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Hydrocarbons in the Water and Bottom Sediments of a Region with Continuous Petroleum Contamination

I. A. Nemirovskaya

Shirshov Institute of Oceanology, Russian Academy of Sciences,
Nakhimovskii prosp. 36, Moscow, 117997 Russia

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Abstract—The abundances and compositions of aliphatic hydrocarbons (AHC) and polyaromatic hydrocarbons (PAH) were investigated in the water and bottom sediments of the southwestern Amur Bay in the Sea of Japan. The water contained from 0 to 129 μg/l AHC (averaging 42.2 μg/l) and from 5 to 85 ng/l PAH (averaging 18 ng/l). The bottom sediments contained 168–2098 μg/g AHC and 7.2–1100 ng/g dry mass PAH. It was shown that the input of anthropogenic HC is better recorded by molecular markers than the distribution of AHC and PAH concentrations. The discovery of elevated HC concentrations in the bottom water layer suggests that the bottom sediments induced secondary contamination of the water body.

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INTRODUCTION

Coastal regions of seas and oceans are zones of high bioproductivity, where considerable amounts of autochthonous biogenic compounds, including HCs, are formed. Furthermore, these regions are affected by the maximum anthropogenic impact, because pollution is mainly confined to ports, oil terminals, and urbanized coastal areas [1].

The extensive development of petroleum production in Russia's Far East results in that increasingly larger marine areas become contaminated with petroleum hydrocarbons. The Sea of Japan is among the most contaminated among the Far East seas [2]. The concentration of HCs in the coastal zone of Amur Bay is often higher than 50 μg/l, and Zolotoi Rog Bay is practically always covered with an oil film, which may be up to 100 μm thick near the shore [3]. Each year Amur Bay receives 121.5 kg benzo(a)pyrene, while only 116.8 kg is removed, which results in that the average content of this carcinogenic polyarene in the bottom sediments (30 ng/g) is much higher than in other basins with a continuous petroleum input [4].

In order to estimate the modern biogenic background, natural and anthropogenic HC components of water and bottom sediments were separated at a model test site in the zone of continuous input of pollutants in the southwestern Amur Bay in April 2005 (Fig. 1).

The contamination of a water basin is usually assessed by comparing the measured contents with the maximum admissible concentrations (MAC) [2, 5]. On the other hand, the use of a bulk concentration for the assessment of the degree of HC contamination of water and bottom sediments casts strong doubt [4, 6]. Considerable amounts of organic matter are buried in semiclosed water reservoirs and productive zones, and HCs may form there in diagenetic processes. During the periods of plankton bloom, petroleum HCs may play a minor role even in regions with a continuous contaminant input [4]. In a basin affected by accidental spills, the influence of pollutants was detected after several years from the distribution of molecular markers rather than from HC contents [6].

METHODS

The investigations were carried out within a single project using the methods accepted at the Analytical Center of the Shirshov Institute of Oceanology, Russian Academy of Sciences (no. ROSS RU. 0001.514963) [4, 7, 8]. Lipids and HCs were extracted with chloroform from seawater (samples of 5 l) and wet samples of bottom sediments [4]. The concentration of the bulk extracted lipid fraction was determined before column chromatography on silica gel, and that of HCs, after column chromatography on silica gel. Hydrocarbon fractions were separated using the method of silica gel column chromatography by hexane (AHC) and a 3 : 2 hexane–benzene mixture (PAH) [9].

The contents of lipids and AHC were determined by IR spectroscopy on an IR-435 Shimadzu instrument (Japan) in the equivalent mixture of 37.5% isooctane, 37.5% hexadecane, and 25% benzene on the basis of the 2930 cm^{-1} band. The contents and compositions of alkanes were determined by capillary gas chromatography using a TBT chromatograph (France) with squalane as a standard (Shirshov Institute of Oceanology, Russian Academy of Sciences, analyst V.I. Peresypkin).

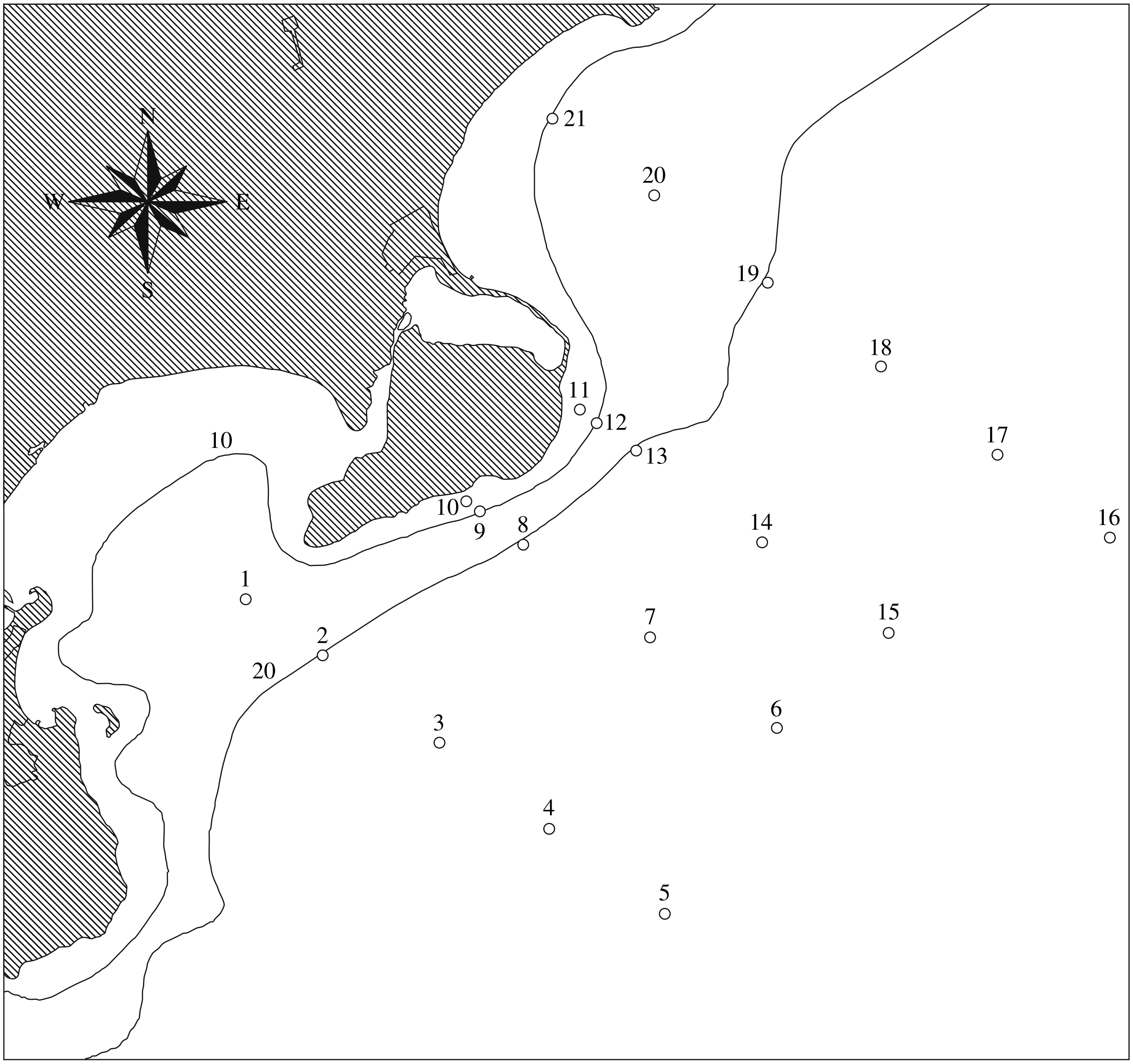

Fig. 1. Sketch map showing sampling sites in the southwestern part of the Amur Bay.

