Original paper

Hydrochemical Composition of the Chernaya River (Crimea) in 2012–2023

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Abstract
The paper aims to evaluate hydrochemical composition of the Chernaya River waters, which is the major supplier of fresh water in Sevastopol, as well as to assess the influence of the river runoff on the ecological state of Sevastopol Bay. Flowing from the Chernorechenskoye Reservoir, the Chernaya River crosses the Baydar Valley and on its way takes in several tributaries, not having passed through the reservoir geochemical filter. Then it loses the most of its flow at several water intakes near the village of Khmelnitskoe and turns into a stream. The stream again becomes a relatively full-flowing river after the inflow of circulating water from the treatment facilities near the village of Sakharnaya Golovka, and finally, it discharges into Sevastopol Bay near the Inkerman basin. In order to investigate the transformation of the river waters hydrochemical composition as it moves from the Chernorechenskoye Reservoir to the river mouth, graphs of average concentration for some hydrochemical elements for four hydrological seasons 2012–2023 were constructed for 10 stations located on the river and two conditional stations in the water area of the bay (averaged data for the Inkerman basin and 30 stations of the bay). The waters of the Chernorechenskoye Reservoir and Chernaya River were revealed to be close in composition along the length of almost the entire channel from the outlet to the water intake near the village of Shturmovoe. Further, the composition of the river waters is determined by wastewater. Directly (without taking into account wastewater), the Chernaya River supplies significant amounts of nitrates, silicic acid and ammonium to Sevastopol Bay, but not phosphates, which come with the wastewater.

Keywords: Chernaya River, Crimea, hydrochemical composition, nutrients, carbonate system, Sevastopol Bay

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Гидрохимическая структура реки Черной (Крым) в 2012–2023 годах

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Аннотация
Цель статьи – оценка гидрохимического состава вод реки Черной, являющейся основным поставщиком пресных вод в г. Севастополе, а также влияния стока этой реки на экологию Севастопольской бухты. Река Черная, вытекающая из Чернореченского водохранилища, на своем пути пересекает Байдарскую долину, вбирает несколько притоков, не прошедших через геохимический фильтр водохранилища, теряет бóльшую часть своего потока на нескольких водозаборах в районе с. Хмельницкого и превращается в ручей. Вновь становится относительно полноводной рекой после поступления в нее оборотных вод очистных сооружений возле с. Сахарная Головка и наконец впадает в Севастопольскую бухту возле Инкерманского ковша. Чтобы проследить за изменением гидрохимического состава вод реки по мере продвижения от Чернореченского водохранилища до устья, для 10 станций, расположенных на реке, и двух условных станций на акватории бухты (осредненные данные для Инкерманского ковша и 30 станций бухты) были построены графики средних значений концентраций некоторых гидрохимических элементов для четырех гидрологических сезонов 2012–2023 гг. Выявлено, что воды Чернореченского водохранилища и реки Черной сходны по составу на протяжении почти всего русла от выхода на поверхность до водозабора под с. Штурмовым, далее состав вод реки определяют сточные воды. Непосредственно река Черная (без учета сточных вод) поставляет в Севастопольскую бухту значительные количества нитратов, кремнекислоты и аммония; фосфаты поступают со сточными водами.

Ключевые слова: река Черная, Крым, гидрохимический состав, биогенные элементы, карбонатная система, Севастопольская бухта

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Introduction

In fact, the Chernaya River flows out of the Skelskaya Cave, almost immediately (two hundred metres from the source) begins to fill the Chernorechenskoye Reservoir (CR), then comes again to the surface through the water intake under the reservoir and flows into the eastern apex of Sevastopol Bay after about 35 km. This river is one of the most important elements of the Sevastopol ecology. Firstly, the Chernaya River is the main external supplier to the bay waters of various hydrochemical components, such as nutrients [1], carbonate system elements [2], trace elements [3], organochlorine compounds [4] and aromatic polycyclic hydrocarbons [5]. Secondly, the waters of the Chernaya River are the main source of fresh water for the city of Sevastopol, and the quality of the water is deemed satisfactory. In accordance with work [1)], a mere 1.7% of the fresh water supplied to Sevastopol fails to meet the requisite sanitary and chemical indicators. This water is drawn from the North Side water supply system.

