Experimental Investigation and Numerical Analysis of Propagation Process for Snow Cover Pollution Near a Major Highway

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Abstract

Snow samples have been taken from ten points according to a special route at a distance of 150 m from the Sovetskoye highway of the Novosibirsk City, in February 2008. The studies on this object are being carried out by the authors for more than 10 years running. With the use of two sample preparation schemes, the major inorganic and organic components of automobile emission chemical composition were determined. The analysis of data concerning almost all the parameters under investigation indicates monotonously decreasing pollutant concentrations with an increase in the distance from the road. A model with a small number of parameters has been developed to estimate the precipitation of a polydisperse contaminant resulting from a linear source. Approbation of the model constructed has been performed using route observations data for snow cover aerosol pollution with polyaromatic hydrocarbons, macro components and heavy metals. Considerable composition heterogeneity of the precipitating aerosol contaminants has been demonstrated. A high level of PAH concentration in the snow was revealed both in the vicinity of and at a long distance from the road, which indicates considerable atmospheric pollution with fine-dispersed components.

Key words: motor transport, snow cover, aerosol pollution, chemical composition, polyaromatic hydrocarbons, lead, numerical modelling

INTRODUCTION

Motor transport is one of the basic pollutants of the atmospheric air environment of the Novosibirsk [1]. Typical polluting substances are presented by sulphur and nitrogen oxides, heavy metals, in particular lead, organic products resulting from an incomplete combustion of fuel components, for example polyaromatic hydrocarbons (PAH) [1–4]. The contribution to atmospheric air environmental pollution is drawn also by dust blowout from the surface of roads by moving motor transport [1]. The

dust composition includes identified substances those are used in order to sprinkle roads (in particular, within the winter period for controlling ice). The elemental structure of them includes sodium, calcium, magnesium, chloride, silicon, *etc.*

For the last years, active measures are taken in order to decrease the pollution level of the Novosibirsk resulting from automobile emission; however, because of a multiparametric character of the processes the efficiency of these actions is frequently ambiguous and unpredictable. So, during 1998–1999 the auto park of Novosibirsk has been entirely transferred

for using unleaded gasoline. As a result, there was a decrease of lead emissions observed, which has positively affected on the state of environment. At the same time, within the same period of time there was a considerable growth of PAH emissions has been fixed, which, to all appearance, could be caused by the lack of preparing the city auto park to gasoline with novel types of antiknock additives [3]. For the last 5−7 years the annual increase in the No-vosibirsk auto park amounts dozens thousand units of vehicles, which cannot positively affect environmental conditions in the city. However, the monitoring of the motor transport impact on the city environmental condition is of occasional character.

It could be appropriate to perform permanent monitoring of the pollution dynamics in vicinity of highways with an intense flow of traffic. Snow cover is considered the most convenient to use as an indicator of territory pollution [3−6]. The aim of the present work consists in the continuation of the studies concerning the spatial dynamics of snow cover pollution by the main components of motor transport emissions in the vicinity of a large highway of the Novosibirsk.

Fig. 1. Scheme of snows sampling along the route (*a*) and data on moisture reserve level (*b*).

