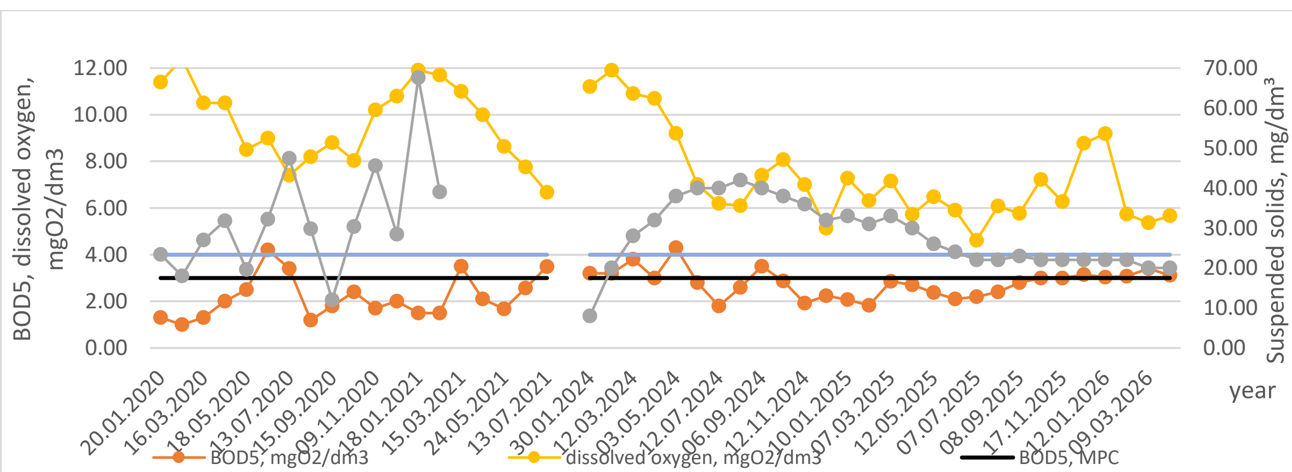


Fig. 3.29 Dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Kiliia, 32 km)

As can be seen, during 2020–2026 the dissolved oxygen content fluctuated within 5–12 $mgO_2/dm^3$ and did not reach the MPC threshold. The $BOD_5$ level, as in the previous section, ranged from 1 to 4 $mgO_2/dm^3$, periodically crossing the MPC level. The dynamics of indicator changes fully correspond to seasonal fluctuations. The COD indicator varied from 12 to 22 $mg/dm^3$. The content of suspended solids changed from 20 to 40 $mg/dm^3$, with virtually no maxima. Thus, in this section, unlike the previous ones, washout and gradual silt deposition are observed, although its volume is insignificant.

Figure 3.30 presents the dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Vylkove, 20 km).

