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WATER QUALITY CONTROL OF THE ZAPORIZKE (DNIPROVSKE) RESERVOIR USING THE AUTONOMOUS HYDROCHEMICAL STATION "NAYADA-2"

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Abstract

The problem of water ecosystem pollution is increasing every year worldwide, and this issue has become even more urgent due to the full-scale military actions on the territory of Ukraine. Monitoring the condition of the Zaporizke (Dniprovske) reservoir is extremely important, as the deterioration of water quality and its sanitary condition can pose risks to both the population and the biota. The aim of the study was to analyze the physicochemical parameters of water in the central section of the Zaporizke (Dniprovske) reservoir, specifically near Monastyrskyi Island, and to assess its suitability for domestic, recreational, and fishery purposes. The research was conducted throughout 2024 near Monastyrskyi Island (Dnipro city). To determine the physicochemical parameters of the water, the stationary station "NAYADA-2" was used. The chemical composition parameters of the water were compared with the regulatory standards for domestic, recreational, and fishery purposes. The study found that most of the physicochemical parameters met the regulatory standards for domestic, recreational, and fishery purposes. However, in the summer months, an exceedance of the chemical oxygen demand (COD_{Cr}) and a decrease in dissolved oxygen concentration were observed, which is a seasonal phenomenon related to the increase in temperature. Additionally, in August, the maximum concentration of total suspended solids was recorded at 24.6 mg/dm^3, which does not meet the regulatory standards for fishery purposes. In the autumn, an exceedance of the BOD_5 (biochemical oxygen demand) values was recorded, which could indicate organic pollution of the water body. Comparing the obtained data with previous studies in 2023, no critical changes were found. According to the study results, the water in the research area met the regulatory standards for domestic, recreational, and fishery purposes for most of the parameters and provides a favorable environment for the existence and reproduction of hydrobionts.

Key words: water quality station, hydrochemical parameters, water quality, Zaporizke (Dniprovske) reservoir, hydroecology.

КОНТРОЛЬ ЯКОСТІ ВОДИ ЗАПОРІЗЬКОГО (ДНІПРОВСЬКОГО) ВОДОСХОВИЩА З ВИКОРИСТАННЯМ АВТОНОМНОЇ ГІДРОХІМІЧНОЇ СТАНЦІЇ "НАЯДА-2"

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Анотація

Проблема забруднення водних екосистем у світі зростає з кожним роком, дана проблема стає ще актуальнішою у зв'язку з повномасштабними воєнними діями на території України. Моніторинг стану Запорізького (Дніпровського) водосховища є надзвичайно важливим, адже погіршення якості води та її санітарного стану може нести небезпеку, як для населення, так і для біоти. Мета роботи – проведення аналізу фізико-хімічних показників води центральної ділянки Запорізького (Дніпровського) водосховища, а саме поблизу о. Монастирський та оцінювання її придатності для комунально-побутових, рекреаційних та рибогосподарських потреб. Дослідження проводили протягом 2024 р. поблизу о. Монастирський (м. Дніпро). Для визначення фізико-хімічних показників води використовували стаціонарну станцію «Наяда-2». Показники хімічного складу води порівнювали з нормативними показниками для комунально-побутового, рекреаційного та рибогосподарського призначення. Дослідженням встановлено, що більшість фізико-хімічних показників відповідали нормативним значенням для комунально-побутового, рекреаційного та рибогосподарського призначення. Однак у літні місяці виявлено перевищення показників $ХСК_{Cr}$ та зниження концентрації розчиненого кисню у воді, що є сезонним явищем та пов'язане зі збільшенням температурного

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концентрації розчиненого кисню у воді, що є сезонним явищем та пов'язане зі збільшенням температурного режиму. Також у серпні встановлено максимальний показник загального вмісту завислих речовин – 24.6 мг/дм^3, що не відповідає нормативним значенням для рибогосподарського призначення. Восени зафіксоване перевищення значень БСК$_5$, що може говорити про органічне забруднення водойми. В порівнянні отриманих даних з попередніми дослідженнями 2023 року критичних змін не виявлено. За результатами досліджень вода дослідної ділянки за більшістю показників відповідає нормативним показникам для комунально-побутового, рекреаційного та рибогосподарського призначення та є сприятливим середовищем для існування та розмноження гідробіонтів.

Ключові слова: станція якості води; гідрохімічні показники; якість води; Запорізьке (Дніпровське) водосховище; гідроекологія.

