

On the role of total ozone in photochemical production of its tropospheric fraction

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Many-year trends in the total ozone content of the atmosphere and that in the troposphere, which have quite the opposite tendencies in Tomsk, are considered. A hypothesis is proposed that a decrease in the near-ground ozone concentration is due to the decrease in the energy of photodissociation, which governs the intensity of photochemical processes in the lower troposphere. The decrease of the photodissociation energy, in its turn, is stipulated by an enhanced attenuation of solar energy in the 295–310 nm spectral range due to the growth of the total ozone content in the stratosphere. This hypothesis was tested by means of balanced estimates based on the data obtained at Tomsk and Kislovodsk stations. The relative variations of the photodissociation energy and the near-ground ozone concentration have close magnitudes.

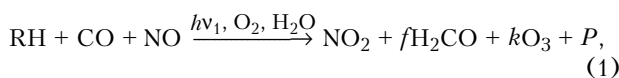
In recent years, the studies of atmospheric ozone have been mainly focused on two principal aspects. One of those appeared almost 100 years ago and deals with the investigation of the total ozone content (TOC), characterizing primarily the behavior of the stratospheric ozone. Such investigations are motivated by the protective role of the ozone layer, preventing the hard ultraviolet solar radiation producing detrimental effect on the Earth's biosphere. The second area of the ozone research that is being intensely developed in few recent decades deals with the investigation of the tropospheric ozone, which is a virulent poisonous gas at a direct contact with biological objects. Besides, ozone is the greenhouse gas and contributes significantly to the climate warming.

The research we present here is based on the data of TOC measurements and measurements of the near-ground ozone concentration (NGOC) near Tomsk. TOC measurements have been carried out with an M-124 ozonometer, which was regularly tested at the Main Geophysical Observatory against a reference Dobson spectrometer. The NGOC was measured with a 3-02P instrument developed by OPTEK (St.-Petersburg), which is calibrated by use of a GS-2 generator of ozone certified at the D.I. Mendeleev All-Russian R&D Metrological Institute. The observations have been started in the early 90's and are being done routinely until now.

Figure 1 shows the time behavior of the near-ground ozone concentration (upper curve) and the total ozone concentration (lower curve) during the period from 1993 to 1999. One can see from Fig. 1 that, regardless of seasonal and long-term variations of the tropospheric ozone concentration and TOC during the period considered, well pronounced opposite trends in the variation of these characteristics were observed. Thus, the near-ground ozone concentration during this period decreased, on the average, from 41.6 to 20.4 $\mu\text{g}/\text{m}^3$ or by 50.7%. And conversely, the TOC

increased during this period from 320 to 363 D.u. or by 11.8%. Such a behavior of the trends makes it possible to assume that the NGOC decrease is connected, in some way, with the TOC increase. This paper presents analysis of the possible mechanism of this interrelation.

It is convenient to consider the mechanism of atmospheric ozone production using the following gross equation¹:



where f and k are the stoichiometric coefficients of the conversion of hydrocarbons of different nature RH; P denotes the products of reactions presenting the sink of photochemical reactions in the form of aerosol.

From Eq. (1) it is evident that entering the real atmosphere with O_2 and water vapor, under the action of ultraviolet solar radiation $h\nu$, the primary impurities of the air, including hydrocarbons of different nature (RH), carbon monoxide and nitric oxide (CO and NO), are transformed, in the course of photochemical processes, into nitric dioxide (NO_2), formaldehyde (H_2CO), and ozone (O_3).

This equation indicates that the ozone concentration depends on two factors, namely the amount of ozone producing substances in the air (the left-hand side of Eq. (1)) and the intensity of ultraviolet solar radiation.

Along with the measurement of ozone concentration we controlled simultaneously the content of other components of the ozone cycle such as CO, HO, NO_2 , CO_2 and, periodically, CH_4 . Based on the data obtained, we can conclude that the concentration of the above-mentioned gases remains unchanged during the period from 1993 to 1999. Consequently, it is believed that such an intense decrease of the near-ground ozone concentration, observed in Fig. 1, may be caused by the variation of the influx of solar radiation.

