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Analysis of processes of chemical transformation of impurities in the atmosphere of the industrial area

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ABSTRACT

Models for estimating the concentration fields of passive and chemically active impurities at large distances from the source have been developed from the data of the route observations. Their validation was made on the data of airborne observations of multicomponent pollution of the winter and summer boundary layer of the atmosphere of the Norilsk industrial region. For winter conditions, the results of estimating the fields of transformation of calcium and sulfur dioxide at distances of 60-100 km from sources of impurities are presented. On the basis of measurements of sulfur dioxide in the summer experiment, the correspondence of the processes of transverse expansion of the impurity flame to theoretical descriptions is shown and the direction of axial drift of the impurity is established.

Keywords: atmosphere, sulfur dioxide, impurity transformation, model, parameter, estimation.

1. INTRODUCTION

To describe the processes of transfer and transformation of impurities from industrial sources, an approach based on numerical modeling of atmospheric hydrothermodynamics can be used. With the necessary input information, it makes it possible to calculate the fields of hydrometeorological elements and impurity concentrations [1-6]. In certain situations, it is possible to apply a compromise approach within the framework of the inverse problems of impurity transfer [7,8]. In this case, it is necessary to obtain stylized descriptions of the contamination processes compatible with the available experimental information.

It should be noted that significant distances from impurity sources are determined by a relatively small number of parameters [9-11]. These include: source power, chemical impurity transformation coefficients, wind speed and mixing layer height, transverse dispersion, which creates the possibility of creating fairly compact models of analysis of observational data.

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2. MODELS FOR ESTIMATING THE FIELDS OF CONCENTRATIONS

The basis of the estimation models is the following balance ratio of a light chemically active impurity coming from a stationary point source to the boundary layer of the atmosphere [9, 10]

$$u(z)\frac{\partial q}{\partial x} = \frac{\partial q}{\partial y}\mu(z)\frac{\partial q}{\partial y} + \frac{\partial}{\partial z}\nu(z)\frac{\partial q}{\partial z} - \alpha q \ , \tag{1}$$

With boundary conditions

$$\nu(z)\frac{\partial q}{\partial z}\Big|_{z=0,\ z=h} = 0\,; \quad q \to 0 \ , \ |y| \to \infty\,; \quad u(z)q|_{x=0} = M\delta(y)\delta(z-H) \ , \tag{2}$$

where the *x* axis is oriented in the direction of the wind, *u(z)* is the wind speed, *μ(z), ν(z)* are the turbulent exchange coefficients, α is the chemical transformation coefficient, M and H are the power and height of the source of the impurity.

It can be shown that [10]

$$q(x,y,z) = p(x,y)\,q'(x,z) \ , \tag{3}$$

where

$$p(x,y) = \frac{1}{2\sqrt{\pi k_0 x}}e^{-\frac{y^2}{4k_0 x}} \ , \tag{4}$$

$$u(z)\frac{\partial q'}{\partial x} = \frac{\partial}{\partial z}k(z)\frac{\partial q'}{\partial z} - \alpha q' \ . \tag{5}$$

At a sufficient distance from the source (7-10 km), the concentration of the light impurity in the mixing layer is equalized in height[9] and in view of the generalized mean value theorem for the function[12].

$$q'(x,\xi) \to Ce^{-\frac{\alpha x}{\overline{U}}} \quad \text{at} \quad x \to \infty \ , \ \xi \in (0,h). \tag{6}$$

Here C is the integration constant, and $\overline{U} = \frac{1}{h}\int_0^h u(z)dz$.

Then, taking into account (3) and (6), in order to estimate the integral concentration in the transverse direction to the direction of the contaminant removal plume, we obtain the following relation

$$P\left(x,\vec{\theta}\right) = Ce^{-\frac{\alpha x}{\overline{U}}}\int_{-\infty}^{\infty}p(x,y)dy = \theta_1 e^{\theta_2 x} \ , \tag{7}$$

Where $\theta_1 = C, \ \theta_2 = -\frac{\alpha}{\overline{U}}$.

