Regularities in the long-term contamination of a motorway surroundings

V.V. Kokovkin, V.F. Raputa, O.V. Shuvaeva, and S.V. Morozov

Institute of Inorganic Chemistry,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk
Institute of Organic Chemistry,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk
Institute of Computational Mathematics and Mathematical Geophysics,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk

Received February 9, 2000

In this paper we describe the regularities of the aerosol pollution distribution in the snow cover near Sovetskoye highway on the left-bank area of the Sovetskii district of Novosibirsk. The experimental data on chemical composition of the snow cover are analyzed using the mathematical models of aerosol emissions from the ground and elevated linear sources. Such basic toxicants as heavy metals and polycyclic aromatic hydrocarbons were used as chemical pollution parameters. Simultaneously, the ion composition of snow samples was determined.

Introduction

The motorized transport, using diesel fuel and gasoline, is one of the main sources of pollution of the environment.[1] The typical contaminants emitted by the vehicles are: sulfur and nitrogen oxides and the products of their transformation – sulfuric acid and nitric acid, heavy metals, in particular, lead, as well as polycyclic aromatic hydrocarbons (PAH). These toxicants enter the environment mainly along with the exhaust gases (EG). The greatest amount of toxicants is observed near motorways.

Moreover, the investigations into the pollution of motorway surroundings are limited in number. Much of the current interest in the subject is focused on the study of the impact of pollutants on cultivated plants,[2,3] contamination of soils by heavy metals. The characteristic feature of such investigations is their laboriousness due to samplings and chemical analysis of the samples.

As to the study of air pollution, such investigations are carried out in regular intervals by the monitoring services of the State Committee of Hydrometeorology and the State Committee of Sanitary Inspection and are aimed at the assessment of the air quality based on the criteria of the maximum permissible concentration (MPC).[4]

An efficient method of studying the pollution regularities of motorway surroundings is the investigation of the snow cover composition.[5,6]

The snow cover during winter period accumulates a great deal of aerosol precipitations and may serve a peculiar indicator of the local contamination.

The goal of this paper was to study the quantitative regularities of distribution of motor transport emissions near motorway on a long-term scale.

1. Experimental investigations of the snow cover pollution

The area of Sovetskoye highway in the left-bank region of Sovetskii district of Novosibirsk was chosen as an object of our study. This area is situated perpendicular to the direction of dominating wind from the southwest typical of the winter periods. In this connection, the irregular distribution of contaminants in the snow cover on the sides of the highway was expected. Therefore, from the windward side (further right-hand side) because of the expectedly enhanced concentrations a larger number of points were taken than from the leeward (left-hand) side of the highway. The distances from the path, on which the snow samples were taken, were the following: (a) the right-hand side of the road: 10 m (1 point); 20 m (2 points); 30 m (3 points); 50 m (4 points); 75 m (5 points); 100 m (6 points); 150 m (7 points); (b) the left-hand side of the road: 20 m (1 point); 100 m (2 points).

The snow samples were taken in the end of February 1999. The snow samples were taken through the whole depth of the snow cover using a titanium tube of 100 mm diameter, and a small scoop made from polyethylene to prevent the capture of soil particles from the ground surface. After melting samples, we analyzed them by applying two different techniques, depending on the nature of the components analyzed. To analyze inorganic components, the liquid sample was filtered using a "blue tape" filter and a membrane filter with pores of 0.45 μm diameter. Thus obtained sediments were air-dried. Both sediments and filtrate were then analyzed. In the filtrate we determined the following parameters of the macro-component

0235-6880/00/08 733-05 $02.00

composition: specific electric conductivity, pH, ion content: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, hydrocarbonate, Cl^{-}, NO_3^{-}, SO_4^{2-}. From the micro-component composition we determined the content of Pb, Cd, Zn, and Cu. The sediments were dried up to the air-dry state. In the sediments the contents of Pb, Cd, Zn, and Cu were also determined. The organic components (PAH) were determined after their extractive concentration to dichlormethane from the entire volume of unfiltered sample.

Analysis was carried out at the analytical laboratories of the Institutes of Inorganic and Organic Chemistry SB RAS authorized by State Standard Agency of the RF. The errors of analysis were within the limits by the State Standard No. 27384–87.[7]

The results of route snow sampling show that the snow mass in the samples along the path under study varied from 85 to 121 kg/m^2. On the average, it was 103 kg/m^2.

