

## ORIGIN OF HYDROCARBONS IN HOLOCENE SEDIMENTS OF THE NORDIK SEAS AND BARENTS SEA

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**Abstract.** The concentrations and composition of hydrocarbons (aliphatic – AHCs and polycyclic aromatic hydrocarbons – PAHs) were determined using molecular markers in Holocene sediments of the Nordik Seas and the Barents Sea (cruise 84 of the R/V *Akademik Mstislav Keldysh*, 2021). A wide range of concentrations in surface bottom sediments has been established:  $C_{org}$  (0.25–2.71%), AHCs (7–182  $\mu\text{g/g}$ ) and PAHs (0–1918  $\text{ng/g}$ ). The distribution of hydrocarbons is determined mainly by the processes occurring in the sedimentary strata (changes in Eh and fluid flows), and to a lesser extent by the lithotype of sediments. At the same time, the formation of autochthonous homologues is observed in the composition of alkanes, and in the composition of PAHs – naphthalenes.

**Keywords:** *aliphatic and polycyclic aromatic hydrocarbons, Nordik Seas, Barents Sea, bottom sediments, fluid flows*

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### INTRODUCTION

The ubiquity of hydrocarbons (HC) in water bodies, their active participation in physicochemical and biochemical processes, interaction with aquatic organisms, as well as the inflow of petroleum HC from various sources leads to difficulties in determining their origin [7, 17, 41–43]. According to the remote sensing data obtained by Sentinel-1A and Sentinel-1B radar satellites, the presence of oil films on the sea surface may indicate not only an anthropogenic but also a natural source of their input [8, 26].

During the inventory of oil HC sources in the World Ocean, it was concluded that their main share (46% of the sum of 1300 thousand tons) comes as a result of natural deposition on the bottom from the underlying sedimentary strata [17]. The Barents and Norwegian Seas are among the largest oil and gas bearing basins of the Arctic [3], on the coasts of which, economic activity is actively carried out [11, 20]. Urbanized territories, ports, oil loading terminals are located here and, accordingly, pollutants coming from the shore and formed in the sea itself as a result of human economic activity are concentrated [5, 18].

For reliable assessment of anthropogenic HC in the marine environment it is necessary to establish the locations and extent of natural oil spills in the sea,

and to assess the natural hydrocarbon background on which this pollution is superimposed. Therefore, the study of HC becomes nowadays a particularly relevant and necessary stage in the environmental monitoring of the Arctic seas for subsequent geo-ecological control during geological exploration and mining [7, 12, 17, 18, 31]. In addition, obtaining reliable estimates of HC characteristics and their role in the ocean carbon balance is one of the important tasks in creating a system for monitoring climate change [13].

The purpose of this study is to determine the concentrations and composition of HCs (aliphatic hydrocarbons and polycyclic aromatic hydrocarbons) in bottom sediments of the Norwegian-Greenland Basin and the Barents Sea in order to establish their origin.

In August 2021, during the 84th cruise of the R/V “Akademik Mstislav Keldysh” the following areas were covered by the research [4, 10]: The deep-water part of the Greenland Basin, the northern part of the East Greenland Ridge, the near-breakup zone near the junction of the Mona and Knipovich Ridges, the western and northwestern extremities of the Svalbard continental shelf (Westnes Ridge, Sofia Basin and the Hinlopen Trog), Fram Strait, the area of the Orli

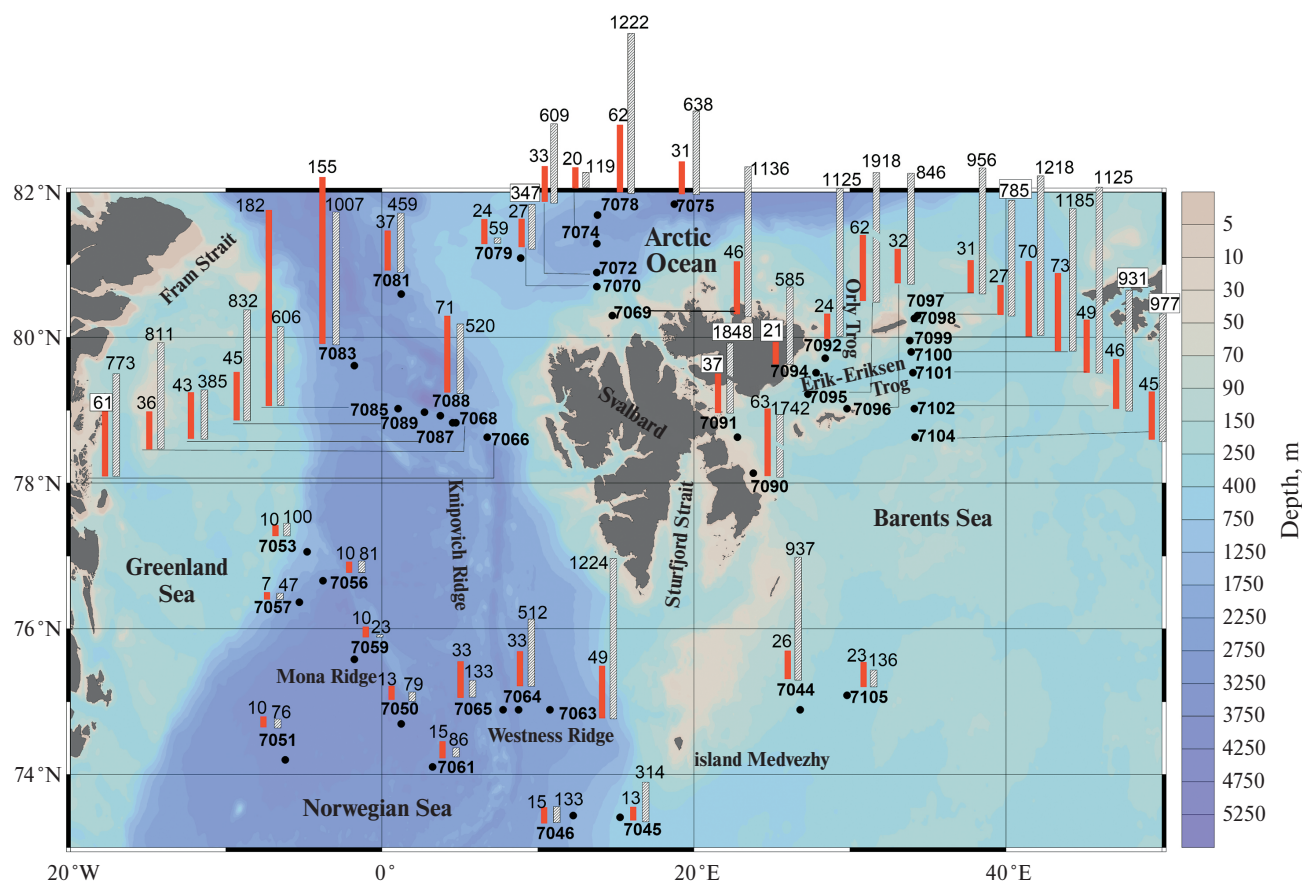


Fig. 1. Sampling map and distribution of PAHs (red columns,  $\mu\text{g/g}$ ) and PAHs (shaded columns,  $\text{ng/g}$ ) in the surface layer of bottom sediments during the 84th cruise of the R/V "Akademik Mstislav Keldysh".

Trough with the intersection of the Erik-Eriksen Trog and the central part of the Barents Sea (Fig. 1).

