

Regional-Scale Numerical Modeling of Gas–Aerosol Dynamics

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A combined mathematical model has been developed to reproduce the spatiotemporal variations in the concentrations of multicomponent gaseous admixtures and aerosols in the atmosphere in the regional and urban scales. The model incorporates the transport of gas components and aerosols in the atmosphere with allowance for photochemical transformation, binary homogeneous nucleation; condensation/evaporation, and coagulation. The meteorological parameters and turbulent characteristics are calculated from a mesoscale nonhydrostatic atmospheric model. The new-particle formation from precursor gases is considered on the basis of a binary homogeneous nucleation mechanism and interaction with background aerosol. Using this model, numerical experiments were performed to investigate spatiotemporal variations in the concentrations of gas components and aerosols as well as the ion composition of aerosol particles in the Baikal region due to strong industrial emission sources. The results of the numerical calculations were compared with field measurement data.

1. Introduction

We consider a combined mathematical model of the transport of atmospheric gas components and aerosols having regard to nucleation, condensation/evaporation, coagulation, and gas- and aqueous-phase chemistry. As these mechanisms are interrelated a single model framework should be used for their incorporation. The general structure of the model without aqueous-phase chemistry can be found in (Aloyan et al., 2010). The model makes it possible to investigate the variability of gas components and aerosols in the atmosphere, the ion composition of aerosol particles with account of their size distribution, as well as to describe the interaction of gas pollutants with aerosol particles or drops.

2. Model of Gas–Aerosol Transport in the Atmosphere

The meteorological parameters and turbulent characteristics were determined on the basis of a three-dimensional mesoscale nonhydrostatic model of atmospheric processes accounting for thermal and orographic inhomogeneities of the underlying surface as

well as heat- and moisture-exchange in soil. A detailed description of this model can be found in (Aloyan, 2008; Aloyan and Piskunov, 2005).

The equations describing the change of concentrations of gas and aerosol components are written in the form (Aloyan, 2008; Aloyan and Piskunov, 2005; Aloyan et al., 2010):

$$\frac{\partial C_i}{\partial t} + u_j \frac{\partial C_i}{\partial x_j} = F_i^{gas} - P_i^{nucl} - P_i^{cond} + P_i^{chem} + \frac{\partial}{\partial x_j} k_{jj} \frac{\partial C_i}{\partial x_j}, \quad (1)$$

$$\frac{\partial \varphi_k}{\partial t} + (u_j - \delta_{j3} w_g) \frac{\partial \varphi_k}{\partial x_j} = F_k^{aer} + P_k^{nucl} + P_k^{cond} + P_k^{coag} + \frac{\partial}{\partial x_j} k_{jj} \frac{\partial \varphi_k}{\partial x_j}, \quad (2)$$

where $(x_1 = x, x_2 = y, x_3 = z)$, $(u_1 = u, u_2 = v, u_3 = w)$; $(j = 1, 2, 3)$; C_i ($i = 1, \dots, N_g$) and φ_k ($k = 1, \dots, N_a$) are the concentrations of gaseous admixtures and aerosols, respectively; N_g and N_a are the numbers of the corresponding components; w_g is the is the gravitational settling; F^{gas} and F^{aer} are the emissions of gaseous admixtures and aerosols, respectively; P^{nucl} , P^{cond} , P^{coag} , P^{chem} are the operators of nucleation, condensation, coagulation, and photochemical transformation, respectively; k_{jj} is the turbulent diffusion coefficient along x, y, z coordinates, respectively.

To set the boundary condition at $z = h$, the surface resistance of an admixture is represented as the sum of three terms: aerodynamic resistance (r_a); quasi-laminar surface-layer resistance (r_b), conditioned by molecular diffusion processes near the Earth's surface; and surface resistance (r_c), conditioned by processes on the deposition surface.

