Hydrocarbons in the Littoral Sediments and March Soils of the Southwestern Coast of the Barents Sea

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Abstract—The genesis, facies conditions of sedimentation, degree of organic matter transformation in the bottom sediments and march soils of the southwestern coast of the Barents Sea are characterized based on results of a GC-MS study of the composition and distribution of hydrocarbons (*n*-alkanes, isoprenoids, steranes, hopanes, polycyclic aromatic hydrocarbons (PAHs), and their alkyl homologues). The effects of the toxicity levels of polyarenes on the biota inhabiting the tidal zones of the coast was assessed, and areas of elevated anthropogenic load were identified (littoral of the eastern Tana Fjord, the village of Kiberg, Abram Cape, the village of Mishukovo, the mouth of the Kulonga River, the apex part of Yarnyshnaya Bay, and Oscar Bay), indicating an unfavorable ecological state of the tidal zones of the Barents Sea coast.

Keywords: hydrocarbons, littoral zones, salt marshes, biomarkers, PAHs, toxicity, coast of the Barents Sea

INTRODUCTION

The Barents Sea and adjacent territories are now one of the largest oil- and gas-bearing basins in the Arctic. The shores of the Barents Sea are impacted by intense anthropogenic activities aimed at developing the infrastructure for shelf hydrocarbon fields and the fields themselves. These anthropogenic activities expose the tidal zones to contamination risks (Bambulyak et al., 2015; Sosnin and Kuranov, 2018; Patin, 2017). The near-shore ecosystems (particularly those in the apex parts of gulfs and bays) are significantly impacted by anthropogenic sources because urbanized techniques, seaports, and hydrocarbon-loading terminals are commonly constrained to these territories, and hence, they are contaminated with compounds brought there from both the shores and the open sea. From this perspective, the shores of the Barents Sea are of particular interest as model territories with regard to their geological, geomorphological, and biological diversity and, hence, the diversity of the organic–geochemical characteristics and susceptibility to contaminants (Panov, 1940; Tarasov and Alekseev, 1985; Aibulatov, 2005; *AMAP*, 2010; Boitsov et al., 2020).

One of the key aspects of chemical stress affecting the Arctic shore is contamination with hydrocarbons (HC) (*AMAP*, 1997; Dahle et al., 2006; Boitsov et al., 2009; Nemirovskaya, 2013). Their detailed studies provide necessary information on the sources of the organic matter (OM), its thermal maturity, and biodegradation processes, whose intensity can be evaluated by comparing characteristics of HC compounds: *n*-alkanes, isoprenoids, steranes, hopanes, and polycyclic aromatic hydrocarbons (PAH) (Eglinton and Murphy, 1969; Peters et al., 2005). In view of this, comprehensive studies of HC of the dispersed OM (DOM) in sediments and soils in the shallow waters of the Barents Sea are an inherent part of the ecological monitoring of the Arctic shores.

PAH is the most important group of molecular markers from the viewpoint of the occurrence of oil HC in the sediments and soils, including hazardous and toxic components of fuel materials and their combustion products (*AMAP*, 1997, 2010; Honda and Suzuki, 2020). The background organic–geochemical characteristics of Arctic territories are traditionally determined and their contamination levels are conventionally assessed using a group of top-priority 16 PAH (*U.S. EPA*, 2005). However, recent studies (Keith, 2015; Meyer et al., 2014; Richter-Brockmann and Achten, 2018) have proved that this list should be significantly appended by other parent and alkylated polyarenes, whose toxicity has been previously disregarded because of their natural origin and/or because they are widespread in natural environments.

In addition, it is important to take into account the different contributions (toxic equivalent, *TEQ*) of individual compounds to the total toxicity of PAH (Nisbet and LaGoy, 1992) and criteria of sediment
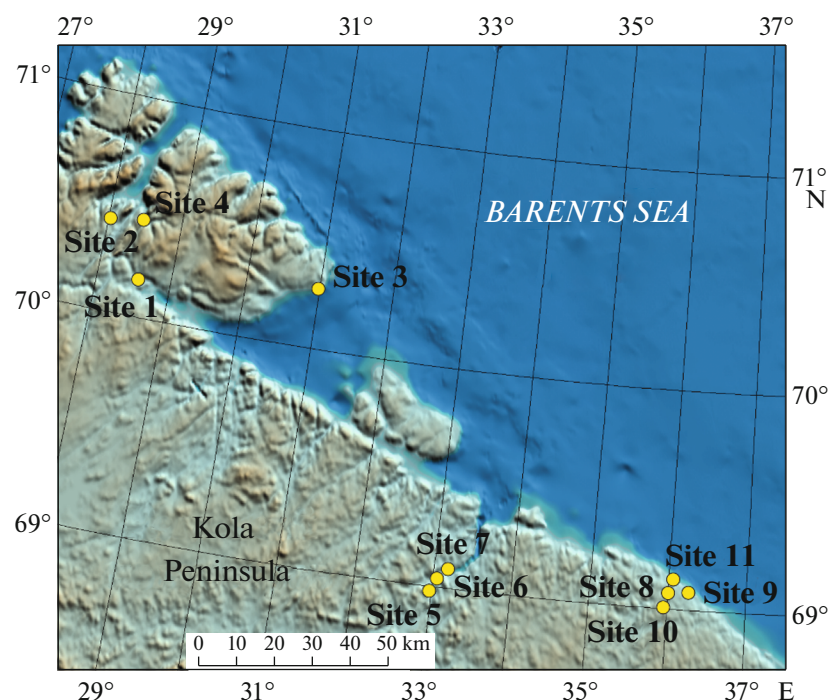
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† Deceased.

Fig. 1. Schematic location map of the sampling sites.

quality for the life of the biota. Below we discuss the criteria that reflect the threshold concentration levels of individual compounds below which their toxicity is possible at a probability of no lower than 10% (effect range low, *ERL*) and no higher than 50% (effect range medium, *ERM*) (Long et al., 1995; MacDonald et al., 2003). This comprehensive approach to the assessment of the ecological state of natural environments and their biological objects is of paramount importance and is indispensable, along with the conventional analysis for the 16 top-priority PAH and their sources (pyrogenic, petrogenic, and biogenic).

Our research was focused on hydrocarbons in the bottom sediments and marsh soils in various tidal zones (saline marshes and rocky and silty–sandy littorals) of the Barents Sea shores in effort to assess their current states and outline areas of elevated anthropogenic pressure.

The studies were aimed at characterizing the group composition of the OM, the molecular composition of the hydrocarbon biomarkers (*n*-alkanes, isoprenoids, and cylanes) and PAH and their alkyl homologues in the bottom sediments and marsh soils of the southwestern shore of the Barents Sea. We have also determined the toxicity levels of the polyarenes for organisms inhabiting the studied sediments and soils.

MATERIALS AND METHODS

In this study, we used samples of bottom sediments and soils collected with a Robur-Il hand-held sampler (piston corer) during low tides at the Norwegian and Russian territories in the Barents Sea shores during summertime in 2019 and 2020 (Fig. 1).

The sampling sites in the territory of Norway were constrained to the apex part of the Varanger Fjord (Site 1), western (Smalfjord) and eastern (Austertana) parts of the Tana Fjord (Sites 2 and 3, respectively), and in the vicinities of the village of Kiberg (Site 4). In the Russian part of the Barents Sea shore, sampling sites were located in the Kola Bay: in the areas of Abram Cape (Site 5), the village of Mishukovo (Site 6), in the mouth of the Kulonga River (Site 7), and in the shore of Eastern Murman: in Yarnyshnaya Bay (Sites 8 and 10), Porchnikha Bay (Site 9), and in Oskar Bay (Site 11). The samples were taken from the tidal zone along transects through the sublittoral–littoral–supralittoral/marsh. Samples at sublittoral sites were taken beneath the water level during the lowest tide period. Samples from the littoral were collected from the intermediate part. The supralittoral was always above the average littoral level, and its location depended on the type of the shore: it occurred in the highest littoral zone (hereafter, *supralittoral*) in open shore segments, in the highest littoral zone in calm areas, and in the zone of halophytic vegetation in the saline marsh (hereafter referred to as *marsh* and *marsh soils*). The core sampling was controlled by the variations in the lithology of the sediments and soils. The total number of the samples was 42, which were collected along 11 transects.

The applied sampling approach allowed us to characterize in detail and identify the spatial distribution of DOM, assess variations in the intensity of the anthro-

pogenic impact depending on the zone and type of the littoral where the samples were taken and on the location of the sampling sites (proximity to population centers and/or a port, pier, etc.). Moreover, this approach was efficient in assessing variations in the character of contamination with time and the effects of natural conditions in the water space (erosion, redeposition of the sedimentary material, and stagnant lagoons) and in evaluating the pressure on the biological communities inhabiting the littoral zone (this was done using geochemical toxicity indexes).

Samples of bottom sediments and soils for laboratory studies were placed into sterile containers and kept frozen at -18^oC. In the laboratory, the samples were freeze dried (Scanvac CoolSafe Freeze Dryer), grinded, their 0.25-mm fraction was separated by sieving, and average subsamples were taken to select material for extracting organic compounds.

The analytical procedure of the study of OM involved: analysis for concentrations of total organic carbon (TOC) and carbonate carbon (CC) by the Knop technique (chemical burning), Soxhlet extraction of bitumoids (A_{ch} is the chloroform extraction, and A_{eb} is ethanol–benzene extraction), analysis for the group composition, including determination of humic acids (HA) and residual OM (ROM), chromatographic fractionation and separation of the sum of the aliphatic and aromatic HC fractions, and GC-MS analysis of n-alkanes, isoprenoids, cyclanes, and polycyclic aromatic hydrocarbons.

