

Hydrocarbon Composition in Water and Coastal Sediments of the Southwestern Sea of Azov: A Case Study

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Abstract

Purpose. The paper aims to study the sources and spatial distribution of hydrocarbons in water, suspended matter and coastal bottom sediments in the southwestern part of the Sea of Azov (Crimean coast) to assess the level of oil pollution in this water area.

Methods and Results. Water and bottom sediment samples were collected in the summer of 2024 along the coast, including areas with high anthropogenic impacts as well as nature conservation zones. Concentrations of hydrocarbons and *n*-alkanes were determined by gas chromatography and diagnostic indices were calculated to identify possible sources of hydrocarbons. Hydrocarbon concentrations varied: 0.048–0.172 mg/L (mean 0.084 ± 0.030 mg/L) in water, 0.01–0.19 mg/L (mean 0.09 ± 0.05 mg/L) in suspended matter, 1.00–3.80 mg/kg (mean 2.48 ± 0.96 mg/kg) in bottom sediments. Hydrocarbon concentrations in water at all stations, except one, exceeded the maximum permissible concentration for fishery water bodies (0.05 mg/L). The distribution of *n*-alkanes in the studied components suggests predominantly natural sources of hydrocarbons: in water and suspended matter, these sources are primarily macrophytes and the bacterial communities, while in coastal sediments, they are organic compounds originating from terrestrial sources. The CPI₂ (> 1) indices and the pristane/phytane ratio (< 1) in most samples, along with the absence of unresolved complex mixtures in the chromatograms, indicate a primarily biogenic rather than petroleum origin for the hydrocarbons.

Conclusions. The observed exceedance of the maximum permissible concentration for total hydrocarbon content in water is attributed to natural processes. The predominantly biogenic origin of hydrocarbons is explained by the influx of organic matter from terrestrial vegetation, as well as the activity of macrophytes and bacterial communities under conditions of summer water warming. Hydrocarbon accumulation in sandy bottom sediments is minimal. Thus, no evidence of oil pollution was detected in the studied water area, and the observed hydrocarbon concentrations are mainly due to natural biogeochemical processes characteristic of the Sea of Azov.

Keywords: aliphatic hydrocarbons, *n*-alkanes, suspended matter, coastal sediments, diagnostic indices, Sea of Azov, Crimean coast, marine pollution

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Introduction

The Azov–Black Sea basin is one of the most developed regions in terms of recreational, tourism, health resort and balneological services, serving not only Russia but also much of Europe [1]. Additionally, the Sea of Azov is a unique water body due to its fishery resources. Many valuable fish species reproduce and grow there [2]. Against the backdrop of global climate change, the anthropogenic pressure on the waters and coastal areas of the Azov region is increasing. This is driven by intensive maritime cargo transportation, port infrastructure development, offshore oil and gas exploration, as well as both spontaneous and planned recreational development along the coast. Significant changes are occurring in the river basins flowing into the Sea of Azov [3, 4]. The lower reaches of these rivers experience the highest anthropogenic pressure, as these areas are the most developed in terms of industry and agriculture and have high population densities along their banks [5]. The Sea of Azov is a unique natural ecosystem with rich flora and fauna; however, its ecosystem is undergoing significant depletion due to human activities. Consequently, the ecological state of the sea water area has been regularly assessed for many years [1, 2, 4–8]. Currently, monitoring of the hydrochemical state and pollution levels in the Sea of Azov is conducted at only a few locations. In the eastern part of Taganrog Bay, monitoring is performed by the Donskaya Estuary Hydrometeorological Station (EHS Donskaya, Azov). In the Kuban River delta and its estuarine coast in Temryuk Bay, monitoring is carried out by the Kubanskaya Estuary Hydrometeorological Station (EHS Kubanskaya, Temryuk). Between the ports of Crimea and Kavkaz, monitoring is conducted by the integrated Laboratory for Environmental Pollution Monitoring (Opasnoe village, Kerch) [1]. Unfortunately, data on the ecological state of the coastal waters of the southwestern part of the sea, from Arabat Bay to Kazantip Bay, which are highly ecologically sensitive, are currently unavailable.

Among the numerous harmful substances of anthropogenic origin entering the Sea of Azov, oil and petroleum products are among the most significant. The primary sources of pollutants entering the Sea of Azov include river runoff, diffuse runoff from wastewater discharged by enterprises in coastal zones, atmospheric precipitation and aeolian fallout, Black Sea waters, shipping, dumping of contaminated bottom sediments and discharges of drilling muds and sludge from oil and gas well drilling. Elevated hydrocarbon (HC) concentrations in water and bottom sediments have been observed in the Kerch region [9], where HC levels in water can be twice the maximum permissible concentration (MPC) [10].

Intensive maritime transportation of various cargoes, including highly toxic substances, exerts a significant impact on the ecosystem. Pollution of the Sea of Azov from ship operations occurs primarily through following mechanisms: leaks of fuel and lubricants, discharges of bilge and ballast water; secondary pollution resulting from the resuspension of bottom sediments during the passage of low-draft loaded vessels; and emissions from marine power plants, which release up to 200 different compounds into the atmosphere via engine and boiler exhausts, as well as through the evaporation of bunker fuel [11].

Additionally, mud volcanoes in Temryuk Bay have repeatedly caused localized pollution of the sea with petroleum products. For example, in October 2015,

the Golubitsky volcano erupted, resulting in the formation of an island composed of mud volcanic material [11, 12].

