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Polyaromatic Hydrocarbons in the Vicinity of the Major Highways of Novosibirsk

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Abstract

The results of field studies, chemical-analytical and numerical investigations of snowpack contamination in the winter season of 2014/2015 in the vicinity of Sovetskoye highway of Novosibirsk after its reconstruction of 2009–2014 years. It was shown that substantial reductions of PAH emissions and the change of the space structure of the field of their fallouts, in comparison with the monitoring data of 2008 were shown. Linear correlations between the precipitation content and that of organic and inorganic components of the samples were established. In the kinematic approximation, the few-parametric model of the field reconstruction of precipitations of the polydisperse impurity from the linear source and the method of its numerical realization in the explicit form was proposed. The approbation of the proposed model on the experimental data obtained was carried out.

Key words: highway, snowpack, monitoring, chemical composition, polyaromatic hydrocarbons

INTRODUCTION

The main source of environmental pollution of big cities is motor transport [1–4]. The emission composition includes polyaromatic hydrocarbons (PAHs) that are the products of the incomplete combustion of gasolines and diesel fuel. PAHs refer to substances of resorptive action, among them, benzo(a)pyrene – to the first class danger. In addition to them, the contribution to the air environment contamination is made by heavy metals, nitrogen, sulphur, carbon oxides, as well as dust emissions raised from the roads surface when moving auto transport. The specific of the emission distribution is determined by the work regime of automobiles, low location of sources, formation of stable contamination zones and virtually around-the-clock impact [5–13]. It seems reasonable to carry out the constant control for the contamination dynamics in the vicinity of highways with intense traffic.

A reliable indicator of Siberian territories contamination is a snow cover which, as a natural tablet-accumulator gives the value of dry and wet aerosol precipitations during the winter period [14, 15]. In comparison with air, snow sampling does not require complex equipment. In comparison with soil and vegetation, snow is also and a convenient analysis object, since after melting the main component is water.

The object of our multi-year year research was the Sovetskoye highway of Novosibirsk,

located in the southwest outskirts of the city [16–18]. The regular investigations of snowpack contamination processes in the vicinity of the highway selected sector have been carried out by the authors for more than 15 years. In the transition period of the city auto transport on the application of unleaded petrol (1998–2001), it was found that the content of various PAH components in snow samples increased in 2–3 times, herewith, the lead content substantially decreased, moreover, due to the large-size solid fraction (particle diameter of more than 3 μm). The contribution of lead into the water-soluble and fine-dispersed (0.45–3 μm) fractions remained practically unchanged. The marked "splash" of PAH emissions, in our opinion, was conditioned by technical reasons related to the unpreparedness of auto transport to the fuel combustion with a new kind of additives. In the subsequent period (till 2008), an emissions increase of PAHs [19] associated with the auto park growth of the city was observed. Since the highway was in the reconstruction mode from 2009 to 2014, full-scale investigations in this period were not conducted by us.

The objective of this work is to estimate the contamination condition of snowpack by major auto transport emissions components in the vicinity of the Sovetskoye highway of Novosibirsk after the conducted reconstruction.

FIELD STUDIES

The route snow survey was carried out in the end of winter season of 2014/2015 in the vicinity of the highway sector located perpendicular to the winds of the southwest direction. This direction of winds is the most characteristic for winter seasons [20]. The snow sampling scheme is presented in Fig. 1, *a*.

Along the route considering the winter repeatability of wind directions, samples were taken in 7 points at the road leeward side and in 2 points at the windward side. The data on their remoteness from the auto road are presented in Table 1. The snow sampling was made by titanium tube of 100 mm in diameter on the full snowpack depth. In Fig. 1, *b*, the dependence of the snow accumulation on the route of the study is presented. According to the data of Fig. 1, *b*, the snow content varies in the range of 95–140 kg/m^2 and, on average, amounts to 121 kg/m^2.

