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## Экологическая безопасность прибрежной и шельфовой зон моря



Ecological Safety of Coastal  
and Shelf Zones of Sea

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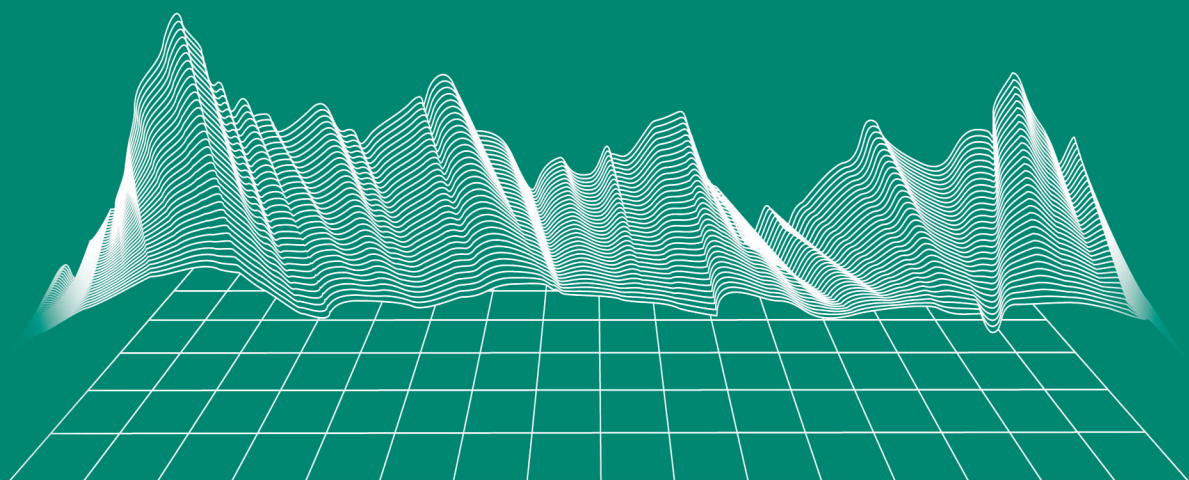
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## Characteristics of Extreme Precipitation in Crimea

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### Abstract

The paper considers the statistical characteristics of extreme precipitation according to long-term (75 years or more) measurements at 5 hydrometeorological stations in Crimea. Quantitative characteristics of the long-term variability of precipitation, the frequency of dry and wet periods, and the interannual variability of extreme precipitation are given. Cumulative distribution functions of extreme precipitation and their approximations based on generalized distributions of extreme values (GEV) are constructed. Both long-term averages and extreme precipitation values take its maxima at the Ai-Petri weather station. This station also has the longest wet periods (2.73 days) and the most intense daily precipitation (6.85 mm/day). The coastal stations of Kerch, Sevastopol and Feodosiya have the longest average duration of dry periods (up to 8 days in Feodosiya), and the total amount of precipitation in Simferopol is greater than that in coastal cities. The analysis of extreme precipitation confirmed that the most intense extreme precipitation is observed in the summer period on Ai-Petri (165 mm/day for a return period of 50 years), as well as in Kerch and Feodosiya. Extreme precipitation in Simferopol and Sevastopol is two times weaker than that on Ai-Petri.

**Keywords:** precipitation, Crimea, precipitation measurements, statistical characteristics, return period, return values

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# Характеристики экстремальных атмосферных осадков в Крыму

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## Аннотация

Рассмотрены статистические характеристики экстремальных осадков по данным долгосрочных (75 лет и более) измерений на пяти гидрометеорологических станциях Крыма. Приведены количественные характеристики многолетней изменчивости осадков, повторяемости сухих и влажных периодов, внутригодовой изменчивости экстремальных осадков. Построены кумулятивные функции распределения экстремальных осадков и их аппроксимации на основе обобщенных распределений экстремальных значений. Как среднепогодные, так и экстремальные значения осадков максимальны на метеостанции Ай-Петри. В этом пункте также отмечаются наиболее продолжительные влажные периоды (2.73 сут) и наиболее интенсивные суточные осадки (6.85 мм/сут). В прибрежных пунктах Керчь, Севастополь и Феодосия отмечается наибольшая средняя продолжительность сухих периодов (до 8 сут в Феодосии), суммарное количество осадков в Симферополе больше, чем в прибрежных городах. Анализ экстремальных осадков подтвердил, что наиболее интенсивные экстремальные осадки отмечаются в летний период на Ай-Петри (165 мм/сут для периода повторяемости в 50 лет), а также в Керчи и Феодосии. Экстремальные осадки в Симферополе и Севастополе в два раза слабее, чем на Ай-Петри.

**Ключевые слова:** атмосферные осадки, Крым, измерения осадков, статистические характеристики, период повторяемости, возвратные значения

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## Introduction

A characteristic feature of precipitation in Crimea is the significant heterogeneity of its distribution over the relatively small area. Most of the steppe region of the peninsula is characterized by insufficient wetness: the average annual precipitation makes 430–550 mm, while under the influence of the Crimean Mountains, much more precipitation falls in mountainous areas [1]. There, the amount of precipitation is approximately 1.5 times higher than that one over the steppe part of the peninsula. The extensive literature on the subject is devoted to the physical mechanisms of disturbances introduced by mountains into the wind and precipitation fields, e.g. [2–5]. At the same time, in the region of the South Coast of Crimea (SCC) – a narrow coastal strip along the southern slope of the Crimean Mountains – an area of subtropical (sub-Mediterranean) climate has been formed [6]. Despite the fact that the average annual precipitation here is close to the amount of precipitation in the steppe regions, most of it, as in the Mediterranean countries, take place during the cold winter period. On the contrary, in the domes-



tic steppe areas of Crimea, the monthly variability is relatively small, with most of the precipitation taking place during the warm summer period <sup>1)</sup>.

A remarkable thing of the distribution of precipitation is the decrease in the amount of precipitation in coastal areas compared to the central regions. For example, in Sevastopol, the average annual precipitation makes about 300 mm, while in Simferopol it makes approximately 500–700 mm <sup>1)</sup>. It is associated with the relative increase in the amount of convective precipitation during the daytime in summer [7] due to the contribution of breeze circulation [8, 9].

The absence of the adequate observational network, as well as insufficient spatial resolution of satellite measurements [7, 10], makes it impossible to study the spatiotemporal structure of precipitation and to assess the probabilistic characteristics of precipitation throughout the peninsula. First of all, such an assessment is very important for the cases of extreme precipitation, the catastrophic manifestations of which are most noticeable in some areas of the peninsula, namely, in mountain valleys and on mountain slopes [11].

One of the cases of heavy summer rain in the SCC region refers to September 6–7, 2018. In Yalta and Feodosiya, almost two to three monthly amounts of rainfall was measured. Two more recent extreme precipitation events refer to the summer of 2021. On the night of June 17, real tropical downpours, the largest ones in the last 100 years, came to Crimea, which had previously suffered from drought. Within a matter of hours, the amount of precipitation corresponding to the norm for 2–3 months fell. The next day, big water came to Yalta. The same thing that had happened in Kerch was repeated there, but on a larger scale.

The purpose of this article is to evaluate the statistical characteristics of extreme precipitation, i.e. those exceeding the 99th percentile [12]. As pointed out above, there are very few long-term meteorological observations suitable for the assessment of the distribution functions and return periods of extreme precipitation in Crimea. The available dataset is comprised of archival meteorological measurements data collected at the hydrometeorological stations (HMSs) in Simferopol, Kerch, on Ai-Petri, in Sevastopol and Feodosiya for the period of at least 75 full years <sup>2)</sup>, as well as the archives of the *RP5* website (URL: <https://rp5.ru/>). At all other locations of meteorological observations in Crimea, there are only fragmentary precipitation measurements available, while continuous measurements cover only the last 10–12 years and are not suitable for climate assessments.

### **Statistical characteristics of the series of daily precipitation at the meteorological stations of Simferopol, Ai-Petri, Kerch, Feodosiya and Sevastopol**

Fig. 1 shows the time series of annual precipitation amounts at meteorological stations. Statistical analysis of these measurements showed that the largest amount of annual precipitation had been observed at the Ai-Petri meteorological station, located in the mountains. Here, the average annual precipitation amounted to 1,003 mm. In Simferopol, the average annual precipitation amounted to 499 mm, and at the coastal stations of Sevastopol, Kerch and Feodosiya, it was

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<sup>1)</sup> Ved, I.P., 2000. [*Climate Atlas of Crimea*]. Simferopol: Tavriya-Plus, 118 p. (in Russian).

<sup>2)</sup> ECA&D Project Team. *European Climate Assessment & Dataset*. 2022. [online] Available at: <https://www.ecad.eu> [Accessed: 31.05.2022].

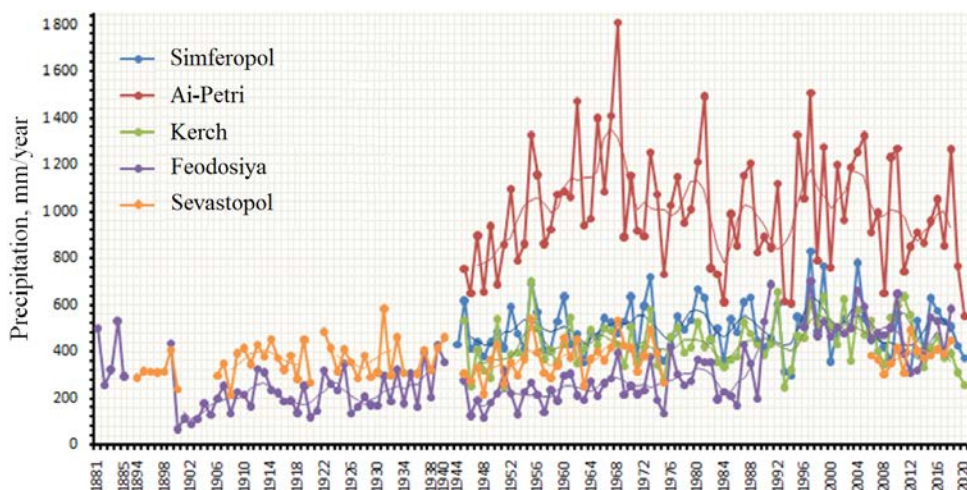


Fig. 1. Annual precipitation amounts and the moving average over 5 points

significantly less and made 365, 437 and 299 mm, respectively. The interannual variability of precipitation amounts on Ai-Petri significantly exceeds the variability at other stations. The decrease in precipitation at all stations in 2019–2020 also calls attention to itself. In particular, the amount of precipitation on Ai-Petri was minimal during the period of interest, which was the main factor in the limited availability of freshwater resources in 2020–2021.

The precipitation series in Simferopol contains 28,125 measurements (77 years) with 18,890 days without precipitation. The precipitation series in Kerch and on Ai-Petri contain 27,759 daily measurements (76 years), while in Kerch there were 20,095 days without precipitation, and on Ai-Petri – 16,635 dry days. The series in Feodosiya consists of 42,733 measurements (111 years) with 34,480 dry days. In Sevastopol, the series contains 30,680 measurements (84 years) with 22,556 dry days. Averages values and maximum amounts of precipitation for the entire period of observations are given in Table 1. It also shows the average and maximum duration of wet and dry periods at meteorological stations and provides estimates of the intensity of daily precipitation, calculated by the following formula

$$P_{\text{int}} = P_{\text{tot}} / N_{\text{wet}},$$

where  $P_{\text{tot}}$  – total precipitation amount,  $N_{\text{wet}}$  – number of wet days.

As could be seen, the intensity of daily precipitation is maximal for the Ai-Petri HMS, located on the top of the Crimean Mountains at an altitude of about 1000 m, and minimal for the Sevastopol HMS in the coastal southwestern part of the peninsula.

Histograms of daily precipitation series are shown in Fig. 2. In this case, the frequency or repeatability of the number of days with a given amount of precipitation is determined in relation to the total length of the series of observations. As is obvious, the repeatability of precipitation monotonically decrease with

Table 1. Statistical characteristics of daily precipitation series: all-time average daily precipitation  $P_{\text{mean}}$  (mm/day), maximum daily precipitation  $P_{\text{max}}$  (mm/day), average duration of dry periods  $T_{\text{drymean}}$  (day), maximum duration of dry periods  $T_{\text{drymax}}$  (day), average duration of wet periods  $T_{\text{wetmean}}$  (day), maximum duration of wet periods  $T_{\text{wetmax}}$  (day), precipitation intensity  $P_{\text{int}}$  (mm/day)

Weather station	$P_{\text{mean}}$	$P_{\text{max}}$	$T_{\text{drymean}}$	$T_{\text{drymax}}$	$T_{\text{wetmean}}$	$T_{\text{wetmax}}$	$P_{\text{int}}$
Simferopol	1.37	119.2	4.29	48	2.15	19	4.16
Ai-Petri	2.75	215.2	4.09	42	2.73	30	6.85
Kerch	1.20	300.0	5.18	57	1.98	13	4.33
Feodosiya	0.82	132.3	8.08	123	1.94	17	4.24
Sevastopol	1.00	209.0	5.57	60	2.01	15	3.78

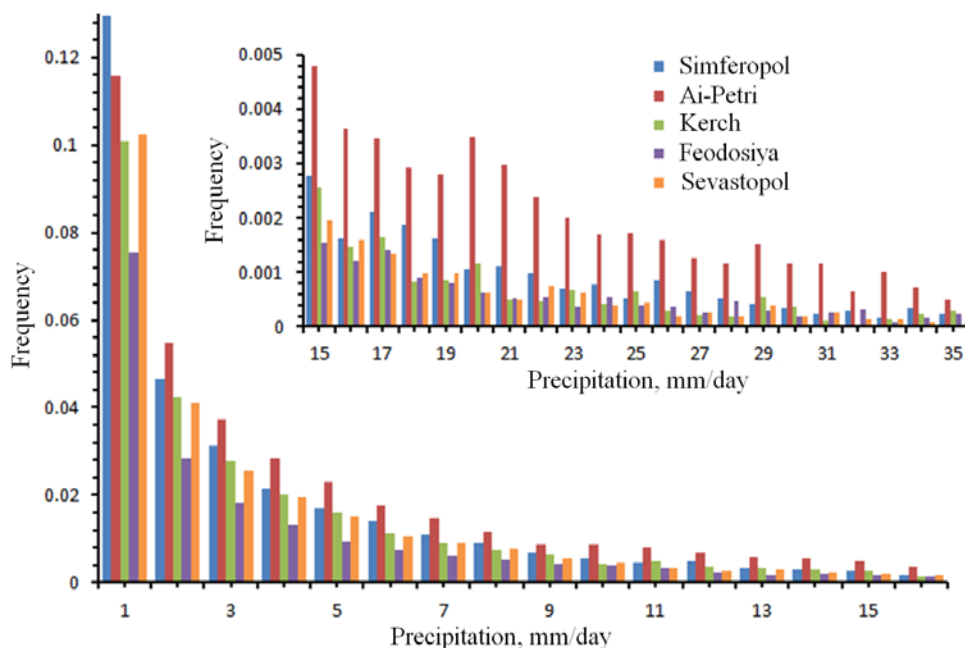


Fig. 2. Histograms of daily precipitation series at weather stations

the increasing amount of precipitation for all the stations. Herewith, extreme precipitation is most frequent at Ai-Petri station.

An important characteristic of precipitation is the distribution function of dry days (i.e., days without precipitation) and wet days. Histograms of the periods of dry and wet days, as well as the probability distribution functions of the duration of dry and wet periods are shown in Fig. 3. For approximation, the following

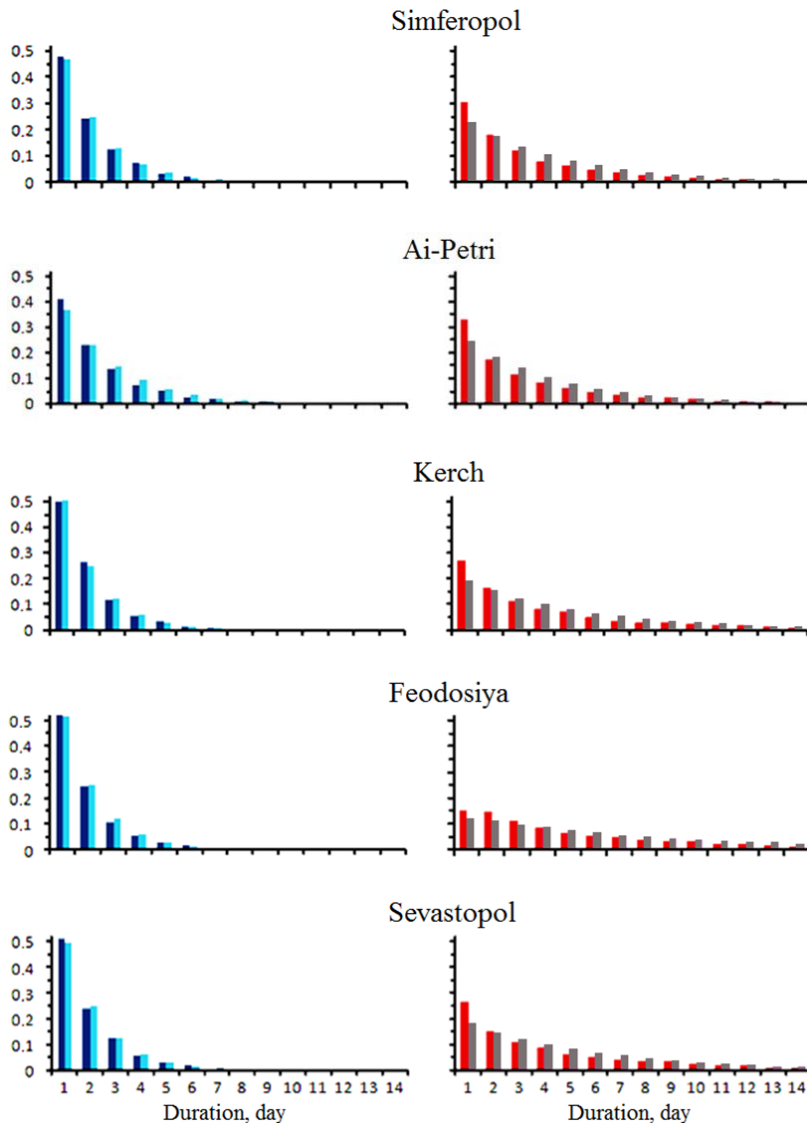


Fig. 3. Distribution histograms of the duration of dry periods and wet periods at weather stations (dark blue – empirical histograms of the precipitation period duration; light blue – approximation by geometric distribution; red – empirical histograms of the precipitation period duration; grey – approximation by geometric distribution)

geometric distribution of the probability density<sup>1)</sup> was used

$$f(x_i = k) = p(1 - p)^{k-1},$$

where  $x_i$  – duration of wet or dry period;  $p = 1/\bar{x}$  – distribution parameter, inverse number of average duration.

For all stations, the frequency of dry periods is approximately two times less than the frequency of precipitation periods; the most frequent are one-day precipitation periods and dry periods lasting 1–4 days. In 90 % of cases, precipitation lasts 3 days or less (4 days – on Ai-Petri), in 50 % of cases – 1 day. There are no significant differences in the duration of wet periods at different stations. At the same time, the frequency of one-day dry periods in Feodosiya is almost two times lower than at other stations, and long dry periods take place more often.

The distributions of dry and wet periods are important characteristics of the temporal structure of precipitation [13], which make it possible not only to judge the moisture regime of the region, but also to assess the possibility of droughts and floods. Indeed, even very heavy precipitation that fell within a short time is not as dangerous as relatively small precipitation falling over a long period. Such indicators as the contribution of wet/dry periods to the total number of days with/without precipitation are also important. Therein, the number of days is analyzed, that is, the proportion of days formed by periods of a given length, and thus the extremeness of the duration of periods of a given length is estimated.

Fig. 4 shows the proportions of periods of different durations to the total number of wet and dry days.

The relative contributions differ for the coastal and land stations. In Kerch, Feodosiya, and Sevastopol, dry periods of 10 days or more contribute more to the total number of dry days due to the reduced frequency of precipitation in summer. Vice versa, wet periods of 5 days or more make a smaller contribution to the total number of days with precipitation. Wet periods lasting 10–15 days take place on Ai-Petri.

### **Annual variation of extreme precipitation**

The most intense extreme precipitation takes place in summer. Fig. 5 shows the amount of daily precipitation in Kerch and the annual variation of the average amount of precipitation exceeding the threshold value of 15 mm/day, which approximately corresponds to the level of 99% of the distribution function, as it will be clear from the subsequent. The maximum amount of daily precipitation, reaching values of more than 50 mm, falls on the summer period. Without giving the same distributions for the other four meteorological stations, it should be noted that they differ slightly from the distribution in Kerch, shown in Fig. 5. What can only be pointed out is that the summer maximum of daily extreme precipitation for Ai-Petri is less noticeable.

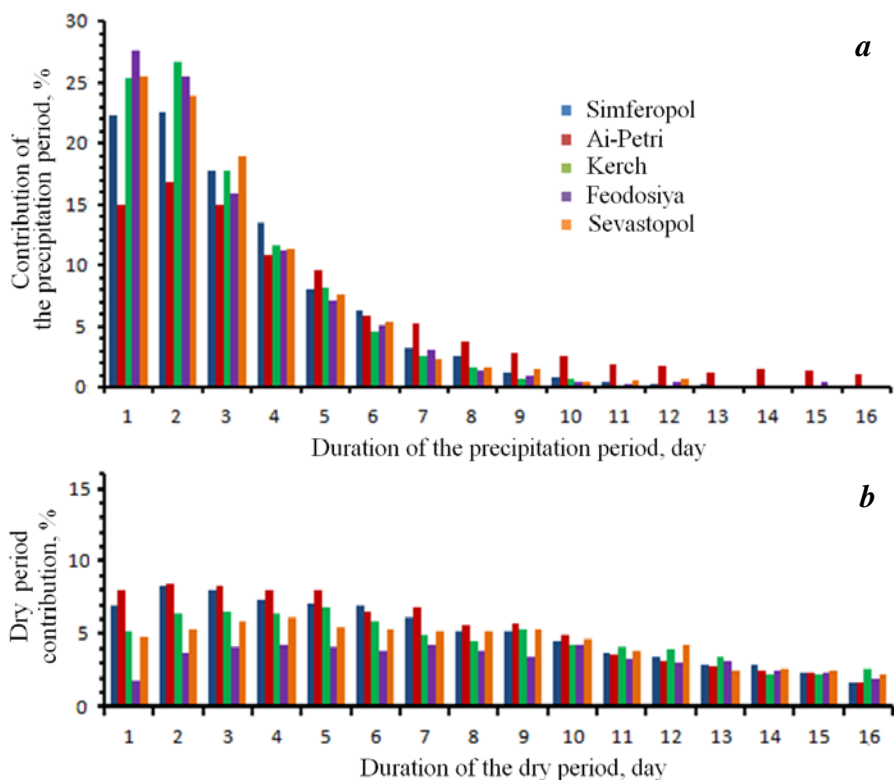


Fig. 4. Empirical histograms of partial contributions of different duration periods to the total number of wet (a) and dry (b) days

The explanation for the summer maximum of extreme precipitation is simple. Intensive precipitation in Crimea is caused by heavy rains associated with convective precipitation during the warm summer season. In winter, cloudiness that forms precipitation refers mainly to nimbostratus clouds. In this case, the source of moisture for continuous rains is the advection of water vapor as a result of transport from neighboring areas due to high airflow velocities [8]. Winter precipitation is long, but less intense and smaller in quantity.

### Characteristics of extreme precipitation

To assess the probability distribution of extreme precipitation exceeding the selected threshold value, i.e., the tail of the full distribution function (usually from the value of 15 mm/day for the daily amount [14, 15]), the generalized extreme value (GEV) distribution is used. The distribution function of extreme values is given by the following formula

$$F(x; \mu; \sigma; \xi) = \exp\left(-\left[1 + \xi\left(\frac{x - \mu}{\sigma}\right)\right]^{-1/\xi}\right),$$

where  $\mu$  – location parameter;  $\sigma$  and  $\xi$  – scale and shape parameters respectively.

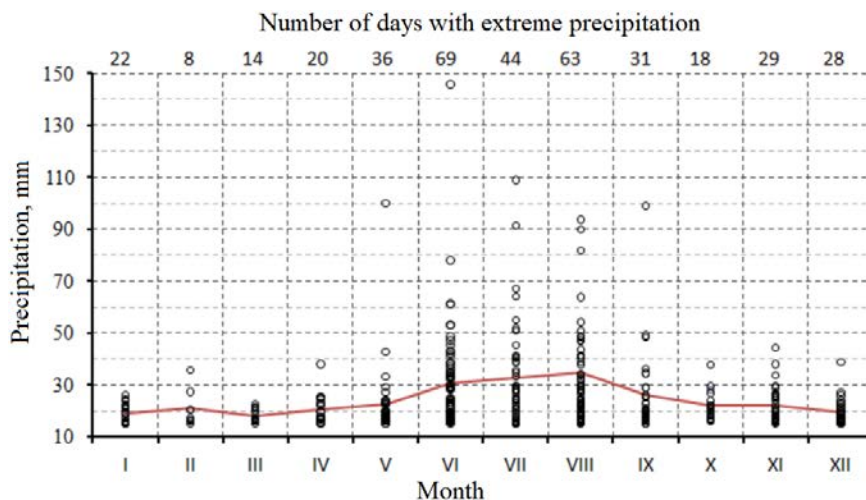


Fig. 5. The monthly numbers of days with extreme (more than 15 mm) daily precipitation in Kerch according to measurement data for 1945–2020. The annual variation of the averages is shown in red

Fig. 6 shows the probability distributions of the daily precipitation series proper (cumulative distribution functions) and their GEV distribution approximation using the maximum likelihood method for five selected weather stations.

As is obvious, there is some difference between the distribution of extreme precipitation at Ai-Petri station and at other HMSs. For the former, the probability values are somewhat shifted towards lower values, i.e., higher values of extreme precipitation have higher probability, which is especially noticeable in comparison with Simferopol.

As an important characteristic of the precipitation absolute extremeness, the so-called return values (that is, values that occur once in a certain number of years) and return periods (that is, the waiting time for a given extreme value) are often used. Return values and return periods are related as follows

$$F_p = \left( 1 - \frac{1}{\tau(R_p)} \right),$$

where  $F_p$  – estimate of the probability density (percentile) for daily precipitation return value  $R_p$  and waiting time of the event  $\tau$ . In particular, for a return period of 100 years, the corresponding percentile would be calculated for a series of daily precipitation by the following formula

$$1 - \frac{1}{365 \cdot 100} = 0.99997.$$

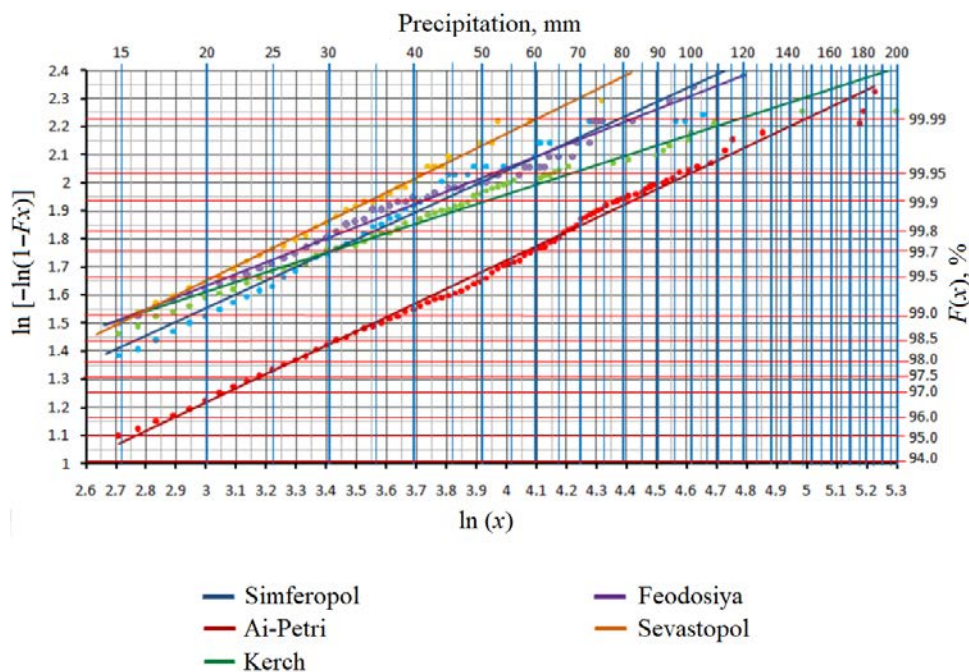


Fig. 6. The probability density of daily precipitation (cumulative distribution functions) at weather stations in logarithmic coordinates and their generalized extreme values distribution approximation using the maximum likelihood method

From the percentile value, using the fitting distribution, it is easy to determine the return value for a given return period. The calculated estimates of extreme precipitation return values at meteorological stations for various return periods are given in Table 2.

Table 2. Daily precipitation (mm/day) at weather stations for various return periods

Weather station	Return period		
	20 years	50 years	100 years
Simferopol	70	85	98
Ai-Petri	137	165	190
Kerch	105	139	169
Feodosiya	76	96	113
Sevastopol	55	67	76

From the percentile value, using the fitting distribution, it is easy to determine the return value for a given return period. The calculated estimates of extreme precipitation return values at meteorological stations for various return periods are given in Table 2.

In general, the return values repeat the behavior of the precipitation intensity values. The highest values are accounted for the Ai-Petri HMS, the lowest ones – for the Sevastopol HMS. The physical reasons for this are rather clear, as the amount of precipitation in the area of high mountains is the highest



one due to the peculiarities of the air flow around the mountains and increased condensation when the air rises to the top of the mountain. And the reduced precipitation intensity in Sevastopol compared to, e. g., Simferopol, as noted above, is explained by the influence of breeze circulation and the shift of the convective cloudiness formation area from the coastal to the land area during the day in the warm period of the year [7, 8]. All these arguments can also be confirmed by the calculated estimates of the maximum duration of dry and wet periods at meteorological stations for the return periods given in Table 3.

Table 3. The duration (days) of dry and wet periods at weather stations for various return periods

Weather station	Return period		
	20 years	50 years	100 years
Simferopol	<u>34</u> 14	<u>38</u> 16	<u>41</u> 17
Ai-Petri	<u>32</u> 20	<u>35</u> 22	<u>38</u> 28
Kerch	<u>41</u> 14	<u>46</u> 16	<u>49</u> 17
Feodosiya	<u>67</u> 12	<u>74</u> 13	<u>79</u> 15
Sevastopol	<u>45</u> 13	<u>50</u> 14	<u>54</u> 15

Note: above the line – duration of dry periods; below the line – that of wet periods.

### Conclusion

The paper considers the daily precipitation measurements at the HMSs of Simferopol, Ai-Petri, Kerch, Feodosiya, and Sevastopol. Statistical analysis of the constructed series shows that the longest and most intense precipitation is observed at the Ai-Petri HMS, which is located in the mountains. The interannual variability of precipitation amounts is also higher there. At the coastal stations of Sevastopol, Kerch, and Feodosiya, the average annual precipitation, its intensity and interannual variability are much lower. In Simferopol, these estimates are in its mean range due to the more continental climate. They are somewhat higher than at coastal stations, but still significantly lower than at the Ai-Petri HMS. A similar pattern can also be traced with the assessment of dry and wet periods duration at these stations. The extreme precipitation takes its annual maximum in summer. This is explained by the fact that intense precipitation in Crimea is caused by heavy rains, which are formed as a result of atmospheric convection during the warm summer period. When assessing the probability of extreme values of precipitation, the GEV distribution was used, which made it possible to determine the return values of daily precipitation at weather stations for different return periods. In general, the ratio of return values is similar to the ratio of precipitation intensity values, as the highest values were obtained for the Ai-Petri HMS, while the lowest ones – for the Sevastopol HMS. The estimates of the dry and wet periods maximum duration given in the paper also follow this pattern.

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**Anatolii E. Anisimov** – presentation of data in the text and their analysis, text editing

**Olga I. Komarovskaya** – calculations, preparation of graphic materials, text editing

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

## Environmental Monitoring System in the Azov and Black Sea Basin

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### Abstract

The paper presents the structure, tasks and features of environmental monitoring of the Black and Azov Seas as well as means and methods thereof adopted in the Russian Federation. The paper describes standards of analysis methods, layouts of offshore sampling stations, analyzed parameters, and specifics of the formation of the State Observation Network adopted by Roshydromet. Differences in the European and Russian systems of marine environmental monitoring and the systems' focus are shown. The features of satellite monitoring of the Azov and Black Sea basin were considered. The latest achievements of satellite monitoring of the Black Sea in the Russian Federation and the prospects for its development were analyzed. Additional opportunities to introduce satellite technologies in solving a number of environmental problems are listed. A new system of satellite monitoring of anthropogenic impacts on the Black Sea shelf of Russia, created by a team of scientists from the Aerocosmos Institute and institutes of the Russian Academy of Sciences, is considered. The possibilities of using mathematical modeling methods as an effective tool for predicting the consequences of anthropogenic impact on marine areas, including oil spills, were analyzed. The long-term changes in the water pollution index of the Black Sea marine areas were estimated in the area of responsibility of the Russian Federation. The implementation stages of the international project EMBLAS developed as part of the Bucharest Convention (1992) were analyzed. The purpose of the project was to develop a system of integrated monitoring of the Black Sea, to collect and manage the obtained data, and to improve the skill level of dedicated experts in the Black Sea states. The paper provides a map of ecological zoning of the eastern Black Sea with description of complex monitoring stations proposed for inclusion in the work program. The paper substantiates the necessity of ecological zoning and allocation of sites, the recreational use of which should be excluded or limited for the sake of people's health until the situation changes.

