

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 (C₁₂–C₄₀), 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 C₁₃–C₃₅. 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_{terr}, $\sum C_{25-35}/\sum C_{15-21(\text{odd})}$) and also signify chronic petroleum contamination (CPI₂, 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 predomination 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 (C₁₂–C₄₀) (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 C₁₃–C₃₅. 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 (*CPI₂*, *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 procedure¹⁾. A sample weight (5–7 g) was placed in a conical flask, 20 cm³ n-hexane was added and

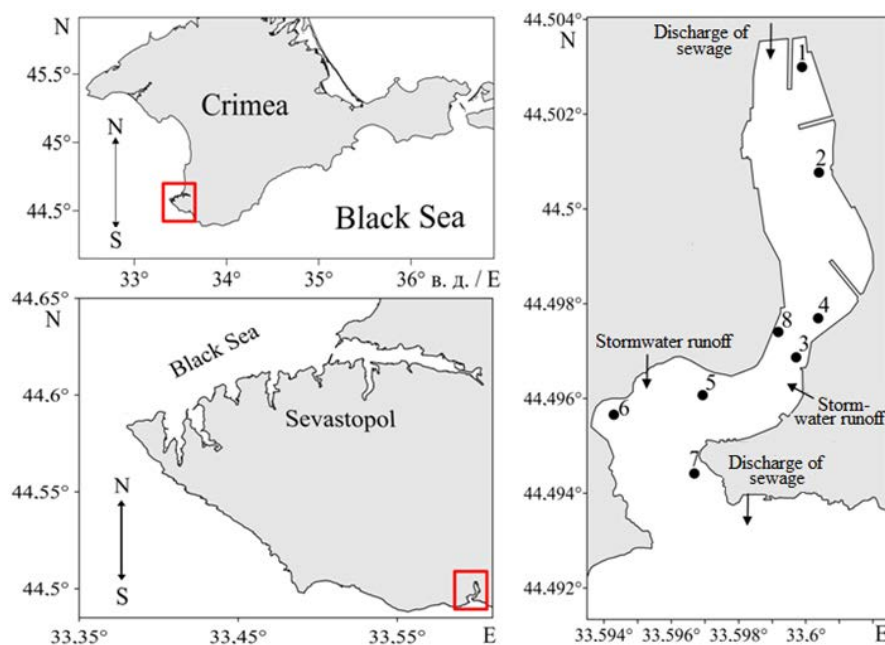


Fig. 1. Map of stations for samplings sea bottom sediments of hydrocarbons analyses in Balaklava Bay, 2019

¹⁾ 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 cm³ 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 cm³.

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 °C¹⁾.

The quantitative determination of the total HC content was performed by calibrating the FID with a HC mixture (C₁₂–C₄₀), 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 %¹⁾.

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 normalization²⁾. Sensitivity of FIDs is proportional to the number of carbon atoms in a molecule²⁾. 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_{C_i} is the number of carbon atoms in the i-th component; n_{H_i} 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 $F_i = 1$ 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];
- C₃₁/C₂₉ [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];

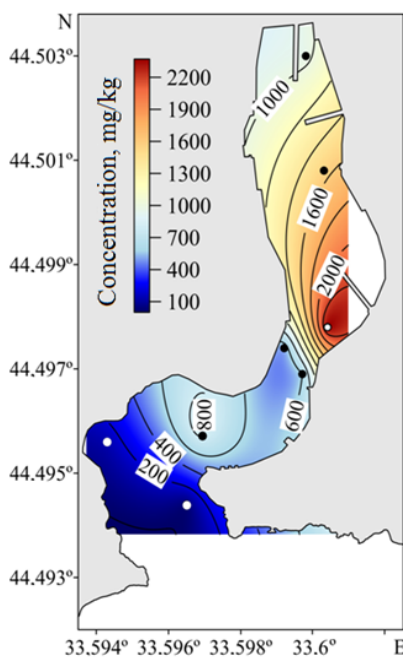
²⁾ Emmanuel, N.M. and Sergeev, G.B., eds., 1980. [Experimental Methods of Chemical Kinetics. A Textbook for Higher Education Students]. Moscow: Vysshaya shkola, 375 p. (in Russian).