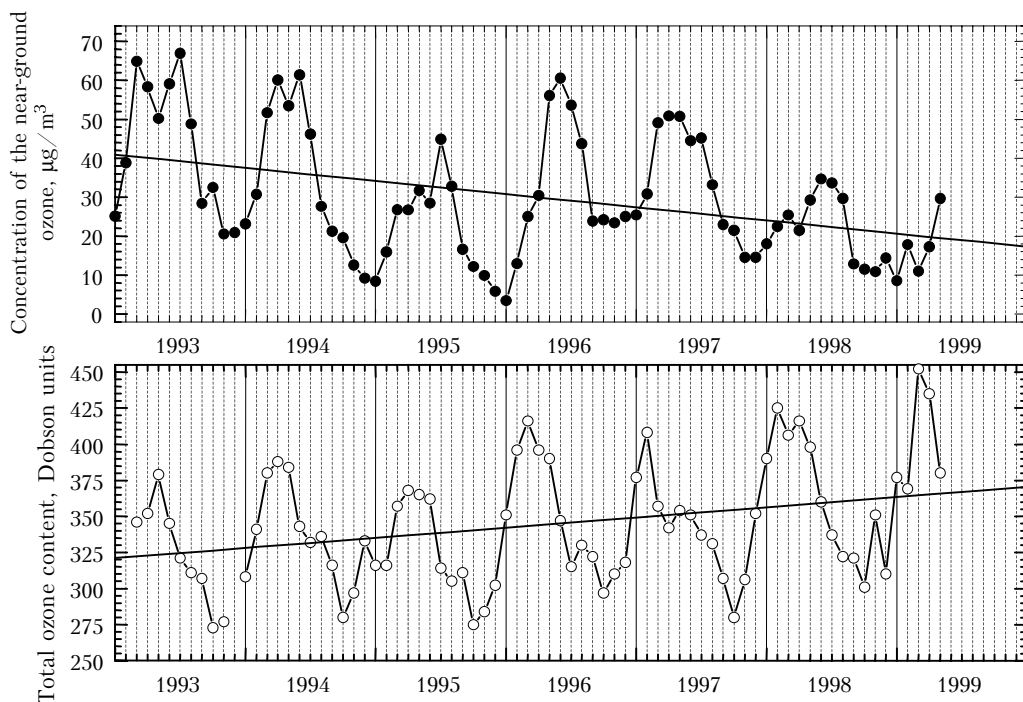


Fig. 1

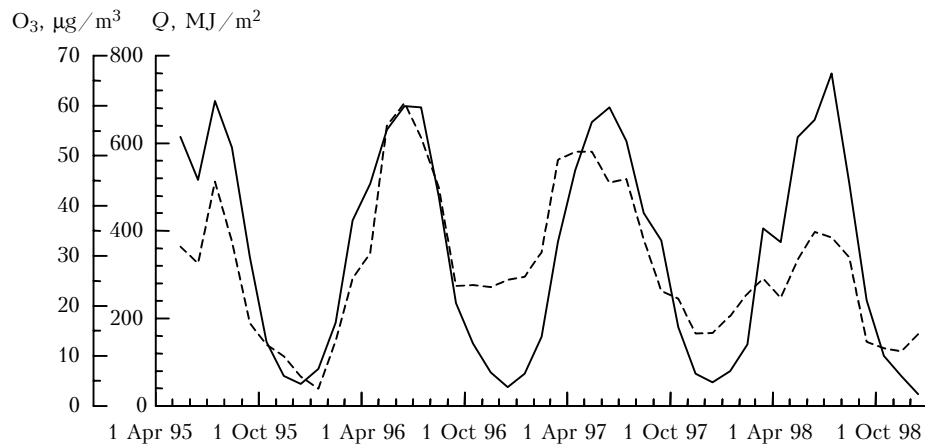
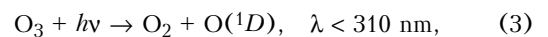
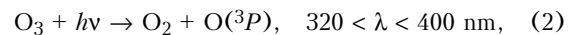


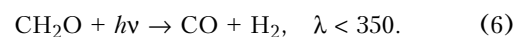
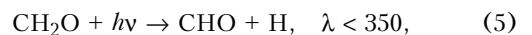
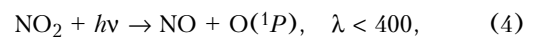
Fig. 2. Long-term variation of the net solar radiation and ozone concentration near Tomsk in 1995–1998; — net radiation; - - - concentration of the near-ground ozone.

