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Distribution of Polycyclic Aromatic Hydrocarbons in Natural Objects over the Territory of Scattering the Emissions from the Irkutsk Aluminum Plant (Shelekhov City, the Irkutsk Region)

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Abstract

Accumulation levels were determined for polycyclic aromatic hydrocarbons (PAHs) in naturally occurring objects over the territory of dispersing the emissions of the Irkutsk Aluminum Plant "IrkAZ-SUAL": in the snow cover, soil, pine needles (*Pinus sylvestris* L.) and larch needles (*Larix sibirica*), in water and the bottom sediments of the. Olkha River, as well as in the near-surface aerosols in Shelekhov City. An estimation was performed for the level of contamination with PAH compounds in the area of the Shelekhov City within the framework of the MPC and background levels, a conclusion has been drawn concerning the distribution of PAH emissions from the source over a limited area. Among the isolated fractions of PAHs, using a gas chromatography-mass spectrometry technique there have been identified and determined 14 arenes including those from the list of priority organic pollutants.

Key words: polycyclic aromatic hydrocarbons, snow cover, soil, pine and larch needles, water and bottom sediments, urban aerosol

INTRODUCTION

According to data received from the Ministry of Natural Resources of the Irkutsk Region, the level of air contamination in the cities of Bratsk, Zima, Irkutsk, Angarsk, Sayansk, Usol'ye Sibirskoye, Ust'-Ilimsk, Cheremkhovo, Shelekhov was rated as high and very high one, with an excess with respect to the MPC level values for suspended solids, carbon dioxide, nitrogen, carbon and sulphur, hydrogen sulphide, benzo(a)pyrene (BaP), formaldehyde, carbon black, hydrogen fluoride. The main sources of air contamination are presented by industrial emissions, whose volume in 2010 amounted to 575 thousand t [1]. A number of substances in the composition of industrial emissions were identified as persistent organic pollutants those can be accumulated in naturally occurring objects within the area of dispersing the contaminated air masses to exert a negative effect on the environment. In particular, the area of Shelekhov City is notable for an extreme accumulation level of polycyclic aromatic hydrocarbons (PAHs, many of those exhibit mutagenic and carcinogenic properties) in the snow cover, soil and vegetation [2–6].

Atmospheric contamination with PAH compounds within the area of the Shelekhov City is determined by the emissions of three major plants of the SUAL-Holding OJSC: the IrkAZ-SUAL JSC, Silicon JSC, SUAL-PM Ltd, and

Irkutsk Heat and Electric Power Plant (IHEPP-5), whereas about 64 % of the total amount of emissions from stationary sources over the city falls to the share of the IrkAZ-SUAL [7]. Since 1962, this plant produces aluminum in amounts of up to 412 thousand t/year. The main part of the facilities of the plant operates using a Söderberg technology with the use of self-baking the anodes with a top current-carrying wire. In 2008, there was launched a 5th series equipped with electrolytic cells with prebaked anodes, which allowed 100–1000-fold reducing the emissions of PAHs [8, 9]. Alongside with the modernization of equipment, at the plant there were introduced recycling water and dry scrubbing systems, wherewith the emissions of fluorine compounds and electrolytic dust exhibited a 99 % decrease [8].

The purpose of this investigation consisted in estimating the current level of PAH accumulation and distribution in naturally occurring objects within the area of dispersing the emissions from the IrkAZ-SUAL, held within the framework of the project "Integrated Ecological Audit of the Baikal Natural Territory and the ecosystem of the Lake Baikal as the World Heritage Site" (No. 01201052127). The objects chosen for studying such as snow cover,

