Experimental and theoretical research of polyaromatic hydrocarbons emitted by coal boiler-houses and power stations

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On the basis of an analysis of route samplings of a snow cover, the fields of specific benzopyrene concentrations in the vicinity of the Belovskaya State Regional Power Station (SRPS) and the Novosibirsk Capacitor-Producing Factory have been reconstructed. Problems of the optimal arrangement of sampling points are analyzed. Relative sedimentation rates of different polyaromatic hydrocarbon (PAH) compounds and their contribution to the snow cover pollution have been estimated. A correlation between the relative molecular weights of the PAH compounds and rates of their aerosol sedimentation has been found.

Introduction

Combustion or thermal treatment of organic substances are accompanied by emissions of mutagenic and carcinogenic compounds. Polycyclic aromatic hydrocarbons (PAHs) comprise a significant part of all carcinogenic compounds. Direct measurements of PAH emissions into the atmosphere and mathematical simulation of pollution fields are complicated problems. This is caused by highly uncertain knowledge of the PAH emission source strengths, description of physical-chemical transformations of gas and aerosol media, and current meteorological conditions.[1–4]

Formation and degradation of PAHs during combustion are competing processes, whose intensities are determined by the temperature regime, surplus of air in boiler furnaces, recirculation of smoke gases, and other factors; therefore, the estimation of PAHs by way of calculations is rather approximate due to the presence of many influencing factors having different intensities and directional patterns. The atmospheric air pollution by PAHs also depends on the efficiency of their settling in the process of ash extraction from emissions.

Benzopyrene (BP) is generally accepted as a PAH indicator. It is rather stable and widespread in the environment. Low efficiency of BP extraction during ash purification is caused by its adsorption on finely dispersed fractions of volatile ash.[2]

On the basis of an analysis of route samplings of the snow cover collected by us in the vicinity of the Belovskaya State Regional Power Station (SRPS) and the Novosibirsk Capacitor-Producing Factory (NCPF), the feasibility of reconstruction of the pattern of snow cover pollution and estimation of the total PAH emission is examined. In the present paper, an arrangement of sampling points is also analyzed by the mathematical methods of optimal experimental planning allowing for the character of the territory, system of roads, and climatic wind characteristics.

The main attention is given to the reconstruction of BP pollution of the snow cover from the data of observations. Despite of significant difference between the examined objects, simulation results have shown similarity in fields of specific BP content in snow. A degree of correspondence between the predicted and measured BP contents at the test points was fairly high. The effect of choice of the observation scheme on the accuracy of pollution field reconstruction has been demonstrated. On an example of the NCPF boiler-house, specific contents and aerosol sedimentation rates of other PAH compounds have been estimated. The feasibility of construction of quantitative dependences has been discussed.

1. Reconstruction of the aerosol pollution of snow from the data of observations

To describe the pattern of long-term pollution of the territory by aerosol emissions of an admixture into the atmosphere, the following regression dependence was constructed in Refs. 5 and 6:

$$p(r, \varphi, \theta) = \theta_1 \, g(\varphi) \, r^{\theta_2} \, e^{-2r_m/r}, \qquad (1)$$

where $p(r, \varphi, \theta)$ is the specific content of the admixture in snow (soil or air); r, φ are the polar coordinates of the calculation point, whose origin coincides with the location of the source; $g(\varphi)$ is the probability that the wind direction is opposite to φ; r_m is the point at which the surface concentration of the weightless admixture emitted from the given point source is maximum; $\theta = (\theta_1, \theta_2)$ is the unknown parameter vector.

Regression dependence (1) was derived under assumption of a narrow (10–15°) smoke plume. Its testing in a number of chemical and metallurgical enterprises has demonstrated fairly good agreement with the available experimental data.[5,6]

If we restrict ourselves to an analysis of the average annual or winter values of the wind velocity, air temperature, and turbulent exchange typical of this territory, then in accordance with Ref. 7 we can estimate the value of r_m from the geometrical characteristics of the source and the parameters of the emitted gas–air mixture. In particular, for the Belovskaya SRPS, r_m is approximately 3.5 km, and for the NCPF boiler-house, it is about 0.8 km.

