



Hydrocarbons composition of sea bottom sediments (Balaklava Bay, Black Sea)

O. V. Soloveva¹ · E. A. Tikhonova¹ · K. I. Gurov² · E. A. Kotelyanets²

Received: 21 January 2022 / Revised: 29 March 2022 / Accepted: 2 April 2022

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Abstract

Coastal regions are zones of active anthropogenic impact. The present environmental problems of Balaklava Bay (Black Sea), which has an increased anthropogenic load for a long time, are of growing interest. It is known that high concentrations of hydrocarbons (HCs) negatively affect the life processes of hydrobionts. The purpose of this work is to determine the content and spatial distribution of HCs as well as to assess the possible sources of their input in the bottom sediments of Balaklava Bay. The identification and quantitative determination of total HC content were carried out by a gas chromatography method on a gas chromatograph “Crystal 5000.2” equipped with a flame ionization detector and calibrated with a mixture of hydrocarbons (C₁₀–C₄₀). *n*-hexane was used as an extractant of HCs. It was found that the total amount of HCs in sediments varied from 21 to 2385 mg/kg, and *n*-alkane concentrations varied from 1 to 154 mg/kg. The HCs are distributed in bottom sediments mosaically with the maximum concentrations in the central part of the bay and the minimum contents in its open part. It was determined that identified *n*-alkanes of bottom sediments ranged from C₁₃ to C₃₅ and had a bimodal distribution, which indicates a mixed origin of hydrocarbons. The calculated markers indicate a predominantly terrigenous origin (TAR, Alk_{terr}, $\sum C_{25-35}/\sum C_{15-21}(\text{odd})$) of HCs as well as chronic oil pollution (CPI₂, UCM/R) of that area. Diagnostic indices used for the differentiation of petroleum from biogenic hydrocarbons allow us to assume the predominant presence of natural HCs.

Keywords Hydrocarbons · *n*-alkanes · Bottom sediments · Diagnostic indices · Balaklava Bay · Black Sea

Introduction

Coastal regions are zones of active anthropogenic load, as well as intensive hydro- and geodynamic processes. This determines the high rate of changes in the characteristics of coastal ecosystems as a result of the simultaneous influence of natural and anthropogenic factors. It is known that bottom sediments are a fairly conservative, and at the same time, it is a complex multicomponent system. This system can accumulate various pollutants, including those of organic origin (in particular, hydrocarbons), and be a source of water

secondary pollution (Kotelyanets et al. 2019; Tikhonova et al. 2019; Kremenchutskii and Gurov 2021).

At present the environmental problems of Balaklava Bay have a significant interest. In recent years, the load on the water area has increased due to its active exploitation as a yacht marina. It is known that the areas of the most anthropogenic hydrocarbons inputs are located in coastal areas, river mouths and near-port waters (Nemirovskaya 2013; Kotelyanets et al. 2019). Balaklava Bay fits all of the above descriptions: its coastline is heavily exploited, Balaklavka River flows into the bay, and the moorage walls of the water body are intensively used as a berth for yachts and small vessels (Orekhova et al. 2019; Tikhonova et al. 2019). The situation is worsened due to the lack of centralized sewage system in waterfront cafes, when untreated wastewaters directly flow into the aquatic environment.

It is known that high concentrations of HCs negatively affect life processes of hydrobionts (Vorobyov 2006). Therefore, many researchers have analyzed the total organic matter content in bottom sediments (Nemirovskaya 2013; Kotelyanets et al. 2019; Tikhonova et al. 2019). This indicator

Editorial responsibility: Jing Chen.

✉ K. I. Gurov
gurovki@gmail.com

¹ A.O. Kovalevsky Institute of Biology of the Southern Seas, Russian Academy of Sciences, Sevastopol, Russia

² Marine Hydrophysical Institute, Russian Academy of Sciences, Sevastopol, Russia



provides an estimation of the organic pollution level in the water area, but it does not allow identifying the nature of these substances.

The genesis of organic matter, including HCs, in bottom sediments allows to determine the molecular composition of normal alkanes (*n*-alkanes), which is one of the possible markers of the origin of organic matter (Nishimura and Baker 1986). Natural sources of HCs, including *n*-alkanes, in marine bottom sediments are vegetable and to lesser extent animal residues. The anthropogenic HC sources in bottom sediments include organic pollutants, the most common among which are oil and petroleum products (Vershinin et al. 2014).

Various markers are used to identify HC genesis. In order to distinguish between the allochthonous and autochthonous origins, the terrigenous/autochthonous ratio (TAR), Alk-terr terrigenous index, $\sum C_{25-35}/\sum C_{15-21(\text{odd})}$, hydrocarbon average chain length (ACL), ratio of low to high molecular weight homologues (LWH/HWH) (Eglinton and Hamilton 1967; Blumer et al. 1971; Duan 2000; Silliman and Schelske 2003; Huang et al. 2011; Zhang et al. 2014) are often used. Individual biomarkers help to specify the biogenic nature of compounds, in particular to assess the contribution of herbaceous and woody vegetation to the formation of the allochthonous component of sediment HCs such as C_{31}/C_{29} , ACL (Ficken et al. 2000; Mead et al. 2005; Huang et al. 2011). To differentiate the petroleum and biogenic origin of the detected HCs, such ratios as the carbon preference index (CPI) and CPI_2 are used. In particular, CPI_2 index, calculated

for the high molecular weight range of the spectrum, is the ratio of the unresolved complex mixture to the aliphatic HC fraction (UCM/R), ACL, LWH/HWH (Mazurek and Simoneit 1984; Simoneit 1986; Silliman and Schelske 2003; Lv and Zhai 2008; Huang et al. 2011).