When assessing HC pollution in a water body, it is essential to consider natural HC levels, which originate from plants, animals and bacterial communities in water, bottom sediments and soils, as well as the influx of organic compounds from land [13]. These components can be of great importance. For example, in areas with high algae accumulation, HC levels may mimic those associated with oil pollution [14]. Biogenic HCs are classified as either autochthonous, produced by planktonic organisms within water bodies, or allochthonous, derived from terrestrial vegetation. As a rule, phytoplankton contributes the largest share to the total mass of biogenic HCs, followed by other organisms in decreasing order of contribution: bacteriobenthos > bacterioplankton > zooplankton [13, 15]. Consequently, when studying oil pollution of water bodies, distinguishing between oil-derived and biogenic HCs becomes critical. Such assessments are fundamental for a deeper understanding of the processes occurring in the water body and for managing the environmental sustainability of specific water areas.

In coastal regions, sea bottom sediments serve as the final repository for both natural and anthropogenic organic matter originating from the water column and various coastal pollution sources. The hydrophobic properties of HCs facilitate their adsorption onto solid particles, leading to their accumulation in suspended matter and various fractions of bottom sediments. Continuous monitoring of the qualitative and quantitative composition of HCs in sea bottom sediments is essential for assessing marine environmental quality and supporting the protection of coastal waters [16–18]. Thus, bottom sediments are among the most critical components for studying pollutants in the marine environment [19, 20].

Monitoring oil pollution is challenging due to the complex and variable composition of oil and petroleum products, which comprise thousands of compounds with diverse properties that can serve as the basis for their analytical determination [21]. Diagnostic indices, derived from *n*-alkane concentration data, are used to identify potential sources of HCs entering the marine environment. A component of crude oil [22, 23], *n*-alkanes are widely used to calculate geochemical markers that can indicate the presence of oil pollution [20, 24]. Numerous studies have identified *n*-alkanes originating from various autochthonous sources (biogenic origin), such as the biosynthesis of higher plants, certain algae and bacteria. Additionally, *n*-alkanes from anthropogenic activities are distinguished, entering the hydrosphere through offshore oil and gas exploration, accidental spills, municipal and industrial discharges, river runoff and waste incineration.

The aim of the study was to identify the sources and distribution patterns of HCs in the aquatic ecosystems of the southeastern Crimean coast (the Sea of Azov).

Material and methods

Water and coastal sediment samples, collected using a hand sampler during expeditionary surveys along a grid of stations (Fig. 1) in the summer of 2024, served as the material for this study. The sampling stations were located in the Sea of Azov along the southwestern coast of Crimea, which includes sectors with high anthropogenic pressure as well as nature conservation zones.



Fig. 1. Map of sampling locations for water, suspended matter and sediments along the southwestern Crimean coast of the Sea of Azov, summer 2024 (<https://yandex.ru/maps>)

Surface water samples were collected in 2 L glass bottles with ground-glass stoppers, pre-washed with a chromic acid mixture, tap water, distilled water, and *n*-hexane. Before sampling, the bottles were rinsed with *n*-hexane and sample water.

A 250 ml water sample was transferred to a separatory funnel, to which 1.5 ml of sulfuric acid (1:1) and 20 ml of *n*-hexane were added. The mixture was shaken for 10 minutes. After phase separation, the aqueous layer was returned to the original bottle, and the hexane extract was passed through a chemical funnel containing freshly calcined sodium sulfate over a cotton substrate into a flask for concentration. The water sample was re-extracted by transferring it back to the separatory funnel, adding 15 ml of *n*-hexane and shaking for 10 minutes. After separating the layers, the aqueous layer was discarded and the hexane extracts were combined. The bottle and the separatory funnel were rinsed with 2–3 ml of *n*-hexane, which was added to the combined extract. The resulting extract was concentrated to a volume of 1 ml using a rotary evaporator.

Coastal sediment samples were collected from the surface horizon (0–5 cm) using a hand sampler in the splash zone at depths not exceeding 2 m. All samples were stored in specialized containers lined with aluminum foil and labeled. In the laboratory, the marine sediments were dried to an air-dry state, with large inclusions such as stones removed beforehand. The sediments were then ground in an inert mortar and sieved through a 0.25 mm mesh for subsequent determination of HC concentrations.

Suspended matter in seawater was collected by filtering water samples through GF/F filters (0.45 μm pore size) using a vacuum pump and a Bunsen flask. The filters were pre-cleaned by boiling three times in distilled water for 10 minutes, air-dried and stored in a desiccator. Before use, the filters were brought to a constant weight, weighed, numbered and placed in sealed transport containers. During filtration, the seawater was continuously stirred to prevent sorption of suspended matter onto the walls of the tank. The filtered volume of 1 L was accounted for when calculating the HC content in the suspended matter. To remove sea salts and avoid distortion of the suspended matter mass, the filters with collected material were rinsed with a small amount of distilled water during filtration without interrupting

suction. The air-dried filters with suspended matter were placed in containers and stored in a freezer at a temperature not exceeding -10°C for no longer than 1 month.

HC detection [25]¹ was performed by extracting HCs from coastal sediment samples or suspended matter collected on filters using an alkaline ethyl alcohol solution, followed by conversion of the analyte into hexane and removal of interfering compounds via sorption on aluminum oxide. The HC content was subsequently measured by gas chromatography. Concentrations of HCs and *n*-alkanes were determined at 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.

