# Dynamics of trace gases in the atmosphere of the Baikal region

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Data on the nitrogen dioxide concentrations in winter 2005–2006 in the vicinity of Irkutsk, obtained using the gas-analyzer, are analyzed and compared with meteorological conditions for the same period. The concentrations of sulfur dioxide and nitrogen oxide in the adjacent to water layer of Lake Baikal vary between 1 and 10 μg/m$^3$. Maximal sulfur dioxide concentrations were recorded in the vicinity of Baikal Pulp and Paper Plant (Southern Baikal). Calculated and measured data on sulfur dioxide and nitrogen dioxide concentrations were found to be in good agreement.

## Introduction

Sulfur dioxide and nitrogen oxides are basic pollutants of the atmosphere, making a harmful impact on the human health and the environment. Participating in photochemical reactions with oxygen and hydrocarbons, these compounds generate other pollutants, such as peroxiacetylnitrates, ozone, etc. It is important to estimate, how these pollutants propagate in the atmosphere, not only around large industrial centers, but also over the background regions, one of which is the Lake Baikal region.

In the recent years, several expeditions were organized to measure $SO_2$, $NO_2$, and NO concentrations in the region of Lake Baikal; rather interesting results were obtained and published.[1–3] The results of measurements were processed with the use of mathematical models of propagation and transformation of impurities.[4] The propagation and transformation of aerosol particles, emitted from five large sources of the Angara region and the Southern Baikal region, were studied with accounting for kinetic processes of condensation, evaporation, and coagulation,[5] where a 10 km step along horizontal coordinates of the grid was used.

## 1. Methods of investigation

The nitrogen oxide and sulfur dioxide were measured in 2005–2006 in Akademgorodok of Irkutsk, in the valley of the river Angara at its left bank, using chemiluminescent gas-analyzers of 310A series. Similar devices were used when measuring pollutants over the water area of Lake Baikal from 9 to 23 June, 2006, along the course of *G.Yu. Vereshchagin* research vessel (Fig. 1). The measurements and recording of results were continual. The device measurement error was 20% at a sensitivity of less than 1 μg/m$^3$. The sampling was made at a 3 m altitude above the water area for to avoid possible impacts of diesel exhausts of the vessel.

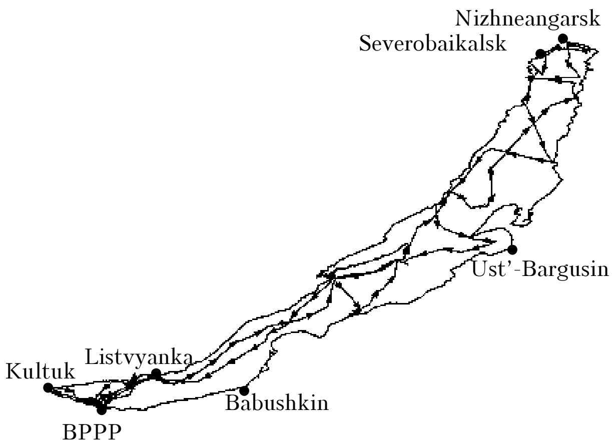


**Fig. 1.** The voyage of *G.Yu. Vereshchagin* research vessel in the Baikal expedition period from 9 to 23 June, 2006.

To investigate the processes of propagation and transformation of aerosols and trace gases in the Lake Baikal water, the nonlinear nonstationary spatial mathematical model of Euler type was chosen,[6] which was earlier used in studies of analogous processes for components emitted by the industrial sources located in the region of Southern Baikal and the valley of river Angara.[7,8] The comparison of calculations with the data of instrumental measurements has shown their satisfactory quantitative agreement.[9]

## 2. Results of field and numerical experiments

Daily variations of nitrogen oxide concentrations were studied with the use of the chemiluminecsent

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gas-analyzer. We have constructed the correlation matrix, which allowed us to distinguish two types of the daily behavior of nitrogen oxide concentrations (Fig. 2), characteristic for urban conditions with continually changing high traffic.

At the warm period, two minima and two maxima are present in the daily behavior of NO concentration (Fig. 2*a*) with morning maximum at 8–9 h. The obtained values are approximately equal to the corresponding values of $NO_2$ for the same time.

