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HYDROCHEMICAL REGIME AND ECOLOGICAL STATE OF SURFACE WATERS IN THE SYNIUKHA RIVER BASIN

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Abstract. Preserving and restoring the ecological status of rivers in the southern regions of Ukraine is long-standing and pressing issue. These territories have a significant permanent water shortage. The problem of water supply has been exacerbated not only by military operations, but also by climatic factors, including the record-breaking hot summer of 2024. The Syniukha River is one of the largest tributaries of the lower part of the Southern Bug, whose water is actively used in various areas of economic activity. The results of the analysis of the dynamics of the hydrochemical regime and the assessment of the quality of surface waters of the Syniukha River for the period from 1993 to 2023 show that the degree of pollution of the river's waters varies according to different indicators. The water quality in the river corresponded to Class II and was described as good. Over the many years, the highest pollution was observed for nitrogen and phosphorus compounds, and the deterioration of dissolved oxygen. The state of the Syniukha River in its upper reaches is not environmentally stable due to the high level of anthropogenic pressure on the river, which exceeds the capacity of the river's aquatic ecosystem to regenerate itself. Deterioration of the ecological state of the Syniukha River requires constant monitoring by environmental institutions and the implementation of water protection measures.

Keywords: hydrochemical regime, water quality assessment, water management activities, anthropogenic impact, ecological status, risk assessment.

1. Introduction

As a result of anthropogenic impact, natural waters are polluted, their composition and properties change, which leads to a deterioration in water quality for water use. Contaminated water may become unusable for a number of water users. Accordingly, when assessing the impact of economic activity on water resources, it is necessary to take into account not only their quantitative but also qualitative changes (Peleshenko & Khilchevskyi, 1997; Osadchyi & Blazhko, 2017). Such an assessment is especially relevant for water bodies that are sources of drinking water supply.

The aim of this study is to investigate the hydrochemical regime and ecological status of surface waters in the Syniukha River basin.

The results of the study of the hydroecology of the Syniukha River are relatively few and are mostly presented in review publication sand specialised reference books. Significant amounts of material devoted to this river are available in the review works of V. M. Timchenko, V. K. Khilchevsky (Khilchevskyi, 2021; Khilchevskyi et al., 2006) and reference books of different periods (Yatsyk et al., 1991; Vyshnevskyi, 2000). The hydrochemical characteristics of the Syniukha waters are given in the works of O. O. Ukhan et al. (Ukhan, 2016; Ukhan et al., 2015). The latest data on the current hydrological characteristics of the rivers and the hydrochemical composition of the water in the Syniukha hydrosystem are available on the websites of the Regional Office of Water Resources in Mykolaiv region, Kirovohrad and Cherkasy regions and the website of the Basin Administration of Water Resources of the Southern Bug River. However, against the background of a significant volume of publications on the Dniester and Southern Bug, the list of publications on the Syniukha

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River is clearly limited, which directly indicates an insufficient level of research on this water body, especially in recent decades.

2. Materials and Methods

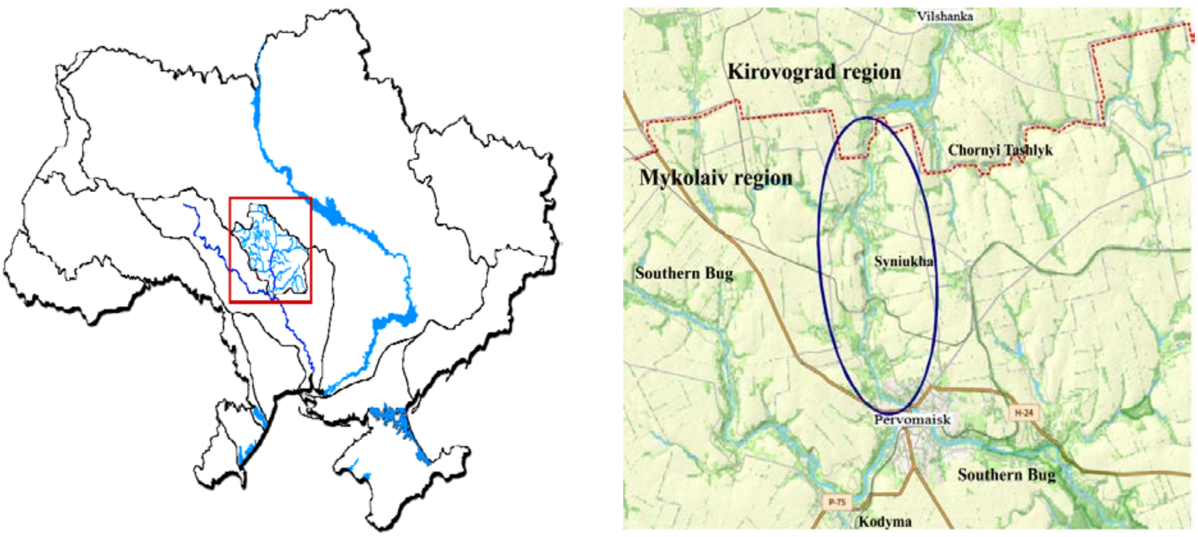
The study was based on official monitoring data on hydrochemical water quality indicators of the Water and soil quality monitoring laboratory of the Regional Office of Water Resources in Mykolaiv region, which were collected at the Pervomaisk post (in the area of drinking water intake) for the period from 1993 to 2023.