The estimation of the parameters $\theta_1, \ \theta_2$ in the regression dependence (7) is carried out from the least-squares observations [13].

With allowance for (2), (4), the estimation of the impurity concentration in the cross section of the flame is carried out using the relation

$$p(x,y,\vec{s}) = \frac{s_1}{\sqrt{x}}e^{-\frac{s_2 y^2}{x}} \ , \tag{8}$$

where $s_1 = \frac{M}{2\sqrt{\pi k_0}}$, $s_2 = \frac{1}{4k_0}$.

The estimation of the parameters s_1, s_2 in the regression dependence (8) for a fixed cross section of the flame $x = x_0$ is also performed from least-squares observations.[13]

3. OBJECT OF RESEARCHES

The object of the study was a total plume of aerosol and gas emissions from three major plants of the Norilsk Mining and Metallurgical Combine (NMMC). Airplane measurements of gases and selection of aerosol admixtures were carried out both in winter and in summer conditions.

In winter, the main observations were carried out on November 10, 2002 at a height of 400 m above sea level in transverse directions (gals) from 58 to 103 km to the west-south-west from Norilsk. In Fig. 1 is a diagram of the flight. Gas components were measured continuously, aerosol samples were taken for AFA-ChP-20 filters - every separate sample was taken on each rectilinear part of the route.

The weather in the Norilsk region on November 10, 2002 determined the central part of a filling cyclone with surface fronts, then a low-gradient reduced-pressure field was observed. The air mass was arctic.

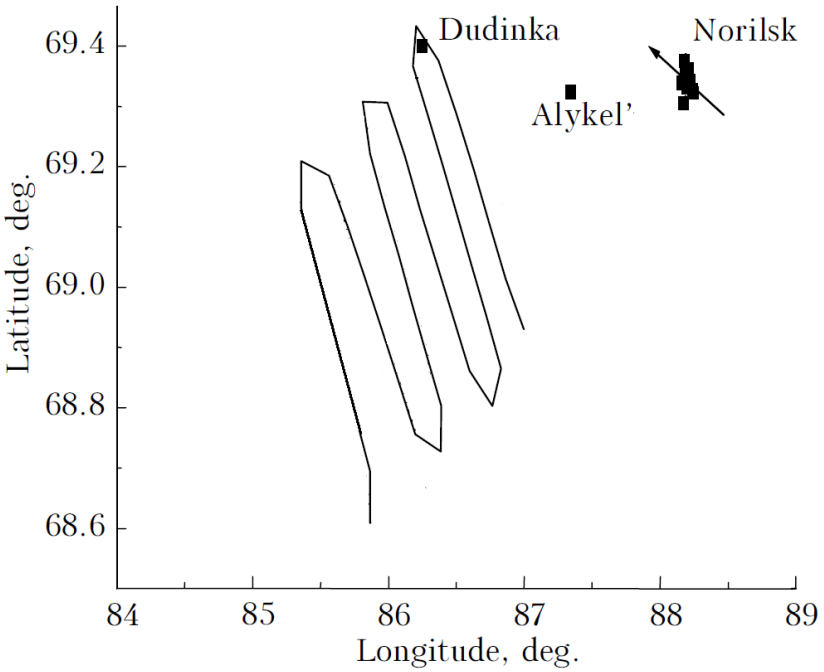

Figure 1. Scheme of airborne sounding on November 10, 2002 of the plume of emissions of Norilsk mining and metallurgical enterprises at an altitude of 400 m.

In summer flights, an attempt was made to route the behavior of impurities along the axis of the plume at a consecutive distance from the source of emissions. In Fig. 2 shows the flight patterns on August 13, 2004 in transverse demolition of impurities directions.