GC-MS analysis of the hydrocarbon fraction was carried out on an Agilent Technologies 6850/5973 GC-MSD system with a quadrupole mass detector, equipped with a program package for processing analytical information (Petrova et al., 2017; Morgunova et al., 2019). All compounds were identified by comparing their retention times and mass spectra with those of external standards (Supelco 47930-U, 46955-U, 49451-U; Chiron AS 2634.27-5UG, AS 0613.30-100-10, AS 2616.31-10UG, AS 2635.27-5UG, AS 0976.29-10-IO, AS 2646.30-10UG, AS 9876.16-50-IO, AS 9877.16-50-IO, AS 1693.16-500-IO), NIST and WILEY libraries, and/or published data (Stout, 1992; George et al., 2008; Meyer et al., 2014).

Aliphatic and cyclic HC were analyzed on a HP DB 30 m × 0.25 mm, the immobile phase was 5% phenyl and 95% methyl silicon, the carrier gas was He, the flow rate was 1.2 mL/min, and the injector temperature was 320°C. The temperature regime of the analysis was as follows: temperature increase from 50 to 320°C at a rate of 3°C/min, and then holding for 7 min at 320°C. The detection was done as a total SCAN (from 50 to 500 m/z, 70 eV). Identification: n-alkanes and isoprenoids by the selective ion with 71 m/z, and cyclane HC by m/z 191 and 217, 218.

Polycyclic aromatic HC were analyzed on the same column, the carrier gas was He, flow rate was 1.2 mL/min, and the injector temperature was 290°C. The temperature regime of the analysis was as follows: temperature increase from 60 to 200°C at a rate of 20°C/min, then to 300 at 10ºC, and holding for 5 min at 300°C. The detection was done as a total SCAN (from 50 to 500 m/z, 70 eV). Parent HC were identified by the selective ions with m/z 128, 166, 178, 202, 228, 252, 276, and 278; and alkylated PAHs were identified by the selective ions with m/z 156, 165, 170, 183, 184, 192, 206, 216, 219, 220, 234, 242, 256, 274, and 324.

RESULTS AND DISCUSSION

The composition of sediments in the littoral zone is controlled primarily by the geological structure and the lithologic–petrographic composition of the rocks that form the bottom of the water area and the shore. Some features of the DOM of the soils/grounds of the shore above the water level are controlled by its type: abrasion (the grain size of the terrigenous formations ranges from boulders to sands) or accumulation (sand and pebble beaches). At low shore segments that are flooded during high tides and surges, marshes are formed, which are wetland meadows with silty or sandy–silty sediments.

Group Composition of the Organic Matter

Concentration of organic carbon (TOC) in the studied sections (Table 1) varies from 0.1 to 9.0%, and a grain-size control is discernible in its distribution, i.e., its concentrations systematically increase in the sequence sands–clays (Vassoevich, 1973).

Most of the sediments and soils are relatively poor in TOC (<2%), except samples taken from the supralittorals/marshes, in which the highest concentrations of humic acids were found (HA up to 12.9%) because the sandy sediments mix with the soils enriched in humus.

The composition of the extractable part of DOM significantly varies in terms of ratios of polar and non-polar compounds (A_{ch}/A_{eb} = 0.2–4.8, Table 1), which indicates that the redox conditions varied during sedimentation.

The degree of OM bituminization (coefficient β) varies from 0.4 to 52.4%, and the sediments with high β usually have the lowest ROM values. A likely reason for this might have been the input of petroleum HCs, because some sampling sites were close to population centers and highways and/or to the ship-repair yard/base/pier for serving vessels and boats (Sites 3, 5, 6, 7, and 11). The group composition of the bitumen does not show any significant deviations from the background characteristics of littoral–shelf sediments of the western Arctic (Romankevich, 1977; Danyushevskaya et al., 1990; Morgunova et al., 2021). HC concentrations in the sediments and soils range from 0.0002 to 0.3%, and the HC are dominated by cyclanes–

Table 1. Geochemical characteristics of DOM

No.	Sample	Location on transect/sampling interval, cm	Lithology	Concentration in sediment, %			A_{ch}/A_{eb}	ROM in OM, %	β^*	% HCs in sed.	HC composition, %	
				CC	TOC	HA					aliph.	arom.
1	**Varanger Fjord (Varangerfjord, Varangerbotn), marsh**											
2	1-0	Sublittoral/0−14	Silt with sandy admixture	0.01	0.3	0.01	0.7	94.5	2.8	0.001	75.0	25.0
3	1-1	Littoral/0−17	Clay	0.01	0.5	0.12	0.5	81.5	2.8	0.003	74.4	25.6
4	1-2	Supralittoral/0−2	Turf	0.03	9.0	8.49	1.0	42.2	5.6	0.021	72.7	27.3
5	1-2	Supralittoral/2−10	Clay	0.01	0.9	0.59	1.4	59.6	3.8	0.002	76.2	23.8
6	**Western Tana Fjord (Tanafjord, Smalfjorden), marsh**											
7	2-0	Sublittoral/0−2	Clay with sandy admixture	0.02	0.3	4.05	1.6	–	40.7	0.006	72.7	27.3
8	2-0	Sublittoral/2−16	Sand, rocks	0.06	0.2	0.01	0.5	88.9	5.1	0.002	75.0	25.0
9	2-1	Littoral/0−2	Clay with sandy admixture and single floral remnants	0.04	0.3	0.20	1.1	56.3	6.8	0.002	83.3	16.7
10	2-1	Littoral/2−10	Dark brown sand	0.07	0.4	0.04	0.3	90.2	1.9	0.002	81.3	18.8
11	2-2	Marsh/0−2	Grass-overgrown surface	0.02	2.0	0.84	1.8	64.7	14.6	0.024	73.3	26.7
12	2-2	Marsh/2−10	Clay with sand, floral remnants, and rocks	0.02	0.6	0.25	1.0	74.9	2.7	0.002	70.0	30.0
13	**Village of Kiberg (Kiberg, Vardø) rocky littoral**											
14	3-0	Sublittoral/1−15	Sand with single shell rock fragments	0.06	0.2	0.00	1.6	97.7	2.6	0.001	71.4	28.6
15	3-1	Littoral/0−15	Sand with single shell rock fragments	0.16	0.4	0.00	1.0	98.8	1.1	0.001	71.4	28.6
16	3-2	Supralittoral/2−10	Turf, rocks	0.04	6.3	4.49	0.7	55.3	4.2	0.012	66.7	33.3
17	**Tana Fjord eastern (Tanafjord, Austertana, Leiropollen), marsh**											
18	4-0	Sublittoral/0−2	Brown clay with sandy admixture	0.03	1.0	0.30	1.5	72.2	13.0	0.004	72.2	27.8
19	4-0	Sublittoral/2−8	Black clay sand and rock fragments	0.01	0.5	0.09	0.2	88.8	0.4	0.000	73.7	26.3
20	4-1	Littoral/0−2	Brown clay	0.01	0.7	0.15	0.9	73.9	11.8	0.004	58.5	41.5
21	4-1	Littoral/2−10	Black clay	0.02	0.2	0.10	1.1	69.2	7.4	0.002	80.0	20.0
22	4-2	Marsh/0−8	Turf, roots	0.08	7.9	12.9	1.6	6.2	4.3	0.020	70.0	30.0
23	**Abram Cape, rocky littoral**											
24	5-0	Sublittoral/0−6	Coarse-grained sand, shingles, rocks, shell rock	0.03	0.2	0.01	3.9	82.2	22.1	0.018	69.2	30.8
25	5-1	Littoral/0−3	Coarse-grained sand, shingles, rocks	0.05	0.1	0.01	1.5	47.0	52.4	0.027	76.2	23.8
26	**Mishukovo, marsh**											
27	6-0	Sublittoral/0−8	Black–brown sand, shingles, rocks	0.04	0.3	0.01	1.0	91.9	5.5	0.004	72.7	27,3
28	6-1	Littoral/0−10	Gray-brown sand with clay admixture	0.03	0.2	0.09	1.1	75.8	3.5	0.002	75.0	25.0
29	6-2	Supralittoral/0−8	Brown sand with clay beneath a turf layer	0.02	2.4	0.69	3.2	55.2	39.9	0.216	65.7	34.3
30	**Mouth of Kulonga R., marsh**											

Table 1. (Contd.)

