Monitoring of the ecological toxicants in the environmental objects of Baikal region. Part 2. Polycyclic aromatic hydrocarbons in snow cover of industrial centers

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We present some results of monitoring the polycyclic aromatic hydrocarbons (PAH) in snow cover of industrial centers in Baikal region (Irkutsk and Shelekhov) obtained in the period from 1996 to 2001. The levels and rates of accumulation for 11 identified compounds included in the priority list of ecological toxins are estimated. The identification of PAH is being done by use of the HPLC method.

Introduction

The level of pollution of the surface atmospheric layer with polycyclic aromatic hydrocarbons (PAH) in Baikal region is characterized by sharp seasonal variability.[1,2] The maximum PAH concentrations are observed in cold seasons because of increased emissions of heat and power stations and the pronounced anticyclonic character of atmospheric circulation. In this period, atmospheric emissions mostly localize nearby their sources, aerosol pollution fields overlap, and solid particles, at which PAH are concentrated, deposit at the surface.[3] As a result, for point sources or sources that occupy a small area, accumulation of PAH in the snow cover directly depends on the PAH concentration in aerosol.[4] Large cities or industrial centers with many pollution sources normally occupy large areas, therefore the level of aerosol pollution at the sampling points depends on the emission rates of local sources and on the particular meteorological situations occurred.[1] At the same time, the effect of "local urban air circulation"[5] should favor additional transport and mixing of pollutants in the atmosphere and following leveling of their concentration on the surface. Therefore, analysis of the snow cover, in contrast to aerosol, allows obtaining integral characteristics of the state of urban environment in winter period.

First, the PAH monitoring in the snow cover was conducted for the period of 1996–2001 to evaluate the degree of pollution in large industrial centers of the Baikal region: Irkutsk and Shelekhov. According to recent data, in Irkutsk occupying the area more than 300 km^2 there are 3267 sources emitting 117 ingredients into the surface atmosphere.[3] Shelekhov is a dormitory of the IrkAZ-SUAL plant, the largest plant in the Eastern Siberia, whose emissions form the powerful source of PAH in the environment. The results of monitoring, levels and rates of PAH accumulation in the regions under study are presented in this paper.

Materials and methods

The snow samples for analysis were collected late in February – early in March in the form of core samples for the whole depth of the snow cover with the base area of 15 × 15 cm. At every point, two samples were taken at the distance of 5–6 m from each other. In all samples, 12 PAH included in the priority list of ecological toxins (see Note to Table 1) were determined by the HPLC method in the liquid and solid phases of the snow water. Benzapilene measurements were conducted by the technique from Ref. 6, and the accompanying PAH were measured by the technique from Ref. 7.

The accumulation levels (surface density) for benzapilene and the sum of identified PAH were calculated taking into account the snow fall per unit area for the whole snow period by the equation

$$Q = m/S,$$

where Q is the PAH accumulation level (surface density), μg/m^2; m is the mass of identified PAH in μg; S is the sampling area in m^2.

The surface density measured using two samples made up the mean value for every point.

The accumulation rate was calculated taking into account the snow period for each winter season by the following equation:

$$\text{Accumulation rate} = Q/\text{number of weeks}.$$

The period from establishment of the snow cover to sampling was 13–16 weeks.

In 1996 and 1998 samples in Irkutsk were collected in the central part of the city and its suburbs (13 points), and in 1996–2001 samples were taken at the points selected for the annual monitoring at late winter season: point 1 – park area of Akademgorodok, point 4 – island of River Angara, central part of the city, point 7 – city suburb, bank of Irkutsk water reservoir (Fig. 1). In the region of Shelekhov, samples were taken at two points: at northeastern and southwestern suburbs in 1996–1999, and in 1996 at nine points beyond Shelekhov about 2 km far from it in the northwestern direction in the rural area.

