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GEOGRAPHY

Indicators of the Pollution of Surface Waters of the Lake Baikal Watershed by Polycyclic Aromatic Hydrocarbons

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Abstract—The content of polycyclic aromatic hydrocarbons (PAH), organic carbon (C_{org}), and mineral nitrogen (N_{min}) in waters of Lake Baikal and its tributaries were analyzed. On the basis of these data, the indicators of the water composition, for Baikal Lake and its tributaries, were worked up for the first time. These indicators—the anthropogenic impact on the ecosystem (PAH/C_{org}) and the indicator of the capacity of the ecosystem to neutralize pollution (N_{min}/C_{org})—show a link between water pollution and the conditions of the watershed basin. It was established that (PAH/C_{org}) and (N_{min}/C_{org}) can be used simultaneously as tracers to calculate the tributary input into organic matter of the lake. It was also revealed that N_{min}/C_{org} is inversely proportional to the C_{org} concentration and directly proportional to N/C in the soil humus. On the basis of the indicators, the watershed areas and water area of the lake were distinguished. The areas are characterized by different levels of the pollution, self-purification capacity, and concentration of carbon in surface waters.

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Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with mutagenic and carcinogenic properties. Lake Baikal is the largest source of drinking water in Eastern Siberia; therefore, the estimation of PAH pollution of the lake and its tributaries is a timely task. Considering the lake water as a mixture of tributary waters, the connection between them is judged by the concentration of the substances studied: in some tributaries the concentration is always higher, while in others it is lower than in the lake. This approach is justified for inorganic substances, because they are scarcely wasted in the intra-waterbody processes. Therefore, based on the comparisons of mineralization, the Sr concentration, etc., in the waters of the Selenga River and Lake Baikal, it was concluded that the input of this tributary into the water composition of Lake Baikal dominates [1, 2]. However, this approach is not applicable to PAHs, because the PAH concentrations in the lake and the tributaries differ by several times (Fig. 1).

PAHs entering with waters of the tributaries are continually utilized by photodecomposition and biodegradation with subsequent emission into the atmosphere in the form of CO_2 or by dissolution in water in the form of HCO_3. The hydrophobic properties of PAHs also encourage their subsidence to the bottom

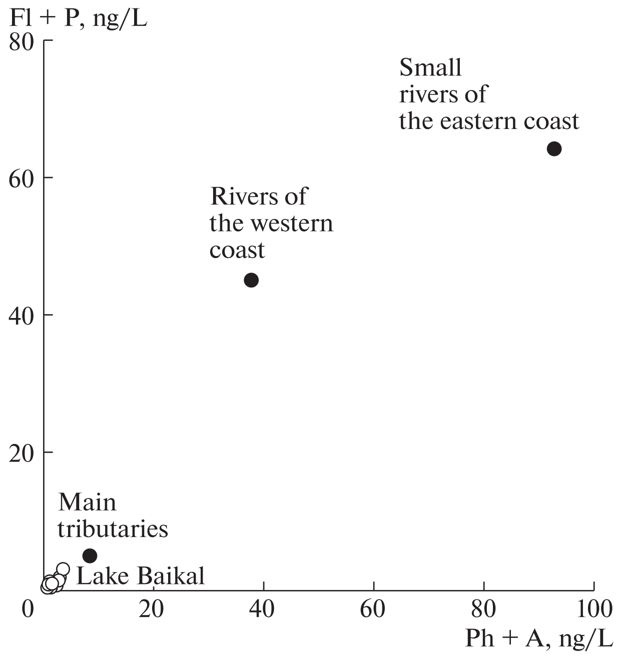

Fig. 1. PAH concentration in the water of Lake Baikal and its tributaries (here and in the other figures, the mean values are designated by black dots).