No.	Sample	Location on transect/sampling interval, cm	Lithology	Concentration in sediment, %			A_{ch}/A_{eb}	ROM in OM, %	β*	% HCs in sed.	HC composition, %	
				CC	TOC	HA					aliph.	arom.
31	7-0	Sublittoral/0–14	Gray sand with black beds, rocks	0.01	0.3	0.01	0.9	83.1	13.1	0.016	77.8	22.2
32	7-1	Littoral/0–6	Brown-gray sand with black sand beds	0.04	0.3	0.08	4.3	68.0	24.2	0.029	71.9	28.1
33	7-2	Supralittoral/0–10	Brown sand with rocks and floral fragments	0.03	4.6	5.69	4.8	14.9	26.7	0.316	79.3	20.7
34			**Yarnyshnaya Bay, rocky littoral**									
35	8-0	Sublittoral/0–5	Shell rock, sand, rocks	0.40	0.7	0.01	0.8	96.6	2.1	0.002	75.0	25.0
36	8-1	Littoral/0–3	Shell rock, sand, rocks	0.00	0.2	0.00	1.7	98.0	2.3	0.001	75.0	25.0
37			**Porchnikha Bay, marsh**									
38	9-0	Sublittoral/0–15	Clay with hydrotroilite admixture	0.04	0.4	0.00	0.6	97.3	1.7	0.002	88.2	11.8
39	9-1	Littoral/0–12	Clay with hydrotroilite admixture	0.02	0.3	0.00	0.9	98.0	1.7	0.001	76.9	23.1
40	9-2	Marsh/0–3	Sand, clay floral remnants and rocks	0.00	0.5	0.25	1.5	67.9	5.6	0.003	73.1	26.9
41	9-2	Marsh/3–12	Clay	0.01	0.4	0.01	0.8	95.8	2.3	0.002	57.9	42.1
42			**Yarnyshnaya Bay, marsh**									
43	10-0	Sublittoral/0–12	Clay with sand	0.00	0.3	0.01	1.2	92.2	5.5	0.002	66.7	33.3
44	10-0	Sublittoral/12–24	Clay with hydrotroilite admixture	0.04	0.4	0.01	0.6	96.2	1.7	0.000	60.0	40.0
45	10-1	Littoral/0–7	Sand, small clay nodules, rocks	0.01	0.1	0.01	2.3	87.0	10.7	0.002	80.0	20.0
46	10-2	Marsh/0–5	Sand with minor clay admixture	0.01	0.8	0.27	1.1	79.0	2.8	0.003	82.6	17.4
47	10-2	Marsh/5–10	Sand with red clay	0.04	0.5	0.16	0.8	77.4	2.4	0.001	72.7	27.3
48			**Oskar Bay, silty–sandy littoral**									
49	11-0	Sublittoral/0–5	Mixture of sand, shingles, clay, rocks, shell rock	0.47	1.0	0.01	1.2	98.0	1.4	0.003	78.6	21.4
50	11-0	Sublittoral/5–15	Clay with shell rock and minor sand admixture	4.67	1.2	0.00	1.6	97.9	2.3	0.007	58.5	41.5
51	11-1	Littoral/0–9	Sand with shell rock, rocks, and minor clay admixture	0.26	0.5	0.00	0.7	96.3	2.8	0.005	80.0	20.0
52	11-1	Littoral/9–23	Sand with shell rock and minor clay admixture	0.02	0.2	0.00	0.4	95.9	2.2	0.001	71.4	28.6
53	11-2	Supralittoral/0–17	Sand with shell rock and minor clay admixture	0.03	0.4	0.00	1.1	95.1	4.7	0.006	61.1	38.9

* $\beta = (A_{ch}/TOC) \times 100\%$, where A_{ch} is the concentration of chloroform bitumoid (Bazhenova et al., 2000).
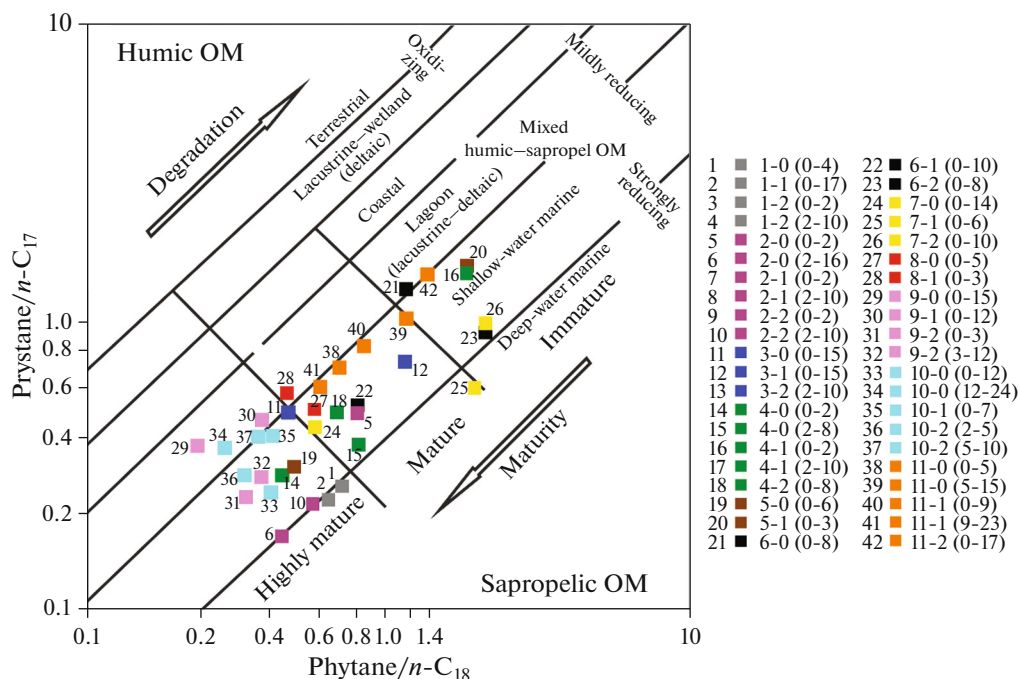
Fig. 2. Connan–Cassou diagram (Connan and Cassou, 1980) of the genetic types and sedimentation facies conditions of DOM.

alkanes (up to 88.2%), although some of the samples contain >40% aromatic compounds (Table 1). The contents of insoluble components reach 99.0%, that is likely due to the input of DOM of post-diagenetic level of transformation during erosion and redeposition of ancient rocks.

Hydrocarbon Molecular Biomarkers

Biomarkers (n-alkanes, isoprenoids, steranes, and hopanes) often inherit their structure and stereochemistry from compounds that form cell components and thus provide information on the genesis of the OM. This makes it possible to assess the input from various sources and characterize their accumulation conditions and level of transformation (Vassoevich, 1958; Eglinton and Murphy, 1969; Uspenskii, 1970; Peters et al., 2005).

n-Alkanes and isoprenoids. In the n-alkanes of the DOM, high-molecular homologues genetically related to terrestrial vegetation dominate over low-molecular compounds (n-$C_{15–19}$/n-$C_{27–31}$ ~ 0.4) associated with OM of hydrobionts (Table 2). The distribution of n-alkanes is not uniform in our samples, which provides evidence of differences in the composition of the source OM and is consistent with the broad variations in the carbon preference index (CPI (1) = 1.1–7.4), degrees of transformations of the short-chain and long-chain n-alkanes ($OEP_{17–19}$ = 0.7–18.2; $OEP_{27–31}$ = 1.7–13.0), and the ratios of isoprenoids (Pr/Phyt = 0.5–1.5).

Sediments from the sublittoral and littoral at most of the sampling sites (Sites 3, 4, 5, 7, 8, 9, 10, and 11) contained low-molecular n-alkanes dominated by n-C_{18}, n-C_{20} compounds, and the CPI (1) = 1.1–2.2. Such a predominance of even n-alkanes in the upper layer of the sediments is likely connected with the input of biodegradation products of petrogenic components, the bacterial decomposition of algae detritus, and/or a contribution of products of microbiota (Nishimura and Baker, 1986; Lein et al., 2013).

We have previously detected the dominance of even n-alkanes in sediments sampled at the sublittoral and littoral of the Tromsø shore, Norway (Morgunova et al., 2021), where their occurrence together with the presence of an "unresolved complex mixture" (UCM) in the high-molecular region and the low values of CPI (1) ~ 1 is reportedly explained by anthropogenic impacts (the influence of an oil terminal and a boat harbor).

The genetic type of the source OM, features of sedimentation, and the level of the thermal maturity of the DOM in the sediments are clearly illustrated by the Connan–Cassou diagram (Fig. 2) (Connan and Cassou, 1980). According to the ratios of isoprenoid coefficients (Pr/C_{17} and Phyt/C_{18}), the DOM of the sediments and soils is of mixed genesis and was formed mostly in shallow-water marine and/or lagoonal conditions.

DOM is most significantly degraded in samples taken on the littoral of the eastern Tana Fjord (Site 4-1 (0–2)), in the eastern Kola Bay (Sites 5-1, 6-0, 6-2,