The purpose of this work is to determine the content and spatial distribution of hydrocarbons, as well as to assess their possible sources in bottom sediments of Balaklava Bay. The identification of probable HC sources was based on the individual composition of *n*-alkanes and diagnostic indices.

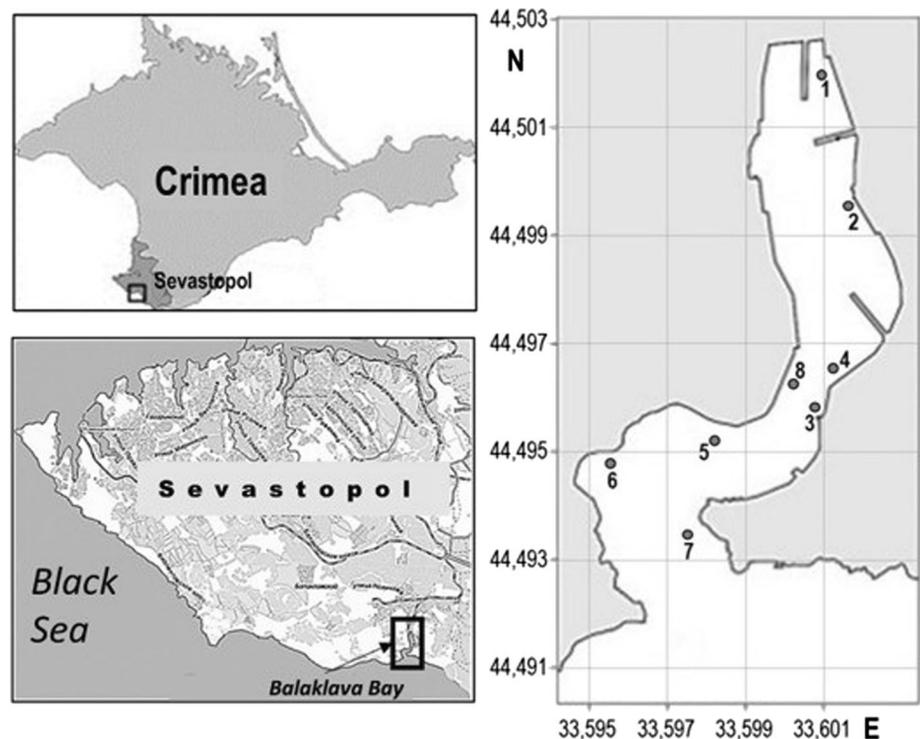
Materials and methods

Study area

Balaklava Bay is located on the southwestern coast of Crimean Peninsula between Cape Fiolent and Cape Aya (Fig. 1). The water area of the bay has an S-shaped configuration. Based on the bottom morphology, shores configuration, and knee-shaped narrowness located in the central part, the bay is divided into two approximately equal water areas—the northern and southern basins, which differ in the features of hydrodynamics and sediments composition.

The central and northern innermost parts of the bay are distinguished by their isolation from the wind effect. Storms are typical only for open and deep-water southern part (Fomin and Repetin 2005). However, despite the isolation of the northern apex of Balaklava Bay from the waves

Fig. 1 Map of sampling stations of bottom sediments for HC analysis in Balaklava Bay, 2019



of the open sea, redistribution of bottom sediment fractions from the western coast to the central part and to the eastern coast under the influence of storms in the southern basin is noted (Gurov and Fomin 2021).

Sampling

Samples of bottom sediment of the upper layer (0–5 cm) were taken in the winter of 2019 in various parts of the coastal area of Balaklava Bay using the Peterson bottom grab (Fig. 1). Sampling stations were selected according to the peculiarities of the bay morphometry, hydrological–hydrochemical structure of waters, probable sources of pollution and nature of the sedimentation process. The presence of river flow and area of pollutant concentration in the central part of the bay also were taken into account (Gurov et al. 2015; Kotelyanets et al. 2019; Orekhova et al. 2019).

Chemical analysis

A weighted sample (5–7 g) was placed into a conical flask with 20 cm³ of *n*-hexane and subjected to ultrasound treatment (ultrasound frequency: 200 Hz; time: 30 min) to extract *n*-alkanes. The extract was allowed to settle (10 min) and then it was transferred to a clean conical flask. A similar extraction was performed three times to fully extract alkane components. In result 60–70 cm³ of the extract was obtained. The obtained extract was passed through a glass column (15 cm × 1 cm) filled with aluminum oxide to separate the polar compounds and was concentrated using rotary evaporation to a volume of 1 cm³.

An aliquot of the concentrated extract (1 μL) was injected with a microsyringe into the evaporator (heated to 250 °C) of a gas chromatograph Krystall 5000.2 with a flame ionization detector (FID). HCs were separated on a 25 m × 0.32 mm HT8 capillary column with a stationary phase, a film thickness of 0.25 μm (SGE Analytical Science). The column temperature was programmed from 40 °C 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.

The *n*-alkanes were identified by matching the retention times observed for samples to those observed for a standard solution of *n*-alkanes. The determination of the total HC content was performed by calibrating the FID with an external standard HC mixture (C₁₀–C₄₀). The standard sample ASTM D2887 Reference Gas Oil (SUPELCO, USA) was used as a mixture of hydrocarbons. The software “Chromatec Analyst 3.0”, the method of absolute calibration and percentage normalization were used for the processing of the results.

Quality assurance and quality control

Before analysis, standard solution of analytes was run to check column performance, peak height and resolution. To ensure quality analyses, standards were injected and analyzed under the same conditions as those used for the samples. Distinct calibration curves, each covering a different range of concentration, were used to quantify the analytes within the linearity range of calibration plot. In this work, the standard addition graph for all *n*-alkanes in sediments extracted was linear with coefficients of determination (R^2) 0.97.

