

# Distribution and Genesis of Hydrocarbons in Water and Sediments of the Kerch Strait

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**Abstract**—The content and composition of hydrocarbons (aliphatic hydrocarbons – AHCs and polycyclic aromatic hydrocarbons – PAHs) in the marine surface suspended particulate matter and surface bottom sediments of the Kerch Strait in April and September 2019 are presented. Despite the high AHCs concentrations in surface waters (56–186 µg/L), their composition differ from oil alkanes due to their rapid degradation and the influence of pyrogenic emissions from watercrafts. Low PAHs concentrations (5–9 ng/L) in marine suspended matter are caused by their lower contents in the emission sources, as well as by the current pattern in the strait. In the coarse-grained bottom sediments, the concentrations of AHCs (1–63 µg/g) and PAHs (1–728 ng/g) were also lower than those in other Black Sea areas. The use of factor analysis showed that the main source of pollution is pyrogenic (combustion products of marine fuel). To a lesser extent, the composition of PAHs is affected by the influence of runoff from the mainland and the flow of oil products from shipping.

**Keywords:** aliphatic and polycyclic aromatic hydrocarbons, Kerch Strait, suspended particulate matter, bottom sediments, factor analysis

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## INTRODUCTION

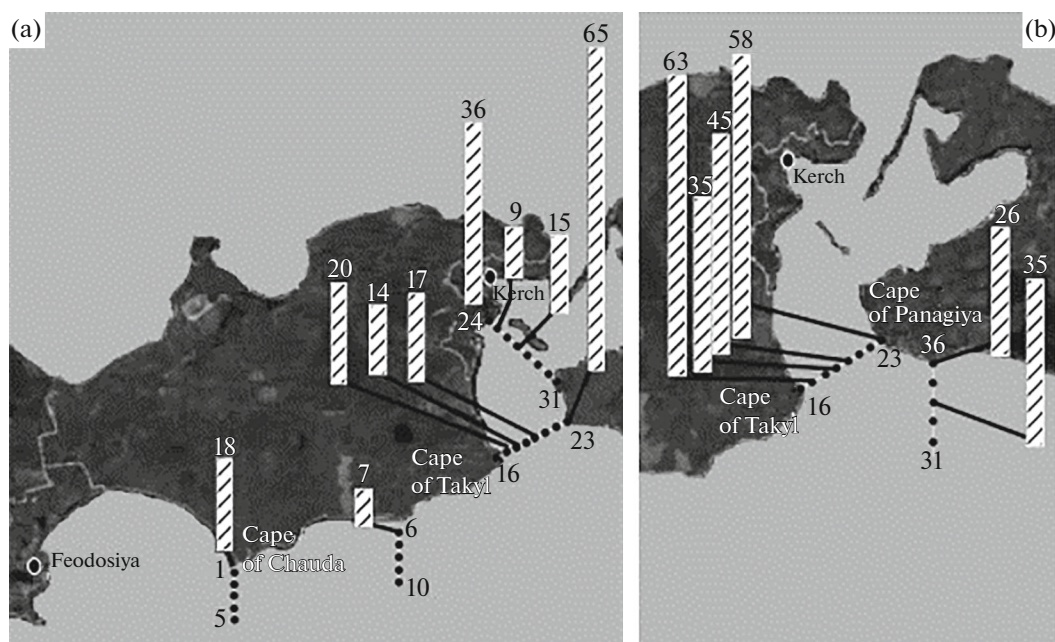
The Black Sea at present is a zone of the Russian oil export (Matishev et al., 2013). Long-term satellite monitoring showed that the oil films in the Russian sector of the sea are mainly accumulated in the Kerch Strait and waters of the Novorossiysk and Tuapse ports (Lavrova et al., 2016; Ivanov et al., 2017). Services for oil delivery, as well as anchorage and high-load recreational sites are restricted to the Kerch Strait. Need for bottom dredging accompanying by dumping of extracted ground, hydrotechnical building, as well as influx of hydrocarbons (HCs) from mud volcanoes in the strait waters affect the biotic and abiotic elements of the Kerch Strait ecosystem (Ovsyanyi et al., 2015; Ereemeev et al., 2003; Lomakin and Spiridonova, 2010; Shnyukov et al., 2010). Therefore, a special attention is focused on study of sea pollution by petrogenic hydrocarbons (PHs) (*Quality of Marine ...*, 2016, 2019; Nemirovskaya et al., 2017; Temerdashev et al., 2017; Tiganus et al., 2013, and others).

Taken into account the wide diversity of HC sources, of great importance is the determination of hydrocarbon genesis. This problem is additionally complicated by the migration species of HCs, phase transitions at the geochemical barriers, and hydrological features of marine environment. Therefore, it is

necessary to choose markers, which provide insight into the genesis of anthropogenic and natural HCs.