## MATERIALS AND METHODS

Bottom sediment samples were collected using an Ocean-50 dredge and undisturbed sediment columns collected using a multicorer (Mini Muc K/MT 410, KUM, Germany), which were divided into layers and frozen until analysis in the laboratory. The thickness of the uncovered sediment layer varied from 1 cm (dredge) to 32 cm (multicorer). Sediment samples were dried at  $50^\circ\text{C}$ , and HC was ultrasonically extracted from the sediment fraction  $< 0.25\text{ mm}$  with methylene chloride (all solvents used were qualified o.s.h.).

The concentration of PAHs was determined by infrared method on an IRAffinity-1 spectrophotometer manufactured by Shimadzu, Japan; alkanes – by gas chromatographic method on a Crystal-Lux 4000-M chromatograph (Russia); PAHs concentration – by fluorimetry [15] on a "Trilogy" device manufactured by Turner (USA), and their composition – by high-performance liquid chromatography (HPLC)

on a Shimadzu LC-20 device, Japan: column – "Envirosep PP", at thermostat temperature  $40^\circ\text{C}$  in gradient mode from 50% to 90% volume fraction of acetonitrile in water, eluent flow rate –  $1\text{ cm}^3/\text{min}$ . A fluorescence detector "RF-20A" with programmable excitation and detection wavelengths was used. The calculation was performed using the software "LC Solution". The instrument was calibrated using individual PAHs and their mixtures produced by "Supelco" (Merck, Germany). As a result, priority polyarenes recommended in the study of pollution of marine objects by EPA (Environmental Pollution Agency) were identified [30]: NAF-naphthalene, MeNAF – 1-methylnaphthalene, 2-MeNAF – 2-methylnaphthalene, ACNF – acenaphthene, FLR – fluorene, FEN – phenanthrene, ANTR – anthracene, FLT – fluoranthene, PR – pyrene, BaA – benz(a)anthracene, CHR – chrysene, BEP – benz(e)pyrene, BbF – benz(b)fluoranthene, BkF – benz(k)fluoranthene, BaP – benz(a)pyrene, DBA – dibenz(a,h)anthracene, BPL – benz(g,h,i)perylene, IND – indeno[1,2,3-c,d]pyrene, PR – perylene.

Organic carbon ( $C_{org}$ ) in bottom sediments was determined by the dry combustion method on a TOC-L instrument (Shimadzu, Japan). The coefficient 0.86 was used to convert HC concentrations to  $C_{org}$  concentrations [7].

## RESULTS AND DISCUSSION

In surface bottom sediments, the content of AHCs varied from 7  $\mu\text{g/g}$  at station 7067 offshore Greenland to 182  $\mu\text{g/g}$  at station 7085 in Fram Strait (Fig. 1), and  $C_{org}$  from 0.25% at station 7053 (also offshore Greenland) to 2.71% at station 7105 east of Medvezhy Island (Table 1).

The concentrations of  $C_{org}$  and AHCs in the Fram Strait sediments also varied in a wide range: 0.81–1.87% and 20–182  $\mu\text{g/g}$ , respectively (Table 1). While on average the fraction of AHCs in the  $C_{org}$  composition of all studied bottom sediments was 0.23%, in Fram Strait it increased at stations 7083 and 7085 up to 0.93%, which is atypical for the background areas of the Arctic lying outside the active anthropogenic activity [7]. The concentrations of AHCs at stations 7083 and 7085 were close (155 and 182  $\mu\text{g/g}$ ). Nevertheless, the content of alkanes (3.9 and 0.1  $\mu\text{g/g}$ ) as well as their composition differed greatly (Fig. 2a). Indeed, at Station 7085, the composition of alkanes was dominated in the low molecular weight region by the  $n\text{-C}_{16}$  homologue, which is of microbial origin [32, 34]. As a result, the ratio of low-molecular to high-molecular alkanes:  $L/H = \sum(C_{12-24})/\sum(C_{25-35})$  increased to 2.0 (Table 2). In contrast, the sediments of st. 7083 were dominated by high-molecular-weight odd terrigenous homologs, and the  $L/H$  value decreased to 0.37. The CPI value (the ratio of odd to even homologs at  $C > 25$ ) in the sediments of these stations was the highest (4.10–6.37) compared to the other studied areas. While at station 7083 the contents of pristan

and phytane were practically equal ( $Pr/Pf = 0.99$ ), at station 7085 phytane dominated ( $Pr/Pf = 0.49$ ). The latter, as well as other markers indicate the different nature of alkanes.

The section along the Vestnes Ridge west of Svalbard was located in the area of the most known active methane seafloor venting in the Arctic [38, 39]. The maximum content of  $C_{org}$  (2.25%), AHCs (49  $\mu\text{g/g}$ ), and PAHs (1224  $\text{ng/g}$ ) in this section is confined to station 7063, located in the fjord cone zone (Horsunn Bay) at a depth of 319 m. The surface layer (0–1 cm) of the sediment contained fragments of bivalve shells, a significant amount of chemosymbiotic benthos – polychaetes of the family *Siboglinidae* and their tubes. In the underlying sediment column (deeper than 1 cm), the content of AHCs increased unevenly in the transition from oxidized to reduced layers (Fig. 3). Their highest concentrations were found at the horizon of 10–11 cm (82  $\mu\text{g/g}$ ) and 15–16 cm (81  $\mu\text{g/g}$ ), but in the lower layers of the column (22–24 cm) their content also remained rather high (49–66  $\mu\text{g/g}$ ), as well as the  $C_{org}$  content (2.01–2.08%). In these layers, the growth of AHCs concentrations was due to the degradation of organic matter, as the  $C_{org}$  content decreased.

The composition of alkanes indicated intensive autochthonous processes occurring in the sedimentary column at station 7063 (Fig. 4): the  $L/H$  ratio increased with burial depth from 0.95 to 1.85 (Table 2), reaching a maximum at the 23–24 cm horizon, as did the pristane/phytane ratio (0.85).

A different distribution in the sediment column at station 7063 was observed for PAHs (Fig. 3). Their concentrations sharply decreased in the surface horizons (from 1224  $\text{ng/g}$  to analytical zero), and in the 7–8 cm layer, they increased reaching 75  $\text{ng/g}$  at the hill. 10–11 cm. Polyarenes were absent in the lower

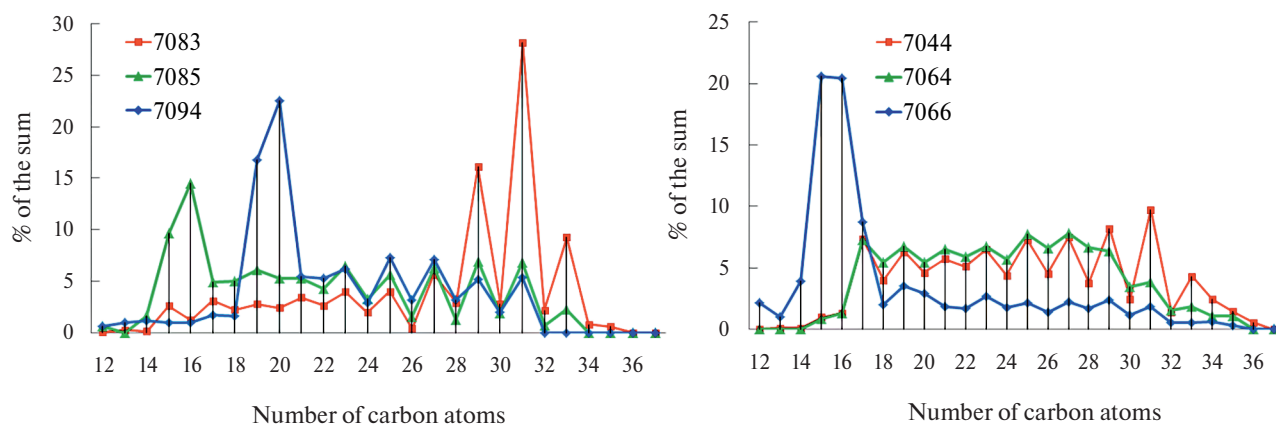


Fig. 2. Composition of alkanes in the surface layer of bottom sediments at selected stations.

