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**Экологическая безопасность  
прибрежной и шельфовой зон моря**



Ecological Safety of Coastal  
and Shelf Zones of Sea

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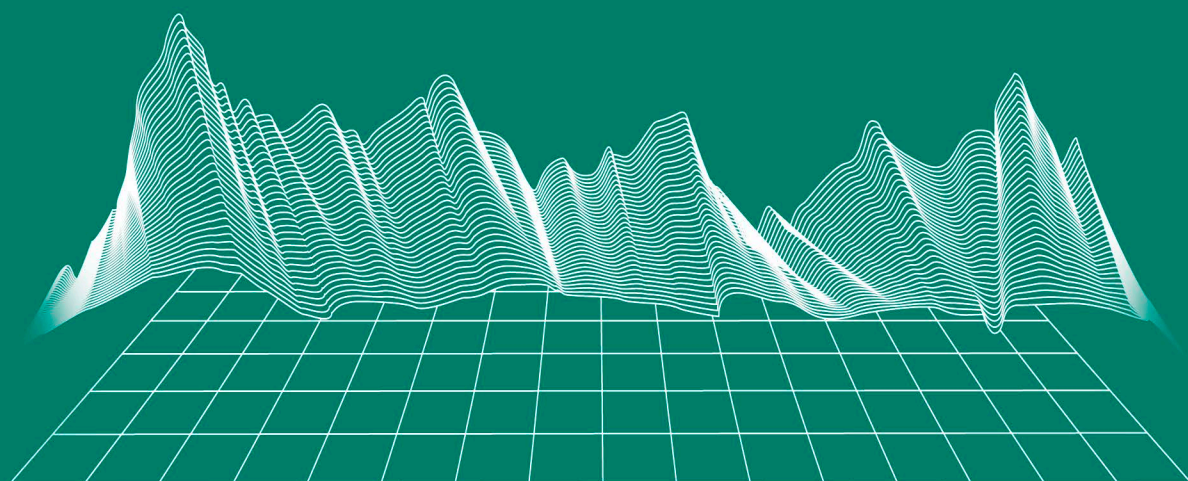
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Original paper

## Geomorphological Resources for the Development of the Tourist and Recreational Complex in the Azov Region

**E. A. Pozachenyuk**

*V.I. Vernadsky Crimean Federal University, Simferopol, Russia*

*e-mail: pozachenyuk@gmail.com*

### Abstract

The integration of the new Azov region territories into the unified tourism space of the Russian Federation requires updating information about their tourist and recreational potential, the most important component of which is geomorphological resources. The paper aims to typify the geomorphological resources of the Azov Sea coast and assess their favourability for recreation. The study is based on the materials of a comprehensive expedition of the Russian Geographical Society (summer 2024), including remote sensing data interpretation, field observations and study of more than 430 key sites, as well as GIS analysis. For the first time, 84 geomorphological sites have been identified and characterised for the entire coast. The typification was carried out according to genesis, morphology, lithology and coastal dynamics. It has been established that the most valuable recreational resources are accumulative spits, bay-reef complexes, the Don River delta and mud volcanoes of Taman. Twenty-six sites (31%) have a high degree of favourability, 22 sites (26%) have a medium one, 23 sites (27%) have a low one and 13 sites (16%) have a very low one. The main limiting factors are intense abrasion (up to 8 m/year), cliff height, landslide processes, eustatic sea level rise causing beach waterlogging, flooding and water scarcity. The results indicate the need to shift from mass beach recreation to adaptive forms of tourism (ecological, sports, health-improving) and to undertake mandatory engineering preparation of the developed areas. The materials can be used to substantiate tourism development strategies and regional master plans for the Azov region.

**Keywords:** Russia, Azov Sea coast, geomorphological resources, resource assessment, recreation, tourism

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# Геоморфологические ресурсы развития туристско-рекреационного комплекса Приазовья

Е. А. Позаченюк

ФГАОУ ВО «Крымский федеральный университет имени В. И. Вернадского»,  
Симферополь, Россия

e-mail: pozachenyuk@gmail.com

## Аннотация

Интеграция новых регионов Приазовья в единое туристское пространство Российской Федерации требует актуализации информации об их туристско-рекреационном потенциале, важнейшей составляющей которого являются геоморфологические ресурсы. Цель работы – типизация геоморфологических ресурсов побережья Азовского моря и оценка степени их благоприятности для рекреации. Исследование базируется на материалах комплексной экспедиции Русского географического общества (лето 2024 г.), включающих данные дешифрирования космических снимков, маршрутных наблюдений и результаты полевых исследований более 430 ключевых участков, а также ГИС-анализ. Впервые для всего побережья выделено и охарактеризовано 84 геоморфологических участка. Типизация проведена по генезису, морфологии, литологии и динамике берегов. Установлено, что наиболее ценными рекреационными ресурсами являются аккумулятивные косы, бухтово-рифовые комплексы, дельта Дона, грязевые вулканы Тамани. Высокую степень благоприятности имеют 26 участков (31 %), среднюю – 22 (26 %), низкую – 23 (27 %), очень низкую – 13 (16 %). Главные лимитирующие факторы – интенсивная абразия (до 8 м/год), высота клифов, оползневые процессы, эвстатическое повышение уровня моря, вызывающее заболачивание пляжей, подтопление и безводность. Результаты свидетельствуют о необходимости перехода от массового пляжного отдыха к адаптивным формам туризма (экологический, спортивный, лечебно-оздоровительный) и обязательной инженерной подготовке осваиваемых территорий. Материалы могут быть использованы для обоснования стратегий развития туризма и региональных мастер-планов Приазовья.

**Ключевые слова:** Россия, побережье Азовского моря, геоморфологические ресурсы, оценка ресурсов, рекреация, туризм

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## Introduction

The accession of the new Azov region territories to the Russian Federation has given a significant impulse to the study of the coastal part of the sea as an integral system. The relevance of these studies today is due to the state demand for the development of a strategy for the development of the Azov Basin water area and the Azov coast. One of the important tasks in the field of tourism is the integration of the new regions into a unified tourism space based on updating information about their tourist and recreational potentials. The geomorphological conditions and resources of the Azov Sea coast are the most important component of the development of tourism and recreation in this macroregion.

It is relief that determines the attractiveness of landscapes, opportunities for beach, educational, sports and health-improving recreation, and also limits the economic development of the territory.

General issues of geomorphology and dynamics of the Azov Sea coasts are considered in works devoted to the characteristics of the coast and types of shores, as well as in atlas materials and other studies <sup>1), 2), 3), 4), 5), 6)</sup>.

Regional studies of the coastal zone were conducted in Crimea <sup>7)</sup> [1, 2], Rostov Oblast <sup>5)</sup> [3, 4] and Krasnodar Krai <sup>8)</sup> [4, 5]. A significant contribution to the study of abrasion processes and sedimentation was made by Yu. V. Artyukhin and V. A. Mamykina <sup>6)</sup>.

Recreational-geographical study of the coast began in the 1960s within the framework of district planning projects (Giprograd). During this period, the prospects for organising treatment and short-term recreation <sup>9)</sup>, as well as the physico-geographical conditions of recreational activity [6], were assessed. A comprehensive description of the Azov recreational region as a “pioneer” type region is presented in the monograph of the Institute of Geography of the USSR Academy of Sciences <sup>10)</sup>, where its role as a “reserve” region for organising recreation for industrial areas of Donbass and the Dnieper region is noted. Dissertation works by N. M. Sazhneva <sup>11)</sup> and D. S. Veselov <sup>12)</sup> specified the territorial organisation and problems of individual

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<sup>1)</sup> Chekunov, A.V., 1972. [*The Structure of the Earth's Crust and Tectonics in the South of the European Part of the USSR*]. Kiev: Naukova Dumka, 176 p. (in Russian).

<sup>2)</sup> Chekunov, A.V., Veselov, A.A. and Gilkman, A.I., 1976. [*The Geological Structure and Evolutionary History of the Black Sea Trough*]. Kiev: Naukova Dumka, 160 p. (in Russian).

<sup>3)</sup> Eremeev, V.N., ed., 2009. *Oceanographic Atlas of the Black Sea and the Sea of Azov*. Kiev: Derzhgidrografiya, 356 p. (in Ukrainian).

<sup>4)</sup> Mamykina, V.A and Khurstalev, Yu.P., 1980. [*The Coastal Zone of the Sea of Azov*]. Rostov-on-Don: Izd-vo RGU, 176 p. (in Russian).

<sup>5)</sup> Arkhipova, O.E., Bulysheva, N.I., Gargopa, Yu.M., Golubeva, N.I., Inzhebeikin, Yu.I., Kovaleva, G.V., Kondakov, A.A., Krasnorutskaya K.V., Lebedeva N.V. [et al.], 2011. *Ecological Atlas of the Sea of Azov*. Rostov-on-Don: SSC RAS, 328 p. (in Russian).

<sup>6)</sup> Artyukhin, Yu.V. and Mamykina, V.A., 1981. [Interannual Variability in the Supply of Abrasion Material to the Coastal Zone of the Sea of Azov and its Role in Coastal Sedimentation]. In: V. P. Zenkovich, E. I. Ignatova, and S. A. Lukianova, eds., 1981. [*The Coastal Zone of Sea*]. Moscow: Nauka, pp. 67–72 (in Russian).

<sup>7)</sup> Reference Materials, 1994. [*Scheme for the Engineering Protection of the Azov Coast of Ukraine*]. Yalta: OOO Inzhazhchita, 120 p. (in Russian).

<sup>8)</sup> Belyaev, V.B., 1973. Addressing Issues Relating to the Engineering Preparation of the Territory in the Regional Planning of the Azov Coast in the Krasnodar Krai. In: Kiev, 1973. *Issues in Regional Planning and Settlement*. Kiev: Budivel'nik, pp. 45–58 (in Russian).

<sup>9)</sup> Rybalov, L.G., 1969. [Architectural and Planning Organisation of a Resort Area on the Azov Sea Coast]. In: Kiev, 1969. [*Design of Resorts and Leisure Areas*]. Kiev: Budivel'nik, pp. 123–135 (in Russian).

<sup>10)</sup> Preobrazhensky, V.S. and Krivosheev, V.M., eds., 1980. [*Geography of Recreational Systems of the USSR*]. Moscow: Nauka, 219 p. (in Russian).

<sup>11)</sup> Sazhneva, N.M., 1988. [*The Spatial Organisation of Coastal Recreational Systems Based on an Oasis Development Model (the case of the Western Azov region)*. PhD Thesis. *Geographical Sciences*]. Leningrad, 210 p. (in Russian).

<sup>12)</sup> Veselov, D.S., 2007. [*The Recreational Potential of the Temryuk District in the Krasnodar Region: Challenges and Prospects for Development*. PhD Thesis. *Geographical Sciences*]. Krasnodar, 168 p. (in Russian).

areas (Western Azov region, Temryuk district). Engineering and technical aspects of territory preparation, including coastal protection measures, were considered in the works of V. B. Belyaev<sup>8)</sup>. In the post-Soviet period, works appeared on the comparative analysis of the Black Sea and Azov Sea coasts [7], assessment of the tourist and recreational potential of the Russian Azov region<sup>13)</sup> and conceptual development models for the Crimean Azov region [8].

An analysis of scientific and methodological materials shows that until recently the Azov region was not considered as a single object of strategic planning in the field of tourism. Most publications are compilative in nature or limited to the administrative boundaries of the old regions. Comprehensive expeditionary studies covering the entire Azov Sea coast within the new borders of the Russian Federation, including field assessment of geomorphological resources for the development of tourist and recreational activity, have not been conducted to date.

The aim of the article is, based on the data of a comprehensive expedition, to typify the geomorphological resources of the Azov Sea coast and assess the degree of their favourability for recreational purposes.

### Materials and Methods

The source of primary information was the materials obtained during the field stage of the comprehensive research expedition along the Azov Sea coast (summer 2024), organised with the support of the Russian Geographical Society.

The conceptual and methodological basis of the research included interpretation of high-resolution satellite images (SAS.Planet program, Bing Satellite map), route observations with description of geomorphological conditions and photo documentation, data processing and mapping in GIS (QGIS 3.16.16).

The typification of relief (geomorphological) resources for the development of recreation and tourism was carried out according to criteria ensuring the relative homogeneity of the identified sites, such as genesis, geological structure, geomorphological conditions (predominant relief), height of the bedrock shore, erosional dissection, depth of vertical dissection, development of negative processes, and the presence of special (attractive) geomorphological objects. Factors limiting the development of recreation were determined. As a result of the analysis, 84 geomorphological sites of the Azov Sea coast were identified. The complete characteristics of the geomorphological sites are given in Table<sup>14)</sup>.

Based on a synthesis of field data and published sources for each geomorphological site<sup>1)-8), 15)</sup> [1–5, 9], the degree of favourability of its use in recreation was determined on a four-point scale: 1 – high degree, 2 – medium, 3 – low, 4 – very low.

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<sup>13)</sup> Kushnir, K.V., 2022. [*Geographical Characteristics of the Tourism and Recreational Potential of the Russian Azov Region. PhD Thesis. Geographical Sciences*]. Rostov-on-Don, 180 p. (in Russian).

<sup>14)</sup> Supplemental materials are available electronically at: [https://ecological-safety.ru/static/assets/files/2026/03/geomorf\\_resursy.pdf](https://ecological-safety.ru/static/assets/files/2026/03/geomorf_resursy.pdf)

<sup>15)</sup> Shnyukov, E.F., Sobolevsky, Yu.V., Gnatenko, G.I., Naumenko, P.I. and Kutniy, V.A., 1986. [*Mud Volcanoes of the Kerch-Taman Region*]. Kiev: Naukova Dumka, 152 p. (in Russian).

## Results and Discussion

The geomorphological structure of the Azov Sea coast is heterogeneous and is determined by the geostructural position within the Black Sea Depression, the junction zone of the East European Platform with the Scythian Platform and the Indolo-Kuban Trough<sup>1), 2)</sup>. The shores are composed mainly of loose rocks (loess-like loams, Neogene clays, sands, shell material), which determines their low resistance to abrasion. The height of the bedrock shores varies from 1–2 to 60–70 m (Taman Peninsula, Kazantip Cape). The coastal shelf (to the 10 m isobath) is characterised by the development of accumulative forms: spits, barrier beaches, bars, limans<sup>4)</sup>. As noted by Yu. V. Artyukhin and V. A. Mamykina<sup>6)</sup>, abrasion material plays an important role in sedimentation in the coastal zone.

As a result of the analysis, 84 geomorphological sites were grouped by region (Fig. 1, additional materials<sup>14)</sup> on the website) and assessed by the degree of favourability of use for recreational purposes (Fig. 2). Below is a description of the regions with an indication of site numbers according to Table<sup>14)</sup>.

The Azov coast of the Republic of Crimea belongs to the Indolo-Kuban Trough of the marginal part of diapiric uplifts and is characterised by subsidence of the shelf zone of the Azov Sea at a rate of 2 mm/year. The Arabat Spit belongs to the Sivash Depression (margin of the Scythian Platform). The relief to the northeast of the Par-pach Ridge is represented by a hilly-ridged plain with alternating small uplifts of ellipsoidal elongated shape and depressions. Ten geomorphological sites have been identified on the coast. Four of them received a high assessment of the degree of favourability for use in recreation (sites 5, 7, 9, 10). Site 5 (Chokrak) is a basin with a lake surrounded by uplands up to 100 m high and possesses valuable therapeutic muds (Fig. 3). The Kazantip site (7) is distinguished by bay relief with bryo-zoan capes up to 106 m high. Sites 1, 2, 4, 6, 8 have a medium assessment. The Zhukovo-Yurkinsky site (3) received a low assessment; landslide processes are actively manifested there<sup>7)</sup> [1, 2]. The limiting factors for the development of recreation are negative processes (abrasion-landslide, abrasion-collapse); the height and steepness of coastal slopes, limited accessibility of beaches; insufficiency of water resources within the Arabat Spit.

The Black Sea Lowland, within which Kherson Oblast is located, is characterised by monotonous accumulative relief forms. The flat surface of the loess-like plain is slightly inclined towards the sea and has low elevations from 1–5 to 20 m, weak relief dissection and a ravine-gully network. There are small rivers here that have no permanent flow. The coast of Kherson Oblast (see Fig. 1) includes three large geomorphological sites (11–13) and is characterised by alternation of abrasion and accumulation areas with the formation of Azov-type spits. According to the degree of favourability of geomorphological conditions for the development of recreation (see Fig. 2), two sites with a high degree of favourability are distinguished: the north of the Arabat Spit (11) and the Biryuchy Island Spit (13) – and one site, Genichesk (12), with a medium one.



Fig. 1. Geomorphological resources of the Azov Sea coast for recreation development



Fig. 2. The degree of favourability of the geomorphological resources of the Azov Sea coast for recreational purposes



Fig. 3. Chokrak Salt Lake (site 5)

The shores of the Arabat Spit, washed by the Sivash waters, are represented by low areas with very narrow beaches or benches, in places waterlogged; in some areas they are steep erosion-collapse shores with ravine dissection, for example Genichesk Kut (Fig. 4). On the Azov Sea side, the shores are accumulative-abrasion. The northern part of the Arabat Spit (11) and the Biryuchy Island Spit (13) received a high assessment. The Arabat Spit on this segment is composed of marine sands with shell material; the height of the barrier beach is 1–5 m; the width of beaches reaches 40–60 m. The Biryuchy Island Spit (13) is an accumulative body 1–1.5 m high with shell-sand beaches. The Genichesk site (12) is characterised by abrasion-collapse cliffs up to 20 m high, composed of loess-like loams and clays. Coastal protection structures in the site have been destroyed, which reduces its potential to a medium degree of favourability. The limiting factors for the development of recreation within the coast of Kherson Oblast are intense abrasion of the Azov Sea coast (the coast of Genichesk – maximum abrasion 4.5 m/year, average 1.1 m/year; to the east – from 1.5 to 3 m/year) and the formation of abrasion-collapse shores, as well as erosion processes in some areas of the western coast of the Arabat Spit.

The Azov Sea coast within Zaporozhye Oblast belongs to the northern coast of the open sea and is washed by the waters of the Utlyuk, Molochnyi, Obytochna limans and Berdyansk Bay. The northern coast is located within the Ukrainian Shield and for the most part is a coastal accumulative-erosional lowland, dissected by river valleys, at the mouths of which beaches have formed. Coastal cliffs are composed of loess-like loams and Scythian clays; spits – of marine sands and shell material. The eastern coast of the oblast from the Berdyanskaya Spit to the administrative border with Donetsk Oblast is washed by the waters of the Azov Sea.



Fig. 4. Steep erosion-collapse shores of the Sivash coast of the Arabat Spit (Genichesk Kut)

According to Fig. 1 and Table <sup>14)</sup>, within the coast of Zaporozhye Oblast, eight geomorphological coastal sites have been identified, characterised by alternation of high coastal slopes (sites 17, 19, 21), spits (sites 16, 18, 20) and river valleys. Coastal slopes have absolute heights of 13–30 m, decreasing towards river valleys and spits to 3–6 m. The northwestern coast of the Utlyuk Liman is distinguished by low slopes of 4–6 m, and in the southeast from the mouth of the Bolshoy Utlyuk River to the southwest, individual sections of slopes have a height of 12 m.

In Zaporozhye Oblast, out of eight sites of the Azov Sea coast, three have a high degree of favourability of geomorphological conditions for recreation, three have a medium one and two have a low one. The accumulative spits have a high degree: Fedotova (16), Obytochna (18), Berdyanskaya (20) (see Fig. 2). Their eastern shores, facing the open sea, have developed beaches of quartz sand and shell material up to 60 m wide. On the western shores of these spits (facing the limans), beaches are mostly absent; the coast is waterlogged and overgrown with reeds (Fig. 5). The bedrock shores (sites 17, 19, 21) are abrasion-landslide and abrasion-collapse cliffs 13–30 m high, composed of loess-like loams and Scythian clays, which determines their medium degree of favourability for recreation (Fig. 6).

The limiting factors for the development of recreation within the coast of Zaporozhye Oblast are abrasion-collapse and abrasion-landslide processes, waterlogging of the western shores of the Berdyanskaya and Obytochna spits, as well as the shores of the Utlyuk and Molochnyi limans. Previously conducted engineering-geological surveys <sup>7)</sup> confirm the high dynamism of these shores.



*a*



*b*

Fig. 5. The Fedotova Spit: *a* – the western shore (Utlyuk Liman); *b* – the eastern shore (the Azov Sea)

In geomorphological terms, the coast of the Donetsk People's Republic (DPR) belongs to coastal accumulative-erosional lowland plains – the margin of the Scythian Platform. On the most elevated sections of the shore, located in the zone of the Zhdanov Horst, Neogene deposits are exposed at the base of the coastal cliff: Middle Sarmatian limestones and Kuyalnik sands. The height of the bedrock shore from the border with Rostov Oblast to the southwest gradually increases from 8–10 to 20 m (near Novoazovsk) and to 40–60 m between the Bezymyanniy farmstead and Shyrokino village, and in the Mariupol area (additional materials <sup>14)</sup> on the website). Abrasion sections of the shore alternate with accumulative sections of various sizes and forms: from large spits to narrow barrier beaches in the mouth areas of river valleys and gullies. In areas where the height of coastal cliffs is



Fig. 6. A steep cliff near the village of Stepanovka (site 17), Obytochna Bay

above 20 m (Yuryevka village, Shyrokinovo village, Bezmyanniy farmstead, Mariupol – Melekino village), the abrasion type of shore passes into the abrasion-landslide type. Landslides are of the block, frontal type with a multi-step surface of landslide terraces. The width of terraces varies from 30–40 to 100–120 m, as, for example, in the area of Zmeiny Cape (Fig. 7). Within Mariupol and to the east, the relief of the bedrock shore is complicated by ancient landslide forms and small anthropogenic landslide foci.

The DPR coast includes six sites (22–27). The Belosarayskaya (23), Bezmyannaya (25) and Krivaya (26) spits are assessed as highly favourable for recreation. They are composed of quartz sand with shell material and have asymmetric shores: eastern – with developed beaches, western – waterlogged. Sites of bedrock shores (22, 24, 27) are characterised by high (up to 65 m) abrasion-landslide cliffs (for example, within the Belosaraysky Graben and Zhdanov Horst) and received medium and low assessments. The Novoazovsk site (27) with developed landslides and collapses has a very low assessment. The data of the “Engineering Protection Scheme”<sup>7)</sup>, as well as our observations, indicate the need for coastal protection in the urbanised areas of this region.

The territory of Rostov Oblast is located within the southern part of the East European Plain. The Azov Sea coast here is represented by coastal lowland accumulative-erosional plains composed of Quaternary loess-like loams and Scythian clays; interlayers of sand, limestone and sandstones occur. The lowland shores are hydromorphic plains, often undrained and waterlogged. Coastal plains are dissected by alluvial and ravine-gully networks. The coast of the oblast occupies most of Taganrog Bay and the entire Mius Liman. The entire eastern coast of Taganrog Bay is formed by the Don River delta. The Beglitskaya, Petrushina, Pavlovo-Ochakovskaya and Chumbur spits extend into the bay within this territory.



Fig. 7. Landslide coast near Zmeiny Cape (site 22), Belosarayskaya Bay

Within the coast of the oblast, 26 geomorphological sites have been identified (28–53), 8 of which have a very low degree of favourability of geomorphological conditions (see Fig. 2), 12 – low, 2 – medium and 5 – high. At the same time, sites with a low (44%) and very low (30%) degree of favourability predominate. This is due to the wide development of active abrasion-landslide and abrasion-talus cliffs from 5–10 to 35–45 m high (sites 28, 29, 31, 33–38, 40, 42–45, 47, 48, 50–53), the shallowness of Taganrog Bay, and the narrowness and poor development of beaches. In most cases, sites with low and very low assessments have narrow or fragmentary beaches composed of sand-clay material with inclusions of semi-rounded fragments of limestone and sandstone rocks, for example the Veselo-Voznesenskiy site (Fig. 8). Sites with bogging and waterlogging of the coastal zone, with dead cliffs and formerly wide beaches, for example the Zolotokosovskiy site (33), also received a very low assessment.

The accumulative spits – Beglitskaya (32), Petrushina (39), Pavlovo-Ochakovskaya (50), Chumbur (52) – and the unique Don River delta (site 46) received a high assessment. The delta is composed of sands, sandy loams, loams and clays, is characterised by numerous branches, islands and kuts, and has high aesthetic and recreational potential, although it is subject to surge floods [3, 4, 9].

Nevertheless, despite the high degree of favourability of spits for use for recreational purposes, they are distinguished by asymmetry in the structure of their shores and the development of negative processes. For example, the northwestern shores of the Pavlovo-Ochakovskaya Spit and the western shores of Chumbur Spit are more intensively abraded (Fig. 9). Stronger winds prevail here, and the water areas are favourable for the development of windsurfing and kitesurfing.



Fig. 8. Active abrasion-talus cliffs in the area of the mouth of the Mokryi Elanchik River (site 28 – Veselo-Voznesenskiy)



Fig. 9. Chumbur Spit: *a* – abraded western coast; *b* – eastern coast – sand-and-shell beach (site 52)

The Azov Sea coast of Krasnodar Krai is for the most part located within the undulating-hilly Azov-Kuban Plain. In the coastal strip from Temryuk to Primorsko-Akhtarsk, it is a lowland hydromorphic plain extending inland up to 25 km with surface elevations of less than 2 m. The southeastern part of the krai is located within the Taman Peninsula, where low hilly ridges of sublatitudinal orientation alternate with flat inter-ridge depressions. This part includes mud volcanoes.

The coast of the krai includes 30 sites (55–84). Nine sites received a high assessment, mainly the “bend” spits – Yeyskaya (61), Kamyshevatskaya (66), Achuevskaya (74), Dolgaya (64), Yasenskaya (70), Chushka (79) – and adjacent territories with wide beaches, for example Glafirovskaya Spit (59). The spits are composed of shell material, detritus and quartz sand. The western shore of the Kamyshevatskaya Spit and the eastern shore of the Dolgaya Spit are subject to intense abrasion, which requires shore protection. A low and very low degree of favourability (40% of the territory) is characteristic of high areas with abrasion-landslide cliffs, such as



Fig. 10. High abrasion-landslide coastal slopes with narrow beaches in the area of Cape Kamenny and the village of Priazovsky (site 78)

Priazovsky-Kamenny (78) with cliff heights up to 60–70 m, as well as the coasts of the Yeysk Liman (60) and Beysug Liman (69), where bogging and waterlogging are noted. For example, the cliff in the area of Cape Kamenny and the village of Priazovsky reaches 70 m in height (Fig. 10). The active development of landslide and erosion processes almost reaches the boundaries of the village of Priazovsky and threatens the destruction of the Church of the Holy Life-Giving Trinity. Due to the height of the coastal cliffs, anti-landslide measures are difficult to implement. The use of this territory for recreational purposes is extremely problematic. A number of authors have examined these processes in detail for this region<sup>5)</sup> [4, 5]. At site 76 (Temryuk), coastal erosion of up to 7 m/year was noted in the area of the Novo-Kurchanskiy branch (Kuban River delta). The unique balneological resources of Taman (mud volcanoes) are described in detail in work<sup>15)</sup>.

### Conclusion

For the first time, based on a unified methodology, a typification and assessment of the geomorphological resources of the entire Azov Sea coast has been carried out. Eighty-four geomorphological sites have been identified, differing in genesis, morphology, lithology and coastal dynamics. It has been established that the geomorphological resources of the region are represented mainly by coastal accumulative-erosional and hydromorphic undrained lowlands, spits, coastal erosional-ridged-hilly plains with bays, as well as bay complexes with bryozoan reef capes.

According to the summary results of the assessment of 84 sites by the degree of favourability of geomorphological resources for recreation, it was established that 26 sites (31%) have a high degree of favourability, 22 (26%) – medium, 23 (27%) – low and 13 (16%) – very low. Thus, 57% of the coast has potential for tourism development, subject to consideration of natural restrictions.

The most valuable geomorphological resources include:

- spits of all types – the main beach zones: Arabat Spit (9–11), Berdyanskaya (20), Belosarayskaya (23), Dolgaya (64), Kamyshevatskaya (66), etc.;
- bay-reef complexes of the Kerch and Taman peninsulas: Kazantip (7), Karalar (6) – objects of educational and ecological tourism;
- the Don River delta (46) – a resource for water tourism and fishing;
- mud volcanoes of Taman (76, 77) and Lake Chokrak (5) – unique balneological resources.

The main geomorphological factors limiting the development of traditional beach recreation:

1. The height of coastal slopes and the loose rocks composing them contribute to the active development of abrasion-landslide, abrasion-collapse and erosion processes; moreover, abrasion (average rate about 1 m/year) in some areas reaches

4–8 m/year (Dolgaya Spit (64), Genichesk (12), Temryuk site (76)), which leads to loss of beaches and destruction of infrastructure.

2. Landslide and collapse processes developed on high cliffs (in Crimea: sites 3, 4, 8; DPR – 22, 24; Rostov Oblast – 28, 43–45, 51; Krasnodar Krai – 55, 78) destroy coastal slopes and make them dangerous for construction.

3. Eustatic sea level rise leads to bogging of formerly wide beaches (50–100 m) and their overgrowth with reeds and bulrush (Yeysk Liman (60), Beysug Liman (69)), which practically excludes these territories from swimming and beach recreation.

4. Flooding, waterlogging and unregulated economic load affect valuable accumulative bodies – spits.

5. The problem of freshwater shortage is acute on the Arabat Spit (sites 9–11) and limits stationary recreation.

Based on the results of the conducted research, the following recommendations for recreational planning are proposed:

- priority development should be given to spits and barrier beaches with a high degree of favourability, but monitoring of abrasion processes and regulated recreational load are necessary;

- sites with a medium degree of favourability are proposed to be used in a limited way: small recreational forms should be developed taking into account local risks;

- sites with a low and very low degree of favourability must be conserved (preserved as natural objects; scientific tourism is possible).

The results obtained indicate the need to shift from the model of mass beach recreation to the development of adaptive, geomorphologically oriented types of tourism: ecological, educational, sports (windsurfing and kitesurfing on spits (sites 23, 32, 52)), and health-improving tourism using the muds of Lake Chokrak (5), limans (68, 69) and mud volcanoes (sites 76, 77).

For areas of intensive recreational use, engineering preparation (shore protection, drainage, water supply, etc.) and the development of coastal protection schemes are mandatory. Promising research is aimed at functional zoning of the coast taking into account the dynamics of geomorphological processes and the creation of GIS monitoring of recreational resources as a basis for sustainable tourism development in the region.

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*About the author:*

**Ekaterina A. Pozachenyuk**, Professor, Professor of the Department of Physical Geography and Geomorphology, Federal State Autonomous Educational Institution of Higher Education “V.I. Vernadsky Crimean Federal University” (4 Akademika Vernadskogo Ave., Simferopol, 295007, Russia), DSc (Geogr.), **ORCID ID: 0000-0002-4837-1009**, **ResearcherID: AAX-4733-2021**, **Scopus Author ID: 57021819500**, [pozachenyuk@gmail.com](mailto:pozachenyuk@gmail.com)

*The author has read and approved the final manuscript.*

Review paper

## The Role of the Marginal Filter and Climate in Changing the Black Sea Ecosystem

V. V. Melnikov

*A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia*

*e-mail: sevlin@ibss-ras.ru*

### Abstract

The paper presents a review of the current state of knowledge regarding the role of the marginal filter and climate in the ecosystem changes of the Black Sea. The marginal filter (MF) is a key buffer zone at the river–sea interface, where the bulk of terrigenous material delivered from land is deposited and transformed. The MF concept was developed by A.P. Lisitsyn, who demonstrated that the five-stage filter in this contact zone retains 93–95% of suspended particulate matter and about 40% of dissolved substances. The study is the first basin-wide synthesis in which the Lisitsyn concept is applied not for local flux calculations, but as an interpretive tool for understanding the cascade of ecosystem collapses across the entire sea, complementing existing local-scale studies of the Black Sea MF. The functioning of the Black Sea MF as an integrated geoeological buffer system remains poorly understood: this sea is distinguished by its extensive shelf, shallow pycnocline, and hydrogen sulphide zone. The limited volume of oxygenated waters, together with the sea's dependence on river runoff, renders the MF critically important for the ecosystem. The author hypothesises that the destruction of the biological block of the MF in the 1960s–1980s by intensive bottom trawling, which eradicated the Phyllophora field and benthic filter-feeders, triggered a cascading degradation: a disaster on the shelf (1950s–1980s), a disaster in the open sea (1980–1988), and a collapse of the entire ecosystem (1988–2000). However, the shift to a novel state (>2000) is already linked to climate: warming caused the disappearance of the Cold Intermediate Layer (2019), which had harboured boreal relicts – key forage zooplankton taxa and commercial fish species. Further warming will fundamentally alter the Black Sea ecosystem.

**Keywords:** Black Sea, marginal filter, deoxygenation, water masses, ecosystem

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# Роль маргинального биофильтра и климата в экосистемных изменениях Черного моря

**В. В. Мельников**

*ФГБУН ФИЦ «Институт биологии южных морей имени А.О. Ковалевского РАН»,  
Севастополь, Россия*

*e-mail: sevlin@ibss-ras.ru*

## **Аннотация**

В статье представлен обзор современного состояния знаний о роли маргинального фильтра и климата в экосистемных изменениях Черного моря. Маргинальный фильтр (МФ) – ключевая буферная зона на границе река – море, где основная масса поступающего с суши терригенного материала осаждается и трансформируется. Концепция МФ разработана А. П. Лисицыным, показавшим, что пятиступенчатый фильтр в этой контактной зоне задерживает 93–95 % взвешенных частиц и около 40 % растворенных веществ. Настоящая работа – первый бассейновый синтез, в котором концепция Лисицына применяется не для локальных расчетов потоков, а как инструмент интерпретации каскада экосистемных коллапсов во всем море, дополняя локальные исследования черноморского МФ. Функционирование черноморского МФ как единой геоэкологической буферной системы остается слабо изученным: это море отличается обширным шельфом, мелким пикноклином и сероводородной зоной. Малый объем кислородных вод и зависимость от речного стока делают МФ критически важным для экосистемы. Автор выдвигает гипотезу, что уничтожение биологического блока МФ в 1960-х–1980-х гг. интенсивными донными тралениями, истребившими филлофорное поле и бентосных фильтраторов, спровоцировало каскадную деградацию: катастрофу на шельфе (1950-е–1980-е гг.), в открытом море (1980–1988 гг.) и коллапс всей экосистемы (1988–2000 гг.). Однако сдвиг к новому состоянию (с 2000 г.) связан уже с климатом: потепление вызвало исчезновение холодного промежуточного слоя (2019 г.), в котором обитали бореальные реликты – ключевые таксоны кормового зоопланктона и промысловые рыбы. Дальнейшее потепление кардинально изменит экосистему Черного моря.

**Ключевые слова:** Черное море, маргинальный фильтр, деоксигенация, водные массы, экосистема

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## Introduction

A large number of works have been devoted to the study of the river–sea contact zone, among which fundamental monographs by G. V. Lopatin<sup>1)</sup>, N. V. Samoylov<sup>2)</sup>, G. I. Shamov<sup>3)</sup>, G. A. Maksimovich<sup>4)</sup>, A. I. Simonov<sup>5)</sup>, O. A. Alekin<sup>6)</sup>, M. I. Budyko and A. A. Sokolov<sup>7)</sup>, N. M. Strakhov<sup>8)</sup>, Yu. P. Zaitsev [1], and V. V. Gordeev [2] should be mentioned. The monograph by Academician A. P. Lisitsyn, *Sedimentation in the Oceans*<sup>9)</sup> shows that more than three-quarters of all sedimentary material enters the ocean with river runoff. The monograph by V. S. Savenko, *Chemical Composition of Suspended Sediments of Rivers* [3] summarises the available information on the geochemistry of river-borne particulate material.

In the work *The Marginal Filter of the Oceans*, A. P. Lisitsyn [4] was the first to formulate the concept according to which natural marginal filters (MFs) arise in zones of mixing of riverine and marine waters; they retain 90–95% of suspended matter and up to 80% of pollutants and other dissolved substances entering the sea<sup>10)</sup> with river runoff [2]. In the water flow before the MF, suspended matter predominates, whereas after it, dissolved substances predominate. The purification of river waters generally described as a five-stage process [4]; the first two stages—physical and geochemical—include *gravitational settling and coagulation* of clay material, i. e. a strong sorbent. During the third purification stage, *sorption and desorption* of organic and inorganic compounds occur as a result of the formation of new powerful sorbents from organic matter and iron oxyhydroxides. The fourth stage is a biofilter, which is usually associated with the transfer of dissolved substances into suspended matter (phytoplankton cells). At the fifth and final stage of water purification, mechanical filtration of all suspended matter is performed by zooplankton, which produces pellets that fall into bottom sediments. Thus, MFs protect marine waters from the direct impact of anthropogenic pollution entering with river waters.

At present, the marginal filters of the Arctic seas—the Kara, White, and Barents Seas—are the most thoroughly described [4–7]. The features of long-term changes

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<sup>1)</sup> Lopatin, G.V., 1952. [*River Alluvial Deposits in the USSR*]. Moscow: Gos. izd-vo geogr. lit-ry, 366 p. (in Russian).

<sup>2)</sup> Samoylov, N.V., 1952. [*River Mouths*]. Moscow: Gos. izd-vo geogr. lit-ry, 526 p. (in Russian).

<sup>3)</sup> Shamov, G.I., 1954. [*River Alluvial Deposits*]. Leningrad: Gidrometeoizdat, 378 p. (in Russian).

<sup>4)</sup> Maksimovich, G.A., 1955. [*Chemical Geography of Land Waters*]. Moscow: Gos. izd-vo geogr. lit-ry, 329 p. (in Russian).

<sup>5)</sup> Simonov, A.I., 1969. [*Hydrology and Hydrochemistry of the Estuarine Coastal Zone in Tideless Seas*]. Moscow: Gidrometeoizdat, 230 p. (in Russian).

<sup>6)</sup> Alekin, O.A., 1970. [*Hydrochemistry Fundamentals: A Study Guide*]. Leningrad: Gidrometeoizdat, 444 p. (in Russian).

<sup>7)</sup> Potapov, O.N., Smirnov, N.S. and Chepelin, L.A., eds., 1974. [*The Global Water Balance and the Earth's Water Resources*]. Leningrad: Gidrometeoizdat, 638 p. (in Russian).

<sup>8)</sup> Strakhov, N.M., 1961–1963. [*Fundamentals of the Theory of Lithogenesis. In 3 volumes*]. Moscow: AN SSSR. Vol. 1, 212 p., Vol. 2, 572 p., Vol. 3, 550 p. (in Russian).

<sup>9)</sup> Lisitsyn, A.P., 1974. [*Sedimentation in the Oceans*]. Moscow: Nauka, 440 p. (in Russian).

<sup>10)</sup> Gordeev, V.V., 1983. [*River Discharge into the Oceans and its Geochemical Characteristics*]. Moscow: Nauka, 160 p. (in Russian).

in the MF of the Volga River have been studied [8]. These works have shown that each sea has its own specific features of sedimentary material formation (river and ice runoff, coastal abrasion, aeolian suspended matter, and others). For example, in the White Sea, coastal abrasion plays an important role [9], while in the Caspian Sea, the export of sedimentary material into the sea by rivers and the deposition of aeolian material from the atmosphere are comparable in order of magnitude [10]. A review of the current state of research on the geochemistry of the Black Sea is given in the work by V. V. Gordeev [11], which shows that although about 1000 rivers flow into this sea, the main part of the runoff is provided by large rivers entering the north-western Black Sea (NWBS).

Despite a considerable volume of local studies covering individual aspects of sedimentation and hydrochemistry, the functioning of the Black Sea MF as an integrated geoecological buffer system has not yet been systemically evaluated. Meanwhile, the specificity of the Black Sea – its extensive shelf, shallow pycnocline, hydrogen sulphide zone, and critically small volume of oxygenated waters – in combination with the determining role of river runoff makes the MF a key regulator of the ecosystem homeostasis of the entire basin. However, to date the Lisitsyn concept has been applied in Black Sea studies mainly for local calculations of suspended matter fluxes and has almost not been used as a tool for explaining cascading basin-wide ecological collapses.

The aim of the present study is to provide, based on A. P. Lisitsyn's concept, a basin-wide analysis and interpretation of the cascade of ecosystem collapses in the Black Sea, considering the MF not as a peripheral geochemical zone but as a system-forming component of ecosystem homeostasis linking processes on the shelf, in the open sea, and climate change. The work advances the hypothesis that the destruction of the biological block of the MF in the 1960s–1980s as a result of intensive anthropogenic pressure (bottom trawling, eradication of the *Phyllophora* field and benthic filter-feeders, regulation of river flow) served as a trigger for ecosystem degradation, while the subsequent transition to a novel state in the 2000s was determined by a climatic factor – warming, which led to the disappearance of the cold intermediate layer and an irreversible replacement of boreal biota by warm-water communities.

## Methods

To test the advanced hypothesis that the destruction of the biological block of the MF acted as a trigger of cascading ecosystem collapse, while climatic warming determined the transition to a novel state, an analytical review approach was applied in this work. Since the study is a basin-wide synthesis rather than an original experimental or expeditionary study, the principal method was a systematic analysis of quantitative and qualitative data accumulated in the literature over an extended period. Such an approach made it possible to reconstruct the chronology of key events, compare disparate local observations, and identify relationships between changes in the MF, eutrophication, deoxygenation, and biotic shifts.

The present work is an analytical review performed on the basis of a systematic analysis of scientific literature devoted to the Black Sea MF, its role in ecosystem processes, and the influence of climate change. The search for sources was carried out in the Russian Science Citation Index (RSCI), Web of Science, and Scopus

databases, as well as in the electronic scientific libraries eLIBRARY.RU and CyberLeninka, using the following keywords: marginal filter, Black Sea, ecosystem collapse, deoxygenation, cold intermediate layer, Zernov's Phyllophora field.

The temporal coverage comprised the period from 1908 (the first description of the Phyllophora field by S. A. Zernov) to 2025. Original research articles, review works, monographs, dissertations, and materials of international conferences in Russian and English were included. The selection of materials was carried out according to the criteria of relevance to the subject (hydrology, geochemistry, biology, ecology of the Black Sea), the availability of quantitative estimates of matter fluxes or biota dynamics, and chronological sequence for reconstructing the cascade of events.

For data processing, content analysis was used to identify key events (eutrophication, degradation of benthos, invasions, and climatic anomalies) and their quantitative characteristics. A comparative-historical approach was then applied to reconstruct the chronology of ecological changes and to compare the state of the MF across different periods (before the 1950s, 1960s–1980s, 1988s–2000s, and the current stage).

### **Black Sea MF Structure**

The largest rivers contributing to runoff in the north-western Black Sea (NWBS) are the Danube (mean runoff  $\sim 200 \text{ km}^3/\text{yr}$ ), the Dnieper ( $\sim 44 \text{ km}^3$ ), the Dniester ( $\sim 10 \text{ km}^3$ ), and the Southern Bug ( $\sim 3 \text{ km}^3$ )<sup>11)</sup>. Their runoff influences the distribution of hydrological-hydrochemical properties, the concentration of nutrients, and the thermohaline stratification of the waters of the entire sea. The runoff of the largest river – the Danube – under the influence of climate and human activity fluctuates from 123 to 313  $\text{km}^3/\text{yr}$  [1]. In low-water periods, the total area of freshened waters in the NWBS amounts to 20–40% of the NWBS water area, while in high-water periods it reaches 70% [1, 12].

Until the middle of the last century, the b functioned as an integrated geoecological buffer system. The block of the Black Sea MF occupied almost the entire north-western shallow shelf and represented a single geoecological buffer system formed by the combined action of the MFs of all large rivers. It was a highly efficient biological filter, a cascade system that transformed a substantial riverine allochthonous flux into the autochthonous production of the marine ecosystem. This block consisted of two circuits: a pelagic one, which produced biological purification in the water column (phyto- and zooplankton), and a benthic one, which ensured the final filtration of river runoff at different depths.

*The pelagic circuit of the MF* before the 1950s was represented by phytoplankton, zooplankton, and macrofilter-feeders (*Aurelia aurita* (Linnaeus, 1758)). Phytoplankton provided the primary uptake of dissolved nutrients, while zooplankton converted them into rapidly sinking organic aggregates (faecal pellets) deposited on the bottom.

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<sup>11)</sup> Dzhaoshvili, Sh.V., 2003. [Rivers of the Black Sea]. Tbilisi: European Environment Agency. Technical Report. Vol. 71, 186 p. (in Russian).

*The benthic circuit of the MF* consisted of three levels:

– *a coastal belt of brown algae–Ericaria crinita* (Duby) Molinari & Guiry, 2020, *Gongolaria barbata* (Stackhouse) Kuntze, 1891, until 2020 included in *Cystoseira sensu lato* – located from the water's edge to a depth of 15 m and performing buffer and recycling functions. Brown algae are capable of absorbing more than 80% of the volume of mineral forms of phosphorus contained in sea-water and daily returning to it up to 16% of its maximum absorbed flux, which makes them an important factor in regulating the nutrient composition of waters [13];

– *a mussel belt* (*Mytilus galloprovincialis* Lamarck, 1819) located at depths of about 30 m. On one square kilometre, mussels filtered 15–20 million m<sup>3</sup> of water per day<sup>12)</sup>, packing suspended matter into heavy pseudofaeces. This maintained stable water transparency of the NWBS, high biodiversity (more than 118 invertebrate species and 48 fish species [1, 14]), and high fish productivity of the entire western basin. Owing to this, the NWBS was a key area of feeding and spawning for species such as mackerel and bonito (whose catches in 1939–1940 amounted to 540,000 t [15]);

– *a Phyllophora belt* (*Phyllophora* spp.) (25–60 m), known as Zernov's Phyllophora field [16–18], which until the early 1950s occupied an area<sup>13), 14)</sup> of more than 10 thousand km<sup>2</sup> with a biomass of up to 10 million t [1, 19]. This field, which was unparalleled in scale in the World Ocean<sup>14)</sup>, was the main part of the sea's MF – the final filter that deposited suspended particles and stabilised bottom sediments. It released up to 2 million m<sup>3</sup> of oxygen daily [1], enriching deep waters and participating in the formation of the Cold Intermediate Layer (CIL).

