Methods of Interpretation of the Data of Snow Cover Pollution Monitoring

VLADIMIR F. RAPUTA¹ and VASILIY V. KOKOVKIN²

¹Institute of Computational Mathematics and Mathematical Geophysics, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 6, Novosibirsk 630090 (Russia)

²Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

E-mail: basil@che.nsk.su

(Received February 15, 2002)

Abstract

A survey of experimental and theoretical methods of the investigation of aerosol pollution of snow cover in the vicinity of man-made sources is performed. On the basis of the formulation of inverse problems of the transport of admixtures in the surface and boundary layers of the atmosphere, a description of the models for the recovery of aerosol precipitation fields for the sources of different types is presented. The results of tests with man-made sources of West and East Siberia are reported. The use of the methods of consequent analysis of the data of monitoring and planning of snow surveys is discussed. The models of optimal decrease in emission from the set of sources are discussed.

INTRODUCTION

Investigation of snow cover is a convenient and economical method to obtain data on the deposition of pollutants from the atmosphere onto the ground surface. The snow cover is of special interest for the investigation of long-term pollution processes (month, season) because the snow as a natural accumulating planetable gives actual values of dry and wet deposition during the cold season [1–4].

The most intensive investigations of the pollution of snow cover were performed within the recent 30–40 years. It was demonstrated that the snow can serve as an indicator of the atmospheric pollution with dust, macrocomponents, heavy metals, polycyclic aromatic hydrocarbons originating from petroleum, proteins, *etc.* Snow cover can be used for remote probing of pollution parameters, including probing from space [2, 5].

The quantitative links between metal content of the atmospheric air and metal deposi-

tion on the surface in cities and suburbs were revealed with the help of geochemical and sanitary hygienic studies. The deposition is observed as anomalies in soil and in snow cover; which are easy to investigate over any previously prescribed network of sampling sites [6-8]. The areas of anomalous concentrations of the compounds present in emission or formed by the transformation of emitted components have been stated in snow cover in the vicinity of industrial enterprises and fueled electric power stations. The intensity and configuration of concentration field are determined by the emission intensity, time of accumulation, location of sources, recurrence of wind directions, etc. Anomalous concentration fields are followed within tens kilometers.

The mathematical methods of quantitative analysis of the data on snow pollution are insufficiently developed yet; they are mainly empirical [1, 6, 7]. On the other hand, the direct application of differential equations of atmospheric dynamics and transport of gas and

aerosol admixtures to the description of long-term pollution is complicated by substantial difficulties connected with the provision of the necessary input meteorological information, description of the interaction with ground surface, assignment of spatial and temporal regime of source operation and disperse composition of the emitted admixtures [9–12]. Such a situation requires a more reasonable analysis of experimental data and theoretical investigations of the spreading of admixtures in the surface and boundary layers of the atmosphere.

When modeling long-term pollution of territory by stationary sources, climatic information can be used instead of the current meteorological data. The application of the methods of similarity and dimensionality theory allows one to decrease the number of determining parameters. Observation planning on the basis of model notions and a priori information on transport processes and sources of admixtures allows one to increase the information content of the experimental data. Thus, all the necessary prerequisites have been created for the monitoring of snow cover to become not passive observation system but also to include the blocks for modeling, analysis, optimal planning of measurements, as well as prediction and situational control [13]. All these constituents of complex monitoring were used and developed in our works. The present paper is a review of results obtained in this area.

SAMPLING PROCEDURE AND CHEMICAL METHODS FOR THE INVESTIGATION OF SNOW POLLUTION

Starting from the conditions of formation and existence, snow cover is a complicated heterogeneous system including solid water as the major component (its content being usually more than 99 %), as well as admixed solid aerosol particles. These aerosol fractions are of the highest interest for the investigation of snow samples because their characteristics can give information on the sources and properties of aerosol precipitated from the atmosphere. There is no general classification of the sources of aerosol particles in snow. One can assume the presence [14] of aerosol particles of natural origin (continental and marine aerosolcosmic dust), as well

as anthropogenic emission of industrial enterprises, transport, agriculture, municipal economy. Depending on sampling sites, contributions of sources and relations between fractions can vary. In addition, aerosol samples differ in phase, disperse, chemical and microbiological composition [15–17]. We are interested in snow sampled near man-made sources. It is evident that aerosol fractions characterizing a specific source are prevailing in such samples.

The sampling of snow for the survey of snow cover pollution is traditionally performed along definite routes, as a rule, connected with the system of rouds. Sampling procedure is usual [1, 2]; number of samples is not regulated. It should be noted that the application of usual approaches for revealing polluted regions requires substantial efforts [6–8].

Sample preparation involving melting is accompanied by the dissolution of a part of aerosol components in water thus bringing changes into the fraction composition [3, 18]. Nevertheless, the resulting data are rather informative to characterize the pollution source. As far as the recovery of the composition of aerosol fractions is concerned, this question requires special consideration.

The effect of regime of snow melting on the results of analysis was investigated [1, 18]. It was demonstrated that it is necessary to separate solid precipitate from solution immediately after sample melting. In case of longtime contact between the solution and precipitate in the air, gradual dissolution of carbonates occurs under the action of carbon dioxide of the air, and precipitation of the formed hydroxides and carbonates of heavy metals (iron, manganese, copper, etc.). The analysis of liquid fraction should be made immediately after filtering, because some macrocomponents of samples are volatile (in particular, ammonium). These conclusions were confirmed by the results of chemical thermodynamic modeling of the equilibrium composition of solutions taking into account complex formation and precipitation (solubility products), and by the results of analytical determination of the concentrations of components of solutions and the dependence of concentrations on pH.

The investigation of disperse composition of precipitation obtained after filtering the

samples collected in the vicinity of various sources (a coal-fueled boiler house, a motorway, etc.) demonstrated that it depends on source type [18]. For example, specific mass of particles in the coarse part of precipitate (more than $2-5 \mu m$) near a coal-fueled boiler house is represented approximately uniformly within the size region up to 60-80 μm. At the same time, a gradual increase in the contribution from larger particles is observed near motorways in the same size range. The permanent presence of calcite and quartz crystals in close ratio independently of source type is characteristic of the phase composition of the investigated precipitates. One may assume that this composition is of soil erosion origin.

