# Polycyclic aromatic hydrocarbons in waters of tributaries of South Baikal

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Results on seasonal and interannual variability of the priority PAH concentrations in waters of the rivers flowing to South Baikal are presented. The degree of pollution of tributary water is estimated based on sanitary-and-hygienic norms.

## Introduction

Polycyclic aromatic hydrocarbons (PAH) are included into the set of priority pollutants and are to be controlled in the environmental objects. Narrow series of priority compounds has been selected for continuous control from hundreds of PAH of different composition observed in natural objects. In Russia, it is only benz(a)pyrene, in European Union there are 6 compounds, and in the USA there are 16 such compounds. The main sources of PAH are plants producing aluminum, enterprises of oil and chemical industry, heat-and-power engineering, motor transport. PAH in the atmosphere are mainly sorbed on solid aerosol particles. Powerful natural sources of PAH in Eastern Siberia are forest fires. PAH come to the rivers of South Baikal mainly due to dry sedimentation of aerosol particles containing them and due to washout by atmospheric precipitation.

Mountains around South Baikal and frequent inversions prevent the exchange between the air masses over the lake and above the surroundings. As a result, technogenic emissions containing PAH propagate along the lake coast and ascend the upper reaches of the rivers along river valleys, which become the places of localization of the technogenic emissions by settling onto the catchment area. Rivers, flowing from northwest slopes of Khamar-Daban ridge occupy small catchment areas (except for river Snezhnaya) but are characterized by high absolute value of the modulus of flow due to significant height of the territory and favorable orientation along the northwest direction of moisture transfer. In Baikal region, the greatest rainfall occurs on the northwest slopes of Khamar-Daban ridge (up to 1500 mm a year), while the rainfall in steppe valley of river Selenga protected by ridges is no more than 250 mm a year. The height of snow cover in the basin of Lake Baikal also changes in a wide range from 200 cm on the slopes of Khamar-Daban ridge to 10 cm in the valley of river Selenga. Prevalence of snow supply and late spring (May) high water are characteristic of rivers of South Baikal.[1] River waters and atmospheric precipitation in the lake basin are studied for already more than 50 years, and the principal peculiarities of the formation of their chemical composition have been revealed during this period.[2,3] Intensive development of industry in Baikal region led to the change of the composition of atmospheric precipitation[4,5] and to the increase of concentrations of the polluting components in the river waters.[6,7]

## Materials and methods

To estimate the levels of the PAH concentrations, investigations were carried out in the mouths of rivers Selenga, Mishikha, Pereemnaya, Snezhnaya, Khara-Murin, Solzan, and Utulik in different seasons of 1996 and 1997 and in May of 2004 and 2005 (Fig. 1).

Collection of snow samples was carried out inside the settlements and at mouths of rivers in March 2005 over the entire depth of snow cover. The samples were prepared for analysis of PAH in snow according to the technique from Ref. 8. Samples of water were collected to glass bottles. The PAH fraction was isolated from water by extraction using $n$-hexane. The extracts were evaporated in a rotational evaporator. Analysis of PAH in extracts was carried out using the "Agilent, GC 6890, MSD 5973 Network" chromato-mass-spectrometer in the Center of Joint Use of LIN SB RAS "Ultramicroanalysis". Different substances were identified according to the time of retaining the peaks on the chromatograms and from the mass-spectra using the database. Quantitative determination of PAH was carried out using the inner standards of "Supelco" corporation, USA: phenanthrene d10, chrysene d12 and perylene d12. The error in measurements did not exceed 10%.

## Results and discussion

Maximum levels of accumulation of PAH in snow cover of the south coast of Baikal are observed in the region of Slyudyanka – 170 μg/m$^2$ that is caused by a significant number of small boiler-houses in the city. Besides, Trans-Siberian railway and a highway pass through this city. The enhanced levels of accumulation, but less than in Slyudyanka are observed