Introduction

The problem of pollution in aquatic ecosystems attracts great attention from scientists worldwide. Pollution of natural waters is part of the broader global environmental pollution issue. Anthropogenic activity affects the natural chemical composition and quality of water. It is known that the hydrochemical state of water depends on a complex of natural and anthropogenic factors [1–10]. According to conducted studies, approximately 1.8 million deaths annually are linked to the consumption of polluted water [11]. The right to safe and clean water is a fundamental human right. In 2010, the UN General Assembly adopted Resolution 64/292 "The human right to water and sanitation," which recognizes the right to safe and clean drinking water and sanitation as essential to the full enjoyment of life and all human rights. In 2015, the UN adopted the Sustainable Development Goals for the period 2015–2030, one of which is Goal No. 6: "Clean Water and Sanitation" [12]. In the European Union, Directive 2000/60/EC "Establishing a framework for Community action in the field of water policy" (dated October 23, 2000) sets out the main (framework) requirements for achieving good water status in water bodies by EU member states. In 2016, Ukraine implemented the provisions of the EU Water Framework Directive at the legislative level by making certain amendments, particularly to the Water Code of Ukraine. Sources of surface water pollution are generally classified as point and diffuse by origin. A point source of pollution is a localized and identifiable discharge source, whereas diffuse sources introduce pollutants from a delocalized area. The most widespread type of pollution, particularly in developing countries, is the discharge of untreated wastewater into natural water bodies from point sources. Diffuse pollution also significantly affects water quality in developed countries. A typical example is the leaching of nitrogen compounds from fertilizers used on agricultural lands [13].

In Ukraine, the problem of water pollution has become even more acute due to the full-scale invasion of the Russian Federation. Since the beginning of the full-scale war, a significant number of direct attacks have been recorded on civilian water supply systems, which are critical for providing the population with safe and high-quality water, as well as on sanitation and irrigation systems that support the agricultural sector. Major oil refineries in Lysychansk, Kramatorsk, and other cities have been destroyed, causing considerable environmental damage and harm to ecosystems, including water resources and water security not only in Ukraine. In countries experiencing armed conflicts and military operations, ensuring water security becomes particularly challenging – namely, providing water supply services and protecting the population from risks associated with water quality and safety . Restrictions in access to water and the environmental damage inflicted on water resources as a result of such actions threaten the overall safety of the population, making the return to peaceful life longer and more difficult [14]. Russia's full-scale war against Ukraine has directly impacted and continues to impact the country's water resources, specifically the water intake and treatment facilities, wastewater treatment plants, water supply networks, and dams. Hostilities have damaged the water quality of the Dnipro River and the Zaporizke (Dniprovske) Reservoir, which serves as a major source of water supply in Ukraine [15]. Therefore, starting in 2022, Ukraine urgently implemented new water body monitoring programs that incorporated the requirements of the EU Water Framework Directive. These include: the "State Monitoring Program of Groundwater for 2022," the "State Monitoring Program of Coastal and Marine Waters of the Black and Azov Seas until 2026," and the "Monitoring Program of Surface Waters for 2022." These documents aim to establish a European model for water body monitoring in Ukraine. The state monitoring of surface waters includes diagnostic, operational, and investigative monitoring, which is conducted according to biological, physicochemical, chemical, and hydromorphological indicators in order to determine the ecological status of surface water bodies [14].

Research on the condition of water bodies located in occupied and frontline territories is extremely important and relevant for providing an adequate assessment of the aquatic environment for specific needs and for estimating the damage caused to water resources. However, such studies are often difficult or impossible to carry out due to security concerns. The Zaporizke (Dniprovske) reservoir is one such water body. Currently, the regime of the reservoir is being shaped under the influence of a complex of external factors, such as water flow, precipitation levels, anthropogenic pressure, water exchange rates, and intra-reservoir processes. The continuously increasing anthropogenic pressure causes significant changes in the chemical composition of water [16; 17]. The Dnipropetrovsk region is a center of concentration for key sectors of heavy industry. The enterprises of metallurgy, chemical production, mechanical engineering, and construction materials manufacturing are located in the Dnipro city. Their industrial activities are the primary sources of negative impact on the environment, particularly on the state of aquatic ecosystems [18]. The formation of the water quality of the Dnipro River is significantly affected by climate change, ongoing military actions, and economic activities in the territory of Ukraine. [15]. Monitoring the condition of the Zaporizke (Dniprovske) Reservoir is currently of critical importance, given the active hostilities that can cause destruction of water infrastructure and the release of pollutants into the water. Deterioration of water quality and its sanitary condition poses risks not only to the population of the Dnipropetrovsk region but to the entire country. It is also crucial to note that water quality directly affects the development and existence of hydrobionts; therefore, degradation of hydroecological conditions may lead to irreversible negative ecological consequences.