CHEMICAL ANALYSIS OF SNOW SAMPLES

The determination of basic 19 PAHs was conducted by the standard method [20], which included the stages of melting snow samples at room temperature, addition of witness-substances allowing estimating extraction concentrating PAHs into methylene chloride from the entire volume of the unfiltered probe, and extract drying by anhydrous sodium sulphate. The dry residue evaporated at a rotational evaporator was dissolved in acetone that was analyzed by the method of chromatography-mass spectrometry using an Agilent Technology (AT) 6890N gas chromatographer with a capillary column HP-5MS and quadruple mass spectromet-

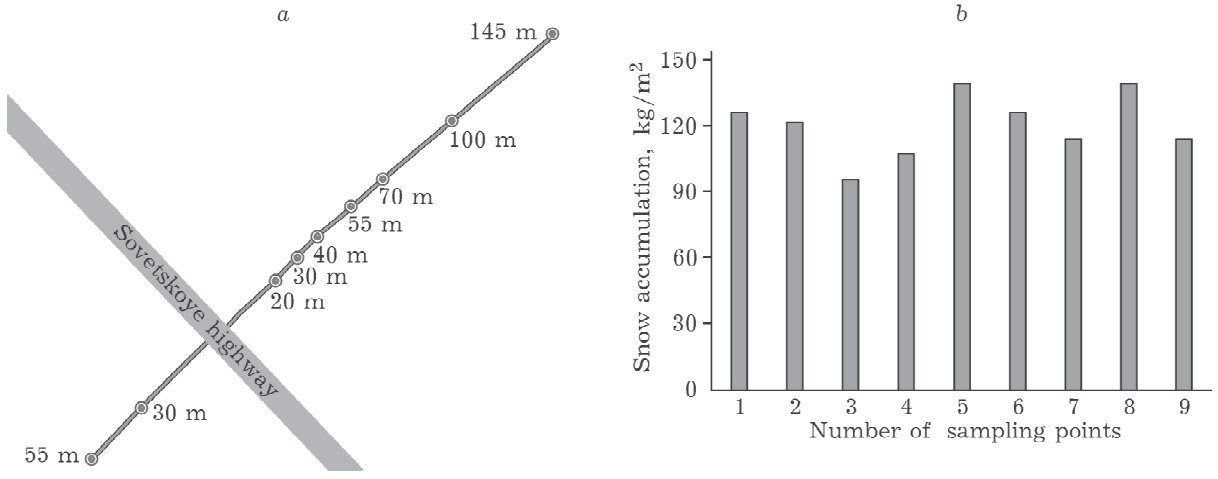

Fig. 1. Scheme of route snow survey (*a*) and data on the moisture content in sampling points (*b*).

ric detector AT 5975N in the regime of detecting by individual characteristics of ions of the compounds under determination. For the concentrations calculation, standard PAH mixture was used (Hewlett Packard No. 8500-6035). The determination error of individual PAHs amounted to no more than 20 %. The results correctness control was carried out by additions of standard samples of bromine and deuterium-derivatives of PAHs into the initial sample volume.

In Table 1, the data on 19 basic PAH component content and PAH total concentration (ΣPAH) are presented. Eight components are marked by bold font because they refer to the carcinogenic class of hazard. The sum of carcinogenic PAHs is presented in the line "ΣCarcinogenic PAHs". The date on the proportion (in %) of carcinogenic PAHs from their total sum are presented in Table 1. The preliminary analysis of the table data shows that for virtually all PAHs, concentrations a monotonic decrease with increasing the distance from the road is observed. Herewith, the proportion of carcinogenic PAHs changes from 20 to 34 % and on average is about 26 %.

