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Original article

Hydrochemical State of the Waters of the Salgir and Biyuk-Karasu Rivers (Crimean Peninsula) in Summer 2023

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Abstract
The paper studies hydrochemical characteristics of waters of the Salgir and Biyuk-Karasu Rivers in summer, when the anthropogenic load is increased. Data were obtained on dissolved oxygen concentration, five-day biochemical oxygen demand (BOD_5), alkaline permanganate oxidizability, concentrations of silicate, mineral and organic forms of nitrogen and phosphorus. The samples were collected in July, August and September 2023 in Simferopol and in the Krasnogvardeisk, Nizhnegorsk and Belogorsk regions in the Republic of Crimea. The analyses were performed according to the generally accepted methods. Compliance of the obtained results on hydrochemical indicators with water quality regulations was assessed. A high level of oxygen content was noted at all stations. BOD_5 values varied from 0.98 to 3.34 mg/L (the village of Molochnoye) and exceeded the limit for fisheries by up to 1.6 times. The oxidizability values exceeded the maximum allowable value by 2 to 4 times. The concentrations of the mineral forms of nitrogen did not exceed maximum permissible concentrations, except for nitrite concentration (maximum exceedance by 2.8 times). The phosphate concentration exceeded the maximum permissible concentrations near the villages of Novogrigoryevka and Molochnoye (maximum by up to 5.6). The study results allow determining the areas of Molochnoye and Novogrigoryevka as most polluted.

Keywords: hydrochemical characteristics, nutrients, anthropogenic load, water quality, Salgir river, Crimea

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Гидрохимическое состояние вод рек Салгир и Биюк-Карасу (полуостров Крым) в летний сезон 2023 года

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Аннотация

Приведены гидрохимические характеристики вод рек Салгир и Биюк-Карасу в летний период при возрастающей антропогенной нагрузке. Получены данные о содержании растворенного кислорода, биохимическом потреблении кислорода на пятые сутки, перманганатной окисляемости в щелочной среде, концентрации кремния, минеральных и органических форм азота и фосфора. Пробы отобраны в июле, августе и сентябре 2023 г. в Симферопольском, Красногвардейском, Нижнегорском и Белогорском районах Республики Крым. Анализы выполнены согласно общепринятой методике. Оценено соответствие полученных результатов по гидрохимическим показателям нормативным требованиям к качеству вод. Отмечен высокий уровень содержания кислорода на всех участках; биохимическое потребление кислорода на пятые сутки изменялось от 0.98 до 3.34 мг/л (с. Молочное) и превышало норматив для водных объектов рыбохозяйственного значения максимум в 1.6 раза, значения окисляемости превышали предельно допустимые показатели в 2–4 раза. Концентрации минеральных форм азота не превышали предельно допустимую концентрацию, кроме нитритов (максимальное превышение в 2.8 раза). Зафиксировано также превышение предельно допустимой концентрации фосфатов в районах с. Новогригорьевка и с. Молочного (максимум в 5.6 раза). Результаты исследований позволяют выделить наиболее загрязненные районы, такие как с. Молочное и с. Новогригорьевка.

Ключевые слова: гидрохимические показатели, биогенные вещества, качество вод, антропогенная нагрузка, река Салгир, Крым

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Introduction

The Salgir River represents the largest water system of the Crimean Peninsula flowing into Sivash Bay of the Sea of Azov during periods of high water. The scientific research of the Salgir River and its basin was initiated in the late 19th century [1)].

[1)] Golovkinskiy, N.A., 1893. [*Springs of Chatyrdag and Babugan*]. Simferopol: Tip. Spiro, 35 p. (in Russian).

The results of expeditionary studies of the Salgir River and its tributary Biyuk-Karasu are described in work [2)]. In 1961, information about the Salgir River basin was presented in the work of M.E. Miller [1] in connection with the construction of the Simferopol Reservoir and the Salgir irrigation system. The study of the natural landscapes and the use of nature in the Salgir River basin as well as the justification of measures to ensure the quantity and quality of water resources in the basin were carried out by A. M. Vlasova [2]. The study considers the main sources of pollution in the Salgir River basin and identifies the areas of the basin with stable and unstable ecological state. The analysis of the factors of water resources formation in the Salgir River under the conditions of climate change and anthropogenic load is presented in the works of E. A. Pozachenyuk et al. [3].