Due to the multicomponent composition of oils, the analyses of bulk HCs contents are of interest only at the initial stages of pollution study. Nevertheless, oil pollution is frequently identified using aliphatic HCs (AHCs) (*Quality*, 2019; Temerdashev et al., 2017, and others), which are ascribed to major oil components. However, the high natural AHC background and variability of their contents and composition under the influence of different processes in the sea significantly complicate the representative estimate of petrogenic pollution. The study of oil pollution mainly involves the determination of two major hydrocarbon classes: AHCs and polycyclic aromatic hydrocarbons (PAHs) (Nemirovskaya, 2013; Alberty and Reif, 1988; AMAP, 2007; Readman et al., 2002; Wakeham, 1996; Yunker et al., 2015, and others), or only PAHs, which are ascribed to resistant organic pollutants (AMAP, 2017; Monitoring, 2011; Morales-Coselles et al., 2017; Tiganus et al., 2013, and others).

In order to establish the pollution of the Kerch Strait, the PAHs content and composition were determined compared to AHCs content in the surface waters and bottom sediments at the end of April and beginning of September, 2019 (Fig. 1). The Kerch



**Fig. 1.** A location scheme of sampling stations along sections in the Kerch Strait and concentrations of aliphatic hydrocarbons ( $\mu\text{g/g}$ , numerals above columns) in the top bottom sediments in April (a) and September (b) in 2019. Station numbers are marked in black under the columns

Strait and Feodosia Gulf were studied in April 2019 (Fig. 1a), whereas in September were analyzed the Kerch pre-strait region: along sections near the Capes of Takyl and Panagiya and the strait proper (Fig. 1b).

The HCs markers are applied to determine the main sources of hydrocarbons: petrogenic, pyrogenic, and biogenic (Nemirovskaya, 2017; Khaustov and Redina, 2017; AMAP, 2007; Savinov et al., 2000). Mainly alkyl-substituted low-molecular-weight arenes are formed under comparatively mild conditions of crude oil formation, whereas high-temperature burning produces non-alkylated overcondensed PAHs: pyrenes, benzo- and indopyrenes (AMAP, 2007). The PAH genesis is determined using concentration ratios of individual polyarenes, in particular, less stable unsubstituted isomers to the more stable ones, kinetic to thermodynamic (Yunker and McDonald, 1995), substituted to unsubstituted, or lighter 2 to 3-ring to the heavier 5–6 ring ones (AMAP, 2007; Savinov et al.; 2000; Yunker et al., 2015). PAHs are characterized by reactions of electrophilic substitution, which leads to the formation of peculiar individual compounds at phase transitions unlike matters involved in addition reactions (AMAP, 2017; Savinov et al., 2000). In particular, hydrophobic properties of PAHs suggest their vertical migration with aerosols from atmosphere in water, and then with suspended particulate matter in bottom sediments.

## METHODS

Water samples were collected by plastic bathometers (Rosette system) at hydrological stations. Sus-

pended particulate matter for study of lipids, AHCs, and  $C_{\text{org}}$  was extracted by filtration at 0.2 atm on preliminarily heated GF/F (0.7  $\mu\text{m}$  pore size) fibrous glass filters. Its content was determined by weighing on 0.45  $\mu\text{m}$  nuclear filters preliminarily washed with HCl. PAHs were determined in April only in sediments, and in suspended matters and bottom sediments in September.

Bottom sediments (layer 0–3 cm) were sampled by bottom grab and frozen at  $-18^{\circ}\text{C}$ . From surface layers of different color, we collected 0–0.5 cm ginger oxidized layer and 0.5–3 cm reduced gray layer. For analysis in stationary laboratory, samples were unfrozen, dried at  $50^{\circ}\text{C}$ , and analyzed for sediment moisture.

Air-dried particulate suspended matter and bottom sediments (fraction 0.25–0.5 mm) dried on a Sappir ultra-sound bath were treated with methylene chloride to extract the total fraction (lipids). HCs were alloted using silica gel column chromatography: AHCs were alloted with hexane, while PAHs, with a hexane–benzene mixture (3 : 2) (Venkatesan and Kaplan, 1987). The concentrations of lipids (prior to applying silica gel column chromatography) and AHCs (after applying column chromatography) were based on  $2930\text{ cm}^{-1}$  band by IR-method on an IRAffinity-1 Shimadzu (Japan) spectrophotometer using a mixture (in volume) of 37.5% isooctane, 37.5% hexadecane, and 25% benzene as standard (GSO 7248-96, manufactured by AOZT Ekros). The sensitivity of the method is  $4\text{ }\mu\text{g/mL}$  of extract (Nemirovskaya, 2013). This method is used as arbitration in analysis of PHs (*Quality...*, 2016, 2019).