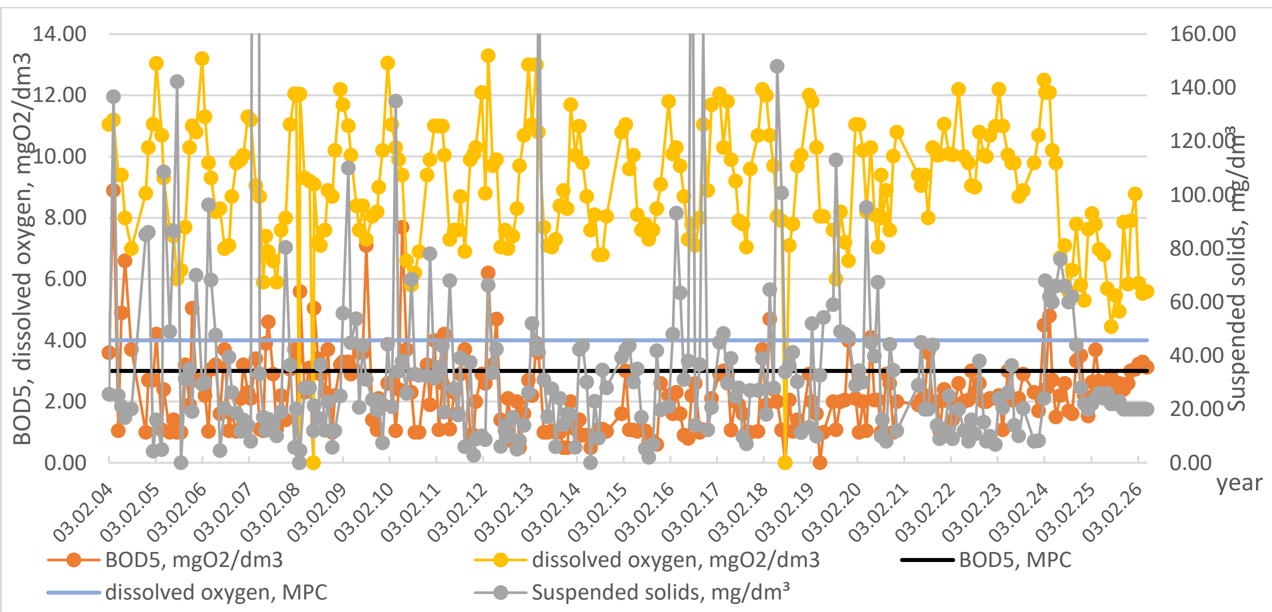


Fig. 3.30 Dynamics of changes in the content of suspended solids, $BOD_5$, and dissolved oxygen in the surface waters of the Danube River (Vylkove, 20 km)

Thus, during 2004–2026 the dissolved oxygen content fluctuated within 5–13 $mgO_2/dm^3$ and did not reach the MPC threshold. The BOD5 level, as in the previous section, ranged from 1 to 4 $mgO_2/dm^3$, periodically crossing the MPC level. The dynamics of indicator changes fully correspond to seasonal fluctuations. The COD indicator varied from 12 to 22 mg/dm$^3$. The content of suspended solids changed from 10 to 50 mg/dm$^3$, with periodic spikes.

The situation in 2024 requires particular analysis, when the level of suspended solids amounted to 40–70 mg/dm$^3$. In the subsequent period of 2025–2026, the content of suspended solids gradually decreased to 20 mg/dm$^3$.

As for the causes of this phenomenon, in our opinion, two sources of influence converged. First, there were the anthropogenic consequences of the war. In April 2024, UAV attacks led to large-scale fires in the Danube Biosphere Reserve (1,080 ha burned). Reed fires had occurred previously, but they were more local in nature and could be extinguished more quickly. In 2024, the fire was much more severe; in addition, due to the ban on navigation, firefighting capacity was limited. As a consequence, soot and ash washed by rain from burned areas of the protected territory entered the surface waters. Second, in 2024 there was first a drought and then Cyclone Boris, with an anomalous flood, which led to the active movement of bottom deposits along the river. Furthermore, given that Vylkove is located in the Danube Delta, storms in the Black Sea have a substantial influence on the hydrological regime. In 2024, Black Sea storms were particularly prolonged and intense, creating wind-driven backwater of seawater and leading to the accumulation of washed-out silt and ash from fires in the reserve; as a result, the content of suspended solids increased. In previous and subsequent years, there was no superposition of these factors, which enabled the self-purification of the surface waters of the Danube River at the Vylkove section.

Figure 3.31 presents the dynamics of changes in the content of suspended solids in the surface waters of the Danube River from Reni (163 km) to Vylkove (20 km).

As can be seen, during the years under study certain fluctuations occurred in the content of suspended solids. The maximum values were recorded precisely at the Vylkove station, which is entirely logical, since it is located in the Danube Delta, 20 km from the point where the Danube flows into the Black Sea.

