Sources of atmospheric pollution with polycyclic aromatic hydrocarbons in the industrial Baikal Region

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Emission of benzapilene and other polycyclic aromatic hydrocarbons to the atmosphere was studied, and it was found that this process depends on the technology of fuel and energy production, aluminum production, building, petrochemical industries and on the type and operating conditions of the equipment used. The correlation was found between benzapilene content and associated pollutants, for example, dust, carbon and nitrogen oxides, resinous substances, polycyclic aromatic hydrocarbons. On this basis, recommendations on the measures necessary for reduction of the benzapilene emissions to the atmosphere are given.

Introduction

Many towns of Eastern Siberia, in particular, in the industrially developed Baikal Region, are characterized by a high level of atmospheric pollution with the products of fuel burning and organic raw material processing.[1] Most hazardous among these products are polycyclic aromatic hydrocarbons (PAH), whose indicator representative is benzapilene (B(a)P) (I class hazard). Usually,[1,2] a source of pollution is identified by analyzing environmental objects for pollutants near industrial, anthropogenic, and traffic emissions. At the same time, PAH investigations directly at sources are limited, although only such measurements can provide for most accurate and reliable information on their quality and quantity.

The aim of this paper was to study the content of B(a)P and associated PAH, as well as various pollutants in organized atmospheric emissions from priority productions, heating systems, and traffic in the industrial Baikal Region (Irkutsk Region).

1. Objects and methods of investigation

1.1. Objects of analysis. Pollution sources

Objects of analysis were organized gas-dust emissions into the atmosphere from various sources of heat and energy production, aluminum production, production of construction materials, petrochemistry, heating systems, and traffic in Irkutsk, Shelekhov, Angarsk, Cheremkhovo. Emissions are the products of combustion, treatment, destruction, and synthesis of fuel, organic raw materials, and materials, which differ significantly in the physical-chemical properties and the nature of associated components.

Heat-and-power engineering sources are boilers of different types corresponding to the fuel burning technologies (coal, firewood, black oil). Coal-fired boilers with the output higher than 50 MW are conditionally classified as objects of "large" heat-and-power engineering. "Medium" heat-and-power engineering includes the layer-type coal-fired boilers with the output from 5 to 50 MW and is characterized by the stationary burning conditions. "Small" heat-and-power engineering includes coal-fired and black oil boilers with the output up to 5 MW.

Heating systems include layer-type coal-fired boilers with an immovable grate and house furnaces with manual fuel loading that are characterized by nonstationary (cyclic) combustion of coal and firewood and classified as low-power heat sources.

Aluminum production sources (IrkAZ-SUAL Ltd., Shelekhov) emit sanctioned, treated (afterburning in specialized burners, treatment in electric filters and foam-vortical scrubbers) gas-dust flows (GDF) of coal-tar pitches in self-baking anodes of tank rooms and untreated sublimates of the same pitches in an aeration lantern and include sanctioned emissions from a calcination oven of an anode mass shop.

Sources of production of construction materials are asphalt concrete plants, different-type Circulite production plants using black oil and oil bitumen in firing of construction materials.

Petrochemical sources (ANKhK Ltd., Angarsk) include various equipment for combustion of gas, black oil, and industrial waste, as well as coal carbonization and pyrolysis facilities.

Cars with gasoline and diesel internal-combustion engines.

1.2. Sampling and analyzing techniques

Samples were collected by the schemes including aspiration of a certain volume (0.01 – 0.5 m^3) of the gas-dust flow through sorption and absorption facilities: fluoroplastic chips, glass fiber, AFAS-PAU aerosol filters (Novopor, Novorossiisk, Russia), *n*-hexane. The volumetric gas discharge was measured by a rheometer with a calibrated diaphragm (prefabricated set up) or

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by Kitoi-M device (OKBA, Angarsk, Russia) for measuring aerodynamic parameters and emission outcome under isokinetic conditions. The equipment used was designed by the NIIOGaz.[3] The gas outflow was activated with an M-822 aspirator (Krasnogvardeets, St. Petersburg, Russia). Depending on the physicochemical properties of emissions (temperature, associated components, disperse composition of solid particles), internal or external filtering methods were applied, and sampling was carried out with or without cooling of emissions while keeping the isokinetic conditions.

In sources under stationary emission conditions, samples were collected consecutively in different days from the same point of the measuring cross section. At nonstationary emissions (burning in a layer-type boiler house, house furnace, asphalt concrete plants, different-type Circulite production plants), samples were collected in a fixed time interval (1, 2, 15, 20 min) during the whole cycle of the technological process.

