Ozone and nitrogen oxide concentrations in near-surface atmospheric layer of Lake Baikal

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The results of synchronous ozone and nitrogen oxide measurements in near-surface atmospheric layer carried out onboard the *G.Yu. Vereshchagin* Research Vessel in August 2003 are presented. Specific features of ozone and nitrogen dioxide distributions in different regions of Baikal are analyzed. Relatively low ozone concentrations are indicated. Anomalously high nitrogen dioxide concentration is revealed in the South Baikal atmosphere. In North Baikal the nitrogen oxide content is found to be 3 times lower than in South Baikal.

Many-year observations of aerosol and gas admixtures in the coastal region of Lake Baikal in summer period revealed spatiotemporal inhomogeneities in distribution of near-surface concentrations of ozone and nitrogen oxides.[1–5]

Literature data on results of numerical simulation of gas admixture concentration distributions have shown that nitrogen oxide and ozone pollution of the South Baikal atmosphere is caused by advective transport of air masses from industrial centers of the region (Irkutsk–Cheremkhovo and Baikalsk); as well as that the lake south zone is more than an order of magnitude stronger polluted than its middle and north zones.[6,7] *In situ* measurements of gas admixture concentrations over entire Lake Baikal water basin are important because they give an objective estimate of actual Baikal pollution and can be used for validation of the mathematical models.

In this paper we present measurements of concentrations of ozone O_3, nitrogen monoxide NO, and nitrogen dioxide NO_2 in the Baikal near-surface atmospheric layer and analyze specific features of spatiotemporal variability of ozone and nitrogen oxides.

Measurement technique

The measurements were carried out onboard the *G.Yu. Vereshchagin* Research Vessel (R/V) of SB RAS in August, 10–13, 2003, during complex expedition along the ship course presented in Fig. 1 (51°47′–55°42′ N, 103°55′–109°37′ E).

The coordinates of measurement points were determined using ship global positioning system (GPS). The observation points, shown by plus-marked circles, correspond to observations at ship stops of one hour and longer duration. The meteorological parameters (temperature of air and water surface, wind speed and direction, air pressure, and cloud type and amount) were determined every hour with the help of the ship meteorological devices at fixed meteorological sites along the ship course.

The O_3, NO, and NO_2 concentrations were measured continuously using chemiluminescent gas analyzers of ozone and nitrogen oxides as a part of the automated system for recording and statistical processing of gas admixture concentrations.

The measurement range of the 3.02-P1 ozone gas analyzer is 0–500 $\mu m/m^3$ at a relative measurement error of ±15%. The detection limit of both R-310 and 3.02-P1 gas analyzers does not exceed 1 $\mu g/m^3$.

The instruments resided in a laboratory room located in the head part of the ship. Air was sampled through a Teflon tube at a height of 6 m above the water surface.

The measurements, having a discretization period of 1 s and a sample volume of up to 250 000 instant values of O_3, NO_2, and NO concentration, were hourly averaged.

At a ship speed of 16 km/h, the spatial resolution of sampling corresponded to 4 m. The measurement conditions excluded the influence of the engine exhausts (aft-located) at any wind direction and an average wind speed of up to 4 m/s. During long ship anchorages, it faced into the wind.

Instrument calibration and zeroing were performed automatically by an instruction from the microprocessor, using built-in sources of microfluxes.

Discussion of measurement results

To analyze the spatial distribution of ozone and nitrogen oxides over the Lake Baikal water basin, as a function of a set of definite characteristics (anthropogenic source locations, specific features of meteorological and climatic conditions), and to identify the causes of variations of their concentrations, the water basin was conventionally divided into three zones. The first zone, the South Baikal (51°28′–52°35′ N), was a zone with the largest influence of anthropogenic sources; while the second

