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Original article

Distribution and Composition of Hydrocarbons in the Bottom Sediments of Kamyshovaya Bay (Black Sea)

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Abstract
Purpose. The purpose of the study is to identify the features of spatial and vertical distribution of hydrocarbons in bottom sediments of the coastal area under constant anthropogenic load, and to assess the likely sources of their inlet into the marine environment (using Kamyshovaya Bay as an example).
Methods and Results. The surface layer of bottom sediments (nine stations) and the sediment column were sampled in July 2021 as a part of long-term monitoring of the Sevastopol bays jointly performed by FRC IBSS and FRC MHI. The features of spatial distribution of hydrocarbons, alkanes and some geochemical markers in the surface layer (0–5 cm) and the vertical profile of bottom sediments are studied. The 30-year accumulation history of the considered substances in the bay bottom sediments is analyzed. The concentration of hydrocarbons in the bottom sediments ranges from 27.6 to 98.5 mg/kg that allows us to classify these sediments as low-polluted. A layer-by-layer study of the hydrocarbon composition in the bay bottom sediments shows that in the course of 30 years the bottom sediments were not significantly polluted with hydrocarbons. The results of analyzing the alkane composition and the geochemical marker values make it possible to establish that, as well as in the surface layer, the predominant source of hydrocarbon inlet was allochthonous and autochthonous organic matter. The increased values of geochemical markers identifying oil pollution indicate the fact that the inlet of oil and oil products can be considered a secondary source of hydrocarbons.
Conclusions. Hydrocarbons in the bottom sediments are distributed unevenly over the Kamyshovaya Bay water area, namely in the central part of the bay, a zone of the increased pollution is formed. It can be a consequence of the processes taking place in the semi-enclosed bay, as well as conditioned by the type of bottom sediments. The results of studying the hydrocarbon composition of bottom sediments show that in the course of the past 30 years and up to the present, Kamyshovaya Bay has been under the anthropogenic load which fluctuated insignificantly due to the degree of economic activity of the port. At the same time, the level of pollution in the bay remains low.

Keywords: bottom sediments, hydrocarbons, n-alkanes, markers, Kamyshovaya Bay, Black Sea

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Introduction

The Sevastopol region is home to over 30 bays, some of which have been developed into ports. Such port water areas are subject to constant anthropogenic impact. Kamyshovaya Bay is no exception [1]. The anthropogenic load on the Kamyshovaya Bay waters is attributable to a number of factors, including the port's operational status, the location of the *Yugtorsan* oil loading enterprise on the bay shores, the presence of treatment facilities, a cement plant and the most powerful boiler house in Crimea (255 MW) [1].

Organic substances of petroleum origin enter seawater not only during the course of marine transport operations, but also with storm and sewage waters, including as a result of the construction of capital construction projects [2, 3]. Additionally, according to previously conducted field observations (June 2012), the bay waters were slightly polluted with oil and petroleum products compared to other port water areas (Sevastopol Bay, Balaklavskaya Bay). The presence of petroleum hydrocarbons was observed at concentrations below the limit of quantitative determination via IR spectrometry in the water [1].

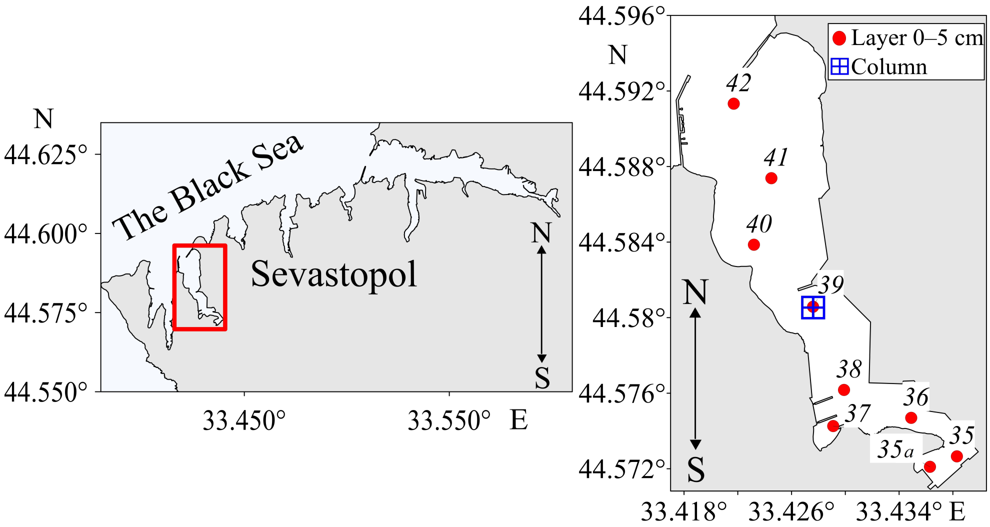
As proposed by the authors [4], the water purification process in Kamyshovaya Bay occurs as a result of the adsorption of organic substances by fine-grained material of bottom sediments. The previously obtained data indicate a slight decrease in the content of chloroform-extractable substances in bottom sediments since 2009. Furthermore, the concentration of petroleum hydrocarbons in the bottom sediments did not exceed 100 mg / 100 g until 2015, which corresponds to the natural content level of this class of substances [5].

However, in later works [6], the results presented by the authors indicate an increase in the organic matter content and the absence of significant permanent sources of its inflow. It is noted that the increase in the organic matter content against the background of decreasing anthropogenic load is explained by the influence of natural factors. The maintenance of such trends may lead to the replacement of suboxic conditions in the bottom sediments by anaerobic ones, with negative consequences for the entire bay area. The natural factors that influence the redistribution of organic matter, including hydrocarbons, in the water area include the following characteristics of the bay: its semi-enclosed nature, the indented coastline, the large number of piers and ship moorings, the uneven anthropogenic load, the presence of a protective jetty that prevents water exchange between the bay and the open sea, etc. In connection with the above, a constant monitoring of the bay water area state is required. Bottom sediments as a "depot" for pollutants are the most informative and indicative in terms of time.

The aim of the study is to identify the characteristics of spatial and vertical distribution of hydrocarbons in bottom sediments of coastal water area under constant anthropogenic load and to assess the probable sources of their input into the marine environment (using Kamyshovaya Bay as an example).

Characteristics of the study area

Kamyshovaya Bay is located in the north of the Heracleian Peninsula. Like Streletskaya Bay, it extends deep into the land (Fig. 1). The length of the bay is 2.75 km, the width at the mouth is 1 km, the depth is 11–18 m; the width in the central part is 300–350 m, the depth is 7–12 m, the width at the top of the bay is 100–130 m, the depth is 6–7 m [7].



