Specific features of the distribution of near-ground ozone and nitrogen oxide in Baikal region under the effect of photochemical processes

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We present some results on the concentration of near-ground ozone, nitrogen monoxide, and nitrogen dioxide, obtained in Ulan-Ude during the observation period of 1998 and 1999. Generation of ozone in the course of photochemical processes involving nitrogen oxides has been observed on the southeast coast of Lake Baikal. The equilibrium concentration of the photochemical ozone has been estimated. It was found that, in the coastal region of Lake Baikal, the processes of NO_2 formation dominate over photolysis processes.

In recent decade, the study of ozone in the near-ground atmospheric layer has been motivated by negative ozone influence on the biota life activity. According to records of the World Health Organization (WHO), the ozone is being currently included into the top group of five substances on the list of general toxicants.

In addition, the atmospheric chemistry studies have revealed in recent decades that the ozone plays a key role in chemical and photochemical processes in the troposphere, causing and governing the tropospheric oxidation capacity.

On the other hand, it was just the growth of ozone content (by 1 to 3% per year) in the troposphere due to photochemical reactions involving NO_x and other gas admixtures that brought a new quality to the ozonometric observations. Measurements of the ozone concentration at only few stations have been expanded to standardized measurement programs at monitoring network stations. Precise systematization and analysis of large measurement data arrays allow a researcher to draw some, though preliminary, conclusions on the near-ground ozone concentration and its variations in space and time.[1,2]

To study specific features of the ozone variations in the near-ground atmospheric layer, data on concentration of basic chemical species reacting with the ozone, such as nitrogen oxides, must also be available. It is noteworthy, that the concentration of a separate photooxidant does not reflect all the complexity of actual interrelations and mutual conversions. Integrated indices characterizing the situation at a given point at a certain time of the day and season are required.

Regular observations of near-ground ozone (O_3), nitrogen oxides (NO, NO_2), carbon monoxide (CO), sulfur dioxide (SO_2), and suspended particles (aerosol < 10 μm in size) in the atmosphere over Ulan-Ude and coastal region of Lake Baikal (Boyarsk village) have been performed since 1998 and do continue now.

The measurements of a gas admixture concentration were made using automated control and data processing system; it includes chemiluminescent gas analyzers for O_3, NO, NO_2, and SO_2 and electrochemical gas analyzer for CO, and a PM-10 sampler of suspended particles. The measurements and data logging have been done continuously with the discretization time 1 s, sample volume of up to 250000 values, and with the subsequent averaging over 1 hr intervals. The instrument calibration and zeroing was made once every 3 days using test gas mixtures. Thus, close coincidence and high accuracy of measurements was maintained at a proper level necessary in studying interrelations and mutual conversions of gas admixtures in photochemical processes. Simultaneously, meteorological parameters were recorded using M-49 meteorological station.

The main features of seasonal ozone variations in Ulan-Ude (Table 1) include late spring (May) maximum and winter (January) minimum. Average O_3 concentration over the period from October 1998 to July 1999 is 41 ppb, annual amplitude being 65 ppb. Transport of the stratospheric ozone to the troposphere, and development of the photochemical processes of ozone production in the course of increase of solar intensity and daylight hours are, obviously, the cause of the springtime increase of the ozone concentration. High springtime values of the ozone concentration are a consequence of the vigorous photochemical process of ozone formation under conditions of seasonally increasing insolation.

The hourly mean O_3 values experience considerable variations, from 4 to 96 ppb, over a year. The ozone concentration varies most strongly in summer while in winter it experiences the weakest variations. The maximum amplitudes of hourly mean values are observed in May and July (51 and 60 ppb, respectively) and minimum in January (9 ppb).

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Table 1. Monthly mean, diurnally mean (daily mean for May and July), and hourly mean values of near-ground ozone concentration (ppb) in Ulan-Ude in 1998–1999

Month	Concentration				
	Monthly mean	Diurnally mean		Hourly mean	
		max	min	max	min
October	14	17	12	36	4
January	9	12	4	13	4
May	74	92	52	96	45
July	66	79	28	84	24

Photochemical ozone formation in the coastal zone of Lake Baikal

Based on the observational data on the near-ground concentration of ozone and nitrogen oxides (NO_2 and NO) in summer period (July – August) of 1999, we have performed analysis of specific features of the photochemical ozone formation in the coastal zone of Lake Baikal.

The observation site was located in Boyarsk village 500 m away from the coastal line. The measurements of ozone and nitrogen oxide concentrations were performed synchronously and continuously over 20 days. In this study, we have also measured the meteorological parameters. On diurnally mean basis, the daylight portion of the day lasted 8–9 h for the all observation period.