**Table 1.** Characterization of the surface layer of bottom sediments of the Norwegian and Barents Seas in different years of study

Neighborhood	$n^*$	AHCs, $\mu\text{g/g}$		PAH**, $\text{ng/g}$		$C_{\text{org}}$ , %		Moisture, %	
		interval	average	interval	average	interval	average	interval	average
August 2021 r.									
All neighborhoods	41	7–182	42	23–1918	663	0.25–2.41	1.56	36.8–82.4	58.2
Southern part	12	7–61	20	23–1224	235	0.25–2.31	1.34	38.3–66.7	50.6
Fram Strait	13	20–182	50	59–1222	635	0.81–1.87	1.45	42.9–82.4	61.2
Northeastern part	16	24–73	48	136–1918	1119	1.46–2.41	1.85	48.1–73.6	61.8
August–September 2016 r.									
All neighborhoods	42	3–44	14	Not defined.	Not defined.	0.07–2.59	1.08	20.1–69.7	45.6
Shtokman landfill	7	9–27	15	Not defined.	Not defined.	0.67–2.57	1.81	23.7–69.7	53.0
Medvezhinsky Trough	10	6–44	17	Not defined.	Not defined.	0.25–1.71	0.79	27.0–58.5	40.6
Russian harbor	7	4–22	11	Not defined.	Not defined.	0.24–1.86	0.96	27.9–60.0	40.1
Svalbard – FJL	8	8–24	16	Not defined.	Not defined.	0.70–1.47	1.21	33.2–68.5	55.5
July–August 2017 r.									
All neighborhoods	48	3–57	12	Not defined.	Not defined.	0.03–2.38	1.02	17.0–72.1	49.5
Western part	16	15–37	10	Not defined.	Not defined.	0.30–1.69	0.65	30.4–60.7	49.6
Svalbard – FJL	14	4–37	13	Not defined.	Not defined.	0.72–2.38	1.52	37.6–72.0	54.3
New Earth	5	6–57	19	Not defined.	Not defined.	0.80–1.66	1.19	40.5–63.4	49.8
Central part	13	4.4–17.2	10.8	Not defined.	Not defined.	0.03–1.94	0.93	17.0–63.4	49.1
May–June 2019 r.									
All neighborhoods	49	6–64	25	24–9934	642	0.05–1.87	0.83	17.1–72.6	56.0
Mona Ridge	7	7–51	18	51–155	91	0.23–0.77	0.51	35.0–72.6	49.8
Lofoten Basin	4	6–28	17	78–286	182	0.49–0.69	0.58	65.2–72.6	68.5
Knipovich Ridge	7	14–37	27	186–751	552	0.52–1.32	0.96	60.1–71.2	66.1
Western Svalbard shelf	6	15–35	27	186–9934	2920	0.58–1.66	0.88	35.3–71.2	54.1
Quaytol chute	5	7–59	23	24–660	170	0.47–0.80	0.63	34.1–61.0	47.2
Meridional r-z at 27.5° E.	6	28–53	40	183–867	472	1.31–1.87	1.70	50.0–76.2	64.3
Meridional r-z 33° E.	14	10–64	23	37–254	109	0.05–1.51	0.52	17.1–68.2	64.3
July–August 2020 r.									
All neighborhoods	21	3–186	45	23–1697	311	0.30–1.56	0.92	22.2–72.9	58.6
Mona Ridge	7	3–27	14	42–65	50	0.30–0.51	0.44	38.5–61.5	49.9
Sturfjord	4	36–186	90	23–830	235	0.69–1.36	1.12	22.2–66.2	46.3
East Svalbard shelf	5	17–86	52	57–1697	780	1.07–1.56	1.29	59.5–72.9	69.6
FJL shelf***	5	17–30	25	78–757	178	0.68–0.87	0.83	67.6–69.6	68.6

Note. \*  $n$  – Number of samples. \*\* Results obtained by fluorescence method. \*\*\* FJL – Franz Josef Land.



**Table 2.** Distribution of main markers in the composition of bottom sediment alkanes at individual stations

Horizon	HC, µg/g	Alkanes, µg/g	Alkanes, % of AAU	L/H*	CPI	$\frac{i-C_{19}}{i-C_{20}}$	Paq	Dominant peaks
Station 7044								
0–1	26	0.1	0.56	0.87	2.38	1.73	0.43	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>21</sub> –C <sub>31</sub>
Station 7046								
0–1	15	0.1	0.53	1.07	1.67	0.19	0.39	C <sub>19</sub> , C <sub>29</sub> , C <sub>31</sub>
3–4	47	0.01	0.03	0.87	2.74	0.32	0.35	C <sub>19</sub> , C <sub>21</sub> , C <sub>29</sub> , C <sub>31</sub>
12–14	25	0.05	0.19	0.75	1.84	0.30	0.34	C <sub>19</sub> , C <sub>29</sub> , C <sub>31</sub>
16–18	49	0.1	0.16	0.57	4.47	0.06	0.38	Nechet. C <sub>23</sub> –C <sub>31</sub>
Station 7063								
0–1	49	0.2	0.43	0.95	1.39	0.53	0.53	C <sub>19</sub> , C <sub>21</sub> , C <sub>23</sub> , C <sub>25</sub>
1–2	39	0.3	0.80	1.18	1.37	0.46	0.61	C <sub>19</sub> , C <sub>21</sub> , C <sub>23</sub> , C <sub>25</sub>
6–7	42	0.1	0.16	1.37	1.20	0.10	0.60	C <sub>19</sub> , C <sub>21</sub> , C <sub>23</sub> , C <sub>25</sub>
10–11	82	0.3	0.35	1.34	1.20	0.46	0.57	C <sub>17</sub> , C <sub>19</sub> , C <sub>21</sub>
14–15	71	0.3	0.40	1.54	1.38	0.48	0.59	C <sub>17</sub> , C <sub>19</sub> , C <sub>21</sub>
19–20	66	0.2	0.33	1.52	1.37	0.34	0.60	C <sub>17</sub> , C <sub>19</sub> , C <sub>21</sub>
23–24	49	0.6	1.28	1.85	1.47	0.85	0.57	C <sub>17</sub> , C <sub>19</sub> , C <sub>21</sub>
Station 7064								
0–1	33	0.3	0.85	1.08	1.29	1.06	0.59	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>21</sub> –C <sub>29</sub>
Station 7066								
0–1	61	0.1	0.20	4.97	1.54	9.28	0.54	C <sub>15</sub> , C <sub>16</sub>
Station 7069								
0–1	49	0.4	0.84	1.09	2.13	2.40	0.45	C <sub>19</sub> , C <sub>25</sub> –C <sub>31</sub>
4–5	66	0.5	0.78	1.01	2.23	0.89	0.45	C <sub>19</sub> , C <sub>25</sub> –C <sub>31</sub>
10–11	76	0.4	0.47	1.16	2.72	1.48	0.43	C <sub>19</sub> , C <sub>25</sub> –C <sub>31</sub>
Station 7083								
0–1	155	3.9	2.50	0.37	6.47	0.99	0.15	C <sub>29</sub> , C <sub>31</sub> , C <sub>33</sub>
Station 7085								
0–1	182	0.1	0.06	2.02	4.10	0.49	0.47	C <sub>15</sub> , C <sub>16</sub>
Station 7094								
0–1	21	0.2	0.75	2.04	2.60	0.31	0.56	C <sub>19</sub> , C <sub>20</sub>
1–2	52	0.2	0.37	1.29	2.78	0.85	0.49	C <sub>19</sub> , C <sub>20</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
7–8	87	0.1	0.10	1.45	2.71	5.93	0.43	C <sub>18</sub> , C <sub>20</sub>
14–15	72	0.1	0.14	1.76	2.93	2.90	0.44	C <sub>18</sub> , C <sub>20</sub>
19–20	47	0.4	0.87	1.19	2.37	1.54	0.50	C <sub>19</sub> , Odds. C <sub>23</sub> –C <sub>31</sub>
31–32	42	0.1	0.36	1.73	2.35	1.78	0.80	C <sub>19</sub> , Odds. C <sub>23</sub> –C <sub>31</sub>
Station 7102								
0–1	46	0.4	0.9	1.39	2.05	1.44	0.55	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>23</sub> –C <sub>31</sub>
1–2	48	0.2	0.4	1.37	2.12	1.02	0.54	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>23</sub> –C <sub>31</sub>
2–3	48	0.3	0.6	1.24	2.20	1.47	0.55	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>23</sub> –C <sub>31</sub>
3–4	47	0.2	0.5	0.88	1.73	0.72	0.44	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>