F i g. 1. Study area (*left*) and scheme of bottom sediment sampling stations in Kamyshovaya Bay, summer 2021 (*right*)

At the apex of the bay there is *Put' Ilyicha* (a fishery collective farm), *Atla* LLC (works on repair, modernisation and adjustment of technological equipment for processing of fish and krill raw materials on fishing vessels and food industry enterprises of the Azov–Black Sea basin) and a reloading port complex for construction aggregates, designed for unloading metal from ships for further processing in the plant. On the eastern side of the bay there is a fishing port, a factory for the production of mosquito nets, *Victoria* (a factory for the production of plastic windows), and on the western side – *Industriya Penoplasta* (a factory for the production of polymer materials), workshops for the repair of marine engines, *Porto Franco* (a residential complex).

According to [8], untreated wastewater from two permanent and one emergency outfall, as well as stormwater runoff, flows into Kamyshovaya Bay.

Material and research methods

Bottom sediment samples were collected in the summer of 2021 using a 0.038 m^2 Peterson grab sampler, then placed in sealed bags, labelled and delivered to the laboratory in refrigerated equipment.

To study the vertical distribution of hydrocarbons, bottom sediments were collected using a hand sampler with a plexiglass tube and a vacuum seal. In the laboratory, the soil column was divided into 2 cm layers, dried, ground in a mortar and a portion of the sample was sieved through 0.25 mm cell diameter sieves.

The data on the granulometric composition of the bottom sediments of Kamyshovaya Bay were taken from [4, 6].

Concentrations of hydrocarbons and n-alkanes were determined at the FRS IBSS Spectrometry and Chromatography Collective Use Centre. A detailed methodology for the determination of hydrocarbons and n-alkanes is presented in [9]. A Kristal 5000.2 gas chromatograph with a flame ionisation detector (FID) was used to analyse the alkanes from the hydrocarbon fraction. Hydrocarbons were separated on a TR-1MS capillary column of 30 m length, 0.32 mm diameter and a stationary phase thickness (100% dimethylpolysiloxane) of 0.25 μm (Thermo Scientific). For absolute calibration of the instrument, the standard ASTM D2887 Reference Gas Oil (*Supelco*, USA) was used as a hydrocarbon mixture. Chromatec Analysis 3.0 software, absolute calibration and percentage normalisation methods were used to process the results.

Nevertheless, it is not feasible to assess all hydrocarbons present in the bottom sediments via gas chromatography due to the transformation of organic matter and formation of more complex compounds. One illustrative example is that of cycloalkanes (naphthenes). A mixture of such organic substances is referred to as an unresolved complex mixture (*UCM*), a chromatographically inseparable background (i/b) or a ‘hump’. The calculation of *UCM* is achieved by subtracting the peak areas of chromatographically separated hydrocarbons from the total area of the chromatogram [9].

To identify the probable genesis of hydrocarbons, a number of diagnostic indices (markers) are employed. To differentiate between compounds of allochthonous and autochthonous origin, the ratio of terrigenous and autochthonous compounds (*TAR*, *TMD*, C_{31}/C_{19}), hydrocarbon average chain length (*ACL*), and the ratio of low-molecular and high-molecular homologues (*LWH*/*HWH*) are used. The application of individual markers enables the clarification of the biogenic nature of compounds, particularly the assessment of the contribution of herbaceous and woody vegetation to the formation of the allochthonous component of hydrocarbons entering bottom sediments. This is achieved through the use of ratios such as: C_{31}/C_{29}, P_{aq}. In order to differentiate between petroleum or biogenic hydrocarbons, a number of ratios are employed, including the carbon preference index (*CPI*), in particular CPI_2 calculated for the high-molecular weight part, the ratio of the unresolved background to the total content of n-alkanes (*UCM*/n-alkanes), *ACL*, and *LWH/HWH* [10–15]. To identify petroleum origin of hydrocarbons, the isoprenoid coefficient ($Ki = (Pr + Ph)/(\text{n-}C_{17} + C_{18})$) and the ratio of isoprenoid alkanes pristane and phytane (*Pr/Ph*) are also frequently applied [16, 17].

In this study we assessed the probable origin of hydrocarbons by analysing the values of the following markers: *Pr/Ph, Ki, UCM/*n-alcanes, *LWH/HWH*, P_{aq}, *TAR*, *ACL*, *TMD*, C_{31}/C_{19}, CPI_2, C_{31}/C_{29} [10–17]. These indices were calculated using the formulas [10–17], as presented in Table 1.

Table 1

Diagnostic molecular ratios and their typical values

Diagnostic index (calculation formula) [10–17]	Value	Decoding the result
1	2	3
UCM/n-alkanes	> 10 < 10	Chronic pollution of bottom sediments Fresh inflow of oil
$LWH/HWH = \sum(C_{11}\text{-}C_{21})/\sum(C_{22}\text{-}C_{35})$	> 1 < 1	Oil origin Terrigenous origin, higher vegetation
$CPI_2 = (1/2)\{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}+C_{35})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32}+C_{34}) + (C_{25}+C_{27}+C_{29}+C_{31}+C_{33}+C_{35})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})\}$	~ 1 < 1 > 1	Large share of hydrocarbons of oil origin Predominantly biogenic origin Biogenic influence on hydrocarbon composition of terrigenous organic matter
$Ki = (Pr + Ph)/(\text{н-}C_{17} + C_{18})$	$0.8 \le Ki \le 1.5$ $0.3 \le Ki \le 0.8$ $Ki \le 0.3$	Presence of medium degraded oil Presence of slightly degraded oil Presence of fresh oil
Pr / Ph	< 1	Presence of oil in bottom sediments
$P_{aq} = (C_{23}+C_{25})/(C_{23}+C_{25}+C_{29}+C_{31})$	0.1 $0.1 < P_{aq} < 0.4$ $0.4 < P_{aq} < 1$	Traces of terrigenous degraded vegetation Fresh macrophytes Aquatic macrophytes
$TAR = (C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$	*High TAR*	Predominance of terrigenous material
$ACL = [25C_{25}+27C_{27}+29C_{29}+31C_{31}+33C_{33}]/[C_{25}+C_{27}+C_{29}+C_{31}+C_{33}]$	Low *ACL*	Oil emissions
$TMD = (C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{15}+C_{17}+C_{19}+C_{21}+C_{23})$	< 0.5 $0.5 < TMD < 1$ > 1	Autochthonous origin Mixed origin Terrestrial vegetation
C_{31}/C_{19}	< 0.4 > 0.4	Autochthonous matter Allochthonous matter
C_{31}/C_{29}	< 0.4 > 0.4	Predominance of woody vegetation Predominance of herbaceous vegetation

The Statistica 12 software package was employed for the processing of statistical data. A cluster analysis of the bottom sediment layers collected in Kamyshovaya Bay (station *39*) was conducted using a combination method based on data on the total hydrocarbon content, *UCM* value, and the composition features of n-alkanes.