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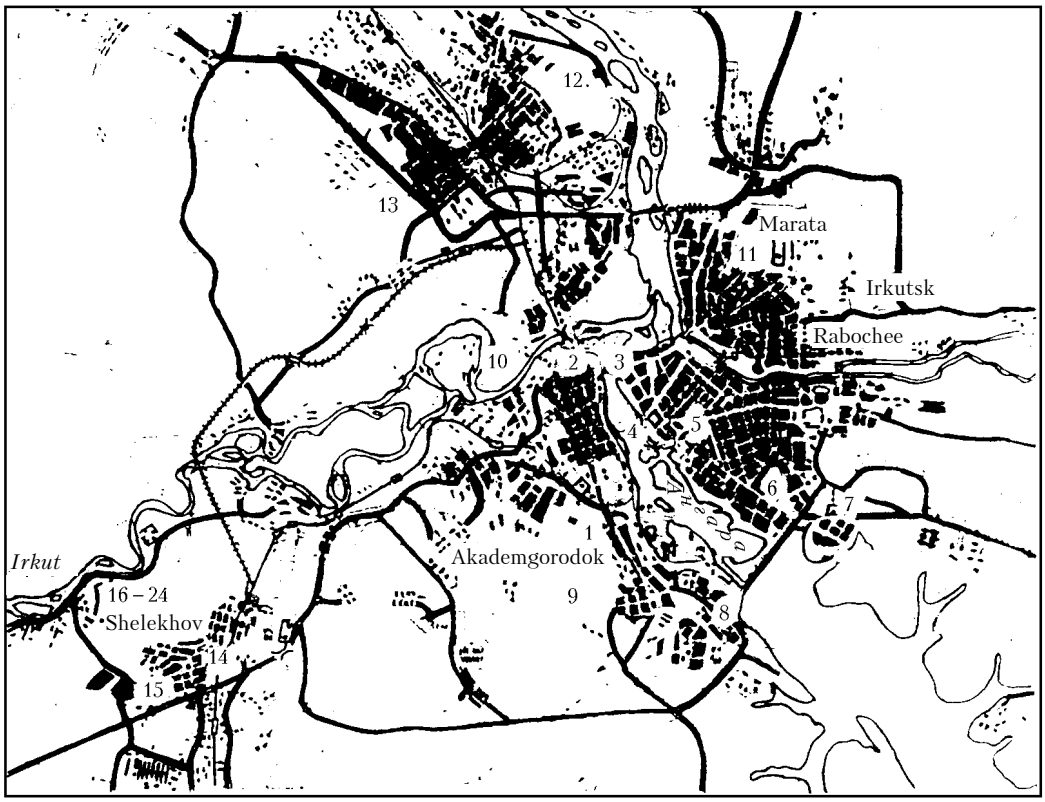

Fig. 1. 1 : 200 000 map of sampling.

Table 1. PAH accumulation levels (μg/m^2) in snow cover of Irkutsk

Sampling points and year		PAH											Total
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
1	1996	88	0.4	55	73	4.7	8.7	6.7	2.3	6.8	5.9	3.6	250
	1998	63	< 0.1	46	30	1.0	6.7	4.3	0.5	< 0.5	< 0.5	0.9	150
	1999	250	2.9	190	110	6.7	25	21	3.3	11	6.2	3.9	640
	2001	90	0.4	78	49	3.1	14	20	4.5	7.6	6.6	5.8	280
2	1996	120	2.7	70	56	5.6	7.1	8.6	15	5.4	5.9	4.0	300
3		310	6.7	150	210	23	27	38	20	21	19	15	840
4	1996	70	2.2	57	40	5.7	6.5	7.3	13	4.3	3.9	2.9	210
	1998	150	< 0.1	85	67	4.5	16	14	2.9	1.1	3.7	3.1	350
	1999	67	< 0.1	75	49	3.4	14	10	41	8.6	< 0.5	5.1	270
	2001	210	1.4	200	140	12	34	56	13	33	20	16	730
5	1996	120	4.7	80	81	3.3	4.6	2.6	< 0.5	3.2	1.9	1.5	300
6		130	0.6	84	83	8.1	7.9	4.9	< 0.5	5.5	5.3	2.9	330
7	1996	9.0	0.2	20	11	6.7	2.2	3.4	< 0.5	< 0.5	5.6	12	71
	1998	40	< 0.1	26	15	0.9	3.1	2.7	0.5	< 0.5	< 0.5	< 0.5	88
	1999	110	< 0.1	100	58	4.4	17	15	19	9.7	7.3	7.0	360
	2001	57	0.9	54	41	2.9	9.2	22	3.2	7.7	6.0	3.7	210
8	1996	170	9.2	160	150	9.3	14	10	< 0.5	8.7	5.8	5.8	540
9	1998	90	< 0.1	62	40	0.6	14	14	2.1	2.2	2.8	3.7	230
10		71	< 0.1	120	71	2.0	25	21	4.1	1.9	2.7	1.8	320
11	1996	18	1.3	15	13	2.1	2.9	0.0	1.3	3.3	2.5	1.7	61
	1998	36	< 0.1	34	17	0.5	4.6	4.6	0.5	< 0.5	1.1	0.8	100
12	1998	120	< 0.1	90	49	3.1	19	19	4.8	1.3	6.0	4.7	320
13		160	< 0.1	87	47	3.9	12	10	2.6	0.8	1.5	1.6	320