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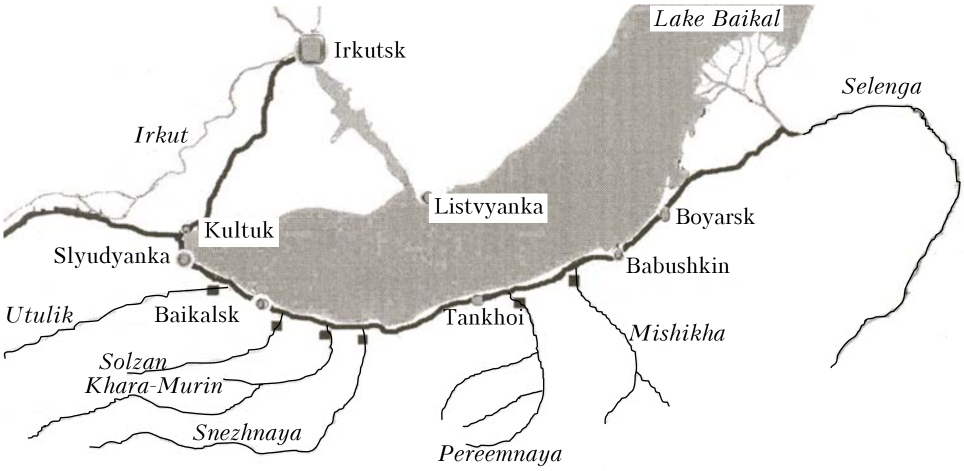


**Fig. 1.** Map-diagram of collection of water samples: black squares correspond to points of collecting samples.

on the territories of small settlements on the south coast of the lake: Kultuk (30 μg/m$^2$), Tankhoi (75), Boyarsk (30). The content of PAH in the samples collected in the region of Baikalsk and in the mouth of river Solzan is low – 28 μg/m$^2$. The observed level of accumulation can be provided both by effective clearance of gaseous emissions of Baikalsk Pulp and Paper Mill and by their spread over vast areas. The level of accumulation of PAH in snow cover in the mouths of rivers of south coast of Lake Baikal is comparable with that in the regions of settlements (r. Utulik – 38, Khara-Murin – 37, Snezhnaya – 60, and Pereemnaya – 90 μg/m$^2$). Minimum level of accumulation of PAH is observed in snow cover of the mouth of river Selenga where the less quantity of precipitation has been fallen, about 10 μg/m$^2$ as low.

Thus, the values of accumulation of PAH in snow cover on the south coast of Lake Baikal exceed that observed in background regions, but are several orders of magnitude lower than in large industrial centers of Baikal region – Irkutsk (400 μg/m$^2$) and Shelekhov (7 thousands μg/m$^2$).[9]

High concentrations of ecotoxicants in water of tributaries of Lake Baikal are observed in spring (Fig. 2) resulting from intense melting of snow, in which PAH are accumulated during the entire cold season.

As was mentioned above, accumulation of pollutants in snow cover in the mouth of river Solzan is lower than in valleys of rivers Utulik and Khara-Murin, and, hence, the same regularity is observed for concentrations in water of the rivers. We assume that emissions of Baikalsk Pulp and Paper Mill, which has high stacks and emissions from them propagate to long distances,[10] affect the pollution of water of tributaries Utulik and Khara-Murin. Emissions of Slyudyanka town also can cause enhancement of concentrations of PAH in water of river Utulik.

Additional source of ecotoxicants in catchment areas of rivers of the south coast of Lake Baikal can be regional atmospheric transfer of PAH along the valley of Angara river. Wet airflows of prevalent northwesterly transfer cause the enhanced rainfall on the slopes of Khamar-Daban ridge that favors enhancement of concentration of pollutants in water of rivers. It is confirmed by the presence of the enhanced concentration of PAH in rivers Snezhnaya and Pereemnaya in comparison with other tributaries of South Baikal. Moreover, the catchment area of Snezhnaya river (3000 km$^2$) is significantly greater than the catchment areas of other rivers of Khamar-Daban ridge.[1]

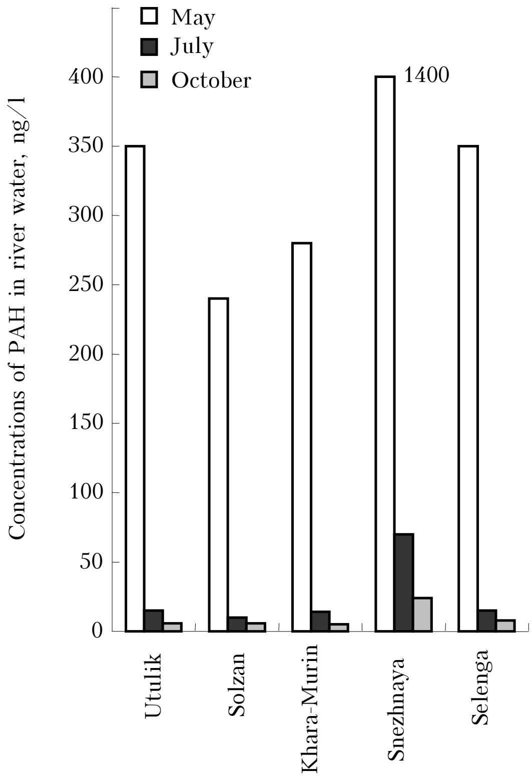


**Fig. 2.** Concentration of PAH in water of tributaries of Lake Baikal in different seasons of 1996.

Regularities of the interannual dynamics of the concentrations of PAH in water of Selenga river are the same as in rivers flowing down from northwest slopes of Khamar-Daban. Concentrations of PAH in