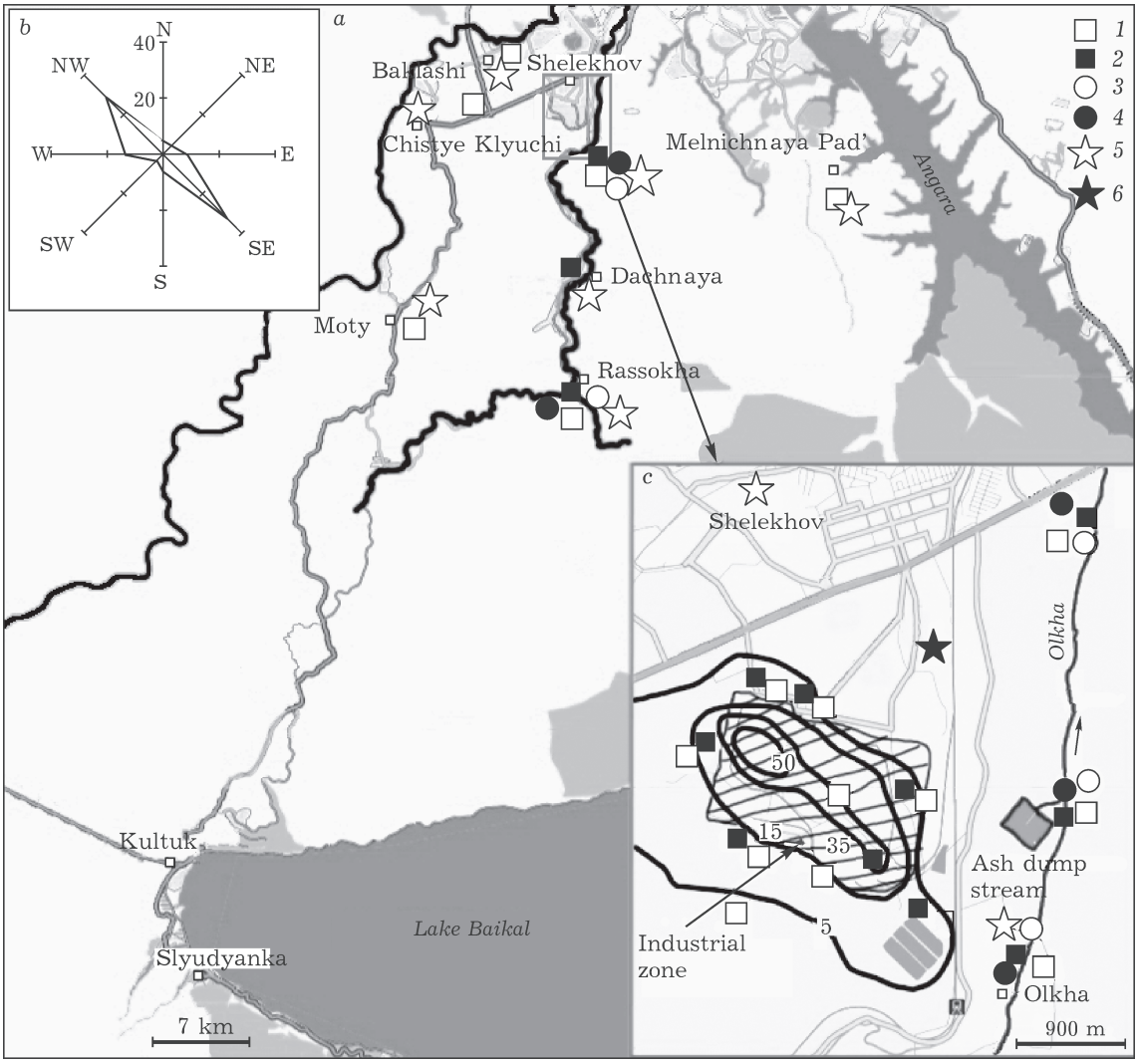

Fig. 1. Schematic map of sampling the natural objects (*a*): *1* – snow cover, *2* – soil, *3* – water, *4* – bottom sediments, *5* – the needles of pine and larch; (*b*) – the repeatability of apparent wind bearing for a year (%); *c* – distribution of the levels of accumulation for total PAHs in snow cover within the area of dispersing the emissions from the IrkAZ-SUAL for the winter time of 2007–2011 (in mg/m^2).

soil, pine needles (*Pinus sylvestris* L.) and larch needles (*Larix sibirica*), water and bottom sediments taken from the Olkha River and near-ground aerosol in the Shelekhov City are characterized by different accumulation abilities and time intervals inherent in affecting by industrial emissions. The analysis thereof would provide a comprehensive assessment of the distribution of PAHs in the environment within the location area of strong and steady source of the pollutants belonging to this class.

EXPERIMENTAL

Sampling of snow, soil, pine needles (*Pinus sylvestris* L.) and larch needles (*Larix sibirica*) was performed at 14 stations within the industrial zone of the IrkAZ-SUAL and beyond the zone at distances of 2, 2.5, 6.5, 11, and 20 km to the north, south, east, west, southeast and northwest (Fig. 1). Snow samples were taken throughout the entire depth of the snow cover in late February, early March, 2009–2010. The samples of surface soil (~10 cm) were taken in September 2009; the samples of conifer needles were taken in August, 2010 and 2012. In the course of sampling the needles we took a subsample at each site from 5–6 pine trees and larch trees about 40 years old.

The samples of surface water and bottom sediments from the Olkha River were taken in August of 2009 at four stations: at a distance of 2 and 20 km from the industrial zone; at the mouth of the drain stream flowing from the ash dump of the IHEPP-5; 2 km downstream of the Olkha River drain from the mouth of the drain stream. The atmospheric aerosol was collected onto glass fibre filters with a diameter 4.7 cm (Munktell, Germany) in the southern part of the Shelekhov City at a distance of 2.5 km northeast from the industrial zone within the period from 20 to 26 March of 2009. The duration of sampling was equal to 2–24 h.

The determination of PAHs in the aerosol, snow, water was carried out with the use of certified procedures [10–12]. The samples of soil and bottom sediments before the analysis were dried up to constant mass and homogenized; the preparation for analysis was carried out as described by the authors of [10]. The determination of PAHs in the analytical termination of the procedures was performed by means of a chromatography-mass spectrometry technique described by the authors of [13]. The determination of PAHs in the needles was carried out according to the procedure described in [13]. The total error in the determination of PAHs in the samples is estimated to amount to 10 % without taking into account sampling error; estimation error for the ratio between individual PAH was equal to 14 %. Determining the distribution of the levels of total PAH accumulation in snow cover within the area of dispersing the emissions of the IrkAZ-SUAL was performed using a Serfer (V 6.04) software package.

RESULTS AND DISCUSSION

Contamination of near-surface aerosol with PAHs

The industrial zone of the IrkAZ-SUAL is located approximately at a distance of 1.5 km from the nearest dwelling houses of the Shelekhov City, so the emissions of the plant, especially in the case of south and southwest winds, represent the main sources of air contamination in the city. According to the governmental reports [1, 14], the maximum concentration of BaP in the air of the Shelekhov in 2010–2011 was registered at the level ranging within 6.2–9.2 MPC (the MPC level for BaP in ambient air is equal to 1 ng/m^3) at the average annual concentration equal to 2.8–3.2 MPC.

In the course of sampling at the distance of 1.5 km from the industrial zone (see Fig. 1) under a stable atmospheric stratification and dead calm, the total concentration of PAHs (ΣPAH) reached 320 ng/m^3, whereas the concentration of BaP amounted to 19 MPC (Table 1). After torrential raining which cleared the atmosphere, the level of ΣPAH fell down to 2.9–14 ng/m^3, but the qualitative composition of the PAH fraction in aerosol samples remained unchanged. Among the PAHs revealed there are 12 compounds identified those are included in the priority list of pollutants such as phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR),