The aim of this study was to analyze the physicochemical parameters of water in the central section of the Zaporizke (Dniprovske) Reservoir, specifically near Monastyrskyi Island, and to assess its suitability for domestic, recreational, and fishery purposes.

Experimental

The study was conducted throughout 2024 near Monastyrskyi Island (Dnipro City) (Fig. 1). Monastyrskyi Island is located in the central part of the city and serves as a recreational and active leisure zone for the population, as well as a permanent site for hydrobiological research by employees of the Scientific Research Laboratory of Hydrobiology, Ichthyology, and Radiobiology of the Scientific Research Institute of Biology at Oles Honchar Dnipro National University (DNU), and by the employees and postgraduate students of the Department of General Biology and Aquatic Bioresources of DNU.

To determine the physicochemical parameters of the water, the stationary station "NAYADA-2" was used. The following parameters were measured: water temperature, pH, total suspended solids, color, nitrate nitrogen content, biochemical oxygen demand in water (BOD_5), dichromate chemical oxygen demand (COD_{Cr}), dissolved oxygen (O_2), organic carbon content (C_{org}), and electrical conductivity. These parameters were measured on a monthly basis.

Fig. 1. Monastyrskyi Island (central section of the Zaporizke (Dniprovske) reservoir)

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The automatic stationary surface water monitoring station "NAYADA-2" is a complex multifunctional device that consists of a cabinet for housing climatic and auxiliary equipment, as well as a measurement and analytical unit (Fig. 2).

Fig. 2. Automatic stationary surface water monitoring station "NAYADA-2"

The system consists of a sensor unit located in the controlled aquatic environment, equipment for data transmission, and a central station for receiving and recording digital signals. The station is equipped with analyzers manufactured by Scan Messtechnik GmbH (Germany), including: the spectro:lyser sensor (for measuring suspended solids, color, organic carbon content (C_{org}), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{Cr}), and nitrate nitrogen content); the ammo:lyser pH sensor (for measuring temperature and pH); the oxi:lyser sensor (for measuring dissolved oxygen); the condu:lyser sensor (for measuring electrical conductivity); the con:cube control and data display unit; and a controller of the hardware-software complex (HSC).

A digital method is used to transmit data on the measured parameters to the central station, ensuring high accuracy. Information is recorded and stored using electronic media. All system operations are controlled by electronic computing machines (ECMs).

The reliability of the obtained results is ensured by the factory calibration certificate for the instruments and the declaration of conformity from the dealer-importer for the first year of use. Subsequent calibration of the sensors is carried out according to the technical regulations, along with annual state verification by the State Standardization and Metrology Authority. To check out the obtained results, water samples were simultaneously collected and analyzed by scientists in the certified Scientific Research Laboratory of Theoretical and Applied Chemistry Problems of the Scientific Research Institute of Chemistry and Geology at DNU (certificate No. ПЧ 06-2/1152-2023 dated September 25, 2023, confirming the technical competence of the laboratory in compliance with the requirements of SSTU ISO 10012:2005 "Measurement management systems. Requirements for measurement processes and measuring equipment") using commonly accepted methods [19]. For the determination of water color, the platinum-cobalt scale was used. The chemical composition indicators of the water were compared with the normative values for municipal and domestic [20] and fishery purposes [21]. Additionally, the data from the Public Health Center of the Ministry of Health of Ukraine [22] were used for analysis in this work.

Results and Discussion

The research findings established that the maximum water temperature was recorded in July at +26.4 °C, while the minimum was in November at +8.9 °C. These values align with the normative indicators for MAC for drinking and household needs (MAC_d) and MAC for fishery needs (MAC_f). Water temperature is an important parameter that affects the physicochemical processes occurring in the waterbody. A number of studies have investigated the impact of temperature on characteristics related to fish and other aquatic organism's reproduction, such as sex determination, gametogenesis dynamics, gamete

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quality, fertility, age and sexual maturity, as well as the duration of the reproductive season [23]. pH levels did not exceed the normative values and remained within the range of 7.0–7.9. The development and vitality of aquatic plants, as well as the stability of various forms of element migration, depend on the pH value.

The highest color index was recorded in May and July, at 4 degrees, while the lowest was in November, at 2.5 degrees. Water color is influenced by the presence of humic and fulvic acids, as well as iron compounds. The intense color of the water in summer is attributed to algae during their mass development, as well as suspended solids.

In August to October, exceedances of the normative values for total suspended solids for fishery purposes were recorded, with the highest value in August at 24.6 mg/dm^3. This is due to the increase in water temperature and the processes of algal "blooming" (table).