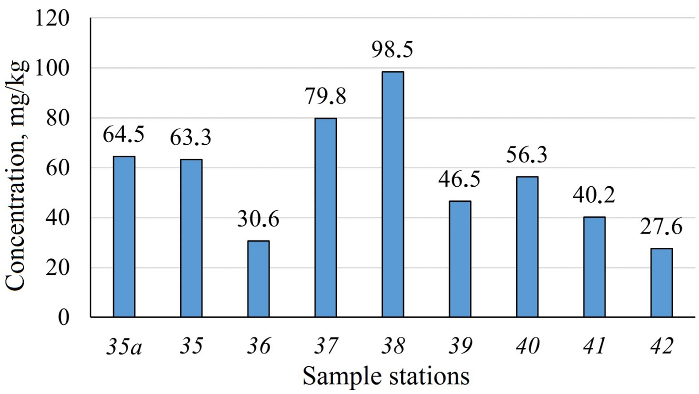
Results and discussion

Content, composition and genesis of hydrocarbons in the surface layer of the Kamyshovaya Bay bottom sediments

The granulometric composition of the collected bottom sediments in Kamyshovaya Bay is heterogeneous [6]. In the apex (stations *35a*, *35*, *36*) and central (stations *37*, *38*, *39*) parts, the sediments were grey silts. At station *40*, the sediments were shell rock with an admixture of sand. At the bay exit (stations *41*, *42*), the sediments were sand with shells and shell detritus. It was observed that the mean particle size of the sediments (1.5 mm) is approximately one order of magnitude larger than that observed in other bays of Sevastopol [6].

As a consequence, the spatial distribution of organic carbon content (C_{org}) in the surface layer of bottom sediments was also not uniform, with figures of 0.3–0.4% in gravel and sand deposits in the bay upper part, 2–2.2% in silt deposits in the central part of the bay, and 1.2–1.8% in the apex parts of the bay [6]. These figures were markedly lower than those observed in the nearby Streletskaya Bay, where the C_{org} content exhibited fluctuations within the range of 4.28 to 6.3% [9], as well as in other bays of Sevastopol [6]. The noted physico-chemical characteristics of the bottom sediments largely determined their sorption capacity in general and the features of hydrocarbon accumulation in them in particular.

The distribution of hydrocarbon content in the bottom sediments of Kamyshovaya Bay exhibits considerable variation across all sampling stations, with a notable unevenness in the distribution across the water area (Fig. 2). The highest values were recorded in the central region of the bay (station *38*, 98.5 mg/kg), followed by the apex (station *35a*, 64.5 mg/kg) and the lowest in the area closest to the bay exit (station *42*, 27.6 mg/kg).



F i g. 2. Concentrations of hydrocarbons in the bottom sediments of Kamyshovaya Bay

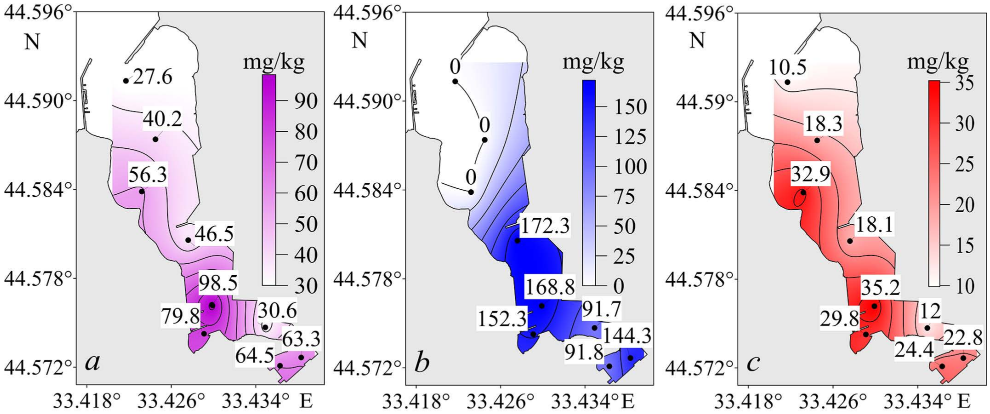
The concentrations of hydrocarbons identified in the various lithological types of bottom sediments were found to exceed background levels. At stations with silty bottom sediments, the concentrations of hydrocarbons were found to be 50 mg/kg, which is above the value typically observed in clean zones [18]. In the bay areas with a predominance of sand and shells, the concentrations of hydrocarbons (10 mg/kg) were also found to be higher than background levels [19]. Nevertheless, it can be assumed that such levels have an insignificant effect on the biota state. As indicated in the data presented in [19, 20], concentrations of up to 50 mg/kg do not result in a notable transformation of the benthic community.

The mean hydrocarbon concentration in the entire water area of Kamyshovaya Bay (nine stations) is 56.4 ± 23.2 mg/kg. For comparison, the hydrocarbon content in the nearby Streletskaya Bay fluctuated within the range of 328 to 2175 mg/kg, with an average value of 1159.8 ± 35.3 mg/kg [9].

The bay water area can be subdivided into three sections: the apex (stations *35a*, *36*), the central region (stations *37–39*), and the bay exit (stations *40–42*). The mean concentration of hydrocarbons in the apex section was found to be 53.3 mg/kg, which is comparable to the overall hydrocarbon concentration observed in the bay. The mean concentration of hydrocarbons in the central region was 74.9 mg/kg, while the concentration at the bay exit was 41.4 mg/kg. Therefore, the silt deposits of the central part of the bay exhibit the highest concentrations of hydrocarbons and C_{org} (Fig. 3, *a*).

The observation of the maximum concentrations of hydrocarbons in the central part of the bay, in conjunction with the granulometric composition of the bottom sediments, may be attributed to the geomorphological features of the water area and the circulating currents, which result in the accumulation of substances entering the marine environment in this particular part of the bay.

It should be noted that the presence of chromatographically unresolved background, indicative of the burial of transformed organic matter, was not observed in all chromatograms. The mean concentration of the unresolved mixture in areas where it was indicated was found to be (91.2 ± 36.4) mg/kg. The maximum value was observed at station *39*, with a concentration of 172.3 mg/kg (Fig. 3, *b*). The absence of the 'hump' in the chromatograms from three stations at the bay exit (stations *40*, *41*, *42*) is primarily attributable to the type of bottom sediments (shell rock and sand), which do not contribute to the accumulation of substances [6]. The relationship between the 'hump' value and the granulometric composition of the bottom sediments (the presence of finely dispersed fractions) is confirmed by the maximum linear positive correlation (0.86) between the *UCM* value and the proportion of the pelitic fraction.