**Keywords:** environmental monitoring, water pollution index, station layout, Azov and Black Sea basin, satellite information, international projects

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Khmara T. V., Pogozeva M. P., 2022



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## Система экологического мониторинга Азово-Черноморского бассейна

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### Аннотация

Представлены структура, задачи и особенности экологического мониторинга Черного и Азовского морей, а также его средства и методы, принятые в Российской Федерации. Описаны используемые в Росгидромете стандарты на методики анализа, схемы расположения морских станций отбора проб, анализируемые параметры и особенности формирования государственной наблюдательной сети. Показаны различия в европейской и российской системах экологического мониторинга морской среды и направленность этих систем. Рассмотрены особенности спутникового мониторинга Азово-Черноморского бассейна. Анализируются последние достижения спутникового мониторинга Черного моря и перспективы его развития в РФ. Перечислены дополнительные возможности внедрения спутниковых технологий при решении ряда природоохранных задач. Рассмотрена новая система спутникового наблюдения за антропогенными воздействиями на шельфе Черноморского побережья России, созданная коллективом ученых института «Аэрокосмос» и институтов РАН. Проанализированы возможности использования математического моделирования как эффективного инструмента для прогнозирования последствий антропогенного воздействия на морские акватории, включая разливы нефти. Представлены оценки многолетних изменений индекса загрязненности вод Черного моря в зоне ответственности РФ. Проанализированы этапы реализации международного проекта *EMBLAS*, разработанного в рамках Бухарестской конвенции (1992 г.), цель которого состояла в развитии системы комплексного мониторинга Черного моря, сборе и управлении полученными данными, повышении уровня квалификации профильных специалистов в причерноморских государствах. Приведена схема экологического районирования восточной части Черного моря с описанием станций комплексного мониторинга, предлагаемых для включения в программу работ. Обоснована необходимость экологического районирования и выделения участков, рекреационное использование которых до изменения ситуации должно быть исключено или ограничено в целях сохранения здоровья людей.

**Ключевые слова:** экологический мониторинг, индекс загрязненности вод, схемы расположения станций, Азово-Черноморский бассейн, спутниковая информация, международные проекты

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## Introduction

The Azov and Black Sea basin is one of the most developed regions in terms of providing recreational-tourist, sanitary-resort and balneological services not only for Russia, but also for Europe as a whole. This is primarily due to the presence of sea beaches, as well as a network of mineral springs and sources of healing mud. Unique climatic and natural recreational conditions contribute to the development of a specific system of medical and resort complexes. At the same time, the catastrophic pollution of the Black and Azov seas is a generally recognized fact [1].

The main federal body of state power of the Russian Federation in the field of use and protection of the environment is the Ministry of Natural Resources and Ecology of the Russian Federation (Ministry of Natural Resources of Russia) (URL: [www.mnr.gov.ru](http://www.mnr.gov.ru)), whose competence includes monitoring environmental pollution. According to [2], monitoring is a systematic diagnosis of a situation with a certain specified frequency and using the same system of indicators. In relation to the monitoring of the hydrochemical state and the level of pollution of the marine environment, monitoring means regular observations in one place by the same or comparable methods. The Ministry of Natural Resources of the Russian Federation establishes requirements for conducting state monitoring of water bodies, including monitoring of the state of the environment and its pollution, collection, processing and storage of data, dissemination of information. The Ministry of Natural Resources of the Russian Federation coordinates and controls the activities of its subordinate the Federal Service for Hydrometeorology and Environmental Monitoring (Roshydromet), the Federal Service for Supervision of Natural Resources, the Federal Agency for Water Resources and the Federal Agency for Subsoil Use. In accordance with the Decree of the Government of the Russian Federation No. 477 dated 06.06.2013 “On the Implementation of State Monitoring of the State and Pollution of the Environment”, Roshydromet was instructed to form and ensure the functioning of the State Observation Network (SON), its stationary and mobile points, as well as ship field research.

At present, the State Observation Network is formed on the basis of Regulations on SON (2003) and includes both regional Departments for Hydrometeorology and Environmental Monitoring (DHEM), and their branches – Centers for Hydrometeorology and Environmental Monitoring, which perform practical work on monitoring<sup>1)</sup>. The results of observations of the marine network of Roshydromet

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<sup>1)</sup> Rosgidromet. *The Structure of Rosgidromet*. 2022. [online] Available at: <http://www.meteorf.ru/about/structure> [Accessed: 06 June 2022].

are published in the Yearbooks of Marine Water Quality by Hydrochemical Characteristics<sup>2)</sup>, which are regularly supplemented by the results of studies and observations of research institutes of Roshydromet and the Russian Academy of Sciences, individual field marine research of state and non-state organizations<sup>2)</sup>, data obtained as part of the international exchange of information.

Contact methods of monitoring observations of the quality of marine waters are supplemented by remote (space) methods of obtaining information. According to the order of the Government of the Russian Federation No. MK-P9-01617 dated 10.02.2003<sup>3)</sup>, the State Institution *Scientific Research Center "Planet"* together with the Hydrometeorological Center of the Russian Federation, the Institute of Oceanology and the Space Research Institute of RAS in the Russian sector of the Black and Azov seas carry out satellite monitoring of the aquatic environment, the technology of which enables to receive processed satellite images of the visible, infrared and microwave ranges from *Meteor-3M*, *Monitor-E*, *Terra Aqua*, *NOAA*, *ERS-2*, *Envisat*, *IRS*, *QuikSCAT*, *Jason*, *TOPEX/Poseidon* and *Meteosat-9* satellites.

Twelve types of final satellite information include not only generalized schematic maps of the state of the aquatic environment, but also the maps of:

- oil pollution of the sea;
- water circulation, sea level changes;
- distribution of phytoplankton and algae, concentration of chlorophyll *a*;
- distribution of diffuse attenuation coefficient;
- sea surface temperature, surface wind;
- results of automated recognition of water bodies, etc.

The purpose of this work is to describe the structure and tasks of the state environmental monitoring of the Black and Azov seas, as well as to evaluate the means and methods for performing observations within the framework of international environmental projects.

### **Materials and methods**

The problems of environmental monitoring of the Black and Azov seas are to be considered in the following order:

- structure and objectives of environmental monitoring. Features, structure and tasks of environmental monitoring in the Black Sea countries;
- means and methods of observations adopted in the Russian Federation, including contact and remote ones, as well as numerical modeling;
- proposals for improving the system of environmental monitoring of the Black Sea based on the results of implementation of international projects and programs.

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<sup>2)</sup> Korshenko, A.N., ed., 2020. *Marine Water Pollution. Annual Report 2019*. Moscow: Nauka, 232 p. (in Russian).

<sup>3)</sup> Roshydromet, 2001. [*On Introduction into Action of the Procedure of Preparation and Submission of General Information on the Environmental Pollution*]. Order by the Head of Roshydromet no. 156 as of 31 October 2000. Available at: <https://docs.cntd.ru/document/901791258> [Accessed: 10 June 2022] (in Russian).

## Results and discussion

Marine environmental monitoring (in this paper, monitoring in the Russian sector of the Black and Azov seas) is aimed at both assessing the current state of the marine environment and predicting the development of environmental risks based on a retrospective analysis of sources and factors of influence. According to this work<sup>4)</sup>, the objects of marine environmental monitoring in the Black and Azov seas are: the marine environment within the exclusive maritime economic zone of the Black Sea states, hydrometeorological and climatic (seasonal) factors of influence, the main pollutants and their impact on the physicochemical parameters of the marine environment, coastal and marine sources of pollution, river and atmospheric runoff, exchange processes between the sea and the atmosphere, the sea and bottom sediments, the sea and living organisms, as well as bi-productivity.

It should be noted that the Russian system of ecological monitoring of the marine environment is significantly different from the European ones. Thus, the Russian system is based on the principle of chemical analysis of water and assessment of its pollution relative to the threshold limit value (TLV) of a particular chemical element in sea water.

The European monitoring system is based on the ecosystem approach, assessing the state of the marine environment using a set of indicators (descriptors) and focusing on assessing the direct impact of human activities on living organisms<sup>5)</sup>. One of the fundamental principles is the subsequent development of a system of measures to prevent or reduce further anthropogenic impact in the event of serious violations of the quality of the marine environment. This methodological approach enables not only to obtain an informative picture of the state of the main components of the marine environment, but also to influence its dynamics in the future. Such a system is currently used in all European seas, including most of the Black Sea<sup>6)</sup>.

In 1992, in Bucharest, specialists from the Black Sea countries (Russia, Turkey, Ukraine, Romania, Bulgaria, and Georgia) signed the Convention for the Protection of the Black Sea from Pollution (Bucharest Convention). Within the framework of the Convention, these states assumed obligations to control and reduce pollution of the Black Sea, to monitor and protect the marine environment<sup>7)</sup>. Specific measures are determined by the three protocols of the Bucharest Convention [3]:

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<sup>4)</sup> Monyushko, M.M., 2007. [Complex Ecological Monitoring of the Azov-Black Sea Basin (Current State)]. In: Publishing house Education and Science s.r.o., 2007. [*International Scientific and Applied Conference "Efficient Tools of Modern Sciences-2007" (3–5 May, 2007)*]. Praha: Publishing house Education and Science s.r.o., 2007.

<sup>5)</sup> European Parliament, 2008. Directive 2008/56/Ec of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive). *Official Journal of the European Union*, L 164, pp. 19–40. Available at: <http://data.europa.eu/eli/dir/2008/56/oj> [Accessed: 02 June 2022].

<sup>6)</sup> UNDP. *EU4EMBLAS*. 2022. [online] Available at: <https://emblasproject.org/> [Accessed: 02 June 2022].

<sup>7)</sup> Black Sea Commission, 1992. *Convention on the Protection of the Black Sea Against Pollution (Bucharest, 21 April 1992)*. Available at: <https://docs.cntd.ru/document/901892843> [Accessed: 02 June 2022] (in Russian).



- Protocol on the Protection of the Marine Environment of the Black Sea from Pollution from Coastal Sources;
- Protocol on Cooperation in Combating Pollution of the Marine Environment of the Black Sea with Oil and Other Harmful Substances in Emergency Situations;
- Protocol on the Protection of the Marine Environment of the Black Sea from Pollution from Discharges.

In 2002, the parties to the Convention signed the Protocol on the Conservation of Biodiversity and Landscapes of the Black Sea, and also compiled a List of Species Important to the Black Sea. The Black Sea Commission (Commission for the Protection of the Black Sea from Pollution) is entrusted with monitoring the implementation of the protocols of the Bucharest Convention, its Strategic Action Plan for the restoration and protection of the Black Sea. The established international advisory groups provide information and expert support to the Black Sea Commission and its permanent Secretariat. The work of the advisory groups is aimed at conducting environmental monitoring and assessing the level of pollution, controlling pollution from land-based sources and developing a unified methodology for the integrated management of the coastal zone, assessing the environmental aspects of regulating fisheries and extraction of other marine biological resources, preserving biodiversity and solving problems of environmental safety of navigation.

The Black Sea Commission manages the activities of the Black Sea regional centers organized on the basis of specialized national institutions <sup>7)</sup>. Support for the Black Sea national monitoring systems is included in the list of international projects carried out within the framework of the Strategic Action Plan for the restoration and protection of the Black Sea.

#### **Monitoring stations of the Russian seas of Roshydromet**

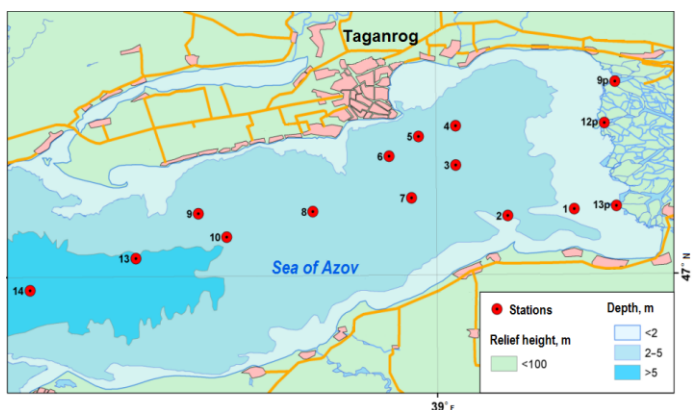
Stations of the State Service for Observation and Control of Pollution of Natural Environment Objects have a certain categorization depending on the composition and frequency of observations. Thus, single control stations of I category with constant monitoring are designed for operational monitoring of pollution level of the marine area. They are located in strategically important areas of the sea or in areas that are constantly subjected to intense pollution. According to the full program, observations of pollution and chemical composition of waters are carried out once a month, and according to the reduced program, monitoring is carried out two to four times a month. Single stations or complexes of stations (sections) of II category cover large areas of the sea, including estuarine sections of rivers, and serve to obtain systematic information, as well as to study the seasonal and interannual variability of controlled parameters. The monitoring is carried out once a month according to the full program (during the freezing period – once a quarter). The information about background levels of pollution, their seasonal and interannual variability is obtained at monitoring stations of III category, located in sea areas with a low level of anthropogenic load in relatively clean waters, where pollutants can get only as a result of their global transfer or regional migration processes. The stations of this category are also designed to determine

the elements of the balance of chemicals. Observations under the full program are carried out once a season. The category and location of monitoring stations can be adjusted depending on the dynamics of the level of pollution of the marine environment or in relation to the emergence of new control objects<sup>2)</sup>.

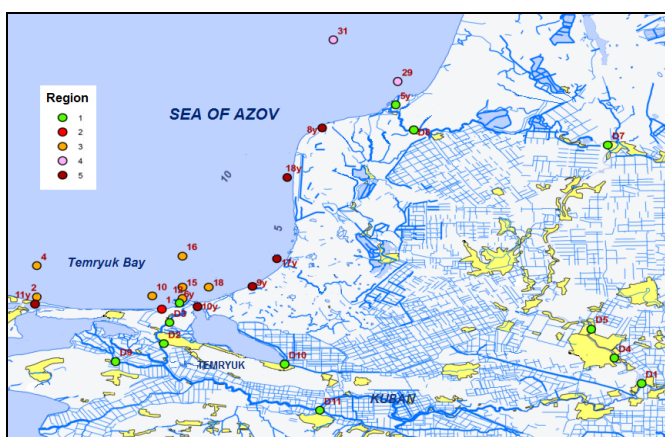
The monitoring programs carried out on the seas of the Russian Federation by the regional departments of Roshydromet are based on a permanent grid of stations of three categories. However, in reality, when implementing plans, it is often not possible to complete stations of the above categories due to constantly arising problems with a small scientific fleet adapted to perform outboard work for sampling water and bottom sediments. An additional complication is the need to analyze the content of chemical compounds and pollutants in seawater in very low concentrations, which requires modern chemical-analytical equipment and pure chemicals.

At present, the monitoring of the hydrochemical state and the level of pollution of the Sea of Azov is carried out in the eastern part of Taganrog Bay by the Don Estuary Hydrometeorological Station; in the delta of the Kuban River and on its estuarine coast in Temryuk Bay – by the Kuban Estuary Hydrometeorological Station (*Kubanskaya* EHS, the city of Temryuk), and at the stations of the section between the ports of Crimea and the Caucasus – by *Opasnoe* – the complex laboratory for monitoring environmental pollution (the city of Kerch). As an example, Fig. 1 shows the layout of stations for monitoring the pollution of the Sea of Azov waters.

In the water area of the Black Sea, the coastal waters of the Caucasian and Crimean coasts of Russia fall under state monitoring. In the coastal areas of the shelf in the area of the cities of Anapa, Novorossiysk, Gelendzhik and Tuapse, observations are carried out by *Kubanskaya* EHS (the city of Temryuk); in the coastal shallow zone in the area of the cities of Sochi and Adler from the mouth of the Sochi River to the mouth of the Mzymta River, the monitoring is carried out by a complex laboratory for monitoring environmental pollution of the Specialized Center for Hydrometeorology and Environmental Monitoring of the Black and Azov Seas (the city of Sochi). Off the Crimean coast of the Black Sea, the monitoring studies of the waters of Sevastopol Bay and the coastal zone of the South-Western Crimea are carried out by the Sevastopol Branch of the Federal State Budgetary Institution *N.N. Zubov State Oceanographic Institute* and the Department of Marine Biogeochemistry of the *Marine Hydrophysical Institute of the Russian Academy of Sciences*, and in the waters of the port of Yalta – a complex laboratory of monitoring of environmental pollution in the city of Yalta – Federal State Budgetary Institution *Crimean* EHS. The samples are taken from the surface and bottom layers, at deep water stations – from standard hydrological horizons of 0, 10, 25 and 50 m. The quality of sea water is controlled by characteristics, which include regime hydrological and hydrochemical characteristics (temperature, salinity, chlorine content, electrical conductivity, pH, total alkalinity and concentration of dissolved oxygen and suspended solids), concentration of biogenic elements (total phosphorus, phosphate phosphorus, ammonium nitrogen, nitrite, nitrate and total nitrogen, silicon) and pollutants such as petroleum hydrocarbons, anionic synthetic surfactants, phenols, organochlorine pesticides



*a*



*b*

Fig. 1. Monitoring stations in the eastern part of Taganrog (a) and Temryuk (b) Bays of the Sea of Azov

of the DDT and HCCH groups, heptachlor, aldrin and polychlorinated biphenyls, as well as heavy metals. All chemical analyzes during work on the marine environment monitoring network are carried out in accordance with the methods of regulatory documents (RD) – guidelines for the chemical analysis of sea water.

### **Satellite monitoring of the Black and Azov seas in the Russian Federation and prospects for its development**

Remote monitoring of the Russian waters of the Azov-Black Sea basin, which are subject to anthropogenic impact, is possible using modern satellite technologies. To do this, the monitoring system uses satellites, measuring equipment on ships and buoys, as well as a centre for receiving and processing information. When arranging satellite monitoring, both the world experience in carrying out such work, as well as the features of the sources of pollutant inflow and the dynamics of the water masses of the Black and Azov seas are taken into account.

For example, according to [4], in 2006, in the course of satellite monitoring of the state of the natural environment in the Russian sector of the Azov and Black seas, more than 1100 satellite images were obtained, processed and analysed from nine specialized Earth remote sensing satellites. Based on the analysis of ground-based observational data from the meteorological stations of Sochi, Tuapse, Novorossiysk, Anapa, Rostov-on-Don and Kerch, as well as previous satellite data, 12 types of operational satellite information and generalized schematic maps of the state and pollution of the marine environment were produced [4].

Modern satellite technologies can provide imaging of marine areas in the visible, infrared and microwave ranges of electromagnetic radiation. Sounding in the infrared and microwave ranges is used to determine the temperature of the sea surface, to study the thermodynamics of sea ice and to determine the salinity of water. Satellite imagery in the visible range makes it possible to monitor the state of the coastal zone and the dynamics of sea coasts, to determine the content of suspended particles, as well as the composition and productivity of phyto- and zooplankton. Spectral imaging can provide qualitative and quantitative analysis of suspensions, determination of chlorophyll in phytoplankton (and indirect water pollution) and detection of oil films on the sea surface.

In 2009, within the framework of the Bucharest Convention, a Strategic Action Plan was adopted to reduce oil pollution of the sea. Its *MONINFO* project is based on the use of satellite technologies for the detection of surface oil pollution in the sea. However, in 2008, even before the implementation of the EU initiative, the first comprehensive project Monitoring of Black Sea Oil Pollution and Environmental Safety of Navigation in Areas of Intensive Navigation in the Kerch Strait, the Water Area of the Port of Novorossiysk and on the Approach Routes to It was successfully implemented in the Russian Federation (with participation of the operator of the satellite data provision service *ScanEx RDC*, which has access to the operating system for positioning vessels (*Automatic Identification System, AIS*), developed by the Federal State Budgetary Institution *Administration of the Black Sea Ports*) [5]. The implementation of the project made it possible to monitor areas of intensive shipping, identify ships involved in unauthorized discharges of oily waters, and provide technical support in planning and conducting search and rescue operations in relation to ships in distress, including ships that do not transmit radio signals.

Space monitoring data from *Sentinel-1B* satellite, received on January 21, 2020, made it possible to detect an oil spill 146 km from Feodosia (Fig. 2). This was reported on January 23, 2020 by the Federal State Budgetary Institution *Scientific Research Centre 'Planeta'*, which identified the object as a film of oil pollution from ships<sup>8)</sup>. The area of pollution was 86.1 km<sup>2</sup>, the length was 55.1 km. Pollution of coastal waters with oil products is one of the main environmental problems of the Black Sea region.

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<sup>8)</sup> Chizhevskiy, A., 2020. [*Space Monitoring Data Showed a Major Oil Spill off the Coast of Crimea*]. Available at: <https://neftgaz.ru/news/incidental/520743-dannye-kosmicheskogo-monitoringa-pokazali-krupnyy-razliv-nefti-u-beregov-kryma/> [Accessed: 10 June 2022] (in Russian).

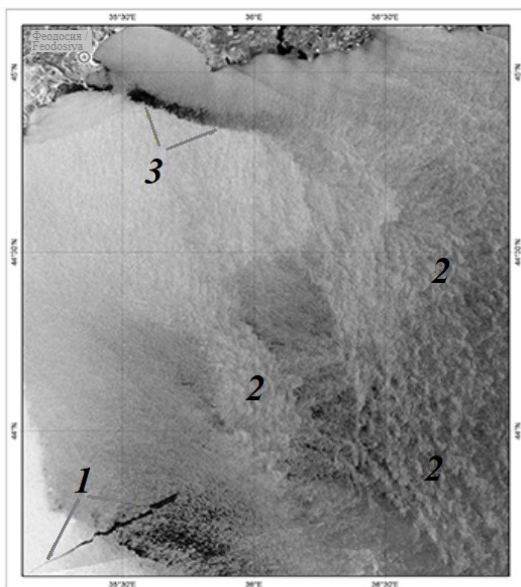


Fig. 2. Radar image of the Black Sea off the Crimean coast: 1 – films of oil pollution from ships; 2 – manifestation of the impact of atmospheric convection on the rough sea surface; 3 – manifestation of the impact of the atmospheric front on the rough sea surface

Another area of environmental monitoring in the Russian sector of the Black Sea was a timely detection and diagnosis of sea water blooming by measuring the concentration of chlorophyll according to satellite observations. Thus, in March 2008, in the northeastern part of the Black Sea, thanks to the timely acquisition of satellite images, the so-called red tide caused by the development of a species of dinophyte algae was recorded for the first time [6, 7]. Optical *MODIS* images taken at that time over the coastal areas of the Black Sea made it possible to trace the spatial and temporal distribution of polluted (blooming) waters. Chlorophyll maps obtained using *Aqua/MODIS* sensors confirmed the results of field observations.

Operational sounding of the optical properties of the Black Sea surface carried out at MHI NASU and regular studies of phytoplankton in its north-eastern part carried out by the staff of the SSC RAS made it possible in May–July 2012 to record an anomalous (over the past 15 years) in intensity and duration blooming of water. According to [8], it was caused by the massive development of the nanoplanktonic species of coccolithophorids.

Currently, a team of scientists from the *Research Institute of Aerospace Monitoring 'Aerokosmos'* with the participation of specialists from the MHI RAS (Sevastopol) and the IO RAS is working on the creation of a system for the integrated monitoring of anthropogenic impacts on the offshore areas of the Black Sea coast of Russia. This system will collect, process and analyze information important for assessing the state of marine areas and the response of coastal ecosystems to human activity, and in the event of a threat, it will be used to develop measures to prevent pollution of the marine environment.

This system for data collection provides for the use of ground-based sources of information, including instruments located on the coast and installed on ships, buoys and fixed platforms, as well as satellite systems that can transmit information

on various characteristics of coastal waters in the operational mode. Such a complex will make it possible to record the direction and speed of the wind, the direction and height of the waves, the speed of the currents, to register vertical distributions of temperature and salinity of the waters, to determine transparency of the waters to identify suspensions, to detect pollution of marine areas, including the presence of oil pollution, surfactant films and plumes of different nature.

To work out the interaction of information flows, test areas were selected that were subject to intense pollution. These were the coast near Sevastopol, the southern coast of Crimea (the village of Katsiveli, where there is an oceanographic platform) and the Krasnodar Territory (the coast near Gelendzhik). The first preliminary results of the integrated system of regional monitoring of coastal waters for the indicated test areas are presented in [9].

It is worth recalling that modern satellite technologies are not limited to studying the surface of the sea. For example, remote sensing makes it possible to register underwater plumes, including those formed as a result of sewage discharges. A plume is a mesoscale formation with anomalous waters of anthropogenic or terrigenous origin [10].

According to [9], starting from 2015, space monitoring of the coast near Sevastopol was carried out based on a detailed analysis of optical multispectral images of high and medium resolution (from 1 to 30 m on the ground) from *Resurs-P No. 1*, *GeoEye*, *WorldView-2*, *WorldView-3*, *Landsat-7*, *Landsat-8*, *Sentinel-2A* satellites. The monitoring revealed the existence of a plume (Fig. 3), which was formed as a result of an emergency rupture of the sewer main of the *Yuzhnye* urban wastewater treatment plant [11]. On satellite images, the plume was distinguished by an anomalous reflectivity spectrum, which differed significantly from the corresponding spectrum for the background areas of the observed water area.

The project was supported by the Federal Target Program “Research and Development in Priority Areas of Development of the Scientific and Technical Complex of Russia for 2014–2020” [12]. The Ministry of Natural Resources and



Fig. 3. Coastal area near the Sevastopol city on a fragment of an optical multispectral image from WorldView-2 satellite (September 17, 2015). The dotted line outlines the characteristic optical anomaly, the solid line shows the position of the underwater sewer line [11]

Ecology of the Russian Federation, the Federal Service for Hydrometeorology and Environmental Monitoring, the Ministry of Emergency Situations of Russia, and others are already interested in its results. These developments are of particular interest to shipbuilding, transport, oil and gas companies, educational and scientific institutions.

### **Mathematical modeling as a tool for assessing the state of the environment**

The use of mathematical modeling makes it possible not only to fill in the gaps at the points of lack of field data, but also to carry out a model assessment of the ecosystem state in the conditions of variability of its components depending on external factors. Modeling enables us to evaluate interactions that occur in real systems, which cannot be or difficult to directly measure.

In addition, the use of the model enables to obtain a forecast of the ecosystem evolution under the mutual influence of natural and anthropogenic factors, to take into account the trends in the state of the ecosystem and the likely consequences of a particular economic program in order to search for a scientifically based set of environmental protection measures. Based on the simulation results, the environmental monitoring program can be optimized.

Complex multi-purpose mathematical models of marine water quality consist of the following blocks: hydrodynamic, impurity transfer, pollutant self-purification, eutrophication and oxygen regime blocks [13].

At present, many mathematical models have been created to predict the spread of an oil slick after a spill. The MHI RAS also developed an operational system for forecasting the spread of oil spills in the Black Sea (*Black Sea Track Web, BSTW*), which is based on the synthesis of the modules of the Baltic oil spill forecast system and the MHI Black Sea circulation model adapted to the physical and geographical conditions of the Black Sea [14, 15].

To assess the quality of waters and compare different marine areas, the calculated values of the water pollution index (WPI) are used, which make it possible to attribute the waters of the study area to a certain purity class. The rules for calculating WPI are determined by methodological recommendations<sup>2)</sup>. The WPI calculation method includes:

- selection of the level of data averaging over space and time;
- calculation of priority pollutant concentrations for the considered water area in a given period of time (in TLV);
- assessment of the water quality class according to the obtained WPI value according to the table “Water quality classes and WPI values”.

For sea waters, when calculating WPI, at least three parameters of pollutants are used and the content of dissolved oxygen is mandatory (TLV = 6 mgO<sub>2</sub>/dm<sup>3</sup>). The WPI calculation formula:

$$WPI = \sum_{i=1}^4 \frac{C_i}{TLV_i} \div 4,$$

where  $C_i$  – concentration of the three most significant pollutants, the average content of which in the water of the study area to the greatest extent exceeded

the corresponding TLVs. Water quality classes depending on WPI values are presented in the Table. Fig. 4 shows the long-term change in the WPI of the Black Sea water areas.

Water quality classes and WPI values <sup>2)</sup>

Water quality class	WPI value range
I. Very clean	$\leq 0.25$
II. Clean	$0.25 \dots \leq 0.75$
III. Moderately contaminated	$0.75 \dots \leq 1.25$
IV. Contaminated	$1.25 \dots \leq 1.75$
V. Polluted	$1.75 \dots \leq 3.00$
VI. Very polluted	$3.00 \dots \leq 5.00$
VII. Extremely polluted	$> 5.00$

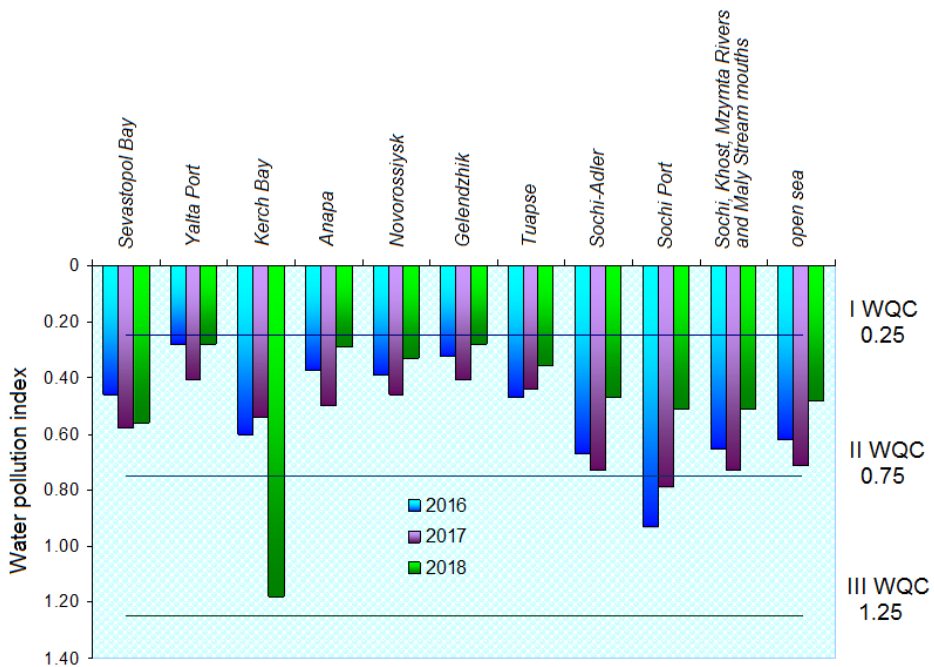


Fig. 4. Long-term change in the WPI value of the Black Sea areas in the area of responsibility of the Russian Federation. WQC – water quality class



### **Proposals for the improvement of the Black Sea environmental monitoring system within the framework of international projects and programs**

On March 15, 2010, the Black Sea Synergy environmental partnership initiative was launched in Brussels to support the efforts of the EU and its partners to find common approaches to the challenges facing the Black Sea region<sup>9)</sup>.

In 2013–2020 a number of Black Sea projects (*EMBLAS-I*, *EMBLAS-II*, *EMBLAS-Plus*) were aimed at improving the methods of marine monitoring and supporting the implementation of the Bucharest Convention in order to develop a monitoring system, collect and systematize the data obtained, and improve the skills of specialized specialists near the Black Sea states. Thus, within the framework of these projects, the FSBI *N.N. Zubov State Oceanographic Institute* conducted, using generally accepted world methods, complex coastal expeditions to assess the ecological state of the marine environment along the Caucasian coast of the Russian Federation, in the Kerch Strait and in more detail in the area of the cities of Sochi and Adler. The purpose of these studies was to improve the quality of monitoring data on the chemical and biological state of the Black Sea by optimizing observation systems, taking into account the practical proposals of the EU Directives *WFD-2000*, *MSFD-2008* and *Black Sea Strategic Action Plan* (2009), as well as expanding the capabilities of the project partner countries for the implementation of marine monitoring, taking into account both the practical recommendations of the EU in the *WFD* and *MSFD* Directives, and the results of the study set out in the *Black Sea Diagnostic Reports I and II*.

