Experimental studies of trace gases in the atmosphere of arid and semi-arid territories of Mongolia

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Results of experimental studies of diurnal variability of the ground ozone, CO_2 and nitrogen oxides in the atmosphere of arid and semi-arid territories of Mongolia for 2005 and 2006 are presented. Factors, leading to increased concentrations of trace gases, their connection with meteorological and turbulent characteristics of the atmosphere are under analysis.

Introduction

The processes of formation of the chemical composition and spatial-temporal variability of aerosol and gas admixtures in the near-ground atmospheric layer are determined by complicated interaction of admixtures from natural and anthropogenic sources and depend on natural climatic factors determining the specific regime of circulation processes in the considered region. Significant anthropogenic impact of trace gases on the state of environment both in regional and global scales causes a necessity of systematic observations of their content in the atmosphere, especially in its near-ground layer.¹

Ozone plays the key role in chemistry and photochemical processes in the troposphere, and its content is determined by its vertical transfer from upper layers of the atmosphere, as well as its formation in the lower troposphere, resulting from photochemical reactions with participation of nitrogen oxides and volatile organic compounds. In spite of tremendous interest to the study of near-ground ozone, the mechanisms of its variability with accounting for the contribution of anthropogenic and natural factors remains poorly studied.^{2–7}

Therefore, investigations of trace gases and their relations with meteorological parameters of the atmosphere under different natural climatic conditions are of great interest, especially in the atmosphere of regions, difficult of access and poorly inhabited, such as vast arid territories of Central Asia, including the Gobi, where such investigations were not carried out earlier.

Conditions of experiment

Joint Russian-Mongolian experiments on the study of conditions of formation, transformation and transfer of atmospheric admixtures in arid and semiarid regions of the Eastern Gobi were started in 2005 by Department of Physical Problems of Buryatia Scientific Center SB RAS and the Institute of Meteorology and Hydrology of Mongolia in the framework of the Treaty on scientific-technical cooperation.

The desert Eastern Gobi covers the eastern part of the Central Asia. It is a plain lying at the level of 1000 m and more. The Gobi is far from seas and oceans, surrounded by high mountains. The nearest coast of Pacific Ocean is at the distance of 1000 km from the eastern boundary of Mongolia, the ridges surrounding the desert reduce the effect of the ocean to minimum. There are less than 100 mm of precipitations in eastern steppe and submountain plains.⁸

Apart from geographical position, such factors as circulation of air masses, relief of the area, and Solar radiation affect formation of the climate in the region. Ridges of Altai, Khangai, Khantii, and Prikhubsugulia affect the properties of air masses and their circulation. In this connection, general circulation of air masses changes, and local circulations are formed.

Measurements of the trace gas concentrations in the atmosphere were carried out in July, 2005 in the Eastern-Gobi district (st. Sainshand) and in June–July, 2006 at st. Sainshand and in Suhe-Bator aimak of Mongolia (st. Baruun-Urt). The observation stations were situated at territories of Hydrometeorological centers located at significant distances from populated areas. Station Sainshand (44°54' N, 110°07' E) is situated in the arid zone (the Gobi) characterized by the absolute absence of any vegetation cover. The station Baruun-Urt (46°41' N, 113°17' E) is situated in steppe zone.

Round-the-clock continuous synchronic measurements of concentrations of near-ground ozone (O_3) , nitrogen oxides (NO_x) , carbon dioxide (CO_2) were carried out at each site by means of automated system for recording and statistical processing of the measurements. The sampling of air was at a height of

2 m above the ground surface. The automated system included: the chemiluminiscent gas analyzers of ozone "3-02P1", nitrogen oxides "R-310" and optical gasanalyzer "Optogas 500.4" designed by OPTEK (Saint-Petersburg), the block for recording and processing of data. The relative error measurements did not exceed $\pm 20\%$.⁹ The data. in The gasanalyzers were calibrated automatically using the built-in sources of microfluxes. To control the accuracy of measurements of $\rm O_3$ and $\rm NO_x$ concentrations, the calibration by the external calibrator Mod ML 8500 ("Monitor Labs," the USA) was periodically carried out. To measure the instant values of the temperature, humidity, wind velocity, as well as direction and turbulent characteristics of the atmosphere, the automated meteorological station "AMK-03" was used; measurements of radiation characteristics were carried out by means of the autonomous sun photometer SP-7.

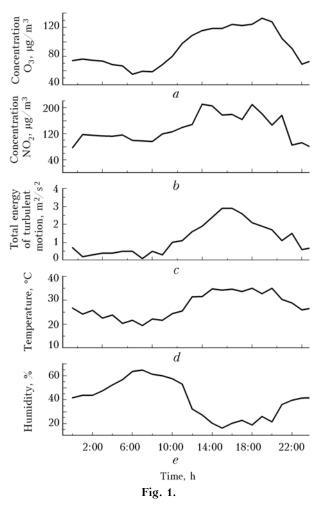
Results of measurements and discussion

Figure 1 presents the daily mean variations of hourly mean concentrations of the near-ground ozone (a), nitrogen dioxide (b), as well as the total energy of turbulent motions (c), temperature and humidity of air (d, e) measured in the region of st. Sainshand in July, 2005.