F i g. 3. Spatial distribution of hydrocarbons (*a*), *UCM* (*b*), and n-alkanes (*c*) in the bottom sediments surface layer of Kamyshovaya Bay

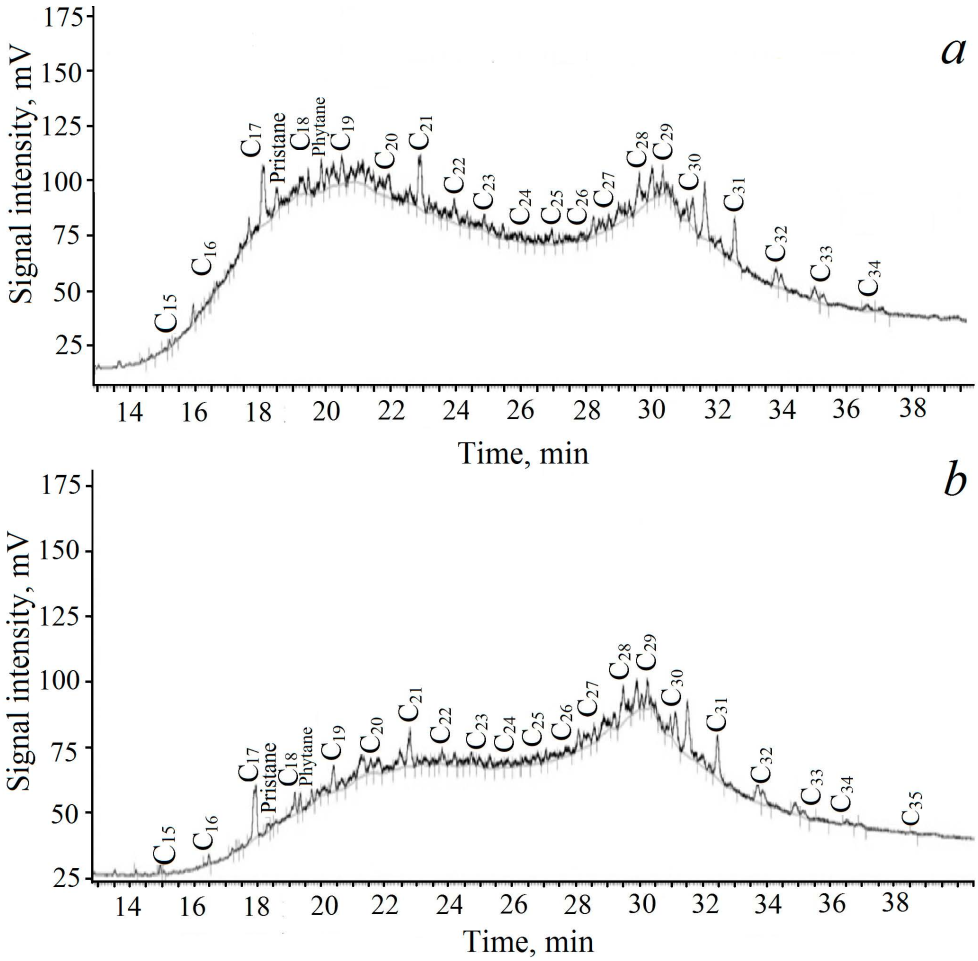
The background in the chromatograms from various recording stations exhibited differences in their outlines. At stations *35*, *36*, *37* and *38*, the 'hump' had bimodal characteristics, with maxima observed in the low-molecular region, indicative of the burial of autochthonous material, and in the high-molecular region, which is typically associated with the burial of oil products [21]. At stations *35a* and *39*, the 'hump' was observed in the high-temperature region, which may indicate the predominant deposition of oil components and oil products (Fig. 4).

The mean concentration of n-alkanes was established at (22.7 ± 8.8) mg/kg. The lowest concentration (10.5 mg/kg) was observed at the point of exit from the bay (station *42*) (Fig. 3, *c*). The spatial distribution of n-alkane concentrations exhibited a similar character to that observed in the distribution of hydrocarbons (Fig. 3, *a*).

The range of C_{15}–C_{34} n-alkanes was identified in all samples obtained from the bottom sediments of the bay (Fig. 5). Isoprenoid alkanes, pristane and phytane, were identified in all samples. The distributions of n-alkanes at stations in the apex, central parts and in the bay exit (Fig. 5) were found to have a similar character.

The principal characteristics of the data set were bimodality (Figs. 4, 5), which suggests two distinct hydrocarbon sources. The presence of odd phytoplankton peaks was observed to reach its highest concentration within the range of C_{17}–C_{21} [21]. The second group of peaks refers to compounds in the range of C_{27}, C_{29} and C_{31}. The odd homologues in this range are genetically related to allochthonous organic matter [22] and are typical for coastal areas [10].

The distribution of n-alkanes at the stations situated in the outer part of the bay had distinctive characteristics. In the low-molecular weight region, the predominant peaks were not of a phytoplanktonic nature, but bacterial in origin (C_{20}, C_{22}) [11]. The bottom sediments at station *40* exhibited a notably elevated concentration of these homologues (57%).