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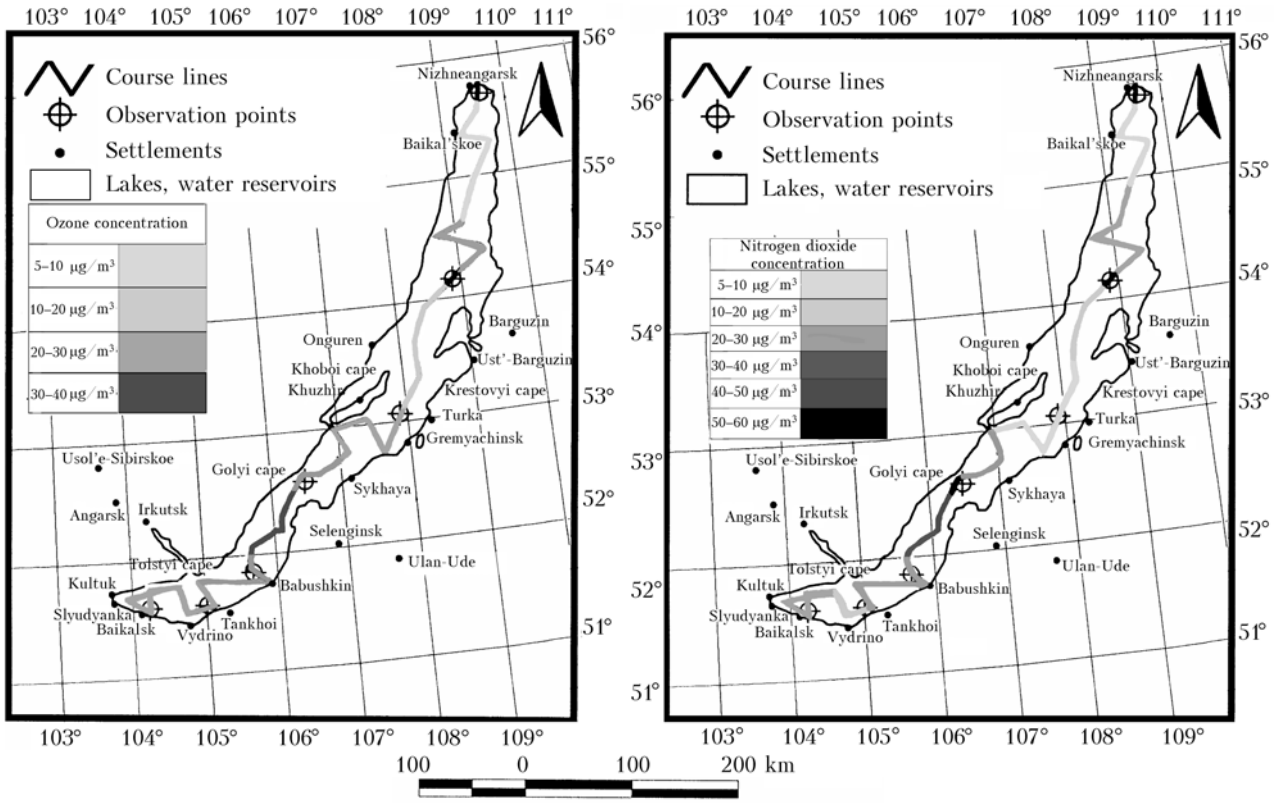

Fig. 1. Schematic map of *G.Yu. Vereshchagin* R/V course.

and the third zones, the Middle Baikal (52°36′–53°48′ N) and the North Baikal (53°49′–55°42′ N), were to a larger degree (depending on climatic and meteorological conditions) under the influence of natural sources of ozone and nitrogen oxides.

As the base data for analysis, 82 hourly mean concentrations of each gas were chosen.

In our estimates of the spatial distribution of the averaged concentrations of O_3, NO, and NO_2 over the Lake Baikal basin, as in Ref. 8, we used the method of arithmetic averaging of hourly mean concentrations of gas admixtures at the points with coordinates (φ_i, λ_i) along the ship course:

$$\overline{x} = \sum_{i=1}^{n} x_i(\varphi_i,\lambda_i)/n,$$

where $x(\varphi_i, \lambda_i)$ are hourly averaged concentrations; φ_i and λ_i are averaged coordinates of the latitude and longitude in hourly air sampling on route; n is the number of hourly mean values of O_3, NO, and NO_2 over averaging interval (0.5° along each coordinate). Within this interval, the hourly mean admixture concentrations were averaged over ~60-km segment in horizontal direction along the ship course. Throughout the course, the interval included approximately 8 hourly mean of O_3, NO, and NO_2 values.

The spatial distribution of average ozone and nitrogen dioxide concentrations in near-surface atmospheric layer of Lake Baikal along the ship course is presented in Figs. 1 and 2.