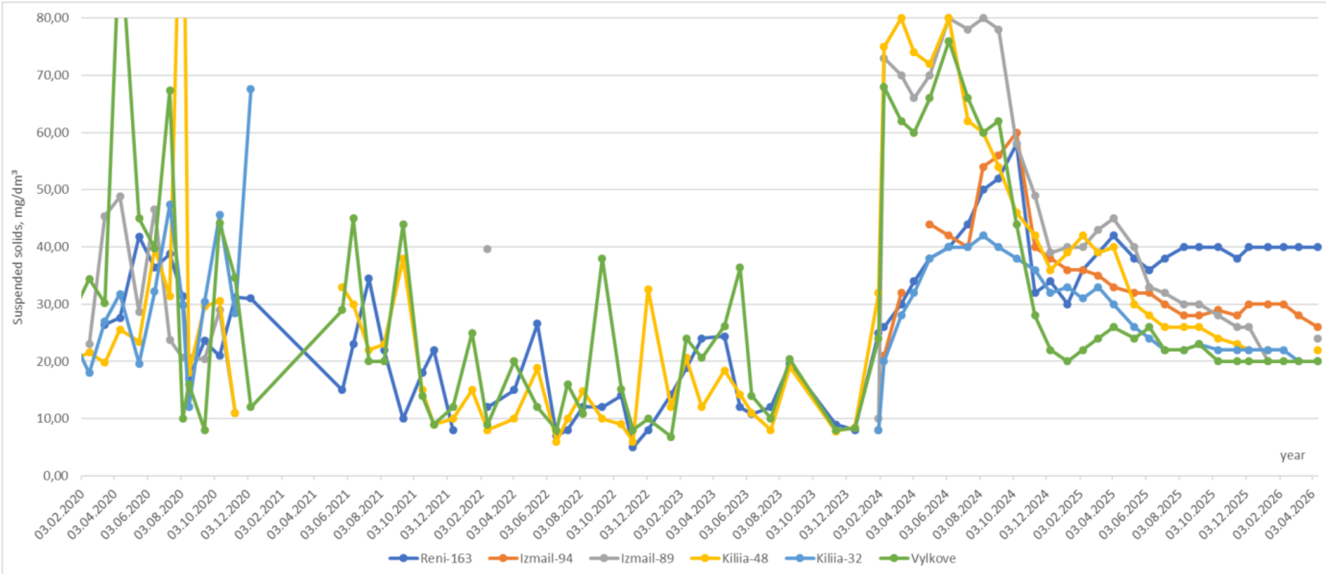


Fig. 3.31 Dynamics of changes in the content of suspended solids in the surface waters of the Danube River from Reni (163 km) to Vylkove (20 km)

With regard to the events of 2024, the maximum amount of suspended solids was recorded at the Izmail 89 km, Kiliia 48 km, and Vylkove stations. The analysis presented above made it possible to conclude that the war exerted an additional anthropogenic impact (shelling of ports) on the state of the surface waters of the Danube River, under conditions of cumulative influence (the combination of war-related and natural impacts). The level of suspended solids at the Izmail 94 km section is also the result of cumulative influence, since, in addition to natural phenomena, the state of surface waters was partly affected by the consequences of shelling of the Port of Reni, located at the 130th km of the Danube River. As regards the Reni 163 km section, the main pollution sources are located upstream, and when this is combined with natural impacts, a cumulative effect is also formed. The situation at the Kiliia 32 km section can be explained by the consequences of natural anomalies; therefore, in the absence of cumulative effects, the negative impacts are minimal.

*Conclusions.* As a result of the analysis of long-term monitoring data on the quality of the surface waters of the Danube River within the Ukrainian section from

Reni to Vylkove, it was established that until 2023 the hydrochemical regime of the studied sections was characterized by relative stability and was determined primarily by natural seasonal fluctuations in runoff, temperature regime, biological productivity of aquatic ecosystems, and the input of substances from the catchment basin. In most cases, the content of dissolved oxygen exceeded the normative values, indicating a satisfactory level of aeration of the water masses and the preservation of favorable conditions for the functioning of aquatic ecosystems. Exceedances of BOD5 standards were predominantly short-lived and were associated with the seasonal inflow of organic matter and changes in the hydrological regime.