During the *EMBLAS* project implementation, the following activities were carried out:

- 1) analysis of national monitoring systems and opportunities for access to the data obtained;
- 2) support for the Black Sea states in the implementation of the Bucharest and other international conventions;
- 3) methodological and technological assistance to countries in the course of marine monitoring, including:
  - assistance in the development and implementation of cost-effective and unified biological and chemical monitoring of the marine environment in accordance with the requirements of international agreements, as well as *WFD* and *MSFD*<sup>5)</sup>;
  - development and implementation of a training program on monitoring methods in order to ensure the quality of the results obtained in accordance with *ISO 17025*;
  - preparation and implementation of the methodology of sea voyages (*Joint Black Sea Surveys*) to assess the state of the open part of the Black Sea;
- 4) development and creation of the Black Sea Water Quality Database (web-based), including hydrological and hydrochemical blocks and most of the biological characteristics of the sea ecosystem (*Black Sea Water Quality Database*);

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<sup>9)</sup> The Commission on the Protection of the Black Sea Against Pollution, 1996. *Strategic Action Plan for the Rehabilitation and Protection of the Black Sea*. [online] Available at: [http://blacksea-commission.org/\\_bssap1996.asp](http://blacksea-commission.org/_bssap1996.asp) [Accessed: 06 June 2022].

5) preparation of proposals for improving the Black Sea marine environment monitoring program in the territorial waters and exclusive economic zones of the Black Sea states.

The FSBI *N.N. Zubov State Oceanographic Institute* and other Russian organizations and laboratories took part in international expeditions, trainings and intercalibrations together with scientists from other Black Sea countries under the guidance of leading world experts. In the course of work, the participants improved their skills and knowledge and at the same time contributed to the acquisition and dissemination of up-to-date knowledge about the ecological state of the Black Sea. Based on the data obtained during coastal expeditions in the spring-summer-autumn periods of 2016, 2017 and 2019, proposals were formed to change the location of stations, unify the measured parameters depending on the depth and frequency of sampling to solve the following tasks:

1) assessment of the current state of hydrochemical and biological parameters of the marine environment;

2) assessment of long-term interannual variability of nutrient concentrations and eutrophication levels in the north-eastern part of the Black Sea with special attention to several local areas (Gelendzhik Bay, Golubaya Bay, Anapa district, Sochi-Adler area);

3) obtaining the necessary data to assess the level of anthropogenic pollution of the marine environment and sources of toxic pollution in the coastal waters of the Caucasus;

4) assessment of the level of pollution by marine macro debris, as well as research into the sources of its entry into the sea;

5) assessment of the structural characteristics of marine communities: concentration of chlorophyll and other photosynthetic pigments, species composition, abundance and biomass of phyto-, meso-, macrozooplankton, zoo- and phytobenthos;

6) assessment of the presence of invasive species (invading species);

7) assessment of the biological consequences of water pollution in coastal waters, the open sea and marine specially protected natural areas.

New stations were proposed covering all ecological regions of the coastal waters of the Caucasus and the central zone of the eastern part of the Black Sea. Particular attention was paid to the Kerch Strait as a narrow channel with intensive navigation and a large source of highly eutrophicated Azov waters. An additional serious source of pollution in the north-eastern part of the sea is anchor transshipment stations (sites) on the shelf south of the Kerch Strait. A narrow strip of heavily polluted waters along the coast from Anapa in the north to Adler in the south is significantly affected by urban sewer discharges, and is also subject to significant pollution due to intensive resort and tourist exploitation. Several stations in the open sea can be considered as background for the calculation of permitted discharges in accordance with Russian legislation. Five stations along the southern maritime border with Abkhazia are needed to control the transboundary

transport of pollutants. For the coastal regions of the Caucasus and the open sea, a new ecological zoning scheme and the optimal spatial arrangement of 51 monitoring stations along the coast and in the open sea, as well as 9 stations in the Kerch Strait were proposed to obtain comprehensive information on hydrological, hydrochemical and biological processes in different parts of the region (Fig. 5).

Based on the data obtained during coastal expeditions of the *EMBLAS* project series in the spring-summer-autumn periods of 2016, 2017 and 2019, some proposals were developed to improve the system of state environmental monitoring of the Black and Azov seas, as well as to form an observation program in the eastern part of the Black Sea, taking into account the principles of ecological zoning. Proposals to expand the capabilities of the national authorities of the Black Sea countries in the implementation of integrated environmental monitoring were based on modern hydrological, hydrochemical and biological data obtained in the course of field research.

Thus, the information obtained using complex methods of modern environmental monitoring will make it possible to identify areas of coastal waters that require priority environmental measures.

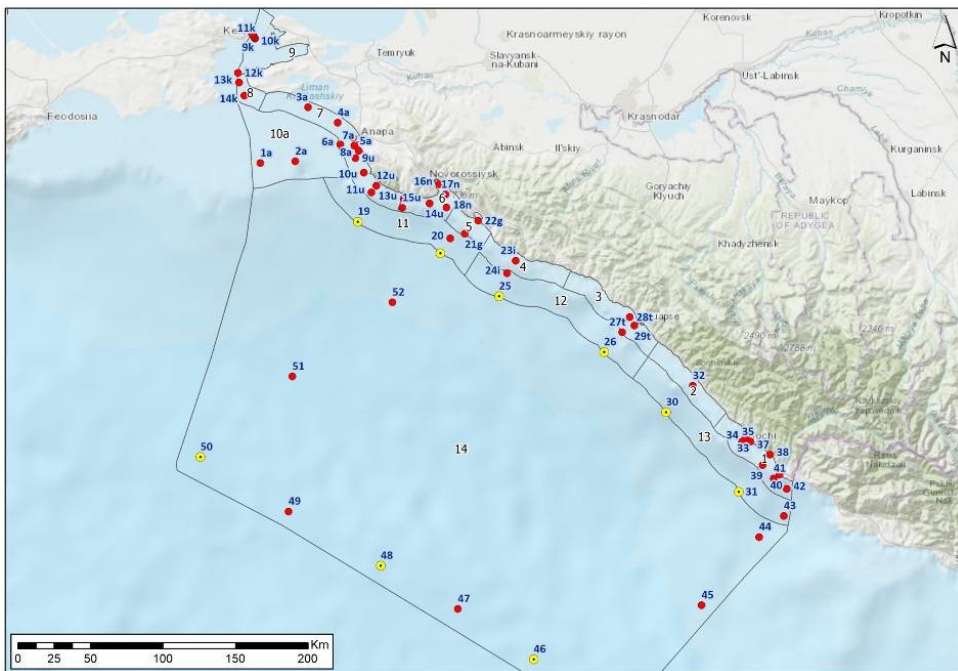


Fig. 5. Scheme of ecological zoning of the eastern Black Sea and integrated monitoring stations proposed for inclusion in the work program. Red dots mark regular stations, yellow ones – background stations

## Conclusions

1. The paper describes the objects and tasks of marine environmental monitoring. Differences in the European and Russian systems of monitoring the marine environment, the orientation of these systems are shown. The Bucharest Convention (1992) is considered, as well as the tasks of the Commission for the Protection of the Black Sea from Pollution and its advisory groups.

2. An analysis of the features, structure and tasks of environmental monitoring of the Black and Azov seas, its means and methods adopted in the Russian Federation is presented. The standards adopted by Roshydromet for the methods of analysis and the layout of offshore sampling stations are described.

3. The directions and possibilities of satellite monitoring of the Azov-Black Sea basin are considered. The latest achievements in the field of remote sensing of the Black Sea in the Russian Federation and the prospects for their development are analyzed. On specific examples for various areas of the Black Sea, the availability of space information systems is shown.

4. The creation of a new system of integrated monitoring of anthropogenic impact on the offshore areas of the shelf regions of the Black Sea coast of Russia and the prospects for its use are considered.

5. It is shown that mathematical models as a modern tool for environmental monitoring make it possible to assess the impact of various types of anthropogenic effect on an ecosystem and obtain a forecast of its evolution.

6. The use of WPI of waters for a comprehensive assessment of the quality of waters in certain areas of the Black Sea is considered. The possibility of comparing the quality of waters in marine areas with different levels of pollution in a retrospective for any selected period is shown.

7. The implementation stages of the international project *EMBLAS* aimed at developing a system of integrated environmental monitoring of the Black Sea in order to fulfil the Bucharest Convention are analysed. A scheme of ecological zoning of the eastern part of the Black Sea with a description of integrated monitoring stations proposed for inclusion in the work program is given.

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**Irina V. Mezentseva** – calculation of WPI for the Black Sea water area, discussion of results

**Tatiyana V. Khmara** – preparation of information of mathematical modelling methods as a tool of ecological monitoring, discussion of results, article editing

**Maria P. Pogozeva** – preparation of illustrations, information of tasks of monitoring as part of EMBLAS project implementation

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

## Variability of Marginal Ice Zone Characteristics and Internal Wave Field near Svalbard according to Sentinel-1 Satellite Data

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### Abstract

The paper presents the results of observations of the ice edge drift and surface manifestations of short-period internal waves according to *Sentinel-1 A/B* spaceborne synthetic aperture radar data in June – September 2019. We analyzed 1200 spaceborne synthetic aperture radar images used to record the ice edge position and 387 surface manifestations of short-period internal waves. During the study period in 2019, the maximum southern position of the drifting ice edge in Fram Strait at 79° N was recorded on 20 June. The ice edge boundary reached its maximum northern position at 82° N on 16 September. The seasonal decrease in ice area in the study region was more intensive in the south-eastern sector. The largest number of surface manifestations of short-period internal waves was detected in August: 162 packets. The maximum probability of short-period internal waves during the study period was observed in the shelf areas to the northwest and south of Svalbard. Internal waves were observed as packets of 4–5 waves. The maximum lengths of the leading wave front were 30–40 km and were observed to the south of Svalbard. Short-period internal waves with leading wave front lengths of 7–10 km prevailed. The highest probability was noted for waves with a packet width of 3–4 km. The paper presents detailed maps of the internal waves' probability and the spatial distribution of their main parameters. The paper analyzes the relationship between the variability of internal wave parameters and that of the ice edge. It is shown that density gradients resulting from ice melting at the ice edge affect the generation and propagation of short-period internal waves. The combination of the melting process, tidal currents and influence of the bottom topography leads to the generation of large packets of short-period internal waves.

**Keywords:** short-period internal waves, spaceborne radar images, marginal ice zone, Svalbard, Fram Strait

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## **Изменчивость характеристик прикромочной ледовой зоны и поля внутренних волн у архипелага Шпицберген по спутниковым данным Sentinel-1**

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### **Аннотация**

Представлены результаты наблюдений за кромкой поля дрейфующих льдов и поверхностными проявлениями короткопериодных внутренних волн по данным спутниковых радиолокаторов с синтезированной апертурой *Sentinel-1 A/B* в июне – сентябре 2019 г. Проанализировано 1200 изображений спутниковых радиолокаторов с синтезированной апертурой, на которых фиксировалось положение границы распространения льдов и было зарегистрировано 387 поверхностных проявлений короткопериодных внутренних волн. В рассматриваемый период 2019 г. максимально южное положение кромки поля дрейфующих льдов в проливе Фрама на 79° с. ш. зафиксировано 20 июня. Крайнего северного положения на 82° с. ш. граница льдов достигла 16 сентября. Сезонное уменьшение количества льда на рассматриваемой акватории происходило более интенсивно в юго-восточном секторе. Наибольшее количество поверхностных проявлений короткопериодных внутренних волн выявлено в августе – 162 пакета. Максимальные значения повторяемости короткопериодных внутренних волн за рассматриваемый период отмечались в шельфовой области к северо-западу и к югу от архипелага Шпицберген. Внутренние волны наблюдались в виде пакетов из 4–5 волн. Максимальные значения длины фронта лидирующей волны составляли 30–40 км и наблюдались к югу от архипелага Шпицберген. Преобладали короткопериодные внутренние волны с длинами фронта лидирующей волны 7–10 км. Наибольшая повторяемость отмечена у волн с шириной пакета 3–4 км. Представлены детальные карты повторяемости внутренних волн и пространственного распределения их основных параметров. Проанализирована связь изменчивости параметров внутренних волн с изменчивостью границы распространения льдов. Получено, что плотностные градиенты, возникающие при таянии льда на кромке ледового поля, оказывают влияние на генерацию и распространение короткопериодных внутренних волн. Сочетание процесса таяния льда, приливных течений и влияния донной топографии приводит к генерации крупных пакетов короткопериодных внутренних волн.

**Ключевые слова:** короткопериодные внутренние волны, спутниковые радиолокационные изображения, прикромочная ледовая зона, архипелаг Шпицберген, пролив Фрама

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## **Introduction**

Currently, there is still interest in the study of internal waves (IWs) in the Arctic seas. Along with studies carried out on the basis of in situ measurements [1–4], satellite observations make it possible to obtain a picture of the spatial distribution of sources of internal wave generation in the entire ice-free water area of the Arctic Ocean. At the moment, studies have been carried out to identify IWs and assess their characteristics with regard to a number of the Arctic seas [5–8]. Yet, the water areas, which are adjacent to Svalbard, were not considered in an integrated manner. At the same time, the waters near the archipelago are characterized by special hydrological parameters, complex system of heat transfer with currents, and constant removal of drifting ice from the northern polar region through Fram Strait [9–11]. Thus, combination of complex bottom topography and tidal water movements near Svalbard establish all the conditions for the possible generation of IWs. According to the results of modeling and in situ measurements made to the north and southeast of the archipelago, short-period IWs (SIWs) were found [1, 8, 12, 13]. In the region under consideration, on the basis of successive measurements of spaceborne synthetic aperture radars (SARs), surface manifestations of SIWs were also identified, and their phase velocities were determined [14].

Nevertheless, a comprehensive study of the sources of generation and propagation of the SIWs near the archipelago and adjacent Fram Strait was not carried out. In this regard, the purpose of this paper is to determine key regions of generation and main spatiotemporal characteristics of the SIWs near Svalbard and in Fram Strait based on the analysis of the array of *Sentinel-1 A/B* satellite SAR images and the consideration of the relationship between the SIW characteristics and the boundary of the drifting ice field in the warm period of 2019.

## **Data and methods**

To analyze the spatial variability of the SIW field in Fram Strait and Svalbard shelf area, *Sentinel-1 A/B* radar images (RI) for June – September 2019 from the archives of the *Copernicus Open Access Hub* system of the European marine forecast centers (<https://scihub.copernicus.eu>) were used.

According to SAR images, the ice edge position and surface manifestations of the SIWs (SM of SIWs) were recorded. Analysis and identification of internal waves in SAR images were carried out in accordance with the technique described in [6]. 1,200 SAR images were analyzed in total, on which 387 SM of SIW were identified. The ice edge position reflecting the ice – open water boundary without taking into account ice concentration was taken as the ice edge.

SAR images were analyzed using *SNAP* © *ESA* (*Sentinel Application Platform*) program (<https://step.esa.int/main/toolboxes/snap/>). This software makes it possible to perform preliminary processing and visualization of SAR images, select the part of interest of the image, draw a section through the SIW packet and determine its main spatial characteristics – the leading wave front length and the packet width.

The procedure of the SAR images analysis was carried out in two stages. At the first stage, the SAR images were subjected to low-pass filtering, i.e., spatial variations of the radar signal field on scales much larger than the IW length were excluded. After this procedure, the manifestations of IW packets on SAR images became more contrasting, and then they were subjected to quantitative analysis.

Fig. 1 shows an example of the IW manifestation on SAR image in the form of three successive packets of SIW. Curve *A–B* is the front length of the leading wave, which made 17.8 km; segment *C–D* is the SIW packet length, which made 11 km. As for the second packet, the front length of the leading wave made 47.4 km, and the SIW packet length made 15 km. The front length of the third packet leading wave made 61.4 km, and the SIW packet length made 15 km.

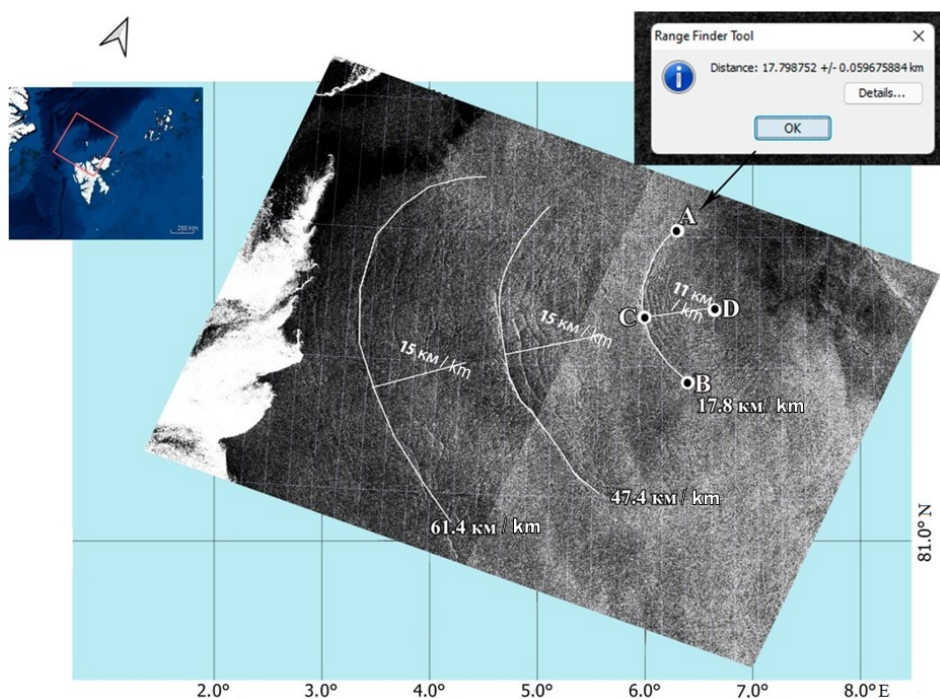


Fig. 1. Enlarged fragment of the original *Sentinel-1 B* SAR image of 15 August 2019 with manifestation of three successive packets of SIWs. *A–B* is the front length of the leading wave of the SIW packet; *C–D* is the SIW packet length

Processing of the analysis results and construction of the spatial maps of various SIW characteristics were carried out in the *MathWorks* © *Matlab* environment.

### **Variability of the ice edge position**

Since the identification of the SM of SIWs is possible only in open water, the ice edge drift position was recorded using the SAR images in order to obtain a general picture of the ice conditions in the study area.

During the study warm period in 2019, the difficult ice conditions in the region took place due to the abnormally increased frequency of atmospheric processes of the eastern (*E*) and meridional (*C*) circulation forms and the intensive transfer of ice from the northern polar area. At the same time, southeasterly and southerly winds prevailed at a speed of up to 6–7 m/s. At the end of the period, in the second half of September, northerly and northwesterly winds with a speed of 7–8 m/s dominated <sup>1)</sup>.

At the beginning of June 2019, the ice edge adjoined the northern coast of Svalbard. The ice spread along the eastern coast of the archipelago up to 75° N (Fig. 2, *a*). To the south of Svalbard, the ice occupied the entire space from 17° E and further eastwards.

In the following days, unlike in previous years, the ice continued to move southward to Fram Strait and by 20 June 2019, near the western coast of the archipelago, it reached its maximum southern position at a latitude of 79° N. At the same time, extended polynyas lying beyond the island were formed on the eastern side of the archipelago, in the ice field. At the end of June, the direction of the general ice drift changed and the ice edge started to move slowly backward to the north.

In early July 2019, ice near the northern coast of Svalbard diverged. By the end of July 2019, the area of open water expanded eastward to Hinlopen Strait (22° E). To the north, the ice edge drift moved slightly, not reaching 81° N. In the south, the ice field shifted to the southern extremity of Edge Island, i.e. to 77° N (Fig. 2, *b*).

The seasonal decrease in the amount of ice in the region under consideration was more intense in the southeastern sector. By the end of August (see Fig. 3, *a*), the ice remained only off the southern coast of Nordaustlandet Island. At the same time, Hinlopen Strait was cleared of the ice completely. In the north, the ice edge shifted beyond 81° N.

In September 2019, the ice edge drift continued to move north (see Fig. 3, *b*). The ice drift, which was located in the southeast of the region under consideration, shifted into Hinlopen Strait, where it remained until the last third of September, when the direction of the prevailing winds changed.

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<sup>1)</sup> Frolov, I.E., ed., 2019. [*Quarterly Review of Hydrometeorological Processes in the Arctic Ocean – 3d Quarter 2019*]. Saint Petersburg: AARI, 71 p. (in Russian).

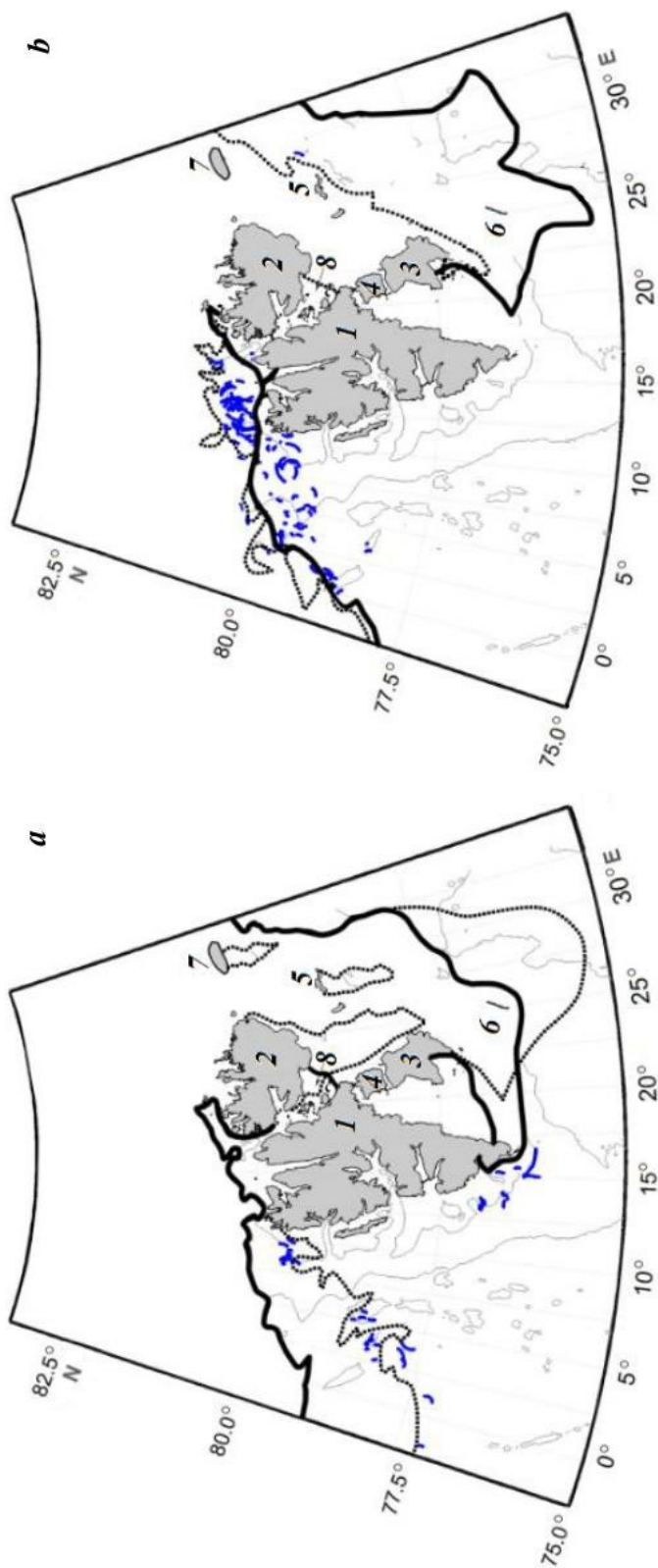


Fig. 2. Position of the ice edge boundary in June (a) and July (b) 2019; the solid line is for the beginning of the month; the dotted line is for the maximum southern position on 16 June 2019 (a) and at the end of July (b). The blue marks denote distribution of leading wave crests in the SIW packets. The numerals stand for: 1 – Spitsbergen Island; 2 – Nordaustlandet Island; 3 – Edge Island; 4 – Barents Island; 5 – King Charles Land; 6 – Hopen Island; 7 – White Island; 8 – Hinlopen Strait

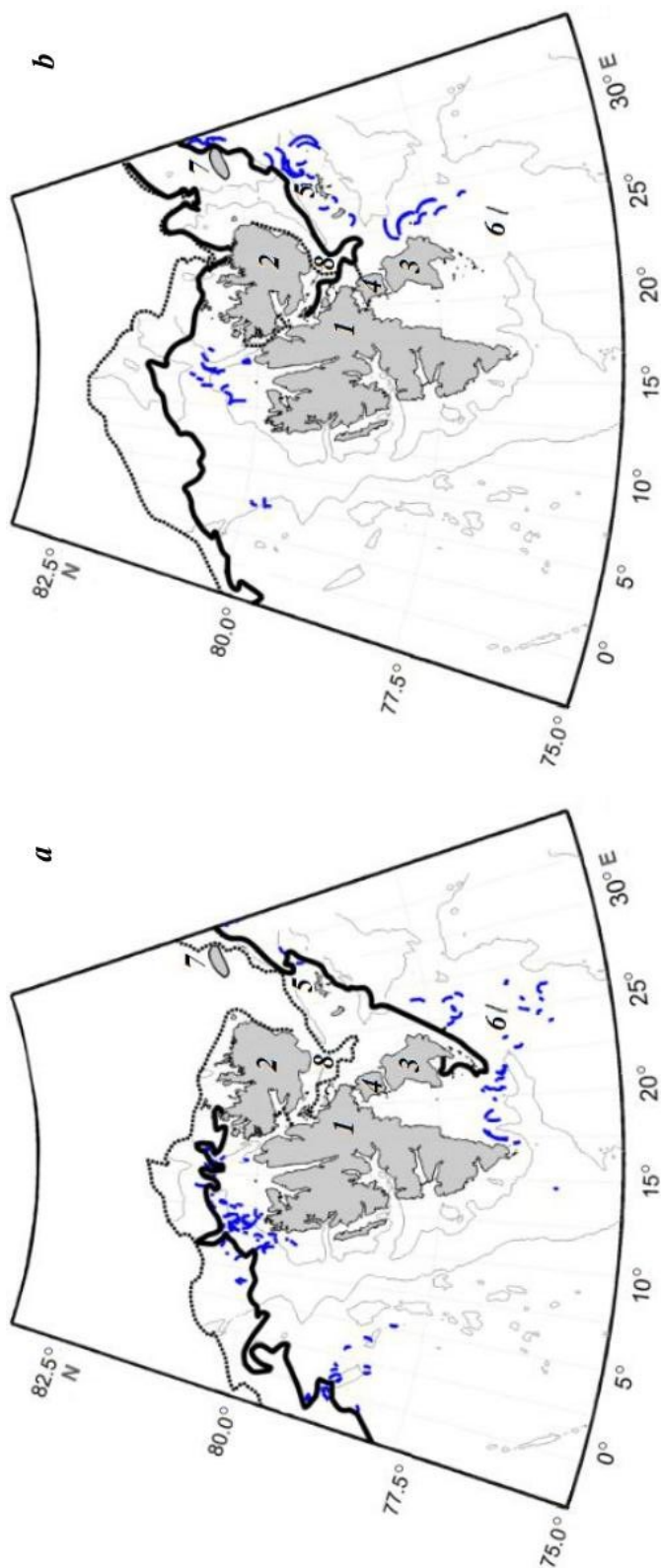


Fig. 3. Position of the ice edge boundary in August (a) and September (b) 2019; the solid line is for the beginning of the month; the dotted line is for the position at the end of August (a) and maximum northern position on 20.09.2019 (b). The blue marks denote distribution of leading wave crests in the SIW packets. The numerals stand for: 1 - Spitsbergen Island; 2 - Nordaustlandet Island; 3 - Edge Island; 4 - Barents Island; 5 - King Charles Land; 6 - Hopen Island; 7 - White Island; 8 - Hinlopen Strait

The maximum northern position ( $82^{\circ}$  N) during the study period was reached by the ice edge on 16 September 2019. Within the next days, the direction of the shift of the ice edge drift changed to the opposite. As of the end of September 2019, in the north, the edge of the ice field was at  $81.5^{\circ}$  N.

#### **Analysis of SAR observations of internal waves**

During the processing of 1200 SAR images, 387 surface manifestations of SIWs were identified in June – September 2019. As a rule, internal waves were observed on RI in the form of packets of 4–5 waves with a characteristic decrease in the distance between them towards the packet tail; single solitons were recorded rarely.

The spatial distribution of leading wave crests in SIW packets in the study area during the warm period of 2019 is shown in Fig. 2 and Fig. 3 by the month and in Fig. 4 in total for the study period. The largest number of waves was detected in August (162 packets) and July (120 packets) (see Table). This is, apparently, due to more pronounced stratification of the upper layer of the ocean, which contributes to a more efficient SIW generation in these months.

In 2019, in the study region, internal waves were observed quite often in the shelf area northwest of Svalbard and in the deep part of Fram Strait. The SM of SIWs were also recorded to the south of Svalbard and near the eastern small islands of the island group of Kong Karls Land and the Kvitøya Island. Most packets were found in these regions.

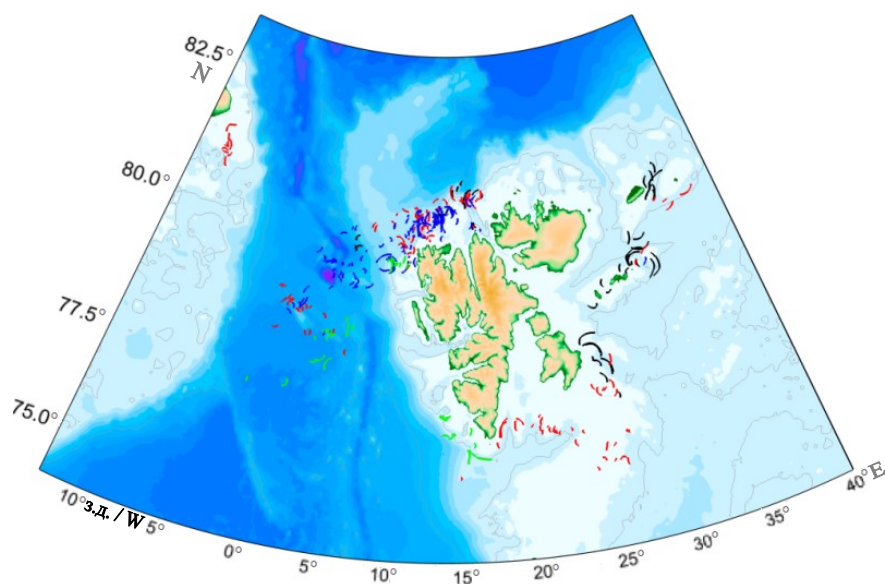


Fig. 4. Spatial distribution of leading wave crests in SIW packets in the study area in June – September 2019 (green – June; blue – July; red – August; black – September)

Number of surface manifestations of short-period internal waves in June – September 2019 identified on 1200 radar images

Month	Number of SM of SIW	Average number of waves per packet
June	44	5–6
July	120	4–5
August	162	5–6
September	61	6–7
Total	387	–

Fig. 5 shows the maps of the spatial distribution of total number of records of SIW packets (see Fig. 5, *a*) and probability of SIW manifestations (see Fig. 5, *b*) on a horizontal grid of  $40 \times 40$  cells.

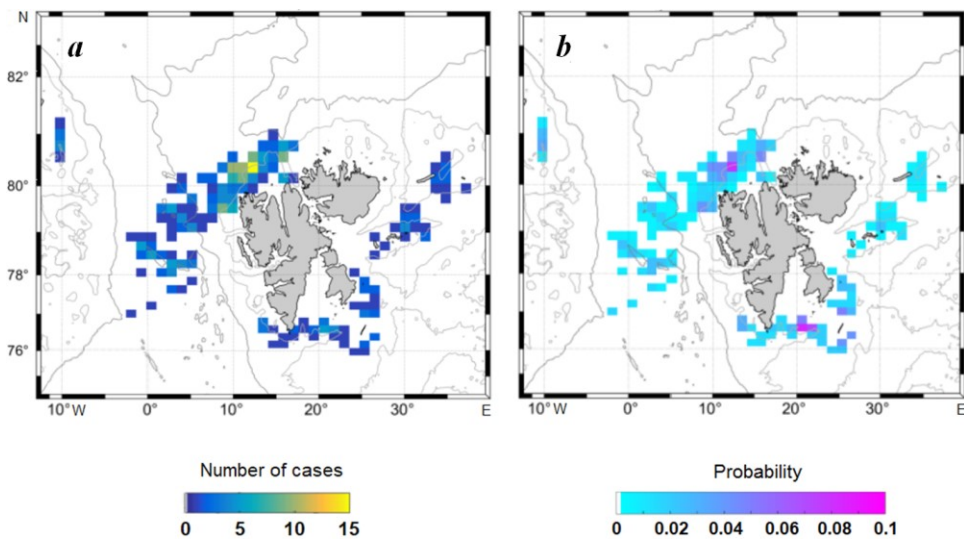


Fig. 5. Spatial distribution of internal wave characteristics in Fram Strait and near Svalbard: *a* – total number of records of SIW packets; *b* – probability of SIW manifestations on satellite radar images

The latter value was calculated as the ratio of the total number of registered SM of SIWs at a given grid node to the number of SAR images of this node. As can be seen from Fig. 5, *b*, the maximum values of SIW probability ( $\sim 0.1$ ) for the period under consideration are registered in the shelf area to the northwest and south of Svalbard.