Figure 1 presents variations of the near-ground NO_2, NO, and O_3 concentrations in the coastal zone of Lake Baikal. The daytime values of the near-ground NO_2, NO, and O_3 concentrations were found to be 73, 24, and 20 ppb, respectively.

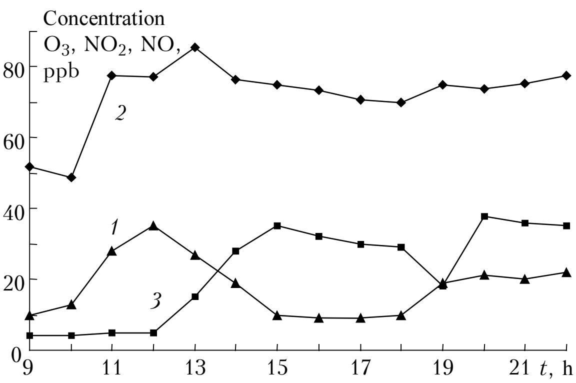

Fig. 1. Diurnal behavior of the near-ground O_3, NO_2, and NO concentrations in the coastal zone of Lake Baikal in August 1999: O_3 (curve *1*); NO_2 (curve *2*); and NO (curve *3*).

In the morning hours, as the solar radiation warms up the soil, the convective fluxes start developing and favor the ozone generation. Between 9 and 12 LT, the increase of NO_2 concentration from 50 to 78 ppb and of ozone concentration from 10 to 35 ppb was observed. At the same time, the NO concentration did not change. This has led to an increase of the $[NO_2]/[NO]$ ratio, suggesting that the ozone concentration can increase due to photochemical reactions. Simultaneously, the air temperature changed from 16 to 25°C, wind speed from 0 to 1 m/s, under conditions of high insolation. In the afternoon (15.00 LT), when airflows changed their direction from northwest to the northeast, the growth of NO concentration to 35 ppb was observed. Probably, the NO increase is primarily caused by the change of admixture emission from anthropogenic sources, located in industrial centers of the region, to the observation site. It should be noted that the atmosphere at this time was characterized by instability, with wind gusts of up to 5 m/s and appearance of clouds. From the plot of diurnal behavior it is seen that for the minimum O_3 concentration of 9 ppb, the corresponding NO value is 32 ppb. These concentrations are observed in the second half of the day at 16:00 LT. Therefore, the process of NO growth is accompanied by the ozone destruction.

Among the photochemical processes involving O_3, NO_2, and NO, one can identify the following three dominating reactions:

$$NO + O_3 \rightarrow NO_2 + O_2, \quad (1a)$$

$$NO_2 + h\nu \rightarrow NO + O, \ \lambda < 420 \text{ nm}, \quad (1b)$$

$$O + O_2 + M \rightarrow O_3 + M. \quad (1c)$$

Subsequently, NO reacts with O_3 to yield NO_2, whose photodissociation then leads to recovery of the NO and O_3 formation. Under these conditions, the cycle of reactions (1a), (1b), and (1c) has a characteristic time on the order of several minutes, and these reactions lead to establishment of the state of photochemical equilibrium (SPE) between O_3, NO_2, and NO.

In a general form, the SPE can be expressed as[3]

$$\frac{[NO_2]}{[NO]} = \frac{1}{J_2} K_1 [O_3], \quad (2)$$

where K_1 is the constant of reaction (1a); and J_2 is the photodissociation rate of reaction (1b).

In a polluted atmosphere, the equality (2) frequently does not hold, because under actual conditions, the O_3–NO_x interaction system involves the products of interaction of CO and hydrocarbons through the reactions[4]:

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2, \quad K_4 = 1.4 \cdot 10^{-13} \text{ cm}^3 \cdot \text{s}^{-1}; \quad (3a)$$

$$HO_2 + NO \longrightarrow OH + NO_2, \quad K_5 = 8.4 \cdot 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}; \quad (3b)$$

$$RH + OH \xrightarrow{O_2} RO_2 + HO_2,$$
$$K_6 = 8.0 \cdot 10^{-15}\ cm^3 \cdot s^{-1}; \qquad (3c)$$
$$RO_2 + NO \longrightarrow NO_2 + HO_2 + carb,$$
$$K_7 = 7.5 \cdot 10^{-12}\ cm^3 \cdot s^{-1}; \qquad (3d)$$
$$HO_2 + NO \longrightarrow OH + NO_2. \qquad (3e)$$

The coefficients K_4–K_7 are taken from Ref. 5. In this scheme, the O_3 formation rate is determined by the reaction of HO_2 with NO (reactions (3b) and (3e)).