The limits of detection (LODs) were calculated as the quotient of three times the standard deviation of the linear coefficient of the calibration line and the slope of the curve. Also, analysis of method blanks ($n = 5$) was performed, and the aliphatic hydrocarbons (AH) concentrations were below their respective limits of quantification (LOQ). The limits of detection (LODs) were calculated as the quotient of three times the standard deviation of the linear coefficient of the calibration line and the slope of the curve, while the LOQs were evaluated as 3 × LODs. For the AHs, the LODs and LOQs were from 0.09 to 0.27 μg/g and from 0.27 to 0.81 μg/g, respectively.

The determination of HCs was carried out on the basis of the Research and Educational Center for Collective Use “Spectrometry and Chromatography” of the Federal Research Center of the Institute of Biology of the Southern Seas.

Determination of hydrocarbon indices to analyze the origin of HCs

The following ratios, i.e., so called markers, were used to determine the probable genesis of *n*-alkanes:

Results and discussion

Results

Geochemistry of bottom sediments

According to (Gurov et al. 2015; Orekhova et al. 2018; Kotelyanets et al. 2019), the sediments of Balaklava Bay are represented by pelite-aleuritic and aleurite-pelitic silts. On average, the proportion of pelite-aleuritic silts was 43%, and that of aleurite-pelitic silts was 24%. The maximum concentrations of silty material were noted in the bottom sediments of the northwestern part of the bay (98–100%). The content of sandy material varied from 0.2% in the innermost part of the northern basin to 69% in the southern basin.



Coarse-grained material in the surface layer of bottom sediments in the innermost part was represented fragmentarily (in the form of separate shells and shell detritus). In the southern basin, the content of gravel fraction (2–8%) was determined by the influx of terrigenous material as a result of coastal abrasion.

Elevated C_{org} concentrations ($\geq 2\%$) were located in the area of pelitic silt accumulations, which was determined by the organic matter feature to be accumulated in fine sediments. In addition, the maximum concentrations of C_{org} ($> 2.5\%$) were associated with the location of sources of untreated municipal wastewater discharge in the southern part of the northern basin and at the outlet of the bay. The minimum C_{org} values ($\leq 1.5\%$), were observed in the apex part of the bay as the result of the input of loose limestone rocks into bottom sediments during their extraction. In the southern basin they were determined in the form of shell detritus as a result of coastal abrasion (Orekhova et al. 2018).

In bottom sediments an increase in pH was noted from the apex of the northern basin (from pH 7.17) to the open part of the southern basin (up to pH 8.00) with increasing depth along the axis of the bay. The maximum values of potential oxidative activity were recorded in the apex of the northern basin (-163 mV), the minimum values were recorded in the southern basin (-236 mV). For comparison, in the background areas located in the open part of the Megalo-Yalo Bay, Eh was $+198$ mV.

The content of hydrocarbons in sea bottom sediments

The amount of HCs, including the aliphatic fraction and chromatographically unresolved complex mixture, in the Balaklava Bay bottom sediments varied from 21 to 2385 mg/kg. The HC distribution across the water area is uneven (Fig. 2). The area of HC concentration as well as that of other pollutants (Kotelyanets et al. 2019) was in the central part of the bay. This fact, according to the publication (Gurov et al. 2015), is associated with both hydrodynamic features of the water area and sedimentation processes in the bay. High levels of pollution were noted in the bottom sediments at the eastern coast of the central part of the bay (St. 2, 3, and 4).

Hydrocarbon composition of sea bottom sediments and calculated values of used indices

n-alkanes in the range of C_{13} – C_{35} have been identified in Balaklava Bay bottom sediments. The C_{13} content was below detection limit in six samples. C_{14} was not detected in one sample. Alkanes with a chain length of C_{34} and C_{35} were not identified in two and one samples, respectively (Table 2).

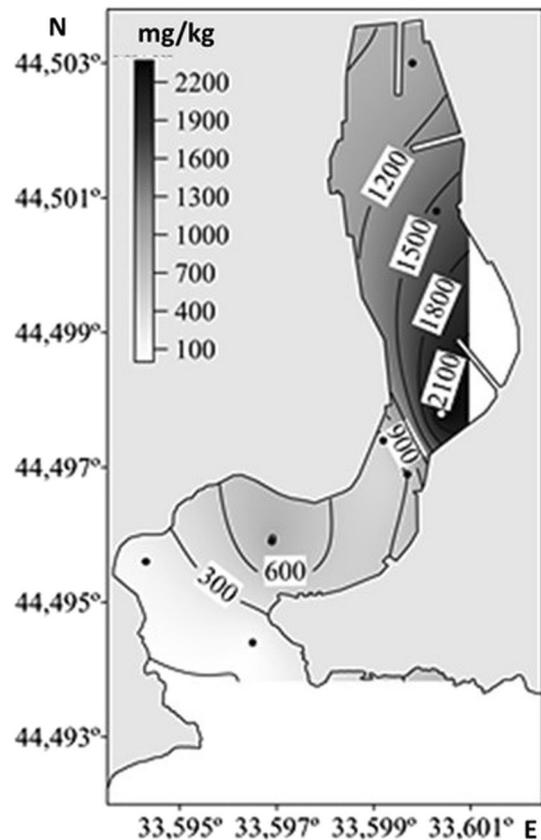


Fig. 2 Spatial distribution of hydrocarbons in Balaklava Bay bottom sediments, 2019