The measurements of the net solar radiation were carried out later, starting from 1995. The measurement data indicated (Fig. 2) that the influx of net radiation during the period from 1995 to 1999 increased by several percent. In this connection, we can assume that the growth of the net solar radiation flux, on the one hand, and the decrease of the radiation flux producing ozone that reaches the underlying surface, on the other hand, are associated with the spectral variation of the intensity of incoming solar radiation. To reveal this spectral range, we shall consider the mechanism of production of the tropospheric ozone.

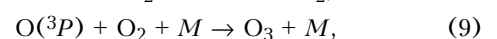
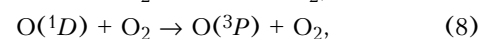
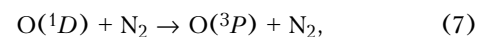
According to Refs. 2 and 3 the onset of photochemical processes in the troposphere is initiated by the photolysis of available ozone by one of the following reactions:



or other substances of the anthropogenic origin:



Approximately 90% of atoms of $\text{O}({}^1D)$, produced from the interaction with the air, transform to the ground state $\text{O}({}^3P)$ and are transformed back to ozone:



where $M = N_2, O_2$.

The remaining 10% of $O(^1D)$ under normal conditions react with water vapor and produce the hydroxyl

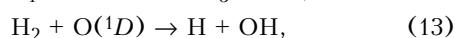


In this case special attention must be given to the fact that the rate of reaction (10) is almost ten times higher than the rate of the cycle (7)–(9) of the ozone reconstruction.

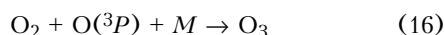
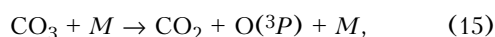
Besides, $O(^1D)$ can interact with nitrous oxide in the air transforming it to the reactive nitric oxide⁴:



with methane and hydrogen yielding hydroxyl:

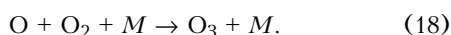
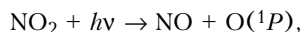
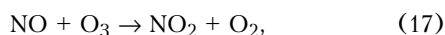


as well as with the stable molecules such as CO_2 (see Ref. 5)



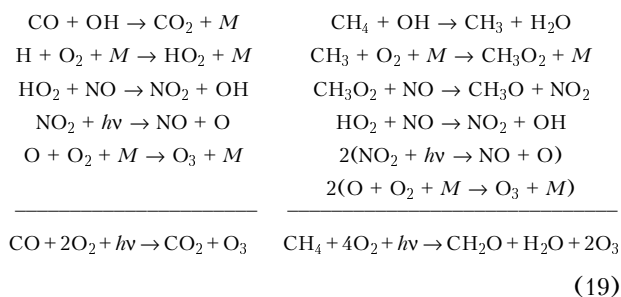
with the subsequent production of ozone molecule.

Further behavior of the air system depends on the concentration of trace gases. In the absence of CO or hydrocarbons in the lower troposphere a photochemical equilibrium is established between nitric oxides and ozone:



If there are CO and other hydrocarbons in the atmosphere, this equilibrium is violated. Subsequent behavior of the system depends on the concentration of nitric oxides, which play the role of cycle switch, in accordance with the theory of chain reactions by N.N. Semenov.⁶ The basic acting substance becomes the hydroxyl OH produced in the reaction (10). Its reaction possibilities are commonly illustrated using, as an example, the oxidation of CO and CH_4 at different NO concentration.

When the NO concentration is more than 15 pptv, the oxidation occurs by the following cycles:

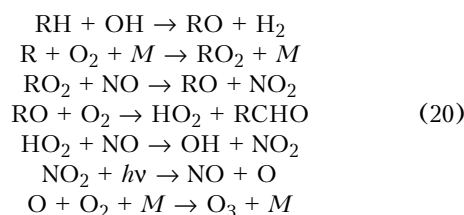


As the final result of these cycles is the fact that simultaneously with the formation of ozone molecules the molecules of OH, HO_2 , NO, and NO_2 are produced, which again enter into photochemical reactions in the new cycles contributing to the formation of new ozone molecules.