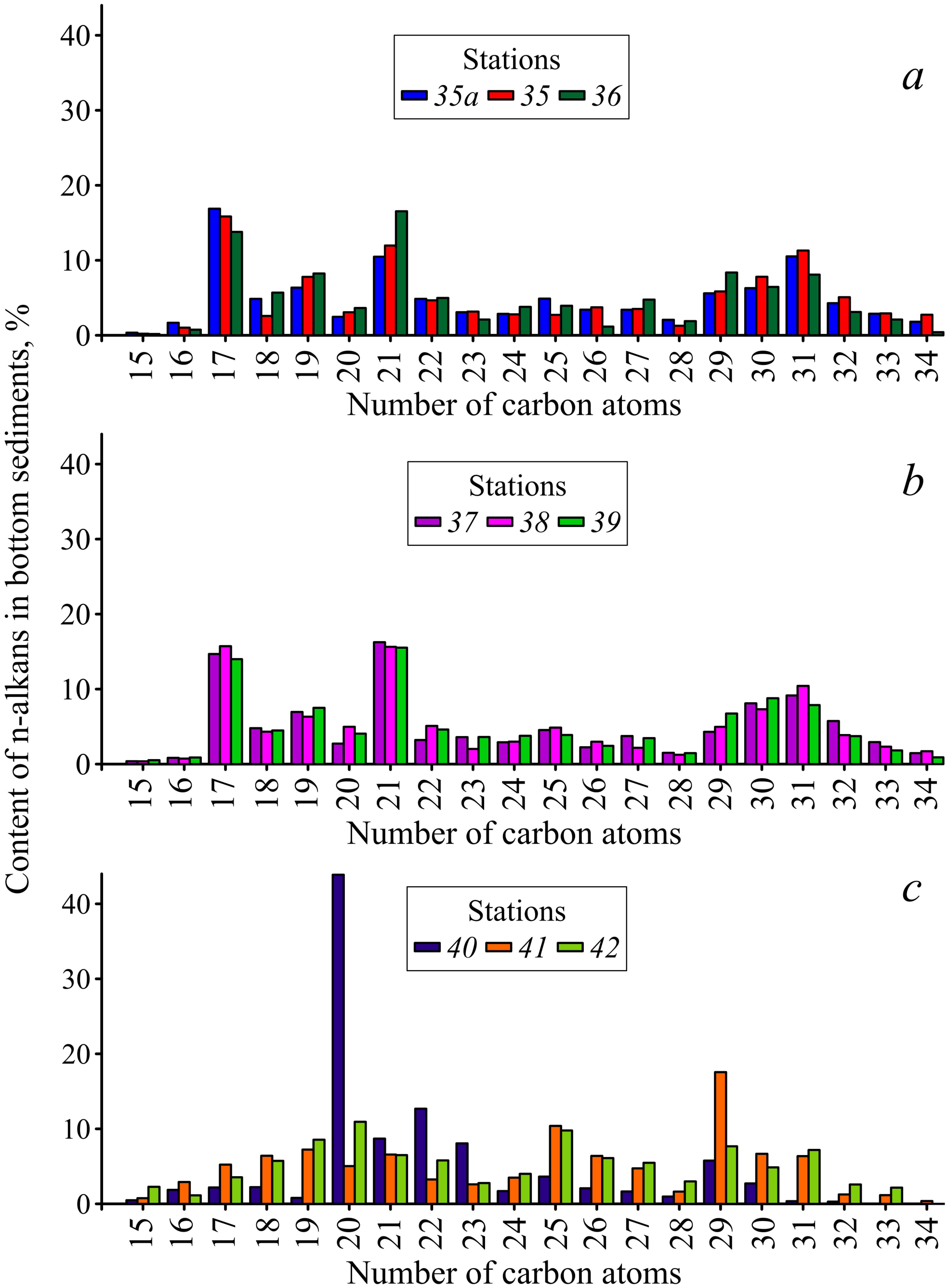


F i g. 4. Typical chromatograms of bottom sediments in Kamyshovaya Bay: a – station *38* (distribution due to a few sources); *b* – station *35a*

It can therefore be concluded that the intensive development of phytoplankton in the inner part of the water area is reflected in the composition of the bottom sediments. Furthermore, this process has a much lower significance for the formation of the hydrocarbon composition of the bottom sediments in the outer part of the bay, where intensive bacterial transformation of organic matter is noted.

In order to establish the source of hydrocarbons in surface bottom sediments, diagnostic indices were calculated and their values at the sampling stations are presented in Table 2.

CPI_2 values at stations *35*, *37*, *38*, *39* were close to 1, which may be an indication of relatively fresh oil pollution [12]. At the remaining stations *35a*, *36*, *40*, *41*, *42*, the marker values were higher than 1, which may be an indicator of the prevalence of biogenic matter (Table 2).



F i g. 5. Composition of n-alkanes in the surface layer of bottom sediments in Kamyshovaya Bay by stations: a – *35a*, *35*, *36*; *b* – *37*, *38*, *39*; *c* – *40*, *41*, *42*

The ratio of pristane to phytane, which is a marker of oil presence, indicated the probable presence of oil pollution (*Pr/Ph* < 1) in almost all the samples collected.

T a b l e 2

Index values in the surface layer of bottom sediments

Indices	Stations								
	35a	*35*	*36*	*37*	*38*	*39*	*40*	*41*	*42*
Pr/Ph	0.71	0.92	0.47	0.08	0.69	0.22	0.33	0.41	0.21
Ki	0.24	0.37	0.30	0.19	0.30	0.22	0.80	0.52	0.71
UCM/n-alkane	3.77	6.32	7.62	5.11	4.79	9.52	0.00	0.00	0.00
LWH/HWH	0.91	0.89	1.16	0.99	1.13	1.06	2.68	0.60	0.80
P_{aq}	0.33	0.26	0.27	0.38	0.31	0.34	0.66	0.35	0.46
TAR	0.83	0.87	0.96	0.78	0.78	0.82	2.25	2.17	1.41
ACL	29.35	29.52	29.09	29.18	29.43	29.36	27.5	28.16	28.35
TMD	0.73	0.67	0.67	0.59	0.62	0.58	0.56	1.80	1.36
C_{31}/C_{19}	1.66	1.45	0.98	1.32	1.65	1.05	0.44	0.88	0.84
CPI_2	1.49	1.20	1.86	1.21	1.34	1.25	1.68	2.25	1.76
C_{31}/C_{29}	1.88	1.93	0.97	2.13	2.10	1.17	0.06	0.36	0.94

The isoprenoid coefficient, which enables the estimation of the extent of oil biodegradation [17], fluctuated within the range typical of fresh and slightly degraded oil pollution. The highest values of this index, which is characteristic of slightly degraded oil (0.52–0.8), were recorded at stations *40–42* (Table 2).

The *UCM*/n-alkanes ratio did not exceed 9.52, which is a value that indicates modern influx of oil products [23]. The analysis of this marker is in accordance with the results obtained from the isoprenoid coefficient.

A study of oil pollution markers allows us to conclude that the current influx of oil and oil products into the bottom sediments, as well as their biotransformation there, is a plausible assumption.

The *LWH/HWH* index at all stations, with the exception of station *40* (situated in the central region of the bay), demonstrates a relatively equal ratio of light and heavy homologues, indicating an equal contribution of autochthonous and allochthonous hydrocarbon sources [24], which is typical for coastal water areas.

The P_{aq} index at all stations, with the exception of stations *40* and *42*, demonstrated a range of 0.26 to 0.38, which suggests that the organic matter present in the bay bottom sediments has a predominantly terrigenous origin [25]. It is possible that aquatic vegetation makes a significant contribution at stations *40* and *42*.

The *TAR* index at stations *35a–39* is less than one, indicating the input of autochthonous material into the bottom sediments. In contrast, at the other stations the terrigenous material input is dominant. The calculated *ACL* index indicates a combination of herbaceous and woody vegetation contributions. The *TMD* index at stations *35a–40* exhibited a range of 0.56 to 0.73, indicative of a mixed contribution from terrestrial and marine sources. At stations *41* and *42*, the contribution of terrestrial vegetation is dominant, indicating a lower content of odd phytoplanktonic n-alkanes in the bottom sediments of these stations. The C_{31}/C_{19} ratio at all stations except station *40* has a high value (0.84–1.66), which reflects the predominant contribution of terrestrial vegetation.