Table 2. Characteristics of n-alkanes and isoprenoids in DOM

No.	Sample	Location on transect/sampling interval, cm	n-alkanes and isoprenoids						
			C_{15-19}/C_{27-31}	OEP_{17-19}	OEP_{27-31}	$Phyt/C_{18}$	Pr/C_{17}	CPI (1)	Pr/Phyt
1	**Varanger Fjord (Varangerfjord, Varangerbotn)**								
2	1-0	Sublittoral/0−14	0.2	2.0	5.1	0.7	0.3	4.2	1.0
3	1-1	Littoral/0−17	0.2	1.8	6.4	0.6	0.2	4.5	1.0
4	1-2	Marsh/0−2	0.2	18.2	12.9	1.1	0.02	6.9	0.7
5	1-2	Marsh/2−10	0.4	10.2	7.8	0.9	0.02	4.7	0.5
6	**Western Tana Fjord (Tanafjord, Smalfjorden)**								
7	2-0	Sublittoral/0−2	0.0	1.6	13.0	0.8	0.5	6.5	1.5
8	2-0	Sublittoral/2−16	0.5	1.7	4.1	0.5	0.2	3.4	0.9
9	2-1	Littoral/0−2	0.3	4.4	6.0	0.7	0.1	5.1	1.0
10	2-1	Littoral/2−10	0.2	3.3	6.2	0.5	0.1	4.7	0.7
11	2-2	Marsh/0−2	0.0	6.3	11.6	0.8	0.1	5.8	1.2
12	2-2	Marsh/2−10	0.0	2.5	7.0	0.6	0.2	4.6	1.1
13	**Village of Kiberg (Kiberg, Vardø)**								
14	3-0	Sublittoral/1−15	0.3	0.9	2.5	0.5	0.5	2.0	0.8
15	3-1	Littoral/0−15	0.5	1.3	2.0	1.1	0.7	1.7	0.9
16	3-2	Supralittoral/2−10	0.0	1.5	12.6	0.8	0.5	6.5	1.4
17	**Eastern Tana Fjord (Tanafjord, Austertana, Leiropollen)**								
18	4-0	Sublittoral/0−2	0.1	1.0	8.1	0.5	0.3	6.4	1.0
19	4-0	Sublittoral/2−8	0.1	1.5	6.8	0.8	0.4	5.0	1.0
20	4-1	Littoral/0−2	2.4	1.0	2.2	2.0	2.3	1.4	0.7
21	4-1	Littoral/2−10	0.1	1.2	8.5	0.7	0.5	6.0	0.9
22	4-2	Marsh/0−8	0.2	1.1	12.7	0.7	0.5	5.1	1.1
23	**Abram Cape**								
24	5-0	Sublittoral/0−6	0.03	1.9	12.5	0.5	0.3	7.4	1.1
25	5-1	Littoral/0−3	3.06	1.0	1.9	1.8	1.5	1.1	0.7
26	**Mishukovo**								
27	6-0	Sublittoral/0−8	0.4	1.0	3.8	1.2	1.3	3.1	1.2
28	6-1	Littoral/0−10	0.1	1.1	3.8	0.8	0.5	4.0	0.8
29	6-2	Marsh/0−8	0.6	1.3	2.3	2.1	0.9	1.9	0.6
30	**Mouth of Kulonga R.**								
31	7-0	Sublittoral/0−14	0.1	1.0	2.0	0.6	0.4	1.8	0.6
32	7-1	Littoral/0−6	0.4	1.7	2.4	2.0	0.6	2.0	0.7
33	7-2	Marsh/0−10	0.5	1.2	2.8	2.1	1.0	1.8	0.6
34	**Yarnyshnaya Bay**								
35	8-0	Sublittoral/0−5	0.4	1.0	1.9	0.6	0.5	1.5	1.0
36	8-1	Littoral/0−3	0.8	0.8	1.9	0.5	0.6	1.5	0.9
37	**Porchnikha Bay**								
38	9-0	Sublittoral/0−15	0.2	0.7	2.9	0.2	0.4	2.2	1.2
39	9-1	Littoral/0−12	0.2	0.8	5.4	0.4	0.5	3.1	0.9
40	9-2	Marsh/0−3	0.1	1.3	6.0	0.3	0.2	4.0	1.4
41	9-2	Marsh/3−12	0.3	1.1	3.6	0.4	0.3	2.3	1.0
42	**Yarnyshnaya Bay, apex part**								
43	10-0	Sublittoral/0−12	0.3	1.3	5.3	0.4	0.3	3.3	1.0
44	10-0	Sublittoral/12−24	0.1	0.8	3.0	0.3	0.4	2.2	0.8
45	10-1	Littoral/0−7	0.3	0.9	4.5	0.4	0.4	2.1	1.2
46	10-2	Marsh/0−5	0.1	1.3	8.6	0.3	0.3	4.5	1.5
47	10-2	Marsh/5−10	0.1	1.0	5.2	0.4	0.4	3.7	1.1
48	**Oskar Bay**								
49	11-0	Sublittoral/0−5	0.2	0.9	4.0	0.7	0.7	2.3	1.1
50	11-0	Sublittoral/5−15	0.8	1.1	3.8	1.2	1.0	2.1	1.0
51	11-1	Littoral/0−9	0.5	1.1	2.1	0.8	0.8	1.5	1.2
52	11-1	Littoral/9−23	0.3	1.0	1.7	0.6	0.6	1.3	0.9
53	11-2	Supralittoral/0−17	1.2	1.0	1.9	1.4	1.4	1.4	1.0

$OEPn = (n\text{-}Cn - 2 + 6 \times n\text{-}Cn + n\text{-}Cn + 2)/(4 \times n\text{-}Cn - 1 + 4 \times n\text{-}Cn + 1)$; $OEP_{17-19} = (OEP_{17} + OEP_{19})/2$ (Peters et. al., 2005); $CPI (1) = 2*(n\text{-}C_{23} + n\text{-}C_{25} + n\text{-}C_{27} + n\text{-}C_{29})/[n\text{-}C_{22} + 2*(n\text{-}C_{24} + n\text{-}C_{26} + n\text{-}C_{28}) + n\text{-}C_{30}]$ (Peters et al., 2005); Pr is pristane, Phyt is phytane.
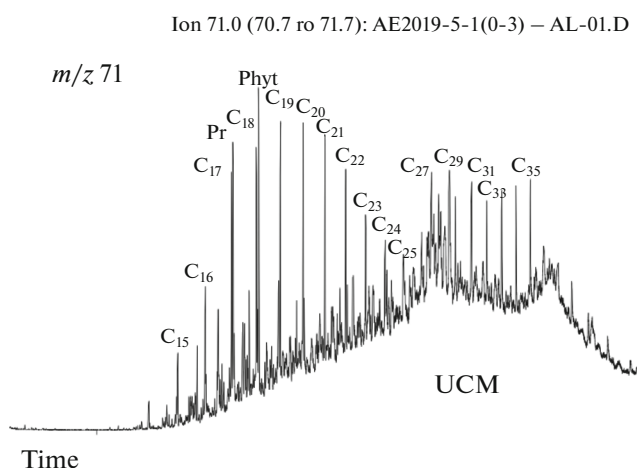
Fig. 3. Mass chromatogram of the distribution of *n*-alkanes in DOM of the bottom sediments (littoral of Abram Cape, Site 5-1).

7-1, and 7-2), and in Oskar Bay (Sites 11-0, 11-2), Dal'nie Zelentsy. It is important to mention that DOM in sediments at Sites 4-1 (0-2), 5-1, 11-2 is dominated by short-chain *n*-alkanes whose CPI (1) is as low as ~1.2, and the chromatograms show a UCM in the high-molecular region (Fig. 3), which confirm the presence of oil derivatives and anthropogenic impact (Bouloubassi and Saliot, 1993b). This is most likely due to the operation of the quartzite-producing open-cast mine and ship terminal in the eastern Tana Fjord, the immediate vicinity of Abram Cape to a port in the Kola Bay, and because of the influence of the mooring for vessels at the settlement of Dal'nie Zelentsy in Oskar Bay.

The distribution of the Pr/C_{17} and Phyt/C_{18} coefficients at most of the noted sampling sites is consistent with the bitumenological data (high β, low ROM, and maximum HC contents in the sediments; Table 1).

Terpanes. The terpane indicators of the conditions of DOM formation in the studied sediments provide evidence of its mixed genesis (H_{35}/H_{34} = 0.0−1.4; H_{29}/H_{30} = 0.0−1.0) (Table 3) and confirm the earlier hypothesis of the dominantly shallow-water marine and/or lagoonal conditions of sedimentation (Kashirtsev, 2003; Peters et al., 2005).

The distribution of terpanes in the DOM is largely controlled by least transformed components: biohopanes and biohopenes (Fig. 4). The dominant compounds are 17β(H)-22, 29, 30-trisnorhopane (Tβ), 22, 29, 30- trisnorhop-17(21)-en (Te) and neohop-13(18)-en, which are produced during diagenetic transformations of bacterial OM.

The maximum biodegradation level of >45% (concentration of weakly transformed biohopanes normalized to the total concentration of hopanes) was detected in the DOM of sediments from the sublittoral of Porchnikha Bay, Site 9-0 (0-15), and Yarnyshnaya Bay, Site 10-0 (12-24) (Fig. 4). Taking into account
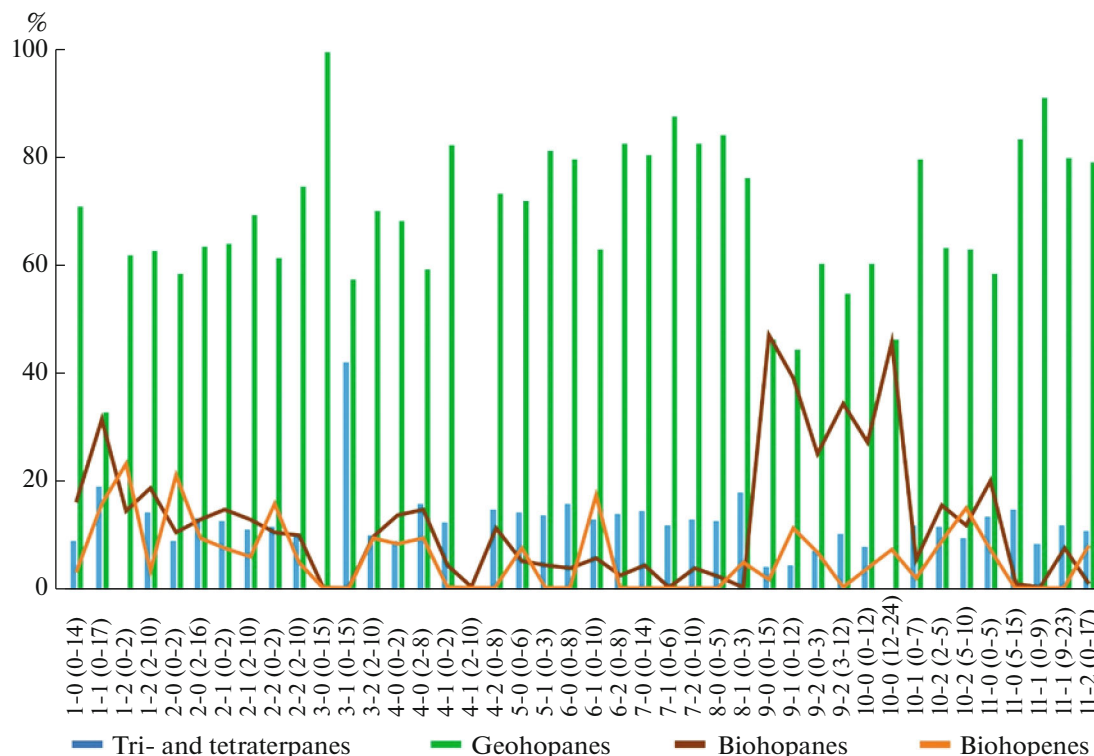

Fig. 4. Distribution of tri- and tetracyclic terpanes, geohopanes, biohopanes, and biohopenes in DOM.

