Monitoring of the ecological toxicants in the environmental objects of Baikal region. Part 1. Determination of polycyclic aromatic hydrocarbons in aerosol of industrial centers (using Irkutsk as an example)

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The possible levels of total concentration of the polycyclic aromatic hydrocarbons (PAH) and individual compounds of this class are determined for the first time in the atmosphere of Irkutsk as a typical industrial center in Baikal region. It is shown that in winter the PAH concentration can reach 300 ng/m^3 (total amount of identified compounds), and the concentration of benzapilene (most dangerous carcinogen) can reach 30 ng/m^3. Under certain meteorological conditions, the extremely high PAH concentration is observed in daytime. The summer PAH concentration does not exceed 1–6 ng/m^3, and that of benzapilene is within 0.2–1 ng/m^3 ($\le$ MPC) due to a wider self-clearing capabilities of the atmosphere. The PAH concentrations were determined by the method of microcolumn high-performance liquid chromatography with multiwave photometric detection.

Development of an up-to-date monitoring system for Baikal region is very important and urgent, especially in view of the fact that Lake Baikal was included into the list of regions of world heritage (UNESCO, 1996). The problem of atmospheric pollution is the most pressing ecological problem in Baikal region.[1] According to data of the State Environmental Protection Committee, seven towns of the Irkutsk Region (Angarsk, Bratsk, Zima, Irkutsk, Usol'e-Sibirskoe, Shelekhov, Cheremkhovo) have been included since 1995 into the list of Russian towns with high level of atmospheric pollution. This about 16% of the total number of towns included in this list.[2]

Polycyclic aromatic hydrocarbons (PAH) are super toxicants of the first class of danger. Pollution of the atmosphere with PAH in Baikal region was not systematically studied earlier, even though powerful sources emitting these compounds (aluminum-producing plants, large heat and power plants, oil and chemistry enterprises) are located there. Emissions of small heat and power plants (thermal power about 1 MW) employing an imperfect solid fuel burning technology (in Irkutsk there are more than 350 such boiler houses)[3] and cars are the main sources of pollution of the near ground atmosphere with PAH.

Specialized divisions of the Irkutsk Hydrology and Meteorology Committee monitor pollution of the urban atmosphere in Baikal region with benzapilene, the most dangerous carcinogen. However, this monitoring does not conform with the current requirements according to such criteria as information content, timeliness, economy, and adequacy of recommendations. We have developed a technique for determination of 12 most important PAH. This technique employs the method of microcolumn high-performance liquid chromatography with multiwave photometric detection. Using it, we have measured the PAH concentration in the samples of atmospheric aerosol from the near ground atmosphere collected in Irkutsk for the period since 1996 until 1999. The obtained data allow estimation of the possible level of aerosol pollution, as well as the seasonal and diurnal dynamics of the PAH concentration typical of Irkutsk (population of 650 000) as a large industrial center in Baikal region.

Experimental technique

Aerosol was sampled at five sites, each having its individual set of local PAHC sources. Site *A* is in the city center near a cross of roads with heavy traffic. Site *B* is also in the city center near the bank of River Angara 250 m far from motorways; there were many houses with stove heating in this district. Site *C* was in the city center, where there were many houses with stove heating, 100 m far from a motorway with heavy traffic. Site *D* is in a park zone 500 m far from a motorway. Site *E* is in a district of private cottages, where there were many houses with stove heating.

Aerosol was sampled for 4–24 hour onto Whatman–41 paper filters (Great Britain), Schllicher & Schnell glass wool filters (Germany), and filters with Al_2O_3, as well as the combination of filters and Octadecyl, Baker

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cartridges. A Gebr. Becker, Wuppertal pump (Germany) with the productivity of 4 m^3/h was used for sampling. The volume of the pumped air was measured with a Schlumberger, Gallus 2000 controller (Germany). A probe with a filter was set at 2 to 10 m above the ground.

The PAH from filters were extracted three times by *n*-hexane in glass retorts (15 ml) on an ultrasonic bath (SANOREX TK-52, Bandelin electronic, Germany). Then the *n*-hexane was separated out from the obtained extracts with a rotor evaporator at 40°q, the residue was diluted in 100–200 μl of methanol, and the methanol solution was analyzed by the method of high-performance liquid chromatography (HPLC).