Organic carbon ( $C_{org}$ ) in bottom sediments was determined by a dry combustion on an AN-7560 analyzer. AHC concentrations in sediments were recalculated for  $C_{org}$  using coefficient of 0.86.

The composition of alkanes was determined by gas chromatography on a Cristall-Lyuk 4000-M device using flame-ionization detector, 30 m × 0.22 mm Supelco capillary column with a phase consisting of 5% phenyl and 95% methylpolyxilane, at temperature programmed from 60 to 300°C, with a rate of 8°/min, and helium as carrier gas (flow velocity of 1.5 mL/min).

The PAHs content and composition were determined by a high-performance liquid chromatography on an LC-20 Shimadzu Prominence chromatograph, using an Envirosep PP column at a thermostat temperature of 40°C, in a gradient regime (from 50 to 90 vol % acetonitrile in water) with an RF-20A fluorescent detector, and at an effluent rate of 1 cm<sup>3</sup>/min. The calculations were made with the LC Solution software. The device was calibrated on individual PAHs and their mixtures (manufactured by Supelco). Thus, the following EPA-recommended individual polyaerenes were determined (*Monitoring...*, 2011): naphthalene (*Naph*), 1-methylnaphthalene (*M\_Naph*), 2-methylnaphthalene (*2M\_Naph*), acenaphthene (*Ace*), fluorene (*Flu*), phenanthrene (*Phen*), anthracene (*Antr*), fluoranthene (*Flt*), pyrene (*Pyr*), benzo[a]anthracene (*BaA*), chrysene (*Chr*), benzo[e]pyrene (*BeP*), benzo[a]pyrene (*BaP*), dibenzo(a,h)anthracene (*DbA*), benzo(g,h,i)perylene (*BPI*), indeno(1,2,3-c,d)pyrene (*Ip*), and benzo(b)fluoranthene (*BbFlu*).

Obtained material is based on the determination of AHCs content in 65 samples of suspended particulate matter and 31 samples of bottom sediments; measurement of alkane composition in 19 samples of suspended particulate matter and 21 sediment samples; and analysis of PAHs content and composition in 5 samples of suspended particulate matter and 21 sediment samples.

The PAHs sources were identified using correlation analysis, as well as factor analysis (principal component analysis in combination with varimax rotation and Kaiser normalization) to reveal optimal (most informative) signs in a multivariate space (Savinov et al., 2000; Yunker et al., 2015).

## RESULTS AND DISCUSSION

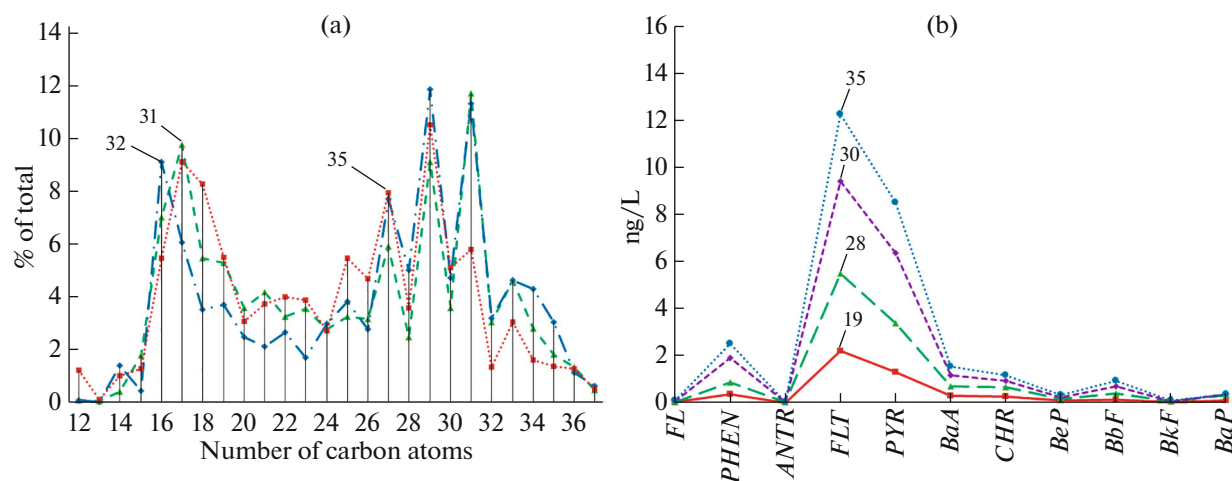
Obtained data showed that the highest AHC concentrations in suspended matter of surface waters occur directly at the Kerch Strait. In particular, the AHC concentrations in April varied within 110–160 µg/L in the Kerch Strait and 70–110 µg/L in the Feodosia Gulf (Nemirovskaya et al., 2020). The elevated average AHC fraction of 72% in lipids compared to 38% in the central part of the sea may indicate the presence of petrogenic HCs. A relative increase of AHC concentrations in lipids is caused by the influx of petrogenic products (Nemirovskaya, 2013).