Table 3. Characteristics of terpanes in DOM

No.	Sample	Location on transect/sampling interval, cm	Terpanes				Steranes			
			C_{31} S/ (S + R)	29Ts/ (29Ts + C_{29})	H_{29}/ H_{30}	H_{35}R/ H_{34}R	C_{27}/ C_{29}	C29αββ/ (αββ + ααα)	C29αα S/ (S + R) (K1)	C29 (αβS + αβR)/ααR (K2)
1	**Varanger Fjord (Varangerfjord, Varangerbotn)**									
2	1-0	Sublittoral/0−14	0.5	0.2	1.0	0.0	0.7	0.5	0.4	1.3
3	1-1	Littoral/0−17	0.4	0.2	0.8	0.0	0.0	0.0	0.0	0.0
4	1-2	Marsh/0−2	0.4	0.2	0.8	0.0	0.0	0.0	0.0	0.0
5	1-2	Marsh/2−10	0.5	0.2	1.0	1.1	0.6	0.5	0.4	1.5
6	**Western Tana Fjord (Tanafjord, Smalfjorden)**									
7	2-0	Sublittoral/0−2	0.5	0.2	0.9	1.2	0.5	0.5	0.3	0.9
8	2-0	Sublittoral/2−16	0.5	0.2	0.7	1.0	0.8	0.4	0.6	2.8
9	2-1	Littoral/0−2	0.5	0.2	0.7	1.0	0.7	0.4	0.4	1.0
10	2-1	Littoral/2−10	0.5	0.2	0.7	1.0	0.5	0.4	0.4	0.9
11	2-2	Marsh/0−2	0.5	0.2	0.7	0.7	0.5	0.4	0.4	1.0
12	2-2	Marsh/2−10	0.5	0.2	0.6	1.0	0.6	0.4	0.5	1.6
13	**Village of Kiberg (Kiberg, Vardø)**									
14	3-0	Sublittoral/1−15	0.5	0.2	0.7	0.0	0.0	0.4	0.0	0.0
15	3-1	Littoral/0−15	0.6	0.2	0.8	0.0	0.7	0.4	0.5	1.4
16	3-2	Supralittoral/2−10	0.5	0.2	0.8	1.0	0.0	0.4	0.0	0.0
17	**Eastern Tana Fjord (Tanafjord, Austertana, Leiropollen)**									
18	4-0	Sublittoral/0−2	0.5	0.2	0.7	0.8	0.7	0.4	0.4	1.1
19	4-0	Sublittoral/2−8	0.5	0.2	0.7	0.9	0.6	0.5	0.4	1.3
20	4-1	Littoral/0−2	0.6	0.2	0.6	0.9	0.4	0.5	0.5	2.2
21	4-1	Littoral/2−10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
22	4-2	Marsh/0−8	0.5	0,.2	0.7	0.0	0.8	0.5	0.4	1.8
23	**Abram Cape**									
24	5-0	Sublittoral/0−6	0.5	0.2	0.8	1.4	0.8	0.5	0.0	0.0
25	5-1	Littoral/0−3	0.6	0.2	0.6	0.9	0.5	0.5	0.6	2.6
26	**Mishukovo**									
27	6-0	Sublittoral/0−8	0.5	0.1	0.6	0.8	0.6	0.5	0.5	2.1
28	6-1	Littoral/0−10	0.5	0.2	0.0	0.9	0.6	0.5	0.4	1.6
29	6-2	Marsh/0−8	0.5	0.2	0.7	0.9	0.7	0.5	0.5	1.8
30	**Mouth of Kulonga R.**									
31	7-0	Sublittoral/0−14	0.5	0.2	0.6	1.0	0.5	0.5	0.4	1.4
32	7-1	Littoral/0−6	0.5	0.3	0.5	0.9	0.4	0.4	0.6	1.9
33	7-2	Marsh/0−10	0.5	0.2	0.7	1.1	0.6	0.4	0.5	2.0
34	**Yarnyshnaya Bay**									
35	8-0	Sublittoral/0−5	0.5	0.2	0.6	1.0	0.7	0.5	0.6	2.5
36	8-1	Littoral/0−3	0.6	0.3	0.6	0.0	0.7	0.4	0.5	1.9
37	**Porchnikha Bay**									
38	9-0	Sublittoral/0−15	0.2	0.0	0.5	0.0	0.0	0.0	0.0	0.0
39	9-1	Littoral/0−12	0.3	0.0	0.6	0.0	0.0	0.0	0.0	0.0
40	9-2	Marsh/0−3	0.5	0.2	0.5	0.9	0.7	0.4	0.6	2.9
41	9-2	Marsh/3−12	0.4	0.3	0.5	0.0	0.0	0.0	0.0	0.0
42	**Yarnyshnaya Bay, apex part**									
43	10-0	Sublittoral/0−12	0.5	0.2	0.5	0.0	0.0	0.0	0.0	0.0
44	10-0	Sublittoral/12−24	0.2	0.0	0.5	0.0	0.0	0.0	0.0	0.0
45	10-1	Littoral/0−7	0.5	0.2	0.6	0.9	0.5	0.4	0.5	1.9
46	10-2	Marsh/0−5	0.5	0.2	0.6	0.7	0.7	0.4	0.8	4.4
47	10-2	Marsh/5−10	0.5	0.2	0.7	0.6	0.0	0.4	0.4	1.2
48	**Oskar Bay**									
49	11-0	Sublittoral/0−5	0.6	0.2	0.6	0.7	0.6	0.4	0.5	2.1
50	11-0	Sublittoral/5−15	0.5	0.2	0.6	0.9	0.6	0.4	0.6	2.5
51	11-1	Littoral/0−9	0.5	0.2	0.5	0.8	0.7	0.5	0.5	2.0
52	11-1	Littoral/9−23	0.5	0.2	0.5	0.8	0.6	0.4	0.5	2.2
53	11-2	Supralittoral/0−17	0.8	0.2	0.6	0.9	0.5	0.5	0.4	1.6

1	1-0 (0-4)	22	6-1 (0-10)
2	1-1 (0-17)*	23	6-2 (0-8)
3	1-2 (0-2)*	24	7-0 (0-14)
4	1-2 (2-10)	25	7-1 (0-6)
5	2-0 (0-2)	26	7-2 (0-10)
6	2-0 (2-16)	27	8-0 (0-5)
7	2-1 (0-2)	28	8-1 (0-3)
8	2-1 (2-10)	29	9-0 (0-15)*
9	2-2 (0-2)	30	9-1 (0-12)*
10	2-2 (2-10)	31	9-2 (0-3)
11	3-0 (0-15)*	32	9-2 (3-12)*
12	3-1 (0-15)	33	10-0 (0-12)*
13	3-2 (2-10)*	34	10-0 (12-24)*
14	4-0 (0-2)	35	10-1 (0-7)
15	4-0 (2-8)	36	10-2 (2-5)
16	4-1 (0-2)	37	10-2 (5-10)*
17	4-1 (2-10)*	38	11-0 (0-5)
18	4-2 (0-8)	39	11-0 (5-15)
19	5-0 (0-6)	40	11-1 (0-9)
20	5-1 (0-3)	41	11-1 (9-23)
21	6-0 (0-8)	42	11-2 (0-17)
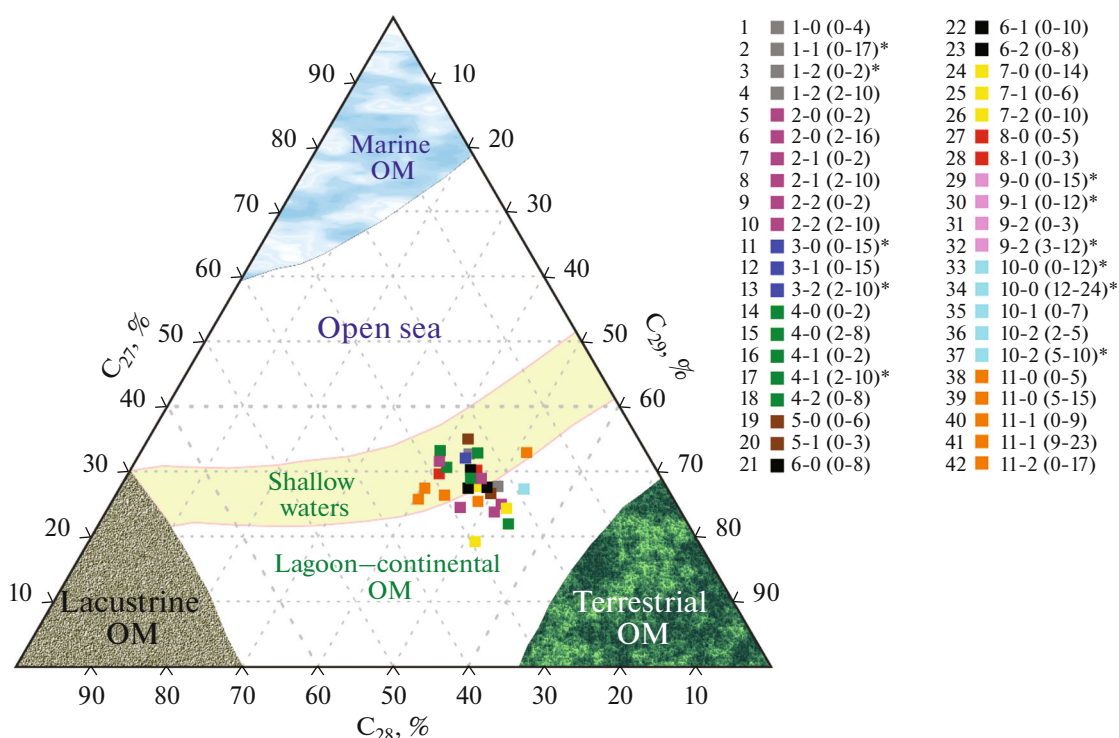
Fig. 5. Facies−genetic characteristics of DOM using the composition of the steranes, * means no steranes.

the predomination of octadecane n-C_{18} in the range of low-molecular n-alkanes (in the absence of the UCM in the chromatograms) and the CPI (1) > 2.0 in the high-molecular region, it is reasonable to suggest that biodegradation was controlled by the bacterial decomposition of algae detritus or by a contribution of the microbiota waste products during diagenesis. Geohopanes in DOM of sediments from the named areas are of lower maturity ($C_{31}S/(S + R) = 0.2$, Table 3), which is consistent with the hypothesis of the biodegradation of the diagenetic DOM.

