=== MARINE CHEMISTRY ===

Variability of Concentration and Composition of Hydrocarbons in Frontal Zones of the Kara Sea

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Received November 20, 2012; in final form, August 7, 2013

Abstract—The distribution and composition of aliphatic and polycyclic aromatic hydrocarbons (HC) in dissolved and particulate forms, as well as in bottom sediments, was studied along the route of a vessel and at stations. It was found that the widest variability of HC concentrations in surface waters was characteristic for the frontal zones of the Yenisei River mouth (4.8–69 μg/L) and for the western branch of the St. Anna Trough (5.5–80.4 μg/L). The increased concentrations of aliphatic HC coincide with those of chlorophyll and particulate matter, as well as with the growth of the intensity of fluorescence, and are caused by natural processes. This is confirmed by HC composition. Bottom sediments are characterized by low HC concentrations, both in terms of dry mass (14 μg/g on average, with the maximum of 36.8 μg/g at station 5018 in the layer of 3–17 cm) and within C_{org} compositions (0.88%). Natural terrigenous homologues are prevailing in alkane composition of the sediments. The marginal filters of the Ob and Yenisei rivers were compared. It is shown that oil HC transferred by the rivers are deposited in the zone of marginal filters without reaching the open waters of the Kara Sea.

DOI: 10.1134/S0001437015040128

INTRODUCTION

The studies of hydrocarbons (HC) in the ecosystems of Arctic seas have become topical in view of the growth of oil production on the Arctic shelf. By now, the facts of local and background pollution of several Arctic regions have been registered, as well as the transboundary transfer of pollutants (Pts) over long distances by air and water masses [3, 20]. By different estimations [16, 20, 24], from 1 to 3% of the total oil output of West Siberia are received by the environment. This amounts to 20–200 million t of spilled oil: a main factor in environmental problems in the basins of the Ob and Yenisei rivers [4, 24]. This fact results in the occurrence of numerous environmental "hot points" and "impact zones" characterized by polluted air, soil, and surface and ground waters, as well as by degraded ecosystems [4, 6].

Untill now, it had been assumed that a key contribution into the total supply of oil HC to the Arctic seas is made by riverine runoff, which provides oil flows of tens and hundreds ton per year [24]. For the Kara Sea, this is provided by the Ob and Yenisei rivers. In reality, in the course of the studies of HC in the Kara Sea, the maximum concentration gradients of HC in water and bottom sediments [15], as well as of many other compounds [2, 19], were registered in the Ob River mouth area. However, hydrocarbon markers showed that Pts were precipitated in the area of the Ob and marine water mixing [15, 17]. At the same time, the question of amount of oil HC supply by rivers to the Arctic seas and of HC distribution between land and sea is still open. Moreover, the seepages in the areas of oil-and-gas fields may provide local sources of oil HC in the basins of the Barents and Kara seas [16, 21].

Studies of HC in surface waters along the route of the 59th cruise of the R/V *Akademik Mstislav Keldysh* and in bottom sediments at the stations in the Kara Sea were performed to determine the content, origin, and transformation of HC in frontal zones (September 2011, Fig. 1). These studies have become especially topical because the exploration of oil fields in the Kara Sea basin is one of the main lines of oil production at the Arctic shelf.

METHODS

Water was sampled with a bucket from the surface during vessel movement and when approaching stations. The bottom sediments were collected using an Okean dredge and a Neimisto tube. Particulate matter was separated by means of GF/F glass-fiber filters (0.7 μm) [13]. Hydrocarbons were extracted on board the vessel immediately after the sampling with a special stirrer from water and with a Sapfir ultrasound bath from the moist samples of particulate matter and from bottom sediments predryed at 50°C. Previously, the fraction of 0.25–0.5 mm used commonly in organic geochemistry to determine HC content [7] was separated by sieving from the treated bottom sediments. Methylene chloride was used as extractant. Lipids (total extractable fraction) and HC, respectively, were determined before and after column chro-
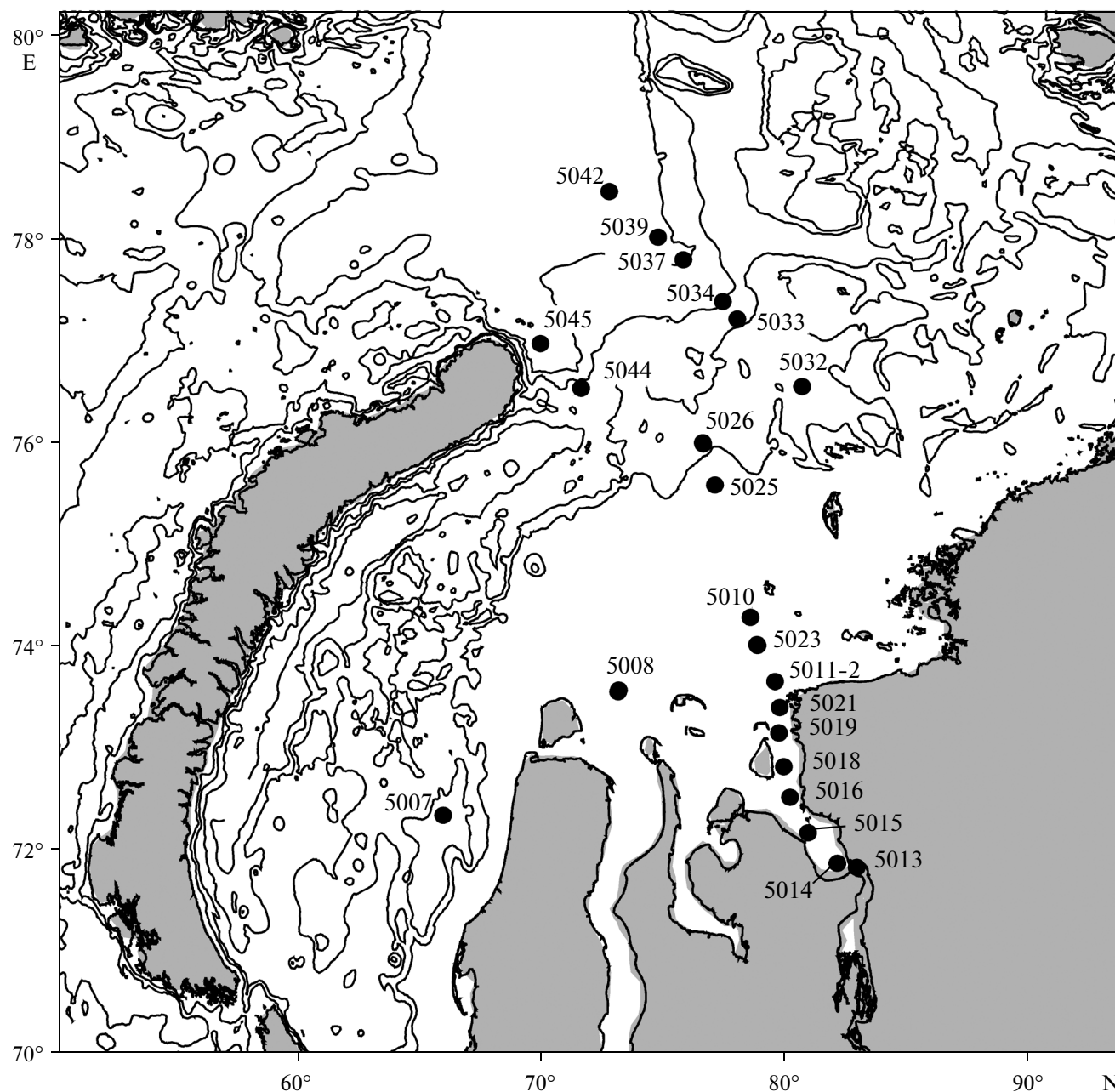
Fig. 1. Scheme of sampling in the Kara Sea.