The unknown parameter vector $\boldsymbol{\theta}$ can be found from the specific content of the admixture at fixed points of the territory, for example, by the least square method.[5]

The component θ_1 is proportional to the emission strength and has rather complicated structure as a function of the climatic characteristics of the wind velocity, turbulent exchange coefficient, and sedimentation rate of the aerosol admixture. Another component of vector θ has the form

$$\theta_2 = -2 - w/[k_1(n + 1)], \qquad (2)$$

where w is the sedimentation rate of aerosol particles, k_1 is the vertical turbulent diffusion coefficient at an altitude of 1 m, and n is the exponent in the approximation of the horizontal wind velocity component by a power-law dependence. The case $\theta_2 = -2$ or $w = 0$ corresponds to a weightless admixture, i.e., $\theta_2 \le -2$.

2. Planning of measurements during route snow sampling

Late in winter of 1997–1998, we collected samples of snow in the vicinity of the Belovskaya SRPS, Kemerovo Region, and the NCPF boiler-house in Novosibirsk. Both enterprises use coal as a fuel.

To optimize the arrangement of the sampling points, cartographic material about the territory, system of roads, arrangement of buildings, forest stands, and state of the snow cover was preliminary analyzed. Using regression dependence (1), data on the PAH emission sources, winter average recurrence of the wind speeds and directions, and locations of the most informative sampling points were numerically modeled. The routes of choice turned out to be oriented north and northeast, according to the highest recurrence of winds of the southern and southwest directions in the examined territories.

The optimum schemes comprised two points which, for example, in case of a low sedimentation rate of the admixture, should be at distances of approximately $0.5r_m$ and $1.5r_m$ from the source.[8] For significant rates of sedimentation of the emitted admixture, the optimal scheme can be numerically modeled only if *a priori* information is available about the parameter vector $\boldsymbol{\theta}$. Otherwise, locally optimal scheme can be used, obtained by application of the step-by-step procedure of sequential analysis and planning of observations.[8,9]

A. Belovskaya SRPS

This thermal power station is in the territory with a comparatively smooth relief. The admixtures generated as a result of the combustion of local coal are emitted into the atmosphere from three 150-m stacks 6 m in diameter with a rate of the gas–air mixture discharge of about 15 m/s. The state of snow cover at the moment of sampling was critical; however, local conditions and technical possibilities had allowed us to collect the samples of snow on the northeast route, taking into account the requirements for the optimal arrangement and the number of the sampling points and including additional points for checking of the reconstructed concentration field. The sampling scheme is illustrated by Fig. 1. Characteristics of the samples and results of their chemical analysis on the benzopyrene content in snow are presented in Table 1.

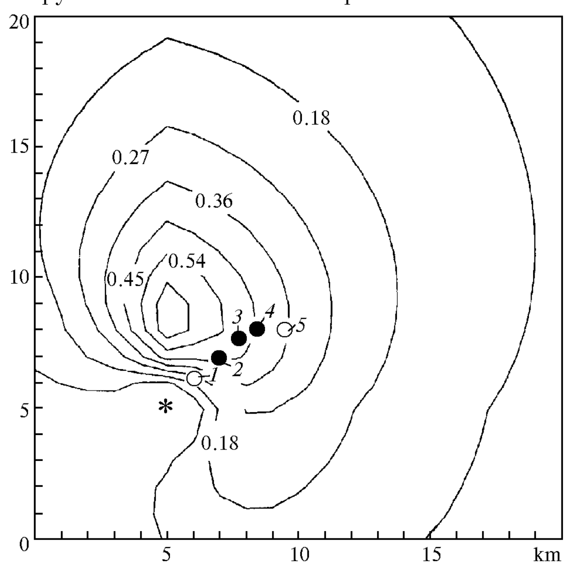

Fig. 1. Reconstructed field of the specific content (in μg/liter) of benzopyrene in snow in the vicinity of the Belovskaya SRPS. Here, * indicates the location of the source, and denote the observation points.