Sorption exposed materials were placed in a conical retort and covered with *n*-hexane, which was first used to wash the internal surfaces of filter holder and carriage. The *n*-hexane washouts from the sampling tube and absorbent solutions were also placed in the retort.

The PAH from sorbents and filters were extracted with an ultrasonic facility with a water bath (Serga-02, Russia) for 15 min. This operation was repeated three times with new portions of *n*-hexane in the retort. Extracts were joined, cleared from particles by filtering through filter of de-ashed paper, and concentrated in vacuum at 30–40°C.

The B(a)P content was determined by the method of low-temperature luminescence at the liquid nitrogen boiling point with a Hitachi 650-10 S fluorescent spectrophotometer (Japan) by the technique developed in Ref. 4. The maximum error in B(a)P determination in a gas-dust flow from the studied sources did not exceed ±25% at the confidence probability of 95%.

Other PAH were determined by the method of high performance liquid chromatography on a Milikhrom A-02 microcolumn liquid chromatograph (EkoNova, Novosibirsk, Russia) by the technique described in Ref. 5. Solid particles, carbon and nitrogen oxides, resinous substances were determined by the techniques considered in Ref. 6.

2. Experimental results

Determination of B(a)P in GDF from all the studied sources of *heat and energy production* and heating systems showed that its content varies in the very wide interval of mass concentrations ($0.005 - 10000\ \mu g \cdot m^{-3}$) and mass emissions ($0.1 - 6000\ \mu g \cdot s^{-1}$) (Table 1). Differentiation of these results with respect to the output and the type of the fuel used revealed the following regularity: as the power of coal-fired heating facilities increases, the mean mass concentrations of B(a)P for different sources decrease in the series: small > medium > large heat-and-power engineering (see Fig. 1).

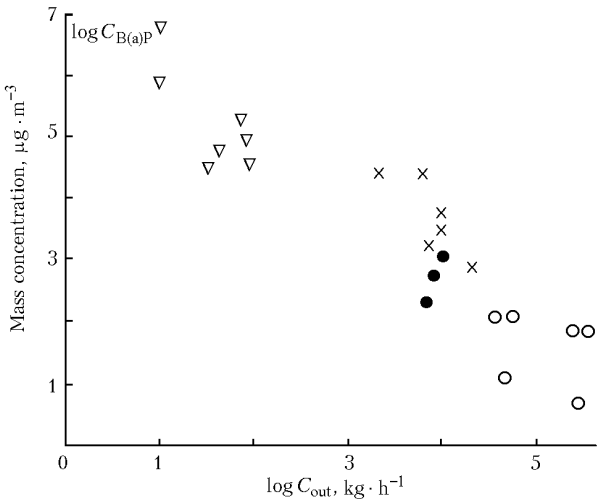

Fig. 1. Dependence of the mass concentration of benzapilene on boiler output for large (○), medium (×), and small (▽) heat-and-power engineering and black oil boilers (●).

It should be noted that the boiler output is determined by the fuel combustion technology. Most high-efficiency coal-fired boilers and gas-cleaning systems (electric filters) provide the lowest atmospheric B(a)P emissions for the large heat-and-power engineering. The results for black oil boilers are close. Chamber combustion of coal dust and black oil favors full contact with air oxygen and, correspondingly, to complete combustion under the stationary conditions. The layer-type boilers of "medium" output with pneumomechanic coal feeding and periodically stationary combustion conditions equipped with gas-flow cleaning systems (battery cyclones and water scrubbers) are characterized by the higher B(a)P content in smoke emissions. The layer combustion method does not provide for the full contact of fuel with oxygen, thus leading to formation of incomplete combustion products – carbon monoxide, soot, PAH.

Even higher levels of the mass concentrations and emissions of the pollutants studied are observed in low-power heat-sources, such as coal boilers and house furnaces characterized by nonstationary combustion of coal and firewood. The mechanism of pollutant formation at layer-type fuel combustion in such sources is considered in detail in Ref. 5.