Extracts were chromatographed in a microcolumn liquid Milikhrom A-02 chromatograph (EkoNova, Novosibirsk, Russia) with a 2 × 75 mm column and Nucleosil 5-C18 PAHC sorbent. The column efficiency against the chrysene peak was 5500 theoretical plates. Chromatographing conditions were as follows: eluent: methanol:water = 65:35 (A), acetonitrile:water = 85:15 (B); gradient: 0–100% 18 min (A), 100% 3 min (B); eluent flow rate of 0.2 ml/min; simultaneous photometric detection at 250, 260, and 290 nm; temperature of 45°q. Acetonitrile and methanol used for analysis had the purity “for HPLC.B

PAH peaks in chromatograms were identified using two parameters: containment time and spectral ratios of the areas of chromatographic peaks of individual PAH at 250, 260, and 290 nm. The PAH amount was determined by the method of external standardization with the use of Supelco Co standards. The measurement error did not exceed 20%.

Results and discussion

The determined levels of the PAH concentration in the samples of atmospheric aerosol collected in different Irkutsk districts for three years are given in the Table. The extreme values and that averaged over 10 to 20 measurements are presented.

The maximum amounts of PAH from 25 to 300 ng/m^3 (total concentrations of all identified compounds) are typical of the winter period. In summer, the total PAH concentration in the atmospheric aerosol is 20 to 100 times lower, and the concentrations of compounds 1–2, 4–5, and 8 (see Note to the Table) only slightly exceed or do not reach the PAHC detection limit of our technique. At the concentration of the solid phase of aerosol from 40 to 260 μg/m^3, the content of PAH in the examined samples does not exceed 0.3%. Marked seasonal variations of both solid phase of aerosol and the relative content of PAH in it were found (Fig. 1).

Table. Levels of PAHC concentration in the solid phase of aerosol, in ng/m^3

Sampling site	Month (year)	PAH											Total
		1	2	3	4	5	6	7	8	9	10	11	
A	February (1996)	$\frac{14-28}{21}$	$\frac{1.0-3.0}{2.0}$	$\frac{50-75}{62}$	$\frac{42-57}{49}$	$\frac{21-22}{21}$	$\frac{18-22}{20}$	$\frac{10-14}{12}$	$\frac{7-11}{9.0}$	$\frac{18-22}{20}$	$\frac{12-14}{8.0}$	$\frac{11-12}{11}$	$\frac{200-280}{240}$
B	January (1996)	$\frac{1.0-3.0}{2.0}$	< 0.01	$\frac{25-37}{31}$	$\frac{26-52}{39}$	$\frac{5.0-10}{7.0}$	$\frac{8-20}{14}$	$\frac{11-14}{12}$	5.0	$\frac{10-18}{14}$	$\frac{6.0-10}{8.0}$	$\frac{5.0-9.0}{7.0}$	$\frac{100-180}{140}$
D	December (1997)	$\frac{1.6-17}{6.0}$	$\frac{0.01-0.55}{0.50}$	$\frac{5.1-43}{15}$	$\frac{2.0-43}{16}$	$\frac{0.70-12}{3.7}$	$\frac{2.8-28}{11}$	$\frac{1.8-23}{8.0}$	$\frac{2.9-31}{11}$	$\frac{0.8-29}{4.0}$	$\frac{0.8-10}{4.0}$	$\frac{1.7-21}{7.4}$	$\frac{25-260}{90}$
D	April (1998)	$\frac{0.1-2.0}{1.0}$	< 0.01	$\frac{0.2-2.5}{1.1}$	$\frac{0.8-3.6}{2.1}$	$\frac{0.1-0.5}{0.2}$	$\frac{0.3-2.4}{1.3}$	$\frac{0.2-2.8}{1.4}$	$\frac{0.1-0.9}{0.4}$	$\frac{0.3-1.8}{0.7}$	$\frac{0.1-0.9}{0.5}$	$\frac{0.1-1.0}{0.5}$	$\frac{3.3-17}{9.3}$
D	June – July (1997)	0.02	< 0.01	$\frac{0.1-0.2}{0.08}$	< 0.1	< 0.1	$\frac{0.1-0.2}{0.07}$	$\frac{0.1-1.1}{0.25}$	$\frac{0.1-0.14}{0.03}$	$\frac{0.3-0.6}{0.16}$	$\frac{0.3-0.8}{0.17}$	$\frac{0.1-0.3}{0.12}$	$\frac{0.12-3.1}{0.94}$
D	July – August (1999)	$\frac{0.1-0.7}{0.3}$	< 0.01	$\frac{0.2-0.9}{0.5}$	$\frac{0.1-0.8}{0.4}$	$\frac{0.1-0.4}{0.2}$	$\frac{0.3-1.3}{0.6}$	$\frac{0.3-3.5}{1.4}$	$\frac{0.1-0.7}{0.3}$	$\frac{0.3-2.2}{1.0}$	$\frac{0.1-1.4}{0.7}$	$\frac{0.1-0.8}{0.5}$	$\frac{2.5-12}{5.8}$
D	October–November (1997)	$\frac{0.1-1.2}{0.5}$	$\frac{0.01-0.08}{0.06}$	$\frac{0.1-3.4}{1.7}$	2.0	$\frac{0.07-1.6}{0.7}$	$\frac{0.08-4.8}{2.4}$	$\frac{0.5-5.2}{2.3}$	$\frac{0.05-3.9}{1.8}$	$\frac{0.3-4.6}{2.2}$	$\frac{0.07-2.5}{1.0}$	$\frac{0.1-3.6}{1.4}$	$\frac{2.7-32}{16}$
D	October (1999)	$\frac{0.4-1.1}{0.4}$	< 0.01	$\frac{0.8-8.0}{2.3}$	$\frac{0.2-4.0}{1.2}$	$\frac{0.2-1.3}{0.4}$	$\frac{0.3-2.9}{0.9}$	$\frac{0.5-3.4}{1.2}$	$\frac{0.1-1.2}{0.4}$	$\frac{0.5-3.8}{1.4}$	$\frac{0.2-2.0}{0.7}$	$\frac{0.2-1.7}{0.6}$	$\frac{3.1-30}{9.5}$