The water quality assessment of the Syniukha River in the control stations was performed using the methodology for environmental assessment of surface water quality by relevant categories (Hrytsenko et el., 2012). This methodology makes it possible to assess trends in the quality of surface waters of land and estuaries of Ukraine in time and space, to determine the impact of anthropogenic pressure on water body ecosystems, and to assess changes in the state of water resources. The level of water suitability of the Syniukha River for various types of water use was determined by the value of the combinatorial water pollution index (Snizhko, 2001).

According to the EU Water Framework Directive (WFD) (EU WFD 2000/60/EC, 2006; Directive 2000/60/EC, 2000) (Directive2000/60/EC, 2000), a management plan should be developed for each of the main river basins of Ukraine, the purpose of which is to achieve environmental objectives within the established timeframe – "good" ecological status of surface bodies, as well as "good" ecological potential of artificial or significantly modified surface water. In order to implement the objectives of EU-Ukraine cooperation in the field of environmental protection and in accordance with paragraph 2 of part two of Article 132 of the Water Code of Ukraine (Vodnyi kodeks Ukrainy, 1995), paragraph 6 of Resolution No. 336 of the Cabinet of Ministers of Ukraine of 18 May 2017, Methodological Recommendations for Determining the Main Anthropogenic Pressures and Their Impacts on the State of Surface Waters were developed (Pro zatverdzhennia Metodyky vyznachennia masyviv poverkhnevykh ta pidzemnykh vod, 2019; Vykhryst et el., 2018). The criterion for assessing the main anthropogenic pressures on the state of surface waters or surface water bodies is to determine the risk of failure to achieve environmental objectives. Depending on the qualitative or quantitative indicators of anthropogenic pressures, 3 categories of anthropogenic impacts are identified: 'no risk'; "possibly at risk"; "at risk". The results of the assessment of the main anthropogenic pressures and their impacts are the basis for the development and implementation of a programme of measures to achieve environmental goals.

3. Results and Discussion

The Syniukha River basin is located in the Novoarkhangelskyi and Vilshanskyi districts of Kirovohrad region and Pervomaiskyi district of Mykolaiv region, a left tributary of the Southern Bug (Vyshnevskyi, 2000) (Fig. 1).



a b

Fig. 1. The basin of the Syniukha River (a) and the study area (b)

The river is 111 km long and drains an area of 16700 km^2. It is formed by the confluence of the Velyka Bys and Tikych rivers and flows through the Prydniprovska Upland mainly in a south-westerly direction. The Syniukha flows into the Pivdennyi Buh on the territory of Pervomaisk and at their confluence, the water comes from about 60 % of the entire basin. The valley is trapezoidal, often asymmetrical, the slopes are dissected by ravines, and rock outcrops are typical. The valley is up to 2.5 km wide and up to 60 m deep. The floodplain in the upper and middle reaches is dry, covered with meadow vegetation. The riverbed is meandering, in some areas rapids; width 40–50 m (in the lower reaches up to 90–120 m). The river slope is 0.46 m/km. Average water discharge at a distance of 12 km from the mouth is 29.4 m^3/s. Main tributaries: Tikich, Yatran (right), Velyka Vysya, Kagarlyk, Sukhyi Tashlyk, Chornyi Tashlyk (left). It is fed mainly by snow. It freezes in December and thaws in March. Ice cover is unstable. There are small hydropower plants; three reservoirs have been created. River water is used for domestic, industrial and agricultural water supply.

At the confluence of the Syniukha with the Southern Bug – Pervomaisk, the river's shore zone is reforested and alkaline Steppe soils are common in this part of the river basin. The climatic conditions upstream in the Syniukha basin are quite different from those of the Steppe zone and have more pronounced signs of a temperate continental climate with precipitation levels of up to 500 mm/year. The lower part of the basin, which is partly located within the Steppe, is characterised by a pronounced similarities to the South Steppe climate, with relatively short winters and hot summers. The negative water balance in this area is caused not so much by a lack of precipitation (480 mm) as by high evaporation (800 mm or more). This is further associated with the extremely low local runoff, which is practically not taken in to account in hydrological calculations of the water budget of Syniukha, which is perennial due to the inflow of water from the upper parts of the collecting basin.

Since 1992, the temperature regime of the Syniukha basin has shown an upward trend, especially in winter. Very hot summer periods accompanied by prolonged dry spells have become more common (Mahas, 2024 a). The average annual temperature in 1961–2023 increased by almost +2.5 °C to 10.2 °C, reaching more than +11 °C in some years.

In the context of climatic instability in recent years, against the background of rising ambient temperatures and a powerful agrogenic transformation of the catchment, there has been a significant, more than 69 %, in water discharge (Q), which has caused a n umber of negative reactions of the river hydrosystem and related natural objects. At present, water discharge is in a prolonged low-water phase, which significantly affects the hydrochemical indicators of river water quality (Mahas, 2024 b).

The negative anthropogenic impact on the water balance of the Syniukha River is also evident, resulting from surface water abstraction, flow regulation by hydraulic structures and an increase in the water surface area with corresponding evaporation losses. The main sources of pollution in the Syniukha River basin include surface runoff from agricultural and urbanised areas, municipal waste water from inoperative or inefficient sewage treatment plants, fish farms, and sugar, fat and sunflower oil industries factories, and mines (Ekolohichnyi pasport Mykolaivskoi Kirovohradskoi oblasti, 2023).

