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Concentrations and Molecular Markers as Indicators of the Origin of Hydrocarbons in Coastal Areas: Evidence from the Southeastern Amur Bay

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The coastal regions of oceans and seas are regions of high biological productivity, where the largest amounts of autochthonous biogenic compounds, HC inclusive, are formed [1]. In addition, these regions are most subjected to anthropogenic load due to the vicinity of ports, oil-loading terminals, and urbanized territories at the coast [2]. The intense gas and oil production in the Russian Far East provokes hydrocarbon pollution, especially in the navigable waters with developed coastal industry. Based on available estimations, the Amur Bay experiences the strongest anthropogenic load in the Peter the Great Bay [1, 3, 5, 6]. The coastal zone of the bay often contains more than 50 ppm HC, reaching up to 2000–2700 ppm in the Zolotoi Rog Bay [1, 6]. The annual inflow of benz(a)pyrene in the Amur Bay is 121.5 kg, whereas annual outflow is only 116.8 kg. As a result, the average concentration of carcinogenic polyarenes in bottom sediments is 30 ppb, which is significantly higher than that in coastal water areas [7].

The pollution of water areas is typically estimated by comparison of measured concentration with maximum permissible concentration (MPC) [2]. At the same time, there are serious doubts about the application of total HC content for the estimation of the degree of water and bottom sediment pollution [3, 4]. In semiclosed water areas and active tectonic zones containing large amounts of buried OM, HC could be formed in diagenetic processes. In particular, during the period of intense plankton growth caused by input of autochthonous biogenic components, anthropogenic HCs can be subordinate even in areas with constant inflow of pollutants [3]. In accidental flooding areas, the influence of pollutants recorded after a few years is at the level of molecular markers rather than the HC concentration [4].

To estimate the recent biogenic hydrocarbon background, we studied the HCs by separating natural and anthropogenic components in water and bottom sediments at the test site in the zone of the constant inflow of pollutants (southwestern part of the Amur Bay; April, 2005; Fig. 1). Organic compounds were extracted by chloroforms immediately after sampling. We determined the contents of lipids prior to silica gel column chromatography and aliphatic hydrocarbons (AHC) after silica gel column chromatography by IR spectroscopy; the composition of alkanes, by gas chromatography; the content and composition of polycyclic aromatic hydrocarbons (PAH), by efficient liquid chromatography; and the content of organic carbon, by dry burning. The methods are described in detail in [3].

The obtained data showed that the AHC concentration in the coastal zone of the Amur Bay varied from 0 to 130 ppm. The average value of 42.2 ± 25.5 ppm is insignificantly higher than the MPC for oil HC in seawater (50 ppm). Only in individual coastal sites (sites 11 and 12) did the AHC concentration in the surface waters exceed those in the water sequence. At the other sites, high AHC contents were found in the leap layer (*liquid bottom*) and the bottom layer. The average concentrations were 27.6 ± 19.6 ppm in the surface waters, 47.2 ± 25.3 ppm in the pycnocline layer, and 51.9 ± 25.5 ppm in the bottom layer.

In the pycnocline layer, the average concentration coefficient of AHC relative to surface waters is 1.7. The mixing of water masses with different density values not only causes HC accumulation but also activates biochemical processes in this layer (in particular, formation of HC-synthesizing microplankton). Elevated contents of AHC in the bottom layer were found in both the coastal zone (sites 1 and 13) and central part (sites 5, 6, and 15). Their concentration reached relatively high values of 61–89 ppm.