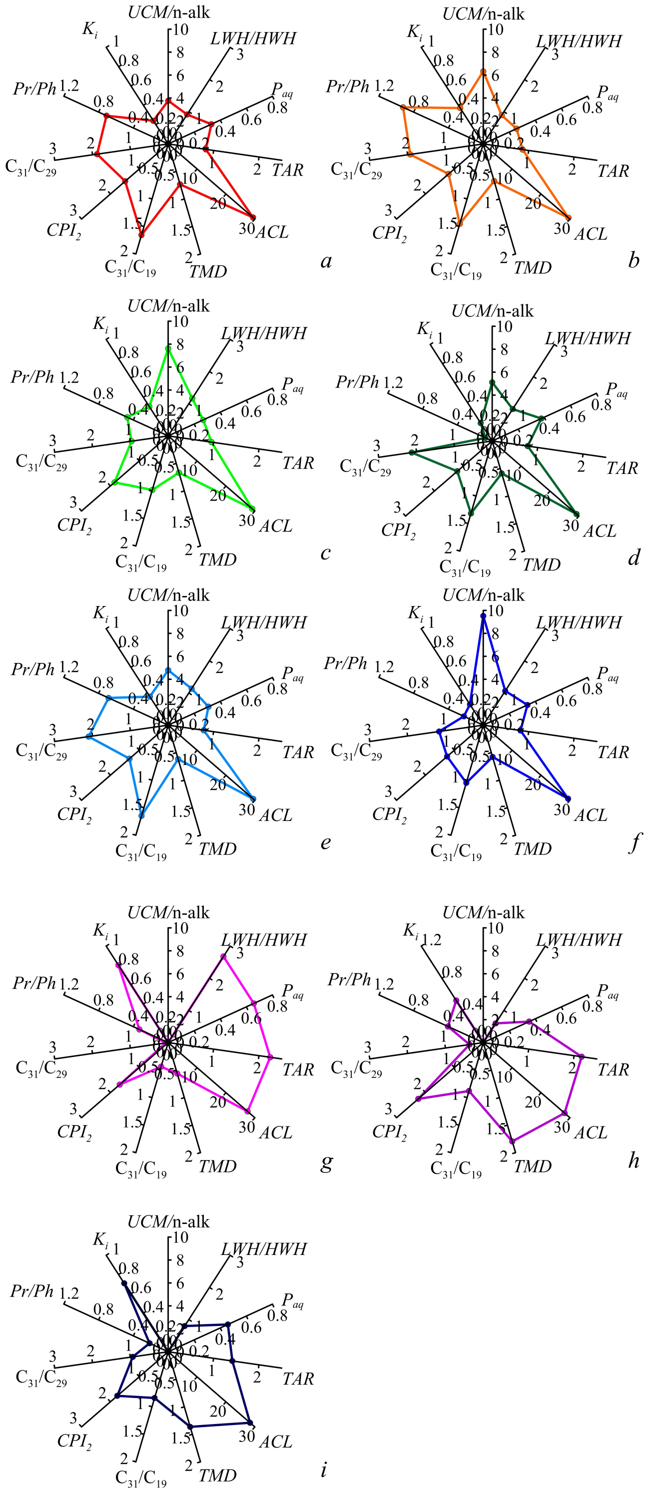
The C_{31}/C_{29} ratio at stations *35a–39*, *42* indicates that herbaceous vegetation is the dominant component, whereas at stations *40*, *41*, woody vegetation plays a more significant role.

The distribution of the principal markers at the sampling stations is illustrated in Fig. 6. The indices at stations *35a*, *35* and *36* are similar in value, which may indicate uniform conditions for the accumulation and transformation of hydrocarbons in the bottom sediments of the specified stations. Furthermore, the indices at stations *37*, *38* and *39* are also comparable on the graph. The indices at station *40* differ from those at the other stations, which is most likely due to the composition of the bottom sediments (the sampling station is located on the limestone slope of the bay). The distribution of markers at stations *41* and *42* is distinctive due to their distance from the bay upper part and a more intense water exchange observed in this area.

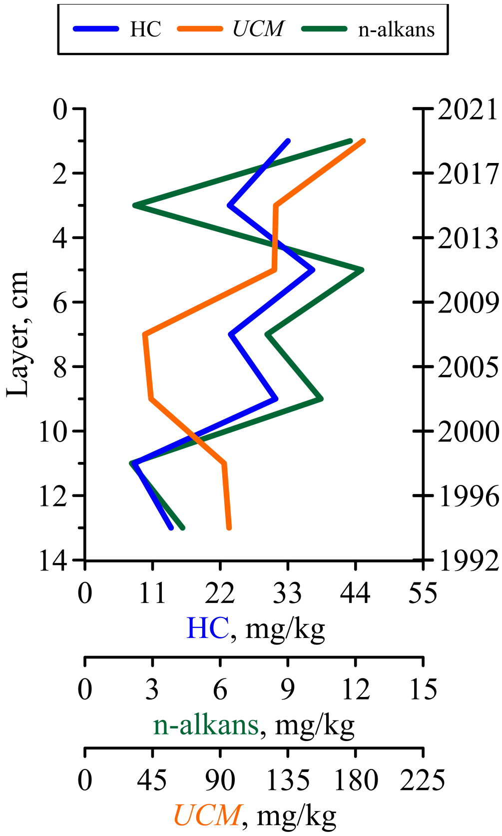
The results of the studies indicated that the concentration of hydrocarbons in the bay bottom sediments demonstrated fluctuations within the range of 27.6–98.5 mg/kg. In regard to the types of bottom sediments (silts, sands, shell rock) with varying degrees of pollution, these indicators align with those observed in relatively healthy water areas experiencing anthropogenic load. The analysis of alkane chromatograms with predominant peaks corresponding to natural sources of hydrocarbons and individual geochemical markers, the values of which correspond to the predominance of biogenic organic matter, allows us to conclude that the main sources of these hydrocarbons in the bottom sediments are natural processes. At the same time, the evidence (CPI_2 values at specific stations are close to 1, $Pr/Ph < 1$, elevated *Ki* values, *UCM*/n-alkanes < 10) indicated a recent flow of oil and oil products.

Long-term changes in the content, composition and genesis of hydrocarbons in the Kamyshovaya Bay bottom sediments

In order to analyse the characteristics of hydrocarbon accumulation by bottom sediments and the temporal variability of their input into the bay water area, a column of bottom sediments was sampled and divided into 2 cm layers. The studies were conducted at one of the stations (station *39*) situated in the central region of the bay. The sampled column had a height of 14 cm.