Note. PAH: phenanthrene 1, anthracene 2, fluoranthene 3, pyrene 4, benzo[a]anthracene 5, chrysene 6, benzo[b]fluoranthene 7, benzo[k]fluoranthene 8, benzapilene 9, benzo[g,h,i]perylene 10, indeno[1,2,3-c,d]pyrene. Dibenzo[a,h]anthracene was not detected in all aerosol samples. The detection limit for compounds 1, 3–7 is 0.1 ng/m^3; that for compound 2 is 0.01 ng/m^3; and the limit for compounds 8–11 is 0.2 ng/m^3 for samples of 100 m^3.

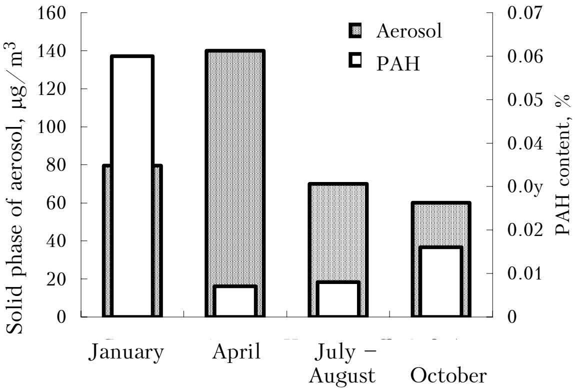


Fig. 1. Total amount of the solid phase of aerosol, in µg/m^3, and total content of PAHC in it, in %. Sampling site *D*, 1998–1999.

The maximum concentration of the solid phase occurs in spring, whereas the maximum content of PAHCs in it is observed in winter.

Significant difference in the PAHC concentration in winter and summer is connected with the following:

(=) heat sources operate more intensely in the cold season;

(b) since November until March the anticyclonic weather is established in the region under study; this weather is characterized by weak winds, strong near-ground temperature inversions, and frequent fogs[1] that favor keeping of the high level of atmospheric pollution;

(c) the phase equilibrium between the content of PAH in the solid and gas phases of aerosol shifts toward the latter as the ambient temperature increases from –20 to 25°q; as a result, PAH transform fully (phenanthrene and anthracene) or partially (fluoranthene and pyrene) into the gaseous component of the atmospheric air.[4]

Sampling of aerosol in summer with a combination of the filters and the cartridge for recovery of PAHCs from the gas phase showed that the probability of PAHCs slipping through the filter could reach 35%. Thus, the total concentration of PAH in the gas and solid phases in summer could reach 10–15 ng/m^3. Nevertheless, this value is still 10–15 times lower than that in the winter period. This result allows the conclusion that the main factors determining the low level of PAH in summer are smaller volume of emissions of these substances and the far higher self-cleaning capability of the atmosphere.

Three compounds prevail in the total mass of PAH identified in the solid phase of aerosol sampled in the winter period. They are phenanthrene, pyrene, and fluoranthene. Their total amount reaches a half of the total mass of detected PAH, whereas the relative concentration of benzapilene is 4–10% (4–22 ng/m^3, 4–22 MPC). The concentrations of PAH and relations between them depend significantly on the sampling site, i.e., on the local sources of pollution. The profile of an aerosol sampled at the site *E* (district of private cottages) differs markedly by high content of benz[g,h,i]perylene and the absence of anthracene and pyrene (Fig. 2).

