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OIL POLLUTION IN THE KERCH STRAIT AFTER THE "VOLGONEFT" TANKER ACCIDENT IN DECEMBER 2024

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In December 2024, up to 4,000 tons of petroleum products entered the marine environment of the Kerch Strait as a result of an accident involving two tankers carrying fuel oil. Considering intensive shipping in the region and chronic hydrocarbon (HC) loading there, the task of determining the extent of pollution and assessing the state of waters has become urgent. The aim of this study was to evaluate the qualitative and quantitative composition of HC in the Kerch Strait waters after the accident. Sampling was carried out in spring 2025 during the 134th cruise of the RV "Professor Vodyanitsky." HC and n-alkane concentrations were determined by gas chromatography. Physicochemical parameters of waters were also assessed (pH, Eh, dissolved oxygen, temperature, and salinity). HC content ranged 0.01 to 0.27 mg·L⁻¹, with the maximum permissible concentration (0.05 mg·L⁻¹) exceeded at 6 stations out of 13. The highest values were recorded in the pre-strait area of the Black Sea. At stations with elevated HC levels, signs of biodegraded oil pollution were recorded. Physicochemical parameters of waters remained within normal limits. The distribution of n-alkanes and HC composition provide evidence for actively occurring self-purification processes.

Keywords: pollution, water, hydrocarbons, Kerch Strait, Black Sea

Oil products remain one of the key pollutants of marine ecosystems. Tanker accidents significantly contribute to their release into the marine environment [Avarii i posledstviya, 2025]. The first large-scale accident occurred in March 1957: over 120 thousand tons of oil entered waters off the coast of Great Britain as a result of the "Torrey Canyon" oil spill. The Kerch Strait is also considered to be an impact area due to intensive shipping, activity of Kavkaz and Krym ports, and the operation of the roadstead transshipment complex in the southern strait [Matishov et al., 2013]. On 11 November, 2007, during a storm, the oil tanker "Volgoneft-139" sank there with 5 thousand tons of fuel oil, and about 1.3 thousand tons entered the water area [Tikhonova et al., 2021]. The second accident occurred in 2017: the bulk carrier "Geroi Arsenala" split in two with 19 tons of diesel fuel and 1.5 tons of motor oil on board [Krushenie sukhogruza, 2020]. On 15 December, 2024, there was another shipwreck in the strait: two tankers, "Volgoneft-212" and "Volgoneft-239," both with a cargo of fuel oil, were caught in a storm. One tanker split in two, and another ran aground. This resulted in a spill of 2.4 to 4 thousand tons of fuel oil out of a total volume of 9.2 thousand tons [Yunusov, 2025].

Due to active water circulation from both the Sea of Azov and Black Sea, pollutants are relatively quickly carried beyond the strait. Currents from the Sea of Azov prevail over the Black Sea ones. River runoff is important in the formation of surge phenomena and water level fluctuations at the ends of the strait and affects the water balance of both seas [Eremeev et al., 2003; The Oil Spill Accident, 2008]. Studies provide evidence that the pre-strait area of the Black Sea is subject to the greatest pollution, while currents from the Sea of Azov mainly transport organic matter of allochthonous and autochthonous origin [Nemirovskaya et al., 2022a]. According to previously obtained data, on 13 November, 2007, the concentration of oil products in the surface water layer at the tanker wreck site was 2.5 mg·L⁻¹, *i. e.*, it reached 50 MPC (maximum permissible concentration) [Matishov et al., 2013]. It was 8 times higher than the mean content of oil products in the strait waters in 1985–1988 [Klenkin et al., 2007]. In the first months after the accident, values of 3–14 thousand MPC of oil products were recorded in water, and clots of fresh fuel oil were found in bottom sediments. By May 2008, the situation with oil pollution of the strait waters and bottom had stabilized; by August 2008, the strait was completely cleared of the consequences of the accidental fuel oil spill [Fashchuk et al., 2010].

Thus, given the high technogenic load, the issue of assessing the state of water masses of the Kerch Strait and adjacent areas of the Black Sea and Sea of Azov is of particular relevance. The aim of this work was to determine the qualitative and quantitative composition of hydrocarbons in the Kerch Strait waters after the tanker accident in December 2024.