FIELD INVESTIGATIONS

As the object for the investigation we have chosen the Sovetskoye Shosse located at the left-bank part of the Soviet District of Novosibirsk. The snow 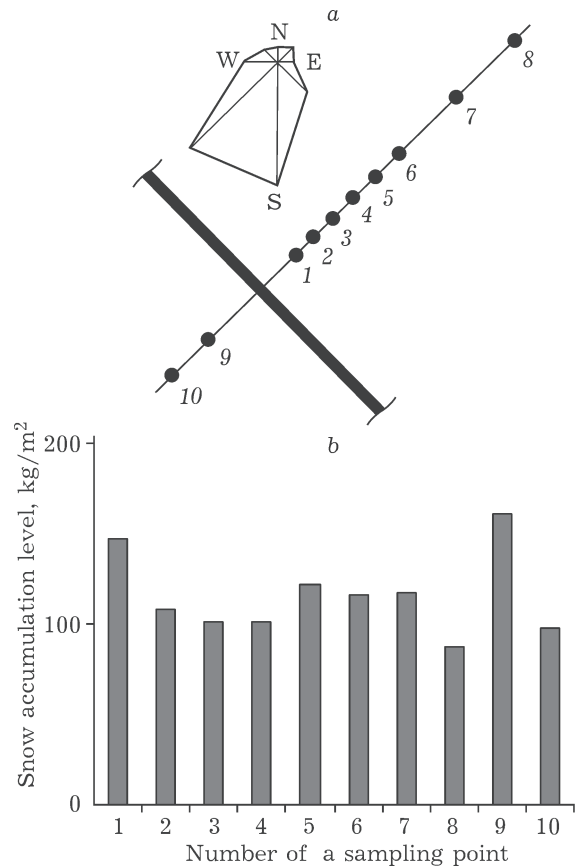sampling along the route was carried out at the end of the winter season of 2007−2008 in the vicinity of the highway range located transversely to the winds of the southwest direction as the most typical one for the winter period of time [7]. We perform regular studies on the processes of snow cover pollution on this site already more than for 10 years.

TABLE 1

Content of macro components in the dissolved part of melt snow samples and the total content of microelements

Sample No.	Distance from the road, m	Ionic macro components, (mg/L)/(mmol/L)					
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}
1	20	19.75/0.859	1.50/0.038	7.65/0.191	1.78/0.073	31.5/0.89	7.6/0.079
2	30	11.6/0.507	0.97/0.025	6.55/0.163	1.22/0.050	16.8/0.47	5.4/0.056
3	40	4.33/0.188	0.45/0.0115	3.91/0.098	0.77/0.032	6.9/0.195	4.8/0.050
4	50	3.59/0.156	0.43/0.011	3.97/0.099	0.83/0.034	5.5/0.155	4.0/0.042
5	65	3.27/0.142	1.42/0.036	3.63/0.091	0.79/0.033	5.7/0.161	4.0/0.042
6	80	2.31/0.10	0.33/0.0084	3.84/0.096	0.88/0.036	3.8/0.107	3.1/0.032
7	110	1.15/0.05	0.26/0.0066	1.85/0.046	0.43/0.0177	4.0/0.113	2.2/0.023
8	150	0.91/0.040	0.20/0.00511	1.79/0.045	0.45/0.0185	5.7/0.161	2.5/0.026
9	−30	0.8/0.035	0.23/0.0059	1.46/0.036	0.43/0.0177	1.4/0.039	2.2/0.023
10	−50	0.34/0.015	0.13/0.0033	1.0/0.025	0.38/0.0156	0.8/0.023	1.9/0.020

The scheme of snow sampling is presented in Fig. 1, *a*. From the windward side of the road we have taken samples at eight points, from the leeward side the sampling was performed at two points. Data concerning the distance from the highway are presented in Table 1. Snow sampling was made with the help of a plastic pipe 45 mm in diameter from all the depth of the snow cover. Figure 1, *b* demonstrates snow accumulation level along the route under study. It can be seen that the content of snow is varying within the range of $90-150$ kg/m^2 amounting on the average to 116 kg/m^2 (see Fig. 1, *b*).

CHEMICAL ANALYSIS OF SNOW SAMPLES

After melting the samples under investigation we used two schemes of sample preparation depending on the nature of components under determination. Prior to the determination of inorganic components a melted sample was filtered through a "blue band" paper filter and a membrane filter with a pore diameter of 0.45 μm. The precipitates obtained were dried in air. We analyzed both the precipitates and filtrate. As far as the filtrate is concerned, we determined the content of sodium, potassium, calcium, magnesium, chlorides, nitrates and sulphates therein. In order to determine sodium, potassium, calcium, magnesium we employed Z 8000 atomic absorption spectrophotometer with Zeeman background correction (Hitachi, Japan), with analyte atomization by means of air−acetylene flame. The detection of sodium and potassium was carried out in the

