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Concentration, composition, and genesis of hydrocarbons in bottom sediments of the Chernaya River estuarine zone (Sevastopol, the Black Sea)

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ABSTRACT

The "river-sea" geochemical barrier is studied slightly in terms of the variety of pollutants, sedimentation, and degradation. At the same time, problems related to oil pollution, in particular the genesis of hydrocarbons, are almost never covered. This study was dedicated to the origin, concentration, and composition of hydrocarbons in the bottom sediments of the Chernaya River (Black Sea, Crimea) estuarine zone. The features of the marginal filter zone of the river were considered. N-alkanes in the range of C_{11}-C_{36} were identified in the bottom sediments of the studied water area. It was noted that there was persistent oil pollution (degraded hydrocarbons) in the water area of Sevastopol Bay, adjacent to the confluence of the river. The accumulation of terrestrial material increased as it moved from the river to the sea. The application of various molecular markers displayed the predominately allochthonous origin of the hydrocarbons in the bottom sediments. As a result of the study of molecular markers by using principal component analysis (PCA) and analysis of variance (ANOVA) analysis, three leading factors responsible for hydrocarbon input to the bottom sediments water area were identified. The first one (36.53 % of the total variation) was associated with n-alkanes of natural and anthropogenic input. The second factor (19.52 % variation) was associated with allochthonous organic matter, including petroleum and bacterial destruction. The third factor (10.74 %) was associated with mainly allochthonous routes of organic substances entering the bottom sediments of the water area.

1. Introduction

The marginal filter is a barrier zone that delays the main part of the sedimentary terrestrial material on the way from the continent to the ocean, and at the same time, delimits the freshwater (river runoff) and marine (ocean) hydrosphere not only geographically, but also by the strength of the processes inside them. Marginal filters of rivers are zones of transformation of terrestrial suspension

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carried out by rivers into marine suspended sedimentary matter. This is a zone of mixing of river and sea waters with salinity from 0 to about 20 ‰, in which there are qualitative and quantitative changes in dissolved and suspended substances coming from the continent. An important element of the marginal filter is the river-sea geochemical barrier with gradients of flow velocities, salinity, and water temperature, where more than 90% of the suspended material of river runoff is removed from the water as a result of various hydrological, physical-chemical, and biological processes [1]. Until recently, the barrier effects occurring in estuarine zones of rivers were the object of study of oceanologists who researched the lithodynamics, physico-chemical and biochemical equilibrium at the land-ocean boundary from the point of view of the balance and redistribution of solid and dissolved runoff [1]. However, estuarine zones of rivers have attracted the attention of researchers in recent years as zones of accumulation and transformation of many classes of pollutants, including those of anthropogenic nature [2]. Drainage and surface waters carry out various chemical compounds from the soils that enter the watercourses that settle in the bottom sediments, while some of the compounds can accumulate, and some can be washed out of them, polluting the surface water for a second time. Bottom sediments are one of the most informative research objects in this chain [3] due to their ability to accumulate various pollutants from the catchment area for a long period of time; they can serve as an indicator of the ecological state of floodplain-channel complexes and are an integral indicator of the surface watercourses pollution degrees [4]. Currently, one of the main types of hydrosphere pollution is oil and its products [5]. A special feature of petroleum products is their ability to accumulate in bottom sediments, turning them into a potential source of secondary pollution of the reservoir; this process is observed when pollutants that have previously passed from water as a result of changes in various physical and chemical processes can migrate from bottom sediments to water, polluting it again [6]. Studies of the content of petroleum hydrocarbons only in surface waters do not always make it possible to characterize the pollution of the floodplain-channel complex fully. River sediments, having a high sorption capacity (especially small fractions), in the process of their movement and deposition in the riverbed, accumulate the entire complex of chemical compounds present in the water [7]. The Chernaya River is the main source of the drinking water supply in the Sevastopol region, being one of the most abundant rivers in the southwestern part of the Crimea. Flowing directly into Sevastopol Bay, the river has a significant impact on the overall ecological state of the main sea area of the city, becoming one of the city-forming elements. The contribution of the river watercourse to the total flow into Sevastopol Bay is about 70% [8,9]. This bay acts like a "terminal station" for most polluted effluents on a regional scale, including the waters of the Chernaya River. The ecological state of Sevastopol Bay has been classified as unfavorable for decades [10]. The available monitoring observations on a wide range of chemical and biological characteristics of various components of the bay ecosystem confirm this conclusion, but they are analyzed mainly in the range of "sea boundaries" of the water area [11]. Multiple research works were devoted to studying these processes in the estuarine zones of large rivers [12]. Only a few research consider the features of the "river-sea" geochemical barrier and concern the dynamics and volumes of river runoff and the content of various biogenic elements, while heavy metals are mainly considered from the variety of pollutants [13]. At the same time, problems related to oil pollution, in particular the genesis of hydrocarbons, are almost never covered. Singular works are devoted to the transformation of hydrocarbons in the marginal filter of large rivers [13,14,15]. A significant difficulty in interpreting the data on oil pollution is associated with the natural biogenic origin of many hydrocarbons. It is also necessary to distinguish between the natural hydrocarbon background and pollutants and their sources of intake [14]. Molecular biomarkers can be the most reliable indicators of the hydrocarbon's genesis [16,17]. They can be used to assess the state of the aquatic ecosystem and the degree of influence of natural and anthropogenic factors. Several indexes can be used to determine the origin of hydrocarbons [18,19,20,21]. Therefore, the processes of hydrocarbon accumulation in the bottom sediments of smaller rivers on a local scale are not currently covered enough. In this regard, the aim of this research was to study concentrations, composition, and origin of hydrocarbons in bottom sediments in the marginal filter area of the mixing zone of fresh waters of the Chernaya River and sea waters of the Sevastopol Bay. The implementation of this goal included the determination of the total concentration of HC (hydrocarbons) and AHC (aliphatic hydrocarbons), the individual composition of n-alkanes in bottom sediments, their spatial and temporal dynamics, as well as a comparison of the HC concentration with safe levels; identification of the most probable ways of HC input into the bottom sediments of the Chernaya River using various diagnostic indexes.