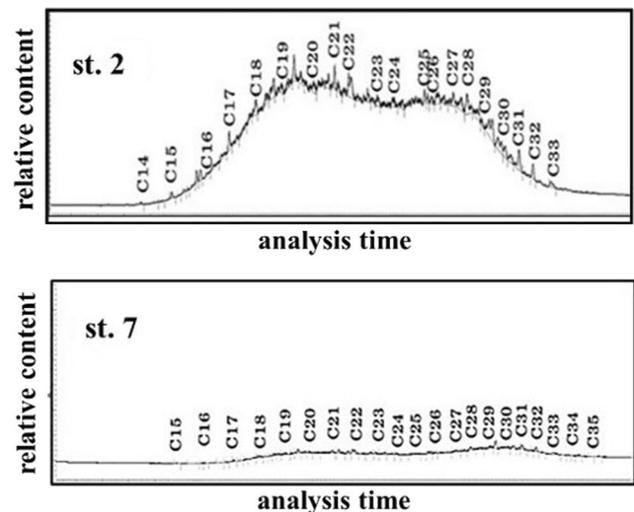


Fig. 3 Typical gas chromatograms of *n*-alkanes obtained from Balaklava Bay bottom sediments, 2019



The remaining compounds were present in all samples. Typical gas chromatograms of HCs of the bay bottom sediments are shown in Fig. 3.

The sum of identified *n*-alkanes in the bay sediments ranged from 1 to 154 mg/kg (Table 2). Their maximum concentrations were observed in the central part of the bay that was consistent with the total HC contents in this area.

Discussion

Assessment of the level of hydrocarbon contamination of bottom sediments

The content of HCs in bottom sediments can be controlled both by the location of their sources and their intensity, and by the physical–chemical characteristics of the sediments themselves. Important indicators affecting the accumulation and transformation of HCs include particle size distribution, content of C_{org} , pH and the redox potential of bottom sediments (Volkman et al. 1980; Taylor et al. 2015; Khaustova et al. 2021; Boguta et al. 2022). In our case, the zones of high HC content coincided with areas of aleurite-pelitic fraction accumulation and high C_{org} content (Gurov et al. 2015; Orekhova et al. 2018).

The particle size distribution of bottom sediments provides additional information about the origin, transport and accumulation of bottom sediments in a particular water area (Folk and Ward 1957; Blott and Pye 2001). Along with this, granulometric composition of sediments controls accumulation of various substances, including pollutants. Increased sorption capacity is usually associated with the presence of fine fractions of bottom sediments (pelite-aleuritic and aleurite-pelitic) (Nemirovskaya 2013; Soloveva et al. 2019, 2021). Thus, increased concentrations of aleurite-pelitic silts in the bottom sediments of the northern basin lead to an increase in the total HC content in them.

The origin of C_{org} of bottom sediments is predominantly natural (Schumacher 2002; Ouyang et al. 2006; Mirsadeghi et al. 2013). The coincidence of the areas of accumulation of C_{org} and HCs, probably, indicates the common origin of these components and the unity of the factors controlling their accumulation in bottom sediments. The researches (Chen et al. 2012; Huang et al. 2012; Bush and McInerney 2015) also indicate that the content of C_{org} is one of the factors controlling the accumulation of hydrocarbons.

The physical–chemical characteristics of bottom sediments, such as pH and Eh, determine the intensity of organic matter decomposition (Taylor et al. 2015; Khaustova et al. 2021; Boguta et al. 2022). According to the obtained pH values, the bottom sediments of the bay are classified as slightly alkaline. On the background of a decrease in the

redox potential, an increase in pH of bottom sediments with increasing depth along the axis of the bay was noted. Low Eh values indicate a constant supply of organic matter (drainage, active shipping, etc.) and active redox processes, including bacterial oxidation.

The obtained values of HC content at most stations are comparable with the data that are typical for bottom sediments of the Black Sea coastal waters (Larin et al. 2011). In particular, similar values were recorded in bottom sediments of the Gelendzhik Bay (11–252 mg/kg), Greater Sochi (5–119 mg/kg) and Feodosiya Gulf (17–80 mg/kg) (Nemirovskaya et al. 2017). The maximum values noted at St. 4 corresponding to the most polluted parts of some coastal water areas, e.g., Sfax (Tunisia) (up to 1729 mg/kg) and Baku (Azerbaijan) (up to 1820 mg/kg) (Zaghden et al. 2007; Sadikhova and Aminbekov 2014). The maximum values of HCs in this section are a consequence of the combined effect of storm, sewer runoff and water circulation, which defines the inflow and accumulation of fine-grained sediments in this area.

HC concentrations in marine bottom sediments are not regulated by Russian statutory instruments. Therefore, researchers (in particular, the Russian Federal Service for Hydrometeorology and Environmental Monitoring) often use foreign standards set out in the so-called Dutch Lists (Neue... 1995). When referring to these standards, 87.5% of samples of Balaklava Bay bottom sediments exceeded the permissible HC level (50 mg/kg). Today, there are other national classifications for HC pollution of bottom sediments. Thus, according to the classification by V.I. Uvarova (Uvarova 1989) bottom sediments can be categorized as follows:

- Clean: 0–5.5 mg/kg
- Slightly contaminated: 5.6–25.5 mg/kg
- Moderately contaminated: 25.6–55.5 mg/kg
- Contaminated: 55.6–205.5 mg/kg
- Polluted: 205.6–500.0 mg/kg
- Highly polluted: over 500.0 mg/kg

In view of this classification, Balaklava Bay bottom sediments belong to slightly contaminated (12.5%), contaminated (12.5%) and highly polluted (75%) categories. As noted in (Kuznetsova and Dzyuban 2006), bacterial communities clearly define the “concentration boundary” of petroleum pollution of bottom sediments (petroleum HC concentration: 40–60 mg/kg), below which water–sediment microbial cenosis intensively decompose organic matter, entering bottom sediments. At higher concentrations these processes are slowed down. In view of this, 87.5% of the examined samples of bottom sediments exceeded the “concentration boundary” of petroleum pollution (contaminated and highly polluted according to V.I. Uvarova's



classification). Unfortunately, all the above approaches to assessment of the HC pollution level of bottom sediments are of relative character and do not allow to identify the nature of HCs. The most informative indicators in terms of identification of the *n*-alkanes origin are various molecular ratios showing the primary pathways by which *n*-alkane can input to the environment (Table 1).

