Pollution of the Basin of the Lake Baikal: Polyaromatic Hydrocarbons

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Abstract

Concentrations of 23 polycyclic aromatic hydrocarbons (PAH) were determined in the bottom sediments of the tributaries: the Selenga, the Turka, the Khaym, the Barguzin, which provide more than 70 % of the water drainage into the Baikal, and in the bottom sediments of the shallow water regions of the lake: the Zmeevaya bay (Chivyrkuy arm) and the Sor-Cherkalovo bay. It was discovered that the level of pollution with PAH is relatively low; the sum of PAH concentrations for the 23 individual compounds is within the range 1.4–5.2 mg/kg (for 5 compounds, the range is 0.15–1.11 mg/kg). The presence of PAH in the samples of bottom sediments is due to local sources of petrogenic and pyrolytic nature.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) occupy a special position among ecotoxicants. The major part of PAH possess high carcinogenic and mutagenic activity, so they are referred to as the ecotoxicant pollutants of priority [1].

Toxicological investigations of many years allowed revealing PAH compounds which are most toxic for the biota. The Environmental Protection Agency of the USA (EPA US) recommends to monitor 16 compounds; a larger number of the initial compounds and their alkylated derivatives is monitored in the countries of Europe [2]. It should be noted that in Russia only one compound belonging to this class, namely, benz(a)pyrene, is prone to the mandatory state control.

The anthropogenic PAH enter the environment from the production of aluminium (combustion of electrodes), from the operation of heat and power plants (combustion of coal and fuel oil), synthesis of organic compounds, petroleum processing, from internal-combustion engines and from spill of combustive-lubricating materials. In nature, PAH are formed in modern diagenesis and in volcanic activity [3]. Because of multiple sources of PAH emission, their identification is an extremely complicated problem.

The major part of PAH is stable and can be transported in the atmosphere, mainly with aerosol particles, over long distance [4].

Recognition of the Lake Baikal by UNESCO as a region of the World Natural Heritage causes the necessity to examine the level of pollution of the lake with ecotoxicants and to reveal their sources. Determination of PAH in water and bottom sediments of the lake itself was not carried out. By present, an estimation of PAH precipitation on the snow cover near the settlements of the southern Pribaikalia has been carried out [5].

To analyze the arrival of PAH into the basin of the Lake Baikal, we chose the bottom sediments of its tributaries. Since PAH are washed off by the surface water and sorbed by bottom sediments, the latter are depositing media and thus integral indicators of the arrival of PAH into the river basins. We examined the bottom sediments of tributaries: Selenga, Turka, Khaim, Barguzin, which provide more than 70 % of the water run-off into the lake; we also studied the bottom sediments of the shallow water region in the Zmeevaya bay (Chivyrkuy arm) and the Sor-Cherkalovo bay.

EXPERIMENTAL

The samples were taken from the subsurface layer of the bottom sediments, down to 10 cm. The samples were dried at room temperature for 5 days, then sieved through the sieve with a mesh size of 0.5 mm. The preparation of the samples of bottom sediments for analysis included twice-repeated extraction of PAH, purification of the resulting extracts with concentrated sulphuric acid, and passing through the column filled with Florisil. PAH were extracted from 20 g of the bottom sediments twice with 40 and 30 ml of hexane for 30 min and 15 min, respectively, at room temperature. The resulting extracts were treated with concentrated H_2SO_4 till decolorization of the acid. The purified extracts were concentrated with a rotary evaporator till the volume of about 1–2 ml, then till dry, and the dry residue was dissolved in 1 ml of hexane and examined with chromatograph.

Identification and quantitative determination of individual PAHs in the samples of bottom sediments were carried out in the Centre for Ecological Research (UFZ, Leipzig, Germany) with the help of chromatography and mass spectrometry procedure (Hewlett Packard HP 5890 gas chromatograph with the HP 5971 mass spectrometer and HP 7673 auto-sampler). The components to be analyzed were separated with a HP Ultra 2 capillary column 25 m long, with an inner diameter of 0.32 mm and coating 0.52 mm thick. Helium (Linde GmbH, Hoelikrigel-skreuth, Germany) was used as a carrier gas. Temperature of the column thermostat was increased from 60 (exposure for 1 min) to 260 °C (exposure for 1 min) at a rate of 10 °C. A standard mixture of deuterated PAH (EC-2044, Promochem, Germany) was used as an internal standard [6].