Comparison of the diurnal dynamics of variations of near-ground ozone and nitrogen dioxide shows that, in general, the characters of variations of their concentrations coincide with each other and are mainly determined by circulation processes. This evidences of a common mechanism of their transfer to the region of observations, obviously, from far distant regions. A quite high correlation between 10-minute average values of ozone and nitrogen dioxide (r = 0.85) was observed during the total period of observations, as well as high concentrations of near-ground ozone.

Diurnal behavior of the near-ground ozone concentration averaged over the total period of observations had a minimum of 55 $\mu\text{g}/\text{m}^3$ in the morning (6 a.m.) at sunrise, then the ozone concentration increased up to $130\;\mu\text{g}/\text{m}^3$ in the daylight time. Maximal values for the total period of observations reached 150–160 μ g/m³. The diurnal behavior of the ozone concentration in the absence of anthropogenic sources of atmospheric pollutions was caused by diurnal dynamics of the mixing layer and the layer of the nighttime temperature inversion near the ground surface. At intensive vertical mixing of air, strongest in the afternoon, ozone of natural origin coming from free troposphere is able to increase the level of the near-ground ozone up to $100-150 \ \mu g/m^3$ [Ref. 3].

Besides, the additional photochemical ozone formation occurs in conditions of enhanced solar activity in the presence of photochemically active reagents, which depends both on meteorological factors and the concentration of pollutants. At quite high observed concentrations of nitrogen dioxide in the atmosphere of the Gobi one should expect intensified processes of NO_2 photodissociation in the daylight time with formation of atomic oxygen and then near-ground ozone.



However, we have not revealed the presence of nitrogen oxides in reactions of photolysis and oxidation with formation or destruction of ozone. Nitrogen oxide, as intermediate product of reactions of photolysis is not observed at st. Sainshand, or its concentration is lower than the gas analyzer R-310 recording threshold; and, taking into account the measurement error, it does not exceed $4 \,\mu\text{g/m}^3$. Perhaps, a quite high rate of formation and oxidation of nitrogen oxide hinders its accumulation in the atmosphere.

The augmented intensity (and the power) of nighttime inversions prevents the income of ozone from the free troposphere to the near-ground layer. This leads to the decrease of the nighttime ozone concentration, its increased sink to the surface, and a decreased ozone lifetime in the near-ground layer. The rate of ozone destruction due to the sink is not as great as in continental regions of tropics and midlatitudes with active vegetation, which is confirmed by relatively high levels of the nighttime ozone concentrations (55 $\mu g/m^3$). Similar behavior of weak destruction of ozone in dry regions, in particular, in the Sahara, was mentioned in Refs. 10 and 11.

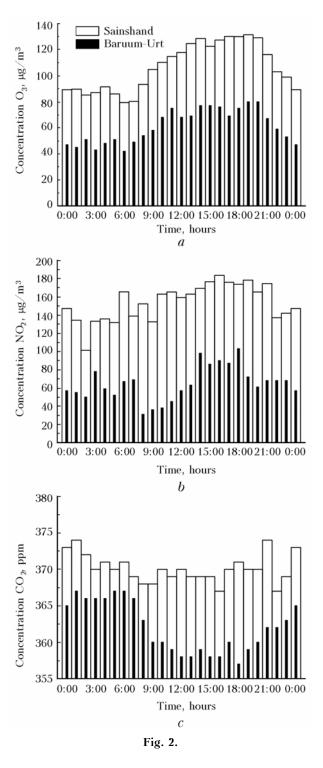
Unfortunately, judging by available publications, data on concentrations of other photochemically active admixtures in the atmosphere of arid territories are practically absent. However, they are needed for comparison and analysis of behavior of the nearground ozone and other trace gases, being the ozone precursors. Perhaps, there exists another source of ozone generation, for example, ozone is generated on the sand surface by some hypothetical mechanism related with static electricity under conditions of the intense solar radiation and weak wind.

The analysis of measurements of the diurnal variability of ozone, nitrogen dioxide, and carbon dioxide at st. Sainshand conducted in summer 2005-2006 has shown that the daily mean concentration of the near-ground ozone in 2006 was by $15 \,\mu g/m^3$ higher than in 2005, nitrogen dioxide – by 19 μ g/m³ higher, and carbon dioxide - by 10 ppm higher. The amplitude of diurnal variations of the near-ground ozone concentration was 52 μ g/m³ (Fig. 2*a*), nitrogen dioxide – 82 μ g/m³ (Fig. 2b) and carbon dioxide – 6 ppm (Fig. 2c) that is, in average, is 1.5-2 times greater than variation of the diurnal amplitudes for atmospheric admixture concentrations, observed in 2005. The differences in the mean values of the atmospheric admixture concentrations in 2005 and 2006 are first of all related with meteorological conditions during the experiments and their effect on the processes of transfer, generation and destruction of ozone.

