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ANALYSIS OF THE HYDROCHEMICAL REGIME OF THE DNIPRO RESERVOIRS

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Abstract. *A complex of issues was considered, namely: hydro-chemical pollution of catchment landscapes, bottom sediments of river basins and groundwater, slowing down of underground flow due to the regulation of the river network, regional development of flooding, presence of landscapes contaminated with radionuclides, and the growth of global climate change. All above as well as the ongoing war in the territory of Ukraine affect the conditions of the formation of the hydro-chemical regime and contribute to the changes in the quantitative and qualitative water indicators in the Dnipro River basin and the Dnipro reservoirs, as the main sources of water supply for Ukraine. The research determined the changes in the hydro-chemical regime of the surface water of the Dnipro reservoirs during 2016–2022 to specify the impact of climate change and anthropogenic factors on the drinking water supply. The dynamics of changes were analyzed for individual qualitative indicators of the surface water of the Dnipro reservoirs in the cold (January) and warm (July) months of the year. It was proven that the accumulation of flood water affects the mineralization of the Dnipro reservoirs along their longitudinal axis, and the mineralization rate and the content of the main ions are significantly affected by the water content of the year. It was established that, in the Dnipro reservoirs, the lower limit of mineralization relative to natural conditions increased by 55%, and the upper limit decreased by 30%. It was determined that despite the seasonal changes in the concentration of ions in the water of the Dnipro reservoirs, their ratio for each reservoir remains practically constant and only sometimes changes in the case of a shift in the carbonate balance and in the confluence of more mineralized waters, which increase the content of* Mg^{2}, Na^{+}, K^{+}, *and* SO_4^{2-}. *The predominant water cation is* Ca^{2+}, *the anion is* HCO_3^{-}, *and the absolute and relative content of other ions is much smaller. The metamorphism of the water of the Dnipro reservoirs changed the ratio of ion concentrations, namely the relative amount of* SO_4^{2-}, Cl^{-}, Na^{+}, *and* K^{+} *ions increased. The obtained results of changes in the quality indicators of surface water in the Dnipro reservoirs have proved the dependence of the formation of the hydro-chemical regime of the reservoirs on the impact of climate change, economic activity, and the consequences of military actions.*
Keywords: *water resources, reservoir, Dnipro, river basin, water quality*

Relevance of research. Global climate change, which is manifesting in a change in the amount of atmospheric precipitation, an increase in the amount of evaporation due to global warming, an increase in anthropogenic load, and unbalanced water use affect the hydrochemical composition of the Dnipro reservoirs water.

Based on hydro-ecological zoning, where hydrogeological structures with dynamic parameters are decisive, hydrochemical pollution of catchment landscapes, bottom sediments of river basins and groundwater, slowing down of underground flow due to the river network regulation, regional development of flooding, presence of radionuclide-contaminated landscapes, and the increasing effect of global climate change become very important, as all these contribute to the change in the conditions of the formation of the hydrochemical regime, which in its turn leads to a change in the quantitative and qualitative characteristics of water the Dnipro River basin.

Russia's full-scale war in Ukraine, starting in February 2022, directly affected the quality of the country's water resources: water intake facilities, water supply, and drainage treatment facilities, water supply networks were destroyed, dams were blown up and water was supplied to Crimea without complying with regulatory standards. The hostilities harmed the water quality of the Dnipro River and Dnipro reservoirs, as the main sources of Ukraine's water supply. Therefore, an urgent task is to identify a mechanism of changes in the hydrochemical composition of the Dnipro water, primarily the water of the Dnipro reservoirs to characterize the state of water resources, which will enable to specify the possibility of using the water of the reservoirs as a source of drinking water supply.

Analysis of recent research and publications. The formation of water quality of the Dnipro River is changing significantly as a result of the impact of climate change, ongoing hostilities, and the economic activity in the territory of Ukraine.

Back in the 50s of the 20th century O.O. Alekin [1], the author of "Fundamentals of Hydrochemistry" revealed the general foundations of studying the chemical composition of river water in the territory of the former USSR, the unity of chemical processes occurring in all natural waters, the systemic conditioning of a complex of natural and anthropogenic factors. When the scientific school of hydrochemical research was developed, the process of hydrochemical regime formation and hydrological characteristics were described. The study of the total anthropogenic impact on the chemical composition of the water of the Dnipro River basin and its reservoirs as well as the differentiated assessment of the impact was given attention to [2–5]. Research on changes in the water quality of the Dnipro River basin is thoroughly covered in the works of V.I. Vyshnevsky, hydrological and hydrochemical characteristics – in the works of O.I. Denysova, processes of formation of the chemical composition of surface waters of reservoirs – in the works of P.M. Lynnyk [6–12]. N.M. Osadcha, V.D. Romanenko, V.M. Timchenko, V.K. Khilchevskyi, et al. developed research on the hydrochemistry of regional basin systems, among which the main place was occupied by both the Dnipro basin as a whole and the basins of some of its tributaries [13–16], however, in the last decade there was a need to update the available data.

