

Modeling of Pollutants in the Atmosphere Based on Photochemical Reactions

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Abstract

This article is devoted to the problem of the propagation of harmful pollutants in the atmosphere from point sources taking into account photochemical transformations. A complete list of typical atmospheric pollutants of the industrial city was determined. The fifteen most common types of harmful substances such as NO₂ (nitrogen dioxide), H₂SO₄ (sulfuric acid) to examine the transformation of impurities were selected. A scheme for the conversion of pollutants by chemical reactions was created. The transfer process and the transformation of substances were described by a system of differential equations. The resulting differential equations are constructed on the basis of stoichiometric formulas and the constant of reaction rate in accordance with the law of mass conservation. To account for the influence of anthropogenic heat sources and heterogeneity of the underlying surface on the propagation of harmful substances taking into photochemical reactions, a model of atmospheric boundary layer and the transport equation and transformation of pollutants by the example of the city of Ust-Kamenogorsk was considered. The schemes of stable and convergent difference for the equations of the atmospheric boundary layer and transport and transformation of admixture of harmful substances were designed.

A software package for numerical simulation of air pollution taking into account photochemical transformations and corresponding visualization of scenarios was developed. The software package allows simulating the spread of pollutants under different weather conditions. The results of the daily monitoring of distribution and dynamics of the formation of chemical substances were obtained. The results of numerical simulation of the propagation and transformation of harmful impurities on mesometeorological background processes taking into account the terrain and water surfaces were presented.

The analysis of the propagation of the substance concentration taking into the transformation of harmful substances of components was carried out.

The results show that the description of photochemical reactions in the mathematical model proposed in this paper allows identifying areas which are heavily contaminated with salts such as MgSO₄, CaSO₄ and acids of H₂SO₄ with a reasonable accuracy due to the sequential chemical reactions taking place in the atmosphere.

Introduction

Environmental problems currently observed in the surface layer of the atmosphere are the result of active human activity. A huge amount of chemicals released by many industries, contributes to environmental pollution. They produce biological effects on the human body. The role of these impurities in chemical reactions in the troposphere is very prominent. Some contaminants are toxic to living organisms, others reduce the transparency of the atmosphere to the Earth's thermal radiation and others

influence the process of the condensation of water vapor in the troposphere. Impurity concentration greatly exceeds the equilibrium concentration and such a distinction between true and equilibrium concentrations indicates that the troposphere is a non-equilibrium reactive system.

Harmful impurities are distributed in the atmosphere contaminating a vast territory. Another important factor is that the problems associated with chemical air pollution are not only of individual regions or states but these challenges have a trans-state character due to the transfer of contaminated air streams.

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Due to its historically socio-economic development, East Kazakhstan region is one of the most disadvantaged regions of the Republic of Kazakhstan in terms of the ecological status of the environment. Ust-Kamenogorsk is an urbanized system with oversaturated industry of a different technological orientation. Large objects of nonferrous metallurgy, nuclear industry and rare-metal complexes, power engineering, transport, food and processing industries, utilities are situated here; moreover, the pollution of the city is supplemented by the emissions of transport and the private sector. Typical pollutants in Ust-Kamenogorsk are sulfur dioxide, nitrogen dioxide, carbon monoxide, phenol, formaldehyde, chlorine, inorganic arsenic compounds, hydrogen chloride, hydrogen fluoride, sulfuric acid, hydrogen sulfide, ammonia, benzopyrene, and metals of 6 elements: lead, zinc, copper, cadmium, beryllium and mercury.

Contribution of sources to urban ambient air pollution is significant, and their negative impact is compounded by the specific features of atmospheric circulation caused by the geographical location of the city. The city is located in the river valley surrounded by mountain ranges on nearly all sides. Such relief forms mountain-valley and katabatic winds causing abnormally adverse weather conditions; they include elevated inversion layer at the calm surface of the earth, fogs and unfavorable direction of wind. Adverse weather conditions are conducive to the transformation of many phytochemical contaminants. The most common contaminant is sulfur dioxide, which dissolves in the fog droplets to form sulfuric acid aerosol that is more toxic than sulfur dioxide emitted by enterprises. The highest levels of contamination are observed in calm conditions combined with fog and inversions. 85% of fogs was observed in calm conditions and 15% was observed at a wind speed of 1-3 m/s.

A number of publications on this subject, in which various aspects of modeling of pollutants in the atmosphere based on photochemical transformations are examined, confirm the relevance of the considered problem. Modeling the process of air pollution is studied by G. Marchuk [1-2], V. Penenko [3, 4], A. Aloyan [5-8], I. Andreeva [11], V. Arguchintsev and A. Arguchintseva [9-10].

In mathematical modeling of impurity transport in mesoscale atmospheric boundary layer, the problem of the recovery of meteorological fields due to the lack of the regular observations over water surface and remote mountain areas is raised.

In [12-14] air quality monitoring was carried out. To determine the pollutants, hardware and measuring tools were used. Air monitoring in urban, rural and industrial areas was carried out. The average

daily concentrations of pollutants taking into account weather conditions (wind speed, wind direction, rainfall, temperature and relative humidity) were determined. To calculate the concentration, empirical functions based on experimental data were used.

Air quality is influenced not only by industry but also by forest fires. After a fire, a large amount of aerosols and smog goes to the global atmosphere [15]. In [16] the cartographic analysis was carried out.

Using metrological data pollutants were determined. The transformation of impurities coming from European countries and its impact on a number of the cities in Turkey is studied. In [17] the sources of pollution are investigated. The continuous monitoring of the industrial city is analyzed. The influence of elevation on the source of air quality is investigated.

The papers [10, 4] are devoted to the investigation of the dynamics of pollution propagation. In [10] a new method for solving the Burgers equation excluding photochemistry is proposed. The inverse problem for the risk assessment of Lake Baikal is considered. This method is used in many problems of modeling environmental problems.