The greatest contribution to the pollution of the water area of the Salgir and Biyuk-Karasu Rivers is made by industrial and municipal wastewater from the city of Simferopol and its suburbs. This phenomenon can be attributed to a confluence of factors, including the proliferation of industrial facilities, high density of buildings, branched transport networks and municipal infrastructure, among others. The work by N.M. Ivanyutin et al. [4] demonstrates that the primary pollutants identified in the investigation of river runoff, for which exceedances of maximum permissible concentrations (MPC) were observed, are petroleum products, ammonium nitrogen, nitrite, nitrate, phosphate, iron, cadmium, manganese, lead and zinc. Furthermore, the BOD_5 permissible levels were exceeded.

In their study, N. M. Ivanyutin et al. [5] identify the increased withdrawal of water from the river and the discharge of inadequately treated wastewater, in addition to precipitation and snowmelt water runoff, as the primary challenges facing the Salgir River. In addition to the previously mentioned sources, E. Yu. Kuznetsova [6] identifies industrial waste settling and livestock farms as contributors to the pollution of surface water. An increase in the concentration of nitrite, phosphate and ammonium nitrogen in the surface waters of the Salgir River was detected. The gradual increase in nitrite content can be attributed to the conversion of ammonia to nitrite as a result of the nitrification. The MPC of ammonium nitrogen was exceeded. The authors conclude that the ecological condition of the river is unsatisfactory.

In the work of G. A. Kiseleva [7], the monitoring of hydrochemical indicators (dissolved oxygen, BOD_5, etc.) revealed significant changes in the environment and benthic ecosystem. This led to the identification of six areas within the Salgir River, characterised by varying degrees of anthropogenic load. The results demonstrated that the river biocenoses underwent a significant transformation as a consequence of intensive anthropogenic activity. It can be stated now with a reasonable degree of certainty that a number of invertebrate species previously recorded in the Salgir River have disappeared.

In general, the water of the Salgir River is characterised as “polluted” according to the classification of surface water quality in the Russian Federation [3)],

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[2)] Kocherin, D.I., 1922. [River Run-Off in the Upper Reaches of the Salgir River up to Simferopol (Main Conclusions)]. In: Simferopol, 1922. [*Materials on the Water Management of Crimea*]. Simferopol: 1-ya Gos. Tipo-lit, iss. 2, 8 p. (in Russian).

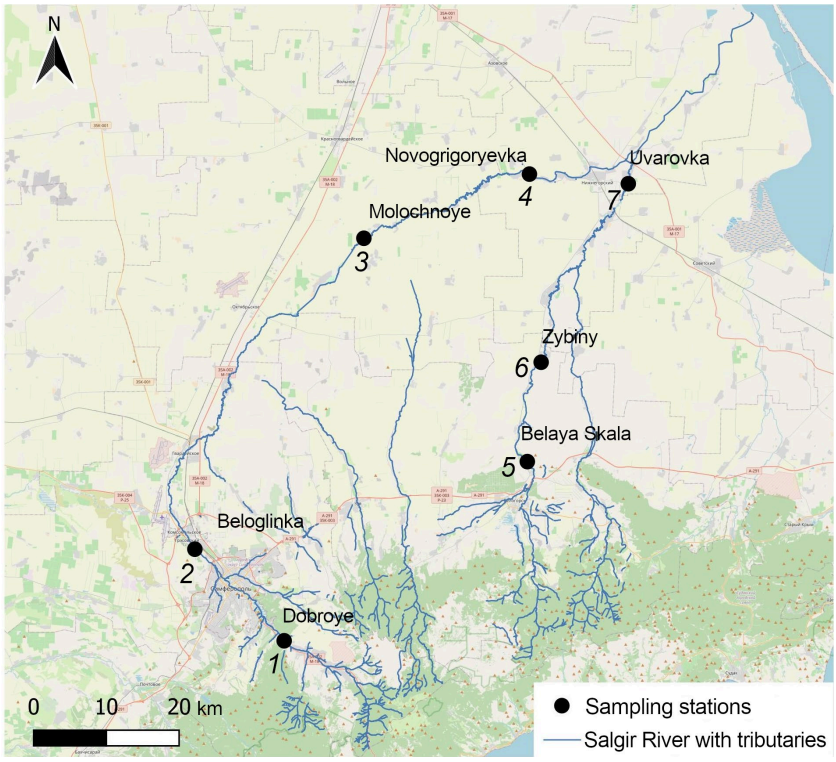
[3)] Council of Ministers of the Republic of Crimea, 2023. [*Report on State and Protection of Environment of Republic of Crimea in 2022*]. Simferopol: OOO Print, 448 p. (in Russian).

as outlined by L. V. Malakhova et al. [8]. Additionally, the river water in the vicinity of the village of Dvurechnoye exhibits high levels of easily oxidizable organic matter, as indicated by elevated BOD and chemical oxygen demand values [4]. In the aforementioned works, insufficient attention is paid to the hydrochemical characteristics of water. Consequently, our work classifies the level of water pollution of the Salgir River on the basis of a hydrochemical analysis of the material in question.