Fig. 6 shows the maps of the spatial distribution of the mean values of the leading wave front length and the width of the SIW packets on a horizontal grid of  $40 \times 40$  cells. As can be seen from Fig. 6, *a*, SIW packets with a leading wave front length of about 20–40 km were mainly observed in the water area in 2019.

The largest packets of internal waves were recorded at some distance from the areas with inhomogeneous topography, which, apparently, is associated with a more developed field of internal waves away from the immediate areas of IW generation. The maximum value of the leading wave front length (40 km) was registered south of Svalbard and the island group of Kong Karls Land. The SIW packets with the lowest values of this parameter within 1–5 km were recorded mainly near the edge of the ice field.

The width of the SIW packets varied from 1 to 12 km. The maximum values were registered south of Svalbard and the island group of Kong Karls Land. The minimum values from 1 to 5 km in most cases characterize the shelf area to the northwest of Svalbard.

The distribution histogram (Fig. 7, *a*) demonstrates clearly the high probability (more than 50% of all cases of observations) of the SIW front length in 2019 in the range from 10 to 12 km with a pronounced peak for the value of 10 km. The second peak of observations can be attributed to the values of the SIW front

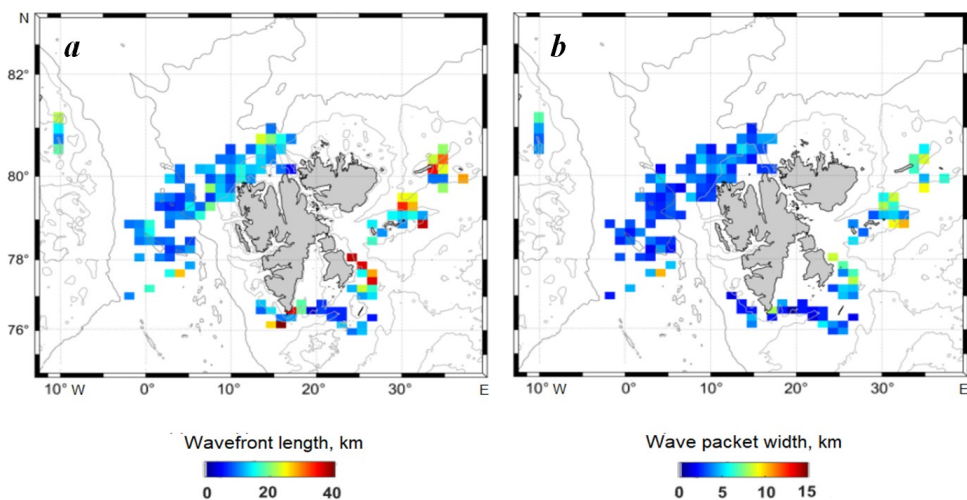


Fig. 6. Spatial distribution of main parameters of internal waves in Fram Strait and near Svalbard in 2019: *a* – length of the leading wave front; *b* – packet width (km)



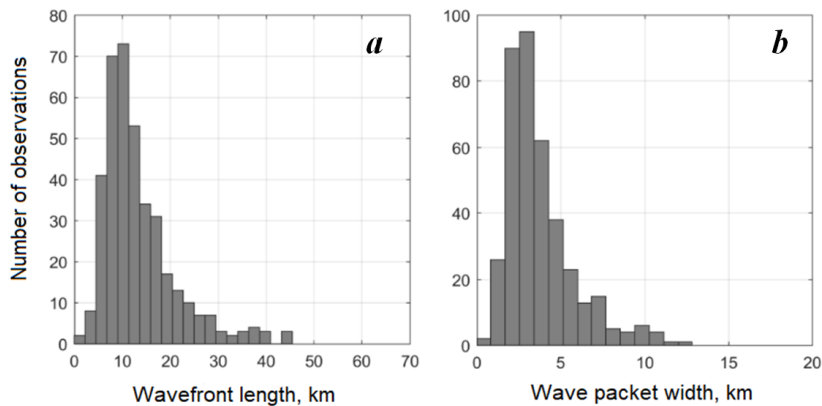


Fig. 7. Histograms of distributions of SIW main parameters in the study area in 2019: *a* – length of the leading wave front; *b* – SIW packet width (km)

length of about 7–8 km. Front length values from 20 to 30 km are found only in 15 % of cases. SIW front lengths from 40 to 50 km were recorded in very rare cases of 5 % only.

Histogram of distribution of SIW packet width (Fig. 7, *b*) shows that its greatest peak took place in the range of 3–4 km. Packet widths of 10–12 km were recorded extremely rarely, in 5 % of observations.

### Results and discussion

Fram Strait and the waters adjacent to Svalbard are characterized by complex water dynamics and specific hydrological conditions, and the topography of the bottom of the study region has significant spatial inhomogeneity. The formation of density stratification is influenced greatly by the presence of a constant ice drift field, which undergoes shifts depending on the season and circulation variability in the polar region. In combination with tidal phenomena, all the above stated features of the study region create conditions for IW generation.

Based on SAR images, an analysis was made concerning the variability of the ice edge position in June – September 2019. It was found that in June 2019, ice spread in Fram Strait to the anomalous southern position off the western coast of Svalbard – up to 79° N. At the same time, the consolidated ice occupied the entire northern shelf area near Svalbard, which in July and August was freed from ice only up to 22° E, shifting to 81° N.

The maximum distance of the ice field from the archipelago was recorded in mid-September 2019 (82° N). The predominance of winds opposite to the ice drift direction in June – August 2019 explains rather high concentration of ice in the study region during this period.

387 SM of SIWs were recorded during the processing of 1200 SAR images. The largest number of SM of SIWs was recorded in August – 162 packets, which is apparently associated with more pronounced stratification of the upper layer of the ocean, which contributes to more efficient IW generation. Internal waves were observed on radar images in the form of packets of 4–5 solitons. The maximum lengths of the leading wave front were 30–40 km and were observed to the south of Svalbard. During the study period of 2019, short-period internal waves with leading wave front lengths of 7–10 km prevailed. The highest probability was noted for waves with a packet width of 3–4 km.

Comparison of the spatial distribution of the surface manifestations of SIWs and the ice edge drift position shows a good correlation (see Fig. 2, Fig. 3), which is confirmed by recent studies [15, 16]. Thus, in June 2019, SIWs were recorded in Fram Strait in deep water and at the southern extremity of the Spitsbergen Island in the immediate vicinity of the ice field edge. In July, SM of SIW were localized in a polynya opened to the north of the Spitsbergen Island, and in Fram Strait to the northwest of the archipelago, but much further to the north than in June.

In August, the position of the ice edge in the north slightly differed from that in July, and, accordingly, SM of SIWs were recorded almost within the boundaries of the same region with a slight shift in the SIW occurrence frequency to the east. To the south and east of Svalbard, SM of SIWs were also recorded mainly along the edge of the ice field, and to the south of the Spitsbergen Island – on the hydrographic polar front.

In September 2019, the main number of SIW manifestations was recorded to the east of Svalbard. At the same time, the length of their front was the largest for the period of the study observations. The generation of large SIW packets in this region was promoted by a combination of two following factors: the interaction of tidal currents and the East Spitsbergen Current with the features of the bottom topography near numerous small islands <sup>2)</sup> and the ongoing process of the melt of the ice preserved in Hinlopen Strait [17]. In September, to the north of the archipelago, at some distance from the ice edge, the minimum number of SM of SIW with short front lengths was recorded.

## Conclusions

Horizontal and vertical density gradients, which can affect the generation and propagation of short-period internal waves, result from ice melt at the ice edge. Since the study region has a certain tidal regime, the interaction of the tidal current and the bottom topography with stratified water layer can also result in the emergence and distribution of internal waves. The combination of the above stated factors leads to the generation of the large SIW packets.

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<sup>2)</sup> Troitskaya, Yu.I., 1995. [*Internal Wave Generation during Passing Round Irregularities by Stratified Shear Flows with Critical Layers*]. Report on Research Project. Grant no. 95-05-15325 (in Russian).

The tasks of future studies are to determine the temporal variability of the SIW parameters, to establish their connection with the tide phase, and to compare the obtained data with the results of numerical modeling using the *Arc5km2018* model.

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**Igor Y. Kozlov** – research task setting, analysis of results, participation in the article writing and arrangement, work on the final manuscript

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

## The Use of Natural Stone in Marine Hydraulic Engineering Construction

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### Abstract

The paper substantiates the feasibility of using natural stone in offshore hydraulic engineering for the purposes of coast protection and construction of protective structures. A review of the Russian and world practice of using natural stone in the construction of offshore structures was made. Russian and foreign scientific, technical and regulatory framework concerning the use of natural stone in marine hydraulic engineering was analyzed. A feasibility study for the need to develop technical requirements for natural stone was completed. A brief assessment of the social, economic and environmental efficiency of the use of natural stone in offshore hydrotechnical construction was carried out, a methodology and criteria for monitoring the compliance of natural stone with the established requirements were developed. At the same time, the actual results of research and development work in the field of studying the properties of building materials and structures, determining the normalized parameters and improving design solutions that meet the safety requirements of structures were used. The accumulated domestic and foreign experience in the use of building materials and technologies, experience in the design, construction and operation of facilities, changes in the legal framework of the Russian Federation are taken into account. The role of natural stone as a building material for structures in marine areas is defined and its key advantages over other materials are identified: environmental friendliness, versatility and simplicity of construction technologies.

**Keywords:** breakwater, coast protection, environmental friendliness, groin, hydraulic engineering, natural stone, protecting structure

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## Применение природного камня в морском гидротехническом строительстве

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### Аннотация

Работа посвящена обоснованию целесообразности применения природного камня в морском гидротехническом строительстве для целей берегозащиты и возведения оградительных сооружений. Выполнен обзор российской и мировой практики применения природного камня в строительстве морских сооружений. Проведен анализ российской и зарубежной научно-технической и нормативной базы, затрагивающей вопрос использования природного камня в морском гидротехническом строительстве. Выполнено технико-экономическое обоснование необходимости разработки технических требований, предъявляемых к природному камню. Выполнена краткая оценка социально-экономической и экологической эффективности применения природного камня в морском гидротехническом строительстве, разработаны критерии контроля соответствия природного камня установленным требованиям. При этом использованы актуальные результаты научно-исследовательских и опытно-конструкторских работ в области изучения свойств строительных материалов и конструкций, определения нормируемых параметров и совершенствования конструктивных решений, отвечающих требованиям безопасности сооружений. Учен накопленный отечественный и зарубежный опыт применения строительных материалов и технологий, опыт проектирования, строительства и эксплуатации сооружений, учтены изменения в законодательстве Российской Федерации. Определена роль природного камня в качестве строительного материала для сооружений в морских акваториях, обозначены его ключевые преимущества перед другими материалами, из которых особого внимания заслуживают экологичность, универсальность и простота технологий строительства.

**Ключевые слова:** берегоукрепление, буна, волнолом, гидротехническое строительство, оградительные сооружения, природный камень, экологичность

**Благодарности:** представленные результаты получены при выполнении работ по государственному заданию на выполнение услуг (работ), в рамках мероприятий по совершенствованию технического регулирования в строительной сфере Государственной программы Российской Федерации «Обеспечение доступным и комфортным жильем и коммунальными услугами граждан Российской Федерации» и в соответствии с Программой разработки национальных стандартов на 2020 г. (1.13.465-1.284.20).

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## **Introduction**

Despite the widespread use of natural stone in marine hydraulic engineering, as well as the reference of natural stone in a number of domestic and foreign regulatory documents, currently there are no formalized technical requirements for natural stone concerning construction in marine areas.

The purpose of the study is to substantiate the utility of the development of technical specifications for natural stone used in hydraulic engineering for the purposes of coastal protection and the construction of protecting structures, as well as checking procedure concerning the compliance of natural stone with established requirements.

To achieve the set goals, the following tasks were solved:

- to review the Russian and world practice of using natural stone in the construction of offshore structures in marine areas;
- to analyze the Russian and foreign scientific, technical and regulatory framework concerning the use of natural stone in marine hydraulic engineering, results of research and development work in the field of studying the properties of building materials and structures, determining the normalized parameters and improving design solutions that meet the safety requirements of structures;
- to substantiate the feasibility of the use of natural stone in marine hydraulic engineering for the purposes of coastal protection and construction of protective structures, determining its key advantages over other materials;
- to complete a feasibility study for the need to develop technical requirements for natural stone;
- to assess the social, economic and environmental efficiency of the use of natural stone in offshore hydrotechnical construction.

### **Analysis of the Russian and world practice of using natural stone in marine hydraulic engineering construction**

As a rule, abroad (England, the Netherlands, France, Italy, Cyprus, the USA, Asian countries) rubble-mound coast protection structures are built in order to protect the coast. Rubble-mound beach-holding groins and breakwaters are widespread in the above stated regions. Moreover, rubble-mound berms are widely used to protect coasts in non-recreational areas. Rubble-mound structures, in comparison with concrete ones, are better combined with the natural coastal landscape and are preferable from the environmental point of view. It should be noted that monitoring of structures and coastal processes is carried out during the entire period of their operation. When performing lithodynamic studies for the purposes of marine coast protection and protecting structures design, it is recommended to consider not a local emergency section of the coast, but the entire lithodynamic system as a whole.

In foreign practice, massive seawalls are also quite often used, as they perceive loads from waves that break directly on the structure. In the USA,



the stability of such walls in the event of erosion of foundation soils is usually provided by pile foundation and a steel sheet-pile shield, which is impervious to the soil underlying the wall. The base of the seawall is often reinforced with a beached bank made of large stone, less often with a protective wave-damping beach<sup>1)</sup>. In Asian countries (Japan, Taiwan), wave-damping covers (aprons) made of stone or profile solid monoliths are used to protect seawalls [1, 2].

Sloping revetments made of one or more layers of stone are used as a more efficient structure compared to seawalls with no destructive effect on the beach located in front of them (Fig. 1).

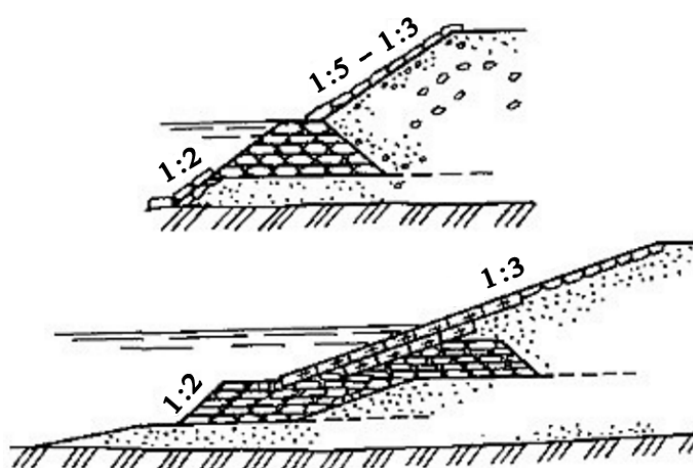


Fig. 1. Design of sloping revetments using natural stone

During the construction of sloping revetments abroad (Holland, England, USA, Japan), the structures can be made of stone in the form of a dump or laying made from a quarry mass of heterogeneous size. In this case, the role of the return filter can be performed by geosynthetic materials. Sloping revetments made of natural stone allow significant subsidence without compromising their functional purpose.

Currently, breakwaters are also widely used in coast protecting construction abroad. They differ in their construction materials and in the cross section design. The materials used for the breakwater construction are natural stone and concrete [3, 4]. The examples of coastal protection with the help of sloping revetments and breakwaters are shown in Fig. 2.

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<sup>1)</sup> U.S. Army Corps of Engineers, 2002. *Coastal Engineering Manual. Engineer Manual 1110-2-1100*. Washington, DC: U.S. Army Corps of Engineers (6 volumes).

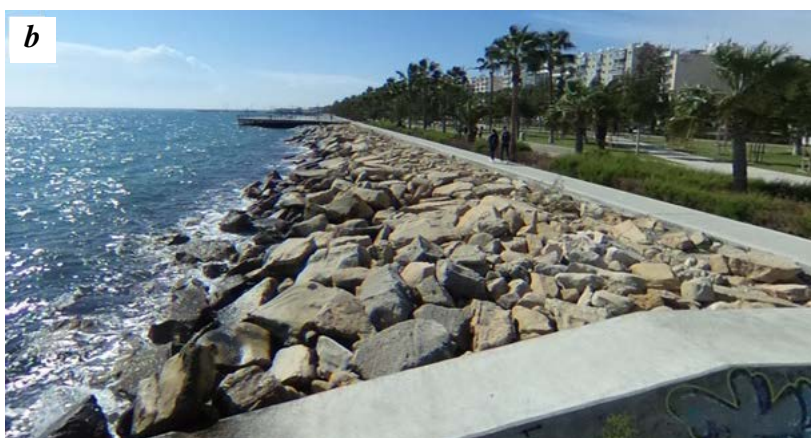


Fig. 2. Examples of coastal protection using natural stone: *a* – stone sloping revetments, Oregon (the USA); *b* – stone sloping revetments, Cyprus; *c* – breakwaters on the Italian Adriatic coast

Groins are most often used to keep beach-forming material (sand or pebbles) from moving along the coast and to accumulate material in the spaces between the groins. To construct groins, stone is usually used, and less often concrete. Wood and steel are not used on the banks with pebble deposits. In the USA, on rocky soils, preference is most often given to gravity-type groins made from a rock blanket or in the form of cells made of steel sheet-pile with stone or sand material and laying on top of a monolithic concrete plate or a natural stone protective covering.

If it is necessary to ensure their imperviousness (on the shores with sand deposits), rubble-mound groins are made with a core of a quarry mass containing a significant amount of fine fractions. In a number of European countries, rubble-mound groins are arranged most often (see Fig. 3).

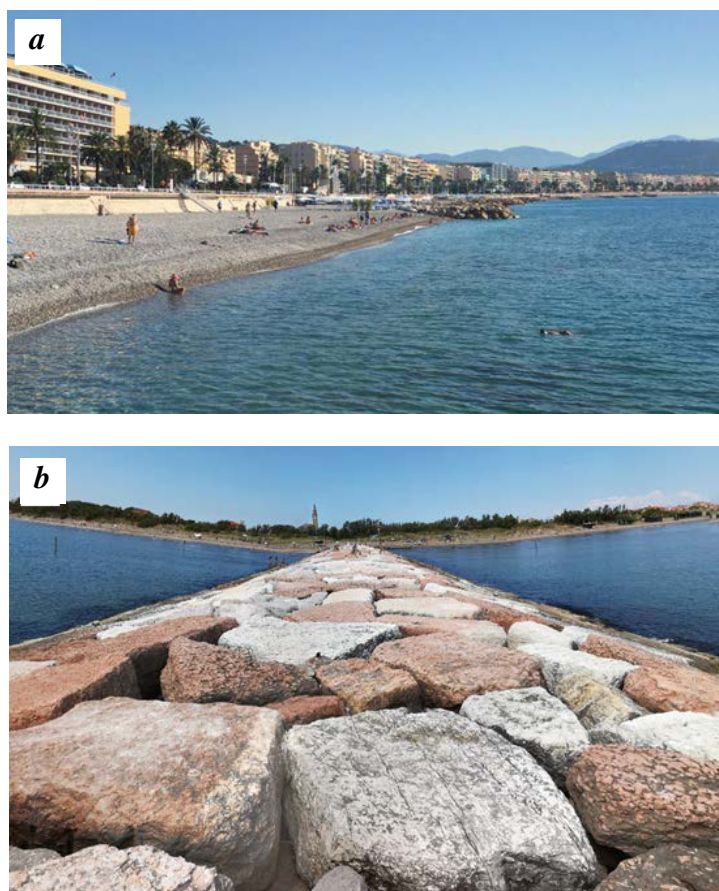


Fig. 3. Rubble-mound groins: *a* – seawalls protected by a beach with rubble-mound groins, Nice (France); *b* – rubble-mound groins Venice (Italy)

In the Russian practice of coast protecting hydraulic structures (HSs) construction, natural stone blanket is the simplest way, and at the same time quite reliable one, to protect the slope against erosion. Nowadays, this structure is used more and more often, since much attention is paid to the possibility of using the coast for recreational purposes and to the environmental component of the project (comfortable habitat for marine fauna) when designing coast protecting measures.

To protect sections of the seacoast that are not used for recreational purposes, the use of rubble-mound berms is most effective. This protecting method is very common due to low labor intensity, ease of repair and restoration. It is disadvantageous in water perviousness, which makes it necessary to protect the bulk soil against sloughing and suffusion, e.g., with the use of geotextiles. The examples of the use of rubble-mound coast protecting structures are shown in Fig. 4, *a*.

In the Russian hydraulic engineering, the practice of coast protecting against erosion with the help of artificial beaches under the protection of groins and breakwaters, including rubble-mound ones, is widespread. Foreign and domestic experience in the design and construction of marine coast protecting hydraulic structures shows that the beach is the best wave-damping structure to protect the coast against erosion. In turn, the protection of beaches with rubble-mound structures is considered to be the best way to protect the coast due to its environmental friendliness, possibility of combining coast protecting and recreational functions, as well as the possibility of preserving the natural landscape. If the requirements of the project are observed and the quality of the laying is good, structures look rather aesthetically pleasing.

It should be noted that there is no prohibition on the construction of natural stone structures in recreational areas. As a rule, signs are installed on such beaches with a warning about the danger of being on rubble-mound structures. An example of the use of coast protecting natural stone structures on the Black Sea coast of Russia is shown in Fig. 4, *b*. Reinforced concrete plates on top of the groins make it possible to increase the accessibility of facilities for vacationers, including disabled people.

Fig. 4, *c* also shows the examples of partly ruined rubble-mound groins at the Tuapse – Sochi section. The shore horizon runs along the deformed heads of such groins. Nevertheless, even partly ruined groins fulfill their function. They hold the beach.

#### **Analysis of the Russian and foreign scientific, technical and regulatory framework concerning the use of natural stone in marine hydraulic engineering**

The method used in Russia to calculate mound coast protection includes determining the required size of a homogeneous stone or deformation of a protecting structure when using non-uniform size materials of a given particle size distribution, as well as the required protection thickness.



Fig. 4. Use of natural stone in Russian hydrotechnical construction: *a* – rubble-mound revetment at the right bank of the Nechespsukho River in the village of Novomikhailovsky (the Krasnodar Region); *b* – a rubble-mound groin with traverses in the village of Nebug (the Krasnodar Region); *c* – partly ruined rubble-mound groins at the Tuapse – Sochi section

The design of marine coast protection and protecting structures is based primarily on the correct consideration of natural geomorphological, lithodynamic and hydrological conditions. Such conditions are considered in the main document regulating the design of marine coast protecting HSs in the Russian Federation, namely, SP 277.1325800.2016 *Coastal Protection Constructions. Design Rules*. This document has been developed for tideless seas (as well as lakes and water-storage basins). It provides approximate areas and conditions concerning the use of groins (without specifying the material of structures), underwater breakwaters (without specifying the material of structures), wave-damping berms and blankets made of large stone. These conditions must be guided by the initial choice of the type of structures. Recommendations are given for choosing the type of beach-holding structures, depending on the type of coast, coastal configuration according to the plan, hydro- and lithodynamic regimes of the sea coastal zone, geological and geomorphological characteristics of the coastal slope, etc. Schemes for the formation of planned outlines and sections of artificial beaches in combination with beach-holding structures are given.

The document also contains requirements for the weight and size of stones in the slope coast protection blanket. The choice of groin design is not regulated by the document (the use of one or another groin design should be determined by a proper feasibility study).

The document recommends to give preference to spreading profile breakwaters of rubble-mound construction when constructing artificial beaches under the protection of underwater breakwaters on the coasts used as recreational areas. Moreover, the requirements for the estimated weight of the groin stones are given.

It is important to note that such Russian seas as the Black Sea, the Sea of Azov, the Caspian and Baltic Seas are tideless (with mild tides). The Arctic seas (the Barents, Kara, Laptev and East Siberian Seas), the Far Eastern seas (the Bering, Okhotsk and Japan Seas), as well as the White Sea are tidal. Ignoring tidal phenomena or insufficient scientific substantiation of design solutions in such areas can lead to a violation of the integrity or to the complete destruction of structures [5]. In this regard, in addition to SP 277.1325800.2016, the document SP 416.1325800.2018 *Engineering Protection of Tidal Sea Coasts. Design Rules* has been developed. According to this document, recommendations are given to pervious (e.g., rubble-mound) breakwaters when constructing artificial beaches under the protection of underwater breakwaters on the coasts used for recreational areas. According to the Russian Industry-Specific Construction Standard VSN 5-84/MMF *Use of Natural Stone in Marine Hydraulic Engineering Construction*, it is recommended to use natural stone for the construction of sloping revetments and wave-damping blankets. In SP 416.1325800.2018, a formula is given for determining the minimum mass of profile blocks (solid monoliths) or large armor blocks for the construction of the outer part of the laying or the mound of sloping revetments and wave-damping blankets exposed to the effects of waves breaking on them. Tidal phenomena can have a significant impact on the timing

of the HSs construction, which once again emphasizes the need for careful consideration and proper accounting of all natural phenomena at the construction site. The same applies to HSs built in the Arctic seas, where, in addition to tidal phenomena, construction is complicated by such natural conditions as high ice forces, as well as a very short navigation period.

In SP 38.13330.2018 *Loads and Impacts on Hydraulic Structures (Wave, Ice and Ship-Produced)*, a requirement is given to take into account the roughness of the slope surface and the filtration properties of the slope material when determining the height of the slope surge. The requirements concerning the weight of the stone are given in Chapter 5. Currently, such requirements should be applied in accordance with the List of National Standards and Codes of Rules (Parts of such Standards and Codes of Rules), which provides obligatory compliance with the requirements of the Federal Law *Technical Regulations on the Safety of Buildings and Structures* approved by the Decree of the Government of the Russian Federation. Formulas are given in order to determine the calculated mass of an individual element when protecting a slope with the rubble stone. When calculating according to these formulas, only its density is taken into account from the characteristics of the stone itself.

In SP 277.1325800.2016 *Marine Coast Protecting Structures. Design Rules*, the conditions for the use of coast protecting structures, including groins, underwater breakwaters, wave-damping berms and blankets made of the large stone are given. The document provides recommendations for the construction of an underwater banquet or underwater breakwater from mound or other structure at the foot of the beach if the design profile of the relative dynamic equilibrium of the artificial beach under construction does not match the natural underwater slope due to the large steepness of the latter. According to this document, recommendations are given to pervious (e.g., rubble-mound) breakwaters when constructing artificial beaches under the protection of underwater breakwaters on the coasts used for recreational areas. As the most effective protective coating of the sea slopes of protective dams against destruction under the impact of waves, ice, currents and precipitation, a sloping-stone coating is given, which significantly dampens wave energy and reduces the surge height. In the document, stone mounds and beached banks also made from the rock mass are considered as one of the recommended types of sloping revetments. It is recommended to use gravity-type groins (including rubble-mound groins) to hold an artificially filled-out beach.

According to this document, in order to construct rubble-mound groins and protective coatings, the homogeneous work stone from sedimentary, crystalline or metamorphic rocks with a compressive strength in the water-saturated state of at least  $6 \cdot 10^7$  Pa, should be used. To determine the minimum mass of stone for the construction of rubble-mound structures, reference is made to Appendix B of SP 38.13330.2018.

The construction rules and regulations SNiP 3.07.02-87 *Hydraulic Marine and River Transport Facilities* contain requirements for the performance of work on the construction of new, reconstruction and expansion of existing marine and river transport hydraulic structures, including ones made from natural stone (Chapter 4). Concerning requirements for the natural stone quality, an instruction is given to use stone materials in construction that comply with VSN 5-84/MMF.

*Guidelines for the Design and Construction of Flexible Reinforced Concrete Slope Coating of Transport Facilities*<sup>2)</sup> are used in the design of wave-damping structures to protect the slopes of transport structures and river banks against the water flow impact. The document provides some requirements for the size of the natural stone in specific structures, but its scope does not allow its provisions to be used for the purposes of this paper.

Regulatory document RD 31.31.55-93 *Instructions for the Design of Marine Berthing and Coast Protecting Structures* as a requirement for the quality of the stone contains the following reference to VSN 5-84/MMF: “The stone for the construction of backings, beds under the berthing facilities and the formation of berthing slopes must meet the requirements of VSN-5-84/Minmorflot.”

The departmental document VSN 5-84/MMF, which is referred to in SP 416.1325800.2018, SNiP 3.07.02-87 and RD 31.31.55-93, contains requirements for the natural stone and applies to the design and construction of marine HSs (mooring, land retention, coast protecting, etc.), located on the coasts of seas, estuaries, lagoons or at the mouths of rivers. The document establishes technical requirements for the natural stone quality (determination of the temporal compressive strength of the rock in dry and water-saturated states, softening coefficient, frost resistance, dry rock density, petrographic composition, water absorption, density of grogs, SO<sub>3</sub> content). Recommendations are given on the ratio of the largest size of the rubble stone to the smallest (for land retention and coast protecting structures it makes no more than 3, for all others – no more than 4).

International strictly formalized regulatory documents in the field of coast protection (*Design Manuals* or *Codes*) have not been developed, since there the design of coast protection is based on accumulated experience and operational engineering assessment [6]. Special *Design Guidelines* are used in foreign countries in the design process, as they contain grounded guidelines. Such guidelines can be applied freely enough and are developed with the involvement of specialized scientific organizations.

In 1984, the British Standards Institution (BSI) developed and issued *Maritime structures. Code of practice for general criteria*<sup>3)</sup>. The document deals

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<sup>2)</sup> TsNIIS, 1984. [*Recommended Practice for the Design and Construction of Flexible Reinforced Concrete Slope Covers for Transport Structures*]. Moscow: TsNIIS, 55 p. (in Russian).

<sup>3)</sup> BSI, 2000. *Maritime Structures: Code of Practice for General Criteria. BS 6349-1:2000*. London: BSI, 254 p.



with the use of the stone as a material for the construction of coast protecting structures. Moreover, the provisions are given regarding the quality control of the stone and the specification of the size of the fractions. Nevertheless, the document is non-regulatory, and its use abroad is advisory.

The following document is also applied in Great Britain – *The Rock Manual. The Use of Rock in Hydraulic Engineering* <sup>4)</sup>. In addition to guidelines for the design, construction and monitoring of the state of natural stone structures, it provides a set of requirements for the stone itself, overview of the properties and functions of the quarry stone, forecast of the rock quality, durability and service life, specification of the stone according to its size, testing and measurement, quality control, etc.

In the USA, where the US Army Corps of Engineers controls coast protection, *Shore Protection Manual* of 1984 had been applied until 2002. This manual was widely used throughout the world. In 2002, the document was republished under the name *Coastal Engineering Manual* taking into account modern European achievements in the field of coast protection. No technical requirements for natural stone are contained in the document.

Requirements for the natural stone used in the construction of rubble-mound structures are contained in *ISO 21650:2007 Actions from Waves and Currents on Coastal Structures*. In particular, the document says that the stone for breakwater construction must be hard and have sufficient resistance to destruction, since it is subject to abrasion and crush.

The document also provides calculation provisions for determining the quantitative characteristics of stone structures. A general formula is given for calculating the minimum mass of individual elements of the mound (the probability of destruction of a stone subject to abrasion and crush is characterized by the energy of the wave impact and the energy required to destroy the stone). The formula takes into account the density of the stone, its dimensions and the height of the waves. The mass of an individual element of the mound is taken into account when calculating the stability of the structure and when determining its dynamic balance profile. In the probabilistic analysis of the durability of structures exposed to waves and currents, the strength parameters of the material are taken into account, as well as the coefficient of friction at the interface between different materials. The slope of rubble-mound breakwaters is a function of the depth and particle size distribution of the mound material.

The Spanish document *ROM 0.5-94 Geotechnical Recommendations for the Design of Maritime and Harbour Works* <sup>5)</sup> contains recommendations for choosing the size of the stone that can be obtained in a particular quarry, as well as for checking its perviousness and mechanical properties (strength and deformability).

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<sup>4)</sup> CIRIA, 2007. *The Rock Manual. The Use of Rock in Hydraulic Engineering*. London: C683, 1304 p.

<sup>5)</sup> Spanish National Port Authorities, 2005. *ROM 0.5-94 Geotechnical Recommendations for the Design of Maritime and Harbour Works*. Puertos del Estado, 430 p. Available at: [https://www.puertos.es/es-es/\\_layouts/download.aspx?SourceUrl=/es-es/BibliotecaV2/ROM%200.5-94%20\(EN\).pdf](https://www.puertos.es/es-es/_layouts/download.aspx?SourceUrl=/es-es/BibliotecaV2/ROM%200.5-94%20(EN).pdf) [Accessed: 10 June 2022].

According to the document, if there is only low-quality rock near the construction site (compressive strength makes less than 50 MPa or specific gravity makes less than 26 kN/m<sup>3</sup>), the area of its use should be limited to the core of the breakwater or at most an intermediate layer. In such cases, the outer mound layer must be constructed with the use of elements of a different type.

Durability can be indirectly determined by laboratory tests, followed by comparison of the results obtained with the recommended reference values of the relevant parameters in each area of the breakwater. The quality of the rock in the laboratory should also be checked when choosing aggregates for concrete. The document also provides recommendations for determining the rubble-mound resistance to shear stress, its perviousness and deformability.