radiation emission mode, whereas calcium and magnesium were detected in the absorption mode for the radiation resulting from a hollow cathode lamp. For the determination of inorganic anions (chlorides, nitrates and sulphates) we used the technique based on "Kapel 103 R" capillary electrophoresis system (Lumex Co., St. Petersburg) with indirect photometric detection at the wavelength of 254 nm. As an electrophoretic buffer solution, we used a mixture of potassium chromate and diethanolamine at pH 9. The separation of anions was carried out using a quartz capillary with an internal diameter of 75 μm at a voltage of 25 kV. The main microelements determined in precipitates and filtrates were Pb, Cu, and Zn. The determination was carried out with the use of PGS-2 atomic emission spectrometer (Germany) in DC arc with the registration by a multichannel analyzer of emission spectra (MAES, VMK-Optoelektronika Co., Novosibirsk).

Organic components (PAH) were determined after triple extractive concentrating into preliminary distilled methylene chloride from the all volume of an unfiltered sample. After gathering the extracts obtained they were dried using anhydrous sodium sulphate. Further, the solvent was removed using a rotary evaporator at the temperature of 35 °C to obtain a dry precipitate. The precipitate obtained was then dissolved in a small volume of acetone ($1-5$ mL). The solution obtained was analyzed for PAH content using a Hewlett-Packard 6890 gas chromatograph with a capillary quartz column and a Hewlett-Packard 5972 MSD. As a carrier gas we have chosen helium with the flow rate equal to 1 mL/min. In order to identify the compounds we used NIST 2002 mass spectral library.

The determination errors for both macro and microelements were within the limits corresponding to the requirements of the State Standard (GOST) [8].

The data obtained corresponding to ionic macro components in the dissolved part of water resulting from melted snow as well as to the sum of main microelements contained in a dissolved part and solid precipitate are presented in Table 1, depending on the distance between the place of sampling and the highway. It can be seen that for all the parameters as a whole the samples' chemical composition the

in the dissolved part and precipitate

NO$_3^-$	Microelements, μg/L		
	Pb	Cu	Zn
2.8/0.045	14.9	21.0	33.8
2.0/0.032	13.7	21.8	18.8
2.3/0.0371	14.2	12.0	14.1
1.5/0.024	11.9	18.1	9.6
2.0/0.032	13.3	10.8	12.9
2.2/0.035	7.4	12.6	9.2
0.6/0.0097	7.3	6.1	8.6
1.8/0.029	11.4	9.1	9.3
0.5/0.0081	7.4	3.9	10.7
0.2/0.0032	4.4	1.9	2.3

concentration is observed to decrease in a monotonous manner with increasing the distance from the highway. Qualitatively, this is in a good agreement with the fact that the highway represents a source of these elements. The level of the content of pollutant substances in snow for the windward side of the road was much higher, than for the leeward side, due to the repeatability of wind direction during the winter period of time [7].

As far as inorganic cations are concerned, the highest content is inherent in sodium: the molar amount of sodium as calculated for 1 L almost coincides with the amount of chlorides. These data are confirmed by the fact that sodium chloride is the main component of the mixture for sprinkling roads in winter. Another component is presented, to all appearance, by magnesium sulphate.

Table 1 presents also data concerning under the total content of heavy metals (lead, copper and zinc) in the sample of snow. The total content of each element was calculated according to the data resulted from the determination of metal content in the fractions of coarse precipitate (with the particle size more than 2−5 μm), fine-disperse precipitate (>0.45 μm) and filtrate. One can see that the content of all the heavy metals, as well as of macro components decreases as the distance from the highway increased.