The combined efficiency of the MF blocks ensured a stable removal of pollutants from the active cycle owing to feedback mechanisms; high biodiversity determined the resistance of the system to fluctuations in external conditions.

### **Functional Role of the MF in the Homeostasis of the Black Sea Ecosystem**

Before the 1950s, the MF of the NWBS was not a peripheral appendage but functioned as a central organ of homeostasis, a kind of “liver” of the entire Black Sea ecosystem. This was because the waters of the shallow area, cooled during winter, flowed into the open sea, forming the CIL and spreading throughout the Black Sea.

At present, there is no consensus on the role played by the NWBS in the formation of the CIL. A number of authors tend to consider it the main source of CIL waters [20–24], others give preference to the open regions of the sea<sup>15), 16)</sup> [25–29],

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<sup>12)</sup> Kiseleva, M.I., 1979. [Bottom Biocoenoses and their Biomass]. In: V. N. Greze, ed., 1979. *Productivity of the Black Sea*. Kiev: Naukova dumka, pp. 218–239 (in Russian).

<sup>13)</sup> Morozova-Vodyanitskaya, N.V., 1948. [Zernov's Phyllophora Field and Causes of its Occurrence]. In: E. N. Pavlovsky, ed., 1948. *[A Commemorative Collection in Honour of Academician Zernov]*. Moscow: Nauka, pp. 216–226 (in Russian).

<sup>14)</sup> Kalugina-Gutnik, A.A., 1975. *[Phytobenthos of the Black Sea]*. Kiev: Naukova Dumka, 246 p. (in Russian).

<sup>15)</sup> Belokopytov, V.N., 2004. *[Thermohaline and Hydroacoustic Structure of the Black Sea Waters. Extended Abstract of PhD Thesis. Geographical Sciences]*. Sevastopol: MHI NASU, 24 p. (in Russian).

<sup>16)</sup> Belokopytov, V.N., 2017. *[Climate Changes of the Black Sea Hydrological Regime. DSc Thesis, Geographical Sciences]*. Sevastopol: MHI RAS, 377 p. (in Russian).

and still others consider the contributions of the two areas approximately equal<sup>17)</sup> [30]. According to various estimates, the total contribution of the NWBS to the formation of this layer in the Black Sea<sup>15), 16)</sup> ranges from 18 to 28% [31]. During most of the year, CIL waters on the north-western shelf persisted, flowing along bottom topography depressions towards the open sea. Usually in November this layer in the NWBS disappeared, being replaced by CIL waters from the open part of the sea, and in January it was renewed again<sup>15), 16)</sup> [32].

Owing to the good aeration of the CIL in those years, the depths of the open central regions of the sea were saturated with oxygen, which allowed forage zooplankton crustaceans to descend to depths inaccessible to fish (below 100 m) [33–35]. All this together ensured the high fish productivity of the Black Sea and especially of its north-western shelf.

Before the onset of active anthropogenic impact, winter cooling and convective mixing on the NWBS shelf led to the formation of dense cold waters, which formed from water already purified by the MF. They were relatively poor in nutrients and organic matter, the bulk of which had time to settle at the previous filtration stages. Thus, during this period, it was not simply cold water that came from the NWBS, but water with a relatively low biochemical potential.

### **Ecological disaster on the NWBS shelf (1950–1980)**

After the Second World War, industrial harvesting of benthic algae began on the Black Sea shelf. It was accompanied by detailed scientific research that determined the commercial areas and strict regulations: for *Phyllophora*, selective harvesting was recommended at four sites with a three-year renewal cycle, while for *Cystoseira* an even stricter regime was recommended, with a 10-year interval and preservation of at least 50% of stocks<sup>14)</sup>. In practice, however, harvesting was conducted without regard for these recommendations – within compressed timeframes, without consideration of reproduction, and against the background of growing pollution [36–41]. *Phyllophora* extraction reached 300 thousand t, significantly exceeding planned targets [40], which resulted in an ecological catastrophe: by the end of the 1970s, *Phyllophora* biomass on the shelf had sharply decreased from 10 to 1.4 million t, and by the mid-1980s it did not exceed 0.2 million t [1].

In parallel, mussels were processed into feed meal<sup>14)</sup>, which caused a several-fold reduction in the area of their biocenosis and a reduction in biomass by an order of magnitude [1]. Before degradation, the total biomass of mussels and oysters on the north-western shelf was estimated at tens of millions of tonnes<sup>18)</sup>. Calculations show that before the 1950s, mollusc communities probably filtered from 100 to 300 km<sup>3</sup> of water per year – a volume comparable to the annual river runoff and to the total volume of waters of the entire shelf. This ensured high water transparency and ecosystem stability.

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<sup>17)</sup> Tuzhilkin, V.S., 2008. [Seasonal and Multiyear Variability of the Thermohaline Structure of the Black Sea and Caspian Sea Waters and the Processes of its Formation. Extended Abstract of DSc Thesis. Geographical Sciences]. Moscow, 46 p. (in Russian).

<sup>18)</sup> Zenkevich, L.A., 1963. [Biology of Seas of the USSR]. Moscow: Izd-vo Akad. Nauk SSSR, 739 p. (in Russian).

The catastrophe was aggravated by the construction of a cascade of dams in the 1950s–1960s, which blocked fish migration routes and led, for example, to an almost tenfold reduction in sturgeon catches compared with the pre-war period [15]. The disappearance of the biological block of the NWBS MF caused staged degradation: nutrient fluxes, no longer retained by the filter, began to enter the shelf directly, which was additionally facilitated by the use of chemicals in agriculture [42]. This provoked rapid phytoplankton growth and then the first mass mortality event in 1973 over an area of 3500 km<sup>2</sup> [1]. Against the background of excess nutrients, a shift occurred towards small-celled phytoplankton forms, as well as species prone to outbreaks. A key indicator of this period was the mass development of mixotrophic dinoflagellates *Prorocentrum cordatum* (Ostenfeld) J. D. Dodge, 1976, whose “blooms” often preceded mortality events [43]. In zooplankton, against the background of a general decline in biodiversity, an increase in the share of rotifers (*Synchaeta* spp.) and some pollution-resistant copepods was noted.

Subsequently, mortality events covering up to 40,000 km<sup>2</sup> became regular and in 1973–1990 led to the loss of 60 million t of biomass of benthic animals [1]. The loss of the main spawning ground and the disappearance of predators that consumed jellyfish provoked an explosive increase in the abundance of gelatinous organisms: the biomass of *Aurelia* jellyfish increased from 670 t to 220 million t, and that of *Noctiluca* tens of times [1].

Turbid, nutrient-enriched waters from the shelf began to form a CIL with low oxygen content. An additional negative factor was the slowdown of water exchange in river systems due to the creation of a cascade of reservoirs, which led to the “ageing” of river waters, a multiple increase in the concentration of pollutants and nutrients, and disruption of sediment transport [43]. These polluted waters, spreading in winter with the CIL throughout the sea, turned hypoxia and eutrophication from a local shelf problem into a basin-wide Black Sea problem, finally disrupting the MF mechanism that had been fine-tuned over millennia. As a result, in the NWBS area the abundance of many species decreased by two to three orders of magnitude – from copepods and benthic crustaceans (hermit crab, crabs) to mullet fry and such bottom fish as sole and seahorse; mackerel visiting the area for feeding disappeared completely [1]. The absence of the MF caused a surge of pathogenic bacteria, leading to cholera epidemics in coastal areas in 1970 [1].

Thus, the destruction of the biological block of the MF launched a series of cascading effects destructive to the entire Black Sea ecosystem: riverine nutrients and organic compounds ceased to be removed by the MF and began to pass through the NWBS in transit, maintaining intense phytoplankton “blooms” and causing eutrophication of the shelf itself and regular mortality events. The transformed CIL became a corridor for the transport of polluted waters. The Black Sea Rim Current facilitated the spread of these poorly aerated and polluted waters throughout the sea. Hypoxia and eutrophication became a common problem for the entire Black Sea, not only for the NWBS, which predetermined the subsequent degradation of the ecosystem of the entire sea.

### **Ecological disaster in the open sea (1980–1988)**

The destruction of the MF became a turning point for the entire Black Sea ecosystem. The loss of function of this natural filter coincided in time with a tenfold increase in nutrient input from the Danube, Dnieper, and Don rivers in the 1960s–1990s [42]. The CIL, which had previously saturated deep waters with oxygen, began to transport biologically active substances into open waters. This led to hyper-eutrophication [44] and rapid phytoplankton development. Masses of dying organic matter began to descend to the main pycnocline, where oxygen became insufficient for their oxidation [45]. As a result, the upper boundary of the oxygen layer shifted upward from 130 m in 1955 to 90 m in 2013 [46]. The deoxygenation process was aggravated by the regulation of river runoff by dams and by the climatic reduction in the volume of incoming water.

The rise of the upper boundary of the anoxic zone disrupted trophic links in the open sea: accumulations of cold-water zooplankton, previously hiding deeper than 100 m, were displaced into the upper layers and became available as prey to sprat, which is confirmed by modelling [35]. In the 1980s–1990s, sprat stocks increased by an order of magnitude, and the contents of its stomachs consisted 100% of *Calanus euxinus* Hulsemann, 1991 [47]. The reduction in the abundance of top predators (mackerel, horse mackerel) that regulated the abundance of gelatinous organisms, combined with the abundance of phytoplankton, led to an explosive growth in the biomass of jellyfish and Noctiluca, completing the total restructuring of the pelagic ecosystem.

### **General crisis of the Black Sea ecosystem (1988–2000)**

The critical event that entailed irreversible consequences was the population outbreak of the invasive ctenophore *Mnemiopsis leidyi* A. Agassiz, 1865 in 1988 [48–51]. The introduction of this organism led to a catastrophic change in the abundance and composition of zooplankton, especially large copepods [49–52]. *Mnemiopsis* actively consumed zooplankton, fish eggs, and larvae. The abundance of detritus, as well as the absence of natural enemies of *M. leidyi*, contributed to the disruption of trophic links and to a catastrophic decline in the stocks of main commercial species – anchovy and sprat, whose catches decreased by more than an order of magnitude [53].

The success of the *M. leidyi* invasion was a consequence of the synergy of several key factors: 1) the destruction of the MF, which weakened the natural stability of the ecosystem; 2) the disruption of trophic links and a sharp reduction in the stocks of the bulk of top predators (Black Sea salmon, mackerel, bluefish, bonito) capable of regulating the abundance of gelatinous organisms [15]; 3) hypoxia and eutrophication, which created favourable conditions for hardy opportunistic species; 4) climatic anomalies (warm winters of the late 1980s), which aggravated the situation.

The general crisis of the Black Sea ecosystem in 1988 was not an isolated event but the culmination of the preceding destabilisation of the biological block of the marginal filter. The balance partially recovered after the appearance in 1997 of another invader: the ctenophore *Beroe ovata* Bruguère, 1789, a predator specialising on *M. leidyi* [54]. By the 2000s, this led to a sharp reduction in the abundance

of *Mnemiopsis* [50, 55] and to the beginning of recovery of populations of some abundant copepods, such as *Acartia clausi* Giesbrecht, 1889 and *Oithona similis* Claus, 1866. However, compared with the initial state, the community as a whole remained simplified, with an increased share of small forms and invaders.

Thus, anthropogenic degradation prepared the ground for the catastrophe, while climate determined its scale. The described dynamics indicates the potential vulnerability of other inland seas, such as the Caspian and Mediterranean, where the combination of climatic warming and anthropogenic degradation of ecosystems may significantly increase the risk of new invasions.

### **Current state of the ecosystem (since 2000)**

To understand the current state of the MF, it is essential to analyse recent changes in environmental conditions. These changes can be divided into several phases.

– As a result of a series of anomalously warm winters (2000, 2005, 2010, 2015, 2020), warming of surface waters began, which led to a reduction in the thickness of the CIL. The contribution of NWBS waters to CIL formation decreased to 5–10% (versus 20% in the middle of the 20th century) [56, 57]. This substantially reduced the functioning of the MF's "oxygen pump". The reduction in nutrient input with river runoff observed in recent decades and, as a consequence, the increase in water transparency did not eliminate hypoxia<sup>19)</sup> in the deep layers of the Black Sea [14, 57, 58], since the established oxygen deficit is maintained not so much by the current flux of organic matter as by the long-term restructuring of the vertical structure of water masses under the influence of warming [14, 57, 58].

– A natural reaction of the biota was the rapid "tropicalisation" of the ecosystem: whereas in 1997, 26 invader species were described [59], by now their number exceeds 300 [60], and traditional native communities have begun to degrade. Against the background of a reduction in mussel banks [61, 62], the ranges of invasive molluscs (*Anadara*, *Mya*, *Rapana*) expanded, and commercial catches in Russian waters sharply decreased from 165–308 thousand t in 1975–1986 to 18.7 thousand t in 2009 [15].

The turning point in the existence of the modern Black Sea ecosystem was the stoppage of the "oxygen pump" of the MF in 2019 [57, 63]. Warming led to the disappearance of the CIL in its classical sense (with boundaries of 8°C) and to the establishment of isothermy throughout the deep-water zone with a temperature of about 8.7°C [57, 63]. This led to the extinction of cold-water relicts, for which a temperature below 8°C was a critical condition of existence [57, 64]. The effects of warming are evident in the accelerated development of the Black Sea sprat: the duration of the development cycle decreased from 7 to 2–3 days [65],

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<sup>19)</sup> Masevich, A.V., 2022. [Oxygen Dynamics in the Main Pycnocline of the Black Sea. Extended Abstract of PhD Thesis. Geographical Sciences]. Sevastopol: MHI RAS, 24 p. (in Russian).

while in *Calanus euxinus* with an increase in temperature from 8 to 18°C the development time from egg to adult is halved [66].

Forecasts indicate that by the end of the 21st century the surface water temperature will increase by another 3.7°C [67] and its salinity will increase (0.18‰ / 10 years), which is characteristic of inland seas dependent on the regional freshwater balance [57, 68]. In the next 25 years, the habitat zone of plankton and fish in the deep-water regions of the sea may rise to the surface by another 9 m [56].

At the current stage, a complex and contradictory transformation of the Black Sea MF is occurring. Complete restoration of the archaic cold-water ecosystem in its original form is impossible because of the fundamental change in physical conditions (warming and disappearance of the CIL) and the mass invasion of warm-water species. The benthic zones of the NWBS MF are in different states:

- Ericaria–Gongolaria communities, which possess a high potential for self-restoration, demonstrate the fastest and most successful recolonisation of the coastal zone [40, 69, 70];

- by the beginning of the 21st century, Phyllophora stocks on Zernov's Phyllophora field on the north-western shelf had catastrophically decreased from 10 million t to 6–50 thousand t, and its area shrunk from 10 to 6.5 thousand km<sup>2</sup>, which made restoration of this biocenosis unlikely even in the long term [71–73]. At the same time, signs of phytobenthos recovery on the bottom of the NWBS are noted, expressed in an increase in its species diversity by a factor of 2–3 [14, 41];

- mussel stocks recover extremely slowly and fragmentarily [61, 62].

At the same time, the observed processes indicate the beginning of the formation of a new filtering system adapting to the changed conditions. The key prerequisites for this were the reduction of eutrophication and the introduction of bans on bottom trawling. The rapid recovery of the Ericaria–Gongolaria phytocenosis and the positive dynamics on the Phyllophora field indicate that, with reduced anthropogenic pressure, the benthic framework of the system retains potential for self-restoration.

Owing to irreversible changes in physicochemical conditions and biotic composition, the formation of an MF identical to the historical one is unlikely. A more probable scenario is the establishment of a system with a different structure and, presumably, lower buffer capacity—a mosaic and potentially less efficient system in which rapidly recovering coastal brown algal communities and regenerating Phyllophora areas play a key role. The pelagic component of the MF has not disappeared but has been transformed into a hybrid system with a new structure and function. Its buffer capacity is probably lower, while its resilience to further disturbances, such as continued warming, remains uncertain.

## Conclusion

This synthesis is the first in which A. P. Lisitsyn's concept is applied not to local flux calculations but as an interpretive framework for explaining the cascade of ecosystem collapses across the entire sea, complementing existing local-scale studies of the Black Sea MF.

The historical MF of the NWBS was not simply a buffer zone but a highly organised ecosystem that for millennia maintained the ecological homeostasis of the entire marine basin. The MF performed two vitally important functions: biological filtration of river runoff and annual oxygen enrichment of the deep waters of the sea through the formation of the CIL, creating a unique cold-water biotope for boreal-Arctic relicts. The destruction of the Phyllophora field and mussel banks under the influence of anthropogenic factors led to an irreversible transformation of this system, which can be considered a bifurcation point in its evolution. Under conditions of climatic warming, ecosystem degradation reached a level that determined its transition to a new unstable state.

The disappearance of the classical CIL with boundaries of 8°C in 2019 and the establishment of isothermy at about 8.7°C initiated an irreversible process of extinction of cold-water species that constituted the basis of the traditional trophic network. The forecasted temperature increase by 3–4°C by the end of the century means an acceleration of mediterraneanisation, which will lead to the dominance of warm-water invaders and the simplification of trophic networks; an increase in the vulnerability of the ecosystem to new invasions, diseases, and anthropogenic loads; and the collapse of traditional fisheries.

Under conditions of the impending crisis, the following measures should be considered:

- 1) creation of a system of continuous integrated monitoring, in which the disappearance of key relict species will become the final signal of the irreversibility of changes;

- 2) an increase in the number of marine reserves with the establishment of a strict conservation regime in them;

- 3) strict limitation of anthropogenic load: reduction of shipping routes over shallow waters, tightening of legislation on mineral extraction, and a fundamental revision of the policy of harvesting and cultivation of living resources;

- 4) preparation for socio-economic consequences, primarily through the intensive development of mariculture as an alternative to commercial fishing;

- 5) implementation of programmes for the cultivation of marine algae, for example, “Sea eco-farms”, the international project KELP FARMS (URL: <https://greenmission.ru/kelp-farms>), with the aim of preserving marine biodiversity and minimising the negative consequences associated with climate change and environmental pollution.

The foregoing analysis warrants a firm and far-reaching conclusion, that the anthropogenic destruction of the biological block of the MF in the 1960s–1980s and the climatic disappearance of the CIL in 2019 are two consecutive, irreversible bifurcation points in the history of the Black Sea ecosystem. Restoration of the initial state is excluded because of the fundamental change in the thermohaline regime. Further ecosystem dynamics will be determined by the ratio of the rates of recolonisation of surviving biotopes and invasion pressure, which requires a transition from a restoration policy to a strategy of adaptive monitoring and management.

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#### *About the author:*

**Viktor V. Melnikov**, Leading Researcher, A. O. Kovalevsky Institute of Biology of the Southern Seas of the Russian Academy of Sciences (299011, Russia, Sevastopol, 2 Nakhimov Ave.), PhD (Biol.), **ORCID ID: 0000-0001-6856-0467**, **ResearcherID: N-9219-2014**, **Scopus Author ID: 57197396948**, [sevlin@ibss-ras.ru](mailto:sevlin@ibss-ras.ru)

*The author has read and approved the final manuscript.*

Original paper

## Seasonal variability of CO<sub>2</sub> content in the surface layer of the Black Sea waters and the intensity of exchange with the atmosphere according to biogeochemical reanalysis data

E. M. Lemeshko \*, M. V. Tsyganova, E. E. Lemeshko

*Marine Hydrophysical Institute of RAS, Sevastopol, Russia*

*\* e-mail: evgeny.lemeshko@mhi-ras.ru*

### Abstract

This article examines the seasonal and interannual spatial variability of the equilibrium partial pressure of carbon dioxide  $p\text{CO}_2$  in the surface water layer and the carbon dioxide flux  $\text{FCO}_2$  at the atmosphere-sea interface for the Black Sea based on biogeochemical reanalysis data. *In situ* measurements for 2015–2024 were used to validate the reanalysis data and compare the seasonal variations of  $p\text{CO}_2$  and  $\text{FCO}_2$ . Additionally,  $p\text{CO}_2$  from reanalysis data in the surface layer of the atmosphere was compared with instrumental measurements. Seasonal cycles of the polygon-averaged  $\text{FCO}_2$  flux and the equilibrium partial pressure in the near-surface layer of the sea, based on instrumental observations and biogeochemical reanalysis data, coincide within 95% confidence intervals, with the exception of the summer season for  $p\text{CO}_2$ . Statistically significant regression relationships ( $p < 0.001$ ) were established between the parameters under consideration. As a result, the reanalysis data provided new insights into the seasonal variability of  $p\text{CO}_2$  and  $\text{FCO}_2$  throughout the sea area. This is particularly relevant when observational data are lacking for the winter and spring periods and the expedition area is limited. Seasonal variability of  $p\text{CO}_2$  and  $\text{FCO}_2$  is primarily influenced by water temperature and the difference in partial CO<sub>2</sub> pressure between the sea and the atmosphere. The distribution of  $p\text{CO}_2$  and  $\text{FCO}_2$  on the shelf and in the coastal zone of the sea demonstrates the significant influence of upwellings near Crimea and river plumes on the seasonal dynamics of  $\text{FCO}_2$ .

**Key words:** carbon dioxide partial pressure,  $p\text{CO}_2$ , carbon dioxide flux,  $\text{FCO}_2$ , seasonal cycle of  $p\text{CO}_2$ , seasonal cycle of  $\text{FCO}_2$ , water temperature, salinity, plume, upwelling, Black Sea, regional climate CO<sub>2</sub>

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# Сезонная изменчивость содержания $\text{CO}_2$ в поверхностном слое вод Черного моря и интенсивности обмена с атмосферой по данным биогеохимического реанализа

Е. М. Лемешко \*, М. В. Цыганова, Е. Е. Лемешко

Морской гидрофизический институт РАН, Севастополь, Россия

\* e-mail: [evgeny.lemeshko@mhi-ras.ru](mailto:evgeny.lemeshko@mhi-ras.ru)

## Аннотация

Исследована сезонная и межгодовая пространственная изменчивость равновесного парциального давления углекислого газа  $p\text{CO}_2$  в поверхностном слое вод Черного моря и потока углекислого газа  $F\text{CO}_2$  на поверхности раздела атмосфера – море на основе данных биогеохимического реанализа. Измерения *in situ* за 2015–2024 гг. использовали для валидации данных реанализа и сопоставления сезонного хода  $p\text{CO}_2$  и  $F\text{CO}_2$ . Дополнительно сопоставляли значения  $p\text{CO}_2$  по данным реанализа в приводном слое атмосферы с инструментальными измерениями. Сезонные циклы осредненного по полигону потока  $F\text{CO}_2$  и равновесного парциального давления в приповерхностном слое моря по данным инструментальных наблюдений и биогеохимического реанализа совпадают в пределах 95%-ных доверительных интервалов за исключением летнего сезона для  $p\text{CO}_2$ . Между рассматриваемыми параметрами установлены статистически значимые регрессионные соотношения ( $p < 0.001$ ), в результате по данным реанализа получены новые представления о сезонной изменчивости  $p\text{CO}_2$  и  $F\text{CO}_2$  во всей акватории моря. Это особенно актуально, когда отсутствуют данные наблюдений в зимний и весенний периоды и ограничен район проведения экспедиций. На сезонную изменчивость  $p\text{CO}_2$  и  $F\text{CO}_2$  основное влияние оказывает температура воды и разность парциальных давлений  $\text{CO}_2$  между морем и атмосферой. Распределение  $p\text{CO}_2$  и  $F\text{CO}_2$  на шельфе и в прибрежной зоне моря показывает значительное влияние апвеллингов у Крыма и речных плюмов на сезонную динамику  $F\text{CO}_2$ .

**Ключевые слова:** парциальное давление углекислого газа,  $p\text{CO}_2$ , поток углекислого газа,  $F\text{CO}_2$ , сезонный цикл  $p\text{CO}_2$ , сезонный цикл  $F\text{CO}_2$ , температура воды, соленость, плюм, апвеллинг, Черное море, региональный климат  $\text{CO}_2$

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## Introduction

Carbon dioxide, as one of the greenhouse gases, influences heat exchange over the land and ocean surfaces, modulating the increase in air temperature, which triggers variations in the climate system at both global and regional scales [1]. Unlike those in the open ocean, the sources and sinks of atmospheric carbon dioxide ( $\text{CO}_2$ ) and its flux at the water–atmosphere interface in coastal seas are insufficiently studied [2–4]. Coastal regions of the World Ocean are characterised by  $\text{CO}_2$  absorption (invasion) at middle and high latitudes and release (evasion) of  $\text{CO}_2$  at low latitudes and in the tropics [2, 3, 5]. At the same time, the annual mean  $\text{CO}_2$  flux values in these regions are comparable to those in the adjacent open ocean. Overall, coastal seas are areas of  $\text{CO}_2$  absorption. The most intense and stationary absorption zones are located in polar and subpolar coastal seas; the ocean region near southern Greenland has the highest  $\text{CO}_2$  flux values (up to  $-7.9 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ ) [5]. The Black Sea ranks second in  $\text{CO}_2$  absorption; the flux of this gas reaches approximately  $-5.0 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  here [5, 6]. Thus, the relevance of this study is due to the importance of studying the  $\text{CO}_2$  flux at the sea–atmosphere interface not only in the shelf zone but also throughout the entire Black Sea area in all seasons.

In the Black Sea, until the 1960s–1970s,  $\text{CO}_2$  invasion from the atmosphere into the water predominated, since the equilibrium partial pressure ( $p\text{CO}_2$ ) remained lower than the partial pressure of carbon dioxide in the atmosphere [7]. In the 1960s–1990s, an increase in total dissolved inorganic carbon ( $\text{TCO}_2$ ) and  $p\text{CO}_2$  and a decrease in pH were observed in the Black Sea, which led to negative trends in the transformation of the sea's carbonate system [7]. In time, this coincided with an increase in the globally averaged concentration of atmospheric  $\text{CO}_2$ , mainly due to anthropogenic impact.

Based on averaged data from high-precision *in situ* measurements of the partial pressure  $p\text{CO}_2$  in the surface water layer, performed during 13 expeditions in 2015–2021 in the north–north-eastern Black Sea, the seasonal cycle of  $p\text{CO}_2$  was calculated. It belongs to the sinusoidal type with variation from 324 to 570  $\mu\text{atm}$  at a mean value of 460  $\mu\text{atm}$  [8]. At the same time, from April to October, the northern Black Sea releases  $\text{CO}_2$  into the atmosphere, and from November to March it absorbs it [8–10]. Calculations of the  $\text{CO}_2$  flux in winter based on spatial hydrochemical survey data for the north–north-eastern Black Sea in December 2022 confirmed the direction of the  $\text{CO}_2$  flux from the atmosphere into the sea, with maxima along the eastern coast of Crimea [10]. It has also been shown that in coastal waters on a synoptic time scale, the  $\text{CO}_2$  flux is characterised by a smaller amplitude of fluctuations compared with seasonal and interannual variability [6].

The main abiotic factors influencing the  $\text{CO}_2$  flux are water temperature, wind speed, and water dynamics [11]. The decadal variability of  $\text{CO}_2$  uptake in the ocean is predominantly influenced by changes in water circulation and biotic factors, which contribute to the redistribution of both natural and anthropogenic carbon in the ocean [11]. The spatial variability of the  $\text{CO}_2$  flux on the Crimean shelf

in December 2022 qualitatively coincided with the distribution of temperature, wind speed, and the partial pressure gradient at the sea–atmosphere boundary  $\Delta p\text{CO}_2$ , although the strongest correlation of the  $\text{CO}_2$  flux was found with wind speed ( $-0.93$ ) [10].

For inland seas, an additional source of  $\text{CO}_2$  is river water, which especially affects  $\text{CO}_2$  fluxes on the shelf [5, 12]. In the Black Sea, the contribution of this source is significant: the Danube, Dniester, Dnieper, and Southern Bug runoff forms an extensive freshened surface layer on the north-western shelf with high  $\text{CO}_2$  concentrations [5, 13]. An additional factor in the absorption of atmospheric  $\text{CO}_2$  by the sea is upwellings, which lead to a decrease in surface water temperature, an inflow of deep carbon-rich waters, and an increase in primary production [4, 14]. The total surface area occupied by upwelling waters can reach 14% of the entire Black Sea area, and interannual variability in the number of upwellings exhibits quasi-biennial cyclicity [15].

Thus, for a more complete description of the spatiotemporal variability of  $\text{CO}_2$  fluxes and their dependence on hydrophysical and meteorological conditions for the entire Black Sea area, it is insufficient to use only high-precision *in situ* hydrochemical measurements due to the limited spatial and temporal sampling (Fig. 1).

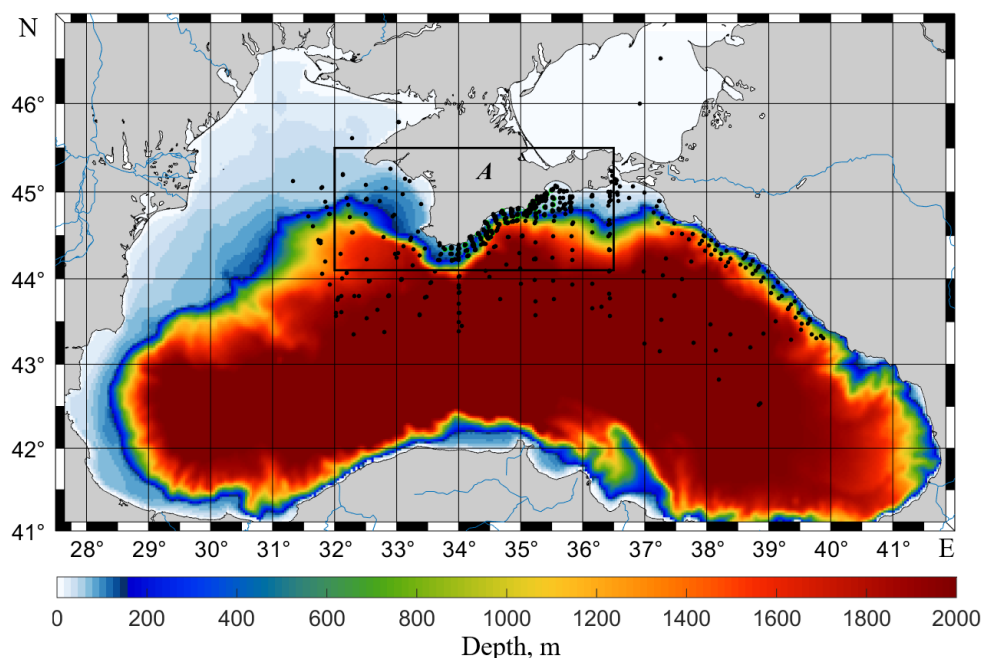


Fig. 1. The study area in the Black Sea. The dots indicate hydrochemical stations for 2015–2024; the rectangle highlights the area of reanalysis data averaging (A)

The present paper aims to:

1) assess the characteristics of the spatiotemporal seasonal and interannual variability of the partial pressure of CO<sub>2</sub> ( $p\text{CO}_2$ ) in the surface water layer and the CO<sub>2</sub> flux at the sea–atmosphere interface ( $FCO_2$ ) based on *in situ* measurements and biogeochemical reanalysis;

2) establish statistically significant regression relationships for  $p\text{CO}_2$  and  $FCO_2$  based on *in situ* measurements and biogeochemical reanalysis and assess the dependence of these parameters on surface water temperature.

## Materials and Methods

The article uses data obtained during expeditionary research on the R/V *Professor Vodyanitsky* in 2015–2024 (Table 1, Fig. 1). The expedition work area includes the northern and north-eastern parts of the Black Sea and the 12-mile (22.2 km) zone of the Crimean coast, where measurements were mainly carried out after 2022 (Fig. 1). Hydrochemical data were collected as a database of concentration gradients and CO<sub>2</sub> fluxes at the water–atmosphere interface from direct  $p\text{CO}_2$  measurements in the northern part of the Black Sea <sup>1)</sup> and are presented in Table 1.

Table 1. Equilibrium partial pressure of CO<sub>2</sub> in the surface water layer ( $p\text{CO}_2$ ), in the atmosphere ( $p\text{CO}_2^{\text{atm}}$ ), CO<sub>2</sub> flux ( $FCO_2$ ) and water temperature ( $T$ ), averaged based on measurement data from R/V *Professor Vodyanitsky* cruises for 2015–2024

| Cruise number | Date                      | $P\text{CO}_2$ ,<br>μatm | $p\text{CO}_2^{\text{atm}}$ ,<br>μatm | $FCO_2$ ,<br>mmol·m <sup>-2</sup> ·day <sup>-1</sup> | $T$ , °C    |
|---------------|---------------------------|--------------------------|---------------------------------------|------------------------------------------------------|-------------|
| 81            | 03.11.2015–<br>10.11.2015 | 329.4 ± 3.7              | 402.9 ± 6.8                           | −3.042 ± 2.76                                        | 15.1 ± 0.46 |
| 87            | 01.07.2016–<br>14.07.2016 | 490.2 ± 21.2             | 389.3 ± 2.7                           | 5.84 ± 2.68                                          | 25.2 ± 0.32 |
| 89            | 06.10.2016–<br>15.10.2016 | 438.2 ± 28.3             | 405.4 ± 4.9                           | 2.07 ± 1.53                                          | 19.2 ± 1.13 |
| 91            | 21.11.2016–<br>01.12.2016 | 392.3 ± 8.6              | 411.4 ± 4.1                           | −0.28 ± 0.15                                         | 12.0 ± 0.82 |
| 94            | 27.04.2017–<br>05.05.2017 | 471.2 ± 17.6             | 413.4 ± 3.8                           | 1.37 ± 0.80                                          | 12.4 ± 0.69 |

<sup>1)</sup> Konovalov, S.K., Orekhova, N.A., Medvedev, E.V., Ingerov, A.V., Galkovskaya, L.K. and Zhuk, E.V., 2023. *A Dataset of CO<sub>2</sub> Concentration Gradients and Fluxes at the Water–Atmosphere Interface, Based on Direct  $p\text{CO}_2$  Measurements for the Northern Part of the Black Sea* [Database]. Moscow. State Registration No. 2023623055 (in Russian).

Table 1 (concluded)

| Cruise number | Date                      | $PCO_2$ ,<br>$\mu\text{atm}$ | $pCO_2^{\text{atm}}$ ,<br>$\mu\text{atm}$ | $FCO_2$ ,<br>$\text{mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ | $T$ , °C        |
|---------------|---------------------------|------------------------------|-------------------------------------------|----------------------------------------------------------------------|-----------------|
| 95            | 16.06.2017–<br>02.07.2017 | $505.3 \pm 6.0$              | $395.2 \pm 1.4$                           | $4.93 \pm 1.11$                                                      | $22.5 \pm 0.63$ |
| 98            | 14.11.2017–<br>28.11.2017 | $366.5 \pm 7.8$              | $410.5 \pm 3.2$                           | $-3.05 \pm 1.33$                                                     | $12.5 \pm 0.59$ |
| 101           | 17.12.2017–<br>26.12.2017 | $355.1 \pm 5.0$              | $413.5 \pm 2.4$                           | $-6.93 \pm 2.46$                                                     | $11.1 \pm 0.36$ |
| 102           | 12.06.2018–<br>27.06.2018 | $500.8 \pm 8.8$              | $404.3 \pm 2.6$                           | $3.05 \pm 1.57$                                                      | $23.6 \pm 0.82$ |
| 108           | 14.07.2019–<br>02.08.2019 | $459.5 \pm 9.1$              | $402.7 \pm 2.8$                           | $3.14 \pm 1.15$                                                      | $24.5 \pm 0.50$ |
| 114           | 21.09.2020–<br>08.10.2020 | $469.4 \pm 30.6$             | $430.3 \pm 5.8$                           | $3.31 \pm 2.65$                                                      | $22.8 \pm 1.20$ |
| 117           | 30.07.2021–<br>08.08.2021 | $515.5 \pm 11.9$             | $409.7 \pm 1.5$                           | $2.69 \pm 1.09$                                                      | $28.1 \pm 0.30$ |
| 119           | 04.09.2021–<br>19.09.2021 | $440.5 \pm 2.6$              | $411.4 \pm 1.28$                          | $1.44 \pm 0.28$                                                      | $22.3 \pm 0.20$ |
| 125           | 02.12.2022–<br>27.12.2022 | $388.2 \pm 2.2$              | $433.9 \pm 1.0$                           | $-2.06 \pm 0.41$                                                     | $13.0 \pm 0.25$ |
| 126           | 16.03.2023–<br>04.04.2023 | $413.4 \pm 2.9$              | $438.1 \pm 1.0$                           | $-2.20 \pm 0.69$                                                     | $9.6 \pm 0.09$  |
| 127           | 14.06.2023–<br>02.07.2023 | $474.5 \pm 3.5$              | $421.9 \pm 1.8$                           | $1.70 \pm 0.52$                                                      | $22.9 \pm 0.21$ |
| 129           | 06.10.2023–<br>22.10.2023 | $423.2 \pm 2.8$              | $437.3 \pm 1.0$                           | $-0.86 \pm 0.38$                                                     | $18.9 \pm 0.41$ |
| 130           | 07.03.2024–<br>21.03.2024 | $370.5 \pm 6.8$              | $435.9 \pm 2.1$                           | $-2.63 \pm 0.60$                                                     | $10.3 \pm 0.17$ |
| 131           | 28.05.2024–<br>18.06.2024 | $497.3 \pm 5.3$              | $434.3 \pm 1.0$                           | $2.24 \pm 0.56$                                                      | $20.4 \pm 0.43$ |

Note: For average values, 95% confidence intervals are given.

Values of the partial pressure of  $CO_2$  were determined using a continuous pumping system for seawater from the surface layer at depths of 1–3 m according to the method described in [16].

Temperature and salinity of the surface water layer were measured with an IDRONAUT OCEAN SEVEN 320PlusM profiling system, and at shallow-water stations with depths less than 50 m, with a GAP-AK 16 hydrological CTD probe. Wind speed was measured with a hydrometeorological information collection system and reduced to the standard 10-m measurement height [17]. The value

of the carbon dioxide flux at the water–atmosphere interface  $FCO_2$  was calculated based on the parameterisations and approach proposed in [18]. In this case, the constants for the range of measured wind speed values and the  $\Delta pCO_2$  gradient between the Black Sea surface and the surface layer of the atmosphere, described in [10], were taken into account.

In addition, biogeochemical reanalysis data based on the NEMO model and the BAMHBI model (Biogeochemical Model for Hypoxic and Benthic Influenced areas)<sup>2)</sup> were used. The work used monthly mean values of  $pCO_2$  and  $FCO_2$  at the sea surface from the NEMO–BAMHBI model reanalysis on a regular  $2.5 \times 2.5$  km grid for 2015–2024<sup>3)</sup>. Instrumental measurements of  $pCO_2$  in the surface layer

Table 2. Regression dependences of parameters ( $pCO_2^{re}$ ,  $pCO_2^{atm-re}$ ,  $FCO_2^{re}$ ,  $T^{re}$ ) according to reanalysis data on *in situ* measurement data ( $pCO_2$ ,  $pCO_2^{atm}$ ,  $FCO_2$ ,  $T$ ) for the significance level  $p < 0.001$

| Regression dependence                 | Period    | Regression equation                                                                                    |
|---------------------------------------|-----------|--------------------------------------------------------------------------------------------------------|
| 1. $T^{re}$ on $T$                    | 2015–2020 | $T^{re} = (0.95 \pm 0.08) \cdot T + 0.11 \pm 1.57$ ,<br>$D = 0.91, R = 0.96$                           |
| 2. $pCO_2$ on $T$                     | 2015–2024 | $pCO_2 = (6.11 \pm 0.97) \cdot T + 333.4 \pm 18.3$ ,<br>$D = 0.56, R = 0.76$                           |
| 3. $FCO_2$ on $T$                     |           | $FCO_2 = (0.35 \pm 0.05) \cdot T - (5.6 \pm 1.0)$ ,<br>$D = 0.58, R = 0.76$                            |
| 4. $FCO_2$ on $(pCO_2 - pCO_2^{atm})$ |           | $FCO_2 = (0.045 \pm 0.004) \cdot (pCO_2 - pCO_2^{atm}) -$<br>$-(0.34 \pm 0.23)$ , $D = 0.81, R = 0.90$ |
| 5. $(pCO_2 - pCO_2^{atm})$ on $T$     |           | $(pCO_2 - pCO_2^{atm}) = (7.2 \pm 1.1) \cdot T - 107.6 \pm 19.9$ ,<br>$D = 0.62, R = 0.79$             |
| 6. $pCO_2^{re}$ on $pCO_2$            | 2015–2020 | $pCO_2^{re} = (1.50 \pm 0.14) \cdot pCO_2 - (192.8 \pm 60.5)$ ,<br>$D = 0.83, R = 0.91$                |
| 7. $pCO_2^{atm-re}$ on $pCO_2^{atm}$  |           | $pCO_2^{atm-re} = (0.43 \pm 0.11) \cdot pCO_2^{atm} +$<br>$+(224.8 \pm 45.7)$ , $D = 0.53, R = 0.73$   |
| 8. $FCO_2^{re}$ on $FCO_2$            | 2015–2024 | $FCO_2^{re} = (0.69 \pm 0.12) \cdot FCO_2 - (0.09 \pm 0.34)$ ,<br>$D = 0.58, R = 0.76$                 |

Note:  $D$  is the coefficient of determination;  $R$  is the correlation coefficient.

<sup>2)</sup> Grégoire, M., Vandenbulcke, L. and Capet, A., 2020. *Black Sea Biogeochemical Reanalysis (CMEMS BS-Biogeochemistry) (Version 1). Data set*. Copernicus Monitoring Environment Marine Service (CMEMS). [https://doi.org/10.25423/CMCC/BLKSEA\\_REANALYSIS\\_BIO\\_007\\_005\\_BAMHBI](https://doi.org/10.25423/CMCC/BLKSEA_REANALYSIS_BIO_007_005_BAMHBI)

<sup>3)</sup> Vandenbulcke, L., Mouchet, A. and Grégoire, M., 2024. *Black Sea MFC BLKSEA\_ MULTI-YEAR\_BGC\_007\_005*. CMEMS, 36 p. (Quality information document ; CMEMS-BLK-QUID-007-005). Available at: <https://documentation.marine.copernicus.eu/QUID/CMEMS-BLK-QUID-007-005.pdf> [Accessed: 12.08.2026].

of the atmosphere were compared with  $p\text{CO}_2$  from atmospheric reanalysis on a  $1^\circ \times 1^\circ$  grid for 2015–2023 [3]. The measurement error of the partial pressure of  $\text{CO}_2$  in the surface layer of the atmosphere was less than 1% [16].

In 2015–2024, the distribution of R/V *Professor Vodyanitsky* expeditions by month was as follows: in August and September, two expeditions each; in June, five; in July, four; in the remaining months, three each (Table 1). No cruises were conducted in January and February. The duration of measurements in each month also varied from a few days to two weeks. The uneven distribution of data by month was taken into account for each month when calculating mean values and standard deviations (SD), as well as the corresponding confidence intervals. The methodology for comparing the means over the instrumental observation polygon and the means over region *A* of the reanalysis data (Fig. 1) was first tested on surface water temperature, for which a regression equation was obtained at the significance level  $p < 0.001$  with a coefficient of determination  $D = 0.91$  and a correlation coefficient  $R = 0.96$  (row 1 in Table 2).

## Results and discussion

The seasonal cycle of the partial pressure of  $\text{CO}_2$  in the sea, averaged over region *A* and over the entire sea, according to reanalysis data and the corresponding cruises from Table 1, is presented in Fig. 2, *a*. According to instrumental observations, the seasonal cycle reached a maximum of 495  $\mu\text{atm}$  (SD – 40.6  $\mu\text{atm}$ ) in summer and a minimum of 364.1  $\mu\text{atm}$  (SD – 6.7  $\mu\text{atm}$ ) in November (in the absence of observations in January and February). The mean value was 440  $\mu\text{atm}$ .

There is a tendency for SD values to decrease in winter compared with summer. According to reanalysis data, the seasonal cycle of  $p\text{CO}_2$  is described by a sinusoidal curve for averaging both over the study region *A* and over the entire sea. For the entire sea, the maximum was reached in June (583  $\mu\text{atm}$ ), and the minimum (369  $\mu\text{atm}$ ) in January, with a mean value of 457  $\mu\text{atm}$ . According to data averaged over study region *A*, the maximum was observed in July (553  $\mu\text{atm}$ ), and the minimum (338  $\mu\text{atm}$ ) in January, with a mean value of 425  $\mu\text{atm}$ .

The spatial arrangement of stations during averaging affects the agreement with reanalysis data (see Fig. 1). The mean instrumental  $p\text{CO}_2$  values for March, April, October, and December agree well with the reanalysis curve averaged over the entire sea, whereas the *in situ* values for May, September, and November correspond better to the curve for region *A* (Fig. 2, *a*). The summer  $p\text{CO}_2$  values according to instrumental observations are approximately 50  $\mu\text{atm}$  lower than the reanalysis values. One possible explanation is the removal of  $\text{CO}_2$  from the surface water layer during the bloom of coccolithophores (May–July) and other biological organisms with a carbonate skeleton [19]. However, according to measurement data, no pronounced statistical relationship was found between the concentration of coccoliths and the  $p\text{CO}_2$  value, which indicates a secondary contribution of the bloom to the variability of  $\text{CO}_2$  concentration in the surface water layer [19].

