Journal of Chemistry and Technologies, 2023, *31*(4), 907-916

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua

UDC 502.3.7.504:543.2

ASSESSMENT OF THE QUALITY AND ECOLOGICAL STATUS OF THE SAKSAGAN RIVER IN THE CONTEXT OF DRINKING WATER AND FISHERY PURPOSES

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Received 27 November 2023; accepted 3 January 2023; available online 31 January 2024

Abstract

The problems of pollution of small rivers of Ukraine and the search for ways to solve them were and remain quite relevant. In connection with the intensive exploitation of Kryvbas iron ore deposits and significant quarry and mine drainage, specific hydrochemical conditions have arisen in this region. It is also important that as of March 1, 2020, the Cabinet of Ministers of Ukraine once again allowed mining enterprises of the Kryvyi Rih Basin to discharge return water from tailings in the Ingulets River and Saksagan River "to prevent an emergency situation at hydrotechnical facilities". The work investigated and analyzed the current physico-chemical state of the Saksagan River with the help of own monitoring studies and online state monitoring data, provided an assessment of the state of the river as a source of economic, drinking and fishery use. The research was conducted in the summer of 2023, 9 monitoring points on the Saksagan River of the Kryvorizka district, Dnipropetrovsk region were selected for chemical analysis of water, previously the points were grouped into 3 groups of three according to territorial characteristics. According to the research results, it was found that the water in all experimental areas does not meet the normative indicators of water quality for fishery needs in terms of sulfates, chlorides and general mineralization. With regard to sulfates, the water does not meet the fishery standards at all moritoring points, and only points 1 and 9 meet the sanitary stan-dards. The water does not meet the normative indicators of water quality for drinking, household and other needs in terms of chlorides and general mineralization, and at almost all points in terms of sulfates (points No. 2, 4–8).
Key words: water quality assessment, Saksagan River, ecological condition, small rivers, hydrochemical parameters.

ОЦІНКА ЯКОСТІ ТА ЕКОЛОГІЧНИЦЙ СТАН РІЧКИ САКСАГАНЬ У КОНТЕКСТІ ГОСПОДАРСЬКО-ПИТНОГО ТА РИБОГОСПОДАРСЬКОГО ПРИЗНАЧЕННЯ

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Анотація

Проблеми забруднення малих річок України та пошук шляхів їх вирішення були та залишаються досить актуальними. У зв'язку з інтенсивною експлуатацією залізорудних родовищ Кривбасу та значним кар'єрним і шахтним водовідливом у даному регіоні виникли специфічні гідрохімічні умови. Також важливим є те, що з 1 березня 2020 року Кабінет Міністрів України знову дозволив гірничорудним підприємствам Криворізького басейну скидати зворотні води з хвостосховищ у р. Інгулець і р. Саксагань «для запобігання виникнення аварійної ситуації на гідротехнічних спорудах». У роботі досліджено та проаналізовано сучасний фізико-хімічний стан річки Саксагань за допомогою власних моніторингових досліджень та онлайн даних державного моніторингу, надано оцінку стану річки, як джерела господарсько-питного і рибогосподарського використання. Дослідження проводились влітку 2023 року, для хімічного аналізу води було обрано 9 моніторингових точок на р. Саксагань Криворізького району, Дніпропетровської області, попередньо точки були скомпановані по три точки у 3 групи за теріторіальною ознакою. За результатами досліджень виявлено, що вода на усіх дослідних ділянках не відповідає нормативним показникам якості води для рибогосподарських потреб за значенням сульфатів, хлоридів та загальної мінералізації. Стосовно сульфатів, вода не відповідає рибогосподарським нормам на всіх моріторінгових точках, і лише точки 1 та 9 відповідають санітарним нормам. Вода не відповідає нормативним показникам якості води для питних, господарсько-побутових та інших потреб за показниками хлоридів та загальної мінералізації, та майже на всіх точках за показниками сульфатів (точки №№ 2, 4–8).
Ключові слова: оцінка якості води, річка Саксагань, екологічний стан, малі річки, гідрохімічні показники.

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doi: 10.15421/jchemtech.v31i4.291632

Introduction

Despite the military actions in our country, Ukraine, in order to maintain the association agreement between Ukraine and the EU, implements the provisions of Directive 2000/60/EU "On establishing the framework of the community's activities in the field of water policy" [1]. According to Directive 2000/60/EC, Member States take the necessary measures to preserve and improve the status of the aquatic environment. Achieving this goal is associated with good water quality, which is ensured by systematic monitoring of the characteristics of the river basin and the impact of human activity on them, as well as economic analysis of water use. Accordingly, Member States must submit summary reports on the analysis of the state of the water basin and monitoring programs, which must be prescribed in the river basin management plan. According to the State Agency of Water Resources of Ukraine, European approaches to water monitoring have been introduced in Ukraine. State monitoring of surface waters is carried out according to the basin principle and provides for a six-year cycle of monitoring and classification of water status according to 5 classes of ecological status and 2 classes of chemical status. It consists of procedures for diagnostic, operational and research monitoring of surface water bodies. In accordance with the "Procedure for State Water Monitoring" (Resolution of the Cabinet of Ministers of Ukraine dated September 19, 2018 No. 758, which entered into force on January 1, 2019) [2], monitoring must be carried out for each water body separately, the comparison of rivers will not take place between themselves or with a mountain river, where the water is very clean, but the same river basin will be compared with itself in different observation periods, in dynamics. According to this system of surface, underground and sea water monitoring, the number of water monitoring points is expected to increase from hundreds to several thousand at clearly defined points. But such measures will hardly cover small rivers, which causes a certain problem, since the number of pollutants that enter with the water of small rivers make up most of the pollution of large reservoirs [3; 4].