In order to compare the results obtained with the data of our previous studies [3, 4] let us discuss the dependence of Pb, Cu and Zn content in the coarse precipitate, as well as total content in the fine precipitate the filtrate on the distance between a sampling point and the motorway. Just as it has been done in [3], in this case it is established that the concentration

TABLE 2

Content of polyaromatic hydrocarbons in the samples of a snow taken in the vicinity of the Sovetskoe Shosse

ComponentS	Content, ng/L									
	Sample No.									
	1	2	3	4	5	6	7	8	9	10
Acenaphtylene	105	113	76.7	65.8	40.9	66.1	32.3	31.9	32.9	20.1
Acenaphtene	64.7	37.0	25.7	14.7	17.5	11.1	11.3	10.6	6.6	9.2
Naphthalene	368	500	376	278	199	420	117	165	141	84.8
Fluorene	262	187	80.7	62.0	63.7	46.9	41.9	39.8	28.5	32.8
Phenanthrene	2270	1650	739	484	447	244	174	117	104	83.8
Anthracene	80.7	57.9	30.0	32.2	29.8	21.9	8.8	9.7	8.2	6.8
Fluoranthrene	769	588	322	200	230	118	75.5	48.1	70.4	44.4
Pyrene	657	428	181.9	102	117	56.3	36.4	26.8	35.7	25.2
Benz(a)anthracene*	118	78.4	34.3	23.0	25.6	14.7	10.3	8.7	37.9	7.8
Chrysene*	562	355	175	95.1	110	57.6	31.6	24.3	138	17.8
Benz(b)fluoranthrene*	244	204	117	79.7	81.7	47.7	32.5	23.5	31.2	22.7
Benz(k)fluoranthrene*	153	112	80.7	49.3	46.8	30.2	20.1	13.8	16.9	12.5
Benz(j) fluoranthrene*	41.3	21.7	15.0	9.7	9.0	7.4	4.0	3.1	4.2	3.4
Benz(e)pyrene	493	302	139	74.7	88.3	46.9	25.4	19.6	22.9	15.0
Benz(a)pyrene*	159	92	53.4	31.3	42.5	24.1	20.1	14.8	27.5	17.6
Perylene	96.7	56.3	27.5	16.2	13.6	4.3	2.8	2.5	3.8	2.4
Dibenz(a,h)anthracene*	95.5	65.9	25.1	11.8	14.4	8.2	2.9	3.9	4.9	2.1
Indeno(1,2,3cd)pyrene*	122	107	68.6	43.6	42.9	25.7	17.6	13.5	23.3	12.0
Benz(g,h,i)perylene	332	241	119	62.0	79.7	43.0	21.5	17.7	18.3	14.8
ΣPAH	6996	5200	2686	1735	1700	1293	686.1	594.4	755.2	435.2
ΣPAH (carcinogenic)	1494.8	1036	568.8	343.5	373.3	215.6	139.1	105.6	283.5	95.9

*Carcinogenic PAH.

of microelements in the coarse fraction decreases with increasing the distance from the highway, for either side near the highway. The maximum of the total microelemental content in fine-disperse and the water-soluble parts is $50-60$ m shifted toward the windward side. It should be also noted that the ratio between the contribution values for the microelements contained in all the three fractions for the samples taken from the point located at a 50 m distance from the highway, coincides with similar results obtained we obtained in $2001-2002$.

Table 2 displays data concerning the content of 19 PAH components in snow, as well as their total concentration (ΣPAH) therein. It can be seen that almost all the PAH components demonstrate a monotonous decrease in the concentration with the increase in the distance from the road is observed.

MODEL FOR ESTIMATING THE AEROSOL PRECIPITATIONS OF A POLYDISPERSE CONTAMINANT

The preliminary analysis of the experimental data obtained for aerosol contaminant precipitations observed demonstrate the variation of the concentration to be rather considerable with increasing the distance from the highway. This fact allows one to assume that there are coarse aerosol fractions present in the structure of the precipitations. For the aprioristic description of the contaminant distribution (N) with respect to the precipitation rate (w) in the atmosphere let us use a two-parametrical function [9, 10]:

$$N(w) = \frac{a^{m+1}}{\Gamma(m+1)} w^m e^{-aw} , \; m \geq -1, a = m/w_m \quad (1)$$

Here w_m is the precipitation rate for the particles of contaminant fraction prevailing by amount; m is the degree of homogeneity for rate distribution of contaminant particles w; $\Gamma(m)$ is Euler's gamma function.