B. NCPF boiler-house

The industrial site of the factory is located in the left-bank part of the Soviet District of Novosibirsk. From the south and west urban settings and industrial enterprises are adjacent to it. The territory to the north from the industrial site is even, with no settings, and is slightly covered with vegetation. The snow cover at the moment of sampling (late in February) was in a good state. In the vicinity of the boiler-house there were no other powerful sources of atmospheric pollution. The admixture was emitted from two closely located stacks 40–50 m high.

Table 1. Benzopyrene pollution of snow in the vicinity of the Belovskaya SRPS and the NCPF boiler-house.

Serial number of point	Distance, km	Concentration, ng/liter	Weight of the sample, g	Sampling area, dm^2
SRPS, northeastern direction				
1	1.5	270	1490	1
2	2.5	680	860	1
3	3.5	710	1080	1
4	4.25	360	1241	1
5	5.5	570	817	2
NCPF boiler-house, northern direction				
1	0.3	2.4	1120	1.45
2	0.45	10.2	1330	1.45
3	0.6	15	1120	1.45
4	1.15	11.1	1390	1.45
5	1.85	6.9	1210	1.45
6	2.85	3.9	730	1.45

Because the southern and southwestern winds are dominant in winter in the given territory, considering the above-discussed, the route to the north of the boiler-house was chosen. Nearby south–to–north highway significantly facilitated the arrangement of the observation points, sampling, and finding distances to the stacks. The results of analysis of snow samples are presented in Table 1.

3. Numerical modeling

The experimental data can be interpreted by means of mathematical modeling. Dependence (1) and data of observations presented in Table 1 enabled us to justify the choice of the reference points – scheme of observations for reconstruction of the fields of benzopyrene pollution of the snow cover in the vicinity of the Belovskaya SRPS and the NCPF boiler-house.

Figures 1 and 2 show the results of reconstruction of the specific BP content along the chosen routes. The comparison of observations with the calculated results demonstrates their good agreement, which confirms the adequacy of the selected model to the running processes of long-term pollution and fairly high accuracy of chemical analyses of snow samples.

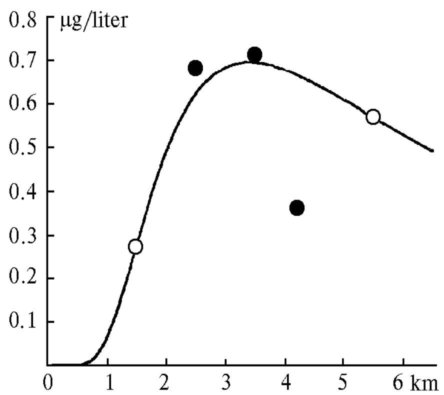

Fig. 2. Benzopyrene concentration in snow to the northwest from the Belovskaya SRPS. Here, the solid curve is for the calculated results, and closed and open circles denote the data of observations in the control and reference points.

A degree of influence of the observation scheme on the quality of estimation is illustrated by Fig. 3.

Despite of significant difference of the source parameters, amounts, and conditions of coal combustion in the SRPS and boiler-house, the estimations of the parameter θ_2 were close in values and equal to 2.05 and 2.21, respectively. This means that most BP is concentrated on fine poorly sedimented aerosol particles. It should be noted that curves in Figs. 2 and 3 will be similar if we proceed to the dimensionless distance $\xi = r/r_m$.