Table

Hydrochemical parameters of water of Zaporizke (Dniprovske) reservoir, 2024.

Parameters	$MMAC_d$	$MMAC_f$	May	June	July	August	September	October	November
t, °C	—	+28	20.7	23.4	26.4	25.6	21.5	16.6	8.9
pH, units	6.5-8.5	6.5-8.5	7.3	7.0	7.01	7.1	7.6	7.8	7.9
Total suspended solids, mg/dm^3	—	20.0	15.65	18.25	19.72	24.6	20.2	21.95	19.75
Color, degrees	10	—	4.0	3.0	4.0	3.3	3.8	2.8	2.5
Nitrate nitrogen, mg N/dm^3	10.15	9.1	0.43	0.61	0.79	1.10	1.07	0.99	0.89
BOD_5 (at 20 °C), mg O_2/dm^3	≤3.00	3.00	1.6	1.1	2.1	2.2	3.9	3.5	4
COD_{Cr}, mg O/dm^3	30	20	36.40	38.20	40.60	30.65	17.12	14.15	9.30
O_2, mg/dm^3	≥ 4	> 6	8.90	9.80	7.30	8.91	9.23	12.81	15.70
C_{org}, мг/дм^3	—	—	19.7	20.5	21.5	22.8	22.7	21.7	19.8
Electrical conductivity, μs/cm	—	—	338.0	333.5	326.0	322.8	321.8	337.5	360.0

Sources of suspended solids may include soil and rock erosion processes, turbidity of bottom sediments, products of metabolism and decomposition of aquatic organisms, chemical reactions, and anthropogenic sources. Suspended solids affect the vitality of aquatic organisms, lead to the siltation of waterbodies, and contribute to the process of eutrophication.

In autumn, exceedances of the BOD_5 values for fishery purposes were recorded – 3.5–4 mg O_2/dm^3. BOD_5 is an important ecological indicator of the condition of natural water bodies, used to assess the degree of contamination of the aquatic environment by organic substances. Compared to previous studies in 2023, the BOD_5 values have slightly increased.

During the spring-summer period of the study, exceedances of the COD_{Cr} values were recorded for both household and fishery purposes – 30.65–40.60 mg O/dm^3. The highest values were recorded in July. The increase in values indicates organic pollution of the water body. The main sources of organic contamination of surface waters are effluents from animal waste farms, industrial wastewater from the processing industry, and others [24]. Starting in September, a decrease in this indicator was observed, with the lowest value recorded in November – 9.3 mg O/dm^3, which may indicate the ability of the waterbody to self-purify. Previous studies showed a constant increase in COD_{Cr}, with the highest value recorded in August 2023 at 41.5 mg O/dm^3. Chemical oxygen demand is one of the integral indicators of water quality, used to assess the total content of organic substances in it. Studies on changes in COD_{Cr} values in waterbodies and comparisons with other integral indicators provide important information regarding the quantity of organic matter, its origin, and processes occurring in these bodies. Therefore, this indicator is widely used in water quality monitoring and in hydrochemical research practice [19].

Regarding the concentration of dissolved oxygen in water, the lowest values of this parameter were recorded in July – 7.3 mg/dm^3, but they fully meet the regulatory values for domestic and fishery purposes. The maximum value was recorded in November – 15.7 mg/dm^3. Compared to the data from the 2023 study, a positive trend in the changes of this parameter can be observed, namely: an increase in the dissolved oxygen content in the water during the summer, which is a positive sign for the existence and reproduction of hydrobionts. This is related to the decrease in water temperature during the

summer months compared to 2023 [25]. The dissolved oxygen content in water is one of the most important physico-chemical parameters, a natural oxidizer that determines water quality and the ability to support the ontogenesis of hydrobionts.

The maximum content of organic carbon (C_{org}) was recorded in the summer period, namely in August – 22.80 mg/dm^3, with the minimum values in November – 19.8 mg/dm^3. A high content of C_{org} in water may indicate organic pollution of both natural and anthropogenic origin. Regarding the nitrate nitrogen levels, no exceedances of the regulatory values were found during the study (see Table 1). However, in the long-term dynamics, an increase in the concentration of nitrate forms of nitrogen was observed in the Zaporizhzhia (Dnipro) Reservoir [25]. The presence of nitrate ions in natural waters is associated with the nitrification processes in the waterbody. Also, a significant amount of nitrate nitrogen enters surface waters with industrial and domestic wastewater, as well as from surface runoff from agricultural lands, especially when applying nitrogen mineral and fresh organic fertilizers [24].

