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The First Data on the Hydrocarbon Composition of Water, Bottom Sediments of the North Crimean Canal and Soils Adjacent to Agricultural Land

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Abstract
The paper presets the results of quantitative and qualitative indicators of the hydrocarbon composition of water, bottom sediments of the North Crimean Canal and soil from adjacent agricultural lands during filling the canal with water after an eight-year break. The material for the study was water, bottom sediments and soil samples taken in the spring of 2022. When planning sampling, the ways of hydrocarbon entry into the canal were taken into account: directly with the Dnieper water, with atmospheric precipitation, and with washout from nearby territories. The qualitative and quantitative composition of hydrocarbons in water, bottom sediments, and soil was determined by gas chromatography in the Scientific and Educational Center for Collective Use «Spectrometry and Chromatography» of IBSS. To identify probable sources of the studied class of substances, biogeochemical markers were used. The obtained concentrations of aliphatic hydrocarbons in water (0.032 ± 0.006 mg·L^{-1}) of the studied section of the North Crimean Canal did not exceed the maximum permissible values (0.05 mg·L^{-1}) and were close to the values typical for unpolluted water areas. The hydrocarbon content in the bottom sediments of the canal (30 mg·kg^{-1} air-dry bottom sediments) and in adjacent fields (18.1 mg·kg^{-1} air-dry bottom sediments) also indicated the absence of high pollution levels. In the canal water, n-alkanes were identified in the C_{17}–C_{32} range; in the bottom sediments and soils of adjacent territories, the n-alkane range was C_{17}–C_{33}. The composition of n-alkanes and the values of biogeochemical markers in water indicated a mixed nature of hydrocarbons with a predominance of compounds of allochthonous origin washed away from the drainage basin of the lower Dnieper. The composition of n-alkanes and the markers calculated for the bottom sediments and soils were typical for the soils of the steppe regions and were significantly similar to them.

Keywords: hydrocarbons, water, bottom sediments, soil, North Crimean canal

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Первые данные об углеводородном составе воды, донных отложений Северо-Крымского канала и почв прилегающих сельскохозяйственных угодий

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Аннотация
Проведено исследование количественных и качественных показателей углеводородного состава воды, донных отложений Северо-Крымского канала и почвы прилегающих земель сельскохозяйственного назначения в период наполнения канала водой после восьмилетнего перерыва. Материалом для исследования послужили пробы воды, донных отложений и почвы, отобранные весной 2022 г. При планировании пробоотбора учитывались пути поступления углеводородов в канал: непосредственно с днепровской водой, выпадение с атмосферными осадками и поступление со смывом с близлежащих территорий. Качественный и количественный состав углеводородов в воде, донных отложениях и почве определяли методом газовой хроматографии на базе НОЦКП «Спектрометрия и хроматография» ФИЦ ИнБЮМ. Для идентификации вероятных источников исследуемого класса веществ использовали биогеохимические маркеры происхождения углеводородов. Полученные концентрации алифатических углеводородов в воде (0.032 ± 0.006 мг·л$^{-1}$) исследуемого участка Северо-Крымского канала не превышают предельно допустимые значения (0.05 мг·л$^{-1}$) и близки к значениям, характерным для незагрязненных акваторий. Содержание углеводородов в донных отложениях канала (30 мг·кг$^{-1}$ воздушно-сухого донного осадка) и на прилегающих полях (18.1 мг·кг$^{-1}$ воздушно-сухого донного осадка) также подтверждало отсутствие высоких уровней загрязнения. В воде канала идентифицированы н-алканы в диапазоне C_{17}–C_{32}, в донных отложениях и грунтах прилегающих территорий диапазон н-алканов был C_{17}–C_{33}. Состав н-алканов и значения биогеохимических маркеров в воде указывают на смешанную природу углеводородов с преобладанием соединений аллохтонного происхождения, смываемых с территории водосборного бассейна нижнего течения Днепра. Состав н-алканов и маркеры, рассчитанные для донных отложений и почв, были характерными для грунтов степных районов и имели существенное сходство с ними.

