

Concentration and Composition of Hydrocarbons in Water and Sediments of The Kara Sea in Different Seasons

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Abstract: The results on the content and composition of aliphatic hydrocarbons (AHCs) and polycyclic aromatic hydrocarbons (PAHs) in surface water and bottom sediments in the Kara Sea were summarized. It was established that the “losses” in AHC concentrations in surface waters in the zone of mixing of river waters (Ob, Yenisei) with sea water exceeded, in some cases, 90% of their removal by the rivers. The composition of AHCs in surface waters depends on the characteristics of the river catchment, sampling season, and time of day (tide, low tide) and coincides with the distribution of the suspended particulate matter (SPM). The highest content of organic compounds and SPM in surface waters was found in the Gulf of Ob in flood: AHCs – up to 514 µg/L, PAHs – up to 15 ng/L, and SPM – up to 15.5 mg/L. In the Kara Sea, the AHC concentrations increased on average from in low water 10–20 µg/L to flood – 325 µg/L, which is associated with the melting of seasonal ice and growth of primary production. In bottom sediments, the particle size distribution determines the AHCs and PAHs; terrigenous n-alkanes dominate the molecular composition. A comparison was made with the behavior of AHCs and PAHs in the SPM of surface waters and bottom sediments in the estuarine areas of other Siberian rivers.

Keywords: hydrocarbons; lipids; Corg; suspended particulate matter; bottom sediments; chlorophyll a; Ob; Yenisei Rivers; Kara Sea.

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1. Introduction

Currently, due to the growing importance of resources, the Arctic region is not considered a periphery but rather a center of international attention [1, 2]. The state of the shelf of Arctic marginal seas is largely influenced by the huge volume of continental runoff, estimated at 2300–2500 km³/year, and its transformation in the river–sea mixing zone [3].

The research of hydrocarbons (HCs) in high-latitude areas is particularly relevant in connection with the exploration of petroleum and gas resources in the Arctic sea shelf. Therefore, the development of monitoring that determines the state of these areas, including cross-border transport of pollutants, is among the main tasks that need to be addressed to ensure environmental safety. Monitoring should consider that the spread of human-made HCs occurs on a naturally sustainable biogeochemical background. Whereas these concentrations are zero for xenobiotics, such as pesticides, then for oil HCs the situation is more complicated. Phytoplankton annually synthesizes 12 million tons of HCs in the ocean, and according to the latest data of the National Academy of Sciences (NAS) of the United States, the mass of HCs

entering from all sources is on average 1.3 million tons per year (at a possible interval of 0.47 to 8.4 million tons per year [4]). To understand the changes taking place in the Arctic, it is necessary to consider not only the availability of natural resources but also new possibilities for their transportation and the fragility of the Arctic environment.

Our studies have shown that natural non-human hydrocarbon geochemical anomalies are constantly in marine environments [5]. Without an examination of the background of the HC concentrations, it is impossible to distinguish their manufactured component. It is of special importance to investigate the geochemical barrier zones, where the most intensive processes of dispersal and concentration of various compounds happen, such as the river–the sea, the atmosphere–the water, the water–the bottom sediments, etc.

The river runoff determines the hydrological regime of the Kara Sea, especially in its southern part. Approximately 58% of annual river runoff enters in May–July, and 80% in June–September [6]. The development of industry and the construction of cities, dams, and power plants are becoming one of the main reasons for the change in river flows [3, 7]. The organic matter (OM) supplied by the rivers extends to the vast expanses of the Arctic basin. The resulting suspended particle matter (SPM), enriched in various compounds, is a kind of “geochemical traps” that contribute to the accumulation of components of river runoff, including man-made ones [4, 8–10]. Therefore, the riverine matter is precipitated at the river–sea boundary, which determines the content of the OM, and the HCs composition [4, 11].

In order to study the processes of input and differentiation of natural and anthropogenic HCs, as well as their possible transformation into various forms of migration, in 2007–2019 in cruises of R/V “Academician Mstislav Keldysh”, a study of aliphatic HCs (AHCs) and polycyclic aromatic hydrocarbons (PAHs) in water, SPM, and bottom sediments was conducted. The study aims to establish patterns of HCs in the distribution and genesis in the water and bottom sediments of the Kara Sea in different seasons. Particular attention is paid to the geochemical barrier zone of the rivers (Ob, Yenisei) – Kara Sea.

The projected amount of HCs in the bottom sediments of the Kara Sea is about 21 billion tons in the petroleum equivalent [12], with strategic reserves on the shelf and in the coastal zone of the sea. In the near future, intensive development might begin, resulting in anthropogenic effects on the basin [3]. It is believed that 1% to 3% of the total petroleum produced in Western Siberia enters the environment [13]. This amounts to 20 to 200 million tons of spilled petroleum, which is still the main factor of environmental disadvantage in the Obi and Yenisei River basins [14].

In the context of the changing climate in recent years, with a significant reduction in the area of perennial ice [15,16], the change in primary production should affect the HC concentrations. Therefore, the study of HCs becomes especially relevant as their natural background changes. When assessing the anthropogenic influence in the extraction and transportation of HCs raw materials, it is necessary to determine it. These studies take on a special urgency before the start of large-scale petroleum production on the Arctic shelf.

The processes in the Arctic seas, especially in coastal areas, vary greatly depending on the study season [17–21]. In particular, in Ob Bay, during the transition season from the flood to the low water, the river runoff current slows down by about three times (from 1.666 to 0.555 m/s) [20]. When Ob Bay becomes free from the ice, the maximum amount of nutrients accumulate in the waters [21].

In addition, the light period became predominant over a day, and the temperature of air and water was set at maximum values in the intra-annual scale. Therefore, in the entire water

area of the Ob Bay, active photosynthesis begins, which results in a difference in specifics of many processes occurring in the bay, and first of all, in such an integral indicator as to the OM [22], as well as in the HCs composition.

It should be noted that due to hydrophobic properties, AHCs and PAHs occur mainly in suspended form during the flood [6]. Our earlier studies in the Gulf of Ob have shown that suspended PAHs concentrations during the summer survey were 35–40 times higher, and during the autumn survey, 25–30 times higher than that in the dissolved form. [22]. However, both in the summer and autumn, the elevated content of PAHs, as well as the OM in general [23], is found in the zones of water mixing: in the southern part of the Taz River flows into the Ob Bay, and in the northern part, where the Ob River water mix with the Kara Sea. This trend in the distribution of PAHs continued in the surface layer of bottom sediments [4]. Their higher concentrations were detected in sandy loams, light loams, and clays. At the same time, there was no direct relationship between the content of the PAH content and the granulometric type of sediments.

According to the model of A.P. Lisitsyn [9, 24], this zone is divided into three parts: 1) the area of gravitational deposition (the fallout of the main part of the sand and coarse silt fractions); 2) the colloidal dispersal area, where sorption and desorption of various elements occur; 3) the outer part is a biological zone, where the productivity of seawater increases due to the growth of the water transparency.

2. Materials and Methods

The HCs study was carried out depending on salinity compared to the contents of SPM, lipids, C_{org} , chlorophyll a (Chl *a*). Water samples were taken using a shipborne sounding system equipped with an SBE-911p hydrophysical probe (Sea-Bird Electronics, Inc., USA) equipped with 10-liter Niskin bottles and combined with a Sequoia LISST laser particle analyzer.

The SPM for determining the organic compounds (OCs) was isolated from surface layer water samples by filtration on GF/F (0.7 μm) fiberglass filters precalcined at 450°C under a vacuum of 200 mbar. In addition, to determine its weight concentration (mg/L), SPM was filtered under a vacuum of 400 mbar through nuclear membrane filters (pore diameter 0.45 μm). Bottom sediment samples were taken by an “Ocean grab sampler”, a multi-corer, and box corer.

Methylene chloride was used to extract lipids from water, SPM, and bottom sediments. All solvents were of high purity qualification. Methylene chloride was used to extract lipids. Individual HC fractions were isolated with hexane by column chromatography on silica gel. The concentrations of lipids (before column chromatography on silica gel) and AHCs (after column chromatography on silica gel) were determined by IR spectroscopy on a Shimadzu IRAffinity-1 instrument (Japan) [25]. The following mixture (by volume) was used as the standard: 37.5% isooctane, 37.5% hexadecane, and 25% benzene [26, 27]. The method's sensitivity is 3 $\mu\text{g}/\text{ml}$ of the extract [6, 25]. This procedure is adopted as an arbitration method for determining petroleum HCs in seawater [27].

To analyze alkanes, we used a Russian Kristall-Lux 4000-M chromatograph equipped with a flame ionization detector (FID) and a capillary column 30 m x 0.22 mm manufactured by Supelco, with the following phase: 5% phenyl and 95% polyxylene, when programmed from 60 to 300°C at a rate of 8⁰/min; the carrier gas is helium (gas flow rate 1.5 ml/min) [25]. To calibrate the instrument and determine the release time of identified alkanes, we used a

mixture of n-C₁₀–C₄₀ calibration standards from Supelco and squalane from Sigma Aldrich as the internal standard.

