INVESTIGATION OF SULFUR AND NITROGEN COMPOUND DISTRIBUTIONS IN THE ATMOSPHERIC LAYER ABOVE LAKE BAYKAL

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Distribution of sulfur and nitrogen aerosol and gaseous compounds is considered based on the experimental data obtained in the Lake Baykal region and the results of mathematical simulation. A series of numerical experiments has been carried out for verification of mathematical models of the atmospheric pollutant transport.

Aerosol and gaseous compounds of sulfur and nitrogen are the principal components of atmospheric pollution not only near industrial centers, but in clear rural regions of the world as well. So it is necessary to study their transport and chemical transformation under specific physical–geographical conditions. Such a study is of especial interest for the Baykal region in connection with stringent requirements for its environmental protection and its essentially inhomogeneous environmental conditions affecting the spread of pollutants. The final purpose of such investigations should be the creation of adequate mathematical models of formation of the field of concentration of atmospheric pollutants under consideration that can be used to predict the state of an air medium over Lake Baykal.

Transformation of sulfur and nitrogen compounds over Lake Baykal was investigated in Ref. 1 for the analytical models, the balance model with elements of statistics,[2,3] and the two-dimensional stationary diffusion model.[4] The essential disadvantage of these models disregarding local topography is the fact that the vertical distribution of pollutants is supposed uniform.

The Lake Baykal region is characterized by essential orographic and thermal inhomogeneities. To describe the mesometeorological processes, in this paper we propose to use the nonhydrostatic model without simplification of the free convection theory,[5] because the regular observations over water surfaces and almost inaccessible mountain areas are lacking. The velocities of movement and the turbulent characteristics, obtained for the hydrothermodynamic model, were used for calculation of aerosol and gaseous pollutant transport for the three-dimensional nonlinear non-stationary model.[6,7]

Experimental data on sulfur and nitrogen compounds in the atmosphere, available to date, allow one to make the first estimates of adequacy of the proposed models of pollutant transport.

In this paper, we consider the distribution of aerosol (SO_4^{2-} and NO_3^-) and gaseous (SO_2 and NO_2) compounds of sulfur and nitrogen obtained from the experimental data and the results of mathematical simulation and compare them. The results of a survey carried out from on board a research vessel in summer 1992 over the lake water area were used as experimental data. The aerosol was collected on the Whatman–41 filters by means of air pumping by a centrifugal pump with a flow rate of 200 l/min. The time of exposure varied from 10 to 20 hours. Chemical composition of the soluble aerosol fraction was analyzed after its extraction from the filter by bidistilled water using the following techniques: The technique of highly efficient liquid chromatography (with the Millichrom chromatograph) was used to detect anions with an error of 4–7% and the atomic absorption technique (with the AAS–30 device) was used to detect cations[2] with an error of 4–6%.

Values of concentration of sulfur and nitrogen dioxides were measured in the atmospheric layer above water by means of a correlation mass–spectrometer designed at the Central Aerological Observatory (Moscow).[8] The device was regularly calibrated by insertion of an optical quartz cell with the known gas content into a received beam (of scattered solar radiation). The device was certified with an error of 10% for SO_2 in the range of its total content from 5 to 500 ppm·m and 15% for NO_2 in the range from 5 to 150 ppm·m. Meteorological parameters and meteorological visibility range were recorded simultaneously with the measurements.

TABLE I. Mean values of the mass concentration of sulfates, nitrates, and sulfur and nitrogen dioxides in the aerosol over different parts of Lake Baykal, μg/m^3.

Region	SO_4^{2-}	NO_3^-	SO_2	NO_2
Northern Baykal	0.4	0.1	3–11	1–3
Middle Baykal	0.3	0.2	3–10	1–2
Southern Baykal	0.4	0.3	5–15	2–5
Near Baykal'sk	1.6	0.7	10–40	2–10

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The survey was carried out in June and July 1992 practically over all water area of the lake. The totality of 227 aerosol samples was collected and analyzed and 64 series of measurements of gaseous pollutants (SO_2 and NO_2) were carried out (10–15 readings in different directions in each series). Table I presents the mean characteristics of aerosol ion composition and gaseous pollutant concentration in three pats of the lake and near Baykal'sk separately with the Baykal'sk Integrated Pulp-and-Paper Mill (BIPPM) being the most intense anthropogenic source of the aerosol on the lake shore.