In the fuel combustion products, PAH are formed and live largely in the adsorbed state on fine particles of volatile ash, soot, aerosols. The maximum B(a)P content was found for low-power heat sources (Table 1). The study of the disperse composition of the volatile ash in Ref. 5 showed that up to 90% of particles have the diameter less than 1 μm at the mean value of 0.6 – 0.7 μm. Particles of such size almost cannot be caught by the existing cleaning systems, and this leads to pollution of the atmosphere with PAH. This result agrees well with the B(a)P distribution over

Table 1. Benzapilene content in organized atmospheric emissions from different productions on the territory of Baikal Region

Production. Technological process. Sources	Benzapilene content (n is sample number)			
	mass concentration, $\mu g \cdot m^{-3}$	mass emission, $\mu g \cdot s^{-1}$	in volatile ash (soot), $\mu g \cdot kg^{-1}$	in nonvolatile ash, $\mu g \cdot kg^{-1}$
Heat-and-power engineering				
Coal and black oil combustions products				
High-power (50 MW)	0.005...0.150 (n = 48)	0.2...8	0.1...0.3	1.4
Medium-power (5...50 MW)	0.6...50 (n = 35)	4...250	$(3...50)\cdot10^3$	–
Low-power (up to 5 MW)	1...10000 (n = 100)	0.1...6000	$(1.2...9)\cdot10^5$ $(1.8..11)\cdot10^5$	3100
Black oil boilers:	0.1...1 (n = 15)	1...6	$5\cdot10^3$ $(8\cdot10^3)$	–
Aluminum production				
Coal pitch combustion, treatment, destruction products				
Electrolysis shop	200...3000 (n = 51)	$(7...50)\cdot10^3$	$(9...10)\cdot10^5$	–
Aeration lantern	0.9...67 (n = 30)	$(4...8)\cdot10^4$	$7\cdot10^5$	–
Anode mass shop	10...100 (n = 33)	$(0.7...12)\cdot10^2$	$(3...8)\cdot10^3$	–
Building				
Black oil and bitumen combustion, treatment, destruction products				
Circulite production	0.05...50 (n = 13)	2...80	$(1..200)\cdot10^2$	1...2
Asphalt concrete production	20...300 (n = 33)	80...1100	$(2...30)\cdot10^4$	$(2...3)\cdot10^3$
Petrochemical production				
Gas, black oil, coke combustion, treatment, destruction products				
Combustion, pyrolysis, and other installations	0...15 (n = 55)	0...40	–	–
Cars				
Internal combustion engines:				
gasoline	0.09...0.23 (n = 20)	–	–	–
diesel	0.20...0.70 (n = 20)	–	$(4...10)\cdot10^3$	–

the size of aerosol particles in the atmosphere, which shows that hydrocarbon is mostly on aerosol particles of 1.2 – 0.3 μm in diameter.[7] From analysis of the chemical composition of volatile ash, it was found that it is enriched with soot, which in the free form consists of condensed particles or covers ash particles of unburnt carbon of the initial fuel. The soot content in the volatile ash is 58...69% for low-output boilers and 67...89% for house furnaces. The high content of B(a)P in soot (see Table 1) causes its biological activity. In general, it should be noted that for heat-and-power engineering sources the levels of B(a)P and PAH content in sanctioned atmospheric emissions is mostly determined by three factors: combustion technology, type of fuel, and the system of cleaning the outgoing gas-dust flow.

Formation of PAH in electrolytic *aluminum production* sources is connected with the use of coke-pitch compositions including coal tar or oil pitches with high contents of resinous substances, mostly hydrocarbons, as an anode mass.[8] Therefore, emissions from different technological processes contain B(a)P in widely varying contents (see Table 1) comparable with the data for gas-dust flows from low-power heat sources. The most nonuniform B(a)P distribution is observed in emissions from aeration lanterns, since this source can be characterized as unorganized one with large gas-dust emissions.

The mass concentrations of B(a)P in GDF from the building production (see Table 1) are significant and comparable with those of aluminum production sources, although in mass emissions they yield to electrolysis shops and aeration lanterns. The comparative analysis of B(a)P concentrations in individual sources of these productions gave the following series in the decreasing order: electrolysis shops, asphalt concrete production, anode mass shop — Circulite production, with the ratio of about 100:10:1. As is seen from Table

1, the B(a)P content is caused by the technological process, rather than the production type. In sources of anode mass shops and Circulite production, emissions are black oil combustion products.

The lowest B(a)P contents are characteristic of the organized sources of atmospheric pollution due to combustion and treatment of gas and black oil in *petrochemical production* and due to *car exhausts* (see Table 1).

For most studied sources, B(a)P was largely found on fine particles of volatile ash and soot (see Table 1) polluting the atmospheric air.