RESULTS AND DISCUSSION

The results of determination of PAH for the tributaries and for shallow water region are shown in Table 1. One can see that the level of pollution with PAH is relatively small; the sum of PAH concentrations for 23 individual compounds is within the range 1.4–5.2 mg/kg (for 5 individual compounds, within the range 0.15–1.11 mg/kg), which is much below the concentrations of PAH in the subsurface bottom sediments in the arctic seas and in the deltas of northern rivers [7, 8]. In the countries with heavy anthropogenic load, the concentrations of PAH are high in the bottom sediments and bring substantial danger for the river ecosystems and for human health due to high degree of biological accumulation of PAH in fish tissues [9]. For example, the sum of PAH over 14 individual compounds in the bottom sediments of the Yangtze river reaches 11.74 mg/kg [10].

The analysis of the origin of PAH is a complicated problem. The analysis is mainly reduced to the identification of the sources of PAH which are conventionally related to the sources of pyrolytic and petrogenic nature [11]. The former are those in which the formation of PAH occurs in the processes of incomplete combustion of the organic matter, for example in the internal combustion engines. A substantial source of PAH in the Baikal region is forest fire. The sources of petrogenic nature are those in which PAH are formed in the transformation of the plant matter (fossil petroleum, gas and coal, products of processing), as well as those in which PAH are formed during the modern diagenesis in soil and in bottom sediments.

The ratios of individual PAH are used for analysis, which allows one to identify the sources both for the regions with highly developed industry and for arctic regions with relatively low pollution. The PAH concentration ratios widely used

TABLE 1

PAH content of the samples of bottom sediments, ng/kg of dry mass

Compound	Sampling sites									
	A1	A2	A3	A4	A5	B1	B2	C	D	E
Naphthalene	16.4	11.0	n/d	20.0	15.6	10.2	22.8	n/d	n/d	n/d
Biphenyl	12.3	4.4	n/d	13.9	12.2	5.4	12.9	n/d	n/d	n/d
Acenaphthylene	4.9	1.8	n/d	11.1	7.8	2.8	10.6	n/d	n/d	n/d
Acenaphthene	13.8	12.8	n/d	17.9	10.1	9.7	16.3	n/d	n/d	n/d
Fluorene	66.8	27.1	n/d	53.4	67.0	30.9	66.1	n/d	n/d	n/d
Phenanthrene	606.0	80.7	297.0	439.0	353.0	141.0	334.0	547.5	376.5	522.0
Anthracene	58.8	3.1	28.0	12.6	7.1	3.4	90.0	13.2	12.8	23.0
3-Methylphenanthrene	310.0	83.8	n/d	226.0	205.0	90.5	380.0	n/d	n/d	n/d
2-Methylphenanthrene	295.0	83.9	n/d	227.0	232.0	88.3	215.0	n/d	n/d	n/d
4-/9-Methylphenanthrene	2854.0	853.0	n/d	2187.0	1965.0	761.0	2457.0	n/d	n/d	n/d
1-Methylphenanthrene	283.0	86.4	n/d	199.0	208.0	89.1	99.0	n/d	n/d	n/d
Fluoranthene	322.0	60.7	469.5	87.2	128.0	67.0	143.0	305.0	152.5	299.0
Pyrene	12.9	5.1	287.0	28.1	11.3	4.4	29.3	126.5	34.0	231.0
Benz(a)anthracene	29.6	12.9	n/d	12.3	16.7	4.7	18.3	n/d	n/d	n/d
Chrysene	72.1	31.2	n/d	20.2	36.2	18.5	60.4	n/d	n/d	n/d
Benz(b)fluoranthene	93.0	57.5	n/d	14.9	57.0	27.5	100.0	n/d	n/d	n/d
Benz(k)fluoranthene	19.5	15.2	n/d	8.3	15.9	4.7	33.0	n/d	n/d	n/d
Benz(e)pyrene	57.9	52.3	n/d	41.1	35.9	25.9	36.3	n/d	n/d	n/d
Benz(a)pyrene	–	–	29.0	6.9	–	–	3.6	25.0	–	–
Perylene	56.3	13.3	n/d	16.9	12.4	12.7	14.4	n/d	n/d	n/d
Indeno(1,2,3)pyrene	–	–	n/d	–	–	–	15.1	n/d	n/d	n/d
Dibenz(a,h)anthracene	–	–	n/d	–	–	–	21.3	n/d	n/d	n/d
Benz(ghi)perylene	–	–	n/d	9.5	3.4	–	20.6	n/d	n/d	n/d
Sum of PAH 23 compounds	5184.3	1496.2	–	3652.3	3399.6	1397.7	4299.0	–	–	–
Sum of PAH 5 compounds	999.7	149.6	1110.5	573.8	499.4	215.8	599.9	1017.2	575.8	1075.0