Selenga and Snezhnaya rivers are close to each other, although these tributaries are different in water amount and the absolute value of the water yield.[1] Additional sources of PAH in water of Selenga river are enterprises of Ulan-Ude city, settlements of Selenginsk and Kamensk. The concentrations of individual PAH near the right bank of the river, where the main part of Ulan-Ude and Selenginsk Cardboard Industrial Complex have been situated, are 3 to 8 times higher than near the left bank. The concentrations of PAH in water decrease in August and October (6–70 ng/l), as water yield from the territory of the basin decreases.

Interannual differences in the concentrations of PAH (Table) are related to both ecological situation in the region and meteorological conditions in the considered years.

The extremely high values in May of 1996 (up to 1400 ng/l) can be explained by strong forest fires on the territory of Baikal region, when the area of burnt forest was 370 thousand ha. Concentrations of benz(a)pyrene in waters of Snezhnaya river in this period exceeded the maximum permissible concentration (MPC) by 5 times, and in Selenga river by 2 times. The total content of 6 PAH (benz(a)pyrene, benz(b)fluoranthene, benz(k)-fluoranthene, benz(g,h,i)perylene, indeno(1,2,3-c,d) pyrene, fluoranthene) in water of Snezhnaya river was 500 ng/l that was 2.5 times greater than MPC for natural and drinkable water accepted in West European countries.[11] Relatively low concentrations of PAH were determined in water samples collected during 1997, except for water of rivers Pereemnaya and Utulik. As is seen in the Table, the observed concentrations of PAH in water of tributaries in May 2004 were 2 and more times higher than the spring values in 2005. Such differences can be explained by enhanced rainfall on the catchment areas of rivers in 2004 (Fig. 3). The 1.2 times excess of the benz(a)pyrene concentration was observed in Snezhnaya river.

The observed concentrations of benz(a)pyrene in river waters are higher than the level of the background concentrations (0.05–6.7 ng/l) determined in the basin of Lake Baikal on the territory of Barguzin Biospheric Reserve in water of Bolshaya river.[12]

The composition and ratio of individual PAH in the samples of natural objects make it possible to identify the dominant sources of pollutants. Among the identified PAH (10 priority compounds), the highest concentrations in surface waters were observed for phenanthrene, fluoranthene, and pyrene: 60–480, 40–185, and 30–330 ng/l, respectively. Their total quantity reached 86% of the total mass of the observed compounds, and 2% of benz(a)pyrene observed in Russia.

**Concentrations of PAH (ng/l) in water of tributaries of South Baikal in spring**

| River | Year | Phenanthrene | Fluoranthene | Pyrene | Benz(a)anthracene | Chrysene | Benz(b)fluoranthene | Benz(k)fluoranthene | Benz(a)pyrene | Benz(g,h,i)perylene | Indeno(1,2,3-c,d)pyrene | Sum of PAH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Utulik | 1996 | 285 | 35 | 100 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 420 |
| | 1997 | 19 | 41 | 62 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 122 |
| | 2004 | 83 | 8 | 2 | < 0.1 | 1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 94 |
| | 2005 | 7 | 60 | 85 | < 0.1 | 5 | 3 | 1 | 9 | 2 | < 0.1 | 172 |
| Solzan | 1996 | 80 | 38 | 59 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 177 |
| | 1997 | 13 | 10 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 23 |
| | 2004 | 85 | 35 | 53 | 2 | 4 | 5 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 184 |
| | 2005 | 47 | 5 | 2 | < 0.1 | < 0.1 | 1 | 3 | 2 | 6 | 5 | 71 |
| Khara-Murin | 1996 | 75 | 70 | 115 | < 0.1 | 35 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 295 |
| | 1997 | 16 | 9 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 25 |
| | 2004 | 52 | 9 | 5 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 66 |
| | 2005 | 49 | 4 | 4 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 57 |
| Snezhnaya | 1996 | 480 | 185 | 330 | 60 | 90 | 70 | 45 | 50 | 85 | 40 | 1435 |
| | 1997 | 22 | 7 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 29 |
| | 2004 | 186 | 52 | 41 | 2 | 3 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 284 |
| | 2005 | 69 | 8 | 6 | < 0.1 | < 0.1 | 5 | < 0.1 | 12 | < 0.1 | < 0.1 | 100 |
| Pereemnaya | 1997 | 29 | 19 | 30 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 78 |
| | 2004 | 142 | 65 | 86 | 2 | 5 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 300 |
| | 2005 | 34 | 4 | 3 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 41 |
| Mishikha | 2004 | 24 | 27 | < 0.1 | 2 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 53 |
| Selenga | 1996 | 150 | 56 | 75 | < 0.1 | 25 | 20 | < 0.1 | 18 | < 0.1 | < 0.1 | 344 |
| | 1997 | 34 | 10 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 44 |
| | 2004 | 67 | 13 | 6 | 1 | 2 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 89 |
| | 2005 | 77 | 7 | 5 | < 0.1 | 2 | 3 | < 0.1 | 1 | 3 | 3 | 101 |