2. Material and methods

2.1. Sampling

The material used in the study were samples of bottom sediments, which were taken monthly in the period from Marth 2019 to February 2020 by a manual grab sampler with a capture area of 0.038 m^2 from the side of a motor boat (Figure 1). Three samples were taken monthly; the total number of samples was 36. In order to carry out sampling at the same place, a GPS-navigator and landmarks on the coast were used. The depth at station 1 was about 4 m, at station 2–1.5 m. At station 3, the selection of bottom sediments was carried out by a grab sampler directly from the Chernaya River at a depth of 0.5 m. Samples of bottom sediments were dried to an air-dry state, ground in an inert mortar with a pestle, and sifted with a sieve with a mesh diameter of 0.25 mm.

2.2. Chemical analysis of bottom sediments

A weighted sample (5–7g) was placed into a conical flask with 20 cm^3 of *n*-hexane and subjected to ultrasonic treatment to extract *n*-alkanes. The extract was allowed to settle (10 min), and then it was transferred to a clean conical flask. A similar extraction was performed three times to fully extract alkane components. As a result, 60–70 cm^3 of the extract was obtained. The obtained extract was passed through a glass column (15cm × 1cm) filled with aluminum oxide to separate the polar compounds and was concentrated using rotary evaporation to a volume of 1 cm^3. An aliquot of the concentrated extract (1 μL) was injected with a micro syringe into the evaporator (heated to 250 °C) of a gas chromatographer, Krystall 5000.2, with a flame ionization detector (FID). HCs were separated on a 25 m × 0.32 mm HT8 capillary column with a stationary phase, a film thickness of 0.25 μm (SGE Analytical Science). The column temperature was programmed from 40 °C to 330°C (temperature elevation rate: 10 °C/min). The carrier gas (helium) flow in the column was 2.5 ml/min without splitting. The detector temperature was 320 °C. The *n*-alkanes were identified by matching the retention times observed for samples to those observed for a standard solution of *n*-alkanes. The total *n*-alkanes content was determined by calibrating the FID with an external standard HC mixture (C10–C40).

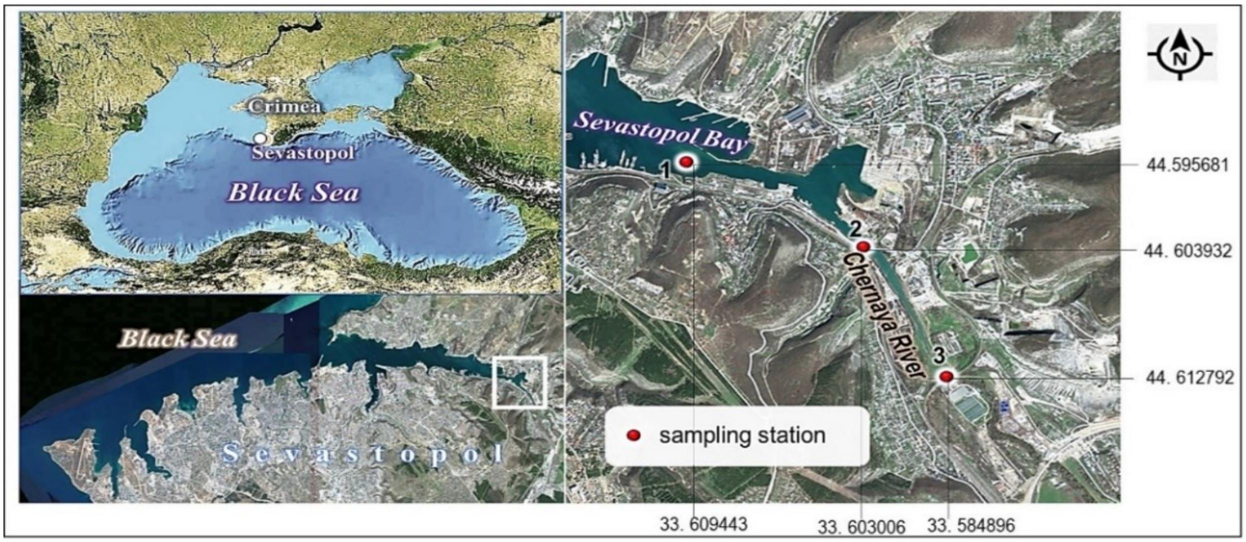

Fig. 1. Map-scheme of bottom sediments sampling in the mixing zone of the river, 2019-2020.

The standard sample ASTMD2887 Reference Gas Oil (SUPELCO, USA) was used as a mixture of HC. The software "Chromatech Analyst 3.0" and the method of absolute calibration and percentage normalization were used to process the results. The determination of hydrocarbons was carried out based on 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.

2.3. Determination of hydrocarbon markers and ratios

Multiple diagnostic indexes and molecular ratios were used to identify hydrocarbon genesis. In the course of the work, a number of ratios were used to determine the biogenic or petrogenic origin of n-alkanes, as well as to differentiate their autochthonous or allochthonous origin to some extent. The indexes and ratios are shown in Table 1.

Table 1. Diagnostic molecular markers and their typical values.