matography using silica gel. Aliphatic and polycyclic aromatic HC were separated with hexane and a 3 : 2 hexane–benzene mixture, respectively [33]. The concentration of organic compounds (Ocs), namely lipids and HC, was determined by IR spectra with 2930-cm^{-1} band using a mixture of 37.5% isooctane, 37.5% hexadecane, and 25% benzene as the standard, by means of an IR 435 (Shimadzu Co.). To convert HC concentrations in sediments into C_{org} values, a parameter of 0.86 was used [13].

The composition of alkanes was determined by capillary gas chromatography (30 m column length, ZB-5

liquid phase) by means of an Intersmat GC 121-2 chromatograph equipped with a flame ionization detector, programming the temperature from 100 to 320°C at the rate of 8°/min.

The content and composition of polycyclic aromatic hydrocarbons (PAH) were determined using the HPLC technique by means of a LC 20 Prominence liquid chromatograph (Shimadzu Co.) equipped with an Envirosep PP column at a 40°C temperature of the column thermostat, in a gradient mode (from 50 to 90 vol % of acetonitrile in water) at an eluant flow rate of 1 cm^3/min. The peaks were registered and the indi-

Table 1. Content of lipids and hydrocarbons (μg/L) in surface waters

Location	n^*	Lipids			Hydrocarbons		
		min	max	average	min	max	average
Kara Sea 2007							
Ob section							
Dissolved	11	35.9	748.2	169.2	6.0	291.1	77.7
Particulate	11	24.8	427.1	182.3	9.7	310.1	101
Kara Sea 2011							
Yenisei section							
Dissolved	15	21.6	133.8	40.2	4.8	69.0	17.6
Particulate	14	21.7	236.5	83.3	7.3	49.1	20.1
Taimyr section							
Dissolved	4	12.9	20.5	16.4	6.4	9.6	8.1
Particulate	4	32.2	41.3	38.2	7.4	16.5	13
St. Anna Trough (east)							
Dissolved	5	8.7	42.0	19.5	2.0	16.2	8.7
Particulate	5	7.5	42.9	26.8	3.2	18.0	6.5
St. Anna Trough (west)							
Dissolved	6	16	125.4	48.8	5.5	41.8	14.4
Particulate	5	35.3	171.7	69.9	5.5	80.4	25.6
Novozemel'skii							
Dissolved	4	9.1	20.3	14	5.5	11.6	6.6
Particulate	4	30.6	52.7	43	16.5	22.5	18.8
Barents Sea 2011							
Dissolved	5	17.5	75.6	34.4	7.5	14.9	10.4
Particulate	5	26.2	77.2	41.6	7.7	20.9	13.1
White Sea 2011**							
Dissolved	5	24.6	50.3	31.0	11.7	28.9	17.0
Particulate	5	65.4	155.7	87.4	30.2	69.2	37.6

* n is a number of samples.

** Samples were collected at the marginal filter of the Severnaya Dvina River.

vidual PAH were determined using an RF 20A fluorescence detector with programmed wavelengths of absorption and excitation. LC Solution software was used for the calculations. The equipment was calibrated by individual and mixed PAH manufactured by Supleco Co. As a result, the following unsaturated polyarenes were identified: naphthalene (N), 1-methylnaphthalene (MN), acenapthene (AcN), fluorene (Flr), phenanthrene (PH), anthracene (A), fluoranthene (FL), pyrene (P), benz(a)anthracene (Baan), chrysene (Chr), benz(e)pyrene (BeP), perylene (PL), benz(a)pyrene (BaP), dibenz(a, h)anthracene (DBaA), benz(g, h, i)perylene (BPL), and indeno[1, 2, 3-c, d]pyrene (IP).

The organic carbon in the bottom sediments was determined by dry combustion with an AH 7529 analyzer.

RESULTS AND DISCUSSION

In surface waters, the sections were executed along the vessel route from the mouth of the Severnaya Dvina to the Kara Sea, as well as in the sea itself at geological sections and frontal zones (Table 1). Special attention was drawn to the zones of the highest gradients of hydrological parameters, chlorophyll content, and fluorescence refined using the data of an UFL 9 lidar (by V.V. Pelevin).