In [4] a model of impurities distribution from the private sector is considered. Issues of the influence of pollutants on visibility and safe operation of the aircraft are examined. Studies carried out in this study show that due to incomplete combustion of coal and terrain features, almost all atmospheric emissions remain in the soil layer at the level of a human growth.

In [9] the transformation processes are considered and 156 chemical reactions between components of 82 contaminants are described in details. Hydrothermodynamic mesoscale processes and the transport of anthropogenic pollutants in the atmosphere and hydrosphere of Lake Baikal region are modeled.

In this article the problem of pollution propagating from point sources taking into account the photochemical transformation is considered. The results of numerical simulation of the propagation and transformation of harmful impurities on mesometeorological background processes by the example of the city of Ust-Kamenogorsk were presented.

Chemical model. To account for the transformation of harmful impurities on transferring the technique proposed in [9] is used. For the simulation of photochemical processes the fifteen most common types of harmful substances such as CH_2O , CO , CO_2 , SO_2 , SO_3 , HSO_3 , NO , NO_2 , NO_3 , HNO_3 , MgO , CaO , H_2SO_4 , MgSO_4 , CaSO_4 and chemical reactions between them are used (Fig. 1).

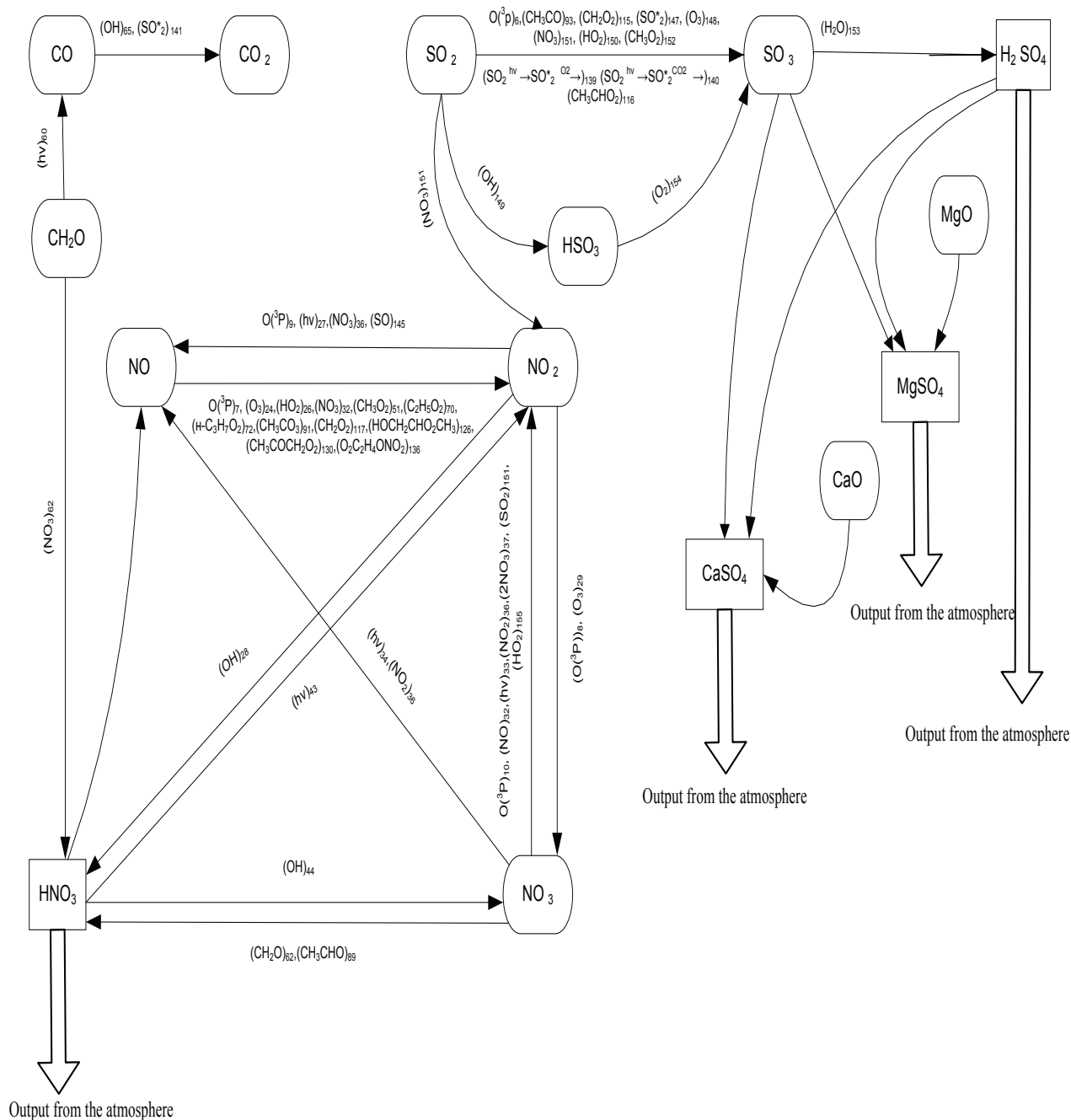


Fig. 1. Diagram of the transformation of pollutants.

For the selected fifteen types of pollutants conversion circuit from one substance to another under the influence of heat and moisture in the impurity was designed (Fig. 1). Each transformation is indicated by arrows, and has its own constant of transformation rate. The scheme shows the substances which are removed from the atmosphere in the form of small solid particles and dust after sequential reactions.

For example, nitric acid is generated by the reaction of nitrogen dioxide NO₂ and OH radical:



Thus, most part of the nitric acid is removed from the atmosphere by the precipitation in the form of HNO₃ solutions and nitrate salts.

Chemical reactions in which SO₂ enters and rate constant of the processes of wet and dry deposition as well as transformations of appropriate reactions k_m are shown in Table 1.