Currently, small rivers of Ukraine suffer from constant anthropogenic pollution, they are more sensitive to pollution than large ones. Small rivers form resources, hydrochemical regime, water quality of medium and large rivers, create natural landscapes in large areas. Accordingly, the state of small rivers is an indicator of the state of the entire river network of each country. That is why it is important to carry out special comprehensive measures to protect small rivers from water loss, pollution and drying up and direct them to eliminate the negative impact of anthropogenic factors.

The main polluters of water in rivers are industrial, municipal and agricultural discharges [5–7]. Despite a significant number of legislative and regulatory acts on their protection, the condition of small rivers is defined as critical. Small rivers are polluted by suspended particles, chemicals and household waste, especially within rural settlements [8; 9].

In most of the small rivers of the Dnipropetrovsk region, the water balance is disturbed, the flow is sharply reduced, they gradually silt up and dry up. The water quality of small rivers deteriorates every year: the water is not suitable not only for drinking water supply, but also for economic needs. Up to 40% of polluted waters from the total volume of these waters in the region are discharged annually into small rivers. A large volumes of soil washed into small rivers as a result of the destruction of coastal strips, placement of economic facilities, livestock farms in water protection zones, secondary pollution with heavy metals, etc. are added to this [10–13].

It is known that since the beginning of the industrial development of iron ore deposits in the Kryvyi Rih district, the nature and intensity of the entry of chemical elements into the hydrosphere has changed significantly, which is due to the man-made movement of large masses of rock with their subsequent redistribution in dumps, hydraulic dumps and tailings, water discharge from quarries and mines, discharges of industrial waste water from beneficiation factories and tailings storage facilities, surface washing from the territory of mining dumps, etc. Almost all rivers of the region are classified as moderately polluted by ecological criteria. The Saksagan River is the main watercourse in this area. The intensive exploitation of iron ore deposits in Kryvbas and significant quarry and mine runoff led to the emergence of specific hydrochemical conditions in this region [14; 15].

The purpose of the work is to study the current physical and chemical state of the Saksagan River with the help of additional monitoring studies and online state monitoring data and to provide an analysis of the ecological state of the river in the context of economic, drinking and fishing use. Providing recommendations on the rational use of natural resources and environmental safety of the area.

The urgency of the work is due to the fact that from March 1, 2020, the Cabinet of Ministers of Ukraine once again allowed the mining enterprises of the Kryvyi Rih Basin to discharge return water from the tailings reservoirs in the Ingulets River and the Saksagan River "to prevent an emergency situation at hydrotechnical structures." Such actions have a significant impact on the quality of water in these rivers precisely because the Kryvyi Rih iron ore basin is located in the basins of the Saksagan and Ingulets rivers.

In total, Kryvbas mining and beneficiation plants (GZK) and preserved mines pump up to the surface up to approximately 40 million m^3 of underground water, of which 16–17 million m^3 – highly mineralized water. The maximum possible amount of underground water, about 28–30 million m^3 per year, are used in the turnover cycles of mining enterprises. Part of the excess return water is temporarily accumulated in storage ponds, which are then discharged into the Ingulets and Saksagan rivers in order to avoid flooding of mines and quarries, their shutdown and to prevent man-made disasters. Also, salted waters from quarries and mines, surface filtration waters, domestic and domestically treated effluents, effluents from treatment facilities are pumped to tailings storage facilities, which are the main accumulator of waste water and occupy a total area of more than 76 km^2. The average water mineralization in the tailings reservoirs reaches 5–8 g/dm^3, and its total volume is 200 million tons. Annual losses from filtration into the soil from tailings are approximately 6–8 million m^3, which causes flooding, salinization of fertile lands and pollution of natural underground and surface water bodies [16].

Priority chemical substances that significantly affect the flora and fauna of rivers are those that determine the mineralization of water. The number of chlorides in tailings reaches 16.5 g/l, sulfates – up to 1.5 g/l, and the dry residue of mineral substances in some cases exceeds 30 g/l. The chemical composition of filtered water practically does not differ from tailings water. Return waters of tailings contain a significant amount of nitrates (23–30 mg/l), oil products are also present (up to 1.0–1.5 mg/l) [17].

Materials and methods

The work examines the river Saksagan, which is located in Ukraine, in the southeastern part of the Dnipro upland, within the Kryvorizky district of the Dnipropetrovsk region. The left tributary of Ingulets (Dnieper basin). It flows mainly to the southwest (in places to the west). It flows into the Ingulets in the southwestern part of the city of Kryvyi Rih. The current speed is insignificant. The river is fed mainly by meltwater, as well as waste water from enterprises and fresh washing water from the Makortivske reservoir. Rainwater and groundwater play a secondary role [17]. Saksagan belongs to the category of small rivers. It is also simultaneously a tributary of the Dnipro of the 2nd order. The natural regime of the river has been greatly changed by the regulatory influence of dams, the discharge of mine and industrial waters, as well as the withdrawal of water for technical needs. In order to enable mining operations for the extraction of minerals in the area «Saksagan» – the Chornogorka the river was transferred to an underground collector (the Saksagan derivation tunnel). For quite a long time, the river has been used for economic needs, industrial water supply, irrigation and fish farming.