It was established that, beginning in 2024, substantial changes in hydrochemical indicators occurred in the studied section of the Danube, primarily in terms of increasing concentrations of suspended solids. Analysis of the spatial and temporal dynamics made it possible to identify the formation of a cumulative effect caused by the simultaneous action of natural and anthropogenic factors. The natural factors include the prolonged summer drought of 2024, the anomalous flood caused by Cyclone Boris, intensive erosion processes in the upper part of the Danube basin, activation of the movement of bottom sediments, and the specific features of the hydrological regime of the river’s delta section. The anthropogenic factors include dredging operations in Romanian and Ukrainian ports, increased shipping intensity, and the consequences of military actions on the territory of Ukraine.

The most pronounced changes were recorded at the Reni section (163 km), where after 2024 a sustained increase in suspended solids to 30–50 $mg/dm^3$ and above was observed, substantially exceeding the long-term level. The simultaneous decrease in dissolved oxygen concentration and increase in $BOD_5$ indicate an intensification of organic-matter oxidation processes and the accumulation of fine-grained sediments. It was established that this section most strongly reflects the transboundary influence of processes occurring in the upper part of the Danube basin.

A comparative analysis of the two sections in the area of Izmail showed substantial differences between the area located upstream of the port and the water area of the port itself. At the Izmail section (94 km), the negative changes were mostly short-lived and were associated with the transit input of suspended solids from upstream sections of the river. By contrast, at the Izmail section (89 km), located directly within the port water area, a more prolonged increase in suspended solids, a decrease in dissolved oxygen, and an increase in COD were recorded. The obtained results indicate a significant local impact of military actions on the state of surface waters. The destruction of port infrastructure, damage to grain terminals and fuel facilities, the outbreak of fires, and the entry of destruction products into the aquatic environment became an additional source of pollution superimposed on natural sediment-redistribution processes.

For the Kiliia section (48 km), located near the Kiliia port point, a sharp increase in suspended solids in 2024, followed by a gradual decrease in 2025–2026, was characteristic. It was found that the principal source of pollution was the migration of suspended and organic substances from upstream sections of the Danube, primarily from the Reni and Izmail areas. The simultaneous decrease in dissolved oxygen concentration and increase in BOD5, with practically unchanged COD values, indicates the accumulation and subsequent oxidation of organic deposits in near-bottom horizons. At the same time, the absence of significant destruction of port infrastructure in the Kiliia area resulted in a less pronounced anthropogenic impact compared with Izmail.

At the Kiliia section (32 km), located downstream, no substantial long-term disturbances of the hydrochemical regime were identified. $BOD_5$, COD, and dissolved oxygen indicators remained within the range of characteristic long-term fluctuations, while the concentration of suspended solids changed mainly in accordance with natural seasonal processes. This indicates effective sedimentation and gradual self-purification of water masses in the lower part of the Kiliia branch.

The specific features of the Danube Delta section were most clearly manifested at the Vylkove section (20 km), where a significant increase in suspended solids was recorded in 2024. It was established that this phenomenon resulted from a combination of several factors: large-scale fires in the Danube Biosphere Reserve caused by military actions, the entry of combustion products into the aquatic environment, and the influence of flood processes and storm activity in the Black Sea. The combination of these factors led to the accumulation of silt, ash, and fine particles in the delta part of the river. In subsequent years, owing to natural self-purification processes and a reduction in the intensity of adverse factors, the concentrations of suspended solids gradually decreased.

The synthesis of the research results makes it possible to conclude that the current state of the surface waters of the Ukrainian section of the Danube is shaped by the complex interaction of natural, transboundary, and military-anthropogenic factors. The year 2024 became the period of the strongest manifestation of the cumulative effect, when the consequences of military actions overlapped with extreme hydrometeorological phenomena. The port water areas and delta sections of the river proved to be the most vulnerable to this impact. The obtained results confirm the need for further development of the water-quality monitoring system, assessment of the consequences of military actions for aquatic ecosystems, and consideration of the combined influence of natural and anthropogenic factors when developing measures for water-resource management in the Danube basin.