The content and composition of PAHs were determined using HPLC and LC 20 Prominence liquid chromatograph (Shimadzu, Japan). An Envirosep PP column was used at 40°C in a thermostat under gradient conditions (up to 50 to 90% in a volume of acetonitrile in water). There was used a 1 cm³/min flow rate of the eluent, and an RF 20A fluorescent detector with programmed wavelengths of absorption and excitation was used. The calculations were performed using LC Solution software [25, 28]. The equipment was standardized with individual PAHs and their mixtures manufactured by Supelco Co. As a result, the key polyarenes recommended for studying the pollution of marine objects [28, 29] were identified.

C_{org} in SPM and bottom sediment samples were determined by dry combustion on a Russian AN-7560 analyzer. The method's sensitivity is 6 µg of carbon in the sample; the accuracy is 3–6 % [30, 31]. To recalculate AHC concentrations to C_{org} concentrations used in bottom sediments, a coefficient of 0.86 was used [6].

The Chl *a* concentration after filtration on GF/F filters was determined by fluorimeter on a Trilogy 1.1 device (Turner Designs, USA) in the “ship’s laboratory according to the method [32]; the SPM composition was determined on a VEGA-3sem scanning electron microscope (TESCAN, Czech Republic).

3. Results and Discussion

3.1. Surface water Ob River–Kara Sea

In 2007, the observation was conducted during the low flow season. In the water, concentrations of dissolved AHC_{s_d} varied 291 to 6 µg/L, while the concentrations of particulate AHC_{s_p} reduced from 310 to 10 µg/L (Table 1), which corresponded to the summer condition of the marginal filter of the Arctic Seas [24]. In the Gulf of the Ob, lipids, and AHCs in surface waters occurred mostly in dissolved form (Figure 1), as the river flows through soils rich in humus. Further, along the transect, there was an increase in concentrations of all organic compounds. In the salinity interval of 0.05-0.6 PSU, the AHC_{s_d}/AHC_{s_p} ratio varied from 1.65 to 1.35. At salinity from 1 to 5.5 PSU, the major part of AHC was removed from the surface water, followed by a decrease in dissolved and particulate forms [25].

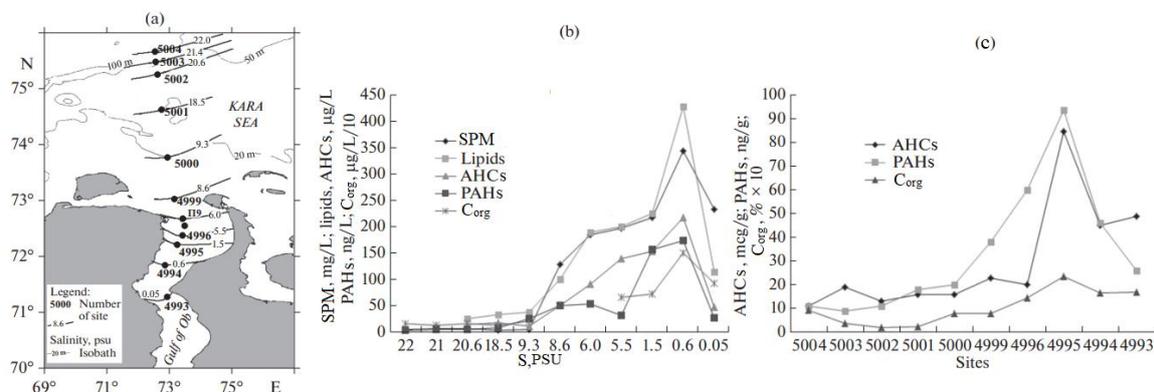


Figure 1. Distributions at the Ob River–Kara Sea boundary in low water (September 2007): (a) – location map of the sampling station, (b) – organic compounds in SPM of the surface water, (c) – organic compounds in the bottom sediments.

While salinity increased, concentrations of the dissolved organic compounds (OCs) decreased, while concentrations of OCs in particulate matter increased, and the minimum

concentration of dissolved forms at $S = 6$ PSU (Site P-9) corresponded to their maximum concentration in particulate matter ($AHCs_d/AHCs_p = 0.18$). In this part of the transect, the AHCs concentration calculated per mg of SPM increased 8.5 times (from 2 to 16.9 $\mu\text{g}/\text{mg}$ of SPM, Figure 1a) [25].

A large amount of sorbents and the salting effect of seawater lead to the transformation of dissolved forms of AHC into particulate ones. While salinity increases, these compounds' dissolved and particulate forms change synchronously.

Table 1. Content of lipids, AHCs, SPM, and salinity in surface waters in river-sea transects in different years of research.

Year, month	n	Lipids, $\mu\text{g}/\text{L}$		AHCs, $\mu\text{g}/\text{L}$		SPM, $\mu\text{g}/\text{L}$		S, PSU
		interval	average	interval	average	interval	average	
Ob River–Kara Sea								
2007.09	12	25–427	182	10–310	101	0.32–34.37	11.62	0.1–20.7
	14d*	27–748	174	6–291	90			
2016.07	13	14–33	163	3–102	40	0.25–10.64	10.31	0.0–31.5
2017.09	5	22–484	166	5–365	100	0.17–5.47	3.52	2.7–25.3
2018.09**	4	35–119	52	17–29	22	0.63–1.85	0.90	24.9–30.0
2019.07	12	192–1637	578	62–514	325	2.93–15.5	7.47	0.16–7.56
Western Part of the Kara Sea								
2019.07	9	64–98	89	51–66	59	0.05–1.07	0.30	28.4–34.5
Yenisei River–Kara Sea								
2011.09	14	22–236	83	7–149	20	0.34–2.93	1.3	0.07–27.93
	15d	22–134	40	5–69	18			
2016.09	22	19–253	68	1.9–53	17	0.18–2.20	1.07	0.4–31.4
Khatanga River–Laptev Sea								
2017.09	17	12–452	108.1	4–189	39	0.1–29.5	7.5	3.5–32.2
Lena River–Laptev Sea								
2015.09	14	18–71	40	4–43	14	0.28–16.23	3.4	2.7–30.1
2017.09	2	22–76	-	7–23	-	0.14–0.86	-	6.8–17.8
Indigirka River–East Siberian Sea								
2017.09	13	145–188.	49	1–61	16	0.09–2.54	0.7	14.8–30.1
Kolyma River–East Siberian Sea								
2017.09	7	11–50	22	2–8	4	0.09–1.7	0.7	17.0–29.4

*4d and 15d concentrations in dissolved form, all other samples – in SPM:

** Samples were taken on the shelf of the Kara Sea

Stratification of the waters in this area was insignificant since at the beginning of the transect, the surface and bottom waters' salinity almost coincided (up to 72°N) [31]. However, in the bottom waters, due to the influence of nepheloid flows, the content of $AHCs_p$ increased with the salinity growth due to the effect of nepheloid flows ($AHCs_d/AHCs_p = 0.56–0.32$). The concentration of $AHCs_s$ in seawater taken from the Neimisto corer was higher than $700 \mu\text{g}/\text{L}$ [25].

The PAH concentration also decreased while the transition from the riverine to seawater. The highest PAH and AHC concentrations were detected at a salinity of 1.5 PSU [25]. However, in more saline water, the maximal AHC concentrations are found to a lesser extent. The likely reason for this is the different nature and sorption capacities of these HCs classes, which depend on their physicochemical characteristics and ability to intermolecular and adsorption interaction. The AHCs are produced by biosynthesis and brought to water bodies with oil contaminants [25, 31]. It is so far uncertain whether polyarenes can be synthesized biogenically, and PAH is thought to be produced mainly by pyrolytic processes [2, 25, 35].

Hydrophobic AHCs are adsorbed mostly by SPM, while the more hydrophilic polyarenes (when dominated by three- and four-cyclic compounds) transfer into dissolved

forms. However, similar to AHCs, the content of SPM controls the PAHs distribution: $r(\text{SPM-PAHs}) = 0.77$ ($n = 9$) [25].

At the same time, in terms of mg SPM, the maximum content was detected at seaward stations, i.e., a decrease in concentrations of polyarens, as a more sustainable hydrocarbon class, occurs to a lesser extent. The PAH was dominated by phenanthrene, which is formed in natural processes. In the surface waters of the Gulf of the Ob, a significant proportion of perylene also has a biogenic origin [29, 36, 37]. Minor components of PAHs in the water and filtered SPM, include benz(a)pyrene, which has carcinogenic and mutagenic properties [2, 5].