Ключевые слова: углеводороды, вода, донные отложения, почва, Северо-Крымский канал

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Introduction

The North Crimean Canal (NCC) and its branches, canals of melioration systems, water supply facilities of drinking water intakes of surface and groundwater sources, and water supply networks are used as water supply routes in the territory of the Republic of Crimea [1)].

The NCC was designed and built not only for land melioration, but also for public water supply. Now, it is an extensive network of main and inter-farm canals, reservoirs, hundreds of pumping stations and hydraulic engineering structures. The canal leaves the Kakhovka water reservoir and reaches Kerch through the Perekop Isthmus. Its length from Novaya Kakhovka (Kherson Region) to Kerch (Republic of Crimea) is 405 km, the length of the main canal and its branches exceeds 10,000 km [1)].

The canal width varies from 15 m to 150 m, with a depth of up to 7 m. The maximum discharge capacity is 300 $m^3 \cdot s^{-1}$, and on the border with the Republic of Crimea it is 1) 225 $m^3 \cdot s^{-1}$.

During its full operation, the NCC covered up to 85 % of the peninsula's total water consumption, of which almost 80 % was for agricultural production. Most of the irrigation water (about 60 %) was used for rice cultivation [1].

In the days of successful development of the melioration water management complex, the irrigated area reached almost 400,000 ha. In 2014, the supply of Dnieper water via the NCC was discontinued. From 2015 to 2022, the NCC route was used to supply water to fill off-stream reservoirs from Nezhin, Prostornoye and Novogrigoryevsk groundwater intakes, as well as from the Belogorsk and Taigan reservoirs supplied through the Biyuk-Karasu River bed to meet the drinking and domestic needs of the Feodosiya–Sudak and Kerch regions and some settlements of the Leninsky district. Since 2022, the supply of Dnieper water to the NCC has been resumed, which undoubtedly has a positive effect on the water supply of the peninsula. At the same time, the poor technical condition of the NCC led and still leads to significant water losses during transportation, to waterlogging of lands, and to salinization of soils in the nearby areas [1)] [1].

When running the Dnieper water through the canal, it is important to control not only the quality of the water in the canal itself but also that of the soil after irrigation. Hydrocarbons (HCs) in soils are a wide range of compounds, the study of which has recently received much attention due to their global distribution and impact on the condition of soils themselves, as well as the environment

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[1)] Tkachuk, V.G., 1971. [*Hydrogeology of the USSR. Volume 8. Crimea*]. Moscow: Nedra, 364 p. (in Russian).

as a whole, including humans. Besides, HCs can serve as indicators of modern geochemical processes in landscapes, therefore it is essential to study the qualitative and quantitative composition of HCs in environments to increase the efficiency of ecological forecasts and ecological monitoring [2].

A group of authors performed a study [2] of soil samples taken from areas with different degrees of anthropogenic load and various soil formation processes and showed that the data on n-alkanes in soils have a certain indicative potential for identifying natural and anthropogenic processes affecting the hydrocarbon state of soils. Also, for aquatic ecosystems, n-alkanes are widely used as an indicator of biogeochemical processes of organic matter transformation [3]. Biogeochemical processes involving HCs occurring in such water bodies, particularly after a break in their functioning, are poorly studied.

Hence, a need arose to obtain information on the safety and quality of the Dnieper water that came through the canal bed and the possibility of using it for irrigated agriculture. Immediately after the filling of the NCC with water, studies were conducted to provide information on the current state of the environment and to become a basis for further observations.