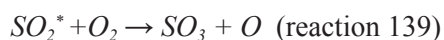
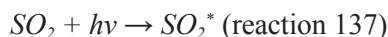
Table 1
Stoichiometric formulas and constants of reaction rate

The number of reactions, m	Reactions	A constant of reaction rate, k_m
6	$O(^3P) + SO_2 \rightarrow SO_3$	$5.68 \cdot 10^{-14}$
93	$CH_3CO_3 + SO_2 \rightarrow CH_3CO_2 + SO_3$	$2 \cdot 10^{-17}$
115	$CH_2O_2 + SO_2 \rightarrow SO_3 + CH_2O$	$1.75 \cdot 10^{-14}$
116	$CH_3CHO_2 + SO_2 \rightarrow SO_3 + CH_3CHO$	$1.75 \cdot 10^{-14}$
134	$n - C_3H_7O_2 + SO_2 \rightarrow SO_3 + n - C_3H_7O$	$1 \cdot 10^{-16}$
135	$CH_3COCH_2O_2 + SO_2 \rightarrow SO_3 + CH_2COCH_2O$	$1 \cdot 10^{-16}$
137	$SO_2 + h\nu \rightarrow SO_2^*$	$1.4 \cdot 10^{-5a}$
138	$SO_2^* + M \rightarrow SO_2 + M$	$1.5 \cdot 10^{-13}$
139	$SO_2^* + O_2 \rightarrow SO_3 + O$	$2.6 \cdot 10^{-15}$
140	$SO_2^* + O_3 \rightarrow SO_3 + O_2$	$1.7 \cdot 10^{-12}$
141	$SO_2^* + CO \rightarrow SO + CO_2$	$4.3 \cdot 10^{-15}$
143	$SO_2^* + C_3H_6 \rightarrow C_3H_5SO_2H$	$2.8 \cdot 10^{-11}$
144	$SO + O_3 \rightarrow SO_2 + O_2$	$6.7 \cdot 10^{-14}$
145	$SO + NO_2 \rightarrow SO_2 + NO$	$1.4 \cdot 10^{-11}$
146	$SO + O_2 \rightarrow SO_2 + O$	$8.4 \cdot 10^{-17}$
147	$SO_2 + SO_2^* \rightarrow SO_3 + O_2$	$6.3 \cdot 10^{-14}$
148	$SO_2 + O_3 \rightarrow SO_3 + O_2$	$1 \cdot 10^{-22}$
149	$SO_2 + OH \rightarrow HSO_3$	$1.5 \cdot 10^{-12}$
150	$SO_2 + HO_2 \rightarrow SO_3 + OH$	$1 \cdot 10^{-18}$
151	$SO_2 + NO_3 \rightarrow SO_3 + NO_2$	$1 \cdot 10^{-20}$
152	$SO_2 + CH_3O_2 \rightarrow CH_3O + SO_2$	$1 \cdot 10^{-17}$
153	$SO_3 + H_2O \rightarrow H_2SO_4$	$9 \cdot 10^{-13}$
154	$HSO_3 + O_2 \rightarrow HO_2 + SO_3$	$4 \cdot 10^{-13}$
156	$SO_2 + CH_3O \rightarrow CH_3OSO_2$	$5 \cdot 10^{-13}$

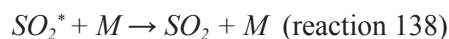
Note: here a is a rate constant of the reaction of first order (s^{-1}), the rest constants are the rate constants of the reactions of the second order (sm^3s^{-1}). Rate constants are given under standard conditions.

Table 1 summarizes the reactions and constants of conversion rates for sulfur oxides SO_2 (tetravalent) and SO_3 (hexavalent), taken from [9].

According to Table 1, the oxidation of sulfur SO_2 occurs in gaseous, liquid and solid phases. Absorbing solar radiation, the molecules of SO_2 are excited and react with oxygen in the excited state and generate SO_3 and O_3 :



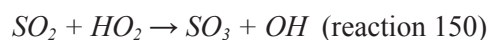
or by the reaction with the third body M:



Sulfur trioxide SO_3 reacts with water to produce sulfuric acid



Free radicals play the leading role in the oxidation of SO_2 :



Sulfur trioxide SO_3 , formed in the oxidation of SO_2 , reacts with atmospheric water droplets and forms a solution of sulfuric acid H_2SO_4 .

For other substances such as CH_2O , CO , CO_2 , HSO_3 , NO , NO_2 , NO_3 , HNO_3 , MgO , CaO , H_2SO_4 , $MgSO_4$, $CaSO_4$ corresponding reactions are selected similarly [9].

Chemical transformations shown in the diagram (Fig. 1) describe a system of fifteen differential equations. Here are some of them; for example, the equations for sulfur oxides SO_2 (tetravalent), SO_3 (hexavalent) and sulfuric acid HSO_3 , H_2SO_4 are in the following form:

$$\begin{aligned} \frac{d\varphi_{\text{SO}_2}}{dt} = & -k_6\varphi_{\text{SO}_2} - k_{93}\varphi_{\text{SO}_2} - k_{115}\varphi_{\text{SO}_2} - k_{116}\varphi_{\text{SO}_2} - k_{139}k_{137}\varphi_{\text{SO}_2} \\ & - k_{140}k_{137}\varphi_{\text{SO}_2} - k_{147}\varphi_{\text{SO}_2} - k_{148}\varphi_{\text{SO}_2} - k_{149}\varphi_{\text{SO}_2} - \\ & - k_{150}\varphi_{\text{SO}_2} - k_{151}\varphi_{\text{SO}_2} - k_{152}\varphi_{\text{SO}_2} + f_{\text{SO}_2} \quad (1) \end{aligned}$$