Diagnostic ratios (calculation formula)	Typical value	Type	Reference
UCM/n-alkanes	<10	Autochthonous and fresh petroleum hydrocarbons	[22]
	>10	Degraded oil products	
LWH/HWH=$\Sigma(C_{11}-C_{21})/\Sigma(C_{22}-C_{35})$	> 1	Oil origin	[23]
	< 1	Terrestrial, high vegetation	
Paq = $(C_{23} + C_{25})/ (C_{23}+C_{25}+ C_{29}+C_{31})$	Paq< 0.1	Traces of degraded vegetation	[24]
	0.1<Paq<0.4	Fres hmacrophytes	
	0.4<Paq<1	Submerged and floating macrophytes	
TAR=$(C_{27}+C_{29}+C_{31})/(C_{15}+C_{17}+C_{19})$	High TAR	Predomination of terrestria lmaterial	[25]
ACL=$[25*C_{25}+27*C_{27}+29*C_{29}+31*C_{31}+33*C_{33}]/[C_{25}+C_{27}+C_{29}+C_{31}+C_{33}]$	Decreased ACL	Oil emissions	[26]
TMD=$(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{15}+C_{17}+C_{19}+C_{21}++C_{23})$	<0.5	Allochthonous substances	[27]
	<0.5		
	0.5<TMD<1	Mixed	
	>1	Ground vegetation	
C_{31}/C_{19}	<0.4	Autochthonous matter	[28]
	>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	Intensive microbial transformation of hydrocarbons	[29,30,31]
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	Oil or biodegradation	
	<1	Biogenic	
	5-10	Higher ground vegetation	
	<3	Oil	
C_{31}/C_{29}	<0.4	Predomination of woody vegetation	[32,33,34]
	>0.4	Predomination of grass vegetation	
NAR=$\Sigma(C_{19-32})-2\Sigma\text{even}(C_{20-32})]/ \Sigma(C_{19-32})$	≈0	Oil	[35]
	≈1	Higher ground vegetation	
Alkterr=$C_{27} + C_{29} + C_{31} + C_{33})/ \Sigma C_{14-38}$	<0.4	Predomination of allochthonous matter	[33]
	>0.4	Predomination of autochthonous matter	
$\Sigma C_{25-35}/\Sigma(C_{15}+C_{17}+C_{19}+C_{21})$	<1	Predomination of autochthonous matter	[36]
	>1	Predomination of terrestrial matter	

UCM – Unresolved Complex Mixture, LWH/HWH – ratio of low to high molecular weight homologues, Paq – the moisture index, TAR – the terrigenous/autochthonous ratio, ACL – hydrocarbon average chain length, TMD – terrigenous vs. marine discriminant, CPI – Carbon Preference Index, NAR - Natural n-alkane ratio.

2.4. Statistical data analysis

A non-Gaussian distribution of the studied values was observed during the data validation. For further statistical processing, the data were normalized using log base 10. The two-factor dispersion analysis ANOVA (factorial main effect ANOVA) was used to test the validity of the hypothesis about the temporal and spatial variability of the HC concentration. Pair wise comparison of HC data in Tukey's different periods was performed according to the criterion of the Tukey honest significant difference (Tukey's HSD test). The differences were considered statistically significant at a level of significance of 0.05. Principal component analysis (PCA) was used to determine (relatively quantitatively) the main sources of HC in water at various sampling stations. This analysis was made by the Varimax rotation method. The number of main components was determined by means of the Stone method [37]. Microsoft Excel and Statistica 12 software packages were used for data processing.

3. Results and discussion

3.1. Spatial-temporal changes in the hydrocarbons content in the bottom sediments of the Chernaya River

The HC concentrations in the bottom sediments (Figure 2A) ranged from 72 to 1739 µs/g. At st. 1, located in the water area of the bay, this indicator varied from 221 to 1739 µg/g, equaling an average of 762±135 µg/g during the study period. At st. 2, in the area of the automobile bridge, the HC content was in the range of 208-943 µg/g, with an average value of 419±63 µg/g. In the riverbed, the content of the studied substances ranged from 72 to 1624 µg/g. Russian regulatory documents do not regulate the content of pollutants in the bottom sediments (there are no normative characteristics of their quality), but it is possible to assess the degree of contamination of bottom sediments in the controlled area based on the compliance of the level of pollutants with the criteria for environmental assessment of soil contamination according to Neue Niederlandische Liste. Altlasten Spektrum 3/95 [38].

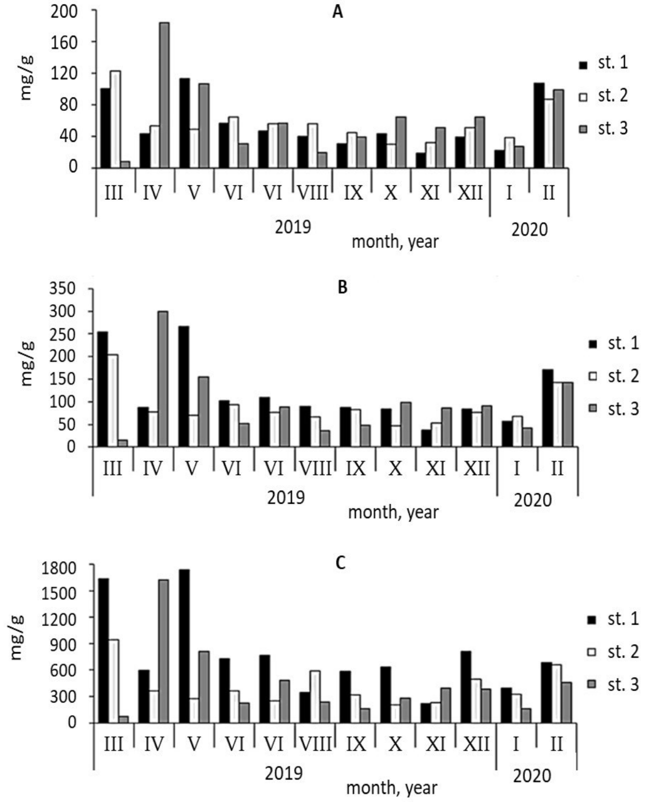

Fig. 2. The content in the bottom sediments of the estuarine zone of the Chernaya River: A-HC, µg/g; B-AHC, µg/g; C-n-alkanes, µg/g.