The contents and compositions of PAH were determined by high-performance liquid chromatography on a Milikhrom-A02 instrument (Russia) operating in the gradient mode with acetonitrile (75–100%) as an eluent. Prontosil-120-5-C_{18} with a grain size of 5 μm was used as a stationary phase. Identification was based on the release time of individual polyarenes obtained from the laboratory of the Environmental Protection Agency (USA) at 220, 254, 280, and 300 nm. Concentrations were determined at 254 nm. The following unsubstituted polyarenes were identified: naphthalene (N), anthracene (AN), phenanthrene (PH), fluoranthene (FL), pyrene (P), triphenylene (TR), chrysene (CR), perylene (PL), benzo(a)pyrene (BP), and 1,12-benzoperylene (BPL).

The content of C_{org} in bottom sediment samples was determined by the method of dry combustion using an AN-7529 analyzer.

RESULTS

The concentration of AHC **in the water** ranged from 0 to 130 μg/l (Table 1). The concentrations of AHC in the density jump layer (Fig. 2b) (“liquid floor”) [10] and in the near-bottom horizon (Fig. 2c) were higher than in the surface water layer (Fig. 2a), which is usually enriched in AHC during the input of fresh petroleum products. Only at shallow near-shore sites (stations 11 and 13) were the concentrations of AHC in

Table 1. Contents of organic compounds in the water of the study area

Station	Depth, m	µl/l		AHC, % of lipids	PAH	BP	PAH*, % of lipids	PH/AN	(P + BP)/(PH + CR)
		lipids	AHC		ng/l				
1	0	35.9	15.5	43.2	3.54	0.1	7.4	1.56	4.17
	5	50.3	37.0	73.6	not determined				
	10	99.2	64.7	65.2	11.25	0.0	8.6	n.d.	1.0
2	0	37.7	7.9	21.0	not determined				
	10	94.2	32.4	34.4	″				
	22	41.0	20.1	49.0	″				
3	0	111.4	28.0	25.1	″				
	10	120.4	36.3	30.1	″				
	26	79.1	15.8	20.0	″				
4	0	37.4	11.1	29.7	″				
	10	59.3	23.7	40.0	″				
	25	59.3	23.7	40.0	″				
5	0	54.6	28.0	51.3	13.7	0.0	18.9	n.d.	36.5
	10	64.7	41.7	64.5	4.99	0.1	5.8	″	7.7
	34	119.0	74.1	62.3	84.57	0.0	53.7	″	
6	0	32.4	20.1	62.0	not determined				
	10	59.3	19.8	33.4	″				
	32	130.5	59.3	45.4	38.25	0.0	22.1	n.d.	0.0
7	0	45.3	20.1	44.4	not determined				
	10	79.1	15.8	20.0	″				
	26	79.1	46.4	58.7	21.44	0.0	20.5	n.d.	0.0
8	0	36.7	0.0	0.0	9.95	0.92	27.1	″	7
	10	68.7	32.4	47.2	4.28	0.07	4.7	″	42.14
	22	90.2	28.4	31.5	not determined				
9	0	130.8	0.0	0.0	″				
	5	74.1	46.0	62.1	13.2	0.0	13.5	n.d.	0.0
	12	59.3	19.8	33.4	2.78	0.0	3.5	″	0.0
10	0	50.3	24.4	48.5	not determined				
	5	67.2	19.8	29.5	″				
	7	96.7	54.6	56.5	″				
11	0	124.7	59.3	47.6	11.38	0.0	6.9	n.d.	0.0
	5	44.9	23.7	52.8	not determined				
	8	102.1	45.3	44.4	49.69	3.5	36.8	31.75	2.0
12	0	118.3	41.3	34.9	17.47	0.29	11.2	3.56	0.93
	5	90.2	19.8	22.0	29.22	0.39	24.5	1.03	2.63
	12	90.2	32.4	35.9	not determined				
13	0	79.1	20.1	25.4	9.33	0.07	8.9	n.d.	0.30
	10	210.3	98.1	46.6	15.45	0.18	5.5	″	1.48
	23	160.7	80.2	49.9	38.98	6.95	18.3	″	0.85
14	0	28.4	11.1	39.1	4.82	0.18	12.8	″	3.59
	10	128.7	45.3	35.2	16.66	0.3	9.8	4.80	5.98
	27	138.0	36.7	26.6	4.92	0.2	2.7		2.62
15	0	59.3	32.4	54.6	not determined				
	10	120.8	54.6	45.2	″				

Table 1. (Contd.)

Station	Depth, m	µl/l		AHC, % of lipids	PAH	BP	PAH*, % of lipids	PH/AN	(P + BP)/(PH + CR)
		lipids	AHC		ng/l				
	34	97.1	36.7	37.8	″				
17	0	50.7	32.4	63.9	″				
	10	94.9	41.3	43.5	″				
	33	64.7	46.0	71.1	″				
18	0	78.0	32.4	41.5	″				
	10	49.6	19.4	39.1	″				
	28	76.2	36.7	48.2	″				
19	0	46.0	20.5	44.6	″				
	10	41.0	18.3	44.6	″				
	22	77.3	19.4	25.1	″				
20	0	33.1	0.0	0.0	4.05	0.37	9.2	6.50	2.44
	5	116.1	54.6	47.0	19.7	0	12.8	n.d.	2.16
	12	82.0	24.1	29.4	5.69	0.13	5.2	″	28.59
21	0	32.4	11.5	35.5	not determined				
	5	104.6	32.4	31.0	″				
	11	64.0	19.8	30.9	″				

* $\times 10^{-3}$.

the surface water higher than in the water body, which may indicate their anthropogenic input from the coast. The following average concentrations were observed: 27.6 ± 19.6 µg/l in the surface water, 47.2 ± 25.3 µg/l in the pycnocline, 51.9 ± 25.5 µg/l in the bottom layer, and 42.2 ± 25.5 µg/l for the whole database. The latter value is somewhat lower than the MAC of petroleum HCs for seawater (50 µg/l).