At present, the physico-chemical parameters of the water of the Saksagan River require constant monitoring, as natural water does not meet sanitary requirements under the influence of return water and tailings from the mining enterprises of Kryvbas. It was the extremely sharp deterioration of water quality that led to the need for a detailed analysis of the physico-chemical composition of the water of the Saksagan River, which is discharged by the mining enterprises of SJSC "Shakhta "Ternivska", which is part of PJSC "KRYVORIZKY IRON ORE PLANT". According to the "Report on the management of PJSC KRYVBASZALIZRUDKOM" for 2020, it is the "Ternivska" and "Oktyabrska" mines that discharge treated wastewater (stormwater) into the Saksagan River. The actual consumption (discharge volume) of return (wastewater) water at the Ternivska mine (release No. 1) in 2019 – 0.730 thousand m^3/year, in 2020 – 0.585 thousand m^3/year, at the Oktyabrska mine (release No. 2) in 2019 – 0.309 thousand m^3/year, in 2020 – 0.393 thousand m^3/year. In order to control the established norms of the maximum allowable discharge of pollutants that enter the water body together with return (rain and melt) water, laboratory tests are carried out in accordance with the control procedure in accordance with the standards of the MPCs and the schedule of laboratory control of the quality of return (storm) water, which annually agreed by the Department of Ecology and Natural Resources of the

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Dnipropetrovsk Regional State Administration. But in addition to control of return sewage, it is absolutely necessary to carry out systematic control of the content of pollutants in the Saksagan and Ingulets rivers, not only in the area of discharges, but also upstream and downstream, in places of recreational areas and water intakes. According to the new "Order..." there are now two state monitoring points on the Saksagan River in the Makroty Village, Makortivske reservoir [18] and Serhiivka Village [19]. is not enough to determine the full picture of pollution and water quality in the river and its impact on the Ingulets River.

Therefore, for a more complete understanding of the state of the water, 9 monitoring points on the Saksagan River of the Kryvorizky District of the Dnipropetrovsk Region were selected (Table 1), from which water samples were taken for chemical water analysis. Previously, the points were combined into three groups in three groups based on territorial characteristics. The first group (points 1–3) is located in the village of Sergiyivka (table 1), which is located on the border of Kryvorizky and Sofiyivsky districts of Dnipropetrovsk region. This group of points is located in the upper part of the Kryvyi Rih District reservoir and can be considered the starting point for water quality. The village of Serhiivka is the largest in this area by the number of inhabitants, located on the banks of the Saksagan River. The second group (points 7–9) is selected in the area of the Ternivska mine, where discharges into the river occur and are located downstream of the first group. The third group (points 4-6) is located in the urban part of Kryvyi Rih, this is a group of points located in the lowest part of the reservoir, where water is withdravaled for the city. Water samples were taken in the summer of 2023: near the bridge in the Serhiivka village – point No. 1; Serhiivka village – point No. 2; water station 1, Serhiivka village – point No. 3; entrance portal I of Saksagan tunnel of the Saksagan river (western bank of the Saksagan reservoir) – point No. 4; the entrance portal of the II Saksagan tunnel of the Saksagan river, (left bank of the Saksagan river) – point No. 5; "Dubky" district (bridge) Saksagan river – point No. 6; 500 m above the discharge of return (rain and melt) waters of the Ternivska mine – point No. 7; place of discharge (rain and melt water) of the mine Ternivska – point No. 8; 500 m below the discharge of return (rain and melt) waters of the Ternivska mine – point No. 9. These points can be attributed to operational monitoring, which is carried out for reservoirs where there is a risk of not achieving a good ecological state of the waters, or water is taken every year for drinking and domestic needs of the population. Operational monitoring data are the basis for the development of specific measures in the river basin management plan to improve or maintain the state of water bodies [20].

Sampling of water samples from an open reservoir was carried out by the method of manual sampling in accordance with regulatory documents and state standards SStU ISO 5667-3-2001, SStU ISO 5667-14-2005, SStU 3920-99, SStU 3913-99, SStU 24481 etc.

Ecological assessment of the quality of surface water characteristics was according to Romanenko [21]. During water research, the following indicators were determined: water temperature, hydrogen index (pH), content of dissolved oxygen, carbon dioxide (CO_2), ammonium nitrogen (NH_4^+), nitrate ions (NO_3^-), nitrite ions (NO_2^-), sulfate ions (SO_4^{2-}), chloride ions (Cl^-), iron ions (Fe^{2+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and indicators of general mineralization.

The pH of water was determined using a pH-150MI ionometer with a glass electrode and a silver chloride reference electrode [22]. The content of dissolved oxygen was determined by the iodometric method by Winkler [23]. The carbon dioxide content was determined by titration with sodium hydroxide solution in the presence of the phenolphthalein indicator [24].

Ammonium nitrogen was determined spectrophotometrically with Nessler's reagent [25]. The content of nitrate ions was monitored using a nitrate-selective electrode ELIS-121NO3 on a pH-150MI ionometer (reference electrode – silver chloride electrode). Nitrite ions were determined spectrophotometrically by a color reaction with the Griess reagent [26].

The content of sulfate ions was determined gravimetrically, using a barium chloride solution as a precipitant [27]. The content of chloride ions was determined mercurimetrically in the presence of a mixed indicator (diphenylcarbazone and bromophenol blue), using a solution of mercury (II) nitrate as a titrant [28]. Iron ions were determined spectrophotometrically by coloration with o-phenanthroline [29]. The content of Calcium and Magnesium ions (Ca^{2+} and Mg^{2+}) was determined by complexometric titration with Trilon B solution [30]. According to the method, two titrations are carried out: first, the content of Calcium and Magnesium ions is determined at pH 10, using Eriochrome black as an indicator, and then the content of Calcium ions is determined at pH 12.5–13 (under these condi-tions, Mg^{2+} ions are precipitated in the form of magnesium hydroxide $Mg(OH)_2$) in the presence of the Murexide indicator. The content of Magnesium ions is calculated by the difference between the total content of Calcium and Magnesium ions and the content of calcium ions.

