POLYCYCLIC AROMATIC HYDROCARBONS IN THE SNOW COVER OF THE SOUTHERN COAST OF LAKE BAIKAL

A.G. Gorshkov, I.I. Marinaite, V.A. Obolkin, G.I. Baram, and T.V. Khodzher

Limnology Institute,
Siberian Branch of the Russian Academy of Sciences, Irkutsk
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Polycyclic aromatic hydrocarbons (PAHs) are detected in the snow cover of the Southern coast of Lake Baikal. Pollution of the snow cover is found to be of local in character. Long winter (150–200 days) and small areas of the spread of pollutants lead to high level of PAH accumulation near the sources of PAH emission. The maximum number of PAHs (11 compounds classified as main ecotoxicants) is found near Slyudyanka where the mean total accumulation is 380 μg/m^2 *for accumulation rates of benz[a]pyrene between* 0.01–1.6 μg/m^2 *per week and fluoranthene between* 0.5–12.6 μg/m^2 *per week.*

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are included in the list of the most important pollutants. Because many compounds of this class have mutagenic and carcinogenic properties,[1] they are continuously monitored in environmental objects. The main anthropogenic sources of PAHs are metallurgy, heat–and–power engineering, and motor transport. This is caused by the fact that PAHs are formed and emitted into the atmosphere as a result of incomplete combustion of an organic fuel. In particular, small boiler houses and individual heating furnaces using coal as a fuel and imperfect combustion technology are intense PAH sources.

In the atmosphere, PAHs are predominantly associated with aerosol particles. Sizes of aerosol particles determine, to a considerable extent the further behavior of PAH, i.e., their sedimentation from the atmospheric air on large particles and transfer by air masses depending on local meteorological conditions and wind direction. Fallout of PAHs with atmospheric precipitation leads to their accumulation in the soil and surface waters. In winter, these ecotoxicants are accumulated in the snow cover. The snow cover, as a deposit, is a convenient object to estimate the pollution of the surface layer of the atmosphere and to establish trajectories of PAH transport from their sources.[2,3]

The Southern coast of Lake Baikal has a developed industrial infrastructure and is an object of heavy anthropogenic pollution. The main sources of air and water pollution are Baikal'sk and the Baikal'sk Paper and Pulp Plant, which produces 160 thousand tons of cellulose per year; Slyudyanka is a big railway junction at the Southern coast of the lake. In winter (150–200 days), the heat–and–power engineering objects become intense sources of PAH emission during the period of their maximum activity. To estimate PAH pollution level in the surface aerosol and to identify the regions of the spread of PAHs from the emission sources, we studied the snow cover of Baikal'sk, Slyudyanka, Tankhoi, Listvyanka, and the Baikal Reservation (basins of the Anosovka and Osinovka rivers). The data presented here are a part of the results obtained under the project Ecologically Pure Power Supply For Baikal Region (Irkutsk) – TACIS.

EXPERIMENTAL PROCEDURE

The arrangement of the stations for snow sampling and aerosol monitoring at the Southern coast of Lake Baikal is shown in Fig. 1: Baikal'sk (with a population of 40 thousand), Slyudyanka (15 thousand), Listvyanka (3.5 thousand), and Tankhoi (5 thousand). Snow samples were taken within the precincts of the towns and settlements and outside them along the coast and on ice of the lake in February–March 1994; aerosol monitoring was performed within the precincts of the towns and settlements in December–February 1993–1994. In addition, monitoring of snow cover and aerosol was performed selectively in 1995–1997. In Irkutsk, sampling of snow and aerosol was performed in park zones of the city during 1994–1996.

Snow samples were taken as cores with a base area of 200×200 mm, no less than 2–3 cores from each point of sampling. Then the snow samples were placed in polyethylene pockets and kept at -15 – -20°C. Prior to analyzing, the snow samples were bottled into glass bottles (washed with acetone and potassium or sodium bichromate dissolved in sulfuric acid and dried at 250°C) and kept at room temperature for 8–10 h. Snow water (1 liter) was filtered through a filter with pore diameter of 2 μm (WHATMAN, England).

