

## Hydrocarbons in Bottom Sediments of the Marginal Filter of the Volga River

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Materials from different spheres of the Earth are ultimately delivered to bottom sediments, which serve as a natural recorder of the functioning of other spheres and originate as a result of the accumulation of their substances [1]. Sedimentary material and species of river-transported elements are subjected to dramatic reworking in marginal filters, where river and sea waters are mixed [1, 2]. These processes are most important for the Caspian Sea, where runoffs of rivers (especially the Volga River) and the intense development and transportation of hydrocarbon fuel by tankers and pipelines (related to the coastal petroleum industry in the Sumgait and Baku ports, Apsheron Peninsula) are potential sources of hydrocarbon pollution [3, 4]. Previously obtained data showed that the total content of hydrocarbon fraction (i.e., the sum of aliphatic hydrocarbons (AHC) and polycyclic aromatic hydrocarbons (PAH)) in bottom sediments varied within 29–1820  $\mu\text{g/g}$  [4]. The content of petroleum hydrocarbons in the northeastern Caspian region varied from 0.052 to 34.09  $\mu\text{g/g}$  with the maximum content in the Tengiz field [3]. The content of six polyarenes in the Volga delta sediments was no more than 40  $\text{ng/g}$  [5].

To determine the recent HC pollution of bottom sediments and trends in the functioning of the Volga marginal filter, in summer of 2003 and 2004 we analyzed bottom sediments (58 samples) in the river waterway; Kirovsk channel; Bakhtemir and Ikryanoe branches; tributaries of the Kizan, Chagan, and other rivers; and the Caspian seashore (Fig. 1, table).

Hydrocarbons were extracted from wet samples with chloroform. Prior to extraction, anhydrous sodium sulfate was added to samples to remove pore, film, and absorbed water. Separate hydrocarbon fractions were

extracted by means of column chromatography on a silicagel. The content of AHC was analyzed by IR spectrophotometry; the composition of alkanes, by gas chromatography; and the content and composition of PAH, by high-resolution liquid chromatography. To convert AHC concentration to  $C_{\text{org}}$  concentration, coefficient 0.86 was used. The technique is described in detail in [6].

Surface samples of bottom sediments taken in 2003 on the Caspian Sea coast are composed of sandy silts with  $C_{\text{org}}$  (0.031–0.59%) and AHC (19.8–142.1  $\mu\text{g/g}$ ) (table). Obtained data show that, although the HC content on the dry sediment basis is low, it is rather high (>1%) in the organic matter (OM) composition. In Station 18, where sediments are dumped during cleaning of the navigation channel, the AHC content accounts for 39.42%, which is typical of near-port waters [6]. The AHC content in the present-day bottom sediments accounts for only 0.1–0.01% of  $C_{\text{org}}$  [7]. The weak correlation between  $C_{\text{org}}$  and AHC ( $r = 0.14$ ) may indicate an input of these compounds from different sources.

Higher contents of  $C_{\text{org}}$  (up to 8.6%) and AHC (up to 3880  $\mu\text{g/g}$ ) were found in sediments taken in 2004 in channels of the Volga River (table). AHC accounts for up to 16.8–23.9% of OM, which is significantly higher than the content in other water areas with constant oil fluxes [6]. In particular,  $C_{\text{org}}$  in the estuarine sediments of the Black Sea varied within 0.08–4.26 wt %. The AHC content varied within 28–472  $\mu\text{g/g}$ , with the maximum content of 2.7% in OM. Our data are comparable with results obtained for harbor waters of navigable areas, such as New York Bay (35–2900  $\mu\text{g/g}$ ) [8] or the western coast of Taiwan (869–10 300  $\mu\text{g/g}$ ) [9].