The requirements of the EU Water Framework Directive 2000/60/EC in the Dnipro River Basin Management Plan (within Ukraine) [17] provide for ensuring a good ecological and chemical state for surface water bodies and performing an analysis of the hydro-chemical regime of reservoirs to implement actions aimed at improving the hydro-ecological situation in the basin, avoiding degradation of regenerative and cleaning capacity of water ecosystems, and establishing the restrictions on water use [18].

The purpose of the research is to specify the mechanism of changes in the hydro-chemical composition of water in the Dnipro reservoirs to characterize the state of water as a source of drinking water supply.

Research materials and methods. Empirical and theoretical methods of scientific research were used, namely collection and analysis of quantitative and qualitative indicators of surface water of the Dnipro reservoirs. The conditions of water use from the Dnipro reservoirs are defined by DSTU4808:2012 "Sources of centralized drinking water supply. Hygienic and ecological requirements for water quality and water withdrawal rules", as well as by the State sanitary standards and rules "Safety indicators and separate indicators of the quality of drinking water in conditions of martial law and emergencies of a different nature" (DSanPiN No. 683) developed for martial law conditions [19; 20].

The change in some quality characteristics of the surface water of the Dnipro reservoirs in 2016–2022 was determined at 6 observation posts, which are characterized by the largest range of data: 1 post – Kyiv Reservoir (Dnipro River, 897 km, Vyshhorod town, tail-water of the Kyiv HPP, Kyiv city potable water intake); 2 post – Kaniv reservoir (Dnipro River, 854.5 km, 500 m downstream the Bortnytska aeration station); 3 post – Kremenchug Reservoir (Dnipro River, 678 km, Sokyrne village, potable water intake of Cherkasy city); 4 post – Kamyanske Reservoir (Dnipro River, 550 km, Horishni Plavni town, town potable water intake); Post 5 – Dnipro Reservoir (Dnipro River, 328 km, Zaporizhzhia city, headwater of the Dnipro HPP, city potable water intake); Post 6 – Kakhovka Reservoir (Dnipro River, 106 km, Lyubymivka village, MPS of the Kakhovka Canal).

Surface water samples were taken by the monitoring service of the State Water Resources Agency of Ukraine and the Central Geophysical Observatory named after Borys Sreznevskyi, the analysis was carried out by an accredited laboratory by general sanitary chemical parameters: the content of ammonium ions (NH_4^+), mg/dm³, hydrogen indicator, units of pH, water hardness, mg-eq/dm³, total iron (Fe_{tot}), mg/dm³, dissolved oxygen, mgO_2/dm^3, color, degree, total alkalinity, mg-eq/dm³, the content of magnesium ions (Mg^{2+}), mg/dm³, nitrate- (NO_3^-) and nitrite- (NO_2^-) ions, mg/dm³, sulfate ions (SO_4^{2-}), mg/dm³, dry residue (dissolved substances), mg/dm³, phosphate ions (PO_4^{3-}), mg/dm³, chemical oxygen demand (COD), mgO_2/dm^3, chloride ions (Cl^-), mg/dm³.

Research results and their discussion. The hydrochemical regime of the reservoir is determined by the following factors: intensity of water exchange; the nature of the soils and vegetation in the areas of flooding and sub-flooding of the catchment area; mode of filling and drawdown of the reservoir; amplitude and intensity of water level fluctuations. An important role in the formation of the hydrochemical regime is also played by: the geographical location of the reservoir, its morphological structure, position in the cascade, atmospheric precipitation, anthropogenic factors (absorption and discharge of water, operation of hydroelectric power stations, water transport, etc.), intrareservoir hydrological and biogeochemical processes.

From the moment the reservoirs are filled, the hydrochemical composition of the Dnipro River water gradually transforms into a lake water type. This transformation is the more pronounced, the slower the water exchange is in the reservoir. Decomposition of the remains of flooded vegetation and disturbing bottom sediments during the operation of reservoirs affect the quality of water entering the upper basin of the reservoir. In reservoirs, in contrast to the river, during their lifetime, shallow, sometimes stagnant zones appeared, in which the oxygen regime deteriorates and organic substances accumulate.