Thus, the permissible concentrations for petroleum hydrocarbons are 50 µg/g. According to the classification [39], the concentrations of petroleum hydrocarbons in the soil at a level of up to 100 µg/g correspond to natural background values: 100–500 µg/g–an elevated background, 500 – 1000 µg/g – a "moderate" level of pollution, 1000–2000 µg/g– "moderately dangerous" pollution, 2000-5000 µg/g– "heavy" pollution, and more than 5000 µg/g – "dangerous" pollution. Thus, according to this classification, it can be noted that the bottom sediments of the water areas studied for oil pollution were from background to moderately dangerous values. At the same time, most of the samples corresponded to a "moderate" level of contamination. The analysis of variance showed the absence of reliable temporal variability of the total HC content in the bottom sediments of the studied water area (Table 2). At the same time, the spatial variability of the studied indicator was revealed. A pairwise comparison showed that the HC content in the bottom sediments at st. 1 was significantly higher than at st. 2 and 3 (Figure 3).

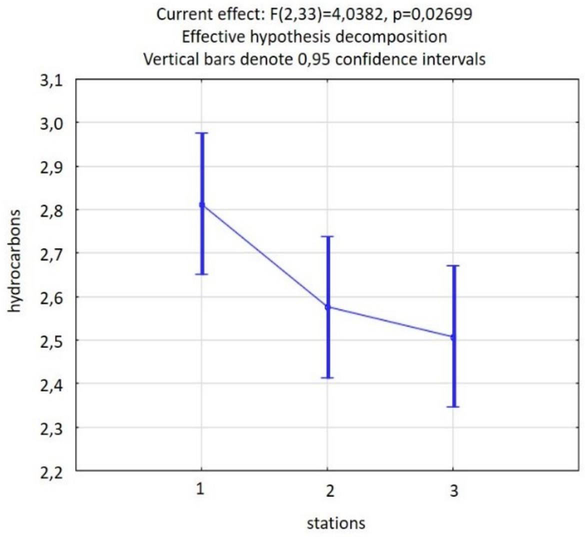

Fig. 3. Corrected mean geometric concentrations of HC (based on the results of Tukey's HSD test, confidence interval 0.95) in the estuary zone of the Chernaya River in 2019-2020.

The average content of HC in the estuary zone of the Chernaya River (st. 2) and the riverbed (st. 3) did not differ. The concentration of AHC (Figure 2B) ranged from 15 to 299 µg/g. At st. 1, this parameter was 37-267 µg/g, with an average of 119±21 µg/g. At st. 2 in the bridge area, the AHC content was from 47 to 204 µg/g, with an average of 88±13. In the riverbed, the content of the aliphatic compounds was 15-299 µg/g, with an average value of 96±22 µg/g. Statistical tests (Table 2) showed no significant differences in the average content of AHC within the study area. During the study period, n-alkanes in the range C_{11}-C_{36} were identified in the estuary zone of the Chernaya River. In most of the samples, the range of the studied compounds was C_{13}-C_{35}. The amount of n-alkanes (Figure 2B) ranged from 8 to 123 µg/g. The average values were 55±9 at st. 1, 57±7 at st. 2, and 63±14 µg/g of dry bottom sediment at st. 3. There were no statistically significant differences in the content of the sum of n-alkanes in different parts of the polygon (Table 2). It is interesting to note that no reliable time dynamics in the content of the studied groups of substances were revealed. At the same time, it is known that during the period of the spring flood, not only the erosion of bottom sediments occurs but also the desorption of mobile forms of metals and their accumulation during the fall [40]. In our case, there was a trend of increasing the content of hydrocarbon components of bottom sediments in the period from February to May (Figure 2). The described phenomenon may be associated with an increase in river flow in the winter-spring period (Figure 4).

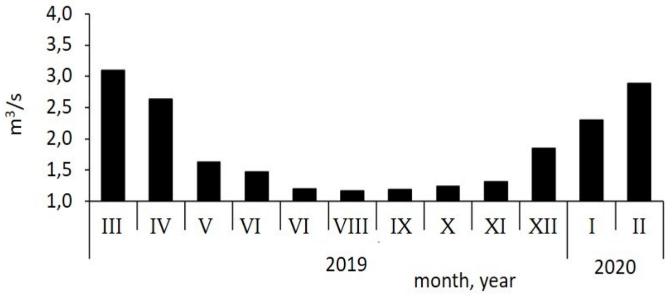

Fig. 4. Average monthly discharge of the Chernaya River [41].

High water is the result of increased runoff from the catchment area, as a result of which organic substances of various genesis can enter the river waters (and, subsequently, into the bottom sediments). The analysis showed that the concentrations of HC and AHC had a significant correlation coefficient with the flow rate of the river only at st. 2 (0.68 and 0.75, respectively). The amount of n-alkanes in the bottom sediments correlated with the river flow at st. 1 (0.51) and at st. 2 (0.70). Thus, in the so-called zone, a significant relationship between the content of individual organic substances in bottom sediments and the intensity of river flow was noted.

Table 2. Results of a two-factor analysis of variance (factorial main effect ANOVA, p=0.05) of the concentration of HC, AHC, and n-alkanes in bottom sediments of the Chernaya River.

Factor	**SS**	**dF**	**MS**	**F**	**p**
			HC concentration, μg/g		
Time of sampling	0,739441	11	0,067222	0,217868	0,964469
Sampling station	0,617089245	2	0,308544623	4,58994091	0,0355309947
Time of sampling* Sampling station	1,781970	22	0,080999	1,000000	0,500000
			AHC concentration, μg/g		
Time of sampling	0,758047585	11	0,0689134168	1,05013287	0,584491992
Sampling station	0,131247	2	0,065624	0,952260	0,415508
Time of sampling* Sampling station	1,544214	22	0,070192	1,000000	0,500000
			n-alkanes concentration, μg/g		
Time of sampling	0,019302	2	0,009651	0,114869	0,892538
Sampling station	0,924186	11	0,084017	8,705535	0,107462
Time of sampling* Sampling station	1,53146451	22	0,069612023	1,000000	0,50000000