Notes. 1. Location of sampling sites: A1 – the Selenga river, 22 km upstream of Ulan-Ude; A2 – the Selenga river, 15 km upstream of Ulan-Ude; A3 – the Selenga river, 1.5 km downstream of the sewage disposal plants of Ulan-Ude; A4 – the Selenga river, 17 km downstream of Ulan-Ude; A5 – the Selenga river, delta; B1 – the Sor-Cherkalovo bay; B2 – the Zmeevaya bay; C – the Turka river, 0.5 km upstream of the site of flowing into the lake; D – the Khaym river, 28 km upstream of the site of flowing into the lake; E – the Barguzin river, 4 km upstream of the site of flowing into the lake. 2. n/d – no data. 3. A dash means that the compound was not detected in a sample.

for the determination of the nature of PAH sources are listed in Table 2. The number of the ratios used for analysis is much larger, but the value ranges indicating the nature of origin have been determined for the three listed ratios. However, this does not mean that these ratios give absolutely correct determination of PAH sources, since the conditions of microbial decomposition of PAH in the bottom sediments depend on temperature, nature of the microbial community, and the presence of other organic pollutants [12].

One can see in Table 3 that phenanthrene to anthracene ratio changes within the range 3.7–49.4. Low values are characteristic of sampling sites in the vicinity of settlements (A1, A3) and traditional recreation areas (B2), where the nature of PAH is mainly pyrolytic. The mean value of the ratio is the evidence of the predominance of petrogenic PAH entering the environment with petroleum products (mineral oils and fuel used in the surface and water transport).

TABLE 2

Ratios of PAH concentrations used for the determination of the nature of pollution sources

Origin	Phenanthrene/anthracene [13]	ΣMethylphenanthrenes/ phenanthrene [14]	Pyrene/perylene [15]
Pyrolytic	<10	<2	
Petrogenic	>15	>2	
Anthropogenic pollution (pyrogenic and petrogenic)			0.8–15

TABLE 3

Ratios of PAH concentrations in the investigated samples

	Sampling sites									
PAH	A1	A2	A3	A4	A5	B1	B2	C	D	E
Phenanthrene/anthracene	10.3	19.1	10.7	34.8	49.4	42.0	3.7	45.0	30.1	16.7
ΣMethylphenanthrenes/ phenanthrene	6.2	13.7		6.5	7.4	7.3	9.7			
Pyrene/perylene	0.2	0.4		1.6	0.9	5.3	2.0			

Predominance of alkylated PAH and those containing 2–3 aromatic rings is characteristic of the samples of petrogenic nature of pollution [16]. The ratio of the sum of methylphenanthrenes to phenanthrene varies from 6.2 to 13.7 for the samples under investigation, which confirms petrogenic nature of PAH origin. The total concentration of the PAH group with 2–3 aromatic rings is substantially higher than the concentrations of other groups (Table 4). These results correlate with the data on the concentrations of petroleum products in the water of the lake itself (anthropogenic pollution) [17]. In addition, exhaust from the internal combustion engines makes a contribution, too.

Perylene is known to be formed in ecosystems in the processes of transformation of the organic matter (modern diagenesis). The pyrene to perylene ratio, introduced by M. I. Venkatasan [15], allows estimating the diagenic perylene. This ratio is small in the bottom sediments sampled from the Selenga river upstream of Ulan-Ude (A1, A2) and from its delta (A5); one can speak of the diagenic perylene; in other samples, petroleum products are exhibited which disguise perylene.