The bulk AHC concentration in the pycnocline is up to 1.7 times higher than that in the surface water layer. At stations 8 and 9, the concentration of AHC in the surface water was below the analytical detection limit, whereas relatively high concentrations were observed in the pycnocline, 43 and 61 µg/l, respectively (Table 1). In addition to the accumulation of various compounds in the pycnocline, the mixing of water masses of different densities promotes the development of biochemical processes (in particular, formation of HC-producing microplankton), which is responsible for such a significant degree of HC accumulation. The highest AHC contents in the near-bottom layer were confined mainly to the shore zone (stations 1 and 13). However, relatively high contents were observed even in the central part of the area (stations 5, 6, and 15), which was most likely due to a local input from the bottom sediments.

The concentrations of PAH in the water ranged within 2.8–84.6 ng/l. Polyarene content fluctuations in the water of the bay were so high that the standard deviation ($\sigma = 18.9$) is comparable with the average value (18.1 ng/l). Similar to AHC, elevated PAH contents were observed in the near-bottom water with a maximum at station 5 (both recalculated to one liter, 84.6 ng/l, and in the composition of lipids, 53.7×10^{-3} %). The most abundant unsubstituted polyarenes are PL, FL, and CR; BP, PH, and AN are minor compounds (Fig. 3a). The average concentrations of polyarenes in the water formed the following sequence (ng/l): PL (5.4) > FL (4.6) > P (1.5) > CR (1.4) > BPL (1.2) > BP (0.57) > N (0.47) > PH (0.40) > AN (0.06). An exception is the near-bottom water from station 13 with 7 ng/l BP (Table 1), which is higher than the MAC of this compound (5 ng/l).

The petroleum nature of PAH from the near-shore zone of the region is indicated by the high PH/AN ratio with a maximum value of 31.8 at station 1. A PH/AN value of more than 10 is an indicator of the extensive input of petroleum polyarenes [11]. In addition, anthropogenic PAH are dominated by high-temperature pyrolysis products – pericondensed (P, BP, BPL, etc.) products prevail in basins with their continuous inflow over PAH produced in natural processes (PH and CR) [4, 12]. The (P + BP)/(PH + AN) ratio is usually no higher than 1 in the absence of pyrogenic input and reaches 20 in basins with a permanent input of pollutants [4]. Trace concentrations of P and BP were found in the water body at some stations (Fig. 3a). On the other hand, at relatively high polyarene concentrations (for instance, at stations 5 and 8), (P + BP)/(PH + AN) reached 36.6–42.1, which is much higher than in the river water of industrial centers. For instance, this ratio was no higher than 1.5 in the water of the Vilnia River

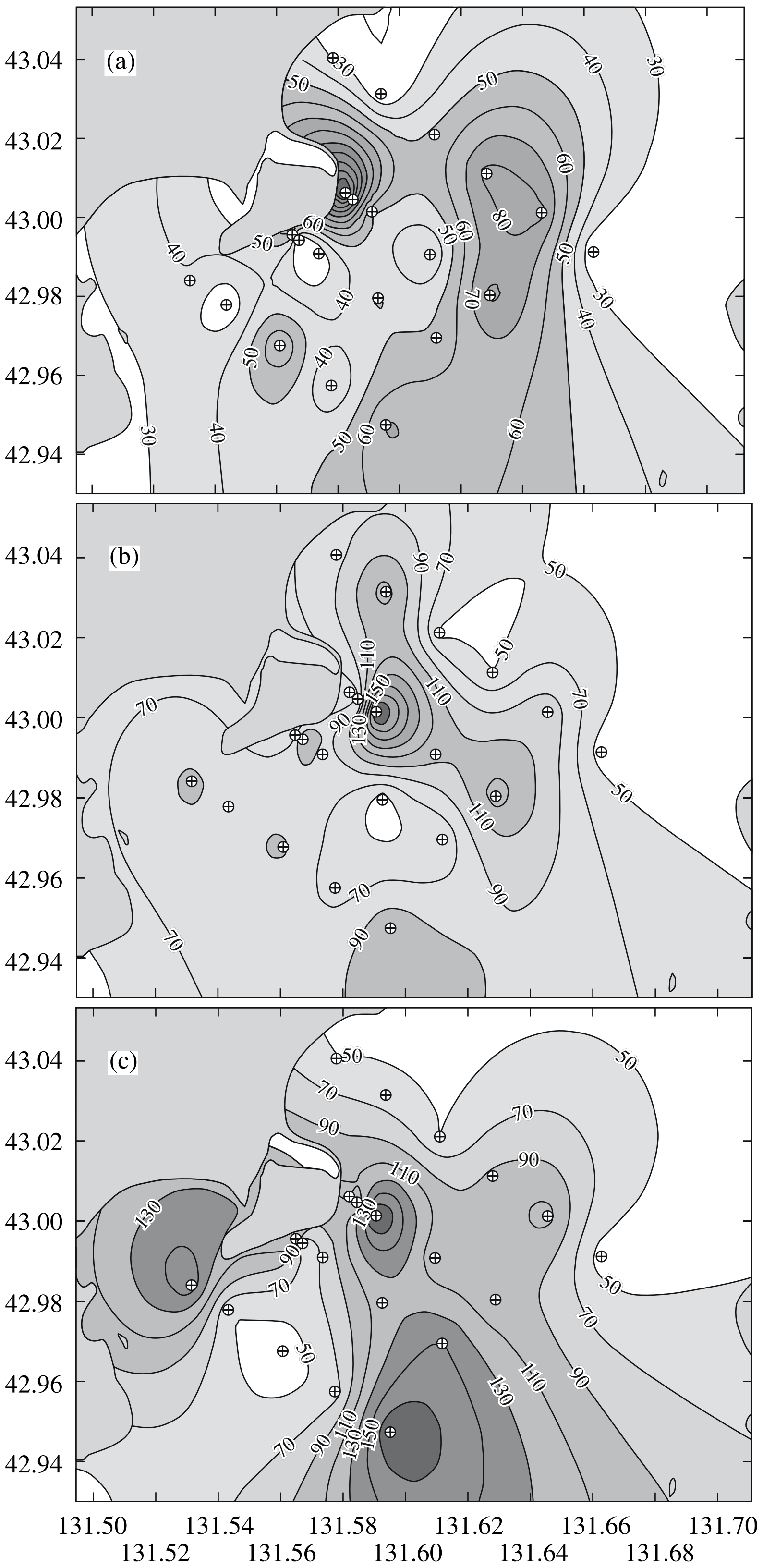

Fig. 2. Distribution of aliphatic hydrocarbons (μg/l) in the water of the test site. (a) Surface, (b) pycnocline, and (c) near-bottom levels.