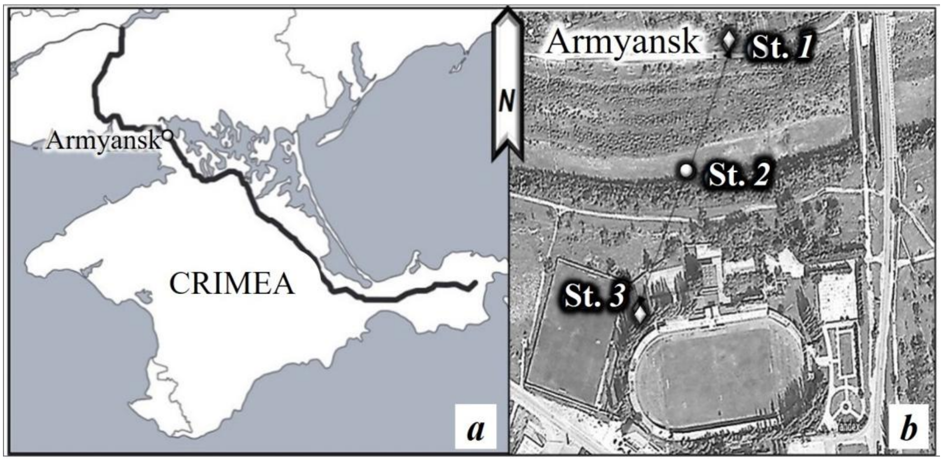
The paper aims at studying quantitative and qualitative indicators of the HC composition of water, bottom sediments of the canal, and soil of the adjacent agricultural lands during the period of canal filling with water after an eight-year break.

Study material and methods

Water, sediment, and soil samples taken in spring 2022 were used as the material for the study. While planning sampling, we considered how HCs had entered the canal: directly from the Dnieper, with atmospheric precipitation, and with washout from nearby territories.

Therefore, water sampling was conducted along the course of the canal water flow from the transect related to a large industrial city of Crimea – Armyansk (Fig. 1). The transect included three water sampling stations, and we took into account the flush from both banks and the intense water flow in the canal: Station *1* – the left bank, Station *2* – the middle part, and Station *3* – the right bank. The bottom sediments were taken by a hand sampler directly in the canal, the soil was taken from the adjacent area. The material was transported on the day of sampling in special containers.

According to guideline FR.1.31.2010.08907 "Methodology for measurement of n-paraffin hydrocarbons mass fraction in samples of soil and bottom sediments of fresh and marine water bodies by gas-liquid chromatography", soil and bottom sediments were dried in the laboratory in natural conditions, then pounded manually in a porcelain mortar and sieved through a 0.25 mm sieve. The dried and sieved sample in an amount of 1–2 g was extracted in 150 mL n-hexane in a Soxhlet extractor for one hour. The obtained extract was purified on a glass column filled with aluminium oxide to remove the polar compounds. The obtained extract was concentrated to 1 mL.



F i g . 1 . Map of the North-Crimean Canal (*a*) and sampling stations for water, bottom sediments and adjacent soil, spring 2022 (*b*)

HCs were extracted with hexane under laboratory conditions from 1 L of water. An aliquot of the concentrated extract (1 μL) for all test objects was injected with a microsyringe into the evaporator of a Crystal 5000.2 gas chromatograph with a flame ionization detector heated to 250 °C. HC separation was performed on a TR-1MS capillary column 30 m long, 0.32 mm in diameter, and with the stationary phase film thickness of 0.25 μm (Termo Scientific). The column temperature was programmed from 70 to 280 °C (rate of temperature rise: 8 $°C·min^{-1}$). The carrier gas (nitrogen) flow in the column was 2.5 $mL·min^{-1}$ without flow splitting. The detector temperature was 320 °C.

Quantitation of HC content was performed by absolute calibration of the flame ionization detector with a mixture of HCs (ASTMD2887 Reference Gas Oil standard (SUPELCO, USA)), that of n-alkanes – by a reference sample of paraffin HCs in hexane with mass concentration of each component 200 $μg·mL^{-1}$, pristane + phytane – 100 $μg·mL^{-1}$ in hexane (SUPELCO, USA).