The construction and operation of the Sabetta port on the western coast of the Ob Bay, intended to ensure the transshipment of HCs raw from the South Tameyskoye gas condensate field in the Yamal Peninsula, and the accompanying intensification of navigation would affect the environmental situation in this region. During the canal's construction to the port of Sabetta, intense dredging operations were carried out in the summer period since 2014, with a total volume of the excavated soil of about 70 mln m³ [38]. This should have led to an increase in the amount of SPM in the water. Indeed, in July 2016, the content of SPM over the whole transect (10.3 mg/L on average) was significantly higher; on the contrary, the concentration of AHCs was lower (Table 1). However, the variability of their concentrations also corresponded to zones of the marginal filter (Figure 2) [6].

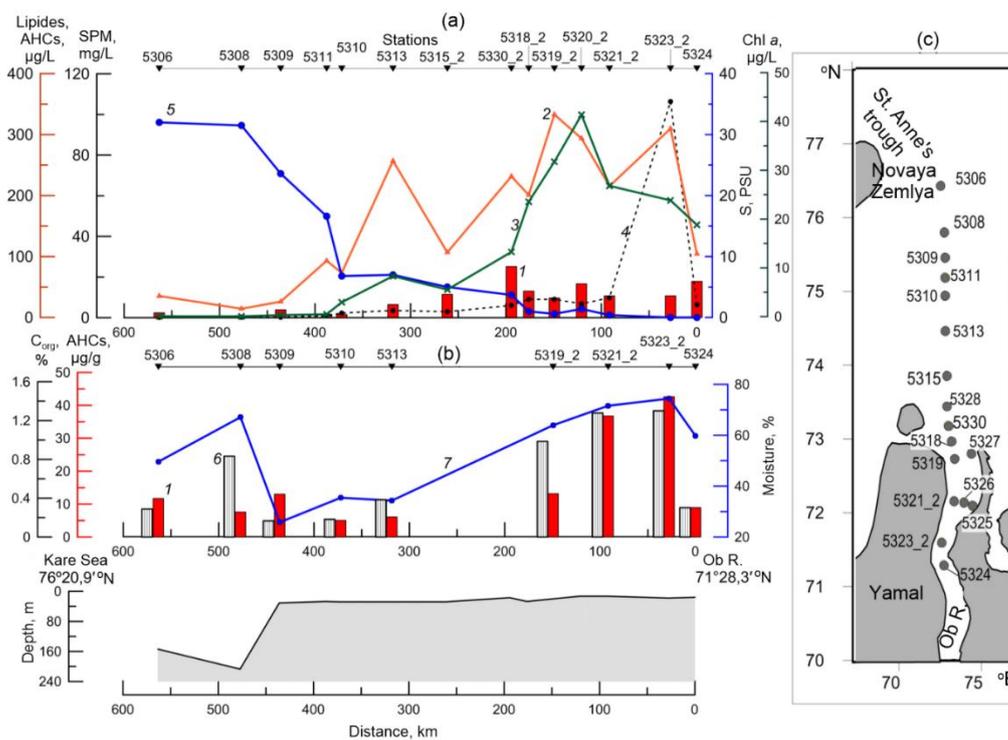


Figure 2. Distribution of various compounds at the transect of the Ob River – the Kara Sea in low water 2016: (a) – in SPM from surface waters, (b) – in bottom sediments, (c) – location of sampling stations: 1 – AHC, 2 – lipids, 3 – Chl a, 4 – SPM, 5 – salinity, 6 – C_{org}, 7 – moisture.

In the Gulf of the Ob, SPM is presented not only by the mineral (smectite, muscovite, quartz, and albite) but the biogenic particles also (diatoms, alga fibers with 50 µm to 1 mm length, and the silicon (opal) skeletons of phytoplankton) (Figure 3). This material is underlain by films of organic matter (OM) and Fe hydroxides [24]. In the seaward part of the profile, particulate matter is dominated by biogenic particles (diatoms and their fibers and spores), while the mineral clay particles, films of Fe hydroxide, and OM were rarer.

A sharp decrease (almost 3 times, up to 3.52 mg/L) in the SPM concentration occurred after the completion of the canal construction in September 2017. On the contrary, the AHC content, especially in the southern part of the bay, increased to 365 $\mu\text{g/L}$ (86 $\mu\text{g/mg}$ of SPM). Weathered petroleum AHCs were dominated in the composition of alkanes in the low molecular weight range [39], which is probably due to the intensification of navigation in this region.

In 2019, researchers working in the Kara Sea and the Gulf of the Ob were carried out immediately after the seasonal ice melting. According to satellite data, samples at stations 6221 and 6222 (Figure 4a) were taken 0–5 days after the ice melting and at stations 6223–6225 and 6234 – directly at the ice edge.

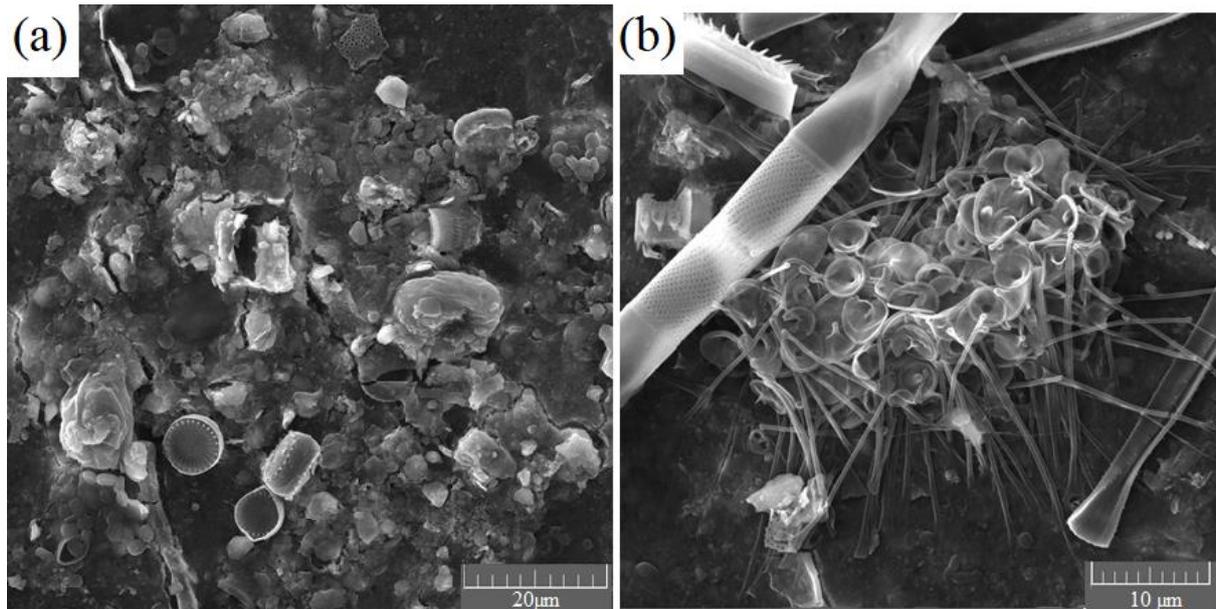


Figure 3. SPM composition in surface waters of various regions of transect: Ob River–Kara Sea: (a) – St. 5323-2, (b) –St. 5308 in 2016. The location of the stations is shown in Figure 2.

In July 2019, the content of SPM varied from 0.05 mg/L (station 6221, shelf of the Novaya Zemlya) to 1.07 mg/L (station 6234, near the ice edge, Figure 4). During the melting of the seasonal ice, the surface water salinity at the ice edge decreased by ~ 5 PSU (to 27.7 PSU), and the ice-loaded material was released. At the ice edge, environmental conditions promoted an increase in the concentrations of Chl *a* and SPM [39]; from our data, the amount of biogenic SPM increased more than 5 times (0.11 to 0.58 $\mu\text{g/L}$).

The content of lipids and AHCs changed to a lesser extent; the AHC concentrations were almost constant (Figure 4b): 51–66 $\mu\text{g/L}$, with an average value of 59 $\mu\text{g/L}$ and a standard deviation of ± 4.6 $\mu\text{g/L}$ (7.8% of the average). The authors observed a similar behavior of SPM and AHCs over the transect along the Antarctic coast [5, 40], where an increase in the SPM content occurred synchronously with an increase in the Chl *a* concentration. At the same time, the AHC values showed almost no change, because AHCs were not the dominant fraction in biosynthesis [25].

At station 6244, located in the outer Ob River estuary, a sharp increase in all studied components was observed, as salinity decreased to 6.1 PSU (Figure 6b): SPM increased 2.7 times (up to 2.93 mg/L), lipids – 4.5 times (up to 417 $\mu\text{g/L}$), AHCs – 2.5 times (up to 169 $\mu\text{g/L}$). This trend was also observed in the Gulf of the Ob, decreasing salinity from the north

to the south. The amount of SPM compared to the open areas of the Kara Sea increased 31 times on average (up to 9.41 mg/L), and AHCs increased 6.2 times on average (up to 372 µg/L).