Depending on the nitrogen oxide content in the air with increasing NO_x, the ozone formation rate will either decrease ($NO_x > 4$ ppb) or increase ($0.3 < NO_x < 2$ ppb).[6]

At a high relative humidity in the coastal zone of Lake Baikal, the hydroxyl OH is primarily produced by the reaction

$$O(^1D) + H_2O \longrightarrow OH + OH,$$
$$K_9 = 2.2 \cdot 10^{-10}\ cm^3 \cdot s^{-1}. \qquad (4)$$

A significant contribution to OH formation may come from photolysis of formaldehyde (H_2CO) via the reactions[7]:

$$H_2CO + h\nu \longrightarrow H + CHO,\ \lambda = 334\ nm; \qquad (5a)$$
$$O_3 + H \longrightarrow OH + O_2,\ K_{11} = 2.8 \cdot 10^{-11}\ cm^3 \cdot s^{-1}. \qquad (5b)$$

Taking into account the reactions mentioned above, the state of photochemical equilibrium (2) can be represented by the equation

$$\frac{[NO_2]}{[NO]} = \frac{1}{J_2}\left(K_1[O_3] + K_5[HO_2] + K_7[RO_2]\right). \qquad (6)$$

Substituting the known K_1, K_5, and K_7 for measured concentrations of O_3, NO, and NO_2 and NO_2 photodissociation rate (J_2), one can calculate the total concentration of ($HO_2 + RO_2$) and the ozone formation rate as follows:

$$[HO_2] + [RO_2] = \frac{J_2\,[NO_2]}{K_5\,[NO]} - \frac{K_1}{K_5}[O_3], \qquad (7)$$
$$\frac{d[O_3]}{dt} = J_2[NO_2] - K_1[NO]\,[O_3]. \qquad (8)$$

It is assumed that $K_5 \approx K_7 \approx 8.4 \cdot 10^{-12}\ cm^3 \cdot s^{-1}$ (Ref. 8). The J_2 calculation was made using measurement data on hourly mean intensity of the total solar radiation for clear atmosphere from the formula suggested in Ref. 9:

$J_2 = Q_{hourly\ mean} \cdot (5.82 \cdot 10^{-4})$ for the solar zenith angle $47° \le \chi < 64°$.

This formula is valid for any cloudy conditions. For the entire observation period in Boyarsk village, 12 clear days were observed. The intensity of total solar radiation was measured using an AP3 × 3 albedometer.

The mean diurnal behavior of photodissociation rate J_2 for summer period in Boyarsk village is presented in Fig. 2. From comparison of diurnal behavior of ozone concentration and photodissociation rate J_2 it is seen that they have maxima nearly coinciding in time, suggesting photochemical ozone formation in the coastal zone of Lake Baikal.

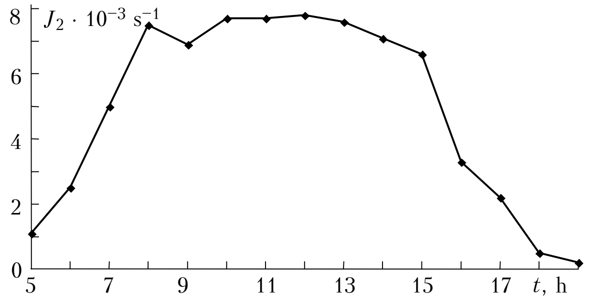

Fig. 2. Diurnal behavior of J_2 based on data of summertime observations (Boyarsk village, summer 1999).

For mean concentrations during summer 1999 under clear-sky conditions in coastal zone of Lake Baikal we have:

$$[NO_2] = 73\ ppb = 18.3 \cdot 10^{11}\ cm^{-3},$$
$$[NO] = 24\ ppb = 6.4 \cdot 10^{11}\ cm^{-3};$$
$$[O_3] = 20\ ppb = 5.0 \cdot 10^{11}\ cm^{-3};$$

$K_1 = 2.2 \cdot 10^{-14}\ cm^3 \cdot s^{-1}$ at air temperature 25°C[5] (Ref. 5);

$J_2 = 3.87 \cdot 10^{-3}\ s^{-1}$ is the mean daytime rate of NO_2 photodissociation.