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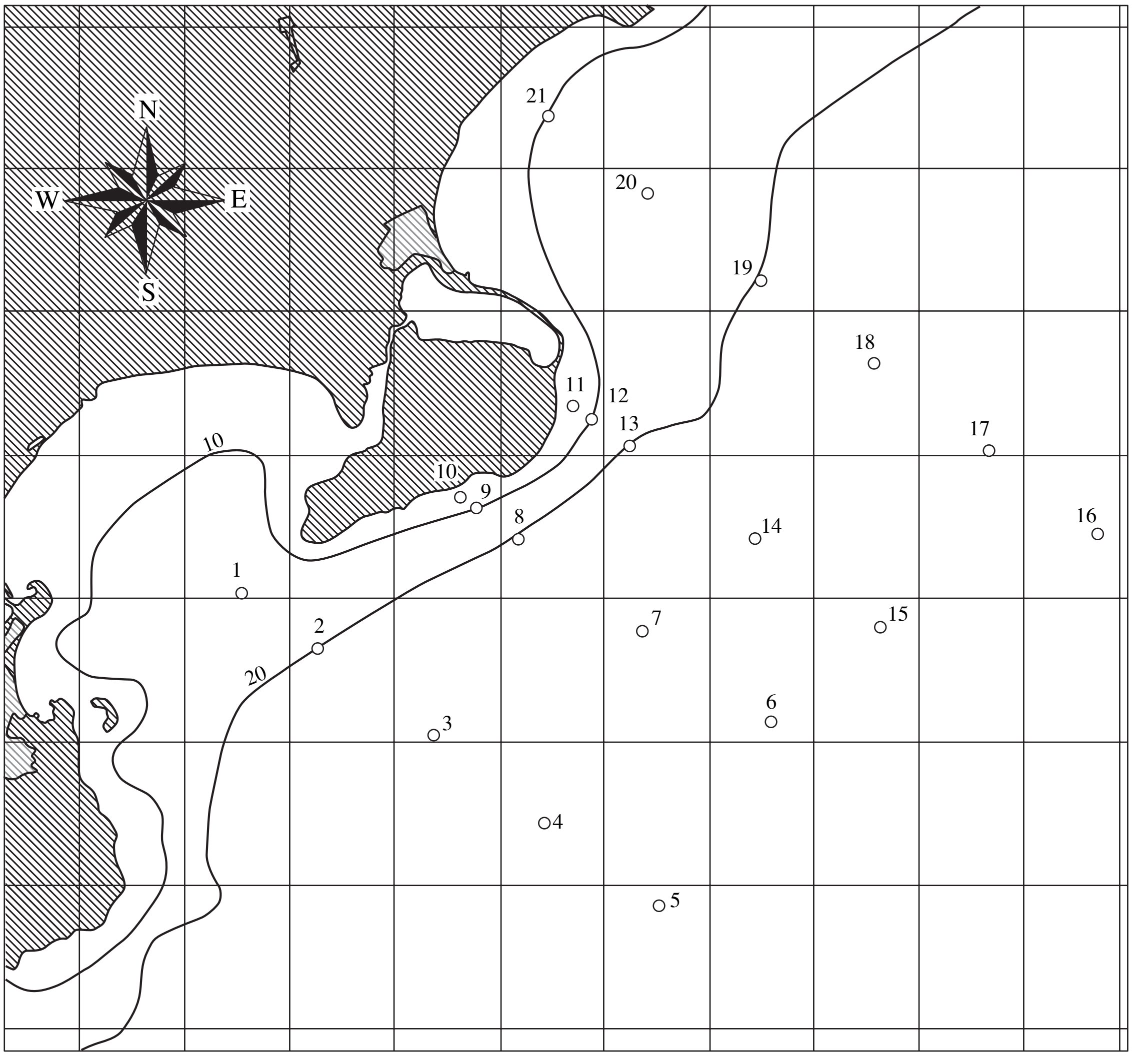

Fig. 1. Sampling scheme in the southeastern part of the Amur Bay (isobaths are given in m).

The high correlation of lipids and AHC ($r = 0.84$) suggests significant transformation of AHC in the bay waters. This is also supported by lower AHC concentration in C_{org} at coastal site 11 (1.6–5.5% at different horizons) as compared to the more offshore stations (11.1–17.2%, site 13). Oil and oil products falling into the marine environment are very rapidly degraded [3]. The transformation of oil pollutants promotes a rapid decrease in AHC and an increase in polar compounds at the expense of resin and asphaltenes [8].

The PAH contents in the Amur Bay waters varied within 2.8–84.6 ppb. Such a high fluctuation of polyarene concentrations in the bay water provides a standard deviation ($\sigma = 18.9$) comparable with the average value of 18.1 ppb. The elevated contents of both PAH and AHC were found at site 5 in the bottom waters (maximum 84.6 ppb) and the lipids (maximum 537 ppm). The unsubstituted polyarenes are dominated by fluoranthene (FL), chrysen (CH), and perylene (PL). Most samples contain phenanthrene (PH), benzperylene (BPL), pyrene (PR), and naphthalene (NP), with minor anthracene (AN), triphenylene (TR), and benz(a)pyrene (BP). The exceptions are bottom water from site 13, where the BP concentration (7 ppb) is higher than the MPC value (5 ppb). The correlation between lipids and PAH ($r = 0.40$) and between AHC and PAH ($r = 0.51$) is lower than that between lipids and AHC.