3.2. Identification of the hydrocarbon's genesis in the bottom sediments of the Chernaya River

The difference in the content of petroleum products in certain sections of the mouth zone of the Chernaya River is determined by the difference in the total content of petroleum hydrocarbons and AHC, which is the so-called "undecomposable background" (UCM). This "background", in the classical approach, is a complex mixture of structured isomers and homologues of iso- and cyclo-hydrocarbons [29]). High values of the undivided fraction are often associated with oil pollution [42,43]. An important diagnostic indicator for the analysis of the genesis of hydrocarbons is the UCM ratio to the sum of aliphatic hydrocarbons. Values of this indicator below 10 are usually associated with the processes of biodegradation of natural organic substances or fresh oil intake. Values exceeding 10 indicate the presence of degraded oil pollution [22]. Although, high values of UCM/n-alkanes may indicate a high intensity of biodegradation of allochthonous and autochthonous organic substances in the absence of oil pollution [44]. The data presented in Table 3shows that the values indicating the presence of oil pollution are most often associated with st. 1, located in the water area of Sevastopol Bay. This ratio, characteristic of oil pollution, was not observed in river bottom sediments. Index values calculated for st. 2 and 3 may be a sign of fresh oil supply. But, in combination with a stable and fairly high ACL (Table 3), they most likely advise the level associated with microbial degradation of nutrients. If we take the average annual indicators, this index is equal to 12±1.1 at st. 1, 6±0.5 at st. 2, and 3±0.6, which indicates the presence of chronic oil pollution in the water area of the bay. It is also evident that the relative share of the "methane-naphthenic hump" is decreasing with the movement upstream of the river. ANAR index [34] close to zero indicates the flow of oil into the environment. On the contrary, values close to 1 are associated with the intake of organic substances from higher terrestrial vegetation. In this study, 64 % of the NAR indexes displayed the probable petroleum nature of n-alkanes. Moreover, at st. 1 located in the bay, there were minimum values of this index. Their values in 100 % of the samples did not exceed 0.5. With the advance from the sea upstream of the river, the percentage of such indicators decreased. The average annual NAR values at sampling stations indicated the oil origin of substances at st. 1 and mixed origin at st. 2 and 3. The low-molecular-weight odd index (CPI_1) was close to 1 in 72% of the cases. However, based on this, it is difficult to assert the presence of anthropogenic pollution. This indicator is not very informative for the identification of oil, and to a greater extent, it is associated with the microbial destruction of organic substances [29]. A more reliable criterion for identifying the origin of hydrocarbons is the CPI_2 index, calculated for high-molecular-weight n-alkanes. Its values ranged from 0.12 to 1.4. Indicators characteristic for the presence of oil pollution were noted only on st. 1. The ratio of LWH/HWH, which reflected the ratio of the mass of light homologues to heavy ones, confidently indicated the influence of higher plants, animals, and bacteria on the formation of n-alkanes in bottom sediments. Its average annual values were in the range of 0.26±0.02 to 0.41±0.08. The ratio C_{31}/C_{19} with values < 0.4 indicated the predominance of autochthonous matter, if > 0.4 – allochthonous. The value of this ratio in 100% of cases indicated a predominantly allochthonous source of hydrocarbons. Moreover, with the approach to the sea, the percentage of allochthonous compounds increased. At the same time, the Paq index in 22% of cases indicated the predominance of traces of terrestrial vegetation, and in 11 %, the presence of fresh macrophytes. The predominance of compounds associated with aquatic plants was confined in all cases at st. 3, located in the riverbed. The accumulation of substances mainly produced by terrestrial plants was more pronounced at st. 1, located in the water area of the bay. The C_{31}/C_{29} ratio allowed us to determine the conditional contribution of woody and herbaceous vegetation as a source of n-alkanes. One hundred percent of the indexes indicated herbaceous vegetation as the predominant source of allochthonous compounds. The TAR index was in the range of 0.22-3.02. In 75% of cases, the values of this indicator indicated the predominance of terrestrial material in the formation of n-alkanes of bottom sediments in these areas. The values of this index increased along the course of the riverbed (st. 1 – 2.15±0.20; st. 2 – 1.47±0.16; st. 3 – 0.98±0.21). The Alkterr ratio reflects the intake of organic substances from the land [32]. In our case, this index varied in the range from 0.06 (a small contribution of allochthonous substances) to 0.35 (a very significant role of terrestrial material). On average, at st. 1, st. 2, and st. 3, it was 0.26 ±0.01, 0.15±0.01, and 0.11±0.01, respectively. This demonstrated the accumulation of terrestrial substances when moving along the riverbed to the sea. The ratio $\Sigma C_{25-35}/\Sigma C_{15,17,19,21}$ makes it possible to identify the autochthonous or allochthonous origin of n-alkanes, excluding such factors as the granulometric composition of bottom sediments and the sedimentation rate in the study area [45]. High values of this indicator characterize the strong influence of terrestrial matter [46]. The index values observed in the Chernaya River ranged from 0.74-10.82. On average, at st. 1, it was 2.65±0,23; at st. 2 – 3.85±0.34; at st. 3 – 3.65±0.83. In general, this indicates a significant influence of allochthonous compounds on the composition of n-alkanes in the bottom sediments of the lower reaches of the Chernaya River and adjacent areas of the Sevastopol Bay. The concentration of petroleum products increased from the river to the sea, which seemed natural to the authors due to the high anthropogenic load on the water area of the bay [10]. At the same time, the content of n-alkanes within the study range had no significant differences. The individual composition of n-paraffins underwent changes (Figure 2). This dynamic was visible in space and time. This fact characterized the variability of the primary sources of receipt of this class of substances in the studied water area [47]. The difference in the substance's deposition on sampling stations (Figure 3) could also be affected by the sediment's grain size change, which is usual for the marginal filter zone [1]. It is known [48] that in the study region, the maximum concentration (99%) of silty material was observed in the Sevastopol Bay water area (st. 1). The silt fractions were distributed as follows: 20% – aleuritic-pelite fraction and 79% – pelitic-aleurite fraction. Directly in the area of the river inflow into the bay (st. 2), accumulation of the sand fraction (7%) and the maximum portion of pelitic silts were noted. In river bottom sediments, the contribution of the finely dispersed fraction was lower and did not exceed 40%. In this case, the proportion of sand increased to 39%, and a gravel fraction (18%) appeared. So, the predominance of silty fractions may explain the elevated concentrations of the studied substances at st. 1. Let us consider in general a group of indexes that allow us to identify the presence of petroleum products in the environment. The values of UCM/n-alkanes, NAR, and CPI_2 indicate the persistence of n-alkanes of petroleum genesis at st. 1. Similar values were isolated at other sampling stations. At the same time, the ACL and LWH/HWH indicators did not demonstrate the presence of light fractions of petroleum products associated with the fresh intake of these pollutants into the environment. Thus, the estuary of the Chernaya River is relatively safe in terms of oil pollution. In the area of the Sevastopol Bay, adjacent to the confluence of the river (st. 1), there is chronic oil pollution (degraded hydrocarbons). Table 3 shows the peaks dominating on the chromatograms of bottom sediments (>10 %).