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## *Conclusions*

The comprehensive assessment of the hydrochemical condition of the Lower Dnipro, Southern Bug, and Ukrainian section of the Lower Danube has demonstrated that the current ecological state of these river systems is determined by the combined influence of long-term anthropogenic transformation, natural hydrological variability, and the unprecedented consequences of the Russian military aggression against Ukraine. Although each river basin possesses specific hydrological, geomorphological, and socio-economic characteristics, the conducted research has revealed common patterns governing the formation of water quality under conditions of increasing environmental stress. Long-term monitoring data covering periods from 2003 to 2026 enabled the identification of statistically significant trends in the dynamics of the principal hydrochemical indicators, the determination of dominant pollution sources, and the evaluation of the adaptive capacity of aquatic ecosystems under rapidly changing environmental conditions.

The results confirm that the ecological status of all investigated river systems has undergone substantial changes since the beginning of the full-scale invasion of Ukraine in 2022. Military activities have introduced an entirely new category of environmental pressure, fundamentally different from conventional anthropogenic pollution. Unlike continuous industrial or municipal discharges, military impacts are characterized by their spatial heterogeneity, episodic occurrence, high intensity, and unpredictable consequences. Explosions, destruction of industrial facilities and hydraulic infrastructure, contamination by fuels, lubricants, combustion products, construction debris, heavy metals, and suspended mineral particles have significantly altered the hydrochemical regime of many river sections. Consequently, hydrochemical processes that previously reflected seasonal natural variability are increasingly governed by short-term extreme events associated with warfare.

One of the principal scientific outcomes of the conducted studies is the confirmation that military impacts should not be regarded as an isolated environmental factor but rather as a catalyst that amplifies the influence of pre-existing anthropogenic pressures. Industrial pollution, agricultural runoff, municipal wastewater discharges, and river regulation had already affected water quality before 2022. However, military actions have intensified these impacts by damaging wastewater treatment facilities, disrupting environmental monitoring systems, increasing uncontrolled pollutant inputs, and altering hydrological connectivity within river basins. Therefore, the present hydrochemical state of Ukrainian rivers reflects the cumulative effects of multiple interacting stressors rather than the influence of any single factor.

The Lower Dnipro basin represents the most striking example of large-scale hydrological transformation caused by military activities. The destruction of the Kakhovka Hydroelectric Power Plant dramatically altered the hydraulic functioning of one of Europe's largest regulated river systems. The disappearance of the Kakhovka Reservoir changed water flow velocities, sediment transport processes, groundwater interactions, and oxygen exchange mechanisms throughout the downstream sections of the river. These changes were immediately reflected in the hydrochemical monitoring data, which recorded increased temporal variability of suspended solids, mineral compounds, and oxygen-related parameters.

The obtained results indicate that suspended solids became one of the most sensitive indicators of wartime environmental disturbance. Their concentrations increased substantially following the destruction of hydraulic structures and intensified shelling activities, reflecting accelerated erosion processes, redistribution of bottom sediments, and the transport of mineral particles generated by explosions and infrastructure collapse. Unlike conventional nutrient pollution, which usually demonstrates gradual seasonal fluctuations, suspended solids exhibited abrupt increases associated with specific military events, making them valuable indicators of immediate environmental disturbance.

Another important conclusion concerns the transformation of the oxygen regime within the investigated river systems. Dissolved oxygen and biochemical oxygen demand ($BOD_5$) traditionally represent integral indicators of ecosystem functioning because they reflect the balance between organic matter decomposition and biological productivity. Under normal hydrological conditions, seasonal fluctuations of these parameters correspond to variations in temperature, primary production, and river discharge. However, since 2022, and particularly after the destruction of the Kakhovka Dam, these natural seasonal patterns have become increasingly disrupted. Local reductions in dissolved oxygen combined with elevated oxygen demand indicate intensified decomposition of organic matter, slower water exchange, increased accumulation of fine sediments, and suppression of natural self-purification processes.