Determination of HCs and n-alkanes was carried out at the Scientific and Educational Center for Collective Use «Spectrometry and Chromatography» of IBSS. To process results during HC concentration determination, Chromatec Analytical 3.0 software (absolute calibration and percentage normalization method) was used.

HC markers were used to identify probable HC sources. In the course of work, a number of ratios were used allowing concluding about biogenic or petrogenic origin of n-alkanes and to some extent to differentiate their autochthonous or allochthonous origin. These ratios were calculated for each sample. The diagnostic indices used to determine the sources of organic compounds are shown in Table 1.

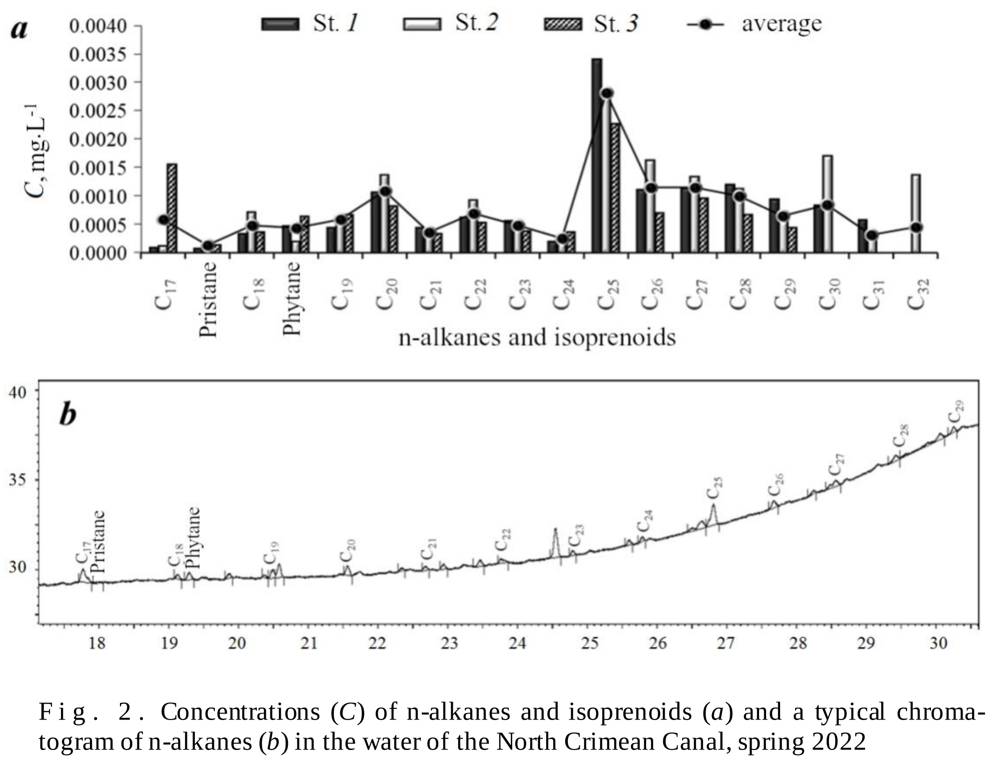
T a b l e 1 . Diagnostic molecular ratios and their value interpretation

Calculation formula	Index value	Entry source	Work
LWH/HWH = $\sum(C_{11} - C_{21})/\sum(C_{22} - C_{35})$	> 1	Oil	[4]
	< 1	Terrigenous, higher plant	
C_{31}/C_{19}	< 0.4	Autochthonous matter	[5]
	>0.4	Allochthonous matter	
$CPI_1 = (^1/_2)\{(C_{15} + C_{17} + C_{19} + C_{21})/(C_{14} + C_{16} + C_{18} + C_{20}) + (C_{15} + C_{17} + C_{19} + C_{21})/(C_{16} + C_{18} + C_{20} + C_{22})\}$	< 1	Intense microbial transformation of hydrocarbons	[6–8]
$CPI_2 = (^1/_2)\{(C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35})\cdot(C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33} + C_{35})\cdot(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})\}$	near 1	Oil or biodegradation	
	< 1	Biogenic	
	5–10	Higher ground plant	
$TMD = (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{15} + C_{17} + C_{19} + C_{21} + C_{23})$	0.5–1	Mixed	[9]
	> 1	Ground vegetation	
C_{31}/C_{29}	< 0.4	Tree vegetation predominance	[10–12]
	> 0.4	Herbaceous vegetation predominance	
Pr/*Ph*	> 1	Biogenic	[13–15]
	< 1	Oil	