Table 2. Continued

Horizon	HC, µg/g	Alkanes, µg/g	Alkanes, % of AAU	L/H*	CPI	$\frac{i-C_{19}}{i-C_{20}}$	Paq	Dominant peaks
4–5	43	0.1	0.2	1.29	2.03	1.36	0.54	C <sub>17</sub> , C <sub>20</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
5–6	36	0.2	0.7	1.14	1.84	0.81	0.57	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>23</sub> –C <sub>31</sub>
6–7	28	0.1	0.4	3.39	2.79	0.77	0.69	C <sub>19</sub> , C <sub>20</sub>
7–8	39	0.2	0.5	1.45	1.94	0.28	0.58	C <sub>19</sub> , C <sub>20</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
8–9	39	0.2	0.5	1.52	1.88	1.20	0.62	C <sub>19</sub> , C <sub>20</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
9–10	30	0.1	0.2	1.51	1.79	1.11	0.57	C <sub>20</sub>
10–11	29	0.2	0.6	1.66	2.42	0.82	0.53	C <sub>17</sub> , C <sub>19</sub>
11–12	29	0.1	0.5	1.46	2.21	1.33	0.54	C <sub>17</sub> , C <sub>19</sub>
12–13	28	0.2	0.7	1.58	2.09	0.67	0.56	C <sub>17</sub>
13–14	29	0.2	0.7	1.41	2.09	2.74	0.56	C <sub>17</sub>
14–15	24	0.2	0.6	1.15	2.08	4.34	0.53	C <sub>17</sub>
15–16	24	0.2	0.6	1.30	2.05	4.03	0.53	C <sub>17</sub> , C <sub>19</sub>
16–17	21	0.0	0.1	1.32	1.85	2.26	0.52	C <sub>17</sub> , C <sub>19</sub>
17–18	35	0.3	0.8	1.20	1.92	4.79	0.54	C <sub>17</sub> , C <sub>19</sub>
18–19	29	0.1	0.5	1.25	2.09	1.75	0.49	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
19–20	29	0.2	0.6	0.97	2.01	1.08	0.45	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
20–21	20	0.1	0.6	1.25	2.31	1.88	0.52	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
21–22	19	0.2	0.9	1.20	2.09	3.73	0.52	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
22–23	32	0.2	0.6	1.04	2.01	0.89	0.52	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
23–24	25	0.1	0.6	1.02	1.57	1.70	0.57	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
24–25	28	0.2	0.7	1.00	1.88	1.39	0.52	Nechet. C <sub>23</sub> –C <sub>31</sub>
25–26	23	0.2	0.8	1.57	1.76	9.99	0.52	C <sub>15</sub>
26–27	31	0.1	0.5	0.98	2.03	0.74	0.48	Nechet. C <sub>23</sub> –C <sub>31</sub>
27–28	25	0.2	0.6	1.07	2.36	3.20	0.47	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
28–29	27	0.2	0.7	1.01	1.88	34.94	0.48	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
29–30	33	0.1	0.3	1.03	2.01	0.63	0.48	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
30–31	22	0.2	0.8	1.08	1.96	6.12	0.49	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
Station 7104								
0–1	45	0.2	0.36	1.44	2.00	0.21	0.50	C <sub>17</sub>
Station 7105								
0–1	23	0.1	0.37	0.71	2.13	2.05	0.47	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
1–2	28	0.1	0.35	0.75	1.49	12.98	0.53	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
2–3	33	0.1	0.18	0.76	2.07	0.30	0.49	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
3–4	25	0.2	0.76	0.29	0.81	4.63	0.31	Nechet. C <sub>27</sub> –C <sub>31</sub>
4–5	21	0.1	0.56	1.13	2.27	1.12	0.48	C <sub>19</sub>
5–6	21	0.1	0.35	0.60	3.39	1.02	0.41	Odds. C <sub>25</sub> –C <sub>31</sub>
6–7	17	0.1	0.37	0.85	2.86	4.10	0.42	C <sub>15</sub> , C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
7–8	19	0.1	0.37	0.52	2.28	1.21	0.33	C <sub>19</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
8–9	20	0.1	0.43	0.54	2.71	4.34	0.37	C <sub>15</sub> , C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
9–10	14	0.04	0.27	0.68	3.54	3.46	0.36	C <sub>19</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>

**Table 2.** The End

Horizon	HC, µg/g	Alkanes, µg/g	Alkanes, % of AAU	L/H*	CPI	$\frac{i-C_{19}}{i-C_{20}}$	Paq	Dominant peaks
10–11	16	0.1	0.53	0.65	2.66	15.80	0.39	C <sub>19</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
11–12	16	0.1	0.58	0.57	2.86	1.34	0.37	C <sub>19</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
12–13	17	0.1	0.59	0.53	2.85	1.62	0.37	Odds. C <sub>25</sub> –C <sub>31</sub>
13–14	17	0.1	0.53	0.59	3.85	3.23	0.35	Odds. C <sub>25</sub> –C <sub>31</sub>
14–15	15	0.1	0.62	0.53	2.99	0.92	0.37	Odds. C <sub>25</sub> –C <sub>31</sub>
15–16	19	0.1	0.38	0.92	1.96	0.71	0.45	C <sub>20</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
16–17	21	0.1	0.50	0.96	1.61	1.04	0.51	C <sub>15</sub> Odds. C <sub>25</sub> –C <sub>31</sub>
17–18	24	0.2	0.68	0.50	3.01	1.77	0.38	C <sub>17</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
18–19	19	0.1	0.67	2.25	1.92	0.13	0.48	C <sub>15</sub>
19–20	20	0.1	0.31	0.60	2.33	2.90	0.43	C <sub>19</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
20–21	19	0.0	0.10	0.59	2.30	2.86	0.39	Odds. C <sub>25</sub> –C <sub>31</sub>
21–22	14	0.1	0.41	0.62	3.13	0.01	0.35	C <sub>17</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
22–23	11	0.1	0.67	0.77	0.36	1.72	0.52	C <sub>15</sub> , Odds. C <sub>25</sub> –C <sub>31</sub>
23–24	13	0.2	1.27	6.34	3.40	5.33	0.47	C <sub>15</sub>
24–25	14	0.1	0.50	0.61	3.02	24.42	0.41	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>
26–27	14	0.01	0.05	1.15	3.54	2.90	0.43	C <sub>17</sub> , C <sub>19</sub> , Odd. C <sub>25</sub> –C <sub>31</sub>

\*  $(L/H - \sum(C_{12-24})/\sum(C_{25-35}))$ ;  $CPI = [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34})] / 2$ ;  $Paq = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31})$ .

part of the column (20–24 cm). At the same time, in the composition of PAHs by hill. 10–11 cm, the number of 2–4 ringed homologs decreased against the background of an increase in 5–6 ringed homologs (Fig. 5), and the  $\sum light/\sum heavy$  ratio decreased from 1.6 to 1.0 (Table 3).

