TIME BEHAVIOR OF THE OZONE AND NITROGEN OXIDES IN THE SURFACE ATMOSPHERIC LAYER NEAR TOMSK

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We analyze the diurnal and annual behavior of the ozone, nitrogen oxide, and nitrogen dioxide based on data of monitoring these components at TOR-station located in Tomsk Akademgorodok. It is shown that balance between O_3, NO, *and* NO_2 *exists during a day. During a year the concentrations of* O_3 *and* NO_2 *vary in antiphase.*

The investigation of the dynamics of ozone and nitrogen oxides is of special interest for two reasons. First, the tropospheric ozone and nitrogen oxides, having strong absorption lines in the solar spectrum, can essentially contribute to the greenhouse effect.[1,2] Second, the ozone and nitrogen dioxide, being the products of photochemical reactions, are toxicants falling in the first and second classes of danger according to the Russian State Standards, what determines their significance in the ecological consequences.

According to data published by Crutzen,[3] photochemical processes in the troposphere start from the photolysis of the available ozone:

$$O_3 + h\nu \rightarrow O_2 + O(^3P), \quad \lambda > 310\ \mathrm{nm},$$

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \quad \lambda < 310\ \mathrm{nm}.$$

Then, up to 90% of the initial ozone content is reduced back[4]

$$O(^3P) + O_2 + M \rightarrow O_3 + M,$$

while rest fraction take part in reactions yielding the hydroxyl

$$O(^1D) + \mathrm{m_2n} \rightarrow 2\mathrm{n\ m}.$$

The hydroxyl can then interact with both organic and inorganic gases.[5–7]

However, interaction of intermediate products with that or other gas depends on the concentration of nitrogen oxides in the atmosphere. According to the Semenov theory of chain reactions,[8] nitrogen oxides act as switches between different reaction cycles. A detailed overview of the possible cycles is presented in Ref. 9.

The source of nitrogen oxides in the atmosphere is evaporation from the underlying surface or anthropogenic activity.[10,11] Nitrogen oxides can exist in the atmospheric air in the following forms: N_2O, NO, N_2O_3, NO_2, N_2O_4, NO_3, and N_2O_5. Among those, NO, NO_2, and NO_3 are free radicals.[12]

Many authors believe that the main source of photochemically active nitrogen oxides is N_2O formed as a result of natural biological processes, which then converts to NO in the reaction:

$$N_2O + O(^1D) \rightarrow NO.$$

Another one source of NO in the atmosphere are combustion processes,[12] that produce the oxide following the scheme:

$$N_2 + O \rightarrow NO + N \quad \text{or} \quad N + O_2 \rightarrow NO + O.$$

In the troposphere NO is converted to NO_2 by ozone or in the following reactions[13]:

$$NO + OH \rightarrow HONO\ ,$$

$$NO + HO_2 \rightarrow NO_2 + OH\ ,$$

$$NO + RO_2 \rightarrow RO + NO_2\ ,$$

where R denotes the organic radical.

At NO concentration higher than 1 ppm, the reaction

$$2NO + O_2 \rightarrow 2NO_2$$

may occur.[14] Under conditions close to the background ones or in regions with low pollution, the main role of nitrogen oxides is that in most cases they favor establishing the photochemical equilibrium between NO, NO_2, and O_3 during daytime[15,16]:

$$NO + O_3 \rightarrow NO_2 + O_2\ ,$$

$$NO_2 + h\nu \rightarrow NO + \mathrm{n}\ , \quad \lambda < 395\ \mathrm{nm},$$

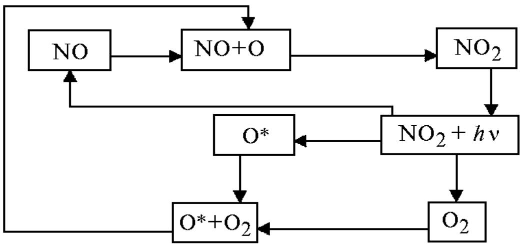
$$\mathrm{n} + \mathrm{n}_2 + \mathrm{l} \rightarrow O_3 + \mathrm{l}\ .$$

In this case the balance between gases is described by the following relation[16]:

$$B = [J_{NO_2}\ (NO_2)]/[k_1\ (NO)\ (O_3)] = 1\ ,$$

where k_1 is the reaction rate constant and J_{NO_2} is the frequency of the NO_2 photolysis.

Schematically it can be presented as follows:



One can see from this scheme that in the absence of other substances the nitrogen oxides and ozone are in constant interaction, which can be broken by termination of the UV radiation influx due to appearance of additional sinks.

The presence or absence of this equilibrium can be easily checked using measurement results. When the equilibrium exists, only single maximum is observed in the diurnal behavior of both NO and O_3. The maxima are somewhat displaced in time,[16,17] what reflects the rate of inflow of substances into the atmosphere and their transformation.[18] If no photochemical equilibrium occurs, the diurnal behavior of NO, O_3, and NO_2 concentrations is much more complicated,[19] what is an indication of smog situations.

