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MARINE CHEMISTRY

Hydrocarbons in the Surface Layer of Bottom Sediments in the Northwestern Caspian Sea

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Abstract—The paper presents research results on the concentrations and compositions of aliphatic and polycyclic aromatic hydrocarbons in the surface layer of bottom sediments in the Northwestern Caspian Sea (2014) and compares them to data for sediments of the Middle and Southern Caspian (2012–2013). The seepage of hydrocarbons out of the sediment mass, resulting in abnormally high concentrations of aliphatic hydrocarbons per dry weight (up to 468 μg/g), as well as within the C_{org} composition (up to 35.2%), is considered the main source of hydrocarbons in sediments in the surveyed area of the Northern Caspian. This is also confirmed by the absence of any correlation between the hydrocarbon and C_{org} distributions, as well as by the transformed oil composition of high-molecular alkanes. The distribution of markers within polycyclic aromatic hydrocarbons points to a mixed genesis—petrogenic and pyrogenic—with prevalence of the latter. Unlike the shallow-water northern part of the Caspian Sea, the content and composition of hydrocarbons in deep-seated sediments are affected by facial conditions of sedimentation and by matter exchange at the water–bottom interface. Therefore, despite high C_{org} concentrations (up to 9.9%), sediments in deep-water depressions are characterized by a quite low concentration of aliphatic hydrocarbons (52 μg/g on average; 0.2% of C_{org}) with prevailing natural allochthonous alkanes.

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INTRODUCTION

The Caspian Sea is the world's second largest (after the Persian Gulf) in terms of oil and gas resources, which are as great as 15 billion t of fuel equivalent, with about 3.3 and 3.6% of the world's oil and gas supply to markets, respectively [26, 27]. Thus, the Azeri–Chirag–Gunashli deposit (Azerbaijan) is among the world's ten largest oil fields [33]. Of great importance for Russia is the Northern Caspian, where even 42 prospecting, exploratory, and productive wells had been drilled by 2014 in Lukoil Co. licensed areas, including 21 productive wells at the operating Yu. Korchagin oil field, at which about 3 million t of oil had been produced and shipped on tankers by 2014 [10]. In 2016, oil production was started at the Filanovsky oil field. At both oil fields, six new stationary structures are projected, including 71 productive wells and about 350 km of submarine big-inch pipelines. This region plays a key role in the formation of the ecosystem and productive biological resources of the Caspian Sea [21]: about 90% of total river runoff enters into the sea here, including 80% of biogenic organic matter (OM) supplied with the Volga River runoff [1]. The concentration of dissolved C_{org} varies within 500–667 μM in the transformed Volga waters supplied from its mouth area.

Assessment of the oil contamination and environmental conditions is complicated by the constant activity of numerous natural hydrocarbon (HC) sources in the Caspian Sea (gryphons and mud volcanoes). About half of the world's 900 mud volcanoes are located at the South Caspian tectonic depression [6]. Satellite monitoring demonstrates that the view of surface contamination by oil films in the Caspian Sea considerably differs from the conditions in the Black and Baltic seas [12]. This is determined in many respects by the large oil and gas resources in the Caspian region. The volume of natural oil seeps is estimated as 3000–16 000 t/year even in the southwestern part of the sea [21]. It is reasonable to assume that similar processes take place also in other areas of the Caspian Sea. In particular, this is confirmed by the discovery of increased concentrations of petrogenic HCs in bottom sediments of the Central Caspian Sea at depths of 220–650 m owing to oil seeps on the seafloor [25]. Areas most subjected to oil contamination are those adjacent to explored and suspended oil fields, as well as to old water-sealed oil wells of the northeastern coasts [7]. Today, vast areas of oil fields are covered by rusty spots: these are traces of oil soaked up thoroughly by the seafloor [6].

To identify the sources of hydrocarbons (HCs) in sediments of the northwestern part of the Caspian Sea, samples were collected in 2014 to analyze for aliphatic and polycyclic aromatic hydrocarbons (AHCs and PAHs, respectively) with comparison to data obtained for sediments of the Middle and Southern Caspian sampled in 2012–2013.

MATERIALS AND METHODS

The surface layer of bottom sediments in the Northern Caspian was sampled in summer 2014 with an Okean dredger. The samples were frozen at –18°C, unfrozen in laboratory conditions, dried at 50°C, then the fraction of 0.25 mm was sift. The total hydrocarbon fraction was extracted with methylene chloride using a Sapfir ultrasound bath at 30°C. The AHC concentration was determined by IR spectrophotometry with a Shimadzu IR Affinity 1 device. As the standard, *GSO 7554-99* for oil products in CCl_4 was used. This procedure is used as an arbitrary technique in analyzing oil hydrocarbons [14].

Organic carbon in the samples of bottom sediments was determined by dry combustion with an AN 7529 analyzer. The sensitivity was 6 μg of carbon in a sample, with the accuracy of 3–6%. To convert the AHC concentrations to C_{org} concentrations, a conversion parameter of 0.86 was used [15, 16].

The composition of alkanes was determined with a Shimadzu 2010 gas-liquid chromatograph equipped with a flame ionization detector and a 50 m column under programmed temperatures from 60 to 300°C at rate of 3°/min with helium as the carrier gas (1.5 L/min gas flow rate). The equipment was calibrated, and the retention time of the identified alkanes was determined using a mixture of n-C_{10}–C_{40} calibration standards (Supelco Co.) and squalane as the internal standard.