The obtained average O_3 values indicate that ozone content in the near-surface layer is low throughout the ship course and experiences insignificant spatial variations (Fig. 2). The maximum ozone concentrations were observed in the south zone of Baikal; while the minimal ones were recorded in the north one. The maximal NO_2 concentration was recorded at 52.5° N and 106.3° E, near the boundary between the south and middle zones, and probably can be attributed to influence of a local pollution source. Minimal NO_2 values were observed in the north zone. The largest variations of hourly mean concentrations were recorded in south and middle zones. Figure 3 presents time variations of hourly mean O_3, NO, and NO_2 values. For comparison, some meteorological and hydrometeorological parameters are shown there: the air and water temperatures, wind speed.

For the period of measurements, from August 10 to 13, the weather was fair and sunny. The atmospheric air pressure varied insignificantly, from 974 mbar in the south to 968 mbar in the north. Under these conditions, the hourly mean concentrations of ozone, nitrogen dioxide, and nitrogen monoxide varied in ranges 15–43, 5–61, and 2–8 μg/m^3, respectively.

In South Baikal, a pronounced characteristic of O_3 and NO_2 temporal distributions is a rapid increase of O_3 in the first half of the day with the afternoon maximum; monotonic increase of NO_2 all the day, with the next day maximum at 04 a.m.

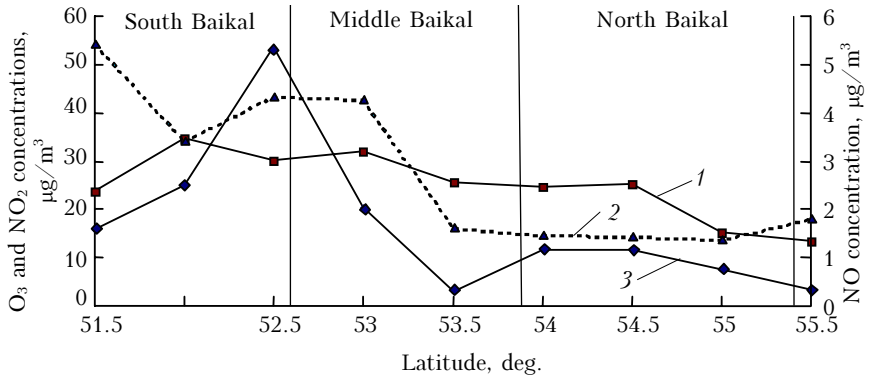

Fig. 2. Spatial variations of ozone and nitrogen oxide concentrations in near-surface layer of Lake Baikal from August 10 to 13, 2003: O_3 (*1*); NO_2 (*2*); and NO (*3*).

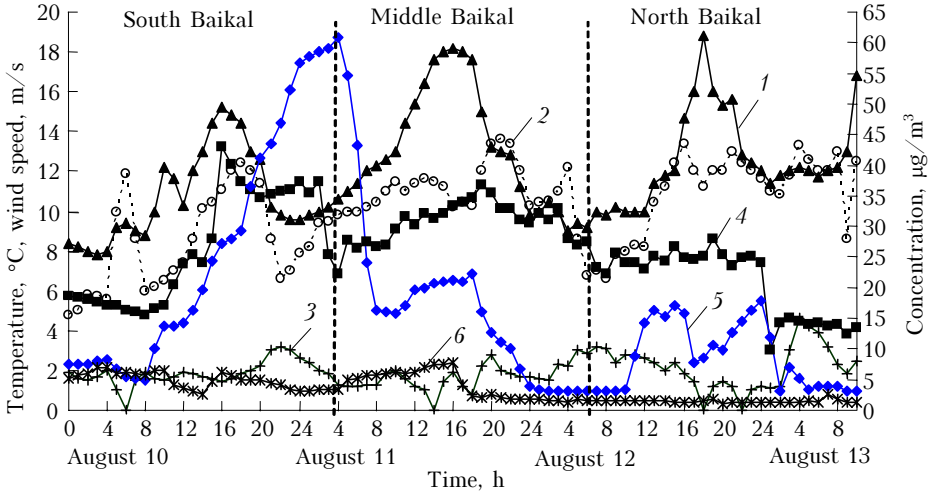

Fig. 3. Time variations of ozone, nitrogen oxides, and meteorological parameters in near-surface atmospheric layer of Lake Baikal: air temperature (*1*), water temperature (*2*), wind speed (*3*); O_3 (*4*); NO_2 (*5*); NO (*6*).

followed by very rapid decrease of concentration in pre-morning hours with the minimum at 08 a.m.