F i g. 6. Ratio of the main markers in bottom sediments of Kamyshovaya Bay by station: a – *35a*; *b* – *35*; *c – 36; d – 37*; *e – 38*; *f – 39*; *g – 40*; *h – 41*; *i – 42*



F i g. 7. Distribution of hydrocarbons, *UCM* and n-alkanes in the bottom sediments column of Kamyshovaya Bay (station *39*)

A relatively uniform distribution of the studied substances was observed across the horizons within the depth range of 0 to 10 cm, with the hydrocarbon content exhibiting fluctuations between 24.5 and 33.0 mg/kg (Fig. 7). In the deeper layers (10–12 and 12–14 cm), a decrease in the hydrocarbon concentration was observed, reaching 8.0–14.0 mg/kg. The concentration of n-alkanes in the columnar layers had a range of 2.5–11.4 mg/kg. The proportion of n-alkanes from hydrocarbons remained relatively consistent, with an average value of 31% and a range of 29 to 36%.

A chromatographically unresolved background was identified in all the layers under investigation. A gradual decline in the 'hump' was observed from the 0–2 cm layer (185 mg/kg) to the 6–8 cm layer (39.9 mg/kg), followed by an increase in the *UCM* concentration towards the 12–14 cm layer (95.9 mg/kg).The change in hydrocarbon, n-alkane and *UCM* content with depth was found to be uneven. The maximum concentration of hydrocarbons (37 mg/kg) was observed in the 4–6 cm layer, while the highest *UCM* values were in the 0–6 cm layer (125–185 mg/kg). This may be a consequence of changes in the intensity and nature of pollution, with the accumulation of an unresolved mixture in the bottom sediments serving as an indicator.

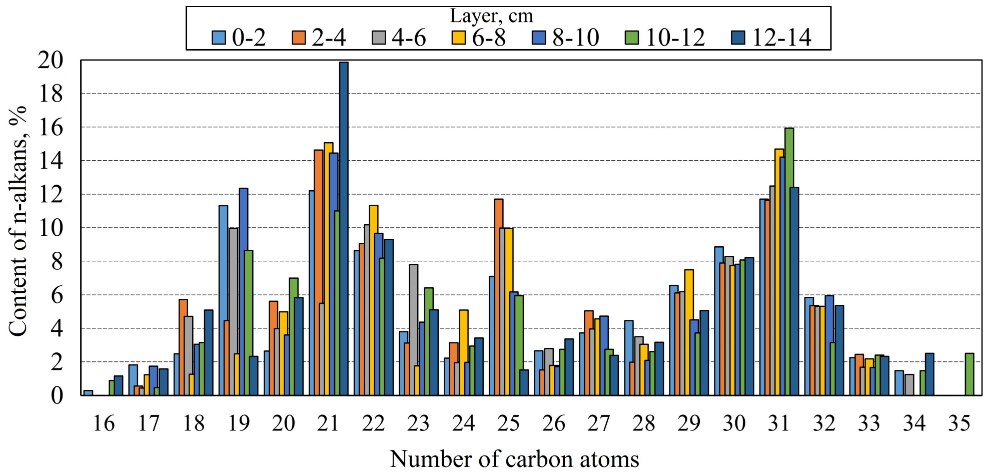
The bottom sediments in the vertical section of the bay are slightly polluted and correspond to the first pollution class [20]. Taking into account the silty nature of the bottom sediments, they can be considered conditionally clean (up to 50 mg/kg). The literature also indicates that during studies of the bottom sediments of Kamyshovaya Bay in the 20th century, slightly elevated levels of petroleum hydrocarbons were recorded, which characterises the water body as slightly polluted [13]. For comparison, in the column of bottom sediments collected in Streletskaya Bay (Sevastopol coast), the concentrations of hydrocarbons were two orders of magnitude higher (1488–4558 mg/kg) [9].

According to the results of [4], the sedimentation rate in the bay, derived from the $^{210}Pb_{exc}$ vertical distribution data, was 0.47 cm/year. At this rate, the 14 cm layer sampled represents 30 years, each 2 cm layer approximately 4.25 years, which allows us to estimate the history of hydrocarbon accumulation.

The maximum concentration of hydrocarbons in the bottom sediments (in terms of sedimentation rate) was observed in 2017–2021 (0–2 cm horizon) and in 2009–2013 (4–6 cm horizon). In 2013–2017 (2–4 cm horizon) the concentration of hydrocarbons was lower compared to 2017–2021 and 2009–2013. The minimum concentrations of hydrocarbons in the periods 1992–2000 may be associated with the economic downturn in Sevastopol and, as a result, a decrease in the turnover of the port: in 1993 it decreased to 349 thousand tons/year. A similar trend was observed in the water area of Streletskaya Bay [9], indicating a reduced anthropogenic load on the coast during this period.

The increase in hydrocarbon concentrations after 2000 may be due to the increased impact on the water surface caused by the construction of new housing estates and the use of the bay as an oil and fishing port. At the same time, given the low levels of hydrocarbons, the observed variations may be largely natural.

In the vertical section, n-alkanes in the range C_{16}–C_{34} were identified (Fig. 8), compounds C_{17}–C_{33} were present in all layers studied. Isoprenoid alkanes, pristane and phytane, were identified in 100% of the samples. The distribution of n-alkanes was bimodal in all the horizons studied. Autochthonous C_{19} (2–11%) and C_{21} (5–20%) predominated. C_{17} (up to 2%), which is probably more bioavailable and transformed, played a minor role. The bacterial peak C_{22} (8–11%) was also present in significant amounts. The most pronounced allochthonous peak was C_{31} (12–16%), which links the hydrocarbons in the bottom sediments to the herbaceous vegetation corresponding to the steppe coast of this region.



F i g. 8. Content of n-alkanes in the bottom sediments column of Kamyshovaya Bay (station *39*)

To determine the genesis of hydrocarbons in bottom sediments, diagnostic indices were calculated (Table 3).