If the NO concentration is less than 10 pptv, then in the troposphere the cycles are realized resulting in the ozone destruction. In this case the substances of hydroxyl groups are removed from the cycles, and ozone and nitric oxide are not reduced. It is evident that this process results in the discontinuance of photochemical processes.

We must pay attention to one circumstance, which is of crucial importance in the tropospheric photochemistry. These are the strongest oxidizing capacities of hydroxyl OH, which in Ref. 7 is named as "the cleaner" of the troposphere. Based on the data from Ref. 8, 90 percent of CO in the air is oxidized by the radical OH and only 10 percent by other oxidants. There also exists selectivity in the reactivity of OH to the other substances. A detailed overview of such peculiar features can be found in Ref. 1.

Except for CO and CH_4 , the other hydrocarbons contribute significantly to the formation of the tropospheric ozone. These hydrocarbons are listed in Ref. 9. A typical mechanism of oxidation of RH (hydrocarbons are collectively called RH independent of their nature), suggested in Ref. 10, is as follows¹¹:



Finally: $RH + 4O_2 + 2h\nu \rightarrow RCHO + 2H_2O + 2O_3$.

As a result, two molecules of O_3 and one molecule of aldehyde RCHO are produced from the initially available one hydrocarbon molecule and one radical OH molecule interacting with it. Another O_3 molecule can subsequently appear in the photolysis of aldehydes in the reactions (5) and (6). In the final phase of the cycle one O_3 molecule more can be produced in the reaction of oxidation of CO by the hydroxyl OH with reducing the hydroperoxide HO_2 in the reactions of the cycle (19).

One can see from the above review that the key substance in the production of supplementary quantity of ozone is the hydroxyl OH group produced in the troposphere in the reaction (10). In order that the reaction (10) be possible, the presence of atom of $O(^1D)$ is necessary, which can occur in the lower atmosphere only under condition of photolysis of ozone by ultraviolet radiation at a wavelength shorter than 310 nm. All the remaining cycles and reactions, given above, result in the conservation of the existing ozone.

Thus, the $\lambda \leq 310$ nm can be considered the upper limit of the spectral range effective for the production of tropospheric ozone.

The lower limit of this spectral range can readily be determined from the experimental data in Fig. 3 taken from Ref. 3. This figure shows that without large error $\lambda = 295$ nm can be taken for the lower limit where the photon flux decreases by five orders of magnitude as compared with that at $\lambda = 300$ nm.

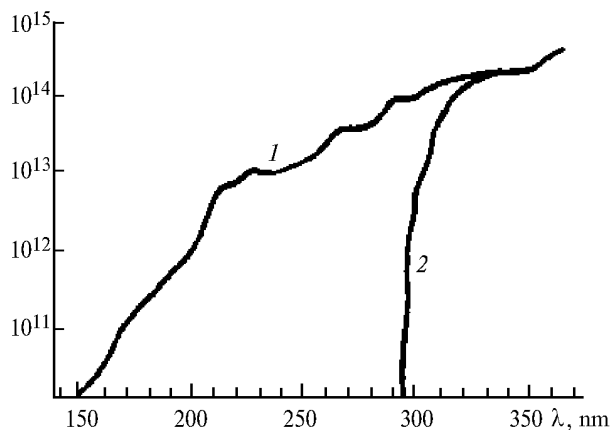


Fig. 3. The photon flux ($\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$) at the upper boundary of the atmosphere (1) and near the ground surface (2) according to Ref. 3.

Thus, from the above data it follows that the production of tropospheric ozone is very sensitive to the change of solar radiation intensity in the spectral range from 295 to 300 nm. In this case the contribution of this radiation to the variation of net solar radiation flux will be practically insignificant because it is about several hundredths of percent.