Figure 3 shows almost synchronous increase of O_3 and NO_2 concentrations and the air temperature at daytime hours. A quite strong interconnection between O_3, NO_2, and the air temperature has been revealed, with correlation coefficients equal to 0.852 ± 0.345 and 0.826 ± 0.364, respectively. The observed relationship can be explained[9,10] by the increase of the convective mixing layer height ($H_{m.l.}$) up to the PBL top at an increase of the air temperature at the observation point. Probably, for this reason in our case the maximum O_3 value in the second half of the day (4 p.m.) corresponds to the maximal air temperature. The high correlation between the near-surface ozone concentration and the air temperature in summer period is also presented in Ref. 11.

Since measurements of the mixing layer height $H_{m.l.}$ were not carried out by us, we can only refer to Ref. 2, which shows this parameter for the south zone of Baikal in summer period to be 1800 m at daytime and 1500 m in the evening. Thus, in the first half-day along the ship course in the south zone the ozone and nitrogen dioxide formation and increase in the near-surface air layer are caused by intensification of the turbulent exchange in PBL. Additional photochemical ozone formation at a low nitrogen oxide concentration is hardly possible. Otherwise, the maximum hourly mean O_3 value at a photochemical equilibrium on the plot (Fig. 3) would lead in time the maximal air temperature, i.e., a lower height of mixing layer would correspond to the maximal ozone concentration.

The high correlation coefficient (0.945) between hourly mean concentrations of ozone and nitrogen dioxide at this time is the evidence of these admixtures arrival to observation points inside the same air mass.

In the second half-day (between 04 and 08 p.m.), at a decrease of the near-surface air temperature from 15 to 13°C, the turbulent exchange decays in the upper PBL and the ozone concentration decreases. Further, more rapid decrease of the air temperature leads to the increase of the ozone sink rate, first in the upper part of PBL, and then throughout the PBL height range. As a result, a small secondary maximum is established at 24:00 LT at the observation site. At the same time, slight variations of ozone concentration between 2 and 2.5 μg/m^3 are observed

(see Fig. 3). Possibly, these variations, as was shown in Ref. 12, are caused by changes in the mixing layer altitude structure due to interplay of local circulations. Also, Figure 3 suggests that daytime amplitudes of ozone variations are much larger than nighttime ones, primarily due to more intensive vertical turbulent exchange because of strong temperature inhomogeneity of water surface and near-surface atmospheric layer in the first half of the day. On the contrary, the nighttime ozone variations in marine boundary air layer[13] are several times higher than the daytime variations, being a consequence of intensification of the ozone exchange between troposphere and the boundary layer. The primary mechanism of this exchange is the interaction between the main flow and the mountain circulation, which under tropical conditions is most effective at nighttime.

In the second half-night, after the stable inversion-type stratification is being established, O_3 rapidly drops.

Almost linear growth of nitrogen dioxide concentration between 20:00 and 00:00 LT (see Fig. 3), providing the turbulent exchange between water surface and near-surface air layer on approaching the borderline between the south and middle Baikal zones, suggests a strong effect of a local surface source there. We attempted to explain this by NO conversion into NO_2 during methane emission from the Baikal surface[14,15] via the cycle of reactions[16]:

$$\text{(R1) } CH_4 + OH \rightarrow CH_3 + H_2O,$$
$$\text{(R2) } CH_3 + O_2 + M \rightarrow CH_3O_2 + M,$$
$$\text{(R3) } CH_3O_2 + NO \rightarrow CH_3O + NO_2,$$
$$\text{(R4) } NO_2 + h\nu \rightarrow NO + O,\ \lambda \le 405 \text{ nm},$$
$$\text{(R5) } CH_3O + O_2 \rightarrow CH_2O + HO_2,$$
$$\text{(R6) } HO_2 + NO \rightarrow OH + NO_2,$$
$$\text{(R7) } NO_2 + h\nu \rightarrow NO + O,\ \lambda \le 405 \text{ nm},$$
$$2(NO_2 + h\nu \rightarrow NO + O),$$
$$2(O + O_2 + M) \rightarrow 2(O_3 + M).$$

The main source of OH may be the reactions:

$$O_3 + h\nu \rightarrow O(^1D) + O_2,\ \lambda \le 320 \text{ nm},$$
$$O(^1D) + H_2O \rightarrow OH + OH.$$

Naturally, the emission of methane and nitrogen monoxide under natural conditions of Lake Baikal is much weaker than in smog situations; nonetheless, the mechanism of ozone formation via the above cycle exists.[17] Moreover, the characteristic methane lifetime is rather long, and by some estimates reaches a few years in the lower troposphere. Therefore, it can be supposed that, in the presence of the methane source, it reacts with OH at any time. Unfortunately, the ship has passed the region of the methane-content local anomaly at night, therefore we failed to verify experimentally the supposition of ozone photochemical formation via the above cycle.

