

# The NO<sub>x</sub>-Limiting Regime of Photochemical Ozone Generation in a Weakly Polluted Convective Boundary Layer: Observations at the ZOTTO Tall Tower Observatory in Central Siberia, 2007–2015

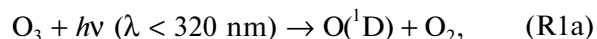
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**Abstract**—Estimates of the photochemical ozone generation rate,  $P_O$ , and the ozone production efficiency (OPE) per molecule of NO<sub>x</sub> (=NO + NO<sub>2</sub>),  $\Delta P$ , are obtained for the region of Central Siberia based on near surface observations of the concentrations of ozone (O<sub>3</sub>) and nitrogen oxides (NO and NO<sub>2</sub>) at ZOTTO (Zotino Tall Tower Observatory) in 2007–2015. The experimental data are approximated well by the power dependences  $P_O \propto [\text{NO}_x]^{-n+1}$ ,  $\Delta P \propto [\text{NO}_x]^{-n}$ ,  $n = 0.82 \pm 0.06$  (the determination coefficient  $R^2 = 0.66$ ), which correspond to the NO<sub>x</sub>-limiting regime of ozone generation in a weakly polluted air mass. The average value for the summer months  $\Delta P \sim 30.0\text{--}43.7$  [mol.O<sub>3</sub>/mol.NO<sub>x</sub>] agrees with the OPE value of 39.8 [mol.O<sub>3</sub>/mol.NO<sub>x</sub>] obtained from the numerical experiments using the GEOS-chem global transport-chemical model. The observation data indicate the significant role of anthropogenic emissions of NO<sub>x</sub> in the regional ozone balance and the necessity of taking this factor into account in predicting ecological risks in the Siberian regions that are traditionally regarded as ecologically pure.

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(1) The content of tropospheric ozone (O<sub>3</sub>) is among the most important factors that determine the level of anthropogenic contamination of the air [1] and the atmospheric budget of climatically significant trace gases, including volatile organic compounds (VOC), carbon monoxide (CO), and methane (CH<sub>4</sub>) [2, 3]. The photochemical lifetime of the stated compounds is limited by the rate of their reaction with the hydroxyl radical, OH, that initiates the oxidation of CO and hydrocarbons by the radical-chain mechanism with the involvement of the family of odd nitrogen NO<sub>x</sub> (=NO + NO<sub>2</sub>). An important reaction of the chain initiation (origination of free radicals) is photolysis of O<sub>3</sub> in the presence of water vapor:



Ozone production occurs in the cycles of chain continuation as a result of photolysis of nitrogen dioxide (NO<sub>2</sub>) formed in the reactions of NO with the hydrogen dioxide radical (HO<sub>2</sub>) and organic peroxy radicals (RO<sub>2</sub>) [4]:

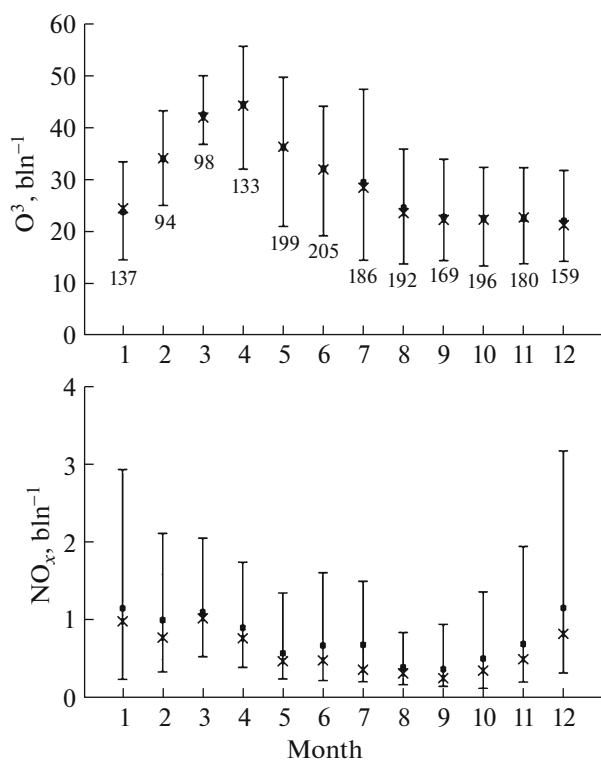


where RH are the primary VOC and R is a hydrocarbon radical. The presence of nonlinear inverse relationships in the O<sub>3</sub>–HO<sub>x</sub>–NO<sub>x</sub>–VOC system is one of the most important properties of the atmospheric photochemical system (APS), which makes it urgent to study the reactions of the tropospheric ozone field to the emissions of its major precursors, VOC and NO<sub>x</sub> [5].