TABLE 1

PAH content in the aerosol samples taken in the Shelekhov City, ng/m^3

Sampling time	PHEN	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BeP	BaP	PER	INP	BP	DBA	ΣPAH	BaP_{MPC}
Average daily PAH content (from 20.03 to 26.03.2009)																
21–22.03.09	6.1	0.8	12.0	11.0	7.1	13.0	18.0	5.5	13.0	6.8	2.2	4.9	6.1	0.7	110	6.8
22–23.03.09	2.1	0.3	5.0	4.6	2.4	4.6	6.3	2.1	3.9	3.4	0.7	1.5	1.8	0.3	39	3.4
23–24.03.09	0.4	0.1	0.3	0.2	0.1	0.2	0.5	0.2	0.4	0.2	0.1	0.2	0.2	<0.1	2.9	0.2
24–25.03.09	2.2	0.1	2.7	2.1	0.6	1.5	1.5	0.5	0.9	0.9	0.1	0.3	0.5	<0.1	14	0.9
25–26.03.09	2.2	0.2	2.6	1.3	0.3	1.4	3.6	0.9	2.4	0.8	<0.1	0.7	0.9	0.1	17	0.8
PAH content during the day (from 14.00, 20.03 to 14.00 21.03. 2009)																
14.00–16.00	4.7	0.5	8.0	5.7	3.8	14.0	41.0	15.0	29.0	17.0	5.6	16.0	20.0	2.9	180	17.0
20.03.09, 16.00–18.00	4.4	0.6	8.6	5.4	3.4	8.6	19.0	7.3	14.0	8.5	2.4	6.0	9.4	1.0	98	8.5
20.03.09, 18.00–21.00	1.4	0.1	0.5	0.4	0.2	0.4	1.3	0.5	1.1	1.0	0.2	0.8	1.4	0.1	9.4	1.0
20.03.09, 21.00–23.00	2.5	0.3	1.0	0.8	0.7	1.0	2.1	0.7	1.6	1.5	0.3	1.0	1.5	0.1	15	1.5
20–21.03.09, 23.00–01.00	3.9	0.5	3.4	2.0	19	23.0	16.0	6.0	13.0	9.5	1.9	5.3	8.3	1.2	110	9.5
21.03.09, 01.00–06.00	0.8	0.1	0.5	0.3	0.2	0.3	0.8	0.3	0.6	0.4	0.1	0.6	0.9	0.1	5.9	0.4
21.03.09, 06.00–08.00	1.5	0.1	0.7	0.5	0.3	0.7	1.5	0.5	1.0	0.9	0.2	0.7	0.9	0.1	9.7	0.9
21.03.09, 08.00–12.00	3.7	0.5	2.7	1.9	2.2	7.8	2.1	8.0	1.6	0.7	1.9	8.1	1.2	1.1	44	0.7
21.03.09, 12.00–14.00	18.0	2.7	45.0	39.0	26.0	44.0	50.0	13.0	36.0	19.0	6.7	10.0	11.0	1.4	320	19.0

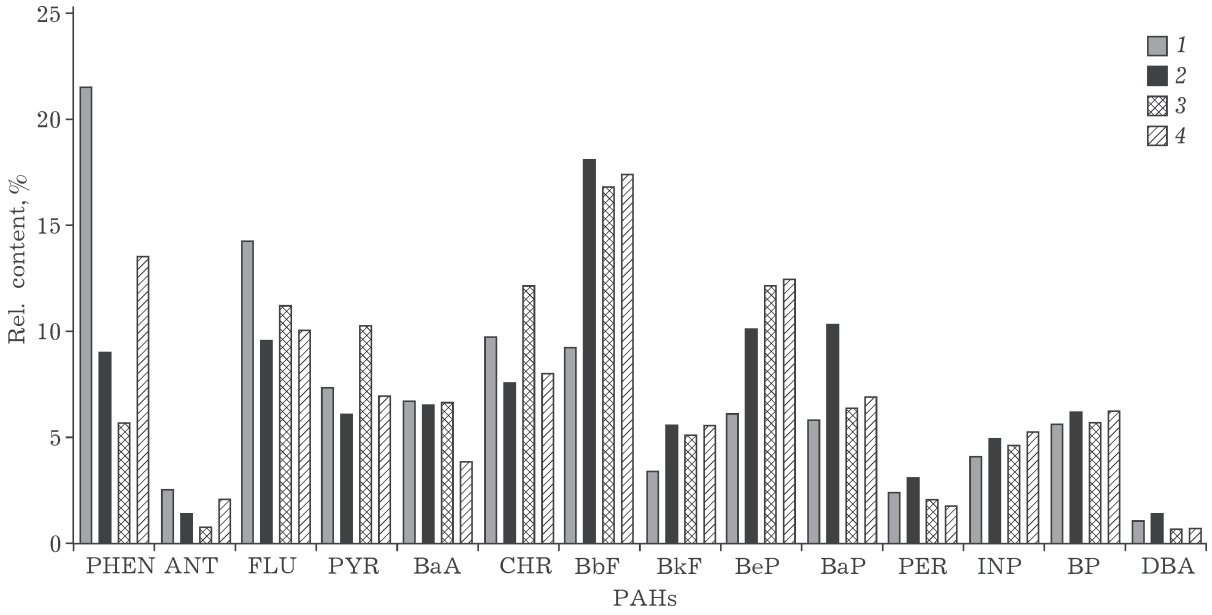

Fig. 2. Relative content of PAHs (in % of ΣPAH): *1*, *2* – in the samples of snow cover (*1* – in the central area of the Shelekhov City, *2* – in the industrial zone of the IrkAZ-SUAL); *3*, *4* – in the aerosol at a distance of 1.5 km from the industrial zone (*3* – at the maximum level of contamination amounting to 110 ng/m^3, *4* – at the lowest level of contamination equal to 2.9 ng/m^3).

benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BKF), BaP, indeno(g,h,i)pyrene (INP), benzo(g,h,i)perylene (BP) dibenz[a,h]anthracene (DBA) and benzo[e]pyrene (BeP) and perylene (PER).

Within the periods of the minimum and maximum air contamination, the aerosol samples exhibit the values of diagnostic parameters (PAH ratio values) BaP/BeP, BaA/CHR and ANT/CHR ranged from 0.50 to 0.55, indicating that there is a local source of arenes [26]. Such a source, in particular, could be presented by aluminum smelter emissions, according to the predominance of BbF in the fraction of PAHs [9], both in the aerosol samples and in samples of snow cover taken from the industrial area (Fig. 2).

In the course of analyzing the profiles of PAHs we used (as a reference for the emissions of the IrkAZ-SUAL) the profile of arene fractions accumulated in the snowpack of the industrial zone for an extended period of time (~100 days). Using the data published in [9, 15] for the analysis was meant as insufficiently justified, taking into account the application of different electrolysis technologies and, accordingly, overlapping the emissions with different composition and PAH ratio.