An aliquot of the concentrated extract (1 μL) was injected with a microsyringe into the evaporator (heated to 250°C) of a Krystall 5000.2 gas chromatograph equipped with a flame ionization detector (FID). HCs were separated on a $30\text{ m} \times 0.32\text{ mm}$ TR-1MS capillary column with a stationary phase thickness of $0.25\text{ }\mu\text{m}$ (Thermo Scientific). The column temperature was programmed from 70 to 280°C at a rate of $8^{\circ}\text{C}/\text{min}$. Helium was used as the carrier gas with a flow rate of $2.5\text{ ml}/\text{min}$ without splitting. The detector temperature was maintained at 320°C .

The total HC content was quantified using absolute calibration of the FID with a HC mixture prepared gravimetrically, ranging from 0.02 to $5.0\text{ mg}/\text{L}$. The ASTM D2887 Reference Gas Oil standard (Supelco, USA) was used as the HC mixture. The total HC content was determined by summing the peak areas of the eluted *n*-alkanes. Chromatographic data were processed using Chromatec Analyst 3.0 software, employing the absolute calibration method and percentage normalization.

Identification of *n*-alkanes was performed using a standard mixture of paraffin HCs in hexane, with each component at a mass concentration of $200\text{ }\mu\text{g}/\text{ml}$, and pristane (Pr) + phytane (Ph) at $100\text{ }\mu\text{g}/\text{ml}$ in hexane (Supelco, USA). For the sanitary assessment of water quality, the MPC in the Russian Federation for fishery water bodies ($0.05\text{ mg}/\text{l}$) was applied².

To identify potential sources of HC inputs, the following diagnostic indices were calculated [26–30]: $(n\text{-C}_{17}+n\text{-C}_{19}+n\text{-C}_{21})/\Sigma n\text{-alkanes}$; Pr/Ph (pristane/phytane ratio); $n\text{-C}_{17}/\text{Pr}$; LWH/HWH (low molecular weight to high molecular weight homologies ratio), defined as $\Sigma(n\text{-C}_{13}-n\text{-C}_{21})/\Sigma(n\text{-C}_{22}-n\text{-C}_{37})$; CPI₂ (carbon preference index), defined as $(\Sigma(n\text{-C}_{23}-n\text{-C}_{31})_{\text{odd}} + \Sigma(n\text{-C}_{25}-n\text{-C}_{33})_{\text{odd}})/2\Sigma(n\text{-C}_{24}-n\text{-C}_{34})_{\text{even}}$; Paq (proxy for aquatic macrophytes), defined as $(n\text{-C}_{23}+n\text{-C}_{25})/(n\text{-C}_{23}+n\text{-C}_{25}+n\text{-C}_{29}+n\text{-C}_{31})$; TAR (terrigenous/aquatic ratio), defined as $(n\text{-C}_{27}+n\text{-C}_{29}+n\text{-C}_{31})/(n\text{-C}_{15}+n\text{-C}_{17}+n\text{-C}_{19})$; ACL (average chain length), defined as $((27 \cdot n\text{-C}_{27} + 29 \cdot n\text{-C}_{29} + 31 \cdot n\text{-C}_{31} + 33 \cdot n\text{-C}_{33} + 35 \cdot n\text{-C}_{35} + 37 \cdot n\text{-C}_{37})/(n\text{-C}_{27}+n\text{-C}_{29}+n\text{-C}_{31}+n\text{-C}_{33}+n\text{-C}_{35}+n\text{-C}_{37}))$.

For correlation analysis, the Pearson correlation coefficient (*r*) was calculated at a significance level of $p = 0.05$.

¹ Ministry of Environmental Protection and Natural Resources of the Russian Federation, 1996. *RD 52.10.556-95: Guidelines. Determination of Pollutants in Samples of Marine Bottom Sediments and Suspensions*. Moscow: Federal Service of Russia for Hydrometeorology and Environmental Monitoring, pp.18-26; 41-49 (in Russian).

² Ministry of Agriculture of the Russian Federation, 2016. *On Approval of Water Quality Standards for Water Bodies of Fisheries Importance, Including Standards for Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Fisheries Importance*. Ministerial Decree No. 552, 13 December 2016. Moscow: Ministry of Agriculture of the Russian Federation (in Russian).

Results

HC Concentrations

Coastal waters. The HC content in the water of the studied section of the Sea of Azov coast ranged from 0.048 to 0.172 mg/L, with a mean of 0.084 ± 0.030 mg/L (Fig. 2, *a*). HC concentrations in the western (stations 1, 2, 3, 9) and eastern (stations 4–8, 10) parts of the study area, separated by the waters adjacent to the Kazantip Nature Reserve (Fig. 1), showed no significant difference, averaging 0.093 ± 0.029 mg/L and 0.078 ± 0.031 mg/L, respectively. No prior studies on HC content in the water of this area have been conducted. The proportion of *n*-alkanes in the HC composition ranged from 24 to 54%, with a mean of $42 \pm 8\%$ (Fig. 2, *b*). These values are slightly higher than the typical proportion of *n*-alkanes (approximately 30%), suggesting an active influx of these compounds.

