MEASURING 3,4-BENZOPYRENE IN ATMOSPHERIC AEROSOLS AND WIND-DRIFTED EMISSIONS FROM SMOKE STACKS OF A HEAT-AND-POWER STATION AND FORECASTING THE LOCAL AND REGIONAL TRANSPORT OF POLLUTANT BY THE MATHEMATICAL SIMULATION METHOD

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The content of 3,4-benzopyrene has been measured in atmospheric aerosols and wind-drifted emissions of a heat-and-power station. These data have been used to estimate the strength of benzopyrene sources by the mathematical simulation method. Average daily values of benzopyrene concentration have been measured in Novosibirsk Akademgorodok and its environs.

INTRODUCTION

Polyaromatic hydrocarbons are most dangerous carcinogens that enter the atmosphere as a result of human activity. Their main sources are heat-and-power stations, motor transport, chemical industry, and other production processes including a heat-treatment of organic substances.

Entering the atmosphere, polyaromatic hydrocarbons either condense to aerosols or are adsorbed on aerosol particles that have already been contained in the atmosphere or in emissions of the source itself. It seems likely that the overwhelming bulk of polyaromatic hydrocarbons occurs as aerosols in the atmosphere.

Among polyaromatic hydrocarbons, 3,4-benzopyrene is a very dangerous carcinogen. Its maximum permissible concentration (MPC) in the atmosphere is $1 \text{ ng} \cdot \text{m}^{-3}$ (10^{-9} g/m^3). Therefore, techniques for reliable measuring such small values of concentration in the atmosphere are of primary importance along with estimating the source strength and the benzopyrene concentration field in territories adjacent to sources and recording diurnal, seasonal, and annual variations of benzopyrene concentration.

It should be noted that direct measurements of the source strength, for example, of a heat-and-power station are rather complicated due to high temperature of a medium inhomogeneously distributed across the stack cross section and with the stack height, almost unpredictable physical-chemical transformations of gaseous and aerodisperse media inside the stack, and so on. Another approach is based on mathematical simulation of the spread and dissipation of aerosol pollutants in the atmosphere and experimental measurements of the concentration of pollutants in the most important points. These data can be used to solve an inverse problem of reconstructing the concentration field and the source strength depending on the meteorological and topographic conditions.

The objective of the present paper is to perform the above-described measurements and mathematical simulation as well as to determine the average daily background values of benzopyrene concentration in Novosibirsk Akademgorodok and its environs.

EXPERIMENTAL PROCEDURE

A mobile physical laboratory mounted in the GAS-66 van was used for aerosol sampling. Aerosol samplers were energized from the AD-10 diesel power station. Aerosols were sampled on AFAKA-20 filters with a volume rate of flow of $5 \text{ m}^3 \cdot \text{h}^{-1}$ at different distances from the source. The sampling time was 20 min. Sampling points were on the source axis down the wind. The wind speed was measured with the ASO-3 anemometer and the wind direction was determined by a wind vane and a compass.

To evaluate the daily concentration of benzopyrene in the atmosphere, two sampling points were arranged: l) on the roof of the Institute in Novosibirsk Akademgorodok, 2) in Klyuchi settlement at a distance of 12 km from Akademgorodok.

Aerosols were sampled on the AFAKA-20 filters of a sample with a volume flow rate of $5 \text{ m}^3 \cdot \text{h}^{-1}$ at the Institute and $13 \text{ m}^3 \cdot \text{h}^{-1}$ in Klyuchi settlement. Measurements were performed from January 25 to

February 8, 1995. The filters were changed every day.

Substances settled on the filters were extracted by dissolving them in n-hexane with a volume of 1—2 ml for every filter. So-obtained extract was subject to gas-chromatography analysis to determine the content of dibutyl phthalate and other halogen-bearing compounds. Then hexane was evaporated from a test tube and it was filled with pure n-octane. The amount of 3,4-benzopyrene was measured by the method of low-temperature selective fluorescence of benzopyrene in the Shpolskii low-temperature glasslike matrix.1 Since many impurities in the solution have no effect on the selective sensitivity of the method, the selective fluorescence of benzopyrene was recorded without preliminary purification. The limiting benzopyrene sensitivity of the method was $5 \cdot 10^{-11}$ g $\cdot$ ml^{-1}.

ABOUT MATHEMATICAL SIMULATION METHOD OF ESTIMATING THE CONCENTRATION FIELDS

Calculation of the surface concentration fields of benzopyrene in wind-drifted emissions from smoke stacks and evaluation of strengths of these sources were based on a solution of inverse problems of reconstructing the values of concentration at arbitrary points from a set of experimental data measured in a limited number of points adjacent to the stacks.