Analysis of the origin of hydrocarbons in bottom sediments of the coastal ecosystem

When discussing the data obtained on the composition of *n*-alkanes in bottom sediments, it is important to take into account the transformation (biological and chemical) of hydrocarbons after they enter the water. The depth of their transformation depends on the combination of physical–chemical and biological conditions in the reservoir. In

Table 1 Diagnostic molecular ratios and their typical values

Diagnostic ratios (calculation formula)	Typical value	Source of HC	References
UCM/R	< 4	Autochthonous and fresh petroleum hydrocarbons	Lv and Zhai (2008), Larin et al. (2011)
	> 4	Degraded oil products	
LWH/HWH = $\sum(C_{13}-C_{21})/\sum(C_{22}-C_{37})$	< 1	Terrigenous, high vegetation	Eglinton and Hamilton (1967), Blumer et al. (1971)
	> 1	Oil origin	
TAR = $\sum C_{27+29+31}/\sum C_{15+17+19}$	High TAR	Predomination of terrigenous material	Silliman and Schelske (2003)
ACL = $(27 \cdot C_{27} + 29 \cdot C_{29} + 31 \cdot C_{31} + 33 \cdot C_{33} + 35 \cdot C_{35} + 37 \cdot C_{37}) / (C_{27} + C_{29} + C_{31} + C_{33} + C_{35} + C_{37})$	Decreased ACL	Oil emissions	Zhang et al. (2014)
CPI ₁ = $(1/2) \{ (C_{15} + C_{17} + C_{19} + C_{21}) / (C_{14} + C_{16} + C_{18} + C_{20}) + (C_{15} + C_{17} + C_{19} + C_{21}) / (C_{16} + C_{18} + C_{20} + C_{22}) \}$	< 1	Intensive microbial transformation of hydrocarbons	Lv and Zhai (2008)
CPI ₂ = $(1/2) \{ (C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34} + C_{36}) \}$	≈ 1	Oil or biodegradation	
	< 1	Biogenic	
	< 3	Oil	
	5–10	Higher ground vegetation	
C ₃₁ /C ₂₉	< 0.4	Predomination of woody vegetation	Ficken et al. (2000), Mead et al. (2005)
	> 0,4	Predomination of grass vegetation	
	≈ 1	Higher ground vegetation	
Alkterr = $(C_{27} + C_{29} + C_{31} + C_{33}) / \sum C_{14-38}$	< 0.4	Predomination of allochthonous matter	Zhang et al. (2014)
	> 0,4	Predomination of autochthonous matter	
$\sum C_{25-35} / \sum C_{15-21(\text{odd})}$	< 1	Predomination of autochthonous matter	Duan (2000)
	> 1	Predomination of terrigenous matter	

Table 2 Content and diagnostic indices of *n*-alkanes in Balaklava Bay bottom sediments

Content/diagnostic indices	St. no							
	1	2	3	4	5	6	7	8
Range <i>n</i> -alkanes	13–35	14–33	13–35	14–35	14–34	15–35	13–35	13–35
Concentration <i>n</i> -alkanes, mg/kg	59	82	53	154	94	1	8	34
$\sum C_{25-35} / \sum C_{15-21}$	2.70	1.52	1.58	2.74	2.47	2.03	0.77	1.18
TAR	2.42	1.71	4.91	3.05	4.36	3.10	1.06	1.74
LWH/HWH	0.27	0.40	0.32	0.24	0.29	0.26	0.64	0.67
Alkterr	0.36	0.25	0.39	0.42	0.38	0.08	0.17	0.20
C ₃₁ /C ₂₉	6.27	4.83	0.65	5.93	0.48	1.11	0.53	1.80
ACL	29.55	29.05	29.64	29.96	29.24	28.85	29.10	29.83
CPI ₁	0.70	0.55	1.03	0.74	0.40	1.30	1.08	0.97
CPI ₂	1.06	0.81	2.39	1.04	1.04	1.23	1.49	0.89
UCM/R	6.13	7.41	4.12	6.45	4.20	4.00	0.67	5.39