(2) An analysis of the sensitivity of the ozone field in the lower troposphere in the European part of Russia (EPR) and in Siberia to the regional emissions of the precursors of O<sub>3</sub> was performed in [6] based on numerical experiments with the GEOS-chem global

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**Fig. 1.** Seasonal variation in  $O_3$  (maximum daytime, 10:00 a.m.–6:00 p.m., hourly average values) and in  $NO_x$  (during the hours corresponding to the daytime maximum of  $O_3$ ), according to the measurements at ZOTTO in 2007–2015. Monthly statistics: average (■), median (×), interval of  $P_{0.5}$ – $P_{9.5}$  (I), total quantity of values used in the calculations (numbers in the upper plot).

transport-chemical model (TCM) [7] using the latest databases for anthropogenic and biogenic sources of atmospheric pollution. A strong dependence of the photochemical ozone production value ( $\Delta[O_3]$ ) in the summer months on the air mass age estimated by the ratio of  $NO_x$  to the total reactive nitrogen  $NO_y$  ( $=NO_x +$  oxidation products) was demonstrated. The atmospheric response in the ozone field to anthropogenic emissions of  $NO_x$  was  $\Delta[O_3] = 10$ – $12$   $bln^{-1}$  on average or  $\sim 30\%$  from the background concentration of  $O_3$  in the summer months at mid-latitudes over the continent ( $35$   $bln^{-1}$ , Fig. 1 from [6]), which indicates the significant role of the anthropogenic factor in regional photochemistry. However, it is extremely hard to perform experimental verification of the obtained results due to strong limitation of representative data for the background composition of the air for the territory of Russia.

In this work, the quantitative analysis of the  $O_3$ – $NO_x$  relationship was performed using the data of observing  $O_3$ ,  $NO$ , and  $NO_2$  at the Zotino Tall Tower Observatory (ZOTTO,  $60^{\circ}47'$  N,  $89^{\circ}21'$  E, 300 m A.S.L.) in Central Siberia in 2007–2015 (Fig. 1). The observatory is located at the base of the Middle Yenisei

Observatory Station of the Institute of Forests, Siberian Branch, Russian Academy of Sciences, 500 km north of Krasnoyarsk in the taiga zone far from large populated areas and industrial facilities. The works include year-round monitoring of the surface concentrations of  $CO_2$ ,  $CH_4$ ,  $CO$ ,  $NO$ ,  $NO_2$ , and  $O_3$ , measurements of the isotopic composition ( $^{13}C/^{12}C/^{14}C$ , etc.) of the basic greenhouse gases, and estimation of carbon flows in the key ecosystems of the region under study ([www.zottoproject.org](http://www.zottoproject.org)). The background character of the station makes it also possible to measure quantitatively the contribution of long-range transport of long-lived precursors of ozone,  $CO$ , and  $CH_4$ , to the regional balance [9–11].

According to [6], the anthropogenic emissions of  $NO_x$  are dominant in the regions of West and East Siberia (0.6 Tg N per year) compared to the other surface sources, biogenic emissions (0.3 Tg N per year), and biomass burning (0.1–0.2 Tg of N per year). The occurrence of a significant anthropogenic signal in the data of  $NO_x$  measurements at the Tall Tower Observatory was established earlier based on the results of calculating the ensembles of inverse trajectories during advection of about 1–2 days [12]. Following [2], we determine the ozone production efficiency (OPE)  $\Delta P$  for one molecule of  $NO_x$ , as a ratio of the ozone accumulation rate  $P_Q$  ( $=P_{O_3} - L_{O_3}$ ) to the photochemical flow rate of  $NO_x$  ( $L_N$ ):