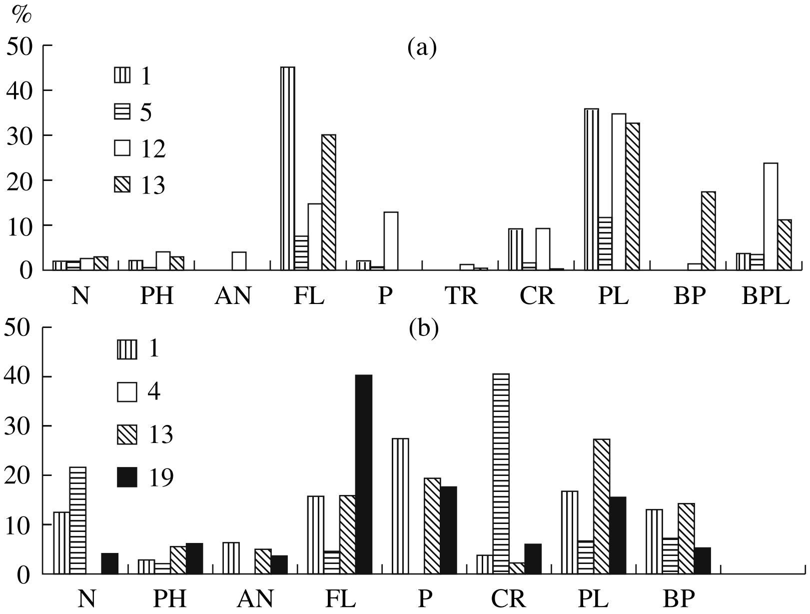

Fig. 3. Proportions of polyarenes in (a) the water of the bottom horizon and (b) the surface layer of bottom sediments at stations 1, 4, 13, and 19. Polyarenes: N, naphthalene; PH, phenanthrene; AN, anthracene; FL, fluoranthene; P, pyrene; CR, chrysene; TR, triphenylene; PL, perylene; BP, benzo(a)pyrene; and BPL, benzoperylene.

within the city of Vilnius [4] and 0.43 at the periphery of Peter the Great Bay [13].

The investigated **bottom sediments** are dominated by the silt–pelite type with a moisture content of 41–65%, 0.56–2.78% C_{org}, and 168–2098 μg/l AHC (Table 2, Fig. 4). An exception is sediments from stations 9 and 12, which are sandy deposits with lower C_{org} (0.086%) and AHC (18.5 μg/l) contents.

The distribution of alkanes and markers in their composition suggests the predominance of weathered petroleum AHC (Table 3). All the samples showed elevated contents of high-molecular-weight homologues (light to heavy AHC ratio ranged from 0.17 to 0.34). Their monotonous distribution in the high-molecular-weight region (Fig. 5a) and the correspondingly low CPI values (odd to even alkane ratio), which are only slightly higher than 1, also indicate the petroleum nature of the polyarenes. Pristane was usually more abundant than heptadecane, and the Pr/n-C_{17} value ranged from 1.07 to 15, which is indicative of *n*-alkane degradation. This is additionally supported by high contents of naphthene and aromatic compounds, which are at least five times more abundant than *n*-alkanes (on average, 271 and 52 ng/g, respectively). For comparison, the bulk concentration of n-alkanes in the sediments of the Baku region is 15–17 μg/g, whereas the naphthene–aromatic hump reached 1300–1500 μg/g [11]. Only at peripheral stations 6 and 7 was the influence of terrigenous components detected in the composition of alkanes (Fig. 5b), and the CPI value increased up to 1.47. Most likely, terrigenous AHC play a passive role during sedimentation, precipitating together with petroleum AHC. The influence of autochthonous alkanes was never detected in the bottom sediments (no positive anomaly at n-C_{17}). This was probably related to low April temperatures, which prevented the development of phytoplankton.

The concentrations of PAH (Table 2) varied from 7.2 to 1100 ng/g dry mass, averaging 162 ng/g (σ = 260 ng/g); the surface layer showed 132 ng/g (σ = 272 ng/g). If polyarene contents in sediments from station 19 are ignored, the average value is 63 ng/g (σ = 52 ng/g). The average composition of PAH from the surface layer of bottom sediments showed the following sequence of identified homologues (ng/g): FL (115.7) > P (50.0) > AN (44.4) > PL (27.6) > CR (18.0) > N (10.0) > BP (8.7) > PH (7.3) > BPL (2.1).

The dominant compounds are FL, which is the most stable among polyarenes, and P, which is mostly of pyrolytic origin [12]. Average (FL + P)/P and (P + BP)/(PH + CR) values of 0.7 and 3.9, respectively, suggest that the sediments are contaminated by pyrogenic PAH. In addition, the content of P in the sediments is higher than that of PL, which is also indicative of the pyrogenic nature of the polyarenes. PL is usually considered as a geochemical background polyarene [11, 12], and a change in the percentage of PL in the composition of PAH is an indicator of diagenetic transformations. The petroleum nature of PAH in the sediments is supported by the elevated fraction of N (averaging 10% and reaching 21%) and the PH/AN ratio (averaging 3.9 and reaching 46.7). The PH/AN value usually increases from surface to subsurface layers and away from the shore, because anthracene is less stable than phenanthrene.