The Yenisei River–Kara Sea section included the area from the outer edge of the delta to the central part of the sea at the depths excee ding 60 m (Figs. 2a, 2b). The water salinity in surface waters varied from 0.069 to 27.927 psu, i.e., just about riverine values at the southernmost station and close to the salinity of the open waters of the Kara Sea in the north. The ratio of particulate and dissolved forms of HC (HC_p and HC_d, respectively) decreased from 1.3 to 0.2 in the southern part of the section. This is caused by the precipitation of coarse grains of particulate matter in the Yenisei waters because of the damming of riverine by marine waters [11]. Along with particulate matter, organic compounds are precipitated, especially hydrophobic high-molecular HC [15, 28]. The water supplied by the river is clarified and a fraction of dissolved Ocs forms. It is notable that the concentrations of dissolved
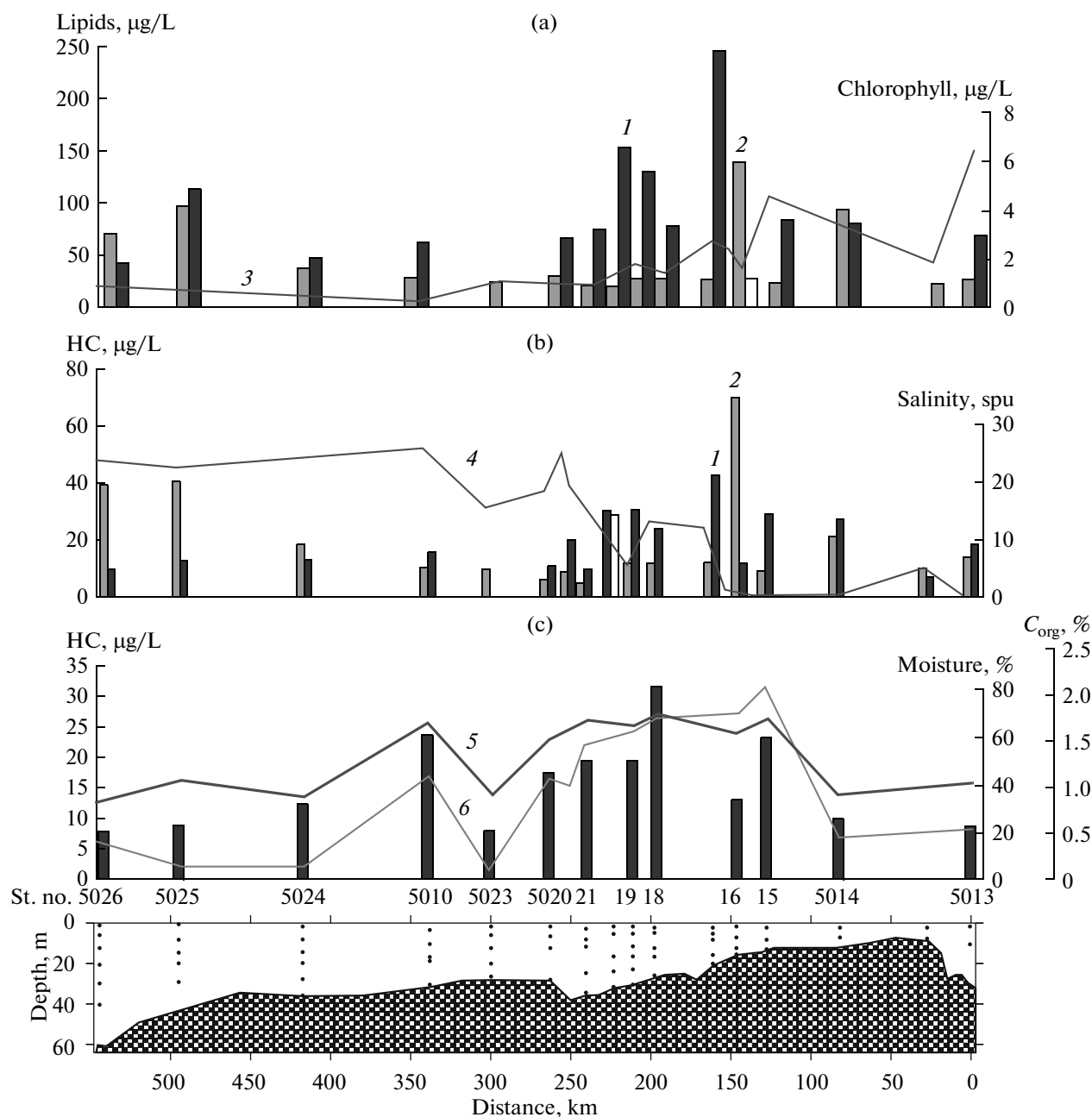
Fig. 2. Distribution of concentrations of lipids (a) and HC in surface waters (b) and bottom sediments (c). *1*—lipids and HC in particulate form; *2*—lipids and HC in dissolved form; *3*—chlorophyll *a*; *4*—salinity; *5*—moisture; *6*—C_{org}.

Ocs in riverine waters are even lower than those in the biological part of the marginal filter (Figs. 2a, 2b). This effect distinguishes the Yenisei River mouth area from those of the Severnaya Dvina and Ob rivers (Arctic rivers flowing over humus-rich soils) in which the dissolved form of HC prevails in the mouth areas [14, 28].