In parallel samples, the content of some inorganic components and precipitate was determined. The scheme of their determination includes filtration through a paper filter of 3–5 μm diameter. The filters with precipitates were dried in open air. The precipitate mass was determined as a difference between masses of filters with precipitates and before filtration. The content of sodium, calcium, chloride, sulphate, *etc.* in the filtrate is determined. The metals were detected by a Z 8000 atomic absorption spectrometer (Hitachi, Japan) with Zeeman background correction and analyte at-

TABLE 1

PAH content in snow samples, ng/L

Nos.	PAH components	Sampling points								
		1	2	3	4	5	6	7	8	9
		Distance from the road, m								
		20	30	40	55	70	100	145	−30	−55
		Sample mass, kg								
		1.00	0.96	0.76	0.85	1.10	1.00	0.90	1.10	0.90
1	Acenaphthylene	5.6	3.1	3.3	4.1	2.7	2.6	2	1.3	0.5
2	Acenaphthene	10.5	13.7	3.6	4.9	4	4	4.4	3.1	0
3	Naphthalene	43.9	18.2	16.4	15.5	9.4	8.6	5.1	3.4	1.4
4	Fluorene	23.9	12.4	10.2	16.9	11.8	10.5	11.5	5.9	1
5	Phenanthrene	282.3	137.9	102.9	132.5	73.9	60	41.7	26.6	15.2
6	Anthracene	7.4	4.3	3.9	7.5	5.3	3.1	4.2	2.5	1.8
7	Fluoranthene	237.2	111.3	95.4	116.3	75.7	54.8	34.9	30.4	20.3
8	Pyrene	108.3	46.6	43	46.8	33.1	22.7	18.2	18.5	13.9
9	**Benzo(a)anthracene**	13.3	6.5	6.7	9.1	6	4.9	4	6.6	3.7
10	**Chrysene**	68.9	29	31.2	36.3	23.7	21.3	21.1	17.4	7.4
11	**Benzo(b)fluoranthene**	40.5	20.6	22.7	24.1	17.2	13.2	9.8	11.8	6.9
12	**Benzo(k)fluoranthene**	28.3	11.7	13.5	14.9	10.7	8.5	5.5	6.4	4.7
13	**Benzo(j)fluoranthene**	2.1	1.3	1.9	1.1	1.1	0.8	0.6	1.1	0.7
14	Benzo(e)pyrene	52.1	20.7	26.6	23.8	16	12.7	8.6	10.9	7
15	**Benzo(a)pyrene**	17.1	6.6	7.4	9.4	6.5	5.9	4.4	5.7	3.3
16	Perylene	8.2	3.3	4.3	3.6	3	2.1	1.2	1.8	1
17	**Indeno(1,2,3-cd)pyrene**	25.6	10.5	12.4	14.8	10.2	8.1	5.2	5.7	4.2
18	**Dibenzo(a,h)anthracene**	6.2	2.2	2.8	3.1	1.8	2	1.2	2.3	0.8
19	Benzo(ghi)perylene	43.4	1	1.4	20.4	13.1	10.4	6.7	6.5	4.2
	ΣPAHs	1025	476	427	506	325	256	190	168	98
	ΣCarcinogenic PAHs	202	88	99	113	77	65	52	57	32
	Carcinogenic PAHs fraction, %	19.7	18.6	23.1	22.3	23.7	25.3	32.6	33.9	32.3

TABLE 2

Snow sample basic inorganic components, mg/L

Nos.	Precipitate	Anions			Cations		
		Chloride	Nitrate	Sulphate	Sodium	Calcium	Magnesium
1	380	35.4	2.42	2.67	12.9	8.55	0.44
2	203	33.9	2.32	2.49	12.4	7.17	0.41
3	150	19.0	2.34	2.43	8.7	6.87	0.67
4	165	17.8	2.43	2.56	8.2	6.13	0.39
5	72	12.5	1.95	2.01	6.8	4.29	0.27
6	60	9.7	2.06	1.68	5.6	5.00	0.35
7	42	4.1	1.01	1.61	2.7	2.72	0.23
8	25	1.7	1.72	1.60	0.99	1.98	0.21
9	22	1.4	1.06	1.38	0.72	1.42	0.20