$$\begin{aligned} \frac{d\varphi_{\text{SO}_3}}{dt} = & k_6\varphi_{\text{SO}_2} + k_{93}\varphi_{\text{SO}_2} + k_{115}\varphi_{\text{SO}_2} + k_{116}\varphi_{\text{SO}_2} + k_{139}k_{137}\varphi_{\text{SO}_2} + \\ & + k_{140}k_{137}\varphi_{\text{SO}_2} + k_{147}\varphi_{\text{SO}_2} + k_{148}\varphi_{\text{SO}_2} + k_{150}\varphi_{\text{SO}_2} + k_{151}\varphi_{\text{SO}_2} + \\ & + k_{152}\varphi_{\text{SO}_2} + k_{154}\varphi_{\text{HSO}_3} - k_{153}\varphi_{\text{SO}_3} + f_{\text{SO}_3} \quad (2) \end{aligned}$$

$$\frac{d\varphi_{\text{HSO}_3}}{dt} = k_{149}\varphi_{\text{SO}_2} - k_{154}\varphi_{\text{HSO}_3} + f_{\text{HSO}_3} \quad (3)$$

$$\frac{d\varphi_{\text{H}_2\text{SO}_4}}{dt} = k_{153}\varphi_{\text{SO}_3} + f_{\text{H}_2\text{SO}_4} \quad (4)$$

Differential equations (1) - (4) are worked out in the way that if the substance reacts it is subtracted from the proportion of the substance and added to the volume of the substance, which is formed in accordance with the law of mass conservation. Sulfur dioxide SO_2 in many cases react in an excited state, so for the convenience of SO_2^* values were taken as $k_7\text{SO}_2$.

Mathematical model. To study the influence of anthropogenic heat sources, pollutants and heterogeneity of the underlying surface on the atmosphere of an industrial city, let's consider the model of the atmospheric boundary layer in the area of three-dimensional area Ω [1, 2, 3]. equations of motion:

$$\frac{\partial u}{\partial t} + \frac{\partial u^2}{\partial x} + \frac{\partial uv}{\partial y} + \frac{\partial u\omega}{\partial z} = -\frac{\partial \pi}{\partial x} + l\nu + \frac{\partial}{\partial z} \left(\nu \frac{\partial u}{\partial z} \right) + \Delta u \quad (5)$$

$$\frac{\partial v}{\partial t} + \frac{\partial uv}{\partial x} + \frac{\partial v^2}{\partial y} + \frac{\partial v\omega}{\partial z} = -\frac{\partial \pi}{\partial y} - l\nu + \frac{\partial}{\partial z} \left(\nu \frac{\partial v}{\partial z} \right) + \Delta v \quad (6)$$

$$\frac{\partial \omega}{\partial t} + \frac{\partial u\omega}{\partial x} + \frac{\partial v\omega}{\partial y} + \frac{\partial \omega^2}{\partial z} = -\frac{\partial \pi}{\partial z} + \lambda\theta + \frac{\partial}{\partial z} \left(\nu \frac{\partial \omega}{\partial z} \right) + \Delta \omega \quad (7)$$

continuity equation under the assumption that the spatial-temporal changes in density are negligible:

$$\text{div} \vec{U} = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial \omega}{\partial z} = 0 \quad (8)$$

equation of heat:

$$\frac{\partial \theta}{\partial t} + \frac{\partial u\theta}{\partial x} + \frac{\partial v\theta}{\partial y} + \frac{\partial \omega\theta}{\partial z} + S\omega = \frac{\partial}{\partial z} \left(\nu \frac{\partial \theta}{\partial z} \right) + \Delta \theta \quad (9)$$

where $\Delta = \frac{\partial}{\partial x} \mu_x \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \mu_y \frac{\partial}{\partial y}$ is a differential operator of horizontal turbulent diffusion.

t is time x, y, z are Cartesian coordinates, \vec{U} is wind velocity with components u, v, ω ; π is pressure, $\lambda = \frac{g}{T}$ is a parameter of convection or buoyancy parameter, $S = \frac{\partial \theta}{\partial z}$ is a stratification parameter, g is gravitational acceleration, T is air temperature, μ_x, μ_y are the coefficients of the horizontal momentum of the turbulence and heat; ν is vertical coefficient of turbulent exchange of momentum and heat, θ is background potential temperature, l is Coriolis parameter.

Simplification and transformation, which were used in the derivation of the systems of equations (5) - (9), generalize the so-called simplification of convection theory, the idea of which was proposed by Boussinesq in 1903, and the physical meaning of these simplifications was identified by Ogura and Phillips in 1962.

For the modeling of the transport and transformation of pollutants the following equation is used:

$$\frac{\partial \varphi_q}{\partial t} + u \frac{\partial \varphi_q}{\partial x} + v \frac{\partial \varphi_q}{\partial y} + \omega \frac{\partial \varphi_q}{\partial z} = \Delta \varphi_q + \frac{\partial}{\partial z} \left(\nu \frac{\partial \varphi_q}{\partial z} \right) + \alpha_q \varphi_q + \beta_q + f_q \quad (10)$$

$$\sum_q \varphi_q = 1$$

where φ_q is a proportion of pollutant concentration in the impurity, f_q describes sources of substances at the level of roughness, α_q, β_q are the coefficients resulting from the transformation equations of the impurities in the atmosphere (1) - (4), the index q means chemical formula of the substance.