$$\Delta P = \frac{P_Q}{L_N} = \tau_N \frac{P_Q}{[NO_x]_e}, \quad (1)$$

where  $\tau_N = (\partial L_N / \partial [NO_x])^{-1}$  is the lifetime of  $NO_x$ ,  $[NO_x]_e = E_N \tau_N$  is the concentration of  $NO_x$  on the assumption of the photochemical equilibrium between the sources ( $E_N$ ) and flows ( $L_N$ ) of  $NO_x$ , and  $P_{O_3}$  and  $L_{O_3}$  [ $mol\ s^{-1}$ ] are the rates of photochemical formation and destruction of  $O_3$ . Under the conditions of a convective boundary layer (CBL) developed above the horizontally homogenous surface, the daytime increase in ozone ( $\Delta[O_3]$ ) is almost totally determined by its photochemical production [2]; in this case, the contribution of the processes of transport and sedimentation in the first approximation can be neglected, whence it follows that

$$\Delta P \cong \frac{\tau_N}{[NO_x]_e} \frac{\Delta[O_3]}{\Delta t}, \quad (2)$$

where  $\Delta[O_3]/\Delta t$  is the average value of  $P_Q$  during the time  $\Delta t$ . Assuming that during the daytime the main flow of  $NO_x$  occurs primarily by the triple reaction (R5) with the formation of nitrogen acid [1, 13],



we obtain the estimate  $\tau_N \approx k_7 \cdot [OH] \cdot [M]$ , where  $k_7$  is the coefficient of the reaction calculated by [8],  $[M]$  is the concentration of air molecules, and  $[OH]$  is

the average daytime concentration of hydroxyl in accordance with the calculations by the GEOS-chem TCM.

(3) For the calculations of  $\Delta P$  and  $P_Q$ , we used the average hourly concentrations of O<sub>3</sub>, NO, and NO<sub>2</sub> at a height of 4 m above the ground, which were obtained based on the initial one-minute series of observations in the summer months of the stated period. The ozone concentration was measured by a Dasibi 1008AH-type gas analyzer, the measurement range was 1–1000 bln<sup>-1</sup>, and the total error was  $\pm 1$  bln<sup>-1</sup>. The concentrations of NO and NO<sub>2</sub> were measured by a Thermo Fisher Scientific TE42C-TL device, and the minimum detectable concentration was 0.05 bln<sup>-1</sup>. To remove the influence of local sources of NO related to the infrastructure facilities and transport, the initial data were filtered by the criterion of  $[\text{NO}]/[\text{NO}_2] < 0.2$ . Additionally, we applied the data on the value of the total cloud cover ( $N_c$ , %) and the maximum daytime temperature of the air ( $T_m$ ) based on the observations at the Vorogovo meteorological station (~40 km northeast of ZOTTO) ([https://rp5.ru/weather\\_archive\\_in\\_Vorogovo](https://rp5.ru/weather_archive_in_Vorogovo)).

To obtain stable quantitative estimates by formula (2), we considered the subset  $\mathbf{P}_a$  of photochemically active days (283 days over all summer months of the observation period under study) that satisfy the criteria  $T_m > 20^\circ\text{C}$  and  $N_c < 30\%$ . The value of photochemical ozone production,  $\Delta[\text{O}_3]$ , was calculated for each day as the difference between the corresponding maximum average hourly concentrations from 02:00 p.m. to 07:00 p.m. and in the morning hours from 09:00 a.m. to 11:00 a.m. local time.

(4) The data from  $\mathbf{P}_a$  are in general characterized by steady diurnal variations in O<sub>3</sub> and NO<sub>x</sub> (Fig. 2) with the maxima before evening and in the morning, respectively. The occurrence of the morning (7:00 a.m.) minimum of ozone is determined by its subinversion flow on the underlying subsurface at nighttime, as well as by the contribution of the NO + O<sub>3</sub> reaction at an increase in the content of nitrogen monoxide in the air in the morning hours due to partial photodissociation of NO<sub>2</sub> and members of the NO<sub>y</sub> (NO<sub>3</sub>, HNO<sub>4</sub>) family that perform the role of reservoir compounds at nighttime. The maximum of the diurnal variation in O<sub>3</sub> is recorded before evening (5:00 p.m.), when the ozone production rate is equated by its chemical flow in the reactions with NO, dry sedimentation, and photodissociation. The diurnal maximum of NO is reached at 10:00 a.m.; in the next few hours, the growth of the concentration of peroxide radicals leads to a redistribution between the members of the NO<sub>x</sub> family towards the increase in the NO<sub>2</sub> content with the subsequent photochemical ozone production (reactions R3, R4) [2].