Table 2. Contents of organic compounds in bottom sediments

Station	Depth, m	Description of sediment	Horizon, cm	Humidity, %	C_{org}, %	AHC		PAH				
						µg/g	% of C_{org}	Total, ng/g	% of C_{org}*	PH**/AN	((P + BP)/(PH + CR)	P/PL
1	14	Clayey mud	1.5–2	54.01	1.562	2098.7	13.44	75.3	0.48	0.44	6.08	1.63
			3–4	44.41	1.545	64.9	0.42	18.8	0.12	4.00	0.64	1.17
2	22	Mud	1.5–2	56.53	1.686	1789.9	10.62	52.1	0.31	–	3.00	1.63
			0–5	52.07	1.603	408.4	2.55	36.7	0.23	1.00	17.45	0.84
3	28	Mud	0–1	62.34	2.241	742.2	3.31	48.8	0.22	3.15	1.23	0.31
			3–5	53.94	1.835	1017.9	5.55	57.2	0.31	3.33	4.43	1.21
4	33	Mud	0–2	64.17	2.672	1214.8	4.55	68.1	0.25	46.67	0.17	0.02
			2–5	55.72	2.374	362.3	1.53	42.2	0.18	–	1.35	0.16
5	35	Mud	0–2	65.10	2.694	257.5	0.96	22.8	0.08	0.83	5.85	0.58
			2–5	62.76	2.694	247.5	0.92	34.6	0.13	6.75	3.13	1.68
6	35	Mud	0–2	61.03	2.875	221.4	0.77	170.2	0.59	3.27	2.88	0.97
			2–5	61.29	2.854	486.7	1.71	130.6	0.42	–	3.93	0.71
7	32	Mud	0–2	57.92	2.223	167.9	0.76	80.0	0.36	3.29	3.73	1.06
			2–5	63.74	2.293	420.2	1.83	118.6	0.52	–	6.67	1.35
9	12	Sand	0–2	26.61	0.237	18.5	0.78	33.3	1.41	0.82	3.13	0.85
12	10	Sand	0–3	30.34	0.086	167.4	19.47	47.5	5.52	4.83	1.45	0.61
13	21	Clayey mud	0–2	58.95	2.127	200.9	0.94	17.6	0.08	1.11	4.21	0.71
			2–5	61.42	2.338	565.9	2.42	126.4	0.54	0.83	5.94	2.28
14	27	Mud	0–3	40.58	0.558	577.9	10.36	170.1	3.05	0.94	2.43	0.59
15	34	Mud	0–3	62.89	2.783	115.5	0.42	–	–	–	–	–
17	33	Mud	0–2	60.37	2.385	385.7	1.62	87.3	0.37	2.45	3.72	1.96
			2–5	56.10	2.667	414.0	1.55	95.6	0.36	1.63	3.27	0.83
18	28	Mud	0–2	21.54	2.175	591.6	2.72	7.2	0.03	3.00	0.64	1.14
			2–5	48.64	0.785	366.4	4.67	171.0	2.18	0.04	5.72	0.89
19	15	Mud	0–1.5–2	47.84	3.674	1570.4	4.28	1099.6	2.99	1.67	1.88	1.14
			2–5	40.59	0.888	733.7	8.26	285.1	3.21	0.24	3.06	0.74
20	14	Mud with H_2S	0–2	38.17	0.927	73.9	0.80	20.0	0.22	–	4.28	1.54
			2–5	42.%55	1.082	514.8	4.76	909.1	8.40	3.32	1.34	0.98

Notes: * $\times 10^{-3}$;

** PH, phenanthrene; AN, anthracene; P, pyrene; BP, benzo(a)pyrene; CR, chrysene; and PL, perylene.

DISCUSSION

The Amur Bay is affected by the highest anthropogenic impact both among the Far East seas and in Peter the Great Bay [2, 3, 5, 14]. The large cities of Vladivostok and Ussuriisk are situated on its shores. The largest seaport of Primorye in Zolotoi Rog Bay also contributes to the contamination of the bay. The material excavated during channel dredging in Zolotoi Rog Bay was dumped at the Tokarevskii Cape region, which enhanced the contamination of the southwestern part of the bay with heavy metals and petroleum HCs [3]. Various mining enterprises are located in the basins of rivers entering the bay. The increasing economic activity of the 1960–1990s was not accompanied by the con-

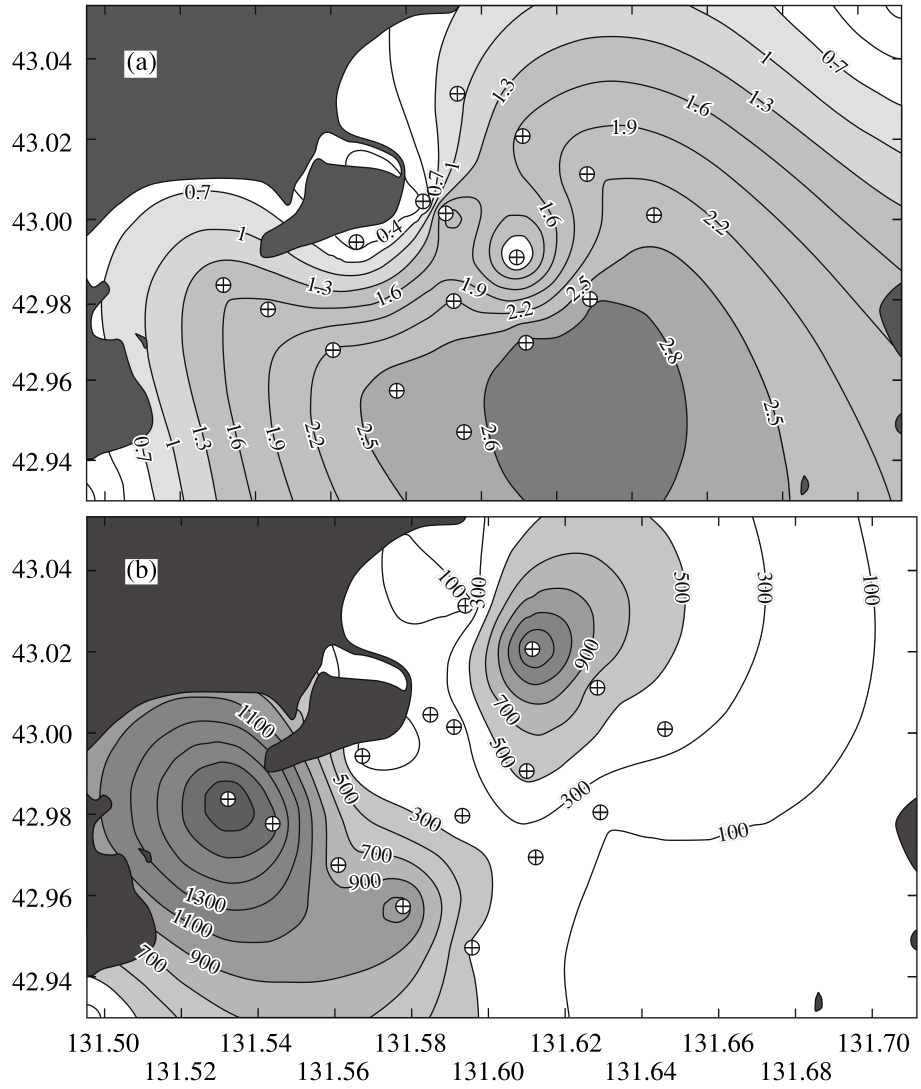

Fig. 4. Distribution of (a) C_{org}-% and (b) AHC- µg/l in the surface layer of bottom sediments over the study area.

struction of efficient sewage treatment facilities, which resulted in that the water of the bay served as an acceptor of untreated sewage [3]. This is the reason why the average concentration of AHC in the water body of the southwestern Amur Bay is more then two times higher than the background level in coastal waters (18–20 µg/l [4]). However, these concentrations are much lower than those of Zolotoi Rog Bay, where they may be as high as 2000–2700 µg/l (Table 3). It should be noted that concentrations of dissolved forms higher than 50 µg/l are rather common in the severely contaminated coastal regions of Russian seas, and values of >1000 µg/l were occasionally reported [6]. Consequently, the concentrations of AHC in the waters of the area under investigation are even lower than those in water regions with a continuous petroleum input. This is related to the fact that the inflowing hydrophobic anthropogenic compounds precipitate in shallow frontal zones (mainly at the areas of their input), which reduces their content in water. This is why the average concentration of AHC in the open waters of Peter the Great Bay and the Sea of Japan (9.2 µg/l) coincides with the background content in the uncontaminated regions of the northern Pacific [13, 14].