With salinity growth with an increase in the amount of colloidally dispersed matter of the riverine particles [11], marine particulate matter of the developed surface is formed, which contains the coarse floccules of loamy minerals and colloidal forms of organic matter

(OM). As a result, the central part of the section at stations 5014–5021 of salinities of 2.3–4.3 psu (the physicochemical zone of the marginal filter) is characterized by the increase of the content of lipids and HC, especially in the particulate form (to 29 µg/mg of particulate matter at station 5018). Tidal effects cause an additional variability of all the parameters. Therefore, no gradual decrease of HC concentrations and HC_p/HC_d ratios take place with the salinity growth. The maximum HC_p/HC_d ratio pertains to st. 5022: 4.67. The water turbidity (by the parameter of light
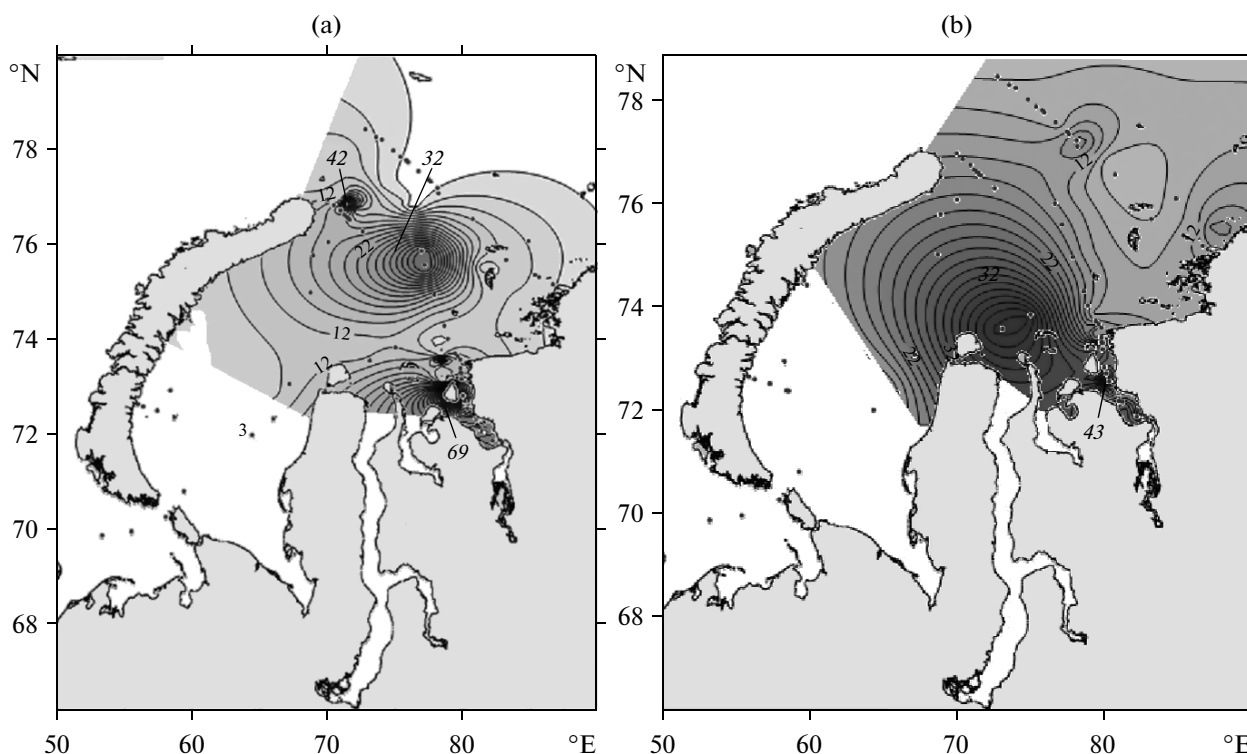
Fig. 3. Distribution of HC concentrations (μg/L) in dissolved (a) and particulate (b) forms in surface waters.

abatement) increased to 3.9 m^{-1} in this region (data of V.A. Artem'ev).

The Ocs concentrations in particulate matter decreased farther seawards along the section. The HC$_p$ content in the biological zone of the marginal filter (stations 5010 and 5024−5026) increased from 9.7 to 28.6 μg/L with an increase of the biogenic fraction of particulate matter (the growth of chlorophyll *a* concentration from 0.482 to 0.995 by S.A. Mosharov). This increase is caused by the changes in the amount of particulate matter (to 1.27 by M.D. Kravchishina). However, a decrease to a higher degree was seen for the dissolved form of HC (to 40.5 μg/L, Fig. 2b). The bio-assimilation of carbon at the Yenisei River mouth was registered even formerly by the ^{13}C isotope composition [3, 27]. The Ocs content at marine stations of the marginal filter increased owing to two main Ocs sources, namely, to marine plankton and to coagulated colloidal and dissolved OM transformed partially into particulate matter (>0.4−0.6 μm) [8]. However, the concentrations of HC in the particulate matter composition decreased to 116 μg per 1 mg of particulate matter.

A strong variability of HC concentrations in surface waters was noticed not only in the mouth areas of the Yenisei and Severnaya Dvina rivers (Table 1) but also in the central part of the sea and near the St. Anna Trough. The HC content was as high as 40−80 μg/L (Fig. 3) here, i.e., it became comparable to or even exceeded the maximum allowable concentrations of

oil HC in fishery basins (50 μg/L). This area was also characterized by the increase of fluorescence along with the concentrations of chlorophyll and particulate matter [5].

HC concentrations showed background values of 6−19 μg/L in the northeastern part of the sea (the St. Anna Trough) and near the Novaya Zemlya Archipelago (Table 1). However, a degree of increase of Ocs content took place in the frontal zone of the temperature−salinity gradient (station 5049) and going toward the coasts, probably due to the coastal abrasion.