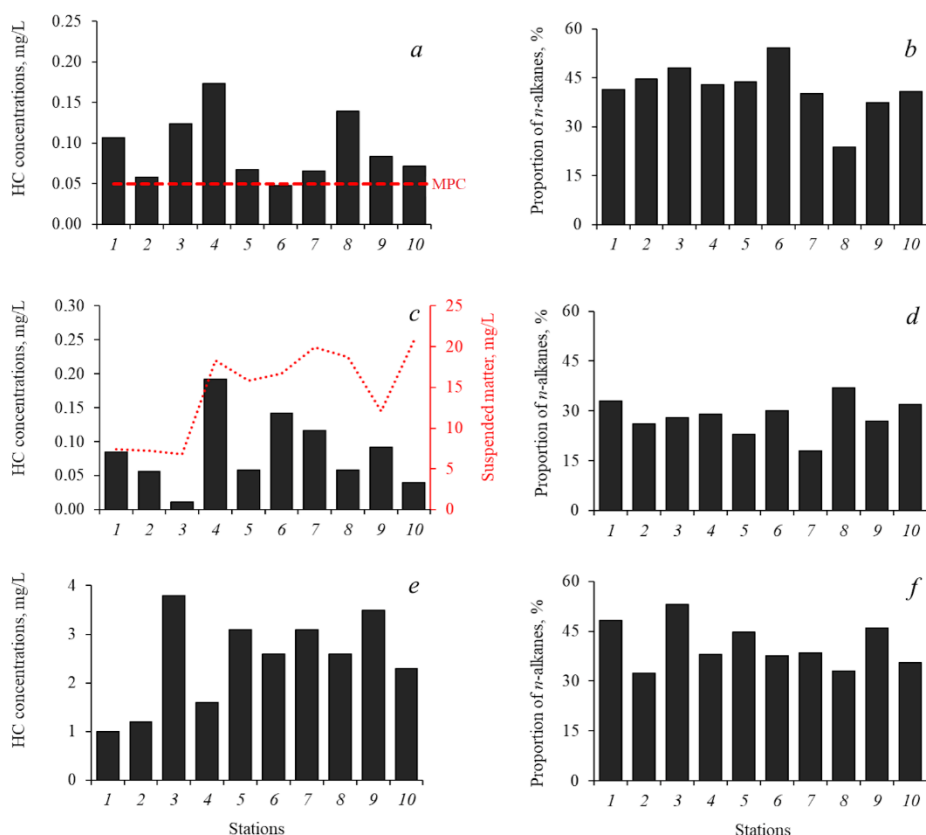


Fig. 2. HC concentrations (*a, c, e*) and *n*-alkane proportions (*b, d, f*) in coastal waters (*a, b*), suspended matter (*c, d*) and coastal sediments (*e, f*) of the southwestern Sea of Azov (Crimean coast), summer 2024

Suspended matter. The suspended matter content in coastal waters ranged from 7 to 21 mg/L, with a mean of 14 ± 6 mg/L (Fig. 2, *c*). The HC content in suspended matter ranged from 0.01 to 0.19 mg/L, averaging 0.09 ± 0.05 mg/L (Fig. 2, *c*). The proportion of *n*-alkanes in the HC composition ranged from 18% to 37%, with a mean of $28 \pm 5\%$ (Fig. 2, *d*).