The AHC of Amur Bay water are already significantly transformed, which is suggested by the strong correlation between the concentrations of lipids and AHC (*r* = 0.84). It is evident that the existence of various HC sources does not disturb this correlation. Even at low spring temperatures, there is an efficient mechanism of transformation providing a rapid recovery of the HC cycle system to the state of dynamic equilibrium. This is also supported by the lower content of AHC in the composition of C_{org} at near-shore station 11 (1.6–4.5% at various levels) compared with more seaward station 13 (11.1–17.2%). The crude oil and petroleum products that enter a marine environment rapidly cease to exist as initial compounds and undergo intense

Table 3. Near-shore regions of Russian seas with the highest concentrations of AHC in water, μg/l [5]

Sea	Region	Concentration range	
		average	maximum
Barents	Kola Bay	50–60	550–1600
White	Dvina Bay	30–40	480–500
Kara	Southwestern part	30–50	460–600
Laptev	Tiksi Bay	30–160	130–1250
East Siberian	Chaunskaya Guba	20–40	90–110
Chukchee	Coastal part	20–30	20–40
Bering	Avacha Bay	10–30	30–2400
Okhotsk	Nagaev Bay	60–290	12–830
Japan	Zolotoi Rog Bay	10–150	2000–2740
	Northern Tatar Strait	30–45	50–1500
Black	Tuapse region	100–160	840–1100
Azov	Taganrog Bay		2100–3000
Caspian	Northern part	70–200	250–1540
Baltic	Neva Guba	70–120	250–1540

degradation [4]. The microbial destruction of petroleum products does not occur from January to May owing to low temperatures [15]. However, their weathering intensifies during this period. The transformation of oil-related pollutants is accompanied by a decrease in AHC fraction and an increase in the content of polar classes at the expense of resins and asphalthenes [16].

The concentration of polyarenes in the waters of the test site (18 ng/l) is practically identical to their concentrations in shelf waters [4]. On the other hand, these values are significantly lower than the concentrations measured in regions with a continuous input of contaminants. For instance, the surface waters of the St. Sebastian and St. Paul channels (near the main oil terminal of Brazil) contain 430–850 ng/l polyarenes [17]. In the region of the port of Leghorn in the Tyrrhenian Sea, whence about 7000 ships call every year, their concentrations are 63–1060 ng/l in the dissolved form and 551–7540 ng/l in the suspended form [18]. However, markers in the composition of dissolved polyarenes from the region studied indicate the influence of petroleum and pyrogenic sources.

The correlations between the contents of lipids and PAH ($r = 0.40$) and between AHC and PAH ($r = 0.51$) are weaker than those between lipids and AHC, which is probably related to their different genesis. The main sources of PAH are the combustion of various fuels and emissions of heating and power systems [12]. The leakage of petroleum products introduces minor amounts of PAH, because their contents in oils are small compared with other hydrocarbon classes (0.3–10.1%).

The distribution of organic matter in bottom sediments is controlled to a significant extent by the degree of sediment dispersion [4]. This is resulted in a correlation between the moisture and C_{org} contents of sediments ($r = 0.77$). The content of C_{org} increases from sands to silts by a factor of more than 30. The AHC sorption capacity of bottom sediments (initially suspension) is controlled by the intensity of ion exchange, which also increases towards fine fractions with high contents of clay minerals. In addition, an increase in the median diameter of sedimentary particles from 0.01 to 1.0 mm results in an increase in their bulk density from 0.8 to 1.9 g/cm^3 [10]. Compared with coarse sediments, finely dispersed materials accumulate more efficiently poorly soluble organic compounds on the surface of particles. This redistribution process depends also on the concentration of organic matter in the solid phase, which serves as a solvent for hydrophobic molecules. This is why the concentrations of AHC in silty deposits are usually higher than those in sandy sediments.

The grain-size control of AHC vanishes in the zone of avalanche sedimentation, in the region of mixing of fresh and saline waters, and in the areas with an extensive input of petroleum products [4]. Therefore, the degree of fluctuations of AHC concentrations in the bottom sediments (averaging 618.8 μg/l for silty sediments at $\sigma = 530$ μg/l) is higher than that of C_{org} (averaging 1.83% at $\sigma = 0.81\%$), both recalculated to dry mass and in the composition of C_{org} (averaging 4.2% at $\sigma = 4.6\%$). These factors can probably be responsible for the difference in the strength of the geochemical correlations and between the distributions of C_{org} and AHC over the area of the test site: r(Moisture–AHC) = 0.12 and r(C_{org}–AHC) = 0.011. Indeed, elevated C_{org} concentrations are confined to the central part of the bay, whereas AHC tend to concentrate in the near-shore regions (Figs. 4a, 4b).

The concentration of AHC in modern marine bottom sediments is usually only several tenths and occasionally hundredth of C_{org} [19]. According to our data, the fraction of AHC in C_{org} varies from 0.42 to 19.47% (Table 2), which indirectly suggests a high HC flux into the bottom sediments. When the concentrations of anthropogenic AHC are high, their content in sandy deposits can increase even at the expense of passive sorption. This results in that the fraction of AHC in the composition of organic matter from the coarse sediment of station 12 (19.5%) is higher than that in the silty sediments of neighboring station 13 (0.94%).

The existence of different sources of HC input (petroleum, pyrogenic, and biogenic) and the complexity of shallow-water sedimentation result in both high fluctuations in HC concentrations and the negligible correlations between the distribution of AHC and PAH

Table 4. Compositions of alkanes from the bottom sediments of the southwestern part of Amur Bay

Station	Depth, m	Horizon, cm	C_{org}, %	AHC, µg/g	AHC, % of C_{org}	Alkanes							
						µg/g	hump, µg/g	alk/hump	Pr/Pf	Pr/C_{17}	Pf/C_{18}	CPI	L/H*
1	14	1.5.–2	1.562	2098.7	13.44	200.8	561.4	2.8	4.4	3.6	0.2	1.06	0.21
		3.–4	1.545	64.9	0.42	4.4	32.8	7.4	4	3.2	1.1	1.18	0.32
2	22	1.5.–2	1.686	1789.9	10.62	191.68	968.8	5	3.3	1.7	0.2	1.06	0.22
		0–5	1.603	408.4	2.55	24.72	208.8	8.4	5	2.5	0.2	1.03	0.34
3	28	0–2	2.241	742.2	3.31	85.8	269.4	3.1	7	5.2	0.2	1.07	0.21
		0–5	1.835	1017.9	5.55	112.9	370	3.3	5.3	5.3	0.4	1.05	0.17
4	33	0–2	2.672	1214.8	4.55	64.16	475.4	7	2.3	1.1	0.2	1.04	0.31
		2–5.	2.374	362.3	1.53	40.36	155.6	3.9	4.2	3.4	0.4	1.08	0.26
5	35	0–2	2.694	257.5	0.96	3.28	172.2	52.5	7.5	7.5	1	1.23	0.25
		2–3.	2.694	247.5	0.92	3.88	78.6	20.25	4.7	4	1.2	1.17	0.26
6	35	0–2	2.875	221.4	0.77	12.06	183	15.2	4	4	1.7	1.47	0.17
		2–5.	2.854	486.7	1.71	11.78	259.2	22	7.3	7.3	0.5	1.14	0.32
7	32	0–2	2.223	167.9	0.76	9.84	107.2	10.9	3.6	3.6	1.7	1.09	0.24
		2–5.	2.293	420.2	1.83	11.18	209.4	2.6	4.6	2.6	0.8	1.12	0.32
9	12	0–2	0.237	18.5	0.78	0.84	9.72	11.6	3.8	15	4	1.2	0.23