Despite these negative developments, one of the most significant scientific findings is the demonstration of the remarkable resilience of large river ecosystems. Long-term observations indicate that the Lower Dnipro retains a measurable capacity for natural recovery when external pressures temporarily decline. In several monitoring stations, reductions in phosphate and ammonium concentrations were observed after periods of decreased industrial activity caused by wartime economic disruption. Although such reductions cannot be interpreted as environmental improvement in a broader socio-economic context, they nevertheless illustrate the capacity of river ecosystems to respond positively when pollutant inputs decrease.

The Southern Bug basin demonstrated a somewhat different pattern of environmental response. Unlike the Lower Dnipro, where hydrological regulation dominates ecosystem functioning, the Southern Bug preserves a relatively more natural flow regime over considerable sections. Consequently, hydrochemical dynamics are more strongly controlled by diffuse pollution originating from agriculture, municipal wastewater, and local industry. Nevertheless, the influence of military activities became increasingly apparent during the last years of observation through intensified fluctuations in nutrient concentrations, organic pollution indicators, and dissolved oxygen content.

The long-term datasets covering more than two decades provide valuable evidence regarding the gradual evolution of anthropogenic impacts within the Southern Bug basin. Statistical analyses revealed that phosphate and ammonium concentrations continue to exhibit pronounced seasonal behavior associated with fertilizer application, agricultural runoff, and biological productivity. However, regression analyses indicate that the overall variability of these compounds has increased considerably since 2020, suggesting that additional external disturbances have become superimposed upon traditional seasonal cycles.

The increasing concentrations of nitrogen compounds, phosphates, surfactants, and herbicides indicate that diffuse pollution originating from agricultural activities remains one of the principal drivers of water quality deterioration. These findings demonstrate that wartime impacts should not divert attention from long-standing environmental problems. Instead, military activities interact with existing agricultural and municipal pollution sources, producing cumulative ecological effects that may exceed the adaptive capacity of river ecosystems if appropriate management measures are not implemented.

Particular attention should be paid to the changing relationships among hydrochemical indicators identified through correlation analysis. The observed shifts in correlation coefficients between sulfate, chloride, phosphate, dissolved oxygen, and $BOD_5$ reflect significant alterations in the functioning of aquatic ecosystems. Correlation matrices constructed for different observation periods demonstrate that the dominant mechanisms controlling water quality are evolving over time. Such changes indicate that the structure of pollution sources has become more complex and that conventional assumptions regarding hydrochemical interactions may no longer adequately describe environmental processes under wartime conditions.

Another important scientific contribution of the conducted research is the application of regression modelling for environmental forecasting. The developed predictive models successfully describe long-term trends in the concentrations of major pollutants and provide quantitative estimates of future environmental risks. Although all forecasting exercises remain subject to uncertainty due to the unpredictable character of military activities, regression analysis has demonstrated its usefulness as a practical decision-support tool for environmental management. The obtained models may serve as an important basis for planning monitoring programmes, prioritizing restoration measures, and evaluating potential scenarios of post-war ecological recovery.

From a methodological perspective, the studies confirm the considerable value of long-term environmental monitoring. Only continuous observations extending over many years make it possible to distinguish natural climatic variability from anthropogenic trends and extraordinary wartime disturbances. Short-term investigations cannot adequately capture the complex interactions among hydrological processes, pollutant transport, ecosystem resilience, and extreme environmental events. Consequently, maintaining uninterrupted monitoring programmes should become one of the highest priorities of Ukraine's environmental policy during both wartime and the subsequent reconstruction period.