It should be noted that there is a significant variation in the ΣPAH and in the ratio between individual arenes in the aerosol during 1 day. In particular, the BaP concentration ranges from 0.4 to 19 MPC (see Table 1). Changing the level of ΣPAH in aerosol up to 30 times within 1 day was accompanied by changing in the ratio values between arenes in the PAH fraction, to all appearance, due to the contribution to air contamination from different sources.

Accumulation of PAHs in snow cover

During the cold season under the conditions of the Siberian anticyclone the pollutants fall on the underlying surface of the earth mainly within the area of the emissions thereof [16]. On this basis, the study of snow cover contamination allows one to reveal the sources thereof, to estimate the area of dispersing the emissions and the level of atmospheric contamination during the cold season (for the Baikal region being up to 160 days). The analysis of snow samples taken within the area of the industrial zone of the IrkAZ-SUAL indicates the accumulation of extreme PAH amounts within a limited area (about 16 km^2, see Fig. 1). At a distance of 1 km from the electrolysis workshop of the plant the value of ΣPAH in snow cover is estimated to amount to 50 000 μg/m^2. Increasing the distance from the industrial zone the amount of PAHs in snow samples exhibited an abrupt decrease: at a distance of 2–2.5 km

TABLE 2

PAH content in the samples of snow cover taken in different areas under study, μg/m^2

PHEN	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BeP	BaP	PER	INP	BP	DBA	ΣPAH
*Industrial zone of the IrkAZ-SUAL**														
2.1–4.5	0.4–0.7	2.1–7.7	1.3–4.8	1.3–3.7	1.9–3.5	3.5–13	1.0–4.2	1.9–7.1	1.4–7.3	0.4–2.2	0.6–3.0	0.8–3.6	0.2–0.9	19–54
Shelekhov City, 2.5 km from the industrial area to the north														
540	63	360	180	170	240	230	85	150	140	61	100	140	27	2500
Olkha Settlement, 2 km from the industrial area to the southeast														
350	39	230	120	82	120	400	140	130	120	79	160	230	51	2300
Baklashi Settlement, 6.5 km from the industrial zone to the northwest														
200	15	210	120	67	150	180	55	110	100	28	60	70	12	1400
Moty Settlement, 20 km from the industrial zone in the southwest														
12	0.7	9.4	5.2	0.8	5.4	4.2	0.5	5.5	3.1	1.7	3.7	<0.2	<0.2	52
Rassokha Settlement, 20 km from the industrial zone to the south														
65	<0.2	43	18	5.5	24	36	15	25	12	3.8	19	23	5.1	300
Melnicnaya Pad' Settlement,20 km from the industrial area to the east														
71	<0.2	39	12	8.0	15	23	12	22	12	5.1	20	22	<0.2	260

* In mg/m^2.

the decrease ranged from 7 to 20 times, ranging from 200 to 1000 times at a distance of 20 km (Table 2). It should be noted that within the area of the Moty Settlement (20 km southwest from the industrial zone) the accumulation level of PAHs amounted to 52 mg/m^2, which value is comparable with the level of accumulation of PAHs in snow within the unpopulated areas of the southern coast of the Lake Baikal [4, 17]. However, this value is almost an order of magnitude higher than the background level (the alpine background monitoring station Mondy, 0.5 μg/m^2 [6]).

It has been found that the qualitative composition of the fraction of PAHs in snow samples is constant (see Table 2), but the ratio between the content of arenes changes with increasing the sampling points distance from the industrial zone. To all appearance, this could be caused by a decrease in the contribution of emissions from the aluminum smelter in snow contamination and by a "manifestation" of arenes from other sources in the fraction of PAHs. These sources could be presented by emissions of HEPPs, boilers, stoves and motor cars, among the arenes thereof there prevail PHEN, FLU and PYR [9, 15, 18]. For example, the fractions of arenes in the snow samples taken from the plant and from the area of the Olkha Settlement PAH exhibit similar profiles, whereas the samples taken at a distance of 20 km from the IrkAZ-SUAL demonstrate an abrupt increase in the fraction of PHEN and FLU and a decrease of the BbF (Fig. 3). The increase in the relative content of PHEN and FLU in the fraction of PAHs in the snow samples taken from the central district of the Shelekhov City could be also caused by the superimposition of pollutants from various sources, therewith the ratio of BaA/BaP = 1.2, indicates a significant contribution of the emissions from motor vehicles to the fraction of PAHs. At the same time, the fact that the snow samples from area of the Rassokha and Moty settlements demonstrate the reduction in the BaA/BaP ratio down to the level ranging within 0.25–0.44 indicates a decrease of the contribution of this factor to the contamination of snow cover [26].

Accumulation of PAHs in larch and pine needles

One of the modern methods for monitoring the environmental contamination consists in assessing the distribution of pollutants within the area under investigation using biological matrices. For example, in order to monitor PAHs in the Baikal region it was proposed to use pine needles, whose wax layer concentrates organic substances coming from the atmosphere. The