The analysis of the chemical composition of liquid solution and solid precipitate is performed, for example, by means of procedures [19, 20]. Let us consider chemical analysis of the samples. Among inorganic components, macrocomponents are usually determined in solution; they are represented by the cations: calcium, magnesium, sodium, potassium, ammonium, and anions: hydrocarbonate, sulphate, chloride, nitrate. Nitrate, ammonium, sulphate, chloride are usually predominant near anthropogenic sources. The components which are prevailing in background regions include calcium, magnesium and hydrocarbonate ions. Among microelements, the highest concentrations in solutions are characteristic of iron, aluminium, copper, zinc, etc. [1, 21-24]. In precipitates, usually the same elements as those listed above for solutions are determined.

Organic components which are of the highest interest in airborne emission include polycyclic aromatic hydrocarbons (PAHs) which possess high carcinogenic activity. It seems important to investigate the content of proteins [8, 25, 26] and microbiological composition [27] of snow for the regions with intensive anthropogenic activity.

Determination of inorganic and organic components is performed separately. Inorganic components are determined in filtrate and in precipitate after sequential filtering through the paper and membrane filters. The PAHs are determined after their preliminary extraction

concentration in hexane from the entire volume of non-filtered sample [28].

The results obtained by means of chemical analysis of snow samples serve as the basis for numerical modeling of environmental pollution from anthropogenic sources of various spatial and temporal structure.

PLANNIG OF OBSERVATIONS

Let us assume that the concentration of an admixture in snow cover is described by the regression dependence $q(\vec{x}, \vec{\theta})$ where \vec{x} is the spatial variable, $\vec{\theta}$ is the vector of unknown parameters. Let the measurements of the admixture content be performed in n sites according to the following plan [29, 30]:

$$\varepsilon_n = \{\vec{x}_i, p_i, i = 1, ..., n\}$$

where p_i is the frequency of observations.

Due to non-linear dependence of $q(\vec{x}, \theta)$ on $\vec{\theta}$, generally speaking, it is impossible to construct an optimal plan of measurements a pri-ori. Because of this, we will limit our consideration to search for locally optimal plans with the help of sequential analysis and observation planning, for unambiguity, we will construct the plans that maximize the determinant of informational matrix $M(\varepsilon, \vec{\theta})$.

1. Let an experiment be performed in N-1 point according to plan ε_{N-1} . Let us find a point \vec{x}_N so that

$$\begin{split} d(\vec{x}_N, \epsilon_{N-1,\vec{\theta}_{N-1}}) &= \max_{\vec{x} \in \Pi} d(\vec{x}, \epsilon_{N-1,\vec{\theta}_{N-1}}) \\ \text{where } d(\vec{x}, \epsilon_{N-1,\vec{\theta}_{N-1}}) &= \nabla^T q M^{-1} \nabla q \,. \end{split}$$

- 2. Additional observation is performed in point \vec{x}_N .
- 3. We search for estimations of $\vec{\theta}$ over N observations according to the plan.

$$\varepsilon_N = \frac{N-1}{N} \varepsilon_{N-1} + \frac{1}{N} \varepsilon(\vec{x}_N)$$

where $\varepsilon(\vec{x}_N)$ is the one-point plan.

If the approximate estimations of $\bar{\theta}$ are available, the procedure 1–3 can be replaced with the following two stages [31]: to build up a locally optimal plan ϵ_1 using the available estimations, and to perform observations in consistency with it; using the measurements

obtained in consistency with the plan ϵ_1 , one should estimate the $\vec{\theta}$ vector.

Examples of the application of the proposed schemes of the optimization of observations are reported in [32-39].

FORMULATION OF INVERSE PROBLEMS

The initial equation for building the models of the recovery of snow pollution on the basis of observation data is

$$\overline{q}_{\overline{\tau}} = \int_{0}^{\infty} q \rho_{\tau,\overline{\tau}}(q) dq \tag{1}$$

that expresses a connection between $\overline{q}_{\overline{\tau}}$, mean concentration over a long period $\overline{\tau}$, and q – one-time concentrations related to time interval $\tau = \overline{\tau}$; $\rho_{\tau,\overline{\tau}}$ is the probability density for one-time concentrations.

The q value can be determined by solving a stationary equation of turbulent diffusion [9-11]

$$u\frac{\partial q}{\partial x} - w\frac{\partial q}{\partial z} = \frac{\partial}{\partial y}K_y\frac{\partial q}{\partial y} + \frac{\partial}{\partial z}K_z\frac{\partial q}{\partial z} + Q\delta(x)\delta(y)\delta(z - H)$$
(2)

Here, the x axis is directed along the wind direction averaged over the period τ ; u is the wind velocity; w is the rate of gravitational sedimentation of admixture particles; K_y , K_z are the exchange coefficients over the axes y and z; Q is the power of source situated in point x = y = 0, z = H; δ is delta function.

Aerosol contamination of local scale

When calculating mean concentrations in the surface layer of the atmosphere, the frequently occurring meteorological conditions are of decisive importance. These conditions include the so-called normal meteorological conditions, for which the following power-type approximation of wind velocity and vertical turbulent exchange coefficient is applicable:

$$u(z) = u_1 \left(\frac{z}{z_1}\right)^n, K_z = K_1 \frac{z}{z_1}$$
 (3)

where u_1 and K_1 are the u and K_z values for $z = z_1$.

Point source. Passing to polar coordinates in (2) and taking into account (1) and (3) we obtain the following representation for the mean surface concentration [12, 40]:

where r, φ are the polar coordinates, P_1 (K_1 , u_1) is the joint probability density for K_1 and u_1 during the averageing period, Ω is the range of real changes of K_1 and u_1 ,

$$q(r, \mathbf{0}, K_1, u_1) = \frac{P(\mathbf{0} + 180^{\circ}) \cdot q_{\Lambda}(r, K_1, u_1)}{r}$$
 (5)

Here $P(\varphi)$ is the wind rose near the ground surface, q_{Λ} is the one-time concentration from a linear source.