Results and discussion

The analysis of the physico-chemical composition of surface water in different sections of the Saksagan River allows us to assess the quality of surface water according to various indicators at the given monitoring points and to draw conclusions about the quality of water in these sections and the water flowing into the Ingulets River (Table 1).

Table 1

Physical and chemical parameters of the Saksagan River

Indicator	LIH_{dh}	Class of danger	MPC_{dh}, mg/dm^3 [24]	LIH_f	MPC_f, mg/dm^3 [25]	Point №1	Point №2	Point №3	Point №4	Point №5	Point №6	Point №7	Point №8	Point №9
	Drinking, household and other needs standarts			Fishery needs standarts										
Temperature, t °C		-	-	-	28	21.00	21.50	21.30	20.80	21.20	21.20	20.20	21.50	20.50
pH	-	-	6.5–8.5	-	6.5–8.5	6.82	7.67	7.17	7.83	6.89	6.59	8.02	8.00	8.01
Dissolved O_2, mg O_2/dm^3	Should not be less than 4 mg/dm^3 in any period of the year			In the winter (under summer) period - not less than 6 mg/dm^3 (first, higher category); 4 mg/dm^3 (second category). In the summer (open) – on all water bodies should be 6 mg/dm^3		9.65	9.55	9.90	4.03	4.73	1.82	9.82	12.4	10.40
BOD full, **mg O_2/dm^3**	Should not exceed 3 mg O_2/dm^3 at a temperature of 20°C				3				3.8	4.55	2.6	2.3	2.2	2.2
COD (Mn), mg O_2/dm^3	15(drinking and household), 30(econimic)			-	20				30.7	35.5	38.8	31.8	26.8	28.1
Chlorides, mg/dm^3	**org.**	**4**	**350**	**с.-т.**	**300**	**635.23**	**962.47**	**500.48**	**459.09**	**506.27**	**694.17**	**782.70**	**736.90**	**664.00**
Sulfates, mg/dm^3	**org.**	**4**	**500**	**с.-т.**	**100**	**366.32**	**569.65**	**476.22**	**857.15**	**864.56**	**734.94**	**1174.8**	**1000.6**	**478.2**
Nitrite nitrogen, mg N/dm^3	s.t.	2	1.0	tox.	0.08	0.43	0.28	0.34	0.05	0.02	0.16	0.01	0.01	0.01
Nitrate nitrogen, mg N/dm^3	s.t.	3	10.2	s.t.	9.1	2.17	5.27	8.68	11.04	14.52	9.15	3.57	2.33	2.54
Ammonium nitrogen, mg N/dm^3	s.t.	3	2	tox.	0.5	0.25	0.21	0.23	0.60	1.04	0.55	0.42	0.38	0.42
Fe^{2+}, mg/dm^3	org.	3	0.3	tox.	0.1	<0.01	<0.01	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Calcium, mg Ca/dm3				s.t.	180	15.03	18.03	20.04						
Magnesium, mg Mg/dm^3				s.t.	50	42.56	45.50	48.64						
General mineraliza-tion, mg/dm^3			**1000**		**1000**	**1660.41**	**2423.09**	**1714.14**	**2368.3**	**2749.3**	**2770.3**	**2825.0**	**2900.0**	**2990.0**

Note: MPC_{dh} – MPCs for meeting drinking, household and other needs of the population; MPC_f – MPCs for fishery needs; LIH_{dh}, LIHf – limiting indicator of harmfulness respectively for drinking, household and fishery needs; org. – organoleptic; s.t. – sanitary and toxicological; tox. – toxicological; point № 1 – near the bridge in the Serhiivka village; point № 2 – Serhiivka village; point № 3 – water station 1, Serhiivka village; point № 4 – entrance portal I of Saksagan tunnel of the Saksagan river (western bank of the Saksagan reservoir); point № 5 – the entrance portal II of the Saksagan tunnel of the Saksagan river, (left bank of the Saksagan river); point № 6 – "Dubky" district (bridge) Saksagan river; point № 7 – 500 m above the discharge of return (rain and melt) waters of the Ternivska mine; point № 8 – place of discharge of return (rain and melt water) of the mine Ternivska; point № 9 – 500 m below the discharge of return (rain and melt) waters of the Ternivska mine.

Indicators of the chemical composition of water were compared with normative indicators for meeting drinking, household and other needs of the population, as well as for fishery needs.

The obtained physicochemical data in Table 2 were compared with the relevant MPCs for meeting drinking, household and other needs of the population (MPC_{dh}) [31] as well as for fishery needs (MPC_f) [32]. As it can be seen from Table 2, the concentration of chlorides and sulfates in almost all points exceeds both the fishery and household water quality standards. At the same time, the most significant water quality norms are violated for chlorides, the concentration of which in monitoring points 1, 2, 6, 7, 8, 9 is more than 2.5 times higher than the MPC_f and almost 2 times higher the MPC_{dh}. With regard to sulfates, there is a 4–5 times exceedance of fishery standards of water quality for the group of points 1–3 and 9, 7–8 times for the group of points 4-6, 10 times for points 7, 8, exceeding drinking and household water quality standards is observed for points 2, 4, 5, 6, 7, 8. High concentrations of chlorides and sulfates in the surface water of the Saksagan River (p. 1–3, 4–6) are due to the content of these pollutants in mine waters and return waters in storage ponds. These waters are accumulated annually, temporarily kept in mine water storage ponds, and the mine is forced to discharge their surplus into surface waters during the inter-vegetation period. At the same time, there is a process of seepage of highly mineralized waters through the soil into the underground water. High values of total mineralization are exceeding the norms by 1.5 to 3 times at all monitoring points. It is also caused by discharges of highly mineralized return water from operating mines [33]. Such high concentrations of chlorides, sulfates and general mineralization are also observed at the state monitoring point located on the Saksagan River, Makorty village, Makortivske reservoir: the concentration of sulfate ions exceeds the norm by 15.31 times, chloride ions by 1.75 times [34].