Note. PAH: I – phenanthrene, II – anthracene, III – fluoranthene, IV – pyrene, V – benzo[a]anthracene, VI – chrysene, VII – benzo[b]fluoranthene, VIII – benzo[k]fluoranthene, IX – benzapilene, X – benzo[g,h,i]perylene, XI – indeno[1,2,3-c,d]pyrene.

Table 2. PAH accumulation levels (μg/m²) in snow cover of Shelekhov

Sampling points and year		PAH											Total
		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
14	1996	520	45	580	670	160	380	240	130	260	180	140	3300
	1997	250	7.1	440	250	41	120	180	39	94	80	67	1600
	1998	560	< 0.1	1100	690	40	300	290	80	120	68	44	3300
	1999	260	< 0.1	340	240	44	130	150	38	110	37	48	1400
15	1996	1100	71	840	1100	220	550	380	130	340	170	170	5100
	1997	3900	160	3700	3000	470	1400	1700	390	770	630	340	16000
	1998	810	< 0.1	1300	670	< 0.5	3200	440	81	28	110	89	3900
	1999	1200	60	1600	1100	240	250	500	150	470	120	130	5800
16	1996	160	9.2	210	140	22	74	59	17	51	16	9	760
17		450	35	410	400	64	180	200	61	190	77	55	2100
18		360	35	410	320	55	120	170	50	160	60	37	1800
19		94	4.1	150	110	25	53	79	28	98	49	33	720
20		170	17	250	190	46	100	140	52	180	84	61	1300
21		57	2.8	70	47	6.9	25	28	10	29	14	11	300
22		110	0.3	130	87	13	49	56	17	61	27	17	580
23		240	0.5	270	200	38	93	130	44	160	73	41	1300

Results and discussion

PAH accumulation levels

The snow cover in Irkutsk and Shelekhov was characterized by a high level of pollution, the content of solid phase from 5 to 73 g/m², and the PAH content (total amount of identified compounds) from 60 to 850 μg/m² in Irkutsk and from 1400 to 16200 μg/m² in Shelekhov. The total amount of phenanthrene, fluoranthene, and pyrene was ~80%, and that of benzapilene was ~2.5% of the amount of the detected PAH. The calculated accumulation levels are given in Tables 1 and 2.

In the central part of Irkutsk, where numerous local sources are located, PAH accumulation in the snow cover ranged from 60 to 840 μg/m² (points 1–8). The maximum level of PAH accumulation from 530 to 840 μg/m² was observed near the highways with heavy traffic (points 3, 8). In the northwestern part of the city (points 12 and 13), the surface PAH density did not exceed 320 μg/m², and in the northeastern upland (point 11) and in the eastern part of the city (point 7, bank of the Irkutsk water reservoir) the PAH accumulation was about five times lower. Benzapilene accumulation in the central part of the city (points 1–8) was from < 0.5 to 33 μg/m², and at suburbs (points 9–13) it ranged from < 0.5 to 3.3 μg/m² (see Table 1).