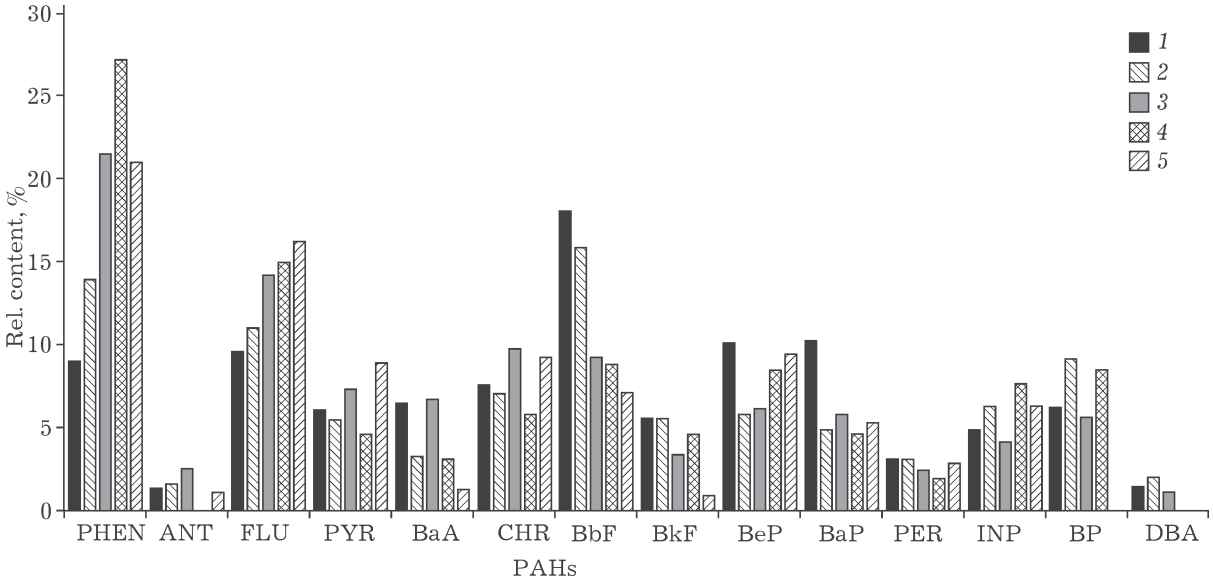

Fig. 3. Relative content of PAHs (in % of ΣPAH) in samples of snow cover: *1* – in the industrial zone of the IrkAZ-SUAL, *2* – in the vicinity of the Olkha Settlement, *3* – in the central area of the Shelekhov City, *4* – near the Melnichnaya Pad' Settlement, *5* – near the Moty Settlement.

TABLE 3

PAH content in pine needles (P) and larch (L) ng/g

Objects	PHEN	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BeP	BaP	PER	INP	BP	DBA	ΣPAH
Shelekhov City, 2.5 km from the industrial area to the north															
P	250	8.5	120	110	38	210	110	49	49	33	8.8	26	28	6.8	1100
L	980	35	1200	850	770	3100	910	320	290	120	21	110	130	24	8900
Olkha Settlement, 2 km from the industrial area to the southeast															
P	144	1.0	230	200	25	162	56	34	30	18	3.9	24	19.3	2.8	950
L	840	19	510	310	260	1800	490	310	160	59	9.2	81	80	21	4900
Baklashi Settlement, 6.5 km from the industrial zone to the northwest															
P	330	37	140	85	14	100	120	1.1	49	29	2.1	0.5	<0.1	0.3	910
L	670	17	580	380	250	1500	300	180	89	31	0.1	34	34	6.2	4100
Chistye Klyuchi Settlement, 11 km from the industrial area to the west															
P	41	4.6	18	11	1.7	12	15	0.1	0.2	0.1	0.3	0.1	<0.1	<0.1	100
L	240	4.6	160	70	80	310	71	36	24	7.6	0.1	11	8.2	0.2	1100
Dachnaya Settlement,11 km from the industrial zone to the south															
P	100	4.4	73	68	18	88	25	14	11	6.0	0.1	<0.1	0.1	<0.1	410
L	560	21	380	270	200	860	170	100	51	24	0.2	23	24	0.7	2700
Melnicnaya Pad' Settlement,20 km from the industrial area to the east															
P	47	1.1	<0.1	<0.1	21	18	5.0	42	<0.1	33	<0.1	<0.1	<0.1	<0.1	170
L	270	4.8	160	120	130	610	180	77	51	16	<0.1	16	14	1.7	1700
Rassokha Settlement, 20 km from the industrial zone to the south															
P	26	0.8	9.9	7.0	0.1	9.8	0.2	0.1	0.3	0.2	<0.1	<0.1	<0.1	<0.1	55
L	260	9.0	140	87	80	260	64	53	24	15	0.2	10	12	<0.1	1000
Moty Settlement, 20 km from the industrial zone ***in to the southwest***															
P	31	0.4	5.2	3.8	0.1	6.3	8.9	0.1	0.2	0.1	0.1	<0.1	<0.1	<0.1	56
L	130	4.7	68	61	56	160	45	23	13	6.3	<0.1	6.6	4.2	0.5	590

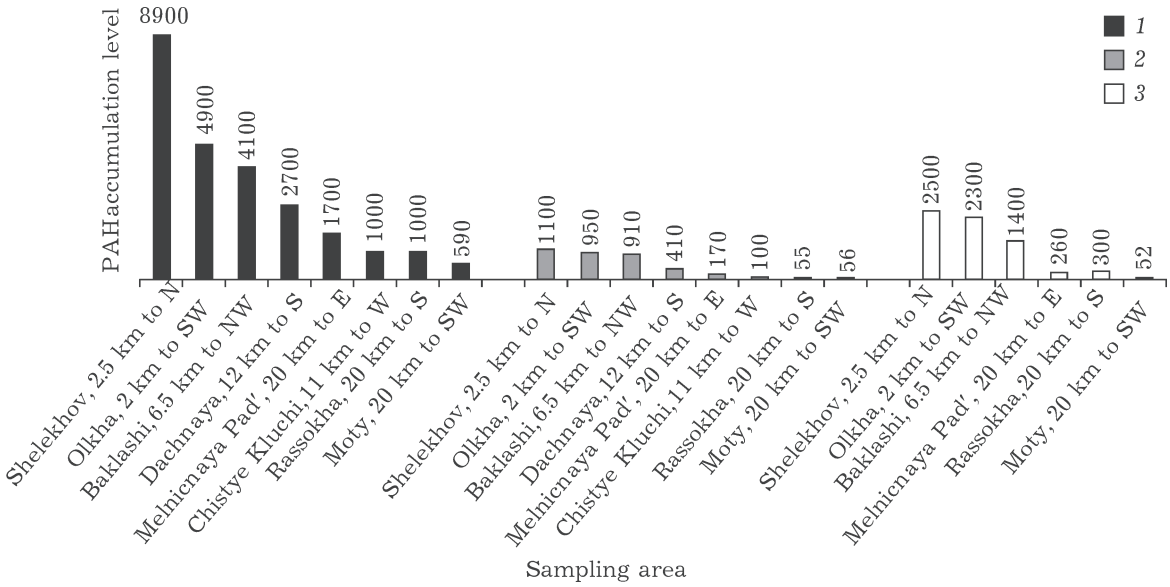

Fig. 4. Levels of PAH accumulation: *1* – in larch needles (ng/g); *2* – in pine needles (ng/g); *3* – in the snow cover (μg/m^2).

further determination of the levels of PAH accumulation in the needles allows one to evaluate the distribution of pollutants within the territory for a chosen observation period [6].