The use of power approximation (3) of wind velocity and turbulent exchange coefficient allows us to represent $q_{\Lambda} = (r, K_1, u_1)$ in the analytical form:

$$q_{\Lambda} = \frac{Q}{(1+n)K_1\phi_0 r\sqrt{2\pi}} e^{-u_1 H^{1+n}/[K_1(1+n)^2 r]}$$
 (6)

It is very difficult to calculate the pollution fields on the basis of (5), (6), because these equations contain large number of parameters, either unknown or requiring more precise determination. Because of this, it is reasonable to transform the eq. (5) into a more convenient form using the generalized integral theorem on the mean meaning of function [41], allowing one to represent the mean concentration in the form:

$$\overline{q}(r, \mathbf{\phi}) = q(r, \mathbf{\phi}, \overline{K}_1, \overline{u}_1) \iint_{\Omega} P_1(K_1, u_1) dK_1 du_1 \tag{7}$$

where \bar{K}_1, \bar{u}_1 are the mean parameters in the Ω region.

Assuming that the concentration of an admixture in snow $\Phi(r, \varphi)$ is proportional to its concentration in the atmosphere, and taking into account (5)–(7), we obtain the following regression dependence:

$$\Phi(r, \mathbf{0}, \vec{\mathbf{0}}) = \theta_1 r^{\theta_2} e^{-2r_m / r} P(\mathbf{0} + 180^{\circ})$$
 (8)

where

$$\theta_1 = \frac{cQB(2r_m)^w}{2(1+n)\sqrt{\pi}\phi_0\Gamma(1+w)}, \theta_2 = -\frac{w}{K_1(1+n)} - 2$$
 (9)

c is the parameter characterizing the deposition of an admixture on snow surface.

Estimations of unknown parameters θ_1 , θ_2 can be made using the observation data, for

example with the help of least squares method [29]. The r_m parameter can be estimated using the geometric characteristics of the source.

A regression dependence (8) allows one to perform recovery of the field of aerosol precipitation of admixtures using relatively small number of reference measurement points. Other sampling sites can be used to check the adequacy of the proposed recovery model. The model (8) was tested in calculating the emission from a series of plants of chemical, metallurgical industry, fuel and energy complex. The pollution of snow with dust, macrocomponents, chemical elements, PAHs was investigated; the disperse and phase composition of admixtures was estimated, as well as their total emission.

The Novosibirsk Electrode Plant. The Plant is situated at a distance of 80 km to the south from Novosibirsk on a plain. It manufactures graphite and carbon electrodes; it is the major source of pollution with PAHs in the Novosibirsk Region [42, 43]. The emission of tar substances including benz(a)pyrene (BP) and other PAHs is formed mainly in the roasting works. Since 1993, periodical sampling of snow and soil is performed in the vicinity of the Plant.

The results of modeling on the basis of observation data and of the dependence (9) are shown in Fig. 1 and in Table 1 [44–46]. The numerical analysis allowed us to make the following conclusions: the major pollution with PAHs is produced in the vicinity of the Plant by 180 m high chimneys of the roasting works; concentration distribution curves for various PAHs are similar to each other, which points to the composite aerosol deposition and is linked firstly with the features of technological processes. The main transport of PAHs is performed by coarse particles with the mean deposition rate of about $0.8-1~\mu/s$.

Eq. (8) was used to analyze the data on PAH content of soil. The character of dependencies obtained for snow depicts the distribution of PAHs in soil. Total accumulation of BP in soil was about 7000 kg. The maximum permissible concentration in soil (20 mg/kg) is exceeded at the territory of more than 100 km².

The Belovo Zinc Plant. The Plant is situated in the north of the central part of Belovo. The major part of heavy metal aerosol is emitted from the industrial area of the plant through a chimney 45 m high. Predominant components

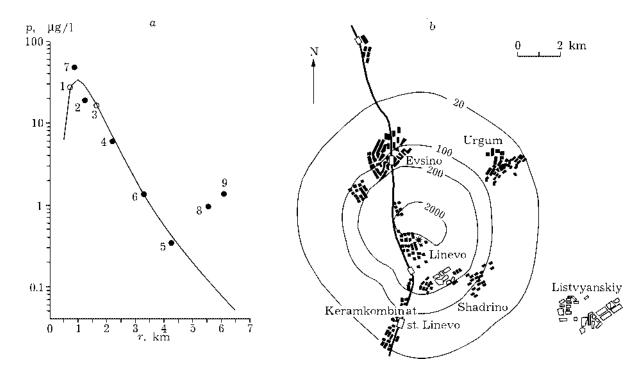


Fig. 1. Specific content of benz(a)pyrene in snow at the route to the north from the NEP (a) and recovered field of benz(a)pyrene concentrations in soil ($\mu g/kg$) (b): \circ reference points, \bullet control points, continuous line – numerical modeling.

TABLE 1

Measured (numerator) and calculated (denominator) PAHs concentrations near the Novosibirsk Electrode Plant

Characteristics	Point No.					Estimation of parameters	
	1*	2	3*	4	5	$\theta_1 \cdot 10^{-3}$	θ_2
Concentration, µg/l:							
fluorene	339/339	272/421	267/267	121/142	7.1/10.4	188	3.84
pyrene	451/451	322/449	254/254	145/121	9.0/6.5	221	4.28
benz(a)anthracene	2427/2427	1850/2712	1610/1610	865/824	61/52.3	1268	4.04
perylene	1571/1571	1139/1877	1165/1165	605/607	41.80/41.84	854	3.92
benz(b)fluoranthene	454/454	311/353	173/173	117/74	10.3/2.8	194	4.76
benz(a)pyrene	27.8/27.8	18.4/28.7	16.4/16.4	6.9/8.03	0.40/0.46	13.9	4.2
Distance, km	0.75	1.25	1.65	2.4	4.2		
Direction	N	N	N	NE	NE		

Note. Asterisk indicates points used to estimate regression parameters (8).

are zinc, lead, and cadmium. Experimental examination of the pollution status of snow cover was performed in the end of 80-ies by the researchers from the Institute of Soil Science and Agricultural Chemistry, SB RAS. Observation data were analyzed in [46, 47] using the model (8).