The concentrations and composition of PAHs were determined by the HPLC technique using a Shimadzu LC 20 Prominence chromatograph with an Envirosep PP column at 40ºC, as well as an RF 20A fluorescence detector, in gradient conditions (from 50 to 90% volume fraction of acetonitrile in water) at the eluent flow rate of 1 cm^3/min. The calculations were done with LC Solution software. The equipment was calibrated on individual PAHs (Supelco Co.) and their mixtures. As a result, 16 individual PAHs recommended by the EPA [30] were identified: naphthalene (N), 1-mehylnaphthalene (MeN), acenaphthene (AcN), fluorene (Flr), phenanthrene (Ph), anthracene (Ac), fluoranthene (Fl), pyrene (P), benz(a)anthracene (BaAn), chrysene (Ch), benz(e) pyrene (BeP), perylene (Pl), benz(a)pyrene (BaP), dibenz(a, h)anthracene (DBaAn), benz(g,h,i)perylene (Bpl), and indeno[1,2,3-c,d]pyrene (IP).

RESULTS AND DISCUSSION

The main feature of bottom sediments in the Caspian Sea is their coarse-grained character at shoals (with depths <100 m). The conventional boundary between the Northern and Middle Caspian is the line joining Chechen' Island and Cape Tyub-Karagan. In terms of the depth distribution over the Caspian Sea, three areas are distinguished: the eastern (the Ural River–the Emba River), with depths shallower than 3 m; the Ural Borozdina depression, 5–8 m in depth; and the western (the Volga River–Caspian plain, 1–5 to 5–12 m in depth) [22]. The waters supplied by the Volga River are subdivided into two branches in the northern part of the sea. Most of the Volga water is directed southward along the western coast and is entrained in the cyclonic water circulation of the Northern Caspian. A minor part of the waters are transported along the northern coast to the east and flows together with the Ural River waters to form a moderate enclosed circulation. The bottom relief of the Northern Caspian Basin shows the evidence of the development of the Quaternary subaerial relief constituted by the fragments of riverine valleys and terraces [4].

The sediments we treated belonged mainly to sandy deposits with an admixture of coquina and, only in certain cases, of siltstone matter (Table 1). The examined sediments were characterized by various grain-size compositions. The sediment moisture was as high as 59% in only one of the samples, 29% on average. The maximum C_{org} content was 0.613% or less (0.315% on average). The correlation coefficients (r) for the <0.063 mm fraction and C_{org} content varied from 0.068 to 0.94 for different regions of the Northern Caspian; i.e., the C_{org} content depended on the grain-size compositions of sediments, with increased C_{org} values in fine-grained material.

For the most part, the AHC distribution is also determined by the grain size of sediments [16]. Silty sediments (especially with prevalence of the <0.1 mm fraction) easily absorb organic compounds, including pollutants from the water column containing particulate matter. However, AHC concentrations in the surveyed area of the Northern Caspian depended neither on the dispersion of sediments nor on the organic matter content. The AHC concentrations at some of the stations appeared high, not only converting into dry mass but also within the C_{org} composition (24–35%, Fig. 1). Both the maximum and minimum concentrations (410–468 and 4–5 μg/g, respectively) were recorded in test area K, with increased C_{org} content within the sediment composition (9–10%). Here, the AHC concentrations varied a hundredfold at neighboring stations, with tenfold variations of the AHC portion within the C_{org} composition. The dispersion of data was so great that the standard deviation ($\sigma = 206$ μg/g) was above the average value (200 μg/g). The lack of a correlation between the C_{org} and AHC

Table 1. Concentrations of organic compounds at key stations in bottom sediments of Northwestern part of the Caspian Sea in summer 2014

Station	Coordinates		Sample composition	Moisture, %	AHCs, μg/g	C_{org}, %	HC fraction, % of C_{org}
	N	E					
1B	43°45′	48°30′	Fine sand	20.6	6.1	0.072	0.72
5B	43°52′30″	48°24′	Fine sand	19.0	114.6	0.028	35.2
D	44°05′53.64″	48°14′29.14″	Grey sand	16.48	2.97	0.110	0.23
K2	44°54′498″	048°56′966″	Fine shells	40.09	410.40	0.416	8.49
K4	44°55′070″	048°57′874″	Fine shells	37.25	4.43	0.496	0.08
K7	44°55′171″	048°57′534″	Fine shells	31.04	5.28	0.421	0.11
K8	44°55′370″	048°57′517″	Fine shells	28.28	216.99	0.550	3.39
K11	44°54′328″	048°57′535″	Shells	27.2	9.21	0.626	0.13
K12	44°54′480″	048°57′510″	Shells	37.0	4.93	0.493	0.09
KK	44°54′059″	048°57′517″	Fine shells	43.58	467.70	0.392	10.27
PK	45°03′0.44″	48°37′51.2″	Sand and shells	22.62	4.85	0.216	0.19
P1	45°03′0.44″	48°37′51.2″	Sand and shells	59.0	11.36	1.613	0.06
P5	45°01′10.0″	48°23′25.9″	Ooze and shells	22.4	200.75	0.206	8.38
P6	44°58′54.0″	48°39′14.0″	Ooze and shells	24.8	116.13	0.165	6.05
P7	45°03′57.5″	48°48′12.1″	Shells and ooze	20.9	136.13	0.101	11.59
C2	44°26′01.99″	48°40′46.91″	Sand and coarse shells	19.75	137.96	0.049	24.21
3C1	44°28′58.188″	48°33′21.063″	Sand and coarse shells	18.54	126.14	0.069	15.72
CK	44°20′00.13″	48°44′33.62″	Shells	41.69	6.14	0.344	0.15
3C2	44°20′00.13″	48°44′33.62″	Sand and coarse shells	19.0	6.17	0.025	2.12
X3	44°07′35.5″	49°01′05.9″	Sand and coarse shells	22.38	5.62	0.024	2.01
X4	44°14′11.4″	49°14′33.7″	Shells	34.74	10.12	0.262	0.33
Sh1	45°03′0.44″	48°37′51.2″	Fine shells	31.67	201.43	0.278	6.23
ShK	44°50′36.5″	48°58′15.8″	Fine shells	30	13.16	0.182	0.62

distributions—r(Moisture–AHC) = 0.15 and r(C_{org}–AHC) = –0.04—might point to different sources of these compounds.