A series of numerical experiments was carried out to verify the mathematical model of transport of sulfur and nitrogen compounds from the data of expedition observations in the Lake Baykal region. Industrial objects of Irkutsk, Angarsk, Usol'e–Sibirskoe, Cheremkhovo, Zima, Shelekhov, and Baykal'sk were considered. The data on the intensity of sources were provided by the Irkutsk Regional Committee on Ecology and Exploitation of Natural Resources.

The domain of integration of 400×250 km^2 area and 1 km high above the underlying surface was selected for simulation.

Temporal and horizontal steps were 300 s and 5 km, respectively. Vertical steps were set as follows:

$$\Delta z = \begin{cases} 50 \text{ m} & \text{for } z \le 150 \text{ m}, \\ 150, & 150 < z \le 300, \\ 200, & 300 < z \le 500, \\ 500, & z > 500. \end{cases}$$

Calculations were carried out for June 6–7 and 24–27, 1992 in the atmospheric boundary layer of Southern Baykal.

The small–gradient baric field prevailed above the underlying surface in the Baykal region on June 6 and 7. It caused predominantly anticyclonic circulations and well-pronounced breeze effects were observed. The weather on June 24 and 25 was determined by a deep cyclone moving from northwest to southeast. The wind had the southwest direction as the cyclonic warm sector passed and the northwest direction as the cold sector passed. The small–gradient baric field was set in on June 26 and the local circulations were observed. Table II presents the results of comparison of the calculated and experimental data.

TABLE II. Mean values of concentration of SO_4^{2-} *and* NO_3^-.

Date	Time of averaging (local), h	Filter location	SO_4^{2-} concentration, μg/m³		Relative error	NO_3^- concentration, μg/m³		Relative error
			Measured	Calculated		Measured	Calculated	
6.06	7–15	Baykal'sk	3.9	2.45	−0.37	0.75	0.55	−0.27
6.06–7.06	22–6	Utulik	4.11	2.82	−0.31	0.49	0.62	0.27
24.06	7–21	Kultuk	1.56	1.55	0.01	0.19	0.10	−0.47
25.06	7–16	Kultuk–Baykal'sk	0.74	0.86	0.16	0.16	0.14	−0.12
25.06–26.06	19–17	Baykal'sk–Murino–Baykal'sk	2.17	1.74	−0.20	0.58	0.35	−0.40
26.06	7–21	Baykal'sk	2.56	3.50	0.37	0.83	0.65	−0.22
26.06–27.06	21–6	Baykal'sk–middle of the lake	4.92	3.14	−0.36	1.30	0.65	−0.50

Correlation coefficients between calculated and measured values of concentration are 0.7 for sulfates and 0.8 for nitrates. Relative errors did not exceed 40% for sulfates and 50% for nitrates. The standard deviations of these errors were 30 and 25%, respectively. The greatest differences between calculated concentration values and experimental ones were connected with the effect of remote sources.

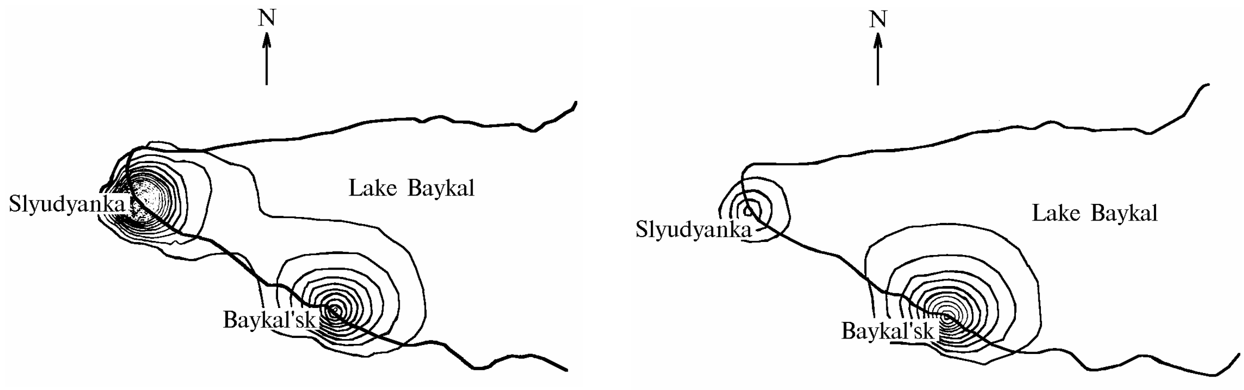
The results of numerical experiments for enterprises of Slyudyanka under typical meteorological conditions are shown in Figs. 1–3.