Table 3. Predominant homologues (>10 %) of hydrocarbons in bottom sediments.

St.	Period											
	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.
st.1	C22, C31, C32	C28, C31	C29, C31, C32	C29, C31	C22, C31	-	C22	C22, C29, C31	C26	C28, C29, C32	C22	C28, C29, C30
st.2	C26, C28, C30	C26, C28, C30	C26, C28, C30	C26, C28, C30	C26, C28, C30	C28, C30	C26, C28	C26, C28, C30	C26, C28, C30	C26, C28, C30	C26, C28, C30	C28, C30
st.3	C17	C26, C28, C30	C26, C28, C31	C28	C28, C30	C30	C26, C29	C26, C28	C26, C28	C26, C28, C30	C26, C28, C31	C26, C28

The following group of indexes (TMD, C_{31}/C_{19}, TAR, $\Sigma C_{25-35}/\Sigma C_{15,17,19,21}$) allows us to establish a nature of organic substances origin in bottom sediments indicating a predominantly allochthonous (terrestrial) origin of n-alkanes (Table 4): The Alkterr index shows how the accumulation of terrestrial material increased as it moved from the river to the sea; this ratio increased from 0.11 to 0.26, which reflected an increase in the proportion of allochthonous compounds. Probably, substances introduced by river runoff were deposited in this area. A similar phenomenon was described in the study of hydrodynamics and transport processes in estuarine areas and adjacent water areas of the other rivers in the world [1,13,49]. At the same time, the C_{31}/C_{29} ratio demonstrated a significant contribution of herbaceous vegetation to the formation of the composition of n-alkanes in the bottom sediments of the Chernaya River. All these peaks are a reflection of the biogenic nature of organic substances. In particular, odd compounds C_{17} are mainly the result of the functioning of the phytoplanktonic community; C_{29} and C_{31} are terrestrial plants. Even homologues, such as C_{22}, are often associated (in combination with CPI values close to 1) with the microbial destruction of organic substances [22,29,50]. From the considered chromatograms, it follows that the peaks C_{29} and C_{31} associated with the high terrestrial vegetation had a significant percentage at st. 1 almost throughout the year. Also, in 25% of cases, such a peak was dominant at st. 3. At st. 2, even high-molecular homologues (C_{26} – C_{32}) prevailed in 100% of the samples. Compounds C_{26}, C_{28}, C_{30}, and C_{32} are evidence of the presence of the so-called sapropel substance [51]. It is mainly formed due to the organic mass of phyto-, zoobenthos, and plankton and is autochthonous for marine and freshwater ecosystems. Apparently, the accumulation of such homologues in the area of st. 2, where the salinity is 16‰, was associated with the intensive synthesis of organic compounds in the "biological zone" of the marginal filter of the river [1,13]. The predominantly biogenic origin of hydrocarbons was also indicated by low CPI_2 values for this zone. Thus, it could be assumed that in the area of the Inkerman automobile bridge (st. 2) there is the last, third section of the marginal filter of the river – a biological one, characterized by high indicators of the content of biogenic hydrocarbons. As a result of the study of diagnostic indexes, a set of information about possible sources of hydrocarbon intake into the waters of the Chernaya River estuarine zone was obtained. The correlation analysis showed the absence of a significant correlation (r = -0.39 – 0.26) between the concentration of n-alkanes and the calculated molecular indexes; therefore, this statistical method didnot allow us to judge the significance of the contribution of certain sources to the formation of n-alkanes in the bottom sediments of the studied area. In order to organize and classify this information, principal component analysis

(PCA) was used (Figure 5). As a result, the "stone filling" method revealed three leading factors that explained most of the variance (66.79 %). Factors describing less than 10 % of the variance are not considered in this paper. The first of them is PC1, which explains that 36.53% of the total variation of c is associated with $C_{15} – C_{25}$, $C_{27 – 35}$ n-alkanes, i.e., it is determined by the content of almost all the identified n-alkanes of different nature. On this basis, we can conclude that there is a mixed path of hydrocarbons entering the water area. It is also closely related to the sum of n-alkanes. In this case, we can judge the low role of homologues $C_{11} – C_{14}$, $C_{26,}$ and C_{36} in the formation of this conditional factor. It can be assumed that this consequence follows from their unstable presence in the analyzed environment. The second factor PC2 (19.52% variability) is associated with heavy even homologues of C_{26} and C_{28}, which have an autochthonous nature; the indexes UCM/n-alkanes, Paq, TAR, ACL, TMD, CPI_2, Alkterr, NAR, and C_{31}/C_{19} in general, connect it with allochthonous organic matter and bacterial destruction. The smallest share of variance is accounted for by the PC3 factor (10.74 %). It is associated with the indexes LWH/HWH, TMD, and $C_{15} – {}_{25}/C_{15,17,19,21}$; this group of parameters, in our case, characterizes mainly allochthonous routes of organic substances entering the bottom sediments of the water area. Judging by the n-alkanes individual composition of the bottom sediments of the Chernaya River estuary, it can be noted that allochthonous intake of HC prevails in the studied polygon. The role of bacterial destruction of organic substances processes is also great. In the area of the river's confluence with the bay (st. 2), the predominance of the processes of biological synthesis of autochthonous organic compounds is highlighted. This is probably due to the fact that the sampling station falls into the "biological zone" of the marginal filter, which is the usual part of the "river-sea" mixing zone and is characterized by high values of primary production [1]. In the marine part of the area (st. 1), the accumulation of petrogenic n-alkanes was noted, which is most likely the result of anthropogenic oil pollution of the water area. An active accumulation of allochthonous compounds of biogenic nature is also recorded in this area.