The composition of individual PAH in the sum of eleven identified compounds for small power production and aluminum production sources is characterized in Table 2.

In all emissions, the prevalent (in mass) substances are volatile pyrene, fluoranthene, and phenanthrene: they make up 40...80% of all PAH. Their contribution increases even more, for example, in treated emissions from the chimney of the electrolysis shop as compared with untreated ones. To the contrary, less volatile PAH, starting from benz(a)anthracene, contribute significantly to gas-dust flows before treatment, while in atmospheric emissions their relative content decreases. Thus, the B(a)P fraction in all PAH emitted by the electrolysis shop is 1.2%, that is, it decreases by about six times relative to the initial GDF, and the content of benz(g,h,i)perylene and indeno(1,2,3-c,d)pyrene decreases by more than order of magnitude. These data show that the treatment systems used in this source is efficient for less volatile PAH adsorbed on solid particles that are well caught by treatment systems. It should be noted that these PAH have higher carcinogenic activity as compared with the volatile ones.

Table 2. Individual PAH in the sum of detected substances for heat and power production and aluminum production sources

PAH	Relative content, %						
	Heat-and-power engineering				Aluminum production		
	house furnace		layer boiler	black oil boiler	ELS* with treatment		AL**
	coal	wood			before	after	
Phenanthrene	21	10	21	26	13	18	18
Anthracene	5	1	4	2.5	2.5	3	4
Fluoranthene	19	11	19	5	22	32	25
Pyrene	24	17	28	13	23	32	26
Benz(a)anthracene	4	7	5	5	4	2.5	5
Chrysene	5	8	6	11	10	7	6
Benz(b)fluoranthene	4	11	4	8	9	2.5	5
Benz(k)fluoranthene	4	9	5	18	2.5	0.8	2
Benz(a)pyrene	**8**	**10**	**5**	**2.5**	**5.8**	**1.2**	**5**
Benz(g,h,i)perylene	3	5	1	4	5	0.6	2
Indeno(1,2,3-c,d)pyrene	3	11	2	5	3.2	0.4	2

* ELS is electrolysis shop; **AL is aeration lantern.

Table 3. Dependence between the B(a)P content ($C_{B(a)P}$, $\mu g \cdot m^{-3}$) and associated pollutants in different pollution sources

Pollutant. Production. Source	Sample number	Correlation coefficient	
		r_{xy}	$r_{xy}(0.05; f^*)$
Solid particles, $C_{s.p}$, $g \cdot m^{-3}$			
Heat-and-power engineering: medium + small	15	0.943	0.514
Aluminum production:			
electrolysis shop + anode mass shop	6	0.947	0.811
Carbon monoxide, C_{CO}, ppm			
Heat-and-power engineering: small	8	0.766	0.707
Resinous substances, $C_{r.s}$, $g \cdot m^{-3}$			
Aluminum production:			
electrolysis shop	4	0.820	0.950
anode mass shop	5	0.956	0.878
Nitrogen oxides, C_{NO_x}, $mg \cdot m^{-3}$			
Aluminum production:			
electrolysis shop + anode mass shop	5	−0.939	0.873
Σ *PAH,* C_{PAH}, $\mu g \cdot m^{-3}$			
Heat-and-power engineering: small	8	0.977	0.707
Aluminum production:			
electrolysis shop, $mg \cdot m^{-3}$	6	0.960	0.811
aeration lantern	24	0.830	0.400

* f is the number of degrees of freedom.

Table 3 gives the correlation coefficients of linear dependences of B(a)P concentrations on the content of associated pollutants. The positive correlation can be found with such components as solid particles, carbon oxides, resinous substances, PAH sum, and the negative correlation is observed with nitrogen oxides. These correlations reflect the possible mechanisms of B(a)P formation. Thus, the high correlation with the concentrations of PAH, nitrogen and carbon oxides is indicative of combustion processes. The correlation with solid particles is caused by the fact that they carry PAH. For aluminum production sources, the B(a)P content depends on the concentration of resinous substances, which contain PAH.

In general, one can conclude that the B(a)P level and PAH content in different pollution sources is determined by technological processes, source operating conditions, used fuel and organic raw material, as well as the presence of the treatment system, rather than by the type of production. The use of efficient methods of cleaning from solid particles and, especially, their fine fraction will favor the decrease of emissions of carcinogenic substances into the atmosphere.

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