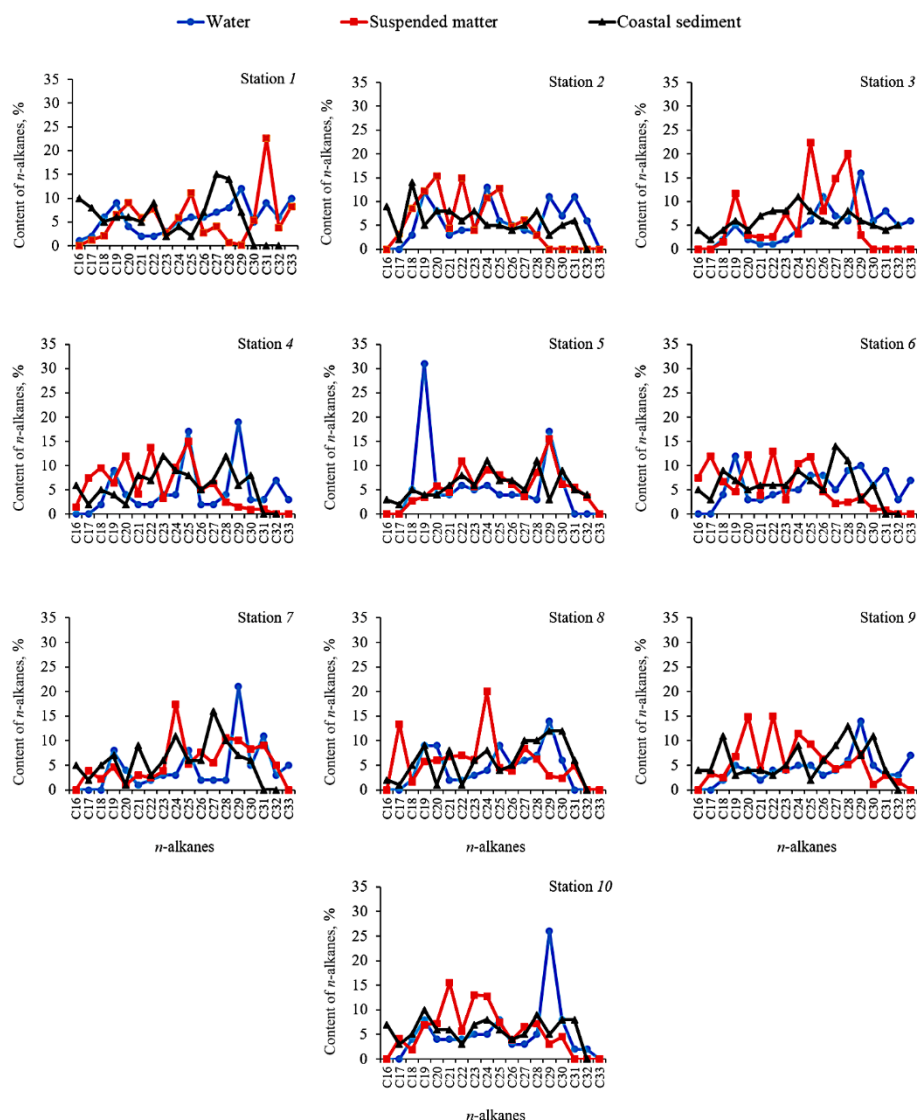


Fig. 3. Relative content of *n*-alkanes in coastal waters, suspended matter and coastal sediments of the southwestern Sea of Azov (Crimean coast), summer 2024

Coastal sediments. The HC content in coastal sediments ranged from 1.00 to 3.80 mg/kg, with a mean of 2.48 ± 0.96 mg/kg (Fig. 2, *e*). The proportion of *n*-alkanes in the HC composition ranged from 32% to 53% (Fig. 2, *f*).

Composition of n-alkanes

Analysis of the individual *n*-alkane composition enabled characterization of HC sources and the processes affecting them in the water of the studied marine coastal ecosystem. The distribution of *n*-alkanes is presented in Fig. 3. The identified *n*-alkanes ranged from *n*-C₁₆ to *n*-C₃₃ in water and suspended matter samples and from *n*-C₁₇ to *n*-C₃₃ in coastal sediment samples.

Diagnostic indices

Based on the HC composition of coastal water, suspended matter and coastal sediments, several geochemical markers of organic matter origin were calculated (Table).

Diagnostic ratios of *n*-alkanes in coastal waters, suspended matter and sediments of the southwestern Sea of Azov (summer 2024)

Index	No. of stations									
	1	2	3	4	5	6	7	8	9	10
<i>Coastal water</i>										
Paq	0.29	0.31	0.23	0.46	0.34	0.42	0.23	0.42	0.31	0.31
TAR	2.54	2.12	5.98	2.58	0.69	2.02	3.99	2.22	4.30	3.70
ACL	30.15	29.56	29.67	29.44	28.59	30.15	29.96	28.37	29.95	28.90
LWH/HWH	0.33	0.42	0.15	0.31	0.97	0.35	0.24	0.46	0.29	0.35
<i>n</i> - C ₁₇ + <i>n</i> -C ₁₉ + <i>n</i> - C ₂₁ / Σ <i>n</i> -alkanes	0.12	0.15	0.07	0.14	0.35	0.15	0.12	0.14	0.10	0.13
CPI ₂	1.60	1.16	1.42	2.29	1.55	1.37	3.23	1.32	1.67	1.87
<i>Suspended matter</i>										
Paq	0.38	1.00	0.91	0.88	0.40	0.78	0.32	0.58	0.57	0.87
TAR	3.45	0.40	1.51	0.64	7.02	0.39	2.90	0.85	1.43	0.86
ACL	30	26	26	26	28	26	29	28	27	26
LWH/HWH	0.33	0.78	0.23	0.70	0.20	0.88	0.17	0.51	0.46	0.56
<i>n</i> - C ₁₇ + <i>n</i> -C ₁₉ + <i>n</i> - C ₂₁ / Σ <i>n</i> -alkanes	0.14	0.20	0.14	0.18	0.08	0.20	0.12	0.26	0.14	0.27
CPI ₂	3.1	1.7	1.4	2.1	1.2	1.6	0.8	1.1	1.3	0.8
<i>Coastal sediments</i>										
Paq	0.49	0.47	0.59	0.44	0.48	0.46	0.47	0.30	0.34	0.39
TAR	1.43	0.70	2.43	2.41	3.67	1.52	2.24	3.76	1.96	1.59
ACL	28	28	28	28	28	28	28	28	28	28
LWH/HWH	0.53	0.60	0.25	0.22	0.22	0.40	0.25	0.22	0.37	0.46
<i>n</i> - C ₁₇ + <i>n</i> -C ₁₉ + <i>n</i> - C ₂₁ / Σ <i>n</i> -alkanes	0.20	0.31	0.12	0.12	0.12	0.19	0.11	0.08	0.20	0.18
CPI ₂	1.0	0.9	1.3	1.3	1.9	1.2	1.0	1.0	1.6	1.0

Discussion

Coastal waters. The HC content in water exceeded the MPC for fishery water bodies (0.05 mg/L) at all sampling stations, except for station 6, where the HC concentration (0.048 mg/L) was almost equal to the MPC. Previous studies [2] reported that, during the summer period from 2016 to 2020, HC concentrations in various parts of the Sea of Azov consistently exceeded the MPC, with an average excess of up to 2.6 times the MPC, consistent with the values observed in this study. According to the data ³ from the State Hydrometeorological Institute in 2023, HC concentrations in the Sea of Azov ranged from analytical zero to 7.2 times the MPC (approximately 0.36 mg/L). The most polluted region of the Sea of Azov is Taganrog Bay, located in the eastern part of the sea. In other regions, HC levels were generally lower, not exceeding 2.2 times the MPC.