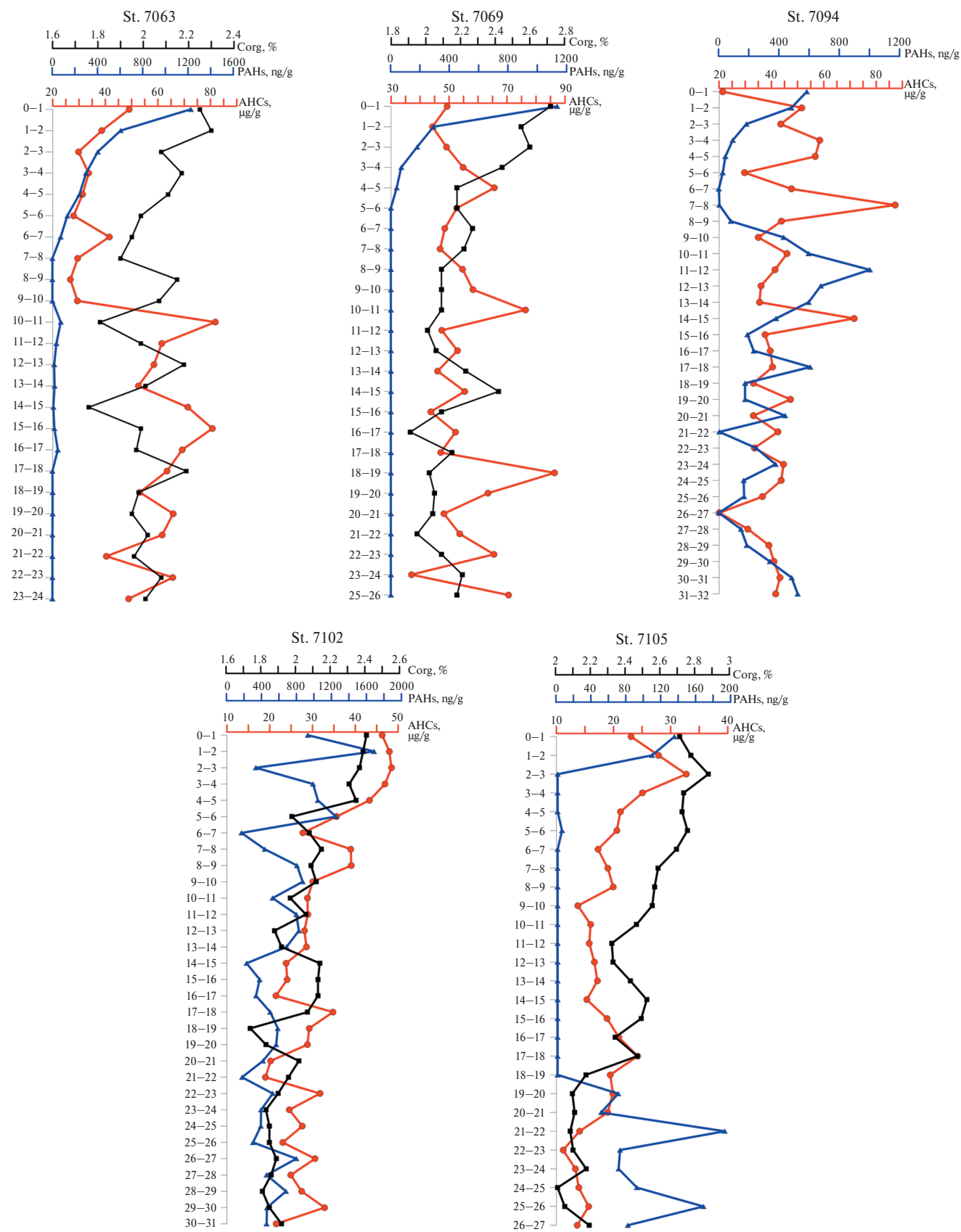
In the surface layer of sediments at stations 7068 and 7087 sampled in the Lumi and Lunde pockmarks, the content of AHCs was rather low both in terms of dry weight (36–43 µg/g) and  $C_{org}$  (0.19–0.26%). A large number of polychaete tubes of the family *Siboglinidae*, as well as hydrocarbon gas escape caverns were observed on the surface and in the sediment column, the number of which increased with sediment depth. The composition of alkanes was dominated by low-molecular-weight homologs, which is determined by their formation, as well as methane [4], in the sediment column.

For surface sediments of the Sofia Basin in the Arctic Ocean, the concentrations of AHCs were even lower: 24–30 µg/g (Fig. 1). Nevertheless, in the oxidized silty-pelitic silt of dark brown color at station 7078, the content of both AHCs (62 µg/g) and PAHs (1222 ng/g) increased. However, in the  $C_{org}$  composition, the fraction of AH in this area did not exceed 0.39%.

The HC content increased in the north of the Barents Sea in the Orli and Erik-Eriksen troughs (Fig. 1): for AHCs up to 73 µg/g (station 7100), and for PAHs up to 1125 ng/g (station 7101). Numerous signs of neotectonic activity were identified on acoustic sections in this area [6].

The highest PAHS content (1848–1918 ng/g), against the background of relatively low concentrations of AHCs (21–63 µg/g), is confined to the Svalbard shelf (stations 7059, 7069, 7090, 7091, 7094, 7095). This anomaly was noted earlier [9, 18, 23–25, 28, 31]. The composition of PAHs was dominated by naphthalene and its homologs formed in the sedimentary strata, as their amount practically did not change with the burial depth (Fig. 5, station 7094).

An unusual HC distribution in the sediment column (31 cm column) was found at station 7102, located in the north of the Barents Sea east of Bely Island at the crossing of the Erik-Eriksen Trough (Fig. 1). White Island at the crossing of the Erik-Eriksen Trough (Fig. 1). Here in the aleurite-pelitic bioturbated sludge, the  $C_{org}$  content decreased unevenly with burial depth from 2.65 to 2.0%, averaging 2.24%, as did the AHCs – 22–47 µg/g, averaging 31 µg/g (Fig. 5). In the composition of alkanes at transition from oxidized to reduced sediment and change in Eh from



**Fig. 3.** Variation of organic compound concentrations in the sedimentary column of selected stations (station locations are given in Fig. 1).