Let us consider this method by the example of a concrete source - Heat-and-Power Station-2 situated in the environs of Novosibirsk Akademgorodok. The station is in a valley of a small river whose northeastern slope is at a distance of 300 m from the Station and has a shape of a step 30 m high. For the most part the field measurements were performed over relatively even area to the north and to the northeast of the Station. The measurements were carried out in the daytime in fall under conditions of intense mixing in the boundary layer of the atmosphere. The Station operates mainly on fuel oil. The combustion products tore discharged into the atmosphere through two closely located stacks 100 and 60 m high.

The lack of information about the source strengths, that is, about the strengths of benzopyrene emissions into the atmosphere, gives no way of direct simulating the spatial spread of pollutants in the atmosphere. Therefore, the method of mathematical simulation, based on a solution of the inverse problem of estimating the polluted zone size from a limited number of experimental data, is most efficient. Because of little information about the meteorological and physical parameters of the atmosphere, we used the OND-86 technique[2] to estimate the concentration fields during the course of experimental measurements. This technique allows the points of maximum surface concentration of pollutants to be determined from the known values of

the wind velocity, air temperature, stack height, and thermophysical parameters of air-gas emission. Then taking these points as the basis, the profiles of the axial surface concentration were calculated assuming the unit strength of each emission source (1 g $\cdot$ s^{-1}).

Hence, the total axial concentration of pollutant can be represented in the form

$$q(x, \overline{\theta}) = \theta_1 \Psi_1(x/x_{1\max}) + \theta_2 \Psi_2(x/x_{2\max}). \qquad (1)$$

Here, the x axis is directed downwind (we consider both sources to be located at $x = 0$); θ_1 and θ_2 are the strengths of benzopyrene emissions from stacks with heights $H_1 = 100$ m and $H_2 = 60$ m, respectively; Ψ_1 and Ψ_2 are the functions describing the values of the axial surface concentration for 1 g$\cdot$s^{-1} strength of each emission source; $x_{1\max}$ and $x_{2\max}$ specify the positions of points with maximum concentration of emissions from the first and second sources, respectively.

According to the Ecological Certificate of the Heat-and-Power Station-2 (HPS-2), the strength of emissions of all pollutants from the first stack is about four times greater than from the second stack. Therefore, we may set

$$\theta_2 = 0,25\theta_1. \qquad (2)$$

in Eq. (1).

DISCUSSION OF OBTAINED RESULTS

Four points to the northeast of the HPS-2 were chosen for numerical reconstruction of the values of axial concentration of benzopyrene in wind-drifted emissions and their comparison with the experimental data. Their positions and wind velocities (at an altitude of 2 m) at the instant of sampling are given in Table I. In Refs. 3 and 4 it was shown that the most important points (for optimal experimental design), when solving the inverse problem of estimating (reconstructing) the source strength from the data of a limited number of experimental measurements of the surface values of concentration, are the points x_{max}. For this reason, the point located at a distance of 1000 m should be chosen for optimal experimental design (according to data presented in Table I) to determine the unknown parameter θ_1. The value of the parameter θ_1, that is, the source strength, can than be determined from the known concentration of surface pollutant at this very point with allowance for Eqs. (1) and (2). The benzopyrene emission strength at the instant of measurements was $2.1 \cdot 10^{-4}$ g $\cdot$ s^{-1} for the first stack and $0.52 \cdot 10^{-4}$ g $\cdot$ s^{-1} for the second stack. These values yield 6.5 and 1.6 kg of 3,4-benzopyrene per year, respectively.

Results of direct simulation of transport of benzopyrene pollutant emitted from the above-considered smoke stacks (with allowance for their

emission strengths determined earlier) are compared with the experimental data measured in several points near the axis of wind-drifted emission in Table I. The reconstructed and experimental data are seen to agree satisfactorily. Their maximum discrepancy is about 40%.

The estimated strengths of the benzopyrene sources allow us to perform prognostic modeling of levels of benzopyrene pollution of atmospheric air at different distances from the source under various meteorological and topographic conditions. Figure 1 illustrates a variant of calculated benzopyrene concentration fields (normalized to its MPC being equal to $1 \text{ ng} \cdot \text{m}^{-3}$) when the emissions from the above-considered stacks drift by the wind to the nearest housing estate of Akademgorodok (to the west of the Station). In this case the wind speed $(3 \text{ m} \cdot \text{s}^{-1})$ taken for our calculations produced the most dangerous values of surface concentration of pollutant.[2] It is seen from the figure that for such distances of the living estate from the Station (longer than 1000 m) the levels of air pollution by 3,4-benzopyrene are less than the MPC, even if very close to it.