The results of estimations of snow pollution fields to the north of the plant are shown

in Fig. 2. Comparison of observations with calculations demonstrates a high correspondence level. Rather rapid decrease in metal concentration with distance points to the fact that the metals are transported mainly in coarse aerosol fractions. Estimations of the θ_2 parameter for snow and for soil are very close to each other. This gives us the reason to assume that the characteristics of aerosol emission remained

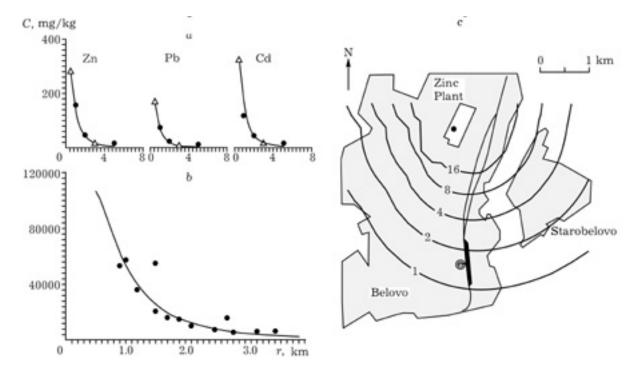


Fig. 2. Concentrations of zinc, lead, cadmium in snow, divided by the background value determined to the north from the Zinc Plant (a); zinc content of soil normalized by the annual mean wind rose (b); recovered field of zinc concentration in soil in MPC units (c).

unchanged for a long time. High heavy metal pollution (especially with zinc) of almost the whole city territory should be stressed. While approaching the industrial area of the Plant, the content of these elements in the soil many times exceeds the MPL (300 mg/kg).

Carbon-fueled boiler houses, gas power plants, oil and gas flares. Processes connected with burning or thermal treatment of organic compounds are accompanied by the emission of mutagenic and carcinogenic compounds. Volatile ash with the particles of the burnt fuel, sulphur, carbon and nitrogen oxides is emitted into the atmosphere. Burning of black oil leads to the emission of flue gas containing sulphur oxides, nitrogen dioxide, solid products of incomplete combustion, and vanadium compounds. Burning of natural gas leads to the emission of nitrogen and carbon dioxides [14]. The PAHs account for the major part of all the carcinogenic compounds. Direct measurement of PAH emission into the atmosphere and mathematical modeling of pollution fields are complicated tasks. This is explained by substantial uncertainty of the assignment of PAH source power, description of physicochemical transformations of gas and aerosol admixtures, current meteorological conditions [48, 49]. An indicator for PAHs is BP. It is very stable and widely spread in the environment. Low degree of capturing BP during ash purification is explained by its adsorption on fine fractions of volatile ash [49]. The above-mentioned processes are typical for all the objects described in this section. Differences are observed in the disperse composition of the emitted mixtures and in source power.

A widespread source of atmospheric pollution is coal-fueled boiler house. As a typical representative of this class of sources, the boiler house of the Novosibirsk Capacitor Plant (NCP) was investigated. The industrial area of the NCP is situated in the left-bank part of the Sovetskiy district of Novosibirsk. Living houses and industrial enterprises stand close to it in the south and in the west. The territory to the north of the industrial area is plain, free of buildings, and vegetation. Other rather powerful sources of atmospheric pollution are absent near the boiler house. The emission is produced by two closely located chomneys of 40–50 m high.

The main experimental stages involved optimal planning of snow surveys, sampling, and chemical analysis of the main parameters of melted snow [28]. The following parameters were selected: macrocomponents of filtrate (including the components of the transformation of kiln gas SO_4^{2-} , NO_3^-), heavy metals (Ba, Fe, Cd, Mn, Cu, Pb, Cr, Ni, Be) in filtrate and in precipitate, PAHs in non-filtered sample, proteins. Sampling characteristics are shown in Table 2. The results of the recovery of BP pollution field near the NCP are shown in Fig. 3, a [50, 51].

The investigations showed that it is necessary to consider aerosol deposition of pollutants in the long-range (0.5 to 3 km) and nearby (up to 0.5 km) regions. For the long-range region, the following results were obtained: the proposed models provide quite adequate description of the pollution of snow cover with different components at relatively small and practically available amount of the input data; the major part of substances emitted into the atmosphere get precipitated on the snow cover at a substantial rate which points to their presence in rather large aerosol particles and requires further correction of the model and also additional experimental studies of the determination of particle size distribution in the aerosol emission of the boiler house. The application of optimal snow sampling schemes

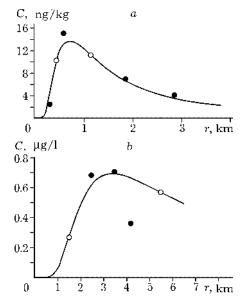


Fig. 3. Distribution of benz(a)pyrene in snow to the north from the NCP (a) and Belovo Power Plant (b).

TABLE 2 Snow pollution with benz(a)pyrene near the Belovo Power Plant and the boiler house of the NCP

Site No.	Distance, km	BP concentration, ng/l	Sample mass, g	Sampling area, dm ²	
		Power plant, to the north-	east		
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	
		Boiler house of NCP, to the	north		
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	

leads to an increase in the accuracy of recovery of pollution regions [[52, 53], and to better stability of the estimations of regression parameters. For optimal planning of observations, it is necessary to take into account aerosol deposition of various components; the deposition rate range is rather wide for PAH components; a connection with relative molecular mass exists. The discovered regularities require additional investigation of physicochemical processes of aerosol formation; the pollution of the nearby region is performed with very large particles with the deposition rate of 0.5-1 m/s. The disperse composition of particles is represented by size distribution up to 100 µm and more. These particles are characterized by the following composition: dissolved macrocomponents, heavy metals, PAHs, proteins. The effect of the vertical turbulent exchange on these particles is small. The deposition of particles can be perfectly described within the kinematic scheme [45]. It is interesting to note that the protein pollution of snow cover is secondary; it occurs due to the capture of the protein component of atmospheric aerosol by the dust emission of boiler house.