The influence of the Chernaya River on the hydrochemical composition of the Sevastopol Bay waters has been the subject of considerable scientific investigation [6–8], including in the most recent works [1–5], yet the changes that occur in the composition of waters on their way from the CR to the river mouth have attracted much less attention from researchers. The population of Sevastopol is so accustomed to the fact that the water supply system provides sufficiently clean water (additional purification is still recommended for food use) that they demonstrate interest in water supply problems only when there are interruptions in supply [2)] or where the quality of running water is uncertain, as was the case following the dam failure on the Baydarka River in 2006 [3)].

In light of the significance of observations pertaining to the impact of the Chernaya River waters on the Sevastopol Bay ecosystem, Marine Hydrophysical Institute (MHI), which initiated its investigation into the hydrological and hydrochemical characteristics of the bay waters towards the end of the 20th century, incorporated the lower Chernaya River waters (from the CR to the Inkerman basin (IB)) into the scope of its study in 2006. The principal findings of the results of the 2006–2011 observations published in [9] indicate that the Chernaya River waters up to the water intake near the village of Shturmovoe exhibit a relatively consistent hydrochemical composition with the CR water, which the surrounding villages have been utilising for food purposes for an extended period without any notable concerns. However, the hydrochemical composition of the water deteriorates significantly between the village of Shturmovoe and the railway bridge across the river.

Thus, the river is conditionally divided into two parts on the basis of water quality. The water from one part is suitable for domestic purposes, while the water from the second part, which contains significant amounts of nutrients, is comparable to phosphorus-containing fertiliser for agricultural needs. All these unfavourable changes in water composition are attributed to the activity of the KOS-3 sewage treatment plant in the village of Sakharnaya Golovka [10], which discharges its wastewater into the river below the water intake near the village of Shturmovoe.

Recent studies devoted to the Chernaya River have addressed the significant issue of water composition alteration during the transition from fresh to saline conditions in the estuary zone between the railway and highway bridges [4, 10–13]. Nevertheless, these studies fail to address the issue of changes in water composition on the route from the reservoir to the IB, which was the objective of the research initiated in 2006 and continued until the present (the most recent survey was conducted in December 2023).

[1)] Antonova, A., 2017. You Can Drink Tap Water. *Sevastopol'skaja Gazeta*. Online available at: https://sevastopol.press/2017/09/04/vodu-iz-krana-mozhno-pit/ [Accessed: 12 April 2024].

[2)] Aleshina, N., 2024. Emergency due to Mud. Sevastopol Remains without Water for the Fourth Day. *KRym.AIF.RU*. Available at: https://krym.aif.ru/society/jkh/chs_iz-za_gryazi_sevastopol_ostayotsya_bez_vody_chetvertye_sutki [Accessed: 12 April 2024].

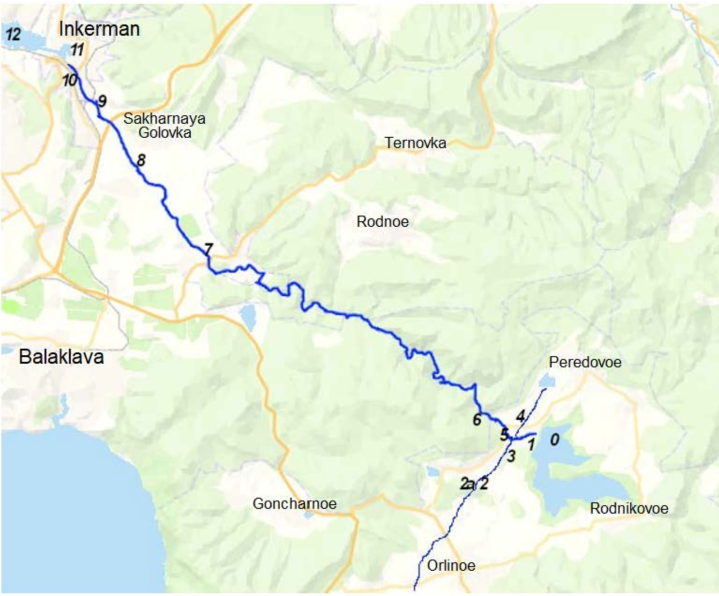
[3)] Ryabov, M., 2006. The Tap Water is Poisoned! *Sevastopol'skaja Gazeta*. Available at: https://sevastopol.press/2006/11/09/voda-otravlena/ [Accessed: 12 April 2024].