* $\Sigma(C_{15} + C_{22})/\Sigma(C_{23} + C_{40})$.

in the sediments: r(AHC–PAH) = 0.26, and $r(C_{org}$–PAH) = –0.21. Similar to AHC, the highest polyarene contents were observed at station 19 in the region of an abrupt increase in water depth.

The OM-rich bottom sediments may contain up to 100 µg/g AHC. Higher concentrations are usually attributed to anthropogenic sources [11, 20]. Biogenic sources provide usually 50 µg/g AHC. Elevated HC concentrations in bottom sediments from shallow semi-closed basins can be caused by the high productivity of plankton coupled with small depths, considerable input of terrigenous organic matter, and high sedimentation rates. Therefore, the shallow-water maximum of AHC concentration (>100 µg/g dry mass) related to natural processes is confined to relatively fine sediments of bays, lagoons, harbors, inland seas, and upper parts of the open oceanic shelf [4].

The concentrations of AHC in the sediments of the studied area were higher than 100 µg/g and reached 500–1000 µg/g at many stations, which is higher in some cases than AHC content in water basins with a continuous petroleum input (Table 5). For instance, the concentration of C_{org} in the estuary sediments of the Black Sea varies over a wider interval (0.08–4.26%) than in the area considered here, whereas AHC contents are restricted to a narrower range of 28–472 µg/g with a maximum of 2.7% in the composition of organic matter [4]. The concentrations of AHC in the Riga and Finnish gulfs of the Baltic Sea are 4–62 µg/g (averaging

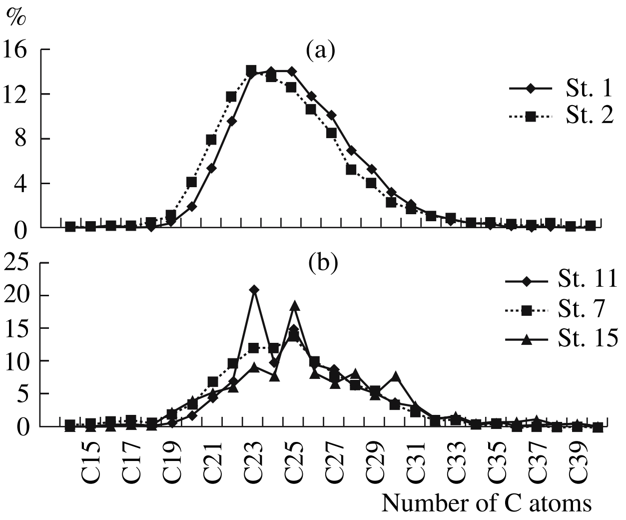

Fig. 5. Compositions of n-alkanes from bottom sediments of mainly (a) petroleum and (b) terrigenous origin.

Table 5. Contents of AHC (μg/g dry weight) in the surface layer of bottom sediments from the regions with a continuous petroleum input

Region	Year	AHC	Reference
Black Sea			
Bulgarian shelf	1989	32–142	[4]
Coastal and central zones	1988–1990	7–153	[21]
Estuary regions of northwestern part (branches of the Danube, Dnestr, and Bug)	1990–1991	5–402	[4]
Bosporus Straight	1995	12–76	[22]
Shore near Sochi		7.6–170	″
Shore near Odessa		110–310	″
Ukrainian shore		2.1–6.6	″
Danube Estuary		49–220	
Baltic Sea, Riga and Finnish bays	1990	1–148	[4]
Caspian Sea			
Azerbaijan shelf	2000	39–1515*	[11]
Iran shelf	2001	14–113*	
Northern part (Russia's territory)	2000	1–42*	
Kazakhstan shelf	2001	2–14*	
Northern shelf	2003	20–142	[23]
Volga delta	2004	59–3881	″
Northern shelf	2004	94–136	″
Caribbean Sea, Cartagena Bay	1997	6–1415	[24]
Continental shelf of the Mississippi R.	1987–1989	1–135	[25]
Persian Gulf	1991–1993	19–671	[26]
Western coast of Taiwan	1990	869–10300	[27]
Victoria Harbor, China	1992	60–646	[28]
Haimen Harbor, China	1993	3–33	″
New York Harbor	1971–1975	35–2900	[29]
Southwestern Amur Bay	2005	19–2099	This study
Antarctica, background	2001, 2003	12–210	[4]

* Sum of alkanes.

0.17% in the composition of OM) and 7–307 μg/g (up to 0.8% of OM), respectively. The level of AHC in the sediments is comparable with their contents in water areas near ports. For instance, the content of AHC in sediments is up to 1415 μg/g in the Cartagena Bay of the Caribbean Sea [24], 671 μg/g in the Persian Gulf [26], and 10300 μg/g at the western coast of Taiwan Island [27]. The concentration of only alkanes in sediments from the coastal zone of Azerbaijan is 1515 μg/s (8.7% of C_{org}) [11].

Such high AHC concentrations in the bottom sediments are most likely related to the high flux of contaminants, most of which enters with sewage and bilge waters as emulsions. The destruction of these emulsions results in that light fractions float to the surface and evaporate, whereas heavy fractions sink to the bottom, i.e., the bottom sediments accumulate petroleum contaminants. However, in the region considered, a high *n*-alkanes/naphthene–aromatic hump ratio, which is an indicator of weathered petroleum products, was detected at AHC concentrations of no higher than 450 μg/g (Fig. 6a), and a maximum ratio of 52.5 was observed at an AHC content of 257.5 μg/g only (Table 4).