A powerful source of the emission of pollutants into the atmosphere is the Belovo Power Plant (Kemerovo Region). The emission occurs through three chimneys of 150 m high and 6 m in diameter. On the basis of geomet-

ric and dynamic characteristics of the sources, r_m is estimated to be 3-3.5 km. Several tens trucks of carbon are usually burnt every day which leads to a large amount of PAH emission. The characteristics of sampling performed in the end of winter season of 1998 are listed in Table 2. The results of modeling using the data of snow survey are shown in Fig. 3, b. These results show [52, 53] that PAHs are spreading on rather small aerosol fractions. The maximum of the surface concentration is smoothed and occurs at a distance of 3-3.5 km to the north of the power plant. The specific content of BP in snow in the maximum was more than 700 ng/l (for comparison, the MPC of BP in water is 5 ng/l).

For after-burning of accompanying gases in the oil and gas flares, the transfer of combustion products is also described by the models of the point source. Results of the recovery of snow pollution with BP near one of the oil and gas flares are shown in Fig. 4 [54]. A distinguishing feature of this type of sources is high burning temperature (700–1000 °C), which causes a substantial increase in the effective height of the emission of all the components, especially PAHs.

A linear source. A characteristic example of the linear sources is a motorway. Such pollutants as sulphur and nitrogen oxides, as well as the products of their transformation, sul-

(10)

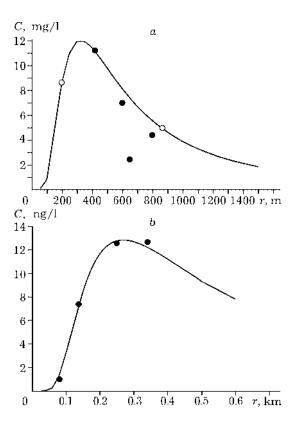


Fig. 4. Specific content of nitrates (a) and benz(a)pyrene (b) in snow near the oil and gas flare.

phuric and nitric acids, heavy metals, in particular lead, and PAHs are characteristic of automobiles [55]. These substances get into the environment mainly with the exhaust and in the form of aerosol. As a consequence, the most large-scale pollution occurs at the motorways.

The long-term aerosol pollution of the territory adjacent to a motorway region can be described as follows [56–60]:

$$q(x,y) = \int\limits_{0}^{2\pi} \int\limits_{L_{1}}^{L_{2}} \frac{S(a)}{2\sqrt{\pi K_{0}a}} \; \mathrm{e}^{-b^{2}/(4K_{0}a)} P(\phi + 180^{\circ}) d\eta d\phi$$

,

where L_1 , L_2 are the ends of the motorway region, $a = x \cos \varphi + (y - \eta) \sin \varphi$, $b = -x \sin \varphi + (y - \eta) \cos \varphi$, φ is the angle between the x axis and the wind direction, S(a) is the surface field of concentrations from a linear source, K_0 is the coefficient characterizing the turbulent diffusion of an admixture in the direction perpendicular to the wind [61].

Calculation according to eq. (10) can be simplified if we use the analytical solution of the turbulent diffusion equation for the case of power approximation of wind velocity and turbulent exchange coefficients over height. In this case [57, 58],

$$S(r, \vec{\theta}) = \frac{\theta_1}{r^{\theta_2}} e^{-r_m / r} \tag{11}$$

$$\text{where} \ \theta_1 = \frac{Gr_m^w}{2(1+n)K_1\Gamma(1+w)} \,, \ \theta_2 = 1 + \frac{w}{K_1(n+1)} \,,$$

G is the power of a linear source, $\Gamma(1 + w)$ is the gamma function.

The models (10), (11) were tested with the data of experimental investigations of the aerosol pollution of snow cover in the vicinity of the Sovetskoye highway in Novosibirsk and the Barnaul motorway. The results of modeling are shown in Table 3 and in Fig. 5.

The performed complex investigation allowed concluding that the distribution of the specific content of macrocomponents is described by the dependencies of two kinds. Within the model of land-based source, quite satisfactory description of the dynamics of distribution with an increase in the distance from the road is obtained. For sulphate, nitrate ions and ammonium, the presence of maximum

TABLE 3

Measured (numerator) and recovered (denominator) concentrations of PAHs near the Sovetskoye highway, ng/l

РАН	Distance from road, m						Estimated 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. Points marked with asterisks were used to estimate regression parameters (11). Only measured PAH concentrations are listed for these points.

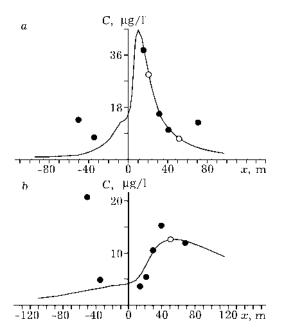


Fig. 5. Distribution of coarse (a), sum of fine and water-dissolved (b) fractions of lead in snow near motorway.

shifted windward by about 30 m is demonstrated. The filed of PAH distribution is formed as a result of the action of two sources: road pollution within 10 m under the action of snow ploughs, and a more remote region polluted by an elevated source [57]. The quantitative description of the remote region of pollution is obtained, which is directly connected with burning regime, and the quantitative dependence of the distribution of microelements between coarse, fine and water-soluble fractions. It is demonstrated that the spread of microelements with coarse fraction occurs under the action of wind-induced blow off the road surface, while the total content of microelements in fine and water-soluble fractions is connected with the automobile exhaust; as a result of the use of non-ethylated petroleum as a fuel in 1999-2001, substantial changes occurred both in the structure of aerosol emission of automobiles and in the mass of the emitted hazardous admixtures. Total decrease in lead emission occurred mainly due to the coarse fraction; the largest changes during the winter season 1999-2000 occurred with the PAH emission. Total emission of benz(a)pyrene into the roadside at a distance of 10 to 50 m increased by a factor of 3, fluoranthene and pyrene by a factor of 1.5 and 2.5, respectively. Mean size

of PAH-containing aerosol particles has also increased substantially. For the PAH components under consideration, it increased 2 to 3 times in comparison with the winter season 1998–1999 [58–60].