The decrease in the concentration of chlorides and sulfates observed in the group of monitoring points of the "Ternivska" mine (items 7–9) is due to the fact that, before discharge, excess return water is treated at local sewage (storm) water treatment facilities. Therefore, there is a significant decrease in the concentration of these indicators in the control structure below the discharge site due to mixing and dilution of return water with natural water. The increased salt content of the water is due to the inflow of water of inappropriate quality from the upper reaches of the river.

In order to understand whether it is possible to use water for communal, household, economic, drinking and fishery water use, in accordance with the Water Code of Ukraine, water quality is assessed based on the standards of ecological safety of water use and ecological standards of water quality of water bodies.

Water bodies are considered suitable for communal and household as well as economic and drinking water use, if the following conditions are met at the same time:

the general requirements for the composition and properties of water for the corresponding category of water use are not violated;

for substances belonging to the third and fourth classes of danger, the condition C ≤MPK is fulfilled, where C – concentration of a substance in a water body, g/m^3;

for substances belonging to the first and second classes of danger, the following condition is fulfilled

$$\sum \frac{C_i}{MPK_i} \leq 1,$$

where C_ii MPC_i – respectively, the concentration and MPC of a substance of the first or second class of danger.

Water bodies are considered suitable for fishery water use if the following conditions are simultaneously met:

the general requirements for the composition and properties of water for the corresponding fishery category are not violated;

the following condition is met for substances belonging to the same limiting indicator of harmfulness (LIH).

$$\sum \frac{C_i}{MPK_i} \leq 1,$$

where C_i, MPK_i – respectively, the concentration and MPC of a substance of the LIH.

The assessment of the quality of surface water at the monitoring points was evaluated by the general parameters of the salt composition. Indicators of salt composition (chlorides, sulfates and general mineralization) are most dependent on the natural conditions of formation of surface water quality. As shown by the obtained results, the ecological assessment of water quality according to the criterion of total mineralization (Table 2) of Saksagan River water in all the indicated monitoring points belongs to the class of brackish waters (II) of the β-mesogaline category (3). This is confirmed by the results of monitoring studies of the Institute of Geological Sciences of the National Academy of Sciences of Ukraine [17; 34].

Monitoring points were also divided into 3 parts according to the content of components of the salt composition (Table 2).

Table 2

Classification of the quality of brackish β-mesogaline waters according to the criteria of pollution by components of the salt composition according to O.A. Allokin [14]

Point of research	1	2	3	4	5	6	7	8	9
Sulfates									
Water quality class	I	II	II	III	III	III	IV	III	II
Water quality category	1	2	2	5	5	4	6	4	2
Chlorides									
Water quality class	III	III	II	II	II	III	III	III	III
Water quality category	4	5	3	3	3	4	4	4	4
Sum of ions									
Water quality class	II	II	II	II	III	III	III	III	III
Water quality category	2	3	2	3	4	4	4	4	4
	II	II	II	II	II	II	III	III	III
Ecological assessment of water quality based on indicators of salt composition									
I_1	2.33	3.33	2.33	3.66	4.00	4.00	4.66	4.00	3.33
According to the state of the water	Good/very good	Good/good	Good/very good	Good/good	Satisfactory/ satisfactory	Satisfactory/ satisfactory	Satisfactory/ satisfactory	Satisfactory/ satisfactory	Good/good
According to the level of water purity	Pure/pure	Pure/quite pure	Pure/pure	Pure/quite pure	Contaminated/slightly contaminated	Contaminated/slightly contaminated	Contaminated/slightly contaminated	Contaminated/slightly contaminated	Contaminated/slightly contaminated

Therefore, in relation to the criteria of salt composition pollution for brackish β-mesogaline waters, water of the Saksagan River in the water intake areas of the urban part of Kryvyi Rih and the village of Sergiyivka, the water quality can be mainly attributed to 3, 4 categories of II, III quality classes, respectively (Pure/ pure or quite pure). According to the content of sulfates, the water quality in the upper part of the Saksagan River (p. 1–3) corresponds to the II class of the 2nd category, in the area of the "Ternivska" mine above the return water discharge, it corresponds to the IVth class of the 6th category, and below the discharge it is already assessed as the IIIrd class of the 5th category (satisfactory / contaminated or slightly contaminated). According to the parameters of the salt composition in the area of the village of Sergiyivka and in the water intake area of the urban part of Kryvyi Rih, the ecological condition of the water can be attributed to good and very good and good, in the area of the "Ternivska" mine – good and good, according to the degree of purity of the water, pure and pure and quite pure, in the area of mines - contaminated and slightly contaminated.

Also, based on the obtained data, a modified water pollution index (WPI) [36] was calculated according to the formula WPI = $(1/6)\sum (C_i/MPK_i)$, where C_i – average arithmetic value of the water quality indicator; MPC^i – maximum permissible concentration.

In the formula, only for O_2, the MPC is divided by the average value of its indicator.