The experimental procedure, the characteristics of gas analyzers and methods for quantitative physical and chemical analysis of aerosol substance on filters are given in the article[14]. It should be noted that the main contribution to air pollution is given by acid oxides of sulfur in the gas phase, obtained as a result of processing of non-ferrous sulphide ores. The processes of chemical transformation of sulfur occur according to the scheme: $\rightarrow SO_2 \rightarrow H_2SO_3 \rightarrow H_2SO_4 \rightarrow M(HSO_4)_m \rightarrow M_2(SO_4)_m$, where M^{m+} is a cation of any metal [15].

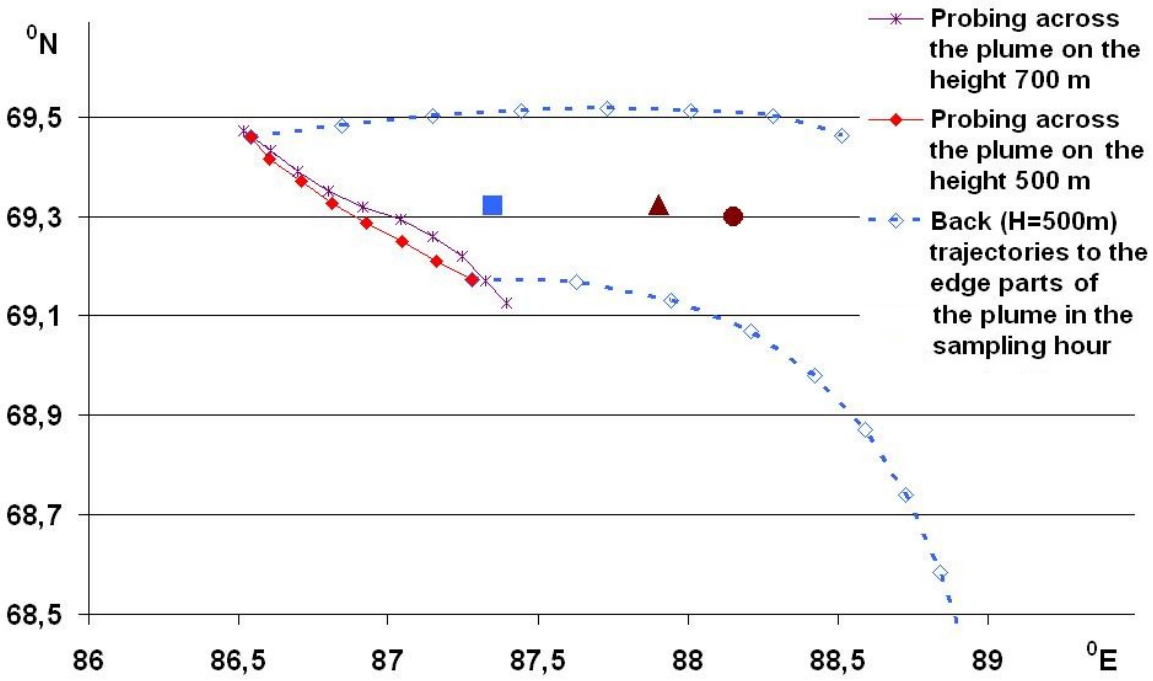

Figure 2. Schemes of transverse airborne sounding of NMMK plume in August 13, 2004 (circle - Norilsk, triangle - Nadezhda Combine, square - Alykel airport)

4. RESULTS AND DISCUSSION

A preliminary analysis of the winter data of measurements showed that in the considered range of distances from the source there are directional changes in the concentrations of calcium, total aerosol and sulfur dioxide. This means that in order to describe the concentration fields of these components, the propagation model of the passive impurity in this case can not be used to the fullest.

For other components of the chemical composition, changes with the distance from the sources have a different behavior. The concentrations of chlorides, bromides and sulfates on sites 1-6 generally change to a much lesser extent. The dynamics of the decrease in the concentrations of lead and nickel with the distance from the source is also less pronounced compared with calcium.

In Fig. 3 shows a pair-wise correlation between the concentrations of calcium and total inorganic aerosol at sites 1-6. The level of statistical connection between the measured concentrations of these impurities is quite high. It should be noted that the graph of the regression line passes above the origin and shows the presence of a noticeable background component in the mass concentration of the aerosol formed by the natural components.