Regional pollution

Industrial centres are powerful sources of emission of pollutants into the atmosphere; many of these pollutants are carried with aerosol particles. Concentration of an admixture from a two-dimensional source S can be represented as

$$Q(x,y) = \frac{1}{2\pi u H} \iint_{S} \frac{m(\xi,\eta) P\left(\operatorname{arctg} \frac{y-\eta}{x-\xi} + 180^{\circ}\right)}{\sqrt{(x-\xi)^{2} + (y-\eta)^{2}}} d\xi d\eta$$

Here (ξ, η) are the current coordinates of the source, $(\xi, \eta) \in S$, $m(\xi, \eta)$ is the emission of an admixture, $P(\varphi)$ is the wind rose in the surface layer of the atmosphere within the time interval under consideration, u and H are the mean wind velocity and the height of mixing layer. It is assumed that the point (x, y) is suffi-

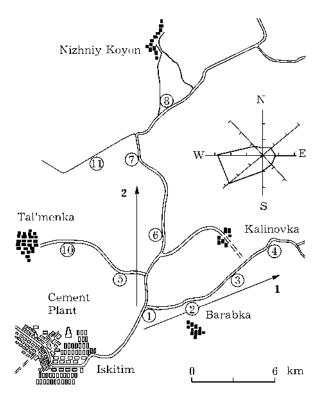


Fig. 6. Scheme of snow survey near Iskitim.

ciently remote from the set S. Using the generalized mean value theorem of integral calculus [41], we obtain the following eq. [62]:

$$Q(x,y) = \frac{\theta \cdot P\left(\operatorname{arctg} \frac{y - \mu}{x - \lambda} + 180^{\circ}\right)}{\sqrt{(x - \lambda)^{2} + (y - \mu)^{2}}}$$
(12)

where $\theta = \frac{M}{2\pi u H}$, $M = \iint_S m(\xi, \eta) d\xi d\eta$ is the total emission of an admixture from the city

territory.

The analysis of eq. (12) shows that in order to determine the Q(x, y) function, it is sufficient to estimate the unknown parameters M, λ , μ , for example using observation data.

The model was tested with the data on snow cover pollution in the areas under the effect of Irkutsk, Tomsk, Iskitim. The investigation allowed obtaining the quantitative regularities for the regional distribution of dust, PAHs, heavy metals, macrocomponents in the vicinity of these cities [62-65]. A scheme of sampling and the results of solving the problem of recovery of the aerosol pollution near Iskitim are shown as examples in Fig. 6 [65]. With increasing distance from the city, a substantial redistribution of the major carry-off directions of aerosol admixtures occurs, connected with the turn of the wind in the boundary layer of the atmosphere. The data of observations and the recovered distribution of the concentration of dust, PAHs, calcium, and cadmium at the routes 1 and 2 are shown in Fig. 7. The obtained regularities can be used to search for correlation links between dust concentration in snow and snow cover reflectance.

MODELS OF GOVERNING THE REDUCTION OF EMISSION

Substantial possibilities of rationalization of measures aimed at the protection of atmospheric air in cities are connected with the optimization of the regime of emission of hazardous admixtures taking into account technological features of sources, building up layout, local atmospheric circulations. To search for optimal solutions, one ought to possess information on the fields of concentrations of the admixtures [66–68], expenses for the de-

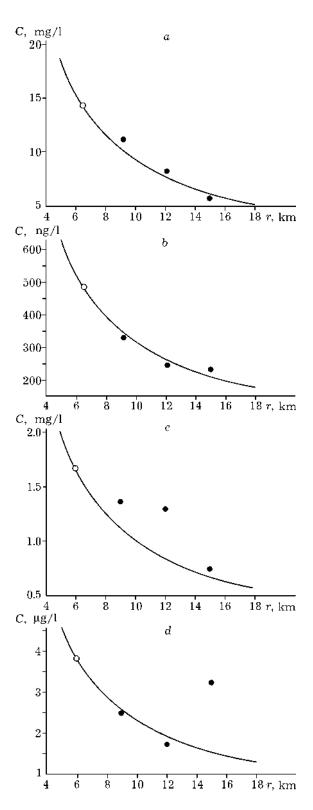


Fig. 7. Recovered and measured at the route 1 content of dust (a), sum of PAHs (b), water-dissolved form of calcium (c) and cadmium (d): a, b – route 1; c, d – route 2.

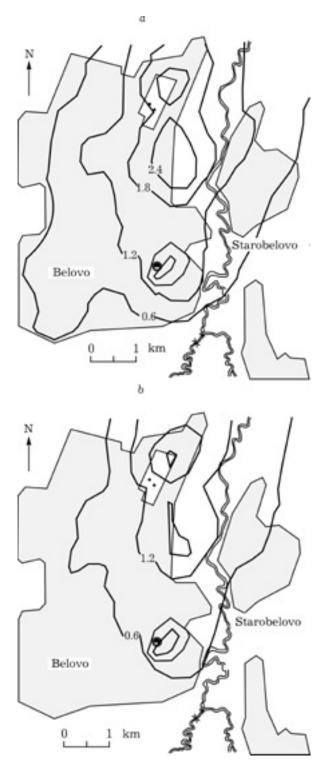


Fig. 8. Isolines of the surface annual mean concentration (mg/m^3) of ash dust in the central part of Belovo (a) and the field of annual mean concentration after optimal decrease of total emission by 300 g/s (b).

crease of emission, and damage produced by environmental pollution. The data of the monitoring of snow cover status allow obtaining the necessary information (Fig. 8). Examples of solution of tasks on governing the long-term pollution processes over city territories are considered in [69, 70]. The efficiency of control is determined using general economic expenses aimed at the decrease in emission of pollutants, taking into account the sanitary and hygienic requirements, as well as social ones.

CONCLUSIONS

Numerical analysis of the data of snow cover monitoring in the vicinity of anthropogenic sources of various structures shows the existence of rather simple regularities of the formation of fields of long-term pollution of the territory. The aggregation of unknown parameters provide a substantial improvement of the efficiency of solving the inverse problems of transformation of admixtures. Using a small number of measurement point and taking into account a very limited input information, it is possible to compose quantitative models of long-term aerosol pollution of the territory from specific sources and industrial centres. For a series of sources, estimations of total emission have been obtained.