Such a high AHC content is presumably caused by the fact that the major portion of pollutants is delivered to the basins with industrial and waste waters as emulsions. After their decomposition, light fractions float to the surface and evaporate, while heavy fractions sink to the bottom [10]. This process is most intense in running waters. According to experimental data, oil absorbed by suspension is the quickest to sink in fresh water, since

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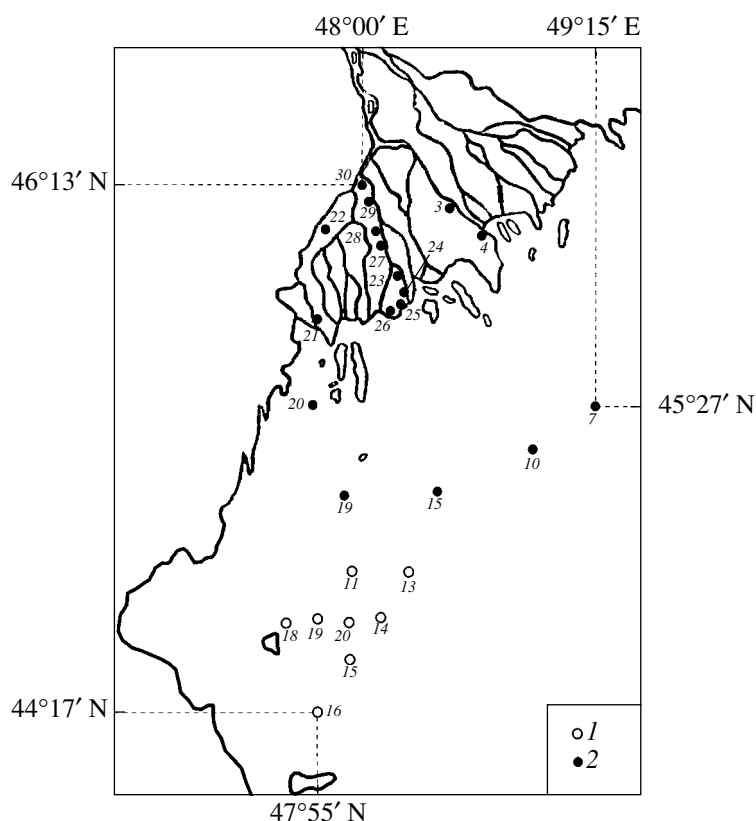


Fig. 1. Sampling scheme of bottom sediments in the Volga River estuary. (1) 2003, (2) 2004.

high salinity decreases the precipitation capacity of petroleum products [11].

The distribution of organic compounds strongly depends on the degree of sediment dispersion. When passing from sands to muds,  $C_{\text{org}}$  content increases more than ten times (table). According to our data of 2004,  $C_{\text{org}}$  content strongly correlates with sediment moisture, which is mainly defined by the grain size composition:  $r = 0.91$  for all data array and  $r = 0.96$  for surface sedimentary layer. A similar pattern is observed for HC distribution. Suspension is quick to accumulate petroleum hydrocarbons, and fine-dispersed sediments (especially if fraction  $< 0.1$  mm is dominant) easily absorb pollutants from suspension-bearing watermass [2]. The AHC content in fine-dispersed sediments (230–3880  $\mu\text{g/g}$ ) is also significantly higher than that in sandy sediments (200–428  $\mu\text{g/g}$ ). If these processes play a leading role, the AHC content in the bottom sediments must correlate with their moisture and  $C_{\text{org}}$  content. In fact, a significant correlation was observed between these parameters:  $r(\text{AHC-Moist}) = 0.58$  and  $r(\text{AHC-}C_{\text{org}}) = 0.54$  for all data;  $r(\text{AHC-}C_{\text{org}}) = 0.69$  for surface layer. However, these correlations are less rigorous than those between  $C_{\text{org}}$  and moisture. For AHC, the granulometric factor ceases to operate in zones of avalanche sedimentation, mixing of fresh and saline waters, and intense input of petroleum products [6].