In September, in spite of some decrease of AHC concentrations (on average, 93 µg/L), their content remained sufficiently high and even at low values at stations 12 (56 µg/L) and 22 (55 µg/L), they exceeded 50 µg/L, which is MAC for petrogenic HCs. These concentrations seemed to be higher than in the surface waters in the Tuapse Harbor area, the other “hot spot” in the Black Sea Zone of the Russian Federation (Larova et al., 2016). In this area, the content of AHC varied from 16 to 49 mg/L, averaging 29 mg/L, and reached 275 µg/L in the Tuapse River at suspended matter content of 16.2 mg/L (Nemirovskaya et al., 2020).

The alkane concentrations in most samples in the Kerch Strait area varied within 0.19–1.05 µg/L, which accounts for as low as 0.4–0.7% AHCs. Chromatogram pattern differs from that of petroleum alkanes, which is characterized by a gentle distribution of homologs (Fig. 2a). The low-molecular region was dominated by either phytoplankton alkanes ( $n-C_{17}$ ) or microbial even-numbered homologs ( $n-C_{16}$ ,  $n-C_{18}$ ) typical of alkanes from surface sea waters (Nishumura and Baker, 1986) and waters of the Black and Azov seas (Temerdashev et al., 2017). The high-molecular-weight homologs were dominated by odd-numbered  $n-C_{25}$ – $C_{31}$  homologs, which is typical of the higher plant wax (Corner, 1998; Yunker et al., 2015).

The PAHs content in the suspended matter of surface waters varied from 5 to 9 ng/L (Table 1). It consists mainly of fluoranthene (*Flt*) and pyrene (*Pyr*) (Fig. 2b). The combustion products of different types of fuel are usually dominated by *Pyr*. However, due to the lower stability, it experienced more rapid degradation than *Flt* (Rovinsky et al., 1988). The *Flt*/(*Flt* + *Pyr*) ratio changed in the different parts of the Kerch pre-strait region within a comparatively narrow range of 0.57–0.63. This is typical of fresh pollution, since *Flt* concentrations in degraded PAHs are much higher than *Pyr* (Nemirovskaya, 2013; Khaustov and Redina, 2017). The low *Naph*/*Phen* ratios (0.05–0.11) could indicate significant an input of oil arenes.

The bottom sediments of the Kerch pre-strait region have the low contents of  $C_{org}$ , AHCs, and PAHs. Their average contents during April and September surveys varied within following ranges: 0.49–0.63%  $C_{org}$ , 21–38 µg/g AHCs –, and 202–277 ng/g PAHs. This is related to the fact that seafloor adjacent to the Kerch Peninsula coast is made up of sands, which are developed to depths of 3–5 m (Ovsyanyi et al., 2015). A shallow coastal, narrow band of strait bottom is occupied by sand, pebble, and shell deposits (Ovsyanyi et al., 2015; Shnyukov et al., 2010). The concentrations of organic compounds are mainly controlled by the grain-size composition of sediments. The  $C_{org}$  content is correlated with moisture of sediments (Mois.), which depends on their lithological composition, with correlation coefficients ( $r$ ) in the surface layer varying from 0.77 in April) to 0.87 in September.



**Fig. 2.** Composition of alkanes (a) and PAHs (b) in samples of suspended matter in separate stations. (19, 28....35 are station numbers).

The PAHs content in the bottom sediments shows wider variations compared to AHCs: 1.2–728 ng/g (by 607 times). Such a wide range of concentrations is caused by diverse sources of polyarene and variability of individual compounds in sedimentation processes. Nevertheless, the grain-size composition of the sediments unambiguously affects the PAHs distribution, since minimum (at st. 6, sandy sediment) and maximum (st. 17, silty ooze) contents are correlated with the minimum (0.017, 20%) and maximum (1.492, 58%) contents of  $C_{org}$  and moisture.

In spite of the different HCs sources,  $C_{org}$  correlates with AHCs in surface sediments, with correlation coefficients varying from 0.84 in September to 0.93 in April. The AHC and PAHs concentrations also show correlation, with similar correlation coefficients for different seasons:  $r(\text{AHCs-PAHs}) = 0.75$ . This is caused by a rapid transformation of different hydrocarbons classes during input in bottom sediments. It should be noted that similar dependences in the AHCs and  $C_{org}$  distribution with  $r(\text{AHCs-}C_{org}) = 0.81$  were noted in sandy sediments during high water periods in the branches of the Severnaya Dvina mouth, in spite of the influx of great amount of suspended particulate matter that absorbed diverse pollutants in the river water during this period (Nemirovskaya, 2013). The latter may also indicate similar pathways for natural and anthropogenic compounds in bottom sediments. Correlation of  $C_{org}$  with AHC concentrations is absent only at extremely high concentrations of the latter (up to 329  $\mu\text{g/g}$ ). In particular, the Kuznichikha arm of the branch of the Severnaya Dvina mouth is characterized by  $r(\text{Mois.-AHCs}) = 0.28$ ,  $r(C_{org}\text{-AHCs}) = 0.19$  ( $n = 8$ ).