Following DSTU4808:2012, surface sources with water quality of 1–3 classes are used for centralized drinking water supply, the assessment of which is obtained by hygienic and ecological criteria [19]. Within the cascade of the reservoirs, the quality of surface water by the specified indicators varies from 1 to 4 class (class 4 is observed by the content of NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, COD in separate periods), and the highest values of the average annual water quality indicators are observed by: NH_4^+ (2.775 mg/dm³), NO_3^- (18.15 mg/dm³) and NO_2^- (0.427 mg/dm³) in Kaniv reservoir, hydrogen index (8.183–8.471 units of pH), in Kyiv reservoir and (8.185–8.313 units of pH) in Kakhovka reservoir, Fe_{tot} (0.094–0.574 mg/dm³) in Kremenchuk reservoir, dissolved oxygen (6.884 mgO_2/dm³) in Kamianske reservoir, PO_4^{3-} (0.969 mg/dm³) in Kyiv reservoir, COD (50.275 mgO_2/dm³) in Kaniv reservoir (Fig. 1).

Within the cascade of reservoirs, the highest values of average seasonal water quality indicators in the cold period are observed by dissolved oxygen (11.075 mgO_2/dm³) in Kyiv reservoir, the content of Ca^{2+} (69.625 mg/dm³), Mg^{2+} (22.55 mg/dm³), suspended substances (8.75 mg/dm³), NH_4^+ (0.945 mg/dm³), PO_4^{3-} (0.635 mg/dm³), Fe_{tot} (0.29 mg/dm³), SO_4^{2-} (69.8 mg/dm³), Cl^- (35.675 mg/dm³) in Kaniv reservoir, color (42 degrees) and COD (31.43 mgO_2/dm³) in Kamianske reservoir, temperature (2.5 °C) in Kakhovka reservoir.

In the summer months, the highest average seasonal indicators are observed by temperature, the content of Ca^{2+} (49.85 mg/dm³), NH_4^+

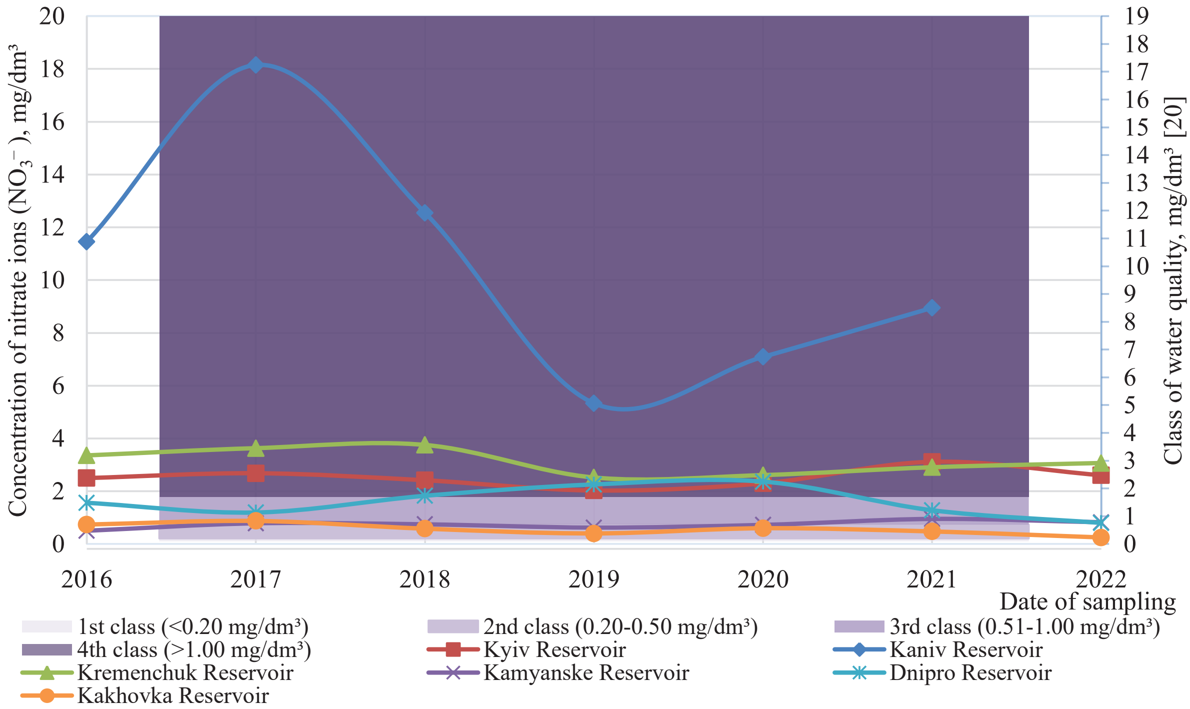
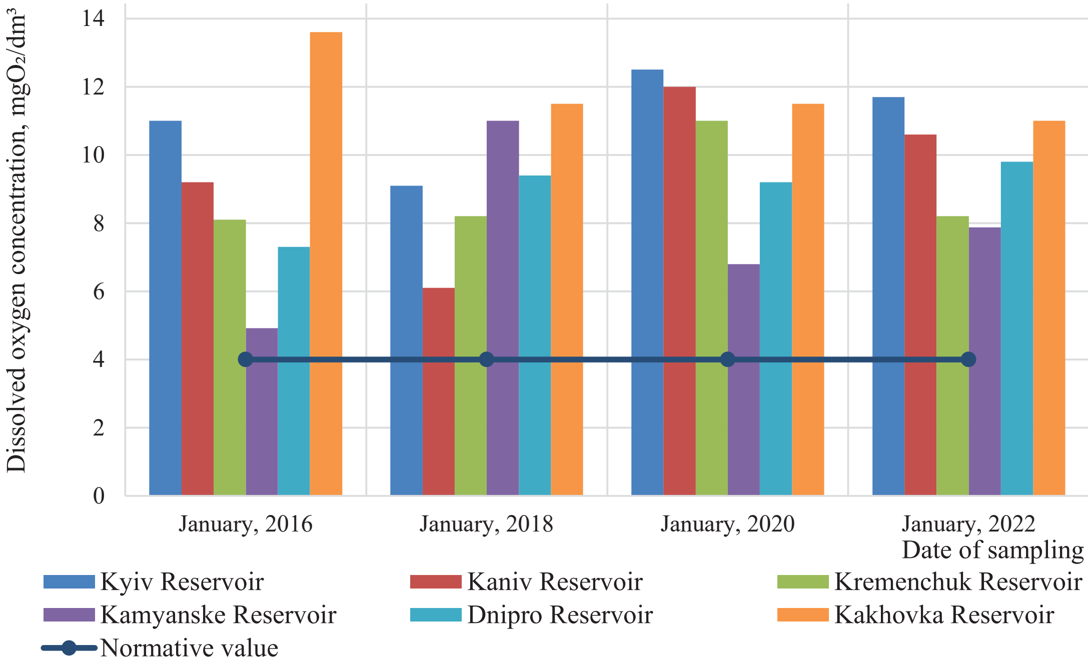