According to spatial dynamics the components can be divided into two groups: (1) exponential (hyperbolic) decrease of concentration with the increase of the distance from the road and (2) a curve with maximum.

2. Simulation of aerosol precipitation distribution

Simulating the processes of long-term pollution of the motorway surroundings has revealed some specific peculiarities. On the one hand, the representation of a motorway as a linear source results in a marked simplification in the statement of the problem. The possibility of replacing the currently available meteorological data on the wind velocity, and state of stability of the atmospheric boundary layer by the climatic data enables us also to remove some restrictions related to uncertainties in the meteorological parameters. On the other hand, the description of the spatiotemporal structure of the contaminating emissions from motor transport faces some difficulties. The location of sources at a low height results in the necessity of detailed consideration for the inhomogeneity of the relief and underlying surface and gives rise to a wide variety of processes of the pollution transport.

Taking the above-mentioned facts into account and having available an appropriate model of the pollutant transport from a point source, the data on the pollution of motorway surroundings can be obtained based on the superposition principle using numerical simulation methods.

In our case, further simplifications are possible. The orientation of the motorway area, near which the investigations are being carried out, enables us to use the approximation of a linear source model because in winter the winds blowing to the right-hand side, prevailed.

Only the contribution of the south and southwest winds is more than 60%. According to Refs. 8–10 the transport of aerosol pollution from a linear source can be described by the following expression:

$$q(x,\boldsymbol{\theta}) = (\theta_1/x^{\theta_2})\ \exp\ (-\ x_{\max}/x),\ \theta_2 \geq 1, \quad (1)$$

where $q(x, \theta)$ is the specific content of contaminants in the snow cover, x is the distance from the source, $x_{\max}$ is the point of maximum surface concentration for nonsettling impurity; $\boldsymbol{\theta} = (\theta_1, \theta_2)$ is the vector of unknown parameters.

Equation (1) follows from analytical solution of a semiempirical equation of turbulent diffusion obtained for power-law profile of wind velocity and the coefficient of vertical turbulent exchange. The component θ_1 is a complicated dependence of meteorological parameters, namely, the height and the source power. The source power enters this dependence linearly. The parameter θ_2 has the form

$$\theta_2 = 1 + W/k\ (n + 1), \quad (2)$$

where W is the rate of sedimentation of aerosol particles; k is the coefficient of vertical turbulent diffusion at 1 m height; n is the exponent in the approximation of horizontal component of wind velocity by a power-law profile.

With *a priori* information at hand, about the parameters of pollutant emissions, Eq. (1) can be further simplified. In the case of ground emission $x_{\max} \to 0$ and from Eq. (1) the following relationship can be derived:

$$q(x,\boldsymbol{\theta}) = \theta_1/x^{\theta_2}. \quad (3)$$

For a weakly settling impurity ($\theta_2 \to 1$), it is convenient in some cases to use the following expression:

$$q(x,\theta) = (\theta/x)\ \exp(-\ x_{\max}/x). \quad (4)$$

The parameters θ_1, θ_2 in the regressions (1), and (3) can be estimated using data collected at two observation points. To evaluate the regression (4), only one point is needed. This concept has some advantages since it enables a precise control over estimating the field of specific content of pollutants based on the data from the remaining observation points. Now we interpret the obtained experimental results based on the above-mentioned dependences for each specific group of chemical parameters.

2.1. Macrocomponents

The exponential decrease was observed for the following components: cations Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+} and anions HCO_3^{-} and Cl^{-}. These components are the main constituents of the road dust. Therefore, the maximum content of these components is observed near the road and decreases with the distance. To describe the component distribution, it is appropriate to use the model (2).

The typical behavior of these components is shown in Fig. 1, where an example is shown of the distribution of sodium ion and the sediment mass. The reconstruction is made using the model (2).