The PAHs composition in the bottom sediments of the Kerch Strait was more diverse compared to that of particulate matter (Figs. 2b and 3). The latter is caused by their higher concentrations in sediments. The frac-

tion of low-molecular-weight PAHs in the suspended matter was no more than 12% and consisted mainly (71–74%) of *Flt* + *Pyr*, whereas naphthalenes in sediments varied within 2.2–23.0%, with maximum at st. 34. The elevated content of naphthalenes marking petrogenic HCs typical of bottom sediments near the Cape of Chauda at st. 1 is 7.9–8.4%, and varies within 14.6–23.0% in the Kerch Strait.

In spite of the wide range of total PAHs, the correlation analysis revealed tight relations between individual polyarenes. The lowest correlation with total PAHs was shown for naphthalene and its homologs, which are the lightest, volatile, and most soluble among identified HCs (Parra et al., 2020).

The results of PAHs accumulation in the bottom sediments and particulate matter are most clearly seen in the dendrogram of the cluster analysis (Ward Method, Euclidean distance, Fig. 4). Based on the molecular weights, PAHs are subdivided into two groups: the lightest (naphthalene and its homologs, fluorene, and phenantrene) and high-molecular weight hydrocarbons forming in pyrogenic processes.

Cluster analysis of PAHs made it possible to divide samples into the following classes.

Class 1: sediments and suspended matter with the highest PAHs contents (from 325 to 728 ng/g in sediments), which were dominated by *Flt* (in 12% of samples);

Class 2: sediments and suspended matter with “average” concentrations of total PAHs (from 18 to 173 ng/g in sediments), with the predominance of *Flt* (in 13% of samples).

Class 3: sediments and suspended particulate matter with low total PAHs concentrations (from 1.20 to 129 ng/g in sediments), which consisted mainly of *Flt*, *Phen*, and *Pyr* (in 17, 12, and 11% of samples, respectively).

**Table 1.** Concentrations of organic compounds at some stations and distribution of markers in PAHs composition

Station	Horizon, cm	AHCs, µg/g	C <sub>org</sub> , %	ΣPAHs, ng/g	% ΣNaph of ΣPAHs	Flt/ Pyr	ΣNaph/ Phen	(Pyr + Flt)/ (Phen + Chr)	Phen/ Antr	Antr/ (Antr+Phen)	BaA/ (BaA+Chr)	Flt/ (Flt + Pyr)	BaP/ (BaP+BeP)
Suspended matter*, September													
14	0	114	130	14	0.93	1.60	0.11	2.46	60.0	0.02	0.65	0.62	0.19
19	0	96	160	11	0.72	1.72	0.10	2.07	41.0	0.02	0.52	0.63	0.49
27	0	111	272	14	0.63	1.55	0.10	2.43	93.0	0.01	0.53	0.61	0.78
30	0	138	240	20	0.59	1.32	0.05	2.23	76.7	0.01	0.60	0.57	0.14
35	0	86	114	17	1.02	1.32	0.11	2.57	75.0	0.01	0.61	0.57	0.14
Sediments, April													
1	0-3	18	0.062	18	7.91	2.58	0.37	0.29	22.7	0.04	0.00	0.45	0.60
6	0-3	7	0.017	1	n.d.	2.50	-	0.50	-	-	-	-	-
17	0.5-3	20	0.752	631	2.25	1.55	0.45	0.93	3.0	0.25	0.41	0.08	0.47
18	0-3	14	0.327	135	7.13	1.48	1.00	0.65	5.6	0.15	0.40	0.15	0.47
20	0-3	17	0.225	71	4.51	1.89	0.53	0.61	10.7	0.09	0.40	0.17	0.45
24	0.5-3	36	1.072	599	3.67	1.49	0.79	0.93	4.0	0.20	0.41	0.10	0.46
25	0-3	9	0.180	79	5.70	1.41	0.52	0.64	9.6	0.09	0.37	0.14	0.48
27	0-3	15	0.21	90	6.22	1.36	0.68	0.67	7.6	0.12	0.38	0.14	0.50
Sediments, September													
1	0-3	18	0.287	129	8.40	1.54	0.75	0.44	10.6	0.09	0.35	0.32	0.44
2	0-3	16	0.215	43	7.29	1.41	1.50	0.67	8.5	0.11	0.33	0.15	0.43
3	0-0.5	40	0.512	173	6.89	1.50	0.80	0.47	11.2	0.08	0.33	0.06	0.48
3	0.5-3	26	0.407	365	2.71	1.71	0.38	0.32	3.1	0.24	0.57	0.19	0.41
4	0.5-3	22	0.507	284	6.38	1.63	0.84	0.59	7.8	0.11	0.43	0.28	0.50
5	0.5-3	40	0.785	489	3.58	1.42	0.79	0.74	7.6	0.12	0.40	0.14	0.48
17	0-0.5	63	1.432	728	4.26	1.44	0.84	0.66	6.4	0.14	0.43	0.16	0.45
17	0.5-3	43	1.132	477	7.70	1.48	0.97	0.60	8.7	0.10	0.37	0.25	0.46
19	0-0.5	35	0.622	325	7.36	1.26	0.95	0.54	9.3	0.10	0.34	0.24	0.48
19	0.5-3	30	0.44	176	6.18	1.41	0.65	0.51	11.7	0.08	0.33	0.21	0.49
20	0-3	45	0.325	86	14.58	1.78	1.01	0.45	15.1	0.06	0.26	0.33	0.40
34	0-3	48	0.123	55	23.02	1.53	1.29	0.70	19.8	0.05	0.16	0.64	0.47
36	0-3	26	0.164	55	16.28	1.53	0.78	0.47	19.8	0.05	0.07	0.41	0.48