The HC origin represents alkane composition. We needed to combine extracts because of the considerably low HC concentrations in water and particulate matter, so the chromatography was carried out on integrated samples. This may be responsible for the quite steady composition of alkanes in different areas of the Kara Sea (Fig. 4a). Low-molecular autochthonous homologues prevailed in all samples. The $\Sigma(C_{12} + C_{24})/\Sigma(C_{25} + C_{35})$ ratio was over 1, with the maximum in the biological part of the marginal filter (Table 2). An exception was registered in the western section at the St. Anna Trough (sample 5) where high-molecular homologues prevailed in the alkane composition. The increased content of $n\text{-}C_{16}$ and C_{22} homologues may testify to the impact of microbial processes; the $n\text{-}C_{17}$ homologue points to phytoplankton alkanes [21, 31]. The decomposition of alkanes by microorganisms is represented by CPI values (the ratio of odd and even homologues) being lower in the low-molecular than in
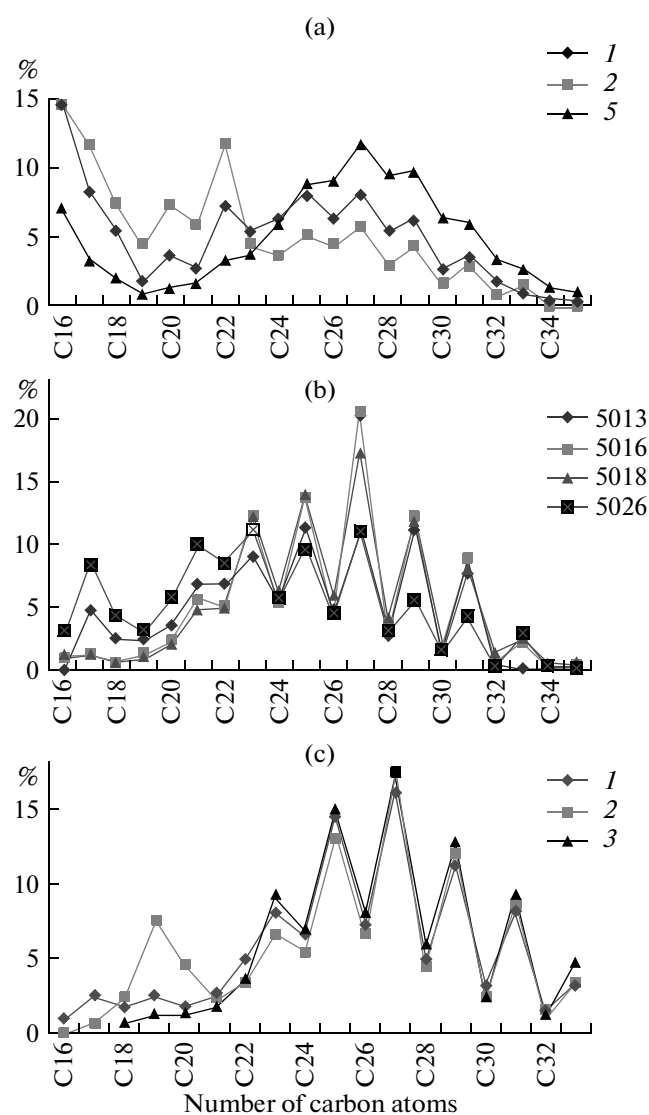
Fig. 4. Composition of alkanes in integrated samples and particulate matter (a): *1*—gravitation; *2*—physicochemical; *5*—western section of the St. Anna Trough; (b)—in the surface layer of bottom sediments: the gravitation (station 5013), physicochemical stations 5016 and 5018), and biological (station 5026) zones of the marginal filter; (c)—within the sediment layer at station 5045: *1*—0–3 cm; *2*—3–7 cm; *3*—24–31 cm.

the high-molecular range (0.86–0.88 and 1.05–1.50, respectively). CPI values in water and in the filtration of particulate matter are commonly close to 1 [14, 30] for high-molecular alkanes, as well as those for the oil alkanes. The supply of terrigenous Ocs causes an increase in CPI values; therefore, the maximum of this value in surface waters (1.5, sample 2, Table 2) is registered in the physicochemical zone of the marginal filter.

The PAH concentrations in surface waters decreased as well from the Yenisei River mouth to open waters within a range of 4.3–2.24 ng/L. The phenanthrene formed in natural processes was prevail-

ing in the PAH composition; the fraction of perylene being also of biogenic origin is also pronounced, especially in the physicochemical zone [25, 31]. The Pts supply affects the fraction of benz(a)pyrene decreasing in the zones of the marginal filter as the gravitation zone (13%) > physicochemical zone (5%) > biological zone (0.4%). The low content of polyarenes in particulate matter is caused by the high flow rate of riverine waters and by the dilution of riverine with marine waters [27].

Bottom sediments are presented by brownish oxidized and greenish-grey reduced aleuropelites with sand admixture on the surface and deeper, respectively [10]. In a number of cases, "crusts" of ice spreading (to $5 \times 3 \times 6$ mm) were found. The sediments in all the cores were bioturbed to the whole penetrated thickness. The low HC content, both converted into dry mass (36.8 µg/g maximum, station 5018, 3–17 cm layer) and within the C_{org} composition (0.88%, station 5013, 19–30 cm layer), is in agreement with the former data [15, 27]. The average HC concentrations in the surface layer of the sediments were similar in different regions of the sea, varying within 11.3–15.7 µg/g (Table 3). Conversely, the C_{org} content varied within a wider range of 0.231–1.050%. The Ocs distribution is more dependent on a grain-size type of sediment compared to that of HC. This assumption is confirmed by the symbatic C_{org} distribution in the sediments and their moisture: $r(C_{org}-\text{moisture}) = 0.83$. The correlation coefficients between these parameters and HC are lower: $r(C_{org}-\text{HC}) = 0.47$ and $r(\text{moisture}-\text{HC}) = 0.44$, which is caused by the rates of utilization and the synthesis of substances in the metabolism of a marine ecosystem [1].

The sorption potential of both HC and OM depends on the dispersion of sediments [15, 17] because the *r* values are statistically significant at $P = 0.95$ (statistical reliability) and $n = 27$ (number of samples). Evidently, the HC content is less affected by the conditions of sedimentation than the OM in general.