Therefore, the AHC content sharply increases in the sediments of the river waterway, causing a deviation from the general trend. In this area, the AHC content (table) in sandy sediments from Station 24 k (746  $\mu\text{g/g}$ ) seemed to be even higher than in muddy sediments from Station 24 (731  $\mu\text{g/g}$ ) and in silty sand in the Belinsk bank channel (Station 4, 319  $\mu\text{g/g}$ ). The same reasons are presumably responsible for differences in the degree of geochemical bonds between  $C_{\text{org}}$  and AHC. The greater part of the suspended terrigenous and organic matter is accumulated during the mixing of river and sea waters at a low salinity ( $S = 0.2\text{‰}$ ) [1]. In the gravitational part of the marginal filter, the primary discharge of river runoff is accompanied by an increase of AHC content in the bottom sediments (stations 3 and 4). With a further salinity increase (up to 2‰), only the finest colloidal and clayey particles remain in the suspension. Under the action of seawater electrolytes, colloids are coagulated to form the larger flocules. Since fine fraction predominates in the suspension, sedimentation is maximal in this area. In addition, the formation of a large amount of fresh sorbents leads to the absorption of not only suspended but also dissolved pollutants from the water [1]. As a result, sediments are enriched in fine-dispersed fractions and, especially, in AHC contents (Station 24, 24kl; table) both in dry sediment and OM (5.5–23.9%). Hence, the depocenter of avalanche

## Content of organic compounds in the bottom sediments

Sample no.	Coordinates		Horizon, cm	Description of sediment	Depth, m	Moisture, %	C <sub>org</sub> , %	AHC, µg/g	AHC, % of C <sub>org</sub>	PAH, ng/g	PAH, 10 <sup>-3</sup> % of C <sub>org</sub>	Ph/An	P + BP Ph + Ch	Pe, % of PAH
	N	E												
2003														
11	44°47'2"	47°54'8"	0-5	SS	6.9	20.8	0.590	83.8	1.22	587	0.10	5.45	0.21	16.0
13	44°45'4"	47°54'8"	0-3	SS	3.8	21.2	0.086	59.9	5.99	9.1	1.06	7	0.12	1.5
14	44°36'2"	47°54'8"	0-5	SS	7.5	26.4	0.500	48.7	0.84	12.7	0.25	3.57	0.70	1.8
15	44°27'1"	47°55'3"	0-3	SS	8.2	20.9	0.068	19.8	0.37	3.6	0.53	2	3.20	20.9
16	44°16'6"	47°44'9"	0-5	S	8.0	20.8	0.220	38.8	0.07	2.8	0.13	23.4	0.08	2.1
18	44°35'9"	47°36'4"	0-5	S	9.1	20.1	0.031	142.1	39.42	16.9	5.45	2.23	0.76	2
19	44°37'0"	47°45'2"	0-5	SS	6.7	26.3	0.550	50.5	0.79	4.7	0.09	2.88	0.48	17.1
20	44°37'1"	47°55'3"	0-5	MS with H <sub>2</sub> S	8.3	28.4	0.400	64.7	1.39	4.9	0.12	-	0.62	6.1
2004														
3-5	45°49'7"	48°50'4"	0-5	MS	2.0	75.8	5.940	235.7	0.34	154.1	0.26	0.61	2.55	20.9
3-4			5-10	MS		42.2	0.687	108.7	1.36	45.5	0.66	0.94	0.77	1.7
3-3			10-15	MS		21.4	0.133	132.1	8.54	810	60.90	0.49	0.56	4.6
3-2			15-20	MS		22.7	0.089	70.1	6.77	not determined				
3-1			20-25	MS		20.5	0.067	45.4	5.83	149.2	22.27	0.56	0.57	4.5
4-1	45°43'5"	48°53'6"	0-5	MS	2.0	70.8	5.320	319.2	0.52	1057	1.99	3.4	3.35	16.6
4-2			5-10	MS		72.8	8.605	365.0	0.36	3258.5	3.79	3.32	3.86	23.9
4-3			10-15	MS		61.4	3.794	486.6	1.10	158.1	0.42	3.32	2.30	24.0
4-4			15-20	S		33.9	0.899	227.3	2.17	140.6	1.56	3.37	2.34	15.7
4-5			20-25	S		28.9	0.540	34.7	0.55	not determined				
20-1	45°22'18"	47°46'7"	0-5	MP	1.0	43.4	1.196	385.5	2.77	36.3	0.30	0.69	0.69	37.7
20-2			5-10	MP		38.3	1.060	163.0	1.32	6.2	0.06	1.88	1.90	14.3
20-3			10-15	MP		41.7	1.241	401.8	2.78	92.8	0.75	4.06	4.06	17.7
20-4			15-20	MP		46.1	1.545	453.4	2.52	1151.4	7.45	4.31	4.32	20.6
20-5			20-25	"		50.1	2.118	803.8	3.26	43.8	0.21	4	5.38	33.8
20-6			25-30	S		29.2	0.439	261.1	5.11	61.5	1.40	0.9	7.43	16.4
21-1	45°28'5"	47°45'9"	0-5	MS	0.5	39.5	0.428	119.4	2.40	35.7	0.83	0.71	4.10	17.9
21-2			5-10	"		27.2	0.498	71.0	1.23	273	5.48	0.69	5.50	12.6
21-3			10-15	"		20.3	0.216	422.0	16.80	162	7.50	1.3	6.20	15.0
21-4			15-20	Mud		41.7	1.027	54.8	0.46	36.7	0.36	0.38	1.20	46.3
22-1	45°35'2"	47°51'3"	0-5	DDSP	0.5	42.4	1.549	181.8	1.01	45.3	0.29	0.65	1.40	28.6
22-2			5-10	MSP		26.3	0.505	125.7	2.14	27.9	0.55	0.26	0.93	28.2
22-3			10-15	"		21.4	0.257	43.8	1.47	9.1	0.35	0.33	1.29	42.4
22-4			15-20	"		26.5	0.376	102.0	2.33	22.6	0.60	0.03	0.21	30.8
23-1	45°50'2"	48°06'8"	0-6	Mud	3.0	75.9	6.035	3880.6	5.53	93.1	0.15	0.35	3.59	29.7
24-k	45°44'9"	48°13'9"	0-5	MS	2.5	25.9	0.312	867.6	23.91	24.5	0.79	5	6.70	24.5
24-1	45°44'9"	48°13'9"	0-5	LM	1.8	66.8	3.982	730.7	1.58	12.3	0.03	20	0.70	14.7
24-2			5-10	"		71.9	4.035	1922.0	4.10	24.7	0.06	5.1	7.06	14.4
24-3			10-15	"		62.0	2.459	1027.4	3.59	not determined				
24-4			15-20	"		45.8	1.075	408.9	3.27	17.9	0.17	-	1.00	39.8
24-5			20-25	MS		26.8	0.493	284.3	4.96	not determined				
24-6			25-30	"		28.5	0.563	181.2	2.77	99.1	1.76	5	6.70	20.8