PAHs were extracted from the filters in glass flasks by *n*-hexane (with a volume of 15 ml, three times) in an ultrasound bath (SANOREX TK–52, Bandelin Electronic, Germany). Then they were extracted from the filtered snow water by *n*-hexane (three times) in the ratio filtrate: *n*-hexane = 20:1. Then *n*-hexane was separated from the obtained extracts

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in a rotor evaporator at 40°C; the residue was dissolved in 100–200 μl of methanol, and the methanol solution was analyzed by the high–performance liquid chromatography (HPLC) method. To check the purity of *n*-hexane used for extraction, 100 ml of the solvent were evaporated in the rotor evaporator and the residue was analyzed by the HPLC method under conditions chosen for PAH determination.

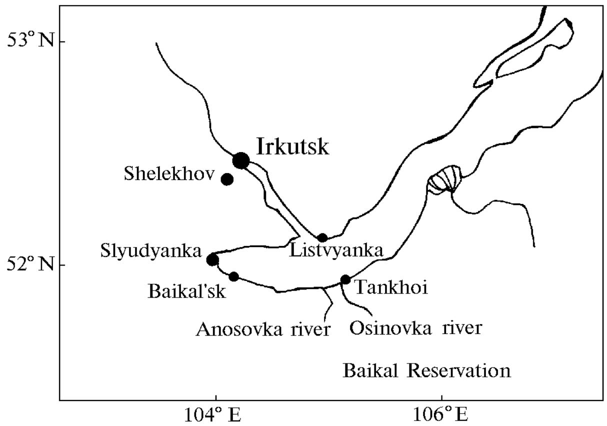

FIG. 1. Southern Baikal. Monitoring stations.

Aerosol sampling and analysis of the PAH extracts were performed by the technique described in Ref. 4.

RESULTS AND DISCUSSION

In all the samples of snow cover in the liquid and solid phases, 12 kinds of PAHs were identified that are classified as main ecotoxicants and recommended for continuous monitoring in environmental objects.[1] In the liquid phase of snow water, a small number of PAHs were found (phenanthrene, fluoranthene, pyrene, and sometimes anthracene and chrysene with concentrations varying from 2 to 500 ng/l). In the solid phase of snow water, i.e., in solid particles with sizes ≤ 6 μm (up to 98% of their number), the maximum number and amount of accumulated PAHs were determined: 11 compounds with concentrations up to 4–8 μg/l (phenanthrene and fluoranthene). The total content of phenanthrene, fluoranthene, and pyrene in all samples was more than 50% of the amount of the detected compounds.

The maximum concentration of PAHs was found in snow samples taken near settlements (Table I). Extremely high value of the mean total concentration (23 μg/l) was detected near Slyudyanka. Local zones of relatively high concentrations were identified in the territory of small settlements, e.g., Tankhoi (0.5–1.9 μg/l), and near junctions of the TransSiberian rails and highways – up to 1.3 μg/l. Far from settlements, the PAH concentration sharply decreased both at the coast (0.2–2.5 μg/l) and on ice of the lake in the direction of prevailing winds (0.02–2 μg/l). In the territory of the Baikal Reservation, the PAH concentration did not exceed 0.1–0.7 μg/l.

As for samples of aerosol, maximum total concentrations of PAHs, from 7 to 100 ng/m^3 (mean value is 53 ng/m^3), were detected in the ambient air in Slyudyanka. At other stations, lower levels of PAH concentration were found (see Table I). The number of individual PAHs identified in the composition of aerosol particles varied from 3 to 11. Phenanthrene, fluoranthene, and pyrene were presented in all samples with concentrations from 0.1 to 12.5 ng/m^3.

As seen from Fig. 2, there is a sufficiently reliable correlation ($R^2 = 0.9759$) between the mean PAH concentration in the aerosols of the ambient air in winter and their accumulation level in the snow cover. So the level of PAH accumulation in the snow cover, as an integral characteristics, permits us to estimate the mean value of the surface aerosol pollution. Taking into account the fact that in winter PAHs are almost completely associated with hard particles (up to 95%), determination of the PAH concentration in aerosol yields an estimate of pollution of the ambient air by these compounds.