The mathematical simulation of pollutant deposition at the territory of Irkutsk predicts the maximum load for the northwestern part of the city.[8] At the same time, because of the temperature gradient of the ambient air and air mass mixing over the city from the center to suburbs and for the surface atmospheric layer – to the center, i.e., the so-called effect of urban air circulation,[5] the pollutant content in the snow cover should become leveled over the city territory. Analysis of the samples taken in 1998 in the central part (points 4 and 10) and at Irkutsk suburbs (points 12 and 13) is interesting from this point of view. At these points, accumulation of the sum of the identified PAH had roughly the same level (from 320 to 350 μg/m²), but the contributions of different PAH varied widely (see Table 1). The concentration ratio (to phenanthrene as a prevailing compound) deviated from the mean level by 2 to 45%. This result is indicative of unequal contributions of different sources to the total PAH amount and, likely, of a minor role of the effect of PAH content leveling in the snow cover. The measurements of the levels of PAH accumulation in 1996–2001 confirm the latter conclusion. In Fig. 2 one can see considerable fluctuations of the PAH accumulation level for one season at different points and in the same region for the observation period.

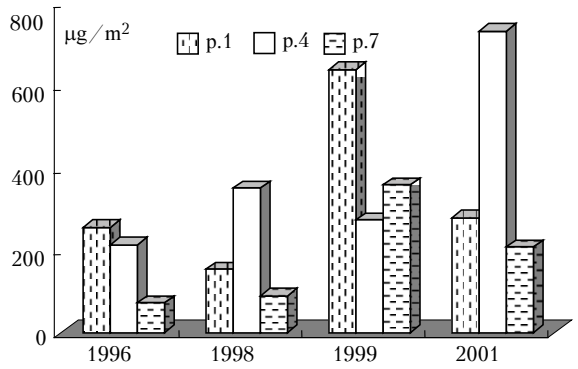

Fig. 2. PAH accumulation level (sum of identified compounds) in the snow cover of Irkutsk for one winter season at sampling points 1, 4, and 7 in 1996–2001.

As for the year-to-year variability, a tendency to doubling of the mean value of PAH accumulation (for three points) is observed (Fig. 3).

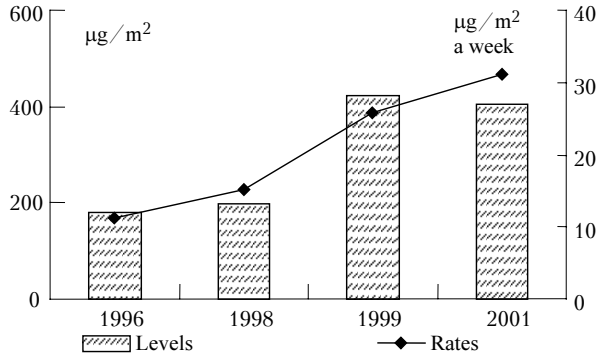

Fig. 3. Year-to-year variability of the mean PAH accumulation level and the mean accumulation rate (for three sampling points 1, 4, and 7) in snow cover of Irkutsk in 1996–2001.

This tendency may be caused by the growing number of cars. Since 1995 until 1998 the lead concentration in snow of the urban regions in Irkutsk increased by more than 30 times against the background of the decreasing content of such technogenic elements as Zn, Cu, and Cd (Ref. 9). Automobiles are mostly run on ethyl gasoline, and it is just the main source of pollution of the surface atmosphere with PAH (Fig. 4).

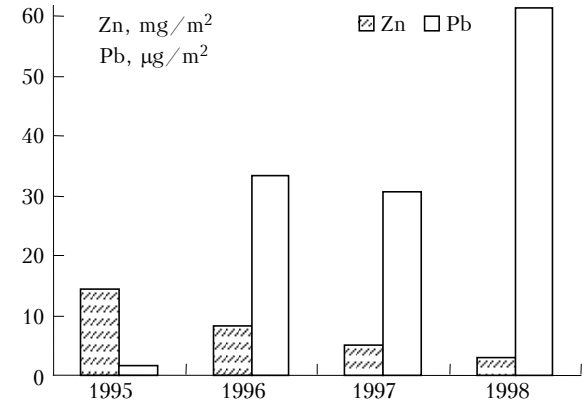

Fig. 4. Year-to-year variability of the level of Pb and Zn accumulation in the snow cover of Irkutsk in 1995–1998 (sampling point 2).