Results and discussion

HCs in the NCC water. HC concentrations in the water of the studied area of the NCC averaged 0.032 ± 0.006 mg·L^{-1}. The obtained values are lower than the maximum permissible concentrations (MPC) for fishery water bodies (0.05 mg·L^{-1}), but slightly higher than those for low-polluted water areas [7]. The content of n-alkanes in the NCC water was in the range of 0.010–0.016 with average 0.013 ± 0.003 mg·L^{-1}.

All the samples recorded n-alkanes in the C_{17}–C_{29} range (Fig. 2, *a*). In two samples C_{30} was present. In one sample it was possible to identify C_{32}. In all three samples the dominant homologue was compound C_{25} (18–26 %). At the same time, the share of other n-alkanes did not exceed 11 %. N-alkane C_{25} is predominantly associated with bacterial and allochthonous production [6]. Along with the presence of C_{20} and C_{22} peaks, also typical of microbial production, we can speak of an active microbial community in the canal waters. Even-numbered n-alkanes with a high molecular weight (C_{28}, C_{30}, C_{32}) are often associated with sapropel matter formed from the organic matter of phyto- and zoobenthos, plankton, and lower plants and is autochthonous for aquatic ecosystems [6]. Such substances accumulate under reducing conditions. Light HCs (up to C_{17}) were not recorded, which indicates the absence of fresh oil inputs. The unresolved complex mixture was absent, which indicates the absence of chronic oil contamination of water (Fig. 2, *b*).



F i g . 2 . Concentrations (*C*) of n-alkanes and isoprenoids (*a*) and a typical chromatogram of n-alkanes (*b*) in the water of the North Crimean Canal, spring 2022

A low weight to high weight HC ratio (LWH/HWH) of less than 1 demonstrates that the source of n-alkanes is higher plants, aquatic animals and bacteria [16]. When the values of this index are close to 1, we can speak of oil pollution, and when the values exceed 2, we can speak of fresh oil input [11]. The calculated LWH/HWH index, according to the received data, was on average 0.35, which indicates the biogenic nature of HCs.

The carbon preference index (CPI) reflects the ratio of odd-numbered to even-numberedn-alkanes. In the low-molecular ($C < 22$) and high-molecular ($C > 22$) spectral regions, the CPI_1 and CPI_2 indices have different interpretations, and therefore it is recommended to calculate them separately [17]. This index may indicate a biogenic or oil origin of hydrocarbons. The contribution of the bacterial community is not excluded. In our case, the average CPI_1 value is 0.62 and CPI_2 is 0.45, which is less than 1 and indicates the biogenic origin of hydrocarbons (Table 2).

The C_{31}/C_{19} ratio is an index showing the ratio of allochthonous to autochthonous components. Its value less than 0.4 indicates predominance of autochthonous substance and more than 0.4 – allochthonous. In our case, the average value of this index is 0.94, which indicates the allochthonous nature of hydrocarbons. The C_{31}/C_{29} ratio of 0.63 indicates the predominance of herbaceous vegetation [18].

