Study of sensitivity of the numerical model describing photochemical oxidation of sulfur to sulfuric acid and ammonium sulfates in the atmosphere of Siberia

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The problem of atmospheric pollution with secondary pollutants is especially urgent now for various aspects of the environmental protection. In this paper, we consider this problem for the sulfuric acid as most typical and toxic secondary pollutant. The results demonstrating the behavior of pollutants in the atmosphere are given. The sensitivity functions of the concentration of chemical components to the parameters of chemical transformations are computed.

Secondary pollution that is very urgent for environmental problems is poorly studied in the Siberian region, although it is often much more toxic than the primary pollution while, at the same time, being much more hard to describe and predict.

In this paper, we consider the problem of atmospheric pollution with sulfur compounds that are among most toxic pollutants. The scheme of chemical transformations of sulfur compounds in the atmosphere is shown in Fig. 1.

The sources of primary anthropogenic emissions of sulfur dioxide into the atmosphere are industrial enterprises, for example, heat power plants. Sulfur compounds can be also emitted by natural sources, for example, volcanoes, which emit hydrogen sulfide that is then oxidized by hydroxyl radical to sulfur dioxide. The latter is then oxidized in the atmosphere to sulfuric acid in two ways. The active way involves excitation by solar radiation to the triplet or singlet state and then reaction with the unexcited molecule of sulfur dioxide. The second, passive, way involves reaction with hydroxyl radical to form sulfuric anhydride and following reaction with the water molecule. The reaction also depends on the amount of solar radiation, because hydroxyl radical is generated at excitation of the ozone molecule by solar radiation. The resulting sulfuric acid is neutralized in the atmosphere through the reaction with ammonia and water to acid ammonium sulfate.

Sink of sulfur compounds from the atmosphere proceeds in several ways: dry sedimentation, wet sedimentation, and removal with aerosols. For sulfur dioxide and sulfuric acid, the scheme shows the processes of wet sedimentation (washing-out by precipitation) and dry sedimentation (adsorption on the surface). Removal with aerosols is typical of ammonium sulfate.

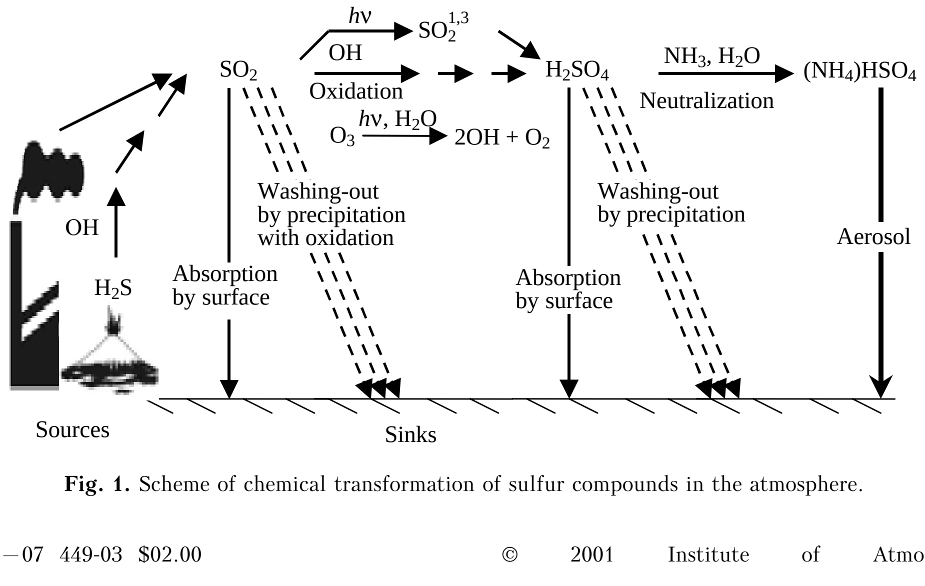

Fig. 1. Scheme of chemical transformation of sulfur compounds in the atmosphere.

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For simulation of transport processes, we used the set of equations of turbulent diffusion for multicomponent admixtures[1]:

$$\frac{\partial}{\partial x}\mu_x\frac{\partial\varphi_i}{\partial x} - u\frac{\partial\varphi_i}{\partial x} + \frac{\partial}{\partial y}\mu_y\frac{\partial\varphi_i}{\partial y} - v\frac{\partial\varphi_i}{\partial y} + \frac{\partial}{\partial z}\nu\frac{\partial\varphi_i}{\partial z} - w\frac{\partial\varphi_i}{\partial z} =$$

$$= \frac{\partial\varphi_i}{\partial t} + B(\varphi)_i - f_i(x, y, z, t), \quad i = \overline{1, n}, \qquad (1)$$

where $\boldsymbol{\varphi} = (SO_2, H_2SO_4, H_2SO_4^{\text{precipitation}}, NH_4HSO_4) \equiv \equiv \{\varphi_i(i = \overline{1, n})\}$ is the vector of concentrations; $\mathbf{u} = (u, v, w)$ is the wind velocity vector; μ_x, μ_y, and ν are the coefficients of turbulence; $f(x, y, z, t)$ is the source function; $B(\varphi)$ is the matrix operator describing the processes of chemical transformation.