As rule, the majority of the smooth Ca-rich spheres (5.6–8.3 μ diameter) in vicinities of urban fossil fuel thermal power plants of Siberia are observed in fly ash deposited in snow [16,17]. However, for the region and type of production under consideration, we do not have such experimental data in order to accurately identify the calcium aerosol. Aerosol sampling for morphological analysis of particles was not performed in our study.

In Fig. 4 presents the results of numerical restoration of calcium and sulfurous gas concentrations on the basis of the dependence of the form (7) on the measurements at two support sites. From the analysis of Fig. 4 it follows that in the considered range of distances the proposed estimation model quite adequately describes the processes of transformation of the impurities in question in the atmosphere.

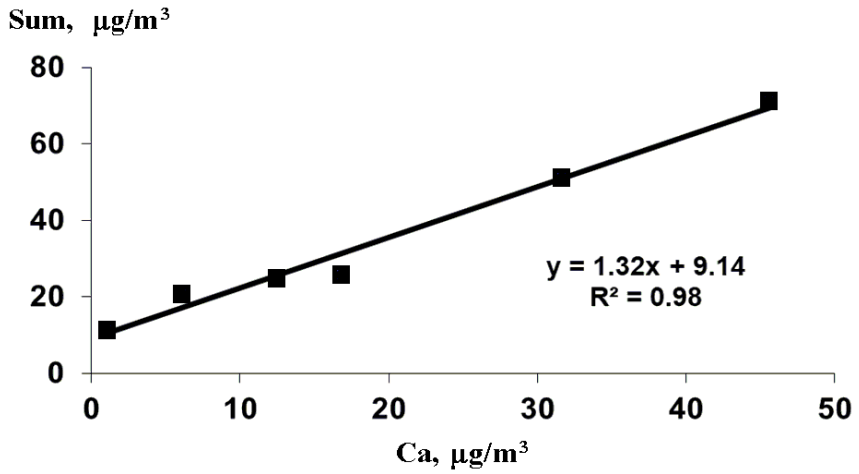

Figure 3. Linear correlation between the concentrations of calcium and total aerosol at sites 1-6.

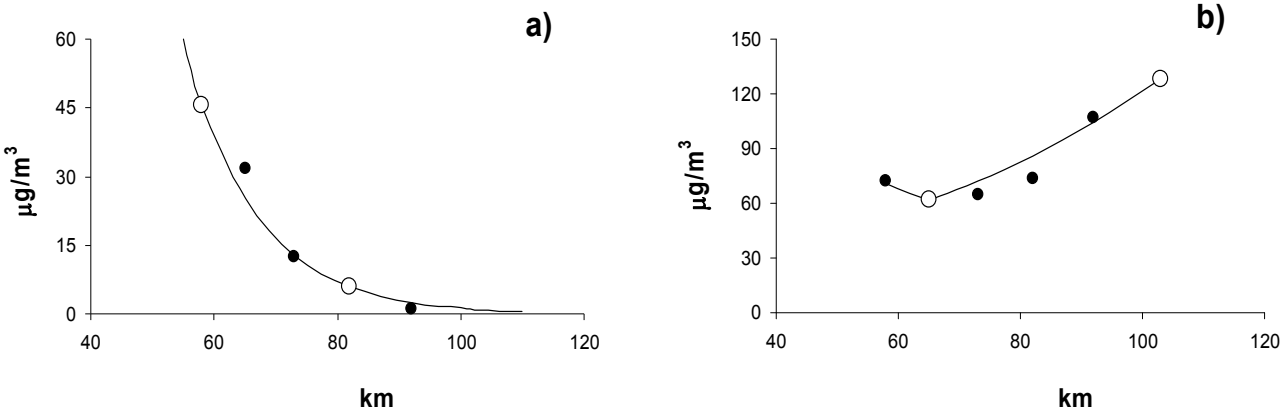

Figure 4. Measured and reconstructed from (7), the concentrations of calcium (a) and SO2 (b) at sites 1 to 6 in the emission plume. ○, ● - the reference measurement and control points.