Since chernozems are common in the upper part of the Syniukha River basin, infiltration water entering the channel network during the period of maximum soil moisture during the recession of spring floods introduces relatively only small amounts of salts, mainly calcium and magnesium bicarbonates (Mahas & Tuz, 2024).

In summer and winter, the river is fed exclusively by groundwater, which also contributes to an increase in the content of hydrocarbonate compounds.

The hydrochemical regime of the Syniukha River is characterised by monitoring data at the Pervomaisk station for the period from 1993 to 2023 (Table 1).

The data averaged over 30 years (Table 1) on the hydrochemical regime of the Syniukha River within the study area indicate the natural presence of quite significant seasonal fluctuations in the content of its components and a certain dependence of the chemical structure of river water on the volume of surface runoff, which is the main source of migratory components of agrogenic origin (nitrates, ammonium compounds, potassium, detritus, etc.). In addition, groundwater has a certain influence on the hydrochemical structure of river water, which is discharged in the erosion cuts of the Syniukha and tributary rivers.

Table 1

Hydrochemical parameters of the Syniukha River at Pervomaisk during the period 1993–2023

Indicator	Values of indicators		
	Average	Maximum	Minimum
Temperature, °C	12.32	29	0
Smell, points	1	1	1
Transparency, cm	37.43	41	3
Mass concentration of suspended solids, mg/dm³	10.87	486	0
Color, hail. PCS	35	101	0.37
Hydrogen index (pH), pH units	8.19	8.83	1.6
Dissolved oxygen, mgO_2/dm³	10.98	34.2	3.44
Measure of oxygen saturation, %	99.28	254	41.3
Calcium, mg/dm³	63.98	108	36
Magnesium, mg/dm³	–.13	58	13
Sodium, mg/dm³	86.56	170.3	5.04
Potassium, mg/dm³	5.31	21.27	1.63
Total calcium and magnesium content (water hardness), mg-eq/dm³	6.33	8.3	4.1
Hydrogen carbonate ions, mg/dm³	383.79	539.9	40.26
Sulfate ions, mg/dm³	86.58	297.6	33.28
Chloride ions, mg/dm³	52.01	82	19.85
Mineralization, mg/dm³	498.04	561.8	432.7
Dry residue (dissolved solids), mg/dm³	564.73	755	340
Phosphate ions(polyphosphates), mg/dm³	0.34	1.068	0
Total phosphorus, mg/dm³	0.25	0.796	0.016
Nitrite ions, mg/dm³	0.09	13.5	0
Nitrate ions, mg/dm³	5.18	45	0
Mass concentration of ammonium ions, mg/dm³	0.09	0.86	0
Silicon (silicon), mg/dm³	4.38	7.769	0.393
Total iron, mg/dm³	0.28	21.6	0
Permanganate oxidizability, mgO/dm³	8.65	14.6	3.64
Biochemical oxygen demand (BOD5), mgO_2/dm³	2.29	15.7	0.2
Biochemical oxygen demand (BOD20), mg/dm³	2.89	14	0.3
Chemical oxygen consumption, mgO/dm³	26.82	49.51	11.76
Total alkalinity, mg-eq/dm³	6.3	8.2	4
Aluminium, mg/dm³	0.02	0.445	0
Manganese, mg/dm³	0.06	1.156	0
Copper, mg/dm³	0.01	0.119	0
Nickel, mg/dm³	0.02	0.67	0
Total chromium, mg/dm³	0	0.015	0
Zinc, mg/dm³	0.04	0.47	0
Mass concentration of anionic surfactants, mg/dm³	0.03	0.6	0
Oil products, mg/dm³	0.14	2.25	0

The chemical composition of the basin's groundwater is characterized by elevated levels of mineralization (4–5 thousand mg/l) with a high content of sulfates and magnesium compounds. Since the groundwater horizons within the river hydraulic system are drained by the Syniukha Valley and its tributaries, they have a direct hydraulic connection with surface water, showing increased sensitivity to pollution. Thus, it is the combination of geological, structural, climatic, and meteorological conditions of the catchment that determine the hydrochemical regime of river waters and, accordingly, the associated groundwater. The latter, in the absence of powerful water-bearing rock horizons, are formed in cracks in Lower Proterozoic crystalline rocks and porous layers of Mesozoic-Cenozoic sediments, which are typical for the entire southern slope of the Ukrainian Crystal Shield (Stan pidzemnykh vod Ukrainy, 2021; Liuta, 2023).

The ionic structure of water is a key hydrochemical parameter by which surface and groundwater are classified and the compliance of the latter with existing standards for different types of water use is assessed. According to the above characteristics (Table 1), the waters of the Syniukha River in its lower reaches are clearly identified within the hydrocarbonate class with a slightly increased content of sulfates and sodium. The most characteristic is the hydrocarbonate complex. According to the monitoring data, the content of hydrocarbonate ions in the water of the Syniukha River ranged from 40.26 to 539.9 mg/dm^3 in the period 1993–2023.

Sulphate ions are present in almost all natural waters and usually rank second in content after hydrocarbonates. They enter the water mainly as a result of chemical weathering with sedimentary rocks, during the oxidation of sulphides, and the dissolution of minerals containing sulphur (usually gypsum). There are also sulphates of anthropogenic origin, the content of which is usually related to the decomposition of industrial and domestic wastewater. The sulphate regime is determined by redox processes, the biological situation in the water body, and human activity. According to the observations, the sulphate content at the Syniukha River station – m. Pervomaisk varied between 33.2 and 297 mg/dm^3.