It should be noted that the highest AHC concentrations were found in sediments sampled in the northwestern part of the area (Table 2). Particularly, the AHC content was 54 μg/g or less in the treated sandy sediments of the Volga River delta [17]. The AHC content in previously studied sediments of the Northern Caspian varied within 1–114 μg/g [19]. The deep-seated sediments (>450 m) of the Middle and Southern Caspian consisting of silty ooze with black hydrotroilite interlayers contained on average 52 μg/g of AHC [17]. The deep-seated bottom sediments of Derbent Depression along with those of the depressions of the Middle and Southern Caspian, characterized by increased content of the light subfraction (up to 99.9%), as well as by the amount of fine claystone within 30–35% [11] and the moisture within 40.5–74.3%, showed the growth of AHC content to 178 μg/g (Fig. 2). Here, the C_{org} concentrations were as high as 9.9% and the sediments smelt of hydrogen sulfide. The high C_{org} content as such was recorded for the first time in sediments of the Caspian Sea. However, the AHC concentrations within the C_{org} composition appeared to be quite low (0.13–0.18%). The AHC content was as low as 7–16 μg/g in near-coastal coarse-grained bottom sediments from stations located near Makhachkala and in the Volga River mouth area (Fig. 2), where pollutants enter with terrigenous and river flows. Owing to the intense alongshore dynamics of shore drifts, bottom sediments accumulate no fine fractions of particulate matter [11, 19], nor any AHCs.

With increased AHC concentrations, the composition of alkanes appeared similar in sediments of the Northern Caspian (Fig. 3a). Low-molecular autochthonous homologs prevailed in all the samples (Table 3)