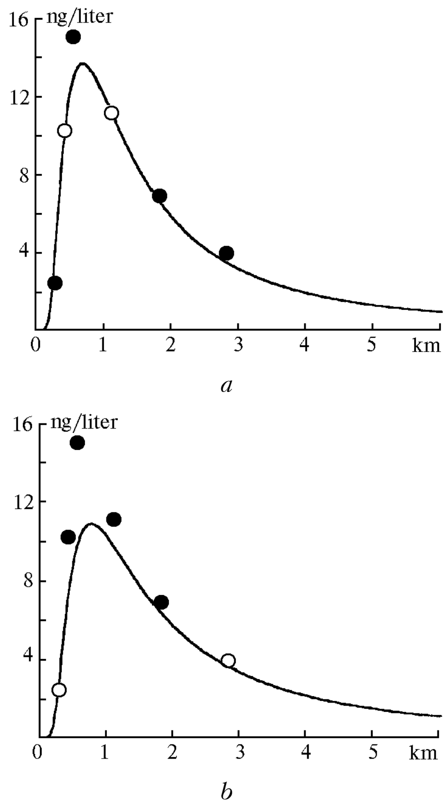

Fig. 3. Calculated and measured benzopyrene concentrations in snow to the north of the NCPF boiler-house for optimal (*a*) and suboptimal (*b*) arrangement of the reference points indicated by open circles.

Table 2. Estimated parameters of the regression dependence for different PAH compounds.

Substance	Estimated parameters		Relative molecular mass
	θ_1	θ_2	
Naphthalene	1301.2	−6.35	128
Acenaphthylene	391.9	−6.25	152
Acenaphthene	112.0	−5.20	154
Fluorene	982.3	−4.48	166
Anthracene	225.1	−3.47	178
Phenanthrene	3238.4	−3.32	178
Pyrene	962.7	−2.66	202
Fluoranthene	1999.5	−2.63	202
Benzanthracene	90.6	−2.39	228
Chrysene	175.8	−2.24	228
Benzofluoranthene	118.4	−2.30	252
Benzopyrene	60.9	−2.21	252
Perylene	14.0	−2.00	252
Dibenz(ah)anthracene	9.2	−2.12	278
Benz(ghi)perylene	77.2	−2.00	276

The field of specific BP concentration shown in Fig. 1 and the data of Table 1 were used to find the total BP emission from the SRPS in winter. Integrating over a 50×50 km area, we obtained 7.7 kg.

Table 2 gives the estimated parameter vector $\boldsymbol{\theta}$ for fifteen PAH compounds, obtained from an analysis of snow sampling in the region of the NCPF boiler-house. With Eq. (2) taken into account, an analysis of Table 2 demonstrates significant differences in the sedimentation rates of different PAHs. For example, sedimentation rates of particles comprising naphthalene are approximately 20 times higher than for benzopyrene. From Table 2 it can be seen that there is a direct proportionality between the relative molecular mass of the PAH compounds and effective rate of their sedimentation. Based on close rates of their sedimentation, they can be divided into the following groups depending on the molecular mass: 228–276, 178–202, and 128–166. More detailed classification and construction of empirical dependences at the given stage of investigations make no sense.

The estimation of another component θ_1 is also of definite interest, because it enables us to establish the relationship between the relative total emissions of the PAH compounds by the NCPF boiler-house.

Conclusion

Based on the results of our investigations, we can conclude the following.

The models for reconstruction adequately describe the BP pollution of snow cover in a wide range of distances given that the observation schemes are nearly optimal. The curves of distribution of the specific BP concentrations obtained for the SRPS and the NCPF boiler-house are similar to each other after proceeding to the dimensionless distance.

Numerical analysis of observations for other PAH compounds allows one to establish the quantitative relationship between the rates of aerosol sedimentation and relative molecular weights and to estimate their long-term relative emission from the source. The method for estimating relative emission of the PAH compounds can be used for identification of pollution sources and efficiency of combustion of organic fuel.

The presence of the PAH compounds with high sedimentation rates calls for additional adjusting of models for reconstruction and arrangement of observation systems.

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