Chloride ions are characterised by high migration capacity due to their good solubility, low sorption on suspended solids and limited consumption by aquatic organisms. Chlorides enter natural waters through the dissolution of chlorine-containing minerals and saline deposits (Khilchevskyi et al., 2019; Khilchevskyi et al., 2013). In recent years, the role of industrial and domestic wastewater in increasing the content of chlorides in water bodies has been identified. Chlorides are found in the waters of the Syniukha River near Pervomaisk in concentrations ranging from 19.8 to 82 mg/dm^3.

Calcium ion is the dominant cation in low-mineralized waters. The main sources of calcium in surface waters are chemical weathering and mineral dissolution. Significant amounts of Ca are introduced with industrial wastewater and from agricultural land. According to observations in the Syniukha River, the calcium content ranged from 36 to 108 mg/dm^3.

Magnesium ions enter surface waters through chemical weathering and dissolution of rocks (dolomites, marls) and wastewater. According to long-term observations (1993–2023), the content of magnesium ions in the water of the Syniukha River ranged from 13 to 58 mg/dm^3.

The total content of calcium and magnesium ions in water forms its total hardness (hardness). According to the monitoring data, the total hardness of the Syniukha River water was 4.1–8.3 mg-eq/dm^3.

Sodium and potassium ions enter surface waters with domestic and industrial wastewater and irrigation water from agricultural land. The sodium content in the mouth of the Syniukha River ranged from 5.04 to 170.3 mg/dm^3, and the potassium content – from 1.63 to 21.27 mg/dm^3.

Water mineralisation (or the sum of ions) is the total content of all minerals detected during chemical analysis of water (Khilchevskyi et al., 2006; Shakirzanova & Kichuk, 2019). Fluctuations in surface water salinity are seasonal. The lowest values are usually observed during spring floods and high waters. The highest values – during the period of low water. During the study period, water salinity ranged from 340 to 755 mg/dm^3.

The hydrogen index (pH) is determined by the presence of free hydrogen ions. Although seasonal fluctuations occur, caused primarily by hydrobiological processes, the pH value is a fairly stable indicator. A sharp change in the pH of water indicates that the water body is polluted by acidic or alkaline wastewater from industrial enterprises. In natural waters, the concentration of hydrogen ions is mainly determined by the ratio of free carbon dioxide and hydrogen carbonate ions, and is also influenced by the high content of humus substances, basic carbonates and metal hydroxides formed as a result of CO_2 absorption during photosynthesis, as well as the presence of hydrolysable salts in the water. In addition, contaminated surface water may contain strong acids or bases that affect the acidity of the water. The concentration of hydrogen ions is of great importance for chemical and biological processes in natural waters (Khilchevskyi, 2021; Khilchevskyi & Chunarov, 2009). The development and vital activity of aquatic plants and the stability of various forms of element migration depend on pH. According to long-term observation data, the pH of the Syniukha River waters ranged from 1.6 to 8.83.

According to the monitoring data, the water of the Syniukha River near Pervomaisk has a significant content of suspended solids (up to 486 mg/dm^3), which is a result of excessive agricultural development of its basin, high degree of ploughing, insufficient forest cover and deterioration of the river's self-purification capacity due to the general deterioration of its condition. Water transparency ranged from 3 to 41 cm.

The content of a large amount of organic and humus compounds in the water of the Syniukha River, especially during periods of increased water content, determines the high dynamics of water colour, which ranges from 0.37 to 101 degrees.

Dissolved oxygen in water is one of the most important physicochemical indicators. At the same time, it is the most significant natural oxidant, determining the quality of water and the ability to maintain the ontogeny of aquatic organisms. The main consumers of dissolved oxygen are the processes of respiration of aquatic organisms and oxidation of organic substances. Low dissolved oxygen content affects the entire range of biochemical and ecological processes in a water body. In surface waters, the oxygen content varies widely and is subject to seasonal and daily fluctuations. Oxygen deficiency is more common in water bodies with high concentrations of polluting organic substances and in eutrophic water bodies containing large amounts of nutrients and humus substances. The dissolved oxygen content in the water of the Syniukha River – Pervomaisk ranged from 3.44 to 34.2 mgO_2/dm^3 or 41.3–254 % saturation.

Chemical oxygen demand COD is an indicative indicator of water pollution. In the water of the Syniukha River, this indicator varied from 11.7 to 49.5 mg/dm^3. The content of organic substances in the water according to the permanganate oxidation index is quite significant and ranged from 3.64 to 14.6 mg O/dm^3.

Biochemical oxygen consumption (BOD_5) provides indirect information about the amount of organic matter in water and allows to assess the degree of pollution of a water body and the content of organic matter that is easily oxidised. This indicator ranged from 0.2 to 15.7 mgO/dm^3 over the entire study period.

Nutrients are among the most important indicators of water quality and the state of the aquatic ecosystem. They determine the level of development of aquatic organisms, the trophic level of water bodies, and the degree of their pollution (Mahas & Trokhymenko, 2009).