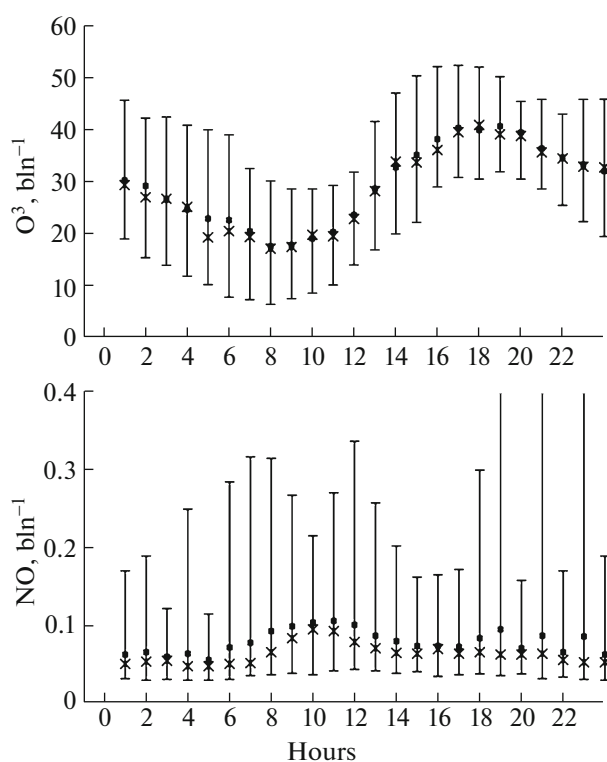


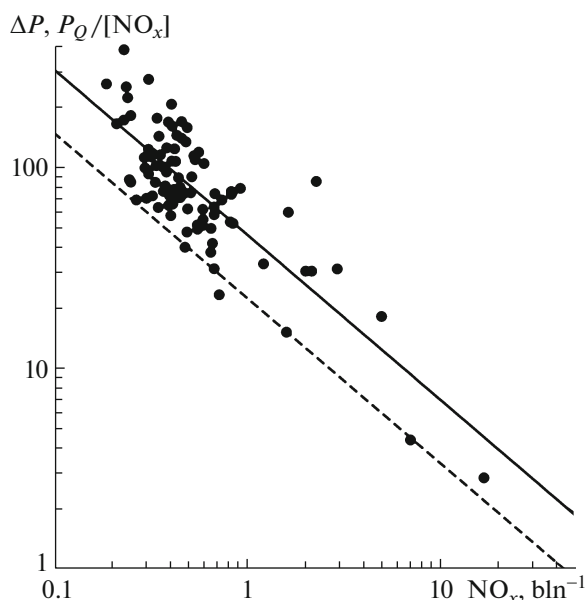
Fig. 2. Diurnal variations in O<sub>3</sub> and NO on the photochemically active days ( $T_m > 20^\circ\text{C}$ ,  $N_c < 30\%$ ) at  $\Delta[\text{O}_3] > 12$  ppbv (notations in Fig. 1); quantity of points for each hour from 28 to 33.

For photochemically active days that satisfy the criterion  $\Delta[\text{O}_3] > 4.9$  bln<sup>-1</sup> (the lower quartile of the frequency distribution of  $\Delta[\text{O}_3]$  in  $\mathbf{P}_a$ ), we calculated the ozone production rates  $P_Q = \Delta[\text{O}_3](24/\Delta t)$ , bln<sup>-1</sup>/day, where  $\Delta t = t_2 - t_1$  (h) is the time interval when ozone was recorded to grow, and then we found the value of  $\Delta P$  by formula (2).  $[\text{NO}_x]_e$  was taken equal to the concentration of NO<sub>x</sub> at the moment  $t = t_2$  (i.e., during the hour when the amplitude of the diurnal variation in O<sub>3</sub> reached a maximum). The results of calculations of the daytime ozone production rate for one molecule of NO<sub>x</sub> ( $P_Q/[\text{NO}_x]_e$ ) and OPE ( $\Delta P$ ) on certain days at  $\tau_N = 0.48$  day<sup>-1</sup> ( $[\text{OH}] = 2 \times 10^6$  mol cm<sup>-3</sup>) are presented in Fig. 3. The corresponding equations of regressive curves have the form

$$P_Q = c_1[\text{NO}_x]_e^{-n+1}, \quad \Delta P = c_2[\text{NO}_x]_e^{-n}, \quad (3)$$

where  $n = -0.82 \pm 0.06$ ,  $c_1 = 46.7 \pm 2.8$ ,  $c_2 = 22.6 \pm 1.4$  ( $R^2 = 0.66$ ).