This study aims at analysing changes in the hydrochemical composition of the waters of the lower Chernaya River in 2012–2023.

Materials and methods

The findings of the quarterly environmental monitoring of Sevastopol Bay at 36 stations and the lower Chernaya River at 10 stations (Fig. 1), conducted by the MHI Marine Biogeochemistry Department were employed in this study. The sequence of the stations is as follows: *1–0–4–6–5–3–2–2a–7–8–9–10*. Stations *11*, *12* were carried out in advance, during the Sevastopol Bay expedition, for details see [15]. From 2012 to December 2023, a total of 36 expeditions were conducted. While surveys were planned in each of the four hydrological seasons, not all of them were carried out. The water samples were transported to a fixed onshore laboratory within a timeframe of 2–3 hours after collection, where they were subjected to immediate analysis. Before analysing dissolved mineral forms of nutrients (silicic acid, phosphates, nitrate, nitrite, ammonium), water samples were pre-filtered through a membrane filter with a pore size of 0.45 µm.

Dissolved oxygen content was determined by the Winkler method [16], mineral forms of nutrients (phosphates, silicon, nitrate and nitrite nitrogen) were analysed photometrically in accordance with work [4)].



F i g . 1 . Map of stations for sampling water from the River Chernaya. Notations are given in the table below

[4)] Bordovsky, O.K. and Ivanenkov, V.N., eds., 1978. [*Methods of Hydrochemical Studies of the Ocean*]. Moscow: Nauka, 271 p. (in Russian).

Station number	Coordinates		Reference points
	N	E	
0	44.492033	33.809025	Reservoir surface over the water intake
1	44.490475	33.805073	Water intake under the reservoir
2	44.475604	33.790574	Baydarka River, former pond
2a	44.475604	33.790574	Concrete trough bypassing the pond
3	44.486921	33.794287	Baydarka River, pipe-bridge outside the village of Ozernoe
4	44.492832	33.792845	Urkusta River
5	44.492115	33.792624	Highway bridge of the village Ozernoe–the village of Peredovoe
6	44.496838	33.784174	Gauging station near Krasnaya Skala
7	44.545083	33.662152	Gauging station near the village of Khmelnitskoe
8	44.574922	33.629644	Highway bridge near the village of Shturmovoe
9	44.595650	33.609477	Railway bridge near Inkerman
10	44.605719	33.601888	Highway bridge near Inkerman

Note: Station *11* – the average over three stations of the Inkerman basin, station *12* – the average over 33 stations in Sevastopol Bay.

Ammonium nitrogen was determined using the modified method of Sagi–Solorzano based on the phenol-hypochlorite reaction using sodium nitroprusside and sodium citrate [5)]. The pH value was determined potentiometrically in an open cell with calibration by NBS scale buffer solutions; total alkalinity was determined by direct titration with potentiometric termination.

The Grafer programme was employed to plot the figures of sequential changes in the composition of each hydrochemical element when progressing from the CR surface to Sevastopol Bay.

[5)] Bordovsky, O.K. and Chernyakova, A.M., eds., 1992. [*Modern Methods of Hydrochemical Studies of the Ocean*]. Moscow: IO AN SSSR, 199 p. (in Russian).

Fig. 2 shows that the contribution of wastewater at st. *9* does not change the values of these parameters too much. But the content of elements of the main biogenic cycle is very much influenced by the wastewater appearing at st. *9* (Fig. 3). The phosphate concentration variations are the most contrasting in this respect. In the CR waters, its content is insignificant in all seasons, at the level of 0.1 µM (Fig. 3, *a*). After the inflow of the Baydarka River waters (phosphates are almost absent in the Urkusta River waters (st. *4*) passing through the geochemical filter), the phosphate concentration at st. *5–7* remains about the same as in the CR. And after wastewater inflow, the minimum phosphate concentration at st. *9* becomes higher than 2 µM, which is 20–50 times higher than its content in the CR waters.