The maturity coefficients of geohopanes in all other studied sediments indicate that the transformation degree of the DOM is mostly high: $C_{31}S/(S + R) \sim 0.5$; $29Ts/(29Ts + C_{29}) \sim 0.2$ (Table 3) (Peters et al., 2005). Such values are commonly typical of material associated with the mineral matrix of ancient rocks, whose particles are brought into the sediment during erosion and redeposition, but this does not exclude an input of postdiagenetic DOM with oil contamination.

Steranes. In the homologous series of (C_{27}−C_{29}) regular steranes, the proportions of cholestanes and ethylcholestanes $C_{27}(\alpha\alpha\alpha + \alpha\beta\beta)/C_{29}(\alpha\alpha\alpha + \alpha\beta\beta) < 1$, that is typical of DOM of mixed marine-terrigenous origin (Table 3) (Petrova et al., 2017). The dominance of C_{29} sterane over C_{27} and C_{28} steranes and roughly equal concentration of the latter indicate that the DOM was accumulated in a shallow marine environ-

ment without input from the open sea (including OM transported by Atlantic currents) (Fig. 5).

The data (Table 3) indicate that the values of the transformation parameters of steranes of terrigenous genesis generally point to a high maturity of the DOM associated with the mineral matrix of the sediments (K1 ~ 0.5; K2 ~ 1.9; $C29\alpha\beta\beta/(\alpha\beta\beta + \alpha\alpha\alpha) \sim 0.5$), which is consistent with the distribution of the geohopanes and the ratios $Pr/C_{17} \sim 0.5$, $Phyt/C_{18} \sim 0.8$ (Tables 3, 2) (Petrov, 1984, 1994a; Gordadze, 2015; Peters et al., 2005). It should also be mentioned that some of the studied sediments (Fig. 4) contain no steranes. This is likely explained by the insufficient transformation level of the source OM of the eukaryotes (Kostyreva et al., 2019; Morgunova et al., 2022).

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons cannot be referred to as biological markers because their direct analogues have not been found in the native biota (Rovinskii et al., 1988). However, polyarenes are an inherent component of the HC and deserve close attention because many of them are widespread, are of natural origin, and are toxic and carcinogenic (*AMAP*, 2010; Dahle et al., 2006; Samburova et al., 2017).

The total concentration of PAH in the sediments widely varies from 31.1 to 12773.2 ng/g (Table 4) and generally does not exceed concentrations in near-shore areas of some bays and gulfs of Arctic seas (Zhi-

Table 4. Geochemical characteristics of PAH in DOM

No.	Sample	Location on transect/sampling interval, cm	ΣPAH	MPI-1	Fl/ (Fl + Pyr)	BaA/ (BaA + Chr)	IP/ (IP + B(ghi)P)	ΣMPh/Ph
1	**Varanger Fjord (Varangerfjord, Varangerbotn)**							
2	1-0	Sublittoral/0−14	135.0	0.5	0.6	0.6	0.4	2.2
3	1-1	Littoral/0−17	156.5	0.3	0.6	0.5	0.0	1.3
4	1-2	Marsh/0−2	77.3	0.3	0.6	0.4	0.0	1.3
5	1-2	Marsh/2−10	103.3	0.3	0.6	0.5	0.4	1.3
6	**Tana Fjord western (Tanafjord, Smalfjorden)**							
7	2-0	Sublittoral/0−2	484.0	0.3	0.6	0.5	0.5	1.2
8	2-0	Sublittoral/2−16	125.2	0.4	0.6	0.6	0.5	2.4
9	2-1	Littoral/0−2	104.5	0.4	0.6	0.5	0.4	1.8
10	2-1	Littoral/2−10	91.9	0.4	0.6	0.5	0.5	2.2
11	2-2	Marsh/0−2	84.3	0.3	0.6	0.5	0.4	0.9
12	2-2	Marsh/2−10	136.3	0.4	0.6	0.5	0.4	2.3
13	**Village of Kiberg (Kiberg, Vardø)**							
14	3-0	Sublittoral/1−15	372.5	0.4	0.6	0.5	0.5	2.0
15	3-1	Littoral/0−15	225.8	0.6	0.6	0.6	0.4	2.8
16	3-2	Supralittoral/2−10	214.8	0.5	0.6	0.5	0.4	2.4
17	**Eastern Tana Fjord (Tanafjord, Austertana, Leiropollen)**							
18	4-0	Sublittoral/0−2	99.8	0.3	0.6	0.5	0.4	1.1
19	4-0	Sublittoral/2−8	1259.2	0.4	0.6	0.6	0.5	1.7
20	4-1	Littoral/0−2	2627.7	0.2	0.6	0.6	0.5	0.5
21	4-1	Littoral/2−10	31.1	0.4	0.6	0.6	0.5	1.8
22	4-2	Marsh/0−8	1680.5	0.4	0.6	0.6	0.5	1.9
23	**Abram Cape**							
24	5-0	Sublittoral/0−6	81.7	0.3	0.6	0.6	0.5	1.3
25	5-1	Littoral/0−3	1400.0	0.2	0.6	0.6	0.5	0.6
26	**Mishukovo**							
27	6-0	Sublittoral/0−8	1142.1	0.4	0.5	0.6	0.4	4.0
28	6-1	Littoral/0−10	212.5	0.4	0.6	0.6	0.5	3.0
29	6-2	Marsh/0−8	1346.9	0.3	0.6	0.6	0.5	1.2
30	**Mouth of Kulonga R.**							
31	7-0	Sublittoral/0−14	39.3	0.7	0.6	0.5	0.4	7.6
32	7-1	Littoral/0−6	119.6	0.3	0.6	0.6	0.4	1.9
33	7-2	Marsh/0−10	1445.0	0.3	0.6	0.6	0.5	1.6
34	**Yarnyshnaya Bay**							
35	8-0	Sublittoral/0−5	2750.3	0.3	0.6	0.6	0.5	0.9
36	8-1	Littoral/0−3	75.6	0.4	0.6	0.4	0.4	2.2
37	**Porchnikha Bay**							
38	9-0	Sublittoral/0−15	144.2	0.3	0.6	0.3	0.4	1.1
39	9-1	Littoral/0−12	88.1	0.3	0.6	0.3	0.4	1.3
40	9-2	Marsh/0−3	158.5	0.4	0.6	0.5	0.4	1.8
41	9-2	Marsh/3−12	226.8	0.3	0.6	0.3	0.4	1.4
42	**Yarnyshnaya Bay, apex part**							
43	10-0	Sublittoral/0−12	1114.3	0.3	0.6	0.6	0.5	1.1
44	10-0	Sublittoral/12−24	96.5	0.5	0.6	0.5	0.0	2.3
45	10-1	Littoral/0−7	2032.8	0.3	0.6	0.6	0.5	0.9
46	10-2	Marsh/0−5	7202.2	0.3	0.6	0.6	0.5	0.8
47	10-2	Marsh/5−10	1169.9	0.3	0.6	0.6	0.4	1.1
48	**Oskar Bay**							
49	11-0	Sublittoral/0−5	1828.3	0.3	0.5	0.6	0.4	1.9
50	11-0	Sublittoral/5−15	12733.2	0.4	0.5	0.6	0.5	1.6
51	11-1	Littoral/0−9	1833.1	0.3	0.6	0.6	0.5	1.8
52	11-1	Littoral/9−23	94.9	0.3	0.6	0.6	0.0	1.4
53	11-2	Supralittoral/0−17	7921.4	0.3	0.6	0.7	0.5	1.4

MPI-1= 1.5 × (3MP + 2MP)/(Pn + 9/4MP + 1MP), where MP is methylphenanthrene (Radke et al., 1982a); Fl is fluoranthene, Pyr is pyrene, B(a)A is benz(a)anthracene, Chr is chrysene, IP is indeno(1, 2, 3-cd)pyrene, B(ghi)P is benzo(ghi)perylene, MPh is methyphenanthrenes, and Ph is phenanthrene.
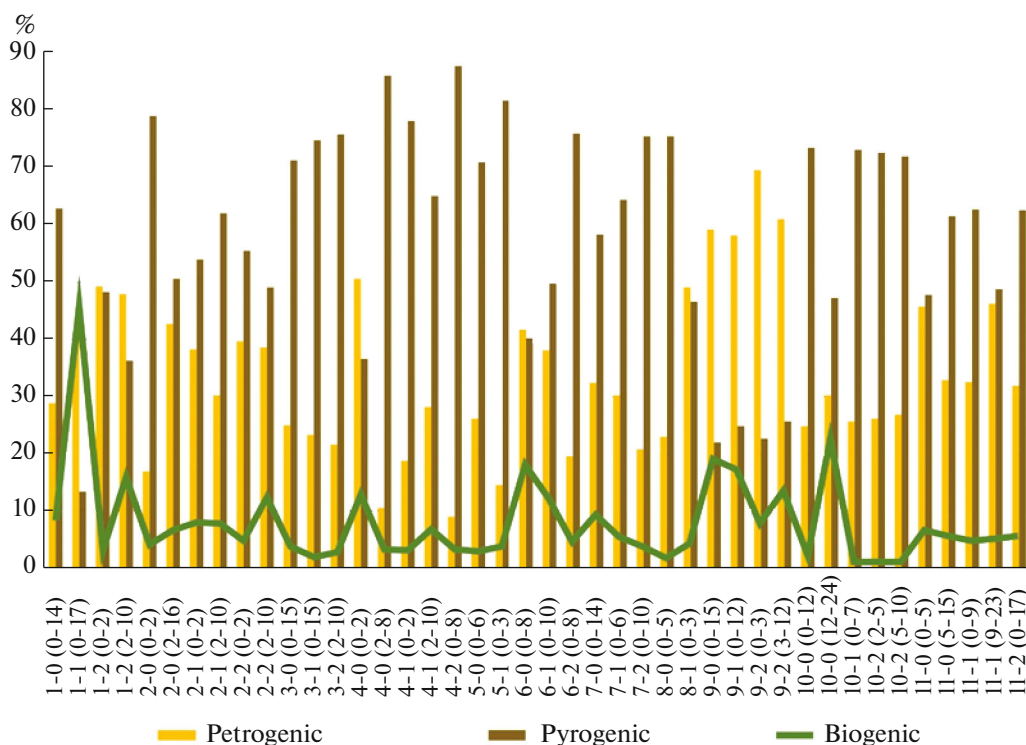
Fig. 6. Contributions (%) of various sources to the PAH composition.