\* In suspended matter concentrations of AHCs and C<sub>org</sub> are given in µg/L



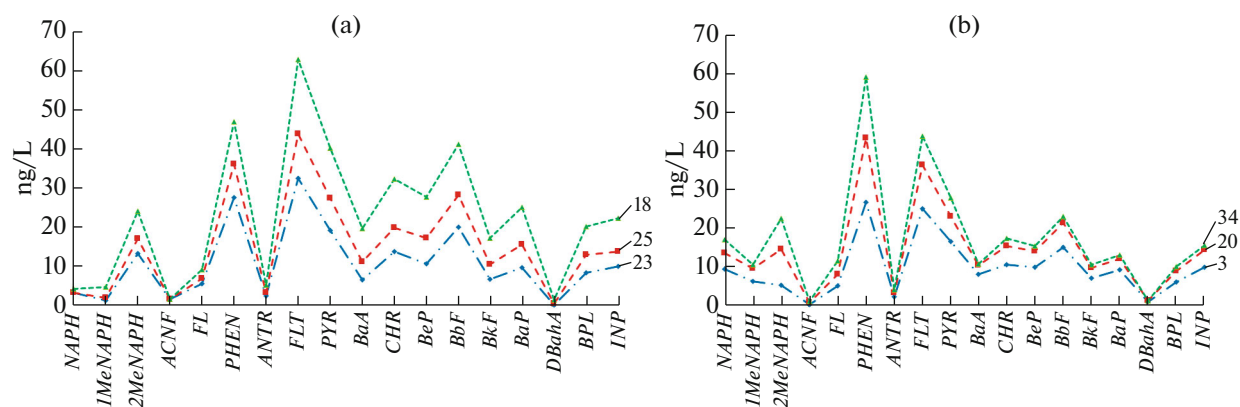


Fig. 3. Typical composition of PAH<sub>s</sub> in the bottom sediments in April (a) and September (b) in 2019. 18, 25 .... are station numbers.

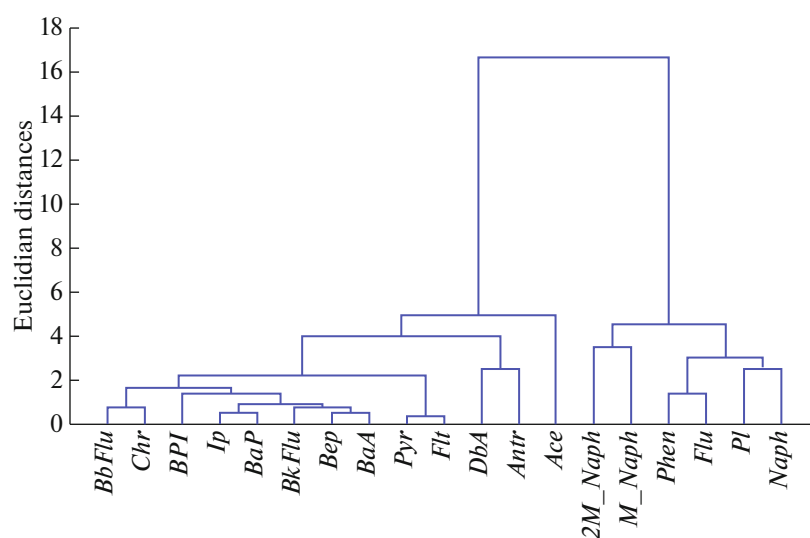


Fig. 4. PAH grouping based on results of cluster analysis of individual compounds.