Nutrients in natural waters include nitrogen, phosphorus and silicon compounds. Nitrogen and phosphorus are most actively involved in the vital activity of aquatic organisms. The most important in biological and biochemical terms are compounds of orthophosphoric and nitric acids, the amount of which in certain periods of the year determines the intensity of organic life in a water body (Mahas & Trokhymenko, 2009). Biogenic substances are catalysts for the process of anthropogenic eutrophication of surface waters. In addition, a significant concentration of nutrients in water can be quite dangerous for humans. The main sources of nutrients (nitrogen and phosphorus compounds) in river waters include residential and urban runoff and wastewaters, industry, agriculture, livestock, agriculture, and precipitation. Internal processes in the water body also play a significant role.

Mineral nitrogen compounds in river waters occur mainly in the form of nitrates, nitrites and ammonium salts dissolved in water. Organic nitrogen compounds are also present in surface waters as a result of the breakdown of protein substances. The main source of nitrogen compounds in river waters is protein degradation processes that occur both in water bodies and in the surrounding soils. One of the indicators of the degree of eutrophication of water bodies is the content of inorganic nitrogen compounds in them.

The main sources of ammonium ions in water bodies are domestic wastewater, surface runoff from agricultural land when ammonium fertilisers are used, and wastewater from various industries. Seasonal fluctuations in ammonium concentration are typically characterised by a decrease in spring and during periods of intensive phytoplankton photosynthetic activity and an increase in summer, when bacterial decomposition of organic matter intensifies. A significant amount of it is a sign of recent water pollution or the result of intensive reduction processes that are common for humic compounds in marsh waters. The concentration of ammonium nitrogen in the water of the Syniukha River – Pervomaisk ranged from 0 to 0.86 mg/dm^3.

Nitrites are intermediate products in the nitrogen cycle (organic ammonium – nitrite – nitrate), so their concentrations in water are usually low compared to ammonium and nitrate nitrogen. The presence of nitrite in uncontaminated water bodies is mainly due to the decomposition of organic matter and nitrification (Mahas & Trokhymenko, 2009). Nitrite is detected in significant concentrations when there is a shortage of oxygen in the water body, and high levels can also be found in areas where wastewater is discharged from enterprises that use nitrite and salt in their production processes. In addition, changes in nitrite content also reflect the self-purification processes of natural waters. The nitrite concentration in the water of the Syniukha River – Pervomaisk ranged from 0 to 13.5 mg/dm^3.

Nitrate nitrogen is formed in natural waters as a result of aqueous nitrification of ammonium ions in the presence of acid under the influence of nitrifying bacteria, which is why nitrate concentrations increase in summer during the massive die-off of phytoplankton (Mahas & Trokhymenko, 2009). Another source of nitrates in surface waters is precipitation. The concentration of nitrate nitrogen in the water of the Syniukha River varied from 0 to 45 mg/dm^3.

Phosphates enter river waters as a result of water erosion of rocks. In natural waters, phosphorus is found in the form of both mineral and organic compounds. Some of it is soluble, while others are found in the form of colloids and suspended solids. Phosphates largely determine the productivity of a water body, as they are a nutrient for aquatic organisms. In river waters, the natural concentration of phosphate is usually low during the growing season due to consumption by biological processes, and is maximised in winter due to the decomposition of organic residues. Elevated phosphorus concentrations in waters sometimes indicate pollution. The content of phosphate ions in the water of the Syniukha River ranged from 0.01 to 1.07 mg/dm^3.

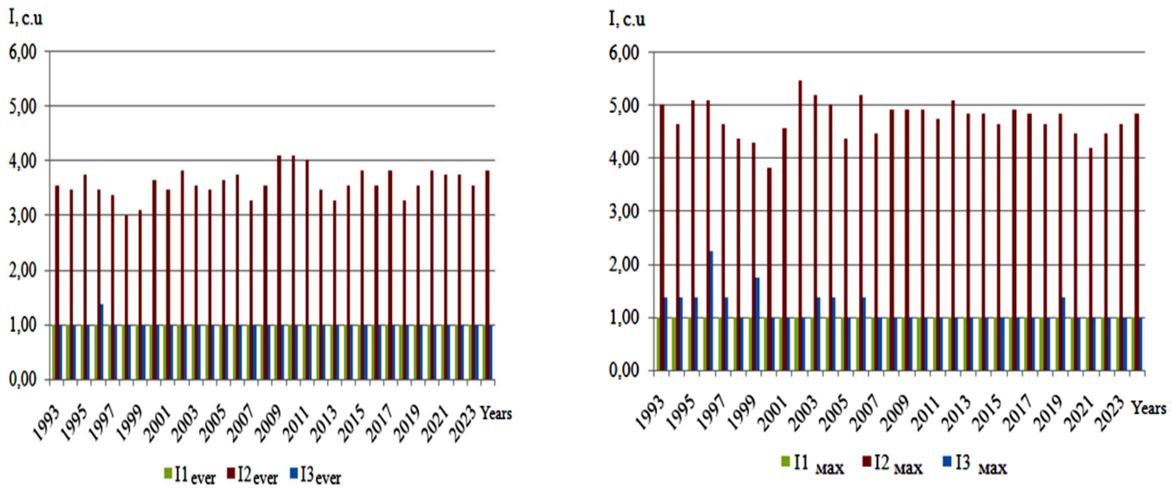
Iron is almost always present in natural waters, as it is ubiquitous in rocks. The concentration of total iron in natural waters is low due to its low migration capacity. The main factors that determine the volume and intensity of Fe inputs to surface waters include the processes of chemical weathering of rocks. A significant amount of soluble iron compounds enters surface water bodies with underground flow, as a result of underground recharge, with wastewater from various industries and agriculture, storm water runoff, surface-slope runoff from urbanised areas and agricultural land. Iron content in the waters of the Syniukha River ranged from 0 to 21.6 mg/dm^3.