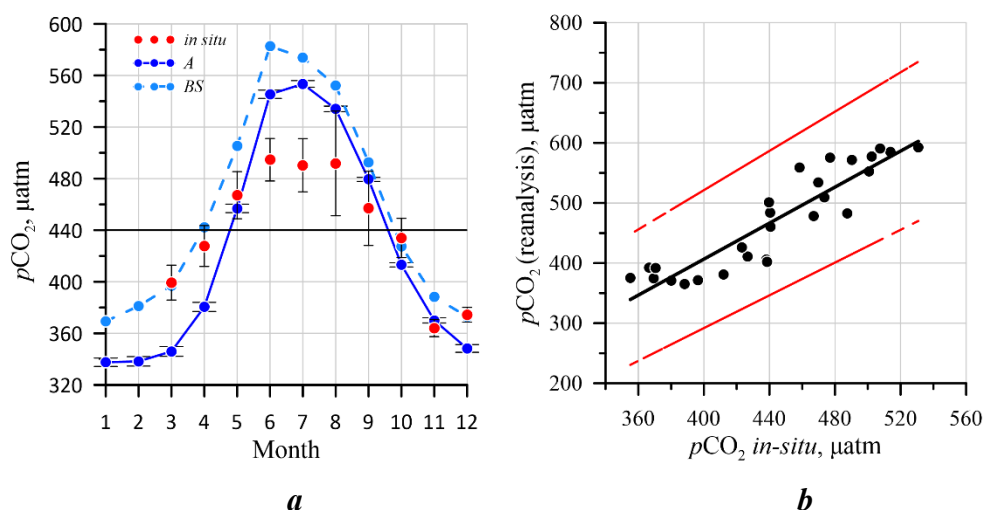


Fig. 2. Seasonal variations in partial pressure of CO<sub>2</sub> in the sea, averaged over the region (*A*), the entire sea (*BS*), and according to *in situ* expedition data (*a*). Regression of *pCO<sub>2</sub>* *in situ* and reanalysis data, averaged over region *A* (solid black line) and 95% confidence intervals (red lines) (*b*)

The decrease in *pCO<sub>2</sub>* values according to instrumental data in summer compared with reanalysis data is apparently explained by the larger number of stations in the coastal zone (see Figs. 1, 3). Therefore, the above-mentioned shift in *pCO<sub>2</sub>* by approximately 50 µatm (Fig. 2, *a*) in summer according to instrumental observation data is explained by the uneven localisation of stations in the coastal zone of Crimea specifically in the summer season of expeditions (Fig. 3), while the reanalysis data are uniformly averaged over the entire region *A*. This can be seen from comparing the distribution of stations over the water area (see Fig. 1) and seasonal maps of *pCO<sub>2</sub>* distribution (Fig. 3). Nevertheless, between the *pCO<sub>2</sub>* *in situ* data and the reanalysis data averaged over region *A*, a regression significant at the  $p < 0.001$  level was obtained with a coefficient of determination of 0.83 and a correlation coefficient of 0.91 (see Fig. 2, *b*); the regression equation is given in Table 2 (row 6). It should be noted that the graphs of the seasonal cycle according to instrumental observations and reanalysis data averaged for region *A* correspond well. At the same time, *pCO<sub>2</sub>* values according to reanalysis data for the entire sea are greater than for region *A*, and the maximum for the entire sea is reached one month earlier (in June) compared with region *A* (July) (see Fig. 2, *a*).

The results of comparing the partial pressure of CO<sub>2</sub> in the surface layer of the atmosphere according to atmospheric reanalysis and direct measurements showed good agreement. For them, a regression relationship was obtained at the significance level  $p < 0.001$  with a coefficient of determination  $D = 0.53$  and a correlation coefficient  $R = 0.73$  (row 7 in Table 2).

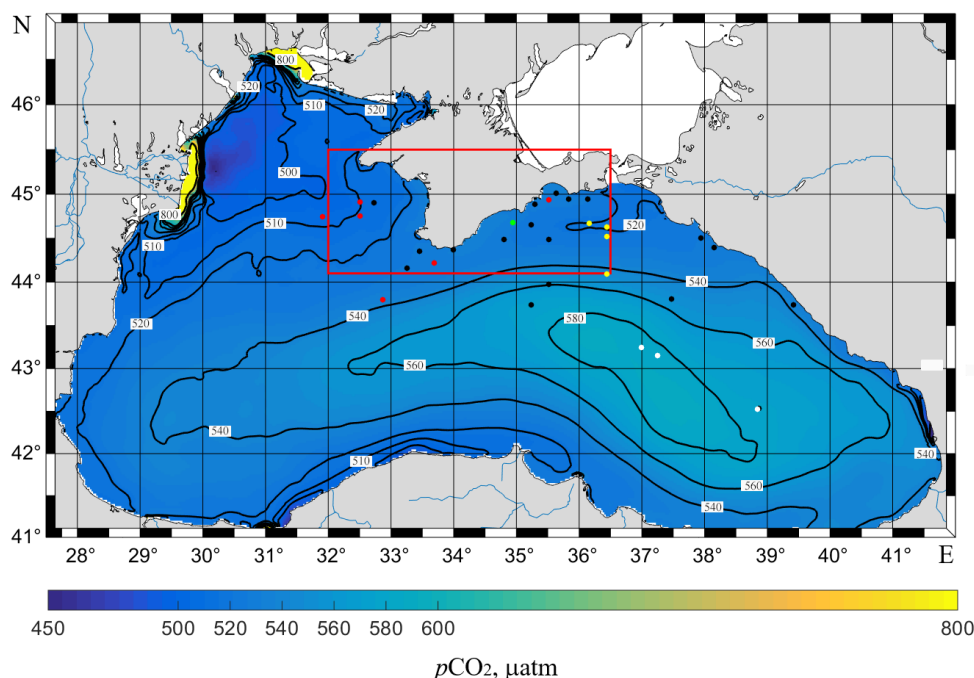


Fig. 3. Annual mean distribution of  $p\text{CO}_2$  for July 2015–2024 from reanalysis data and the locations of hydrochemical stations for which an estimate of the seasonal variation was obtained based on instrumental data from cruises: No. 87 (2016, red dots), No. 95 (2017, yellow dots), No. 108 (2019, black dots), No. 117 (2021, white dots), No. 127 (2023, green dots)

In the cold period of the year, from January to April and from October to December, absorption of atmospheric  $\text{CO}_2$  occurred in study region *A*. The maximum negative values of the mean  $\text{FCO}_2$  flux over region *A* were  $-3 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  in March and December according to instrumental data and up to  $-4 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  according to reanalysis data (Fig. 4, *a*). In the warm period of the year, from May to September, the  $\text{FCO}_2$  flux in study region *A* was directed into the atmosphere, reaching a maximum of  $3.4 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  in August (Fig. 4, *a*). The mean temperature of the surface sea layer also reached a maximum ( $27^\circ\text{C}$ ) according to instrumental observations in August. At the same time,  $\text{FCO}_2$  flux values according to reanalysis data for the entire sea are greater than those for region *A* (Fig. 4, *a*). Averaged over the entire sea, the  $\text{FCO}_2$  flux changes direction from absorption to emission approximately one month earlier (in April) than in region *A* (in May) (Fig. 4, *a*).

The maximum  $\text{FCO}_2$  according to reanalysis data is reached in summer one month earlier (in July) and exceeds the mean flux according to instrumental data

by approximately  $1 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$  (Fig. 4, *a*). Nevertheless, the underestimation of instrumental estimates of the seasonal cycle of  $p\text{CO}_2$  in summer (see Fig. 2, *a*) leads to an underestimation of  $\text{FCO}_2$  according to measurement data relative to reanalysis in July (Fig. 4, *a*). However, from monthly mean  $\text{FCO}_2$  data (*in situ* measurements and reanalysis) for region *A* for 2015–2024, a regression significant at the  $p < 0.001$  level was obtained (Fig. 4, *b*) with coefficients of determination and correlation of 0.58 and 0.76, respectively (row 8 in Table 2). Qualitatively, the seasonal variability of the mean  $\text{FCO}_2$  flux over the study area coincided with the seasonal cycle of mean temperature and the mean partial pressure gradient  $\Delta p\text{CO}_2$ , for which significant regression equations were obtained (rows 3 and 4 in Table 2, respectively). It should be noted that the graphs of the seasonal cycle of  $\text{FCO}_2$  according to instrumental observations and reanalysis averaged for region *A* correspond well (Fig. 4, *a*).

Based on reanalysis data, the seasonal spatial distribution of partial pressure (see Figs. 3, 5) and  $\text{CO}_2$  flux (Figs. 6, 7) was obtained. In July, region *A* was characterised by  $p\text{CO}_2$  values up to  $560 \text{ } \mu\text{atm}$ , which corresponds to elevated values on the seasonal cycle graph, since most stations are located in the coastal and shelf zones with  $p\text{CO}_2$  up to  $520 \text{ } \mu\text{atm}$  (see Fig. 3). Minimum values (up to  $500 \text{ } \mu\text{atm}$ ) were recorded on the north-western shelf of the sea. At the same time, the coastal areas of the runoff of the Southern Bug, Dnieper, and Dniester rivers give maximum  $p\text{CO}_2$  values (up to  $800 \text{ } \mu\text{atm}$ ) (see Fig. 3). The largest source of  $\text{CO}_2$  flux

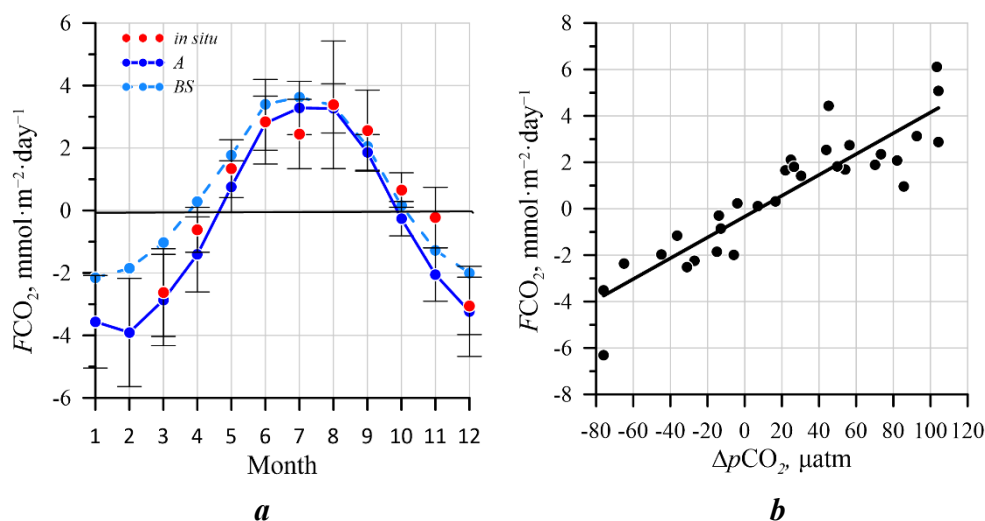


Fig. 4. Seasonal variation of the  $\text{FCO}_2$  flux averaged over region *A*, over the entire sea (*BS*) and according to *in situ* expedition data (*a*). Regression of  $\text{FCO}_2$  and the partial pressure gradient of  $\text{CO}_2$  at the sea-atmosphere interface  $\Delta p\text{CO}_2$  based on monthly average *in situ* data (*b*)

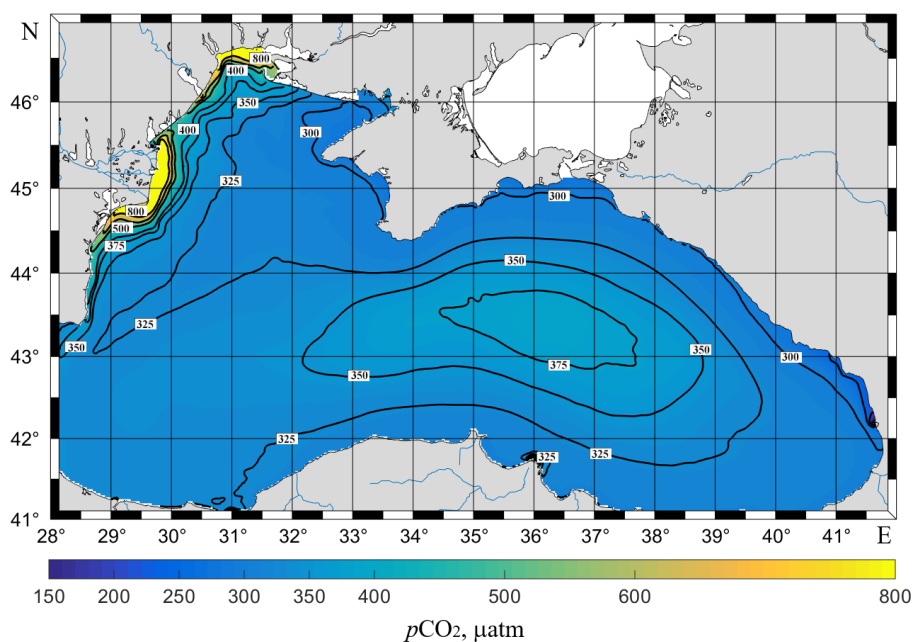


Fig. 5. Annual mean distribution of  $p\text{CO}_2$  according to reanalysis data for January 2015–2024

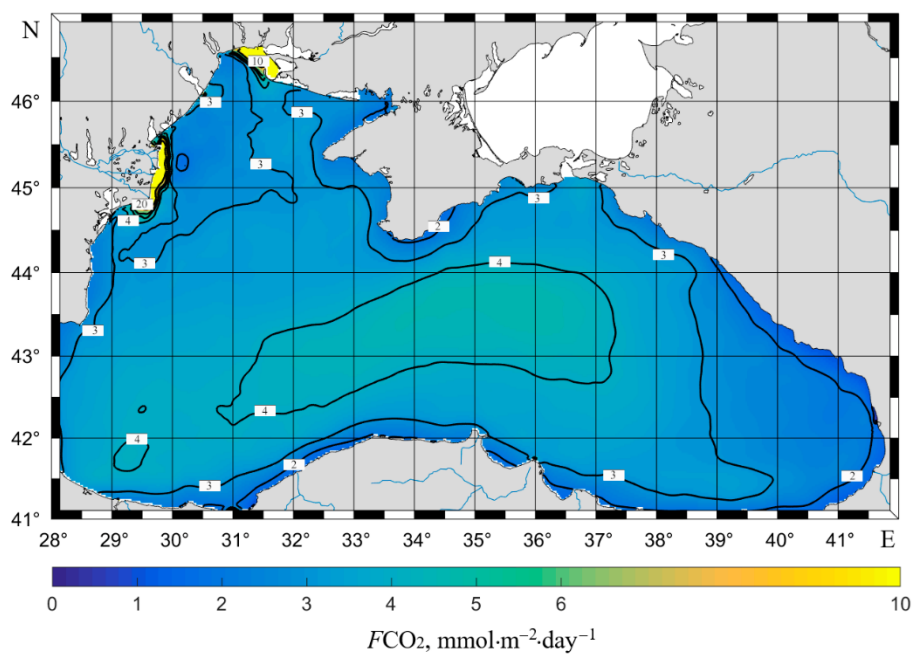


Fig. 6. Annual mean distribution of  $\text{FCO}_2$  according to reanalysis data for July 2015–2024

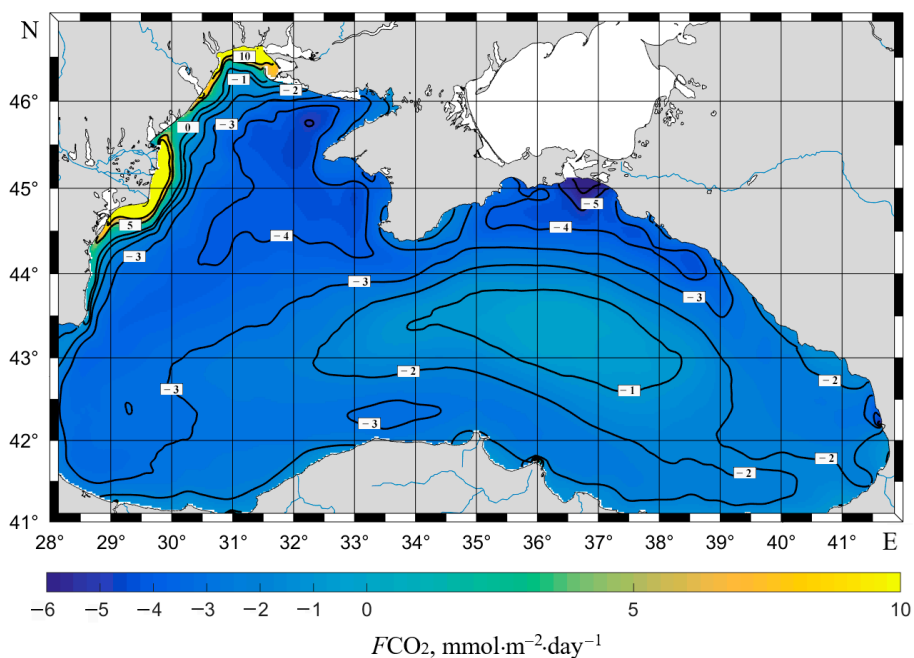


Fig. 7. Annual mean distribution of  $FCO_2$  according to reanalysis data for January 2015–2024

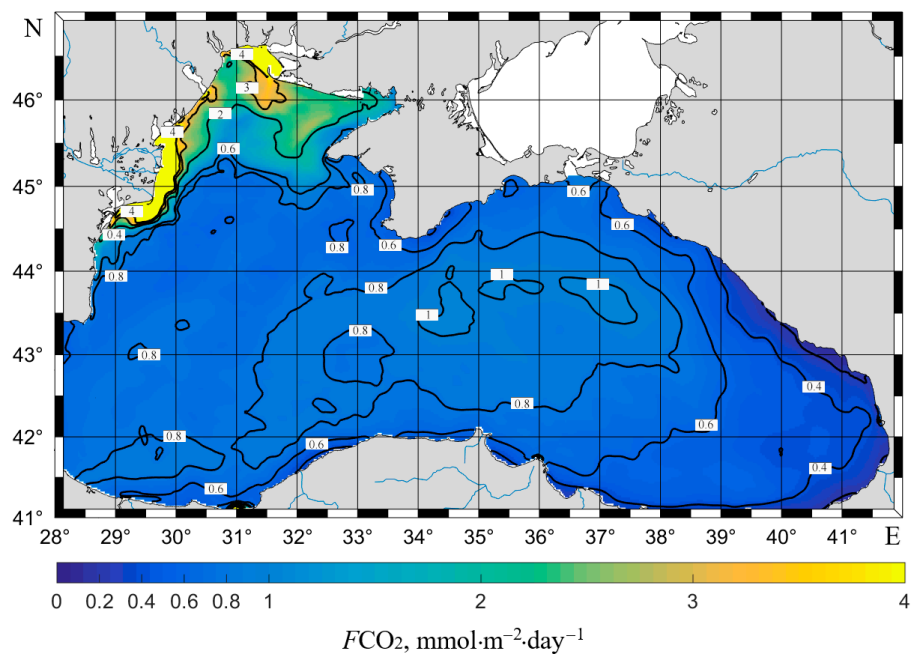


Fig. 8. Annual mean distribution of  $FCO_2$  standard deviation according to reanalysis data for July 2015–2024

into the sea is associated with the Danube plume, where  $p\text{CO}_2$  values reach more than 800  $\mu\text{atm}$  (see Fig. 3). In the central and western deep-water parts,  $p\text{CO}_2$  values up to 560  $\mu\text{atm}$  are also noted (see Fig. 3). In January, in the central part of the sea,  $p\text{CO}_2$  values decrease to 350  $\mu\text{atm}$ , and in the coastal and shelf areas of the north and north-east of the sea, to 250–300  $\mu\text{atm}$  (see Fig. 5). In winter, the area of river plumes decreases due to reduced river runoff, but the surface freshened layer still remains a source of  $\text{CO}_2$  for the sea with  $p\text{CO}_2$  values up to 800  $\mu\text{atm}$  (see Fig. 5).

In summer, the  $\text{CO}_2$  flux is directed from the sea into the atmosphere; in July it reaches a maximum  $F\text{CO}_2$ , according to reanalysis data, of up to 4  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  in the central part of the sea and more than 10  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  in the areas of river plumes on the north-western shelf (see Fig. 6). Minimum values, up to 2  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ , were localised in the coastal areas of Crimea (see Fig. 6) and coincided with areas of temperature decrease during seasonal upwellings, statistical data on which are given in [15], while local minima of the  $F\text{CO}_2$  flux were observed in the eastern and southern regions of the Crimean Peninsula according to measurement data [10]. In Fig. 8, the upwelling areas near Crimea are outlined by the isoline of the standard deviation (SD) of  $F\text{CO}_2$  at 0.6  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ . On the north-western shelf, variability due to the combined effect of river runoff and upwellings reaches maximum values for the entire sea area, 2–4  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ , while in the deep-water part of the sea it does not exceed 1  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  (Fig. 8).

In winter, the  $\text{CO}_2$  flux is directed from the atmosphere into the sea. In January,  $F\text{CO}_2$  reaches a maximum (in absolute value) of up to –4  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  on the north-western shelf and in the Kerch region, and a minimum of up to –1  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  in the central part of the sea (see Fig. 7). In winter, the areas of river plumes on the north-western shelf still remain a source of  $\text{CO}_2$  for the sea; the  $\text{CO}_2$  flux is positive and directed from the sea into the atmosphere with  $F\text{CO}_2$  values in January exceeding 10  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  (see Fig. 7). River plumes of the Southern Bug, Dnieper, and Dniester rivers are characterised by maximum  $p\text{CO}_2$  values (up to 800  $\mu\text{atm}$ ) on the north-western shelf and serve as a source of  $\text{CO}_2$  for the sea (see Fig. 5). The  $\text{CO}_2$  flux is positive and directed from the sea into the atmosphere with mean  $F\text{CO}_2$  values exceeding 10  $\text{mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  (see Figs. 3–8). The role of the Danube as the main source of  $\text{CO}_2$  on the north-western shelf of the sea is manifested in the seasonal cycle of  $\text{CO}_2$ : the maximum  $\text{CO}_2$  concentration in the Danube delta and branches is observed in May and October [20]. Since the maximum river runoff on the north-western shelf occurs at the end of April–May, the areas of river plumes and, accordingly, the  $F\text{CO}_2$  flux into the atmosphere reach a maximum in May–June [13].

## Conclusions

Comparison of instrumental observation data on the equilibrium partial pressure  $p\text{CO}_2$  in the near-surface sea layer and the  $F\text{CO}_2$  flux at the sea–atmosphere interface in 19 expeditions in 2015–2024 at control polygon A in the north–north-eastern Black Sea with biogeochemical reanalysis data showed that the reanalysis

data describe, with statistical significance, the seasonal and interannual spatio-temporal variability of the partial pressure and CO<sub>2</sub> flux in the surface sea layer. The following results were obtained:

- Statistically significant regression relationships and cross-correlations were determined for the parameters  $p\text{CO}_2^{\text{re}}$ ,  $p\text{CO}_2^{\text{atm-re}}$ ,  $F\text{CO}_2^{\text{re}}$ ,  $T^{\text{re}}$  according to re-analysis data and the results of measurements of  $p\text{CO}_2$ ,  $p\text{CO}_2^{\text{atm}}$ ,  $F\text{CO}_2$ ,  $T$  *in situ* at the significance level  $p < 0.001$ .

- The seasonal cycles of the equilibrium partial pressure  $p\text{CO}_2$  averaged over region *A* in the near-surface sea layer according to instrumental observations and biogeochemical reanalysis coincide within 95% confidence intervals, except for the summer season, which is explained by the non-homogenous location of hydrochemical stations (casts) near the Crimean coast during summer expeditions.

- The seasonal cycles of the  $F\text{CO}_2$  flux averaged over region *A* at the sea–atmosphere interface according to instrumental observations and biogeochemical reanalysis coincide within 95% confidence intervals.

- For the first time, quantitative estimates of the spatial variability of seasonal CO<sub>2</sub> fluxes were obtained for the entire Black Sea area: in the cold period (October–April), uptake predominates ( $F\text{CO}_2 < 0$ ), while in the warm period (May–September), emission predominates ( $F\text{CO}_2 > 0$ ).

- For the first time, for the entire Black Sea area, the seasonal cycle of the partial pressure  $p\text{CO}_2$  in the near-surface water layer was quantitatively determined: a maximum of 580 μatm in June and a minimum of 365 μatm in January.

- For region *A* in the northern part of the sea around Crimea, the maximum  $p\text{CO}_2$  (up to 557 μatm) is observed already in July, and the minimum in January reaches 340 μatm. This makes it possible to reconstruct the seasonal values of  $p\text{CO}_2$  and  $F\text{CO}_2$  in the winter months (January and February), when expeditions were not conducted.

For the first time for the entire Black Sea area, long-term mean spatial estimates of the equilibrium partial pressure  $p\text{CO}_2$  in the near-surface sea layer and the  $F\text{CO}_2$  flux at the sea–atmosphere interface were obtained for each month.

- Part of the north-western shelf and the Kerch region are characterised by maximum CO<sub>2</sub> invasion from the atmosphere into the sea in winter (in January  $F\text{CO}_2$  reaches  $-4 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ), while in the deep-water part of the sea the invasion is weak (about  $-1 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ). In summer, maximum evasion (in July  $F\text{CO}_2$  reaches  $5 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) covers the central and western parts of the sea, while in the river plume zones on the north-western shelf values can exceed  $10 \text{ mmol}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ .

- The spatial distribution of the CO<sub>2</sub> flux on the north-western shelf indicates the influence of river plumes (especially the Danube) on the seasonal dynamics of  $F\text{CO}_2$ .

- Comparison of the distribution of the CO<sub>2</sub> flux and its SD in the coastal zone of Crimea with statistical data on seasonal upwellings allows a qualitative conclusion about the significant influence of upwellings on  $F\text{CO}_2$ , especially in summer, when the frequency and intensity of upwellings are maximal.

On the basis of the obtained significant regression relationships and cross-correlations, it can be concluded that among the considered factors, water temperature has the main influence on  $p\text{CO}_2$ , while water temperature and the difference in partial  $\text{CO}_2$  pressures between the sea and the atmosphere have the main influence on  $\text{FCO}_2$ .

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#### *About the authors:*

**Evgeny M. Lemeshko**, Leading Researcher, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russia), PhD (Phys.-Math.), **ORCID ID: 0000-0003-4676-1940**, **ResearcherID: S-7815-2018**, [evgeny.lemeshko@mhi-ras.ru](mailto:evgeny.lemeshko@mhi-ras.ru)

**Marina V. Tsyganova**, Junior Researcher, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russia), **ORCID ID: 0000-0003-2398-1756**, **ResearcherID: S-5426-2018**, [m.tsyganova@mhi-ras.ru](mailto:m.tsyganova@mhi-ras.ru)

**Egor E. Lemeshko**, Researcher, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russia), PhD (Geogr.), **ORCID ID: 0000-0001-5612-000X**, **ResearcherID: C-5691-2016**, **Scopus Author ID: 57205681264**, [e.lemeshko@mhi-ras.ru](mailto:e.lemeshko@mhi-ras.ru)

*Contribution of the authors:*

**Evgeny M. Lemeshko** – conceptualisation, selection of data analysis methods, analysis of research results, writing – original draft, writing – review and editing

**Marina V. Tsyganova** – selection and processing of hydrochemical data, analysis and visualisation of calculation results, conducting the research, writing – original draft

**Egor E. Lemeshko** – processing of reanalysis data, visualisation of results, statistical analysis of data, conducting the research, writing – original draft

*All authors have read and approved the final manuscript.*

Original paper

## Diurnal Cycle of the Black Sea Waters Temperature in the Area of the Southern Coast of Crimea Based on High-Frequency Measurements of the Thermoprofilemeter

V. A. Rubakina \*, A. A. Kubryakov, P. V. Gaisky

*Marine Hydrophysical Institute of RAS, Sevastopol, Russia*

\* e-mail: valenru93@mail.ru

### Abstract

The aim of this article is to analyse the vertical variability of the diurnal temperature cycle in coastal waters off the Southern Coast of Crimea. The study is based on data from a thermoprofilemeter with a high temporal resolution of 0.5 s, installed on the oceanographic platform in Katsiveli, covering the period from August 24, 2021, to November 26, 2023. It was found that the diurnal temperature cycle is expressed at all measurement depths and is most pronounced at the uppermost level (0.75 m) from May to August. Maximum anomalies of the mean diurnal cycle are observed in May–July during the morning and afternoon hours. The strongest warming occurs from 11:00 to 16:00 in layers down to 6–8 m, and during the warm season it reaches depths of 14–16 m. Selected events of significant daytime warming in both cold and warm seasons are examined. The diurnal amplitude is 1.3°C in the cold season and 3.5°C in the warm season. Statistical analysis of daytime warming  $\Delta T$  shows that  $\Delta T$  is most often less than 0.3°C, while events with  $\Delta T$  exceeding 2–3°C are rare. The highest temperatures are observed in June–August at the uppermost levels under wind speeds of 2–4 m/s, with warming penetrating down to 18 m. During the cold season (November–April), under strong winds, temperatures are low at all depths. The highest mean  $\Delta T$  values occur in summer at wind speeds up to 6 m/s, decreasing with increasing wind speed. The lowest  $\Delta T$  values are characteristic of the cold season. In layers down to 4–6 m,  $\Delta T$  exceeds 0.8–1°C in summer, while in winter it is close to 0°C at all measurement levels. Thus, thermoprofilemeter data can be successfully used to analyse the diurnal variability of water temperature in the coastal zone. The results obtained in this study complement the existing understanding of diurnal temperature variability in the coastal Black Sea. In particular, it was determined that the vertical distribution of diurnal temperature fluctuations strongly depends on the season and wind conditions, and in summer daytime warming can penetrate to depths of 14–18 m.

**Keywords:** temperature diurnal cycle, distributed temperature sensor, thermoprofilemeter, thermistor chain, Black Sea, Southern Coast of Crimea

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## **Суточный ход температуры вод Черного моря в районе Южного берега Крыма по данным высокочастотных измерений термопрофилемера**

**В. А. Рубакина \*, А. А. Кубряков, П. В. Гайский**

*Морской гидрофизический институт РАН, Севастополь, Россия*

*\* e-mail: valenru93@mail.ru*

### **Аннотация**

Целью настоящей работы является анализ вертикальной изменчивости суточного хода температуры прибрежных вод в районе Южного берега Крыма. Исследование выполнено с использованием данных термопрофилемера с высоким временным разрешением 0.5 с, установленного на океанографической платформе в п. Кацивели, за период с 24.08.2021 по 26.11.2023. Определено, что суточный ход температуры выражен на всех горизонтах измерений, наиболее ярко – на верхнем горизонте 0.75 м с мая по август. Максимальные аномалии среднего суточного хода отмечаются в мае – июле в утренние и дневные часы. Максимальный прогрев происходит с 11:00 до 16:00 в слоях до 6–8 м, а в теплый период достигает горизонтов 14–16 м. Рассмотрены отдельные события значительного дневного прогрева в холодный и теплый периоды года. Амплитуда суточного хода составляет 1.3 °C в холодный и 3.5 °C в теплый период. Статистический анализ дневного прогрева  $\Delta T$  показал, что чаще всего  $\Delta T$  составляет менее 0.3 °C, а события с  $\Delta T$  более 2–3 °C редки. Наибольшая температура наблюдается в июне – августе на верхних горизонтах при ветре 2–4 м/с, прогрев может проникать до 18 м. В холодный период (ноябрь – апрель) при сильном ветре температура имеет низкие значения на всех горизонтах. Наибольшие средние значения  $\Delta T$  отмечаются летом при ветре до 6 м/с, с усилением ветра они снижаются; наименьшие – характерны для холодного периода года. В слоях до 4–6 м значения  $\Delta T$  летом превышают 0.8–1 °C, а зимой близки к 0 °C на всех горизонтах измерений. Таким образом, данные термопрофилемера могут быть использованы для анализа суточной изменчивости температуры вод прибрежной зоны. Результаты, полученные в исследовании, дополняют уже имеющуюся картину суточной изменчивости температуры в прибрежной зоне Черного моря. В частности, определено, что вертикальное распределение суточных колебаний температуры вод сильно зависит от сезона и ветровых условий, а в летний период дневной прогрев может проникать до глубин 14–18 м.

**Ключевые слова:** суточный ход температуры, распределенный датчик температуры, термопрофилимер, термокоса, Черное море, Южный берег Крыма

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## Introduction

Monitoring of the state of the coastal sea zone, such as the Southern Coast of Crimea (SCC), is necessary for understanding and predicting the natural processes occurring in it and their impact on the environment. The study of temperature variability of the coastal waters of the Black Sea in the SCC region is important for assessing ecosystem dynamics, identifying climate changes, and understanding processes at the sea–land boundary. Among the many hydrophysical parameters, the vertical thermal structure of waters is the most informative, since it determines the dynamics of biogeochemical components of the marine environment, the state of the coastal zone, and its recreational potential. Of particular interest is temperature variability, which reflects both seasonal and intraseasonal fluctuations that affect ecosystem processes and sea–land interaction.

The coastal zone of the SCC is characterised by high dynamism of the temperature regime due to its geographic location and climatic conditions. Since significant tidal oscillations are absent here, upwellings and wave processes of various origins play a decisive role in the formation of the thermal structure. The identification of such difficult-to-predict events, whose duration varies from several minutes to several days, is possible only through long-term continuous observations [1].

The study of the diurnal cycle of temperature in the upper ocean layer is among the priority tasks of modern oceanology, since it is diurnal fluctuations that make a substantial contribution to the turbulent exchange of heat and momentum between the ocean and the atmosphere and affect the formation of wind fields [2, 3]. Changes in water stratification caused by diurnal fluctuations in heat fluxes affect physical and biogeochemical processes in the upper ocean [2]. As shown in [4], diurnal temperature variability in the near-surface ocean layer is closely related to the radiation balance and turbulent exchange. The diurnal temperature cycle is recorded almost throughout the World Ocean, and its consideration is mandatory for a correct assessment of near-surface water temperature, which plays a significant role in heat and mass exchange across the water–air interface. Modelling results

confirm that diurnal temperature variability substantially modulates water stratification, turbulence conditions, and the formation of the upper quasi-homogeneous layer [5–7].

This problem has been addressed in many studies by both foreign and domestic authors [8–13] using *in situ* measurements and satellite monitoring. Fundamental works on the general circulation and climatology of the Black Sea, for example [14, 15], rely on standard hydrological sections, which cannot adequately reproduce high-frequency diurnal variability and coastal processes characteristic of the SCC coastal zone.

It should be noted that one of the main factors forming the thermal regime off the Crimean coast is upwelling. The overwhelming majority of modern studies of the variability of the coastal thermal structure of waters are devoted to it [1, 16–19]. Thus, in [1], based on thermistor chain data with a temporal resolution of 60 s, the seasonal cycle of synoptic thermal variability of waters at the Black Sea Hydrophysical Subsatellite Polygon, Katsiveli, in 2013 was estimated, and upwelling events not related to wind forcing were considered. In [20], the vertical thermal structure of Black Sea waters was studied using temperature-profiling drifters, and in [21], high-frequency SEVIRI scanner data combined with results of coastal *in situ* measurements made it possible to successfully study sea surface temperature (SST) variability in the coastal zone of the SCC.

The thermal structure of waters at the Black Sea Hydrophysical Subsatellite Polygon in Katsiveli has been studied from the stationary oceanographic platform of MHI since the mid-1990s using various instruments, including a thermistor chain installed from the near-surface to the bottom layer. In [22], information is given about the platform itself and its capabilities for long-term hydrometeorological measurements, as well as long-term data on the vertical distribution of sea temperature (1981–2003), which showed a positive trend in annual mean sea temperature. In [23], results of long-term measurements of water temperature off the SCC, performed in the area of the oceanographic platform at depths up to 25 m, as well as corresponding data on the wind field in this region, are presented. For the warm half-year, monthly changes in temperature at six standard levels (1, 5, 10, 15, 20, and 25 m) are detailed, and wind-induced upwelling/downwelling processes and their temporal variability are recorded.

The widespread use of thermistor chains and thermoprofilemeters has not led to a detailed study of the diurnal temperature cycle, since most works are devoted to upwellings and internal waves. An exception is [24], where water temperature in Balaklava Bay at depths from 14.5 to 29 m was measured with a thermistor chain (29.01.2022–04.02.2022). At each sensor, 303 water temperature values were recorded. Over the entire measurement period, the maximum temperature was 9.075°C and the minimum was 8.375°C. As a result, it was concluded that the diurnal cycle is not observed in the thermistor chain data. The features of the vertical variability of the diurnal temperature cycle in Black Sea waters are considered in more detail in [25], which studied significant diurnal warming events for the cold

and warm seasons. However, these measurements relate mainly to the deep-water part of the Black Sea. In addition, the vertical resolution of temperature-profiling drifters [20] in the surface layer is insufficient and is limited to data from only two sensors – at levels 0.2 and 12.2–12.5 m. Remote sensing data from the SEVIRI scanner [26] allow estimating the diurnal cycle of SST, as well as extreme warming events, but the vertical temperature distribution is not recorded by this scanner. The model study [27] reproduces, based on NEMO calculation results, the vertical distribution of the diurnal temperature cycle for the Black Sea basin in different seasons of 2015; however, no similar works have been carried out for the SCC region.

Thus, at present there are no studies that, on the basis of long-term *in situ* measurements, analyse the vertical distribution of the diurnal temperature cycle in the coastal zone of the SCC in different seasons.

The aim of our work is to estimate the diurnal variability of the temperature of the upper water layer in the SCC region using high-frequency thermoprofilemeter data over a period of more than two years. To achieve this aim, the following tasks were performed: the vertical distribution of diurnal oscillations and its features in different seasons were studied and described, a statistical analysis of diurnal warming events in the upper water layer was carried out, and the relationship of diurnal temperature variability with wind forcing was analysed.

## Methods

*Region and measurement period.* The study was carried out using data obtained at the stationary oceanographic platform of Marine Hydrophysical Institute, Russian Academy of Sciences, located in Katsiveli (SCC) at a distance of about 500 m from the shore. The sea depth at the measurement point was about 30 m. Measurements were performed from 24.08.2021 to 26.11.2023.

*Thermoprofilemeter data.* Vertical temperature profiles were obtained using a distributed temperature sensor (thermoprofilemeter) with a total length of 24 m, consisting of 16 1.5-m temperature-sensitive sections [28]. The sensor installation anchored on the bottom near the platform provided continuous measurements of the interpolated temperature profile to a depth of 19.5 m. The remaining sections (4.5 m) were located vertically above the water and at the interface in the surface sea-wave zone. In this work, data from 16 measurement levels were analysed: 0.75, 2.25, 3.75 m above sea level; –0.75, –2.25, –3.75, –5.25, –6.75, –8.25, –9.75, –11.25, –12.75, –14.75, –15.75, –17.25, –18.75 m relative to sea level. The primary polling period of all sections was 0.5 s, which made it possible to obtain an almost instantaneous picture of vertical temperature stratification. The instrumental resolution of the sensor measuring channels was 0.0026°C. The declared measurement error at the profile sections is 0.1°C. The thermal inertia of the sensor is about 30 s [29].

*Wind speed data.* Measurements <sup>1)</sup> were carried out on the same platform at a height of 21 m above sea level with subsequent reduction to the standard observation height of 10 m [30]. The marine part of the platform, oriented approximately 50°–230° relative to north, was used. The direction range available for wind measurements is 340°–0°–270°. All data passed quality control with rejection of unreliable fragments.

*Data processing.* To analyse temporal variability and the diurnal cycle of temperature, the initial thermoprofiler data (polling period 0.5 s) were averaged to hourly values. Data for levels 0.75 m and lower were analysed. For each measurement level, time series of temperature were constructed, on the basis of which seasonal and diurnal variability was estimated.

To quantify diurnal oscillations, two parameters were used:

- the amplitude of the diurnal cycle (*A*), calculated as the difference between the maximum and minimum temperature values over a calendar day. This parameter characterises the total range of diurnal oscillations, but can be distorted by upwellings leading to sharp cooling;

- diurnal warming ( $\Delta T$ ) – the difference between temperature at 17:00 and 4:00 local time:

$$\Delta T = T_{17:00} - T_{04:00}.$$

The choice of these hours is justified by the fact that, according to preliminary analysis of the mean diurnal cycle, 04:00 corresponds to the temperature minimum and 17:00 to the maximum in most months. The use of  $\Delta T$  allows a more objective assessment of diurnal warming itself, excluding the influence of upwellings and other short-term cooling events that can falsely overestimate the amplitude *A*.

*Statistical analysis.* To estimate the frequency of occurrence of diurnal warming events, histograms of the  $\Delta T$  distribution were constructed for the entire measurement period, as well as separately for the warm (May–September) and cold (November–March) seasons. Only positive  $\Delta T$  values were analysed (cases when the temperature at 17:00 exceeded the temperature at 04:00).

*Limitations.* The analysis was performed for one fixed measurement location; therefore, the obtained results reflect local features of the diurnal cycle and may not fully correspond to open-sea conditions. The profiler data cover only the upper layers at depths of 0–19.5 m, which limits the possibility of analysis at deeper levels.

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<sup>1)</sup> Kuznetsov, A.S., Garmashov, A.V. and Zima, V.V., 2023. Database for Wind Characteristics Monitoring for the Black Sea Coastal Ecotone at Cape Kikineiz of the Southern Coast of Crimea for 2013–2022 [Database]. Moscow. State Registration No. 2023622482 (in Russian).

## Results and Discussion

### *Diurnal and seasonal cycles of water temperature in the upper layer*

The time course of water temperature at the 0.75 m level from 24.08.2021 to 26.11.2023 (Fig. 1) demonstrates a clearly pronounced seasonal cycle and diurnal variability. The lowest temperature at this level was 7.4°C (23:00 10.03.2022), and the highest was 29°C (16:00 22.08.2023). In the pattern of the temperature time course, events of upwellings and extreme diurnal warming events stand out, with an amplitude of the diurnal temperature cycle at the upper level exceeding 10°C (examples are marked by ellipses in Fig. 1).

Fig. 2, *a* presents the distribution of mean temperature at the 0.75 m measurement level by months and hours of the day. From the obtained distribution it is seen that the seasonal cycle makes the most substantial contribution to temperature variability. Maximum temperatures during the year occur in August (in the afternoon hours) and average 26.6°C; minimum values are observed in February–March (at night and in the morning) and are 8.9–9°C.

The temperature anomaly diagram (Fig. 2, *b*) shows the deviation of the diurnal temperature cycle at the 0.75 m level from the mean seasonal value. The largest absolute anomalies are observed in May–August, when the diurnal temperature cycle is most pronounced. Maximum values are recorded in June–July and range from  $-0.9\ldots-0.8^{\circ}\text{C}$  (2:00–5:00) to approximately  $+1^{\circ}\text{C}$  at 17:00. Such a distribution of the mean diurnal cycle is in good agreement with estimates obtained earlier from SST data [26] and with the distribution pattern obtained in [27] from NEMO

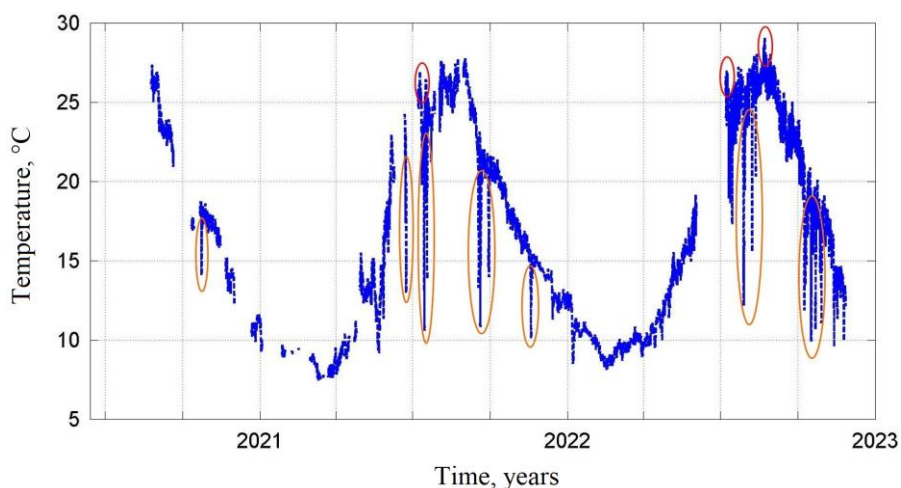


Fig. 1. Temporal variability of temperature at a depth of 0.75 m from 24.08.2021 to 26.11.2023, based on thermoprophilemeter data (examples of extreme daytime warming are marked with red ellipses; examples of upwelling events are marked with orange ellipses)

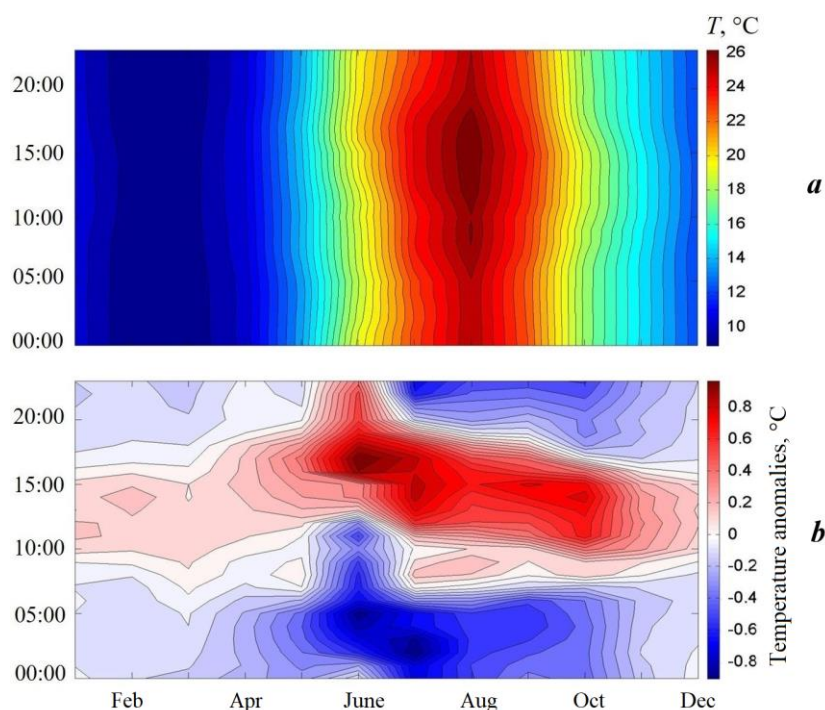


Fig. 2. Seasonal variability based on thermoprofile-meter data for 2021–2023: temperature at a depth of 0.75 m by hour of day and month (a); temperature anomalies at a depth of 0.75 m by hour of day and month (b)

model calculations. The discrepancy with temperature-profiling drifter data [25] at the 0.2 m level (maximum anomalies in April–May, reaching  $\pm 0.4^{\circ}\text{C}$ ) is most likely explained by the fact that the thermoprofilemeter was located in the coastal shallow-water zone and measurements were carried out at one fixed point. In summer, breeze winds make an additional contribution to the variability of the diurnal cycle in the coastal zone. Temperature-profiling drifters, by contrast, operated mainly in the deep-water part of the Black Sea and constantly changed their position.