HC accumulation in both the bottom sediments and the surface waters of the Yenisei River–Kara Sea section proceeded in the physicochemical area of the marginal filter (Fig. 2c), where their concentrations are as high as 32 µg/kg in the surface layer (station 5018). These concentrations at the edge stations of the section were little different (8.4 and 7.3 µg/g). The distribution of the markers within the alkane composition showed a similar genesis of HC in different parts of the sea (Table 2, Fig. 4b). Compounds related genetically to the land vegetation prevailed, with $\Sigma C_{(12-24)}/\Sigma C_{(25-35)} < 1$ and CPI > 1. The odd $C_{25}-C_{31}$ homologues were dominant and n-alkanes prevailed over isoprenoids (pristane and phytane). The CPI value in the physicochemical zone of the Yenisei marginal filter was as high as 4.21 (station 5019). Conversely, the biological zone (station 5026) was characterized by an increased content of low-molecular homologues with the preva-

Table 2. Typical alkane composition for individual samples of particulate matter and bottom sediments

Station	HC*, µg/g	Pristane/Phytane	CPI			$\dfrac{\Sigma(C_{12-24})}{\Sigma(C_{25-35})}$	Dominant peaks
			$\Sigma odd/\Sigma even$	(C_{12-24})	(C_{25-35})		
Integrated samples of water and particulate matter							
1**	23.2	0.7	0.48	0.80	1.05	1.00	C_{16}, C_{17}, C_{25}
2	24.5	1.0	0.47	0.88	1.50	1.97	C_{16}, C_{17}, C_{22}
3	24.1	1.1	0.55	0.89	1.20	2.00	C_{16}, C_{17}, C_{25}
5	19.8	0.6	0.55	0.76	1.12	0.34	C_{16}, C_{26}, C_{29}
Bottom sediments							
5013 (0−1)	8.4	0.3	1.09	1.25	3.83	0.46	C_{25}, C_{27}, C_{29}
5016 (0−3)	13.0	1.3	1.19	1.57	4.16	0.27	C_{25}, C_{27}, C_{29}
5018 (0−2)	31.7	1.2	1.05	1.43	2.81	0.27	$C_{25}, C_{27}, C_{29}, C_{31}$
5019 (0−3)	19.4	0.5	1.19	1.31	4.21	0.20	C_{27}, C_{29}, C_{31}
5019 (3−17)	26.8	1.0	1.21	1.62	4.19	0.19	C_{27}, C_{29}, C_{31}
5010 (0−1)	23.6	0.8	1.10	1.18	2.87	0.17	C_{27}, C_{29}, C_{31}
5011-2 (0−3)	17.1	0.7	1.20	1.53	3.96	0.18	C_{27}, C_{29}, C_{31}
5023 (0−2)	7.8	1.0	1.04	1.25	3.16	0.29	C_{25}, C_{27}, C_{29}
5026 (0−2)	7.31	1.20	0.85	1.35	2.40	0.89	C_{17}, C_{25}, C_{27}
5044 (0−2)	10.8	1.32	1.01	1.43	2.98	0.45	C_{17}, C_{25}, C_{27}
5044 (14−18)	15.3	1.00	0.86	1.19	2.42	0.35	C_{25}, C_{27}, C_{29}
5045 (0−3)	11.0	1.0	0.92	1.06	2.28	0.29	C_{25}, C_{27}, C_{29}
5045 (3−7)	9.5	0.9	0.98	1.10	2.78	0.34	C_{25}, C_{27}, C_{29}
5045 (24−30)	7.7	1.1	1.00	1.00	2.43	0.18	C_{25}, C_{27}, C_{29}

 * Concentrations in particulate matter are given in µg/L.

** 1æ gravimetric; 2æ physicochemical; 3æ biological zone of the marginal filter; 5æ western section across the St. Anna Trough.

Table 3. Content of organic compound at the surface layer of bottom sediments

Stations	Section	HC, µg/g		C_{org}, %		Moisture, %	
		range	average	range	average	range	average
2011							
5007−5009	−	6.1−16.6	12.9	0.127−0.738	0.341	30.5−63.7	48.2
5010−5026	Yenisei	7.3−31.7	15.6	0.062−0.715	0.231	35.8−68.0	53.8
5028−5029	Taimyr	11.6−19.8	15.7	0.690−0.830	0.760	55.8−57.0	56.5
5032−5042	St. Anna Trough, west	2.7−25.4	14.6	0.226−1.213	0.750	37.3−65.5	56.7
5044−5054	St. Anna Trough, east	4.5−18.8	11.3	0.699−1.791	1.050	55.2−68.1	63.0
2007							
5946−4960	Yamal	4.6−76.6	45.8	0.01−2.36	0.75	23.4−76.6	48.1
4993−5004	Ob	3.7−42.4	13.65	0.21−2.36	1.01	21.5−85.6	57.03

lence of n-C_{17} alkane of phytoplankton and CPI value decreased to 2.4.

The PAH content in the surface layer of the sediments at the Yenisei marginal filter varied from 11 to 36.2 ng/g. These values are lower than those obtained formerly [23, 26], which may be caused by the variability of the riverine runoff. The maximum was associated with the physicochemical zone of the marginal filter similarly to that of aliphatic HC (Fig. 5). Perylene and phenanthrene of natural origin were prevailing within PAH composition, amounting to 24 and 20%, respectively, of the total PAH [26, 31, 32]. The fraction of perylene in the zone of avalanche sedimentation was 12% or below; the relative amounts of phenanthrene and fluoranthene increased to 27 and 17%, respectively (Fig. 5). The fractions of phenanthrene and fluoranthene were as high as 32 and 17%,

respectively, at the seaward stations in the biological zone of the marginal filter, with a decrease of perylene content to 9%. The anthropogenic impact was pronounced in riverine waters as the increased content of naphthalene (to 12%) and pyrene marking the oil fields and the pyrogenic PAH, respectively. The transformation of polyarenes results in the increase of fluoranthene content, hence, Fl/P = 0.8. Low-molecular polyarenes pass through the mixing zone of riverine and marine waters as transit matter, which causes an increase of the phenanthrene fraction to 38% of the total value on the background of the decrease of PAH concentrations.