The calculation of the precipitation field of polydisperse contaminant (p) resulting from a point source is based on the relationship [9, 11]

$$p = \int_0^\infty w q_w N(w) dw \quad (2)$$

where q_w is the field of concentration for a monodisperse contaminant with the precipitation rate w.

In the calculation of average concentration in the surface atmospheric layer, frequently occurring meteorological conditions are of determining significance. They represent so-called normal meteorological conditions for those one uses power function for the approximation of wind speed u (z) and the factor of vertical turbulent exchange K_z [12]:

$$u(z) = u_1(z/z_1)^n, \; K_z = k_1 z/z_1 \quad (3)$$

where u_1 and k_1 are the values of u and K_z at $z = z_1$.

Using the relationships (3) and the analytical solutions of the turbulent diffusion equation for low-intensity sources, the concentration field q_w near to the ground could be presented as [11, 13]

$$q_w(x,y) = \frac{Mc^\omega}{2(1+n)\sqrt{\pi k_0}\Gamma(1+\omega)x^{1.5+\omega}}$$

$$\times \exp(-\frac{c}{x} - \frac{y^2}{4k_0 x}) \quad (4)$$

Here the axis x is oriented along the wind direction; the axis y is directed along the direction transverse with respect to wind; M is the intensity of a contaminant source; k_0 is the turbulent exchange parameter along the direction the axis y;

$$c = u_1 H^{1+n}/(1+n)^2 k_1, \; \omega = w/(k_1(1+n)) \quad (5)$$

Taking into account relationships (1), (4), expression (2) can be presented in the form

$$p(x,y) = \frac{Ma^{m+1}}{2(1+n)\sqrt{\pi k_0}\Gamma(1+m)x^{1.5}} \exp(-\frac{c}{x} - \frac{y^2}{4k_0 x})$$

$$\times \int_0^\infty \frac{w^{m+1}\exp(-aw)}{\Gamma(1+\omega)} \left(\frac{c}{x}\right)^\omega dw = \frac{Q}{x^{1.5}} \exp(-\frac{c}{x} - \frac{y^2}{4k_0 x})$$

$$\times \int_0^\infty \frac{\omega^{m+1}\exp(-R\omega)}{\Gamma(1+\omega)} \left(\frac{c}{x}\right)^\omega d\omega, \quad (6)$$

$$Q = \frac{MR^{m+2}}{2(1+n)a\sqrt{\pi k_0}\Gamma(1+m)}, \quad R = a(1+n)k_1$$

Then, the concentration field created by an infinite linear source is located on the basis of the superposition of precipitation fields from point sources:

$$p_{\text{lin}}(x,y) = \int_{-\infty}^\infty p(x_p, y_p) d\eta \quad (7)$$

Here $x_p = s_1 - \eta\sin\beta$; $y = s_2 - \eta\cos\beta$; $s_1 = x\cos\beta + y\sin\beta$; $s_2 = -x\sin\beta + y\cos\beta$; b is the angle between wind direction and axis x.

The most simple form (7) the expression acquires at $\beta = \pi/2$. In this case we obtain:

$$p_{\text{lin}}(x) = \frac{\theta_1}{x} \exp\left(-\frac{c}{x}\right) \int_0^\infty \frac{\omega^{\theta_2} \exp(-\theta_3 \omega)}{\Gamma(1+\omega)} \left(\frac{c}{x}\right)^\omega \, d\omega \tag{8}$$

$$\theta_1 = \frac{MR^{m+2}}{(1+n)a\Gamma(1+m)}, \quad \theta_2 = m+1, \quad \theta_3 = R$$

The investigation of the properties of function (8) demonstrate that within the range of x values $x \in (0,\infty)$ the function reaches a maximum at certain point x_0, monotonously increases at $x \in (0,x_0)$ and, correspondingly, monotonously decreases within the range of x values $x \in (x_0,\infty)$ tending to zero at $x \to 0$, $x \to \infty$. The estimation of unknown parameters θ_1, θ_2, θ_3, included in the relationship (8), was performed by means of the technique of least squares using the data of measurements concerning the density of contaminant precipitations at the points of snow sampling [14]. One should also note that the value of c corresponds to the distance where a sample exhibits the maximal concentration of a light contaminant [11].