The comparative analysis of the investigated river basins further demonstrates that ecological vulnerability depends not only on pollution intensity but also on hydrological characteristics, river regulation, catchment land use, and ecosystem resilience. Rivers with heavily modified hydrological regimes, such as the Lower Dnipro, respond differently to external disturbances than more naturally flowing systems such as the Southern Bug. Understanding these differences is essential for developing basin-specific management strategies rather than applying uniform restoration approaches across all Ukrainian river systems.

The present study provides a comprehensive assessment of the ecological condition of the surface waters of the Ukrainian section of the Lower Danube River (Reni–Izmail–Vylkove), combined with an analysis of the functioning of Danube river ports under changing environmental and socio-economic conditions. The obtained results allow for the formulation of several integrated scientific conclusions regarding long-term hydrochemical dynamics, the role of anthropogenic pressure, and the emerging influence of military activities on the river ecosystem and regional transport systems. The analysis of monitoring data for the period 2010–2024 demonstrates that the hydrochemical regime of the Ukrainian Danube was relatively stable during most of the studied period. Until approximately 2023, variations in the main water quality indicators were predominantly governed by natural seasonal processes, including river discharge fluctuations, temperature regime changes, and sediment transport dynamics. Within this phase, concentrations of phosphates, ammonium, sulfates, chlorides, $BOD_5$, and dissolved oxygen generally remained within characteristic long-term ranges, with only episodic and spatially limited deviations. However, despite this overall stability, the system already exhibited signs of chronic anthropogenic influence. In particular, nutrient compounds such as phosphates and ammonium demonstrated recurrent seasonal peaks, which are typically associated with agricultural runoff, untreated or insufficiently treated wastewater discharges, and organic loading from adjacent settlements. Chloride concentrations, although relatively stable, reflected a persistent background anthropogenic pressure, indicating long-term accumulation processes rather than short-term pollution events. Sulfate variability suggested a mixed origin, combining both natural geochemical processes and anthropogenic inputs, while the behavior of $BOD_5$ and dissolved oxygen indicated that the ecosystem retained a moderate capacity for self-purification. Nevertheless, periodic oxygen depletion events highlighted the sensitivity of the system to localized organic pollution and hydrodynamic disturbances. A significant shift in the hydrochemical state of the river was identified starting from 2024. This period is characterized by a noticeable increase in the variability and amplitude of key water quality indicators, especially suspended solids concentration and oxygen regime parameters. The observed changes indicate a transition from a relatively stable hydrochemical system to a more dynamic and disturbance-sensitive state. The main drivers of this transformation include intensified anthropogenic pressure, extreme hydrometeorological events, increased erosion processes, and enhanced transboundary transport of pollutants. Of particular importance is the emergence of military-related impacts, which have become a new destabilizing factor for the Lower Danube ecosystem. These impacts are indirect in nature but significant in scale, influencing hydrological connectivity, sediment redistribution, and local pollution patterns. The most pronounced deterioration in water quality was observed in port-adjacent and deltaic zones, where hydrodynamic conditions amplify pollutant accumulation and resuspension processes. These areas are characterized by higher variability in hydrochemical indicators and reduced resilience to external stressors. In contrast, downstream sections of the river demonstrated partial stabilization tendencies, suggesting the presence of natural recovery mechanisms under conditions of reduced localized pressure. Despite increasing anthropogenic stress, the Lower Danube continues to exhibit a significant, though not unlimited, capacity for self-regulation and self-purification. The interaction between flow velocity, sediment transport, and biogeochemical cycling allows the system to partially mitigate pollution impacts, particularly in less disturbed sections. However, the efficiency of these natural processes is strongly dependent on hydrological continuity and the absence of excessive pollutant loading. When thresholds of organic and mineral contamination are exceeded—especially in confined or semi-enclosed port areas—the self-purification capacity becomes significantly reduced. This leads to temporary oxygen deficits, accumulation of nutrients, and increased eutrophication risk. The findings indicate that the ecological resilience of the system remains intact but is increasingly under pressure. Continued intensification of anthropogenic activities without adequate mitigation