The spatial distribution of objects was analyzed by the Principal Component Analysis, which allows the most efficient analysis of multivariate data. Obtained scheme of object distribution in planes PC<sub>1</sub> and PC<sub>2</sub> (Fig. 5) strongly supports the model of cluster classification, since data points are mainly grouped in a single cloud. “Anomalous” samples spaced far apart from the general group (Fig. 5a) are confined to stations: 19 (September, 0–0.3 cm), 17 (April, September 0–0.5, 0.5–3 cm); 5 (September, 0.5–3 cm), and 24 (April, 0–3 cm). Factor analysis of PAHs distribution in the objects (Fig. 5b) showed that the “anomalous” values are typical of PAHs presented in samples with the highest concentrations of *Flt*, *Phen*, and *Pyr*. Other polyarenes fall closely to each other and are arranged along PC<sub>1</sub> axis (Fig. 5b). This indicates similar dispersion of concentrations relative to the average values and comparatively homogenous hydrological–geochemical conditions of sedimentation.

The indicator ratios calculated for individual PAHs from available data made it possible to determine their origin (Table 2). Most part of markers indicate a pyrogenic origin of polyarenes in the suspended matter and bottom sediments. This is especially clearly confirmed by the *Flt*/(*Flt* + *Pyr*) ratio, which falls in the “pyrogenic” interval of values in 100% cases. A pyrogenic source of PAHs was also justified by the *BaA*/(*BaA* + *Chr*) ratio in 88.5% cases. Some markers point to a mixed origin of polyarenes (pyrogenic + petrogenic) in the objects; while others suggest the influence of photolysis caused by the pollution from oil-fired ships (Table 2).

Thus, our studies established the high AHC concentrations in suspended particulate matter of surface waters (>50 µg/L) and in the bottom sediments (>10 µg/g), which is the background level for AHCs in sandy sediments (*Quality of Marine...*, 2016, 2019; Tolosa et al., 2004). In spite of such high AHC con-

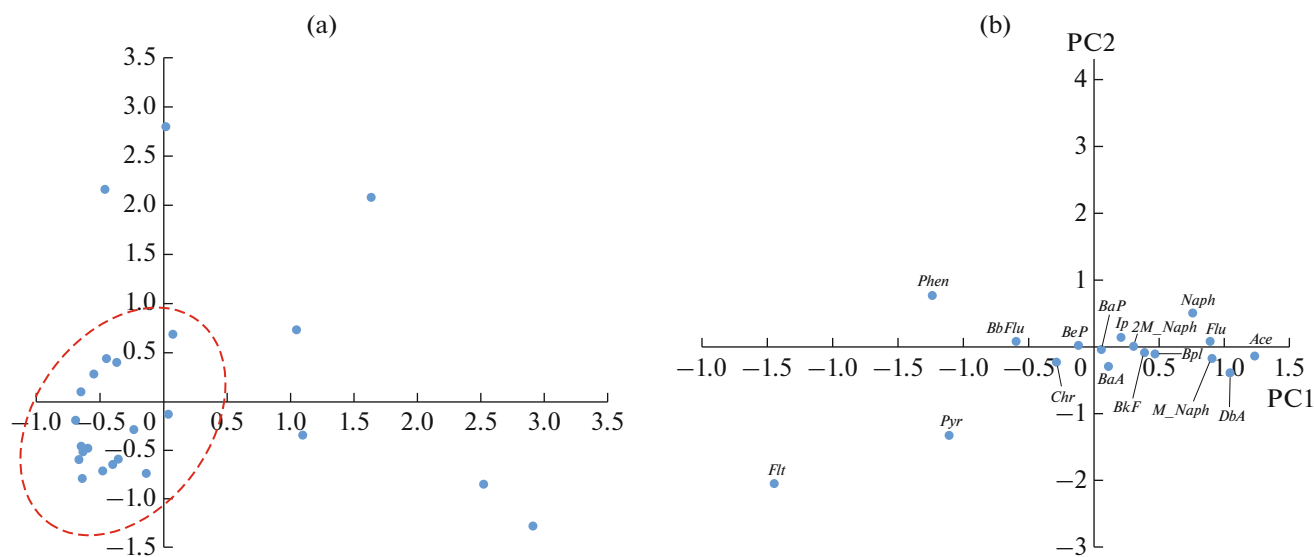


Fig. 5. Distribution of samples (a) and relationship of individual PAHs (b) based on results of component analysis.

centrations, the transformation of petrogenic HCs in marine environment and at the water–floor boundary leads to a radical change of their initial chemical composition, mainly due to the loss of light fractions and dissolution. The intensity of bacterial transformation increases with increasing water temperature. Therefore, the fraction of even-numbered low-molecular weight homologs in alkanes in surface waters increased during September survey. It was noted previously that the low-molecular-weight alkanes in the Black Sea waters were dominated by *n*-C<sub>16</sub>, -C<sub>17</sub>, -C<sub>18</sub> homologs, which have an autochthonous origin (Nemirovskaya et al., 2017; Temerd-

shev et al., 2017). As a result, the alkanes differed from petrogenic alkanes.