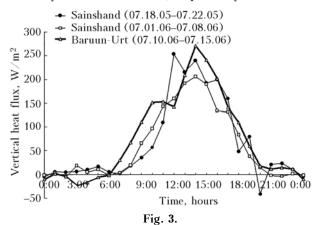
The meteorological conditions in July, 2005 were characterized by clear, dry, and hot weather with a high daily-average temperature up to 38 °C (some days the temperature exceeded 40 °C). Unstable weather was observed in June–July, 2006, the daytime air temperature was quite high, but did not exceed 30–32 °C. Such conditions, due to the increased turbulence, favored more intensive mixing of air masses and the income of ozone from upper atmospheric layers.

The reasons of high concentrations of trace gases in the atmosphere of arid territories are the following: the near-full absence of precipitations in summer, which favors washing-out of admixtures from the atmosphere; the enhanced heating of the ground surface, which does not allow light admixtures to settle to the underlying surface, that, in general, leads to their accumulation in the atmosphere. This is confirmed by Fig. 3, in which the diurnal behavior of the vertical flux of heat between the atmosphere and the ground surface is shown based on the observation data from st. Sainshand and st. Baruun-Urt.

It is seen that maximal development of thermal turbulence (near-ground convection) is observed in daytime hours. At this time, the near-ground air strongly mixes with air from the above layer, and a significant vertical flux of heat directed upward from the underlying surface is observed.



A high correlation between gas admixture concentrations in the atmosphere and meteorological parameters is observed. The correlation coefficients for near-ground values of ozone, nitrogen dioxide, and air temperature are 0.9 and 0.8, respectively. The correlation coefficients for the near-ground concentrations of ozone, nitrogen dioxide and relative humidity are -0.9 and -0.7, respectively.



Investigations of the trace gas behavior were carried out in 2006 at st. Baruun-Urt situated at the same latitude as st. Sainshand but 340 km easterly. According to climatic and natural conditions, st. Baruun-Urt is related to semi-arid territories. The climate here is affected by the Pacific marine air masses.

Analysis of the data on concentrations of trace gases in the near-ground layer of the atmosphere at st. Baruun-Urt has shown that the values of the atmospheric admixtures are significantly lower than at st. Sainshand. For example, the daily mean concentrations of ozone in the near-ground layer of the atmosphere at st. Baruun-Urt are by $45 \ \mu\text{g/m}^3$ less than the daily mean concentrations observed at st. Sainshand, nitrogen dioxide – by 89 $\ \mu\text{g/m}^3$, and carbon dioxide – by 8 ppm (see Fig. 2).

The concentrations of trace gases and the character of their temporal distribution at st Baruun-Urt correspond to the data for continental stations in mid-latitudes.

Observations of the carbon dioxide content in the atmosphere of arid and semi-arid zones show the difference in its diurnal variations. The curves of temporal variability of the CO_2 concentrations obtained on July, 6 and 7 at st. Sainshand and on July, 13 and 14 at st. Baruun-Urt are shown in Fig. 4 for comparison.

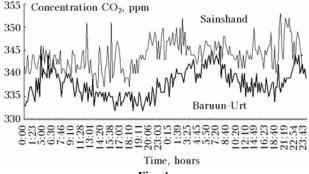


Fig. 4.

It is seen that the diurnal behavior of the carbon dioxide concentrations at st. Baruun-Urt is better pronounced than at st. Sainshand. Its content in the atmosphere at st. Sainshand is higher than at st. Baruun-Urt and comparatively weakly changes during a day, that is related with the absence of the processes of photosynthesis. The content of CO_2 in the near-ground layer of air at st. Baruun-Urt in clear days decreases in the daytime and increases in the night hours due to vegetation, which assimilates CO_2 with participation of solar light.

Conclusions

High concentrations of near-ground ozone, nitrogen dioxide, and other trace gases in the atmosphere of arid territories at the absence of close anthropogenic sources are related mainly with dynamical processes and circulation of air masses in these latitudes, known as "belt of deserts" favoring remote transfer of trace gases, including the territories, which undergone the anthropogenic pollution.

The absence of precipitation, enhanced heating of the underlying ground surface, and vertical convective fluxes during long period of time favor the accumulation of atmospheric admixtures in the near-ground layer of the atmosphere, the intensification of the daytime air exchange between the near-ground layer and above layers, and photochemical generation of ozone, that leads to its high daytime concentrations.

Acknowledgements

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