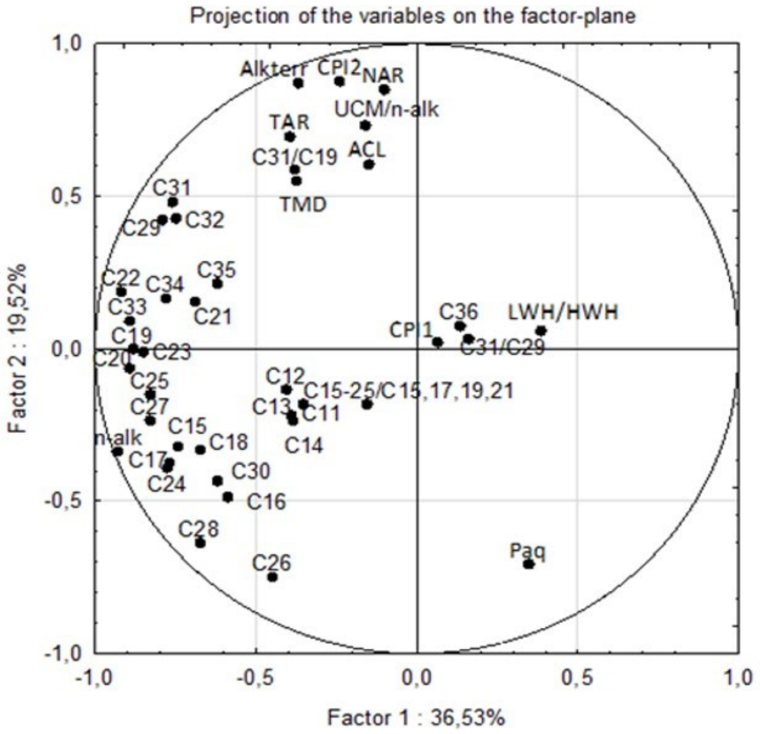

Fig. 5. Principal component analysis (PCA) for n-alkanes and diagnostic molecular markers for bottom sediments of the of the Chernaya River estuarine zone.

Table 4. Molecular markers of hydrocarbons in bottom sediments.