The ratio of terrigenous to autochthonous matter is estimated by the TMD index [19]. A value of this diagnostic index of less than 0.5 indicates the predominance of autochthonous matter. The range 0.5–1 indicates a mixed input. In this study,

Table 2. Average values of diagnostic indices and the origin of hydrocarbons in the water of the North Crimean Canal, spring 2022

Index	Average	Hydrocarbon origin
LWH/HWH	0.35	Biogenic
CPI_1	0.62	Biogenic
CPI_2	0.45	Biogenic
Pr/Ph	0.40	Oil
C_{31}/C_{19}	0.94	Allochthonous
TMD	3.15	Terrigenous
C_{31}/C_{29}	0.63	Plant (herbaceous vegetation)

the mean value of this indicator was 3.15, which is more than 1 and indicates an intensive input of terrigenous matter produced by higher ground plants (Table 2). This fact is natural for river systems, as their filling with water occurs due to runoff from the river basin [18, 20].

An important diagnostic index [2)] is the ratio of pristane, which is predominantly of natural origin, to phytane, which is present mostly in oil [21]. This ratio ranged from 0.22 to 0.82 with an average of 0.40, which most likely indicates the presence of oil products in the water. At the same time, other markers diagnose the biogenic nature of HCs.

HCs in the bottom sediments of the NCC and the soils of the adjacent areas. The sediments sampled from the canal bottom were not river sediments but rather soil that was in the canal bed and was flooded when the canal started working. It should be noted that soils in the area are dark brown [3)], which are characterised by a neutral pH. In terms of mechanical composition, brown soils are mostly heavy. Due to deep (from 1 m) penetration of humus, a significant part of brown soils is highly fertile [4)].

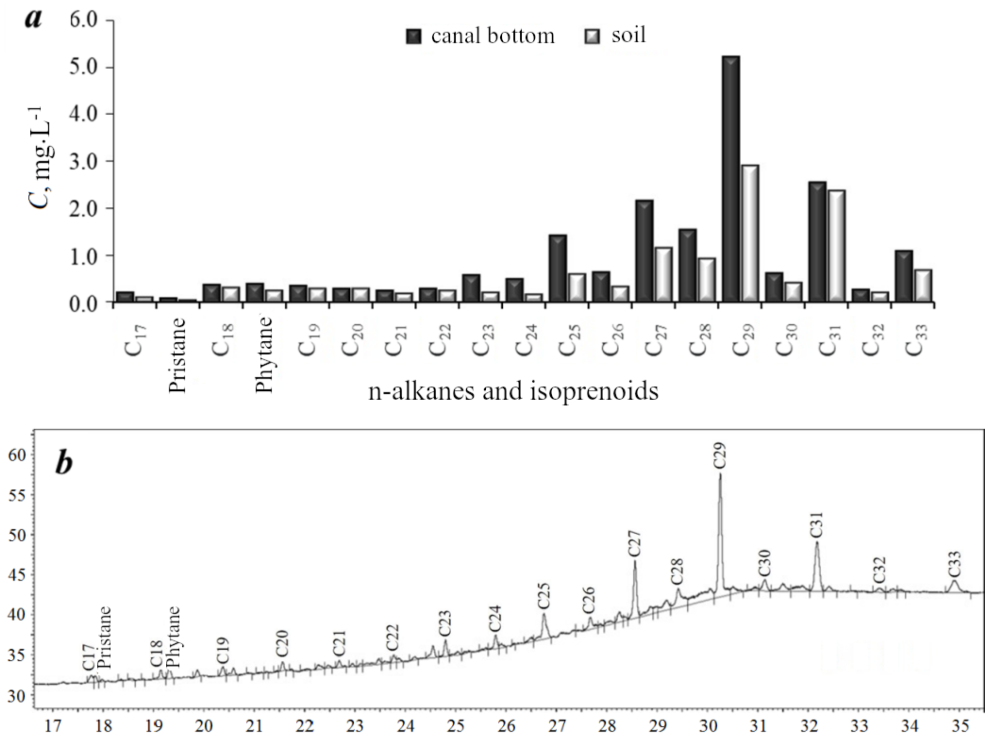
The HC concentration in bottom sediments of the NCC studied area was 30 $mg \cdot kg^{-1}$ air-dry bottom sediment (a.d.b.s.) (Fig. 3, *a*), which corresponds to naturally clean water areas [22]. The n-alkane content in the NCC bottom sediments was 18.7 $mg \cdot kg^{-1}$ a.d.b.s. In the soil sampled from the farmland adjacent to the canal, HC content was 18.1 $mg \cdot kg^{-1}$, n-alkanes accounted for 11.2 $mg \cdot kg^{-1}$ a.d.b.s., i. e. the proportion of n-alkanes in soil (62 %) was the same as in bottom sediments (62 %). The recorded HC content is low and characterizes the soils and bottom sediments as unexposed (in terms of oil contamination) [22].