The problem was solved within the domain $D_t = \{[a \le x \le b], \quad [c \le y \le d], \quad [\delta(x, y) \le z \le H], [0 \le t \le T]\}$, where $\delta(x, y)$ is the function of terrain with the boundary conditions:

$$\left.\frac{\partial\varphi_i'}{\partial x}\right|_{a,\,b} = 0, \quad \left.\frac{\partial\varphi_i'}{\partial y}\right|_{c,\,d} = 0, \quad \left.\frac{\partial\varphi_i'}{\partial z}\right|_{H} = 0;$$

$$\nu\left.\frac{\partial\varphi_i'}{\partial z}\right|_{\delta(x,\,y)} = \alpha_i(\varphi_{si} - \varphi_i'), \qquad (2)$$

α is the coefficient of pollutant absorption by surface; φ_s is the surface concentration of the pollutant, φ_i' are deviations of the pollutant concentrations from the background values. At the boundary points, where the direction of the velocity vector coincides with the direction of the external normal to the boundary, the pollutant is allowed to leave the domain under conditions (2).

The block of chemical transformations is described using an operator in the matrix form. To find it for all the considered reactions, the effective constants of the pseudofirst order for monomolecular processes were calculated from the time averaged concentrations of the reagents and the reaction rate constants.[3]

The rate constant of oxidation of sulfur dioxide to sulfuric acid was estimated as $4.01 \cdot 10^{-5}\ s^{-1}$, and for neutralization of sulfuric acid it was $5.56 \cdot 10^{-6}\ s^{-1}$. For washing-out of sulfur dioxide and sulfuric acid, the rate constants were taken equal to $2.78 \cdot 10^{-6}\ s^{-1}$; for adsorption by the surface, the constant for sulfur dioxide was $4.16 \cdot 10^{-6}\ s^{-1}$ and that for sulfuric acid it was taken $1.39 \cdot 10^{-6}\ s^{-1}$; the constant for the process of removal of ammonium sulfate with aerosol was $1.35 \cdot 10^{-6}\ s^{-1}$.

To construct discrete approximations, the splitting method was applied: transport was computed at the first two splitting steps, and chemical transformations were computed at the third step.[2] The obtained numerical scheme possesses the properties of stability, transportation, and monotony; the laws of conservation of mass and energy are assumed to hold in it. The scheme has the second order of accuracy relative to the spatial coordinates and the first order of accuracy with respect to time.[4]

Using this mathematical model, we have conducted a series of numerical experiments.

Analysis of the results shows that the model adequately describes hydrodynamic and chemical aspects of pollutant diffusion in the atmosphere against the background of the inhomogeneous wind field in a region with complex terrain.

With the proper selection of model parameters and source activities, the stationary spatial distribution of a pollutant is established in a stationary wind field. For example, in a region of the size of 100 km with a 300-m high hill at the initial background wind of 8 m/s at the height of 1.5 km, the stationary distribution is established within 8.5 h after the source starts to operate.

For the chemical block of the model, we obtained the time dependences of the concentrations (Fig. 2) typical of the considered mechanism of transformations.

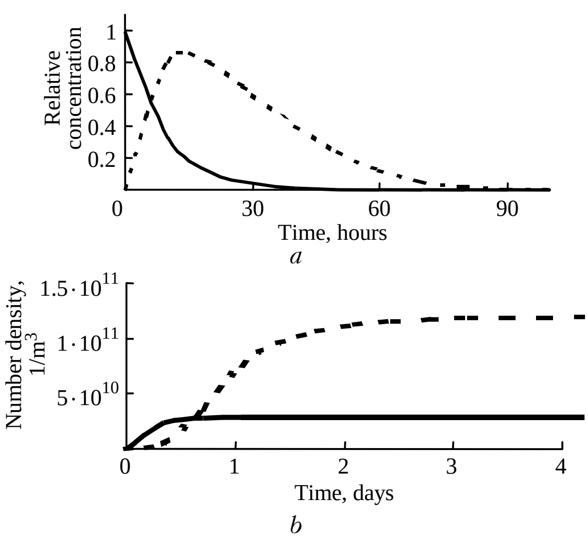

Fig. 2. Temporal distribution of the concentration for sulfur compounds at one-time (*a*) and continuous (*b*) emission: SO_2 (———) and H_2SO_4 (- - -).