The silicon concentration in the water of the Syniukha River at the Pervomaisk control point ranged from 0.39 to 7.76 mg/dm^3 in 1993–2023.

The content of heavy metals (copper, zinc, nickel, chromium, manganese) in the waters of the Syniukha River is limited by high pH, water turbidity, and intensive biological processes. Sources of heavy metals include industrial wastewater, quarry water, various reagents containing copper, and runoff from agricultural land. In many cases, the content of heavy metals in the water of the Syniukha River is highest during floods and high water, which is explained by their washing away from the catchment surface. That is why, over the entire period of observation, the content of copper in the river water ranged from 0 to 0.12 mg/dm^3, zinc from 0 to 0.47 mg/dm^3, nickel from 0 to 0.67 mg/dm^3, chromium from 0 to 0.015 mg/dm^3, and manganese from 0 to 1.16 mg/dm^3.

The content of pollutants, such as oil products, synthetic surfactants and phenols, in natural waters mainly depends on the anthropogenic load on water bodies. Large quantities of oil products enter surface waters with wastewater from oil refineries, chemical and other industries, and with domestic wastewater. The main source of synthetic surfactants in natural water bodies is domestic and industrial wastewater. When these compounds enter water bodies they can affect their physicochemical state, worsening the oxygen regime and organoleptic properties. At the same time, these compounds remain in river water for a long time and slowly decompose. The content of synthetic surfactants in the Syniukha River near Pervomaisk ranges from 0 to 0.6 mg/dm^3.

Water quality was assessed by three sets of indicators: components of the salt composition (total ions, chlorides, sulfates), tropho-saprobiological criteria (suspended solids, transparency, pH, ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, phosphorus phosphate, dissolved oxygen measure of oxygen saturation, permanganate oxidizability, bichromate oxidizability, BOD_5), the content of specific substances of toxic effect (copper, zinc, chromium, manganese, total iron, nickel, oil products and synthetic surfactants). The analysis of water quality monitoring and assessment data showed that the degree of water pollution in the Syniukha River is not the same according to different indicators. The results of the generalized ecological assessment of the water quality of the Syniukha River for the period 1993–2023 show that, according to the average and worst values of mineralization indicators, the river water belonged to fresh water, and its ionic composition was of the hydrocarbonate class, calcium group, type III. In both cases, among the block indices, the index of the ecological and sanitary block worsens water quality the most (Fig. 2). That is, the water of the Syniukha River has excessive concentrations of nitrogen and phosphorus compounds, and a rather unstable oxygen regime and pH.



a b

Fig. 2. Temporal changes in water quality in the Syniukha River according to the environmental block indices: a – for annual average values; b – for the worst values

During the entire study period, there was significant water pollution with organic substances, characterizedby an increase in the BOD_5. In terms of maximum values, the 4–5th class of water quality is predominant (“poor-very poor” in terms of condition, “dirty-very dirty” in terms of purity). The deterioration of water quality to Class 3 is observed in terms of oxidation (PO, COD). The oxygen regime of the Syniukha River corresponds to Class 3 (“mediocre”, “moderately polluted”) using average values of the indicator, but using the worst values it is much worse - Classes 4–5. That is, in most samples, the oxygen regime of the river is mostly at an acceptable level, but there are still frequent cases of a critical decrease in dissolved oxygen content, up to and including frostbite. This can be explained by the fact that the river and its tributaries are regulated by numerous reservoirs that have limited water exchange at depth in them. The deterioration of the oxygen regime occurs as a result of seasonal hydrobiological processes, as well as pollution by domestic and industrial wastewater and surface runoff from agricultural land. It is also worth noting the very high level of biogenic pollution of the Syniukha River waters in terms of nitrogen and phosphorus compounds, where the water quality varied from class 4 to 5 (in terms of condition “bad, very bad’ and in terms of purity “dirty-very dirty”). It is the high content of such compounds caused by anthropogenic factors that leads to “blooming” of water in the created reservoirs and deterioration of the oxygen regime.

According to the integrated assessment, during the study period, the waters of the Syniukha River in the Pervomaisk city reach correspond to Class II, Category 2 and are assessed as “very good-clear” in terms of their average values of indicators. According to the worst values of indicators, the water corresponds to Class II, Category 3 and the water quality of the Syniukha River is assessed as “good – quite clean”.

If we look at the results for individual years (Fig. 3), we can see that the situation has not changed significantly over the entire observation period. The water quality in terms of average and worst indicators fluctuated within the second class, with only the quality categories changing. Among the block indices, the highest values are for the block of environmental and sanitary indicators.

The indice variations at their maximum values indicate limited fluctuations in pollution levels and a tendency to stabilize the hydrochemical state of the water in the Syniukha River. Such changes can be explained by a decrease in uncontrolled wastewater discharges and surface runoff in the river basin. However, against the backdrop of a decline in economic activity in the river basin and the volume of its pollution, there is a tendency for water quality to deteriorate in terms of average indicators, which is explained by a significant decrease in water flow in the river and the accumulation of pollutants near the river mouth.

Thus, in general, the ecological condition of the river is not good due to high anthropogenic pressure and limited capacity for self-purification of water. This requires attention from environmental institutions and the need to develop and implement an effective environmental program aimed at both improving the condition of the watershed and limiting further pollution of the water body.