The system of equations (5) - (10) is solved with the following initial and boundary conditions:

$$\begin{aligned}
\vec{U} &= \vec{U}^0(x, y, z), \quad \theta = \theta^0(x, y, z), \quad \varphi_q = \varphi_q^0(x, y, z) \text{ at } t = 0, \\
u &= u_1(y, z, t), \quad v = v_1(y, z, t), \quad \omega = 0, \quad \frac{\partial \theta}{\partial x} = 0, \quad \varphi_q = \varphi_q^0 \text{ at } x = 0, \quad 0 \leq y \leq Y, \\
\frac{\partial u}{\partial x} &= 0, \quad v = 0, \quad \omega = 0, \quad \frac{\partial \theta}{\partial x} = 0, \quad \frac{\partial \varphi_q}{\partial x} = 0 \text{ at } x = X, \quad 0 \leq y \leq Y, \\
u &= u_2(x, z, t), \quad v = v_2(x, z, t), \quad \omega = 0, \quad \frac{\partial \theta}{\partial y} = 0, \quad \varphi_q = \varphi_q^0 \text{ at } y = 0, \quad 0 \leq x \leq X, \\
u &= 0, \quad \frac{\partial v}{\partial y} = 0, \quad \omega = 0, \quad \frac{\partial \theta}{\partial y} = 0, \quad \frac{\partial \varphi_q}{\partial y} = 0 \text{ at } y = Y, \quad 0 \leq x \leq X, \\
u &= 0, \quad v = 0, \quad \omega = 0, \quad \theta = 0, \quad \pi = 0, \quad \varphi_q = 0 \text{ at } z = H \\
\omega &= 0, \quad h \frac{\partial u}{\partial z} = a_u u, \quad h \frac{\partial v}{\partial z} = a_v v, \quad h \frac{\partial \theta}{\partial z} = a_\theta (\theta - \theta_0), \quad \varphi_{q,0} = \frac{f_q + a_\theta \varphi_{q,h} v}{\beta + a_\theta v} \text{ at } z = h,
\end{aligned} \tag{11}$$

where H is conventional height of atmospheric boundary layer; X, Y are lateral boundaries of the area, $\varphi_{q,0}, \varphi_{q,h}$ are share concentrations of the substance q at the level of roughness and surface layer, θ_0 is a temperature at the level of roughness,

$a_u = \frac{\psi_u(\zeta_h)}{\eta_u(\zeta_h, \zeta_0)}$ is the parameter caused by the friction of airflows with the underlying surface, $a_\theta = \frac{\psi_\theta(\zeta_h)}{\eta_\theta(\zeta_h, \zeta_0)}$ is the parameter of turbulent heat exchange, β is a quantity having the dimensions of velocity and characterizing the interaction with the underlying surface impurities, h is the height of the surface layer, ζ_0, ζ_h are dimensionless parameters of height, ψ_u, ψ_θ are Businger interpolation functions obtained by the experimental data. Full review of other interpolation formulas proposed by various authors, was prepared by A. Yaglom [18]. In our case, we used interpolation functions of the following form:

$$\psi_u(\zeta) = 1 + 4.7\zeta, \quad \psi_\theta(\zeta) = 0.74 + 4.7\zeta \text{ if } \zeta > 0, \tag{12}$$

$$\eta_u(\zeta, \zeta_u) = \int_{\zeta_u}^{\zeta} \frac{\psi_u(\zeta)}{\zeta} d\zeta, \quad \eta_\theta(\zeta, \zeta_0) = \int_{\zeta_0}^{\zeta} \frac{\psi_\theta(\zeta)}{\zeta} d\zeta.$$

The boundary conditions $u = u_1(y, z, t), v = v_1(y, z, t)$ are determined on the basis of meteorological conditions. For modeling the atmospheric boundary layer at $z=h$, the Monin-Obukhov similarity theory and the empirical function of [1, 3] are selected. In determining the boundary conditions for a surface layer θ, φ_q at $z=h$, the equation of the terrain $z=\delta(x, y)$ is taken into account. The remaining boundary

conditions are set to perform smoothness disturbances and the continuity equation on the boundary integrable field.

Numerical solution method proposed in this paper allows considering the following classes of atmospheric motions:

- large-scale, which horizontal scale lengths are of several hundred kilometers or more;
- medium-sized, which length scales are of the order of about 100 km;
- small-scale, which horizontal length scales are of 10 km or less.

For the considered classes of atmospheric motions the impact of molecular viscosity forces of air is always very small, therefore these forces can be face neglected. In the boundary layer the intense turbulent transport of momentum is observed. The mathematical model (5) - (11) is developed under these assumptions. There are different approaches of describing the turbulent exchange coefficients μ_x, μ_y, ν . One can set the numerical values or the variation law of these coefficients [18].

Numerical Implementation of the Algorithm

To solve the task (5) - (11), the finite difference method is used and it is numerically implemented by splitting into physical processes, which has been successfully used in the numerical solutions of equations aerohydrodynamics in natural variables [19].

Let's introduce the following uniform grids in the area

$$\Omega = \{0 \leq x \leq l_1, 0 \leq y \leq l_2, 0 \leq z \leq l_3\}$$

$$\begin{aligned} \Omega_h &= \{(x_i, y_j, z_k) = (ih_1, jh_2, kh_3), i = 0, 1, \dots, N_1, j = 0, 1, \dots, N_2, k = 0, 1, \dots, N_3\} \\ \Omega_{x,h} &= \{(x_{i-1/2}, y_j, z_k) = ((i-1/2)h_1, jh_2, kh_3), i = 1, 2, \dots, N_1, j = 0, 1, \dots, N_2, k = 0, 1, \dots, N_3\} \\ \Omega_{y,h} &= \{(x_i, y_{j-1/2}, z_k) = (ih_1, (j-1/2)h_2, kh_3), i = 0, 1, \dots, N_1, j = 1, 2, \dots, N_2, k = 0, 1, \dots, N_3\} \\ \Omega_{z,h} &= \{(x_i, y_j, z_{k-1/2}) = (ih_1, jh_2, (k-1/2)h_3), i = 0, 1, \dots, N_1, j = 0, 1, \dots, N_2, k = 1, 2, \dots, N_3\} \end{aligned}$$

where

$$h_1 = l_1/N_1, \quad h_2 = l_2/N_2, \quad h_3 = l_3/N_3.$$

In the method of splitting into physical processes the components u, v and ω of the wind speed are determined in the grid nodes $\Omega_{x,h}, \Omega_{y,h}$ and $\Omega_{z,h}$, respectively; pressure π , temperature θ and the proportion of pollutant concentrations φ_q are determined in the grid nodes Ω_h .