omization in air-acetylene flame. The detection of sodium and potassium was carried out by irradiation emission, however, calcium and magnesium – by irradiation absorption using hollow cathode lamps. For inorganic anions (chlorides, nitrates, sulphates and fluorides), the determination was based on the application of a Metrohm 883 Basic IC plus ion chromatograph with a conductometric detector and chromatographic column Metrosep A sup 5 – 150/4.0; eluent – 3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$. The analysis uncertainties were in the rates regulated by State Standard (GOST) [22].

The mentioned data are presented in Table 2. One can see that for all parameters of the chemical composition, the monotonic decrease of concentrations with increasing the distance from the motorway is observed as was noted and for PAH components.

Qualitatively, this agrees with the fact that the highway is the source of emissions. The level of fallouts from the leeward side of the road is much higher than from the windward side, which is the consequence of the repeatability of wind directions in the winter period of time [20]. Among inorganic cations, sodium prevails; its mole concentration is close to the content of chlorides. This accordance confirms the fact that sodium chloride is the basic component of mixture for winter bedding course roads.

Figure 2 presents pairwise correlation dependences between sulphates and precipitates with the sum of PAHs.

From Fig. 2, one can see that between compared variables close linear associations are observed. In case of the precipitate and sum of PAHs, a high correlation level indicates PAHs preferential spreading in the dust composition. In case of PAHs and sulphates, a similar relationship is less obvious, but it can testify one of the mechanisms of sulphates formation as a result of the transformation of their precursor SO_2 from exhaust gases at dust particles [14].

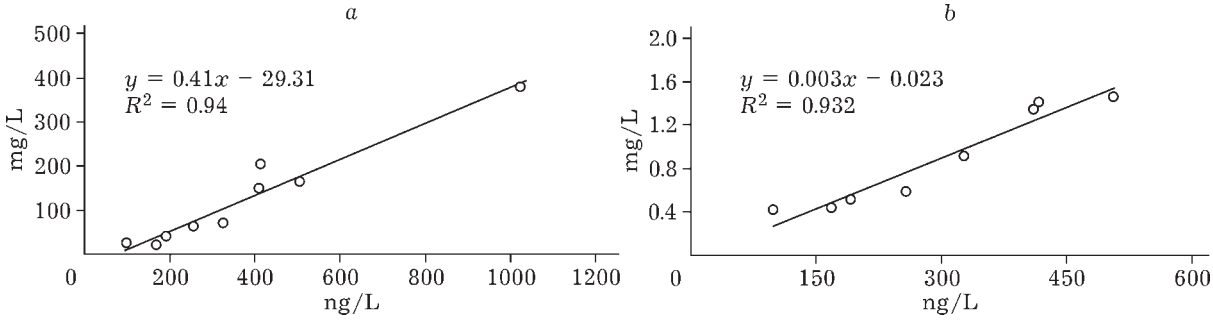

Fig. 2. Linear correlations between the contents of the sum of PAHs and precipitates (*a*), and sum of PAHs and sulphates (*b*) in samples of melted snow water.

NUMERICAL RECONSTRUCTION OF PAH FALLOUT FIELDS

The analysis of Table 1 shows that the change of PAH concentrations in snow, as moving away from the highway, is quite substantial and indicates the presence in the fall-outs composition of large aerosol fractions. In this case, when constructing the models of assessing fall-out fields of PAHs, the kinematic scheme of spreading particles in the atmosphere from the linear source and impurity transfer can be described by the following equation:

$$u\frac{\partial q}{\partial x} - w\frac{\partial q}{\partial z} = 0 \qquad (1)$$

with boundary condition

$$q\big|_{x=0} = \psi(z) \equiv Q\delta(z - H) \qquad (2)$$

where $q(x, z)$ is concentration of the admixture in the plane (x, z); u is mean of horizontal wind in the direction of x axis; w is velocity of particles sedimentation in the vertical direction, axis z oriented directly upward; Q, H are power and effective height of the source, respectively; δ is Dirac delta function.