There is quite intense Huggins absorption band of ozone in the range being studied.¹² Therefore if the ozone concentration varies, as well as its total content, on the way of solar radiation to the surface layer in the stratosphere, then the radiation flux intensity varies in the 295–310 nm range, and, respectively, the photodissociation rate varies according to Eq. (3), which is determined by this flux¹³:

$$J = \int_{295}^{310} F_{\lambda} \sigma_{\lambda} \phi_{\lambda} d\lambda, \quad (21)$$

where F_{λ} is the radiation spectral density; σ_{λ} is the absorption cross section by ozone molecules for the radiation at a wavelength λ ; ϕ_{λ} is the quantum yield, characterizing the probability of dissociation of a molecule after absorbing the light quantum at a wavelength λ .

The radiation flux F_{λ} , determining the ozone photodissociation at the level z , is described by Eq. (22)¹³

$$F_{\lambda}(z) = F_{\lambda}^0 \exp[-(\tau_a + \tau_s)] + F_{\lambda}^s(z, A), \quad (22)$$

where F_{λ}^0 is the extra terrestrial solar radiation flux; τ_a and τ_s are the optical thickness values due to absorption and scattering of radiation along the propagation path; F_{λ}^s is the radiation flux scattered by gases, aerosol, and underlying surface with the albedo A .

Because the measurements of solar radiation intensity in the 295–310 nm range were not carried out, the balance estimates were made to check the above considerations of the variation of the photodissociation rate using Eqs. (3), (21), and (22) due to the change of the total ozone content and then these estimates were compared with the trend of the near-ground ozone concentration observed.

We have made the estimates assuming that the TOC increase was mainly observed in the layer of 10–30 km. The variables in Eqs. (21), (22) varied only slightly during this period except for τ_a , which directly depends on the vertical ozone distribution¹³:

$$\tau_a(z, \lambda) = \int_z^{\infty} dz O_3(z) \sigma(\lambda) \sec \theta, \quad (23)$$

where $O_3(z)$ is the ozone molecular concentration, cm^{-3} ; $\sigma(\lambda)$ is the absorption cross section, cm^2 ; θ is the solar zenith angle determining the length of the propagation path in the atmosphere.

The estimates are given in Table 1, from which it follows that the TOC increase by 11.8% can decrease the photodissociation rate of tropospheric ozone by 55.5% according to Eqs. (3) and (21) that must result in the decrease of the intensity of ozone production by the same amount. In fact this amount is 50.9% that, with the allowance made for a series of assumptions, is close to the calculated value.

Table 1. The relative variation (%) of the TOC, the ozone photodissociation rate, and the near-ground ozone concentration in the vicinity of Tomsk during the period from 1993 to 1999

$\frac{\text{TOC}_{99} - \text{TOC}_{93}}{\text{TOC}_{93}}$	$\frac{J_{99} - J_{93}}{J_{93}}$	$\frac{O_3[99] - O_3[93]}{O_3[93]}$
+ 11.8	- 55.5	- 50.9

If our estimates and considerations are valid, they must also be made in the other regions, which are not strongly subjected to active anthropogenic effect, since in this case the schematic drawing of ozone production can vary within wide limits.^{1–4}

To check this conclusion, we used the data published in Ref. 14 from the background station “Kislovodsk” where the similar trends are observed.

From Table 2 as well as from Table 1 it follows that the TOC increase gives rise to a decrease in the ozone photodissociation rate in the 295–310 nm spectral range. The actual decrease of the near-ground ozone concentration is approximately close to the above decrease in the ozone photodissociation rate.

Table 2. The relative variation (%) of the TOC, the ozone photodissociation rate, and the near-ground ozone concentration for the station "Kislovodsk" during the period from 1991 to 1995

$\frac{\text{TOC}_{95} - \text{TOC}_{91}}{\text{TOC}_{91}}$	$\frac{J_{95} - J_{91}}{J_{91}}$	$\frac{\text{O}_3[95] - \text{O}_3[91]}{\text{O}_3[91]}$
+ 4.9	- 27.6	- 22.2

Thus, the above-mentioned balance estimates have shown that the variation of TOC may result in a decrease of the ozone photodissociation rate in the troposphere in the spectral range of 295–310 nm and, correspondingly, in an increase in the near-ground ozone concentration, which is found to be commensurate with the actually recorded value of the decrease of the near-ground ozone.

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