The investigation of PAH distribution in the snow cover of the Irkutsk Region revealed an intensive source of these compounds, namely, the Irkutsk Aluminium Plant [18], at which the combustion of electrodes occurs, accompanied by the emission of large amounts of PAH. Substantial difference in the qualitative composition of PAH of snow cover and bottom sediments was revealed in the analysis of

TABLE 4

Total concentration of the groups of PAH with different number of aromatic rings in the molecule, ng/kg

Number of aromatic rings	A1	A2	A4	A5	B1	B2
2–3	4521	1248	3407	3083	1232	3804
4	493	123	165	205	107	265
5	170	125	81	112	58	215
6	–	–	–	–	–	15

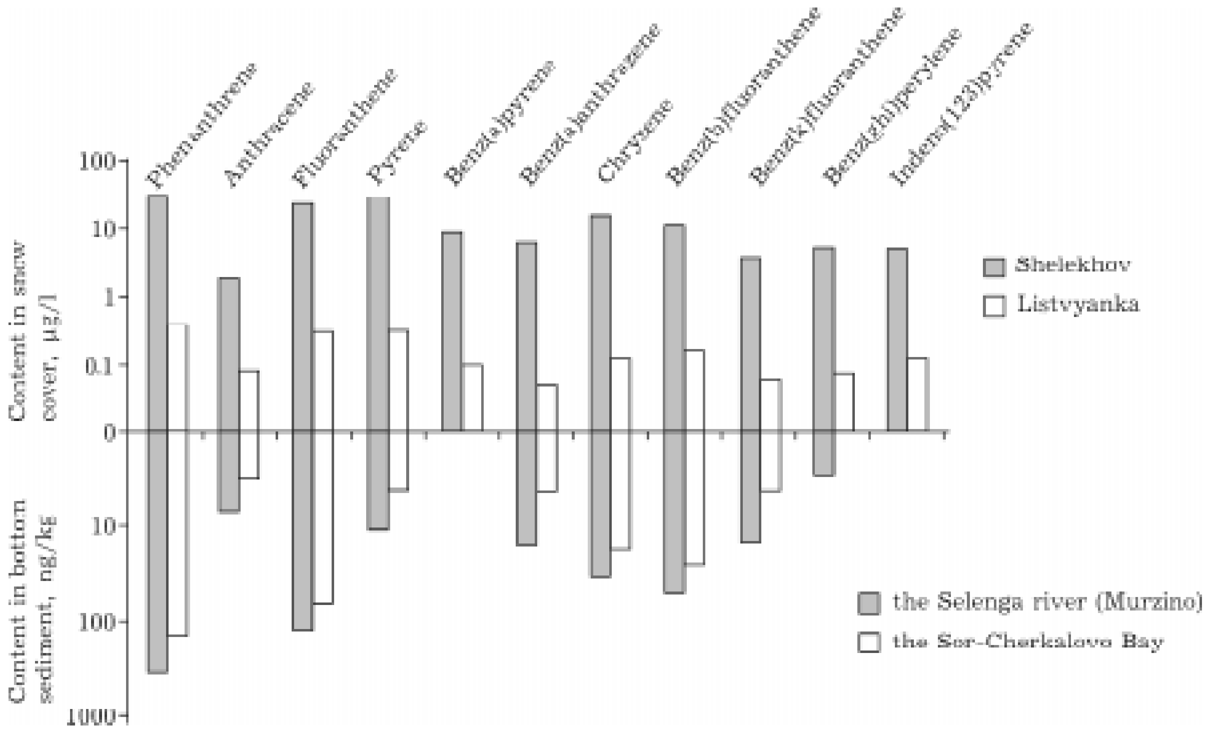

Fig. 1. PAH content in the snow cover of Shelekhov sity and Listvyanka settlement and in the bottom sediments of the Selenga river (Murzino) and the Lake Baikal (the Sor-Cherkalovo bay).