The maximum surface PAH density in the snow cover was found in the region of Shelekhov (points 14 and 15). Accumulation of the identified compounds of this class for the season of 1997 achieved the total value of 16 mg/m², and that of benzapilene was 0.7 mg/m² (see Table 2). In other years, the surface PAH density (the mean over two points: 14 and 15) did not exceed 5 mg/m² and 0.5 mg/m² for benzapilene.

With the dominant northwestern wind, the territory of Shelekhov is beyond the main zone polluted by the IrkAZ-SUAL plant. Nevertheless, the plant is the main source of pollution of the urban atmosphere. The concentration ratios of the detected PAH to phenanthrene in the samples collected in 1996–1999 in Shelekhov (points 14 and 15) and beyond it (points 16–24) have close values. The observed spread in the PAH concentrations is characterized by the relative standard deviation (S_r) ≤ 11% (except for the anthracene, for which S_r = 16%). The constant concentration ratio is indicative of the same dominant source, and the level of PAH accumulation in some seasons is likely determined by the value of the contribution from the plant emissions to pollution of the urban atmosphere and, consequently, the snow cover.

PAH accumulation rates

There are only few data, in the literature, on the rates of PAH accumulation in the snow cover that allows comparative estimates of the pollution level to be obtained for different periods and different regions. The calculation of PAH accumulation rates from the results of snow cover monitoring in Irkutsk (see Fig. 3) confirms the 2.5 times increase of the PAH flow onto the surface, that is, the increase in pollution of the surface atmosphere for the period since 1996 until 2001. For Shelekhov, the calculated accumulation rates point to a strong effect of IrkAZ-SUAL emissions on the pollution of the atmosphere. In some seasons, the PAH flow rate changed from 25 to 1000 μg/m² a week at the mean (for the observation period) rate of 300 μg/m² a week. The comparison with the background levels for the Western Europe (Pyrenees – 0.09, the Alps – 0.26, Tatra Mountains – 0.77 μg/m² a week[10]) and with the highland background monitoring station in Mondy (0.04 μg/m² a week[11]) shows that the total PAH flows in the regions of Irkutsk and Shelekhov are, respectively, 700 and 7500 times higher.

Measurement of the accumulation rates allows us to assess pollution with the substances of highest environmental and human hazard. Thus, in the central part of Irkutsk for the period since 1996 until 2001, the benzapilene accumulation rate increased four times and in 2001, it was 2.5 μg/m² a week. In Shelekhov the mean benzapilene accumulation rate for the period since 1996 until 1999 was 17 μg/m² a week. Comparison of benzapilene flows in large German cities (Berlin, Frankfurt, Dusseldorf – 0.5–2.0 μg/m² a week[12]), along roadside in Finland (0.3–1.9 μg/m² a week[13]), and in the industrial centers of Baikal region suggests that the pollution of Irkutsk atmosphere with this carcinogen has a comparable level, and in Shelekhov it is up to 50 times higher.

Identification of PAH sources

It is rather difficult to identify a source (sources) of PAH emission from the concentration ratio of different PAH in snow of industrial centers, because pollution fields of different sources overlap in the process of accumulation. An exclusion may be the regions with a powerful dominating source, for example, the pollution zone of the IrkAZ-SUAL plant, or sources, whose emissions are equivalent in the composition, such as, for example, areas with buildings having furnace heating at Irkutsk suburbs (point 9).

The PAH/benzapilene concentration ratios in the snow cover of the studied regions calculated for source identification are given in Table 3.