Mathematical models that were developed for the spread of anthropogenic suspended solid pollutants in the surface layer of the atmosphere can be used for forecasting of regions of PAH dispersion from their emission sources based on quantitative detection of PAHs on solid particles of the snow cover (up to 70–90%). Such models for the region of Southern Baikal were considered in Ref. 5. The authors demonstrated that in winter, under conditions of the Siberian anticyclone solid particles of gas emission settle mainly near their sources. Winds with the monsoon component in the Southern Baikal region can transport pollutants from the emission sources toward the lake.

Experimentally established levels of PAH accumulation persuasively agree with the results of mathematical simulation. The PAH accumulation is, in fact, bounded by the precincts of the town. And the small value of PAH concentrations in snow samples collected on ice of the lake near Slyudyanka and Baikal'sk is more likely caused by shorter accumulation time and instability of the snow cover on ice as compared with the coast than by the absence of the PAH dispersion in this direction.

An attempt to identify emission sources from the ratio of individual PAHs detected in aerosol (pyrene/benz[a]pyrene and benz[g,h,i]perylene/benz[a]pyrene) was undertaken in Ref. 6. As seen from Table II, major contribution of PAH to the composition of aerosol is made by boiler houses and house heating furnaces in Slyudyanka and house heating furnaces in Tankhoi. Low levels of concentration and possible superposition of emissions from different sources (heat–and–power stations, the Paper and Pulp Plant, and motor transport) made it impossible to identify major sources of PAH emission in Baikal'sk.[6]

TABLE I. PAH concentration range in aerosol (ng/m^3) *and snow cover** (ng/l)*. PAH accumulation level in snow cover (150 days, total content of detected compounds,* μg/m^2*).*

Station and year of monitoring		PAN											Accumulation level
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
Slyudyanka	Aerosol, 1993–1994	0.1–2.5	< 0.01–1	2.5–25	1–15	1–6	0.5–10	0.2–10	< 0.1	0.3–22	< 0.2–15	< 0.2–3.0	–
	Snow, 1994, 1997	200–4700	< 1–320	250–8100	< 10–3500	< 10–1000	10–200	10–200	< 10–200	20–1000	< 20–1300	< 20–2500	150–680
Listvyanka	Aerosol, 1993–1994, 1995–1996	0.5–5.5	< 0.01–0.1	< 0.1–12.5	< 0.1–12	0.5–4	0.5–4	0.1–5.5	< 0.1–2.0	< 0.1–5	< 0.2–3	< 0.2–2.5	–
	Snow, 1994, 1996, 1997	240–250	< 1–8	190–300	< 10–300	< 10–50	43–115	85–140	< 10–55	< 10–90	40–85	55–65	60–120
Baikal'sk	Aerosol, 1993–1994	< 0.1	< 0.01	< 0.1–3	< 0.1	0.2–0.4	< 0.1–0.2	< 0.1–0.2	< 0.1	< 0.1	< 0.2	< 0.2	5
	Snow, 1994, 1997	< 15–300	< 1–4	< 10–300	< 10–55	< 10–30	< 10–160	< 10–240	< 10–55	< 10–90	< 20–40	< 20–25	5–65
Tankhoi	Aerosol, 1993–1994	< 0.1–0.2	< 0.01	< 0.1–2.0	< 0.1–1.0	0.5–0.6	0.3–0.7	0.2–0.6	< 0.1–0.3	< 0.1–0.5	< 0.2	< 0.2	
	Snow, 1994, 1997	100–500	< 1–7	100–670	< 10–175	< 10	< 10–160	20–170	< 10–115	60–115	< 20–30	< 20	100–440
Baikal Reservation	Snow, 1994, 1997	10–170	< 1–10	< 10–150	< 10–50	< 10	< 10–190	< 10–55	< 10–30	< 10–60	< 20	< 20	18–50

*The table presents total concentrations of PAH detected on solid particles and in the liquid phase of snow water: phenanthrene (I), anthracene (II), fluoranthene (III), pyrene (IV), benz[a]anthracene (V), chrysene (VI), benz[b]fluoranthene (VII), benz[k]fluoranthene (VIII), benz[a]pyrene (IX), benz[g,h,i]perylene (X), indeno[1,2,3-c,d]pyrene (XI).