Thus, we obtain the mean ozone formation rate to be:

$$d[O_3]/dt = 3.87 \cdot 10^{-3}\ s^{-1} \times$$
$$\times\ 18.3 \cdot 10^{11}\ cm^{-3} - 2.2 \cdot 10^{-14}\ cm^3 \cdot s^{-1} \times$$
$$\times\ 6.4 \cdot 10^{11}\ cm^{-3} \times 5 \cdot 10^{11}\ cm^{-3} \approx$$
$$\approx 5 \cdot 10^8\ cm^{-3} \cdot s^{-1} \approx 7\ ppb/hr.$$

Figure 3 shows the diurnal behavior of the hourly mean ($HO_2 + RO_2$) concentrations calculated by the equation of photochemical equilibrium. At high relative humidity ($r = 92\%$) at the coast of Lake Baikal, during first half day there occurs rapid growth of peroxy radicals ($HO_2 + RO_2$) according to reaction (3c) at a relatively low NO concentrations. Maximum ($HO_2 + RO_2$) value was observed at 11:00 LT and was found to be $8.3 \cdot 10^9\ cm^{-3}$.

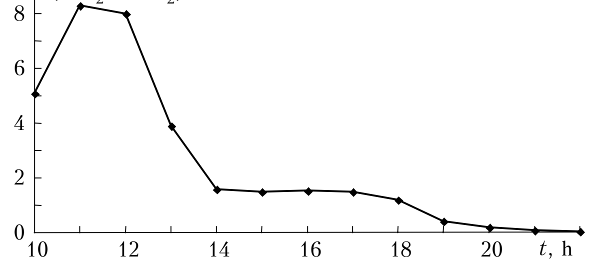

Fig. 3. Daytime behavior of ($HO_2 + RO_2$) concentrations for summer observation period (Boyarsk village, summer 1999).

Table 2

Date	t, hr	$[O_3]$, ppm	$\frac{[NO]}{[NO_2]}$	T, °C	Calculated NO_2 photolysis rate	$\frac{[NO_2]}{[NO_x]}$	Calculated NO − NO_2 transformation rate
07.25	15.00	0.014	0.8	23	0.258	0.55	0.52
07.26	14.00	0.012	1.05	22	0.290	0.486	0.45
07.30	15.00	0.016	0.27	21	0.099	0.78	0.5
08.01	14.00	0.008	1.22	18	0.244	0.499	0.46
08.02	13.00	0.015	1.52	24	0.524	0.4	0.455
08.03	13.00	0.007	0.737	18	0.118	0.585	0.46
08.04	17.00	0.01	0.38	20	0.076	0.72	0.52
08.05	14.00	0.008	0.96	20	0.081	0.7	0.49
08.07	13.00	0.02	1.1	20	0.484	0.47	0.488
08.09	15.00	0.012	0.75	23	0.207	0.567	0.55
08.10	16.00	0.011	1.2	25	0.304	0.45	0.52

A significant contribution to $(HO_2 + RO_2)$ may come from photolysis of formaldehyde via reactions (5). At the average daytime NO concentrations of 24 ppb in Boyarsk village it was determined that:

$$(HO_2 + RO_2) \approx 2.5 \cdot 10^9 \text{ cm}^{-3} \approx 0.094 \text{ ppb} \approx 94 \text{ ppt},$$

$$d[O_3]/dt \approx 7 \text{ ppb/hr}.$$

Calculation of $[O_3]$ formation rate and concentrations of peroxy radicals has shown that their values in the air of Lake Baikal coast are considerable.

High concentration of $[HO_2 + RO_2]$ radicals suggests that the intense hydrocarbon oxidation occurs in the atmosphere of the southeast coast of Lake Baikal, possibly because of high concentration of the OH hydroxyl in the air.

Since $[HO_2 + RO_2]$ measurements were not performed, the results presented in Fig. 3 can be considered as a rough estimate.

The measurements of gas admixtures in the coastal zone of Lake Baikal have shown that the characteristic of interaction between nitrogen oxides and ozone is more complex, and that it cannot be correctly described by relation (8). However, expression (8) can be used to estimate the photochemical ozone sources.

Table 2 presents the results of calculation of NO_2 photolysis rate and the rate of transformation of NO to NO_2 (using formulas presented in Refs. 10 and 11) based on the data of summertime observations in 2000 (July – August).

It should be noted that in this period, atmospheric instability was observed, with frequent change of air masses, clouds, and precipitation.

On clear days, a photochemical equilibrium was observed as well as cases close to this state, what is supported by data of Table 2. Most probable $[NO]/[NO_2]$ concentration ratio was found to be 0.92. Overall, the processes of NO_2 formation dominate over the processes of NO_2 photolysis, probably leading to relatively low O_3 concentrations.

In the summer period, the ozone concentration in Ulan-Ude is much higher than on the coast of Lake Baikal.

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