

EXPERIMENTAL STUDY AND NUMERICAL SIMULATION OF AEROSOLS AND GASEOUS POLLUTION IN THE ATMOSPHERE OVER SOUTHERN BAYKAL

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This paper considers the spread of aerosol and gaseous sulfur and nitrogen compounds obtained from experimental data and results of numerical simulation for Baykal Lake region. From measurement results, aerosol mass concentration was estimated, as well as the size spectrum (up to 100 μm) and chemical composition. Using a 3-D numerical model of pollution spread and transformation, averaged fields of sulfur and nitrogen oxides, as well as sulfates and nitrates were calculated that well agree with the experimental data.

Up to date a lot of papers are published devoted to experimental study of atmospheric aerosol in the Baykal Lake region.¹⁻⁷ Since *in situ* experiments are rather expensive, when evaluating anthropogenic impact upon the atmosphere, of significant importance become mathematical simulations along with instrumental research.

Reference 8 briefly reviews the papers dealing with the use of models of aerosol and gaseous pollution spread and transformation over Baykal Lake. Using the Euler type model an attempt was made to estimate the effect of anthropogenic pollution with dust, sulfur and nitrogen oxides on Baykal Lake and its neighboring territories in different meteorological situations⁹⁻¹¹ with regard for the evolution of atmospheric aerosols due to coagulation.¹² It should be noted that all numerical experiments in these papers were done with a 25 km spatial step, that is greater than the average width of ridges in this region. Studies of the spread and transformation of sulfur, nitrogen, and carbon compounds from industrial objects of the Irkutsk-Cheremkhovsk integrated plant, Slyudyanka, and Baykal'sk and their influence on Baykal Lake were made using nonlinear nonstationary 3-D Euler model¹³ verified against the data of field measurements in Baykal region in 1992.⁸ Numerical calculations of the South Baykal pollution with dust emitted from the same enterprises were also done.¹⁴

In this paper we present some results of additional analysis of data obtained in summer of 1991 when conducting complex study of Baykal aerosol.^{6,7} The measurements were done at two stationary sites at the south Baykal coast in Listvyanka settlement and using a mobile facility on a research vessel. Aerosol was sampled upon «Vatman-41» and AFA-KhA-20 filters with a high-volume sampler with air bleeding rate about 0.5 m³/min. To separate the aerosol by size, a

five-stage cascade impactor with quartz resonators as bases and a ten-stage grid diffusion battery of TSI-3040 type were used. Aerosol particle number density for particles smaller than 1 μm in diameter was measured with a TSI-3020 condensation nuclei counter (10% measurement accuracy) and a PKZV photoelectric counter. The technique of size spectrum reconstruction is described in Ref. 6.

Chemical analysis of soluble aerosol fraction after extraction from filters with bidistilled water was performed relative to anions by methods of liquid chromatography with 4-5% error, and to cations by atom absorption methods with 4-6% error.

The processed measurement data on Baykal aerosol were then used to estimate its mass concentration, to obtain the size spectrum up to 100 μm and chemical composition. According to this estimation, the mass concentration of submicron (diameter up to 1 μm) particles averaged over the observation period was 12 $\mu\text{g}/\text{m}^3$, while the concentration of large (diameter greater than 1 μm) particles was about 5 $\mu\text{g}/\text{m}^3$. The analysis of aerosol chemical composition revealed the prevalence of sulfate component among anions (35-40% of total mass) and calcium and sodium among cations.

The dependence of the particle number density on aerosol particle size was found. Two peaks in the diurnal behavior of the aerosol particle number density were revealed, namely, the morning and evening ones. We have shown that it is due to photochemical transformations of gaseous ingredients into aerosol particles and the change of atmospheric boundary layer depth.

All observations over atmospheric aerosol were accompanied with standard meteorological measurements performed at a hydrometeorological network. The analysis of synoptic maps (surface) and

baric topography allowed us to reveal a noticeable prevalence of northwest winds during the observation period. These winds transport pollutants to the lake from industrial enterprises situated along the Angara valley. Such air flows appear, in particular under the effect of high-pressure area over the Enisei upper course. During the complex field measurements three rain periods were observed.