The use of natural stone in marine hydraulic engineering construction is considered in the published works of one of the authors of this paper [7, 8]. The published paper proposes qualitative and quantitative criteria for the applicability of some types of structures of artificial islands in marine areas. Specifically, the slope profile structures with the natural stone slope protection are considered. It is important to note that when constructing slopes of natural embedding (sandy or pebble ones, which are not reinforced with the stone), significant deformations of the slopes are often predicted or observed, up to their complete erosion [9, 10].

Natural stone slope protection is recommended with its sufficient feasibility study: as a rule, such protection makes it possible to increase the slope steepness and, accordingly, reduce the consumption of materials and the cost of construction. The expediency of the use of thrust elements of an underwater banquet, e.g. made of large stone, is determined by a decrease in the volume of the stone filled into the banquet body. At the same time, it is emphasized that the economic feasibility of the artificial island sloping structures construction depends primarily on the depth of the water area at the construction site. As a rule, it is more appropriate to use vertical structures at significant depths. What is more, it is necessary to provide for regular measures to replenish the loss of beach material in accordance with the results of calculations and (or) modeling.

### **Technical requirements for the natural stone characteristics**

The natural stone, along with profile solid monoliths (such as hexabits, tetrapods, etc.), is one of the most common types of elements used for the construction of coast protection and protecting HSs. The stone, as well as profile solid monoliths, is used in the construction of stone wave-damping blankets (berms), designed to provide protection of natural coastal cliffs (including dune slopes), sloping revetments, seawalls and other facilities located in the inshore and near-shore zones of the sea against wave impact (slaps, surges and underwashing).

Stone blankets in areas, which are composed of non-eroded soils and are not used for resort purposes, are equivalent to beaches in terms of wave-damping efficiency, but unlike the latter, they are more stable and practically do not require any regular replenishment of volumes.

According to the experience of design (including the use of physical modeling methods), construction and operation of wave-damping blankets, among the main factors determining the wave-damping capacity, the accent is given to the porosity of the mound, the shape of the stone, the steepness of the slope from the sea side and the mark of the mound top.

The stone and crushed stone are the main materials for the construction of wave-damping coast protection and protecting structures. In recent decades, stone has been used in the construction of hydraulic structures in the ports of Sochi, Imeretinskiy, Vanino, Kuryk, etc.

It is important to understand that the stone of proper quality with strictly defined characteristics should be used for effective wave damping. Otherwise, there is a rapid destruction of wave-damping coast protection and protecting structures due to the erosion by waves, which causes significant economic and environmental damage. To achieve these goals, the staff of the Subdivision of JSC TsNIITS "Research Center "Sea Coasts" in the City of Sochi developed and approved the national standard GOST R 70021-2022 *Natural Stone for Marine Coast protection and protecting Structures. Specifications*. This document stipulates the technical requirements for the natural stone used for the construction of marine coast protection and protecting structures of all classes, as well as berthing slopes and beaches.

The developed standard will contribute to the following:

- reduction of the level of danger during the operation of the stone wave-damping coast protection and protecting structures;
- reduction of the risk of emergencies and subsequent social and economic, environmental and other types of damage;
- reliability improvement of the stone wave-damping coast protection and protecting structures;
- reduction in expenses for repair and reconstruction of the stone wave-damping coast protection structures;
- increase of the wave-damping efficiency of the stone structures.

### **Conclusions**

Currently, the natural stone is used everywhere in the construction of coast protection and protecting structures in marine areas, since it has such significant advantages as environmental friendliness, free deformability, versatility and easy handling.

In the Russian hydraulic engineering, the natural stone mounds are used increasingly due to the simplicity of construction technology, high reliability and significant effectiveness of slope protection against erosion. Such structures are used more and more often, since when designing coast protecting structures, much attention is paid to the recreational function of the coast, as well as to the environmental component.

Rubble-mound berms have also found wide application due to their low labor intensity during construction, ease of repair and restoration. At the same time, it is necessary to provide for the protection of bulk soil from sloughing and suffusion (using geotextiles or other means).

In the hydraulic engineering practice, beaches are considered the best wave-damping structures with good reason. In turn, the protection of beaches with rubble-mound structures is generally accepted as the best way to protect the coast due to the possibility of combining coastal protection and recreational functions, environmental friendliness, as well as the possibility of preserving the natural landscape. With the proper quality of construction work, such structures look rather aesthetically pleasing. It is important to note that laying the top layer of a natural stone structure in order to form a flat surface is not necessary in many cases, since it is more of an aesthetic nature and is associated with additional labor costs. Therefore, the implementation of such laying is advisory.

Foreign and domestic experience in the design and construction of marine coast protecting HSs, as well as the accumulated experience of surveying coastal sections protected by rubble-mound structures, such as groins and breakwaters, have shown their high efficiency as beach-holding structures. In the water area protected by such structures, no dead regions are formed, since even with weak waves stable water exchange processes are observed. Structures in the form of rubble mounds are freely deformable. Therefore, with deformation or even destruction of individual parts, the structure continues to perform its functions. Moreover, elimination of the resulting damage does not require large expenses. As a rule, the natural stone porous mounds are biopositive, as favorable conditions are created in the pores for the habitat of mollusks and other marine fauna representatives.

The method used in Russia to calculate mound coast protection includes determining the required size of a homogeneous stone or deformation of a protecting structure (when using non-uniform size materials of a given particle size distribution), as well as the required protection thickness. At the same time, the basis for the marine HSs design is the correct consideration of the natural conditions of the site. Abroad, design standards for marine coast protection structures are generally non-regulatory and advisory.

For effective wave damping, a stone with certain characteristics and of the proper quality should be used. To improve the reliability of wave-damping coast protection and protecting structures due to the wave impact and to prevent significant economic and environmental damage from such destruction, the staff of the Subdivision of JSC TsNIITS “Research Center “Sea Coasts” in the City of Sochi developed and approved the national standard GOST R 70021-2022. The application of the newly approved standard will prevent significant economic and environmental damage caused by the rapid destruction of wave-damping coast protection and protecting structures due to the erosion through exposure to the waves.

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**Elisey A. Vyaly** – review of the literature on the research problem, development of the research concept, processing and description of the research results, formulation of conclusions

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

## Long-term Dynamics of Underwater Landscapes of the Coastal Zone Cape Kosa Severnaya – Cape Tolsty (Sevastopol)

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### Abstract

Data on the long-term dynamics of underwater landscapes of the coastal zone at Cape Kosa Severnaya–Cape Tolsty are given for the first time for the period from 1964 to 2017. Landscape maps of the water area are made on the basis of landscape and hydrobotanical studies. The distribution of bottom natural complexes with key Black Sea phytocenoses is shown. It is found that the spatial distribution of underwater landscapes and the qualitative and quantitative indicators of their vegetation component have changed over a period of more than 50 years. It is probably due to both natural factors and increased anthropogenic activity. The bottom natural complexes of the boulder benches and upper shoreface consisting of psephitic sediments with dominance of *Ericaria crinita* and *Gongolaria barbata* typical of depths of 0.5–5 m, have changed the least. These changes touched only the configuration of their boundaries and the depth of their distribution. Changes were noted in the vegetation component: macrophytobenthos biomass values increased, a high proportion of phytocenosis edificators was identified, epiphytes made a significant contribution, macrophytes appeared that prefer areas with higher levels of marine eutrophication. The most significant transformation of the bottom natural complexes occurred at a depth of 5–15 m. It was noted that the depth of distribution of the following bottom complexes had changed: 1) that of a gently dipping accumulation plain formed by psammitic deposits with admixed shell fragments and predominated by *Phyllophora crispa*, and 2) that of the upper shoreface formed by psephitic deposits predominated by *Gongolaria barbata* with alternation of pebble and gravel deposits and broken shells, where *Phyllophora crispa* predominates. The vegetation component is characterized by a sharp decrease in the contribution of phytocenosis edificators, substitution of perennial macrophyte species by annual ones, and a vertical decrease of the depth of habitat of deep-water species. This is probably due to a decrease in light exposure.

**Keywords:** coastal zone, bottom natural complex, dynamics, macrophytobenthos, Black Sea, Sevastopol

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## **Многолетняя динамика подводных ландшафтов прибрежной зоны мыс Коса Северная – мыс Толстый (Севастополь)**

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### **Аннотация**

Впервые приведены сведения о многолетней динамике подводных ландшафтов прибрежной зоны м. Коса Северная – м. Толстый за период с 1964 по 2017 г. На основе проведенных ландшафтных и гидробиотических исследований составлены ландшафтные карты исследуемой акватории, показано распространение донных природных комплексов с ключевыми черноморскими фитоценозами. Установлено, что за более чем 50-летний период изменилось пространственное распределение подводных ландшафтов, а также качественные и количественные показатели их растительной компоненты, что, вероятно, связано как с влиянием природных факторов, так и с возросшей антропогенной деятельностью. Выявлено, что наименьшие изменения претерпели донные природные комплексы глыбово-валунного бенча и подводного склона, сложенного грубообломочными отложениями, с доминированием эрикарии косматой и гонголарии бородатой, характерные для глубин 0.5–5 м. Эти изменения коснулись лишь конфигурации их границ и глубины распространения. В донных природных комплексах отмечены изменения растительной компоненты: увеличились значения биомассы макрофитобентоса, выявлены высокая доля эдификаторов фитоценозов и значительный вклад эпифитов, появились макрофиты, предпочитающие районы с повышенным уровнем эвтрофирования морской среды. Наиболее существенная трансформация донных природных комплексов произошла на глубинах 5–15 м. Отмечены изменения глубины распространения донного комплекса слабонаклонной аккумулятивной равнины, сложенной псаммитовыми отложениями с примесью битой ракушки, где доминирует филлофора курчавая, и донного комплекса подводного склона, сложенного грубообломочными отложениями, где преобладает гонголария бородатая, с мозаичным чередованием галечно-гравийных с битой ракушкой донных осадков, где господствует филлофора курчавая. Растительная компонента этих комплексов характеризуется резким снижением вклада эдификаторов фитоценозов, заменой многолетних видов макрофитов на однолетние и вертикальным снижением глубин обитания глубоководных видов, которое, вероятно, связано с уменьшением освещенности.

**Ключевые слова:** прибрежная зона, донный природный комплекс, динамика ландшафтов, макрофитобентос, Черное море, Севастополь

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## Introduction

Modern environmental management in the coastal zone of the sea leads to the formation of an unfavorable environmental situation, a decrease in the quality and quantity of natural resources, a reduction in biological and landscape diversity. To solve the issues of rational environmental management in the coastal area, it is necessary to “determine in which direction, at what speed and how specifically the properties of the landscape change both in space and time” [1, p. 198]. According to V.B. Sochava and colleagues, landscape dynamics can only be understood by studying spatial and temporal aspects “in their inextricable connection”<sup>1)</sup>. In the works of G.A. Isachenko [2], the main provisions of the concept of long-term dynamics of landscapes were considered. Questions on the study of the dynamics of territorial landscapes were widely covered in the works of V.N. Sukachev [3], N.A. Solntsev [4], N.L. Beruchashvili<sup>2)</sup>, A.A. Krauklis<sup>3)</sup>, V.A. Bokov<sup>4)</sup>, A.G. Isachenko [5], and I.I. Mamai [6].

However, there are few scientific works devoted to the study of the dynamics of underwater landscapes due to the limited experience of such studies, the lack of methodological foundations<sup>5)</sup> and the accumulated data array [7–9]. In this regard, the study of spatio-temporal changes in underwater landscapes is an urgent task of geographical science.

Until now, the issue of indicators of the dynamics of underwater landscapes remains debatable. It is known that for marine geosystems, the leading functional role in the formation of the environment and ensuring the sustainable development of the biotic component of the coastal ecosystem of the shelf is played by macrophytes, which are considered a landscape-forming factor and an indicator of the originality of morphological complexes of horizontal division of underwater landscapes<sup>5)</sup>. Being a vulnerable component of the coastal zone, macrophytobenthos actively responds to environmental changes, which

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<sup>1)</sup> Sochava, V.B., Krauklis, A.A. and Mikheev, V.S., 1974. [Landscape Dynamics and the Idea of Epifacies]. In: Yu. M. Matarzin, ed., 1974. [*Current State of the Landscape Study Theory: Proceedings of the 7th All-Union Meeting on Landscape Study*]. Perm, p. 9 (in Russian).

<sup>2)</sup> Beruchashvili, N.L., 1972. [Seasonal Dynamics of the Facies Structure and Functioning]. In: TGU, 1972. [*Landscape Collection*]. Tbilisi: Izd-vo TGU, pp. 100–115 (in Russian).

<sup>3)</sup> Krauklis, A.A., 1979. [*Issues of Experimental Landscape Study*]. Novosibirsk: Nauka, 232 p. (in Russian).

<sup>4)</sup> Bokov, V.A., 1983. [*Spatial and Temporal Organization of Geosystems*]. Simferopol: SGU, 55 p. (in Russian).

<sup>5)</sup> Petrov, K.M., 1989. [*Underwater Landscapes: Theory, Study Approaches*]. Leningrad: Nauka, 126 p. (in Russian).

makes it possible to use its quantitative and qualitative indicators to study the state of underwater landscapes [10].

The coastal zone of Cape Kosa Severnaya – Cape Tolsty (Sevastopol) was chosen as a model polygon, which is distinguished by biological and landscape diversity. As part of the bottom vegetation of the studied area, there are species of macrophytes listed in the Red Book of the Russian Federation<sup>6)</sup> and the Red Book of Sevastopol<sup>7)</sup> – *Phyllophora crispa* (Huds.) P.S. Dixon and *Stilophora tenella* (Esper) P.C. Silva.

In this regard, the purpose of the article is to identify spatio-temporal changes in the landscape structure of the coastal zone between Cape Kosa Severnaya and Cape Tolsty based on the quantitative and qualitative characteristics of macrophytobenthos over more than a 50-year period (1964–2017).

### Materials and methods of research

The authors collected, analyzed and summarized the materials of field landscape and hydrobotanical studies (summer period of 1997, 2006 and 2017) carried out in the coastal zone of Cape Kosa Severnaya – Cape Tolsty. Works in the coastal area were carried out with the use of light diving equipment and small boats. When studying the structure of bottom landscapes, the method of landscape profiling was used with a detailed description of key areas (see work<sup>5)</sup> and [8]). In 2017, three landscape and one hydrobotanical profiles were laid, and in 1997 and 2006, hydrobotanical surveys were carried out (Fig. 1). Transect coordinates were determined using a portable GPS receiver (*Oregon 650*) (Table 1).

Divers-researchers passed along the profile, taking photographs and shooting videos, visually describing bottom sediments, using the classification of marine clastic sediments according to their granulometric composition [8]. Sampling of macrophytobenthos was carried out according to the standard method<sup>8)</sup>. Algae were identified by the guide<sup>9)</sup> taking into account the latest nomenclature changes. Isolation of phytocenoses was carried out according to the dominant classification of A.A. Kalugina-Gutnik<sup>8)</sup>. A total of 64 quantitative samples were collected and processed. When analyzing the structure of phytocenoses, the Shannon diversity index ( $H$ ) was used. To analyze long-term changes in the composition and structure of macrophytes (depths of 1–15 m), archival materials from the Institute of Biology of the Southern Seas for 1964 and published data known for this region and collected using a similar method [11] were used.

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<sup>6)</sup> Bardunov, L.V. and Novikov, V.S., eds., 2008. [*Red Data Book of the Russian Federation (Plants and Fungi)*]. Moscow: Tovarishestvo Nauchnykh Izdaniy KMK, 885 p. (in Russian).

<sup>7)</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).

<sup>8)</sup> Kalugina-Gutnik, A.A., 1975. [*Phytobenthos of the Black Sea*]. Kiev: Naukova Dumka, 248 p. (in Russian).

<sup>9)</sup> Zinova, A.D., 1967. [*Identification Guide for Green, Brown and Red Algae of the South Seas of the USSR*]. Leningrad: Nauka, 397 p. (in Russian).

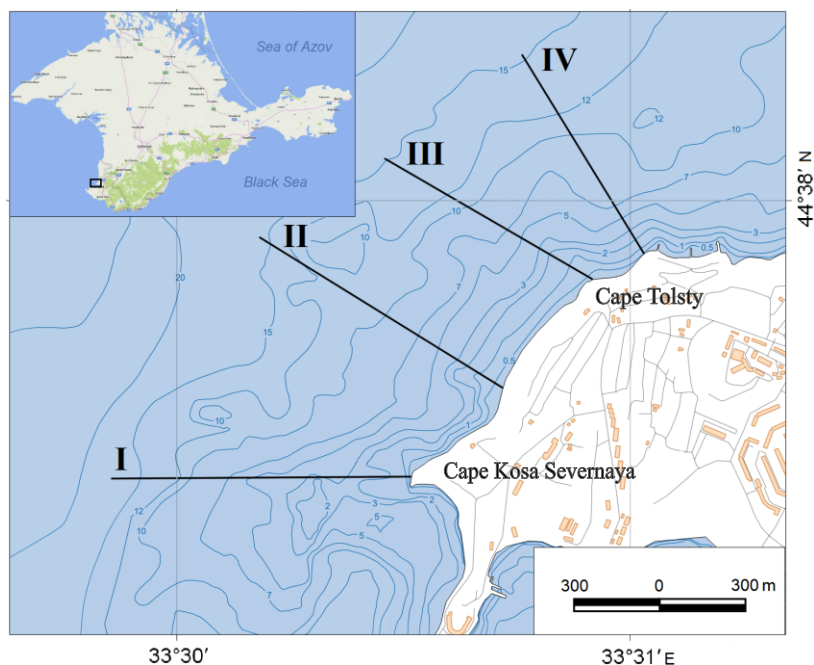


Fig. 1. Schematic map of the location of landscape and hydrobotanical profiles in the coastal zone Cape Kosa Severnaya – Cape Tolsty (2017) (Roman numerals stand for profiles)

Table 1. Coordinates and depth range of hydrobotanical profiles in the coastal zone Cape Kosa Severnaya – Cape Tolsty

Profile	Coordinates		Depth range, m
	Northern latitude	Eastern longitude	
I	44°37.887'	33°30.653'	0.5–15
II	44°37.984'	33°30.811'	0.5–15
III	44°38.306'	33°31.254'	0.5–15
IV	44°38.305'	33°31.440'	0.5–15

To create a landscape map, the *QGIS* 2.14.18 software package and the electronic basis of the bathymetric map were used. The conjugated analysis of the geological structure maps, the topographic map, and the information from the field surveys made it possible to extrapolate water areas with similar parameters to identify the boundaries of bottom natural complexes (BNCs). BNCs are relatively homogeneous bottom areas characterized by the unity of interrelated components: the lithogenic base, the bottom water mass, and

the marine organisms inhabiting them [8]. The georeferencing of the boundaries of landscape complexes was carried out using the *QGIS* program. The landscape map is a cartographic basis, and the BNCs are aquatic units for studying long-term changes in the spatial distribution of the composition and structure of macrophytobenthos.

Statistical data processing was performed using the *MS Excel 2000* (*Microsoft Corp.*) and *Statistica 6.0* (*Statsoft Inc., OK, USA*) software packages. As a result of processing the obtained materials, landscape maps of different years were created (Fig. 2).

### Results and discussion

In the landscape structure of the coastal zone of Cape Kosa Severnaya – Cape Tolsty, BNCs were identified (4 – in 1964; 3 – in 1997; 2 – in 2006; 4 – in 2017) with the participation of dominant macrophyte species of *Ericaria crinita* (*Ericaria crinita* (Duby) Molinari & Guiry = *Cystoseira crinita*), *Gongolaria barbata* (*Gongolaria barbata* (Stackhouse) Kuntze = *Cystoseira barbata*) and *Phyllophora crispa* (*Phyllophora crispa* (Huds.) P.S. Dixon)) (Fig. 2).

#### Landscape structure of the coastal zone Cape Kosa Severnaya – Cape Tolsty (1964) (Fig. 2, a):

1. A boulder bench predominated by *Ericaria crinita* was recorded at depths of 0.5–1 m. The phytocenosis of *Ericaria crinita* – *Cladostephus spongiosus* – *Gelidium crinale* was described in this BNC. The contribution of the community edificator was high (Table 1). As part of the algocenosis, *Ulva rigida* C. Ag. and occasionally *Padina pavonica* (L.) Thivy were noted. Epiphytic synusia was poorly represented (species of the genus *Ceramium*) (Table 2). The values of the Shannon diversity index were low, which indicated a homogeneous structure of the phytocenosis with a predominance of the dominant species (Table 3).

2. An upper shoreface, composed of psephitic deposits, predominated by *Ericaria crinita* and *Gongolaria barbata*, was located at depths of 1–5 m. The phytocenosis *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Gelidium crinale* was described in this BNC. The values of biomass in general in the 1–5 m layer and at shallower depths were comparable (Table 2). The proportion of dominants was the highest for the entire observation period (Table 2). *Ulva rigida* was also noted in the composition of algocenosis. *Vertebrata subulifera* (C. Ag.) Kuntz was noted among epiphytes. The value of the species diversity index indicated the oligodominant structure of the phytocenosis (Table 3).

3. An upper shoreface, composed of psephitic deposits, predominated by *Gongolaria barbata*, with mosaic alternation of pebble and gravel deposits with shell fragments, predominated by *Phyllophora crispa*, was located at depths of 5–10 m. The phytocenosis (*Gongolaria barbata*) – *Phyllophora crispa* – *Gelidium spinosum* was described in this BNC. Its biomass and the contribution of *Gongolaria barbata* dropped by almost half, while the proportion of *Phyllophora crispa* more than tripled with the increasing depth (Table 2). Epiphytic species of algae were practically non-existent (Table 2). The values of the species diversity index were low, which indicated a small contribution of associated and epiphytic macrophyte species (Table 3).

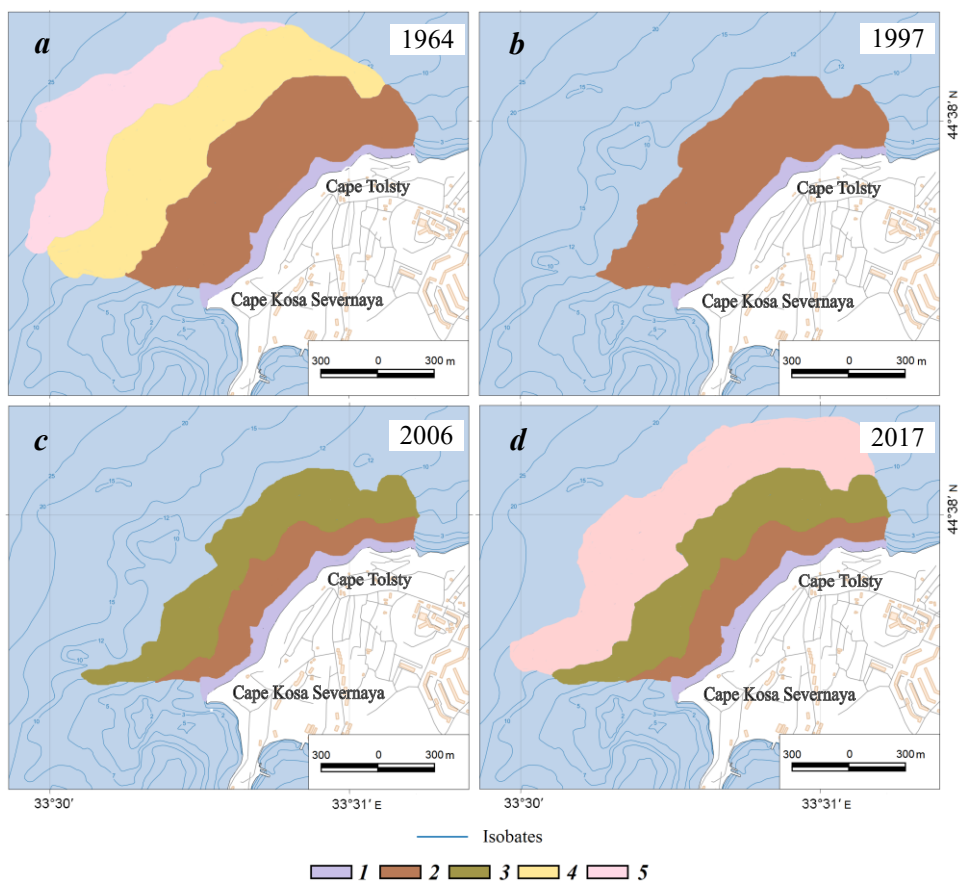


Fig. 2. Schematic map of the landscape structure of the coastal zone Cape Kosa Severnaya – Cape Tolsty:

1 – boulder benches with dominance of *Ericaria crinita*; 2 – upper shoreface consisting of psephitic sediments predominated by *Ericaria crinita* and *Gongolaria barbata*; 3 – upper shoreface consisting of psephitic deposits predominated by *Gongolaria barbata* with mosaic alternation of pebble and gravel deposits and shell fragments predominated by *Phyllophora crispa*; 4 – upper shoreface consisting of psephitic sediments predominated by Dietyota; 5 – gently dipping accumulation plain consisting of psammitic deposits with inclusion of shell fragments predominated by *Phyllophora crispa*.

Table 2. Total biomass of macrophytes, percentage of dominant species and their epiphyts in BNC of the coastal zone Cape Kosa Severnaya – Cape Tolsty (Fig. 2) in various years

Year	BNC	Depth, m	Total biomass of macrophytes, g·m <sup>-2</sup>	Proportion, %		
				<i>Ericaria crinita, Gongolaria barbata</i>	<i>Phyllophora crispa</i>	Epiphytic
1964	1	0.5–1	3040.0 ± 550.9	93	0	1
	2	1–5	3109.0 ± 273.9	94	0	2
	3	5–10	2451.0 ± 236.1 – 1615.0 ± 163.1	84–42	16–52	0
	5	10–15	826.0 ± 51.4	0	75	0
1997	1	0.5–1	3506.7 ± 572.9 – 1492.3 ± 451.5	89–32	0	1–3
	2	1–5	1444.0 ± 381.6	58	0	0
	3	5–10	1141.6 ± 319.3 – 571.1 ± 42.5	68–44	13–20	1
2006	1	0.5–1	3984.2 ± 771.1 – 2786.2 ± 136.1	86–67	0	12–29
	2	1–10	2247.0 ± 538.4 – 591.2 ± 151.9	48–38	0	51–57
2017	1	0.5–1	11457.8 ± 2031.5 – 12888.7 ± 4380.1	94–96	0	5–4
	2	1–10	5572.2 ± 825.2 – 3157.1 ± 501.9	78–65	0	16–33
	4	10–15	130.6 ± 41.2	5	0	15
	5	15–20	74.6 ± 18.6	0	96	3

Table 3. Changes in the values of the Shannon (H) index of species diversity at Cape Kosa Severnaya – Cape Tolsty in various years

Year	Depth, m					
	0.5	1	3	5	10	15
1964	–	0.46	0.45	0.68	0.98	0.99
1997	0.77	2.31	1.58	1.93	2.48	–
2006	0.87	2.03	2.43	1.90	1.84	–
2017	0.45	0.35	1.23	1.90	1.77	0.32

5. A gently dipping accumulation plain consisting of psammitic deposits with admixed shell fragments predominated by *Phyllophora crispa* was located at depths of 10–15 m. The phytocenosis *Phyllophora crispa* was described in this BNC. Its biomass and the proportion of the dominant species were relatively high (Table 2). The epiphytes were absent (Table 1). As part of the algocenosis, *Cladostephus spongiosus* (Huds.) C. Ag., *Gracilaria dura* (C. Ag.) J. Ag. and *Dictyota* sp. were present. The values of the *H* index indicate a low species diversity of the phytocenosis (Table 3).

Landscape structure of the coastal zone Cape Kosa Severnaya – Cape Tolsty (1997) (Fig. 2, b):

1. A boulder bench predominated by *Ericaria crinita* was recorded at depths of 0.5–1 m. In this BNC of 1997, as in 1964, the phytocenosis of *Ericaria crinita* – *Cladostephus spongiosus* – *Gelidium crinale* was described. Its biomass and the proportion of *Ericaria crinita* dropped by more than half with the increasing depth, while at a depth of 0.5 m their values were relatively comparable with those in 1964, and at a depth of 1 m they were two and three times lower, respectively, than in 1964 (Table 2). *Gelidium crinale* (Hare ex Turner) Gaillon (35 % of the total biomass of macrophytes) was abundant in the structure of the algocenosis at a depth of 1 m; *Gelidium spinosum* (S. G. Gmel.) P. C. Silva, *Ellisolandia elongata* (J. Ellis & Sol.) K.R. Hind & G.W. Saunders and *Ulva rigida* were also present. The role of epiphytic synusia was small (Table 1). The values of the species diversity index indicate the polydominant structure of the algocenosis (Table 3).

2. An upper shoreface, composed of psephitic deposits, predominated by *Ericaria crinita* and *Gongolaria barbata*, was located at depths of 1–5 m in 2006, as in 1964. The phytocenosis of *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Gelidium crinale* was described in this BNC. Its biomass was two times lower than in 1964. The share of edificators was low, almost two times lower than in 1964 (Table 2). A significant contribution of *Gelidium crinale* (33 % of the total biomass of macrophytes) was noted in the community; *Ulva rigida*, *Ellisolandia elongata* were also found, and *Phyllophora crispa* was found sporadically. Epiphytic algae were practically non-existent (Table 2). Relatively high values of the species diversity index testify to the polydominant structure of the phytocenosis (Table 3).

3. An upper shoreface, composed of psephitic deposits, predominated by *Gongolaria barbata*, with mosaic alternation of pebble and gravel deposits with admixed shell fragments, where *Phyllophora crispa* predominates, was recorded in 1997 at depths of 5–10 m, as in 1964. This BNC described the same phytocenosis (*Gongolaria barbata*) – *Phyllophora crispa* – *Gelidium spinosum*. Its biomass decreased by half with increasing depth, while being 2–3 times lower than in 1964. The contribution of *Gongolaria barbata* dropped almost by half, while the contribution of *Phyllophora crispa* increased by the same factor with the increasing depth (Table 2). The community included *Ericaria crinita*, *Cladostephus spongiosus*, *Ulva rigida*. Epiphytic synusia was poorly developed (Table 2). The values of the *H* index indicate the complex structure of phytocenosis, where a high contribution of associated algae species is noted (Table 3).

Landscape structure of the coastal zone Cape Kosa Severnaya – Cape Tolsty (2006) (Fig. 2, c):

1. A boulder bench predominated by *Ericaria crinita* was recorded at depths of 0.5–1 m. In this BNC of 2006, the phytocenosis of *Ericaria crinita* – *Cladostephus spongiosus* – *Gelidium crinale* was described. Its biomass in the studied depth range slightly decreased with the increasing depth (Table 2). The contribution of the community edificator as a whole reached significant values (Table 2). In the structure of algocenosis, *Cladophoropsis membranacea* (Hofm. Bang ex C. Ag.), *Ulva rigida*, and *Gelidium spinosum* were occasionally noted. As part of the community, a significant contribution of epiphytic algae to the total biomass of macrophytes was noted (more than an order of magnitude higher than at the same depths in 1964 and 1997). The epiphytic synusia was dominated by *Vertebrata subulifera*, *Laurencia coronopus* J.Ag. and species of the genus *Cladophora*. The values of the Shannon diversity index indicate a high species diversity of phytocenosis (Table 3).

2. An upper shoreface, composed of psephitic deposits, predominated by *Ericaria crinita* and *Gongolaria barbata*, was located, unlike in 1964 and 1997, at depths of 1–10 m. The same phytocenosis (*Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Gelidium crinale*) was described in this BNC. In 2006, its biomass decreased by almost four times with the increasing depth and was at the upper boundary of the community about one and a half times lower than in 1964, and by the same amount higher than in 1997 (Table 2). The contribution of algocenosis dominants was minimal for the entire observation period. Species of the genus *Ulva* occasionally occurred in the composition of phytocenosis in the depth range of 1–5 m, while *Carradoriella elongata* (Huds.) Savoie & G.W. Saunders was registered at the depths of 5–10 m, and *Phyllophora crispa* – sporadically. The contribution of epiphytic synusia reached maximum values and accounted for about half of the total macrophyte biomass (Table 1). Among epiphytes, *Vertebrata subulifera* dominated at all depths; *Laurencia coronopus*, *Chondria capillaris* (Huds.) M. J. Wynne, and species of the genus *Cladophora* were recorded at the depths of 3–5 m. The values of the *H* index indicate the complex structure of phytocenosis, where a high contribution of associated and epiphytic algae species is noted (Table 3).

Landscape structure of the coastal zone Cape Kosa Severnaya – Cape Tolsty (2017) (Fig. 2, d):

1. A boulder bench predominated by *Ericaria crinita* was located at depths of 0.5–1 m. At present, the phytocenosis of *Ericaria crinita* was described in this BNC. Its biomass in the studied depth range was characterized by high quantitative indicators, the value of which increased slightly with the increasing depth (Table 2). The contribution of the community edificator was also high (Table 2). Among the thickets of *Ericaria crinita*, *Cladostephus spongiosus* and *Gelidium crinale* are found sporadically. Epiphytes are poorly represented; their maximum contribution falls on *Vertebrata subulifera*. At these depths, *Laurencia coronopus*, *Myriactula rivulariae* (Suhr ex Aresch.) Feldmann, and *Corynophlaea umbellata* (C. Ag.) Kütz were also found in the epiphytic synusia. The values of the Shannon diversity index were low, which indicated a homogeneous structure of the phytocenosis with a predominance of the dominant species (Table 3).