In the samples of bottom sediments and soil, we identified n-alkanes in the range from C_{17} to C_{33}, which corresponded to the presence of these compounds in water at the sampling station and is also typical of the soil mantle of steppe areas [23]. The maximum concentrations of n-alkanes were in the high-molecular-weight range dominated by odd-numbered compounds indicating the predominance of compounds synthesized by land organisms. The even-numbered peaks in the C_{18}–C_{22} range were not pronounced indicating no active microbial degradation of organic matter in the bottom sediments of the canal and adjacent field areas. The autochthonous peaks corresponding to C_{17}, C_{19} etc. were also not pronounced. Active microbial processes were probably confined to the water column at the moment of sampling and were not characteristic of bottom sediments.

[2)] AMAP, 2007. *AMAP (Arctic Monitoring and Assessment Programme). Chapter 4. Sources, inputs and concentrations of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, and other contaminants related to oil and gas activities in the Arctic*. Oslo: AMAP, 87 p.

[3)] Soboleva, E.V. and Guseva, A.N., 2010. [*Chemistry of Fossil Fuels*]. Moscow: Izd-vo Mosk-ovskogo Un-ta, 312 p. (in Russian).

[4)] Shoba, S.A., ed., 2011. [*National Atlas of Soils of the Russian Federation*]. Moscow: Astrel, 632 p. (in Russian).



F i g . 3 . Concentrations (*C*) of n-alkanes and isoprenoids (*a*) and typical chromatogram of n-alkanes (*b*) in bottom sediments of the North Crimean Canal and adjacent soil, spring 2022

The n-alkane C_{29} (26–29 %) of plant origin (terrestrial herbaceous plants) was dominant in concentration both in soil and in bottom sediments [24]. This fact is consistent for soils in steppe areas. In addition, this, along with the lower proportion of C_{29} (5 %) in the canal water, confirms the assumption that the large amount of allochthonous compounds in the canal bottom sediments may be associated with their accumulation in the canal bed during the eight-year period of no-runoff in the canal.

Today, it can be assumed that the canal bottom sediments can be a significant source of input of various compounds into the canal waters. The peaks from C_{27} to C_{31}, which also indicate the presence of allochthonous compounds in the studied environment [5], are also sufficiently pronounced. It should be noted that separation of alkanes originating from aquatic and terrestrial plants is rather conventional. This is due to the fact that this approach is strictly applicable only to fresh organic matter [6], while in bottom sediments, transformed compounds are mostly presented.

The ratio of light to heavy n-alkanes in the mixture was low and averaged 0.10 (Table 3). These values are consistent with the biogenic nature of organic matter.

Table 3. Average values of diagnostic indices and the origin of hydrocarbons in the bottom sediments and adjacent soil of the North Crimean Canal, spring 2022

Index	Average		Hydrocarbon origin
	in bottom sediments	in soil	
LWH/HWH	0.09	0.11	Biogenic
CPI_1	1.06	0.81	Biogenic
CPI_2	7.64	8.42	Biogenic
Pr/Ph	0.18	0.14	Oil
C_{31}/C_{19}	7.26	8.56	Terrigenous
TMD	9.04	10.35	Terrigenous
C_{31}/C_{29}	0.49	0.81	Plant (herbaceous vegetation)

The CPI_1 marker for the low-molecular-weight region for both studied media is almost equal to 1 (Table 3), but one cannot conclude from this about the presence of petroleum products in the sediments. Similar CPI_1 values, along with a pronounced peak of C_{29}, are most likely indicative of natural ways of HC input and transformation [6]. In the high-molecular-weight region, where CPI_2 is more informative as a criterion of biogenicity, its value exceeded 7 indicating a large fraction of biogenic matter [13–15].