To obtain the spatial field of sulfur and nitrogen compounds in the atmosphere of South Baykal, we used a mathematical model.¹³ The model is based on the solution of semiempirical equation of turbulent diffusion and takes into account chemical interactions of 82 substances. The following system of equations is used as the initial one:

$$\frac{\partial S}{\partial t} + \mathbf{V} \text{grad } S - W_g \frac{\partial S}{\partial x_3} = \sum_{i=1}^3 \frac{\partial}{\partial x_i} K_i \frac{\partial S}{\partial x_i} - A S + F. \quad (1)$$

Here t is time; $\mathbf{V} = (u, v, w)$ is the velocity vector; u and v are horizontal components and w is the vertical component of wind velocity vector along the axes of Cartesian rectangular coordinate system (x_1, x_2, x_3) ; $S = \{S_j\}$ is the tensor of mass concentration of substances under study; $K_1, K_2,$ and K_3 are the coefficients of turbulent diffusion along the axis $x_1, x_2,$ and $x_3,$ respectively; $A(x_i, t) = \{A_{jk}(x_i, t)\}$ is the matrix operator describing the interactions between different substances and their local variations; $i = \overline{1, 3}, \quad k = \overline{1, K};$ $K = (n+1)(n+2)(n+3)/6,$ $F(x_i, t)$ is the vector-function describing sources of pollutants; $W_g = \{W_{gj}\}$ is the tensor of substance precipitation rate due to gravitation; n is the number of substances in a multicomponent medium.

As the initial conditions we took $S_j = 0.$ Boundary conditions have the form:

$$\begin{aligned} \frac{\partial S_j}{\partial x_1} &= 0 \quad \text{at } x_1 = 0, X; \\ \frac{\partial S_j}{\partial x_2} &= 0 \quad \text{at } x_2 = 0, Y; \\ \frac{\partial S_j}{\partial x_3} &= 0 \quad \text{at } x_3 = H, \end{aligned} \quad (2)$$

where $x_1 = 0, x_1 = X; x_2 = 0, x_2 = Y; x_3 = H$ are the boundaries of the area under study. At the level of underlying surface, $x_3 = \delta(x_1, x_2),$ the boundary condition is stated that takes into account substance reflection and absorption depending on the properties of the underlying surface.

To construct the computing algorithm for solution of discrete analogs of Eq. (1) we used the splitting method.¹⁵ At every short-time period a two-stage scheme was considered. The first stage is the transport and diffusion for each substance independently; the second stage is the stage of local

transformations and sources effects, assumes mutual adaptation and interaction of all substances:

$$\frac{\partial S_j}{\partial t} + \sum_{p=0}^n \sum_{q=p}^n \sum_{r=q}^n a_j(p, q, r) S_p S_q S_r = F_j, \quad (3)$$

$$\left\{ \sum_{p=0}^n \sum_{q=p}^n \sum_{r=q}^n a_j(p, q, r) S_p S_q S_r \right\} = A_{jk}, \quad S_0 = 1,$$

$$j = \overline{1, n}, \quad k = \overline{1, K}, \quad K = (n+1)(n+2)(n+3)/6.$$

The method of numerical integration of the system (1) – (3) is described in Ref. 16 in detail.