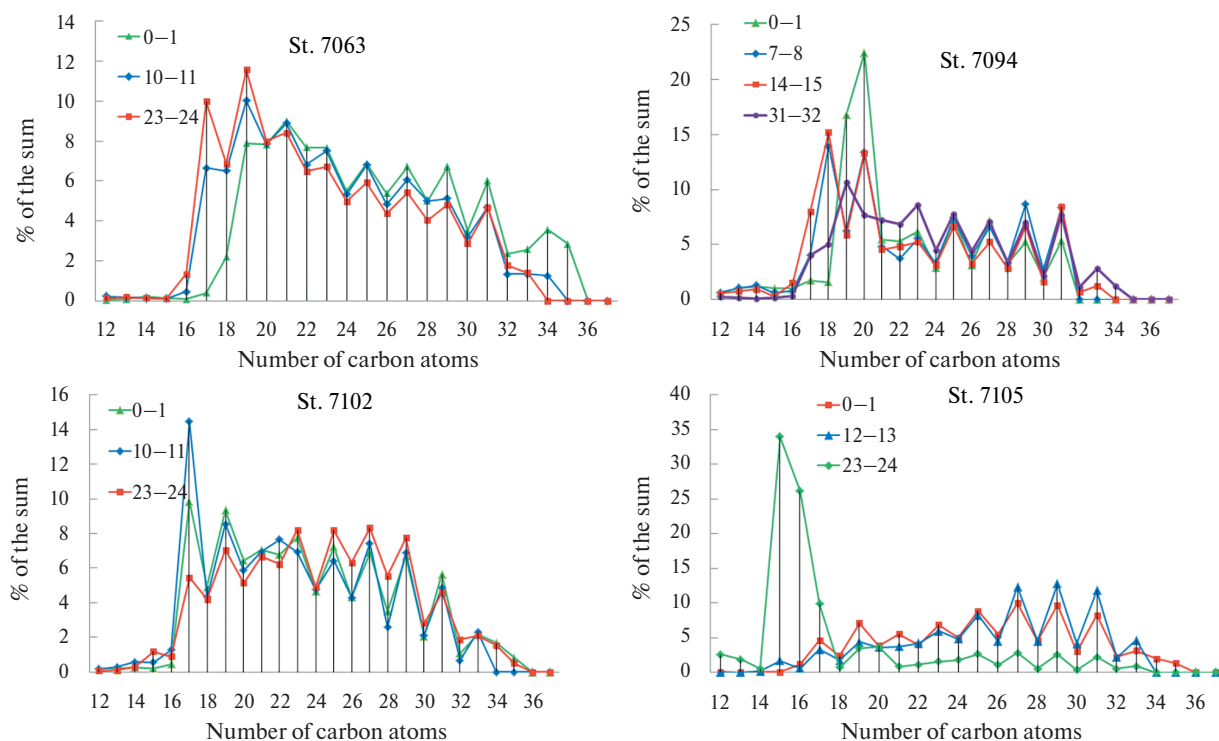


Fig. 4. Composition of alkanes in the sedimentary column of selected stations (station locations are given in Fig. 1).

175 (0–1 cm horizon) to -137 (10–11 cm horizon) the formation of autochthonous homolog *n*-C17 occurred (Fig. 4), and the C17/C25 ratio (2.25) increased 4.7 times compared to the 9–10 cm horizon.

The content of PAHs at station 7102 decreased 2-fold in the sediment thickness: from 931 to 459 ng/g. However, their concentration sharply increased at the transition from the surface oxidized layer to the underlying reduced layer (1–2 cm, up to 1690 ng/g, Fig. 5, Table 3). In contrast to St. 7063, naphthalenes were not among the dominant homologs here (Fig. 5). The PAHS composition was dominated by phenanthrene, the most stable and widespread polyarene in bottom sediments [7, 14, 18, 41].

An anomalous distribution of PAHS concentrations that increased in the lower horizons of the column (Fig. 3) and dominated by 2-methylnaphthalene (Fig. 5), a marker of petroleum genesis [14, 16, 18], was found in the sediments of station 7105 located in the eastern part of the Medvezhinsky Trough [8]. 7105 located in the eastern part of the Medvezhinsky Trough [8]. Sediments at this station were characterized by rather high concentrations of  $C_{org}$  in both the surface (2.71%) and lower (2.19%, 25–26 cm) horizons (Fig. 3). In contrast, the content of AHCs was rather low, and their values decreased irregularly from 23  $\mu\text{g/g}$  in the surface layer to 14  $\mu\text{g/g}$  in the lower layer. Nevertheless, autochthonous alkanes occurred

in the composition of alkanes in the lower horizons of the column (Fig. 4) and the L/H ratio (Table 2) at the 26–27 cm horizon was almost 2 times higher (1.21) than at the 24–25 cm horizon (0.61). All this indicates natural HC formation in the sedimentary strata. In addition, the formation of PAHs (Fig. 3) occurred in the lower horizons of the core, in the composition of which the share of naphthalenes increased (Fig. 5).

The sediment at station 7044, located in the crater at the site of a volley methane release as a result of dissociation of gas hydrates in the sedimentary strata in the postglacial time, contained a large number of polychaetes and their tubes, as well as shale rubble and driftwood [10]. Such structures are very characteristic of Arctic sea floor topography and are related to the fact that during glaciations, methane from the subsurface reservoir was concentrated in massive mounds beneath the ice sheet [19]. When glaciations retreated, the methane was abruptly released, forming explosive craters. Here, the surface sediment layer (Fig. 1) was characterized by a rather high  $C_{org}$  concentration (2.65%), a relatively low AHCs content (26  $\mu\text{g/g}$ ), and an elevated PAHS concentration (937 ng/g). Nevertheless, the composition of alkanes in the low molecular weight region showed peaks characteristic of phytoplanktonogenic OM (Fig. 2), and phytane dominated over pristane ( $i\text{-C}_{19}/i\text{-C}_{20} = 1.73$ ,

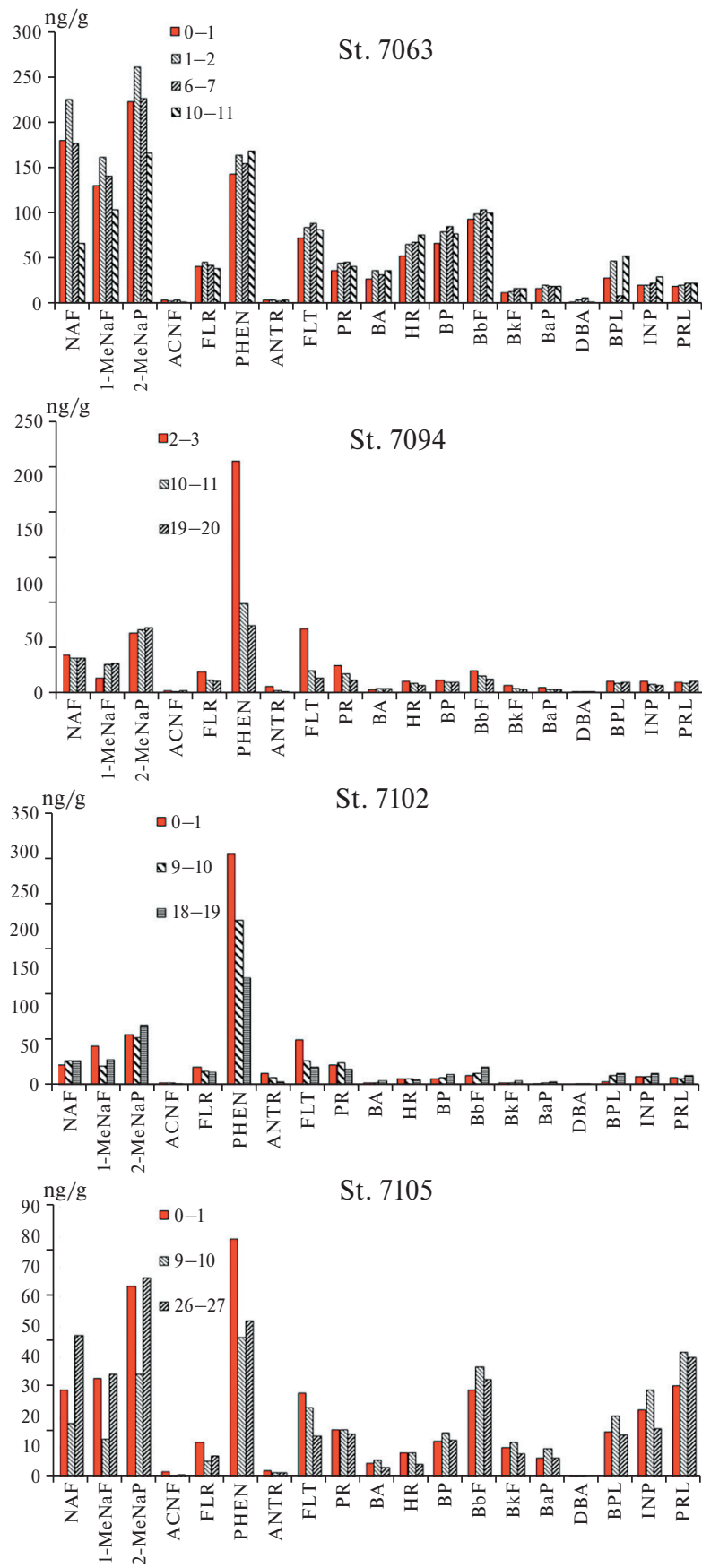


Fig. 5. PAHS composition in the sedimentary column of selected stations (station locations are given in Fig. 1).