3. Nucleation

The nucleation model used here is based on the model of homogeneous nucleation in the $\{H_2O-H_2SO_4\}$ system (Vehkamaki et al., 2002). Stratospheric sulfate particles are generated due to low air temperatures. In the troposphere, due to higher (compared to the stratosphere) temperatures, the generation of nucleation-mode particles is governed by higher H_2SO_4 concentrations and relative humidity values. Based on this model, we calculated the nucleation rates (cm^{-3}), radius of critical cluster, and threshold concentration of sulfuric acid. The sulfuric acid concentration had been derived from the chemical model.

4. Condensation and Coagulation

The equation describing the evolution of particle-size distribution through outer and newly formed particles (due to nucleation) can be represented in the following form (Aloyan and Piskunov, 2005) (for the sake of simplicity, the terms of advective transport and turbulent mixing are omitted as they can be found in equations (1)–(2):

$$\frac{\partial \phi_g}{\partial t} + \frac{\partial v_g \phi_g}{\partial g} = J_{nucl}(g, t) + \frac{1}{2} \int_0^g K(g, g_1) \phi_{g-g_1} \phi_{g_1} dg_1 - \int_0^\infty K(g, g_1) \phi_{g_1} dg_1 \quad (3)$$

where g_l is the particle mass, ϕ_g is the concentration of particles of masses between g and $g + dg$, $K(g, g_l)$ is the coagulation coefficient (kernel) characterizing the rate of collisions of particles of masses g and g_l , and $J_{nucl}(\phi_g, t)$ is the nucleation rate. Here, the kernel accounts for diffusion, free-molecular, and transition regimes of particle collisions. The second term in the left-hand side of the equation describes the rate of condensational growth of particles (v_g). The regime of growth and evaporation of particles depends on the ratio of particle size to path length of vapor molecules in medium l_l . The interpolation formula for v_g for an arbitrary regime of exchange between the vapor and particle surface is written as

$$v_g = \frac{\alpha \pi d^2 n V_T g^{2/3}}{4(1 + 3dg^{1/3}/8l_l)} \left(1 - \exp\left\{ \frac{\lambda \theta}{kT} \right\} \left[\frac{g^{1/3}}{g^*} - 1 \right] \right) \quad (4)$$

where d is the particle diameter, α is the accommodation coefficient.

5. Gas- and Aqueous-Phase Chemistry

In the spatially homogeneous case, the gas- and aqueous-phase transport is described by the nonlinear differential equations (Aloyan et al., 2010; Hermann, 2000; Yermakov et al., 2003):

$$\frac{d[C_g^i]}{dt} = w_{gen,g}^i - w_{loss,g}^i - \left([C_g^i] k_i - [C_{aq}^i] \frac{k_i}{K_H^i k_b T} \right) L \quad (5)$$

$$\frac{d[C_{aq}^j]}{dt} = w_{gen,aq}^j - w_{loss,aq}^j + \left([C_g^i] k_i - [C_{aq}^j] \frac{k_i}{K_H^i k_b T} \right) \frac{1}{N_A} \quad (6)$$

where C_g^i and C_{aq}^j are the concentrations of the i -th gas-phase component (cm^{-3}) and j -th aqueous-phase component (mole/l), $i = 1, \dots, N_g$; $j = 1, \dots, N_{aq}$; N_g and N_{aq} are the numbers of species in gas and aqueous phases, respectively, $w_{gen,g}^i$ and $w_{loss,g}^i$ are the generation and loss rates of the i -th component in gas-phase reactions ($\text{cm}^{-3}\text{s}^{-1}$), $w_{gen,aq}^j$ and $w_{loss,aq}^j$ are the generation and loss rates of the j -th component in aqueous-phase reactions (mole/(l·atm)), k_b is the Boltzmann constant, and N_A is the Avogadro number. The transition between gas and aqueous phases is described by the resistance model (Schwartz, 1988). Equations (5) and (6) describe the balance of flows of a given species in the gas and aqueous phases, respectively. The model incorporates 51 aqueous-phase (HO_2 , H_2O_2 , OH^- , H^+ , OH , HO_2^- , HSO_3^- , SO_4^{2-} , O_2 , O_2^- , SO_3^{2-} , SO_3^- , HSO_5^- , O_3 , SO_2 , HSO_4^- , SO_5^- , SO_4^- , SO_3^{2-} , $\text{S}_2\text{O}_8^{2-}$, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})^+$, Fe^{2+} , Fe^{3+} , FeHSO_3^+ , FeSO_3^+ , $\text{FeOHSO}_3\text{H}^+$, FeSOH^+ , FeSO_4 , FeOHSO_3 , NO_2^- , HNO_2 , O_2^{2-} , O_3^- , O^- , CO_2 , H_2CO_3 ,