Table. (Contd.)

Sample no.	Coordinates		Horizon, cm	Description of sediment	Depth, m	Moisture, %	C <sub>org</sub> , %	AHC, µg/g	AHC, % of C <sub>org</sub>	PAH, ng/g	PAH, 10 <sup>-3</sup> % of C <sub>org</sub>	Ph/An	P + BP / Ph + Ch	Pe, % of PAH
	N	E												
25-1	45°43'1"	48°13'5"	0-5	S	1.6	27.6	0.461	58.9	1.10	8	0.17	0.35	3.77	8.2
26-1	45°42'6"	48°13'7"	0-5	DS	1.6	26.9	0.595	119.0	1.72	13.8	0.23	0.36	4.21	7.9
26-2			5-10	"		22.7	0.232	5.5	0.20	13.4	0.58	0.83	11.50	4.2
26-3			10-15	"		29.3	0.398	199.4	4.31	19.7	0.49	0.35	10.00	4.2
27-1	46°00'5"	48°07'1"	0-6	DDSP	0.6	22.5	0.354	222.4	5.40	9.1	0.26	0.64	3.00	18.6
27-2			6-12	"		32.3	0.534	101.2	1.63	7.7	0.14	0.58	3.10	18.9
28-1	46°08'3"	48°03'6"	0-7	DDSP	0.7	23.5	0.298	130.0	3.75	36	1.21	0.46	3.94	22.8
28-2			7-14	"		33.4	0.607	124.9	1.77	34.8	0.57	0.31	3.90	38.0
29-1	46°11'2"	48°00'4"	0-5	DDSP	0.6	26.3	0.455	340.0	6.43	44.9	0.99	0.76	5.25	29.1
29-2			5-10	"		25.9	0.415	102.5	2.12	42.7	1.03	0.44	3.97	21.7
29-3			10-15	"		23.7	0.516	158.7	2.65	521.3	10.10	0.84	4.43	28.2
29-4			15-20	"		24.9	0.171	101.2	5.09	71.9	4.20	0.53	4.18	15.0
30-1	46°13'6"	48°00'9"	0-4	DMS	5.0	25.6	0.160	109.1	5.86	12.6	0.79	0.33	5.09	17.1
30-2			4-8	"		31.3	0.279	70.3	2.17	5.8	0.21	0.3	4.20	17.3
7	45°27'48"	49°15'3"	0-5	FS	5.3	20.6	0.106	93.5	7.59	6.5	0.61	0.75	0.31	20.1
10	45°15'5"	48°55'6"	0-5	"	5.8	23.7	0.205	135.9	5.70	11.9	0.58	0.86	0.31	20.1
15	45°04'6"	48°23'3"	0-5	"	6.9	27.6	0.233	116.2	4.29	3.4	0.15	0.35	0.28	32.1
19	45°03'2"	47°45'4"	0-5	Mud	4.3	49.5	1.548	113.6	0.63	76.4	0.49	0.32	0.54	18.8