**Table 3.** Distribution of markers within PAHs (HPLC method) of bottom sediments at some stations

Horizon	AHCs, μg/g	ΣPAU, ng/g	ΣNaf/ ΣPAHs,%	FLT/PR	ΣNuff/ PHEN	(PR+FLT)/ (PHEN+ XP)	FEN/. ANTR	Σ2–3 col./ Σ 5–6 col.	FLT/. (FLT + PR)
Station 7044									
0–1	26	681	30.8	1.7	1.7	0.4	25.3	1.2	0.6
Station 7046									
0–1	15	81	29.6	1.8	1.5	0.4	25.8	1.1	0.6
2–3	78	90	44.1	2.2	2.4	0.3	32.6	2.0	0.7
3–4	47	70	58.1	4.3	3.5	0.3	39.3	3.9	0.8
16–18	49	466	52.5	0.9	7.3	0.4	33.8	1.6	0.5
Station 7063									
0–1	49	1170	45.7	2.0	3.7	0.6	39.5	1.6	0.7
1–2	39	1400	46.3	1.9	3.9	0.6	42.1	1.6	0.7
6–7	42	1270	42.9	2.0	3.5	0.6	47.0	1.4	0.7
10–11	82	1100	30.5	2.0	2.0	0.5	42.2	1.0	0.7
Station 7069									
0–1	49	450	23.5	2.2	0.9	0.5	36.1	1.2	0.7
1–2	44	517	29.0	2.6	1.4	0.5	39.0	1.2	0.7
4–5	66	579	30.2	2.5	1.9	0.6	44.6	1.0	0.7
10–11	76	513	27.5	2.6	1.8	0.6	44.9	0.9	0.7
Station 7078									
0–1	62	1222	35.2	2.0	1.8	0.4	41.3	1.4	0.7
Station 7090									
0–1	63	387	37.3	1.3	2.2	0.4	31.8	1.4	0.6
Station 7091									
0–1	148	626	37.6	1.1	2.5	0.4	14.1	1.4	0.5
Station 7092									
0–1	24	366	38.8	2.2	1.8	0.4	24.5	2.0	0.7
2–3	44	520	19.8	2.3	0.5	0.4	38.1	1.9	0.7
3–4	58	505	24.2	2.1	0.6	0.3	40.8	2.5	0.7
6–7	48	603	25.1	1.6	0.6	0.3	30.5	2.3	0.6
Station 7094									
10–11	46	327	35.9	1.2	1.4	0.4	34.3	1.9	0.5
11–12	41	353	31.8	1.2	1.0	0.3	15.0	2.5	0.5
14–15	72	313	36.5	1.3	1.2	0.3	19.6	2.9	0.6
19–20	47	294	40.9	1.1	1.9	0.4	34.6	2.1	0.5
Station 7095									
0–1	62	441	31.5	1.5	1.3	0.3	21.6	1.6	0.6
Station 7099									
0–1	70	400	30.9	1.5	1.2	0.4	13.2	1.7	0.6
Station 7101									
0–1	49	1125	32.7	1.2	1.2	0.3	16.8	2.0	0.5

Table 3. The End

Horizon	AHCs, μg/g	ΣPAU, ng/g	ΣNaf/ ΣPAHs,%	FLT/PR	ΣNuff/ PHEN	(PR+FLT)/ (PHEN+ XP)	FEN/ ANTR	Σ2–3 col./ Σ 5–6 col.	FLT/ (FLT + PR)
Station 7102									
0–1	46	625	22.8	2.3	0.5	0.3	19.4	3.4	0.7
6–7	28	804	20.6	1.6	0.4	0.3	14.3	3.3	0.6
8–9	39	614	23.3	1.2	0.5	0.3	16.0	2.8	0.5
9–10	30	502	23.6	1.1	0.6	0.3	21.7	2.6	0.5
18–19	29	455	31.4	1.1	1.0	0.3	31.6	2.0	0.5
Station 7104									
0–1	45	710	32.7	1.8	1.1	0.2	18.2	2.4	0.6
Station 7105									
0–1	23	406	31.0	1.8	1.6	0.5	31.8	1.2	0.6
1–2	28	335	22.0	1.9	1.8	0.8	29.9	0.6	0.7
2–3	33	256	21.2	1.8	1.8	0.7	30.5	0.6	0.6
3–4	25	317	19.2	1.7	1.6	0.8	27.0	0.5	0.6
4–5	21	303	24.7	1.7	2.3	0.8	23.0	0.6	0.6
5–6	21	316	16.7	1.8	1.3	0.8	25.4	0.5	0.6
6–7	17	331	19.5	1.7	1.6	0.9	23.5	0.5	0.6
7–8	19	375	19.2	1.7	1.1	0.7	23.9	0.6	0.6
8–9	20	351	19.8	1.6	1.2	0.7	21.9	0.6	0.6
9–10	14	342	19.3	1.5	1.4	0.7	26.0	0.5	0.6
10–11	16	318	25.1	1.6	1.7	0.6	26.3	0.8	0.6
11–12	16	344	21.2	1.6	1.3	0.7	30.6	0.7	0.6
12–13	17	296	22.4	1.4	1.7	0.7	24.8	0.6	0.6
13–14	17	287	19.4	1.4	1.3	0.7	26.2	0.6	0.6
14–15	15	286	19.2	1.4	1.3	0.7	30.3	0.6	0.6
15–16	19	299	18.5	1.5	1.5	0.8	27.9	0.5	0.6
16–17	21	397	25.1	1.5	1.7	0.6	24.8	0.8	0.6
17–18	24	437	27.2	1.9	1.2	0.4	28.3	1.2	0.6
18–19	19	203	26.3	0.8	2.0	0.6	24.2	0.7	0.5
19–20	20	240	29.3	0.9	2.2	0.6	22.7	0.8	0.5
20–21	19	246	35.3	0.9	2.7	0.6	21.4	1.0	0.5
21–22	14	294	36.2	1.0	2.8	0.6	23.7	1.1	0.5
22–23	11	344	41.8	0.9	2.6	0.4	27.9	1.6	0.5
23–24	13	323	36.0	0.9	2.2	0.5	26.1	1.2	0.5
24–25	14	349	35.8	0.7	2.8	0.5	26.5	1.1	0.4
25–26	16	377	39.5	0.8	2.3	0.4	32.3	1.5	0.5
26–27	14	381	39.0	0.9	2.8	0.5	27.6	1.2	0.5



Table 2), which may indicate active biogeochemical processes in the sediment [34].