The application of procedures of optimal planning of the regression experiments allows elevating the accuracy of estimation of the parameters and fields of pollution. The results of the analysis of snow cover monitoring data can be used to govern the decrease in aerosol emission of hazardous admixtures. Economical profitableness and special efficiency of the monitoring of snow cover for the control of emission and pollution levels near the plants should be stressed.

The set of performed investigations is the basis for a complex system of monitoring of environmental pollution for a series of anthropogenic sources and their totality. This set includes the following main elements of the system: measurements involving the mathematical methods of planning snow surveys, chemical analysis of the normalized parameters of emission, interpretation of the data of point

observations, elaboration of recommendations on optimization of the decrease in emission.

Acknowledgements

The authors thank researchers from SIA Vector: A. P. Sadovsky, S. E. Ol'kin, I. K. Reznikova, researchers from the IIC, SB RAS: O. V. Shuvaeva, N. F. Beizel', B. S. Smolyakov; from NIOC, SB RAS: S. V. Morozov, from ICKC, SB RAS: K. P. Koutsenogii, T. V. Yaroslavtseva; from LIN, SB RAS: A. G. Gorshkov, T. V. Khodzher, V. M. Domysheva, I. I. Marinaite for participation in definite stages of the joint investigations and for useful discussions of the obtained results. The work has been partly supported by the RFBR Grant No. 00–015–98–543.

REFERENCES

- 1 V. N. Vasilenko, I. M. Nazarov, Sh. D. Fridman, Monitoring zagryazneniya snezhnogo pokrova, Gidrometeoizdat, Leningrad, 1985.
- 2 V. G. Prokacheva, V. F. Usachev, Snezhny pokrov v sfere vliyaniya goroda, Gidrometeoizdat, Leningrad, 1989.
- 3 A. P. Boyarkina, V. V. Baykovskiy, N. V. Vasilyev, et al., Aerozoli v prirodnykh landshaftakh Sibiri, Tomsk, 1993.
- 4 K. Van de Velde, Ch. Ferrari, C. Barbante et al., Environ. Sci. and Technol., 33 (1999) 3495.
- 5 V. N. Vasilenko, V. G. Prokacheva, Sh. D. Fridman, Trudy GGI, Moscow, 1981, issue 285, p. 56.
- 6 Yu. E. Saet, B. A. Revich, E. P. Yanin et al., Geokhimiya okruzhayushchey sredy, Nedra, Moscow, 1990.
- 7 Metodicheskiye rekomendatsii po otsenke stepeni zagryazneniya atmosfernogo vozdukha naselennykh punktov metallami po ikh soderzhaniyu v snezhnom pokrove i pochve, Moscow, 1990.
- 8 G. P. Koroleva, A. G. Gorshkov, T. P. Vinigradova et al., Khimiya v interesakh ustoychivogo razvitiya, 6 (1998) 327.
- 9 M. E. Berland, Sovremennye problemy atmosfernoy diffuzii i zagryazneniya atmosfery, Gidrometeoizdat, Leningrad, 1975.
- 10 N. L. Byzova, E. K. Karger, V. K. Ivanov, Eksperimental'nye issledovaniya atmosfernoy diffuzii i raschety rasseyaniya primesi, Gidrometeoizdat, Leningrad, 1975.
- 11 M. E. Berland, Prognoz i regulirovaniye zagryazneniya atmosfery, Gidrometeoizdat, Leningrad, 1985.
- 12 Atmosfernaya diffuziya i zagryazneniye vozdukha, Trudy glavnoy geofizicheskoy observatorii, issue 417, Gidrometeoizdat, Leningrad, 1979, p. 3.
- 13 Yu. A. Israel, Ekologiya i kontrol' sostoyaniya okruzhayushchey sredy, Gidrometeoizdat, Leningrad, 1984.
- 14 N. F. Tishchenko. Okhrana atmosfernogo vozdukha, Khimiya, Moscow, 1991.
- 15 L. S. Ivlev, Yu. A. Dovgalyuk, Fizika atmosfernykh aerozol'nykh sistem, St. Petersburg, 1999.
- 16 E. Meszaros, Fundamental of Atmospheric Aerosol Chemistry, Ak. Kiado, Budapest, 1999.