When passing from the upper oxidized (0−3 cm) to the reduced layer (3−17 cm) of the sediments, the C_{org} and HC concentrations decreased in several cases (e.g., at stations 5010, 5013, 5015, etc.). At other sta-
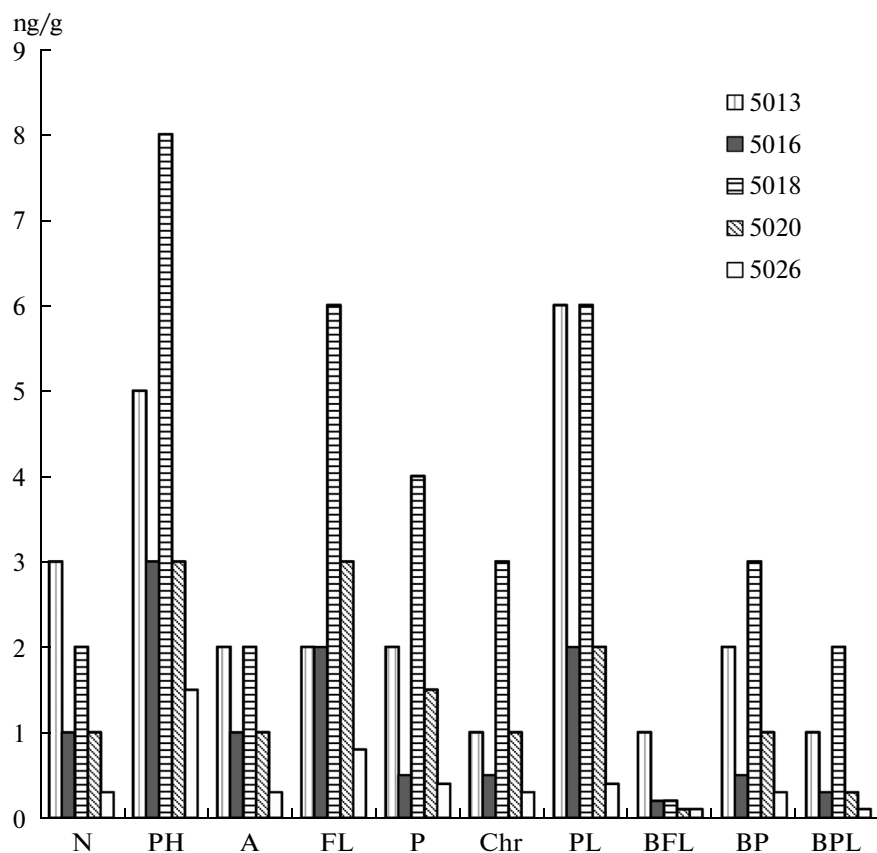
ng/g

Fig. 5. Composition of unsubstituted PAH in the Yenisei River−Kara Sea section.

tions, these concentrations increased, especially in the zone of avalanche sedimentation, in the physicochemical zone of the Yenisei marginal filter (stations 5016–5020), and at the St. Anna Trough (stations 5033 and 5051). This is caused by the changes in the material composition and redox conditions in the sediment mass. The HC content in these layers decreased even faster than that of OM [14, 15]. Thus, the HC maximum at station 5045 coincided to the C_{org} minimum (Fig. 6). The alkane composition in the layer of 3–7 cm appeared to be more biogenic that in the surface layer of the sediment, because of the registered n-C_{19} maximum caused by the microbial transformation of HC (Fig. 4c). The initial stage of sedimentation is characterized by the intense OM transformation by microorganisms [10]. The development of the reduction processes in the sediments under the supply of labile OM being assimilable for bacteria results in a change of redox potential of the environment and HC transformation.

The PAH content within the sediment mass varied synchronously with aliphatic HC. The content of polyarenes increased owing to PH, FL, P, and Chr from the oxidized to reduced layer in the sediments of station 5008 affected by the Ob River waters. The PAH concentrations at station 5033 varied irregularly with the burial depth, being twice as high in the layer of 30–

38 cm as those in the surface layer (13 and 6 ng/g, respectively) owing mainly to phenanthrene.

Summarizing the presented data, one may conclude that the increased gradient of Ocs concentrations was registered in the frontal zones, not only in the mouth areas of the Yenisei and Severnaya Dvina rivers but also in the western part of the section at the St. Anna Trough (to 60−80 μg/L, Table 1, Fig. 3). The HC concentrations in surface waters in September 2011 showed much wider variability compared to 2007, when the HC content did not exceed the background values (10−20 μg/L) and conformed to the levels for the Arctic open seas [15]. These concentrations varied within 216−10 μg/L from riverine to marine waters exclusively in the Ob River mouth. During our surveys at the St. Anna Trough, the content of HC in dissolved and particulate forms at neighboring stations in the frontal zones increased by factors of 4 and 11, respectively. The growth of HC concentrations at the southern extremity of the St. Anna Trough (Fig. 3) is caused by natural processes despite the excess of maximum allowable concentrations for oil HC. This growth proceeded in the area of high gradients of temperature between Arctic waters and those desalinized by continental runoff [5]. This area was also marked by high concentration gradients of chlo-

rophyll, dissolved OM, and particulate matter. It was also noted that the location of frontal zones varied considerably from year to year and was probably determined by the effect of intense wind events.

In the Yenisei marginal filter, concentrations of both aliphatic HC and PAH in surface waters and sediments in September 2011 varied within a narrower range than those in September 2007. This difference is caused by the character of the rocks constituting the drainage basins of these two rivers [9, 11]. Unlike the Ob River, the Yenisei river runoff is regulated, which results in a decrease by more than a half of the supply of river drifts (from 13 to 4.9 million t/year) [12].