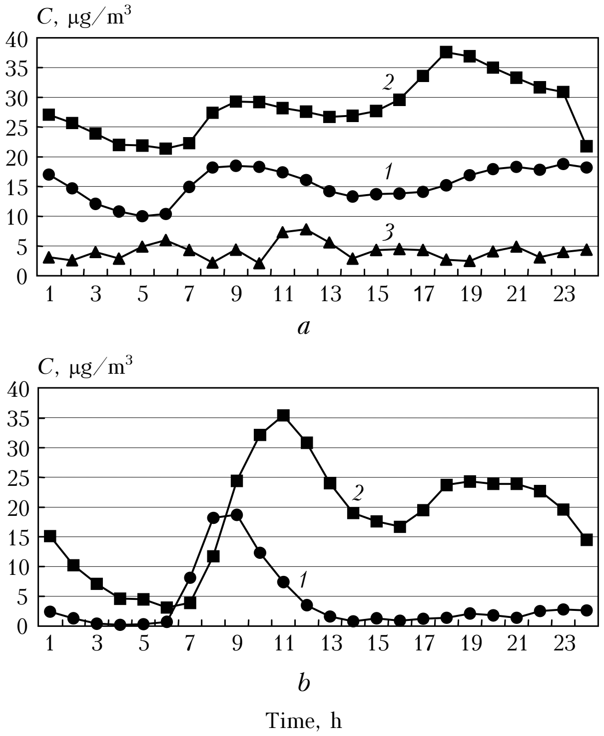


**Fig. 2.** Distribution of $NO_2$ (*a*) and NO (*b*) characteristic for warm (*1* – May–September) and cold (*2* – October–February) periods, as well as over a period of field investigations in the Baikal Region in June, 2006 (*3*).

At the rest of the daily time, the NO concentrations are significantly lower (by about an order of magnitude). Note that the values of calculated correlation coefficients between the daily distribution of $NO_2$ concentration averaged for the period from May to September and the daily distribution averaged separately for each of these months exceeds 0.8 (for NO concentrations – 0.9).

For the cold period (October–February) in the daily behavior of the nitrogen dioxide concentration three maxima and three minima are observed, and for the nitrogen oxide concentration – two maxima and two minima (Fig. 2*b*). The values of calculated correlation coefficients in the period October–February for $NO_2$ exceed 0.85, for NO – 0.8. In general, the observed daily behavior in Irkutsk corresponds to the daily behavior in other cities.[10,11]

Morning and evening maxima of the nitrogen dioxide concentration coincide with periods of the most intensive traffic; the day-time and deeper night minima – with periods of low traffic. The local maximum of $NO_2$ at 1 hour in the cold period can be connected with formation of the ground inversion, favorable for accumulation of nitrogen dioxide in the process of oxidation of NO to $NO_2$ [Ref. 11]. Daily behavior of the nitrogen dioxide concentration in the cold period in Irkutsk coincides qualitatively with the daily behavior of $NO_2$ concentration in the suburbs of Sarvash, Hungary.[12]

Studies of processes of propagation and transformation of nitrogen oxides and sulfur dioxide were continued in the above-water layer of Lake Baikal, where $NO_2$, NO, and $SO_2$ concentrations were analyzed in summer 2005 and in June, 2006. The results of measurements testify that the values of $NO_2$ concentration in the southern and middle basins of the lake in 2006 and 2005 differ slightly. The values of $NO_2$ concentrations did not exceed 10 μg/m$^3$, the nitrogen oxide concentrations were less than 1 μg/m$^3$, and the values for sulfur dioxide did not exceed 5 μg/m$^3$. When approaching the shore, where the impacts of diesel exhausts of the vessel and pollutions of the shore sources influenced, the values of $NO_2$ concentrations increased by 1–2 orders of magnitude (the corresponding values for $NO_2$ approached 300 μg/m$^3$, for NO – exceeded 200 mg/m$^3$). Since in June, 2006 the forest fires were not observed close to Lake Baikal (as opposite to 2005) the values of NO concentrations in the northern basin of the lake differed slightly from the corresponding values in the middle and southern basins. Maximal values of $SO_2$ concentrations, equal to 35 μg/m$^3$, were recorded near the Baikal Pulp and Paper Plant at a distance of 1–4 km under the smoke plume.

The results of instrumental investigations were supplemented with calculations based on the mathematical model of propagation and transformation of impurities. The integration was conducted in the area of 32×6 km$^2$ and at 3 km altitude over the Lake Baikal water surface. Time and horizontal steps were 20 s and 100 m, respectively; vertical steps were set as follows: up to 400 m height the step was equal to 50 m, at a height higher than 400 m up to 1400 m the step was 500 m; up to 2000 m – 600 m, and higher – 1000 m. The initial concentration of molecular nitrogen was taken equal to 0.93 kg/m$^3$, molecular oxygen – 0.297 kg/m$^3$, water vapor – $7 \cdot 10^{-4}$ kg/m$^3$, molecular hydrogen – $10^{-7}$ kg/m$^3$.

The turbulent diffusion coefficients were calculated with the use of relations of semiempirical theory of turbulence. The block of chemical reactions, taken into account in numerical experiments, is given in Ref. 6. As opposite to Ref. 6, we took in calculations the value of the reaction rate constant R27 (photochemical dissociation of $NO_2$), which is equal to $7.8 \cdot 10^{-4}$ s$^{-1}$.

To estimate the value of the turbulent diffusion coefficient at maximal measured $SO_2$ concentrations under the emission plume of the Baikal Pulp and Paper Plant (BPPP), we have conducted a series of numerical experiments. It is difficult to determine the turbulent diffusion coefficient from direct measurements. A combination of model calculations and measurements allowed us to estimate this parameter with a sufficient accuracy.

Figure 3 shows the distributions of calculated values of $SO_2$ concentrations at the west wind velocity of 2 m/s and different values of the horizontal component of the turbulent diffusion coefficient of the impurity in the ground layer.