MATERIAL AND METHODS

Water from the Kerch Strait surface layer was sampled in glass containers with a bathometer on 15–16 March, 2025 (the 134th cruise of the RV "Professor Vodyanitsky") along a grid of stations (Fig. 1). The work was carried out at a wind speed of 2.4–9.4 m·s⁻¹, wave height of 0.3–1.2 m, and air temperature of +10.1...+11.9 °C. Physical and chemical parameters of water (temperature, salinity, pH, Eh, and dissolved oxygen content) were measured with a verified portable logging multiparameter meter HI-98194 (Hanna Instruments, Germany). This tool provides measurements in the following ranges:

- temperature, 0.0 to +50.0 °C (resolution 0.1 °C, and error ± 0.1 °C);
- salinity, 0.00 to 70.00 psu (resolution 0.01 psu, and error ±0.01 psu);
- pH, 0.0 to 14.0 (resolution 0.01, and error ± 0.02);
- Eh (redox potential), -2,000 to +2,000 mV (resolution 0.1 mV, and error ± 1.0 mV);
- dissolved oxygen, 0.00 to 50.00 mg·L $^{-1}$ (resolution 0.01 mg·L $^{-1}$, and error ± 0.10 mg·L $^{-1}$).

Extracts with hexane were prepared according to the state standard GOST R 52406-2005 directly onboard the research vessel (IBSS core facility RV "Professor Vodyanitsky"). The content of hydrocarbons (hereinafter HC) and n-alkanes in water was determined by gas chromatography on a Crystal 5000.2 chromatograph ("Chromatec," Russia) with a flame ionization detector at the IBSS core facility "Spectrometry and Chromatography." The method ensures obtaining results with an accuracy not exceeding the following values (with a confidence probability *P* of 0.95): at an oil product concentration 0.02 to 0.5 mg·dm⁻³ inclusive, the relative standard deviation of reproducibility is 25%, and at a concentration over 0.5 mg·dm⁻³, 13%. To process the results, Chromatec Analytic 3.0 software was used, and absolute calibration and percentage normalization were applied. HC origin was determined based on the chromatogram character, n-alkane distribution, and biogeochemical markers. The difference in means of two samples was assessed based on box plots (MS Office Excel) with outliers showing the distribution of data by quartiles; the median and outliers were highlighted.

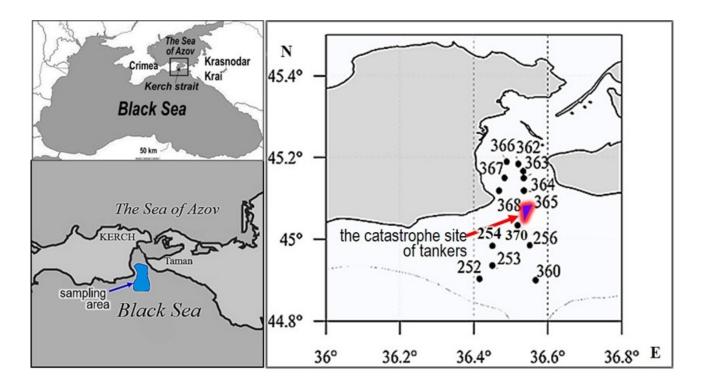


Fig. 1. Schematic map of water sampling from the surface layer in the Kerch Strait water area (the 134th cruise of the RV "Professor Vodyanitsky," March 2025)

RESULTS AND DISCUSSION

The physical and chemical parameters of water (Table 1) are sensitive indicators of pollution, including fuel oil one, and allow for the rapid detection of deviations from the natural state of seawater in the ecosystem. The values of pH in the surface layer at the stations surveyed varied 8.2 to 8.4 indicating a slight alkaline reaction of the aquatic environment. No dependence of water pH on HC concentration in it was revealed. The values of Eh varied +85 to +134 mV; this characterizes the aquatic environment as an oxidizing one. The lowest values of Eh were recorded in water of shallow stations (e. g., +85 mV at sta. 366); higher values were registered at deeper stations (+134 mV at sta. 256). Oxygen saturation ranged 101 to 105%, and the concentration of dissolved oxygen ranged 9.6 to 10.9 mg·L⁻¹. The highest values (105% and 10.9 mg·L⁻¹) were revealed at sta. 366 and 367, while the minimum one, at sta. 254 (101%). Water masses of the surveyed area were characterized by saturation and slight supersaturation with oxygen. At all the stations, the content of dissolved oxygen was above the standard value of 6 mg·L⁻¹. According to the Order of the State Fisheries Committee of Russia No. 96 of 28.04.1999, this may indicate optimal aeration. In case of fuel oil pollution, a sharp decrease in these parameters is usually observed due to oxygen consumption for HC oxidation and toxic effects on phytoplankton and microfauna. In this case, the recorded levels of dissolved oxygen may indirectly evidence the lack of large-scale fuel oil pollution in water. In the surface layers, salinity varied 18.52 to 18.74 psu. These values are typical for the water area surveyed. Water temperature in the surface layer varied +8.5 to +10.0 °C. In terms of organoleptic properties, inter alia the absence of a film on the surface and the lack of changes in color, odor, and turbidity, no traces of fuel oil were registered in the surface water layer.