Thus, for the entire data set obtained in 2021, a correlation ( $r = 0.52$ ,  $n = 41$ ) was observed between precipitation moisture, which varied in the range of 31.6–82.4%, and  $C_{org}$ . It is known that the porosity and moisture content of precipitation, to a certain extent, are determined by its particle size distribution [2]. Sediments with high moisture content (up to 80% or more) are usually formed by fine suspended sediments with a high proportion of biogenic matter (e.g., fragments of dying planktonic organisms). Low moisture values (less than 40%) are characteristic of coarse bottom sediments formed by lithogenic material entering the seas as a result of coastal erosion and slope runoff.

Between AHCs and moisture ( $r = 0.24$ ) and  $C_{org}$  and AHCs ( $r = 0.22$ ) these relationships were much weaker. The distribution of HC determines not so much the lithotype of bottom sediments, but the level of primary production in the water area, the contribution of terrigenous OM, and the influence of benthic macro- and microorganisms [21, 22]. Therefore, in many investigated areas there were no relationships in the distribution of  $C_{org}$  and AHCs, AHCs and PAHs. Different nature of formation of AHCs (phytoplankton and oil pollution) and PAHs (fuel combustion processes, to a lesser extent oil pollution) lead to the lack of relationship in the distribution of these hydrocarbon classes:  $r(\text{AHCs} - \text{PAHs}) = -0.23$ .

In most cores, there is a decrease in  $C_{org}$  concentrations in the upper part of the core (10–12 cm) and an insignificant change in the lower horizons. This pattern corresponds to the general trend of organic matter change in Arctic shelf sediments [31] and rather low CPI values in the composition of alkanes ( $< 3$ , Table 2) in the studied water areas indicate an increase in the input of biogenic HCs. Their formation occurred directly in the sedimentary strata, which often had a hydrogen sulfide odor due to a large amount of undecomposed organic compounds (stations 7063, 7068, 7087, 7105).

In Fram Strait, such a large range of concentrations is largely due to the peculiarities of the hydrological regime conditions [33, 36, 39]. Two main currents interact here: the warm West Spitsbergen Current and the cold East Greenland Current. Due to these currents, there is an exchange between Arctic and Atlantic water masses [38]. In the Marginal Ice Zone (MIZ), according to data obtained in 2021, phytoplankton productivity increases to 450–650  $\text{mgC} \times \text{m}^{-2} \times \text{day}^{-1}$  [29]. Increased concentrations of nutrients, chlorophyll-a, high level of phytoplankton production

in surface waters, as well as high rates of vertical matter flux lead to accumulation of organic compounds in sediments at some bottom areas. The latter leads to mosaicity in the distribution and composition of organic matter in the surface layer. Earlier it was considered that the main source of HC in the bottom sediments of Fram Strait was phytoplankton (ice algae) and biogeochemical processes at the water-bottom boundary [22]. The contribution of HC of terrestrial origin was minimal. However, our studies showed that terrigenous high-molecular-weight alkanes dominated in the sediments at station 7082. Therefore, the CPI values were higher compared to other areas (Table 2).

The study of the differentiation of the molecular composition of PAHs during transport through the Fram Strait allowed us to establish that the more volatile/light polyarenes, which are formed in emissions at low latitudes, are transported long distances in the atmosphere. In contrast, high molecular weight PAHs are deposited predominantly in coastal shelf water areas as a result of gas exchange between the atmosphere and water [27, 41].

The Westnes Ridge is a drift, the southeastern part of which is complicated by numerous hydrocarbon gas outcrops [37, 40, 43]. At the same time, deep fluids migrate in the sediment column and form not only methane but also high-molecular hydrocarbons. Therefore, at station 7063 in the sedimentary stratum there was a correlation between  $C_{org}$  distribution and sediment moisture ( $r = 0.58$ ,  $n = 25$ ), and there were no correlations between AHCs distribution and  $C_{org}$  ( $r = -0.38$ ). The latter is most likely due to the presence of a source of organic compounds genetically unrelated to suspension and sedimentation processes. This confirms the distribution of molecular markers in the composition of AHCs and PAHs.

Depending on the conditions in oil and gas bearing horizons and geological structures beneath the seafloor, gas-liquid flows of methane and other HCs from sedimentary strata can become active, temporarily cease their activity, or disappear altogether, and then reappear [11, 35]. This can explain the difference in concentrations of AHCs and PAHs in different years of the study in the same area (Table 1).

The origin of HC differed significantly depending on the study area. It turned out that more stable terrigenous alkanes dominated in sediments only in some areas. That is why CPI values of alkane composition were so low (Table 2). The distribution of methane unloading areas reveals an extremely wide and diverse range of sedimentation settings: landscape-morphological, geodynamic, and climatic [1]. The lack of correlation between  $C_{org}$  and AHCs concentrations, the increase in the share of AHCs in the composition

of  $C_{org}$  with the depth of sediment burial, and the distribution of markers in the composition of alkanes may testify in favor of the deep nature of AHCs [1, 9]. The local character of these processes is indicated by the lateral variability of AHCs concentrations in sediments.

On the Svalbard shelf, the concentration levels and composition of polyarenes are formed by eroded coal rocks of the archipelago [25, 31]. Therefore, the highest concentrations of PAHs are found here.

The depth processes influence the formation of the modern morphostructure and relief of the Eric-Eriksen and Orly troughs [6]. The general picture of the unloadings location reveals an extremely wide and diverse range of settings of their distribution – landscape-morphological, geodynamic and climatic. The latter is confirmed by anomalously high values of heat flux, in particular, in the Orly trough more than 300 mW/m<sup>2</sup>. The activity of deep processes is noted in different segments of the trough because of the tectonic nature of these structures. The western part of the Orly Trough is promising in terms of detecting areas of methane outcrops, which was confirmed by a shipboard echo sounder that established a profile with a flare [10]. That is why there were such high concentrations of HCs, especially PAHs, in the sediments here. The uniqueness of sampling in this area was also due to the fact that in the recent past the troughs of the north of the Barents Sea, were inaccessible for research due to the ice cover and difficult ice situation in the short summer season.

In conclusion, it should be emphasized that the study of HC composition and biogeochemical processes in bottom sediments is now becoming an integral part of research to assess the effects of the changing environment and climate in the Arctic on ecosystems.

## CONCLUSION

The HC sources differed significantly for the studied water areas of the Norwegian-Greenland Basin and the Barents Sea with different sedimentation conditions and deep fluid flows from the bottom. Therefore, large ranges of variation in the concentrations of organic compounds in the surface layer of sediments were established, which amounted to 0.25–2.71% for  $C_{org}$ , 7–182 µg/g for AHCs and 0–1918 ng/g for PAHs.

The obtained correlations between sediment moisture and  $C_{org}$  content indicate the joint content of biogenic and lithogenic components. The absence of correlations between the  $C_{org}$  content and HC concentration, as well as between the concentrations of AHCs and PAHs indicate the

simultaneous presence of different sources that form these organic compounds in sediments.

In Fram Strait, such a large range of concentrations is largely due to the hydrological conditions of the water area. Both microbial and terrigenous alkanes dominated in the composition of AHCs, and high-molecular-weight homologs prevailed in the composition of PAHs.

In many investigated Holocene sediments, the behavior of organic compounds is mainly due to microseepage of natural HCs (Westness Ridge, Orly Trough area, central part of the Barents Sea, etc.). The composition of alkanes and the composition of PAHs indicated intensive deep fluid flows occurring in the sedimentary strata, which in some cases (st. 7105) can lead to the formation of oil films on the sea surface, registered from space using radar satellites.

The composition of specific biomarkers (e.g., st. 7963) reflects lateral and vertical variability of HC sources in the sediment column. In the water areas of pockmarks and sips, enrichment of the uncovered sedimentary strata with light alkanes in the composition of AHCs and naphthalenes in the composition of PAHs was revealed.

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## CONFLICT OF INTERESTS

The authors of this paper have no conflict of interests.

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