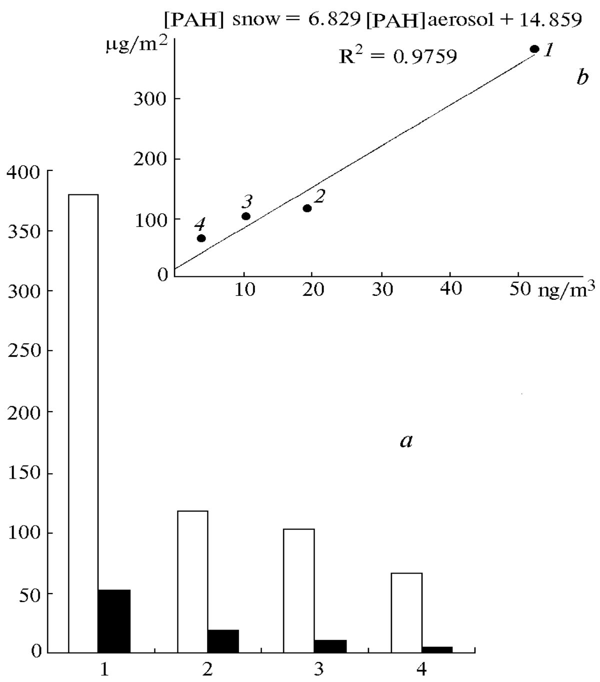

FIG. 2. Data on snow cover and aerosol monitoring for 1993/94 at the Southern coast of Lake Baikal. Mean total concentrations of PAHs (a) and their correlation (b) in Slyudyanka (1), Listvyanka (2), Tankhoi (3), and Baikal'sk (4); PAHs in the snow cover (μg/m^2) *(empty squares); PAHs in aerosol* (ng/m^3) *(filled squares).*

TABLE II. Ratio of individual PAHs in the content of examined aerosols and gaseous emissions from different sources.

Monitoring station	PAH ratio	
	IV/IX	X/IX
Slyudyanka	0.7–3.3	< 0.2–0.7
Listvyanka	< 1–2.4	0.6
Tankhoi	< 1–2.0	< 2
Baikal'sk	< 1	< 2
Gaseous emissions		
Individual heating furnaces	1.5–5.2	0.15–0.93
Small heat–and–power stations	–	0.46

Relatively low concentrations of PAH in aerosol and snow cover near Baikal'sk should be mentioned particularly. The Baikal'sk Paper and Pulp Plant burns tremendous amounts of different fuels (coal, lignuine made from black liquor, petroleum products, and bark) in pulp production. The observed low level of PAHs may be caused by both efficient purification of gaseous emissions and emission of combustion products into higher atmospheric layers and their dispersion on large areas.

A comparative estimate of pollution with PAHs in the region of the Southern coast of Lake Baikal is possible with the use of two parameters: (a) concentration of benz[a]pyrene in the ambient air as a "carcinogenity index; (b) PAH accumulation rate in the snow cover.

Near Slyudyanka, where the level of PAH accumulation in the snow cover is maximum, the benz[a]pyrene concentration in aerosol varied widely (Table III).

Minimum values correspond to the level of concentrations detected in background regions. Maximum values correspond to atmospheric pollution in large industrial centers. This indicates a certain periodicity of high PAH concentrations in the ambient air and considerable purification capacity of the atmosphere. The mean concentration of benz[a]pyrene is 0.8 ng/m^3, which is less than the maximum permissible concentration in the ambient air by the Russian law equal to 1 ng/m^3. Near Baikal'sk and Tankhoi, the detected concentrations of benz[a]pyrene in the aerosol of the ambient air are close to the values determined in background regions (see Table III).