We suppose that velocity field $\vec{U}_h = (u_h, v_h, \omega_h)$ pressure field π_h^n , the proportion of pollutant concentrations $\varphi_{q,h}^n$ and temperature θ_h^n are known in nodal points of grid areas $\Omega_{x,h}, \Omega_{y,h}, \Omega_{z,h}, \Omega_h$ at the time t^n . Then, for calculating the unknown velocity and pressure fields, temperature, concentration at the time t^{n+1} , the splitting scheme is used which comprises the following steps [19]:

1. Determination of intermediate $\vec{U}_h^{n+1/2}$ speeds considering the Coriolis force and the effect of temperature:

$$\frac{\vec{U}_h^{n+1/2} - \vec{U}_h^n}{\tau} = -L_h \vec{U}_h^n + \Lambda_h \vec{U}_h^n + \vec{G}_h^n \quad (13)$$

where $L_h \vec{U}_h^n, \Lambda_h \vec{U}_h^n$ are the difference analogs of members describing convective transport and turbulent exchange, $\vec{G}_h^n = (lv_h^n, -lu_h^n, \lambda\theta_h^n)$ are the members describing the influence of Coriolis forces and temperature.

At this stage, it is assumed that the transfer of momentum is carried out by convection, turbulent exchange, Coriolis forces and temperature. Despite the fact that the intermediate velocity field $\vec{U}_h^{n+1/2}$ does not satisfy the continuity equation, the interior points of the grid areas describe vortex flow characteristics.

2. Using the found intermediate velocity $\vec{U}_h^{n+1/2}$ field, we obtain the following equation for the pressure field taking into account the solenoidal velocity $div_h \vec{U}_h^{n+1} = 0$:

$$\Lambda_h \pi_h^{n+1} = \frac{div_h \vec{U}_h^{n+1/2}}{\tau} \quad (14)$$

For the numerical solution of the Poisson equation (14) at each time step, an iterative method is used.

3. It is assumed that the transfer of amount of motion is carried out only due to the pressure gradient and to determine the velocity \vec{U}_h^{n+1} on the time layer t^{n+1} we have

$$\frac{\vec{U}_h^{n+1} - \vec{U}_h^{n+1/2}}{\tau} = -\nabla_h \pi_h^{n+1} \quad (15)$$

where ∇_h is the difference analogue of the nabla operator

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

4. Using the found velocity fields, transfer and diffusion of temperature are calculated by the following difference scheme.

$$\frac{\theta_h^{n+1} - \theta_h^n}{\tau} = -L_h \theta_h^n + \Lambda_h \theta_h^n \quad (16)$$

Now it is necessary to determine the transport and transformation of proportions $\varphi_{q,h}^{n+1}$ of pollutant concentrations in the impurity.

5. Transport of proportions of pollutant concentrations in the impurity due to convection and turbulent exchange is defined from the following equation:

$$\frac{\varphi_{q,h}^{n+1/2} - \varphi_{q,h}^n}{\tau} = -L_h \varphi_{q,h}^n + \Lambda_h \varphi_{q,h}^n \quad (17)$$

6. The calculation of the transformation of the concentration proportion of harmful substances in the impurity and the influence of external sources are defined from the following equation:

$$\frac{\varphi_{q,h}^{n+1} - \varphi_{q,h}^{n+1/2}}{\tau} = \alpha_q \varphi_{q,h}^{n+1} + \beta_q + f_q \quad (18)$$

where $\varphi_{q,h}^{n+1}$ is the proportion of pollutant concentration q in the impurity on the $n+1$ -th time layer, the coefficients α_q, β_q are determined from the differential equations (1)-(4).

For example, from the equation (3) for a concentration of proportion of the substance HSO_3 we have:

$$\varphi_{HSO_3}^{n+1} = \frac{\varphi_{HSO_3}^{n+1/2} + \tau\beta_{HSO_3} + \mathcal{F}_{HSO_3}}{1 - \tau\alpha_{HSO_3}}$$

where

$$\alpha_{HSO_3} = -k_{154}\varphi_{HSO_3}$$

$$\beta_{HSO_3} = k_{149}\varphi_{SO_2}$$

Results and Discussion

Using the model described above and the proposed algorithm, numerical calculations for different values of the input parameters were carried out. Dimensions of the considered area were 35×35 km, the height of the surface layer is 3500 meters, convection parameter $\lambda = 0.16$ m/(s·deg), the parameter of stratification S from the physical viewpoint deter-

mines changes in temperature with a change in the height, therefore it was calculated based on the vertical temperature gradient; Coriolis force is $l = 10^{-4} s^{-1}$.

Values of horizontal and vertical turbulent exchange coefficients are taken as $\mu_x = \mu_y = 6 \cdot 10^3 m^2/s$, $\nu = 30 m^2/s$.

As the characteristic length scale, wind speed and temperature, the following numerical values were used: $L = 35000$ m, $U^* = 10$ m/s, $\theta^* = 20$ °C.

To determine the dimensionless quantities of input parameters $\lambda, l, S, \mu_x, \mu_y, X, Y, H$ the following formula were used:

$$\bar{\lambda} = \frac{\lambda \cdot \theta^*}{U^*}, \bar{l} = \frac{l \cdot L}{U^*}, \bar{S} = \frac{S \cdot L}{\theta^*}, \bar{\mu}_x = \frac{\mu_x}{L \cdot U^*}, \bar{\mu}_y = \frac{\mu_y}{L \cdot U^*}, \bar{X} = \frac{X}{L}, \bar{Y} = \frac{Y}{L}, \bar{H} = \frac{H}{L}$$

where U^* is characteristic velocity, θ is characteristic temperature, L is the length scale.