2. An upper shoreface, composed of psephitic deposits and predominated by *Ericaria crinita* and *Gongolaria barbata*, was recorded in 2017 at depths of 1–10 m, as in 2006. The same phytocenosis *Ericaria crinita* + *Gongolaria barbata* – *Cladostephus spongiosus* – *Gelidium crinale* was described in this BNC. Its biomass dropped by almost half with the increasing depth, while at the upper and lower boundaries of the community it was 2.5–5 times higher, respectively, than in 2006 (Table 2). The proportion of edificators in this depth interval was characterized by high values, which were approximately twice as high as in 2006 (Table 2). Representatives of the genus *Ulva* were registered in the community. At these depths, a significant role of epiphytic algae was noted (Table 2). Among them, *Vertebrata subulifera* prevailed, *Stilophora tenella* (Esper) P.C. Silva and *Ectocarpus siliculosus* (Dillwyn) Lyngb were also noted. The values of the Shannon diversity index were significantly higher compared to those at shallower depths, which indicates a more complex structure of the algocenosis (Table 3).

4. An upper shoreface composed of psephitic deposits predominated by a species of the genus *Dictyota* was located at depths of 10–15 m. The phytocenosis *Dictyota* sp was described in this BNC. Its biomass was low, while the community edificator accounted for 50 % of the total biomass of macrophytes (Table 2). At these depths, the lithophytic form of *Chondria capillaris* was abundant. *Ericaria crinita*, *Gongolaria barbata*, *Osmundea pinnatifida* (Huds.) Stackh., *Cladostephus spongiosus* were also registered in the algocenosis. Epiphytic synusia was represented mainly by *Callithamnion corymbosum* (Smith) Lyngb. The complex structure of phytocenosis is confirmed by the value of the Shannon diversity index (Table 3).

5. A gently dipping accumulation plain consisting of psammitic deposits with admixed shell fragments and predominated by *Phyllophora crispa* was located at depths of 15–20 m. *Phyllophora crispa* phytocenosis was described in this BNC. Its biomass was low, while at the upper boundary of the community it was more than an order of magnitude lower than in 1964 (Table 2). Algocenosis edificator dominated. The community included *Zanardinia typus* (Nardo) P.C. Silva. *Ectocarpus siliculosus* dominated among epiphytes. The value of the species diversity index indicates the oligodominant structure of the phytocenosis (Table 3).

Thus, the analysis of the material obtained showed that over more than a 50-year period in the coastal zone of Cape Kosa Severnaya – Cape Tolsty, there were changes in the spatial distribution of underwater landscapes, as well as in the qualitative and quantitative indicators of their plant component.

It is characteristic that the BNC of the boulder bench predominated by *Ericaria crinita* (1) was noted at depths of 0.5–1 m throughout the entire period under study. However, in 2017, at these depths, a significant increase in the total biomass of macrophytes was recorded, mainly due to *Ericaria crinita*, compared with its values in earlier years (Fig. 2; Table 2). The values of the Shannon diversity index show that the composition and structure of phytocenoses have changed over 53 years, they have become more homogeneous, and not polydominant. The share of the algocenosis edificator during the study period remained generally

high and varied from 96 % to 32 % of the total macrophyte biomass, while its maximum value was noted in 2017 and the minimum – in 1997 (Table 2). In this BNC of 2006, the macrophytobenthos included the most significant contribution of epiphytes (12–29 %), while in 1997 and 2017, their share did not exceed 5 %, in 1964 it was about 1 % of the total macrophyte biomass (Table 2).

The BNC of the upper shoreface, composed of psephitic deposits and predominated by species of *Ericaria crinita* and *Gongolaria barbata* (2), was also recorded during the entire study period. However, the depth of its distribution varied over the years. Thus, if in 1964 and 1997 the BNC was described at depths of 1–5 m, in 2006 and 2017 it was recorded at depths of 1–10 m (Fig. 2; Table 2). This BNC was characterized by a more complex structure of algocenosis. Its edificators, in addition to *Ericaria crinita*, include *Gongolaria barbata*, which prefers areas protected from waves at greater depths for growth<sup>8</sup>). The dominance of *Ericaria crinita* at shallow depths is explained by the high surf zone of the near-shore zone of Cape Kosa Severnaya – Cape Tolsty. At the upper boundary of the BNC, the proportion of dominant species is quite high and varies from 48 % (2006) to 94 % (1964), while at the lower boundary it decreases to 38 % (2006) – 65 % (2017) of the total macrophyte biomass (Table 2).

It is indicative that the spatial distribution of BNCs 1 and 2, where *Ericaria crinita* and *Gongolaria barbata* predominate, is determined by the stability of the bottom lithogenic base, which is a substrate for the attachment of macrophytes. However, in the composition and structure of macrophytobenthos of these BNCs, significant changes occurred, which apparently are a response to changes in environmental conditions. It is known that since the end of the last century, in many areas of the Crimean shelf, where an increase in the level of eutrophication of water masses has been recorded, an increase in the density of thickets of *Ericaria crinita* and *Gongolaria barbata* in the upper sublittoral zone (depths of 0.5–3 m) has been observed, which is probably associated with a decrease in water transparency [12]. Such changes at the depths of growth of these species caused a shift in their ecological and phytocenotic optimum<sup>8</sup>), which was previously located at depths of 3–5 m.

The abundant development of epiphytic species growing on the thalli of *Ericaria crinita* and *Gongolaria barbata* and having a high surface area of thalli may be a response to an increase in dissolved organic matter in the coastal zone of the sea. The most significant proportion of epiphytic synusia at depths of 0.5–1 and 1–10 m (12–29 % and 51–57 % of the total macrophyte biomass, respectively) was recorded in 2006, which may be due to the continuing increase in water pollution compared to 1964 and 1997. Indirectly, an increase in the level of trophicity of the environment in the area of Capes Kosa Severnaya and Tolsty is evidenced by the index of species diversity, which was minimal in 1964 and varied from 0.46 to 0.99, then increased in 1997 (0.77–2.48) and 2006 (0.87–2.43), and slightly decreased in 2017 (0.32–1.90). In 2017, in BNCs 1 and 2, the total biomass of macrophytobenthos, the proportion of *Ericaria crinita* and *Gongolaria barbata* increased, while the contribution of epiphytic algae decreased, which allows us to conclude that the state of the marine environment has improved (Table 1). Our assumption can be confirmed by information about

the current classification of this water area as conditionally clean. Thus, in 2018, the *E-TRIX* value varied from 1.44 to 2.20 (according to this criterion, the water corresponds to a low trophic level), while in 2007 this indicator was about 4 [13].

In 1964 and 1997 at depths of 5–10 m, the BNC of an upper shoreface composed of psephitic deposits was described, where *Gongolaria barbata* predominated, with mosaic alternation of pebble and gravel deposits with admixed shell fragments, where *Phyllophora crispa* dominated (3). In 2006 and 2017 the BNC was not observed at these depths. This phytocenosis is typical for the Black Sea coast of Crimea. The existence of a "transition zone" where several phytocenoses meet at the same depth at the same time was pointed out by A.A. Kalugina-Gutnik<sup>8)</sup> as early as the end of the previous century. This intermediate zone previously extended at depths of 15–20 m. At present, it has shifted to depths of 7–10 m. According to U.V. Simakova [14], these areas represent an ecocline, a zone with a gradual change in the composition of bottom vegetation along the illumination gradient [8]. However, the existence of "transitional" BNCs largely depends on the intensity of hydro- and lithodynamic processes occurring in the coastal zone. The studied area is characterized by an active redistribution of deposits, where the direction and intensity of alongshore flows depend on the wind-wave regime [15].

More than 50 years ago, at depths of 10–15 m, the BNC of a gently dipping accumulation plain was recorded, it was composed of psammitic deposits with admixed shell fragments, where *Phyllophora crispa* dominated. At these depths, relatively significant concentrations of the dominant species were noted (Table 2). Based on the analysis of archival material collected along the Crimean coast in the 1960s–1970s<sup>8)</sup>, it can be assumed that at depths of more than 15 m, the phyllophora biomass would have been much higher (in the area of Laspi Bay at depths of 15–25 m it was about 5000 g m<sup>-2</sup>). In 2017, single specimens of *Phyllophora crispa* were found at depths of 15–20 m, and one-year-old *Dictyota* sp. grew abundantly at depths of 10–15 m and *Gongolaria barbata* and *Ericaria crinita* were occasionally noted (Table 1).

For the Black Sea coast of Crimea in the 1960s–1970s at depths of more than 25 m, phytocenoses with the participation of deep-water species of *Zanardinia typus*, *Nereia filiformis*, and *Carradoriella elongata* were described. At present (2017), in the region of Cape Kosa Severnaya – Cape Tolsty, these species have been found in BNCs 4 and 5 at depths of 10–15 m. It is characteristic that in 1964 they were not registered at these depths, which indicates a vertical decrease in the depths of their habitat, which is probably associated with a decrease in illumination.

Thus, the BNC of a gently dipping accumulation plain, composed of psammitic deposits with admixed shell fragments, where *Phyllophora crispa* prevails, and the BNC of an upper shoreface, composed of psephitic deposits, predominated by *Gongolaria barbata* with a mosaic alternation of pebble and gravel deposits with admixed shell fragments of bottom sediments dominated

by *Phyllophora crispa* turned out to be more susceptible to transformation, which was reflected in a change in the depth of their distribution, degradation of the plant component, and a sharp decrease in the contribution of edificatory species.

It is significant that over the period from 1964 to 2017, the anthropogenic load on the coastal zone of Cape Kosa Severnaya – Cape Tolsty increased sharply. In the last decade, there has been an active development of this coast with residential and recreational facilities. Intensive construction has led to activation of gravitational processes in the coastal zone. In addition, the volume of wastewater discharge into the water area of this region has significantly increased.

Spatio-temporal changes in the BNC in the landscape structure are probably associated with the influence of both natural factors and increased economic activity. Thus, in modern conditions, under the influence of natural and anthropogenic fluctuations, new BNCs are formed, containing elements of the previous ones. According to L.A. Bespalova [16], who studied the anthropogenic impact on the landscape structure of the Sea of Azov, its return to a pre-existing state is impossible due to irreversible changes in landscape components. In favor of the proposed assumption, one can also cite Dollo's law known in the theory of evolution, from which it follows that a decrease in the influence of anthropogenic and natural factors acting on the system does not mean that it will return to its previous state<sup>10</sup>).

In general, the question of the reasons for the restructuring of the BNC, including structural changes in the vegetation component of the landscape of the coastal zone of Cape Kosa Severnaya – Cape Tolsty, remains debatable. Many of the stated provisions require further elaboration and comprehensive research [8].

### Conclusion

The analysis of the obtained materials showed that during the period of research in the coastal zone of Cape Kosa Severnaya – Cape Tolsty, the spatial distribution of underwater landscapes, as well as the qualitative and quantitative indicators of their plant component, have changed, which is probably due to the influence of both natural factors, and increased anthropogenic activity.

The BNCs of the boulder bench and the upper shoreface, composed of psephitic deposits and predominated by *Ericaria crinita* and *Gongolaria barbata*, located at depths of 0.5–5 m, underwent the least changes. These changes affected only the configuration of their boundaries and the depth of distribution, which is probably due primarily to the stability of the lithogenic base, which is the substrate for the strong attachment of macrophytes. The plant component of these BNCs is distinguished by the maximum values of macrophyte biomass, a high proportion of phytocenosis edificers, and a significant contribution of epiphytes.

The most significant restructuring occurred in the BNCs located at depths of 5–15 m: the BPC of a gently dipping accumulation plain composed of psammit-

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<sup>10</sup> Dollo, L., 1893. Les Lois de l'évolution. *Bulletin de la Société belge de géologie, de paléontologie et d'hydrologie*, 7, pp. 164–166. Available at: <https://www.biodiversitylibrary.org/item/159645#page/183/mode/1up> [Accessed: 25 May 2022].

ic deposits with admixed shell fragments, where *Phyllophora crispa* dominates, and the BPC of an upper shoreface composed of psephitic deposits, where *Gongolaria barbata* dominates, with a mosaic alternation of pebble and gravel deposits with admixed shell fragments, where *Phyllophora crispa* dominates. During the period under study (1964–2017), there were changes in the depth of their distribution, degradation of the plant component, a sharp decrease in the contribution of edificators of phytocenoses, replacement of perennial macrophyte species with annual ones, and a vertical decrease in the depth of habitat of deep-sea species, which is, probably, associated with a decrease in illumination.

The study of the dynamics of underwater landscapes will make it possible to predict their development and behavior under certain conditions, to scientifically substantiate the type of environmental management, to provide for nature conservation measures, and to determine the value of the maximum allowable load on the BNC.

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**Nataliya V. Mironova** – macrophytobenthos sample processing (1998, 2006, 2017), analysis and description of the study results, preparation of the article text

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

# Contamination of Sandy Beaches with Marine Litter Microparticles (the Eastern Part of the Gulf of Finland of the Baltic Sea)

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## Abstract

This article discusses the features of the distribution of marine microlitter (particles less than 5 mm) in 2019–2020 on 13 beaches of St. Petersburg and the Leningrad Region located on the coast of the Russian part of the Gulf of Finland (the Baltic Sea). Microlitter was found on all beaches, however, its composition and amount varied significantly depending on the beach exposure and other factors. The concentration of microlitter ranged from 0.1 to 55.5 particles/m<sup>2</sup>. The largest amount of microlitter in the wrack zone was found on the beach in the center of St. Petersburg, the least – in Alexandria Park on the south coast; the predominant type of microlitter on most beaches is plastic. Using a cluster analysis, the beaches were classified according to the degree of their contamination: the most contaminated beaches are located within the city on the coasts of the Neva Bay, the least contaminated beaches are either outside the Neva Bay or at a considerable distance from the center of St. Petersburg. In the Neva Bay and on the northern coast of the open part of the Gulf of Finland, the concentrations of microlitter are higher, which may be due to the peculiarities of currents and winds determining the removal of particles coming with the Neva River runoff and their transport to the north. Comparison of the obtained data with the results of other studies in this region showed that, as compared with the beaches of other parts of the Baltic Sea, the Eastern Gulf of Finland has the highest values of the number of microparticles on the beaches.

**Keywords:** marine litter, microlitter, Neva Bay, Gulf of Finland, beaches, microplastics, contamination, marine ecosystems

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# Загрязнение микрочастицами морского мусора песчаных побережий восточной части Финского залива Балтийского моря

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## **Аннотация**

Рассмотрены особенности распределения морского мусора (частиц размером менее 5 мм) в 2019–2020 гг. на 13 пляжах Санкт-Петербурга и Ленинградской области, расположенных на побережье российской части Финского залива Балтийского моря. Мусор обнаружен на всех пляжах, однако его состав и количество значительно варьируют в зависимости от экспозиции пляжа и других факторов. Концентрация мусора составила от 0.1 до 55.5 частиц/м<sup>2</sup>. Самое большое количество мусора в зоне заплеска обнаружено на пляже в центре Санкт-Петербурга, меньше всего – в парке Александрия на южном побережье. Преобладающим типом мусора на большинстве пляжей является пластик. С помощью кластерного анализа пляжи охарактеризованы по степени их загрязненности: наиболее загрязненные пляжи расположены в черте города на побережьях Невской губы, наименее загрязненные пляжи – либо за пределами Невской губы, либо на значительном отдалении от центра Санкт-Петербурга. В Невской губе и на северном побережье открытой части Финского залива концентрации мусора выше, чем на южном побережье, что может быть связано с особенностями течений и ветров, обуславливающих вынос и перенос к северу частиц, поступающих со стоком реки Невы. Сравнение полученных данных с результатами других исследований в данном регионе показало, что, по сравнению с побережьями других частей Балтийского моря, в восточной части Финского залива наблюдаются более высокие значения количества микропластика на пляжах.

**Ключевые слова:** морской мусор, мусор, Невская губа, Финский залив, пляж, микропластик, загрязнение, морские экосистемы

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## **Introduction**

For a long time, waste was considered a problem for areas near industrial sites and densely populated urban areas, but not for marine ecosystems. However, after the discovery of the Great Pacific Garbage Patch, the problem of marine litter became known to a wide audience [1]. Currently, marine litter is having a negative impact on the economy and well-being of people living near the sea, as well as on marine ecosystems [2]. Every year, up to 20 million tons of plastic waste enter the World Ocean [3]. Marine litter easily crosses borders between countries; it can be found near its place of origin or it can be carried by currents and winds. This makes it difficult to assess the distribution of marine litter and to find its sources.



Microplastic is particles of both natural and synthetic materials with the largest dimension of up to 5 mm. Microplastics can be primary (pre-production pellets are small polymer particles used in the manufacture of various products) and secondary (fragments resulting from the destruction of larger plastic products) [4]. Microplastics have been found in filter feeders and other benthic organisms [5]. Laboratory studies have shown that many marine invertebrates such as bivalves, echinoderms, amphipods, and zooplankton can ingest microplastics [6, 7]. Plastic often contains hazardous additives, can adsorb hydrophobic persistent organic pollutants and transfer these substances into marine food chains [8].

Monitoring studies of marine and, in particular, beach litter are important for identifying the sources of its entry into the marine environment. In the Baltic region, the studies of beach litter have been carried out for several years (see report<sup>1)</sup> and works [9–11]). The first large-scale studies of beach litter were carried out in 2011–2013 within the framework of the *MARLIN* project, during which from 75 to 236 fragments of macrolitter per 100 m of beach<sup>1)</sup> were found on the coasts of Sweden, Finland, Estonia and Latvia. It was discovered that the main sources of marine litter in the Baltic Sea were maritime transport, fishing, domestic sewage, as well as recreational activities on the coast [9].

Large scale research on microplastics in 2014–2016 on German beaches showed that the upper layer of sand on the beaches of the Baltic coast of Germany contained an average of 2–11 microplastic particles per kilogram of dry mass [12], and on the beaches of the Kiel Fjord – from 2 to 30 particles per kilogram of dry mass [13]. At the same time, on the beaches of the German island of Rügen, the amount of microplastics was already 80–100 particles per kilogram of dry mass in the sand layer [14]. The beaches in Poland were also contaminated with microplastics, their concentrations on the sand surface ranged from 25 to 43 particles per kilogram of dry weight in 2014 [15].

Beaches can be contaminated with microlitter of various sizes: from tens of microns to 5 mm. In 2014–2016, on the beaches of Germany and Lithuania, monitoring studies [10] of contamination with visually distinguishable microlitter (2–5 mm) were carried out using the methods that were later used in this work. The following results were obtained: the occurrence of microlitter particles ranged from 0.02 to 3.9 particles/m<sup>2</sup>. Studies by various authors show that microlitter is found on all beaches. However, it is very difficult to compare contamination assessment results due to differences in the methodologies used. In addition, the authors can describe contamination by all types of microlitter, as well as focus only on microplastics.

On the Russian coast of the Baltic Sea, studies of microplastics in beach sands have been conducted since 2016. It was established that on the beaches of the Kaliningrad region, microplastics were present both on the surface of the sand

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<sup>1)</sup> European Commission, 2013. *Final Report of Baltic Marine Litter Project MARLIN – Litter Monitoring and Raising Awareness 2011–2013*. Available at: [https://www.pidasaaristosiistina.fi/files/1994/Marlin\\_Final\\_Report\\_2014.pdf](https://www.pidasaaristosiistina.fi/files/1994/Marlin_Final_Report_2014.pdf) [Accessed: 06 March 2022].

and at a depth of more than 1 m, and the concentrations varied from 2 to 572 particles per kilogram of dry mass [16]. On the coasts of the eastern part of the Gulf of Finland, the study of marine litter was started by the Russian State Hydrometeorological University (RSHU) in 2018 [17]. It was found that all the coasts of the Gulf of Finland and the Neva Bay were polluted with plastic litter of all fractions – from macro- to microlitter. A parallel study at the stations of RSHU in 2019 [18] showed a distribution of microplastic concentrations in beach sediments from 15 to 210 particles per kilogram of dry mass in the Neva Bay. Model studies in 2019 revealed the trends in the distribution of microplastics in the Neva Bay [19]. In general, studies in the Neva Bay and the Gulf of Finland indicate much higher concentrations of microplastics on the Russian coast compared to the coastal zone of other Baltic countries.

In this region, only the Russian State Hydrometeorological University annually investigates the contamination of beaches with microlitter, which makes it possible to analyze dynamic characteristics and perform statistical processing of data. Therefore, the purpose of this study is to analyze the contamination of the beaches of the Neva Bay and the eastern part of the Gulf of Finland with marine litter microparticles based on the seasonal surveys of the RSHU in 2019–2020. In this regard, the following tasks were performed: the features of the distribution of marine microlitter on the beaches of the Russian coast of the Gulf of Finland were considered, the beaches were classified according to their contamination degree in 2019–2020, and the data obtained were compared with the results of other studies in the region.

The selected materials used in the preparation of this work were previously presented at the conference<sup>2)</sup>.

### **Materials and methods**

The eastern (Russian) part of the Gulf of Finland is the final reservoir of accumulation of substances from Lake Ladoga and the Neva River. In this part of the bay, the Neva Bay deserves special attention, as it is a man-made lagoon bounded by the Western High-Speed Diameter, a the Flood Protection Barrier of St. Petersburg and the Marine Facade, which contributes to the accumulation of material coming with the waters of the Neva River. The eastern part of the Gulf of Finland is experiencing a strong anthropogenic impact, as more than 5 million people live on the shores of this water body.

Almost everywhere within the Eastern Gulf of Finland and its coastal zone, the upper part of the geological section is represented by late and postglacial Quaternary deposits. On the beaches, these deposits are represented by medium-grained river sands, and within the boundaries of the Neva Bay – by coarse-grained river sands [20].

The studies were carried out on 13 beaches of St. Petersburg and the Leningrad region (Fig. 1) in the summer months of 2019–2020.

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<sup>2)</sup> Kuzmina, A.S. and Ershova, A.A., 2021. Comparative Characterization of Marine Microlitter Monitoring Techniques for Sandy Beaches of the Gulf of Finland in the Baltic Sea. In: IBSS, 2021. *Pont Evksinskiy – 2021 : Materials of XII All-Russian Scientific and Applied Conference for Young Scientists on the Water Systems Problems, Dedicated to the 150 th Anniversary of the Sevastopol Biological Station – A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS. Sevastopol, 20–24 September, 2021*. Sevastopol: IBSS, p. 78–80. doi:10.21072/978-5-6044865-8-0 (in Russian).

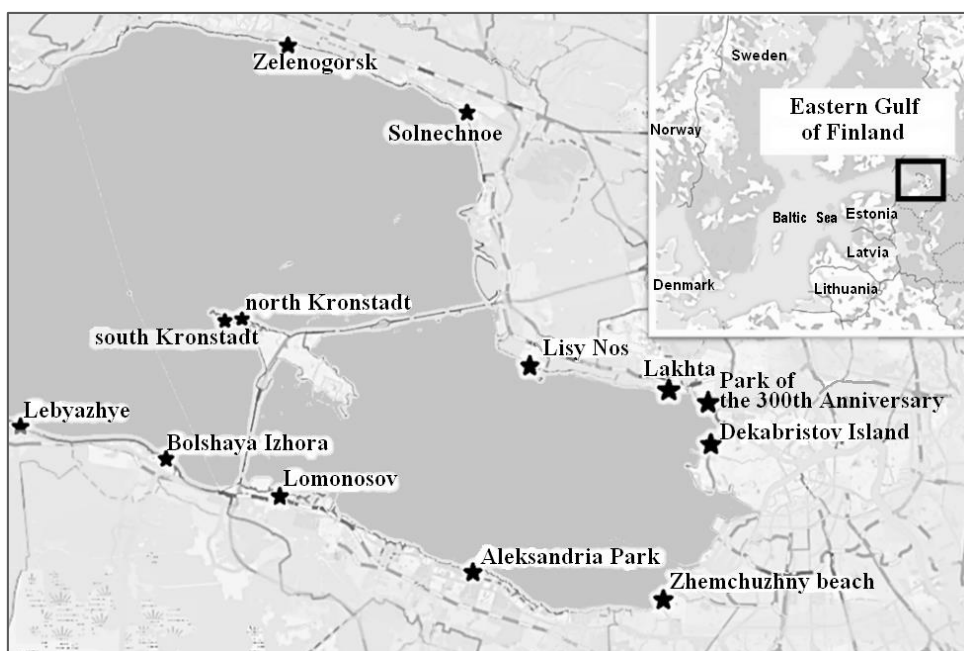


Fig. 1. Microlitter sampling locations on the coasts of the Eastern Gulf of Finland

When sampling microlitter, two international beach survey methods [10, 21] were used. These methods were developed for the Baltic coasts based on the monitoring experience of the *OSPAR* project. The first is the Frame-method, which aims at wrack zone with a 40 m<sup>2</sup> survey polygon for collecting large litter (more than 5 mm) with two squares of 1 m<sup>2</sup> for collecting microlitter 2–5 mm in size (using a sieve with a 2 mm cell). The second is the Rake-method, which involves the entire coast from the waterline to the vegetation line with an area of at least 50 m<sup>2</sup>; the sand is sieved with the use of a special rake with a cell of 2 mm (Fig. 2). Both methods aim at a visually distinguishable fraction of microlitter (2–5 mm), but in the two functionally different zones of the beach.

The selected particles of microlitter were counted and classified according to the type of material: plastic, glass, paper, metal and other materials (Fig. 3).

The obtained data were entered into protocols (by beaches) and processed using Microsoft Excel and PAST4 software (Ward's method). This algorithm uses methods of dispersion analysis to estimate distances between clusters. It minimizes the sum of the squares of the distance for the two clusters that are formed at each step. Ward's method leads to the formation of clusters of approximately equal sizes with minimal intraclass dispersion. In general, Ward's method is effective, but it tends to create small clusters, which has almost no effect on the quality

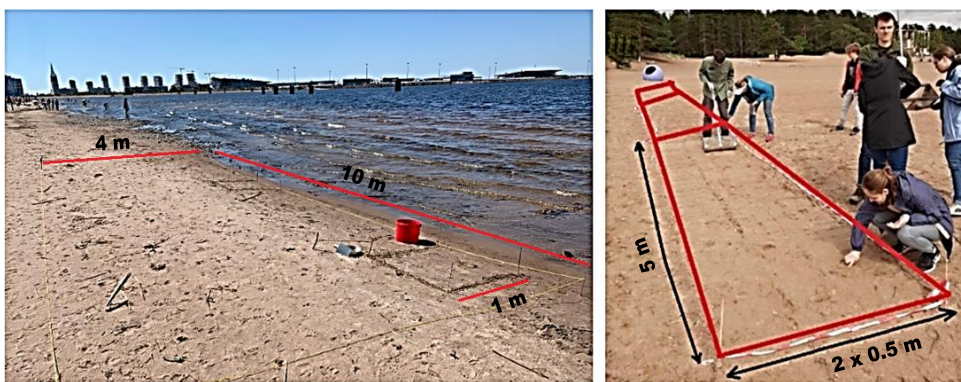


Fig. 2. Microlitter sampling methods: *a* – Frame-method, *b* – Rake-method

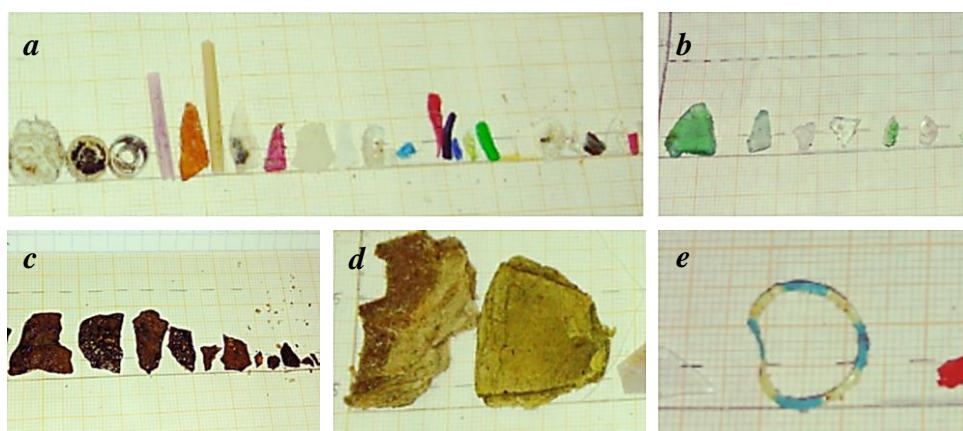


Fig. 3. Types of microlitter particles on the beaches of the Eastern Gulf of Finland: plastic (*a*), glass (*b*), metal (*c*), paper (*d*), other (*e*)

of classification with a relatively small size of the original selection<sup>3)</sup>. This method was applied because in 2019-2020 the survey was carried out once a year and the dataset included no more than 20 values of microlitter concentrations in the wrack zone.

### Results

The studies were carried out for the two functionally different parts of the beach. On all coasts, contamination of the wrack zone was studied, that is, the presence of microlitter directly at the waterline. Most likely, the source of microlitter was sea waves splashing the material onto the shore. The entire width of the beach (including the dry part) was surveyed by the Rake-method only

<sup>3)</sup> Soshnikova, L.A., Tamashevich, V.N., Uebe, G. and Shefer, M., 1999. *Multidimensional Statistical Analysis in Economics*. Moscow: Unity, 598 p. (in Russian).

on selected representative beaches in order to establish the significance of other sources of beach contamination (waste from tourists, wind transfer, etc.).

#### *Wrack zone*

Among all the studied beaches in the summer seasons of 2019 and 2020, the largest amount of microlitter particles per square meter in the wrack zone was found on the beach in the very center of St. Petersburg on Dekabristov Island in the Neva Bay. Within the same period, the smallest amount of microlitter particles was found on the beaches remote from the center – on Laskovy beach in the village of Solnechnoye in the open part of the Gulf of Finland in 2019 and on the beach in Lomonosov in 2020 (Fig. 4). At the same time, less microlitter was found on the beaches in the wrack zone in 2020 than in 2019.

On the beaches of the Neva Bay, microlitter is mainly represented by plastic, with the exception of the beach in Alexandria Park, where it is represented only by glass. Outside the Neva Bay, the situation is different – the microlitter mainly consists of metal on the beaches of Kronstadt, and it consists of glass on the northern coast of the open part of the bay (Fig. 5). Most of the microplastic particles were found on Dekabristov Island, while plastic was absent in the samples from the village of Solnechnoye and Alexandria Park. In general, more microplastics can be found in the wrack zone of the beaches in the Neva Bay than in the open part of the gulf behind the Flood Protection Barrier.

During the study, the number of microlitter particles and, in particular, microplastics on the beaches of the Neva Bay and the open part of the Gulf of Finland was determined. The obtained data were analyzed using statistical

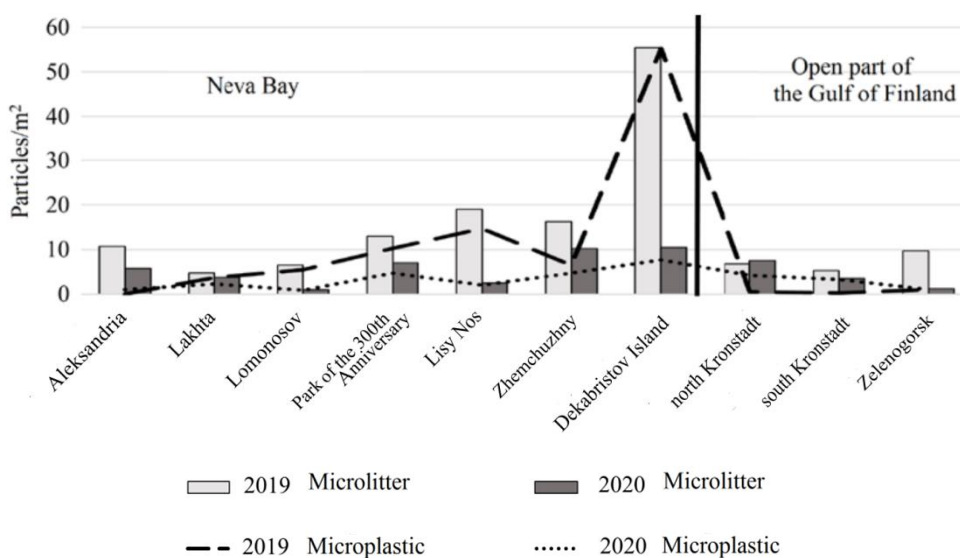


Fig. 4. The number of particles of microlitter and microplastics in the wrack zone, 2019–2020

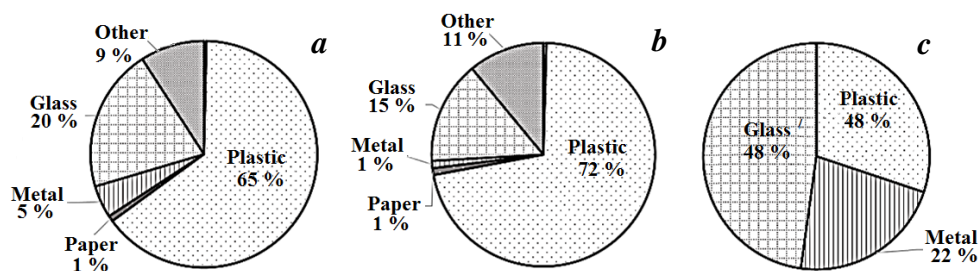


Fig. 5. The percentage of microlitter of each type on all the studied beaches in 2019–2020 (a), in the Neva Bay (b), in the open part of the Gulf of Finland (c)

processing methods. The average statistical characteristics for these sections of the coastal zone of the Eastern Gulf of Finland were obtained: arithmetic mean ( $\bar{x}$ ), median ( $M_e$ ), standard deviation ( $\sigma$ ), maximum and minimum (Table 1). Thus, in the Neva Bay, the average number of particles ( $\bar{x}$ ) is higher than in the open part of the gulf, while the standard deviation  $\sigma$  exceeds the average value, which indicates large differences between the beaches of the Neva Bay. Indeed, in 2019, 55.5 particles/m<sup>2</sup> were found on the beach on Dekabristov Island, and 1 particle/m<sup>2</sup> was found in Alexandria Park. At the same time, in the open part of the Gulf of Finland, the standard deviation does not exceed the mean value, and the median is much closer to the mean than for the data from the Neva Bay, which indicates greater data homogeneity.