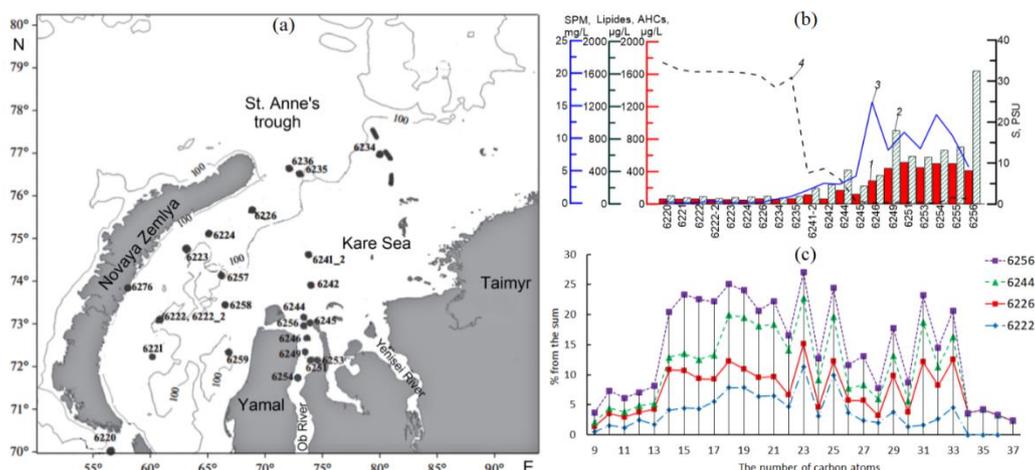


Figure 4. Location of sampling stations in cruise 76 of the R/V Akademik Mstislav Keldysh in July 2019 (a); distributions of: 1 – AHCs, 2 – lipids, 3 – suspended particulate matter, 4 – salinity in surface waters (b); composition of alkanes in SPM in surface waters at different stations (c).

The SPM maximum content (15.5 mg/L), in contrast to the maximum AHC values, was detected at station 6246, where the surface salinity was 0.22 PSU. The SPM content decreased southwards and then increased again to 13.62 mg/L at station 6254, where salinity was 0.16 PSU. The AHC content also increased 1.8 times up to 114 µg/L at the entrance to the Gulf of the Ob, from station 6245 to 6246. Southwards, in the Ob Gulf water, the average content of SPM and AHC reached 10 and 469 µg/L, respectively. The observed correlations in the distribution of AHCs and lipids ($r=0.79$), AHCs and SPM ($r=0.85$), as well as lipids and SPM ($r=0.55$) indicated mainly the natural biogenic composition of the studied compounds.

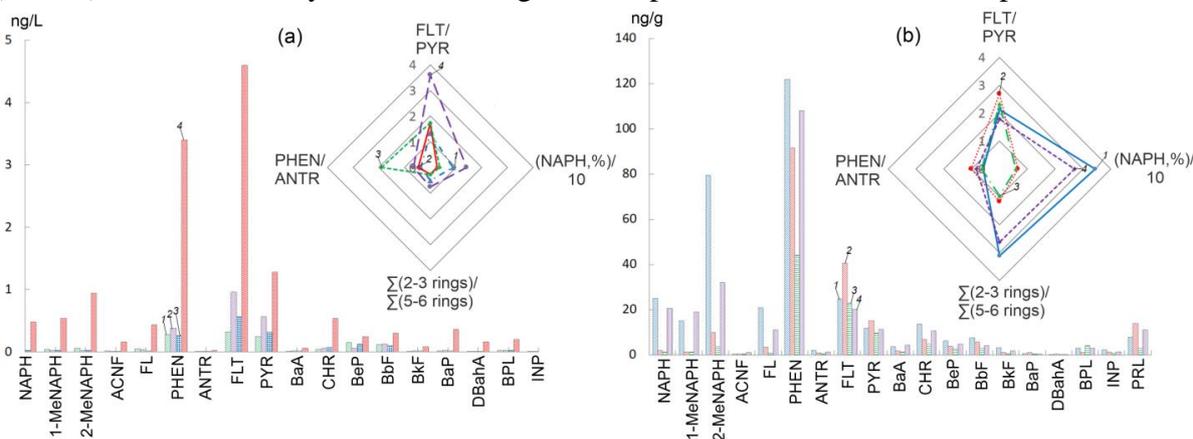


Figure 5. Composition of PAHs in the suspended particulate matter of surface water (a) and in the bottom sediments (b) at individual stations. The insets show the distribution of the main markers in the composition of PAH. Naph – naphthalene, 1-MeNaph – 1-methylnaphthalene, 2- MeNaph – 2-methylnaphthalene, Ace – acenaphthene, Flr – fluorene, Phen – phenanthrene, Antr – anthracene, Flu – fluoranthene, Pyr – pyrene, BaA – benzo(a)anthracene, Chr – chrysene, BeP – benzo(e)pyrene, BaP – benzo(a)pyrene, BbFlu – benzo(b)fluoranthene, BkFlu – benzo(k)fluoranthene, DbAntr – dibenzo(a,h)anthracene, BPl – benzo(g,h,i)perylene, Ip – indeno [1,2,3-c,d] pyrene, Pl – perylene. 1 – st. 6234, 2 – st. 6235, 3 – 6242, 4 – st. 6254. The location of the stations is shown in Figure 4a.

The homologs of low molecular weight dominated among alkanes in SPM, since the ratio $(\sum(C_9+C_{24})/\sum(C_{25}+C_{37}))=L/H$ varied in the range 0.92–2.29 (on average, 1.84). The

smooth character of the alkanes' distribution (Figure 4c) likely indicates the influence of weathered petroleum hydrocarbons on their composition. The latter was also confirmed by the dominance of phytane over pristane, as *i*-C₁₉/*i*-C₂₀ ratio averaged 0.56, and the C₁₇/C₂₅ ratio was only slightly higher 1 (1.15, on average).

The concentrations of PAHs in the surface waters of the Kara Sea were low, 1.6 ng/L on average; their amount increased significantly in the Ob Gulf, up to 14.7 ng/L on average. The most stable polyarenes (phenanthrene and fluoranthene) dominated the PAH composition [35] (Figure 5a). In this case, the contents of naphthalene's and the high-molecular polyarenes were generally lower than their detection limits. Only at station 6254 in the Gulf of the Ob, in the low-molecular range, a peak of 2-methylnaphthalene, characteristic of the petroleum PAHs, was distinguished.

The insignificant amount of the pyrogenic PAHs in the samples also confirms the phenanthrene/anthracene ratio, which varied in a range of 65–190, since only at values <10 this ratio indicate a significant portion of ship fuel combustion's products in the PAH composition. The fluoranthene/(fluoranthene + pyrene) ratio, which marks the pyrogenic PAHs at values <0.5 [34, 41, 42], was 0.62 on average in our determinations. This also confirms the insignificant effect of ship fuel combustion's products on their composition.

3.2. Bottom sediments Ob River–Kara Sea

Bottom sediments in the Ob Bay – Kara Sea section in 2007 in the innermost part consisted of black (station 4993) and fine silt silts (stations 4995–5000), while large silts and medium-grained sands were recorded at peripheral stations (stations 5001 and 5002, location of the stations is shown in Figure 1a). Silty–pelitic oozes were found only at deep-water station 5004. The variability in OM content in the uppermost layers of the sediments is quite significant: C_{org} varies from 0.21 to 2.36% (Table 2), and the contents of AHCs and PAHs were 5–42 μg/g (0.04–0.21% C_{org}) and 11–94 ng/g (0.12–0.84 × 10⁻³ C_{org}), respectively. The maximum concentrations of OCs were detected at station 4995 (Figure. 1c), which occurs in the physicochemical zone of the marginal filter in the zone of avalanche sedimentation. In this zone, changes in the charges of colloid particles (*S*=1.5 PSU) are associated with the transition of OCs in SPM (maxima of their concentrations, Figure 1b) of the near-bottom and sediments [25].

Table 2. Content of organic compounds and moisture in the surface layer of bottom sediments of the Arctic seas in different years of research.