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

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

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 Lists³⁾. When comparing

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

³⁾ 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 [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 C₁₃–C₃₅ range were identified. In six samples, C₁₃ content was below the detection limit. C₁₄ was not detected in one sample. Alkanes with chain length of C₃₄ and C₃₅ 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.

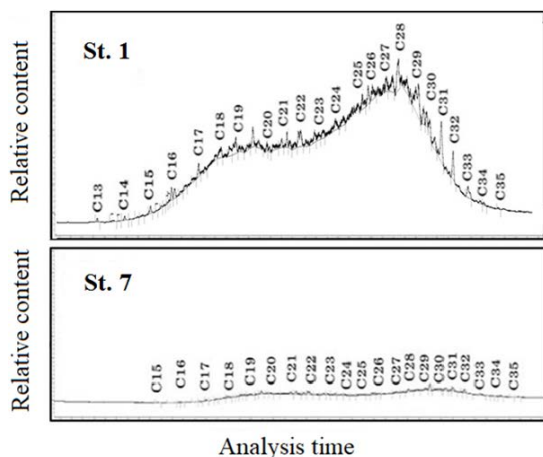


Fig. 3. Typical chromatograms of n-alkanes from sea bottom sediments of Balaklava Bay

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 ₃₁ /C ₂₉	ACL	CPI ₁	CPI ₂	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 C₂₀–C₂₂ range and the second peak fell predominantly on C₂₈–C₃₁ (Fig. 4). In particular, at Sts. 3, 6–8, a high proportion of C₂₁ was observed. At Sts. 5 and 8 a predominance of C₂₀ was noted. The C₂₂ 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 C₂₈–C₃₂ range. Odd-numbered compounds in this part of the spectrum are mainly of terrigenous origin [18].

The source of even-numbered n-alkanes C₂₈, C₃₀, C₃₂ 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.

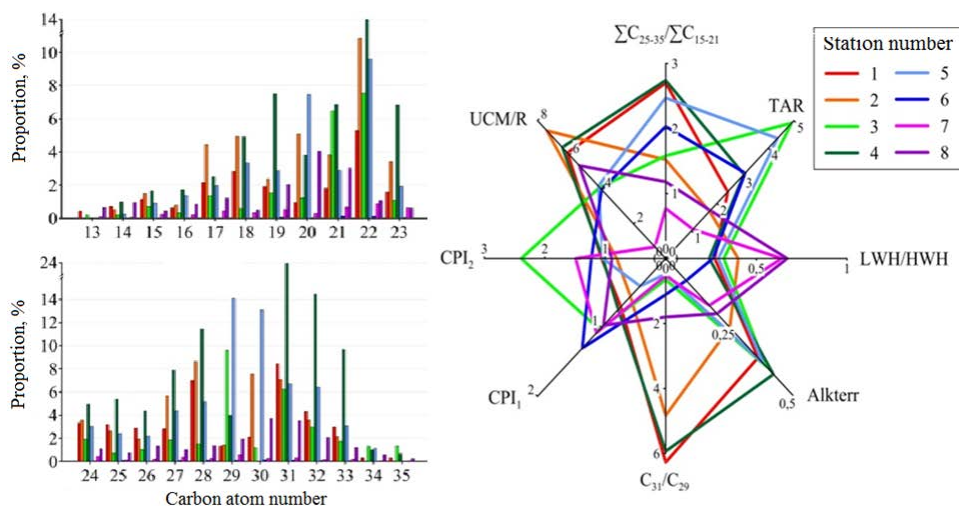


Fig. 4. Distribution of n-alkanes and main markers in the sea bottom sediments of Balaklava Bay

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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