Table 1. The number of detected particles of microlitter on the beaches of the eastern part of the Gulf of Finland in 2019–2020, particles/m<sup>2</sup>

Beach location	$\bar{x}$	$M_e$	$\sigma$	max	min
<i>Microlitter</i>					
Neva Bay	11.9	8.6	13.6	55.5	1.0
Open part of the Gulf of Finland	5.7	6.0	3.0	9.8	1.3
<i>Including microplastics</i>					
Neva Bay	8.5	4.8	14.4	55.3	0.0
Open part of the Gulf of Finland	1.7	1.0	1.6	4.3	0.3

A classification of data on microlitter contamination for 2019–2020 was carried out using Ward’s method together with the Euclidean distance. A division into three classes was chosen: the most contaminated beaches, moderately contaminated beaches and the least contaminated beaches. The average values in each class were calculated (Table 2) and a comparison was made between the 2<sup>nd</sup> and 3<sup>rd</sup> classes according to Student’s *t*-test. As a result, it was found that  $t^*$  (2.64) >  $t_{cr}$  (2.12) (calculated at a significance level of  $\alpha = 0.05$ ), which means that the classes should not be combined with each other. It is advisable to consider them as separate groups.

The most contaminated is the beach on Dekabristov Island, located in the city center (Fig. 6) right at the confluence of one of the largest branches of the Neva River into the Neva Bay, which, apparently, determines the large amount of microlitter found. At the same time, the beach is one of the most contaminated with macro- and mesolitter, according to our observations [22], and is not cleaned by municipal services. Moderately polluted beaches are also located within the city on the coasts of the Neva Bay. The least contaminated beaches are located either outside the Neva Bay, or at a considerable distance from the center of St. Petersburg. The exception is the beach in the village of Lakhta, which turned out to be the least contaminated according to the above classification, which may be due to the presence of dense reed beds that partially trap particles.

Table 2. Beach classification by microlitter concentrations in the Eastern part of the Gulf of Finland in 2019–2020

Class	$\bar{x}$ , particles/m <sup>2</sup>	Beach location
1 (most contaminated)	33	Dekabristov Island
2 (moderately contaminated)	10.6	Alexandria Park of the 300th Anniversary Lisy Nos Zhemchuzhny
3 (least contaminated)	5	Lakhta Lomonosov North Kronstadt South Kronstadt Zelenogorsk

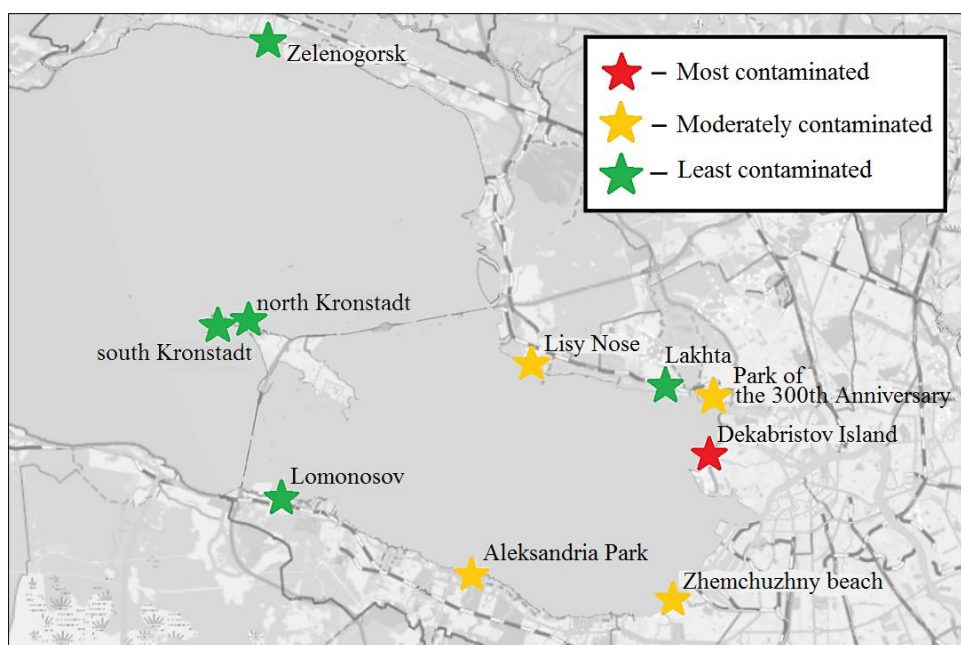


Fig. 6. Classification of the Gulf of Finland beaches according to the degree of microlitter contamination

#### *Selective study of beaches across the entire width*

In addition to the wrack zone, in 2019 and 2020, beaches on the northern and southern coasts of the open part of the Gulf of Finland were selectively studied using the Rake-method to assess the contamination of the beach along the entire width from the waterline to the vegetation line (Fig. 1), including its entire dry part. At the same time, in contrast to 2019, in 2020 only two beaches, characterizing the situation on the southern and northern coasts of the eastern part of the Gulf of Finland, were selected for the study. The selected beaches differ not only in hydrodynamic conditions, but also in the level of recreational load, as well as in the cleaning frequency.

In 2019–2020, the number of microparticles varied within a very wide range: in 2019, the largest number of microlitter particles per square meter was found on the northern beach of Kotlin Island, and the least – on the beach in Bolshaya Izhora, while in 2020 the most of the particles were found on the beach in Bolshaya Izhora, and the least – on the beach in Zelenogorsk. The microlitter from the beaches of Kronstadt (Kotlin Island) is mostly represented by metal, while on the other beaches of the open part of the Gulf of Finland the microlitter is mostly plastic. In general, more microplastics are observed on the northern coast of the open part of the gulf, and relatively many microplastic particles (more than 1 particle/m<sup>2</sup>) were found on the southern beach of Kotlin Island in 2019.

The amount of microlitter from the waterline to the vegetation line varies from beach to beach (Fig. 7). Thus, in 2019 on the beaches of Kronstadt



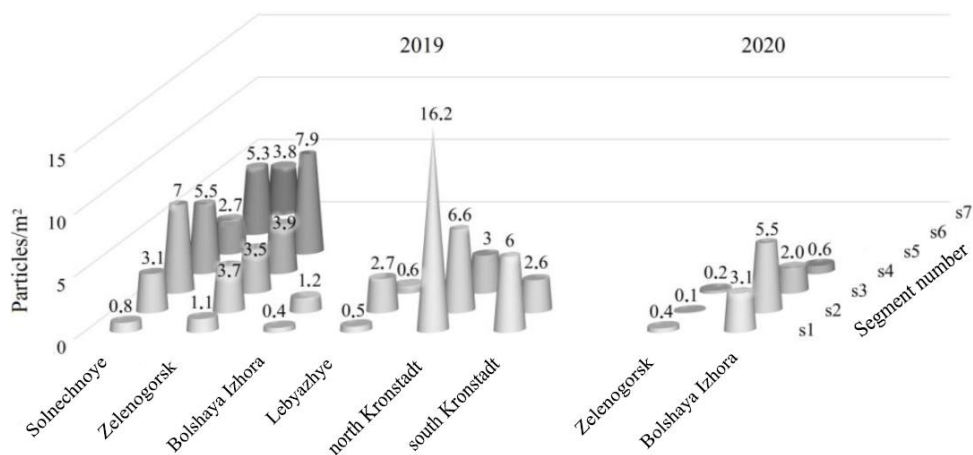


Fig. 7. Distribution of microlitter by beach segments from waterline (S1) to vegetation line (S7) in 2019 and 2020

(Kotin Island) the amount of microlitter decreases with distance from the water line, that is, most likely, the microlitter on the beach is of marine origin and comes with waves; this is also indirectly indicated by its composition – mostly rusty metal. It should be noted that here, on the territory of the *Western Kotlin* Nature Reserve, regular cleaning of large litter is carried out and this reserve is visited infrequently due to the large distance from the city – the number of tourists here is much smaller than on the coasts of the mainland of the Gulf of Finland. On the beaches of Zelenogorsk and the village of Solnechnoye on the northern coast of the Gulf of Finland, the situation is reverse – there is more microlitter far from the water, although Zelenogorsk and Solnechnoye are the popular beaches of the Kurortny District of St. Petersburg that are daily cleaned. A large amount of microlitter in the sands of these beaches probably indicates the insufficiency of mechanical cleaning tools that allow small fractions of litter (for example, the remains of cigarette butts) to pass through, collecting only large litter. However, another reason for the accumulation of microparticles (mainly plastic) in the dry part of these beaches cannot be indicated – spring and autumn storms, throwing suspended material far into the beach. This is evidenced by a large number of pellets in the microlitter composition, the source of which is the wash-out into the sea from construction sites.

The beaches of the southern coast of the Gulf of Finland – Bolshaya Izhora and Lebyazhye – are the so-called wild beaches, which are cleaned only by local volunteers. Both beaches have a high recreational load in the summer, however, in 2019, the lowest amount of microlitter was found there along the entire width of the beach. Using the example of these beaches, the theory of influence of the dominant currents in the Gulf of Finland is confirmed, according to which the suspended material coming from the city and the Neva River, is carried out to the northern coast [23].

The 2020 study showed a different pattern of microlitter distribution on the beaches of the northern and southern coasts: more litter was found in Bolshaya Izhora with the maximum accumulation in the middle of the beach, and the smallest amount of microparticles was observed on Zelenogorsk beach, which may be due to an artificial renewal of the beach with clean imported sand.

### **Discussion**

The conducted studies showed that microlitter in one form or another was found on all the beaches of the Eastern Gulf of Finland and the Neva Bay. The most contaminated beaches with particles smaller than 5 mm are located within the boundaries of St. Petersburg, closer to its center, in the area of one of the main branches of the Neva River. A similar situation is observed in other parts of the Baltic Sea: in the Kaliningrad region, the most microplastics were found in the wrack zone on the most visited beaches, as well as on the Vistula Spit [17]; the beaches of Finland are also characterized by higher contamination of urban beaches [9]. Thus, the beaches of urban areas are the most contaminated with microlitter in the Baltic region.

The studies conducted within the *MARLIN* project showed that the most contaminated beaches in the Baltic were the beaches of Finland, located on the northern coast of the Gulf of Finland [9], and more than half of all objects found there were plastic. In this work, it is revealed that the northern coast of the Gulf of Finland and the Neva Bay is more contaminated with microlitter than the southern one, and microplastics are the predominant type of microlitter here – approximately 65% of the total volume. In general, the variety of materials that make up the microlitter of the Gulf of Finland is great; in addition to microplastics, there are microparticles of metal, glass, plaster and other materials, while, for example, on the coast of the Kaliningrad region in the South-East Baltic, anthropogenic marine litter consists mainly of plastic – a total of about 90% of all collected samples [17].

The comparison of concentrations of microlitter and microplastics found on the Baltic coasts of Germany, Lithuania [11] and Russia using the methods discussed in this study showed that, unlike the beaches of Germany and Lithuania, in the Neva Bay of the Gulf of Finland, the maximum number of microparticles in the Baltic region was discovered. On the beaches of the Russian coast of the Gulf of Finland, an average of 11.5 particles/m<sup>2</sup> was found in the wrack zone and 3 particles/m<sup>2</sup> – along the entire width of the beach, while in Germany and Lithuania these values are on average 0.1 and 3.9 particles/m<sup>2</sup>, respectively, for the wrack zone and 0.2 and 0.02 particles/m<sup>2</sup> – for the entire width of the beach. The beaches of the Neva Bay and Germany are characterized by the predominance of plastic particles in the wrack zone.

Unlike the Baltic coasts of other countries, where the main source of marine litter is tourism, in the Neva Bay and the open part of the Russian coast of the Gulf of Finland, the sources of microlitter vary from beach to beach and may probably depend on the type of industrial activity nearby. Thus, for example, the predominance of metal particles in the microlitter structure of the beaches of

Kronstadt (Kotlin Island) can be explained by active navigation and ships moored in the immediate vicinity of sampling sites, and the source of glass on the beach in Alexandria Park (regularly cleaned) can be the Petrovsky Glass Manufactory, located on the shore near the park. A large amount of plaster residues on some beaches (the “other” category) also indicates the proximity of construction sites and places where construction waste is disposed of. It is also impossible to exclude the role of incompletely treated municipal and industrial wastewater as a source of microplastics on the studied coasts: the microplastic samples were often represented by nurdles or pellets, and by fragments of household hygiene items. Due to the predominance of southwestern winds, as well as complex currents, the northern coast of the open part of the Gulf of Finland is more contaminated with microlitter than the southern one, since the particles coming from the Neva River runoff are transferred to the north [23].

### Conclusion

On the whole, the conducted study confirms the main pattern of microparticle distribution in the waters of the Neva Bay and on its coasts: higher concentrations of microlitter are typical of the Neva Bay and the northern coast of the open part of the Gulf of Finland, which is explained by the peculiarities of currents and prevailing winds. Quite naturally, the beaches closer to the city center are more contaminated. However, the conducted research also shows a significant variability in the concentrations and conditions for the formation of microplastic load on the beaches; a more detailed research, obviously, requires more frequent studies, taking into account the seasons and hydrometeorological phenomena.

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**Aleksandra A. Ershova** – setting the goal of the study, general scientific guidance, editing the text of the article, formulating conclusions

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

## Hydrocarbons in the Surface Layer of Bottom Sediments of Balaklava Bay (Black Sea)

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### Abstract

The purpose of this work is to determine the content and spatial distribution of hydrocarbons in the upper (0–5 cm) layer of bottom sediments of Balaklava Bay and to assess probable sources of hydrocarbons in this water area. The quantitative determination of the total content of hydrocarbons was carried out by calibration of the flame ionization detector with a mixture of hydrocarbons (C<sub>12</sub>–C<sub>40</sub>), which had been prepared by the gravimetric method, with the content ranging 0.1–5.0 mg/L. N-hexane was used as an extractant. The measurements were carried out using *Kristall 5000.2* gas chromatograph. The total amount of hydrocarbons in the bottom sediments of Balaklava Bay reached 2385 mg/kg, with an average of 880 mg/kg, and that of n-alkanes – 154 mg/kg, with an average of 61 mg/kg. The maximum concentrations of hydrocarbons are noted in the central part of the bay and the minimum ones – in its seaward part. In the sea bottom sediments of Balaklava Bay n-alkanes were identified in the range of C<sub>13</sub>–C<sub>35</sub>. The total content of hydrocarbons in the sea bottom sediments of Balaklava Bay corresponded to the levels noted in the polluted zones of coastal areas of the World Ocean. The presence of bimodality in the n-alkanes distribution chromatograms apparently indicates the mixed origin of hydrocarbons. The calculated markers indicate that normal alkanes in the sea bottom sediments of the water area are of predominantly terrigenous origin (TAR, Alk<sub>terr</sub>,  $\sum C_{25-35}/\sum C_{15-21(odd)}$ ) and also signify chronic petroleum contamination (CPI<sub>2</sub>, UCM/R). The hydrocarbon composition of sea bottom sediments in the seaward area of Balaklava Bay differed from that recorded in the inner parts of the water area. Calculated for this area, diagnostic indices, which allow differentiation of oil and biogenic hydrocarbons, indicate predominance of natural hydrocarbons.

**Keywords:** hydrocarbons, n-alkanes, sea bottom sediments, diagnostic indices, Balaklava Bay, Black Sea

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## **Углеводороды в поверхностном слое донных отложений Балаклавской бухты (Черное море)**

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### **Аннотация**

Цель работы – определение содержания и пространственного распределения углеводородов в поверхностном (0–5 см) слое донных отложений б. Балаклавской, а также оценка вероятных источников поступления углеводородов в эту акваторию. Количественное определение суммарного содержания углеводородов проводили путем калибровки пламенно-ионизационного детектора смесью углеводородов (C<sub>12</sub>–C<sub>40</sub>) (в диапазоне 0.1–5.0 мг/л), которую готовили гравиметрическим методом. В качестве экстрагента использовали н-гексан. Измерение проводили на газовом хроматографе «Кристалл 5000.2». Суммарное количество углеводородов в донных отложениях б. Балаклавской достигало 2385 мг/кг при среднем 880 мг/кг, а н-алканов – 154 мг/кг при среднем 61 мг/кг. Максимальные концентрации углеводородов отмечены в центральной части бухты, а минимальные – в ее мористой части. В донных отложениях б. Балаклавской идентифицированы н-алканы в диапазоне C<sub>13</sub>–C<sub>35</sub>. Общее содержание углеводородов в донных отложениях б. Балаклавской соответствовало уровням, отмеченным на загрязненных участках прибрежных районов Мирового океана. Наличие бимодальности на хроматограммах распределения н-алканов, по-видимому, указывает на смешанное происхождение углеводородов. Рассчитанные маркеры свидетельствуют о преимущественно терригенном происхождении нормальных алканов в донных отложениях акватории (*TAR*, *Alkterr*,  $\sum C_{25-35}/\sum C_{15-21(неч.)}$ ), а также о присутствии хронического нефтяного загрязнения (*CPI<sub>2</sub>*, *UCM/R*). Состав углеводородов донных осадков для мористого участка б. Балаклавской отличался от зафиксированного во внутренних частях акватории. Рассчитанные для этого района диагностические индексы, позволяющие дифференцировать нефтяные и биогенные углеводороды, указывают на преобладающее присутствие природных углеводородов.

**Ключевые слова:** углеводороды, н-алканы, донные отложения, диагностические индексы, бухта Балаклавская, Черное море

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## **Introduction**

Today, the interest in the environmental problems of Balaklava Bay has intensified. In recent years, the pressure on the water area has been increasing due to the active operation of the small fleet. It is known that the input areas of the major part of anthropogenic hydrocarbons (HCs) are limited to the coastal areas, river mouths and port water areas [1, 2]. Balaklava Bay has all the above features: its coast is intensively used, the Balaklava River flows into the bay and the quay walls of the waterbody are heavily used as a berth for yachts and small vessels [3, 4]. The situation is also worsened by the lack of centralized sewage systems in the cafe on the embankment, from which untreated sewage flows directly into the aquatic environment.

High HC concentrations negatively affect the life processes of hydrobionts [5, 6]. Therefore, many researchers analyzed the total amount of organic matter in bottom sediments [1, 3, 4, 6]. This indicator makes it possible to estimate the level of organic pollution of the water areas, but not to identify the nature of these substances.

The genesis of organic matter, including HCs, in bottom sediments can be defined by knowing the molecular composition of normal alkanes (n-alkanes), which is one of the possible markers of the organic matter origin [7]. Natural sources of HCs, including n-alkanes, in marine soils are plant and to a lesser extent animal residues [8]. Anthropogenic sources of HCs in bottom sediments include organic pollutants, among which oil and oil products are the most common [9, 10].

The purpose of this work is to determine the content and spatial distribution of HCs in recent bottom sediments of Balaklava Bay as well as to assess the probable sources of hydrocarbon input in this water area. These sources were identified on the basis of data on the individual composition of n-alkanes and diagnostic indices.

Various markers are used to identify the genesis of HCs. To differentiate allochthonous and autochthonous origin of HCs the following are applied: the terrigenous/aquatic ratio (TAR), Alkterr terrigenous index (percentage of terrestrial alkanes),  $\sum C_{25-35} / \sum C_{15-21(\text{odd})}$ , average chain length (ACL), ratio of low-molecular-weight homologues to high-molecular-weight (LWH/HWH) homologues [11–16]. Certain biomarkers allow specifying the biogenic component of compounds, in particular to estimate the contribution of herbaceous and woody



vegetation to the formation of the allochthonous component of HCs entering bottom sediments. These are, for example,  $C_{31}/C_{29}$  and ACL ratios [14, 17, 18]. To differentiate the oil and biogenic origin of detected HCs such ratios are used as the Carbon Preference Index (CPI), in particular  $CPI_2$  calculated for the high-molecular-weight n-alkanes, the ratio of the value of the unresolved complex mixture (UCM/R) to the aliphatic fractions of HCs, ACL, LWH/HWH [11, 14, 19–21].

### Material and methods

The material for the study was bottom sediment samples of the upper layer (0–5 cm) taken by a diver with Plexiglas pipes with sealed top and bottom during the winter of 2019 in different parts of the coastal water area of Balaklava Bay (Fig. 1). Sampling stations were selected with regard to the peculiarities of the bay morphometry, hydrological-hydrochemical structure of waters, probable sources of pollution and the nature of the sedimentation process. At the same time, the presence of river flow and the zone of pollutant concentration in the central part of the bay was considered [2, 3, 22].

The sample preparation was done according to the procedure<sup>1)</sup>. A sample weight (5–7 g) was placed in a conical flask, 20 cm<sup>3</sup> n-hexane was added and

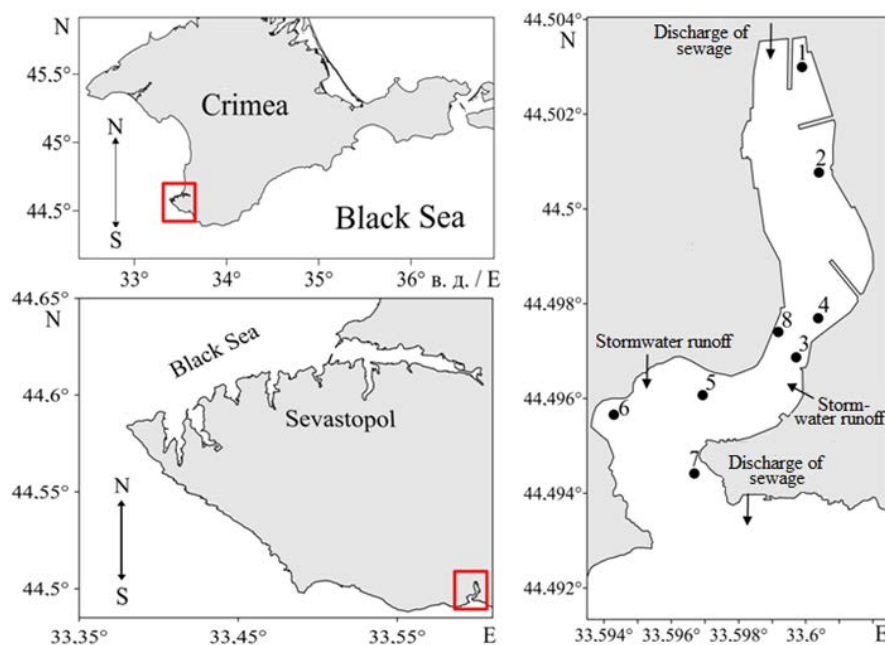


Fig. 1. Map of stations for samplings sea bottom sediments of hydrocarbons analyses in Balaklava Bay, 2019

<sup>1)</sup> Drugov, Yu.S. and Rodin, A.A., 2020. [Ecological Analyses for Oil and Oil Product Spills: Practical Guide]. Moscow: Laboratoriya znaniy, 273 p. (in Russian).

shaken for 30 minutes. The extract was allowed to stand (10 min), then transferred to a clean conical flask. A similar extraction was carried out two more times and 60–70 cm<sup>3</sup> of the extract was obtained. The obtained extract was passed through a glass column (15 cm × 1 cm) with a tapered tip and filled with aluminium oxide to separate the polar compounds, and then concentrated to a volume of 1 cm<sup>3</sup>.

An aliquot of the concentrated extract (1 µL) was injected with a microsyringe into the Crystal 5000.2 Gas Chromatograph evaporator with a flame ionization detector (FID) heated to 250 °C. Hydrocarbons were separated on a HT8 Capillary Column 25 m × 0.32 mm with a stationary phase film thickness of 0.25 µm (SGE Analytical Science). The column temperature was programmed from 40 to 330 °C (temperature elevation rate 10 °C/min). The carrier gas (helium) flow in the column was 2.5 mL/min without splitting. The detector temperature was 320 °C<sup>1)</sup>.

The quantitative determination of the total HC content was performed by calibrating the FID with a HC mixture (C<sub>12</sub>–C<sub>40</sub>), which was prepared gravimetrically, with the HC content within the range of 0.1–5.0 mg/L. The error of the chromatographic method is 4 %<sup>1)</sup>.

To process the results and determine the individual n-alkane content the authors used Chromatec Analytic 3.0 software, the absolute calibration method and percentage normalization<sup>2)</sup>. Sensitivity of FIDs is proportional to the number of carbon atoms in a molecule<sup>2)</sup>. This relation is especially obvious for a hydrocarbon series. Correction mass coefficients of sensitivity *Fi* for the peak areas of sample components were calculated according to state standard GOST 33012-2014 (ISO 7941:1988) by the formula

$$F_i = \frac{(12.01 \cdot n_{C_i} + 1.008 \cdot n_{H_i}) \cdot 0.851}{12.01 \cdot n_{C_i}},$$

where *n<sub>C<sub>i</sub></sub>* is the number of carbon atoms in the i-th component; *n<sub>H<sub>i</sub></sub>* is the number of hydrogen atoms in the i-th component; 0.851 is the mass fraction of carbon in heneicosan used to obtain equality *Fi* = 1 for heneicosan.

HC determination was carried out at the scientific and educational centre of collective use “Spectrometry and Chromatography” of A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS.

The following ratios (markers) were used to determine the probable genesis of n-alkanes:

- $\sum C_{25-35} / \sum C_{15-21(\text{odd})}$  [13];
- TAR =  $\sum C_{27+29+31} / \sum C_{15+17+19}$  [11];
- UCM/R [20, 21];
- C<sub>31</sub>/C<sub>29</sub> [17, 18];
- LWH/HWH =  $\sum (C_{13}-C_{21}) / \sum (C_{22}-C_{37})$  [15, 16];
- Alkterr =  $(C_{27}+C_{29}+C_{31}+C_{33}) / \sum C_{14-38}$  [12];
- ACL =  $(27 \cdot C_{27} + 29 \cdot C_{29} + 31 \cdot C_{31} + 33 \cdot C_{33} + 35 \cdot C_{35} + 37 \cdot C_{37}) / (C_{27} + C_{29} + C_{31} + C_{33} + C_{35} + C_{37})$  [12];

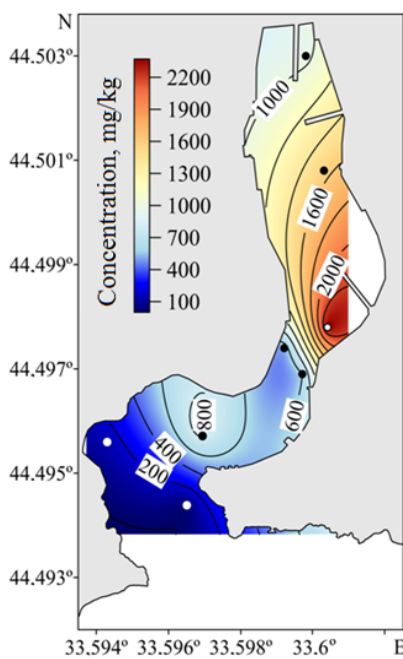
<sup>2)</sup> Emmanuel, N.M. and Sergeev, G.B., eds., 1980. [Experimental Methods of Chemical Kinetics. A Textbook for Higher Education Students]. Moscow: Vysshaya shkola, 375 p. (in Russian).

$$- CPI_1 = (1/2) \{ (C_{15} + C_{17} + C_{19} + C_{21}) / (C_{14} + C_{16} + C_{18} + C_{20}) + (C_{15} + C_{17} + C_{19} + C_{21}) / (C_{16} + C_{18} + C_{20} + C_{22}) \} [19];$$

$$- CPI_2 = (1/2) \{ (C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36}) \} [19].$$

## Results and discussion

The particle size distribution of bottom sediments in Balaklava Bay is not homogeneous [4]. The bottom sediments are represented by grey silt, mainly with an admixture of sand. The proportion of silt is greater in the apex part of the bay, whereas at the bay mouth the marine soils are represented by sand with an admixture of shells, which affects the accumulation capacity of the sediments. The amount of HCs, including aliphatic fraction and unresolved complex mixture, in bottom sediments of Balaklava Bay ranged from 21 mg/kg to 2,385 mg/kg and corresponded to the nature of marine soils. They were distributed unevenly across the water area (Fig. 2). High levels of contamination were registered in the bottom sediments at Stations 2–4 located near the eastern shore of the central part of the bay. The zone of their concentration as well as that of other pollutants [2] was in the central part of the bay. This fact, as indicated in the literature [22], is related not only to hydrodynamic features of the water area but also to the nature of marine soils. At most stations, the obtained HC content values were comparable with data typical for bottom sediments of the Black Sea coastal waters [23]. In particular, similar values were recorded for bottom



sediments in Gelendzhik Bay (11–252 mg/kg), Feodosiya Bay (17–80 mg/kg) and the Bolshoi Sochi coastal area (5–119 mg/kg) [24]. The maximum values noted at St. 4 correspond to the most polluted areas of some coastal waters, e. g. Sfax, Tunisia (up to 1729 mg/kg) and Baku, Azerbaijan (up to 1820 mg/kg) [25, 26].

HC concentrations in marine bottom sediments are not regulated by Russian regulatory documents, so researchers (including Roshydromet staff) often use foreign standards set out in the Dutch Lists<sup>3)</sup>. When comparing

Fig. 2. Spatial distribution of hydrocarbons in Balaklava Bay bottom sediments (2019)

<sup>3)</sup> EarthScience Information Systems. *Dutch Target and Intervention Values, 2000 (the New Dutch List)*. 2000. [online] Available at: [esdat.net/Environmental%20Standards/Dutch/annexS\\_I2000Dutch%20Environmental%20Standards.pdf](https://esdat.net/Environmental%20Standards/Dutch/annexS_I2000Dutch%20Environmental%20Standards.pdf) [Accessed: 3.06.2022].

sediments of Balaklava Bay with the mentioned norms, the HC content exceeded the permissible level (50 mg/kg) in 87.5 % of bottom sediment samples. Today, there are other domestic classifications of bottom sediments contamination with HC. For example, according to the classification of V. I. Uvarova [27], bottom sediments can be divided into

- clean – 0÷5.5;
- slightly contaminated – 5.6÷25.5;
- moderately contaminated – 25.6÷55.5;
- contaminated – 55.6÷205.5;
- polluted – 205.6÷500.0;
- very polluted – over 500.0 mg/kg.

According to this classification, the bottom sediments of Balaklava Bay are classified as slightly contaminated (12.5 %), contaminated (12.5 %) and very polluted (75 %). As noted by I. A. Kuznetsova and A. N. Dzyuban [28], bacterial communities clearly show a “concentration boundary” (40–60 mg/kg) of oil contamination of bottom sediments, below which the water-soil microbial communities can manage HCs entering the bottom sediments and stabilize the situation. According to this data, 87.5 % of the studied bottom sediment samples exceeded the “concentration boundary” of oil pollution (contaminated and extremely polluted according to V. I. Uvarova's classification). All mentioned approaches to assessment of HC pollution level in bottom sediments are of relational character and do not allow identification of HC nature. The most informative in terms of identification of the origin of n-alkanes are various molecular ratios indicating the preferential ways of HC entry into the environment.

In the bottom sediments of Balaklava Bay, n-alkanes in the C<sub>13</sub>–C<sub>35</sub> range were identified. In six samples, C<sub>13</sub> content was below the detection limit. C<sub>14</sub> was not detected in one sample. Alkanes with chain length of C<sub>34</sub> and C<sub>35</sub> were not identified in two and one samples, respectively (see table). The other compounds were present everywhere. Typical chromatograms of the bay bottom sediment HCs are shown in Fig. 3.