Station number	t, °C	рН	Eh, mV	DO, %	DO, mg·L ⁻¹	S, psu
366	+8.81	8.3	+85	104.5	10.9	18.54
362	+9.47	8.4	+88	103.9	10.6	18.67
363	+9.70	8.2	+96	102.0	9.6	18.67
364	+9.73	8.2	+102	104.4	10.5	18.73
365	+9.88	8.2	+88	103.6	10.5	18.73
368	+9.19	8.2	+103	103.5	10.6	18.69
367	+8.71	8.2	+113	105.0	10.9	18.52
252	+9.57	8.2	+100	104.8	10.7	18.74
253	+9.32	8.2	+117	102.7	10.5	18.48
254	+10.63	8.2	+132	100.5	10.3	18.60
370	+9.72	8.2	+120	101.6	10.2	18.49
256	+9.94	8.2	+134	101.2	10.2	18.65
360	+10.00	8.2	+130	101.4	10.3	18.65

Table 1. Physical and chemical parameters of the surface water in the Kerch Strait, March 2025

Note: DO, dissolved oxygen; S, salinity.

HC concentration in the water area surveyed varied within the range of 0.01–0.27 mg·L⁻¹ (Fig. 2A). At 6 stations out of 13, HC content in water exceeded the MPC (0.05 mg·L⁻¹) or was at its level. Stations with a slight excess of sanitary standards (1 to 1.6 MPC) were grouped near the western coast of the strait (Kerch area). At stations located in the eastern strait, the values were within the MPC. A significant excess was revealed at 2 stations in the pre-strait area of the Black Sea, southward of the tanker wreck site (Fig. 2A).

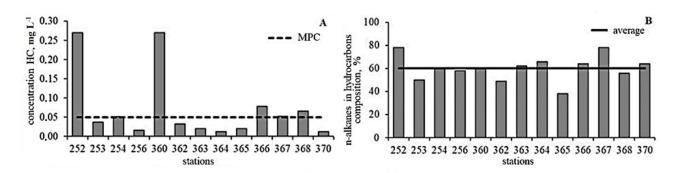


Fig. 2. Hydrocarbon concentration (A) and n-alkanes/hydrocarbons ratio (B) in the surface layer of the Kerch Strait waters (the 134th cruise of the RV "Professor Vodyanitsky," March 2025)

In the surface water layer, the n-alkanes/hydrocarbons ratio varied 38 to 78% averaging 60% (Fig. 2B). These values are elevated and provide evidence for an intensive flow of n-alkanes into the strait water area.

Statistical analysis (Fig. 3a–c) showed the presence of outliers among the obtained values of HC concentration, unresolved complex mixture (hereinafter UCM), and n-alkanes/hydrocarbons ratio. Thus, we revealed stations with indicators significantly exceeding HC values characteristic of the water area surveyed.

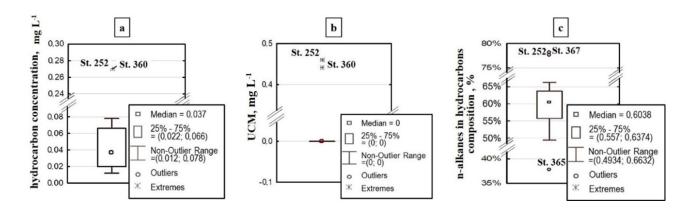


Fig. 3. Box plots showing the presence of statistical outliers in the data: a, hydrocarbon concentration; b, unresolved complex mixture (UCM); c, n-alkanes/hydrocarbons ratio

As noted above, sta. 252 and 360 were characterized by elevated HC values. At these stations, HC concentration significantly exceeded the MPC: by 5.4 times. In terms of n-alkanes/hydrocarbons ratio, elevated values were recorded at sta. 252 and 367, and reduced ones, at sta. 365 (Fig. 3c). HC content noted at other stations was typical for this area [Nemirovskaya et al., 2022a]. Furthermore, at sta. 252 and 360, UCM was determined: 0.46 and 0.44 mg·L⁻¹, respectively. The presence of UCM in water indicates oil pollution [Wang et al., 2015]. In this area, similar values were observed before (in 2019–2021): oil pollution reached 0.25 mg·L⁻¹ [Nemirovskaya et al., 2022b], while the presence of UCM was not recorded at that time. There was no UCM at other sites surveyed.