The water circulation in the Kerch pre-strait and a heterogeneity of the velocity field in the transverse section of the strait (Izhitskii and Zav'yalov, 2017) facilitate the accumulation of most pollutants not only in the strait, but also in the western part of the studied area, near the Capes of Chauda and Takyl.

The concentrations of AHCs and C<sub>org</sub> decreased during transition from oxidized to reduced layer, while the PAH content, in contrast, increased. The latter is likely determined by the elevated emission of pol-

Table 2. Indicator PAHs ratios, which characterize their genesis

Ratios	Possible PAHs genesis	% of cases
<i>Phen/Antr</i>	<10—fuel combustion >10—petrogenic origin	50 50
<i>Antr/(Antr + Phen)</i>	>0.1—fuel combustion <0.1—petrogenic origin	62 38
<i>BaA/(BaA + Chr)</i>	> 0.50—fuel combustion <≈0.20—petrogenic origin	89 11
<i>Flt/(Flt + Pyr)</i>	> 0.50—petrogenic oil origin	100
<i>BaP/BP</i>	>0.6—fuel combustion <0.60—not navigable source	81 19
<i>BaP/(BaP + BeP)</i>	≈0.5—fresh pollution <0.5—subjected to photolysis	16 84
<i>Ip/(Ip + BPI)</i>	< 0.2—petrogenic origin >0.2—pyrogenic origin	19 81
$\Sigma(2-3 \text{ rings})/\Sigma(5-6 \text{ rings})$	>1—petrogenic origin <1—fuel combustion	19 81

yarenes in 1950s in response to the coal combustion (Rovinsky et al., 1988).

It should be noted that owing to the coarse-grained composition of sediments, the PAHs content in the Kerch Strait was lower (Table 1) than in other regions of the Black Sea. In particular, in the mud sediments of the Romanian shelf, their concentrations ( $\Sigma 16$  PAHs) varied within 141–6983 ng/g, and were within 0.4–1703 ng/g in the Stambul Strait, Turkey ( $\Sigma 8$  PAHs) (Tiganuş et al., 2013)

Due to their structural features, PAHs most completely reflect the kinetics of vertical and horizontal migration of anthropogenic HCs fluxes (Khaustov and Redina, 2017; Morales-Coselles et al., 2017; Yunker et al., 2015). The indicator ratios of PAHs composition applied to reveal sources of anthropogenic pollution demonstrated high-temperature fuel combustion (Kucuksezgin et al., 2013), as follows from the pyrogenic genesis of PAHs in most samples. This can be confirmed also by the distribution of total PAHs concentration. In particular, the highest pollution levels were established at stations 17, 19, and 24 with silted sediments (Table 1). The main source of the pollution is the emission of oil combustion products by ships. The same conclusion was made during the study of the Black Sea shelf of Romania (Tiganuş et al., 2013), where the proportions of markers (PAHs) of bottom sediments indicated that the pollution was caused by high-temperature pyrolytic processes. Thereby, 2011–2012 data showed that the bottom sediments of the Asian Black Sea sector were classified as polluted (17% of samples) and strongly polluted (65%) sediments (Traven et al., 2008).

The discovery of naphthalene and its homologs in all samples among PAHs of bottom sediments was unexpected because they were practically completely absent in the suspended matter. Obviously, these arenes supplying in bottom sediments in response to maritime activity are accumulated at shallow depths. Partially petrogenic nature of PAHs in sediments of the Kerch Strait was also determined from *Phen/Antr* and *Antr/(Antr + Phen)* ratios.

## CONCLUSIONS

Waters and sediments of the Kerch Strait differ in the high AHC concentrations. Due to the rapid transformation, alkanes differed from oil alkanes in composition. The influx of pollutants in marine environment leads to the increase of the HCs content in water and bottom sediments, thus creating the modern hydrocarbon background.

The influence of pollutants is best expressed in the composition of the more stable hydrocarbon class, PAHs. The low PAHs concentrations in water (5–9 ng/L) and in bottom sediments (1–728 ng/g) are caused by a scheme of currents and coarsely-grained composition of sediments of the Kerch Strait.

Correlations between organic compounds and molecular markers PAHs could indicate homogenous hydrological–geochemical conditions of sedimentation.

The PAHs distribution in bottom sediment samples from the considered area makes it possible to identify the pollution mainly as pyrogenic and to lesser extent, as degraded oil. The most probable source of pollution is HCs released during combustion of marine fuel.

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