Year	n	Lithological type	Moisture (average), %	AHCs interval (average), μg/g	C _{opr} , interval (average), %
Ob River–Kara Sea					
2007	2	Silty sand	28.9	5–10 (9)	0.21–0.36 (0.28)
	8	Aleuropelite	68.0	7–42 (16)	0.63–2.36 (1.29)
2016	5	Sand	36.3	5–13 (9)	0.14–0.67 (0.35)
	9	Aleuropelite	69.8	4–43 (21)	0.30–1.38 (1.07)
2017	4		65.4	15–44 (26)	0.64–1.55 (1.14)
2019	1*		63.9	38	1.07
Yenisei River–Kara Sea					
2011	14	Aleuropelite	56.7	3–25 (16)	0.23–1.21 (0.75)
2016	6		69.5	15–30 (23)	0.09–0.17 (0.15)
Western part of the Kara Sea					
2011	14	Aleuropelite	53.8	20–37 (28)	0.35–0.99 (0.75)
2019	10		52.2	20–37 (29)	0.35–0.99 (0.78)
Khatanga River–Laptev Sea					
2017	3	Aleuropelite with sand	64.7	7.7–32.4 (23.0)	0.90–1.42 (1.12)
	1	Silty sand	29.9	8.9	0.46

Year	n	Lithological type	Moisture (average), %	AHCs interval (average), µg/g	C _{org} , interval (average), %
Lena River–Laptev Sea					
2015	8	Aleuropelite	56.6	3.3–40.0 (12.4)	0.446–3.05 (1.32)
	2	Sand	29.3	3.2–7.4 (5.3)	0.29–0.58 (0.43)
Indigirka River–East Siberian Sea					
2017	6	Aleuropelite	50.1	13.9–5.5 (26.9)	0.41–0.80 (0.78)
Kolyma River–East Siberian Sea					
2017	5	Aleuropelite	49.4	4.2–13.6 (10.0)	0.40–0.77 (0.59)

*Station 6242, Figure 4

Between C_{org} and AHC concentrations, a significant correlation was revealed: $r(\text{AHCs–PAHs})=0.75$, $r(\text{AHCs–C}_{\text{org}})=0.87$, $r(\text{PAHs–C}_{\text{org}})=0.81$ ($n=10$). Weaker correlations were determined between the moisture (Ms) of the sediments and OCs: $r(\text{Ms–C}_{\text{org}})=0.76$, $r(\text{Ms–AHCs})=0.51$, and $r(\text{Ms–PAHs})=0.57$. Therefore, the OC concentrations are controlled not only by the sediment composition but also by processes in the marginal filter of the Ob River. A slight increase in the concentrations at station 5003 might be attributed to the changes in the grain size composition [4].

In the uppermost sediment layer in the Kara Sea, PAHs were dominated by phenanthrene (Figure 1c), which accounts for 65% PAHs in the Ob Bay, and up to 100% in sediments of the Kara Sea. In the apex part of the Ob Bay (station 4995), naphthalene is one of the dominant compounds (25% of the total PAH concentration), and the naphthalene/phenanthrene ratio is there > 1 , which might suggest the presence of the petroleum HCs [2, 6, 35, 41]. Sediments at station 4995 also contain a higher percentage of fluoranthene (64% from ΣPAHs), which indicates, with regard to the low fluoranthene/pyrene ratio of 0.6, the presence of pyrogenic compounds [41–44]. The dominance of anthropogenic polyarenes over natural ones was also reflected in the relatively low (for the estuarine zone) percentage of perylene (<20%), which commonly marks terrigenous OM [36]. The highest perylene percentage (50%) is constrained to sediments at station 4996, which have the highest Eh (+476 mV) among all values in this profile [45].

The change in the redox conditions of sedimentation is reflected in the origin of this polyarene in the sediments. The most likely source of the perylene was the decomposed peat constituents transported by the Ob River [4].

In sediments at the transect of the Ob Bay – the Kara Sea, the OC concentrations varied synchronously (the correlation coefficient ranged in the interval of 0.54–0.94). At st. 4993, the black sapropel became denser with depth (layer 0–35 cm). The sediment characteristics varied: moisture, 71–64.5%, AHC – 25–17 µg/g, C_{org} – 1.68–1.72% [25]. The Eh values in sediments remained constant, + 20 mV. However, at station 4995, in the area of avalanche sedimentation, the AHC content in a layer of 0–14 cm decreased almost 3 times (42 to 15 µg/g), with a minimum (11 µg/g) in a layer of 2–4 cm, where sediments changed from oxidized to reduced conditions [4].

Later studies of bottom sediments at this profile yielded similar ranges of AHC concentrations (Table 2). An exception was detected in 2016, when the average AHC concentration was as low as 9 µg/g [25]. The most likely reason for this was the coarser grained composition of sediments because the C_{org} content (0.35% on average) was also relatively low.

The composition of alkanes in bottom sediments differed from that in the SPM by higher CPI values. The odd, most stable terrigenous homologs C₂₅–C₃₁, associated with

terrestrial vegetation, dominated. During sedimentation, the amount of autochthonous alkanes decreases because they are more susceptible to biological degradation [46, 47].

In 2019, the investigated bottom sediments belonged to silty-pelitic ones, whose average concentration of C_{org} was 0.78%, AHCs – 29 $\mu\text{g/g}$, and moisture – 52.2 % (Table 2). The range of measured concentrations was mainly (Figure 6) due to the variability of the grain-size composition of sediments, as can be seen from correlation dependence in the distribution of AHCs and C_{org} : $r=0.76$. The AHC was dominated by odd $C_{23} - C_{33}$ alkanes (Figure 6b), and the CPI values (the ratio of odd to even alkanes in the high molecular weight range) varied from 2.44 to 3.30. The predominantly terrigenous composition of the AHCs is also seen from the low values of the ratios $L/H = 0.62$ and $C_{17}/C_{25} = 0.12$.

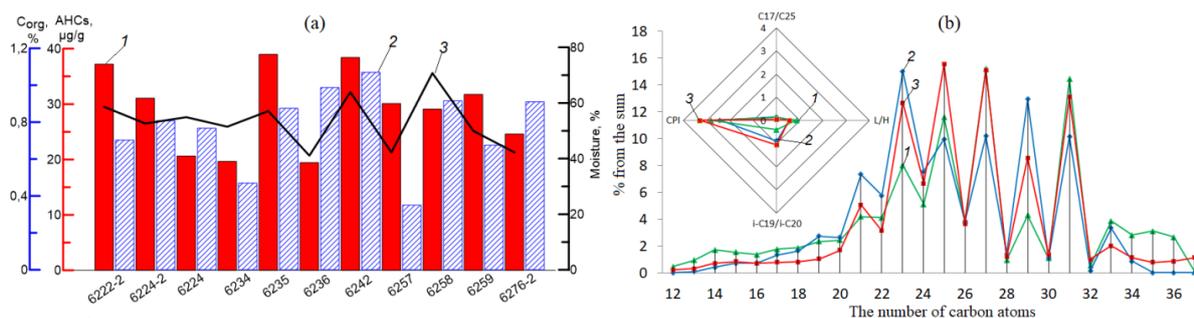


Figure 6. Distribution in the surface bottom sediments (a): 1 – AHCs, 2 – C_{org} , and 3 – moisture, (b) – composition of alkanes 1 – station 6235, 2 – station 6259, 3 – station 6276-2, inset – distribution of main markers. The location of the stations is shown in Figure 4a.

At the inner Kara Sea shelf adjacent to the Ob Bay, the PAH content in the bottom sediment (station 6242) was 328 ng/g , exceeding the average concentration in other areas of the sea, 252 ng/g . The composition of PAHs differed from that of SPM by the predominance of 1-methylnaphthalene (Figure 5b), which indicates the petroleum origin of polyarenes [36]. The minimum content of naphthalene’s (5.9%) was found in the Kara Sea at station 6236 at the northern tip of the Novaya Zemlya, and the maximum (50%) – at station 6258, i.e., at a shelf of the central part of the western basin. The low proportion of 6-core PAH (1–15%) and low concentrations of benzo(a)pyrene (on average 0.75 ng/L) confirm the insignificant effect of pyrolysis products of organic raw materials. Our data fit into a wide range of variability of PAH concentrations in the upper layer of bottom sediments in a different area of the Kara Sea: 52–353 ng/g [25, 35].

3.3. Surface water Yenisei River – the Kara Sea

In September 2011, surveys at the Yenisei River – the Kara Sea transect were conducted from the outer edge of the river delta to the central part of the sea, where depths exceeded 60 m (Figure 7 a, b). In surface waters, the salinity varied strongly: 0.069 to 27.927 PSU; that is, at the southernmost station, the salinity was closer to the riverine values, while on the northernmost ones – to the open Kara Sea. In the southern part of the transect, a ratio of the AHCs particulate and dissolved forms, AHC_{sp}/AHC_{sd} , decreased from 1.3 to 0.2, which was caused by precipitation of coarse-grained particulate matter in the Yenisei waters due to the damming riverine by seawater [9]. Together with SPM, the organic compounds are precipitated, especially hydrophobic high-molecular AHC [4, 47]. The riverine flows are clarified, followed by a growth of the dissolved OC portion. Note that dissolved OC

concentrations in river waters are even lower than those in the biological part of the marginal filter (Fig. 7 a, b) [6].