#### *Vertical distribution of the diurnal temperature cycle*

At the 0.75 m level, the mean diurnal cycle is traced throughout the year (Fig. 3). Maximum temperatures were recorded from 11:00 to 16:00; the time of maximum varied by month: in February at 14:00, in May at 17:00, in August at 15:00, and in November at 12:00 (Fig. 3, *a–d*).

One of the parameters analysed in this work is the amplitude (*A*) of the diurnal cycle. *A* takes maximum values in June–October. At the upper measurement level in June, it reached  $1.8^{\circ}\text{C}$ , in July  $1.7^{\circ}\text{C}$ . In the cold season, the mean amplitude

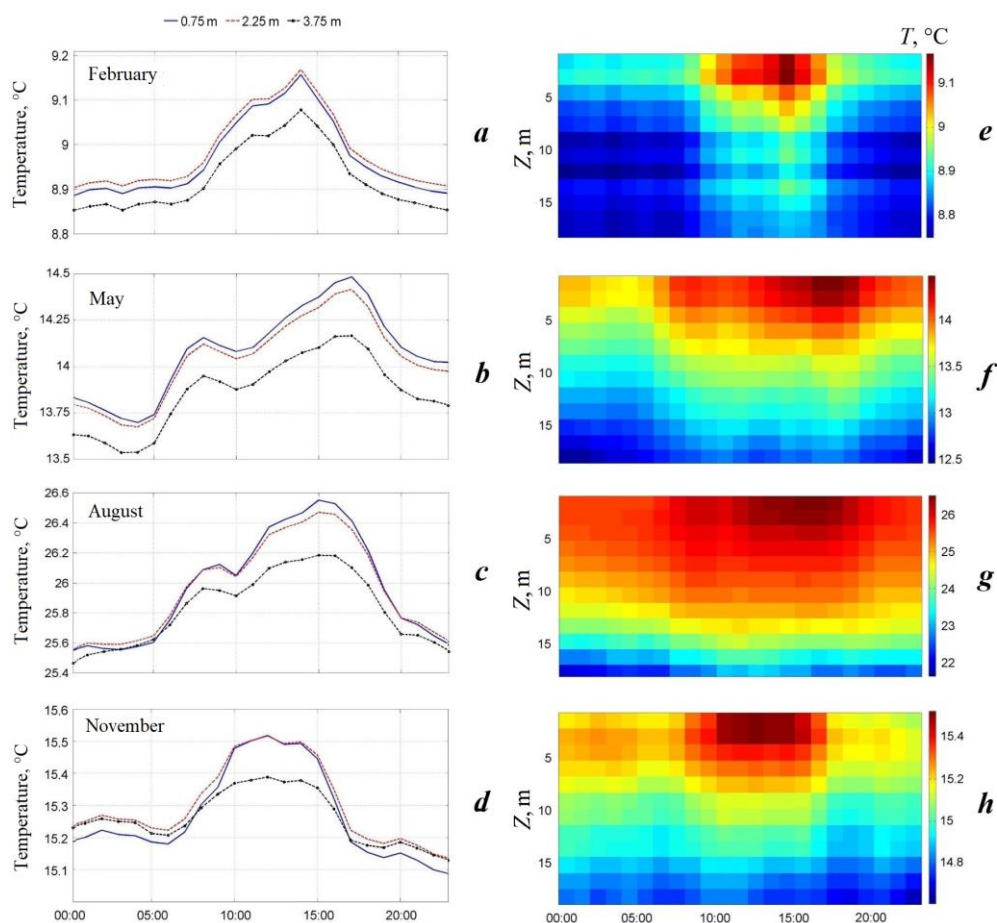


Fig. 3. The mean diurnal temperature cycle at depths of 0.75, 2.25 and 3.75 m (*a–d*) and vertical distribution of the mean diurnal temperature cycle (*e–h*) for February (*a, e*); May (*b, f*); August (*c, g*); November (*d, h*) 2021–2023

did not exceed  $0.4^{\circ}\text{C}$ . Maximum warming was noted predominantly in the upper layers down to 6–8 m depth. However, in the warm season it extended to the lower measurement levels, 14–16 m (Fig. 3). At the 18.75 m level, the mean diurnal temperature cycle was expressed to a greater or lesser extent in all months except July and November. It was most clearly manifested in June ( $A = 1.5^{\circ}\text{C}$ ), August ( $A = 1.4^{\circ}\text{C}$ ), and October ( $A = 0.7^{\circ}\text{C}$ ).

It should be noted separately that in the cold period (November–March) and in the period of seasonal temperature decrease (August–October), during the morning and evening–night hours, the water temperature at the upper measurement level was lower than in the underlying layers. This is clearly seen in Fig. 3, *a, c, d*. In December–March, the temperature at the 0.75 m level was lower than

at the 2.25 m level. From August to November, during the evening and morning hours, the temperature in the upper layer was lower than at the 3.75 m level (Fig. 3), and only from 10:00 to 15:00 did it become higher than in the underlying layers.

In [25], which studied the mean diurnal cycle for levels 0.2 and 12.2 m, such a vertical temperature distribution in the diurnal cycle is associated with the fact that during daytime the waters of the upper layer warm up, while during night and morning hours nocturnal convection cools this upper layer, and the temperature at the lower levels turns out to be higher than in the upper layer.

#### *Features of the diurnal cycle and diurnal warming*

Diurnal warming events in the warm season. The time range of thermoprofilemeter measurements included two warm periods – May–August 2022 and 2023. The thermoprofilemeter data well reflect seasonal warming. The highest temperature values were recorded in August. A number of pronounced upwelling events are observed.

Let us consider in more detail the events of significant diurnal warming in the warm season. In May 2023, for example (Fig. 4, *a*), it is clearly seen that on average the  $A$  values at the upper level did not exceed  $3.5^{\circ}\text{C}$ .  $A$  values above  $4^{\circ}\text{C}$  correspond to upwelling events (highlighted in blue). For example, on 28 May  $A$  reached  $13.4^{\circ}\text{C}$  due to cooling, when the water temperature at the 0.75 m level on that day almost equalled the temperature at the 18.75 m level (Fig. 4, *a*).

An event of intense diurnal warming was recorded on 22.07.2023 (Fig. 4, *b*). The temperature of the upper layer increased from  $23.7$  to  $27.2^{\circ}\text{C}$ ,  $A = 3.5^{\circ}\text{C}$ . On that day, wind speed was lower than on the previous and following days and did not exceed  $6\text{ m/s}$ ; air temperature reached  $29^{\circ}\text{C}$ . At the same time, on 21 and 23 July, when wind speed exceeded  $10\text{ m/s}$ , no similar warming was observed despite the high air temperature (Fig. 4, *b*). Stable stratification formed: the water temperature at the 18.75 m level remained at  $18\text{--}19^{\circ}\text{C}$ .

The mean amplitude of the diurnal cycle  $A$  was  $2^{\circ}\text{C}$ , reaching  $3\text{--}3.5^{\circ}\text{C}$  in some cases (Fig. 4, *b*). As an example, consider the warming event of 22 July: over the day  $A$  reached  $3.5^{\circ}\text{C}$ , and water temperature rose from  $23.7$  to  $27.2^{\circ}\text{C}$  (Fig. 4, *b*). This was due to hydrometeorological conditions: wind speed during that day did not exceed  $6\text{ m/s}$ , and air temperature increased from  $24.5$  to  $25^{\circ}\text{C}$ . At the same time, on 23 July, despite a substantial increase in air temperature to  $27.5^{\circ}\text{C}$ , no such water warming was observed because of wind intensification to  $10\text{ m/s}$ . Temperature stratification was noted: at the 18.75 m level, water temperature during this time interval did not exceed  $17^{\circ}\text{C}$ , which was substantially lower than in the upper layers.

Diurnal warming events in the cold season. In the cold season (Fig. 5, *a*), from December 2022 to March 2023, the mean amplitude of the diurnal cycle at the upper 0.75 m level was  $0.5^{\circ}\text{C}$ , somewhat higher than estimates obtained in [11] from thermistor chain data in the Baltic Sea for the analogous period of 2014 ( $0.1\text{--}0.3^{\circ}\text{C}$ ).

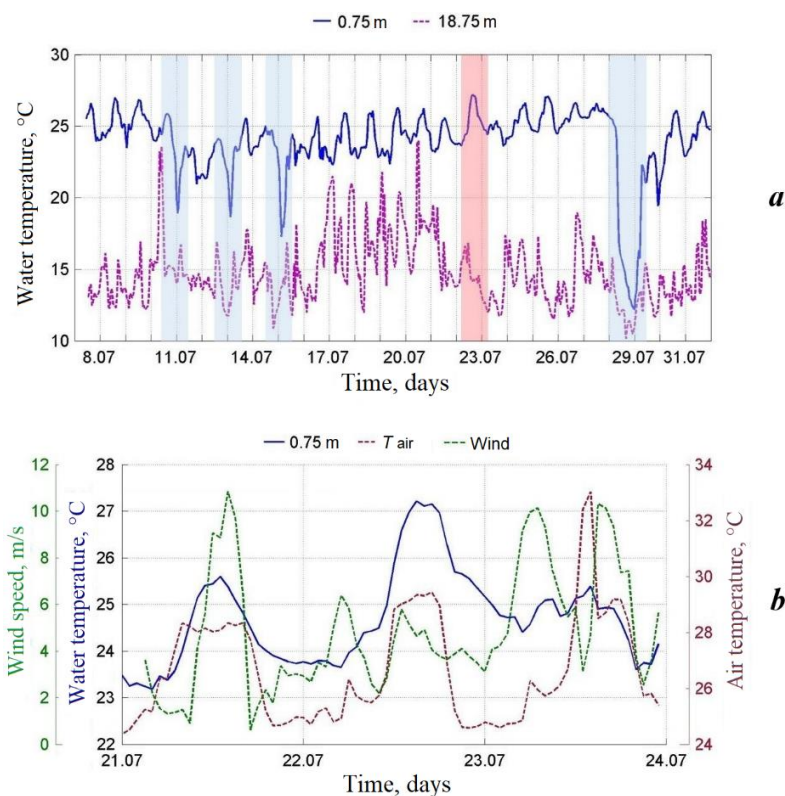


Fig. 4. Temporal variability of temperature at depths of 0.75 m and 18.75 m from 7.07.2023 to 31.07.2023 (the warming event on 22 July 2023 is highlighted with red shading; upwelling events are highlighted with blue shading) (a); time series of air temperature, water temperature at a depth of 0.75 m, and wind speed (b)

This difference is probably related to different measurement regions: in this work, profiler data in the coastal zone of the Black Sea were used, whereas in [11] measurements were carried out with a thermistor chain in the open part of the Baltic Sea.

Four warming events were identified for which  $A$  values reach and exceed  $1^{\circ}\text{C}$ : 21.12.2022 ( $1.3^{\circ}\text{C}$ ), 29.12.2022 ( $1^{\circ}\text{C}$ ), 08.01.2023 ( $1.2^{\circ}\text{C}$ ), and 06.03.2023 ( $1^{\circ}\text{C}$ ).

Let us consider in more detail the warming event of 21.12.2022 (Fig. 5, b). On that day, water temperature and the amplitude of its diurnal cycle reached fairly high values – 14 and  $1.3^{\circ}\text{C}$ , respectively. Wind speed during the day under consideration did not exceed 6 m/s, and in the daytime hours almost calm conditions persisted (2–4 m/s). At the same time, air temperature reached a maximum and was  $12\text{--}14^{\circ}\text{C}$  in the daytime. In addition, on the previous day, 20 December,

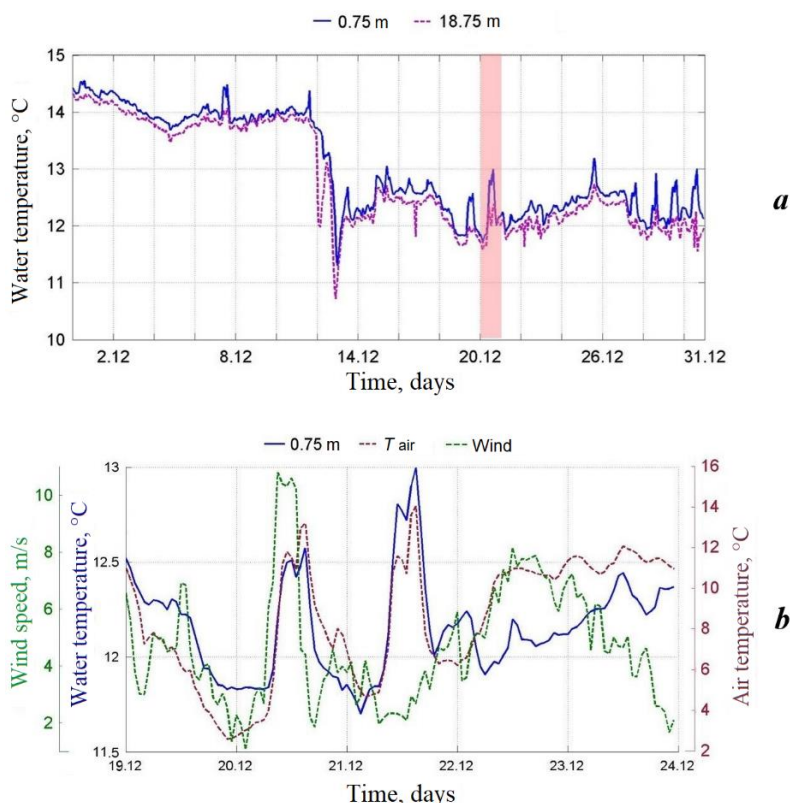


Fig. 5. Temporal variability of temperature at depths of 0.75 m and 18.75 m from 1.12.2022 to 31.01.2023 (the warming event on 21.12.2022 is highlighted with red shading) (a); time series of water temperature, air temperature, and wind speed for the period from 19.12.2022 to 23.12.2022 (b)

substantial diurnal warming event was also noted with  $A = 0.75^{\circ}\text{C}$  at a fairly high air temperature ( $13.2^{\circ}\text{C}$ ). It is clearly seen that with a gradual increase in wind speed and a decrease in air temperature, the intensity of diurnal warming decreases significantly: on 22 and 23 December,  $A$  values did not exceed  $0.4^{\circ}\text{C}$  (Fig. 5, b).

During the same period, two upwellings were recorded – on 13.12.2022 and 07.01.2023 (Fig. 5, a), when water temperature at the upper 0.75 m level decreased from 14 to  $11.3^{\circ}\text{C}$  and from 12.2 to  $8.6^{\circ}\text{C}$ , respectively.

Extreme warming events can be observed both from remote sensing data and from temperature-profiling drifter measurement results. The conditions of its formation are similar to those described in [25, 26]: low wind speed and absence of cloud cover.

Amplitude of the diurnal temperature cycle, diurnal warming, and statistical distribution of diurnal warming value in the upper water layer. For statistical analysis of diurnal warming events, the amplitude  $A$ , calculated as the difference between the maximum and minimum temperature values over the considered day, may not always be an appropriate measure. This is because during the day not only warming but also cooling can occur, often associated with upwellings. Fig. 6 compares time series of  $A$  and  $\Delta T$  (difference in temperature values at 17:00 and 4:00) at the 0.75 m level. Such a temperature difference allows an objective assessment of diurnal warming, since at these hours the diurnal maximum and minimum temperatures are observed, respectively (see Fig. 2, *b*). It is clearly seen that for events with extremely high  $A$  values, in the overwhelming majority of cases  $\Delta T$  values are negative, indicating cooling.

Statistical analysis of diurnal warming events was carried out only for positive  $\Delta T$  values (warming cases). Distributions for the entire period as a whole, as well as separately for the warm and cold seasons, show (table) that warming with  $\Delta T$  less than  $0.3^{\circ}\text{C}$  is most common.

Events with  $\Delta T = 2\text{--}3^{\circ}\text{C}$  were rare and accounted for no more than 2% of the total number of warming events and 6% in the warm season. In the warm period (May–September),  $\Delta T$  can reach  $5^{\circ}\text{C}$  and higher, whereas in the cold period (November–March),  $\Delta T$  does not exceed  $3^{\circ}\text{C}$ , and warming events with  $\Delta T > 1^{\circ}\text{C}$  constitute less than 1%.

Variability of water temperature and diurnal warming for different months of the year and the relationship of these quantities with the wind field and measurement level. The dependence of water temperature and diurnal warming  $\Delta T$  on measurement level and wind speed in different months of the year was studied.

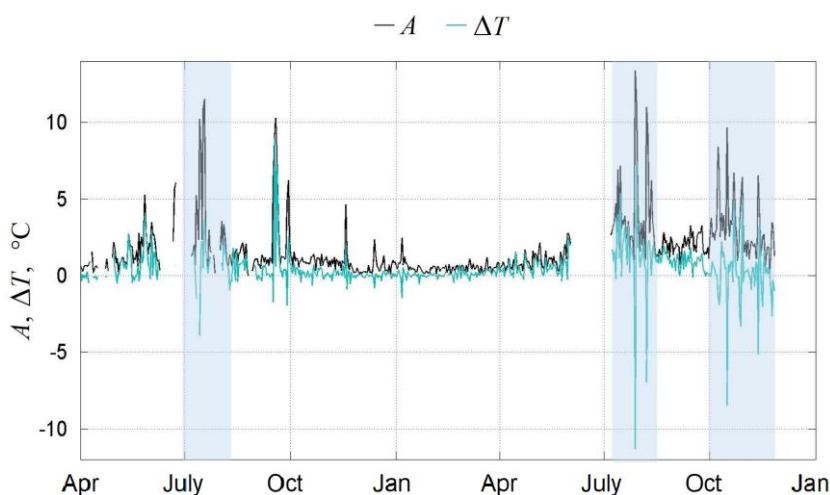


Fig. 6. Temporal variability of  $A$  values and the temperature difference  $\Delta T$  (events with  $A$  corresponding to upwelling are highlighted with blue shading)

Statistical distribution of daytime warming  $\Delta T$ , %

| $\Delta T$ ,<br>°C        | May–<br>September | November–<br>March | Entire<br>period |
|---------------------------|-------------------|--------------------|------------------|
| $\Delta T < 0.3$          | 28                | 84                 | 57               |
| $0.3 \leq \Delta T < 0.5$ | 12                | 11                 | 13               |
| $0.55 \leq \Delta T < 1$  | 25                | 4                  | 14               |
| $1 \leq \Delta T < 1.55$  | 17                | < 1                | 8                |
| $1.55 \leq \Delta T < 2$  | 8                 | < 1                | 4                |
| $2 \leq \Delta T < 2.9$   | 6                 | < 1                | 2                |
| $2.9 \leq \Delta T < 3.5$ | ~1                | 0                  | < 1              |
| $3.5 \leq \Delta T < 4.5$ | ~1                | 0                  | < 1              |
| $4.5 \leq \Delta T < 5$   | ~1                | 0                  | < 1              |
| $5 \leq \Delta T < 8$     | < 1               | 0                  | < 1              |
| $\Delta T \geq 8$         | 0                 | 0                  | < 1              |

For each interval of wind speed, month, and measurement level, the mean  $\Delta T$  value was determined. The obtained dependence is presented as a diagram;  $\Delta T$  was calculated as the difference in temperature at 17:00 and 4:00 to exclude the influence of upwellings and situations when there were few temperature measurements during the day and the difference between maximum and minimum values cannot be considered the amplitude of the diurnal cycle.

At the upper measurement level, the highest  $\Delta T$  values (1.8–2°C) are observed in the summer months (June–August), with a maximum in July (2.3°C) at wind speeds up to 4 m/s (Fig. 7, *a*). With increasing wind speed,  $\Delta T$  decreases. The lowest  $\Delta T$  values occur in the cold season and on average do not exceed 0.3–0.4°C.

A similar dependence for the amplitude of the diurnal cycle  $A$ , constructed from satellite data over a multi-year period [31], has a similar character; however, the maximum of  $A$  is shifted to April–June, with the highest values in June. Such a difference may be related both to the different duration of the data time series and to the measurement level and method of data acquisition.

According to the vertical distribution (Fig. 7, *b*), the highest  $\Delta T$  values also occur in June–August, with a maximum in July in the upper water layers down to 4–6 m, exceeding 1°C at the surface. At levels down to 8 m,  $\Delta T$  reaches 1°C. From April,  $\Delta T$  in the upper layers increases, and in September it decreases. Minimum  $\Delta T$  values are noted in December–February for all considered levels.

The main feature of the obtained dependence is a local maximum of  $\Delta T$  in the 14–18 m layer in June–July. Temperature at the lower levels fluctuates substantially due to internal waves, as well as local currents and advection. In June–July, the seasonal thermocline layer is located at this depth, and its oscillations lead

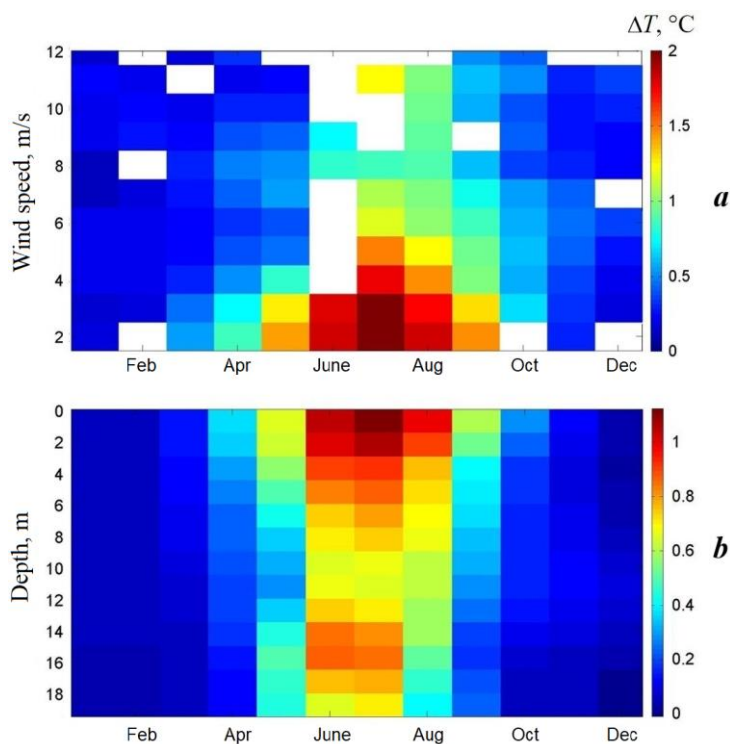


Fig. 7. Dependence of diurnal warming for different months: on wind speed at a depth of 0.75 m (a) and on the depth (b)

to an increase in  $\Delta T$ . In addition, in the summer months, in the 16–20 m layer, there is a maximum of spectral energy of inertial oscillations [13], coinciding with a local maximum of spectral energy of diurnal oscillations.

### Conclusion

The vertical distribution of the diurnal variability of water temperature in the Black Sea in the SCC region was studied using thermoprofilemeter data with a high temporal resolution (0.5 s). It was determined that the thermoprofilemeter data well display the diurnal, seasonal, and interannual course of temperature, as well as upwelling and extreme warming events.

The diurnal cycle is traced to a greater or lesser extent for all analysed levels in each month of the year. At the upper 0.75 m level, it is most pronounced in May–August. The largest absolute values of anomalies in the mean diurnal cycle occur in May–July at 4:00–5:00 and 15:00–17:00.

The mean diurnal temperature cycle at different levels in different months was analysed. Maximum warming was observed from 11:00 to 16:00 (the time varied

by month), predominantly in the upper layers down to 8 m. However, in the warm season, warming extended to the lower measurement levels, 14–16 m. In the cold season (November–March), as well as during the period of seasonal cooling (August–October), during the morning and evening–night hours, the temperature at the upper 0.75 m level was lower than in the underlying layers.

Events of extreme diurnal warming in the cold and warm seasons were considered. The amplitude  $A$  of the diurnal temperature cycle was 1.3 and 3.5°C, respectively. The formation of such significant warming was favoured by calm conditions and elevated air temperature. Data on the vertical temperature distribution allow the conclusion that stable stratification formed: vertical mixing of water, especially in the warm season, was almost absent.

A statistical analysis of diurnal warming  $\Delta T$  was performed. Warming of less than 0.3°C is most common. Events in which temperature increased by more than 2–3°C per day were rare and accounted for no more than 2% of the total number of warming events and 6% in the warm season. In the warm season,  $\Delta T$  can reach 5°C and higher, whereas from November to March  $\Delta T$  does not exceed 3°C, and warming events with  $\Delta T > 1^\circ\text{C}$  during this period are rare and account for no more than 1%. The highest water temperature is reached in June–August in the upper layers at wind speeds of 2–4 m/s. In the warm season, at minimum wind speed, water warmed to a depth of 16–18 m. From November to April, under high wind speed, temperature variability was minimal at all considered measurement levels.

The highest  $A$  values at the 0.75 m level (1.5°C and higher) were observed at wind speeds up to 6 m/s from May to September, with maximum values in July (on average 2.5°C). Minimum  $A$  values were noted from November to April at almost any wind speed. During the spring warming period, amplitude  $A$  increased at wind speeds below 5 m/s. In the vertical distribution, the highest  $A$  values occurred in July; maximum values were concentrated in the 8–17 m layer.

The variability of  $\Delta T$  in different months at different wind speeds and at different measurement levels was analysed. For the upper level, the highest  $\Delta T$  values (1.8–2°C) were observed in the summer period, from June to August, with a maximum in July (2.3°C) at wind speeds up to 4–6 m/s. With increasing wind speed,  $\Delta T$  decreases. The lowest  $\Delta T$  values were recorded in the cold season and on average did not exceed 0.3–0.4°C.

The highest  $\Delta T$  values occur in June–August, with a maximum in July in the upper water layers. In the layer down to 4–6 m,  $\Delta T$  exceeds 1°C in the summer months, whereas in the 10–12 m layer it does not exceed 0.65°C in the summer months. Minimum  $\Delta T$  values, close to 0°C, were observed at the lower measurement levels in November–March.

This work demonstrates the successful use of thermoprofilemeter data for analysing the diurnal variability of water temperature in the coastal zone. These data can be used for verification of numerical models of hydrothermodynamics of coastal zones, as well as for studying upwelling events, which will be presented

in further works. The obtained results complement existing understanding of diurnal temperature variability in the coastal zone of the Black Sea. It was determined that the vertical distribution of diurnal water temperature fluctuations strongly depends on the season and wind conditions, and in the summer period diurnal warming can penetrate to depths of 14–18 m.

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#### *About the authors:*

**Valentina A. Rubakina**, Junior Researcher, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russia), PhD (Phys.-Math.), **ORCID ID: 0000-0001-5028-5911**, **SPIN-code: 2924-8373**, **ResearcherID: U-5746-2019**, **Scopus Author ID: 57209578281**, [valenru93@mail.ru](mailto:valenru93@mail.ru)

**Arseniy A. Kubryakov**, Deputy Director for Research, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russia), DSc (Phys.-Math.), **ORCID ID: 0000-0003-3561-5913**, **ResearcherID: F-8921-2014**, **Scopus Author ID: 37072750100**, [arskubr@yandex.ru](mailto:arskubr@yandex.ru)

**Pavel V. Gaisky**, Leading Researcher, Head of Laboratory, Marine Hydrophysical Institute of RAS (2 Kapitanskaya St., Sevastopol, 299011, Russia), PhD (Techn.), **ORCID ID: 0000-0003-3110-848X**, **ResearcherID: HQZ-3112-2023**, **Scopus Author ID: 57222760697**, [gaisky@inbox.ru](mailto:gaisky@inbox.ru)

*Contribution of the authors:*

**Valentina A. Rubakina** – review of literature on the research problem, analysis of the data used, description of the research results, writing the text of the article, formulation of conclusions

**Arseniy A. Kubryakov** – formulation of the problem, analysis of the data used, description of the research results, formulation of conclusions

**Pavel V. Gaisky** – review of literature on the research problem, provision of data, analysis of the data used, preparation of article materials, formulation of conclusions

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

Original paper

## Concentrations of Nutrients in the Pore Waters of the Sevastopol Bay Bottom Sediments

K. I. Gurov \*, A. V. Varenik, M. A. Myslina

*Marine Hydrophysical Institute of RAS, Sevastopol, Russia*

*\* e-mail: gurovki@gmail.com*

### Abstract

The paper aims to assess features of the spatio-temporal distribution of nutrient concentrations in the pore waters of the upper sediment layer based on modern *in situ* data. Samples were collected using a DCh-0.025 bottom grab sampler. Pore water was extracted by centrifugation (Elmi CM-6MT centrifuge). Concentrations of inorganic nutrients were determined photometrically using a KFK-3KM spectrophotometer and a Skalar San++ continuous flow autoanalyser (the Netherlands) after filtration (0.45 µm membrane), except for ammonium samples. Ammonium nitrogen was measured by a modified Sagi–Solorzano method. Correlation coefficients and their significance were calculated using the Statistica software. Qualitative and quantitative characteristics of the spatial distribution of nutrient concentrations in pore waters from the upper sediment layer were obtained for samples collected in Sevastopol Bay in 2024. Seasonal variability was revealed, and relationships with station location, sediment type and geochemical properties of the solid phase were established. In the upper sediment layer of Sevastopol Bay, a weakly alkaline reducing environment predominated: pH and Eh values ranged from 7.1 to 7.8 and from 0 to –270 mV, respectively. Over the year, mean concentrations varied within the following ranges: nitrites were 0.23–0.37 µM; nitrates were 0.71–3.61 µM; phosphates were 11.91–25.84 µM; silicic acid was 21.14–297.30 µM; and ammonium was 139.64–543.76 µM. A negative correlation was found between ammonium and phosphate concentrations and Eh ( $r = -0.8$  and  $-0.7$ , respectively), while phosphates and silicic acid showed positive correlations with pH ( $r = 0.7$  and  $0.6$ , respectively). The weakly alkaline reducing conditions observed in the sediments of Sevastopol Bay are the main factor controlling elevated ammonium and phosphate concentrations and low nitrate levels. Intra-annual dynamics of nutrient concentrations in pore waters are influenced by hydrological parameters (water temperature), hydrodynamic conditions in different parts of the bay (autumn–winter mixing), as well as by additional local inputs of nutrients with stormwater and sewage discharges.

**Keywords:** Sevastopol Bay, bottom sediments, redox conditions, pore waters, nutrients, nitrates, nitrites, phosphorus, silicon, ammonium

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## **Содержание биогенных элементов в поровых водах поверхностного слоя донных отложений Севастопольской бухты**

**К. И. Гуров \*, А. В. Вареник, М. А. Мыслина**

*Морской гидрофизический институт РАН, Севастополь, Россия*

*\* e-mail: gurovki@gmail.com*

### **Аннотация**

Цель работы – оценить особенности пространственно-временного распределения концентрации биогенных элементов (нитратов, нитритов, аммония, фосфатов и кремнекислоты) в поровых водах поверхностного слоя донных отложений Севастопольской бухты по современным натурным данным. Пробы были отобраны с помощью дночерпателя ДЧ-0,025. Поровые воды извлекали с помощью центрифуги *Elmi CM-6MT*. Концентрации минеральных форм биогенных элементов определяли фотометрически с использованием спектрофотометра КФК-3КМ и проточного автоматического анализатора биогенных элементов *Scalar San++* (Нидерланды) после фильтрации (фильтр 0.45 мкм), за исключением проб для определения ионов аммония. Аммонийный азот определяли с помощью модифицированного метода Сэджи – Солорзано. Коэффициенты корреляции и степень их достоверности были рассчитаны с помощью программы *Statistica*. Получены качественные и количественные характеристики пространственного распределения концентраций биогенных элементов в поровых водах из верхнего слоя донных отложений, отобранных в Севастопольской бухте в 2024 г. По результатам анализа была выявлена их сезонная изменчивость, установлены связи с географическим расположением станций, типом донных отложений и геохимическими характеристиками их твердой фазы. В верхнем слое донных отложений Севастопольской бухты формируется преимущественно слабощелочная восстановительная среда: значения pH и Eh изменяются в диапазоне от 7.1 до 7.8 и от 0 до –270 мВ соответственно. Установлено, что в течение года средние концентрации нитритов изменяются в диапазоне 0.23–0.37 мкМ; нитратов – 0.71–3.61 мкМ; фосфатов – 11.91–25.84 мкМ; кремнекислоты – 21.14–297.30 мкМ; ионов аммония – 139.64–543.76 мкМ. Выявлена отрицательная корреляция концентраций аммония и фосфатов с Eh ( $r$  равно –0.8 и –0.7 соответственно), положительная – фосфатов и кремнекислоты с pH ( $r$  равно 0.7 и 0.6 соответственно). Наблюдаемые для донных отложений Севастопольской бухты слабощелочные восстановительные условия являются определяющим фактором повышенных концентраций аммонийного азота и фосфатов, а также низких концентраций нитратов. Внутригодовая динамика концентраций биогенных элементов в поровых водах донных отложений бухты определяется влиянием гидрологических параметров вод (изменение температуры вод), гидродинамических условий в отдельных районах бухты (осенне-зимнее перемешивание), а также дополнительным локальным поступлением биогенных элементов с ливневыми и канализационными стоками.

**Ключевые слова:** Севастопольская бухта, донные отложения, окислительно-восстановительные условия, поровые воды, биогенные элементы, нитраты, нитриты, фосфаты, кремнекислота, ионы аммония

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## Introduction

Sevastopol Bay, a classic semi-enclosed water area with hindered water exchange and intense anthropogenic load, is a complex dynamic ecosystem where the hydrological, hydrochemical, and geochemical regimes are formed under the influence of natural and anthropogenic factors. It is known that organic matter is actively accumulated in the bottom sediments of the bay [1].

The functioning of marine ecosystems is largely limited by the availability of nutrients. The balance of these elements regulates biological productivity, determines the character of biogeochemical cycles, and ultimately influences the evolution of the marine environment, since it directly controls the scales of photosynthesis and organic matter degradation [2].

Studies devoted to analysis of the variability of the content of inorganic nutrients in the Sevastopol Bay waters have been carried out in the Marine Biogeochemistry Department of Marine Hydrophysical Institute for more than 20 years [2–5]. In the recent study [2], the authors indicate that the influence of the anthropogenic factor on the hydrochemical regime of the bay prevails over natural processes, and note an increase in concentrations of almost all studied nutrients in 2007–2016.

When the level of anthropogenic load in aquatic ecosystems is assessed, bottom sediments are one of the most informative objects of study. The surface layer of bottom sediments (0–5 cm) is a dynamic geochemical structure in which exchange occurs most intensively between the solid and liquid phases, as well as between the sediment and the water column. An important parameter determining the intensity of all occurring processes is the redox potential (Eh). At the same time, pore waters are also one of the key links in the transformation of the main nutrients and maintain the productivity of marine ecosystems. The regeneration and binding in sediments of nitrogen, phosphorus, and silicon, which serve as nutrient sources for phytoplankton, largely determine the trophic status of the entire water column [13, 14].

It is worth noting that the study of nutrient fluxes is important for understanding eutrophication processes. However, despite systematic investigation of the physicochemical characteristics of bottom sediments (including the chemical composition of pore waters [11, 12]) and the accumulation patterns of organic and inorganic

pollutants in them [6–10], data on the quantitative characteristics and spatial distribution of nutrients in pore waters are absent.

The present paper aims to assess features of the spatio-temporal distribution of nutrient concentrations in the pore waters of the surface layer of bottom sediments based on modern in situ data.

## Methods and Materials

**Characteristics of the study area.** The Sevastopol Bay water area has long been a base of the Russian Navy with various types of industrial and economic infrastructure, as well as a zone of active navigation and hydraulic engineering works. In addition, a large urban agglomeration, the city of Sevastopol, is located on the shores of the bay. As a result, the water area experiences an extremely high integrated level of anthropogenic load, which leads to disruption of existing ecological equilibria. For a long time, seafood was harvested and cultivated in the bay, but now this is impossible due to depletion of biological resources and a high level of pollution [3]. Currently, the bay is among the most polluted coastal water areas in the Black Sea and, according to model estimates [15], is characterised by a low self-purification capacity.

The hydrological and hydrochemical regimes of Sevastopol Bay have been the subject of long-term studies [2–5, 15–24] and are formed as a result of the complex interaction of a number of factors: the intensity of water exchange between the bay and the adjacent open part of the Black Sea, the features of water circulation inside the bay [18, 19], the runoff of the Chernaya River, the input of storm-water and sewage waters, as well as atmospheric deposition [3, 4, 16, 21, 22].

According to [3, 15, 17], wind has the greatest effect on the hydrological regime of the bay. Northern and northeastern winds cause a regime of blocked water exchange and accumulation of pollutants. A change of wind to southerly, on the contrary, promotes removal of accumulated polluted waters, including domestic sewage, toward the northern coast of Sevastopol Bay [1, 15].

In [15, 18, 19], a pronounced two-layer structure of water circulation in the bay was noted: in the surface layer (0–5 m), a current directed into the bay along its northern shore prevails, while in the near-bottom layer, a compensatory outflow current along the southern shore prevails. At the same time, the average current velocities in the near-bottom flow over most of the water area do not exceed 10–15 cm/s.

An anticyclonic structure with convergence in the centre and rising isosurfaces at the periphery forms in the central part of the bay a quasi-stationary area that influences water dynamics, the distribution of hydrochemical parameters, and modern bottom sediments [25].

Density stratification of water column is typical of Sevastopol Bay, especially in summer. This hinders oxygen supply to the near-bottom layer and leads to the formation of hypoxia [3, 23].

The influence of the Chernaya River runoff is clearly seasonal and spatially limited [3, 4, 16, 21]. Fresh river waters form a plume propagating in the surface layer and creating an additional baroclinic component of currents, enhancing the horizontal heterogeneity of thermohaline fields [17]. During floods, a clearly pronounced freshened current forms, propagating along the northern shore, which leads to significant stratification and transport of suspended matter into the head of the bay [4, 21]. During low-water periods, the influence of runoff is localised at the head of the bay [16, 21].

The variability of natural processes is additionally affected by the anthropogenic factor. First of all, this is expressed in the input of stormwater and sewage runoff, which act as a powerful pulsed factor and have a sharper and more local effect on the hydrochemical regime compared with river runoff [20]. In [24], the authors record the formation of contrasting freshened plumes at storm sewer outlets after rainstorms, which leads to rapid and significant changes in water temperature, salinity, and turbidity, as well as in the content of nutrients in the surface layer; their excess, in turn, leads to eutrophication of the water body, hypoxia, and a change in the structure of plankton communities [3, 16].

**Sampling.** Samples of the surface (0–5 cm) layer of bottom sediments were collected using a BG-0.025 bottom grab sampler during quarterly expeditions of the Marine Biogeochemistry Department of Marine Hydrophysical Institute, RAS, onboard small vessel *Gidrograf-4*. In total, 32 sediment samples were collected in different hydrological seasons (spring, autumn, winter), from which pore waters

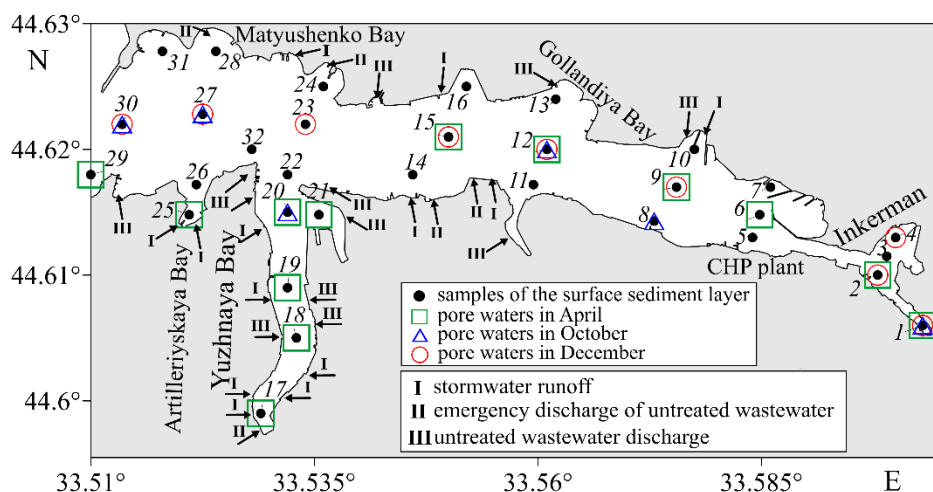


Fig. 1. Location of the bottom sediment sampling stations, as well as stormwater and emergency wastewater outlets [20]

were extracted using an Elmi CM-6MT centrifuge (rotation speed 3000 rpm, rotation time 35 min). The sampling map is shown in Fig. 1.

The pH and redox potential (Eh) values in sediment samples were determined potentiometrically using I-160MP ion meters, a Hanna Instruments HI 10530 combination electrode (pH), and an EPV-1 platinum electrode (Eh).

Grain-size analysis was carried out in two stages in accordance with GOST 12536-2014. At the first stage, wet sieving of samples was performed to isolate and gravimetrically quantify the pelitic-aleuritic fraction (particles smaller than 0.05 mm). At the second stage, the remaining material (fraction larger than 0.05 mm) was dried and separated by dry sieving on a standard set of sieves.

Concentrations of inorganic nutrients were determined photometrically using a KFK-3KM spectrophotometer and a Skalar San++ continuous flow autoanalyser (the Netherlands) after filtration (0.45 µm membrane), except for samples for determination of ammonium ions<sup>1)</sup>. The silicic acid concentration was determined with a salinity correction<sup>1)</sup>:

$$C_{\text{true}} = C_{\text{obs}} \cdot (1 + 0.0045S),$$

where  $C_{\text{true}}$  is the true silicic acid concentration;  $C_{\text{obs}}$  is the observed silicic acid concentration;  $S$  is the final salinity of the analysed sample, PSU<sup>1)</sup>.

Ammonium nitrogen was determined using a modified Sagi – Solorzano method for seawater, which is based on the phenol-hypochlorite reaction using sodium nitroprusside and sodium citrate<sup>2)</sup>. Nitrite concentrations and combined nitrite and nitrate concentrations were determined according to the procedure (RD 52.10.745-2020).

Correlation coefficients and their significance were calculated using the Statistica software. The confidence level of the obtained correlation coefficients was 95%.

## Results and Discussion

In Sevastopol Bay, fine-grained silts predominate (on average ~ 85%), with a maximum in Yuzhnaya Bay and the deep-water part on the fairway. The spatial distribution of grain-size fractions is determined by the flood regime of the Chernaya River (eastern part of the bay), the intense input of stormwater and sewage discharges, which are the main source of terrigenous suspended matter in the central part of the bay, and by the contribution of abrasion processes in the coastal strip (western part of the bay). The maximum silt content on the fairway in the central part of the bay is associated with great depths in this area and the features of water

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<sup>1)</sup> 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).

<sup>2)</sup> UNESCO, 1987. *Thermodynamic of the carbon dioxide system in seawater*. UNESCO technical papers in marine science. Vol. 51, pp. 3–21.

circulation [25], which promote deposition of fine particles due to weakened wind-wave mixing and reduced rate of input of new clastic material.

The high content of organic carbon (up to 5%) in the bottom sediments of Yuzhnaya and Artileriyskaya bays is determined by the presence in these areas of a large number of stormwater and emergency sewage outlets [8, 12]. The minimum organic carbon content of 0.5–2.5% in the western part of the bay is explained by the input of gravel–sand and silty material as a result of abrasion activity [8]. The absence of abrasion processes in the central part of the bay is associated with anthropogenic transformation of the shoreline, expressed in the construction of concrete embankments and piers [26].

This promotes the formation of weakly alkaline reducing conditions in bottom sediments (pH 7.1–7.8, Eh from 0 to –300 mV) (Fig. 2). During the year, pH and Eh values change insignificantly and average 7.4 and –190 mV, respectively.

The minimum Eh values of sediments in the central part of Sevastopol Bay (from –190 to –270 mV) and in Yuzhnaya Bay (from –140 to –310 mV) can be explained by the features of sedimentation in these areas (Fig. 2, *b*). In the central part of the bay at maximum depths under conditions of low water exchange with the open sea, a thick layer of fine-grained silty sediments with elevated organic carbon content forms. The features of circulation [18, 19, 25] prevent oxygen supply to the near-bottom water layer [23], as a result of which oxygen is consumed in bottom sediments

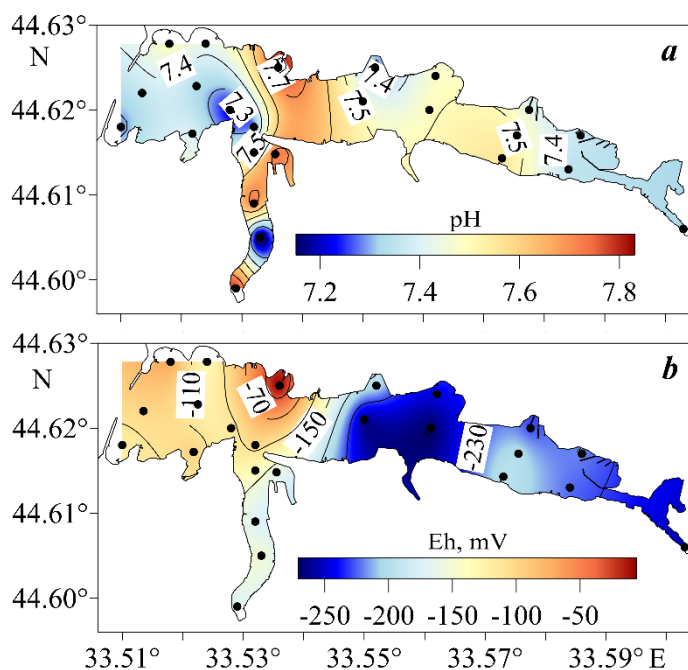


Fig. 2. Spatial distribution of pH (*a*) and Eh (*b*) values in the surface layer of the Sevastopol Bay bottom sediments

for oxidation of organic matter, and anaerobic conditions form in the sediments [11]. In Yuzhnaya Bay, the analogous situation is complicated by additional input of organic matter with numerous sewage discharges.