The obtained estimates were stable relative to the variations in the initial parameters: threshold values of  $T_m$  and  $N_c$ , and the selection of the algorithm for calculating the values of  $\Delta[\text{O}_3]$  and  $[\text{NO}_x]_e$ . For the subset of the days that satisfy the criterion  $T_m > 15^\circ\text{C}$ ,  $N_c \leq 100\%$ , the corresponding coefficients of proportional-



**Fig. 3.** Values of  $P_Q/[\text{NO}_x]_e$  (solid line,  $R^2 = 0.66$ ) and  $\Delta P$  at  $\tau_N = 0.48 \text{ days}^{-1}$  (dashed line) on the photochemically active days ( $T_m > 20^\circ\text{C}$ ,  $N_c < 30\%$ ) at  $\Delta[\text{O}_3] > 4.9 \text{ bln}^{-1}$ .

ity in formulas (3) were  $46.3 \pm 1.7$  and  $22.4 \pm 0.8$ , and the value of the indicator amounted to  $-0.80 \pm 0.04$ , i.e., the stated values remained unchanged within the accuracy of the selected procedure at a much greater spread of the experimental points ( $R^2 = 0.52$ ). In a similar way, we can take the average concentration of  $\text{NO}_x$  in  $\Delta t$  as  $[\text{NO}_x]_e$ .

(5) It was shown in [12] that the observations of the increased concentrations of  $\text{NO}_x$  ( $>0.5\text{--}1 \text{ bln}^{-1}$ ) at ZOTTO are related to the passage of strongly smeared plumes of anthropogenically polluted air from sources located at  $>500 \text{ km}$  from the tall tower. In accordance with the results of the trajectory analysis, at a typical time of advection of about one day, the air in the plume at a height of up to  $850 \text{ mbar}$  can be taken uniformly mixed along the vertical. This allows us to consider cautiously the estimates of the OPE obtained empirically in the surface layer as characterizing the photochemical system of the lower troposphere in general. In [6], the distribution of the OPE value above the continent was calculated based on the fields of concentrations from the GEOS-chem model as the inclination of the corresponding line during regression of  $[\text{O}_3]$  on  $[\text{NO}_z]$  ( $=[\text{NO}_y] - [\text{NO}_x]$ ) [14]. For the model cell, including ZOTTO, we obtained  $\langle \Delta[\text{O}_3]/\Delta[\text{NO}_z] \rangle = 39.8$ ,  $\langle [\text{NO}_x] \rangle = 0.63 \text{ bln}^{-1}$ , where  $\langle \cdot \rangle$  means average for the summer months. For the mostly cloudless weather, the range of variations in  $[\text{OH}]$  was  $1.5\text{--}2.2 \times 10^6 \text{ mol cm}^{-3}$ . Using the values of  $\langle [\text{NO}_x] \rangle$  and  $[\text{OH}]$  obtained in (2), we have  $\Delta P =$

$30.0\text{--}43.7$ , which is in good agreement with the above estimate of the value of  $\Delta[\text{O}_3]/\Delta[\text{NO}_z]$ .

The spread of the experimental points observed in Fig. 2 is determined by a broad range of conditions of ozone generation in the CBL on certain days depending on particular meteorological conditions and the photochemical prehistory of the air mass. In general, however, for the interval of  $[\text{NO}_x]$  from  $0.2$  to  $5 \text{ bln}^{-1}$ , there is a stable tendency to a decrease in  $P_Q$  with the growth of  $[\text{NO}_x]$  with respect to the common properties of the atmospheric photochemical system. The established power dependence within the accuracy of the experimental data is extrapolated to the region of higher values of  $\text{NO}_x$  (points in Fig. 2 at  $[\text{NO}_x] = 7.0$  and  $16.8 \text{ bln}^{-1}$ ), for which at the background concentration of VOC in the region at the level of  $100\text{--}150 \text{ bln}^{-1}$  [15], we can expect the transition from the  $\text{NO}_x$ -limiting ( $n \rightarrow 0+$ ) to the VOC-limiting ( $n \rightarrow 2$ ) mode of ozone generation [5]. The strong dependence of the rate of photochemical ozone production on the  $\text{NO}_x$  content that was found from the model experiments and confirmed experimentally under the conditions of a weakly polluted convective boundary layer over the continent makes urgent the problem of limiting regional anthropogenic emissions of  $\text{NO}_x$  as a part of the general problem of air quality control in the regions of the Russian Federation.

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