F i g . 3 . Contents of phosphates (*a*), silicic acid (*b*), nitrates (*c*) and ammonium (*d*) at the stations of the lower Chernaya River in 2012–2023

The concentration of silicic acid in the CR waters during the summer months is approximately equivalent to that observed in the waters of the IB and the entire bay, ~ 5 µM (Fig. 3, *b*). In other seasons, the concentration of silicic acid in the CR waters is noticeably higher, at 20 µM. This value increases markedly after the inflow of tributaries containing silicic acids about 5 to 8 times higher than in the CR, ranging from 80 to 160 µM. This results in a slight increase in silicic acid content at st. *5–7*, which then almost doubles at st. *9* after wastewater intake. Thereafter, a monotonic decrease in silicic acid concentration upon contact with seawater at st. *10*, *11*, *12* takes place.

Seasonal variations in nitrate content in the CR waters have been observed, with accumulation during winter, extraction in spring, and increased consumption during summer and autumn. At the same time, nitrate concentration in the CR waters is always higher than in the bay waters (Fig. 3, *c*). The Baydarka River has a nitrate concentration that is 3–4 times higher than that of the CR (it is important to note again that the geochemical filter in the Urkusta River has a similar nitrate concentration to that of the CR). This has a negligible impact on the water composition at st. *5–7* upstream of the water intake. Below the water intake, wastewater inflow leads to a 2–4 times increase in nitrate concentration at st. *9* which then remains at a stable level of 80 µM. The decrease in nitrate content upon contact with seawater is gradual; at st. *10* nitrate concentrations become approximately the same as in the CR, after which they decrease by an order of magnitude in the IB and subsequently throughout the bay.

The dynamics of ammonium content in the CR surface waters are qualitatively opposite to those of nitrate content. During the winter and spring months, when nitrate levels are elevated, ammonium concentrations are typically low, with an average value of less than 0.5 µM (Fig. 3, *d*). In summer, nitrate begins to be consumed during photosynthesis, while ammonium accumulates as a result of decomposition of suspended organic matter (SOM) (SOM decomposition process provides higher ammonium concentrations in the CR bottom waters compared to the surface waters). By autumn, the process of ammonium accumulation in the CR surface waters intensifies (photosynthesis weakens, SOM decomposition continues). It is also noteworthy that while the nitrate concentration in the CR surface and bottom waters is approximately equivalent, ammonium is consistently present at higher levels in bottom waters than in surface ones. It can be assumed that this is caused by the decomposition of deposited SOM near the bottom. Wastewater increases ammonium content at st. *9* predictably, about 2–4 times higher than at st. *5–7*. The decrease in ammonium as well as nitrate concentrations in contact with seawater during the progression from st. *10* to st. *12* is not immediate, but gradual.

Discussion

Among the above results, the main ones should be highlighted: the role of the tributaries of the Chernaya River (the Baydarka and Urkusta Rivers) and the sewage treatment plants in changing the composition of the CR waters; the rate of assimilation of the river waters by the bay seawater.

Figs. 2, 3 demonstrate that the inflow of tributary waters (st. *2–4*) containing significantly more of all nutrients and having higher alkalinity than the CR waters does not significantly affect the composition of the Chernaya River waters. Only silicic acid content at st. *5–7* (river waters up to the intake) exhibits a notable increase following the inflow of tributary waters. In contrast, the concentrations of other nutrients and alkalinity value remain approximately at the same level as in the CR.

With regard to the waters of wastewater treatment facilities, the impact of which is evident just before the mouth at st. *9*, they contain significantly higher levels of nutrients throughout the year than the waters of the Chernaya River at st. *5–7*: phosphates by 10–100 times, silicic acid, nitrates and ammonium by about 2 times.

Such an increase in concentrations is almost levelled out before the river water enters the IB, the concentrations of all biogenic elements are markedly reduced at st. *10* compared to st. *9*, and the composition of water in the IB is almost the same as in Sevastopol Bay. That is, the main decrease in the content of nutrients and alkalinity value occurs at the river mouth, between st. *9* and st. *10*, where the Chernaya River waters are diluted with marine waters and finally turn into them at st. *10*, where salinity is rarely less than 17. It is no coincidence that this area has attracted increased attention from the scientific community [4, 5, 10–13].