Experiment No. 1. The small–gradient baric field was set in over Southern Baykal, and windless weather prevails. Isolines of the field of calculated surface concentration of sulfur dioxide are shown in Fig. 1*a* as fractions of the average daily maximum permissible concentration (MPC) being equal to 0.05 mg/m^3. In all figures, the isolines are drawn in 0.1 steps of the average daily MPC of the corresponding ingredient. Zones of enhanced concentration appear in the vicinity of the emission sources. Zones of the enhanced average daily MPC of sulfur dioxide around Slyudyanka and Baykal'sk are 20 and 5 km^2, respectively.

Experiment No. 2. The west wind prevailed that caused the pollutant transport toward the lake water area (Fig. 2*a*). The sulfur dioxide concentration decreases in the vicinity of the emission sources in comparison with experiment No. 1.

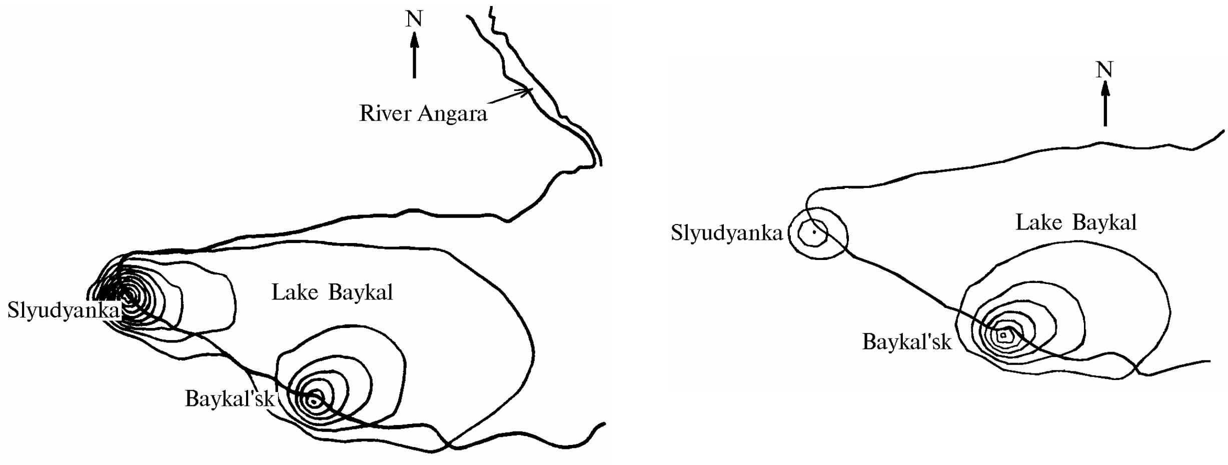
Experiment No. 3. The southwest wind prevailed. The emissions of enterprises of Slyudyanka and Baykal'sk settled almost completely on the open surface of the lake and reached the opposite shore when the sulfur dioxide concentration was equal to 0.1 of its average daily MPC (Fig. 3*a*).

Experiment Nos. 4–6. The nitrogen dioxide distribution over Southern Baykal was studied for the same types of the wind field as in experiments Nos. 1–3. Figures 1*b*–3*b* illustrate the distribution of NO_x concentration for the windless weather, west and southwest wind, respectively, with the NO_x concentration above the average daily MPC being equal to 0.04 mg/m^3 only in calm weather in Baykal'sk on an area of 5 km^2.