	March	April	May	June	July	Aug.	Sept.	Oct,	Nov,	Dec.	Jan,	Feb.	Av.	±
UCM/n-alkanes														
st.1	14	12	13	11	14	6	16	13	10	18	15	5	12	1,1
st.2	6	5	4	4	3	9	5	5	5	8	7	6	6	0,5
st.3	7	7	6	6	7	10	3	3	6	5	5	3	6	0,6
ACL														
st.1	29,6	29,6	29,8	29,7	30,0	29,8	29,2	29,6	29,9	29,2	28,8	29,4	29,54	0,10
st.2	28,6	29,1	29,1	28,9	28,8	29,4	28,5	28,6	28,7	29,7	30,1	29,3	29,07	0,14
st.3	29,7	29,2	29,5	28,7	29,8	29,4	28,9	28,4	29,3	29,0	28,5	28,5	29,07	0,14
TMD														
st.1	1,86	1,21	2,66	1,78	1,83	1,21	0,99	2,66	1,65	2,67	1,25	1,90	1,81	0,17
st.2	1,46	1,78	1,06	0,85	1,59	1,33	0,95	1,31	1,78	2,50	1,40	1,83	1,49	0,13
st.3	0,36	1,24	1,28	0,74	0,82	0,61	0,79	1,78	1,59	2,79	0,79	0,63	1,12	0,19
NAR														
st.1	-0,08	-0,24	0,02	-0,03	-0,11	-0,05	-0,01	0,01	-0,17	-0,24	-0,18	-0,21	-0,11	0,03
st.2	-0,48	-0,55	-0,57	-0,45	-0,64	-0,59	-0,34	-0,27	-0,38	-0,41	-0,54	-0,26	-0,46	0,04
st.3	-0,23	-0,63	-0,62	-0,36	-0,37	-0,26	-0,71	-0,60	-0,51	-0,58	-0,40	-0,57	-0,49	0,05
CPI 1/CPI2														
st.1	1,23/ 1,12	1,15/ 0,62	1,34/ 1,21	0,91/ 1,15	0,92/ 1,09	1,42/ 0,97	1,42/ 1,08	1,03/ 1,40	1,11/ 0,80	0,95/ 0,81	1,05/ 0,84	1,08/ 0,73	1,13/ 0,98	0,05/ 0,07
st.2	1,36/ 0,38	1,04/ 0,30	1,33/ 0,24	1,11/ 0,28	0,84/ 0,22	0,99/ 0,23	1,13/ 0,43	1,49/ 0,56	1,17/ 0,42	0,97/ 0,46	0,98/ 0,31	1,13/ 0,64	1,13/ 0,37	0,05/ 0,04
st.3	1,34/ 0,46	0,98/ 0,23	1,04/ 0,24	0,96/ 0,45	1,06/ 0,46	1,06/ 0,50	1,20/ 0,12	1,33 /0,24	1,34/ 0,35	1,23/ 0,28	1,12/ 0,34	1,13/ 0,21	1,15/ 0,32	0,04/ 0,03
LWH/HWH														
st.1	0,26	0,35	0,23	0,38	0,39	0,40	0,55	0,27	0,32	0,21	0,32	0,30	0,33	0,03
st.2	0,23	0,19	0,26	0,34	0,17	0,21	0,41	0,33	0,23	0,15	0,25	0,30	0,26	0,02
st.3	1,06	0,21	0,23	0,61	0,59	0,73	0,18	0,15	0,20	0,08	0,43	0,42	0,41	0,08
Paq														
st.1	0,33	0,39	0,16	0,19	0,18	0,27	0,34	0,17	0,25	0,32	0,38	0,19	0,26	0,02
st.2	0,44	0,46	0,32	0,39	0,44	0,34	0,47	0,35	0,45	0,23	0,36	0,20	0,37	0,03
st.3	0,52	0,45	0,42	0,40	0,23	0,42	0,53	0,52	0,37	0,48	0,53	0,42	0,44	0,02
C31/C19														
st.1	4,23	3,30	4,24	2,96	3,41	1,74	1,37	2,98	2,23	0,68	4,22	1,75	2,76	0,35
st.2	0,73	2,38	1,05	1,18	1,65	1,83	1,06	1,39	1,92	2,50	3,77	2,08	1,80	0,24
st.3	0,43	1,75	1,50	0,87	1,62	0,78	1,03	1,03	1,54	3,94	1,28	0,71	1,37	0,26
C31/C29														
st.1	2,30	5,85	1,35	0,77	1,75	1,22	1,40	0,73	1,50	0,12	0,89	0,65	1,54	0,43
st.2	0,48	3,53	1,10	1,18	1,49	2,03	1,25	0,79	2,21	0,77	8,03	0,83	1,97	0,60
st.3	1,62	1,22	1,37	1,30	1,75	1,71	1,38	1,52	1,07	5,09	1,81	0,63	1,71	0,32
TAR														
st.1	2,38	1,55	3,45	2,21	1,91	1,60	1,10	3,27	1,86	2,46	2,04	2,00	2,15	0,20
st.2	1,22	1,36	0,94	0,99	1,41	1,48	1,01	1,36	1,87	2,92	1,26	1,80	1,47	0,16
st.3	0,22	1,00	1,08	0,62	0,77	0,52	0,74	1,39	1,26	3,02	0,65	0,55	0,98	0,21
Alkterr														
st.1	0,26	0,18	0,35	0,29	0,28	0,25	0,21	0,35	0,25	0,25	0,20	0,25	0,26	0,01
st.2	0,13	0,13	0,12	0,12	0,11	0,12	0,13	0,18	0,16	0,20	0,14	0,24	0,15	0,01
st.3	0,07	0,11	0,12	0,12	0,15	0,12	0,06	0,12	0,15	0,13	0,10	0,08	0,11	0,01
ΣC25-35/ ΣC15,17,19,21														
st.1	2,98	2,43	3,90	2,18	2,10	1,91	1,40	3,17	2,70	4,12	2,15	2,80	2,65	0,23
st.2	3,87	5,20	3,61	2,57	5,56	4,55	1,99	2,58	3,93	5,53	3,85	2,92	3,85	0,34
st.3	0,74	4,24	4,71	1,34	1,55	1,12	4,78	6,22	4,31	10,82	1,98	2,00	3,65	0,83

4. Conclusions

1. The content of HC ranged from 72 to 1739 μg/g in the bottom sediments of the Chernaya River estuarine zone. The concentration of HC in the bottom sediments in the marine part of the study area was statistically significantly higher than in the estuarine and riverine. The concentration of AHC ranged from 15 to 299 μg/g. The amount of n-alkanes ranged from 8 to 123 μg/g. No statistically significant differences were marked in the content of AHC and n-alkanes at different sites of the polygon.

2. The annual dynamics of the content of HC, AHC, and n-alkanes in the bottom sediments of the studied area were not revealed. At the same time, there is a trend towards an increase in the content of the studied components of the hydrocarbon composition of bottom sediments from February to May.

3. During the study period, n-alkanes in the range C_{11}-C_{36} were identified in the estuary zone of the Chernaya River. In most of the samples, the range of the studied compounds was C_{13}-C_{35}. The spatial-temporal variability of the individual composition of n-alkanes is noted. It can be assumed that in the area of the Inkerman automobile bridge, there is the last biological section of the marginal filter, characterized by high indicators of the biogenic hydrocarbon content.

4. The estuary of the Chernaya River is relatively safe in terms of oil pollution. Chronic oil pollution (degraded hydrocarbons) was noted in the area of the river's confluence into the Sevastopol Bay.

5. A group of diagnostical indexes displayed a predominantly allochthonous (terrestrial) origin of n-paraffins. The accumulation of terrestrial material increased as it moved from the river to the sea.

6. As a result of the study of diagnostic indexes, three leading factors were identified that explained most of the variance (66.79 %). The most significant one was PC1, which explains 36.53 % of the total variation; it was associated with n-alkanes of length C_{15}-C_{25}, C_{27}- C_{35}, i.e., it is determined by the content of almost all identified n-alkanes of different nature. The second factor of PC2 (19.52% variability) was associated with heavy even homologues of C_{26} and C_{28}, which have an autochthonous nature. The indexes UCM/n-alkanes, Paq, TAR, ACL, TMD, CPI_2, Alkterr, NAR, and C_{31}/C_{19}, in general, connect it with allochthonous, including oil, organic matter, and bacterial destruction. The smallest percentage of variance was accounted for by the PC3 factor (10.74 %). It is associated with the indexes LWH/HWH, TMD, and $C_{15-25}/C_{15,17,19,21}$; this group of parameters, in our case, characterized mainly allochthonous routes of organic substances entering the bottom sediments of the water area.

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