measures may lead to a gradual weakening of natural regulatory mechanisms. The integrated analysis of river transport activity and port dynamics demonstrates a strong interconnection between navigation intensity and environmental state. The activation of Ukrainian Danube ports (Reni, Izmail, and Ust-Dunaisk) under wartime conditions has significantly increased shipping intensity and cargo turnover in the region. This shift was driven primarily by the blockade of alternative maritime routes and the strategic importance of Danube corridors for national logistics. While dredging activities and the use of alternative navigation channels (including the Bystre estuary) have improved transport accessibility and economic resilience, they have also contributed to hydromorphological alterations. These include changes in sediment distribution patterns, increased turbidity, and localized disturbances of aquatic habitats. Comparative analysis of regional port systems indicates that increased activity in Ukrainian and Romanian Danube ports has led to uneven spatial redistribution of cargo flows. Some ports, such as Constanța, have experienced sustained growth, while others, such as Galați, have shown declining trends due to shifting transport preferences. Overall, river-sea transport routes have gained importance, reinforcing the strategic role of the Danube as a transboundary logistics corridor. Importantly, while navigation expansion has clear economic and geopolitical advantages, it simultaneously introduces additional environmental pressure, particularly in ecologically sensitive delta zones. One of the key outcomes of this study is the confirmation that the hydrochemical state of the Lower Danube is shaped by the combined action of natural variability, long-term anthropogenic loading, and emerging military-related impacts. These factors do not act independently but rather interact synergistically, amplifying system instability under certain conditions. Natural drivers, including seasonal discharge variation and extreme hydrometeorological events, establish the baseline variability of the system. Anthropogenic pressures – such as agriculture, industry, navigation, and wastewater discharge – overlay this natural variability, creating chronic stress conditions. Military impacts, although temporally concentrated, act as episodic high-intensity stressors that can significantly disrupt sediment regimes and water quality patterns. This multifactorial structure of influence explains the increasing heterogeneity of hydrochemical conditions observed in recent years and highlights the need for integrated basin-scale management approaches. The developed regression models and statistical analyses provide a reliable basis for forecasting future trends in water quality under different scenarios, including continued peacetime development and post-conflict recovery. The results indicate that without targeted environmental interventions, there is a high probability of continued variability and periodic deterioration in key hydrochemical parameters, particularly in heavily used port and delta zones. At the same time, the system retains sufficient regenerative potential, which can be enhanced through appropriate management measures. These include modernization of wastewater treatment infrastructure, stricter control of pollutant sources, regulation of navigation intensity in sensitive zones, and restoration of natural hydrological regimes where possible. Strengthening long-term monitoring systems is essential for early detection of негативні тенденції and for supporting adaptive management strategies. Equally important is the integration of Ukrainian monitoring efforts into broader international frameworks governing the Danube River basin. In summary, the Ukrainian section of the Lower Danube River represents a complex and highly dynamic aquatic system characterized by the interaction of natural processes, long-term anthropogenic pressure, and emerging geopolitical factors. While the river maintains a considerable capacity for self-regulation, recent trends indicate increasing environmental vulnerability, particularly in relation to suspended solids dynamics, nutrient loading, and oxygen balance instability. The dual role of the Danube – as both an ecological corridor and a strategic transport artery-creates inherent tensions between economic development and environmental sustainability. The results of this study emphasize that sustainable management of the river basin requires an integrated approach that simultaneously considers hydrological processes, water quality dynamics, transport infrastructure development, and the broader context of regional security and climate variability. Only through coordinated monitoring, international cooperation, and implementation of adaptive environmental policies can the long-term ecological stability of the Lower Danube be ensured, alongside the continued functioning of its critical socio-economic infrastructure.

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# ASSESSMENT OF CURRENT STATE AND CONSEQUENCES OF MILITARY IMPACTS ON THE RIVERS OF THE UKRAINIAN BLACK SEA REGION

MONOGRAPH

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