the qualitative composition of PAH in the samples of snow cover in the Shelekhov city and Listvyanka settlement, as well as in the bottom sediments of the Sor-Cherkalovo bay and the Selenga river near Murzino (the sites located geographically most close to the sources of PAH in the Irkutsk Region and supplementing the profile: Shelekhov/Listvyanka – the Sor-Cherkalovo bay/the Selenga river near Murzino. An increased content of pyrene, benz(a)pyrene, benzo(ghi)perylene and indeno(1,2,3)pyrene is characteristic of the samples collected in Shelekhov and Listvyanka (Fig. 1). Qualitatively different composition of the samples from the Irkutsk Region and from Buryatia provides evidence of different origin of the samples, which in the first case are due to the gas emissions of the Irkutsk Aluminium Plant and in the second case come from various local sources. Though a substantial transfer of PAH with air masses along the direction from Irkutsk to Listvyanka was revealed [18], the differences in the qualitative composition of the samples along the profile Shelekhov/Listvyanka – the Sor-Cherkalovo bay/the Selenga river allow us to assume that such a transport does not make a determinant contribution into the pollution of the tributaries of the Baikal with PAH. This is connected with the fact that PAH are sorbed by aerosol particles (the material of electrodes) and undergo rapid sedimentation [4, 5].

CONCLUSION

The results obtained and the analysis of the ratios of individual PAH for the identification of the sources from which PAH arrive into the ecosystems of the Baikal region allow us to make the following conclusions:

1. The concentrations of PAH in the bottom sediments of the tributaries of the Baikal are small, in comparison with the concentrations of PAH in the bottom sediments of the Arctic seas, and come mainly from local sources.

2. For the sampling sites situated within settlements and near them, the nature of PAH is pyrolytic, due to the use of coal and firewood as fuel for heating in winter.

3. For sampling sites situated far from settlements, PAH originating from petroleum

products (water and surface transport are characteristic.

4. The diagenic perylene is discovered in the samples from the sites where the level of pollution with petroleum products is low.

5. The sources of PAH situated in the Irkutsk Region do not make any noticeable contribution into the pollution of bottom sediments of the investigated rivers.

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REFERENCES

1 R. J. Irwin, M. VanMouwerik, L. Stevens *et al.,* Environmental Contaminants Encyclopedia, National Park Service, Water Resources Division, Fort Collins, Colorado, 1997.
2 Ya. Bartulevich, G. V. Yagov, *Pityevaya voda*, 6 (2001) 11.
3 L. I. Kuzubova, S. V. Morozov, Organicheskiye zagryazniteli pityevoy vody, Novosibirsk, 1993.
4 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin *et al., Optika atmosfery i okeana*, 6 (1999) 540.
5 A. G. Gorshkov, I. I. Marinayte, V. A. Obolkin *et al., Ibid.,* 11 (1998) 913.
6 A. Hubert, K.-D. Wenzel, M. Manz *et al., Analyt. Chem.*, 72 (2000) 1294.
7 J. L. Sericano, J. M. Brooks. M. A. Champ *et al., Marine Pollution Bull.*, 42 (2001) 1017.
8 V. M. Savinov, T. N. Savinova, J. Carroll *et al., Ibid.,* 40 (2000) 807.
9 P. Baumard, H. Budzinski, Q. Michon *et al., Estuarine, Coastal and Shelf Sci.*, 47 (1998) 77.
10 M. Liu, P. J. Baugh, S. M. Hutchinson *et al., Environ. Pollution*, 110 (2000) 357.
11 M. B. Yunker, L. R. Snowdon, R. W. MacDonald *et al., Environ. Sci. Technol.*, 30 (1996) 1310.
12 H.-M. Schulz, K.-C. Emeis, *Environ. Geology*, 39 (2000) 839.
13 H. Soclo, Etude de la Distribution des Hydrocarbures Aromatiques Polycycliques dans les Serdiments Marins Rercents, Identification des Sources, Ph.D. Thesis, University Bordeaux I, Bordeaux, France, 1986.
14 P. Garrigues, H. Budzinski, M. P. Manitz, S. A. Wise, *Polycyclic Aromatic Compounds*, 7 (1995) 275.
15 M. I. Venkatasan, *Marine Chem.,* 25 (1988) 1.
16 M. Notar, H. Leskovsek, J. Faganeli, *Marine Pollution Bull.*, 42 (2001) 36.
17 Obzor zagryazneniya okruzhayushchey prirodnoy sredy v Rossiyskoy Federatsii za 2001 g., Rosgidromet, Moscow, 2002.
18 G. P. Koroleva, A. G. Gorshkov, T. P. Vinogradova *et al., Khimiya v interesakh ustoichivogo razvitiya,* 6 (1998) 327.