Fig. 1. Average annual change in the content of nitrate, mg/dm³, in the surface water of the Dnipro reservoirs in 2016–2022 (samples were taken from the Kakhovka reservoir in 2016–2021)

(0.636 mg/dm³), Fe_{tot} (0.408 mg/dm³) in Kaniv reservoir, PO_4^{3-} (0.473 mg/dm³) in Kremenchuk reservoir, COD (35.978 mgO_2/dm³), color (51.75 degrees) in Kamianske reservoir, Mg^{2+} (15.85 mg/dm³), dissolved oxygen (8.65 mgO_2/dm³), Cl^- (35.45 mg/dm³) in Dnipro reservoir, SO_4^{2-} (52.6 mg/dm³) in Kakhovka reservoir.

Comparison of average monthly data with normative ones allowed to plot changes in the content of dissolved oxygen, mgO_2/dm³, Fe_{tot}, mg/dm³ and COD, mgO_2/dm³ (Figs. 2–4) [21–23].



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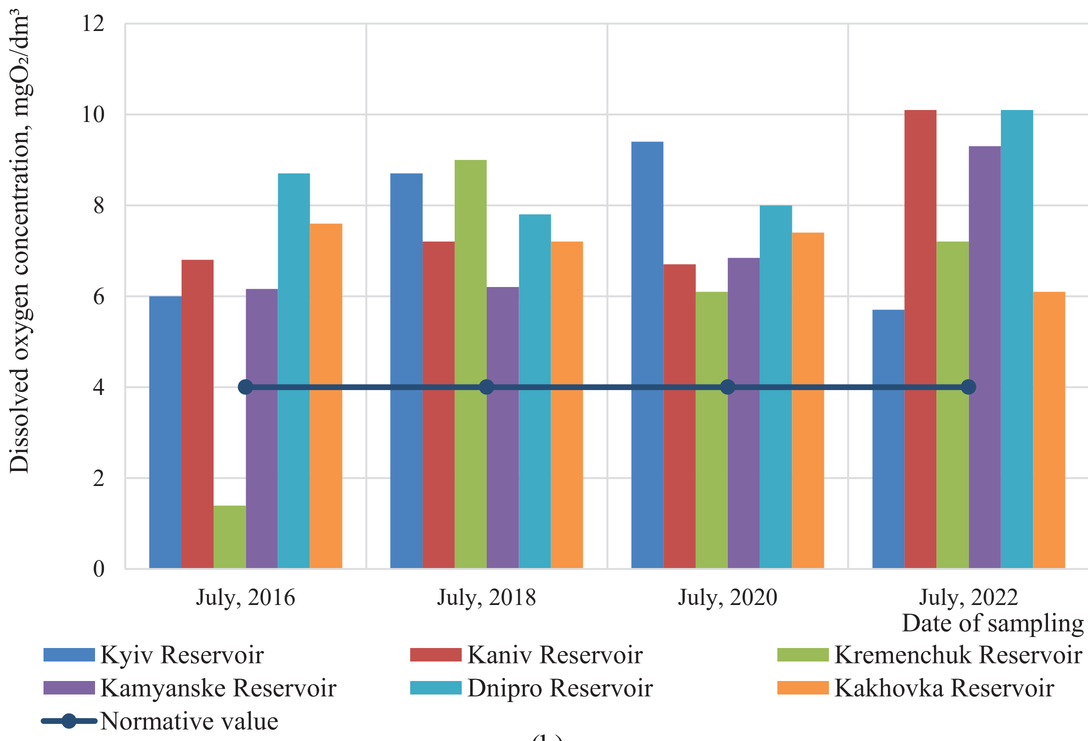
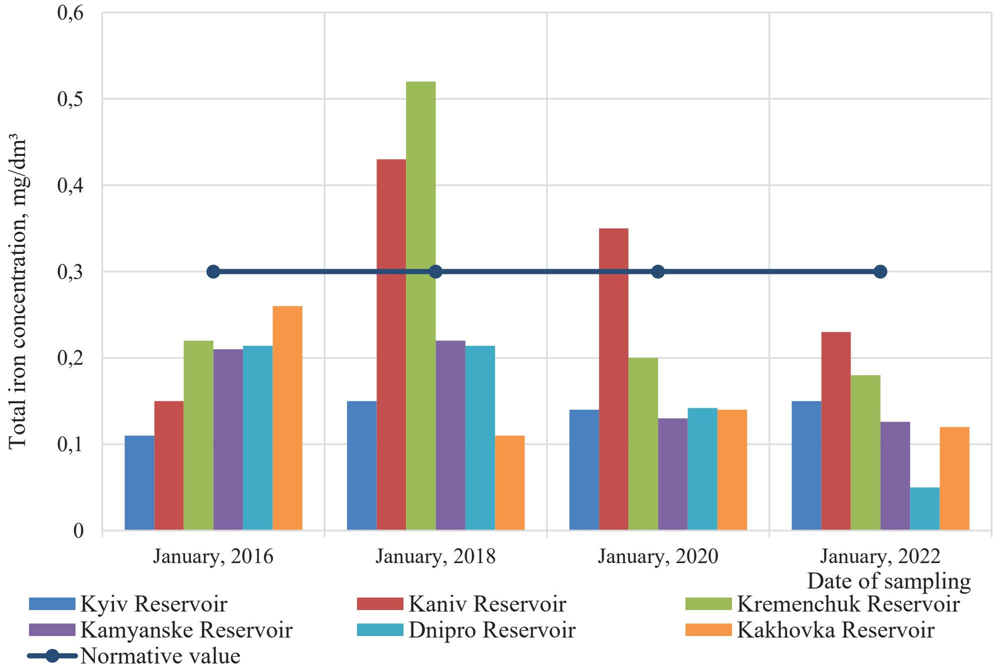
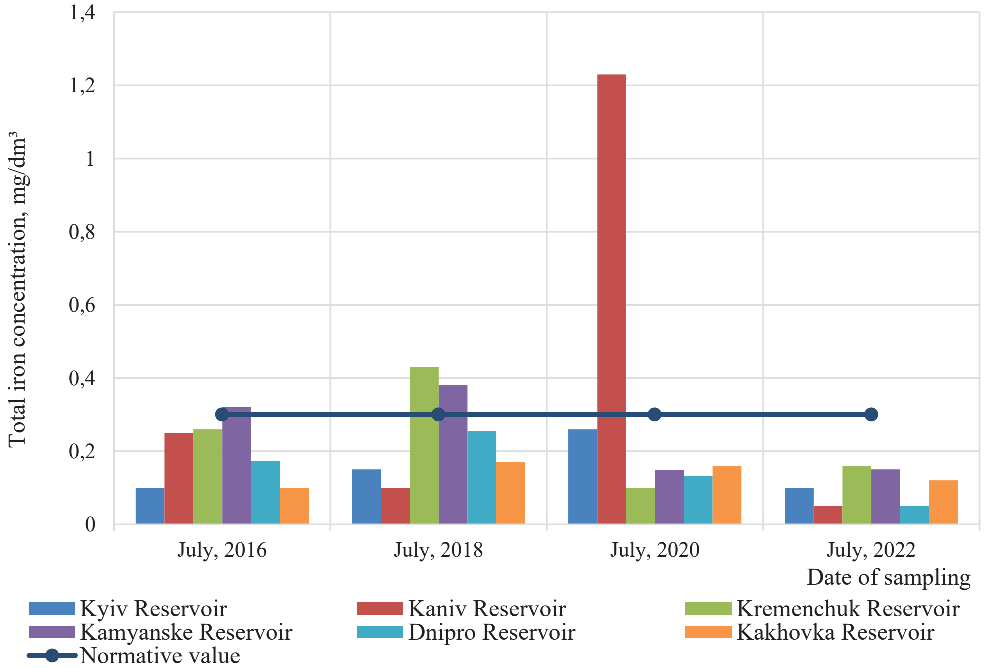