lin and Plotitsyna, 2009). The concentrations of polyarenes in sediments sampled at Sites 1, 3, 5, 6, and 7 correspond to values previously determined in these areas (Savinov et al., 2003; *AMAP*, 2007; Dahle et al., 2006, 2009). The lowest PAH concentrations were found in sediments sampled along a sublittoral–littoral–marsh transect in the Varanger Fjord (Site 1) and Porchnikha Bay (Site 9). The highest PAH concentrations were detected in sediments sampled in the apex part of Yanrnyshnaya Bay (Sites 10-2 (0-5)), in the sublittoral of Oskar Bay (Site 11-2) and reach a maximum in the sublittoral of the latter (Site 11-0 (5-15)), where a pier for vessel mooring is located. The data are consistent with concentrations of the aromatic fraction of HCs in these sediments (>40%) (Table 1).

The contributions of various sources (pyrogenic, petrogenic, and biogenic) to the composition of PAH in the sediments are distinguished based on analysis of the proportions of molecular groups of polyarenes that reflect their genesis (Petrova et al., 2009; Yunker et al., 2014; Dahle et al., 2006, 2009).

The traditionally used ratios of less stable "kinetic" isomers to more stable "thermodynamic" PAH are one of the most powerful tools for distinguishing between different HC sources. In contrast to the thermodynamic isomers (phenanthrene, chrysene, benzo(*ghi*)perylene, etc.), which are generated mostly in the process of long-lasting diagenetic and catagenetic maturation, kinetic isomers (anthracene, benz(α)anthracene, indeno(1, 2, 3-*cd*)pyrene, etc.) are formed at relatively

short-lasting pulses of temperature effect, and their high concentrations in samples are usually interpreted as an indicator of anthropogenic influence and/or the input of combustion products (Garrigues et al., 1988; Yunker et al., 2014). Our data (Table 4, Fig. 6) indicate that pyrogenic components played a leading role in controlling the composition of the PAH. The ratios of thermodynamic and kinetic isomers (Table 4) testify that most of the samples are dominated by combustion products of biomass and solid fuels (coal and wood) and the combustion products of diesel fuel: (Fl/(Fl + Pyr) > 0.5; BaA/(BaA + Chr) > 0.5; IP/(IP + BghiP) > 0.2; ΣMPh/Ph > 1) (Yunker et al., 1996, 2014; Tobiszewski and Namiesnik, 2012).

At the same time, one should be aware that PAH formed by pyrolytic processes may have both anthropogenic and natural postdiagenetic sources.

Along with parent PAH compounds, the sediments contain groups of alkylated homologues, including alkylnaphthalenes, alkylphenanthrenes, methylanthracene, methylfluorantehnes, methylpyrenes, alkylchrysenes, and trimethyltetrahydropyrenes. Differences in the distribution of alkyl-substituted PAH in the sediments also enable the identification of their genesis and the thermal maturity of the DOM (Yunker et al., 2014; Xu et al., 2019).

For example, anthropogenic PAH, which are products of high-temperature pyrolysis, are mostly structures of mono-, dimethyl-, and ethyl-substituted components. The pyrene derivatives are dominated by
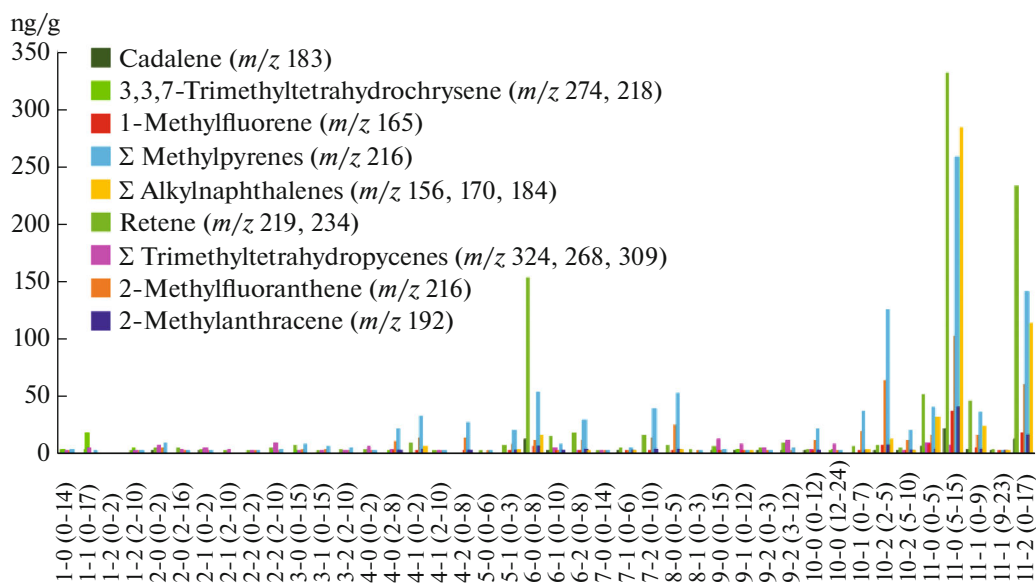
Fig. 7. Concentration and distribution of alkylated PAH in DOM.

1- and 3-methylpyrenes (*m/z* 216) (Rovinskii et al., 1988). The sediments contain 1-methylfluorene (*m/z* 165), which is formed during cyclization of 2,3-dimethylbiphenyl and is a marker of diesel engine exhaust (Alexander et al., 1988; Rhead et al., 2003; Sun et al., 2013). The occurrence of 2-methylanthracene (*m/z* 192) in the sediments suggests high concentrations of combustion products of diesel fuel and/or exhaust gases (Yunker et al., 2014).

The ratios of isomers of methylphenanthrene (3-, 2-, 9/4-, and 1-), which are diagenetic derivatives of diterpenoids, are based on their different thermodynamic stability and resistance to biodegradation (MPI-1; Garrigues et al., 1988; Hossain et al., 2013). The dominance of the former two homologues testifies to a high degree of transformation of DOM associated with the mineral matrix of the rocks (Yunker et al., 2015).

The most typical compounds of natural processes related to low-temperature OM transformations are structures containing one or several partly or completely hydrogenated rings and polysubstituted HC with different degrees of substitution: 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysene (*m/z* 274, 218); 1,2,9- and 2,2,9-trimethyltetrahydropicenes (*m/z* 324, 268, 309), and 1-methyl-7-isopropyl-phenanthrene (retene) (*m/z* 219). These structures are thought to be formed by early diagenetic transformations of source OM (Rovinskii et al., 1988).

According to this, our data on concentrations and distributions of alkylated PAH (Table 4, Fig. 7) indicate that the DOM has various sources and was variably transformed.

Most of our samples contain relatively high percentage of products of high-temperature pyrolysis,

and their concentrations are at a maximum in sediments sampled in the marsh of the apex part of Yarnyshnaya Bay (Sites 10-2 (0-5)) and in the sub- and supralittoral of Oskar Bay (Sites 11-0 (5-15); 11-2 (0-17)). Along with this, sediments at the latter two are dominated by retene and alkylhomologues of naphthalene, indicating that the OM is of biogenic and petrogenic origin. The lowest concentrations of high-temperature pyrolysis products of PAH were found in sediments along the whole traverse (sublittoral–littoral–marsh) in the Varanger Fjord (Site 1) and Porchnikha Bay (Site 9).

The methylphenanthrene index (MPI-1) (Table 4) varies from 0.2 to 0.7, reflecting variations in the degree of transformation of DOM of the sediments, which is consistent with the thermal maturity indicators of other groups of HC markers.

Assessment of Sediments According to PAH Toxicity Criteria

It is known that PAH are carcinogenic and mutagenic, and the intensities of their adverse effects on the environments are different for various individual compounds (Long et al., 1995; Keith, 2015; Samburova et al., 2017). When brought to sediments and/or soils, polyarenes are bound by microparticles and dissolved OM and are thus accumulated in the sediments and soils, which are true indicators of the contamination of the ecosystem.