With respect to PAH content, the sediments can be classified as weakly contaminated, because the sum of 3–6-memebered ring polyarenes is usually lower than 100 ng/g [11]. At a continuous input of pollutants, the concentration of PAH in bottom sediments is usually higher than 1000 ng/g, and the sediments become toxic at values of >4000 ng/g. The obtained data are comparable with the concentrations of PAH in the bottom sediments of Antarctica, which is an uncontaminated background region (Table 6). Even at station 19 (Table 2), where the content of PAH was 1100 ng/g in the surface layer and 285 ng/g in the subsurface layer, and that of BP was 60 and 26 ng/g, respectively (MAC of BP in soils is 20 ng/g), the fraction of BP in the PAH composition was no higher than 5%. The relative content of BP at station 19 was lower than in other sediments of the area (Fig. 3b), although the (P + BP)/(PH + CR) ratio was only 1.7 and 0.2. In contrast, this ratio is significantly higher at lower PAH concentrations in sediments (for instance at station 13) (Table 2). Therefore, the degree of sediment contamination with pyrogenic and petroleum polyarenes is independent of the bulk concentrations of PAH (Fig. 6b). It is obvious that polyarenes can be formed in diagenetic processes in the zones of enhanced sedimentation, where considerable amounts of OM are buried. For instance, in the water body of the Bengal upwelling at the coast of southeastern Africa, the content of PAH in the sediments reached 555–815 ng/g at (B + BP)/(PH + CR) < 1 [4]. A transition from the surface to subsurface layer is often accompanied by an increase in HC concentration, especially significant for PAH, which can be related to the elevated flux of polyarenes in the 1950s.

Thus, even in the coastal regions with a continuous input of contaminants (southwestern Amur Bay), the

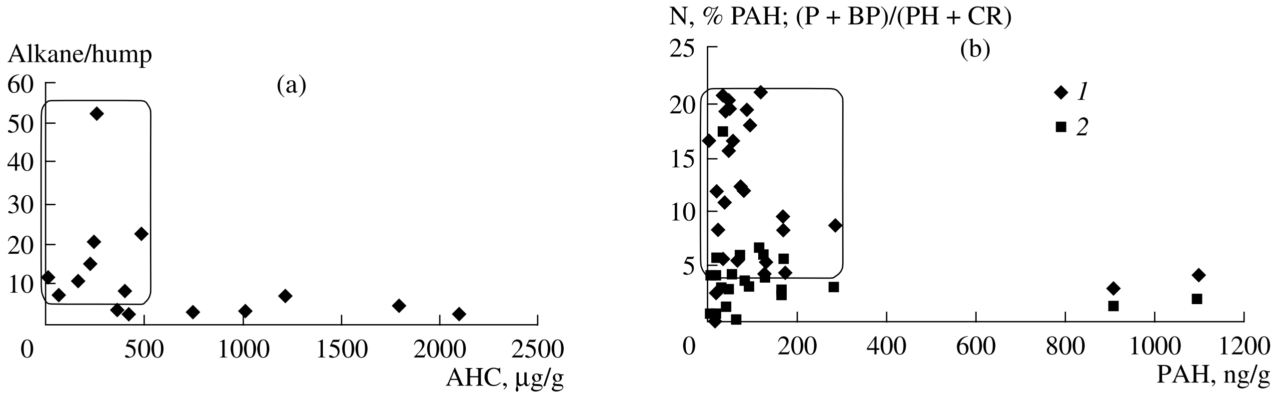

Fig. 6. Distribution of markers in the composition of (a) AHC and (b) PAH. (*1*) Fraction of naphthalene in the composition of PAH, %, and (*2*) (P + BP)/(PH + CR).

bulk content of HC in water and bottom sediments cannot always be used as a measure of their pollution. Anthropogenic HC are more adequately recorded by molecular markers. Therefore, the assessment of the degree of contamination of water areas must include not only a comparison of the obtained concentrations with MAC values but also the determination of HC composition.

Table 6. Contents of PAH (ng/g dry mass) in the bottom sediments of regions with a continuous input of contaminants

Region	Year	Content	Reference
Persian Gulf	1991–1993	<20–4740 (Σ13 PAH)	[26]
San Quentin Bay, Mexico	1992	0–<50 (Σ44 PAH)	[30]
Haimen Harbor, China	1993	70–33000 (Σ9 PAH)	[27]
Victoria Harbor, Hong Kong, China	1992	350–3450 (Σ9 PAH)	[28]
Hsin-ta Harbor, Taiwan	2000	98.1–3382 (Σ30 PAH)	[31]
Kyeondggi Bay, Korea	1995	9.1–1400 (Σ23 PAH)	[32]
Boston Harbor, USA	1999	487–718360 (Σ14 PAH)	[33]
Western coast, Australia	1991	1.0–3200 (Σ11 PAH)	[34]
Sidney Bay, Australia	1998	<100–380000 ((Σ16 PAH)	[35]
Riga and Finnish bays, Baltic Sea	1991	42–444 (Σ8 PAH)	[4]
Baltic Sea	1993	9.5–1871 (Σ15 PAH)	[36]
Estuary regions of the northwestern Black Sea	1991	11.5–339 (Σ8 PAH)	[4]
Ravenna Harbor, Adriatic Sea, Italy	1998–1999	30–112000 (Σ13 PAH)	[37]
Todos–Santos Bay, northwestern coast of Brazil	2000	8–4163 (Σ13 PAH)	[38]
Southwestern part of the Amur Bay	2004	19–1010 (Σ9 PAH)	This study
Antarctica	2001	12.9 (Σ8 PAH)	[4]

CONCLUSIONS

The concentration of AHC in the water of the southwestern part of Amur Bay ranges from 0 to 129 μg/l, averaging 42.2 μg/l, which is twice the background level of near-shore regions. However, their contents are lower than those of water areas with a continuous petroleum input. Although our investigations were carried out during a relatively cold period, the AHC were already significantly transformed, because their contents in the surface layer were lower than in the pycnocline and bottom water layer.

The concentration of dissolved PAH varied from 5 to 85 ng/l, and the average value (18 ng/l) is comparable with the polyarene level in near-shore seawater, 18–22 ng/l, and much lower than in water areas with a continuous input of pollutants. Nonetheless, the composition of polyarenes suggests the influence of petroleum and pyrogenic sources.

The pollutants entering the bay are accumulated in bottom sediments. The discovery of higher HC concentrations in the water of the near-bottom layer suggests that the bottom sediments promote secondary contamination in the basin.

The average content of AHC in silty sediments is 619 μg/g ($\sigma = 530$ μg/g), which is much higher than the background biogenic level (~100 μg/g). Alkane markers indicate the presence of weathered petroleum HC.

The contents of PAH in the bottom sediments varies from 7.2 to 1100 ng/g dry mass (averaging 162 ng/g at $\sigma = 260$ ng/g). Based on these values, most of the sediments can be classified as weakly contaminated with polyarenes. However, the presence of markers in their composition indicates the influence of petroleum and pyrogenic sources.

A comparison of the obtained results with the data for regions with a continuous input of contaminants allowed us to conclude that the introduction of anthropogenic HC is better recognized at the level of molecular markers than from the distribution of AHC and PAH concentrations.

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