HCO_3^- , H_2SO_4 , CO_3^{2-} , HNO_3 , HNO_4 , NO_4^- , NO , NO_2 , NH_4^+ , NH_3 , N_2O_5 , NO_3^- , NO_3 , NO_2^- , HNO_2 , H_2O) and 31 gas-phase (CO_2 , SO_2 , HSO_3 , SO_3 , H_2SO_4 , O_2 , O_3 , OH , H , HO_2 , H_2O_2 , NO , NO_2 , NO_3 , N_2O_5 , NH_3 , HNO_2 , HNO_3 , HNO_4 , $\text{O}^1(\text{D})$, $\text{O}^3(\text{p})$, CO , HCO , CH_3O , CH_2O , CH_3O_2 , CH_3OOH , CH_3OH , CH_2OH , CH_4 , CH_3) species. Thus, this is a system of 82 nonlinear nonstationary equations to be solved at each point of the three-dimensional domain.

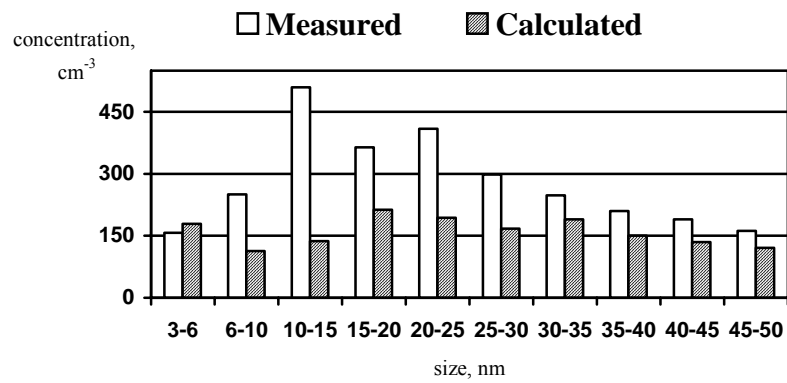
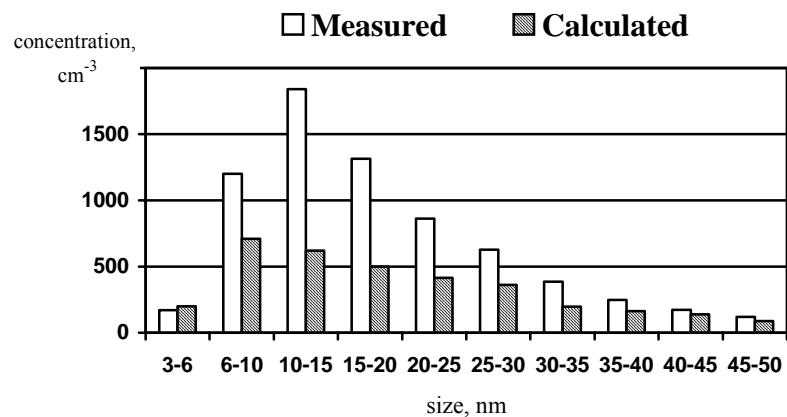
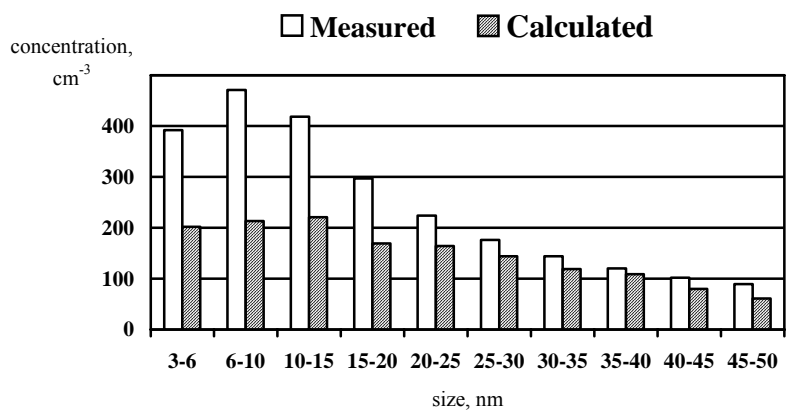
6. Results of Numerical Experiments