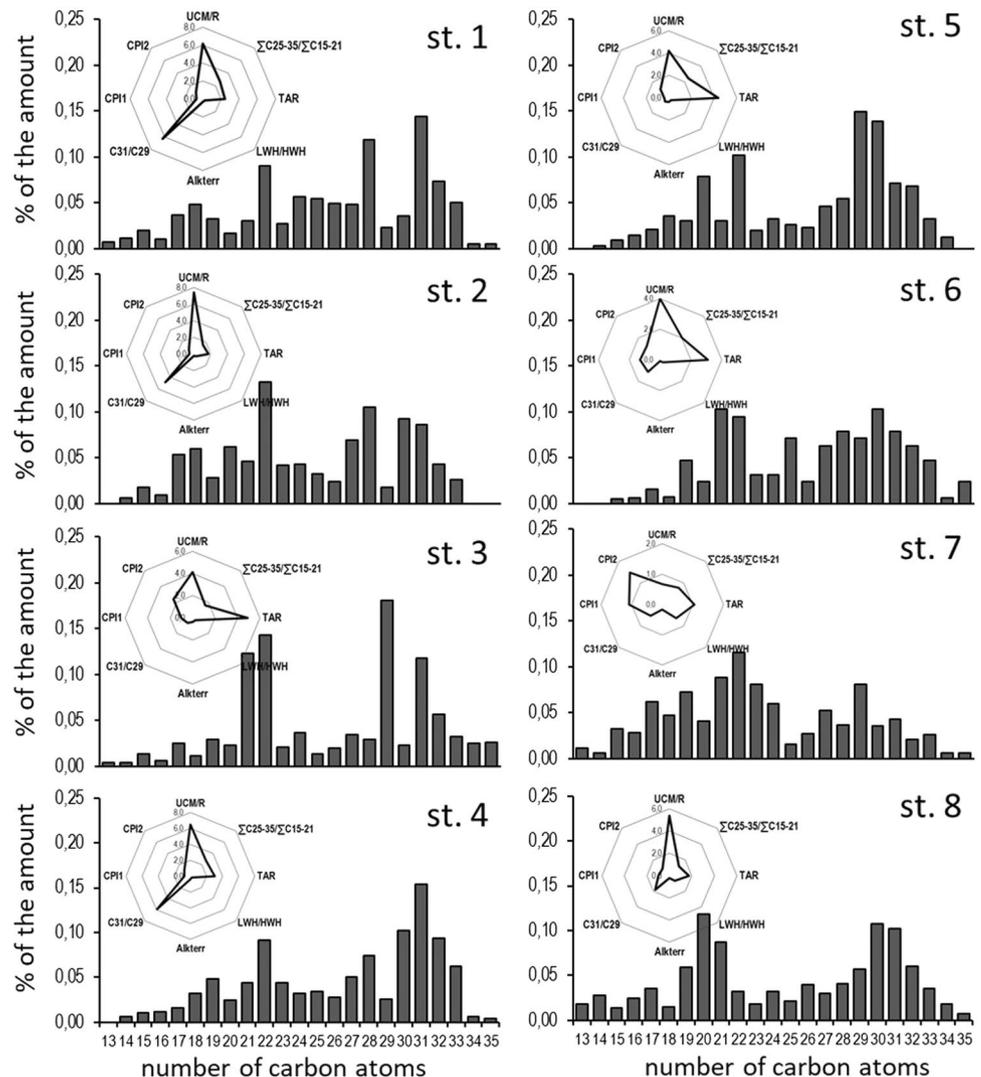
the works (Volkman et al. 1980; Nemirovskaya 2013; Wenzel et al. 2007) it was found that aerobic bacteria can play a significant role in the formation of HC composition when oil products enter to sediments, due to the consumption of light homologues. Low Eh values (from -163 to -236) indicate active redox processes, including bacterial oxidation (Chekalov 2018). As a result, a partially transformed hydrocarbon mixture was identified in the bottom sediments of the bay, which does not contain hydrocarbons with a chain shorter than C_{13} (Table 2).

It was found that the distribution of *n*-alkanes on the gas chromatograms was bimodal. At all the stations, the first peak accounted for compounds in the range of C_{20} – C_{22} and the second peak accounted predominantly for C_{28} – C_{31} (Fig. 4). In particular, at St. 3, 6, 7, and 8, a high proportion of C_{21} was noted. C_{20} was prevailed on St. 5 and 8. The concentration of C_{22} homologue was high at all survey stations (except for St. 8). Together with the CPI values (Table 2), which in most cases were close to 1, this indicates

accumulation of phytoplankton biosynthesis products in the bottom sediments and microbial HC destruction (Beiger et al. 1997; Nemirovskaya 2013). In the high molecular weight range of the spectrum, the maximum concentrations were noted in the homologues of C_{28} – C_{32} range. Odd-numbered compounds in this range of the spectrum are predominantly of terrigenous origin (Mead et al. 2005).

The source of C_{28} , C_{30} , and C_{32} *n*-alkanes is the sapropel matter, which is autochthonous for marine ecosystems. It is formed from organic mass of phyto- and zoobenthos, plankton and lower plants (Petrova and Shanina 2014). According to the available data, typical chromatograms of bottom sediments of different origin can be divided into three types: bimodal distribution, predominance of high molecular weight fractions, and predominance of low molecular weight alkanes (Zhang et al. 2014). A bimodal distribution is usually attributed to sediment input from both land and water. As a result, analysis of the peaks indicates a simultaneous

Fig. 4 Distribution of *n*-alkanes and main markers in Balaklava Bay bottom sediments, 2019



input of allo- and autochthonous compounds and their bacterial degradation.

The sum of C_{15} – C_{21} *n*-alkanes ($\sum C_{15-21}$) points to the autochthonous compounds (Blumer et al. 1971). The sum of odd-numbered C_{25} – C_{35} homologues ($\sum C_{25-35}$) represents predominantly terrigenous alkanes (Eglinton and Hamilton 1967). The ratio of these groups allows identifying the organic matter origin more accurately, excluding the influence of such factors as sediments grain size and sedimentation rate (Duan 2000). A high (> 1) ratio ($\sum C_{25-35}/\sum C_{15-21}$) indicates the strong influence of terrigenous matter. A decrease in the values of this index indicates a decrease in the influence of terrigenous matter. In our case, this index values were ranged between 0.77 and 2.74 (Table 2). The lowest value was noted at St. 7. At St. 8 this index was slightly exceeded 1 (1.18). The average value was 1.87. High ratios of these groups of *n*-alkanes indicate a significant input of HCs from the land.