At the Institute of Atmospheric Optics of SB RAS, continuous monitoring of ozone and the components of ozone cycles has been being carried out since 1992. Therefore, enough data have already been compiled up to now to check what cycles predominate in the region under study.

The measurements are performed with 3–02P and R310–31 OPTEK ozonometers. These instruments employ the chemiluminescence principle; they allow one to carry out measurements accurate to 12–15%. The detection threshold is 1 μg/m^3 (for O_3), 0.1 μg/m^3 (NO), and 0.2 μg/m^3 (NO_2).

Gas analyzers are among the equipment of the automated TOR-station operating every hour whole day round.

Figure 1 shows the monthly mean diurnal behavior of O_3, NO, and NO_2 recorded in June of 1998 at the TOR-station.

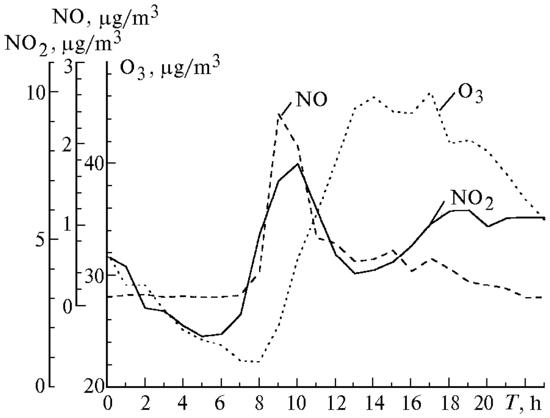


FIG. 1. Monthly mean diurnal behavior of the ozone, nitrogen oxide, and nitrogen dioxide near Tomsk in June, 1998.

It is seen from Fig. 1 that in night-time the ozone destruction occurs, causing reduction of the ozone concentration by the morning hours (8:00 L.T.). The sunrise and correspondingly the start up of the nitrogen oxide inflow into the atmosphere in this period take place at 3:00–4:00 L.T. Therefore, disbalance is greatest in the morning, what manifests itself in the maximum of NO concentration at 9:00 and that of NO_2 at 10:00 as shown in Fig. 1. Obviously, the most probable reaction during this period is interaction of NO and OH as demonstrated by the time shift between maxima in the NO and NO_2 concentrations. The photochemical equilibrium among NO, NO_2, and O_3 molecules establishes as the ozone concentration increases. The concentrations of NO and NO_2 decrease, what is apparently not only because of the balance between them, but also due to the outflow of the reaction products into the upper layers through turbulent mixing.

In the evening hours, when the processes of NO evaporation and NO_2 photolysis weaken, the reaction of NO oxidation to NO_2 with constant consumption of O_3 and NO begins to predominate.

The data presented agree well with the results obtained in other regions,[15–19] where other components of ozone cycles were monitored and no photochemical smog occurred. It allows a conclusion to be drawn that monitoring at the TOR-station is carried out under the conditions close to the background ones with no smog situations, at least in summer.

As was mentioned above, O_3 and NO_2 are the secondary toxicants, for which the State Standard establishes the maximum permissible concentrations. Moreover, their effects may sum up. Therefore it is worth to consider the dynamics of these components for a longer period.

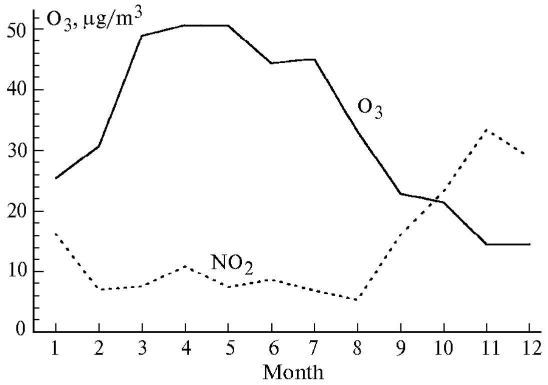


FIG. 2. Annual behavior of the ozone and nitrogen dioxide near Tomsk in 1997.

It is seen from Fig. 2 that the concentrations of ozone and nitrogen dioxide vary in antiphase during a year. The O_3 concentration is maximum from spring to summer (from March to July) and minimum from fall to winter (from November to December). The situation with nitrogen dioxide is just the opposite: it reaches maximum from fall to winter (from September to January) and minimum from spring to summer (from February to August).

Thus, the total concentration ($O_3 + NO_2$) is almost constant during a year, what is indicative of no photochemical smogs in the region. Similar annual behavior of O_3 and NO_2 was observed at the territory of Ukraine,[20] Germany,[21] and some regions of Great Britain.[17] This can be explained by seasonal inflow of the ozone-producing substances into the atmosphere and by an increase in the outflow of reaction products into the upper layers in summer.

Summarizing, we can conclude that near Tomsk there occurs the balance between concentrations of ozone and nitrogen oxides established during daytime. During a year their contents vary in antiphase depending both on the seasonal dynamics of inflow of the ozone-producing substances into the atmosphere and on the intensity of vertical mixing processes.

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