The distribution of *n*-alkanes in the coastal waters exhibited a bimodal pattern, indicating dual sources of HC inputs. At most stations, the low molecular weight region was dominated by the autochthonous *n*-alkane *n*-C₁₉ [28], with its proportion ranging from 5% to 31%. This presence is attributed to phytoplankton production. In contrast, the phytoplankton-derived *n*-C₁₇ was less prominent, likely due to its higher bioavailability. In the high molecular weight region, the allochthonous *n*-alkane *n*-C₂₉ (10–26%) was predominant across all stations, with *n*-C₃₁ also dominant in some samples. The predominance of odd-numbered high molecular weight *n*-alkanes is characteristic of coastal waters and is attributed to the influx of terrigenous organic matter [28]. In some samples, peaks of even-numbered *n*-alkanes (*n*-C₁₈, *n*-C₂₀, *n*-C₂₄, *n*-C₂₆) were prominent, likely associated with bacterial production [31, 32]. This was probably due to the active development of heterotrophic communities, with abundances ranging from 10³ to 10⁶ cells/ml, driven by elevated water temperatures (up to 29.5 °C). Additionally, peaks of *n*-C₂₅ were observed, with proportions ranging from 4% to 17%. This *n*-alkane is commonly found in macrophytes [33, 34], where its proportion often exceeds 40% [35]. In particular, *Zostera*, which was abundant in the coastal zone during sampling, contains significant amounts of *n*-C₂₅ [36, 37]. The isoprenoid *n*-alkane pristane was detected only at station 1, at a low concentration (approximately 10⁻⁴ mg/L). At other sampling stations, only phytane was detected, with concentrations an order of magnitude higher than pristane (0.001–0.002 mg/L, mean 0.001 ± 0.001 mg/L). Overall, the chromatogram profiles were characteristic of natural HC sources. The absence of pristane suggests a lack of recent oil pollution in the coastal waters.

To identify the most likely sources of HC inputs into the environment, molecular biogeochemical markers were employed. They enabled differentiation between biogenic and petroleum-derived HCs (Pr/Ph, CPI₂) and between autochthonous and allochthonous origins (Paq, TAR, LWH/HWH, C₁₇+C₁₉+C₂₁/Σ*n*-alkanes) (Table).

³ Federal Service for Hydrometeorology and Environmental Monitoring (ROSHYDROMET), 2024. *An Overview of the State and Pollution of the Environment in the Russian Federation for 2024*. Moscow, 222 p. (in Russian). [online] Available at: https://www.meteorf.gov.ru/product/infomaterials/90/41118/?sphrase_id=937357 [Accessed: 25 September 2025].

For the coastal waters, the aquatic macrophyte proxy (Paq) ranged from 0.29 to 0.46, indicating an influx of HCs from fresh and decomposed macrophytes [33]. This is consistent with the presence of significant amounts of algae washed ashore in the coastal zone during the sampling period. At most stations, the TAR and LWH/HWH markers indicated a predominant contribution of terrestrial vegetation to HC formation in the water. Similarly, low values of the ratio of autochthonous compounds ($n\text{-C}_{17}$, $n\text{-C}_{19}$, $n\text{-C}_{21}$) to the sum of n -alkanes further confirmed the predominantly allochthonous origin of HCs. This pattern is typical for inland and coastal waters. However, station 5 was an exception, with a high proportion of phytoplankton-derived C_{19} (31%), indicating that autochthonous production was the predominant source of HCs. At station 1, where both pristane and phytane were detected, the Pr/Ph ratio was 0.14, a value characteristic of fresh oil presence [20, 38]. Given the low concentrations of these compounds, their presence may also result from natural sources. A Pr/Ph ratio < 1 can also indicate a marine environment with anoxic conditions [39]. Consequently, this ratio could reflect either minor oil contamination or the influence of natural factors.

The predominance of autochthonous components is also supported by the C_{17}/Pr ratio of 2.9 [40]. The carbon preference index for the high molecular weight region (CPI_2) ranged from 1.16 to 3.23, with a mean of 1.75, indicating a predominance of biogenic, primarily allochthonous compounds [41, 42].

In the summer of 2024, the HC content in the coastal waters of the southwestern Sea of Azov (northeastern coast of Crimea) ranged from 0.048 to 0.172 mg/L, with a mean of 0.084 ± 0.030 mg/L. These values exceeded the MPC for fishery water bodies. Analysis of the n -alkane composition indicated no evidence of oil pollution in the waters. The primary sources of HC inputs during this period were both allochthonous and autochthonous production. Allochthonous compounds, primarily from terrestrial vegetation, were predominant, while autochthonous compounds were derived from the activity of micro- and macroalgae. Additionally, the bacterial community contributed to HC formation, with its active development driven by elevated water temperatures.

Suspended matter. The suspended matter content in the coastal waters ranged from 7 to 21 mg/L. For example, in Taganrog Bay, this parameter ranged from 3 to 20 mg/L [43]. In the open waters of the Sea of Azov, where river runoff, which contributes significant amounts of suspended matter, is less pronounced, concentrations ranged from 2.8 to 53.1 mg/L [44] and from 2 to 37 mg/L [45]. Thus, the suspended matter concentrations observed near the studied coast were consistent with typical values for the Sea of Azov.