(b)

Fig. 2. Changes in the content of dissolved oxygen, mgO_2/dm³, in the water of the Dnipro reservoirs in the cold (a) and warm (b) months of 2016–2022 (samples were collected in the warm months from the Kakhovka reservoir in 2016–2021)



(a)

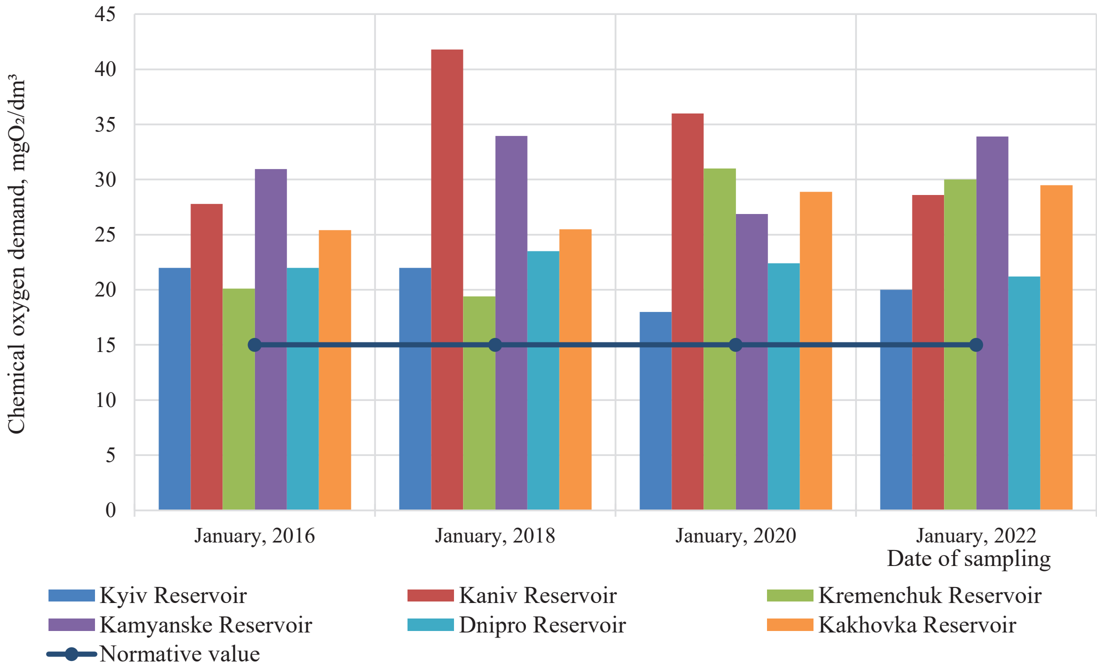


(b)