A comparison of the composition of the waters of the CR (st. *0–1*) and the bay (st. *12*) reveals that the waters of the Chernaya River contribute only silicic acid and nitrates to the bay, while phosphates enter the bay exclusively from the waters of the Sakharnaya Golovka wastewater treatment facilities. Furthermore, the effluent from the wastewater treatment facilities contains silicic acid, nitrates and ammonium.

Conclusions

The hydrochemical monitoring of the Chernaya River waters shows the following:

1. The oxygen saturation of the waters of the CR and the lower Chernaya River up to the water intakes is approximately 100% in all seasons, and the pH value is within the range of 8.25–8.30.

2. The total alkalinity of the CR and the Chernaya River exhibits seasonal variations. During the winter and spring months, it is higher than the alkalinity of the Sevastopol Bay waters. Conversely, during the summer and autumn, it is lower.

3. The waters of the CR and the Chernaya River exhibit elevated concentrations of silicic acid and nitrates throughout the year, in comparison to the Sevastopol Bay waters. The ammonium concentrations in the river and bay waters are found to be approximately equivalent.

4. The phosphate content of the reservoir and river waters is approximately equivalent, yet the river subsequently becomes the source of phosphates for the bay following the introduction of wastewater from the treatment plant.

5. The waters of the Baydarka River (a tributary of the Chernaya River), which have not undergone geochemical filtration via the CR, consistently exhibit markedly elevated concentrations of silicic acid, nitrates, ammonium and phosphates as well as a higher alkalinity value than the river waters. This presents a potential risk to the quality of the water supplied to Sevastopol.

REFERENCES

1. Orekhova, N.A., Medvedev, E.V. and Ovsyany, E.I., 2018. Influence of the River Chernaya Water on Hydrochemical Regime of the Sevastopol Bay (the Black Sea). *Ecological Safety of Coastal and Shelf Zones of Sea*, (3), pp. 84–91. https://doi.org/10.22449/2413-5577-2018-3-84-91 (in Russian).
2. Moiseenko, O.G., Khoruzhiy, D.S. and Medvedev, E.V., 2014. Carbonate System in the Chernaya River Waters and in the Zone of the Chernaya River – Sevastopol Bay Biogeochemical Barrier (the Black Sea). *Morskoy Gidrofizicheskiy Zhurnal*, (6), pp. 47–60 (in Russian).
3. Malakhova, L.V., Proskurnin, V.Yu., Egorov, V.N., Chuzhikova-Proskurnina, O.D. and Bobko, N.I., 2020. Trace Elements in the Chernaya River Water and Evaluation of their Income with the Riverine Inflow into the Sevastopol Bay in Winter 2020. *Ecological Safety of Coastal and Shelf Zones of Sea*, (3), pp. 77–94. https://doi.org/10.22449/2413-5577-2020-3-77-94 (in Russian).
4. Malakhova, L.V., Egorov, V.N., Malakhova, T.V., Lobko, V.V., Murashova, A.I. and Bobko, N.I., 2020. Organochlorine Compounds Content in the Components of the Black River Ecosystem and Assessment of their Inflow to the Sevastopol Bay in the Winter Season 2020. *International Journal of Applied and Fundamental Research*, (5), pp. 7–14. https://doi.org/10.17513/mjpfi.13061 (in Russian).
5. Soloveva, O.V., Tikhonova, E.A., Mironov, O.A. and Barabashin, T.O., 2021. Polycyclic Aromatic Hydrocarbons in the Bottom Sediments of the River – Sea Mixing Zone on the Example of the River Chernaya and the Sevastopol Bay (the Black Sea). *Physical Oceanography*, 28(3), pp. 338–347. https://doi.org/10.22449/1573-160X-2021-3-338-347
6. Ovsyany, E.I., Romanov, A.S., Min'kovskaya, R.Ya., Krasnovid, I.I., Ozyumenko, B.A. and Zymbal, I.M., 2001. Basic Polluting Sources of Sea near Sevastopol. In: MHI, 2001. *Ekologicheskaya Bezopasnost' Pribrezhnoy i Shel'fovoy Zon i Kompleksnoe Ispol'zovanie Resursov Shel'fa* [Ecological Safety of Coastal and Shelf Zones and Comprehensive Use of Shelf Resources]. Sevastopol: ECOSI-Gidrofizika. Iss. 2, pp. 138–152 (in Russian).
7. Ivanov, V.A., Ovsyany, E.I., Repetin, L.N., Romanov, A.S. and Ignatyeva, O.G., 2006. *Hydrological and Hydrochemical Regime of the Sebastopol Bay and its Changing under Influence of Climatic and Anthropogenic Factors*. Sevastopol: Marine Hydrophisical Institute NAS of Ukraine, 90 p. (in Russian).
8. Ovsyany, E.I., Artemenko, V.M., Romanov, A.S. and Orekhova, N.A., 2007. The Chernaya River Discharge as a Factor Affecting the Water-Salt Regime Forming and Ecological State of the Sevastopol Bay. In: MHI, 2007. *Ecological Safety of Coastal and Shelf Zones and Comprehensive Use of Shelf Resources*. Sevastopol: MHI. Iss. 15, pp. 57–65 (in Russian).
9. Kondratiev, S.I., 2014. [Study of the Hydrochemical Structure of the Chernaya River (Crimea) in 2006–2011]. In: MHI, 2014. *Ekologicheskaya Bezopasnost' Pribrezhnoy i Shel'fovoy Zon i Kompleksnoe Ispol'zovanie Resursov Shel'fa* [Ecological Safety of Coastal and Shelf Zones and Comprehensive Use of Shelf Resources]. Sevastopol: MHI. Iss. 28, pp. 176–185 (in Russian).
10. Narivonchik, S.V., 2024. Variability of Nutrient Concentration in Waters of the Chernaya River Estuarine Zone (Sevastopol Region). *Ecological Safety of Coastal and Shelf Zones of Sea*, (1), pp. 82–97.
11. Boltachev, A.R., Karpova, E.P. and Danilyuk, O.N., 2010. Peculiarities of thermohaline parameters and ichthyocenosis of the Chernaya River estuary (the Sevastopol Bay). *Marine Ekological Journal*, 9(2), pp. 23–36 (in Russian).