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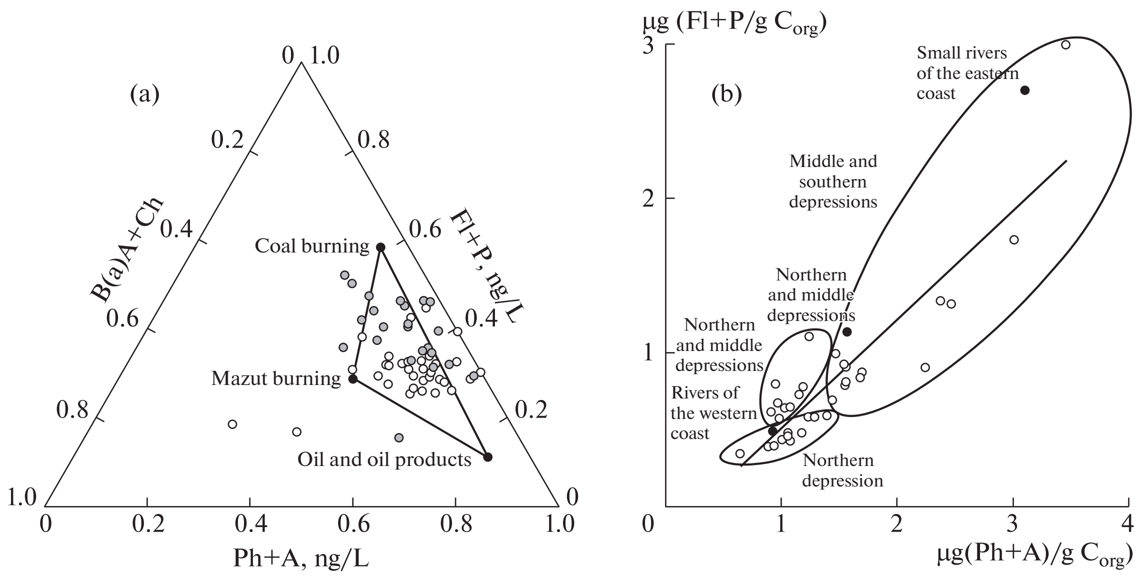

Fig. 2. Normalization of PAH concentrations in the water of Lake Baikal (white dots) and its tributaries (gray dots) (a) to reveal the emission sources and (b) estimate the intensity of pollution.

with suspended matter. The purpose of this work was to estimate comprehensively PAH pollution of the water objects in the Lake Baikal basin on the basis of the nondimensional indicators of the chemical composition of waters.

For this purpose, the indicators were sought and approbated to reveal the PAH sources and pollution levels and to estimate the tributary input to the lake pollution and self-purification capacity of the waters.

Data on the content of PAHs and several natural components in the lake and river waters were used. To determine PAHs, we sampled water at the end of May and beginning of June in 2015 and 2016. Because of the low concentration, PAHs were determined in unfiltered water samples. Substances with the maximum concentrations were considered: phenanthrene (Ph), anthracene (A), fluoranthene (Fl), pyrene (P), benz[a]anthracene (B (a) A) and chrysene (Ch). The data on the May and June concentrations of the natural components in the tributaries were obtained in part by the authors and in part taken from published sources [1, 3]. Information about the natural components of Lake Baikal was taken from the publications reflecting results of the current episodic observations [4–8] or perennial monitoring [8, 10]. No considerable differences in the values and spatial distribution of the concentrations of the elements were revealed. The connection between waters of the tributaries and Lake Baikal was judged on the basis of the proximity of their points in the mixing diagrams. For convenience, all tributaries were divided into three categories according to the specific features of the chemical composition. The water sample (point) from Lake Baikal lies within the mixing field bordered by the lines connecting the tributary points. This water sample is polluted by all rivers. The water sample lying beyond this field is polluted only by the tributaries that border the side adjacent to the sample; the closer the sample to the tributary, the more significant its contribution.

It was established that the normalization of the concentrations of several PAHs on the basis of other PAHs (in our case, on the sum of concentrations) indicates the emission sources (Fig. 2a). Therefore, the PAH composition for both Lake Baikal and the tributaries is determined by the PAHs of oil and oil products and mazut and coal boilers. The oil share is higher in Baikal, because the river samples lie above the lake samples in relation to this source. Such differentiation shows that the oil sources are mostly situated in Lake Baikal itself [11]. In addition, the variance is attributable to a different amount of suspended matter, because PAHs were determined in unfiltered water samples: heavier Fl, P, B (a) A, and Ch, which are typical for boiler-house emissions, are sorbed on organic particles present in the rivers in larger amounts.

To estimate the pollution level, it is necessary to reconcile the PAHs in all samples to the C_{org} content (Fig. 2b). The resulting ratio of PAH/C_{org} is the relative contents of PAHs or the enrichment of organic matter (OM) by PAHs. Organic matter of the rivers of the western coast (Krestovka, Goloustnaya, and Buguldeika) is less enriched in PAHs. The maximum enrichment is observed for the rivers of the southeastern coast (Slyudyanka, Snezhnaya, Utulika, and Pereemnaya). Intermediate values are typical for the waters of the large tributaries (Selenga, Verkhnyaya Angara, and Bargusin). The most significant pollution of the rivers is caused by the northwestern transportation of pollutants [12] and an enormous amount of