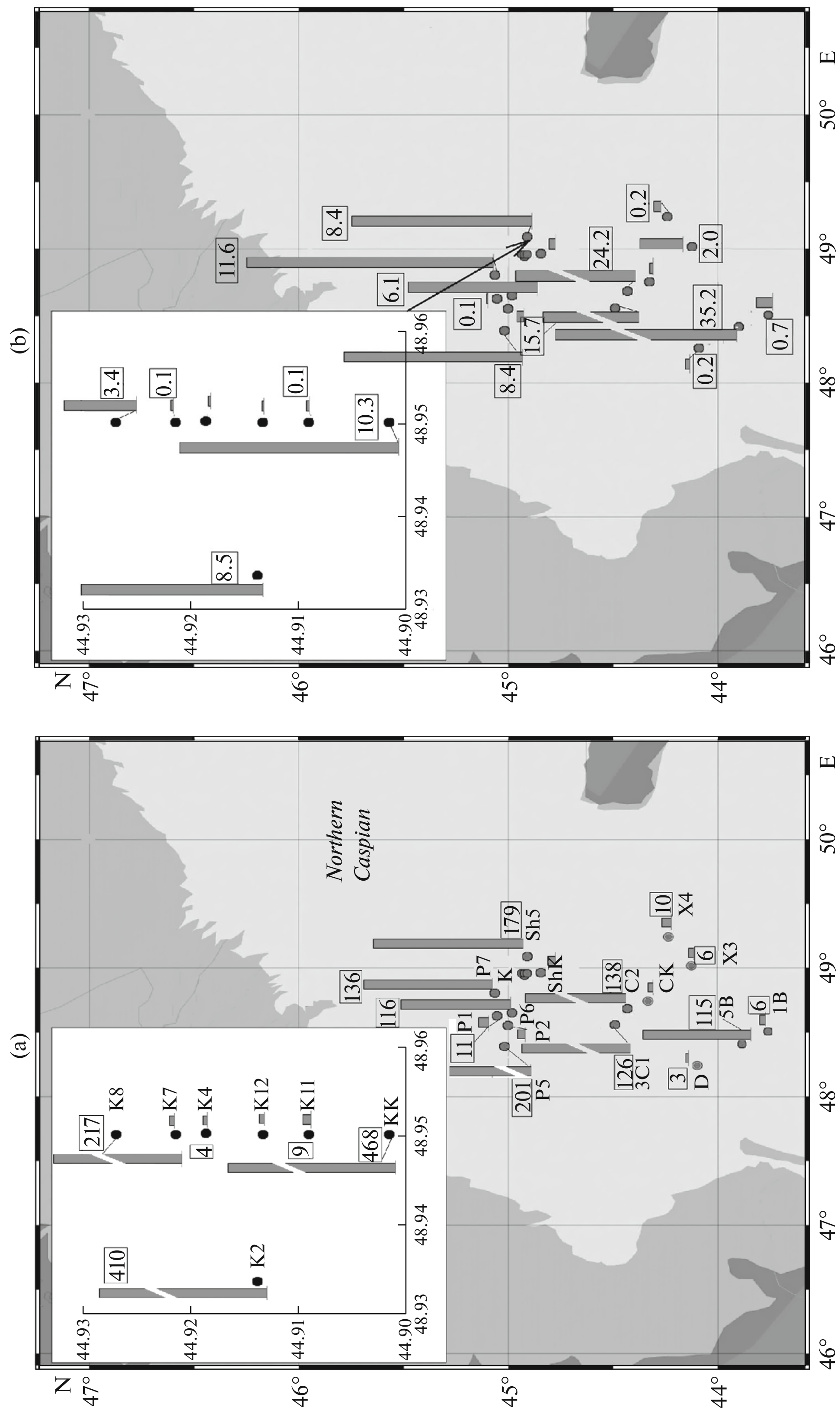

Fig. 1. AHC concentrations (a, μg/g; in squares and columns) and fractions within C_{org} (b, %; in squares and columns) in bottom sediments of Northwestern part of the Caspian Sea (summer 2014).

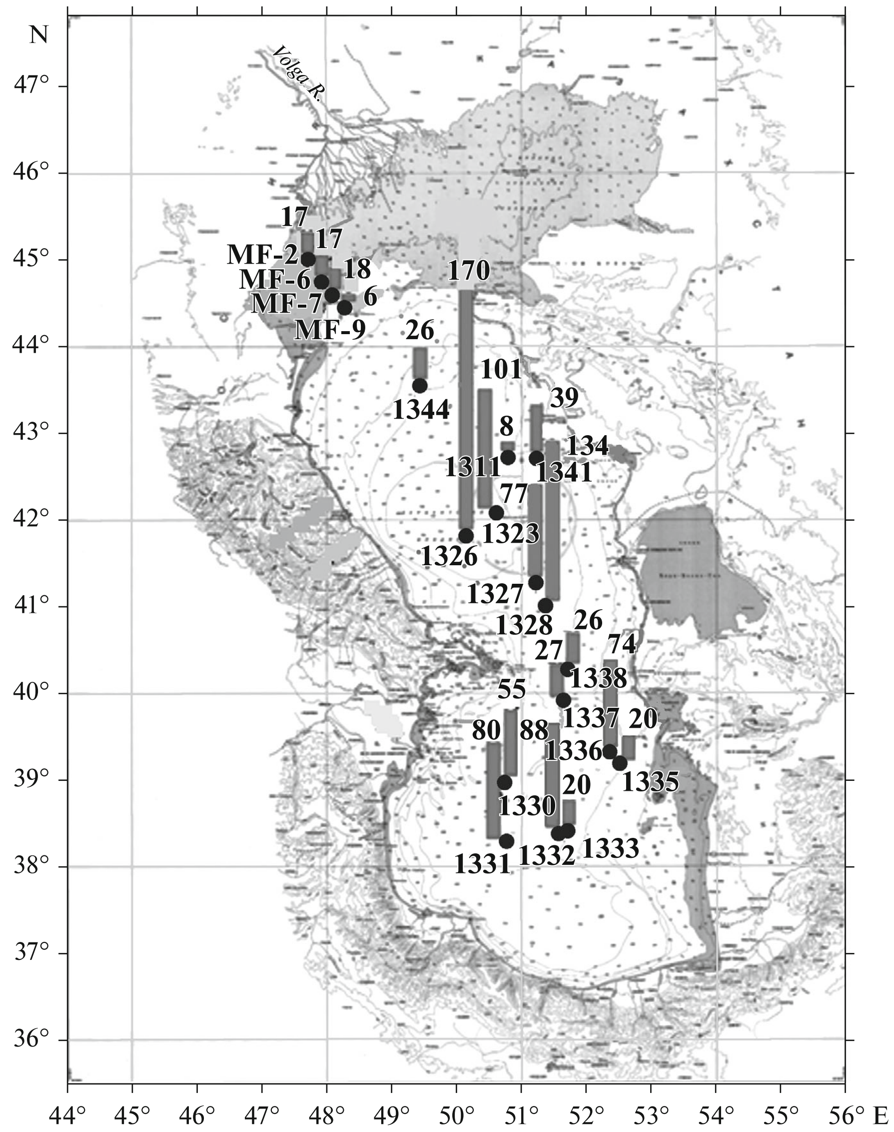

Fig. 2. Scheme of sampling (station nos. under columns) and AHC concentrations (μg/g; columns and numbers above) in bottom sediments of the Caspian Sea in summer 2013.

Table 2. Concentrations of organic compounds in surface layer of bottom sediments of the Caspian Sea in various years of surveys

Season and year	AHCs, μg/g		C_{org}, %		Moisture, %	
	range	average	range	average	range	average
Branches of the Volga River mouth						
Summer 2009	2.0–33.2	15.3	0.110–1.348	0.35	17.8–54.5	28.5
Summer 2010	13.4–54.5	27.9	0.006–0.555	0.21	17.3–50.2	26.0
North, Middle, and South Caspian Sea						
Summer 2010	18.0–38.9	25.6	0.212–3.752	1.590	24.3–57.6	40.5
Spring 2012	13.5–97.5	45.0	0.365–3.539	1.990	37.1–94.6	74.3
Autumn 2012	2.3–31.4	13.3	0.015–3.511	1.608	18.2–95.9	61.0
Autumn 2013	19.7–178.4	51.8	0.054–9.884	2.560	18.0–94.1	55.2
Northwestern Caspian Sea						
Summer 2014	3.0–467.7	103.9	0.028–0.613	0.315	16.5–59.0	29.3