12. Mezentseva, I.V. and Sovga, E.E., 2019. Self-Purification Ability of the Ecosystem of the East Part of the Sevastopol Bay with Respect to Inorganic Nitrogen. *Ecological Safety of Coastal and Shelf Zones of Sea*, (1), pp. 71–77. https://doi.org/10.22449/2413-5577-2019-1-71-77 (in Russian).
13. Rudneva, I. and Shayda, V., 2019. Bioassay of the Estuary Waters of the Chernaya River (Bay of Sevastopol, Black Sea) Using the Brine Shrimp Artemia (Crustacea: Brachiopoda). *Ecosystem Transformation*, 2(3), pp. 76–84. https://doi.org/10.23859/estr-190213
14. Sovga, E.E. and Khmara, T.V., 2020. Influence of the Chernaya River Runoff during High and Low Water on the Ecological State of the Apex of the Sevastopol Bay Water Area. *Physical Oceanography*, 27(1), pp. 28–36. https://doi.org/10.22449/1573-160X-2020-1-28-36
15. Orekhova, N.A. and Varenik, A.V., 2018. Current Hydrochemical Regime of the Sevastopol Bay. *Physical Oceanography*, 25(2), pp. 124–135. https://doi.org/10.22449/1573-160X-2018-2-124-135
16. Carpenter, J.H., 1965. The Chesapeake Bay Institute Technique for the Winkler Dissolved Oxygen Method. *Limnology and Oceanography*, 10(1), pp. 141–143. https://doi.org/10.4319/lo.1965.10.1.0141
17. Kondratev, S.I. and Orekhova, N.A., 2023. Potential Threats to the Ecological State of Water in the Sevastopol Bay. *Lomonosov Geography Journal*, 78(6), pp. 3–14. https://doi.org/10.55959/MSU0579-9414.5.78.6.1 (in Russian).

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