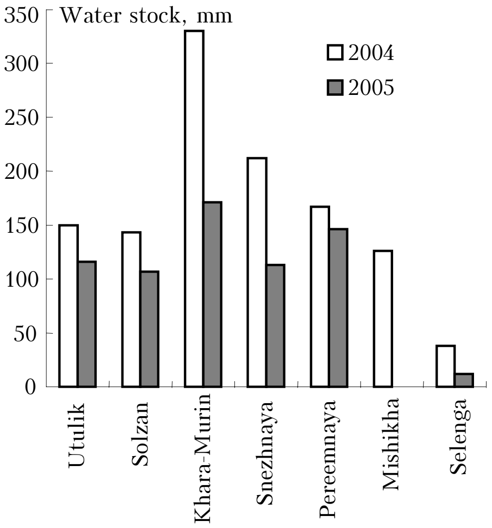


**Fig. 3.** Water stock in winter 2004–2005.

The percentage of phenanthrene, fluoranthene and pyrene in the samples of snow cover and water is evidence of the fact that emissions of municipal power engineering are the dominating sources of pollution of the natural environment on the south coast of Baikal (Fig. 4).

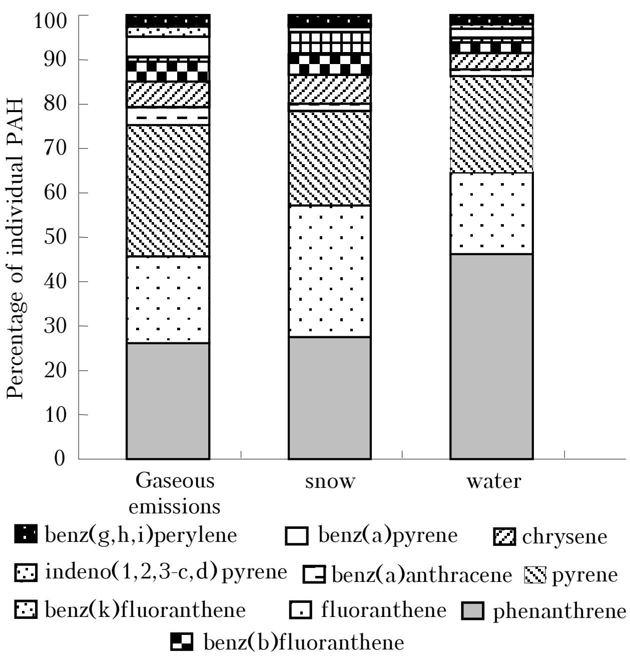


**Fig. 4.** Percentage of individual PAH in samples of gaseous emissions of enterprises of heat-and-power engineering (from the data of Ref. 14) in snow cover and in water of tributaries of South Baikal.

The fraction of benz(g,h,i)perylene and indeno-(1,2,3-c,d)pyrene, the signs of pollution of the natural environment by motor transport,[13] in the samples is, on the average, about 3%.

# Conclusions

The obtained concentrations of the sum of PAH in tributaries of South Baikal have seasonal and interannual dynamics. It has been revealed that waters of tributaries during spring high water and during forest fires on the territory of Baikal region are characterized by relatively high concentrations of PAH. The dependence of the concentrations of PAH in water on the precipitation during winter is observed. Three compounds, phenanthrene, fluoranthene, and pyrene, are prevalent among 10 priority PAH. The degree of pollution of water of tributaries as compared with the sanitary-hygienic standards has been estimated.

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