The indicator was calculated based on six indicators: BOD_5 and O_2 were mandatory, the other four indicators were chosen with the highest ratio to the MPC (in our case, it is SO_4^{2-} , Cl^-, NO_2^-, NO_3^- for the calculation of household drinking water consumption and SO_4^{2-}, Cl^-, NH^{4+}, NO_2^- for the calculation of fish farming water consumption).

The calculation of the modified WPI according to the economic and drinking standards made it possible to establish that only at points 1–3 in the village of Serhiyivka the water is classified as clean ($0.3 < WPI \leq 1.0$) class II, and in other monitoring points it is mainly classified as moderately polluted ($1.0 < IZV \leq 2.5$) class III. The calculation of the modified IZV according to the fisheries regulations made it possible to establish that only in points 1–3 in the area of Serhiivka village the water is classified as dirty ($4.0 < IZV \leq 6.0$) class V, and in other monitoring points it is classified mainly as contaminated ($2.5 < IZV \leq 4.0$) Class IV. It should be noted that in this case the effect of summation with the same LIH was not taken into account.

Tropho-saprobiological (ecological-sanitary) quality assessment of the surface waters of land and estuaries was carried out according to the following hydrochemical parameters: hydrogen ion concentration, ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, phosphorus, phosphates, dissolved oxygen, permanganate and bichromate oxidation, biochemical oxygen demand [14; 35].

Oxygen dissolved in water is the most important physical and chemical indicator of natural water, it is a natural oxidizer that determines water quality and the possibility of supporting the ontogenesis of hydrobionts. The oxygen content in the experimental areas near the village of Serhiivka (points 1–3) and the mine "Ternivska" (points 7–9) meet the standards, and corresponds to class I, category 1 of water quality ("excellent"). The worst situation is observed in monitoring points No. 4–6, where low concentrations of oxygen in water were detected, especially in point No. 6, where the indicator was 1.82 mg/dm^3 and belongs to class V, the 7th category of water quality ("very bad"). Such a low value of dissolved oxygen in the recreation area indicates that the processes of rotting, decomposition of organic products, and algae growth (overgrowth of the reservoir) are taking place in the water. In order to prevent further deterioration of the sanitary state of the water body, it is necessary to introduce biomelioration measures, and possibly mechanical cleaning (dredging), which will indirectly increase the amount of oxygen. This does not correspond to either economic and drinking or fishery standards [36; 37].

Direct indicators of organic pollution of river water are ammonium nitrogen, nitrites and nitrates. If ammonium nitrogen is detected in the water, this indicates fresh pollution of organic origin, which is formed at the first stage of mineralization of nitrogen-containing ammonium substances. Exceeding its maximum permissible level has a harmful effect on the health of animals. The detection of nitrites in the water indicates that the water is already polluted and continues to be polluted with organic substances, since a certain period of time is necessary for the first stage of ammonia mineralization (its transformation into nitrites) to take place. Therefore, the detected nitrites are a manifestation of recent water pollution by organic substances. The presence of nitrates in water indicates the end of the process of mineralization of organic substances, which indicates long-term contamination of natural water with organic substances. It should be noted that nitrates, which in themselves are not very harmful, but inside the body they turn into nitrites, which are ten times more toxic than nitrates themselves.

At all monitoring points, according to the indicator of ammonium nitrogen, there was no excess of economic and communal norms, the water corresponded to class II, the 3rd category of water quality ("good"). In the water of the experimental sites near the Ternivska mine and in the area of the Saksagansky tunnel, the water according to the content of ammonium nitrogen corresponds to water quality class III, category 4 ("satisfactory") – the water meets the economic and drinking standards, but does not meet the fishery standards. Adding to this explanation the non-compliance with nitrate standards in items 4 and 5, it can be concluded that the water in the area of the city of Kryvyi Rih in the recreation area "Dubky" and near the entrance portals I and II has been systematically polluted by organic substances for a relatively short period of time, which is why the lowest concentrations of dissolved oxygen were observed at these points. According to nitrates, the water at these points does not meet the standards. What does it say about the fact that household waste gets into the water in the area of the city of Kryvyi Rih. However, the increased content of ammonium nitrogen in the waters of reservoirs can be observed not only in case of excessive pollution with organic substances, but also when some part of nitrogen-containing fertilizers from agricultural fields enters the river network together with rainwater or groundwater.

The increased amount of nitrite nitrogen in the first group of points (p. 1–3) and in the recreation zone (Dubky – p. 6) relative to fishery norms and indicators in other points indicates fresh water pollution in the area of the village of Serhiivka. This signals the intensive application of nitrogen to fields and gardens especially in spring and summer. According to the content of nitrite ions in the water near the village of Serhiivka (p. 1–3), the water can be classified as V class, the 7th category of water quality ("very bad"). Indicators of NO^{2-} at scientific research stations in the area of the Terniv mine allow it to be classified as II class, 3rd category of water quality ("good"). Within Kryvyi Rih, the concentration of NO^{2-} mostly corresponds to class III, category 4 of water quality ("satisfactory").

The concentration of nitrate ions (NO^{3-}) in the water near the entrance portals of the Saksagan tunnel did not meet either the economic, communal or fishery standards, it corresponds to class V, category 7 of water quality ("very bad").

Conclusions

According to the results of research, water quality at all studied points does not meet the standards for fishery needs in terms of sulfates, chlorides, and general mineralization. With regard to sulfates, the water does not meet the fishery standards at all moritoring points, and only points 1 and 9 meet the sanitary standards. Based on the data of state monitoring and conducted analyses, it can be assumed that the increased salt content of the water is due to the inflow of water of inappropriate quality from the upper reaches of the Saksagan River, waste water from untreated enterprises, return water and tailings from mining enterprises.