The main part of our research was the consideration of interaction of different substances in the atmosphere which can be considered as a tremendous oxidizing medium with high content of the main oxidizer – oxygen. The compounds containing atoms of C, H, S, and N of natural and anthropogenic origin when entering the atmosphere transform into stable long-living compounds (for example, CO₂) or short-living substances of acid character (nitrogen and sulfur oxides). Along with the oxygen, ozone O₃, the HO radical, hydroperoxide radical HO₂, organic peroxide radicals (ROO), peroxyacetyl nitrate (PAN), hydrogen peroxide H₂O₂, and nitrate ion NO₃⁻ participate in the transformations. Existing theoretical and experimental results strongly support the key part of hydrogen radicals in the entire complex of problems of atmospheric photochemistry.¹⁷ Most reactive is the HO radical (Ref. 18); it takes part in oxidizing of nitrogen and sulfur oxides into nitrogen and sulfur acids (reactions R25, R28, R42, R149, R153, R154 (Ref. 13), as well as initializes oxidizing of CO, CH₄, C₂H₆, C₃H₈, CH₃CHO, CH₃OH, CH₃SCH₃, C₃H₆, and a number of other components of natural and anthropogenic origin (reactions R47, R57, R65, R71, R74, R82, R83, R87, R99, R101, R105, R125, R129 (Ref. 13)). The HO radical is generated in the troposphere mainly due to reaction R3. Atoms O(¹D) appear as a result of photolysis (R1), therefore the rate of HO generation strongly depends on scattering of solar radiation by clouds.

HO is also generated in O(¹D) interaction with methane (R48). HO₂ radicals are generated in reactions R14, R23, R45, R46, R58, R64, R66, R68, R75, R76, R83, R131, and R154.

Gas-phase photochemical sinks of HO_x in the troposphere are related to reaction in which H₂O molecules are generated (R18, R23, R57). At the same time, the presence of liquid-droplet water results in increasing role of heterogenous processes in destruction of "odd" hydrogen.¹⁷ This means, in particular, that the processes of washing-out of some reservoir components produced with participation of HO and HO₂ in gas phase (reactions R19 and R28) are the sink for HO_x family.

Peroxyacetyl nitrate being the active component of photochemical smog is generated in reaction of acylperoxide radical with nitrogen

dioxide (reaction R92). The nitrate-ion NO_3^- is produced in reaction R29, which results in a sharp decrease in the ozone concentration in cities at night.¹⁹ Stationary concentration of nitrate-ion is determined by equilibrium process of N_2O_5 formation (reactions R35, R39). NO_3^- is rather active and interacts with C-H bonds of aldehydes and aromatic compounds of phenol type with formation of nitrite acid (R62, R89).

We have conducted numerical experiments characterizing the spread of atmospheric pollutants from industrial enterprises situated in south of Irkutsk region. Industrial objects of such towns as Irkutsk, Angarsk, Usol'e-Sibirskoe, Cheremkhovo, Shelekhov, Slyudyanka, and Baykal'sk were included into consideration. The data about the source intensity were presented by the Irkutsk regional committee on ecology and nature exploration. It should be noted that in large cities of middle Russia the total daily amount of sulfur and nitrogen oxides emitted in cold season is 4 to 5 times higher than in warm season.¹⁸

For simulation we chose, the integration domain with $400 \times 250 \text{ km}^2$ area and 2 km high over the underlying surface. The step in time was 300 s, while the horizontal step was 5 km, the vertical steps were set in the following way:

$$\Delta z = \begin{cases} 50 \text{ m} & \text{for } x_3 \leq 300 \text{ m} \\ 200 \text{ m} & \text{--- } 300 < x_3 \leq 500 \text{ m} \\ 1000 \text{ m} & \text{--- } 500 < x_3 \leq 1500 \text{ m} \\ 2000 \text{ m} & \text{--- } x_3 > 1500 \text{ m.} \end{cases}$$

The coefficient of vertical turbulent diffusion was set equal to $10 \text{ m}^2/\text{s}$; $k_1 = (0.5 + \sqrt{\mathbf{V}^2/2}) \Delta x_1 \text{ m}^2/\text{s}$; $k_2 = (0.5 + \sqrt{\mathbf{V}^2/2}) \Delta x_2 \text{ m}^2/\text{s}$. The constants of reaction rates used in our calculations were taken from Refs. 19 – 24.

As a result of numerical experiments performed, we calculated the fields of nitrogen and sulfur oxides, sulfates and nitrates averaged over the considered period of complex *in situ* research. These fields well agree with the measurement results (relative error was below 40%). Figures 1 and 2 show the isolines of fields of sulfates and nitrates surface concentrations.