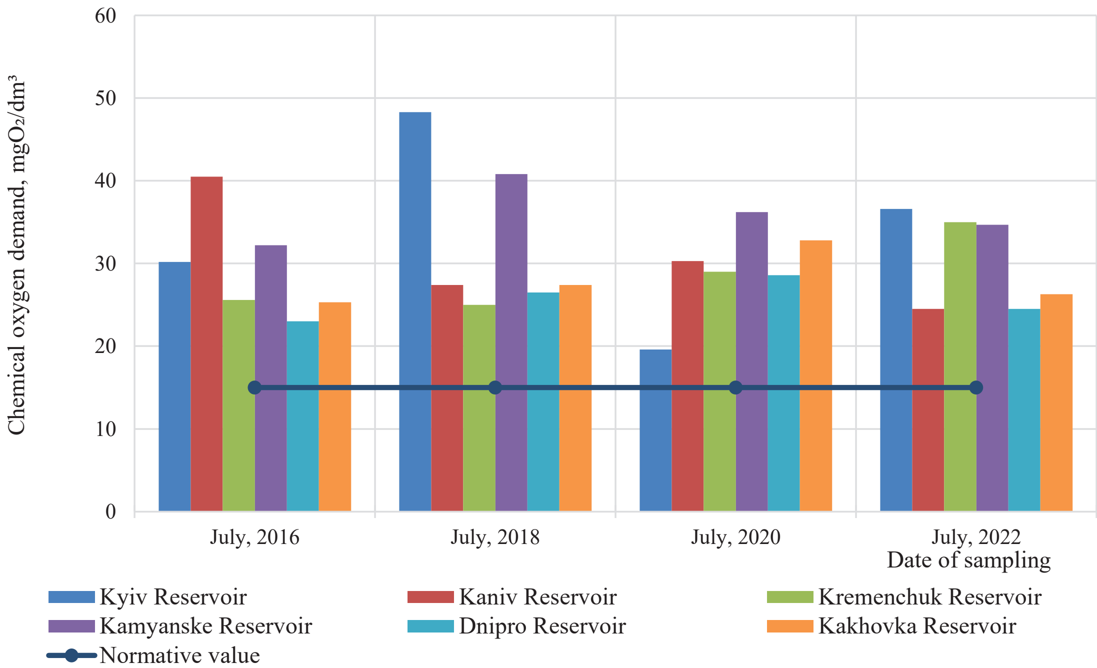
Fig. 3. Changes in the content of total iron, mg/dm³, in the water of the Dnipro reservoirs in the cold (a) and warm (b) months of 2016–2022 (samples were collected in the warm months from the Kakhovka reservoir in 2016–2021)

It is known that the construction of reservoirs leads to a seasonal or multi-year redistribution of river runoff. Changes in the dynamics of mineralization and the concentration of the basic ions occur along with the redistribution of river runoff.

As a result of the accumulation of low-mineralized floodwater in the reservoirs and their mixing with more mineralized river water arriving in subsequent seasons, the annual amplitude of fluctuations in mineralization and the concentration of individual ions decrease. The accumulation of flood water leads to a change in the mineralization of reservoirs along their longitudinal axis. The surface and bottom water



(a)



(b)

Fig. 4. Changes in COD, mgO_2/dm^3, in the water of the Dnipro reservoirs in the cold (a) and warm (b) months of 2016–2022 (samples were collected in the warm months from the Kakhovka reservoir in 2016–2021)

layers of the Dnipro reservoirs usually have the same mineralization. The level of mineralization and the content of basic ions is significantly affected by the water content of the year. In medium-water and high-water years, the water mineralization of the Dnipro reservoirs is lower than in low-water years [21]. Thus, in the Dnipro reservoirs, the lower limit of mineralization relative to natural conditions increased by 55 %, and the upper limit decreased by 30 %. Currently, the upper limit of mineralization down the Dnipro cascade increases from 400 mg/dm³ in the Kyiv reservoir to 460 mg/dm³ in the Dnipro reservoir (Table 1).

1. Range of the concentration of basic ions and water mineralization of the Dnipro reservoirs in 1985–2021, mg/dm^3 [24]

Reservoir	Ca^{2+}	Mg^{2+}	Na^+ i K^+	HCO_3^-	CO3$^-$	SO_4^{2-}	Cl^-	Sum of ions
Kyiv	17.0–70.0	5.0–27.0	5.0–25.0	106.0–246.0	0.0–15.0	11.0–89.0	1.0–29.0	196.0–394.0
Kaniv	31.0–79.0	5.0–35.0	9.0–59.0	106.0–217.0	0.0–27.0	19.0–112.0	11.0–59.0	198.0–398.0
Kremenchug	29.0–70.0	5.0–30.0	3.0–40.0	109.0–220.0	0.0–28.0	17.0–54.0	11.0–41.0	216.0–420.0
Kamyanske	29.0–59.0	5.0–17.0	9.0–35.0	88.0–219.0	0.0–12.0	20.0–54.0	17.0–31.0	171.0–393.0
Dnipro	33.0–62.0	5.0–22.0	1.0–43.0	131.0–219.0	0.0–21.0	26.0–86.0	21.0–44.0	207.0–460.0
Kakhovka	31.0–55.0	5.0–22.0	7.0–59.0	73.0–217.0	0.0–25.0	33.0–94.0	21.0–54.0	210.0–450.0

The predominant cation in the water in the Dnipro reservoirs is Ca^{2+}, and the anion is carbonate (HCO_3^-). The absolute and relative content of other ions is much lower. Despite the seasonal changes in the concentration of ions in the water of reservoirs, their ratio for each reservoir remains practically constant and only sometimes changes in the case of a shift in the carbonate balance and in the confluence of more mineralized water, which increases the content of Mg^{2+}, sodium (Na^+), potassium (K^+) and SO_4^{2-}. The metamorphism of the water of the Dnipro reservoirs changed the ratio of ion concentrations, namely the relative amount of SO_4^{2-}, Cl^-, Na^+, and K^+ ions increased.