The features of the spatial distribution of pH in the surface sediment layer are also explained by a number of factors of both natural (sediment type, local sources of fresh water) and anthropogenic (input of suspended matter and organic carbon with sewage discharges) origin. The weakly alkaline environment ( $\text{pH} = 7.8$ ) in the area of station 24 (Fig. 2, *a*) is explained by the sandy type of sediments, which promotes good water exchange between the sediment and the near-bottom water layer, while the analogous weakly alkaline environment ( $\text{pH} = 7.7\text{--}7.8$ ) at stations 17, 20, 21 is explained by reducing conditions in the silty sediments of Yuzhnaya Bay, which are characterised by a distinct smell of hydrogen sulfide, and Eh reaches  $-170$  mV (Fig. 2, *b*). The minimum Eh values ( $-260\text{--}-270$  mV) recorded in the central part of the bay (stations 12, 15) are explained by the features of water circulation in the bay (the stations are located at equal distances from the western part of the bay, which is characterised by intense water exchange with the open sea, and from the eastern part with a predominant contribution of river runoff), bottom topography (maximum depth on the fairway), and the geochemical composition of bottom sediments (the fraction of fine-grained silts with increased organic carbon content predominates).

The main sources of nutrient input to the bottom sediments of the bay have a mixed natural-anthropogenic origin: phosphorus and various forms of nitrogen enter with sewage and surface terrigenous runoff; silicon is primarily of natural origin and is transported with terrigenous runoff as a result of weathering, and can also enter bottom sediments as a result of economic activity (e.g., construction). Thus, the large number of stormwater and sewage outlets located along the perimeter of the entire bay is the determining factor of the spatial heterogeneity of concentrations of the studied substances.

The distribution of nutrients in the pore waters of the upper sediment layer changes both in space and in time (during the year). The concentration variation ranges are  $0\text{--}7.10$   $\mu\text{M}$  for nitrates,  $0.02\text{--}0.89$   $\mu\text{M}$  for nitrites,  $25.74\text{--}1380.95$   $\mu\text{M}$  for ammonium,  $0.20\text{--}94.68$   $\mu\text{M}$  for phosphates, and  $36.04\text{--}628.09$   $\mu\text{M}$  for silicic acid (Figs. 3–6).

For comparison, [2] shows the ranges of nutrient concentration variation in the bay waters in 2007–2016: nitrates –  $0\text{--}286.35$   $\mu\text{M}$ , nitrites –  $0\text{--}6.37$   $\mu\text{M}$ , ammonium –  $0\text{--}40.70$   $\mu\text{M}$ , phosphates –  $0\text{--}5.20$   $\mu\text{M}$ , and silicic acid –  $0\text{--}97.98$   $\mu\text{M}$ .

The physicochemical characteristics of sediments – weakly alkaline reducing conditions (low pH values, Eh values below  $-100$ ) and increased organic carbon content – largely determine the features of organic matter decomposition and the associated transformation of nutrients.

In general, nitrate concentrations in pore waters are extremely low and on average an order of magnitude lower than in the near-bottom and surface water layers [2]. Thus, the average nitrate concentrations in pore waters are minimal in April (0.37  $\mu\text{M}$ ), in October they increase to 1.42  $\mu\text{M}$ , and in December they reach maximum values (3.61  $\mu\text{M}$ ). This is explained by the fact that in reduced sediments at high negative Eh values denitrification no longer occurs. At the same time, intra-annual variability of the values persists, which the authors of [2] associate with increased vertical mixing in the autumn–winter period, as well as with a decrease in light availability. This is confirmed by an increase in nitrate concentrations in the western, most hydrodynamically active part of the bay (Fig. 3).

On the other hand, for this range of sediment Eh and pH values, active ammonification is characteristic, including decomposition of organic matter with release of ammonium ( $\text{NH}_4^+$ ). This is confirmed by high values (on average from 139.64  $\mu\text{M}$  in April to 543  $\mu\text{M}$  in October) of ammonium ion concentrations in pore waters

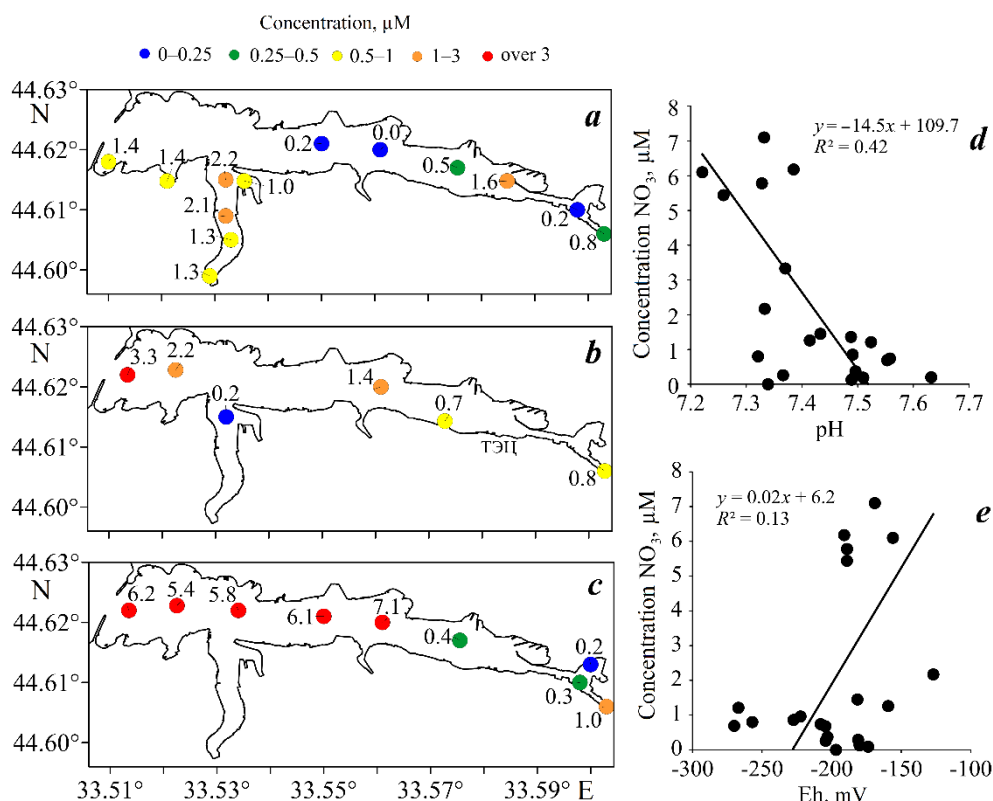


Fig. 3. Nitrate concentrations in pore waters of the Sevastopol Bay sediments in April (a), October (b) and December (c) 2024, as well as the ratio of nitrate concentrations to the characteristics of the sediment solid phase: pH (d) and Eh (e)

(Fig. 4), which are several orders of magnitude higher than the concentrations of this compound in the surface and near-bottom water layers [2].

Anaerobic conditions are also characterised by anammox, i.e., anaerobic oxidation of ammonium, which is of great importance for understanding the nitrogen balance in bottom sediments and nitrate/nitrite fluxes [27].

The maximum concentration of ammonium nitrogen in pore waters (1380.95  $\mu\text{M}$ ) was noted at station 8 (Fig. 4), located in the area of discharge of local treatment facilities near the thermal power plant (Fig. 1), which is consistent with the maximum ammonium concentrations in the near-bottom water layer noted in [2]. An elevated concentration (1185.33  $\mu\text{M}$ ) of ammonium nitrogen was also noted at station 1, located at the boundary of the river–bay geochemical barrier. This area is characterised by increased accumulation of the fine-grained pelitic fraction (silt proportion – 98%), mineralisation of organic matter ( $C_{\text{org}}$  content more than 2% [8, 12]), and carbon dioxide production, accompanied by an increase in  $p\text{CO}_2$  content in water [4]. For such sediments, characterised by black colour,

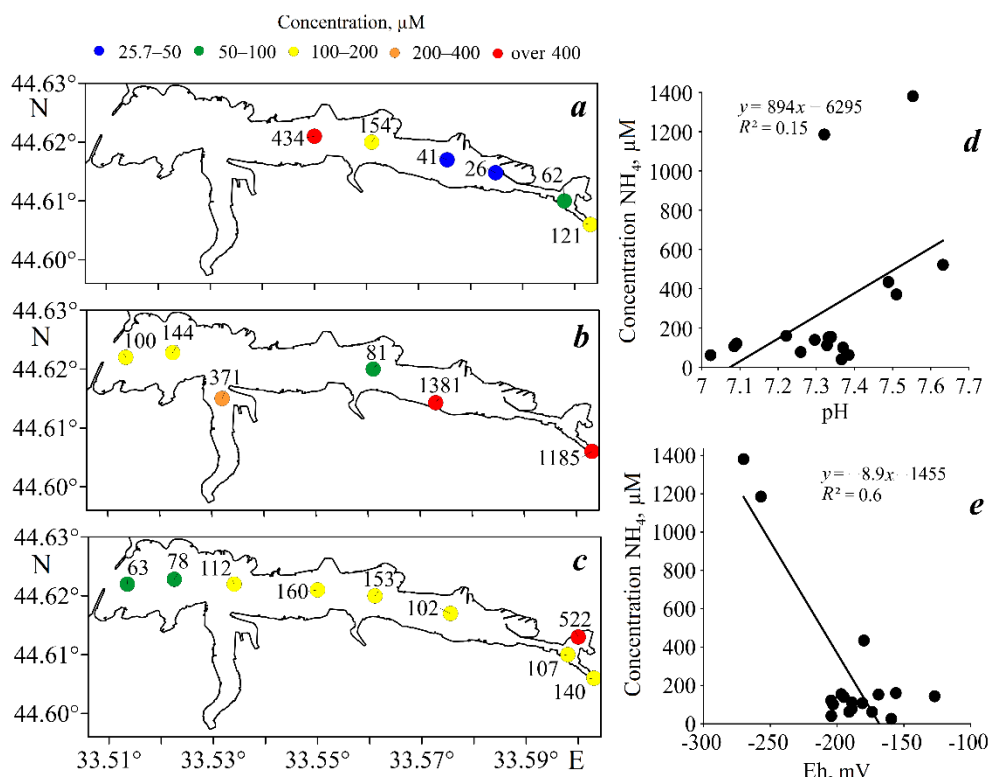


Fig. 4. Ammonium concentrations in pore waters of the Sevastopol Bay sediments in April (a), October (b) and December (c) 2024, as well as the ratio of ammonium nitrogen concentrations to the characteristics of the sediment solid phase: pH (d) and Eh (e)

intense putrefactive odour, a low Eh value ( $-257$  mV), and enrichment in organic matter, oxygen-free conditions are noted [11]. This leads to the fact that under hypoxia, denitrification and ammonification become the dominant pathways of nitrogen transformation, while nitrification is minimised [13]. This is confirmed by a high statistically significant negative correlation between ammonium concentration and sediment Eh ( $r = -0.8$ ,  $n = 21$ ,  $p < 0.05$ ).

In the reducing environment of the silty sediments of Sevastopol Bay, active sorption of phosphorus can occur on iron, manganese and aluminium (oxy-hydr)oxide particles. Similar processes are observed in reduced sediments of the large, anthropogenically loaded Lake Onega [28]. Upon transition to anaerobic conditions (which is typical for the bottom sediments of the bay), iron oxides are reduced ( $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ ) and dissolve, and bound phosphorus is massively released into pore waters [28–30].

Average phosphate concentrations in pore waters ( $11.91\text{--}25.84\text{ }\mu\text{M}$ ) are significantly higher than in the near-bottom and surface water horizons of the bay [2].

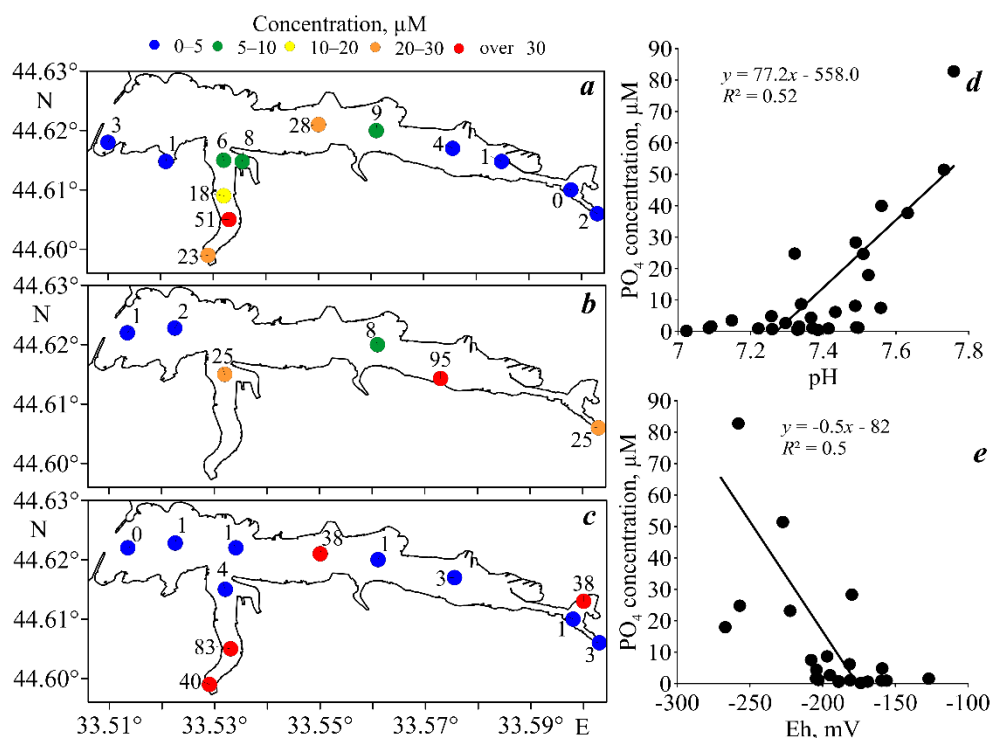


Fig. 5. Phosphate concentrations in pore waters of the Sevastopol Bay sediments in April (a), October (b) and December (c) 2024, as well as the ratio of phosphate concentrations to the characteristics of the sediment solid phase: pH (d) and Eh (e)

The maximum average phosphate concentrations in pore waters are noted in October (25.84  $\mu\text{M}$ ), and the minimum in April (11.91  $\mu\text{M}$ ) (Fig. 5). This is due to the influence of hydrological water parameters, primarily temperature, as a result of which the rate of chemical reactions slows down. In addition, the autumn–winter period is characterised by mixing of the water column, and therefore maximum concentrations in the near-bottom and surface water layers are observed in December [2]. Elevated phosphate concentrations (18–83  $\mu\text{M}$ ) during the study period are noted mainly in the sediments of Yuzhnaya Bay, and in October also in the area of station 8 (95  $\mu\text{M}$ ), located near the thermal power plant (Fig. 5). In December, phosphate concentrations in the pore waters of Yuzhnaya Bay sediments are two orders of magnitude higher than the values obtained for the fairway area in the central part of Sevastopol Bay. This is explained by additional input of nutrients with stormwater and sewage discharges, as well as by limited water exchange in the southern and central parts of Yuzhnaya Bay. The correlation between phosphate concentrations and sediment pH is  $r = 0.7$ ,  $n = 31$ ,  $p < 0.05$ , and between phosphate concentrations and Eh is  $r = -0.7$ ,  $n = 31$ ,  $p < 0.05$ .

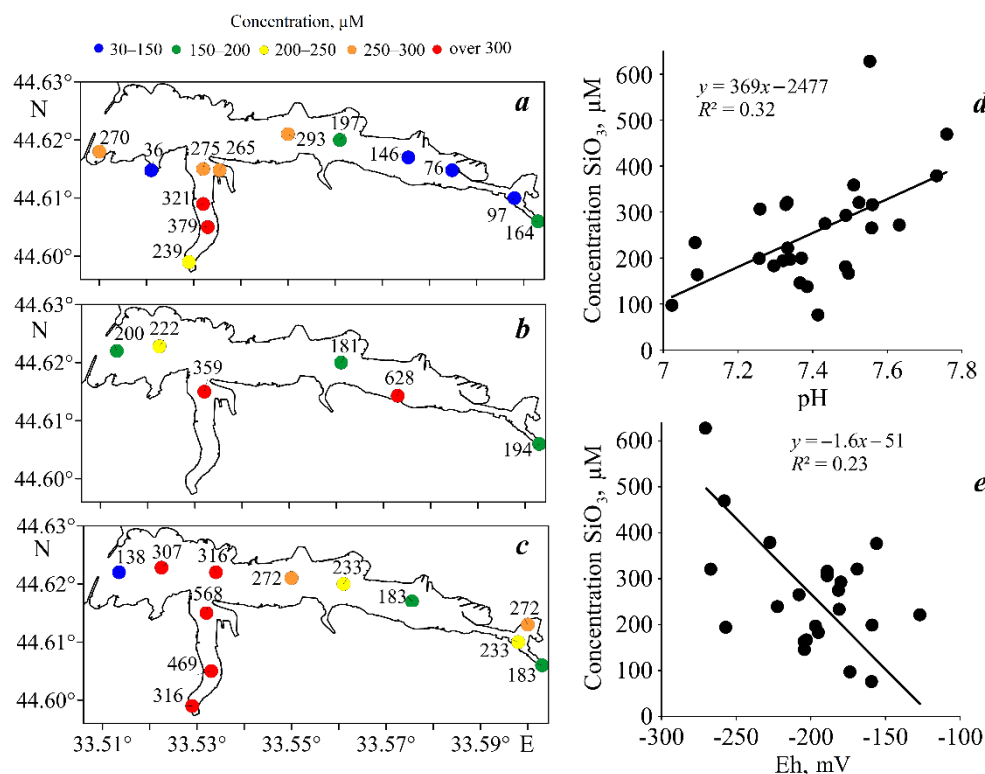


Fig. 6. Silicic acid concentrations in pore waters of the Sevastopol Bay sediments in April (a), October (b) and December (c) 2024, as well as the ratio of silicic acid concentrations and the characteristics of the sediment solid phase: pH (d) and Eh (e)

In the pore waters of Sevastopol Bay, the silicic acid concentration (21.14–297.30  $\mu\text{M}$ ), like that of phosphates, is significantly (by several orders of magnitude) higher than in the near-bottom and surface water layers. Silicic acid concentrations in pore waters are minimal in spring, increase in summer, and reach their maximum in autumn and winter. The main sources of silicon input are river and stormwater runoff, which explains the elevated silicic acid concentrations noted for Yuzhnaya Bay (239–568  $\mu\text{M}$ ), which persist throughout the year, and the low values observed on the fairway (76–293  $\mu\text{M}$ ) and in the western part of the bay (138–307  $\mu\text{M}$ ) (Fig. 6).

Redox conditions do not have a direct effect on the solubility of silicic acid, unlike that of phosphorus. However, under anaerobic conditions, as a result of active sulfate reduction, pH and total alkalinity increase [31, 32]. The intensity of sulfate reduction is determined by the amount and availability of organic matter, which serves as an electron-donor substrate [33]. During oxidation, sulfate ions are reduced to sulfides, and organic carbon passes into an inorganic form. As a result of this reaction, bicarbonate ions appear and protons are consumed, which naturally leads to an increase in both total alkalinity and pH values in pore waters. This indirect mechanism of accelerating silica dissolution under alkaline conditions has been quantitatively confirmed in experimental and field studies [34].

The statistically significant positive correlation between silicic acid concentration and sediment pH ( $r = 0.6$ ,  $n = 31$ ,  $p < 0.05$ ), as well as the negative correlation ( $r = -0.5$ ,  $n = 31$ ,  $p < 0.05$ ) between silicic acid concentration and Eh, confirms the leading role of this mechanism. Thus, sulfate reduction acts as a powerful biochemical catalyst: by creating alkaline conditions, it substantially accelerates the dissolution of silicon-containing compounds, which ultimately determines the high silicic acid concentrations in the pore waters of anaerobic sediments.

## Conclusion

Thus, a complex of natural and anthropogenic factors, including limited water exchange, features of the shoreline configuration, river runoff, and the input of stormwater and domestic wastewater, forms a specific redox condition in the bottom sediments of the bay. It is this setting that is the primary factor determining the direction, sequence, and intensity of all chemical and microbiological processes occurring in the sediments.

Analysis of the chemical composition of pore waters revealed a sharp contrast in the distribution of nutrients between bottom sediments and the water column.

Concentrations of labile nitrogen forms (nitrates and nitrites) in pore waters were lower than in the near-bottom and, especially, surface water. The low content of nitrates and nitrites indicates an almost complete absence of oxygen and active denitrification in the sediments, where these compounds are used as alternative oxidants (electron acceptors) for decomposition of a large amount of organic matter.

On the contrary, concentrations of ammonium, phosphates, and silicic acid in the pore waters of bottom sediments were one to two orders of magnitude higher than in water. High ammonium concentrations are a consequence of anaerobic mineralisation (ammonification) of nitrogen-containing organic matter. Phosphates accumulate as a result of release from iron (oxyhydr)oxide complexes, which lose sorption capacity under reducing conditions. The high silicic acid content confirms intense dissolution of biogenic silica, characteristic of anaerobic bottom sediments.

The spatial heterogeneity in the distribution of nutrients is a direct reflection of diagenetic processes occurring in the sediments and their key role in the ecosystem. This heterogeneity may also indicate the formation in the sediments of strong concentration gradients (directed for ammonium, phosphates, and silicic acid from sediment to water) and determine a constant diffusive flux of these nutrients into the near-bottom layer. This process can not only maintain phytoplankton productivity during periods of reduced external runoff but also contribute to eutrophication even after a technical reduction of direct anthropogenic load on the water area.

As a result, silty sediments rich in organic carbon under weakly alkaline reducing conditions can act not only as a passive store of all incoming substances but also as a biogeochemical reactor – an important link in the element cycle in marine ecosystems.

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*About the authors:*

**Konstantin I. Gurov**, Researcher, Marine Hydrophysical Institute of RAS (299011, Russia, Sevastopol, Kapitanskaya St., 2), PhD (Geogr.), **ORCID ID: 0000-0003-3460-9650**, **Scopus Author ID: 57200248245**, **ResearcherID: L-7895-2017**, [gurovki@gmail.com](mailto:gurovki@gmail.com)

**Alla V. Varenik**, Senior Researcher, Marine Hydrophysical Institute of RAS (299011, Russia, Sevastopol, Kapitanskaya St., 2), PhD (Geogr.), **ORCID ID: 0000-0001-5033-4576**, **ResearcherID: H-1880-2014**, **Scopus Author ID: 56960448000**, [alla.varenik@mhi-ras.ru](mailto:alla.varenik@mhi-ras.ru)

**Mariya A. Myslina**, Junior Researcher, Marine Hydrophysical Institute of RAS (299011, Russia, Sevastopol, Kapitanskaya St., 2), **ORCID ID: 0000-0002-0054-0379**, [myslina@mhi-ras.ru](mailto:myslina@mhi-ras.ru)

*Contribution of the authors:*

**Konstantin I. Gurov** – sampling, formulation of the aims and objectives of the study, analysis and synthesis of the research results, preparation of graphic and textual materials, writing of the original draft of the paper

**Alla V. Varenik** – general scientific supervision of the study, data preparation, discussion of the results of the work, revision of the text

**Mariya A. Myslina** – data processing, participation in discussion of the paper materials

*All the authors have read and approved the final manuscript.*

Original paper

## Interannual Changes in the Hydrochemical Parameters of the Chernaya River from 2019 to 2024 (Sevastopol, Southwestern Crimea)

J. A. Petrova \*, N. A. Milchakova, J. A. Gavrilova

*A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia*

*\* e-mail: juliacosac@gmail.ru*

### Abstract

The study aims to assess the quality of the Chernaya River waters by analysing interannual changes and spatial distribution of hydrochemical parameters for 2019–2024, and to develop evidence-based scientific and practical recommendations for improving the condition of the water body. The article analyses the monitoring data of the Chernaya River for 36 standardised and non-standardised hydrochemical parameters, including nutrients, organic and inorganic substances, heavy metals and pesticides, at five observation points in its upper, middle and lower reaches. The material was collected during state monitoring under the Ecology and Environmental Protection of the City of Sevastopol program. Sampling was carried out once per season. A hydrochemical analysis was performed on 120 samples using standard methods. We found significant spatial differences in the content of standardised and non-standardised indicators. It was shown that the concentration of certain nutrients, chlorides, sulfates and metals (Fe, Cu) in the lower reaches exceeded the standard values for water bodies by more than four times. The content of Ca, Mn, and Mg varied sharply throughout the observation period, exceeding the maximum permissible levels by a factor of two or more. In 2024, an increase was observed in the content of suspended solids and nutrients ( $\text{NH}_4^+$ , Si), and in chemical oxygen demand, while at all monitoring sites, by 2024, the content of phenols (since 2021) and petroleum products (since 2023) had decreased, whereas the concentrations of organochlorine pesticides, nickel, hexavalent chromium, and nitrates were below the maximum permissible concentrations and varied little across years and regions. In the estuarine part of the Chernaya River, a slight improvement in water quality was recorded in terms of phenol content. Despite the improvement in organic indicators, the exceedance of the maximum permissible concentrations for heavy metals and nutrients requires continued monitoring and the implementation of measures: inventory of sources, introduction of reed filter strips and strengthening of bioindication monitoring.

**Keywords:** monitoring of water bodies, hydrochemical indicators, pollutants, spatial dynamics, water quality, Chernaya River, Sevastopol city

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## **Межгодовые изменения гидрохимических показателей реки Черной с 2019 по 2024 годы (Севастополь, Юго-Западный Крым)**

**Ю. А. Петрова \*, Н. А. Мильчакова, Ю. А. Гаврилова**

*ФГБУН ФИЦ «Институт биологии южных морей имени А.О. Ковалевского РАН»,  
Севастополь, Россия*

*\* e-mail: juliacosac@gmail.ru*

### **Аннотация**

Целью исследования является оценка качества вод р. Черной на основе межгодовых изменений гидрохимических параметров и особенностей их пространственного распределения за 2019–2024 гг., а также разработка на основе полученных данных научно-практических рекомендаций по улучшению состояния водного объекта. Проанализированы данные мониторинга 36 нормируемых и ненормируемых гидрохимических показателей, включая биогенные, органические и неорганические вещества, тяжелые металлы и пестициды, в пяти пунктах наблюдений в верхнем, среднем и нижнем течении р. Черной. Материал собран в ходе государственного мониторинга по программе «Экология и охрана окружающей среды города Севастополя». Отбор проб проводили один раз в сезон. Гидрохимический анализ проведен для 120 проб по стандартным методикам. Выявлены значительные пространственные различия содержания нормируемых и ненормируемых показателей, показано, что концентрация некоторых биогенных элементов, хлоридов, сульфатов и металлов (Fe, Cu) в нижнем течении более чем в четыре раза превышает нормативные значения для водных объектов. Содержание Са, Mn и Mg резко менялось в течение всего периода наблюдений с превышением предельно допустимых нормативов вдвое и более. К 2024 г. отмечен рост содержания взвешенных веществ, биогенных элементов ( $\text{NH}_4^+$ , Si) и химического потребления кислорода, тогда как на всех участках наблюдений к 2024 г. содержание фенолов (с 2021 г.) и нефтепродуктов (с 2023 г.) снизилось, а концентрации хлорорганических пестицидов, никеля, хрома шестивалентного и нитратов были ниже ПДК и слабо варьировали по годам и районам. В устьевой части р. Черной зафиксировано незначительное улучшение качества воды по содержанию фенолов. Несмотря на улучшение по органическим показателям, превышение ПДК по тяжелым металлам и биогенным элементам требует продолжения мониторинга и принятия мер: инвентаризации источников, внедрения фильтрующих полос из тростника и усиления биоиндикационного контроля.

**Ключевые слова:** мониторинг водных объектов, гидрохимические показатели, загрязняющие вещества, качество вод, река Черная, Севастополь

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## Introduction

The quality of fresh waters, water supply problems and protection of water bodies are global environmental issues included in the list of Sustainable Development Goals of the UN General Assembly <sup>1)</sup> and in the Ministerial Declaration of the 10th World Water Forum <sup>2)</sup>. In the development programme of the Russian Federation for achieving the targets of the Sustainable Development Goals <sup>3)</sup>, national target indicators for the period up to 2030 have formed a list of measures to preserve the quality of fresh waters, including monitoring of water bodies <sup>1), 3)</sup>. For the federal city of Sevastopol, this task has not only environmental but also socio-economic significance. The region is classified as water-scarce and arid, while in recent decades water consumption in it has increased significantly due to intensification of economic and recreational activity and population growth. The main source of drinking water supply for the city has been and remains the Chernaya River. For this water body, a wide range of measures is being implemented within state environmental programmes, including federal programmes – “Water of Russia” and “Clean Banks” <sup>4)</sup>, aimed at preserving water quality, reducing discharge volumes of untreated or poorly treated wastewater, and ensuring rational water use.

The first studies assessing the water quality of the Chernaya River were carried out by M. A. Galadzhieva <sup>5)</sup> and G. M. Gasovsky [1, 2] using indicator organisms as early as the beginning of the 20th century. From the 1980s, monitoring of hydrochemical indicators and the ecological state of the river was conducted by the Center for Hydrometeorology in the Autonomous Republic of Crimea, and from 2015 by the Federal State Budgetary Institution “Crimean Directorate for Hydrometeorology and Environmental Monitoring” and the Federal Service for Hydrometeorology and Environmental Monitoring (Roshydromet). From 1980 to 2008,

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<sup>1)</sup> Available at: <https://www.ungeneva.org/ru/about/topics/sustainable-development-goals> [Accessed: 20 June 2025].

<sup>2)</sup> Ziganshina, D.R., Usmanova, O.K., Beglov, I.F. and Degtyareva, A.S., eds., 2024. *The 10th World Water Forum. Water for Shared Prosperity: Collection of Papers*. Tashkent. p. 53. Available at: <https://www.cawater-info.net/library/rus/10wwf-ru.pdf> [Accessed: 20 June 2026] (in Russian).

<sup>3)</sup> President of the Russian Federation, 2024. *Decree No. 309 of 24.05.2024 “On the National Development Goals of the Russian Federation for the Period up to 2030 and for the Future up to 2036”*. Available at: <https://rspp.ru/activity/social/nacionalnye-celi-razvitiya-Rossii/> [Accessed 20 June 2026] (in Russian).

<sup>4)</sup> Government of the City of Sevastopol, 2025. [Annual State Report on the State and Protection of the Environment of the City of Sevastopol for 2024]. Sevastopol. Available at: <https://spn.sev.gov.ru/ekologicheskoe-sostoyanie-sevastopolya/doklad-o-sostoyanii-i-ob-okhranekruzhayushchey-sredy-goroda-sevastopolya/> [Accessed: 30 July 2025] (in Russian).

<sup>5)</sup> Galadzhieva, M.A., 1927. [Materials on the Fauna of Protozoa of Fresh Waters in the Environs of Sevastopol]. In: I. I. Puzanov, ed., 1927. [Proceedings of the Crimean Research Institute]. Simferopol: Krymskoye Gosudarstvennoye Izdatelstvo. Vol. 1, iss. 2, pp. 106–117 (in Russian).

the water quality of the Chernaya River was determined by 29 indicators, including various organic and inorganic pollutants and dissolved gases [3, 4], and from 2015 to 2024 by 22 parameters taking into account data on fresh water discharge<sup>4)</sup>. Over the entire observation period, the largest volume of data was collected for the gauging station near the village of Khmelnitskoye, 2 km from the river mouth<sup>4)</sup>. Episodically, studies of the river channel were performed at four gauging stations [5, 6], mainly at the observation point (OP) in the village of Khmelnitskoye, the mouth of the Chernaya River and in sections of some of its tributaries – the Baidarka River and the Urkusta River [4, 6, 7].

Generalisation of data on water quality of the Chernaya River for 1980–2015 by 16 hydrochemical indicators revealed a significant increase in concentrations of phenols, synthetic surfactants, petroleum products and heavy metals (HMs), especially in the last decade [4, 7]. Thus, from 2016 to 2019, at the gauging station in the village of Khmelnitskoye, exceedances of maximum permissible concentrations (MPCs) of nitrites, phenols and HMs were found [3, 7, 8]. At other gauging stations, according to seasonal observations from 2010 to 2023, an increase in concentrations of nitrates and silicic acid was also recorded [6]. At the same time, a tendency toward an increase in the content of nitrites and ammonium nitrogen was also revealed for averaged values, and along the entire river course, exceedance of the standard for  $\text{NH}_4^+$  for fishery water bodies was recorded [5].

Taking into account the high ecosystem, environmental and socio-economic significance of the Chernaya River, a significant increase in water consumption and wastewater disposal volumes, as well as increased pollution risks due to intensification of economic activity, in 2021 a programme of regular monitoring of waters and bottom sediments was developed within the state programme “Ecology and Environmental Protection of the City of Sevastopol”<sup>6)</sup>. Since 2015, state monitoring of the ecological state of the Chernaya River waters has been carried out by 38 indicators, and since 2020 by 43 at five OPs in the upper, middle and lower reaches. In 2019–2024, water quality at all OPs was assessed by seasons, which made it possible to prepare an extensive database, although without taking into account chronic and short-term pollution<sup>7)</sup>.

Since the technogenic influence of the urban environment has a significant impact on the ecological state of the Chernaya River, the relevance of the conducted studies is beyond doubt.

The aim of the work is, based on interannual changes in 36 hydrochemical indicators and the features of their spatial distribution for 2019–2024, to assess the water quality of the Chernaya River in its upper, middle and lower reaches and to develop scientific and practical recommendations for improving the condition of the water body.

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<sup>6)</sup> Government of the City of Sevastopol, 2021. [On the Approval of the State Program of the City of Sevastopol “Ecology and Environmental Protection of the City of Sevastopol”]: Resolution of the Government of the City of Sevastopol no. 660-III as of 20 December 2021. Published 21 December 2021. Available at: <https://sev.gov.ru/docs/253/163582/> [Accessed: 11 August 2026] (in Russian).

<sup>7)</sup> Ministry of Ecology and Natural Resources of the Republic of Crimea, 2025. [Report on the State and Protection of the Environment in the Territory of the Republic of Crimea in 2024]. Available at: [https://meco.rk.gov.ru/uploads/meco/container/2025/07/16/2025-07-16-15-31-21\\_2024.pdf](https://meco.rk.gov.ru/uploads/meco/container/2025/07/16/2025-07-16-15-31-21_2024.pdf) [Accessed: 18 August 2026] (in Russian).

## Materials and Methods

### *Characteristics of the study area*

The Chernaya River, whose length is 35 km, belongs to the main rivers of the north-western slope of the Crimean Mountains and is one of the three largest rivers of Sevastopol<sup>4)</sup>. The watercourse originates in the Baidar Basin from the Skelsky Spring and flows into the Black Sea [9]; the river catchment area is 669 km<sup>2</sup>, its average elevation is 395 m [10], and the main recharge is provided by the Skelsky Spring (discharge 40–220 L/s) and atmospheric precipitation<sup>4)</sup>. The hydrographic network is represented by 11 tributaries (the Uzundzha, Bosa, Baga Nizhnyaya, Baga Verkhnyaya, Urkusta, Ay-Todorka, Sukhaya Rechka, Baidarka, Uppa, Armanka, Kalenda rivers) with a total catchment area of 287.02 km<sup>2</sup>, as well as the Chernorechenskoye Reservoir (catchment area  $S = 6.04$  km<sup>2</sup>, volume  $V = 64$  million m<sup>3</sup>)<sup>4)</sup>. The width of the river water protection zone is 100 m<sup>8)</sup>; within its boundaries there are specially protected natural areas (SPNAs), lands of rural settlements, their sewage treatment facilities and agricultural lands.

The Chernaya River is the only full-flowing and perennial watercourse of Sevastopol. A significant part of its channel (7.5 km) is within the boundaries of the state natural landscape reserve of regional significance “Baidarsky”, on whose territory the Chernorechensky Canyon is located<sup>4), 7)</sup>. Despite the fact that many types of economic activity on the territory of the reserve, the largest in the network of SPNAs of Sevastopol, are prohibited or limited, sources of river pollution are industrial, agricultural and other facilities located near its boundaries. According to 2024 data, up to 2.23 million m<sup>3</sup> of water entered the Chernaya River channel, of which one third was transit water from the Kadykovsky quarry (0.78 million m<sup>3</sup>), and the main part (two thirds) was wastewater from sewage treatment facilities of the State Unitary Enterprise “Vodokanal”<sup>4)</sup>. In addition, the Chernaya River is among the most flood-prone rivers [11], and runoff from the entire catchment basin during a flood can significantly worsen water quality due to the entry of various pollutants [11–13].

### *Sampling and research methods*

The territorial system for monitoring the water quality of the Chernaya River is represented by five OPs (Fig. 1): OP-1 – Inkerman, OP-2 – Zelenaya Gorka settlement (wastewater discharge), OP-3 – Oktyabrsky settlement (wastewater discharge), OP-4.1 (site 1), OP-4.2 (site 2) – Sakharnaya Golovka settlement (background and control sites), OP-5 – Rodnikovoye village (SPNA “State Natural Landscape Reserve of Regional Significance ‘Baidarsky’”).

Samples for assessing the water quality of the Chernaya River were collected within the framework of state monitoring of surface water bodies from 2019 to 2024

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<sup>8)</sup> Government of the City of Sevastopol, 2016. [On Approval of the Regulations on the State Natural Landscape Reserve of Regional Significance “Baidarsky”]: Resolution of the Government of the City of Sevastopol no. 408-III as of 29 April 2016. Available at: <https://docs.cntd.ru/document/438883181?ysclid=mtiqivyg5882718582> [Accessed: 18 August 2026] (in Russian).

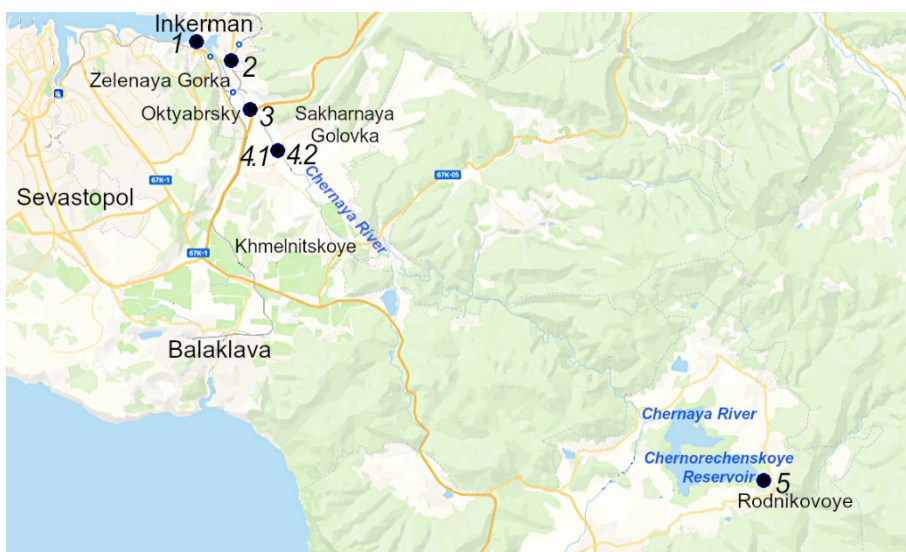


Fig. 1. Map of observation points on the Chernaya River (the dots denote observation points and their numbers). The map is from: <https://map.ru/pkk/sevastopol> (Accessed: 28 August 2026)

under the programme “Ecology and Environmental Protection of the City of Sevastopol” once per season at five OPs in accordance with GOST R 59024–2020.

A hydrochemical analysis was performed for 120 samples; 43 parameters were determined, including the content of dissolved gases (3) and nutrients (12), organoleptic indicators (6), organic (10) and inorganic (12) compounds. Of these, 25 indicators were standardised and 18 were non-standardised. The samples were studied in the testing laboratories of RusInteCo LLC, EkoSvet Firm LLC and Biopotentsial LLC.

In this work, data on 36 hydrochemical indicators were analysed. These include standardized indicators: dissolved oxygen ( $O_2$ ) content, five-day biochemical oxygen demand ( $BOD_5$ ), chemical oxygen demand (COD), suspended solids, nutrients (silicon Si, nitrites  $NO_2^-$ , nitrates  $NO_3^-$ , ammonium nitrogen  $NH_4^+$ , total nitrogen  $N_{total}$ , phosphates  $PO_4^{3-}$ ), ions of the main salt composition (sulfates  $SO_4^{2-}$ , carbon dioxide  $CO_2$ , chlorides  $Cl^-$ ), macroelements (Mg, Ca, Na and K total), microelements and heavy metals (Fe, Cu, Zn, Ni, Mn,  $Cr^{6+}$ ), as well as non-standardised indicators: pH, oxygen saturation  $O_2$  (%) and bicarbonate concentration  $HCO_3^-$ . In addition, the concentrations of organic pollutants were determined, including petroleum products, phenols, anionic surfactants (ASs) and organochlorine pesticides ( $\alpha$ -,  $\beta$ -,  $\gamma$ -HCH, DDT, DDD, DDE, HCB).

To assess the water quality of the Chernaya River, a comparative analysis of the obtained data and water quality standards for water bodies of fishery

significance was carried out in accordance with Order of the Ministry of Agriculture No. 552 of 13.12.2016<sup>9)</sup>, and SanPiN 1.2.3685–21<sup>10)</sup>.

The PAST 4.0 software package and Microsoft Excel were used for statistical analysis.

## Results

### *Interannual dynamics of standardised hydrochemical indicators*

The concentration of dissolved oxygen from 2019 to 2024 at all OPs varied insignificantly – from 6.82 to 8.3 mg/dm<sup>3</sup> (with a standard of 6.0 mg/dm<sup>3</sup>).

The content of suspended solids in the upper reaches of the river (OP-5 Rodnikovoye) from 2019 to 2024 was within the range of standard values (2.8–23.9 mg/dm<sup>3</sup>); at other sections it was 1.2–1.9 times higher (27.1–46.12 mg/dm<sup>3</sup>) (Fig. 2, *a*). Maximum values were observed in the middle and lower reaches of the river in 2023 and 2024.

The content of nutrients during the study period exceeded the MPC at most OPs. Thus, in 2024, the maximum NH<sub>4</sub><sup>+</sup> content at OP-4.1 Sakharnaya Golovka reached 0.685 mg/dm<sup>3</sup> with an MPC of 0.5 mg/dm<sup>3</sup> (1.4-fold exceedance) (Fig. 2, *b*). A single peak in NO<sub>2</sub><sup>–</sup> concentration was observed at OP-3 Oktyabrsky (0.48 mg/dm<sup>3</sup> with an MPC of 0.08 mg/dm<sup>3</sup>) in 2021; by 2024 the value had decreased to 0.0025 mg/dm<sup>3</sup>. The NO<sub>3</sub><sup>–</sup> content varied within the MPC (40 mg/dm<sup>3</sup>) from 0.447 to 4.26 mg/dm<sup>3</sup> in 2021 and 2023, respectively<sup>7)</sup>; the highest values were recorded in the middle reaches of the river at OP-3 Oktyabrsky.

High concentrations of SO<sub>4</sub><sup>2–</sup> (11–1174 mg/dm<sup>3</sup> with an MPC of 100 mg/dm<sup>3</sup>) and Cl<sup>–</sup> (17–10467 mg/dm<sup>3</sup> with an MPC of 300 mg/dm<sup>3</sup>) were revealed at all OPs (Fig. 2, *c, d*), while in the lower reaches of the river at OP-1 Inkerman, exceedance of the MPC for these indicators was noted throughout the entire observation period.

BOD<sub>5</sub> throughout the entire study period at all monitoring sites, except OP-4.2 Sakharnaya Golovka in 2019 (2.0 mg O<sub>2</sub>/dm<sup>3</sup>) and OP-5 Rodnikovoye in 2021 (2.1 mg O<sub>2</sub>/dm<sup>3</sup>), exceeded the standards (2.1 mg O<sub>2</sub>/dm<sup>3</sup>), amounting to 2.7–5.82 mg O<sub>2</sub>/dm<sup>3</sup>. Maximum BOD<sub>5</sub> values (more than 1.9 times above the norm) were recorded in 2023 and 2024 at OP-4.1 Sakharnaya Golovka and OP-3 Oktyabrsky.

The pH values at all OPs were within the range of natural variation (from 7.69–8.35 to 7.3–7.7) from 2019 to 2024, whereas COD increased from 4.5–5.9 mg/dm<sup>3</sup> in 2019–2022 to 78.5–98.5 mg/dm<sup>3</sup> in 2023 and 2024, exceeding the standard value by a factor of more than 2.6.

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<sup>9)</sup> Ministry of Agriculture of Russia, 2016. *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. Moscow: Ministry of Agriculture of Russia (in Russian).