The Saksagan flowing into the Ingulets in the area of the Fedir Mershavtsev Park affects the quality of water, therefore it is very important to establish and eliminate the factors of water pollution upstream of the Saksagan River outside the village of Makorty, Makortivske reservoir.

Increasing the number of monitoring points will allow to identify sources of pollution and introduce additional measures to preserve water resources. The obtained results can be also used in conducting water quality studies, monitoring studies of water ecosystems, and developing scientific and biological justifications and regulations for the use of aquatic biological resources and meliorations.

References

[1] The European Parliament and the council of the European Union. (2020). [*Directive of the European Parliament and of the Council establishing a framework for Community action in the field of water policy*]. Kyiv, Ukraine. (in Ukrainian). https://zakon.rada.gov.ua/laws/show/994_962#Text

[2] Cabinet of ministers of Ukraine. (2018). [*Decree on the approval of the Procedure for State Water Monitoring*]. Kyiv, Ukraine. (in Ukrainian) https://www.kmu.gov.ua/npas/pro-zatverdzhennya-poryadku-zdijsnennyaderzhavnogo-monitoringu-vod

[3] Yesipova, N., Marenkov, O., Sharamok, T., Nesterenko, O., Kurchenko, V. (2022). Development of the regulation of hydrobiological monitoring in circulation cooling system of the Zaporizhzhia Nuclear Power Plant. *Eastern-European Journal of Enterprise Technologies*, *2*(10), 116. https://doi.org/*10.15587/1729-4061.2022.255537*

[4] Meyer, A. M., Klein, C., Fünfrocken, E., Kautenburger, R., Beck, H. P. (2019). Real-time monitoring of water quality to identify pollution pathways in small and middle scale rivers. *Science of the Total Environment*, *651*, 2323–2333. https://doi.org/10.1016/j.scitotenv.2018.10.069

[5] Mylatska, O.I., Strocal, V.P. (2023). [The state of the problem of ecological degradation of small rivers of Ukraine]. *IX International scientific and practical conference of students, postgraduates and young scientists "Ecology – philosophy of human existence*, 55–57. (in Ukrainian).

[6] Mandaric, L., Mor, J. R., Sabater, S., Petrovic, M. (2018). Impact of urban chemical pollution on water quality in small, rural and effluent-dominated Mediterranean streams and rivers. *Science of the Total Environment*, *613*, 763–772. https://doi.org/10.1016/j.scitotenv.2017.09.128

[7] Dutta, S., Dwivedi, A., & Suresh Kumar, M. (2018). Use of water quality index and multivariate statistical techniques for the assessment of spatial variations in water quality of a small river. *Environmental monitoring and assessment*, *190*, 1–17. https://doi.org/10.1007/s10661-018-7100-x

[8] Tarariko, O. H., Ilienko, T. V., Kuchma, T. L. (2013). Formation of ecologically sustainable agrolandscapes in the conditions of climate change. *Agroecological journal*, 4, 13–20. https://doi.org/10.15407/ugz2016.03.056

[9] Kabir, A. E., Sekine, M., Imai, T., Yamamoto, K., Kanno, A., Higuchi, T. (2021). Assessing small-scale freshwater microplastics pollution, land-use, source-to-sink conduits, and pollution risks: Perspectives from Japanese rivers polluted with microplastics. *Science of the Total Environment*, *768*, 144655. https://doi.org/10.1016/j.scitotenv.2020.144655

[10] Serdiuk, S.M., Lunova, O.V., Ahieieva, O.F., Kamianska, V.O. (2017). [Small rivers of Ukraine: geoecological survey of problems. *Bulletin of the Donetsk Mining Institute*], (1), 101–106. (in Ukrainian).

[11] Pasichnyi, H. V., Bulava, L. M., Horb, A. S., Hrytsenko, N. V., Dodatko, E. L., Duk, N. M., Dushyn, B. V., Zelenska, L. I., Krymtsov, A. O., Masiuk, M. T., Mikulinskyi, I. B., Myroshnyk, N. V., Pasichnyi, V. H., Pakhomov, O. Ye., Shmatkov, H. H. (1992). [*Physical and economic geography of Dnipropetrovsk region*]. Dnipropetrovsk: DSU. (in Ukrainian)

[12] Paraniak, R. P., Ostasha, T. P. (2014). [Mechanisms of ecological risk formation of anthropogenic pollution of small rivers of Lviv region]. *Scientific Messenger of Stepan Gzhytskyi National University of Veterinary Medicine and Biotechnologies of Lviv*, 16, *3*(60), part 3, 371–379. (in Ukrainian)

[13] Bohynia, O. S. (2020). [Chemical composition of bottom sediments of the Saksagan River]. *Collection of scientific works of the Dnipro State Technical University (technical sciences)*, *1*(36), 138–142. (in Ukrainian) https://doi.org/10.31319/2519-2884.36.2020.24

[14] Sherstiuk, N.P., Nosova, L.O., Bielik, V.N. (2011). [Analysis of hydrochemical characteristics of surface waters in the territory of the Northern Mining and Processing Plant]. *Bulletin of Dnipropetrovsk University.*