Another parameter widely used for HC source identification is the ratio of individual compounds with the odd number of atoms—TAR. It also allows to estimate the ratio of allochthonous to autochthonous alkanes. In this work TAR ratio varied from 1.06 to 4.36 (Table 2), averaging 2.79. On the whole, this coefficient characterizes the predominance of allochthonous matter coming from the land.

The components of $\sum C_{21-}$ indicate predominance of autochthonous matter (Blumer et al. 1971), whereas $\sum C_{22+}$ suggests terrigenous input (Eglinton and Hamilton 1967). The ratio $\sum C_{21-}/\sum C_{22+}$ (LWH/HWH) is often used to estimate the predominant pathway of organic matter input. This ratio was in the range of 0.24–0.67 at all sampling stations (Table 2). On average, it was 0.39, which shows a significant terrigenous input of organic matter.

The Alkterr index calculated using formula $(C_{27} + C_{29} + C_{31} + C_{33})/\sum C_{14-38}$ is one of the indicators of terrigenous input (Zhang et al. 2013). This index ranged from 0.08 to 0.39 (Table 2), averaging 0.28. Together with other markers, it indicated a high content of terrigenous matter in the bottom sediments.

Woody and herbaceous land vegetation often plays an essential role in the formation of the qualitative composition of bottom sediment HCs. The main peak associated with woody vegetation, in particular, with higher plant epicuticular waxes accounts for C_{29} , while that associated with herbaceous vegetation is predominantly accounts for C_{31} (Volkman et al. 1980; Ficken et al. 2000; Mead et al. 2005). These indicators ratio (C_{31}/C_{29}) was varied widely from 0.53 to 6.27 (Table 2), averaging 2.70 at the study area. Thus, it can be said that, in general, bottom sediments contain traces of herbaceous plants. An exception was noted for St. 5 and 7, where the proportion of C_{29} associated with tree species is high. The contribution of both components was approximately equal at St. 6.

The average carbon chain length (ACL) of *n*-alkanes also relates to their genesis. The HCs of woody plants are characterized by low ACL values. High ACL values indicate the predominance of herbaceous vegetation in HC formation (Huang et al. 2011). The presence of fresh oil pollution also leads to a reduction in ACL (Jeng 2006). It was found that the values of the parameter ranged from 28.85 to 29.96 (Table 2), which reflected approximately the same role of herbaceous and woody plants in the organic matter formation of bottom sediments in the water area. However, it should be considered that this approach is strictly applicable only to “fresh” organic matter (Nemirovskaya 2013).

The main criterion of HC biogenicity is the widely used Carbon Preference Index (CPI), the ratio of sums of odd- and even-numbered homologues (Bray and Evans 1961; Kuhn et al. 2010; Sojinu et al. 2012; Nemirovskaya 2013). In the presence of oil pollution, CPI's values are often close to 1. It is known that during decomposition of oil and petroleum products, light HCs are the first to disappear and the share of more stable compounds increases. It happens due to both chemical (oxidation) and biological (aerobic microbial degradation) decomposition (Volkman et al. 1980; Nemirovskaya 2013; Wentzel et al. 2007). Therefore, the ratio of high molecular weight *n*-alkanes is more stable and informative for determination of the HC nature.

The groups of short- and long-chain alkanes tend to have different CPIs, which are denoted as CPI_1 and CPI_2 , respectively. It was shown that for the lighter *n*-alkanes CPI_1 ranged from 0.40 to 1.30 (Table 2), averaging 0.84. The CPI was low at St. 1, 2 and 5, while at the other stations, it was close to 1. High content of low molecular weight even-numbered *n*-alkanes in these areas may be the result of microbial degradation of organic matter (Nishimura and Baker 1986; Pavlenko et al. 2011; Nemirovskaya 2013). The shares of these compounds were approximately equal at St. 1, 2 and 5. The CPI_2 values describing the ratio of long chain *n*-alkanes ranged from 0.81 to 2.39 (Table 2), averaging 1.24. The predominance of odd-numbered compounds was noted at St. 3 and 7. For other sites, the index was around 1, which is a characteristic of oil pollution of bottom sediments. The CPIs values were higher in the high molecular weight range than in the low molecular weight range.

It is known that a clear predominance of odd or even components is not typical for *n*-alkanes in the case of trace oil pollution (Han and Calvin 1969). The presence of oil pollution, detected in the low molecular weight range of *n*-alkanes, can be noted at St. 3, 4, 6, 7, and 8. Probably, we have recorded relatively fresh oil hydrocarbons that have not degraded yet. However, the simultaneous presence of the CPI indice of about 1 and C_{29} peaks on the chromatograms of these stations may indicate the planktonogenic rather than petroleum nature of the detected aliphatic hydrocarbons (Nemirovskaya 2013). This phenomenon was noted for St.

3 and 7. The value close to 1 (St. 1, 2, 4, 5, 6, and 8) in the high molecular weight range of the CPI spectrum, suggests chronic oil pollution of the water area.

The predominance of compounds with an odd number of carbon atoms in the low molecular weight range may indicate not only recent input of oil products but also HC production by microorganisms (Han and Calvin 1969; Reddy et al. 2000) and macrophytes (Ficken et al. 2000; Mead et al. 2005). Thus, it can be assumed that short chain *n*-alkanes identified in the bottom sediments of the inner parts of Balaklava Bay were of mixed origin, which is typical for the coastal areas of the Black Sea (Nemirovskaya et al. 2019).