<sup>10)</sup> Chief State Sanitary Doctor of the Russian Federation, 2021. *Decree No. 2 of 28.01.2021 "On the Approval of Sanitary Rules and Norms SanPiN 1.2.3685-21 'Hygienic Standards and Requirements for Ensuring the Safety and (or) Harmlessness of Environmental Factors for Humans'"*. Available at: [https://mru31.fmba.gov.ru/upload/iblock/56a/cj7i0jx6pyscza503n4t3zo3ljv79cyi/Postanovlenie-Glavnogo-gosudarstvennogo-sanitarnogo-vracha-RF\\_-2-ot-28.01.2021.pdf](https://mru31.fmba.gov.ru/upload/iblock/56a/cj7i0jx6pyscza503n4t3zo3ljv79cyi/Postanovlenie-Glavnogo-gosudarstvennogo-sanitarnogo-vracha-RF_-2-ot-28.01.2021.pdf) [Accessed: 20 August 2026] (in Russian).

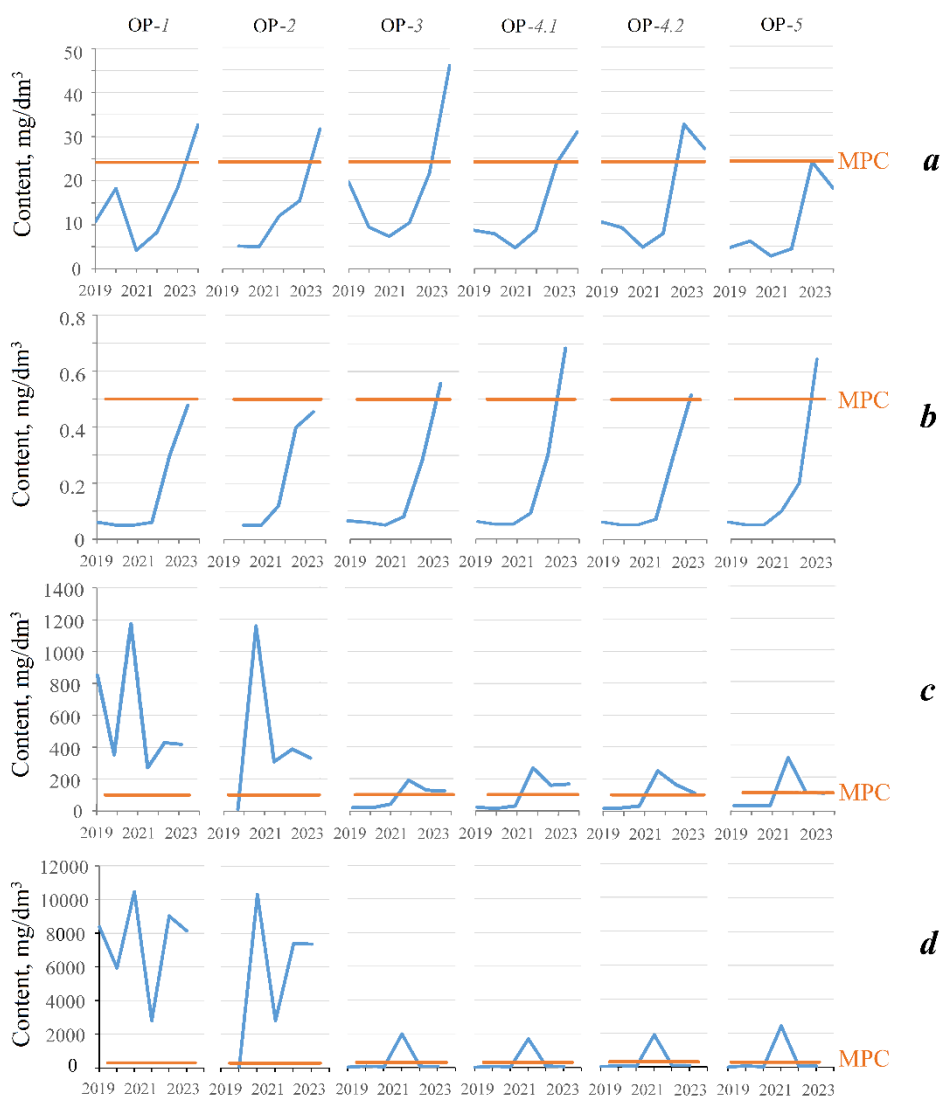


Fig. 2. Content dynamics of solids (*a*),  $\text{NH}_4^+$  (*b*),  $\text{SO}_4^{2-}$  (*c*),  $\text{Cl}^-$  (*d*) in the Chernaya River water in 2019–2024

Concentrations of microelements, including some HMs, were characterised by significant interannual variability; exceedances of the MPC were revealed from 2019 to 2024. An above-standard Mn concentration (from 0.0166 to 0.0282 mg/dm<sup>3</sup> with an MPC of 0.001 mg/dm<sup>3</sup>) was noted at all OPs from 2022 to 2024, with a maximum at OP-1 Inkerman in 2019 (0.062 mg/dm<sup>3</sup>).

The content of Fe (0.11–0.49 mg/dm<sup>3</sup> with an MPC of 0.1 mg/dm<sup>3</sup>) and Cu (0.00147–0.0096 mg/dm<sup>3</sup> with an MPC of 0.001 mg/dm<sup>3</sup>) at OP-1 Inkerman also exceeded the MPC throughout the observation period, except 2021 and 2022 (Fig. 3, *a*, *b*).

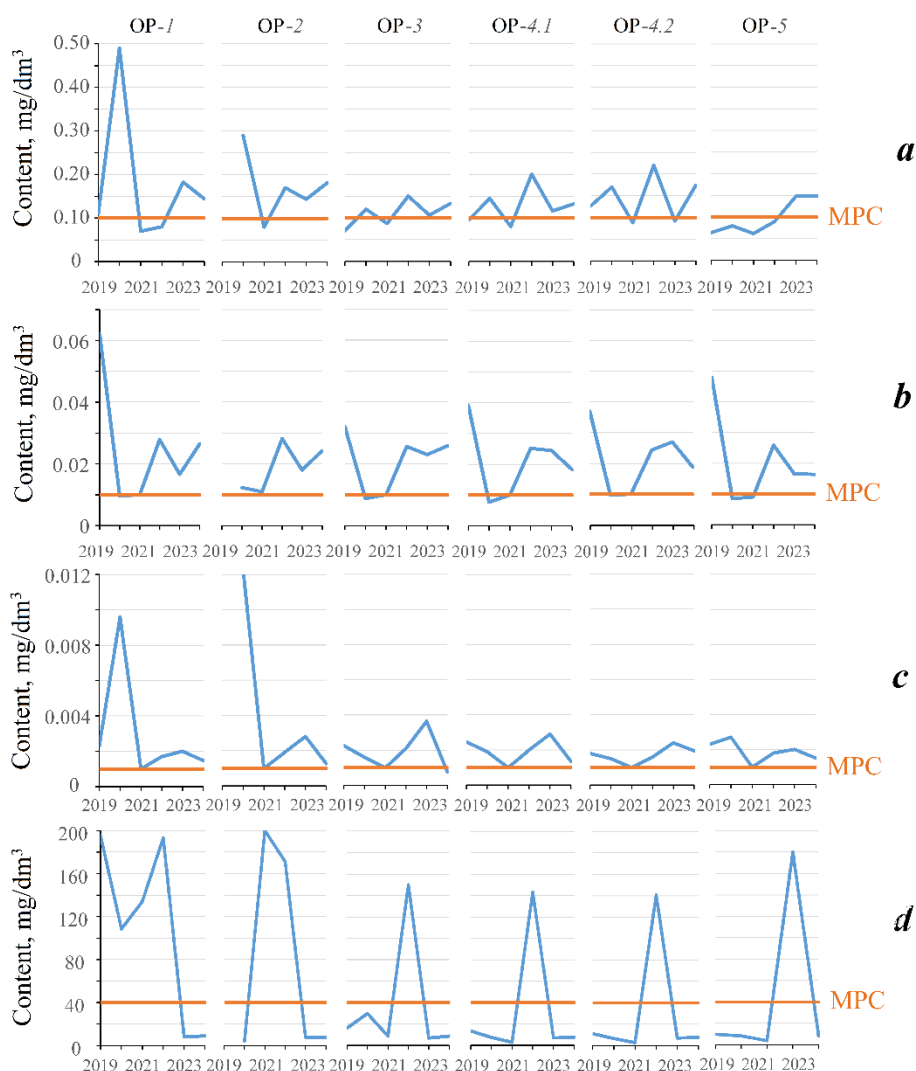


Fig. 3. Interannual content of Fe (*a*), Mn (*b*), Cu (*c*), Mg (*d*) in the Chernaya River water in 2019–2024

Concentrations of Cr and Ni ( $< 0.01 \text{ mg/dm}^3$ ) were within the standards at all sites.

The Mg concentration in 2022 at all sites exceeded the MPC ( $40 \text{ mg/dm}^3$ ) by a factor of more than three ( $140.7\text{--}193.4 \text{ mg/dm}^3$ ), and in 2023 and 2024 it decreased by more than an order of magnitude (to  $6.88\text{--}11.2 \text{ mg/dm}^3$ ) (Fig. 3, *c*, *d*). An above-standard Ca concentration in 2022 was also observed at all OPs ( $213.3\text{--}423.3 \text{ mg/dm}^3$  with an MPC of  $180 \text{ mg/dm}^3$ ); at OP-1 Inkerman and OP-2 Zelenaya Gorka from 2021 to 2024, exceedance of its MPC by a factor of more than 1.6 was recorded.

Among organic pollutants, the highest concentration was found for phenols (0.0021–0.0029 mg/dm<sup>3</sup> with an MPC of 0.001 mg/dm<sup>3</sup>) at all OPs in 2019 and 2020 (Fig. 4, *a*). From 2021 to 2024, a significant decrease in the average annual phenol content was observed (to 0.0002 mg/dm<sup>3</sup>), with a minimum at OP-5 Rodnikovoye in 2023.

The content of petroleum products throughout the entire observation period at all OPs was insignificant: in 2019 and 2020 it did not exceed 0.02 mg/dm<sup>3</sup>. In 2022, a ubiquitous slight increase to 0.058–0.074 mg/dm<sup>3</sup> was noted (MPC 0.05 mg/dm<sup>3</sup>), except at OP-2 Zelenaya Gorka; in 2023–2024, values varied from 0.0165 to 0.0268 mg/dm<sup>3</sup> (Fig. 4, *b*). The content of ASs in the middle and lower reaches of the river in 2022 increased to 0.09–0.21 mg/dm<sup>3</sup> (MPC 0.1 mg/dm<sup>3</sup>); by 2024, the values of this indicator had decreased threefold, except at OP-1 Inkerman, where exceedance of the MPC persisted (Fig. 4, *c*). The concentration of organochlorine pesticides at all OPs was below the MPC throughout the entire observation period.

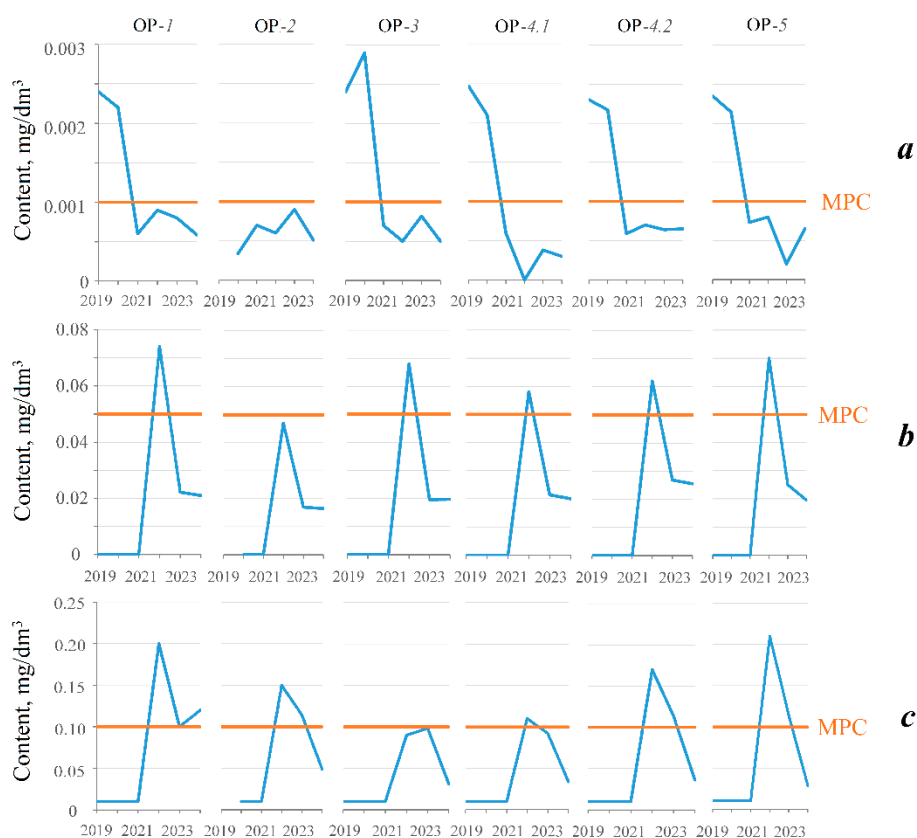


Fig. 4. Content dynamics of phenols (*a*), petroleum products (*b*), ASs (*c*) in the Chernaya River water in 2019–2024

*Interannual dynamics of non-standardised water indicators*

The  $\text{HCO}_3^-$  concentration varied between 53–128.8 mg/dm<sup>3</sup> during the observation period, peaking at OP-4.2 Sakharnaya Golovka in 2022. The concentrations of CO<sub>2</sub> and total nitrogen did not exceed 1 mg/dm<sup>3</sup>.

The total content of Na<sup>+</sup> and K<sup>+</sup> was maximum at all OPs in 2020 (518–10 489 mg/dm<sup>3</sup>), and minimum in 2019 (0.064–0.127 mg/dm<sup>3</sup>). In the lower reaches of the river in 2021, the values of this indicator varied in the range of 5906–6646 mg/dm<sup>3</sup>, and in the upper and middle reaches – 21.5–31.5 mg/dm<sup>3</sup>. In subsequent years, at all OPs, the total content of Na<sup>+</sup> and K<sup>+</sup> was 26–38.75 mg/dm<sup>3</sup>.

The average values for 2019–2024 of the hydrochemical indicators of the Chernaya River that determine water quality are presented in the table.

Average values of the Chernaya River water quality indicators in 2019–2024

| Indicator                                            | Observation point |       |       |       |       |
|------------------------------------------------------|-------------------|-------|-------|-------|-------|
|                                                      | OP-1              | OP-2  | OP-3  | OP-4* | OP-5  |
| pH                                                   | 7.5               | 7.38  | 7.69  | 7.66  | 7.4   |
| Dissolved oxygen, mg/dm <sup>3</sup>                 | 7.6               | 7.58  | 7.63  | 7.65  | 7.58  |
| Suspended solids, mg/dm <sup>3</sup>                 | 15.4              | 13.84 | 18.93 | 14    | 10    |
| Petroleum products, mg/dm <sup>3</sup>               | 0.02              | 0.02  | 0.02  | 0.02  | 0.02  |
| BOD <sub>5</sub> , mgO <sub>2</sub> /dm <sup>3</sup> | 3.77              | 3.56  | 3.89  | 3.4   | 3.5   |
| COD, mg/dm <sup>3</sup>                              | 39.16             | 44.26 | 38.29 | 37.2  | 34.86 |
| Anionic surfactants, mg/dm <sup>3</sup>              | 0.075             | 0.066 | 0.04  | 0.044 | 0.064 |
| Oxygen saturation, %                                 | 93.6              | 63.2  | 74.9  | 75.39 | 73.6  |
| Sulfates, mg/dm <sup>33</sup>                        | 582.8             | 439   | 86.89 | 108.6 | 96.16 |
| Chlorides, mg/dm <sup>3</sup>                        | 7456              | 5593  | 375   | 323   | 449   |
| Nitrates, mg/dm <sup>3</sup>                         | 1.5               | 1.67  | 2.19  | 1.95  | 1.77  |
| Nitrites, mg/dm <sup>3</sup>                         | 0.053             | 0.016 | 0.031 | 0.024 | 0.026 |
| Ammonium ions, mg/dm <sup>3</sup>                    | 0.16              | 0.215 | 0.182 | 0.2   | 0.184 |

| Indicator                                                                    | Observation point |           |           |           |           |
|------------------------------------------------------------------------------|-------------------|-----------|-----------|-----------|-----------|
|                                                                              | OP-1              | OP-2      | OP-3      | OP-4*     | OP-5      |
| Carbon dioxide, mg/dm <sup>3</sup>                                           | 0.5               | 0.5       | 0.5       | 1.0       | 0.5       |
| Phosphates, mg/dm <sup>3</sup>                                               | 0.054             | 0.055     | 0.086     | 0.078     | 0.059     |
| Bicarbonates, mg/dm <sup>3</sup>                                             | 279.0             | 270.7     | 233.6     | 175.8     | 264.6     |
| Phenols, mg/dm <sup>3</sup>                                                  | 0.0012            | 0.0006    | 0.0013    | 0.0009    | 0.001     |
| Calcium, mg/dm <sup>3</sup>                                                  | 512               | 360       | 100       | 94        | 93        |
| Magnesium, mg/dm <sup>3</sup>                                                | 108               | 78        | 37        | 30        | 37        |
| Sodium and potassium<br>(in total), mg/dm <sup>3</sup>                       | 4778              | 1454      | 147       | 127       | 121       |
| Total iron, mg/dm <sup>3</sup>                                               | 0.179             | 0.173     | 0.110     | 0.128     | 0.098     |
| Manganese, mg/dm <sup>3</sup>                                                | 0.025             | 0.015     | 0.020     | 0.020     | 0.020     |
| Copper, mg/dm <sup>3</sup>                                                   | 0.003             | 0.003     | 0.002     | 0.002     | 0.002     |
| Zinc, mg/dm <sup>3</sup>                                                     | 0.036             | 0.0154    | 0.010     | 0.01      | 0.0124    |
| Chromium (VI), mg/dm <sup>3</sup>                                            | 0.005             | 0.005     | 0.005     | 0.01      | 0.005     |
| Nickel, mg/dm <sup>3</sup>                                                   | 0.005             | 0.005     | 0.005     | 0.005     | 0.005     |
| Total nitrogen, mg/dm <sup>3</sup>                                           | 1.69              | 0.92      | 1.00      | 0.90      | 1.00      |
| Phosphorus, mg/dm <sup>3</sup>                                               | 0.040             | 0.005     | 0.050     | 0.025     | 0.025     |
| Silicon, mg/dm <sup>3</sup>                                                  | 3.00              | 3.69      | 2.67      | 2.77      | 2.83      |
| Pesticides<br>( $\alpha$ -, $\beta$ -, $\gamma$ -HCH, DDT,<br>DDD, DDE, HCB) | < 0.00001         | < 0.00001 | < 0.00001 | < 0.00001 | < 0.00001 |

\* For OP-4, mean values are given (site 1 and site 2).

The lower reaches of the Chernaya River (OP-1, OP-2) are characterised by increased content of chlorides, sulfates, calcium, magnesium, sodium and potassium in total, compared with the upper and middle reaches (table). The  $\text{NO}_2^-$  concentration in the lower reaches of the river was twice as high as in the upper reaches, and the  $\text{NO}_3^-$  content reached a maximum in the middle reaches of the river (table), which indicates chronic pollution (washout with storm runoff).

The phosphate content at all OPs in the Chernaya River is below the MPC for mesotrophic water bodies <sup>7)</sup> (table).

An increase in the concentration of some HMs (Mn, Fe, Cu, Zn) was observed from the upper reaches (OP-5 Rodnikovoye) to the lower reaches (OP-1 Inkerman).

The average values of  $\text{Cr}^{6+}$ , Ni, petroleum products and pesticides were within the MPC limits at all monitoring sites. For 2019–2024, the average COD value was an order of magnitude greater than  $\text{BOD}_5$  (table). This is probably due to the presence of difficult-to-degrade organic compounds of plant origin. It is indicative that the high content of dissolved oxygen (7.58–7.65 mg/dm<sup>3</sup>) determines biochemical equilibrium and normal functioning of the biota of the Chernaya River.

## Discussion

According to the results of water quality monitoring of the Chernaya River in 2019–2024, exceedances of the MPC were revealed for a number of hydrochemical indicators, such as COD and the content of HMs (except  $\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$ ), nutrients, phenols, chlorides and sulfates (see Figs. 2, 4).

Throughout the entire observation period, one-time or periodic spikes in the concentrations of Mn, Fe, Mg and Cu and suspended solids were noted, exceeding the standards for fishery water bodies (see Figs. 2, 3), which may be associated with intensive bank erosion, erosion and washout of fertilisers from agricultural fields. The high content of Mg and Ca in the waters of the Chernaya River in 2022, exceeding the MPC (see Fig. 3), proved comparable to data for 1989–2008 [3], which may be the result of specific hydrochemical conditions in the mixing zone of river and sea waters, given the absence of mining and chemical enterprises in the area of OP-1 Inkerman and OP-2 Zelenaya Gorka.

Exceedance of the COD standard and above-standard concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  (see Fig. 2) were observed annually. Peaks in the concentrations of phenols, ASs and petroleum products exceeding the MPC for fishery water bodies were recorded (see Fig. 4). From 2019 to 2024, an increase in the content of nutrients  $\text{NH}_4^+$  and Si was noted.

It should be noted that the increase in the concentration of nutrients in the upper and lower reaches of the Chernaya River revealed by us is comparable to the results of other researchers for 2012–2023 [5, 6]. Apparently, the high concentration of pollutants in the Chernaya River is associated with their entry from agricultural lands located mainly along the middle reaches of the river (including in the coastal and water protection zones), as well as with economic wastewater from industrial enterprises. In addition, sources of pollution include the inflow of sea waters during storm surges in the estuarine zone, discharges of centralised and

local sewage treatment facilities and storm runoff [3, 5, 6]. Nevertheless, at all river sections we revealed a decrease in the content of Cu, ASs and petroleum products from 2019 to 2024.

Analysis of the spatial distribution of some hydrochemical indicators revealed fairly high concentrations of chlorides, sulfates and HMs, as well as exceedance of the BOD<sub>5</sub> and COD standards in the estuarine zone of the Chernaya River (OP-1, -2, see Figs. 2, 3) compared with other sections (OP-3, -4, -5). At the same time, the high content of sulfates and chlorides exceeding the MPC proved comparable to data for 1989–2008 [3]. This may be due to the high content of organic substances in water because of the entry of insufficiently treated or untreated wastewater and natural precipitation.

Overall, researchers noted a deterioration in the water quality of the Chernaya River in 2012–2023 and associated it with the entry into the channel of some pollutants from its tributaries [5, 6].

Analysis of monitoring data for 2019–2024 showed some deterioration in the water quality of the Chernaya River. The main reason is the entry into the channel of significant volumes of insufficiently treated industrial wastewater from enterprises, as well as untreated domestic wastewater from unorganised wastewater disposal sources. The situation was aggravated by the restriction of control (supervisory) measures<sup>4)</sup>. A slight increase in the content of ASs, phenols, petroleum products and some metals is associated with their accumulation on the river catchment area during low-water periods and subsequent washout with intensive storm runoff, as well as during short-term extreme floods (June 2021, June and December 2022)<sup>4)</sup>.

Nevertheless, in the lower reaches of the river and the estuarine part, a decrease in phenol concentration to a level below the MPC for water bodies of fishery importance was recorded<sup>9)</sup>. This indicates some improvement in water quality in terms of this indicator compared with data for 1980–2020 [8, 14]. In addition, a decrease in concentrations of nitrites and nitrates was noted, which proved below the standards<sup>7)</sup> compared with 2015–2020 [5, 11].

At all observation points, low concentrations of organochlorine and other pesticides were revealed, not exceeding the MPC, which corresponds to data for 1980–2015 and 2020 [14, 15]. The stable oxygen content at different river sections proved similar to 2015 data [11].

A comparative analysis of interannual changes in the hydrochemical indicators of the Chernaya River with data on the other largest watercourses of Crimea and water bodies of fishery importance for 2022–2024 revealed a similar tendency toward an increase in COD<sup>5), 6)</sup>. Apparently, this is associated with leaching from the soils of the catchment basin of persistent organic compounds and the entry of nutrients, metals and other pollutants as part of insufficiently treated wastewater from sewage treatment facilities.

Based on the conducted studies and analysis of published data for 2019–2024<sup>4)</sup>, some decrease in the water quality of the Chernaya River – the main source of drinking water supply for the city of Sevastopol – was established. This requires the adoption of comprehensive measures and the implementation of water protection

measures. First of all, these include restriction or prohibition of the placement of unorganised recreation areas in the river water protection zone and increased requirements for environmental expertise during the construction of permanent structures in this zone. In our opinion, the inclusion in the water quality monitoring system of bioindication studies using indicator species from representatives of coastal aquatic vegetation, such as common reed (*Phragmites australis*), will make it possible not only to improve the assessment of environmental quality but also to develop scientifically substantiated recommendations for reducing the negative impact on the water body.

## Conclusion

Analysis of the interannual dynamics of the water quality of the Chernaya River by 36 standardised and non-standardised hydrochemical indicators for 2019–2024 revealed their significant variation at five OPs located in the upper, middle and lower reaches of the river.

The variability of the content of elements of the main salt composition of river waters ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , Ca, Mg), nutrients ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , Si) and microelements, including some HMs (Fe, Cu, Mn, Ni and  $\text{Cr}^{6+}$ ), was analysed. The dynamics of a number of organic pollutants (phenols, petroleum products, organochlorine pesticides, ASs) was assessed.

The greatest degree of pollution of the Chernaya River waters was revealed in the lower reaches, which is directly associated with the entry into the water-course of insufficiently treated industrial wastewater, organic compounds and heavy metals with intensive storm runoff from the catchment basin, during extreme floods, as well as with polluted waters of tributaries.

During the study period, the content of Fe and Cu increased by a factor of more than four, and the Mn concentration exceeded the MPC by more than an order of magnitude. In addition, increased concentrations of Ca and Mg, suspended solids,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  were revealed. Interannual changes in the content of  $\text{NO}_3^-$ , Ni and  $\text{Cr}^{6+}$  were insignificant. The concentration of organic pollutants at all OPs decreased by 2024; the concentration of phenols fell below the MPC from 2021, and that of petroleum products from 2023.

Non-standardised hydrochemical indicators varied to a lesser extent than standardised ones: pH decreased to neutral values, Si concentration and COD indicators increased more than twofold, and the total content of Na and K decreased by two orders of magnitude by 2021, changing insignificantly in subsequent years.

Thus, the water quality of the Chernaya River by 36 hydrochemical indicators for the specified period can be considered satisfactory, especially with respect to organic pollutants. Exceedances were noted only for some heavy metals and nutrients, mainly in the lower reaches of the river and at its mouth.

Since the Chernaya River is the main surface source of water supply for Sevastopol, monitoring of its water quality remains a priority task. To improve the effectiveness of control, it is recommended to:

- conduct an inventory of pollution sources;

- develop a set of measures aimed at reducing the volumes of incoming untreated wastewater;
- introduce reed filter strips for sedimentation of suspended solids and absorption of pollutants;
- supplement water monitoring with bioindication studies using indicator species of coastal aquatic vegetation.

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*About the authors:*

**Julia A. Petrova**, Postgraduate, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Ave., Sevastopol, 299011, Russia), **ORCID: 0009-0008-4317-5931**, [juliacosac@gmail.ru](mailto:juliacosac@gmail.ru)

**Natalia A. Milchakova**, Leading Researcher, Head of the Laboratory of Phytoresources, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Ave., Sevastopol, 299011, Russia), PhD (Biol.), **ORCID ID: 0000-0001-5407-7706**, **Researcher ID: I-1280-2016**, [nmilchakova@ibss-ras.ru](mailto:nmilchakova@ibss-ras.ru)

**Julia A. Gavrilova**, Postgraduate, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Ave., Sevastopol, 299011, Russia), **ORCID: 0009-0004-1243-8912**, [u.gavrilova@gs.sev.gov.ru](mailto:u.gavrilova@gs.sev.gov.ru)

*Contribution of the authors:*

**Yulia A. Petrova** – analysis of state monitoring results, preparation of the manuscript text

**Natalia A. Milchakova** – formulation of the problem, analysis of results, preparation of the manuscript text

**Yulia A. Gavrilova** – analysis of state monitoring results, preparation of the manuscript text

*All authors have read and approved the final manuscript.*

Original paper

## Distribution of macrophytobenthos in the landscapes of the natural monument “Coastal Aquatic Complex at Cape Sarych”

N. V. Mironova, T. V. Pankeeva \*

*A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia*

*\* e-mail: tatyapankeeva@yandex.ru*

### Abstract

For the first time, based on a landscape approach, the features of the spatial distribution of benthic vegetation, floristic composition, and qualitative and quantitative characteristics of the macrophyto-benthos of the regional natural monument “Coastal Aquatic Complex at Cape Sarych” (Southern Coast of Crimea, Sevastopol region) are shown. The study used materials from hydrobotanical and landscape surveys conducted in this area in the summer of 2021. A landscape map of the water area was compiled, and seven underwater landscapes were identified, featuring the key macrophyte species *Ericaria crinita*, *Gongolaria barbata* and *Phyllophora crispa*. For each landscape contour, the total macrophyte biomass (TMB) and the proportion of key macrophyto-benthic species were calculated. The comparative analysis showed that the landscape of the shallow zone (0.5–1 m) has the greatest variability in TMB values ( $2036.5 \pm 264.6$ )–( $8167.6 \pm 465.7$ ) g·m<sup>-2</sup> raw mass and proportions of *E. crinita*, *G. barbata* (4–83%). The contribution of epiphytes does not exceed (3–21% TMB). Maximum values of TMB ( $6972.8 \pm 371.2$ )–( $10\,673.3 \pm 654.8$ ) g·m<sup>-2</sup> raw mass and high contribution of *E. crinita*, *G. barbata* (53–77%) were observed in the landscapes upper shoreface (1–5 m), where the highest proportion of epiphytic algae was also recorded (23–34%). The TMB in landscapes of the gently (5–15 m) dipping accumulation plain was characterized by relatively low values, which varied slightly ( $1312.7 \pm 141.3$ )–( $2463.0 \pm 196.7$ ) g·m<sup>-2</sup> raw mass, with the contribution of *P. crispa* increasing sharply with depth (from 20 to 87%), whereas that of *E. crinita* and *G. barbata* significantly decreasing (from 66 to 2%); the proportion of epiphytic plants was 8–23%. It was established that the marine flora contained a significant number of algal species listed in Red Data Books, which confirms the conservation value of the studied aquatic area. However, species of macrophytes, indirectly indicating pollution of the protected water area, were found in the algoflora of the nature monument. In the coastal zone under recreational pressure, a mass development of green algae (*Ulva rigida*, *Ulva intestinalis*, *Cladophora laetevirens*) was observed, along with the highest proportion of polysaprobic and the maximum contribution of annual and summer macrophyte species inhabiting waters with an elevated organic content. The obtained results can be utilized for optimizing the conservation regime of the natural monument.

**Keywords:** bottom vegetation, *Ericaria crinita*, *Gongolaria barbata*, *Phyllophora crispa*, specially protected natural areas, landscape structure, Black Sea, Sevastopol

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## **Распределение макрофитобентоса в ландшафтах памятника природы «Прибрежный аквальный комплекс у мыса Сарыч»**

**Н. В. Миронова, Т. В. Панкеева \***

*ФГБУН ФИЦ «Институт биологии южных морей имени А. О. Ковалевского РАН»,  
Севастополь, Россия*

\* e-mail: [tatyanapankeeva@yandex.ru](mailto:tatyanapankeeva@yandex.ru)

### **Аннотация**

Впервые на основе ландшафтного подхода оцениваются флористический состав, качественные и количественные характеристики макрофитобентоса и особенности его распределения в акватории памятника природы регионального значения «Прибрежный аквальный комплекс у мыса Сарыч» (Южный берег Крыма, район г. Севастополя). Использованы материалы гидробиотанической и ландшафтной съемок, проведенных в этом районе летом 2021 г. Составлена ландшафтная карта акватории, выделено семь подводных ландшафтов с участием ключевых видов макрофитов *Ericaria crinita*, *Gongolaria barbata* и *Phyllophora crispa*. Для каждого ландшафтного контура рассчитаны общая биомасса макрофитов и доля ключевых видов макрофитобентоса. Сравнительный анализ показал, что ландшафты мелководной зоны (глубина 0.5–1 м) отличаются наибольшей вариабельностью общей биомассы макрофитов –  $(2036.5 \pm 264.6) - (8167.6 \pm 465.7) \text{ г} \cdot \text{м}^{-2}$  сырой массы – и доли *E. crinita*, *G. barbata* (4–83 %). Вклад эпифитов не превышает (3–21 % общей биомассы макрофитов). Максимальные значения общей биомассы макрофитов –  $(6972.8 \pm 371.2) - (10\,673.3 \pm 654.8) \text{ г} \cdot \text{м}^{-2}$  сырой массы – и высокий вклад *E. crinita*, *G. barbata* (53–77 %) отмечены в ландшафтах, относящихся к подводному склону (глубина 1–5 м), где также зарегистрирована наибольшая доля эпифитных водорослей (23–34 %). Показатели общей биомассы макрофитов в ландшафтах слабонаклонной равнины (глубина 5–15 м) относительно невысоки и слабо варьируют – от  $(1312.7 \pm 141.3)$  до  $(2463.0 \pm 196.7) \text{ г} \cdot \text{м}^{-2}$  сырой массы; при этом вклад *P. crispa* резко возрастает с глубиной (с 20 до 87 %), а доля *E. crinita* и *G. barbata* – существенно снижается (с 66 до 2 %), доля эпифитной синузии составляет 8–23 %. В составе морской флоры зарегистрировано значительное количество видов водорослей, занесенных в Красные книги, что подтверждает высокую природоохранную ценность изучаемой акватории. Однако в альгофлоре памятника природы обнаружены виды макрофитов, которые косвенно указывают на загрязнение охраняемой акватории. В прибрежной зоне, испытывающей рекреационную нагрузку, отмечено массовое развитие зеленых водорослей (*Ulva rigida*, *U. intestinalis*, *Cladophora laetevirens*), наибольшая доля полисапробионтов и максимальный вклад однолетних и сезонно-летних видов макрофитов, обитающих в воде с повышенным уровнем антропогенной эвтрофикации. Полученные результаты могут быть использованы для оптимизации природоохранного режима памятника природы.

**Ключевые слова:** донная растительность, *Ericaria crinita*, *Gongolaria barbata*, *Phyllophora crispa*, особо охраняемые природные территории, ландшафтная структура, Черное море, Севастополь

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## Introduction

Recent hydrobiological studies have shown that global environmental and climatic changes, together with an increase in storm intensity, pose a significant threat to the ecosystems of the world's coastal zones, 30% of which are covered by macrophyte beds [1–3]. Increased eutrophication of seawater and a substantial rise in anthropogenic pressure on the coastal zones of the world's oceans, including the Black Sea, are also leading to adverse changes in the seabed vegetation cover [4–9]. The area of water bodies with bottom vegetation is known to be shrinking significantly. Thus, according to data from the United Nations Environment Programme (UNEP), the area of macrophyte habitats has been decreasing by 7% since 1930. For example, the average annual rate of decline in the area where kelp grows is 2% [10]. It is telling that the destruction of phytobenthos habitats, leading to a reduction in macrophyte biomass, is also characteristic of protected marine areas [11, 12].

In Sevastopol, there are six protected areas, which include a marine protected area (MPA). A significant proportion of the MPA's area is occupied by the “Cape Aya” and “Karansky” state-owned natural landscape reserves of regional importance. Hydrological natural monuments cover 391.9 hectares, accounting for 54.6% of the total protected water area in Sevastopol. Within these protected areas, the ericaria–gongolyaria and phyllophora phytocenoses, as well as communities of higher aquatic vegetation, are of scientific and conservation value; these constitute key components of the Black Sea ecosystem and have a protected status at international, national and regional levels [13].

The scientific literature contains data on the floristic composition of macrophytic benthos and landscape diversity in protected areas in the Republic of Crimea and the federal city of Sevastopol [11, 12, 14]. However, information on the spatial distribution and biomass of macrophytes in the underwater landscapes of protected water bodies remains limited.

The aim of this study is to assess the distribution of macrophyte benthos and its quantitative and qualitative indicators in the landscapes of the “CAC at Cape Sarych” natural monument.

## Study materials and methods

The “Coastal Aquatic Complex (CAC) at Cape Sarych” hydrological natural monument of regional significance is located in the southern part of Sevastopol. The coastline stretches for 1,900 metres, and the water area is 300 metres wide. The total area of the monument is 62.28 hectares, of which 3.51 hectares are land and 58.77 hectares are water [13].

Along most of the coastline, there is a boulder bench that merges into sections of a pebble one [15]. The narrow bench drops off sharply to a considerable depth. The underwater slope is rather steep. The open shores near Cape Sarych promote active mixing of water masses, ensuring high water clarity and low trophic levels [16]. Anticyclonic currents prevail here throughout the year. In summer, the water temperature near the shore drops significantly due to the upwelling of deep waters, which renew the water column during surges [17].

In the summer of 2021, hydrobotanical and landscape surveys were carried out in the waters of the “CAC at Cape Sarych” natural monument. As part of these surveys, three profiles were set, running perpendicular to the shoreline (Fig. 1). A portable Oregon 650 GPS receiver was used to determine their coordinates. When selecting the locations for the profiles, consideration was given to the characteristics of the geological and geomorphological structure of the coastal zone and the type of land use. Profiles I ( $44^{\circ}23.566' \text{ N}$ ,  $33^{\circ}43.624' \text{ E}$ ) and III ( $44^{\circ}23.244' \text{ N}$ ,

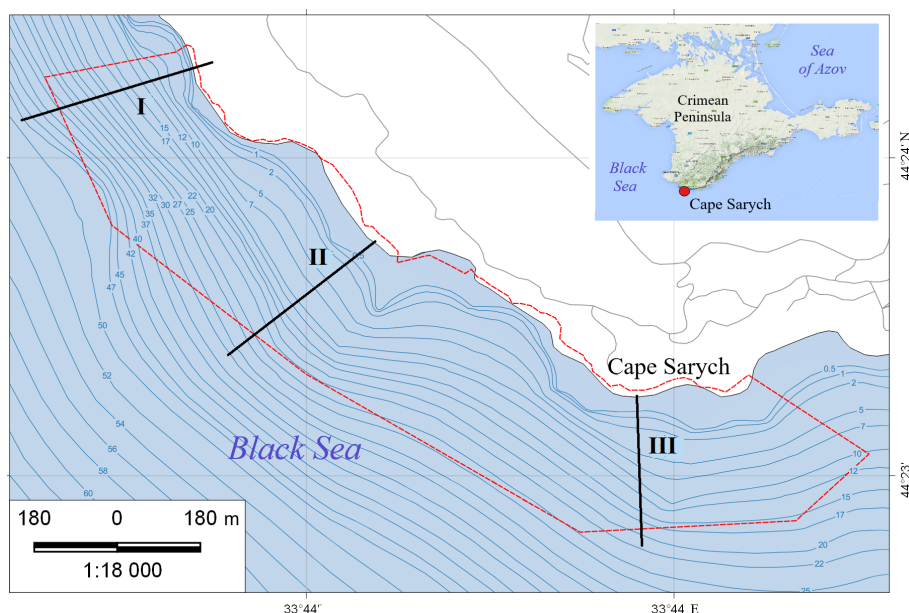


Fig. 1. A schematic map of the waters of the “Coastal Aquatic Complex (CAC) at Cape Sarych” natural monument, showing the boundaries of the protected area (red outline) and location of the profiles (I–III), 2021. The inset shows the Crimean Peninsula, with the study area marked by a red circle

33°43.266' E) run at the foot of the cliffs, where the coastal zone consists of boulder deposits and a sharp drop in depth is observed. At present, the adjacent coastline in the area of profile I is under active development, while at Cape Sarych, where profile III is located, there is virtually no human activity. Profile II (44°23.477' N, 33°43.836' E) runs along a section of a pebble bench on which the beach is situated, while the adjacent area is occupied by a cottage estate.

To study the landscape structure of the water body, the landscape profiling method was applied, involving a detailed description of the profiles and key areas. Samples were collected in accordance with the standard methodology<sup>1)</sup> at depths of 0.5–15 m. A total of 84 quantitative samples were collected and analysed (28 samples per profile). Algal species were identified using an identification guide<sup>2)</sup>, taking into account the latest changes in nomenclature (available at: <http://www.algaebase.org>). The level of seawater pollution was assessed indirectly using Cheney's floristic ratio [18]. The structure and composition of the macrophytobenthos were analysed using Shannon's species diversity index (H) [19]. The distribution of algal species by ecological groups (vegetation duration and saprobity) is presented in accordance with the classification by A. A. Kalugina-Gutnik<sup>3)</sup>.

The QGIS 3.28.13 software package and a digitised, georeferenced navigation map were used to create the landscape map. The landscape structure was studied at the local area level.

## Results and discussion

Within the landscape structure of the “CAC at Cape Sarych” natural monument, seven underwater landscapes were identified; six of these differ in terms of their dominant macrophyte species: *Ericaria crinita* (Duby) Molinari et Guiry = *Cystoseira crinita*), *Gongolaria barbata* (Stackh.) Kuntze = *Cystoseira barbata*) and *Phyllophora crispa* (Huds.) P. S. Dixon; landscape 7 is devoid of vegetation (Fig. 2).

**A boulder bench predominated by *Ericaria crinita* and *Gongolaria barbata* (I)** occupies depths of 0.5–1 m in the western (profile I) and eastern (profile III) parts of the nature monument (see Fig. 2). The projected coverage of the bed by macrophytes (PC) at these depths is up to 100%.

The total macrophyte biomass (TMB) ranged from  $(2,036.5 \pm 264.6)$  to  $(7,197.3 \pm 494.5)$  g·m<sup>-2</sup> wet weight (Table 1). The proportion of *E. crinita* and *G. barbata* varied widely from 4 to 83% of the TMB: the maximum was recorded in the waters of profile I at a depth of 1 m, and the minimum was in the waters of the same profile at a depth of 0.5 m, where the bottom vegetation was dominated

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<sup>1)</sup> Kalugina-Gutnik, A.A., 1969. [Black Sea Benthic Vegetation Survey Using Light-Weight Diving Equipment]. In: AS USSR, 1969. [Marine Underwater Studies]. Moscow: Nauka, pp. 105–113 (in Russian).

<sup>2)</sup> Zinova, A.D., 1967. [Field Guide to Green, Brown and Red Algae of the Southern Seas of the USSR]. Leningrad: Nauka, 397 p. (in Russian).

<sup>3)</sup> Kalugina-Gutnik, A.A., 1975. [Phytobenthos of the Black Sea]. Kiev: Naukova Dumka, 248 p. (in Russian).

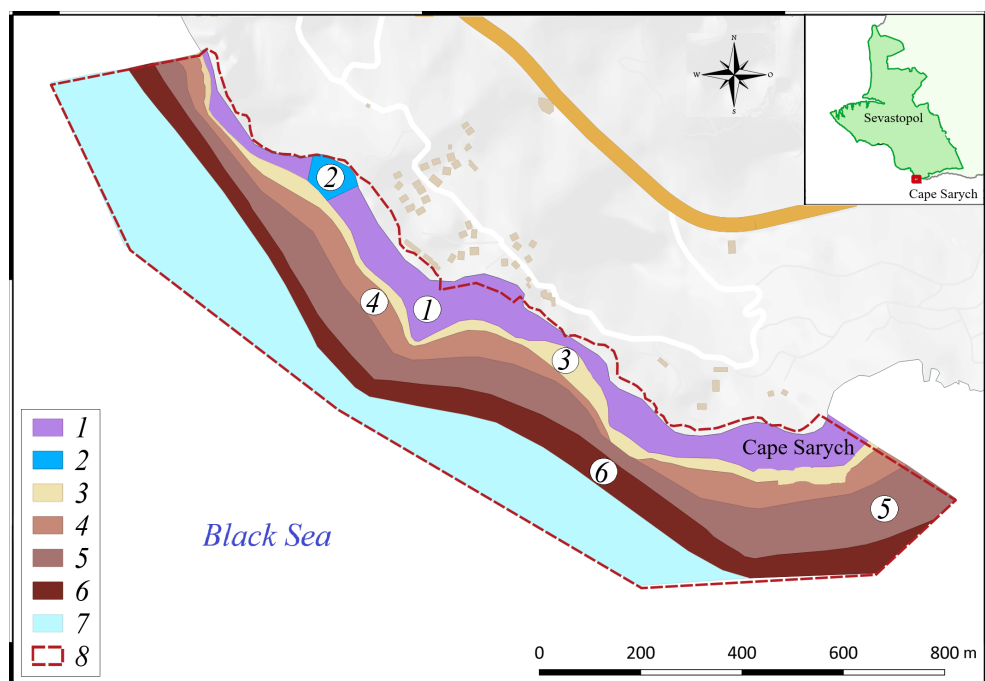


Fig. 2. Schematic map of the landscape structure of the water area of the natural monument CAC at Cape Sarych with defined underwater landscapes: 1 – boulder benches predominated by *Ericaria crinita* and *Gongolaria barbata*; 2 – pebble-boulder benches with individual blocks, predominated by *Ericaria crinita* and *Gongolaria barbata*; 3 – upper shoreface consisting of psephitic sediments predominated by *Ericaria crinita* and *Gongolaria barbata*; 4 – upper shoreface consisting of psephitic deposits predominated by *Ericaria crinita* and *Gongolaria barbata* with mosaic alternation of pebble and gravel deposits and shell fragments predominated by *Phyllophora crispa*; 5 – gently dipping accumulation plain formed by gravel-psammitic deposits with inclusion of shell fragments predominated by *Phyllophora crispa*, and individual blocks predominated by *Ericaria crinita* and *Gongolaria barbata*; 6 – gently dipping accumulation plain formed by psammitic deposits with inclusion of shell fragments predominated by *Phyllophora crispa*; 7 – gently dipping accumulation plain formed by sandy sediments, with no bottom vegetation; 8 – boundaries of the natural monument.