- 17 K. Ya. Kondratyev, Optika atmosfery i okeana, 14, 3 (2001) 171.
- 18 V. V. Kokovkin, O. V. Shuvaeva, V. F. Raputa et al., in: Estestvennye i antropogennye aerozoli, in L. S. Ivlev (Ed.), St. Petersburg, 2001, p. 66.
- 19 Unifitsirovannye metody issledovaniya kachestva vod. Metody chimicheskogo analiza vod, Moscow, 1977.
- 20 O. V. Shuvaeva, Analiticheskiy obzor, Novosibirsk, 1996, issue 41.
- 21 R. Gragnani, C. Smiraglia, B. Stenni, S. Torcini, Annals of Glaciology Cambridge: Intern. Glaciol. Soc., 27 (1998) 679.
- 22 R. C. Ferrier, J. S. Anderson, J. D. Miller, N. Christophersen, Water, Air and Soil Pollut., 44, 3-4 (1989) 321.
- 23 J. L. Colin, J. L. Jaffrezo, J. Pinart, S. Roulette-Cadene, *Atmos. Environ.*, 21, 5 (1987) 1147.
- 24 E. W. Wolff, M. R. Legrand, P. Wagenbach, J. Geophys. Res. D, 103, 9 (1998) 10927.
- 25 S. Gruber, R. Jaenicke, J. Aerosol Sci., 31 (2000) S737.
- 26 A. Darbe (Ed.), Practical Protein Chemistry: A Handbook, J. Wiley&Sons, 1986.
- 27 V. V. Anikeev, K. A. Lukomskaya, Rukovodstvo k prakticheskim zanyatiyam po mikrobiologii, Prosveshcheniye, Moscow, 1977.
- 28 V. V. Kokovkin, V. F. Raputa, O. V. Shuvaeva, Khimiya v interesakh ustoychivogo razvitiya, 7 (1999) 477.
- 29 V. V. Fedorov, A. B. Uspenskiy, Vychislitel'nye aspekty metoda naimen'shikh kvadratov pri analize i planirovanii regressionnykh eksperimentov, Izd-vo MGU, Moscow, 1975.
- 30 V. V. Fedorov, Teoriya optimal'nogo eksperimenta, Nauka. Moscow, 1971.
- 31 A. B. Uspenskiy, V. V. Fedorov, Kibernetika, 4 (1974) 123.
- 32 A. I. Krylova, V. F. Raputa, K. A. Sutorikhin, Meteorologiya i gidrologiya, 5 (1993) 5.
- 33 V. F. Raputa, A. I. Krylova, Ibid., 3 (1995) 49.
- 34 A. I. Krilova, V. F. Raputa, Bull. NCC. Ser. Num. Mod., 2 (1995) 41.
- 35 V. F. Raputa, A. I. Krylova, G. T. Yakovenko, Preprint No. 1032, Novosibirsk, 1994.
- 36 K. P. Koutsenogii, V. F. Raputa, A. I. Krylova, *Optika atmosfery i okeana*, 9, 6 (1996) 786.
- 37 V. F. Raputa, A. I. Krilova, J. Aerozol Sci., 27 (1996) 131.
- 38 V. F. Raputa, A. I. Krilova, K. P. Koutsenogii, in M. Kulmala and P. Wagner (Eds.), Nucleation and Atmospheric Aerosols, Pergamon Press, London – New York, 1996, p. 726.
- 39 A. I. Krylova, V. F. Raputa, Preprint No. 995, Novosibirsk, 1993.
- 40 E. L. Genikhovich, M. E. Berland, I. G. Gracheva et al., in E. Yu. Bezuglaya (Ed.), Trudy glavnoy geofizicheskoy observatorii, issue 549, Gidrometeoizdat, St. Petersburg, 1998, p. 11.
- 41 L. I. Kamynin, Kurs matematicheskogo anliza, vol. 2, Izd-vo MGU, Moscow, 1995.
- 42 Sostoyaniye okruzhayushchey prirodnoy sredy v Novosibirskoy oblasti v 1993 godu, in A. I. Petrik and Yu. R. Shirokov (Eds.), Novosibirsk, 1994.
- 43 Sostoyaniye okruzhayushchey prirodnoy sredy v Novosibirskoy oblasti v 1994 godu, in A. I. Petrik and Yu. R. Shirokov (Eds.), Novosibirsk, 1995.
- 44 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin, Meteorologiya i gidrologiya, 2 (1997) 33.
- 45 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin et al., Optika atmosfery i okeana, 13, 9 (2000) 886.

- 46 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin, *Ibid.*, 1, 6 (1997) 616.
- 47 V. F. Raputa, A. P. Sadovskiy, T. A. Kuzovkova, Ekologiya i ekonomika, vol. 2, Kemerovo, 1997, p. 74.
- 48 S. P. Belyaev, S. P. Beschastnov, G. M. Khomushku et al., Meteorologiya i gidrologiya, 12 (1997) 54.
- 49 L. I. Bolotneva, P. A. Bryukhanov, I. M. Nazarov et al., in: Dal'niy atmosferny perenos zagryaznyayushchikh veshchestv, Gidrometeoizdat, Moscow, 1988, p. 143.
- 50 V. F. Raputa, V. V. Kokovkin, O. V. Shuvaeva, J. Aerozol Sci., 30 (1999) 657
- 51 I. S. Andreeva, A. I. Borodulin, G. A. Buryak et al., Optika atmosfery i okeana, 14, 6-7 (2001) 547.
- 52 V. F. Raputa, V. V. Kokovkin, O. V. Shuvaeva et al., Ibid., 12, 6 (1999) 540.
- 53 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin et al., Ekologicheskiye problemy ugledobyvayushchey otrasli v regione pri perekhode k ustoychivomu razvitiyu, vol. 2, Kemerovo, 1999, p. 29.
- 54 V. F. Raputa, B. S. Smolyakov, K. P. Koutsenogii, *Sib. ekol. zhurn.*, 7 (2000) 103.
- 55 V. Yu. Aleksandrov, L. I. Kuzubova, E. P. Yablokova, Ekologicheskiye problemy avtomobil'nogo transporta: Analit. obzor, Novosibirsk, 1995, issue 34.
- 56 V. V. Kokovkin, O. V. Shuvaeva, V. F. Raputa, J. Aerozol Sci., 31 (2000) 526.

- 57 V. V. Kokovkin, V. F. Raputa, O. V. Shuvaeva, Optika atmosfery i okeana, 13, 8 (2000) 788.
- 58 V. F. Raputa, V. V. Kokovkin, O. V. Shuvaeva, *Ibid.*, 14, 3 (2001) 240.
- 59 V. V. Kokovkin, O. V. Shuvaeva, V. F. Raputa, J. Aerozol Sci., 32 (2001) 526.
- 60 V. F. Raputa, V. V. Kokovkin, O. V. Shuvaeva, Vych. tekhnologii, 6 (2001) 348.
- 61 Klimat Novosibirska, Gidrometeoizdat, Leningrad, 1979. 62 V. F. Raputa, T. V. Khodzher, A. G. Gorshkov *et al.*,
- Optika atmosfery i okeana, 11, 6 (1998) 650. 63 V. F. Raputa, T. V. Khodzher, A. G. Gorshkov et al.,
- J. Aerozol Sci., 29 (1998) 807.64 V. F. Raputa, G. P. Koroleva, A. G. Gorshkov et al.,
- Optika atmosfery i okeana, 14, 6-7 (1998) 623. 65 V. F. Raputa, V. V. Kokovkin, O. V. Shuvaeva, *Ibid.*,
- 14, 6-7 (2001) 554. 67 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin *et al.*, *Ibid.*,
- 11, 6 (1998) 602.68 V. F. Raputa, A. P. Sadovskiy, I. V. Demchenko, Ekologi-
- ya i ekonomika, vol. 2, Kemerovo, 1997, p. 76. 69 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin *et al.*, *Optika*
- atmosfery i okeana, 14, 3 (2001) 233.
- 70 V. F. Raputa, A. P. Sadovskiy, S. E. Ol'kin et al., Sib. ekol. zhurn., 5 (2001) 599.