In the frontal zone of the Yenisei river, changes in hydrophysical and hydrobiological characteristics under the mixing of riverine and marine waters causes a particular type of sedimentation process, as well as variability of HC content and composition. Oil HC supplied into the aquatic environment of natural basins are distributed in a short time over different forms of migration (dissolution, sorption by particulate matter or by sediments, etc.) [14, 30]. Anthropogenic HC transferred by the rivers are transformed quite rapidly despite the low temperatures in the marine environment [15]. The microplankton of high latitudes utilizes and assimilates intensively both autochthonous and allochthonous OM due to low activation energies of the main reactions of metabolism (3–6 kcal/M), comparable to exchange intensity in warm waters [1]. Therefore, the composition of n-alkanes pointed to a high degree of degradation of the hydrobiont component (Table 2). Moreover, one must note that the main role in OM supply to the Kara Sea is played not by young biogenic substance but by the older terrigenous matter supplied by the rivers [12, 25]. All these effects result in the prevailing of autochthonous compounds in the alkane composition of water and particulate matter and the domination of allochthonous matter in bottom sediments (Fig. 4).

The obtained data are contradictory to current opinion about the existence of numerous "hot points" of maximum pollution of the Ob–Yenisei region in the Kara Sea [4, 6]. It is probable that such points occur at the drainage basin of the Kara Sea. It was found that the waters of the lower courses of the Ob, Pur, and Nadym rivers must be characterized as extremely polluted, and the Taz River waters are considerably polluted [6]. This means that the maximum allowable concentrations of pollutants are sufficiently exceeded. Particularly, the HC concentrations in the waters of the Antipayuta area of the Taz Estuary varied within 50–280 µg/L in summer 2009 and were considerably higher than those in autumn (20–50 µg/L). HC content at the considered aquatic area in 2011 was over maximum allowable concentrations in waters at 68% of the stations, amounting on average to 127 and 118 µg/L in the surface and near-bottom layer, respectively. HC content in the bottom sediments of Ob Bay
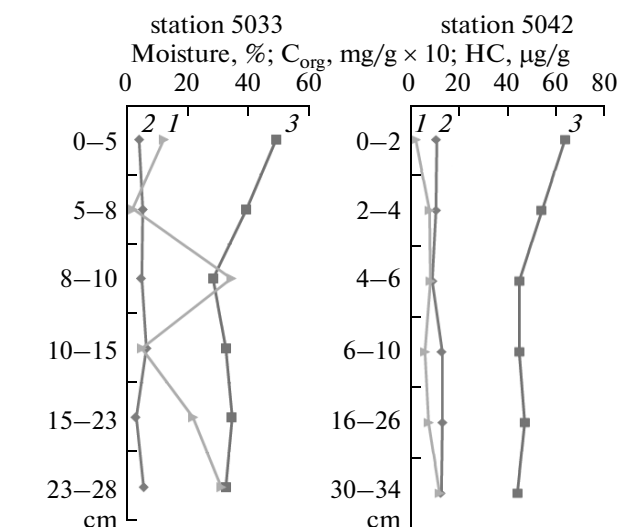

Fig. 6. Distribution within the sediment mass at stations 5033 and 5042: *1*—HC; *2*—C_{org}; *3*—moisture.

(150 µg/g) was three times as high as the EU allowable concentrations for oil hydrocarbons.

At the same time, according to our studies and published data, HC composition in the Yenisei and Ob estuaries was characterized by mainly natural terrigenous genesis, even despite its high concentration [15, 17, 22]. A greater importance in the pollution of bottom sediments may obtain from the distant transfer of Pts by waters of streams crossing regions of oil production [3] where Pts are supplied by surface and underground runoff from drilling and technological areas. As a result, HC content in the Taz Estuary is higher than that in the Ob Bay, owing to the waters flowing over the Pur oil-producing area. Because of this, HC concentrations in the surface layer of sediments increased to 55–205 µg/kg in 2002–2003 during the drilling activity in the Ob Bay [17]. The decrease of these concentrations in 2007 (42.4 µg/g maximum value) might testify both to the decomposition of oil HC and to the burial of bottom sediments by a layer of newly supplied relatively clear matter.

Based on data on the amounts of supplied oil and of HC in various marine matter and bearing in mind that crude oil contains on average 5.8% n-alkanes and 4.7% PAH, fluxes of alkanes and PAH to the Arctic seas were evaluated [21]. According to these evaluations, the amount of oil HC supplied in the course of the oil production, transportation, and usage is considerably lower compared to supply by natural seepage. The Arctic is still characterized by a relatively clear environment, even in coastal waters [4, 17, 21].

CONCLUSIONS

A pronounced interannual variability of HC concentrations compared to September 2007 is revealed (especially in surface waters). This variability is deter-

mined by hydrodynamic conditions, and the growth of HC content coincides with an increase of the concentrations of particulate matter and chlorophyll *a*. HC concentration in surface waters (up to 80 µg/L in the adjacent aquatic area of the northern extremity of the Novaya Zemlya Archipelago) appears to be even higher than those in the Yenisei River mouth area (to 43 µg/L).

The distribution of HC is caused by their grain-size composition in the surface layer of bottom sediments and by redox conditions within the sediment mass.

HC distribution follows the regularities of marginal filters both in the Yenisei River–Kara Sea and in the Ob River–Kara Sea sections [11]. The HC are accumulated in surface waters and bottom sediments of the physicochemical zone, so quite clear waters are supplied to the pelagic area.

Lower HC concentrations in the Yenisei River mouth area compared to the Ob Bay result from a difference in the character of the rocks constituting the drainage basins of these two rivers, as well as from the regulation of the Yenisei runoff. Unlike the Ob Bay–Kara Sea section [15], the Yenisei section showed no successive decrease of Ocs concentrations seawards from the mouth; this is caused by the jump in salinity and by tidal events during sampling.

In view of the mainly natural HC composition in the water and bottom sediments of the Kara Sea coastal area, one may conclude that the marginal filters of the rivers eliminate supplied pollutants. Hence, the notion of the rivers as the main sources of oil pollution on the shelf of Arctic seas [24] is quite hyperbolic.

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Translated by A. Rylova