The oil nature of PAH in the coastal zone of the study area follows from the high NP concentration and PH/AN ratio > 10, which confirms a significant input of oil polyarenes [9]. The NP accounts for 2% of dissolved PAH, reaching maximum at site 9 (4.5%). The maximum PH/AN ratio of 31.8 was found at proximal site 1. In addition, in areas with the constant PAH inflow, anthropogenic PAH, mainly represented by products of high-temperature pyrolysis of organic material (pericondensed PAHs, such as PR, BP, BPL, and others), The content of organic compounds in bottom sediments

Site	Depth, m	Sediment	Horizon, cm	Moisture, %	C_{org}, %	AHC		PAH				
						ppm	% of C_{org}	Total, ppb	% of $C_{org} \cdot 10^{-3}$	PH/AN	(PR + BP)/(PH + CH)	PR/PL
1	14	Glay	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	Glay	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	Glay	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	Glay	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	Glay	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	Glay	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	Glay	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	Glay	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	Glay	0–3	40.58	0.558	577.9	10.36	170.1	3.05	0.94	2.43	0.59
15	34	Glay	0–3	62.89	2.783	115.5	0.42	–	–	–	–	–
17	33	Glay	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	Glay	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	Glay	0–2	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	Glay 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

Note: (PH) Phenanthrene; (AN) anthracene; (PR) pyrene; (BP) benz(a)pyrene; (CH) chrysene; (PL) perylene.

dominate over PAH formed in natural processes (PH, CH) [3, 10]. If pyrogenic input is absent, the (PR + BP)/(PH + CH) ratio is typically more than 1, reaching up to 20 in water areas with a constant inflow of pollutants [3].

This ratio is close to zero at some sites characterized by trace contents of PR and BP. At the same time, sites 5 and 8, with relatively high contents of polyarenes, are characterized by higher values of this ratio (36.6–42.1), which is significantly higher than those in the riverine waters within industrial centers (in particular, in the waters of the Vilnyale River within the city of Vilnius [11]).

The AHC content in bottom sediments varied within 168–2098 ppm (table), which accounts for 0.42–19.47% of C_{org} (average 4.2%, $\sigma = 4.6\%$). The fluctuation of AHC contents in bottom sediments (the average value for silts is 618.8 ppm, $\sigma = 530$ ppm) is higher than that for C_{org} (average 1.83%, $\sigma = 0.81\%$). The AHC concentration is not controlled by grain size in the avalanche sedimentation zones and in areas of large-scale input of oil products [3]. Actually, the elevated contents of C_{org} are confined to the central parts of the study area, while the AHCs are mainly accumulated in the coastal zones. Therefore, one can see different geochemical relations between C_{org}, moisture content (M) of sediments (controlled by granulometric composition), and AHC. For example, $r(\text{M–C}_{org}) = 0.77$, $r(\text{M–AHC}) = 0.12$, $r(\text{C}_{org}\text{–AHC}) = 0.011$.