Results of measuring the daily average surface concentration of benzopyrene in Akademgorodok and in Klyuchi settlement are shown in Fig. 2 (curves *1* and *2*, respectively). It is seen that in Akademgorodok the measured daily average concentration is 1.5—3 times larger than its maximum permissible value. At the same time, in Klyuchi settlement situated slightly farther than Akademgorodok the measured values of concentration were, as a rule, markedly smaller than the MPC. It is reasonable to assume that enhanced values of benzopyrene concentration in Akademgorodok were due to heavy traffic. It seems likely that the observed level of benzopyrene pollution in Kluchi settlement is representative of its average regional value. This is in agreement with the published data.

Results of measuring the concentration of another widespread atmospheric pollutant - dibutyl phthalate - are also shown in Fig. 2 for comparison. Dibutyl phthalate is commonly used for plastic and furniture production and its MPC is $100 \text{ ng} \cdot \text{m}^{-3}$. The correlation is also seen between the values of dibutyl phthalate surface concentration and the degree of urbanization of sampling sites.

TABLE I. *Experimental and reconstructed values of the 3,4-benzopyrene concentration* $(\text{ng} \cdot \text{m}^{-3})$ *in the wind-drifted emissions from the smoke stacks of the HPS-2.*

Distance from the source, m	Wind speed $(\text{m} \cdot \text{s}^{-1})$ and direction	Concentration	
		Measured	Calculated
1000	4.0 SW	1.20*	1.20*
1300	3.0 SW	0.96	1.12
1500	2.0 SSW	0.60	1.00
2200	2.5 S	0.64	0.72

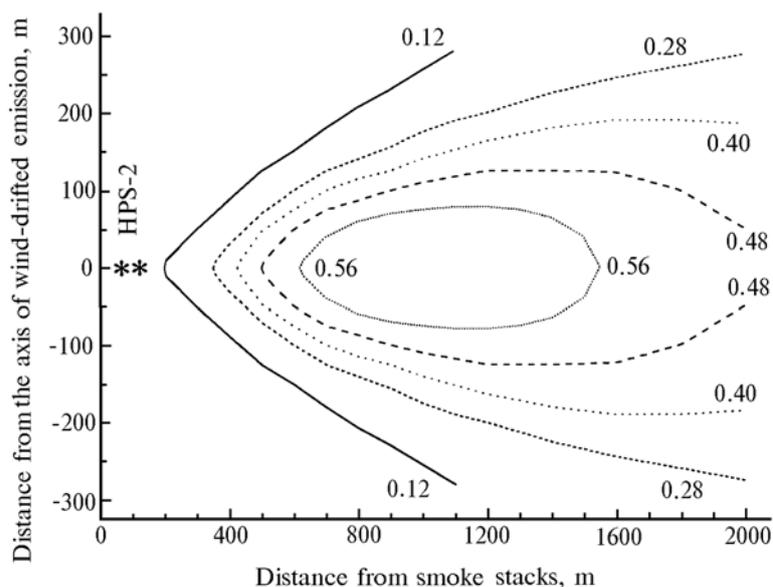Note: Asterisks denote the values of concentration used to estimate the source strengths.

FIG. 1. *Field of the surface concentration of benzopyrene normalized to its MPC (wind speed u = 3 m/s).*
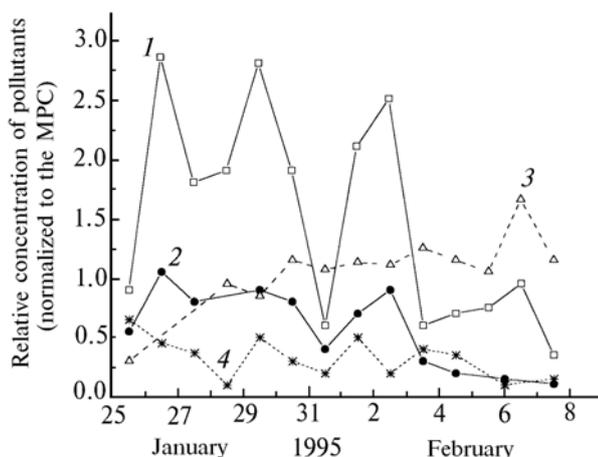
Fig. *2. Values of 3,4-benzopyrene (curves 1 and 2) dibutyl phthalate (curves 3 and 4) concentration erosols of the surface layer of the atmosphere in Akademgorodok (curves 1 and 2) and Klyuchi settlement (curves 3 and 4).*

On the basis of the performed work, the following fusions can be drawn:

The results of calculation of the fields of surface entration of atmospheric pollutant agree satisfactorily with the observation data when the local topography, meteorological conditions, and data on the structural peculiarities of the emission sources have been correctly taken into account.

In these experiments, special attention should be given to optimal experimental design.

To determine the relative contribution of near-surface sources to the field of hydrocarbon concentration and to estimate more correctly the parameters of their emissions, additional examination is required.

This joint experiment including different stages was successively performed and the accumulated experience can be useful for investigation of other sources of atmospheric pollution.

ACKNOWLEDGMENT

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