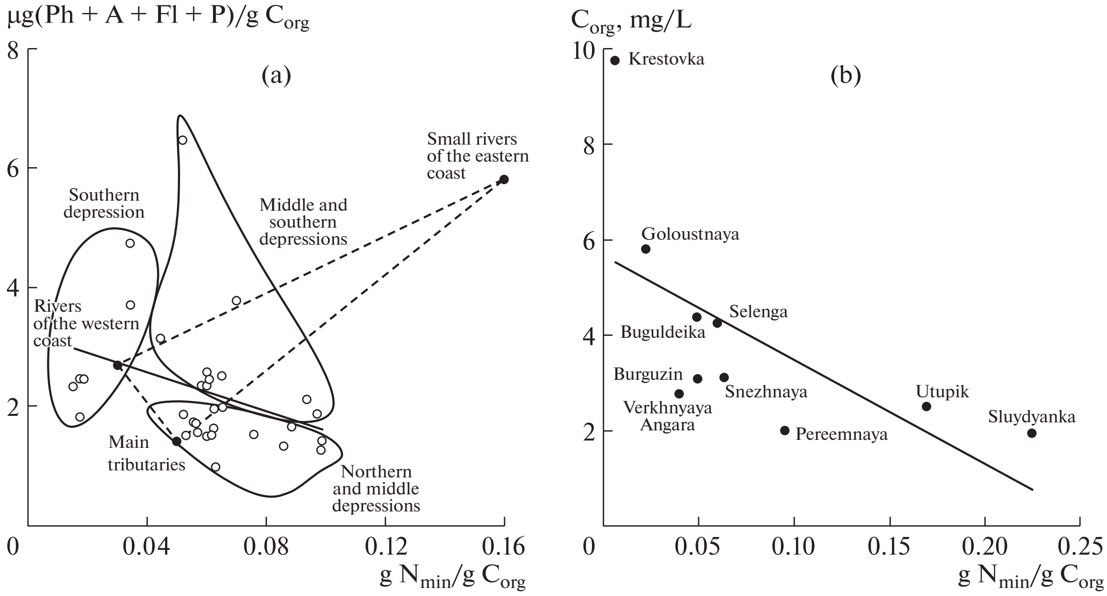

Fig. 3. The dependence of (a) the relative PAH content in the water of Lake Baikal and (b) the C_{org} concentration in the waters of its tributaries on the intensity of OM mineralization.

precipitation [11, 12]. The relative content of PAHs in the waters of Lake Baikal grows from north to south. The pollution of the Middle Baikal waters is likely associated with natural oil seepage.

To estimate the contribution of the tributaries to the pollution of Lake Baikal, the water of the lake was considered as a mixture of waters of the tributaries. The presence of three components of the mixture (categories of tributaries) suggests the use of two negatively correlated substances as the tracers [13]. Therefore, PAHs and N_{min} were used. The negative correlation between them is due to the attribution of PAHs to the surface runoff and N_{min} to the soil-ground and underground runoff [2]. Like PAHs, N_{min} was normalized to C_{org}. Figure 3 shows that the enrichment of organic matter by PAHs decreased with an increase in the N_{min} content, i.e., PAHs are decomposed simultaneously with natural OM, from which nitrogen is released. Therefore, N_{min}/C_{org} can be considered an indicator of OM mineralization. The close values of N_{min}/C_{org} in the waters of Lake Baikal and its main tributaries show the high value of their contribution to the pollution of the lake and confirm the current hypothesis on the allochthonous origin of OM of Lake Baikal [6–8]. The small contribution of the small rivers of the eastern coast is caused by the high mineralization of OM in spite of the high enrichment in PAHs. The high mineralization makes OM a bioavailable substance and encourages its decomposition by lake bacterioplankton. Waters of the rivers of the western coast with a high content of OM probably participate in the pollution of Southern Baikal along with the main tributaries. The high OM content in these rivers compensates for its low enrichment in PAHs.

Though the OM content in Lake Baikal is mostly due to the processes within the water body, the revealed dependence of the PAH content on OM mineralization is nonetheless valuable. This means that the water areas where the ratio of N_{min}/C_{org} is higher and the enrichment of OM by PAHs is lower than in the tributaries or other areas are characterized by a higher rate of self-purification. In this case, the smallest rate is observed in Southern Baikal because of pollution by the waters of the western tributaries. The high contribution of the main tributaries means a similarity in the OM composition between them and Lake Baikal and, consequently, their eutrophication, because the share of the phytoplankton participating in OM formation has to be smaller in the rivers than in the lake. The water areas of Lake Baikal with a different self-purification capacity were distinguished on the basis of N_{min}/C_{org} (Fig. 4a).