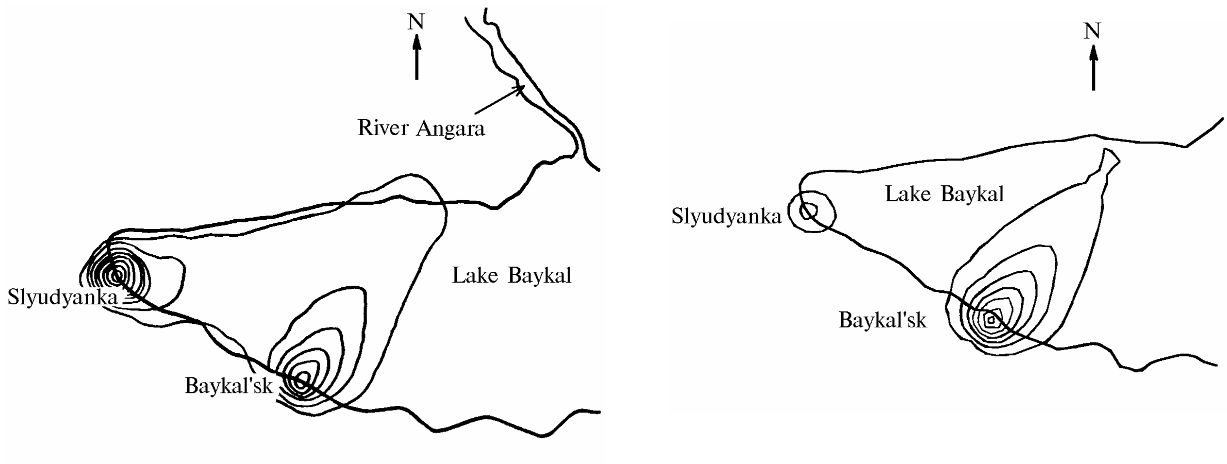
a *b*

FIG. 1. Isolines of concentration in calm weather: a) SO_2, *b)* NO_x.



a *b*

FIG. 2. Isolines of concentration at west wind: a) SO_2, *b)* NO_x.



a *b*

FIG. 3. Isolines of concentration at southwest wind: a) SO_2, *b)* NO_x.

Generalizing the results of our investigations, let us note the following. The prevalent anions are everywhere sulfates, hydrocarbonates, and chlorides. However, their relative contents are different in different parts of the lake. The content of sulfates in southern part is much greater than that of other anions. In addition, the enhanced average background contents of all ions and more pronounced variability of sulfates are observed here in comparison with other parts of the lake, which is connected with additional contribution of anthropogenic sources that are mainly located in the southern part of the lake.

The survey carried out over the water area near the most intense source - Baykalsk - showed a significant excess of concentration of the ions considered here in comparison with their average background level in the southern part of the lake. The relative contents of ions in the aerosol are also different in this region. The anions of sulfates and chlorides predominate.

Na occupies the first place among cations. Such a composition of ions near the BIPPM is connected with application of such substances as NaOH, Cl_2, ClO_2 and H_2SO_4 in the technology of the pull production. It is interesting that the average values of mass concentration of sodium and chloride ions in southern part of the lake are insignificantly different from other ions. This means that the principal contribution of atmospheric emissions of the plant is made up of coarse aerosol fractions that sediment near the source.

Investigations of the chemical composition of atmospheric precipitation carried out earlier show that rain waters in this region become sulfate–sodium in contrast with hydrocarbonate–calcium ones characteristic of the rest part of Baykal.[9]

Being precursors of sulfate and nitrate aerosols, spatial distributions of SO_2 and NO_2 gases reveal the regions of anthropogenic pollution, where the high content of the SO_4^{2-} and NO_3^- ions is observed in the aerosol (see Table I). Concentration of NO_2 increases along the Angara River from Baykal to Irkutsk, but is less than its maximum permissible values for settlements. Nitrogen dioxide often was not recorded in the middle part of the lake due to its low concentration (less than the threshold of its detection).

The verification of mathematical model of pollutant transport in the atmosphere makes it possible to classify meteorological situations and atmospheric pollutant in the lake Baykal region just now.

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