The red rectangular in the inset shows the study area

by *Palisada perforata* (Bory) K. W. Nam (31%), *Corallina officinalis* L. (24%), *Cladophora sericea* (Huds.) Kütz. (14%) and species of the genus *Ceramium* (21%).

In the waters of profile III, in addition to the dominant species *E. crinita* and *G. barbata*, *Cladostephus spongiosus* (Huds.) C. Agardh (2–6%) was recorded, whilst at a depth of 0.5 m, *Padina pavonica* (L.) Thivy (3%) was noted, and at a depth of 1 m, *Carradoriella elongata* (Huds.) Savoie et G. W. Saunders (16% of the TMB) was recorded.

Within this depth range, epiphytes predominated within the boundaries of the landscape under study: *Vertebrata subulifera* (C. Agardh) Kuntze (1–17%), *Ceramium ciliatum* (Ell.) Ducl. (3–5%), *Ceramium diaphanum* (Lightf.) Roth (1–3%), and *Laurencia coronopus* J. Agardh (1–2% of the TMB).

Significant variation in the values of the species diversity index *H* indicates rather a complex structure of the macrophytobenthos community, due to the alternation of dominant algal species in the profiles area, with a high contribution from epiphytes (Table 1).

Table 1. Total biomass of macrophytes, percentage of dominant species and their epiphytes species, diversity index *H* in the landscape structure of natural monument CAC at Cape Sarych by depth in 2021

| Landscapes | Depth, m | Biomass of macrophytes, g·m <sup>-2</sup> | Proportion of, %                                       |                           |                  | <i>H</i>      |
|------------|----------|-------------------------------------------|--------------------------------------------------------|---------------------------|------------------|---------------|
|            |          |                                           | <i>Ericaria crinita</i> ,<br><i>Gongolaria barbata</i> | <i>Phyllophora crispa</i> | epiphytic plants |               |
| 1          | 0.5–1    | (2036.5 ± 264.6)–<br>(7197.3 ± 494.5)     | 4.1–82.8                                               | 0                         | 3.0–19.6         | 1.12–<br>2.87 |
| 2          | 0.5–1    | (6772.2 ± 403.8)–<br>(8167.6 ± 465.7)     | 55.3–72.7                                              | 0–0.1                     | 8.2–21.4         | 1.92–<br>2.46 |
| 3          | 1–3      | (6972.8 ± 371.2)–<br>(8195.3 ± 481.4)     | 68.3–77.0                                              | 0.6–6.0                   | 22.7–24.3        | 0.95–<br>1.77 |
| 4          | 3–5      | (7681.9 ± 397.8)–<br>(10 673.3 ± 654.8)   | 53.5–62.0                                              | 11.5–22.8                 | 15.2–34.4        | 1.47–<br>1.78 |
| 5          | 5–10     | (1370.3 ± 126.8)–<br>(2463.0 ± 196.7)     | 30.8–65.9                                              | 19.7–51.9                 | 8.4–17.3         | 1.43–<br>1.91 |
| 6          | 10–15    | (1312.7 ± 141.3)–<br>(1967.6 ± 164.2)     | 0–1.8                                                  | 76.9–87.1                 | 11.1–23.1        | 0.59–<br>0.78 |

Note: The numbering and description of underwater landscapes correspond to the information presented in the text and in Fig. 2.

**A pebble-boulder bench with individual blocks, predominated by *Ericaria crinita* and *Gongolaria barbata* (2)**, is situated at a depth of 0.5–1 m in the central (profile II) part of the natural monument (see Fig. 2). The PC values at these depths reached 60–70%. The TMB varied slightly within the range from  $(6,772.2 \pm 403.8)$  to  $(8,167.6 \pm 465.7)$  g·m<sup>-2</sup> wet weight (Table 1). Of note, in the waters of this profile, at a depth of 0.5 m, where *E. crinita* and *G. barbata* (55%) dominated the macrophytobenthos, significant clusters of *Ulva rigida* C. Agardh (29%) and *U. intestinalis* L. (2% of wet weight) were found in the water column of this profile at a depth of 0.5 m, where *E. crinita* and *G. barbata* (55%) dominated the macrophytobenthos composition. At a depth of 1 m in this landscape, the contribution of *E. crinita* and *G. barbata* increases by a factor of 1.3, whilst the proportion of species of the genus *Ulva* decreased to 1.4% of the TMB. It is noteworthy that, with increasing depth, the role of representatives of the epiphytic synusia more than doubled (Fig. 2); at a depth of 0.5 m, *Cladophora laetevirens* (Dillwyn) Kütz. (4%), whilst at a depth of 1 m, *V. subulifera* (17% of the TMB) predominated.

The species diversity of the phytocenosis is confirmed by high values of Shannon's index H (Table 1).

**An upper shoreface consisting of psephitic sediments predominated by *Ericaria crinita* and *Gongolaria barbata* (3)** is situated along the coastline at a depth of 1–3 m (see Fig. 2). The underwater slope is steep and complicated by boulder deposits. The PC values at these depths were at their maximum (100%). The TMB varied within a fairly narrow range from  $(6,972.8 \pm 371.2)$  to  $(8,195.3 \pm 481.4)$  g·m<sup>-2</sup> of wet weight (Table 1). The contribution of *E. crinita* and *G. barbata* varied from 68 to 77% of the TMB. The composition of the benthic vegetation included *C. spongiosus* (1–3%) and *P. crispa* (1–6%). It is characteristic that epiphytic synusia was abundant in this depth range; among the epiphytes, *V. subulifera* (19–22%) predominated, while *Antithamnion cruciatum* (Agardh) Nägeli (1–3% of the TMB) was also present.

The relatively low values of the species diversity index H (Table 1) indicate a homogeneous structure of the macrophytobenthos community, with a prevalence of dominant species.

**An upper shoreface consisting of psephitic deposits predominated by *Ericaria crinita* and *Gongolaria barbata* with mosaic alternation of pebble and gravel deposits and shell fragments predominated by *Phyllophora crispa* (4)**, extends to depths of 3–5 m (see Fig. 2). The underwater slope is steep, with areas covered with pebbles, gravel and broken shells situated between the boulders. The PC values at these depths were high (90–100%). The TMB ranged from  $(7,681.9 \pm 397.8)$  to  $(10,673.3 \pm 654.8)$  g·m<sup>-2</sup> wet weight (Table 1). The proportion of *E. crinita* and *G. barbata* varied from 53 to 62%, while the contribution of *P. crispa* ranged from 11 to 23% of the TMB. *V. subulifera* dominated the epiphyte community (12–32%); *A. cruciatum* (1–3% of the TMB) was noted; the maximum contribution of the epiphytic synusia was recorded in the water column of profile II, and the minimum was in the area of profile III.

The complex polydominant structure of the macrophytobenthos community, in which a significant proportion of epiphytic algal species was observed, is confirmed by the values of the species diversity index  $H$  (Table 1).

**A gently dipping accumulation plain formed by gravel-psammitic deposits with inclusion of shell fragments predominated by *Phyllophora crispa* and individual blocks predominated by *Ericaria crinita* and *Gongolaria barbata* (5),** is found at a depth of 5–10 m (see Fig. 2). The relief is a plain characterised by smoothed forms and randomly arranged boulders and stones. The PC values were 90%. The TMB varied from  $(1,370.3 \pm 126.8)$  to  $(2,463.0 \pm 196.7)$  g·m<sup>-2</sup> wet weight (Table 1). The proportion of *E. crinita* and *G. barbata* ranged from 31 to 66%, whereas that of *P. crispa* ranged from 20 to 52% of the TMB. The composition of the benthic vegetation included *Codium vermilara* (Olivi) Delle Chiaje (3%) and *Nereia filiformis* (J. Agardh) Zanard (1% of the TMB). The contribution of epiphytic algae was relatively low, with *Rhodochorton purpureum* (Light.) Rosenv. predominating (8–17% of the TMB).

The values of the species diversity index  $H$  indicate a high contribution of dominant algal species to the composition of the macrophytobenthos community (Table 1).

**A gently dipping accumulation plain formed by gravel-rubble deposits with inclusion of shell fragments predominated by *Phyllophora crispa* (6),** extends to depths of 10–15 m (see Fig. 2). The relief consists of a sloping plain with a slight gradient. The PC values in this depth range reached 90%. The TMB varied within a narrow range from  $(1312.7 \pm 141.3)$  to  $(1967.6 \pm 164.2)$  g·m<sup>-2</sup> wet weight (Table 1). The contribution of *P. crispa* ranged from 77 to 87%, while the proportion of *E. crinita* and *G. barbata* did not exceed 2% of the TMB. *N. filiformis* was recorded in the benthic vegetation (1% of the TMB). Among the epiphytes, *R. purpureum* predominated (11–23% of the TMB).

Low values of the Shannon  $H$  species diversity index indicate a fairly homogeneous structure of the macrophytobenthos community, with a single dominant species (Table 1).

**A gently dipping accumulation plain formed by sandy sediments, with no bottom vegetation (7),** extends to depths of over 15 m (see Fig. 2).

According to the obtained data, the greatest variability within the boulder bench landscape (1) was observed in the TMB values and the proportion of key species (*E. crinita* and *G. barbata*). At the same time, in the landscape of the pebble-boulder bench with individual blocks (2), the TMB indices and those of the same dominant species showed only slight variation. The highest TMB values and the greatest contribution from *E. crinita* and *G. barbata* were recorded in landscapes belonging to the upper shoreface (3–4). The highest proportion of epiphytic algae was also recorded in these landscapes. TMB indices in the gently dipping plain landscapes (5–6) are characterised by relatively low values, which varied only slightly. The contribution of the key species, *P. crispa*, increased sharply with increasing depth, whilst that of *E. crinita* and *G. barbata* decreased significantly; the role of the epiphytic sinusia also diminished.

Thus, the ratio of biomass values for key species of macrophytes and lithophytic algae comprising the macrophytobenthos of underwater landscapes depends not only on the change in the light gradient with increasing depth, but also on the characteristics of the seabed lithology and the hydrodynamic regime of the coastal zone under study [20].

The TMB values in the boulder bench landscapes of the natural monument and the adjacent coastal area, which is not part of it, were found to be broadly comparable. At the same time, in the landscapes of the upper shoreface, this indicator was 2–3 times higher, whilst in the landscapes of the gently dipping plain it was approximately twice as high as in the unprotected water area [21].

Today, eight species of algae listed in the Red Data Books of the Russian Federation (2024)<sup>4)</sup> and Sevastopol (2018)<sup>5)</sup>; of these, two species—*P. crisper* and *Stilophora tenella* (Esper) P.C. Silva—are listed in both registers; six species—*C. vermilata*, *N. filiformis*, *Dictyota spiralis* Montagne, *D. dichotoma* (Huds.) J. V. Lamour., *Spermatococcus paradoxus* (Roth) Kütz. and *Dermocorynus dichotomus* (J. Agardh) Gargiulo, M. Morabito et Manghisi—are listed only in the Sevastopol Red Data Book.

It is noteworthy that a comparative analysis of protected macrophyte species (listed in the Red Data Books of the Russian Federation and Sevastopol), forming part of Sevastopol's hydrological natural monuments, revealed that the highest number of such species (eight) was recorded specifically in the waters of the “CAC at Cape Sarych” natural monument, whilst the minimum (three species) was recorded in the waters of the “CAC at Cape Lucullus” site. In the waters of the “CAC at Chersonesos Taurica” and “CAC at Cape Fiolent” sites, an equal number (five species each) was found [13].

Thus, the “CAC at Cape Sarych” natural monument, established to preserve species and landscape diversity, is functioning as such under current conditions. This is evidenced by the species composition of the phytobenthos, the significant number of algal species protected at regional and national levels, the high TMB values and the substantial proportion of dominant macrophyte species within its composition in the underwater landscapes.

Notably, macrophyte species were identified in the algal flora of the natural monument, a finding that indirectly indicates seawater pollution. It is well known that algae and seagrasses respond markedly to changes in the quality of the coastal environment, so their communities can be used as indicators of the trophic status of the environment [6, 12, 22, 23]. A study by A. A. Kalugina-Gutnik<sup>3)</sup> shows that as eutrophication in a water body increases, the total number of macrophyte species rises, and red (Rhodophyta) and green (Chlorophyta) algae tend to become more abundant than brown (Heterokontophyta) algae<sup>3)</sup>.

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<sup>4)</sup> Geltman, D.V., ed., 2024. *Red Data Book of the Russian Federation. Plants and Fungi*. Moscow: VNI “Ekologiya”, 944 p. (in Russian).

<sup>5)</sup> Dovgal, I.V. and Korzhenevsky, V.V., eds., 2018. [*Red Data Book of Sevastopol*]. Kaliningrad; Sevastopol: Izdatelsky Dom “ROST-DOLFK”, 432 p. (in Russian).

A comparative analysis of the floristic composition of algae was carried out using an annotated list of macrophyte species compiled during a hydrobotanical survey conducted jointly with I. K. Evstigneeva and I. N. Tankovskaya [14]. It was shown that the greatest number of macrophyte species and the most extensive growth of green algae were recorded on landscapes of a pebble-and-boulder bench with individual boulders and on an upper shoreface composed of coarse-grained clastic sediments within the water area of profile II, where the beach and sewage treatment facilities are located (Table 2). By contrast, in the area of profile III, where access to the shore is difficult and there are no residential developments or recreational activity, the lowest number of species was recorded. Furthermore, the Cheney index, which reflects the ratio of green, brown and red algae, also had the lowest value, indirectly confirming the relative cleanliness of the seawater in this part of the nature reserve's waters [18] (Table 2). The highest value of the Cheney index was recorded in the area of profile I, where the construction of recreational facilities in the adjacent area is likely to negatively affect the species composition of macrophytobenthos (Table 2).

The macroalgae growing in the area of the “CAC at Cape Sarych” natural monument differ in their saprobiont composition, which indirectly confirms the varying trophic status of the seawater in the waters of the three profiles<sup>3)</sup>. Thus, the highest proportion of oligosaprobic species and the lowest proportion of mesosaprobic macrophytes were recorded in the area of profile III, whilst the waters of profile II showed the highest proportion of polysaprobic species and the lowest proportion

Table 2. The floral and saprobiont composition of macrophytes in the water area of the natural monument CAC at Cape Sarych in the summer of 2021

| Profile | Total number of species | Of these, |    |    | Proportion, % |          | $K_{Ch}$ | Proportion of species by saprobicity, % |       |       |
|---------|-------------------------|-----------|----|----|---------------|----------|----------|-----------------------------------------|-------|-------|
|         |                         | Ch        | H  | Rh | <i>A</i>      | <i>P</i> |          | Oligo-                                  | Meso- | Poly- |
| I       | 52                      | 7         | 12 | 33 | 63            | 37       | 3.33     | 71                                      | 23    | 6     |
| II      | 58                      | 14        | 17 | 27 | 67            | 33       | 2.63     | 62                                      | 26    | 12    |
| III     | 50                      | 7         | 14 | 29 | 58            | 42       | 2.57     | 74                                      | 20    | 6     |
| Total   | 77                      | 19        | 19 | 39 | 65            | 35       | 3.05     | 61                                      | 30    | 9     |

Note: the annotated list of macrophyte species of the natural monument was compiled by I. K. Evstigneyeva and I. N. Tankovskaya [14].

Notations:  $K_{ch}$  – Cheney's index; Ch – Chlorophyta; H – Heterokontophyta; Rh – Rhodophyta; A – annual macrophytes; P – perennial macrophytes.

of species inhabiting clean coastal waters (Table 2). The algal contribution indices on the saprobiont scale in the waters of profile I occupy an intermediate position (Table 2). However, an abundance of *C. officinalis* was observed in the vicinity of this profile, suggesting a moderate degree of environmental pollution. This is supported by studies conducted in the Mediterranean Sea, which found that in the areas close to sewage outfalls, a plant cover dominated by coralline algae species forms [4, 8]. In the waters of profiles I and II, *Ulothrix implexa* (Kütz.) Kütz. is found—a species indicative of water eutrophication. This species was not recorded in the area of profile III. However, *Codium vermilara* (a typical inhabitant of clean waters) was found in its waters.

It should be noted that, under anthropogenic pressure, perennial algal species are replaced by seasonal and annual species within the benthic vegetation [12, 24]. A comparative analysis of the species composition of the microphytobenthos showed that the highest proportion of perennial algal species was recorded in the area of profile III, whilst the lowest one was found in the waters of profile II (Table 2).

It is well known that macrophytobenthos biomass reduces as a result of the adverse effects of pollutants entering the water [12, 22, 24]. Thus, in the waters of profile II, the key perennial species (*E. crinita* and *G. barbata*), which prefer clean areas of the open littoral zone, were observed to reduce their contribution to the TMB. At the same time, there was an increase in the proportion of annual and summer-seasonal green algae belonging to the genera *Ulva* and *Cladophora*, which inhabit environments with elevated levels of organic compounds. It is noteworthy that, under current conditions in the Black and Baltic Seas, species of the genus *Ulva* dominate in eutrophicated areas [7, 12, 23–25]. It is characteristic that not only along the Black Sea coast, but also in the Mediterranean Sea, in areas under excessive recreational pressure and sewage inflow, dominant algal species are being replaced [4, 9, 22]. In these areas of the water body, a decline in the biomass of perennial species of the genus *Cystoseira* was recorded, accompanied by a shrinkage of their habitat area.

At present, the waters adjacent to the “CAC at Cape Sarych” natural monument are under adverse human impact due to the presence of recreational facilities and a cottage estate on the coast.

To optimise the nature conservation regime, it is important to observe the 500-metre-wide water protection zone, as specified in Article 65 of the Water Code of the Russian Federation. Special regulations governing economic and other activities apply within this zone. In future, it will be necessary to clarify the boundaries of the natural monument and its buffer zone, taking into account the natural features and the impact of human activity on the coastline. The creation of a south-coast land-and-sea reserve, comprising the “Cape Aya” and “Laspy Cliffs” protected areas, the “Laspy Cliffs” protected stow and the “CAC at Cape Sarych” natural monument [20].

## Conclusions

1. As a result of underwater surveys carried out in the waters of the “CAC at Cape Sarych” natural monument, seven landscapes were identified, each characterised by dominant macrophyte species: *Ericaria crinita*, *Gongolaria barbata* and *Phyllophora crispa*.

2. Shallow-water landscapes (1–2) (depth 0.5–1 m) are characterised by the greatest variability in TMB values—ranging from  $(2036.5 \pm 264.6)$  to  $(8167.6 \pm 465.7) \text{ g} \cdot \text{m}^{-2}$  of wet weight—and in the proportion of *E. crinita* and *G. barbata* (4–83%). The contribution of epiphytes did not exceed 3–21% of the TMB. Maximum TMB values—ranging from  $(6,972.8 \pm 371.2)$  to  $(10,673.3 \pm 654.8) \text{ g} \cdot \text{m}^{-2}$  wet weight—and a high contribution from *E. crinita*, *G. barbata* (53–77%) were recorded in the upper shoreface landscapes (3–4) at depths of 1–5 m, where the highest proportion of epiphytic algae (23–34%) was also recorded. In the gently sloping plain landscapes (5–6) at depths of 5–15 m, the TMB is characterised by relatively low values, which vary only slightly: from  $(1,312.7 \pm 141.3)$  to  $(2,463.0 \pm 196.7) \text{ g} \cdot \text{m}^{-2}$  of wet weight; with increasing depth, the contribution of *P. crispa* rose sharply from 20 to 87%, while the contributions of *E. crinita* and *G. barbata* fell from 66 to 2%, and the proportion of the epiphytic sinusia ranged from 8 to 23%.

3. Significant variation in the values of the species diversity index H was observed in the underwater landscapes of the nature reserve, indicating a complex structure of the macrophytic benthic communities. The relatively low values of Shannon’s diversity index H (0.59–1.77) are characteristic of a fairly homogeneous structure of macrophyte communities, where dominant species prevail. The species diversity of phytocommunities, which is mainly due to the significant contribution of epiphytes, is confirmed by high values of the H index (1.92–2.87).

4. Eight species of algae (*Phyllophora crispa*, *Stilophora tenella*, *Codium vermilara*, *Nereia filiformis*, *Dictyota spiralis*, *D. dichotoma*, *Spermatocnusus paradoxus*, *Dermocorynus dichotomus*), which are listed in the Red Data Books of the Russian Federation and Sevastopol, were identified in the marine flora of the natural monument confirming the high conservation value of the study area.

5. In the area of profile II, which experiences the greatest recreational pressure and the greatest impact from sewage treatment facilities, signs of eutrophication were observed: the highest proportion of green algae species (24%), the lowest contribution from perennial plants (33%), and the highest proportion of polysaprobic species (12%). In the waters of profile III (with the lowest anthropogenic pressure), these indicators corresponded to relatively clean water (oligosaprobionts – 74%, polysaprobionts – 6%, perennials – 42%, and lowest Cheney’s index (2.57)).

The obtained results can be used for monitoring studies of benthic vegetation and rare and protected species of macrophytes, as well as for addressing issues relating to optimisation of the conservation regime for Sevastopol’s natural monuments and protected areas.

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#### *About the authors:*

**Nataliya V. Mironova**, Senior Researcher, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), PhD (Biol.), **ORCID ID: 0000-0001-7110-7081**, **ResearcherID: AAC-9421-2022**, [dr.nataliya.mironova@yandex.ru](mailto:dr.nataliya.mironova@yandex.ru)

**Tatyana V. Pankeeva**, Leading Researcher, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Av., Sevastopol, 299011, Russian Federation), DSc (Geogr.), **ORCID ID: 0000-0002-8933-6103**, **ResearcherID: FAA-2365-2022**, [tatyapankeeva@yandex.ru](mailto:tatyapankeeva@yandex.ru)

#### *Contribution of the authors:*

**Nataliya V. Mironova** – processing of macrophytobenthos samples, analysis and description of the study findings, preparation of the article text, selection, systematisation and analysis of literature sources

**Tatyana V. Pankeeva** – sampling, systematisation and analysis of literature sources, preparation of the article text, cartographic materials and references

*All the authors have read and approved the final manuscript.*

Original paper

## Assessment of Toxicity of Two Drilling Fluids on the Early Development of Russian Sturgeon *Acipenser gueldenstaedtii*

I. I. Rudneva<sup>1</sup>, V. G. Shayda<sup>2</sup>, M. V. Medyankina<sup>3</sup>

<sup>1</sup> Marine Hydrophysical Institute of RAS, Sevastopol, Russia

<sup>2</sup> Company “EcoService-A”, Moscow, Russia

<sup>3</sup> Moscow State University of Technology and Management K. G. Razumovsky  
(First Cossack University), Moscow, Russia

\* e-mail: [svg-41@mail.ru](mailto:svg-41@mail.ru)

### Abstract

Early ontogenetic stages of aquatic organisms are most susceptible to the effects of pollutants. Drilling fluids are toxic for aquatic environment and can impair the growth, development and survival of aquatic organisms. The paper studies the effect of two water-based drilling fluids (WBF 1 and WBF 2) at concentrations of 0.025, 0.05, 0.1, 0.5 and 1 mg/L on the survival of fertilized eggs and prelarvae of Russian sturgeon *Acipenser gueldenstaedtii* as well as the dynamics of their hatching in fresh and 5‰ saline water for 5 days. The studied drilling fluids exhibited varying toxicity. The survival of embryos in the control groups in fresh water and exposed to a medium with WBF 1 at a concentration of 0.1–0.5 mg/L did not differ, but at a concentration of 1 mg/L, all the embryos died. In salt water, at WBF 1 concentrations of 0.025 mg/L and higher, a decrease in survival by 87% was observed ( $p < 0.01$ ). WBF 2 did not affect the survival of the sturgeon embryos. In both control groups, larval hatching occurred on the first day, but embryos exposed to the medium with WBF 1 at a concentration of 0.025–0.5 mg/L hatched only on the second day. The number of prelarvae in the medium with all tested concentrations was less than in the control. At a concentration of 1 mg/L, prelarvae did not hatch. Significant differences in the survival rate of prelarvae in the experimental groups compared to the control were found at a WBF 1 concentration of 1 mg/L. A high positive correlation was established between the concentration of the toxicant and the mortality of fish prelarvae ( $R^2 = 0.87$ ). No differences were found between the survival rates of fish prelarvae in the control and experimental groups maintained in WBF 2. Based on these studies, it can be concluded that WBF 2 had no toxic effect on fish prelarvae at the tested concentrations and is therefore more environmentally safe than WBF 1. Fish embryos are adequate bioindicators for assessing the toxicity of drilling fluids and can be used to assess the ecological status of coastal waters in offshore oil and gas fields.

**Keywords:** drilling fluids, fish eggs, fish prelarvae, pollution, bioassay, Russian sturgeon, *Acipenser gueldenstaedtii*

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## Оценка токсичности двух видов буровых растворов для раннего развития русского осетра *Acipenser gueldenstaedtii*

И. И. Руднева<sup>1</sup>\*, В. Г. Шайда<sup>2</sup>, М. В. Медянкина<sup>3</sup>,

<sup>1</sup> Морской гидрофизический институт РАН, Севастополь, Россия

<sup>2</sup> ООО «ЭкоСервис-А», Москва, Россия

<sup>3</sup> МГУТУ Московский государственный университет технологий и управления  
имени К. Г. Разумовского (Первый казачий университет), Москва, Россия

\* e-mail: svg-41@mail.ru

### Аннотация

Гидробионты на ранних онтогенетических стадиях в наибольшей степени подвержены воздействию загрязнителей. Буровые растворы токсичны для водной среды и могут нарушать рост, развитие и выживаемость водных организмов. Исследовали действие двух буровых растворов на водной основе (*WBF 1* и *WBF 2*) в концентрации 0.025, 0.05, 0.1, 0.5 и 1 мг/л на выживаемость оплодотворенной икры и предличинок русского осетра *Acipenser gueldenstaedtii*, а также на динамику их вылупления в пресной и соленой (5 ‰) воде в течение 5 сут. Исследуемые буровые растворы проявляли различную токсичность. Выживаемость эмбрионов в контрольных группах в пресной воде и экспонированных в среде с *WBF 1* при концентрации 0.1–0.5 мг/л не различалась, но при концентрации 1 мг/л все эмбрионы погибли. В соленой воде при концентрации *WBF 1* 0.025 мг/л и выше наблюдали сокращение выживаемости на 87 % ( $p < 0.01$ ). *WBF 2* не повлиял на выживаемость эмбрионов осетра. В обеих контрольных группах вылупление личинок произошло в первые сутки, но эмбрионы, экспонированные в среде с *WBF 1* при концентрации 0.025–0.5 мг/л, вылупились только на вторые сутки. Количество предличинок в среде со всеми тестируемыми концентрациями было меньше, чем в контроле. При концентрации 1 мг/л предличинки не вылупились. Достоверные различия в выживаемости предличинок в опытных группах по сравнению с контрольными были обнаружены при концентрации *WBF 1* 1 мг/л. Установлена высокая отрицательная корреляция между концентрацией токсиканта и выживаемостью предличинок рыб ( $R^2 = 0.87$ ). Различий между выживаемостью предличинок в контрольной и опытной группах, содержащихся в *WBF 2*, не выявлено. На основании проведенных исследований можно заключить, что *WBF 2* не оказал токсического действия на предличинок рыб в тестируемых концентрациях; следовательно, этот раствор является более экологически безопасным, чем *WBF 1*. Эмбрионы рыб являются адекватными биоиндикаторами для оценки токсичности буровых растворов и могут быть использованы для определения экологического статуса прибрежных акваторий в районах разработки нефтегазовых месторождений на шельфе.

**Ключевые слова:** буровые растворы, загрязнение воды, икра рыб, предличинки, биотестирование, русский осетр, *Acipenser gueldenstaedtii*

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## Introduction

The development of offshore oil and gas fields in the seas and oceans is carried out using drilling fluids, for which information on their toxicity to marine life is limited and contradictory [1–3]. Drilling fluids are mixtures of various chemical components, as well as water, suspensions, emulsions and aerated liquids, organic solvents, heavy metals and clay, and are used to flush boreholes during drilling. Depending on the liquid phase, drilling fluids are divided into three groups: water-based (WBF), oil-based (OBF) and synthetic fluid-based, mainly ether-based (SBF) <sup>1)</sup>. WBFs are the most commonly used; they consist of barite (over 90%), bentonite, brown coal, lignosulphonate and heavy metals, with other components accounting for 8–12% [4].

Spent drilling fluids are classified as industrial waste and must be disposed of, since many of them are toxic, mutagenic and carcinogenic [1, 5, 6]. When released into the aquatic environment, these substances can cause adverse effects, alter the physical and chemical properties of the hydrobionts' habitat, disrupt their vital functions, behaviour, metabolic processes, reproduction, growth and development, lead to the death of organisms, and also alter the structure of aquatic communities [7]. Therefore, study of the toxicity of drilling fluids, their impact on biota, and determination of their permissible concentration levels in water bodies are of significant practical and theoretical importance. For these purposes, various toxicological tests are used to assess the hazard posed by these substances, understand the mechanisms by which they affect aquatic ecosystems and determine the ecological risk based on the responses of test organisms and their biomarkers [8].

Fish embryos and larvae are sensitive to various toxicants and are therefore widely used as test organisms for analysing water quality. The fish embryo toxicity test is mandatory when determining permissible levels of pollutants in both fishery waters and marine waters in areas of active economic activity [8]. Given the intensive

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<sup>1)</sup> Deka, B., 2023. Oil-based drilling fluid's composition. Chapter 2. In: K. Hazarika, ed., 2023. *Theory of Drilling Fluid*. India, Noida: CIIR Scientific Publications, pp. 3–6.

development of offshore oil and gas fields in the seas and oceans, as well as the risks associated with this activity, the pollution of the marine environment by drilling fluids could have disastrous consequences for the ecosystem and its inhabitants [9]. Nowadays, the biological effects of drilling fluids remain poorly studied, which makes determining their toxicity for aquatic organisms particularly important.

The Russian sturgeon, *Acipenser gueldenstaedtii* (Brandt & Ratzeberg, 1833), is a bottom, anadromous, euryhaline species of fish that spawns in rivers, after which the juveniles migrate to the sea to grow and mature, before returning to the rivers to reproduce [10]. In spring and summer, sturgeons inhabit the sea shelf and lay their eggs in rivers at depths of 3 to 10 metres, favouring areas temporarily flooded by spring floodwaters. The fertilised eggs develop for 8–10 days, after which the larvae are carried downstream along the spawning rivers and enter a brackish water environment. Sturgeons are found in the Caspian and Black Seas as well as in the Sea of Azov, where the water salinity is lower than in the ocean. Fertilised eggs and the subsequent stages of embryonic development are highly sensitive to changes in the environment and the presence of pollutants, which adversely affect the embryonic development, hatching and survival of the larvae [11].

The study is aimed to determine the toxicity of two types of drilling fluid, WBF 1 and WBF 2, at concentrations of 0.025, 0.05, 0.1, 0.5 and 1 mg/L to fertilised eggs and prelarvae of the Russian sturgeon *Acipenser gueldenstaedtii*.

### Material and methods

Fertilised Russian sturgeon eggs at stages 31–35 (with clearly distinguishable embryos and eye spots) were obtained at the Temryuk Fish Farm in May 2021. The eggs were placed in glass containers (10 fertilised eggs in each, at a ratio of one egg per 15 mL of the appropriate medium) and incubated at an ambient temperature of 16.3 to 18.0°C throughout the period of embryogenesis. The water was changed once every two days. All experiments were carried out in triplicate <sup>2)</sup> over a period of 5 days.

Natural fresh water from the Kuban River, which had undergone special water treatment at a fish farm, was used as the control and background medium in the experiments. Artificial seawater was prepared using the same freshwater base, with the addition of sea salt at a concentration of 5‰, which corresponds to the average salinity of the Sea of Azov, where sturgeon are found. Thus, the experiment included two control groups: freshwater (Control 1) and 5‰-saline water (Control 2).

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<sup>2)</sup> 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 Federal Agency for Fishery dated May 26, 2025, No. 296 (in Russian).

Two water-based drilling fluids were used:

- WBF 1 is a clear liquid with a boiling point of over 100°C, a pH of 3.1–3.3 and a relative density of 1.4 g/mL. It is water-soluble, stable under normal conditions, and is used in the oil and gas industry as a biocide containing ammonium salts of nitrilotriacetic acid;

- WBF 2 is a clear liquid with an ammonia odour, containing bis[tetrakis(hydroxymethyl)phosphonium] sulphate. Its boiling point is 100°C, pH is 7.5–9.9 and relative density is 1.15 g/mL.

The concentrations of the drilling fluids were 0.025, 0.05, 0.1, 0.5 and 1 mg/L.

During the experiment, the percentage of live embryos at the end of embryogenesis, the hatching rate of prelarvae and their survival rate were recorded.

The results were analysed statistically: the mean and standard error of the mean ( $M \pm m$ ) were calculated. The survival index was defined as the ratio of the number of live embryos and prelarvae in the experimental groups to the control values. Statistical significance of differences was assessed using the Mann–Whitney U test at  $p < 0.05$ . To determine the relationship between drilling fluid concentration and the survival rates of embryos and prelarvae, the CURUEFIT computer programme (version 2.10-L) was used.

## Results

Incubation of embryos exposed to two drilling fluids for 5 days showed varying results. No statistically significant differences were found between the survival rates of sturgeon embryos in fresh water and in salt water (5%). No differences were found between the survival rates of embryos in the control group in fresh water and those exposed to WBF 1 at concentrations of 0.1–0.5 mg/L; while a statistically significant ( $p < 0.01$ ) reduction in this parameter was observed at a concentration of 1 mg/L (Table 1). In salt water, significant differences were observed even at a toxicant concentration of 0.025 mg/L.

A moderate negative correlation was found between the concentration of the WBF 1 toxicant and the survival of fish embryos in fresh and salt water ( $y = 15.5 - 17.4x$ ,  $R^2 = 0.37$ ). The survival index of fish embryos at various concentrations of WBF 1 relative to the control in fresh and salt water showed a similar trend: differences were insignificant in the two control groups, whilst the indices tended to decrease as the concentration of the toxicant increased (Fig. 1, *a*).

WBF 2 had no significant effect on the survival of sturgeon embryos (Table 1); the survival index varied only slightly (Fig. 1, *b*). No correlations were found between the concentrations of the WBF 2 drilling fluid and the embryo survival.

In both control groups, the prelarvae hatched on the first day of incubation. At WBF 1 concentrations ranging from 0.025 to 0.5 mg/L, the prelarvae only began to hatch on the second day (Fig. 2). At a concentration of 1 mg/L, no hatching occurred. At concentrations of 0.025 and 0.05 mg/L, hatching continued on the third day, but ceased as the concentration increased. The number of hatched prelarvae in all experimental groups was lower than in the control groups. The onset of hatching of prelarvae from eggs exposed to WBF 2 occurred simultaneously with the control group.

Table 1. The influence of drilling fluids on the embryos survival rate ( $n = 30$  embryos for each group)

| Experiment conditions | Embryos survival percentage ( $M \pm m$ ) |                 |
|-----------------------|-------------------------------------------|-----------------|
|                       | WBF 1                                     | WBF 2           |
| Control 1             | $26.7 \pm 3.4$                            | $26.7 \pm 5.4$  |
| Control 2             | $33.3 \pm 2.7$                            | $33.3 \pm 2.7$  |
| Concentration, mg/L   |                                           |                 |
| 0.025                 | $10.0 \pm 0.0 *$                          | $23.3 \pm 7.2$  |
| 0.05                  | $10.0 \pm 0.0 *$                          | $23.3 \pm 10.9$ |
| 0.1                   | $6.7 \pm 2.7 *$                           | $20.3 \pm 7.9$  |
| 0.5                   | $6.7 \pm 2.4 *$                           | $20.3 \pm 6.9$  |
| 1.0                   | $0 \pm 0 **$                              | $23.3 \pm 10.9$ |

\* Significant difference relative to control in fresh water ( $p \leq 0.01$ ).

\*\* Significant difference relative to control in fresh water ( $p \leq 0.01$ ) and in 5‰ saline water ( $p \leq 0.01$ ).

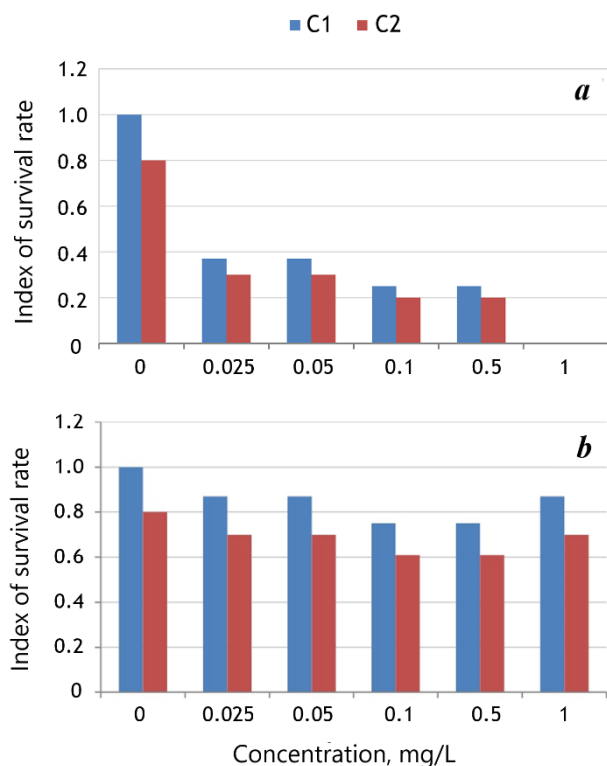


Fig. 1. Index of survival rate of fish embryos relative to control in fresh water (C1) and in 5‰ saline water (C2) with drilling fluid WBF 1 (a) and WBF 2 (b)

Table 2. Effect of drilling fluids on survival rate of sturgeon prelarvae ( $n = 30$  embryos for each group)

| Experiment conditions | Prelarvae survival percentage ( $M \pm m$ ) |                 |
|-----------------------|---------------------------------------------|-----------------|
|                       | WBF 1                                       | WBF 2           |
| Control 1             | $75.0 \pm 11.8$                             | $75.0 \pm 11.8$ |
| Control 2             | $66.7 \pm 6.8$                              | $66.7 \pm 6.8$  |
| Concentration, mg/L   |                                             |                 |
| 0.025                 | $66.7 \pm 0.5$                              | $58.3 \pm 6.8$  |
| 0.05                  | $66.7 \pm 7.7$                              | $66.7 \pm 3.7$  |
| 0.1                   | $25.0 \pm 17.7^*$                           | $66.3 \pm 12.8$ |
| 0.5                   | $20.0 \pm 16.3^*$                           | $63.5 \pm 4.6$  |
| 1.0                   | $0 \pm 0^{**}$                              | $66.7 \pm 13.6$ |

\* Significant difference relatively to control in fresh water ( $p \leq 0.01$ ) and in 5 % saline water ( $p \leq 0.01$ ).

\*\* Significant difference relatively to control in fresh water ( $p \leq 0.01$ ).

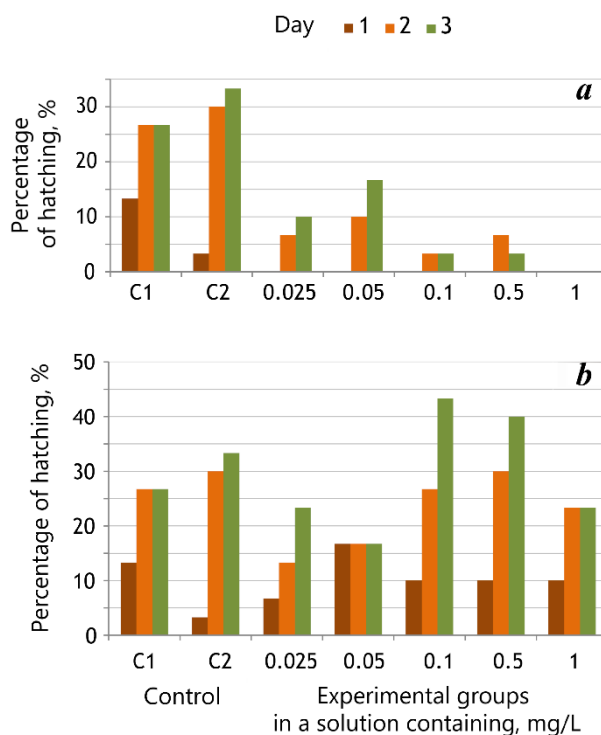


Fig. 2. The dynamics of the embryos hatching exposed in the drilling fluids *WBF* 1 (a) and *WBF* 2 (b) in the control groups (C1 – in fresh water; C2 – in 5% saline water) and experimental groups at concentrations of 0.025–1 mg/L on days 1, 2 and 3 of hatching

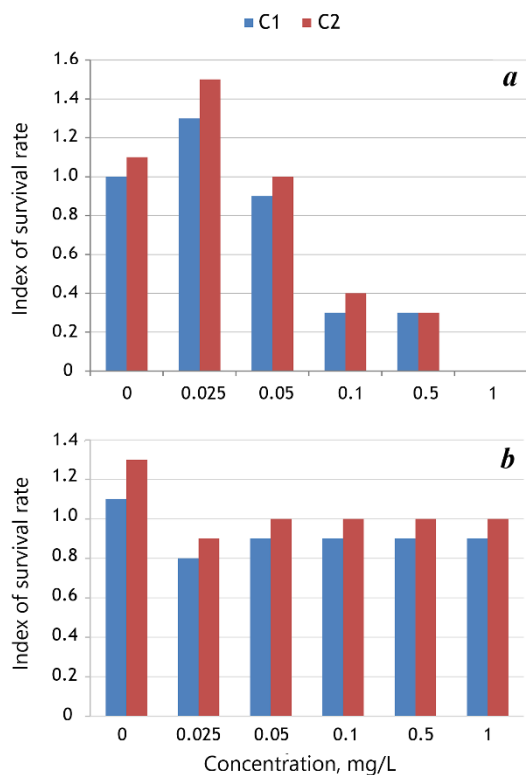


Fig. 3. Index of fish prelarvae survival relative to control in fresh water (C1) and in 5‰ saline water (C2) with drilling fluid *WBF 1* (a) and *WBF 2* (b)

Maximum hatching was recorded on the third day at a drilling fluid concentration of 0.1–0.5 mg/L. The concentration of the toxicant *WBF 2* that did not affect the dynamics of prelarvae hatching from eggs was 0.05 mg/L.

The survival of sturgeon prelarvae exposed to drilling fluids at various concentrations is presented in Table 2. Statistically significant differences in the survival of prelarvae between the experimental and control groups were observed when *WBF 1* was used at concentrations of 0.1–0.5 mg/L, whereas at a concentration of 1 mg/L the prelarvae died. A strong positive correlation was established between the concentration of the toxicant and the mortality of the prelarvae ( $y = 1.1 - 0.01x$ ,  $R^2 = 0.87$ ). No differences were found in the survival of the prelarvae between the control and experimental groups exposed to *WBF 2*.

The survival indices of fish prelarvae at the tested concentrations of *WBF 1* in fresh and salt water differed only slightly in the two control groups, while in the experimental groups they showed a downward trend as the toxicant concentration increased to 0.05 mg/L and above (Fig. 3, a). The survival index of prelarvae exposed to a medium containing *WBF 2* varied only slightly (Fig. 3, b).

### Discussion of the study results

The results of a study into the effect of two water-based drilling fluids on the survival of sturgeon embryos and prelarvae, and their hatching, showed that *WBF 1* is more toxic than *WBF 2*. Anadromous fish, to which sturgeon belong, reproduce in freshwater bodies and return to the sea for further growth and development. They are of particular interest for ecotoxicological studies, as they allow

the effects of toxicants on the same fish species to be compared in both freshwater and saltwater [12]. As the spawning grounds of the Russian sturgeon are located in the lower reaches of rivers, wave action and wind-induced surges can cause changes in salinity in the spawning areas and affect survival rates, hatching of prelarvae from the eggs and their further development.

Furthermore, variations of sea level resulting from global climate changes may alter the ecological conditions in river estuaries and affect the development of marine organisms, including sturgeon [13, 14]. Toxicants can rapidly travel from well-drilling sites downstream along rivers, posing a significant threat to the development of fish eggs and larvae and to their reproduction [15]. Thus, we analysed two control groups of sturgeon embryos: one in fresh water and the other in 5‰-salt water.

The survival rate of sturgeon embryos exposed to WBF 1 solutions at various concentrations differed significantly from that of the control. At a toxicant concentration of 1 mg/L, the embryos died in both fresh and salt water. In salt water, statistically significant differences from the control were observed even at a toxicant concentration of 0.025 mg/L, indicating that WBF 1 is more toxic in salt water. Previously, other researchers had noted that salt water had a negative effect on the early development of chum salmon eggs [14]. Thus, in fresh water, WBF 1 at a concentration of 0.5 mg/L had no effect on embryo survival, whereas in salt water the threshold concentration fell to 0.025 mg/L. For WBF 2, no differences were observed between the experimental and control groups.

Our results are consistent with those of other authors, who showed that exposure to a medium containing 2.5% XP-07 drilling fluid caused degeneration (atresia) of maturing oocytes in the gonads of *Tilapia guineensis*, leading to their complete disappearance and subsequent disruption of the fish's reproductive process [16]. In study [17], the toxicity of oil-based drilling mud (OBDM), which contains heavy metals, was investigated using zebrafish embryos. The embryo mortality, heart rate and larval hatching rate were measured daily over a 96-hour period. The 96-hour lethal concentration of OBDM at which 50% of the test organisms died ( $LC_{50}$ ) was 0.005 mg/mL (5 ppm).