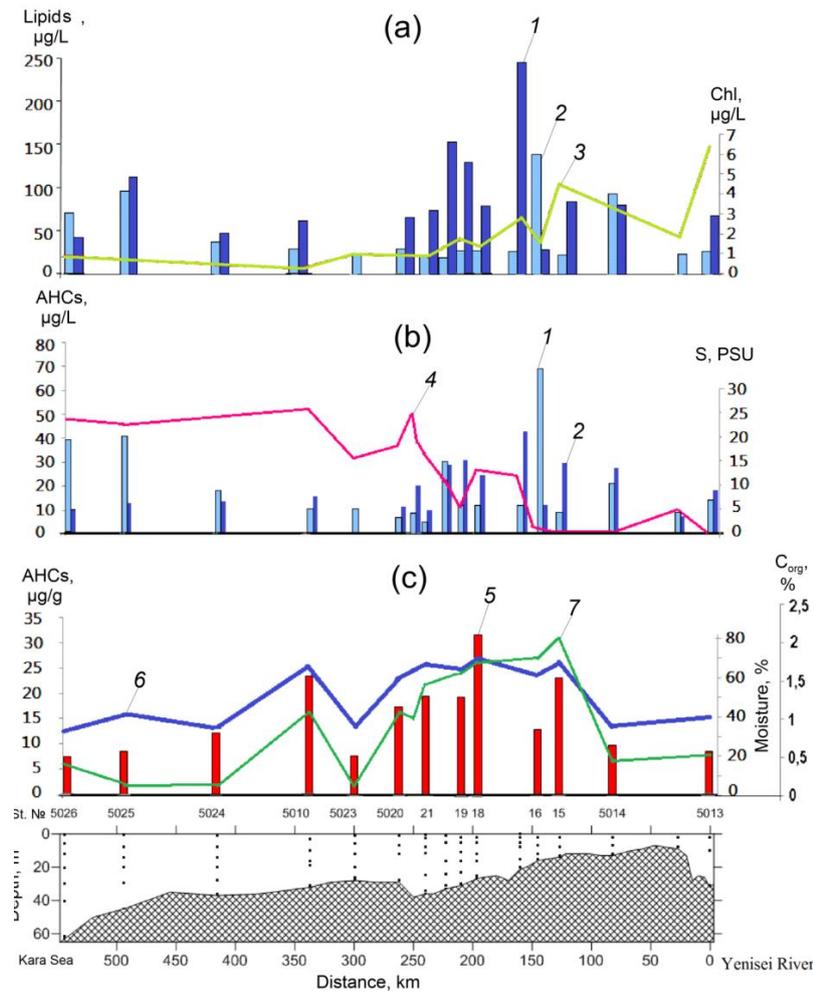


Figure 7. Distribution of concentrations in surface waters (a, b) and in bottom sediments (c) at the transect of the Yenisei River – the Kara Sea in 2011, September. (a): 1– lipids in dissolved form, 2—lipids in SPM, 3– Chl a; (b): 1 – AHCs in dissolved form, 2 – AHCs in SPM, 4 – Salinity; (c): 4–AHCs, 5–Moisture; 6–C_{org}.

As the salinity increases, the amount of colloidal-dispersive material grows, leading to the formation of SPM with a developed surface, such as floccules of clay minerals and colloidal forms of OM. As a result, in the central part of the transect, at stations 5014–5021 in the salinity range 2.3–4.3 PSU (physical-chemical zone of the marginal filter), the content of lipids and AHCs increased, especially in the particulate form (to 29 µg/mg of SPM at station 5018). High tide and low tide events lead to additional variability of all parameters. Therefore, no gradual decrease in AHC concentrations and AHC_{Sp}/AHC_d ratios was observed when salinity grew. The maximum AHC_{Sp}/AHC_d ratio (4.67) was recorded at St. 5022.

Seawards along the transect, the OCs concentrations in SPM decreased. In the biological zone of the marginal filter (stations 5010, and 5024–5026), the AHC_p content increased from 10 to 29 µg/L synchronously to the biogenic fraction of SPM, which is related to a growth of Chl *a* concentration from 0.482 to 0.995 [47, 48], that was accompanied by an increase of the amount of SPM (to 1.27 mg/L). However, the dissolved form of AHC_d grew to a higher degree (to 40.5 µg/L, Figure 7b). The bioassimilation of carbon at the Yenisei River mouth was registered earlier by the ¹³C_{org} isotope composition [7, 49]. Seawards the marginal filter, the OCs content increased due to two main OCs sources, namely, marine plankton and

coagulated colloidal and dissolved OM, which transformed partially into particulate matter (>0.4–0.6 μm) [4, 18]. However, the concentrations of AHC_{sp} decreased to 12 μg/mg in the SPM.

The existence of different zones in the Yenisei – Kara Sea section was confirmed by the results of bacterioplankton studies [50]. The abundance and activity of bacterioplankton in these zones varied by order of magnitude. In waters with salinities less than 2.5 PSU, the mean bacterial abundance values were 254×10^3 , $(2741 \pm 394) \times 10^3$, and $(2069 \pm 185) \times 10^3$ cells/mL in spring, summer, and fall, respectively. At salinities greater than 18 PSU, the bacterial abundance in the same seasons was $(196 \pm 50) \times 10^3$, $(683 \pm 184) \times 10^3$, and $(125 \pm 24) \times 10^3$ cells/mL, respectively. Similar patterns were observed in the biomass distribution in the summer period [51].

A strong variability of AHC concentrations in surface waters was recorded not only in the Yenisei mouth (Table 1) but also in the central part of the sea, as well as near the St. Anna Trough. Here, the AHC content was as high as 40–80 μg/L (Figure 8). This area was also characterized by increased fluorescence, Chl *a*, and SPM [52]. Changes in the species structure of phytoplankton here are more associated with seasonal rearrangements in the community than with the impact on the region of river runoff and waters of the Barents Sea and Atlantic origin [6].

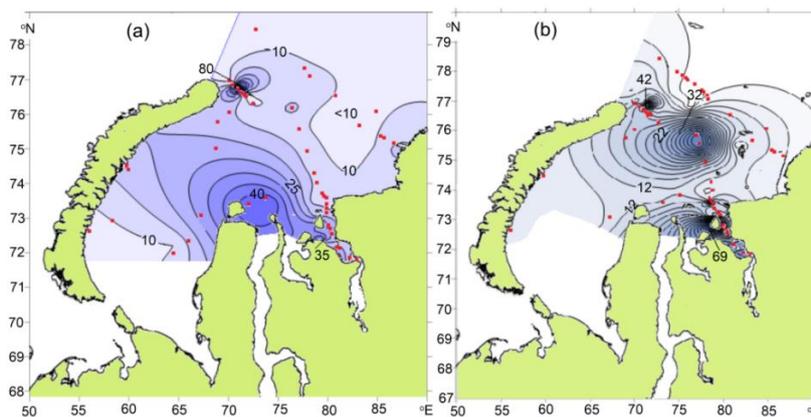


Figure 8. Distribution of AHC concentrations (μg/L) is dissolved (a) and in SPM (b) forms in surface waters of the Kara Sea.

In the northeastern Kara Sea (the St. Anna Trough) and near the Novaya Zemlya Archipelago, the AHC concentrations showed background values 19 μg/L (Table 1) [47]. However, the pronounced increase in OCs content took place in the frontal zone of the temperature-salinity gradient (station 5049), which continued toward the coasts, probably due to the coastal abrasion.

In July 2016, in surface waters, the variability interval of AHC concentrations in SPM was similar to that in 2011 and lower than in the Ob mouth (Table 1). Like the previous years, AHC concentration in the surface water gradually changed while salinity increased. The close concentrations of AHCs (50–60 μg/L) were determined in various zones of the marginal filter, and they showed no correlation with either SPM content ($r = 0.21$) or the Chl *a* concentration ($r = 0.40$). It is worth mentioning that the distribution of Chl *a* weakly correlated with the total content of SPM ($r = 0.44$) because of the terrigenous nature of the latter [25]. The synchronous growth of the Chl *a* and AHC concentrations was recorded only in the biological zone of the marginal filter, and the alkanes' composition was predominantly autochthonous [47].

3.4. Bottom sediments Yenisei River – the Kara Sea

Bottom sediments in the freshwater section of the Yenisei River – the Kara Sea profile are silty-pelitic with sand admixture, which are oxidized of brown color on the surface, and transferred to reduced greenish-gray ones deeper. At places “crusts” of ice-rafted material (up to $5 \times 3 \times 6$ mm) were found. The average AHC concentration, both recalculated to dry weight ($16 \mu\text{g/g}$) and in C_{org} (0.15%), was in 2011 lower than that in July 2016 ($23 \mu\text{g/g}$ and 0.20%, respectively) [25]. The C_{org} distribution was more strongly (than the AHC distribution) correlated with the sediment moisture, evidently due to the synchronous distribution of C_{org} and moisture: $r(C_{\text{org}}-M_s)=0.83$ (in 2011). The correlation coefficients between these parameters and AHCs are lower: $r(C_{\text{org}}-AHCs)=0.47$ and $r(M_s-AHCs)=0.44$, which is likely attributed to utilization and/or synthesis rates of organic compounds in the marine ecosystem [25, 51]. The AHCs were accumulated in the bottom sediments (similar to the surface waters) in the physicochemical zone of the marginal filter [24, 35].