The conductivity values did not exceed the regulatory limits. The lowest value was recorded in September – 321.8 μs/cm, and the highest in November – 360.0 μs/cm. The electrical conductivity of natural water primarily depends on the concentration of dissolved mineral salts and temperature. Comparing the obtained data with previous studies, the electrical conductivity of the water has changed little.

It is known that water quality and hydrological parameters are the main indicators of the state of waterbodies used for recreational purposes. Special attention needs to be given to the biological (microbiological) water quality indicators, as they include pathogenic microorganisms – disease-causing agents. Monastyrskyi Island has been one of the popular recreational spots in the city of Dnipro for many years. In the long-term dynamics of bacterioplankton development in the Zaporizhzhia (Dnipro) reservoir, periods of maximum and minimum values are observed, which are related to varying degrees of anthropogenic load [27]. It is a regular pattern that the total number of microorganisms and saprophytes increases in the autumn when mass die-off of aquatic vegetation occurs. Conversely, in the summer, during the mass development of algal flora ("water blooming"), the number of surface bacterioplankton decreases due to the antagonism between saprophytes and cyanobacteria. Regarding microbiological indicators, the total number of microorganisms and saprophytes in all sections of the Zaporizke (Dniprovske) reservoir is 1–2 times lower compared to fishery MACs [27].

The World Health Organization (WHO) pays significant attention to the quality of recreational water, developing relevant documents (reviews, guidelines, recommendations), which serve as a benchmark for national bodies dealing with recreational issues on water bodies [28]. The European Union has the "Directive on the management of bathing water quality" [29]. It is worth noting that Ukraine lacks separate regulatory documents concerning recreational water quality or the quality of waterbodies for bathing. Currently, this issue is addressed as part of more general regulatory requirements. Scientists study the impact of water quality on recreational water use. Along with the normative evaluation of beach conditions by controlling state authorities, the global system of voluntary international environmental certification of beach management is developing. One such program is the "Blue Flag" program of the international Foundation for Environmental Education [30]. In 2001, the foundation became a global organization and began collaborating with the United Nations Environment Programme (UNEP) and the World Tourism Organization (UNWTO). It actively conducts five environmental programs. The goal of the "Blue Flag" program is to ensure sustainable beach management and yacht and boat moorings through the implementation of strict criteria regarding water quality, environmental education, and environmental management. Since clear regulatory parameters are needed for water quality assessment, the 2006/7/EC directive on the management of bathing water quality, adopted in the European Union, has been used as the basis [29]. Beaches that have received the certification are included in the World Tourism Organization's list as recommended for visits. In 2010, Ukraine joined the "Blue Flag" program. In 2021, 19 Ukrainian beaches were awarded the "Blue Flag" certification [31]. All 10 freshwater beaches are located on the Dnipro River or within its basin, including a beach in the Dnipropetrovsk region (Pishchanka village, Novomoskovsk district, Dnipropetrovsk region, Samara River) [32].

Laboratories of the territorial centers for disease control and prevention of the Ministry of Health of Ukraine regularly monitor the quality of

water in recreational water bodies used for bathing. In May-June 2024, 1218 water samples from surface water bodies in recreational and leisure areas on rivers and lakes in Ukraine were tested for microbiological indicators. According to the results obtained by the Center for Public Health of the Ministry of Health of Ukraine, in the Dnipropetrovsk region, water quality met the standards only at two beaches: namely, on Monastyrskyi Island in the city of Dnipro and at the city beach in the town of Zelendolsk [22]. Therefore, the water of the Zaporizke (Dniprovske) Reservoir near Monastyrskyi Island meets the regulatory water quality standards for recreational purposes and simultaneously provides a favorable environment for the existence of biota.

Conclusion

The water of the study area meets the normative standards for municipal, recreational, and fishery purposes according to most hydrochemical parameters. In terms of microbiological indicators, the water quality of the study area also fully complies with the normative standards and is safe for bathing.

Compared to last year's studies, in the summer, a decrease in the average temperature indicators and an increase in oxygen concentration in the water were observed, which is a favorable sign for the existence and reproduction of fish and other aquatic organisms. However, an increase in the COD_{Cr} values and the total suspended solids in the water was detected, although from September, a gradual decrease in the chemical oxygen demand was observed, indicating the self-purification capacity of the water body. In the fall, the BOD_5 indicators were found to be exceeded during the study.

The prospects for further research lie in the continuation of a comprehensive systematic assessment of the water quality of the Zaporizke (Dniprovske) reservoir to detect changes and improve the condition of the waterbody. The obtained data will also be useful in the development of monitoring and water use programs.

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