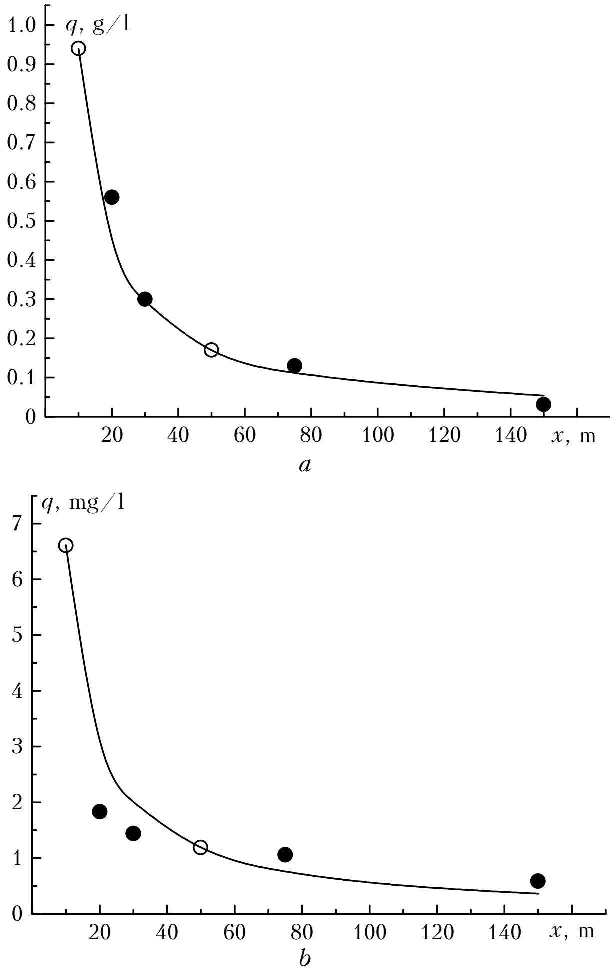

Fig. 1. Distribution of specific content of undissolved part (*a*) and water dissolved sodium (*b*) (Φ – reference points; M – control points).

The control over the remaining points shows satisfactory agreement between the calculated and observation data.

According to data from Table 1, the distribution, corresponding to the model (1), is observed for NO_3^-, SO_4^{2-}, and NH_4^+. The concentration peaks at a certain distance from the motorway (30 m) for NO_3^- and SO_4^{2-} are caused by the fact that these ions have as their immediate predecessors such ions, as NO_x and SO_2 as well as ammonia contained in the exhaust gases. The exhaust gases temperature is elevated. For this reason, the exhaust gases do not settle immediately near the road but are transported across a certain area along the wind. The NO_x and SO_2 in the atmosphere are transformed into the sulfuric and nitric acids. The low pH values revealed at 30 m distance are also caused by this fact. We did not manage to assess, for the above components, the model parameters because of a sharp maximum. This only indicates to a qualitative agreement of the model and the presence of some interrelations that were neglected.

Table 1. Spatial dynamics of specific content of SO_4^{2-}, NO_3^-, and NH_4^+, mg/l

Element	Distance from the right-hand side of the motorway, m					
	10	20	30	50	75	150
SO_4^{2-}	8.93	5.96	22.6	3.46	2.31	2.50
NO_3^-	2.11	1.84	12.6	2.54	3.84	3.72
NH_4^+	0.16	0.11	0.32	0.07	0.22	0.17

2.2. Polycyclic aromatic hydrocarbons (PAH)

The experimental dependences obtained of the most studied PAH are the following. Near the motorway the PAH content is maximum. In what follows we observe a smooth fall of the PAH content at the distances of 20 to 40 m. Then starting with the distance about 50 m the nearly linear drop of the PAH content is observed. Now we illustrate the results of reconstruction, based on the model (1), of the specific content of benz(a)pyrene, fluoranthene, and pyrene in the snow cover in Table 2. The model parameters for selected PAH are calculated on the basis that x_{max} is positioned at 30 m distance. The model parameters are estimated based on data from two points located at 20 and 50 m distance from the road. The remaining 4 points characterize the reconstruction accuracy.

Table 2. The measured (numerator) and reconstructed (denominator) concentrations, mg/l, of PAH in the motorway surrounding

PAH	Distance from the motorway, m						Estimates of the parameters	
	10	20*	30	50*	75	100	$\theta_1/10^3$	θ_2
Benz(a)pyrene	209/29	47	45/43.2	31	16/20.9	16/15.2	16.3	1.45
Fluoranthene	1314/250	370	334/319	210	127/143	74/94	200	1.6
Pyrene	842/163	196	150/149.7	85	51/48	35/31	260	1.9

Note. The points indicated as "*" were used to assess the regression parameters (1). Here the measured values of PAH are given.