Calculations were carried out on grids of dimensions $50 \times 50 \times 25$ and $100 \times 100 \times 50$. Harmful substances released into the atmosphere from industrial plants and motor vehicles were set in proportions under the assumption that the sum of the proportions is a unit (Table 2).

Table 2
Percentage of chemical substances in the atmosphere

The number of a substance	Chemical name	Chemical formula	Proportioning of the material
1	Formaldehyde	CH ₂ O	$\varphi_{CH_2O} = 0.33$
2	Carbon monoxide	CO	$\varphi_{CO} = 0.08$
3	Carbon dioxide	CO ₂	$\varphi_{CO_2} = 0.02$
4	Sulfur oxide	SO ₂	$\varphi_{SO_2} = 0.08$
5	Sulfur trioxide	SO ₃	$\varphi_{SO_3} = 0.12$
6	Sulfurous acid	HSO ₃	$\varphi_{HSO_3} = 0.02$
7	Nitric oxide	NO	$\varphi_{NO} = 0.10$
8	Nitrogen dioxide	NO ₂	$\varphi_{NO_2} = 0.10$
9	Nitrate	NO ₃	$\varphi_{NO_3} = 0.02$
10	Nitric acid	HNO ₃	$\varphi_{HNO_3} = 0.02$
11	Magnesia	MgO	$\varphi_{MgO} = 0.04$
12	Calcium oxide	CaO	$\varphi_{CaO} = 0.06$
13	Sulfuric acid	H ₂ SO ₄	$\varphi_{H_2SO_4} = 1 \cdot 10^{-15}$
14	Magnesium sulfate	MgSO ₄	$\varphi_{MgSO_4} = 2 \cdot 10^{-15}$
15	Calcium sulfate	CaSO ₄	$\varphi_{CaSO_4} = 1 \cdot 10^{-15}$

To determine the dynamics of the formation of harmful substances, computational experiments and comparative analysis were carried out. At the initial time the chemicals MgSO₄, CaSO₄, H₂SO₄ make up a very small part. Using numerical simulation, harmful substances released by industrial

sources react with short-wave solar radiation, water vapor (photochemical reactions) and form a sequence of reactions (Table 1). As a result of complex chemical reactions the proportion of MgSO₄, CaSO₄, H₂SO₄ significantly increases with a time (Fig. 2).

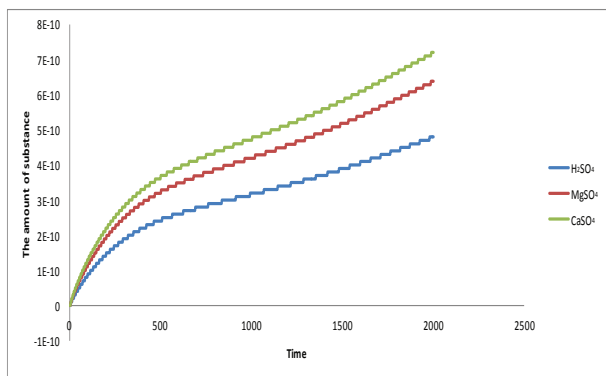


Fig. 2. Dynamics of harmful substances in the atmosphere.

Daily monitoring of the changes of pollutants in the atmosphere was carried out. The monitoring has shown that during the night production plants work at full capacity and emit more harmful substances than in the daytime (Fig. 3).

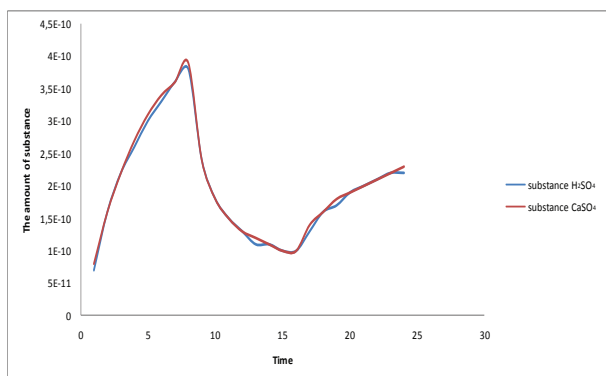


Fig. 3. Monitoring of air pollution by harmful substances.

Currently the main anthropogenic source of carbon monoxide CO is the exhaust gases of internal combustion engines. Carbon dioxide is formed during the combustion of fuel in internal combustion engines at low temperatures or inadequate setting of the air supply (insufficient amount of oxygen being fed for the oxidation of carbon monoxide CO to carbon dioxide CO₂). Under natural conditions, on the surface of the Earth, carbon monoxide CO is formed during incomplete anaerobic decomposition of organic compounds and biomass combustion, primarily during the forest and wildfires. Figure 4 shows the propagation of these substances over the city of Ust-Kamenogorsk at a wind speed of 2 m/s.

Among more than 7.000 chemical compounds polluting the environment the 10 most dangerous groups of substances that include nitrogen dioxide NO₂ in the air are distinguished. The ratio of oxides

NO and NO₂ in the troposphere varies, they can easily be converted into each other, therefore we can use the same symbol (NO)_x for them. Figure 5 shows the distribution of this substance over the city of Ust-Kamenogorsk at a wind speed of 2 m/s.

Nitric acid HNO₃ is formed as a result of chemical reactions of nitrogen oxides in the troposphere. Nitric acid, unlike sulfuric acid, may remain in a gaseous state for a long time as it condenses badly. Nitric acid is more volatile than sulfuric. Couple drops of nitric acid are absorbed by clouds and aerosol particles. Most of the nitric acid is removed from the atmosphere by the precipitation in the form of solutions HNO₃ and nitrate salts.