Series: Geology. geography, *19*(13), 31–38. (in Ukrainian)
[15] Khilchevskyi, V. K., Sherstiuk, N. P. (2021). Long-term changes in the chemical composition of the water of the Inhulets and Saksahan rivers within the Kryvorizkyi Iron Ore Basin (1980–2020). *Journal of Geology, Geography and Geoecology*, *30*(3), 470–479. https://doi.org/10.15421/112143
[16] Kozin, Ya. V., Gatskyi, A. K. General characteristics of the condition of the environment in the conditions of Kryvorizky tail storage. *Ecological page.* (in Ukrainian) https://kdpu.edu.ua/pryroda-kryvorizhzhia/pryroda-ta-liudy/ekolohichna-storinka/3217-konstruktyvno-heohrafichni_oso_blyvosti-polipshennya-suchasnoho-stanu-hirnychopromyslovykh-landshaftiv.html
[17] Bagriy, I. D., Blinov, P. V., Belokopitova, N. A. (2002). [*Geo-ecological problems of the Kryvyi Rih basin in conditions of restructuring of the mining industry*]. Kyiv, Feniks. (in Ukrainian)
[18] Monitoring and environmental assessment of water resources of Ukraine. State Agency of Water Resources of Ukraine. (in Ukrainian). http://monitoring.davr.gov.ua/EcoWaterMon/GDKMap/Index
[19] Khilchevskyi, V. K., Kravchynsky, R. L., Chunaryov O. V. (2012). [*Hydrochemical regimen and water quality of river Ingulets under technogenesis conditions*]. Kyiv, Nika Center. (in Ukrainian)
[20] Lototska, O. V., Bitsyura, L. O. (2021). Monitoring of surface water resources in Ukraine and its legislative basis. *Bulletin of Social Hygiene and Health Protection Organization of Ukraine*, (2), 79–84. (in Ukrainian) https://doi.org/10.11603/1681-2786.2021.2.12386
[21] Arsan, O. M., Davydov, O. A., Diachenko, T. M., Evtushenko, M. Yu., Zhukynskyi, V. M., Kyrpenko, N. I., Yakushyn, B. M. (2006). [*Methods of hydroecological research of surface waters*]. Under the editorship of V.D. Romanenko. NASU: Institute of Hydrobiology, K: Lohos. (in Ukrainian)
[22] State Standard of Ukraine (2003). [Water quality. Determination of pH]. (SStU 4077-2001). (in Ukrainian)
[23] State Standard of Ukraine (2006). [Water quality. Determination of dissolved oxygen. Iodometric method]. (SStU ISO 5813:2004). (in Ukrainian)
[24] Khilchevskyi, V. K., Zabokrytska, M. R. (2021). [*Chemical analysis and assessment of the quality of natural waters*]. Lutsk. Vezha-Druk. (in Ukrainian)
[25] State Standard of Ukraine (2004). [Determination of ammonium. Part 1. Manual spectrometric method]. (SStU ISO 7150- 1:2003). (in Ukrainian)
[26] State Standard of Ukraine (2003). [Water quality. Determination of nitrites. Spectrometric method of molecular absorption]. (SStU ISO 6777:2003 (ISO 6777:1984, IDT)). (in Ukrainian)
[27] The methodology for measuring 081/12-0007-01 (2002). [Surface and treated wastewater. The methodology for measuring the mass concentration of sulfates by the gravimetric method]. (in Ukrainian)
[28] State Standard of Ukraine (2016). [Soil quality. Determination of chloride ion in aqueous extract]. (SStU 7908:2015). (in Ukrainian)
[29] State Standard of Ukraine (2004). [Water quality. Determination of iron. Spectrometric method using 1,10-phenanthroline]. (SStU ISO 6332:2003). http://docs.dbn.co.ua/5744_1583178494823.html (in Ukrainian)
[30] State Standard of Ukraine (2004). [Water quality. Determination of the total content of calcium and magnesium. Titrimetric method using ethylenediaminetetraacetic acid]. (SStU ISO 6059:2003). (in Ukrainian). https://zakon.isu.net.ua/sites/default/files/normdocs/1-10437-dstu_iso_6059_2003_yakist_vody._vyznachannya_sumarnog.pdf
[31] Ministry of Health of Ukraine (2022). [Hygienic water quality standards of water bodies to meet drinking, household and other needs of the population]. Kyiv, Ukraine. (in Ukrainian) https://zakon.rada.gov.ua/laws/show/z0452-10#Text
[32] Maximum permissible values of water quality indicators for fishery reservoirs. (1990). [*The general list of MPCs and ASELs of harmful substances for the water of fishing reservoirs*]. Kyiv, Ukraine, Ministry of Fisheries. (in Ukrainian)
[33] Report on the management of PJSC «KRYVORIZKY IRON ORE PLANT» (2020). (in Ukrainian) https://www.krruda.dp.ua/wp-content/uploads/2021/04/uprav_2020.pdf
[34] Hrytsenko, A.V., Vasenko, O.H., Vernichenko, H. A. (2012). [*Methods of ecological assessment of surface water quality by relevant categories*]. Kharkiv, UkrNDIEP (In Ukrainian).
[35] Snizhko, S. (2001) [*Assessment and forecasting of natural water quality*]. Kyiv, Nika Center. (in Ukrainian).
[36] Fedonenko, O. V., Marenkov, O. M. (2018). [*Industrial development of the ichthyofauna of the Zaporizhzhya (Dnipro) reservoir*]. Dnipro, Lira. (in Ukrainian)
[37] Agostinho, A. A., Alves, D. C., Gomes, L. C., Dias R. M., Petrere, Jr. M., Pelicice, F. M. (2021). Fish die-off in river and reservoir: A review on anoxia and gas supersaturation. *Neotropical Ichthyology*, *19*(03), e210037 https://doi.org/10.1590/1982-0224-2021-0037.