The calculations made using the model allowed us to evaluate annual mean precipitation of sulfate sulfur and nitrate nitrogen in South Baykal; these amounts were evaluated as 0.32 and 0.06 $\text{g}/(\text{m}^2 \cdot \text{year})$. Note that from the observational data of the snow cover monitoring network for 1987 (Ref. 25) these values for South Baykal are estimated as 0.17–0.33 $\text{g}/(\text{m}^2 \cdot \text{year})$ for sulfur and 0.02–0.04 $\text{g}/(\text{m}^2 \cdot \text{year})$ for nitrogen. The estimates of sulfur and nitrogen precipitation at South Baykal obtained in model calculations are close to the values obtained from measurement data

on precipitation at the territory of the USA and Canada in oak forests in spring–summer season¹⁸ that are respectively 0.323 and 0.091 $\text{g}/(\text{m}^2 \cdot \text{year})$.

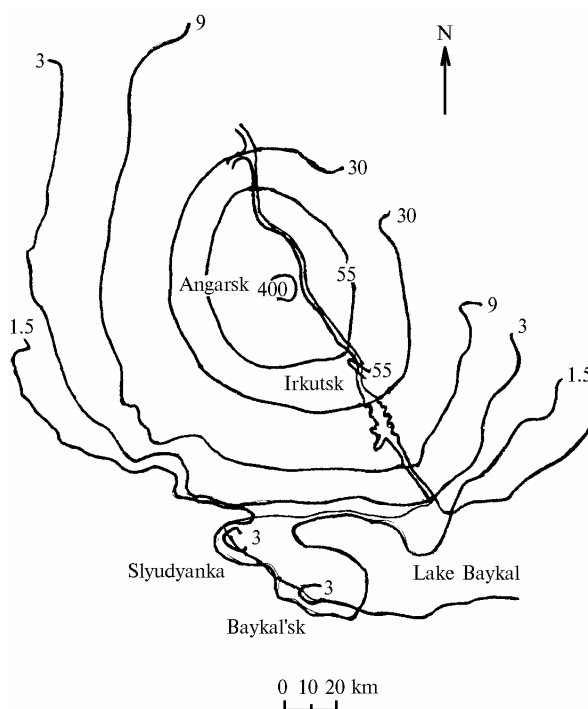


FIG. 1. Isolines of averaged SO_4^{2-} concentration near the underlying surface (in $\mu\text{g}/\text{m}^3$).

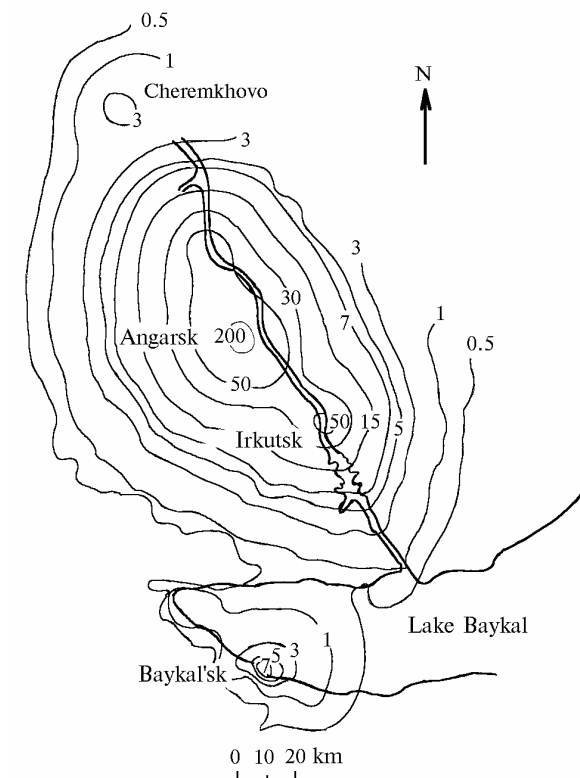


FIG. 2. The same as in Fig. 1 but for NO_3^- .

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