In the case of one-time emission of sulfur dioxide at the initial time with zero initial concentrations of other reagents, it turned out that sulfuric acid (secondary pollution) is formed in the atmosphere in some time after the emission. The maximum of its concentration was observed in 11.3 h after the emission. In this case, sulfur compounds were removed from the atmosphere roughly in 3 days. In the case of a continuously operating source, the stationary concentration of sulfur dioxide and sulfuric acid was established within 21 h and 85 h, respectively. At this stage, the behavior of the concentrations was analyzed by comparing the values of some parameters calculated from the modeled data with their theoretical values. Namely, we have obtained the analytical equations for time, at which the concentration of sulfuric acid is maximum, and the time of establishment of the stationary concentration for oxides and acids in the case of a continuously operating source. The values obtained from analytical calculations agreed well with those computed with the model.

The joint operation of the hydrodynamic and chemical blocks gave an interesting result. It turned out that the maximum in the concentration of secondary pollutants was shifted with respect to the maximum in the concentration of primary ones. It is seen from the spatial distribution of oxides and acids (cross section at the fixed vertical coordinate) for sulfur compounds (Fig. 3).

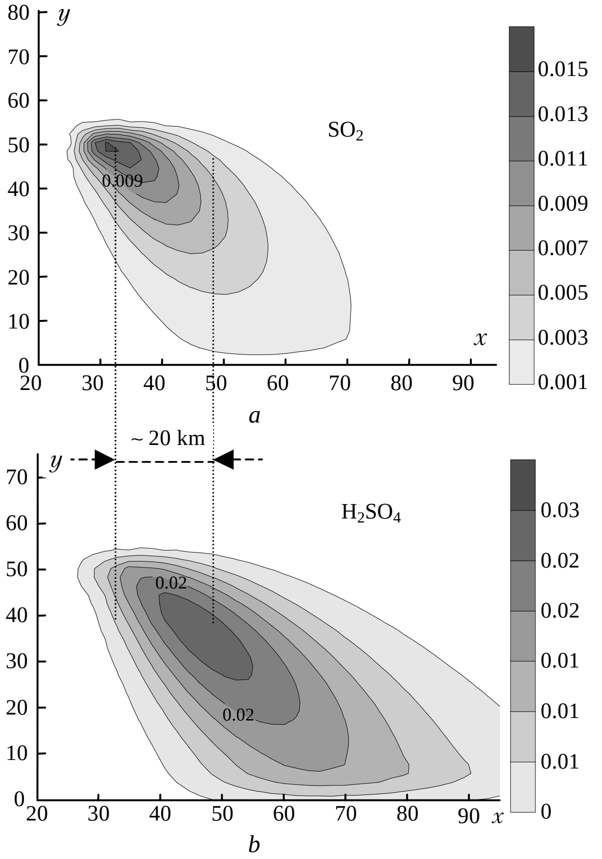

Fig. 3. Spatial distribution of sulfur dioxide (*a*) and sulfuric acid (*b*). Stationary solution of 3D problem; horizontal cross section at the ground level; distance in km is plotted along the axes; the source of sulfur dioxide is located at the point ($x = 25$ km, $y = 50$ km) at the altitude $z = 300$ m.

The stationary spatial distribution of sulfur dioxide is established roughly in 6 h and in 7 h for sulfuric acid.

Calculation of sensitivity functions

Diagnostics and optimization of the numerical model as applied to the chemical block are impossible without studying the sensitivity of the state function to the input parameters of the model. The effect of variations of the rate constants of chemical reactions on the air quality was studied using the algorithms of the theory of sensitivity of models.[2] We have calculated the functions of sensitivity of the goal functionals describing the atmospheric quality to variations of all parameters of the block of chemical transformations.

The parameters of the block of chemical transformations are the rate constants of chemical reactions and parameters of sources. We used three methods: direct simulation, variational equations, and variational approach.

The values of the sensitivity functions calculated by the second and the third methods were the same, but different from those calculated by the first method. This can be explained by drawbacks of the first method, that is efficient only at large variations.

The Table gives the values of the normalized sensitivity functions SF^*_{ij} connecting relative variations of the parameters and concentrations:

$$\frac{\Delta\varphi_i}{\varphi_i} = \frac{\Delta Y_j}{Y_j} SF^*_{ij}. \quad (3)$$

Table. Normalized functions of sensitivity of chemical system components to rate constants of chemical reactions for the scheme of chemical transformation of sulfur compounds

Reaction	Component	
	SO_2	H_2SO_4
Oxidation of SO_2	−0.93	0.82
Washing-out of SO_2	−0.12	−0.05
Washing-out of H_2SO_4	0	−0.10
Neutralization of H_2SO_4	0	−0.22
Source of SO_2 emissions	1	0.75

Analysis of the obtained values shows that the highest sensitivity functions for sulfur dioxide and sulfuric acid are characteristic of the processes of oxidation and the function of source of sulfur dioxide.

The sensitivity functions obtained by the method of variations or the method using sensitivity ratios for integral identity give the additional information for studying models of chemical kinetics. This is especially important for multicomponent mixtures with a large number of parameters determining the behavior of an atmospheric chemical system.

Acknowledgments

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