Note: (SS) Shelly sand, (MS) muddy sand, (S) sand, (MP) mud with plant remains; (DDSP) dense dust-sized sand with plants; (MSP) muddy sand with plants; (LM) liquid mud; (DS) dust-sized sand; (FS) fine-grained sand; (DMS) dense muddy sand.

sedimentation of the Volga River mouth is located in this part of the marginal filter. The more intense increase in C<sub>org</sub> content relative to AHC in the muddy sediments can be caused by fluxes of other organic compounds in addition to HC, since a transformation of petroleum HC may facilitate the formation of resins and asphaltenes.

This conclusion is also confirmed by alkane composition. All samples are dominated by high-molecular homologues, because they have a greater capacity for hydrophobic bonding at the water-suspension interface as compared to lower-molecular hydrocarbons [6]. Transformed petroleum HCs were occasionally found in the river channels (stations 24k and 29). Alkanes in this area are characterized by a lower oddness index for the high-molecular region (CPI = 1.17-1.58) and by a predominance of phytane over pristane (Pr/Pf = 0.35-0.87 (pristane is mainly of biogenic origin)).

Low-molecular hydrocarbons in practically all samples of bottom sediments show a maximum at n-C<sub>17</sub>, which is typical of phytoplankton alkanes [6, 13]; this

is probably because petroleum HCs occur in bottom sediments, when precipitation rate exceeds transformation rate. For the same reason, alkanes in most samples show a bimodal distribution, and AHCs are of mixed (autochthonous-allochthonous) genesis. The presence of the naphthenic-aromatic hump in the C<sub>22</sub>-C<sub>28</sub> region may also indicate the influence of weathered petroleum HC. The hump in the high-molecular region (more than 10 µg/g) is caused by constant petroleum fluxes; the hump in the low-molecular region, by the transformation of natural terrigenous compounds [4, 13]. In particular, the total content of n-alkanes is 15-17 µg/g and the naphthenic-aromatic hump is recorded at 1300-1500 µg/g in the vicinity of Baku [4].

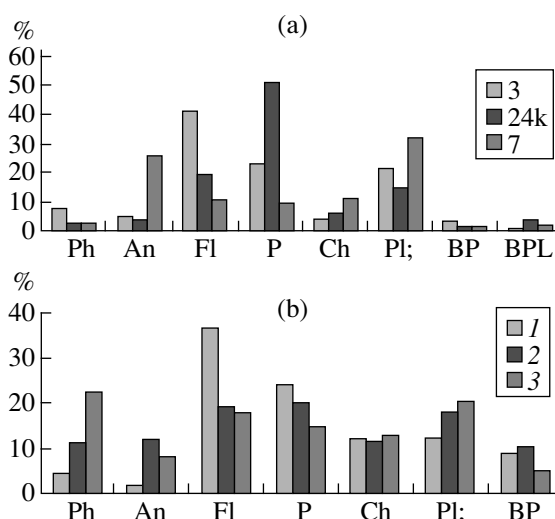
At relatively low AHC contents (6.5-76.4 µg/g, stations 7, 19, 15, 19), sandy-muddy sediments at the periphery of the Volga River mouth are also enriched in biogenic components. The high vital activity of plankton in the outer (biological) part of the marginal filter [2] (salinity 2.1-6.6‰) leads to an increase of planktonogenic alkanes. In this area, C<sub>org</sub> increases from sandy