The HC content in suspended matter ranged from 0.01 to 0.19 mg/L. For comparison, in the Kerch Strait, connecting the Black Sea and the Sea of Azov, HC concentrations ranged from 0.11 to 0.16 mg/L [46], which were interpreted as high by the authors. In the Sea of Azov, summer HC concentrations varied from < 0.02 to 0.20 mg/L, with weighted average values exceeding the MPC by 0.08–2.60 times [2]. Thus, the HC levels observed in this study were consistent with typical values for the Sea of Azov and exceeded the MPC in 80% of cases.

The n -alkane composition in suspended matter included compounds $n\text{-C}_{16}$ – $n\text{-C}_{33}$, with $n\text{-C}_{17}$ – $n\text{-C}_{31}$ present at all stations. Among the low molecular weight n -alkanes, both odd-numbered phytoplankton-derived $n\text{-C}_{17}$ and $n\text{-C}_{19}$ [47] and even-numbered $n\text{-C}_{18}$, $n\text{-C}_{20}$, $n\text{-C}_{22}$, potentially of bacterial origin [48], were detected

in high proportions (> 10%). Among the high molecular weight *n*-alkanes, *n*-C₂₄, associated with bacterial activity [49] and *n*-C₂₅, commonly linked to macrophytes [28], were predominant. In contrast, allochthonous *n*-C₂₉ and *n*-C₃₁, which are widespread in coastal areas [50], were of secondary importance. The limited presence of allochthonous *n*-alkanes was likely due to the composition of suspended matter, which in coastal areas is primarily represented by mineral particles and diatoms [51]. Elevated water temperatures (up to 29.5 °C) also promoted the active development of bacterioplankton [46]⁴, resulting in a high proportion of bacterially derived *n*-alkanes. The isoprenoid alkane pristane was detected only in isolated cases at low concentrations. Phytane was present at all stations, though its concentrations were also low (about 10⁻³ to 10⁻⁴ mg/L). The dominance of *n*-C₂₅ was likely attributed to the abundance of macrophytes in the coastal zone of the sea.

The values of CPI₂ index fluctuated in a wide range from 0.8 to 3.1, with a mean of 1.51 ± 0.68 (Table). Typically, these values for suspended matter are close to 1 [28]. However, at several stations, values were significantly higher, likely due to the elevated *n*-C₂₅ content attributed to the abundance of macrophytes in the coastal zone of the Sea of Azov.

The humidity index (Paq) ranged from 0.32 to 1.00, indicating a predominance of *n*-alkanes derived from aquatic macrophytes, which was particularly pronounced at stations 2, 3, 4, 6, 8, 10 [28]. The terrigenous ratio (TAR) varied from 0.9 to 7.02, with a mean of 1.94 ± 2.06. On average, this suggests a predominance of allochthonous organic matter; however, at stations 2, 4, 6, 8, 10, autochthonous compounds were strongly dominant. The ACL ranged from 26 to 30 and showed a strong negative correlation with the Paq index ($r = -0.95$), indicating that the influx of macrophyte-derived organic matter reduced the ACL. The LWH/HWH ratio varied from 0.17 to 0.78, which also indicates heterogeneity in HC sources across individual stations. When interpreting this marker, it is important to consider that such values arise mainly from the high content of *n*-C₂₄ and *n*-C₂₅, rather than from higher-molecular-weight odd homologues of allochthonous origin. As a result, it is not possible to conclude that allochthonous material predominates. At the same time, the proportion of phytoplankton-derived compounds at all stations was low, not exceeding 27%, with a mean of 17 ± 6%.

Natural compounds predominated in the *n*-alkane composition along the studied coast. Among these, compounds derived from the metabolic activity of aquatic vegetation played a significant role in the suspended matter.

The HC content in the suspended matter of coastal waters in the southwestern Sea of Azov during the summer of 2024 ranged from 0.01 to 0.19 mg/L, with a mean of 0.09 ± 0.05 mg/L. These values are characteristic of the Sea of Azov. Analysis of the *n*-alkane composition revealed no evidence of oil pollution in the suspended matter. The primary sources of HCs in the water during this period were the activities of bacterial communities and macroalgae. Autochthonous compounds were produced through the metabolic processes of both the bacterial communities and macroalgae.

⁴ Arctic Monitoring and Assessment Programme, 2007. *Arctic Oil and Gas 2007*. Oslo, Norway: AMAP, 40 p. [online] Available at: <https://www.amap.no/documents/download/1017/inline> [Accessed: 25 September 2025].

Coastal sediments. The coastal sediments of the studied water area were predominantly composed of fine sands. The average HC content in these sediments was 2.48 ± 0.96 mg/kg. These values, being below 10 mg/kg, are considered trace levels for sandy sediments [40]. The proportion of *n*-alkanes in the HC composition was elevated, suggesting a recent influx of these compounds [28].