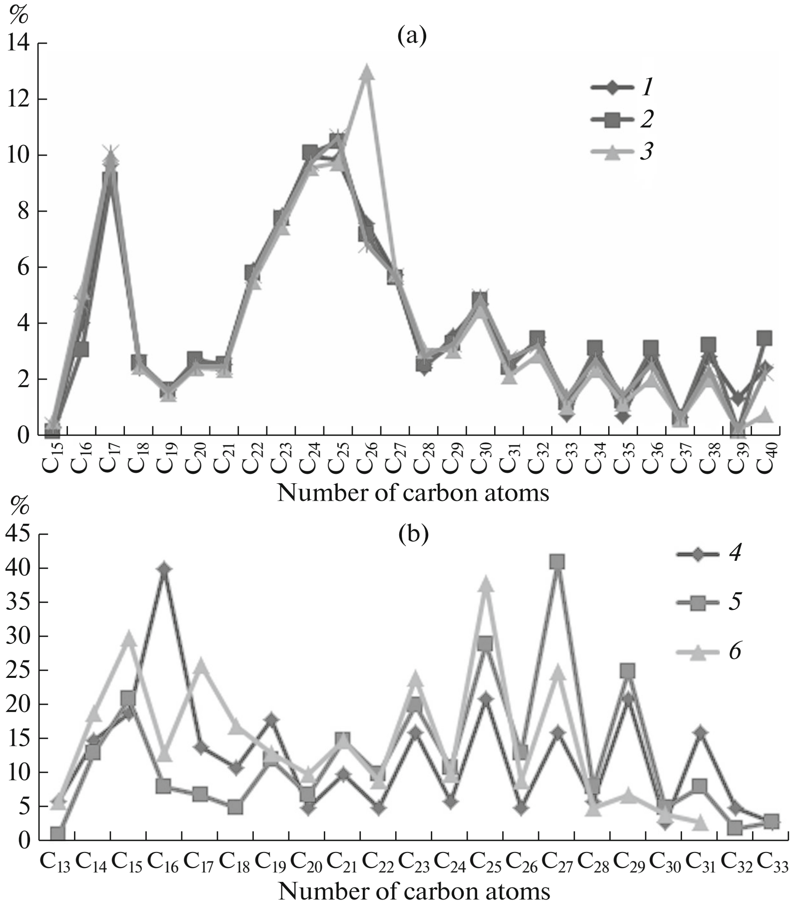

Fig. 3. Composition of *n*-alkanes in bottom sediments of Northwestern part of the Caspian Sea in (a) 2014 and (b) 2013: (*1*) station 5B, (*2*) K2, (*3*) KK, (*4*) station 1323, (*5*) station 1330, and (*6*) station 1336 (see Figs. 1 and 2 for location of stations).

except for sediment from station KK, where the fraction of n-C_{26} homolog was 7%. The alkane n-C_{17} has its origin in phytoplankton and the phytobenthos; n-C_{24}–C_{25} alkanes are of bacterial origin [28, 31]. The concentrations of n-C_{17} and n-C_{24} homologs were 9–10%, which indicates intense transformation of alkanes. Therefore, the CPI values were 1 or lower within the range of C_{12-24}.

The high-molecular range was characterized by only a slight excess of odd over even homologs (CPI = 0.82–1.26), which might testify to transformed oil alkanes. This is also confirmed by the prevalence of phytane over pristane in all the samples, because the ratio i-C_{19}/i-C_{20} varied within 0.42–0.60 (Table 3). It is notable that sediments from the Volga River Delta and the Middle Caspian were characterized by a greater contribution of terrigenous homologs, since the odd alkanes prevailed and the CPI values were higher than those in sediments of the Northern Caspian (1.65–1.90). The various sorption capacities of sediments determined by their grain size were demonstrated in the variability of alkane compositions near Makhachkala. n-C_{16}, C_{21}, and C_{23} alkanes (those dependent on the intensity of microbial processes) are more prevalent in silty than in sandy sediments.

In the course of field surveys in the Middle and Southern Caspian in summer 2013, the warp [13] was sampled by means of a multicorer from the near-bottom layer (fluffy layer), and it contained 1.4–2 times more AHCs than the surface layer of sediments [17]. The fraction of n-C_{17} homolog in the warp was as high as 11% of the total alkanes, whereas the surface layer of sediments contained 5% or less. The water–bottom interface is characterized by intense autotrophic processes resulting in the formation of autochthonous organic compounds including AHCs [13].

The total content of PAHs in bottom sediments of the Northern Caspian in 2014 varied within 3.9–41.6 ng/g (Table 4) that was comparable to the concentrations for the same region in 2001–2002 (0.3–40.5 ng/g [23]), as well as to those in the sediments of the Sarmatskoe oil field in 2009 (10–30 ng/g [20]). The low PAH content as such is caused by the coarse-grain composition of sediments. According to 2000 data, the content of polyarenes was within 4–30 ng/g in most sediment samples from the Russian sector of

Table 3. Distribution of markers in bottom sediments at individual stations (see Figs. 1 and 3 for location of stations)