3.1. Discussion.

At the river–the sea geochemical barrier, a common tendency for all estuarine areas was revealed: with an increase in salinity, there is a decrease in AHC concentrations in SPM (Figure 9). In some cases, losses in the AHC concentrations exceeded 90% of the riverine input. Whereas, in the pelagic zone of these seas, the AHC content is close to the background ($2-7 \mu\text{g/L}$ in low water [25, 47]), in the mixing zones, the HC content is much higher.

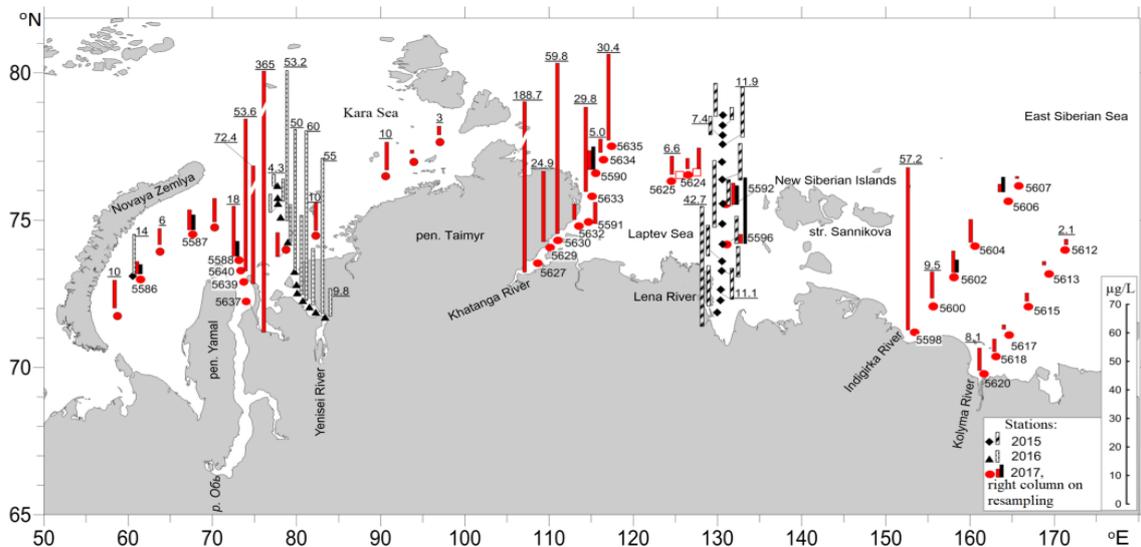


Figure 9. Distribution of AHCs ($\mu\text{g/L}$, underlined above the columns) in the surface waters' suspended particulate matter in different years of the study (at the bottom of the columns - station numbers).

The distribution of the components at the boundary between the Ob estuary and the Kara Sea is controlled by processes that occur in the geochemical barrier (marginal filter [8]), forming the estuarine frontal zone. At the same time, local maxima and minima were observed in the SPM and OC distribution, which is determined by latitudinal displacements of the estuarine frontal zone due to the tides and wind forcing.

The sampling season is of great importance since large amounts of contaminants accumulate in winter and enter the rivers during floods [53–59]. In June 2019, during the ice melting season, the average values of concentrations of lipids and AHCs (89 and $59 \mu\text{g/l}$,

respectively) in SPM in the Kara Sea were significantly higher than those in autumn 2018 (52 and 22 $\mu\text{g/l}$, respectively; Table 1). The latter is associated with the intense development of phytoplankton during and after the melting of seasonal ice when biological production reaches an annual maximum, and the main volumes of continental runoff enter the sea [6, 60]. The vegetation of marine phytoplankton, both at the lower edge of the ice and in sub-ice water, begins as early as the end of February, and as a result, significant volumes of autochthonous OC are produced [60].

The composition of AHCs and PAHs in the bottom sediments of the southern part of the Kara Sea evidenced the influence of petroleum HCs associated with the production of AHCs and the intensification of navigation. Our data fit into a wide range of variability of PAH concentrations in the upper layer of bottom sediments in different regions of the Kara Sea: 52–353 ng/g [25, 35].

The sum of naphthalene's shows an inverse relationship with the sum of PAHs (Figure 7b), since $r(\sum\text{PAH} - \sum\text{naphthalene's}) = -0.49$. The dominance of naphthalene's is also seen in the dendrogram of cluster analysis ('Ward's method, Figure 10). In addition, the proportion of phenanthrene formed in diagenetic processes is significant. At the same time, a correlation was observed between phenanthrene and perylene: $r(\text{PHEN-PL} = 0.52)$, the formation of which occurs in the thickness of the sediments.

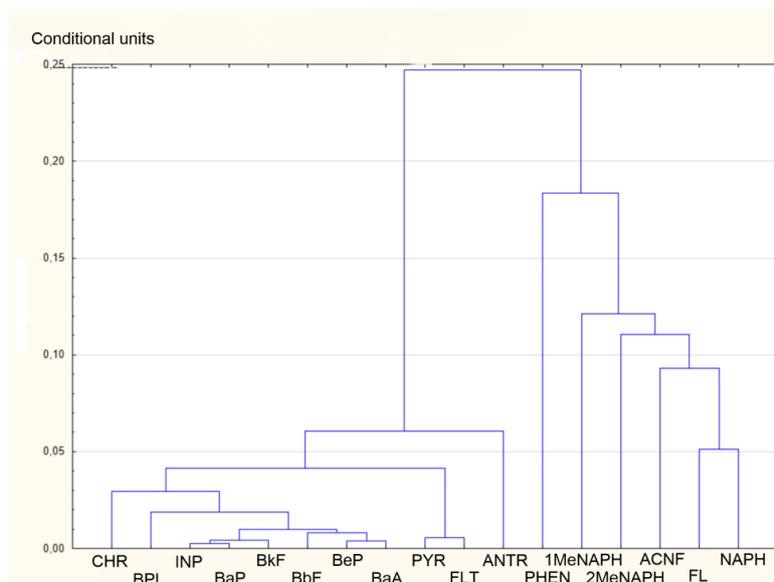


Figure 10. Groupings of PAHs based on the results of cluster analysis of individual compounds.

The dominance of petroleum polyarens in PAHs is also confirmed by the low values of the ratio $(\text{FLP} + \text{PYR})/(\text{PHEN} + \text{CHR})$, which at values <0.5 characterizes petrogenic PAHs [35, 38], and in the sediments of the Kara Sea averaged 0.38. In addition, a low proportion of 6-ring PAHs (1–15%) and low concentrations of benzo(a)pyrene (Figure 5b), can also indicate a predominantly petroleum origin of polyarens.

In addition, wind direction influences the HC distribution in the Ob estuary; in early September 2017, based on satellite imagery data, the desalinated surface layer was reduced against the east coast. A month later, due to changes in wind conditions, the desalinated layer loaded with SPM, spread northwards and to the northwest. Therefore, in the surface layer of st. 5588_2 compared to station 5588, the SPM content increased sharply (0.46 to 2.60 mg/L), while the AHC content decreased from 18 to 6 $\mu\text{g/L}$ (Figure 9), possibly due to decomposition

during weathering. Therefore, in this area, SPM had almost no effect on the AHC distribution, as there were no strong correlation: $r(\text{SPM-AHCs})=0.42$ ($n=7$).

The tidal phenomena contributed more to AHCs behavior at this geochemical barrier, particularly at the Yenisei River mouth; therefore, a gradual decrease in AHC concentrations does not always occur with an increase in salinity.

During sedimentation in the early summer season, rapid decomposition of autochthonous SPM and OCs, showed no observed increase in the concentrations of C_{org} , AHCs, and PAHs in the bottom sediments, unlike its concentration in the surface waters. In the water and sediments of the Ob estuary, the qualitative and quantitative composition of OCs indicated a rapid utilization not only of the components supplied with the river runoff but also those produced locally in the estuary [25].