Considering that the systems contain PAH not only from anthropogenic but also from a broad spectrum of natural sources, sediments in the tidal zones were studied using the toxicity factors of individual compounds (Toxic Equivalency Factor, TEF) and low and medium effective ranges (ERL, ERM) (Nisbet and
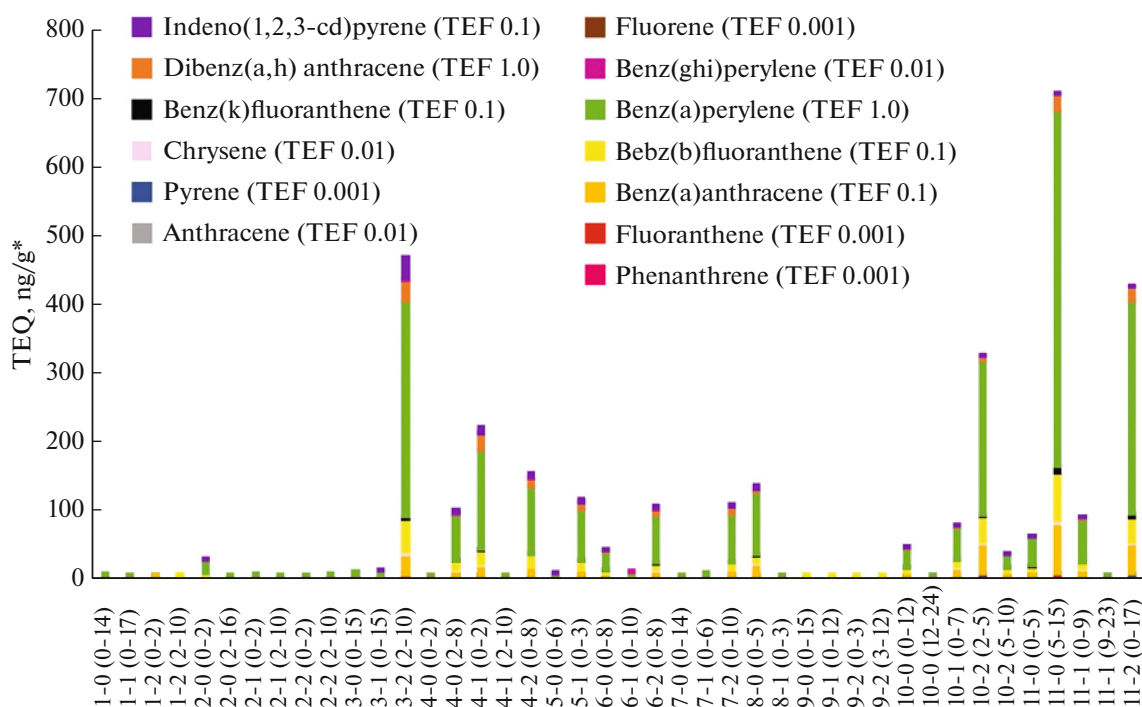
Fig. 8. Toxic equivalents (TEQ) of individual PAH compounds with respect to benz(a)pyrene in DOM, ng/g. *TEQ = Σ (CiTEFi), where Ci is the concentration of individual compound i, and TEFi is the total equivalency factor of compound i (Nisbet and LaGoy, 1992).

LaGoy, 1992; Long et al., 1995). ERL reflects the borders of safe effects of toxins contained in sediments on organisms inhabiting these sediments, whereas sediments with ERM are potentially hazardous for these organisms.

The TEQ factor (Fig. 8) is an indicator of the toxicity of main PAH compounds with respect to benz(a)pyrene, which is assumed as a reference compound whose internationally approved equivalent toxicity factor is 1: (I-TEF) = 1. All other compounds are characterized by their own individual toxicity equivalents calculated with respect to this reference compound (Nisbet and LaGoy, 1992; Savinov et al., 2003; Samburova et al., 2017).

According to our data, the total toxicity level (TEQ) reaches a maximum in the supralittoral of the shore near the village of Kiberg (Site 3-2: 470.7 ng/g), in the apex part of the marsh of Yarnyshnaya Bay (Site 10-2 (0-5): 325.9 ng/g), and in the supralittoral of Oskar Bay (Site 11-2: 426.6 ng/g). The sediments in the sublittoral of the latter (Site 11-0 (5-15)) show a much higher TEQ = 710.3 ng/g. The minimal toxicity of PAH was detected in sediments along the whole transect in the area of the Varanger Fjord (Site 1: 7.9 ng/g) and in Porchnikha Bay (Site 9: 2.7 ng/g) (Fig. 8).

Our data are generally consistent with literature data on TEQ in the Norwegian and Russian sectors of the Barents Sea shore: 472−733 ng/g in Vardø, 40−66 ng/g

in Vadsø, and 71−583 (∼483) ng/g in the Kola Bay (Savinov et al., 2003; Zhilin and Plotitsina, 2009).

The ERM and ERL toxicity levels of PAH in the sediments for organisms inhabiting these sediments are presented in Fig. 9. Our estimates based on the toxicity criteria show that the effect of ΣPAH (Table 4) at all sampling sites does not exceed the published intermediate level: ERL = 4 022, ERM = 44 792 (Long et al., 1995).

However, most of the samples contained at least one compound whose concentration was higher than ERL: phenanthrene, fluorene, pyrene, benz(a)anthracene, anthracene, chrysene, and benz(a) pyrene. This means that the sediments are potentially hazardous for the biota but do not acutely affect organisms inhabiting them. Toxic effects were at a maximum in marsh samples from Yarnyshnaya Bay (Site 10-2) and the supralittoral of Oskar Bay (Site 11-2), and sediments sampled in the sublittoral of the latter (Site 11-0 (5-15)) show the maximum values of the contamination criteria.

CONCLUSIONS

Our studies of bottom sediments and marsh soils in the tidal zones of the southwestern Barents Sea shore led us to collect data on the distribution of DOM and its components: hydrocarbon molecular biomarkers (n-alkanes, isoprenoids, steranes, and hopanes) and on an extended list of hydrocarbon molecular markers
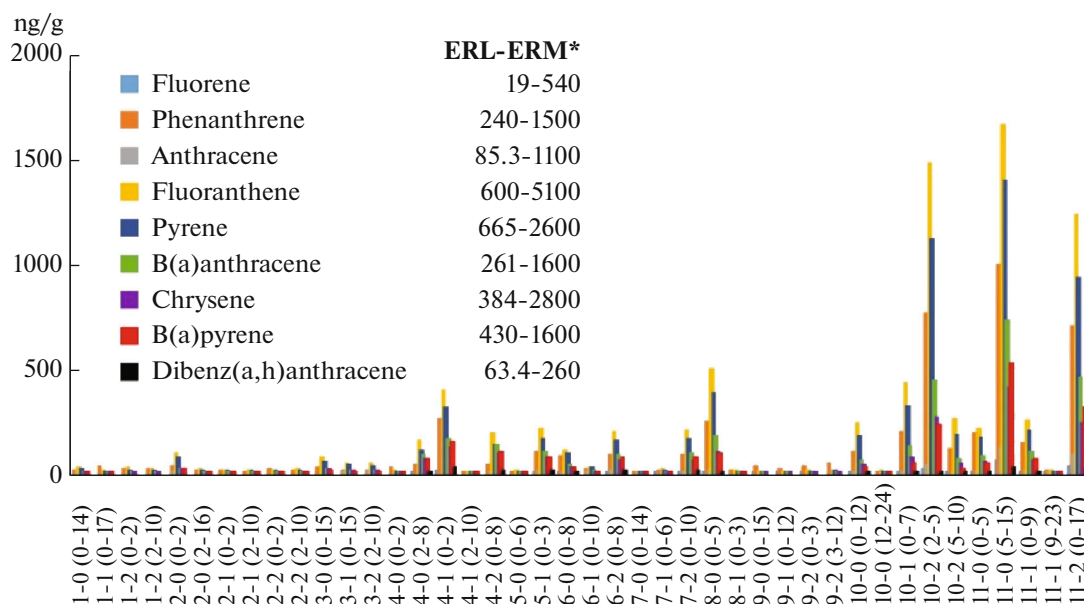
Fig. 9. Contamination criteria (ELR, ELM) with PAH in DOM, * criteria of toxic effect ERL, ERM (Long et al., 1995).

(parent and alkylated PAH), which allowed us to assess the current state of the shore segments and to outline areas of elevated anthropogenic impact.

We have found out that the PAH were formed in shallow-water marine and/or lagoonal facies conditions of sedimentation. We have proved that no PAH is brought from the open sea, including organic matter transported with Atlantic currents.

Biodegradation processes detected in the sediments of the sublittoral of Porchnikha Bay and Yarnyshnaya Bay (short-chain n-alkanes maximum at n-C_{18}, >45% of biogenic compounds in the total hopanes, and the low maturity of the latter) are of local character and are related to stagnant environmental conditions favorable for blooming (boggy marsh, apex area).

We have demonstrated that DOM maturity parameters (ROM, proportions of geohopanes and steranes, and MPI-1) indicate that the sediments contain OM of postdiagenetic transformation level, which was trapped into the sediments during erosion and redeposition of ancient rocks and/or contamination with petroleum hydrocarbons.

The PAH and their alkylated homologues contain a lot of components of pyrogenic genesis (Fl/(Fl + Pyr > 0.5; BaA/(BaA + Chr) > 0.5; IP/(IP + BghiP) > 0.2; ΣMP/Ph>1; Σmethylphenanthrenes; 1-methylfluorene; 2-metylanthracene), which are products of biomass burning and combustion products of diesel fuel and/or exhaust gases.

The highest total PAH concentrations were fond in sublittoral sediments (ΣPAH = 7921 ng/g) and subsurface sediments of the sublittoral (ΣPAH = 12733 ng/g) in Oskar Bay, where a pier and mooring for vessels is situated. The minimum variations in the total PAH concentration (ΣPAH = 77−227 ng/g) were detected in sediments sampled along a marsh−littoral−sublittoral transect in the Varanger Fjord and Porchnikha Bay.

The toxicity factors (TEQ) and levels of PAH effects (ELR and EMR) on organisms inhabiting the sediments (which included at least one individual PAH compound in a concentration higher than ERL) indicate that most of the tidal zones of the Barents Sea shores are polluted. However, we have not detected acute toxic effect of PAH onto the biota of the studied shore segments (levels > ERM). At the same time, elevated anthropogenic impact identified in some areas (eastern Tana Fjord and Kiberg in Norway; Abram Cape, area of the settlement of Mishukovo, Kulonga River, apex part of Yarnyshnaya Bay, and Oskar Bay in Russia) testify that the ecological state of the Barents Sea shores is adverse.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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