One of the important parameters used for assessing the presence of oil pollution as well as the intensity of HC biodegradation processes is the presence of an indecomposable background or an unseparated naphthenic-aromatic “hump” (Unresolved Complex Mixture, UCM) on chromatograms, with a maximum in the high molecular weight range (Nemirovskaya 2013). The UCM is a mixture of complex isomers and homologues, branched and cyclic HCs, which cannot be split in a chromatographic column (Gough and Rowland 1990). The number of oil components representing the UCM can be as high as 250,000 compounds. This indicates that the UCM is the most complex mixture of organic compounds on Earth (Sutton et al. 2005). That said, despite the obvious relation to oil sources, the presence of the UCM in the low concentration range may also be due to bacterial decomposition of autochthonous organic matter (Venkatesan and Kaplan 1982). The configuration of the UCM depends on its composition. Natural and anthropogenic HCs have different “humps” (Nemirovskaya 2013). The anthropogenic compounds are characterized by a “hump” in the high molecular weight range. This kind of maximum in the low temperature region occurs due to microbial degradation of natural organic compounds, in particular plant detritus (Bouloibassi and Saliot 1993). The UCM curve was “double humped” at St. 1, 2, 3, 4, 5 and 8 (an example is given in Fig. 3) and, the steeper “hump” was in the low temperature region (St. 2 and 8) indicating the predominant degradation of autochthonous matter. As for other stations (St. 1, 3, 4, 5), we can speak about the presence of unseparated mixture, both due to microbial destruction and to accumulation of anthropogenic organic compounds. The value of UCM was insignificant at St. 6 and 7, located closer to the exit from the bay and having a significantly lower level of *n*-alkanes in the bottom sediments than at other stations (by 1 or 2 order of magnitude). It should be noted that the bottom sediments at seaward stations (St. 6 and 7) were represented by sand with an admixture of shells unlike other parts of the studied water area, where silty sediments predominate. As a result, the deposition of organic matter in this area is probably not as intense as in the inner part of the bay.

The ratio of UCM value to the *n*-alkane content at most of the sampling stations varied from 4 to 7 (Table 2), which was a diagnostic sign of chronic oil pollution (Mazurek and Simoneit 1984; Simoneit 1986). The exception was St. 7, where at low HC concentrations, the proportion of the “hump” was also 0.67, which most likely corresponds to bacterial transformation of organic substances (Venkatesan and Kaplan 1982).

Based on markers calculated for Balaklava Bay sediments (Fig. 4), it can be assumed that terrigenous HCs predominate in the bottom sediments of the water area, as well as oil contamination was observed. In this aspect St. 7 was notable: as can be seen from the marker values, autochthonous HCs prevailed in the bottom sediments in this area, CPI and UCM/R markers at this station indicated the presence of natural HCs (Mazurek and Simoneit 1984; Simoneit 1986). Based on their overall content, the outer part of the bay (St. 6 and 7) can be characterized as having low levels of HCs in the bottom sediments. This part of the studied water area is the most open to the sea and located behind the circular eddies that “lock” the bay and limit its water exchange with the sea (Fomin and Repetin 2005). The low HC values in the seaward part of the studied site (St. 6 and 7) may also be attributed to the nature of the sediments represented by sand with an admixture of shells, which effects the sediment accumulation capacity. However, the absence of oil pollution and predominance of autochthonous *n*-alkanes in the bottom sediments was characteristic of the eastern part of this water area.

Conclusions

1. The total HC amount in Balaklava Bay bottom sediments varied from 21 to 2385 mg/kg and was consistent with the nature of the bottom sediments. The recorded pollution levels mainly corresponded to those observed in polluted areas of the World Ocean. It was found that HCs were distributed unevenly throughout the water area. The main concentration zone was in the central part of the bay. The minimum HC content in the bottom sediments was registered in the seaward part of the bay.
2. The content of *n*-alkanes in Balaklava Bay bottom sediments ranged from 1 to 154 mg/kg. The maximum values were observed in the central part of the water area (in the bay constriction area), in particular at its eastern coast. The minimum values were registered in the open part of the bay.
3. Gas chromatograms of examined *n*-alkanes of bottom sediments showed a bimodal distribution which indicates a mixed origin of HCs
4. The molecular markers indicate a predominantly terrigenous origin of HCs in the bottom sediments of the area



as well as the presence of chronic oil pollution in the inner part of the bay.

- The HC composition of bottom sediments in the most open seaward part of Balaklava Bay differed from that in the inner parts of the water area. The values of molecular markers indicate the predominance of autochthonous origin of HCs in the bottom sediments of the bay.

Acknowledgements Present work was carried out within framework of the State assignment of the IBSS on the theme “Molismological and biogeochemical foundations of the marine ecosystems homeostasis” (No. 0556-2021-0001, No. state registration 121031500515-8), the State assignment of the MHI on the theme No. 0555-2021-0005 “Complex interdisciplinary investigations of the oceanologic processes conditioning functioning and evolution of the Black and Azov seas’ ecosystems of the coastal zones”. The authors appreciate deeply the lead engineer of the Marine sanitary hydrobiology Department (IBSS) Alyomova T. E. for determining aliphatic hydrocarbons in the studied bottom sediments.

Author’s contribution OVS: setting goals, describing the qualitative and quantitative composition of PAHs, assessing potential sources of PAHs entering the bottom sediments, formulating conclusions, writing a paper. EAT: preparation of bottom sediment samples for chemical analysis, assessment of the relationship between the granulometric composition of bottom sediments and the content of PAHs in them, formulation of conclusions. KIG: taking samples of bottom sediments, assessment of the relationship between the granulometric composition of bottom sediments and the content of PAHs in them, preparation of the paper in accordance with the journal requirements. EAK: taking samples of bottom sediments, participation in the discussion of the paper materials.

Declarations

Competing interests The authors declare that they have no conflict of interest.

Consent for publication All authors mutually agreed to publish the work in this journal.

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