NUMERICAL ANALYSIS OF EXPERIMENTAL RESULTS

According to the data presented in Fig. 1, the highway section under investigation ranges from the southeast to the northwest. In this connection, in order to estimate the fields of aerosol contaminant precipitations, a simplified model (8) could be used, since the average winter repeatability of southern, southwest and western winds amounts to about 70 % [7]. Correspondingly, the northern, northeast and east wind contribution is equal to 14 % only, which allows one to select conventionally "leeward" and "windward" sides as well as to determine the ration of contaminant carryover on corresponding sides of the highway as 5 : 1.

Figure 2, *a* demonstrates the results of estimating the precipitation fields for the sum of PAH components, obtained on the basis of model (8). The results of the numerical reconstruction of the concentration field are in a quite good agreement with the data of measurements for observation points. Some discrepancy between the measured and calculated values for point No. 4, in our opinion, could be caused by a considerable deviation of moisture reserve
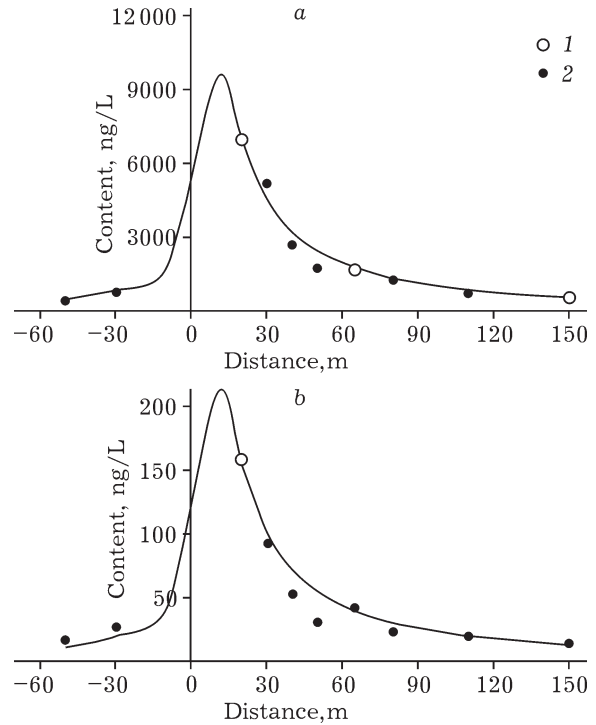

Fig. 2. Data concerning the total content of PAH (*a*) and benz(a)pyrene (*b*) in snow, measured and reconstructed according to model (8). Here and in Fig. 3: *1*, *2* − reference and observation points, respectively.

level at this point from the average level (see Fig. 1, *b*), as well as by the presence of a large-scale gradient in the concentration field. The obtained estimations of parameters θ_2, θ_3, directly connected with the dispersity characteristics, were used for reconstruction of the concentration field for benz(a)pyrene (see Fig. 2, *b*). In this case, with use of model (8) we have estimated parameter θ_1 only, and for its determination we used the observation in the reference point at a distance of 20 m from the road.