(0.106%, Station 7) to muddy sediments (up to 1.55%, Station 19), without significant changes in AHC contents (93 and 114  $\mu\text{g/g}$ , respectively). This is caused by the fact that, if the biogenic factor prevails in sedimentation, complex planktonic lipids, which compose the main part of lipids of primary producers, have no time to decompose on passing from surface to deep waters. As a result, lipids become further enriched in polar compounds and depleted in AHC [6].

Depending on study area and lithology, PAH contents varied from 3 to 3258 ng/g dry sediment (table). Differences in HC sources (petroleum, pyrogenic, and biogenic), as well as the complicated sedimentation in shallow waters, disrupt the correlation between PAH and AHC in sediments:  $r(\text{AHC-PAH}) = 0.03$ . However, as with AHC, the highest PAH contents in the surface layer are typical of fine-dispersed sediments in the Volga River channels (about 100 ng/g, stations 3, 4). At the offshore stations, the PAH content sharply decreases: 3–12 ng/g in sandy sediments (stations 7–15) and 76 ng/g in muddy sediment (Station 19). These data are close to the previous data [4], showing that PAH content in the outer shelf of the northern Caspian region varies from 20 ng/g in the surface layer of sandy sediments to 184 ng/g in muddy sediments. Only a weak correlation was observed between  $C_{\text{org}}$  and total polyarenes:  $r(C_{\text{org}}\text{-PAH}) = 0.27$  ( $n = 20$ ) [4].

The phenanthrene/anthracene ratio (Ph/An) is typically more than 10 at large fluxes of petroleum polyarenes or their active transformation during diagenetic processes [4]. According to obtained data,  $\text{Ph/An} > 1$  was observed only at stations 16 in 2003 and 4 in 2004, indicating the pyrogenic nature of PAH in this area. In addition, anthropogenic pericondensed PAHs, which are produced by the high-temperature pyrolysis of organic raw material, such as pyrene, benz(a)pyrenes, benzperylene, and others, prevail over natural PAHs (phenanthrenes, chrysenes, and picenes) [14]. Therefore, the ratio of anthropogenic–“natural” PAHs (for example, pyrene + benz(a)pyrene/(phenanthrene + chrysene)) was used to determine the effect of pyrogenic sources [6]. This ratio in the surface sediments of the Volga River delta is typically more than 1, occasionally reaching up to 10–11.5 (table). At offshore stations 7–15, this ratio decreases to 0.3–0.5 because of pyrene precipitation (Fig. 2a). A similar dependence was found in the Daugava River estuary (Fig. 2b).

Thus, HC composition in marginal filters undergoes regular changes owing to the precipitation of petroleum and pyrogenic homologues. Therefore, the anthropogenic index of polyarenes in sediments of the Volga delta branches varies within 1–10 and decreases to 0.3–0.5 after the marginal filter. Hence, anthropogenic (petroleum and pyrogenic) HCs do not cross the marginal filter and enter the open sea. Therefore, the northern part of the sea is the least polluted as compared to the other Caspian regions, especially the area adjacent to Apsheron Peninsula [4]. The precipitation of anthro-



**Fig. 2.** Proportions of polyarenes in the surface layer of bottom sediments at the geochemical barrier. (a) Volga River–Caspian Sea; (b) Daugava River–Gulf of Riga: (1) mouth; (2) mixing area; (3) bay. (Ph) phenanthrene, (An) anthracene, (F) fluoranthene, (P) pyrene, (Ch) chrysene, (Pl) perylene, (BP) benz(a)pyrene, (BPL) benzperylene.

pogenic HCs in the water mixing zone leads to a relative increase in the concentration of perylene in PAH at the offshore stations, reaching up to 32% in the surface layer of Station 15. It was shown that, in addition to AHC, some PAHs are formed in the outer (biological) part of the marginal filter. This phenomenon is common for river marginal filters, since a similar dependence was previously found for the estuaries of the Daugava, Yenisei, and Ob rivers [6, 15].

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