To estimate the spatial variability of the self-purification capacity of the river waters, the relationship between the N_{min} and C_{org} contents in the land ecosystems was analyzed. In the process of OM decomposition in soils and draining waters, N_{min} increases and C_{org} decreases [14], i.e., the self-purification capacity of the river N_{min}/C_{org} is inversely proportional to the C_{org} concentration (Fig. 3b). Due to the fact that the increase in temperature enhances OM decomposition, an increase in N_{min}/C_{org} and decrease in C_{org} are expected from north to south and with a decrease in the land elevation (Fig. 4b). Actually, the smallest C_{org} concentrations are observed in the rivers of the eastern

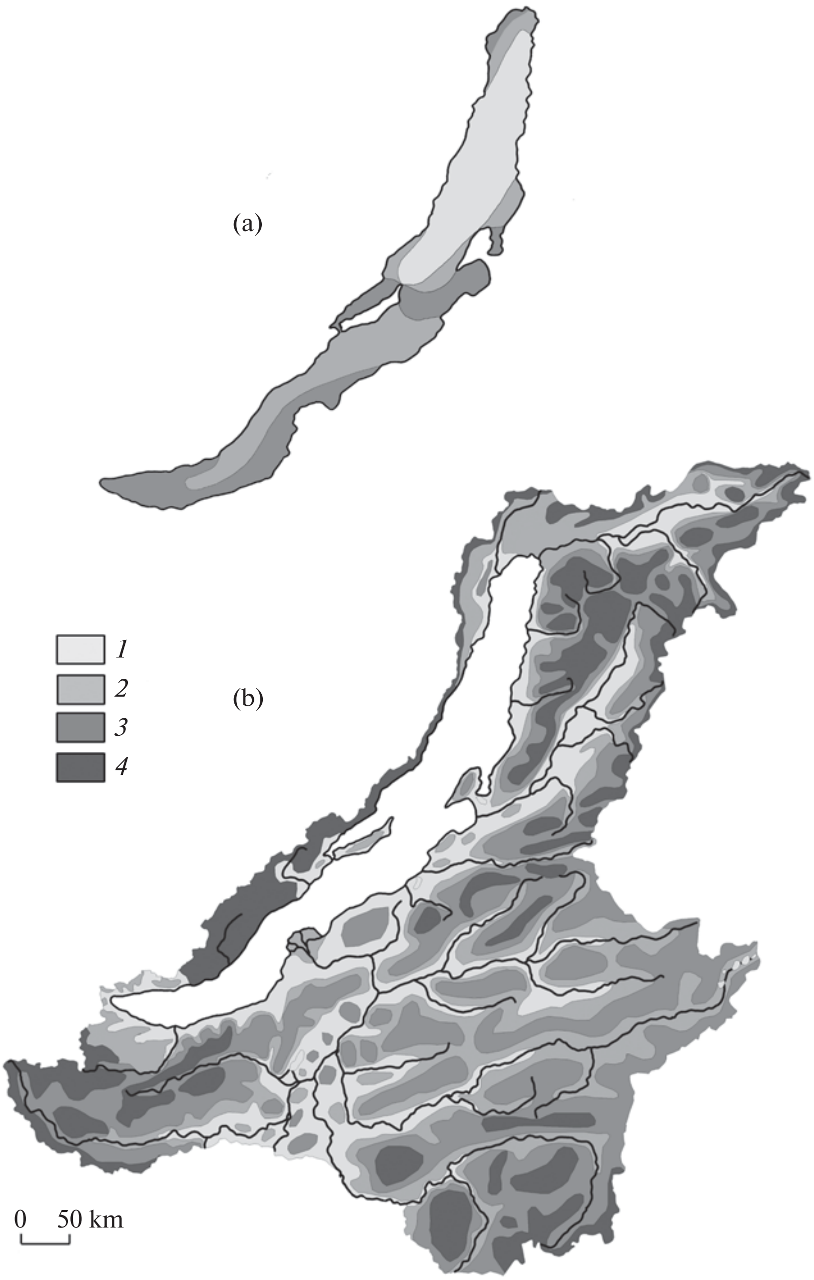

Fig. 4. Self-purification capacity of (a) the waters of Lake Baikal and (b) river waters of its basin: 1, high ($N_{min}/C_{org} > 0.8$); 2, medium–high ($N_{min}/C_{org} = 0.8–0.6$); 3, medium–low ($N_{min}/C_{org} = 0.6–0.4$); 4, low ($N_{min}/C_{org} < 0.4$); C_{org} content in the river waters of Lake Baikal (b): 2–3 mg/L (*1*), 3–4 mg/L (*2*), 4–5 mg/L (*3*), >5 mg/L (*4*).

coast; brown soils, developing under positive mean annual temperatures, dominate in the basins of these rivers. The highest C_{org} concentrations are observed in the rivers of the western coast, which drain the cool soils of the podzolic row. For the largest tributaries, the basins of which differ by the great diversity of bioclimatic conditions, medium C_{org} concentrations are typical. The ratio of N_{min}/C_{org} also decreased within the slopes, where the surface runoff dominates, and increased in the valleys (excluding swamped areas), where the soil-ground and underground runoffs dominate.

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