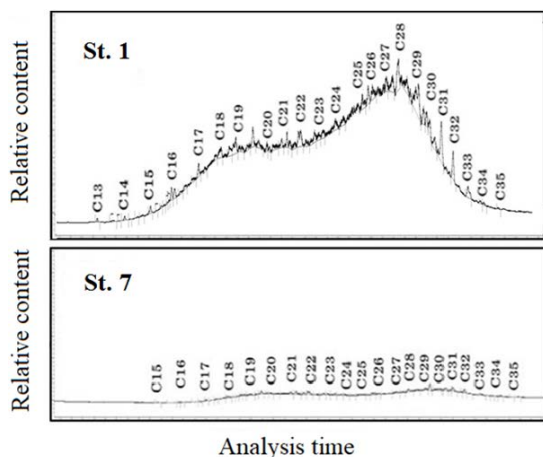


Fig. 3. Typical chromatograms of n-alkanes from sea bottoms sediments of Balaklava Bay

Concentration and diagnostic indexes of n-alkanes in Balaklava Bay bottom sediments

Station number	D	K	$\frac{\sum C_{25-35}}{\sum C_{15-21}}$	TAR	$\frac{LWH/H}{WH}$	Alkterr	C <sub>31</sub> /C <sub>29</sub>	ACL	CPI <sub>1</sub>	CPI <sub>2</sub>	UCM/R
1	13-35	59	2.70	2.42	0.27	0.36	6.27	29.55	0.70	1.06	6.13
2	14-33	82	1.52	1.71	0.40	0.25	4.83	29.05	0.55	0.81	7.41
3	13-35	53	1.58	4.91	0.32	0.39	0.65	29.64	1.03	2.39	4.12
4	14-35	154	2.74	3.05	0.24	0.42	5.93	29.96	0.74	1.04	6.45
5	14-34	94	2.47	4.36	0.29	0.38	0.48	29.24	0.40	1.04	4.20
6	15-35	1	2.03	3.10	0.26	0.08	1.11	28.85	1.30	1.23	4.00
7	13-35	8	0.77	1.06	0.64	0.17	0.53	29.10	1.08	1.49	0.67
8	13-35	34	1.18	1.74	0.67	0.20	1.80	29.83	0.97	0.89	5.39

Note: D – range of identified n-alkanes; K – concentration of identified n-alkanes, mg/kg.

The content of the sum of identified n-alkanes in the bay area ranged from 1 mg/kg to 154 mg/kg (see table). Similar to the total HC content, maximum concentrations were registered in the central part of the bay.

The distribution of n-alkanes on the chromatograms was bimodal. At all stations, the first peak corresponded to compounds in the C<sub>20</sub>–C<sub>22</sub> range and the second peak fell predominantly on C<sub>28</sub>–C<sub>31</sub> (Fig. 4). In particular, at Sts. 3, 6–8, a high proportion of C<sub>21</sub> was observed. At Sts. 5 and 8 a predominance of C<sub>20</sub> was noted. The C<sub>22</sub> homologue had a high concentration at all study stations (except for St. 8). Together with the CPI values (table), which in most cases are close to 1, this indicates the accumulation of products of phytoplankton organism biosynthesis and microbial HC degradation in bottom sediments [1, 29]. For the high-molecular-weight n-alkanes, the maximum concentrations were in the homologues within the C<sub>28</sub>–C<sub>32</sub> range. Odd-numbered compounds in this part of the spectrum are mainly of terrigenous origin [18].

The source of even-numbered n-alkanes C<sub>28</sub>, C<sub>30</sub>, C<sub>32</sub> is the sapropel matter, which is formed on the basis of organic mass of phyto- and zoobenthos, plankton, lower plants and is autochthonous for marine ecosystems [30]. According to available data, chromatograms characteristic of bottom sediments of different genesis show three types of distribution: bimodal distribution, predominance of high-molecular-weight fractions and predominance of low-molecular weight alkanes [12, 31]. The bimodality of distribution is usually attributed to sediment input from both the land and water layer. Consequently, analysis of the peaks on chromatograms of the Balaklava Bay sediment suggests simultaneous inputs of allochthonous, autochthonous compounds and their bacterial degradation.

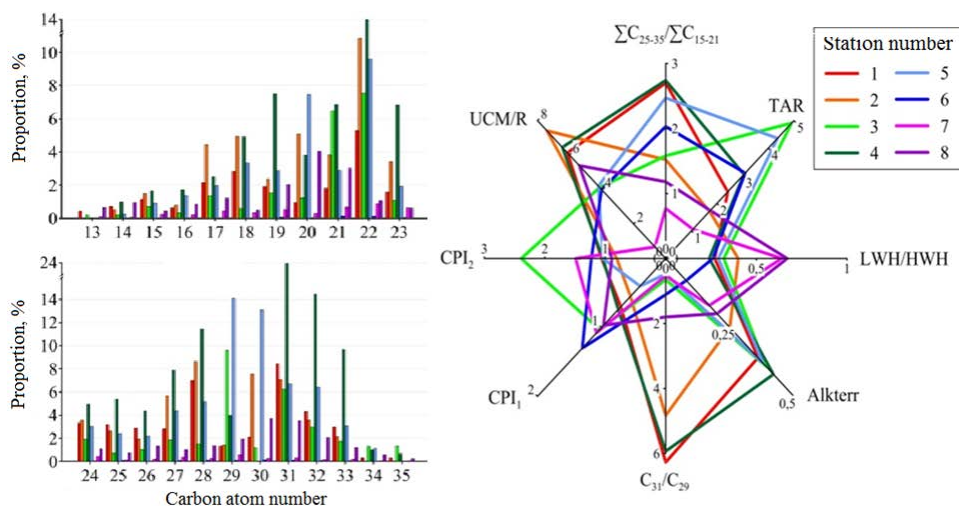


Fig. 4. Distribution of n-alkanes and main markers in the sea bottom sediments of Balaklava Bay

The sum of  $C_{15}$ – $C_{21}$  n-alkanes ( $\sum C_{15-21}$ ) gives an idea of autochthonous compounds [15]. The sum of odd-numbered homologues  $C_{25}$ – $C_{35}$  ( $\sum C_{25-35}$ ) represents mainly terrigenous alkanes [16]. The ratio of these groups allows identifying the origin of organic matter more reliably while excluding the influence of factors such as the sedimentary particle size distribution and sedimentation rate [13]. A high (more than 1) ratio ( $\sum C_{25-35}/\sum C_{15-21}$ ) indicates a strong influence of terrigenous matter. In our case, the values of this index ranged within 0.77–2.74 (see table). The minimum value was noted at St. 7 and at St. 8 this parameter slightly exceeded 1 (1.18). The average value was 1.87. High ratios of the mentioned groups of n-alkanes indicate a significant input of HC from the land.

Another parameter widely used to identify HC sources is the ratio of individual compounds with an odd number of atoms – TAR. It also allows estimating the ratio of allochthonous to autochthonous alkanes. This ratio varied from 1.06 to 4.36 (see table), with an average of 2.79. In general, this ratio characterizes the predominance of allochthonous material coming from the land.

The components  $\sum C_{21-}$  reflect autochthonous substances [15], and  $\sum C_{22+}$  reflect the terrigenous input [16]. The ratio  $\sum C_{21-}/\sum C_{22+}$  (LWH/HWH) is often used to estimate the preferential pathway of organic matter input. The mentioned ratio at the sampling stations ranged within 0.24–0.67 (see table). On average, it was 0.39, which demonstrates terrigenous input of organic matter.

The Alkterr index calculated using the formula  $(C_{27}+C_{29}+C_{31}+C_{33})/\sum C_{14-38}$  is one of the indicators of inputs from the land [32]. The index ranged from 0.08 to 0.39 (see table), with an average of 0.28. Together with other markers, this indicates a high content of terrigenous matter in the bottom sediments.

Terrestrial woody and herbaceous vegetation often contributes significantly to formation of the qualitative composition of bottom sediments. The main peak associated with woody vegetation falls on  $C_{29}$ , while that associated with herbaceous vegetation falls largely on  $C_{31}$  [17, 18]. The ratio of these markers ( $C_{31}/C_{29}$ ) varied widely: 0.53–6.27 (see table), with an average of 2.70 for the water area. Thus, we can say that in general the bottom sediments in the water area contain traces of herbaceous plants. Except for St. 5 and 7, where the proportion of  $C_{29}$  associated with woody species was high. At St. 6 the contribution of both components was approximately equal.

The average carbon chain length (ACL) of n-alkanes is also related to their genesis. Low ACL values are characteristic of woody plant HCs, whereas high ones indicate the predominance of herbaceous vegetation in the formation of HCs [14]. In case of fresh oil contamination, a decrease in ACL is also observed [33]. This parameter varied from 28.85 to 29.96 (see table), with an average value of about 30. This shows approximately the same role of herbaceous and woody plants

in the formation of organic matter of the bottom sediments of the area. However, it should be noted that this approach is only applicable to “fresh” organic matter [1].

It is known that when oil and oil products degrade, the light HCs are the first to disappear and the concentration of more stable compounds increases. Therefore, the ratio of high-molecular-weight n-alkanes is more informative to determine the nature of HCs. The main criterion of HC biogenicity for high-molecular-weight n-alkanes is the widely used CPI coefficient, the ratio of the sum of odd- and even-numbered homologues [1, 34–36]. In case of oil contamination its values are often close to 1.

Groups of alkanes with short and long carbon chains tend to have different odd number indices, which are denoted as  $CPI_1$  and  $CPI_2$ , respectively. Calculations showed that for the lighter n-alkanes  $CPI_1$  ranged within 0.40–1.30 (see table), with an average of 0.84. The CPI was low at sites 1, 2, 5. At the other sites, it was close to 1. The high content of low-molecular-weight even-numbered n-alkanes in the indicated water areas may be the result of microbiological degradation of organic substances [1, 7, 37]. At the other stations, the proportions of the above mentioned compounds were approximately equal.  $CPI_2$  values describing the ratio for n-alkanes with long chains ranged from 0.81 to 2.39 (see table), with an average of 1.24. The predominance of odd-numbered compounds was registered at Sts. 3 and 7. For other areas the index was about 1, which indicates oil contamination of the bottom sediments. For the high-molecular-weight n-alkanes the CPIs were higher for the low-molecular-weight ones.

For n-alkanes containing traces of oil contamination, a clear predominance of odd- or even-numbered components is not characteristic [38]. Therefore, in terms of low-molecular-weight, oil contamination can be supposed at Sts. 3, 4, 6–8. It is likely that relatively fresh oil HCs, which have not yet degraded, have been registered. But the simultaneous detection of CPI about 1 and  $C_{29}$  peaks at these stations may indicate not the oil but planktonogenic nature of the detected aliphatic HCs [1]. This phenomenon was noted for Sts. 3, 7. For the high-molecular-weight n-alkanes the CPI close to 1 at Sts. 1, 2, 4–6, 8 is evidence of chronic oil pollution of the water area.

The prevalence of compounds with an odd number of carbon atoms in the low-molecular-weight n-alkanes may indicate not only fresh input of oil products but also their production as a result of activity of microorganisms [38, 39] and macrophytes [17, 18]. So, we can assume that n-alkanes with short carbon chains identified in the bottom sediments of the inner parts of Balaklava Bay were of mixed origin, which is characteristic of the coastal areas of the Black Sea [40].



One of the important parameters in assessing the presence of oil contamination as well as the intensity of biodegradation of HCs is the occurrence of unresolved background or unresolved naphtheno-aromatic “hump” (Unresolved Complex Mixture, UCM) on chromatograms, with a maximum in the high-molecular-weight n-alkanes [1]. UCM is a mixture of complex isomers and homologues, branched and cyclic HCs, which cannot be separated in a chromatographic column [41]. The number of oil components representing UCM can be up to 250,000 compounds. This indicates the fact that UCM is the most complex mixture of organic compounds existing on Earth [42]. However, in spite of the obvious association with oil sources, the presence of UCM in the low concentration range may also be due to bacterial degradation of autochthonous organics [43].

The unresolved background configuration depends on its composition. The “humps” of natural and anthropogenic HCs differ [1]. Anthropogenic compounds are characterized by a “hump” in the region typical of high-molecular-weight n-alkanes. This maximum in the low temperature region occurs due to microbial degradation of natural organic compounds, in particular plant detritus [44]. At Sts. 1–5 and 8, the unresolved background curve was “double-humped” (an example is shown in Fig. 3). At Sts. 2 and 8, the steeper “hump” was in the low-temperature region indicating the predominant degradation of autochthonous matter.

At other stations (Sts. 1, 3–5), we can speak about the presence of an unresolved mixture due to both microbial degradation and accumulation of anthropogenic organic compounds. At Sts. 6 and 7 located closer to the bay mouth and having a significantly lower (1–2 orders of magnitude) level of n-alkanes in the bottom sediments than at the other stations, the unresolved background was subtle. It should be noted that at Sts. 6 and 7, located in the seaward part of the study area, the soil nature differed from that in other areas of the water area with a muddy structure. These sediments were composed of sand and/or sand with an admixture of shells. As a result, in this area organic matter is likely to be deposited to a lesser extent than in the inner part of Balaklava Bay.

The ratio of unresolved background value to n-alkanes content at most of the sampling stations ranged within 4–7 (Table 1), which is a diagnostic sign of chronic oil pollution [20, 21]. The exception was St. 7, where at low HC concentrations the “hump” fraction was 0.67, which most likely corresponds to the result of bacterial transformation of organic substances [43].

The marker values calculated for the bottom sediments of Balaklava Bay (Fig. 4) indicate the predominance of terrigenous HCs in the bottom sediments of the water area as well as the presence of oil contamination. In this aspect, St. 7 stands out: in the bottom sediments thereof, judging by the marker values, HCs of autochthonous nature prevailed. CPI and UCM/R markers at this station indicate the presence of natural HCs [20, 21]. Given their total content, the outer part of

the bay (St. 6 and 7) can be characterized as having low HC levels in the bottom sediments. It is the most seaward part of the study water area located behind the circular eddies “locking” the bay and limiting its water exchange with the sea [45]. The low HC values in the area of the seaward part of the study area (St. 6 and 7) may also be attributed to the nature of the marine soils represented by sand with an admixture of shells, which affects the sediment accumulation capacity. However, the absence of oil contamination and predominance of autochthonous n-alkanes in the bottom sediments are only noted in the eastern part of this area.

### Conclusions

1. The total amount of HCs in bottom sediments of Balaklava Bay varied from 21 mg/kg to 2385 mg/kg and corresponded to the nature of the bottom sediments. The recorded pollution levels were mostly consistent with those observed in contaminated areas of the World Ocean. The mentioned substances were distributed unevenly over the water area. Their concentration zone was in the central part of the bay. Minimal HC content in the bottom sediments was registered in the open part of the bay.

2. The content of n-alkanes in the bottom sediments of Balaklava Bay. Balaklava ranged from 1 to 154 mg/kg. The maximum values were recorded in the central part of the water area (in the area of constriction), particularly near its eastern shore, and the minimum values were recorded in the open part of the bay.

3. The distribution of n-alkanes in the chromatograms showed signs of bimodality throughout the water area of Balaklava Bay, which indicates a mixed origin of HCs.

4. The molecular markers indicate a mainly terrigenous origin of HCs in the bottom sediments of the water area as well as the presence of chronic oil pollution in the inner part of the bay.

5. The bottom sediment composition of the most open seaward part of Balaklava Bay differed from that of the bottom sediments in the inner parts of the water area. Given the marker values, HCs of autochthonous nature prevailed there.

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**Ekaterina A. Kotelyanets** – sampling and primary processing of samples, calculation of diagnostic indices

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## Assessment of Mazut Toxicity for Embryos of Two Sea Fish Species

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### Abstract

Shelf areas of the seas and oceans characterizing high level of bioproductivity are significantly affected by anthropogenic pollution, including oil contamination. Early developmental stages of marine organisms are very sensitive to pollutants, which generate oxidative stress in them and provoke further pathological processes. We studied the influence of mazut in a concentration of 0.01 and 0.1 ml/L on the developing embryos of two benthic fish species: peacock blenny *Salaria pavo* and round goby *Neogobius melanostomus* in Stage VI. We studied the following biomarkers: superoxide dismutase (SOD), catalase (CAT), peroxidase (PER) and glutathione reductase (GR) spectrophotometrically. The results showed high toxicity of mazut accompanied with the changes in the activity of key antioxidant enzymes in the embryos of both tested fish species, which generated oxidative stress in developing fish exposed to mazut. The general trends and peculiarities of the responses of embryo enzymes to the oil intoxication were shown, which depended on the morphological peculiarities of eggs of the tested fish species. The peacock blenny egg has thicker shell than the round goby egg, therefore, it is protected better from the environmental impact. The paper discusses possibilities of use of the demersal fish eggs for the assessment of ecological status of shelf areas in case of oil pollution.

**Keywords:** Black Sea, mazut, pollution, fish embryos, biomarkers, antioxidant enzymes

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# Оценка токсичности мазута для икры двух видов морских рыб

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## Аннотация

Шельфовые зоны морей и океанов, характеризующиеся высокой биопродуктивностью, в наибольшей степени подвержены антропогенному загрязнению, включая нефтяное. Ранние онтогенетические стадии гидробионтов очень чувствительны к действию загрязнителей, приводящих к возникновению окислительного стресса и развитию последующих патологических процессов. Исследовали влияние мазута в концентрации 0.01 и 0.1 мл/л на активность антиоксидантных ферментов, являющихся маркерами окислительного стресса, у эмбрионов собачки-павлина *Salaria pavo* и бычка-кругляка *Neogobius melanostomus* на VI этапе развития. В качестве биомаркеров спектрофотометрическими методами исследовали активность ключевых антиоксидантных ферментов супероксиддисмутазы (СОД), каталазы (КАТ), пероксидазы (ПЕР) и глутатионредуктазы (ГР). Результаты позволили выявить токсичность мазута, что выразилось в изменении активности тестируемых ферментов в эмбрионах обоих видов рыб, свидетельствующем о развитии окислительного стресса у развивающихся зародышей, инкубированных в растворах токсиканта. Установлены характерные общие закономерности и особенности ответных реакций ферментов эмбрионов на интоксикацию мазутом, зависящие от морфологического строения икринок исследуемых видов. Икринка собачки-павлина имеет более толстую внешнюю оболочку, чем у бычка-кругляка и, следовательно, она лучше защищена от внешних воздействий. Обсуждается возможность использования демерсальной икры донных рыб в качестве тест-объектов для оценки экологического состояния прибрежных акваторий при нефтяном загрязнении.

**Ключевые слова:** Черное море, мазут, загрязнение, эмбрионы рыб, биомаркеры, антиоксидантные ферменты

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## Introduction

Ecotoxicological methods of the assessment of the effects of various pollutants are recognized for the analysis of the state of aquatic ecosystems and their inhabitants, since they have a number of advantages, namely: they do not require any expensive equipment, they are quick, and owing to the responses of test organisms they allow to identify adverse changes in ecosystems within a fairly short period of time. From this perspective, the ecotoxicological approach has found wide application in ecology and aquatic toxicology. It is an integral part of some monitoring programs, which is widely used in environmental risk analysis [1]. The choice of test objects is of great importance here, as their reactions make



it possible to assess the effect of pollutants. One of the informative test systems is represented by fish embryos and larvae, which are sensitive to the effects of various pollutants and, therefore, are widely used on the practical side to establish legal levels of environmental pollution and assess the state of the aquatic environment. The fish embryos embryotoxicity test is an obligatory component of the standard technique<sup>1)</sup> for the threshold limit value (TLV) concerning fishery water bodies, including marine areas with high economic activities [2]. First of all, it is referred to the shelf zones of the seas and oceans, which are most susceptible to anthropogenic influence, which negatively affects the ecosystem and its inhabitants.

One of the most common and dangerous pollutants of the marine environment has still been oil and its products [3, 4]. At the same time, an increase in shelf area oil production, as well as the development of new areas, including in the Black Sea, inevitably cause an increase in pollution of the marine environment with petroleum hydrocarbons, drilling mud and other associated pollutants [5–7]. They include components characterizing different levels of toxicity [7], which affect marine organisms in different ways. Concurrently, the sea shelf is the most biologically productive area, where reproduction and development (at early developmental stages) of organisms occur, for which even the smallest concentration of oil pollution poses a significant danger [8–11]. Moreover, researchers note the manifestation of diverse disorders at different stages of biological organization. Such disorders are characterized by a delay in growth and development, deterioration of body functions [12, 13], appearance of anomalies, increase in mortality, and change in the time of hatching of larvae from fish eggs [14]. All these indicators can serve as convenient bioindicators of the toxic effect of oil on the early developmental stages of fish, so they are widely used in aquatic toxicology. However, primary toxic reactions unfold at the molecular level, and informative biomarkers in this case are represented by antioxidant enzymes that protect the body from oxidative stress [15–18]. The responses of the protective antioxidant system can depend on the fish species, stage of their development, and toxicant dose, which should be taken into account when planning ecotoxicological experiments and monitoring programs, including the determination of legal levels of pollutants in the marine environment.

The aim of this work is a comparative analysis of the responses of biomarkers, in terms of which the activity of four antioxidant enzymes in the fish eggs of peacock blenny *Salaria pavo* and round goby *Neogobius melanostomus* were analyzed at developmental stage VI upon incubation exposed in the mazut solution in a concentration of 0.01 and 0.1 ml/L.

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<sup>1)</sup> Russian Federal Fishery Agency, 2009. [*Guidelines for the Development of Water Quality Standards for Fishery Water Bodies, Including Standards for Threshold Limit Values of Harmful Substances in the Water of Fishery Water Bodies*]: Approved by Order no. 695 as of 4 August 2009 by the Russian Federal Fishery Agency (in Russian).

## Materials and methods

The fish eggs of round goby *Neogobius malanostomus* and peacock blenny *Salaria pavo* at developmental stage VI were collected in the Sevastopol coastal waters. The fish eggs are benthic, and the embryos develop in the coastal area. Stage VI is the stage of the mobile embryo, which is characterized by the beginning of the moving activity of the embryo simultaneously with the heart pulsation [19].

Mazut in a concentration of 0.01 and 0.1 ml/L was added to filtered sea water, stirred for 20–30 minutes, settled for 30 minutes, and poured into aerated aquariums, in which the fish eggs in the amount of 50 pieces were placed at a water temperature corresponding to the sea water temperature [20]. Control fish eggs without any oil products were kept under similar conditions. At the end of stage VI, fish eggs were taken to determine the activity of enzymes, and the whole procedure was replicated three times.

The activity of such antioxidant enzymes as superoxide dismutase (SOD), catalase (CAT), peroxidase (PER), and glutathione reductase (GR) was analyzed with the help of Specol-211 spectrophotometer (Carl Zeiss, Iena, Germany) in accordance with the methods that we had described previously [21]. The SOD activity was expressed in arbitrary units, the CAT activity – in milligrams  $H_2O_2$ . The PER activity was expressed in absorbance units, that of GR – in nanomoles NADPH. All units of enzyme activity were adjusted to milligram of protein per minute.

The research results were processed statistically by standard methods, and the arithmetic mean ( $M$ ) and the error of the mean ( $m$ ) were calculated. Significance of differences was determined by the Mann–Whitney test; differences were considered significant at  $p < 0.05$ .

## Results

The obtained results made it possible to establish certain patterns and discover features of changes in the antioxidant enzyme activity in developing embryos of two fish species during incubation in a mazut solution in both concentrations (Table). In a concentration of 0.01 ml/L, the SOD activity decreased by 83.5 % significantly ( $p < 0.05$ ) in peacock blenny embryos, but with an increase in the toxicant content, it increased almost 3 times as against the control (Table, Fig. 1). Concerning round goby embryos, a decrease in the enzyme activity was also stated in both mazut concentrations by 51–71 % (Fig. 2).

The CAT activity in peacock blenny embryos increased by almost 140 % in a low mazut concentration, and in a high concentration it remained 40 % higher as against the control. Concerning round goby, other relationship was established: in a concentration of 0.01 ml/L, the enzyme activity showed no changes, and in a concentration of 0.1 ml/L, it decreased by 50 % (Fig. 2).

The PER activity in peacock blenny embryos did not change in a low mazut concentration, but it increased by 150 % with a toxicant dose increase (Fig. 1). Round goby embryos showed a significant decrease in enzyme activity in both mazut concentrations by 79–81 % (Fig. 2). Under the influence of the toxicant, the GR activity decreased in peacock blenny embryos by 38–53 % as against the control, and in round goby embryos – by 69–54 %, respectively (Fig. 1).

Antioxidant enzyme activity (mg protein/min,  $M \pm m$ ) in the peacock blenny and round goby embryos at developmental stage VI exposed to mazut at a concentration of 0.01 and 0.1 ml/L

Enzymes	Peacock blenny				Round goby			
	0		0.01		0.1		0	
	Mazut concentration, %							
SOD	137.4 ± 18.6	22.2 ± 8.6	489.5 ± 28.3	150.8 ± 29.0	43.7 ± 8.6	74.2 ± 12.3	0.01	0.1
CAT	0.05 ± 0.01	0.14* ± 0.08	0.07 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0.05 ± 0.01	0.11 ± 0.01	0.05 ± 0.01
PER	0.04 ± 0.003	0.040 ± 0.003	0.10 ± 0.02	0.44 ± 0.01	0.080 ± 0.005	0.08 ± 0.01	0.080 ± 0.005	0.08 ± 0.01
GR	4.35 ± 1.38	2.7* ± 0.8	2.04 ± 0.15	27.53* ± 1.50	7.6 ± 0.9	12.7 ± 1.5	7.6 ± 0.9	12.7 ± 1.5

Note: SOD – superoxide dismutase, CAT – catalase, PER – peroxidase, GR – glutathione reductase.

\* The differences are significant at  $p < 0.05$  between the enzyme activity to the control.

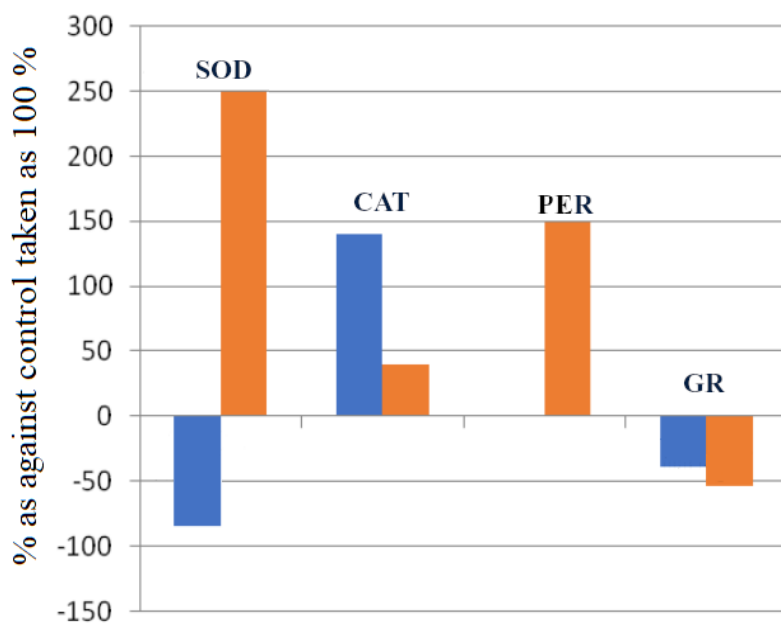


Fig. 1. The changes of the antioxidant enzyme activity in the developing peacock blenny embryos exposed to mazut as against the control taken as 100 % (mazut concentration: blue – 0.01 ml/L; orange – 0.1 ml/L)

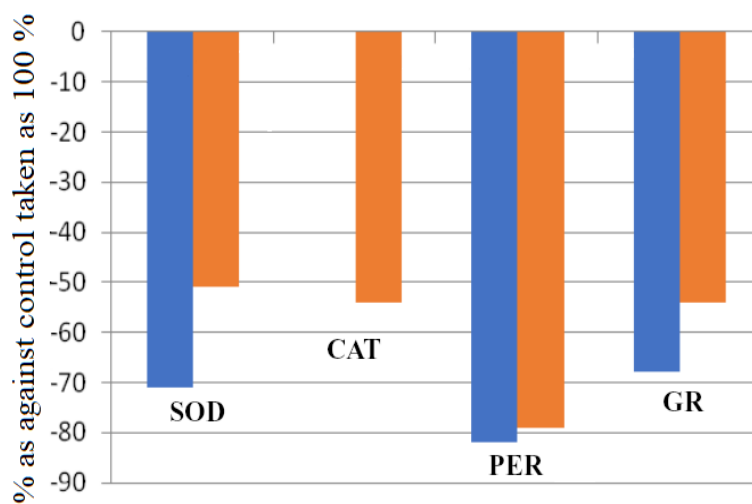


Fig. 2. The changes of the antioxidant enzyme activity in the developing round goby embryos exposed to mazut as against the control taken as 100 %. The other nomenclatures are the same as for Fig. 1

## Discussion

Thus, the obtained results showed significant differences in the responses of antioxidant enzymes in the embryos of two fish species exposed to mazut. At the same time, the antioxidant system of the round goby embryos turned out to be more sensitive to the effect of mazut if we compare it with the peacock blenny defense system. The activity of all the studied enzymes in the round goby embryos under the influence of the tested mazut concentrations was reduced by 50–89 % as against the control, while the peacock blenny indicators changed ambiguously and depended on the toxicant dose. Thus, the peacock blenny embryos SOD activity during the incubation in the mazut solution with a lower concentration decreased, but with its increase, it increased by more than 2 times as against the control. This indicates that intoxication with mazut develops a protective reaction on the part of the antioxidant system key enzyme, which converts the superoxide radical to less toxic products, in particular, to hydrogen peroxide. The activity of CAT decomposing hydrogen peroxide increased by 40–145 % under the action of the toxicant as against the control in peacock blenny embryos, which also indicated the processes of H<sub>2</sub>O<sub>2</sub> detoxification as a protective reaction of embryos to the effect of oil products [22]. The same response was stated for PER, which degrades organic peroxides. In the studied mazut concentrations, GR activity in peacock blenny embryos was slightly inhibited.

The obtained data demonstrate the development of oxidative stress in the embryos of two fish species in response to mazut exposure, which is consistent with the results of other authors. These data showed that oil caused multiple stress in marine organisms, accompanied by an increase in the production of free radical products, impaired reproduction, DNA damage, and developmental and behavioral abnormalities, as well as a decrease in immunity [23, 24].

An increase in enzyme activity indicates the formation of an adaptive response of the antioxidant system of embryos to neutralize the products of reactive oxygen species, while a decrease in the activity of enzymes is due to intoxication, which causes their inhibition and leads to their inability to perform protective functions. In all cases, there is an outflow of energy for antioxidant protection, which reduces the metabolic rate of the developing embryo, impairs the provision of normal processes of growth, development, and hatching [17, 25]. The presented data are indicative of the informative value of the antioxidant system parameters for the assessment of the toxic effects in marine organisms under the action of oil pollution. In this connection, they were chosen within this research as biomarkers for the analysis of the mazut embryotoxicity.

Our research showed the reorganization of the enzyme antioxidant system in developing embryos of peacock blenny and round goby depending on different concentrations of the toxicant. As previously noted [16], before the larvae emerge from the shell of the fish egg, which protects it from the adverse effects of the external environment, there is an increase in the antioxidant enzyme activity,

which is associated with the protection of the body from the upcoming oxidative stress. However, under the influence of the tested mazut concentrations in the developing fish eggs, the response reactions of antioxidant protection were modified. Subject to the existence of a toxicant, additional efforts are required for the processes of its detoxification, which results in corresponding metabolism reorganization. It is necessary to note the species-specific reaction of fish embryos to the mazut action, which can be stipulated by the peculiarities of the morphological structure of the fish eggs. The fish egg shell thickness of round goby makes 4  $\mu\text{m}$ , and of peacock blenny – 5  $\mu\text{m}$  [19]. This means that a peacock blenny fish egg is better protected against the environmental impact than a round goby fish egg, which corresponds to the biochemical studies data. In addition, a round goby fish egg is almost twice as large (1.9 mm in diameter) as a peacock blenny fish egg (0.75–0.80 mm in diameter). The larger surface of a round goby fish egg makes it possible to adsorb more of the toxicant, which penetrates and accumulates in the developing embryo up to the concentrations that cause intoxication of the body and decrease in its protective reactions expressed in the enzyme inhibition.

### Conclusion

The results of this research demonstrate the effectiveness of the use of molecular biomarkers represented by the protective antioxidant system enzymes in order to assess the state of the early ontogenetic stages of fish that respond to a stressor (oil). At the same time, the species specificity of the responses of the peacock blenny and round goby embryos to the action of mazut due to the specific structure of the fish eggs of the two tested species was established. A peacock blenny fish egg is better protected from external influences than a round goby fish egg, since the thickness of its shell is greater than that of the round goby (5  $\mu\text{m}$  and 4  $\mu\text{m}$ , respectively). Aside from that, a round goby fish egg is almost 2 times larger than a peacock blenny fish egg and, thus, it is able to adsorb more toxicant that penetrates inside and accumulates in the developing embryo, which causes intoxication and decrease in protective reactions. This should be taken into account when choosing test objects and their biomarkers in order to develop biotesting methods, systems of rapid response and elucidation of the mechanisms of adaptation of marine fish early developmental stages to environmental impact.

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