UCM accumulation is also possible as a result of biodegradation of saturated oil components [Hu et al., 2018]. The "hump" on chromatograms is shifted to the high-molecular weight region (Fig. 4), which also provides evidence for the oil nature of UCM [Nemirovskaya, 2013] and, consequently, the presence of oil pollution in water.

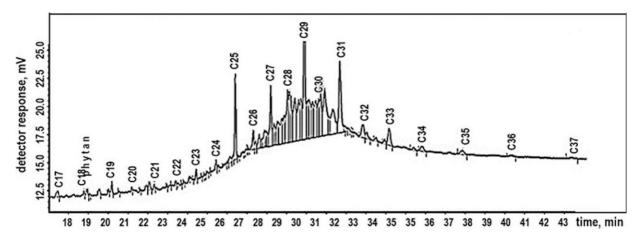


Fig. 4. Example of a chromatogram showing the presence of an unresolved complex mixture (UCM) in the surface layer of the Kerch Strait waters (sta. 360) (the 134th cruise of the RV "Professor Vodyanitsky," March 2025)

In water studied, n-alkanes were identified within the range of C_{17} – C_{37} , with C_{36} and C_{37} recorded at sta. 252 and 360. At other sites, n-alkanes were found within C_{17} – C_{35} ; this range is typical for coastal waters.

Based on the data obtained, a significant difference in the content of oil products at sta. 252 and 360 was established compared to that at other stations surveyed. Due to this fact, the composition of n-alkanes was analyzed for selected groups of stations separately. The stations were divided into two groups: G1 (sta. 252 and 360) and G2 (stations 363, 365, 367, 368, 353, 352, 370, and 356). At the stations with low and moderate HC content (G2), the distribution of n-alkanes was of a bimodal character (Fig. 5a). For G2, the peaks in the low-molecular weight region fell on autochthonous C_{17} (10%) and C_{19} (8%) [Nemirovskaya, 2013]. Allochthonous n-alkanes, C_{27} (8%), C_{29} (14%), and C_{31} (13%), dominated over autochthonous ones and formed the second maximum. The revealed pattern of the distribution of n-alkanes corresponds to that in coastal waters, where natural sources of HC prevail. However, given the sampling area where chronic oil pollution was recorded (a shipping artery) [Nemirovskaya et al., 2022b], it can be assumed that in this case, traces of oil products that underwent biotransformation were also present. Thus, active self-purification processes are taking place in the studied components in waters of the Kerch Strait ecosystem.

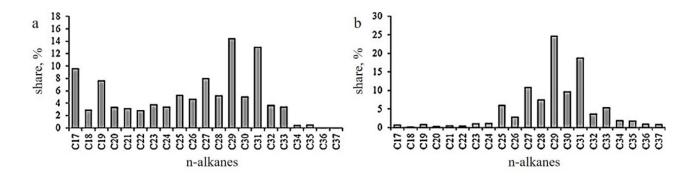


Fig. 5. Distribution of n-alkanes in water at stations with low and moderate hydrocarbon content (a) and high hydrocarbon content (b) in the Kerch Strait (the 134th cruise of the RV "Professor Vodyanitsky," March 2025)

At stations with high HC concentration (G1), the distribution of n-alkanes differed significantly from that for G2. The content of autochthonous C_{17} and C_{19} was minor (lower than 1%). The distribution was unimodal, with maximums of C_{27} , C_{29} , and C_{31} (Fig. 5b) and with a fairly high proportion of C_{28} and C_{30} . The distribution pattern is similar to that recorded in biodegraded oil aggregates [Nemirovskaya, 2013]. The distribution of n-alkanes during biodegradation was characterized by the absence of peaks in the low-molecular weight region, typical of oil pollution, and the predominance of peaks of C_{26} – C_{29} , which may indicate a high degree of HC weathering. The predominance of odd n-alkanes, typical of allochthonous matter, seems to be related to the active decomposition of even high-molecular weight homologues [Nemirovskaya, 2013]. As established before, in some cases, after oil spills, allochthonous homologues predominated in the composition of n-alkanes [Wang, Fingas, 2003].