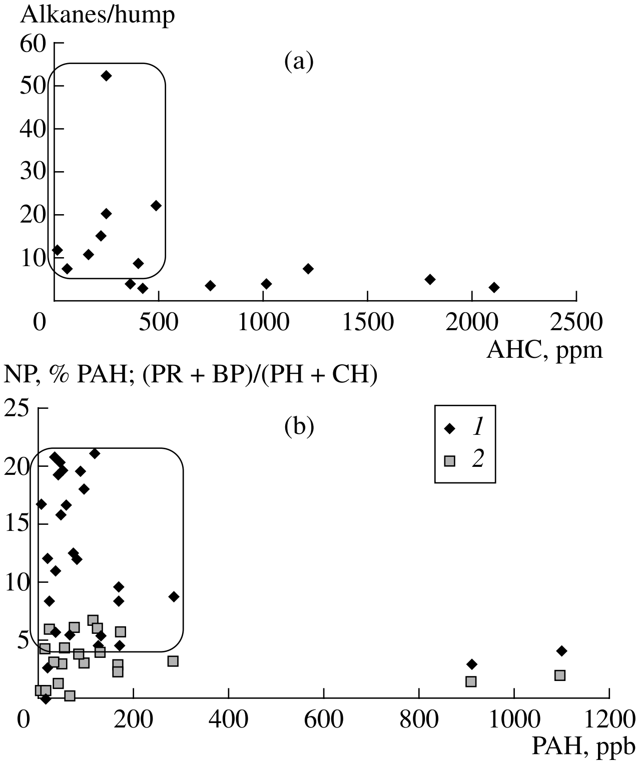

Fig. 2. Distribution of markers in HC depending on their total content and regions of stronger influence of anthropogenic factors: (a) AHC, (b) PAH. (*1*) Naphthalene fraction in PAH (%); (*2*) (PR + BP)/(PH + CH).

In modern marine bottom sediments, the AHCs usually account for only tenths and occasionally hundredths the fraction of C_{org} [12]. According to our data, the AHC concentration in the C_{org} composition of the bottom sediments of the Amur Bay is as much as 19.5%, indirectly suggesting elevated inflow of anthropogenic HC in bottom sediments. If the anthropogenic AHC concentration in water (even related to passive sorption) is high, their share in the C_{org} composition of sandy deposits can increase [3]. Therefore, the AHC concentration in the coarse-dispersed sediment of site 12 (19.5%) is higher than that in silts from nearby site 13 (0.94%).

In the most proximal area, AHC markers testify to the predominance of weathered oil HC. Alkanes are characterized by an even distribution of homologues in the high-molecular region and, as a result, low CPI ratio (the ratio of odd and even homologues) of 1.03–1.47. The hump of naphthene aromatic compounds is more than five times higher than the average content of *n*-alkanes (on the average, 271 and 52 ppb, respectively). The ratio of light and heavy compounds varied within 0.17–0.34. For comparison, the content of naphthene aromatic hump was as high as 1300–1500 ppm near Baku, while the total content of *n*-alkanes in the sediments was 15–17 ppm [9]. Only alkanes from peripheral sites of the study area were affected by terrigenous components, as shown by the increase in CPI. The absence of the influence of autochthonous alkanes on bottom sediments is presumably caused by low temperatures in April, preventing development of biogenic processes. For the same reason, pristane dominated over heptadecane in all samples: the Pr/n-C_{17} ratio varied from 1.07 to 15.

The table shows that the PAH concentration (on a dry weight basis) varied from 7.2 to 1100 ppb (average value 162 ppb, $\sigma = 260$ ppb) in the bottom sediments and 132 ppb ($\sigma = 272$ ppb) in the bottom sediments. Omitting the concentration in sediment from site 19, the average value is 63 ppb ($\sigma = 52$ ppb). The different (oil, pyrogenic, and biogenic) sources of HC and the complexity of biogeochemical processes in shallow waters presumably results in such a wide variation of their concentration. The same factors are responsible for the absence of correlation between AHC and PAH in sediments: r(AHC–PAH) = 0.26, r(C_{org}–PAH) = –0.21. However, as for AHC, the maximum concentration of polyarenes was found at site 19 in the depth drop zone.

The oil nature of PAH in sediments is seen from the elevated NP contents (average 10%, maximum 21%) and the average PH/AN ratio of 3.9 (maximum 47). Most sediments demonstrate high values of (PR + BP)/(PH + CH) and PR/PL ratios (>1), while FL/(Fl + PR) < 0.5, indicating the presence of pyrogenic polyarenes [3, 13]. Since PL is typically considered as a polyarene of the geochemical background [10, 11], its variations in PAH serve as an indicator of diagenetic transformations. In the samples under study, the PR content is higher than the PL concentration, which also indicates a pyrogenic nature of polyarenes in sediments.

It should be noted in conclusion that the average AHC concentration in the water of the study area is two times higher than their level in coastal waters (15–20 ppm [3]). However, the AHC concentration is lower than that in other waters with constant oil inflows. In particular, the AHC content in the Zolotoi Rog Bight (Amur Bay) was as much as 2000–2740 ppm (average 10–150 ppm) [6]. The concentration of dissolved PAH (on the average, 18 ppb) is comparable with the concentration in the coastal waters (18–22 ppb) [3]. At the same time, waters at the test site show high contents of polyarenes (40–85 ppb), which is two to four times higher than the background.