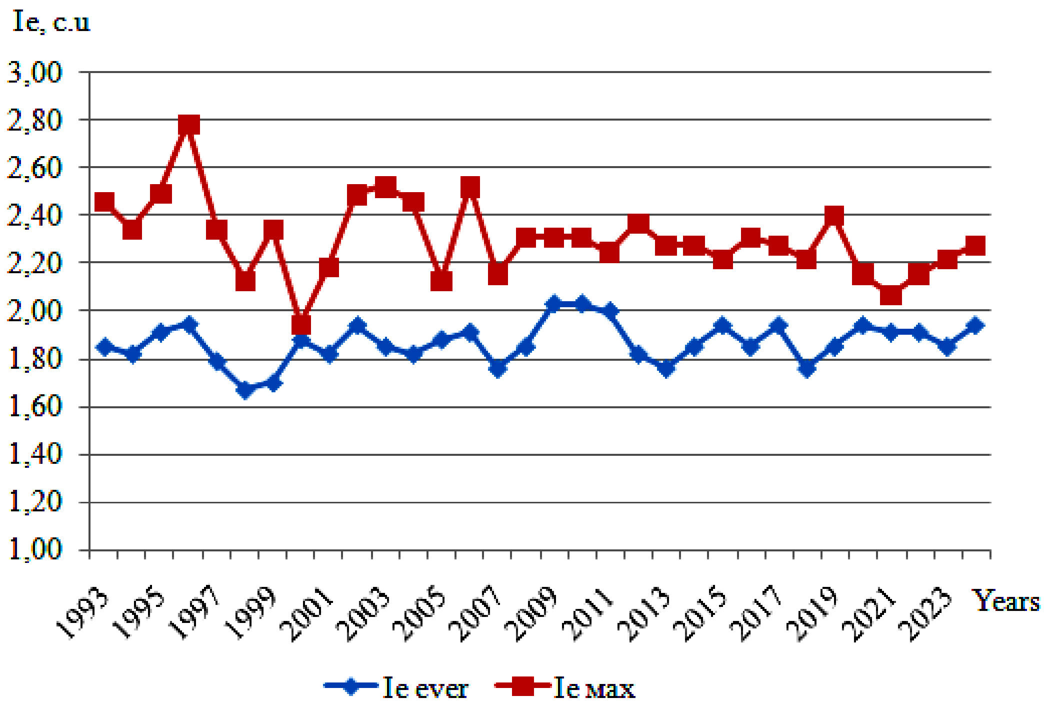


Fig. 3. Changes in the environmental indices of water quality in the Syniukha River

The level of water suitability of the Syniukha River for various types of water use was determined by the value of the combinatorial water pollution index (CWPI) using the values of maximum permissible concentrations for water bodies of fishery significance (MPC) (Table 2).

Table 2

Results of water quality assessment of the Syniukha River according to fishery MPC standards

Water quality indicators of the Syniukha River – Pervomaisk city according to fishery MPC standards					
n=24; *n′*=17; *K*=71 %; CWPI=77; quality class III b – "dirty"					
1	2	3	4	5	6
Indicator	**[O_2]**	**[Ca]$^{2+}$**	**[Mg]$^{2+}$**	**[Na]$^{+}$**	**[K]$^{+}$**
MPC, mg/dm^3	6	180	40	120	50
N	378	378	378	278	278
N′	359	0	140	14	0
No	95.0	0.0	37.0	5.0	0.0
Evaluation indices	4	1	3	1	1
Ki	1.83	0.36	0.95	0.72	0.11
Valuation indices	1	1	1	1	1
Evaluation points Si	4	1	3	1	1
Indicator	**[Cl]$^{-}$**	**[SO_4]$^{2-}$**	**[P_{min}]**	**[NO_2]$^{-}$**	**[NO_3]$^{-}$**
MPC, mg/dm^3	300	100	1	0.02	9.1
N	378	378	51	378	378
N′	0	93	0	307	52
No	0.0	24.6	0.0	81.2	13.8
Evaluation indices	1	2	1	4	2
Ki	0.17	0.87	0.25	4.61	0.57
Valuation indices	1	1	1	2	1

Continuation of Table 2

1	2	3	4	5	6
Evaluation points Si	1	2	1	8	2
Indicator	**$[NH_4]^+$**	**$[Fe_{sum}]$**	**[COD]**	**$[BOD_5]$**	**Suspended matter**
MPC, mg/dm^3	0.39	0.1	20	2.25	15
N	378	378	266	378	378
N′	6	323	232	148	79
No	1.6	85.4	87.2	39.2	20.9
Evaluation indices	1	4	4	3	2
Ki	0.24	2.77	1.34	1.02	0.72
Valuation indices	1	2	1	1	1
Evaluation points Si	1	8	4	3	2
Indicator	**pH**	**Mineralization**	**$[Cu]^{2+}$**	**$[Zn]^{2+}$**	**$[Cr]^{6+}$**
MPC, mg/dm^3	6.5–8.5	1000	0.001	0.01	0.001
N	378	378	375	375	378
N′	9	0	307	310	18
No	2.4	0.0	81.9	82.7	4.8
Evaluation indices	1	1	4	4	1
Ki	0.96	0.56	7.14	3.57	0.20
Valuation indices	1	1	2	2	1