Reactions (R3) and (R6) are key chains in the conversion of NO to NO_2; they can proceed also in the absence of solar radiation like the reactions of ozone and nitrogen monoxide in the main cycle, resulting in formation of an additional amount of nitrogen dioxide. This can be deduced from maximum NO_2 in the region of the anomalous methane content (Fig. 2).

In the Middle Baikal, the diurnal dynamics of ozone is less pronounced (Fig. 3). With increase of the distance from the borderline between south and middle zones, the concentration of nitrogen dioxide rapidly decreases. The NO variations during first half-day are considerable and have a noon maximum; however, the hourly mean concentrations are low. For this reason, NO_2 slightly increases at daylight hours. Possibly, such dynamics of nitrogen oxides at low NO_2 values in the morning hours does not favor the photochemical ozone formation.[18]

In daylight hours, the temperature of near-surface air layer practically does not depend on the water surface temperature, and the coefficient of correlation between them is low (0.209 ± 0.374). This is an indication of a significant weakening of vertical turbulent exchange in PBL and a considerable decrease of the mixing layer height.

During the ship movement in the middle zone close to the eastern part of Olkhon island at a distance of up to 10 km off the coastline, the air temperature increase from 15 to 18°C was observed between 12:00 and 16:00 LT at the measurement point, while the ozone concentration increased only by 3 $\mu g/m^3$. This means that during advection within a single air mass, the warmer air contains less ozone than the colder one; therefore, the ozone concentration does not increase significantly in the second half-day. In evening, the decrease of air temperature and increase of wind speed up to 3 m/s indicate an increase of the rate of downward ozone flux from the PBL top and the establishment of O_3 maximum at the observation point by 07 p.m. At nighttime hours, when inversion stratification develops in the near-surface atmospheric layer, a slow sink and deposition of ozone and nitrogen oxides to the water surface take place at the measurement point.

In the North Baikal zone, as compared to the south and middle ones, the spatiotemporal distributions of O_3, NO_2, and NO are characterized by their relatively low concentrations. Considerable variations of air and water surface temperatures all the day do not lead to variations of ozone and nitrogen oxide concentrations; the values of correlation coefficients for the air temperature and O_3 (NO) are insignificant: -0.217 and -0.24, respectively. A significant correlation between O_3 and NO_2, (0.536 ± 0.346), can be explained by the common mechanism of transport to the observation site, namely: advection of gas admixtures from the industrial centers in North Baikal in the case of the northwesterly wind. During night, at 24:00 LT,

when the air mass turns its direction to the northeast and the wind speed increases to 5 m/s, both O_3 and NO_2 rapidly decrease, with nitrogen dioxide concentration dropping almost to zero (see Fig. 3). The presence of these processes at nighttime and morning hours is supported by quite high negative correlation coefficients between wind speed and O_3 NO_2: –0.644 and –0.66, respectively.

Conclusions

Thus, almost all observed variations of gas admixture concentrations along ship course reflect the characteristic features of influence of mesoscale dynamical and local convective processes on the distribution of gas admixtures in atmosphere of Lake Baikal.

In South Baikal, the observed ozone variations under daylight conditions are caused by the vertical turbulent exchange in the atmospheric boundary layer.

The revealed maximum of O_3 at afternoon time, presumably, corresponds to the maximal height of mixing layer equal to 1800 m. Nighttime short-term ozone variations may be due to local (breeze, within-depression) circulations.

The photochemical processes do not play a significant role in additional ozone formation for the measurement period; but local maxima of nitrogen dioxide concentration, revealed near natural pollution sources (methane emission), may indicate that photochemical ozone generation at daytime is possible.

In the Middle Baikal, because of weakly developed turbulent exchange in PBL, the ozone distribution at the measurement site is more uniform, with maximum in evening. When concentration of nitrogen oxides is low, the photochemical processes do not reproduce ozone.

In the North Baikal, the revealed low admixture concentrations of gases, probably, reflect the general regional background for this zone. Because this region is poorly studied, the investigation of the gas admixture distribution mechanisms there is urgent.

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