Good agreement between the calculated and experimental data at the distances of 30, 75, and 100 m points to the high accuracy of the dependence choice. According to the general form of the dependence, we can conclude that in reality there exists bimodal distribution with the first peak at about 10 m and the second one in 25 m area. It is evident that the first peak is due to the effect of snowplow machinery and the second one is due to the emissions of exhaust gases.

The calculated values of θ_1 enable us to determine the PAH relative emission in the atmosphere. Taking into account the moisture reserves and the estimates of θ_1, θ_2, we can calculate the total PAH emission from the motorway during winter season. The value of θ_2 differs from 1 that is indicative of the contribution of sedimentation effects.

2.3. Microelements

The distribution of microelements among the fractions (water-soluble, finely dispersed, and coarse-dispersed) is shown in Table 3. It is evident that the contribution of microelements in the coarse-dispersed fraction decreases with the increase of the distance from the road when the total insoluble part is reduced. On the contrary, the part of microelements in the water-soluble fraction grows. The part of fine fraction also increases.

Heavy particles of dust and soot, forming the coarse-dispersed fraction, contribute significantly to the pollution of the snow cover at a distance of 50 m from the motorway. The particle behavior can be described as sedimentation of heavy monodisperse aerosol by the model (3). Figure. 2*a* shows the reconstructed results obtained using the lead as an example of typical contaminant of motorway surroundings. The model parameters were estimated based on data from the points at 10 and 150 m. Good agreement between the calculated and experimental data on specific contents of metal is indicative of the usefulness of the model chosen.

The distribution of microelements in the water-soluble fraction does not provide information on a reasonably pronounced dynamics of the content variation with the increase of the distance from the motorway. It is evident that this is due to the solubility of microelement compounds in different aerosol fractions in preparation for samples. If we assume that the contribution to the solubility of microelements of the fine aerosol fraction is a determining factor, especially in a direction away from the road where the contribution of the fine fraction increases, then the net microelement content in the fine and water-soluble fractions can be considered. Based on the fine fraction a well-defined peak at 30 m distance was observed. Then, for reconstructing the pattern of pollution, we can use the model (4) where the number of parameters being determined reduces to a single parameter. The results of modeling are shown in Fig. 2*b*, where the lead is used as an example. The point at 150 m is chosen as a reference one. It is evident that the model agrees well with the experimental data.

Table 3. Distribution of microelements in fractions, %

Element	Fraction	1 (right)	2 (right)	3 (right)	4 (right)	1 (left)	2 (left)
	W	27	36	47	49	84	80
Cu	F	1.0	1.0	8.0	4.0	4.0	2.0
	C	72	63	45	47	12	18
	W	0.4	1.4	2.7	2.8	20	41
Pb	F	0.8	0.4	6.1	2.5	8.0	3.0
	C	98.8	98.2	91.2	94.7	72	56
	W	0.2	2.0	5.3	3.0	10	1.4
Zn	F	1.2	2.0	8.3	4.0	10	0.8
	C	98.6	96	86.4	93	80	97.8

N o t e . W – water-soluble fraction, F – finely dispersed fraction, C – coarse-dispersed fraction.