The paper analyses new data on the hydrochemical characteristics of waters from the Salgir and Biyuk-Karasu Rivers in summer, when the water area is subjected to an increased anthropogenic load.

Materials and methods

To assess the hydrochemical state of waters of the Salgir River and its most full-flowing tributary, the Biyuk-Karasu River, studies were carried out in July, August and September 2023 in four sections of the Salgir River from its head to its mouth and in three sections of the Biyuk-Karasu River along the main stream to the mouth (Figure).



Map of water sampling stations on the Salgir River and its tributary Biyuk-Karasu

[4] Trofimchuk, M.M., ed., 2021. [*Quality of Surface Waters of the Russian Federation. Information on the Most Polluted Water Bodies of the Russian Federation (Annex to Year-Book for 2020)*]. Rostov-on-Don, 160 p. (in Russian).

On the Salgir River, samples were taken upstream of the Simferopol Reservoir (the village of Dobroye, station *1*) at a station with a presumably low anthropogenic impact, downstream of the city of Simferopol (the village of Beloglinka, station *2*) at a station with a high anthropogenic load, downstream of the river in the developed agricultural area, following an extensive network of fishery ponds (the village of Molochnoye, station *3*), and closer to the mouth, in the area with agricultural land and livestock production (the village of Novogrigoryevka, station *4*). On the Biyuk-Karasu River, samples were taken downstream of Belogorsk (the village of Belaya Skala, station *5*) in the area of orchards, further downstream in the area of grain crops cultivation (the village of Zybiny, station *6*) and closer to the mouth after the settlement where a cattle farm and feed mill are located (the village of Uvarovka, station *7*). Samples were obtained from the surface in triplicate, resulting in a total of 45 samples and 405 hydrochemical analyses.

The following parameters were identified in the samples: dissolved oxygen, five-day biochemical oxygen demand (BOD_5), alkaline permanganate oxidizability, silicate, mineral and organic forms of nitrogen and phosphorus. The analyses were performed according to generally accepted methods [5), 6)]. The oxygen concentration was determined by the Winkler method, while the nutrients were determined photometrically. Phosphates were determined by the Murphy–Riley method; nitrites were quantified photometrically using the Griess method, while nitrates were first reduced to nitrites with copper-plated cadmium. Ammonium nitrogen was determined by the Sagi–Solorzano method, while silicon was quantified by the Koroleff method.

Results and discussion

Dissolved oxygen concentration in the waters of the Salgir and Biyuk-Karasu Rivers (Table) varied from 5.30 (the village of Novogrigoryevka) to 6.57 mL/L (the village of Beloglinka) in July; and from 5.48 (the village of Molochnoye) to 7.12 mL/L (the villages of Dobroye and Beloglinka) in August. The range of variability was 6.09–7.66 mL/L in September. The minimum oxygen content was recorded near the village of Uvarovka and the maximum one was near the village of Novogrigoryevka. In general, the oxygen concentration in the waters of the Salgir River and its tributary Biyuk-Karasu is high; even its minimum content is above the MPC according to the limit for fisheries [7)] by 1.3 mL/L.

Such indicators as BOD_5 and alkaline permanganate oxidizability were used to characterise water pollution of the studied river sections. The first indicator reflects pollution of the environment by non-persistent organic matter, the second one indicates the degree of water pollution by persistent organic matter. BOD_5 values varied from 0.98 (the village of Belaya Skala) to 3.34 mg/L (the village of Molochnoye)

[5)] Sapozhnikov, V.V., ed., 2003. [*Guidelines for the Chemical Analysis of Marine and Freshwater in Environmental Monitoring of Fishery Waters and Prospective Fishing Areas of the World Ocean*]. Moscow: Izd-vo VNIRO, 202 p. (in Russian).

[6)] HMSO, 1984. *The permanganate index and permanganate value tests for waters and effluents 1983*. London: HMSO, 21 p.