Taking into account that the solution of equations (1) and (2) can be expressed in the form of $q(x,z) = \psi(z + \frac{w}{u}x)$ [23], we get the following result for the density of polydisperse admixture fallout in the perpendicular direction to the linear source [24]:

$$\sigma(x,\vec{\theta}) = \int_0^\infty wq\big|_{z=0} N(w)dw = \frac{Hu^2}{x^2}N(\frac{Hu}{x}) = \theta_1 x^{-\theta_2}\exp(-\frac{\theta_3}{x}) \qquad (3)$$

where $N(w) = \frac{n^{n+1}}{w_k\Gamma(n+1)}\left[\frac{w}{w_k}\exp(-\frac{w}{w_k})\right]^n$,

$$\theta_1 = \frac{u}{\Gamma(n+1)}\left(\frac{nHu}{w_k}\right)^{n+1}, \quad \theta_2 = n+2, \quad \theta_3 = \frac{nHu}{w_k},$$

w_k characterises the velosity of admixture fraction in which particle quantity prevails; n is the degree of uniformity of particles distribution on velocities w; $\Gamma(n)$ is Euler gamma function.

In the general case, the estimation of parameters θ_1, θ_2, θ_3 is done by the least square method using PAH data [25]. In particular, when the number of parameters and supporting points coincides, the problem reduces to the solution of the following non-linear equations:

$$\theta_1 x_j^{-\theta_2}\exp(-\frac{\theta_3}{x_j}) = m_j, \quad j = \overline{1, 3}$$

where m_j is measured density of admixture fallout at the distance of x_j from the source.

Then, the sought parameters θ_1, θ_2, θ_3 are calculated in an explicit form by the following formulas:

$$\theta_2 = \frac{\ln(m_1/m_2) - a\ln(m_1/m_3)}{\ln(x_2/x_1) - a\ln(x_3/x_1)},$$

$$\theta_3 = \frac{\ln(m_1/m_2) - b\ln(m_1/m_3)}{(b-1)/x_1 + 1/x_2 - b/x_3},$$

$$\theta_1 = m_1 x_1^{\theta_2} e^{\frac{\theta_3}{x_1}}, \quad a = \frac{1/x_2 - 1/x_1}{1/x_3 - 1/x_1}, \quad b = \frac{\ln(x_2/x_1)}{\ln(x_3/x_1)}$$

The highway section, in the vicinity of which the selection of snow samples was conducted, is oriented across the winds, prevailing in the winter season of the southwest sec-

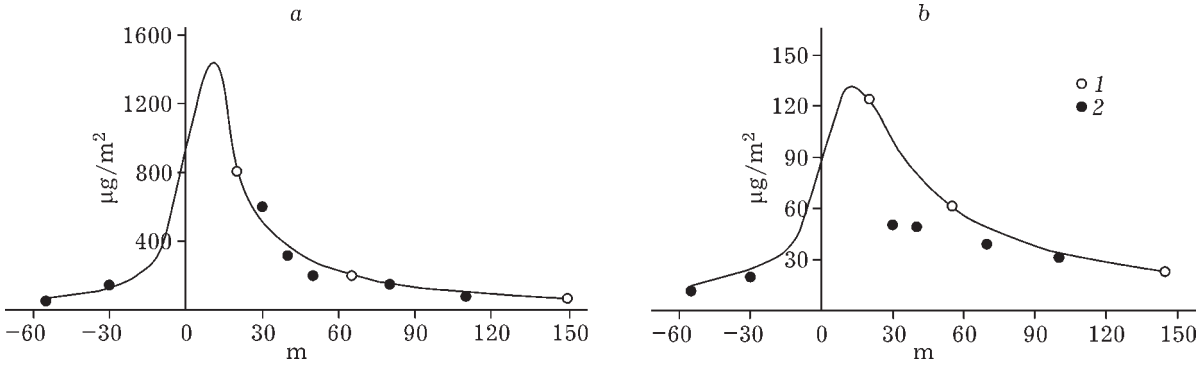

Fig. 3. Measured and reconstructed by model (3) fallouts densities of the PAH sum on the snowpack for the winter seasons of 2007/2008 (*a*) and 2014/2015 (*b*): *1* and *2* – supporting and control points of observations, respectively.