Based on the models described above, numerical experiments were performed to reproduce the spatial and temporal variations of gas admixtures and aerosol particles in the Lake Baikal region in Russia. The input parameters are: a modeling domain of 600 x 600 km with a horizontal step size of 10 km, height of 2050 m from the Earth's surface with 20 variable-size vertical steps ($\Delta z = 50$ m for $z \leq 100$ m, $\Delta z = 75$ m for $100 \leq z \leq 250$ m, $\Delta z = 100$ m for $250 \leq z \leq 1450$ m, $\Delta z = 150$ m for $1450 \leq z \leq 2050$ m), time step is 600 s. The initial time of simulations was taken to be 6 h local time. The background wind was $U_b = 4$ m/s and $V_b = 0$ at the upper boundary ($z = 2050$ m). The aerosol size spectrum was divided into 30 size bins in the range from 0.003 to 1.5 μm . The emission sources (SO_2 , NO_x , and CO) from local industrial plants were taken into account.

The algorithm of numerical calculations was as follows. First, the parameters of atmospheric circulation with wind flow and turbulence characteristics were obtained with the help of the hydrodynamic model. Next, in the background of resulting atmospheric circulation, the transport and chemical transformation of gas species was considered resulting in the formation of sulfuric acid vapors and other secondary pollutants. Then, the new-particle formation within the binary $\{\text{H}_2\text{O}-\text{H}_2\text{SO}_4\}$ homogeneous nucleation mechanism was calculated. And, finally, the dynamics of aerosol particles in the atmosphere was simulated taking into account condensation/evaporation and coagulation, as well as chemical processes at the surface of aerosol particles in gas and aqueous phases.

The results of numerical calculations show that the large quantity of SO_2 emitted from local power plants in the Baikal region is converted into H_2SO_4 . Here, the interaction of sulfuric acid and water vapors at low temperatures contributed to the formation of nucleation-mode particles. Then, these particles interact both with one another and with natural aerosol particles. We investigated the variability of gas components in the atmosphere and their content in the drop phase (or, at wet surfaces of aerosol particles). The ion composition of aerosol particles was shown to be essentially variable during the day, depending on the particle size distribution.

We conducted a comparison of the numerical calculations with observation data collected at Listvyanka (NIFHI campaign). Figure 1 shows the results of comparison for particles with sizes in the range between 3 and 50 nm at different time instants: $t = 12$ h (a), $t = 15$ h (b), and $t = 24$ h (c). The model satisfactorily reproduces the formation of nucleation-mode particles from precursor gases. Some discrepancy between calculated and observed values can be explained by uncertainties in the current understanding of appropriate nucleation mechanisms (for example, the involvement of biogenic emissions and ion nucleation, in addition to sulphuric acid and ammonia species).



Comparison between calculated and measured concentrations of nucleation-mode particles in Listvyanka, at $t=12$ h (a), $t=15$ h (b), and $t=24$ h (c).

Table 1 shows the results of comparisons between calculated and measured data of daily -mean content of some ions in aerosol particles in the surface layer of Irkutsk town. In the numerical calculations, the ion composition was calculated by integrating over the entire aerosol size range. It can be seen that the ion composition is generally well reproduced by the model.

Table 1. Comparison between experimental and calculated mass concentrations of aerosol ion composition in the atmosphere of the Baikal region.

ions	calculated ($\mu\text{g}/\text{m}^3$)	measured ($\mu\text{g}/\text{m}^3$)
H^+	0.0024	0.0081
NH_4^+	0.7	0.93
NO_3^-	0.65	0.47
HSO_4^-	2.66	4.33

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