TABLE III. Benz[a]pyrene (B[a]P) concentration in the ambient air.

Monitoring station	Monitoring year	B[a]P, ng/m^3	Reference
Background level			
Molodezhnaya, Antarctica	1980	0.02	7
Great Lakes, USA	1980	0.1–2	8
Borovoe, Russia	1976–1983	0.3–0.5	9
Coast of Lake Baikal			
Slyudyanka	1994–1995	0.3–20	–
Listvyanka	1995–1996	< 0.02–5	–
Baikal'sk	1994–1995	< 0.02	–
Tankhoi	1994–1995	<0.02–0.5	–
City districts			
Valencia, Spain	1989	13	10
Irkutsk, Russia	1995–1996	10–22	–

Accumulation rates of benz[a]pyrene and fluoranthene in the snow cover near Slyudyanka, Baikal'sk, Listvyanka, and Tankhoi exceed those for background regions but are almost 5–30 times smaller than for industrial regions of Baikal (e.g., Irkutsk and Shelekhov) and industrial centers of Western Europe (Table IV). These data are indicative of smaller ecotoxicant flow from the atmosphere to the underlying surface and, consequently, lower pollution of the atmospheric air. In the territory of the Baikal Reservation, the PAH accumulation rates in the snow cover are comparable with those for background regions.

TABLE IV. Rates of PAH accumulation in snow cover (μg/m² *per week).*

Monitoring station	PAH			
	I	III	IV	IX
Slyudyanka	0.4–7.3	0.5–12.6	0.1–6.5	0.1–1.6
Listvyanka	0.6–2.3	0.2–1.6	0.6–1.7	0.1–0.4
Baikal'sk	0.2–1.0	0.2–0.8	0.1–0.4	0.2–0.5
Tankhoi	0.2–0.6	0.6–1.2	0.5–1.2	0.2–0.8
Irkutsk	4.2–20	3.0–15.3	2.2–15.6	0.5–1.3
Sault Ste. Marie, Canada*	2.2–34	1.5–64	0.9–37	0.5–5.5
Berlin, Frankfurt, Dusseldorf, Germany**	–	4.5–15.4	2.7–9.8	0.5–2.0
Baikal'sk Reservation	–	0.1–0.3	–	0.02
Background level*	–	0.14–0.33	–	< 0.001–0.022*

* Findings of Ref. 11.
** Mean values for Berlin, Frankfurt, and Dusseldorf; findings of Ref. 12

It should be noted that, due to long winter (150–200 days), the level of PAH accumulation (see Table I) in snow cover near the sources is of the same order as the accumulation level in industrial, commercial, and residential districts of big cities.[10,11] This may be a cause of the sharp increase of PAH concentration level in melt water in spring. At the same time, taking into account that PAHs have limited solubility in water and most of them are sorbed on solid particles, most of these ecotoxicants will remain on the coastal surface or pass into bottom sediments of the lake and its tributaries.

CONCLUSION

We have identified eleven PAHs (recommended for continuous monitoring in environmental objects) in the snow cover of the Southern coast of Lake Baikal in the regions of possible sources. Maximum accumulation levels were found near Slyudyanka with accumulation rates 5–30 times less than in industrial centers of the Baikal region. In the territory of the Baikal Reservation, PAH accumulation rates are close to that in background regions.

Based on PAH monitoring in snow cover and on the data of numerical simulation of the spread of solid suspensions from gaseous emissions, we have concluded that the pollution of snow cover and aerosol is local in character. This leads to high level of PAH accumulation in the regions of emission sources due to long winter and small area of pollutant dispersion.

Small boiler houses and individual heating furnaces using coal as a fuel are classified as main sources of PAH. Therefore, improvement of the technology of fuel combustion and the system of gaseous emission purification, replacement of coal with gas, and use of electric power for heating will favor the decrease of PAH pollution level in the examined regions.

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