Table 3. PAH/benzapilene concentration ratio in atmospheric emissions from different sources and in snow samples

Source	PAH									
	I	II	III	IV	V	VI	VII	VIII	X	XI
Atmospheric emissions										
Boiler houses*:										
coal	1.1–18	0.10–2.6	2.6–8.0	4.0–13	0.47–1.6	0.45–0.77	0.53–0.94	0.23–1.8	0.09–0.52	0.31–0.60
black oil	9.3	1.0	1.7	4.7	1.7	4.0	3.0	6.3	1.3	1.7
Furnaces*:										
coal	1.1–10	0.28–3.1	1.6–8.9	2.0–11	0.43–1.5	0.47–2.0	0.45–1.3	0.30–0.63	0.13–0.40	0.39–0.59
firewood	1.0	0.14	1.2	1.8	0.74	0.78	1.1	0.95	0.57	1.2
Carburetor engine **	–	–	9.9–76	14	1.1–7.4	4.4–15	1.4–7.4	9.1	1.9–8.7	–
Diesel engine**	36	0.1–1.5	23	23	0.9–4.0	2.6	–	1.1–1.0	0.4–2.0	–
IrkAZ-SUAL emissions ***	0.39–4.1	0.06–0.51	3.4–5.2	1.6–4.4	0.23–0.73	0.36–1.3	1.0–1.6	0.27–0.37	0.38–0.54	0.21–0.30
Snow cover										
Shelekhov	0.95–5.3	0.01–0.22	1.4–9.0	1.1–5.7	0.01–0.65	0.54–2.5	0.77–2.9	0.28–0.66	0.26–0.87	0.18–0.71
Irkutsk center, p. 1–8	13–37	0.1–1.5	7.1–25	9.3–25	0.7–1.5	1.3–1.6	0.8–1.8	0.3–3.0	1.0	0.59–1.1
Irkutsk suburbs:										
point 11	5.4	0.38	4.6	3.8	0.63	0.88	–	0.38	0.75	0.50
point 9	41	< 0.1	28	18	0.27	6.4	6.4	0.95	1.3	1.7
point 10	37	< 0.1	63	37	1.1	13	11	2.2	1.4	0.95
point 12	92	< 0.1	69	38	2.4	15	15	3.7	4.6	3.6
point 13	200	< 0.1	109	59	4.9	15	13	3.3	1.9	2.0

* Data from Ref. 14. ** Data from Ref. 15. *** Sampling (n = 10) was carried out by Dr. L.I. Belykh, senior researcher of the Biology Institute at the Irkutsk State University, PAH were determined by the technique from Ref. 14.

In the snow samples from Shelekhov, the PAH concentration ratios fall within a narrow range of values and coincide with those in the plant emissions, while the concentration ratios in the samples from Irkutsk suburbs (point 9) coincide with those in emissions of boiler houses and coal burning furnaces. In the snow cover of the central part of Irkutsk (points 1–8), the concentration ratios for the most PAH coincide with their values in automobile exhausts, but their wide ranges likely point to the contributions of other sources to pollution in this part of the city (boiler house and furnace emissions, building and repair works, trash burning). Analysis of the PAH concentrations in the snow cover at points 9, 10, 12, and 13 (see Fig. 1) indicates the contributions of several PAH sources to local pollution.

Conclusion

For 90–110 days of the winter season, the snow cover of industrial centers in the Baikal region accumulates from 60 to 840 μg/m^2 of PAH in Irkutsk and from 1400 to 16000 μg/m^2 in Shelekhov (sum of 11 identified compounds). From the concentration ratios of the found PAH it was determined that the dominant pollution sources are emissions of the IrkAZ-SUAL plant in Shelekhov, automobile exhausts in the central part of Irkutsk, and emissions from boiler houses and furnaces in the Irkutsk suburbs. For the period of monitoring, since 1996 until 2001, the mean level of PAH accumulated in Irkutsk increased from 240 to 420 μg/m^2 and the mean PAH accumulation rate increased from 11 to 31 μg/m^2 a week, while that of benzapilene increased from 0.5 to 2.5 μg/m^2 a week. In the region of Shelekhov, at the mean PAH accumulation rate equal to 4600 μg/m^2, the PAH flow rate was estimated as 300 and that of benzapilene as 17 μg/m^2 a week. The benzapilene accumulation rate in Irkutsk is comparable with those in large cities of the Western Europe, and that in Shelekhov is 50 times as high.

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