As the concentration of OBDM increased, the hatching rate of larvae and the heart rate of embryos in the experimental group decreased. The results indicated the high toxicity of OBDM and its teratogenic effect on fish embryos, which was concentration-dependent [17]. Thus, fish embryos and the early developmental stages of various aquatic organisms provide a suitable and adequate model for assessing the toxicity of drilling fluids [18–21].

Another informative test used to characterise the toxicity of the drilling fluids under study was the hatching rate of prelarvae from eggs. In both control groups, hatching occurred on the first day, while in the experimental groups, exposed to WBF 1 at concentrations of 0.025–0.5 mg/L, hatching only took place on the second day. Furthermore, the number of hatched larvae was lower than in the control group, and at a concentration of 1 mg/L, no hatching occurred.

WBF 2 had no effect on this process: in both the experimental and control groups, hatching occurred simultaneously at all concentrations under study.

Incubation of Atlantic cod embryos and early larval stages in solutions of formation water (FW) and drilling waste discharges also revealed no effect on larval survival or hatching. However, at minimal concentrations of the toxicant in cod eggs, abnormalities were detected in the cytoskeletal and signalling proteins that regulate muscle development, the function of the retinal rods, cellular signalling and the tissue integrity of juveniles, all of which are essential for swimming and escaping predators. After hatching, maldevelopment was observed in the majority of larvae: due to jaw malformations, fish kept in a 1% FW solution were unable to feed and died of starvation. Furthermore, when incubated in FW at this concentration, abnormalities in the normal pigmentation of the fish larvae were noted. No adverse effects were seen following exposure to 0.1 and 0.01% FW [22].

The survival rate of prelarvae decreased when incubated in a solution containing 0.1–0.5 mg/L of WBF 1, whereas that of the fish, exposed to the tested concentrations of WBF 2, did not change significantly and did not differ from the control. Thus, the studied drilling fluids have varying effects on the early stages of sturgeon ontogenesis, which is consistent with the findings of other authors [22]. It is worth noting the positive effect of water-based drilling mud (WBM) waste at concentrations of 1–10 mg/L on the feeding efficiency, growth and survival of cod larvae after 14 days of exposure, which, as suggested, was caused by particles of a certain size that stimulated feeding activity [23].

Individual components of drilling fluids had a negative impact on fish, with their toxicity differing from that of the mixture as a whole. This may be due to both synergistic and antagonistic interactions between the components [24]. Benthic fish and invertebrates, which come into direct contact with toxicants, suffer most from xenobiotics entering the aquatic environment [25]. Experiments conducted on *Tilapia mossambica*, *Mugil persia* and the benthic mollusc *Boleophthalmus boddarti* showed that water-insoluble components have a lesser effect on these organisms than water-soluble drilling fluids [24].

The adverse effects of drilling fluids entering the water were observed in the open sea, where, even at a distance of 5 km from the oil platform, significant damage was caused to benthic organisms, mainly bivalves, with the most severe damage being detected at a distance of 0.5–1 km from the oil well [23]. Studies on fish (haddock and herring) from wild populations in areas of intensive oil production have shown significant induction of the body's defence systems, increased activity of cytochrome P-450 family enzymes in the liver, damage to and alterations in DNA and fatty acid composition, indicating a complex negative impact of oil and associated components used in oil fields during well drilling [26].

The main risk stems from the large volumes, high concentrations and discharges of water-soluble drilling fluids. However, the rapid migration of these fluids over long distances and the sedimentation of solid components at a depth of 80 m may mitigate the anticipated harm. An impact of these substances on benthic filter-feeders has been observed, but no adverse effects on the epibenthic fauna and fish near the mesotrophic reef have been identified [27].

The toxic effects of drilling fluids on aquatic ecosystems can occur via three mechanisms [28]: a) changes in the physical and chemical properties of water resulting from the release of drilling fluids into the marine environment; b) the formation of a film on the water's surface that impedes normal gas exchange, creating hypoxic and anoxic conditions leading to the death of aquatic organisms; c) the formation of anoxic zones due to the decomposition of organic components by microbial consortia [29]. Consequently, deterioration in habitat conditions, the accumulation of solid particles on the surface of the egg shell and delayed hatching, the direct toxic effects of toxicants (particularly heavy metals present in the drilling fluid) as well as the development of oxidative stress create extremely unfavourable conditions for the viability of fish eggs and embryos [30]. We have also observed the negative consequences of drilling fluids entering the marine environment for members of the benthic community in the shelf zone, namely *zostera* and amphipods [31].

Therefore, the main objective of analysing the toxicity of drilling fluids during early ontogenetic development of aquatic organisms is to assess risks to these organisms and human health, evaluate water quality and develop criteria for establishing maximum permissible concentrations of toxicants.

## Conclusion

Sturgeon embryos and prelarvae proved to be appropriate models for assessing the toxicity of drilling fluids. The response of the tested developmental stages of sturgeon to drilling fluids depended on the duration of exposure, concentration and type of toxicant. The most sensitive tests were the sturgeon embryo survival and the hatching dynamics of prelarvae from eggs. There was no difference in embryo survival between the control groups in fresh water and those exposed to a medium containing WBF 1 at concentrations of 0.1–0.5 mg/L; however, at a concentration of 1 mg/L, all embryos died.

In salt water at a WBF 1 concentration of 0.025 mg/L and above, a reduction in survival of 87% was observed ( $p < 0.01$ ). WBF 2 had no effect on the survival of sturgeon embryos. In both control groups, the larvae hatched on the first day, but the embryos exposed to a medium containing WBF 1 at concentrations of 0.025–0.5 mg/L hatched only on the second day. The number of prelarvae in the medium containing all tested concentrations was lower than in the control. At a concentration of 1 mg/L, the prelarvae did not hatch. Statistically significant differences in prelarvae survival between the experimental groups and the controls were observed at a WBF 1 concentration of 1 mg/L.

The toxicity test results presented here for drilling fluids at early life stages of sturgeon may be of practical value for assessing the consequences of climatic disasters and storm events, when seawater containing drilling fluids can enter rivers at sturgeon spawning grounds and potentially harm this species.

Fish embryos and larvae can be used as test organisms in diagnostic tests. The results of this study will be applied in the development of methods for assessing the toxicity of drilling fluids, as well as in the creation of environmentally safe drilling fluids and new technologies. It should be noted that, in order to reach a definitive conclusion regarding the toxicity of drilling fluids, further studies are required on other taxonomic groups, in particular planktonic organisms, aquatic vegetation and benthic molluscs and crustaceans.

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#### *About the authors:*

**Irina I. Rudneva**, Leading Researcher, Marine Hydrophysical Institute of RAS (2 Kapitan-skaya St., Sevastopol, 299011, Russia), DSc (Biol.), Professor, **ORCID ID: 0000-0002-9623-9467**, **Scopus Author ID: 9266541700**, **ResearcherID: L-3758-2016**, [svg-41@mail.ru](mailto:svg-41@mail.ru)

**Valentin G. Shaida**, Researcher Engineer, Company “EcoService-A” (17A Verkhnyaya Krasnoselskaya Str., Bldg. 1B, Of. 8, Moscow, 107140, Russia)

**Maria V. Medyankina**, Associate Professor, Ecology and Nature Use Chair of Department of Biotechnologies and Fisheries, Moscow State University of Technology and Management K. G. Razumovsky (First Cossack University) (14 Shabolovskaya Str., Bldg. 9, Moscow, 119049, Russia), PhD (Biol.), **ORCID ID: 0000-0002-9195-0399**, [medyankina@mail.ru](mailto:medyankina@mail.ru)

#### *Contribution of the authors:*

**Irina I. Rudneva** – concept development, task statement

**Valentin G. Shaida** – development of methods and carrying out the experimental studies

**Maria V. Medyankina** – processing and description of the study results

*All the authors have read and approved the final manuscript.*

Original paper

## Organic Matter–Destructing Bacteria in Bottom Sediments of the Southern Kamchatka: Distribution Patterns under Variable Geochemical Conditions

G. V. Frolkin<sup>1</sup>\*, K. M. Zaripova<sup>2</sup>, E. A. Tikhonova<sup>2, 3</sup>,  
N. V. Burdiyan<sup>2</sup>, Yu. V. Doroshenko<sup>2</sup>, K. A. Selivanova<sup>4</sup>

<sup>1</sup> Research Center for Freshwater and Brackish-Water Hydrobiology – Branch of the A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia

<sup>2</sup> A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russia

<sup>3</sup> Far Eastern Federal University, Vladivostok, Russia

<sup>4</sup> Herzen State Pedagogical University of Russia, Saint Petersburg, Russia

\* e-mail: egor.frolkin@ibss-ras.ru

### Abstract

The paper aims to assess the organic pollution level of the coastal waters of the southern part of the Kamchatka Peninsula based on microbiological and physical and chemical parameters of bottom sediments. During cruise 25/2 aboard PV *Professor Multanovsky* (July–August 2025), samples of surface-layer bottom sediments were collected at 16 stations in the north-western Pacific Ocean and the Sea of Okhotsk. The grain size distribution, organic matter content (determined by the loss-on-ignition method), physical and chemical parameters of the bottom water (temperature, salinity, pH, redox potential), as well as the abundance of heterotrophic and hydrocarbon-oxidising bacteria (determined by the limiting dilution method) were determined. The study revealed that the organic matter content in silty soils (5.0–14.7%) was significantly higher than in sandy-gravelly soils (less than 2.3%); an inverse relationship was identified between this parameter and the redox potential ( $\rho = -0.72$ ;  $p < 0.01$ ). The abundance of heterotrophic bacteria ranged from  $10^2$  to  $10^7$  cells·g<sup>-1</sup>, whilst that of hydrocarbon-oxidising bacteria ranged from  $10$  to  $10^4$  cells·g<sup>-1</sup>. The highest abundance values for both groups were recorded in Avacha Bay ( $10^7$  and  $10^3$  cl·g<sup>-1</sup>, respectively) and in the recreational bays (Vilyuchenskaya, Listvennichnaya), indicating a high anthropogenic load. The minimum values ( $10^2$  and  $10$  cells·g<sup>-1</sup>) were recorded in the background area at the mouth of the Nalycheva River. A positive correlation was found between the abundance of hydrocarbon-oxidising bacteria and organic matter content ( $\rho = 0.6$ ,  $p < 0.05$ ), as well as a negative relationship was found between the abundance of both groups and the redox potential (for heterotrophic bacteria  $\rho = -0.7$ ,  $p < 0.01$ ; for hydrocarbon-oxidising bacteria  $\rho = -0.8$ ,  $p < 0.001$ ). The soil type has a statistically significant effect on the abundance of hydrocarbon-oxidising bacteria ( $p < 0.05$ ). The results confirm the effectiveness of using heterotrophic bacteria and hydrocarbon-oxidizing bacteria abundance indicators as bioindicators of organic pollution and show the self-purification potential of the studied waters.

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Doroshenko Yu. V., Selivanova K. A., 2026



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**Keywords:** bottom sediments, heterotrophic bacteria, hydrocarbon-oxidizing bacteria, coastal waters, Kamchatka Peninsula, Sea of Okhotsk

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## **Особенности распределения основных групп бактерий – деструкторов органического вещества в различных геохимических условиях донных отложений прибрежных акваторий южной части полуострова Камчатка**

**Г. В. Фролкин<sup>1</sup>\*, К. М. Зарипова<sup>2</sup>, Е. А. Тихонова<sup>2, 3</sup>,  
Н. В. Бурдиян<sup>2</sup>, Ю. В. Дорошенко<sup>2</sup>, К. А. Селиванова<sup>4</sup>**

<sup>1</sup> Научно-исследовательский центр пресноводной и солоноватоводной  
гидробиологии – филиал ФИЦ ИнБЮМ, Севастополь, Россия

<sup>2</sup> ФГБУН ФИЦ «Институт биологии южных морей имени А.О. Ковалевского РАН»,  
Севастополь, Россия

<sup>3</sup> Дальневосточный федеральный университет, Владивосток, Россия

<sup>4</sup> Российский государственный педагогический университет имени А. И. Герцена,  
Санкт-Петербург, Россия

\* e-mail: egor.frolkin@ibss-ras.ru

### **Аннотация**

Цель исследования – оценить уровень органического загрязнения прибрежных акваторий южной части полуострова Камчатка по микробиологическим и физико-химическим показателям донных отложений. В ходе экспедиции рейса 25/2 ПС «Про-

фессор Мультановский» (июль – август 2025 г.) на 16 станциях в северо-западной части Тихого океана и Охотском море отобраны пробы поверхностных донных отложений. Определены гранулометрический состав, содержание органического вещества методом потерь при прокаливании, физико-химические параметры придонной воды (температура, соленость, pH, окислительно-восстановительный потенциал), а также численность гетеротрофных и углеводородоокисляющих бактерий методом предельных разведений. Установлено, что содержание органического вещества в илистых грунтах (5.0–14.7 %) значительно выше, чем в песчано-гравийных (менее 2.3 %), выявлена обратная зависимость между этим показателем и окислительно-восстановительным потенциалом ( $\rho = -0.72$ ;  $p < 0.01$ ). Численность гетеротрофных бактерий варьировала от  $10^2$  до  $10^7$  кл·г<sup>-1</sup>, углеводородоокисляющих – от 10 до  $10^4$  кл·г<sup>-1</sup>. Максимальные значения численности обеих групп зафиксированы в Авачинской губе ( $10^7$  и  $10^3$  кл·г<sup>-1</sup> соответственно) и рекреационных бухтах (Вилученская, Лиственничная), что указывает на высокую антропогенную нагрузку. Минимальные значения ( $10^2$  и  $10$  кл·г<sup>-1</sup>) отмечены в фоновом районе устья р. Налычева. Выявлена положительная корреляция между численностью углеводородоокисляющих бактерий и содержанием органического вещества ( $\rho = 0.6$ ,  $p < 0.05$ ), а также отрицательная связь численности обеих групп с окислительно-восстановительным потенциалом (для гетеротрофных бактерий  $\rho = -0.7$ ,  $p < 0.01$ , углеводородоокисляющих –  $\rho = -0.8$ ,  $p < 0.001$ ). Тип грунта статистически влияет на численность углеводородоокисляющих бактерий ( $p < 0.05$ ). Полученные данные подтверждают эффективность использования численности гетеротрофных и углеводородоокисляющих бактерий в качестве биоиндикаторов органического загрязнения и отражают потенциал самоочищения исследованных акваторий.

**Ключевые слова:** донные отложения, гетеротрофные бактерии, углеводородоокисляющие бактерии, прибрежные акватории, полуостров Камчатка, Охотское море

**Благодарности:** отбор проб в ходе научного рейса проводился в рамках Всероссийской научно-образовательной программы «Плавучий университет» по теме «Подготовка молодого кадрового резерва в области морских наук по научно-образовательной программе „Плавучий университет“ на основе комплексных исследований экосистемы дальневосточных морей России» (проекты № 075-03-2025-662/8 и № 075-03-2025-421/5). Подготовка питательных сред для определения численности индикаторных групп бактерий, пробоподготовка донных отложений, определение физико-химических характеристик донных отложений выполнены в рамках государственного задания ФИЦ ИнБЮМ по теме «Изучение биогеохимических закономерностей радиоэкологических и хемоэкологических процессов в экосистемах водоемов Азово-Черноморского бассейна в сравнении с другими акваториями Мирового океана и отдельными водными экосистемами их водосборных бассейнов для обеспечения устойчивого развития на южных морях России» (№ гос. регистрации 124030100127-7). Определение содержания органического вещества в донных отложениях и анализ особенностей распределения индикаторных групп бактерий выполнены при поддержке Минобрнауки России в рамках направления «Экология и биоразнообразие Камчатки» Межведомственной программы исследований Камчатского полуострова и сопредельных акваторий 2024–2026 гг., проект № FZNS-2024-0037 «Комплексный экологический мониторинг прибрежных морских и наземных экосистем Камчатки».

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## Introduction

Coastal marine ecosystems play a key role in the global biogeochemical cycle. Coastal sediments act as the main reservoir for organic pollutants, including petroleum products and other hydrocarbon compounds from human activities (port operations, shipping, recreation) and natural processes (river discharge, natural oil seeps) [1–3]. Under slow water exchange, bottom sediments become a long-term store for pollutants, underscoring their particular ecological significance as indicators of anthropogenic pressure on marine ecosystems.

Assessing the condition of bottom sediments requires a comprehensive approach combining physico-chemical and microbiological analytical methods. The physico-chemical parameters of the bottom layer (temperature, salinity, pH, redox potential) shape the habitat conditions for microbial communities and determine the direction of biogeochemical transformations of organic matter (OM). In turn, microbiological indicators—the abundance of heterotrophic bacteria (HB) and hydrocarbon-oxidising bacteria (HOB)—can serve as bioindicators of organic pollution and reflect the ecosystem's self-purification potential [4–7]. In polluted water bodies, an increase in the abundance of certain bacterial groups is often observed before any detectable change in the chemical parameters of the water. Thus, microbiological methods can be significantly more sensitive than sanitary-chemical ones [8–10].

Despite the available data on the state of Kamchatka's coastal waters, information on the quantitative composition and distribution of functional groups of degrading bacteria in bottom sediments remains scarce [11], particularly when comparing background and anthropogenically impacted areas spatially. Since some of the studied sampling stations are located at a mooring site where fuel is constantly being transported and bunkered, oil was selected as the model pollutant and the sole substrate for degrading microorganisms [12, 13].

This study is the first to comprehensively investigate the spatial distribution of HB and HOB in the bottom sediments of coastal waters of various types in Kamchatka, including port areas (Avacha Bay), recreational bays (Vilyuchinskaya, Listvennichnaya) and background sites (the mouth of the Nalychev River), while considering the grain size distribution of the sediments, organic matter content and levels of key physico-chemical parameters of the bottom environment. This approach aims to assess the level of organic pollution and identify the factors determining the spatial heterogeneity of microbial communities.

The aim of this study is to study the microbiological and physico-chemical characteristics of bottom sediments in the coastal waters of the north-western Pacific Ocean and the Sea of Okhotsk in order to assess the level of organic pollution.

## Materials and methods

The work was carried out in the summer of 2025 during a cruise of passenger vessel *Professor Multanovsky* in the north-western Pacific Ocean and the Sea of Okhotsk (Fig. 1).

A total of 16 stations were surveyed. Stations 1–3 were located within Avacha Bay; station 4 was at the mouths of the Vakhil and Ostrovnoy Rivers; station 16 was at the mouth of the Nalychev River, where “red tides” were recorded in 2020 [14, 15]; Station 17 was near Khalaktyrsky Beach; Station 40 was in the strait connecting Avacha Bay with the ocean; station 41 was in the Sarannaya Bay; station V1 was in the waters of the Vilyuchinskaya Bay, into which the Vilyucha and Zhirovaya rivers flow; stations R1 and 48 were in Russkaya Bay; station L2 was in Listvennichnaya Bay, into which the river of the same name flows; station 91 was opposite the villages of Ust-Bolsherechsk and Oktyabrsky; station 115 was near the mouth of the Ozeraya River by the village of Ozerovsky; station 129 was at Cape Kambalny, into which the river of the same name flows; station 142 was in Maria Bay, where the mouths of the Krivoy and Lysaya Rivers are situated.

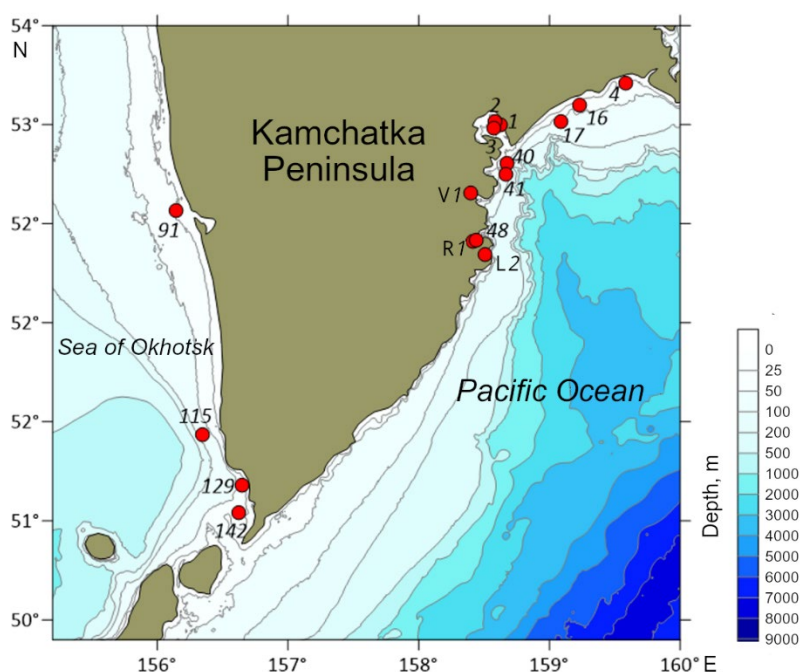


Fig. 1. Map of the sediment sampling stations (red dots) in the northwestern Pacific Ocean and the Sea of Okhotsk (2025)

The stations at the river mouths were selected because of the organic matter transport by river waters. At these sites, salinity decreases slightly, which may influence the spatial distribution of the microbiological community. By contrast, bays have limited water exchange, leading to a sharp increase in OM concentration; they also often serve as mooring sites for vessels and form part of tourist routes.

Samples of surface bottom sediments (top layer up to 5 cm) were collected using a box corer. Immediately after sampling, the physical properties of the bottom sediments were assessed visually and the type of seabed was determined <sup>1)</sup>. The temperature, salinity of the bottom water layer and depth at the sampling stations were determined using a CTD probe. The pH and redox potential (Eh) were measured using a Nitron-pH pH-metre with a temperature compensator. For analysis, the upper oxidised layer of the bottom sediments was collected.

The total OM content in bottom sediment samples was determined by loss on ignition (LOI) according to GOST (State Standard) 23740-2016 <sup>2)</sup>. Sample preparation involved grinding air-dried samples and sieving them through a 0.2-mm mesh sieve. A sub-sample weighing 3–5 g was dried in duplicate at  $(105 \pm 2)^{\circ}\text{C}$  to constant weight and then ignited in a muffle furnace. Ignition began with a cold furnace: the temperature was gradually raised to  $(525 \pm 25)^{\circ}\text{C}$ , and the samples were held at this temperature for 3 h until constant weight was reached. The LOI was calculated from the difference in mass. The final result was the arithmetic mean of two replicate determinations, with the acceptable discrepancy between them being less 10%.

The abundance of HB and HOB in bottom sediment samples was determined by limiting dilution using liquid nutrient media <sup>3)</sup>. A peptone medium was used for HB, and the Dianova–Voroshilova medium was used for HOB. Sterile oil was added to each tube after inoculation at a concentration of 1% as the sole source of carbon and energy. The samples were processed within 2 h of collection.

Initial data processing and calculation of correlation coefficients were performed using Microsoft Excel. Statistical analysis was performed using R. To assess the influence of environmental factors on bacterial abundance in bottom sediments, a correlation analysis was conducted. The primary method for assessing bacterial abundance data was Spearman's nonparametric correlation coefficient ( $\rho$ ).

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<sup>1)</sup> Oradovsky, S.G., ed., 1979. [*Methodical Guidance no. 43 on the Determination of Pollutants in Marine Sediment*]. Moscow: Gidrometeoizdat, 36 p. (in Russian).

<sup>2)</sup> GOST, 2016. *GOST 23740-2016. Soils. Methods of Laboratory Determination of Organic Composition*. Moscow: Standartinform. (Interstate Standard). Introduced 1 July 2017.

<sup>3)</sup> Netrusov, A.I., ed., 2005. [*Practical Course on Microbiology*]. Moscow: Akademiya, 608 p. (in Russian).

Pearson's parametric correlation coefficient ( $r$ ) was additionally used to assess linear relationships between variables whose distribution satisfied the assumptions for its application [16–17]. To assess the effect of sediment type on bacterial abundance, all stations were divided into three groups based on sediment descriptions in the sampling documentation: 1) predominantly silty sediments; 2) sandy (including silty sand) ones; 3) sand-and-gravel ones. Since abundance data did not follow a normal distribution, the nonparametric Kruskal–Wallis H test was used to compare the groups; when significant differences were found, pairwise comparisons were performed with Holm–Bonferroni correction (to control the family-wise error rate in multiple comparisons). Differences were considered statistically significant at  $p < 0.05$ .

### Results and discussion

The bacterial groups under study were isolated from samples collected under a wide range of physico-chemical environmental conditions (table). At most stations, the bottom sediments consisted of sandy soils mixed with silt. In areas with limited water exchange, the bottom sediments more frequently contained

Physical and chemical properties of bottom water and sediments at sampling stations

| Station number | $t$ , °C | $S$ , PSU | Depth, m | pH  | Eh, mV |
|----------------|----------|-----------|----------|-----|--------|
| 1              | 3.0      | 29.7      | 23       | 7.5 | –192   |
| 2              | 4.0      | 27.3      | 24       | 7.5 | –385   |
| 3              | 2.6      | 31.8      | 26       | 7.6 | –199   |
| 4              | 2.5      | 29.7      | 30       | 7.2 | –35    |
| 16             | 1.2      | 32.9      | 41       | 7.7 | +197   |
| 17             | 1.2      | 33.1      | 56       | 7.6 | +192   |
| 40             | 1.4      | 33.9      | 62       | 7.5 | +169   |
| 41             | 1.3      | 33.1      | 87       | 7.8 | +104   |
| V1             | 8.5      | 27.8      | 5        | 7.2 | +53    |
| R1             | 7.8      | 28.1      | 5        | 7.8 | +129   |
| 48             | 2.7      | 32.4      | 32       | 7.4 | –219   |
| L2             | 8.7      | 28.5      | 12       | 7.5 | +61    |
| 91             | 9.9      | 29.0      | 25       | 8.2 | +228   |
| 115            | 3.4      | 33.0      | 76       | 7.6 | –30    |
| 129            | 6.6      | 32.4      | 37       | 7.5 | +338   |
| 142            | 7.1      | 32.6      | 33       | 7.8 | +284   |

a higher proportion of fine-grained material (Appendix A). The temperature of the bottom layer during the studies ranged from 1.2 to 9.9 °C. The lowest values were recorded at station 16 (the mouth of the Nalychev River) and station 17 (Khalaktyrsky Beach). The salinity of the water in the bottom layer ranged from 27.3 (in Avacha Bay) to 33.9 PSU (at the bay's outlet). The pH varied from 7.2 to 8.2. The lowest pH values were recorded in the silty sediments of Vilyuchinskaya Bay, whilst the highest ones were found in the Sea of Okhotsk near the villages of Ust-Bolsherechsk and Oktyabrsky. On average, the pH was 7.7 (close to neutral conditions), which favours the growth and development of HOB [18]. The redox potential (Eh) varied widely, ranging from –385 to +338 mV. The lowest values were recorded in the bottom sediments of Vilyuchinskaya Bay, whilst the highest were recorded opposite Cape Kambalny in the Sea of Okhotsk.

An analysis of samples from the surface layer of bottom sediments, collected at 16 stations in the coastal waters of Kamchatka, revealed high spatial variability in OM content (Fig. 2). The values varied widely from 0.6% (station 17) to 14.7% (station 48), indicating the combined influence of local factors on the accumulation and retention of OM.

One of the factors influencing the accumulation and retention of OM in bottom sediments is the grain size distribution of the sediments<sup>4), 5)</sup> [19–21]. The highest concentrations of OM (ranging from 5.0 to 14.7%) were in silty soils (stations 1–3, 48, 115). Fine-grained silt particles, with their large specific surface area, effectively

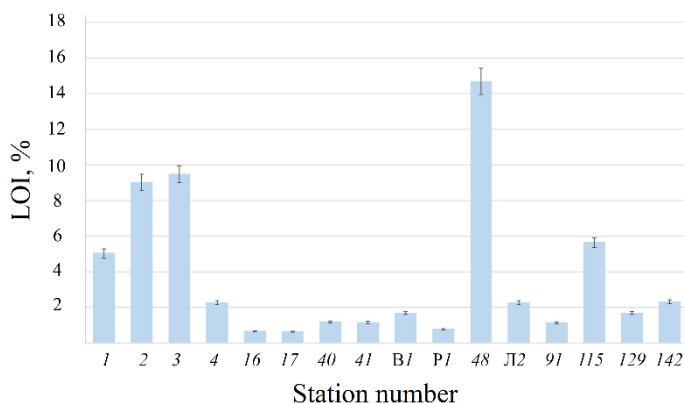


Fig. 2. Content of organic matter (LOI, %) in surface-layer bottom sediments of the coastal waters off the Kamchatka Peninsula, 2025

<sup>4)</sup> Dauvalter, V.A., 2002. [Formation Factors for the Chemical Composition of Lacustrine Sediments]. Murmansk: Izd-vo MGTU: 75 p. (in Russian).

<sup>5)</sup> Romankevich, E.A., 1977. [Geochemistry of Organic Matter in the Ocean]. Moscow: Nauka, 256 p. (in Russian).

sorb organic material and create conditions for its burial. By contrast, in sandy and gravelly sediments typical of areas with high hydrodynamic activity (stations 16, 17, R1, 91, 40, 41), the OM content did not exceed 2.3%. Coarse soil particles of this type have a low capacity to retain OM, whilst good aeration promotes its rapid oxidation. Stations with transitional soil types (silty sand, silted sand) – 4, L2, 129, 142, VI – showed intermediate LOI values (1.1–2.3%), apparently depending on the proportion of the silty fraction.

For silty facies, which are favourable for the accumulation of OM, the key parameter that comprehensively reflects the conditions for its preservation is the redox potential. In the studied sediments, a consistent inverse relationship was observed ( $r = -0.80$ ;  $p < 0.001$ ;  $\rho = -0.72$ ;  $p < 0.01$ ): all stations with the OM content above 5% (stations 1, 2, 3, 48, 115) were characterised by negative Eh values (ranging from  $-385$  to  $-30$  mV), indicating the formation of reducing (anaerobic) conditions.

This relationship was particularly pronounced at stations 2, 3 and 48, where low Eh values (down to  $-385$  mV) were accompanied by signs of hydrogen sulphide (a characteristic odour, hydrothroilite spots) and maximum LOI values (9.0–14.7%). Low redox potential values in such sediments may result from oxygen consumption during the oxidation of OM and may cause a rapid deceleration in its further degradation, as anaerobic processes (e. g. sulphate reduction) become dominant, effectively preserving the organic material. An exception to this pattern is station VI with silty soils, where, despite a soil structure favourable for OM accumulation, a relatively low LOI value (1.7%) and a positive Eh value ( $+53$  mV) were recorded. This is likely due to the shallow depth in the vicinity of this station (5 m), since wave action and the absence of stable stratification of the water column prevent the formation of reducing conditions near the seabed.

Thus, the distribution of OM in the study area is shaped by several interrelated factors. The hydrodynamic regime influences the localisation of silty (accumulative) and sandy-gravelly (transitional) facies. It is the fine-grained composition of the sediments that creates the conditions for sorption and burial of OM. An additional factor increasing the influx of OM to the seabed is anthropogenic pressure. In Avacha Bay, which is under chronic pollution due to shipping and discharge of domestic and industrial effluents, an increased amount of allochthonous OM enters the silty sediments. This leads to a higher OM content compared with background water bodies of similar grain size composition. Redox conditions play an important role in maintaining high concentrations of OM: in this case, a positive feedback mechanism is at work, since the intensive inflow and accumulation of OM (of both natural and anthropogenic origin) in silty sediments leads to active oxygen consumption by microorganisms and the formation of reducing conditions (negative Eh values

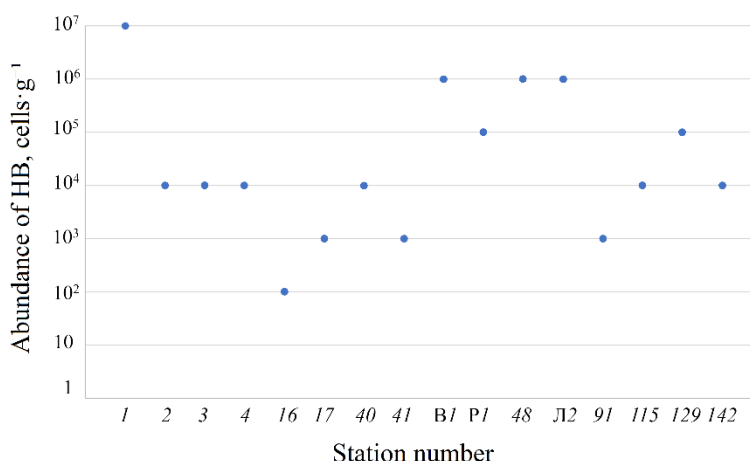


Fig. 3. Abundance (cells·g<sup>-1</sup>) of heterotrophic bacteria in the surface layer of bottom sediments at the study stations

at stations 1–3, 48, 115). The resulting anaerobic conditions, in turn, sharply decelerate the further degradation of the OM, thereby helping to preserve it.

OM destructing bacteria were detected in all samples of the bottom sediments (Fig. 3). The abundance of these bacteria ranged from 10<sup>2</sup> to 10<sup>7</sup> cells·g<sup>-1</sup>. The highest values were recorded in Avacha Bay (10<sup>7</sup> cells·g<sup>-1</sup>), as well as in Vilyuchinskaya and Listvennichnaya Bays (10<sup>6</sup> cells·g<sup>-1</sup>). Avacha Bay (station 1) is home to one of Kamchatka's largest ports, while Vilyuchinskaya and Listvennichnaya Bays (stations VI and L2, respectively) are of high recreational value. The high microorganism abundance in these areas indicates water pollution by organic compounds and the ability of microbial communities to degrade them. Furthermore, the mouths of small rivers are situated in the bays, which are potential sources of OM for the studied water bodies. The lowest values for HB abundance were recorded in the vicinity of the Nalychev River mouth (10<sup>2</sup> cells·g<sup>-1</sup>). The mouth of this river has the largest catchment area among the rivers of the Avachinskaya volcanic group and probably lies within the zone of increased turbidity of the river plume.

HOB were also detected in all samples analysed (Fig. 4), with concentrations ranging from 10 to 10<sup>4</sup> cells·g<sup>-1</sup>. At half of the stations under study, the HOB concentration was 10<sup>2</sup> cells·g<sup>-1</sup>. The lowest values were recorded at station 41 in Sarannaya Bay and at station 16 near the mouth of the Nalychev River (10 cells·g<sup>-1</sup>). High concentrations of HOB (10<sup>3</sup> cells·g<sup>-1</sup>) were recorded in Avacha Bay, Vilyuchinskaya Bay and Russkaya Bay, near the village of Ozernovsky (station 115) and Cape Marii (station 142). The highest values (10<sup>4</sup> cells·g<sup>-1</sup>) were recorded at station 48, which is situated in the area of Russkaya Bay. The high abundance of HOB in these areas may be due to high anthropogenic pressure on the bay's ecosystem as a result of recreational activities.

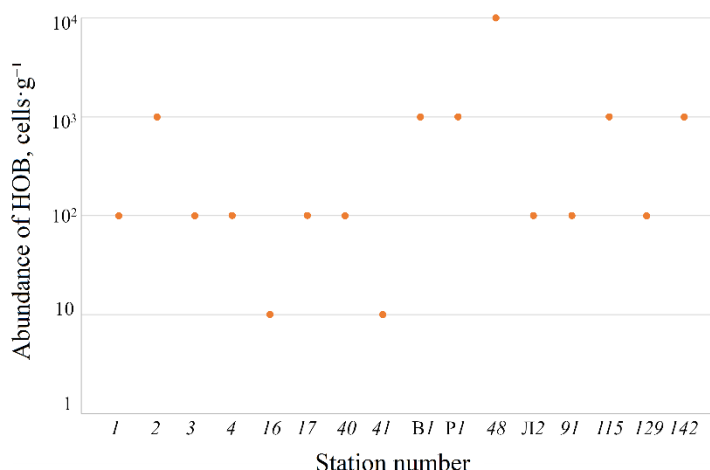


Fig. 4. Abundance (cells·g<sup>-1</sup>) of hydrocarbon-oxidizing bacteria in the surface layer of bottom sediments at the study stations

A statistically significant positive correlation was found between the total abundance of HB and HOB in bottom sediments (Spearman's rank correlation coefficient  $\rho = 0.7$ ,  $p = 0.005$ ). This relationship may indicate the combined influence of common abiotic factors on both groups, as well as possible trophic interactions or functional coupling within the microbial community. The proportion of HOB in the total HB abundance varied widely: from 0.001 to 10%. At six stations (2, 16, 17, 91, 115 and 142), this proportion was highest, reaching 10%. The average proportion of HOB across all stations was about 3.8%, while the median proportion of HOB relative to total HB abundance was 1.0%.

A statistical analysis revealed no significant relationship between bacterial abundance in bottom sediments and near-bottom water temperature. At the same time, a moderate negative correlation was found between HB abundance and near-bottom water salinity ( $\rho = -0.6$ ,  $p < 0.05$ ), as well as between HB abundance and depth ( $\rho = -0.6$ ,  $p < 0.05$ ). These relationships appear to be indirect and reflect general hydrological and trophic conditions. Lower salinity was observed at coastal shallow-water stations, which receive continental runoff that serves as a source of labile OM and nutrients, creating conditions for the development of the bacterial community [22]. For HOB, no statistically significant relationships with salinity or depth were found.

A correlation analysis revealed a significant positive correlation between the HOB abundance and OM content (Pearson's correlation coefficient  $r = 0.6$ ,  $p < 0.05$ ; Spearman's rank correlation coefficient  $\rho = 0.6$ ,  $p < 0.05$ ). No such relationship was found for HB.

Negative correlations were found between redox potential (Eh) and the abundance of both HB ( $\rho = -0.7$ ,  $p < 0.01$ ) and HOB ( $\rho = -0.8$ ,  $p < 0.001$ ). These correlations probably indirectly reflect a relationship with sediment type. Silty sediments, characterised by a high specific surface area, tend to accumulate OM and form poorly aerated reducing conditions (low Eh values). At the same time, an abundance of substrate for adhesion and the availability of OM may create favourable conditions for the development of bacterial communities. pH values within the studied range had no significant effect on the bacterial abundance.

A statistical analysis (Kruskal–Wallis H test) revealed a significant effect of sediment type on the abundance of both HB ( $H = 7.14$ ,  $p = 0.028$ ) and HOB ( $H = 8.55$ ,  $p = 0.014$ ). A pairwise comparison with Holm–Bonferroni correction showed that pronounced and significant differences occurred for HOB between silty and sandy-gravelly sediments (Mann–Whitney U test,  $p < 0.01$ ). Silty sediments were characterised by a higher abundance of this group, whereas coarse-clastic sediments had the lowest values [23, 24].

A comparison with data from 2023–2024 for the studied region reveals some general spatial patterns in the distribution of OM destructing bacteria. In both studies, the maximum abundance of functional bacterial groups (HB and HOB) was recorded in anthropogenically impacted water areas—Avacha Bay and recreational bays (Vilyuchinskaya and Listvennichnaya)—which confirms the role of these bacteria as bioindicators of organic pollution [11]. Minimum abundance values were recorded in background areas near the mouth of the Nalychev River. In bottom sediments, the bacterial abundance varied over a wider range than in the water column, reflecting the role of bottom sediments as the main accumulator of OM and microorganisms. The both studies confirm the effectiveness of using HB and HOB abundance as an indicator of the organic pollution level in the coastal waters of Kamchatka.

## Conclusions

The HB abundance in the bottom sediments varied widely: from  $10^2$  to  $10^7$  cells·g<sup>-1</sup>, while the HOB ranged from  $10$  to  $10^4$  cells·g<sup>-1</sup>. This variability reflects the influence of local factors: anthropogenic pressure, hydrodynamic and geochemical conditions.

The analysis of the abundance of the studied bacterial groups shows that the most contaminated areas, based on microbiological parameters, are Avacha, Vilyuchinskaya and Listvennichnaya Bays. This is due to increased anthropogenic pressure and the inflow of organic pollutants from rivers. The high abundance of destructing bacteria in these areas indicates both the input of organic pollutants (including hydrocarbons) and the maintenance of the ecosystem's self-purification potential.

The lowest bacterial abundances were recorded in the background area at the mouth of the Nalychev River ( $10^2$  cells·g<sup>-1</sup> for HB,  $10$  cells·g<sup>-1</sup> for HOB), which, together with the low OM content (0.68%) in the bottom sediments, may indicate minimal anthropogenic impact.

Silty soils (stations 1–3, 48, 115) accumulate OM (5.0–14.7% of LOI) and support higher bacterial counts than sandy-gravelly sediments (< 2.3% of LOI).

The correlation between the location of port areas and recreational bays and the maximum abundance of HOB confirms the role of these bacteria as bioindicators of oil pollution. The spatial correlation between the increased abundance of the studied microbial groups areas of human activity supports the use of HB and HOB abundance in bottom sediments as bioindicators of the ecological status of the coastal waters near the Kamchatka Peninsula.

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## Appendix A

Table A 1. Sediment types <sup>6)</sup> at sampling stations

| Station number | Description                                                                                                                                                     |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1              | Dark gray silt with an admixture of sand, semi-liquid, viscous                                                                                                  |
| 2              | Dark gray silt with greenish spots, soft, viscous, dark smears, strong hydrogen sulfide odor                                                                    |
| 3              | Dark gray silt with greenish spots, soft, viscous, strong hydrogen sulfide odor                                                                                 |
| 4              | Dark gray sandy silt, compact, plastic, plant remains                                                                                                           |
| 16             | Dark gray medium-grained sand with an admixture of silt, soft, loose, dominance of fine- and medium-grained gravel, occasional fine- and coarse-grained pebbles |
| 17             | Dark gray medium-grained sand with an admixture of silt, soft, loose, shell inclusions, dominance of fine- to medium-grained gravel                             |
| 40             | Dark gray silty sand, compact, plastic to loose, with an admixture of shells, with occasional fine-grained gravel inclusions                                    |

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<sup>6)</sup> Oradovsky, S.G., ed., 1979. [Methodical Guidance no. 43 on the Determination of Pollutants in Marine Sediment]. Moscow: Gidrometeoizdat, 36 p. (in Russian).

Table A1 (concluded)

| Station number | Description                                                                                                  |
|----------------|--------------------------------------------------------------------------------------------------------------|
| 41             | Dark grayish-brown silt, compact, plastic, shell detritus inclusions                                         |
| B1             | Dark gray fine- to medium-grained sand                                                                       |
| P1             | Dark gray heterogeneous silt with light spots, semi-liquid, very viscous, strong hydrogen sulfide odor       |
| 48             | Dark gray silty sand, soft, loose, with decomposition odor                                                   |
| J12            | Dark gray medium- to fine-grained gravel, soft, loose, algae, occasional benthic organisms, shell inclusions |
| 91             | Dark gray silt, soft, viscous                                                                                |
| 115            | Dark gray silty sand, soft, loose, shell detritus inclusions                                                 |
| 129            | Dark gray silty sand, soft, plastic, shell detritus inclusions                                               |
| 142            | Dark grayish-brown silt, compact, plastic, shell detritus inclusions                                         |

*About the authors:*

**Georgii V. Frolkin**, Junior Researcher, Research Center for Freshwater and Saltwater Hydrobiology, Branch of IBSS, (2 Nakhimov Ave, Sevastopol, 299011, Russia), **ORCID ID: 0009-0002-2260-5230**, **ResearcherID: NIU-5117-2025**, [egor.frolkin@ibss-ras.ru](mailto:egor.frolkin@ibss-ras.ru)

**Ksenia M. Zaripova**, Junior Research Associate, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimova Ave., Sevastopol, 299011, Russia), **ORCID ID: 0009-0001-1160-4139**, **Scopus Author ID: 59173430600**, **ResearcherID: GWV-4575-2022**, [zaripova\\_km@ibss-ras.ru](mailto:zaripova_km@ibss-ras.ru)

**Elena A. Tikhonova**, Leading Researcher, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimov Ave., Sevastopol, 299011, Russia); Far Eastern Federal University (10 vil. of Ayaks, Russky Island, Vladivostok, Primorsky Krai, Russia), PhD (Biol.), **ORCID ID: 0000-0002-9137-087X**, **Scopus Author ID: 57208495804**, **ResearcherID: X-8524-2019**, [tihonoval@mail.ru](mailto:tihonoval@mail.ru)

**Nataliya V. Burdiyan**, Senior Researcher, A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimova Ave., Sevastopol, 299011, Russia), PhD (Biol.), **ORCID ID: 0000-0001-8030-1556**, **Scopus Author ID: 57208497483**, **ResearcherID: AAD-1704-2022**, [burdiyan@mail.ru](mailto:burdiyan@mail.ru)

**Yuliya V. Doroshenko**, Researcher, A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS (2 Nakhimova Ave., Sevastopol, 299011, Russia), PhD (Biol.), **ORCID ID: 0000-0003-0498-3369**; **Scopus Author ID: 57211643141**, **ResearcherID: AAD-1706-2022**, [julia\\_doroshenko@mail.ru](mailto:julia_doroshenko@mail.ru)

**Katerina A. Selivanova**, Graduate Student, Herzen State Pedagogical University of Russia (48 Moyka River Embankment, Saint Petersburg, 191186, Russia), [katarina1107@yandex.ru](mailto:katarina1107@yandex.ru)

*Contribution of the authors:*

**Georgii V. Frolkin** – writing and formatting the article, justifying the study and preparing the literature review, sampling, microbiological analyses to determine the abundance of indicator bacterial groups, processing and describing the study results, analysing and discussing the results

**Ksenia M. Zaripova** – concept development, writing and formatting the article, justifying the study and preparing the literature review, creating graphical materials, processing and describing the study results, analysing and discussing the results

**Elena A. Tikhonova** – concept development, setting study aims and objectives, discussing the results, justifying the study, sampling

**Nataliya V. Burdiyan** – description of the methodology, discussion of the results, preparation of culture media

**Yuliya V. Doroshenko** – description of the methodology, discussion of the results, preparation of culture media

**Katerina A. Selivanova** – sampling, microbiological analyses to determine the abundance of indicator bacterial groups, determination of the organic matter content in bottom sediments

*All the authors have read and approved the final manuscript.*