To clarify HC origin, additional parameters were also considered, in particular, the CPI₂ marker (carbon preference index). It is the key one for revealing the presence of oil products and is described by the ratio of the number of odd homologues in the high-molecular weight region to even ones [Peters, Moldowan, 1993]. In the presence of fresh oil pollution, the marker values are close to 1. At stations of G1, its values were 2.3 and 2.8, which corresponds to those for a biogenic

substance [Ficken et al., 2000]. If we assume the influx of fuel oil, we can conclude as follows: its relatively light components are likely to have degraded after two months; a trace of its presence could be the "hump" on the chromatogram (see Fig. 4).

UCM/n-alkanes ratio for stations of G1 was 2.1 and 2.75 (> 2), and this is typical for degraded oil products [Shirneshan et al., 2016]. As already noted, the "hump" is shifted to the high-molecular weight region and is located under the dominant peaks; it is typical for oil pollution.

Based on the nature of the chromatograms and the values of individual markers of HC origin at stations of G1, it can be assumed that elevated HC concentrations in water masses of these sites are related to the presence of biodegraded oil components.

Thus, traces of oil pollution were recorded in the Black Sea water area adjacent to the Kerch Strait. Importantly, its components were heavily biodegraded, which may indicate active self-purification processes.

Conclusions. The values of hydrocarbon (HC) concentration in the surveyed water area, the Kerch Strait, fluctuated within the range of 0.01 to 0.27 mg·L⁻¹. At 6 stations out of 13 analyzed, HC content in the surface water layer exceeded the MPC (0.05 mg·L⁻¹) or was at its level. Stations with a slight excess of sanitary standards (1–1.6 MPC) were grouped near the western coast of the strait (Kerch area). At the stations situated in the eastern Kerch Strait, the values were within the MPC. A significant excess of the MPC for the HC content was registered at two stations in the pre-strait area of the Black Sea.

At the stations with low and moderate HC pollution, the distribution pattern of n-alkanes corresponds to that in coastal waters, where natural sources of HC prevail. However, given the intensity of shipping in the sampling area, where chronic oil pollution was recorded, it can be assumed as follows: in this case, there were traces of oil products that underwent biotransformation.

At the stations with an increased HC content – in the Black Sea water area adjacent to the Kerch Strait – traces of oil pollution were revealed based on the presence of an unresolved complex mixture. The origin of this pollution remains unclear, as it is impossible to clarify the composition of the fuel oil by the methods used. Strong biodegradation of oil components was recorded, which may evidence active self-purification processes in this water area.

This work was carried out within the framework of IBSS state research assignment "Assessment of oil pollution of coastal marine waters of the Crimean Peninsula resulting from the Kerch Strait disaster in December 2024 and development of recommendations for improving coastal waters by stimulating natural self-purification processes" (No. 125050605819-8).

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НЕФТЯНОЕ ЗАГРЯЗНЕНИЕ КЕРЧЕНСКОГО ПРОЛИВА ПОСЛЕ АВАРИИ ТАНКЕРОВ «ВОЛГОНЕФТЬ» В ДЕКАБРЕ 2024 Г.

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В декабре 2024 г. в результате аварии двух танкеров, перевозивших мазут, в Керченском проливе в морскую среду поступило до 4 тыс. т нефтепродуктов. С учётом судоходного характера региона и хронической нагрузки углеводородами (УВ) актуальными задачами стали выявление масштабов загрязнения и анализ состояния воды. Цель работы — определить качественный и количественный состав УВ в воде Керченского пролива после аварии. Пробоотбор проведён весной 2025 г. в рамках 134-го рейса НИС «Профессор Водяницкий». Концентрации УВ и н-алканов определены методом газовой хроматографии. Оценены физико-химические параметры воды (рН, Еh, содержание растворённого кислорода, температура и солёность). Значения концентрации УВ колебались от 0,01 до 0,27 мг·л⁻¹, при этом на 6 из 13 станций была превышена ПДК (0,05 мг·л⁻¹). Максимальные величины зафиксированы в акватории Чёрного моря, прилегающей к проливу. На станциях с высокими уровнями содержания УВ в воде обнаружены признаки биодеградированного нефтяного загрязнения. Физико-химические показатели воды оставались в пределах нормы. Распределение н-алканов и состав УВ указывают на активно происходящие процессы самоочищения.

Ключевые слова: загрязнение, вода, углеводороды, Керченский пролив, Чёрное море