The ratio of the pristane (predominantly biogenic) to phytane (observed in oil) was low, suggesting the possible presence of traces of oil contamination in sediments and soil [25]. With a similar ratio of pristane to phytane, the transformation of organic matter in reducing condition [3)] can also be stated. This is a more likely explanation of this isoprenoid ratio, since the values of other markers indicate the biogenic nature of HCs.

The ratio of C_{31} and C_{19} n-alkanes in sediments from the canal bottom indicates a strong predominance of terrigenous matter in the composition of organic compounds in the bottom sediments [9]. The high TMD value (9.04) also indicates an active input of HC from land. In addition to direct outwash of substances from the land, their accumulation on the canal bottom during the period of water absence can also be assumed. On the whole, the predominantly terrigenous origin of HCs was indicated by the corresponding indices. The indices were higher in the soil than on the canal bottom. This fact seems to be expected, since organic matter is produced in the water column of the canal and is partially deposited on the bottom increasing the share of autochthonous n-alkanes of the bottom sediments.

The ratio of n-alkanes, which characterises the proportions of herbaceous and tree vegetation, averaged 0.49 for sediments and 0.81 for soil. This indicator shows the predominance of organic compounds associated with ground vegetation in soil rather than in canal bottom sediments. In the water column, the value of this index was 0.63, which was the average between its values in the two mentioned solid media.

Thus, the interpretation of the diagnostic relationships for the bottom sediments of the NCC and adjacent fields is generally consistent. A high correlation of soil organic compounds with ground vegetation was noted.

Conclusion

The obtained HC concentrations in the water (0.032 ± 0.006 mg·L^{-1}) of the studied section of the NCC do not exceed the MPC and are close to the values characteristic of values typical of uncontaminated water areas. The HC content in the canal bottom sediments (30 mg·kg^{-1} a.d.b.s.) and in the adjacent fields (18.1 mg·kg^{-1} a.d.b.s.) also indicated the absence of high pollution levels.

In the NCC water, n-alkanes were identified in the C_{17}–C_{32} range with an average concentration of 0.013 ± 0.003 mg·L^{-1}. In the bottom sediments and soils of the adjacent areas, the range of n-alkanes was C_{17}–C_{33} and their concentrations were 18.7 and 11.2 mg·kg^{-1} a.d.b.s., respectively.

The composition of n-alkanes in water indicates the mixed nature of HCs, with the predominance of compounds of allochthonous origin, which are washed away from the river basin of the lower Dnieper. The compositions of n-alkanes of the bottom sediments and soils were significantly similar and were typical of soils of steppe areas. This is probably due to the accumulation of soil in the canal bed during the period of water absence in it.

Most of the markers for water, sediments and soil, which allow differentiating between oil and biogenic HCs (LWH/HWH, CPI_2, Pr/Ph), indicate the predominance of natural components. The presence of oil HCs (Pr/Ph < 1) cannot be excluded, although this is unlikely due to the absence of other signs of oil contamination. At the same time, the markers which allow revealing predominance of autochthonous or allochthonous compounds (C_{31}/C_{19}, TMD) definitely indicate predominance of allochthonous ones. This fact is expected for river systems, as their filling with water occurs due to runoff from the river basin. The high amount of allochthonous compounds may also be due to their accumulation in the canal during the eight-year period of no-washout in it. The C_{31}/C_{29} ratio indicates the predominant formation of allochthonous organic matter by HCs originating from herbaceous plants. This fact is consistent with the fact that the NCC and adjacent parts of the Dnieper are located in steppe areas.

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Elena A. Tikhonova – sample preparation, determination of hydrocarbons in water, bottom sediments and soil, discussion of the results

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