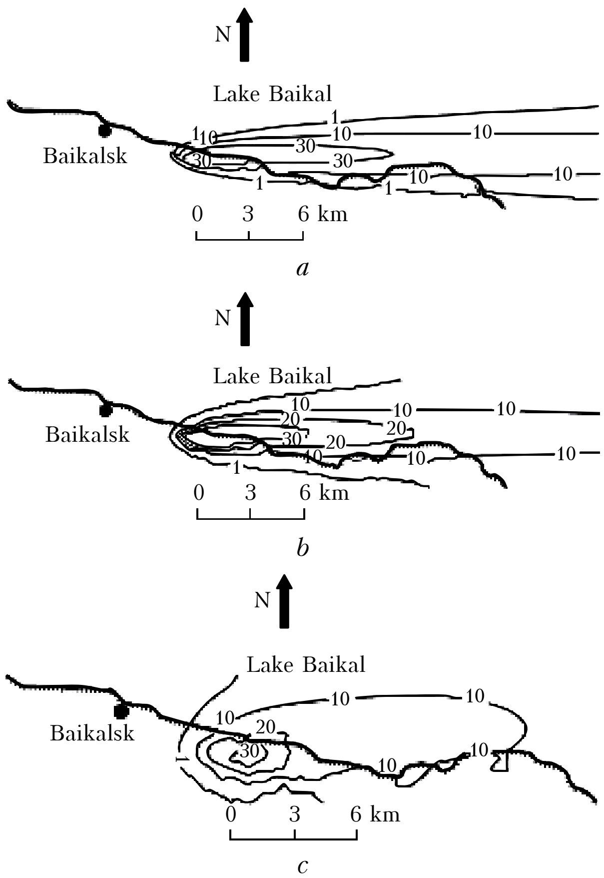


**Fig. 3.** Isolines of calculated values of $SO_2$ concentrations in the vicinity of BPPP at different values of horizontal component of the coefficient of turbulent diffusion of impurity in the ground layer $K_x = K_y$: $K_x = 50$ (*a*); 100 (*b*); 500 $m^2/s$ (*c*).

The values of meteorological characteristics in calculations corresponded to those observed in the expedition on June 12, 2006 in the vicinity of BPPP. The comparison of calculated and measured values of $SO_2$ concentrations are presented in Table.

**Table. $SO_2$ concentration values for the above-water layer of Lake Baikal**

| Number of measurement point | Concentrations, μg/m³ | | | |
|---|---|---|---|---|
| | measured | calculated at $K_x$, $m^2/s$ | | |
| | | 50 | 100 | 500 |
| 1 | 30 | 32 | 28 | 16 |
| 2 | 31 | 33 | 32 | 20 |
| 3 | 35 | 57 | 34 | 19 |

Thus, numerical results have shown the horizontal component of the turbulent coefficient on June 12, 2006 near BPPP to be 100 $m^2/s$ (Fig. 3*b*). Maximal concentrations were observed in the air flow direction. Values of $SO_2$, exceeding 20 μg/m³, were recorded at a distance about 10 km from BPPP, and higher 30 μg/m³ – within 6 km. At weak turbulent processes the impurity cloud was elongated along the wind direction; at distinctly expressed ones the impurity plume blurred.

Figure 3*c* shows isolines of calculated values of $SO_2$ concentration at west wind velocity of 2 m/s and the horizontal component of the turbulent diffusion coefficient of the impurity equal to 500 $m^2/s$. As is seen, a smoother distribution of $SO_2$ concentrations was obtained. The values of $SO_2$ concentrations equal to 30 μg/m³ and more were not recorded over the lake. The plume axis was oriented from the west-southwest to the east-northeast. At further increase of the horizontal component of the impurity turbulent diffusion coefficient the character of $SO_2$ distribution and the values of concentrations virtually did not change. Thus, a comparison of measured and modeled values of $NO_2$ concentrations allowed us to determine more precisely the atmospheric turbulent characteristics, which could not be calculated by direct methods. In fact, the inverse problem was solved.

## Conclusions

When investigating 24-hour concentration variations of nitrogen oxides in 2005–2006 in Irkutsk, two types of daily behavior were revealed. The distribution of concentrations of the first type (May–September) in the daily behavior of $NO_2$ concentrations is characterized by two maxima and two minima, for NO concentrations it is characterized by one maximum and one minimum. At the second type (from October to February), the daily behavior of the $NO_2$ concentration distribution is characterized by three minima and three maxima, and in the daily behavior of NO concentration the distribution, characterized by two maxima and two minima, prevails.

Above the water area of Lake Baikal the daily behavior of $SO_2$, $NO_2$, and NO concentrations for the observation period in June, 2006 was weakly expressed (2–9 μg/m³). This evidences the absence of local sources. The southern basin of the lake, which is under impact of high-power sources of industrial emissions, such as Slyudyanka and Baikalsk, is the most polluted.

The comparison of measured and modeled values of gas concentrations allowed us to estimate the horizontal component of the turbulent diffusion coefficient above Lake Baikal in summer period. Its value varies between 100 and 200 $m^2/s$. The $SO_2$ concentration near BPPP reaches 35 μg/m³.

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