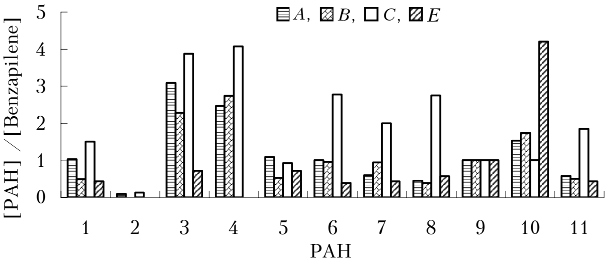


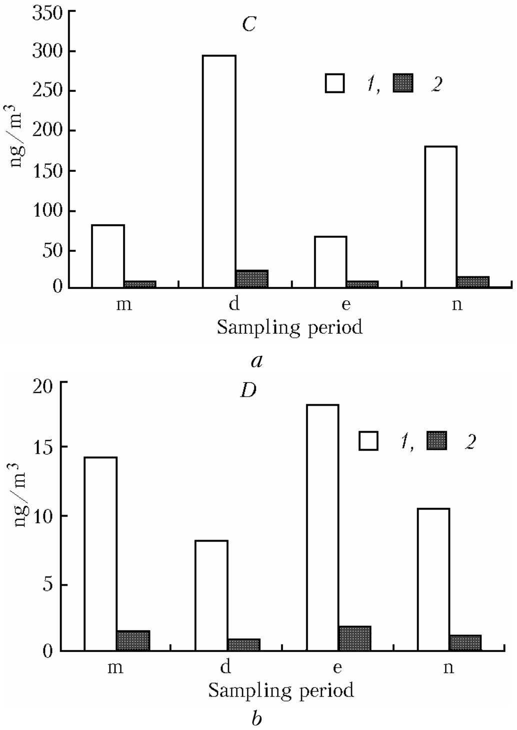
Fig. 2. Concentrations of individual PAH normalized to the content of benzapilene in aerosol sampled at different districts of Irkutsk. January–February 1996 (for compound numbers see the Table).

In this district, the main sources of PAH are stoves. In the central part (sites *A* and *B*), the main pollution sources are car exhausts, so the PAH profiles for these sites are similar.

To estimate the diurnal dynamics of PAHC concentration in aerosol, we have analyzed the samples taken at the sites *A* and *B* under two meteorological situations:

Situation 1: t_{night} = – 30 … – 40°q, t_{day} = – 25 … –30°q, thick fog in the morning;

Situation 2: t_{night} = –15 … –20°q, t_{day} = – 7 … –12°q, snowfall during day or night.



a

b

Fig. 3. Diurnal dynamics of the total PAH concentration (*1*) and the concentration of benzapilene (*2*) in aerosol of Irkutsk. Sampling sites *C* and *D*, sampling periods: from 7:00 to 11:00 a.m. (m), from 11:00 a.m. to 4:00 p.m. (d), from 4:00 p.m. to 10:00 p.m. (e), from 10:00 p.m. to 7:00 a.m. (n); January 1999.

At the site *C* in situation 1 in daytime (from 11:00 to 16:00 LT), the extremely high total concentration of PAH was observed (up to 300 ng/m^3, including 25 ng/m^3 of benzapilene). These values are almost three times higher than those in the morning and evening. This maximum likely results from the shift of the temperature inversion to the daytime, as well as from more intense emissions from cars. The night increase of the total concentration of PAH and that of benzapilene up to, respectively, 180 and 13 ng/m^3 may be a consequence of emissions from stoves in the districts of private cottages. At the site *D* in situation 2, the diurnal change of the PAHC concentration is a typical diurnal behavior of a pollutant in the atmospheric air.[5] In the morning (from 7:00 to 11:00 a.m.) and evening (from 4:00 to 10:00 p.m.), the PAH concentration is maximum, and in daytime it is almost halved (Fig. 3).

Conclusion

The possible levels of the PAH concentrations in the near-ground atmospheric aerosol in Irkutsk (population of 650 000), which is a typical industrial center in Baikal region, have been estimated. The maximum total PAH level of 300 ng/m^3 (concentration of benzapilene of 30 ng/m^3) was observed in a winter period because of most intense operation of heat and power plants and pronounced anticyclonic character of atmospheric circulation leading to accumulation of pollutants in the near-ground atmospheric layer. It has been shown that extremely high accumulation of PAHCs is possible under certain meteorological conditions during daytime. In summer, due to higher self-cleaning capabilities of the atmosphere, the concentration of PAH does not exceed 1–6 ng/m^3, and that of benzapilene is within 0.2–1 ng/m^3 ($\leq$ MPC).

Our studies have shown that microcolumn high-performance liquid chromatography with multiwave photometric detection is an optimal and economical method of analysis. The developed technique is characterized by high selectivity, sufficient sensitivity for determination of 12 PAH in a wide range of concentrations, and a total error no more than 20%.

References

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