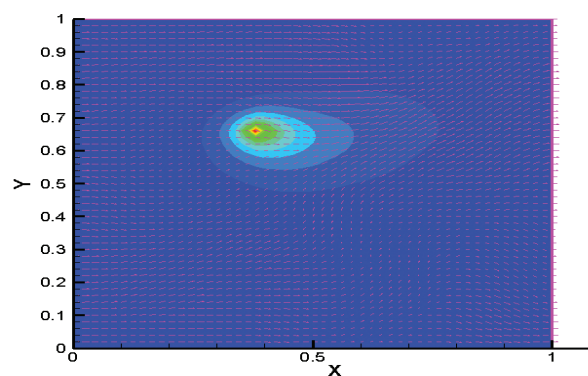


Fig. 4. Distribution of CO₂ (carbon dioxide) at a wind speed of 2 m/s.

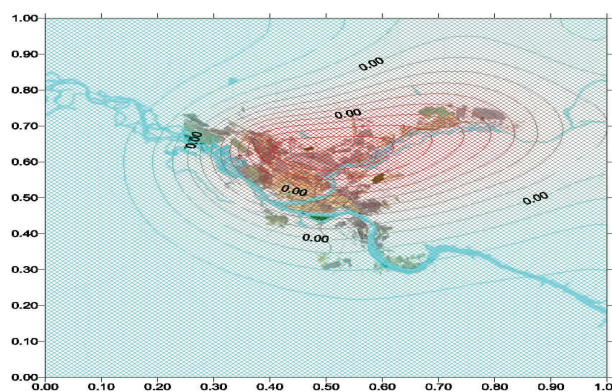


Fig. 5. Contours of pollutant NO₂ (nitrogen dioxide) at a wind speed of 2 m/s.

The reason for toxic smog is the increased sulfur dioxide SO₂ concentration in the atmosphere. In the presence of acid products at high humidity leads to the formation of dense fog which also captures the particles of dust and soot. Such toxic fog is called toxic smog. SO₂ and its oxidation product, SO₃, cause the main damage to the environment.

Waste coal - preparation plants contain SiO_2 , CaO , K_2O and Na_2O . They are dumped that raises the amount of dust and smoke and dramatically worsen the atmosphere and surrounding areas.

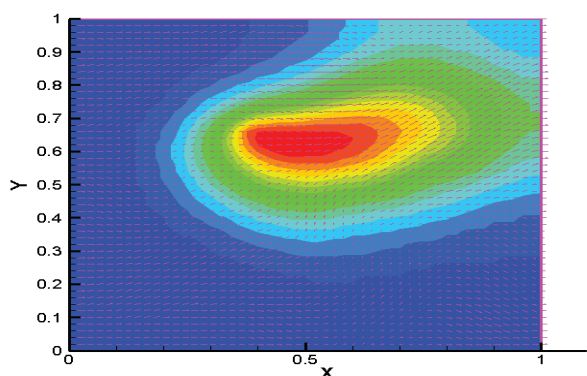


Fig. 6. Distribution of CaSO_4 (calcium sulfate) at a wind speed of 2 m/s.

Sulfur is contained in aerosols in the form of sulphates CaSO_4 and MgSO_4 . This makes up 30% of all wastes of sulfur in the troposphere in the form of inorganic compounds. Figure 6 shows the distribution of CaSO_4 mesometeorological on background processes.

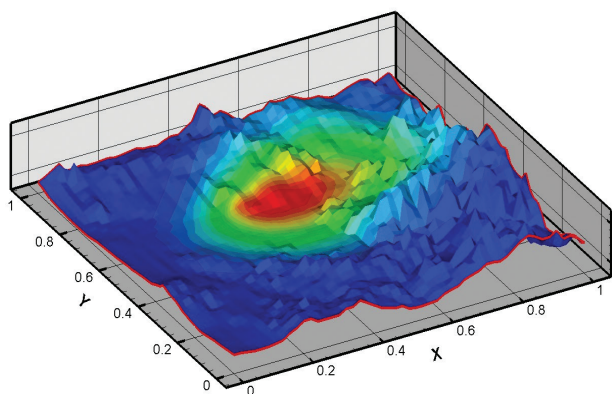


Fig. 7. Simulation of H_2SO_4 (sulfuric acid) at a wind speed of 2 m/s in the horizontal sections, taking into account the terrain.

Most of the gaseous impurities coming from the Earth's surface in the troposphere are in reduced form or in the form of oxides with a low oxidation state, for example, H_2S , NH_3 , CH_4 and others. Impurities that come from the troposphere to the surface are compounds with a high oxidation state. This family includes sulfuric acid H_2SO_4 , which causes the formation of acid rain. Figure 7 shows the distribution of H_2SO_4 (sulfuric acid) taking into account the terrain.

Conclusion

In this paper a mathematical model of mesoscale atmospheric processes in non hydrostatic approximation, transport and transformation of pollutants based on topography and thermal inhomogeneities of the underlying surface was developed. A new model describing the process of transformation of the proportion of impurity substances by photochemical reactions in the atmospheric surface layer using emission data specific to the industrial regions was designed. Basic mathematical model describing the photochemistry was completed with new members taking into the obtained results of the atmosphere generated in the form of droplets, fine particles, dust and particles, etc.

Atmosphere is a constantly changing environment varying in time and space where processes proceed. All the processes proceed in the atmosphere during air irradiation by sunlight but they take place at different rates in different ways depending on the intensity of light emission. These processes take place in one direction in the daytime and proceed in the reverse direction at night. Pressure and air movement affect the processes proceeding in the atmosphere. Taking into account these processes, the monitoring of air pollution and the dynamics of harmful chemicals was carried out.

For the selected 15 substances the separate and the total distribution were calculated. The model considers the terrain and water surfaces of Ust-Kamenogorsk. Calculations were carried out at different directions and wind speeds.

Numerical calculations revealed that as a result of photochemical reactions, salts such as MgSO_4 , CaSO_4 and H_2SO_4 , HNO_3 are formed, and the most contaminated areas by these substances were identified.

At moderate wind speeds one can observe the effect of water surfaces and terrain orography on the dispersion of pollutants, and at high wind speeds, these factors do not cause specific abnormalities.

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Received 6 February 2013