In general, for the period from 1993 to 2023, out of 24 indicators 17 exceeded the MPC with varied extent, so the pollution complexity index was 71 %. Referring to individual indicators, the level of water pollution was distributed as follows:

– The content of chlorides, mineralization, phosphates, nickel, chromium, and surfactants was recorded as “single low-level contamination” and the water was “slightly contaminated”;

– The content of suspended solids, sulfates, and nitrates was recorded as “unstable low-level pollution” and the water was “polluted”;

– The BOD content was recorded as “persistent low-level pollution” and the water was “dirty”;

– Dissolved oxygen and COD indicators showed “characteristic low-level contamination” and the water was “dirty”;

– The content of petroleum products was recorded as “stable medium-level pollution” and the water as “very dirty”;

– In terms of iron, copper, and chromium, “characteristic medium-level contamination” was recorded, and the water was “very dirty”;

– In terms of nitrite, iron, manganese, copper, and zinc, the water was found to be “characteristically medium polluted” and “very dirty”.

In general, the water quality of the Syniukha River corresponded to the CWPI index of 77 points, which indicates that the investigated water body belongs to the III b class of water quality. The state of pollution of the water body can be characterized as “dirty”, which indicates that its waters are unsuitable for safe fish farming.

According to hydrochemical monitoring data, the Syniukha River is polluted and is under the influence of a high anthropogenic load (the river's waters are heavily polluted by domestic and industrial wastewater). The presence of significant volumes of discharges causes an unacceptably high content of organic and, in many cases, toxic substances in the river waters. The main pollutants are biogenic substances (nitrogen and phosphorus compounds). The high and persistent level of pollution over time indicates the poor efficiency of the waste water treatment plants that discharge water in to the Syniukha River basin.

The analysis of long-term data on hydrochemical water quality indicators (Tablj 3) showed that the risk of not achieving environmental objectives arises from the high content of ammonium nitrogen and phosphates in the water of the Syniukha River, for which the corresponding actual values exceed the critical ones. Water pollution with these substances indicates the presence of point sources of untreated municipal wastewater, which may be caused by the absence and improper operation of treatment facilities in the studied surface water massif. There are no risks in terms of oxygen, BOD_5 and *pH*.

Table 3

Risk assessment of anthropogenic load for chemical and physical-chemical indicators based on monitoring data of the Syniukha River inPervomaisk for1993–2023

Indicator	Actual values	Critical values	Risk assessment
Oxygen*, % saturation	99.28	70	without risk
BOD_5 **, mg/dm^3	2.29	6	without risk
NH_4 **, mg/dm^3	0.76	0.6	at risk
NH_4 ***, mg/dm^3	0.47	0.2	at risk
PO_4 ***, mg/dm^3	0.34	0.3	at risk
pH	8.19	6.5–8.5	without risk

* 10 th percentile.
** 90 th percentile.
*** Average annual value.

The results of the assessment can serve as a basis for developing ways to address economic and social issues related to river protection, planning and implementing water protection measures to achieve good ecological status of the river, and evaluating the effectiveness of such measures.

4. Conclusions

This paper investigates the ecological state and water quality of the Syniukha River, a large tributary of the Southern Bug River, based on long-term observations in its estuary, the area of drinking water intake at the Pervomaisk post (1993–2023, 24 indicators).

An indicative ecological assessment of the water quality of the Syniukha River showed that the degree of pollution of the river's waters varies according to different indicators. In general, for the period 1993–2023, the value of the ecological index of water quality of the Syniukha River in terms of average concentrations of indicators corresponded to the 2nd Class of Category 2 (very good water quality, clean water quality). Using the worst values of indicators, the environmental index corresponded to Class II, Category 3 (water condition “good”, water clarity “fairly clean”). Therefore, the water quality class is relatively consistent over the entire study period.

Comparison of the block indices of the environmental assessment shows that the water of the Syniukha River in its estuary has been most polluted over the years by substances of the environmental and sanitary block, namely nitrogen and phosphorus compounds, poor dissolved oxygen conditions, and high organic matter content.

In terms of chronological trends, the average values of the indicators show an increase in the environmental index, which indicates a certain deterioration in the water quality and ecological status of the Syniukha River. The main reasons for such changes include a decrease in water flow in the river over the past 100 years, a high level of anthropogenic pressure and limited capacity for water self-purification.

The assessment results of water quality in the mouth of the Syniukha River, according to fishery MPC standards, correspond to Class III (b) and characterize as the water as “dirty” and unsuitable for safe fish farming. The deterioration in water quality is caused by elevated concentrations of nitrite and COD, which can be explainned by the significant development of agriculture in the river catchment, including the use of fertilizer sand plant protection products that are periodically washed into the river with surface and groundwater runoff. The high concentrations of iron, manganese, copper, zinc, and oil products are caused by the discharge of polluted industrial wastewater.

The results of the study indicate that for the period 1993–2023, the state of the Syniukha River in the estuary cannot be considered ecologically stable and optimal due to the high level of anthropogenic pressure on the river, which clearly exceeds the capacity of the river’s aquatic ecosystem to regenerate itself. This situation indicates an increased level of environmental hazard in the river basin. Given the importance of the Syniukha River as the largest tributary of the Southern Bug in its lower reaches and a source of drinking water supply in Mykolaiv region, the problem of deterioration ecological state of the Syniukha River requires attention from environmental protection agencies and the need to develop comprehensive water quality management based on the identification and assessment of the impact of major sources of pollution, and regulation of water management activities in the river basin.

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