[7)] *On the Approval of Water Quality Standards for Water Bodies of Commercial Fishing Importance, Including Standards for Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Commercial Fishing Importance*: Order of the Ministry of Agriculture of Russia dated December 13, 2016, No. 552 (in Russian)

The main hydrological and hydrochemical parameters of the Salgir and Biyuk-Karasu Rivers in July–September 2023

Sampling date	Station number	*T*, °C	O_2, mL/L	BOD_5, mg/L	Concentration, μg/L					Oxidizability, mgO/L
					NO_2^-	NO_3^-	NH_4^+	PO_4^{3-}	Si	
July										
06.07.23	*1*	22.5	6.57	1.67	23.0	964	56.7	15	2186	4.56
06.07.23	*2*	23.0	5.42	1.90	15.7	986	35.2	31	2303	3.88
18.07.23	*3*	23.5	5.37	3.34	49.4	944	54.3	687	4881	5.86
18.07.23	*4*	25.0	5.30	1.63	39.0	962	41.4	612	5708	6.26
26.07.23	*5*	22.0	5.82	0.98	16.2	967	35.7	3	1920	4.16
27.07.23	*6*	23.5	5.70	1.03	10.3	1013	25.2	10	2373	3.58
27.07.23	*7*	26.5	6.50	1.91	3.7	848	39.4	8	2739	5.12
August										
03.08.23	*1*	24.0	7.12	2.42	23.7	3500	336.0	45	3690	7.90
03.08.23	*2*	21.5	7.12	2.35	31.8	7328	63.0	46	4300	8.95
09.08.23	*3*	21.6	5.48	2.26	23.0	6930	31.0	1120	2660	7.27
09.08.23	*4*	25.3	6.71	2.57	6.2	3767	204.0	612	6370	5.63
September										
13.09.23	*5*	18.2	6.09	ND	2.2	2804	18.9	9	1263	ND
14.09.23	*6*	17.3	6.41	ND	21.2	5629	29.9	22	875	ND
20.09.23	*3*	18.0	7.08	ND	44.7	2766	54.1	614	4142	5.85
20.09.23	*4*	19.2	7.66	ND	55.9	2518	45.2	64	8196	3.28

Note: ND – not determined. MAC O_2 – 4.20 μg/L; MAC NO_2^- – 20.0; MAC NO_3^- – 9000 μg/L; NH_4^+ – 390 μg/L. Limit for 5-day biochemical oxygen demand (BOD_5) – 2.1 mg/L; limit for oxidizability – 4.00 mgO/L.

in July. At the same time, the maximum BOD_5 values exceeded the limit (2.1 mgO/L) by 1.6 times. In July, the limit exceedance was observed only once; in August and September, the exceedance was persistent (maximum by 1.3 times). According to the integrated ecological classification of surface water quality [8)], the BOD_5 values of the Salgir River waters made it possible to classify them as satisfactorily clean (3rd class of water quality) in July and polluted (4th class) in August and September.

Water oxidizability varied from 3.58 to 20.10 mgO/L. The minimum value was observed in July (the village of Zybiny) and the maximum in September (the village of Molochnoye). The average oxidizability exceeded the MPC (4.0 mgO/L) of the limit for fisheries by 1.6 times in July, by 1.9 times in August and by 4.8 times in September. According to the oxidizability values, waters of the Salgir and Biyuk-Karasu Rivers in July were classified as the 2nd class of quality, corresponding to clean water [8)], but in August it was classified as the 3rd class, corresponding to satisfactorily clean waters. In September, the waters were classified to be of the 4th class, indicating a deterioration in quality. Therefore, in terms of oxidizability, a deterioration in the river water quality was observed from July to September, which can be attributed to increased anthropogenic impact and recreational load.

Forms of nitrogen

Water *nitrite nitrogen concentrations* in the waters of the Salgir and Biyuk-Karasu Rivers ranged from 2.2 to 55.9 μg/L; the minimum and maximum values were recorded in September (the villages of Uvarovka and Novogrigoryevka, respectively). Increased NO_2^- concentrations (49.4 and 44.7 μg/L) were observed near the village of Molochnoye in July and September. Exceedance of MPC (20 μg/L) was noted at three out of seven stations in July, at three out of four stations in August, and at three out of four stations in September. The maximum MPC exceedance was by a factor of 2.8. The average value of nitrite concentration equal to 24.4 μg/L exceeded the MPC by 1.2 times.