Within the area of dispersing the emissions of the IrkAZ-SUAL (with the predominance of the northwest and southeast winds), the needles of pine and larch accumulate PAHs in the amounts ranging within 55–4900 ng/g (Table 3). The PAH fraction contains 14 arenes, those were identified in aerosol and snow as well. The maximum concentration of ΣPAH was found in the samples of larch needles sampled at a distance of 2.5 km from the IrkAZ-SUAL. With increasing the distance from the plant amounting to 20 km, the ΣPAH value exhibits a 3–10-fold decrease, the minimal amounts of PAHs being registered for the samples taken from the area of the Moty Settlement (see Fig. 1, southwest direction). Pine needles accumulate the PAHs in smaller amounts as compared to the larch needles in the case of samplings from the sample sites. With increasing the distance from the industrial zone up to

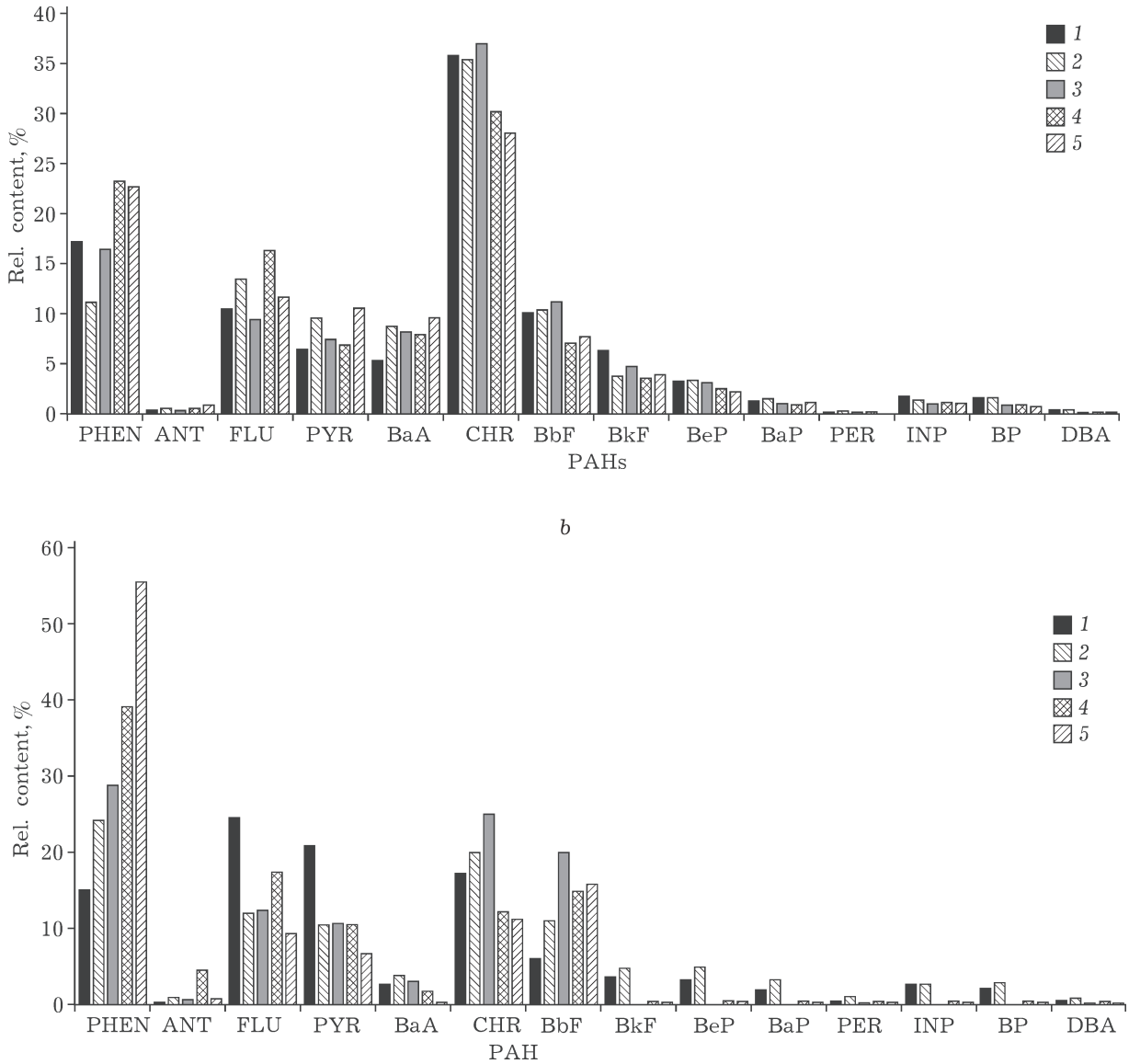

Fig. 5. Relative content of PAHs (in % of ΣPAH) in larch needles (*a*) and pine needles (*b*): *1* – near the Olkha Settlement; *2* – central area of the Shelekhov City; *3* – the Melnicnaya Pad' Settlement area; *4* – near the Chistye Klyuchi Settlement; *5* – near the Moty Settlement.

20 km the ΣPAH content in pine needles also decreases (15 times in the vicinity of the Moty and Rassokha settlements, Fig. 4), reaching the background level (20–30 ng/g [6]).

The fraction of arenes accumulated in the larch needles near the Olkha Settlement (2 km southeast from the aluminum plant) and an uninhabited area of Melnichnaya Pad' Settlement (20 km east from the aluminum plant), are characterized by a similar PAH ratio values. However, the content of CHR in PAHs is higher (~35 %) as compared with the samples of snow from these areas. Furthermore, the samples taken at a considerable distance from the industrial area, exhibit decreasing the CHR fraction with increasing the PHEN fraction (Fig. 5, *a*).