Station	AHCs, μg/g	CPI			$\frac{\Sigma C_{(12-24)}}{\Sigma C_{(25-35)}}$	Dominant peaks
		∑odd/∑even	(C_{12-24})	(C_{25-35})		
Northern Caspian, 2014						
5B	114.6	0.87	0.88	0.97	1.06	C_{17}, C_{24}, C_{25}
K2	410.4	0.84	0.87	1.00	1.00	″ ″
KK	467.7	0.82	0.87	0.82	0.97	C_{17}, C_{24}–C_{26}
P5	200.8	0.98	0.82	1.13	1.26	C_{17}, C_{24}, C_{25}
Sh1	201.4	0.91	0.97	1.26	1.04	″ ″
Middle Caspian, 2013						
MF-2	17.39	1.23	0.87	1.87	0.88	C_{23}, C_{25}, C_{27}
1323	101.09	2.00	1.35	2.89	0.82	C_{29}, C_{31}
1328	134.48	1.56	0.87	3.72	1.25	C_{18}, C_{25}, C_{27}
1330	54.94	2.16	1.26	3.23	0.35	C_{17}, C_{27}, C_{29}, C_{31}
1331, fluffy layer	157.23	2.14	1.30	3.33	0.77	C_{17}, C_{27}, C_{29}
Sediment 0–2	80.52	1.21	0.97	1.30	0.29	C_{27}, C_{29}
1336	74.48	1.85	1.23	3.46	0.43	C_{17}, C_{25}, C_{27}, C_{29}

Table 4. PAH concentrations and ratios of molecular markers in individual samples of bottom sediments of Northwestern part of the Caspian Sea (2014)

% of total	Station									
	P1	P7	X4	Sh5	KK	K2	P5	3C1	5B	Ш1
Naphthalene	3.2	2.2	2.6	3.6	2.5	2.3	1.0	1.7	1.8	0.8
1-methyl naphthalene methyl naphthalene	3.2	0.1	0.4	0.2	0.4	0.6	0.2	1.0	0.8	0.1
2-methyl naphthalene	1.3	1.2	0.4	1.5	3.6	2.6	2.2	1.0	0.7	0.4
Acenaphthene	n.d.	0.2	n.d.	0.1	0.3	0.3	0.1	n.d.	0.1	0.1
Fluorene	n.d.	2.0	n.d.	3.1	2.9	2.1	4.6	0.7	1.4	1.6
Phenanthrene	25.8	68.6	7.9	59.6	63.9	67.1	56.7	61.6	52.9	35.9
Anthracene	0.3	2.5	n.d.	1.7	2.5	3.0	2.4	2.0	1.9	1.4
Fluoranthene	29.0	8.6	35.0	13.9	6.7	5.1	17.4	11.8	22.6	24.2
Pyrene	15.5	11.1	31.0	11.6	11.5	12.1	10.2	15.6	12.2	17.1
Benz(a)anthracene	3.9	2.0	4.8	2.3	2.9	2.6	3.2	2.7	3.1	4.5
Chrysene	5.8	1.3	5.2	1.4	2.1	1.5	1.7	1.4	2.1	4.4
Benz(e)pyrene	10.3	0.2	11.4	0.5	0.6	0.6	0.1	0.2	0.3	6.1
Benz(b)fluoranthene	n.d.	n.d.	0.4	0.1	n.d.	n.d.	0.1	0.1	n.d.	0.3
Benz(k)fluoranthene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.
Benz(a)pyrene	n.d.	n.d.	0.3	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	1.0
Dibenz(a.1)pyrene	1.4	n.d.	0.3	0.1	0.1	n.d.	n.d.	0.1	0.1	0.5
Benz(g.h.i)perylene	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.
Inden[1.2.3-c.d.]pyrene	n.d.	n.d.	0.087	0.098	n.d.	n.d.	0.014	n.d.	n.d.	0.027
Dibenz(a.e)pyrene	n.d.	n.d.	n.d.	0.012	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Anthanthrene	n.d.	n.d.	n.d.	0.092	n.d.	n.d.	0.014	n.d.	n.d.	0.163
Markers										
Naphthalene/methyl naphthalenes	0.71	1.69	3.02	2.10	0.62	0.70	0.40	0.83	1.18	1.51
Naphthalene/phenanthrene	0.13	0.03	0.33	0.06	0.04	0.03	0.02	0.03	0.03	0.02
Fluoranthene/pyrene	1.88	0.78	1.13	1.20	0.58	0.42	1.71	0.76	1.85	1.41