The *n*-alkane profile ranged from *n*-C₁₇ to *n*-C₃₃, with *n*-C₃₂ and *n*-C₃₃ detected at all stations. The predominant *n*-alkane was the allochthonous *n*-C₂₉ [52] (Fig. 3). Plant-derived *n*-C₂₅ and *n*-C₃₁ [53], as well as bacterial *n*-C₂₄, *n*-C₂₈, *n*-C₃₀ [54, 55]⁵, were present in high proportions (>10 %) at certain stations. In some samples, elevated levels of phytoplankton-derived *n*-C₁₇ and *n*-C₁₉ [56] were observed. Overall, odd-numbered *n*-alkanes in the high molecular weight range predominated. However, the slightly elevated presence of even-numbered homologues (*n*-C₂₄, *n*-C₂₆, *n*-C₂₈, *n*-C₃₀) may reflect the active proliferation of bacterial communities in coastal sediments. These even-numbered homologues are likely formed through anaerobic transformation of specific compounds and microbial processes [55, 57].

This distribution is typical for coastal waters during periods of significant water warming, which promotes the proliferation of bacterioplankton communities [46]. Consequently, this leads to the active degradation of autochthonous compounds. The isoprenoid alkane pristane, typically indicative of oil pollution [28], was absent. Phytane, however, was detected at all stations in concentrations of 0.020–0.061 mg/kg. No chromatographically unresolved complex mixture was observed.

To identify the primary sources of organic matter in coastal sediments, diagnostic ratios, commonly referred to as markers, were employed (Table). The CPI₂ index averaged 1.24 ± 0.32 . CPI₂ values close to 1 in bottom sediments are typically interpreted as indicative of oil pollution [41, 42], suggesting potential contamination of the water body that was not detected in the water column during the study period but may have accumulated previously. However, sandy bottom sediments are not conducive to the accumulation of such substances. The absence of pristane and a chromatographically unresolved complex mixture (UCM) further supports the lack of oil product accumulation in the sediments. CPI marker values close to 1 may reflect a low contribution of terrestrial plant-derived material [58], attributed to the elevated presence of compounds (*n*-C₂₄, *n*-C₂₆, *n*-C₂₈, *n*-C₃₀). As noted earlier, these compounds are likely associated with the proliferation of bacterial communities in coastal sediments.

Consequently, organic matter from various ecosystem components is actively incorporated and transformed within coastal sediments. The humidity index (Paq) ranged from 0.30 to 0.59 (mean: 0.44 ± 0.08), indicating a significant contribution of macrophytes to organic matter formation [33]. The terrigenous index (TAR) exhibited a wide range, from 0.70 (indicative of predominant autochthonous compounds) to 3.76 (indicative of predominant allochthonous compounds), with an average of 2.17 ± 0.97 . This reflects the quantitative dominance of allochthonous *n*-alkanes at most stations, a pattern typical for coastal waters [28].

⁵ Poshibaeva, A.R., 2015. [*Bacterial Biomass as a Source of Petroleum Hydrocarbons*]. Thesis Cand. Chem. Sci. Moscow, 24 p. (in Russian).

The average hydrocarbon chain length (ACL) was stable, with a mean of 28. The ratio of low molecular weight and high molecular weight *n*-alkanes ranged from 0.22 to 0.66 (mean: 0.35 ± 0.14), indicating a significant contribution of terrestrial vegetation to organic matter formation [59]. This ratio varied from 0.22 to 0.60, reflecting the predominance of autochthonous *n*-alkanes at station 2, allochthonous *n*-alkanes at stations 3, 4, 5, 7, 8, 9, and an approximately equal balance at stations 1, 6, 10. The proportion of autochthonous *n*-alkanes did not exceed 31% (station 2), with a mean of 0.16 ± 0.07 . Thus, the coastal sediments of the studied area contained low levels of HCs, primarily derived from natural processes in the water column and adjacent terrestrial areas. Despite the dominance of terrigenous *n*-alkanes, aquatic vegetation contributed significantly to the organic matter pool. No significant burial of organic matter was observed in the coastal sediments.

The HC content in the coastal sediments of the of the southwestern Sea of Azov (Crimean coast) during the summer of 2024 ranged from 1.00 to 3.80 mg/kg, with a mean of 2.48 ± 0.96 mg/kg. These low values correspond to trace concentrations, likely attributable to the grain size of the coastal sediments, which is not conducive to the accumulation of significant HC quantities. Analysis of the *n*-alkane composition showed no evidence of oil pollution in the sediments. The primary sources of HCs in the coastal sediments during this period were allochthonous and autochthonous compounds, the latter formed through the metabolic activity of macroalgae.

Conclusion

During the summer of 2024, water and suspended matter in the coastal waters of the southwestern Sea of Azov (Crimean coast) exhibited elevated HC concentrations. In contrast, HC concentrations in coastal sediments were at trace levels, likely due to the grain size of the sandy sediments, which is not conducive to the accumulation of significant HC quantities. The *n*-alkane composition suggests that their presence was driven by natural processes. Despite exceeding the MPC for total hydrocarbon content in water and suspended solids, analysis of the *n*-alkane composition indicates that this contamination is predominantly biogenic rather than petroleum-based.

This suggests a low level of oil pollution in the studied coastal waters, consistent with the environmental conditions of the Sea of Azov. Macrophytes were a key contributor to HC formation across all studied components. During the sampling period, significant amounts of stranded aquatic vegetation were observed in the coastal zone, serving as a major source of HCs entering the coastal ecosystem. The microbial community actively consumes and transforms readily available autochthonous compounds, particularly those of phytoplankton origin, leading to a reduced proportion of these compounds in the total hydrocarbon pool. Coastal sediments predominantly accumulated allochthonous compounds.

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