Pine needles, unlike larch needles, can be characterized by prevailing PHEN among the arenes (see Fig. 5, *b*). It should be noted that the sample of needles taken on the sites near the Chistye Klyuchi and Moty settlements, characterized by an abrupt increase in the relative content of the PHEN (down to 45–55 %) and a considerable scatter of the relative content of FLU, PYR, CHR and BbF. Such a composition of the fractions of PAHs contained in pine needles, to all appearance, could be caused by a more prolonged accumulation of pollutants as compared with the larch needles (as a biological indicator we chose pine needles of the second year of life [6]), and, as a consequence, coming the PAH from different sources. At the same time, the higher level of PAH accumulation in larch needles, and the maximum content of the CHR in the arene fraction could be connected, to all appearance, with the absorption properties and the surface morphology of the wax layer thereof [19].

The accumulation of PAHs in the larch needles occurs only during the growing season, so the needles as a biological indicator could characterize the air contamination only with respect to the warm season. The warm season differs from the winter season by dispersing the contaminated air masses over a larger area [16]. However, the data presented in Fig. 4 indicate that the content of arenes in the larch needles decreases abruptly at a distance from the boundary of the industrial zone higher than 20 km, which indicates the fact that the area of the propagation of polluted air masses is quite limited. Perhaps, this could be connected with the terrain of the Shelekhov region [20].

PAH content in soil

The determination of ΣPAH in soil as an environmental indicator allows one to assess the contamination of an area under investigation with this class of organic pollutants. The PAH profiles established for the soil samples taken from the territory of dispersing the emissions of the IrkAZ-SUAL, are individual and they reflect the intake of arenes from different sources during a long time under the conditions of chemical and microbiological degradation of the contaminants.

We have established the following PAH content in the soil of the industrial zone (ng/g): ΣPAH 19 000–55 000, BaP 500–2400 ng/g (25–

TABLE 4

PAH content in soil, ng/g

PHEN	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BeP	BaP	PER	INP	BP	DBA	ΣPAH	BaP_{MPC}
Industrial zone of the IrkAZ-SUAL *															
1.1–8.0	0.2–2.2	2.1–11	1.6–8.2	0.9–6.8	1.0–7.7	0.5–2.5	0.2–1.0	0.3–1.7	0.5–2.4	0.1–0.7	0.2–1.6	0.3–2.0	0.1–0.5	19–55	25–120
Olkha Settlement, 2 km from the industrial zone to the south															
84	13	210	160	75	94	140	49	97	110	30	79	97	19	1300	4.8
Dachnya Settlement, 11 km from the industrial zone to the south															
7.4	0.8	7.9	6.0	2.2	2.8	57	12	19	21	<2.0	5.0	58	<2.0	200	1.0
Rassokha Settlement, 20 km from the industrial zone to the south															
21	5.0	43	34	15	33	27	25	39	21	<2.0	18	24	6.0	140	1.0

* In μg/g.

120 MPC, the MPC for BaP in soils being equal to 20 ng/g). The BaP concentration exceeds the regional geochemical background (1–3 ng/g, [21]) by 800 times; the value of this parameter characterizes the soil as an object with an extreme level of contamination [22].

Outside the industrial zone (near the Olkha Settlement), the content ΣPAH is 40 times lower, whereas the soil contamination according to the concentration of BaP could be rated as high. The results obtained earlier for this area (ΣPAH 260–1200 ng/g [21], the content of BaP 5–210 ng/g [21], 11–155 ng/g [23]) indicate remaining the same level of soil contamination (Table 4). It should be noted, that with increasing the distance from the territory of the plant up to 11 and 20 km the ΣPAH content in the soil is abruptly reduced down to 140–200 ng/g, whereas the level of soil contamination according to the concentration of BaP could be rated as moderate.

PAH content in water and bottom sediments of the Olkha River

The catchment basin of the Olkha River is located within the area of dispersing the industrial emissions of the IrkAZ-SUAL, so the river water are subjected to the contamination ith PAHs, especially in the spring, during the snow-melting period and discharging the accumulated pollutants together with meltwater. Water samples collected at the distances of 2 and 20 km upstream from the industrial zone (see Fig. 1, *a*) exhibit the range of content ΣPAH to vary within 4.2–11 (March), 68–110 (April) and 19–52 ng/dm^3 (the summer months of June, July) (Table 5). The BaP concentration in the samples taken during the snow-melting period (April), does not exceed the MPC level thereof for drinking water (5 dm^3), but the value is 20–30 times higher than the background level (0.1 ng/dm^3 [24]). The content of

TABLE 5

PAH content in the water of the Olkha River, ng/dm^3

Sampling date	PHEN	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BeP	BaP	PER	INP	BP	ΣPAH	ΣPAH_{EEC}	BaP_{MPC}
Mouth of the IHEPP-5 ash dump drainage stream																
03.03	32	2.1	53	48	6.5	28	20	5.3	12	21	<0.2	15	16	260	77	4.2
06.04	43	7.3	32	17	3.8	3.6	5.8	2.3	5.8	2.7	<0.2	8.6	12	140	31	0.54
25.06	2.8	<0.2	15	8.5	2.0	5.8	3.4	1.4	2.0	1.2	<0.2	<0.2	<0.2	42	6.0	0.24
25.07	200	17	410	240	130	290	340	93	210	160	49	98	120	2400	810	32
2 km downstream the Olkha River from the mouth of the IHEPP-5 ash dump drainage stream																
03.03	38	2.8	32	23	15	33	39	11	25	22	<0.2	34	38	310	140	4.4
06.04	31	5.3	15	9.4	8.2	10	13	5.3	12	5.1	<0.2	15	19	150	57	1.0
25.06	2.9	<0.2	2.6	3.0	<0.2	2.4	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	11	–	–
25.07	13	0.9	8.3	4.5	2.2	5.5	2.5	1.0	2.0	1.5	1.2	2.2	4.7	50	12	0.30
2 km upstream the Olkha River from the industrial zone (the Olkha Settlement)																
03.03	4.3	<0.2	2.5	2.0	0.9	1.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	11	–	–
06.04	33	5.7	12	8.9	5.9	11	8.2	3.4	6.9	3.2	<0.2	4.4	5.4	110	25	0.64
25.06	7.0	1.2	5.0	3.4	<0.2	4.1	1.2	<0.2	0.9	1.1	<0.2	<0.2	<0.2	24	2.3	0.22
25.07	11	2.0	16	6.5	2.4	5.7	2.5	1.0	1.8	1.2	1.0	1.0	<0.2	52	5.7	0.24
20 km upstream of the Olkha River from the industrial zone (the Rassokha Settlement)																
03.03	4.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	4.2	–	–
06.04	30	3.0	7.9	4.9	0.9	1.4	4.0	2.1	3.8	2.1	<0.2	3.2	4.4	68	16	0.42
25.06	6.5	0.9	4.0	1.6	<0.2	3.5	0.9	0.5	0.8	0.7	<0.2	<0.2	<0.2	19	2.1	0.14
25.07	8.0	<0.2	4.2	3.2	<0.2	2.4	2.2	<0.2	1.3	1.6	<0.2	<0.2	<0.2	23	3.8	0.32