The earlier revealed differences between SPM contents in fluff and the upper layer of bottom sediments might indicate a rapid transformation of OCs in the processes of early diagenesis since the intense formation of SPM during the ice melting period, or the short-term changes in primary production, are significantly lower than the rate of “typical geological” processes in the bottom sediment cores [61]. To study the OM transformation of the water-bottom boundary at st. 6222-2 in 2019, a sample of the fluff (the uppermost part of a thin, easily turbid sediment layer) was taken from the multicore. Fluff is a transitional form of material from bottom suspension into bottom sediment. The chemical composition of SPM is much more susceptible to seasonal changes than bottom sediments. In the fluff layer, the content of all studied components was higher than the upper layer of compact bottom sediments: its moisture content was 77.6%, the $C_{\text{org}} - 2.05\%$, and the AHC content – 120 $\mu\text{g/g}$. In this case, the amount of AHC was more than 3 times higher than the upper 0–1 cm layer of sediment. On the contrary, the concentration of alkanes increased from 0.7 to 0.9 $\mu\text{g/g}$ when the transition from fluff to sediment by reducing low molecular weight and growth of odd high molecular weight homologs. The CPI values increased from 2.68 to 3.09 (Figure 11a).

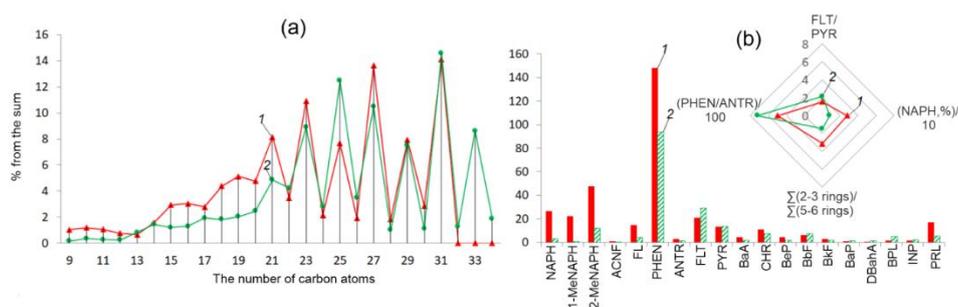


Figure 11. Composition of alkanes (a) and PAHs (b) in the fluffy layer (1) and in the 0–1 cm sediment layer (2) at st. 6222-2, the inserts show the distribution of the main markers.

The PAH concentration in the fluffy layer was lower than in the surface layer of bottom sediments, 300 and 346 ng/g , respectively. The composition of the fluff concerning the naphthalene’s content (32.2%) was seven times higher than that of the upper sediment layer (4.6%, Figure 11 b).

During sedimentation, the composition of alkanes changed. Therefore, the data obtained in 2018 from sediment traps are indicative. In the Ob River nearshore area (St. 5943, Figure 12), at a depth of 10 m, the composition of alkanes was closest to the dissolved AHC, while the CPI value was only 0.92. However, even at a depth of 20 m, the odd terrigenous alkanes dominated in the high molecular weight field, which SPM of the nepheloid layer supplied; CPI values increased to 1.75. A close distribution of homologs was also observed in

sedimentary material collected with sediment traps moored in the Vilkitsky Strait (St. 5944). Here, at a depth of 50 m, smooth distribution of homologs was observed, and at a depth of 160 m, a series of odd alkanes C₂₇–C₃₅ dominated in the high molecular weight field (Figure 12).

During the mass generation of SPM by phytoplankton in the upper photic layer, the biogenic SPM dominates [6, 18], and the role of autochthonous biogenic markers increases *n*-C₁₅, -C₁₇ [46]. In this layer, terrigenous components account for less than 5%. There, seasonal differences in the composition of alkanes related to phyto- and zooplankton production may also be significant [47, 61]. In deep layers, with the massive disintegration of pellets and input of SPM from the nepheloid layers, the amount of high molecular weight odd alkanes, which are most resistant to decomposition, increases (Figure 12).

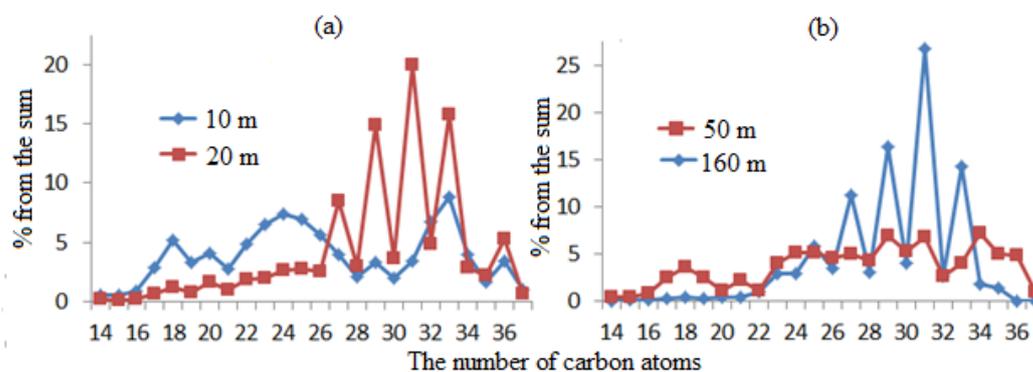


Figure 12. Composition of alkanes in sediment traps in 2018: (a) st. 5943 in the nearshore of the Ob River; (b) Vilkitsky Strait.

The AHC distribution is also influenced by the composition of the river catchment areas. In particular, the differences between the AHC and SPM contents in the Ob and Yenisei Rivers estuaries are associated with the nature of rocks in the basins of these two rivers. After regulation of the Yenisei River runoff, there was a decrease in sediment input by more than twice, from 13 to 4.9 million tons/year [62, 63]. For the Ob estuary, as well as for the Northern Dvina [6, 58], in the salinity interval of 0.05–0.6 PSU, the dissolved form dominated, and the (AHC_d/AHC_p) ratio varied from 1.65 to 1.35 [25]. With an increase in salinity, AHC_d decreased, while AHC_p increased, and at S = 6 PSU, the minimum of the dissolved forms corresponding to the maximum of the suspended forms (AHC_{s_d}/AHC_{s_p}=0.18), since the dissolved organic compounds transferred into the suspended ones [4]. In this case, the AHC_{s_p} content, calculated in terms of SPM mg, increased 8.5 times (from 2 to 16.9 μg/mg).

Conversely, at the Yenisei River mouth, with an increase in salinity, the AHC_d/AHC_p ratio increased from 0.77 to 5, while the concentrations of dissolved organic compounds in river water were even lower than those in the biological part of the marginal filter. This distinguishes the mouth area of the Yenisei River from the Northern Dvina and Ob Rivers – the arctic rivers draining the humus-rich soils, where dissolved AHC_d forms dominate in mouth areas [25]. In addition, it should be taken into account that the main role in the OM supply to the Kara Sea is played by not the newly formed biogenic matter but by terrigenous, ancient material brought by rivers [63].

In bottom sediments, just like sedimentary material from sediment traps moored in bottom layers, a predominance of odd terrigenous homologs was typical [6, 41]. Climate change leading to accelerated degradation of the coastal ice might contribute to increased SPM contents in the estuarine areas of the Lena and Kolyma Rivers, as well as in most coastal areas of the East Siberian Sea [64, 65].

In particular, despite the increased oil-related industrial activity, the Beaufort Sea sediments were also dominated by biogenic, mainly terrigenous HCs. In the last three decades, sediments have generally remained unpolluted [66]. Therefore, in the balance calculations carried out for the Kara Sea, the fraction of terrigenous C_{org} has been estimated at 1.15×10^6 (85% of the total mass), and marine C_{org} , at 0.23×10^6 t/year [11, 67].

4. Conclusions

The studies carried out at the trans-Arctic transect (the Kara–Laptev–East Siberian Seas) showed that the highest AHC concentrations were found in the river mouth areas. At the same time, at the river (Ob, Yenisei, Khatanga, Lena, Indigirka, and Kolyma) – the sea barrier, with an increase in salinity, HC concentrations in SPM decrease. In some cases, loss in concentrations at the river–sea barrier exceeded 90% of AHCs riverine input.

The greatest variability in AHC concentrations is confined to the mouth of the Ob River. During the descent of seasonal ice in surface waters, the average AHC content increased from 20 to 59 $\mu\text{g/L}$. These concentrations are caused by the formation of autochthonous processes after the ice melting and the Ob River flood rather than by the oil pollution. However, during that period, at the Ob River – the Kara Sea geochemical barrier, with a change in salinity, there was a sharp decrease in the concentrations of all OCs and SPM.

The accumulation of naphthalene's in sediments promotes their growth in the composition of PAHs compared to the surface SPM and fluff, which makes it possible to assess the pollution in the western part of the Kara Sea as mainly the oil one. The most likely source of pollution is the input of PAHs from 'ship's bilge waters. The fuel combustion products are of a subordinate nature.

No anthropogenic petroleum AHCs were found in open waters of the studied Arctic seas. Mainly terrigenous HCs enter bottom sediments, and compounds of autochthonous genesis are almost completely transformed during the sedimentation.

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Conflicts of Interest

The authors declare no conflict of interest.

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