The data resulting from the simulation of spatial dynamics for ionic components are presented by the example of sodium and sulphate ions in Fig. 3. It is seen that the model curve, whose parameters were estimated from three experimental points describes well the decrease of sodium concentration at the sites located on either side of the highway. For sulphate ions, the direct estimations of the model parameters from experimental data gave a regular deviation at the points of the windward side of the road (see Fig. 3, *b*). Subtracting the background concentration of sulphate ions (1.4 mg/L) there
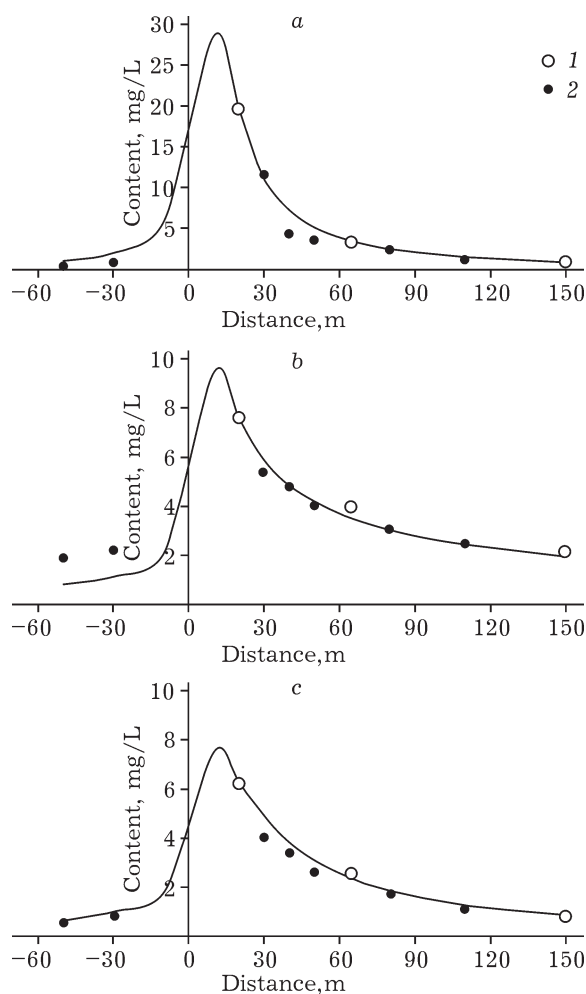
Fig. 3. Measured and reconstructed data concerning the content of in a snow of ions Na^+ (a) and SO_4^{2-} (b) ions taking into account (b) and with no account (c) of background values. For design. see Fig. 2.

is a good coincidence between experimental points and the model curve observed.

As far as heavy metals are concerned, the results of simulation both for the part concerning coarse precipitate, and those related in total to fine-disperse precipitate and filtrate are in a good agreement with the results obtained earlier [3].

CONCLUSIONS

The chemical analysis and numerical studies concerning snow cover pollution in the vicinity of the highway allow us to make the following conclusions.

With the use of two sample preparation schemes, main inorganic and organic components of chemical composition have been de-

termined in the samples taken from ten points along a special route at a distance up to 150 m from the highway. Inorganic components included eight macro components and three microelements, organic components included 19 PAH components. The analysis of the data with respect to almost all the parameters of the composition indicates monotonously decreasing concentration of elements with increasing the distance from the highway.

Basing on analytical relationships (1), (4) we have developed small-number parameter models for estimating the contaminant precipitation taking into account the heterogeneity of the aerosol composition. The models obtained could be used for estimating the fields both of one-time, and of long-term territory contamination.

The approbation of the model suggested has demonstrated to be in a satisfactory agreement with the data concerning observed PAH, macro components. In order to reconstruct the fields of aerosol precipitations a relatively small quantity of reference observation points is required. Taking into account the polydisperse nature of contaminant composition within the framework of unified model one could perform the interpretation of the results of experimental studies for a considerable range of distances.

One should note a rather high level of PAH content in snow both near to, and at a great distance from the highway, which indicates a significant atmospheric air pollution by fine-disperse components.

Taking into account a predominant impact of motor transport emissions on the environment of the Novosibirsk, one should extend theoretical and applied studies concerning this problem, to involve more widely the methods of instrumental monitoring of current atmospheric air pollution of as well as to develop effective measures aimed at the reduction of negative impact.

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