T a b l e 3

Values of n-alkane genesis markers in the vertical profile of bottom sediments in Kamyshovaya Bay (station *39*)

Markers	Layer, cm						
	0–2	2–4	4–6	6–8	8–10	10–12	12–14
Pr/Ph	1.40	0.16	0.28	0.25	1.01	2.37	1.19
Ki	1.50	0.70	1.20	1.30	1.60	1.60	1.20
CPI_2	1.29	2.03	1.55	1.93	1.69	1.71	0.98
UCM/n-alkane	18.03	15.04	11.02	5.49	4.54	37.22	23.54
LWH/HWH	0.80	0.83	0.66	0.74	1.09	0.88	1.06
P_{aq}	0.37	0.45	0.49	0.35	0.36	0.39	0.28
TAR	1.67	4.54	2.17	7.21	1.66	2.46	5.07
ACL	30.00	29.90	30.0	30.0	30.00	30.90	30.30
TMD	1.10	1.60	1.40	1.90	1.00	1.30	0.80
C_{31}/C_{19}	1.00	2.60	1.30	5.90	1.20	1.80	5.30
C_{31}/C_{29}	1.30	1.90	2.00	2.00	3.20	4.30	2.40

In the thickness of the bottom sediments, except for layers 2–4, 4–6, 6–8 cm, a predominance of pristane (mainly biogenic) over phytane was observed. In other layers this ratio indicates the presence of oil pollution. The isoprenoid coefficient *Ki* in the 2–4 cm layer corresponded to the presence of slightly degraded oil products, in the other layers its values indicated presence of oil and oil products of medium degradation [17]. Thus, the isoprenoid n-alkane composition in the vertical section of the bay bottom sediments corresponds to the periodic uptake and further degradation of petroleum hydrocarbons.

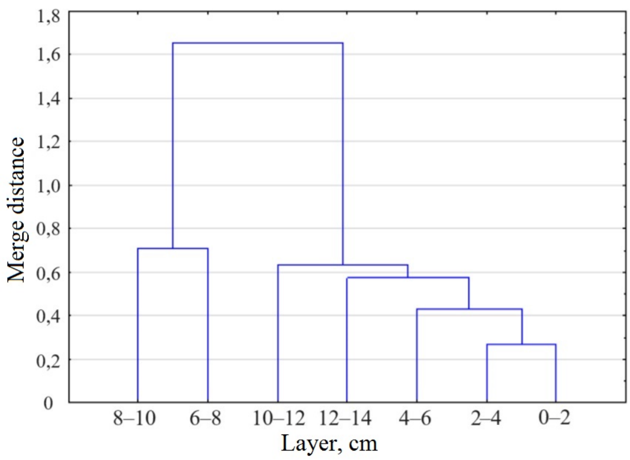
CPI_2 values, which ranged from 0.98 to 2.03 in the high molecular weight range (average 1.60), may indicate both transformed oil contamination and the biogenic nature of OM [14, 26, 27].

The ratio *UCM*/n-alkanes varied from 4.54 to 37.22. The minimum ratios were noted at the 6–8 and 8–10 cm layers from 2001 to 2009. The maximum value of this ratio (37.22) was observed at the 10–12 cm layer corresponding to the period 1996–2000. The *LWH/HWH* index values were 0.66–1.09 with an average of 0.87 indicating the influx of terrigenous material [24].

The P_{aq} index varied from 0.28 to 0.49, which corresponds to the predominant accumulation of allochthonous compounds. The obtained *TAR* index values varied from 1.66 to 7.21, also indicating the accumulation of allochthonous matter in the bottom sediments [25].

The average hydrocarbon chain length (*ACL*) varied within a small range of 29.90–30.90, which characterises the stability of the organic matter accumulation and transformation processes in the water basin.

The *TMD* index with values of 1.00–1.90 and the C_{31}/C_{19} n-alkane ratio indicate the predominant burial of high molecular weight hydrocarbons in the bottom sediments.



F i g. 9. Results of cluster analysis of the bottom sediments layers sampled in Kamyshovaya Bay (station *39*)

In order to identify periods with different characteristics of hydrocarbon background of the bottom sediments of Kamyshovaya Bay, clustering of the bottom sediment layers (Fig. 9) was performed according to the total hydrocarbon content, *UCM* value and n-alkane concentration.

Over the 30-year period studied, layers corresponding to the period 2000–2009 were identified (6–8 and 8–10 cm), when the *UCM*/n-alkane ratio was lower. It can be assumed that during this period conditions for the inflow and accumulation of hydrocarbons changed. At the same time, the quality of the bottom sediments characterised the state of the bay as favourable in all periods studied.

It can be concluded that the hydrocarbon content in the bottom sediment layers of different depths fluctuated slightly and was within the range of 8.0–37.0 mg/kg, which corresponds to the indicators for clean water areas. At the same time, a chromatographically unresolved background was detected, indicating the burial of transformed organic compounds. Based on the analysis of alkane chromatograms and individual geochemical markers, the predominant source of hydrocarbons in the bottom sediments over the last 30 years has been the natural flux of organic matter. Traces of transformed oil are also present.

Conclusion

Despite its small size, Kamyshovaya Bay has a clear zoning, which, as shown in the literature, is associated with different conditions of organic matter accumulation in bottom sediments. As a consequence, hydrocarbons in the bottom sediments of Kamyshovaya Bay are distributed unevenly throughout the water area, and a zone of increased pollution is formed in the central part of the bay. The recorded distribution of hydrocarbon content in the bottom sediments of the bay is a consequence of the processes occurring in the semi-enclosed bay and is also determined by the heterogeneity of the granulometric composition of bottom sediments, which contributes to the accumulation of substances of different nature to a different extent. The concentration of hydrocarbons in bottom sediments ranged from 27.6 to 98.5 mg/kg, which allows us to classify them as slightly contaminated. Judging by the character of chromatograms with predominant peaks corresponding to natural sources of hydrocarbons and some geochemical markers (*LWH*/*HWH*, P_{aq}, *TAR*, *ACL*, *TMD*, C_{31}/C_{19}, C_{31}/C_{29}), the values of which correspond to the predominance of biogenic organic matter, the main source of hydrocarbons in bottom sediments is the input of autochthonous and allochthonous compounds. Markers (CPI_2 values at some stations are close to 1, $Pr/Ph < 1$, increased *Ki* values, *UCM*/n-alkanes < 10) of recent oil and oil product input were recorded.

A layer-by-layer study of the hydrocarbon composition of the bay bottom sediments revealed that they had not been significantly contaminated by hydrocarbons over the past 30 years. The predominant source of hydrocarbons, based on analysis of alkane composition and geochemical marker values, and in the surface layer, was allochthonous and autochthonous organic matter. Judging from the values of geochemical markers diagnosing oil contamination, the influx of oil and oil products can be considered as a secondary source of hydrocarbons.

Thus, both over the past 30 years and at present, Kamyshovaya Bay has been subject to anthropogenic pollution, with minor fluctuations due to the level of economic activity in the port, while the level of pollution in the bay has remained low.

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Konstantin I. Gurov – formulation of goals and objectives of the study; presentation of data in the text and their analysis; paper correction; discussion of the study results; preparation of graphic and text materials; formulation of the conclusions.

The authors have read and approved the final manuscript.

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