Nitrate nitrogen concentrations were 1–2 orders of magnitude higher than nitrite nitrogen concentrations and varied over a wide range from 848 to 7328 μg/L. The NO_3^- minimum was observed in July near the village of Uvarovka, and the maximum (0.8 MPC) in August in the vicinity of the village of Beloglinka. Other NO_3^- values were lower and ranged from 0.1 to 0.77 MPC with an average nitrate concentration of 2795 μg/L. It is notable that there was an increase in nitrate concentration from July to September. This can be explained by an increase in the recreational load and anthropogenic impact on the region.

Ammonium nitrogen concentrations were recorded between 19 and 336 μg/L. The minimum NH_4^+ concentration was observed in September near the village of Uvarovka, and the maximum one in August near the village of Dobroye. High ammonium nitrogen content can be impacted by domestic runoff from the village

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[8)] State Committee on Water Management, 2018. [*Scheme of Integrated Use and Protection of Water Bodies of the Republic Of Crimea, Including Norms of Permissible Impact on Water Bodies, and Water Quality Targets for Water Bodies Located in the Territory of the Republic of Crimea. Book 2: Assessment of the Environmental Condition and Key Problems of River Basins Located in the Territory of the Republic of Crimea*] (in Russian).

of Dobroye; settlements along the Salgir riverbed do not have centralized sewerage systems. All the NH_4^+ concentrations were significantly below the MPC (390 μg/L) according to the fishery regulations. The average NH_4^+ content in the river waters was 72 μg/L, which is 5.4 times lower than MPC.

Organic nitrogen (N_{org}) was determined only in September; its concentrations were high and varied from 2990 to 8110 μg/L. The minimum was recorded near the village of Belaya Skala, and the maximum near the village of Novogrigoryevka. The maximum concentration of nitrite (56 μg/L) and high oxidizability values (18.40 mgO/L) were also recorded there. The presented hydrochemical characteristics show that this area is polluted with organic matter. The average N_{org} content was 5070 μg/L in September.

Mineral phosphorus (PO_4^{3-}) concentrations varied from 3.5 to 1120 μg/L in the waters of the Salgir and Biyuk-Karasu Rivers. The minimum was observed in July (the village of Belaya Skala) and the maximum in August (the village of Molochnoye). In the vicinity of the villages of Molochnoye and Novogrigoryevka, PO_4^{3-} is 1–2 orders of magnitude higher than in other areas. This is likely attributable to the impact of domestic and other anthropogenic sources, as evidenced by the elevated organochlorine concentrations observed in the vicinity of the village of Molochnoye [8]. The average PO_4^{3-} concentration was 260 μg/L in July–September; therefore, the waters under study can be classified as polluted ones [8)].

Silicate concentrations had high values and varied in wide ranges from 875 to 8200 μg/L. The minimum and maximum were observed in September near the village of Belaya Skala and the village of Novogrigoryevka, respectively. Increased Si concentrations in the water near the village of Novogrigoryevka are caused by the chemical composition of soils, including aluminosilicates as the main component. In the vicinity of the village of Molochnoye, the concentrations of silicates are about 2 times lower than in the village of Novogrigoryevka. In the other areas, the concentration of Si was almost 4 times lower than the maximum concentrations. The average silicate concentration in July–September was 3574 μg/L.

Conclusions

The analysis of the hydrochemical data obtained in the period between July and September 2023 in the waters of the Salgir and Biyuk-Karasu Rivers has led to the following conclusions:

– the oxygen level in water is high at all river sections;

– the exceedance of BOD_5 and oxidizability limits by a maximum of 1.6 and 4.8 times, respectively, were recorded in the vicinity of the village of Molochnoye. This resulted in the river waters being assigned to the 4th class of water quality in September, down from the 2nd class they were assigned to in July;

– nitrite MPC was exceeded by a factor of 2.5 (the village of Molochnoye). Nitrate concentrations were below MPC and increased from July to September. Ammonium nitrogen concentrations were low and did not exceed MPC;

– high concentrations of phosphates, 1-2 orders of magnitude higher than in other areas, were recorded in the vicinity of the villages of Molochnoye and Novogrigoryevka due to the influence of domestic and household wastewater;

– the results of all hydrochemical analyses of the Salgir River waters indicate that the areas of the villages of Molochnoye and Novogrigoryevka are most polluted.

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Diana S. Borisova – participation in expeditionary sampling, sample processing, obtaining of hydrochemical indicatiors, analysis and discussion of the results, article writing

Sergey V. Ovechko – problem statement, discussion of the results, article editing

Vitaly I. Ryabushko – problem statement, work planning, discussion of the results, final editing

All the authors have read and approved the final version of the manuscript.