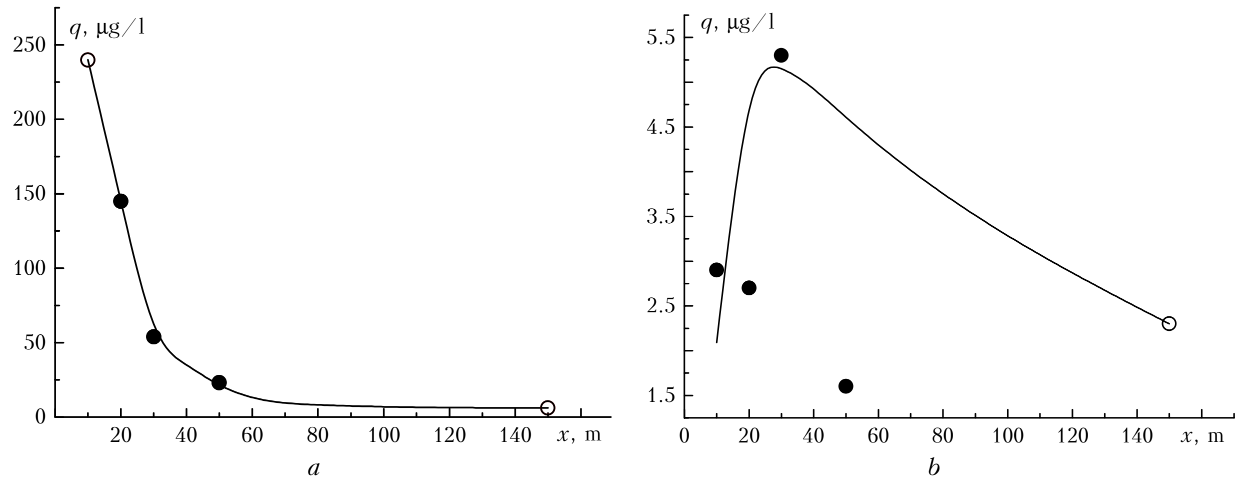

Fig. 2. The specific lead content in the coarse-dispersed fraction (*a*) and the net lead content in the fine and water-soluble fractions (*b*) (Φ – reference points, M – control points).

Conclusion

The paper describes the complex investigation that enabled us to draw the following conclusions:

– The distribution of the specific content of macrocomponents is described by the dependences of two types. In the framework of the model of the ground source, a satisfactory description is obtained of the distribution dynamics with the increase of the distance from the motorway. For sulfate-, nitrate-ions, and ions of ammonium the presence of the peak is shown, which was shifted to the windward side at a distance of 30 m.

– The field of PAH was formed by the action of two sources: the motorway pollution within 10 m occurred under the action of snow removal machinery and the distant zone was formed under the action of the elevated source. The distant zone of pollution connected directly with the regime of exhaust gas burning was described quantitatively.

– The quantitative interrelation of microelement distributions in the coarse-dispersed, fine and water-soluble fractions has been revealed. It has been shown that the distribution of microelement related to coarse-dispersed fraction occurs under the influence of wind drift from the road, and the net content of microelements in the fine and water-soluble fractions is due to the exhaust gases from the motor vehicles.

References

1. V.Yu. Aleksandrov, L.I. Kuzubova, and E.P. Yablokova, *Ecological Problems of Motor Transport. Analytical Review* Issue 4 (Publishing House of the State Public Scientific-Technical Library of SB RAS, Novosibirsk, 1995), 32 pp.

2. M. Treshow, ed., *Air Pollution and Life of Plants*, (Gidrometeoizdat, Leningrad, 1988), 250 pp.

3. A.N. Silant'ev and I.L. Shkuratova, *Detection of Industrial Contamination of Soil and Atmospheric Precipitation Against the Background of Global Contamination* (Gidrometeoizdat, Leningrad, 1983), 136 pp.

4. *The Environment and Ecological Situation in the Novosibirsk Science Center SB RAS* (Publishing House of SB RAS, Novosibirsk, 1995), 186 pp.

5. V.N. Vasilenko, I.M. Nazarov, and Sh.D. Fridman, *Monitoring of Snow Cover Pollution* (Gidrometeoizdat, Leningrad, 1985), 185 pp.

6. V.P. Pchelintsev, in: *The Influence of Human Activities on the Environment of Komi ASSR*, (Syktyvkar, 1982), pp. 103–112.

7. *Water. Current Standards of Measurement Errors of Indices of Content and Characteristics.* All-Union State Standard 27384–87 (Publishing House of Standards, Moscow, 1988), 14 pp.

8. M.E. Berlyand, *Modern Problems in Atmospheric Diffusion and Pollution* (Gidrometeoizdat, Leningrad, 1975), 448 pp.

9. V.F. Raputa, A.P. Sadovskii, and S.E. Ol'kin, Meteorol. Gidrol., No. 2, 33–41 (1997).

10. V.F. Dunskii, N.V. Nikitin, and M.S. Sokolov, *Pesticide Aerosols* (Nauka, Moscow, 1982), 288 pp.