In the surface layer of bottom sediments, the AHC concentrations were higher than 100 ppm (biogenic background level in silts [3, 9]) and were as much as 500–1000 ppm at many sites, which is comparable with their concentration in harbor waters. In particular, the AHC concentration was as much as 1415 ppm in the Cartagena Bay (Caribbean Sea) [14] and 671 ppm in the Persian Gulf [15]. However, the elevated *n*-alkanes/naphthene–aromatic hump ratio, which marks weathered oil products in the sediments of the southeastern Amur Bay, was found at AHC concentrations of no more than 450 ppm (Fig. 2a), with a maximum ratio of 20.2 at an AHC concentration of 248 ppm.

In terms of PAH concentration, the sediments of the study area can be ascribed to weakly polluted sediments, because the total content of three to six annulated polyarenes is mainly less than 100 ppb [9]. At a constant inflow of pollutants, the PAH concentration in the bottom sediments is typically >1000 ppb, while sediments become toxic at a PAH concentration of >4000 ppb. Even at site 19 (table), the (PR + BP)/(PH+ CH) ratio was only 1.7 and 0.2 at a PAH concentration in the surface and subsurface layer of 1100 and 285 ppb, respectively. At the same time, this ratio at lower PAH contents in sediments is significantly higher (table, Fig. 2b). Therefore, the degree of sediment pollution by pyrogenic and oil polyarenes does not depend on total PAH concentration. Evidently, OM was buried together with PAH in the intense sedimentation zones. In particular, the PAH concentration reaches 555–815 ppb, while (PR + BP)/(PH + CH) < 1 in sediments in the Bengel upwelling zone near the coast of southeastern Africa, where pollution is virtually absent [3].

Thus, the total HC content in water and bottom sediments cannot serve as the measure of their pollution even in coastal areas with a constant inflow of pollutants (southeastern Amur Bay). The influence of anthropogenic HC is better recorded by molecular markers. Therefore, the degree of water pollution can be estimated not only by comparison of measured concentrations with the MPC value but also on the basis of HC composition.

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REFERENCES

1. N. A. Aibulatov, *Activity of Russia in the Coastal Zone and Ecological Problems* (Nauka, Moscow, 2005) [in Russian].
2. *GESAMP Joint Group of Experts on the Scientific Aspects of Marine Pollution. Reports and Studies. No. 50* (IMO, London, 1993).
3. I. A. Nemirovskaya, *Hydrocarbons in Oceans (Snow–Ice–Water–Bottom Sediments)* (Nauchnyi Mir, Moscow, 2004) [in Russian].
4. V. I. Petrova, G. I. Batova, M. A. Galishev, and G. I. Ivanov, Oceanology **4**, 490 (1999) [Okeanologiya **4**, 539 (1999)].
5. A. V. Tkalin, T. A. Belan, and E. N. Shapovalov, Mar. Pollut. Bull. **26**, 418 (1993).
6. E. S. Lebedeva, in *Geoecology of Shelf and Coasts of Russian Seas* (Noosfera, Moscow, 2001), pp. 289–327 [in Russian].
7. V. V. Anikeev, I. A. Nemirovskaya, and M. Yu. Urbanovich, Geokhimiya, No. 10, 1525 (1994).
8. A. N. Kuznetsov, Candidate's Dissertation in Geography (Rostov-on-Don, 2005) [in Russian].
9. I. Tolosa, S. Mora, M. R. Sheikholeslami, et al., Mar. Pollut. Bull. **48**, 44 (2004).
10. F. Ya. Rovinskii, T. A. Teplistkaya, and T. A. Alekseeva, *The Background Monitoring of Polycyclic Aromatic Hydrocarbons* (Gidrometeoizdat, Leningrad, 1988) [in Russian].
11. S. A. Zaretskas and I. A. Nemirovskaya, Vodn. Res., No. 3, 136 (1991).
12. N. B. Vassoevich, in *Nature of Organic Matter in Recent and Fossil Sediments* (Nauka, Moscow, 1973), pp. 11–59 [in Russian].
13. M. B. Yunker, L. R. Snowdon, R. W. Macdonald, et al., Environ. Sci. Technol. **30**, 1310 (1996).
14. C. H. Pargo-Losano, A. J. Marrugo–Conzalelez, and R. Fernandez-Maestre, Mar. Pollut. Bull. **44**, 71 (2002).
15. S. W. Fowler, J. W. Readman, B. Oregioni, et al., Mar. Pollut. Bull. **27**, 171 (1993).