The analysis of the obtained results proved that the position of the individual reservoir in the cascade and the features of its hydrological regime largely determine the seasonal and multi-year dynamics of water mineralization and the content of the basic ions, which change significantly along with the seasonal redistribution of the river runoff [21; 24].

Today, the surface water of the Dnipro reservoirs, as a source of water supply, is characterized by long-term and seasonal fluctuations in the chemical composition and physical properties, water pollution degree, etc., which occur under the effect of climatic change, economic activity and ongoing hostilities on some adjacent territories to the Dnipro reservoirs cascade.

Improper water use and agricultural pollution of water bodies against the background of the increase in average annual temperature led to the scarcity of water capacity of water ecosystems in the Dnipro basin and its reservoirs.

The water of the Dnipro River, as the main source of drinking water supply, was especially acutely affected by the war unleashed by Russia, namely the uncontrolled discharge of water at the Kakhovka HPP. The volume of water discharge from the Kakhovka Reservoir at the moment exceeds the filling volume; there is irrational use of water from the reservoir, which causes the need to provide alternative technological solutions for the uninterrupted operation of water intakes in the Kherson, Zaporizhzhia, and Dnipropetrovsk regions. Toxins that appear after all aquaculture in the Kakhovka Reservoir dies, which is already happening, will begin to spread and threaten other countries.

Conclusions. The conducted research on the hydro-chemical regime of the surface water of the Dnipro reservoirs for 2016–2022 showed:

– the ionic composition is dominated by hydro carbonate ions, there is a decrease in the number of calcium ions due to an increase in the concentrations of magnesium and sodium;

– there are above-limit values of certain quality characteristics of the surface water of the Dnipro reservoirs in the cold (January) and warm (July) months of the year compared to the normative ones (by the content of NH_4^+ twice, COD in three times and by color twice) [19]. In certain periods, the quality of the surface water of the Dnipro reservoirs corresponds to 4 class 4 by the content of NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, and COD [20].

The obtained data proved the need to improve water treatment technologies with the use of biological methods of water treatment, the use of membrane technologies, etc.

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АНАЛІЗ ГІДРОХІМІЧНОГО РЕЖИМУ ДНІПРОВСЬКИХ ВОДОСХОВИЩ

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Анотація. *Розглянуто комплекс питань, а саме: гідрохімічне забруднення водозбірних ландшафтів, донних відкладів річкових басейнів та ґрунтових вод, уповільнення підземного стоку внаслідок зарегулювання річкової мережі, регіональний розвиток підтоплення, наявність забруднених радіонуклідами ландшафтів, зростання глобальних змін клімату, за яким зміна умов формування гідрохімічного режиму та війна на території України сприяють зміні кількісних та якісних показників водних ресурсів у басейні річки Дніпро та дніпровських водосховищ, як основного джерела водопостачання України. Дослідженнями визначено зміни гідрохімічного режиму поверхневих вод дніпровських водосховищ упродовж 2016–2022 років для встановлення впливу кліматичних змін та антропогенних чинників на питне водопостачання. Проаналізовано динаміку змін окремих якісних показників поверхневих вод дніпровських водосховищ у холодні (січень) та теплі (липень) місяці року. Засвідчено, що накопичення повеневих вод продовжує призводити до зміни мінералізації дніпровських водосховищ по їх повздовжній осі, а на її рівень та вміст головних іонів значно впливає водність року. Встановлено, що, на дніпровських водосховищах нижня межа мінералізації відносно природних умов підвищилась на 55 %, а верхня – знизилась на 30 %. Визначено, що незважаючи на сезонні зміни концентрацій іонів у воді дніпровських водосховищ, їх співвідношення для кожного водосховища залишається практично сталим і лише інколи змінюється в разі зміщення карбонатної рівноваги та в місцях впадіння більш мінералізованих вод, які збільшують вміст* Mg^{2}, Na^{+}, K^{+} *і* SO_4^{2-}. *Переважним катіоном води є* Ca^{2+}, *аніоном –* HCO_3^{-}, *абсолютний і відносний вміст інших іонів значно менший. Метаморфізація вод дніпровських водосховищ змінила співвідношення концентрацій іонів: підвищилась відносна кількість іонів* SO_4^{2-}, Cl^{-}, Na^{+}, K^{+}. *Отримані результати зміни якісних показників поверхневих водних ресурсів у дніпровських водосховищах підтвердили залежність формування гідрохімічного режиму водосховищ від впливу кліматичних змін, господарської діяльності та наслідків військових дій.*

Ключові слова: *водні ресурси, водосховище, Дніпро, річковий басейн, якість води*