tor. Their repeatability is about 70 % [20]. It gives the possibility to use the simplified model (3), conditionally identify the leeward and windward sides and determine fractions of the removal of impurities on both sides of the highway, as 4 : 1, respectively.

In Fig. 3, *a* and *b*, presents the results of estimation the sum fallout fields of PAHs on the basis of model (3) calculated from the data of tables of PAH concentrations taking into account the water content of snow for the winter seasons of 2007/2008 [19] and 2014/2015 snow moisture content.

The results of the numerical reconstruction of fields quite satisfactorily agree with fit the measurements data in control points. A high degree of the curve slope in the region of maximal PAH fallout in the winter season 2007/2008 indicates that the disperse composition of PAHs contained particles was more heterogeneous than in winter season 2014/2015. Beginning from the distance approximately 50–60 m from the road, the curves in Fig. 3, *a* and *b* acquire a more slopping character and PAH fallout densities are correlated as 3 : 1. In general, the total fallouts of PAHs from the highway in the winter season of 2014/2015 were reduced in more than 5 times, in comparison with the season of 2007/2008.

CONCLUSIONS

The conducted field studies, chemicoanalytical and numerical investigations of snowpack contamination in the vicinity of the Sovetskoye highway of Novosibirsk, showed a substantial decrease of PAH emissions, in comparison with the season of 2008. Besides, the space structure of their fallout field substantially changed after the reconstruction made in the period of 2009–2014. There linear correlations between inorganic and organic components were determined, which specifies the unified source of emissions. On the other hand, the presence of such correlations allows making additional control of chemicoanalytical data.

In the kinematic approach, a few-parameter model of the reconstruction of the fallout field of the polydisperse admixture from the linear source was developed and in the explicit form, the method for its numerical realization was proposed. The approbation of the model presented showed its satisfactory agreement with experimental PAH data. For the reconstruction of aerosol fallout fields, a relatively small number of supporting observation points is required. The consideration of the polydisperse composition of impurities allows making interpretation of experimental investigations results in a quite substantial distance range.

Taking into account the dominating effect of emissions of auto transport on the environment of Novosibirsk, the further development of theoretical and applied investigations on this problem, involvement of methods of instrumental monitoring of both the current and long-term pollution of atmospheric air and snowpack, developments of models of the numerical analysis of gas aerosol admixtures from highways, developing effective measures on decreasing their negative influence are necessary.

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Полиароматические углеводороды в окрестностях крупной автомагистрали Новосибирска

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Аннотация

Приведены результаты полевых, химико-аналитических и численных исследований загрязнения снегового покрова в зимнем сезоне 2014–2015 гг. в окрестностях Советского шоссе Новосибирска после ее реконструкции 2009–2014 гг. Показано, что по сравнению с данными мониторинга 2008 г. произошло существенное снижение выбросов ПАУ и изменение пространственной структуры поля их выпадений. Установлены линейные корреляционные связи между содержанием осадков и неорганическими и органическими компонентами проб. В кинематическом приближении разработана малопараметрическая модель реконструкции поля выпадений полидисперсной примеси от линейного источника и предложен в явном виде метод ее численной реализации. Проведена апробация предложенной модели на полученных экспериментальных данных.

Ключевые слова: автомагистраль, снежный покров, мониторинг, химический состав, полиароматические углеводороды