TABLE 6

PAH content of in the bottom sediments of the Olkha River, ng/g

PHEN	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BeP	BaP	PER	INP	BP	DBA	ΣPAH	BaP_{MPC}
Mouth of the IHEPP-5 ash dump drainage stream															
85	15	190	120	93	110	97	35	60	76	23	44	46	16	1000	3.8
2 km downstream the Olkha River from the mouth of the IHEPP-5 ash dump drainage stream															
95	20	220	170	100	160	170	57	120	100	43	70	96	18	1500	5.0
2 km upstream the Olkha River from the industrial zone (the Olkha Settlement)															
25	7.0	50	36	23	29	31	12	21	26	14	16	16	<2.0	300	1.3
20 km upstream of the Olkha River from the industrial zone (the Rassokha Settlement)															
14	3.0	18	13	6.0	11	18	6.0	15	12	9.0	4.0	6.0	2.8	140	0.6

the five arenes those are under monitoring in drinking water in the EEC countries (BbF, BkF, BaP, INP and BP, see Table 5), in the waters of Olkha River within the period of the maximum PAH contamination is 8 times lower than MPC_{EEC} (200 ng/dm^3 [25]).

Polycyclic aromatic hydrocarbons have high hydrophobic properties, so at the water-bottom boundary layer they are redistributed to be accumulated in bottom sediments. On this basis, the surface bottom sediments can serve as indicators with respect to water contamination and as potential secondary sources of the contamination of a water reservoir. It has been found that the bottom sediment samples of the Olkha River (Table 6) taken 2 and 20 km upstream from the industrial zone exhibit the content of ΣPAH equal to 300 and 140 ng/g, respectively, whereas the BaP concentration therein corresponds to 1.3 and 0.6 MPC, respectively (the MPC for BaP in the bottom sediments is equal to 20 ng/g). This indicates that at a distance of 20 km from the potential source (the IrkAZ-SUAL) in the Olkha River there is a background level of water contamination with PAH compounds. Thereby the content of BaP corresponding to the regional background levels (for the tributaries of South Baikal 0.7–65 ng/g, for the Angara River 5–65 ng/g), remain almost unchanged within the period from 1993 [24].

It has been found that the ratio between PAHs revealed in the Olkha River bottom sediments near the ash dump stream of IHEPP-5 (see Fig. 1, c) and 2 km downstream the river from the confluence of the stream, are comparable. The ratio values differ from the profile of PAHs accumulated within the snowpack of the industrial zone in a more high level of FLU and PYR, as well as in a decrease in the relative concentration of BbF. The noted change in the ratio between the arenes could be caused by coming the PAHs both with the emissions from the IrkAZ-SUAL, and from another source such as IHEPP-5. This assumption can be confirmed by data concerning the extreme content of the УPAH in water samples taken within the area of discharging the ash dump water drainage stream (July, see Table 5), as well as by a high level of PAH accumulation in bottom sediments 2 km downstream the Olkha Rver from the place of the drainage stream confluence.

CONCLUSIONS

PAHs distribution was studied in natural objects over the territory of dispersing the emissions from the IrkAZ-SUAL aluminum plant, a strong and steady source of such type pollutants. An extreme PAH accumulation has been revealed within the range from 19 to 54 mg/m^2 for the snow cover and within the range from 19 to 55 μg/g for the soil surface layer of the industrial zone of the plant. The BaP concentration in the soil is 120 times higher than the MPC level being 800 times higher than the regional geochemical background. At a distance from the source equal to 20 km, the PAH accumulation level in snow exhibits an abrupt decrease ranging from 200 to 1000 times, however being up to 10 times higher than the back-

ground levels up to 10 times; the content of PAHs in soil exhibits a 400-fold decrease, and the contamination could be assessed as moderate with respect to BaP concentration.

Larch needles have been demonstrated to exhibit a high efficiency as a biological indicator of air contamination. The accumulation level of PAHs in larch needles is almost an order of magnitude higher than that for of pine needles and reflects the distribution of pollutants only during the summer. Basing on the analysis of the levels of PAH accumulation in snow cover as well as in larch and pine needles there has been concluded that the PAHs propagation occurs from the source of the emission thereof within a limited area.

The emissions of IrkAZ-SUAL do not affect the southern part of the catchment basin of the Olkha River. At a 20 km distance from the industrial area the purity of water in the Olkha River meets the requirements for drinking water, whereas the content of BaP in bottom sediments is consistent with the regional background level.

Studies have been performed concerning the atmospheric contamination in the Shelekhov City during a stable atmospheric stratification under dead calm. The concentration of BaP under these conditions is 19 times higher than the MPC level. There is a considerable daily variability revealed for the ΣPAH content in aerosol, which variability is characterized by an increase in the total PAH content up to 30 times and the BaP content fluctuations from 0.4 to 19 MPC.

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