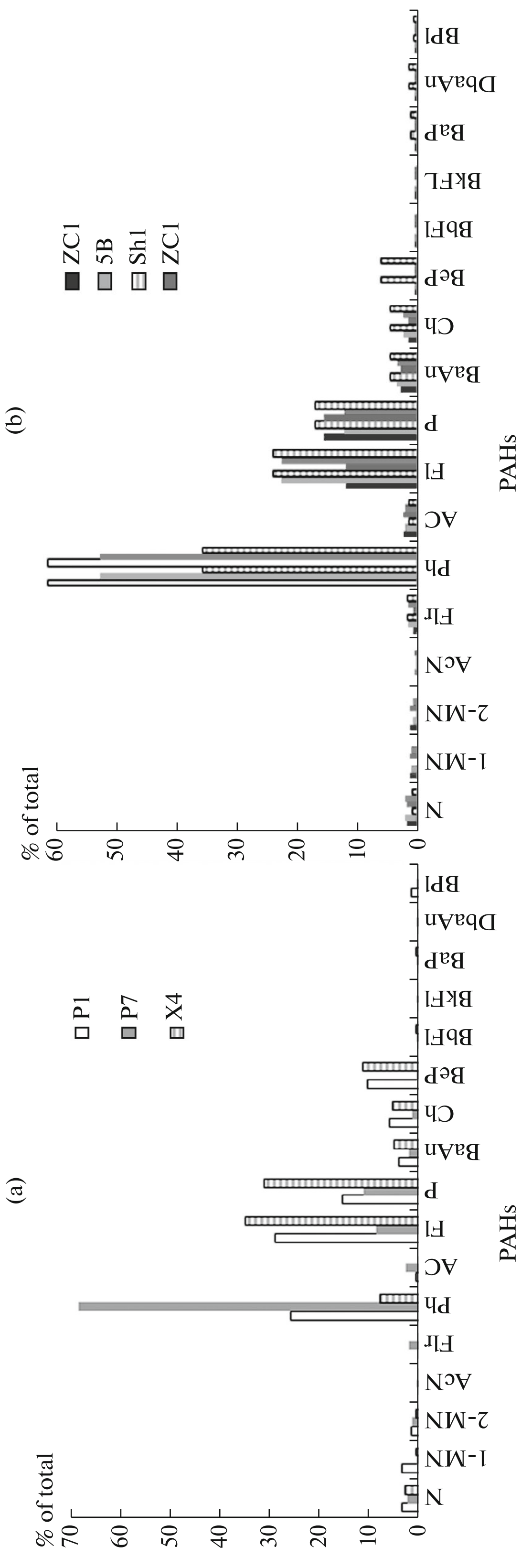

Fig. 4. Typical composition of PAHs in bottom sediments sampled in Northwestern part of the Caspian Sea in 2014 (see Fig. 1 for location of stations).

the Caspian Sea, but increasing to 284–345 ng/g in some of the samples [31]. The highest concentrations of polyarenes (up to 1600 ng/g) were recorded in silty sediments of the Azerbaijan sector of the Caspian Sea.

The lack of correlation between the AHC and PAH distribution ($r = 0.34$; $n = 10$) in the treated sediments of the Northern Caspian is due to the different natures of these classes of hydrocarbons. The main source of PAHs is the supply of fuel combustion products from polluted air [24, 31, 32]. Biosynthesis in living organisms, biogeochemical transformation of various nonhydrocarbon compounds, and oil pollution are considered the key AHC sources [16, 28].

According to the authors' data, the concentrations of dominant individual polyarenes in sediments of the Northern Caspian varied on average (%) as Ph (50.1) > Fl (17.4) > P (14.8) > N (4.4) > BaAn (3.28) > BeP (3.0) > Ch (2.7). Phenanthrene is found in all environments, both natural and those under anthropogenic impact [24, 32]; hence, high its concentrations are not unexpected. The petrogenic origin of PAHs is represented by an increased content of naphthalene and especially of its methylated homologs. The N/MeN ratio varied within a wide range of 0.4–3.2, which may indicate different origins of them. This ratio was over 1 exclusively in several sediments where AHC content was also high (stations KK, K2, and P5, Table 4). An N/Ph ratio indicating unweathered oil products for the values >1 [31, 32] shows that polyarenes in sediments are pronouncedly transformed. This conclusion is also confirmed by a higher content of fluoranthene compared to pyrene (Table 4). Fluoranthene, the most stable of the identified PAHs, prevails in many aquatic objects even in the regions distant from the pollution sources [16]. Conversely, sediments from stations P7, KK, K2, P5, and 3C1 contained more pyrene than fluoranthene (Fig. 4), which points to their pyrogenic origin [16, 32].

It should be noted that the fraction of high-molecular homologs in the total PAHs amounted to 1% or less (Fig. 4). An exception was recorded at station Sh1, where this fraction was as high as 9.5% for the maximum PAHs content of 41.6 ng/g. The concentration of benzopyrene (BP) showing the highest carcinogenic activity among the unsubstituted PAHs characterizes the degree of environment pollution with carcinogenic polyarenes [9]. In view of this, BP receives much attention in PAHs studies. However, the fraction of BP is usually small in marine environments [16], so this is a minor component, on average 0.15% on the total PAH concentration. Biotic and abiotic natural processes result in the formation of the current biogenic background of BP and PAHs as a whole.

Factor analysis has also shown that PAHs in sediments of the Middle Caspian were of mixed genesis. Three principal components were distinguished. The first component, characterized by the greatest load of pyrogenic polyarenes (0.88–0.97), contributed 48.9%

to the total dispersion. The second component (26.9%) showed considerable loads of naphthalene and its alkylated homologs, which indicates a PAHs supply from oil sources (shipping spills and oil seeps). Owing to the third component (7.4%), a high load of phenanthrene (0.89), the influence of diagenetic processes on the formation of PAHs composition was revealed. According to [31], the contributions of pyrogenic and diagenetic sources to the composition of sedimentary PAHs were as high as 60 and <20%, respectively, in the Russian sector of the Caspian Sea, with >90% in sediments of Iran and Kazakhstan.

According to the authors' data, deep-seated sediments of the Middle and Southern Caspian contained from 19 to 42 ng/g of PAHs. Their composition was also characterized by the prevalence of light homologs among which the phenanthrene portion was as high as 73% of the total, with 13–17% of pyrene, 6–11% of fluoranthene, and 4–7% of chrysene. The naphthalene portion was 1.6% or less. The low methylnaphthalene content (N/MeN = 5.5–6.8) may indicate a minor oil contribution. This is also confirmed by low values of (P + BP)/(Ph + Ch) ratios (0.17–0.26). The Fl/P ratio was below 0.5 in all the samples, which testifies to intense pyrolytic processes generating polyarenes (probably due to the supply with fluidal flows, i.e. by mud volcanism).