According to Fig. 4 at a distance of 65 km, the concentration of sulfur dioxide as a result of chemical transformation reached a minimum value. With increasing distance, the process of its transformation in the atmosphere was reduced. At the same time, a fairly rapid decrease in the calcium concentration occurred up to a distance of 92 km. The estimation of transformation ratios for average and maximum concentrations of sulfur dioxide was 0.019 and 0.039, respectively. According to literary sources[18], the average rate of its oxidation in the atmosphere is 0.027.

In Fig. 5 shows the results of a numerical estimation of the concentration of sulfur dioxide on the basis of the dependence of the form (8) on the measurements in the transverse plume direction at two reference points in the summer experiment of 2004. The flight was conducted at an altitude of 500 m and a distance of 35 km from the industrial site of the plant.

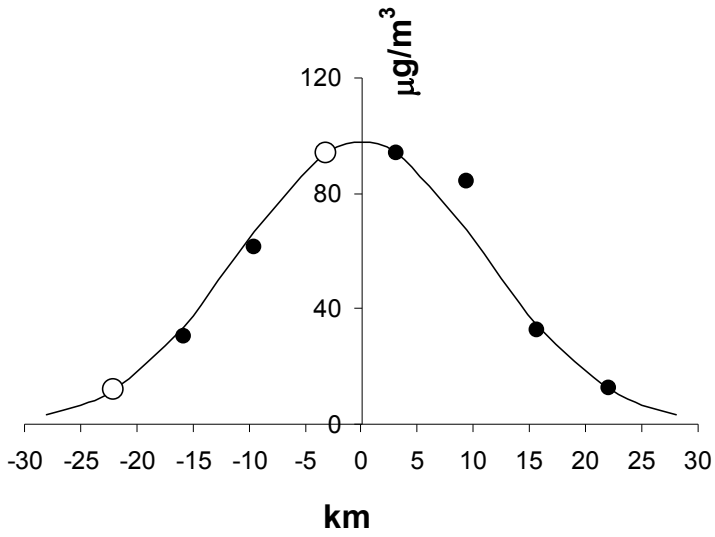

Figure 5. The concentration of SO_2 measured and restored in dependence (8) across the ejection plume in the summer experiment. ○, ● - the reference measurement and control points.

The analysis of Fig. 5 shows a high level of agreement between the observational data and the model dependence and determine the direction of the impurity plume axis at the altitudes of the atmospheric boundary layer. The concentration of SO_2 in the range of distances from -5 km to 5 km practically does not change, the width of the plume is quite significant, which creates favorable conditions for the realization of the flight route and for carrying out experimental studies along the axis of the plume.

5. CONCLUSION

With the use of stationary models for the assessment of long-range transport fields and impurity transformation, a numerical analysis of airborne probing data was carried out in the winter and summer atmosphere of the Norilsk industrial region. Under conditions of the experimental studies, the active gas-particle transition was experimentally recorded in the winter at a distance of 60-100 km from the source of emissions, and confirmed the average estimates of the life time of sulfur dioxide in the real atmosphere. The developed two-parameter model of transformation at certain distances from sources quite adequately describes the variation of the fields of average concentrations of calcium, sulfur dioxide in transverse direction of the plume of impurities.

Within the framework of the linear correlation analysis of the measurement results, a close relationship was established between the concentration of calcium and the mass concentration of atmospheric aerosol, and an estimate of its background component due to components of natural origin was made.

Analysis of the sulfur dioxide measurement data in the summer experiment showed quite adequate correspondence of the processes of transverse expansion of the torch of the impurity in question to theoretical concepts and confirmed the reliability of determining the position of the axis of the jet. This creates a basis for further numerical studies of atmospheric transport processes and the chemical transformation of impurities from NGMK in summer conditions.

6. ACKNOWLEDGMENTS

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