Thus, the performed studies have shown that mainly coquina sediments in the Northwestern part of the Caspian Sea were characterized by abnormally high AHC concentrations and by wide spatial variability. As well, the AHC content in bottom sediments did not depend on the degree of their dispersion, i.e., independent of the prevalence of either fine or coarse fractions. Considering that the natural AHC background in sandy sediments is usually 10 μg/g or less [16, 31], only some individual samples from the surveyed region of the Northern Caspian contained AHCs conforming to this background level. In most cases, the determined concentrations were considerably higher. It was found earlier that bottom sediments in the central part of the Northern Caspian usually consisted of coarse-grain fractions with low concentrations of AHCs and alkanes showed minor oil pollution [17, 23, 29, 31]. The concentrations of alkanes varied within 2.2–3.2 μg/g [23] (from <0.1 to 0.2 μg/g according to other authors [31]) in the central part of the Dagestan coast in the runoff area of the Terek River (the Staryi Terek branch) and of its tributaries, as well as in the western part of the runoff area of the Volga River Delta. According to our data, bottom sediments of the Northwestern part of the Caspian Sea contained 4.0–14.2 μg/g of alkanes—only 2.5–3.5 of AHCs and 0.2–1.4% of C_{org}.

The lack of a correlation between the grain size of bottom sediments and the C_{org} and AHC concentrations might be caused by the existence of a source having no genetic relation to particulate matter and sedimentation processes. Probably, natural seepage is to consider the main source of AHCs. Hydrogeological anomalies were repeatedly recorded in oil-and-gas-bearing provinces during the exploration of oil and gas deposits [3]. Hydrocarbons break out from the subsurface not only through drilling wells, but also from seeps due to the activation of seismic-tectonic or other natural forces. The local character of these anomalies can be confirmed by the wide variability of AHC concentrations over the test areas. The subsurface dynamics and pulsating activity of intracrustal systems appear as various "splashes" of gas and liquids onto the bottoms of aquatic areas and on surrounding coasts. In particular, various types of natural seepage have been recorded at all depths in the Gulf of Mexico and, as it is thought [2], appeared to be among the causes of the Deepwater Horizon accident. Under such conditions, outbursts of fluids should be not only quite regular, but also occasionally inevitable, and wells only accelerate discharge.

The data on the composition and background concentrations of these seeping AHCs are quite contradictory [24]. Oil with a low chilling temperature commonly seeps. Such oil is quite susceptible to the impact of microorganisms, and its composition includes biogenic AHCs. This probably explains the prevalence of low-molecular homologs within the compositions of alkanes and PAHs in bottom sediments of the Northwestern part of the Caspian Sea.

Both the AHC and PAHs concentrations in natural systems are determined not only by their content in the supply sources but also by the physicochemical properties of compounds and the processes affecting them in a basin: the impacts of solar radiation, temperature, the occurrence of oxygen, microorganisms, plants, fungi, etc. [16, 20, 24]. Oil in the seepage zone is a much reduced energy source exposed to microbial oxidation [21]. Therefore, the content of microbial homologs within the alkane composition is increased, which is also proved in sediments of the Northwestern part of the Caspian Sea (Fig. 4a). Besides seepage, the products of fuel combustion (the prevalence of light polyarenes) can also be considered sources of PAHs (a more stable class of hydrocarbons) as well.

The authors' data on the origin of HCs in bottom sediments have been confirmed by the satellite monitoring of oil spills in the Northern Caspian since 2010 [8, 18], which have recorded no oil pollution caused by the oil production there. This is due to the effective preventive measures applied against environmental and industrial hazards by the LUKOIL–Nizhnevolzhskneft Co., especially the use of "zero discharge," i.e., the transfer of all wastes to coast. Most of filmy pollutions are associated with shipping routes, some of which cross the company's licensed areas; they have also been recorded in the vicinities of shipping channels, the Tyuleniy Archipelago, and Cape Tyub-Karagan in the Kazakhstan sector of the sea, as well as near the ports of Aktau and Makhachkala [18]. Most of the found oil slicks consisted of discharged bilge water and other liquid wastes containing oil products, often mixed with fish-processing waste. Numerous small oil slicks were found on the seawater surface near the Mangyshlak Peninsula with the submarine extension separating the depressions of the Northern and Middle Caspian [5]. The area of occurrence of these slicks was mainly associated with the young Scythian–Turan Plato, as well as with the neighboring parts of the Caspian depression on the ancient East European Craton. It was found that seepage outlets as "travelling waves" represent increased subsurface geodynamic activity of the Caspian Sea tectonic depression [5].

Unlike the sediments we examined, increased concentrations of AHCs in deep-seated sediments of the Middle and Southern Caspian containing a large amount of C_{org} are caused by the formation of AHCs under natural sedimentation and diagenetic processes [12]. This is also confirmed by the composition of alkanes with prevalent C_{25}–C_{29} odd homologs.

CONCLUSIONS

Coarse-grained bottom sediments in the Northwestern Caspian Sea are characterized by a wide range of AHC concentrations, both converted into dry mass (3–468 μg/g) and within the C_{org} composition (0.13–35.2%), which is much higher than the values recorded in deep-seated fine-grained sediments from the depressions of the Middle and Southern Caspian.

Alkanes in the sediments are of mixed origin, consisting of transformed autochthonous and oil AHCs in the low- and high-molecular parts, respectively.

The PAHs in bottom sediments are characterized by quite low total concentrations (3.9–41.6 ng/g). Their composition is of mixed genesis with a prevalent pyrogenic constituent.

In view of the unusual AHC distribution in sediments of the Northern Caspian and of the lack of a correlation between the AHC, C_{org}, and PAH concentrations, seepage from the sediment mass is considered the main source of HCs, not sedimentation and diagenetic processes, unlike sediments of the Middle and Southern Caspian.

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